

Transient analysis of localised defect states in semiconductors

Author:

Debuf, Didier

Publication Date:

2003

DOI:

<https://doi.org/10.26190/unsworks/4625>

License:

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/55708> in <https://unsworks.unsw.edu.au> on 2024-05-01

TRANSIENT ANALYSIS OF LOCALISED DEFECT STATES
IN SEMICONDUCTORS

BY

DIDIER ROLAND DEBUF,
B. Eng(Electrical). (UNSW)
MEngSci. (UNSW)

A DISSERTATION SUBMITTED TO

THE SCHOOL OF ELECTRICAL ENGINEERING AND TELECOMMUNICATIONS

THE UNIVERSITY OF NEW SOUTH WALES

IN FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Copyright © D. R. Debuf 2003

All rights reserved

U N S W

2 0 OCT 2003

LIBRARY

Declaration

I hereby declare that this submission is my own work and to the best of my knowledge it contains no material previously published or written by another person, nor material which to a substantial extent has been accepted for the award of another degree or diploma at UNSW or any other educational institution, except where due acknowledgement is made in the thesis. Any contribution made to the research by others, with whom I have worked at UNSW or elsewhere, is explicitly acknowledged in the thesis.

I also declare that the intellectual content of the thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

Didier Roland Debuf

Abstract

This thesis presents a theoretical evaluation of the differential rate equations governing recombination, emission and trapping via the single-level defect and multiple-level defects. A solution is derived to the governing differential rate equations for the single-level defect first developed in 1952 by Shockley, Read and Hall. This is extended to multiple levels by application of the single-level solution method to the multiple level rate equations, developed using a first principles approach, for two defect level systems. The intention is that this theory be applied to measurement techniques and modeling to evaluate the effects of defect levels in the bandgap at both the interface of silicon and silicon dioxide, and in the bulk region. Further, being of a general nature, the theory may be applied to other semiconductor systems and structures.

The decay of excess carriers via a single-level defect in non-degenerate semiconductors generated by a light impulse $\delta(t)$ is governed by the differential equations referred to as the Shockley-Read-Hall (SRH) rate equations. In the past, linear approximations were used or restrictive conditions imposed to obtain an analytical solution limited to low or high injection. For defect level parameters of practical interest, the non-linear differential equations were numerically solved. Whereas carrier decay is often approximated by one time constant τ , in the present work it is shown that recombination occurs with both the minority (τ_1) and majority (τ_2) time constants present in the decay. Expressions for τ_1 and τ_2 are derived without an approximation at a given temperature, for arbitrary non-degenerate excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . A general analytic solution to the SRH rate equa-

tions represented by an infinite series of mono-exponential terms, the frequencies or inverse time constants of which, are a linear combination of the fundamental frequencies $\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$, is derived without an approximation. The solution is the sum of the responses of an infinite number of linear systems and in this sense represents the impulse response. A critical point representing the transition between the linear and non-linear variation of fundamental frequency with excess carrier density is identified. The analytic solution is verified by analysing the numerical solution of the SRH rate equations for the fundamental frequencies using a multi-transient technique. The trapping behaviour of the minority carrier at a single level defect, with excess carrier concentration is examined.

Experimental evaluation of semiconductor defect parameters is usually accomplished by applying the Shockley-Read-Hall (SRH) recombination time constant expression. It is shown that this expression is an approximation due to the nature of the definition of the time constant. Furthermore, a recent analytic solution to the SRH rate equations which is derived without an approximation for near equilibrium and non-equilibrium situations, is shown to unify the work of previous authors for the single-level defect and small departures of carrier concentration from equilibrium. The method of this solution is applied to derive the steady state solution. It is found that the resulting two time constants or eigenvalues of the steady state linear system, are in agreement with the order of the underlying second order differential equation. In this work the author describes the nature of the approximation in the original work and compares the approximation, the exact solution and the analysis of the numerical solution for component time constants.

Acknowledgments

This work is born out of an interest in solid state physics and as such credit should be given to those who went before me and laid the foundations upon which I hope I have contributed to. I might add that it is my belief that the single-level work came into being by the observation of an effect of cooling a silicon sample with the subsequent warming to room temperature, and the attempt to explain multiple defects affecting the changing oscilloscope trace. I still have not found the reason for the effect. However, with some patience and some help from my colleagues Dr Yash Shrivastava and Alec Dunn, the final result of my search is the single-level solution to the Shockley-Read-Hall rate equations. The multiple-level theory is a natural extension of the single-level theory first presented fifty years ago by Shockley, Read and Hall in 1952. Sufficient detail is presented to enable students like myself to follow the argument. Further, it should be noted that in the scheme of things the mathematics involved is simple although tedious to work out. The solutions to the single-level equations and the multiple-level equations are what I would call engineering solutions. This is because they could be useful in practice.

The path I have followed has been a varied one, however along the way many people have contributed to varying degrees and I would like to thank them all. I would also like to give credit to those teachers at the University of New South Wales who through their patience gave me the basic knowledge to pursue a number of interesting avenues of thought in relation to the above. In particular I would like to thank, Professor Martin Green and Dr Peter Ladbroke for their encouragement in developing an interest in electrically active defects in semiconductors. Further I would like to thank Mark Murray for continuing inspiration and to what may be said

to be the start of the beginning of the path some thirty years ago. My appreciation is also extended to Dr R. Corkish, K. Rosolen, S. Zecevic, D. Brown, Dr I. Gardiner and Dr B. St. George for helpful discussions. Lastly, my appreciation is warmly extended to Dianne Clarke for her support and encouragement.

regards Didier

Contents

Declaration	i
Abstract	i
Acknowledgments	iii
1 Introduction	1
1.1 Discussion	1
1.2 Thesis Organisation	4
2 General Analytic Solution to the Shockley-Read-Hall Rate Equations with a Single Level Defect	7
2.1 Introduction	7
2.2 Non-Linear Rate Equation with Series Solution	11
2.3 Derivation of λ_1 and λ_2 for Arbitrary Injection Level	14
2.4 Derivation of an Analytic Solution for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$.	20
2.5 Numerical Solution of SRH Equations: Ideal Impulse $\delta(t)$	24
2.6 Further Aspects of Trapping	31
2.7 Proposed Experimental Conditions	34
2.8 Discussion	35
3 Accuracy of the Shockley-Read-Hall Time Constant for a Single-Level Defect Species	37
3.1 Introduction	37
3.2 Analytic Steady State SRH Solution	43

3.3	Numerical Solution for the Steady State	44
3.4	Discussion	46
3.5	Conclusions	46
4	Multiple Defect Energy Levels and Isothermal Trapping in Semi-conductors	
	48	
4.1	Introduction	48
4.2	Multiple Discrete Energy Levels: Derivation of Frequencies λ for Arbitrary Injection Level	52
4.3	Ground Excited State System: Derivation of Frequencies λ for Arbitrary Injection Level	61
4.4	Numerical Solution for the Multiple Level and Excited State Systems: Ideal Impulse $\delta(t)$	68
4.5	Discussion	74
5	Multiple level Defect Species Evaluation from Average Carrier Decay	79
5.1	Introduction	79
5.2	Impulse Response and Average Excess Carrier Concentration	82
5.3	Ground and Excited State System: Fundamental frequencies λ . . .	87
5.4	Experimental Constraints	90
5.5	Experimental Conditions	92
5.6	Experimental Results	93
5.7	Discussion	98
6	Accuracy of Semiconductor Multiple-Level-Defect Measurements Using Deep Level Transient Spectroscopy and Lifetime Spectroscopy	
	100	
6.1	Introduction	100
6.2	Existing DLTS	102
6.3	Accuracy of Existing DLTS	105

6.4	Discussion	111
6.5	Accuracy of Existing Lifetime Spectroscopy	112
6.6	Proposed Analytic Lifetime Spectroscopy, Single-Level	116
6.7	Limitations on Materials Characterisation	123
6.8	Discussion	123
7	Conclusions	125
7.1	Discussion	125
7.2	Concluding Remarks	128
	Appendix	128
A	Evaluation of $\eta_n(t_0)$ and $\eta_p(t_0)$	129
B	Derivation of an Analytic Solution for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$	131
C	Calculation of Coefficients F_{10}, F_{01} and $N_{i,j}$	137
D	Rate Equation: Quadratic Form	139
E	Analytic Solution: Infinity of Linear Systems	140
F	Differential Rate Equation for Multiple Discrete Levels	141
G	Evaluation of $\eta_{nk}(t_0)$ and $\eta_{pk}(t_0)$	146
H	Differential Equations for Ground and Excited State System	149
I	Evaluation of $\eta_{ng}(t_0)$, $\eta_{pg}(t_0)$ and $\eta_{nx}(t_0)$, $\eta_{px}(t_0)$	152
	Addendum	153
J	Addendum: Referees' Reports and Author's Comments	154
J.1	Introduction	154
J.2	Comments by Referee A	155
J.3	Author's comment to Referee A	158
J.4	Comments by Referee B	160

J.5	Author's comment to Referee B	162
J.6	Comments by Referee C	163
J.7	Author's comment to Referee C	166
Publications List		166
K Publications List		167
K.1	Publications in Refereed Journals	167
K.2	Publications submitted to Refereed Journals	168
K.3	Publications in Conference Proceedings	169
K.4	Publications in Preparation	170
Bibliography		170

List of Tables

2.1	Typical Parameters for Numerical Solution.	25
2.2	TLS analysis of numerical data $\Delta n(t + \Delta t)$ and evaluation of Eq. (2.32). Note the prediction of Eq. (2.39) with frequencies a linear combination of the fundamental frequencies and calculated coefficients $N_{i,j}$. $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$	30
2.3	Requirements for an electron trap, hole trap, recombination center and generation center.	33
4.1	Typical defect level parameters for numerical solution of the discrete multiple defect level system.	68
4.2	TLS analysis of numerical data $\delta_n(t + \Delta t)$ for the case of level one, level two and level three included in the model. Evaluation of Eq. (4.33) and Eq. (4.36) for $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$	73
4.3	Typical defect level parameters for numerical solution of the ground excited state system.	77
5.1	Defect level parameters used for the fit of experimental data of the ground excited state system, for CZ sample 6_1, (carbon interstitial - oxygen interstitial).	96
5.2	Defect level parameters used for the fit of experimental data of the ground excited state system, for CZ sample 6_1, (vacancy - oxygen complex).	98

6.1	Defect level parameters for the analytical solution of time constants from Eqs. (6.8) for the multiple discrete defect level system.	107
-----	---	-----

List of Figures

- 2.1 Phase diagram indicating convergence to the equilibrium point for the given example where $\Delta n(t)$ is normalised to $\Delta n(0)$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$ 26
- 2.2 A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 2.1 for defect level parameters. Continuous line: τ_1 and τ_2 predicted by Eq. (2.32) Circles: τ_1 and τ_2 derived from multi-transient analysis of the numerical solution 27
- 2.3 Decay time constant $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus the Fermi level E_F eV for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. Continuous line: τ_1 and τ_2 calculated by Eq. (2.32) Circles: TLS analysis of numerical solution $\Delta n(t + \Delta t)$ 28
- 2.4 Normalised error ε Eq. (2.47) between predicted values of $N_{i,j}E_{i,j}$ and numerical solution $\Delta n(t + \Delta t)$ for $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$ to $\Delta n(0) = 5 \times 10^{14} \text{ cm}^{-3}$. This corresponds to the linear and non-linear regions of variation of $\Delta n(0)$ with $\lambda_{1,2}$. $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ and $\Delta t = 1 \times 10^{-8} \text{ sec}$ 30
- 2.5 A graph of $\tau_1 = 1/\lambda_1$ and τ_{L-SRH} , τ_{H-SRH} versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 2.1 for defect level parameters. 36

- 3.1 A graph of fundamental time constant τ_1 and SRH time constant $\tau_{ss} = \tau_{SRH}$ versus excess carrier concentration $\Delta n(0^+)$. Circles: τ_1 derived from multi-transient analysis of the numerical solution. There is a relative error $\varepsilon \approx 30\%$ between τ_1 and τ_{SRH} in the linear region. 42
- 3.2 A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$ for the steady state. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. Continuous line: τ_1 and τ_2 predicted by equation (3.12) Circles: τ_1 and τ_2 derived from multi-transient analysis of the numerical solution. 45
- 3.3 A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$. Comparison between the transient ([1]) and steady state solutions. Continuous line: τ_1 and τ_2 predicted by equation (3.12). . 47
- 4.1 Band diagram for three discrete defect levels indicating carrier transitions with the respective band. 52
- 4.2 Band diagram for the ground excited state system indicating carrier transitions with the respective band. 62
- 4.3 A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$, $\tau_3 = 1/\lambda_3$ and $\tau_4 = 1/\lambda_4$ versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 4.1 for defect level parameters. Continuous line: $\tau_1, \tau_2, \tau_3, \tau_4$ predicted by Eq. (4.33) Circles: $\tau_1, \tau_2, \tau_3, \tau_4$ derived from multi-transient analysis of the numerical solution 70
- 4.4 Decay time constant $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$, $\tau_3 = 1/\lambda_3$ and $\tau_4 = 1/\lambda_4$ versus the Fermi level E_F eV for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. The intrinsic Fermi level is shown as E_i . Continuous line: $\tau_{1,2,3,4}$ calculated by Eq. (4.33). 71

- 4.5 A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system versus excess electron concentration $\Delta n(0)$. The doping concentration N_D of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 4.3 for defect level parameters. Continuous line: τ_1 , τ_2 , τ_3 predicted by Eq. (4.55) Circles: τ_1 , τ_2 , τ_3 derived from multi-transient analysis of the numerical solution 75
- 4.6 Decay time constant $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system versus the Fermi level E_F eV for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. The intrinsic Fermi level is shown as E_i . Continuous line: $\tau_{1,2,3}$ calculated by Eq. (4.55). 76
- 5.1 A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system of $C_i - O_i$ (carbon interstitial - oxygen interstitial) versus excess carrier concentration $\Delta n(0) = \Delta p(0)$. The doping concentration N_D of the sample is $8.34 \times 10^{14} \text{ cm}^{-3}$. See Table 5.1 for defect level parameters. Continuous line: Fit of τ_1 and τ_2 determined from the characteristic equation, to the experimental data. Circles: Experimental data for n-type CZ sample 6_1. 95
- 5.2 A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system of $V - O$ (vacancy - oxygen complex) versus excess carrier concentration $\Delta n(0) = \Delta p(0)$. The doping concentration N_D of the sample is $8.34 \times 10^{14} \text{ cm}^{-3}$. See Table 5.2 for defect level parameters. Continuous line: Fit of τ_1 and τ_2 determined from the characteristic equation, to the experimental data. Circles: Experimental data for n-type CZ sample 6_1. 97
- 6.1 A graph of fundamental time constant τ_1 , from the root of Eq. (6.10) versus $1/kT$, for the combined effect of three levels in Table 6.1 and for the case of each level in the Table as if it were the only level present in the semiconductor sample. Solid line: plot of τ_1 for each level. Solid line with circles: combined effect of three levels. 109

- 6.2 A graph of fundamental time constant τ_2 , from the root of Eq. (6.10) versus $1/kT$, for the combined effect of three levels in Table 6.1 and for the case of each level in the Table as if it were the only level present in the semiconductor sample. Solid line: plot of τ_2 for each level. Solid line with circles: combined effect of three levels. 110
- 6.3 A graph of fundamental time constant τ_1 and SRH time constant $\tau = \tau_{SRH}$ versus excess carrier concentration $\Delta n(0^+)$. Circles: τ_1 derived from multi-transient analysis of the numerical solution. There is a relative error $\varepsilon \approx 30\%$ between τ_1 and τ_{SRH} in the linear region at $T = 300\text{ K}$ 114
- 6.4 For this p-type semiconductor example, the existing Lifetime Spectroscopy technique shows curves for the indicated energy level depths $E_t - E_v$. The temperature variation is from 80K to 400K. 115
- 6.5 For this p-type semiconductor example, the Analytic Lifetime Spectroscopy technique shows curves for the indicated energy level depths $E_t - E_v$. The temperature variation is from 20K to 400K. 122
- F.1 Carrier transitions between the k' level in the conduction band and the k^{th} level defect state in the bandgap. 142

Chapter 1

Introduction

1.1 Discussion

The basic concepts of the recombination of excess carriers in semiconductors via a defect level within the bandgap were developed in the 1950s. The Shockley-Read-Hall (SRH) rate equations of Shockley and Read [2], Hall [3] describe the evolution with time of recombination, capture and emission of excess carriers via a single defect energy level in the bandgap of a semiconductor. Analyses of the recombination process were based primarily on numerical solutions of the differential equations, with analytic solutions provided in some limiting cases such as low or high excess carrier concentration Nomura and Blakemore [4]. Using linear approximations of the Shockley-Read-Hall rate equations, it has been shown that, for a single-level defect, there are two fundamental time constants, the inverse of which are referred to as the fundamental frequencies. These two time constants appear in steady-state conditions Shockley and Read [2] with an approximation, as well as transient carrier decay situations Streetman [5], Sandiford [6] also with an approximation.

A brief survey of developments related to the partial solutions of the SRH rate equations follows. A partial solution to the rate equations Fan [7] yielded two time constants in terms of a "recombination time", "a time to trap a carrier" and "a time to release a trapped carrier". In this case the recombination time constant is defined as in Eq. (3.1) discussed later in the text. In Rose [8] the defect problem

is addressed with approximations introduced to elucidate the different features of types of defects. For the transient case, an approximate solution of Sandiford [6], yields two time constants comprising an initial decay and a transient decay. A set of differential rate equations for multiple discrete levels based on a summation of the single level SRH equations is stated in Wertheim [9]. Approximations were introduced to provide a linear solution to the non-linear differential equations for small changes in Δp and Δn from the equilibrium values. For the single-level, two time constants result from this solution for the transient case which were simplified to one time constant and an "adjustment time" which agree with Sandiford [6].

In Nomura and Blakemore [4] approximations were applied to the solution not of the rate equations but to the second order differential equation in Δp that results from the rate equations and the charge neutrality condition. As pointed out by Ref. [4], all previous methods of solution of the second order equation including perturbative methods, were unsuccessful in yielding a solution. For this reason previous attempts at solving the rate equations have inherently involved approximations in order to gain some insight into the carrier dynamics. However, Streetman [5] confirmed the existence of two time constants, as also indicated by Wertheim [9], for small departures from equilibrium for the transient case applied to the single-level defect. In Choo [10], application of the rate equations to coupled states and two independent states is investigated for the transient and steady state situations. The transient time constant expressions agree with Ref. [5] and Ref. [9] for small departures of the carrier concentration from equilibrium for the single-level case. There are two time constants in these solutions which are in agreement with the exact solution of Debuf [1]. This is consistent with the governing second order differential equation since there are two eigenvalues of the linear system because the equation is second order.

The present work extends that of previous authors for the single-level by presenting an analytic solution to the SRH rate equations. Furthermore, in the next Section 1.2, an application of this solution method to the multiple level situation is indicated. For the single-level the decay of excess carriers in non-degenerate semiconductors, generated by a light impulse $\delta(t)$, is governed by the differential equations referred

to as the Shockley-Read-Hall (SRH) rate equations. In the past, linear approximations were used or restrictive conditions imposed to obtain an analytical solution limited to low or high injection. For defect level parameters of practical interest, the non-linear differential equations were numerically solved. Whereas carrier decay is often approximated by one time constant τ , in the present work it is shown that recombination occurs with both the minority (τ_1) and majority (τ_2) time constants present in the decay. Expressions for τ_1 and τ_2 are derived without an approximation at a given temperature, for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . A general analytic solution to the SRH rate equations is derived without an approximation by the present author. This solution is in the form of an infinite series of mono-exponential terms, the frequencies or inverse time constants of which, are a linear combination of the fundamental frequencies $\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$. The solution is the sum of the responses of an infinite number of linear systems and in this sense represents the impulse response. A critical point representing the transition between the linear and non-linear variation of fundamental frequency with excess carrier density is identified. The analytic solution is verified by analysing the numerical solution of the SRH rate equations for the fundamental frequencies using a multi-transient technique. The trapping behaviour of the minority carrier at a single level defect, with excess carrier concentration is examined.

Experimental evaluation of semiconductor defect parameters is usually accomplished by applying the Shockley-Read-Hall (SRH) recombination time constant expression. It is shown that this expression is an approximation due to the nature of the definition of the time constant. Furthermore, a recent analytic solution to the SRH rate equations which is derived by the present author without an approximation for near equilibrium and non-equilibrium situations, is shown to unify the work of previous authors for the single-level defect and small departures of carrier concentration from equilibrium. The method of this solution is applied to derive the steady state solution. It is found that the resulting two time constants or eigenvalues of the steady state linear system, are in agreement with the order of the underlying second order differential equation. In this work the author describes the nature of

the approximation in the original work and compares the approximation, the exact solution and the analysis of the numerical solution for component time constants.

1.2 Thesis Organisation

The sequence of theory presented in the current work is intended to bring the reader forward from the single-level theory to the multiple-level theory in a natural progression. A solution to the single-level SRH rate equations is derived in Chapter 2. This is approached by a simple example for which the solution is given by two methods. The first method is differentiation of the linear solution and the second follows direct integration. Both methods converge to the same solution. This solution is in the form of an infinite series of monexponential terms with frequencies or inverse time constants the linear combination of the eigenvalues of the linear solution. It is shown that the SRH equations may be similarly solved and this solution is derived in more detail by the integral method in Appendix B. Independent verification of the series solution is achieved by analysing the numerical solution for the component time constants by a multitransient technique. This analysis reveals time constants in good agreement with those fundamental time constants predicted by the theory. Furthermore, this analysis indicates that for the single-level the series solution with the frequencies a linear combination of the fundamental frequencies, is to be expected.

In Chapter 3 the accuracy of the steady state SRH time constant expression is examined. It is shown that this expression is not accurate in the linear (constant) region of variation of time constant with excess carrier concentration. This region corresponds to an excess carrier concentration in the neighbourhood of the equilibrium value. For small departures from equilibrium referred to as the small signal case, the SRH expression is often used for the "transient" interpretation of experimental data. This small signal case corresponds to the transient solution of Ref. [1], which has at least two time constants. The steady state solution for near equilibrium is shown to be identical to the small signal transient solution. The SRH expression is compared with the exact solution for the steady state and an analysis

of the numerical solution for component time constants. There is good agreement between the exact solution and the analysis of the numerical solution. The SRH expression is found to be thirty percent in error relative to the exact solution, in the linear region.

The Shockley-Read-Hall (SRH) rate equations determine on average the carrier transitions via a single level defect in the bandgap of a non-degenerate semiconductor. Multiple discrete level defects are usually described by a summation of the single level SRH equations. This formulation of the differential equations is difficult to extend to other defect level systems and has not been verified. In Chapter 4 the differential equations for the multiple discrete level system and the ground excited state level system are derived from first principles. Verification of the two sets of rate equations is performed by applying the method of solution for the single level rate equations developed recently. Given a general analytic solution to the SRH rate equations for the single defect level, represented by an infinite series of mono-exponential terms, the frequencies or inverse time constants of which are a linear combination of the fundamental frequencies $\lambda = 1/\tau$, the multiple defect level solution expression is derived. Expressions for the minority carrier time constant τ_1 and time constants τ_{k+1} are derived for m with $k = 1, 2, \dots, m$ discrete defect levels without an approximation at a given temperature, for excess carrier concentration below non-degenerate doping, arbitrary doping concentration $N_{A,D}$, defect level concentration N_{tk} , cross section $\sigma_{nk,pk}$ and energy level E_{tk} . A similar expression for the minority carrier time constant τ_1 for the ground excited state system is derived. The minority carrier trapping behaviour is examined. A more accurate measure of semiconductor quality is proposed which is based on a measure of the time constant τ_1 whether the decay is a transient or steady state response for both defect level systems.

In Chapter 5 an expression for the average decay is determined by solving the carrier continuity equations, which include terms for multiple defect recombination. This expression is the decay measured by techniques such as the contactless photoconductance decay method which determines the average or volume integrated decay. Implicit in the above is the requirement for good surface passivation such

that only bulk properties are observed. A proposed experimental configuration is given to achieve the intended goal of an assessment of the type of defect in an n-type CZ silicon semiconductor with an unusually high relative lifetime. The high lifetime is explained in terms of a ground excited state multiple defect level system. Also, minority carrier trapping is investigated.

Semiconductor material evaluation in terms of defect parameters is presently determined experimentally by applying the Shockley-Read-Hall (SRH) recombination time constant expression. Two current methods of determining defect level depth, namely Lifetime Spectroscopy and Deep Level Transient Spectroscopy (DLTS), are shown to yield incorrect results. The source of the error in each case is identified in Chapter 6. It is shown in Chapter 3 that the SRH lifetime expression is approximate. A recent analytic solution to the SRH rate equations extended to differential rate equations for two multiple defect level systems, yields a solution derived without an approximation. In terms of material characterisation, this exact solution is shown to provide more detailed information on multiple level depths than the existing theory, which relies on a dominant single level. Furthermore, for semiconductor samples known to be predominantly doped with one defect species, it is shown that the dominant decay time constant is influenced by the other defect species present in the semiconductor sample. A new method of semiconductor material evaluation for a single-level, called Analytic Lifetime Spectroscopy (ALS) is proposed. This method is based on the exact solution.

Chapter 2

General Analytic Solution to the Shockley-Read-Hall Rate Equations with a Single Level Defect

2.1 Introduction

As outlined in Chapter 1, the basic concepts of the recombination of excess carriers in semiconductors via a defect level within the bandgap were developed in the 1950s. The Shockley-Read-Hall (SRH) rate equations of Shockley and Read [2], Hall [3] describe the evolution with time of recombination, capture and emission of excess carriers via a single defect energy level in the bandgap of a semiconductor. Analyses of the recombination process were based primarily on numerical solutions of the differential equations, with analytic solutions provided in some limiting cases such as low or high excess carrier concentration Nomura and Blakemore [4]. Using linear approximations of the Shockley-Read-Hall rate equations, it has been shown that, for a single-level defect, there are two fundamental time constants, the inverse of which are referred to as the fundamental frequencies. These two time constants appear in steady-state conditions in Ref. [2] with an approximation, as well as transient

carrier decay situations Streetman [5], Sandiford [6] also with an approximation.

The equation describing the time evolution of the normalised excess electron concentration $\Delta n_{nm}(t)$, is a second order non-linear differential equation and has a term in the cubic power of $\Delta n_{nm}(t)$ Ref. [4]. We expect at least two time constants in the solution (the eigenvalues of the linear system) as the differential equation is second order. However the existing interpretation of experimental data relies on one time constant τ_{ss} (steady state case) or τ_b (bulk decay - transient case). This implies a first order differential equation. While this situation may be sufficient as an approximation it lacks the provision for predicting behaviour and a unified approach to interpretation. For example with regard to the effect of a defect energy level in bulk silicon or in low dimensional structures, a consistent theoretical basis is required.

While the above findings were based on linear approximations of the underlying rate equations, in the present paper we derive a solution to the rate equations to obtain the time dependent response to a light impulse $\delta(t)$ without an approximation. Our analytical solution shows that the entire decay curve consists of an infinity of mono-exponential terms and that all inverse time constants or frequencies are a linear combination of the two fundamental frequencies. One expression for the minority (τ_1) and one expression for the majority (τ_2) carrier decay time constant, is derived without an approximation at a given temperature for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . A critical point representing the transition between the linear and non-linear variation of excess carrier density with fundamental frequency is identified. This has not been previously given (see Ref. [5] and Ref. [6]) with the result that the linear approximations above were difficult to apply in practice. The theory presented addresses the whole decay process from $0^+ < t < \infty$ as the excess carrier decay is expressed by a sum of mono-exponential terms with coefficients and time constants calculated from the above parameters. As such the sum of exponentials is non-linear. However each mono-exponential term is the response to a linear system and the series represents the sum of the responses to an infinite sum of linear systems. Hence in this sense, the derived solution represents the impulse

response. To our knowledge the impulse response of the SRH rate equations for the transient case has not been derived for low through to high injection, and presents a unified approach to analysis of the single-level defect. As the present work extends the theory of the original SRH papers of 1952 which describe a simple case of uniform excess carrier concentration and a single level, it is intended to provide a clear theoretical basis for further work.

To verify the theory this chapter contains a numerical solution of the SRH rate equations which is analysed by a multi-transient analysis method for the component exponentials. This analysis of the numerical simulation confirms time constants predicted by the theory presented. We provide a consistent solution to the differential equations, with supporting evidence the multi-transient analysis of the numerical solution. Notwithstanding this, provision for the experimental position is also given. This work extends that of Streetman [5] and Sandiford [6] for the transient case, and Shockley and Read [2] for the steady-state case, by providing an analytical solution from low through to high injection. Note also that the SRH rate equations are valid for the non-degenerate statistics which indicates the high injection level limit Sze [11]. Further work seeks to address the multi-level and interface or surface effects, in terms of the analytical solution to the SRH rate equations.

For practical device operation the effect of defect levels at the surface or interface is minimised by passivation which limits the concentration of such energy levels. As a result the bulk levels may have a significant impact on device operation such as solar cell efficiency and stable FET threshold voltage. However device operation occurs under varying injection levels from low through to high injection. Hence the requirement to model the effect of defects accurately and under varying conditions. Minority carrier decay is usually modeled by one time constant τ_b (representing bulk recombination, which is approached asymptotically for $t \gg \tau_b$), derived from the simplified carrier continuity equations incorporating the law of mass action. Sah [12] points out that the law of mass action is valid for the equilibrium situation.

The linear approximation referred to above infers low excess carrier concentration in relation to the equilibrium majority carrier concentration, for which approximate time constant expressions are deemed to apply in Ref. [2] depending on defect level

concentration N_t . An experimental restriction of low excess carrier concentration is often imposed to facilitate interpretation of the data using the approximations in order to determine defect level parameters such as cross sections, energy level and concentration. It is shown that for the transient case whereas at high injection τ_1 is adequate to model recombination, at low injection τ_2 is also required as the magnitude of the coefficient can be significant. For the steady state, in low injection the frequencies are the same as the transient case although the coefficients may be markedly different and furthermore the coefficient for the τ_2 term may be significant.

The Chapter is organised as follows. The section 2.2 demonstrates the solution to a non-linear differential equation represented by a quadratic. In effect the SRH rate equations have a quadratic form and the example given is intended to illustrate the infinite series of mono-exponential terms in the solution, the bounds of the solution and in particular the non-linear nature of the solution. Two approaches to obtaining the indicated solution demonstrate a consistency in its derivation. This is further expanded in a more rigorous approach in section 2.4. However the eigenvalues λ_1 and λ_2 of the linear solution to the SRH rate equations are first determined in section 2.3. The fundamental frequencies λ_1 and λ_2 are derived isothermally for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . An excess electron concentration $\Delta n(t)$ and hole concentration $\Delta p(t)$ is assumed to be uniformly generated throughout the wafer thickness at $t = 0^+$ (see Section 2.7). It is shown that the non-linear terms in the rate equations for $\Delta n(t)$ and $\Delta p(t)$ go to zero at $t = 0^+$ or some time $t = t_i$ where $t_i > 0^+$. The resulting linear differential equations may be solved at $t = 0^+$ or $t = t_i$ for the two fundamental frequencies λ_1 and λ_2 . In section 2.4, the response to a light impulse $N_o\delta(t)$ is determined for a p-type semiconductor with a single-level defect, including the effect of arbitrary injection level $\Delta n(0) = N_o$. Having obtained the fundamental time constants, a general solution for $\Delta n(t)$ and $\Delta p(t)$, represented by the impulse response as stated above is found from the non-linear rate equations being expressed in integral form. A section 2.5 contains a multi-transient analysis of the numerical solution to determine the component exponentials in the sum of exponentials. Comparison of the predictions of the analytic solution with

the results of the multi-transient analysis of the numerical solution is very good. Also the theory indicates calculated magnitudes in agreement with those derived from the numerical analysis. In particular the linear combination of fundamental frequencies in the exponents predicted by the analytic solution and the variation of the time constants $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ with injection level, indicate close agreement. An indication of recombination only and the onset of minority carrier trapping is discussed. Note the defect level concentration is assumed to be uniformly distributed throughout the silicon sample.

2.2 Non-Linear Rate Equation with Series Solution

The processes of capture and emission of carriers from a defect level and recombination and trapping via a defect level are governed by the SRH rate equations. These processes determine the average lifetime of minority carriers and hence device characteristics. As stated in the introduction current methods of analysis to determine defect level parameters are approximate in nature. Despite the probability that many defect levels may be present in a given semiconductor sample, an effective lifetime τ_e is often evaluated as if they may be represented by one dominant level. A major contribution of the current work is the derivation of a general analytic solution to the SRH rate equations for a single level defect in order to provide a basis for future work.

It is shown in Ref. [4] that the SRH equations can be represented by a second order non-linear dynamical system. Further as discussed in section 2.4 the nonlinearity is quadratic in nature. Derivation of a general analytic solution for such a system is quite tedious and involved (as is demonstrated in later sections). However, the fundamental concepts involved in such a solution are very simple. The main aim of this section is to illustrate these concepts through a simple first order example. Towards this end, consider the following first order non-linear dynamical system:

$$\frac{dn(t)}{dt} = N_1 n(t) + N_2 n^2(t) \tag{2.1}$$

Note the nonlinearity is a quadratic term. In fact when $N_2 = 0$ the system is linear and has the usual solution $n(t) = n(0) \exp(N_1 t)$. When $N_2 \neq 0$ the system has two equilibrium points 0 and $-N_1/N_2$. It is an easy matter (by linearising the system about the equilibrium points) to show that for $N_1 < 0$, 0 is a stable equilibrium point and $-N_1/N_2$ is an unstable equilibrium point. Further the domain of attraction of the stable equilibrium point 0 is rather large. Any trajectory starting from an initial condition in the range $-\infty < n(0) < -N_1/N_2$ for $N_2 > 0$ and in the range $-N_1/N_2 < n(0) < \infty$ for $N_2 < 0$ converges to this equilibrium point. From a mathematical standpoint, trajectories outside this domain of attraction can be shown to diverge to infinity. From a physical standpoint the effect of the non-linearity for an initial condition starting inside the stated ranges and given an appropriate value of N_2 , may enhance generation of minority carriers corresponding to the impurity photovoltaic effect Keevers and Green [13]. This effect indicates an improved infrared response of solar cells by the addition of defect levels such as produced by indium. The effect is not evaluated in the present work.

Suppose that we have an initial condition that lies within the domain of attraction. Then what is the exact nature of the solution? A solution to the linearised system would suggest that $n(t) = n(0) \exp(N_1 t)$ and indeed it is a good approximation if $n(0)$ is sufficiently small. However, for large $n(0)$ we need to take the non-linear nature of the system into account. Because of the quadratic nature of the nonlinearity, it is possible to integrate the system Eq. (2.1) exactly to arrive at:

$$n(t) = \frac{N_1 n(0) e^{N_1 t}}{(N_1 + N_2 n(0)) - N_2 n(0) e^{N_1 t}} \quad (2.2)$$

Another method to obtain the above solution is the following that highlights certain points. A solution to the linearised system suggests that we should try solutions of the form $n(t) = n(0) \exp(N_1 t)$. However when we substitute this into Eq. (2.1), a term involving $\exp(2N_1 t)$ is generated on the right hand side. This suggests that we should try solutions of the form $n(t) = n_1 \exp(N_1 t) + n_2 \exp(2N_1 t)$. Proceeding in this way a possible solution takes the form:

$$n(t) = n_1 e^{N_1 t} + n_2 e^{2N_1 t} + n_3 e^{3N_1 t} + n_4 e^{4N_1 t} + \dots \quad (2.3)$$

where:

$$\frac{dn(t)}{dt} = n_1 N_1 e^{N_1 t} + n_2 2N_1 e^{2N_1 t} + n_3 3N_1 e^{3N_1 t} + \dots \quad (2.4)$$

Substituting Eqs. (2.3) and (2.4) into Eq. (2.1) and noting that $\exp(N_1 t)$, $\exp(2N_1 t)$, $\dots$ are linearly independent functions and the equality in Eq. (2.1) can only be achieved when the coefficients on both sides of the equation match. Solving for the n_k where $k = 1, 2, 3, \dots$ a geometric series results in:

$$\begin{aligned} n(t) &= n_1 e^{N_1 t} + \frac{N_2}{N_1} n_1^2 e^{2N_1 t} + \left(\frac{N_2}{N_1}\right)^2 n_1^3 e^{3N_1 t} + \dots \\ &= \frac{n_1 e^{N_1 t}}{1 - \frac{N_2}{N_1} n_1 e^{N_1 t}} \end{aligned} \quad (2.5)$$

Using the initial condition:

$$n(0) = \frac{n_1}{1 - \frac{N_2}{N_1} n_1} \quad (2.6)$$

results in the following which is equivalent to Eq. (2.2) that was obtained by direct integration:

$$n_1 = \frac{N_1 n(0)}{N_1 + N_2 n(0)} \quad (2.7)$$

So despite their differences both methods lead to the same solution. It is essentially the first method that we use to obtain the general solution of the SRH rate equations. However it is shown that this leads to equivalent expressions when equating coefficients as derived from the assumption of the solution being a series of exponential terms (second method). Note that if Eq. (2.1) is modified to include a constant term N_0 on the right side, then for initial conditions in the domain of attraction, the trajectories reach a nonzero steady state value. This can easily be accommodated in the second method by including a constant term n_0 on the right side of Eq. (2.3).

A few salient points in the above development should be noted. These are also true for our general solution developed in section 2.4. A solution to the linearised system is a good approximation only for initial conditions that are sufficiently close to the equilibrium point. Following the second method, within the domain of attraction the general solution is a linear combination of what could be said to be an

infinity of exponential terms. Further the frequencies of these exponential terms are integer multiples of a fundamental frequency (in the above example they are multiples of N_1). Finally the fundamental frequency is associated with the linearised system. In the next section it is shown that there are two fundamental frequencies for the single level defect system associated with the linear solution of the SRH rate equations.

2.3 Derivation of λ_1 and λ_2 for Arbitrary Injection Level

Neglecting the effect of excited states of a defect energy level, Auger recombination and radiative recombination, the carrier continuity equations for the one-dimensional case are given as follows:

$$\frac{dn(x, t)}{dt} = G_n - U_n + \frac{1}{q} \frac{dJ_n}{dx} \quad (2.8)$$

$$\frac{dp(x, t)}{dt} = G_p - U_p + \frac{1}{q} \frac{dJ_p}{dx} \quad (2.9)$$

with $n(x, t)$ and $p(x, t)$ being the electron and hole concentrations having a time t and a spatial x , dependence. $G_{n,p}$ is the generation rate, $U_{n,p}$ is the recombination rate, and $J_{n,p}$ is the current density given by respectively:

$$J_n = q\mu_n n(x, t)\xi + qD_n \frac{\partial n(x, t)}{\partial x} \quad (2.10)$$

$$J_p = q\mu_p p(x, t)\xi - qD_p \frac{\partial p(x, t)}{\partial x} \quad (2.11)$$

Simplifications are made such that the generation rate $G_{n,p}$, diffusion components $qD_n dn(x, t)/dx$ and $qD_p dp(x, t)/dx$, and the electric field ξ are considered negligible. Hence the continuity equations simplify to:

$$\frac{dn(t)}{dt} = -U_n \quad (2.12)$$

$$\frac{dp(t)}{dt} = -U_p \quad (2.13)$$

Note that n and p do not depend on x . The excess electron concentration $\Delta n(t)$ and the excess hole concentration $\Delta p(t)$ are written in terms of normalised excess carrier concentration $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ respectively. Note $\Delta n_{nm}(0^+) = 1$ and $\Delta p_{nm}(0^+) = 1$.

$$\Delta n_{nm}(t) = \frac{\Delta n(t)}{\Delta n(0)} \quad (2.14a)$$

$$\Delta p_{nm}(t) = \frac{\Delta p(t)}{\Delta p(0)} \quad (2.14b)$$

The defect level electron concentration $N_t f(t)$ is written in terms of the departure from equilibrium $N_t \Delta f(t)$ and the equilibrium concentration $N_t f_o$. As such the electron and hole concentrations, and the defect level concentration may be written respectively with N_t being the defect level concentration:

$$n(t) = \Delta n_{nm}(t) \Delta n(0) + n_{po} \quad (2.15a)$$

$$p(t) = \Delta p_{nm}(t) \Delta p(0) + p_{po} \quad (2.15b)$$

$$N_t f(t) = N_t \Delta f(t) + N_t f_o \quad (2.15c)$$

with the corresponding equilibrium concentrations n_{po} and p_{po} and where at equilibrium the electron occupancy of the defect level is $f_o = f(0^-)$ given in terms of p_{po} by:

$$f_o = \frac{p_1}{p_{po} + p_1} \quad (2.16a)$$

and in terms of n_{po} by:

$$f_o = \frac{n_{po}}{n_{po} + n_1} \quad (2.16b)$$

with

$$n_1 = N_c \exp \left(-\frac{(E_c - E_t)}{kT} \right) \quad (2.17a)$$

$$p_1 = N_v \exp \left(-\frac{(E_t - E_v)}{kT} \right) \quad (2.17b)$$

A charge neutrality relation indicates the conservation of charge with time.

$$\Delta p_{nm}(t)\Delta p(0) = \Delta n_{nm}(t)\Delta n(0) + N_t\Delta f(t) \quad (2.18)$$

$N_t\Delta f(t)$ may be written as $\Delta n_t(t)$ with $\Delta n_t(t)$ being the defect level excess electron concentration. By rewriting the charge neutrality relation with $\Delta n(0) = \Delta p(0)$, the valence, conduction and defect level electron concentrations may be directly compared since the three quantities are normalised to one injection level $\Delta n(0)$.

$$\Delta p_{nm}(t) = \Delta n_{nm}(t) + \frac{\Delta n_t(t)}{\Delta n(0)} \quad (2.19)$$

From Eqs. (2.15) and (2.18) the SRH rate equations in Ref. [4] may be written in normalised form as:

$$\begin{aligned} -\frac{d\Delta n_{nm}(t)}{dt} = & \gamma_0\Delta n_{nm}(t) - \sigma_0\Delta p_{nm}(t) \\ & - C_n [\Delta p_{nm}\Delta p(0) \\ & - \Delta n_{nm}\Delta n(0)] \Delta n_{nm}(t) \end{aligned} \quad (2.20)$$

$$\begin{aligned} -\frac{d\Delta p_{nm}(t)}{dt} = & \alpha_0\Delta p_{nm}(t) - \beta_0\Delta n_{nm}(t) \\ & + C_p [\Delta p_{nm}\Delta p(0) \\ & - \Delta n_{nm}\Delta n(0)] \Delta p_{nm}(t) \end{aligned} \quad (2.21)$$

where:

$$\alpha_0 = C_p N_t \left\{ \frac{p_1}{p_{po} + p_1} + \frac{p_{po} + p_1}{N_t} \right\} \quad (2.22a)$$

$$\beta_0 = C_p N_t \left\{ \frac{p_{po} + p_1}{N_t} \right\} \quad (2.22b)$$

$$\gamma_0 = C_n N_t \left\{ \frac{n_1}{n_{po} + n_1} + \frac{n_{po} + n_1}{N_t} \right\} \quad (2.22c)$$

$$\sigma_0 = C_n N_t \left\{ \frac{n_{po} + n_1}{N_t} \right\} \quad (2.22d)$$

with $C_n = v_{thn}\sigma_n$ and $C_p = v_{thp}\sigma_p$ being the capture coefficients for electrons and holes respectively.

By extending the work of Streetman [5] and Sandiford [6] to cover the wider range of injection levels from low through to high injection, the rate equations are re-written so as to make the non-linear terms go to zero at some time t . To do this the differential equation (2.20) may be written with the inclusion of, $-\eta_n(t)C_n\Delta n^2(0)\Delta n_{nm}(t)$ and $+\eta_n(t)C_n\Delta n^2(0)\Delta n_{nm}(t)$ for the minority carrier, and $-\eta_n(t)C_n\Delta n^2(0)\Delta p_{nm}(t)$ and $+\eta_n(t)C_n\Delta n^2(0)\Delta p_{nm}(t)$ for the majority carrier, where $\eta_n(t) = \Delta f(t)$. Inclusion of the $\eta_n(t)$ terms above in Eq. (2.20) and a corresponding set of terms in $\eta_p(t)$ into Eq. (2.21) is a construction which allows the application of the boundary conditions to evaluate the non-linear terms in both equations and determine the precise time at which the equations can be treated as linear. If the resulting Eqs. (2.23) and (2.24) are multiplied out, the $\eta_n(t)$ and $\eta_p(t)$ terms cancel, reducing the equations to Eq. (2.20) and Eq. (2.21) respectively. Effectively the equations are unchanged by inclusion of the above terms.

$$\begin{aligned}
 -\frac{d\Delta n_{nm}(t)}{dt} = & C_n N_t \left[\Delta n_{nm}(t) \left(\frac{n_{po} + n_1}{N_t} + \frac{n_1}{n_{po} + n_1} + \frac{\eta_n(t)\Delta n(0)}{N_t} \right) \right. \\
 & - \Delta p_{nm}(t) \left(\frac{(n_{po} + n_1)}{N_t} + \frac{\eta_n(t)\Delta p(0)}{N_t} \right) \\
 & \left. + \frac{1}{N_t} [\Delta n_{nm}(t)\Delta n(0) - \Delta p_{nm}(t)\Delta p(0)] (\Delta n_{nm}(t) - \eta_n(t)) \right]
 \end{aligned} \tag{2.23}$$

Similarly for Eq. (2.21) substitutions of a corresponding set of terms containing $\eta_p(t)$ result in Eq. (2.24).

$$\begin{aligned}
 -\frac{d\Delta p_{nm}(t)}{dt} = & C_p N_t \left[\Delta p_{nm}(t) \left(\frac{p_{po} + p_1}{N_t} + \frac{p_1}{p_{po} + p_1} + \frac{\eta_p(t)\Delta p(0)}{N_t} \right) \right. \\
 & - \Delta n_{nm}(t) \left(\frac{(p_{po} + p_1)}{N_t} + \frac{\eta_p(t)\Delta n(0)}{N_t} \right) \\
 & \left. + \frac{1}{N_t} [\Delta p_{nm}(t)\Delta p(0) - \Delta n_{nm}(t)\Delta n(0)] (\Delta p_{nm}(t) - \eta_p(t)) \right]
 \end{aligned} \tag{2.24}$$

Using the charge neutrality relation with $\eta_n(t) = \Delta f(t)$, the non-linear term in Eq. (2.23) referred to as $g^n(t)$ may be written as follows:

$$g^n(t) = -(\Delta n_{nm}(t) - \eta_n(t))\eta_n(t) \tag{2.25}$$

From Eq. (2.25) two cases exist for the non-linear function $g^n(t)$ to vanish at a certain time t_0 . Either $\Delta n_{nm}(t_0) - \eta_n(t_0) > 0$ and $\eta_n(t_0) = 0$ or, $\Delta n_{nm}(t_0) - \eta_n(t_0) = 0$ and $\eta_n(t_0) > 0$.

The first case is satisfied at $t_0 = 0^+$ as $\eta_n(0^+) = 0$ since $\Delta f(0^+) = 0$ and from the charge neutrality relation, $\eta_p(0^+) = 0$. This corresponds to a linear region of frequency variation with excess carrier concentration as is further explained at the end of this section. At $t_0 = 0^+$ the non-linear term vanishes and the Eq. (2.20) becomes linear.

In the second case which corresponds to a non-linear region of frequency variation with excess carrier concentration (see end of section), $\eta_n(t_0) > 0$ and $\eta_p(t_0) > 0$ with $t_0 = t_i$ such that $\Delta n_{nm}(t_i) - \eta_n(t_i) = 0$. Again $g^n(t_i)$ goes to zero with $\eta_n(t_i) = \Delta f(t_i) = \Delta n_{nm}(t_i)$. Effectively there is an intersection of $\Delta f(t)$ and $\Delta n_{nm}(t)$ whereas in the linear region of frequency variation above there is no intersection.

Similarly the non-linear term in Eq. (2.24) referred to as $g^p(t)$ may be expressed using the charge neutrality relation for $\Delta p_{nm}(t)$.

$$g^p(t) = \left(\Delta n_{nm}(t) + \Delta f(t) \frac{N_t}{\Delta n(0)} - \eta_p(t) \right) \eta_n(t) \quad (2.26)$$

At low injection $\eta_p(0^+) = 0$ and at high injection the choice of $\eta_p(t_0) > 0$, given $\Delta f(t_i) = \Delta n_{nm}(t_i)$ results in $g^p(t) = 0$ at $t_0 = t_i$.

$$\eta_p(t_i) = \Delta f(t_i) \left(1.0 + \frac{N_t}{\Delta n(0)} \right) \quad (2.27)$$

The differential equations (2.23) and (2.24) are written in a simplified linear form similar to that by Streetman [5] at $t_0 = 0^+$ or $t_0 = t_i$ as Eqs. (2.28). Constants $\eta_n(t_0)$ and $\eta_p(t_0)$ are dependent on the injection level. In Appendix A $\eta_n(t_0)$ and a condition for $\eta_n(t_0) > 0$, at some $t_0 = t_i$ is evaluated.

$$-\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=t_0} = \alpha \Delta p_{nm}(t_0) - \beta \Delta n_{nm}(t_0) \quad (2.28a)$$

$$-\left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=t_0} = \gamma \Delta n_{nm}(t_0) - \sigma \Delta p_{nm}(t_0) \quad (2.28b)$$

where α , β , γ and σ now contain the $\eta_n(t_0)$ and $\eta_p(t_0)$ terms for the two cases indicated above such that $t_0 = 0^+$ or $t_0 = t_i$, with $\Delta n(0) = \Delta p(0)$.

$$\alpha = C_p N_t \left\{ \frac{p_1}{p_{p0} + p_1} + \frac{p_{p0} + p_1}{N_t} + \frac{\eta_p(t_0) \Delta p(0)}{N_t} \right\} \quad (2.29a)$$

$$\beta = C_p N_t \left\{ \frac{p_{po} + p_1}{N_t} + \frac{\eta_p(t_0) \Delta n(0)}{N_t} \right\} \quad (2.29b)$$

$$\gamma = C_n N_t \left\{ \frac{n_1}{n_{po} + n_1} + \frac{n_{po} + n_1}{N_t} + \frac{\eta_n(t_0) \Delta n(0)}{N_t} \right\} \quad (2.29c)$$

$$\sigma = C_n N_t \left\{ \frac{n_{po} + n_1}{N_t} + \frac{\eta_n(t_0) \Delta p(0)}{N_t} \right\} \quad (2.29d)$$

The method using the differential operator $D = d/dt$ in Jordan [14] and Kreyszig [15] whereby the determinant of the matrix of equations (2.28) equals zero, allows the formation of the characteristic equation.

$$(D^2 + (\alpha + \gamma) D + (\alpha\gamma - \sigma\beta)) e^{-\lambda t} = 0 \quad (2.30)$$

The characteristic equation at $t = t_0$ (where the non-linear terms go to zero) may be written as Eq. (2.31). As such the fundamental frequencies λ_1 and λ_2 (inverse time constants) may be evaluated.

$$\lambda^2 - (\alpha + \gamma) \lambda + (\alpha\gamma - \sigma\beta) = 0 \quad (2.31)$$

By evaluating the roots of Eq. (2.31) such that the frequency $\lambda_1 = 1/\tau_+$ and $\lambda_2 = 1/\tau_-$ by comparison with Ref. [5].

$$\lambda_1 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left(1 + \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2} \right)^{\frac{1}{2}} \right) \quad (2.32a)$$

$$\lambda_2 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left(1 - \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2} \right)^{\frac{1}{2}} \right) \quad (2.32b)$$

The linear solution of Eqs. (2.28) for $\Delta p_{nm}(t)$ and $\Delta n_{nm}(t)$ is $\Delta_l p_{nm}(t)$ and $\Delta_l n_{nm}(t)$ respectively with $\Delta_l f(t)$ derived from the charge neutrality relation.

$$\Delta_l p_{nm}(t) = P_{10} e^{-\lambda_1 t} + P_{01} e^{-\lambda_2 t} \quad (2.33a)$$

$$\Delta_l n_{nm}(t) = N_{10} e^{-\lambda_1 t} + N_{01} e^{-\lambda_2 t} \quad (2.33b)$$

$$\Delta_l f(t) = F_{10} e^{-\lambda_1 t} + F_{01} e^{-\lambda_2 t} \quad (2.33c)$$

The range of excess carrier density where the fundamental frequencies change with injection level is expressed by Eqs. (2.29) and (2.32). Low injection refers to the situation where the excess carrier density is much less than the equilibrium majority carrier density as in Ref. [11]. The linear region of variation of fundamental frequencies $\lambda_{1,2}$ with injection level or excess carrier density is defined by Eq. (2.34). This condition is satisfied upon expansion of Eq. (2.34) for $\eta_n(t_0) = 0$ and $\eta_p(t_0) = 0$ at $t_0 = 0^+$. The requirement is found from $\eta_n(t) = \Delta f(t)$ which equals zero at $t = 0^+$ as $\Delta f(t)$, the defect level excess electron concentration, is zero at $t = 0^+$. An upper limit for the linear region of excess carrier density exists referred to as $\Delta n(0)_{critical}$, is evaluated in Appendix A. Hence $\eta_n(0^+) = 0$ and $\eta_p(0^+) = 0$, renders Eqs. (2.23) and (2.24) linear for all injection levels less than $\Delta n(0)_{critical}$.

$$\frac{d\lambda_{1,2}}{d\Delta n(0)} = 0 \quad (2.34)$$

The non-linear region of variation of fundamental frequencies $\lambda_{1,2}$ with injection level or excess carrier density is defined by Eq. (2.35). This corresponds to the range of excess carrier density whereby the change in fundamental frequency with injection level is non-zero as expressed by Eq. (2.35). This condition is satisfied for $\eta_n(t_0) > 0$ and $\eta_p(t_0) > 0$ for some value of t_0 . As such $\Delta f(t) > 0$ can only be achieved with $t_0 > 0^+$ as $\Delta f(t)$ is greater than zero except at $t = 0^+$ and $t = \infty$. The equations (2.23) and (2.24) are linear at $t_0 = t_i$.

$$\left| \frac{d\lambda_{1,2}}{d\Delta n(0)} \right| > 0 \quad (2.35)$$

2.4 Derivation of an Analytic Solution for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$

Having evaluated the frequencies λ_1 and λ_2 derived from the linear equations at time $t = 0^+$ or t_i , it now remains to find a solution for the rate equations away from the equilibrium points 0^+ and t_i . It is shown below that the general solution for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$, consists of the same infinite series of mono-exponential terms with different coefficients respectively, the inverse time constants of which are

a linear combination of those frequencies of the linear solution. The non-linear differential rate equations for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ are re-written as indefinite integral expressions for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ respectively. These expressions are solved by repeated integration by parts, to reveal an infinity of mono-exponential terms for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$. In this format the coefficients may be derived recursively in a nested fashion which is not computationally convenient. Having established that the solution is an infinity of exponential terms, equating coefficients on both sides of the rate equations, realises simultaneous equations which are independent provided λ_1/λ_2 is irrational. This uniquely identifies, and allows the evaluation of the coefficients by a recurrence relation. A definition of linearity is provided in Ref. [16] which includes the state of the system prior to application of the impulse $\delta(t)$. Since each mono-exponential term in $\Delta n_{nm}(t)$ is the solution of a linear differential equation with a constant coefficient, the solution is the response to an infinite number of linear systems. As such the solution for $\Delta n_{nm}(t)$ represents the impulse response and provides a general solution to the rate equations. The region of convergence about the equilibrium point $t = 0^+$ is examined.

The unconstrained coupled differential equations we are interested in are of the form of Eqs. (2.36), (2.37) and (2.38) taken from Eqs. (2.20) and (2.21), and substituting the charge neutrality relation.

$$\begin{aligned} -\frac{d\Delta n_{nm}(t)}{dt}\Delta n(0) &= (\gamma_0 - \sigma_0)\Delta n_{nm}(t)\Delta n(0) \\ &\quad - \sigma_0 N_t \Delta f(t) \\ &\quad - C_n N_t \Delta n_{nm}(t)\Delta n(0)\Delta f(t) \end{aligned} \quad (2.36)$$

$$\begin{aligned} -\frac{d\Delta p_{nm}(t)}{dt}\Delta n(0) &= (\alpha_0 - \beta_0)\Delta p_{nm}(t)\Delta n(0) \\ &\quad + \beta_0 N_t \Delta f(t) \\ &\quad + C_p N_t \Delta p_{nm}(t)\Delta n(0)\Delta f(t) \end{aligned} \quad (2.37)$$

$$\Delta p_{nm}(t)\Delta n(0) = \Delta n_{nm}(t)\Delta n(0) + N_t \Delta f(t) \quad (2.38)$$

An insight is gained into the solution of the above non-linear rate equations as follows. On substitution of the linear solutions Eqs. (2.33) for $\Delta n_{nm}(t)$ $\Delta p_{nm}(t)$

and $\Delta_I f(t)$ into the above coupled differential equations (2.36) and (2.37) representing the global evolution of $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ respectively, we find that for example $\exp(-2\lambda_1 t)$, $\exp(-2\lambda_2 t)$ and $\exp(-(\lambda_1 + \lambda_2)t)$, are generated on the right hand side and not on the left. Continuing by including $\exp(-2\lambda_1 t)$ etc. in a solution and further inclusion of exponents which do not match, we intuitively expect an infinity of exponential terms in the solution form for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and via the charge neutrality relation for $\Delta f(t)$. We expect the non-linear solution to have an infinite number of exponential terms and the time constants to be a linear combination of the two fundamental frequencies λ_1 and λ_2 , where the eigenvalues of the linearised system are given by $-\lambda_1$ and $-\lambda_2$. A more rigorous analysis is given in Appendix B.

The following solution form is proposed for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and via the charge neutrality relation $\Delta f(t)$, with the notation $E_{i,j} = \exp(-i\lambda_1 t - j\lambda_2 t)$.

$$\begin{aligned}\Delta n_{nm}(t) &= \sum_i^{\infty} \sum_j^{\infty} N_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \\ &= \sum_i^{\infty} \sum_j^{\infty} N_{i,j} E_{i,j}\end{aligned}\tag{2.39a}$$

$$\begin{aligned}\Delta p_{nm}(t) &= \sum_i^{\infty} \sum_j^{\infty} P_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \\ &= \sum_i^{\infty} \sum_j^{\infty} P_{i,j} E_{i,j}\end{aligned}\tag{2.39b}$$

$$\begin{aligned}\Delta f(t) &= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} F_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \\ &= \sum_i^{\infty} \sum_j^{\infty} F_{i,j} E_{i,j}\end{aligned}\tag{2.39c}$$

The coefficients of the exponential terms are determined by solving simultaneous equations. The procedure for evaluating the coefficients $P_{i,j}$, $N_{i,j}$ and $F_{i,j}$ is to substitute Eq. (2.39) into Eqs. (2.36), (2.37) and (2.38). Note that the $\exp(-(i\lambda_1 + j\lambda_2)t)$ are linearly independent functions for various (i, j) provided λ_1/λ_2 is irrational. So equality for all t can only be attained by matching the coefficients of appropriate

exponentials on both sides. For $i = 0$ and $j = 0$ the coefficients N_{00} , P_{00} and F_{00} are defined to be equal to values at $t_0 = 0^+$ or $t_0 = t_i$. As $t \rightarrow 0^+$, $E_{i,j} \rightarrow 1$ and hence $\Delta n_{nm}(0^+) = N_{00}$ with $N_{00} = 1$. Confirmation of the above method of equating coefficients is given in Appendix B and the coefficients F_{10} and F_{01} are determined in Appendix C. Hence N_{10} and P_{10} may be evaluated in terms of F_{10} as follows.

$$((\gamma_0 - \sigma_0) - \lambda_1) N_{10} - \sigma_0 \frac{N_t}{\Delta n(0)} F_{10} = C_n N_t (2N_{00} F_{10}) \quad (2.40a)$$

$$((\alpha_0 - \beta_0) - \lambda_1) P_{10} + \beta_0 \frac{N_t}{\Delta p(0)} F_{10} = -C_p N_t (2P_{00} F_{10}) \quad (2.40b)$$

Three simultaneous equations may be formed by equating coefficients for $i = 1, j = 1$, such that N_{11} and P_{11} may be evaluated in terms of N_{10} , N_{01} , P_{10} and P_{01} given F_{10} and F_{01} .

$$((\gamma_0 - \sigma_0) - (\lambda_1 + \lambda_2)) N_{11} - \sigma_0 \frac{N_t}{\Delta n(0)} F_{11} = C_n N_t (N_{10} F_{01} + N_{01} F_{10} + 2N_{00} F_{11}) \quad (2.41a)$$

$$((\alpha_0 - \beta_0) - (\lambda_1 + \lambda_2)) P_{11} + \beta_0 \frac{N_t}{\Delta p(0)} F_{11} = -C_p N_t (P_{10} F_{01} + P_{01} F_{10} + 2P_{00} F_{11}) \quad (2.41b)$$

$$P_{11} \Delta p(0) - N_{11} \Delta n(0) - N_t F_{11} = 0 \quad (2.41c)$$

Continuing to solve the simultaneous equations for further coefficients, a solution set for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ may be realised in terms of F_{10} and F_{01} . A global solution for $f(t)$ is obtained by substitution of solutions for $\Delta n(t)$ and $\Delta p(t)$ into the expression for the charge neutrality relation Eq. (2.18). From Eq. (2.36) a recurrence relation may be formed which simplifies the calculation of the coefficients $N_{i,j}$ and $F_{i,j}$ with $i = 1, 2, \dots \infty$ and $j = 1, 2, \dots \infty$. Similarly a recurrence relation for $P_{i,j}$ may be formed.

$$\begin{aligned} \sum_i \sum_j (i\lambda_1 + j\lambda_2) N_{i,j} E_{i,j} &= (\gamma_0 - \sigma_0) \sum_i \sum_j N_{i,j} E_{i,j} \\ &\quad - \sigma_0 \frac{N_t}{\Delta n(0)} \sum_i \sum_j F_{i,j} E_{i,j} \\ &\quad - C_n N_t \sum_i \sum_j S_{i,j} \end{aligned} \quad (2.42)$$

where $E_{0,0} = 1$ and

$$S_{i,j} = \sum_u^i \sum_v^j N_{i-u,j-v} F_{u,v} E_{i-u,j-v} E_{u,v} \quad (2.43)$$

The nature of the quadratic form for the SRH differential equation representing $\Delta n_{nm}(t)$ is determined in Appendix D. Further the sum of the responses to an infinity of linear systems which the solution represents is examined in Appendix E.

2.5 Numerical Solution of SRH Equations: Ideal Impulse $\delta(t)$

The unconstrained coupled differential equations we are interested in are of the form of equations (2.44), (2.45) and (2.46) taken from Eqs. (2.20) and (2.21), and substituting the charge neutrality relation.

$$\begin{aligned} -\frac{d\Delta n_{nm}(t)}{dt} \Delta n(0) &= (\gamma_0 - \sigma_0) \Delta n_{nm}(t) \Delta n(0) \\ &\quad - \sigma_0 N_t \Delta f(t) \\ &\quad - C_n N_t \Delta n_{nm}(t) \Delta n(0) \Delta f(t) \end{aligned} \quad (2.44)$$

$$\begin{aligned} -\frac{d\Delta p_{nm}(t)}{dt} \Delta n(0) &= (\alpha_0 - \beta_0) \Delta p_{nm}(t) \Delta n(0) \\ &\quad + \beta_0 N_t \Delta f(t) \\ &\quad + C_p N_t \Delta p_{nm}(t) \Delta n(0) \Delta f(t) \end{aligned} \quad (2.45)$$

$$\frac{d\Delta p_{nm}(t)}{dt} \Delta n(0) = \frac{d\Delta n_{nm}(t)}{dt} \Delta n(0) + N_t \frac{d\Delta f(t)}{dt} \quad (2.46)$$

The three equations (2.44), (2.45) and (2.46) form a set of second order coupled differential equations Nomura and Blakemore [4] which are non-linear and solved numerically. No a priori knowledge is known about $\Delta n_{nm}(t + \Delta t)$ as it represents the time evolution of the excess carrier concentration derived numerically. A correlation between the numerical solution and the predictions of the analytical solution is made and found to indicate close agreement. This confirms the method used to analyse the decay as a useful tool.

Table 2.1: Typical Parameters for Numerical Solution.

T	300.0	temperature [K]
nn	2048	number of time samples
Δt	2×10^{-8}	time sample interval sec
N_A	5×10^{13}	majority carrier concentration cm^{-3}
$E_t - E_v$	0.65	energy level depth from valence band eV
$\Delta n(0)$	5×10^9	excess carrier concentration cm^{-3}
N_t	5×10^{11}	discrete level concentration cm^{-3}
σ_p	8.5×10^{-17}	cross section for holes cm^2
σ_n	9×10^{-15}	cross section for electrons cm^2

A fourth and fifth order Runge-Kutta scheme in Refs. [17] and [18], is chosen to represent discrete values of $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$, to ensure convergence to the equilibrium concentration for the minority carrier as $t \rightarrow \infty$. Figure 2.1 representing the phase diagram as in Ref. [19] indicates the convergence to the equilibrium point for the example given by table 2.1. The normalised excess carrier concentrations at $t = 0^+$ are given by $\Delta n_{nm}(0^+) = 1.0$ and $\Delta p_{nm}(0^+) = 1.0$. The defect level initial occupation is assumed not to change from $t = 0^-$ to $t = 0^+$ ($f(0^+) = f(0^-)$). Table 2.1 indicates typical data used in the numerical solution.

Multi-transient analysis refers to the extraction of component exponential terms from a sum of exponentials comprising the signal. The methods available Yeramian and Claverie [20], Claverie [21] and Alam [22] present a means of analysing signals with additive white gaussian noise. In addition where the data matrix and the observation matrix may be subject to noise fluctuations, the Total Least Squares method in Ref. [23] (TLS) is employed. This method models the multi-exponential signal as an autoregressive process. For the present analysis the TLS method of Refs. [22] and [24] multi-transient analysis using Singular Value Decomposition (SVD) Klema [25] is applied to the analysis of the multi-component exponential decay.

TLS multi-transient analysis of the numerical solution of Eqs. (2.44), (2.45) and (2.46) results in the determination of frequencies which are compared with

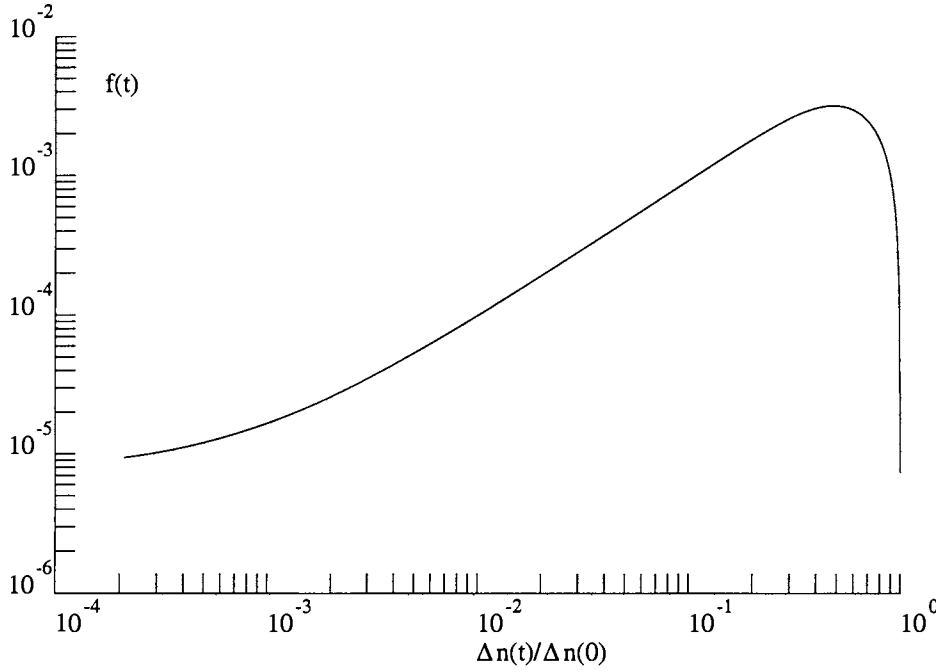


Figure 2.1: Phase diagram indicating convergence to the equilibrium point for the given example where $\Delta n(t)$ is normalised to $\Delta n(0)$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$

the existing theoretical expressions Eqs. (2.32) for low through to high injection. Figure 2.2 shows the comparison between the decay time constants $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ as calculated from Eq. (2.32) and as evaluated by TLS analysis of numerical data ($\Delta n(t + \Delta t)$) for $T = 300 \text{ K}$. The figure indicates the variation from low injection through to high injection. Note the excess carrier concentration $\Delta n(0)$ varies from $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is excellent and as such contributes to the confidence in the TLS method of analysis. The onset of the non-linear variation of frequencies λ_1 and λ_2 with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{\text{critical}}$ is clearly seen in the figure where the linear portion extends to $5 \times 10^{11} \text{ cm}^{-3}$ and begins to diverge for $\Delta n(0)$ greater than $5 \times 10^{11} \text{ cm}^{-3}$. This indicates that the linear region is in close agreement with the definition given by Eq. (2.34). See Appendix A for the evaluation of $\Delta n(0)_{\text{critical}}$. For parameters listed in table 2.1, $\Delta n(0)_{\text{critical}} = 5.44 \times 10^{11} \text{ cm}^{-3}$. Note also that TLS multi-transient analysis of the numerical solution results in τ_1 and τ_2 in close agreement with that predicted by the solution for τ_1 and τ_2 of Eq. (2.32) for high injection.

Figure 2.3 shows the comparison between the decay time constants τ_1 and τ_2

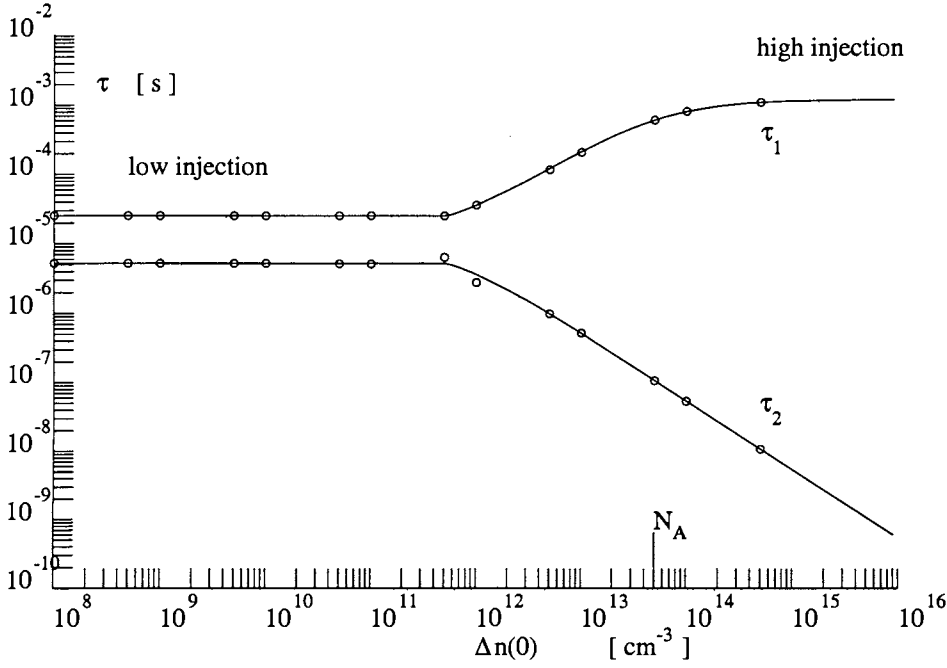


Figure 2.2: A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 2.1 for defect level parameters. Continuous line: τ_1 and τ_2 predicted by Eq. (2.32) Circles: τ_1 and τ_2 derived from multi-transient analysis of the numerical solution.

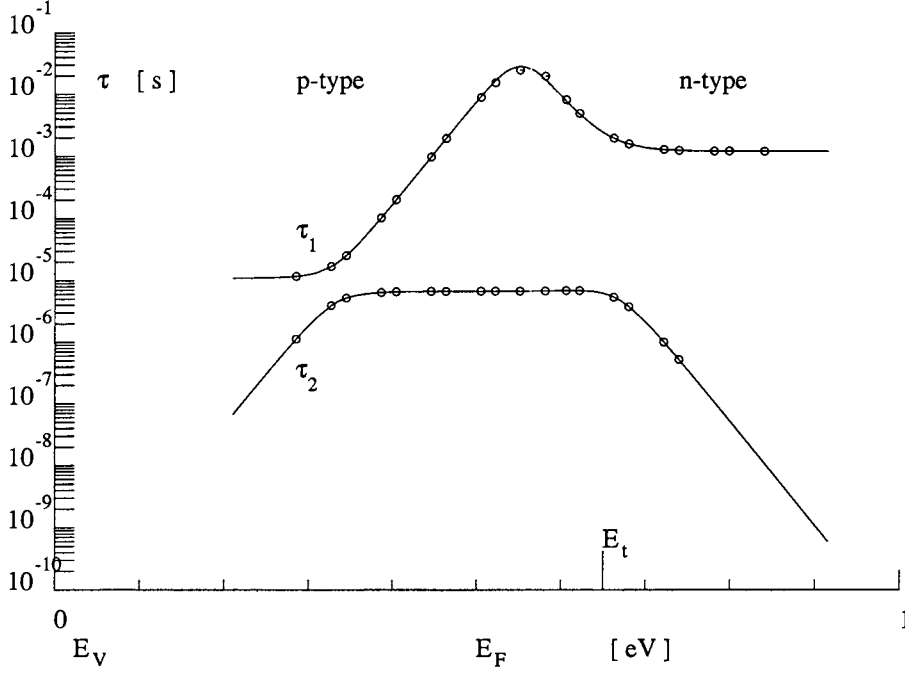


Figure 2.3: Decay time constant $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus the Fermi level E_F eV for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. See Table 2.1 for parameters. Continuous line: τ_1 and τ_2 calculated by Eq. (2.32). Circles: TLS analysis of numerical solution $\Delta n(t + \Delta t)$.

as calculated from Eq. (2.32) and as evaluated by TLS analysis of numerical data ($\Delta n(t + \Delta t)$) for $T = 300 \text{ K}$, versus the Fermi level E_F . The doping concentration for the p-type and n-type samples varies from $5 \times 10^{10} \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is very good for the numerical solution and the calculated τ_1 and τ_2 . From this figure τ_1 describes the minority carrier decay constant and τ_2 , the majority carrier decay constant, by analogy with Shockley and Read [2] for the steady state. As such they represent fundamental decay time constants.

Figure 2.2 indicates that for $\Delta n(0) > \Delta n(0)_{\text{critical}}$, τ_1 increases realising a situation where the minority carrier (p-type) time constant represented by τ_1 is becoming longer. The minority carriers (electrons) are remaining in the conduction band for a longer average time indicating that there are fewer holes at the defect level to recombine with. As such the defect level electron population is increasing and electrons are remaining at the defect level for a longer average time. This is referred to as minority carrier trapping. The time constant τ_1 remains constant in the linear re-

gion of variation of $\tau_{1,2}$ with $\Delta n(0)$. This region corresponds to recombination only whereas the non-linear region undergoes recombination and trapping. Eventually the trapping saturates as $\Delta n(0)$ is increased to high injection and the time constant τ_1 reaches a maximum becoming almost constant.

Further by recalling the expression Eq. (2.39) for the decay $\Delta n_{nm}(t)$ the infinity of time constants is found to be linear combinations of two fundamental frequencies λ_1 and λ_2 . Table 2.2 indicates the correlation with the prediction of Eqs. (2.32) and (2.39), and TLS analysis of the decay $\Delta n(t + \Delta t)$ within the limitations of the TLS method. No a priori knowledge is known about time constants associated with the numerical solution, yet the agreement of the analytical and TLS methods with respect to the linear combination of λ_1 and λ_2 and their magnitude, is excellent. The TLS multi-transient analysis also reveals the same magnitudes of the coefficients of the exponential terms as by the analytical approach (see Appendix C). Note the magnitudes of the coefficients decrease rapidly. In addition for the transient case in low injection, the magnitude of the coefficient for τ_2 is significant. By evaluating an error term ε Eq. (2.47), being the difference between the series with calculated coefficients as determined in Appendix C, and the numerical solution, an estimate of the agreement of the two approaches may be made.

$$\varepsilon = \left| \frac{\sum_i^\infty \sum_j^\infty N_{i,j} E_{i,j} - \Delta n(t + \Delta t)}{\Delta n(0)} \right| \quad (2.47)$$

Figure 2.4 indicates the agreement for the linear and non-linear regions of variation of $\lambda_{1,2}$ with $\Delta n(0)$. The indicated closeness of fit between the two approaches is good for the initial part of the decay and diverges for large time. This may be explained by accumulation of error in the Runge Kutta numerical method. Further the value for $d\Delta n_{nm}(t)/dt$ at $t = 0^+$ for the series $N_{i,j}$ at $t = 0^+$ at the indicated injection levels, is 9.15075×10^4 which is in close agreement with the predicted value (see Eq. (C.1)). This verifies the calculated values of the coefficients $N_{i,j}$ by the method outlined in Appendix C.

Table 2.2: TLS analysis of numerical data $\Delta n(t + \Delta t)$ and evaluation of Eq. (2.32). Note the prediction of Eq. (2.39) with frequencies a linear combination of the fundamental frequencies and calculated coefficients $N_{i,j}$. $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$.

λ	Eq. (2.32) $\lambda \text{ sec}^{-1}$	TLS frequency $\lambda \text{ sec}^{-1}$	TLS coefficient normalised to $\Delta n(0)$	calculated coefficient $N_{i,j}$
λ_1	3.92871×10^4	3.92871×10^4	$N_{10} = 6.5804 \times 10^{-1}$	6.5804×10^{-1}
$2\lambda_1$		7.99744×10^4	$N_{20} = -2.135 \times 10^{-4}$	-2.024×10^{-4}
λ_2	19.10753×10^4	19.1069×10^4	$N_{01} = 3.3825 \times 10^{-1}$	3.3783×10^{-1}
$\lambda_1 + \lambda_2$		23.3579×10^4	$N_{11} = 3.0767 \times 10^{-3}$	3.4045×10^{-3}
$2\lambda_2$		38.3739×10^4	$N_{02} = 8.4177 \times 10^{-4}$	8.3745×10^{-4}
$3\lambda_2$		60.1207×10^4	$N_{03} = 1.3457 \times 10^{-6}$	1.8820×10^{-6}

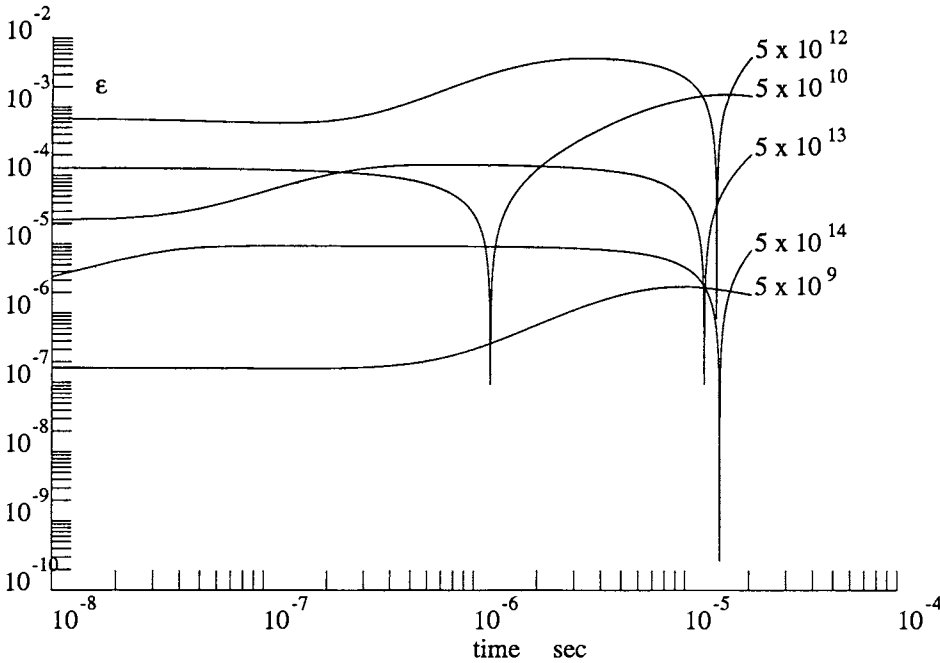


Figure 2.4: Normalised error ε Eq. (2.47) between predicted values of $N_{i,j}E_{i,j}$ and numerical solution $\Delta n(t + \Delta t)$ for $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$ to $\Delta n(0) = 5 \times 10^{14} \text{ cm}^{-3}$. This corresponds to the linear and non-linear regions of variation of $\Delta n(0)$ with $\lambda_{1,2}$. $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ and $\Delta t = 1 \times 10^{-8} \text{ sec}$.

2.6 Further Aspects of Trapping

The definition of trapping is further addressed in order to clarify past definitions and a definition that encompasses trapping, recombination and generation. For the present case of a p-type semiconductor the first definition of minority carrier (electrons) trapping may be expressed as:

- The defect level electron concentration Δn_t increases with increasing excess carrier concentration effectively accumulating electrons at the level.

In this work the above definition gives insight into the unique behaviour of the fundamental time constant τ_1 with excess carrier concentration in both n-type and p-type semiconductor as opposed to the other fundamental time constants τ_{k+1} (see also Chapter 4 on multiple defect levels). However it may be that a further definition that follows from a discussion on carrier transitions via defects by Blakemore [26] and Sah [27] is more acceptable from the physics of the trapping process. This extended second definition may be expressed in terms of the SRH rate equations [2] of Eq. (2.48) with the terms determined from the first principles approach to the carrier transitions in Appendix F.

$$\frac{dn(t)}{dt} = e_n N_t f(t) - C_n N_t n(t)[1 - f(t)] \quad (2.48a)$$

$$\frac{dp(t)}{dt} = e_p N_t [1 - f(t)] - C_p N_t p(t)f(t) \quad (2.48b)$$

Eqs. (2.48) describe carrier transitions via a single-level defect and the following indicate required conditions for electron trapping, hole trapping, recombination and generation.

- electron trap: The probability or rate that a defect state captures a conduction band electron ($C_n N_t n(t)[1 - f(t)]$) is greater than capturing a valence band electron - or emitting a hole to the valence band ($e_p N_t [1 - f(t)]$). In addition the trapped electron is emitted to the conduction band ($e_n N_t f(t)$) rather than emit an electron to the valence band or equivalently capture a hole from the valence band ($C_p N_t p(t)f(t)$).

- hole trap: The probability or rate that a defect state captures a valence band hole ($C_p N_t p(t) f(t)$) is greater than capturing a hole from the conduction band or equivalently emitting an electron to the conduction band ($e_n N_t f(t)$). In addition the trapped hole is emitted to the valence band ($e_p N_t [1 - f(t)]$) rather than emit the hole to the conduction band or equivalently capture an electron from the conduction band ($C_n N_t n(t) [1 - f(t)]$).
- recombination center: The probability or rate that a defect state captures a conduction band electron ($C_n N_t n(t) [1 - f(t)]$) is greater than capturing a valence band electron or emitting a hole to the valence band ($e_p N_t [1 - f(t)]$). In addition the trapped electron is emitted to the valence band or a hole is captured from the valence band ($C_p N_t p(t) f(t)$) rather than hole captured from the conduction band or equivalently an electron emitted to the conduction band ($e_n N_t f(t)$).
- generation center: The probability or rate that a defect state captures a valence band electron or equivalently emits a hole to the valence band ($e_p N_t [1 - f(t)]$) is greater than capturing a conduction band electron ($C_n N_t n(t) [1 - f(t)]$). In addition the trapped electron is emitted to the conduction band ($e_n N_t f(t)$) rather than the electron emitted to the valence band or equivalently capturing a hole from the valence band ($C_p N_t p(t) f(t)$).

These definitions may be summarised in Table 2.3.

From Table 2.3 an expression for the recombination characteristics of a center at low excess carrier concentration may be evaluated. The first criteria or inequality for recombination is determined with $n(t) = n_{po} + \Delta n(t)$. Eq. (2.49) with $e_p = C_p p_1$. Equation (2.49) is determined from Eqs. (C.1) and (C.2) of Appendix C and Eq. (2.16a).

$$-\left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=0+} [n_{po} + \Delta n(t)] > -p_{po} \left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=0+} \quad (2.49)$$

Eq. (2.49) indicates that for the present case (see Table 2.1 for parameters) with $dn/dt = 9.15 \times 10^4$ and $dp/dt = 8.25 \times 10^2$ at $t = 0^+$ this inequality is not satisfied

Table 2.3: Requirements for an electron trap, hole trap, recombination center and generation center.

Type of center	Definition
electron trap	$C_n n(t) > e_p$ $e_n > C_p p(t)$
hole trap	$C_p p(t) > e_n$ $e_p > C_n n(t)$
recombination center	$C_n n(t) > e_p$ $C_p p(t) > e_n$
generation center	$e_p > C_n n(t)$ $e_n > C_p p(t)$

in the linear region (constant region) of variation of τ_1 with excess carrier concentration. Hence, this level center acts neither as a recombination center only nor an electron trap only in this region. It may still act as a hole trap together with recombination in this linear region. Furthermore, electron (minority carrier) trapping occurs for $\Delta n(0) > 4.5 \times 10^{11} \text{ cm}^{-3}$, which is close to $\Delta n(0)_{critical} = 5.44 \times 10^{11} \text{ cm}^{-3}$. Effectively, electron trapping occurs near $\Delta n(0)_{critical}$ and for $\Delta n(0) > \Delta n(0)_{critical}$. Hence, in the linear region there is no electron trapping except near $\Delta n(0)_{critical}$ for the defect example given in Table 2.1. This validates the use of the first definition of trapping and the explanation of the increase of τ_1 for $\Delta n(0) > \Delta n(0)_{critical}$ with minority carrier (electrons) trapping given in Section 2.5.

However, for a level near the band edge (conduction band) it is expected that emission e_n is more probable as is capture of electrons as n_1 is greater and electron trapping may be more likely. The theory may be similarly applied to other defect parameters and doping concentration. The defect level parameters of cross section, level depth and concentration determine the unique values of the fundamental frequencies and so the series of monoexponential terms may be constructed as in Section 2.4 and Appendix C. From the series of terms the values of the differentials in Eq. (2.49) at $t = 0^+$ may be evaluated and the trapping characteristics of the

center determined according to the definitions of Table 2.3. This may be done either by resolving the fundamental frequencies from the experimental decay using a multitransient technique and constructing the exponential series or directly evaluating the terms.

2.7 Proposed Experimental Conditions

Specifically with regard to a p-type silicon wafer, for infra red light pulses produced by a YAG laser at $t = 0^+$ with a wavelength of $1.064\mu m$, a uniform excess carrier concentration may be generated within a sample of $50\mu m$ thickness Luke [28]. This produces the initial condition $\Delta n(0) = \Delta p(0)$ at $t = 0^+$. Silicon nitride passivated surfaces provide a low effective surface recombination velocity (S_{eff}) on a float zone p-type silicon wafer as in ref. [29]. Similarly a low surface recombination velocity may be attained with the $Si - SiO_2$ system as in Ref. [30]. The effective surface recombination velocity is taken to be injection level dependent in Refs. [29] and [30]. For excess carrier concentrations $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$ an $S_{eff} < 50 \text{ cm/s}$ is assumed to be attainable with appropriate processing with the $Si - SiO_2$ system for a wafer resistivity of the order of $250 \Omega cm$ ($5 \times 10^{13} \text{ cm}^{-3}$). The decay of excess carriers may be detected by a contactless microwave photoconductance measurement. Furthermore a dominant level with an energy near midgap (such as one of the gold levels at $E_t - E_v = 0.65eV$) which represents an efficient recombination centre, is the basis for the single level model. The defect level concentration is assumed to be uniformly distributed throughout the sample.

In terms of direct application a possibility immediately arises from the present work where a silicon sample is processed as above. Minority carrier trapping for a dominant defect level may be evaluated by an analysis of the decay due to an impulse of light as previously indicated to determine τ_1 and a plot of this quantity against the excess carrier concentration $\Delta n(0)$. Since τ_1 represents the minority carrier for a dominant defect level, a measure of material quality is attained by an assessment of minority carrier trapping. From the charge neutrality relationship increasing the excess carrier concentration in the sample means that both $\Delta n(t)$ and $\Delta p(t)$ are

measured. However from the present work both quantities contain the same decay constants. The decay may be analysed for τ_1 and given the relative magnitude of excess carrier concentration wafers may be compared for quality. Ideally the range of excess carrier concentration should encompass the linear region and the non-linear region of variation of $\tau_{1,2}$ with excess carrier concentration.

2.8 Discussion

As stated previously the steady state decay time constant is the same as the transient decay time constant with only the magnitudes of the coefficients of the exponential terms differing from steady state to transient. Existing experimental data are largely interpreted using the expressions derived in Ref. [2] with approximations as indicated in the introduction. The current work seeks to address the anomalies arising from such an interpretation in terms of the defect level parameters such as level depth. To this effect for example figure 2.5 indicates the variation of τ_1 with excess carrier concentration and that of τ_{L-SRH} and τ_{H-SRH} of Ref. [2] representing equations (5.3) and (6.1) respectively of that paper. Note that τ_{L-SRH} is the low excess carrier time constant and τ_{H-SRH} is the high excess carrier concentration time constant. From the figure τ_{L-SRH} underestimates τ_1 by approximately thirty percent in the linear region. Although τ_{H-SRH} is a good fit in the non-linear region in terms of determining material quality for a dominant defect again the degree of trapping is unknown. However for defect level parameter estimation decay experiments are usually conducted in the linear region (low excess carrier concentration). The reason for the discrepancy in the linear region is that in the original paper of Ref. [2] the change in charge density produced by changing concentration in the traps is neglected. The present work makes no such assumption. Referring to the figure from the low and high excess carrier concentration time constants the $\Delta n(0)_{critical}$ cannot be determined. As a result the extent of the linear region is unknown from these time constants. The extent of the linear region is also unknown with the work of Streetman [5]. Without knowing the limit on excess carrier concentration defining the linear region reduces the application of Ref. [2] and Ref. [5] in practice unless

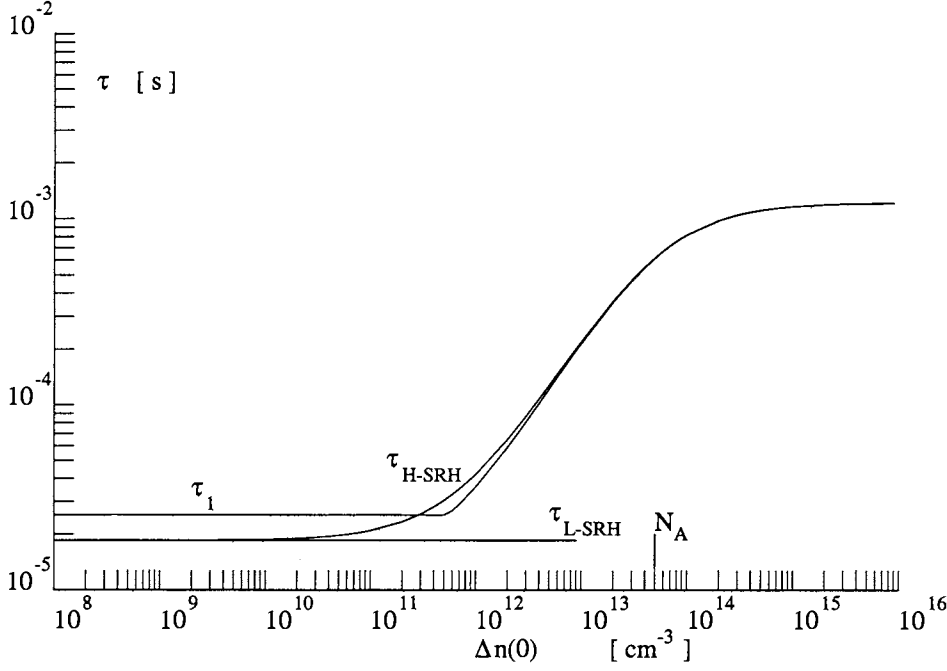


Figure 2.5: A graph of $\tau_1 = 1/\lambda_1$ and τ_{L-SRH} , τ_{H-SRH} versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 2.1 for defect level parameters.

the time constants are plotted against a range of excess carrier concentrations to ascertain the onset of trapping.

Chapter 3

Accuracy of the Shockley-Read-Hall Time Constant for a Single-Level Defect Species

3.1 Introduction

A dominant recombination mechanism in semiconductors, apart from Auger recombination, is Shockley-Read-Hall (SRH) recombination as described by the SRH rate equations in 1952 [2] [3]. Shockley and Read developed an expression for the recombination time constant in the steady state τ_{ss} . Although developed for the steady state, the theory has been applied to the transient case in the neighbourhood of the equilibrium point (small signal) and the time constant is referred to as τ_b . This applies to a single-level defect although in practical situations multiple defect levels occur. These rate equations have been applied to the analysis of experimental data assuming a dominant defect energy level. The literature indicates conflicting partial solutions to the rate equations, notably the expression with a single time constant [2] which is defined as (3.1), where U represents the recombination rate,

and expressions of several authors with two time constants, indicated below.

$$\tau_{ss} = \frac{\Delta n}{U} \quad (3.1)$$

The focus of the present work is to show that the SRH expression is an approximation, indicate the source of the approximation which for the given example amounts to a relative error of thirty percent, and resolve the conflicting issues. The recent general analytic method of solution [1], for the transient case developed without an approximation, is applied to the SRH rate equations (3.2) to obtain a new steady state solution. This solution is compared to the existing steady state SRH time constant expression.

$$-\frac{dp(t)}{dt} = C_p N_t p(t) f(t) - e_p N_t (1 - f(t)) \quad (3.2a)$$

$$-\frac{dn(t)}{dt} = C_n N_t n(t) (1 - f(t)) - e_n N_t f(t) \quad (3.2b)$$

In Eq. (3.2), N_t is the defect concentration, $n(t)$, $p(t)$ are the electron and hole concentrations respectively, $f(t)$ is the defect occupancy function or probability function, C_n and C_p are the electron and hole capture coefficients and, e_n and e_p are the electron and hole emission rates.

In the present work the theoretical predictions of time constants from the analytic solution are compared with the analysis of the numerical solution for component time constants in the steady state case. Good agreement is found for this comparison. Previous analyses in the literature have assumed the validity of the single time constant expression (3.3) (Eq. 5.3 of Ref. [2]) derived from Eq. (3.1) without such a comparison.

$$\tau_{ss} = \frac{(n_{po} + n_1 + \Delta n)}{C_p N_t (n_{po} + p_{po} + \Delta n)} + \frac{(p_{po} + p_1 + \Delta p)}{C_n N_t (n_{po} + p_{po} + \Delta n)} \quad (3.3)$$

It is shown that the definition, Eq. (3.1), leads to an incorrect theoretical prediction of one time constant τ_{ss} of Eq. (3.3) for the steady state whereas at least two time constants are predicted by the analytic steady state theory presented in this work.

This indicates that the definition Eq. (3.1) is not related to the physics of the carriers.

The present work demonstrates that the steady state solution, determined both analytically and by analysis of the numerical solution, converges to the transient solution of Ref. [1] in the small signal transient limit. This confirms the transient and steady state multiple time constant solutions to be consistent. The single SRH time constant τ_{ss} of Eq. (3.3) is inaccurate which implies from Eq. (3.1) that the recombination term $U = \Delta n / \tau_{ss}$ is also inaccurate. In the literature this recombination term is included in the carrier continuity equation which describes the flux of carriers into and out of a volume of semiconductor [31]. Within the volume there may be recombination and generation. The definition of Eq. (3.1) leads to a recombination term, which at best is convenient as a means to represent the SRH equations in the carrier continuity equation in a mathematical context, is however not physically meaningful. A more accurate recombination term is derived in terms of the concept of fundamental frequencies in Chapter 5.

A brief survey of developments related to the partial solutions of the SRH rate equations follows. A partial solution to the rate equations [7] yielded two time constants written in terms of a "recombination time", "a time to trap a carrier" and "a time to release a trapped carrier". In this case the recombination time constant is defined as in (3.1). In [8] the defect problem is addressed with approximations introduced to elucidate the different features of types of defects. For the transient case, an approximate solution of [6], yields two time constants comprising an initial decay and a transient decay. A set of differential rate equations for multiple discrete levels based on a summation of the single level SRH equations is stated in [9]. Approximations were introduced to provide a linear solution to the non-linear differential equations for small changes in Δp and Δn from the equilibrium values. For the single-level, two time constants result from this solution for the transient case which were simplified to one time constant and an "adjustment time" which agree with [6].

In [4] approximations were applied to the solution not of the rate equations but to the second order differential equation in Δp (3.4) that results from the rate

equations and the charge neutrality condition.

$$\begin{aligned}
 & \frac{N_t}{p_o} \left\{ y'' \left(y + 1 + \frac{p_1}{p_o} \right) - y'^2 \left(1 - \frac{C_n}{C_p} \right) \right\} \\
 & + y' \left\{ y^2 \left(1 + \frac{C_p}{C_n} \right) + y \left[\left(1 + \frac{p_1}{p_o} \right) \left(1 + \frac{n_1}{p_o} + \frac{2C_p}{C_n} \right) \right. \right. \\
 & \quad \left. \left. + \frac{N_t}{p_o} \left(1 + \frac{2p_1}{p_o} \right) / \left(1 + \frac{p_1}{p_o} \right) \right] \right. \\
 & \quad \left. + \left[\left(1 + \frac{p_1}{p_o} \right)^2 \left(\frac{n_1}{p_o} + \frac{C_p}{C_n} \right) + \frac{N_t}{p_o} \left(1 + \frac{C_p p_1}{C_n p_o} \right) \right] \right\} \\
 & + y \frac{C_p}{C_n} \left\{ y^2 + y \left[\left(2 + \frac{p_1}{p_o} + \frac{n_1 p_1}{p_o p_o} \right) + \frac{N_t p_1}{p_o p_o} / \left(1 + \frac{p_1}{p_o} \right) \right] \right. \\
 & \quad \left. + \left[\left(1 + \frac{p_1}{p_o} \right) \left(1 + \frac{n_1 p_1}{p_o p_o} \right) + \frac{N_t p_1}{p_o p_o} / \left(1 + \frac{p_1}{p_o} \right) \right] \right\} \\
 & = 0
 \end{aligned} \tag{3.4}$$

where $y = \Delta p / p_o$ and similarly for Δn and,

$$n_1 = N_c \exp \left(-\frac{(E_c - E_t)}{kT} \right) \tag{3.5a}$$

$$p_1 = N_v \exp \left(-\frac{(E_t - E_v)}{kT} \right) \tag{3.5b}$$

As pointed out by [4], all previous methods of solution of (3.4) including perturbative methods, were unsuccessful in yielding a solution. For this reason previous attempts at solving the rate equations have inherently involved approximations in order to gain some insight into the carrier dynamics. However, Streetman [5] confirmed the existence of two time constants, as also indicated by [9], for small departures from equilibrium for the transient case applied to the single-level defect. In [10], application of the rate equations to coupled states and two independent states is investigated for the transient and steady state situations. The transient time constant expressions agree with [9] and [5] for small departures of the carrier concentration from equilibrium for the single-level case. There are two time constants in these solutions which are in agreement with the exact solution of [1]. This is consistent with the governing second order differential equation (3.4) since there are two eigenvalues of the linear system because the equation is second order.

However, the equations in the multiple level and single level cases, were stated but the resulting time constants were not verified against an analysis of the numerical solution for the component time constants. In Section 3.2 the exact steady state analytic solution is discussed and the steady state fundamental time constants presented. In Section 3.3 the theoretical prediction of these fundamental time constants and analysis of the numerical solution for component time constants are shown to be in close agreement. This solution comprises, for the single-level, two fundamental time constants, τ_1 and τ_2 , which are in agreement with previous derivations notably Refs. [9] [5] for the small signal case and the order of the underlying second order differential equation. In Ref. [1] the minority carrier time constant is defined as τ_1 and the majority carrier as τ_2 . In this respect these two fundamental time constants are directly related to the physics of carrier decay which affect structures such as solar cells. In this case it is the minority carrier represented by τ_1 which is involved in the physics of trapping [1].

In [7] and [10] the steady state time constant is defined as (3.1) as in [2] (Eq. 5.2), without justification. Although two time constants are derived for the minority carrier in n-type and p-type semiconductor material in the appendix of [2], these time constants are defined similar to (3.1). It may be shown that these time constants as defined, for the linear region (constant region) of variation of the dominant time constant τ_1 with excess carrier concentration, corresponding to the small signal case of [1], do not agree with the exact solution as given in [1].

For the single level case, the equation describing the time evolution of the normalised excess electron concentration (3.4), $\Delta n_{nm}(t)$, is a second order non-linear differential equation and has a cubic power of $\Delta n_{nm}(t)$ given as Eq. (9) in [4]. Since the differential equation for $\Delta n_{nm}(t)$ is second order, at least two time constants are expected in the solution (the eigenvalues of the linear system) for all excess carrier concentrations less than the Auger limit and the non-degenerate doping concentration. The steady state is realized with the boundary condition $dn(t)/dt = 0$ at $t = 0^+$ for electrons in the conduction band. Application of the boundary condition is still expected to realize two time constants in the solution since the underlying differential equation is second order.

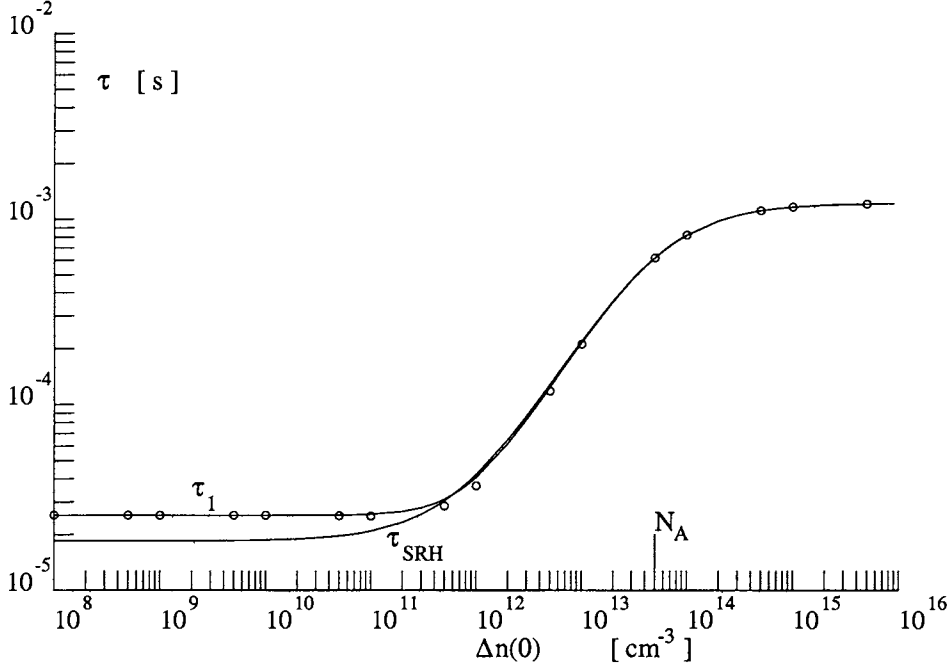


Figure 3.1: A graph of fundamental time constant τ_1 and SRH time constant $\tau_{ss} = \tau_{SRH}$ versus excess carrier concentration $\Delta n(0^+)$. Circles: τ_1 derived from multi-transient analysis of the numerical solution. There is a relative error $\varepsilon \approx 30\%$ between τ_1 and τ_{SRH} in the linear region.

In [2] the steady state is realised by setting $U_n = U_p$ given as Eq. 4.1 of [2]. They define only a single time constant (Eq. 5.2 of [2] repeated as Eq. (3.1) of this work), τ_{ss} , implying the solution of a first, rather than second, order governing differential equation. For a second order equation to become first order, a zero must be cancelled by a pole of the same magnitude and frequency as the zero for all excess carrier concentrations. A zero that is not cancelled should be realized in the solution.

It is shown in Figure 3.1 that the time constant $\tau_{ss} = \tau_{SRH}$ is approximately equal to the dominant time constant τ_1 for only part of the range of excess carrier concentration. Furthermore, the analysis of the numerical solution for component time constants (see Section 3.3) yields close agreement with the predicted value of τ_1 for the steady state. Parameters used for the evaluation are given in [1]. Hence the definition of τ_{ss} in [2], as stated above, yields a time constant expression which is inaccurate.

3.2 Analytic Steady State SRH Solution

A recent analytic solution (3.6) [1] to the SRH rate equations (3.2) is obtained without any approximations for uniform arbitrary non-degenerate doping concentration $N_{A,D}$, defect energy depth E_t , defect concentration N_t and cross sections σ_n and σ_p . The exact solution (3.6) for the single-level comprises an infinity of monoexponential terms with frequencies or inverse time constants a linear combination of two fundamental frequencies $\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$.

$$\Delta n_{nm}(t) = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} N_{u,v} \exp(-u\lambda_1 t - v\lambda_2 t) \quad (3.6a)$$

$$\Delta p_{nm}(t) = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} P_{u,v} \exp(-u\lambda_1 t - v\lambda_2 t) \quad (3.6b)$$

$$\Delta f(t) = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} F_{u,v} \exp(-u\lambda_1 t - v\lambda_2 t) \quad (3.6c)$$

The magnitude, of the coefficients $N_{u,v}$ and $P_{u,v}$ of the exponential terms, falls away rapidly to a very small value so that less than eight terms are significant in the series. The first two coefficients are the most significant, $(u, v) = (1, 0)$ and $(0, 1)$. Expressions for the minority carrier time constant τ_1 and majority time constant τ_2 are derived and given as (3.12). The dominant time constant is τ_1 and its behaviour with excess carrier concentration indicates the onset of trapping. A critical point, representing the transition between the linear (constant) and non-linear variation of fundamental frequency with excess carrier density, is identified.

Application of the method of solution derived in [1] as indicated above, to the steady state is performed as follows. Fundamental frequencies are derived by scaling the differential equations and solving the linear form (3.7) of the non-linear differential equations.

$$-\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=t_0} = \alpha \Delta p_{nm}(t_0) - \beta \Delta n_{nm}(t_0) \quad (3.7a)$$

$$-\left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=t_0} = \gamma \Delta n_{nm}(t_0) - \sigma \Delta p_{nm}(t_0) \quad (3.7b)$$

where α , β , γ and σ now contain the $\eta_n(t_0)$ and $\eta_p(t_0)$ terms (see [1]), with $\Delta n(0) = \Delta p(0)$ and $\eta_n(t_0)$ defined as follows,

$$\eta_n(t_0) = f_s(0^+) - f_o \quad (3.8)$$

From the charge neutrality relation with $\Delta n(t_0) = \Delta f_s(t_0) = \eta_n(t_0)$ the quantity $\eta_p(t_0)$ may be defined as Eq. (3.9),

$$\eta_p(t_0) = \left(1 + \frac{N_t}{\Delta n(0)}\right) \eta_n(t_0) \quad (3.9)$$

The steady state definition of the occupancy function $f_s(t)$ (Eq. 4.2 of [2]), with $n(t) = n_{po} + \Delta n(t)$ and $p(t) = p_{po} + \Delta p(t)$ and corresponding equilibrium concentrations n_{po} and p_{po} , is given as Eq. (3.10).

$$f_s(0^+) = \frac{C_n n(t) + C_p p_1}{C_n n(t) + C_p p(t) + C_n n_1 + C_p p_1} \quad (3.10)$$

At equilibrium the electron occupancy of the defect level is $f_o = f(0^-)$ given in terms of p_{po} by:

$$f_o = \frac{p_1}{p_{po} + p_1} \quad (3.11a)$$

and in terms of n_{po} by:

$$f_o = \frac{n_{po}}{n_{po} + n_1} \quad (3.11b)$$

The fundamental frequencies $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ are given as Eqs. (3.12) (see Ref [1]).

$$\lambda_1 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left(1 + \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2}\right)^{\frac{1}{2}}\right) \quad (3.12a)$$

$$\lambda_2 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left(1 - \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2}\right)^{\frac{1}{2}}\right) \quad (3.12b)$$

3.3 Numerical Solution for the Steady State

The unconstrained coupled differential equations are of the form (3.2) and (3.13), where (3.13) results from the steady state condition $U_n = U_p$ [2] or:

$$\frac{dp(t)}{dt} = \frac{dn(t)}{dt} \quad (3.13)$$

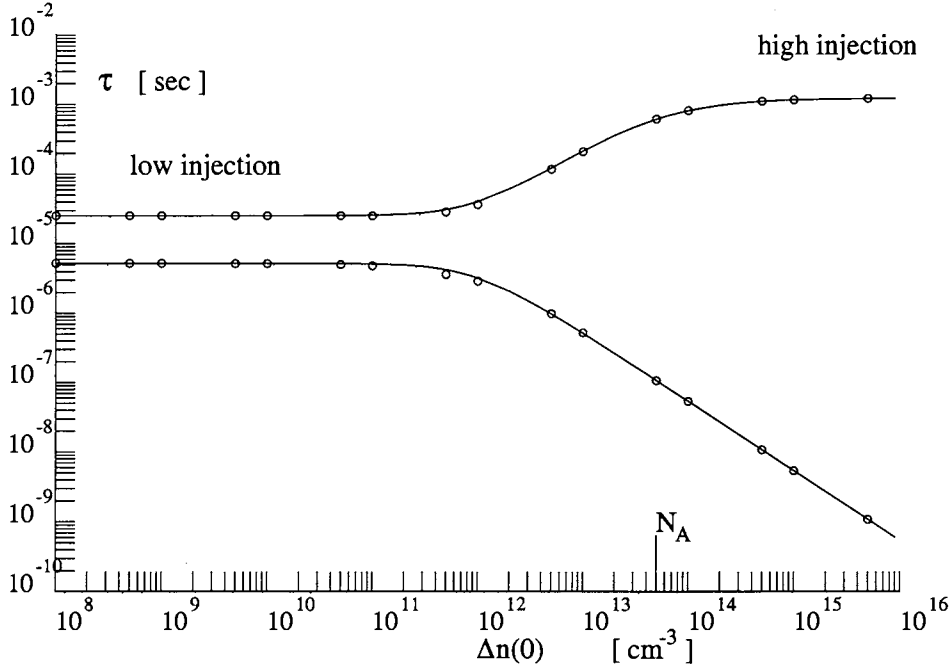


Figure 3.2: A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$ for the steady state. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. Continuous line: τ_1 and τ_2 predicted by equation (3.12) Circles: τ_1 and τ_2 derived from multi-transient analysis of the numerical solution.

The initial conditions are $n(0^+) = p(0^+)$ due to the generation rate G and $f(0^+)$ determined Eq. 4.2 of [2] for the steady state.

For small deviations from equilibrium (low excess carrier concentrations) referred to as the linear region (constant region) of variation of time constant with excess carrier concentration at least two time constants are expected in the steady state as with the transient case. This is because the governing equation is second order. For higher excess carrier concentrations away from equilibrium the time constants are expected to differ from the transient case because $dn(t)/dt = dp(t)/dt$ will necessarily give a different $\Delta n(0)_{\text{critical}}$ [1]. See [1] for the fifth order Runge-Kutta scheme and typical data used in the numerical solution.

Multi-transient analysis using the Total Least Squares (TLS) method, refers to the extraction of component exponential terms from a sum of exponentials comprising the signal (see [1]). Figure 3.2 shows the comparison between the decay time constants $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ as calculated from equation (3.12) and as eval-

uated by TLS analysis of numerical data ($\Delta n(t + \Delta t)$) for $T = 300\text{ K}$. The figure indicates the variation from low injection through to high injection. Agreement is very good. Also, the steady state values for τ_1 and τ_2 agree with the transient values for the constant region.

3.4 Discussion

The steady state solution converges to the transient solution for low excess carrier concentrations and hence confirms the transient solution for the near equilibrium case referred to as the small signal case. This steady state solution is independently determined from a different set of boundary conditions and yet converges to the transient solution as expected from the physics for the small signal case. Furthermore, for the case of intermediate excess carrier concentration the steady state and transient solutions for the time constants are different as shown in Figure 3.3. The present work independently addresses the solution of the steady state, proving consistency in the solution and indicating a more accurate set of time constants than that of the 1952 SRH time constant.

3.5 Conclusions

From a theoretical standpoint, the SRH lifetime expression τ_{ss} for the dominant single level model, is shown to be approximate. The existing interpretation of experimental data relies on one time constant τ_{ss} (steady state case) or τ_b (bulk decay - transient case) derived from the definition Eq. 5.2 of [2] (repeated as Eq. (3.1) here). Figure 3.1 and Figure 3.2 indicate that for low injection the SRH single time constant expression, applied to both the steady state and transient situations (small signal), does not adequately reflect the actual decay. Whereas at high injection τ_1 is adequate to model recombination and trapping, at low injection τ_2 is also required as the magnitude of the coefficient can be significant. For the steady state, in low injection the frequencies are the same as the transient case. From the above it can be seen that the single SRH time constant expression is not sufficient as an ap-

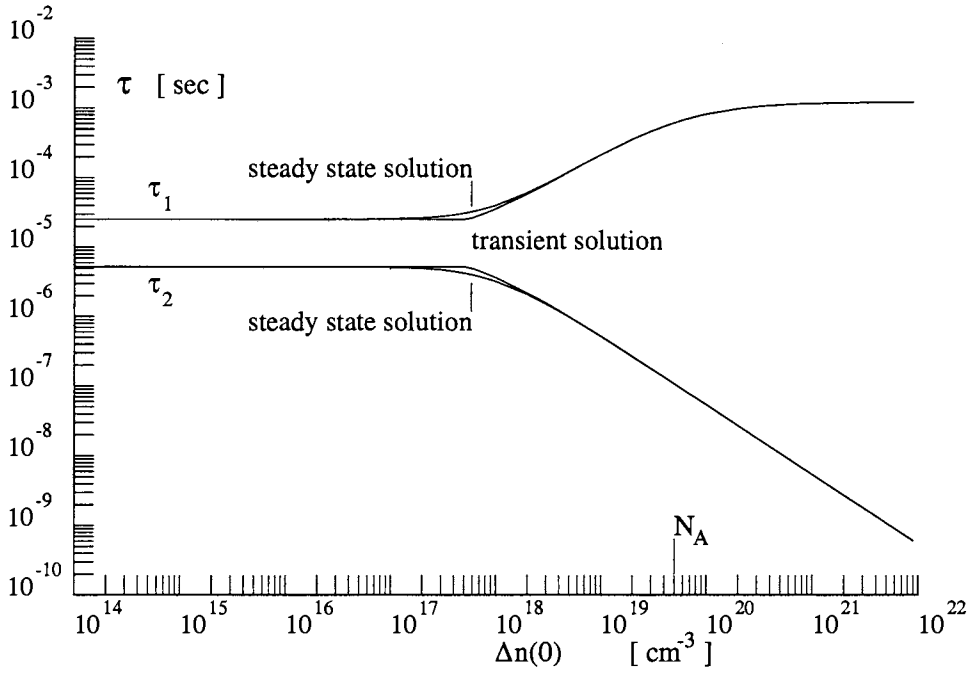


Figure 3.3: A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$. Comparison between the transient ([1]) and steady state solutions. Continuous line: τ_1 and τ_2 predicted by equation (3.12).

proximation and it lacks the ability to predict behaviour. Furthermore, the steady state solution together with the TLS analysis of the numerical solution, confirms the presence of at least two time constants in the decay. This unifies the existing solutions of the rate equations in the literature, as expected from inspection of the second order differential equation (3.4), for small departures from the equilibrium carrier concentration where the transient and steady state solutions are identical.

Chapter 4

Multiple Defect Energy Levels and Isothermal Trapping in Semiconductors

4.1 Introduction

Consider the decay response of a semiconductor to a light impulse $\delta(t)$. The Shockley-Read-Hall (SRH) rate equations Shockley and Read [2], and Hall [3] describe the evolution with time of recombination, capture and emission of excess carriers via a single defect energy level in the bandgap of a semiconductor. These rate equations have been applied to date to the analysis of experimental data assuming a dominant defect energy level. Multiple defect energy levels were discussed in Rose [8] with approximations introduced to elucidate features of types of defects. A set of differential rate equations for multiple discrete levels based on a summation of the single level SRH equations is given in Wertheim [9] and Choo [10]. Again approximations were introduced to provide a linear solution to the non-linear differential equations. The time constants resulting from this solution were applied to data where the sample semiconductor probably contained concentrations of unintentional defects in excess of what is currently acceptable today. A requirement exists such that the effect of low concentrations of defect levels may be assessed without

introducing approximations.

The validation of the summation of the single level SRH equations for the multiple discrete level case has not been previously confirmed. This is especially important since many analyses applied to the multiple defect situation have involved approximations. The approach taken to determine the accuracy of the above formulation of the rate equations is firstly to derive the equations from first principles and secondly to analyse the numerical solution. The validity of the set of rate equations is confirmed by applying the method of solution developed in Chapter 2 Ref. [1]. This solution represents the impulse response and is given by an infinite number of monoexponential terms, the inverse time constants or frequencies, of which are the linear combination of fundamental frequencies. The fundamental frequencies are derived from the linear form of the differential equations. In this Chapter the differential rate equations and the solution of the rate equations, for two multiple defect state systems, are derived. The first is the multiple discrete energy level situation where there are m discrete levels in the bandgap and the second is a ground state with an excited state. These two systems represent the multiple defect energy levels commonly encountered in the physics of device operation.

Major contributions of the current work are the derivation of the differential rate equations for the two defect level systems, derivation of expressions representing the analytic solution to the rate equations for the stated multiple defect level systems and verification of the rate equations. As with the single level solution of Chapter 2 Ref. [1] the fundamental frequencies or inverse time constants are derived from the linear form of the scaled rate equations. Expressions for the minority (τ_1) and majority (τ_{k+1} with $k = 1, 2 \dots m$) carrier decay time constants for the discrete case and $\tau_{1,2,3}$, for the ground excited state system are given. These are derived without an approximation at a given temperature for an excess carrier concentration below the non-degenerate doping concentration, arbitrary doping concentration $N_{A,D}$, defect level concentration N_{tk} , cross section $\sigma_{nk,pk}$ and energy level E_{tk} . The theory presented here addresses the whole decay process from $0^+ < t < \infty$. The analytic solution is verified by showing agreement with an analysis of the numerical solution of the rate equations for component time constants for the above given parameters

using a multi-transient technique.

The processes of capture and emission of carriers from multiple defect levels and recombination and trapping via multiple defect levels are described by the derived rate equations. These processes determine the average lifetime of minority carriers and hence device characteristics. A considerable effort is being expended on improving the quality of semiconductor material to minimise the mostly detrimental effects of defect levels on device performance. Current methods of analysis to determine defect level parameters or semiconductor quality are approximate in nature. Despite the probability that many defect levels may be present in a given semiconductor sample, an effective lifetime τ_e is often evaluated as if they may be represented by one dominant level. However τ_e is a cumulative quantity and by definition cannot be related to the physics of one carrier type over all excess carrier concentrations. A more accurate measure of semiconductor quality is proposed here. It is based on a measure of one time constant τ_1 which is shown to represent the minority carrier over all excess carrier concentrations whether the decay is produced by an impulse $N_o\delta(t)$ or in the steady state. The behaviour of τ_1 with excess carrier concentration gives an indication of the onset of minority carrier trapping. Note that the time constants for the impulse response and the steady state response are the same in the neighbourhood of the equilibrium point, only the coefficients of the exponential terms in the series change. A critical point representing the transition between the linear (constant) and non-linear variation of fundamental frequency with excess carrier density is identified. For practical assessment of semiconductor material quality a contactless isothermal method is required. The photoconductance decay method may be applied for a range of silicon conductivities suitable for device fabrication. Given an ideal surface passivation, namely surface recombination velocity $S = 0$, a measure of τ_1 may be extracted from the decay.

The paper is organised as follows. The differential equations for the multiple discrete defect level system are derived from first principles in Appendix F and the fundamental frequencies evaluated in section 4.2. Fundamental frequencies λ_{k+1} representing m , $k = 1, 2 \cdots m$ discrete energy levels are derived for isothermal conditions for arbitrary excess carrier concentration below non-degenerate doping, uni-

form doping concentration $N_{A,D}$, defect level concentration N_{tk} , cross section $\sigma_{nk,pk}$ and energy level E_{tk} . An excess electron concentration $\Delta n(t)$ and hole concentration $\Delta p(t)$ is assumed to be uniformly generated throughout the wafer thickness at $t = 0^+$. It is shown that the non-linear terms in the rate equations for $\Delta n(t)$ and $\Delta p(t)$ go to zero at some time $t = t_0$. The resulting differential equations may be solved at $t = 0^+$ or $t = t_0$ for the fundamental frequencies or eigenvalues $-\lambda_{k+1}$. Having obtained the fundamental time constants, a general solution for $\Delta n(t)$ and $\Delta p(t)$, represented by the impulse response is given.

The ground excited state defect level system is evaluated in section 4.3. Here the differential rate equations are derived from first principles for carrier transitions between the ground and excited state. Again the linear form of the rate equations indicates the fundamental frequencies involved in the decay.

A section 4.4 contains a multi-transient analysis of the numerical solution to determine the component exponentials in the sum of exponentials. Comparison of the predictions of the analytic solution for the multiple discrete and ground excited state systems with the results of the multi-transient analysis of the numerical solution is very good. In particular the linear combination of fundamental frequencies in the exponents predicted by the analytic solution and the variation of the time constant $\tau_1 = 1/\lambda_1$ with excess carrier concentration, indicate close agreement. An indication of recombination only and of trapping is discussed.

A section 4.5 discusses the implications of the theoretical results determined above. In particular, defect level parameters for the same level as in Chapter 2 Ref. [1] are retained in the present analysis and it is shown that with additional levels the minority carrier time constant τ_1 is lower. This is to be expected, however since τ_1 is the dominant decay time constant, it has implications in terms of interpretation of experimental data which relies on measuring the dominant decay term. The reason for this is that different semiconductor samples may have different concentrations of background defect species leading to variable impact on τ_1 even though a dominant defect species may be present in the samples.

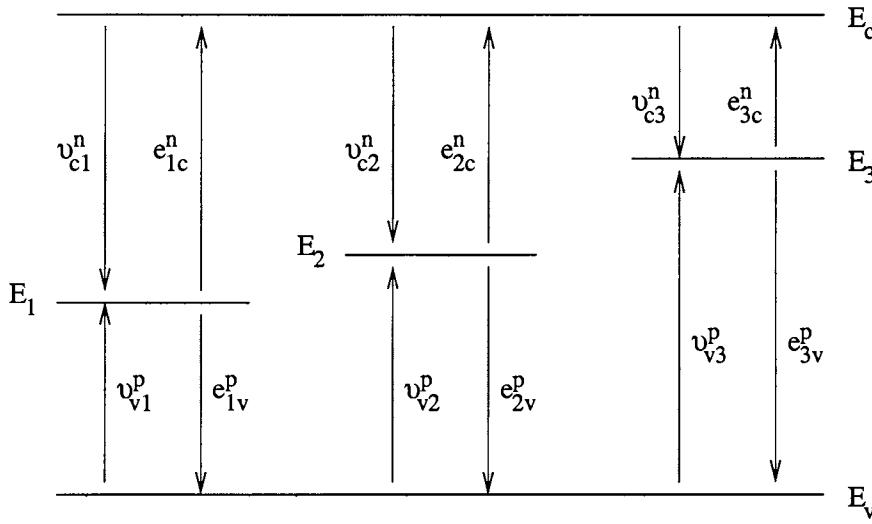


Figure 4.1: Band diagram for three discrete defect levels indicating carrier transitions with the respective band.

4.2 Multiple Discrete Energy Levels: Derivation of Frequencies λ for Arbitrary Injection Level

Consider m discrete defect energy levels in the bandgap where the processes of recombination and emission proceed with the respective band for each level independently. Interaction between levels is not considered. In Ref. [9] the rate equations are given without formal derivation as a summation of the SRH single level level rate equations. It is shown in Appendix F that this formulation is effectively correct although one can not, strictly speaking, define individual level carrier recombination rates. There is only one recombination rate for each carrier. With reference to Figure 4.1 for three defect levels ($m = 3$) the following rate equations apply as in Refs. [2] [9] for the recombination via and emission from the k^{th} defect level:

$$\frac{dn(t)}{dt} = \sum_{k=1}^m [e_{kc}^n N_{tk} f_k(t) - v_{ck}^n N_{tk} n(t) (1 - f_k(t))] \quad (4.1)$$

$$\frac{dp(t)}{dt} = \sum_{k=1}^m [e_{kv}^p N_{tk} (1 - f_k(t)) - v_{vk}^p N_{tk} p(t) f_k(t)] \quad (4.2)$$

where e_{kc}^n and e_{kv}^p represent the emission rates for electrons and holes respectively (for the k^{th} defect level) and, v_{ck}^n , v_{vk}^p are the capture coefficients for electrons and holes respectively. The following are defined from the first principles approach in Ref. [2] and Appendix F to simplify notation used in the text.

$$C_{nk} n_{1k} = e_{kc}^n \quad (4.3a)$$

$$C_{pk} p_{1k} = e_{kv}^p \quad (4.3b)$$

$$C_{nk} = v_{ck}^n \quad (4.3c)$$

$$C_{pk} = v_{vk}^p \quad (4.3d)$$

where $C_{nk} = v_{thn} \sigma_{nk}$ and $C_{pk} = v_{thp} \sigma_{pk}$, with σ_{nk} and σ_{pk} , the cross sections for electrons and holes respectively. The quantities v_{thn} and v_{thp} are the average thermal velocity of electrons and holes respectively, and

$$n_{1k} = N_c \exp \left(-\frac{(E_c - E_{tk})}{kT} \right) \quad (4.4a)$$

$$p_{1k} = N_v \exp \left(-\frac{(E_{tk} - E_v)}{kT} \right) \quad (4.4b)$$

The excess electron concentration $\Delta n(t)$ and the excess hole concentration $\Delta p(t)$ are written in terms of normalised excess carrier concentration $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ respectively where the subscript nm denotes a normalised quantity. Note that $\Delta n_{nm}(0^+) = 1$ and $\Delta p_{nm}(0^+) = 1$.

$$\Delta n_{nm}(t) = \frac{\Delta n(t)}{\Delta n(0)} \quad (4.5)$$

$$\Delta p_{nm}(t) = \frac{\Delta p(t)}{\Delta p(0)} \quad (4.6)$$

The defect level occupancy function $f_k(t)$ for the k^{th} level is written in terms of the departure from equilibrium $\Delta f_k(t)$ and the equilibrium occupation f_{ok} . The electron and hole concentrations, and occupancy terms may be written:

$$n(t) = \Delta n_{nm}(t)\Delta n(0) + n_{po} \quad (4.7a)$$

$$p(t) = \Delta p_{nm}(t)\Delta p(0) + p_{po} \quad (4.7b)$$

$$f_k(t) = \Delta f_k(t) + f_{ok} \quad (4.7c)$$

where the corresponding equilibrium concentrations n_{po} and p_{po} and where the equilibrium defect level occupation $f_{ok} = f_k(0^-)$ is given for the k^{th} level by:

$$f_{ok} = \frac{p_{1k}}{p_{po} + p_{1k}} = \frac{n_{po}}{n_{po} + n_{1k}} \quad (4.8)$$

A charge neutrality relation requires the conservation of nett charge with time as in Ref. [2] with N_t being the defect level concentration.

$$\Delta p_{nm}(t)\Delta p(0) = \Delta n_{nm}(t)\Delta n(0) + \sum_{k=1}^m N_{tk}\Delta f_k(t) \quad (4.9)$$

$\Delta f(t)$ may be written as $\Delta n_t(t)/N_t$ with $\Delta n_t(t)$ being the defect level excess electron concentration. By rewriting the charge neutrality relation with $\Delta n(0) = \Delta p(0)$, the valence, conduction and defect level electron concentrations may be directly compared since the three quantities are normalised to an injection level $\Delta p(0)$.

$$\Delta p_{nm}(t) = \Delta n_{nm}(t) + \frac{\Delta n_{tk}(t)}{\Delta n(0)} \quad (4.10)$$

For multiple discrete energy levels in the bandgap the rate equations are given by the first principles derivation in Appendix F as Eqs. (F.11) and (F.12) which correspond to the rate equations Eqs. (4.1) and (4.2) and are written as follows:

$$\frac{dn(t)}{dt} = -U_n \quad (4.11)$$

$$\frac{dp(t)}{dt} = -U_p \quad (4.12)$$

The differential equations (4.1) and (4.2) are scaled Fulford et al [32] by a normalising factor $\Delta n(0) = \Delta p(0)$ where $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ represent the scaled electron and hole concentrations. It is shown that the non-linear terms in the rate equations for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ go to zero at some time $t = t_0$. The resulting differential equations contain terms in only λ_{m+1} . As there are $m + 1$ equations and $m + 1$ unknowns the equations may be solved for the fundamental frequencies λ_{m+1} . The scaled equations are written as Eqs. (4.13) and (4.14) for the normalised electron and hole excess carrier concentrations respectively.

$$\begin{aligned}
 -\frac{d\Delta n_{nm}(t)}{dt} &= \Delta n_{nm}(t) \sum_{k=1}^m (\gamma_{0k} - \sigma_{0k}) \\
 &\quad - \sum_{k=1}^m \frac{\sigma_{0k}}{\Delta n(0)} N_{tk} \Delta f_k(t) \\
 &\quad - \sum_{k=1}^m C_{nk} N_{tk} \Delta n_{nm}(t) \Delta f_k(t)
 \end{aligned} \tag{4.13}$$

$$\begin{aligned}
 -\frac{d\Delta p_{nm}(t)}{dt} &= \Delta p_{nm}(t) \sum_{k=1}^m (\alpha_{0k} - \beta_{0k}) \\
 &\quad + \sum_{k=1}^m \frac{\beta_{0k}}{\Delta n(0)} N_{tk} \Delta f_k(t) \\
 &\quad + \sum_{k=1}^m C_{pk} N_{tk} \Delta p_{nm}(t) \Delta f_k(t)
 \end{aligned} \tag{4.14}$$

where:

$$\alpha_{0k} = C_{pk} N_{tk} \left\{ \frac{p_{1k}}{p_{po} + p_{1k}} + \frac{p_{po} + p_{1k}}{N_{tk}} \right\} \tag{4.15a}$$

$$\beta_{0k} = C_{pk} N_{tk} \left\{ \frac{p_{po} + p_{1k}}{N_{tk}} \right\} \tag{4.15b}$$

$$\gamma_{0k} = C_{nk} N_{tk} \left\{ \frac{n_{1k}}{n_{po} + n_{1k}} + \frac{n_{po} + n_{1k}}{N_{tk}} \right\} \tag{4.15c}$$

$$\sigma_{0k} = C_{nk} N_{tk} \left\{ \frac{n_{po} + n_{1k}}{N_{tk}} \right\} \tag{4.15d}$$

It is shown that the non-linear terms in the second order differential equation describing $\Delta n_{nm}(t)$ vanish at time $t = t_0$ for two conditions. This allows the eigenvalues to be determined. Two variables are defined and the conditions on these

two variables determine how the non-linear terms in the second order differential equation go to zero at time $t = t_0$. For a given excess carrier concentration one defect level occupancy function $\Delta f_k(t)$ for some k may intersect $\Delta n_{nm}(t)$ at some time t_0 . A further increase in $\Delta n(0^+)$ may result in two defect level occupancy functions intersecting $\Delta n_{nm}(t)$ concurrently at $t = t_0$. These two intersections occur simultaneously at $t = t_0$ although the times t_{ik} for a given k of each intersection are different. The important point is that in intersecting simultaneously, the values of $\eta_{nk}(t)$ and $\eta_{pk}(t)$ are the values of the individual defect level intersecting with $t = t_{ik}$. Let $\eta_{nk}(t_{ik}) = \Delta f_k(t_{ik}) = \Delta n_{nm}(t_{ik})$ at the point of intersection for some k . There is also a corresponding term $\eta_{pk}(t_{ik})$ to be described below. Note that the occupancy functions in intersecting simultaneously with $\Delta n_{nm}(t)$ at $t = t_0$, the values of $\eta_{nk}(t_{ik})$ and $\eta_{pk}(t_{ik})$ are from intersections that occur at different t_{ik} . Eqs. (4.13) and (4.14) may be written as Eq. (4.16) and Eq. (4.17) respectively, which include the terms $\eta_{nk}(t_{ik})$ and $\eta_{pk}(t_{ik})$

$$-\frac{d\Delta n_{nm}(t)}{dt} = \sum_{k=1}^m \left[\Delta n_{nm}(t) [\gamma_k - \sigma_k] - \frac{\sigma_k}{\Delta n(0)} N_{tk} \Delta f_k(t) - C_{ck}^n \Delta n(0) N_{tk} \Delta f_k(t) [\Delta n_{nm}(t) - \eta_{nk}(t)] \right] \quad (4.16)$$

Similarly for Eq. (4.14) substitution of a corresponding set of terms containing $\eta_{pk}(t_{ik})$ result in Eq. (4.17).

$$-\frac{d\Delta p_{nm}(t)}{dt} = \sum_{k=1}^m \left[\Delta p_{nm}(t) [\alpha_k - \beta_k] + \frac{\beta_k}{\Delta n(0)} N_{tk} \Delta f_k(t) + C_{vk}^p \Delta n(0) N_{tk} \Delta f_k(t) [\Delta p_{nm}(t) - \eta_{pk}(t)] \right] \quad (4.17)$$

where α_k , γ_k , β_k and σ_k now contain the $\eta_{nk}(t_{ik})$ and $\eta_{pk}(t_{ik})$ terms for the two cases indicated above at $t = t_0$ with $\Delta n(0) = \Delta p(0)$.

$$\alpha_k = C_{vk}^p N_{tk} \left\{ \frac{p_{1k}}{p_{po} + p_{1k}} + \frac{p_{po} + p_{1k}}{N_{tk}} + \frac{\eta_{pk}(t_{ik}) \Delta p(0)}{N_{tk}} \right\} \quad (4.18a)$$

$$\beta_k = C_{vk}^p N_{tk} \left\{ \frac{p_{po} + p_{1k}}{N_{tk}} + \frac{\eta_{pk}(t_{ik}) \Delta n(0)}{N_{tk}} \right\} \quad (4.18b)$$

$$\gamma_k = C_{ck}^n N_{tk} \left\{ \frac{n_{1k}}{n_{po} + n_{1k}} + \frac{n_{po} + n_{1k}}{N_{tk}} + \frac{\eta_{nk}(t_{ik}) \Delta n(0)}{N_{tk}} \right\} \quad (4.18c)$$

$$\sigma_k = C_{ck}^n N_{tk} \left\{ \frac{n_{po} + n_{1k}}{N_{tk}} + \frac{\eta_{nk}(t_{ik}) \Delta p(0)}{N_{tk}} \right\} \quad (4.18d)$$

and

$$[\gamma_{0k} - \sigma_{0k}] = [\gamma_k - \sigma_k] \quad (4.19a)$$

$$[\alpha_{0k} - \beta_{0k}] = [\alpha_k - \beta_k] \quad (4.19b)$$

Inclusion of the $\eta_{nk}(t)$ terms above in Eq. (4.16) and a corresponding set of terms in $\eta_{pk}(t)$ in Eq. (4.17) is a construction which allows the application of the boundary conditions to evaluate the non-linear terms in both equations. The non-linear terms in the differential equations go to zero at time t_0 at which the equations contain only the terms in λ_k . If the resulting equations (4.16) and (4.17) are multiplied out, the $\eta_{nk}(t)$ and $\eta_{pk}(t)$ terms cancel. Effectively the equations are unchanged by inclusion of those terms.

The non-linear term in Eq. (4.16) labeled as $g_k^n(t)$ may be written as follows with $t = t_0$:

$$g_k^n(t_0) = -[\Delta n_{nm}(t_0) - \eta_{nk}(t_0)] \eta_{nk}(t_0) \quad (4.20)$$

Similarly, the non-linear term in Eq. (4.17) referred to as $g_k^p(t_0)$ may be expressed as follows.

$$\begin{aligned} g_k^p(t_0) &= (\Delta p_{nm}(t_0) - \eta_{pk}(t_0)) \eta_{nk}(t_0) \\ &= \left(\Delta n_{nm}(t_0) + \Delta f_k(t_0) \frac{N_{tk}}{\Delta n(0)} - \eta_{pk}(t_0) \right) \eta_{nk}(t_0) \end{aligned} \quad (4.21)$$

Two conditions exist for the non-linear terms to vanish (go to zero at time t_0) in Eqs. (4.16) and (4.17) at a certain time t_0 . For example, two quantum levels ($m = 3$) the charge neutrality relation Eq. (4.9) is written as Eq. (4.22) with two

intersecting occupancy functions $\Delta f_1(t_{i1})$ and $\Delta f_2(t_{i2})$. Note that for a light impulse $\delta(t)$, carriers are generated with $\Delta n(0) = \Delta p(0)$ and $\Delta n_{nm}(t)$ is normalised.

$$\begin{aligned}\Delta p_{nm}(t_0) = & \Delta n_{nm}(t_0) + \frac{N_{t1}}{\Delta n(0)} \Delta f_1(t_0) \\ & + \frac{N_{t2}}{\Delta n(0)} \Delta f_2(t_0) + \frac{N_{t3}}{\Delta n(0)} \Delta f_3(t_0)\end{aligned}\quad (4.22)$$

At $t = t_0$, the following constants are defined.

$$\eta_{nk}(t_0) = \eta_{n1}(t_{i1}) + \eta_{n2}(t_{i2}) \quad (4.23a)$$

$$\eta_{pk}(t_0) = \eta_{p1}(t_{i1}) + \eta_{p2}(t_{i2}) \quad (4.23b)$$

with

$$\eta_{p1}(t_{i1}) = \phi_1 \eta_{n1}(t_{i1}) \quad (4.24a)$$

$$\eta_{p2}(t_{i2}) = \phi_2 \eta_{n2}(t_{i2}) \quad (4.24b)$$

and ϕ_k Eq. (4.25) defined with $k = 1$

$$\phi_1 = \left[1 + \frac{N_{t1}}{\Delta n(0)} \right] \quad (4.25)$$

now from equations (4.23b) and (4.24)

$$\begin{aligned}\eta_{pk}(t_0) = & \phi_1 \eta_{n1}(t_{i1}) \\ & + \phi_2 \eta_{n2}(t_{i2})\end{aligned}\quad (4.26)$$

so that the charge neutrality relation Eq. (4.22) and Eq. (4.26) may be written as Eq. (4.27) where the constant $\eta_{pk}(t_0)$ is defined by $\eta_{pk}(t_0) = \Delta p_{nm}(t_0)$.

$$\begin{aligned}\Delta p_{nm}(t_0) = & \eta_{pk}(t_0) \\ & + \frac{N_{t3}}{\Delta n(0)} \Delta f_3(t_{i3})\end{aligned}\quad (4.27)$$

Therefore $\Delta f_3(t_{i3}) = 0$ and this can only occur if the condition $t_{i3} = 0^+$ for which $\Delta f_3(0^+) = 0$ since $f_k(0^-) = f_k(0^+)$ for $k = 3$. The other condition is $t_{i1} > 0^+$ and $t_{i2} > 0^+$ for which $\Delta f_1(t_{i1}) > 0$ and $\Delta f_2(t_{i2}) > 0$, the points of intersection. Hence

constants $\eta_{n1}(t_{i1}) > 0$ and $\eta_{n2}(t_{i2}) > 0$ and similarly for $\eta_{pk}(t_{ik}) > 0$ for $k = 1, 2$. The constant $\eta_{n3}(t_{i3}) = 0$ and similarly for $\eta_{pk}(t_{ik}) = 0$ for $k = 3$.

The linear (constant) region of frequency variation with excess carrier concentration corresponds to the case of $\eta_{nk}(0^+) = 0$ and $\eta_{pk}(0^+) = 0$ for all k . When $\eta_{nk}(t_{ik}) > 0^+$ for some k , this corresponds to the non-linear region of frequency variation with excess carrier concentration (see at the end of this section). Effectively there is an intersection of $\Delta f_k(t_{ik})$ and $\Delta n_{nm}(t)$ whereas at low injection there is no intersection.

For a light impulse $\delta(t)$, carriers are generated such that $\Delta n(0) = \Delta p(0)$. The differential equations (4.16) and (4.17) are written in a simplified linear form at $t = t_0$ as equations (4.28) and (4.29) respectively. Constants $\eta_{nk}(t_{ik})$ and $\eta_p(t_{ik})$ are dependent on the excess carrier concentration. In Appendix G $\eta_{nk}(t_{ik})$ and a condition for the $\eta_{nk}(t_{ik}) > 0$, at some $t = t_0$ is evaluated.

$$-\frac{d\Delta n_{nm}(t)}{dt} = \Delta n_{nm}(t) \sum_{k=1}^m (\gamma_k - \sigma_k) - \sum_{k=1}^m \frac{\sigma_k}{\Delta n(0)} N_{tk} \Delta f_k(t) \quad (4.28)$$

$$-\frac{d\Delta p_{nm}(t)}{dt} = \Delta p_{nm}(t) \sum_{k=1}^m (\alpha_k - \beta_k) + \sum_{k=1}^m \frac{\beta_k}{\Delta n(0)} N_{tk} \Delta f_k(t) \quad (4.29)$$

In addition the following expression indicates the k^{th} defect level electron rate of occupation given by Eq. (F.14) (see Appendix F) which corresponds to an equivalent expression in Ref. [9]:

$$N_{tk} \frac{d\Delta f_k(t)}{dt} = U_n|_k - U_p|_k \quad (4.30)$$

A set of linear equations is formed similar to that in Chapter 2) Ref. [1] from Eqs. (4.28) and (4.30) and is written as follows with the differential operator $D = d/dt$

Eq. (4.31) where Eq. (4.29) is dependent and not included.

$$\det \begin{bmatrix} D + \sum_{k=1}^3 (\gamma_k - \sigma_k) & 0 & -\frac{N_{t1}\sigma_1}{\Delta n(0)} & -\frac{N_{t2}\sigma_2}{\Delta n(0)} & -\frac{N_{t3}\sigma_3}{\Delta n(0)} \\ -(\gamma_1 - \sigma_1) & (\alpha_1 - \beta_1) & \frac{N_{t1}(D + \sigma_1 + \beta_1)}{\Delta n(0)} & 0 & 0 \\ -(\gamma_2 - \sigma_2) & (\alpha_2 - \beta_2) & 0 & \frac{N_{t2}(D + \sigma_2 + \beta_2)}{\Delta n(0)} & 0 \\ -(\gamma_3 - \sigma_3) & (\alpha_3 - \beta_3) & 0 & 0 & \frac{N_{t3}(D + \sigma_3 + \beta_3)}{\Delta n(0)} \\ 1 & -1 & \frac{N_{t1}}{\Delta n(0)} & \frac{N_{t2}}{\Delta n(0)} & \frac{N_{t3}}{\Delta n(0)} \end{bmatrix} = 0 \quad (4.31)$$

As mentioned in Chapter 2 the method using the differential operator $D = d/dt$ Jordan [14] and Kreyszig [15] whereby the determinant of the matrix of linear equations (4.31) equals zero, allows the formation of the characteristic equation at $t = t_0$ (where the non-linear terms go to zero). The characteristic equation is given by Eq. (4.32) and may be solved for the time constants where the coefficients (b, c, d, e) are determined from the determinant of the matrix formed from Eq. (4.31).

$$(D^4 + bD^3 + cD^2 + dD + e) \exp(-\lambda t) = 0 \quad (4.32)$$

As such the fundamental frequencies λ_k (inverse time constants) may be evaluated.

$$\lambda^4 - b\lambda^3 + c\lambda^2 - d\lambda + e = 0 \quad (4.33)$$

By evaluating the four roots of Eq. (4.33) the fundamental frequencies are given by $\lambda_1 = 1/\tau_1$, $\lambda_2 = 1/\tau_2$, $\lambda_3 = 1/\tau_3$ and $\lambda_4 = 1/\tau_4$

The linear region of variation of fundamental frequencies λ_k with injection level or excess carrier density is defined by Eq. (4.34). This condition is satisfied upon expansion of Eq. (4.34) for $\eta_n(t_0) = 0$ and $\eta_p(t_0) = 0$ at $t_0 = 0^+$. The requirement is found from $\eta_n(t) = \Delta f(t)$ which equals zero at $t = 0^+$ as $\Delta f(t)$, the defect level excess electron concentration, is zero at $t = 0^+$. An upper limit for the linear region of excess carrier density exists referred to as $\Delta n(0)_{critical}$, is evaluated in Appendix G.

$$\frac{d\lambda_k}{d\Delta n(0)} = 0 \quad (4.34)$$

The non-linear region of variation of fundamental frequencies λ_{k+1} with injection level or excess carrier density is defined by Eq. (4.35). This condition is satisfied for $\eta_n(t_0) > 0$ and $\eta_p(t_0) > 0$ for some value of t_0 . $\Delta f(t) > 0$ can only be achieved with $t_0 > 0^+$ as $\Delta f(t)$ is greater than zero except at $t = 0^+$ and $t = \infty$.

$$\left| \frac{d\lambda_{k+1}}{d\Delta n(0)} \right| > 0 \quad (4.35)$$

Having evaluated the fundamental frequencies for $m = 3$, an analytic solution of the differential rate equations for $\Delta n(t)$ and $\Delta p(t)$ may be written as Eqs. (4.36) and (4.37) respectively following the derivation for a single level in Chapter 2 Ref. [1].

$$\Delta n(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{i,j,u,v} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t - v\lambda_4 t) \quad (4.36)$$

$$\Delta p(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} P_{i,j,u,v} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t - v\lambda_4 t) \quad (4.37)$$

4.3 Ground Excited State System: Derivation of Frequencies λ for Arbitrary Injection Level

Consider a single defect energy level E_{gnd} representing the ground state with an excited state E_x in the bandgap of an n-type semiconductor. The processes of recombination and emission proceed inter-dependently between the ground and excited state and with the respective band. With reference to Figure 4.2 the following equations apply similar to Refs. [2] [4] for the recombination via and emission from the ground and excited state system (see Appendix H for relevant expressions for U_{xg}^n , U_{xg}^p , U_{gx}^n and U_{gx}^p):

$$\frac{dn(t)}{dt} = e_{gc}^n N_t f_g(t) + e_{xc}^n N_t f_x(t) - v_{cg}^n n(t) N_t [1 - f_g(t)] - v_{cx}^n n(t) N_t [1 - f_x(t)] \quad (4.38)$$

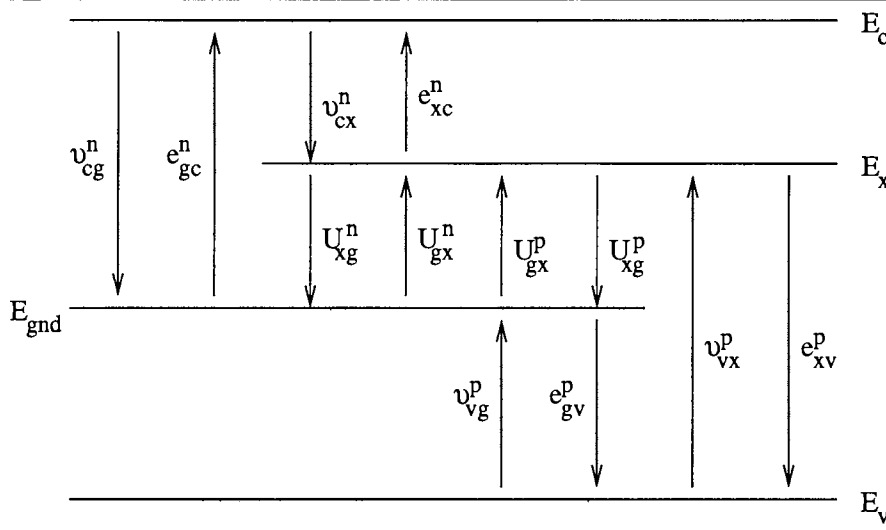


Figure 4.2: Band diagram for the ground excited state system indicating carrier transitions with the respective band.

$$\frac{dp(t)}{dt} = e_{gv}^p N_t [1 - f_g(t)] + e_{xv}^p N_t [1 - f_x(t)] - v_{vg}^p p(t) N_t f_g(t) - v_{vx}^p p(t) N_t f_x(t) \quad (4.39)$$

$$\begin{aligned} N_t \frac{df_g(t)}{dt} &= (v_{cg}^n n(t) + e_{gv}^p) N_t + (U_{xg}^n - U_{gx}^n) - (U_{xg}^p - U_{gx}^p) \\ &\quad - [v_{cg}^n n(t) + v_{vg}^p p(t) + e_{gv}^p + e_{gc}^n] N_t f_g(t) \end{aligned} \quad (4.40)$$

$$\begin{aligned} N_t \frac{df_x(t)}{dt} &= (v_{cx}^n n(t) + e_{xv}^p) N_t + (U_{gx}^n - U_{xg}^n) - (U_{gx}^p - U_{xg}^p) \\ &\quad - [v_{cx}^n n(t) + v_{vx}^p p(t) + e_{xv}^p + e_{xc}^n] N_t f_x(t) \end{aligned} \quad (4.41)$$

where the superscript denotes the carrier for example, $C_{cg}^n = v_{thn} \sigma_{cg}^n$ and $C_{vg}^p = v_{thp} \sigma_{vg}^p$ represent the capture coefficients for electrons and holes respectively. The quantities σ_{cg}^n and σ_{vg}^p represent the cross sections for electrons and holes from the conduction and valence bands to the ground state respectively. The quantities v_{thn} and v_{thp} are the average thermal velocity of electrons and holes respectively:

$$e_{gc}^n = C_{cg}^n n_{1g} \quad (4.42a)$$

$$e_{xc}^n = C_{cx}^n n_{1x} \quad (4.42b)$$

$$e_{gv}^p = C_{vg}^p p_{1g} \quad (4.42c)$$

$$e_{xv}^p = C_{vx}^p p_{1x} \quad (4.42d)$$

$$v_{cg}^n = C_{cg}^n = v_{thn} \sigma_{cg}^n \quad (4.42e)$$

$$v_{cx}^n = C_{cx}^n = v_{thn} \sigma_{cx}^n \quad (4.42f)$$

$$v_{vg}^p = C_{vg}^p = v_{thp} \sigma_{vg}^p \quad (4.42g)$$

$$v_{vx}^p = C_{vx}^p = v_{thp} \sigma_{vx}^p \quad (4.42h)$$

with:

$$n_{1g} = N_c \exp \left(-\frac{(E_c - E_{gnd})}{kT} \right) \quad (4.43a)$$

$$p_{1g} = N_v \exp \left(-\frac{(E_{gnd} - E_v)}{kT} \right) \quad (4.43b)$$

$$n_{1x} = N_c \exp \left(-\frac{(E_c - E_x)}{kT} \right) \quad (4.43c)$$

$$p_{1x} = N_v \exp \left(-\frac{(E_x - E_v)}{kT} \right) \quad (4.43d)$$

From the charge neutrality relation,

$$\begin{aligned} \frac{d\Delta p_{nm}(t)}{dt} &= \frac{d\Delta n_{nm}(t)}{dt} + \frac{N_t}{\Delta n(0)} \left(\frac{d\Delta f_g(t)}{dt} + \frac{d\Delta f_x(t)}{dt} \right) \\ &= \frac{d\Delta n_{nm}(t)}{dt} + \frac{N_t}{\Delta n(0)} \frac{d\Delta f(t)}{dt} \end{aligned} \quad (4.44)$$

The rate equations (4.38) and (4.39) are re-written so as to make the non-linear terms go to zero at some time t_0 . For a given excess carrier concentration one defect level occupancy function $\Delta f_{g,x}(t)$ for some k may intersect $\Delta n(t)$ at some

time t_0 . A further increase in $\Delta n(t)$ may result in the two defect level occupancy functions intersecting $\Delta n(t)$ concurrently at $t = t_0$. These two intersections occur simultaneously at $t = t_0$ although the times t_{ig} and t_{ix} of each intersection are different. The important point is that in intersecting simultaneously the values of $\eta_{ng}(t)$ and $\eta_{nx}(t)$ are the values of the individual defect level occupancy function intersecting, at $t = t_{ig}$ and $t = t_{ix}$. Inclusion of $\eta_{ng}(t)$ and $\eta_{nx}(t)$ terms into Eq. (4.45) and a corresponding set of terms in $\eta_{pg}(t)$ and $\eta_{px}(t)$ into Eq. (4.45) follows the derivation in the previous section. It is a construction which allows the application of the boundary conditions to evaluate the non-linear terms in both equations and determine the precise time at which the equations become linear. See Appendix H for a derivation of the carrier transition equations for the ground excited state system.

$$\begin{aligned}
-\frac{d\Delta n_{nm}(t)}{dt} = & \Delta n_{nm}(t) [(\gamma_g - \sigma_g) \\
& + (\gamma_x - \sigma_x)] \\
& - \frac{\sigma_g}{\Delta n(0)} N_t \Delta f_g(t) \\
& - \frac{\sigma_x}{\Delta n(0)} N_t \Delta f_x(t) \\
& - C_{cg}^n \Delta n(0) \Delta f_g(t) [\Delta n_{nm}(t) - \eta_{ng}(t)] \\
& - C_{cx}^n \Delta n(0) \Delta f_x(t) [\Delta n_{nm}(t) - \eta_{nx}(t)] \quad (4.45)
\end{aligned}$$

Similarly for Eq. (4.39) substitutions of a corresponding set of terms containing $\eta_{p(g,x)}(t)$ result in Eq. (4.46).

$$\begin{aligned}
-\frac{d\Delta p_{nm}(t)}{dt} = & \Delta n_{nm}(t) [(\alpha_g - \beta_g) \\
& + (\alpha_x - \beta_x)] \\
& + \frac{\beta_g}{\Delta n(0)} N_t \Delta f_g(t) \\
& + \frac{\beta_x}{\Delta n(0)} N_t \Delta f_x(t) \\
& + C_{vg}^p \Delta n(0) \Delta f_g(t) [\Delta p_{nm}(t) - \eta_{pg}(t)] \\
& + C_{vx}^p \Delta n(0) \Delta f_x(t) [\Delta p_{nm}(t) - \eta_{px}(t)] \quad (4.46)
\end{aligned}$$

where the for example the symbols α_g and α_x are represented below as $\alpha_{g,x}$ where either g or x applies. See H for the relevant expressions for $f_g(t)$ and $f_x(t)$.

$$\alpha_{(g,x)} = C_{v(g,x)}^p N_t \left\{ \frac{p_{1(g,x)}}{p_{po} + p_{1(g,x)}} + \frac{p_{po} + p_{1(g,x)}}{N_t} \right\} + \frac{\eta_{p(g,x)}(t_i) \Delta n(0)}{N_t} \quad (4.47a)$$

$$\beta_{(g,x)} = C_{v(g,x)}^p N_t \left\{ \frac{p_{po} + p_{1(g,x)}}{N_t} + \frac{\eta_{p(g,x)}(t_i) \Delta n(0)}{N_t} \right\} \quad (4.47b)$$

$$\gamma_{(g,x)} = C_{c(g,x)}^n N_t \left\{ \frac{n_{1(g,x)}}{n_{po} + n_{1(g,x)}} + \frac{n_{po} + n_{1(g,x)}}{N_t} \right\} + \frac{\eta_{n(g,x)}(t_i) \Delta p(0)}{N_t} \quad (4.47c)$$

$$\sigma_{(g,x)} = C_{c(g,x)}^n N_t \left\{ \frac{n_{po} + n_{1(g,x)}}{N_t} + \frac{\eta_{n(g,x)}(t_i) \Delta p(0)}{N_t} \right\} \quad (4.47d)$$

The non-linear term in Eq. (4.45) referred to as $g^n(t)$ may be written as Eq. (4.48) with $\eta_{ng}(t) = \Delta f_g(t)$ and $\eta_{nx}(t) = \Delta f_x(t)$.

$$g^n(t) = - [\Delta n_{nm}(t) - \eta_{ng}(t)] \eta_{ng}(t) - [\Delta n_{nm}(t) - \eta_{nx}(t)] \eta_{nx}(t) \quad (4.48)$$

Similarly, the non-linear term in Eq. (4.46), referred to as $g^p(t)$, may be expressed as Eq. (4.49).

$$g^p(t) = \left(\Delta n_{nm}(t) + \Delta f_g(t) \frac{N_t}{\Delta n(0)} - \eta_{pg}(t) \right) \eta_{ng}(t) + \left(\Delta n_{nm}(t) + \Delta f_x(t) \frac{N_t}{\Delta n(0)} - \eta_{px}(t) \right) \eta_{nx}(t) \quad (4.49)$$

The two conditions for evaluating $\eta_{ng}(t_0) > 0$ and $\eta_{nx}(t_0) > 0$, and the choice of $\eta_{pg}(0^+) > 0$ and $\eta_{px}(0^+) > 0$ at some $t = t_0$, are determined similar to the method in Section 4.2. For example, at low injection $\eta_{pg}(0^+) = 0$ and $\eta_{px}(0^+) = 0$ and the choice of $\eta_{pg}(0^+) > 0$ and $\eta_{px}(0^+) > 0$ at some $t = t_0$ given $\Delta f_g(t_{ig}) = \Delta n_{nm}(t_{ig})$ and $\Delta f_x(t_{ix}) = \Delta n_{nm}(t_{ix})$ results in $g^p(t) = 0$ at t_0 .

$$\eta_p(t_{ig}) = \Delta f(t_{ig}) \left(1 + \frac{N_t}{\Delta n(0)} \right) \quad (4.50a)$$

$$\eta_p(t_{ix}) = \Delta f(t_{ix}) \left(1 + \frac{N_t}{\Delta n(0)} \right) \quad (4.50b)$$

For a light impulse $\delta(t)$, carriers are generated such that $\Delta n(0) = \Delta p(0)$. The differential equations (4.45) and (4.46) at $t_0 = 0^+$ or $t = t_0$ are represented by equations (4.51) and (4.52). Constants $\eta_n(t_0)$ and $\eta_p(t_0)$ are dependent on the injection level. In Appendix I $\eta_n(t_0)$ and a condition for the existence of $\eta_n(t_0) > 0$, at some t_0 is evaluated.

$$\begin{aligned} -\frac{d\Delta n_{nm}(t)}{dt} \Big|_{t=t_0} &= \Delta n_{nm}(t_0) [(\gamma_g - \sigma_g) \\ &\quad + (\gamma_x - \sigma_x)] \\ &\quad - \frac{\sigma_g}{\Delta n(0)} N_t \Delta f_g(t_0) \\ &\quad - \frac{\sigma_x}{\Delta n(0)} N_t \Delta f_x(t_0) \end{aligned} \quad (4.51)$$

$$\begin{aligned} -\frac{d\Delta p_{nm}(t)}{dt} \Big|_{t=t_0} &= \Delta n_{nm}(t_0) [(\alpha_g - \beta_g) \\ &\quad + (\alpha_x - \beta_x)] \\ &\quad + \frac{\beta_g}{\Delta n(0)} N_t \Delta f_g(t_0) \\ &\quad + \frac{\beta_x}{\Delta n(0)} N_t \Delta f_x(t_0) \end{aligned} \quad (4.52)$$

The set of linear equations representing the ground excited state system are expressed as follows, where $D = d/dt$. See Appendix H for $\Delta f_g(t)$ and $\Delta f_x(t)$. The values of f_{og} and f_{ox} are determined from $df_g/dt = 0$ and $df_x/dt = 0$ respectively.

$$\begin{bmatrix} [D + (\gamma_{(g)} - \sigma_{(g)}) + (\gamma_{(x)} - \sigma_{(x)})] & 0 & -\sigma_{(g)} & -\sigma_{(x)} \\ -(\gamma_{(g)} - \sigma_{(g)}) & (\alpha_{(g)} - \beta_{(g)}) & \{ [D + (\sigma_{(g)} + \beta_{(g)})] + N_{t(x)} \left[C_{(xg)}^n \frac{f_{ox}}{(1-f_{ox})} + C_{(xg)}^p \frac{(1-f_{og})}{(1-f_{og})} \right] \} & -N_{t(g)} \left[C_{(xg)}^p \frac{f_{og}}{(1-f_{ox})} + C_{(xg)}^n \frac{(1-f_{og})}{(1-f_{ox})} \right] \\ -(\gamma_{(x)} - \sigma_{(x)}) & (\alpha_{(x)} - \beta_{(x)}) & -N_{t(x)} \left[C_{(gx)}^p \frac{f_{ox}}{(1-f_{og})} + C_{(gx)}^n \frac{(1-f_{ox})}{(1-f_{og})} \right] & \{ [D + (\sigma_{(x)} + \beta_{(x)})] + N_{t(g)} \left[C_{(gx)}^n \frac{f_{og}}{(1-f_{ox})} + C_{(gx)}^p \frac{(1-f_{og})}{(1-f_{ox})} \right] \} \\ 1 & -1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \Delta n_{nm}(t_0) \\ \Delta p_{nm}(t_0) \\ \Delta f_g(t_0) \\ \Delta f_x(t_0) \end{bmatrix} = 0 \quad (4.53)$$

The method using the differential operator D as in Refs. [14] [15] whereby the determinant of the matrix of equations (4.53) equals zero, allows the formation of the characteristic equation.

$$(D^3 + bD^2 + cD + d) \exp(-\lambda t) = 0 \quad (4.54)$$

The fundamental frequencies $\lambda_{1,2,3}$ (inverse time constants) may be evaluated by solving for the three roots of Eq. (4.55)

$$-\lambda^3 + b\lambda^2 - c\lambda + d = 0 \quad (4.55)$$

with the frequencies given by $\lambda_1 = 1/\tau_1$, $\lambda_2 = 1/\tau_2$ and $\lambda_3 = 1/\tau_3$.

The linear region (constant) of variation of fundamental frequencies $\lambda_{1,2,3}$ with injection level or excess carrier density is defined by Eq. (4.56). This condition is satisfied upon expansion of Eq. (4.56) for $\eta_{ng}(t_0) = 0$, $\eta_{nx}(t_0) = 0$ and $\eta_{pg}(t_0) = 0$, $\eta_{px}(t_0) = 0$ at $t_0 = 0^+$. An upper limit for the linear region of excess carrier density exists, referred to as $\Delta n(0)_{critical}$, is evaluated in Appendix I.

$$\frac{d\lambda_{1,2,3}}{d\Delta n(0)} = 0 \quad (4.56)$$

The non-linear region of variation of fundamental frequencies $\lambda_{1,2,3}$ with injection level or excess carrier density is defined by Eq. (4.57). This corresponds to the range of excess carrier density whereby the change in fundamental frequency with injection level is non-zero as expressed by Eq. (4.57).

$$\left| \frac{d\lambda_{1,2,3}}{d\Delta n(0)} \right| > 0 \quad (4.57)$$

This condition is satisfied for $\eta_{ng}(t_0) > 0$, $\eta_{nx}(t_0) > 0$ and $\eta_{pg}(t_0) > 0$, $\eta_{px}(t_0) > 0$ for some value of t_0 . $\Delta f_{g,x}(t) > 0$ can only be achieved with $t_0 > 0^+$ as $\Delta f_{g,x}(t)$ is greater than zero except at $t = 0^+$ and $t = \infty$.

Having evaluated the fundamental frequencies for the ground excited state system, an analytic solution of the differential rate equations for $\Delta n(t)$ and $\Delta p(t)$ may

Table 4.1: Typical defect level parameters for numerical solution of the discrete multiple defect level system.

parameter	level one	level two	level three
$E_t - E_v$ energy depth [eV]	0.55	0.65	0.75
N_t concentration [cm^{-3}]	5×10^{12}	5×10^{11}	5×10^{10}
σ_p cross section holes [cm^2]	$\sigma_{v1} = 8.5 \times 10^{-15}$	$\sigma_{v2} = 8.5 \times 10^{-17}$	$\sigma_{v3} = 8.5 \times 10^{-12}$
σ_n cross section electrons [cm^2]	$\sigma_{c1} = 9.0 \times 10^{-17}$	$\sigma_{c2} = 9.0 \times 10^{-15}$	$\sigma_{c3} = 9.0 \times 10^{-14}$

be written as Eqs. (4.58) and (4.59) respectively.

$$\Delta n(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t) \quad (4.58)$$

$$\Delta p(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} P_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t) \quad (4.59)$$

4.4 Numerical Solution for the Multiple Level and Excited State Systems: Ideal Impulse $\delta(t)$

Considering the multiple discrete defect level system the coupled differential equations we are interested in are of the form of Eqs. (4.1) and (4.2) with df_k/dt from Eq. (4.30). These equations form a set of second order coupled differential equations Nomura and Blakemore [4] which are non-linear and are normally solved numerically. There is no a priori knowledge about $n(t + \Delta t)$ as it represents the time evolution of the excess carrier concentration derived numerically. A correlation between the numerical solution and the predictions of the analytical solution is made and found to indicate close agreement. This confirms the method used to analyse the decay as a useful tool.

A fifth order Runge-Kutta scheme as in Refs. [17] [18], is chosen to represent discrete values of $n(t)$, $p(t)$ and $f_k(t)$, to ensure convergence to the equilibrium

concentration for the minority carrier as $t \rightarrow \infty$. The normalised excess carrier concentrations at $t = 0^+$ are given by $\Delta n_{nm}(0^+) = 1$ and $\Delta p_{nm}(0^+) = 1$. The defect level initial occupation is assumed not to change from $t = 0^-$ to $t = 0^+$ ($f(0^+) = f(0^-)$). Table 4.1 indicates typical data used in the numerical solution.

As mentioned in Chapter 2 the component exponentials, of a sum of exponentials, are determined by a multi-transient technique. Multi-transient analysis refers to the extraction of component exponential terms from a sum of exponentials comprising the signal. The methods available as in Refs. [20] [21] [22] present a means of analysing signals with additive white gaussian noise. In addition, where the data matrix and the observation matrix may be subject to noise fluctuations, the Total Least Squares method Van Huffel [23] (TLS) is employed. This method models the multi-exponential signal as an autoregressive process. For the present analysis the TLS technique of Refs. [22] and [24] multi-transient analysis using Singular Value Decomposition (SVD) Klema [25] is applied to the analysis of the multi-component exponential decay.

TLS multi-transient analysis of the numerical solution of equations (4.1), (4.2) and (4.30) results in the determination of frequencies which are compared with those derived from a theoretical expression represented by Eq. (4.33). Figure 4.3 shows the comparison between the decay time constants $\tau_{m+1} = 1/\lambda_{m+1}$ for $m = 3$ as calculated from Eq. (4.33) and as evaluated by TLS analysis of numerical data $[\Delta n(t + \Delta t)]$ for $T = 300 \text{ K}$. The figure indicates the variation of fundamental frequencies with excess carrier concentration. Agreement is excellent and as such contributes to the confidence in the TLS method of analysis. The onset of the non-linear variation of frequencies λ_{m+1} with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{critical}$ is clearly seen in the figure. The linear portion extends to $5 \times 10^{11} \text{ cm}^{-3}$ and begins to diverge for $\Delta n(0)$ greater than $5 \times 10^{11} \text{ cm}^{-3}$. This indicates that the linear region is in close agreement with the definition given by Eq. (4.34). See Appendix G for the evaluation of $\Delta n(0)_{critical}$. For parameters listed in Table 4.1, $\Delta n(0)_{critical} =$

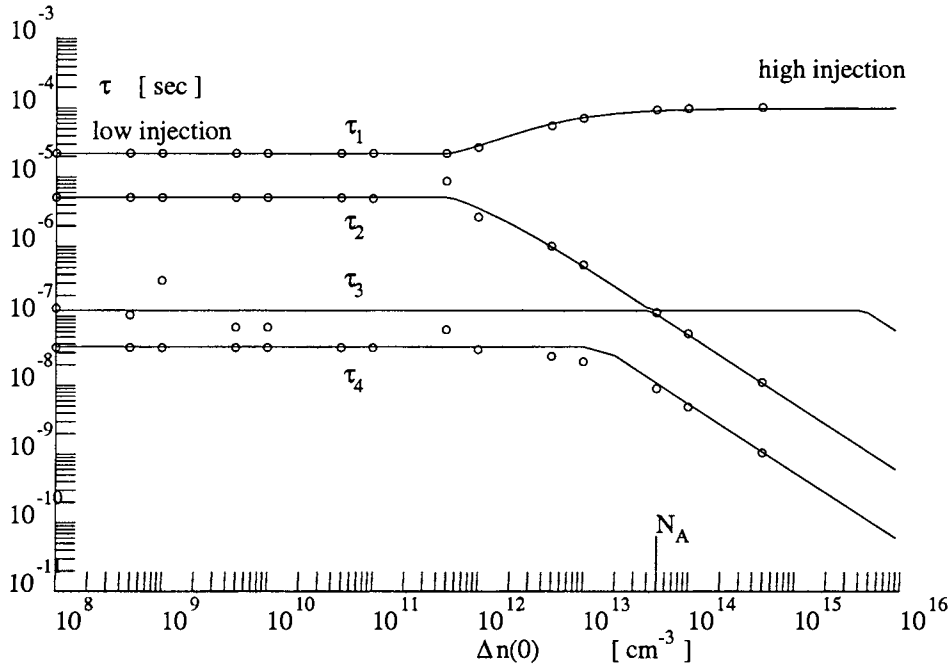


Figure 4.3: A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$, $\tau_3 = 1/\lambda_3$ and $\tau_4 = 1/\lambda_4$ versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 4.1 for defect level parameters. Continuous line: τ_1 , τ_2 , τ_3 , τ_4 predicted by Eq. (4.33) Circles: τ_1 , τ_2 , τ_3 , τ_4 derived from multi-transient analysis of the numerical solution

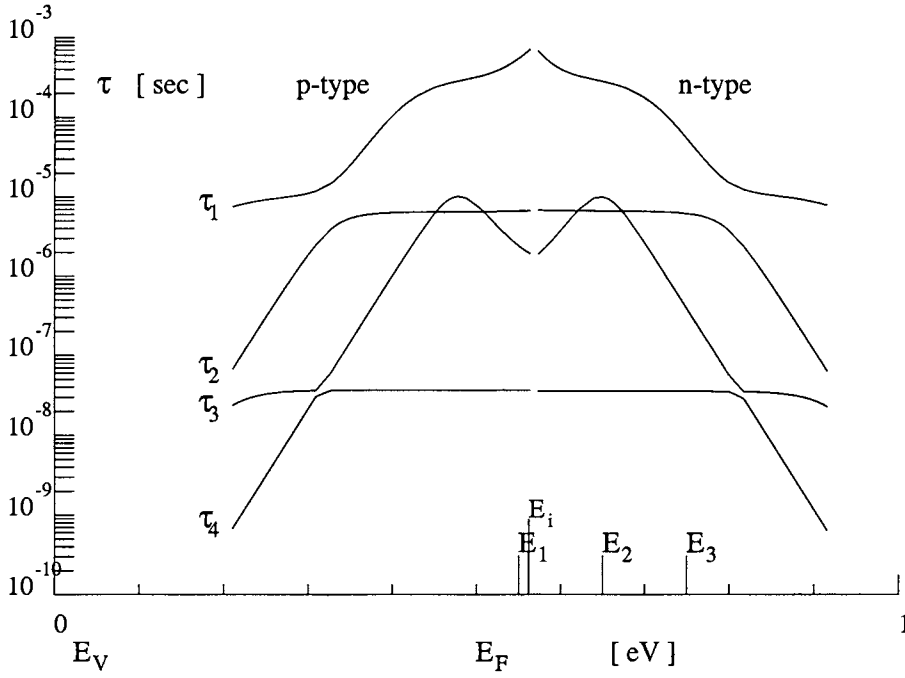


Figure 4.4: Decay time constant $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$, $\tau_3 = 1/\lambda_3$ and $\tau_4 = 1/\lambda_4$ versus the Fermi level E_F eV for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. The intrinsic Fermi level is shown as E_i . Continuous line: $\tau_{1,2,3,4}$ calculated by Eq. (4.33)

$5.44 \times 10^{11} \text{ cm}^{-3}$. Note also that TLS multi-transient analysis of the numerical solution results in τ_{m+1} in close agreement with that predicted by the solution for τ_{m+1} of Eq. (4.33) for high injection. Some values from the analysis of the numerical solution (circles), could not be resolved due to the very small magnitude of the coefficient of the exponential term.

Figure 4.4 shows the comparison between the decay time constants $\tau_{1,2,3,4}$ as calculated from Eq. (4.33) for $T = 300 \text{ K}$, versus the Fermi level E_F . The doping concentration for the p-type and n-type samples varies from $5 \times 10^{10} \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. From this figure τ_1 describes the minority carrier decay constant and τ_{k+1} with $k > 1$, the majority carrier decay constants, by analogy with Shockley and Read [2] for the steady state. As such they represent fundamental decay time

constants.

Figure 4.3 indicates that for $\Delta n(0) > \Delta n(0)_{critical}$, τ_1 , the minority carrier (p-type) time constant is becoming longer. The minority carriers (electrons) are remaining in the conduction band for a longer average time indicating that there are fewer holes at the defect level for them to recombine with. The defect level electron population is increasing and electrons are remaining at the defect level for a longer average time. This is referred to as minority carrier trapping. The time constant τ_1 remains constant in the linear region of variation of τ_{k+1} with $\Delta n(0)$. This region corresponds to recombination only whereas the non-linear region undergoes recombination and trapping. Eventually the trapping saturates as $\Delta n(0)$ is increased to high injection and the time constant τ_1 , becomes almost constant.

Further, by recalling the expression Eq. (4.36) for the decay $\Delta n_{nm}(t)$, the infinity of time constants is found to be linear combinations of $m+1$ fundamental frequencies λ_{k+1} . Table 4.2 indicates the correlation with the prediction of equations (4.33) and (4.36), and TLS analysis of the decay $\Delta n(t + \Delta t)$ within the limitations of the TLS method. No a priori knowledge is known about time constants associated with the numerical solution, yet the agreement of the analytical and TLS methods with respect to the linear combination of λ_{k+1} is excellent. Note the magnitudes of the coefficients decrease rapidly. In addition for the transient case in low injection, the magnitude of the coefficient for τ_2 is significant.

The equations describing the time evolution of the decay for the ground excited state system are given by Eqs. (4.38), (4.39), (4.40) and (4.41). A fifth order Runge-Kutta scheme as in Refs. [17] [18], is chosen to represent discrete values of $n(t)$, $p(t)$ and $f_k(t)$. TLS multi-transient analysis of the numerical solution of the given equations results in the determination of frequencies which are compared with the derived theoretical expressions represented by Eq. (4.55). Figure 4.5 shows the comparison between the decay time constants $\tau_{1,2,3} = 1/\lambda_{1,2,3}$ as calculated from Eq. (4.55) and as evaluated by TLS analysis of numerical data $[\Delta n(t + \Delta t)]$ for $T = 300$

Table 4.2: TLS analysis of numerical data $\delta_n(t + \Delta t)$ for the case of level one, level two and level three included in the model. Evaluation of Eq. (4.33) and Eq. (4.36) for $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$.

	Eq. (4.33)	TLS frequency	TLS coefficient
λ	$\lambda [\text{secs}^{-1}]$	$\lambda [\text{secs}^{-1}]$	
λ_1	4.52402×10^4	4.523774×10^4	$N_{1000} = 6.27774 \times 10^{-1}$
$2\lambda_1$		8.785162×10^4	$N_{2000} = 6.72298 \times 10^{-4}$
λ_2		19.40604×10^4	$N_{0100} = 3.62217 \times 10^{-1}$
$\lambda_1 + \lambda_2$	19.4182×10^4	22.47085×10^4	$N_{1100} = 4.97937 \times 10^{-3}$
$2\lambda_2$		38.37658×10^4	$N_{0200} = 9.82831 \times 10^{-4}$
$2\lambda_1 + 2\lambda_2$		50.62222×10^4	$N_{2200} = 1.41584 \times 10^{-5}$
λ_3	820.513×10^4	677.3815×10^4	$N_{0010} = 3.03147 \times 10^{-10}$
$2\lambda_3$		1989.850×10^4	$N_{0020} = 6.42367 \times 10^{-8}$
λ_4	2735.61×10^4	2736.545×10^4	$N_{0001} = 3.35857 \times 10^{-3}$

K . The figure indicates the variation of fundamental frequencies with excess carrier concentration. Agreement is excellent. Again the onset of the non-linear variation of frequencies $\lambda_{1,2,3}$ with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{critical}$ is clearly seen in the figure.

Figure 4.6 shows the comparison between the decay time constants τ_1 , τ_2 and τ_3 as calculated from Eq. (4.55) for $T = 300\text{ K}$, versus the Fermi level E_F . The doping concentration for the p-type and n-type samples varies from $5 \times 10^{10}\text{ cm}^{-3}$ to $1 \times 10^{16}\text{ cm}^{-3}$. Agreement is very good for the numerical solution and the calculated $\tau_{1,2,3}$. From this figure τ_1 describes the minority carrier decay constant and $\tau_{2,3}$, the majority carrier decay constants.

4.5 Discussion

From the theory presented it is evident that τ_1 represents an important parameter in terms of the minority carrier trapping behaviour. This extends to both the multiple discrete defect level system and the ground excited state defect level system. These two systems are considered to be the most significant sources of defect level effects on the minority carrier. The measurement of τ_1 with excess carrier concentration for a given temperature in the linear and non-linear region realises a basis for evaluating semiconductor material quality. In particular the linear region which represents recombination-only allows comparison of semiconductor time constants (τ_1). Comparison of time constants in the non-linear region is at best unreliable as the degree of trapping is unknown and the range of variation of τ_1 with excess carrier concentration is significant.

The ground excited state system may be applicable to the boron-acceptor complex Zhao [33]. This is not explored further in the present work. It is also evident that even a very low concentration of ground excited state defect levels (see table 4.3) has a dramatic effect on the time constant τ_1 . Also, for such a system the effect is significantly different for p-type as opposed to n-type (see Figure 4.6). Again

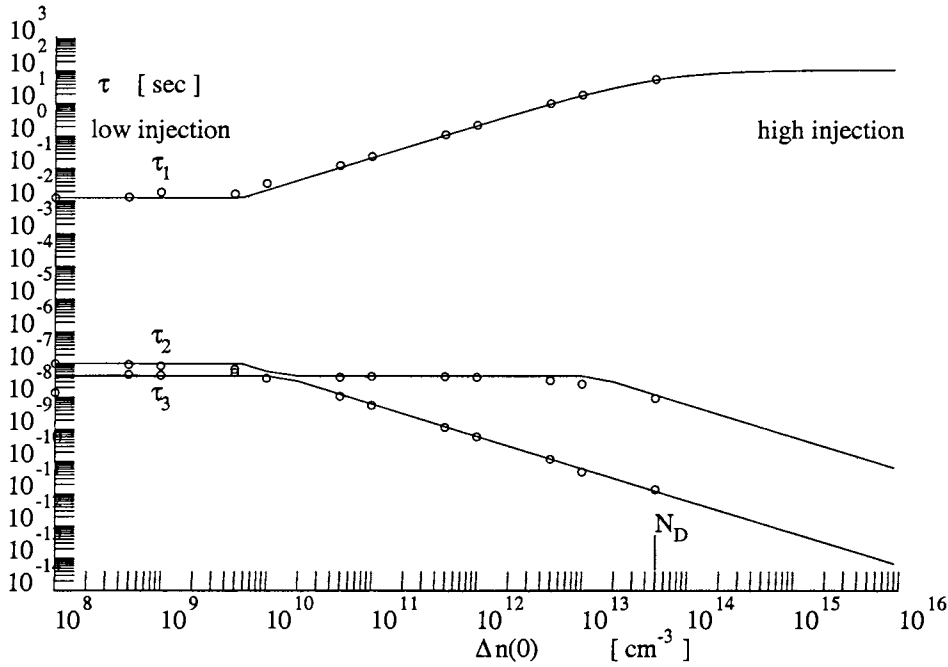


Figure 4.5: A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system versus excess electron concentration $\Delta n(0)$. The doping concentration N_D of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table 4.3 for defect level parameters. Continuous line: τ_1 , τ_2 , τ_3 predicted by Eq. (4.55) Circles: τ_1 , τ_2 , τ_3 derived from multi-transient analysis of the numerical solution

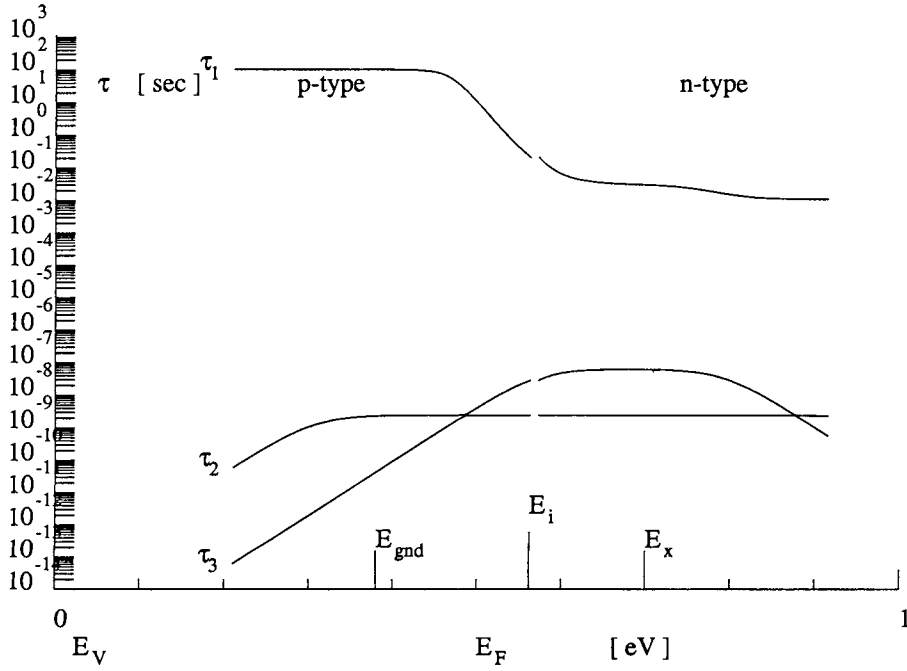


Figure 4.6: Decay time constant $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system versus the Fermi level E_F eV for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. The intrinsic Fermi level is shown as E_i . Continuous line: $\tau_{1,2,3}$ calculated by Eq. (4.55)

Table 4.3: Typical defect level parameters for numerical solution of the ground excited state system.

parameter	ground state	excited state
$E_c - E_x$ energy depth [eV]		0.425
$E_x - E_{gnd}$ energy depth [eV]	0.320	
N_t concentration [cm^{-3}]	5×10^4	5×10^4
σ_p cross section holes [cm^2]	$\sigma_{vg}^p = 8.5 \times 10^{-14}$	$\sigma_{vx}^p = 8.5 \times 10^{-11}$
σ_n cross section electrons [cm^2]	$\sigma_{cg}^n = 8.5 \times 10^{-17}$	$\sigma_{cx}^n = 8.5 \times 10^{-15}$

a measurement of τ_1 from the linear to the non-linear regions indicates material quality (see Figure 4.5).

The defect level parameters for the single defect level in Chapter 2 Ref. [1] were intentionally retained in the present analysis of the multiple discrete level case (see table 4.1). Comparison of $\tau_1 = 2.55 \times 10^{-5} sec$ for the single defect state of Chapter 2 Ref. [1] and that for the multiple discrete level state $\tau_1 = 2.21 \times 10^{-5} sec$ (see Table 4.2) reveals that additional levels results in a faster minority carrier time constant. This represents a relative error greater than ten per cent in addition to measurement errors. This has obvious implications for interpretation of experimental data where τ_1 is the dominant decay time constant. It thus becomes imperative that a multiple level model such as proposed in the present work be used to interpret data as the dominant level model is not sufficient to provide accurate defect level parameters. Further, the above discussion may help to explain the anomalies arising from interpreting data in experimental methods such as Deep Level Transient Spectroscopy (DLTS) which determine the dominant decay time constant for a given rate window at a given temperature.

Furthermore, from the multitransient analysis of the numerical solution the num-

ber of fundamental frequencies is directly related to the number of electrically active defect levels present in the semiconductor sample. In both the multiple discrete level system and the coupled level system the number of fundamental frequencies is $m + 1$ where there are m defect levels. Hence from a practical viewpoint the total number of defects may be determined by analysing the decay for the fundamental frequencies.

Chapter 5

Multiple level Defect Species

Evaluation from Average Carrier

Decay

5.1 Introduction

As previously noted, decay of carriers due to an impulse of light $N_0\delta(t)$ via a single level defect in the bandgap is described by the Shockley-Read-Hall (SRH) differential rate equations Shockley and Read [2]. These equations refer to the average rate of transitions via the defect level for the processes of recombination, capture and emission. The recent analytic solution to the SRH rate equations of Chapter 2 Ref. [1] is composed of an infinity of monoexponential terms, the frequencies λ_{k+1} or inverse time constants ($\lambda_{k+1} = 1/\tau_{k+1}$) of which are a linear combination of two fundamental frequencies for the single level case. The fundamental frequency $\lambda_1 = 1/\tau_1$ refers to the minority carrier decay. Application of the single-level method of solution to two multiple defect systems in 4 indicates that the decay contains $k+1$

fundamental frequencies or inverse time constants for k discrete defect levels. The time constant τ_1 is the dominant decay time constant. A plot of τ_1 versus the excess carrier concentration indicates the recombination only and trapping with recombination regions.

These analytic solutions for the single level differential equations and consequently for the multiple level case were derived without any approximation for arbitrary doping concentration $N_{A,D}$, non-degenerate excess carrier concentration and defect level parameters, N_{tk} , the concentration and σ_{nk} , σ_{pk} , the electron and hole cross sections for the k^{th} level respectively. Note that the differential equations apply for non-degenerate statistics so that there is an upper limit on the excess carrier concentration N_{ex} [11].

A contribution of this chapter is the solution of the carrier continuity equation including a multiple defect level recombination term. This solution is determined, with constraints which reflect the experimental conditions, in order to ascertain the nature of the decay as predicted by theory in Chapter 4 and the average decay determined in section 5.2. The diffusion term $D_{n,p}$, which is expressed in terms of the mobility $\mu_{n,p}$, may be taken to first order at low frequency N_{ex} [34]. The first order dependence of the diffusion term, expressed in terms of the mobility as above also applies for non-degenerate statistics. The differential rate equations referred to as the Shockley-Read-Hall rate equations for the single level defect Ref. [2] and the differential rate equations for the multiple defect systems of Chapter 4 apply for non-degenerate statistics. Furthermore, in the derivation of the SRH rate equations, the carriers are assumed to reside at the band edge and so Boltzmann statistics apply and non-parabolic, multiple bands are not considered.

The relatively long lifetime of the particular CZ silicon sample under consideration suggests that the impurity levels are close to the band edges, yielding a long time constant τ_1 . The current work investigates two-level carrier transitions for the ground and excited state or coupled levels system of Chen et al [35] and Frens et

al [36]. Experimental results are explained in terms of defect complexes which have these ground and excited states near the band edges. For the particular silicon CZ sample, three defect complexes are identified as possible sources of the relatively long time constant τ_1 . The first is the carbon interstitial - oxygen interstitial $C_i - O_i$ complex Ref. [36], the second is the vacancy - oxygen $V - O$ complex Ref. [36] and the third is the phosphorus donor (n-type) and the ground state of the $V - O$ complex or $C_i - O_i$ complex Ref. [35]. These complexes have energy levels near the band edges.

It is shown that multiple level fundamental time constants for the ground excited state or coupled levels system, for one of the complexes above, are in agreement with experimental data determined by a contactless photoconductance technique. This technique measures the average or volume integrated decay. The average decay in a semiconductor wafer (silicon) with an ideal surface passivation described by the surface recombination velocity $S = 0 \text{ cm/s}$ is derived in Luke [28]. An assessment of the effect of bulk minority carrier recombination and trapping is not performed in Ref. [28] although an effective bulk lifetime is included. The effective bulk lifetime describes the effect of a dominant defect level. For the more accurate case of multiple defect levels the average decay is determined analytically from the theory of Chapter 4. This forms the basis for interpreting the experimental results. An evaluation of recombination and or trapping is performed in the present work by plotting the τ_k versus excess carrier concentration. For the complexes stated above a difference is found in the nature of the plots. This represents a method of identifying particular defect species.

The paper is organised as follows. In Section 5.2 the method of solving the carrier continuity equations analytically for the above constraints is presented. The average decay which indicates the volume integrated decay measured by the photoconductance decay method is evaluated. Section 5.3 describes the derivation of the ground excited state system equations and the excess carrier concentration decay equation.

This equation includes the fundamental frequencies for this defect system. Sections 5.4, 5.5 and 5.6 describe the experimental constraints, the experimental conditions and the experimental results respectively. This is followed by a Section 5.7 on a discussion of the results.

5.2 Impulse Response and Average Excess Carrier Concentration

For the purposes of illustrating the method of solution, a multiple-level defect analytic solution of Chapter 4 to the rate equations is used in the carrier continuity equation solution method. Consider a p-type silicon wafer with a defect with a ground excited state uniformly distributed. The analytic solution to the rate equations with excess minority carrier concentration $\Delta n(t)$, in the absence of a field ξ and diffusion $D_{n,p}$ is represented by Eq. (5.1). This expression is the impulse response $\Delta n(t)$ as derived in Chapter 2 Ref. [1] to a light impulse $N_o\delta(t)$ with a single level defect. In the above derivation the excess carrier concentration $\Delta n(0)$ is uniformly distributed throughout the sample at $t = 0^+$. The non-uniform excess carrier generation, through the thickness of the sample, for the multiple defect system equations of Chapter 4 is considered in section 5.3.

$$\begin{aligned}\Delta n(t) &= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t) \\ &= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} E_{i,j,u}\end{aligned}\tag{5.1}$$

The recombination rate $U_n(t)$ is defined as follows Wertheim [9] where $\Delta n(t)$ represents the impulse response for recombination.

$$U_n(t) = -\frac{d\Delta n(t)}{dt}\tag{5.2}$$

and from Eq. (5.1):

$$U_n(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} (i\lambda_1 t + j\lambda_2 t + u\lambda_3 t) N_{i,j,u} E_{i,j,u} \quad (5.3)$$

where

$$E_{i,j,u} = \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t) \quad (5.4)$$

In the present analysis the carrier and recombination spatial profile as well as the time evolution, is sought normal to the surface at the point of the incidence of light. For the single-level, neglecting excited states, Auger recombination and radiative recombination, the carrier continuity equation for the one dimensional case is given as follows Sze [11]. Simplifications are made such that the generation $G_{n,p}$ at $t = 0^+$ after cessation of the impulse, is negligible. The electric field ξ in the bulk is also considered negligible.

$$\frac{\partial \Delta n(x, t)}{\partial t} = D_n \frac{\partial^2 \Delta n(x, t)}{\partial x^2} - U_n(x, t) \quad (5.5)$$

Consider the following expressions for the recombination rate $U_n(x, t)$ and the excess carrier concentration $\Delta n(x, t)$, which include the spatial dependence in the term $u(x, t)$.

$$U_n(x, t) = u(x, t) \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} (i\lambda_1 t + j\lambda_2 t + u\lambda_3 t) N_{i,j,u} E_{i,j,u} \quad (5.6)$$

$$\Delta n(x, t) = u(x, t) \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} E_{i,j,u} \quad (5.7)$$

It remains to find an expression for $u(x, t)$.

The following are the boundary conditions due to the surface passivation where S is the surface recombination velocity and D_n is the diffusion constant. Consider both surfaces to be identically passivated such that they both have the same value of S .

$$D_n \left. \frac{\partial \Delta n(x, t)}{\partial x} \right|_{x=-d/2} = S \Delta n(-d/2, t) \quad (5.8a)$$

$$-D_n \frac{\partial \Delta n(x, t)}{\partial x} \Big|_{x=+d/2} = S \Delta n(+d/2, t) \quad (5.8b)$$

and where the boundary conditions transform to:

$$D_n \frac{\partial u(x, t)}{\partial x} \Big|_{x=-d/2} = S u(-d/2, t) \quad (5.9a)$$

$$-D_n \frac{\partial u(x, t)}{\partial x} \Big|_{x=+d/2} = S u(+d/2, t) \quad (5.9b)$$

Using the principle of the separation of variables, the required solution of Eq. (5.5) is represented by,

$$u(x, t) = X(x)T(t) \quad (5.10)$$

such that by substitution of Eq. (5.10) into Eq. (5.5) realises an expression Eq. (5.11) whereby the two functions of x and t can only attain equality if equal to a constant.

$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} = \frac{1}{D_n T(t)} \frac{dT(t)}{dt} = -\alpha^2 \quad (5.11)$$

The respective solutions become,

$$T(t) = e^{-\alpha^2 D_n t} \quad (5.12)$$

$$X(x) = A \cos(\alpha x) + B \sin(\alpha x) \quad (5.13)$$

An equation for $u(x, t)$ (excess carriers) results from the separation of variables McKelvey [37], where the A_m and B_m are given in Ref. [28]. A linear superposition of solutions Eq. (5.10) is required to satisfy the boundary conditions Eq. (5.9). Each term in the summation (each value of m) satisfies the boundary conditions.

$$\begin{aligned} u(x, t) &= \sum_m u_m(x, t) \\ &= \sum_m \left[A_m e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right. \\ &\quad \left. + B_m e^{-\alpha_m^2 D_n t} \sin(\alpha_m x) \right] \end{aligned} \quad (5.14)$$

Due to symmetry, the spatial dependence of excess carrier concentration $\Delta n(x, t)$ must be an even function of x so $B_m \rightarrow 0$. However the boundary condition Eq. (5.9) must also be satisfied, requiring agreement of Eq. (5.14) and Eq. (5.9) resulting in the equation (5.15), using the method for finding the coefficients of a Fourier series (see appendix of Ref. [28]).

$$\Delta u(x, t) = \sum_m \left[A_m(\lambda) e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right] \quad (5.15)$$

where,

$$\begin{aligned} A_m(\lambda) = & \frac{4g'_o \alpha_m e^{-\alpha_\lambda d/2} (1 + R e^{-\alpha_\lambda d})}{(\alpha_\lambda^2 + \alpha_m^2) [\alpha_m d + \sin(\alpha_m d)]} \\ & \times \left[\alpha_\lambda \sinh \left(\frac{\alpha_\lambda d}{2} \right) \cos \left(\frac{\alpha_m d}{2} \right) \right. \\ & \left. + \alpha_m \cosh \left(\frac{\alpha_\lambda d}{2} \right) \sin \left(\frac{\alpha_m d}{2} \right) \right] \end{aligned} \quad (5.16)$$

A general solution $\Delta n(x, t)$ is found by multiplying the impulse response given by Eq. (5.1) by that of Eq. (5.15) as shown in Eq. (5.17).

$$\begin{aligned} \Delta n(x, t) = & \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} E_{i,j,u} \\ & \times \sum_m \left[A_m(\lambda) e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right] \end{aligned} \quad (5.17)$$

Similarly for the solution $U_n(x, t)$ given by Eq. (5.18).

$$\begin{aligned} U_n(x, t) = & \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} (i\lambda_1 t + j\lambda_2 t + u\lambda_3 t) N_{i,j,u} E_{i,j,u} \\ & \times \sum_m \left[A_m(\lambda) e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right] \end{aligned} \quad (5.18)$$

It may be shown by substitution for each value of the mode of decay m that equations (5.17) and (5.18) are a solution to the carrier continuity equation (5.5). These solutions include the spatial dependence, a term related to the diffusion of carriers to the surfaces and a recombination via multiple levels defect term.

The value α_m is found by substituting Eq. (5.15) into one of Eq. (5.9), resulting in the following condition to be satisfied by the selection of an appropriate surface recombination velocity S .

$$\cot\left(\frac{\alpha_m d}{2}\right) = \frac{\alpha_m D_n}{S} \quad (5.19)$$

The average excess carrier concentration is now sought. Integrating Eq. (5.17) with respect to x Eq. (5.20), realises an expression for the average density of minority carriers representing the impulse response given by Eq. (5.21).

$$\Delta n_{av}(t) = \frac{1}{d} \int_{-d/2}^{d/2} \Delta n(x, t) dx \quad (5.20)$$

The integral Eq. (5.20) may be evaluated yielding the result Eq. (5.21).

$$\begin{aligned} \Delta n_{av}(t) &= \left[\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - \lambda_3 t) \right] \\ &\times \frac{8g_o e^{-\alpha_\lambda d/2}}{d} \sum_m^{\infty} \frac{\sin(\alpha_m d/2)}{(\alpha_\lambda^2 + \alpha_m^2) [\alpha_m d + \sin(\alpha_m d)]} \\ &\times \left[\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) \cos\left(\frac{\alpha_m d}{2}\right) + \alpha_m \cosh\left(\frac{\alpha_\lambda d}{2}\right) \sin\left(\frac{\alpha_m d}{2}\right) \right] e^{-(\alpha_m^2 D_n)t} \end{aligned} \quad (5.21)$$

As $S \rightarrow \infty$, from equation (5.19), $\alpha_m d/2 = \pi/2, 3\pi/2, 5\pi/2 \dots$ such that for $m = 1, 2, 3, \dots$, α_m is given by Eq. (5.22).

$$\alpha_m = \frac{(2m-1)\pi}{d} \quad (5.22)$$

The average density of minority carriers representing the impulse response for $S \rightarrow \infty$, is given by Eq. (5.23) with $m = 1, 2, 3, \dots$ being the mode of decay.

$$\begin{aligned} \Delta n_{av}(t) &= \left[\sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - \lambda_3 t) \right] \\ &\times \frac{8g_o e^{-\alpha_\lambda d/2}}{d} \sum_{m=1}^{\infty} \frac{\sin(\alpha_m d/2)}{(\alpha_\lambda^2 + \alpha_m^2) [\alpha_m d + \sin(\alpha_m d)]} \\ &\times \left[\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) \cos\left(\frac{\alpha_m d}{2}\right) + \alpha_m \cosh\left(\frac{\alpha_\lambda d}{2}\right) \sin\left(\frac{\alpha_m d}{2}\right) \right] e^{-(\alpha_m^2 D_n)t} \end{aligned} \quad (5.23)$$

The initial average minority carrier profile is exponential with a peak at $x = -d/2$ normal to the incidence of light.

For the case where the surface recombination velocity S approaches zero in the limit, the condition given by Eq. (5.19) indicates that $\alpha_m d/2 = 0, 2\pi, 4\pi, 6\pi, \dots$, and all the terms in the summation of equation (5.21) vanish except for $\alpha_m d/2 = 0$. The mode of decay is $m = 0$. This results in an indeterminate form for the limit which is solved by the use of L'Hopital's rule. The result for the $S = 0$, case given by Eq. (5.24), indicates that only the bulk term is involved in the decay.

$$\begin{aligned} \lim_{\alpha_0 \rightarrow 0} \Delta n_{av}(t) &= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - \lambda_3 t) \\ &\times \left[\frac{4g_o \alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) e^{-\alpha_\lambda d/2}}{d} \right] \end{aligned} \quad (5.24)$$

$$\begin{aligned} \lim_{\alpha_0 \rightarrow 0} \Delta p_{av}(t) &= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} P_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - \lambda_3 t) \\ &\times \left[\frac{4g_o \alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) e^{-\alpha_\lambda d/2}}{d} \right] \end{aligned} \quad (5.25)$$

Note that the coefficient of the exponential terms contains the absorption coefficient α_λ which is related to the wavelength of the incident light. The expressions for average decay indicate that the fundamental frequencies are unaffected by the absorption coefficient.

5.3 Ground and Excited State System: Fundamental frequencies λ

As mentioned in Chapter 4 consider a defect energy level E_{gnd} representing the ground state with an excited state E_x in the bandgap of an n-type semiconductor. The set of linear equations representing the ground excited state system are Eqs. (5.26) with the differential operator $D = d/dt$, where C_{gx}^n , C_{gx}^p , C_{xg}^n and C_{xg}^p are

constants related to the carrier transitions between states. The values of f_{og} and f_{ox} are determined from $df_g/dt = 0$ and $df_x/dt = 0$ respectively.

$$\begin{bmatrix}
 [D + (\gamma_{(g)} - \sigma_{(g)}) & 0 & -\sigma_{(g)} & -\sigma_{(x)} \\
 + (\gamma_{(x)} - \sigma_{(x)})] & & & \\
 -(\gamma_{(g)} - \sigma_{(g)}) & (\alpha_{(g)} - \beta_{(g)}) & \{ [D + (\sigma_{(g)} + \beta_{(g)})] & -N_{t(g)} \left[C_{(xg)}^p \frac{f_{og}}{f_{ox}} \right. \\
 & & + N_{t(x)} \left[C_{(xg)}^n \frac{f_{ox}}{f_{og}} & + C_{(xg)}^n \frac{(1-f_{og})}{(1-f_{ox})} \right] \\
 & & + C_{(xg)}^p \frac{(1-f_{ox})}{(1-f_{og})} \} & \\
 -(\gamma_{(x)} - \sigma_{(x)}) & (\alpha_{(x)} - \beta_{(x)}) & -N_{t(x)} \left[C_{(gx)}^p \frac{f_{ox}}{f_{og}} & \{ [D + (\sigma_{(x)} + \beta_{(x)})] \right. \\
 & & + C_{(gx)}^n \frac{(1-f_{ox})}{(1-f_{og})} & + N_{t(g)} \left[C_{(gx)}^n \frac{f_{og}}{f_{ox}} \right. \\
 & & & + C_{(gx)}^p \frac{(1-f_{og})}{(1-f_{ox})} \} \\
 1 & -1 & 1 & 1
 \end{bmatrix}
 \begin{bmatrix}
 \Delta n_{nm}(t_0) \\
 \Delta p_{nm}(t_0) \\
 \Delta f_g(t_0) \\
 \Delta f_x(t_0)
 \end{bmatrix}
 = 0
 \quad (5.26)$$

where constants $\eta_{n(g,x)}(t_0)$ and $\eta_{p(g,x)}(t_0)$ in Eq. (5.27) may be evaluated as in Chapter 2 Ref. [1].

$$\begin{aligned}
 \alpha_{(g,x)} = & C_{v(g,x)}^p N_{t(g,x)} \left\{ \frac{p_{1(g,x)}}{p_{po} + p_{1(g,x)}} + \frac{p_{po} + p_{1(g,x)}}{N_{t(g,x)}} \right. \\
 & \left. + \frac{\eta_{p(g,x)}(t_0) \Delta p(0)}{N_{t(g,x)}} \right\}
 \end{aligned} \quad (5.27a)$$

$$\begin{aligned}
 \beta_{(g,x)} = & C_{v(g,x)}^p N_{t(g,x)} \left\{ \frac{p_{po} + p_{1(g,x)}}{N_{t(g,x)}} + \frac{\eta_{p(g,x)}(t_0) \Delta n(0)}{N_{t(g,x)}} \right\}
 \end{aligned} \quad (5.27b)$$

$$\begin{aligned}
 \gamma_{(g,x)} = & C_{c(g,x)}^n N_{t(g,x)} \left\{ \frac{n_{1(g,x)}}{n_{po} + n_{1(g,x)}} + \frac{n_{po} + n_{1(g,x)}}{N_{t(g,x)}} \right. \\
 & \left. + \frac{\eta_{n(g,x)}(t_0) \Delta n(0)}{N_{t(g,x)}} \right\}
 \end{aligned} \quad (5.27c)$$

$$\begin{aligned}
 \sigma_{(g,x)} = & C_{c(g,x)}^n N_{t(g,x)} \left\{ \frac{n_{po} + n_{1(g,x)}}{N_{t(g,x)}} + \frac{\eta_{n(g,x)}(t_0) \Delta p(0)}{N_{t(g,x)}} \right\}
 \end{aligned} \quad (5.27d)$$

with

$$n_{1g} = N_c \exp \left(-\frac{(E_c - E_{gnd})}{kT} \right) \quad (5.28a)$$

$$p_{1g} = N_v \exp \left(-\frac{(E_{gnd} - E_v)}{kT} \right) \quad (5.28b)$$

$$n_{1x} = N_c \exp \left(-\frac{(E_c - E_x)}{kT} \right) \quad (5.28c)$$

$$p_{1x} = N_v \exp \left(-\frac{(E_x - E_v)}{kT} \right) \quad (5.28d)$$

The method using the differential operator D as in Refs. [14] [15] whereby the determinant of the matrix of equations (5.26) equals zero, allows the formation of the characteristic equation.

$$(D^3 + bD^2 + cD + d) \exp(-\lambda t) = 0 \quad (5.29)$$

The fundamental frequencies $\lambda_{1,2,3}$ (inverse time constants) may be evaluated by solving for the three roots of Eq. (5.30)

$$-\lambda^3 + b\lambda^2 - c\lambda + d = 0 \quad (5.30)$$

with the frequencies given by $\lambda_1 = 1/\tau_1$, $\lambda_2 = 1/\tau_2$ and $\lambda_3 = 1/\tau_3$.

Following the analysis in Chapter 2 Ref. [1], Chapter 4 and Choo [10], the following equations for the excess carrier concentrations $\Delta n_{av}(t)$ Eq. (5.31) and $\Delta p_{av}(t)$ Eq. (5.32) may be written for the multiple level or ground excited state system. There are three fundamental time constants.

$$\begin{aligned} \Delta n_{av}(t) = & \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} N_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t) \\ & \times \left[\frac{4g_o \alpha_\lambda \sinh \left(\frac{\alpha_\lambda d}{2} \right) e^{-\alpha_\lambda d/2}}{d} \right] \end{aligned} \quad (5.31)$$

and:

$$\Delta p_{av}(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} P_{i,j,u} \exp(-i\lambda_1 t - j\lambda_2 t - u\lambda_3 t) \times \left[\frac{4g_o\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) e^{-\alpha_\lambda d/2}}{d} \right] \quad (5.32)$$

Equations 5.31 and 5.32 indicate that for ideal surface passivation ($S = 0$) there are an infinity of exponential terms in the decay and the frequencies are a linear combination of the fundamental frequencies.

5.4 Experimental Constraints

In Sections 5.2 and 5.3 the theoretical analysis reveals that for ideally passivated surfaces ($S = 0$) the fundamental frequencies may be determined from the average decay. Furthermore, the diffusion term vanishes due to conditions imposed on the modes of decay. For this case of a very low surface recombination velocity ($S \approx 0$) the modes of decay are restricted to $m = 0$. Also, in the previous Section 5.3 it is shown that for average decay the fundamental time constants are unaffected by the wavelength of light. The absorption coefficient only affects the magnitudes of the coefficients of the exponential terms in the decay. For the purpose of illustrating the range of excess carrier concentrations over which the fundamental frequencies may be measured an impulse of light $N_o\delta(t)$, with a single wavelength and a energy slightly greater than the bandgap, is chosen to represent the light source. In the limit of weak absorption, an impulse of light $\delta(t)$ generates a uniform excess carrier concentration in the semiconductor material where $\Delta n(0)$ and $\Delta p(0)$ are equal and represent the photo-excited excess carrier density. The relative change in conductivity of sample wafers of different resistivity when photo excited defines a criteria for decay detection by a microwave or inductively coupled detector. Low resistivity ρ implies

high conductivity σ and the relative change $\Delta\sigma/\sigma$ may be small.

$$\Delta\sigma = \int_{-d/2}^{d/2} q(\mu_n\Delta n(x,t) + \mu_p\Delta p(x,t))dx \quad (5.33)$$

For sufficiently small $\Delta p(0)$ (n-type silicon) the contribution to conductivity in the majority band is negligible as opposed to the sudden increase in minority carriers above the equilibrium concentration in the minority band (for n type $\Delta p(0) \ll n_{po}$). As the photoconductivity perturbation $\Delta\sigma$ is small compared to the wafer conductivity, the time dependence of the microwave signal is the same as the average excess carrier density $\Delta p_{av}(x,t)$ proportional to $\Delta\sigma$. Although the microwave reflectance is a non-linear function of wafer conductivity, the above is true for high ($\rho = 0.2\Omega cm^2$) and low ($\rho = 100\Omega cm^2$) conductivity samples considered here where the values in brackets represent resistivity. The difference is that for high conductivity wafers, high order modes of decay Luke [28] ($m \gg 1$) decay much faster and are not observed by the microwave system. As the excess carrier concentration is increased the contribution to conductivity of the majority band is not negligible and both carriers contribute to the conductivity $\Delta\sigma$ as in Eq. (5.33).

After the optical excitation pulse in the absence or low concentration of discrete levels (trapping centers), the decrease in the average minority carrier concentration and subsequent observed decay is determined by bulk and surface recombination and diffusion of carriers to the surfaces. The average carrier concentration, proportional to the sheet conductance of the wafer, decays with a characteristic time constant τ_m for a given surface recombination velocity $S \gg 1 \text{ cm/s}$. This volume integrated concentration is measured by the microwave reflectance photoconductance decay method Luke [28]. Equation (5.31) represents the impulse response with $k + 1$ fundamental frequencies due to $k = 2$ multiple defect levels in the bandgap for $S = 0$, indicating that only the three fundamental time constants are involved in the decay.

Analysis of the decay for τ_k , the fundamental time constants, is performed using

a multi-transient technique as mentioned in Chapter 2. Multi-transient analysis refers to the extraction of component exponential terms from a sum of exponentials comprising the signal. The methods available as in Refs. [20] [21] [22] present a means of analysing signals with additive white Gaussian noise. In addition, where the data matrix and the observation matrix may be subject to noise fluctuations, the Total Least Squares method Van Huffel [23] (TLS) is employed. This method models the multi-exponential signal as an autoregressive process. For the present analysis the TLS method of Refs. [22] [24] multi-transient analysis using Singular Value Decomposition (SVD) Klema [25] is applied to the analysis of the multi-component exponential decay.

From equation (5.33), increasing the excess carrier concentration in the sample means that both $\Delta n(t)$ and $\Delta p(t)$ contribute to the conductivity $\Delta\sigma$. However, from the present work, both quantities contain the same decay constants Eqs. (5.31) and (5.32). Hence the decay may be analysed for τ_1 with arbitrary excess carrier concentration. Ideally the range of excess carrier concentration should encompass the linear (constant) region and the non-linear region of variation of τ_1 with excess carrier concentration. Longer minority carrier time constants (τ_1) indicate lower defect level effects and an estimate of the linear region of τ_1 with excess carrier concentration realises a range of excess carrier concentration before the onset of trapping.

5.5 Experimental Conditions

Experimental conditions for determining bulk decay are discussed below. Specifically with regard to a n-type CZ silicon wafer, a uniform excess carrier concentration may be generated within a sample of $400\mu m$ thickness Luke [28] by light of a wavelength of the order of $1\mu m$. For a light source with multiple wavelengths, whether it be blue light (strongly absorbing) or infra red light (weakly absorbing), a variation in

generation of excess carrier concentration is expected at the surface with respect to the bulk. The high excess carrier concentration generated at the surface produces a long time constant τ_{long} contribution given a good surface passivation. This is due to trapping at bulk states near the surface (see Chapter 2 Ref. [1] for an explanation of minority carrier trapping). From equation (5.34) it may be seen that the effective time constant τ_e is that of the bulk states τ_{short} away from the surface, which is shorter.

$$\frac{1}{\tau_e} = \frac{1}{\tau_{long}} + \frac{1}{\tau_{short}} \quad (5.34a)$$

$$\tau_e \approx \tau_{short} \quad (5.34b)$$

Simulations indicate that the infra-red light produces a near uniform excess carrier concentration away from the surface in the bulk. The light source produces the initial condition $\Delta n(0) = \Delta p(0)$ at $t = 0^+$. A low surface recombination velocity may be attained with the $Si-SiO_2$ system as in Ref. [30]. A phosphorus surface diffusion (n-type) of Ref. [38] or boron surface diffusion (p-type) of Ref. [39] provides a surface field that limits the injection of carriers into the surface states. However it may be modulated by the excess carrier concentration, so the effective surface recombination velocity is taken to be injection level dependent in Refs. [30] and [29]. For excess carrier concentrations $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$ an $S_{eff} < 50 \text{ cm/s}$ is assumed to be attainable with appropriate processing with the $Si-SiO_2$ system for a wafer resistivity of the order of $5 \text{ } \Omega\text{cm}$ ($5 \times 10^{14} \text{ cm}^{-3}$ doping density). The decay of excess carriers may be detected by a contactless microwave as in Ref. [40] or inductively coupled as in Ref. [41] photoconductance measurement.

5.6 Experimental Results

The following is the author's experimental results. As indicated in the introduction three candidate complexes are considered for assessment as to the unusually long

lifetime of the CZ silicon sample by application of the theory developed in Chapter 4. This theory describes the decay due to pulse of light for the coupled levels system in terms of the fundamental frequencies $\lambda_1 = 1/\tau_1$, $\lambda_2 = 1/\tau_2$ and $\lambda_3 = 1/\tau_3$. The first defect complex is the carbon interstitial - oxygen interstitial $C_i - O_i$ complex Ref. [36], the second is the vacancy - oxygen $V - O$ complex Ref. [36] and the third is the phosphorus donor (n-type) and the ground state of the $V - O$ complex or $C_i - O_i$ complex Ref. [35]. These complexes have energy levels near the band edges which may give rise to the long lifetime.

The resistivity of the n-type CZ silicon sample is $5.5 \Omega \text{ cm}$ which corresponds to a doping concentration, N_D , of $8.34 \times 10^{14} \text{ cm}^{-3}$. An n^+ surface diffusion is performed as in Ref. [38], followed by an oxidation step. The thickness of the wafer is $411 \mu\text{m}$. The photoconductance measurement is performed with an inductively coupled system similar to Ref. [41] except that the frequency is lower (8-10MHz) and the light source is a tungsten flash. The major component in terms of intensity, in a tungsten flash, is infra-red light. This light is assumed to generate near uniform excess carrier concentration throughout the thickness of the wafer except near the surface. The dominant time constants are expected to be that of the bulk states away from the surface (see Section 5.5). Furthermore, the silicon sample is not subjected to high energy radiation of electrons which would be expected to create vacancies in the silicon lattice as in Ref. [36].

The first fit of experimental data by theoretical values of τ_1 and τ_2 Eq. (5.30), determined by adjusting excited state defect parameters, is shown in Figure 5.1. The defect parameters adjusted were the defect concentration N_t , the electron and hole cross sections, σ_{nx} and σ_{px} respectively, for the excited state and the electron and hole cross sections, σ_{ng} and σ_{pg} respectively, for the ground state, shown in Table 5.1. Energy levels for this coupled state system correspond to the carbon interstitial - oxygen interstitial complex ($C_i - O_i$) Ref. [36], with $E_c - E_x = 0.04 \text{ eV}$ for the excited state, and $E_c - E_g = 0.84 \text{ eV}$, for the ground state. From Figure

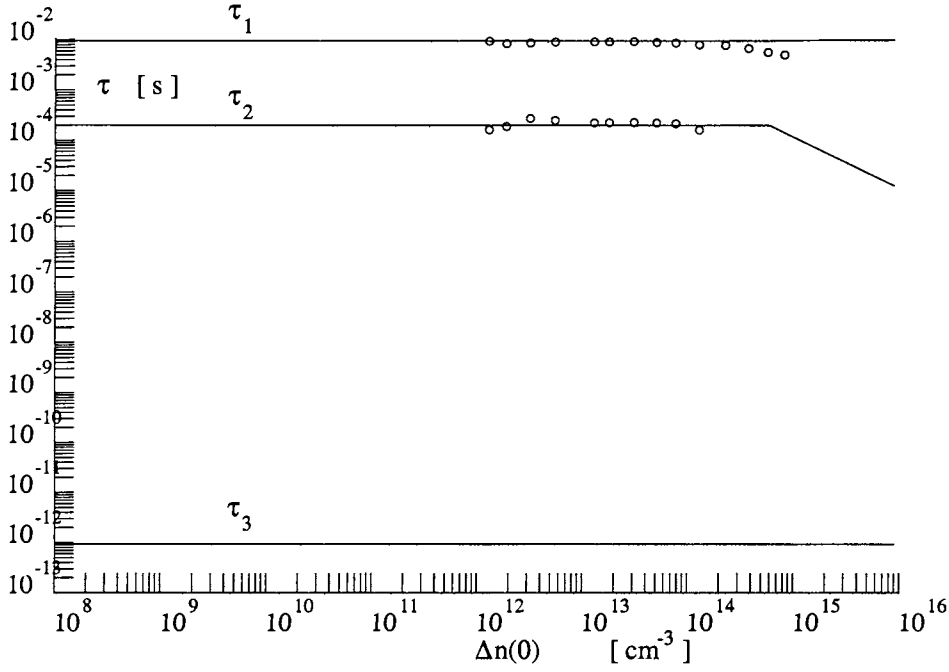


Figure 5.1: A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system of $C_i - O_i$ (carbon interstitial - oxygen interstitial) versus excess carrier concentration $\Delta n(0) = \Delta p(0)$. The doping concentration N_D of the sample is $8.34 \times 10^{14} \text{ cm}^{-3}$. See Table 5.1 for defect level parameters. Continuous line: Fit of τ_1 and τ_2 determined from the characteristic equation, to the experimental data. Circles: Experimental data for n-type CZ sample 6_1.

Table 5.1: Defect level parameters used for the fit of experimental data of the ground excited state system, for CZ sample 6_1, (carbon interstitial - oxygen interstitial).

parameter	ground state	excited state
$E_c - E_x$ energy depth [eV]		0.04
$E_c - E_{gnd}$ energy depth [eV]	0.84	
N_t level concentration [cm^{-3}]	5×10^6	5×10^6
σ_p cross section holes [cm^2]	$\sigma_{vg}^p = 4.5 \times 10^{-19}$	$\sigma_{vx}^p = 6.5 \times 10^{-9}$
σ_n cross section electrons [cm^2]	$\sigma_{cg}^n = 2.5 \times 10^{-20}$	$\sigma_{cx}^n = 8.5 \times 10^{-15}$

5.1 the agreement is good for τ_1 and τ_2 with the adjusted parameters of Table 5.1. Experimental data for τ_3 could not be determined because this time constant is very short.

A fit of theory for the ground excited state system of Table 5.2 corresponding to the vacancy-oxygen complex ($V - O$) Ref. [36] is shown in Figure 5.2. Again, the concentration N_t and cross sections of the defect were adjusted to provide as close a fit to the experimental data with the theoretical values of τ_1 and τ_2 Eq. (5.30). The energy levels for the $V - O$ complex are $E_c - E_x = 0.17$ eV for the excited state, and $E_c - E_{gnd} = 0.76$ eV, for the ground state. From Figure 5.2 agreement is relatively poor for τ_1 as the theoretical curve enters a trapping region. This is because at low excess carrier concentrations the minority carrier is the major contributor to the decay which corresponds to τ_1 . At higher excess carrier concentrations the time constant τ_1 is becoming longer indicating that for the n-type silicon there are fewer electrons at the defect levels to recombine with. Hence the minority carrier holes are accumulating or being trapped at the defect levels. Experimental data points do not follow this trapping behaviour. It is concluded that the vacancy-oxygen complex is not a major contributor to the decay. This is to be expected since the silicon sample

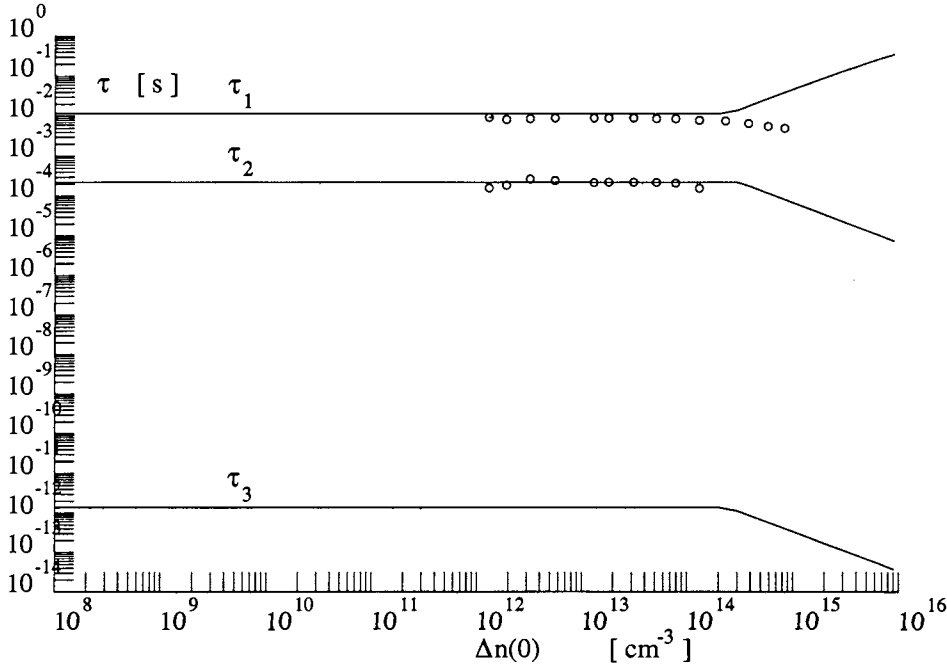


Figure 5.2: A graph of $\tau_1 = 1/\lambda_1$, $\tau_2 = 1/\lambda_2$ and $\tau_3 = 1/\lambda_3$ for the excited state system of $V - O$ (vacancy - oxygen complex) versus excess carrier concentration $\Delta n(0) = \Delta p(0)$. The doping concentration N_D of the sample is $8.34 \times 10^{14} \text{ cm}^{-3}$. See Table 5.2 for defect level parameters. Continuous line: Fit of τ_1 and τ_2 determined from the characteristic equation, to the experimental data. Circles: Experimental data for n-type CZ sample 6.1.

Table 5.2: Defect level parameters used for the fit of experimental data of the ground excited state system, for CZ sample 6.1, (vacancy - oxygen complex).

parameter	ground state	excited state
$E_c - E_x$ energy depth [eV]		0.17
$E_c - E_{gnd}$ energy depth [eV]	0.76	
N_t level concentration [cm^{-3}]	2.8×10^4	2.8×10^4
σ_p cross section holes [cm^2]	$\sigma_{vg}^p = 7.5 \times 10^{-19}$	$\sigma_{vx}^p = 6.5 \times 10^{-9}$
σ_n cross section electrons [cm^2]	$\sigma_{cg}^n = 2.5 \times 10^{-19}$	$\sigma_{cx}^n = 8.5 \times 10^{-13}$

did not undergo radiation with high energy electrons to create vacancies in the silicon lattice. A fast time constant τ_3 is shown in Figure 5.2, could not be resolved by the contactless photoconductance method because the sampling time is too large.

A fit of the experimental data with theory for the phosphorus donor with a concentration of $8.34 \times 10^{14} \text{ cm}^{-3}$ and cross sections $\sigma_p = 5 \times 10^{-21} \text{ cm}^2$ and $\sigma_n = 5 \times 10^{-15} \text{ cm}^2$ Ref. [35] and ground states of the complexes could not be achieved. The phosphorus donor lies at an energy level $E_c - E_D = 0.045 \text{ eV}$. The ground states were $E_c - E_t = 0.17 \text{ eV}$ and $E_c - E_t = 0.76 \text{ eV}$, corresponding to the vacancy-oxygen complex and $E_c - E_t = 0.84 \text{ eV}$, corresponding to the carbon interstitial - oxygen interstitial complex Ref. [36].

5.7 Discussion

Given a silicon wafer sample with a well passivated surface, the fundamental time constants τ_1 and τ_2 may be determined from the photoconductance decay by multi-transient analysis. A relatively long time constant is attributed to defect levels near the band edges. Examples of coupled levels used to fit the experimental data have

levels near the band edges. A consistent fit to the experimental data is provided by the $C_i - O_i$ complex. The vacancy - oxygen complex $V - O$ shows trapping behaviour which is not apparent in the experimental data. The phosphorus $V - O$ ground state complex could not be fitted to the data given the concentration of the doping concentration N_D and the much smaller ground state concentrations of the $C_i - O_i$ and $V - O$ complexes. Also, the history of the silicon sample indicates that it is unlikely to have a high vacancy concentration. This indicates that the $V - O$ complex is less likely than the $C_i - O_i$ complex. A plot of the fundamental time constants versus excess carrier concentration may be a method of identifying a defect species.

The small concentration of the defects ($5 \times 10^{-6} \text{ cm}^{-3}$) determined from the fit, is consistent with the theory of Chapter 4 for the ground excited state system. The dip in τ_1 of the experimental data points, at higher excess carrier concentration, is attributed to the beginning of Auger recombination.

Chapter 6

Accuracy of Semiconductor

Multiple-Level-Defect

Measurements Using Deep Level

Transient Spectroscopy and

Lifetime Spectroscopy

6.1 Introduction

In materials' characterisation, the defect level depth, which is directly related to carrier recombination, is predominantly determined from rate equations. A dominant recombination mechanism (apart from Auger recombination) is Shockley-Read-Hall (SRH) recombination [2] [3] as described by the SRH rate equations. Strictly, these rate equations apply to a single-level defect although interpretation of experimental

data has usually relied on the assumption of a dominant defect energy level. A set of differential rate equations for multiple discrete levels based on the summation of the single-level equations is given in [9] and [10]. A recent analytic solution to the SRH rate equations [1], extended to include multiple defect levels in a first principles approach, indicates that the equations of [9] and [10] for multiple discrete levels are correct only in the neighbourhood of the equilibrium point.

The Deep Level Transient Spectroscopy (DLTS) technique of semiconductor defect level depth measurement, first developed in 1974 by Lang [42], is extended in the present work by including all multiple-level carrier transitions in a full set of rate equations. The method of solution of the recent analytic solution [1] to the single-level (SRH) rate equations, is extended to the two multiple level systems, namely the multiple discrete level system and the ground excited states or coupled levels system. This proposed theory indicates that the accuracy of the usual method of DLTS measurement is affected by additional defect levels comprising the multiple-level systems. These two defect systems have a major effect on the minority carrier and hence the physics of device operation. In the present work the three-multiple-discrete-level system, using the exact solution in the neighbourhood of the equilibrium point, provides a clear distinction of the effect between one and multiple levels on the dominant time constants in the decay. The extended solution is obtained without approximation for arbitrary excess carrier concentration below non-degenerate doping, uniform arbitrary doping concentration $N_{A,D}$, defect energy depth $E_{t,k}$, defect concentration $N_{t,k}$ and cross sections $\sigma_{n,k}$ and $\sigma_{p,k}$ (for the k^{th} level). The solution is comprised of an infinity of mono-exponential terms, the frequencies (inverse time constants) of which are a linear combination of the fundamental frequencies $\lambda_{k+1} = 1/\tau_{k+1}$. Expressions for the minority carrier time constant τ_1 and time constants τ_{k+1} arising from majority carrier transitions are derived for m discrete defect levels with $k = 1, 2, \dots, m$ (the magnitude of the time constants is in descending order $\tau_1 > \tau_2 > \tau_3 > \dots \tau_{k+1}$). The dominant time con-

stant is τ_1 for n-type or p-type semiconductor and its behaviour with excess carrier concentration indicates the onset of trapping.

This Chapter is organised as follows. Section 6.2 briefly discusses the principle underlying DLTS. Then a detailed account of the theory related to multiple defect levels is addressed so as to provide a basis for assessing the impact of additional levels on the dominant decay time constant τ_1 . It is the dominant decay time constant that DLTS measures. Section 6.5 discusses the theory of the SRH rate equations and how accepted theory which yields one time constant expression τ , is incorrect. This has an impact on the existing defect level measurement method known as Lifetime Spectroscopy. Then in Section 6.6 a detailed account of the proposed lifetime spectroscopy method termed Analytic Lifetime Spectroscopy is given for the single level case as an illustration of the method. Section 6.7 indicates the limitations on material characterisation due to theoretical approximations and both theory and material properties that may lead to erroneous parameter determination as discussed in the previous sections.

6.2 Existing DLTS

In order to place the extended solution in context, a brief review of DLTS is warranted to see what emerges when it is applied to a multiple defect level system, as may often exist in practice. In DLTS, a pulse is applied to a device with a depletion layer, which is reduced in width by the forward bias of the pulse to fill deep levels with carriers. On application of a reverse bias pulse the depletion layer widens and the carriers in each band travel to the depletion layer edge in a matter of picoseconds. Due to thermal emission, carriers in the deep levels are emitted to the respective band and this is detected as a change in capacitance ΔC of the depletion layer. The thermal emission rate determines the decay rate of the depletion layer. In order to detect the decay rate, a rate window $t_1 - t_2$ is usually employed although similar

schemes (correlator) are available. At low temperatures the decay rate is slow and the difference in the decay ΔC at times t_1 and t_2 is small. At intermediate temperatures, the difference is greater. However, at high temperatures the decay rate is very fast as thermal emission is greater and again the difference is small. Hence, a peak in the emission rate versus inverse temperature occurs. A plot of several peaks, corresponding to different rate windows, produces a straight line plot with the slope proportional to the level depth. This plot is referred to as an Arrhenius plot. For multi-exponential decays rate windows may be selected to resolve the different time constants resulting in several Arrhenius plots.

As originally conceived, DLTS assumes that the effect of each level may be independently determined from the multi-exponential decay of a capacitance transient with the dominant time constant τ arising directly from a dominant defect species. One carrier type is assumed to be emitted from the defect levels. The thermal emission rate $e_{n,p} = 1/\tau$ derived from the detailed balance relations is given by Eq. (6.1) [43].

$$e_{n,p} = \frac{\sigma_{n,p}^t v_{th(n,p)} N_{c,v}}{g} \exp \left[\frac{-\Delta G_{n,p}}{kT} \right] \quad (6.1)$$

where $\sigma_{n,p}^t$ is the thermal cross section for electrons or holes, $v_{th(n,p)}$ is the thermal velocity of electrons or holes, $N_{c,v}$ is the effective density of states for electrons or holes, g is the degeneracy and $\Delta G_{n,p}$ is defined by (6.2).

$$\Delta G_{n,p} = \Delta H_{n,p} - T \Delta S_{n,p} \quad (6.2)$$

$\Delta G_{n,p}$ represents the change in Gibbs's free energy required to emit an electron (hole) from the center at constant temperature. Eq. (6.2) expresses this quantity in terms of the change in enthalpy ΔH and the change in entropy ΔS . By substitution of the relevant terms, where ΔG is replaced by ΔE , implying no change in entropy (adiabatic process), an emission time constant τ results in Eq. (6.3).

$$\tau = \frac{g}{\sigma_{n,p}^t \gamma_{n,p} N_{c,v}} \frac{1}{T^2} \exp \left[\frac{-\Delta E}{kT} \right] \quad (6.3)$$

where

$$\gamma_{n,p} = 2\sqrt{3}k^2m_{c,v}^* \left[\frac{2\pi}{h^2} \right]^{\frac{3}{2}} \quad (6.4)$$

with k being Boltzmann's constant, $m_{c,v}^*$ the effective mass for electrons or holes and h is Planck's constant.

Modulation by a pulse of the depletion layer of a Schottky barrier or pn junction produces a change in capacitance where the capacitance of the depletion layer is given by Eq. (6.5).

$$C(t) = C(0^+) \exp\left(\frac{-t}{\tau}\right) - C_{\infty} \quad (6.5)$$

A rate window is defined by $t_1 - t_2$ representing two points on the decay curve. A change in capacitance of the depletion layer may be expressed by Eq. (6.6).

$$\Delta C(t) = C(t_1) - C(t_2) \quad (6.6a)$$

$$\frac{\Delta C(t)}{C(0^+)} = \exp\left(\frac{-t_1}{\tau}\right) - \exp\left(\frac{-t_2}{\tau}\right) \quad (6.6b)$$

Differentiating equation (6.6b) with respect to τ yields the familiar expression relating the rate window $t_1 - t_2$ to the maximum emission time constant τ as Eq. (6.7).

$$\tau = \frac{t_1 - t_2}{\ln\left(\frac{t_1}{t_2}\right)} \quad (6.7)$$

Laplace Deep Level Transient Spectroscopy (LDLTS) [44] is a mathematical refinement of the usual Deep Level Transient Spectroscopy (DLTS), giving better resolution of the spectral peaks. Although LDLTS is used to resolve multiple defect level depths, it may not lead to the direct identification of the defect species. However this may be possible in conjunction with other methods both theoretical and experimental. The DLTS method has limitations on the sensitivity or detection of low defect concentrations. LDLTS or the usual DLTS uses the concept of a rate

window to resolve the dominant time constant in the decay. Over a temperature range a time constant expression containing the rate window Eq. (6.7), which is proportional to the emission time constant of Eq. (6.1) ($\tau = 1/e_{n,p}$), is evaluated. The emission rate $e_{n,p}$ is related to the dominant decay time constant through this expression. A maximum emission rate is expected at a particular temperature. This maximum is related to the defect level energy depth via Eq. (6.3). A plot of several maxima versus the inverse of the temperature allows the defect energy depth to be resolved from the slope of the linear plot.

6.3 Accuracy of Existing DLTS

Having discussed the DLTS method, the proposed extended multiple-level theory, comprising the full set of carrier transitions using the recent method of solution in Ref. [1], is now applied to the three level system. A review of the DLTS method applied to the actual resulting time dependent decay and how the rate window scheme interprets it is examined later in the Chapter. Fundamental frequencies are derived by scaling the differential rate equations and solving the linear form of the non-linear differential equations. The determinant of the matrix of these differential equations, Eq. (6.8), is reduced to a polynomial of the differential operator $D = d/dt$, termed the characteristic equation, Eq. (6.9) [15]. From this polynomial the fundamental frequencies may be determined as in Eq. (6.10). For m defect levels there are $m+1$ fundamental frequencies where $\tau_1 = 1/\lambda_1$ is the dominant time constant. This matrix concept may be seen in [10] for low excess carrier concentration where the carrier concentration does not deviate appreciably from the equilibrium concentration, and so can be neglected. In this case the non-linear rate equations become linear. For higher excess carrier concentrations the matrix terms are modified as in [1]. Eqs. (6.8) describe the full set of carrier transitions whereas Eq. (6.1) is an approximation involving only the emission of one carrier type.

$$\begin{aligned}
 & \begin{bmatrix} D + \sum_{k=1}^3 (\gamma_{0k} - \sigma_{0k}) & 0 & -\frac{N_{t1}\sigma_{01}}{\Delta n(0)} & -\frac{N_{t2}\sigma_{02}}{\Delta n(0)} & -\frac{N_{t3}\sigma_{03}}{\Delta n(0)} \\
 -(\gamma_{01} - \sigma_{01}) & (\alpha_{01} - \beta_{01}) & \frac{N_{t1}}{\Delta n(0)} \times (D + \sigma_{01} + \beta_{01}) & 0 & 0 \\
 -(\gamma_{02} - \sigma_{02}) & (\alpha_{02} - \beta_{02}) & 0 & \frac{N_{t2}}{\Delta n(0)} \times (D + \sigma_{02} + \beta_{02}) & 0 \\
 -(\gamma_{03} - \sigma_{03}) & (\alpha_{03} - \beta_{03}) & 0 & 0 & \frac{N_{t3}}{\Delta n(0)} \times (D + \sigma_{03} + \beta_{03}) \\
 1 & -1 & \frac{N_{t1}}{\Delta n(0)} & \frac{N_{t2}}{\Delta n(0)} & \frac{N_{t3}}{\Delta n(0)} \end{bmatrix} \begin{bmatrix} \Delta n_{nm}(t_0) \\ \Delta p_{nm}(t_0) \\ \Delta f_1(t_0) \\ \Delta f_2(t_0) \\ \Delta f_3(t_0) \end{bmatrix} \\
 & \qquad \qquad \qquad = 0 \qquad \qquad \qquad (6.8)
 \end{aligned}$$

where the α_{0k} , β_{0k} , γ_{0k} and σ_{0k} , with $k = 1, 2, 3$, refer to the near equilibrium case.

The characteristic equation is given by equation (6.9) and may be solved for the time constants where the coefficients (b, c, d, e) are determined from the determinant of the matrix formed from Eq. (6.8).

$$[D^4 + bD^3 + cD^2 + dD + e] \exp(-\lambda t) = 0 \quad (6.9)$$

The fundamental frequencies λ_{k+1} (inverse time constants) may be evaluated from the polynomial of degree $m + 1$ given by Eq. (6.10).

$$\lambda^4 - b\lambda^3 + c\lambda^2 - d\lambda + e = 0 \quad (6.10)$$

By evaluating the four roots of the polynomial (6.10) the fundamental frequencies are given by $\lambda_1 = 1/\tau_1$, $\lambda_2 = 1/\tau_2$, $\lambda_3 = 1/\tau_3$ and $\lambda_4 = 1/\tau_4$.

The square matrix, with the differential operator D in the off diagonal entries as in the matrix of Eq. (6.8), is of order $m + 2$. Similarly for the square matrix of Ref. [10] for the near equilibrium case of two levels. This means that when more levels are added the order of the matrix increases by the additional number of levels and the degree of the polynomial or characteristic equation increases correspondingly. It is important to note that with additional defect levels, the size of the matrix changes and the coefficients of the polynomial Eq. (6.10) change. Hence, the roots or fundamental frequencies of the polynomial change. This alters the values of all the fundamental frequencies. For instance with additional defect levels, τ_1 becomes

Table 6.1: Defect level parameters for the analytical solution of time constants from Eqs. (6.8) for the multiple discrete defect level system.

parameter	level one	level two	level three
$E_c - E_t$ energy depth [eV]	0.55	0.35	0.25
N_t concentration [cm^{-3}]	5×10^{11}	5×10^{10}	5×10^9
σ_p cross section holes [cm^2]	$\sigma_{v1} = 8.5 \times 10^{-15}$	$\sigma_{v2} = 8.5 \times 10^{-17}$	$\sigma_{v3} = 8.5 \times 10^{-12}$
σ_n cross section electrons [cm^2]	$\sigma_{c1} = 9.0 \times 10^{-17}$	$\sigma_{c2} = 9.0 \times 10^{-15}$	$\sigma_{c3} = 9.0 \times 10^{-14}$

lower in value, and is not a linear change. Hence the effect of all the defect levels is not the sum or linear superposition of the individual effects of each defect level.

The main assumption inherent in the multiple-level theory is that the matrix of Eqs. (6.8), which strictly describe the full set of carrier transitions in a field free region, also apply within the depletion region where an electric field ξ is present. Equivalently, the resulting fundamental frequencies (which are the irrational eigenvalues of the linear system [1]) are unique for the given defect level properties (see Table 6.1) and are independent of the electric field ξ being determined by equilibrium values of defect level occupancy, cross sections and concentration. Hence, it may be concluded that the level depths may be recovered from these same fundamental frequencies in a field or field free region because they reflect the same level depths. Although the depletion electric field ξ may enhance emission through the Poole-Frenkel effect [45], the effect is neglected in the present analysis.

In order to recover the true level depths, decay measurements are performed at constant temperature over a temperature range. The fundamental frequencies λ_{k+1} must be resolved using a multi-transient analysis technique [1] from each experimental decay and a set of simultaneous equations formed at each temperature from the polynomial of Eq. (6.10). Each equation in the set contains a different λ . The coefficients (b,c,d,e) of Eq. (6.10) are determined in terms of the λ_{k+1} from the simultaneous equations. From expressions for each coefficient, found by expanding

the matrix Eq. (6.8), the level depths may be evaluated from the slope of the plot of each coefficient in terms of the λ_{k+1} versus $1/kT$. A graph of linear plots, with the x abscissa in units of $1/kT$, is obtained with the slopes of each line representing the level depths. This measurement technique is termed Fundamental Frequency Spectroscopy.

To place the DLTS method of measurement in context with the foregoing multiple-level theory an example set of three defect levels from Table 6.1 is examined with respect to the resolution of the levels using the rate window concept. For the combined effect of three levels, the best a rate window can do is to resolve a τ (Eq. (6.3)) with time constants $\tau = \tau_1$ and $\tau = \tau_2$. The time constants $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ make the most significant contribution to the respective exponential decay term, whether all three levels or just one level is included in the matrix of Eqs. (6.8). The fundamental frequencies (λ_1, λ_{k+1} for $k = 1, 2 \cdots m$), for the two cases of three levels ($m = 3$) and one level ($m = 1$), are the respective roots of the polynomial of Eq. (6.10) resulting from Eqs. (6.8) for each case.

For a doping concentration of $N_D = 5 \times 10^{13} \text{ cm}^{-3}$ in a silicon sample, Figure 6.1 indicates the variation of the dominant time constant τ_1 for the combined effect of the three levels in Table 6.1, and for each level as if it were the only defect present in the semiconductor sample. A rate window may be chosen corresponding to the dominant time constant τ_1 . Figure 6.1 is a log plot of τ versus $1/kT$, from which the energy level depth may be recovered from the slope of each line as described by equation (6.3).

It is seen from Figure 6.1 that level one is resolved as the plot of τ_1 for level one alone almost coincides with the time constant τ_1 for the combined effect of all three levels. In resolving the level there is a relative error of a few percent. From Eq. (6.10), the next significant contribution to the decay comes from the component with τ_2 as the time constant. Examining this time constant, τ_2 , from Figure 6.2, the combined effect of all levels produces a τ_2 which does not coincide

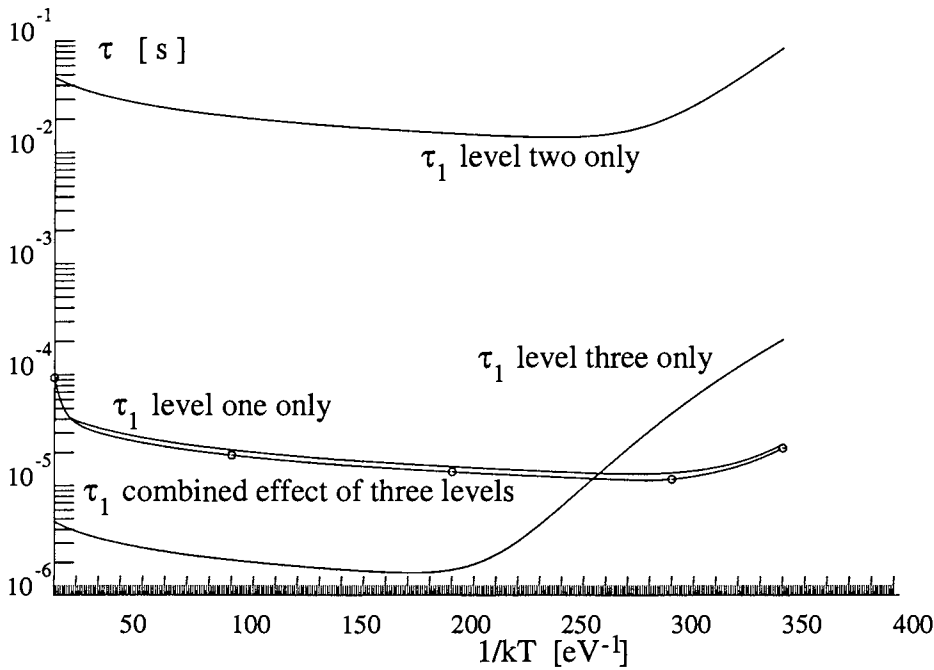


Figure 6.1: A graph of fundamental time constant τ_1 , from the root of Eq. (6.10) versus $1/kT$, for the combined effect of three levels in Table 6.1 and for the case of each level in the Table as if it were the only level present in the semiconductor sample. Solid line: plot of τ_1 for each level. Solid line with circles: combined effect of three levels.

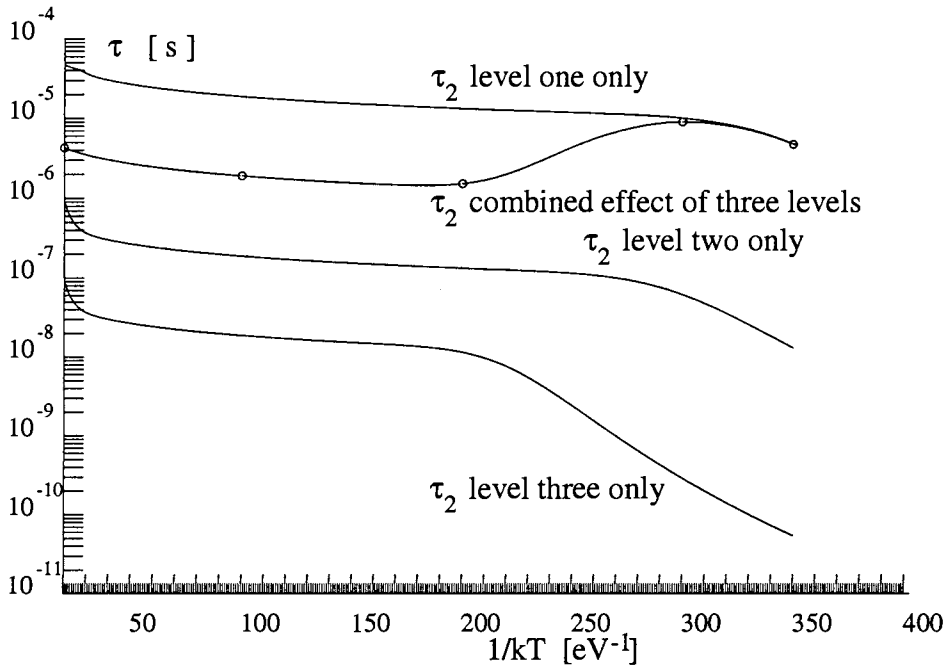


Figure 6.2: A graph of fundamental time constant τ_2 , from the root of Eq. (6.10) versus $1/kT$, for the combined effect of three levels in Table 6.1 and for the case of each level in the Table as if it were the only level present in the semiconductor sample. Solid line: plot of τ_2 for each level. Solid line with circles: combined effect of three levels.

with any level except at low temperatures (with a different slope). The closest level to the combined time constant of τ_2 is the level one. However, the level resolved is effectively a "ghost level" because it does not exist. It is evident that level one has the dominant effect on the dominant time constant τ_1 and the time constant τ_2 , for the combined levels, due to a combination of deep level depth and concentration (see Table 6.1).

As shown in Figure 6.1 at any one temperature τ_1 is lowered by the addition of other defect levels arising from other defects which are electrically active. That means that since τ_1 is the dominant decay time constant in both n-type and p-type, it varies in an unpredictable manner with each semiconductor sample. Without taking into account all the other fundamental time constants and linear combination of them, DLTS effectively measures τ_1 , the dominant decay constant, via the rate window concept. Given a dominant defect species in two semiconductor samples, but with different numbers of background defect species in each sample, the values of τ_1 in each sample will be different. Each DLTS peak will shift in an unpredictable way if the background defects are unknown. Hence, in the two cases the level is resolved with an error compared to the case where the dominant defect species level exists on its own, without any other defect levels present. A similar argument applies for time constant τ_2 .

6.4 Discussion

In conclusion the above discussion may help to shed some light on the anomalies arising from interpreting data in experimental methods such as LDLTS which determine the dominant decay time constant for a given rate window at a given temperature. In the literature there is a spread of values reported for defect level parameters such as level depth. This is because a given sample with, for example, iron as the dominant defect will have different background defect levels to another

similarly doped sample, resulting in a different time constant τ_1 as well as different resultant fundamental frequencies $\lambda_{k+1} = 1/\tau_{k+1}$.

6.5 Accuracy of Existing Lifetime Spectroscopy

Although developed for the steady state, the SRH theory has been applied to the transient case in the neighbourhood of the equilibrium point (small signal) and the time constant is referred to as τ_b . This applies to a single-level defect although in practical situations multiple defect levels occur. These rate equations have been applied to the analysis of experimental data assuming a dominant defect energy level. The literature indicates conflicting partial solutions to the rate equations, notably the single time constant expression of Ref. [2] which is defined as Eq. (6.11), where U represents the recombination rate, and expressions with two time constants of several authors indicated below.

$$\tau = \frac{\Delta n}{U} \quad (6.11)$$

The definition Eq. (6.11) is given without justification in the literature in Ref. [2] and subsequently.

For the single level case, the equation describing the time evolution of the normalised excess electron concentration, $\Delta n_{nm}(t)$, is a second order non-linear differential equation and has a cubic power of $\Delta n_{nm}(t)$ given as Eq. (9) in Ref. [4]. Since the differential equation for $\Delta n_{nm}(t)$ is second order, at least two time constants are expected in the solution (the eigenvalues of the linear system) for all excess carrier concentrations less than the Auger limit and the non-degenerate doping concentration. The steady state is realized with the boundary condition $dn(t)/dt = 0$ at $t = 0^+$ for electrons in the conduction band ie. the population of carriers remains constant with time. Application of the boundary condition is still expected to realize two time constants in the solution since the underlying differential equa-

tion is second order. These two time constants are the fundamental time constants determined from the response to an impulse (transient solution of Chapter 2 Ref. [1]).

As mentioned in Chapter 3, in Ref. [2], the steady state is realised by setting $U_n = U_p$ given as Eq. 4.1 of Ref. [2]. They define only a single time constant (Eq 5.2 of Ref. [2] repeated as Eq. (6.11) of this work), τ , implying the solution of a first, rather than second, order governing differential equation. For a second order equation to become first order, a zero must be cancelled by a pole of the same magnitude and frequency as the zero for all excess carrier concentrations. A zero that is not cancelled should be realized in the solution. It is shown in Figure 6.3 (from Chapter 3) that the time constant $\tau = \tau_{SRH}$ is approximately equal to the dominant time constant τ_1 for only part of the range of excess carrier concentration. Furthermore, the analysis of the numerical solution yields close agreement with the predicted value of τ_1 for the steady state. Parameters used for the evaluation are given in Chapter 2 Ref. [1]. Hence the definition of τ in Ref. [2], as stated above, yields a time constant expression which is inaccurate.

An existing method of lifetime spectroscopy Rein et al [46] using the SRH expression for lifetime τ (Eq. 5.3 of Ref. [2]) proposes the following expression (Eq. 18 of Ref. [46]) for determining the level depth $E_c - E_t$ where τ is the dominant decay constant for low level injection.

$$\ln \left(\frac{\tau}{T} \right) = -\frac{E_c - E_t}{kT} + \text{const} \quad (6.12)$$

As indicated in the above the dominant time constant value does not accurately reflect the effect of a single defect level given there may be other defect species present in the semiconductor sample. It is an effective lifetime. Figure 6.4 indicates a plot of Eq. (6.12)

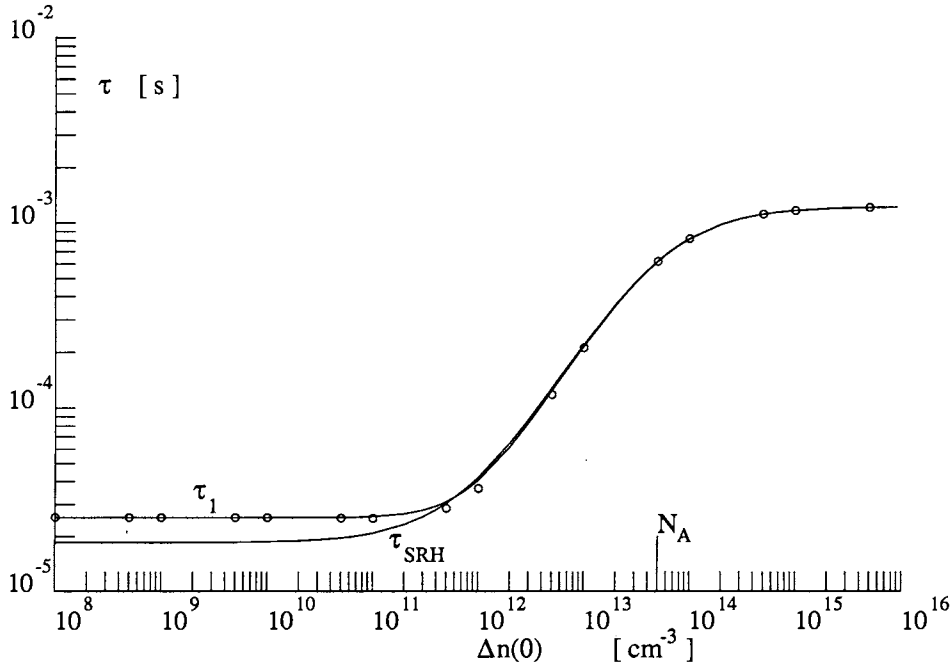


Figure 6.3: A graph of fundamental time constant τ_1 and SRH time constant $\tau = \tau_{SRH}$ versus excess carrier concentration $\Delta n(0^+)$. Circles: τ_1 derived from multi-transient analysis of the numerical solution. There is a relative error $\varepsilon \approx 30\%$ between τ_1 and τ_{SRH} in the linear region at $T = 300$ K.

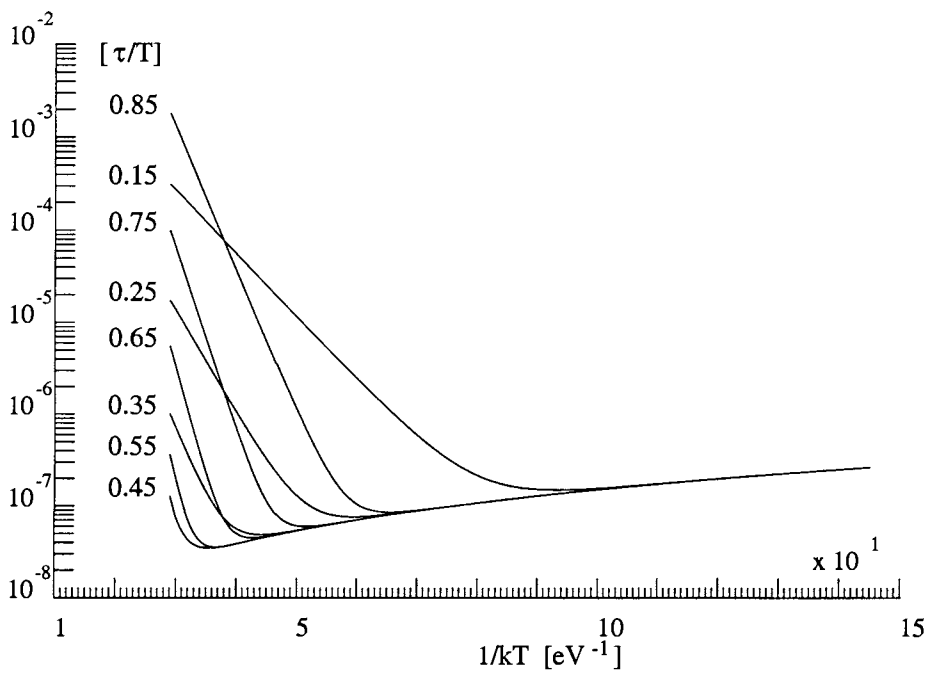


Figure 6.4: For this p-type semiconductor example, the existing Lifetime Spectroscopy technique shows curves for the indicated energy level depths $E_t - E_v$. The temperature variation is from 80K to 400K.

6.6 Proposed Analytic Lifetime Spectroscopy, Single-Level

A single level is considered for the purposes of illustrating the method of the proposed Analytic Lifetime Spectroscopy described below, for low excess carrier concentration where the deviation from equilibrium is small. Multitransient analysis of the numerical solution of the governing differential equations has independently verified the fundamental frequencies predicted by the theory of Chapter 2 Ref. [1].

The following rate equations apply as in Refs. [9] [10] for the recombination via and emission from the defect level k :

$$\begin{aligned} \frac{dn(t)}{dt} = & [e_{kc}^n N_{tk} f_k(t) \\ & - v_{ck}^n N_{tk} n(t) (1 - f_k(t))] \end{aligned} \quad (6.13)$$

$$\begin{aligned} \frac{dp(t)}{dt} = & [e_{kv}^p N_{tk} (1 - f_k(t)) \\ & - v_{vk}^p N_{tk} p(t) f_k(t)] \end{aligned} \quad (6.14)$$

where e_{kc}^n and e_{kv}^p represent the emission rates for electrons and holes respectively (for the k^{th} defect level) and, v_{ck}^n , v_{vk}^p are the capture coefficients for electrons and holes respectively. The following are defined to simplify notation used in the text.

$$C_{nk} n_{1k} = e_{kc}^n \quad (6.15a)$$

$$C_{pk} p_{1k} = e_{kv}^p \quad (6.15b)$$

$$C_{nk} = v_{ck}^n \quad (6.15c)$$

$$C_{pk} = v_{vk}^p \quad (6.15d)$$

where $C_{nk} = v_{thn} \sigma_{nk}$ and $C_{pk} = v_{thp} \sigma_{pk}$, with σ_{nk} and σ_{pk} , the cross sections for electrons and holes respectively. The quantities v_{thn} and v_{thp} are the average thermal

velocity of electrons and holes respectively, and

$$n_{1k} = N_c \exp \left(-\frac{(E_c - E_{tk})}{kT} \right) \quad (6.16a)$$

$$p_{1k} = N_v \exp \left(-\frac{(E_{tk} - E_v)}{kT} \right) \quad (6.16b)$$

For the present let $m = 1$ signifying one defect energy level. The excess electron concentration $\Delta n(t)$ and the excess hole concentration $\Delta p(t)$ are written in terms of normalised excess carrier concentration $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ respectively. The defect level electron concentration $N_t f(t)$ is written in terms of the departure from equilibrium $N_t \Delta f(t)$ and the equilibrium concentration $N_t f_o$. The electron and hole concentrations, and the defect level concentration may be written as follows from Chapter 2 Ref. [1] with N_t being the defect level concentration:

$$n(t) = \Delta n_{nm}(t) \Delta n(0) + n_{po} \quad (6.17a)$$

$$p(t) = \Delta p_{nm}(t) \Delta p(0) + p_{po} \quad (6.17b)$$

$$N_t f(t) = N_t \Delta f(t) + N_t f_o \quad (6.17c)$$

with the corresponding equilibrium concentrations n_{po} and p_{po} and where at equilibrium the electron occupancy of the defect level is $f_o = f(0^-)$ given in terms of p_{po} by:

$$f_o = \frac{p_1}{p_{po} + p_1} \quad (6.18a)$$

and in terms of n_{po} by:

$$f_o = \frac{n_{po}}{n_{po} + n_1} \quad (6.18b)$$

A charge neutrality relation indicates the conservation of charge with time.

$$\Delta p_{nm}(t) \Delta p(0) = \Delta n_{nm}(t) \Delta n(0) + N_t \Delta f(t) \quad (6.19)$$

$N_t \Delta f(t)$ may be written as $\Delta n_t(t)$ with $\Delta n_t(t)$ being the defect level excess electron concentration. By rewriting the charge neutrality relation with $\Delta n(0) = \Delta p(0)$, the valence, conduction and defect level electron concentrations may be directly compared since the three quantities are normalised or scaled to one injection level $\Delta n(0)$.

$$\Delta p_{nm}(t) = \Delta n_{nm}(t) + \frac{\Delta n_t(t)}{\Delta n(0)} \quad (6.20)$$

The differential equations (6.13) and (6.14) are scaled Ref. [32] by a normalising factor $\Delta n(0) = \Delta p(0)$ where $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ represent the scaled electron and hole concentrations. It is shown that the non-linear terms in the rate equations for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ go to zero at some time $t = t_0$. The resulting differential equations contain terms in only λ_{m+1} . As there are $m + 1$ equations and $m + 1$ unknowns the equations may be solved for the fundamental frequencies λ_{m+1} . From equations (6.17) and (6.19) the SRH rate equations of Ref. [4] may be written for $m = 1$ in normalised form as Eqs. (6.21) and (6.22).

$$\begin{aligned} -\frac{d\Delta n_{nm}(t)}{dt} &= \Delta n_{nm}(t)(\gamma_0 - \sigma_0) \\ &\quad - \frac{\sigma_0}{\Delta n(0)} N_{tk} \Delta f_k(t) \\ &\quad - C_{nk} N_{tk} \Delta n_{nm}(t) \Delta f_k(t) \end{aligned} \quad (6.21)$$

$$\begin{aligned} -\frac{d\Delta p_{nm}(t)}{dt} &= \Delta p_{nm}(t)(\alpha_0 - \beta_0) \\ &\quad + \frac{\beta_0}{\Delta n(0)} N_{tk} \Delta f_k(t) \\ &\quad + C_{pk} N_{tk} \Delta p_{nm}(t) \Delta f_k(t) \end{aligned} \quad (6.22)$$

where:

$$\alpha_0 = C_p N_{tk} \left\{ \frac{p_{1k}}{p_{po} + p_{1k}} + \frac{p_{po} + p_{1k}}{N_{tk}} \right\} \quad (6.23a)$$

$$\beta_0 = C_p N_{tk} \left\{ \frac{p_{po} + p_{1k}}{N_{tk}} \right\} \quad (6.23b)$$

$$\gamma_0 = C_n N_{tk} \left\{ \frac{n_1}{n_{po} + n_{1k}} + \frac{n_{po} + n_{1k}}{N_{tk}} \right\} \quad (6.23c)$$

$$\sigma_0 = C_n N_{tk} \left\{ \frac{n_{po} + n_{1k}}{N_{tk}} \right\} \quad (6.23d)$$

with $C_n = v_{thn}\sigma_n$ and $C_p = v_{thp}\sigma_p$ being the capture coefficients for electrons and holes respectively.

The following solution of Eqs. (6.21) and (6.22) is derived for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ respectively and via the charge neutrality relation $\Delta f_k(t)$.

$$\Delta n_{nm}(t) = \sum_i^\infty \sum_j^\infty N_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \quad (6.24a)$$

$$\Delta p_{nm}(t) = \sum_i^\infty \sum_j^\infty P_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \quad (6.24b)$$

$$\Delta f(t) = \sum_{i=0}^\infty \sum_{j=0}^\infty F_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \quad (6.24c)$$

The characteristic equation (6.16) formed from the scaled differential equations (6.21) and (6.22) where the non-linear terms go to zero at time t_0 . Measurement of the fundamental frequencies λ_1 and λ_2 (inverse time constants) from the decay allows the determination of $(\alpha_0 + \gamma_0)$ and $(\alpha_0\gamma_0 - \sigma_0\beta_0)$ as indicated below.

$$\lambda^2 - (\alpha_0 + \gamma_0)\lambda + (\alpha_0\gamma_0 - \sigma_0\beta_0) = 0 \quad (6.25)$$

The frequencies $\lambda_1 = 1/\tau_+$ and $\lambda_2 = 1/\tau_-$ by comparison with Ref. [5] are given as Eq. (6.26).

$$\lambda_1 = \frac{1}{2} \frac{\alpha_0 + \gamma_0}{\alpha_0\gamma_0 - \sigma_0\beta_0} \left(1 + \left(1 - 4 \frac{\alpha_0\gamma_0 - \sigma_0\beta_0}{(\alpha_0 + \gamma_0)^2} \right)^{\frac{1}{2}} \right) \quad (6.26a)$$

$$\lambda_2 = \frac{1}{2} \frac{\alpha_0 + \gamma_0}{\alpha_0\gamma_0 - \sigma_0\beta_0} \left(1 - \left(1 - 4 \frac{\alpha_0\gamma_0 - \sigma_0\beta_0}{(\alpha_0 + \gamma_0)^2} \right)^{\frac{1}{2}} \right) \quad (6.26b)$$

The linear (constant) region of variation of fundamental frequencies $\lambda_{1,2}$ with injection level or excess carrier density is defined by Eq. (6.27) It is the linear region

that is independent of excess carrier concentration. For the proposed Analytic Lifetime Spectroscopy method the frequencies λ_1 and λ_2 as determined in this region allows the direct application of Eq. (6.25). An upper limit for the linear region (constant) of excess carrier density exists and is referred to as $\Delta n(0)_{critical}$, as evaluated in Chapter 2 Ref. [1].

$$\frac{d\lambda_{1,2}}{d\Delta n(0)} = 0 \quad (6.27)$$

Re-writing Eq. (6.25) and substituting the values of the fundamental frequencies λ_1 and λ_2 determined from the measured decay yields an expression developed below, that allows the evaluation of the level depth.

$$-\lambda_1^2 = -(\alpha_0 + \gamma_0) \lambda_1 + (\alpha_0 \gamma_0 - \sigma_0 \beta_0) \quad (6.28a)$$

$$-\lambda_2^2 = -(\alpha_0 + \gamma_0) \lambda_2 + (\alpha_0 \gamma_0 - \sigma_0 \beta_0) \quad (6.28b)$$

Equations (6.28) are solved for $(\alpha_0 + \gamma_0)$ and $(\alpha_0 \gamma_0 - \sigma_0 \beta_0)$ in terms of λ_1 and λ_2 :

$$(\alpha_0 + \gamma_0) = \frac{\begin{vmatrix} -\lambda_1^2 & 1 \\ -\lambda_2^2 & 1 \end{vmatrix}}{\Delta} \quad (6.29a)$$

$$(\alpha_0 \gamma_0 - \sigma_0 \beta_0) = \frac{\begin{vmatrix} -\lambda_1 & -\lambda_1^2 \\ -\lambda_2 & -\lambda_2^2 \end{vmatrix}}{\Delta} \quad (6.29b)$$

where

$$\Delta = \lambda_2 - \lambda_1 \quad (6.29c)$$

Expressions for $(\alpha_0 + \gamma_0)$ and $(\alpha_0 \gamma_0 - \sigma_0 \beta_0)$ are formed from Eq. (6.23), yielding the following.

$$C_n (n_{po} + n_1) = \frac{g_n}{C_n N_t (1 - f_o) - C_p N_t f_o} \quad (6.30a)$$

$$C_p(p_{po} + p_1) = \frac{g_p}{C_n N_t (1 - f_o) - C_p N_t f_o} \quad (6.30b)$$

where:

$$g_n = (\alpha_0 + \gamma_0) C_n N_t (1 - f_o) - (\alpha_0 \gamma_0 - \sigma_0 \beta_0) - [C_n N_t (1 - f_o)]^2 \quad (6.31a)$$

$$g_p = (\alpha_0 + \gamma_0) C_p N_t f_o - (\alpha_0 \gamma_0 - \sigma_0 \beta_0) - [C_p N_t f_o]^2 \quad (6.31b)$$

and at $t = 0^+$ from Eqs. (6.21) and (6.22) with $\Delta f(0^+) = 0$:

$$-\left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=0^+} = C_n N_t (1 - f_o) \quad (6.32a)$$

$$-\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=0^+} = C_p N_t f_o \quad (6.32b)$$

By dividing Eq. (6.30a) by Eq. (6.30b), yields an equation (6.33) that is the basis of the proposed Analytic Lifetime Spectroscopy.

$$\ln(g_n) = -\frac{E_c - E_t}{kT} + \ln \left[\frac{C_n N_c}{C_p p_{po}} g_p \right] \quad (6.33)$$

The quantity g_n expressed as Eq. (6.31a) in terms of measured quantities from the decay, such as $(\alpha_0 + \gamma_0)$ and $(\alpha_0 \gamma_0 - \sigma_0 \beta_0)$ in terms of λ_1 and λ_2 , and $dn(t)/dt$ at $t = 0^+$ as given by Eq. (6.32a). This quantity is plotted against $1/kT$ as indicated by Eq. (6.33) and the slope of the plot yields the level depth $E_c - E_t$. Figure 6.5 indicates a number of plots of simulations of various single level depths.

However, this implementation may not be realised in a practical sense over a wide range of temperatures and requires low excess carrier concentrations to remain in the linear (constant) region.

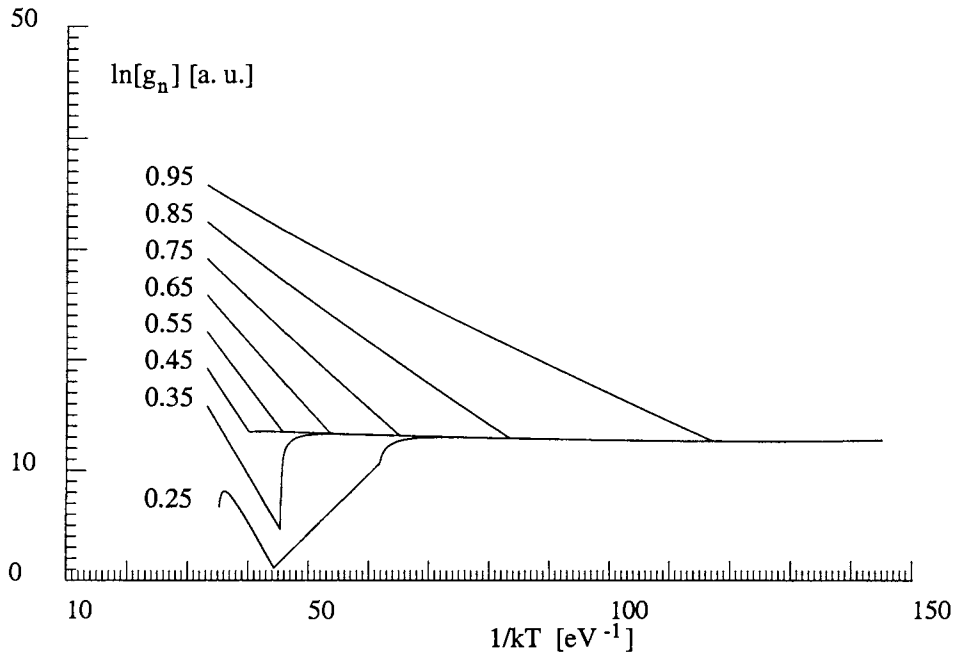


Figure 6.5: For this p-type semiconductor example, the Analytic Lifetime Spectroscopy technique shows curves for the indicated energy level depths $E_t - E_v$. The temperature variation is from 20K to 400K.

6.7 Limitations on Materials Characterisation

As indicated above, the limitations on material characterisation using the existing method of lifetime spectroscopy of Ref. [46] become apparent as follows. As outlined in the Introduction, from a theoretical standpoint the lifetime expression τ for the dominant single level model is approximate. Furthermore, from both a theoretical consideration as indicated and the differences in background defect species of physical semiconductor samples known to be predominantly doped with one defect species, the dominant time constant in the decay is influenced by the other defect species present in the semiconductor sample.

As indicated in Section 6.6, the new Analytic Lifetime Spectroscopy is based on theory which is an extension of the single-level theory developed in Chapter 2 Ref. [1]. A multitransient analysis of the numerical solution yields very good agreement with the theoretical prediction of the fundamental frequencies λ_1 and λ_2 for the single level case. This independent verification of the theory, derived from the differential rate equations determined from first principles, and the Shockley-Read-Hall rate equations, confirms the properties of the above solution.

6.8 Discussion

The Analytical Lifetime Spectroscopy method presented in this Chapter has a significant advantage over the present Lifetime Spectroscopy method. The advantage is that variables resolved by multitransient analysis from the measured decay may be plotted against $1/kT$ to determine a single-level defect level depth without ambiguity. With Lifetime Spectroscopy from Figure 6.4 a plot (linear part) for a level in the lower half of the bandgap intersects that of a level in the upper half. Effectively the two level depths cannot be distinguished from one measurement technique. In effect Two defect level depth measurement methods are required to identify the level

depth and which half of the bandgap the level resides (see Rein et al [46]). It is clear from the graph of Figure 6.5 for Analytic Lifetime Spectroscopy that the level depth represented by the slope of the plots (linear part indicated by a level depth) does not have this ambiguity as there are no intersections. Only one measurement and one wafer is required to determine level depth making the procedure very straight forward and simple. This is a very practical outcome of the new theory.

Chapter 7

Conclusions

7.1 Discussion

Initially at $t = 0^+$, for the situations examined in this thesis $\Delta n(0)$ electrons and $\Delta p(0)$ holes are uniformly generated in the material. Expressions for the minority (τ_1) and majority (τ_2) carrier decay time constants are derived without an approximation at a given temperature for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . The transition from low to high injection is also given. A general analytic expression for the carrier decay $\Delta n(t)$ for $t > 0^+$ derived from the rate equations is represented by an infinity of exponential terms, the frequencies of which are linear combinations of the two fundamental frequencies λ_1 and λ_2 . These frequencies are attributed to minority λ_1 and majority λ_2 decay frequencies (inverse time constants). Very good agreement is found between the decay frequencies λ_1 and λ_2 for the theory presented and by TLS multi-transient analysis of the numerical solution, at one temperature. This independent verification of the theory derived from the Shockley-Read-Hall rate equations confirms the properties of the above solution. Further, the solution represents the impulse response as the exponential terms are

the response of an infinite sum of linear systems.

From a theoretical standpoint, the SRH lifetime expression τ for the dominant single level model, is shown to be approximate. The existing interpretation of experimental data relies on one time constant τ_{ss} (steady state case) or τ_b (bulk decay - transient case) derived from the definition Eq. 5.2 of Ref. [2] (repeated as Eq. (3.1) here). Figure 3.1 and Figure 3.2 indicate that for low injection the SRH time constant expression, applied to both the steady state and transient situations, does not adequately reflect the actual decay. It is the low injection region that is commonly used to interpret experimental data and determine defect level parameters. Whereas at high injection τ_1 is adequate to model recombination and trapping, at low injection τ_2 is also required as the magnitude of the coefficient can be significant. For the steady state, in low injection the frequencies are the same as the transient case. From the above it can be seen that the single SRH time constant expression is not sufficient as an approximation and it lacks the provision for predicting general behaviour. Deviations could be at their most significant when the magnitude of the coefficient, of the exponential terms of the minority and majority decay time constants, are similar in magnitude.

Furthermore, the recent general analytic solution of Chapter 3 (also published elsewhere Debuf [1]) applied to the steady state, together with the TLS analysis of the numerical solution, confirms the presence of at least two time constants in the decay. This unifies the existing solutions of the rate equations in the literature, as expected from inspection of the second order differential equation (3.3), for small departures from the equilibrium carrier concentration where the transient and steady state solutions are identical.

Using the method of solution developed in Chapter 3 Ref. [1] it is shown that the differential rate equations derived for the two-defect-level systems are consistent with the numerical solution of the rate equations. The linear form of the rate equations predicts fundamental time constants which agree with those determined from

the analysis of the numerical solution. As previously mentioned, the analytic solution to the differential rate equations for the multiple defect state systems indicates an infinity of exponential terms, the frequencies of which are a linear combination of fundamental frequencies. The fundamental frequencies are derived from the linear form of the rate equations without an approximation at a given temperature for arbitrary, excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . The transition from the linear to non-linear variation of fundamental frequency with excess carrier concentration is also given. Trapping behaviour of the minority carrier τ_1 is discussed and a measure of semiconductor quality is proposed based on the value and behaviour of τ_1 . Expressions for the minority (τ_1) and majority carrier decay time constants are given. There is no priori knowledge of the number and value of time constants in the numerical solution. This independent verification of the theory, determined from the first principles derivation of the rate equations, confirms the properties of the above solution and the method of multi-transient analysis.

The fundamental theory of transient decay due to the two-multiple-defect level systems given in the present work may find a wide range of applications. Some of these applications may be comparing the quality of crystalline silicon, polycrystalline silicon and cast silicon in the case of solar cells. Further, the effectiveness of different experimental techniques may be refined with the measurement of the fundamental decay time constants associated with multiple defect levels. Hence a uniform interpretation of defect level parameters across the techniques may ensue.

This work introduces the solution of the carrier continuity equation which includes multiple defect levels in the carrier recombination terms. The recombination term is expressed as an infinite number of exponential terms with frequencies which are multiples of fundamental frequencies. The resulting expressions for the excess carrier concentrations $\Delta n_{av}(x, t)$ and $\Delta p_{av}(x, t)$, may be readily formulated by analysing the decay for a well passivated surface ($S = 0$) for τ_1 and τ_2 , the fun-

damental time constants. Simplifications are made which reflect the experimental situation envisaged to carry out a simple contactless photoconductance decay measurement. A silicon CZ wafer with both surfaces well passivated is shown to yield consistent experimental time constants, with an exact theory.

Existing experimental data are largely interpreted using the time constant expression τ derived by Shockley, Read and Hall in Refs. [2] [3] and for multiple levels with approximations, as indicated in the introduction. The current work seeks to address the anomalies arising from such an interpretation in terms of the defect level parameters such as level depth, using exact theory developed recently. The accuracy of the existing measurement techniques, DLTS and Lifetime Spectroscopy, is demonstrated and the limitations of each method presented. A proposed Analytic Lifetime Spectroscopy for a single level defect is outlined.

7.2 Concluding Remarks

The fundamental frequencies uniquely identify the defect level properties of capture cross section $\sigma_{n,p}$, level concentration N_t and energy E_t , as a signature of time constants. The numerical solution at temperature T_i , excess carrier concentration $\Delta n(0)$ and doping concentration N_A , indicates the evolution of the decay with the given defect level parameters and indicates that the theory is consistent having been derived without approximations and independently verified by a multitransient analysis of the numerical solution.

Appendix A

Evaluation of $\eta_n(t_0)$ and $\eta_p(t_0)$

For low injection $\eta_n(t_0)$ and $\eta_p(t_0)$, at $t_0 = 0^+$ are both zero. It remains to find a value for $\eta_n(t_0)$ and $\eta_p(t_0)$ at $t_0 = t_i$. Firstly a relationship between the differential terms in equations (2.27) is established and subsequently an expression for $\eta_n(t_i)$ is developed. Secondly having determined an expression for $\eta_n(t_i)$ in terms of the excess carrier concentration $\Delta n(0)$, a critical value of excess carrier concentration $\Delta n(0)_{critical}$ may be evaluated. This value represents the transition between the linear variation of fundamental frequency with excess carrier concentration and the non-linear variation with $\eta_n(t_0) = 0$. A requirement for the selection of $\eta_n(t_i) = \Delta f(t_i) = \Delta n_{nm}(t_i)$ is found from the charge neutrality relation Eq. (2.18) with $\Delta p(0) = \Delta n(0)$ as follows.

$$\Delta p_{nm}(t_i) = \left(1 + \frac{N_t}{\Delta n(0)}\right) \Delta n_{nm}(t_i) \quad (\text{A.1})$$

where,

$$\phi = \left(1 + \frac{N_t}{\Delta n(0)}\right) \quad (\text{A.2})$$

Equating coefficients on both sides of Eq. (A.1) considering the first two components.

$$\begin{aligned} P_{10} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{10} \\ P_{01} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{01} \end{aligned} \quad (\text{A.3})$$

Now, multiplying the first equation of Eqs. (A.3) by $\lambda_1 \exp(-\lambda_1 t_i)$ and the second equation by $\lambda_2 \exp(-\lambda_2 t_i)$ yields

$$\begin{aligned} P_{10}\lambda_1 e^{-\lambda_1 t_i} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{10}\lambda_1 e^{-\lambda_1 t_i} \\ P_{01}\lambda_2 e^{-\lambda_2 t_i} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{01}\lambda_2 e^{-\lambda_2 t_i} \end{aligned} \quad (\text{A.4})$$

Summing the left hand side of Eqs. (A.4) and equating that to the sum of the right hand side results in a relationship between the differentials as follows.

$$\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t_0=t_i} = \left(1 + \frac{N_t}{\Delta n(0)}\right) \left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t_0=t_i} \quad (\text{A.5})$$

Having established this relationship equation (2.28) may be solved for $\eta_n(t_i)$. The value of $\eta_p(t_i)$ is evaluated from Eq. (2.27).

$$\eta_n(t_i) = \frac{(\phi\alpha_0 - \beta_0) - (\phi\gamma_0 - \phi^2\sigma_0)}{\phi\Delta n(0)(1 - \phi)(C_n + C_p)} \quad (\text{A.6})$$

where α_0 , β_0 , γ_0 and σ_0 are given by Eq. (2.22). Solving the following quadratic resulting from equation (A.6) with $\eta_n(t_i) = 0$, corresponding to the linear region of variation of $\lambda_{1,2}$ with $\Delta n(0)$, indicates the onset of the non-linear region. For $\Delta n(0) > 0$, the onset of the non-linear region is termed $\Delta n(0)_{critical}$.

$$\begin{aligned} 0 &= \Delta n^2(0) ((\alpha_0 - \beta_0) - (\gamma_0 - \sigma_0)) \\ &\quad + \Delta n(0) (N_t\alpha_0 - N_t\gamma_0 + 2N_t\sigma_0) \\ &\quad + N_t^2\sigma_0 \end{aligned} \quad (\text{A.7})$$

Note also from Eqs. (2.28) and (A.2) the following may be established for t_i :

$$t_i = -\frac{1}{(\gamma - \sigma\phi)} \ln(\eta_n(t_i)) \quad (\text{A.8})$$

Appendix B

Derivation of an Analytic Solution for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$

More formally the non-linear equation (2.36) may be written in the following form given $r_n(t)$ and $q_n(t)$ where $\Delta n(t) = \Delta n_{nm}(t)\Delta n(0)$

$$\frac{d\Delta n(t)}{dt} + r_n(t)\Delta n(t) = q_n(t) \quad (\text{B.1})$$

where $\Delta f(t)$ is the non-linear occupation function.

$$r_n(t) = (\gamma_0 - \sigma_0) - C_n N_t \Delta f(t) \quad (\text{B.2})$$

$$q_n(t) = \sigma_0 N_t \Delta f(t) \quad (\text{B.3})$$

An analytic solution for $\Delta n(t)$ may be written as follows (see Kreyszig [47]).

$$\Delta n(t) = e^{-\int r_n(t)dt} \left(\int q_n(t) e^{\int r_n(t)dt} dt + C \right) \quad (\text{B.4})$$

It is assumed that the non-linear function $\Delta f(t)$ may be given by $\Delta_l f(t)$, Eq. (2.33). A solution of equation (B.4) is obtained by substitution of $\Delta_l f(t)$ and evaluating the indefinite integral by repeated integration by parts. An infinite sum of exponentials with exponents a linear combination of the fundamental frequencies λ_1 and λ_2 is revealed for $\Delta n(t)$ (Eq. (B.10)).

The solution of Eq. (B.4) is briefly outlined as follows. let,

$$I_{qn}(t) = \int \sigma_0 N_t (F_{10} e^{-\lambda_1 t} + F_{01} e^{-\lambda_2 t}) e^{(\gamma_0 - \sigma_0)t} e^{\frac{C_n N_t F_{10}}{\lambda_1} e^{-\lambda_1 t} + \frac{C_n N_t F_{01}}{\lambda_2} e^{-\lambda_2 t} + c'} dt \quad (\text{B.5})$$

and

$$\begin{aligned} I_{rn}^-(t) &= e^{-\int r_n(t) dt} \\ &= e^{-(\gamma_0 - \sigma_0)t} e^{-\frac{C_n N_t F_{10}}{\lambda_1} e^{-\lambda_1 t} - \frac{C_n N_t F_{01}}{\lambda_2} e^{-\lambda_2 t} - c'} \end{aligned} \quad (\text{B.6})$$

such that, where C is a constant of integration to be determined by the boundary conditions.

$$\Delta n(t) = I_{rn}^-(t) (I_{qn}(t) + C) \quad (\text{B.7})$$

and performing the integration by parts for the first term of $I_{qn}(t)$ as follows,

$$\begin{aligned} I &= \int u dv \\ &= uv - \int v du \end{aligned} \quad (\text{B.8})$$

where,

$$u = e^{\frac{C_n N_t F_{10}}{\lambda_1} e^{-\lambda_1 t} + \frac{C_n N_t F_{01}}{\lambda_2} e^{-\lambda_2 t} + c'} \quad (\text{B.9a})$$

$$du = e^{\frac{C_n N_t F_{10}}{\lambda_1} e^{-\lambda_1 t} + \frac{C_n N_t F_{01}}{\lambda_2} e^{-\lambda_2 t} + c'} (-C_n N_t F_{10} e^{-\lambda_1 t} - C_n N_t F_{01} e^{-\lambda_2 t}) \quad (\text{B.9b})$$

$$v = \frac{\sigma_0 N_t F_{10}}{((\gamma_0 - \sigma_0) - \lambda_1)} e^{((\gamma_0 - \sigma_0) - \lambda_1)t} \quad (\text{B.9c})$$

$$dv = e^{((\gamma_0 - \sigma_0) - \lambda_1)t} \quad (\text{B.9d})$$

Multiplying equation (B.5) through by $I_{rn}^-(t)$ and collecting terms yields an expression for $\Delta n(t)$ where $R_{xyz}(t)$ is an integral which may be further integrated by parts. The equation representing the function $\Delta n(t)$ is given by Eq. (B.10) indicating a series of exponential terms which on further integration goes to an infinity of

terms. Effectively the integration is performed until the magnitude of the remainder ($R_{xyz}(t)$) is less than some ϵ . The constant of integration C is evaluated at the end of this section.

$$\begin{aligned} \Delta n(t) = & \phi_{10}^n F_{10} \left\{ e^{-\lambda_1 t} + \psi_{20}^n F_{10} \left[e^{-2\lambda_1 t} + \psi_{30}^n F_{10} (e^{-3\lambda_1 t} + R_{111}(t)) + \psi_{21}^n F_{01} (e^{-(2\lambda_1 + \lambda_2)t} + R_{112}(t)) \right] \right. \\ & + \psi_{11}^n F_{01} \left[e^{-(\lambda_1 + \lambda_2)t} + \psi_{21}^n F_{10} (e^{-(2\lambda_1 + \lambda_2)t} + R_{121}(t)) + \psi_{12}^n F_{01} (e^{-(\lambda_1 + 2\lambda_2)t} + R_{122}(t)) \right] \left. \right\} \\ & + \phi_{01}^n F_{01} \left\{ e^{-\lambda_2 t} + \psi_{02}^n F_{01} \left[e^{-2\lambda_2 t} + \psi_{03}^n F_{01} (e^{-3\lambda_2 t} + R_{222}(t)) + \psi_{12}^n F_{10} (e^{-(\lambda_1 + 2\lambda_2)t} + R_{221}(t)) \right] \right. \\ & + \psi_{11}^n F_{10} \left[e^{-(\lambda_1 + \lambda_2)t} + \psi_{21}^n F_{10} (e^{-(2\lambda_1 + \lambda_2)t} + R_{211}(t)) + \psi_{12}^n F_{01} (e^{-(\lambda_1 + 2\lambda_2)t} + R_{212}(t)) \right] \left. \right\} \\ & + I_{rn}^-(t)C \end{aligned} \quad (B.10)$$

where

$$\phi_{ij}^n = \frac{\sigma_0 N_t}{(\gamma_0 - \sigma_0) - (i\lambda_1 + j\lambda_2)} \quad (B.11)$$

$$\psi_{ij}^n = \frac{C_n N_t}{(\gamma_0 - \sigma_0) - (i\lambda_1 + j\lambda_2)} \quad (B.12)$$

Consider now the second non-linear expression Eq. (2.37) for $\Delta p_{nm}(t)$ which may be similarly written in the following form with $\Delta p(t) = \Delta p_{nm}(t)\Delta n(0)$:

$$\frac{d\Delta p(t)}{dt} + r_p(t)\Delta p(t) = q_p(t) \quad (B.13)$$

where,

$$r_p(t) = (\alpha_0 - \beta_0) + C_p N_t \Delta f(t) \quad (B.14)$$

$$q_p(t) = -\beta_0 N_t \Delta f(t) \quad (B.15)$$

An analytic solution for $\Delta p(t)$ may be written as follows (see Ref. [47]).

$$\Delta p(t) = e^{-\int r_p(t)dt} \left(\int q_p(t) e^{\int r_p(t)dt} dt + C \right) \quad (B.16)$$

Similarly an analytic solution for $\Delta p(t)$ is available by integrating equation (B.16) by parts to reveal an infinite series of mono-exponential terms with inverse time constants, a linear combination of the frequencies λ_1 and λ_2 .

$$\begin{aligned} \Delta p(t) = & \phi_{10}^p F_{10} \left\{ e^{-\lambda_1 t} - \psi_{20}^p F_{10} \left[e^{-2\lambda_1 t} - \psi_{30}^p F_{10} (e^{-3\lambda_1 t} + R_{111}(t)) - \psi_{21}^p F_{01} (e^{-(2\lambda_1 + \lambda_2)t} + R_{112}(t)) \right] \right. \\ & - \psi_{11}^p F_{01} \left[e^{-(\lambda_1 + \lambda_2)t} - \psi_{21}^p F_{10} (e^{-(2\lambda_1 + \lambda_2)t} + R_{121}(t)) - \psi_{12}^p F_{01} (e^{-(\lambda_1 + 2\lambda_2)t} + R_{122}(t)) \right] \left. \right\} \\ & + \phi_{01}^p F_{01} \left\{ e^{-\lambda_2 t} - \psi_{02}^p F_{01} \left[e^{-2\lambda_2 t} - \psi_{03}^p F_{01} (e^{-3\lambda_2 t} + R_{222}(t)) - \psi_{12}^p F_{10} (e^{-(\lambda_1 + 2\lambda_2)t} + R_{221}(t)) \right] \right. \\ & - \psi_{11}^p F_{10} \left[e^{-(\lambda_1 + \lambda_2)t} - \psi_{21}^p F_{10} (e^{-(2\lambda_1 + \lambda_2)t} + R_{211}(t)) - \psi_{12}^p F_{01} (e^{-(\lambda_1 + 2\lambda_2)t} + R_{212}(t)) \right] \left. \right\} \\ & + I_{rp}^-(t)C \end{aligned} \quad (B.17)$$

where

$$\phi_{ij}^p = \frac{-\beta_0 N_t}{(\alpha_0 - \beta_0) - (i\lambda_1 + j\lambda_2)} \quad (\text{B.18})$$

$$\psi_{ij}^p = \frac{C_p N_t}{(\alpha_0 - \beta_0) - (i\lambda_1 + j\lambda_2)} \quad (\text{B.19})$$

From the charge neutrality relation as follows, a solution for the non-linear function $\Delta f(t)$ should also contain an infinity of exponential terms contradicting the assumption that $\Delta f(t)$ be represented by $\Delta_l f(t)$

$$N_t \Delta f(t) = \Delta p(t) - \Delta n(t) \quad (\text{B.20})$$

Hence mono-exponential terms containing the linear combination of the fundamental frequencies should also be included in $\Delta f(t)$ as follows:

$$\begin{aligned} \Delta f(t) = & \Delta_l f(t) + \gamma_{20} e^{-2\lambda_1 t} + \gamma_{02} e^{-2\lambda_2 t} \\ & + \gamma_{11} e^{-(\lambda_1 + \lambda_2)t} + \dots \end{aligned} \quad (\text{B.21})$$

As such the following solutions for $\Delta n(t)$ and $\Delta p(t)$ may be determined.

$$\begin{aligned} \Delta n(t) = & \phi_{10}^n F_{10} e^{-\lambda_1 t} + (\phi_{10}^n \psi_{20}^n F_{10}^2 + \phi_{20}^n \gamma_{20}) e^{-2\lambda_1 t} + (\phi_{10}^n \psi_{20}^n \psi_{30}^n F_{10}^3 + \phi_{30}^n \gamma_{30}) e^{-3\lambda_1 t} \\ & + (\phi_{10}^n \psi_{20}^n \psi_{21}^n F_{10}^2 F_{01} + \phi_{10}^n \psi_{11}^n \psi_{21}^n F_{10}^2 F_{01} + \phi_{01}^n \psi_{11}^n \psi_{21}^n F_{10}^2 F_{01} + \phi_{21}^n \gamma_{21}) e^{-(2\lambda_1 + \lambda_2)t} \\ & + (\phi_{10}^n \psi_{11}^n F_{10} F_{01} + \phi_{01}^n \psi_{11}^n F_{10} F_{01} + \phi_{11}^n \gamma_{11}) e^{-(\lambda_1 + \lambda_2)t} \\ & + (\phi_{10}^n \psi_{11}^n \psi_{12}^n F_{10} F_{01}^2 + \phi_{01}^n \psi_{11}^n \psi_{12}^n F_{10} F_{01}^2 + \phi_{01}^n \psi_{02}^n \psi_{12}^n F_{10} F_{01}^2 + \phi_{12}^n \gamma_{12}) e^{-(\lambda_1 + 2\lambda_2)t} \\ & + \phi_{01}^n F_{01} e^{-\lambda_2 t} + (\phi_{01}^n \psi_{02}^n F_{01}^2 + \phi_{02}^n \gamma_{02}) e^{-2\lambda_2 t} + (\phi_{01}^n \psi_{02}^n \psi_{03}^n F_{01}^3 + \phi_{03}^n \gamma_{03}) e^{-3\lambda_2 t} \\ & + R^n(t) + I_{rn}^-(t) C \end{aligned} \quad (\text{B.22})$$

and

$$\begin{aligned}
 \Delta p(t) = & \phi_{10}^p F_{10} e^{-\lambda_1 t} + (\phi_{10}^p \psi_{20}^p F_{10}^2 + \phi_{20}^p \gamma_{20}) e^{-2\lambda_1 t} + (\phi_{10}^p \psi_{20}^p \psi_{30}^p F_{10}^3 + \phi_{30}^p \gamma_{30}) e^{-3\lambda_1 t} \\
 & + (\phi_{10}^p \psi_{20}^p \psi_{21}^p F_{10}^2 F_{01} + \phi_{10}^p \psi_{11}^p \psi_{21}^p F_{10}^2 F_{01} + \phi_{01}^p \psi_{11}^p \psi_{21}^p F_{10}^2 F_{01} + \phi_{21}^p \gamma_{21}) e^{-(2\lambda_1 + \lambda_2)t} \\
 & + (\phi_{10}^p \psi_{11}^p F_{10} F_{01} + \phi_{01}^p \psi_{11}^p F_{10} F_{01} + \phi_{11}^p \gamma_{11}) e^{-(\lambda_1 + \lambda_2)t} \\
 & + (\phi_{10}^p \psi_{11}^p \psi_{12}^p F_{10} F_{01}^2 + \phi_{01}^p \psi_{11}^p \psi_{12}^p F_{10} F_{01}^2 + \phi_{01}^p \psi_{02}^p \psi_{12}^p F_{10} F_{01}^2 + \phi_{12}^p \gamma_{12}) e^{-(\lambda_1 + 2\lambda_2)t} \\
 & + \phi_{01}^p F_{01} e^{-\lambda_2 t} + (\phi_{01}^p \psi_{02}^p F_{01}^2 + \phi_{02}^p \gamma_{02}) e^{-2\lambda_2 t} + (\phi_{01}^p \psi_{02}^p \psi_{03}^p F_{01}^3 + \phi_{03}^p \gamma_{03}) e^{-3\lambda_2 t} \\
 & + R^p(t) + I_{rp}^-(t)C
 \end{aligned} \tag{B.23}$$

Using the charge neutrality relation and equating coefficients, the factor γ_{20} for example may be evaluated.

$$\begin{aligned}
 N_t \gamma_{20} e^{-2\lambda_1 t} = & (\phi_{10}^p \psi_{20}^p F_{10}^2 + \phi_{20}^p \gamma_{20}) e^{-2\lambda_1 t} \\
 & - (\phi_{10}^n \psi_{20}^n F_{10}^2 + \phi_{20}^n \gamma_{20}) e^{-2\lambda_1 t}
 \end{aligned} \tag{B.24}$$

such that

$$\gamma_{20} = \frac{(\phi_{10}^p \psi_{20}^p - \phi_{10}^n \psi_{20}^n) F_{10}^2}{N_t - \phi_{20}^p + \phi_{20}^n} \tag{B.25}$$

Using the notation in the text an expression for N_{20} may be evaluated and is equivalent to that derived by equating coefficients of like exponential terms.

$$N_{20} = \frac{(N_t \phi_{10}^n \psi_{20}^n + \phi_{10}^p \phi_{20}^n \psi_{20}^p - \phi_{10}^n \phi_{20}^p \psi_{20}^n) F_{10}^2}{N_t - \phi_{20}^p + \phi_{20}^n} \tag{B.26}$$

Evaluation of the constant of integration C and confirmation of the method of equating coefficients to realise simultaneous equations, is as follows. Equation (B.10) may be expressed as Eq. (B.27).

$$\Delta n(t) = I_{rn}^-(t) I_{qn}(t) + I_{rn}^-(t) C \tag{B.27}$$

and the constant C determined at $t_0 = 0^+$ or $t_0 = t_i$ which represent boundary conditions where the value of $\Delta n(t)$ is known.

$$C = \frac{\Delta n(t_0) - I_{rn}^-(t_0) I_{qn}(t_0)}{I_{rn}^-(t_0)} \tag{B.28}$$

Differentiating equation (B.27) results in an expression Eq. (B.29) (with the value of C Eq. (B.28) included) which may be equated with Eq. (2.20) and substituting the charge neutrality relation.

$$\begin{aligned} \left. \frac{d\Delta n(t)}{dt} \right|_{t=t_0} &= \left. \frac{d[I_{rn}^-(t)I_{qn}(t)]}{dt} \right|_{t=t_0} + \\ &\quad [\Delta n(t_0) - I_{rn}^-(t_0)I_{qn}(t_0)] \\ &\quad \times [-(\gamma_0 - \sigma_0) + C_n N_t F_{10} e^{-\lambda_1 t_0} + C_n N_t F_{01} e^{-\lambda_2 t_0} + \dots] \end{aligned} \quad (\text{B.29})$$

At $t_0 = t_i$ for example equating like exponential terms for λ_1 yields the following where $\eta_n(t_i) = \Delta f(t_i)$:

$$((\gamma_0 - \sigma_0) - \lambda_1 - C_n N_t \eta_n(t_i)) N_{10} e^{-\lambda_1 t_i} = \left(\sigma_0 \frac{N_t}{\Delta n(0)} + 2C_n N_t (N_{00} + \eta_n(t_i)) \right) F_{10} e^{-\lambda_1 t_i} \quad (\text{B.30})$$

and for $i = 1, j = 1$:

$$\begin{aligned} ((\gamma_0 - \sigma_0) - (\lambda_1 + \lambda_2) - C_n N_t \eta_n(t_i)) N_{11} e^{-(\lambda_1 + \lambda_2) t_i} &= \left(\sigma_0 \frac{N_t}{\Delta n(0)} + 2C_n N_t (N_{00} + \eta_n(t_i)) \right) \\ &\times F_{11} e^{-(\lambda_1 + \lambda_2) t_i} \\ &\quad + C_n N_t (N_{10} F_{01} + N_{01} F_{10}) \\ &\times e^{-(\lambda_1 + \lambda_2) t_i} \end{aligned} \quad (\text{B.31})$$

Appendix C

Calculation of Coefficients F_{10} , F_{01} and $N_{i,j}$

All coefficients $N_{i,j}$ and $P_{i,j}$ are a function of F_{10} , F_{01} , λ_1 , λ_2 and $\eta_n(t_i)$. Note that the differentials of the normalised variables $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ at $t = 0^+$ are equal to a constant independent of the injection level and derived from equations (2.20) and (2.21).

$$\left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=0^+} = -C_n N_t (1 - f_o) \quad (\text{C.1})$$

$$\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=0^+} = -C_p N_t f_o \quad (\text{C.2})$$

At $t = 0^+$, the normalised expressions Eqs. (2.39) are represented by Eq. (C.3), given Eq. (C.1).

$$1 = N_{10} + N_{01} + \varepsilon_N \quad (\text{C.3a})$$

$$C_n N_t (1 - f_o) = \lambda_1 N_{10} + \lambda_2 N_{01} + \varepsilon'_N \quad (\text{C.3b})$$

where ε and ε' are error terms representing the series:

$$\begin{aligned} \varepsilon_N &= N_{11} + N_{20} + N_{02} + N_{12} + N_{21} \\ &+ N_{30} + N_{03} + \cdots \end{aligned} \quad (\text{C.4a})$$

$$\begin{aligned}\varepsilon'_N &= (\lambda_1 + \lambda_2)N_{11} + 2\lambda_1 N_{20} + 2\lambda_2 N_{02} \\ &\quad + (\lambda_1 + 2\lambda_2)N_{12} + \cdots\end{aligned}\tag{C.4b}$$

From equation (B.30) with $\eta_n(t_i) = 0$, the values of F_{10} and F_{01} may be evaluated, given N_{10} and N_{01} , as follows:

$$F_{10} = \frac{[(\gamma_0 - \sigma_0) - \lambda_1] N_{10}}{\frac{\sigma_0 N_t}{\Delta n(0)} + 2C_n N_t}\tag{C.5}$$

$$F_{01} = \frac{[(\gamma_0 - \sigma_0) - \lambda_2] N_{01}}{\frac{\sigma_0 N_t}{\Delta n(0)} + 2C_n N_t}\tag{C.6}$$

At $t = t_i$, the values of F_{10} and F_{01} may be determined from Eq. (B.30).

Let $\varepsilon_N = 0$ and $\varepsilon'_N = 0$ and calculate N_{10} and N_{01} from Eq. (C.3). With an initial value of N_{10} and N_{01} , the components $N_{i,j}$ of the series for ε_N and ε'_N may be evaluated by equating coefficients and solving simultaneous equations. Similarly for P_{10} and P_{01} , the $P_{i,j}$ for the series ε_P and ε'_P may be evaluated. The coefficients N_{10} and N_{01} are re-evaluated from Eq. (C.3) corrected for the error terms ε_N and ε'_N as follows:

$$N_{10} + N_{01} = 1 - \varepsilon_N\tag{C.7a}$$

$$\lambda_1 N_{10} + \lambda_2 N_{01} = C_n N_t (1 - f_o) - \varepsilon'_N\tag{C.7b}$$

N_{10} and N_{01} are re-evaluated, and the $N_{i,j}$, $P_{i,j}$ and $F_{i,j}$ determined from the simultaneous equations such that the sum of the coefficients at $t = 0$ equals one. Note that at $t = 0^+$ the resulting series for $N_{i,j}$ should yield a value for $d\Delta n_{nm}(t)/dt$ given by Eq. (C.1) for arbitrary injection $\Delta n(0)$.

Appendix D

Rate Equation: Quadratic Form

At $t = 0^+$ the following quadratic applies for the transient case at hand. As such the easiest way to deal with this is to do a co-ordinate change so that the N_0 term disappears in the new co-ordinates.

$$0 = N_0 + N_1 n(0^+) + N_2 n^2(0^+) \quad (\text{D.1})$$

Now $n(0^+)$ approaches n_t the non-zero solution of the above quadratic and using the co-ordinate change $\tilde{n} = n(0^+) - n_t$, the N_0 term is eliminated. In terms of Eq. (2.42), Eq. (2.1) is written as follows such that for all (i, j) we have:

$$\begin{aligned} \sum_i^\infty \sum_j^\infty \frac{dN_{i,j} E_{i,j}}{dt} = & - \sum_i^\infty \sum_j^\infty \left(\frac{(\gamma_0 - \sigma_0) N_{i,j} - \sigma_0 \frac{N_t}{\Delta n(0)} F_{i,j} - C_n N_t \Phi_{i,j}}{\sum_i^\infty \sum_j^\infty N_{i,j} E_{i,j}} \right) \sum_i^\infty \sum_j^\infty N_{i,j} E_{i,j} \\ & + C_n N_t \sum_i^\infty \sum_j^\infty \frac{F_{i,j}}{N_{i,j}} N_{i,j}^2 E_{i,j}^2 \end{aligned} \quad (\text{D.2})$$

where $\Phi_{i,j}$ is the sum of the cross terms and:

$$N_0 = C_n N_t (1 - f_o) \quad (\text{D.3})$$

$$N_1 = - \left((\gamma_0 - \sigma_0) - C_n N_t \sum_i^\infty \sum_j^\infty \Phi_{i,j} \right) \quad (\text{D.4})$$

$$N_2 = C_n N_t \sum_i^\infty \sum_j^\infty \frac{F_{i,j}}{N_{i,j}} \quad (\text{D.5})$$

Appendix E

Analytic Solution: Infinity of Linear Systems

It may be shown as follows that the infinite series solution represents the sum of responses of an infinite number of linear systems to an impulse $\delta(t)$. Given the infinity of exponential terms comprising the solution for $\Delta n_{nm}(t)$ each $N_{i,j}E_{i,j}$ term may be written as:

$$u_{i,j} = N_{i,j}E_{i,j} \quad (\text{E.1})$$

which is a solution of a linear differential equation with a constant coefficient and $\lambda_1 > 0$ and $\lambda_2 > 0$:

$$\frac{du_{i,j}}{dt} = -(i\lambda_1 + j\lambda_2)u_{i,j} \quad (\text{E.2})$$

As such the infinite series of exponential terms comprising the solution of the differential equation for $\Delta n_{nm}(t)$ is a sum of linear responses and the solution represents the impulse response. Stability for linear ordinary differential equations Stuart [48] is assured if the eigenvalues $-i\lambda_1$ and $-j\lambda_2$, lie on the real axis in the left half plane ie. $Re(-i\lambda_1) < 0$ and $Re(-j\lambda_2) < 0$. This is certainly the case here.

Appendix F

Differential Rate Equation for Multiple Discrete Levels

A first principles approach is adopted as in Shockley and Read [2] in deriving the differential rate equations for carrier transitions via multiple discrete defect energy levels in the bandgap. The recombination rate for electrons at a discrete defect energy level is the difference in the rate of electron capture and the rate of electron emission Ref. [2]. Consider m discrete defect levels where there is no carrier exchange between levels. Furthermore, a carrier at the k' level in the range of energy $dE_{k'}$ makes a transition to the k^{th} discrete defect level as shown in Figure F.1. A rate of electron capture from the conduction band to multiple levels may be expressed as being proportional to the number of electrons in the conduction band $f(E_{k'})N(E_{k'})dE_{k'}$ ($f(E_{k'})$ is the electron occupation probability function) and the number of holes $\sum_{k=1}^m N_{tk}(1 - f_k(E_{tk}))$ at the defect levels where $f_k(E_{tk})$ is the electron defect level occupation function for a given k . The constant of proportionality is $\sum_{k=1}^m c_n(E_k, E_{k'})$. Similarly the rate of electron emission from the defect levels to the conduction band is proportional to the number of available empty states $f_p(E_{k'})N(E_{k'})dE_{k'}$ (where $f_p(E_{k'}) = (1 - f(E_{k'}))$) in the conduction band and

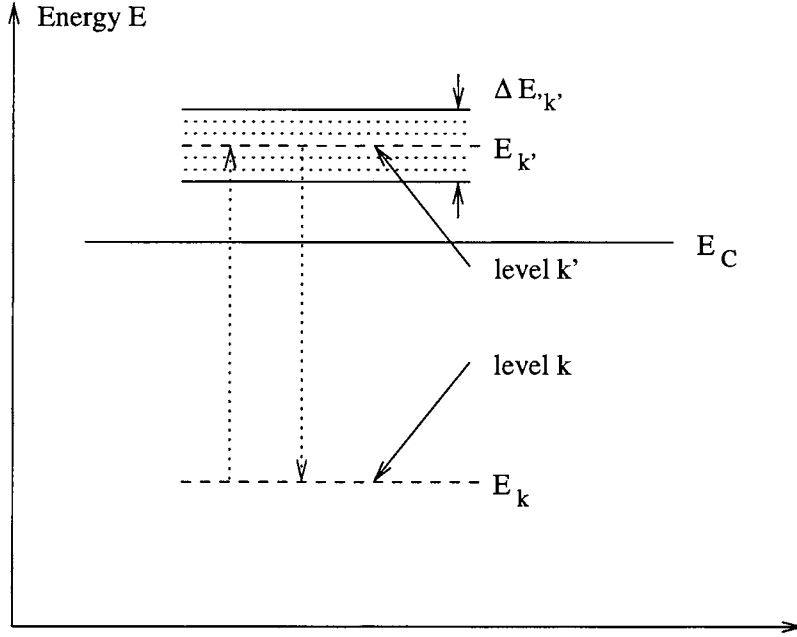


Figure F.1: Carrier transitions between the k' level in the conduction band and the k^{th} level defect state in the bandgap.

the number of electrons $\sum_{k=1}^m N_{tk} f_k(E_{tk})$ at the defect levels. Again, the constant of proportionality is $\sum_{k=1}^m e_n(E_{k'}, E_k)$.

$$\begin{aligned}
 dU_n &= \left[\sum_{k'=1}^m c_n(E_k, E_{k'}) \right] \left[\sum_{k=1}^m N_{tk} (1 - f_k(E_{tk})) \right] \\
 &\times f(E_{k'}) N(E_{k'}) dE_{k'} \\
 &- \left[\sum_{k'=1}^m e_n(E_{k'}, E_k) \right] \left[\sum_{k=1}^m N_{tk} f_k(E_{tk}) \right] \\
 &\times f_p(E_{k'}) N(E_{k'}) dE_{k'}
 \end{aligned} \tag{F.1}$$

where:

$$f_k(E_{tk}) = \frac{1}{1 + \exp\left(\frac{E_{tk} - E_{f_{tk}}(t)}{kT}\right)} \tag{F.2}$$

and:

$$f(E_{k'}) = \frac{1}{1 + \exp\left(\frac{E_{k'} - E_f(t)}{kT}\right)} \tag{F.3}$$

At equilibrium the recombination rate dU_n is zero and $E_{f_{tk}}(0^-) = E_f$ where $E_{f_{tk}}$ is the k^{th} defect level occupancy Fermi level and E_f is the equilibrium Fermi level.

The proportionality constant $c_n(E_k, E_{k'})$ is non-zero for a carrier transition involving a particular (k, k') pair, otherwise it is zero. From the equilibrium condition, it may be established that $e_n(E_{k'}, E_k)$ is also non-zero for the same (k, k') pair since the occupancy functions are non-zero at equilibrium. Hence carrier transitions occur in unique pairs (k', k) , so that equation (F.1) is only valid for a corresponding pair to the exclusion of all other pairs. The mathematical equivalent for the discrete level case where there is no interaction between levels is that the quantities $f_k(E_{tk})$ (and hence $[1 - f_k(E_{tk})]$) and $f_k(E_{tk'})$ (and hence $[1 - f_k(E_{tk'})]$) are orthogonal functions with respect to functions of $c_n(E_k, E_{k'})$ and $e_n(E_{k'}, E_k)$ Kreyszig [49] as follows.

$$dU_n = 0 \text{ for } k \neq k' \quad (\text{F.4a})$$

$$|dU_n| > 0 \text{ for } k = k' \quad (\text{F.4b})$$

From equation (F.1) the following may be established from the given equilibrium condition by summing over all (k', k) pairs.

$$\begin{aligned} \left[\sum_{k'=1}^m e_n(E_{k'}, E_k) \right] &= \left[\sum_{k'=1}^m c_n(E_k, E_{k'}) \right] \\ &\times \sum_{k=1}^m \exp\left(\frac{E_{tk} - E_{k'}}{kT}\right) \end{aligned} \quad (\text{F.5})$$

Substitution of Eq. (F.5) into Eq. (F.1) results in the following integral, similar to Ref. [2] for the single-level case.

$$\begin{aligned} U_n &= \int_{E_c}^{\infty} \left[1 - \sum_{k=1}^m \exp\left(\frac{E_{fk} - E_f(t)}{kT}\right) \right] \\ &\times \left[\sum_{k=1}^m N_{tk} (1 - f_k(E_{tk})) \right] \\ &\times \left[\sum_{k'=1}^m c_n(E_k, E_{k'}) \right] f(E_{k'}) N(E_{k'}) dE_{k'} \end{aligned} \quad (\text{F.6})$$

In the conduction band most of the carriers are near E_c and so $f_p(E_{k'})$ is nearly unity.

$$n(t) = \int_{E_c}^{\infty} N(E_{k'}) f(E_{k'}) dE_{k'} \quad (\text{F.7})$$

Together with the following equation expressing $n(t)$ using Fermi-Dirac statistics, an expression for N_c is derived Eq. (F.9a) as in Ref. [2] where $f(E_{k'})$ is written in terms of $f_p(E_{k'})$.

$$n(t) = N_c \exp\left(\frac{E_f(t) - E_c}{kT}\right) \quad (\text{F.8})$$

When the following substitutions are made together with the orthogonal relation Eq. (F.4) an average value for $c_n(E_k, E_{k'})$ is determined Eq. (F.9c). It is the average value that is measured experimentally.

$$N_c = \int_{E_c}^{\infty} \left[\exp\left(\frac{E_c - E_{k'}}{kT}\right) \right] N(E_{k'}) dE_{k'} \quad (\text{F.9a})$$

$$C_{nk} = \left\langle \sum_{k'=1}^m c_n(E_{k'}) \right\rangle \quad (\text{F.9b})$$

where

$$\begin{aligned} & \left\langle \sum_{k'=1}^m c_n(E_k, E_{k'}) \right\rangle \\ &= \frac{\int_{E_c}^{\infty} \left[\exp\left(\frac{E_c - E_{k'}}{kT}\right) \right] [\sum_{k'=1}^m c_n(E_k, E_{k'})] N(E_{k'}) dE_{k'}}{N_c} \end{aligned} \quad (\text{F.9c})$$

the resulting equation for the recombination rate U_n is as follows:

$$\begin{aligned} U_n &= \sum_{k=1}^m C_{nk} \left[1 - \exp\left(\frac{E_{tk} - E_f(t)}{kT}\right) \right] \\ &\quad \times N_{tk} [1 - f_k(E_{tk})] n(t) \end{aligned} \quad (\text{F.10})$$

This may be further refined such that with n_{1k} given by Eq. (4.4a):

$$\begin{aligned} U_n &= \sum_{k=1}^m [C_{nk} N_{tk} (1 - f_k(E_{tk})) n(t) \\ &\quad - C_{nk} N_{tk} f_k(E_{tk}) n_{1k}] \end{aligned} \quad (\text{F.11})$$

Similarly an expression for U_p may be derived with p_{1k} given by Eq. (4.4b):

$$\begin{aligned} U_p &= \sum_{k=1}^m [C_{pk} N_{tk} f_k(E_{tk}) p(t) \\ &\quad - C_{pk} N_{tk} (1 - f_k(E_{tk})) p_{1k}] \end{aligned} \quad (\text{F.12})$$

It may be shown that the equations (4.13) and (4.14) may be directly derived from Eq. (F.11) and Eq. (F.12). Note there is only one recombination rate. The summation of $N_{tk}\Delta f(E_{tk})$ over all discrete defect levels is equal to $\Delta p(t) - \Delta n(t)$ from the charge neutrality relation. From the charge neutrality relation one may write:

$$\left[\sum_{k=1}^m N_{tk} \frac{df(E_{tk})}{dt} \right] = U_n - U_p \quad (\text{F.13})$$

and from the orthogonality condition Eq. (F.4) for each k the following is established:

$$\left[N_{tk} \frac{df(E_{tk})}{dt} \right] = U_n|_k - U_p|_k \quad (\text{F.14})$$

where the following are defined to simplify the notation and do not indicate a level recombination rate:

$$\begin{aligned} U_n|_k &= C_n(k) N_{tk} (1 - f_k(E_{tk})) n(t) \\ &\quad - C_n(k) N_{tk} f(E_{tk}) n_{1k} \end{aligned} \quad (\text{F.15})$$

and:

$$\begin{aligned} U_p|_k &= C_p(k) N_{tk} f(E_{tk}) p(t) \\ &\quad - C_p(k) N_{tk} (1 - f_k(E_{tk})) p_{1k} \end{aligned} \quad (\text{F.16})$$

Appendix G

Evaluation of $\eta_{nk}(t_0)$ and $\eta_{pk}(t_0)$

For low injection $\eta_{nk}(t_0)$ and $\eta_{pk}(t_0)$, at $t_0 = 0^+$ are both zero. It remains to find a value for $\eta_{nk}(t_0)$ and $\eta_{pk}(t_0)$ at $t = t_{ik}$ for a k value. Firstly a relationship between the differential terms in Eqs. (4.28) and (4.29) is established and subsequently an expression for $\eta_{nk}(t_{ik})$ is developed. Secondly having determined an expression for $\eta_{nk}(t_{ik})$ in terms of the excess carrier concentration $\Delta n(0)$, a critical value of excess carrier concentration $\Delta n(0)_{critical}$ may be evaluated. This value represents the transition between the linear variation of fundamental frequency with excess carrier concentration and the non-linear variation. A requirement for the selection of $\eta_{nk}(t_{ik}) = \Delta f(t_{ik}) = \Delta n_{nm}(t_{ik})$ is found from the expression Eq. (4.24) with $\Delta p(0) = \Delta n(0)$ as follows.

$$\Delta p_{nm}(t_{ik}) = \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) \Delta n_{nm}(t_{ik}) \quad (G.1)$$

where for p-type:

$$\phi_k = \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) \quad (G.2)$$

and for n-type:

$$\phi_k = \left(1 - \frac{N_{tk}}{\Delta n(0)}\right) \quad (G.3)$$

In relation to p-type, equating coefficients on both sides of Eq. (G.1) and considering the first two components.

$$\begin{aligned} P_{10} &= \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) N_{10} \\ P_{01} &= \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) N_{01} \end{aligned} \quad (G.4)$$

Now, multiplying the first equation of Eqs. (G.4) by $\lambda_1 \exp(-\lambda_1 t_{ik})$ and the second equation by $\lambda_2 \exp(-\lambda_2 t_{ik})$ yields

$$\begin{aligned} P_{10} \lambda_1 e^{-\lambda_1 t_{ik}} &= \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) N_{10} \lambda_1 e^{-\lambda_1 t_{ik}} \\ P_{01} \lambda_2 e^{-\lambda_2 t_{ik}} &= \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) N_{01} \lambda_2 e^{-\lambda_2 t_{ik}} \end{aligned} \quad (G.5)$$

Summing the left hand side of Eq. (G.5) and equating that to the sum of the right hand side results in a relationship between the differentials as follows.

$$\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=t_{ik}} = \left(1 + \frac{N_{tk}}{\Delta n(0)}\right) \left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=t_{ik}} \quad (G.6)$$

Having established this relationship equations (4.28) and (4.29) may be solved for a given k for $\eta_n(t_{ik})$. The value of $\eta_p(t_{ik})$ is evaluated from Eq. (4.24).

$$\eta_{nk}(t_{ik}) = \frac{(\phi_k \alpha_{0k} - \beta_{0k}) - (\phi_k \gamma_{0k} - \phi_k^2 \sigma_{0k})}{\phi_k \Delta n(0) (1 - \phi_k) (C_{nk} + C_{pk})} \quad (G.7)$$

where α_{0k} , β_{0k} , γ_{0k} and σ_{0k} are given by Eq. (4.15). Solving the following quadratic resulting from equation (G.7) with $\Delta\eta_{nk}(t_{ik}) = 0$, corresponding to the linear region of variation of λ_{k+1} with $\Delta n(0)$, indicates the onset of the non-linear region. For $\Delta n(0) > 0$, the onset of the non-linear region is termed $\Delta n(0)_{critical}$. For p-type $\Delta n(0)_{critical}$ is evaluated from:

$$\begin{aligned} 0 &= \Delta n^2(0) ((\alpha_{0k} - \beta_{0k}) - (\gamma_{0k} - \sigma_{0k})) \\ &+ \Delta n(0) (N_{tk} \alpha_{0k} - N_{tk} \gamma_{0k} + 2N_{tk} \sigma_{0k}) \\ &+ N_{tk}^2 \sigma_{0k} \end{aligned} \quad (G.8)$$

and for n-type, $\Delta n(0)_{critical}$ is evaluated from:

$$\begin{aligned}
 0 = & -\Delta n^2(0) ((\alpha_{0k} - \beta_{0k}) - (\gamma_{0k} - \sigma_{0k})) \\
 & + \Delta n(0) (N_{tk}\alpha_{0k} - N_{tk}\gamma_{0k} + 2N_{tk}\sigma_{0k}) \\
 & + N_{tk}^2\sigma_{0k}
 \end{aligned} \tag{G.9}$$

Note also from Eqs. (4.19) and (G.2) the following may be established for t_{ik} :

$$t_{ik} = -\frac{1}{(\gamma_k - \sigma_k\phi_k)} \ln(\eta_{nk}(t_{ik})) \tag{G.10}$$

Appendix H

Differential Equations for Ground and Excited State System

Carrier transitions at the ground and excited states are described the recombination rates as follows:

$$N_t \frac{df_g(t)}{dt} = U_{ng} - U_{pg} + (U_{xg}^n - U_{gx}^n) - (U_{xg}^p - U_{gx}^p) \quad (\text{H.1a})$$

$$N_t \frac{df_x(t)}{dt} = U_{nx} - U_{px} + (U_{gx}^n - U_{xg}^n) - (U_{gx}^p - U_{xg}^p) \quad (\text{H.1b})$$

Expressions for $U_{ng} - U_{pg}$ and $U_{nx} - U_{px}$ may be derived similar to that for multiple levels in Appendix F. Due to the orthogonality relation in Section F only transitions between the ground and excited state need be considered. It remains to find expressions for $U_{xg}^n - U_{gx}^n$ and $U_{xg}^p - U_{gx}^p$ for the excited state and similarly for the ground state.

The recombination rate for holes at the excited state is the difference in the rate of hole capture and the rate of hole emission Eq. (H.1). A rate of hole capture from the ground state to the excited state may be expressed as being proportional to the number of holes at the ground level and the number of electrons at the excited

level. The constant of proportionality is C_{gx}^p . Similarly the rate of hole emission from the excited state to the ground state is proportional to the number of holes in the excited state and the number of electrons on the ground state. Again a constant of proportionality is e_{xg}^p Ref. [2].

$$\begin{aligned} U_{gx}^p - U_{xg}^p &= C_{gx}^p N_t (1 - f_g(t)) N_t f_x(t) \\ &\quad - e_{xg}^p N_t (1 - f_x(t)) N_t f_g(t) \end{aligned} \quad (\text{H.2})$$

At equilibrium the recombination rate U_{gx}^p is zero and $E_{fg}(0^-) = E_{fx}(0^-) = E_F$ where E_F is the equilibrium Fermi level. From equation (H.1) and equation (F.2) where in this case the k^{th} level is the excited state, the following may be established from the given equilibrium condition.

$$e_{xg}^p = C_{gx}^p \exp \left(-\frac{(E_x - E_{gnd})}{kT} \right) \quad (\text{H.3})$$

On substitution of Eq. (H.3) into Eq. (H.1) the recombination rate for holes at the excited state is given as:

$$\begin{aligned} U_{gx}^p - U_{xg}^p &= C_{gx}^p N_t^2 [(1 - f_g(t)) f_x(t) \\ &\quad - \exp \left(-\frac{(E_x - E_{gnd})}{kT} \right) (1 - f_x(t)) f_g(t)] \end{aligned} \quad (\text{H.4})$$

The recombination rate for electrons at the excited state is the difference in the rate of electron capture and the rate of electron emission Eq. (H.5). A rate of electron capture from the ground state to the excited state may be expressed as being proportional to the number of electrons at the ground level and the number of holes at the excited level. The constant of proportionality is C_{gx}^n . Similarly the rate of electron emission from the excited state to the ground state is proportional to the number of electrons in the excited state and the number of holes on the ground state. Again a constant of proportionality is e_{xg}^n .

$$\begin{aligned} U_{gx}^n - U_{xg}^n &= C_{gx}^n N_t f_g(t) N_t (1 - f_x(t)) \\ &\quad - e_{xg}^n N_t f_x(t) N_t (1 - f_g(t)) \end{aligned} \quad (\text{H.5})$$

At equilibrium the recombination rate $U_{gx}^n - U_{xg}^n$ is zero and $E_{fg}(0^-) = E_{fx}(0^-) = E_F$ where E_F is the equilibrium Fermi level. From Eq. (H.5) the following may be established from the given equilibrium condition.

$$e_{xg}^n = C_{gx}^n \exp\left(\frac{E_x - E_{gnd}}{kT}\right) \quad (\text{H.6})$$

On substitution of Eq. (H.6) into Eq. (H.5) the recombination rate for electrons at the excited state is given as:

$$\begin{aligned} U_{gx}^n - U_{xg}^n &= C_{gx}^n N_t^2 [(1 - f_x(t)) f_g(t) \\ &\quad - \exp\left(\frac{E_x - E_{gnd}}{kT}\right) (1 - f_g(t)) f_x(t)] \end{aligned} \quad (\text{H.7})$$

A similar analysis may be performed for the ground state. The rate of change of electron occupation at the excited state from the ground state may be expressed as.

$$\begin{aligned} N_t \frac{df_{gx}(t)}{dt} &= (U_{gx}^n - U_{xg}^n) - (U_{gx}^p - U_{xg}^p) \\ &= N_t^2 \left[- \left(C_{gx}^n \exp\left(\frac{E_x - E_{gnd}}{kT}\right) + C_{gx}^p \right) (1 - f_g(t)) f_x(t) \right. \\ &\quad \left. + \left(C_{gx}^n + C_{gx}^p \exp\left(-\frac{(E_x - E_{gnd})}{kT}\right) \right) (1 - f_x(t)) f_g(t) \right] \end{aligned} \quad (\text{H.8})$$

Similarly the rate of change of electron occupation at the ground state from the excited state may be expressed as.

$$\begin{aligned} N_t \frac{df_{xg}(t)}{dt} &= (U_{xg}^n - U_{gx}^n) - (U_{xg}^p - U_{gx}^p) \\ &= N_t^2 \left[\left(C_{xg}^n \exp\left(\frac{E_x - E_{gnd}}{kT}\right) + C_{xg}^p \right) (1 - f_g(t)) f_x(t) \right. \\ &\quad \left. - \left(C_{xg}^n + C_{xg}^p \exp\left(-\frac{(E_x - E_{gnd})}{kT}\right) \right) (1 - f_x(t)) f_g(t) \right] \end{aligned} \quad (\text{H.9})$$

Appendix I

Evaluation of $\eta_{ng}(t_0)$, $\eta_{pg}(t_0)$ and $\eta_{nx}(t_0)$, $\eta_{px}(t_0)$

For low injection $\eta_{ng}(t_0)$, $\eta_{pg}(t_0)$ and $\eta_{nx}(t_0)$, $\eta_{px}(t_0)$, at $t_0 = 0^+$ are both zero. It remains to find a value for $\eta_{ng}(t_0)$, $\eta_{pg}(t_0)$ and $\eta_{nx}(t_0)$, $\eta_{px}(t_0)$, at $t_0 > 0^+$. Following the derivation similar to Appendix G, the relevant expressions are given below.

For example for the ground state a requirement for the selection of $\eta_{ng}(t_{ig}) = \Delta f(t_{ig}) = \Delta n_{nm}(t_{ig})$ (p-type) is found from the charge neutrality relation Eq. (4.9) with $\Delta p(0) = \Delta n(0)$ as follows.

$$\Delta p_{nm}(t_{ig}) = \left(1 + \frac{N_t}{\Delta n(0)}\right) \Delta n_{nm}(t_{ik}) \quad (\text{I.1})$$

where for p-type:

$$\phi = \left(1 + \frac{N_t}{\Delta n(0)}\right) \quad (\text{I.2})$$

and for n-type:

$$\phi = \left(1 - \frac{N_t}{\Delta n(0)}\right) \quad (\text{I.3})$$

A relationship between the differentials is as follows:

$$\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t_0=t_{ig}} = \left(1 + \frac{N_t}{\Delta n(0)}\right) \left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t_0=t_{ig}} \quad (\text{I.4})$$

Having established this relationship equation (4.19) may be solved for $\eta_n(t_{ig})$. The value of $\eta_p(t_{ig})$ is evaluated from Eq. (4.20).

$$\eta_{ng}(t_{ig}) = \frac{(\phi\alpha_{0g} - \beta_{0g}) - (\phi\gamma_{0g} - \phi^2\sigma_{0g})}{\phi\Delta n(0)(1 - \phi)(C_{cg}^n + C_{vg}^p)} \quad (I.5)$$

where α_{0g} , β_{0g} , γ_{0g} and σ_{0g} are given by Eq. (4.15). Solving the following quadratic resulting from equation (I.5) with $\Delta\eta_{ng}(t_{ig}) = 0$, corresponding to the linear region of variation of λ with $\Delta n(0)$, indicates the onset of the non-linear region. For $\Delta n(0) > 0$, the onset of the non-linear region is termed $\Delta n(0)_{critical}$. For p-type $\Delta n(0)_{critical}$ is evaluated from:

$$\begin{aligned} 0 = & \Delta n^2(0) ((\alpha_{0g} - \beta_{0g}) - (\gamma_{0g} - \sigma_{0g})) \\ & + \Delta n(0) (N_t\alpha_{0g} - N_t\gamma_{0g} + 2N_t\sigma_{0g}) \\ & + N_t^2\sigma_{0g} \end{aligned} \quad (I.6)$$

and for n-type, $\Delta n(0)_{critical}$ is evaluated from:

$$\begin{aligned} 0 = & -\Delta n^2(0) ((\alpha_{0g} - \beta_{0g}) - (\gamma_{0g} - \sigma_{0g})) \\ & + \Delta n(0) (N_t\alpha_{0g} - N_t\gamma_{0g} + 2N_t\sigma_{0g}) \\ & + N_t^2\sigma_{0g} \end{aligned} \quad (I.7)$$

A similar analysis to the above may be made for the excited state.

Appendix J

Addendum: Referees' Reports and Author's Comments

J.1 Introduction

This thesis extends the work of Shockley, Read and Hall by presenting a detailed account of an exact solution to the single-level and multiple-level differential equations describing carrier transitions via defect levels in semiconductors. The predicted fundamental frequencies derived from this theory are independently verified by a multitransient analysis of the numerical solution of the differential equations. This provides a consistent theory or basis for experimental analysis and modeling. I believe the new theory may enhance our understanding of the effect of multiple levels in semiconductor devices and may even be used to identify defect species.

The respective referees' comments, in the following sections, of this Addendum are included in the present work in an effort by the author to bring into the discussion a balanced viewpoint. A few major points raised by the referees about the present work may require further investigation. The defect examples given in the thesis may be somewhat limiting. These examples are intended to reveal the salient features of the theory presented in the thesis. More future work is required to demonstrate the theory by exploring the complexity of defect species with a wider range of defect parameters. The experimental work may require significant development. In this respect, the theory may lead to the implementation of new techniques of multiple level measurement namely Fundamental Frequency Spectroscopy and, single-level measurement namely Analytic Lifetime Spectroscopy, described in this thesis. The thesis is heavily reliant on the mathematics underpinning the theory. This is because the physics of the carrier transitions via defect levels is described by nonlinear differential equations. The problem then becomes a mathematical one in terms of obtaining a general solution. These equations present a significant problem in terms of finding a general solution by virtue of their nonlinearity. This mathematical context may detract from the physics of the problem to the extent that the readability and comprehension of the theory can be demanding. A stronger effort to simplify the presentation of the theory may be required.

Nevertheless, it is my view that a large problem can be made more manageable by judiciously choosing smaller pieces of the puzzle and solving the related problems. The reader may note that there are three paths leading to the same series solution in the thesis. One is differentiation of an assumed solution, the second, integration which leads to a series solution and the third, multitransient analysis of the numerical solution of the differential equations, which confirms the predicted fundamental frequencies. Furthermore, the physics of a problem can lead to assumptions which simplify or reduce the complexity in terms of understanding the phenomena, but at the same time one has to quantify those assumptions. I believe this is best done by understanding the relationship between the quantities through a mathematical description so that the variables may be quantified. This may be said to be just common sense. However, just as the description of the physics can be misleading via assumptions, so too can the mathematics via approximations. In this event, several paths leading to the same solution provide a consistent means of understanding the problem, which in this case is a general solution without approximation to the multiple-level differential equations.

I would like to take the opportunity to thank the referees for their time and their constructive comments. I look forward to an extension of the work in the form of improvements in defect level measurement and refinement of the theory, presented in this work. NOTE: The referees' comments were transcribed from the photocopy of the original reports into latex text format.

regards Didier

J.2 Comments by Referee A

The main objective of this thesis to solve a mathematical problem that is at the heart of semiconductor physics, the complex dynamics of electrons and holes mediated by discrete defect levels within the energy band gap. It is an old problem and it has been investigated quite exhaustively. Yet, its general mathematical treatment has remained too difficult a task for most researchers. Mr. Debuf has demonstrated impressive mathematical skills and achieved the goal of obtaining analytical solutions.

Although I am impressed by the quality of the mathematical work, the thesis contains a serious misconception of the physical mechanism of minority carrier trapping that, in my opinion, should be precluded from being passed on to future scholars. I would rate this as a major correction, and recommend that it be properly addressed in an Addendum to the thesis. The reasons for this are given at the end of this report.

The main outcome of such an impressive amount of mathematical derivations seems to be that it is not possible to talk of a single carrier lifetime parameter, because the detailed theory predicts two time constants to characterise recombination via the SRH mechanism. This in itself is not new, but Mr. Debuf gives new and ample proof of it. Yet I have reservations about this result being of much practical significance. The concept of carrier lifetime has proven to be powerful enough to interpret experimental data and perform device modeling. The fact that it is in general an effective parameter that represents a host of physical mechanisms (with corresponding time constants) is well known. It is a fact that the lifetime varies in numerous and frequently unpredictable ways, and this in most cases is more important than the possible impact of there being two or more time constants. Nevertheless, the theoretical models in the thesis are powerful tools to study the complexities of recombination in semiconductors.

The thesis is mathematically overwhelming, but fails to be physically convincing. After reading it, one gets the impression that the physical understanding is inversely proportional to the mathematical sophistication. Compared to earlier work, which focused on the physics and used mathematics as a means towards clarifying them, this thesis achieves the opposite, with mathematics becoming an end. In some circumstances the thesis seems to try to bend the physics and so they conform to the mathematics.

The thesis purports that the physical models for carrier recombination that have so effectively allowed the progress of semiconductor technology of the last 50 years are wrong and should be replaced with new methods. Indeed, those physical models have approximations and limits of applicability and it is worth reminding experts in the field of that. Yet, to make the more accurate models acceptable would require a much more exhaustive study than is presented here. It is scientifically unacceptable to base such strong statements on just one case study of one specific defect level that happens to lead to a 30% discrepancy with the simplified SRH model. This case is used ad nauseam throughout the thesis (in chapters 2, 3 and 6), together with large chunks of text and other figures, which, incidentally, makes the thesis presentation quite awkward. Surely it should be possible to apply the theory to other cases, unless the computations are so time consuming that they can only be performed once or twice during a whole PhD research?

A serious assessment of the exact solutions in this thesis compared to the simpler models is lacking. It is obvious that the error depends on the specific parameters of the defects and that the simple models are perfectly adequate in many cases. A systematic study, perhaps similar to that of Rein (reference [46]), would be necessary to make the arguments of this thesis more convincing and clarify what their real significance is. As it stands, I am afraid that Chapter 3 is not a scientifically sound discussion of the accuracy of the SRH model. This chapter provides zero extra information compared to chapter 2. In page 46 it is said that the time constants (please refrain from using the word "decay" in steady-state situations, and amend also section 2.7 in this regard) in the steady-state case can be difference from those in the transient case. It would be good to show this by plotting both in the same graph, although it is possible that a different defect center may have to be chosen to reveal such difference.

Chapter 4 successfully tackles the still more complex problem of several defects simultaneously present. As shown in Fig. 4.1, the approach taken is that these defects are independent, that is transitions between themselves are not considered. Once again, the conclusions of the chapter ("it thus becomes imperative...", p. 77) are not substantiated by the study of just one example. It would have been interesting if the detailed model had been compared to the usual way in which multiple defects are dealt with, by adding the recombination rates (the inverse lifetimes) produced by each of those centers.

Chapter 5 contains the only experimental results in the thesis, showing the type of work that would be desirable to consolidate the models. It is a pity that only one wafer has been measured, because the diversity of situations that can be found in the physical world is enormous, and their study would have assisted to demonstrate the applicability of theoretical models and raise some interest among experimental researchers. As it stands, the comparison between theory and experiment presented in this chapter is not convincing, partially because this particular wafer shows practically no features of interest (the time constants are practically flat as a function of

excess carrier density, Fig. 5.1), and also because it is possible to fit almost anything to the experimental points, considering that there are so many free variables. In fact, the two defect properties attempted in Fig. 5.1 and 5.2 do a pretty good job at explaining the data, considering that there are extra reasons for the drop of τ at high carrier densities than those considered in the model. (Please choose a vertical axis that allows to see the real quality of the theoretical fit; ten orders of magnitude makes things look artificially close).

Instead of dismissing the IDLS and TDLS methods (in Chapter 6), the author should consider more carefully the work by Schmidt, Rein, Macdonald etc., to cite a few, showing that it is not possible to conclusively identify the properties of a defect using just one wafer (unless TDLS and IDLS are combined). The Analytical Lifetime Spectroscopy method proposed in Chapter 6 has, in my opinion, very little value in practice, because it relies on the knowledge of too many, usually unknown, parameters (density of defects, capture cross sections, etc.). This chapter does not explore in sufficient depth the TDLS and IDLS methods, certainly not enough to show their limitations (using again the same Fig. 6.4 as in chapters 2 and 3 seems a poor effort).

Finally, I come to the most important point of this report. There are not many instances in which the author ventures to discuss physics, but there is one (repeated too many times in the thesis by virtue of word processing, p.28, p.71, etc) where he explains the behaviour of the first time constant with excess carrier density in terms of carrier trapping. In my opinion, he shows a misconception of trapping effects, possibly due to the double meaning given to this word in early literature. In page 28, the author explains the behaviour of τ_1 shown in Fig. 2.2, in terms of "minority carrier trapping". He affirms that at very low carrier densities (the "linear region") there is recombination only, whereas beyond the critical carrier density both trapping and recombination are at work. In actual fact, it is the other way around; it is well documented that trapping effects are more important the lower the carrier density is. The "linear region" is actually where trapping effects are more significant, while the dynamics of carrier retention and release that occur in the "non linear region" are to be seen, in my opinion (and that of most researchers), as part of the normal statistics of SRH recombination.

I will use the author's statement in section 2.7 as an argument to support my interpretation. He concludes that "the reason for the discrepancy in the linear region is that in the paper of Shockley and Read the change in charge density produced by changing the (carrier) concentration in the traps is neglected". Indeed, that is so, and this is no other but the definition of minority carrier trapping, which is discernible because it alters the balance of charge between excess electrons and holes. So the difference between this thesis' model and SRH's is the inclusion of trapping effects, which results in the observed discrepancy in the linear region (and only there!). Hence it is the linear region that is affected by trapping, while the recombination only model of SRH is perfectly adequate to explain the rest of the curve.

I would like to encourage Mr. Debuf to read sections of the excellent book by Blakemore (reference below). I will paraphrase this book (p. 256): "What makes the problem so complicated is that the flaws indulge in both recombination and trapping...they behave primarily as recombination centers if, after capturing an electron...they capture a hole. On the other hand, the flaw is acting primarily as an electron trap if it more likely to return the electron to the conduction band". Additional clarifications are offered in p. 249: "...trapping effect, in the sense that the flaws produce a marked disparity between the excess of electrons and excess holes", and elsewhere in the book. I would also strongly recommend a correction of the author's distorted perception of the physics of trapping in the papers he has submitted for publication. A much stronger trapping effect than the 30% discrepancy observed by him is frequently found in many types of silicon wafers. Such strong trapping requires specific theoretical modeling, as discussed by Fan (ref. 6 of the thesis) and more comprehensively, by Hornbeck and Haynes. Reference to these authors is obliged for any person seriously interested in understanding trapping effects. I am almost certain that the author's model is capable of explaining strong trapping as well, simply by choosing the appropriate parameters for the defect level. What Hornbeck, Haynes, Fan, Blakemore and others point out is that such parameters would not lead to that defect being an effective recombination center, which leads to their models having at least two types of defect (or the same level having a dual role), one mainly for recombination, the other mainly a trapping center. I would also recommend consulting some recent papers by Macdonald given below. Of particular relevance is a paper in Phys. Rev. B that precisely discusses the limitations of the SRH model at low carrier densities, reaching very similar conclusions to this thesis, although with a simpler approach and clearer physics.

The relevant references are:

- J. S. Blakemore, *Semiconductor Statistics* (Pergamon Press, Oxford, 1962)
- J. A. Hornbeck and J. R. Haynes, *Phys. Rev.* **97**, 311 (1955)
- D. Macdonald and A. Cuevas, *Minority carrier trapping in multicrystalline silicon*, *Appl. Phys. Lett.* vol 74 (12), pp. 1710-1712 (1999)

- D. Macdonald and A. Cuevas, Validity of Shockley-Read-Hall statistics for modeling carrier lifetimes in silicon, Phys. Rev. B. vol 67, No 15 (II), p 075203 (2003)

Part C

After examination of the thesis I recommend that:

2. The thesis merits the award of the degree subject to minor corrections as listed being made to the satisfaction of the head of school.

NOTE: the word minor above was crossed out in favour of substantial.

J.3 Author's comment to Referee A

General comments:

- Section 2.6, Further Aspects of Trapping, was included to expand on the concept of trapping and encompass the more realistic situation of electron trapping, hole trapping, recombination and generation. In this section the rates of carrier capture and emission from the original SRH rate equations define the processes of electron trapping, hole trapping, recombination and generation by means of inequalities. These definitions indicate that the unique behaviour of τ_1 in both n-type and p-type semiconductor may be explained as corresponding to minority carrier trapping with increasing excess carrier concentration as discussed in Section 2.5, for the given example. However, the author feels that the theory presented in this thesis is applicable generally.
- With the fundamental frequencies either resolved from the measured decay or calculated from known defect parameters the multiple level defect species carrier transitions may be modeled exactly as they occur in the real world.
- The fundamental frequency $\lambda_1 = 1/\tau_1$ behaves in a unique way in both n-type and p-type semiconductor as opposed to the other fundamental frequencies λ_{k+1} . Referee A does not address this behaviour in the new theory. The author gives an explanation of the behaviour of τ_1 , which is the primary fundamental time constant.
- With the current effective lifetime theory significant multiple level transition information is lost as only a lumped effect is given. The new theory presents possibilities of more detailed defect species analysis by the concept of the fundamental frequencies which present more information on defect level parameters. This presents possibilities of new research such as ultra-pure semiconductors with a more detailed picture of multiple level effects.
- From Chapter 3 the expression for the original SRH single-level time constant Eq. (5.3) of [2] is shown to be incorrect. In effect this expression is strictly an inadequate description of the physics of carrier transitions for the single-level defect but more so for multiple level defects. Strictly, the concepts of minority carrier time constant and majority carrier time constant, in terms of Eq. 5.3 of Shockley and Read [2] often quoted in the literature, also inadequately describe the physics of minority carrier decay.

Specific comments:

- paragraph 6: Chapter 3 proves that the source of the error resulting in the single time constant expression Eq. (5.3) of [2], is the definition of recombination $U = \Delta n/\tau$. This definition is given in [2] without justification. In Chapter 2 there is no mention of the role played by this SRH recombination term. As a consequence of the new theory this SRH recombination term strictly has no physical meaning. Paragraph 3 of Section 3.1 was added to Chapter 3 to show this inaccuracy. An accurate recombination term derived in terms of fundamental frequencies of the new theory is given in Chapter 5. As indicated by Referee A, a graphical demonstration of the steady state and the transient solutions would clarify the distinction between the two solutions. Figure 3.3 was added to Chapter 3 to show the difference between the steady state solution and the transient solutions. Furthermore, the steady state defined in the original 1952 SRH paper by setting the recombination rates equal, $U_n = U_p$, suggests that the slopes of the variation of excess carrier concentration with time (see Eqs. (2.12) and (2.13)), may vary but steady state is maintained as long as they are equal. This implies "decay" and as I understand it is the principle behind the Quasi-Static technique of measurement.
- paragraph 7: Chapter 4 indicates that the fundamental time constants should be derived from the determinant of the matrix of the governing equations. This is further expanded in Chapters 4 and 6 on the accuracy of DLTS, which shows that the multiple level time constants are the roots of a polynomial. The frequencies of the exponential terms in the series solution are a linear combination of the fundamental frequencies. These frequencies become very large (very rapid time constant). By summing all the frequencies or inverse time constants, the overall inverse time constant may be taken to correspond to that of the shortest time constant (see Eq. (5.34) of Chapter 5). This would give an unrealistic value for this sum. Hence, the time constant for the overall carrier transitions cannot be modeled by the summation of the individual inverse time constants.

- paragraph 8: The Experimental work provides proof of concept in applying the new theory with given experimental constraints or boundary conditions to identify a particular defect species in CZ grown silicon. A paper has been accepted for publication (2003) in J. Appl. Phys.
- paragraph 9: The Analytical Lifetime Spectroscopy method presented in Chapter 6 has a significant advantage over the present Lifetime Spectroscopy method. The advantage is that variables resolved by multitransient analysis from the measured decay may be plotted against $1/kT$ to determine a single-level defect level depth without ambiguity. With Lifetime Spectroscopy from Figure 6.4 a plot (linear part) for a level in the lower half of the bandgap intersects that of a level in the upper half. Effectively the two level depths cannot be distinguished from one measurement technique. In effect two defect level depth measurement methods are required to identify, the level depth, and which half of the bandgap the level resides (see Rein et al [46]). It is clear from the graph of Figure 6.5 for Analytic Lifetime Spectroscopy that the level depth represented by the slope of the plots (linear part indicated by a level depth) does not have this ambiguity as there are no intersections. Only one measurement and one wafer is required to determine level depth making the procedure very straight forward and simple. This is a very practical outcome of the new theory. In Chapter 6, Section 6.3, paragraphs 4 and 5 were added to clarify the application of the new theory to a practical measurement technique namely DLTS. Here I include a new measurement method termed Fundamental Frequency Spectroscopy for resolving multiple defect level depths. This further enhances the application of the new theory to practical problems.
- paragraph 10. I agree that trapping effects may be more significant for device performance at low excess carrier concentrations. This part of the text is intended to explain the unique behaviour, of τ_1 of the new theory, with excess carrier concentration in both p-type and n-type semiconductor. I feel referee A has applied existing concepts of trapping usually applied in terms of an effective lifetime to explain the behaviour of τ_1 . In my view this is not appropriate as τ_1 is not the same as the effective lifetime although they appear to behave similarly with excess carrier concentration.
- paragraph 11. The 30% error in the linear region is not a trapping effect (see also response to paragraph 13). The new theory takes care of trapping and recombination over the whole range of excess carrier concentration below non-degenerate doping, so it is not necessary to think in terms of regions of trapping and regions of recombination. The new theory provides an analytic solution over this range of excess carrier concentration, arbitrary defect parameters and arbitrary uniform doping. However, as Referee A points out evaluation of the theory over such a range with an extensive set of example defect parameters, may be required to clearly demonstrate the application of the theory.
- paragraph 12. I agree that a center may act as both a recombination and trapping center.
- paragraph 13. Again the 30% error is not a trapping effect. It is the relative error between the SRH single time constant and the exact time constant τ_1 with excess carrier concentration derived from the new theory. This demonstrates graphically that the single SRH time constant expression is inaccurate and strictly interpretation of the physics of carrier transitions in terms of this expression is also incorrect. As referee A indicates earlier in paragraph 3 that for the single level there are in reality two time constants and the physics of trapping, recombination and generation should be investigated using the full set of time constants as in Section 2.6 of Chapter 2.

J.4 Comments by Referee B

Part A

1. Objective

The main objective of this work is the theoretical evaluation of the differential equations describing charge carrier recombination and trapping via defect centers in semiconductors. The result of this calculation is compared with the standard Shockley-Read-Hall (SRH) statistics which is normally used for the description of charge carrier recombination.

The relevance of the calculations is demonstrated on practical examples and a new evaluation scheme based on the theoretical calculations is presented.

The theoretical derivation of the carrier kinetics via single and multiple defect levels is on a very high level and shows the thorough working style of the author. Thus, the main objective of the work is fully met by the author. The very high standard of the calculations and theoretical analysis is rewarded in several publications in journals with a very high standard (Physical Review Letters).

Nevertheless, the demonstration of the practical relevance of the new model and its application to the experiment is not absolutely convincing.

2. Originality

The theoretical calculation and the new model of the author are very original, since the use of the standard SRH model is widespread usually without any critical questions about possible assumptions underlying the calculations. Thus, the author's work can have an important impact on the characterization of defect centers in semiconductors.

3. Presentation

The presentation of calculations and conclusions is clearly written and understandable. Nevertheless, since the calculation are on high mathematical level it would have been very good to keep the reader a bit more motivated by giving more insight in the practical importance of the new model.

Part B

1. Literature Review

The literature review is complete especially in the field of the theoretical background of carrier recombination in semiconductors.

2. Method

The methods chosen for the theoretical evaluation of the carrier kinetics and the comparison to the standard SRH model demonstrate the very high mathematical skills of the author. This excellent theoretical description of physical processes is reflected in the impressive publication list of the author. However, the analysis of the experimental results using the new model (chapter 5) is not absolutely convincing. While the principal experimental constraints (surface passivation,...) are discussed properly, the description of the practical determination of the physical values from the experimental curve is not appropriate. Only the result of the multi-exponential fit is shown (Fig.5.1) while the decay curve itself, the fit and especially the error bars of the determined values are missing. This weakens the conclusions drawn by the author concerning the defect type observed in the investigated sample.

3. Results and findings

The theoretical findings and results shown in this work are on a very high level. Since the description of carrier kinetics via defect levels in semiconductors is of great importance, they can be very significant. Nevertheless, the demonstration of this significance and the deviation which is

achieved if the standard SRH model is used for evaluating practical measurements is not demonstrated satisfactory.

4. Discussion of results

As said above, the discussion of the theoretical results is very comprehensive and thorough. In Chapter 6 the practical importance of his calculations for important experimental methods such as Deep-Level Transient Spectroscopy or Lifetime Spectroscopy is shown. Nevertheless, this discussion remains on a theoretical level although especially here it would have been extremely important to demonstrate the practical relevance by showing the deviation when applying the author's new model instead of the standard SRH theory to an experimental example.

5. Style

The writing style is very good and the virtual presentation is good.

Part C

After examination of the thesis I recommend that:

2. The thesis merits the award of the degree subject to minor corrections as listed being made to the satisfaction of the head of school.

Corrections:

Fig 6.5: The lifetimes are deceasing with increasing temperature. The opposite trend is observed in reality. The underlying calculation of this figure seems to be not correct.

J.5 Author's comment to Referee B

- Figure 6.4 was amended to reflect the correct slope of the linear portion of the plots in the graph.

specific comments

- part B 2. see author's response to Referee A, paragraph 9.
- part B 3 and 4. see author's response to Referee A, paragraph 9 and 13.

J.6 Comments by Referee C

Part A

A1 Objective

- A full analytical solution to the widely-used Shockley-Read-Hall (SRH) rate equations for carrier recombination through defects in semiconductors.
 - Transient and steady state illumination conditions;
 - single-level defect types;
 - multiple single-level defects
 - single multiple-level defect types;
- Numerical confirmation;
- Demonstration of error in original SRH theory;
- Impact on experimental time constant measurements and on deep level transient spectroscopy (DLTS).

The objectives were definitely achieved in a theoretical sense, although the real-world impact of the differences of the new theory from that which is in general use will need in the future, to be better demonstrated than in the present thesis. However, the extent of the theoretical development alone is easily adequate to justify the award of the degree.

A2 Originality

The work is highly original and some may think almost heretical in its challenge to experimental techniques so widespread and generally accepted and to the theory developed by scientists of such stature and repute as Shockley.

A3 Presentation

The subject matter is heavily reliant on mathematics and, consequently the thesis is very mathematical. I think the candidate should have made more effort, in an engineering thesis, to make the work more accessible to readers who have not lived and breathed SRH recombination theory for as many years as he has himself, particularly by greater use of explanatory diagrams, graphs and tables.

Part B

B(1) Literature Review

The literature referenced in the text is relevant and its coverage minimally adequate. There is a German language reference cited by [6] that is probably relevant to the early development and should have been included in the review. However, the reader is faced by a bewildering array of conditions, approximations and special cases for which approximate solutions have been found in the past. This could have been clarified somewhat by, for example, tabulation of prior theoretical work with clear labeling of whether transient or steady state conditions were assumed, type and number of defect types considered and the resulting expressions in each case. Consideration of such a table should help the reader quickly grasp the differences and agreements between the various results and how they relate to each other and to the candidate's results.

The sentence about Fan's work (pages 1 and 39) is confusing in that it speaks of two time constants "in terms of" three listed time constants. While this is not incorrect, it is also unclear and the reader deserves an explanation. Fan, in his equations 24, 25 does have two constants defined in terms of the three listed times. This thesis should either (1) detail how the two are defined in terms of the three or (2) simply say that Fan's work yielded two time constants, which is the important point here.

B(2) Method

This work uses highly appropriate methods to produce the first complete solutions to these equations that are of great technological importance. I hope the candidate will proceed to develop the practical application of his theory and demonstrate convincingly the sorts of cases in which it is important to consider his more comprehensive model in preference to the erroneous model in common sense.

I felt concerned about the strict conditions (negligible drift and diffusion) and whether they are compatible with the oft-repeated "without any approximation". However, those conditions are in the SRH derivation and are not additional conditions in the solution of the SRH equations.

B(3) Results and Findings

The project examines in great detail, from a mathematical and, to a lesser extent, a physical, point of view. It gives importantly and for the first time, a full analytical solution to the widely-used Shockley-Read-Hall (SRH) rate equations for carrier recombination through defects in semiconductors. Transient and steady-state solutions are given for single, single-level defect types; multiple single-level defects at different energy levels that each interact with the conduction and valence bands; and single multiple-level defect types whose energy levels each interact with each other and with the conduction and valence bands. The solutions are verified numerically.

An important aspect of the work is the confirmation that in the simplest case, for single, single-level defect, the solution of the SRH rate equations contains at least two time constants, not a single one as was rather arbitrarily proposed in the original SRH theory and is usually assumed by experimentalists and theorists today. That assumption occurs despite the several credible prior theoretical developments, cited in the thesis, that have shown the existence of a minimum of two time constants. The solution is an infinite series of terms whose decay rates are linear combinations of two fundamental time constants. The thesis shows that the solutions for the more complicated cases of multiple single-level defect types and single multiple-level defect types are similarly expressible as infinite series of terms whose decay rates are linear combinations of a known number of fundamental time constants.

The impact of the acceptance of the original SRH treatment on deep level transient spectroscopy (DLTS) is considered and a different method is proposed. Chapter 6 is about inaccuracies due to multiple defect levels so it is odd that the proposed new method is illustrated in Sect. 6.4 with a single level case.

The work is of great theoretical performance although its practical importance for experimentalists still needs to be better demonstrated.

B(4) Discussion of Results

The candidate has demonstrated a full understanding of the work but could probably have presented it in a form less challenging to the reader with greater use of tables and diagrams. These results are very important, theoretically and almost certainly also in the interpretation of at least some experimental results but the present method of analysis is deeply embedded and experimentalists will need to see a valid and convincing reason to adopt a change. Even the stimulation of further research will require the wide acceptance of the practical need for reconsideration of the currently accepted methods.

B(5) Style

I found the style rather confusing and presumptive of a greater familiarity of the reader with the details of the subject matter than is reasonable. A more tutorial and gentle treatment, written as if aimed at a less expert student, say, would have been preferable. Particularly in chapters 2, 4 use could have been made of dot points or, better, flow charts to clarify the solution methods. References could then be made in the text to such charts to help clarify the explanation.

The style of literature referencing in the thesis is novel and slightly irritating since it spoils the flow of sentences. If the names of authors are to be given then they should be included as parts of the sentences, not as if they were in parentheses but aren't. The Harvard referencing style would have been a preferable way to incorporate the authors' names.

Corrections:

There are a number of minor corrections or changes that could optionally be made:

- 1. The title page misses "Engineering" from the School name;
- 2. p. 5: the "thirty per cent error" refers only to some particular set of parameters;
- 3. p. 17: the rewriting of (2.20) with inclusion of given terms was obscure to me.
- 4. p. 18: The mathematical development is obscure and insufficient effort has been expended by the candidate to explain it clearly enough for this examiner to grasp it easily without significant study. For example, the connections of (2.25) to (2.23) and (2.26) to (2.24) are not obvious since terms in the later equations cannot be seen in the earlier. It would help if (2.23) and (2.24) were rewritten with g^n and g^p included.
- 5. p 55: It is unclear whether the presented work is a whole new mathematical method for solution of differential equations or just the application of a known method to this particular problem. This must be clarified. A flowchart would be helpful.
- 6. p. 71, line 2: I don't see that Fig. 4.4 compares numerical and analytical results as the text implies it does.
- 7. p.77: Is a 10% error serious ?
- 8. Eq.(5.6): It is confusing that u is used here, with unspecified meaning, while u was used in Eq. (5.4) and previously as an index;
- 9. p.90: The absorption coefficient seems to affect both the coefficients and the decay rates in Eqs. (5.31), (5.32) but the text states that it only affects the magnitudes;
- 10. p91/92: Text implies a single characteristic time constant but one point of the thesis is that there are more than one;
- 11. p 102: It is not the polarity of the pulse that reduces the layer width;
- 12. p 126: Is the existing SRH method adequate for comparisons on samples anyway even though it is erroneous ?

Part C

After examination of the thesis I recommend that:

2. The thesis merits the award of the degree subject to minor corrections as listed being made to the satisfaction of the head of school.

J.7 Author's comment to Referee C

general comment

- Referee C would like to see more practical application of the new theory and in this context my response to Referee A paragraph 9 may satisfy this requirement.

optional corrections

1. The word Engineering was added to the school title
2. Although the theory allows for the evaluation of the fundamental time constants for arbitrary defect level parameters and subsequent assessment of the error, this was not extensively demonstrated in the thesis.
3. The reference [4] is given and expansion of the equations in this reference with Eqs. (2.15) and (2.18) results in Eq. (2.20). This is straight forward and inclusion of the working is not thought to be warranted.
4. The differential rate equations for the single level and the multiple levels are scaled as indicated in the text. This is a standard method of solution developed in the 1960's although independently developed by the author for this problem. A reference is cited [32]. The scaling allows all variables to be compared on the same basis. The method of solution relies on making the non-linear component of the differential equations go to zero at a particular time t_0 . At this point in time the equations in the matrix only contain terms in λ_{k+1} and there are exactly $k + 1$ equations. Hence, all the fundamental frequencies λ_{k+1} may be evaluated from the simultaneous equations. The λ_{k+1} are independent of time. Since the equations are normalised or scaled the magnitude of the coefficient, of the highest degree term in the resulting polynomial, is unity. This effectively reduces the number of variables to be solved for by one and allows the solution for λ_{k+1} to be found. Equally, the solution may be assumed and substituted into the differential equations, which results in the infinite series. Furthermore, the multi-transient analysis of the numerical solution confirms the existence of the same time constants in the decay as that predicted by the theory.
6. This line was removed from the text
7. The 10% error is Further expanded in Chapter 6. Here the theory is applied to the existing DLTS measurement technique, which is shown to yield discrepancies in level depth measurement for the multiple level case.
8. Unfortunately I discovered a problem with the consistent use of so many symbols throughout the thesis. Being limited with alphabetic symbols I set u to mean a symbol and a function, with the function differentiated from the symbol by the brackets.
9. The absorption coefficient α_λ occurs in an exponent which does not have a time variable t . Hence, this exponential term is a constant and applies directly to the magnitude not the exponential terms with a time variable t .
10. Luke and Cheng [28] refer to modes of decay, which become apparent in the development of their solution. These modes of decay are in addition to the fundamental frequencies determined in this work. The modes are only significant for the surface recombination velocity $S \gg 0$ ie. a poorly passivated surface.
11. The sentence containing the word polarity was clarified to indicate that forward bias reduces the depletion layer width and reverse bias extends the depletion layer width.
12. The existing method may be adequate for comparison in a relative sense. However, in an absolute sense it is not adequate. Furthermore, the existing SRH theory cannot adequately predict or model behaviour of carrier dynamics via multiple defect states, which exists in the real world. The fact is that the original SRH theory is not designed for multiple levels and so does not strictly apply to the real world. Why is it that a high effective lifetime wafer does not necessarily produce a highly efficient solar cell? The new theory encompasses a significant aspect of the theory of carrier transitions via multiple levels for what may be said to be arbitrary defect level parameters and uniform doping. This may lead to resolving such issues as raised by the above question.

Appendix K

Publications List

K.1 Publications in Refereed Journals

- General analytic solution to the Shockley-Read-Hall rate equations with a single-level defect

Didier Debuf, Yash Shrivastava and Alec Dunn

Phys. Rev. B volume **65**, article number 245211, June 19 (2002)

- Multiple level defect species evaluation from average carrier decay

Didier Debuf

accepted for publication J. Appl. Phys. (2003)

General analytic solution to the Shockley-Read-Hall rate equations with a single-level defect

Didier Debuf*

Centre for Photovoltaic Engineering, The University of New South Wales, Sydney, New South Wales 2052, Australia

Yash Shrivastava†

School of Electrical and Information Engineering, The University of Sydney, Sydney, New South Wales 2006, Australia

Alec Dunn

9/16 Vimiera Road, Eastwood, New South Wales 2122, Australia

(Received 21 August 2001; revised manuscript received 22 January 2002; published 19 June 2002; publisher error corrected 26 June 2002)

The decay of excess carriers in nondegenerate semiconductors generated by a light impulse $\delta(t)$ is governed by the differential equations referred to as the Shockley-Read-Hall (SRH) rate equations. In the past, linear approximations were used or restrictive conditions imposed to obtain an analytical solution limited to low or high injection. For defect level parameters of practical interest, the nonlinear differential equations were numerically solved. Whereas carrier decay is often approximated by one time constant τ , in the present paper it is shown that recombination occurs with both the minority (τ_1) and majority (τ_2) time constants present in the decay. Expressions for τ_1 and τ_2 are derived without an approximation at a given temperature, for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$, and energy level E_t . A general analytic solution to the SRH rate equations represented by an infinite series of monoexponential terms, the frequencies or inverse time constants of which are a linear combination of the fundamental frequencies $\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$, is derived without an approximation. The solution is the sum of the responses to an infinite number of linear systems and in this sense represents the impulse response. A critical point representing the transition between the linear and nonlinear variation of fundamental frequency with excess carrier density is identified. The analytic solution is verified by analyzing the numerical solution of the SRH rate equations for the fundamental frequencies using a multitransient technique. The trapping behavior of the minority carrier at a single-level defect, with excess carrier concentration, is examined.

DOI: 10.1103/PhysRevB.65.245211

PACS number(s): 72.20.Jv

I. INTRODUCTION

The basic concepts of the recombination of excess carriers in semiconductors via a defect level within the band gap were developed in the 1950s. The Shockley-Read-Hall (SRH) rate equations,^{1,2} describe the evolution with time of recombination, capture and emission of excess carriers via a single defect energy level in the band gap of a semiconductor. Analyses of the recombination process were based primarily on numerical solutions of the differential equations, with analytic solutions provided in some limiting cases such as low or high excess carrier concentration³. Using linear approximations of the Shockley-Read-Hall rate equations, it has been shown that, for a single-level defect, there are two fundamental time constants, the inverse of which are referred to as the fundamental frequencies. These two time constants appear in steady-state conditions¹ with an approximation, as well as in transient carrier decay situations^{4,5} also with an approximation.

The equation describing the time evolution of the normalized excess electron concentration $\Delta n_{nm}(t)$ is a second-order nonlinear differential equation and has a cubic power of $\Delta n_{nm}(t)$.³ We expect at least two time constants in the solution (the eigenvalues of the linear system) as the differential equation is second order. However the existing interpretation of experimental data relies on one time constant τ_{ss} (steady-state case) or τ_b (bulk decay, transient case). This implies a first-order differential equation. While this situation may be

sufficient as an approximation, it lacks the provision for predicting behavior and a unified approach to interpretation. For example, with regard to the effect of a defect energy level in bulk silicon or in low-dimensional structures, a consistent theoretical basis is required.

While the above findings were based on linear approximations of the underlying rate equations, in the present paper we derive a solution to the rate equations to obtain the time-dependent response to a light impulse $\delta(t)$ without an approximation. Our analytical solution shows that the entire decay curve consists of an infinity of monoexponential terms and that all inverse time constants or frequencies are a linear combination of the two fundamental frequencies. One expression for the minority (τ_1) and one expression for the majority (τ_2) carrier decay time constant is derived without an approximation at a given temperature for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$, and energy level E_t . A critical point representing the transition between the linear and nonlinear variation of excess carrier density with fundamental frequency is identified. This has not been previously given (see Refs. 4 and 5) with the result that the linear approximations above were difficult to apply in practice. The theory presented addresses the whole decay process from $0^+ < t < \infty$ as the excess carrier decay is expressed by a sum of monoexponential terms with coefficients and time constants calculated from the above parameters. As such the sum of exponentials is nonlinear. However each monoexpo-

nential term is the response to a linear system and the series represents the sum of the responses to an infinite sum of linear systems. Hence in this sense, the derived solution represents the impulse response. To our knowledge the impulse response of the SRH rate equations for the transient case has not been derived for low through to high injection, and presents a unified approach to the analysis of the single-level defect. As the present work extends the theory of the original SRH papers of 1952 which describe a simple case of uniform excess carrier concentration and a single level, it is intended to provide a clear theoretical basis for further work.

To verify the theory the present work contains a numerical solution of the SRH rate equations, which is analyzed by a multitransient analysis method for the component exponentials. This analysis of the numerical simulation confirms time constants predicted by the theory presented. We provide a consistent solution to the differential equations, with supporting evidence being the multitransient analysis of the numerical solution. Notwithstanding this, provision for the experimental position is also given. This work extends that of Streetman⁴ and Sandiford⁵ for the transient case, and Shockley and Read¹ for the steady-state case, by providing an analytical solution from low through to high injection. Note also that the SRH rate equations are valid for the nondegenerate statistics, which indicates the high injection level limit.⁶ Further work seeks to address the multilevel and interface or surface effects in terms of the analytical solution to the SRH rate equations.

For practical device operation the effect of defect levels at the surface or interface is minimized by passivation, which limits the concentration of such energy levels. As a result the bulk levels may have a significant impact on device operation such as solar cell efficiency and stable field effect transistor threshold voltage. However device operation occurs under varying injection levels from low through to high injection. Hence the requirement to model the effect of defects accurately and under varying conditions. Minority-carrier decay is usually modeled by one time constant τ_b (representing bulk recombination, which is approached asymptotically for $t \gg \tau_b$), derived from the simplified carrier continuity equations incorporating the law of mass action. Sah⁷ points out that the law of mass action is valid for the equilibrium situation.

The linear approximation referred to above infers low excess carrier concentration in relation to the equilibrium majority carrier concentration, for which approximate time constant expressions are deemed to apply¹ depending on defect level concentration N_t . An experimental restriction of low excess carrier concentration is often imposed to facilitate interpretation of the data using the approximations in order to determine defect level parameters such as cross sections, energy level, and concentration. In addition to the approximate expressions, the transition to high injection, where a different expression applies for the given sample, is not known. It is shown that for the transient case, whereas at high injection τ_1 is adequate for modeling recombination, at low injection τ_2 is also required as the magnitude of the coefficient can be significant. For the steady state, at low injection the frequencies are the same as the transient case although the coeffi-

cients may be markedly different and, furthermore, the coefficient for the τ_2 term may be significant.

The paper is organized as follows. Section II demonstrates the solution to a nonlinear differential equation represented by a quadratic. In effect the SRH rate equations have a quadratic form and the example given is intended to illustrate the infinite series of monoexponential terms in the solution, the bounds of the solution, and, in particular, the nonlinear nature of the solution. Two approaches to obtaining the indicated solution demonstrate a consistency in its derivation. This is further expanded in a more rigorous approach in Sec. IV. However the eigenvalues λ_1 and λ_2 of the linear solution to the SRH rate equations are first determined in Sec. III. The fundamental frequencies λ_1 and λ_2 are derived isothermally for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$ and energy level E_t . An excess electron concentration $\Delta n(t)$ and hole concentration $\Delta p(t)$ is assumed to be uniformly generated throughout the wafer thickness at $t=0^+$. It is shown that the nonlinear terms in the rate equations for $\Delta n(t)$ and $\Delta p(t)$ go to zero at $t=0^+$ or at some time $t=t_i$, where $t_i > 0^+$. The resulting linear differential equations may be solved at $t=0^+$ or $t=t_i$ for the two fundamental frequencies λ_1 and λ_2 . In Sec. IV, the response to a light impulse $N_o \delta(t)$ is determined for a p -type semiconductor with a single-level defect, including the effect of arbitrary injection level $\Delta n(0)=N_o$. Having obtained the fundamental time constants, a general solution for $\Delta n(t)$ and $\Delta p(t)$, represented by the impulse response as stated above, is found from the nonlinear rate equations being expressed in integral form. Section V contains a multitransient analysis of the numerical solution to determine the component exponentials in the sum of exponentials. The agreement of the predictions of the analytic solution with the results of the multitransient analysis of the numerical solution is very good. Also the theory indicates calculated magnitudes in agreement with those derived from the numerical analysis. In particular, the linear combination of fundamental frequencies in the exponents predicted by the analytic solution and the variation of the time constants $\tau_1=1/\lambda_1$ and $\tau_2=1/\lambda_2$ with injection level indicate close agreement. An indication of recombination only and of trapping is discussed. Section VI indicates the proposed experimental conditions for determining the time constants τ_1 and τ_2 and the onset of minority-carrier trapping is indicated. Note that the defect level concentration is assumed to be uniformly distributed throughout the silicon sample.

II. NONLINEAR RATE EQUATION WITH SERIES SOLUTION

The processes of capture and emission of carriers from a defect level and recombination and trapping via a defect level are governed by the SRH rate equations. These processes determine the average lifetime of minority carriers and hence device characteristics. As stated in the Introduction, current methods of analysis to determine defect level parameters are approximate in nature. Despite the probability that many defect levels may be present in a given semicon-

ductor sample, an effective lifetime τ_e is often evaluated as if they may be represented by one dominant level. A major contribution of the current work is the derivation of a general analytic solution to the SRH rate equations for a single-level defect in order to provide a basis for future work.

It is shown in Ref. 3 that the SRH equations can be represented by a second-order nonlinear dynamical system. Further as discussed in Sec. IV the nonlinearity is quadratic in nature. Derivation of a general analytic solution for such a system is quite tedious and involved (as is demonstrated in later sections). However, the fundamental concepts involved in such a solution are very simple. The main aim of this section is to illustrate these concepts through a simple first-order example. Towards this end, consider the following first-order nonlinear dynamical system:

$$\frac{dn(t)}{dt} = N_1 n(t) + N_2 n^2(t) \quad (1)$$

Note the nonlinearity due to a quadratic term. In fact when $N_2 = 0$ the system is linear and has the usual solution $n(t) = n(0)\exp(N_1 t)$. When $N_2 \neq 0$ the system has two equilibrium points 0 and $-N_1/N_2$. It is an easy matter (by linearizing the system about the equilibrium points) to show that for $N_1 < 0$, 0 is a stable equilibrium point and $-N_1/N_2$ is an unstable equilibrium point. Further the domain of attraction of the stable equilibrium point 0 is rather large. Any trajectory starting from an initial condition in the range $-\infty < n(0) < -N_1/N_2$ for $N_2 > 0$ and in the range $-N_1/N_2 < n(0) < \infty$ for $N_2 < 0$ converges to this equilibrium point. From a mathematical standpoint, trajectories outside this domain of attraction can be shown to diverge to infinity. From a physical standpoint the effect of the nonlinearity for an initial condition, starting inside the stated ranges and given an appropriate value of N_2 , may enhance generation of minority carriers corresponding to the impurity photovoltaic effect.⁸ This effect indicates an improved infrared response of solar cells by the addition of defect levels such as produced by indium. The effect is not evaluated in the present work.

Suppose that we have an initial condition that lies within the domain of attraction. Then what is the exact nature of the solution? A solution to the linearized system would suggest that $n(t) = n(0)\exp(N_1 t)$ and indeed it is a good approximation if $n(0)$ is sufficiently small. However, for large $n(0)$ we need to take the nonlinear nature of the system into account. Because of the quadratic nature of the nonlinearity, it is possible to integrate the system (1) exactly to arrive at

$$n(t) = \frac{N_1 n(0) e^{N_1 t}}{[N_1 + N_2 n(0)] - N_2 n(0) e^{N_1 t}} \quad (2)$$

Another method to obtain the above solution is the following that highlights certain points. A solution to the linearized system suggests that we should try solutions of the form $n(t) = n(0)\exp(N_1 t)$. However when we substitute this into Eq. (1), a term involving $\exp(2N_1 t)$ is generated on the right-hand side. This suggests that we should try solutions of the

form $n(t) = n_1 \exp(N_1 t) + n_2 \exp(2N_1 t)$. Proceeding in this way a possible solution takes the form

$$n(t) = n_1 e^{N_1 t} + n_2 e^{2N_1 t} + n_3 e^{3N_1 t} + n_4 e^{4N_1 t} + \dots, \quad (3)$$

where

$$\frac{dn(t)}{dt} = n_1 N_1 e^{N_1 t} + n_2 2N_1 e^{2N_1 t} + n_3 3N_1 e^{3N_1 t} + \dots \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (1) and noting that $\exp(N_1 t)$, $\exp(2N_1 t)$, $\dots$ are linearly independent functions, the equality in Eq. (1) can only be achieved when the coefficients on both sides of the equation match. Solving for the n_k , where $k = 1, 2, 3, \dots$, a geometric series results:

$$\begin{aligned} n(t) &= n_1 e^{N_1 t} + \frac{N_2}{N_1} n_1^2 e^{2N_1 t} + \left(\frac{N_2}{N_1}\right)^2 n_1^3 e^{3N_1 t} + \dots \\ &= \frac{n_1 e^{N_1 t}}{1 - \frac{N_2}{N_1} n_1 e^{N_1 t}}. \end{aligned} \quad (5)$$

Using the initial condition

$$n(0) = \frac{n_1}{1 - \frac{N_2}{N_1} n_1} \quad (6)$$

results in the following, which is equivalent to Eq. (2) that was obtained by direct integration:

$$n_1 = \frac{N_1 n(0)}{N_1 + N_2 n(0)}. \quad (7)$$

So despite their differences both methods lead to the same solution. It is essentially the first method that we use to obtain the general solution of the SRH rate equations. However it is shown that this leads to equivalent expressions when equating coefficients as derived from the assumption of the solution being a series of exponential terms (second method). Note that if Eq. (1) is modified to include a constant term N_0 on the right side, then for initial conditions in the domain of attraction, the trajectories reach a nonzero steady-state value. This can easily be accommodated in the second method by including a constant term n_0 on the right side of Eq. (3).

A few salient points in the above development should be noted. These are also true for our general solution developed in Sec. IV. A solution to the linearized system is a good approximation only for initial conditions that are sufficiently close to the equilibrium point. Following the second method, within the domain of attraction the general solution is a linear combination of what could be said to be an infinity of exponential terms. Further, the frequencies of these exponential terms are integer multiples of a fundamental frequency (in the above example they are multiples of N_1). Finally the fundamental frequency is associated with the linearized system. In the following section it is shown that there are two

fundamental frequencies for the single-level defect system associated with the linear solution of the SRH rate equations.

III. DERIVATION OF λ_1 AND λ_2 FOR ARBITRARY INJECTION LEVEL

Neglecting the effect of excited states of a defect energy level, Auger recombination, and radiative recombination, the carrier continuity equations for the one-dimensional case are given as follows:

$$\frac{dn(x,t)}{dt} = G_n - U_n + \frac{dJ_n}{dx}, \quad (8)$$

$$\frac{dp(x,t)}{dt} = G_p - U_p + \frac{dJ_p}{dx} \quad (9)$$

with $n(x,t)$ and $p(x,t)$ being the electron and hole concentrations having a time t and a spatial x dependence. $G_{n,p}$ is the generation rate, $U_{n,p}$ is the recombination rate, and $J_{n,p}$ is the current density given by, respectively,

$$J_n = q\mu_n n(x,t)\xi + qD_n \frac{\partial n(x,t)}{\partial x}, \quad (10)$$

$$J_p = q\mu_p p(x,t)\xi - qD_p \frac{\partial p(x,t)}{\partial x}. \quad (11)$$

Simplifications are made such that the generation rate $G_{n,p}$, diffusion components $qD_n dn(x,t)/dx$ and $qD_p dp(x,t)/dx$, and the electric field ξ are considered negligible. Hence the continuity equations simplify to

$$\frac{dn(t)}{dt} = -U_n, \quad (12)$$

$$\frac{dp(t)}{dt} = -U_p. \quad (13)$$

Note that n and p do not depend on x . The excess electron concentration $\Delta n(t)$ and the excess hole concentration $\Delta p(t)$ are written in terms of normalized excess carrier concentrations $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$, respectively. Note $\Delta n_{nm}(0^+) = 1$ and $\Delta p_{nm}(0^+) = 1$,

$$\Delta n_{nm}(t) = \frac{\Delta n(t)}{\Delta n(0)}, \quad (14a)$$

$$\Delta p_{nm}(t) = \frac{\Delta p(t)}{\Delta p(0)}. \quad (14b)$$

The defect level electron concentration $N_t f(t)$ is written in terms of the departure from equilibrium $N_t \Delta f(t)$ and the equilibrium concentration $N_t f_o$. As such the electron and hole concentrations and the defect level concentration may be written as follows, respectively, with N_t being the defect level concentration:

$$n(t) = \Delta n_{nm}(t)\Delta n(0) + n_{po}, \quad (15a)$$

$$p(t) = \Delta p_{nm}(t)\Delta p(0) + p_{po}, \quad (15b)$$

$$N_t f(t) = N_t \Delta f(t) + N_t f_o \quad (15c)$$

with the corresponding equilibrium concentrations n_{po} and p_{po} and where at equilibrium the electron occupancy of the defect level is $f_o = f(0^-)$ given in terms of p_{po} by

$$f_o = \frac{p_1}{p_{po} + p_1} \quad (16a)$$

and in terms of n_{po} by

$$f_o = \frac{n_{po}}{n_{po} + n_1}, \quad (16b)$$

with

$$n_1 = N_c \exp\left[-\left(\frac{E_c - E_t}{kT}\right)\right], \quad (17a)$$

$$p_1 = N_v \exp\left[-\left(\frac{E_t - E_v}{kT}\right)\right]. \quad (17b)$$

A charge neutrality relation indicates the conservation of charge with time,

$$\Delta p_{nm}(t)\Delta p(0) = \Delta n_{nm}(t)\Delta n(0) + N_t \Delta f(t). \quad (18)$$

$N_t \Delta f(t)$ may be written as $\Delta n_t(t)$ with $\Delta n_t(t)$ being the defect level excess electron concentration. By rewriting the charge neutrality relation with $\Delta n(0) = \Delta p(0)$, the valence, conduction and defect level electron concentrations may be directly compared, since the three quantities are normalized to one injection level $\Delta n(0)$,

$$\Delta p_{nm}(t) = \Delta n_{nm}(t) + \frac{\Delta n_t(t)}{\Delta n(0)}. \quad (19)$$

From Eqs. (15) and (18) the SRH rate equations³ may be written in normalized form as

$$\begin{aligned} -\frac{d\Delta n_{nm}(t)}{dt} &= \gamma_0 \Delta n_{nm}(t) - \sigma_0 \Delta p_{nm}(t) \\ &\quad - C_n [\Delta p_{nm} \Delta p(0) - \Delta n_{nm} \Delta n(0)] \Delta n_{nm}(t), \end{aligned} \quad (20)$$

$$\begin{aligned} -\frac{d\Delta p_{nm}(t)}{dt} &= \alpha_0 \Delta p_{nm}(t) + \beta_0 \Delta n_{nm}(t) \\ &\quad + C_p [\Delta p_{nm} \Delta p(0) - \Delta n_{nm} \Delta n(0)] \Delta p_{nm}(t), \end{aligned} \quad (21)$$

where

$$\alpha_0 = C_p N_t \left\{ \frac{p_1}{p_{po} + p_1} + \frac{p_{po} + p_1}{N_t} \right\}, \quad (22a)$$

$$\beta_0 = C_p N_t \left\{ \frac{p_{po} + p_1}{N_t} \right\}, \quad (22b)$$

$$\gamma_0 = C_n N_t \left\{ \frac{n_1}{n_{po} + n_1} + \frac{n_{po} + n_1}{N_t} \right\}, \quad (22c)$$

$$\sigma_0 = C_n N_t \left\{ \frac{n_{po} + n_1}{N_t} \right\} \quad (22d)$$

with $C_n = v_{thn} \sigma_n$ and $C_p = v_{thp} \sigma_p$ being the capture coefficients for electrons and holes, respectively.

By extending the work of Streetman⁴ and Sandiford⁵ to cover the wider range of injection levels from low through to high injection, the rate equations are rewritten so as to make the nonlinear terms go to zero at some time t . To do this, the differential equation (20) may be written with the inclusion of $-\eta_n(t) C_n \Delta n^2(0) \Delta n_{nm}(t)$ and $+\eta_n(t) C_n \Delta n^2(0) \Delta n_{nm}(t)$ for the minority carrier, and $-\eta_n(t) C_n \Delta n^2(0) \Delta p_{nm}(t)$ and $+\eta_n(t) C_n \Delta n^2(0) \Delta p_{nm}(t)$ for the majority carrier, where $\eta_n(t) = \Delta f(t)$. Inclusion of the $\eta_n(t)$ terms above in Eq. (20) and a corresponding set of terms in $\eta_p(t)$ into Eq. (21) is a construction which allows the application of the boundary conditions to evaluate the nonlinear terms in both equations and determine the precise time at which the equations become linear. If the resulting Eqs. (23) and (24) are multiplied out, the $\eta_n(t)$ and $\eta_p(t)$ terms cancel, reducing to Eqs. (20) and (21), respectively. Effectively the equations are unchanged by inclusion of the above terms,

$$\begin{aligned} & - \frac{d\Delta n_{nm}(t)}{dt} \\ & = C_n N_t \left[\Delta n_{nm}(t) \left(\frac{n_{po} + n_1}{N_t} + \frac{n_1}{n_{po} + n_1} + \frac{\eta_n(t) \Delta n(0)}{N_t} \right) \right. \\ & \quad - \Delta p_{nm}(t) \left(\frac{(n_{po} + n_1)}{N_t} + \frac{\eta_n(t) \Delta p(0)}{N_t} \right) \\ & \quad + \frac{1}{N_t} [\Delta n_{nm}(t) \Delta n(0) - \Delta p_{nm}(t) \Delta p(0)] \\ & \quad \left. \times [\Delta n_{nm}(t) - \eta_n(t)] \right]. \end{aligned} \quad (23)$$

Similarly for Eq. (21), substitutions of a corresponding set of terms containing $\eta_p(t)$ result in Eq. (24):

$$\begin{aligned} & - \frac{d\Delta p_{nm}(t)}{dt} = C_p N_t \left[\Delta p_{nm}(t) \left(\frac{p_{po} + p_1}{N_t} + \frac{p_1}{p_{po} + p_1} \right. \right. \\ & \quad + \frac{\eta_p(t) \Delta p(0)}{N_t} \left. \right) - \Delta n_{nm}(t) \left(\frac{(p_{po} + p_1)}{N_t} \right. \\ & \quad + \frac{\eta_p(t) \Delta n(0)}{N_t} \left. \right) + \frac{1}{N_t} [\Delta p_{nm}(t) \Delta p(0) \\ & \quad - \Delta n_{nm}(t) \Delta n(0)] [\Delta p_{nm}(t) - \eta_p(t)] \left. \right]. \end{aligned} \quad (24)$$

Using the charge neutrality relation with $\eta_n(t) = \Delta f(t)$, the nonlinear term in Eq. (23) referred to as $g^n(t)$ may be written as follows:

$$g^n(t) = -[\Delta n_{nm}(t) - \eta_n(t)] \eta_n(t). \quad (25)$$

From Eq. (25) two cases exist for the nonlinear function $g^n(t)$ to vanish at a certain time t_0 . Either $\Delta n_{nm}(t_0) - \eta_n(t_0) > 0$ and $\eta_n(t_0) = 0$, or $\Delta n_{nm}(t_0) - \eta_n(t_0) = 0$ and $\eta_n(t_0) > 0$.

The first case is satisfied at $t_0 = 0^+$ as $\eta_n(0^+) = 0$ since $\Delta f(0^+) = 0$ and from the charge neutrality relation, $\eta_p(0^+) = 0$. This corresponds to a linear region of frequency variation with excess carrier concentration as is further explained at the end of this section. At $t_0 = 0^+$ the nonlinear term vanishes and Eq. (20) becomes linear.

In the second case, which corresponds to a nonlinear region of frequency variation with excess carrier concentration (see end of section), $\eta_n(t_0) > 0$ and $\eta_p(t_0) > 0$ with $t_0 = t_i$, such that $\Delta n_{nm}(t_i) - \eta_n(t_i) = 0$. Again $g^n(t_i)$ goes to zero with $\eta_n(t_i) = \Delta f(t_i) = \Delta n_{nm}(t_i)$. Effectively there is an intersection of $\Delta f(t)$ and $\Delta n_{nm}(t)$, whereas in the linear region of frequency variation above there is no intersection.

Similarly the nonlinear term in Eq. (24) referred to as $g^p(t)$ may be expressed using the charge neutrality relation for $\Delta p_{nm}(t)$,

$$g^p(t) = \left(\Delta n_{nm}(t) + \Delta f(t) \frac{N_t}{\Delta n(0)} - \eta_p(t) \right) \eta_n(t). \quad (26)$$

At low injection $\eta_p(0^+) = 0$ and at high injection the choice of $\eta_p(t_0) > 0$, given $\Delta f(t_i) = \Delta n_{nm}(t_i)$, results in $g^p(t) = 0$ at $t_0 = t_i$.

$$\eta_p(t_i) = \Delta f(t_i) \left(1.0 + \frac{N_t}{\Delta n(0)} \right). \quad (27)$$

The differential equations (23) and (24) are written in a simplified linear form similar to that by Streetman⁴ at $t_0 = 0^+$ or $t_0 = t_i$ as Eqs. (28). Constants $\eta_n(t_0)$ and $\eta_p(t_0)$ are dependent on the injection level. In Appendix A $\eta_n(t_0)$ and a condition for $\eta_n(t_0) > 0$, at some $t_0 = t_i$ is evaluated,

$$- \frac{d\Delta p_{nm}(t)}{dt} \Big|_{t=t_0} = \alpha \Delta p_{nm}(t_0) - \beta \Delta n_{nm}(t_0), \quad (28a)$$

$$- \frac{d\Delta n_{nm}(t)}{dt} \Big|_{t=t_0} = \gamma \Delta n_{nm}(t_0) - \sigma \Delta p_{nm}(t_0), \quad (28b)$$

where α , β , γ , and σ now contain the $\eta_n(t_0)$ and $\eta_p(t_0)$ terms for the two cases indicated above such that $t_0 = 0^+$ or $t_0 = t_i$, with $\Delta n(0) = \Delta p(0)$,

$$\alpha = C_p N_t \left\{ \frac{p_1}{p_{po} + p_1} + \frac{p_{po} + p_1}{N_t} + \frac{\eta_p(t_0) \Delta p(0)}{N_t} \right\}, \quad (29a)$$

$$\beta = C_p N_t \left\{ \frac{p_{po} + p_1}{N_t} + \frac{\eta_p(t_0) \Delta n(0)}{N_t} \right\}, \quad (29b)$$

$$\gamma = C_n N_t \left\{ \frac{n_1}{n_{po} + n_1} + \frac{n_{po} + n_1}{N_t} + \frac{\eta_n(t_0) \Delta n(0)}{N_t} \right\}. \quad (29c)$$

$$\sigma = C_n N_t \left\{ \frac{n_{po} + n_1}{N_t} + \frac{\eta_n(t_0) \Delta p(0)}{N_t} \right\}. \quad (29d)$$

The method using the differential operator $D = d/dt$,^{9,10} whereby the determinant of the matrix of equations (28) equals zero, allows the formation of the characteristic equation

$$[D^2 + (\alpha + \gamma)D + (\alpha\gamma - \sigma\beta)]e^{-\lambda t} = 0. \quad (30)$$

The characteristic equation at $t = t_0$ (where the nonlinear terms go to zero) may be written as Eq. (31). As such the fundamental frequencies λ_1 and λ_2 (inverse time constants) may be evaluated,

$$\lambda^2 - (\alpha + \gamma)\lambda + (\alpha\gamma - \sigma\beta) = 0. \quad (31)$$

By evaluating the roots of Eq. (31) such that the frequency $\lambda_1 = 1/\tau_+$ and $\lambda_2 = 1/\tau_-$ by comparison with,⁴

$$\lambda_1 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left[1 + \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2} \right)^{1/2} \right], \quad (32a)$$

$$\lambda_2 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left[1 - \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2} \right)^{1/2} \right]. \quad (32b)$$

The linear solution of Eqs. (28) for $\Delta p_{nm}(t)$ and $\Delta n_{nm}(t)$ is $\Delta_i p_{nm}(t)$ and $\Delta_i n_{nm}(t)$, respectively, with $\Delta_i f(t)$ derived from the charge neutrality relation,

$$\Delta_i p_{nm}(t) = P_{10} e^{-\lambda_1 t} + P_{01} e^{-\lambda_2 t}, \quad (33a)$$

$$\Delta_i n_{nm}(t) = N_{10} e^{-\lambda_1 t} + N_{01} e^{-\lambda_2 t}, \quad (33b)$$

$$\Delta_i f(t) = F_{10} e^{-\lambda_1 t} + F_{01} e^{-\lambda_2 t}. \quad (33c)$$

The range of excess carrier density where the fundamental frequencies change with injection level, is expressed by Eqs. (29) and (32). Low injection refers to the situation where the excess carrier density is much less than the equilibrium majority carrier density.⁶ The linear region of variation of fundamental frequencies $\lambda_{1,2}$ with injection level or excess carrier density is defined by Eq. (34). This condition is satisfied upon expansion of Eq. (34) for $\eta_n(t_0) = 0$ and $\eta_p(t_0) = 0$ at $t_0 = 0^+$. The requirement is found from $\eta_n(t) = \Delta f(t)$, which equals zero at $t = 0^+$ as $\Delta f(t)$, the defect level excess electron concentration, is zero at $t = 0^+$. An upper limit for the linear region of excess carrier density exists referred to as $\Delta n(0)_{critical}$ and is evaluated in Appendix A. Hence $\eta_n(0^+) = 0$ and $\eta_p(0^+) = 0$ render Eqs. (23) and (24) linear for all injection levels less than $\Delta n(0)_{critical}$,

$$\frac{d\lambda_{1,2}}{d\Delta n(0)} = 0. \quad (34)$$

The nonlinear region of variation of fundamental frequencies $\lambda_{1,2}$ with injection level or excess carrier density is defined by Eq. (35). This corresponds to the range of excess carrier density whereby the change in fundamental frequency with injection level is nonzero as expressed by Eq. (35). This condition is satisfied for $\eta_n(t_0) > 0$ and $\eta_p(t_0) > 0$ for some value of t_0 . As such $\Delta f(t) > 0$ can only be achieved with $t_0 > 0^+$ as $\Delta f(t)$ is greater than zero except at $t = 0^+$ and $t = \infty$. Equations (23) and (24) are linear at $t_0 = t_i$,

$$\left| \frac{d\lambda_{1,2}}{d\Delta n(0)} \right| > 0. \quad (35)$$

IV. DERIVATION OF AN ANALYTIC SOLUTION FOR $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$, AND $\Delta f(t)$

Having evaluated the frequencies λ_1 and λ_2 derived from the linear equations at time $t = 0^+$ or t_i , it now remains to find a solution for the rate equations away from the equilibrium points 0^+ and t_i . It is shown below that the general solution for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$, and $\Delta f(t)$ consists of the same infinite series of monoexponential terms with different coefficients, respectively, the inverse time constants of which are a linear combination of those frequencies of the linear solution. The nonlinear differential rate equations for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ are rewritten as indefinite integral expressions for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$, respectively. These expressions are solved by repeated integration by parts, to reveal an infinity of monoexponential terms for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$. In this format the coefficients may be derived recursively in a nested fashion which is not computationally convenient. Having established that the solution is an infinity of exponential terms, equating coefficients on both sides of the rate equations realizes simultaneous equations which are independent, provided λ_1/λ_2 is irrational. This uniquely identifies and allows the evaluation of the coefficients by a recurrence relation. A definition of linearity is provided in Ref. 11, which includes the state of the system prior to application of the impulse $\delta(t)$. Since each monoexponential term in $\Delta n_{nm}(t)$ is the solution of a linear differential equation with a constant coefficient, the solution is the response to an infinite number of linear systems. As such the solution for $\Delta n_{nm}(t)$ represents the impulse response and provides a general solution to the rate equations. The region of convergence about the equilibrium point $t = 0^+$ is examined.

The unconstrained coupled differential equations we are interested in are of the form (36)–(38) taken from Eqs. (20) and (21), and substituting the charge neutrality relation:

$$-\frac{d\Delta n_{nm}(t)}{dt} \Delta n(0) = (\gamma_0 - \sigma_0) \Delta n_{nm}(t) \Delta n(0) - \sigma_0 N_t \Delta f(t) - C_n N_t \Delta n_{nm}(t) \Delta n(0) \Delta f(t), \quad (36)$$

$$-\frac{d\Delta p_{nm}(t)}{dt} \Delta n(0) = (\alpha_0 - \beta_0) \Delta p_{nm}(t) \Delta n(0) + \beta_0 N_t \Delta f(t) + C_p N_t \Delta p_{nm}(t) \Delta n(0) \Delta f(t), \quad (37)$$

$$\Delta p_{nm}(t)\Delta n(0) = \Delta n_{nm}(t)\Delta n(0) + N_t \Delta f(t). \quad (38)$$

An insight is gained into the solution of the above nonlinear rate equations as follows. On substitution of the linear solutions (33) for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and $\Delta f(t)$ into the above coupled differential equations (36) and (37) representing the global evolution of $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$, respectively, we find that, for example, $\exp(-2\lambda_1 t)$, $\exp(-2\lambda_2 t)$ and $\exp[-(\lambda_1 + \lambda_2)t]$ are generated on the right-hand side and not on the left. Continuing by including $\exp(-2\lambda_1 t)$, etc. in a solution and further inclusion of exponents which do not match, we intuitively expect an infinity of exponential terms in the solution form for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and via the charge neutrality relation for $\Delta f(t)$. We expect the nonlinear solution to have an infinite number of exponential terms and the time constants to be a linear combination of the two fundamental frequencies λ_1 and λ_2 , where the eigenvalues of the linearized system are given by $-\lambda_1$ and $-\lambda_2$. A more rigorous analysis is given in Appendix B.

The following solution form is proposed for $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$ and via the charge neutrality relation $\Delta f(t)$, with the notation $E_{i,j} = \exp(-i\lambda_1 t - j\lambda_2 t)$,

$$\begin{aligned} \Delta n_{nm}(t) &= \sum_i \sum_j N_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \\ &= \sum_i \sum_j N_{i,j} E_{i,j}, \end{aligned} \quad (39a)$$

$$\begin{aligned} \Delta p_{nm}(t) &= \sum_i \sum_j P_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) \\ &= \sum_i \sum_j P_{i,j} E_{i,j}, \end{aligned} \quad (39b)$$

$$\Delta f(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} F_{i,j} \exp(-i\lambda_1 t - j\lambda_2 t) = \sum_i \sum_j F_{i,j} E_{i,j}. \quad (39c)$$

The coefficients of the exponential terms are determined by solving simultaneous equations. The procedure for evaluating the coefficients $P_{i,j}$, $N_{i,j}$, and $F_{i,j}$ is to substitute Eq. (39) into Eqs. (36)–(38). Note that $\exp[-(i\lambda_1 + j\lambda_2)t]$ are linearly independent functions for various (i,j) provided λ_1/λ_2 is irrational. So equality for all t can only be attained by matching the coefficients of appropriate exponentials on both sides. For $i=0$ and $j=0$ the coefficients N_{00} , P_{00} , and F_{00} are defined to be equal to values at $t_0=0^+$ or $t_0=t_i$. As $t \rightarrow 0^+$, $E_{i,j} \rightarrow 1$ and hence $\Delta n_{nm}(0^+) = N_{00}$ with $N_{00}=1$. Confirmation of the above method of equating coefficients is given in Appendix B and the coefficients F_{10} and F_{01} are determined in Appendix C. Hence N_{10} and P_{10} may be evaluated in terms of F_{10} as follows:

$$[(\gamma_0 - \sigma_0) - \lambda_1]N_{10} - \sigma_0 \frac{N_t}{\Delta n(0)} F_{10} = C_n N_t (2N_{00}F_{10}), \quad (40a)$$

$$[(\alpha_0 - \beta_0) - \lambda_1]P_{10} + \beta_0 \frac{N_t}{\Delta p(0)} F_{10} = -C_p N_t (2P_{00}F_{10}). \quad (40b)$$

Three simultaneous equations may be formed by equating coefficients for $i=1, j=1$, such that N_{11} and P_{11} may be evaluated in terms of N_{10} , N_{01} , P_{10} and P_{01} given F_{10} and F_{01} ,

$$\begin{aligned} [(\gamma_0 - \sigma_0) - (\lambda_1 + \lambda_2)]N_{11} - \sigma_0 \frac{N_t}{\Delta n(0)} F_{11} \\ = C_n N_t (N_{10}F_{01} + N_{01}F_{10} + 2N_{00}F_{11}), \end{aligned} \quad (41a)$$

$$\begin{aligned} [(\alpha_0 - \beta_0) - (\lambda_1 + \lambda_2)]P_{11} + \beta_0 \frac{N_t}{\Delta p(0)} F_{11} \\ = -C_p N_t (P_{10}F_{01} + P_{01}F_{10} + 2P_{00}F_{11}), \end{aligned} \quad (41b)$$

$$P_{11}\Delta p(0) - N_{11}\Delta n(0) - N_t F_{11} = 0. \quad (41c)$$

Continuing to solve the simultaneous equations for further coefficients, a solution set for $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ may be realized in terms of F_{10} and F_{01} . A global solution for $f(t)$ is obtained by the substitution of solutions for $\Delta n(t)$ and $\Delta p(t)$ into the expression for the charge neutrality relation (18). From Eq. (36) a recurrence relation may be formed which simplifies the calculation of the coefficients $N_{i,j}$ and $F_{i,j}$ with $i=1, 2, \dots, \infty$ and $j=1, 2, \dots, \infty$. Similarly a recurrence relation for $P_{i,j}$ may be formed,

$$\begin{aligned} \sum_i \sum_j (i\lambda_1 + j\lambda_2) N_{i,j} E_{i,j} \\ = (\gamma_0 - \sigma_0) \sum_i \sum_j N_{i,j} E_{i,j} - \sigma_0 \frac{N_t}{\Delta n(0)} \sum_i \sum_j F_{i,j} E_{i,j} \\ - C_n N_t \sum_i \sum_j S_{i,j}, \end{aligned} \quad (42)$$

where $E_{0,0} = 1$ and

$$S_{i,j} = \sum_u^i \sum_v^j N_{i-u, j-v} F_{u,v} E_{i-u, j-v} E_{u,v}. \quad (43)$$

The nature of the quadratic form for the SRH differential equation representing $\Delta n_{nm}(t)$ is determined in Appendix D. Further, the sum of the responses to an infinity of linear systems which the solution represents is examined in Appendix E.

V. NUMERICAL SOLUTION OF SRH EQUATIONS: IDEAL IMPULSE $\delta(t)$

The unconstrained coupled differential equations we are interested in are of the form (44)–(46) taken from Eqs. (20) and (21), and substituting the charge neutrality relation:

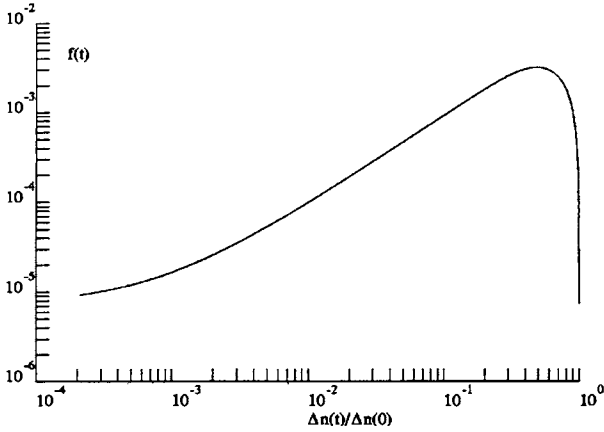


FIG. 1. Phase diagram indicating convergence to the equilibrium point for the given example, where $\Delta n(t)$ is normalized to $\Delta n(0)$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$.

$$-\frac{d\Delta n_{nm}(t)}{dt} \Delta n(0) = (\gamma_0 - \sigma_0) \Delta n_{nm}(t) \Delta n(0) - \sigma_0 N_t \Delta f(t) - C_n N_t \Delta n_{nm}(t) \Delta n(0) \Delta f(t), \quad (44)$$

$$-\frac{d\Delta p_{nm}(t)}{dt} \Delta n(0) = (\alpha_0 - \beta_0) \Delta p_{nm}(t) \Delta n(0) + \beta_0 N_t \Delta f(t) + C_p N_t \Delta p_{nm}(t) \Delta n(0) \Delta f(t), \quad (45)$$

$$\frac{d\Delta p_{nm}(t)}{dt} \Delta n(0) = \frac{d\Delta n_{nm}(t)}{dt} \Delta n(0) + N_t \frac{d\Delta f(t)}{dt}. \quad (46)$$

The three equations (44)–(46) form a set of second-order coupled differential equations³ which are nonlinear and solved numerically. No *a priori* knowledge is available for $\Delta n_{nm}(t + \Delta t)$ as it represents the time evolution of the excess carrier concentration derived numerically. A correlation between the numerical solution and the predictions of the analytical solution is made and found to indicate close agreement. This confirms the method used to analyze the decay as a useful tool.

A fourth- and fifth-order Runge-Kutta scheme,^{12,13} is chosen to represent discrete values of $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$, and $\Delta f(t)$, to ensure convergence to the equilibrium concentration for the minority carrier as $t \rightarrow \infty$. Figure 1 representing the phase diagram¹⁴ indicates the convergence to the equilibrium point for the example given by Table I. The normalized excess carrier concentrations at $t = 0^+$ are given by $\Delta n_{nm}(0^+) = 1.0$ and $\Delta p_{nm}(0^+) = 1.0$. The defect level initial occupation is assumed not to change from $t = 0^-$ to $t = 0^+$ [$f(0^+) = f(0^-)$]. Table I indicates typical data used in the numerical solution.

Multitransient analysis refers to the extraction of component exponential terms from a sum of exponentials comprising the signal. The methods available^{15–20} present a means of analyzing signals with additive white Gaussian noise. In addition, where the data matrix and the observation matrix may be subject to noise fluctuations, the total least-squares

TABLE I. Typical parameters for numerical solution.

T	300.0	Temperature (K)
nn	2048	Number of time samples
Δt	2×10^{-8}	Time sample interval (sec)
N_A	5×10^{13}	Majority carrier concentration (cm^{-3})
$E_t - E_v$	0.65	Energy level depth from valence band (eV)
$\Delta n(0)$	5×10^9	Excess carrier concentration (cm^{-3})
N_t	5×10^{11}	Discrete level concentration (cm^{-3})
σ_p	8.5×10^{-17}	Cross section for holes (cm^{-2})
σ_n	9×10^{-15}	Cross section for electrons (cm^{-2})

method²¹ (TLS) is employed. This method models the multiexponential signal as an autoregressive process. For the present analysis the TLS (Refs. 15 and 22) multitransient analysis method using singular value decomposition²³ is applied to the analysis of the multicomponent exponential decay.

The TLS multitransient analysis of the numerical solution of Eqs. (44)–(46) results in the determination of frequencies which are compared with the existing theoretical expressions (32) for low through to high injection. Figure 2 shows the comparison between the decay time constants $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ as calculated from Eq. (32) and as evaluated by the TLS analysis of numerical data [$\Delta n(t + \Delta t)$] for $T = 300 \text{ K}$. The figure indicates the variation from low injection through to high injection. Note that the excess carrier concentration $\Delta n(0)$ varies from $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is excellent and as such contributes to the confidence in the TLS method of analysis. The onset of the nonlinear variation of frequencies λ_1 and λ_2 with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{\text{critical}}$ is clearly seen in the figure where the linear portion extends to $5 \times 10^{11} \text{ cm}^{-3}$ and begins to diverge for $\Delta n(0)$ greater than $5 \times 10^{11} \text{ cm}^{-3}$. This indicates that the linear region is in close agreement with the definition given by Eq. (34). See Appendix A for the

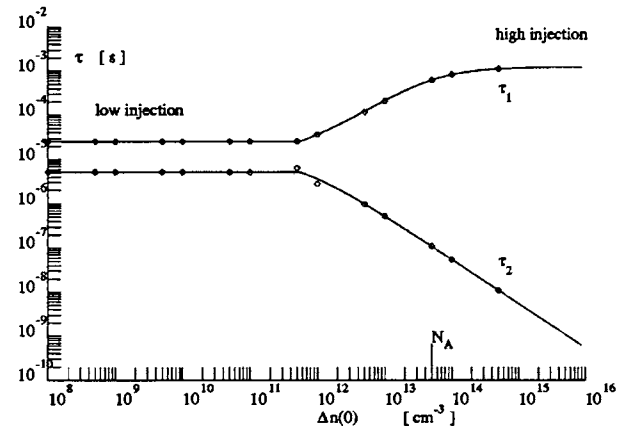


FIG. 2. A graph of $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table I for defect level parameters. Continuous line: τ_1 and τ_2 predicted by Eq. (32). Circles: τ_1 and τ_2 derived from multitransient analysis of the numerical solution

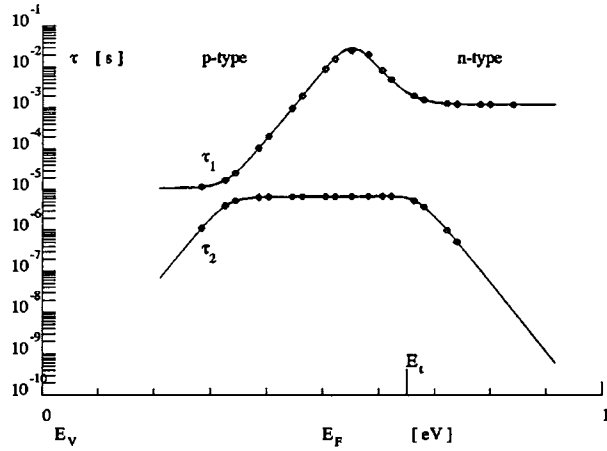


FIG. 3. Decay time constant $\tau_1 = 1/\lambda_1$ and $\tau_2 = 1/\lambda_2$ versus the Fermi level E_F (eV) for doping concentrations of $N_{A,D} = 5 \times 10^{10} \text{ cm}^{-3}$ to $N_{A,D} = 1 \times 10^{16} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$. Continuous line: τ_1 and τ_2 calculated by Eq. (32). Circles: TLS analysis of numerical solution $\Delta n(t + \Delta t)$.

evaluation of $\Delta n(0)_{\text{critical}}$. For parameters listed in Table I, $\Delta n(0)_{\text{critical}} = 5.44 \times 10^{11} \text{ cm}^{-3}$. Note also that the TLS multitransient analysis of the numerical solution results in τ_1 and τ_2 , in close agreement with that predicted by the solution for τ_1 and τ_2 of Eq. (32) for high injection.

Figure 3 shows the comparison between the decay time constants τ_1 and τ_2 as calculated from Eq. (32) and as evaluated by the TLS analysis of numerical data $[\Delta n(t + \Delta t)]$ for $T = 300 \text{ K}$ versus the Fermi level E_F . The doping concentration for the *p*-type and *n*-type samples varies from $5 \times 10^{10} \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is very good for the numerical solution and the calculated τ_1 and τ_2 . From this figure, τ_1 describes the minority-carrier decay constant and τ_2 the majority-carrier decay constant, in analogy with Shockley and Read¹ for the steady state. As such they represent fundamental decay time constants.

Figure 2 indicates that for $\Delta n(0) > \Delta n(0)_{\text{critical}}$, τ_1 increases realizing a situation where the minority carrier (*p*-type) time constant represented by τ_1 is becoming longer. The minority carriers (electrons) remain in the conduction band for a longer average time indicating that there are fewer holes at the defect level to recombine with. As such the de-

fect level electron population is increasing and electrons remain at the defect level for a longer average time. This is referred to as minority-carrier trapping. The time constant τ_1 remains constant in the linear region of variation of $\tau_{1,2}$ with $\Delta n(0)$. This region corresponds to recombination only, whereas the nonlinear region undergoes recombination and trapping. Eventually the trapping saturates as $\Delta n(0)$ is increased to high injection and the time constant τ_1 reaches a maximum becoming almost constant.

Further by recalling the expression (39) for the decay $\Delta n_{nm}(t)$, the infinity of time constants is found to be a linear combination of two fundamental frequencies λ_1 and λ_2 . Table II indicates the correlation with the prediction of Eqs. (32) and (39) and the TLS analysis of the decay $\Delta n(t + \Delta t)$ within the limitations of the TLS method. No *a priori* knowledge is available for time constants associated with the numerical solution, yet the agreement of the analytical and TLS methods with respect to the linear combination of λ_1 and λ_2 and their magnitude is excellent. The TLS multitransient analysis also reveals the same magnitudes of the coefficients of the exponential terms as by the analytical approach (see Appendix C). Note that the magnitudes of the coefficients decrease rapidly. In addition, for the transient case in low injection, the magnitude of the coefficient for τ_2 is significant. By evaluating an error term ε , Eq. (47), being the difference between the series with calculated coefficients as determined in Appendix C and the numerical solution, an estimate of the agreement of the two approaches may be made,

$$\varepsilon = \left| \frac{\sum_i \sum_j N_{i,j} E_{i,j} - \Delta n(t + \Delta t)}{\Delta n(0)} \right|. \quad (47)$$

Figure 4 indicates the agreement for the linear and nonlinear regions of variation of $\lambda_{1,2}$ with $\Delta n(0)$. The indicated closeness of fits between the two approaches is good for the initial part of the decay and diverges for large time. This may be explained by accumulation of error in the Runge-Kutta numerical method. Further, the value for $d\Delta n_{nm}(t)/dt$ at $t = 0^+$ for the series $N_{i,j}$ at $t = 0^+$ at the indicated injection levels is 9.15075×10^4 , which is in close agreement with the

TABLE II. TLS analysis of numerical data $\Delta n(t + \Delta t)$ and evaluation of Eq. (32). Note the prediction of Eq. (39) with frequencies being a linear combination of the fundamental frequencies and calculated coefficients $N_{i,j}$. $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ with $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$.

λ	Equation (32) $\lambda \text{ (sec}^{-1}\text{)}$	TLS frequency $\lambda \text{ (sec}^{-1}\text{)}$	TLS coefficient normalized to $\Delta n(0)$	Calculated coefficient $N_{i,j}$
λ_1	3.92871×10^4	3.92871×10^4	$N_{10} = 6.5804 \times 10^{-1}$	6.5804×10^{-1}
$2\lambda_1$		7.99744×10^4	$N_{20} = -2.135 \times 10^{-4}$	-2.024×10^{-4}
λ_2	19.10753×10^4	19.1069×10^4	$N_{01} = 3.3825 \times 10^{-1}$	3.3783×10^{-1}
$\lambda_1 + \lambda_2$		23.3579×10^4	$N_{11} = 3.0767 \times 10^{-3}$	3.4045×10^{-3}
$2\lambda_2$		38.3739×10^4	$N_{02} = 8.4177 \times 10^{-4}$	8.3745×10^{-4}
$3\lambda_2$		60.1207×10^4	$N_{03} = 1.3457 \times 10^{-6}$	1.8820×10^{-6}

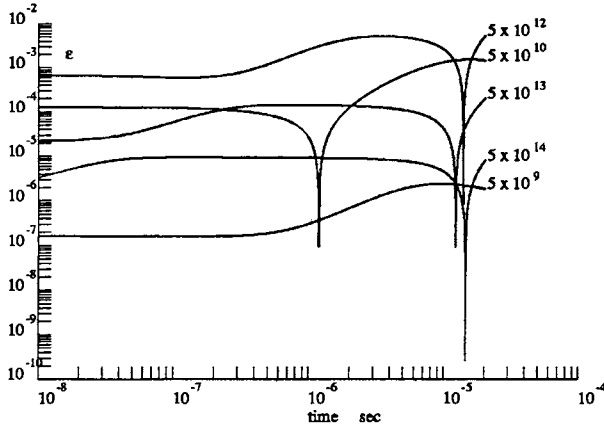


FIG. 4. Normalized error ϵ , Eq. (47), between predicted values of $N_{i,j}E_{i,j}$, and numerical solution $\Delta n(t + \Delta t)$ for $\Delta n(0) = 5 \times 10^9 \text{ cm}^{-3}$ to $\Delta n(0) = 5 \times 10^{14} \text{ cm}^{-3}$. This corresponds to the linear and nonlinear regions of variation of $\Delta n(0)$ with $\lambda_{1,2}$. $N_A = 5 \times 10^{13} \text{ cm}^{-3}$ and $\Delta t = 1 \times 10^{-8} \text{ sec}$.

predicted value [see Eq. (C1)]. This verifies the calculated values of the coefficients $N_{i,j}$ by the method outlined in Appendix C.

VI. PROPOSED EXPERIMENTAL CONDITIONS

Specifically with regard to a *p*-type silicon wafer, for infrared light pulses produced by a yttrium aluminum garnet (YAG) laser at $t = 0^+$ with a wavelength of $1.064 \mu\text{m}$, a uniform excess carrier concentration may be generated within a sample of $50 \mu\text{m}$ thickness.²⁴ This produces the initial condition $\Delta n(0) = \Delta p(0)$ at $t = 0^+$. Silicon nitride passivated surfaces provide a low effective surface recombination velocity S_{eff} on a float-zone *p*-type silicon wafer.²⁵ Similarly a low surface recombination velocity may be attained with the Si-SiO₂ system.²⁶ The effective surface recombination velocity is taken to be injection level dependent in Refs. 25 and 26. For excess carrier concentrations $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$, $S_{\text{eff}} < 50 \text{ cm/s}$ is assumed to be attainable with appropriate processing with the Si-SiO₂ system for a wafer resistivity of the order of $250 \Omega \text{ cm}$ ($5 \times 10^{13} \text{ cm}^{-3}$). The decay of excess carriers may be detected by a contactless microwave photoconductance measurement. Furthermore a dominant level with an energy near midgap (such as that of the gold levels at $E_t - E_v = 0.65 \text{ eV}$), which represents an efficient recombination center, is the basis for the single-level model. The defect level concentration is assumed to be uniformly distributed throughout the sample.

In terms of direct application a possibility immediately arises from the present work where a silicon sample is processed as above. Minority-carrier trapping for a dominant defect level may be evaluated by an analysis of the decay due to an impulse of light as previously indicated to determine τ_1 and a plot of this quantity against the excess carrier concentration $\Delta n(0)$. Since τ_1 represents the minority-carrier for a dominant defect level, a measure of material quality is attained by an assessment of minority carrier trapping. From the charge neutrality relationship, increasing the

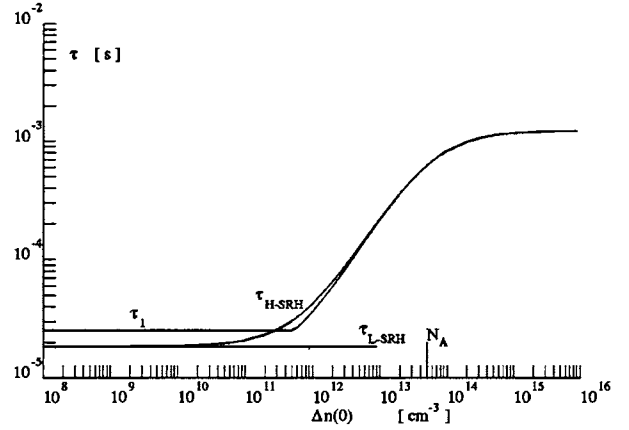


FIG. 5. A graph of $\tau_1 = 1/\lambda_1$ and τ_{L-SRH} , τ_{H-SRH} versus excess electron concentration $\Delta n(0)$. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. See Table I for defect level parameters.

excess carrier concentration in the sample means that both $\Delta n(t)$ and $\Delta p(t)$ are measured. However from the present work both quantities contain the same decay constants. The decay may be analyzed for τ_1 and given the relative magnitude of excess carrier concentration, wafers may be compared for quality. Ideally the range of excess carrier concentration should encompass the linear region and the nonlinear region of variation of $\tau_{1,2}$ with excess carrier concentration.

VII. DISCUSSION

As stated previously the steady-state decay time constant is the same as the transient decay time constant with only the magnitudes of the coefficients of the exponential terms differing from steady state to transient. Existing experimental data are largely interpreted using the expressions derived in Ref. 1 with approximations as indicated in the Introduction. The current work seeks to address the anomalies arising from such an interpretation in terms of the defect level parameters such as level depth. To this effect, for example, Fig. 5 indicates the variation of τ_1 with excess carrier concentration and that of τ_{L-SRH} and τ_{H-SRH} of Ref. 1 representing Eqs. (5.3) and (6.1) respectively of that paper. Note that τ_{L-SRH} is the low excess carrier-concentration time constant and τ_{H-SRH} is the high excess carrier-concentration time constant. From the figure τ_{L-SRH} underestimates τ_1 by $\approx 30\%$ in the linear region. Although τ_{H-SRH} is a good fit in the nonlinear region in terms of determining material quality for a dominant defect, again the degree of trapping is unknown. However for defect level parameter estimation decay experiments are usually conducted in the linear region (low excess carrier concentration). The reason for the discrepancy in the linear region is that in the original paper¹ the change in charge density produced by changing concentration in the traps is neglected. The present work makes no such assumption. Referring to the figure from the low and high excess carrier concentration time constants the $\Delta n(0)_{\text{critical}}$ cannot be determined. As a result the extent of the linear region is unknown from these time constants. The extent of the linear

region is also unknown with the work of Ref. 4. Without knowing the limit on excess carrier concentration defining the linear region reduces the application of Refs. 1 and 4 in practice unless the time constants are plotted against a range of excess carrier concentrations to ascertain the onset of trapping.

VIII. CONCLUSIONS

Initially at $t=0^+$, $\Delta n(0)$ electrons and $\Delta p(0)$ holes are uniformly generated in the material. Expressions for the minority- (τ_1) and majority- (τ_2) carrier decay time constants are derived without an approximation at a given temperature for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_t , cross section $\sigma_{n,p}$, and energy level E_t . The transition from low to high injection is also given. A general analytic expression for the carrier decay $\Delta n(t)$ for $t>0^+$ derived from the rate equations is represented by an infinity of exponential terms, the frequencies of which are linear combinations of the two fundamental frequencies λ_1 and λ_2 . These frequencies are attributed to minority λ_1 and majority λ_2 decay frequencies (inverse time constants). Very good agreement is found between the decay frequencies λ_1 and λ_2 for the theory presented and by the TLS multitransient analysis of the numerical solution at one temperature. This independent verification of the theory derived from the Shockley-Read-Hall rate equations confirms the properties of the above solution. Further, the solution represents the impulse response as the exponential terms are the response to an infinite sum of linear systems.

The fundamental frequencies uniquely identify the defect level properties of capture cross section $\sigma_{n,p}$, level concentration N_t , and energy E_t , as a signature of time constants. The numerical solution at temperature T_i , excess carrier concentration $\Delta n(0)$ and doping concentration N_A indicates the evolution of the decay with the above defect level parameters. This unifies the theory of minority-carrier decay via a single-level defect by providing a means of modeling such decay.

ACKNOWLEDGMENTS

D.D. would like to thank Professor M. Green and Dr. P. Ladbroke for their encouragement in developing an interest in electrically active defects in semiconductors, and M. Murray for continuing inspiration. A special thanks to Dr. A. Aberle and Dr. J. Atai for reading the manuscript and indicating corrections. Appreciation is also extended to D. Clarke for her support and encouragement, and K. Rosolen, S. Zecevic, D. Brown, Dr. I. Gardiner, and Dr. B. St. George for helpful discussions.

APPENDIX A: EVALUATION OF $\eta_n(t_0)$ AND $\eta_p(t_0)$

For low injection $\eta_n(t_0)$ and $\eta_p(t_0)$ at $t_0=0^+$ are both zero. It remains to find a value for $\eta_n(t_0)$ and $\eta_p(t_0)$ at $t_0=t_i$. First, a relationship between the differential terms in Eqs. (27) is established and subsequently an expression for

$\eta_n(t_i)$ is developed. Second, having determined an expression for $\eta_n(t_i)$ in terms of the excess carrier concentration $\Delta n(0)$, a critical value of excess carrier concentration $\Delta n(0)_{critical}$ may be evaluated. This value represents the transition between the linear variation of fundamental frequency with excess carrier concentration and the nonlinear variation with $\eta_n(t_0)=0$. A requirement for the selection of $\eta_n(t_i)=\Delta f(t_i)=\Delta n_{nm}(t_i)$ is found from the charge neutrality relation (18) with $\Delta p(0)=\Delta n(0)$ as follows:

$$\Delta p_{nm}(t_i) = \left(1 + \frac{N_t}{\Delta n(0)}\right) \Delta n_{nm}(t_i), \quad (A1)$$

where

$$\phi = \left(1 + \frac{N_t}{\Delta n(0)}\right). \quad (A2)$$

Equating coefficients on both sides of Eq. (A1) considering the first two components,

$$\begin{aligned} P_{10} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{10}, \\ P_{01} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{01}. \end{aligned} \quad (A3)$$

Now, multiplying the first equation of Eq. (A3) by $\lambda_1 \exp(-\lambda_1 t_i)$ and the second equation by $\lambda_2 \exp(-\lambda_2 t_i)$ yields

$$\begin{aligned} P_{10} \lambda_1 e^{-\lambda_1 t_i} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{10} \lambda_1 e^{-\lambda_1 t_i}, \\ P_{01} \lambda_2 e^{-\lambda_2 t_i} &= \left(1 + \frac{N_t}{\Delta n(0)}\right) N_{01} \lambda_2 e^{-\lambda_2 t_i}. \end{aligned} \quad (A4)$$

Summing the left-hand side of Eq. (A4) and equating that to the sum of the right-hand side results in a relationship between the differentials as follows:

$$\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t_0=t_i} = \left(1 + \frac{N_t}{\Delta n(0)}\right) \left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t_0=t_i}. \quad (A5)$$

Having established this relationship, Eq. (28) may be solved for $\eta_n(t_i)$. The value of $\eta_p(t_i)$ is evaluated from Eq. (27),

$$\eta_n(t_i) = \frac{(\phi \alpha_0 - \beta_0) - (\phi \gamma_0 - \phi^2 \sigma_0)}{\phi \Delta n(0) (1 - \phi) (C_n + C_p)}, \quad (A6)$$

where α_0 , β_0 , γ_0 , and σ_0 are given by Eq. (22). Solving the following quadratic resulting from Eq. (A6) with $\Delta \eta_n(t_i)=0$, corresponding to the linear region of variation of $\lambda_{1,2}$ with $\Delta n(0)$, indicates the onset of the nonlinear region. For $\Delta n(0)>0$, the onset of the nonlinear region is termed $\Delta n(0)_{critical}$,

$$\begin{aligned} 0 &= \Delta n^2(0) [(\alpha_0 - \beta_0) - (\gamma_0 - \sigma_0)] \\ &+ \Delta n(0) (N_t \alpha_0 - N_t \gamma_0 + 2N_t \sigma_0) + N_t^2 \sigma_0. \end{aligned} \quad (A7)$$

Note also that from Eqs. (28) and (A2), the following may be established for t_i :

$$t_i = -\frac{1}{(\gamma - \sigma\phi)} \ln[\eta_n(t_i)]. \quad (\text{A8})$$

APPENDIX B: DERIVATION OF AN ANALYTIC SOLUTION FOR $\Delta n_{nm}(t)$, $\Delta p_{nm}(t)$, AND $\Delta f(t)$

More formally, the nonlinear equation (36) may be written in the following form, given $r_n(t)$ and $q_n(t)$, where $\Delta n(t) = \Delta n_{nm}(t)\Delta n(0)$:

$$\frac{d\Delta n(t)}{dt} + r_n(t)\Delta n(t) = q_n(t), \quad (\text{B1})$$

where $\Delta f(t)$ is the nonlinear occupation function.

$$r_n(t) = (\gamma_0 - \sigma_0) - C_n N_t \Delta f(t), \quad (\text{B2})$$

$$q_n(t) = \sigma_0 N_t \Delta f(t). \quad (\text{B3})$$

An analytic solution for $\Delta n(t)$ may be written as follows (see Ref. 27):

$$\Delta n(t) = \exp\left[-\int r_n(t)dt\right] \left(\int q_n(t)e^{\int r_n(t)dt}dt + C\right). \quad (\text{B4})$$

It is assumed that the nonlinear function $\Delta f(t)$ may be given by $\Delta f(t)$, Eq. (33). A solution of Eq. (B4) is obtained by substitution of $\Delta f(t)$ and evaluating the indefinite integral by repeated integration by parts. An infinite sum of exponentials, with the exponents being a linear combination of the fundamental frequencies λ_1 and λ_2 is revealed for $\Delta n(t)$ [Eq. (B10)].

The solution of Eq. (B4) is briefly outlined as follows. Let

$$I_{qn}(t) = \int \sigma_0 N_t (F_{10}e^{-\lambda_1 t} + F_{01}e^{-\lambda_2 t})e^{(\gamma_0 - \sigma_0)t} \times e^{(C_n N_t F_{10}/\lambda_1)e^{-\lambda_1 t} + (C_n N_t F_{01}/\lambda_2)e^{-\lambda_2 t} + c'} dt \quad (\text{B5})$$

and

$$I_{rn}^-(t) = \exp\left[-\int r_n(t)dt\right] = e^{-(\gamma_0 - \sigma_0)t} e^{-(C_n N_t F_{10}/\lambda_1)e^{-\lambda_1 t} - (C_n N_t F_{01}/\lambda_2)e^{-\lambda_2 t} - c'}. \quad (\text{B6})$$

such that

$$\Delta n(t) = I_{rn}^-(t)(I_{qn}(t) + C), \quad (\text{B7})$$

where C is a constant of integration to be determined by the boundary conditions. Performing the integration by parts for the first term of $I_{qn}(t)$ as follows:

$$I = \int u dv = uv - \int v du, \quad (\text{B8})$$

where

$$u = e^{(C_n N_t F_{10}/\lambda_1)e^{-\lambda_1 t} + (C_n N_t F_{01}/\lambda_2)e^{-\lambda_2 t} + c'}, \quad (\text{B9a})$$

$$du = e^{(C_n N_t F_{10}/\lambda_1)e^{-\lambda_1 t} + (C_n N_t F_{01}/\lambda_2)e^{-\lambda_2 t} + c'} (-C_n N_t F_{10}e^{-\lambda_1 t} - C_n N_t F_{01}e^{-\lambda_2 t}), \quad (\text{B9b})$$

$$v = \frac{\sigma_0 N_t F_{10}}{[(\gamma_0 - \sigma_0) - \lambda_1]} e^{[(\gamma_0 - \sigma_0) - \lambda_1]t}, \quad (\text{B9c})$$

$$dv = e^{[(\gamma_0 - \sigma_0) - \lambda_1]t}. \quad (\text{B9d})$$

Multiplying Eq. (B5) through by $I_{rn}^-(t)$ and collecting terms yields an expression for $\Delta n(t)$ in which $R_{xyz}(t)$ is an integral which may be further integrated by parts. The equation representing the function $\Delta n(t)$ is given by Eq. (B10) indicating a series of exponential terms, which on further integration goes to an infinity of terms. Effectively the integration is performed until the magnitude of the remainder $[R_{xyz}(t)]$ is less than some ϵ . The constant of integration C is evaluated at the end of this section.

$$\begin{aligned} \Delta n(t) = & \phi_{10}^n F_{10} (e^{-\lambda_1 t} + \psi_{20}^n F_{10} [e^{-2\lambda_1 t} + \psi_{30}^n F_{10} \{e^{-3\lambda_1 t} + R_{111}(t)\} + \psi_{21}^n F_{01} \{e^{-(2\lambda_1 + \lambda_2)t} + R_{112}(t)\}]) \\ & + \psi_{11}^n F_{01} [e^{-(\lambda_1 + \lambda_2)t} + \psi_{21}^n F_{10} \{e^{-(2\lambda_1 + \lambda_2)t} + R_{121}(t)\} + \psi_{12}^n F_{01} \{e^{-(\lambda_1 + 2\lambda_2)t} + R_{122}(t)\}]) \\ & + \phi_{01}^n F_{01} (e^{-\lambda_2 t} + \psi_{02}^n F_{01} [e^{-2\lambda_2 t} + \psi_{03}^n F_{01} \{e^{-3\lambda_2 t} + R_{222}(t)\} + \psi_{12}^n F_{10} \{e^{-(\lambda_1 + 2\lambda_2)t} + R_{221}(t)\}]) \\ & + \psi_{11}^n F_{10} [e^{-(\lambda_1 + \lambda_2)t} + \psi_{21}^n F_{10} \{e^{-(2\lambda_1 + \lambda_2)t} + R_{211}(t)\} + \psi_{12}^n F_{01} \{e^{-(\lambda_1 + 2\lambda_2)t} + R_{212}(t)\}]) + I_{rn}^-(t)C, \end{aligned} \quad (\text{B10})$$

where

$$\phi_{ij}^n = \frac{\sigma_0 N_t}{(\gamma_0 - \sigma_0) - (i\lambda_1 + j\lambda_2)}, \quad (\text{B11})$$

$$\psi_{ij}^n = \frac{C_n N_t}{(\gamma_0 - \sigma_0) - (i\lambda_1 + j\lambda_2)}. \quad (\text{B12})$$

Consider now the second nonlinear expression (37) for

$\Delta p_{nm}(t)$, which may be similarly written in the following form with $\Delta p(t) = \Delta p_{nm}(t) \Delta n(0)$:

$$\frac{d\Delta p(t)}{dt} + r_p(t) \Delta p(t) = q_p(t), \quad (\text{B13})$$

where

$$r_p(t) = (\alpha_0 - \beta_0) + C_p N_t \Delta f(t), \quad (\text{B14})$$

$$q_p(t) = -\beta_0 N_t \Delta f(t). \quad (\text{B15})$$

An analytic solution for $\Delta p(t)$ may be written as follows (see Ref. 27).

$$\Delta p(t) = \exp \left[- \int r_p(t) dt \right] \left(\int q_p(t) \exp \left[\int r_p(t) dt \right] dt + C \right). \quad (\text{B16})$$

Similarly an analytic solution for $\Delta p(t)$ is available by integrating Eq. (B16) by parts to reveal an infinite series of monoexponential terms with inverse time constants, a linear combination of the frequencies λ_1 and λ_2 ,

$$\begin{aligned} \Delta p(t) = & \phi_{10}^p F_{10} (e^{-\lambda_1 t} - \psi_{20}^p F_{10} [e^{-2\lambda_1 t} - \psi_{30}^p F_{10} \{e^{-3\lambda_1 t} + R_{111}(t)\} - \psi_{21}^p F_{01} \{e^{-(2\lambda_1 + \lambda_2)t} + R_{112}(t)\}]) \\ & - \psi_{11}^p F_{01} [e^{-(\lambda_1 + \lambda_2)t} - \psi_{21}^p F_{10} \{e^{-(2\lambda_1 + \lambda_2)t} + R_{121}(t)\} - \psi_{12}^p F_{01} \{e^{-(\lambda_1 + 2\lambda_2)t} + R_{122}(t)\}]) \\ & + \phi_{01}^p F_{01} (e^{-\lambda_2 t} - \psi_{02}^p F_{01} [e^{-2\lambda_2 t} - \psi_{03}^p F_{01} \{e^{-3\lambda_2 t} + R_{222}(t)\} - \psi_{12}^p F_{10} \{e^{-(\lambda_1 + 2\lambda_2)t} + R_{221}(t)\}]) \\ & - \psi_{11}^p F_{10} [e^{-(\lambda_1 + \lambda_2)t} - \psi_{21}^p F_{10} \{e^{-(2\lambda_1 + \lambda_2)t} + R_{211}(t)\} - \psi_{12}^p F_{01} \{e^{-(\lambda_1 + 2\lambda_2)t} + R_{212}(t)\}]) + I_{rp}^-(t) C, \quad (\text{B17}) \end{aligned}$$

where

$$\phi_{ij}^p = \frac{-\beta_0 N_t}{(\alpha_0 - \beta_0) - (i\lambda_1 + j\lambda_2)}, \quad (\text{B18})$$

$$\psi_{ij}^p = \frac{C_p N_t}{(\alpha_0 - \beta_0) - (i\lambda_1 + j\lambda_2)}. \quad (\text{B19})$$

From the charge neutrality relation as follows, a solution for the nonlinear function $\Delta f(t)$ should also contain an infinity of exponential terms contradicting the assumption that $\Delta f(t)$ be represented by $\Delta f(t)$,

$$N_t \Delta f(t) = \Delta p(t) - \Delta n(t). \quad (\text{B20})$$

Hence monoexponential terms containing the linear combination of the fundamental frequencies should also be included in $\Delta f(t)$ as follows:

$$\Delta f(t) = \Delta f(t) + \gamma_{20} e^{-2\lambda_1 t} + \gamma_{02} e^{-2\lambda_2 t} + \gamma_{11} e^{-(\lambda_1 + \lambda_2)t} + \dots \quad (\text{B21})$$

As such the following solutions for $\Delta n(t)$ and $\Delta p(t)$ may be determined.

$$\begin{aligned} \Delta n(t) = & \phi_{10}^n F_{10} e^{-\lambda_1 t} + (\phi_{10}^n \psi_{20}^n F_{10}^2 + \phi_{20}^n \gamma_{20}) e^{-2\lambda_1 t} + (\phi_{10}^n \psi_{20}^n \psi_{30}^n F_{10}^3 + \phi_{30}^n \gamma_{30}) e^{-3\lambda_1 t} + (\phi_{10}^n \psi_{20}^n \psi_{21}^n F_{10}^2 F_{01} + \phi_{10}^n \psi_{11}^n \psi_{21}^n F_{10}^2 F_{01} \\ & + \phi_{01}^n \psi_{11}^n \psi_{21}^n F_{10}^2 F_{01} + \phi_{21}^n \gamma_{21}) e^{-(2\lambda_1 + \lambda_2)t} + (\phi_{10}^n \psi_{11}^n F_{10} F_{01} + \phi_{01}^n \psi_{11}^n F_{10} F_{01} + \phi_{11}^n \gamma_{11}) e^{-(\lambda_1 + \lambda_2)t} \\ & + (\phi_{10}^n \psi_{11}^n \psi_{12}^n F_{10} F_{01}^2 + \phi_{01}^n \psi_{11}^n \psi_{12}^n F_{10} F_{01}^2 + \phi_{01}^n \psi_{02}^n \psi_{12}^n F_{10} F_{01}^2 + \phi_{12}^n \gamma_{12}) e^{-(\lambda_1 + 2\lambda_2)t} + \phi_{01}^n F_{01} e^{-\lambda_2 t} \\ & + (\phi_{01}^n \psi_{02}^n F_{01}^2 + \phi_{02}^n \gamma_{02}) e^{-2\lambda_2 t} + (\phi_{01}^n \psi_{02}^n \psi_{03}^n F_{01}^3 + \phi_{03}^n \gamma_{03}) e^{-3\lambda_2 t} + R^n(t) + I_{rn}^-(t) C \quad (\text{B22}) \end{aligned}$$

and

$$\begin{aligned} \Delta p(t) = & \phi_{10}^p F_{10} e^{-\lambda_1 t} + (\phi_{10}^p \psi_{20}^p F_{10}^2 + \phi_{20}^p \gamma_{20}) e^{-2\lambda_1 t} + (\phi_{10}^p \psi_{20}^p \psi_{30}^p F_{10}^3 + \phi_{30}^p \gamma_{30}) e^{-3\lambda_1 t} + (\phi_{10}^p \psi_{20}^p \psi_{21}^p F_{10}^2 F_{01} \\ & + \phi_{10}^p \psi_{11}^p \psi_{21}^p F_{10}^2 F_{01} + \phi_{01}^p \psi_{11}^p \psi_{21}^p F_{10}^2 F_{01} + \phi_{21}^p \gamma_{21}) e^{-(2\lambda_1 + \lambda_2)t} + (\phi_{10}^p \psi_{11}^p F_{10} F_{01} + \phi_{01}^p \psi_{11}^p F_{10} F_{01} \\ & + \phi_{11}^p \gamma_{11}) e^{-(\lambda_1 + \lambda_2)t} + (\phi_{10}^p \psi_{11}^p \psi_{12}^p F_{10} F_{01}^2 + \phi_{01}^p \psi_{11}^p \psi_{12}^p F_{10} F_{01}^2 + \phi_{01}^p \psi_{02}^p \psi_{12}^p F_{10} F_{01}^2 + \phi_{12}^p \gamma_{12}) e^{-(\lambda_1 + 2\lambda_2)t} \\ & + \phi_{01}^p F_{01} e^{-\lambda_2 t} + (\phi_{01}^p \psi_{02}^p F_{01}^2 + \phi_{02}^p \gamma_{02}) e^{-2\lambda_2 t} + (\phi_{01}^p \psi_{02}^p \psi_{03}^p F_{01}^3 + \phi_{03}^p \gamma_{03}) e^{-3\lambda_2 t} + R^p(t) + I_{rp}^-(t) C. \quad (\text{B23}) \end{aligned}$$

Using the charge neutrality relation and equating coefficients, the factor γ_{20} , for example, may be evaluated,

$$N_t \gamma_{20} e^{-2\lambda_1 t} = (\phi_{10}^p \psi_{20}^p F_{10}^2 + \phi_{20}^p \gamma_{20}) e^{-2\lambda_1 t} - (\phi_{10}^n \psi_{20}^n F_{10}^2 + \phi_{20}^n \gamma_{20}) e^{-2\lambda_1 t}, \quad (\text{B24})$$

such that

$$\gamma_{20} = \frac{(\phi_{10}^p \psi_{20}^p - \phi_{10}^n \psi_{20}^n) F_{10}^2}{N_t - \phi_{20}^p + \phi_{20}^n}. \quad (\text{B25})$$

Using the notation in the text an expression for N_{20} may be evaluated and is equivalent to that derived by equating coefficients of like exponential terms,

$$N_{20} = \frac{(N_t \phi_{10}^n \psi_{20}^n + \phi_{10}^p \phi_{20}^n \psi_{20}^p - \phi_{10}^n \phi_{20}^p \psi_{20}^n) F_{10}^2}{N_t - \phi_{20}^p + \phi_{20}^n}. \quad (\text{B26})$$

Evaluation of the constant of integration C and confirmation of the method of equating coefficients to realize simultaneous equations are as follows. Equation (B10) may be expressed as Eq. (B27):

$$\Delta n(t) = I_{rn}^-(t) I_{qn}(t) + I_{rn}^-(t) C \quad (\text{B27})$$

and the constant C determined at $t_0 = 0^+$ or $t_0 = t_i$, which represent boundary conditions where the value of $\Delta n(t)$ is known,

$$C = \frac{\Delta n(t_0) - I_{rn}^-(t_0) I_{qn}(t_0)}{I_{rn}^-(t_0)}. \quad (\text{B28})$$

Differentiating Eq. (B27) results in an expression (B29) (with the value of C [Eq. (B28)] included) which may be equated with Eq. (20) and substituting the charge neutrality relation,

$$\begin{aligned} \left. \frac{d\Delta n(t)}{dt} \right|_{t=t_0} &= \left. \frac{d[I_{rn}^-(t) I_{qn}(t)]}{dt} \right|_{t=t_0} \\ &+ [\Delta n(t_0) - I_{rn}^-(t_0) I_{qn}(t_0)] [-(\gamma_0 - \sigma_0) \\ &+ C_n N_t F_{10} e^{-\lambda_1 t_0} + C_n N_t F_{01} e^{-\lambda_2 t_0} + \dots]. \end{aligned} \quad (\text{B29})$$

At $t_0 = t_i$ for example, equating like exponential terms for λ_1 yields the following, where $\eta_n(t_i) = \Delta f(t_i)$:

$$\begin{aligned} &[(\gamma_0 - \sigma_0) - \lambda_1 - C_n N_t \eta_n(t_i)] N_{10} e^{-\lambda_1 t_i} \\ &= \left(\sigma_0 \frac{N_t}{\Delta n(0)} + 2 C_n N_t [N_{00} + \eta_n(t_i)] \right) F_{10} e^{-\lambda_1 t_i} \end{aligned} \quad (\text{B30})$$

and for $i = 1, j = 1$,

$$\begin{aligned} &[(\gamma_0 - \sigma_0) - (\lambda_1 + \lambda_2) - C_n N_t \eta_n(t_i)] N_{11} e^{-(\lambda_1 + \lambda_2) t_i} \\ &= \left(\sigma_0 \frac{N_t}{\Delta n(0)} + 2 C_n N_t [N_{00} + \eta_n(t_i)] \right) F_{11} e^{-(\lambda_1 + \lambda_2) t_i} \\ &+ C_n N_t (N_{10} F_{01} + N_{01} F_{10}) e^{-(\lambda_1 + \lambda_2) t_i}. \end{aligned} \quad (\text{B31})$$

APPENDIX C: CALCULATION OF COEFFICIENTS

F_{10} , F_{01} , AND $N_{i,j}$

All coefficients $N_{i,j}$ and $P_{i,j}$ are a function of F_{10} , F_{01} , λ_1 , λ_2 , and $\eta_n(t_i)$. Note that the differentials of the normalized variables $\Delta n_{nm}(t)$ and $\Delta p_{nm}(t)$ at $t = 0^+$ are equal to a constant independent of the injection level and derived from Eqs. (20) and (21),

$$\left. \frac{d\Delta n_{nm}(t)}{dt} \right|_{t=0^+} = -C_n N_t (1 - f_o), \quad (\text{C1})$$

$$\left. \frac{d\Delta p_{nm}(t)}{dt} \right|_{t=0^+} = -C_p N_t f_o. \quad (\text{C2})$$

At $t = 0^+$, the normalized expressions (39) are represented by Eq. (C3), given Eq. (C1),

$$1 = N_{10} + N_{01} + \varepsilon_N, \quad (\text{C3a})$$

$$C_n N_t (1 - f_o) = \lambda_1 N_{10} + \lambda_2 N_{01} + \varepsilon'_N, \quad (\text{C3b})$$

where ε and ε' are error terms representing the series

$$\varepsilon_N = N_{11} + N_{20} + N_{02} + N_{12} + N_{21} + N_{30} + N_{03} + \dots, \quad (\text{C4a})$$

$$\begin{aligned} \varepsilon'_N &= (\lambda_1 + \lambda_2) N_{11} + 2\lambda_1 N_{20} \\ &+ 2\lambda_2 N_{02} + (\lambda_1 + 2\lambda_2) N_{12} + \dots. \end{aligned} \quad (\text{C4b})$$

From Eq. (B30) with $\eta_n(t_i) = 0$, the values of F_{10} and F_{01} may be evaluated, given N_{10} and N_{01} , as follows:

$$F_{10} = \frac{[(\gamma_0 - \sigma_0) - \lambda_1] N_{10}}{\sigma_0 N_t + 2 C_n N_t}, \quad (\text{C5})$$

$$F_{01} = \frac{[(\gamma_0 - \sigma_0) - \lambda_2] N_{01}}{\sigma_0 N_t + 2 C_n N_t}. \quad (\text{C6})$$

At $t = t_i$, the values of F_{10} and F_{01} may be determined from Eq. (B30).

Let $\varepsilon_N = 0$ and $\varepsilon'_N = 0$ and calculate N_{10} and N_{01} from Eq. (C3). With an initial value of N_{10} and N_{01} , the components $N_{i,j}$ of the series for ε_N and ε'_N may be evaluated by equating coefficients and solving simultaneous equations. Similarly for P_{10} and P_{01} , the $P_{i,j}$ for the series ε_P and ε'_P may

be evaluated. The coefficients N_{10} and N_{01} are reevaluated from Eq. (C3), corrected for the error terms ε_N and ε'_N as follows:

$$N_{10} + N_{01} = 1 - \varepsilon_N, \quad (C7a)$$

$$\lambda_1 N_{10} + \lambda_2 N_{01} = C_n N_t (1 - f_o) - \varepsilon'_N. \quad (C7b)$$

N_{10} and N_{01} are reevaluated, and the $N_{i,j}$, $P_{i,j}$, and $F_{i,j}$ are determined from the simultaneous equations such that the sum of the coefficients at $t=0$ equals 1. Note that at $t=0^+$ the resulting series for $N_{i,j}$ should yield a value for $d\Delta n_{nm}(t)/dt$ given by Eq. (C1) for arbitrary injection $\Delta n(0)$.

APPENDIX D: RATE EQUATION, QUADRATIC FORM

At $t=0^+$ the following quadratic form applies for the transient case at hand. As such the easiest way to deal with this is to do a coordinate change so that the N_0 term disappears in the new coordinates.

$$0 = N_0 + N_1 n(0^+) + N_2 n^2(0^+). \quad (D1)$$

Now $n(0^+)$ approaches n_t , the nonzero solution of the above quadratic, and using the coordinate change $\tilde{n} = n(0^+) - n_t$, the N_0 term is eliminated. In terms of Eq. (42), Eq. (1) is written as follows such that for all (i,j) we have

$$\sum_i \sum_j \frac{dN_{i,j} E_{i,j}}{dt} = - \sum_i \sum_j \left(\frac{(\gamma_0 - \sigma_0) N_{i,j} - \sigma_0 \frac{N_t}{\Delta n(0)} F_{i,j} - C_n N_t \Phi_{i,j}}{\sum_i \sum_j N_{i,j} E_{i,j}} \right) \sum_i \sum_j N_{i,j} E_{i,j} + C_n N_t \sum_i \sum_j \frac{F_{i,j}}{N_{i,j}} N_{i,j}^2 E_{i,j}^2, \quad (D2)$$

where $\Phi_{i,j}$ is the sum of the cross terms and

$$N_0 = C_n N_t (1 - f_o), \quad (D3)$$

$$N_1 = - \left((\gamma_0 - \sigma_0) - C_n N_t \sum_i \sum_j \Phi_{i,j} \right), \quad (D4)$$

$$N_2 = C_n N_t \sum_i \sum_j \frac{F_{i,j}}{N_{i,j}}. \quad (D5)$$

APPENDIX E: ANALYTIC SOLUTION, INFINITY OF LINEAR SYSTEMS

It may be shown as follows that the infinite series solution represents the sum of responses of an infinite number of linear systems to an impulse $\delta(t)$. Given the infinity of ex-

ponential terms comprising the solution for $\Delta n_{nm}(t)$, each $N_{i,j} E_{i,j}$ term may be written as

$$u_{i,j} = N_{i,j} E_{i,j}, \quad (E1)$$

which is a solution of a linear differential equation with a constant coefficient and $\lambda_1 > 0$ and $\lambda_2 > 0$:

$$\frac{du_{i,j}}{dt} = -(i\lambda_1 + j\lambda_2) u_{i,j}. \quad (E2)$$

As such the infinite series of exponential terms comprising the solution of the differential equation for $\Delta n_{nm}(t)$ is a sum of linear responses and the solution represents the impulse response. Stability for linear ordinary differential equations²⁸ is assured if the eigenvalues $-i\lambda_1$ and $-j\lambda_2$ lie on the real axis in the left half plane, i.e., $\text{Re}(-i\lambda_1) < 0$ and $\text{Re}(-j\lambda_2) < 0$. This is certainly the case here.

*Email address: didier@ee.usyd.edu.au

†Email address: yash@ee.usyd.edu.au

¹W. Shockley and W. T. Read, Phys. Rev. **87**, 835 (1952).

²R. N. Hall, Phys. Rev. **87**, 387 (1952).

³K. C. Nomura and J. S. Blakemore, Phys. Rev. **112**, 1607 (1958).

⁴B. G. Streetman, J. Appl. Phys. **37**, 3137 (1966).

⁵D. J. Sandiford, Phys. Rev. **105**, 524 (1957).

⁶S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1981).

⁷C. T. Sah, Solid-State Electron. **19**, 95 (1976).

⁸M. J. Keevers and M. A. Green, Sol. Energy Mater. Sol. Cells **41/42**, 195 (1996).

⁹D. W. Jordan and P. Smith, *Nonlinear Ordinary Differential Equations An Introduction to Dynamical Systems* (Oxford University Press, Oxford, 1999), p. 63.

¹⁰E. Kreyszig, *Advanced Engineering Mathematics* (Wiley, New York, 1988), p. 89.

¹¹C. Chen, *Linear System Theory and Design* (Harcourt Brace College, New York, 1984), p. 87.

¹²J. R. Dormand, *Numerical Methods for Differential Equations: A Computational Approach* (CRC Press, New York, 1996).

¹³W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in C: The Art in Scientific Computing* (Cambridge University Press, Cambridge, 1992).

- ¹⁴D. W. Jordan and P. Smith, *Nonlinear Ordinary Differential Equations An Introduction to Dynamical Systems* (Oxford University Press, Oxford, 1999), p. 3.
- ¹⁵J. Alam, Master's thesis, The University of Calgary, Alberta, Canada, 1990.
- ¹⁶E. Yeramian and P. Claverie, *Nature* (London) **326**, 169 (1987).
- ¹⁷P. Claverie, A. Denis, and E. Yeramian, *Comput. Phys. Rep.* **9**, 247 (1989).
- ¹⁸D. Maier, P. Hug, M. Fiederle, C. Eiche, D. Ebling, and J. Weese, *J. Appl. Phys.* **77**, 3851 (1995).
- ¹⁹D. A. Batovski and C. M. Hardolov, *J. Appl. Phys.* **74**, 291 (1993).
- ²⁰D. Eiche, C. Maier, J. Weese, J. HonerKamp, and K. W. Benz, *J. Appl. Phys.* **75**, 1242 (1994).
- ²¹S. Van Huffel and J. Vandewalle, *The Total Least Squares Problem Computational Aspects and Analysis* (SIAM, Philadelphia, 1991).
- ²²D. R. Debuf, Master's thesis, The University of New South Wales, Sydney, Australia (1993).
- ²³V. J. Klema and A. J. Laub, *IEEE Trans. Autom. Control* **AC-25**, 164 (1980).
- ²⁴K. L. Luke and L. J. Cheng, *J. Appl. Phys.* **61**, 2282 (1987).
- ²⁵J. Schmidt and A. G. Aberle, *J. Appl. Phys.* **85**, 3626 (1999).
- ²⁶A. G. Aberle, S. Glunz, and W. Warta, *J. Appl. Phys.* **71**, 4422 (1992).
- ²⁷E. Kreyszig, *Advanced Engineering Mathematics* (Wiley, New York, 1988), p. 34.
- ²⁸A. M. Stuart and A. R. Humphries, *Dynamical Systems and Numerical Analysis* (Cambridge University Press, New York, 1998), p. 127.

Multiple-level defect species evaluation from average carrier decay

Didier Debuft^{a)}

*Centre of Excellence for Advanced Silicon Photovoltaics and Photonics,
The University of New South Wales, Sydney, New South Wales 2052, Australia*
(Dated: Received 3 March 2003; accepted 4 June 2003)

An expression for the average decay is determined by solving the the carrier continuity equations, which include terms for multiple defect recombination. This expression is the decay measured by techniques such as the contactless photoconductance decay method, which determines the average or volume integrated decay. Implicit in the above is the requirement for good surface passivation such that only bulk properties are observed. A proposed experimental configuration is given to achieve the intended goal of an assessment of the type of defect in an n-type Czochralski-grown silicon semiconductor with an unusually high relative lifetime. The high lifetime is explained in terms of a ground excited state multiple-level defect system. Also, minority carrier trapping is investigated.

PACS numbers: 72.20.Jv, 72.40.+w, 85.30.De

I. INTRODUCTION

Decay of carriers due to an impulse of light $N_0\delta(t)$ via a single-level defect in the band gap is described by the Shockley-Read-Hall (SRH) differential rate equations by Shockley and Read¹. These equations refer to the average rate of transitions via the defect level for the processes of recombination, capture and emission. The recent analytic solution to the SRH rate equations of Ref.² is composed of an infinity of monoexponential terms, the frequencies ω_{k+1} or inverse time constants ($\omega_{k+1} = 1/\tau_{k+1}$) of which are a linear combination of two fundamental frequencies for the single level case. The fundamental frequency $\omega_1 = 1/\tau_1$ refers to the minority carrier decay. Application of the single-level method of solution to two multiple defect systems in Ref.³ indicates that the decay contains $k + 1$ fundamental frequencies or inverse time constants for k discrete defect levels. The time constant τ_1 is the dominant decay time constant. A plot of τ_1 versus the excess carrier concentration indicates the recombination only and trapping with recombination regions.

These analytic solutions for the single-level differential equations, and consequently for the multiple-level case, were derived without any approximation for uniform arbitrary doping concentration $N_{A,D}$, nondegenerate excess carrier concentration and defect-level parameters, the concentration N_{tk} , and the electron and hole cross sections for the k th level, σ_{nk} , σ_{pk} , respectively. Note that the differential equations apply for nondegenerate statistics so that there is an upper limit on the excess carrier concentration⁴.

A contribution of the present work is the solution of the carrier continuity equation including a multiple-level defect recombination term. This solution is determined, with constraints which reflect the experimental conditions, in order to ascertain the nature of the decay as

predicted by theory in Ref.³ and the average decay determined in Sec. II. The diffusion term $D_{n,p}$, which is expressed in terms of the mobility $\mu_{n,p}$, may be taken to first order at low frequency⁵. The first-order dependence of the diffusion term, expressed in terms of the mobility as above, also applies for nondegenerate statistics. The differential rate equations referred to as the Shockley-Read-Hall rate equations for the single-level defect¹ and the differential rate equations for the multiple defect systems of Ref.³ apply for nondegenerate statistics. Furthermore, in the derivation of the SRH rate equations, the carriers are assumed to reside at the band edge, and so Boltzmann statistics apply and nonparabolic, multiple bands are not considered.

A silicon wafer grown by the Czochralski method (Cz) often contains a defect species complex related to oxygen. The relatively long lifetime of the particular Cz silicon sample under consideration suggests that the impurity levels are close to the band edges, yielding a long time constant τ_1 . The current work investigates two-level carrier transitions for the ground and excited states or the coupled level system of Chen et al⁶ and Frens et al⁷. Experimental results are explained in terms of defect complexes which have these ground and excited states near the band edges. For the particular silicon Cz sample, three defect complexes are identified as possible sources of the relatively long time constant τ_1 . The first is the carbon interstitial-oxygen interstitial $C_i - O_i$ complex⁷, the second is the vacancy-oxygen $V - O$ complex Ref.⁷ and the third is the phosphorus donor (n-type) and the ground state of the $V - O$ complex or $C_i - O_i$ complex⁸. These complexes have energy levels near the band edges.

It is shown that multiple-level fundamental time constants for the ground excited state or coupled level system, for one of the complexes above, are in agreement with experimental data determined by a contactless photoconductance technique. This technique measures the average or volume integrated decay. The average decay in a semiconductor wafer (silicon) with an ideal surface passivation described by the surface recombination velocity $S = 0$ cm/s is derived in Luke⁸. An assessment

^{a)} Electronic mail: didier@ee.usyd.edu.au

of the effect of bulk minority carrier recombination and trapping is not performed in Ref.⁸ although an effective bulk lifetime is included. The effective bulk lifetime describes the effect of a dominant defect level. For the more accurate case of multiple defect levels the average decay is determined analytically from the theory of Ref.³. This forms the basis for interpreting the experimental results. An evaluation of recombination and or trapping is performed in the present work by plotting the τ_{k+1} versus excess carrier concentration. For the complexes stated above a difference is found in the nature of the plots. This represents a method of identifying particular defect species.

The article is organized as follows. In Sec. II the method of solving the carrier continuity equations analytically for the above constraints is presented. The average decay, which indicates the volume integrated decay measured by the photoconductance decay method, is evaluated. Section III describes the derivation of the ground excited state system equations and the excess carrier concentration decay equation. This equation includes the fundamental frequencies for this defect system. Sections IV, V, and VI describe the experimental constraints, the experimental conditions, and the experimental results, respectively. This is followed by a Sec. VII on a discussion of the results.

II. IMPULSE RESPONSE AND AVERAGE EXCESS CARRIER CONCENTRATION

For the purposes of illustrating the method of solution, a multiple-level defect analytic solution of Ref.³ to the rate equations is used in the carrier continuity equation solution method. Consider a p-type silicon wafer with a defect with a ground excited state uniformly distributed. The analytic solution to the rate equations with excess minority carrier concentration $\Delta n(t)$, in the absence of a field ξ and diffusion D_n , is represented by Eq. (1). This expression is the impulse response $\Delta n(t)$ as derived in Ref.² to a light impulse $N_0\delta(t)$ with a single level defect. In the above derivation the excess carrier concentration $\Delta n(0)$ is uniformly distributed throughout the sample at $t = 0^+$. The non-uniform excess carrier generation, through the thickness of the sample, for the multiple defect system equations of Ref.³ is considered in Sec. III.

$$\Delta n(t) = \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t), \quad (1)$$

$$= \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} E_{j,u,v}(t). \quad (2)$$

The recombination rate $U_n(t)$ is defined as follows Wertheim,⁹ where $\Delta n(t)$ represents the impulse response

for recombination:

$$U_n(t) = -\frac{d\Delta n(t)}{dt}, \quad (3)$$

and from Eq. (1):

$$U_n(t) = \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (j\omega_1 + u\omega_2 + v\omega_3) N_{j,u,v} E_{j,u,v}(t), \quad (4)$$

where

$$E_{j,u,v}(t) = \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t). \quad (5)$$

In the present analysis the carrier and recombination spatial profile, as well as the time evolution, is sought normal to the surface at the point of the incidence of light. For the single level, neglecting excited states, Auger recombination, and radiative recombination, the carrier continuity equation for the one-dimensional case is given as follows:¹⁰ Simplifications are made such that the generation $G_{n,p}$ at $t = 0^+$ after cessation of the impulse, is negligible. The electric field ξ in the bulk is also considered negligible:

$$\frac{\partial \Delta n(x, t)}{\partial t} = D_n \frac{\partial^2 \Delta n(x, t)}{\partial x^2} - U_n(x, t). \quad (6)$$

Consider the following expressions for the recombination rate $U_n(x, t)$ and the excess carrier concentration $\Delta n(x, t)$, which include the spatial dependence in the term $u(x, t)$:

$$U_n(x, t) = u(x, t) \times \left[\sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (j\omega_1 + u\omega_2 + v\omega_3) N_{j,u,v} E_{j,u,v}(t) \right], \quad (7)$$

$$\Delta n(x, t) = u(x, t) \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} E_{j,u,v}(t). \quad (8)$$

It remains to find an expression for $u(x, t)$.

The following are the boundary conditions due to the surface passivation where S is the surface recombination velocity and D_n is the diffusion constant. Consider both surfaces to be identically passivated such that they both have the same value of S .

$$D_n \frac{\partial \Delta n(x, t)}{\partial x} \bigg|_{x=-d/2} = S \Delta n(-d/2, t), \quad (9a)$$

$$-D_n \frac{\partial \Delta n(x, t)}{\partial x} \bigg|_{x=+d/2} = S \Delta n(+d/2, t), \quad (9b)$$

and where the boundary conditions transform to

$$D_n \frac{\partial u(x, t)}{\partial x} \Big|_{x=-d/2} = Su(-d/2, t), \quad (10a)$$

$$-D_n \frac{\partial u(x, t)}{\partial x} \Big|_{x=+d/2} = Su(+d/2, t). \quad (10b)$$

Using the principle of the separation of variables, the required solution of Eq. (6) is represented by

$$u(x, t) = X(x)T(t), \quad (11)$$

such that by substitution of Eq. (11) into Eq. (6) realizes expression Eq. (12), whereby the two functions of x and t can only attain equality if equal to a constant:

$$\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} = \frac{1}{D_n T(t)} \frac{dT(t)}{dt} = -\alpha^2. \quad (12)$$

The respective solutions become,

$$T(t) = e^{-\alpha^2 D_n t}, \quad (13)$$

$$X(x) = A \cos(\alpha x) + B \sin(\alpha x). \quad (14)$$

An equation for $u(x, t)$ (excess carriers) results from the separation of variables,¹¹ where the A_m and B_m are given in Ref.⁸. A linear superposition of solutions Eq. (11) is required to satisfy the boundary conditions Eq. (10). Each term in the summation (each value of m) satisfies the boundary conditions:

$$\begin{aligned} u(x, t) &= \sum_m u_m(x, t) \\ &= \sum_m \left[A_m e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right. \\ &\quad \left. + B_m e^{-\alpha_m^2 D_n t} \sin(\alpha_m x) \right]. \end{aligned} \quad (15)$$

Due to symmetry, the spatial dependence of excess carrier concentration $\Delta n(x, t)$ must be an even function of x , so $B_m \rightarrow 0$. However the boundary condition Eq. (10) must also be satisfied, requiring agreement of Eq. (15) and Eq. (10), resulting in Eq. (16), using the method for finding the coefficients of a Fourier series (see the Appendix of Ref.⁸):

$$\Delta u(x, t) = \sum_m \left[A_m(\lambda) e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right], \quad (16)$$

where

$$\begin{aligned} A_m(\lambda) &= \frac{4g'_0 \alpha_m e^{-\alpha_\lambda d/2} (1 + Re^{-\alpha_\lambda d})}{(\alpha_\lambda^2 + \alpha_m^2) [\alpha_m d + \sin(\alpha_m d)]} \\ &\times \left[\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) \cos\left(\frac{\alpha_m d}{2}\right) \right. \\ &\quad \left. + \alpha_m \cosh\left(\frac{\alpha_\lambda d}{2}\right) \sin\left(\frac{\alpha_m d}{2}\right) \right]. \end{aligned} \quad (17)$$

A general solution $\Delta n(x, t)$ is found by multiplying the impulse response given by Eq. (1) by that of Eq. (16), as shown in Eq. (18).

$$\begin{aligned} \Delta n(x, t) &= \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} E_{j,u,v}(t) \\ &\times \sum_m \left[A_m(\lambda) e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right]. \end{aligned} \quad (18)$$

Similarly, for the solution $U_n(x, t)$ given by Eq. (19).

$$\begin{aligned} U_n(x, t) &= \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} (j\omega_1 + u\omega_2 + v\omega_3) N_{j,u,v} E_{j,u,v}(t) \\ &\times \sum_m \left[A_m(\lambda) e^{-\alpha_m^2 D_n t} \cos(\alpha_m x) \right] \end{aligned} \quad (19)$$

It may be shown by substitution for each value of the mode of decay m that Eqs. (18) and (19) are a solution to the carrier continuity Eq. (6). These solutions include the spatial dependence, a term related to the diffusion of carriers to the surfaces and a recombination via the multiple-level defect term.

The value α_m is found by substituting Eq. (16) into one of Eq. (10), resulting in the following condition to be satisfied by the selection of an appropriate surface recombination velocity S .

$$\cot\left(\frac{\alpha_m d}{2}\right) = \frac{\alpha_m D_n}{S}. \quad (20)$$

The average excess carrier concentration is now sought. Integrating Eq. (18) with respect to x , Eq. (21), realizes an expression for the average density of minority carriers representing the impulse response given by Eq. (22):

$$\Delta n_{av}(t) = \frac{1}{d} \int_{-d/2}^{d/2} \Delta n(x, t) dx. \quad (21)$$

The integral Eq. (21) may be evaluated yielding the result in Eq. (22):

$$\begin{aligned}
\Delta n_{av}(t) = & \left[\sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t) \right] \\
& \times \frac{8g_o e^{-\alpha_\lambda d/2}}{d} \sum_m \frac{\sin(\alpha_m d/2)}{(\alpha_\lambda^2 + \alpha_m^2) [\alpha_m d + \sin(\alpha_m d)]} \\
& \times \left[\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) \cos\left(\frac{\alpha_m d}{2}\right) + \alpha_m \cosh\left(\frac{\alpha_\lambda d}{2}\right) \sin\left(\frac{\alpha_m d}{2}\right) \right] e^{-(\alpha_m^2 D_n)t}.
\end{aligned} \tag{22}$$

As $S \rightarrow \infty$, from Eq. (20), $\alpha_m d/2 = \pi/2, 3\pi/2, 5\pi/2, \dots$, such that for $m = 1, 2, 3, \dots$, α_m is given by Eq. (23):

$$\alpha_m = \frac{(2m-1)\pi}{d}. \tag{23}$$

The average density of minority carriers representing the impulse response for $S \rightarrow \infty$, is given by Eq. (24) with $m = 1, 2, 3, \dots$, being the mode of decay:

$$\begin{aligned}
\Delta n_{av}(t) = & \left[\sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t) \right] \\
& \times \frac{8g_o e^{-\alpha_\lambda d/2}}{d} \sum_{m=1}^{\infty} \frac{\sin(\alpha_m d/2)}{(\alpha_\lambda^2 + \alpha_m^2) [\alpha_m d + \sin(\alpha_m d)]} \\
& \times \left[\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) \cos\left(\frac{\alpha_m d}{2}\right) + \alpha_m \cosh\left(\frac{\alpha_\lambda d}{2}\right) \sin\left(\frac{\alpha_m d}{2}\right) \right] e^{-(\alpha_m^2 D_n)t}.
\end{aligned} \tag{24}$$

The initial average minority carrier profile is exponential with a peak at $x = -d/2$ normal to the incidence of light.

For the case where the surface recombination velocity S approaches zero in the limit, the condition given by Eq. (20) indicates that $\alpha_m d/2 = 0, 2\pi, 4\pi, 6\pi, \dots$, and all the terms in the summation of Eq. (22) vanish except for $\alpha_m d/2 = 0$. The mode of decay is $m = 0$. This results in an indeterminate form for the limit, which is solved by the use of L'Hopital's rule. The result for the $S = 0$, the case given by Eq. (25), indicates that only the bulk term is involved in the decay.

$$\begin{aligned}
\lim_{\alpha_0 \rightarrow 0} \Delta p_{av}(t) = & \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} P_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t) \\
& \times \left[\frac{4g_o \alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) e^{-\alpha_\lambda d/2}}{d} \right].
\end{aligned} \tag{26}$$

Note that the coefficient of the exponential terms contains the absorption coefficient α_λ , which is related to the wavelength of the incident light. The expressions for average decay indicate that the fundamental frequencies are unaffected by the absorption coefficient.

III. GROUND AND EXCITED STATE SYSTEM: FUNDAMENTAL FREQUENCIES ω_{k+1}

$$\begin{aligned}
\lim_{\alpha_0 \rightarrow 0} \Delta n_{av}(t) = & \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t) \\
& \times \left[\frac{4g_o \alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) e^{-\alpha_\lambda d/2}}{d} \right],
\end{aligned}$$

As mentioned in Ref.³ consider a defect energy level E_{gnd} representing the ground state with an excited state E_x in the band gap of an n-type semiconductor. The set of linear equations representing the ground excited

state system are Eqs. (27) with the differential operator $D = d/dt$, where C_{gx}^n , C_{gx}^p , C_{xg}^n and C_{xg}^p are constants related to the carrier transitions between states. The

values of f_{og} and f_{ox} are determined from $df_g/dt = 0$ and $df_x/dt = 0$, respectively:

$$\begin{bmatrix} [D + (\gamma_{(g)} - \sigma_{(g)}) + (\gamma_{(x)} - \sigma_{(x)})] & 0 & -\sigma_{(g)} & -\sigma_{(x)} \\ -(\gamma_{(g)} - \sigma_{(g)}) & (\alpha_{(g)} - \beta_{(g)}) & \{ [D + (\sigma_{(g)} + \beta_{(g)})] + N_{t(g)} \left[\frac{C_{(xg)}^n f_{og}}{f_{ox}} + C_{(xg)}^p \frac{(1-f_{ox})}{(1-f_{og})} \right] \} & -N_{t(g)} \left[\frac{C_{(xg)}^p f_{og}}{f_{ox}} + C_{(xg)}^n \frac{(1-f_{og})}{(1-f_{ox})} \right] \\ -(\gamma_{(x)} - \sigma_{(x)}) & (\alpha_{(x)} - \beta_{(x)}) & -N_{t(x)} \left[\frac{C_{(gx)}^p f_{ox}}{f_{og}} + C_{(gx)}^n \frac{(1-f_{og})}{(1-f_{ox})} \right] & \{ [D + (\sigma_{(x)} + \beta_{(x)})] + N_{t(x)} \left[\frac{C_{(gx)}^n f_{og}}{f_{ox}} + C_{(gx)}^p \frac{(1-f_{ox})}{(1-f_{og})} \right] \} \\ 1 & -1 & 1 & 1 \end{bmatrix} \begin{bmatrix} \Delta n_{nm}(t_0) \\ \Delta p_{nm}(t_0) \\ \Delta f_g(t_0) \\ \Delta f_x(t_0) \end{bmatrix} = 0, \quad (27)$$

where constants $\eta_{n(g,x)}(t_0)$ and $\eta_{p(g,x)}(t_0)$ in Eq. (28) may be evaluated as in Ref.²:

$$\alpha_{(g,x)} = C_{v(g,x)}^p N_{t(g,x)} \left[\frac{p_{1(g,x)}}{p_{po} + p_{1(g,x)}} + \frac{p_{po} + p_{1(g,x)}}{N_{t(g,x)}} + \frac{\eta_{p(g,x)}(t_0) \Delta p(0)}{N_{t(g,x)}} \right], \quad (28a)$$

$$\beta_{(g,x)} = C_{v(g,x)}^p N_{t(g,x)} \left[\frac{p_{po} + p_{1(g,x)}}{N_{t(g,x)}} + \frac{\eta_{p(g,x)}(t_0) \Delta n(0)}{N_{t(g,x)}} \right], \quad (28b)$$

$$\gamma_{(g,x)} = C_{c(g,x)}^n N_{t(g,x)} \left[\frac{n_{1(g,x)}}{n_{po} + n_{1(g,x)}} + \frac{n_{po} + n_{1(g,x)}}{N_{t(g,x)}} + \frac{\eta_{n(g,x)}(t_0) \Delta n(0)}{N_{t(g,x)}} \right], \quad (28c)$$

$$\sigma_{(g,x)} = C_{c(g,x)}^n N_{t(g,x)} \left[\frac{n_{po} + n_{1(g,x)}}{N_{t(g,x)}} + \frac{\eta_{n(g,x)}(t_0) \Delta p(0)}{N_{t(g,x)}} \right], \quad (28d)$$

with

$$n_{1g} = N_c \exp \left(-\frac{(E_c - E_{gnd})}{kT} \right), \quad (29a)$$

$$p_{1g} = N_v \exp \left(-\frac{(E_{gnd} - E_v)}{kT} \right), \quad (29b)$$

$$n_{1x} = N_c \exp \left(-\frac{(E_c - E_x)}{kT} \right), \quad (29c)$$

$$p_{1x} = N_v \exp \left(-\frac{(E_x - E_v)}{kT} \right). \quad (29d)$$

The method using the differential operator D , as in Refs.¹² and¹³ whereby the determinant of the matrix of Eqs. (27) equals zero, allows the formation of the characteristic equation:

$$(D^3 + bD^2 + cD + d) \exp(-\omega t) = 0 \quad (30)$$

The fundamental frequencies $\omega_{1,2,3}$ (inverse time constants) may be evaluated by solving for the three roots of Eq. (31):

$$-\omega^3 + b\omega^2 - c\omega + d = 0 \quad (31)$$

with the frequencies given by $\omega_1 = 1/\tau_1$, $\omega_2 = 1/\tau_2$ and $\omega_3 = 1/\tau_3$.

Following the analysis in Refs.^{2,3}, and¹⁴, the following equations for the excess carrier concentrations $\Delta n_{av}(t)$, Eq. (32), and $\Delta p_{av}(t)$, Eq. (33), may be written for the multiple-level or ground excited state system. There are three fundamental time constants:

$$\Delta n_{av}(t) = \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} N_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t) \times \left[\frac{4g_o \alpha_\lambda \sinh \left(\frac{\alpha_\lambda d}{2} \right) e^{-\alpha_\lambda d/2}}{d} \right], \quad (32)$$

and

$$\Delta p_{av}(t) = \sum_{j=0}^{\infty} \sum_{u=0}^{\infty} \sum_{v=0}^{\infty} P_{j,u,v} \exp(-j\omega_1 t - u\omega_2 t - v\omega_3 t) \times \left[\frac{4g_o\alpha_\lambda \sinh\left(\frac{\alpha_\lambda d}{2}\right) e^{-\alpha_\lambda d/2}}{d} \right]. \quad (33)$$

Equations (32) and (33) indicate that for ideal surface passivation ($S = 0$) there is an infinity of exponential terms in the decay and the frequencies are a linear combination of the fundamental frequencies.

IV. EXPERIMENTAL CONSTRAINTS

In Secs. II and III the theoretical analysis reveals that for ideally passivated surfaces ($S = 0$) the fundamental frequencies may be determined from the average decay. Furthermore, the diffusion term vanishes due to conditions imposed on the modes of decay. For this case of a very low surface recombination velocity ($S \approx 0$) the modes of decay are restricted to $m = 0$. Also, in the previous Sec. III, it is shown that for average decay the fundamental time constants are unaffected by the wavelength of light. The absorption coefficient only affects the magnitudes of the coefficients of the exponential terms in the decay. For the purpose of illustrating the range of excess carrier concentrations over which the fundamental frequencies may be measured, an impulse of light $N_o\delta(t)$, with a single wavelength and a energy slightly greater than the band gap, is chosen to represent the light source. In the limit of weak absorption, an impulse of light $\delta(t)$ generates a uniform excess carrier concentration in the semiconductor material where $\Delta n(0)$ and $\Delta p(0)$ are equal and represent the photoexcited excess carrier density. The relative change in conductivity of sample wafers of different resistivity when photoexcited, defines a criteria for decay detection by a microwave or inductively coupled detector. Low resistivity ρ implies high conductivity σ and the relative change $\Delta\sigma/\sigma$ may be small:

$$\Delta\sigma = \int_{-d/2}^{d/2} q(\mu_n\Delta n(x,t) + \mu_p\Delta p(x,t))dx. \quad (34)$$

For sufficiently small $\Delta p(0)$ (n-type silicon) the contribution to conductivity in the majority band is negligible as opposed to the sudden increase in minority carriers above the equilibrium concentration in the minority band [for n-type $\Delta p(0) \ll n_{p0}$]. As the photoconductivity perturbation $\Delta\sigma$ is small compared to the wafer conductivity, the time dependence of the microwave signal is the same as the average excess carrier density $\Delta p_{av}(x,t)$ proportional to $\Delta\sigma$. Although the microwave reflectance is a nonlinear function of wafer conductivity, the above is true for high ($\rho = 0.2\Omega\text{cm}^2$) and low ($\rho = 100\Omega\text{cm}^2$)

conductivity samples considered here where the values in brackets represent resistivity. The difference is that for high conductivity wafers, high-order modes of decay⁸ ($m \gg 1$) decay much faster and are not observed by the microwave system. As the excess carrier concentration is increased the contribution to conductivity of the majority band is not negligible and both carriers contribute to the conductivity $\Delta\sigma$ as in Eq. (34).

After the optical excitation pulse in the absence or low concentration of discrete levels (trapping centers), the decrease in the average minority carrier concentration and subsequent observed decay is determined by bulk and surface recombination and diffusion of carriers to the surfaces. The average carrier concentration, proportional to the sheet conductance of the wafer, decays with a characteristic time constant τ_m for a given surface recombination velocity $S \gg 1\text{ cm/s}$. This volume integrated concentration is measured by the microwave reflectance photoconductance decay method⁸. Equation (32) represents the impulse response with $k+1$ fundamental frequencies due to $k=2$ multiple defect levels in the band gap for $S=0$, indicating that only the three fundamental time constants are involved in the decay.

Analysis of the decay for τ_{k+1} , the fundamental time constants, is performed using a multitransient technique. Multi-transient analysis refers to the extraction of component exponential terms from a sum of exponentials comprising the signal. The methods available, as in Refs.^{15,16,17} present a means of analyzing signals with additive white Gaussian noise. In addition, where the data matrix and the observation matrix may be subject to noise fluctuations, the total least squares method Van Huffel¹⁸ (TLS) is employed. This method models the multiexponential signal as an autoregressive process. For the present analysis the TLS method of Refs.¹⁷ and¹⁹ multitransient analysis, using singular value decomposition (SVD),²⁰ is applied to the analysis of the multicomponent exponential decay.

From Eq. (34), increasing the excess carrier concentration in the sample means that both $\Delta n(t)$ and $\Delta p(t)$ contribute to the conductivity $\Delta\sigma$. However, from the present work, both quantities contain the same decay constants Eqs. (32) and (33). Hence, the decay may be analyzed for τ_1 with arbitrary excess carrier concentration. Ideally, the range of excess carrier concentration should encompass the linear (constant) region and the nonlinear region of variation of τ_1 with excess carrier concentration. Longer minority carrier time constants (τ_1) indicate lower defect level effects and an estimate of the linear region of τ_1 with excess carrier concentration realizes a range of excess carrier concentration before the onset of trapping.

V. EXPERIMENTAL CONDITIONS

Experimental conditions for determining bulk decay are discussed below. Specifically, with regard to a n-type

Cz silicon wafer, a uniform excess carrier concentration may be generated within a sample of $400\ \mu\text{m}$ thickness⁸ by light of a wavelength of the order of $1\ \mu\text{m}$. For a light source with multiple wavelengths, whether it be blue light (strongly absorbing) or infrared light (weakly absorbing), a variation in generation of excess carrier concentration is expected at the surface with respect to the bulk. The high excess carrier concentration generated at the surface produces a long time constant τ_{long} contribution given a good surface passivation. This is due to trapping at bulk states near the surface (see Ref.² for an explanation of minority carrier trapping). From Eq. (35) it may be seen that the effective time constant τ_e is that of the bulk states τ_{short} away from the surface, which is shorter.

$$\frac{1}{\tau_e} = \frac{1}{\tau_{\text{long}}} + \frac{1}{\tau_{\text{short}}}, \quad (35a)$$

$$\tau_e \approx \tau_{\text{short}}. \quad (35b)$$

Simulations indicate that the infrared light produces a near uniform excess carrier concentration away from the surface in the bulk. The light source produces the initial condition $\Delta n(0) = \Delta p(0)$ at $t = 0^+$. A low surface recombination velocity may be attained with the $\text{Si} - \text{SiO}_2$ system as in Ref.²¹. A phosphorus surface diffusion (n type) of Ref.²² or boron surface diffusion (p type) of Ref.²³ provides a surface field that limits the injection of carriers into the surface states. However it may be modulated by the excess carrier concentration, so the effective surface recombination velocity is taken to be injection level dependent in Refs.²¹ and ²⁴. A subsequent oxidation step²² provides the surface passivation. For excess carrier concentrations $1 \times 10^8\ \text{cm}^{-3}$ to $1 \times 10^{16}\ \text{cm}^{-3}$ an $S_{\text{eff}} < 50\ \text{cm/s}$ is assumed to be attainable with appropriate processing with the $\text{Si} - \text{SiO}_2$ system for a wafer resistivity of the order of $5\ \Omega\text{cm}$ ($5 \times 10^{14}\ \text{cm}^{-3}$ doping density). This value of the surface recombination velocity is an upper limit with the value of S_{eff} decreasing with increasing excess carrier concentration from the injection level dependence of S_{eff} . The decay of excess carriers may be detected by a contactless microwave as in Ref.²⁵ or inductively coupled as in Ref.²⁶ photoconductance measurement.

VI. EXPERIMENTAL RESULTS

The following is the author's experimental results. As indicated in the Introduction, three candidate complexes are considered for assessment as to the unusually long lifetime of the Cz silicon sample by application of the theory developed in Ref.³. This theory describes the decay due to pulse of light for the coupled levels system in terms of the fundamental frequencies $\omega_1 = 1/\tau_1$, $\omega_2 = 1/\tau_2$ and $\omega_3 = 1/\tau_3$. The first defect complex is the carbon interstitial-oxygen interstitial $C_i - O_i$ complex Ref.⁷, the second is the vacancy-oxygen $V - O$ complex

Ref.⁷ and the third is the phosphorus donor (n type) and the ground state of the $V - O$ complex or $C_i - O_i$ complex Ref.⁶. These complexes have energy levels near the band edges, which may give rise to the long lifetime.

The resistivity of the n-type Cz silicon sample is $5.5\ \Omega\text{cm}$ which corresponds to a doping concentration, N_D , of $8.34 \times 10^{14}\ \text{cm}^{-3}$. An n^+ surface diffusion is performed as in Ref.²², followed by an oxidation step. The thickness of the wafer is $411\ \mu\text{m}$. The photoconductance measurement is performed with an inductively coupled system similar to Ref.²⁶ except that the frequency is lower (8-10 MHz) and the light source is a tungsten flash. The major component in terms of intensity, in a tungsten flash, is infrared light. This light is assumed to generate near-uniform excess carrier concentration throughout the thickness of the wafer except near the surface. The dominant time constants are expected to be that of the bulk states away from the surface (see Sec. V). Furthermore, the silicon sample is not subjected to high energy radiation of electrons, which would be expected to create vacancies in the silicon lattice as in Ref.⁷.

The first fit of experimental data by theoretical values of τ_1 and τ_2 Eq. (31), determined by adjusting excited state defect parameters, is shown in Fig. 1. The defect parameters adjusted were the defect concentration, N_t , the electron and hole cross sections, σ_{nx} and σ_{px} , respectively, for the excited state and the electron and hole cross sections; and σ_{ng} and σ_{pg} respectively, for the ground state, shown in Table I. Energy levels for this coupled state system correspond to the carbon interstitial-oxygen interstitial complex ($C_i - O_i$)⁷, with $E_c - E_x = 0.04\ \text{eV}$ for the excited state, and $E_c - E_g = 0.84\ \text{eV}$, for the ground state. From Fig. 1 the agreement is good for τ_1 and τ_2 with the adjusted parameters of Table I. Experimental data for τ_3 could not be determined because this time constant is very short.

A fit of theory for the ground excited state system of Table II, corresponding to the vacancy-oxygen complex ($V - O$)⁷ is shown in Fig. 2. Again, the concentration N_t and cross sections of the defect were adjusted to provide as close a fit to the experimental data with the theoretical values of τ_1 and τ_2 , Eq. (31). The energy levels for the $V - O$ complex are $E_c - E_x = 0.17\ \text{eV}$ for the excited state, and $E_c - E_{\text{gnd}} = 0.76\ \text{eV}$, for the ground state. From Fig. 2 agreement is relatively poor for τ_1 as the theoretical curve enters a trapping region. This is because at low excess carrier concentrations the minority carrier is the major contributor to the decay, which corresponds to τ_1 . At higher excess carrier concentrations the time constant τ_1 is becoming longer, indicating that for the n-type silicon there are fewer electrons at the defect levels to recombine with. Hence, the minority carrier holes are accumulating or being trapped at the defect levels. Experimental data points do not follow this trapping behavior. It is concluded that the vacancy-oxygen complex is not a major contributor to the decay. This is to be expected since the silicon sample did not undergo radiation with high energy electrons to create

vacancies in the silicon lattice. A fast time constant τ_3 , shown in Fig. 2, could not be resolved by the contactless photoconductance method because the sampling time is too large.

A fit of the experimental data with theory for the phosphorus donor with a concentration of $8.34 \times 10^{14} \text{ cm}^{-3}$ and cross sections $\sigma_p = 5 \times 10^{-21} \text{ cm}^2$ and $\sigma_n = 5 \times 10^{-15} \text{ cm}^2$ and ground states of the complexes could not be achieved. The phosphorus donor lies at an energy level $E_c - E_D = 0.045 \text{ eV}$. The ground states were $E_c - E_t = 0.17 \text{ eV}$ and $E_c - E_t = 0.76 \text{ eV}$, corresponding to the vacancy-oxygen complex and $E_c - E_t = 0.84 \text{ eV}$, corresponding to the carbon interstitial-oxygen interstitial complex⁷.

VII. DISCUSSION

Given a silicon wafer sample with a well-passivated surface, the fundamental time constants τ_1 and τ_2 may be determined from the photoconductance decay by multi-transient analysis. A relatively long time constant is attributed to defect levels near the band edges. Examples of coupled levels used to fit the experimental data have levels near the band edges. A consistent fit to the experimental data is provided by the $C_i - O_i$ complex. The vacancy-oxygen complex $V - O$ shows trapping behavior which is not apparent in the experimental data. The phosphorus $V - O$ ground state complex could not be fitted to the data given the concentration of the doping concentration N_D and the much smaller ground state concentrations of the $C_i - O_i$ and $V - O$ complexes. Also, the history of the silicon sample indicates that it is unlikely to have a high vacancy concentration. This indicates that the $V - O$ complex is less likely than the $C_i - O_i$ complex. A plot of the fundamental time constants versus excess carrier concentration may be a method of identifying a

defect species.

The small concentration of the defects ($5 \times 10^{-6} \text{ cm}^{-3}$) determined from the fit, is consistent with the theory of Ref.³ for the ground excited state system. The dip in τ_1 of the experimental data points, at higher excess carrier concentration, is attributed to the beginning of Auger recombination.

VIII. CONCLUSIONS

This work introduces the solution of the carrier continuity equation, which includes multiple defect levels in the carrier recombination terms. The recombination term is expressed as an infinite number of exponential terms with frequencies which are multiples of fundamental frequencies. The resulting expressions for the excess carrier concentrations $\Delta n_{av}(x, t)$ and $\Delta p_{av}(x, t)$, may be readily formulated by analyzing the decay for a well passivated surface ($S = 0$) for τ_1 and τ_2 , the fundamental time constants. Simplifications are made which reflect the experimental situation envisaged to carry out a simple contactless photoconductance decay measurement. A silicon Cz wafer with both surfaces well passivated is shown to yield consistent experimental time constants, with an exact theory.

Acknowledgments

The Special Research Centre of Excellence for Advanced Silicon Photovoltaics and Photonics is supported by the Australian Research Council's Special Research Centres scheme. The author's appreciation is extended to Dr. J. Zhao for supplying the silicon sample and Dr. R. Corkish for helpful discussions.

- ¹ W. Shockley and W. T. Read. *Phys. Rev.*, **87**:835, (1952).
- ² D. Debuf, Y. Shrivastava, and A. Dunn. *Phys. Rev. B*, **65**:245211, (2002).
- ³ D. Debuf. *unpublished*, (2003).
- ⁴ S. M. Sze. *Physics of Semiconductor Devices*. (Wiley And Sons, New York 2nd Ed. p30, 1981).
- ⁵ S. M. Sze. *Physics of Semiconductor Devices*. (Wiley And Sons, New York 2nd Ed. p29, 1981).
- ⁶ W. M. Chen, B. Monemar, E. Janzen, and J. L. Lindstrom. *Phys. Rev. Lett.*, **67**:1914, (1991).
- ⁷ A. M. Frens, M. T. Bennebroek, A. Zakrzewski, J. Schmidt, W. M. Chen, , E. Janzen, J. L. Lindstrom, and B. Monemar. *Phys. Rev. Lett.*, **72**:2939, (1994).
- ⁸ K. L. Luke and L. J. Cheng. *J. Appl. Phys.*, **61** (6):2282-2293, 1987.
- ⁹ G. K. Wertheim. *Phys. Rev.*, **109**:1086, 1958.
- ¹⁰ S. M. Sze. *Physics of Semiconductor Devices*. (Wiley And Sons, New York 2nd Ed. p51, 1981).
- ¹¹ J. P. McKelvey. *Solid State and Semiconductor Physics*.

- Harper and Row, New York, Evanston and London, 1966.
- ¹² D. W. Jordan and P. Smith. *Nonlinear Ordinary Differential Equations An Introduction to Dynamical Systems*. (Oxford University Press, Oxford p63, 1999).
- ¹³ E. Kreyszig. *Advanced Engineering Mathematics*. (Wiley And Sons, New York p89, 1988).
- ¹⁴ S. C. Choo. *Phys. Rev. B*, **1**:687, (1970).
- ¹⁵ E. Yeramian and P. Claverie. *Nature*, **326**:169, (1987).
- ¹⁶ P. Claverie, A. Denis, and E. Yeramian. *Comp. Phys. Rep.*, **9**:247, (1989).
- ¹⁷ J. Alam. Master's thesis, (The University of Calgary, Alberta, Canada, 1990).
- ¹⁸ S. Van Huffel and Vandewalle J. *The Total Least Squares Problem Computational Aspects and Analysis*. (Society for Industrial and Applied Mathematics SIAM, Philadelphia, 1991).
- ¹⁹ D. R. Debuf. Master's thesis, (The University of New South Wales, Sydney, Australia, 1993).
- ²⁰ V. J. Klema and A. J. Laub. *IEEE Trans Automatic Con-*

- trol, **AC-25:164**, (1980).
- ²¹ A. G. Aberle, S. Glunz, and W. Warta. *J. Appl. Phys.*, **71:4422**, (1992).
 - ²² R. R. King, R. A. Sinton, and R. M. Swanson. *IEEE Trans. Elect. Dev.*, **37:365**, (1990).
 - ²³ R. R. King and R. M. Swanson. *IEEE Trans. Elect. Dev.*, **38:1399**, (1991).
 - ²⁴ J. Schmidt and A. G. Aberle. *J. Appl. Phys.*, **85:3626**, (1999).
 - ²⁵ P. A. Basore and B. R. Hansen. Microwave detected photoconductance decay. *21st IEEE Photovoltaic Specialists Conference*, 1990.
 - ²⁶ R. K. Ahrenkiel and S. Johnston. *26th IEEE Photovoltaic Specialists Conference Sept 29 - Oct 3, Anaheim, California*, (1997).

TABLE I: Defect level parameters used for the fit of experimental data of the ground excited state system, for Cz sample 6-1, (carbon interstitial - oxygen interstitial).

Parameter	Ground state	Excited state
$E_c - E_x$ energy depth from conduction band [eV]		0.04
$E_c - E_{gnd}$ energy depth [eV]	0.84	
N_t discrete level concentration [cm^{-3}]	5×10^6	5×10^6
σ_p cross section for holes [cm^2]	$\sigma_{vg}^p = 4.5 \times 10^{-19}$	$\sigma_{vx}^p = 6.5 \times 10^{-9}$
σ_n cross section for electrons [cm^2]	$\sigma_{cg}^n = 2.5 \times 10^{-20}$	$\sigma_{cx}^n = 8.5 \times 10^{-15}$

TABLE II: Defect level parameters used for the fit of experimental data of the ground excited state system, for Cz sample 6-1, (vacancy - oxygen complex).

Parameter	Ground state	Excited state
$E_c - E_x$ energy depth from conduction band [eV]		0.17
$E_c - E_{gnd}$ energy depth [eV]	0.76	
N_t discrete level concentration [cm^{-3}]	2.8×10^4	2.8×10^4
σ_p cross section for holes [cm^2]	$\sigma_{vg}^p = 7.5 \times 10^{-19}$	$\sigma_{vx}^p = 6.5 \times 10^{-9}$
σ_n cross section for electrons [cm^2]	$\sigma_{cg}^n = 2.5 \times 10^{-19}$	$\sigma_{cx}^n = 8.5 \times 10^{-13}$

Figure Captions

FIG. 1. Graph of $\tau_1 = 1/\omega_1$, $\tau_2 = 1/\omega_2$, and $\tau_3 = 1/\omega_3$ for the excited state system of $C_i - O_i$ (carbon interstitial - oxygen interstitial) vs excess carrier concentration $\Delta n(0) = \Delta p(0)$. The doping concentration N_D of the sample is $8.34 \times 10^{14} \text{ cm}^{-3}$. See Table I for defect level parameters. Continuous line: fit of τ_1 and τ_2 determined from the characteristic Eq. (31), to the experimental data. Circles: experimental data for n-type Cz sample

6_1.

FIG. 2. Graph of $\tau_1 = 1/\omega_1$, $\tau_2 = 1/\omega_2$, and $\tau_3 = 1/\omega_3$ for the excited state system of $V - O$ (vacancy - oxygen complex) vs excess carrier concentration $\Delta n(0) = \Delta p(0)$. The doping concentration N_D of the sample is $8.34 \times 10^{14} \text{ cm}^{-3}$. See Table II for defect level parameters. Continuous line: fit of τ_1 and τ_2 determined from the characteristic Eq. (31), to the experimental data. Circles: experimental data for n-type Cz sample 6_1.

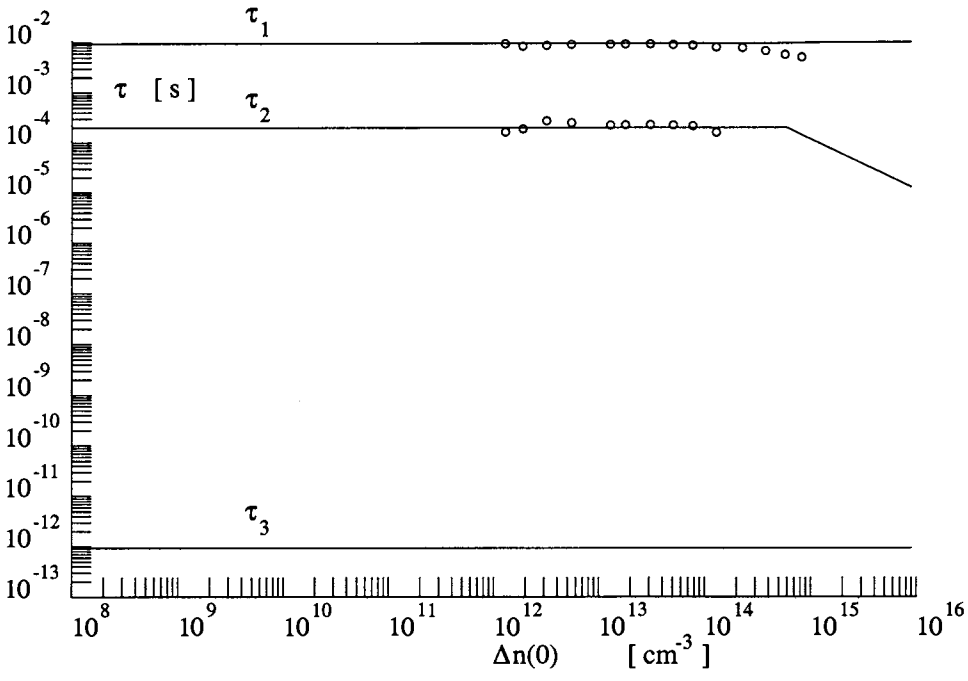


FIG. 1: Didier Debuf, J. Appl. Phys.

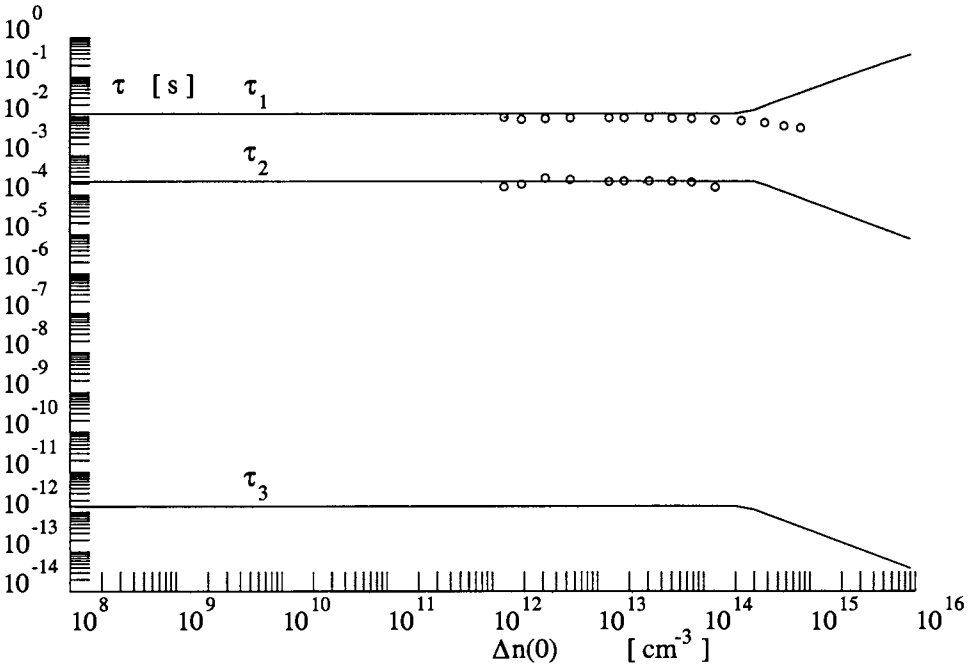


FIG. 2: Didier Debuf, J. Appl. Phys.

K.2 Publications submitted to Refereed Journals

- General theory of carrier lifetime with multiple localised defect states
in semiconductors

Didier Debuf

submitted to Phys. Rev. B May 2 (2002)

- Accuracy of the Shockley-Read-Hall time constant for a
single-level defect species

Didier Debuf, Yash Shrivastava, Richard Corkish

submitted to Phys. Rev. Lett. Dec 22 (2002)

resubmitted to Phys. Rev. B (2003)

- Accuracy of semiconductor multiple-level-defect measurements

Using Deep Level Transient Spectroscopy

Didier Debuf, Peter H Ladbrooke

submitted to Phys. Rev. Lett. (2003)

Accuracy of the Shockley-Read-Hall Time Constant for a Single-Level Defect Species

Didier Debuf*

*Centre of Excellence for Advanced Silicon Photovoltaics and Photonics,
The University of New South Wales, Sydney NSW 2052, Australia*

Yash Shrivastava†

*School of Electrical and Information Engineering,
The University of Sydney, Sydney NSW 2006, Australia*

Richard Corkish‡

*Centre of Excellence for Advanced Silicon Photovoltaics and Photonics,
The University of New South Wales, Sydney NSW 2052, Australia*

(Dated: July 22, 2003)

The recent analytic solution to the Shockley-Read-Hall (SRH) rate equations for the transient case is derived without an approximation for near equilibrium and non-equilibrium situations. The method of this solution is applied to derive a new steady state solution. It is shown that the resulting two time constants or eigenvalues of the linear system, are in agreement with the order of the underlying second order differential equation. In this work we describe the nature of the approximation in the original SRH work that leads to one time constant and compare the approximation, the new exact solution and the analysis of the numerical solution for component time constants. The new exact solution is in agreement with the analysis of the numerical solution. Furthermore, this solution is shown to unify the work of previous authors for the single-level defect and small departures of carrier concentration from equilibrium (small signal).

PACS numbers: 72.20.Jv, 72.40.+w, 85.30.De

I. INTRODUCTION

A dominant recombination mechanism in semiconductors, apart from Auger recombination, is Shockley-Read-Hall (SRH) recombination as described by the SRH rate equations in 1952 [1] [2]. Shockley and Read developed an expression for the recombination time constant in the steady state τ_{ss} . Although developed for the steady state, the theory has been applied to the transient case in the neighbourhood of the equilibrium point (small signal) and the time constant is referred to as τ_b . This applies to a single-level defect although in practical situations multiple defect levels occur. These rate equations have been applied to the analysis of experimental data assuming a dominant defect energy level. The literature indicates conflicting partial solutions to the rate equations, notably the expression with a single time constant [1] which is defined as (1), where U represents the recombination rate, and expressions of several authors with two time constants, indicated below.

$$\tau_{ss} = \frac{\Delta n}{U} \quad (1)$$

The focus of the present work is to show that the SRH expression is an approximation, indicate the source of the approximation which for the given example amounts to

a relative error of thirty percent, and resolve the conflicting issues. The recent general analytic method of solution [3], for the transient case developed without an approximation, is applied to the SRH rate equations (2) to obtain a new steady state solution. This solution is compared to the existing steady state SRH time constant expression.

$$-\frac{dp(t)}{dt} = C_p N_t p(t) f(t) - e_p N_t (1 - f(t)) \quad (2a)$$

$$-\frac{dn(t)}{dt} = C_n N_t n(t) (1 - f(t)) - e_n N_t f(t) \quad (2b)$$

In Eq. (2), N_t is the defect concentration, $n(t)$, $p(t)$ are the electron and hole concentrations respectively, $f(t)$ is the defect occupancy function or probability function, C_n and C_p are the electron and hole capture coefficients and, e_n and e_p are the electron and hole emission rates.

In the present work the theoretical predictions of time constants from the analytic solution are compared with the analysis of the numerical solution for component time constants in the steady state case. Good agreement is found for this comparison. Previous analyses in the literature have assumed the validity of the single time constant expression (3) (Eq. 5.3 of Ref. [1]) derived from Eq. (1) without such a comparison.

$$\tau_{ss} = \frac{(n_{p0} + n_1 + \Delta n)}{C_p N_t (n_{p0} + p_{p0} + \Delta n)} + \frac{(p_{p0} + p_1 + \Delta p)}{C_n N_t (n_{p0} + p_{p0} + \Delta n)} \quad (3)$$

*Electronic address: didier@ee.usyd.edu.au

†Electronic address: yash@ee.usyd.edu.au

‡Electronic address: R.Corkish@unsw.edu.au

It is shown that the definition, Eq. (1), leads to an incorrect theoretical prediction of one time constant τ_{ss} of Eq. (3) for the steady state whereas at least two time constants are predicted by the analytic steady state theory presented in this work. This indicates that the definition Eq. (1) is not related to the physics of the carriers.

The present work demonstrates that the steady state solution, determined both analytically and by analysis of the numerical solution, converges to the transient solution of Ref. [3] in the small signal transient limit. This confirms the transient and steady state multiple time constant solutions to be consistent. The single SRH time constant τ_{ss} of Eq. (3) is inaccurate which implies from Eq. (1) that the recombination term $U = \Delta n / \tau_{ss}$ is also inaccurate. In the literature this recombination term is included in the carrier continuity equation which describes the flux of carriers into and out of a volume of semiconductor. Within the volume there may be recombination and generation. The definition of Eq. (1) leads to a recombination term, which at best is convenient as a means to represent the SRH equations in the carrier continuity equation in a mathematical context, is however not physically meaningful.

A brief survey of developments related to the partial solutions of the SRH rate equations follows. A partial solution to the rate equations [4] yielded two time constants written in terms of a "recombination time", "a time to trap a carrier" and "a time to release a trapped carrier". In this case the recombination time constant is defined as in (1). In [5] the defect problem is addressed with approximations introduced to elucidate the different features of types of defects. For the transient case, an approximate solution of [6], yields two time constants comprising an initial decay and a transient decay. A set of differential rate equations for multiple discrete levels based on a summation of the single level SRH equations is stated in [7]. Approximations were introduced to provide a linear solution to the non-linear differential equations for small changes in Δp and Δn from the equilibrium values. For the single-level, two time constants result from this solution for the transient case which were simplified to one time constant and an "adjustment time" which agree with [6].

In [8] approximations were applied to the solution not of the rate equations but to the second order differential equation in Δp (4) that results from the rate equations

and the charge neutrality condition.

$$\begin{aligned} & \frac{N_t}{p_o} \left\{ y'' \left(y + 1 + \frac{p_1}{p_o} \right) - y'^2 \left(1 - \frac{C_n}{C_p} \right) \right\} \\ & + y' \left\{ y^2 \left(1 + \frac{C_p}{C_n} \right) + y \left[\left(1 + \frac{p_1}{p_o} \right) \left(1 + \frac{n_1}{p_o} + \frac{2C_p}{C_n} \right) \right. \right. \\ & \quad \left. \left. + \frac{N_t}{p_o} \left(1 + \frac{2p_1}{p_o} \right) / \left(1 + \frac{p_1}{p_o} \right) \right] \right\} \\ & + \left[\left(1 + \frac{p_1}{p_o} \right)^2 \left(\frac{n_1}{p_o} + \frac{C_p}{C_n} \right) + \frac{N_t}{p_o} \left(1 + \frac{C_p p_1}{C_n p_o} \right) \right] \left\{ \right. \\ & + y \frac{C_p}{C_n} \left\{ y^2 + y \left[\left(2 + \frac{p_1}{p_o} + \frac{n_1 p_1}{p_o p_o} \right) + \frac{N_t p_1}{p_o p_o} / \left(1 + \frac{p_1}{p_o} \right) \right] \right. \\ & \quad \left. \left. + \left[\left(1 + \frac{p_1}{p_o} \right) \left(1 + \frac{n_1 p_1}{p_o p_o} \right) + \frac{N_t p_1}{p_o p_o} / \left(1 + \frac{p_1}{p_o} \right) \right] \right\} \right\} \\ & = 0 \end{aligned} \quad (4)$$

where $y = \Delta p / p_o$ and similarly for Δn and,

$$n_1 = N_c \exp \left(- \frac{(E_c - E_t)}{kT} \right) \quad (5a)$$

$$p_1 = N_v \exp \left(- \frac{(E_t - E_v)}{kT} \right) \quad (5b)$$

As pointed out by [8], all previous methods of solution of (4) including perturbative methods, were unsuccessful in yielding a solution. For this reason previous attempts at solving the rate equations have inherently involved approximations in order to gain some insight into the carrier dynamics. However, Streetman [9] confirmed the existence of two time constants, as also indicated by [7], for small departures from equilibrium for the transient case applied to the single-level defect. In [10], application of the rate equations to coupled states and two independent states is investigated for the transient and steady state situations. The transient time constant expressions agree with [7] and [9] for small departures of the carrier concentration from equilibrium for the single-level case. There are two time constants in these solutions which are in agreement with the exact solution of [3]. This is consistent with the governing second order differential equation (4) since there are two eigenvalues of the linear system because the equation is second order.

However, the equations in the multiple level and single level cases, were stated but the resulting time constants were not verified against an analysis of the numerical solution for the component time constants. In Section II the exact steady state analytic solution is discussed and the steady state fundamental time constants presented. In Section III the theoretical prediction of these fundamental time constants and analysis of the numerical solution for component time constants are shown to be in close agreement. This solution comprises, for the single-level, two fundamental time constants, τ_1 and τ_2 , which are in agreement with previous derivations notably Refs. [7] [9] for the small signal case and the order of the underlying second order differential equation. In Ref. [3] the

minority carrier time constant is defined as τ_1 and the majority carrier as τ_2 . In this respect these two fundamental time constants are directly related to the physics of carrier decay which affect structures such as solar cells. In this case it is the minority carrier represented by τ_1 which is involved in the physics of trapping [3].

In [4] and [10] the steady state time constant is defined as (1) as in [1] (Eq. 5.2), without justification. Although two time constants are derived for the minority carrier in n-type and p-type semiconductor material in the appendix of [1], these time constants are defined similar to (1). It may be shown that these time constants as defined, for the linear region (constant region) of variation of the dominant time constant τ_1 with excess carrier concentration, corresponding to the small signal case of [3], do not agree with the exact solution as given in [3].

For the single level case, the equation describing the time evolution of the normalised excess electron concentration (4), $\Delta n_{nm}(t)$, is a second order non-linear differential equation and has a cubic power of $\Delta n_{nm}(t)$ given as Eq. (9) in [8]. Since the differential equation for $\Delta n_{nm}(t)$ is second order, at least two time constants are expected in the solution (the eigenvalues of the linear system) for all excess carrier concentrations less than the Auger limit and the non-degenerate doping concentration. The steady state is realized with the boundary condition $dn(t)/dt = 0$ at $t = 0^+$ for electrons in the conduction band. Application of the boundary condition is still expected to realize two time constants in the solution since the underlying differential equation is second order.

In [1] the steady state is realised by setting $U_n = U_p$ given as Eq. 4.1 of [1]. They define only a single time constant (Eq. 5.2 of [1] repeated as Eq. (1) of this work), τ_{ss} , implying the solution of a first, rather than second, order governing differential equation. For a second order equation to become first order, a zero must be cancelled by a pole of the same magnitude and frequency as the zero for all excess carrier concentrations. A zero that is not cancelled should be realized in the solution. It is shown in Figure 1 that the time constant $\tau_{ss} = \tau_{SRH}$ is approximately equal to the dominant time constant τ_1 for only part of the range of excess carrier concentration. Furthermore, the analysis of the numerical solution for component time constants (see Section III) yields close agreement with the predicted value of τ_1 for the steady state. Parameters used for the evaluation are given in [3]. Hence the definition of τ_{ss} in [1], as stated above, yields a time constant expression which is inaccurate.

II. ANALYTIC STEADY STATE SRH SOLUTION

A recent analytic solution (6) [3] to the SRH rate equations (2) is obtained without any approximations for uniform arbitrary non-degenerate doping concentration $N_{A,D}$, defect energy depth E_t , defect concentration N_t

and cross sections σ_n and σ_p . The exact solution (6) for the single-level comprises an infinity of monoexponential terms with frequencies or inverse time constants a linear combination of two fundamental frequencies $\omega_1 = 1/\tau_1$ and $\omega_2 = 1/\tau_2$.

$$\Delta n_{nm}(t) = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} N_{u,v} \exp(-u\omega_1 t - v\omega_2 t) \quad (6a)$$

$$\Delta p_{nm}(t) = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} P_{u,v} \exp(-u\omega_1 t - v\omega_2 t) \quad (6b)$$

$$\Delta f(t) = \sum_{u=1}^{\infty} \sum_{v=1}^{\infty} F_{u,v} \exp(-u\omega_1 t - v\omega_2 t) \quad (6c)$$

The magnitude, of the coefficients $N_{u,v}$ and $P_{u,v}$ of the exponential terms, falls away rapidly to a very small value so that less than eight terms are significant in the series. The first two coefficients are the most significant, $(u, v) = (1, 0)$ and $(0, 1)$. Expressions for the minority carrier time constant τ_1 and majority time constant τ_2 are derived and given as (12). The dominant time constant is τ_1 and its behaviour with excess carrier concentration indicates the onset of trapping. A critical point, representing the transition between the linear (constant) and non-linear variation of fundamental frequency with excess carrier density, is identified.

Application of the method of solution derived in [3] as indicated above, to the steady state is performed as follows. Fundamental frequencies are derived by scaling the differential equations and solving the linear form (7) of the non-linear differential equations.

$$-\frac{d\Delta p_{nm}(t)}{dt} \Big|_{t=t_0} = \alpha \Delta p_{nm}(t_0) - \beta \Delta n_{nm}(t_0) \quad (7a)$$

$$-\frac{d\Delta n_{nm}(t)}{dt} \Big|_{t=t_0} = \gamma \Delta n_{nm}(t_0) - \sigma \Delta p_{nm}(t_0) \quad (7b)$$

where α , β , γ and σ now contain the $\eta_n(t_0)$ and $\eta_p(t_0)$ terms (see [3]), with $\Delta n(0) = \Delta p(0)$ and $\eta_n(t_0)$ defined as follows,

$$\eta_n(t_0) = f_s(0^+) - f_o \quad (8)$$

From the charge neutrality relation with $\Delta n(t_0) = \Delta f_s(t_0) = \eta_n(t_0)$ the quantity $\eta_p(t_0)$ may be defined as Eq. (9),

$$\eta_p(t_0) = \left(1 + \frac{N_t}{\Delta n(0)}\right) \eta_n(t_0) \quad (9)$$

The steady state definition of the occupancy function $f_s(t)$ (Eq. 4.2 of [1]), with $n(t) = n_{po} + \Delta n(t)$ and $p(t) = p_{po} + \Delta p(t)$ and corresponding equilibrium concentrations n_{po} and p_{po} , is given as Eq. (10).

$$f_s(0^+) = \frac{C_n n(t) + C_p p_1}{C_n n(t) + C_p p(t) + C_n n_1 + C_p p_1} \quad (10)$$

At equilibrium the electron occupancy of the defect level is $f_o = f(0^-)$ given in terms of p_{po} by:

$$f_o = \frac{p_1}{p_{po} + p_1} \quad (11a)$$

and in terms of n_{po} by:

$$f_o = \frac{n_{po}}{n_{po} + n_1} \quad (11b)$$

The fundamental frequencies $\tau_1 = 1/\omega_1$ and $\tau_2 = 1/\omega_2$ are given as Eqs. (12) (see Ref [3]).

$$\omega_1 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left(1 + \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2} \right)^{\frac{1}{2}} \right) \quad (12a)$$

$$\omega_2 = \frac{1}{2} \frac{\alpha + \gamma}{\alpha\gamma - \sigma\beta} \left(1 - \left(1 - 4 \frac{\alpha\gamma - \sigma\beta}{(\alpha + \gamma)^2} \right)^{\frac{1}{2}} \right) \quad (12b)$$

III. NUMERICAL SOLUTION FOR THE STEADY STATE

The unconstrained coupled differential equations are of the form (2) and (13), where (13) results from the steady state condition $U_n = U_p$ [1] or:

$$\frac{dp(t)}{dt} = \frac{dn(t)}{dt} \quad (13)$$

The initial conditions are $n(0^+) = p(0^+)$ due to the generation rate G and $f(0^+)$ determined Eq. 4.2 of [1] for the steady state.

For small deviations from equilibrium (low excess carrier concentrations) referred to as the linear region (constant region) of variation of time constant with excess carrier concentration at least two time constants are expected in the steady state as with the transient case. This is because the governing equation is second order. For higher excess carrier concentrations away from equilibrium the time constants are expected to differ from the transient case because $dn(t)/dt = dp(t)/dt$ will necessarily give a different $\Delta n(0)_{critical}$ [3]. See [3] for the fifth order Runge-Kutta scheme and typical data used in the numerical solution.

Multi-transient analysis using the Total Least Squares (TLS) method, refers to the extraction of component exponential terms from a sum of exponentials comprising the signal (see [3]). Figure 2 shows the comparison between the decay time constants $\tau_1 = 1/\omega_1$ and $\tau_2 = 1/\omega_2$ as calculated from equation (12) and as evaluated by TLS analysis of numerical data ($\Delta n(t + \Delta t)$) for $T = 300$ K. The figure indicates the variation from low injection through to high injection. Agreement is very good. Also, the steady state values for τ_1 and τ_2 agree with the transient values for the constant region.

IV. DISCUSSION

The steady state solution converges to the transient solution for low excess carrier concentrations and hence confirms the transient solution for the near equilibrium case referred to as the small signal case. This steady state solution is independently determined from a different set of boundary conditions and yet converges to the transient solution as expected from the physics for the small signal case. Furthermore, for the case of intermediate excess carrier concentration the steady state and transient solutions for the time constants are different as shown in Figure 3. The present work independently addresses the solution of the steady state, proving consistency in the solution and indicating a more accurate set of time constants than that of the 1952 SRH time constant.

V. CONCLUSIONS

From a theoretical standpoint, the SRH lifetime expression τ_{ss} for the dominant single level model, is shown to be approximate. The existing interpretation of experimental data relies on one time constant τ_{ss} (steady state case) or τ_b (bulk decay - transient case) derived from the definition Eq. 5.2 of [1] (repeated as Eq. (1) here). Figure 1 and Figure 2 indicate that for low injection the SRH single time constant expression, applied to both the steady state and transient situations (small signal), does not adequately reflect the actual decay. Whereas at high injection τ_1 is adequate to model recombination and trapping, at low injection τ_2 is also required as the magnitude of the coefficient can be significant. For the steady state, in low injection the frequencies are the same as the transient case. From the above it can be seen that the single SRH time constant expression is not sufficient as an approximation and it lacks the ability to predict behaviour. Furthermore, the steady state solution together with the TLS analysis of the numerical solution, confirms the presence of at least two time constants in the decay. This unifies the existing solutions of the rate equations in the literature, as expected from inspection of the second order differential equation (4), for small departures from the equilibrium carrier concentration where the transient and steady state solutions are identical.

Acknowledgments

The Special Research Centre of Excellence for Advanced Silicon Photovoltaics and Photonics is supported by the Australian Research Council's Special Research Centres scheme.

-
- [1] W. Shockley and W. T. Read. *Phys. Rev.*, **87**:835, (1952).
 - [2] R. N. Hall. *Phys. Rev.*, **87**:387, (1952).
 - [3] D. Debuf, Y. Shrivastava, and A. Dunn. *Phys. Rev. B*, **65**:245211, (2002).
 - [4] H. Y. Fan. *Phys. Rev.*, **92**:1424, (1953).
 - [5] A. Rose. *Phys. Rev.*, **97**:322, (1955).
 - [6] D. J. Sandiford. *Phys. Rev.*, **105**:524, (1957).
 - [7] G. K. Wertheim. *Phys. Rev.*, **109**:1086, 1958.
 - [8] K. C. Nomura and J. S. Blakemore. *Phys. Rev.*, **112**:1607, (1958).
 - [9] B. G. Streetman. *J. Appl. Phys.*, **37**:3137, (1966).
 - [10] S. C. Choo. *Phys. Rev. B*, **1**:687, (1970).
 - [11] S. M. Sze. *Physics of Semiconductor Devices*. (Wiley And Sons, New York, 1981).
 - [12] J. P. McKelvey. *Solid State and Semiconductor Physics*. Harper and Row, New York, Evanston and London, 1966.
 - [13] K. L. Luke and L. J. Cheng. *J. Appl. Phys.*, **61** (6):2282–2293, 1987.

Figure Captions

FIG. 1. A graph of fundamental time constant τ_1 and SRH time constant $\tau_{ss} = \tau_{SRH}$ versus excess carrier

concentration $\Delta n(0^+)$. Circles: τ_1 derived from multi-transient analysis of the numerical solution. There is a relative error $\varepsilon \approx 30\%$ between τ_1 and τ_{SRH} in the linear region.

FIG. 2. A graph of $\tau_1 = 1/\omega_1$ and $\tau_2 = 1/\omega_2$ versus excess electron concentration $\Delta n(0)$ for the steady state. The doping concentration N_A of the sample is $5 \times 10^{13} \text{ cm}^{-3}$. Continuous line: τ_1 and τ_2 predicted by equation (12) Circles: τ_1 and τ_2 derived from multi-transient analysis of the numerical solution.

FIG. 3. A graph of $\tau_1 = 1/\omega_1$ and $\tau_2 = 1/\omega_2$ versus excess electron concentration $\Delta n(0)$. Comparison between the transient ([3]) and steady state solutions. Continuous line: τ_1 and τ_2 predicted by equation (12).

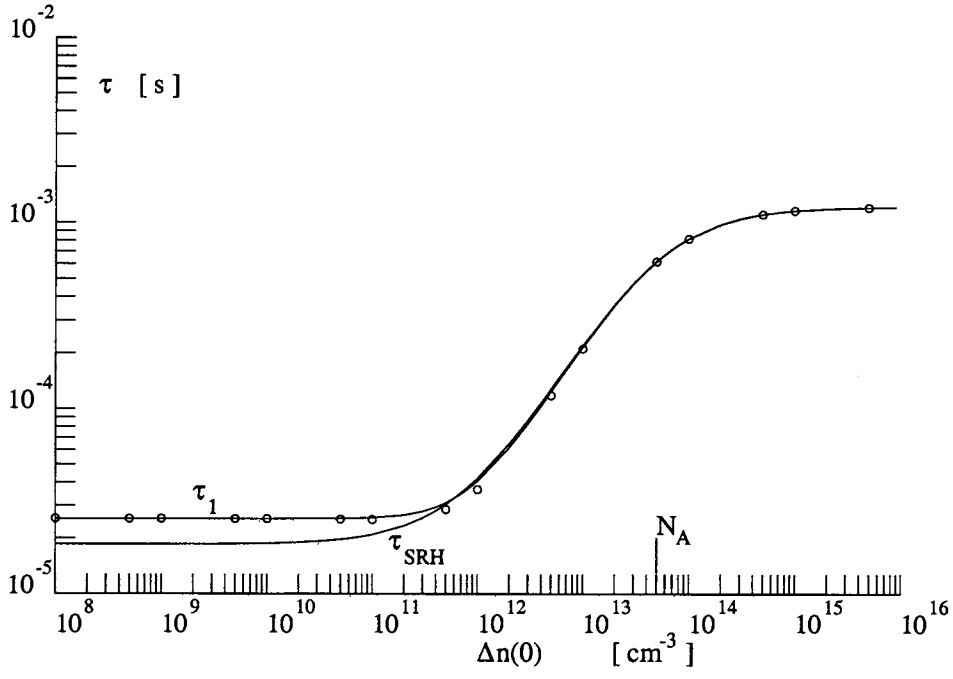


FIG. 1: Didier Debuf, Phys. Rev. B

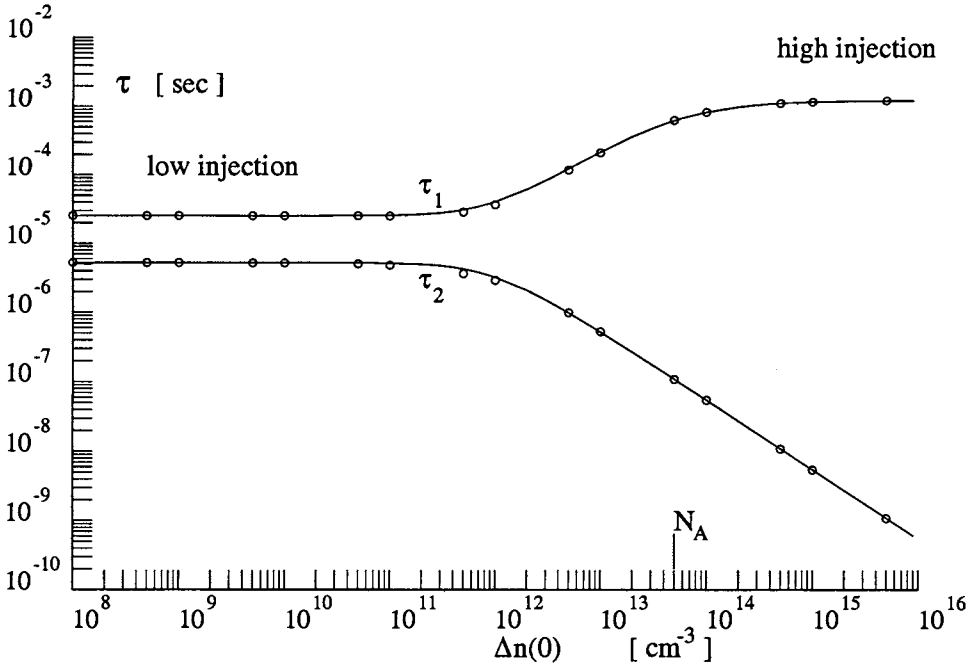


FIG. 2: Didier Debuf, Phys. Rev. B

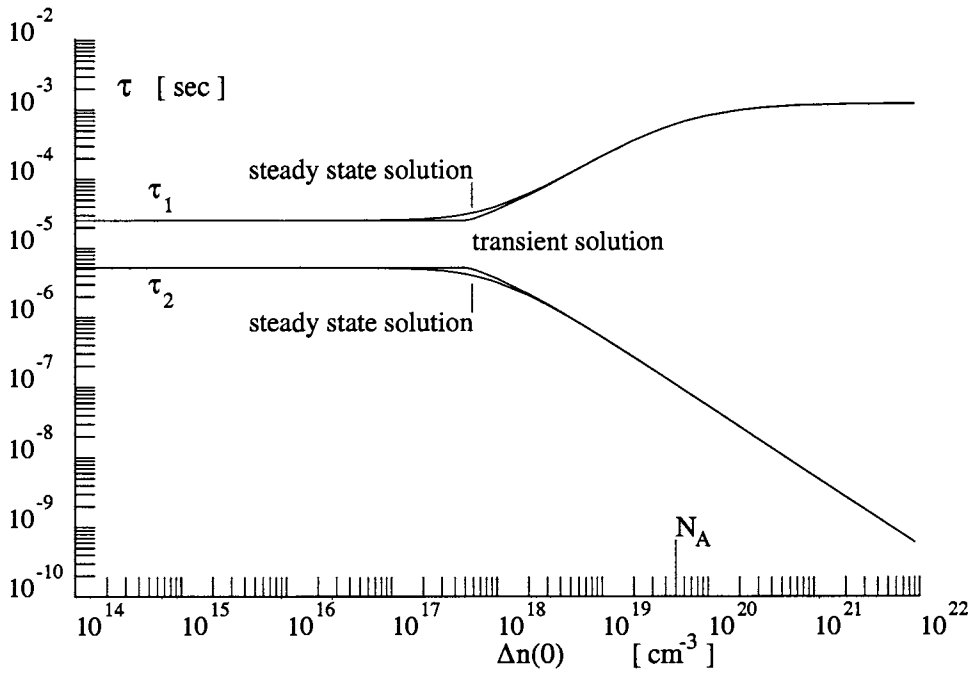


FIG. 3: Didier Debuf, Phys. Rev. B

Accuracy of Semiconductor Multiple-Level-Defect Measurements Using Deep Level Transient Spectroscopy

Didier Debuf*

*Centre of Excellence for Advanced Silicon Photovoltaics and Photonics,
The University of New South Wales, Sydney NSW 2052, Australia*

Peter H. Ladbroke†

GaAs Code Ltd., Wilbraham Road, Fulbourn, Cambridge, CB1 5ET, England

(Dated: July 22, 2003)

The accuracy of defect level depth determined by a current measurement method, namely Deep Level Transient Spectroscopy (DLTS), is shown to be sensitive to the number of defect levels present in the semiconductor sample. A recent analytic solution method of the Shockley-Read-Hall (SRH) rate equations, extended to differential rate equations for two multiple defect level systems, yields a multiple-level solution derived without approximation. In terms of semiconductor material characterisation, this exact solution including the full set of carrier transitions is shown to provide more detailed information on multiple level depths than the existing theory, which relies on independent dominant single levels.

PACS numbers: 72.20.Jv, 72.40.+w, 85.30.De

In materials' characterisation, the defect level depth, which is directly related to carrier recombination, is predominantly determined from rate equations. A dominant recombination mechanism (apart from Auger recombination) is Shockley-Read-Hall (SRH) recombination [1] [2] as described by the SRH rate equations. Strictly, these rate equations apply to a single-level defect although interpretation of experimental data has usually relied on the assumption of a dominant defect energy level. A set of differential rate equations for multiple discrete levels based on the summation of the single-level equations is given in [3] and [4]. A recent analytic solution to the SRH rate equations [5], extended to include multiple defect levels in a first principles approach, indicates that the equations of [3] and [4] for multiple discrete levels are correct only in the neighbourhood of the equilibrium point.

The Deep Level Transient Spectroscopy (DLTS) technique of semiconductor defect level depth measurement, first developed in 1974 by Lang [6], is extended in the present work by including all multiple-level carrier transitions in a full set of rate equations. The method of solution of the recent analytic solution [5] to the single-level (SRH) rate equations, is extended to the two multiple level systems, namely the multiple discrete level system and the ground excited states or coupled levels system. This proposed theory indicates that the accuracy of the usual method of DLTS measurement is affected by additional defect levels comprising the multiple-level systems. These two defect systems have a major effect on the minority carrier and hence the physics of device operation. In the present work the three-multiple-discrete-level system, using the exact solution in the neighbourhood of the equilibrium point, provides a clear distinction of the effect between one and multiple levels on the dominant

time constants in the decay. The extended solution is obtained without approximation for arbitrary excess carrier concentration below non-degenerate doping, uniform arbitrary doping concentration $N_{A,D}$, defect energy depth $E_{t,k}$, defect concentration $N_{t,k}$ and cross sections $\sigma_{n,k}$ and $\sigma_{p,k}$ (for the k^{th} level). The solution is comprised of an infinity of mono-exponential terms, the frequencies (inverse time constants) of which are a linear combination of the fundamental frequencies $\omega_{k+1} = 1/\tau_{k+1}$. Expressions for the minority carrier time constant τ_1 and time constants τ_{k+1} arising from majority carrier transitions are derived for m discrete defect levels with $k = 1, 2, \dots, m$ (the magnitude of the time constants is in descending order $\tau_1 > \tau_2 > \tau_3 > \dots, \tau_{k+1}$). The dominant time constant is τ_1 for n-type or p-type semiconductor and its behaviour with excess carrier concentration indicates the onset of trapping.

In order to place the extended solution in context, a brief review of DLTS is warranted to see what emerges when it is applied to a multiple defect level system, as may often exist in practice. In DLTS, a pulse is applied to a device with a depletion layer, which is reduced in width by the polarity of the pulse to fill deep levels with carriers. On application of a reverse pulse the depletion layer widens and the carriers in each band travel to the depletion layer edge in a matter of picoseconds. Due to thermal emission, carriers in the deep levels are emitted to the respective band and this is detected as a change in capacitance ΔC of the depletion layer. The thermal emission rate determines the decay rate of the depletion layer. In order to detect the decay rate, a rate window $t_1 - t_2$ is usually employed although similar schemes (correlator) are available. At low temperatures the decay rate is slow and the difference in the decay ΔC at times t_1 and t_2 is small. At intermediate temperatures, the

difference is greater. However, at high temperatures the decay rate is very fast as thermal emission is greater and again the difference is small. Hence, a peak in the emission rate versus inverse temperature occurs. A plot of several peaks, corresponding to different rate windows, produces a straight line plot with the slope proportional to the level depth. This plot is referred to as an Arrhenius plot. For multi-exponential decays rate windows may be selected to resolve the different time constants resulting in several Arrhenius plots.

Laplace Deep Level Transient Spectroscopy (LDLTS) [7] is a mathematical refinement of the usual Deep Level Transient Spectroscopy (DLTS), giving better resolution of the spectral peaks. Although LDLTS is used to resolve multiple defect level depths, it may not lead to the direct identification of the defect species. However this may be possible in conjunction with other methods both theoretical and experimental. The DLTS method has limitations on the sensitivity or detection of low defect concentrations.

As originally conceived, DLTS assumes that the effect of each level may be independently determined from the multi-exponential decay of a capacitance transient with the dominant time constant τ arising directly from a dominant defect species. One carrier type is assumed to be emitted from the defect levels. The thermal emission rate $e_{n,p} = 1/\tau$ derived from the detailed balance relations is given by Eq. (1) [8].

$$e_{n,p} = \frac{\sigma_{n,p}^t v_{th(n,p)} N_{c,v}}{g} \exp \left[\frac{-\Delta G_{n,p}}{kT} \right] \quad (1)$$

where $\sigma_{n,p}^t$ is the thermal cross section for electrons or holes, $v_{th(n,p)}$ is the thermal velocity of electrons or holes, $N_{c,v}$ is the effective density of states for electrons or holes, g is the degeneracy and $\Delta G_{n,p}$ is defined by (2).

$$\Delta G_{n,p} = \Delta H_{n,p} - T \Delta S_{n,p} \quad (2)$$

$\Delta G_{n,p}$ represents the change in Gibb's free energy required to emit an electron (hole) from the center at constant temperature. Eq. (2) expresses this quantity in terms of the change in enthalpy ΔH and the change in entropy ΔS . By substitution of the relevant terms, where ΔG is replaced by ΔE , implying no change in entropy (adiabatic process), an emission time constant τ results in Eq. (3).

$$\tau = \frac{g}{\sigma_{n,p}^t \gamma_{n,p} N_{c,v}} \frac{1}{T^2} \exp \left[\frac{-\Delta E}{kT} \right] \quad (3)$$

where

$$\gamma_{n,p} = 2\sqrt{3}k^2 m_{c,v}^* \left[\frac{2\pi}{h^2} \right]^{\frac{3}{2}} \quad (4)$$

with k being Boltzmann's constant, $m_{c,v}^*$ the effective mass for electrons or holes and h is Planck's constant.

Modulation by a pulse of the depletion layer of a Schottky barrier or pn junction produces a change in capacitance where the capacitance of the depletion layer is given by Eq. (5).

$$C(t) = C(0^+) \exp \left(\frac{-t}{\tau} \right) - C_\infty \quad (5)$$

A rate window is defined by $t_1 - t_2$ representing two points on the decay curve. A change in capacitance of the depletion layer may be expressed by Eq. (6).

$$\Delta C(t) = C(t_1) - C(t_2) \quad (6a)$$

$$\frac{\Delta C(t)}{C(0^+)} = \exp \left(\frac{-t_1}{\tau} \right) - \exp \left(\frac{-t_2}{\tau} \right) \quad (6b)$$

Differentiating equation (6b) with respect to τ yields the familiar expression relating the rate window $t_1 - t_2$ to the maximum emission time constant τ as Eq. (7).

$$\tau = \frac{t_1 - t_2}{\ln \left(\frac{t_1}{t_2} \right)} \quad (7)$$

LDLTS or the usual DLTS uses the concept of a rate window to resolve the dominant time constant in the decay. Over a temperature range a time constant expression containing the rate window Eq. (7), which is proportional to the emission time constant of Eq. (1) ($\tau = 1/e_{n,p}$), is evaluated. The emission rate $e_{n,p}$ is related to the dominant decay time constant through this expression. A maximum emission rate is expected at a particular temperature. This maximum is related to the defect level energy depth via Eq. (3). A plot of several maxima versus the inverse of the temperature allows the defect energy depth to be resolved from the slope of the linear plot.

Having discussed the DLTS method, the proposed extended multiple-level theory, comprising the full set of carrier transitions using the recent method of solution in Ref. [5], is now applied to the three level system. A review of the DLTS method applied to the actual resulting time dependent decay and how the rate window scheme interprets it is examined later in the paper. Fundamental frequencies are derived by scaling the differential rate equations and solving the linear form of the non-linear differential equations. The determinant of the matrix of these differential equations, Eq. (8), is reduced to a polynomial of the differential operator $D = d/dt$, termed the characteristic equation, Eq. (9) [9]. From this polynomial the fundamental frequencies may be determined as in Eq. (10). For m defect levels there are $m + 1$ fundamental frequencies where $\tau_1 = 1/\omega_1$ is the dominant time constant. This matrix concept may be seen in [4] for low excess carrier concentration where the carrier concentration does not deviate appreciably from the equilibrium

concentration, and so can be neglected. In this case the non-linear rate equations become linear. For higher excess carrier concentrations the matrix terms are modified

as in [5]. Eqs. (8) describe the full set of carrier transitions whereas Eq. (1) is an approximation involving only the emission of one carrier type.

$$\begin{bmatrix} D + \sum_{k=1}^3 (\gamma_{0k} - \sigma_{0k}) & 0 & -\frac{N_{t1}\sigma_{01}}{\Delta n(0)} & -\frac{N_{t2}\sigma_{02}}{\Delta n(0)} & -\frac{N_{t3}\sigma_{03}}{\Delta n(0)} \\ -(\gamma_{01} - \sigma_{01}) & (\alpha_{01} - \beta_{01}) & \frac{N_{t1}(D + \sigma_{01} + \beta_{01})}{\Delta n(0)} & 0 & 0 \\ -(\gamma_{02} - \sigma_{02}) & (\alpha_{02} - \beta_{02}) & 0 & \frac{N_{t2}(D + \sigma_{02} + \beta_{02})}{\Delta n(0)} & 0 \\ -(\gamma_{03} - \sigma_{03}) & (\alpha_{03} - \beta_{03}) & 0 & 0 & \frac{N_{t3}(D + \sigma_{03} + \beta_{03})}{\Delta n(0)} \\ 1 & -1 & \frac{N_{t1}}{\Delta n(0)} & \frac{N_{t2}}{\Delta n(0)} & \frac{N_{t3}}{\Delta n(0)} \end{bmatrix} \begin{bmatrix} \Delta n_{nm}(t_0) \\ \Delta p_{nm}(t_0) \\ \Delta f_1(t_0) \\ \Delta f_2(t_0) \\ \Delta f_3(t_0) \end{bmatrix} = 0 \quad (8)$$

where the α_{0k} , β_{0k} , γ_{0k} and σ_{0k} , with $k = 1, 2, 3$, refer to the near equilibrium case.

The characteristic equation is given by equation (9) and may be solved for the time constants where the coefficients (b, c, d, e) are determined from the determinant of the matrix formed from Eq. (8).

$$[D^4 + bD^3 + cD^2 + dD + e] \exp(-\omega t) = 0 \quad (9)$$

The fundamental frequencies ω_{k+1} (inverse time constants) may be evaluated from the polynomial of degree $m + 1$ given by Eq. (10).

$$\omega^4 - b\omega^3 + c\omega^2 - d\omega + e = 0 \quad (10)$$

By evaluating the four roots of the polynomial (10) the fundamental frequencies are given by $\omega_1 = 1/\tau_1$, $\omega_2 = 1/\tau_2$, $\omega_3 = 1/\tau_3$ and $\omega_4 = 1/\tau_4$.

The square matrix, with the differential operator D in the off diagonal entries as in the matrix of Eq. (8), is of order $m+2$. Similarly for the square matrix of Ref. [4] for the near equilibrium case of two levels. This means that when more levels are added the order of the matrix increases by the additional number of levels and the degree of the polynomial or characteristic equation increases correspondingly. It is important to note that with additional defect levels, the size of the matrix changes and the coefficients of the polynomial Eq. (10) change. Hence, the roots or fundamental frequencies of the polynomial change. This alters the values of all the fundamental frequencies. For instance with additional defect levels, τ_1 becomes lower in value, and is not a linear change. Hence the effect of all the defect levels is not the sum or linear superposition of the individual effects of each defect level.

The main assumption inherent in the multiple-level theory is that the matrix of Eqs. (8), which strictly

describe the full set of carrier transitions in a field free region, also apply within the depletion region where an electric field ξ is present. Equivalently, the resulting fundamental frequencies (which are the irrational eigenvalues of the linear system [5]) are unique for the given defect level properties (see Table I) and are independent of the electric field ξ being determined by equilibrium values of defect level occupancy, cross sections and concentration. Hence, it may be concluded that the level depths may be recovered from these same fundamental frequencies in a field or field free region because they reflect the same level depths. Although the depletion electric field ξ may enhance emission through the Poole-Frenkel effect [10], the effect is neglected in the present analysis.

In order to recover the true level depths, decay measurements are performed at constant temperature over a temperature range. The fundamental frequencies ω_{k+1} must be resolved using a multi-transient analysis technique [5] from each experimental decay and a set of simultaneous equations formed at each temperature from the polynomial of Eq. (10). Each equation in the set contains a different ω . The coefficients (b,c,d,e) of Eq. (10) are determined in terms of the ω_{k+1} from the simultaneous equations. From expressions for each coefficient, found by expanding the matrix Eq. (8), the level depths may be evaluated from the slope of the plot of each coefficient in terms of the ω_{k+1} versus $1/kT$. A graph of linear plots, with the x abscissa in units of $1/kT$, is obtained with the slopes of each line representing the level depths. This measurement technique is termed Fundamental Frequency Spectroscopy.

To place the DLTS method of measurement in context with the foregoing multiple-level theory an example set of three defect levels from Table I is examined with respect to the resolution of the levels using the rate win-

dow concept. For the combined effect of three levels, the best a rate window can do is to resolve a τ (Eq. (3)) with time constants $\tau = \tau_1$ and $\tau = \tau_2$. The time constants $\tau_1 = 1/\omega_1$ and $\tau_2 = 1/\omega_2$ make the most significant contribution to the respective exponential decay term, whether all three levels or just one level is included in the matrix of Eqs. (8). The fundamental frequencies (ω_1, ω_{k+1} for $k = 1, 2 \dots m$), for the two cases of three levels ($m = 3$) and one level ($m = 1$), are the respective roots of the polynomial of Eq. (10) resulting from Eqs. (8) for each case.

For a doping concentration of $N_D = 5 \times 10^{13} \text{ cm}^{-3}$ in a silicon sample, Figure 1 indicates the variation of the dominant time constant τ_1 for the combined effect of the three levels in Table I, and for each level as if it were the only defect present in the semiconductor sample. A rate window may be chosen corresponding to the dominant time constant τ_1 . Figure 1 is a log plot of τ versus $1/kT$, from which the energy level depth may be recovered from the slope of each line as described by equation (3).

It is seen from Figure 1 that level one is resolved as the plot of τ_1 for level one alone almost coincides with the time constant τ_1 for the combined effect of all three levels. In resolving the level there is a relative error of a few percent. From Eq. (10), the next significant contribution to the decay comes from the component with τ_2 as the time constant. Examining this time constant, τ_2 , from Figure 2, the combined effect of all levels produces a τ_2 which does not coincide with any level except at low temperatures (with a different slope). The closest level to the combined time constant of τ_2 is the level one. However, the level resolved is effectively a "ghost level" because it does not exist. It is evident that level one has the dominant effect on the dominant time constant τ_1 and the time constant τ_2 , for the combined levels, due to a combination of deep level depth and concentration (see Table I).

As shown in Figure 1 at any one temperature τ_1 is lowered by the addition of other defect levels arising from other defects which are electrically active. That means that since τ_1 is the dominant decay time constant in both n-type and p-type, it varies in an unpredictable manner with each semiconductor sample. Without taking into account all the other fundamental time constants and linear combination of them, DLTS effectively measures τ_1 , the dominant decay constant, via the rate window concept. Given a dominant defect species in two semiconductor samples, but with different numbers of background defect species in each sample, the values of τ_1 in each sample will be different. Each DLTS peak will shift in an unpredictable way if the background defects are unknown. Hence, in the two cases the level is resolved with an error compared to the case where the dominant defect species level exists on its own, without any other defect levels present. A similar argument applies for time constant τ_2 .

In conclusion the above discussion may help to shed some light on the anomalies arising from interpreting data in experimental methods such as LDITS which determine the dominant decay time constant for a given rate window at a given temperature. In the literature there is a spread of values reported for defect level parameters such as level depth. This is because a given sample with, for example, iron as the dominant defect will have different background defect levels to another similarly doped sample, resulting in a different time constant τ_1 as well as different resultant fundamental frequencies $\omega_{k+1} = 1/\tau_{k+1}$.

The Special Research Centre of Excellence for Advanced Silicon Photovoltaics and Photonics is supported by the Australian Research Council's Special Research Centres scheme.

* Electronic address: didier@ee.usyd.edu.au

† Electronic address: gaascode@aol.com

- [1] W. Shockley and W. T. Read. *Phys. Rev.*, **87**:835, (1952).
- [2] R. N. Hall. *Phys. Rev.*, **87**:387, (1952).
- [3] G. K. Wertheim. *Phys. Rev.*, **109**:1086, 1958.
- [4] S. C. Choo. *Phys. Rev. B*, **1**:687, (1970).
- [5] D. Debuf, Y. Shrivastava, and A. Dunn. *Phys. Rev. B*, **65**:245211, (2002).
- [6] D. V. Lang. *J. Appl. Phys.*, **45**:3023, 1974.
- [7] K. Gosinski, L. Dobaczewski, K. B. Nielsen, A. N. Larsen, and A. R. Peaker. *Phys. Rev. B*, **63**:235309, (2001).
- [8] H. G. Grimeiss, E. Janzen, and B. Skarstam. *J. Appl. Phys.*, **51**:3740, (1980).
- [9] E. Kreyszig. *Advanced Engineering Mathematics*. (Wiley And Sons, New York 6thEd p74, p89, 1988).
- [10] J. Frenkel. *Phys. Rev.*, **54**:647, (1938).

Table Captions

TABLE 1. Defect level parameters for the analytical solution of the rate equations of Eqs. (8) for the multiple discrete defect level system.

Figure Captions

FIG. 1. A graph of fundamental time constant τ_1 , from the root of Eq. (10) versus $1/kT$, for the combined effect of three levels in Table I and for the case of each level in the Table as if it were the only level present in the

semiconductor sample. Solid line: plot of τ_1 for each level. Solid line with circles: combined effect of three levels.]

FIG. 2. A graph of fundamental time constant τ_2 , from the root of Eq. (10) versus $1/kT$, for the combined effect of three levels in Table I and for the case of each level in the Table as if it were the only level present in the semiconductor sample. Solid line: plot of τ_2 for each level. Solid line with circles: combined effect of three levels.]

TABLE I: Didier Debuf, Phys. Rev. Lett.

parameter	level one	level two	level three
$E_c - E_t$ energy depth from conduction band [eV]	0.55	0.35	0.25
N_t discrete level concentration [cm^{-3}]	5×10^{11}	5×10^{10}	5×10^9
σ_p cross section for holes [cm^2]	$\sigma_{v1} = 8.5 \times 10^{-15}$	$\sigma_{v2} = 8.5 \times 10^{-17}$	$\sigma_{v3} = 8.5 \times 10^{-12}$
σ_n cross section for electrons [cm^2]	$\sigma_{c1} = 9.0 \times 10^{-17}$	$\sigma_{c2} = 9.0 \times 10^{-15}$	$\sigma_{c3} = 9.0 \times 10^{-14}$

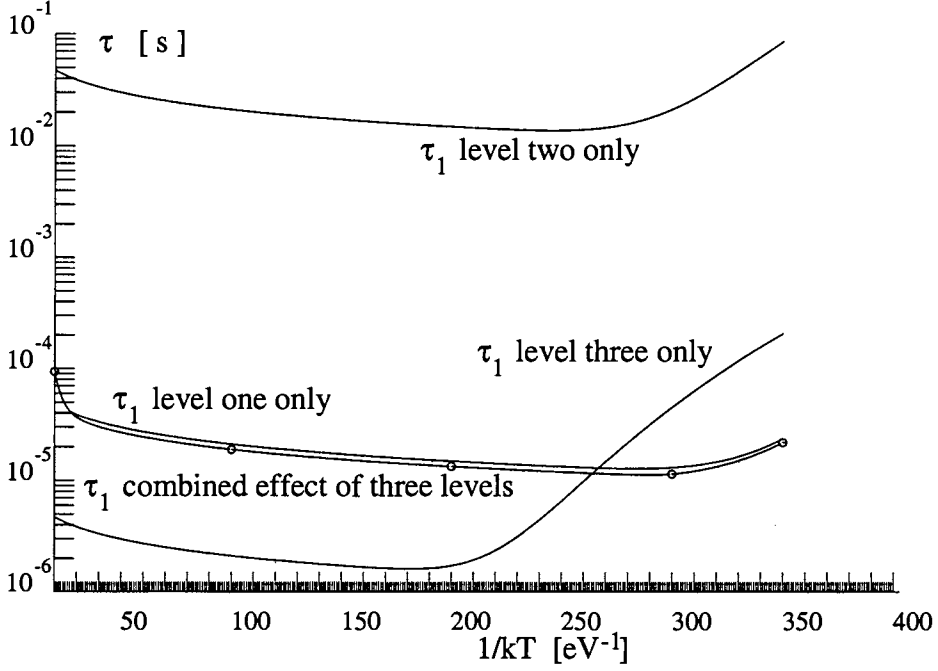


FIG. 1: Didier Debuf, Phys. Rev. Lett.

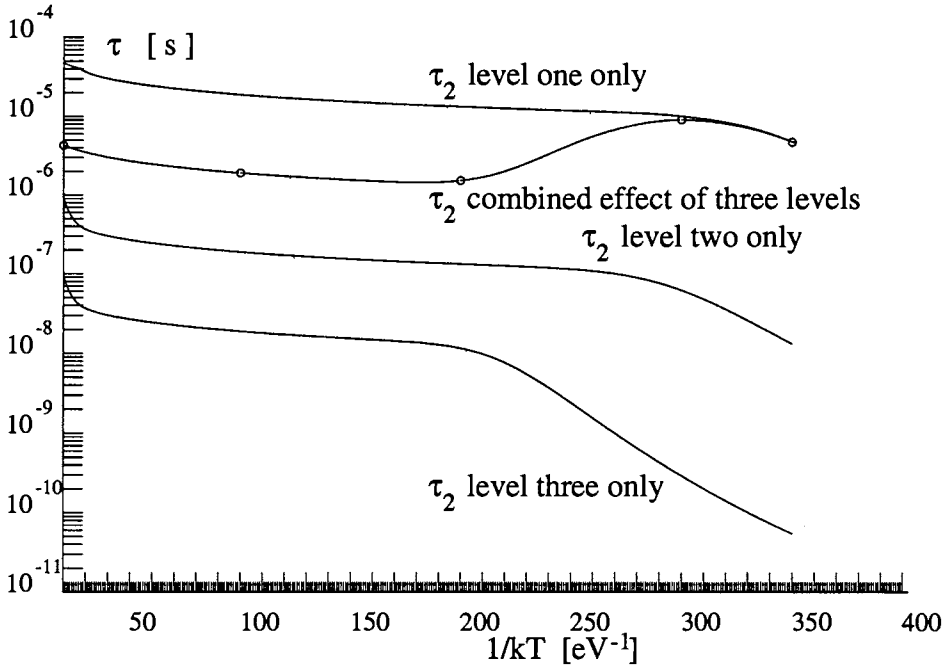


FIG. 2: Didier Debuf, Phys. Rev. Lett.

K.3 Publications in Conference Proceedings

- A general analytic solution to the Shockley-Read-Hall rate equations with a single-level defect
Didier Debuf, Yash Shrivastava
Proceedings PV in Europe from PV Technology to Energy Solutions
Conference and Exhibition
Photovoltaics for Europe Conference and Exhibition on Science, Technology and Application, Palazzo dei Congressi, Rome, Italy, 7-11 October (2002).
- Multiple defect levels and isothermal trapping: semiconductor material quality evaluation
Didier Debuf, Armin G. Aberle
Proceedings PV in Europe from PV Technology to Energy Solutions
Conference and Exhibition
Photovoltaics for Europe Conference and Exhibition on Science, Technology and Application, Palazzo dei Congressi, Rome, Italy, 7-11 October (2002).
- Unified theory of recombination and trapping via multiple defect levels
Didier Debuf, Martin A. Green
Proceedings ANZES, Newcastle Australia, 27-29 November (2002)
Solar 2002, Newcastle, November 2002 (Australian and New Zealand Solar Energy Society).
- Recombination via discrete defect levels with application to semiconductor material characterisation
Didier Debuf, Richard Corkish
Proceedings COMMAD, UNSW, Sydney Australia, 11-13 December (2002)
2002 Conference on Optoelectronic and Microelectronic Materials and Devices, Sydney, 11-13 December 2002.

A GENERAL ANALYTIC SOLUTION TO THE SHOCKLEY-READ-HALL RATE EQUATIONS WITH A SINGLE LEVEL DEFECT

Didier Debuf^a, Yash Shrivastava^b

a: Centre for Third Generation Photovoltaics, The University of New South Wales, Sydney NSW 2052, Australia

b: School of Electrical and Information Engineering, The University of Sydney, Sydney NSW 2006, Australia

ABSTRACT: A recent derivation of an analytic solution to the Shockley-Read-Hall rate equations is compared to the currently accepted steady state expression. The new solution is written as an infinite sum of monoexponential terms, the frequencies or inverse time constants of which are a linear combination of two fundamental frequencies. Whereas the analytic solution is derived without approximation it is shown that the usual steady state expression is approximate and the source of the approximation is identified. Independent agreement between theory and the numerical solution of the non-linear rate equations is provided by multitransient analysis which determines the component exponentials in a sum of exponentials. Minority carrier recombination and trapping is discussed and a definition for the minority carrier time constant is proposed.

Keywords: Lifetime Defects Recombination

1 INTRODUCTION

The average rate of processes of recombination and trapping, capture and emission via a single-level defect is given by the Shockley-Read-Hall (SRH) rate equations first developed in 1952 [1][2]. A steady state solution given in [1] is often used with approximations to interpret experimental data in the literature. In this respect the assumption of a dominant electrically active defect is made to simplify the interpretation. A recent derivation of an analytic solution to the SRH rate equations [3] indicates that the solution is an infinite series of monoexponential terms, the frequencies or inverse time constants of which are a linear combination of two fundamental frequencies λ_1 and λ_2 . The solution is determined without approximation for doping concentration $N_{A,D}$ limited to non-degenerate doping and, arbitrary defect level concentration N_t , defect level depth E_t and cross sections $\sigma_{n,p}$ for electrons and holes respectively. As each exponential term in the series solution represents the response to a linear system, the solution is the sum of responses to an infinite number of linear systems. In this sense the analytic solution is the impulse response. A spatially uniform defect concentration and uniform excess carrier concentration are assumed as initial conditions. Note the SRH equations apply for non-degenerate statistics.

In the present paper it is shown that approximations were introduced in the steady state solution of [1]. The present work seeks to address the effect of the introduced approximations in interpreting decay data using the steady state solution of [1] in the light of the analytic solution of [3]. The paper is organized as follows. Section 2 begins by stating the carrier continuity equation and indicating constraints in order to delineate the boundary conditions under which consideration of the transient and steady state solution is found to apply. The transient solution due to an impulse $N_0\delta(t)$ is first considered and the solution of [3] given. Then the implications of the usual SRH time constant expression are discussed. Section 3 confirms the time constants determined from the theory of [3] by a multitransient analysis of the numerical solution. Included is the definition of minority carrier time constant and minority carrier trapping in the light of the

theory of [3]. The conclusions follow.

2 TRANSIENT AND EXISTING STEADY STATE SOLUTION

2.1 Carrier continuity equations

The carrier continuity equations (1) and (2) describe the flux of carriers into and out of a volume and apply for low excess carrier concentration, low electric field E and parabolic bands (Boltzmann statistics) [4].

$$\begin{aligned} \frac{\partial n(x,t)}{\partial t} = & G_n - U_n + \mu_n n(x,t) \frac{\partial E}{\partial x} \\ & + \mu_n E \frac{\partial n(x,t)}{\partial x} + D_n \frac{\partial^2 n(x,t)}{\partial x^2} \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{\partial p(x,t)}{\partial t} = & G_p - U_p - \mu_p p(x,t) \frac{\partial E}{\partial x} \\ & - \mu_p E \frac{\partial p(x,t)}{\partial x} + D_p \frac{\partial^2 p(x,t)}{\partial x^2} \end{aligned} \quad (2)$$

Consider a single parabolic band such as that found in p-type silicon where U_n represents the recombination rate for electrons. For the transient solution given in [3] the generation rate G_n , the electric field E and diffusion D_n terms are considered negligible. Similarly terms in the carrier continuity equation for $p(x,t)$ are considered negligible. These conditions are imposed in order to determine the impulse response as stated above. In the steady state the term G_n and a corresponding term G_p in the $p(x,t)$ expression is not negligible and effectively is required to maintain the steady state.

2.2 Non-linear SRH Rate Equations

The recombination rates U_n and U_p are given by the first principles' derivation given in [1] known as the SRH rate equations.

$$U_n = C_n N_t n(t)(1 - f(t)) - C_n n_1 N_t f(t) \quad (3)$$

$$U_p = C_p N_t p(t)f(t) - C_p p_1 N_t (1 - f(t)) \quad (4)$$

Given an impulse of light that generates excess carriers in equal concentrations such that $\Delta n(0) = \Delta p(0)$ the above two equations (3) and (4), with the carrier continuity equations and the constraints indicated, yield the following.

$$U_n = -\frac{\partial n(x, t)}{\partial t} \quad (5)$$

$$U_p = -\frac{\partial p(x, t)}{\partial t} \quad (6)$$

Applying the charge neutrality condition with (5) and (6) a second order differential equation for the excess carrier concentration $\Delta n(t)$ may be determined [5]. Perturbative methods of solution were unable to yield satisfactory forms of solution for this non-linear second order equation. So the rate equations have traditionally been solved numerically.

2.3 Infinite Series Solution to SRH Rate Equations

The infinite series transient solution to the SRH rate equations is given in [3] and may be written as follows with $\lambda_1 = 1/\tau_1$ and $\lambda_2 = 1/\tau_2$.

$$\Delta n(t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} N_{i,j} \exp[-(i\lambda_1 + j\lambda_2)t] \quad (7)$$

Since the differential equation for $\Delta n(t)$ is second order, two time constants are expected in the solution for all excess carrier concentrations less than the Auger limit. The two fundamental frequencies are determined from the linear form of the non-linear rate equations. The minority carrier time constant is defined to be τ_1 and the majority carrier time constant is defined to be τ_2 . The dominant time constant is τ_1 .

2.4 Steady State SRH Time Constant Expression

The steady state is realized with the boundary condition $dn(t)/dt = 0$ at $t=0^+$ for electrons in the conduction band where the population remains constant with time. Application of the boundary condition is still expected to realize two time constants (the eigenvalues of the linear system) in the solution as the underlying

differential equation is second order. These two time constants are the fundamental time constants determined from the response to an impulse (transient solution of [3]). In [1] the steady state is realized by $U_n = U_p$ as in Eqn. 4.1 of [1]. Shockley and Read define only a single time constant Eqn. 5.2 of [1], τ , implying the solution of a first, rather than a second order governing differential equation. For a second order equation to become first order, a zero must be cancelled by a pole of the same magnitude and frequency as the zero for all excess carrier concentrations. In effect the zero that is not cancelled should be realized in the solution as for the transient case. It is shown below that the time constant $\tau = \tau_{H-SRH}$ (where the subscript H-SRH refers to Eqn. 5.3 of [1] with agreement for high excess carrier concentration) is approximately equal to τ_1 for only part of the range of excess carrier concentration.

Hence the definition of τ in [1] as stated above, results in an approximation for the time constant expression τ_{H-SRH} (Eq. 8) with τ_{L-SRH} indicating the low excess carrier concentration limit for $\Delta n = 0$.

$$\tau_{H-SRH} = \frac{\tau_{po}(n_{po} + n_1 + \Delta n) + \tau_{no}(p_{po} + p_1 + \Delta n)}{n_{po} + p_{po} + \Delta n} \quad (8)$$

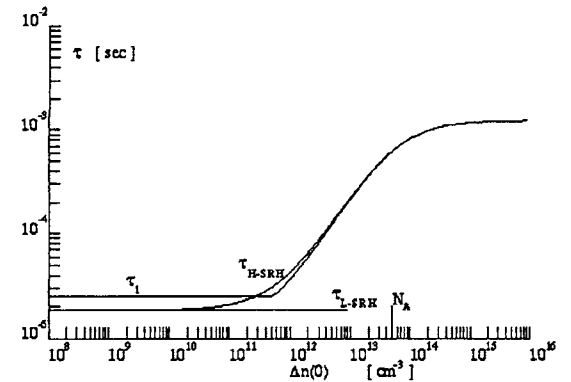


Figure 1 Variation of τ_1 with excess carrier concentration for parameters in Table 1 and calculated by the method of Ref. [3]. Also shown is τ_{H-SRH} (Eq. 8)

Fig. 1 indicates the variation of τ_1 with excess carrier concentration $\Delta n(t)$ for $t=0^+$. In addition the components τ_{H-SRH} and τ_{L-SRH} are shown with the τ_{H-SRH} solution providing partial zero cancellation for moderate to high excess carrier concentrations such that $\tau_1 \approx \tau_{H-SRH}$. At low excess carrier concentrations the SRH expression varies in a non-linear manner towards the lower limit. In this region the linear region of τ_{H-SRH} is not clearly defined and is difficult to apply in practice. For the series solution of [3], the linear region of variation of τ_1 with excess carrier concentration is independent of excess carrier concentration. The critical point at which the excess carrier concentration departs from the linear region is also clearly defined.

Table I: Parameters for the single defect modeled in Fig. 1

parameter	value	units
temperature T	300	K
doping concentration N_A	5×10^{13}	cm^{-3}
defect concentration N_t	5×10^{11}	cm^{-3}
defect level depth $E_t - E_v$	0.65	eV
electron capture cross section σ_n	9×10^{-15}	cm^2
hole capture cross section σ_p	8.5×10^{-17}	cm^2

3 MULTITRANSIENT ANALYSIS AND MINORITY CARRIER TRAPPING

The analysis of the numerical solution of the rate equations (3),(4) provides a means of confirming the theory developed in [3]. No a priori knowledge of time constants is known about the numerical solution as it represents the evolution with time of the rate equations for parameters listed in Table 1.

3.1 Numerical solution of rate equations

A fifth order Runge Kutta scheme [3] is employed to numerically solve the non-linear rate equations (3),(4) for the transient case. Fig. 2 shows the variation of τ_1 and τ_2 with excess carrier concentration for both that predicted by theory and that determined by multitransient analysis of the numerical solution. Multitransient analysis refers to the extraction of component exponential terms from a sum of exponentials comprising the signal. In addition where the data matrix and the observation matrix may be subject to noise fluctuations, the Total Least Squares method [3] is employed. This method models the multi-exponential signal as an autoregressive process.

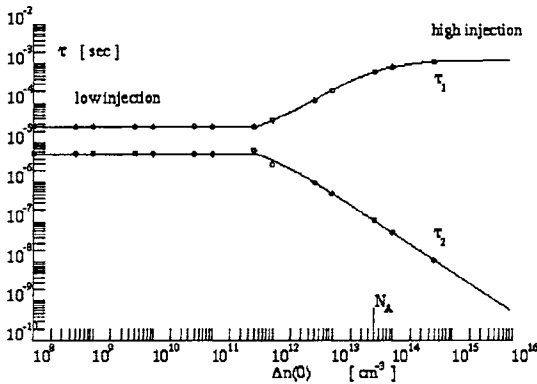


Figure 2 Variation of τ_1 and τ_2 with excess carrier concentration. Continuous line: theory derived in Ref. [3]. Circles: multitransient analysis of numerical solution. Parameters for the calculations are listed in Table 1.

Agreement is good and indicates independent verification of the theory.

3.2 Minority carrier trapping

Fig. 2 indicates that the time constant τ_1 increases as the excess carrier concentration is increased. At low excess carrier concentration the time constant is independent of excess carrier concentration. For high injection the time constant saturates and is almost constant. An earlier definition of the minority carrier time constant is now examined for consistency in the light of the above behaviour of τ_1 .

Consider the p-type sample with electrons being the minority carrier. As τ_1 increases the electron population in the conduction band is increasing as the average time they remain before recombination is increasing. This means fewer holes exist at the defect level for recombination and the defect occupancy or population of electrons is also increasing. Effectively the minority carrier is being trapped at the defect level.

As high injection is approached the hole population although small becomes relatively constant and the electron occupancy at the defect level saturates. For low excess carrier concentration the time constant corresponds to recombination only as there is very little trapping. The evidence for this is that τ_1 is independent of excess carrier concentration. As τ_1 is increasing, τ_2 significantly decreases. The time constant τ_2 corresponds to the majority carrier (holes) which are in abundance in the valence band. Together with the increasing electron occupancy at the defect level considerable recombination takes place decreasing the majority carrier time constant. This implies that the rate of change of the holes in the valence band is increasing with excess carrier concentration.

3.3 Variation of τ_1 and τ_2 with doping concentration

Fig. 3 indicates the variation of τ_1 and τ_2 with Fermi level which effectively implies that the doping concentration is varied.

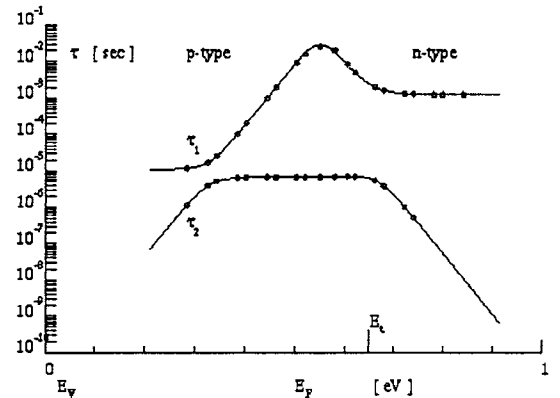


Figure 3 Variation of τ_1 and τ_2 with Fermi level. Continuous line: theory developed in Ref. [3]. Circles: multitransient analysis of numerical solution.

The figure shows close agreement with the predictions of [3] and the multitransient analysis of the numerical solution.

4 DISCUSSION

For the example listed in Table 1 the relative error in the value of τ_1 and τ_{H-SRH} in the linear region of Fig. 1, is of the order of thirty percent. Further the governing differential equation is second order so two time constants are expected in the decay whether it be transient or steady state. Therefore the usual SRH time constant expression represents an approximation.

It is evident from Fig. 2 that τ_1 and τ_2 are significant decay components in the linear region of variation of time constant with excess carrier concentration. This is the region most often employed to determine defect parameters from experiment. The magnitude of the coefficients of the exponential terms determines the contribution of the components to the decay for the transient and steady state. The magnitudes may be modeled as in [3] with known defect parameters.

In the Appendix of [1] two time constant expressions are derived for small departures from equilibrium. However these expressions do not agree with the two time constant expressions derived in [6] for exactly the same conditions of small departures from equilibrium. Although [6] applies to the transient case, the steady state is expected to have the same time constants with only the magnitudes of the coefficients differing from transient to steady state. This is because the steady state is a boundary condition and does not change the underlying governing second order differential equation. The results of [3] agree with those of [6]

The SRH approximate time constant expression is difficult to apply in practice as the extent of the linear region is unknown. Further the degree of the approximation is unknown as the relative error changes in this region. As such the SRH approximate time constant expression indicates trends only.

Fig. 3 indicates that τ_1 behaves uniquely for p-type and n-type and so the definition of τ_1 as the minority carrier time constant is consistent. The proposed infinite series solution indicates the recombination-only region and a trapping region. The variation of time constant components with excess carrier concentration should be plotted in order to determine the onset of the trapping region.

5 CONCLUSIONS

A general analytic solution to the SRH rate equations derived in [3] is shown to be consistent by the multitransient analysis of the numerical solution. There are few constraints which amount to non-degenerate statistics, spatially uniform defect concentration and uniform excess carrier concentration. Further the theory is developed without an approximation. This work presents a unified approach to recombination and trapping.

6 ACKNOWLEDGMENTS

The Special Research Center for Third Generation Photovoltaics is supported by the Australian Research Council's Special Research Centres scheme. A special thanks to Dr R. Corkish for helpful discussions.

7 REFERENCES

- [1] W. Shockley and W. T. Read Phys. Rev. **87**, 835 (1952)
- [2] R. N. Hall Phys. Rev. **37**, 387 (1952)
- [3] Didier Debuf, Yash Shrivastava, Alec Dunn Phys. Rev. B **65**, 245211 (2002)
- [4] S. M. Sze, Physics of Semiconductor Devices (Wiley, New York, 1981)
- [5] K. C. Nomura and J. S. Blakemore, Phys. Rev. **112**, 1607 (1958)
- [6] B. G. Streetman, J. Appl. Phys. **37** 3137 (1966)

MULTIPLE DEFECT LEVELS AND ISOTHERMAL TRAPPING: SEMICONDUCTOR MATERIAL QUALITY EVALUATION

Didier Debuf and Armin G. Aberle

Centre for Third Generation Photovoltaics, The University of New South Wales, Sydney NSW 2052, Australia
didier@ee.usyd.edu.au

ABSTRACT: A solution to the single level Shockley-Read-Hall rate equations developed recently is applied to two multiple level systems. The two systems considered are the multiple discrete level system and the ground excited state or coupled level system. It is shown that the solution to the differential rate equations for the two multiple level systems derived without an approximation lead to a consistent interpretation of the minority carrier time constant. Hence a measure of semiconductor quality may be determined by an assessment of the variation of minority carrier time constant with excess carriers due to an impulse or after steady state conditions.

Keywords: Recombination Lifetime Defects

1 INTRODUCTION

The processes of capture and emission of carriers from multiple defect levels and recombination and trapping via multiple defect levels are governed by rate equations. These processes determine the average lifetime of minority carriers and hence device characteristics. A recent exact solution of the single-level rate equations is derived in [1] and extended to the multiple level case in [2]. A brief overview of the multiple level solution is given in the present work.

Consider the decay response of a semiconductor to a light impulse $\delta(t)$. The Shockley-Read-Hall (SRH) rate equations [3][4] describe the evolution with time of recombination, capture and emission of excess carriers via a single defect energy level in the bandgap of a semiconductor. These rate equations have, to date been applied to the analysis of experimental data assuming a dominant defect energy level. Multiple defect energy levels were discussed in [5] with approximations introduced to elucidate features of types of defects. A set of differential rate equations for multiple discrete levels based on a summation of the single level SRH equations is given in [6]. Again, approximations were introduced to provide a linear solution to the non-linear differential equations.

The validation of the summation of the single level SRH equations for the multiple discrete level case has not previously been confirmed. This is especially important since many analyses applied to the multiple defect situation have involved approximations. The validity of the set of multiple-defect rate equations is confirmed in the present work by applying the method of solution developed in [1]. This solution represents the impulse response and is given by an infinite number of mono-exponential terms the inverse time constants or frequencies of which are the linear combination of fundamental frequencies. The fundamental frequencies are derived from the linear form of the differential equations. Expressions for the minority τ_1 and majority τ_{k+1} with $k=1,2,\dots,m$ carrier decay time constants for the discrete case (see Figure 1) and $\tau_{1,2,3}$, for the ground excited state system (see Figure 2) are given. These are derived without any approximation at a given temperature for excess carrier concentration limited to non-degenerate doping, arbitrary doping concentration $N_{A,D}$, defect level concentration N_{tk} , cross section $\sigma_{pk,nk}$

and energy level E_{tk} . The theory presented addresses the whole decay process from $0^+ < t < \infty$.

Despite the probability that many defect levels may be present in a given semiconductor sample, an effective lifetime, τ_e , is often evaluated as if all the levels may be represented by one dominant level. In photoconductance decay for example, at low excess carrier concentration, the decay is due to minority carriers. At high excess carrier concentration both carriers contribute to the decay. Since τ_e is a cumulative time constant the exact definition of the physics of what τ_e represents from low to high excess carrier concentration is difficult to address. In the exact solution representing all defect levels, the time constant τ_1 represents the minority carrier decay for low and high excess carrier concentration. Its behaviour with excess carrier concentration gives an indication of the onset of minority carrier trapping whether the decay is produced by an impulse $N_0\delta(t)$ or in the steady state. A more accurate measure of semiconductor quality is proposed [1][2] which is based on a measure of time constant τ_1 . A critical point representing the transition between the linear and non-linear variation of fundamental frequency with excess carrier density is identified. For practical assessment of semiconductor material quality a contactless isothermal method is required. The photoconductance decay method may be applied for a range of silicon conductivities suitable for device fabrication. Given ideal surface passivation, $S=0$, where S is the surface recombination velocity, a measure of τ_1 may be extracted from the decay. Proposed experimental details are given in [1]. In particular the following are addressed in the present paper as a result of the implications derived from the theory developed.

- τ_1 is more naturally defined as the minority carrier decay constant
- τ_1 is the dominant decay process in p-type and n-type material.
- A measure of semiconductor quality is determined from the linear region of τ_1 versus excess carrier concentration
- The value of τ_1 is influenced by the presence of other defect levels in the bandgap
- For multiple defect states, all the fundamental time constants should be measured.

The paper is organized as follows. Section 2 contains a multi-transient analysis of the numerical solution to determine the component exponentials in the sum of exponentials. Comparison of the predictions of the analytic solution for the multiple discrete system and ground excited state system with the results of the multi-transient analysis of the numerical solution is very good. An indication of recombination only and of trapping is discussed. An excess electron concentration $\Delta n(t)$ and hole concentration $\Delta p(t)$ is assumed to be uniformly generated throughout the wafer thickness at $t=0^+$. The differential rate equations are scaled [7] and when the normalised excess carrier concentration versus time, intersects the defect occupancy function the non-linear terms in the rate equations for $\Delta n(t)$ and $\Delta p(t)$ go to zero at $t = t_0 > 0^+$. The differential equations may be solved at $t = 0^+$ or $t = t_0$ for the fundamental frequencies or eigenvalues $-\lambda_{i+1}$. Having obtained the fundamental time constants, a general solution for $\Delta n(t)$ and $\Delta p(t)$, represented by the impulse response may be evaluated. An analysis for the ground excited state system may be similarly performed.

Section 3 discusses the implications of the theoretical results determined above. In particular defect level parameters for the same level as in [1] are retained in the present analysis and it is shown that with additional levels the minority carrier time constant τ_1 becomes shorter. This has implications in terms of interpretation of experimental data that relies on measuring the dominant decay constant.

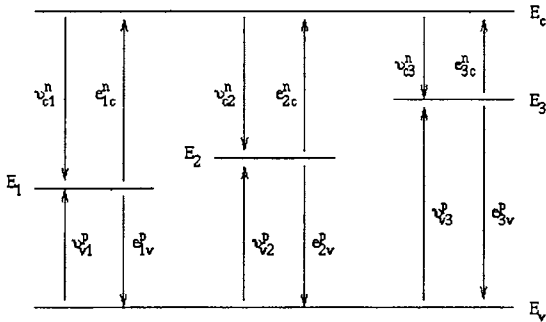


Figure 1 Band diagram for three discrete levels ($m=3$) indicating carrier transitions with the respective band.

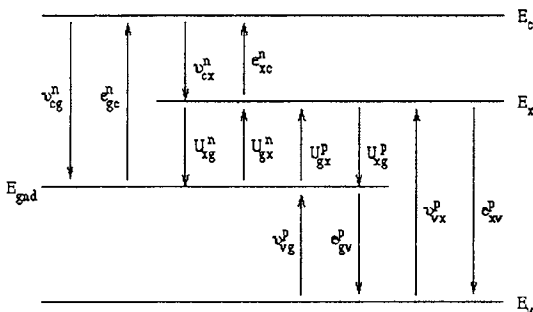


Figure 2 Band diagram for the ground excited

state system indicating carrier transitions.

2 NUMERICAL SOLUTION FOR MULTIPLE AND EXCITED STATE SYSTEMS

2.1 Multiple Discrete level System

In the multiple discrete defect level system the coupled differential equations form a second order differential equation in $n(t)$ [8] which is non-linear. The coupled equations are solved numerically. No a priori knowledge is known about $\Delta n(t + \Delta t)$ as it represents the time evolution of the excess carrier concentration derived numerically. Table 1 indicates the defect parameters for the discrete case. A comparison is made between the numerical solution and the predictions of the analytical solution and found to indicate close agreement [2]. This confirms the method used to analyse the decay. A fifth-order Runge-Kutta scheme [9] is chosen to represent discrete values of $n(t)$, $p(t)$ and $f_k(t)$, to ensure convergence to the equilibrium concentration for the minority carrier as $t \rightarrow \infty$. The defect level initial occupation is assumed not to change from $t = 0^-$ to $t = 0^+$ ($f(0^+) = f(0^-)$).

Table 1: Parameters for multiple discrete level system

parameter	value	units
state one E_c-E_v	0.55	eV
defect concentration N_{H1}	5×10^{12}	cm^{-3}
cross section holes state 1 σ_{v1}	8.5×10^{-15}	cm^2
cross section electrons state 1 σ_{e1}	9.0×10^{-17}	cm^2
state two E_c-E_v	0.65	eV
defect concentration N_{H2}	5×10^{11}	cm^{-3}
cross section holes state 2 σ_{v2}	8.5×10^{-17}	cm^2
cross section electrons state 2 σ_{e2}	9.0×10^{-15}	cm^2
state three E_c-E_v	0.75	eV
defect concentration N_{H3}	5×10^{10}	cm^{-3}
cross section holes state 3 σ_{v3}	8.5×10^{-12}	cm^2
cross section electrons state 3 σ_{e3}	9.0×10^{-14}	cm^2

Table 2: Parameters for ground excited state system

parameter	value	units
excited state E_c-E_x	0.320	eV
ground state E_c-E_{gnd}	0.745	eV
defect concentration N_t	5×10^4	cm^{-3}
cross section holes gnd state σ_{vg}	8.5×10^{-14}	cm^2
cross section holes excited state σ_{vx}	8.5×10^{-11}	cm^2
cross section electrons gnd state σ_{cg}	8.5×10^{-17}	cm^2
cross section electrons excited σ_{cx}	8.5×10^{-15}	cm^2

The Total Least Squares method (TLS) multitransient analysis of the numerical solution [1] results in the determination of frequencies which are

compared with those derived from a theoretical expression. Figure 3 shows this comparison between the decay time constants $\tau_{m+1} = 1/\lambda_{m+1}$ for $m=3$ as calculated theoretically and as evaluated by TLS analysis of numerical data $\Delta n(t + \Delta t)$ for $T=300$ K. The figure indicates the variation of fundamental frequencies with excess carrier concentration. Note that the excess carrier concentration $\Delta n(0)$ varies from $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is excellent and confirms the TLS method of analysis. The onset of the non-linear variation of frequencies λ_{i+1} with $\Delta n(0)$ at $\Delta n(0) = \Delta n(0)_{\text{critical}}$ is clearly seen in the figure where the linear portion extends to $5 \times 10^{11} \text{ cm}^{-3}$ and begins to diverge for $\Delta n(0)$ greater than $5 \times 10^{11} \text{ cm}^{-3}$. This indicates the linear region is in close agreement with the definition given by Ref. [1]. For parameters listed in Table 1, $\Delta n(0)_{\text{critical}} = 5.44 \times 10^{11} \text{ cm}^{-3}$ [2]. Note also that TLS multitransient analysis of the numerical solution results in τ_{i+1} are in close agreement with that predicted by the analytic solution [2]. Some values (circles) could not be resolved due to the very small magnitude of the coefficient of the exponential term.

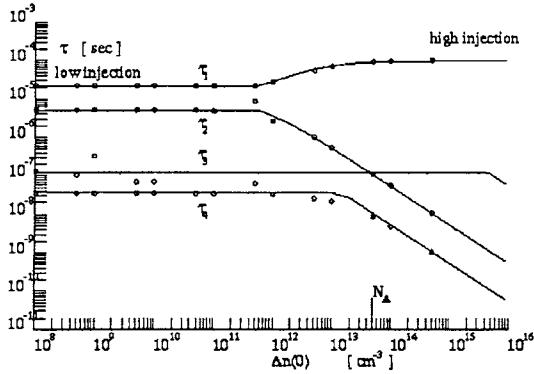


Figure 3 A graph of τ_1, τ_2, τ_3 and τ_4 versus the excess electron concentration for the multiple discrete level system. Continuous line: $\tau_{1,2,3,4}$ as predicted by analytic solution [2]. Circles: $\tau_{1,2,3,4}$ derived from multitransient analysis of numerical solution.

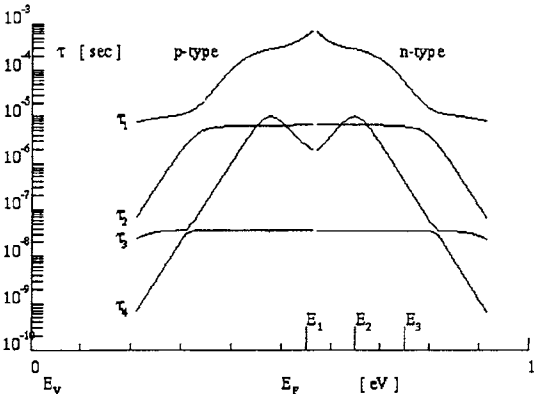


Figure 4 Decay time constants $\tau_{1,2,3,4}$ versus Fermi level E_F for the discrete level system.

Continuous line: as predicted by analytic solution [2].

Figure 4 shows the comparison between the decay time constants $\tau_{1,2,3,4}$ versus the Fermi level E_F for the discrete level system with $m=3$ discrete levels and $T=300$ K. The doping concentration for the p-type and n-type samples varies from $5 \times 10^{10} \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is very good between the numerical solution and the calculated τ_{k+1} . From this figure τ_1 describes the minority carrier decay constant for p-type and n-type, and τ_{k+1} with $k>1$, the majority carrier decay constants, by analogy with [3] for the steady state. As such they represent fundamental decay time constants.

Figure 3 indicates that for $\Delta n(0) > \Delta n(0)_{\text{critical}}$, τ_1 , being the dominant time constant, increases. The minority carriers (electrons) are remaining in the conduction band for a longer average time indicating a shortage holes at the defect level with which to recombine. The defect level electron population is increasing and electrons are remaining at the defect level for a longer average time. This is referred to as minority carrier trapping. The time constant τ_1 remains constant in the linear region of variation of τ_{k+1} with $\Delta n(0)$. This region corresponds to recombination only whereas the non-linear region undergoes recombination and trapping. Eventually the trapping saturates as $\Delta n(0)$ is increased to high injection and the time constant τ_1 reaches a maximum becoming almost constant.

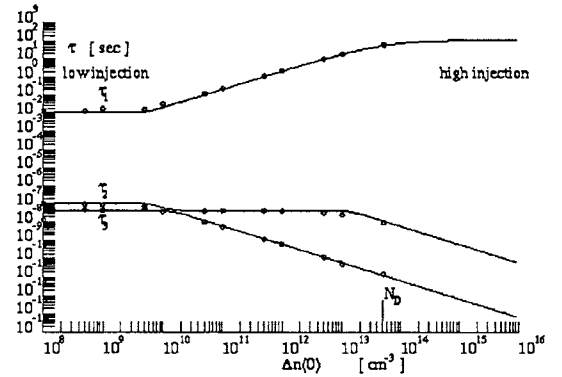


Figure 5 A graph of $\tau_{1,2,3}$ versus excess electron concentration for the ground excited state system. Continuous line: as predicted by analytic solution [2]. Circles: multitransient analysis of numerical solution.

2.2 Ground Excited State System

The equations describing the time evolution of the decay for the ground excited state system are given in [2]. Table 2 indicates the defect parameters for this case. Again, a fifth-order Runge-Kutta scheme is chosen to represent discrete values of $n(t)$, $p(t)$ and $f_{g,x}(t)$ for an n-type silicon sample. TLS multi-transient analysis of the numerical solution of the given equations results in the determination of frequencies which are compared with the derived theoretical expressions [2]. Figure 5 shows

the comparison between the decay time constants $\tau_{1,2,3} = 1/\lambda_{1,2,3}$ as calculated theoretically and as evaluated by TLS analysis of numerical data $\Delta n(t + \Delta t)$ for $T=300$ K. The figure indicates the variation of fundamental frequencies with excess carrier concentration. Agreement is excellent. Again the onset of the non-linear variation of frequencies $\lambda_{1,2,3}$ with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{\text{critical}}$ is clearly seen in the figure.

3 DISCUSSION

It is evident from the theory presented that τ_1 represents an important parameter in terms of the minority carrier behaviour of a semiconductor sample. This extends to both the multiple discrete defect level system and the ground excited state defect level system. These two systems are considered to be the most significant sources of defect level effects on the minority carrier. As such the measurement of τ_1 with excess carrier concentration for a given temperature in the linear and non-linear region realises a basis for evaluating semiconductor material quality. In particular the linear region which represents recombination only allows comparison of time constants τ_1 . A longer dominant decay time constant may indicate a defect level close to the band edge. Comparison of time constants in the non-linear region is at best unreliable as the degree of trapping is unknown and the range of variation of τ_1 with excess carrier concentration is significant.

The ground excited state system may be applicable to the boron-acceptor complex [10]. It is evident that even the very low concentration of the ground excited state levels (see table 2) has a dramatic effect on τ_1 (see Fig. 5) compared to the discrete case. Further experimental evidence for coupled states is provided in Refs. [11][12].

The defect level parameters for the single defect level in [1] were intentionally retained in the present analysis of the multiple discrete level case in [2]. Comparison of $\tau_1=2.55 \times 10^{-5}$ secs for the single defect state [1] and that for the multiple discrete level state $\tau_1=2.21 \times 10^{-5}$ secs in the linear region (see Figure 3), reveals that additional levels results in a lower minority carrier time constant. This represents a relative error greater than ten per cent in addition to measurement errors. This has obvious implications for interpretation of experimental data where τ_1 is the dominant decay time constant. It thus becomes imperative that a multiple level model such as proposed in the present work be used to interpret data since the dominant level model is not sufficient to provide accurate defect level parameters. Further, the above discussion may help to explain the anomalies arising from interpreting data in experimental methods such as Deep Level Transient Spectroscopy (DLTS) which determine the dominant decay time constant for a given rate window at a given temperature. In the literature there is a spread of values reported for defect level parameters such as level depth from such methods. This is because a given sample with, for example, iron as the dominant defect will have different background defect levels to another similarly doped sample, resulting in a different time constant τ_1 for each sample.

4 CONCLUSIONS

It is shown using the method of solution developed in [1] that the differential rate equations derived for the two defect level systems are consistent with the numerical solution of the rate equations. The transition from the linear to non-linear variation of fundamental frequency with excess carrier concentration is indicated. Trapping behaviour of the minority carrier τ_1 is discussed and a measure of semiconductor quality is proposed based on the value and behaviour of τ_1 . A priori knowledge of the number and value of time constants in the numerical solution is not known. This independent verification of the theory determined from the first-principles derivation of the rate equations confirms the properties of the above solution and the method of multi-transient analysis.

The fundamental theory of transient decay due to the multiple defect level system given in the present work may find a wide range of application. Some of these applications may be comparing the quality of crystalline silicon, polycrystalline silicon and cast silicon used for solar cells. Furthermore, the effectiveness of different experimental techniques may be refined with the measurement of the fundamental decay time constants associated with multiple defect levels. Hence a uniform interpretation of defect level parameters across the techniques may ensue.

5 ACKNOWLEDGMENTS

The Special Research Centre for Third Generation Photovoltaics is supported by the Australian Research Council's Special Research Centres scheme. A special thanks to Dr R. Corkish for helpful discussions.

6 REFERENCES

- [1] Didier Debuf, Yash Shrivastava, Alec Dunn
Phys. Rev. B **65** 245211 (2002).
- [2] Didier Debuf, in preparation (2002)
- [3] Shockley W., Read W. T.
Phys. Rev. **87** p835. (1952)
- [4] Hall R. N. Phys. Rev. **87** p387. (1952)
- [5] Rose A. Phys. Rev. **97** p322. (1955)
- [6] Wertheim G. K. Phys. Rev. **109** p1086. (1958)
- [7] Fulford G. R., Broadbridge P., Industrial Mathematics, Case Studies in the Diffusion of Heat and Matter, Cambridge U. P., Cambridge (2002) p29
- [8] Nomura K. C., Blakemore J. S.
Phys. Rev. **112** p1607. (1958)
- [9] Dormand J. R. Numerical Methods for Differential Equations A Computational Approach, CRC Press , New York. (1996)
- [10] Zhao S., Assali L. V. C., Justo J. F., Gilmer G. H., Kimerling L. C., J. Appl. Phys. **90** p2744 (2001)
- [11] Chen W. M., Monemar B., Janzen E.,
Phys. Rev. Lett. **67** p1914 (1991)
- [12] Frens A. M., Bennebroek M. T., Zakrzewski A., Schmidt J., Phys. Rev. Lett. **72** p2939 (1994)

Unified Theory of Recombination and Trapping via Multiple Defect Levels

Didier Debuf and Martin A. Green
Centre for Photovoltaic Engineering
The University of New South Wales
Sydney NSW 2052
AUSTRALIA

Telephone: +61 02 9385 4018
Facsimile: +61 02 9662 4240
E-mail: didier@ee.usyd.edu.au

Abstract

Based on the solution of the Shockley-Read-Hall differential rate equations for the single level defect developed recently, the multiple level solution indicates that the dominant single level model is inadequate. The solution of differential equations for a multiple discrete level defect system and a ground excited state system is derived without an approximation. It applies for a given doping concentration, defect level concentration, defect level depth and electron and hole cross sections. A consequence of the unified solution for a range of excess carrier concentrations is that a measure of semiconductor quality may be assessed by measuring the minority carrier time constant τ_1 . This applies for single crystal, polycrystalline and cast silicon. Further the solution has implications in terms of defect level measurement and modelling of device structures such as solar cells.

1 INTRODUCTION

The processes of capture and emission of carriers from multiple defect levels and recombination and trapping via multiple defect levels are governed by rate equations. These processes determine the average lifetime of minority carriers and hence device characteristics. The solution of the single-level rate equations is derived in Ref. Debuf et al, (2002) and extended to the multiple level case in Ref. (Debuf, 2002). A brief overview of the multiple level solution is given in the present work for the purpose of elucidating the features of the solution with application to determining the properties of electrically active defects. A considerable effort is being expended on improving the quality of semiconductor material to minimise the mostly detrimental effects of defect levels on device performance. Current methods of analysis to determine defect level parameters or semiconductor quality are approximate in nature. Despite the probability that many defect levels may be present in a given semiconductor sample, an effective lifetime τ_e is often evaluated as if they may be represented by one dominant level. A more accurate measure of semiconductor quality is proposed which is based on a measure of one time constant τ_1 whether the decay is produced by an impulse $N_0\delta(t)$ or in the steady state. This time constant τ_1 represents the minority carrier decay and its behaviour with excess carrier concentration gives an indication of the onset of minority carrier trapping. A critical point representing the transition between the linear and non-linear variation of fundamental frequency with excess carrier density is identified. For practical assessment of semiconductor material quality a contactless isothermal method is required. The photoconductance decay method may be applied for a range of silicon conductivities suitable for device fabrication. Given the degree of surface passivation $S=0$ where S is the surface recombination velocity, a measure of τ_1 may be extracted from the decay. Proposed experimental details are given in Ref. Debuf et al, (2002).

Consider the decay response of a semiconductor to a light impulse $\delta(\tau)$. The Shockley-Read-Hall (SRH) rate equations Shockley et al (1952), (Hall, 1952) describe the evolution with time of recombination, capture and emission of excess carriers via a single defect energy level in the bandgap of a semiconductor. These rate equations have been applied to date to the analysis of experimental data assuming a dominant defect energy level. Multiple defect energy levels were discussed in (Rose, 1955) with approximations introduced to elucidate features of types of defects.

A set of differential rate equations for multiple discrete levels based on a summation of the single level SRH equations is given in Ref. (Wertheim, 1958). Again approximations were introduced to provide a linear solution to the non-linear differential equations. The validation of the summation of the single level SRH equations for the multiple discrete level case has not been previously confirmed. This is especially important since many analyses applied to the multiple defect situation have involved approximations. The validity of the set of multiple defect rate equations is confirmed in the present work by applying the method of solution developed in Debuf et al, (2002). This solution represents the impulse response and is given by an infinite number of mono-exponential terms the inverse time constants of which or frequencies are the linear combination of fundamental frequencies. The fundamental frequencies are derived from the linear form of the differential equations. Expressions for the minority τ_1 and majority τ_{k+1} with $k=1,2,\dots,l+1$ carrier decay time constants for the discrete case (see Figure 1) and $\tau_{1,2,3}$ for the ground excited state system (see Figure 2) are given. These are derived without an approximation at a given temperature for arbitrary excess carrier concentration, doping concentration $N_{A,D}$, defect level concentration N_{tk} , cross section $\sigma_{pk,nk}$ and energy level E_{tk} . The theory presented addresses the whole decay process from $0^+ < t < \infty$. The analytic solution is verified by analysing the numerical solution of the rate equations for the above given parameters using a multitransient technique.

In particular the following are addressed in the present paper as a result of the implications derived from the theory developed.

- τ_1 is more naturally defined as the minority carrier decay constant
- τ_1 is the dominant decay process in p-type and n-type
- A measure of semiconductor quality is determined from the linear region of τ_1 versus excess carrier concentration
- The value of τ_1 is influenced by the presence of other defect levels in the bandgap
- For multiple defect states, all the fundamental time constants should be measured.

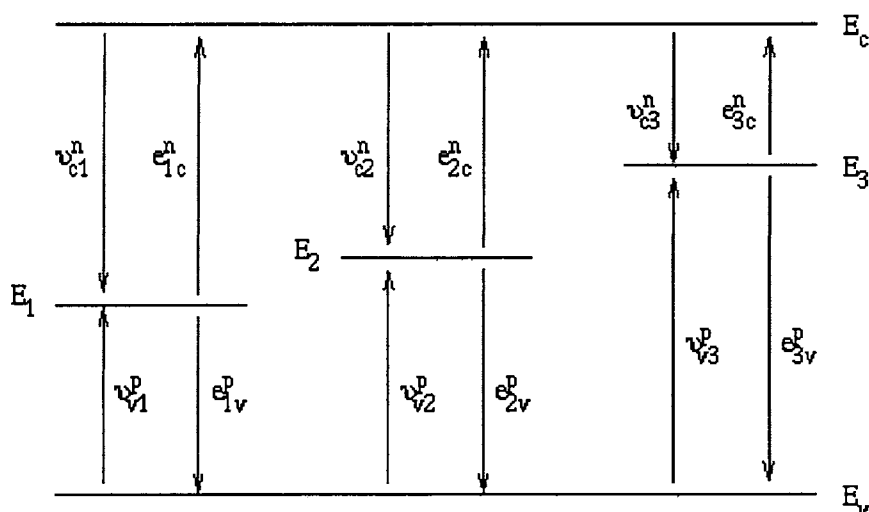


Figure 1 Band diagram for three discrete levels indicating carrier transitions with the respective band.

The paper is organized as follows. A section 2 contains a multi-transient analysis of the numerical solution to determine the component exponentials in the sum of exponentials. Comparison of the predictions of the analytic solution for the multiple discrete system and ground excited state system with the results of the multi-transient analysis of the numerical solution is very good. An indication of recombination only and of trapping is discussed. An excess electron concentration $\Delta n(t)$ and hole concentration $\Delta p(t)$ is assumed to be uniformly generated throughout the wafer thickness at $t=0^+$. It is shown that the non-linear terms in the rate equations for $\Delta n(t)$ and $\Delta p(t)$ go to zero at $t=0^+$ or some time $t = t_0$ where $t_0 > 0^+$. The resulting linear differential equations may be solved at $t = 0^+$ or $t = t_0$ for the fundamental frequencies or eigenvalues $-\lambda_{i+1}$. Having obtained the fundamental time constants, a general solution for $\Delta n(t)$ and $\Delta p(t)$, represented by the impulse response may be evaluated. An analysis for the ground excited state system may be similarly performed. A section 3 discusses the implications of the theoretical results determined above. In particular defect level parameters for the same level as in (Debuf et al, 2002) are retained in the present analysis and it is shown that with additional levels the minority carrier time constant τ_1 becomes faster. This has implications in terms of interpretation of experimental data that relies on measuring the dominant decay constant. As such the minority carrier lifetime represented by τ_1 is degraded with the presence of other levels.

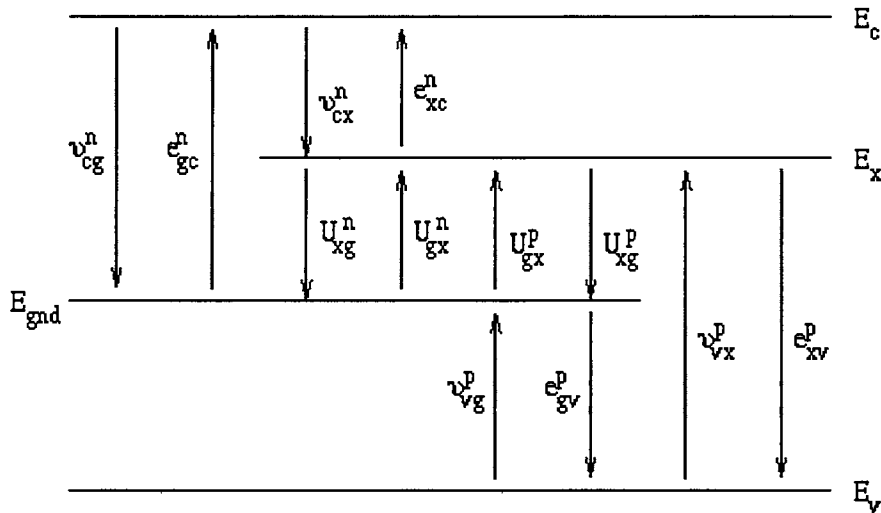


Figure 2 Band diagram for the ground excited state system indicating carrier transitions.

2 NUMERICAL SOLUTION FOR MULTIPLE AND EXCITED STATE SYSTEMS

Considering the multiple discrete defect level system the coupled differential equations form a second order differential equation in $n(t)$ Nomura et al (1958) which is non-linear. The coupled equations are solved numerically. No a priori knowledge is known about $\Delta n(t + \Delta t)$ as it represents the time evolution of the excess carrier concentration derived numerically. A correlation between the numerical solution and the predictions of the analytical solution is made and found to indicate close agreement. This confirms the method used to analyse the decay as a useful tool. A fifth order Runge-Kutta scheme (Dormand, 1996), Press et al, (1992), is chosen to represent discrete values of $n(t)$, $p(t)$ and $f_k(t)$, to ensure convergence to the equilibrium concentration for the minority carrier as $t \rightarrow \infty$. The normalised excess carrier concentrations at $t = 0^+$ are given by $\Delta n_{nm}(0^+) = 1.0$ and $\Delta p_{nm}(0^+) = 1.0$ where the subscript nm indicates normalised quantities. The defect level initial occupation is assumed not to change from $t = 0^-$ to $t = 0^+$ ($f(0^-) = f(0^+)$).

The Total Least Squares method (TLS) multi-transient analysis of the numerical solution Debuf et al, (2002) results in the determination of frequencies which are compared with those derived from a theoretical expression. Figure 3 shows the comparison between the decay time constants $\tau_{l+1} = 1/\lambda_{l+1}$ for $l=3$ as calculated from and as evaluated by TLS analysis of numerical data $\Delta n(t + \Delta t)$ for $T=300$ K. The figure indicates the variation of fundamental frequencies with excess carrier concentration. Note the excess carrier concentration $\Delta n(0)$ varies from $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is excellent and as such contributes to the confidence in the TLS method of analysis. The onset of the non-linear variation of frequencies λ_{l+1} with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{\text{critical}}$ is clearly seen in the figure where the linear portion extends to $5 \times 10^{11} \text{ cm}^{-3}$ and begins to diverge for $\Delta n(0)$ greater than $5 \times 10^{11} \text{ cm}^{-3}$. This indicates the linear region is in close agreement with the definition given by Ref. Debuf et al, (2002). See Ref. (Debuf, 2002) for the evaluation of $\Delta n(0)_{\text{critical}}$. For parameters listed in (Debuf, 2002), $\Delta n(0)_{\text{critical}} = 5.44 \times 10^{11} \text{ cm}^{-3}$. Note also that TLS multitransient analysis of the numerical solution results in τ_{l+1} in close agreement with that predicted by the analytic solution (Debuf, 2002). Some values (circles) could not be resolved due to the very small magnitude of the coefficient of the exponential term.

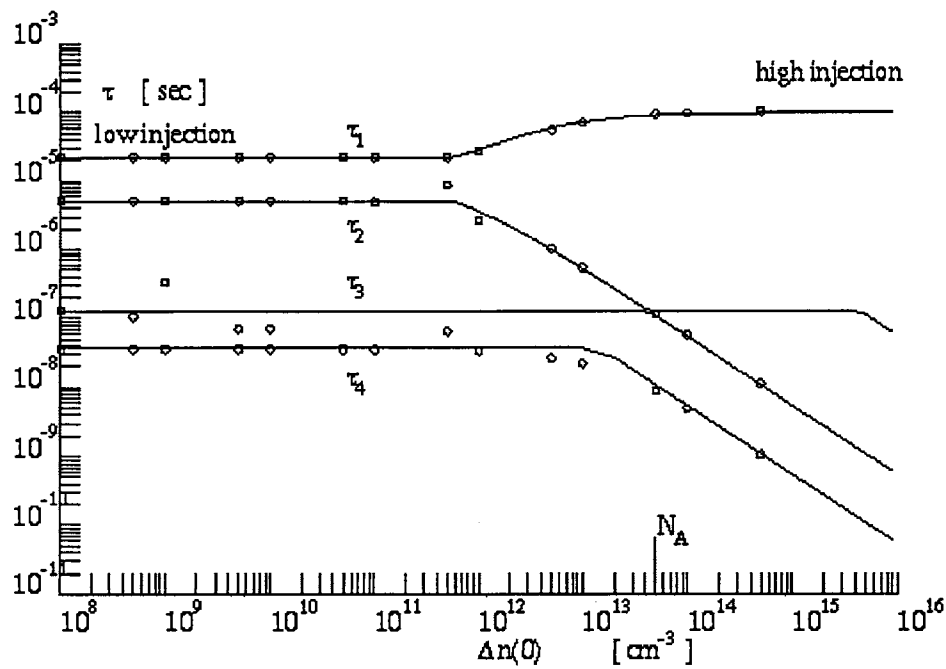


Figure 3 A graph of τ_1 , τ_2 , τ_3 and τ_4 versus the excess electron concentration for the multiple discrete level system. Continuous line: $\tau_{1,2,3,4}$ as predicted by analytic solution (Debuf, 2002). Circles: $\tau_{1,2,3,4}$ derived from multitransient analysis of numerical solution.

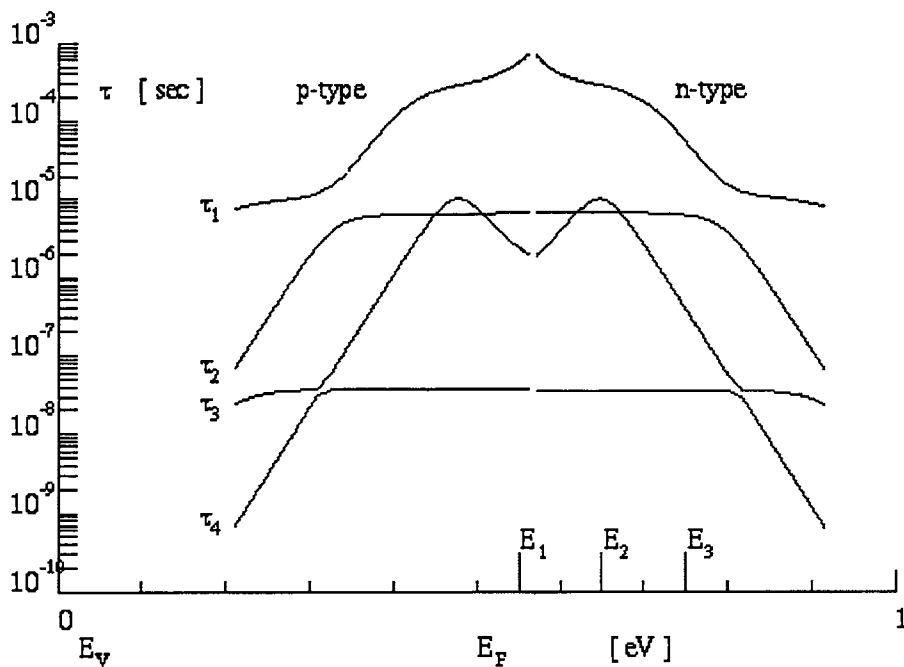


Figure 4 Decay time constants $\tau_{1,2,3,4}$ versus Fermi level E_F for the discrete level system. Continuous line: as predicted by analytic solution (Debuf, 2002).

Figure 4 shows the comparison between the decay time constants $\tau_{1,2,3,4}$ versus the Fermi level E_F for the discrete level system with $l=3$ and $T=300$ K. The doping concentration for the p-type and n-type samples varies from $5 \times 10^{10} \text{ cm}^{-3}$ to

$1 \times 10^{16} \text{ cm}^{-3}$. Agreement is very good for the numerical solution and the calculated τ_{k+1} . From this figure τ_1 describes the minority carrier decay constant for p-type and n-type, and τ_{k+1} with $k > 1$, the majority carrier decay constants, by analogy with Shockley et al (1952) for the steady state. As such they represent fundamental decay time constants.

Figure 3 indicates that for $\Delta n(0) = \Delta n(0)_{\text{critical}}$, τ_1 increases realising a situation where the carrier (p-type) time constant represented by τ_1 is becoming longer. The minority carriers (electrons) are remaining in the conduction band for a longer average time indicating that there are fewer holes at the defect level to recombine with. As such the defect level electron population is increasing and electrons are remaining at the defect level for a longer average time. This is referred to as minority carrier trapping. The time constant τ_1 remains constant in the linear region of variation of τ_{k+1} with $\Delta n(0)$. This region corresponds to recombination only whereas the non-linear region undergoes recombination and trapping. Eventually the trapping saturates as $\Delta n(0)$ is increased to high injection and the time constant τ_1 reaches a maximum becoming almost constant.

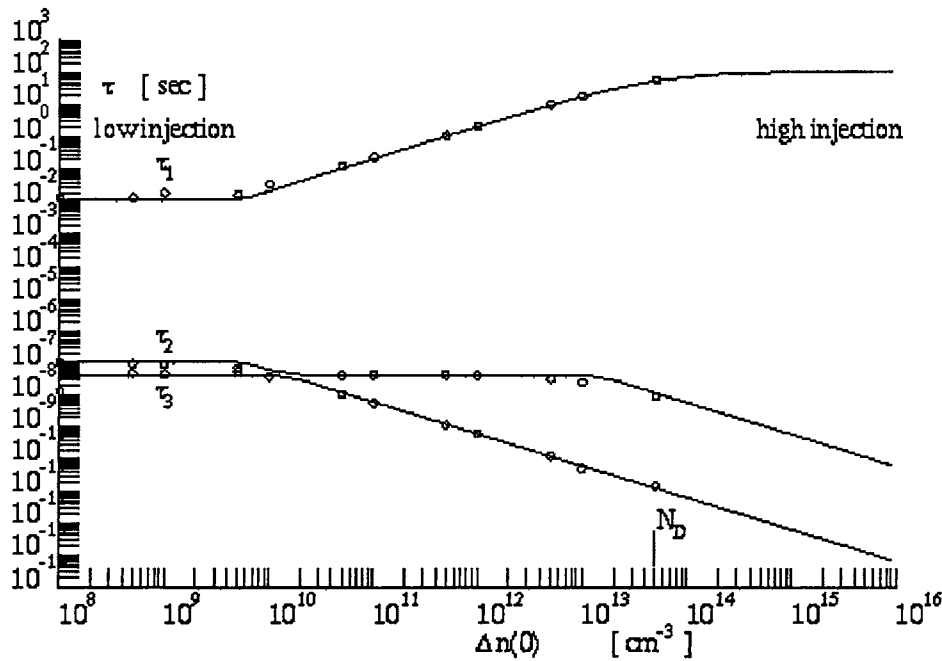


Figure 5 A graph of $\tau_{1,2,3}$ versus excess electron concentration for the ground excited state system. Continuous line: as predicted by analytic solution (Debuf, 2002). Circles: multitransient analysis of numerical solution.

The equations describing the time evolution of the decay for the ground excited state system are given in Ref. (Debuf, 2002). Again a fifth order Runge-Kutta scheme is chosen to represent discrete values of $n(t)$, $p(t)$ and $f_{(g,x)}(t)$. TLS multi-transient analysis of the numerical solution of the given equations results in the determination of frequencies which are compared with the derived theoretical expressions (Debuf, 2002). Figure 5 shows the comparison between the decay time constants $\tau_{1,2,3} = 1/\lambda_{1,2,3}$ as calculated and as evaluated by TLS analysis of numerical data $\Delta n(t + \Delta t)$ for $T=300 \text{ K}$. The figure indicates the variation of fundamental frequencies with excess carrier concentration. Note the excess carrier concentration $\Delta n(0)$ varies from $1 \times 10^8 \text{ cm}^{-3}$ to $1 \times 10^{16} \text{ cm}^{-3}$. Agreement is excellent. Again the onset of the non-linear variation of frequencies $\lambda_{1,2,3}$ with $\Delta n(0)$ for $\Delta n(0) = \Delta n(0)_{\text{critical}}$ is clearly seen in the figure.

3 DISCUSSION

From the theory presented it is evident that τ_1 represents an important parameter in terms of the minority carrier trapping behaviour of a wafer sample. This extends to both the multiple discrete defect level system and the ground excited state defect level system. These two systems are considered to be the most significant sources of defect level effects on the minority carrier. As such the measurement of τ_1 with excess carrier concentration for a given temperature in the linear and non-linear region realises a basis for evaluating semiconductor material quality. In particular the linear region which represents recombination only allows comparison of wafer time constants (τ_1) so that the longer time constant wafers may be preferentially processed. A longer dominant decay time constant may indicate a defect level

close to the band edge. Comparison of wafer time constants in the non-linear region is at best unreliable as the degree of trapping is unknown and the range of variation of τ_1 with excess carrier concentration is significant. The defect level parameters for the single defect level in Debuf et al, (2002) were intentionally retained in the present analysis of the multiple discrete level case in Ref. (Debuf, 2002). Comparison of $\tau_1=2.5453 \times 10^{-5}$ secs for the single defect state Debuf et al (2002) and that for the multiple discrete level state $\tau_1=2.2104 \times 10^{-5}$ secs (see Figure 3) reveals that additional levels results in a faster minority carrier time constant. This represents a relative error greater than ten per cent in addition to measurement errors. This has obvious implications for interpretation of experimental data where τ_1 is the dominant decay time constant. It thus becomes imperative that a multiple level model such as proposed in the present work be used to interpret data as the dominant level model is not sufficient to provide accurate defect level parameters. Further, the above discussion may help to explain the anomalies arising from interpreting data in experimental methods such as Deep Level Transient Spectroscopy (DLTS) which determine the dominant decay time constant for a given rate window at a given temperature. In the literature there is a spread of values reported for defect level parameters such as level depth from such methods. This is because a given wafer sample with for example iron as the dominant defect will have different background defect levels to another similarly doped sample.

4 CONCLUSIONS

Using the method of solution developed in Ref. Debuf et al, (2002) it is shown that the differential rate equations derived for the two defect level systems are consistent with the numerical solution of the rate equations. The linear form of the rate equations predicts fundamental time constants which agree with those determined from the analysis of the numerical solution. The analytic solution to the differential rate equations for the multiple defect state systems indicates an infinity of exponential terms, the frequencies of which are a linear combination of fundamental frequencies. The fundamental frequencies are derived from the linear form of the rate equations without an approximation. The transition from the linear to non-linear variation of fundamental frequency with excess carrier concentration is indicated. Trapping behaviour of the minority carrier τ_1 is discussed and a measure of semiconductor quality is proposed based on the value and behaviour of τ_1 . A priori knowledge of the number and value of time constants in the numerical solution is not known. This independent verification of the theory determined from the first principles derivation of the rate equations confirms the properties of the above solution and the method of multi-transient analysis. The fundamental theory of transient decay due to the multiple defect level system given in the present work may find a wide range of application. Some of these applications may be comparing the quality of crystalline silicon, polycrystalline silicon and cast silicon as described in the case of solar cells. Further the effectiveness of different experimental techniques may be refined with the measurement of the fundamental decay time constants associated with multiple defect levels. Hence a uniform interpretation of defect level parameters across the techniques may ensue.

5 REFERENCES

- Didier Debuf, Yash Shrivastava, Alec Dunn (2002). *General analytic solution to the Shockley-Read-Hall rate equations with a single-level defect*. Phys. Rev. B (65) 245211.
- Didier Debuf (2002). *Multiple defect levels and isothermal trapping*. Paper presented to Solid State Electronics.
- Dormand J. R. (1996) Numerical Methods for Differential Equations A Computational Approach, CRC Press , New York.
- Hall R. N. (1952). *Electron-hole Recombination in Germanium*. Phys. Rev. (87) p387.
- Nomura K. C., Blakemore J. S. (1958). *Decay of Excess Carriers in Semiconductors*. Phys. Rev. (112) p1607.
- Press W. H., Flannery B. P., Teukolsky S. A., Vetterling W. T. (1992) *Numerical Recipes in C: The Art of Scientific Computing* . Cambridge University Press, Cambridge.
- Rose A. (1955). *Recombination Processes in Insulators and Semiconductors*. Phys. Rev. (97) p322.
- Shockley W., Read W. T. (1952). *Statistics of the Recombination of Holes and Electrons*. Phys. Rev. (87) p835.
- Wertheim G. K. (1958). *Transient Recombination of Excess Carriers in Semiconductors*. Phys. Rev. (109) p1086.

RECOMBINATION VIA DISCRETE DEFECT LEVELS WITH APPLICATION TO SEMICONDUCTOR MATERIAL CHARACTERISATION

Didier Debuf ^a and Richard Corkish

Centre for Third Generation Photovoltaics, The University of New South Wales, Sydney NSW 2052, Australia
a:email didier@ee.usyd.edu.au

ABSTRACT

Semiconductor material characterization in terms of defect parameters is presently evaluated experimentally by applying the Shockley-Read-Hall (SRH) recombination time constant expression. A recent analytic solution to the SRH rate equations extended to differential rate equations for two multiple defect level systems, yields a solution derived without an approximation. In terms of material characterisation, this exact solution is shown to provide detailed information on multiple level depths in contrast to the existing theory, which relies on one dominant single level. Furthermore, for semiconductor samples known to be predominantly doped with one defect species, it is shown theoretically that the dominant decay is influenced by the other defect species present in the semiconductor sample.

INTRODUCTION

Materials' characterisation, in particular the defect level depth, which is directly related to carrier recombination, is predominantly determined from rate equations. A dominant recombination mechanism apart from Auger recombination is Shockley-Read-Hall (SRH) [1][2] recombination as formulated by the SRH rate equations. This applies to a single-level defect and interpretation to date of experimental data has relied on the assumption of a dominant defect energy level. A set of differential rate equations for multiple discrete levels based on the summation of the single-level equations is given in [3]. However approximations were introduced in [3] to simplify the analysis by reducing the non-linear differential equations to a linear form. A recent derivation of an analytic solution to the SRH rate equations [4], extended to include multiple defect levels in a first principles approach [5], indicates that the equations of [3] for multiple discrete levels are correct.

This extended solution is obtained without any approximations for a given doping concentration $N_{A,D}$, defect energy depth E_{ik} , defect concentration N_{ik} and cross sections σ_{nk} and σ_{pk} (for the k th level). The solution is comprised of an infinity of mono-exponential terms, the frequencies (inverse time constants) of which are a linear combination of the fundamental frequencies $\omega_k = 1/\tau_{k+1}$. Expressions for the minority carrier time constant τ_1 and time constants τ_{k+1} are derived in [5] for m with $k=1,2,\dots,m$, discrete defect levels. The dominant time constant is τ_1 and its behaviour with excess carrier concentration indicates the onset of trapping. The time constants τ_{k+1} are associated with the majority carrier and the defect energy levels.

In this work the focus is on determining the level depth as a means of assessing material quality. From this measurement other defect parameters may be determined from the equations. Laplace Deep Level Transient Spectroscopy (LDLTS) [7] is commonly used to ascertain defect level parameters. Although LDLTS is used to resolve multiple defect level depths, it may not lead to the direct identification of the defect species. However this may be possible in conjunction with other methods both theoretical and experimental. Another method in recent use is Lifetime Spectroscopy [8]. Both methods have limitations on the sensitivity or detection of low defect concentrations.

There are two main barriers to the determination of defect level depth for a useful assessment of material quality. The first is the inherent approximations in the derivation of the SRH lifetime expressions in common use. The recent solution indicated above [5] is determined without an approximation. The second barrier is that methods that measure the dominant time constant, such as LDLTS, may be in error for another reason. This is because from the first principles' analysis for multiple defect levels the dominant time constant is influenced by the presence of other defects, as discussed below. This may lead to a level resolution that is in error.

The defect level parameters for the single defect level in [4] were intentionally retained in the analysis of the multiple discrete level case in [5]. Comparison of $\tau_1 = 2.55 \times 10^{-5}$ s for the single defect state [4] and that for the multiple discrete level state $\tau_1 = 2.21 \times 10^{-5}$ s in the linear region, reveals that additional levels result in a lower minority carrier time constant. This represents a relative error greater than ten per cent in addition to measurement errors. This has obvious implications for interpretation of experimental data since the level depth is

contained in the time constant of the exponential term. Furthermore, the above discussion may help to explain the anomalies in terms of defect parameters arising from interpreting data in experimental methods such as LDLTS which determine the dominant decay time constant for a given rate window at a given temperature. In the literature there is a spread of values reported for defect level parameters such as level depth. This is because a given sample with, for example, iron as the dominant defect will have different background defect levels to another similarly doped sample, resulting in a different time constant τ_1 for each sample.

The paper is organised as follows. Section 2 briefly discusses the existing lifetime spectroscopy method of defect level depth evaluation. Then an account of the proposed lifetime spectroscopy method, termed Analytic Lifetime Spectroscopy, is given for the single level case as an illustration of the method which may be applied to multiple levels in Section 3. Section 4 indicates the limitations on material characterisation due to theoretical approximations and material properties that may lead to erroneous parameter determination as discussed in the Introduction. The conclusions are given in Section 5.

2 LIFETIME SPECTROSCOPY

An existing method of lifetime spectroscopy [8] using the SRH expression Eq. (1) for lifetime τ (Eqn. 5.3 of [1]) proposes the following expression Eq. (2) (Eqn. 18 of [8]) for determining the level depth $E_c - E_t$ where $\tau = \tau_1$ is the dominant decay constant for low level injection.

$$\tau = \frac{\tau_{no}(p_{po} + \Delta p + p_1) + \tau_{po}(n_{po} + \Delta n + n_1)}{n_{po} + p_{po} + \Delta n} \quad (1)$$

$$\ln\left(\frac{\tau}{T}\right) = -\frac{E_c - E_t}{kT} + \text{const} \quad (2)$$

As indicated in the introduction the dominant time constant value does not accurately reflect the effect of a single defect level if there are other defect species present in the semiconductor sample. It is an effective lifetime only. Furthermore, Eq. (1) is inaccurate for low injection [6].

3 ANALYTIC LIFETIME SPECTROSCOPY

Consider a single level for the purposes of illustrating the proposed method of the Analytic Lifetime Spectroscopy [9] described below. Multitransient analysis of the numerical solution of the governing differential equations has independently verified the fundamental frequencies predicted by the theory [4]. Re-writing the characteristic equation as Eqs. (3) and substituting the values of the fundamental frequencies ω_1 and ω_2 determined from the measured decay, yields an expression developed below, that allows the evaluation of level depth.

$$-\omega_1^2 = -(\alpha_o + \gamma_o)\omega_1 + (\alpha_o\gamma_o - \sigma_o\beta_o) \quad (3a)$$

$$-\omega_2^2 = -(\alpha_o + \gamma_o)\omega_2 + (\alpha_o\gamma_o - \sigma_o\beta_o) \quad (3b)$$

Eqs. (3) are solved for $(\alpha_o + \gamma_o)$ and $(\alpha_o\gamma_o - \sigma_o\beta_o)$ in terms of ω_1 and ω_2 . Expressions for $(\alpha_o + \gamma_o)$ and $(\alpha_o\gamma_o - \sigma_o\beta_o)$ yield the following Eqs (4).

$$C_n(n_{po} + n_1) = \frac{g_n}{C_n N_t(1 - f_o) - C_p N_t f_o} \quad (4a)$$

$$C_p(p_{po} + p_1) = \frac{g_p}{C_n N_t(1 - f_o) - C_p N_t f_o} \quad (4b)$$

where,

$$g_n = (\alpha_o + \gamma_o)C_n N_t (1 - f_o) - (\alpha_o \gamma_o - \sigma_o \beta_o) - [C_n N_t (1 - f_o)]^2 \quad (5a)$$

$$g_p = (\alpha_o + \gamma_o)C_p N_t (1 - f_o) - (\alpha_o \gamma_o - \sigma_o \beta_o) - [C_p N_t (1 - f_o)]^2 \quad (5b)$$

and at $t=0^+$

$$-\frac{d\Delta n_{nm}(t)}{dt}\bigg|_{t=0^+} = C_n N_t (1 - f_o) \quad (6)$$

By dividing Eq. (5a) by Eq. (5b), yields Eq. (7) that is the basis of the proposed Analytic Lifetime Spectroscopy.

$$\ln(g_n) = -\frac{E_c - E_t}{kT} + \ln\left[\frac{C_n N_c}{C_p p_{po}} g_p\right] \quad (7)$$

In expression (7), C_n and C_p are the capture rates of electrons and holes respectively, N_c is the effective density of states and p_{po} is the equilibrium carrier concentration for a p-type semiconductor. From an analysis of the decay, dn/dt at $t=0^+$ and the time constants $\tau_1=1/\omega_1$ and $\tau_2=1/\omega_2$, are evaluated. The quantity g_n for a p-type semiconductor may be determined from quantities which can be measured such as τ_1 , τ_2 and dn/dt . This is plotted against $1/kT$. The slope of the plot yields the level depth $E_c - E_t$. Figure 1 indicates a number of plots of various single level depths.

In the multiple level case, the graph has a simultaneous plot of lines with slopes corresponding to the multiple level depths for the fundamental time constants determined from the decay. Since the fundamental time constants are related to the level depths via the characteristic equation [4][5], more information is available to determine the multiple levels. This contrasts with the single line plot for an effective lifetime for a dominant single level used in equation (1), which is approximate

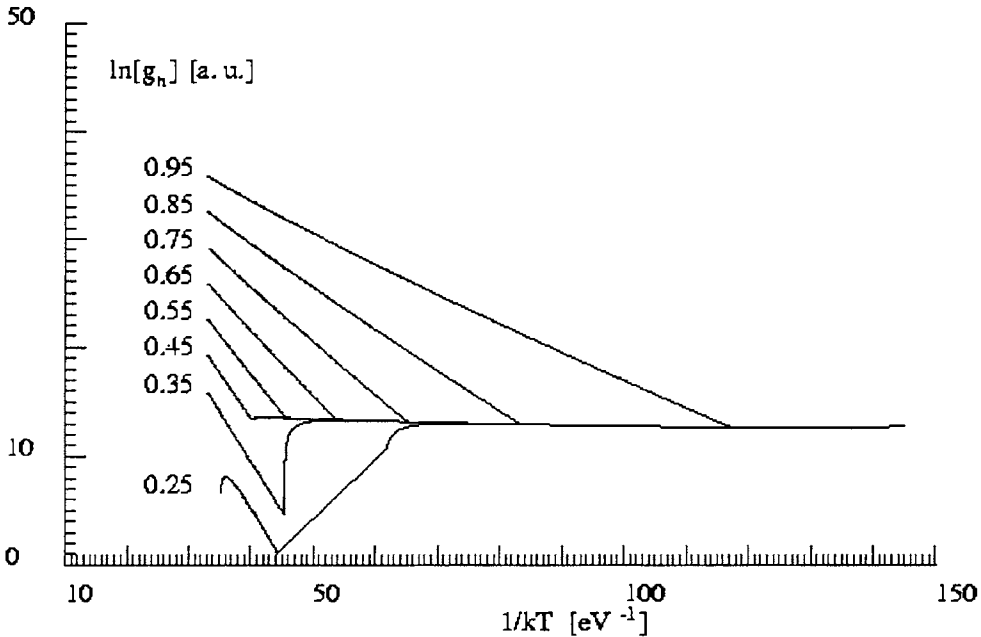


Figure 1 Proposed Analytic Lifetime Spectroscopy plot for various single level depths from the valence band edge.

4 DISCUSSION

As indicated above the limitations on material characterisation using the existing method of lifetime spectroscopy [8] become apparent as follows. From a theoretical standpoint the lifetime expression τ for the dominant single level model, is approximate. Furthermore, from both a theoretical consideration as indicated and the differences in background defect species of physical semiconductor samples known to be predominantly doped with one defect species, the dominant time constant in the decay is influenced by the other defect species present in the semiconductor sample. As indicated in Section 3, the new Analytic Lifetime Spectroscopy is based on theory which is an extension of the single level theory developed in [4]. A multitransient analysis of the numerical solution yields very good agreement with the theoretical prediction of the fundamental frequencies ω_{k+1} for the multiple discrete level case. This independent verification of the theory derived from the differential rate equations determined from first principles, confirms the properties of the above solution. An advantage of the proposed lifetime spectroscopy is that multiple levels, corresponding to the fundamental frequencies determined from the decay, may be resolved. This increases the capability of identifying defect species.

5 CONCLUSIONS

Existing experimental data are largely interpreted using the time constant expression τ derived in [1] and for multiple levels with approximations as indicated in the introduction. The current work seeks to address the anomalies arising from such an interpretation in terms of the defect level parameters such as level depth using exact theory developed recently.

6 ACKNOWLEDGMENTS

The Special Research Centre for Third Generation Photovoltaics was supported by the Australian Research Council's Special Research Centres scheme.

7 REFERENCES

- [1] W. Shockley and W. T. Read, Phys. Rev., **87** 835, (1952)
- [2] R. N. Hall, Phys. Rev., **87** 387, (1952)
- [3] G. K. Wertheim, Phys. Rev., **109** 1086, (1958)
- [4] D. Debuf, Y. Shrivastava and A. Dunn, Phys. Rev. B, **65** 245211, (2002)
- [5] D. Debuf, in preparation, (2002)
- [6] D. Debuf and Y. Shrivastava, Proceedings PV in Europe, from PV Technology to Energy Solutions, Rome, Italy, Oct (2002)
- [7] K. Gosinski, L. Dobaczewski, K. B. Nielsen, A. N. Larsen and A. R. Peaker, Phys. Rev. B, **63** 235309, (2001)
- [8] S. Rein, T. Rehr, W. Warta and S. W. Glunz, J. Appl. Phys., **91** 2059, (2002)
- [9] D. Debuf, in preparation (2002)
- [10] K. C. Nomura and J. S. Blakemore, Phys. Rev., **112** 1607, (1958)

K.4 Publications in Preparation

- The theory of fundamental frequency spectroscopy for semiconductor material characterisation

Didier Debuf

in preparation : to be submitted to J. Appl. Phys. (2003)

Bibliography

- [1] D. Debuf, Y. Shrivastava, and A. Dunn. *Phys. Rev. B*, **65**:245211, (2002).
- [2] W. Shockley and W. T. Read. *Phys. Rev.*, **87**:835, (1952).
- [3] R. N. Hall. *Phys. Rev.*, **87**:387, (1952).
- [4] K. C. Nomura and J. S. Blakemore. *Phys. Rev.*, **112**:1607, (1958).
- [5] B. G. Streetman. *J. Appl. Phys.*, **37**:3137, (1966).
- [6] D. J. Sandiford. *Phys. Rev.*, **105**:524, (1957).
- [7] H. Y. Fan. *Phys. Rev.*, **92**:1424, (1953).
- [8] A. Rose. *Phys. Rev.*, **97**:322, (1955).
- [9] G. K. Wertheim. *Phys. Rev.*, **109**:1086, 1958.
- [10] S. C. Choo. *Phys. Rev. B*, **1**:687, (1970).
- [11] S. M. Sze. *Physics of Semiconductor Devices*. (Wiley And Sons, New York, 1981).
- [12] C. T. Sah. *Solid-State Electron.*, **19**:975, (1976).
- [13] M. J. Keevers and M. A. Green. *Solar Energy Materials and Solar Cells.*, **41/42**:195, (1996).

- [14] D. W. Jordan and P. Smith. *Nonlinear Ordinary Differential Equations An Introduction to Dynamical Systems*. (Oxford University Press, Oxford p63, 1999).
- [15] E. Kreyszig. *Advanced Engineering Mathematics*. (Wiley And Sons, New York 6thEd p74 p89, 1988).
- [16] C. Chen. *Linear System Theory and Design*. (Harcourt Brace College Publishers, New York p87, 1984).
- [17] J. R. Dormand. *Numerical Methods for Differential Equations A Computational Approach*. CRC Press, New York, 1996).
- [18] W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling. *Numerical recipes in C : The Art in Scientific Computing*. (Cambridge University Press, Cambridge, 1992).
- [19] D. W. Jordan and P. Smith. *Nonlinear Ordinary Differential Equations An Introduction to Dynamical Systems*. (Oxford University Press, Oxford p3, 1999).
- [20] E. Yeramian and P. Claverie. *Nature*, **326**:169, (1987).
- [21] P. Claverie, A. Denis, and E. Yeramian. *Comp. Phys. Rep.*, **9**:247, (1989).
- [22] J. Alam. Multi exponential signal analysis using the total least squares method. Master's thesis, (The University of Calgary, Alberta, Canada, 1990).
- [23] S. Van Huffel and Vandewalle J. *The Total Least Squares Problem Computational Aspects and Analysis*. (Society for Industrial and Applied Mathematics SIAM, Philadelphia, 1991).
- [24] D. R. Debuf. Analysis of multi exponential signals applied to photoconductance decay. Master's thesis, (The University of New South Wales, Sydney, Australia, 1993).

-
- [25] V. J. Klema and A. J. Laub. *IEEE Trans Automatic Control*, **AC-25**:164, (1980).
- [26] J. S. Blakemore. *Semiconductor Statistics*. Pergamon Press, Oxford p250, 1962.
- [27] C. T. Sah. *Fundamentals of Solid State Electronics*. World Scientific, London p231, 1991.
- [28] K. L. Luke and L. J. Cheng. *J. Appl. Phys.*, 61 (6):2282–2293, 1987.
- [29] J. Schmidt and A. G. Aberle. *J. Appl. Phys.*, **85**:3626, (1999).
- [30] A. G. Aberle, S. Glunz, and W. Warta. *J. Appl. Phys.*, **71**:4422, (1992).
- [31] C. T. Sah. *Fundamentals of Solid State Electronics*. World Scientific, London p265 p268, 1991.
- [32] G. R. Fulford and P. Broadbridge. *Industrial Mathematics, Case Studies in the Diffusion of Heat and Matter*. (Cambridge University Press, Cambridge p29, 2002).
- [33] S. Zhao, L. V. C. Assali, Justo J. F., Gilmer G. H., and Kimerling L. C. *J. Appl. Phys.*, **90**:2744, (2001).
- [34] S. M. Sze. *Physics of Semiconductor Devices*. (Wiley And Sons, New York Second Ed. p29, 1981).
- [35] W. M. Chen, B. Monemar, E. Janzen, and J. L. Lindstrom. *Phys. Rev. Lett.*, **67**:1914, (1991).
- [36] A. M. Frens, M. T. Bennebroek, A. Zakrzewski, J. Schmidt, W. M. Chen, , E. Janzen, J. L. Lindstrom, and B. Monemar. *Phys. Rev. Lett.*, **72**:2939, (1994).
- [37] J. P. McKelvey. *Solid State and Semiconductor Physics*. Harper and Row, New York, Evanston and London, 1966.

- [38] R. R. King, R. A. Sinton, and R. M. Swanson. *IEEE Trans. Elect. Dev.*, **37**:365, (1990).
- [39] R. R. King and R. M. Swanson. *IEEE Trans. Elect. Dev.*, **38**:1399, (1991).
- [40] P. A. Basore and B. R. Hansen. Microwave detected photoconductance decay. *21st IEEE Photovoltaic Specialists Conference*, 1990.
- [41] R. K. Ahrenkiel and S. Johnston. *26th IEEE Photovoltaic Specialists Conference Sept 29 - Oct 3, Anaheim, California*, (1997).
- [42] D. V. Lang. Deep level transient spectroscopy : A new method to characterise traps in semiconductors. *J. Appl. Phys.*, 45:3023, 1974.
- [43] H. G. Grimeiss, E. Janzen, and B. Skarstam. *J. Appl. Phys.*, **51**:3740, (1980).
- [44] K. Gosinski, L. Dobaczewski, K. B. Nielsen, A. N. Larsen, and A. R. Peaker. *Phys. Rev. B*, **63**:235309, (2001).
- [45] J. Frenkel. *Phys. Rev.*, **54**:647, (1938).
- [46] S. Rein, T. Rehrl, W. Warta, and S. W. Glunz. *J. Appl. Phys.*, **91**:2059, (2002).
- [47] E. Kreyszig. *Advanced Engineering Mathematics*. (Wiley And Sons, New York 6thEd p34, 1988).
- [48] A. M. Stuart and A. R. Humphries. *Dynamical Systems and Numerical Analysis*. (Cambridge University Press, New York p127, 1998).
- [49] E. Kreyszig. *Advanced Engineering Mathematics*. (Wiley And Sons, New York 6thEd p218, 1988).