

Theoretical investigation of materials and performance for the hot carrier solar cell

Author:

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Publication Date:

2014

DOI:

<https://doi.org/10.26190/unsworks/2532>

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Theoretical Investigation of Materials and Performance for the Hot Carrier Solar Cell

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PLEASE TYPE**THE UNIVERSITY OF NEW SOUTH WALES
Thesis/Dissertation Sheet**Surname or Family name: **Feng**First name: **Yu**

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Abbreviation for degree as given in the University calendar:
PhDSchool: **School of Photovoltaics and Renewable Energy Engineering**Faculty: **Engineering**Title: **Theoretical Investigation on Materials and Performances for the Hot Carrier Solar Cell****Abstract 350 words maximum: (PLEASE TYPE)**

The hot carrier solar cell (HCSC) is a novel concept on solar energy conversion, which has the potential of exceeding the Shockley-Queisser efficiency limit. Such device extracts the hot photo-generated carriers before their thermalization. It requires an absorber layer that inhibits the energy dissipation of hot carriers, and two energy selective contacts (ESC) that extract electrons and holes respectively, through small energy windows. This is to prevent excessive entropy generation during the extraction processes.

In this thesis several device models are developed for calculating the conversion efficiency of the hot carrier solar cell. Incorporation of actual impact ionization and Auger recombination rates into the model enables self-modulation of the carrier average energies, allowing for stable solutions when carriers are extracted merely at specific energy levels. The carrier-carrier scattering also takes an important role as they contribute to the renormalisation of carrier energy distributions. The proposed model of energy/particle conservations applies to the case of normalized carrier populations while the relaxation-time model can apply to arbitrary carrier statistics. These device models are then generalized to any solid-state systems, yielding a generalized version of the opto-electronic reciprocal relation. The effect of energy-selective contacts on the device performance has also been quantitatively analyzed. Accounting for real properties of carrier ballistic tunneling through the contacts, the efficiency variation has been calculated for different transmission profiles, yielding optimized contact structures.

To optimize the selection of materials for this device, the electronic and phononic properties of multiple-quantum-well superlattices have been calculated. Tight-binding methods and bond charge models are adopted for the calculation of electronic and phononic structures respectively. The rates of hot electrons emitting phonons are then calculated for various structural parameters, with the carrier screening effect being formularized and incorporated. The anharmonic interactions between phonons are also calculated to evaluate the phonon-bottleneck effect. In correspondence to the proposed device model, the relaxation times of carrier renormalisation has been evaluated by calculating the rates of carrier-carrier scattering using real material parameters. The electron tunneling properties through real material systems have also been calculated, with inelastic scattering by phonons incorporated. The work on material modeling provides comprehensive tools for theoretical analysis of real material systems, whose results are to be readily adopted by the device models for accurate performance predications.

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ABSTRACT

The hot carrier solar cell (HCSC) is a novel concept on solar energy conversion, which has the potential of exceeding the Shockley-Queisser efficiency limit. Such a device extracts the hot photo-generated carriers before their thermalization. It requires an absorber layer that inhibits the energy dissipation of hot carriers, and two energy selective contacts (ESC) that extract electrons and holes respectively, through small energy windows. This is to prevent excessive entropy generation during the extraction processes.

In this thesis, several device models are developed for calculating the conversion efficiency of the hot carrier solar cell. Incorporation of actual data, from literature, for impact ionization and Auger recombination rates, into the model enables self-modulation of the carrier average energies, allowing for stable solutions when carriers are extracted at specific energy levels. The carrier-carrier scattering also takes an important role as it contributes to the renormalisation of carrier energy distributions. The proposed model of

energy/particle conservations applies to the case of normalized carrier populations while the relaxation-time model can apply to arbitrary carrier statistics. These device models are then generalized to any solid-state systems, yielding a generalized version of the opto-electronic reciprocal relation. The effect of energy-selective contacts on the device performance has also been quantitatively analyzed. Accounting for real properties of carrier ballistic tunneling through the contacts, the efficiency variation has been calculated for different transmission profiles, yielding optimized contact structures.

To optimize the selection of materials for this device, the electronic and phononic properties of multiple-quantum-well superlattices have been calculated. Tight-binding methods and bond charge models are adopted for the calculation of electronic and phononic structures respectively. The rates of hot electrons emitting phonons are then calculated for various structural parameters, with the carrier screening effect being formulated and incorporated. The anharmonic interactions between phonons are also calculated to evaluate the phonon-bottleneck effect. In correspondence to the proposed device model, the relaxation times of carrier renormalisation are evaluated by calculating the rates of carrier-carrier scattering using real material parameters. The electron tunneling properties through real material systems have also been calculated, with inelastic scattering by phonons incorporated. The work on material modeling provides comprehensive tools for theoretical analysis of real material systems, whose results are to be readily adopted by the device models for accurate performance predictions.

DEDICATION

To my beloved wife and parents

ACKNOWLEDGEMENT

I would like to express my deepest gratitude to my supervisor Prof. Gavin Conibeer first. He has provided me the greatest support during my PhD study. I am grateful for his trust and consistent teaching that allow me to complete this challenging theoretical project. Our regular academic talking has inspired me a lot and leads me to fruitful research outcomes.

I would like to thank one of my co-supervisors Dr. Santosh Shrestha for guiding me into the wonderful area of hot carrier solar cell. He has constantly provided me suggestions and support on my work and life. I am also thankful to Dr. Shujuan Huang for providing me professional knowledge on the area of colloidal nano-particles. Many thanks to my co-supervisor Prof. Martin Green for his precious advices and guidances on my research outcomes, especially on the work of optoelectronic reciprocity.

I am grateful to Dr. Pasquale Aliberti for his kindness and hard work during our collaboration on the theoretical device model of the hot carrier

solar cell. He guided me into this area and we together developed beautiful numerical models. I much appreciate the great help provided by Dr. Robert Patterson and Dr. Binesh Puthen Veettil throughout my PhD study. I would also like to thank Mr. Hongze Xia and Dr. Xiaoming Wen for our happy collaboration.

I would like to thank all of my great friends who have supported me and helped me during the recent three years, especially Lihui Song, Hongze Xia, Xuguang Jia, Linfeng Wu, Pengfei Zhang, for their company through both good and bad times. I am also grateful to Prof. Gavin Conibeer, Dr. Santosh Shrestha, Dr Ivan Perez-Wurfl and Dr Alison Lennon for providing me tutoring positions, which has allowed me to enjoy the great charm of teaching.

Thanks to the University of New South Wales and School of Photovoltaics and Renewable Energy Engineering for providing me this unforgettable experience of doctoral study. Three years ago I met my wife Shu Lin in the campus, who was also a student studying in this school. Since then she has granted me so much happiness and great spiritual support. I am quite grateful to her and to our love.

Finally I would like to give a lot of thanks to my parents, grandparents and other family members for their constant love and wonderful support.

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NOMENCLATURE

DOS	density of states
EC	energy conservation
ehs	electron-hole scattering
eq	equilibrium
ESC	selective energy contact
HCSC	hot carrier solar cell
HH	heavy hole
IA	impact ionization/Auger recombination
LH	light hole
MPP	maximum power point
RT	room temperature
RTA	relaxation time approximation
RTD	resonant tunneling diode
SO	split-off (band)
TH	thermalisation
TRPL	time resolved photoluminescence

INTRODUCTION

The hot carrier solar cell (HCSC) is a solar energy converting device that can potentially have efficiency figures higher than the limitation for conventional (single-junction) solar cells.[1] The underlying physical principle for this high conversion efficiency comes from the suppression of energy relaxation processes of photo-generated carriers.[2, 3] These highly energetic carriers, excited by the blue spectrum part of solar irradiation, are immediately thermalized to the respective band edges in conventional solar cells, while in HCSC the carriers can maintain hot populations. These hot carriers are then extracted from their respective contacts with rectification of both carrier type and transmittable energies. Such selective energy contacts (ESCs) serve as brownian heat engines, converting the thermal energy of hot carriers into free energy with little entropy generation.[4]

There are several models being proposed since the concept of HCSC was first introduced in 1980s, but most of them adopted over-simplified assumptions resulting in unrealistic efficiency figures.[1, 5] An important issue is the use of conservation laws. Some work assumed the incoming and outgoing quanta fluxes are balanced but with no considerations on energetics[1], while

others treated the conservation of system total energy only[5, 6]. The former assumption is problematic and leads to unrealistically high temperature predictions[7], and the latter can give physical solutions only with the assumption of zero electro-chemical potential of carrier system[5]. The author of this thesis has developed a model incorporating both considerations on particle conservation and energy conservation. By modeling realistic quantum processes, the number of assumptions is significantly reduced leading to more reliable performance predictions.

Due to the significant contrast of effective masses between electrons and holes, electrons get most of the photon energy and thermalize slower in most semiconductors[8], leading to a much hotter distribution than that of holes. Here the term “thermalization” refers to the process that carriers dissipate their energies to the lattice via various scattering mechanisms. There have been two arguments on the temperature distributions between electrons and holes. Some researchers believed that the holes are completely thermalized and a normal contact for them is sufficient[8], while others argued that the interactions between electrons and holes are sufficiently fast to maintain a uniform temperature[5, 9]. This disagreement has been tested quantitatively by the author, with significant implications for the operation of a real device. Moreover, the author treated the existence of non-equilibrium carrier system with arbitrary statistical functions, instead of the distributions in thermal equilibrium. It is proved that the steady-state carrier energy distribution is away from that in thermal equilibrium and the device performance largely depends on such non-equilibrium properties. The author has also related the device non-equilibrium property with intrinsic material properties, providing new aspects for material selection.

To make a good HCSC device, there are requirements for the photonic,

electronic and phononic properties of the absorber material. It is preferable to have good absorption properties with low band gaps, the dissociation of photo-generated excitons should be quick enough and the carrier transport property should also be good. However, among all the quantum processes happening in such devices, the energy relaxation of carriers is the most crucial one to realize the HCSC device. As demonstrated in some recent quantitative works[10, 9], a slower carrier cooling rate can dramatically increase the conversion efficiency over that of conventional cells. By investigating the microscopic nature of the carrier energy relaxation, we found it possible to suppress the energy dissipation by blocking one of its sequential processes. A promising way for this is to minimize the rate of electron-phonon interactions, hence preventing hot electrons from emitting phonons in the time order of femtoseconds. Among these interactions, the Fröhlich (polar) scattering[11] with optical modes is the dominant contribution for polar semiconductors.[12] Another approach is to utilize the so-called “phonon bottleneck effect” to block the decay paths from optical phonons to acoustic phonons, e.g. Klemens decay.[13] If maintained as a hot population, optical phonons can actually feed energy back to electrons, as they diffuse much slower than acoustic phonons and are prone to be reflected at interfaces.[14, 15]

In the literature, the phonon-electron scattering rate and hence the carrier energy relaxation time have been reported for both elementary semiconductors, such as Si and Ge, and diatomic polar semiconductors, such as GaAs and GaN.[12] The results have shown a slight increase in the conversion efficiency due to a moderate warm temperature of electrons. Another observation is that elemental semiconductors perform better than compound materials in terms of electron-phonon decoupling, because the energy dissipation rates due to polar Fröhlich interaction are much faster than those caused

by deformation potential. However, though compound semiconductors suffer strong electron-phonon interactions, there may be decoupling between optical phonons and acoustic phonons which contributes to the phonon bottleneck effect. If with a large mass contrast between the two component atoms, Klemens decay may be effectively prevented due to a large frequency splitting between acoustic modes and optical modes.[16] The splitting may allow the violation of energy conservation law, thus blocking the decay passage.[17]

Among all types of semiconductors, type III-V is a good choice as the component atoms can be mixed with accurate stoichiometric control and crystallinity. However, as the performances of solar cells are strongly affected by dislocations, traps and other defects, elaborate deposition techniques are required to get good material qualities. In fact, III-N materials are notoriously difficult to grow due to phase separation and limitation of available substrates. Nevertheless, their simple crystal structures (cubic or hexagonal) and tunable atomic masses make them attractive, as the phonon energy splitting can be sufficiently large. In addition, the polarity of such material is not as strong as that of the II-VI group, leading to a less strong Fröhlich interaction. With careful examination, InN (Indium Nitride) was selected as a close to ideal candidate for HCSC absorber[9]. Its large phononic bandgap, resulting from the large mass contrast between indium and nitrogen atoms, indicates a significant suppression of Klemens decay. Its narrow optical bandgap (0.7eV) also allows broad-band light absorption. This is preferable, as for a HCSC the open-circuit voltage is no longer limited by the electronic bandgap. Experimentally there is evidence showing a lower carrier cooling rate of InN than that of GaAs[18].

Apart from bulk semiconductors, nanostructured materials have been investigated and there is experimental evidence that multiple-quantum-well

superlattice (MQW-SL) structures can reduce the electron energy relaxation significantly.[19] Some explanations have been proposed involving phonon-bottleneck effects and dynamic carrier screening[20]. However the theoretical prediction in terms of the steady-state energy relaxation rates of electrons remains a problem. Its dependence on the variation of layer thicknesses is also still unclear. Therefore a comprehensive theoretical and computational framework is required with consideration of all relevant processes and effects.

During PhD study, the author has constructed a theoretical framework of the electron cooling processes in quantum-well semiconductor superlattice structures and has applied it to the InN/In_xGa_{1-x}N MQW-SL. Processes involving the screened Fröhlich interaction and the anharmonicity-based phonon decay are modeled and computed. A model that deals with the static carrier screening in any MQW-SL structures has been developed with sufficient accuracy. These are all powerful tools for engineering the absorber of HCSC and have already generated some useful results.

Apart from the electronic, photonics and phononic properties of the absorber, the transmission properties of electrons through the contacts (ESCs) cannot be neglected. The final conversion efficiency significantly relies on the contact resistance and the entropy generation during extraction. To prove this, the author has improved the existing model with consideration on realistic properties of carrier extraction. By using this quantitative model, a sample contact structure of InGaN/InN/InGaN has been optimized, aiming to minimize both the contact resistance and the entropy generation. In general these two effects counter against each other so that a trade-off is required for optimization. Other material systems have also been evaluated with a complicated tight-binding method taking into account the phonon scattering effect during the transmission.

DEVICE MODELING

2.1 Hybrid model for steady-state operation of the HCSC

In this section the theoretical efficiencies of an ideal hot carrier solar cell (HCSC) device considering indium nitride (InN) as the absorber material have been calculated. A hybrid model has been suggested to incorporate both the particle (quanta) conservation and the energy conservation during the opto-electronic energy conversion. Real electronic dispersions of wurtzite-structured InN have been taken into account yielding actual rates of impact ionization (II) and Auger recombination (AR). The model reveals that the interplay of AR/II, carrier thermalization and extraction affects the cell performance in a complex way. This indicates the necessity of incorporating electronic, photonic, phononic structures and their coupling properties when designing material structures to achieve high energy conversion efficiency. The work in this section has been published in “Investigation of theoretical efficiency limit of hot carriers solar cells with a bulk indium nitride absorber” by P. Aliberti, Y. Feng, et al., 2010, Journal of Applied Physics, 108(9):094507-094507.

In a hot carrier solar cell, highly energetic carriers are extracted from the device before their thermalisation to room temperature (Fig. 2.1). At steady state, a hot population of carriers in the absorber layer may be established by engineering the material for a slow heat dissipation[17]. The thermally populated carriers are then extracted from the energy selective contacts (ESCs). Such a contact works as a carrier filter only allowing a certain type of carriers with a specified energy to transmit through it[21]. It is a reversible Brownian heat engine if operating quasi-statically[4]. Thereby the thermal energy of carrier populations can be converted to electrical work with minimized entropy generation.

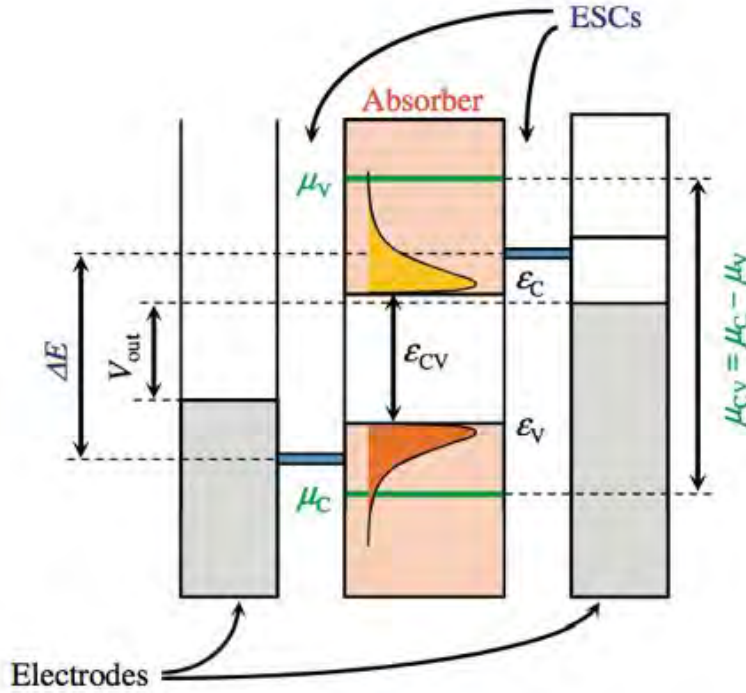


Fig 2.1: Schematic diagram on the operation principle of the hot carrier solar cell[22]

This proposed device allows higher efficiencies in comparison to conven-

tional solar cells. In fact, the excess energy of energetic photons, which is lost in a conventional solar cell, is first converted to the thermal energy of carriers and then converted to electricity in a HCSC. Previous reports[1, 5] on the efficiency calculation of the HCSC predicted high efficiency (50% to 80%); however the methodologies adopted in their analyses are problematic[7]. These models all belong to two different theoretical frameworks, either the particle conservation (PC) model (Sec. ??) or the impact ionization/Auger recombination (II/AR) model (Sec. ??). These two models rely on respective over-simplified assumptions and hence are only valid in particular extreme conditions. In addition an ideal absorber material with the approximation of parabolic bands has always been considered in the past.

PC models[1, 23] assume the relevant microscopic processes conserve the total number of photons and electron-hole (e-h) pairs. In the case of a band-to-band absorption or emission process, an e-h pair is created or annihilated, accompanied by annihilation/emission of an associated photon. The number of e-h pairs does not change during the processes until they are extracted at the electrodes. However, in the static operation of the HCSC the carriers are basically hot and away from equilibrium, yielding a strong trend towards impact ionization or Auger recombination. This is especially true if extracting carriers with ideal ESCs. As pointed out by Würfel et al.[7], if the extraction energy deviates from the average energy of the absorbed photons, the static carrier temperature varies significantly unless the process of impact ionization or Auger recombination is fast enough.

II/AR models[5] utilize the energy conservation (EC) law to calculate the conversion efficiency. It includes an assumption that the electro-chemical potential of the e-h pairs in the absorber is maintained at zero. This is the case of chemical equilibrium between the electrons and holes. However

under external disturbance (e.g. photons) such equilibrium state can only be retrieved by super-fast inter-band carrier scattering. Such scattering includes impact ionization and Auger recombination as its reverse process. In actual operation of HCSC devices the exact chemical equilibrium cannot be obtained as the rates of these processes are limited by the intrinsic electronic properties of the absorber material.

2.1.1 Combination of PC and EC models

In this recently proposed model, the laws of particle conservation and energy conservation are both included to eliminate any over-simplified assumptions. The actual rates of impact ionization and Auger recombinations are calculated within the framework of Fermi's golden rule. Actual electronic band structures of the model material are adopted for this calculation, which will be discussed in the following sub-sections.

The HCSC device has been treated as a system which can interact with the external environment through particles and energy exchange. Hot electrons and holes dissipate their energies by interacting with the lattice, and are then extracted to the external circuit through ESCs. Both contacts in this model have been considered to be ideal, such that they have infinite conductivity and an infinitesimal allowed energy range for transmission. The particle fluxes and energy fluxes between the device and the environment are illustrated in Fig. 2.2.

We assume the electron system and the hole system are separately in equilibrium, i.e. the statistics of electrons and holes are normalized due to fast electron-electron or hole-hole scattering processes, respectively. Their energy distributions are described by respective Fermi functions with altered electrochemical potentials and temperatures. In this part a common temperature

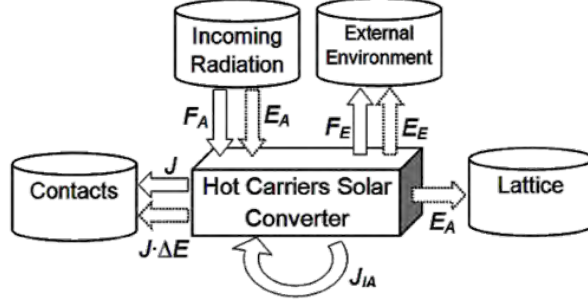


Fig 2.2: Schematic diagram of the energy and particle fluxes used in the model (particle fluxes: full arrows; energy fluxes: dotted arrows).[9]

value for hot electrons and holes has also been assumed[24]. These assumptions have been included in other reports[7, 12], though other authors considered holes to be completely thermalized, due to their high effective mass, with only electrons being at a higher non-equilibrium temperatures[8, 25].

Corresponding to Fig. 2.2, the particle fluxes are expressed in Eq. 2.1 to Eq. 2.5. The incoming photon flux coming from the sun can be approximated with a blackbody radiation spectrum as shown in Eq. 2.1.

$$F_A = \int_{E_g}^{\infty} \frac{2\Omega_A}{h^3 c^2} \frac{\epsilon^2 d\epsilon}{e^{\epsilon/kT_S} - 1} \quad (2.1)$$

$$\Delta\mu = \mu_e + \mu_h + E_g \quad (2.2)$$

where μ_e and μ_h represent quasi-Fermi energies of electrons and holes measured from the conduction and valence band edges, respectively. $\Delta\mu$ is the quasi-Fermi level separation, which includes the band gap E_g , as shown in Eq. 2.2. F_A represents the number of incoming particles (photons) per unit area per unit time, Ω_A is the solid angle subtended by the sun and is proportional to the concentration ratio, $T_S = 5760$ K is the temperature of the blackbody.[26] The outgoing particle flux, due to radiative recombination of electrons and holes in the device is calculated using a generalized Planck

equation[27] and assuming a flat geometry for the cell (Eq. 2.3).

$$F_E = \int_{E_g}^{\infty} \frac{2\pi}{h^3 c^2} \frac{\epsilon^2 d\epsilon}{e^{(\epsilon - \Delta\mu)/kT_s} - 1} \quad (2.3)$$

In Eq. 2.3 T_C is the common Fermi-temperature for the electron and hole distributions. Particle fluxes due to AR and II are calculated using coefficients derived for bulk InN. Details of the derivation are reported in Sec. 2.1.2.2.

$$F_{IA} = d_{abs} R_{II}(\mu_e, \mu_h, T_C) - d_{abs} R_{AR}(\mu_e, \mu_h, T_C) \quad (2.4)$$

where F_{IA} is the particle flux associated with AR and II events. This is directly related to total AR-II rates (R_{AR} , R_{II}) and to the absorber thickness d_{abs} . The current density in steady state can be calculated by balancing incoming and outgoing particle and energy fluxes

$$J = e(F_A - F_E + F_{IA}) \quad (2.5)$$

The calculation of current density as a function of carrier temperature and quasi-Fermi levels, according to Eq. 2.5, is completely general and allows computation of extracted current for a given carrier statistics in the absorber.

AR and II rates depend on the quasi-Fermi level separation. A net AR rate is obtained for positive $\Delta\mu$ and a net II rate for negative $\Delta\mu$. The rigorous PC condition is only accomplished when there is no splitting of quasi-Fermi levels, i.e. there is chemical equilibrium between the electron reservoir and the hole reservoir.

The flux of energy due to incoming solar illumination (E_A) is considered together with the energy flux emitted by the cell due to emission of photons (E_E) and the flux due to the carrier thermalisation process (E_{TH}). The

expressions of these energy fluxes are listed in Eq. 2.6~2.8.

$$E_A = \int_{E_g}^{\infty} \frac{2\Omega_A}{h^3 c^2} \frac{\epsilon^3 d\epsilon}{e^{\epsilon/kT_S} - 1} \quad (2.6)$$

$$E_E = \int_{E_g}^{\infty} \frac{2\pi}{h^3 c^2} \frac{\epsilon^3 d\epsilon}{e^{(\epsilon-\Delta\mu)/kT_C} - 1} \quad (2.7)$$

$$E_{TH} = n_e d_{abs} \frac{\bar{\epsilon}_e(\mu_e, T_C) - \bar{\epsilon}_e(\mu_e, T_{RT})}{\tau_{TH}} + n_h d_{abs} \frac{\bar{\epsilon}_h(\mu_h, T_C) - \bar{\epsilon}_h(\mu_h, T_{RT})}{\tau_{TH}} \quad (2.8)$$

The energy flux due to electron and hole thermalisation losses is shown in Eq. 2.8. T_{RT} is room temperature (300 K), τ_{TH} is the characteristic thermalisation lifetime for hot carriers, n_e and n_h are the electron and hole densities, respectively, $\bar{\epsilon}_e$ and $\bar{\epsilon}_h$ are the average energy values for electron and hole populations. The net thermalisation loss is a function of the carrier temperature and quasi-Fermi potentials, as shown in Eq. 2.8. The average energy decays during thermalisation toward $\bar{\epsilon}_e(\mu_e, T_{RT})$ and $\bar{\epsilon}_h(\mu_h, T_{RT})$, which are close to the thermal energy value $3kT_{RT}$. The energy reference levels are the corresponding band edges.

$$\bar{\epsilon}_e = \frac{\int_0^{\infty} \epsilon D_e(\epsilon) f_e(\mu_e, T_C) d\epsilon}{\int_0^{\infty} D_e(\epsilon) f_e(\mu_e, T_C) d\epsilon} \quad (2.9)$$

$$\bar{\epsilon}_h = \frac{\int_0^{\infty} \epsilon D_h(\epsilon) f_h(\mu_h, T_C) d\epsilon}{\int_0^{\infty} D_h(\epsilon) f_h(\mu_h, T_C) d\epsilon} \quad (2.10)$$

In Eq. 2.9 and 2.10 $D_e(\epsilon)$ and $D_h(\epsilon)$ represent the electron and hole densities of states while f_e and f_h are the electron and hole occupancy probabilities. In this model it is assumed that hot populations are distributed according to Fermi-Dirac statistics and hence f_e and f_h will depend exponentially on T_C , E_e and E_h respectively, although in reality its validity strongly depends on the rates of carrier-carrier scattering. E_{TH} represents an exponential decay in energy of photo-generated carriers. However, the consideration of nonequilibrium AR and II coefficients can modify occupancies but

conserve total energy of the electronic system. The product of the extracted current and the extraction energy represents the extracted hot carrier energy flux and can be calculated by balancing the three energy fluxes as in Eq. 2.11.

$$J\Delta E = e(E_A - E_E - E_{TH}) \quad (2.11)$$

where J is the extracted current as in Eq. 2.5 while ΔE represents the extraction energy of hot carriers from the absorber as shown in Fig. 2.1. This value is assumed to be fixed and depends on the properties of the ESC structure[21]. Even assuming ideal ESCs, and hence isoentropic carrier transfer, the voltage of carriers in the external circuit, ΔV , must be lower than $\Delta E/e$. This is described by a Carnot type relation between the voltage across the device and the extraction energy[1].

$$\Delta V = \frac{1}{e} \left[\Delta E \left(1 - \frac{T_{RT}}{T_C} \right) + \Delta \mu \frac{T_{RT}}{T_C} \right] \quad (2.12)$$

Being every flux mentioned in the previous sections a function of $\Delta \mu$ and T_C , these two parameters can be calculated, together with current density J , solving numerically Eq. 2.5, 2.11, and 2.12. The solar cell efficiencies have been calculated as the ratio of extracted power at the maximum power point (MPP) of operation and the total power in the incoming spectrum, P_{in} .

$$\eta = \frac{J\Delta V}{P_{in}} \quad (2.13)$$

where P_{in} is the sum of all the photon energies, multiplied by their individual intensities, I_A .

$$P_{in} = \int_0^\infty \epsilon I_A d\epsilon \quad (2.14)$$

2.1.2 Performance prediction for an InN-based HCSC

In this part bulk indium nitride InN has been chosen as the modeling material for the absorber. The main reason for this is the desirable electronic and

phononic properties of the wurtzite-structured InN. It has a small electronic band gap (0.7 eV) for a wide-band light absorption. At the same time due to the strong contrast between the atomic masses of its component elements, it has a very wide gap between acoustic and optical branches in its phonon dispersion characteristic. This allows slower thermalisation of hot carriers by suppression of optical to acoustic phonon decay via the specific Klemens' decay processes[28, 29, 12, 13].

2.1.2.1 Electronic structures and Carrier density calculation

To enable the calculations of the electronic properties of InN, an accurate description of its electronic structure is required. $E - k$ relations for high purity wurtzite InN have been calculated by Fritsch *et al.*[29] using empirical pseudopotential methods. Results of the calculations illustrate that, in the energy range of interest for solar cells, InN shows two separated bands at the Γ point plus a satellite band at the $M - L$ symmetry point, along the Σ crystal direction for the conduction band. For the valence band the calculation confirms two main bands with a point of degeneration at Γ , which can be identified as heavy and light hole bands. In addition, a separated split-off band is considered as shown in Tab. 2.1.

A multivalley approximation for the bulk InN band structure which takes into account the three lowest conduction band minima (Γ_1 , Γ_3 , and $M - L$) and three valence bands [heavy hole(HH), light hole(LH) and split-off(SH) bands] has been used for calculations. Parameters for effective masses in satellite bands and nonparabolicity coefficients have been extracted from Fritsch and numeric values are reported in Tab. 2.1.[29, 30]

To be able to calculate the J - V characteristic of the HCSC using the equations described above, a relation between carrier density, electron and

Table 2.1: Model parameters for bulk indium nitride conduction and valence bands. Values have been extracted from Fritsch *et al.* [29].

	Conduction band			Valence band		
	Γ_1	Γ_3	$M - L$	$\Gamma_1(H)$	$\Gamma_2(L)$	$\Gamma_3(S)$
Effective mass m/m_0	0.04	0.25	1	2.827	0.235	0.479
Nonparabolicity factor	1.43	0	0	0	0	0
Intervalley energy separation (eV)	0	1.77	2.71	0	0	0.25
Number of equivalent valleys	1	1	6	1	1	1

hole quasi-Fermi levels, and carrier temperatures for bulk wurtzite InN is necessary. The carrier density can be calculated from the electron and hole densities of states, which can be obtained from the respective electronic dispersion relations.

2.1.2.2 AR and II coefficients calculation

The influence of AR-II on the efficiency of the HCSC has been taken into account amending the expression for the total current from the cell, as shown in Eq. 2.5. Such a modeling approach allows consideration of actual II-AR effects for all operating points of the HCSC. AR-II rates have been calculated by considering the three most probable processes for bulk InN, i.e. CCCH, CHHS, and CHHL (Fig. 2.3), as reported by Dutta and Nelson[31], and neglecting high k -vector mechanisms[32, 33, 34]. The band structure used for the II-AR rate computation is the same as for carrier density calculations. The CCCH AR process involves three conduction band electrons and one heavy hole. A conduction band electron recombines with a hole, giving energy to a second conduction band electron and raising it to a higher energy level. CCCH was first investigated by Beattie and Landsberg[35] (Eq. 2.15).

$$R_{CCCH} = \frac{32e^4 m_{c0} \alpha_{CH} \beta}{h^3 \epsilon^2 E_g} I \quad (2.15)$$

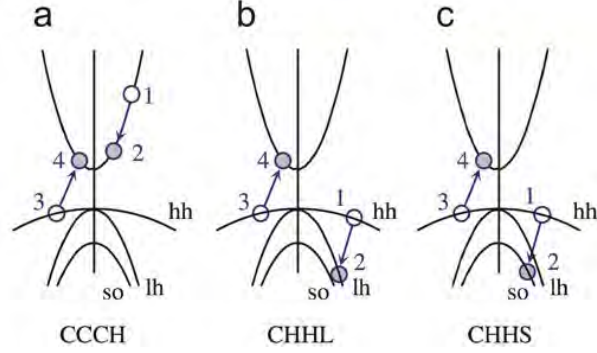


Fig 2.3: Schematic diagram of impact ionisation processes: CCCH, CHHS, CHHL. Adapted from “Hot carrier solar cells operating under practical conditions” by Y. Takeda et al., 2009, Journal of Applied Physics, 105(7):074905.

A simplification of the rate expression has been calculated by Dutta and Nelson[31] and is used in Eq. 2.15 with a technique developed by Sagimura[36]. The integral I can be evaluated according to Eq. 2.16. Definitions for functions F and G can be found in Dutta and Nelson[31], Z_1 and Z_2 are calculated as in Eq. 2.17.

$$I = \int_0^\infty dZ_1 \int_{|A|Z_1}^\infty dZ_2 F(Z_1, Z_2) G(Z_1, Z_2) Z_1^2 Z_2^2 J_0[1 - f_c(2')] \quad (2.16)$$

$$Z_1 = k'_1 + \frac{k'_2}{1 + 2\mu}; \quad Z_2 = k'_2; \quad \mu = \frac{m_{c0}}{m_v} \quad (2.17)$$

The CHHS AR process involves one electron, two heavy holes and a split-off band hole (Fig. 2.3). A conduction band electron recombines with a hole in the HH band, giving energy to another hole which can then move from the HH band to the SO in the valence band. The rate for this process has also been investigated by Beattie and Landsberg and has been used here as in Eq. 2.18~2.20, with same approach as for Eq. 2.15~2.17.

$$R_{CHHS} = \frac{32e^4 m_{c0} \alpha_{CH} \alpha_{SH}}{h^3 \mu \epsilon^2 E_g} \int_0^\infty dZ_1 \int_{A_1 Z_1}^\infty dZ_2 \int_{-1}^1 dt J_1 L f_c(1') \times \left(Z_1 - \frac{Z_2}{1 + 2/\mu} \right) F \left(Z_1 - \frac{Z_2}{1 + 2/\mu}, Z_2 \right) \quad (2.18)$$

$$J_1^2 = \frac{2}{\mu} a_S Z_2^2 - \left(1 + \frac{2}{\mu}\right) Z_1^2 - \frac{8\pi m_{c0}}{h\mu} (E_g - \Delta)$$

$$a_S = \mu_S - 1 + \frac{2}{2 + \mu} \quad \mu = \frac{m_{c0}}{m_s} \quad (2.19)$$

$$L = \frac{h^2 + j_1^2}{(4\lambda^2 + h^2 + j_1^2)^2}$$

$$A_1(Z_1) = \frac{1}{a_S} \left(1 + \frac{\mu}{2}\right) Z_1^2 + \frac{4\pi m_{c0}}{a_S h^2} (E_g - \Delta) \quad (2.20)$$

The function F is the same as in Eq. 2.16, α_{SH} and α_{CH} are due to the modulating part of Bloch functions in the conduction band and have been calculated numerically, m_s is the effective mass of holes in the split-off band for a particular value of energy E^* [31].

$$E^* = \frac{2m_v + m_{c0}}{2m_v + m_{c0} - m_s} (E_g - \Delta) \quad (2.21)$$

The CHHL process is similar to CHHS but involves a hole from the light hole band instead of the split-off band. Hence calculation of the AR rates for the two processes is very similar. The AR rate for CHHL can be written as in Eq. 2.22. Its expressions are close to those for calculating CHHS rates.

$$R_{CHHL} = \frac{32e^4 m_{c0} \alpha_{CH} \alpha_{LH}}{h^3 \mu \epsilon^2 E_g} \int_0^\infty dZ_1 \int_{A_2 Z_1}^\infty dZ_2 \int_{-1}^1 dt J_2 L f_c(k'_1) Z_1^2 Z_2^2 F[k'_1, k'_2] \quad (2.22)$$

$$J_2^2 = \frac{2}{\mu} a_L Z_2^2 - \left(1 + \frac{2}{\mu}\right) Z_1^2 - \frac{8\pi m_{c0}}{h\mu} E_g$$

$$a_L = \mu_L - 1 + \frac{2}{2 + \mu} \quad \mu_L = \frac{m_{c0}}{m_l} \quad (2.23)$$

$$L = \frac{h^2 + j_1^2}{(4\lambda^2 + h^2 + j_1^2)^2}$$

$$A_2(Z_1) = \frac{1}{a_L} \left(1 + \frac{\mu}{2}\right) Z_1^2 + \frac{4\pi m_{c0}}{a_L h^2} E_g E^{**} = \frac{2m_v + m_{c0}}{2m_v + m_{c0} - m_l} E_g \quad (2.24)$$

The overall AR rate can be calculated by adding the AR rates from different processes

$$R_{AR} = R_{CCCH} + R_{CHHS} + R_{CHHL} \quad (2.25)$$

Impact ionization, as the reverse process of Auger recombination, has a rate that differs from that of Auger recombination only if the system is not at chemical equilibrium (microscopic reversibility). In this process highly energetic carriers impact with bound carriers in the lattice, ionizing them, and creating new electron-hole pairs. The total II rate is the summation of II rates for different mechanisms and is calculated from the total AR rate[31].

$$R_{II} = R_{AR}e^{-\Delta\mu/k_B T} \quad (2.26)$$

Thus, for $\Delta\mu = 0$, the II and AR rates are the same and cancel out, such that particle number is conserved and both electron and holes populations can be described by the same thermal temperature. If $\Delta\mu$ is positive the II rate is less than that for AR. This is the case when carrier extraction is not immediate and there is a build up of generated carriers such as to create a positive chemical potential, $\Delta\mu$. There is, therefore, a tendency to reduce the particle number and AR processes dominate. On the other hand, if $\Delta\mu$ is negative then the II rate is greater than that for AR, implying a faster carrier extraction compared to carrier photo-generation. This will in turn suppress emission and drive the particle number to increase through II.

2.1.3 Numerical results and discussion

The system of equations reported in the previous section of this paper can be solved using numerical methods and assuming particular constraints for the operation of the solar cell. The current density J can be calculated for a given voltage V across the device terminals, fixing absorber thickness and thermalisation velocities. Results presented in this section have been calculated for the case of no concentration ($\Omega_A = 6.8 \times 10^{-5}$), the maximum concentration ratio ($\Omega_A = 1$) and a concentration ratio of 1000 suns

$\Omega_A = 0.068$, the last of which appears to be the upper limit for achievable concentration in solar cells. An absorber thickness of $d_{abs} = 50$ nm has been used, unless otherwise noted. In fact the optimal absorber thickness is affected by both carrier thermalisation and absorption. The absorption issue is a drawback of the HCSC, as the absorber is required to be thin as a consequence of Eq. 2.8. A thermalisation constant $\tau_{TH} = 100$ ps has been adopted, as a reasonable compromise between values recently reported in the literature[18, 37, 38, 39]. In fact the thermalisation velocity of hot carriers in InN is still under debate and depends strongly on the quality of the material and deposition technique[18, 37].

2.1.3.1 Variation in conversion efficiency with carriers extraction energy

Fig. 2.4 shows the dependence of the calculated efficiency on the extraction energy ΔE . For 1000 suns the efficiency curve reaches a peak value of 43.6% for hot carrier extraction energy of 1.44 eV. Maximum efficiencies of 52% and 22.5% have been calculated, respectively, for full concentration and nonconcentrated spectra. For the maximum concentration case the dependence on extraction energy is very flat. This is because, at these very high illumination levels, thermalisation only plays a minor role compared to energy flux associated with carrier generation. For the 1 sun and 1000 suns cases, there is a broad optimum in extraction energy (at 1.47 eV and 1.45 eV, respectively) between not having it too low in order to maintain voltage, while not having it too high such as to reduce current. This current limiting effect is most marked when the extraction energy is higher than 1.62 eV, which is close to the average energy of the incoming photon population. At the MPP, in order to provide carriers with sufficient energies to fill the gap denuded at the extraction energy, carriers are forced to undergo AR. For these extrac-

tion energies the AR rate is larger than the II rate, with a large positive quasi-Fermi gap and a very low carrier temperature.

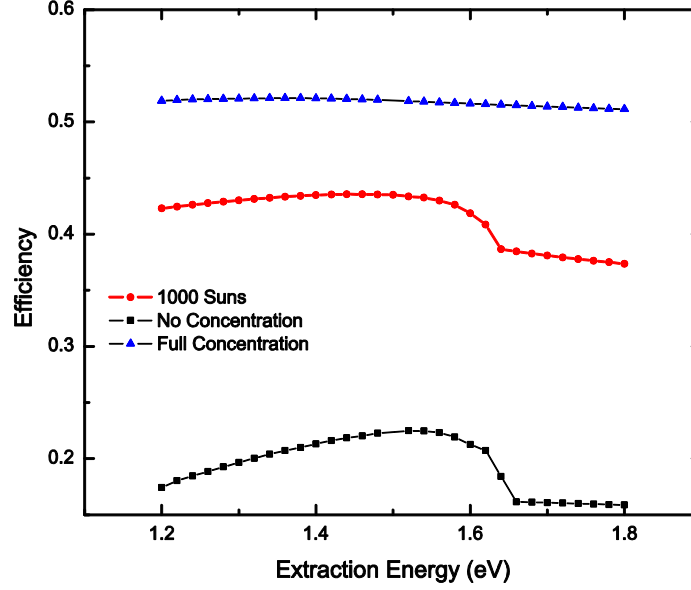


Fig 2.4: HCSC efficiency as a function of carrier extraction energy level[9]. Thermalisation time is 100 ps, lattice temperature is 300 K. Absorber layer thickness is 50 nm.

2.1.3.2 HCSC parameters analysis

In this section relations between the main HCSC parameters and extraction voltage are discussed, all the results presented here and in following sections have been calculated considering a concentration ratio of 1000 suns, if not otherwise stated. Fig. 2.5(a) shows J - V characteristics for the HCSC for four different extraction energies. The value of V_{OC} increases when the extraction energy is increased according to Eq. 2.12. Under open circuit conditions, as the carrier temperature T_C is very high (~ 1000 K), the V_{OC} is directly re-

lated to ΔE . The short circuit current decreases monotonically as a function of extraction energy due to the increase in AR events, which are necessary to raise the carrier energies to the extraction level and drive down $\Delta\mu$.

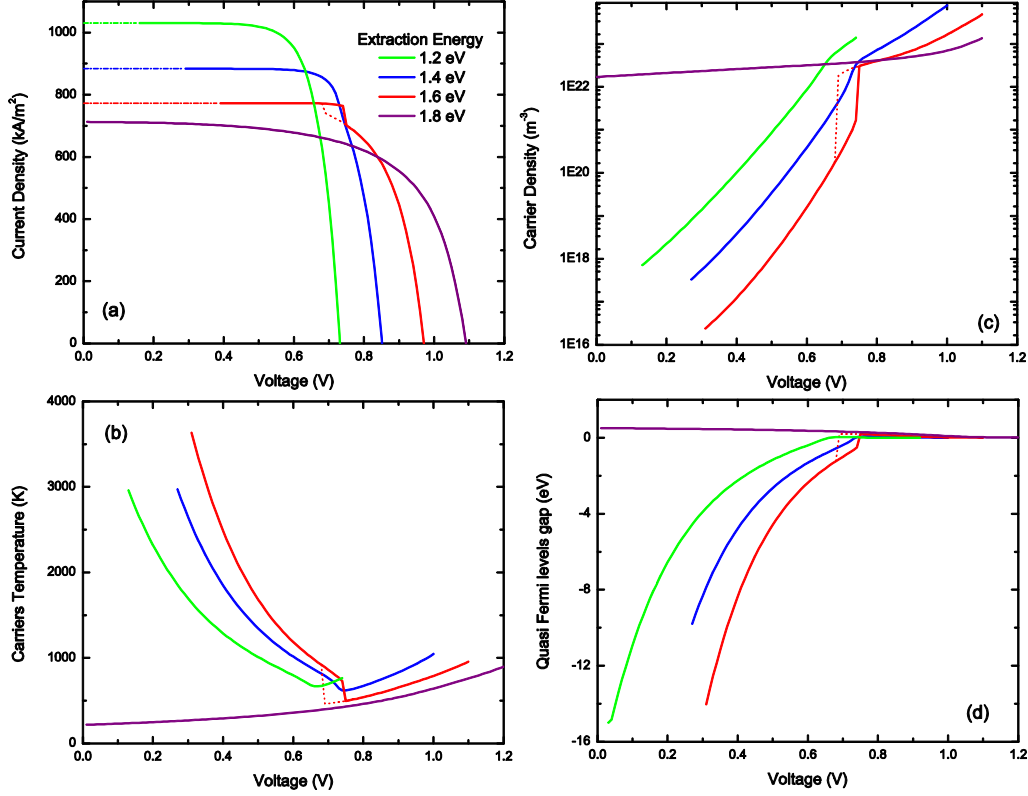


Fig 2.5: (a) J - V relations, (b) carrier temperature, (c) carriers densities, and (d) quasi-Fermi potentials separation vs extraction voltage for different extraction energies.[9]

The low voltage part of the relationships, Fig. 2.5(a) (dash-dot lines), has been calculated considering unlimited II and AR rates. In fact, according to the model, carrier temperatures at very low extraction voltages tend to be extremely high, as shown in Fig. 2.5(b). Such high temperatures can enlarge II rates in order to decrease carrier energies to extraction level. In

this regime the theoretical II and AR rates, calculated as explained in the previous sections, are not exact, since other multiple carrier generation mechanisms, other than CCCH, CHHL and CHHS, can be involved and prevent further increase in carrier temperature. This allows T_C to remain in a physically acceptable range, and thus, addresses the objection to the PC model discussed by Würfel[7].

The value of 3000 K for carrier temperature has been used as the threshold between current values calculated with the hybrid model presented here ($T_C < 3000$ K) and values computed using the unlimited II/AR rates ($T_C > 3000$ K)[38]. This particular temperature value allows matching of the two currents, calculated with the two methods. It is because in this range a strong II is required to lower the average carrier energy for extraction, which is only possible if with a large negative $\Delta\mu$ [Fig. 2.5(d)]. This reduces carrier density [Fig. 2.5(c)] and makes thermalisation losses negligible. Thus, the hybrid model at low voltages becomes similar to II-AR model with zero thermalization loss[5, 40].

For an extraction energy of 1.6 eV the J - V curve of Fig. 2.5(a) shows two possible stable steady states of operation at voltages close to the MPP, which correspond to two possible solutions of the model. For this particular value of ΔE (bistable region) the device can work both in AR regime and II regime, due to the interplay of AR and II processes with carrier thermalisation. For the first solution (dotted line) the quasi-Fermi level separation is positive, hence the AR rate is higher than the II rate, increasing the average energy of the carrier distribution as shown in Fig. 2.5(d). A fast thermalisation rate will offset this average energy increase. For the second solution (continuous line) the quasi-Fermi level separation is negative, hence the net II rate decreases the average carrier energy. However the thermalization loss is less due to a

low carrier density, creating a second steady state. The operation state in II regime has a larger current density, as unlike carrier thermalisation, II also involves an increase in the number of carriers. The exact operation state depends on the initial condition and the transition processes.

Fig. 2.5(b) shows that for a quite high extraction energy, the temperature of carriers is low, e.g. 500 K for $\Delta E = 1.8 \text{ eV}$ at MPP. In this case the extraction energy is higher than the average energy of absorbed photons and hence J should be decreased, due to very significant AR (Eq. 2.5). Although a net AR rate is always present to increase the average energy of carriers, due to a high carrier density the role of even a moderate thermalisation rate is enhanced in this regime and hence the carrier temperature is reduced at all extraction voltages. II becomes negligible and the efficiency is basically related to the limitation of the AR rate, which depends on the material intrinsic properties. On the other hand for $\Delta E < 1.62 \text{ eV}$ the MPP is in II regime. Here, the carrier temperatures increase with extraction energy for a lower carrier density and hence a smaller thermalization energy loss. High values of carrier temperature are observed at low voltages due to high II rates. Instead temperature drops if increasing the voltage, reaching acceptable values around the MPPs.

For $\Delta E < 1.62 \text{ eV}$, the quasi-Fermi level gap $\Delta\mu$ changes from large negative values, at low voltages, to very small positive values, at open circuit conditions as shown in Fig. 2.5(d). At low voltages radiative recombination is suppressed and most of the photo-generated carriers are extracted from the device as current. For such voltages multiple electron-hole pairs generation due to II is dominant and AR is negligible. The high extraction current also keeps the carrier density in the absorber low ($10^{11} \sim 10^{12} \text{ cm}^{-3}$), although extra carriers are generated by II. With increasing voltage toward the V_{MPP} ,

$\Delta\mu$ increases toward small negative values as shown in Fig. 2.5(c), contributing to the increase in thermalisation losses [Fig. 2.7(a)]. Despite the increase in the emission, higher carrier densities are reported when voltage is increased because of the decrease in extraction current. At MPP carrier density values about 10^{16} cm^{-3} are shown in Fig. 2.5(c) with carrier temperatures below 1000 K for all extraction energies considered, these being feasible values for an InN absorber[38]. A very high carrier temperature has been found at low voltages for extraction energies $\Delta E < 1.62 \text{ eV}$, Fig. 2.5(b), with values reaching above 3000 K when approaching short circuit. In these conditions additional II mechanisms will occur limiting the carrier temperature and the quasi-Fermi level gap from reaching extremely high values, which are unrealistic, as explained in the previous section. This process acts as a self-limiting mechanism for carrier temperature, which is intrinsic in the nature of the device and highlights the influence of II for cell operation[29]. After reaching a minimum around the MPP due to increased emission and thermalisation, the carrier temperature increases again with voltage due to rapid increase in AR. This is because at high voltages the thermalization energy loss becomes significant [Fig. 2.7(a)], leading to the necessity of lifting energies of carriers to re-supply the extracted ones.

The fast increase in carrier temperature at low voltages is not observed with extraction energies higher than 1.62 eV. For $\Delta E = 1.8 \text{ eV}$ the carrier temperature carries on decreasing monotonically as the voltage approaches short circuit, reaching values lower than the lattice temperature, $T_C < T_{RT}$. This condition, which appears unphysical, is due to the fact that the extraction energy is too high compared to the average energy distribution of incoming photons. As previously discussed a very high AR rate is necessary to increase the average carrier energy for extraction, requiring a large

positive $\Delta\mu$ that suppresses temperature below T_{RT} , as shown in Fig. 2.5(b) and (d). In addition the lattice feeds energy back to the electrons instead of taking their energies away because of the reversed temperature gradient, i.e. $T_C < T_{RT}$.

The absorber carrier density, Fig. 2.5(c), has a very strong influence on cell performance, being strongly related to thermalisation losses (Eq. 2.8). We may view the change on carrier density as a result of the transient process after starting operating the device. At open circuit, which is the initial operating condition of the solar cell, a relatively high carrier density is calculated ($n_C \approx 10^{17} \text{ cm}^{-3}$) due to low extraction. In this case the value of n_C is mainly related to the incoming particles flux, radiative emission and AR. On decreasing the contact voltage the carrier density decreases to about 10^{16} cm^{-3} at V_{MPP} . A further decrease in the voltage causes an additional reduction in n_C related to the temporary large increase in carrier extraction rate. The carrier density drop is only partially compensated by the increase in II rate, but this is only a second order effect. On the other hand only a very moderate decrease in n_C is observed for extraction energy of 1.8 eV, which indicates a relatively faster stabilization of n_C in response to voltage variation.

2.1.3.3 AR and II rates

Total rates for AR and II as function of voltage have been calculated using Eq. 2.26 and results are plotted in Fig. 2.6(a) and 2.6(b). AR and II lifetimes are calculated dividing the carrier density by the rates

$$\tau_{AR} = \frac{n_C}{R_{AR}}; \quad \tau_{II} = \frac{n_C}{R_{II}} \quad (2.27)$$

Under open circuit conditions the lifetime for AR is shorter than the lifetime for II. AR lifetime is slightly higher than the carrier thermalisation

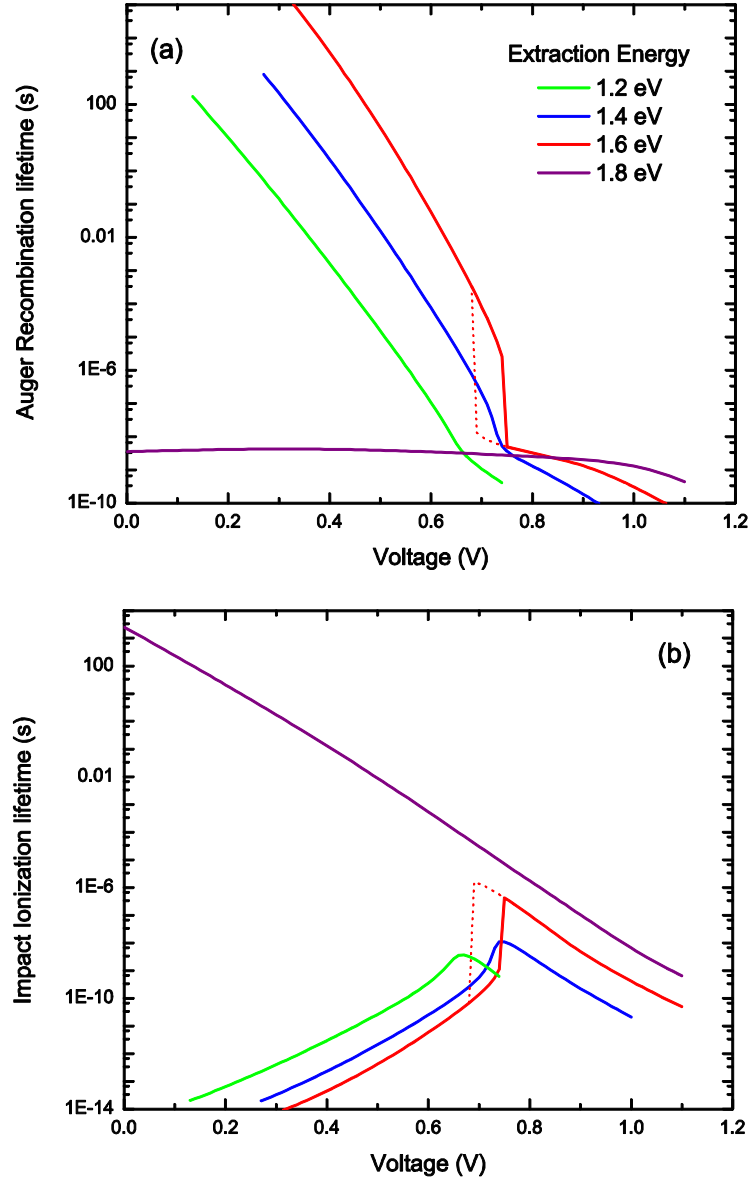


Fig 2.6: (a) AR and (b) II lifetimes vs extraction voltage for different extraction energies.[9]

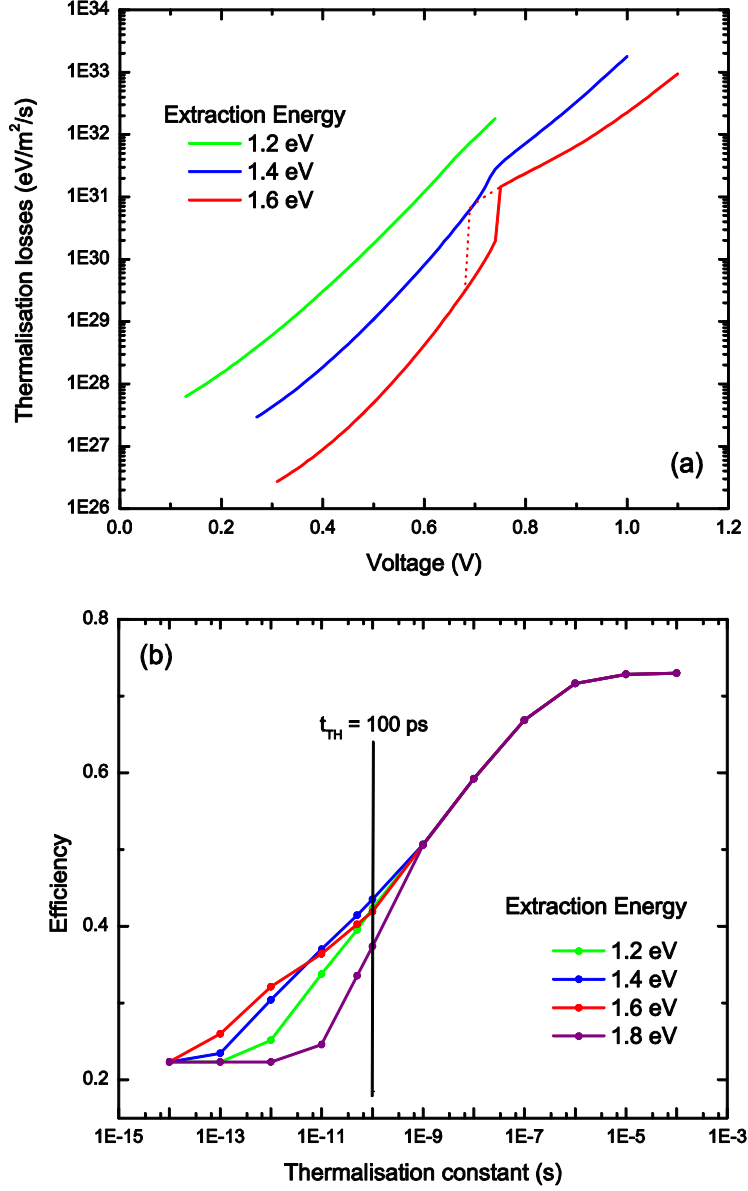


Fig 2.7: (a) Thermalisation losses vs extraction voltage for different extraction energies. Thermalisation constant is 100 ps. (b) Calculated efficiency limit versus thermalisation constant. [9]

constant 100 ps. This implies that the average energy increase due to AR is negligible compared to thermalisation losses, hence the average kinetic energy of new photo-generated carriers is dissipated by thermalisation. On decreasing the voltage toward V_{MPP} an increase in AR and II lifetimes is observed together with decreasing of thermalisation losses, Fig. 2.7(a). For further decrease in the voltage, AR and II rates show opposite trends due to the inversion of the quasi-Fermi energy gap. In terms of device operation this means that AR is negligible at low voltages and II plays the dominant role in determining the carrier distribution properties ($\Delta E < 1.62$ eV) and allowing the temperature to be maintained while increasing the number of carriers available for extraction. For higher extraction energies (e.g. 1.8 eV) no inversion of $\Delta\mu$ is observed and the carrier temperature drops monotonically toward the lattice temperature in the low voltage regime.

2.1.3.4 Thermalisation losses and efficiency versus thermalisation time

Most of the conclusions reached by analyzing AR and II rates match quite well with results shown in Fig. 2.7(a), where the energy losses due to hot carrier thermalisation are reported in units of eV per unit area per unit time. The quasi-exponential increase in thermalisation losses with extraction voltage, given a constant τ_{TH} , is mainly due to the increase in carrier density. These results confirm that, even considering AR and II in the calculation, the value of τ_{TH} has still a major influence on the final device efficiency. Fig. 2.7(b) shows calculated efficiency as a function of the τ_{TH} for different extraction energies. For very fast thermalisation ($\tau_{TH} = 10^{-14}$ s) an efficiency of 22.3% is observed. This value does not depend on ΔE and is very close to the Shockley-Queisser efficiency limit for bulk InN when AR is taken into account. Increasing the value of τ_{TH} , a splitting of the efficiency curves

for different ΔE has been found. This is due to the complex interplay between carrier thermalisation and the influence of AR and II. A monotonic fast increase in efficiency is shown for all extraction energies when τ_{TH} is between 0.1 ps and 1 μ s. For $\tau_{TH} = 10^{-10}$ s, which is the value used for all the calculations presented in the previous sections, four different values of efficiency can be identified along the black vertical line in Fig. 2.7(b). In this particular case τ_{TH} is closer to the AR and II lifetimes at the MPP. These are, respectively, $\tau_{AR} = 4.5 \times 10^{-9}$ s and $\tau_{II} = 3.21 \times 10^{-7}$ s for $\Delta E = 1.6$ eV and $\Delta V = 0.72$ V. This implies that AR/II processes begin to have enough time to supply carriers for extraction before complete thermalisation. A further increase in τ_{TH} leads to a significant increase in efficiency until it reaches saturation at $\tau_{TH} = 1$ ms, $\eta = 73\%$. In this region η does not depend on ΔE , indicating that the II-AR model can be applied with a high accuracy. This result determines the region of validity of the II-AR model, which was demonstrated to be valid only in particular conditions by Takeda et al.[41] In this region $\tau_{AR,II} \ll \tau_{TH}$, which implies that the carrier energy distribution can always be adjusted for extraction by AR and II before thermalisation, hence the extraction energy does not play a major role when the thermalisation process is reasonably slow.

2.1.3.5 Efficiency computation with actual Indium Nitride absorption coefficients

The results of calculations shown in the previous sections of this report assume ideal absorption properties, which imply that every incoming photon with energy above the band gap is absorbed and generates an electron-hole pair.

In this section, results of efficiency computation and J - V characteristics are reported based on the actual bulk InN absorption coefficients. Real

absorption properties have also been used to modify the ingoing and outgoing particle fluxes, F_A and F_E , according to the generalized Kirchhoff law for thermal photon currents emitted by a nonblack emitter[27].

$$F'_A = \int_{E_g}^{\infty} a(\epsilon) \frac{2\Omega_A}{h^3 c^2} \frac{\epsilon^2 d\epsilon}{e^{\epsilon/kT_S} - 1} \quad (2.28)$$

$$F'_E = \int_{E_g}^{\infty} a(\epsilon) \frac{2\pi}{h^3 c^2} \frac{\epsilon^2 d\epsilon}{e^{(\epsilon-\Delta\mu)/kT_C} - 1} \quad (2.29)$$

In Eq. 2.28 and 2.29 $a(\epsilon)$ represents absorptivity as a function of the energy for bulk wurtzite InN. Data for InN absorption coefficient α can be found in the literature and are plotted in Fig. 2.8 together with the photoluminescence signal and the approximation used in the calculation[42]. Details on photoluminescence measurement configuration are reported elsewhere[43]. The value of absorptivity can be calculated from the absorption coefficient according to Eq. 2.30, if assuming the incident light passes the planar absorber perpendicularly with negligible front and rear surface reflection.

$$a(\epsilon) = 1 - e^{-\alpha(\epsilon) \times d_{abs}} \quad (2.30)$$

where d_{abs} is the InN layer thickness. In Fig. 2.9(a) and 2.9(b) the efficiencies of the HCSC for different thicknesses of the absorber layer are shown. For all the extraction energies the efficiency increases in the first region of the plot, $d_{abs} < 1000$ nm, and decreases for a thicker absorber. The opposite trend is due to the influence on efficiency of the competitive interplay between thermalisation and absorption. On increasing d_{abs} a larger quantity of light is absorbed, thus more photo-generated carriers are available for extraction, which results in an efficiency increase. At the same time there is a net increase in losses due to hot carriers thermalisation, as evidenced in Eq. 2.8. In reality on increasing d_{abs} there is also a net decrease in carrier density which would lead to smaller thermalisation losses but this is a second order effect. Instead, when thermalisation losses begin to play a major

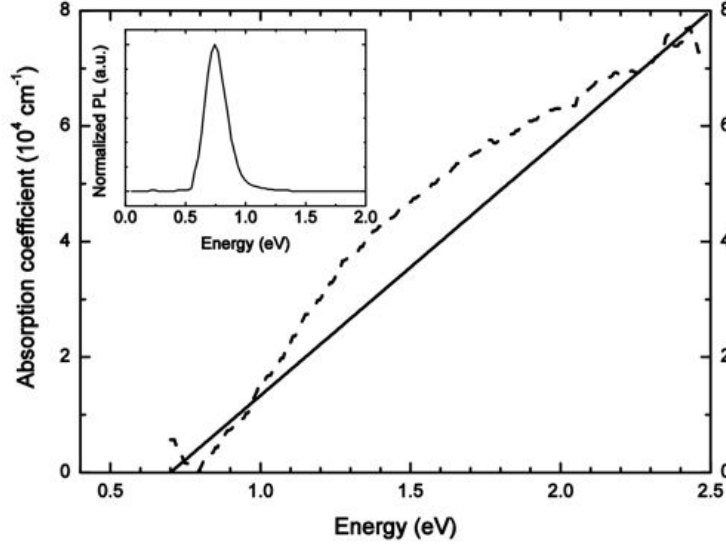


Fig 2.8: Bulk InN absorption coefficient from [42] (dashed line) and approximation used for calculation (solid line), (inset) InN photoluminescence signal.

role, the efficiency starts to drop. Such behavior is more or less pronounced depending on ΔE . Fig. 2.9(b) shows that at higher extraction energies the efficiency peak occurs at lower absorber thickness and in addition the slope of the curve is more pronounced. This confirms that high thermalisation losses cause a drop in the average carriers energy making extraction more difficult and so requiring a higher AR rate for larger extraction levels.

The value of maximum efficiency is considerably lower when real absorption properties are taken into account, Fig. 2.9(c), compared to the case of ideal absorption, 32.2% and 43.6%, respectively. This implies that to gain both the increased absorption and reduced thermalisation a light trapping technique has to be implemented on a thin absorber. Using an effective light trapping scheme the effective light path in the absorber can be enlarged, increasing absorption without changing physical thickness and allowing thermalisation losses to remain moderate. Different techniques to implement

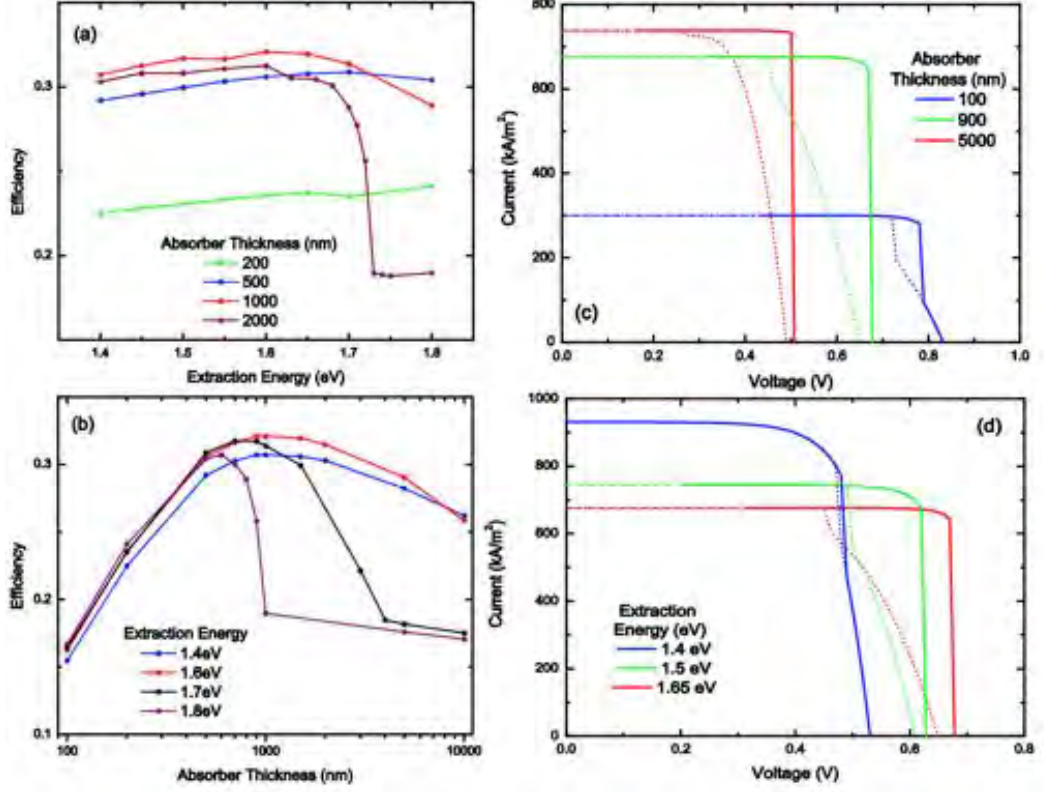


Fig 2.9: Performances of the InN-based HCSC with actual absorption properties: (a) Efficiency limit vs extraction energy for different absorber thicknesses. (b) Efficiency limits vs absorber thickness for different extraction energies. (c) J - V relations for different absorber thicknesses at their respective optimal extraction energies. (d) J - V relations for different extraction energies at their respective optimal absorber thicknesses. Thermalisation constant is 100 ps.

light multiple passes are currently used in conventional and thin film solar cells and could potentially be transferred to HCSCs[44].

In summary the HCSC is a very promising way to implement a next generation photovoltaics device. Several models have been proposed over the last few years for calculating limiting efficiencies. In this section maximum achievable efficiencies for HCSC have been calculated, using bulk wurtzite

InN as absorber layer. A hybrid model which takes into account both particle balance and energy balance has been implemented and adopted for calculations. The model also considers influence of real AR and II rates on cell performance for the first time, in addition actual thermalisation losses are included. AR-II rates have been calculated including the most important three-carrier interaction mechanisms which can occur in InN at energies of interest for solar applications. The real InN dispersion relation has been reconstructed using actual effective masses for different bands and nonparabolicity coefficients. The limiting efficiency as a function of carrier extraction energy has been studied for a fixed absorber thickness and thermalisation constant. A maximum efficiency of 43.6% has been found for 1000 suns solar concentration and energy extraction level of 1.44 eV, assuming a thermalisation constant of 100 ps. An efficiency of 0.52 was found for full solar concentration. Current-voltage relationships have been calculated for different extraction energies. In addition the influence of thermalisation constant on maximum efficiency has been investigated, showing a very close correlation between the two parameters. The influence of real InN absorption properties has also been studied, proving that a light trapping scheme is mandatory to achieve sensible efficiency improvements in HCSCs.

From the results, when a real material is considered for efficiency calculation of HCSC, values of efficiency limits can be considerably different as compared to an ideal hot carrier absorber that has little carrier thermalization. This implies that the gain in efficiency which can be achieved using bulk materials as absorbers in HCSCs is limited due to the electronic and phononic properties of the material. The thermalisation constant used 100 ps is thought to be a good approximation, but could be different for specific high quality material, as it depends on the exact suppression of phonon

decay mechanisms in the sample. Nevertheless the fact that an efficiency of 43.6% can be obtained with a bulk absorber is an optimistic outcome, which encourages further investigation on electronic and phononic properties of semiconductors to slow down carrier cooling and achieve more significant efficiency gains for HCSCs.

2.2 Impact of contact properties on cell performance

Apart from the absorber the energy selective contacts (ESC) are the other vital components of the hot carrier solar cell. For a high conversion efficiency a small contact resistance is required as well as a low entropy generation on extracting carriers. In this section it will be shown that these two requirements generally conflict with each other. A trade-off between them that leads to optimal properties of the ESCs is demonstrated. The optimal efficiency taking into account the non-ideality of the ESC is about 5% lower than that calculated in Sec. 2.1. The work in this section has been published in “Non-ideal energy selective contacts and their effect on the performance of a hot carrier solar cell with an indium nitride absorber” by Y. Feng, P. Aliberti, et al., 2012, Applied Physics Letters, 100(5):053502-053502.

2.2.1 Performance evaluation of an InN-based HCSC with the thermalization time constant of 100 ps

In this section actual properties of the energy selective contacts (ESC) have been taken into account, yielding more realistic performance figures of the HCSC. The impact on different contact properties has been analyzed under the assumption of ballistic transport. A potential practical implementation of a hot carrier solar cell, with contacts based on an $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{InN}/\text{In}_x\text{Ga}_{1-x}\text{N}$

quantum well structure, has been proposed, with calculated maximum efficiency of 37.15% under 1000 suns.

Most of the previous modelling work on the performance of the HCSC treated the ESCs as ideal Carnot heat engines, i.e. the entropy is conserved when carriers are extracted to the electrodes. This condition immediately leads to a relation between the electro-chemical potentials and the thermal energies, shown in Eq. 2.12. However in the actual case the contact cannot be in such an ideal configuration, as it can only work quasi-statically to achieve zero entropy generation[4]. In the actual operation of the HCSC a finite current density is required for reasonable efficiency, which yields a trade-off between the current extraction and the entropy generation. In this work the extraction properties of the ESCs attached to a wurtzite InN absorber have been formulated by a generalized Landauer formula; cell efficiencies with different transmission profiles of such contacts have been computed. The maximal efficiency has been found while the trade-off between the contact resistive loss and the extraction-related entropy generation is discussed in detail.

2.2.1.1 Expressions of carrier ballistic transport from the absorber

A 50 nm InN layer with a wurtzite structure has been adopted as the absorber with a carrier thermalization time of 100 ps, the same with that being assumed in the previous model (Sec. 2.1). Spatially-independent Fermi-Dirac carrier energy distributions are assumed for the electron and hole systems throughout the absorber. The same system temperature for electrons and holes has been assumed due to ultrafast carrier-carrier interaction[5]. At steady state the conservation of total energy and number of carriers gives the operating points of the cell, for given illumination and voltage condi-

tions. Carrier transport through the ESCs can be regarded as ballistic due to the ultra-thin resonant tunneling structure[21]. The relation between the current density around a given energy level, the carrier transmission properties and the state occupation probabilities is shown in Eq. 2.31 and 2.32.

$$J_{e,h}(\epsilon) = C_{e,h}(\epsilon) P_{e,h}(\epsilon) [f(T_C, \mu_{e,h}; \epsilon) - f(T_{RT}, \mu_{e,h}; \epsilon)] \quad (2.31)$$

$$C_{e,h}(\epsilon) = -\frac{e}{\pi^3 \hbar} \sum_{\min \epsilon} \left(\int_0^\epsilon \int_0^{\epsilon-\epsilon_z} \frac{dk_y}{d\epsilon_y} \frac{dk_z}{d\epsilon_z} d\epsilon_y d\epsilon_z \right) \quad (2.32)$$

The energy-dependent current density $J_{e,h}(\epsilon)$ is proportional to the carrier transmission probability $P_{e,h}(\epsilon)$ and to the difference of occupation probabilities at the two sides of the contact, i.e. $f(T_C, \mu_{e,h}; \epsilon)$ for hot electrons or holes in the absorber and $f(T_{RT}, \mu_{e,h}; \epsilon)$ for electrons or holes in the cold contact. The band-structure factor $C_{e,h}(\epsilon)$ takes into account the carrier density of states and the carrier group velocity in wurtzite InN. This is calculated by assuming that the extracted carriers are close to the local energy minimum points with approximately parabolic $E - k$ relations. This assumption is justified by the fact that the maximum extraction level considered in the computation is about 1.5 eV, which is lower than any transition energy from one valley to another in the conduction band[29]. The derivation of Eq. 2.32 assumes that the electron energy around band minima is composed of three parts (E_x, E_y, E_z) corresponding to the three different x, y, z -components of the wave vector, which is the case if the constant energy surfaces are ellipsoids, and along the three coordinate axes parabolic dispersion relations exist close to the band minima. An InN band structure, calculated using an empirical pseudo-potential method, has been adopted to obtain the proportionality factors[29, 45]. In Eq. 2.32 x is designated as the thin film growth direction, i.e. $\Gamma - A$ direction for wurtzite InN, along which carrier extraction has been considered[30].

To prove the carrier transport equation (Eq. 2.31 and 2.32) we shall look into the derivation of the one-dimensional Landauer formula. Briefly it represents the current along a one-dimensional structure with the ballistic assumption, i.e. the dimension of the scattering region is much shorter than the carrier mean free path.

$$I = -\frac{2e}{h} \int_0^\infty M(\epsilon)T(\epsilon)[f_1(\epsilon) - f_2(\epsilon)]d\epsilon \quad (2.33)$$

where $T(\epsilon)$ denotes the energy-dependent transmission probability across the scattering region. $f_1(\epsilon)$ and $f_2(\epsilon)$ are the average occupation numbers at the left and the right leads. $M(\epsilon)$ is the number of planar modes of the scattering region that lies at energy ϵ . A brief proof of Eq. 2.33 deals with the $E - k_x$ relation (carriers transport along x -axis) by representing the current

$$\begin{aligned} I &= -2e\rho \sum_{k_x} v_x(\epsilon)T(\epsilon)M(\epsilon)\Delta f(\epsilon) \\ &= -2e\frac{1}{L} \cdot \frac{L}{2\pi} \int_0^\infty \frac{1}{h} \frac{d\epsilon}{dk_x} dk_x \cdot T(\epsilon)M(\epsilon)\Delta f(\epsilon) \\ &= -\frac{2e}{h} \int_0^\infty M(\epsilon)T(\epsilon)\Delta f(\epsilon)d\epsilon \end{aligned} \quad (2.34)$$

where L is the dimension of the left lead along x -axis and the occupation difference $\Delta f(\epsilon) = f_1(\epsilon) - f_2(\epsilon)$. The carrier density of each planar-wave state is $1/L$ after normalization. The pre-factor 2 takes the spin degeneracy into account. In the derivation of Eq. 2.34 the summation over one-dimensional states $\sum_{k_x} = \frac{L}{2\pi} \int d\epsilon$ and the group velocity of electron wave-packets is represented by $v_x(\epsilon) = \frac{1}{h} \frac{d\epsilon}{dk_x}$.

In terms of the generalized Landauer formulae for three-dimensional crystal structures the derivation in Eq. 2.33 is still valid. But instead the planar modes $M(\epsilon)$ should have a quasi-continuous spectrum. In such case the summation over three-dimensional states may be converted into integrals

by $\sum_{k_x > 0, k_y, k_z} = \frac{V}{8\pi^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} dk_x dk_y dk_z$. In the modeling material of wurtzite InN, the conduction band minima include two valleys at Γ and another six valleys at L . For its valence band, the minima all centre at Γ (HH, LH, SO). The integration over the states for the current may merely take the neighbourhood of these band minima into account, as their low energies offer reasonable occupation probabilities. The three-dimensional $E - k$ relation at the neighboring region of a band minima can be treated with a diagonal tensor of effective mass, i.e. $\epsilon(\mathbf{k}_0 + d\mathbf{k}) = \epsilon(\mathbf{k}_0) + d\epsilon_x + d\epsilon_y + d\epsilon_z$. This assumption leads to ellipsoid-shaped constant energy surfaces around $\mathbf{k}_0$. In analog to Eq. 2.33 we have derived the expression of tunneling current for one band minimum in Eq. 2.35

$$\begin{aligned}
I &= -2e \frac{1}{L} \cdot \frac{V}{8\pi^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} dk_x dk_y dk_z \cdot \frac{1}{\hbar} \frac{d\epsilon_x}{dk_x} T(\epsilon) \Delta f(\epsilon) \\
&= -\frac{Ae}{4\pi^3 \hbar} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_0^{\infty} d\epsilon_x dk_y dk_z \cdot T(\epsilon) \Delta f(\epsilon) \\
&= -\frac{Ae}{4\pi^3 \hbar} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} d\epsilon_x d\epsilon_y d\epsilon_z \cdot 2 \frac{dk_y}{d\epsilon_y} \cdot 2 \frac{dk_z}{d\epsilon_z} T(\epsilon) \Delta f(\epsilon) \\
&= -\frac{Ae}{\pi^3 \hbar} \int_0^{\infty} T(\epsilon) \Delta f(\epsilon) d\epsilon \int_0^{\epsilon} d\epsilon_z \int_0^{\epsilon - \epsilon_z} d\epsilon_y \frac{dk_y}{d\epsilon_y} \frac{dk_z}{d\epsilon_z} \quad (2.35)
\end{aligned}$$

where A denotes the cross section area of the yz plane. Eq. 2.35 proves the current expression in Eq. 2.31 and 2.32. For real contact structures the transmission probability $T(\epsilon)$ could be calculated from the time-independent Schrödinger equation and will be shown in the following sections. The inverse group velocity $dk_{y,z}/d\epsilon_{y,z}$ may be calculated explicitly by considering $d\epsilon_{y,z} = \hbar^2(k_{y,z} - k_{0\ y,z})/m_{y,z}^* \cdot dk_{y,z}$.

2.2.1.2 Device model with carrier extraction properties incorporated

With non-ideal ESCs the expression of reversible extraction Eq. 2.12 is no longer valid. Instead the particle exchange and heat exchange between the

absorber and the external electrodes need to be incorporated into Eq. 2.5 and 2.11.

$$F_A - F_E - F_{IA} + J/e = 0 \quad (2.36)$$

$$E_A - E_E - E_{TH} - E_J/e = 0 \quad (2.37)$$

The extraction current density J is represented in Eq. 2.31 while the extraction power density E_J is shown in Eq. 2.38 similarly.

$$E_{J;e,h}(\epsilon) = C_{e,h}(\epsilon)P_{e,h}(\epsilon)[f(T_C, \mu_{e,h}; \epsilon) - f(T_{RT}, \mu_{e,h}; \epsilon)] \cdot \epsilon \quad (2.38)$$

Similarly to Eq. 2.5 and 2.11, Eq. 2.36 and 2.37 illustrate the balance of carrier and energy fluxes under steady state conditions. F_A , F_E , F_{IA} , and J/e correspond to the absorbed and emitted photon fluxes, impact ionization/Auger recombination flux and carrier extraction flux respectively. F_{IA} has a positive value if impact ionization is predominant over Auger recombination. E_A , E_E , E_{TH} , E_J/e represent the corresponding absorption and emission energy fluxes, the energy flux due to thermalisation of carriers with phonons and the energy flux due to carrier extraction. Under steady state conditions each of the fluxes depends only on the properties of the carrier energy distribution $(\Delta\mu, T_C)$, which are then determined by Eq. 2.36 and 2.37.

2.2.1.3 Calculation results for rectangular transmission windows

To introduce a simple description of the ESC non-ideality into the calculation of the performance of an InN based HCSC, it is assumed that ESCs have a rectangular energy transmission window for both electrons and holes. The transmission probability of carriers with energies inside the transmission window is assumed to be unity, whereas zero transmission probability is assumed for carriers with energy out of this range (see inset in Fig. 2.10). For

simplicity the same transmission window configuration has been adopted for both electrons and holes.

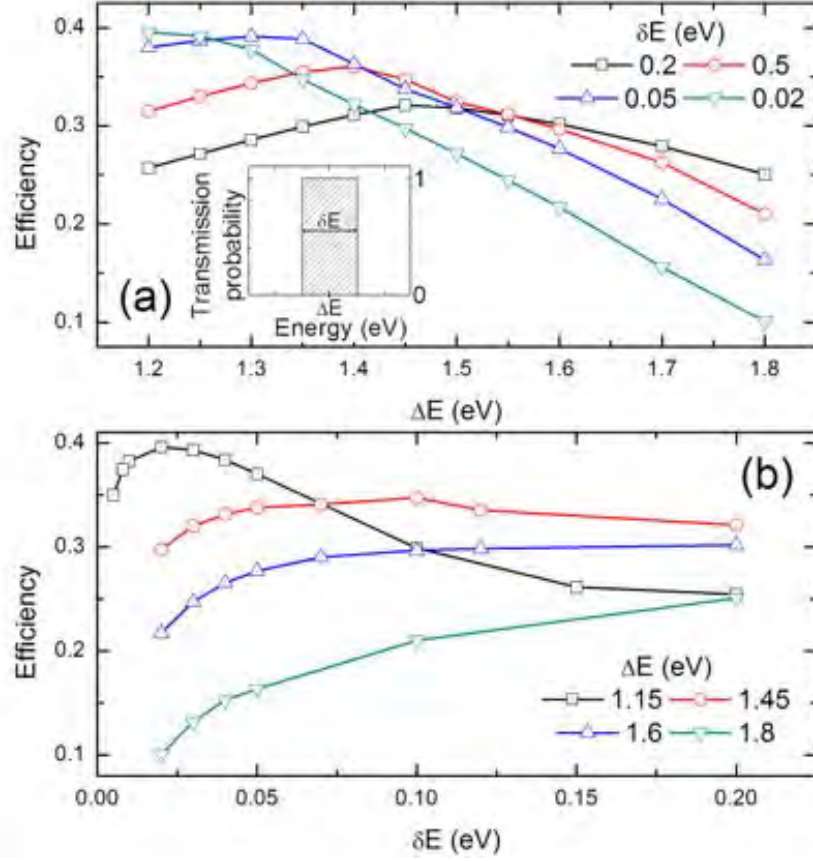


Fig 2.10: (a) Calculated HCSC efficiency versus extraction energy, ΔE , under 1000-sun illumination, for different extraction energy window width, δE . (b) Calculated HCSC efficiency versus extraction energy window, δE , under 1000-sun illumination, for different extraction energies, ΔE .

Fig. 2.10 shows calculated efficiency data corresponding to different hot carrier extraction levels (ΔE) and different extraction energy window width (δE) for complete absorption of 1000-sun illumination. The maximum achievable efficiency is 39.6%, which occurs for $\Delta E = 1.15$ eV and $\delta E = 0.02$ eV. It is relevant to highlight that, considering ideal ESCs, the efficiency reaches the

peak value of 43.6% for $\Delta E = 1.44$ eV (Sec. 2.1). With non-ideal ESCs, the optimum extraction energy value shifts from 1.44 eV to 1.15 eV. This is because carrier extraction at higher energies is associated with a higher resistive loss because of the lower carrier density at these energy levels. Fig. 2.10(b) shows that the optimum value of δE is related to ΔE due to the same reason. In fact, for increasing values of ΔE , δE which gives the optimum efficiency increases in order to maintain the carrier extraction rate. But the calculated efficiency is low if the transmission window is too wide, particularly for the device with semi-selective contacts (i.e. no upper bound), demonstrating a disagreement with the efficiency reduced to a less extent proposed in the literature, calculated without consideration of Auger recombination[46]. In reality Auger recombination continues to supply high energy carriers well above ΔE , which for a wide transmission window are extracted and then thermalised in the contacts giving a larger entropy increase. Electron-hole pairs are lost due to the fast Auger recombination while their excess energies are always lost due to entropy generation. In this sense the Auger recombination should be inhibited to achieve higher efficiency; however without proper rates of Auger recombination the carrier temperature can be extremely high or low unless the extraction energies strictly match the average carrier energies[7].

2.2.1.4 A practical ESC structure with cell performance predicted

Fig. 2.11 shows four J - V curves corresponding to different extraction energies. For each value of ΔE the curve corresponding to the respective optimal value of δE is shown. The optimal δE increases from 0.03 eV to 0.5 eV when ΔE rises from 1.2 eV to 1.8 eV. The one-order-of-magnitude increase of optimal δE when ΔE changes from 1.4 eV to 1.6 eV is due to a large contrast of the carrier temperatures in these two cases. For carrier extrac-

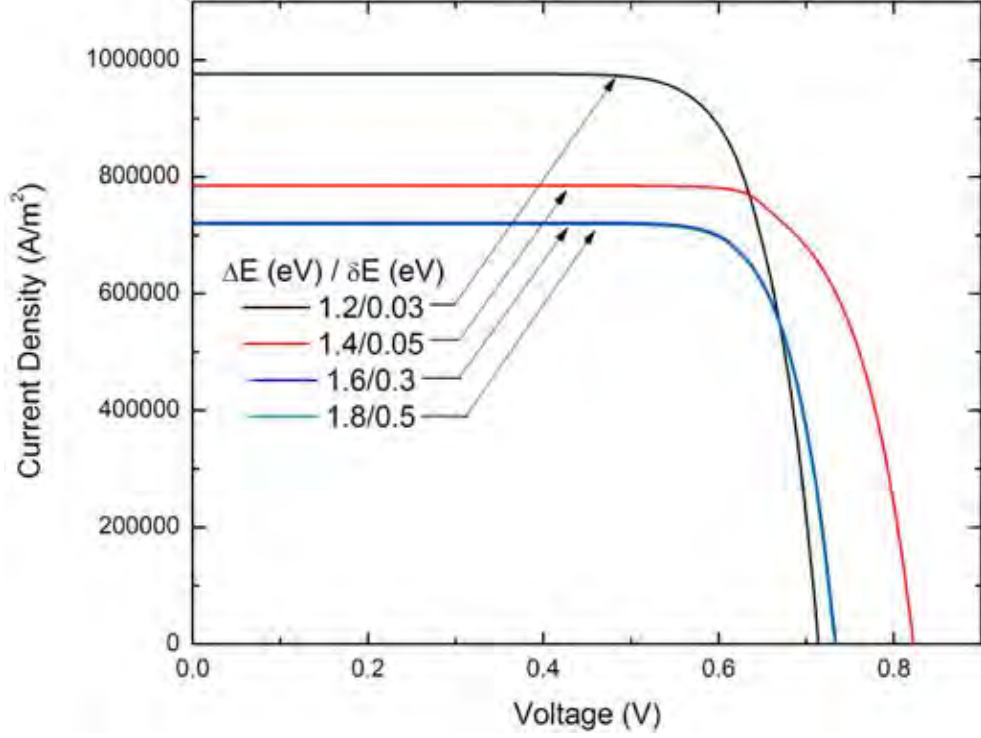


Fig 2.11: Current - Voltage characteristics for different extraction energies, ΔE . For each value of ΔE the optimal value of the transmission energy window δE , giving the highest efficiency, has been used.

tion at 1.2 eV or 1.4 eV, carriers with low energies are extracted while the extraction of highly energetic carriers is blocked, as the impact ionization rate is limited depending on material properties, leading to increased average carrier energy. The occupation probability at extraction level increases with temperature, requiring a narrower transmission window for the highest efficiency. In Fig. 2.11 it can be observed that the curves corresponding to $\Delta E = 1.6$ eV and $\Delta E = 1.8$ eV overlap. The reason for this is that in both cases the minimum allowed transmission energy coincides at 0.3 eV above the band edges. This energy level is located high up in the tail of the carrier distribution; hence the majority of the extracted carriers are concentrated around the bottom of the transmission window. Fig. 2.11 also shows

that increasing ΔE from 1.4 eV to 1.6 eV the open-circuit voltage decreases. This is in disagreement with the direct proportionality relation between ΔE and ΔV adopted in the previous model. The higher carrier temperature for $\Delta E = 1.4$ eV results in a higher efficiency of the carrier extraction process, which compensates for the low extraction energy leading to a high value of open-circuit voltage.

For a practical HCSC device ESCs can potentially be realized using an $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{InN}/\text{In}_x\text{Ga}_{1-x}\text{N}$ single quantum well structure[47]. This structure shows energy selectivity due to the resonant tunneling of carriers at the confined energy levels[48]. Under 1000-sun illumination the carrier extraction rate through thermionic emission has been calculated as negligible compared to the total extracted current for cells operating at MPP. Another advantage of using the $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{InN}/\text{In}_x\text{Ga}_{1-x}\text{N}$ structure is the possibility of optimizing both the electron and hole contacts independently by varying the indium fraction.

The methods of calculating the transmission probability of carriers across such structures will be discussed in the following sections. The calculated $T(\epsilon)$ is then adopted for the evaluation of cell performance. It was found that the best extraction performance for electrons is achieved using a $\text{GaN}/\text{InN}/\text{GaN}$ quantum well structure, while the extraction of heavy holes[29] requires a lower barrier height. It is found that the optimal barrier material for the hole ESC is $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$, which has a bandgap of 2.72 eV and hence a barrier height of 1.01 eV, assuming a symmetrical alignment of band diagrams for InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ [49]. The reduction on barrier height significantly improves hole transmission properties, allowing a reasonable thickness for the hole contact.

The ESCs parameters have been optimized in order to obtain the max-

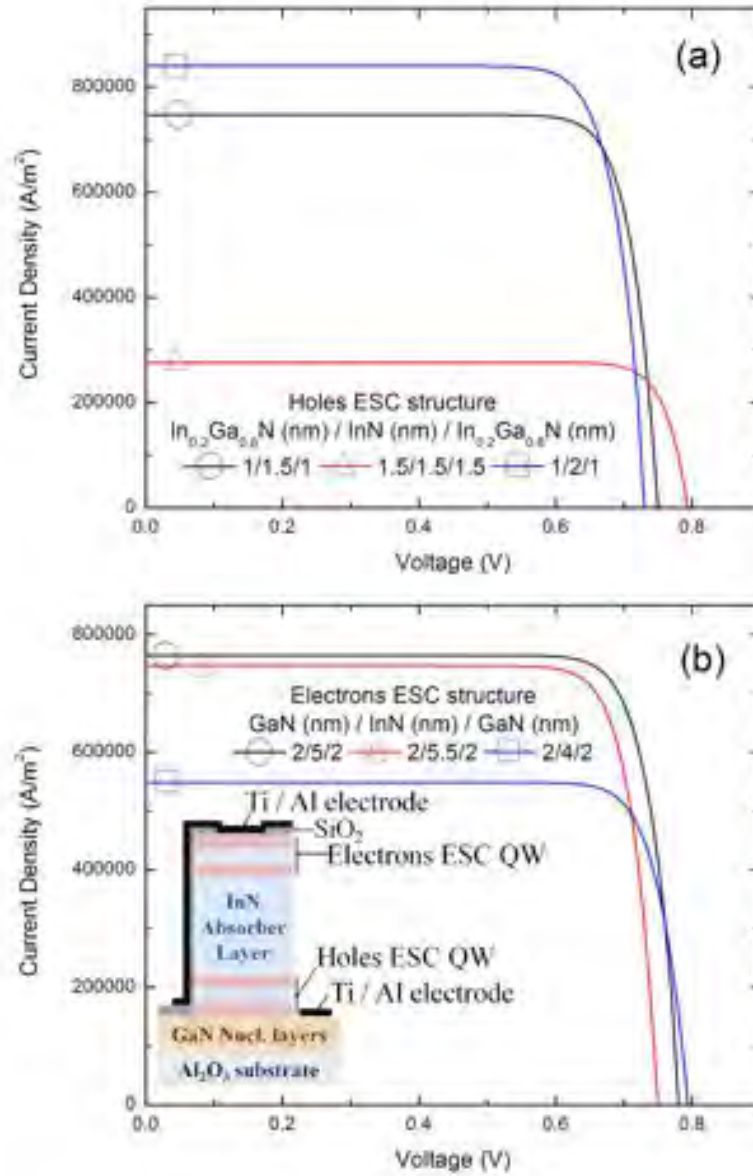


Fig 2.12: Current - Voltage characteristics of the HCSC with $In_xGa_{1-x}N$ quantum wells as ESCs, with different well/barrier thicknesses. (a) Adopted electron ESC structure is $GaN(2nm)/InN(5nm)/ GaN(2nm)$; (b) Hole ESC structure is $In_{0.2}Ga_{0.8}N$ (1 nm) / InN (2 nm) / $In_{0.2}Ga_{0.8}N$ (1 nm).

imum achievable efficiency for the device, assuming a 1000-sun incoming spectrum. The maximum calculated efficiency is 37.1% and occurs with a GaN (2 nm) / InN (5nm) / GaN (2 nm) quantum well as the electron ESC and an $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ (1 nm) / InN (2 nm) / $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ (1 nm) quantum well as the hole ESC. Fig. 2.12 shows that a thinner well layer increases the discrete energy levels inside the resonant tunneling structure, leading to a lower short-circuit current but a higher open-circuit voltage. The band alignment of the ESCs adopted in this calculation, with the assumption of symmetric distributions between the CB and the VB, is demonstrated in the schematic figure Fig. 2.13. The transmission peak becomes wider with thinner barrier

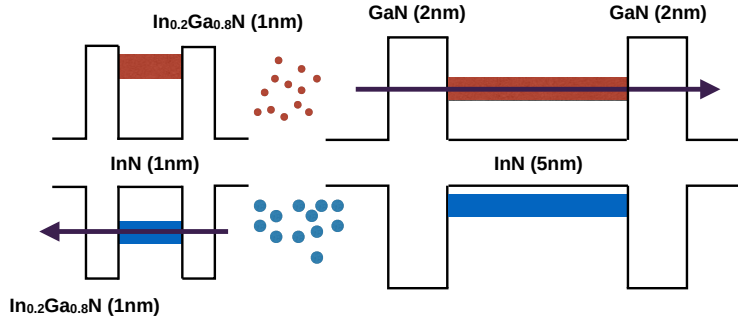


Fig 2.13: Schematic diagram on band alignments of the optimal InN/InGaN ESC structures for the InN absorber, with the assumption of symmetric distributions between the CB and the VB.

layers thus reducing resistive losses, but introducing an additional entropy increase in the carrier extraction process. Given a fixed double barrier structure, the transmission energy peak is much higher and wider for electrons than for holes, due to the small effective mass of electrons[50]. Therefore, the best device performance is achieved by extracting electrons using a relatively thick barrier layer, to narrower the transmission window width, and a reasonably large well layer, to lower the extraction energy value. Due to the assumption of equal temperature for electron and hole populations, the hole

ESC has to match the extraction properties of the electron ESC. To achieve this very thin barrier and well layers are required due to the relatively high effective mass of holes.

2.2.1.5 Conclusions

In conclusion, the 1000-sun performance of a hot carrier solar cell with an InN absorber layer have been calculated considering more realistic carrier extraction properties. The previously reported thermalization time constant of 100 ps has been adopted. By assuming a rectangular carrier transmission window the maximum efficiency reaches 39.6%. For a real system, an $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{InN}/\text{In}_x\text{Ga}_{1-x}\text{N}$ double barrier resonant quantum well structure can be used to extract carriers at a certain energy level. This configuration gives a highest efficiency of 37.1%. The hot carrier solar cell based on the III-Nitrides structure presented in this paper is a viable and a realistic solution to realize a device prototype to demonstrate the hot carrier effect in solar energy conversion.

2.2.2 Predicted cell performance based on experimental thermalization time constants

The value of the thermalization time constant τ_{TH} of carriers in wurtzite InN is still an object of scientific debate and appears to be closely related to the film quality[51, 52, 38]. As shown in Sec. 2.1 the conversion efficiency of the HCSC strongly relies on the magnitude of τ_{TH} . An empirical range of τ_{TH} is required in order to investigate the feasibility of adopting a specified material as the absorber. My colleague and collaborators have fabricated a thin film of InN and characterized its carrier cooling properties with time resolved photoluminescence (TRPL). In this section the details of the experimental work are demonstrated with brief explanations on the results, as well

as conversion efficiency figures of the InN-based HCSC predicted from the measured data. This work has been published in “Effects of non-ideal energy selective contacts and experimental carrier cooling rate on the performance of an indium nitride based hot carrier solar cell” by P. Aliberti and Y. Feng et al., 2011, Applied Physics Letters, 99(22):223507-223507.[53]

2.2.2.1 TRPL measurement on a MBE deposited InN layer

The hot carrier cooling transients have been measured by TRPL on a $1.4\ \mu\text{m}$ InN layer grown by MBE on a LT-GaN and GaN buffer layers with respective thicknesses of $1\ \mu\text{m}$ and $25\ \text{nm}$. The samples have been excited by a pulsed Ti:sapphire laser at $1.59\ \text{eV}$. The energy of the pulse was $35\ \mu\text{J}$ at $150\ \text{kHz}$. The carrier mobility was $2000\ \text{cm}^2/\text{Vs}$ with a background carrier density of $1.5 \times 10^{18}\ \text{cm}^{-3}$. The photo-excited carrier density has been calculated considering a beam diameter of $0.8\ \text{mm}$ (FWHM) and a penetration depth of $\alpha(\lambda)^{-1}$, where $\alpha(\lambda)$ is the absorption coefficient measured by conventional spectrophotometry[54, 55].

The PL has been probed for energies from the InN bandgap to $1\ \text{eV}$. PL transients for different photon energies are reported in Fig. 2.14(a) and 2.14(c). At higher energies, the PL signal shows a longer rise time and a very fast decay. This is due to the larger time constant needed for the carriers to fill high energy states and to the rapid relaxation of the hot carriers towards the respective band edges. In InN and several other polar semiconductors, the carriers relax mainly through electron-LO phonon interactions[56]. At lower photon energies, a faster rising of the PL signal is observed together with a longer carrier relaxation transient. This is evidence that, after photo-excitation, the states with energies close to the band edge are populated by photo-generated carriers almost immediately. The slower carrier cooling is

due to hot phonon effect and to the screening of the electrons-LO phonon interaction, caused by the higher local carrier density[57]. Fig. 2.14(b) shows the calculated carrier temperature as a function of time. The temperature values have been calculated by fitting the high-energy tail of PL spectrum with a Boltzmann distribution. The fitted relaxation time constant is $\tau_{TH} = 6.87$ ps. This is higher than the theoretical value, demonstrating that the hot phonon effect has a major role for the relaxation of hot carriers in InN, although this is not sufficient to allow a consistent gain in efficiency for a HCSC based on InN[58].

2.2.2.2 Cell efficiency prediction based on the measured thermalization rates

The maximum conversion efficiency of the HCSC has been calculated as a function of the ESCs transmission window width (δE) and extraction energy (ΔE), for a concentration factor of 1000 suns and for the maximum concentration (46000 suns). Fig. 2.15(a) shows that, at 1000 suns, the efficiency of the cell increases when the value of ΔE is enlarged, due to the larger number of carriers available for extraction. The maximum achievable efficiency in this case is 24%, which is close to the value predicted by the detailed balance limit for an InN based solar cell at 300 K[59]. An efficiency value of 33% has been reported for the same value of τ_{TH} and ideal ESCs (Sec. 2.1). This implies that the low value of efficiency is due to two combined effects, the thermodynamic losses in the ESCs and the high carriers thermalisation velocity. At the time of extraction, the carriers have lost most of their excess energy due to the very fast thermalisation rate. Thus, extraction is only possible at energies close to the band edges. Fig. 2.16 shows the temperature of extracted carriers as a function of δE , confirming a carrier temperature around 330 K at any value of ΔE , for values of δE corresponding to the

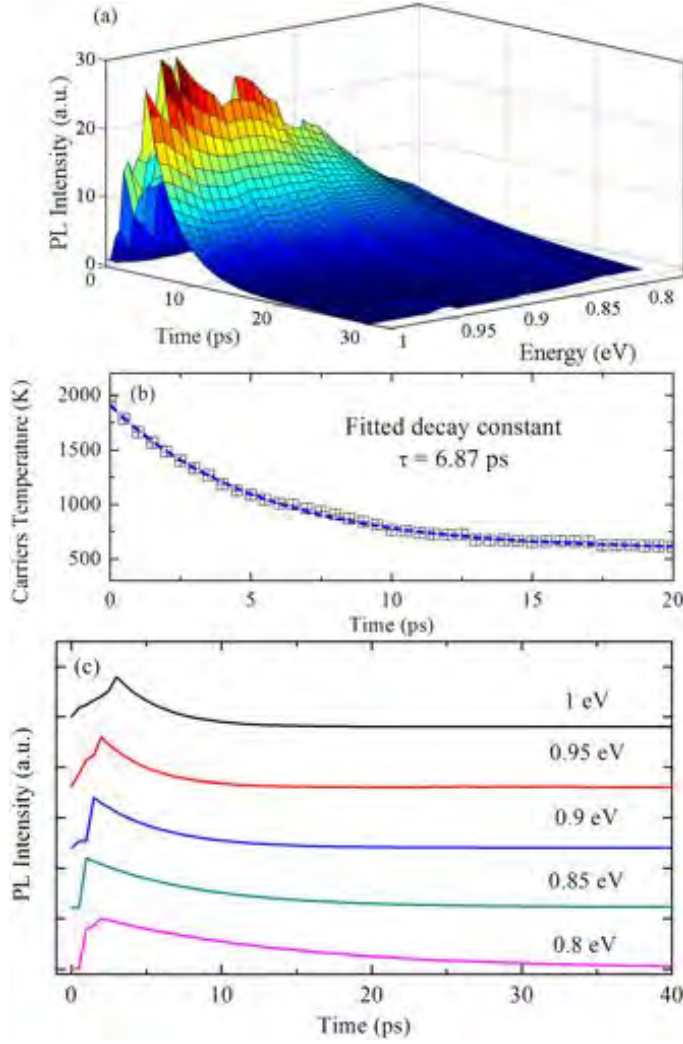


Fig 2.14: (a) Time resolved photoluminescence for a $1.4 \mu\text{m}$ epitaxial InN film. Photo-excited carrier density is $1.5 \times 10^{19} \text{ cm}^{-3}$; (b) Calculated hot carrier temperature transient (the dashed line is a single exponential fitting); (c) Photoluminescence intensity versus delay time for different probed energies.

maximum efficiency and 1000-sun illumination.

A conversion efficiency of 36.2% can be achieved for maximum concentration of the solar spectrum, Fig. 2.15(b). The increase in efficiency is due to the much higher average energy of the carrier system. The maximum efficiency is obtained for $1.0 \text{ eV} < \Delta E < 1.2 \text{ eV}$ and $0.05 \text{ eV} < \delta E < 0.1 \text{ eV}$. With

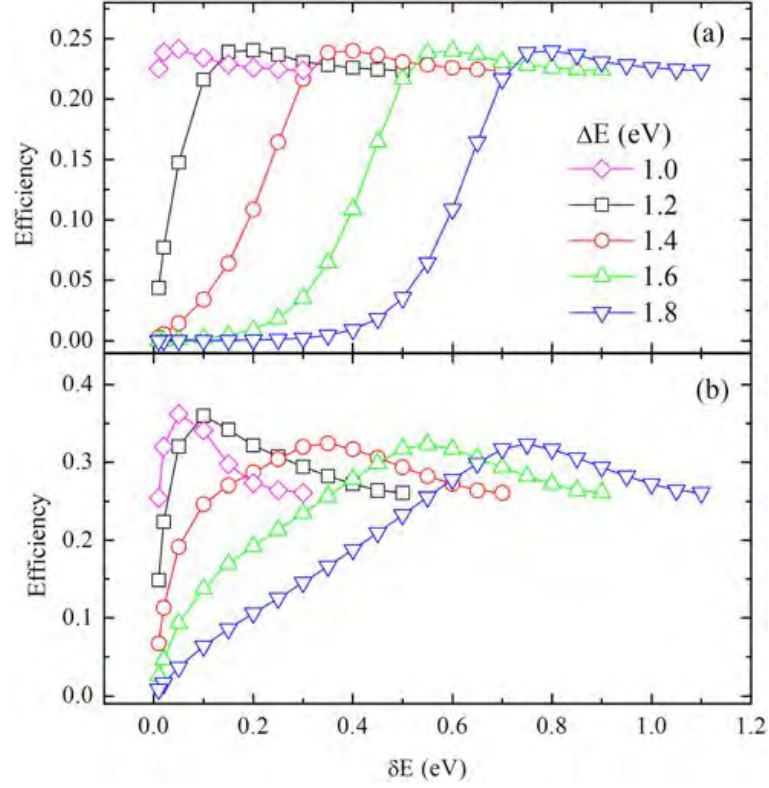


Fig 2.15: Hot carrier solar cell efficiency versus width of energy selective contacts calculated with the experimental thermalisation data, for different extraction energies. (a) 1000 suns and (b) maximal concentration.

this ESCs configuration, II is the predominant carrier scattering mechanism in the system, increasing the number of carriers available for extractions at low energy states. However, realizing highly selective ESCs has been found to be a very complex technological task[43]. For values of ΔE higher than 1.2 eV, the AR rate is higher than the II rate, allowing promotion of carriers to higher energy states. In this case, the constraints on the value of δE are more relaxed, as shown by the gentle peaks in Fig. 2.15(b). For maximum concentration, the average carrier temperature at maximum power point is between 500 K and 650 K, as reported in Fig. 2.16(b).

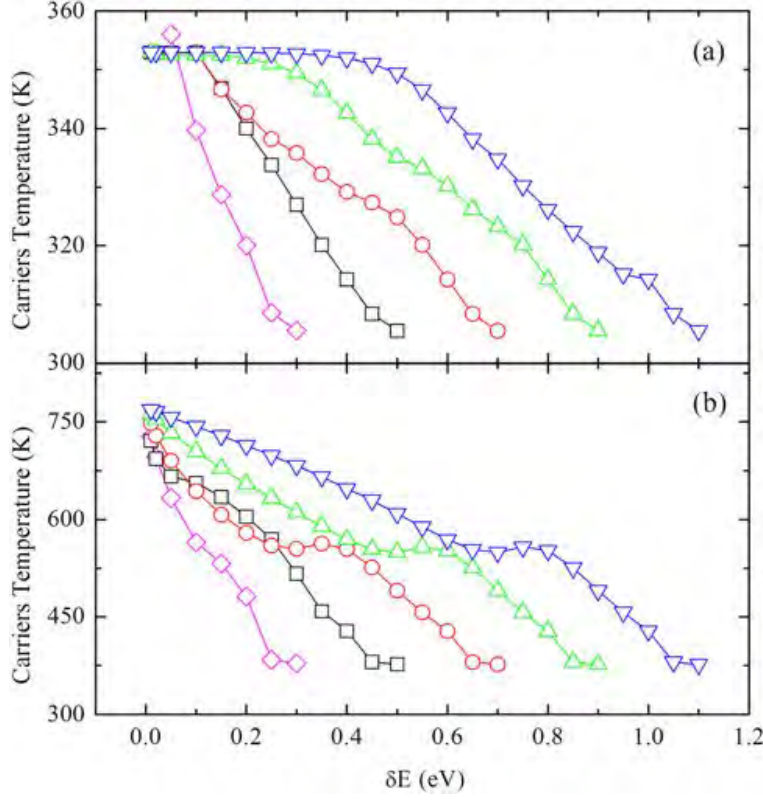


Fig 2.16: carrier temperature at maximum power point versus δE , for different values of ΔE . (a) 1000 suns and (b) maximal concentration.

2.2.2.3 Conclusion

In conclusion, the limiting performance of a HCSC based on bulk wurtzite InN have been calculated considering non-ideal electronic properties of absorber and ESCs. The hot carrier relaxation rate of InN has been measured by TRPL. It was found that, although the presence of hot phonon effect in InN, the hot carriers cool down too fast to the respective band edges to allow a sufficient efficiency gain in the conversion process of the solar radiation. The consequence is that the limiting efficiencies of the HCSC are 24% for 1000 suns, which is close to the Shockley-Queisser limit, and 36.2% for maximal concentration. These results narrow down the possibilities of

using bulk III-V semiconductors to implement HCSC absorbers. This inconvenience can be potentially tackled by designing absorber layers based on multiple quantum well systems, which may further slow the cooling process of hot carriers[60, 19].

2.3 Relaxation time model and carrier scattering effects

In the previous sections the cell efficiencies are evaluated by assuming Fermi distributions of electrons and holes at the same temperature. However in reality the reservoir of carriers may be far away from equilibrium, hence requiring a method that deals with arbitrary distribution functions. Their variations from the Fermi functions should depend numerically on the various rates of microscopic scattering processes.

In this section performance of the HCSC has been analyzed using a model incorporating the relaxation times of the relevant electronic processes. The variation in the maximum efficiency as well as the carrier statistics are demonstrated according to different carrier-carrier scattering rates. The significant dependance of cell performance on Coulomb scattering properties is quantitatively demonstrated and explained by carrier depletion, asymmetric electron and hole statistics and unmatched transmission properties for carrier extraction. The inter-relation between the electronic properties of the absorber material and the contact properties implies that an integrated design with both parts is required. The work here has been published in “Investigation of carrier-carrier scattering effect on the performance of hot carrier solar cells with relaxation time approximation” by Y. Feng et al., 2013, Applied Physics Letters, 102:243901 [61].

2.3.1 Carrier statistics on the operation of HCSC

In the previous sections the limiting efficiency for a hot carrier solar cell has been obtained with the assumption that carriers are in equilibrium at an elevated temperature.[9] In reality the cell efficiency could deviate from this prediction due to the non-equilibrium of electrons and holes.[8] Some researches argued that the electrons and holes are at the same temperature due to their fast interaction.[5, 9] Others argued that holes remain at room temperature in spite of the presence of hot electrons, since photo-generated holes have lower energies and suffer quicker cooling.[8, 25] Both of the two arguments are over-simplified. The actual carrier distributions and energy exchange rates depends critically on the details of interactions such as electron and hole scattering, impact ionization and its inverse process.

In addition to the difference between the respective distributions of electrons and holes, their occupancies may not strictly follow the Fermi statistics. This is in contrast with the assumption in previous reports.[10, 7] The electron-electron (or hole-hole) elastic scattering rate is generally proportional to the square of the electron (or hole) concentration. Therefore if there are not sufficient densities of carriers the scattering rates may be too low to maintain the respective carrier system in equilibrium. The carrier occupancy can deviate most substantially from equilibrium at the extraction energy levels of the ESCs. This is especially true if a large number of carriers are extracted in this narrow energy window and the scattering rates that lead to renormalization are insufficiently rapid. The depletion of carriers within this energy range may lead to significant efficiency loss.

In this section the performance of a hot carrier solar cell device has been evaluated taking into account the non-equilibrium distributions of electrons and holes as well as different rates of Coulomb scattering between charge

carriers. This includes processes of electron-electron (e-e) scattering, hole-hole (h-h) scattering and electron-hole (e-h) scattering. Their effects on the carrier renormalization and the electron-hole energy transfer have been quantitatively examined under the relaxation time approximation (RTA). Other processes relevant to an operating device, including photo-generation, radiative recombination, carrier extraction, carrier cooling (inelastic carrier scattering) and impact ionisation/Auger recombination (AR-II), have also been incorporated with RTA.

2.3.2 Relaxation time model on the static statistics of carriers

The energy distributions of electrons, $n(\epsilon)$, and holes, $p(\epsilon)$, are affected by several microscopic processes. Each of them evolves simultaneously towards the respective equilibrium distributions $n_{eq}(\epsilon)$, $n_{ehs}(\epsilon)$, $n_{th}(\epsilon)$ and $n_{ai}(\epsilon)$. The kinetic equation for electrons is shown as Eq. 2.39 and that for holes has a similar form. Only steady-state solutions are required, hence $dn(\epsilon)/dt$ and $dp(\epsilon)/dt$ can be set to zero in Eq. 2.39.

$$\begin{aligned} \frac{\partial n(\epsilon)}{\partial t} = & -\frac{n(\epsilon) - n_{eq}(\epsilon)}{\tau_{eq}} - \frac{n(\epsilon) - n_{ehs}(\epsilon)}{\tau_{ehs}} - \frac{n(\epsilon) - n_{th}(\epsilon)}{\tau_{th}} \\ & - \frac{n(\epsilon) - n_{ai}(\epsilon)}{\tau_{ai}} + G_e(\epsilon) - R_e(\epsilon) - E_e(\epsilon; V) \end{aligned} \quad (2.39)$$

The characteristic relaxation times, τ_{eq} , τ_{ehs} , τ_{th} , τ_{ai} correspond to their respective processes, i.e. e-e scattering (leading to electron distribution renormalisation), e-h scattering, thermalization and AR-II. The energy-dependent carrier density, n_{eq} , n_{ehs} , n_{th} , n_{ai} are given by their distributions in thermal equilibrium. The rates, $G_e(\epsilon)$, $R_e(\epsilon)$, $E_e(\epsilon)$ are those for photo-generation, radiative recombination and electron extraction.

Equilibrium energy distributions $n_{eq}(\epsilon)$, $n_{ehs}(\epsilon)$, $n_{th}(\epsilon)$ and $n_{ai}(\epsilon)$ are ap-

appropriate representations of charge carrier populations if the renormalizing processes are much faster than those that move the population away from equilibrium. In this case they can be expressed as Fermi functions with a dependence on the quasi-Fermi levels μ_e, μ_h and the carrier temperature T_e, T_h . From arbitrary distributions $n(\epsilon)$ and $p(\epsilon)$, the equilibrium distributions can be found by minimizing the system free energy.[5] The e-e elastic scattering conserves the particle number $N[n(\epsilon)]$ and total energy $E[n(\epsilon)]$ of electrons, only re-normalizing the distribution. Its respective equilibrium distribution can be found from Eq. 2.40, where $D(\epsilon)$ denotes the density of states at energy ϵ . Electron-hole scattering exchanges energy between electrons and holes, moving the populations towards a common temperature. It also conserves respective particle numbers and the system total energy. The equilibrium distributions are described by Eq. 2.41. The thermalization process transfers electronic energy to phonons and serves to reduce the overall carrier temperature toward room temperature T_{RT} . The numbers of electrons and holes are still conserved through this process, with the equilibrium distributions shown in Eq. 2.42. Auger recombination and its reverse process, impact ionization exchange both thermal energy and electro-chemical energy between electrons and holes until a common temperature and zero total electro-chemical potential are reached.[5] The first equation of Eq. 2.43 is obtained using the conservation of the system's total energy and requires knowledge of the potential energy of an e-h pair, i.e. the electronic bandgap E_g . The second equation is based on the condition of charge neutrality resulting from the pair-wise generation and annihilation of electrons and holes.

$$\begin{aligned} N[n_{eq}(\epsilon; \mu_e, T_e)] &= \int_0^\infty D(\epsilon)n(\epsilon)d\epsilon \equiv N[n(\epsilon)] \\ E[n_{eq}(\epsilon; \mu_e, T_e)] &= \int_0^\infty \epsilon D(\epsilon)n(\epsilon)d\epsilon \equiv E[n(\epsilon)] \end{aligned} \quad (2.40)$$

$$N[n_{ehs}(\epsilon; \mu_e, T)] = N[p_{ehs}(\epsilon; \mu_h, T)] = N[n(\epsilon)] \quad (2.41)$$

$$E[n_{ehs}(\epsilon; \mu_e, T)] + E[p_{ehs}(\epsilon; \mu_h, T)] = E[n(\epsilon)] + E[p(\epsilon)]$$

$$N[n_{th}(\epsilon; \mu_e, T_{RT})] = N[p_{th}(\epsilon; \mu_h, T_{RT})] = N[n(\epsilon)] \quad (2.42)$$

$$\begin{aligned} E[n_{ai}(\epsilon; \mu, T)] + E[p_{ai}(\epsilon; -E_g - \mu, T)] + E_g N[n_{ai}(\epsilon; \mu, T)] \\ = E[\epsilon; n(\epsilon)] + E[\epsilon; p(\epsilon)] + E_g N[\epsilon; n(\epsilon)] \\ N[n_{ai}(\epsilon; \mu_e, T)] = N[p_{ai}(\epsilon; -E_g - \mu, T)] \end{aligned} \quad (2.43)$$

Generally the relaxation times are dependent on the carrier distributions and the specific energy levels considered. For simplicity here we only consider the carrier density dependences of τ_{eq} and τ_{ehs} while setting other relaxation times as constants. The scattering relaxation times τ_{eq} and τ_{ehs} are both inversely proportional to the respective carrier densities while the former is also inversely proportional to the respective carrier effective mass m_e^* or m_h^* [62]. To compare the performance of the HCSC with different levels of material-related scattering properties we varied the proportionality coefficients A and B in Eq. 2.44. Superscript e or h indicates the type of carriers to which the parameter refers.

$$\begin{aligned} \tau_{eq}^e &= \frac{A}{m_e^* N[n(\epsilon)]} & \tau_{eq}^h &= \frac{A}{m_h^* N[p(\epsilon)]} \\ \tau_{ehs}^e &= \tau_{ehs}^h & &= \frac{B}{N[n(\epsilon)]} \end{aligned} \quad (2.44)$$

For carrier photo-generation, only direct transitions from the heavy-hole valence band to the lowest conduction band are considered. The two bands are assumed to be parabolic, characterized by their effective masses. The energy-dependent generation rates of electrons $G_e(\epsilon)$ and of holes $G_h(\epsilon)$ are expressed in Eq. 2.45. The radiative emission is treated with a generalized

Planck's law (Eq. 2.46) taking into account direct transitions only.[8] The energy-dependent carrier extraction rate is given by Landauer formalism due to its ballistic nature (Eq. 2.47)[10].

$$G_e(\epsilon) = R_c j_{sun} [E_g + (1 + m_e^*/m_h^*)\epsilon] \quad (2.45)$$

$$R(\epsilon) = \frac{2\pi}{h^3 c^2} \frac{[E_g + (1 + m_h^*/m_e^*)\epsilon]^2}{(\rho_e(\epsilon)/n(\epsilon) - 1)(\rho_h(\epsilon)/n(\epsilon) - 1) - 1} \quad (2.46)$$

$$E_e(\epsilon) = \begin{cases} 0 & \epsilon < \frac{\Delta E - E_g - \delta E}{2}, \quad \epsilon > \frac{\Delta E - E_g + \delta E}{2} \\ C_e(\epsilon) \cdot [n(\epsilon)/\rho_e(\epsilon) - f(T_{rt}, V_e; \epsilon)] & \frac{\Delta E - E_g - \delta E}{2} < \epsilon < \frac{\Delta E - E_g + \delta E}{2} \end{cases} \quad (2.47)$$

Where $j_{sun}(\epsilon)$ is the solar spectral photon flux and $R_c = 1000$ is the concentration ratio of interest. The energy dependent densities of states $\rho_e(\epsilon)$ and $\rho_h(\epsilon)$ are for electrons and holes respectively. The carrier extraction rate is proportional to the difference between the occupancy in the absorber and the thermalised occupancy in the contact $f(T_{rt}, V_e; \epsilon)$, with the proportionality coefficient $C_{e,h}(\epsilon)$ relevant to the electronic band structure.[10] The ESCs of electrons and holes are assumed to be symmetric, i.e. they share the same extraction levels, $\frac{\Delta E - E_g}{2}$ relative to the respective band edges and have the same transmission window width δE .

2.3.3 Numerical results and discussions

The 1000-sun performance has been predicted for the cell configuration of an intrinsic InN absorber (thickness: 50 nm) with two symmetric ESCs, in accordance with the previous work.[10, 9]. The material parameters adopted in this work are consistent with those adopted in the previous sections (Tab. 2.1). Additional parameters are required for characterizing the properties of relevant processes, which are listed in Tab. 3.8. The thermalisation relaxation

time of holes is assumed to be shorter than that of electrons by an order of magnitude to demonstrate the asymmetric carrier cooling properties. The transmission window properties adopted here are from the results shown in Sec. 2.2.1.3, i.e. the calculated optimal ΔE and δE with the assumption of rectangular transmission probability profiles.

Table 2.2: Appropriate material and structural parameters adopted in the performance calculation of HCSCs with different carrier-carrier scattering rates

II-AR τ_{ai}	Thermalisation τ_{th}		Transmission window	
	electrons	holes	ΔE	δE
10^{-10}s [9, 31]	10^{-10}s [10, 9]	10^{-11}s	1.15eV [10]	0.02eV [10]

2.3.3.1 Efficiency variations with different e-e/h-h and e-h scattering parameters

The maximum efficiencies have been computed with different relaxation time parameters, following the A and B given in Eq. 2.44. The results are demonstrated in Fig. 2.17. The values of A and B are in SI units (A : kgs/m^3 , B : s/m^3). For simplicity the units of A and B are not shown explicitly in the following content. In the upper figure efficiency decreases with A , suggesting insufficient rates of e-e and h-h elastic scattering could reduce the efficiency. This is because the carriers with energies within the transmission window of the ESCs could be depleted unless the elastic scattering is quick enough to supply new carriers with these energies. The curve at $B = 10^8$ is almost flat, for e-h elastic scattering is quick enough to prevent carrier depletion, noting that e-h scattering allows both carriers to exchange their energies, providing possibilities of supplying carriers with the energies of extraction. For the same reason, with negligible e-e and h-h scattering ($A > 10^{-16}$) the efficiency

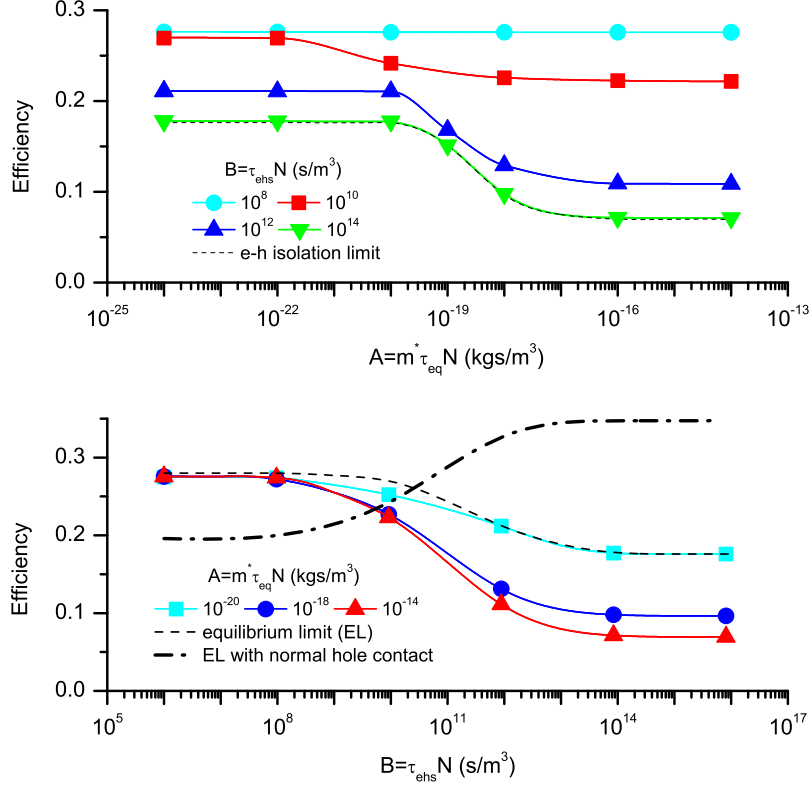


Fig 2.17: Maximum efficiency with different A and B (Eq. 2.44). The e-h isolation limit indicates no scattering between electrons and holes. The equilibrium limit indicates ultrafast e-e scattering and h-h scattering.

tends toward a constant value instead of dropping to zero. The lower figure in Fig. 2.17 shows that the efficiency decreases with the relaxation time of e-h scattering. It is partly due to the carrier depletion especially with insufficient e-e and h-h scattering, as shown in Fig. 2.18 at $A = 10^{-14}$. With sufficient e-e and h-h scattering, for example the equilibrium limit in which carriers are completely re-normalised, the same trend still exists. In fact a long relaxation time of e-h scattering blocks the energy flow from electrons to holes, allowing the holes to relax rapidly due to their fast thermalisation events

compared to electrons. This would limit the hole flux out of the device since only holes with an elevated energy and within a small energy window could be extracted. On contrary, the efficiency goes up with B if we replace the hole ESC with a normal contact, one that is transmissive for all holes, since less e-h scattering means less energy loss from hot electrons. From Fig. 2.17, to optimize the cell performance the selection of the hole contact depends on the e-h scattering rate in the absorber. A normal contact is beneficial for slow scattering rates ($B > 10^{11}$) while the ESC configuration adopted here has a greater advantage for rapid scattering rates ($B < 10^{11}$).

2.3.3.2 Energy-dependent distributions of carriers under static cell operation

The energy-dependent distributions of electrons and holes are shown in Fig. 2.18, corresponding to the Maximum Power Points (MPPs) with different A and B values. From left to right the figures show the trend of increasing carrier temperature with e-e and h-h scattering rates (A varies from 10^{-14} to 10^{-19}), as with less carrier depletion a faster extraction rates occur reducing the retention time of carriers. From top to bottom the figures demonstrate a larger deviation between electron distribution and hole distribution with less e-h scattering (B varies from 10^{10} to 10^{14}). The carrier depletion within the transmission window of ESCs is illustrated in the corresponding insets. The resupply of depleted holes is more rapid than electrons because of the proportionality between the scattering rate and the carrier effective mass.[62] With a small A , i.e. fast e-e/h-h scattering rates, the supply of holes is sufficient for the carrier extraction, leading to a larger current density and a higher overall efficiency. In this case the electron depletion could be even more severe since the increase in current depletes electrons more quickly. This is observed with $B = 10^{10}$ and 10^{12} . Apart from the region of carrier depletion

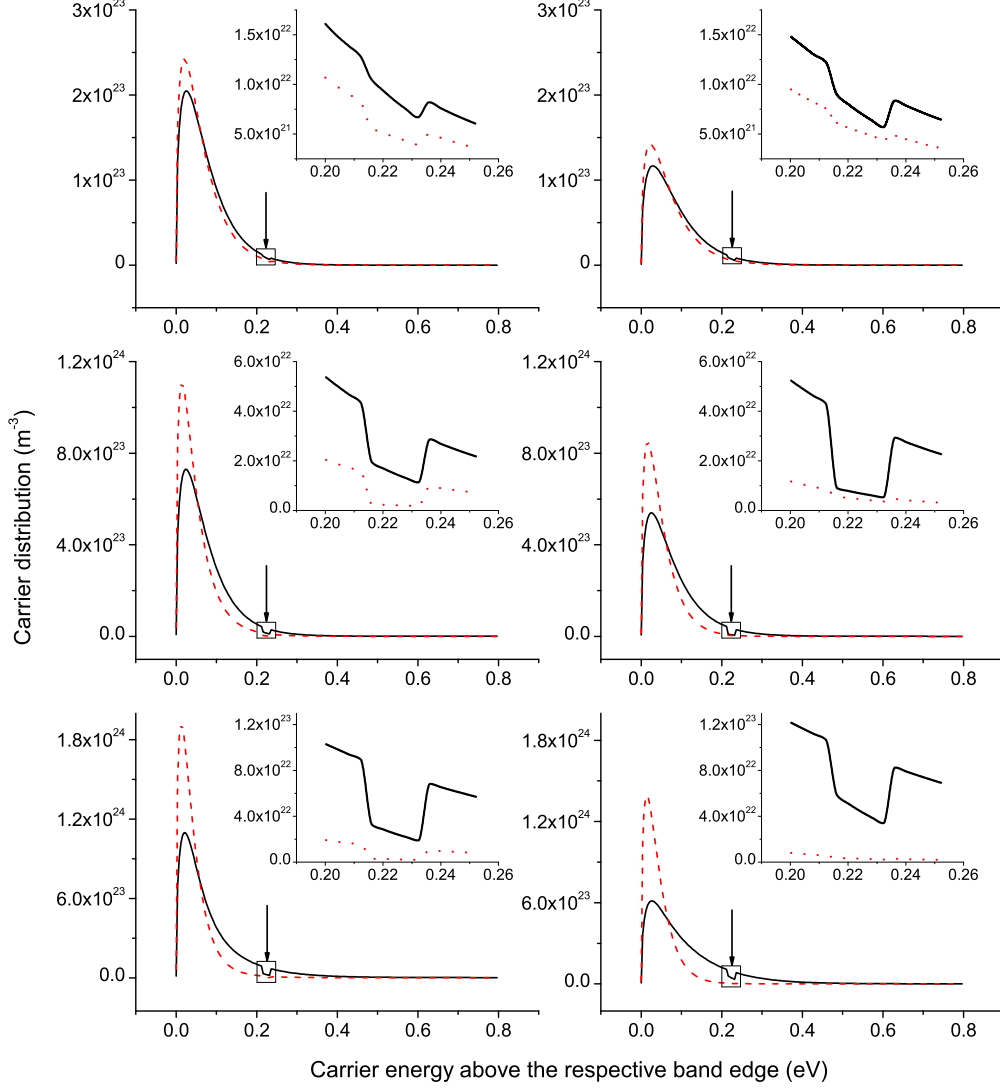


Fig 2.18: Energy-dependent distributions of electrons (black solid line) and holes (red dashed line) when operating at the Maximum Power Points (MPPs) with different A and B : $A = 10^{-14}$ (left), $A = 10^{-19}$ (right); $B = 10^{10}$ (upper), $B = 10^{12}$ (middle), $B = 10^{14}$ (lower). The depleted region within the transmission window is enlarged in the corresponding inset.

the distributions are close to Fermi functions, which may be used for defining a “quasi-temperature” for each type of carriers. The quasi-temperature

variations with A and B are depicted in the insets of Fig. 2.19.

2.3.3.3 Current - Voltage characteristics of the HCSC with various carrier scattering parameters

The calculated current-voltage curves are shown in Fig. 2.19. With faster e-h scattering (smaller B) the short-circuit current density is increased while the open-circuit voltage is reduced. It is difficult to extract holes at the elevated energy level required by ESCs unless e-h scattering is quick enough to resupply highly energetic holes. On the other hand the increase of voltage with slower e-h scattering comes from the hotter electron distribution at the open-circuit condition, with less energy lost to the thermalised holes. If an HCSC is designed with the narrow high energy transmission window for holes, as adopted in this thesis, the maximum efficiency is always higher for quicker e-h scattering. The drawback of slow e-h scattering would be pronounced for insufficient e-e and h-h scattering rates, since the significant carrier depletion would inhibit the carrier extraction resulting in a colder carrier distribution. As a result, the upper inset of Fig. 2.19 shows that the quasi-temperatures of both electrons and holes are low at MPPs, if e-h interaction is weak, while in the lower inset the contrast between them increases. The carrier quasi-temperature insets also provide a test of the validity of commonly used assumptions: electrons and holes share the same temperature only for fast e-h scattering ($B < 10^{10}$) while holes are completely thermalised when e-h scattering rates are slow ($B > 10^{14}$).

For real materials the choice of parameters A and B can be determined by computing the realistic scattering rates between carriers. We have calculated the scattering relaxation times for bulk cubic-InN, taking into account both the direct Coulomb potential and the exchange one. The results closely follow the relation shown in Eq. 2.44, with $A = 2.5 \times 10^{-19}$ and $B = 2.4 \times 10^{11}$.

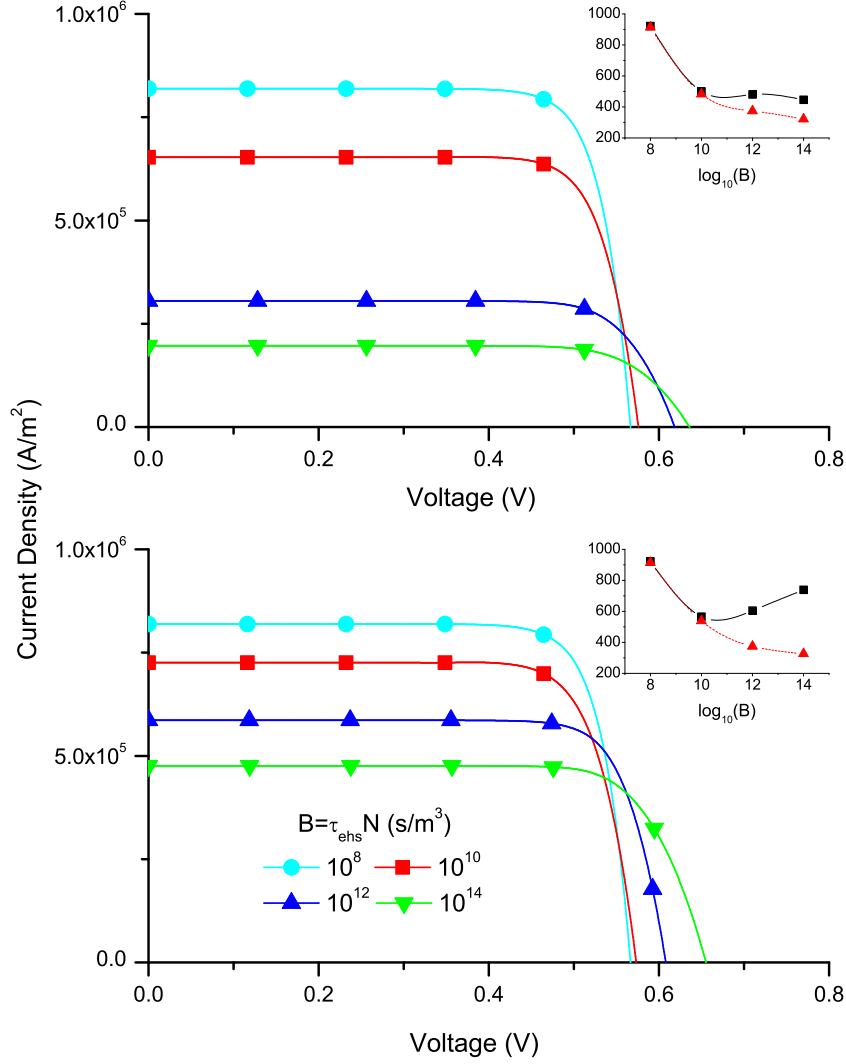


Figure 2.19: Current-voltage characteristics with four values of B . The upper figure is for slow e-e/h-h scattering ($A = 10^{-14}$) while the lower figure is for quick e-e/h-h scattering ($A = 10^{-20}$). The insets show the quasi-temperatures (in Kelvin) at MPPs for electrons (black square) and for holes (red triangle)

Overall the importance of carrier-carrier scattering has been revealed in terms of the performance of HCSC. Two types of scattering have been dis-

cussed: e-e/h-h scattering and e-h scattering. Both of these contribute to the re-normalisation of carriers while the latter also contributes to the energy transfer from hot electrons to partially thermalized holes. The results show the maximum efficiency varies significantly with the carrier scattering properties due to energy-dependent carrier depletion and asymmetric statistics of electrons and holes. With different hole contacts the dominant loss mechanism switches: with an ESC at an elevated energy the hole extraction is blocked until significant heat is transferred from hot electrons. Thus at the hole side an ESC is more suitable for fast e-h scattering while a normal contact is beneficial for slow e-h scattering rates. In addition, the RTA model suggested here provides the possibility of analyzing any realistic HCSC device. This is done by adopting the material-related relaxation times of all relevant processes. The model also serves to optimize the transmission properties of both contacts. According to this work it heavily depends on the carrier scattering properties in the absorber.

2.4 Unified framework of any optoelectronic devices

During the recent decades lots of new concepts have been developed as alternative approaches for solar energy conversion. Among them some focus on advanced operating principles different from conventional cells, such as the solar-thermo-electric cell, hot carrier cell, multiple-excitation-generation (MEG) cell, intermediate-level cell and tandem cell. These proposals aim to improve the conversion efficiency by enhancing or inhibiting some electronic processes. For instance the hot carrier cell decouples photo-generated carriers from acoustic phonons, while solar-thermo-electric cell feed energies to carriers from the lattice. The MEG cell works in a similar way to the hot carrier cell but a dominant impact ionization process is utilized to improve the quantum efficiency above the unity. The intermediate-level cell and tandem cell utilize the inter-band electronic transitions with different resonant frequencies to maximize use of the broad-band photon spectrum.

Other concepts dealt with the adoption of novel materials and structures. Apart from the conventional crystallized semiconductors, disordered systems and nano-structures have been investigated for the purpose of solar energy conversion. Amorphous materials has been shown to have potential benefit on improving cell performance while nano-structures (quantum-wells, quantum dots, nanotubes, graphene etc.) have been demonstrated to have fancy electronic or photonic properties. Molecular systems have already been widely used in organic solar cells and dye-sensitized cells.

Although we could investigate on those different concepts individually, this may involve repeated labor work ignoring their common properties. They share a common trait that the major processes relevant to the energy conversion are actually quantum interactions between elementary excitations

with sufficiently high frequencies. The interactions are so fast (duration time $\sim 1/\omega$) that they may be regarded as quasi-classical scattering processes. Each scattering involves a certain probability of change on the system quantum state. With the fluctuations being smoothed by time averaging, the static macroscopic condition of any solid-state system exists. These considerations lead to a unified theoretical framework suitable for describing any opto-electronic devices.

2.4.1 Introduction to quantized excitations in solids and the unified approach for steady-state operations

Up to now the known material systems at room temperature have three forms: gas, liquid and solid. Macroscopic quantum systems, including Bose-Einstein condensate, superfluids, etc., exist only at very low temperatures. Gas and liquid have atoms move around with limited interactions while in solids the positions of atoms are fixed except for vibrations. Here the fixed position of the nucleus does not rule out the quantum uncertainty, i.e. $\sigma_x \sigma_p \geq \hbar/2$, where σ_x and σ_p denote the standard deviations of one-dimensional position x and momentum p . In the non-relativistic limit the momentum of a free particle is expressed as $p = m dx/dt = \sqrt{2mE_k}$, where m and E_k denote its static mass and kinetic energy, respectively. As the static mass of a nucleus is much larger than that of an electron, the uncertainty of its position is much smaller.

Gases and liquids are not under consideration as they have a random distribution of atoms. Though statistically average properties may be found for these systems, random algorithms (e.g. Monte Carlo simulation) have to be invoked in their numerical treatments. In addition phases of gas and liquid are generally not suitable for an electrical device since the inter-atomic

coupling is low that may only yield a small current.

2.4.1.1 Elementary excitations in solids

In solids the positions of nuclei are fixed within the range allowed by the quantum uncertainty. The total system energy may be represented by $E = E_e^k + E_n^k + E_{e,e} + E_{e,n} + E_{n,n}$ where $E_{e,n}^k$ denotes the kinetic energies of electrons and nucleus respectively. $E_{e,e}$, $E_{e,n}$ and $E_{n,n}$ denote the respective potential energies between electrons and nuclei. The system wave function can be broken into its electronic and nuclear components (Born-Oppenheimer approximation), and at the ground state E_e^k , $E_{e,e}$ and $E_{e,n}$ are the only potentials required to calculate the electronic states (adiabatic approximation).

At the system ground state the electrons occupy these electronic states from the bottom up to the Fermi energy. At its excited states additional energies need to be added to the system. These excitation energies can be quantized to their respective elementary excitations (quasi-particles). For instance, an electron excited to the conduction band contributes to an (single) electron excitation and an (single) hole excitation, while the kinetic energy of vibrating atoms is quantized as phonons (or molecular vibrations). Other elementary excitations, including photons, excitons, plasmons, polarons, etc., have their effects in the whole process of solar energy conversion. The system Hamiltonian may be expressed by $H = \sum_i \hbar \omega_{f_i} c_i^\dagger c_i + \sum_j \hbar \omega_{b_j} a_j^\dagger a_j + H_I$, where ω_{f_i} and ω_{b_j} denote the frequencies of those excitations that obey Fermi statistics and Bose statistics respectively. The annihilation operators c_i and a_j are also for fermion and boson respectively. H_I includes all the interaction terms between different elementary excitations.

The quantization of these excitations in solids makes it possible to deal with the many-body interaction processes from a unified treatment. In terms

of solar energy conversion, the quanta of excitations come from the sources of injected photons. On the other hand, they finally flow to quanta sinks, including a sink of fermion excitations (for current extraction) and a sink of bosons (for heat dissipation). These sinks are external reservoirs and normally assumed as being in equilibrium. The internal many-particle processes within the system have various physical origins. However in terms of the device modeling we can neglect the underlying physics of those processes and simply parameterize their respective coupling strengths.

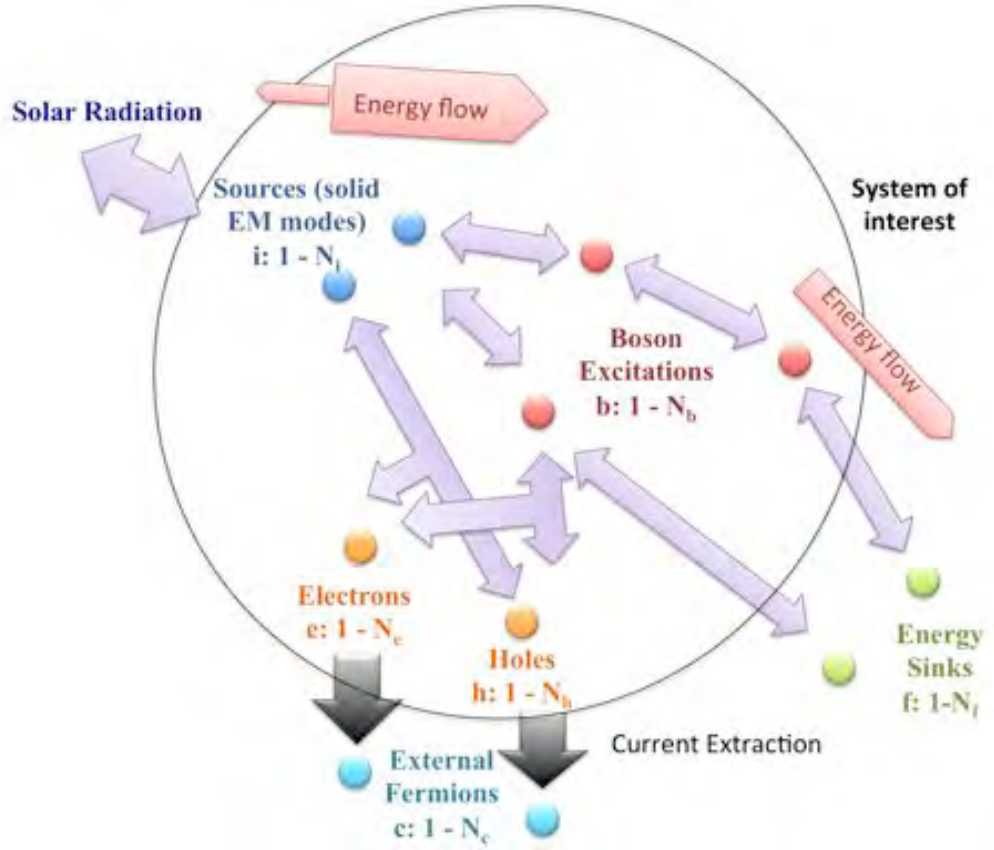


Figure 2.20: Schematic diagram of the energy and quanta transfer between different type of excitations when a solid-state opto-electronic device is in its operation.

2.4.1.2 Interactions of excitations under standard perturbation theory and theoretical approach towards the performance of steady-state operation

From quantum field theory the interaction Hamiltonian H_I includes various coupling terms. The major coupling terms between two bosons are $g_{b_1 b_2} \cdot a_{b_1}^+ a_{b_2}$ and its hermitian conjugate $g_{b_1 b_2}^* \cdot a_{b_1} a_{b_2}^+$. Three bosons are involved in coupling terms like $g_{b_1 b_2 b_3} \cdot a_{b_1}^+ a_{b_2}^+ a_{b_3}$ and $g_{b_1 b_2 b_3}^* \cdot a_{b_1} a_{b_2} a_{b_3}^+$. a^+ and a denote the creation and annihilation operators of the corresponding boson mode. Note here the reduced Planck's constant $\hbar$ is set to unity for convenience. From the 1st order time-dependent perturbation theory, the time-evolution of the final-state probability has a rate proportional to the square of the respective Hamiltonian matrix component. Such component is evaluated by adopting the rules of boson state operation, i.e. $a^+ |n\rangle = \sqrt{n+1} |n+1\rangle$ and $a |n\rangle = \sqrt{n} |n-1\rangle$. This leads us to the quanta flux (or rate of change on the occupation number) due to a specified interaction. For instance $dn_{b_1}/dt = -dn_{b_2}/dt = \alpha_{b_1 b_2} \cdot (n_{b_1} + 1)n_{b_2}$ is derived from the interaction Hamiltonian of $g_{b_1 b_2} \cdot a_{b_1}^+ a_{b_2}$, while $dn_{b_1}/dt = dn_{b_2}/dt = -dn_{b_3}/dt = \alpha_{b_1 b_2 b_3} \cdot (n_{b_1} + 1)(n_{b_2} + 1)n_{b_3}$ is derived from $g_{b_1 b_2 b_3}^* \cdot a_{b_1} a_{b_2} a_{b_3}^+$. If accounting for their hermitian conjugate those expressions above will include rates of respective reverse processes. This results in a strict conformance of the principle of detailed balance.

The interaction Hamiltonian involving fermion excitations should include the same number of electron creation operators and electron annihilation operators, as the number of electrons shall be conserved during the interaction. The most usual term is the hopping Hamiltonian $g_{e_1 e_2} \cdot c_{e_1}^+ c_{e_2}$ that leads to a quanta flux of $\alpha_{e_1 e_2} \cdot (1 - n_{e_1})n_{e_2}$. The scattering terms like $g_{e_1 e_2 e_3 e_4} \cdot c_{e_1}^+ c_{e_2}^+ c_{e_3} c_{e_4}$ corresponds to a quanta flux of $\alpha_{e_1 e_2 e_3 e_4} \cdot (1 - n_{e_1})(1 - n_{e_2})n_{e_3}n_{e_4}$. Such process involves four electronic states. In semiconductors the processes of impact

ionization, Auger recombination, carrier-carrier scattering are all sub-classes of this type of coupling.

The interaction Hamiltonian that involves both fermion and boson excitations includes the boson-assisted electronic transition as its lowest-order term. Such term may be expressed as $g_{e_1 e_2 b} \cdot c_{e_1}^+ c_{e_2} a_b^+$ whose corresponding quanta flux is $\alpha_{e_1 e_2 b} \cdot (1 - n_{e_1}) n_{e_2} (n_{b_2} + 1)$. It is worthwhile to mention that for the process of photon-assisted electronic transition the term $\alpha_{e_1 e_2 b} \cdot (1 - n_{e_1}) n_{e_2}$ corresponds to the spontaneous emission while $\alpha_{e_1 e_2 b} \cdot (1 - n_{e_1}) n_{e_2} n_{b_2}$ is for the stimulated emission. Its reverse process yields an absorption term $\alpha_{e_1 e_2 b} \cdot (1 - n_{e_2}) n_{e_1} n_{b_2}$ that has the same pre-factor with the stimulated emission (if $n_{e_1} = 0$ and $n_{e_2} = 1$)[63].

Higher-order terms of the interaction Hamiltonian may exist, through some of them are ruled out by specified selection rules (e.g. electron number, energy, momentum, angular momentum, etc.). These terms include higher orders of small quantities and hence are much weaker (with the assumption of weak perturbative fields). For instance the higher-order terms of the electron-phonon coupling include higher orders of the atomic displacements, which is small compared to the equilibrium separation between atoms.

Though all the processes due to weak coupling can be incorporated by the Fermi's golden rule, it does not explicitly include the transport of excitations. This is because some modes defined here are not stationary states even of the unperturbed Hamiltonian; hence their spatial distributions vary with time (at the speed of group velocity). However from the theory of quantum ballistic transport, the quanta flux from $(\mathbf{r}, \mathbf{p})$ to $(\mathbf{r} + \Delta\mathbf{r}, \mathbf{p})$ and the flux from $(\mathbf{r} + \Delta\mathbf{r}, -\mathbf{p})$ to $(\mathbf{r}, -\mathbf{p})$ can be regarded as reverse processes (by time reversal for T-symmetric process). As the momentum relaxation processes are ultrafast in solids, the internal modes $(\mathbf{r}, \mathbf{p})$ and $(\mathbf{r}, -\mathbf{p})$ have the same

average occupation number, as long as their energies are the same (e.g. homogeneous space). In this case the two modes of opposite momenta may be combined together with a net flux $F = \alpha[n(\mathbf{r} + \Delta\mathbf{r}, \pm\mathbf{p}) - n(\mathbf{r}, \pm\mathbf{p})]$. A strong deviation between occupations of $(\mathbf{r} + \Delta\mathbf{r}, -\mathbf{p})$ to $(\mathbf{r}, -\mathbf{p})$ only occur at the boundary of the system, i.e. at the coupled photon modes or electrical terminals. Assuming the external mode $(\mathbf{r}, \mathbf{p})$ points to the system, then the mode $(\mathbf{r}, -\mathbf{p})$ is towards the environment and is irrelevant to the operation of the system. The coupled internal mode $(\mathbf{r} + \Delta\mathbf{r}, \pm\mathbf{p})$ gains a net flux $F = \alpha[n(\mathbf{r} + \Delta\mathbf{r}, -\mathbf{p}) - n(\mathbf{r}, \mathbf{p})]$. In conclusion the net flux for excitation transport is expressed by $F = \alpha_{12}(n_1 - n_2)$ at both system interior and interfacial regions.

For solid-state systems that work for optoelectronic functions, it is possible to calculate the static operation performance by taking into account the steady-state conditions for all relevant modes. This condition requires that the average occupation numbers of each mode does not vary with time. As all the quanta fluxes merely rely on the occupation numbers, it is a self-consistent problem and has finite number of solutions (normally there is only one solution). The coefficient of each process is a constant that can be parameterized accounting for the physical nature of the interaction. In the future this framework can be adopted to conduct a theoretical performance analysis for any novel optoelectronic proposals.

2.4.2 Generalized optoelectronic reciprocity derived from the framework

In recent years the fundamental reciprocity of the operation of a solar cell and its reverse operation, i.e. a light-emitting device (LED), has triggered lots of interest among researchers, since the pioneering work done by Donolato[64].

This work developed a reciprocity for a p-n junction diode, which can operate both as a solar cell and as a LED. The relation has been developed from a viewpoint of the junction-edge minority carrier concentrations, which is then linked to the collection and emission efficiency[65, 66, 67]. Most recently Wong and Green[68, 69] took the parasitic resistances of the diode into account, yielding an incremental version of this reciprocal relation.

Although these relations are proven, at a macroscopic level, to be suitable for describing a semiconductor p-n junction, it does not apply to other materials and devices. The proof does not explicitly include processes of photon recycling, exciton formation, phonon scattering, etc. In addition the proof is specified for a two-terminal device and does not give any conclusions on the energy spectrum of injected carriers. In this work a generalized version of this reciprocity is derived, simply as a deduction from the detailed balance of microscopic processes. The relation has no specification on the type of the material system; it works for amorphous and molecular systems as well as for periodically ordered systems. As the proof no longer relies on the help of the minority carrier concentrations, it does not rely on any empirical knowledge of semiconductor junctions. The derived reciprocity is general and valid for any pairs of photon sources and current terminals. Furthermore, parasitic processes can be incorporated without much effort, enabling a wider range of application.

We start from the calculation of steady-state mode occupations for an arbitrary static system state. For each excitation mode, there is an equation balancing its outgoing quanta flux to its incoming flux. Eq. 2.48 links the steady-state occupation numbers of these modes to the statistics of the external excitation reservoirs. This equation is obtained by linearizing the expression of the net quanta flux for each microscopic process, i.e.

$dF_k = \sum_i \beta_{ki} df_{ki} + \sum_j \beta_{kj} dn_{kj}$, where k is the index of the process, df_{ki} and dn_{kj} denote the respective occupation numbers of the involved fermion mode (f_i) and boson excitation (n_j), deviated from their equilibrium values. Such linearization is only sufficiently accurate up to the 1st order of such deviation and hence requires $dn_i \ll 1$. The equilibrium state of the system refers to the state where every process is in dynamic equilibrium, i.e. with a net flux of zero.

$$\begin{aligned}
\mathbf{0} = \frac{\partial}{\partial t} \begin{bmatrix} df_1 \\ df_2 \\ \vdots \\ dn_1 \\ dn_2 \\ \vdots \end{bmatrix} &= \begin{bmatrix} q_{11} & q_{12} & \cdots & & \\ q_{21} & q_{22} & \cdots & & \\ \vdots & \vdots & \ddots & & \\ \hline & & & \mathbf{0} & \\ \hline & & & p_{11} & p_{12} & \cdots \\ & & & p_{21} & p_{22} & \cdots \\ & & & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} dg_1(f_1^t) \\ dg_2(f_2^t) \\ \vdots \\ dh_1(n_1^s) \\ dh_2(n_2^s) \\ \vdots \end{bmatrix} \\
- \begin{bmatrix} \sum q_{1i} + t_{11} & t_{12} & \cdots & x_{11} & x_{12} & \cdots \\ t_{21} & \sum q_{2i} + t_{22} & \cdots & x_{21} & x_{21} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots \\ \hline y_{11} & x_{12} & \cdots & \sum p_{1i} + s_{11} & s_{12} & \cdots \\ y_{21} & y_{21} & \cdots & s_{21} & \sum p_{2i} + s_{22} & \cdots \\ \vdots & \vdots & \ddots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} dg_1(f_1) \\ dg_2(f_2) \\ \vdots \\ dh_1(n_1) \\ dh_2(n_2) \\ \vdots \end{bmatrix} \\
&= \begin{bmatrix} \mathbf{Q} & \mathbf{0} \\ \mathbf{0} & \mathbf{P} \end{bmatrix} \begin{bmatrix} \delta \mathbf{g}^t \\ \delta \mathbf{h}^s \end{bmatrix} - \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{D} & \mathbf{C} \end{bmatrix} \begin{bmatrix} \delta \mathbf{g} \\ \delta \mathbf{h} \end{bmatrix} \quad (2.48)
\end{aligned}$$

f_i and n_j are average occupation numbers of the fermion mode and the boson mode in the system respectively. In the following content these symbols denote both the average occupation numbers and the modes themselves. Their deviations from the equilibrium values are represented by df_i and dn_i . g_i and h_j are functions depending on f_i and n_i respectively, whose deviations $dg_i(f_i)$ and $dh_j(n_j)$ are due to the respective deviated occupation numbers (df_i and dn_i). Each of these internal modes may interact with external modes,

i.e. either terminal fermion modes f_i^t (carrier extraction/injection) or source boson modes n_j^s (heat/photon exchange). The exact expression of the net flux of such interactions has the form of $\alpha_{ie}(n_i - n_e)$ (for bosons) or $\alpha_{ie}(f_i - f_e)$ (for fermions), where i and e are the respective indices of the internal and the external modes. To clarify the dimensions of the matrix blocks in Eq. 2.48, n and m are used to denote the respective numbers of fermion modes and boson modes involved internally in the system, while n_e and m_e denote the numbers of coupled external fermion modes and boson modes respectively. The matrices $\mathbf{Q}$ and $\mathbf{P}$ are of the dimension $n \times n_e$ and $m \times m_e$, while $\mathbf{A}$, $\mathbf{B}$, $\mathbf{C}$ and $\mathbf{D}$ are blocks of $n \times n$, $n \times m$, $m \times m$ and $m \times n$, respectively.

2.4.2.1 block-matrix representation of light-induced current and current-induced radiation

By utilizing identities of block matrix the illumination-induced current and the current-induced radiation of the system may be expressed linearly, if the external disturbance is only slightly varied from its equilibrium condition. This is in consistent with Eq. 2.48 since all processes are treated as linear with the deviated occupation numbers (df_i and dn_j).

$$\begin{aligned}
\mathbf{A}\delta\mathbf{g} + \mathbf{B}\delta\mathbf{h} &= \mathbf{Q}\delta\mathbf{g}^t \\
\mathbf{D}\delta\mathbf{g} + \mathbf{C}\delta\mathbf{h} &= \mathbf{P}\delta\mathbf{h}^s \\
\Rightarrow \mathbf{C}^{-1}\mathbf{D}\delta\mathbf{g} + \delta\mathbf{h} &= \mathbf{C}^{-1}\mathbf{P}\delta\mathbf{h}^s \\
\Rightarrow (\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})\delta\mathbf{g} &= \mathbf{Q}\delta\mathbf{g}^t - \mathbf{B}\mathbf{C}^{-1}\mathbf{P}\delta\mathbf{h}^s \tag{2.49}
\end{aligned}$$

$$(\mathbf{C} - \mathbf{D}\mathbf{A}^{-1}\mathbf{B})\delta\mathbf{h} = -\mathbf{D}\mathbf{A}^{-1}\mathbf{Q}\delta\mathbf{g}^t + \mathbf{P}\delta\mathbf{h}^s \tag{2.50}$$

In terms of the photo-generated current, we can set all terminal fermion modes in their equilibrium condition (no external bias), i.e. $\delta\mathbf{g}^t = \mathbf{0}$, plus a small disturbance of external boson occupations from their equilibrium values (e.g. light photon injection), i.e. $|\delta\mathbf{n}^s| \ll \mathbf{1}$. From Eq. 2.49 the static

internal occupation deviation $\delta \mathbf{g}$ is expressed in Eq. 2.51 as a linear response of the external disturbance $\delta \mathbf{h}^s$. Such internal deviation then contributes to the *terminal* current expressed in Eq. 2.52.

$$\delta \mathbf{g} = -(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}\delta \mathbf{h}^s \quad (2.51)$$

$$\begin{aligned} \delta \mathbf{I}|_{\delta \mathbf{g}^t=0} &= \mathbf{Q}^T \delta \mathbf{g} \\ &= -\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}\delta \mathbf{h}^s \end{aligned} \quad (2.52)$$

On the other hand if we apply a small bias whilst not injecting any light except for the background radiation (i.e. $\delta \mathbf{h}^s = \mathbf{0}$ and $|\delta \mathbf{g}^t| \ll 1$), a variation on the steady-state occupations of internal boson modes occurs (Eq. 2.53), which then leads to a net emission flux demonstrated in Eq. 2.54.

$$\delta \mathbf{h} = -(\mathbf{C} - \mathbf{D}\mathbf{A}^{-1}\mathbf{B})^{-1}\mathbf{D}\mathbf{A}^{-1}\mathbf{Q}\delta \mathbf{g}^t \quad (2.53)$$

$$= -\mathbf{C}^{-1}\mathbf{D}(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{Q}\delta \mathbf{g}^t \quad (\text{Binomial inverse theorem})$$

$$\begin{aligned} \delta \phi|_{\delta \mathbf{h}^s=0} &= \mathbf{P}^T \delta \mathbf{h} \\ &= -\mathbf{P}^T\mathbf{C}^{-1}\mathbf{D}(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{Q}\delta \mathbf{g}^t \end{aligned} \quad (2.54)$$

The expressions of photon-induced current (Eq. 2.52) and current-induced radiation (Eq. 2.54) are rigorous up to the 1st order of $\mathbf{g}^t$ and $\mathbf{h}^s$. The reciprocity between them depends on the transpose relation between the matrices of $-\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}$ and $-\mathbf{P}^T\mathbf{C}^{-1}\mathbf{D}(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{Q}$. This relation is proved in the following sections.

2.4.2.2 Symmetry properties of A and C for a system in equilibrium accounting for arbitrary microscopic reversible processes

Consider any microscopic process with fermion modes involved. As the number of electrons has to be conserved we may regard the process as several electronic transitions assisted by bosons: $f_i \rightarrow f_j$, $i, j = 1, 2, \dots, m$ where

i and j denote indices of the two fermion modes. Correspondingly the net transition rate between electronic states f_i and f_j may be represented by $F_k = A_k f_i(1 - f_j) - B_k f_j(1 - f_i)$, where k denotes the index of pair-wise transitions while A_k and B_k are functions of occupation numbers of other relevant modes. From the principle of detailed balance $F_k = 0$ for a system in equilibrium. If the average occupation numbers f_i and f_j deviate from their equilibrium values then a net flow may occur. It is possible to represent each fermion occupation number f_i by a “semi-chemical potential” μ_i that gives rise to the Fermi function $f_i = 1/\{1 + \exp[\beta(\epsilon_i - \mu_i)]\}$. Note that $\beta = 1/k_b T$ is the inverse thermal energy of the equilibrium temperature T . ϵ_i is the energy of the fermion excitation mode whose reference is at its equilibrium chemical potential (Fermi level for electron system) so that $\mu_i = 0$ in equilibrium. Here μ_i is regarded as pseudo for any deviation of the occupation number f_i is contributed merely by variation on μ_i , while T is always regarded as a constant, i.e. $\Delta f_i = F(\Delta \mu_i; \epsilon_i, \mu_i, T)$. Substituting this Fermi function into f_i and f_j we find that $f_j(1 - f_i) : f_i(1 - f_j) = e^{\beta(\epsilon_i - \epsilon_j)} : e^{\beta(\mu_i - \mu_j)}$. As long as $\mu_i = \mu_j$, the ratio of $f_j(1 - f_i)$ to $f_i(1 - f_j)$ remains the same as that in equilibrium. Since the interaction pre-factors A_k and B_k are constants, the net quanta flux $F_k = 0$ as long as $\mu_i = \mu_j$.

For small deviations from the equilibrium condition the net quanta flux of an arbitrary pair-wise transition may be linearized to $dF_k = \alpha_i df_i + \alpha_j df_j$, $i < j$, where a positive dF_k is defined to increase the occupation number of f_i while to decrease that of f_j . We assume that the deviation function of the occupation number can undertake a variable separation procedure, i.e. $df_i(\mu_i; \epsilon_i) = M^f(\epsilon_i)N^f(d\mu_i)$ (the validity of this variable separation is given in the next section). This makes it possible to express the net flux as $dF_k = \alpha_{ki} M^f(\epsilon_i)N^f(d\mu_i) + \alpha_{kj} M^f(\epsilon_j)N^f(d\mu_j)$. From the discussion in

the last paragraph $dF_k = 0$ when $d\mu_i = d\mu_j$. It leads to $\alpha_{ki}M^f(\epsilon_i) = -\alpha_{kj}M^f(\epsilon_i)$; this term is denoted by t_k . Following this procedure we adopt the function $N^f(d\mu_i)$ for $\delta\mathbf{g}$ (Eq. 2.55). Then $\mathbf{A}$ in Eq. 2.48 can be expressed as a symmetric matrix. As an example we may express the relevant matrix blocks in Eq. 2.55 for the special case of only three correlated fermion states.

$$\begin{aligned}\delta\mathbf{g}^t &= \begin{bmatrix} dN^f(\mu_1^t) \\ dN^f(\mu_2^t) \\ dN^f(\mu_3^t) \end{bmatrix} & \delta\mathbf{g} &= \begin{bmatrix} dN^f(\mu_1) \\ dN^f(\mu_2) \\ dN^f(\mu_3) \end{bmatrix} \\ \mathbf{A} &= \begin{bmatrix} q_1 + t_1 + t_2 & -t_1 & -t_2 \\ -t_1 & q_2 + t_1 + t_3 & -t_3 \\ -t_2 & -t_3 & q_3 + t_2 + t_3 \end{bmatrix}\end{aligned}\quad (2.55)$$

In general we may express elements of the matrix $\mathbf{A}$ as $A_{ij} = A_{ji} = -\sum_k t_k$, $i \neq j$, where k denotes the index of all possible electronic transitions between f_i and f_j .

Similarly, to find an expression for the matrix $\mathbf{C}$, it is necessary to select the occupation-dependent function $\delta\mathbf{h}$ first. As we did for fermion modes, we can adopt the variable separation strategy for boson modes. However in this case two different types of pair coupling exist, which is fundamentally due to the lack of particle conservation law for bosons. For the 1st type of pair-wise processes boson modes n_i and n_j gain or lose an occupation number simultaneously (pair-wise production/annihilation). On the other hand, in the 2nd-type processes one mode gains an occupation number while the other lose one (pair-wise boson transition). In the case of pair-wise production/annihilation the net quanta flux $F_k = A_k(n_i+1)(n_j+1) - B_k n_i n_j$. Like the treatment of fermions we define the semi-chemical potential μ_j for the boson mode n_j , i.e. $n_j = 1/\{\exp[\beta(\epsilon_j - \mu_j)] - 1\}$. Following the previous reasoning routine F_k remains zero if $\mu_i = -\mu_j$. In the case of pair-wise transitions $F_k = A_k(n_i+1)n_j - B_k n_i(n_j+1)$ where the condition of zero net

flux corresponds to $\mu_i = \mu_j$.

Using the same linearization technique the net quanta flux of an arbitrary pair-wise process is expressed by $dF_k = \beta_{ki}dn_i + \beta_{kj}dn_j$, $i < j$. It is defined that a positive dF_k is to increase the occupation number of n_i . Here we separate the function $dn_i(\mu_i; \epsilon_i)$ into $M^b(\epsilon_i)dN^b(\mu_i)$. $dn_i(\mu_i; \epsilon_i)$ is obviously not an even function of $d\mu_i$, which indicates the primary order of $d\mu_i$ in its Taylor expansion is the 1st order. If merely accounting for this primary order, $dN^b(\mu_i)$ is an odd function, i.e. $-dN^b(\mu_j) = dN^b(-\mu_j)$. In the processes of pair-wise production/annihilation the detailed balance principle leads to $dF_k = 0$ when $\mu_i = -\mu_j$. This gives the term $\beta_{ki}M^b(\epsilon_{ki}) = \beta_{kj}M^b(\epsilon_{kj})$, which is denoted by s_k . On the other hand $s_k \equiv \beta_{ki}M^b(\epsilon_{ki}) = -\beta_{kj}M^b(\epsilon_{kj})$ is valid in pair-wise boson transitions. If $dN^b(\mu_i)$ is used to define $\delta\mathbf{h}$ then $\mathbf{C}$ is a symmetric matrix. As an example $\delta\mathbf{h}$ and $\mathbf{C}$ are listed below for the case of three correlated phonon modes (and three fermion modes).

$$\delta\mathbf{h} = \begin{bmatrix} dN^b(\mu_1) \\ dN^b(\mu_2) \\ dN^b(\mu_3) \end{bmatrix} \quad \mathbf{C} = \begin{bmatrix} p_1 + s_1 & s_1 & -s_1 \\ s_1 & p_2 + s_1 & -s_1 \\ -s_1 & -s_1 & p_3 + s_1 \end{bmatrix} \quad (2.56)$$

In general $C_{ij} = C_{ji} = \sum_{k_1} s_{k_1} - \sum_{k_2} s_{k_2}$ for $i \neq j$, where k_1 denotes index of processes of pair-wise production and annihilation (between mode n_i and n_j) while k_2 refers to indices of transition processes. It is noted that Eq. 2.56 describes a boson process $|1\rangle + |2\rangle \leftrightarrow |3\rangle$. A good example of this is the phonon coupling due to the third-order anharmonicity of crystal potential, which plays a vital rule in the operation of hot carrier solar cells.

2.4.2.3 Selection of functions $N^f(\mu)$ and $N^b(\mu)$

To find the most suitable expressions for functions $N^f(\mu)$ and $N^b(\mu)$, we need to first examine the Taylor series of the Fermi function $n^F(\mu; \epsilon)$ (and

similarly the Bose function $n^B(\mu; \epsilon)$:

$$\begin{aligned} dn^F(\mu; \epsilon)|_{\mu=0} &= \frac{1}{\exp[\beta(\epsilon - d\mu)] + 1} - \frac{1}{\exp[\beta(\epsilon)] + 1} \\ &= \frac{\beta e^{\beta\epsilon}}{(e^{\beta\epsilon} + 1)^2} d\mu + \frac{\beta^2 e^{\beta\epsilon}}{2!} \frac{e^{\beta\epsilon} - 1}{(e^{\beta\epsilon} + 1)^3} d\mu^2 + O(d\mu^3) \end{aligned} \quad (2.57)$$

It is impossible to separate the variables ϵ and $d\mu$ exactly. This is because terms in Eq. 2.57 involve different orders of $\exp(\beta\epsilon)$, while in a rigorous variable separate, i.e. $df(\epsilon; d\mu) = M^f(\epsilon)N^f(d\mu)$, terms of its Taylor expansion over $d\mu$ should involve the same order of $\exp(\beta\epsilon)$. Accounting for the linearization of rates of all processes it is not a fault problem as we could simply assign $N^f(d\mu) = N^b(d\mu) = d\mu$, accompanied by $M^f(\epsilon) = \beta e^{\beta\epsilon}/(e^{\beta\epsilon} + 1)^2$ and $M^b(\epsilon) = \beta e^{\beta\epsilon}/(e^{\beta\epsilon} - 1)^2$. This leads to an error on $df(\epsilon; d\mu)$ of the order of $d\mu^2$. Error of such order has already been introduced when linearizing the microscopic processes by $F = \sum_i \beta_{ki} dn_i + \sum_{ij} O(dn_i dn_j)$.

Just for the mathematical completeness, we could separate the variables accurately when treating non-degenerate occupations, i.e. $n^F(\epsilon - d\mu) \approx \beta e^{\beta\epsilon}/(e^{\beta\epsilon} + 1)^2 [\beta d\mu + (\beta d\mu)^2/2! + \dots] = \beta e^{\beta\epsilon}/(e^{\beta\epsilon} + 1)^2 \cdot [\exp(d\mu) - 1]$. In this case we can assign $N^{f,b}(d\mu) = \exp(d\mu) - 1$. However if we need to deal with pair generation/annihilation of boson modes we need to have $N^b(-d\mu) = -N^b(d\mu)$ for that particular mode. The optimal expression in this case is a hyperbolic function $N^{f,b}(d\mu) = \sinh(d\mu)$. However this introduces non-consistency on the definition of $N^f(d\mu)$ and $N^b(d\mu)$ and this additional accuracy is unnecessary for a 1st-order problem. We will still use $N^f(d\mu) = N^b(d\mu) = d\mu$ in the following content.

2.4.2.4 Transpose properties between **B** and **D**

For evaluating blocks of **B** and **D** we need to consider the behavior of each fermion-boson pair if they are involved in a certain process. Their occupation

numbers have interaction only if the quanta flux of such process involves products of their occupation functions. For the interaction between a fermion mode f_i and a boson mode n_j , there are only two types of terms existing, i.e. $A_k(n_j+1)f_i - B_k n_j(1-f_i)$ and $A_k(n_j+1)(1-f_i) - B_k n_j f_i$. The physical picture of the 1st term is an electronic transition from a state with lower energy to f_i , by absorbing a photon n_{kj} , plus its reverse process. The 2nd type illustrates a transition to a state with higher energy. Using the same reasoning technique as above, it is readily proved that in the 1st-type interaction $dF_k = 0$ if $d\mu_j = d\mu_i$, while the 2nd type of the flux term becomes zero when $d\mu_j = -d\mu_i$. As usual we linearize the quanta flux, i.e. $dF_k = \alpha_{ki}df_i + \beta_{kj}dn_j$ (positive dF_k is to emit bosons), and adopt the same equations for variable separation, i.e. $df_i(\mu_i; \epsilon_i) = M^f(\epsilon_i)N^f(d\mu_i)$ and $dn_j(\mu_j; \epsilon_j) = M^b(\epsilon_j)N^b(d\mu_j)$. From the previous section we adopt $N^f(d\mu) = N^b(d\mu) = d\mu$ so $t_k = -s_k$ for the 1st type and $t_k = s_k$ for the 2nd type, where the coefficients t_k and s_k are defined previously as $t_k = \alpha_{ki}M^f(\epsilon_i)$ and $s_k = \beta_{kj}M^b(\epsilon_j)$.

From the definition of Eq. 2.48 one readily finds that the matrix component B_{ij} equals to $\sum_{k_1} s_{k_1} - \sum_{k_2} s_{k_2}$, where k_1 denotes index of 1st-type pair-wise processes and k_2 refers to 2nd-type processes. Correspondingly D_{ji} equals to $-\sum_{k_1} t_{k_1} - \sum_{k_2} t_{k_2}$. This proves that $B_{ij} = D_{ji}$ thus the matrix $\mathbf{B}$ is always the transpose of the matrix $\mathbf{D}$.

2.4.2.5 Generalised reciprocity relation in a matrix form

From all the discussion in previous sections we derive the following form (Eq. 2.58) of the current-induced radiation $\delta\phi|_{\delta\mathbf{h}^s=0}$.

$$\begin{aligned}
\delta\phi|_{\delta\mathbf{h}^s=0} &= -\mathbf{P}^T\mathbf{C}^{-1}\mathbf{D}(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{Q}\delta\mathbf{g}^t \\
&= -[\mathbf{Q}^T(\mathbf{A}^T - \mathbf{D}^T\mathbf{C}^{-1}\mathbf{B}^T)^{-1}\mathbf{D}^T\mathbf{C}^{-1}\mathbf{P}]^T\delta\mathbf{g}^t \\
&= -[\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}]^T\delta\mathbf{g}^t
\end{aligned} \tag{2.58}$$

The reciprocity relation between $\delta\phi|_{\delta\mathbf{h}^s=0}$ and $\delta\mathbf{I}|_{\delta\mathbf{g}^t=0}$ is given in Eq. 2.58 and Eq. 2.59.

$$\delta\mathbf{I}|_{\delta\mathbf{g}^t=0} = -\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}\delta\mathbf{h}^s \quad (2.59)$$

If adopting $\mathbf{T} = -\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}$ as the transfer matrix between the terminal current function $\delta\mathbf{I}|_{\delta\mathbf{g}^t=0}$ and the source photon function $\delta\mathbf{h}^s$, the reciprocity is expressed in a simplified form in Eq. 2.60.

$$\begin{aligned} \delta\phi|_{\delta\mathbf{h}^s=0} &= \mathbf{T}^T \delta\mathbf{g}^t \\ \delta\mathbf{I}|_{\delta\mathbf{g}^t=0} &= \mathbf{T} \delta\mathbf{h}^s \end{aligned} \quad (2.60)$$

Eq. 2.60 quantitatively exhibits the fluxes of emitted photons into the m external photon modes, n_j^s ($j = 1, \dots, m$), as linear responses of deviated occupation numbers of the n terminals, f_i^t ($i = 1, \dots, n$). By expanding Eq. 2.58 into a linear equation for each *source-terminal* pair, we obtain $d\phi_j|_{\delta\mathbf{h}^s=0} = T_{ij} \cdot d\mu_i^t$, while $dI_i|_{\delta\mathbf{g}^t=0} = T_{ij} \cdot d\mu_j^s$ from the matrix equation Eq. 2.59. In the right sides of these equations a summation over all relevant external modes is neglected for simplicity. In the following content this is regarded as a convention without any further notification. It is also noted that the condition $\delta\mathbf{g}^t = 0$ is equivalent to $\delta\mathbf{f}^t = 0$. Similarly $\delta\mathbf{h}^s = 0$ is equivalent to $\delta\mathbf{n}^s = 0$.

2.4.2.6 Differential optoelectronic reciprocity for near-equilibrium system

According to Planck's law the net photon flux of a vacuum mode (source mode) n_j^s , i.e. the blackbody radiation, is $\phi_{bb}^j(\mu_j) = 2(\epsilon_j^s)^2/h^3c^2 \cdot n_j(\mu_j)$. Denoting $p_m(\epsilon) = 2\epsilon^2 M^b(\epsilon)/h^3c^2 = 2\epsilon^2/h^3c^2 \cdot \beta e^{\beta\epsilon}/(e^{\beta\epsilon} - 1)^2$, this flux deviated from the equilibrium is expressed by $d\phi_{bb}^j(\mu_j) = p_m(\epsilon_j^s)d\mu_j$, if only with small

deviation from equilibrium. Thereby a *mode-dependent external quantum efficiency* can be defined as $Q_{ij} = dI_i|_{\delta\mathbf{f}^t=0}/d\phi_{bb}^j(\mu_j^s) = \delta I_i|_{\delta\mathbf{f}^t=0}/[p_m(\epsilon_j^s) \cdot d\mu_j^s] = T_{ij}/p_m(\epsilon_j^s)$. The emission due to current injection is then expressed by $d\phi_j|_{\delta\mathbf{n}^s=0} = T_{ij} \cdot d\mu_i^t = p_m(\epsilon_j^s) \cdot Q_{ij} \cdot d\mu_i^t = Q_{ij} \cdot d\phi_{bb}^j(\mu_i^t)$. The physical meaning of this expression is that the current-induced emission by applying a voltage equals to the blackbody radiation induced by this voltage, multiplied by the corresponding external quantum efficiency.

In general this differential reciprocity is strictly valid up to the 1st order of deviation from the equilibrium value. It is valid for any system in equilibrium, i.e. as long as each relevant process has zero net flux. Therefore we may apply this relation to systems of arbitrary temperature T or even with a strong bias V (splitting of chemical potentials). With the bias there are two reservoirs of electrons with separation of their respective electro-chemical potentials; one of them includes all electrons outside the Fermi surface and the other refers to electron energies below the Fermi level. In a semiconductor it refers to the splitting of “quasi-fermi levels” between electrons and holes. The proof on the reciprocity is the same but with a different unperturbed equilibrium condition: all fermions have the occupations described by $f(\epsilon; \pm qV/2, T)$; bosons involved in band-to-band (across the Fermi level) transitions are described by $n(\epsilon; qV, T)$ while those involved in “free carrier absorption” are described by $n(\epsilon; 0, T)$, assuming they are two separate reservoirs with merely limited coupling. The sign in the Fermi function depends on the sign of energy ϵ . Note the energy reference is chosen to be the same as before, i.e. the Fermi energy of electrons at the condition of zero bias.

Similar to $d\phi_{bb}^j(\mu)$ defined in the previous paragraphs, we define the incremental blackbody radiation if increasing the boson chemical potential from qV to $qV + d\mu$ as $d\phi_{bb}^j(\mu; T, V) = 2\epsilon^2/h^3c^2 \cdot dn^B(\mu; \epsilon_j^s)|_{\mu=qV} =$

$p_m(\epsilon_j^s; V, T)d\mu$, where $p_m(\epsilon_j^s; V, T)$ is defined as $2\epsilon^2/h^3c^2 \cdot M(\epsilon_j^s - qV, T) = 2\epsilon^2/h^3c^2 \cdot \beta e^{\beta(\epsilon_j^s - qV)} / [e^{\beta(\epsilon_j^s - qV)} - 1]^2$. There is a relation between $d\phi_{bb}^j(\mu; T, V)$ and $d\phi_{bb}^j(\mu; T, 0)$ shown in Eq. 2.61.

$$d\phi_{bb}^j(\mu; T, V) = d\phi_{bb}^j(\mu; T, 0) \cdot e^{q\beta V} \left[\frac{e^{\beta(\epsilon_j^s - qV)} - e^{\beta(-qV)}}{e^{\beta(\epsilon_j^s - qV)} - 1} \right]^2 \quad (2.61)$$

In the non-degenerate regime (photon energy $\epsilon_j^s \gg qV + 1/\beta$) the term in the square brackets is close to unity. With the bias V the *mode-dependent external quantum efficiency* is defined as $Q_{ij}^V = dI_i|_{\delta\mathbf{f}t=0}^V / d\phi_{bb}^j(\mu_j^s; T, V) = T_{ij}^V / p_m(\epsilon_j^s; T, V)$. Correspondingly the current-induced radiation is expressed by $d\phi_j|_{\delta\mathbf{n}^s=0}^V = T_{ij}^V d\mu_i^t = Q_{ij}^V \cdot d\phi_{bb}^j(\mu_i^t; T, V)$. In the non-degenerate regime it is approximated by $Q_{ij}^V \cdot e^{q\beta V} \cdot d\phi_{bb}^j(\mu_i^t; T, 0)$. With the accuracy up to the 1st-order of $d(\beta\mu_i^t)$, $d\phi_{bb}^j(\mu_i^t; T, 0) = \phi_{eq}(\epsilon_j^s) d(\beta\mu_i^t) \cdot \exp(\beta\epsilon_j^s) / [\exp(\beta\epsilon_j^s) - 1] \approx \phi_{eq}(\epsilon_j^s) d(\beta\mu_i^t)$, where $\phi_{eq}(\epsilon_j^s)$ denotes the equilibrium emission of the source photon mode with energy ϵ_j^s . It is noted that the approximation is only valid for photon energy $\epsilon_j^s \gg 1/\beta$. In the case that the *mode-dependent external quantum efficiency* does not vary with the bias, i.e. $Q_{ij}^V = Q_{ij}^0$, $d\phi_j|_{\delta\mathbf{n}^s=0}^V \approx Q_{ij}^0 \phi_{eq}(\epsilon_j^s) e^{q\beta V} d(\beta\mu_i^t)$. This is the near-equilibrium form of the junction-terminal reciprocity relation derived in literature[69]. It is rigorous only if $\epsilon_j^s \gg qV + 1/\beta$. In fact if accounting for quantum statistics the exact expression of current-induced emission is

$$d\phi_j|_{\delta\mathbf{n}^s=0}^V = Q_{ij}^V \phi_{eq}(\epsilon_j^s) e^{q\beta V} d(\beta\mu_i^t) \cdot \frac{e^{\beta\epsilon_j^s}}{e^{\beta\epsilon_j^s} - 1} \left[\frac{e^{\beta(\epsilon_j^s - qV)} - e^{\beta(-qV)}}{e^{\beta(\epsilon_j^s - qV)} - 1} \right]^2 \quad (2.62)$$

2.4.2.7 Summary on the reciprocity for near-equilibrium system

In conclusion, if the chemical potential of the unperturbed condition is 0 then $d\phi_j|_{\delta\mathbf{n}^s=0} = Q_{ij} d\phi_{bb}^j(\mu_i^t; T, 0)$, where the *mode-dependent external quantum efficiency* is defined as $Q_{ij} = dI_i|_{\delta\mathbf{f}t=0} / d\phi_{bb}^j(\mu_j^s; T, 0)$. If the chemical potential

of the unperturbed condition is V then $d\phi_j|_{\delta\mathbf{n}^s=0}^V = Q_{ij}^V d\phi_{bb}^j(\mu_i^t; T, V)$. The latter relation is only rigorous if there is no free carrier absorption (strictly speaking bosons involved in band-to-band absorption cannot be involved in free carrier absorption and vice versa, and the specified mode n_j is for band-to-band absorption only). This is because in cases of boson-assisted electronic transition which do not cross the Fermi surface, the equilibrium chemical potential of the boson should be 0 rather than qV . Thus if a type of bosons can have both band-to-band interactions and interactions without electronic transition across the Fermi surface, its equilibrium occupation function cannot be defined, making the relation less rigorous.

In the non-degenerate regime, i.e. $\epsilon_j^s \gg qV + 1/\beta$, the Bose-Einstein quantum statistics converges to the classical Boltzmann statistics. This enables the approximate reciprocity relation $d\phi_j|_{\delta\mathbf{n}^s=0}^V = Q_{ij}^V \phi_{eq}(\epsilon_j^s) e^{q\beta V} d(\beta\mu_i^t)$. A brief table is provided in Tab. 2.3 describing the incremental reciprocity relations for systems in equilibrium, including their respective system conditions and approximations. Note in Tab. 2.3 the summation over modes is expressed explicitly to conclude appropriately.

2.4.2.8 Analysis of systems far away from the equilibrium for an approximate reciprocal relation

Strictly speaking the reciprocity derived in the previous sections is not valid for a system significantly deviated from its equilibrium condition. However with some assumptions an approximate relation can be derived in this case. This is important in actual applications of this principle, as solar cells and light emitting devices generally operate away from the equilibrium. Assuming the system operates in an initial steady state (away from equilibrium), i.e. $\partial f_i / \partial t = \partial n_j / \partial t = 0$ for any internal modes. With incremental change of the external condition (bias or illumination), a new steady state is reached with

Table 2.3: Reciprocal relations for systems in equilibrium (i and j denote indices of external fermion/boson modes that couple to the system)

condition	system in equilibrium (zero chemical potential)
solar cell	$dI_i _{\delta \mathbf{f}^t=0} = \sum_j Q_{ij} d\phi_{bb}^j(\mu_j^s; T, 0)$
LED	$d\phi_j _{\delta \mathbf{n}^s=0} = \sum_i Q_{ij} d\phi_{bb}^j(\mu_i^t; T, 0)$
condition	system in equilibrium (nonzero chemical potential V)
assumption	relevant photons involved purely in band-to-band transition
solar cell	$dI_i _{\delta \mathbf{f}^t=0}^V = \sum_j Q_{ij}^V d\phi_{bb}^j(\mu_j^s; T, V)$
LED	$d\phi_j _{\delta \mathbf{n}^s=0}^V = \sum_i Q_{ij}^V d\phi_{bb}^j(\mu_i^t; T, V)$
assumption	non-degenerate occupations ($\epsilon_j^s \gg qV + 1/\beta$)
solar cell	$dI_i _{\delta \mathbf{f}^t=0}^V = \sum_j Q_{ij}^V d\phi_{bb}^j(\mu_j^s; T, V)$
LED	$d\phi_j _{\delta \mathbf{n}^s=0}^V = \phi_{eq}(\epsilon_j^s) e^{q\beta V} \sum_i Q_{ij}^V d(\beta \mu_i^t)$

$f_i \rightarrow f_i + df_i$ and $n_j \rightarrow n_j + dn_j$; steady-state condition gives $\partial(df_i)/\partial t = \partial(dn_j)/\partial t = 0$. Eq. 2.48 is still applicable to this non-equilibrium situation.

The first assumption that needs to be incorporated is that the system operates in a non-degenerate regime; this indicates that the occupations of both boson and fermion modes are described by Maxwell-Boltzmann statistics with sufficient accuracy. It requires that the modes of primary effects should have small occupation, i.e. $e^{-\beta(\epsilon-\mu)} \ll 1$ or equivalently $\epsilon \gg \mu + 1/\beta$.

The second assumption is that primary fermion-boson interactions between modes of significant non-equilibrium are band-to-band absorption and emission. With this assumption the fermion-fermion flux $F_k = A_k f_i (1 - f_j) - B_k f_j (1 - f_i)$ does not change in the non-degenerate regime, if f_i and f_j vary according to $\Delta \mu_i = \Delta \mu_j$. This is because $f_i \approx e^{-\beta(\epsilon_i - \mu_i)} \cdot e^{\beta \Delta \mu_i}$ and $1 - f_j \approx e^{\beta(\epsilon_j - \mu_j)} \cdot e^{-\beta \Delta \mu_j}$, where i and j refer to fermion modes above and below the Fermi energy respectively. In $f_i(1 - f_j)$ the two terms $e^{\beta \Delta \mu_i}$ and $e^{-\beta \Delta \mu_j}$ cancel with each other. In the term of its reverse process, $f_i \approx 1$ and

$1 - f_j \approx 1$ give no dependence on $\Delta\mu_i$ up to the 1st order. If linearizing the fermion-fermion flux in terms of $dN^f(\mu) = d\mu$, the symmetric property of matrix $\mathbf{A}$ still exists. Other recombination processes can also be included in this way.

To accommodate the symmetric property of $\mathbf{C}$, the boson occupation vector $\delta\mathbf{n}$ uses dn instead of $d\mu$, i.e. $dN^b(\mu) = dn$. This is because the photon mode has little interaction and hence it is possible to have largely contrasted occupation numbers. The photon transport process $F_k = \alpha_k(n_i - n_j)$ cannot be linearized to an opposite pair of coefficients if $d\mu$ is adopted. On the contrary the electrons transport to their neighbouring ones without significant differences from equilibrium. One reason for this is that electrons suffer ultrafast momentum relaxation, hence a right-moving electron may quickly turns into a left-moving one, being scattered back. Therefore we could still use $dN^f(\mu) = d\mu$ without much bias. In fact if adopting other parameters the band-to-band absorption would yield unbalanced coefficients. To keep $\mathbf{A}$ symmetric $d\mu$ should be chosen to represent the occupations of fermion modes. The drawback of this approximation is that a device operating in the ballistic transport regime may not be modeled appropriately.

It is noted that processes that involve modes with statically near-equilibrium occupations can be included. In a conventional bulk semiconductor device such processes involve carrier-phonon interactions, phonon-phonon interaction, carrier-carrier scattering due to their thermalized occupation statistics on steady-state operation. In this case carriers and phonons are at least locally in thermal equilibrium; their net flux can be linearized in the neighbourhood of the equilibrium point. According to the analysis in the previous sections this always leads to a symmetric kinetic matrix.

However in general Auger recombination and impact ionization cannot

be explicitly included as the reservoirs of electrons and holes are not in a chemical equilibrium, demonstrated by the splitting of their electrochemical potentials. In fact Auger recombination can be regarded as sequential processes of a radiative recombination followed by a free carrier absorption. There is no reciprocity for free carrier excitations; however in the case of ultra-fast thermalization its effect may be neglected. This is because the static carrier statistics are fixed by frequently interacting with the lattice; free carrier absorption does not impact on their occupation numbers and hence has no effect on emission/current. In Auger recombination only the recombination part is to be considered while the excitation part is neglected, offering the completely same effect as a defect-induced recombination. This is inclusive for the reciprocity to be valid. However, the validity might be violated in a hot carrier solar cell as here carriers and phonons might not have a sufficient number of interactions to maintain a thermalized distribution.

In the fermion-boson pair-wise processes $F_k = A_k(n_j + 1)f_i - B_k n_j(1 - f_i)$ if f_i has energy above the Fermi level, or $F_k = A_k(n_j + 1)(1 - f_i) - B_k n_j f_i$ if the energy of f_i is below the Fermi level, there must be another fermion state f_w involved for the transition of f_i . From the previous discussion we know that after linearizing the flux expression the coefficients before $d\mu_i$ and $d\mu_w$ are always differ by sign. We then assume each electronic transition is associated with a unique boson mode n_k . If a boson mode n_j is involved in a series of transitions then n_k all refer to the same value by adopting large transport coefficients between them (in matrix **C**).

After this treatment there are merely two elements in each column of **B** and in each row of **D**. The two elements only differ in sign. Therefore **B** and **D** may be represented:

$$\mathbf{B} = \begin{bmatrix} s_1 & 0 & s_3 & \cdots & 0 \\ -s_1 & s_2 & 0 & \cdots & 0 \\ 0 & -s_2 & -s_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & s_m \\ 0 & 0 & 0 & \cdots & -s_m \end{bmatrix} \quad (2.63)$$

$$\mathbf{D} = \begin{bmatrix} t_1 & -t_1 & 0 & \cdots & 0 & 0 \\ 0 & t_2 & -t_2 & \cdots & 0 & 0 \\ t_3 & 0 & -t_3 & \cdots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & s_m & -s_m \end{bmatrix} \quad (2.64)$$

A linear transformation from $\mathbf{B}$ to $\mathbf{D}$ is derived:

$$\mathbf{B} = \mathbf{D}^T \mathbf{J} \quad (2.65)$$

$$\mathbf{J} = \begin{pmatrix} s_1/t_1 & 0 & 0 & \cdots & 0 \\ 0 & s_2/t_2 & 0 & \cdots & 0 \\ 0 & 0 & s_3/t_3 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & \cdots & s_m/t_m \end{pmatrix} \quad (2.66)$$

In addition each internal mode can only interact with one external reservoir at maximum. This assumption enables re-constructing $\mathbf{Q}$ and $\mathbf{P}$ to diagonal square matrices. The proof of reciprocity in a matrix form is demonstrated in Eq. 2.67 and Eq. 2.68.

$$\begin{aligned} \delta\phi|_{\delta\mathbf{n}_i^s=0} &= -\mathbf{P}^T \mathbf{C}^{-1} \mathbf{D} (\mathbf{A} - \mathbf{B} \mathbf{C}^{-1} \mathbf{D})^{-1} \mathbf{Q} \delta \mathbf{g}^t \\ &= -[\mathbf{Q}^T (\mathbf{A}^T - \mathbf{D}^T \mathbf{C}^{-1} \mathbf{B}^T)^{-1} \mathbf{D}^T \mathbf{C}^{-1} \mathbf{P}]^T \delta \mathbf{g}^t \\ &= -[\mathbf{Q}^T (\mathbf{A} - \mathbf{B} \mathbf{J}^{-1} \mathbf{C}^{-1} \mathbf{J} \mathbf{D})^{-1} \mathbf{B} \mathbf{J}^{-1} \mathbf{C}^{-1} \mathbf{P}]^T \delta \mathbf{g}^t \end{aligned} \quad (2.67)$$

As $\mathbf{C}$ and $\mathbf{J}$ are both symmetric matrices, they commute: $\mathbf{C}\mathbf{J} = \mathbf{C}^T\mathbf{J}^T = \mathbf{J}\mathbf{C}^T = \mathbf{J}\mathbf{C}$. Same relation holds for $\mathbf{C}^{-1}$, $\mathbf{J}^{-1}$ and $\mathbf{P}$.

$$\begin{aligned}
\delta\phi|_{\delta\mathbf{n}^s=0} &= -[\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{J}^{-1}\mathbf{J}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{J}^{-1}\mathbf{P}]^T\delta\mathbf{g}^t \\
&= -[\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}\mathbf{J}^{-1}]^T\delta\mathbf{g}^t \\
&= \mathbf{J}^{-1}\mathbf{T}^T\delta\mathbf{g}^t \\
\delta\mathbf{I}|_{\delta\mathbf{f}^t=0} &= -\mathbf{Q}^T(\mathbf{A} - \mathbf{B}\mathbf{C}^{-1}\mathbf{D})^{-1}\mathbf{B}\mathbf{C}^{-1}\mathbf{P}\delta\mathbf{h}^s \\
&= \mathbf{T}\delta\mathbf{h}^s
\end{aligned} \tag{2.68}$$

Eq. 2.68 builds a linear relation between the n terminal occupation functions $dN^f(\mu_i^t)$ ($i = 1, \dots, n$) to the net radiation $\delta\phi_j|_{\delta\mathbf{n}^s=0}$ ($j = 1, \dots, m$), emitted to m external photon modes n_j^s : $d\phi_j|_{\delta\mathbf{n}^s=0} = t_j/s_j \cdot T_{ij}dN^f(\mu_i^t)$.

2.4.2.9 The non-equilibrium version of reciprocity and its relation to literature work

If we further examine the physical meaning of the term $t_j/s_j \cdot dN^f(\mu_i^t)$ we will find its relation to the blackbody radiation. The electronic transition associated with n_j has a net quantum flux $dF_j = t_{j1}dN^f(\mu_p) - t_{j2}dN^f(\mu_q) - s_jdN^b(\mu_j)$, where the positive sign before $dN^f(\mu_p)$ indicates the electron at f_p has a higher energy. This net flux is a linearized version of the expression $F_j = \alpha_j f_p(1 - f_q)(n_j + 1) - \alpha_j f_q(1 - f_p)n_j$. Then $t_{j1} = \alpha_j(n_j + 1 - f_q) \cdot df_p/dN^f(\mu_p)$, $t_{j2} = \alpha_j(n_j + f_p) \cdot df_q/dN^f(\mu_q)$ and $s_j = \alpha_j(f_q - f_p)dn_j/dN^b(\mu_j)$. For a system operated as a light-emitting device, $\mu_j \leq \mu_p - \mu_q$; hence $n_j = e^{-\beta(\epsilon_j - \mu_j)} \leq e^{-\beta(\epsilon_j - \mu_p + \mu_q)} = f_p(1 - f_q)$ in the non-degenerate regime. As both f_p and $1 - f_q$ are much smaller than unity, n_j may be neglected in the expressions of t_{j1} and t_{j2} . If adopting $dN^f(\mu_p) = d\mu_p$ then $df_p/dN^f(\mu_p) = \beta f_p$ and $df_q/dN^f(\mu_q) = \beta(1 - f_q)$; therefore $t_j \equiv t_{j1} = t_{j2}$.

The ratio $t_j/s_j = \beta f_p(1-f_q) \cdot [dn_j/dN^b(\mu_j)]^{-1}$. If adopting $dN^b(\mu_j) = dn_j$ we have $t_j/s_j = \beta f_p(1-f_q) = \beta e^{-\beta\epsilon_j} e^{\beta(\mu_p-\mu_q)}$. The reciprocity relation derived above gives a corresponding illumination-induced current $dI_i|_{\delta\mathbf{f}^t=0} = T_{ij} \cdot dn_j = T_{ij}/p_m(\epsilon_j) d\phi_{bb}^j$, where $p_m(\epsilon_j) = \epsilon^2/h^3c^2$. The EQE is defined as $Q_{ij} = dI_i|_{\delta\mathbf{f}^t=0}/d\phi = T_{ij}/p_m(\epsilon_j)$. Hence it is possible to express the current-induced emission in terms of equilibrium radiation (Eq. 2.69). It is noted that the equilibrium emission $\phi_{eq} = p_m(\epsilon_j)e^{-\beta\mu_j}$ if Bose-Einstein statistics degrades to Maxwell-Boltzmann statistics, i.e. in the non-degenerate regime.

$$\begin{aligned}
d\phi_j|_{\delta\mathbf{n}^s=0} &= d\phi_j|_{\delta\mathbf{n}^s=0} = t_j/s_j \cdot T_{ij} d\mu_i^t \\
&= \beta e^{-\beta\epsilon_j} e^{\beta(\mu_p-\mu_q)} \cdot T_{ij} d\mu_i^t \\
&= Q_{ij} \cdot p_m(\epsilon_j) e^{-\beta\epsilon_j} \cdot e^{\beta(\mu_p-\mu_q)} d(\beta\mu_i^t) \\
&= Q_{ij} \phi_{eq}(\epsilon_j) e^{\beta(\mu_p-\mu_q)} d(\beta\mu_i^t)
\end{aligned} \tag{2.69}$$

In this treatment a photon mode interacting with several fermion pairs is calculated separately, say $n_{j_1}, \dots, n_{j_p}$ involved in fermion pair-wise transition $f_{j_{11}} \rightarrow f_{j_{12}}, \dots, f_{j_{l1}} \rightarrow f_{j_{l2}}$. If combining the fluxes due to all those processes together, the illumination-induced current is expressed by $dI_i|_{\delta\mathbf{f}^t=0} = \sum_q Q_{ij_q} \cdot d\phi_{bb}^j$. Correspondingly the current-induced radiation is $d\phi_j|_{\delta\mathbf{n}^s=0} = \sum_q Q_{ij_q} e^{\beta(\mu_{j_{q1}}-\mu_{j_{q2}})} \cdot \phi_{eq}(\epsilon_j^s) d(\beta\mu_i^t)$. More accurately speaking, this is the radiation from the internal photon mode n_j , which is assumed to couple to a certain external reservoir but might not only coupled with one external mode.

Therefore it is most appropriate to describe the non-equilibrium reciprocity in terms of external reservoirs. Supposing there are n external fermion reservoirs and m external photon reservoirs, then $dI_i(\epsilon_i)|_{\delta\mathbf{f}^t=0} = \sum_{p,q} Q_{i_p j_q} \cdot d\phi_{bb}^j(\epsilon_j)$, where i_p denotes index of all internal fermion modes with energy ϵ_i that couple to the external reservoir i , and j_q refers to all

internal photon modes, with energy ϵ_j , coupling to the photon reservoir j . Correspondingly $d\phi_j(\epsilon_j)|_{\delta\mathbf{n}^s=0} = \sum_{p,q} Q_{i_p j_q} e^{\beta(\mu_{j_{q1}} - \mu_{j_{q2}})} \cdot \phi_{eq}(\epsilon_j) d(\beta\mu_i^t)$, where μ_i^t is the semi-chemical potential of this external electron reservoir, at a mode energy of ϵ_i . The indices j_{q1} and j_{q2} refer to the internal electronic states, which recombined, emitting to j_q with energy ϵ_j , which then couples to the photon source reservoir j .

In a semiconductor diode $\mu_{j_{q1}} - \mu_{j_{q2}}$ describes the local junction voltage $qV_J(\mathbf{r})$, which contributes to a local photon emission $d\phi_j(\mathbf{r}, \epsilon_j)$. This equation turns into its special form: $\phi_j(\mathbf{r}, \epsilon_j) = EQE_{ij}(\epsilon_i, \epsilon_j) \phi_{eq}(\epsilon_j) e^{q\beta V_J(\mathbf{r})} d(\beta\mu_i^t)$, where the “partial external quantum efficiency” between electron reservoir i and photon reservoir j [located at (x,y)] is defined by $EQE_{ij}(\epsilon_i, \epsilon_j) = \sum_{p,q} Q_{i_p j_q} = dI_i(\epsilon_i)|_{\delta\mu^t=0}/d\phi_{bb}^j(\epsilon_j)$. A ϵ_i -independent relation is readily derived by summing equations of all possible ϵ_i together. Its two-terminal special case has been derived in literature[69], however here the relation is generalized to any source-terminal pairs.

A further assumption may be adopted for a two-terminal (or two types of terminal) system. The chemical potentials at the two terminals are denoted by $\frac{V}{2}$ and $-\frac{V}{2}$. If neglecting the resistive loss, in a diode with forward bias the chemical potentials of internal electron and hole excitations (the “junction voltage”) may be assumed as being in respective equilibrium with their external modes. Thus the splitting between them is V , i.e. $\mu_{j_{q1}} - \mu_{j_{q2}} \equiv V$. The differential current-induced emission is then expressed as $d\phi_j(\epsilon_j)|_{\delta\mathbf{n}^s=0} = \sum_{p,q} Q_{1_p j_q} e^{q\beta V} \cdot \phi_{eq}(\epsilon_j) d(q\beta V/2) + \sum_{2_p, q} Q_{1_p j_q} e^{q\beta V} \cdot \phi_{eq}(\epsilon_j) d(-q\beta V/2)$, where 1_p and 2_p denote indices of respective electronic modes with energies larger than the Fermi energy (injected from reservoir 1) and those smaller than the Fermi energy (extracted to reservoir 2). j_q refers to all internal photon modes, with energy ϵ_j , which couple to the photon reservoir j . It leads

to the absolute value of the radiation with only background incident light, demonstrated in Eq. 2.70.

$$\begin{aligned}\phi_j(\epsilon_j) &= \frac{1}{2} \sum_{p,q} \int_0^V \beta Q_{1pj_q} \phi_{eq}(\epsilon_j) e^{q\beta v} dv - \frac{1}{2} \sum_{2p,q} \int_0^V \beta Q_{2pj_q} \phi_{eq}(\epsilon_j) e^{q\beta v} dv \\ &= \frac{1}{2} \left(\sum_{p,q} Q_{1pj_q} - \sum_{2p,q} Q_{2pj_q} \right) \phi_{eq}(\epsilon_j) (e^{q\beta V} - 1)\end{aligned}\quad (2.70)$$

At steady state the summation of electron fluxes over all terminals is zero, i.e. $0 = \sum_i dI_i|_{\delta \mathbf{f}^t=0} = (\sum_{p,q} Q_{1pj_q} + \sum_{2p,q} Q_{2pj_q}) d\phi_{bb}^j(\epsilon_j)$. This leads to $\sum_{p,q} Q_{1pj_q} = -\sum_{2p,q} Q_{2pj_q}$, which then yield expression of the current-induced radiation: $\phi_j(\epsilon_j) = \sum_{p,q} Q_{1pj_q} \phi_{eq}(\epsilon_j) (e^{q\beta V} - 1)$. It is noted that the term $\sum_{p,q} Q_{1pj_q}$ is the “partial external quantum efficiency” $EQE_j^*(\epsilon_j)$ defined in literature[67]. It is noted that $EQE_j^*(\epsilon_j) = \sum_{\epsilon_1} EQE_{1j}(\epsilon_1, \epsilon_j) = -\sum_{\epsilon_2} EQE_{2j}(\epsilon_2, \epsilon_j)$, which links this EQE to the one defined in the last paragraph, by summing over all electron energy levels. As the relation is valid for any photon reservoir j , macroscopically it is suitable for describing emission flux with specified location, orientation, polarization, etc. In this case EQE^* may be defined with fine resolution, e.g. $EQE^*(\mathbf{r}, \theta, \phi, \epsilon)$.

2.4.2.10 Summary on the reciprocity derived in this work

Unlike the reciprocal principle for a system in equilibrium, there is no reciprocity in general for non-equilibrium systems. However for non-degenerate statistics of excitations, the differential reciprocity may still be valid, if only certain interactions are included between modes, although interactions between modes in near-equilibrium are all inclusive. Tab. 2.4 describes the evolution of the form of this relation, if further assumptions are adopted.

This principle has a wide range of applications as its equilibrium version is presented at a microscopic level (quantum modes), i.e. for any pair of external photon source mode and terminal electronic mode. Its non-equilibrium

Table 2.4: Reciprocal relations for systems away from equilibrium. A_i refers to indexed assumptions; all these assumptions refer to excitations of significant non-equilibrium; excitations with close thermodynamic parameters, e.g. thermalized electrons and phonons, does not impair the reciprocity.

A_1	excitations have non-degenerate occupations ($\epsilon_{i,j} \gg \mu_{i,j} + 1/\beta$)
A_2	primary fermion-boson interactions are band-to-band transitions
A_3	gradual variation on electron spatial occupation (ballistic excluded)
cell	$dI_i(\epsilon_i) _{\delta \mathbf{f}^t=0} = \sum_j \sum_{p,q} Q_{ipjq} \cdot d\phi_{bb}^j(\epsilon_j)$
LED	$d\phi_j(\epsilon_j) _{\delta \mathbf{n}^s=0} = \sum_i \sum_{p,q} Q_{ipjq} e^{\beta(\mu_{jq1} - \mu_{jq2})} \cdot \phi_{eq}(\epsilon_j) d(\beta \mu_i^t)$
A_4	$\mu_{jq1} - \mu_{jq2}$ only relies on position (local “junction voltage” $V_J(\mathbf{r})$)
define	partial external quantum efficiency $EQE_{ij}(\epsilon_i, \epsilon_j) = \sum_{p,q} Q_{ip,jq}$
cell	$dI_i(\epsilon_i) _{\delta \mu^t=0} = \sum_j EQE_{ij}(\epsilon_i, \epsilon_j) d\phi_{bb}^j(\mathbf{r}, \epsilon_j)$
LED	$d\phi_j(\mathbf{r}, \epsilon_j) = \sum_i EQE_{ij}(\epsilon_i, \epsilon_j) \phi_{eq}(\epsilon_j) e^{q\beta V_J(\mathbf{r})} d(\beta \mu_i^t)$
A_5	all μ_{jq1} equal to the potential of their coupled terminals ($qV/2$)
A_6	all μ_{jq2} equal to the potential of their coupled terminals ($-qV/2$)
define	$EQE_j^*(\epsilon_j) = \sum_{\epsilon_1} EQE_{1j}(\epsilon_1, \epsilon_j) = -\sum_{\epsilon_2} EQE_{2j}(\epsilon_2, \epsilon_j)$
cell	$I_1 = -I_2 = \sum_j EQE_j^*(\epsilon_j) \phi_{bb}^j(\epsilon_j)$
LED	$\phi_j(\epsilon_j) = EQE_j^*(\epsilon_j) \phi_{eq}(\epsilon_j) (e^{q\beta V} - 1)$
i, j	indices of external fermion reservoir and boson reservoir respectively
i_p	index of all internal fermion modes with energy ϵ_i that couple to i
j_q	index of all internal photon modes with energy ϵ_j that couple to j
ϕ_{bb}^j	radiation to the system from photon sources with energy ϵ_j in j
μ_i^t	semi-chemical potential of the terminal electron reservoir i , at energy ϵ_i
j_{q1}	internal fermion states above Fermi level, transition with j_{q2} emit to j_q
j_{q2}	internal fermion states below Fermi level, transition with j_{q1} emit to j_q

version requires some assumptions and is expressed in terms of external reservoirs. This is still much more general than relations discussed in literature work, as it applies to systems with arbitrary numbers of terminals. More important, unlike the literature works based on properties of the p-n junction, this model does not rely on any requirement of the structure or material,

generalizing the relation to a fundamental principle.

By classifying all the solid-state elementary excitations into fermions and bosons while treating their interactions in the framework of quantum statistics, it includes all the possible processes including particle diffusions, photon recycling, phonon emission/decay, exciton generation/dissociation, plasmon generation/relaxation, etc. The equilibrium version of this principle is a completely rigorous and general one. As long as microscopic processes (with T-symmetry) are within the framework of Fermi's golden rule, the relation is rigorous up to the 1st order of the deviated occupation number from the equilibrium condition.

2.4.2.11 Applications of the differential reciprocity principle

This work proves that electroluminescence (EL) technique can be adopted to measure the quantum efficiency of any proposed solar cell device (amorphous, organic, nano-structured, tandem, hot carrier, solar-thermoelectric, etc.) if the device operates close to its equilibrium state.

The characterization may be conducted on an energy-resolved level. We could obtain the wavelength-dependent response of illumination from measuring the energy spectrum of EL radiation. In addition, the spatial response and angular response of solar cells with arbitrary geometry can be mapped from an EL image.

It is also possible to obtain the energy spectrum of the extracted current from a solar cell by injecting carriers at different energy level (e.g. through a barrier) and measuring the emitted spectrum. Though this characterization is trivial for conventional cell, it has vital applications in characterizing the hot carrier solar cell (HCSC). Furthermore, the contacts can be placed anywhere without violation of the reciprocity; therefore optimal contact po-

sitions may be found by injecting carriers from different locations for EL characterization.

On the other hand, we can reverse this relation and obtain properties of a light-emitting device (LED) by characterizing its current generation properties. The angular/wavelength/polarization dependences of a LED can be figured out, if we vary an incident laser beam and measure the induced current.

2.4.2.12 Limitation of the reciprocity and its further development

Although this work provides an incremental reciprocal principle that is much more generalized than those derived in literature[69, 67], it still has several limitations and requires further work.

Only the equilibrium version of this relation is completely generalized, and it is possible to incorporate any processes of T-symmetry. However it has limited applications, as it only applies for a system that operates with an incremental variation from its equilibrium state.

The non-equilibrium version does apply to any operational point of a conventional solar cell or a LED; but it requires assumptions of non-equilibrium statistics and carrier diffusive transport. In addition, electron excitations and hole excitations are assumed to be separate systems in equilibrium, at least locally, with the lattice. This is problematic when applying it to the HCSC. In the normal operation of a HCSC the carriers shall have much lifted thermal temperatures compared to that of the lattice. If there is still much interactions between them then the reciprocity is not valid; further variations are introduced by the fast Auger recombination and impact ionization rates as well as the free carrier absorption. These processes now alter the static occupations of internal states, yielding deviation from reciprocity.

In particular situations the reciprocity may still apply to the HCSC. One of these is that the deviation from a universal equilibrium state is not large. Otherwise there should be complete decoupling between any two systems in the chain of carrier cooling. In principle a complete block of the electron-phonon coupling makes this reciprocity valid; however it seems very unrealistic. Other approaches, including blocking the phonon decay path or localizing/confining phonons, contribute to additional situations in which the reciprocity may work. In general possibly there is no reciprocal relation for the HCSC, or maybe it exists but in a quite different form. This creates a very good position for future theoretical work.

MATERIAL MODELING

3.1 Computation of electronic and phononic structures

The microscopic foundation of the electrical and thermal properties of a specific material involves its electronic structure and phononic structure. They are stationary states of the respective excitations in the crystal field. For periodic structures, the dispersion relations between their frequencies and wave-vectors are of special importance. In this section, these dispersions are demonstrated for wave-vectors along highly symmetric axes, calculated using empirical models, including the tight-binding method for electrons and the bond charge model for phonons. The calculations focus on the multiple-quantum-well superlattices (MQW-SLs) as they have been experimentally demonstrated to show slowed carrier cooling and are potential absorber layers for realizing the HCSC.

3.1.1 Tight-binding methods on electronic structures

In this section electronic band structures are calculated for different periodic structures, using tight-binding (or LCAO, linear combination of atomic

orbitals) methods. The calculated band structures of bulk III-V semiconductors are shown first, followed by those calculated for superlattice structures. The details of the adopted model have been described in Sec. ??.

3.1.1.1 Sources of parameters required in the tight-binding model

The calculation of electronic dispersion relations requires tight-binding potentials (hopping between neighbouring atoms), i.e. the Hamiltonian matrix elements $\langle \phi_i | H_{TB} | \phi_j \rangle$. These elements are evaluated in terms of atomic orbitals $|\phi_i\rangle$. To calculate band structures of different materials, we may adopt different sets of atomic orbitals, e.g. sp^3 , sp^3s^* or sp^3d^5 , and different number of neighbouring atoms with non-zero hopping potentials, e.g. up to the 1st-nearest neighbours or the 2nd-nearest neighbours. For common binary semiconductors the literature sources of tight-binding potentials are listed in Tab. 3.1. These parameters were retrieved from fitting the electronic dispersion relations to those obtained from *ab-initio* calculations.

Table 3.1: Summary on the data sources of tight-binding parameters

Author	Material	Crystal structure	Basis set	Nearest-neighbour
Priester[70]	III-V	Zinc-blende	sp^3s^*	1st
Vogl[71]	Group IV, III-V	Zinc-blende	sp^3s^*	1st
Molina[72]	InN	Wurtzite	sp^3	1st
hernández[73]	AlGaN, InGaN	Zinc-blende	sp^3s^*	1st, 2nd
Yang[74]	InGaN	Wurtzite	sp^3d^5	1st, 2nd
Jancu[75]	AlN, GaN, InN	Wurtzite, cubic	sp^3d^5	1st, 2nd
Kobayashi[76]	III-V	Wurtzite	sp^3	1st
Jancu[77]	Group IV, III-V	Zinc-blende	sp^3d^5	1st
Osbourne[78]	GaAs, AlAs	Zinc-blende	sp^3	1st, 2nd

3.1.1.2 Calculated band structures of bulk semiconductors

The incorporation of d orbitals can predict the dispersion relation with higher accuracy; however with more fitting parameters the physical significance of each potential parameter is reduced. As we are mainly concerned with the dispersion of compound superlattices and scattering/interaction properties, the adoption of five d orbitals per atom is not appropriate. In the following calculations, we adopted Priester's parameters for cubic III-V semiconductors[70], Hernández's data for c-InN and c-GaN[73], and Molina's for w-InN[72]. The calculated electronic band structures are shown in Fig. 3.1, for GaAs and GaP, and in Fig. 3.2, for InAs and AlAs. It is noted that the materials considered here are all of the cubic (zinc blende) phase.

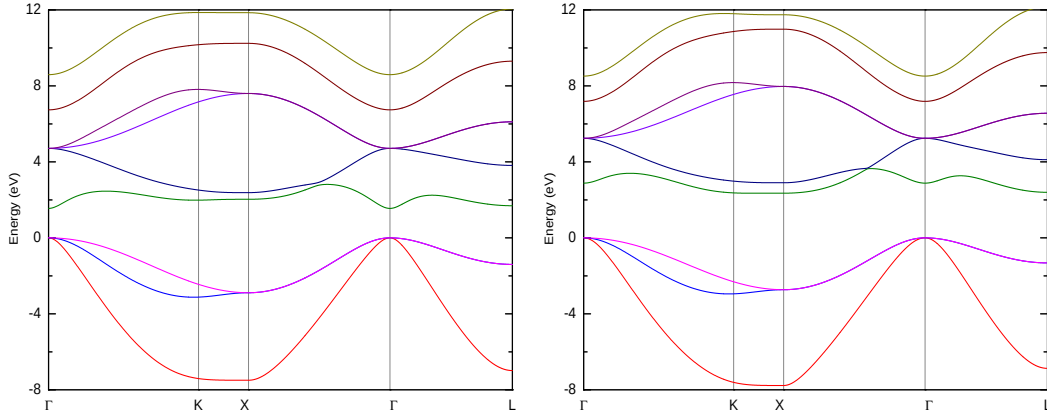


Fig 3.1: Calculated bulk band structures of GaAs (left) and GaP (right). The tight-binding parameters are taken from Priester's paper[70].

The spin-orbit splitting between valence bands has been taken into account with parameters adopted from Priester's work[70]. Here different spin states for $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$ are taken into account. The reason for choosing this basis set is the same as in Sec. ??: non-zero coupling terms only arise

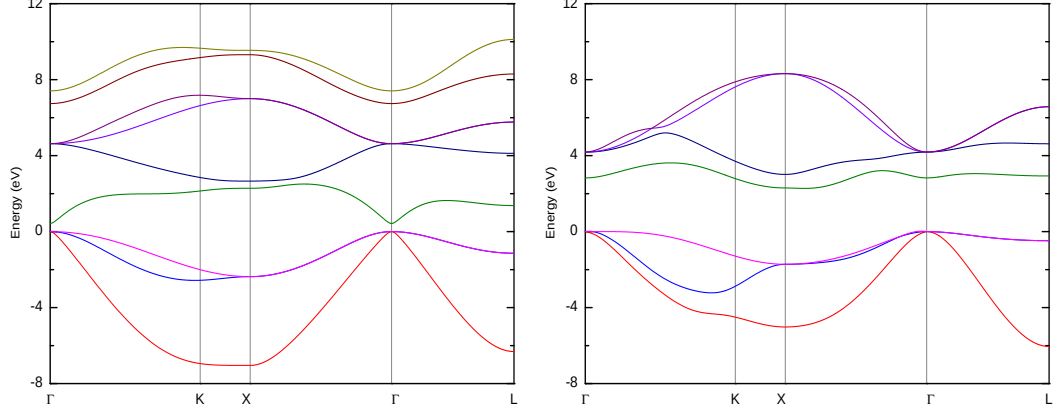


Fig 3.2: Calculated bulk band structures of InAs (left) and AlAs (right). The tight-binding parameters are taken from Priester's paper[70].

between states that involve components of the same total angular momenta. A comprehensive analysis on choosing the spin states for an appropriate basis set has been provided in literature[79].

In Sec. ?? we have expressed the spin-orbit coupling Hamiltonian in the same form as that in the Kane model[80]. To recapitulate this term is presented in Eq. 3.1.

$$H_{so} = \frac{\hbar}{4m^2c^2} \vec{\nabla}V \times \mathbf{p} \cdot \vec{\sigma} \quad (3.1)$$

This term arises by solving the Dirac equation for an electron in external fields[81]. For a centrally symmetric field this term may be simplified, by taking into account $\vec{\nabla}V = \mathbf{r}/r \cdot dV/dr$,

$$H_{so} = \frac{\hbar}{2m^2c^2} \cdot \frac{dV(r)}{dr} \frac{\mathbf{r}}{r} \times \mathbf{p} \cdot \frac{\vec{\sigma}}{2} = \frac{\hbar^2}{2m^2c^2} \frac{dV(r)}{rdr} \hat{\mathbf{l}} \cdot \hat{\mathbf{s}} \quad (3.2)$$

Now the spin-orbit coupling Hamiltonian yields a more usual form in electronic dispersion calculations: $H_{so} = \lambda \hat{\mathbf{l}} \cdot \hat{\mathbf{s}}$. Following Luttinger-Kohn

representations[82] (Sec. ??), $|p_x\rangle$, $|p_y\rangle$, $|p_z\rangle$ can be linearly decomposed into orthogonal states $|jm\rangle$, where j and m are respectively the total angular momentum and its projection along the z -axis. Evaluation of the spin-orbit Hamiltonian elements, i.e. terms like $\langle p_x \uparrow | H_{so} | p_z \downarrow \rangle$ becomes straight forward, with the help of these orthogonal states. The spin-orbit Hamiltonian matrix represented under the basis set of $(p_x \uparrow, p_y \uparrow, p_z \downarrow)$ is provided in Eq. 3.3[79].

$$H_{so} = \begin{pmatrix} 0 & -i\lambda & \lambda \\ i\lambda & 0 & -i\lambda \\ \lambda & i\lambda & 0 \end{pmatrix} \quad (3.3)$$

The constant λ can be obtained by measuring the atomic spin-orbit splitting. The data source[70] followed the same convention of defining λ , and $\lambda_{a/c} = \Delta_{a/c}/3$, with $\Delta_{a/c}$ being the renormalized atomic spin-orbit splitting of the anion and cation p states[83]. Actually the relation between λ and Δ can be readily found by evaluating Eq. ?? for the case of central symmetry, and then comparing it with Eq. 3.2. For cubic InN, the data source provided $\lambda_a = 0.003$ for Nitrogen $\lambda_c = 0.002$ for indium by adjusting the spin-orbital splitting to match *ab-initio* results. The calculated band structure for cubic InN is shown in Fig. 3.3 (a).

To compare with the band structure of cubic InN, electronic dispersion relations for wurtzite InN have also been calculated. A sp^3 tight-binding model that merely incorporates interactions from the 1st-nearest neighbours has been adopted for this calculation, in correspondence to Molina's work[72]. The tight-binding parameters have been adjusted for a more accurate estimation of the band gap. The calculated band structure is provided in Fig. 3.3 (b). The band gaps of the modeled bulk semiconductor materials are listed in Tab. 3.2, in comparison with the widely accepted figures.

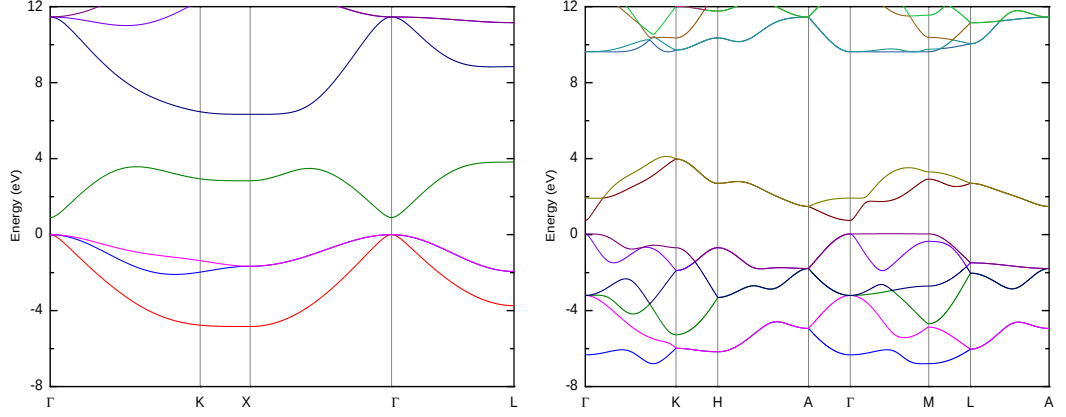


Fig 3.3: Calculated bulk band structures of cubic InN (left), and wurtzite InN (right). The tight-binding parameters are taken from Hernández's paper[73] for the cubic phase, and from Molina's work[72] for the hexagonal phase.

Table 3.2: TB Modeled band gaps of bulk semiconductors compared with widely accepted values

Material	GaAs	GaP	InAs	AlAs	c-InN	w-InN
Modeled bandgap (eV)	1.5	2.3	0.4	2.2	0.8	0.7
Accepted values (eV)	1.42	2.26	0.35	2.17	0.5	0.7

3.1.2 Band structures of InGaAs-GaAsP quantum-well superlattices

In this section the calculated electronic band structures of InGaAs-GaAsP multiple-quantum-well superlattices (MQW-SL) are demonstrated, with various structural parameters (especially layer thicknesses). This calculation was accomplished by an empirical tight-binding model, whose parameters were adopted from Priester's work[70].

3.1.2.1 Reasons for investigating MQW-SL structures

Recently a great deal of work has focused on the many novel properties of nanostructures including MQW-SLs in terms of their electronic and optical properties. One of the major effects, the reduced hot carrier cooling rate, is of particular interest in the field of hot carrier solar cell [17, 6]. This phenomenon was observed in GaAs quantum well superlattices [19] and is possibly due to the phonon bottleneck effect [24]. This effect is expected to be enhanced in materials with large phononic bandgap due to the reduction of Klemens decay [84]. In fact under high injection of charge carriers non-equilibrium dynamics appear between the hot polar phonons emitted by hot carriers and the acoustic phonon reservoir, which maintains an equilibrium with the environment [84]. Not only in bulk compounds do people search for suitable material to block phonon decay, also a great deal of research effort is devoted to superlattices. The GaAs-AlGaAs quantum well has been demonstrated experimentally with a many hundreds of picoseconds hot carrier relaxation rate in the 1990s [19]. In addition to the slow hot carrier cooling rate, MQW-transistor-based nitride compounds are also interesting due to their high electron mobility [85]. There are other applications in optics such as the InN/GaN MQW light emitting diode which has shown promising performance at the ultra-violet end of the spectrum [86]. To investigate the electrical and thermal properties of these structures, the microscopic properties of the system stationary states need to be computed first. This includes properties such as electronic band structures and phononic dispersion relations (treated in the following section).

InGaAs-GaAsP MQW-SL is of particular interest, for its strain-balanced structure is easy to be deposited by MOVPE[87]. In addition, GaAs based MQW-SLs has been demonstrated experimentally with a longer carrier re-

laxation time, although they do not have a large phononic energy gap. This indicates that certain mechanisms exist in MQW-SL structures to prevent energies of hot carriers relaxing. Candidate mechanisms involve the localization of hot carriers or hot phonons, screened electron-phonon coupling, and reduced interaction due to flattening of dispersion relations. To figure out the dominant effects on the carrier cooling mechanism in such structures, the electronic band structures for various structural parameters is the first step in our investigation.

3.1.2.2 Methods and results

This calculation is based on the “virtual crystal approximation” (VCA)[88], which treats the tight-binding potentials of a ternary material as the weighted average of the corresponding potentials of two binary compounds. Though better approximations have been suggested for the electronic structures of ternary materials[89], VCA is adopted here due to its simplicity. For instance, the tight-binding parameters of the ternary compounds $AB_{1-x}C_x$ are obtained by Eq. 3.4.

$$V^{ABC}(x) = (1 - x)V^{AB} + xV^{AC} \quad (3.4)$$

For InGaAs-GaAsP MQW-SL, the component binary compounds include InAs, GaAs and GaP. As we did for calculating the band structures of these bulk materials, we have adopted the same tight-binding parameters for the calculation of MQW-SLs. This model involves sp^3s^* atomic orbitals and only interactions from the 1st-nearest neighbours. The compositions of elements have been selected to match our experimental work. The well layer is made of $In_{0.17}Ga_{0.83}As$, and the barrier layer is $GaAs_{0.8}P_{0.2}$. Thicknesses of both the well layer and the barrier layer were varied for calculation, in order to figure out the variation on the band structures. The calculated band structures are

demonstrated in Fig. 3.4 - Fig. 3.9, for six sets of layer thicknesses (Tab. 3.3). In the future samples of these structures will be fabricated for experimental analysis, with samples B1 and B2 representing the strain balanced condition.

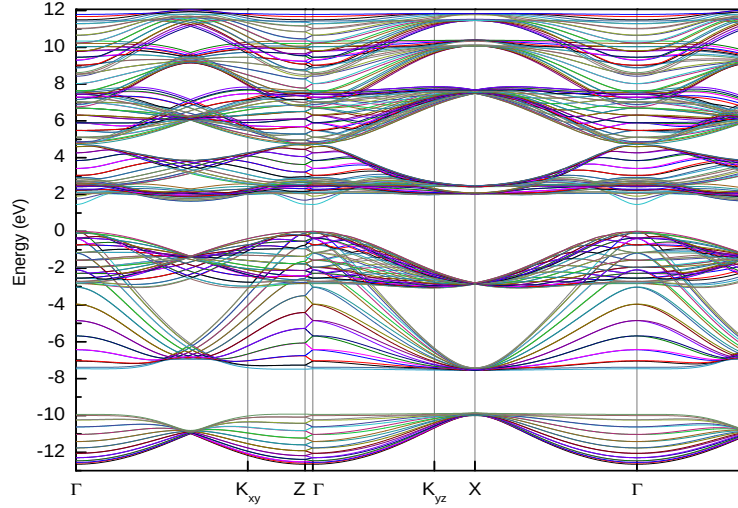


Fig 3.4: Calculated electronic band structures of the MQW-SL structure A1

Table 3.3: Six sets of MQW-SL structures for electronic calculation

Material	Set No.	A1	B1	C1	A2	B2	C2
$\text{In}_{0.17}\text{Ga}_{0.83}\text{As}$	Well (nm)	3.5	3.5	3.5	7	7	7
$\text{GaAs}_{0.8}\text{P}_{0.2}$	Barrier (nm)	2.5	5.5	15	5	11	30

The electronic density of states (DOS) has been calculated for each of the six samples, by accounting for the energies of an evenly-distributed $\mathbf{k}$ -point mesh in the reduced Brillouin zone. A Gaussian smearing with small energy spreading (standard deviation $\sigma=26\text{meV}$) has been adopted to smooth the DOS profiles.

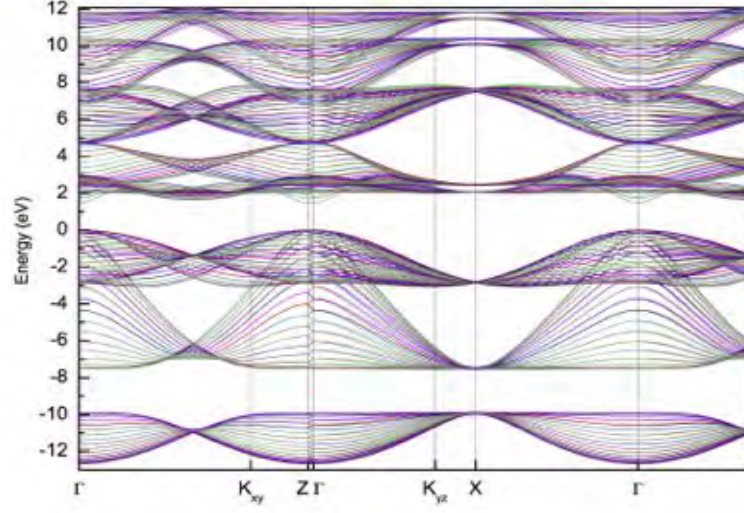


Fig 3.5: Calculated electronic band structures of the MQW-SL structure B1

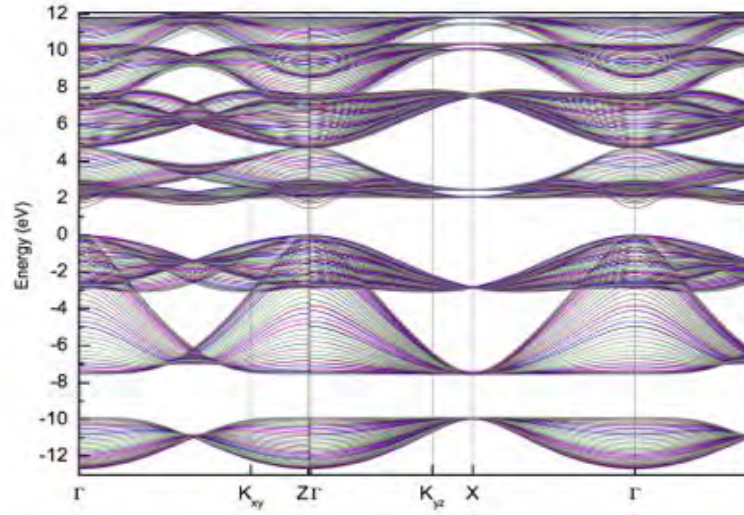


Fig 3.6: Calculated electronic band structures of the MQW-SL structure C1

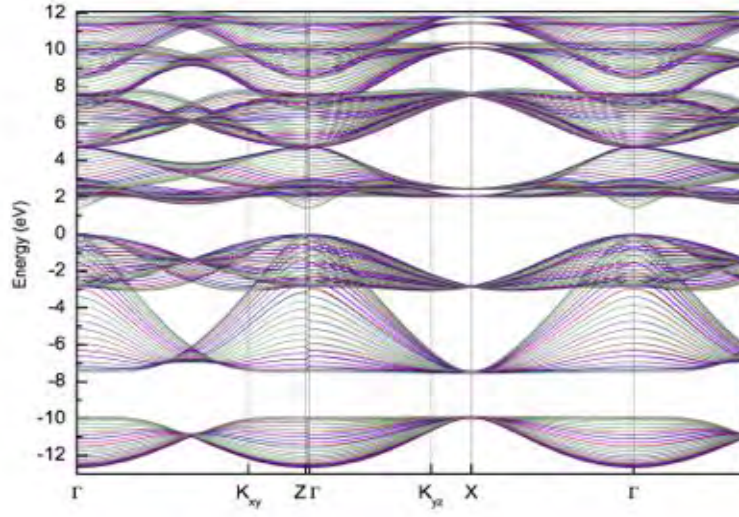


Fig 3.7: Calculated electronic band structures of the MQW-SL structure A2

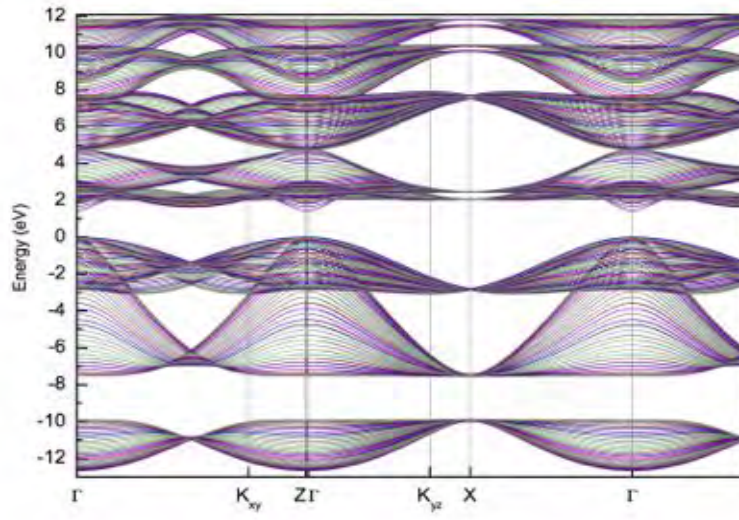


Fig 3.8: Calculated electronic band structures of the MQW-SL structure B2

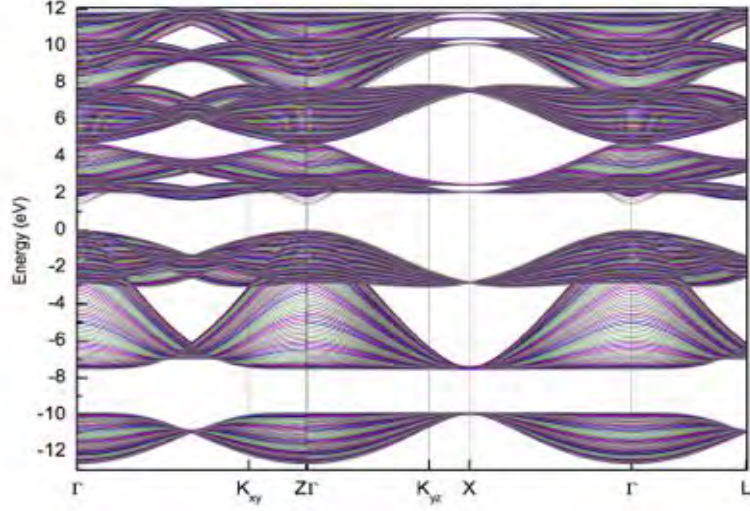


Fig 3.9: Calculated electronic band structures of the MQW-SL structure C2

From Fig. 3.10(b) the DOS profiles at the conduction band edge varies with different layer thicknesses. This variation is mainly contributed by the variation of the thickness ratio, i.e. the ratio of the well thickness to the barrier thickness. For a smaller thickness ratio, the density of well-confined states is reduced; these states are effectively shifted up, above the barrier height. This leads to a smaller sub-barrier DOS and a higher 1st conduction-band DOS peak, as shown in Fig. 3.10(b). On the other hand, the joint variation of both layer thicknesses, with a fixed thickness ratio, merely has a secondary effect on the electronic DOS. In fact such variation simply folds the reduced Brillouin zone, creating mini-gaps at the zone edge due to destructive interference. These mini-gaps contribute to the fluctuations of the sub-barrier DOS profiles, demonstrated by comparison between curves of sample A1 (B1, C1) and A2 (B2, C2) in Fig. 3.10(b).

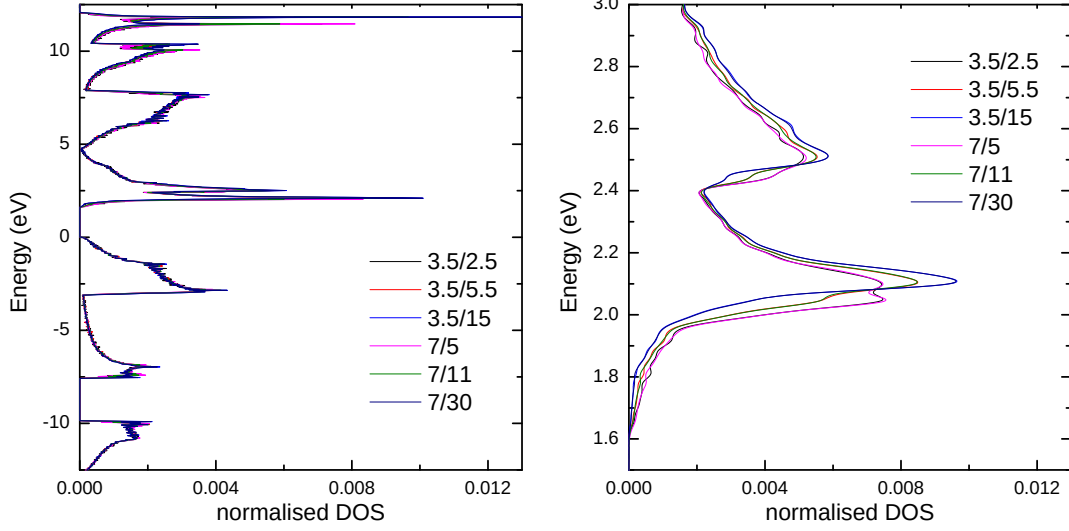


Fig 3.10: Electronic density of states (DOS) for the whole considered energy range (left figure), and at the conduction-band edge (right figure).

3.1.3 Bond charge model on calculating phononic structures for MQW-SL structures

In this section, the phonon dispersion of a wurtzite InN-GaN multiple quantum well superlattice was produced using a modified adiabatic bond charge model (ABCM). Bulk binary compound parameters obtained from *ab-initio* calculations were used as input parameters for the modified bond charge model. The phononic bandgap, visualization of the vibrational modes, specific heat and thermal conductivity in the quantum confined direction for the superlattice material are reported. The size of the phononic bandgap is predicted to be between that of the two bulk materials in all symmetry directions and insufficient to prevent first order phonon decay. Surprisingly the A1-like mode has a greater vibration frequency than the E1-like mode,

which is opposite to what was believed to be the case in the bulk counterparts. The specific heat of the superlattice is similar to that of GaN despite similar volumetric fractions of the materials. The low thermal conductivity of InN limits the thermal conduction in the confined direction. This work has been published in “Theoretical calculation of the vibrational and thermal properties of wurtzite inn-gan multiple quantum well superlattice” by H Xia, Y Feng et al., 2013, Journal of Applied Physics, 113:164304[90].

3.1.3.1 Methodology

This is a theoretical study of the indium-Nitride and gallium-Nitride quantum well system. The strategy adopted here is to use the *ab-initio* calculation for the bulk InN and GaN as an input, then extract the force constants from these two bulk dispersions for the adiabatic bond charge model and use these extracted force constants to predict the phonon dispersions for the InN-GaN MQW-SL.

A semi-classical model, the adiabatic bond charge model (ABCM), was selected to predict phonon dispersions for the superlattice structure (Sec. ??). Like most semi-classical models, the ABCM contains a number of physically appealing physical features and has been shown to provide accurate predictions of phonon dispersions in covalently bonded solids [91]. It has been shown to be applicable to materials with appreciable bond dipoles[92, 93, 94]. Compared with a Valence Force Field Model (VFFM), which has 4 free parameters for elemental semiconductors [95] and 7 for binary compounds [96], the ABCM offers advantages in that it requires a minimum number of 4 free parameters for the former and 6 for the latter and the physical meaning of each parameter is generally clear. It performs well in simulating covalently bonded system like the nitrides.

Additionally the computational savings associated with semi-classical methods are attractive when applied to systems involving large numbers of atoms like quantum wells and quantum dots compared to any *ab-initio* methods.

Several kinds of modified ABCM have been developed, one of which revised by B. D. Rajput and D. A. Browne [93] is selected as reference. In this modified ABCM, six adjustable parameters are incorporated, namely the short range ion-ion interaction Φ''_{ii} , bond charge (BC)-anion interaction Φ''_n , BC-cation interaction Φ''_p , BC-anion-BC bending force β_n , BC-cation-BC bending force β_p and the long range Coulombic interaction. The dynamic equations for ABCM are derived in the way that the BCs are treated as points sitting between the two atoms involved, with a specified partition ratio. In the dynamic equation Eq(3.5) the dimensions of bond charges are eliminated by the adiabatic approximation.

$$M\omega^2 u = \{R + 4(z^2/\epsilon) - [T - 2(z^2/\epsilon)C_T] \\ \times [S + (z^2/\epsilon)C_S]^{-1}[T^+ - 2(z^2/\epsilon)C_T^+]\} \quad (3.5)$$

In Eq(3.5), M is the mass matrix for the system and u is the displacement vector. R , T and S are the Fourier transformed force constant matrices of short range ion-ion, ion-BC and BC-BC interactions, while the long range Coulombic counterparts are denoted by the capital C . The Coulombic pre-factor, z^2/ϵ , determines the contribution from the long range interaction.

The ABCM should be modified so that it can produce reasonable phonon dispersions for the nitride binary compounds which are highly polarized. There are several feasible ways to account for this polarization effect, one of which is to shift the bond charges towards the nitrogen ions. This method is intuitive and has been proved to be effective in producing phonon dispersions for II-VI compounds[93]. It is worth mentioning that the short range interaction cannot produce any LO-TO splitting despite the fact that the

bond charges have been shifted and the force constant difference has been taken into consideration for both anion and cation. This splitting observed in polarized materials can only be obtained by the long range Coulombic interaction. Numerically the LO-TO splitting is caused by the non-analytical term in the Ewald summation when k approaches zero. Physically it is due to the macroscopic electric field induced by the dipole-dipole interaction[97].

Force constants for the cubic phase of InN and GaN were obtained from *ab-initio* simulations and used to produce dispersion curves for the MQW-SL. The phonon modes for the zinc blende phase of these materials are all Raman active, which is an advantage over the wurtzite phase where this is not the case [98]. The fitting algorithm can also make use of this experimental data as input for the cubic phases. As the atomic bonding structure for both zinc blende and wurtzite is tetrahedral, it is reasonable to assume that the short range interaction potentials should stay the same and the force constants should apply for both structures.[94]

The phonon dispersions for bulk materials from the ABCM were fitted to some high symmetry points in the Brillouin Zone (BZ) (Γ , X and L). From this, the force constants relevant to the ABCM were extracted. Throughout this work it is assumed that short-range bonding force constants are similar for bulk materials as well as superlattices. This is a reasonable assumption given that the force constant only has an appreciable effect on neighbouring BCs and next nearest neighbouring atoms. Hence a deviation in bulk-like behaviour would only occur for atoms immediately either side of an interface. The bonding force constants are averaged at the interface between InN and GaN. The non-bonding potential (long-range Coulomb potential) has been included depending on the structure of the MQW-SL with its Fourier transformed force constant obtained using the Ewald summation. It has also been

idealized that there is no lattice mismatch at the interface and the lattice constant is the same for these two materials. For strain-balanced quantum wells, the in-plane lattice constants are equal to that of the substrate, while the out-of-plane constants depend on the respective Poisson's ratios[99]. However, the averaged lattice constant between InN and GaN is adopted here for simplicity. From this, the phonon dispersions for the superlattice were produced.

3.1.3.2 *ab-initio* calculation and fitted force constants

A self-consistent-field method and ultra-soft pseudo-potentials with a *Perdew-Burke-Ernzerhof* (PBE) exchange functional were used in performing the *ab-initio* calculation. The software package Quantum Espresso was used here. [100] The lattice constants were extracted for each material and found to be quite accurate compared with existing experimental data [101, 102]. The kinetic energy cutoffs for the electronic wave-function have been carefully tested for convergence (A cutoff wave function kinetic energy of 80 Ry for both InN and GaN with a k-point mesh grid of $4 \times 4 \times 4$). Phonon frequencies at some high symmetry points are reported in Table 3.4.

After the frequencies at Γ , X and L points are extracted and by using a Nelder-Mead simplex algorithm [106], the ABCM was fitted and the force constants were extracted and are presented in Table 3.5.

3.1.3.3 Comparison of the Phonon dispersions in bulk by ABCM and DFT

The bulk phonon dispersions for InN and GaN produced from both *ab-initio* and the ABCM show reasonable agreement for interpolations across the Brillouin zone. The frequencies of the zone center modes fit well even though the shapes of the curves are less complex in ABCM than in *ab-initio* (see Figure

Table 3.4: Lattice constants and frequencies at high symmetry points for Cubic InN and GaN. The lattice constant was calculated by minimizing the system energy.

	Cubic InN			Cubic GaN		
	This calc.	expt.	expt.[103]	This calc.	expt.[101]	expt.
Lattice constant/ $\text{\AA}$	5.08	5.01[104]	4.97	4.47	4.50	4.50[105]
LO at Γ /THz	17.1	17.6[102]	17.6	21.7	22.2	22.2[102]
TO at Γ /THz	13.5	14.2[102]	13.7	16.4	16.6	16.7[102]
LO at X /THz	16.9			19.8		
TO at X /THz	15.6			17.6		
LA at X /THz	6.4			10.4		
TA at X /THz	3.9			6.0		
LO at L /THz	17.3			20.4		
TO at L /THz	14.7			16.5		
LA at L /THz	6.6			10.1		
TA at L /THz	3.4			4.4		

3.11 and Figure 3.12). This is because in the *Density Functional Theory* (DFT), the quantized and distributive electron configuration for each atom is taken into account while in ABCM bond electrons are assumed as being placed between two atoms. The system energy and hence vibrational modes are different due to their different electron configurations. For a semi-classical model with only six free parameters, the ABCM performs well between the frequencies in some symmetry directions. It has been demonstrated that ABCM with nine free parameters can be better fitted for some nitride compounds, however at the cost of three more parameters.[107] The primary point of this work is to present that ABCM is capable of producing phonon dispersions for a MQW-SL and therefore ABCM with fewer free parameters is preferred.

Table 3.5: Force constants for the ABCM. All the FCs are in unit N/m except for z^2/ϵ which was calculated by taking the lattice constant and electron charge as 1. The subscript n and p denote a negatively or positively charged target ion. Φ''_{ii} is the ion-ion interaction force constant while Φ''_n and Φ''_p are the force constant for anion-BC and cation-BC respectively. β denotes the bond bending force constant while z^2/ϵ is the Coulombic pre-factor.

	Φ''_{ii}	Φ''_n	Φ''_p	β_n	β_p	z^2/ϵ
InN	2.37	33.74	1.42	13.94	0.001	0.01245
GaN	4.55	42.45	1.14	23.96	0.101	0.01830

The bulk wurtzite phases of both materials were also generated in order to test the assumptions and the algorithm itself. Based on the assumption that the bonding force constants stay the same in zinc blende and in wurtzite, the generated dispersions show a good quality compared with results of some existing dispersion models[108]. Phonon frequencies at some high symmetry points are tabulated and compared with previous works (Table 3.7 and 3.6).

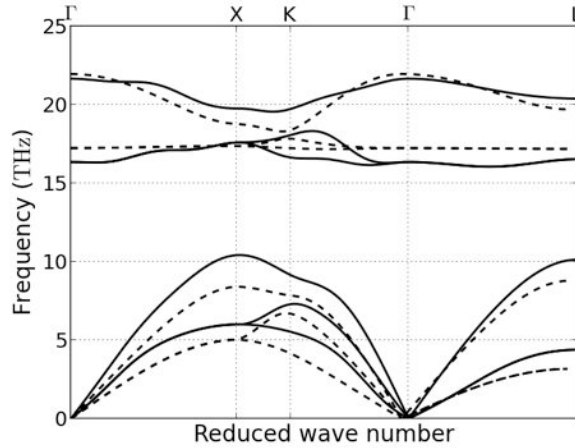


Fig 3.11: Phonon dispersions of cubic GaN. The dispersions produced by DFT are denoted by the solid line while the one in dashed line is produced by the ABCM.

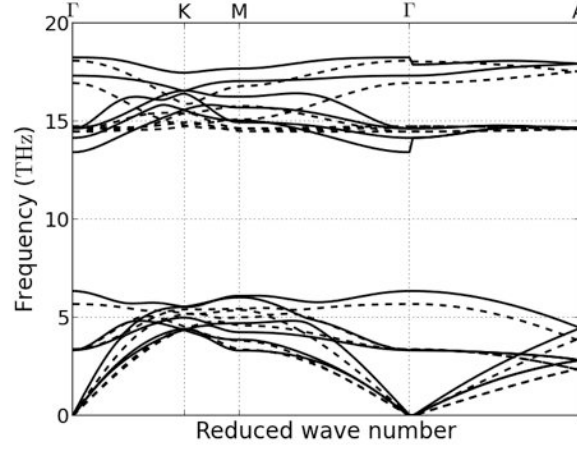


Fig 3.12: Phonon dispersions of wurtzite InN. The dispersions produced by DFT are denoted by the solid line while the one in dashed line is produced by the ABCM. This figure aims to show how ABCM works for a wurtzite lattice.

3.1.3.4 Structural configuration of the Wurtzite InN-GaN MQW-SL

In this study we have constructed an InN-GaN quantum well of 10 subunit cells, 5 of which are InN while the rest are GaN (40 atoms within the unit cell). Each layer is about 2.6nm to 2.9nm thick, which can be grown by epitaxial methods [114]. Due to the high symmetry and easy growth on the [0001] direction in wurtzite structure, these 10 subunit cells stacking along this direction form the primitive cell of the superlattice. This configuration is shown in Fig. 3.13(a) while the schematic picture for the structure is presented in Fig. 3.13(b). We also varied the thickness from 2 sub-unit cells to 8 units and tested the trend of the phonon dispersions and thermal conductivity at the [0001] direction.

Table 3.6: Wurtzite InN phonon frequencies at high symmetry points (in unit THz). Data of the column *This work* was generated by the modified ABCM. The Inelastic X-ray Scattering (IXS) is from the Serrano *et al* group [109].

Symmetry points	Phonon Mode	<i>ab initio</i> [110]	Raman [111]	IXS [109]	This work
Γ	E1(LO)	17.85			18.09
	A1(LO)	17.58	17.88		18.05
	B1	17.28			16.95
	E2	14.49	14.85		14.75
	E1(TO)	14.01			14.68
	A1(TO)	13.29			14.48
	B1(low)	6.75			5.69
	E2(low)	2.49			3.34
A	LO	17.55			17.54
	LA	4.50			3.90
M	B1(low)	7.50		6.60	5.45
	E2	4.80		6.15	5.38
	E2(low)	3.90		4.65	5.01
	TA _z	3.75		3.69	4.61
	TA _x	2.40		2.49	3.80
K	B1(low)	6.00		5.94	5.43
	TA	4.20		4.26	4.38

Table 3.7: Wurtzite GaN phonon frequencies at high symmetric points (in unit THz). Data of the column *This work* was generated by the modified ABCM.

Symmetry points	Phonon mode	IXS [112]	Raman [113]	<i>ab initio</i> [112]	This work
Γ	E1(LO)		22.40	22.57	23.57
	A1(LO)	21.87	22.18	22.54	23.51
	B1	20.76		21.57	21.43
	E2		17.08	17.43	19.30
	E1(TO)		16.80	17.15	19.21
	A1(TO)		16.01	16.36	18.65
	B1(low)	9.87		10.16	9.08
	E2(low)		4.33	4.34	5.58
A	LO	21.33		22.06	22.57
	LA	6.93		7.18	6.17
M	A1(TO)	17.28		18.05	18.57
	E2	7.14		7.22	8.16
	E2(low)	5.79		5.99	7.56
	TA _z	5.52		5.65	6.20
	TA _x	4.11		4.22	5.70
K	TO	18.42		18.81	18.79
	TA	6.45		6.47	7.17

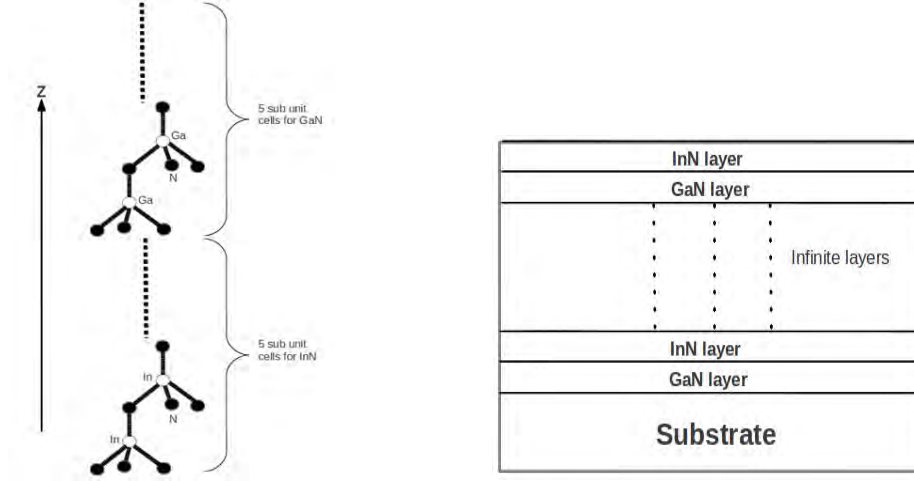


Fig 3.13: (a) Schematic graph of the atomic arrangement inside one unit cell. The direction of z-axis is the same as the $[0001]$ direction. Note that planes perpendicular to the z axis have no quantum confinement. (b) Schematic graph for the quantum well device. The periodic boundary conditions imply an infinite number of InN-GaN layers inside the device. The phonon bands derived apply best to the region well away from the substrate and surface.

3.1.3.5 Phonon dispersion in the Wurtzite InN-GaN MQW-SL

Assumptions have been made so that this ABCM can output reasonable phonon dispersions for the superlattice as was mentioned in Sec. 3.1.3.1. The dispersion is shown in Figure 3.14. It is worth reporting that the dispersion curves are quite flat along the Γ -A direction for a 10 sub-unit cell MQW. This is because several folds of quantum confinement are built along that direction and the Brillouin Zone edge at A shrinks accordingly. The high-lying modes are confined along the Γ -A while the low-lying modes are more or less mixed. But the zone-folding is exactly along Γ -A, and hence contributes to the flatness. Additionally, the phonon energy gap in this quantum well structure is slightly smaller than that in the bulk materials. This is also reasonable because the increased number of particles inside one unit cell will naturally introduce more allowed modes in the dispersion. Hence the energy

gap is decreased to around 20.06 meV.

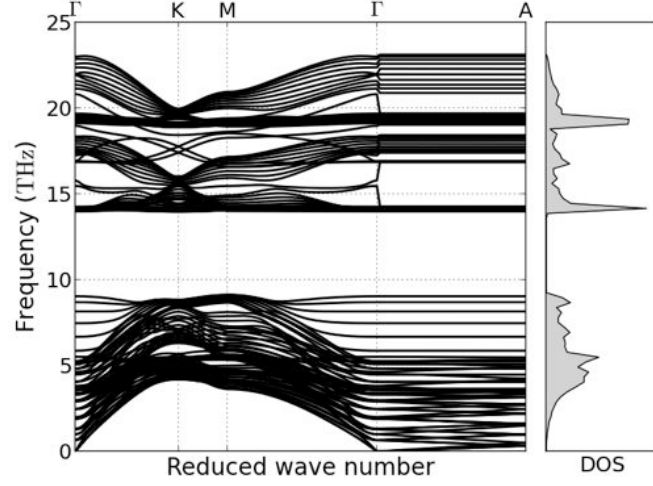


Fig 3.14: Phonon dispersion for the InN-GaN MQW with 10 sub-unit cells. Note that the flatness along Γ -A direction is due to the phonon confinement.

For a system with fewer sub-unit cells, it behaves more like an alloy whose unit cell is relatively small. The confinement along Γ -A is not as strong as the one with 10 sub-unit cells (see Fig. 3.15). On the contrary, systems with thicker InN/GaN layers behave more like bulk materials.

We identified that the highest optical frequency at Γ is the A1-like mode in the 2 sub unit cell MQW (see the points with the highest frequency in Fig. 3.16). It is caused by the out-of-phase vibrations of the cations and anions at the Γ -A direction. The second highest mode is the E1-like mode which has a similar type of vibration but in the Γ -M direction. However, in the bulk materials, E1 mode usually has a greater frequency than the A1 mode (Tab. 3.6 and Tab. 3.7). Another substantial discrepancy was found in the splitting of E1 and A1 modes between the bulk and the MQW. The splitting in the 2 sub unit cells MQW is 10.7% compared to the A1 mode while in bulk GaN it is only 0.26% (in Tab. 3.7) and 0.22% in bulk InN (in Tab. 3.6).

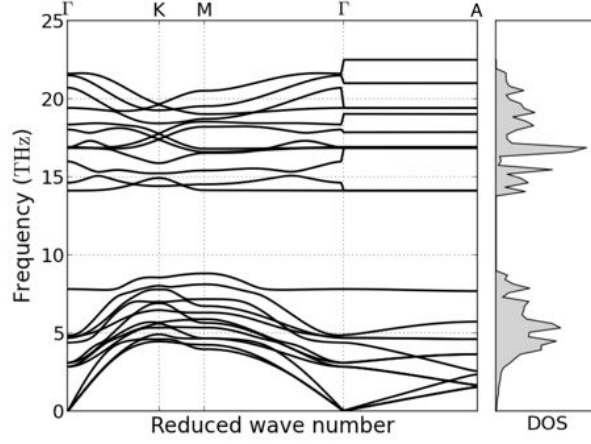


Fig 3.15: Phonon dispersion for the InN-GaN MQW with 2 sub-unit cells. Note that the confinement along the Γ -A direction is reduced compared with Figure 3.14. The frequency splitting at the Γ point can be explained by the nonequivalent dipole moment viewed from different directions (Γ -A or Γ -M). This dipole moment is expected to be present in nitride compounds in the wurtzite phase.

This is attributed to the combination of long-range Coulombic and phonon confinement effects induced from the Γ -A direction. The highest vibrational frequency of the Γ -point mode along the Γ -M direction is reduced, for the accumulated surface charge induced by the longitudinal wave is discontinued by the non-vibrating layers. This effect is most enhanced for those MQW structures with thin layers.

On the contrary, the three acoustic modes which pass through the origin along the Γ -A direction consist of two mixed modes and one transverse mode. This is similar in the Γ -M direction except that the plane where the atoms vibrate is different.

It is found that for MQW the phononic bandgap becomes smaller than that of its bulk components. This is because that the two types of bulk-like modes are mixed together, and some interfacial modes form within the

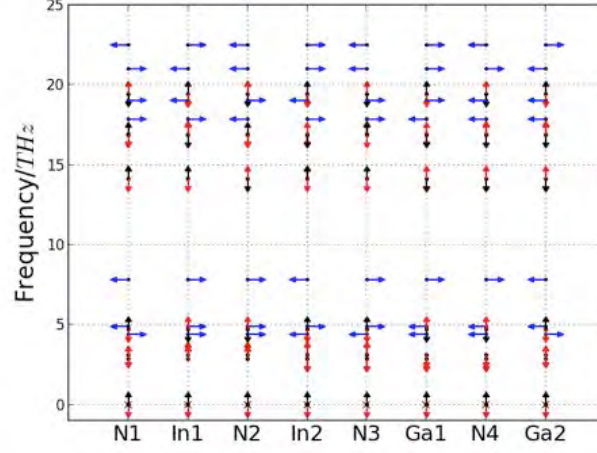


Fig 3.16: Vibrations in the InN-GaN MQW with 2 sub-unit cells at Γ -A direction. The stacking order along the Γ -A direction is N1/In1/N2/In2/N3/Ga1/N4/Ga2. A horizontal arrow (in blue) denotes a longitudinal mode while a vertical (in red and black) one denotes a transverse mode. The cross mark in the plot represents the mixed mode. Note that the arrows only show the vibrating direction and do not contain information on magnitudes. The arrows in red and black denote a different vibration pattern within the plane perpendicular to the Γ -A direction.

original gap. is not large enough to completely block the Klemens decay, in terms of the carrier cooling rate it may not be beneficial compared to its bulk counterparts.

3.1.3.6 Thermal properties

The Debye specific heat was calculated via Eq. 3.6 while the thermal conductivity at c or the $[0001]$ direction was evaluated using Boltzmann transport theory (Eq. 3.7) [115]. The bulk specific heats are estimated well and are close to the ones in literature (see Figure 3.17 with the specific heat of a MQW-SL shown as comparison). For thermal conductivity, the reason why only the c direction was investigated is that it is the most common direction

on which people grow a hexagonal crystal and so this is the direction most likely to be compared against experiment. Besides, in the plane perpendicular to c direction, there is no confinement and the thermal conductivity in each layer should well be close to that in the bulk counterpart.

$$C_p = \frac{1}{N_q} \sum_{\lambda q} \left[k_B \left(\frac{\hbar \omega_{\lambda q}}{k_B T} \right)^2 \frac{e^{\hbar \omega_{\lambda q}/k_B T}}{(e^{\hbar \omega_{\lambda q}/k_B T} - 1)^2} \right] \quad (3.6)$$

$$\kappa_{\alpha\beta} = \hbar \sum_{\lambda} \int \frac{d^3 q}{(2\pi)^3} v_{\alpha\lambda}(q) v_{\beta\lambda}(q) \omega_{\lambda}(q) t_{\lambda}(q) \left\{ \frac{dn_B[\omega_{\lambda}(q)]}{dT} \right\} \quad (3.7)$$

In Fig. 3.18, thermal conductivity for both bulks and MQW-SLs with various thicknesses is shown. No clear trend with respect to the thickness of MQW-SL was observed. This is probably because phonon frequency and its group velocity do not explicitly depend on the thickness of MQW-SL. As one would notice in Fig. 3.19, the contribution from the higher frequencies to the thermal conductivity is almost zero. This is because the group velocity of those phonons is very small due to the confinement in the Γ - A direction, and thus contributes less to the thermal conductivity.

In Eq. 3.7, λ denotes the polarisation of a phonon mode while α and β refer to the direction of a phonon. In this example, only the Γ - A direction is considered. v is the group velocity of phonon while n_B is the Boson occupation function. t is the relaxation time of phonon for which we assume a constant value.

3.1.3.7 Conclusion

In this study, an *ab-initio* method as well as a modified ABCM were employed to produce the phonon dispersion of an InN-GaN MQW superlattice. Due to the fact that its phononic bandgap is not large enough to completely

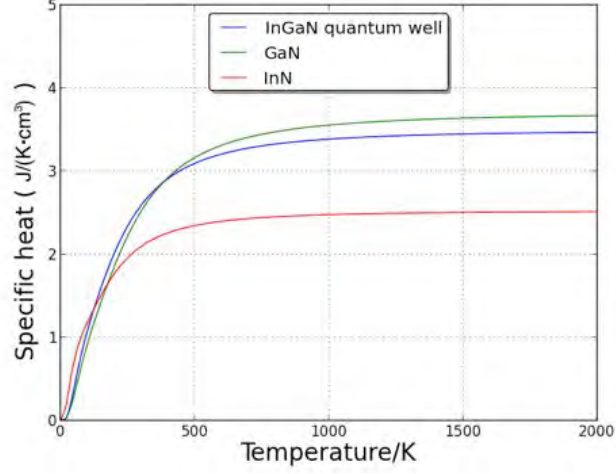


Fig 3.17: Specific heat for the InN-GaN MQW with 10 sub-unit cells. The specific heat curve of the MQW falls between the curves of InN and GaN. The specific heats of the bulk materials at 300K are $2.5 \text{ JK}^{-1}\text{cm}^{-3}$ and $2.1 \text{ JK}^{-1}\text{cm}^{-3}$ for GaN and InN respectively. In the previous work, specific heat of GaN was measured within $(2.42\text{-}2.64) \text{ JK}^{-1}\text{cm}^{-3}$ [116] while that of InN was around $(2.00\text{-}2.11) \text{ JK}^{-1}\text{cm}^{-3}$ [117, 118]

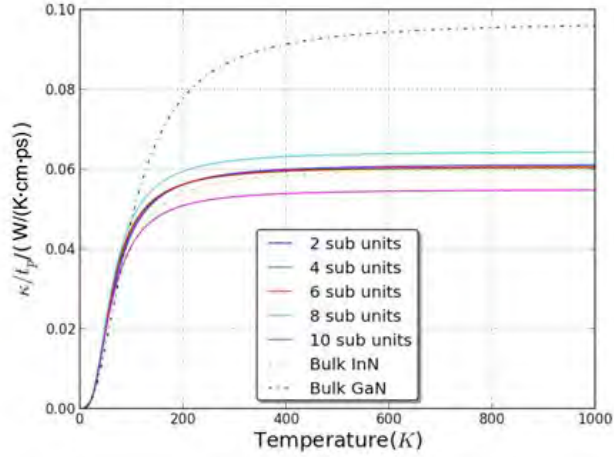


Fig 3.18: Thermal conductivity at c direction for the InN-GaN MQW and the bulk counterparts. Though the thermal conductivity of bulk GaN is quite high, the overall thermal conductivity of the MQW is limited by that of the bulk InN.

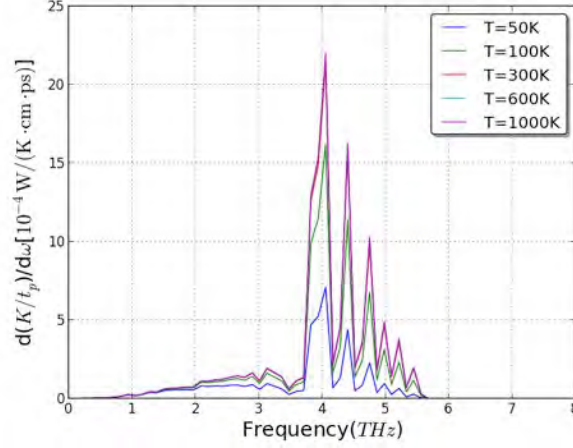


Fig 3.19: Frequency dependent thermal conductivity in c direction for the 10 sub-unit cells InN-GaN MQW. Only the low frequency phonon modes contribute to the thermal conductivity in this direction.

block the Klemens decay, in terms of the carrier cooling rate it may not be beneficial compared to its bulk counterparts. However, due to the confinement properties of polar modes, the diffusion of hot phonons is suppressed. This could potentially prevent the re-distribution of hot phonons, enhance the phonon bottleneck effects and create more chances for these phonons to feed energy back to electrons. Future work will examine the rate of electron-phonon interactions in these structures. This will give a better idea of which of the allowed phonon modes couple most strongly. Experiments such as Raman spectroscopy, neutron scattering, inelastic X-ray scattering or FTIR can also be conducted on fabricated superlattices to measure the phonon frequencies directly.

3.2 Many-body interactions for electrons and phonons

In this section, several types of many-body interactions have been analysed theoretically, and their rates have been evaluated for some sample material structures. The first type of interaction considered here is the polar interaction between electrons and polar phonon modes. In the first part the carrier screening effect has been incorporated to reformulate the polar interaction rates in MQW-SL structures. Effects of variations on the thicknesses of the barrier and the well layers have been demonstrated quantitatively for the modeling material of strain-balanced $\text{In}_{0.25}\text{GaAs}/\text{GaAsP}_{0.33}$ MQW-SLs. In the second part the actual carrier cooling lifetimes have been calculated in wurtzite InN-InGaN MQW-SLs with different layer thicknesses and gallium compositions. In this part the polar electron-phonon interaction and the phonon-phonon interaction are both incorporated. The phonon-bottleneck effect has been evaluated quantitatively by regarding the carrier cooling as a multiple-step process. In the third part the Coulombic interactions between carriers (i.e. electron/hole excitations) have been computed in a cubic- InN modeling material. The corresponding relaxation times have been obtained by fitting the computed results, providing realistic parameters for the device model described in Sec. 2.3.

3.2.1 Theoretical work on the static carrier screening and its effect on carrier cooling rate in MQW-SL structures

In this section an electro-static model has been formulated to analyze the effect of carrier screening on the energy relaxation of electrons in polar-semiconductor multiple-quantum-well superlattices. The screened polar po-

tential in this structure has been obtained in terms of its 0-th order and 1-st order Fourier components. The 1-st order correction gives a further reduction of the coupling strength due to the uneven spatial distribution of carriers, and it heavily depends on the relative bi-layer thickness compared to the Debye screening length. The reductions of electron energy relaxation in $\text{In}_{0.25}\text{GaAs}/\text{GaAsP}_{0.33}$ multiple-quantum-well superlattices have been numerically analysed yielding conclusions which agree with the recent experiments. The model provides a quantified approach to optimize the structure configuration in terms of the carrier cooling rate, allowing the multiple-quantum-well superlattice to be an excellent absorber candidate for realizing the hot carrier solar cell. The work in this section has been published in “Effect of static carrier screening on the energy relaxation of electrons in polar-semiconductor multiple-quantum-well superlattices” by Y. Feng et al., 2013, Journal of Applied Physics, 113(2):02431-024317[119].

3.2.1.1 Introduction

The multiple-quantum-well superlattice (MQW-SL) has been experimentally proven to be a material structure with a significantly reduced cooling rate compared to bulk materials.[19, 99] Potentially it can work as an absorber structure for realizing the HCSC device[15]. A fine design of this structure aiming for a minimized carrier energy relaxation requires a theoretical method to treat the electron-phonon coupling. In the literature the Fröhlich-type interaction between electrons and polar phonons in MQW-SL has been formulated, in which only the interactions with “bare” phonons were considered[120, 121]. In fact with sufficient carrier density the polarization field generated by lattice waves is screened by carriers, leading to a significantly reduced coupling strength. Although in bulk materials[122] and in

single quantum wells[123, 124, 125] the static screening and plasmon-phonon coupling have been theoretically studied[126, 127], this screening effect on the electron relaxation in polar-semiconductor multiple-quantum-well superlattices requires a practical method to be quantified.

Recent experimental results demonstrate a relatively long energy relaxation time of carriers in the InGaAs/GaAsP MQW-SL structure with thick layers compared to that with thin layers[99]. The phenomenon is not appropriately explained by the phonon-bottleneck effect that has frequently been adopted as the reason of a reduced cooling rate[13, 128]. On the contrary the MQW-SL with thick layers has a less confined acoustic property and hence a better transport of hot phonons. In this work the carrier screening effect is suggested to be responsible for this observation. An electro-static model has been adopted to formulate the screened electron-phonon coupling in polar-semiconductor MQW-SLs. The reduced coupling strength between electrons and phonons has been analysed in terms of their Fourier transformed potentials. Compared to the interaction with the “bare” phonons, the reduced cooling rates of the hot electrons due to the carrier screening have been calculated. The numerical results are presented for different structure configurations of the MQW-SL. They demonstrate an indicative variation of the electron cooling rates with layer thicknesses which matches the experimental results well. Apart from the numerical results this work provides a theoretical framework of optimizing the MQW configuration for solar applications. The optimizable structure parameters are the respective layer thicknesses and the compositions of materials involved.

3.2.1.2 Fourier components of screened potential in MQW-SL

The MQW-SL structure involves two component materials with electronic band offsets. The bi-layers consisting of both layers of respective materials are positioned periodically along the direction perpendicular to the layer planes. This direction is defined as the z-axis for convenience. The coordinate zero is set as being at the middle of a well layer, i.e. the z-coordinate of this well layer is $[-\frac{W}{2}, \frac{W}{2}]$.

With significant mismatch between the acoustic properties of the component materials there is no optical resonant mode vibrating in both types of layers[129, 130] (strictly speaking, only for layers with sufficient thickness). In this case all the polar modes[131] are confined within a single type of layers. Take the well-confined mode as an example, whose polarization field is described in Eq. 3.8[120]. The field shrinks to zero at the two edges of the layer of confinement.

$$\begin{aligned} \mathbf{P}(\mathbf{r}, \mathbf{k}_0, l) &= \frac{1}{\sqrt{V}} \sqrt{\frac{\hbar}{2\gamma\omega}} \frac{\mathbf{k}_0}{k_0} e^{i\mathbf{k}_0\mathbf{r}} \Phi_l \\ \Phi_l &= A \sin \left\{ \frac{l\pi}{W} \left[z - m(W+B) + \frac{W}{2} \right] \right\} e^{-ik_{0z}[z-m(W+B)]} \\ &\quad m(W+B) - \frac{W}{2} \leq z \leq m(W+B) + \frac{W}{2} \end{aligned} \quad (3.8)$$

Where $\mathbf{P}(\mathbf{r}, \mathbf{k}_0, l)$ is the polarization field at coordinate $\mathbf{r}$, generated by a polar mode at the l -th branch and with a wave-vector $\mathbf{k}_0 = k_{0x}\hat{\mathbf{x}} + k_{0y}\hat{\mathbf{y}} + k_{0z}\hat{\mathbf{z}}$. V is the volume of the structure; W and B are the respective layer thicknesses of the well and the barrier. γ and ω are the coupling strength constant and the frequency of the mode of concern. Φ_l represents the modulation function of the mode, containing $l-1$ nodes within one well[120]. A is the normalization factor, and $m = 0, \pm 1, \pm 2, \dots$ denotes the index of the periodic region along z-axis. From Eq. 3.8 the periodicity over the bi-layers follows

the Bloch theorem; hence only the region $[-\frac{W}{2}, \frac{W}{2}]$ will be considered in the following part. The density of bound charge ρ_b has been calculated as the negative divergence of the polarization field, shown in Eq. 3.9.

$$\rho_b = \sum_{k=\frac{2\pi n}{W+B}} \left(\frac{k_{0xy}^2}{|\mathbf{k}_0|} S_{k+k_{0z}}^1 + \frac{k_{0z}}{|\mathbf{k}_0|} S_{k+k_{0z}}^2 \right) e^{ikz} e^{i\mathbf{k}_0 \mathbf{r}} \quad (3.9)$$

Where $k_{0xy}^2 = k_{0x}^2 + k_{0y}^2$; S_k^1 and S_k^2 are k -dependent charge parameters defined in Eq. 3.10 with $\alpha = A\sqrt{\frac{\hbar}{2\gamma\omega V}}$.

$$\begin{aligned} S_k^1 &= \frac{i\alpha e^{ikW/2}}{2(W+B)} \left[\frac{e^{-i(kW-l\pi)} - 1}{-k + l\pi/W} + \frac{e^{-i(kW+l\pi)} - 1}{k + l\pi/W} \right] \\ S_k^2 &= \frac{i\alpha l\pi e^{ikW/2}}{2W(W+B)} \left[\frac{e^{-i(kW-l\pi)} - 1}{-k + l\pi/W} - \frac{e^{-i(kW+l\pi)} - 1}{k + l\pi/W} \right] \end{aligned} \quad (3.10)$$

Assuming carriers are gaseous with the spatial concentration denoted by $n_{e,h}(z)$, the relation between the electric potential and the charge density is described by the electro-static Poisson equation (in SI units).

$$\nabla^2 \phi = -\frac{\rho_b}{\epsilon} + \frac{q}{\epsilon} \Delta(n_e - n_h) \quad (3.11)$$

Where $q\Delta(n_e - n_h)$ indicates the variation of the charge concentration resulting from the extra potential ϕ of the lattice wave. For non-degenerate carrier statistics it is proportional to the total density of free carriers $n(z)$ (denoted by n_w in the well and n_b in the barrier) including both electrons and holes[132], shown in Eq. 3.12. q , k_B and ϵ denote the elementary charge, Boltzmann constant and the permittivity respectively.

$$\Delta(n_e - n_h) \approx \begin{cases} \frac{q\phi}{k_B T} n_w & z \in n(W+B) + \left[-\frac{W}{2}, \frac{W}{2}\right] \\ \frac{q\phi}{k_B T} n_b & z \in n(W+B) + \left[\frac{W}{2}, \frac{W}{2} + B\right] \end{cases} \quad (3.12)$$

Fourier transformation of Eq. 3.11 leads to Eq. 3.13, where $k = \frac{2\pi n}{W+B}$ ($n = 0, \pm 1, \pm 2, \dots$).

$$\begin{aligned}
 -|k\mathbf{u} + \mathbf{k}_0|^2 F_{k+k_{0z}}[\phi] = & -\frac{1}{\epsilon} \left(|\mathbf{k}_0| S_{k+k_{0z}}^1 + \frac{k_{0z}}{|\mathbf{k}_0|} S_{k+k_{0z}}^2 \right) e^{i\mathbf{k}_0\mathbf{r}} \\
 & + \frac{q^2}{\epsilon k_B T} \sum_{k'=\frac{2\pi n}{W+B}} F_{k'}[n(z)] F_{k+k_{0z}-k'}[\phi]
 \end{aligned} \quad (3.13)$$

The Fourier transformed expression of the spatially non-uniform carrier concentration $n(z)$ (Eq. 3.14) involves a direct component with $k = 0$ (i.e. the average carrier concentration $\bar{n}$) and alternative components with $k = \pm \frac{2\pi}{W+B}, \pm \frac{4\pi}{W+B}, \dots$; the alternative components are all proportional to the contrast between n_w and n_b . As all the Fourier components of the polar potential $F_k[\phi]$ contain $e^{i\mathbf{k}_0\mathbf{r}}$, the term will be neglected in the following relevant expressions for convenience.

$$F_k[n(z)] = \begin{cases} \frac{n_w - n_b}{W+B} \frac{\sin(kW/2)}{k/2} & k \neq 0 \\ \frac{n_w W + n_b B}{W+B} \equiv \bar{n} & k = 0 \end{cases} \quad (3.14)$$

The symmetric series $F_k[n(z)]$ has the maximum value at $k = 0$. Therefore in the summation part of Eq. 3.13 the term with $k' = 0$ generally makes a major contribution. By only taking this term into account we obtain the 0-th order approximation of the potential, shown in Eq. 3.15.

$$F_{k+k_{0z}}^{(0)}[\phi] = \frac{\frac{k_{0xy}^2}{|\mathbf{k}_0|} S_{k+k_{0z}}^1 + \frac{k_{0z}}{|\mathbf{k}_0|} S_{k+k_{0z}}^2}{\epsilon |k\mathbf{u} + \mathbf{k}_0|^2 + q^2 \bar{n} / k_B T} \quad (3.15)$$

The 1-st order correction of the Fourier transformed potential is obtained by substituting Eq. 3.15 into Eq. 3.13 for the summation of all the alternative components. This summation is denoted by $\sum_{k' \neq k}$ in Eq. 3.16 where $k - k' = \pm \frac{2\pi}{W+B}, \pm \frac{4\pi}{W+B}, \dots$

$$F_{k+k_{0z}}^{(1)}[\phi] = -\frac{\sum_{k' \neq k} F_{k-k'}[n(z)] F_{k'+k_{0z}}^{(0)}[\phi]}{\epsilon |k\mathbf{u} + \mathbf{k}_0|^2 k_B T / q^2 + \bar{n}} \quad (3.16)$$

If regarding the Fourier transformed potential (i.e. $F_k^{(0)}[\phi]$ and $F_k^{(1)}[\phi]$) as consisting of two parts: the terms of S_k^1 and the terms of S_k^2 , then they have definite and opposite parities in the reciprocal space. In fact for an odd l , S_k^1 has the parity of +1, while S_k^2 has the parity of -1. The inverse parities exist for an even l . The nature of symmetry ensures that only terms of a certain symmetric type would appear when accompanying the transitions of electronic states with definite parities. In the MQW-SL if only considering the intra-sub-band transitions then the potential terms with -1 parity would cancel out, as is proved in the following sections. Hence for the Fourier transformed potential of the polar coupling, only the terms of S_k^1 are of interest for an odd l , while only the terms of S_k^2 are considered for an even l . The symmetric rule has been applied when deriving Eq. 3.17. The summation in this expression converges, and the contribution of each term peaks at k' values around $\pm l \frac{\pi}{W}$.

$$F_{k+k_{0z}}^{(1)}[\phi] = \begin{cases} \frac{-4ik_{0xy}^2 \alpha l \pi (n_w - n_b) / W}{|\mathbf{k}_0|(W+B)^2 \left(\epsilon |k\mathbf{u} + \mathbf{k}_0|^2 + \frac{q^2 \bar{n}}{k_B T} \right)} \sum_{k' \neq k} \left[\frac{\cos\left(\frac{k'+k_{0z}}{2} W\right)}{\left(l \frac{\pi}{W}\right)^2 - (k' + k_{0z})^2} \frac{\sin\left(\frac{k-k'}{2} W\right)}{\bar{n} + |k'\mathbf{u} + \mathbf{k}_0|^2 \epsilon k_B T / q^2} \right] & \text{for odd } l \\ \frac{-4k_{0z} \alpha l \pi (n_w - n_b) / W}{|\mathbf{k}_0|(W+B)^2 \left(\epsilon |k\mathbf{u} + \mathbf{k}_0|^2 + \frac{q^2 \bar{n}}{k_B T} \right)} \sum_{k' \neq k} \left[\frac{(k' + k_{0z}) \sin\left(\frac{k'+k_{0z}}{2} W\right)}{\left(l \frac{\pi}{W}\right)^2 - (k' + k_{0z})^2} \frac{\sin\left(\frac{k-k'}{2} W\right)}{\bar{n} + |k'\mathbf{u} + \mathbf{k}_0|^2 \epsilon k_B T / q^2} \right] & \text{for even } l \end{cases} \quad (3.17)$$

3.2.1.3 special cases of the screened potential of polar modes in MQW-SL

The screened potentials of the polar phonon modes have simplified forms with clear physical meaning in some special cases, although in general the complicated expressions appear as shown in Eq. 3.15 and Eq. 3.17.

Case 1. $\bar{n} \ll \frac{\epsilon k_B T}{q^2(W+B)^2}$. In Eq. 3.15 the screening term $q\bar{n}/k_B T$ in the denominator becomes negligible for $k \neq 0$, which corresponds to the case

with minimal carrier screening. In fact the contribution from the term of $k = 0$ is small except for the long-wavelength modes at the reciprocal zone center. This is because S_k^1 and S_k^2 are generally double-peak functions with the peak positions far away from the zone center. The 1st-order correction $F_{K+k_{0z}}^{(1)}[\phi]$ is negligible as well, as proved in Case 3. One thing to notice is that the form degenerates to that of the bulk material by setting $W \rightarrow \infty$: as S_k^1 turns into a delta function centered at $\pm \frac{\pi l}{W}$, the only existing terms are $F_{\frac{\pi l}{W}+k_{0z}} + F_{-\frac{\pi l}{W}+k_{0z}} \propto 1/\sqrt{(\pi l/W)^2 + \mathbf{k}_0^2}$. Eq. 3.15 presents the unscreened Fröhlich-type coupling strength in bulk materials[133].

Case 2. $W + B \gg \sqrt{\frac{\epsilon k_B T}{q^2 \bar{n}}}$ and $n_w \gg n_b$. In this case the 1st-order correction on the screened potential reaches a maximum. It indicates that the correction due to the non-uniformity of the carrier spatial distributions (i.e. $n_w - n_b$) becomes the most important, when the periodic length of the MQW-SL structure is large compared to the Debye screening length $\lambda_D = \sqrt{\frac{\epsilon k_B T}{q^2 \bar{n}}}$. [134, 124, 122] Its physical meaning lies in the long-range nature of the carrier screening effect: electrons and holes which contribute to the screening of a charged particle are located in a region with the Debye length as its dimension. Therefore only if the thickness of a single layer is significantly larger than the screening length, it is sufficient to effectively screen the field of a confined polar mode. In the case of the MQW-SL structure with thick layers the well-confined modes are screened by carriers merely in the well layers, with the concentration n_w higher than $\bar{n}$. This leads to a large reduction term $F_k^{(1)}[\phi]$ on the Fourier transformed potential.

Case 3. $n_w - n_b \ll \min \left\{ \bar{n}, \frac{\epsilon k_B T}{q^2 (W+B)^2} \right\}$. In this case the 1st-order correction term is negligible compared to the 0th-order screened potential. This means that for the MQW-SL structure either with an even carrier distribution or with ultra-thin bi-layers, the 0-th order approximation shown in Eq. 3.15

is sufficiently accurate. In fact with relatively thin bi-layers ($W + B \ll \lambda_D$) carriers of multiple layers perform the screening collectively within a range characterized by the Debye length, and only the average carrier density $\bar{n}$ has its effect.

3.2.1.4 Evaluation of the screening effect on electron cooling

To evaluate the electron cooling rate due to the screened polar coupling, the electronic structure of the MQW-SL is necessary. For sufficiently large layer thicknesses ($\gtrsim 10\text{nm}$)[135] the Kronig-Penney model is suitable to yield the dispersion relation and the envelope wave functions corresponding to states with mixed parities.[136] Here we only consider structures with sufficient barrier height ($\geq 0.4\text{eV}$) and layer thicknesses ($\geq 7\text{nm}$), allowing more than one electron sub-bands below the conduction band edge of the barrier; with ultrafast carrier re-normalization only these states with low energies have non-zero occupancies. The parities of these states are almost definite (+1 for odd sub-bands and -1 for even sub-bands). Within one sub-band the wavefunctions of states with different wave-vectors have very similar forms in the well layers, while their weak decaying terms away from the well have some differences[136]. For intra-band transitions the overlap of envelope wavefunctions can be represented by the expression of the zone-center state without any significant error. Eq. 3.18 evaluates the wavefunction overlap in a single period.

$$u_c^* u_c = \begin{cases} \frac{\cos^2(k_w z)}{\cos^2(k_w W/2)} & |z| < \frac{W}{2} \\ \frac{\cosh^2[k_b(z + \frac{W+B}{2})]}{\cosh^2(k_b B/2)} & \frac{W}{2} < |z| < \frac{W+B}{2} \end{cases} \quad (3.18)$$

where $k_w = \sqrt{2m^*E}$ and $k_b = \sqrt{2m^*(V - E)}$ with the respective electron

effective mass denoted by m^* . V is the conduction band offset between the well and the barrier, and E is the carrier kinetic energy above the band edge of the well layer. Using Fermi's Golden Rule, the transition rate from the initial electronic state $|\psi_i\rangle$ to the final state $|\psi_f\rangle$ is proportional to $|\langle\psi_f|\phi|\psi_i\rangle|^2$. According to the Bloch's theorem the electron wavefunction can be expressed as $\psi_{f,i} = \{u_{f,i}(z)e^{ik_{f,i}[m(W+B)-z]}\}e^{ik_{f,i}z}$, $z \in m(W+B) + [-W/2, W/2 + B]$. The term in the brace is a periodic function, corresponding to the Fourier series $F_{2n\pi/(W+B)+k_{f,i}}[u_{f,i}]$, $n = 0, \pm 1, \pm 2, \dots$. Eq. 3.19 evaluates the Hamiltonian element $\langle\psi_f|\phi|\psi_i\rangle$ in the reciprocal space by replacing $u_f^*u_i$ with $u_c^*u_c$. The previously neglected term $e^{i\mathbf{k}_0\mathbf{r}}$ in the polarization potential contributes to the delta function.

$$\langle\psi_f|\phi|\psi_i\rangle = \sum_{k=\frac{2\pi n}{W+B}} F_{k+k_i-k_f}[u_c^*u_c] \left\{ F_{-k+k_{0z}}^{(0)}[\phi] + F_{-k+k_{0z}}^{(1)}[\phi] \right\} \delta(\mathbf{k}_i - \mathbf{k}_f + \mathbf{k}_0) \quad (3.19)$$

As discussed before, due to the $+1$ parity of $F_k[u_c^*u_c]$ the asymmetric components of the Fourier transformed potential only make minor contributions to the term $\langle\psi_f|\phi|\psi_i\rangle$. This effect is especially for the dominant transition processes, i.e. emitting phonons near the zone center ($k_{0z} \sim 0$). Therefore the major contribution comes from S_k^1 for the odd l or from S_k^2 for the even l . To characterize the reduction effect on the energy relaxation rate of electrons, Eq. 3.20 shows the ratio of the screened polar electron-phonon coupling strength (G_0 to the 0th order and G_1 to the 1st order) to the unscreened strength G_u . The integral over the whole reduced Brillouin zone needs to be incorporated, as well as a summation over the branches of polar phonons and the electronic sub-bands[129, 130]. In Eq. 3.20 the summation $\sum_{k'}$ is over the Fourier series with $k' = \frac{2\pi n}{W+B}$ ($n = 0, \pm 1, \pm 2, \dots$) and kdk denotes the integral element over the planar wave vector k of the polar mode (i.e. k_{0xy} in the previous sections). a_l represents the lattice constant. For

simplicity the average lattice constant of the component materials has been adopted for the numerical calculation, allowing little error as the MQW-SL structure is strain-balanced.

$$\begin{aligned}
 G_u &= \int_{-\frac{\pi}{W+B}}^{\frac{\pi}{W+B}} \int_0^{\frac{\pi}{a_l}} \left| \sum_{k'} F_{k'+k_z} [u_c^* u_c] F_{k'+k_z}^{(0)} [\phi] \Big|_{\bar{n}=0} \right|^2 k dk dk_z \\
 G_{0,1} &= \int_{-\frac{\pi}{W+B}}^{\frac{\pi}{W+B}} \int_0^{\frac{\pi}{a_l}} \left| \sum_{k'} F_{k'+k_z} [u_c^* u_c] F_{k'+k_z}^{(0,1)} [\phi] \right|^2 k dk dk_z \\
 R_0 &= \frac{G_0}{G_u} \quad R_1 = \frac{G_0 + G_1}{G_u}
 \end{aligned} \tag{3.20}$$

The spatially dependent carrier concentrations n_w and n_b are calculated in Eq. 3.21 by summing over the populations from the lowest sub-bands until being converged. The energy of a low-lying sub-band has negligible dispersion[136] and is denoted by a constant E_j . With ultra-fast carrier scattering their statistics can be described by the Fermi functions.

$$n_{w,b} = \frac{\sum_{e,h} \sum_j n_{w,b}^j \int_0^\infty f(E_j + E_{xy}) D^j(E_{xy}) dE_{xy}}{W + B} \tag{3.21}$$

In Eq. 3.21, $\sum_{e,h}$ indicates the summation of electron and hole concentrations, and $\sum_j$ ($j = 1, 2, \dots$) is the summation from the lowest energy sub-bands. $n_{w,b}^j$ is the respective probability of a carrier in the well or barrier layers, corresponding to an electronic state at the j -th sub-band. It is calculated from the envelope wavefunction of the state. $f(E)$ is the Fermi function with dependence on the carrier temperature and the electro-chemical potential. The two-dimensional density of states $D^j(E_{xy})$ relates to the two-dimensional effective mass of the carrier.

Under the effective mass approximation the Hamiltonian on the envelope wavefunction may be written as $-\frac{\hbar^2 \Delta}{2m_w} u_w(z) - (\frac{\hbar^2 \Delta}{2m_b} - V) u_b(z)$ in the MQW-SL

structure, where u_w, u_b are the periodic rectangular functions. Eq. 3.22 has been obtained by separating Δ into $\frac{\partial^2}{\partial z^2} + \Delta_{xy}$ where $\Delta_{xy} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$. The envelope wave function $\phi(x, y, z) = \phi_z(z)\phi_{xy}(x, y)$. It includes a conventional one-dimensional MQW-SL equation and an equation describing the planar wavefunctions across the stacking layers.

$$\begin{aligned}
 E_z^j \phi_z^j &= \left[-\frac{\hbar^2}{2m_w} \frac{\partial^2}{\partial z^2} u_w(z) - \left(\frac{\hbar^2}{2m_b} \frac{\partial^2}{\partial z^2} - V \right) u_b(z) \right] \phi_z^j \quad (3.22) \\
 (E^j - E_z^j) \phi_{xy}^j &= \frac{1}{2} \left\{ \left[-\frac{\hbar^2}{n_w^j W + n_b^j B} \left(\frac{n_w^j W}{m_w} + \frac{n_b^j B}{m_b} \right) \Delta_{xy} \right] + H_p^j \right\} \phi_{xy}^j \\
 H_p^j &= - \left(\frac{1}{m_w} - \frac{1}{m_b} \right) \left[\frac{n_b^j B}{n_w^j W + n_b^j B} u_w(z) - \frac{n_w^j W}{n_w^j W + n_b^j B} u_b(z) \right] \hbar^2 \Delta_{xy}
 \end{aligned}$$

$n_{w,b}^j$ is calculated from the solution of the 1st equation in Eq. 3.22 where the superscript j refers to the j -th sub-band. In the case of $m_w \approx m_b$, if considering H_p as the perturbation Hamiltonian which characterizes the small spatial fluctuation of the potential, the 1st-order perturbed energy shift $E^{j(1)} = \langle \phi^j | H_p^j | \phi^j \rangle = 0$. This indicates the unperturbed Schrödinger equation gives the sufficiently accurate energy values up to the 1st order. Eq. 3.23 shows the two-dimensional effective mass corresponding to the j -th sub-band, obtained from the 2nd equation in Eq. 3.22. The two-dimensional density of states $D^j(E_{xy}) = m_{xy}^{*j} / \pi \hbar^2$.

$$m_{xy}^{*j} = (n_w^j W + n_b^j B) \left(\frac{n_w^j W}{m_w} + \frac{n_b^j B}{m_b} \right)^{-1} \quad (3.23)$$

3.2.1.5 Numerical results and discussion

The model has been adopted to calculate the reduction factors $R_{0,1}$ for the $\text{In}_{0.25}\text{GaAs}/\text{GaAsP}_{0.33}$ MQW-SL structure, of which the steady-state carrier temperatures have been measured by Hirst[99]. Prior to the calculation the carrier distributions need to be pre-set in order to compare the screening

effects between structures with different layer thicknesses. Here normalized carrier statistics with the carrier temperature of 400K have been assumed, in correspondence to the fitting results in Hirst's experiment. A large splitting between the quasi-Fermi levels (1eV) has also been adopted. As a result, the carrier concentrations within the well layers and the barrier layers are calculated as being around 10^{23} m^{-3} and 10^{21} m^{-3} , respectively.

The compositions of the ternary semiconductors adopted in the computation are in correspondence to Hirst's report. The values of the respective bandgaps and the carrier effective masses are calculated from empirical expressions[137, 138]. It is noted that strain effects are neglected in this calculation. The results of the reduction factors are illustrated in Fig. 3.20.

Table 3.8: Material parameters for $\text{In}_{0.25}\text{GaAs}/\text{GaAsP}_{0.33}$ MQW-SLs

Component	Bandgap (in unit of eV)	Electron/hole effective mass (in unit of the free electron mass)
$\text{In}_{0.25}\text{GaAs}$	1.077	0.0539 / 0.4644
$\text{GaAsP}_{0.33}$	1.858	0.0868 / 0.5263

From Fig. 3.20, due to the carrier screening the electron cooling rate is the most reduced for the MQW-SL structure with a thick well layer and a thin barrier layer. The left figure shows the 0-th order reduction factor R_0 which is relevant to the average carrier concentration $\bar{n}$. For the structure with a thick well layer or a thin barrier layer the energies of the electronic sub-bands are lowered. This leads to a higher average carrier concentration and therefore a more reduced coupling strength.

The right figure in Fig. 3.20 illustrates the 1st-order approximation R_1 of the reduction factor. Its difference from R_0 results from the contrast between the carrier concentrations in different layers. The polar coupling in

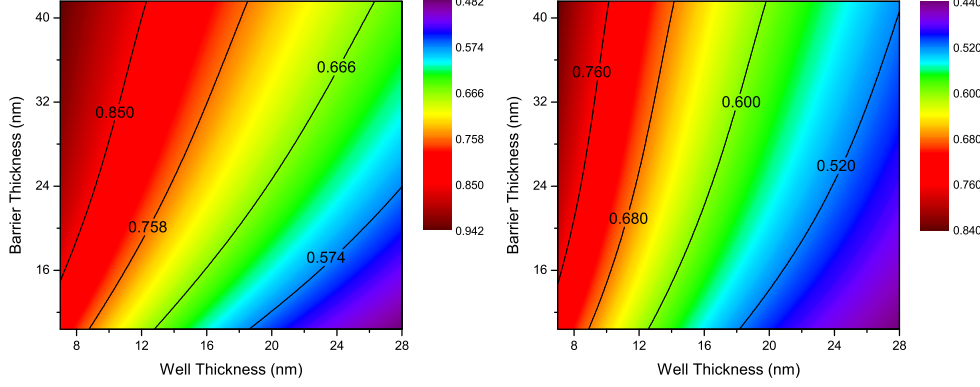


Fig 3.20: The reduction factor of the polar phonon emission rate (or electron cooling rate) for $\text{In}_{0.25}\text{GaAs}/\text{GaAsP}_{0.33}$ MQW-SL structures with different layer thicknesses (Left: R_0 , Right: R_1)

the MQW-SL predominantly comes from the well-confined modes due to their large overlap with wavefunctions of the low-lying electronic states. On the other hand these modes are strongly screened by the high carrier populations in the wells. Therefore a large spatial contrast of the carrier concentrations results in a further reduction of the coupling strength. This corresponds to the decrease of the reduction factor in the right figure compared to the left figure.

The difference between R_0 and R_1 is minimized if the layer thicknesses in the MQW-SL structure are insufficient compared to the Debye length, which characterizes the effective dimension of carriers taking part in the static screening[134]. With thicker layers the confined polar mode in the MQW-SL has a greater tendency to be screened merely within the layer of confinement. It leads to a more significant reduction of the coupling strength as the well-confined modes are screened by a higher carrier population. The phenomenon is illustrated in the right figure of Fig. 3.20, in which the values for structures with thicker layers are more reduced compared to those in the

left figure.

To compare the theoretical analysis with the experimental data, two sets of $\text{In}_{0.25}\text{GaAs}/\text{GaAsP}_{0.33}$ MQW-SL structures are carefully examined. The relevant measurements demonstrated steady-state PL results of two samples: one with 7nm well and 10.4nm barrier while the other with 14nm well and 20.8nm barrier[99]. The carrier temperatures fitted from the PL data are relatively high for the sample with thicker layers, indicating a reduced carrier cooling rate. Correspondingly the theoretical reduction of electron energy relaxation has been calculated for these two structures. The 0-th order/1-st order reduction factors are 0.80/0.73 for the one with thinner layers and 0.73/0.62 for the other. As illustrated in this numerical result, the MQW-SL structure with thicker layers demonstrates a larger reduction on the polar coupling strength and hence the electron cooling rate. This is consistent with the experimental conclusions.

Here the ratio of $G_{0,1}$ to G_u has been calculated, as the indicative value showing the trend when varying the layer thicknesses. In addition the detailed relaxation rate due to the screened electron-phonon coupling can be obtained, merely by incorporating the actual dispersion relations[139, 140, 135] and the mode-dependent wavefunctions [135, 136] in Eq. 3.19 and Eq. 3.20. This technique is especially useful for designing the HCSC with minimized carrier cooling rate as it helps to optimize the component materials and the layer thicknesses of the MQW-SL absorber.

3.2.1.6 Conclusion

The effect of carrier screening on the energy relaxation of electrons in polar-semiconductor multiple-quantum-well superlattices has been theoretically analyzed with an electro-static model. The Fourier transformed potentials

generated by the polar phonon modes have been calculated up to the 1-st order approximation. The screening effects due to the average carrier density and the concentration contrast have been treated separately, corresponding to the 0-th and 1-st corrections of the solution respectively. The 1-st order correction heavily depends on the relative thickness of the bi-layers compared to the characterization length of the static screening. As a result, for thick layers the spatial non-uniformity of the carriers leads to a further reduction of the polar coupling strength compared to the case of a uniform distribution. The numerical results demonstrate that the energy relaxation rates of electrons are more reduced in the superlattice structure with thicker layers, especially when the 1-st order correction is taken into account. The model correctly explains the recent experimental observations. It also helps the design of the MQW-SL absorber for the realization of HCSC.

3.2.2 Calculation of energy relaxation properties of polar interactions and phonon anharmonicity coupling

In this section the energy relaxation time of electrons in $\text{InN} - \text{In}_x\text{Ga}_{1-x}\text{N}$ superlattices is computed considering the multi-stage energy loss of electrons. As a result the effect of each stage in the relaxation process is revealed for superlattice absorbers. The energy relaxation rate figures are obtained for different material systems of the absorber, i.e. for different combinations of indium compositions and the thicknesses of well and barrier layers in the superlattices. The optimum material system for the absorber has been suggested, with the potential to realize HCSCs with high efficiency. This work has been presented orally in SPIE Optics + Photonics 2012, and then has been published in “Analysis on carrier energy relaxation in superlattices and its implications on the design of hot carrier solar cell absorbers” by Y. Feng

et al., 2012, in SPIE Solar Energy and Technology, pages 847103-847103, International Society for Optics and Photonics[141].

3.2.2.1 Introduction

The crucial criteria to obtain high efficiency from the hot carrier effect is to minimize the energy relaxation rates of carriers in the absorber layer, where most of the electron-hole pairs are generated from absorbing photons.[9] The energy relaxation of carriers occurs with several sequential processes. For polar materials carriers loss energy by emitting polar optical phonons.[142, 12] The increased occupancy of polar phonon modes feeds energy back to carriers, unless the occupied populations are relaxed by phonon decay and phonon diffusion. Due to the anharmonicity of the crystal potential, three-phonon interaction or even higher-order phonon-coupling can occur, resulting in an energy relaxation of polar modes.[84, 143] Phonon diffusion, on the other hand, comes from the spatial non-uniformity and continually relaxes the occupancies of phonon modes generated from hot electrons or hot phonons.

The electron-phonon interaction lifetimes [144, 12] and the lifetimes of the polar optical modes [145, 108] have been computed in bulk III - V semiconductors, but in superlattice materials the carrier cooling processes are not completely understood. Experimental evidence demonstrates a reduced cooling rate in some superlattice system.[19] The explanation partly lies on the non-equilibrium distribution of hot electrons and high-lying optical phonons. The detailed computation, based on the balance at steady state of the flow of phonon emission, decay and diffusion, have not been well studied.

Here InN/In_xGa_{1-x}N multiple quantum-well superlattices (MQW-SL) with a wurtzite crystal structure are studied as the absorber of the hot carrier solar cell, due to the significant hot-phonon-bottleneck effects of their com-

ponent materials.[146] The reason mainly comes from the large contrast of the atomic masses, and hence a large band-gap between high-lying and low-lying phonon modes.[28, 108] The phonon band-gap effectively stop Klemens decay, i.e. one high-lying phonon decaying into two low-lying phonons[84], and produces a hot population of polar phonons, feeding energy back to electrons.[107] InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ have very similar lattice structures, with almost the same lattice constant (for large x). This benefits the solar energy conversion, in terms of both the carrier transport and the reduction of recombination sites. The 1-dimensional superlattice structure ensures a continuous density of electronic states and hence a broad-band absorption. The absorption is further enhanced by the small electronic band-gap of InN.

3.2.2.2 Phononic model

The dispersion relations of phonon modes in superlattices have been computed with a 1-dimensional atomic-plane model. Since the epitaxial growth is intended to be along the high-symmetry $\Gamma - A$ direction for both InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers, the periodicity of MQW-SL and hence the zone-folding is also along this direction. For simplicity we assume that the mode frequency of each zone-folded mini-band only depends on the vertical component of the wave-vector (i.e. along $\Gamma - A$). The reason for the assumption partly comes from the high concentration of electron-emitted polar phonons around the zone-centre, where the dispersions are relatively flat compared to the mini-gaps. In the wurtzite structure periodic atomic planes with alternating elements align perpendicular to the $\Gamma - A$ direction. If only considering the vertical component of wave-vectors, all atoms in one atomic plane vibrate in phase and can be treated as one uniform displacement. The phononic model adopted here treats a 1-dimensional chain with an equal length of

the superlattice periodicity, taking into account the plane-to-plane force constants. The plane-to-plane force constants are calculated by adopting the conventional Keating potentials for all bonds. (Eq. 3.24)

$$U_k = \frac{3\alpha}{16r_0^2} \sum_{j=1}^4 (\mathbf{r}_{ij}^2 - r_0^2)^2 + \frac{3\beta}{8r_0^2} \sum_{j=1}^4 \sum_{k>j}^4 (\mathbf{r}_{ij} \mathbf{r}_{ik} + \frac{r_0^2}{3})^2 \quad (3.24)$$

where α and β are the bond-stretching and bond-bending force constants. $\mathbf{r}_{ij}$ is the vector from a given atom i to one of its four nearest neighbours j . The two types of atoms are modeled as positive-charged and negative-charged points respectively to take into account the long-range Coulomb interatomic forces. *Ab-initio* calculated Born effective charges[147], as well as the bond-stretching and bond-bending force constants[148, 149], are adopted for InN and GaN. Under harmonic approximation the planar interaction model generates the phonon dispersions along $\Gamma - A$ direction for InN and GaN. The calculated zone-centre LO and TO energies are around 9.1eV and 6.8eV for GaN, and 7.2eV and 5.5eV for InN.

For the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layer we have atomic planes which consist of both indium and gallium. The force constants and atomic mass for these planes are regarded as weighted averages of these parameters for pure InN and GaN. The reason comes from the large number of atoms in one atomic plane, where indium and gallium atoms are mixed uniformly, following the mole ratio of $x : 1 - x$. The computed phonon dispersions of superlattices show confined optical modes and zone-folded acoustic branches. The confined nature of the optical modes comes from the large contrast between the atomic masses and the force constants of the two component materials, i.e. InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$.

3.2.2.3 Electronic model

The electronic structures, involving the wavefunctions and energies of all the states, can be calculated by using the Kronig-Penney model for superlattices.[150] By doing that the band structure of each component, i.e. InN or $\text{In}_x\text{Ga}_{1-x}\text{N}$, is assumed as parabolic, and is characterized by two parameters: the bandgap and the carrier effective mass. The theoretical bandgap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ has been expressed as a function of x [49], while the effective mass of GaN has been adopted for the barrier layer. In equilibrium conditions space charges occur in the well layers (negative) and in the barrier layers (positive) due to the difference of their electron affinities. The electron affinity of GaN is significantly lower than that of InN, giving a larger off-set of the conduction band edge rather than that of the valence band edge. In the superlattices consisting of InN and $\text{In}_x\text{Ga}_{1-x}\text{N}$, similar band shifts are expected. The conduction band off-set V_B , or the barrier height of electrons, has been taken into Eq. 3.25 for the dispersion relation.

$$\begin{aligned} \cos[k_z(L_W + L_B)] &= \frac{1}{2} \left(\frac{k_W L_B}{k_B L_W} + \frac{k_B L_W}{k_W L_B} \right) \sin(k_W L_W) \sin(k_B L_B) \\ &\quad + \cos(k_W L_W) \cos(k_B L_B) \end{aligned} \quad (3.25)$$

$$k_W = \sqrt{2mE(k_z)}$$

$$k_W = \sqrt{2m(E(k_z) - V_B)}$$

where k_z is the Bloch wave-vector of electrons in superlattice and $E(k_z)$ is its corresponding energy, with the reference level of the conduction band edge of the well material. L_W and L_B are the well thickness and the barrier thickness. Apart from the dispersion relations the electron envelope wavefunction for each state has been calculated, as the evaluation of the electron-phonon coupling strength requires calculation of the overlap integral. Coupling of electronic waves in different layers generates widely-spread wavefunctions

with mixed parities.[150]

3.2.2.4 Electron-phonon interaction

For polar semiconductors the energy relaxation of electrons is predominantly through polar interactions with optical modes rather than through electron-phonon coupling due to the deformation potential.[12] In bulk wurtzite-structured materials only one branch of optical modes are infrared-active.[144] Free carriers are able to respond to the high-frequency polarization field generated by these polar modes. In the MQW-SL consisting of two component wurtzite-structured layers, the polar modes sit in similar positions. For $\text{InN}/\text{In}_x\text{Ga}_{1-x}\text{N}$ superlattices these modes lie in the high-lying optical branches, separated from the low-lying modes by a significant energy gap. Therefore the generated polar phonons stay in high-lying branches with a long relaxation time in terms of decay into low-lying modes, leading to a non-equilibrium phonon distributions. This phonon-bottleneck effect has been investigated during the recent decades for both bulk materials[146, 151] and nano-structured materials[19, 152].

The calculation of the rate of polar interaction between hot electrons (here emission by holes is not of our concern) and polar phonons are based on the Fröhlich-type Hamiltonian and the 1-st order perturbation theory. In 1-dimensional superlattices the elements of the Fröhlich-type Hamiltonian can be represented in Eq. 3.26, with an overlap integral between the envelope wavefunction of electrons and the effective electric potential generated by the lattice mode. The effective potential can be calculated by taking the divergence of the polarization field of each mode. For confined modes the potential decays exponentially when being away from the layer of confinement[121]. The effect of static screening from the populated car-

rier density has been taken into account by adopting the Debye screening length, which is proportional to the carrier density N [153]. A recent report has proved the significant effect of screening on the polar interactions in heavily-doped InN[38].

$$H_{k'k}^2 = \frac{e^2 \hbar \omega}{8V} \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon} \right) \left[n(\mathbf{q}, \omega) + \frac{1}{2} \mp \frac{1}{2} \right] \frac{1}{q^2} R_1(\mathbf{q}) \times \delta(\mathbf{k}' - \mathbf{k} \pm \mathbf{q}) [A_l \int dz \phi_j^*(z) \phi_{j'}(z) I_l(z)]^2 \quad (3.26)$$

where ω is the angular frequency of the lattice mode of interest and $\mathbf{q}$ is its wavevector. V is the volume of the superlattice. ϵ and ϵ_∞ are the static permittivity and the optical permittivity respectively. $n(\mathbf{q}, \omega)$ is the occupation number of the mode $(\mathbf{q}, \omega)$; the term $n(\mathbf{q}, \omega) + 1$ corresponds to the process of phonon emission of the mode while $n(\mathbf{q}, \omega)$ corresponds to phonon absorption. $R_1(\mathbf{q})$ is the $\mathbf{q}$ -dependent reduction factor due to carrier screening whose form has been given in Sec. 3.2.1. Notice here only the major order is included, i.e. the order $k' = 0$ in Eq. 3.20, for simplicity. The delta function $\delta(\mathbf{k}' - \mathbf{k} \pm \mathbf{q})$ indicates the conservation of the crystal momentum. $\phi_j(z)$ is the one-dimensional electron envelope function and $I_l(z)$ is the effective potential of the l -th confinement mode, of which the corresponding modulation function requires a normalization factor A_l [154].

3.2.2.5 Phonon-phonon interaction

The interactions between phonons are due to the anharmonicity of the crystal potential. The dominant anharmonicity is of the 3rd-order and leads to a three-particle process[84]. Fission of one phonon into two can happen as well as fusion of two phonons. The potential of anharmonicity is taken as the interaction Hamiltonian, and ideally a tensor coefficient presents

the interaction strengths between different polarizations of the three modes involved[16]. However the tensor of the anharmonicity coefficient is hard to determine experimentally and it is still not clear for some nitrides. Therefore we have adopted a mode-average coefficient instead which can be easily determined from experiment $F = \gamma/\bar{c}$, where γ is the temperature dependent Grüneisen's constant and $\bar{c}$ is the average acoustic speed. The reported values for InN/In_xGa_{1-x}N have been adopted for the lifetime calculation of two types of confined modes respectively[108].

$$c(\omega, \omega', \omega'') = -\frac{i}{\sqrt{N}} \frac{2M}{\sqrt{3}} F \omega \omega' \omega'' \quad (3.27)$$

where c is the three-phonon coupling strength. M is the average atomic mass and N is the atom density. ω , ω' and ω'' are the respective angular frequencies of the three modes involved in the interaction. The elements of the interaction Hamiltonian due to the 3rd order anharmonicity contain an overlap integral of modulation functions of all three modes[155].

$$H_{qq'q''}^2 = \frac{\hbar^3}{MM'M''V^2} \frac{|c(\omega, \omega', \omega'')I(\mathbf{k}, \mathbf{k}', \mathbf{k}'')|^2}{\omega\omega'\omega''} \times [(n(n'+1)(n''+1) - (n+1)n'n'')] \quad (3.28)$$

3.2.2.6 Energy relaxation time of systems in equilibrium

To compare the relaxation properties of hot electrons and hot polar phonons under constant illumination (for simulating the operation of solar cells) between different superlattice structures, the energy relaxation times are computed for each material structure. The energy relaxation time of electrons due to the emission of polar phonons is defined as $\Gamma_e = \frac{E_e}{\sum \epsilon_p w_p}$, where E_e is the total energy of the electron system and the summation in the denominator is over the polar modes, with ϵ_p and w_p referring to the energy and emission rate of each mode. To give indicative and comparable relaxation

time values for all MQW-SL structures the distributions of electrons and phonons are pre-set. In the case of phonon emission the electrons are set as be in equilibrium at $T_C=1000\text{K}$, while the reservoir including all phonons maintains at room temperature (300K).

For the decay of excess polar phonons, all phonons can no longer be assumed to be in equilibrium, in order to avoid zero net transition rates. Here we assume the high-lying modes are in equilibrium at 1000K while the low-lying modes are at room temperature. The setting is physical since the energies of the emitted polar phonons are quickly re-distributed into other high-lying modes due to the phonon-phonon interaction (through Ridley channel or Barman-Srivastava channel).[108] Therefore the high-lying branches are populated very fast which can be regarded as a particle system with high-level interactions. On the other hand, the low-lying branches are very difficult to populate partly due to the large phononic gap. Another reason is that the energies of the decayed low-lying phonons are immediately re-distributed into the whole system of the low-lying phonons, because their interactions are very fast due to the quasi-continuous phonon density of states and their higher occupancies. Besides, the excess phonons in acoustic branches will quickly diffuse out, being relaxed into an equilibrium occupancy at room temperature. Therefore the low-lying phonons can be regarded as a reservoir at room temperature. The energy relaxation time of the hot phonons is defined as referring to the energy flow out of the high-lying LO phonon system, i.e. $\Gamma_{ph} = \frac{E_{hph}}{\sum \epsilon_{lph} w_{lph}}$, where E_{hph} is the total energy of the high-lying LO phonons and the summation in the denominator is over the modes of high-lying LO phonons, with ϵ_{lph} and w_p indicating the energy and annihilation rate of each mode.

The transition rates are calculated from the 1st order perturbation the-

ory: $w = \frac{2\pi}{\hbar} |H_i|^2 \delta(\Delta E)$, where H_i is the interaction hamiltonian given by Eq. 3.26 and Eq. 3.28 and ΔE is the energy change during the transition, i.e. the difference of the total energy of the final states and that of the initial states. The 1st order perturbation theory is only valid for the case that the interaction energy much weaker than the self-energy of particles involved, and the interaction should last for sufficient long time. For electron-phonon interaction, although there is some deviation resulting from the further decay of the emitted phonons, the approximation is still accurate enough and has been adopted in most of the relevant work. [156, 108]

3.2.2.7 Method for steady-state carrier cooling mechanism

In reality the high-lying phonon modes have occupancies which deviate from equilibrium, for they interact with two reservoirs with very different statistics: in some branches of the high-lying region (i.e. polar optical modes) phonons are quickly generated by interacting with the hot electrons, while each high-lying phonon then decays into a low-lying phonon and a high-lying phonon with relatively lower frequency (Ridley channel or Barman-Srivastava channel). The hot electron system is regarded as a reservoir in equilibrium, with temperature higher than room temperature, because of their quick mutual interactions and continuous photon energy supply when the device operates at steady state. The low-lying phonons are assumed to be in equilibrium at room temperature. Only the high-lying phonons are assumed as being in non-equilibrium, and for which the occupancies are to be calculated.

In this work the non-equilibrium occupancies of high-lying modes have been computed under the steady-state condition, with the assumptions that the emission of polar phonons are merely due to hot electrons (assumed as 1000K). In fact holes gain less energy from photo-generation than electrons

and are more easy to be thermalised due to their larger effective mass.[157] The computational strategy is based on the time-domain iteration and Monte Carlo simulation. Initially a guessed occupancy function is adopted for high-lying modes and the fixed step-time is set for the iteration. Each iteration starts from the generation of a random set of electrons according to the Fermi statistics, with information of their energies and momentums. For each electron the probability of emitting phonons for each polar mode is calculated; after one iteration the occupancies of the polar modes increase accordingly. Then the transition rates of all possible three-phonon processes are calculated within the same time interval, leading to a re-normalization of all phonon modes. The computation process is iterated until saturation on the mode occupancies is reached, resulting in the steady-state occupancies of all high-lying modes.

In order to simulate the dynamics of particle interactions it is necessary to consider the phonon diffusion, which is an alternative relaxation path of hot phonons. In fact both Ridley and Barman-Srivastava channels conserve the phonon number in high-lying branches, while at steady state the emission of optical phonons from hot electrons must be balanced by some relaxation path. In ideal InN/In_xGa_{1-x}N SL the relaxation is from phonon diffusion most probably. A simplified model has been suggested, where an average product of mean free path and group velocity is adopted for all optical modes. In fact the wave-vector-dependent diffusion rates are smeared, for the wave-vector of a phonon will be randomized after several successive three-phonon processes.

$$\frac{\partial n_{\mathbf{q},w}}{\partial t} = B_{\mathbf{q},w} - A_{\mathbf{q},w}n_{\mathbf{q},w} + \tau v^2 \frac{\partial^2 n_{\mathbf{q},w}}{\partial \mathbf{x}^2} \quad (3.29)$$

where $n_{\mathbf{q},\omega}$ is the occupation number at mode $(\mathbf{q}, \omega)$. $G(\mathbf{q}, \omega, \mathbf{x}, t)$ is the generation rates of polar phonons, emitted by hot electrons. With a

linear approximation, $A_{\mathbf{q},w}$ is defined as its averaged occupancy-derivative $A_{\mathbf{q},w} = -\overline{\partial G(\mathbf{q},\omega)}/\overline{\partial n_{\mathbf{q},w}}$. At steady state Eq. 3.29 gives the solution Eq. 3.30 if canceling the dependance on $B_{\mathbf{q},w}$.

$$\tau v^2 \frac{\partial^2 n_{\mathbf{q},w}}{\partial x^2} \Big|_{x=0} = \frac{A_{\mathbf{q},w}}{\cosh(W/2\sqrt{\alpha_{\mathbf{q},w}}) - 1} [n_{\mathbf{q},w} - n_{\mathbf{q},w}^{eq}(T_{rt})] \quad (3.30)$$

where $\alpha_{\mathbf{q},w} = \tau v^2 / A_{\mathbf{q},w}$, $n_{\mathbf{q},w}^{eq}(T_{rt})$ is the occupation number of each mode, in equilibrium at room temperature T_{rt} . W is the dimension along the direction of phonon diffusion, and the superlattice slab is placed from $-W/2$ to $W/2$. The equation provides the occupation annihilation rate at the middle of the system, i.e. $x = 0$.

3.2.2.8 Numerical results: polar phonon emission

The energy relaxation times referred to the polar phonon emission are illustrated in Fig. 3.21, for all the MQW-SL configurations, i.e. for different well and barrier thicknesses and different barrier materials. 18×18 combinations of the thicknesses are sampled as representing all the possible structures from 2nm to 9nm. The number of combinations comes from the fact that a complete well/barrier layer should include a integer number of unit cells. Fig. 3.21 is generated by interpolating the relaxation time data of the sampling combinations.

From Fig. 3.21 the general trend indicates that the thinner barrier layer gives the longer energy relaxation time of the electrons. There are several possible reasons to explain the observation. The screening of polar modes strongly depends on the carrier concentration, which favours a wide well layer and a thinner barrier layer. In fact the MQW-SL structure with a wider well layer has lower confined energy levels, leading to a higher electron occupancy, while in SL with a thinner barrier layer the average potential of electrons is reduced resulting in lower energy levels of non-bound states. Thicker wells

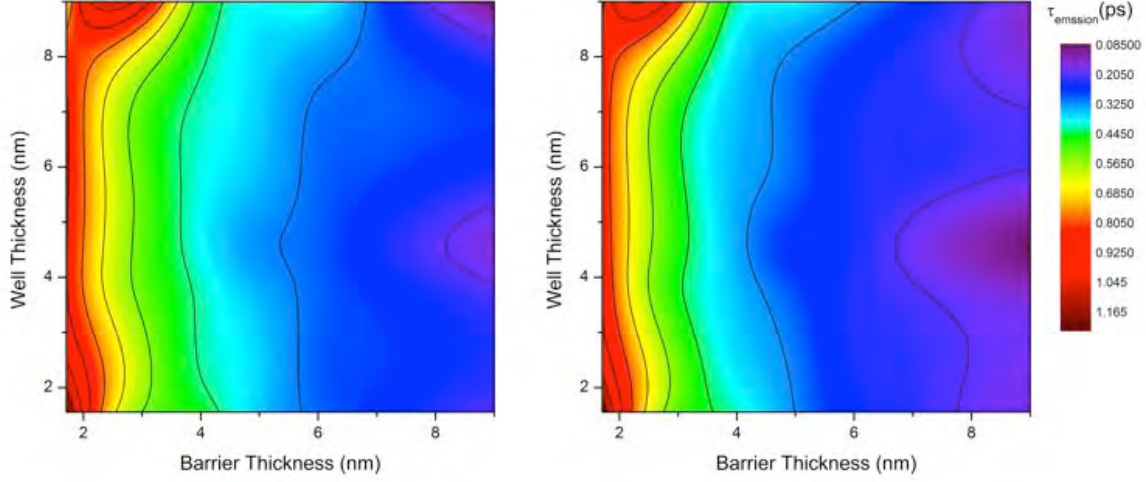


Fig 3.21: Energy relaxation times of the hot electron system (1000K), in the reservoir of phonons (300K), with superlattice structures of different well/barrier thicknesses and $\text{In}_x\text{Ga}_{1-x}\text{N}$ compositions (Left: $x=0$ Right: $x=0.2$)

also have a greater total number of states which can be occupied and a greater density of these states leading to higher concentrations. The high carrier concentration significantly screens the potential of polar modes, and hence demonstrates a reduced cooling rate of electrons. It is also possible that the larger well-to-barrier ratio increases the relaxation time because InN has flatter dispersions than that of GaN . For MQW-SL the zone-folding of flat dispersions results in very narrow mini-bands, which slows down the rates of intra-band transitions, while the inter-band transitions are prevented by the mini-gaps. Another reason of the trend results from the multiple energy levels of the confined polar modes in the MQW-SL. If the periodic dimension of the SL becomes larger then the increased number of these energy levels could increase the number of allowed transitions, and hence the cooling rate. This effect favours a thinner well layer as well, which balances off its benefits

due to the first two reasons. Therefore the preferable SL structure involves a thinner barrier layer, while having little dependence on the well thickness, as shown in Fig. 3.21.

As to the effect of different indium content x in the barrier material $\text{In}_x\text{Ga}_{1-x}\text{N}$, the contrast between the minimum and maximum relaxation times becomes smaller for a larger x , if comparing the two figures in Fig. 3.21. In fact with a larger indium content, the electronic and phononic properties of $\text{In}_x\text{Ga}_{1-x}\text{N}$ are closer to those of bulk InN , and hence the relaxation time values will shift towards the value of bulk InN . Hence the optimal structure with the longest relaxation time (in terms of the hot phonon emission) exists in the case of $x=0$, while on the other hand the high potential barrier is detrimental to the carrier transport. In terms of designing hot carrier solar cells, a comprehensive consideration is necessary to take all these properties into account.

3.2.2.9 Numerical results: three-phonon process

The energy relaxation times of high-lying longitudinal optical phonons are demonstrated in Fig. 3.22, for different combinations of well and barrier thicknesses. For indium mole fraction $x=0$ (left figure), the contrast of relaxation times are larger than that of the case for $x=0.2$ (right figure); this is reasonable as more indium content in the barrier layer would make the structure closer to bulk InN . Both figures show the same trend with different barrier/well thicknesses: the relaxation time increases with thicker well layers and thinner barrier layers, in spite of some irregular local variations. The regular variation mainly results from the change of numbers of InN -like modes and InGaN -like modes.

To explain the variation, we need to first examine the phonon dispersions

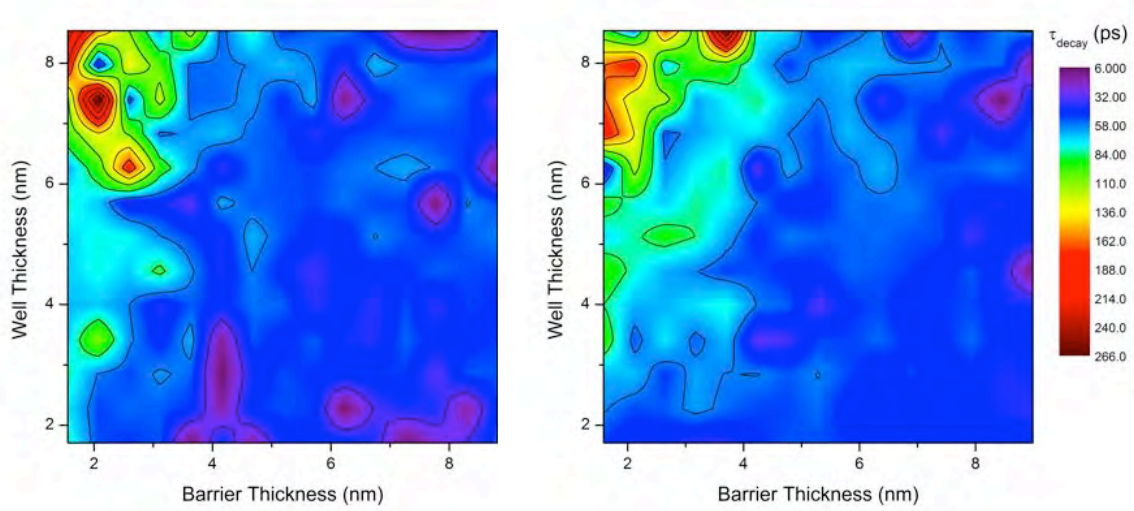


Fig 3.22: Energy relaxation times of the high-lying LO phonon system (1000K), in the reservoir of 1000K high-lying phonons and 300K low-lying phonons, with superlattice structures of different well/barrier thicknesses and $\text{In}_x\text{Ga}_{1-x}\text{N}$ compositions (Left: $x=0$ Right: $x=0.2$)

of the MQW-SL. Taking $x=0$ as an example, the left figure in Fig. 3.23 shows the dispersions of InN/GaN SL structure, with 6 layers of nitrogen atoms inside each layer (same for the InN layer and the GaN layer). From the number of atomic layers involved we could expect the same number of high-lying optical modes which are InN-like and GaN-like respectively. The GaN-like optical modes (blue color: solid line for LO, dashed line for TO) have much higher frequencies than the InN-like optical modes (green color), for the bond force constants of GaN are larger and the atomic mass of gallium is smaller. There are also four branches (orange color: two of LO and two of TO) corresponding to the interfacial (IF) modes, with frequencies between GaN-like modes and InN-like modes. From the right figure of Fig. 3.23, the vibrations are almost completely confined in the respective type of layers, for InN-like and GaN-like optical modes. For IF modes most of the vibrational

energy is within the 1st and 2nd nitrogen atoms from the interface, and hence has little overlap with InN-like or GaN-like modes.

Considering all three-phonon processes, only the Ridley channel and the S-B channel (decaying into a high-lying optical phonon and a low-lying optical phonon) are allowed due to the energy conservation law. As in wurtzite-structured SL, the difference between the acoustic branches and the low-lying optical branches becomes unimportant, and the low-lying branches can be separated into two categories: GaN-confined modes (red lines) and GaN-InN mixed modes (gray lines). In fact the InN-like low-lying modes sit within the allowed frequency band of GaN, which also excite vibrations in GaN layers. Therefore no InN-confined modes exist in the low-lying branches. Among all allowed three-phonon processes, GaN-like optical modes can decay into both types of low-lying modes (See the solid arrow and the dashed arrow in Fig. 3.23), while InN-like optical modes can only decay into the mixed modes for it only overlaps with the mixed modes. Besides, the energy gap between GaN-like LO modes and GaN-like TO modes is relatively large; hence the resulting low-lying phonons have relatively high energies, compared to the decayed low-lying phonons from the InN-like modes. Since the low-lying branches with high energies are generally flatter, leading to a larger joint density of states of transition, the decay rates of GaN-like LO modes could be enhanced further. Due to the two reasons explained above the GaN-like LO modes decay faster than the InN-like LO modes. Therefore with a thicker well layer (or a thinner barrier layer), the energy relaxation time of the high-lying LO phonon system becomes longer, for it introduces more InN-like modes (or fewer InGaN-like modes).

The energy relaxation time of 1000K high-lying LO phonon system (in the reservoir of 1000K high-lying phonons and 300K low-lying phonons) varies

from several picoseconds to several hundreds of picoseconds. The resulting order of magnitude matches reported experimental observations.[19, 56, 57] The irregular local variation occurs due to the formation of mini-gaps in the phonon energy spectrum. Some decays are blocked if resulting in phonon energies within the mini-gaps. Therefore by finely engineering the InN/In_xGa_{1-x}N SL structure (i.e. well/barrier thicknesses and indium composition), the effect of mini-gaps may significantly reduce the phonon decay rate, although practically this technique may be too idealized to be reliable. In reality the spatial non-uniformity of fabricated well/barrier layers (including defects and uneven indium distribution in In_xGa_{1-x}N) is hard to control, and could significantly affect the energy-dependent density of states of phonon modes. Its energy spectrum also strongly depends on the interfacial conditions. In the calculation we assume the InN/GaN interface strictly lies on the same atomic plane without any interfacial mixture of indium and gallium atoms. Finally even with ideal fabrication conditions there must be several layers of stressed atoms due to the lattice mismatch, whose equilibrium positions are shifted as well as their potentials in the crystal.

3.2.2.10 Numerical results: non-equilibrium distributions of high-lying modes

The non-equilibrium occupancies of all high-lying modes have been computed considering the processes of polar phonon generation, three-phonon interaction and hot phonon diffusion. Due to the limited resources of computation, only a fixed InN/In_xGa_{1-x}N MQW-SL structure has been taken into account, with three layers of unit cells stacking in each layer (layer thickness $\approx 2\text{nm}$). The slab is assumed to have a thickness of $100\mu\text{m}$ (around 25,000 bi-layers of InN and In_xGa_{1-x}N). For simplicity we only focus on the statistics at the middle of the slab, and hence Eq. 3.30 can be used to treat the phonon diffusion.

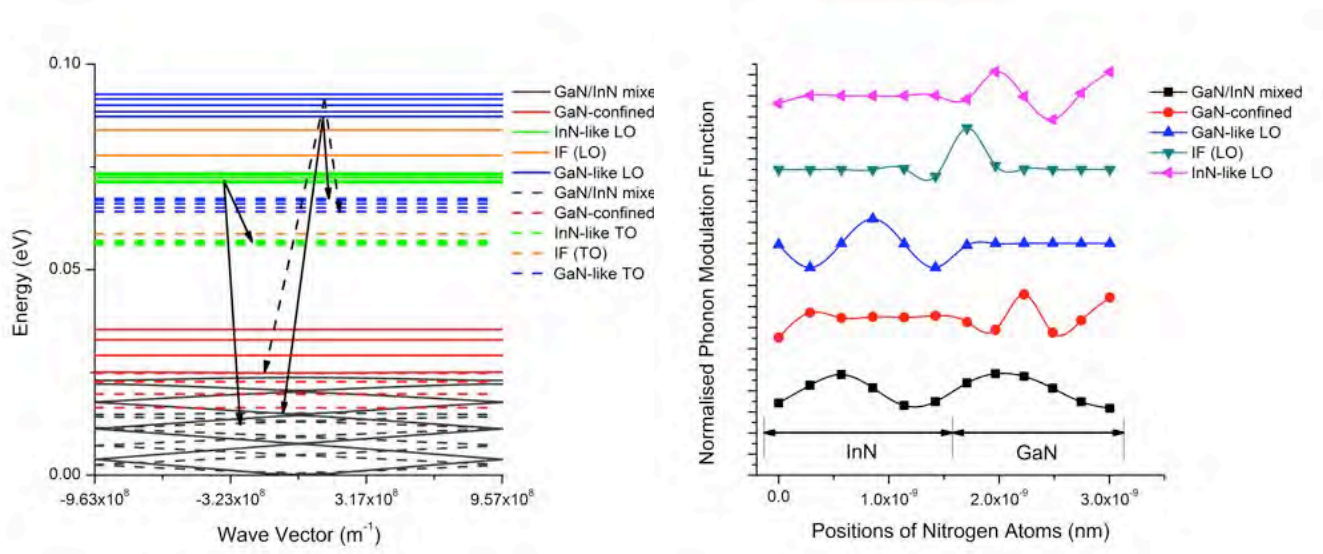


Fig 3.23: The left figure shows the calculated phonon dispersions of the InN/GaN MQW-SL along the $\Gamma - A$ direction, with two decay paths of GaN-like LO modes and one decay path of InN-like LO modes indicated by respective arrows. The right figure shows the phonon modulation function of a representative mode from each category of modes, computed from the eigenfunctions of the lattice dynamic equation. The transverse modes have similar modulation functions and hence only that of longitude modes are shown.

The left figure in Fig. 3.24 demonstrates the steady-state energy relaxation times of electrons for both cases of $x=0$ and $x=0.2$. With a larger diffusion parameter τv^2 , the hot high-lying phonons diffuse away faster creating a less occupied steady-state distribution. For $\tau v^2 > 1 \text{ m}^2/\text{s}$ the hot distribution of high-lying phonons no longer exist (thermalised phonon limit), and hence the relaxation time reaches the lower limit which is merely determined by the electron-polar phonon interaction. On the other hand due to the lack of Klemens decay the relaxation time does not have an upper limit, as the number of high-lying phonons can only be relaxed by hot phonon diffusion.

The right figure in Fig. 3.24 shows the occupation number of all the six

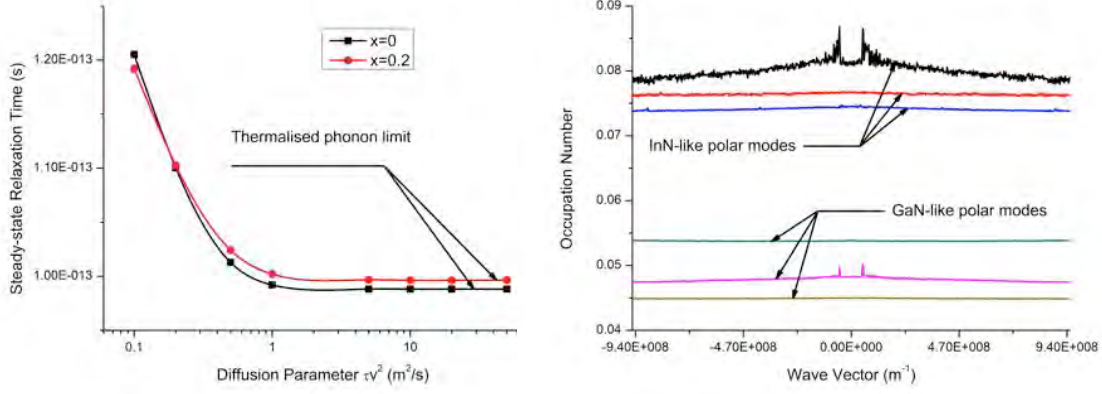


Fig 3.24: The left figure is the variation of energy relaxation times of electrons in a MQW-SL with three unit cells in each layer, on different diffusion parameters τv^2 ; the right figure shows the non-equilibrium occupation numbers of polar modes, for $\tau v^2 = 1\text{m}^2/\text{s}$ and $x=0$.

polar mode branches in the same structure ($x=0$). The value of the diffusion parameter adopted here is $\tau v^2 = 1\text{m}^2/\text{s}$. The three upper branches correspond to the InN-like polar modes and the lower three are for the GaN-like polar modes; a branch with a higher occupancy corresponds to a phonon branch with a lower frequency. From the figure the polar branch with the lowest energy has the steady-state distribution which deviates most from the equilibrium distribution, the reason for which lies in the overlap integral between the electronic state and the polar mode involved in the interaction. The first InN-like polar mode has a modulation function with a zero node, i.e without change of sign within one InN layer; therefore it interacts most strongly with the lowest confined electronic state which also involves a zero node. The other InN-like polar modes have weaker (odd number of nodes) or no interaction (even number of nodes) with the first confined electronic state due to their symmetry properties. As to the GaN-like polar modes, they are hard to populate because of the small electron concentration in the barrier

layers. Generally the occupation number gradually decreases from the zone center to the zone edge, while in the region close to zone center the occupancy drops because of the carrier screening effect on polar interactions. In fact by taking the screening of polar modes into consideration, the electrons can only interact with the ionic dipoles within the region characterized by the screening length, instead of the larger region between two neighbouring vibrational nodes. This reduces the interaction strength most for phonons located at the zone center.

3.2.2.11 Implication for the design of hot carrier solar cells

The nature of confinement in InN/In_xGa_{1-x}N MQW-SLs (with small x) enables different carrier relaxation properties from those in bulk materials, and hence provide possibilities to realize a long cooling time of electrons. In terms of the emission of polar phonons, a InN/In_xGa_{1-x}N MQW-SL structure with a thin barrier layer has a long relaxation time, while the phonon decay favours a SL structure with a thin barrier layer and a thick well layer. On the other hand, in terms of blocking the hot phonon diffusion, a thinner bi-layer of InN and In_xGa_{1-x}N benefits more, for in this structure phonon modes have a reduced group velocity along the vertical direction. With very thin barrier layers (less than two unit cells) the In_xGa_{1-x}N-like modes can no longer be completely confined and are mixed with the interfacial modes; in conclusion a SL structure with a reasonably thin barrier layer (around 2nm) and a reasonably thick well layer (around 10nm) has the potential benefit of reducing the overall carrier cooling rate. Increase of the indium content in the barrier layer could shift the material properties towards that of the bulk, which is not favourable in terms of the relaxation properties. But the design of hot carrier solar cells require the combined benefits of different material

properties: a high barrier height is inappropriate for the carrier transport, and hence practically some amount of indium in the barrier layer may benefit the overall performance of the cell.

3.2.3 Coulombic interaction between carriers based on a tight-binding treatment

In Sec. 2.3 the device model based on a relaxation time approximation has revealed a strong correlation between the carrier-carrier scattering rates and conversion efficiency of the device. It is important, when designing a hot carrier solar cell, to know the carrier scattering rates of the selected absorber material. However, until now there has not been a direct method to measure them experimentally. This thereby emphasizes the requirement of developing a theoretical method to predict these rates. For such purpose, the author has applied existing theoretical models to real material calculations (cubic InN), and then incorporated the results into the device model (Sec. 2.3).

The screened Coulomb potential $V(\mathbf{r})$ has been adopted for evaluating the e-h interaction. As widely adopted in the literature, this type of carrier-carrier scattering is purely Coulomb and could be thought of as a scattering process involving ionized impurities.[62, 158] The scattering rate from the initial states $(\mathbf{k}_1, \mathbf{k}_2)$ to the final states $(\mathbf{k}'_1, \mathbf{k}'_2)$ is given in Eq. 3.31.

$$S(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}'_1, \mathbf{k}'_2) = \frac{2\pi}{\hbar} |M|^2 f_{\mathbf{k}_1} f_{\mathbf{k}_2} (1 - f_{\mathbf{k}'_1}) (1 - f_{\mathbf{k}'_2}) \times \delta(E_{\mathbf{k}'_1} + E_{\mathbf{k}'_2} - E_{\mathbf{k}_1} - E_{\mathbf{k}_2}) \quad (3.31)$$

$$M = \langle \mathbf{k}'_1, \mathbf{k}'_2 | V(\mathbf{r}_1 - \mathbf{r}_2) | \mathbf{k}_1, \mathbf{k}_2 \rangle = \frac{e^2}{V\epsilon} \frac{\delta_{\mathbf{k}_1+\mathbf{k}_2, \mathbf{k}'_1+\mathbf{k}'_2}}{|\mathbf{k}'_1 - \mathbf{k}_1|^2 + \beta^2}$$

$$\beta = \frac{e^2 \overline{n_e} + \overline{n_h}}{\epsilon k_B T_c} \quad (3.32)$$

where M is the corresponding element of the Hamiltonian matrix and $f_{\mathbf{k}}$ is the occupation probability of an electronic state $\mathbf{k}$. In equilibrium it is

merely the Fermi function of the energy level. ϵ is the dielectric constant of the material and V is the system volume. β is the inverse Debye screening length, which is proportional to the average carrier concentrations, $\bar{n}_e$ for electrons and $\bar{n}_h$ for holes. T_c is the carrier temperature at equilibrium.

To calculate the relaxation times of carrier-carrier elastic scattering processes, carrier systems in thermal equilibrium are considered. The reason for using equilibrium distributions partly lies in the simplicity when evaluating parameters in Eq. 3.31 and Eq. 3.32, including the screening length and the occupation probability of each state. From results of device modeling, the state occupancies are accurately described by Fermi functions except for energies within the narrow extraction window. This indicates that it is physically feasible to treat the scattering process under the equilibrium approximation. For states at the extraction energies the re-supply of extracted carriers comes from the collisions of two random states spread over the whole energy range. Therefore their rates can be regarded as determined merely by the equilibrium distribution. The calculation can be simply performed by integrating Eq. 3.31 over the whole reduced Brillouin zone (for $\mathbf{k}_2$, $\mathbf{k}'_1$ and $\mathbf{k}'_2$). The result is a “scattering-out” rate for the state $\mathbf{k}_1$. In fact this is sufficient for an equilibrium distribution, as the re-supply rate of a state is always balanced by the scattering-out rate of the same state (detail balance).

The relaxation times are calculated using the formulae in Eq. 3.33, for five different sets of equilibrium distributions. Each corresponds to a certain carrier temperature from 400K to 800K. The material is assumed to be intrinsic. An aligned Fermi level for both electrons and holes is calculated for each carrier temperature, listed in Tab. 3.9. Due to the relatively heavy effective mass and the high degeneracy of hole bands the Fermi level is closer to the conduction band edge. The carrier concentrations vary exponentially

with different carrier temperatures, allowing for a sufficiently wide and evenly distributed logarithmic scale used to fit the calculated relaxation times. The relaxation time is calculated by Eq. 2.44.

$$\tau_{ehs}(\mathbf{k}_1) = \frac{f_{\mathbf{k}_1}}{\sum_{\mathbf{k}_2, \mathbf{k}'_1, \mathbf{k}'_2} S(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}'_1, \mathbf{k}'_2)} \quad \overline{\tau_{ehs}} = \frac{\sum_{\mathbf{k}_1} f_{\mathbf{k}_1}}{\sum_{\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}'_1, \mathbf{k}'_2} S(\mathbf{k}_1, \mathbf{k}_2; \mathbf{k}'_1, \mathbf{k}'_2)} \quad (3.33)$$

where $\tau_{ehs}(\mathbf{k}_1)$ is the relaxation time for the carriers at state $\mathbf{k}_1$ being scattered away by the opposite type of carriers. The average relaxation time $\overline{\tau_{ehs}}$ is defined as the ratio of the total occupation probability to the total scattering rate, for states along different crystal directions. In this work all the electron states with energies from the conduction band edge up to the 0.4eV have been taken into account, scattering with the entire mesh of hole states. The electron states at the high-energy tail (with energies higher than 0.4eV) have negligible levels of interaction due to their low occupation probabilities.

Table 3.9: Five equilibrium carrier distributions adopted as the sample set for the relaxation time calculation. The Fermi level positions are evaluated from the valence band edge.

temperature (K)	concentration (m^{-3})	Fermi level (eV)
400	2.19×10^{18}	0.495
500	3.11×10^{19}	0.510
600	1.89×10^{20}	0.526
700	7.07×10^{20}	0.542
800	1.95×10^{21}	0.557

For e-e scattering or h-h scattering, states with energies close to the extraction levels are considered, as the deviation from the normalized distribution occurs only at these states. For each such state we have evaluated its scattering rate with the same type of carrier states over the whole mesh within the reduced Brillouin zone. Being different from the e-h scattering,

the interaction between two indistinguishable fermions involves an exchange term in addition to the direct scattering term [159]. To incorporate this term, the Coulomb Hamiltonian elements are evaluated with the orthogonal basis set of states with definite total angular and magnetic quantum numbers, including spin-orbit coupling [160]. For this purpose we adopted an atomic orbital basis set with the Luttinger-Kohn representation adopted for hole states [79, 82]. The size of this basis set is 16, involving 8 eigenstates for each atom (cation or anion): $\{\phi^{LK}\} = \{s_{1/2}^{1/2}, s_{-1/2}^{1/2}, p_{3/2}^{3/2}, p_{1/2}^{3/2}, p_{-1/2}^{3/2}, p_{-3/2}^{3/2}, p_{1/2}^{1/2}, p_{-1/2}^{1/2}\}$. For each electronic state the wave function with the tight-binding basis set $\{\phi^{TB}\}$ has been calculated from Eq. ???. It was then transformed to the wave function with the basis set $\{\phi^{LK}\}$. Conventionally the two-particle wave function is presented as a Slater-type function. Their corresponding Hamiltonian element has been recently formalized in Eq. 3.34 by Dolguikh et al. [160].

$$\langle \mathbf{k}'_1, \mathbf{k}'_2 | V | \mathbf{k}_1, \mathbf{k}_2 \rangle = \frac{e^2}{V\epsilon} \left(\frac{F_+ \delta_{\mathbf{k}_1+\mathbf{k}_2, \mathbf{k}'_1+\mathbf{k}'_2}}{|\mathbf{k}'_1 - \mathbf{k}_1|^2 + \beta^2} - \frac{F_- \delta_{\mathbf{k}_1+\mathbf{k}_2, \mathbf{k}'_1+\mathbf{k}'_2}}{|\mathbf{k}'_2 - \mathbf{k}_1|^2 + \beta^2} \right) \quad (3.34)$$

$$F_+ = \sum_{n=1}^{16} \sum_{m=1}^{16} c_n^{\mathbf{k}'_1*} c_n^{\mathbf{k}_1} c_m^{\mathbf{k}'_2*} c_m^{\mathbf{k}_2} \quad F_- = \sum_{n=1}^{16} \sum_{m=1}^{16} c_n^{\mathbf{k}'_1*} c_n^{\mathbf{k}_2} c_m^{\mathbf{k}'_2*} c_m^{\mathbf{k}_1}$$

Eq. 3.34 includes two terms, the 1st term comes from the direct Coulomb scattering and the 2nd term is the exchange term. An illustrative diagram for this could be found in a recent paper by Glazov [159].

The scattering relaxation times have been calculated for each type of process, shown in Fig. 3.25. Five sets of carrier distributions with temperatures from 400K to 800K have been taken into account as they cover the possible range of carrier temperatures for an operating HCSC. For each scattering process the proportionality factor in Eq. 2.44 has been obtained by fitting the respective relaxation time with the carrier concentration. We adopted a fixed-slope linear regression as the fitting method, illustrated in Eq. 3.35.

The data points, i.e. carrier concentrations, are evenly distributed in a logarithmic scale. By converting the original data into logarithmic values before fitting, each data point can share an even fitting weight.

$$\begin{aligned}
Y &= X + c & (3.35) \\
e - e : Y &= \lg(\tau_{eq}^e) \quad X = -\lg\{N[n(\epsilon)]\} \quad c = \lg\left(\frac{A}{m_e^*}\right) \\
h - h : Y &= \lg(\tau_{eq}^h) \quad X = -\lg\{N[p(\epsilon)]\} \quad c = \lg\left(\frac{A}{m_h^*}\right) \\
e - h : Y &= \lg(\tau_{ehs}) \quad X = -\lg\{N[n(\epsilon)]\} \quad c = \lg(B)
\end{aligned}$$

We have obtained the intercept c for each type of carrier scattering, by fitting the logarithmic data X and Y according to Eq. 3.35. The simulation data and fitted curves are plotted in Fig. 3.25. Proportionality coefficients proposed in Eq. 2.44 have been obtained and listed in Tab. 3.10. The fitting scheme is based on the least square error.

Table 3.10: The proportionality coefficients and the adjusted R-square values from the regression calculation

scattering type	proportionality	value	adj. R-square
e-e	A/m_e^*	4.15×10^{12}	0.8849
h-h	A/m_h^*	8.45×10^{10}	0.9994
e-h	B	2.41×10^{11}	0.9996

From the results the adjusted R-square values are close to unity, indicating a good match between the regression line and the original data. The only deviation occurs for e-e scattering. This type of scattering shows a shorter relaxation time than the fitting result at high carrier temperatures. This is purely due to the incorporation of electron-electron exchange interactions. In fact an electronic transition to a nearby state in the k-space is the most rapid due to its small momentum change. The intra-band electron

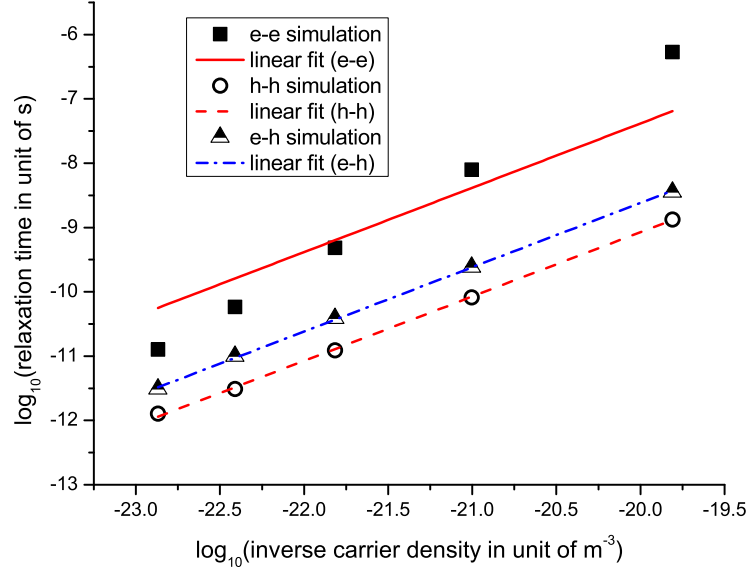


Figure 3.25: The simulation data of the scattering relaxation times with the inverse carrier density plus the fitting results for three types of carrier-carrier elastic scattering. The carrier reservoir is assumed as being in thermal equilibrium. The five levels of carrier density correspond to the respective carrier temperatures of 400K, 500K, 600K, 700K and 800K.

transition is preferred as the initial and final tight-binding eigenvectors are approximately the same. Therefore for intra-band electron-electron interactions both the direct transition and the exchange transition are significant, i.e. $F_+ \approx F_-$, if the final states lie in the same band. In Eq. 3.34 the exchange term largely reduces the magnitude of the overall Hamiltonian. For inter-band interactions the direct term of intra-band transition is significant while the exchange term is much smaller, as illustrated in Fig. 3.26. This leads to a stronger interaction. As the energy range of carrier extraction lies at the lowest non-degenerate conduction band, its interaction with high order bands strongly relies on the spread of the electron energy distribution.

With a higher carrier temperature these interactions occur more often due to the larger occupation probabilities at the high-energy tail. This finally leads to a super-linear relation between the scattering relaxation time and the inverse carrier concentration. On the other hand, for h-h scattering this dependance does not exist due to the degeneracy of three bands (if neglecting the spin-orbit splitting).

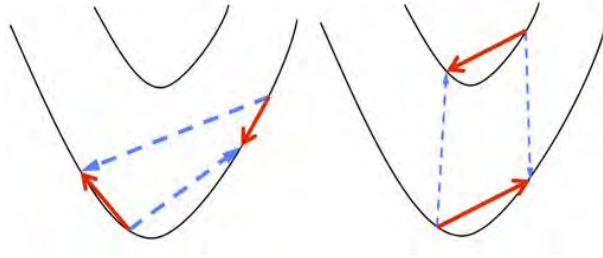


Figure 3.26: Illustration diagram explaining the difference between intra-band and inter-band electron scattering. The intra-band scattering between electrons (left) includes both strong direct and exchange components (both intra-band transition); the inter-band scattering (right) has a strong direct component (intra-band transition) but a weak exchange component (inter-band transition)

The proportionality factor B for e-h scattering is 2.4×10^{11} , lying at the middle of the possible range (See Fig. 2.17). Accordingly at the equilibrium limit the selective hole contact corresponds to an maximum efficiency of 23.1%. This is much lower than the efficiency value of 30.5% for the device with a normal hole contact. The proportionality factor A has been calculated as being 2.5×10^{-19} , by taking the realistic carrier effective masses into account. This e-e/h-h scattering rate is insufficient to maintain equilibrium carrier statistics; accordingly the maximum efficiency is well below the value at equilibrium limit. A detailed calculation gives the efficiency value of 17.7%, taking into account the same symmetric energy-selective contact structure as

adopted in the last section. However with a normal hole contact the efficiency could exceed 20%.

Using the model proposed in this work, the energy-dependent contact extraction profiles could be optimized for any suggested absorber material. If a selective energy contact is used we may still vary the transmission window width and the centre-point energy as they have a strong effect on the power output of the device. Due to the different statistics of electrons and holes individual optimizations are necessary for their respective contacts, generally leading to non-symmetric contact structures. Such contact optimization heavily depends on the carrier scattering properties in the absorber. Despite this complexity it is essential to enhance the solar-electricity conversion efficiency above the Shockly-Queisser limit. This provides possibilities for future work.

3.3 Tight-binding models for the contacts

Apart from the absorber layer, the energy selective contacts (ESC) form another important component of the HCSC. The ESC is used to extract a specified type of carriers within a small energy window, so that the heat exchange associated with the carrier transport is minimized. This leads to only a small entropy generation on carrier extraction. Its energy selectivity can be fulfilled by resonant tunneling, which is a well studied effect in semiconductor physics.

However, in most of the relevant works the carrier transmission properties were calculated using the effective mass approximation (EMA). This approximation is only sufficiently accurate for ordered structure with sufficient number of periods (i.e. bulk structure); a reasonable requirement is that each layer should have a thickness larger than 10nm[135]. On the other

hand, according to the work on device modeling of the HCSC (Sec. 2.2), the resonant tunneling diode (RTD) used for carrier extraction purposes must be an ultra-thin structure ($<2\text{nm}$ per layer). Otherwise the resonant tunneling probability is too small (decays exponentially with the thickness) to extract any current for practical energy conversion.

In this work a tight-binding (TB) based model has been adopted for calculating the electron transmission properties through an ultra-thin scattering region. To simulate the resonant tunneling structure, three lattice-matched layers are modeled, i.e. a well layer sandwiched between two barrier layers. The left contact (i.e. absorber) and the right contact (i.e. electrode) of this structure are assumed with the same material of the well layer. This simplification enables us to merely vary two materials instead of four different types of material.

Another problem comes from the unperturbed treatment of a single electron through the RTD. In fact there are elastic scattering, e.g. scattering off impurity atoms, and inelastic scattering, e.g. electron-electron and electron-phonon interactions, happening to a single electron during transmission. These processes may alter its transmission profile and requires theoretical approaches for a better simulation on real systems. In polar semiconductors like GaAs, the dominant scattering process is due to electrons coupling to LO phonons[161]. In this work the phonon scattering has been incorporated with a simplified method. The model significantly reduces the computational complexity without much loss on its accuracy. The numerical results demonstrate that phonon scattering in general impairs the energy selectivity.

3.3.1 One-electron transmission without scattering

The method described here has been given in the literature[162]. The transmission probability between any pair of modes $\psi_L(\mathbf{k}, n)$ and $\psi_R(\mathbf{k}', n')$ can be calculated simply by solving the time-independent Schrödinger equation with appropriate boundary conditions. Note that the subscript L or R indicates that the mode is at the left or right contact. n and n' denote the respective band indexes.

3.3.1.1 General model for layer-based scattering problem

To solve the Schrödinger equation with the tight-binding method, the Hamiltonian matrix needs to be presented explicitly in terms of atomic orbitals. Supposing the crystal structure includes a primitive cell with n atoms, each of which has m atomic orbitals, which are included in the basis set, then wave functions of electron stationary states may be expressed as linear combinations of these mn orbitals. The components of the Hamiltonian matrix correspond to different types of nearest-neighbour interactions; their values may be obtained from the literature or by fitting the bulk band structure. To accommodate the lateral uniformity and the vertical variation of the RTD, the system is divided into N layers of atoms, normal to the transport direction. Correspondingly the system Hamiltonian may be divided into its intra-layer and inter-layer sub-matrices, H_i and B_j .

If assuming the inter-layer interaction only exists between neighbouring layers (nearest-neighbour coupling assumption), the system Hamiltonian ma-

trix is expressed in Eq. 3.36.

$$\mathbf{H} = \begin{pmatrix} \ddots & \dots & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \vdots & \mathbf{H}_{i-1} & \mathbf{B}_{i-1}^+ & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{B}_{i-1} & \mathbf{H}_i & \mathbf{B}_i^+ & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{B}_i & \mathbf{H}_{i+1} & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \dots & \ddots \end{pmatrix} \quad (3.36)$$

Corresponding to the division into layers the eigenvector (e.g. stationary-state wave function) may also be divided into N sub-vectors (Eq. 3.37).

$$\psi = \begin{pmatrix} \vdots \\ \mathbf{c}_{i-1} \\ \mathbf{c}_i \\ \mathbf{c}_{i+1} \\ \vdots \end{pmatrix} \quad (3.37)$$

Our next step is to calculate the bulk modes in the left and right contacts. This is because we are treating with the transmission property of each pair of bulk modes; thus the wave functions of these bulk modes need to be obtained first. Indeed these contact modes provide the boundary conditions for solving the Schrödinger equation problem.

In bulk crystals the width of each layer is chosen to include at least a whole primitive cell in order to make sure all the layers are completely equivalent. In fact if the crystal has a primitive vector (l_x, l_y, l_z) , $l_z \neq 0$, where z denotes the electron transport direction, then the layer located at $Z+l_z$ is equivalent with the layer at Z , including a lateral displacement along $\mathbf{l}_{\parallel} = (l_x, l_y)$. Therefore all the Hamiltonian sub-matrices are the same, i.e. $\mathbf{H}_i = \mathbf{H}_{L/R}$ and $\mathbf{B}_i = \mathbf{B}_{L/R}$. From Sec. ?? the time-independent Schrödinger equation can be expressed in a matrix form: $\mathbf{H}\psi = E\psi$. This immediately

leads to

$$-\mathbf{B}_{L/R}\mathbf{c}_{i-1} + (E\mathbf{I} - \mathbf{H}_{L/R})\mathbf{c}_i - \mathbf{B}_{L/R}^+\mathbf{c}_{i+1} = \mathbf{0} \quad (3.38)$$

where $\mathbf{I}$ denotes the identity matrix. According to the Bloch theorem we may define a Bloch factor λ to represent the phase shift between two atoms separated by (l_x, l_y, l_z) . Note that $\lambda = \exp(i\mathbf{k} \cdot \mathbf{l})$. The wave functions of neighbouring layers have the same phase shift, i.e. $\mathbf{c}_i = \lambda\mathbf{c}_{i-1} = \lambda^{-1}\mathbf{c}_{i+1}$. Substituting this into Eq. 3.38 we obtain Eq. 3.39.

$$\lambda^{-1}\mathbf{B}_{L/R}\mathbf{c} + \mathbf{H}_{L/R}\mathbf{c} + \lambda\mathbf{B}_{L/R}^+\mathbf{c} = E\mathbf{c} \quad (3.39)$$

where $\mathbf{c}$ denotes $\mathbf{c}_{i-1}$. If knowing the Bloch factor λ , E and $\mathbf{c}$ can be solved from this secular equation. Furthermore, if defining $\mathbf{d} = \lambda\mathbf{c}$ one can convert Eq. 3.39 into

$$\begin{pmatrix} \mathbf{0} & \mathbf{I} \\ -\mathbf{B}_{L/R} & E\mathbf{I} - \mathbf{H}_{L/R} \end{pmatrix} \begin{pmatrix} \mathbf{c} \\ \mathbf{d} \end{pmatrix} = \lambda \begin{pmatrix} \mathbf{I} & \mathbf{0} \\ \mathbf{0} & \mathbf{B}_{L/R}^+ \end{pmatrix} \begin{pmatrix} \mathbf{c} \\ \mathbf{d} \end{pmatrix} \quad (3.40)$$

This is a generalized eigenvalue problem that allows us to calculate λ and $\mathbf{c}$ from any value of E . The eigenvector $\mathbf{c}$ has a dimension of mn ; so Eq. 3.40 has $2mn$ solutions, including mn right-going modes and mn left-going modes. Some of them are propagating modes that correspond to $|\lambda| = 1$ while the others are evanescent modes. We denote the right-going modes and left-going modes by their respective Bloch factors $(\lambda_{\pm,p})$ and eigenvectors $(\mathbf{u}_{\pm,p})$, $p = 1, 2, \dots, nm$. The Bloch velocity (group velocity) is given in Eq. 3.41[162].

$$v_{\pm,p} = -\frac{2a}{\hbar} \text{Im}(\lambda_{\pm,p} \mathbf{u}_{\pm,p}^+ \mathbf{B}^+ \mathbf{u}_{\pm,p}) \quad (3.41)$$

where a denotes the thickness of the layer. From Eq. 3.40 we obtain $2mn$ eigenvectors; however unlike a standard secular equation, here these

eigenvectors may not be orthogonal. So it is convenient to define dual vectors $\tilde{\mathbf{u}}_{\pm,p}$ that obey $\tilde{\mathbf{u}}_{\pm,p} \mathbf{u}_{\pm,q} = \delta_{p,q}$ for arbitrary p and q . A generalized matrix version of the Bloch factor can be defined in Eq. 3.42.

$$\mathbf{F}_{\pm} = \sum_{p=1}^{nm} \lambda_{\pm,p} \mathbf{u}_{\pm,p} \tilde{\mathbf{u}}_{\pm,p}^+ \quad (3.42)$$

Now the mode matching between the contact modes and the wave functions in the scattering region is to be discussed. The details of the contact modes provide boundary conditions for solving the Schrödinger equation. Immediately left of the scattering region we have

$$\begin{aligned} \mathbf{c}_{-1} &= \mathbf{F}_{L,+}^{-1} \mathbf{c}_{+,0} + \mathbf{F}_{L,-}^{-1} \mathbf{c}_{-,0} \\ &= (\mathbf{F}_{L,+}^{-1} - \mathbf{F}_{L,-}^{-1}) \mathbf{c}_{+,0} + \mathbf{F}_{L,-}^{-1} \mathbf{c}_0 \end{aligned} \quad (3.43)$$

where $\mathbf{c}_{+,0}$ is the incoming source wave. At the right of the scattering region there is $\mathbf{c}_{S+2} = \mathbf{F}_{R,+} \mathbf{c}_{+,S+1}$ similarly. Substituting these equations into Eq. 3.38 we reach a final matrix equation[162].

$$(\mathbf{E}\mathbf{I} - \mathbf{H}')\psi = \mathbf{Q}_{L,p} \quad (3.44)$$

$$\begin{aligned} \mathbf{H}' &= \begin{pmatrix} \mathbf{H}_L + \Sigma_L(E) & \mathbf{B}_1^+ & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{B}_1 & \ddots & \mathbf{B}_{i-1}^+ & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{B}_{i-1} & \mathbf{H}_i & \mathbf{B}_i^+ & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{B}_i & \ddots & \mathbf{B}_S^+ \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{B}_S & \mathbf{H}_R + \Sigma_R(E) \end{pmatrix} \\ \psi &= \begin{pmatrix} \mathbf{c}_0 \\ \vdots \\ \mathbf{c}_i \\ \vdots \\ \mathbf{c}_{S+1} \end{pmatrix} \quad \mathbf{Q}_{L,p} = \begin{pmatrix} \mathbf{B}_L(\mathbf{F}_{L,+}^{-1} - \mathbf{F}_{L,-}^{-1})\mathbf{u}_{L,+,p} \\ \vdots \\ \mathbf{0} \\ \vdots \\ \mathbf{0} \end{pmatrix} \end{aligned}$$

where $\Sigma_L(E) = \mathbf{B}_L \mathbf{F}_{L,-}^{-1}$ and $\Sigma_R(E) = \mathbf{B}_R^+ \mathbf{F}_{R,+}$. Eq. 3.44 enables us to calculate the eigenfunction of layers $\mathbf{c}_i$ that are within and at the edges of the scattering region ($i = 0, 1, \dots, S, S+1$). Among them $\mathbf{c}_{S+1}$ is of special importance because it includes all the information on the transmission coefficient. In fact $\mathbf{c}_{S+1}$ is a linear combination of the right contact modes, weighted by respective transmission coefficients (Eq. 3.45).

$$\mathbf{c}_{S+1} = \sum_{q=1}^{mn} \mathbf{u}_{R,+,q} t'_{q,p} \quad (3.45)$$

The transmission coefficients shall be normalized by their Bloch velocities to ensure an unitary scattering matrix[162]:

$$t_{q,p} = \sqrt{\frac{v_{L,+,p}}{v_{R,+,q}}} t'_{q,p} = \sqrt{\frac{v_{L,+,p}}{v_{R,+,q}}} \tilde{\mathbf{u}}_{R,+,q}^+ \mathbf{c}_{S+1} \quad (3.46)$$

The total transmission (over all the pairs of contact modes) at the specified energy E and planar mode $\mathbf{k}_{\parallel}$ is $T(E, \mathbf{k}_{\parallel}) = Tr(\mathbf{t}^+ \mathbf{t})$. Note all the contact modes are for the same energy and planar mode according to Eq. 3.40.

3.3.1.2 Modeling the lattice-matched RTD of zinc blende structure for ESC applications

In this section an AlAs/GaAs/AlAs RTD has been modeled as AlAs and GaAs have close lattice constants and they are both zinc blende lattice. Such lattice is among the simplest crystal structures, providing much modeling convenience.

In a zinc blende lattice the primitive vectors may be represented by $(1 \ 1 \ 0)a/2$, $(1 \ 0 \ 1)a/2$ and $(0 \ 1 \ 1)a/2$. We use $(1 \ 0 \ 1)a/2$ as the transfer vector (l_x, l_y, l_z) between neighbouring layers (transport is along z (001) direction). Each layer includes primitive cells placed along the planar direction, formed by two 2D vectors $(1 \ 1)a/2$ and $(1 \ -1)a/2$. As there are two atoms, an anion and a cation in one primitive cell, with a *sp*-TB method

there are merely eight atomic orbits included in the basis set. The intra-layer sub-matrix $\mathbf{H}_{L/R}$ is divided into four 4×4 blocks:

$$\mathbf{H}_{L/R} = \begin{pmatrix} \mathbf{E}_a + \mathbf{H}_a^{(2)} & \mathbf{H}_{ac}^{(1)} \\ \mathbf{H}_{ca}^{(1)} & \mathbf{E}_c + \mathbf{H}_c^{(2)} \end{pmatrix} \quad (3.47)$$

where $\mathbf{E}_a$ and $\mathbf{E}_c$ are diagonal matrices including all the self-energies, i.e. terms like $\langle s_{a/c} | \hat{H} | s_{a/c} \rangle$. $\mathbf{H}_{ac}^{(1)}$ and $\mathbf{H}_{ca}^{(1)}$ are hermitian conjugate matrices, including Hamiltonian elements of the 1st nearest-neighbour interactions, i.e. terms like $\langle s_{a/c} | \hat{H} | s_{c/a} \rangle$. $\mathbf{H}_{a/c}^{(2)}$ includes elements of the 2nd nearest-neighbour interactions, i.e. terms like $\langle s_{a/c}^1 | \hat{H} | s_{a/c}^2 \rangle$. Here superscripts 1 and 2 denote two neighbouring primitive cells. Each 4×4 block includes four orbitals: s , p_x , p_y , p_z . The matrix elements shall also include the phase shift due to $\mathbf{k}_{\parallel}$, if two interacting ions are in different primitive cells. Following the same routine the sub-matrix $\mathbf{B}_{L/R}$ is divided in Eq. 3.48.

$$\mathbf{B}_{L/R} = \begin{pmatrix} \mathbf{B}_a^{(2)} & \mathbf{0} \\ \mathbf{B}_{ca}^{(1)} & \mathbf{B}_c^{(2)} \end{pmatrix} \quad (3.48)$$

where $\mathbf{B}_a^{(2)}$ and $\mathbf{B}_c^{(2)}$ includes the coupling terms between the same type of ions at neighbouring layers (2nd nearest neighbours). $\mathbf{B}_{ca}^{(1)}$ refers to the inter-layer 1st nearest-neighbour interactions, i.e. the covalent bond between anion and cation that is across the layer interface. It is noted that only interactions up to the 2nd nearest neighbour are included here; this is sufficient to describe a covalent bonded crystal.

Substituting the expressions of $\mathbf{H}_{L/R}$ and $\mathbf{B}_{L/R}$ into Eq. 3.40 the Bloch factor λ is solved for any specified E . λ in fact characterizes the phase shift associated with the vector (l_x, l_y, l_z) . For a specified planar mode, i.e. fixed $\mathbf{k}_{\parallel}$, the Bloch wave-vector along the transport direction is unique for each propagating mode (Eq. 3.49).

$$k_z = \frac{\arg \lambda - \mathbf{k}_{\parallel} \cdot \mathbf{l}_{\parallel}}{l_z} \quad (3.49)$$

In conclusion at a specified energy E and a planar mode $\mathbf{k}_{\parallel}$, there is a finite number (mn) of electronic modes (defined by Bloch factor λ). Among them there are propagating modes that couple to the scattering region; each of them has an unique Bloch wave-vector k_z . The transmission coefficient between two arbitrary propagating modes at the left and the right contacts, respectively, is calculated by solving Eq. 3.44. Summation over their squared amplitudes gives a total transmission that is specified to E and $\mathbf{k}_{\parallel}$. To obtain a complete transmission at the energy level E another summation is required over all the planar modes, i.e. $T(E) = \sum_{\mathbf{k}_{\parallel}} T(E, \mathbf{k}_{\parallel})$.

$T(E)$ has already included all the transmission probabilities of different incoming electronic modes. Thereby unlike the method we adopted in Sec. 2.2.1.1, the summation over modes is no longer required in a Landauer formulae. In the $x - y$ plane each primitive cell occupy an area of $a^2/2$, constructed by the 2D primitive vectors $(1 \ 1)a/2$ and $(1 \ -1)a/2$. Following this, the ballistic current is derived in Eq. 3.50, if sampling evenly-distributed $N_{\parallel}$ planar modes within the 2D reduced Brillouin zone.

$$\begin{aligned}
J &= -\frac{2e}{h} \int_0^{\infty} \frac{2}{N_{\parallel} a^2} \sum_{t=1}^{N_{\parallel}} T(\epsilon, \mathbf{k}_{\parallel,t}) [f_L(\epsilon) - f_R(\epsilon)] d\epsilon \\
&= -\frac{4e}{h N_{\parallel} a^2} \int_0^{\infty} T(\epsilon) [f_L(\epsilon) - f_R(\epsilon)] d\epsilon \\
&= -\frac{4e}{h a^2} \int_0^{\infty} \bar{T}(\epsilon) [f_L(\epsilon) - f_R(\epsilon)] d\epsilon
\end{aligned} \tag{3.50}$$

where a is the lattice constant of a zinc blende lattice and $N_{\parallel}$ is the sampling number for planar modes. $\bar{T}(\epsilon)$ denotes the average transmission, i.e. $T(\epsilon) = N_{\parallel} \bar{T}(\epsilon)$. $f_L(\epsilon)$ and $f_R(\epsilon)$ denote the average occupation numbers in the left and the right contacts respectively. Eq. 3.50 describes the current density due to electron transport by summation over its whole energy scale. The current density due to holes has the same form.

3.3.2 Incorporation of phonon scattering

As discussed before, electron-phonon coupling has the primary effect on electrons transmitting through a polar-material structure[161]. Following the same method as in Sec. ??, we can derive the interaction Hamiltonian between a localized electron and an atomic vibration. First the full potential energy of electron-phonon system is expanded into different orders of atomic displacement $\mathbf{u} = \mathbf{R} - \mathbf{R}_0$.

$$V_{ei}(\mathbf{r} - \mathbf{R}^{(0)} - \mathbf{u}) = V_{ei}(\mathbf{r} - \mathbf{R}^{(0)}) - \mathbf{u} \cdot \vec{\nabla} V_{ei}(\mathbf{r} - \mathbf{R}^{(0)}) + O(\mathbf{u}^2) \quad (3.51)$$

The second quantization gives $\mathbf{u} = i\boldsymbol{\xi}\sqrt{\hbar/2M\omega}(a + a^\dagger)$, where $\boldsymbol{\xi}$ is the polarization vector, M and ω denote the atomic mass and the vibrational frequency, respectively. a and $a^\dagger$ are the respective annihilation and creation operators of the atomic vibration. This provides a total Hamiltonian of the atom $H_p + H_{ep}$. Using the linear transformation technique in Sec. ??, a polaron self-energy is derived in Eq. 3.52.

$$\begin{aligned} \Delta E &= - \left[\boldsymbol{\xi} \cdot (-q) \vec{\nabla} V_{ei}(\mathbf{r} - \mathbf{R}^{(0)}) \sqrt{\frac{\hbar}{2M\omega}} \right]^2 \frac{1}{\hbar\omega} \\ &= - \frac{[q\boldsymbol{\xi} \cdot \vec{\nabla} V_{ei}(\mathbf{r} - \mathbf{R}^{(0)})]^2}{2M\omega^2} \end{aligned} \quad (3.52)$$

For simplicity we denote the projected potential energy gradient $q\boldsymbol{\xi} \cdot \vec{\nabla} V_{ei}(\mathbf{r} - \mathbf{R}^{(0)})$ by γ [161], so $\Delta E = -\gamma^2/2M\omega^2$. It is noted that this derivation is strictly only for a localized electron coupled with an ionic vibration. However in a lattice strong ion-ion coupling leads to phonon wave that propagate in the whole lattice. In this case a frequency ω can only be specified to a phonon mode, instead of atomic vibrations. Correspondingly the lattice vibrational energy is quantized by $H_p = \sum_p \hbar\omega_p(a_p a_p^\dagger + a_p^\dagger a_p)$. Thereby the electron-phonon interaction Hamiltonian should also be evaluated in terms of phonon occupation states.

The analysis starts from considering the interaction between a transmitting electron and a confined phonon mode p that spreads over L_p primitive cells. The atomic displacement is expressed in correspondence to Eq. ??.

$$\mathbf{u}_{j,a/c} = i\sqrt{\frac{\hbar}{2ML_p\omega_p}}\boldsymbol{\xi}_{p,a/c}(a_p + a_p^+) \quad (3.53)$$

where the subscript j is the index of the primitive cell ($j = 1, \dots, L_p$). The subscripts a or c denotes the anion or the cation and M is the total mass of a primitive cell. If we still keep the same definition of γ , i.e. $\gamma_{a/c} = q\boldsymbol{\xi}_{p,a/c} \cdot \vec{\nabla}V_{ei}(\mathbf{r}_{a/c} - \mathbf{R}_{a/c}^{(0)})$, the self-energy of the polaron in Eq. 3.52 needs to be re-expressed:

$$\Delta E_p = - \frac{\sum_{j,k}(\psi_{j,a_k}^* \psi_{j,a_k} \gamma_a^2 + \psi_{j,c_k}^* \psi_{j,c_k} \gamma_c^2)}{2ML_p\omega_p^2} \quad (3.54)$$

where $\psi_{j,a/c_k} = \langle \psi | \phi_{a/c_k} \rangle$ is the the electron wave function projected at the k -th basis function of the anion/cation in the j -th primitive cell. If using the sp^3 basis set, $\phi_{a/c_{1,2,3,4}} = s_{a/c}, p_{x,a/c}, p_{y,a/c}, p_{z,a/c}$. The electron wave function follows the normalization condition $\sum_{j,k}(\psi_{j,a_k}^* \psi_{j,a} + \psi_{j,c_k}^* \psi_{j,c}) = 1$. This enables us to define an average coupling strength $\tilde{\gamma}_p$ that is normalized by L_p (Eq. 3.55). This definition is in fact the same as the treatment in the literature [161].

$$\begin{aligned} \tilde{\gamma}_p &\equiv \sqrt{\frac{\sum_{j,k}(\psi_{j,a_k}^* \psi_{j,a_k} \gamma_a^2 + \psi_{j,c_k}^* \psi_{j,c_k} \gamma_c^2)}{L_p}} \\ &= -2M\omega_p^2 \Delta E_p \end{aligned} \quad (3.55)$$

A conventional way of defining the self-energy shift is by its fractional reduction compared to the unperturbed energy, i.e. $g = -\Delta E/\hbar\omega$. The quantities ΔE and g are referred to as the Franck-Condon energy and the Huang-Rhys factor, respectively[163]. They are both used to characterize the

strength of electron-phonon coupling. In GaAs $g = 2.02/L_0$ where L_0 is the linear extent of the localized state in angstroms[161, 164, 165].

If defining g_p as the g -factor of the polaron formed from the coupled phonon mode p , which is localized within one planar primitive cell. we can express the coupling constant $\tilde{\gamma}_p$ by g_p : $\tilde{\gamma}_p = \sqrt{2M\hbar\omega_p^3 g_p}$. It is noted that the total number of primitive cells equals to the product of cell numbers along the vertical and transverse directions, i.e. $L_p = L_{p,\perp} L_{p,\parallel}$. For states that spread along the planar directions, the coupling constant is $\tilde{\gamma}_p = \sqrt{2M\hbar\omega_p^3 g_p / L_{p,\parallel}}$. The next step is to express the Hamiltonian H_{ep} in terms of $\tilde{\gamma}_p$, as demonstrated in Eq. 3.56.

$$\begin{aligned} H_{ep} &= \sum_p \sqrt{\frac{\hbar}{2M L_p \omega_p}} \sum_{j,k} (\psi_{j,a_k}^* \psi_{j,a_k} \gamma_{p,a} + \psi_{j,c_k}^* \psi_{j,c_k} \gamma_{p,c}) (a_p + a_p^+) \\ &\approx \sum_p \tilde{\gamma}_p \sqrt{\frac{\hbar}{2M \omega_p}} (a_p + a_p^+) \end{aligned} \quad (3.56)$$

If within one layer there are in total $L_\perp$ primitive cells along the carrier transport direction and $L_\parallel$ cells along the planar directions, the total number of normal modes are $6L_\perp L_\parallel$ for the zinc blende structure. As the major scattering mechanism comes from the polar interaction, which requires a microscopic electric field that can only be contributed by the longitudinal optical (LO) phonons. Merely $L_\perp L_\parallel$ LO phonon modes need to be considered for their interactions with the incoming electron. In nano-layers the scattering probability decays with $1/q_\parallel^2$, when the planar wave-vector $q_\parallel$ deviates from zero. As an approximation we assume that scattering with all these $L_\perp L_\parallel$ phonon modes does not change the planar wave-vector of the incoming electron, i.e. $\Delta k_\parallel = q_\parallel = 0$. This assumption of planar wave-vector conservation simplifies the problem, as we only need to consider one primitive cell along the planar direction (and hence one planar mode). Correspondingly

we treat the incoming electron being scattered by only $L_\perp$ phonon modes, each of which involves a planar-mode-averaged coupling constant $\tilde{\gamma}_{p,\perp}$.

The electron-phonon scattering involves absorption or emission of phonons, leading to the change on occupation numbers. To evaluate its effect phonon states with different occupation numbers need to be incorporated. The stationary state of the system is to be solved with a basis set that includes states $|f_i, n_1, n_2, \dots, n_{L_\perp}\rangle = |f_i\rangle \otimes |n_1\rangle \otimes |n_2\rangle \cdots \otimes |n_{L_\perp}\rangle$, where f_i ($f = s, p_x, p_y, p_z$) denotes the atomic electronic state at the i -th atom; i has $2(S+1)$ values, i.e. an anion and a cation in each layer, from layer 0 to layer $S + 1$. n_j ($j = 1, 2, \dots, L_\perp$) is the occupation number of the j -th vibrational mode of the layer of interest (barrier or well). The total system Hamiltonian is $H = H_e + H_p + H_{ep}$. The matrix elements of H_e are irrelevant to the phonon state, and have been given by the tight-binding parameters. On the other hand, the matrix element of H_p only depends on the phonon state; hence it is merely an additional term to the diagonal elements of the total system Hamiltonian matrix. The matrix elements are illustrated in Eq. 3.57.

$$\begin{aligned} \langle f_i, n_1, \dots, n_{L_\perp} | H_e | f_j, m_1, \dots, m_{L_\perp} \rangle &= \langle f_i | H_e | f_j \rangle \prod_{k=1}^{L_\perp} \delta_{n_k, m_k} \quad (3.57) \\ \langle f_i, n_1, \dots, n_{L_\perp} | H_p | f_j, m_1, \dots, m_{L_\perp} \rangle &= \delta_{f_i, f_j} \sum_{k=1}^{L_\perp} \left(n_k + \frac{1}{2} \right) \hbar \omega_k \prod_{k=1}^{L_\perp} \delta_{n_k, m_k} \end{aligned}$$

In principle these $L_\perp$ phonon modes are treated independently as shown in Eq. 3.57 to accommodate their different occupation numbers. However this leads to a Hamiltonian matrix with the dimension of $8L_\perp(N+1)^{L_\perp} \times 8L_\perp(N+1)^{L_\perp}$, where N denotes the maximal phonon occupation numbers that are taken into account. The complexity of this problem increases exponentially with the layer thickness $L_\perp$, which is not practical for numerical calculation. A practical method has been proposed to solve this problem by adopting

collective parameters ω and γ to express the Hamiltonians of all the $2L_\perp$ modes. This method is verified by noticing that the frequencies of all LO Γ -point modes are quite close. The collective parameter γ is simply the algebraic average of $\tilde{\gamma}_p$, if it is defined to be proportional to the average self-energy $\Delta\bar{E}_p$.

$$\begin{aligned}\gamma &= -2M\omega^2\Delta\bar{E}_p = -\frac{2M\omega^2}{2L_\perp} \sum_{p=1}^{2L_\perp} \Delta E_p \\ &= \frac{1}{2L_\perp} \sum_{p=1}^{2L_\perp} \tilde{\gamma}_p = \frac{1}{L_\perp} \sum_{p=1}^{2L_\perp} \sqrt{\frac{M\hbar\omega_p^3 g_p}{L_\parallel}}\end{aligned}\quad (3.58)$$

It is noted that, as discussed before, we only consider one planar primitive cell; hence $L_\parallel = 1$. In correspondence to the adoption of collective parameters, we transform the basis states from $|f_i, n_1, n_2, \dots, n_{L_\perp}\rangle$ to $|f_i, n\rangle$, where $n = \sum_{k=1}^{L_\perp} n_k$. The expression of $|f_i, n\rangle$ is given in Eq. 3.59.

$$|f_i, n\rangle = \binom{n + L_\perp - 1}{L_\perp - 1}^{-\frac{1}{2}} \cdot \sum_{n_k \in [0, 1, \dots, n]}^{\sum_{k=1}^{L_\perp} n_k = n} |f_i, n_1, n_2, \dots, n_{L_\perp}\rangle \quad (3.59)$$

From Eq. 3.59 the new state $|f_i, n\rangle$ only depends on the total phonon occupation number n , and is irrelevant to its distribution in each mode. This is done by a summation over all the possible states $|f_i, n_1, n_2, \dots, n_{L_\perp}\rangle$ that contribute to a total occupation number n , i.e. $\sum_{k=1}^{L_\perp} n_k = n$. In addition each occupation number n_k is an integer from 0 to n . A normalization factor, shown in Eq. 3.59, appears before this summation, which is expressed as a binomial coefficient:

$$\binom{n + L_\perp - 1}{L_\perp - 1} = \frac{(n + L_\perp - 1)!}{n!(L_\perp - 1)!} \quad (3.60)$$

The new basis $|f_i, n\rangle$ set only has $8L_\perp^2(N + 1)$ states, in correspondence to a Hamiltonian matrix of the dimension $8L_\perp^2(N + 1) \times 8L_\perp^2(N + 1)$. The

computational complexity is reduced to a polynomial level that is numerically soluble.

Now we can evaluate the Hamiltonian matrix element $\langle f_i, n | H_{ep} | f_j, m \rangle$ by substituting Eq. 3.56 and Eq. 3.59. After some algebraic rearrangement, the matrix element is expressed analytically, as demonstrated in Eq. 3.61.

$$\begin{aligned} \langle f_i, n | H_{ep} | f_i, n+1 \rangle &= \langle f_i, n+1 | H_{ep} | f_i, n \rangle \\ &= \gamma \sqrt{\frac{\hbar}{2M\omega}} \cdot \left[\frac{n!}{(n+L_\perp-1)!} \cdot L_\perp(L_\perp-1) \right. \\ &\quad \left. \cdot \sqrt{\frac{n+1}{n+L_\perp}} \sum_{p=1}^{n+1} \frac{(n-p+L_\perp-1)!}{(n-p+1)!} \sqrt{p} \right] \end{aligned} \quad (3.61)$$

Except for the elements expressed in Eq. 3.61, all the other matrix elements of H_{ep} equal to zero. For convenience we define the average occupation number per mode as $\tilde{n} = n/(L_\perp)$. From the numerical results shown in Fig. 3.28, the factor within the square bracket (Eq. 3.61) increases with the number of modes, $L_\perp$, and increases with the occupation number per mode $\tilde{n}$. Fig. 3.28 (b) provides evidence that the factor within the square bracket at the right side of Eq. 3.61 is proportional to the number of modes. If accounting for an arbitrary number of planar primitive cells ($L_\parallel$), γ is reduced by a factor of $\sqrt{L_\parallel}$, and this factor is multiplied by a factor of $\sqrt{L_\parallel}$. The term in Eq. 3.61 does not change, which implies that the solution is independent on the number of planar cells considered, for any transversely periodic system (if assuming the planar wave-vector is conserved during transmission). This verifies the validity of calculation with only one planar primitive cell.

With the basis set of $|f_i, n\rangle$, the matrix elements for Hamiltonians H_e and H_p have similar expressions to those shown in Eq. 3.57.

$$\begin{aligned} \langle f_i, n | H_e | f_j, m \rangle &= \delta_{n,m} \langle f_i | H_e | f_j \rangle \\ \langle f_i, n | H_p | f_j, m \rangle &= \delta_{f_i, f_j} \delta_{n,m} \left(n + \frac{1}{2} L_\perp \right) \hbar \omega \end{aligned} \quad (3.62)$$

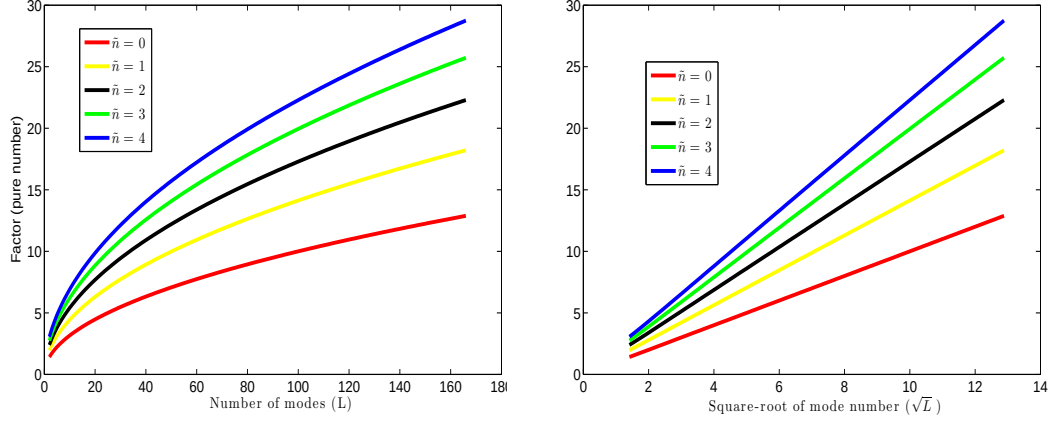


Fig 3.27: (a) the factor within the square bracket at the right side of Eq. 3.61 varies with number of modes L ; (b) the same factor varies with the square root of number of modes, demonstrating its proportionality to $\sqrt{L}$. Different curves correspond to different average occupation numbers per mode, $\tilde{n}$.

The transmission profile for each initial phonon state is then calculated by incorporating all the Hamiltonian components into the matrix equation Eq. 3.44. Statistically, the phonon system at room temperature can be regarded as a grand canonical ensemble. The probability of each microstate is then described by the exponential law $p_i = \exp[(N_i\mu - E_i)/kT]/Z$, where the phonon chemical potential $\mu_i \equiv 0$ and Z is the partition function. Therefore, the transmission profile at room temperature can be obtained by averaging the transmission profiles of all the possible phonon states, weighted by their respective probabilities.

$$T_{av}(\epsilon_e) = \frac{\sum_{n=0}^{n_{max}} T(\epsilon_e, n) C(n + L_{\perp} - 1, L_{\perp} - 1)}{\sum_{n=0}^{n_{max}} C(n + L_{\perp} - 1, L_{\perp} - 1)} \quad (3.63)$$

$$C(n + L_{\perp} - 1, L_{\perp} - 1) = \frac{(n + L_{\perp} - 1)!}{n!(L_{\perp} - 1)!}$$

3.3.2.1 Numerical results and discussion

By adopting the one-electron TB scattering model and the interaction with optical phonons, the transmission profiles of several RTD structures have been calculated. Due to the required intensive computational work, the RTD structure has not been optimized in order to match the maximal efficiency of the hot carrier solar cell. However some traits can be revealed from this numerical work.

The first structure considered here is an AlAs/GaAs/AlAs RTD, in which each layer consists of three atomic monolayers (layer thickness = $3/2 \times$ lattice constant). A reference energy-dependent transmission curve has been calculated first, without consideration of the electron-phonon scattering. From Fig. 3.29(b) the resonant peaks appear to be ideal for ESC application, if only accounting for electrons propagating normal to the layers. The first significant peak goes up to unity at 2.14 eV (above the valence band edge), with FWHM of around 0.02eV. And the next peak (at around 2.2eV) is not close enough to ruin the selective property, as the energy separation from the first peak (68meV) is much higher than the thermal smearing at room temperature ($kT \approx 26\text{meV}$).

If incorporating the electron-phonon polar interaction Hamiltonian, the coherence of the transmitting electron is potentially destroyed, by absorbing or emitting phonons. The red solid curve in Fig. 3.29(b) shows the transmission profile for an initial state of zero optical phonons in the well. Compared to the reference case, the main peak suffers a red shift of about 16meV. This is probably due to the negative polaron self-energy arisen from the electron-phonon coupling (Sec. ??). A side peak appears at the right side of the main peak (2.16eV), separated from the main peak by about 36meV. This corresponds to the electron losing its energy by emitting a LO-phonon in the well,

then transmitting out resonantly. As initially there are no LO phonons, the side peak at the left of the main peak does not exist. For the other solid curves shown in Fig. 3.29(b), the initial phonon numbers are all higher than the average value at room temperature, thus the 1st main peak completely disappears, accompanied by multiple side peaks at both sides. The peaks at the left side correspond to the absorption of one or more phonons, while those at the right are for the emission of phonons.

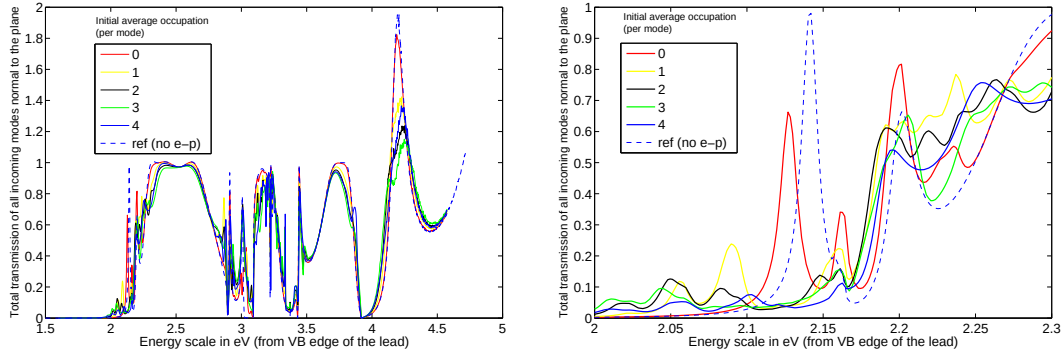


Fig 3.28: Total transmission profiles for right-going modes vertically propagating into an AlAs/GaAs/AlAs RTD, in the energy range of whole conduction bands (a), and the conduction band edge (b), of the contact material (GaAs). The two barrier layers and one well layer are both of the thicknesses of three monolayers. Curves with different colors refer to different initial occupation numbers of the well-confined LO phonon modes. The dashed line corresponds to the transmission profile if electron-phonon coupling has been neglected.

The transmission profile at room temperature has been calculated and demonstrated in Fig. 3.30, by averaging over all the transmissions at different initial phonon states (Eq. 3.63). When incorporating the electron-phonon coupling, the transmission at the red-shifted main peak becomes lower, while side peaks emerge at both sides. We can conclude that electron-phonon scattering introduces side peaks while weaken the main resonant peaks. The

selectivity of the ESC is impaired by the phonon scattering. To prevent this problem, materials with small coupling constants are preferred, and the well layer shall be made as thin as possible.

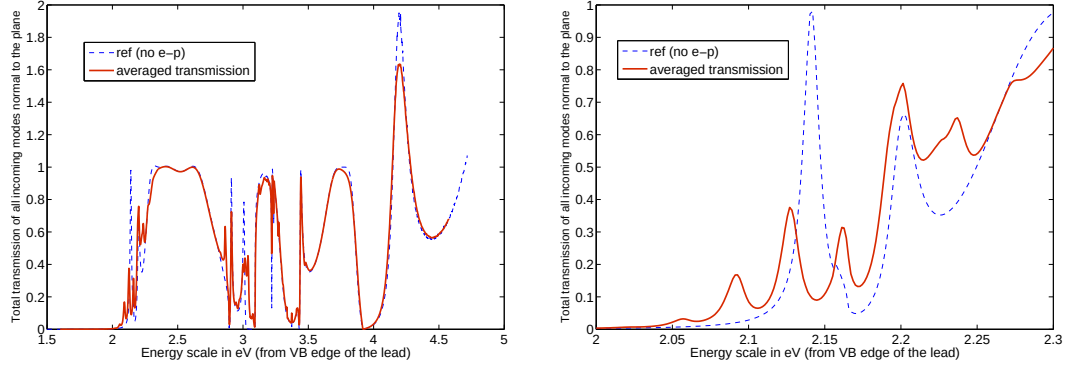


Fig 3.29: Total transmission profile for right-propagating modes vertically propagating into an AlAs/GaAs/AlAs RTD at room temperature, in the energy range of whole conduction bands (a), and the conduction band edge (b), of the contact material (GaAs), averaged by the statistical probabilities of different phonon occupation numbers. The two barrier layers and one well layer are both of the thicknesses of three monolayers. The dashed line corresponds to the transmission profile if electron-phonon coupling has been neglected.

However, there is an inherent problem when the well layer is as thin as we adopted in this calculation. As shown in Fig. 3.31, if accounting for the incoming electrons at all incident angles, the transmission profile is completely smoothed with no significant resonant peaks. Actually the first confined level of the thin well layer is close to the barrier height. Those resonant-tunneling electrons with a non-zero incident angle have extra kinetic energy due to their transport along the planar directions, and are able to travel across the barrier in a classical way. From the logarithmic plot shown in Fig. 3.31(b), the resonant peaks, which begins from 2.14eV, are merged by the broad plateau of classical transport. For high initial phonon numbers,

there are multiple transmission lumps appearing at the energy range below 2.14 eV, which are contributed by the electron resonant tunneling after absorbing multiple phonons. The transmission profile at room temperature is demonstrated in Fig. 3.31, calculated using the same averaging technique as that in Fig. 3.30.

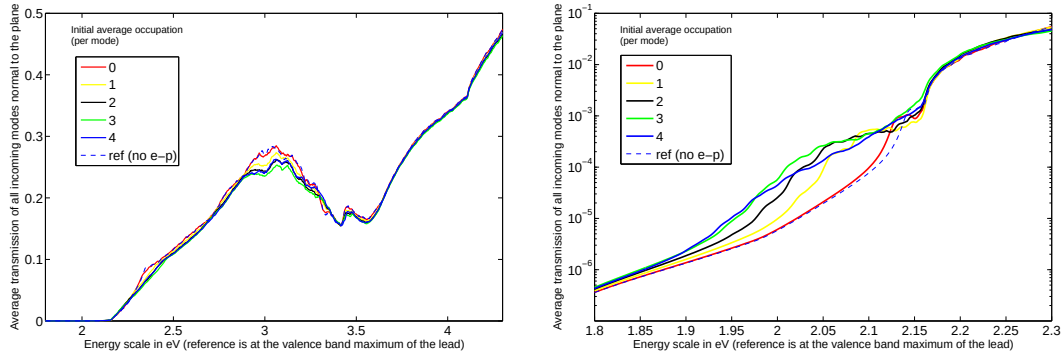


Fig 3.30: Average transmission profile including all right-propagating modes into an AlAs/GaAs/AlAs RTD, in the energy range of whole conduction bands (a), and the conduction band edge in logarithmic scale (b), of the contact material (GaAs). The two barrier layers and one well layer are both of the thicknesses of three monolayers. Curves with different colors refer to different initial occupation numbers of the well-confined LO phonon modes. The dashed line corresponds to the transmission profile if electron-phonon coupling has been neglected.

From the results shown above, we conclude that the AlAs/GaAs/AlAs RTD each of three monolayers cannot fulfill the ESC requirements for the HCSC application. Apart from using a thicker well layer, we could also use a different well material that has a smaller band gap. Among the III-V zinc-blende-structured materials, InAs can fulfill the demand well. As the lattice constant of AlAs (and GaAs) is smaller than that of InAs, the InAs layer has compressive strain along the planar directions. This strain reduces its band gap further, so it is even more beneficial. To calculate the transmission

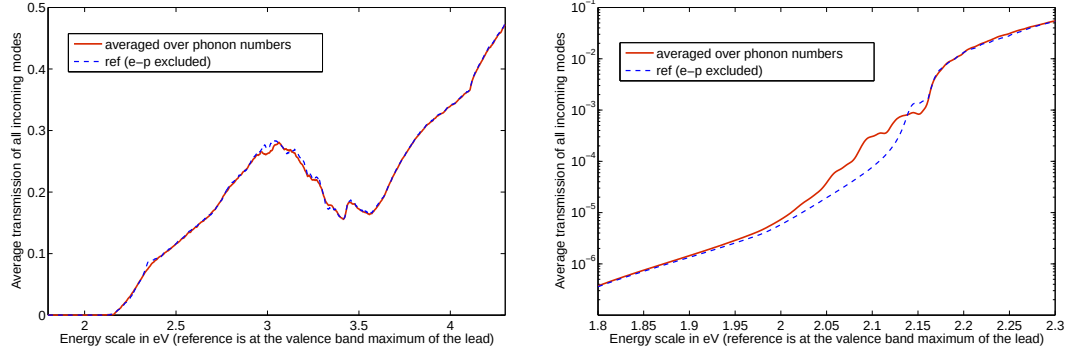


Fig 3.31: Average transmission profile including all right-propagating modes into an AlAs/GaAs/AlAs RTD at room temperature, in the energy range of whole conduction bands (a), and the conduction band edge in logarithmic scale (b), of the contact material (GaAs). The two barrier layers and one well layer are both of the thicknesses of three monolayers. Curves with different colors refer to different initial occupation numbers of the well-confined LO phonon modes. The dashed line corresponds to the transmission profile if electron-phonon coupling has been neglected.

profiles of this structure, we still adopt the lattice-matched GaAs as the left and right contacts, and AlAs as the barriers. The lateral atomic separation of the strained-InAs layer is reduced to match the lattice constant of AlAs, while the vertical separation is enlarged, accruing to its Poisson's ratio. The band structure of this deformed InAs has been calculated using a separation-dependent tight-binding model[70].

The result shown in Fig. 3.33 demonstrates two resonant peaks around 1.8eV and a higher peak close to 2eV, if electron-phonon coupling is neglected. Here electrons of all possible incident angles are included, so the appearance of resonant peaks suggests the feasibility of using this structure as ESC. The higher resonant peak is at least one order of magnitude stronger than those low peaks, while its energy level is around 0.2eV higher. At room temperature this peak will not have significant impact on carrier transmis-

sion, but it becomes important when transmitting hot electrons ($T > 1000\text{K}$).

Although the transmission profile of no electron-phonon coupling seems promising, it is significantly impaired when taking phonon scattering into account. From Fig. 3.33, we could find a clear resonant peak only for the case of zero initial phonon number. The average transmission probability of this peak is very low ($< 10^{-3}$) so that the contact resistance can be an issue. If we plot the average transmission at room temperature using a normal scale (Fig. 3.34), the resonant transmission peaks are mostly smoothed when accounting for the phonon scattering.

In conclusion it is still hard to overcome both problems and get to a structure with both little phonon scattering and deep confined levels. The two requirements in fact counter each other: in order to get a deep confined level the well layer should not be too thin, while little scattering requires an ultrathin well layer (a few monolayers). To get a trade-off between them, a comprehensive computational analysis is required to optimise the structure. The material selection is also an important issue: a small electron-phonon coupling constant is required, and large electron effective mass is also preferred. The latter is because that lower confined levels appear in materials with heavy carriers. If we adopt heavy-carrier materials for the well, it might be possible to make an ultra-thin layer without being afraid of the disappearance of resonant peaks. In addition, thin barrier layers made of high band gap materials are preferred to prevent the impact of classical transport. Further restrictions are introduced from considerations on actual fabrication issues. For instance, the high degree of lattice mismatch when growing InAs on GaAs allows only a few monolayers before island formation. Thus a uniform structure would not have an InAs layer thicker than 6 atomic monolayers.

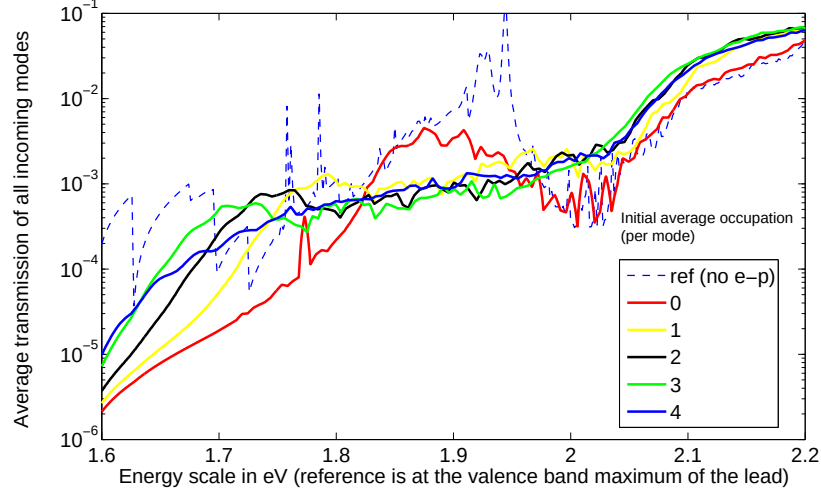


Fig 3.32: Average transmission profile including all right-propagating modes into an AlAs/strained-InAs/AlAs RTD of the contact material (GaAs) with different numbers of phonons. The numbers of monolayers are 3(AlAs)/6(InAs)/3(AlAs). The dashed line corresponds to the transmission profile if electron-phonon coupling has been neglected.

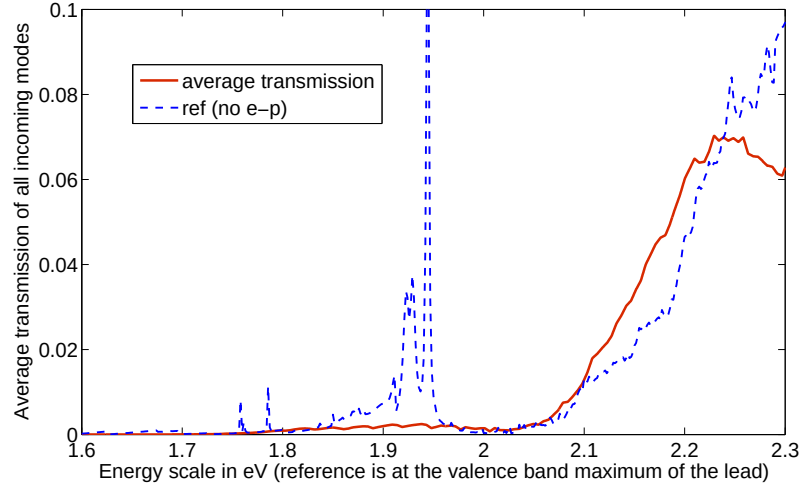


Fig 3.33: Average transmission profile including all right-propagating modes propagating into an AlAs/strained-InAs/AlAs RTD of the contact material (GaAs) at room temperature, averaged by the statistical probabilities of different phonon occupation numbers. The numbers of monolayers are 3(AlAs)/6(InAs)/3(AlAs).

CONCLUSIONS AND FUTURE WORK

This thesis describes the research work the author has done during his PhD study. It is separated into two parts. The first part deals with the theoretical investigation of the device concept of the hot carrier solar cell, and using non-specific material parameters to calculate the performance of such device. The second part concerns the calculation of these material parameters by applying theoretical models to real materials.

To conclude, the work on device modeling is listed below, including its description and results:

1. Establishment of the first hybrid model that is capable of determining optoelectronic properties over the whole operational range of this solar cell. The previous concepts of particle conservation and energy conservation have been reformulated and combined together, yielding a series of equations to determine the current at each voltage. To overcome the gap between the two conservation laws, real rates of impact ionization and Auger recombination occurring in the hot carrier device have been calculated and incorporated into this model. The efficiency figure predicted by this model is still high (43.2%

for 1000-sun concentration), although it has been significantly reduced from the efficiency limit reported in literature by taking into account a close-to-realistic carrier thermalization time (100ps).

2. Incorporation of non-ideal selective energy contacts into the previous device model. In the previous model the carrier extraction is regarded as being reversible, while in this improved model the entropy generation through realistic ballistic contacts has been included. The overall device efficiency now depends on both the absorption (optical-to-thermal) efficiency and the extraction (thermal-to-electrical) efficiency. A nitride-based device prototype has been proposed, whose maximal efficiency has been predicted. However, experiments of InN thin film suggest an ultrafast cooling lifetime of 6.87ps, which reduces the efficiency down to 24% for 1000-sun concentration.

3. To avoid oversimplified assumptions, especially those with large disagreement (such as the temperature difference between electrons and holes), a relaxation-time model has been proposed, with in-device carrier distributions described by arbitrary energy-dependent functions. All types of relevant microscopic processes have been included in this model, and the only required material parameters are their respective relaxation times. This model enables us to look into the details of the steady-state operation of the hot carrier solar cell. In addition, it helps to clarify some arguments on the working principle.

4. A unified theoretical framework has been proposed, aiming to solve any device problem in the far-from-equilibrium regime. As an important application of this framework, a generalized opto-electronic reciprocal principle has been deduced, which has a similar form with that reported in literature. Instead of using the knowledge of semiconductor p-n junction just as the previous work did, this generalized reciprocity only depends on the validity of Fermi's golden rule, and is capable of being applied to any solid-state devices.

In addition, it can apply to a system with any numbers of optical sources and electrical terminals, with a even finer resolution.

The part on material modeling includes the following works:

1. Electronic modeling on both bulk semiconductors and multiple-quantum-well-superlattice structures. A *sps** tight-binding model has been adopted for these calculations. The results on superlattices show electronic band structures varying with different superlattice structures, whose trends have been explained. This work contributes to the fundamental considerations of material selection for the hot carrier solar cell.

2. Phononic modeling on InN-GaN multiple-quantum-well-superlattice structures. A modified bond charge model has been used, incorporating the force constants interpolated from *ab-initio* calculations. The phonon structure varies with different layer thicknesses, as well as the macroscopic properties such as specific heat and thermal conductivity. This work provides quantitative insight on the phonon-bottleneck effect in multiple-quantum-wells.

3. Many-particle processes, including carrier-phonon, phonon-phonon and carrier-carrier interactions, are of great importance on realizing the hot carrier solar cell. The electron-phonon and phonon-phonon interactions need to be prohibited in order to keep the electrons hot, while the optimization for carrier-carrier interaction is much more complicated, as demonstrated in the device modeling part. Here relevant material models are presented to evaluate these rates (or lifetimes) of many-body processes. This work leads to calculations on the material parameters and properties, which are to be adopted into the device model. It helps the designer of the hot carrier solar cell to optimize the material selection.

4. The transmission problem of electron through ultra-thin material sys-

tem. Tight-binding models are incorporated so that scattering regions of only a few monolayers are modeled appropriately. The author has formulated the phonon-scattering effect and incorporated this into the tight-binding transmission model. To convert the problem from an exponential-time (EXP-TIME) one to a polynomial (P) problem, a simplified method has been introduced. This enables the incorporation of phonon scattering into problems of large-scale system. The results suggest that phonon-scattering can impair the energy selectivity significantly. This contributes to the consideration when designing the energy selective contacts.

This thesis provides theoretical frameworks for future researchers to optimize the structure and materials of the hot carrier solar cell. The study of electronic and phonon properties of both bulk and QW superlattice materials, sheds light on the optimum structures, materials and mechanisms for slowed carrier cooling. It enables the design of optimised materials and structures for both hot carrier absorbers and ESCs such as to design full hot carrier working devices. Some possible future developments are listed as below.

1. The further development of the device model of the hot carrier solar cell. The spatial dependence of carrier distributions is possible to be incorporated. Random algorithm such as Monte Carlo simulation may be explored for providing an alternative approach to simulate such devices.

2. The co-optimisation of the absorber and the contacts. As revealed from this thesis, the optimized properties of the absorber and the contacts have strong correlation. Therefore they need to be optimized together. The optimal extraction energy levels and transmission window widths largely depends on the interaction properties of the absorber material. Therefore a detailed co-optimization on both material and device structure would be very helpful

to the design of the cell.

3. Investigation on the cooling mechanism in nano-structured materials. Although this thesis provides some preliminary analysis on the multi-step cooling processes of hot electrons, further investigations are required for in-depth understanding on the carrier and lattice dynamics in nano-structures. Many-body interactions are required to be incorporated as well as the transport of quasi-particles.

4. Design and optimization on the resonant tunneling contacts. From the real material modeling work described in this thesis, it is not an easy task to design a resonant tunneling contact that fulfills all demands of the hot carrier solar cell. A fine design is required for both the material and width of each layer, and the selection of material needs considerations on inhibiting scattering mechanisms. Other types of contacts may be investigated as alternative ways to harvest the thermal energy of hot electrons with a high efficiency.

5. Fabrication of the device prototype. As suggested in this thesis, an all-nitride-based structure may be fabricated using MBE or MOCVD to fulfill the device requirements of the hot carrier solar cell. In future this structure is to be fabricated for preliminary device characterizations. Other similar structures, such as all-arsenide-based device, are also possible prototypes to realize the hot carrier solar cell.

LIST OF PUBLICATIONS

[1] Feng, Y, Patterson, R, Lin, S, Shrestha, S, Huang, S, Green, MA, and Conibeer, G, 2013, "Investigation of carrier-carrier scattering effect on the performance of hot carrier solar cells with relaxation time approximation", Applied Physics Letters, vol. 102, no. 24, pp. 243901, <http://dx.doi.org/10.1063/1.4811263>

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[3] Feng, Y, Aliberti, P, Veettil, BP, R. Patterson, Shrestha, SK, Green, MA and Conibeer, G, 2012, 'Non-ideal energy selective contacts and their effect on the performance of a hot carrier solar cell with an indium nitride absorber', Applied Physics Letters, vol. 100, no. 5, pp. 053502, <http://dx.doi.org/10.1063/1.3680594>

[4] Feng, Y, Aliberti, P, R. Patterson, Puthen-Veettil, B, Lin, S, Shrestha,

5. List of Publications

SK, Green, MA and Conibeer, G, 2012, 'Analysis on carrier energy relaxation in superlattices and its implications on the design of hot carrier solar cell absorbers', in Proceedings of SPIE Vol. 8471, The international society for optics and photonics (SPIE), presented (oral) at SPIE 2012: Optics+Photonics, San Diego, 12-16 August 2012, 10.1117/12.928459

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