

Defects in silicon solar cell materials

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DEFECTS IN SILICON SOLAR CELL MATERIALS

by

Benjamin O. Chan, B. Sc.

A thesis submitted to the University of New South Wales in fulfilment of the requirements for the degree of Doctor of Philosophy

March 1993

To my wife, Mimi and my deceased son, Isaac

ABSTRACT

This thesis aims to evaluate defects in the different Si solar cell materials in use and being developed at the Centre for Photovoltaic Devices and Systems, University of New South Wales with a view to understanding how they affect solar cell performance A wide range of characterisation techniques (defect etching, optical microscopy, electron microscopy, IR microscopy, FTIR, PL, EBIC, EDX, PIXE, PIGE, RBS, hot probe, four point probe and C-V) were implemented on the various materials investigated in this thesis. These investigations involved a qualitative evaluation of free carrier absorption in solar cells; the identification of processinduced defects and clarification of their role in gettering processes in novel lasergrooved solar cells; a systematic evaluation of intrinsic defects in cast polycrystalline Si received from different manufacturers and correlating these defects to the open circuit voltage, short circuit current density, fill factor and efficiency of laser-grooved solar cells fabricated on these substrates; and the characterisation of novel solutiongrown Si layers being developed at the UNSW. Preferential defect etching coupled with microscopy and EBIC techniques proved indispensible in these investigations.

Free carrier absorption in Si was reviewed and an empirical model for solar cells presented Rough calculations from the model indicated that such absorption can affect the long wavelength response of solar cells. This effect is enhanced in solar cells incorporating light-trapping schemes

For the laser-grooved solar cell processing sequence, oxidation-induced defects exposed via defect etching and previously thought to be dislocation etch pits were correctly identified as S-pits. It was consequently shown that no dislocations were induced by oxidation of planar or textured surfaces using normal oxidation procedures. Thermal wave effects produced by pulsed-laser scribing of Si was observed for the first time and was shown to getter oxidation-induced precipitates Dislocation generation was observed in the groove region during P-diffusion and drive-in Preferential P diffusion along these dislocations was also observed and

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believed to enhance the gettering and passivating properties of P in laser-grooved solar cells

For cast polycrystalline Si materials, spreadsheet analysis of interstitial oxygen and subsitutional carbon, video microscopy and image processing of dislocations and IR microscopy of inclusions allowed densitometric measurements for these defects EBIC studies have suggested that dislocations were electrically active in grain boundaries. An EBIC linescan technique for the evaluation of grain boundary recombination velocities and intragrain diffusion lengths was also suggested Preliminary correlations between intrinsic defects and solar cell output showed that low interstitial oxygen concentrations resulted in higher cell short circuit current density and efficiency.

For solution-grown Si, it was shown that the dominant dopant impurity came from melt material (e g., Bi for Au-Bi melts and Al for Sn-Al melts). A major obstacle to successful device fabrication was the formation of inclusions due to melttrapping mechanisms at the epilayer-substrate interface However, they were not observed at the interface of solution grown layers Strain was observed for solutiongrown dilute-Ge Si_{1-x}Ge_x layers via PL measurements Such layers can potentially contribute to efficiency enhancements in solar cells. EDX probing of an interfacial layer between Si and glass have suggested the formation of an AlSiMgO compound from which Si growth can proceed. The properties of this compound and Si growth mechanisms on it are undergoing further investigation.

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CHAPTER 1

INTRODUCTION

1.1 The Promise of Photovoltaic Energy Conversion

Ever-increasing energy demand due to development is leading to depletion of finite fossil fuel reserves. Furthermore, the concern over emission of greenhouse gases and their environmental impact by burning fossil fuel may not make it possible to utilise all of the known available reserves. Photovoltaic energy conversion via solar cells have long been available as a 'clean' alternative energy source. However, the prohibitive cost and low energy conversion efficiency of solar cells limited their early use to remote area power generation (e.g., space exploration (Green, 1993))

The development of the laser-grooved solar cell by Wenham in 1986, saw a vast improvement (50% relative) in solar cell efficiencies compared to commercially available screen-printed cells at that time with no significant changes in cell processing costs. Optimisation of cell processing led to efficiencies above 20% (Chong, 1989) Recent pilot-line production at the University of New South Wales are turning out efficiencies as high as 19.6% on large (45 cm²) and small area (8 cm²) cells. The theoretical limit for Si solar cell efficiency is 30% for the Auger-recombination limited cell (Green, 1987, pp. 96-98). Further improvements to cell efficiency are possible by a proper understanding of device characteristics, specially gettering and passivation mechanisms occurring during laser groove processing

The main bulk of the cost in Si solar cell fabrication lies in the fabrication of the starting Si substrate (Hunt, 1976) Cost reduction in the following areas in Si growth will enhance the economic viability of photovoltaic energy conversion:

1) the inefficient and energy-intensive Siemens process for purifying metallurgical grade Si to semiconductor grade Si,

 Czochralski (CZ) growth of Si ingot from semiconductor grade Si and subsequent slicing.

Cast polycrystalline material replaces CZ growth with a cheaper casting process The quicker growth and relatively impure conditions save a lot of energy from energy-intensive CZ growth. With a cheaper ingot, wastage from low yield slicing processes become less significant.

Slicing of the ingot wastes half of the already costly Si material and produces wafers which are thicker than required for optimum cell performance For a cell with a randomised texture, this thickness is $\approx 100 \ \mu m$ (Green, 1987, p. 96). The object of solution-grown Si is to substitute the CZ growth with a less energy-intensive (low-temperature) process The direct deposition of Si sheets on glass substrates eliminates wastage from normal ingot slicing practices. With light trapping schemes included, a sheet thicknesses of 20 μm will result in insignificant losses in cell performance compared to the savings made in producing the Si substrate. For such thin sheets, the glass substrate is expected to provide the necessary mechanical strength for cell processing. Glass is the usual encapsulant for solar cell modules and actually acts as a superstrate for the solar cell structures envisioned for solution-grown Si layers.

For the low cost materials mentioned above, defects are inevitable because of their relatively fast and impure growth conditions. Some of these defects may be electronically neutral and remain relatively unchanged during cell processing and, therefore, contribute insignificantly to cell output characteristics. Such defects can be tolerated in starting solar cell substrates. Most defects, however, impede carrier photogeneration and collection by creating non-carrier generating light absorption processes or by acting as carrier recombination or scattering sites (Chapter 3). A need then exists for the proper evaluation of the impact of these defects on large area devices like solar cells. Defect correlation studies on polycrystalline Si (Martinuzzi,

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1987, El Ghitani and Martinuzzi, 1989a, b; Brenneman, 1990; Doolittle et al., 1990 and Hide et al., 1990) have underlined this need.

Defects need not be a liability to cell performance as extrinsic gettering studies have proven (Rozgonyi et al., 1975; Schwuttke et al , 1977; Pearce and Zaleckas, 1979; Yang and Schwuttke, 1980; Hayafuji et al., 1981; Eggermont et al , 1983, Swaroop, 1983 and Elwell and Hahn, 1984). It is believed that defects introduced during laser groove processing provide potential but unproven gettering mechanisms (Wenham, 1986 and Chong, 1989) Such possibilities have been reported for intrinsic defects in polycrystalline material as well (Sopori, 1988 and Seiter, 1987).

Characterisation of intrinsic (crystal growth) and extrinsic (material processing) defects in Si solar cell materials then sheds light on the device characteristics of solar cells and presents avenues for improving solar cell performance.

1.2 Objective of Thesis

The objective of this thesis is to evaluate defects in the different Si solar cell materials in use and being developed at the Centre for Photovoltaic Devices and Systems, UNSW with a view to understanding how they affect solar cell performance Process-induced defects in laser-grooved solar cells are to be identified and their role in gettering clarified. Intrinsic defects in cast polycrystalline Si received from different manufacturers are to be characterised systematically and correlated to cell open circuit voltage, short circuit current density, fill factor and efficiency Solution-grown Si layers being developed at the UNSW are to be characterised in the hope of providing direction to appropriate strategies for the growth of Si on glass for solar cell fabrication

1.3 Scope of Thesis

An understanding of defects and how they affect solar cell performance will be essential in understanding the results presented in this thesis. A brief description of defects occurring in the Si lattice is presented in Chapter 2 with more extensive treatments cited in references Chapter 3 is a general discussion on how defects affect solar cell performance. The electrical activity arising from them is described in some detail The discussion on free carrier absorption is a first attempt in considering its effect on solar cell performance. A suggestion on how to incorporate it satisfactorily into solar cell equations is made. It will be shown that the red response and, hence, the light trapping property of solar cells will be affected the most by such absorption.

Chapter 4 describes the development of characterisation equipment and techniques necessary to identify defects (described in Chapter 2) and their effects (Chapter3) Particular attention is given to the techniques used to extract the results in Chapters 5, 6 and 7 Electron Beam Induced Current (EBIC), preferential-defect etching and microscopy will prove to be indispensable tools in all three chapters.

Chapter 5 re-examines oxidation-induced damage identified by Chong (1989) in laser-grooved solar cells Defect-etching of wafers will show that the previously identified dislocation etch pits are actually S-pits which come from precipitate formation due to contamination from polishing, furnace materials during thermal processing and/or chemical baths for device processing or material evaluation The laser-grooving procedure will be identified as the main defect-generating step in the process and the extent and nature of the damage will be discussed in detail. An interesting 'gettering' effect during pulsed laser processing will be explained in terms of thermal waves as are dark bands surrounding a laser scribed oxide observed only in a scanning electron microscope. This is the first time that such an effect has been reported during pulsed laser processing of Si and provides interesting material for future processing applications not only for solar cells but for other devices as well. The chapter concludes by providing a gettering model for laser-grooved solar cells The sintering step will be identified as the most effective gettering step in the process where all the gettering mechanisms (P, Al and laser damage) act in unison over the whole cell volume.

Chapter 6 concerns the development of characterisation techniques for the systematic evaluation of intrinsic defects in cast polycrystalline Si material produced by different manufacturers Dislocations, inclusions, substitutional carbon content and interstitial oxygen content are the main defects to be considered in this chapter Only grain boundaries show significant recombination activity during EBIC investigations Dislocations seem to be active only when located along grain boundaries Recombination activity from inclusions is difficult to observe although they are expected to hinder the generation of carriers in the solar cell. Comparison of EBIC linescans along grain boundaries with an existing model (Dimitriadis, 1985) makes possible the interpretation of such linescans in terms of grain boundary recombination velocity and grain diffusion lengths. An initial attempt to correlate defects to cell open circuit voltage, short circuit current density, fill factor and efficiency indicates that effects due to interstitial oxygen concentration dominate effects coming from It will be shown that decreasing interstitial oxygen concentration other defects improves cell short circuit current and efficiency This result is consistent with previously reported results (Doolittle et al., 1990 and Hide et al., 1990)

Chapter 7 deals mainly with the characterisation of Liquid Phase Epitaxial Si (Lee, 1990 and Shi, 1992a) and Si_{1-x}Ge_x (Healy et al., 1991) layers. The main reason for this is to be able to identify the appropriate strategy for growing Si on glass for solar cell fabrication Liquid-Phase Epitaxial layers grown at very low temperatures with Au60wt%Bi melts are shown be n-type with dopant concentrations in the 10^{17} - 10^{18} cm⁻³ as spreading resistance analysis shows. Proton-Induced X-ray Emission (PIXE) measurements identify large amounts of Au and Bi in the sample due to trapped melt material at the interface between the grown layer and the substrate This is verified by IR microscopy and Energy Dispersive X-ray (EDX) analysis on an exposed inclusion particle along a cleaved edge of a typical LPE Si layer grown from Au60wt%Bi. Arsenic, a suspected impurity in Au material, is also detected in concentrations comparable to dopant concentrations from spreading resistance analysis. Photoluminescence analysis, however, positively identifies Bi as the dopant

impurity Arsenic identified in PIXE analysis can then be attributed to an artifact arising from the random summing of L X-rays from Au and Bi as curve-fitting experiments on Au-Bi melts showed a better fit assuming As was not present (Hotchkis, 1991).

EBIC studies on epilayer substrate interfaces show strong electrical activity arising from inclusions as they are located right at the junction area. Defect etching of similar layers reveal similar inclusion distribution to the EBIC contrast observed Dislocations are also apparent in the defect etched epilayer Junctions fabricated from n/p LPE layers produced a cleaner interface with weaker electrical activity from epilayer-substrate inclusions as they are located farther away from the active junction region Improved epilayer characteristics using Sn-based melts have resulted in solar cells with open circuit voltages exceeding 600mV and efficiencies up to 8 5 % (Shi et al., 1992a)

Strain in dilute-Ge Si_{1-x}Ge_x alloys grown with the same melt is identified via photoluminescence measurements (Chan et al., 1992). An attempt to expose misfit dislocations is obscured by the already high dislocation density of the layers The order of magnitude difference observed in dislocation density for x = 0.03 and x = 0.19 layers may indicate that the observed dislocations are threading dislocations originating from misfit dislocations. Cells fabricated from unstrained Si_{1-x}Ge_x alloys show recombination activity arising from the observed dislocations when examined under EBIC. Activity from inclusions are likewise observable These strained layers may find application in solar cell fabrication (Healy and Green, 1992).

Finally, the realisation of Si growth on glass via rheotaxy (Shi et al, 1992b) allowed the use of higher temperatures for solution-growth. EDX probing of an interface layer apparent along a cleaved section of a Si on glass sample reveal a possible nucleation mechanism for such growth The presence of Mg and Al indicates that O on the surface is being depleted by these elements exposing a Si-rich surface suitable for crystal growth. Defect etching of Si on glass layers display a twinning structure reminiscent of Si on sapphire (Nolder et al., 1965).

Acronyms, relating mostly to characterisation techniques, have been explained in appropriate locations in the text of this thesis. However, a list is given in Appendix C in case they prove too hard to locate.

CHAPTER 2

DEFECTS IN SILICON

2.1 Classification of Defects

Defects in the Si diamond lattice can be classified into the following categories[•] point, line, area and volume (van Bueren, 1960). This is a 'dimensional' classification of the defects, i. e., zero-dimensional, one-dimensional, two-dimensional and three-dimensional respectively One may think that such a classification puts too much emphasis on structure and ignores the electrical activity of the defects However, such activity actually stem out from the actual physical imperfections in the Si lattice (broken lattice bonds). Defects in semiconductors have been recently reviewed by Boer (1990, Part V).

2.1.1 Point Defects

Figure 2.1 illustrates a variety of point defects on a two-dimensional lattice. Figure 2 1a) shows a self-interstitial, 2 1b) is a vacancy, 2.1c) is a substitutional impurity atom, 2.1d) is an interstitial impurity atom. A more exhaustive listing of such defects (including systems of point defects) is given by Boer (1990, pp. 432-434) Such defects introduce lattice strain among its neighbouring lattice sites. The amount of strain present is determined by the size and concentration of the point defect.

Point defects move through the Si lattice by diffusion. Diffusion can proceed in several ways depending on the point defect involved. Self-diffusion occurs among lattice atoms at high temperatures. Impurities normally associate with a vacancy, a



Figure 2.1. Point defects in Si: a) vacancy, b) self-interstitial, c) substitutional impurity and d) interstitial impurity.

lattice atom, or an interstitial site for diffusion. The diffusion of the impurity in the Si crystal depends on the temperature and impurity concentration of the Si crystal The maximum amount of impurity the Si lattice can support at a certain temperature is usually expressed in terms of solid solubility

The investigation of point defects in Si is a very large field. The subject of dopant impurities alone comprises a major field of study in device processing (dopant diffusion, ion implantation, heavy doping, etc...). The behaviour of point defects has been of vital importance in understanding these processes. A good review on the creation and motion of point defects is given by Boer (1990, Chapter 19)

2.1.2 Line Defects

Line defects come in the form of dislocations Two types of dislocations are possible in the Si lattice, namely, edge and screw dislocations Figure 2.2 shows the distinction between the two⁻ the lattice deformation brought about by the defect We can think of edge dislocations as the result of inserting or removing partial planes of atoms in the lattice and screw dislocations as a fault in stacking the atoms in which part of the upper plane of atoms join part of the lower plane This difference is normally quantified in terms of the burger's vector of the defect The burger's vector is formed by drawing a polygon consisting of an equal number of lattice atoms on each side around the defect (Boer, 1990, p. 440) In a perfect lattice, these polygons are closed However, in the presence of a dislocation, an additional vector is needed to close the polygon. This vector is the burger's vector of the defect It can easily be seen that the burger's vector of an edge dislocation is perpendicular to it while that of a screw dislocation is parallel to it. For the materials used in this thesis, screw dislocations were rarely observed and more emphasis is placed on the edge dislocation in the following discussion. Examples of dislocations in Si are illustrated in Figure 5.2.

Dislocations can move through the lattice via glide or climb Dislocation glide normally proceeds parallel to its burgers vector along its slip plane, the plane defined



Α

В



Figure 2.2. Types of dislocations in Si: a) edge dislocation and b) screw dislocation. The burgers vector **b** is shown for each dislocation type.

by the burgers vector and the line defect This is more easily pictured as sideways motion of the inserted plane of atoms. If the motion proceeds perpendicular to its slip plane, the motion is referred to as dislocation climb which can be pictured as upwards motion of the extra plane of atoms. Partial climb, which is more likely to occur, is referred to as a jog. Dislocation motion ends when it encounters another defect (the Si surface, an impurity atom, another dislocation, an inclusion or a grain boundary, etc .) They are then said to be 'pinned' down by the defect

An interesting effect occurs when a pinned dislocation is subject to shear stress perpendicular to the dislocation Dislocation loops (Frank and Read, 1950) are formed sequentially with the process repeating itself periodically as long as the stress is present

When a layer composed of material with lattice constant a is grown on a substrate with lattice constant b ($a \neq b$), the resulting misfit can generate edge dislocations along their interface These dislocations are called misfit dislocations and are illustrated in Figure 2.3. These dislocations come from grown-in threading dislocations (Matthews and Blakeslee, 1974) which propagate from the sample surface through the interface and into the other layer. When the misfit between the two layers cannot be accommodated by strain, threading dislocations bow and elongate along the interface creating a segment of interfacial misfit dislocation Si_{1-x}Ge_x on Si (section 7.3) and heavily diffused layers (section 2.2.2) are examples of structures where misfit dislocations can be observed.

2.1.3 Area Defects

The most obvious area defect in any crystal is its surface. The numerous broken lattice bonds on the top, bottom and side surfaces of the crystal easily make it the largest crystal defect. The surface of Si crystals is normally covered with native oxide \approx 3 nm thick. This easily oxidised surface makes Si the most commonly used semiconductor for device fabrication as the oxide layer is capable of neutralising surface defects



Figure 2.3. Misfit dislocations (\perp) in the interface of a layer with lattice constant *a* grown on a substrate of lattice constant *b* (*a*<*b*). In the absence of strain, the dislocations propagate along the interface and form a rectangular array.

Grain boundaries are the next most important defect in polycrystalline Si These can be classified according to how much misorientation is present in the adjacent crystals. A twin boundary is formed when lattice atoms from one side of the boundary form the mirror image of the ones on the other side. The simplest form of a twin boundary is a stacking fault where no dangling bonds are formed along the boundary Stacking faults are terminated by partial dislocations (Nabarro, 1967) Stacking faults can grow or shrink by the emission or absorption of vacancies or selfinterstitials

Twin boundaries are classified as coherent or incoherent depending on whether the twin plane is identical to the boundary plane (Matare, 1971, p 149) Coherent twins have twin planes identical to the boundary planes and with minimum disorder resulting along the boundaries. Incoherent twins have boundary planes different from the twin planes resulting in twinning dislocations. Such higher order twins contain vacancy lines similar to an array of edge dislocations in low angle grain boundaries (Boer, 1990, p. 450).

Low-angle grain boundaries consist of a few degrees ($\theta < 5^{\circ}$) misorientation between the adjacent crystals (Matare, 1971, pp 91-94). The angle of misorientation θ can normally be described in terms of dislocation spacing d $\theta \approx b/d$ where b is the magnitude of the burgers vector. As the angle of misorientation increases, the number of dislocations along the boundary increases. Large angle grain boundaries may incorporate other defects like vacancies, precipitates or inclusions.

Interfaces arising from the growth of Si on a foreign substrate or of a $Si_{1-x}Ge_x$ alloy on Si constitute a surface defect Point defects, misfit dislocations and grain boundaries may arise from lattice mismatch between the grown layer and the substrate. Under suitable conditions, lattice mismatch can be entirely accommodated by lattice strain with resultant changes in the electrical property of the strained layer (section 7 3).

2.1.4 Volume Defects

Volume defects come in the form of precipitates and inclusions They are lumps of foreign material in the Si lattice These defects act as nucleation or pinning sites for other defects like point defects and dislocations. The surface of the volume defect in itself represents a defect. Small precipitates (occupying <3 atomic planes) are normally classified as point defects since they are still minuscule in the macroscopic sense. Thermal donors formed from oxygen precipitates are examples of small precipitates which can be classified as a point defect A more general term covering large point defects and defects extending up to 100 μ m in length is microdefect (Zulehner, 1989a, p 391) Stacking faults are the largest microdefects with some extending more than 100 μ m in the crystal They are more appropriately classified as area defects (2.2.3) as the precipitated vacancies or self-interstitials from which stacking faults originate normally aggregate on a plane.

2.2 Generation of Defects

Defects are generated during crystal growth and during device processing Defects arising from growth are called intrinsic defects since they are the inevitable defects in the starting material for device fabrication Defects due to handling and processing of Si material into devices are called extrinsic defects. The following section discusses intrinsic defects generated by the growth techniques used for the materials considered in this thesis. the Float Zone (FZ) and Czochralski (CZ) techniques for single crystal silicon, the casting process for polycrystalline Si and solution growth for thin film Si. This will then be followed by a discussion of extrinsic defects related to solar cell processing. This discussion will concentrate on the novel laser-grooved solar cell processing sequence (Wenham, 1986 and Chong, 1989) Shimura (1989, pp 279-377) reviews issues concerning intrinsic and extrinsic defects in Si microelectronic device fabrication.

2.2.1 Intrinsic Defects

2.2.1.1 Single Crystal Si

The CZ and FZ techniques (Shimura, 1989, pp 121-146) are the more common growth techniques for current Si wafers with CZ-Si accounting for \approx 80% of wafers used in the semiconductor industry Vastly improved control over growth conditions has made possible the growth of dislocation-free crystals The term dislocation-free means that dislocations are not observable on the grown ingots and is, therefore, limited by the technique used to observe the dislocations. For the manufacturer of the FZ-Si wafers used in this thesis, this would mean a density less than 100 cm⁻² (Chong, 1989, p 169). This density varies as the dopant concentration in the wafer increases due to increased lattice stress caused by the differing size of the impurity. Typical densities for commercially available wafers are from 10² to 10⁴ cm⁻² (Boer, 1990, p 445) Dislocation-free growth has, however, resulted in the formation of swirl defects (Shimura, 1989, p 282) These microdefects are believed to originate from the high density of self-interstitials and vacancies inherent in dislocation-free Si

An important difference between FZ and CZ grown crystals lies in the interstitial oxygen (O_i) content of the resultant crystals. Table 2.1 lists impurities present in typical CZ and FZ Si (Zulehner, 1989b). It can be seen that the O_1 concentration in FZ-Si is one to two orders of magnitude less than for CZ-Si The greater O_i content of CZ-Si is mainly due to contamination from the quartz crucible used to contain the melt during crystal growth O_i contributes to the mechanical strength of Si wafers (Shimura, 1982) reducing breakages due to wafer handling and processing This is one of the main reasons why CZ-Si is more commonly used than FZ-Si in device fabrication. The larger O_i content, however, increases the possibility of precipitation during device processing Oxygen precipitation generates bulk defects (section 2.3) which degrade solar cell performance (section 3.3.1) FZ-Si has been used for the fabrication of research laser-grooved solar cells in order to have more control over oxygen precipitation. The best results in research and pilot-line

| Impurity | Impurity Concentration (cm ⁻³) | |
|----------|--|---|
| | CZ-Si | FZ-Si |
| С | 1×10 ¹⁵ - 5×10 ¹⁶ | 1×10 ¹⁵ - 3×10 ¹⁶ |
| Ν | <1014 | <1014 |
| 0 | 1×10 ¹⁷ - 1×10 ¹⁸ | 1×10 ¹⁵ - 1×10 ¹⁶ |
| Na | $\leq 5 \times 10^{12}$ | $\leq 2 \times 10^{12}$ |
| Cr | < 2×10 ¹¹ | < 2×10 ¹¹ |
| Fe | < 2×10 ¹² | < 2×10 ¹² |
| Ni | < 1×10 ¹² | < 1×10 ¹² |
| Cu | < 5×10 ¹³ | < 5×10 ¹³ |

 Table 2.1. Typical impurities found in FZ Si and their respective concentrations

 (adapted from Zulehner, 1989b)

production of laser-grooved solar cells have been attained using FZ-Si wafers

Transition metal contamination in both CZ and FZ Si has dropped to levels below the ppb range (Table 2 1) mainly due to improved growth techniques This, together with dislocation-free growth reduces concern over intrinsic defects for single crystal solar cells. More attention needs to be directed towards extrinsic defects

2.2.1.2 Cast Polycrystalline Si

Low cost Si materials usually come in the form of polycrystalline Si The savings comes from the less energy-intensive growth processes Various materials from different growth techniques (ribbon, dendritic web, sheet and cast) have been tried with cast polycrystalline Si producing better cells (Narayanan, 1989, p 36) The large grain sizes (\approx 4 mm on average) achieved on this substrate make the term semicrystalline more appropriate for this type of material. The casting process has

many variations depending on the particular manufacturer The basic casting technique involves pouring a Si melt into a mould, cooling it down and removing the mould (Brenneman and Tomlinson, 1988) The large amount of stress generated during the cooling process generates grain boundaries, grain sub-boundaries, and dislocations in the growing polycrystal. Impurities coming from the mould material (commonly quartz) introduce a large amount of oxygen into the cast ingot. Carbon is introduced via the heating elements in the furnace and in the starting Si material C precipitation forms SiC inclusions in the cast ingot. Electromagnetic casting (Kaneko et al , 1990) replaces the mould with an electromagnetic field. Contact with a mould and, hence, contamination from it is eliminated Defects identified in this type of material are described in greater detail in Chapter 6.

2.2.1.3 Solution-Grown Si

The growth of Si layers on foreign substrates has always been an attractive proposition to cut down on solar cell production cost (Lee, 1990 and Shi, 1992a) The savings in wafer sawing alone is enormous (\approx 50%). Low temperature processes further improve the economy of such material. At low temperatures, impurity solubilities are very low and the growth of high quality material is feasible. Thermal stress (see next section) is an important issue for solution growth of Si where the substrate lies horizontally on a heat susceptor Substrate flatness will be a crucial factor in eliminating thermal stresses during crystal growth Another concern for solution growth is to avoid melt trapping between the grown layer and the substrate and between grown layers. Chapter 7 will give a full account of defects observed in solution-grown Si and Si_{1-x}Ge_x

2.2.2 Extrinsic Defects

Solar cell device processing can introduce defects in the substrate. This is usually related to high temperature processes that accompany such steps and is dependent on the defects and stresses already present in the material. In this thesis, the defects generated by buried contact solar cell processing will be the focal point of discussion. Appendix A summarises the laser-groove solar cell processing sequence Defect generation can occur during oxidation, laser scribing, P diffusion and sintering.

High temperatures change the elastic properties of Si and can introduce thermomechanical stresses in the Si wafer When thermal stress exceeds the elastic limit of the wafer, plastic deformation takes place via dislocation generation and propagation This results in permanent warping of wafers (Hu, 1977, p 24) Radial temperature gradients are well-known sources for thermal stress during device processing They depend on how wafers are positioned in the furnace, the quartz boat holder in use and the rate at which the wafers are heated up or cooled down (Shimura, 1989, p. 286). Vertical furnaces (Singer, 1986) have been developed for the purpose of minimising thermal stress due to the weight of the wafer straining its bottom part in conventional horizontal furnaces.

Another important consideration during thermal processing of Si is the incorporation of impurities from furnace material and ambient gas The solubility of metals increases dramatically as the melting point of Si is approached Heavy and transition metals from furnace material can diffuse then into the Si substrate during high temperature treatments. Subsequent cooling of the substrate decreases the solubility of impurities and they will start precipitating on defects in the substrate (Pearce and McMahon, 1977). In dislocation-free FZ Si, precipitation mainly occurs at the surface.

For CZ-Si, O precipitation occurs at certain temperatures leading to the formation of undesirable bulk defects Some of these precipitates give rise to thermal donors of which 16 species have been identified so far (Gotz et al , 1992) Thermal donor formation can reverse the polarity of p-type substrates frustrating attempts to make a junction on such a substrate. For thermal treatments between 1000 - 1100 °C, oxygen out-diffuses from the wafer surface (O'Mara, 1988, p. 42) and precipitation occurs only in the bulk of the wafer. These precipitates can then act as sinks for other defects leaving a defect-free region near the surface for device fabrication. This

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gettering effect (section 3 5 1) is commonly used in microelectronic device fabrication

Heat treatments accompany most of the cell processing steps and are the main defect generating mechanism in these processing steps Other effects inherent in the processing step can, likewise, generate defects. The following discussion will concentrate on these aspects of laser-groove solar cell processing.

Oxidation-induced defects manifest themselves in the form of precipitates, stacking faults and dislocations The furnace is a main source of transition metal precipitates as has been described above. Stacking faults from oxidation are wellknown with extensive studies carried out by earlier workers (Hu, 1977, p 26) They are believed to originate from the nucleation of self-interstitials generated during oxidation on intrinsic defects or surface damage (Katz, 1988, p 133) For FZ-Si swirl defects (section 2.2.1 1) will be the relevant intrinsic defect. Dislocations generated by thermal stress have already been discussed earlier in this section and can be generated during oxidation by virtue of the high temperatures used in the process (Appendix A). Additional stress because of the different thermal expansion coefficients of the Si wafer and the oxide layer (thermal mismatch) is generated during the cool down process after oxidation. Dislocation generation in the oxidation of mechanically or laser damaged wafers (Schwuttke et al, 1977, Pearce and Zaleckas, 1979, Yang and Schwuttke, 1980, Hayafuji et al, 1981, Swaroop, 1983, p 99 and Elwell and Hahn, 1984) clearly demonstrates thermal mismatch. Although texturing of the wafer surface presents similar stress points during oxidation, no dislocations have been observed on oxidised textured wafers (section 5.2). Oxidation-induced defects in the laser-grooved solar cell processing will be investigated further in Chapter 5

An important effect during oxidation is the redistribution of dopant impurities (Katz, 1988, pp. 129-131) Oxidation is usually performed on P diffused surfaces As the Si-SiO₂ interface advances into the wafer, P will redistribute on each side of the interface until its chemical potential is the same on both sides This effect occurs

apart from the expected drive-in of P deeper into the wafer due to the high temperature treatment accompanying the oxidation step

In the laser scribing step, Si is being vaporised along the path of the laser Although the temperature affected regions are highly localised, the large thermal gradient between the scribed region and the surrounding area generates stress resulting in the generation of defects (Hayafuji et al , 1981) In laser-grooved solar cell processing, most of this damage is removed by a KOH chemical etch (section 5 3.2). Residual damage after the KOH etch will be investigated in Chapter 5 Further processing of the groove (P diffusion and sintering) will be shown to generate dislocations around the groove.

Phosphorous diffusion proceeds mainly by the migration of self-interstitials (Ourmazd and Schroter, 1984). These point defects are generated during the diffusion itself and allows fast diffusing impurities to migrate towards the diffused region and be paired with the P atom Under certain conditions, heavy diffusion can create a network of misfit dislocations (Lawrence, 1966) due to the lattice strain caused by the different size of the dopant impurity.

Rear Al treatments (Mandelkorn and Lamneck, 1973; Roorda et al, 1988; Narayanan and Green, 1989; Chong, 1989, pp. 27-41 and Pasquinelli et al., 1991) create an Al-Si alloy at the rear mainly for the creation of a back surface field Temperature gradient zone melting (Chong, 1989, pp 31-37) has been identified as a potential defect generating mechanism for such treatments. Temperature gradients across the wafer cross section can make the Al-Si alloy migrate through the substrate creating deleterious effects on cell performance Localised inhomogeneities can lead to holes appearing in the substrate. The annealing of Al layers on Si is believed to generate hydrogen at the interface (Janssens et al., 1981) which can be linked to gettering mechanisms accompanying rear Al treatments (Pasquinelli et al., 1991) At low annealing temperatures (425°C) Poitevin et al., 1988 suspect that point defects and dissolved oxygen in the Al-Si interface are present and likewise contribute to gettering.

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Aging effects are important when delay in device processing occurs. Interface roughness increases for oxidised Si in a few days time (Grundner et al, 1989) For hydrophobic surfaces, native oxide formation occurs in roughly the same time frame depending on the dopant concentration of the exposed surface.

Having identified intrinsic defects in single crystal FZ/CZ, cast polycrystalline and solution-grown Si and knowing how extrinsic defects can be introduced into them, we now proceed to evaluate their influence on solar cell performance

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CHAPTER 3

DEFECTS AND SOLAR CELL PERFORMANCE

3.1 Basic Solar Cell Operation

In order to understand how defects can influence solar cells, we need to know how a solar cell operates Figure 3.1 is a schematic diagram of a textured lasergrooved solar cell When light with energy greater than the indirect bandgap of Si shines on the cell, electrons from the valence band are excited to the conduction band leaving holes in the valence band. These photogenerated electron-hole pairs are then separated by the built-in electric field of the p-n junction. The electrons are then collected by the top/buried metal contacts and travel the circuit load until they eventually reach the rear metal contact of the cell where they recombine with holes which have accumulated there As can be clearly seen, any impedance to photogeneration of charge carriers and their collection degrades the performance of the solar cell Examples of carrier photogeneration attenuation are competing light absorption processes that do not generate charge carriers, shading by the top metal grid and the presence of non-carrier generating materials in the cell (inclusions). The main impedance to carrier collection are recombination processes in the solar cell material: deep level impurities, surfaces, ohmic contact interfaces, grain boundaries, stacking faults, dislocations and other structural defects. Scattering processes are likewise important and will be discussed in terms of photon scattering and charge Inelastic photon scattering via defects may improve cell carrier scattering. performance via light trapping mechanisms (e g, the textured surface of the cell) Carrier scattering via defects directly affects carrier mobility and thus represents an



Figure 3.1. Schematic diagram for a textured laser grooved solar cell. N^+ and N^{++} layers come from P diffusion and P⁺ comes from Al alloying.
impedance to carrier collection Phonon scattering mechanisms are important but are beyond the scope of this thesis and will not be discussed. K. Boer (1990, Chapter 11) provides a good review on this topic. A discussion of gettering and passivating effects during cell processing will then make the high efficiency features of the lasergrooved solar cell illustrated in Figure 3.1 apparent.

3.2 Free Carrier Absorption

Free carriers present in the lattice due to dopant impurities can absorb incoming photons by moving to a higher energy level in their respective energy bands (intra-band absorption) or to a different energy band (inter-band absorption) They then quickly lose their energy via phonon emission and relax back to their original energy state This type of absorption does not lead to carrier generation and competes with absorption processes that generate electron-hole pairs (charge carriers) in Si It is thus an undesirable effect in Si solar cells and needs to be minimised Moreover, the subsequent relaxation of the carrier to its original state is one of the heat generating processes in the solar cell During solar cell operation this heating effect can degrade solar cell performance (Green, 1986, pp. 91-92)

3.2.1 Absorption Mechanisms

Free carrier absorption depends on the wavelength of the incident radiation and carrier type and concentration in Si. The classical model for free carrier absorption predicts a λ^2 dependence on the incident light wavelength (Boer, 1990, p 310) For $\omega \tau_e >>1$, where ω is the frequency of the incident radiation ($\omega=2\pi c/\lambda$) and τ_e is the energy relaxation time, the free carrier absorption coefficient α_{FC} can be expressed as

$$\alpha_{FC} = \frac{3 \times 10^{-4} N}{10^{16} (cm^{-3})} \frac{m_o}{m'} \frac{10}{\varepsilon_o} \frac{10^{-13}}{\tau_e} \frac{\lambda^2}{n}$$
[3 1]

where N is the free carrier concentration (in cm⁻³), m'/m_o is the carrier effective mass, n is the refractive index of Si, ε_o its dielectric constant and λ is in μ m

Current theory shows that this wavelength dependence can be modified by carrier scattering mechanisms through the term τ_e (Boer, 1990, pp 310-315) The total free carrier absorption can then be thought of as a superposition of the absorption due to the different scattering mechanisms (Gladden and Baghdadi, 1986)

$$\alpha_{FC} = \alpha_{acoustic} + \alpha_{ions} + \alpha_{interband}$$
 [3.2]

with the different components having wavelength dependencies

$$\alpha_{acoustic} = A\lambda^{15}$$
 [3 3a]

$$\alpha_{ions} = B\lambda^3$$
 [3 3b]

$$\alpha_{interband} = C(\lambda)$$
 [3 3c]

Expressions for the proportionality constants A and B can be found in Boer (1990 pp 310-315). Spitzer and Fan (1956) identify $C(\lambda)$ as a broad peak in the 1 to 5 μ m wavelength range for n-type Si. A, B and C are all directly proportional to the carrier concentration in the material

Intervalence band absorption for p-type Si has not yet been observed although some workers have corrected hole effective mass by considering such transitions A possibility is that this effect is incorporated in a very broad peak extending from $\lambda = 1$ to 15 µm This is possible because of the doubly-degenerate structure of the topmost valence band in Si (Kane, 1956). This provides an explanation for the kink at the long-wavelength end of IR absorption spectra in p-type Si (Leung, 1971, pp. 67-70).

Free carrier absorption in n-type Si has been measured by Spitzer and Fan (1956). They have shown that the IR absorption is due to acoustic phonon and ionised impurity scattering Gladden and Baghdadi (1986) made curve fits on IR spectra of n-type wafers and obtained a λ^2 dependence This is consistent with the

Drude model for free carrier absorption, however, Dumke (1961) has shown that this theory is only applicable for $\omega \ll T$ which yields $\omega \ll 200 \text{ cm}^{-1}$ ($\lambda \gg 50 \mu m$) Quantitative agreement between experimental measurements and classical theory is therefore not to be expected as has been observed by Schroeder et al (1978) Nevertheless, a successful fit to acoustic phonon scattering was made by Gladden and Baghdadi (1986) for n-type Si

Similar calculations from phonon scattering for p-type Si by Gladden and Baghdadi (1986) gave values in error by about 500%. Drude model calculations were off by an order of magnitude. The results of Schroeder et al. (1978) were much better with only a 100% difference between theoretical and experimental values.

In this thesis, the IR transmission spectra of variously doped p-type FZ <100>Si wafers (Table 3 1) were obtained mainly for a proper baseline evaluation of moderately doped. The resistivity of each wafer was measured with a four point probe and was converted to carrier concentration using ASTM F723-82(87) Absorption coefficients α were obtained from the IR transmission spectra using equation 4 4. The α peaks for a high resistivity wafer (PFZ0) are mainly due to lattice These peaks are eliminated from the calculated phonon peaks (Figure 41) absorption spectra by subtraction of the high resistivity wafer α No other peaks show up in all the subtracted spectra and it can be assumed that $\alpha_{impurity}=0$. The resulting α value calculated is then equal to the free carrier absorption coefficient α_{FC} A scatter plot of α_{FC} for $\lambda=5\mu m$ (last column of Table 3.1) against carrier concentration N reveals the direct proportion relationship expected from equation 3.1To extract the wavelength dependence of α_{FC} , a logarithmic plot of α_{FC} against λ (Figure 3.3) was made The slope of the curve should then indicate the appropriate exponent of λ The calculated slopes using the base 10 logarithm of α_{FC} and λ are listed in Table 3 2. It was observed that the curves in Figure 3.3 bent down slightly at $\lambda \approx 15 \ \mu m$ The slopes were likewise calculated for the bent part of the curve and is tabulated in Table 3.2. Table 3.2 indicates a λ^2 dependence for $\lambda=5$ to 15 µm which then falls to $\lambda^{1.4}$ beyond 15 µm. The $\lambda^{1.4}$ dependence is consistent with acoustic

Table 3.1. FZ wafers used to evaluate free carrier absorption in p-type <100> Si Resistivities were measured using a four-point probe and converted to carrier concentrations using ASTM F723-82(87). The free carrier absorption at λ =5 µm is plotted against carrier concentration in Figure 3.2.

| SAMPLE | ρ (Ω cm) | N (cm ⁻³) | α _{FC} (5μm) |
|--------------|----------|------------------------|-----------------------|
| PFZ 0 | 1000 | $1.3 	imes 10^{13}$ | 0.00 |
| PFZ1 | 2.0 | 6.9×10^{15} | 0.22 |
| PFZ2 | 1.0 | 1.5×10^{16} | 0.54 |
| PFZ3 | 0 46 | 3.5 × 10 ¹⁶ | 1 52 |
| PFZ4 | 0 22 | 9 0 × 10 ¹⁶ | 4.48 |
| PFZ5 | 0 096 | $2.9 	imes 10^{17}$ | 14 85 |
| PFZ6 | 0.062 | 5.7 × 10 ¹⁷ | 33.17 |

phonon scattering processes (equation 3.3a). The transition from a $\lambda^{1.4}$ to a λ^2 dependence towards shorter λ indicates the superposition of a process with a higher λ dependence over acoustic phonon scattering Ionised impurity scattering (equation 3.3b) is the obvious answer in this case

Leung (1971, pp 63-83) observed the same wavelength dependence for λ =5 to 15 µm and the kink at ≈15 µm in his work but was not able to observe any particular wavelength dependence after the kink as was observed in this work He concluded from his work that the wavelength dependence he observed can be thought of as a superposition of the absorption mechanisms considered in equations 3.3a and b The temperature dependence of the free carrier absorption is, however, unexplainable via these mechanisms. IR absorption curves obtained by him for a sample taken at two different temperatures intersected each other at long wavelengths while the models predict monotonically increasing absorption curves



Figure 3.2. A scatter plot of $\alpha(5\mu m)$ listed in Table 3.1 against carrier concentration indicating a direct proportionality between the two.



Figure 3.3. Logarithmic plot of free carrier absorption against λ for the p-type FZ <100> Si wafers in Table 3.1. The slope of the curves for $\lambda = 5$ to 15 µm is 2.0 and reduces to 1.4 for longer wavelengths (see Table 3.2).

Table 3.2. Calculated slopes of the curves in Figure 3.3 for λ =5 to 15 µm (s₁) and 15 to 25 µm (s₂). The base 10 logarithm of α_{FC} and λ were used to calculate s₁ and s₂ The slopes then represent the exponent of λ for the particular wavelength ranges considered

| SAMPLE _ | SLOPE | |
|----------|----------------|----------------|
| | s ₁ | s ₂ |
| PFZ1 | 2.0 | 1.4 |
| PFZ2 | 2.0 | 14 |
| PFZ3 | 18 | 14 |
| PFZ4 | 2.0 | 14 |
| PFZ5 | 2.0 | 1.5 |
| PFZ6 | 2.0 | _ a |

 $^a~$ The IR spectra was saturated with free carrier absorption for $\lambda > 15~\mu m$

Other workers (Hara and Nishi, 1966 and Schroeder et al., 1978) have reported similar λ^2 dependence. Vavilov (1960) has reported $\lambda^{1.85}$ and $\lambda^{1.5}$ for hole and electron free carrier absorption respectively Photo-induced free carrier absorption in indium-doped Si was measured by Staflin (1965) He observed a wavelength dependence of $\lambda^{1.5}$ consistent with acoustic phonon scattering models Such measurements have a bearing on actual free carrier absorption processes during solar cell operation.

3.2.2 Free Carrier Absorption in Solar Cells

Free carrier absorption in a solar cell is largely dependent on the carrier concentration profile across it during device operation. This will require treating the solar cell emitter (diffused region) and base (substrate) separately It will be assumed that the emitter doping level is N_D , the base doping level is N_A , the electron

concentration across the device is n(x) and the hole concentration is p(x) At a specific depth x into the solar cell, these concentrations represent the majority and minority carrier concentration. Two cases need to be considered during device operation 1) low injection (n(x) << p(x) or vice versa) and 2) high injection levels $(n(x) \approx p(x))$ Electron and hole concentrations are limited by available states in the conduction and valence bands respectively

The carrier concentration profile across a solar cell is determined by the photogeneration rate G and the transport rates from the point of generation For monochromatic radiation, we have (Green, 1987, p. 42)

$$G = \alpha_{eh} N_p \qquad [3.4]$$

$$dN_{p}/dx = (\alpha_{eh} + \alpha_{FC})N_{p}$$
 [3.5]

where x is the distance in the direction of the photon flux, N_p is the photon flux and α_{eh} is the absorption coefficient for electron-hole pair creation. α_{FC} will be dependent on x firstly because of the presence of dopant-diffused regions necessary for device operation and second, because of the dependence of G on x as is evident from equations 3.4 and 3.5. During device operation, the carrier concentration profile across the solar cell becomes more complicated as the charge carriers are being collected. The expression for α_{FC} will then take the form

$$\alpha_{FC}(x,\lambda) = K_e \lambda^a n(x) + K_h \lambda^b p(x)$$
[3 6]

where K_e and K_h are constants which can be derived empirically (Schroeder et al, 1978 and Appendix B) and n(x) and p(x) are the electron and hole concentration profile across the device respectively. An appropriate set of exponents for λ would be a=b=1.5. This will be consistent with Staflin's results (Staflin, 1965) on photoinduced free hole absorption and Fan's results (Fan et al, 1956) on free electron absorption. For a rough approximation of the magnitude of α_{FC} it can be assumed that a=b=2 which is what most workers claim (section 3.2.1). In this case, Schroeder's empirical results (Schroeder et al., 1978) can be used yielding

$$\alpha_{FC}(x,\lambda) = 1 \times 10^{-18} \lambda^2 n(x) + 2.7 \times 10^{-18} \lambda^2 p(x)$$
[3 7]

where α_{FC} is in cm⁻¹ and λ is in μ m

Under low injection conditions, $n(x) = N_D$ in the emitter assuming uniform doping conditions while $p(x) \approx 0$. For typical laser-grooved solar cells, $N_D \sim 5 \times 10^{18}$ cm⁻³ For $\lambda = 1.1 \ \mu\text{m}$, $\alpha_{eh} \approx 3.5 \ \text{cm}^{-1}$ (Green, 1987, p 230) and $\alpha_{FC} \approx 6.1 \ \text{cm}^{-1}$ from equation 3.7. This means that, under the most favourable conditions, the fraction of photons ($\lambda = 1.1 \ \mu m$) which can contribute to cell short circuit current in the emitter region is 3.5/(3.5 + 6.1) = 0.36 (Green, 1987, pp. 85-86). In the bulk of the solar cell, where $p(x) = N_A \approx 10^{16} \text{ cm}^{-3}$ for a 1 Ω cm substrate and $n(x) \approx 0$, α_{FC} = 3.3 cm^{-1} and nearly half the near-bandgap photons are lost to free carrier absorption The more heavily doped regions near the metal contacts further attenuate the number of useful near-bandgap photons which contribute to current generation The collective effect of free carrier absorption from diffused layers and the bulk of the cell is to decrease cell current generated by near-bandgap radiation This effect should become evident in spectral response measurements (section 4.5.3) on cells made on different resistivity substrates. The drop in long wavelength response observed by Chong (1989, p.72) can be partially explained by free carrier absorption effects Careful consideration of measurement conditions and other effects arising from varying bulk resistivity (e. g., series resistance) should, however, be made in interpreting these curves.

The preceding discussion shows that free carrier absorption plays an important role in sub-bandgap absorption processes. Although such processes are very weak in Si, light trapping mechanisms significantly enhance their carrier generating ability with a path length enhancement factor of 50 deemed feasible for randomising schemes (Green, 1987, pp. 70-73). The rough calculation of α_{FC} made for a laser-grooved solar cell under low-injection conditions indicates that half the current gained by light trapping can be easily lost due to free carrier absorption An exact calculation of free carrier absorption losses is possible with the incorporation of equations 3 4 to 3 6 into device simulation programs like PC-1D (Basore, 1991).

Free carrier absorption under low injection conditions involved only one term in equation 3 7. Under high injection conditions $(n(x) \approx p(x))$, the other term starts to make a significant contribution. High injection is, however, difficult to achieve in the diffused regions because of limits imposed on the electron-hole product. When the cell diffusion length is much greater than the cell thickness, the electron-hole product across the cell can be expressed as (Green, 1987, p.91)

$$n(x)p(x) = n_i^2 e^{qV_{oc}/kT}$$
 [3.8]

where $n_i = 1.01 \times 10^{10} \text{ cm}^{-3}$ (Sproul et al., 1990). For $V_{oc} \approx 670 \text{mV}$ (the best result obtained on laser-grooved solar cells by Chong (1989, p 160)), $n(x)p(x) \approx 2 \times 10^{31}$ cm⁻⁶. It can easily be seen that minority carrier concentrations in the diffused regions of the cell will remain well below majority carrier concentrations. For the 1 Ω cm substrate considered in the previous example, $n(x) \approx 10^{31} \text{ cm}^{-3}/\text{N}_{\text{A}} \approx 10^{15} \text{ cm}^{-3}$ in the bulk of the solar cell and α_{FC} for $\lambda = 1.1 \ \mu\text{m}$ increases slightly to 3.4 cm⁻¹ The contribution from n(x) increases for higher resistivity substrates

3.2.3 IR Spectra Analysis

The original reason for modelling free carrier absorption is to be able to facilitate quantitative FTIR measurements of impurity concentrations in moderately doped Si substrates (10^{16} to 10^{17} cm⁻³). Section 4.2.1.1 discusses the subtraction of free carrier absorption from IR spectra to determine C and O impurity peak heights from polycrystalline Si substrates. The modelled baseline does not always have a λ^2 dependence Good fits have been obtained for exponents in the range 1 4 to 2 0

3.3 Recombination

When light of energy greater than the indirect gap of Si is incident on a Si wafer, an electron-hole pair is generated. These charge carriers quickly relax to the band edges by successive phonon emission. In the absence of internal or external electric fields, the photogenerated electron-hole pairs move randomly about the crystal lattice and eventually recombine via band-to-band processes or via defect levels (Green, 1987, pp 44-54). Recombination can proceed either radiatively or non-radiatively. Radiative recombination involves the emission of photons while non-radiative recombination involves the emission of photons (thermal energy).

Band-to-band radiative recombination is merely the inverse mechanism for carrier generating processes in Si and can lead to further creation of electron-hole pairs by the emission of sub-bandgap photons. The absorption coefficient for such photons is, however, very small. Nevertheless, such an absorption process can significantly reduce electron-hole pair disappearance rates if light trapping mechanisms are used Band-to-band non-radiative recombination occurs via the excitation of another charge carrier (Auger process) The excited carrier quickly relaxes back to the band edge by successive emission of phonons.

Recombination via defect levels is, however, the most efficient recombination mechanism for Si devices with mid-gap levels being the more effective recombination centres (Green, 1986, p. 55). The carriers give up their excess energy via radiative and non-radiative processes as well although the particular mechanisms involved are not yet fully understood (Jaros, 1982). Green (1987, pp. 50-54) discusses four mechanisms through which carriers can lose their excess energy optical (radiative), cascade, multiphonon and Auger.

Defects in Si contribute to recombination by introducing energy levels in the forbidden gap of Si. The following sections discuss the nature of the defect levels generated by each class of defect and the consequent recombination arising from them. During device operation, recombination via these defect levels should be kept to a minimum to ensure efficient carrier collection in the solar cell. In some instances,

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however, these defect levels may be used to the advantage of the solar cell through the impurity photovoltaic effect (Wolf, 1960 and Guttler and Queisser, 1970)

3.3.1 Point Defects

The electrical activity of point defects comes from the incomplete chemical bonding of the normally tetravalent Si lattice atom resulting in a net charge in the Si lattice. Group III and Group V impurities are well-known to introduce incomplete covalent bonds (holes) or extra/dangling bonds (electrons) in the Si lattice. The low ionisation energies of these impurities create energy levels close to the valence or conduction bands. Such shallow levels are essential for junction fabrication and do not contribute much to recombination processes in the solar cell

Deeper level impurities are more of a concern for Si device processing with mid-gap levels being identified as the more efficient recombination centre for charge carriers (Green, 1986, p.55). Noble and transition metal recombination centres have been studied by Graff and Pieper (1983). Cr, Fe, Ni and Cu form only one donor in Si with their activation energies decreasing with increasing atomic number. Ag and Au form two levels. Ti, V and Mn form three deep levels of equal concentration. The concentration of electrically active defects at a certain temperature increases with increasing atomic numbers. Graff (1989) reviews the behaviour of transition metals in Si. The intentional introduction of Au has been used to control substrate lifetimes for particular devices (Coffa et al, 1989). Au creates an acceptor level at 0 54 eV and a donor level at 0 83 eV (Sze, 1981, p. 21) A second donor level has also been identified by Jang and Bosman (1989). Cu, Fe and Ni are the main transition metals that are easily introduced from furnace material. Ni and Cu are also the usual plating metals for laser-grooved solar cells. Ag is sometimes used to thicken the rear ohmic contacts of solar cells. Au (together with Bi) has been used as a melt in the lowtemperature liquid-phase epitaxy of Si (section 7.2).

Oxygen in CZ Si or cast polycrystalline Si (section 2.2) exists mainly as an interstitial impurity. It is believed to be electrically benign. However, its precipitates

can introduce recombination centres (Hwang and Schroder, 1986) or change the resistivity of the material by thermal donor formation (Cazcarra and Zunino, 1980) Carbon, which is normally present in cast polycrystalline Si is likewise isoelectronic. It is believed to trigger O precipitation (Leroueille, 1981) resulting in the formation of bulk defects It is believed that C-induced precipitation of interstitials/vacancies contribute to the formation of swirl defects (Zulehner, 1989a, p 401) Sn, like C (Group IV), is isoelectronic as well and for this reason has been used as a melt in the solution growth of Si (section 7 2)

3.3.2 Line Defects

The local stress around a dislocation deforms the forbidden bandgap of Si due to a change in deformation potential relation (Matare, 1971, p.157). The result is a wider bandgap at the dislocation site For dislocations separated by more than a lattice constant, the resulting undulation along the band edges can effectively increase the bandgap of Si. This effect is responsible in generating potential barriers along grain boundaries (section 3.3 3)

Free dangling bonds along the dislocation line introduce energy levels in the forbidden gap. Kimerling and Patel (1979); Weber and Alexander (1983) have shown that a 0 4 eV donor level and 0.35 and 0.54 eV acceptor levels can be associated with dislocations generated by plastic deformation. Further evidence of these energy levels have been observed in photoluminescence spectra (Sauer et al., 1985). However, recombination via dislocations was observed only for high dislocation densities ($\approx 10^6 \text{cm}^{-2}$). High dislocation densities ($\geq 10^5 \text{cm}^{-2}$) are known to change the resistivity of Si (Matare, 1971, p. 443).

A well-known effect of dislocations in microelectronic device fabrication is the enhanced diffusion of dopant impurities along them (Shimura 1989, pp. 343-344) This effect creates diffusion pipes in the junction region of a device resulting in junction leakage currents and reduced minority carrier lifetimes. Junction leakage introduce shunt resistances in the cell which degrade cell performance (section 4 6 1)

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It has been suggested that dislocations are electrically active only when they are decorated by an impurity and that undecorated dislocations have a negligible electrical effect (Monkowski, 1981 and Lawrence, 1973).

3.3.3 Area Defects

The abrupt termination of the Si lattice at its surface leaves a large amount of dangling bonds which create a high density of defect levels in the Si bandgap. Even with the growth of a passivating oxide on the surface, surface recombination activity can still persist depending on the quality of the oxide. The study of such activity is one of the more important considerations for current high efficiency solar cell design (Green, 1987, pp 111-121)

Metal contacts to Si present a different problem with barrier formation giving rise to undesirable contact resistance (Green, 1987, p. 121-122) The elimination of such barriers by heavily doping the contact regions gives rise to surface recombination problems. The minimisation of metal/silicon interface recombination has led to the fabrication of the world's highest efficiency solar cell (Green, 1991).

The electrical activity of stacking faults is quite similar to that of dislocations as they are normally terminated by partial dislocations (section 2 1 3) They have been more widely studied, however, because of their occurrence in oxidation processes, a common device fabrication step. Impurity decorated stacking faults have proven the particularly active in generating leakage currents (Shimura, 1989, p 344)

Coherent twins are known to be electrically inactive due to the absence of dangling bonds along such boundaries (Matare, 1971, p. 148). Satisfactory devices have been made on single-crystal Si substrates with the intentional inclusion of twin boundaries. Incoherent twins, however, have been found to be active (Ast et al., 1991) Stacking faults are likewise well-known for their electrical activity (Ravi et al, 1973)

The activity of low-angle grain boundaries can be derived from the density of dislocations present along the boundary. Larger angle grain boundaries may include

point defects, precipitates, inclusions and other defect clusters and, hence, are the most electrically active centres in polycrystalline Si. The advent of large grain (>1mm grain width) polycrystalline Si produced by casting have lessened the importance of grain boundary activity on devices fabricated on them The world's highest efficiency polycrystalline cell to date was made on such a substrate (Narayanan et al , 1990)

3.3.4 Volume Defects

The bulk of volume defects act as non-carrier generating volumes and as carrier scattering points in the Si lattice. The resulting defect level structure from volume defects depends mainly on the characteristics of its interface with Si Depending on the material the volume defect is made of, this interface may present surface states which act as recombination centres. Such an interface may act as nucleation points for point and line defects further increasing its recombination activity

Recombination due to oxygen precipitates has been described in terms of the surface recombination velocity at the Si-precipitate interface and their average density and size (Hwang and Schroder, 1986). Density distribution of interface states from Deep Level Transient Spectroscopy (DLTS) spectra show that these interface states are quite similar to as-oxidised Si-SiO₂ interface states.

3.4 Scattering Processes

3.4.1 Photon Scattering

Photons incident on defects are scattered by them This is demonstrated very clearly by surface reflection. Surface reflection on a solar cell without Anti-Reflection (AR) coating can result in a 30% loss in photogenerated carriers. AR coatings and light trapping schemes have been developed precisely to minimise such losses In polycrystalline Si, grain boundaries and inclusions provide further photon scattering

sites The photons may either be backscattered or deflected across the cell giving desirable light trapping effects

3.4.2 Carrier Scattering

In contrast to photon scattering, carrier scattering degrades solar cell performance. Carrier scattering impede their collection by decreasing their diffusion lengths and, hence, their mobility. Lattice strain surrounding the defect is the main source of scattering in electrically neutral defects. Space-charge accumulation on electrically active defect sites act as stronger scattering sites because of Coulombic interactions between the charge carriers and the space charge (Boer, 1990, p 879)

Dislocations generate a positive space-charge cylinder around negatively charged dangling bonds. Parallel to the dislocations, the mobility of carriers remain as would have been expected from a dislocation free substrate. Perpendicular to the dislocations, carriers are scattered more efficiently and a consequent decrease in carrier mobility results. These results have been verified by Schroter (1969) and Podor (1974) Scattering in devices with hetero-interfaces like Si_{1-x}Ge_x/Si is an important process as the misfit dislocations present in the interface are perpendicular to the direction of carrier flow

Grain boundaries are efficient scattering sites as dislocations, point defects and defect clusters are usually present specially for large angle grain boundaries. Such scattering can be reduced significantly in solar cells if finger spacing widths are less than grain widths. This is easily achieved in large grain cast polycrystalline Si where the average grain width is \approx 4 mm (section 6.2.2).

3.5 Defect Gettering and Passivation

It has already been pointed out in section 3.3 that defects do not necessarily have to be a liability during device operation. Some of them, like dopant impurities, are essential for the device to function at all. Some deep level impurities may also be turned into an advantage via the impurity photovoltaic effect (Wolf, 1960 and Guttler and Queisser, 1970). Recent calculations have shown that a marginal boost in cell performance is feasible via the In defect level (Keevers, 1993). Moreover, defects can act as sinks for other defects rendering them neutral or taking them away from the active device region The intentional introduction of defects to achieve these effects is called gettering and has proved useful in improving device yields in microelectronic device fabrication (Swaroop, 1983) Gettering action in solar cell processing will be considered in the next section For larger immobile defects like grain boundaries, defect passivation will be the main recourse to reduce recombination activity arising from such defects. This will be tackled in section 3 5.2.

3.5.1 Gettering

Gettering is the main mechanism for neutralising point defects, specially transition metals and heavy metals It normally involves the intentional creation of defects where impurities can later on nucleate onto and be passivated after subsequent heat treatment. Gettering techniques can be classified as intrinsic, extrinsic or chemical (Shimura, 1989, p. 346-347).

Intrinsic gettering involves the creation of defects in the bulk of the substrate by oxygen out-diffusion and precipitation (section 2.2.2). Defects are then collected and trapped in the bulk of the wafer leaving a denuded zone near its surface. This technique is not suitable for solar cell processing as the bulk of the wafer participates in carrier generation and transport during device operation

Extrinsic gettering involves the use of external means to generate defects which will act as gettering sinks during device processing. Damage (usually at the rear of the wafer) is introduced first by laser or mechanical damage followed by oxidation, Al or P diffusion or the deposition of silicon nitride or polysilicon layers Subsequent thermal treatments allow impurities to diffuse to the gettering sites and be trapped or neutralised.

For the laser-grooved solar cell processing sequence, the relevant extrinsic gettering techniques are laser damage, P diffusion and Al diffusion. Laser scribing is

necessary for the fabrication of buried metal contacts. It is known to introduce damage in scribed regions of the wafer (section 2.2). KOH or NaOH baths etch some of the damaged regions including material ejected during the actual scribe. Chapter 5 will consider the extent of this damage in more detail It will be shown that thermal wave effects considerably enlarge the scribe affected area A thermal wave gettering effect will also become apparent in the experiments carried out in that chapter

Heavy P diffusion along the grooves creates an n^+ layer suitable for metallisation and is believed to passivate residual groove damage P gettering can proceed by the creation of point defects in the diffused region (Lecrosnier et al, 1980) or misfit dislocations at the interface of the Si substrate and the diffused region (Fair, 1978). Studies have shown that transition metals and Au are efficiently gettered in P diffused regions (Rozgonyi et al., 1975; Lecrosnier et al., 1980 and Ourmazd and Schroter, 1984).

Al alloying at the rear of the wafer creates a p⁺ layer likewise suitable for metallisation Although workers have concentrated more on back surface field effects and thermal gradient zone melting problems (section 2 2), Al gettering has been claimed to occur during the creation of the rear p⁺ layer (Roorda et al , 1988; Chong, 1989, pp 38-39 and Pasquinelli et al., 1991). Pasquinelli et al., 1991 observed that rear Al treatments appear to be additive or complemental to P gettering and explains this behaviour via additional gettering of impurities by Al. They also note that the introduction of H during the annealing of the Al-Si interface (Janssens et al., 1981) can explain this result as well. H, like P, has very strong passivating qualities (see next section) and can associate with impurities in the bulk and neutralising them This process can account for the Al gettering effects so far observed. At low annealing temperatures (425°C), Poitevin et al (1988) believe that point defects and dissolved oxygen at the Al-Si interface contribute to gettering.

The sintering step necessary for Al-Si alloy formation also provides the heat treatment necessary for laser damage and P gettering to occur. It is then the most

effective gettering treatment for the solar cell and, being the last heat treatment for the process, cannot be more strategically placed in the process

Chemical gettering involves the elimination of defects in the Si wafer via suitable chemical reactions. HCl volatilisation (Robinson and Heiman, 1971) eliminates transition metals as a result of Cl reacting with them forming volatile metal chlorides Oxidation-induced stacking faults are likewise reduced with the creation of vacancies at the Si surface. Trichloroethylene (TCA) oxidation produces a similar effect on oxidation-induced stacking faults (Hattori, 1976). In chemical gettering, transition metal impurities are actually extracted from the Si wafer and expelled through the gas stream For intrinsic and extrinsic gettering, the gettered defects remain in the Si wafer at the appropriate gettering sites

3.5.2 Passivation

Passivation refers to the neutralisation of dangling bonds created by the presence of a defect. For transition metal impurities, dislocations, grain boundaries and inclusions, this usually means pairing an appropriate impurity (H or P) to the dangling bond For surfaces, O is more appropriate. When the passivating impurities (H, P or O) attach themselves to the dangling bonds, they modify the defect levels associated to the dangling bonds and recombination via the defect levels is eliminated

Oxidation of the Si surface is an effective way of passivating it The resulting oxide also plays an important masking role in subsequent dopant diffusion and metallisation processes. The amount of recombination at the Si-SiO₂ interface depends a lot on the quality of the oxide grown. Chemical gettering of impurities (see previous section) is an effective way of improving oxide quality. Such treatments during oxidation improves oxide quality by catching metal impurities and exhausting them via the gas stream Pre-oxidation cleaning procedures using similar treatments removes impurities before they can contaminate the wafer

H passivation of grain boundaries is a well known technique for polycrystalline solar cells The main disadvantage of this technique is that further device processing

may release the H and reactivate the defect centre. The use of P is more consistent with device processing and is believed to passivate grain boundaries just as well The preferential diffusion of P along grain boundaries (Holloway, 1982) enhances the passivating action of P along grain boundaries. Evidence for the passivating effect of P on grain boundaries will be presented in Chapter 6 Chapter 5 will likewise show that P passivation works well for laser grooves. In this case, the enhanced diffusion of P along extrinsic defects in the groove is evident

The effectiveness of gettering and passivating strategies during device processing depends on the intrinsic defects in the material and on the entire processing sequence schedule to which the material is exposed. Most of the gettering and passivation techniques discussed have the potential of introducing additional defects into the material (section 2.2) Subsequent device processing or gettering/passivating procedures may then lead to the undoing of previous gettering and passivation steps In the laser-grooved solar cell processing sequence, the optimal position of gettering and passivating steps coincides with normal cell processing steps.

The next chapter will now discuss how the effects considered in this chapter can be quantitatively or qualitatively evaluated for Si materials and solar cells

CHAPTER 4

CHARACTERISATION OF SILICON MATERIALS AND SOLAR CELLS

4.1 Monitoring Intrinsic and Extrinsic Defects

The recombination activity of defects and its potential to degrade solar cell performance warrant the need for monitoring intrinsic and extrinsic defects in solar cell materials This entails correctly identifying the defects and quantitatively or qualitatively evaluating their recombination activity via appropriate characterisation techniques. Non-destructive techniques would be more useful as they allow us to proceed with device fabrication while monitoring how defects are introduced and transformed at different processing stages. However, the use of destructive techniques is sometimes necessary and several wafers have to be processed in a batch with one wafer being pulled out and tested at certain processing stages. This chapter briefly summarises the characterisation techniques used in this thesis. The field of defect characterisation is very wide and varied with whole conferences being dedicated to this topic (e. g., Stavola et al., 1988; Roberts et al., 1989 and Wolford et al, 1990). Consequently, emphasis will be put on features of the characterisation technique essential for understanding the results to be presented in succeeding chapters.

Looking back at the way defects were classified, we note that all of them are actual physical defects in the Si lattice. Microscopy is the main technique for the direct observation of defects. The largest point defects are normally a few lattice constants wide (≈ 1 nm) and are below the resolution of a Scanning Electron

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Microscope (SEM) and just above the resolution of a Scanning Transmission Electron Microscope (STEM) (Holt, 1990). The development of the High Resolution Transmission Electron Microscope (HRTEM) has allowed the observation of such small defects and has even been used to evaluate the structure of semiconductor interfaces at resolutions smaller than the Si lattice constant (Hutchison, 1990) The sample preparation techniques necessary for HRTEM techniques are, however, complicated and often difficult to implement on the structures being studied in this thesis

Indirect observation of defects via the exposure of the strain field around them using appropriate chemical baths allows their direct observation under conventional optical microscopes and SEM's. This is very effective for line (dislocations), area (grain boundaries, microcracks, stacking faults) and volume (inclusions and precipitates) defects TEM techniques remain the most effective in the direct observation of point defects. Spectroscopic techniques provide a way to identify impurities in the Si lattice and determine their concentration without having to image them The evaluation of the electrical nature of defects will be discussed together with solar cell characterisation towards the end of this chapter.

4.2 Point Defect Characterisation

The following techniques are mainly for impurity identification and evaluation of impurity concentration. Some of these techniques can ascertain the actual configuration of the impurity in the lattice (substitutional or interstitial).

4.2.1 Optical Beam Techniques

4.2.1.1 Fourier Transform Infrared (FTIR) Spectroscopy

This is a well-known non-destructive characterisation technique for a wide range of materials (Griffiths and de Haseth, 1986) in which variations in their optical absorption properties as a function of the wavelength of incident light can lead to the identification of impurities present in them. The optical transmittance T of Si for monochromatic radiation is defined as

$$T = I/I_o$$
 [4.1]

where I_o is the intensity of the incident beam and I the intensity of the transmitted beam. The attenuation of the transmitted beam is determined by absorption processes in the material, the thickness x of the sample and the reflectivity R of the sample surfaces Thus,

$$T = \frac{(1-R)^2 e^{-\alpha x}}{1-R^2 e^{-2\alpha x}}$$
[4.2]

where α is the absorption coefficient for absorption processes in Si and is a function of the wavelength of the incident radiation. In the medium to far infrared wavelengths (2 to 45 µm) R=0.3 and the absorption processes of interest are:

$$\alpha = \alpha_{lattice} + \alpha_{impurity} + \alpha_{FC}$$
 [4.3]

where $\alpha_{lattice}$ relates to lattice absorption, $\alpha_{impurity}$ to impurity absorption and α_{FC} to free carrier absorption (section 3.2). For $\lambda > 7\mu m$, $\alpha_{lattice}$ dominates in high resistivity Si samples. Figure 4.1 displays the phonon peaks in a 1000 Ω cm p-type FZ Si substrate with C_s and O_i concentrations below detection limits. A summary of phonon peak assignments are identified according to Krishnan et al. (1990, pp 290-292) The strongest peak at 16.4 μm (610 cm⁻¹) is known as the two-phonon band. For $\rho < 2 \Omega$ cm (p-type Si), α_{FC} starts appearing at the longer wavelengths (see PFZ1 in Figure 3.2 for an example). For $\rho < 0.1 \Omega$ cm, α_{FC} dominates the spectra and $\alpha_{lattice}$ and $\alpha_{impurity}$ are obscured. At 300°K, impurity peaks from O_i and C_s appear for impurity concentrations ≥ 0.5 ppm atomic (ppma). To observe shallow level



Figure 4.1. Infrared Absorption spectrum (resolution=8 cm⁻¹) for a 1000 Ω cm ptype FZ Si at room temperature showing lattice absorption ($\alpha_{lattice}$). A summary of phonon peak assignments can be found in Krishnan et al. (1990, pp. 290-292). The strongest peak at 16.4 µm (610 cm⁻¹) is known as the two-phonon (TO + TA) band.

impurity peaks, the samples will have to be cooled to low temperatures. At near liquid He temperatures, donor and acceptor levels are filled and absorption characteristic of the energy level of the impurity occurs. This has enabled the precise measurement of shallow impurity levels in the Si bandgap (Krishnan et al., 1990, pp. 324-326). Low temperatures also sharpen and intensify absorption peaks (Griffiths and de Haseth, 1986, p 516). A consequent fivefold increase in the sensitivity of C_s and O_i concentration measurements can be achieved at 20°K (Mead, 1980) Overlapping peaks are also resolved

Impurities present in the lattice absorb the incident energy according to how they are attached to the Si lattice atoms. These bonds have unique vibrational modes particular to the given defect (Krishnan et al, 1990, p 299) and allows the identification of the impurity. Impurity concentrations can then be calculated by measuring the impurity absorption peak height and multiplying it with an appropriate conversion factor (ASTM F123-86 and ASTM F1188-88) Impurity peak heights can be determined by solving equation 4.2 for α .

$$\alpha = -\frac{1}{x} \ln \left(\frac{-0.49 + \sqrt{0.241 + 0.36T^2}}{0.18T} \right)$$
 [4.4]

 $\alpha_{impurity}$ can then be extracted from equation 4.3 as

$$\alpha_{impurity} = \alpha - \alpha_{lattice} - \alpha_{FC} \qquad [4.5]$$

 $\alpha_{lattice}$ can be calculated from the transmission spectra of a high resistivity low impurity concentration reference sample (Figure 4.1) In low resistivity samples, α_{FC} (the spectrum baseline) can be modelled with an appropriate wavelength dependence (section 3 2) and subtracted from the absorption spectra Figure 4.2 shows the spectrum of a low resistivity sample obtained at room temperature with a resolution of 8 cm⁻¹ and with $\alpha_{lattice}$ from Figure 4.1 already subtracted. At this stage, the



Figure 4.2. Room temperature IR absorption coefficient spectrum (····) of a 0.5 Ω cm cast polycrystalline Si substrate after the subtraction of α_{lattice} (resolution=8 cm⁻¹). The increasing baseline (---) of the curve is due to free carrier absorption which is modelled here by a $\lambda^{1.55}$ wavelength dependence.

impurity peaks are already apparent. For this spectrum, α_{FC} was modelled using a $\lambda^{1.55}$ wavelength dependence. The resulting baseline model (solid curve) is superimposed in Figure 4.2 and shows a good fit to the spectrum baseline. Figure 4.3 shows the result of subtracting the modelled α_{FC} from Figure 4.2. The peak at 9.0 μ m (1107 cm⁻¹) is due to O_i and that at 16 5 μ m (607 cm⁻¹) is due to C_s The 19.5 μm (515 cm^{-1}) peak is due to absorption by a weaker vibrational mode of O_1 $\,$ The stronger O_1 peak (9.0 µm) is due to asymmetric stretching of the Si-O-Si molecule while the weaker peak (19.5 μ m) is due to symmetric stretching of the same molecule (Krishnan et al., 1990, pp. 296-300). The C_s peak is observable only after subtraction of $\alpha_{lattice}$ as the strongly absorbing two-phonon peak obscures it. The impurity peak coefficients are easily extracted and converted into impurity concentrations. For this particular sample, the O_i concentration $[O_i] = 9.8$ ppma and C_s concentration $[C_s] =$ 10 4 ppma. At a resolution=1 cm⁻¹, a more accurate result (13 1 ppma) for $[C_s]$ is obtained as the peak half-width for C_s (6 cm⁻¹) is much greater than the resolution (Stallhofer and Huber, 1983). The peak half-width of O_1 is 32 cm⁻¹

A similar effect can be obtained by using a background sample having the same thickness and resistivity as the sample but containing impurity concentrations below the detection limit (<<1 ppma) of the FTIR technique This is, in fact, the recommended ASTM method for evaluating C and O concentrations in Si (ASTM F123-86 and F1188-88). Such references are, however, hard if not impossible to prepare specially in the case of cast polycrystalline Si (Chapter 6) where the samples come from different manufacturers and resistivities and thicknesses are likely to vary from sample to sample

In this thesis, a computer controlled Nicolet 520 FTIR bench was used to take IR transmission spectra. It was fitted with a DTGS detector with a CsI window and CsI beamsplitter. The use of CsI enables spectra to be acquired in the 225 to 5000 cm⁻¹ (2 to 44 μ m wavelength) wavenumber range The bench was constantly purged with N₂ eliminating CO₂ and H₂O peaks from the spectra and protecting the extremely hygroscopic CsI material. Figure 4.4 represents a simplified diagram of the



Figure 4.3. Absorption peaks due to interstitial oxygen (O_i) and substitutional carbon (C_s) in Si after subtracting the modelled baseline from the absorption curve in Figure 4.2. The peak position for O_i is 9.0 µm (1109 cm⁻¹) and for C_s is 16.5 µm (607 cm⁻¹). The small peak at 19.4 µm (515 cm⁻¹) is a secondary O_i peak. If $\alpha_{lattice}$ was not subtracted from the spectra, the C_s peak would be obscured by the two-phonon peak indicated in Figure 4.1.

apparatus which is basically a Michelson interferometer. Radiation from the IR source is split into two parts by the beam splitter The fixed and moving mirror parts then introduce a path difference between the two beams generating an interference pattern is detected by an appropriate detector This interference pattern is usually referred to as an interferogram and can be resolved into individual wavelengths composing it by a mathematical process called Fourier transformation. Griffiths and de Haseth (1986, pp. 1 - 25) discuss the physics and mathematics of the Michelson interferometer and Fourier transformation of the interferogram in greater detail To obtain a transmission spectrum, a background spectrum is first acquired after sufficient N₂ purging of the chamber The sample is then taken and ratioed against the background spectra. This procedure eliminates ambient atmosphere absorption from the spectrum. A sample shuttle (Figure 4 4) is used to bring the sample into and out of the beam path for the two measurements mentioned above This minimises disturbances to the ambient atmosphere in bringing the sample out of the beam for a background spectrum and into the beam for the sample spectrum.

Samples were polished to mirror-like finish on both sides with NALCO 2350 silica slurry using a modified metallographic polisher. Sample thicknesses varied from 200 to 400 μ m. To eliminate oxides on the sample surface, it is dipped into a dilute HF solution and subsequently rinsed in deionised water. Measurements were done at room temperature for free carrier absorption measurements (section 3.2) and C and O concentration measurements (section 6.2.4). The sample chamber needed to be purged for 15 to 30 minutes to ensure consistent ambient atmospheres for the measurements O measurements were done at a resolution of 8 cm⁻¹ to avoid interference fringes in the spectra. C measurements (Stallhofer and Huber, 1983) In this case, IR spectra had to be smoothed before being analysed. Internal curve-smoothing routines were available in the Nicolet FTIR software.

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Figure 4.4. A simplified diagram for the FTIR set-up used in this thesis. It is basically a Michelson interferometer fitted with an appropriate beamsplitter and detector for the required wavelengths.

Sample thicknesses can be calculated from the generated interference fringe patterns in high resolution spectra of thin ($<500 \mu$ m) double side polished wafers using the equation.

$$x = \frac{N_f}{2n(v_1 - v_2)}$$
 [4.6]

where N_f is the number of interference fringes contained in the wavenumber (10000/ λ) range v_1 to v_2 (Griffiths and de Haseth, 1985, p 350). This technique ensures that the thickness value used in the subsequent analysis is the thickness at the sampled area

Spectral data was converted to ASCII format and analysed with a customised Excel spreadsheet (Appendix B). With the advent of high speed personal computers and vastly improved spreadsheet software, values of α are easily calculated, free carrier absorption modelled and subtracted and impurity concentrations determined. For a high resolution spectra (1 cm⁻¹) over the 400 to 2000 cm⁻¹ range, Excel spreadsheet size together with the two linked charts exceed 1MB. The use of an IBM PC compatible 486 computer with a built-in maths co-processor and 4MB RAM allows spectrum analysis to be performed in a matter of minutes. Similar analysis on a similarly configured 386 computer can take 15 to 20 minutes This type of analysis is impossible to carry out with the existing Nicolet FTIR software

4.2.1.2 Photoluminescence (PL)

When light of energy greater than the Si bandgap is incident on a Si wafer, electron-hole pairs are created. An electron may bind itself to a hole creating an exciton with a binding energy E_x of 14.7 meV. In the absence of defects, these electron hole pairs recombine via the mechanisms mentioned in the previous chapter Radiative exciton recombination emits a photon with an energy characteristic of the bandgap and the phonons or impurity levels assisting in the process At near liquid He temperatures the energy of the emitted phonon E_{v} can be expressed as

$$E_{v} = E_{g} - E_{x} - E_{ph} - E_{l} \qquad [4\ 7]$$

where E_g is the indirect bandgap of Si, E_{ph} is the assisting phonon energy and E_t is the impurity-bound exciton ionisation energy The emitted photon is the luminescent signal When Group III or V impurities are present, some of these excitons can bind themselves to the impurity before recombining By measuring the energy of the luminescent signal, the particular impurity involved in the recombination can be identified (Dean et al, 1967). E_t is related to the ionisation level of the impurity via Haynes' rule (Haynes, 1960). Impurity concentrations can be worked out from the ratios of the bound to free exciton TO phonon replica peaks (Tajima, 1977) This only works for single impurity systems, however, since complicated interactions occur between impurities in double impurity systems (Mitchard and McGill, 1980; Brown et al, 1982)

The experimental set-up of the PL apparatus used in this thesis is shown in Figure 4.5 Samples are prepared by cutting them into 4 mm \times 4 mm sizes Bulk Si samples are etched 10 μ m with a 10:1 HF HNO₃ to expose a fresh surface for the measurement. Solution-grown layers are etched 0.1 to 1 μ m to ensure that their substrates do not contribute to the PL signal. The samples are mounted on a quartz chuck with vacuum grease and cooled down to 10°K by a closed-cycle He refrigerator The 514 nm line of an Ar⁺ laser is then used to generate excitons in the sample A cooled (77°K) Ge detector detects the luminescent signal as the grating monochromator sweeps the 1 05 to 1 30 μ m wavelengths Conventional lock-in techniques (light chopper and lock-in amplifier) eliminate random noise from the laser itself. The luminescent signal is then collected by a computer and the spectra is displayed via appropriate software.



Figure 4.5. Experimental set-up for photoluminescence measurements.

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to Dean et al. (1967).

Figure 4.6 shows the PL spectra of an n-type (P-doped) Si wafer The Prelated peaks and its phonon replicas are labelled according to Dean et al. (1967) In Chapter 7, it will be seen that the PL peak positions for solution grown n-type Si are different to these and, hence, indicate the presence of a different dopant impurity

4.2.2 Ion Beam Techniques

These techniques involve impurity identification by bombarding Si with ions electrons, protons or alpha particles. These techniques are non-destructive so long as the particle energies are kept low The effects of ion bombardment has been well studied for Si in ion implantation processes for junction creation Since protons are a lot smaller than the normal dopant atoms (B, P, As, Sb) less damage is expected from it. Proton irradiation damage in solar cells has been considered by (Tada et al., 1982, pp 3-26 to 3-36). Electrons are still a lot smaller than protons and are the preferred ions for non-destructive examination of Si. Electron microscopy (section 4.3) has evolved into a powerful non-destructive technique for material characterisation in the microelectronics industry (Holt, 1990). Alpha particles are mainly used in RBS measurements The larger size of the particle results in a shallower penetration depth making it suitable for the analysis of thin film or layered Si

4.2.2.1 X-ray Analysis

When an ion of sufficient energy impinges on a Si wafer, it can knock out inner shell electrons from the lattice atoms. The 'holes' left by the knocked out electrons are quickly filled up by outer shell electrons depending on their transition probability In so doing, the electrons give up their energy by x-ray or electron emission (Auger effect). The emitted x-rays have energies which are unique to the particular atom it came from. This allows us to finger print the x-ray emission of an atom Impurities in the Si lattice can then be identified

In this thesis, two techniques were used for x-ray analysis of Si. The first technique to be discussed is Energy Dispersive X-ray (EDX) Analysis. This technique

uses electrons as the probing ion beam and is normally incorporated in a SEM. The second technique uses a proton beam instead to generate the required x-rays and will be referred to as Proton-Induced X-ray Emission (PIXE) Analysis The particular set-up used in this thesis was developed at the Australian Institute of Nuclear Science and Engineering (Golja et al., 1981).

Sufficient x-ray excitation in EDX Analysis requires a beam energy twice the particular line energy being investigated (Kevex Corporation, 1988). For thin specimens (<10 µm thick), the penetration depth of electrons will have to be controlled to ensure the probe beam does not go through the sample For typical electron energies (5 to 35 keV) available in an SEM, the electron penetration depth varies from 0 3 to 10 µm. Polished surfaces are required for quantitative analysis In the absence of standards for elemental analysis, a semi-quantitative routine can be used to approximate elemental concentrations in the material being studied This analysis has a sensitivity of 0.1 at% and an accuracy of 10%. This does not make it suitable for impurity analysis in Si which are typically in the ppma range However, it is sufficient for the analysis of $Si_{1-x}Ge_x$ layers (section 7.3) Quantitative analysis on Si_{1-x}Ge_x layers were confirmed with PIXE and RBS measurements. Qualitative elemental analysis can also be carried out for unknown samples with irregular shapes The identification of elements present in an inclusion can lead to its correct identification (section 6 2.3)

In this thesis, EDX analysis was carried out using a Cambridge Stereoscan 360 SEM equipped with a Kevex x-ray detector and analyser. The detector consisted of Li-doped Si with a Be window. The window material allows the detection of elements with atomic numbers as low as 5 (Boron).

PIXE measurements are more sensitive than EDX measurements with impurity concentrations in the ppma range being detected for some elements (Golja et al., 1981). Protons are accelerated by a Van de Graaf accelerator to an energy of 2 MeV The probe diameter for the proton beam is typically 1 mm and is much larger than for an electron beam in an SEM ($\approx 1 \mu m$) Samples, cut to a size of 1 cm², are
mounted with a 7° tilt with respect to the beam to avoid channelling. Samples were cleaned by etching 0.1 to 1 μ m off their surfaces using a 20 HF:1 HNO₃ solution The proton penetration depth for a 2 MeV beam is 47 μ m (Feldman and Picraux, 1977) and the useful x-rays come from the first quarter of this range (Hotchkis, 1991). Lower proton energies, although decreasing this depth, result in poorer x-ray production Low x-ray yields are likewise obtained for elements with Z<21.

4.2.2.2 Proton Induced Gamma-ray Emission (PIGE)

This technique is mainly used to determine elements with Z<21 that have low x-ray yields using PIXE. It is limited mainly by the gamma-ray yield of the elements. Rare elements (Li, F, B) have larger gamma-ray yield than abundant (C, Si, O) (Anttila et al, 1981). H yields undesirable reactants and is not suitable for measurement. For heavier elements, PIXE gives greater resolution due to better x-ray yields PIGE and PIXE are normally used as complementary techniques with PIXE determining heavier elements and PIGE lighter elements. PIGE spectra can be acquired simultaneously with PIXE spectra with beam energies similar for PIXE measurements (1 to 3 MeV).

4.2.2.3 Rutherford Backscattering Spectroscopy (RBS)

RBS is a well-known characterisation tool which is very useful in profiling thin films (Dean et al 1980 p.193). A 2 MeV α -particle is used to probe the surface of the thin film or bulk material. Backscattered particles are then used to generate an RBS profile (see Figure 4 7) The edges generated in the profile are characteristic of the atoms present in the material and at what depth they appear Surface sputtering allows profiling of the surface up to 2 μ m deep (α -particle penetration at the indicated energy is 8 μ m (Feldman and Picraux, 1977)). The edges generated can then be modelled for a depth up to 2 μ m by specifying elements and their assumed concentration levels (Figure 4.7). The particular set-up used in this thesis (Meglicki



Figure 4.7. RBS profile (---) of solution-grown $Si_{1-x}Ge_x$ layer on Si. The Si and Ge edges have been modelled (---)with a proper set of concentrations accurate to 0.1 at% for a 2 μ m thickness. The addition of the modelled edges (---) approximate the experimental curve.

et al., 1987) had a sensitivity of the order of 0.1 at%. The same sample chamber was used for RBS, PIXE and PIGE measurements

4.3 Line, Area and Volume Defect Characterisation

This section will be mainly be concerned with the observation of line area and volume defects. Some volume and area defects can be observed without chemical treatments using IR microscopy. However, chemical etching allows better delineation of such defects, making them easier to identify with conventional optical and electron microscopy. Such a treatment usually alters the surface of the sample and further processing of the sample may prove difficult without repolishing the surface

4.3.1 Chemical Etching

Chemical solutions are very commonly used in device processing for damage removal, polishing, cleaning, removal of oxide layers, texturing and exposure of defects These solutions are classified according to whether they remove Si uniformly (isotropic) or non-uniformly (anisotropic). Isotropic etchants are useful for stock removal or polishing while anisotropic etchants are used for surface texturing and defect delineation. The more common etchants that have been used in this thesis are discussed below

4.3.1.1 Isotropic Etching

The more common isotropic etchant for Si is a mixture of HF and HNO_3 The etch rate for this solution depends on how much HNO_3 is present in the solution. CP4 (Mader, 1984, p. 283) consists of the same chemicals with acetic acid added to it. The acetic acid acts as a buffer solution, reducing the etch rate of the HF:HNO₃ solution. This properties make it a good polishing solution.

The exposure of a fresh surface of Si is a common procedure to clean Si surfaces prior to characterisation This has been done in PL and x-ray measurements using an appropriate mixture of HF and HNO₃ (section 4.2.1.2 and section 4.2.2)

Chemical polishing is normally sufficient for surface flatness requirements in FTIR measurements. However, better surface flatness can be achieved via chemomechanical polishing. OH molecules in the silica sol (NALCO 2350) slurry oxidise the Si surface. The oxide can then be removed by abrasive action using an appropriate pad. Reasonable polishing rates (0 1 to 0.25 μ m/min) have been attained using this technique on a modified metallographic polisher.

Material inclusions which are resistant to the etching solution or which etch more slowly than Si will become visible after a chemical polishing etch Figure 4 8 is a Si_3N_4 inclusion in electromagnetically cast polycrystalline Si exposed after a chemical polishing treatment. The elemental composition of the inclusion was determined via EDX analysis and the image obtained by an SEM.

4.3.1.2 Anisotropic Etching

Surface texturing of <100> Si surfaces is easily done with a KOH or NaOH chemical baths These chemical etchants are well known to etch very slowly in the <111> direction Hence, etching practically stops after (111) surfaces have been exposed On a (100) surface, random pyramids are formed. KOH or NaOH etching has also been successfully used in cleaning laser-scribed grooves and giving them an acceptable shape for metallisation (Wenham, 1986, pp. 112-121).

Several preferential defect etchants are available (Mader, 1984, pp. 299-300) Some of these are, however sensitive to crystal orientation. The shape of the delineated defect then depends on the crystallographic orientation of the exposed Si surface For polycrystalline Si, an etchant which is insensitive to crystal orientation is preferable for easier defect identification. Etch pits will appear rounded due to this property of the etchant. Several such etchants are available, namely the Dash (Dash, 1956), Secco (Secco d'Aragona, 1972) and Sopori (Sopori, 1984) etch.

The Dash etch usually requires long etching times (15 minutes to a few hours) The Sopori and Secco etchants have reasonable etch times (5 minutes). The Sopori etch has a slight edge in the ease of handling. It is composed of an 36:20:1-2 mixture

Figure 4.8. Si_3N_4 inclusion in cast polycrystalline Si exposed after an isotropic etch. Around 40 μ m of material was removed from the wafer surface. A grain boundary can be seen running underneath the inclusion. This implies that the inclusior was located along a grain boundary before the chemical etching step.



of HF, glacial CH₃COOH and HNO₃ These acids are easily disposable and pose a lesser health risk. The Secco etch (1:2 0.15M KCr₂O₇ and HF) contains chromates which must be treated as suspect carcinogen and pose an eco-hazard Special disposal has to be arranged for used Secco etch In these days of environmental awareness, such considerations cannot be taken for granted One minor drawback in using the Sopori etch is the appearance of stains on the etched wafer surface. These do not, however, interfere with defect observation and are easily removed by a $H_2SO_4:H_2O_2$ cleaning solution. The amount of HNO₃ in a Sopori etch determines the etching rate and the size of the delineated defects. This is usually kept to within 1 to 2 parts in the solution. In order to attain this formula consistently, large volumes of etchant has to be formulated at a time. Fortunately, this solution has a long shelf life (Sopori, 1984) The Secco etch is, however, the more popular etching solution and in order to compare my results with other work, it was used throughout this thesis Its delineation properties are excellent and well established (Miller and Rozgonyi, 1980, pp 225-228)

Secco-etching normally proceeds with ultrasonic stirring or mechanical agitation to ensure uniform defect delineation. Care has to be exercised in the number of samples etched in a particular solution to avoid contamination of the Si surface from the etching solution. A good rule would be to use 50 ml per 50.8 mm wafer for a 5-minute etching time (ASTM F416-88). Fresh solutions minimise cross contamination and, therefore, give the best results. A used Secco etch can result in contamination of the samples. In this case a knowledge of the history of the solution is essential in deciding whether it can be used again. After etching LPE films or finished cells, heavy wafer staining can result in succeeding etching with the same solution.

The etch rate for a Secco-etch is $\approx 1.5 \,\mu$ m/minute. In a normal 5-minute etch, 8 μ m of material is removed. The defect structures exposed are then 8 μ m below the actual surface. For the evaluation of layers less than 10 μ m thick, the etching time can be reduced. For the solution grown layers in Chapter 7, etch times were typically 2 to 3 minutes For thinner samples, a Cu decoration technique (Lawrence, 1965) can be used Defects decorated with Cu are resistant to a 30-second Sirtl etch (Sirtl and Adler, 1961) creating topographic irregularities observable by conventional microscopy. Another alternative for defect evaluation of thin samples is the use of a HRTEM.

4.3.2 Microscopy

Microscopy is essential in order to observe the defects delineated by the technique mentioned above. Optical and electron microscopes are the common tools used for such purposes in this thesis. Infrared microscopy can, however, detect inclusions in Si material even before they are etched and is applied to cast polycrystalline and solution-grown Si. The incorporation of image processing capabilities with these techniques greatly enhanced the ease of defect density and feature measurements. Nomarski microscopy is the main tool for evaluating polished surfaces. It is useful in evaluating topographic features in epitaxial surfaces as well

4.3.2.1 Optical Microscopy

An optical microscope is used to observe defect etch pits and other features exposed by chemical etching. Although four imaging modes (brightfield, darkfield, polarised light and Nomarski) are available on the microscope, it is normally operated in the brightfield (reflected light) mode. A CCD camera (JVC TK900-E) allows the recording of microscope images on a Video Cassette Recorder (VCR) and displaying them on a TV screen. This makes defect counting much more comfortable and allows the use of image processing (Bioscan Inc, Optimas image processing software and Imaging Technology Inc., PC Vision⁺ frame-grabber) available on the IR microscope which is also equipped with a VCR Good quality colour and black and white prints can be obtained quickly via video printers (SONY UP3000P and UP-860) The setup for this microscope system is very similar to that for the IR microscope (see next section) shown in Figure 4 9 with the exclusion of the IR source and computer The inclusion of the VCR allows the storage, review and analysis of the images without generating a large volume of prints A 3-hour VHS cassette can store about 2200 frames at 5 seconds recording time per frame This is even more efficient than computer storage which needs 570 MB of memory to store the same number of images A quicker review of the images enhances the advantages of video recording After processing the recorded images, the VHS cassettes can then be reused or filed appropriately.

The Nomarski Differential Interference Contrast (NDIC) mode of the microscope allows the observation of 3 nm vertical features on the Si surface. This is an excellent way of evaluating polished surfaces With this method, a polarised beam is split by a Nomarski prism inserted between the sample and the objective lens In the presence of vertical reliefs, the two beams do not travel the same distance and interference contrast is generated. (Miller and Rozgonyi, 1980, pp. 229-233) NDIC is a good method to evaluate stacking fault density in epitaxial layers with very little sample preparation required (ASTM F522-88)

4.3.2.2 Infrared Microscopy

A metallographic microscope (Olympus BHM) was modified in order to get an IR image of Si substrates (Brenneman et al., 1990). Figure 4.9 shows a schematic of the IR microscope developed in the course of this thesis A tungsten-halogen lamp illuminates the backside of a wafer on the microscope stage The visible wavelengths of light are strongly absorbed by the Si wafer ensuring that no visible light passes through it. Near the bandgap, the absorption coefficient of Si drops rapidly and some near-infrared light can get through the wafer. Using a low-light-intensity camera (DAGE MTI series 68 with UltriconTM camera tube) sensitive to these wavelengths, an infrared image of the wafer can be generated. Inclusions and grain boundaries in polycrystalline Si readily generate contrast as they absorb or scatter incident infrared radiation (Figure 4.10).



Figure 4.9. Schematic diagram of the IR microscope. The set-up is similar to the one used by Brenneman et al. (1990) except for the inclusion of the video cassette recorder and video printer.

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Figure 4.10. Infrared image of grain boundaries and inclusions in cast polycrystalline Si The dark patches with spikes are Si_3N_4 inclusions while the rest are SiC inclusions The contrast is generated by light scattering and absorption mechanisms



The IR microscope includes the features of the optical microscope mentioned in the previous section and, hence, can be used as such. The light-sensitive camera, however, permits only black and white images to be recorded and is more sensitive to uneven sample illumination Initial focusing with the brightfield mode of the microscope is necessary for the proper placement of the sample within the IR focusing range. On switching to the IR mode (transmitted light), a correction has to be made for chromatic aberration due to the longer IR wavelengths To focus on the sample surface, it has to be moved a bit farther from the objective lens.

The effect of the refractive index of Si n_{Sl} , which is greater than that of air, is to make the wafer appear thinner when focussing at the bottom and top of the wafer Figure 4 11 represents a ray diagram of the transmitted infrared light collected by the objective lens of the microscope. The apparent thickness of the wafer can be read off the calibrated focussing knob in microns If the actual thickness of the Si wafer is known, we can calculate the refractive index $n_{Sl}=l'/l$ where *l* is the apparent thickness of the wafer and *l* its actual thickness. Since the response of the camera cuts off at around 1.2 µm, this represents n_{Sl} for $\lambda=1$ to 1.2 µm which is roughly constant (Philipp and Taft, 1960). A careful measurement for a sample with *l*=304 µm yielded *l*=88 µm and $n_{Sl}=3.45$ which is in agreement with Philipp and Taft's results (1960)

With n_{Sl} known, wafer thickness can be measured using $l=n_{Sl}l'$ The resolution r of this technique is limited by the depth of field of the microscope This depth of field is inversely related to the total magnification in use (Olympus instruction manual) For a 500× magnification, the depth of field is 1 3 µm and r=45 µm This thickness measurement technique will be difficult to carry out for samples thinner than 10 µm and is hampered by the need to focus on surface features to act as reference points for the measurements

Inclusion density measurement with the IR microscope is possible by counting inclusions as they come into focus during a depth scan of the substrate (section 6.2.3). The actual depth d of the inclusions can be determined from their apparent depth d with some accuracy using the technique mentioned above $d=n_{Si}d$ The resolution of





Figure 4.11. The effect of the refractive index of Si n_{Si} in IR imaging. The wafer appears thinner by a factor of n_{Si} ($\lambda \approx 1.1 \ \mu m$). The thickness *l* of the wafer can be calculated knowing its apparent thickness *l*. This is done by focusing on a top surface feature then focusing on the bottom surface. The focus knob (see Figure 4.8) is calibrated in microns and the difference calculated from the above adjustment gives the apparent thickness *l* in microns. The actual thickness of the wafer is then $l=n_{Si}l$.

the microscope limits the size of inclusions observable with the IR microscope For a magnification of 200×, this size is $\approx 0.8 \ \mu m$ (Olympus BHSM Microscope Instruction Manual). Thus, inclusion density measurements at this magnification will not include inclusions less than 0.8 μm in diameter. Interference from surface features should be eliminated by polishing the samples on both sides. Polished samples also increase the intensity of the transmitted light resulting in better images.

A similar depth scan can also be used to determine whether a particular grain boundary runs through the whole substrate and whether it is normal to the wafer surface Moreover, the type of boundary (twin, low-angle, large angle) should be distinguishable with this technique as increasing disorder along the boundary scatters more light (section 3 4 1) Front and back surface features on defect etched substrates can likewise be observed and correlated with ease using IR microscopy (Figure 4.12). Other defects can be observed with the IR microscope via Cu decoration (Miller and Rozgonyi, 1980, p 235). In this case, when the Cu precipitates are too small to be individually resolved, oblique lighting techniques can generate Tyndall light scattering (Lawson, 1972, p. 274) from the precipitates allowing the observation of the decorated dislocations.

4.3.2.3 Electron Microscopy

An optical microscope is quite limited by its depth of field of the image This can sometimes lead to ambiguity in the identification of dislocation etch pits and saucer pits (section 5.2). The smaller apertures achievable by electromagnetic lenses in an electron microscope give a depth of field typically two orders of magnitude greater than that for optical microscopes (Holt, 1990, p. 71). The shorter electron wavelengths also result in better resolution as well. The various analytical and imaging modes available in an electron microscope make it indispensable for semiconductor characterisation. Nevertheless an optical microscope is easier to operate and more readily accessible.

Figure 4.12. The top (A) and bottom (B) surface of a Secco-etched polycrystalline Si A correlation between dislocation etch pits and grain boundaries on both surfaces is evident This indicates that the dislocations and grain boundary traverse the wafer cross section.





Six imaging modes are available in an SEM emissive, charge collection, x-ray, luminescence, transmitted electrons and electroacoustic (Holt, 1990, p 71) The transmission mode is available in a STEM and is not available on the SEM used in this investigation. The SEM also lacks a detector for cathodoluminescence (CL) making the luminescent mode unavailable. PL (section 4.2.1.2) is very similar to CL and is used in its place. The main difference between the two techniques is that luminescence mapping is unavailable in the PL technique The electroacoustic effects discussed in Chapter 5. The x-ray mode has already been discussed to some extent in section 4 2 2 1 The charge collection mode of an electron microscope is normally referred to as Electron Beam Induced Current (EBIC) and normally applies to semiconductor materials. EBIC will be discussed in conjunction with solar cell characterisation in section 4.6.2

When an electron beam impinges on a solid, electrons in the beam collide with electrons and nuclei in the lattice and are scattered according to how heavy the nuclei are In Si, this volume of interaction is spherical (Hanoka and Bell, 1981) Figure 4.13 illustrates this interaction volume and the signal source for the emissive and x-ray modes of the SEM The emissive mode consists of low energy (secondary) electrons and high energy (backscattered) electrons Secondary electrons emanate mainly from the surface irradiated by the electron beam and are collected by a scintillator detector above the specimen Most of the topographical images in this thesis were obtained in this mode and will be referred to as Secondary Emission Images (SEI's). Secondary emission is enhanced by tilted surfaces and by edges Such topographical features will normally appear bright and may interfere with the acquisition of a good image

This effect is less pronounced in a Backscattering Image (BSI). Specimen charging due to the presence of insulating materials is also minimised and elemental contrast is obtainable with a BSI. The BSI comes from the collection of higher energy electrons with energy close to the primary electron energy (the incident

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Figure 4.13. The interaction volume between an electron beam and Si showing the sources of the signals for electron and x-ray emission in the SEM (Reimer, 1985, p. 5). PE=Primary Electrons, SE=Secondary Electrons, BSE=Back-Scattered Electrons, AE=Auger Electrons and X=X-rays.

electron beam). Reimer (1985, pp. 227-271) discusses the emissive mode in greater detail.

The electron microscope used in this thesis is a Cambridge Stereoscan 360 SEM equipped with a scintillator detector for secondary emission imaging, a Robinson detector for backscattering imaging, a Kevex x-ray detector for x-ray analysis and a GW Electronics specimen current amplifier for EBIC imaging

4.4 Crystallographic Orientation of Si Crystals

Crystallographic orientation is a bulk property of the Si crystal and does not represent a defect X-ray diffraction is the most common way of determining crystallographic orientation of Si wafers (ASTM F26-87a). An easier but less accurate method has been devised by Sopori (1981) which involves randomly texturing the surface of the wafer (KOH or NaOH etching) and diffracting light on the surface This technique is easily implemented in determining the orientation of <100>, <110> and <111> wafers and is mentioned as an alternative to x-ray diffraction in ASTM F26-87a Misorientations shift the diffraction pattern across the screen and result in very complicated diffraction patterns. Attempts to use this technique on large-grain polycrystalline Si used in this thesis proved difficult as the beam position is hard to ascertain and the complicated diffraction patterns are hard to interpret.

A more useful technique for cast polycrystalline Si using an SEM is the generation of Electron Channelling Patterns (ECP). By rocking the electron beam $\pm 5^{\circ}$ off-axis, Kikuchi bands are generated in the backscattering mode (Reimer, 1985, p. 11) The resulting bands can be matched to a particular crystallographic orientation Typical resolutions are of the order 1 to 10 µm This is more than enough for studying large grain polycrystalline Si with grain diameters exceeding 1 mm. Studies on crystallographic dependence of diffusion and oxidation, effects of grain boundary types on device characteristics and grain orientation of solution grown

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Si on glass can be carried out with ECP This technique provides material for future device studies on polycrystalline and solution-grown Si

4.5 Characterising the Electrical Activity of Defects

It has been pointed out in Chapter 3 that dopant impurities are necessary defects for device fabrication (section 3.3.1). Thus, the evaluation of dopant concentration and concentration profiles forms a major part of this section. Carrier type and bulk resistivity are directly linked to dopant impurities in the material. Their characterisation provides vital information for p-n junction fabrication which is the heart of solar cell operation Bulk resistivity (along with ohmic contact resistance) contributes to series resistance during device operation High resistivity substrates tend to yield lower cell fill factors although an increase in open circuit voltage may compensate for this effect and cell efficiency remains constant These aspects of solar cell performance will be discussed in greater detail in section 4.6. Carrier lifetime or mobility is linked to substrate quality and surface passivation. Crucial oxidation steps are routinely checked for oxide quality by measuring carrier lifetime after oxidation EBIC, the main tool for evaluating the recombination activity of bulk and intrinsic defects, will also be discussed in section 4.6.

4.5.1 Hot probe and four point probe

Hot probe measurements (ASTM F42-77(87)) determine the carrier type in the substrate. Measurements were improvised by heating one probe of two in contact with the Si material. The thermally generated carriers create a potential difference between the two probes which can be measured by a voltmeter. Although this technique is normally applied to bulk material, it can also be applied to epitaxial layers provided the substrate is of the opposite polarity or of sufficiently high resistivity These conditions are similar to four point probe requirements.

Four point probe measurements determine the resistivity of Si bulk material (ASTM F84-84a) It can also measure the sheet resistivity of epitaxial layers

provided they are grown on a substrate with opposite polarity (ASTM F374-84) or on a sufficiently high resistivity substrate (about 3 orders of magnitude higher than that of the epilayer). Hot probe measurements should be performed on an epilayer to check its carrier type against its substrate prior to four point probe measurements The presence of a junction or a high resistivity substrate 'reflects' majority carriers in the epilayer region away from the substrate Thus, current is made to pass along the epilayer exclusively. The measured voltage V and current I can be converted into sheet resistivity by using the thin slice approximation (Uhlir, 1955):

$$\rho_s = \frac{\pi}{\ln 2} \frac{V}{I} = 4.53 \frac{V}{I}$$
 [48]

This is valid for sample thickness x < s/2 where s is the probe spacing. $s\approx 1.6$ mm for the particular configuration used in this thesis and the approximation is valid for $x<800 \ \mu\text{m}$ Smits (1958) gives correction factors for finite sample shapes (circular and rectangular) For a 50.8 mm wafer a 1% reduction in ρ_s occurs and the corrected sheet resistivity $\rho_s' = 0.99\rho_s$. For a 2 cm × 2 cm sample (typical for solution-grown Si layers), $\rho_s' = 0.97\rho_s$. Even for half this size, the resistivity only drops by around 11% from that calculated from equation 4.8. Only when the sample size is nearly equal to the total probe spacing will a significant 50% reduction in ρ_s be observed. The four point probe then gives us a good estimate of the epilayer sheet resistance

If the thickness x of the epilayer can be measured, the resistivity ρ of the epilayer can be calculated using $\rho = \rho_s x$ This resistivity value can be converted into a dopant concentration value (ASTM F723-82(87)) provided the carrier type in the epilayer is known For unknown solution-grown epilayers, the standard procedure for measuring resistivities used in this thesis was to etch oxide layers off the sample, determine the carrier type of both epilayer and substrate with the hot probe, measure the sheet resistivity of the epilayer and the resistivity of the substrate with the four point probe and measure the epilayer thickness with a Dektak IIA Surface Profile

Measuring System (Sloan Technology) Thicknesses from 0.5 nm to 65.5 μ m are measurable with Dektak IIA If surface roughness and warping interfere with thickness measurements, a reasonable estimate of the average sample thickness is made A reasonable estimate of the epilayer resistivity is then obtained and an effective epilayer dopant concentration estimated from ASTM F723-82(87).

4.5.2 Capacitance-Voltage (C-V) Measurements

The computer-controlled C-V apparatus used in this thesis has been described in detail by Ong (1988). The C-V technique can generate dopant concentration profiles of bulk, epitaxial, diffused or implanted Si wafers (Heime, 1979) The device structure for profiling epitaxial layers in this thesis is shown in Figure 4 14. Schottky barriers and ohmic contacts are fabricated on the surface to be profiled This coplanar structure works for layers on a high resistivity or opposite polarity substrate. It can also be implemented on diffused or implanted regions (Wilson and Jamba, 1982) The ohmic contacts on n-type Si were mainly evaporated Al. In most cases, the rough surface of the epilayers ensured good ohmic contact Schottky diodes consisted of evaporated Pd. For p-type Si, the Al ohmic contacts were sintered at 450°C for half an hour before Al schottky diodes were evaporated onto the surface. The dark Current-Voltage (*I-V*) curves of the diodes were plotted to verify successful diode fabrication and to check reverse breakdown voltage

For an abrupt junction,

$$C = \varepsilon_{\rm s} A/w \qquad [4.9]$$

and

$$w = \sqrt{\frac{2\varepsilon_s(V_{bl} + V - 2kT/q)}{qN}}$$
[4 10]



.

Figure 4.14. C-V test structure for epilayers on opposite polarity or high resistivity substrates. If the epilayer is on a heavily doped substrate, it is easier to make the ohmic contact (hatched circle) at the rear of the substrate. Several schottky diode sizes are available (open circles).

where ε_s is the permittivity of Si, q the electronic charge, A is the area of the junction and w is the depletion width, N is the dopant concentration of the epilayer and V is the applied reverse bias (Sze, 1985, pp 76-86). Substituting equation 4.10 into equation 4.9, solving for C^{-2} and differentiating with respect to V yields

$$\frac{d(C^{-2})}{dV} = \frac{2}{q\varepsilon_s NA^2}$$
[4 11]

By plotting C^{-2} against V and calculating slopes along the curve at various points, a doping profile can be generated with

$$w = \varepsilon_{\rm s} A/C \qquad [4\ 12]$$

since w extends mainly into the epilayer.

Diodes on wafers with known resistivities were first tested to ensure correct capacitance measurements. Although the technique did not give accurate results initially, proper cable shield grounding solved the problem. Figure 4.15 shows the concentration profile for diodes fabricated on uniformly-doped n-type substrates with resistivities of 0.1 Ω cm (N1) and 1 Ω cm (N2). The measured concentrations are 8 8 $\times 10^{16}$ for N1 and 4.5 $\times 10^{15}$ for N2 and are in good agreement with the expected concentrations: 7.8 $\times 10^{16}$ for N1 and 4.9 $\times 10^{15}$ for N2 obtained via four point probe measurements. The shallower profile generated for N1 is due to its lower breakdown voltage. *C-V* measurements become unstable near the diode breakdown voltage

The C-V technique is limited by the dopant concentration of the layer to be profiled. A very low concentration introduces a large series resistance between the contacts and part of the applied voltage is dropped across this resistance For $N\approx10^{18}$ cm⁻³, the capacitance of the diode at zero bias is very high and exceeds the range of



Figure 4.15. C-V carrier concentration profiles for schottky diodes fabricated on n-type Si substrates with bulk resistivities of 0.1 Ω cm (N1) and 1 Ω cm (N2). The lower resistivity substrate N1 has a shallower profile due to its higher carrier concentration and, hence, lower breakdown voltage.

the capacitance meter. In this case, very small diodes (0.3 to 1mm in diameter) have to be fabricated. From equation 4.11, N is inversely proportional to A^2 Small errors in the calculation of A lead to significant differences in the calculated N. This means that the diode area A has to be measured very accurately. Moreover, the breakdown voltage of the diode decreases with increasing N (20 V for $N=5\times10^{15}$ cm⁻³ and 5V for $N=10^{17}$ cm⁻³) resulting in shallower profiles. Profiles for $N>10^{17}$ cm⁻³ are <0.5 µm deep as can be seen from Figure 4.15.

The limitations mentioned above together with the difficulty in fabricating Schottky diodes on the epilayers frustrated attempts to profile solution-grown epilayers (Figure 7 1). More successful profiles were obtained with spreading resistance measurements obtained from SOLECON Laboratories (USA).

4.5.3 Microwave Photoconductance Lifetime Tester

The microwave photoconductance technique for measuring minority carrier lifetime has been described by Basore and Hansen (1990). This tool has proven to be very useful in monitoring oxidation, diffusion, and sintering processes. This is routinely achieved by putting an n-type Si control wafer in the appropriate furnace and measuring its carrier lifetime after the process. Comparison with previous measurements can detect problems during the processing step (e.g., a large drop in lifetime can represent contamination of the wafer). Minority carrier lifetime depends on recombination (section 3.3) and scattering process (section 3.4.2) in the Si wafer Lifetime degradation then indicates the introduction of defects in the Si wafer Lifetime measurements on cast polycrystalline and solution-grown Si are, however, hard to implement.

4.6 Solar Cell Characterisation

It is essential to evaluate the final result of device processing and be able to see what effect gettering or passivation steps had on the device. Since the resulting solar cell is basically a photodiode, light and dark I-V measurements provide us with

very useful information about the device. These measurements have to be complemented by appropriate characterisation techniques to find out the source of unideal cell performance. EBIC measurements can identify recombination centres in the finished solar cell. Careful defect etching experiments have to be performed to actually correlate a particular physical defect with the EBIC recombination centre Successful junction creation and junction depth measurement can be evaluated using EBIC Spectral response measurements give useful information on the effects of defects on carrier photogeneration and collection.

4.6.1 Current-Voltage (I-V) measurements

Under constant illumination, the current and voltage output of a solar cell is governed by the circuit load. Figure 4.16 illustrates a typical *I-V* curve for an illuminated solar cell. From this curve, the three important cell parameters (open circuit voltage V_{oc} , short circuit current I_{sc} and fill factor *FF*) are defined (Green, 1986, pp 79-81). The curve is described by the illuminated diode equation

$$I = I_o(e^{qV/kT} - 1) - I_L$$
 [4.13]

where I_o is the diode saturation current, I_L is the light generated current, k is Boltzmann's constant and T is the cell temperature (°K). The cell short circuit current I_{sc} is equivalent to the light-generated current I_L in the solar cell. I_L is determined by the carrier generation and collection properties of the solar cell. Carrier recombination and inactive solar cell areas directly result in a drop in I_{sc} . Localised lighting (e. g., Light Beam Induced Current) can then yield useful information on cell properties. The next section will discuss a similar technique (EBIC) that can perform a similar task A consideration of I_{sc} alone is sufficient to characterise defects and their effects on solar cell performance. I_{sc} is usually normalised to the solar cell area and is then referred to as the cell short circuit current density J_{sc} .

The open circuit voltage V_{oc} of a solar cell is defined as



Figure 4.16. *I-V* curve for a solar cell under illumination. V_{oc} and I_{sc} are merely the x- and y-intercepts of the curve. V_m and I_m refer to the maximum power point in the curve.

$$V_{oc} = \frac{kT}{q} \ln \frac{I_L + I_o}{I_o}$$
 [4 14]

where I_o , under the simplest conditions, is given by

$$I_o = Aqn_1^2 (D_e/L_e N_A + D_h/L_h N_D)$$
 [4.15]

where A is the area of the device, q is the electronic charge, n_l is the intrinsic carrier concentration, D_e and D_h are the electron and hole diffusivities, L_e and L_h are the electron and hole diffusion lengths and N_D and N_A are the dopant concentrations in the n and p-type layers. Consideration of the limits on V_{oc} have shown that bulk and surface recombination are the fundamental processes determining V_{oc} . (Green, 1987, pp 100-105). Electron Beam Induced Voltage (EBIV) (Romanowski and Buczkowski, 1985) can then be used in place of EBIC for imaging recombination centres in solar cells.

The solar cell Fill Factor (FF) is defined as

$$FF = V_m I_m / V_{oc} I_{sc}$$
[4.16]

where V_m and I_m represent the maximum power point along the *I-V* curve. Ideally, *FF* is a function of V_{oc} alone (Green, 1986, p.80) Therefore, bulk and surface recombination is expected to reduce the cell *FF*. The cell *FF* is also very sensitive to parasitic resistances, namely (Green, 1986, pp. 96-98). One type of parasitic resistance is series resistance. This mainly comes from the bulk resistance of a solar cell and the associated contact resistance at semiconductor-metal interface. The other type of parasitic resistance is shunt resistance and is caused by leakage across the p-n junction of the solar cell. Dislocations, precipitates, inclusions and cleaved junction regions are a common source of junction leakage.

The three factors (V_{oc} , I_{sc} and FF) just discussed can be lumped into one factor defined as the cell efficiency η :

$$\eta = V_{oc} I_{sc} FF/P_{in}$$
[4.17]

where P_{in} is the power of the incident light on the cell η is the ultimate parameter for evaluating solar cell performance and needs to be maximised From equation 4.17, it is clear that any gain in V_{oc} , I_{sc} or FF will result in improved cell performance The theoretical limit for an Auger-recombination limited Si solar cell is 30% (Green, 1987, p 97).

Lighted *I-V* measurements were made using a computer-controlled solar simulator designed at the UNSW Centre for PV Devices and Systems After a warm up time of 20 minutes, a calibrated cell was used to obtain an illumination intensity of 100 mW/cm². Four-probe measurements ensured minimisation of contact resistance problems. The copper chuck on which the cell is vacuum-mounted is kept at a constant temperature to minimise unwanted thermal effects during measurement A more detailed description of solar simulator operations and limitations can be found in Kurianski (1990)

4.6.2 Electron Beam Induced Current (EBIC)

The charge collection mode of the SEM is more commonly known as the Electron Beam Induced Current (EBIC) mode. This mode mainly applies to semiconductors where carrier generation in the material is possible. The collected current is typically orders of magnitude larger than the probe current. In Si, whose bandgap is 1.1 eV at room temperature, an electron with an energy of 20 keV is capable of generating 18,000 electron-hole pairs. However, the actual number generated is around 6000 pairs because the incident electron interacts with inner shell electrons of the atoms in the lattice (Reimer, 1985, p. 275). The induced-current image of the sample is generated by collection and amplification of these generated

carriers The collection of these carriers require that an electric field be present across the Si sample. This can be done by fabricating a p-n junction via diffusion or ion implantation, by making an MIS or Schottky barrier on the wafer surface or by applying a bias across the wafer The first mentioned is the more natural method for solar cells studied in this thesis. Bulk defects are more commonly studied using an MIS (Ast et al., 1991) or Schottky barrier structure (Jakubowicz et al., 1987)

EBIC is very useful in imaging recombination centres and inactive cell regions Recombination represents a loss of the generated carriers and will usually appear as dim or dark areas in the EBIC image. Features which inhibit carrier generation (metal fingers, dirt on surface, inclusions) likewise generate similar features Quantitative techniques allow the measurement of recombination velocities and diffusion lengths An excellent review of the capabilities of EBIC can be found in Leamy (1982)

Profiling the EBIC signal from bulk defects is possible by varying the electron energy from 5 to 35 keV This allows us to study recombination centres 0 3 to 10 μ m deep. The profile depth is dependent on the depth and distribution of the generated charge carriers (Figure 4.17). Resolution is obviously lost for deeper penetration due to larger carrier generation volumes. Deeper profiles can be obtained by STEM-EBIC techniques (Ast et al, 1991). This has the added feature of being able to directly correlate EBIC contrast with bulk defects and solar cell output Caution has to be exercised in interpreting EBIC images because of the limited carrier generation depths achievable by this technique. Recombination activity of defects may appear strong at shallow penetration depths due to depletion layer or surface effects but contributes only slightly to bulk recombination (Ast et al, 1991, p. 46).

EBIC is easily implemented in an SEM. Initial EBIC micrographs were made using the built in specimen current amplifier of a Cambridge Stereoscan 360 SEM A bias of 0 7 V due to the touch alarm was inevitable and the EBIC currents were hard to control. Reasonable images were generated using very slow scan speeds (TV/1000) with this set-up A specimen current amplifier from GW Electronics was later acquired and installed in the same microscope. This allowed the precise

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Figure 4.17. Carrier generation profile in Si for an incident electron accelerated at 10, 15, 25, 30, 35 and 40 kV (Vyatskin and Pilyankevich, 1964). The area under the curves represent the total number of electron-hole pairs created.

measurement of EBIC currents and resulted in more consistent imaging Figure 4 18 illustrates the sample configurations used for EBIC imaging in this thesis Figure 4.18A is used for normal EBIC images. A limited depth profile can be performed in this planar configuration by varying the electron beam accelerating voltage. Figure 4 19 is an EBIC image of an array of defects in a chemically polished cast polycrystalline Si solar cell. The dark stripes running from top to bottom are due to shading from the metal fingers on top of the cell. Grain boundaries (dark curves) and electrically active dislocations (black spots) are apparent in the figure Some of the black spots may be due to inclusions. This can be verified via defect etching or IR microscopy Dimitriadis (1985) developed a quantitative analysis of grain boundary recombination velocities for polycrystalline Si using this planar configuration. Assuming low carrier injection; grain diffusion length $L \gg r_e$, the carrier generation radius; zero internal electric field in the grains; a semi-infinite semiconductor, depletion width $w \ll L$ and that the influence of the grain boundary on the minority carrier distribution can be treated as a perturbation, a grain boundary normal to the Si surface with a recombination velocity S_{GB} will give rise to a normalised EBIC I_N given by.

$$I_N = 1 - \frac{S_{GB} r_e L^{1/2} e^{(r_e - x)/L}}{2\sqrt{2\pi} D x^{1/2}}$$
[4.18]

where x is the distance from the grain boundary and D is minority carrier diffusion constant. This model will be used in section 6.3 2 to explain EBIC features observed in cast polycrystalline Si solar cells. An interesting application of this model will also be made in the analysis of laser scribes (section 5 3 3 3).

The sample configuration in Figure 4 18B is normally used for junction imaging and junction depth measurement. The cleaved edge of the solar cell is polished to remove cleaving damage. In most instances, however, a clean cleaved section is sufficient for junction imaging and junction depth measurement (section



Figure 4.18. EBIC configurations for A) the usual planar observation of the junction and B) junction imaging and measuring junction depth.

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Figure 4.19. EBIC micrograph of a cast polycrystalline Si solar cell showing different types of defects. The dark strips from top to bottom are due to shading from metal fingers on the cell surface. The dark curves are due to recombination at grain boundaries while the dark spots originate from dislocations.


7 2) The minimum depth measurable by the EBIC technique depends on its resolution The best resolution attainable with EBIC is $\approx 1 \ \mu m$ and junction depths less than 1 μm will be difficult to measure Junction imaging is demonstrated in section 5 3 4 where the high surface recombination velocity along the polished cleaved edge ensures that the bright areas correlate to the extent of P-diffusion into the grooves.

Polished surfaces are preferred for EBIC measurements since surface features may interfere with the observation of recombination activity. Figure 4 20 shows topographic EBIC contrast generated by a laser-textured surface The image on the left is a BSI of a laser-textured solar cell The image on the right is the EBIC image corresponding to the same area Recesses appear brighter as they tend to trap scattered electrons and edges appear darker as electron emission is enhanced (see section 4 3 2 3). Enhanced electron emission also occurs at tilted surfaces which consequently appear darker Shading effects due to metal fingers or dirt on the cell surface normally generate dark patches in an EBIC image The resulting contrast is reduced if the electron beam is energetic enough to penetrate through the shading material.

4.6.3 Spectral Response

Spectral response measurements were made using the facilities at SANDIA laboratories The illuminated current of a solar cell is monitored as the wavelength of incident light is varied over its response band (ASTM E1021-84) The resulting spectra shows how well the solar cell is converting each wavelength of light to current. Knowing the wavelength dependence of the generation rate of charge carriers and the penetration depth of each wavelength, problems can be identified.

In section 3.2, it was noted that free carrier absorption effects can affect the near infrared response of solar cells. The spectral response of cells made on substrates with varying resistivities should record a fall in response in the $1\mu m$ wavelength region for decreasing resistivities Dead layers from heavy diffusions

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Figure 4.20. Topographic contrast in EBIC images. The image on the left is a BSI of a laser-textured solar cell. The image on the right is the EBIC image corresponding to the same area. Recesses appear brighter as they tend to trap scattered electrons, edges appear darker as electron emission is enhanced, tilted surfaces appear darker for similar reasons.



reduce diffusion lengths in the diffused area and results in a decrease in the blue (short wavelength) response of commercial screen-printed cells (Lindmayer and Allison, 1972) Spectral response was likewise used with limited success by Chong to evaluate the effect of different substrate resistivities on cell output (Chong, 1989, pp 69-80, 148-150)

4.7 Overview of the Use of Characterisation Techniques in this Thesis

Having described how defects can be evaluated in Si materials and solar cells, we now turn to the study of defects in specific solar cell processing procedures and in future solar cell materials Chapter 5 will deal with extrinsic defects generated in the laser-grooved solar cell processing sequence developed at the University of New South Wales, Chapter 6 will deal with the identification of intrinsic defects in cast polycrystalline Si and their effects on device performance and Chapter 7 will mainly involve the characterisation of solution-grown material being developed at the University of New South Wales. Preferential defect etching coupled with optical and electron microscopy will prove indispensable in exposing extrinsic and intrinsic line, area and volume defects to be considered in these chapters. EBIC will find applications in all these chapters for evaluating the recombination activity of certain defects or in junction imaging and depth measurement. IR microscopy and EDX analysis will prove useful in evaluating inclusions in cast polycrystalline Si and solution-grown Si layers. FTIR measurements of free carrier absorption has already been discussed in Chapter 3 and will again find application in evaluating $[O_i]$ and $[C_s]$ in cast polycrystalline Si. Specialised application of the hot-probe, four-point probe and C-V technique to solution grown layers will be discussed in Chapter 7. PIXE and PL analyses will prove useful in identifying the dopant impurity for solution-grown Si EDX, RBS and PIXE will be used in evaluating alloy composition of solution-grown Bandgap reductions in these alloys will be evaluated via PL $Si_{1-x}Ge_x$ layers. measurements

CHAPTER 5

LASER-GROOVED SOLAR CELLS

5.1 Introduction

Pilot-line production of laser-grooved solar cells at the UNSW have achieved efficiencies up to 19.6% on both large area (45 cm²) and small area (8 cm²) cells The success of this design lies in the efficient and economical metallisation process achieved via laser grooves (Wenham, 1986). An understanding of the groove characteristics will be essential in understanding cell characteristics and in identifying future improvements to laser-grooved solar cell processing.

Figure 3.1 shows a cross-section of the laser-grooved solar cell. By burying the front metal contacts, shading losses are minimised. The large aspect ratio of the metal fingers also allows the top surface of the cell to be lightly diffused increasing the short wavelength ('blue') response of the cell. The incorporation of heavily doped metal contact regions (P in the grooves and Al at the rear) have made gettering possible Gettering minimises unwanted activity from intrinsic and extrinsic defects Optimisation of heavy P diffusion of grooves and Al sintering steps have led to efficiencies up to 20 6% on 12 cm² cells (Chong, 1989) Only high efficiency solar cell structures (e.g., Passivated Emitter Solar Cell (PESC), Passivated Emitter and Rear Cell (PERC) and Passivated Emitter Rear Locally-diffused (PERL) solar cell) have exceeded such efficiencies on low resistivity (0.2 to 0.5 Ω cm) substrates (Green et al., 1989 and Zhao et al., 1990). However, the photolithographic requirements of such structures make them more costly. Consequently, these cells find applications where cell cost is not the primary concern like space cells or concentrator cells Because of its economy and vastly improved efficiency, the laser-grooved or buried contact approach will become the dominant terrestrial solar cell structure with the design already licensed to several companies for commercial production (Wenham, 1992).

A testimony to the excellent performance of laser-grooved solar cells is its superior open circuit voltage on 1 Ω cm FZ Si substrates compared to that of PESC structures (648mV (Chong, 1989, p. 94) compared to 640mV (Narayanan and Green, 1989) for planar solar cells) Both structures benefit from the same high efficiency features P and Al gettering. The main difference lies in the oxide growth and thicknesses used and the laser-grooving step. There are then two possibilities that can explain this result: 1) lower top surface recombination velocities and/or 2) laser damage gettering. The latter has been claimed by previous workers (Wenham, 1986, p. 30 and Chong, 1989, pp. 104-107) although no physical evidence of laser damage after cell processing was presented. Chong (1989, p. 26) found the optimum groove depth to be around 45 µm. Deeper grooves attained by increasing KOH etch times have led to poorer cell performance. This effect can be attributed to the removal of residual damage around the grooves necessary for gettering. This chapter of the thesis reveals the damage caused by laser-groove processing for the first time, examines the extent of the damage and explores gettering mechanisms that arise from it

The next section will review some of the results on oxidation-induced defects previously reported by Chong (1989, pp. 162-169) and will discuss the nature of the oxidation-induced defects observed. Some experiments have been repeated and will show that dislocation generation does not occur during oxidation of planar and random-pyramid textured surfaces The observed defects are S-pits which may arise from furnace contamination during high temperature processes The remaining sections will be devoted to the characterisation of the grooving procedure in lasergrooved solar cell processing. Some attention is directed at thermal wave effects that have not been considered before. Gettering via laser scribes is demonstrated and is

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shown to proceed from thermal wave effects. The resulting interaction between thermal wave effects and P diffusion sheds new light on laser-groove characteristics These observations lead to a better understanding of gettering processes in lasergrooved solar cells.

5.2 Oxidation-Induced Defects

Previous work in evaluating oxide quality have shown a correlation between oxide thickness and etch pit density (Chong, 1989, p. 178). Although these pits were identified as dislocation etch pits, not all of them were A closer look at some of the pits show that they are saucer pits (S-pits). S-pits are shallow pits formed by the removal of precipitates on the Si surface. They appear rounded for isotropic defect etchants like the Secco etch used in this work Dislocation etch pits are conical in shape The cone recedes in the direction where the line defect propagates (Figure 5.1) Under an optical microscope, it is often hard to distinguish between S-pits and dislocation pits because of the limited depth of field of the instrument. Outright identification is, however, possible with electron microscopy. Figure 5.2A shows Spits on a Secco-etched oxide grown in a heavily contaminated furnace. In Figure 5.2B, the conical shape of dislocation etch pits in a polycrystalline Si sample is quite distinct under SEM observation

Secco-etched bare wafers were found to have much lower dislocation densities than previously reported (Chong, 1989, p. 169) owing to the difficulty of correctly identifying dislocation etch pits with an optical microscope when S-pits are present Figure 5.3A shows a Secco-etched virgin wafer The pits present are S-pits and may have come from contaminants during wafer polishing and handling SEM scanning of the surface revealed no dislocation etch pits in the scanned frames Etching of textured surfaces confirms this result (see Figure 5.4). Subsequent etching of an oxidised Si wafer, reveals a greater density of S-pits (Figure 5.3B). An SEM scan of the sample has likewise revealed no dislocations. The S-pit density for this sample is $\approx 7 \times 10^4$ cm⁻² and is consistent with transition metal contamination



Figure 5.1. Feature characteristics of dislocation etch pits (A and B) and S-pits (C). The dislocation etch pits have a conical structure receding in the direction where the line defect propagates (after ASTM F47-87).

Figure 5.2. A) SEM micrograph showing the structure of shallow pits. B) Dislocation etch pits on a polycrystalline Si sample. The conical features indicated in Figure 5 1 are clearly seen.





Figure 5.3. A) S-pits on a Secco-etched virgin wafer. The S-pits originate from wafer polishing Wafer cleaning before defect etching minimises this effect. B) S-pits on a Secco-etched oxidised wafer. The density of 7×10^4 cm⁻² is consistent with the expected S-pit density due to transition metal contamination from an unclean furnace (Tsuya and Shimura, 1983).





Figure 5.4. Secco-etched random pyramid textured surfaces: A) 10 μ m pyramid base width and B) 25 μ m pyramid base width. The pyramids have been smoothed out by the etch. Around 30 frames were inspected for each sample revealing no dislocations and S-pits on the surface.





observed when 'unclean' furnaces are used for oxidation (Tsuya and Shimura, 1983) The etch pits reported by Chong (1989, p 178) are consistent with such contamination although they are more likely due to contamination during the removal of a large portion of the wafer surface before defect etching (Wenham, 1993, private communication). Figure 5.3B shows that the stress due to thermal mismatch between the oxide layer and the Si wafer is not enough for dislocations to be generated Thermal gradients across the wafer (section 2.2.2) represent a potentially more efficient source of dislocations during oxidation.

Textured surfaces present stress points along the pyramid edges and peaks during oxidation and have been reported to cause a consequent drop in V_{oc} and FF of the finished cell (Chong, 1989, pp 93-94). This drop in cell output has been attributed to dislocation generation during oxidation with a correlation between etch pit density and oxide thickness being observed (ibid., pp 162-182). If this were so, increasing the size of the pyramids should then reduce the density of stress points during oxidation and consequently reduce the number of dislocations generated in the process To verify this effect, two wafers were textured with pyramid base widths of 10 μ m and 25 μ m. A 300 nm oxide layer was then grown on the wafers by wet oxidation at 900°C After the oxidation step, both wafers were chemo-mechanically polished (section 4 3.1) on one side for optimal defect delineation A mirror-like finish was usually attained after the removal of 20 to 30 μ m of material from the surface The remaining oxide was then etched off with a 10% HF solution just before the Secco etching step.

Figures 5 4A and B are SEM micrographs of the Secco-etched 10 μ m and 25 μ m random pyramid textured side of the wafers. The pyramids have been rounded off by the etching step. No dislocations are observable in the micrographs Around 30 other frames were examined for each sample revealing no dislocation etch pits. The previously reported pits are then suspected to be S-pits as has already been mentioned for bare and planar oxidised wafers. The reported densities (2×10⁵ to 1×10⁶ cm⁻²) and highly inhomogenous distribution of the pits are consistent with S-pit formation

Close-up SEM micrographs for the reported pits reveal S-pit characteristics (Figure 5.1 and Figure 5.2A). Contamination during oxidation, which is the likely source of these pits, can cause a similar drop in V_{oc} and blue response of cells due to the higher surface recombination velocities for such oxides. It can also account for the observed correlation between oxide thickness and etch pit density with longer oxidation times enhancing contamination. The greater density of S-pits observed by Chong (1989, p 186) on a textured cell compared to a planar cell is probably due to the fact that a textured surface presents more stress points at which contaminants may precipitate We can safely conclude then that stresses present in an oxidised textured wafer is not sufficient to generate dislocations. These stress points may, however, play a more important role

S-pits observed on the polished side of the samples in Figure 5.4 probably come from slurry precipitates adhering to the Si surface during chemomechanical polishing The absence of S-pits on the textured side of the samples is consistent with this assumption It also shows that there are no precipitates from furnace contamination This result may be due to improved oxidation conditions used for the samples, in particular, the consistent use of TCA precleaning of furnaces TCA precleaning has proven effective in minimising oxide contamination as lifetime measurements have shown on oxides grown with and without TCA precleaning in our laboratory (Ebong, 1992).

5.3 Laser Processing of Si

5.3.1 Scribe Damage and Appearance

Figure 5.5 shows a simplified diagram of the laser scribing apparatus used in the production of experimental laser-grooved solar cells. Precise details of the laser scriber have been described by Wenham (1986). A pattern for the top ohmic contact of a solar cell is defined first and is converted into a computer program which, by controlling the shutter and x-y table, is able to recreate the desired pattern on the Si



motorised x-y table



wafer. Before running the program, the desired pulse frequency and laser intensity is set for the Q-switched, 1.06µm Nd:YAG laser. A wafer is then placed on the wafer holder and held in place by vacuum Optimum conditions for the scribes are listed in Appendix A The viewing lens allows in situ observation of the scribing process The suction tube allows the removal of reject material during the scribing process minimising damage to the wafer surface.

Damage certainly occurs in the heat-affected region around the laser scribe Figure 5.6 is part of a typical metal ohmic contact pattern generated by a laser scribe which has been Secco-etched. It shows regions of strain at the bottom and sides of the resultant groove generated by laser scribing The regular drilled-hole pattern is a result of Q-switched laser pulsing. The appearance of this pattern depends on the pulse frequency, *f*, the scribe speed, *s*, and the diameter of the hole opening, *d* This is normally expressed in terms of an overlap factor G=df/s (Quantronix Corporation, 1973a, p. 65) Figure 5 7 is a typical laser-drilled hole generated by a single pulse revealing a distinct cone shape In this figure, $d\approx 22 \ \mu m$ and does not vary much for different pulse frequencies and peak powers ($d\approx 15 \ to 25 \ \mu m$)

The cosmetic appearance of a scribe with $G\approx 1$ can be seen in Figure 5.8. In this case, the holes just overlap. For $G\approx 3$ (Figure 5.10A), the edges of the scribe will appear straight and the scribe will look clean because of the large trajectory angle ($\approx 45^{\circ}$) of the rejected material (ibid.). Ejected particles, typically 5 µm in diameter, are scattered around the groove region For G>6 (Figure 5.10C), the scribe will appear cluttered with refuse material because of the lower trajectory angle of rejected material. The rejected material accumulates behind the scribe front and can be easily removed by a KOH or NaOH etch (section 4.3.1.2).

Two laser scribers were used for the scribes studied in this thesis. Laser 1 was initially used until it had to be upgraded. Later scribes were done with Laser 2 which distinctly had a more powerful beam. Scribing conditions on Laser 1 were unrepeatable with Laser 2 as the laser beam became unstable at low power for Laser 2 Actual table speeds (Table 5.1) for the different table speed settings (1 to 5)

Figure 5.6. Scribe damage exposed by Secco etch on a typical laser scribe. The Spits away from the groove are due to precipitates formed during oxide growth in a . heavily contaminated furnace. The low density of S-pits around the scribed region will be explained in section 5.3.3.



Figure 5.7. A hole created by a single laser pulse on a Si wafer The hole has a conical shape. The hole opening in this case is 22 μ m and does not vary much with pulse frequency and peak power.



Figure 5.8. Cosmetic appearance of a scribe with an overlap factor $G \approx 1$ The dark band surrounding the scribe is attributed to thermal wave effects (section 5 3 3) For $G \approx 3$ and G > 6, see Figures 5.10A and C respectively.



Table 5.1. Table speed measurements and G-factors for f=8 kHz using Laser 2. For G calculations, d was taken to be 20 μ m and s, the actual table speed. A large discrepancy in expected and actual speeds exist for settings 1 and 4.

| Speed Setting | Expected Speed | Actual Speed | G (8 kHz) |
|---------------|-----------------------|-----------------------|-----------|
| | (cm s ⁻¹) | (cm s ⁻¹) | |
| 1 | 0.3 | 0.6 | 27 |
| 2 | 1.3 | 1.9 | 8.4 |
| 3 | 2.5 | 2.8 | 5.7 |
| 4 | 5.1 | 7.3 | 2.2 |
| 5 | 7.6 | 7.5 | 2.1 |

available on Laser 2 was determined by measuring distances between drilled holes at a pulse frequency of 200 Hz. Measurements were made only when the dots attained uniform spacing between them. For the highest table speed used (7.5 cm s⁻¹), the table accelerates for a distance of 3.5 mm before attaining uniform speed. The distance needed to stop is 2.5 mm. These distances decrease for lower table speeds. Actual table speeds for Laser 1 were not possible to check because they were modified during the upgrade. Rough estimates can, however, be obtained from Table 5.1 as Laser 1 and 2 were built similarly.

5.3.2 Extent of the Heat Affected Zone

Measurements made by the laser manufacturers show that the temperature rise is negligible 30 μ m from an area irradiated by a single pulse of laser (Quantronix Corporation, 1973b). Moreover, for pulse frequencies less than 35 kHz, the Si material should cool down to ambient temperature before the next laser pulse arrives. Most of the heat in this process is carried away via the heat of vaporisation of the vaporised Si material. Laser damage should then be highly localised and can be removed by a subsequent KOH etch (Wenham, 1986, pp. 112-121). This etching step rids the groove of loose slag and, more importantly, defines the groove shape for the buried metal contacts. Figure 5.9 shows a Secco-etched laser scribe after the normal KOH etch step. The oxide layer was etched off prior to the Secco etch. Damage depicted in Figure 5.6 has been successfully removed. The following discussion will, however, present evidence that residual laser-induced damage may still be present around the grooved region.

In Figure 5.8, a dark band surrounding the scribe can be observed. Dark regions in the SEI mode of the SEM (section 4.3.2.3) mean that the secondary (low energy) electrons are being 'trapped' in the oxide layer or in the Si/SiO₂ interface. Such charge trapping is well-known to occur for insulators under the SEI mode of observation in an SEM.. The contrast with the surrounding oxide layer suggests that the oxide layer around the scribe has been affected by the scribing process. Moreover, the fringes of the dark region are brighter than the surrounding oxide and appear to be frayed. Such bright features represent the enhanced emission of secondary electrons (section 4.3.2.3). This normally occurs along edges and inclined surfaces in the sample. Its presence at the edges of the dark band indicates the presence of a stressed oxide layer where damage is producing enhanced secondary electron emission.

The above-mentioned dark band feature is not observable with backscattered (high energy) electrons and is hardly visible under an optical microscope (brightfield and Nomarski mode). Wafers with varying surface conditions (bare or oxidised, P-diffused and oxidised, n-type or p-type, textured or planar, polycrystalline, nitridised) were similarly scribed and consistently displayed the dark bands. The bare wafer sample has a native oxide which makes it possible to see dark band the feature although faintly. KOH and HF treatments on these wafers make them fade. Apparently stress in the oxide is released during such treatments making it impossible to generate the dark band. Complete removal of the oxide layer results in the disappearance of the dark bands. It is then established that the oxide layer is the source of the SEI contrast generating the dark bands.

Figure 5.9. Secco-etched laser groove after the KOH etch step. Scribe damage indicated in Figure 5.6 has completely disappeared.



The dark band in Figure 5.8 is more than 400 µm wide and its observation is reported for the first time in this thesis. Its explanation may hold the key to the unusually good output of laser-grooved solar cells and provide a new gettering mechanism for laser-processed devices. The following sections will attempt to explain the dark bands in terms of thermal wave generation during the laser scribing process, an effect which has, until now, been overlooked in pulsed-laser processing of Si. The study of thermal wave phenomena has been of great concern in photoacoustic (PA) and electroacoustic characterisation of materials (Rosencwaig, 1980). Thermal waves are the main source of the acoustic signal in these techniques. More recently, PA techniques have been applied to monitoring material removal in laser drilling processes (Miyazaki and Tanaka, 1991). However, the technique was not attempted Groove depth is a major concern in laser-grooved solar cells. Often, on Si. destructive techniques like cleaving and imaging the grooves for depth measurement have to be done. PA methods promise in situ and non-destructive evaluation of groove depth during laser scribing. They also allow the investigation of thermal dissipation in solar cells (Flaisher et al, 1989). This may have important applications in evaluating device performance for concentrator cells. The exploitation of the vast potential offered by PA techniques justifies a deeper investigation of the source of the PA signal: thermal waves.

5.3.3 Thermal Waves

5.3.3.1 Theory

Repeated laser-pulsing of Si periodically heats it up resulting in the generation of thermal waves (Favro et al, 1987, pp. 70-71). The flow of heat in Si is diffusive in nature and is thus governed by a diffusion equation:

$$\nabla \cdot [\kappa \nabla T(\mathbf{r}, t)] - \rho c(\partial T(\mathbf{r}, t) / \partial t) = -f(\mathbf{r}, t)$$
[5.1]

where ρ is the density of Si, c its specific heat and κ its thermal conductivity. The term 'thermal wave' refers to the time-dependent solutions T(r,t) to the equation 5.1 with a periodic heat source f(r,t):

$$\mathbf{f}(\mathbf{r},\mathbf{t}) = \mathbf{f}(\mathbf{r})\mathbf{e}^{-i\omega \mathbf{t}}$$
 [5.2]

with $T(\mathbf{r},t)$ taking a similar form. Equation 5.1 then takes the form:

$$\nabla \cdot [\kappa \nabla T(\mathbf{r})] + \kappa q^2 T(\mathbf{r}) = -\mathbf{f}(\mathbf{r})$$
[5.3]

where a complex thermal wave number q has been defined as:

$$q = (1+i)(\omega \rho c/2\kappa)^{\frac{1}{2}}$$
 [5.4]

The diffusion length for these waves can then be expressed as:

$$\mu_{\rm L} = (2\kappa/\omega\rho c)^{\frac{1}{2}}$$
 [5.5]

where μ_L will be referred to as the thermal diffusion length. Note the $f^{\frac{1}{2}}$ dependence of μ_L . ($f=\omega/2\pi$).

A solution to equation 5.3 can be determined via a Green's function technique which yields

$$T(\mathbf{r}) = (iCe^{iqz})/\kappa q \qquad [5.6]$$

for a uniform surface source (ibid., p. 78-79). In this equation, z is the distance from the Si surface and C specifies the source strength per unit area (laser beam power density). From equations 5.4 and 5.5, $q=(1+i)/\mu_L$. Substituting this in equation 5.6, it can be seen that T(r) is directly proportional to e^{-z/μ_L} . The amplitude of the wave, which is proportional to the real part of T(r), then drops by $\approx 1/500$ in one thermal wavelength ($z=2\pi\mu_{\rm I}$).

Stearns and Kino (1987, p. 209) have identified three mechanisms for the generation of heat during laser probing of Si: 1) de-excitation of electrons and holes to conduction or valence band edges, 2) bulk recombination and 3) surface recombination. The resulting PA signal for a near-bandgap Nd:YAG laser is believed to originate from free carrier relaxation. No reports have yet been published on similar processes for laser ablation of Si. For the laser scribing process described in this thesis, heat generation is described in terms of optical absorption and its temperature dependent nature (Wenham, 1986, p. 45). In the next section, the large temperature gradients experienced by the Si substrate during such laser scribing will be shown to generate thermal wave effects previously not taken into consideration.

5.3.3.2 Experimental Evidence for Thermal Waves During Laser Scribing

Figure 5.10 A to D shows how the dark band feature observed in Figure 5.8 changes with pulse frequency. A table speed setting of 1 was used for all scribes. The laser power was not adjusted and resulted in increasing peak powers for decreasing pulse frequencies. For a constant table speed, the increase in pulse peak power is compensated by less frequent pulsing ensuring that roughly the same energy is delivered for the same scribe length. It can be seen from Figure 5.10 that the widths of the dark bands depend inversely on the pulse frequency. Table 5.2 summarises the scribing conditions for each scribe and lists the calculated thermal diffusion lengths calculated from equation 5.5 and the 'range' of the dark bands which will be defined here as half the dark band width. The dark-band ranges roughly correspond to the calculated thermal diffusion lengths except for scribes A and B which are larger than expected. A scatter plot of the data obtained in Table 5.2 plus an additional scribe at 16 kHz yielding a dark band range of 44 microns is shown in Figure 5.11. The solid curve is equation 5.5. The agreement between the dark band range and the theoretical μ_L at higher frequencies is remarkable since this implies that

Figure 5.10. SEI of laser scribes taken at pulse frequencies of A) 1 kHz, B) 2 kHz, C) 4 kHz and D) 8 kHz. Table speed was kept constant for all scribes. Roughly the same energy is delivered for each scribe.





Figure 5.11. A scatter plot of the dark-band ranges in Table 5.2 against $f^{-\frac{1}{2}}$. The solid curve is generated by equation 5.5. The dark band ranges agree remarkably with equation 5.5 except for the low frequency pulses. The deviation may be caused by ablation artifacts indicated in Figure 5.10. This agreement implies that the dark bands are generated by thermal waves.

Table 5.2. Scribing conditions for the scribes presented in Figure 5.10 including an additional scribe (E) done at 16 kHz. The dark-band range is determined by measuring the dark-band widths and dividing by two. μ_L is calculated from equation 5.5.

| Sample | Speed | f | μ_{L} | Dark-band Range |
|--------|---------|-------|-----------|-----------------|
| | Setting | (kHz) | (µm) | (µm) |
| Α | 1 | 1 | 171 | 265 |
| В | 1 | 2 | 121 | 163 |
| С | 1 | 4 | 86 | 90 |
| D | 1 | 8 | 61 | 66 |
| E | 1 | 16 | 43 | 44 |

the dark bands are generated by thermal waves! For smaller frequencies, deviation from the μ_L curve increases due probably to differences in pulse overlap (G factor) or some unknown interaction between the ablation process and the propagation of thermal waves.

Differences due to varying G can be exploited easily by varying the table speed while keeping the pulse frequency and average peak power constant. Figures 5.12A to D show the effect of increasing table speed on the dark bands for f=8 kHz. Table speed settings are indicated for each scribe. It is observed that a decrease in G results in a larger dark-band range. This result is probably due to scattering of thermal waves. As the amount of overlap decreases, less damage is encountered by the laser pulse resulting in reduced thermal wave scattering. The thermal wave is then expected to diffuse more into the Si material and is manifested by an increase in the dark-band range. The damage accompanying the generation of thermal waves may also be producing as yet, unknown interactions with the thermal wave. This area needs further study.
Figure 5.12. The dependence of the widths of the dark bands observed in Figure 5.10 as a function of table speed (Laser 1): A) setting=2, B) setting=3, C) setting=4 and D) setting=5. Typical table speeds for Laser 2 are given in Table 5.1 and are expected to be roughly the same for Laser 1. The pulse frequency (8 kHz) and peak power were held constant.



5.3.3.3 Thermal Wave Induced Damage

There have been very few reports on the effects of thermal wave probing on semiconductors. Rosencwaig (1987, p. 122) has observed a transient surface annealing effect in the PA probing of Si wafers. This effect can extend 50 to 100 μ m from the illuminated point. This range is an order of magnitude larger than the expected thermal diffusion lengths for their modulated PA set-up. Stearns and Kino (1985) have concluded that electronic strain is the main source of PA signals using near bandgap laser radiation. Flaisher (1990) has reported anomalous PA effects which can be related to thermal surface deformations resulting from pulsed-laser probing. All of these effects were, however, for non-destructive laser probing of Si. To the author's knowledge, no study on thermal wave effects during pulsed laser ablation of semiconductors has been reported so far. Miyazaki and Tanaka (1991) applied PA techniques in monitoring laser drilling of materials but did not consider drilling Si. In this section, an attempt is made to identify possible damage caused by thermal waves in laser scribing of Si.

Scribe damage has already been described in section 5.3.1 (Figure 5.6). Figure 5.13 A is an optical micrograph of the same scribed region showing better contrast between the almost S-pit-free regions and the dense S-pit region. The unusually dense S-pits $\approx 100 \,\mu\text{m}$ away from the scribe, were initially thought to arise from etching solution contamination (section 4.3.1.2). However, etching of scribes with a fresh solution still exposes the same features (Figure 5.13B). This rules out solution contamination.

Figure 5.13B was obtained with the light source slightly off the perpendicular to the sample surface. The S-pit-free regions do not scatter light and appear dark. Regions with high S-pit densities scatter the incident light generating a hazy appearance of the wafer surface. A well-known cause for haze-generation is the presence of precipitates formed during oxidation (section 5.2). The oxidation furnace was then checked and discovered not to have been cleaned properly prior to oxidation of the wafer samples in Figures 5.6 and 5.13. The S-pits which generate haze on the

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Figure 5.13. A) Optical micrograph of a Secco-etched laser grooved wafer shown in Figure 5.6 showing the relatively uncontaminated region $\approx 100 \ \mu m$ from the groove. This artifact may be due to thermal wave effects during scribing. B) Similarly etched scribes showing table speed (top 3 pairs) and frequency (top pair and bottom 3 scribes) dependence of the gettered region. Scribing conditions are given in Table 5.3.





| Scribe Position from the top | f (kHz) | Table Speed Setting |
|---------------------------------|---------|---------------------|
| 1 and 2 | 8 | 1 |
| 3 and 4 | 8 | 3 |
| 5 and 6 | 8 | 5 |
| 7 | 0 5 | 5 |
| 8 | 0 2 | 5 |
| 9 | 4 | 1 |
| 10 | 2 | 1 |
| 11 | 1 | 1 |

 Table 5.3.
 Scribing conditions for the Secco-etched scribes in Figure 5 13B.

wafers are then a result of furnace contamination during oxidation

Having identified the S-pits as arising from precipitates from furnace contamination, the S-pit-free region extending $\approx 100 \ \mu m$ away from the scribed region can then be attributed to some form of gettering activity during the scribing process. The extent of such gettering activity displays similar table speed and frequency dependence as the SEI dark bands described in the previous section. Table 5.3 summarises the scribing conditions for the scribes presented in Figure 5.13B. The top three pairs show the increasing dark-band range effect due to decreasing *G* and the top pair and three bottom scribes display the inverse proportion to $f^{\frac{1}{2}}$. One obvious conclusion is that gettering occurs via thermal wave effects. The scribes done at 500 and 200 Hz displayed smaller gettered widths as a result of the pulses being separated too far apart (*G*<1) for thermal wave generation. This implies that the observed gettering effect reaches a maximum at a certain $G \ge 1$.

Gettering normally requires defect generation followed by high temperature processing during which impurities can diffuse to the gettering sites and be neutralised (section 3 5.1). For the thermal wave gettering effect observed above, the only clear damage exposed by preferential defect etching is that along the scribe itself (Figure 5.6) More refined characterisation techniques are required for the revelation of point defects and micro-precipitates which are not delineated by chemical etching procedures (section 4.3.1). Furthermore, hardly any temperature rise is expected 50 μ m away from the scribed region (section 5.3.2). It is then unclear how the precipitates can diffuse to the gettering sites A possible gettering scenario for the surface precipitates mentioned above is that lattice deformations due to thermal wave propagation expel the precipitates from the Si surface into the oxide Another possibility is that the lattice deformations lead to the breakdown of these precipitates

The remaining part of this section is an attempt to uncover thermal-wave induced defects The influence of thermal waves can potentially extend more than 100 μ m for cells scribed using the usual pulse frequency of 6 kHz (Appendix A). The groove-etching step produces a groove 20 to 30 μ m wide leaving most of the thermal-wave affected region. Defects arising from thermal waves then become significant considering that they may act as recombination centres or contribute to gettering mechanisms in succeeding cell processing steps It has already been suggested that the induced defects may be too small to be exposed via chemical defect etching techniques However, if these defects are electrically active, EBIC can be used to image them indirectly. This can be done by scribing a solar cell and evaluating recombination centres arising from the scribed region.

Figure 5 14A shows a laser scribe (8 kHz and table speed setting of 2) adjacent to a metal finger on a planar solar cell. The particular EBIC set-up (Figure 4.18A) plus the finished solar cell structure may have affected the generation of the dark-band feature which appears very faintly in this micrograph. The thinned oxide for this cell (110 nm) may have contributed towards this effect as well At any rate, the presence of the dark band is only a manifestation of thermal wave effects and its faint appearance or disappearance during processing is not an indication that thermal wave effects have not occurred. Thermal wave effects are dictated by the laser beam power density, frequency and scribe speed (sections 5 3 3 1 and 5 3.3.2)

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Figure 5.14. EBIC depth profile of scribe done at 8 kHz and a table speed setting of 2: A) SEI of scribe, B) EBIC at E=10 keV, C) EBIC at E=20 keV and D) EBIC at E=30 keV. The metal finger at the right hand side of the micrographs is used as a reference in generating the EBIC image of the scribe.



An EBIC depth profile of the scribe in Figure 5.14 A was made by using an electron probe energy E = 10, 20 and 30 keV (Figures 5 14 B, C and D) The metal finger to the right of the scribe was used as a reference point for generating the EBIC contrast EBIC linescans provide a means of evaluating the extent of the electrical activity of the scribe and allows comparison between Figures 5.14 B, C and D At a probing depth of 1 5 μ m (E=10 keV) recombination activity (dark regions) around the scribe is very strong with the width of the dark region roughly corresponding to the width of the dark band in Figure 5 14A A linescan across the scribe indicates a narrower region (120 μ m width) where no EBIC signal is recorded. The decay in EBIC towards this region resembles an inverted exponential curve. For deeper probe depths (5 μ m, E=20 keV and 10 μ m, E=30 keV), the width of the region where there is no EBIC signal is drastically reduced to 32 and 25 μ m respectively and the tail of the inverted exponential curve becomes sharper

To interpret the EBIC contrast generated by the laser scribe, a model for grain boundary EBIC (section 4.6.2) developed by Dimitriadis (1985) can be used as a first order approximation The depth of the scribe in Figure 5 14 (\approx 70 µm) is much larger than the probe depths (1 to 10 μ m) used and the assumption that the grain boundary is a surface with a finite recombination velocity S_R is well in agreement for the scribed region Plotting I_N as a function of x in equation 4.18 then yields the equivalent of an EBIC linescan across the scribe. Figure 5.15 shows calculated EBIC linescans (shown normalised) for the probe depths used in Figure 5.14. The diffusion length Lwas assumed to be 100 μm and $S_R{=}80{,}000$ cm s^{-1} $\,$ It can be seen that the region where no EBIC signal is generated expands dramatically as the probe depth increases The opposite is observed for the scribes in Figure 5.14. This effect can be explained by the presence of recombination at the Si-oxide interface affected by thermal waves As the electron beam penetrates deeper into the material, more of the generated carriers are unaffected by the surface recombination centres and the recombination centres along the scribe dominate the EBIC image For E=30 keV, the region where no EBIC current is recorded roughly corresponds to the width of the scribe.



Figure 5.15. Calculated EBIC current at accelerating voltages used in Figure 5.14 as a function of distance from a surface with $S_R = 80,000$ cm/s.

Examination of the same scribe along a cleaved edge (Figures 5.16 A and B) reveals no significant effects on the p-n junction due to the scribe The junction deformation near the opening of the scribe is due to dopant redistribution caused by laser ablation and is highly localised. The large recombination velocity of the cleaved surface allows the location of the actual physical junction in the solar cell

EBIC probing of scribes done at different table speeds provides further argument for thermal wave generated surface recombination corresponding to the dark bands discussed in previous sections. Figure 5.17 shows EBIC linescans generated by scribes made at 8 kHz and table speed settings of 1, 2, 3 and 4 for Figures 5.17 A, B, C and D respectively. A metal finger on the left-hand-side was used as a reference for generating the EBIC contrast in a similar fashion to Figure 5 14 Faster table speeds should result in less scribe damage and, thus, lower S_R The extent of the inverted tail in the EBIC linescan should, therefore, decrease (see Figure 6 16) In Figure 5 17, the extent of the inverted tail increases as has been observed with SEI dark-band widths. Moreover, the shape of the inverted exponential tail suggests the superposition of recombination centres other than the ones along the scribe. The extent of the superimposed recombination feature corresponds roughly to the previously mentioned dark-band widths.

EBIC imaging of the scribes has shown that substantial surface recombination activity can be generated via thermal waves. Flaisher (1990) has reported anomalous PA behaviour that may be due to thermal surface deformations. It is probable that similar deformations occur in the thermal wave affected regions via the generation of point defects or microprecipitates It is still not clear whether similar defects in the bulk exist as the resolution of the EBIC technique is insufficient to resolve such defects. Electrically active hole traps in the bulk have been identified via Deep Level Transient Spectroscopy (DLTS) in laser annealed Si (Hartiti et al., 1989 and references therein). Hayafuji et al. (1981) has observed the formation of thermally stable pseudo-swirl defects generated by low power laser irradiation of Si Bulk defects, if they are present, may take a similar form to these pseudo-swirl defects Figure 5.16. A) SEI of a scribed solar cell along a cleaved edge perpendicular to the scribe The scribe depth is $\approx 77 \ \mu m$. B) EBIC image of A). The distorted junction image near the scribe is due to topographic contrast (section 4.6 2)





Figure 5.17. EBIC images for an 8 kHz scribe done at different table speed settings (Table 5.1): A) SEI, B) speed setting=1, C) speed setting=3 and D) speed setting=5



This will be very fortunate as such defects have been reported to act as effective gettering sites (ibid.).

5.3.4 Characteristics of the Final Groove

Figure 5.18 shows a laser groove in the cross section of an experimental lasergrooved solar cell with the corresponding EBIC signal superimposed The bright regions surrounding the groove and very close to the cell's top surface represent the EBIC image The surface of the cleaved edge has been ground with 600 and 1200 grit SiC paper before polishing with 1 μ m Al₂O₃ powder Such a surface is expected to yield a high surface recombination velocity and the bright regions should correspond very closely to where a junction has been formed via P diffusion into the area. The region between the groove and the bright region represents the diffusion depth of P (\approx 5 μ m) and is consistent with diffusion depths made on planar wafers (Chong, 1989, pp. 113-117). The top surface junction depth is likewise within the expected range of 1 to 2 μ m (ibid., pp. 107-114).

The branching of the bright regions from the groove suggests that P has diffused preferentially along certain directions Such preferential diffusion have been known to occur in grain boundaries (Holloway, 1982) and dislocations (Shimura, 1989, p 343). To determine the defects involved for the preferential diffusion of P in the grooves, a similar planar experimental laser-grooved solar cell was stripped of metal contacts, the oxide layer etched off and subjected to a 5-minute Secco-etch. Figure 5.19 shows the groove region of the etched solar cell. Dislocations are revealed up to 50 μ m from the groove with the area in between the grooves remaining dislocation-free. There is a definite correlation then between the groove and the dislocations surrounding it. In section 5.2, dislocations were not observed in unprocessed wafers. This discounts the possibility that dislocations on the substrate were gettered toward the grooves during cell processing. Etching of the grooves at different stages of processing suggests that they originate from the heavy P diffusion step and are enhanced by the subsequent sintering step.

Figure 5.18. EBIC image of a finished laser groove superimposed on its SEI The roughly polished cleaved surface has a high recombination velocity. The bright regions then correspond very closely to where P has diffused. For planar surfaces, a similar diffusion and drive-in process allows P to penetrate 5 μ m into the Si This micrograph shows that with laser grooves, P diffuses deeper than expected (up to 30 μ m) and in certain directions only. This implies the presence of defects along which P diffuses preferentially.



Figure 5.19. Dislocations decorating the groove region of an experimental lasergrooved solar cell. Dislocations are likewise present at the bottom and sides of the groove but are not visible in this micrograph.



Figure 5.20 shows how the dislocations arise in the pilot line laser-grooved solar cell processing sequence (Appendix A). A wafer was pulled out during processing after the KOH groove etch, after groove diffusion and after the sintering step. Oxides were then stripped prior to a Secco etch. All the wafers were textured. After the KOH etch step, no dislocations or S-pits are observable along the surface and grooves (Figure 5.20A). This is consistent with results already mentioned in section 5.2 (Figure 5.9). After heavy P diffusion into the grooves (3 hours at 940°C). some dislocations begin to appear (only one dislocation etch pit is visible in Figure The observed dislocation etch pits extend up to 15 µm away from the 5.20B). groove. For a <100> oriented wafer, misfit dislocation networks (section 2.2.2) are confined to the diffused region (Fairfield and Schwuttke, 1968). Even with the assumption of preferential P diffusion, the dislocations are too far to be due to P diffusion and is, hence, attributed to diffusion-induced damage resulting from an interaction between P diffusion and residual (thermal wave-induced) laser damage. An alternative source is the stress exerted by a large concentration of P at corners in the groove. This process is similar to dislocation generation in U grooves reported by Tamaki et al. (1988). However, in their case, stress was applied via oxidation of the groove. After sintering at 980°C for 14 hours, the density of dislocations increase dramatically (Figure 5.20C) and extend up to 30 µm away from the groove. This is roughly the same distance P diffuses preferentially into the grooves (Figure 5.18). It may be assumed then that, after the dislocations were generated, P diffused along them yielding roughly the same P-diffusion depth and dislocation generation depth. A closer look down the groove (Figure 5.20 D) reveals both dislocation etch pits and Spits along the sides and at the bottom of the groove. The S-pits probably come from P clustering during thermal processing of the heavily-doped groove.

Figures 5.21A and B compares dislocation densities in heavily grooved areas of the wafer. Figure 5.21A is an area near the metal contact pad which was scribed heavily (parallel grooves) in order to have a thicker metallisation. Figure 5.21B is an area which had parallel grooves. Roughly the same dislocation densities $(2 \times 10^6 \text{ cm}^{-2})$

Figure 5.20. Secco-etched grooves on pilot line wafers in the process of being fabricated into solar cells (45 cm²): A) after the KOH etch step, B) after groove diffusion, C) after sintering and D) close up view of the groove bottom in C).



Figure 5.21. Dislocations in different regions of the laser grooved wafer after the sintering step: A) parallel grooves near the metal contact pad, B) at the intersection of two sets of parallel grooves at the metal contact pad and C) rear of the wafer.



are observed for these regions. A similar density is observed at the bottom of the groove in Figure 5.20 D including the region 10 μ m from its sides. Figure 5.21C shows dislocations at the rear of the cell suggesting that some of the dislocations generated from the grooves extend through to the rear of the wafer. The micrograph shown is an unusually dense concentration of etch pits. A scan of 20 frames shows a density of $\approx 10^4$ cm⁻². There is no strong evidence that these dislocations come from the Al sintered at the rear of the wafer. It is expected that most of the Al diffused layer would have been etched away by the Secco etch. A spreading resistance profile of the rear of such a cell shows that Al diffuses up to a depth of around 8 μ m (Chong, 1989, p. 42). A 5-minute Secco etch removes 8 μ m off the sample surface.

Additional information on the structure of the dislocations can be revealed by examining dislocation distribution deeper into the wafer. This can be accomplished by polishing the samples before the Secco-etch. In Figure 5.22 A, most of the groove has been polished off. It can be seen that most of the dislocations originate from the groove. Moreover, they appear to be bowed and occasionally join other dislocations. Butterfly patterns result from such an interaction. Figure 5.22 B shows a region similar to Figure 5.21 B polished very close to the bottom of the grooves. The large holes are where the grooves have crossed over each other. The dislocations present here display the same features shown in Figure 5.22 A. When the grooves are. completely polished off, most of the dislocations disappear even along the region where the scribe is expected to be. This implies that most of the dislocations are located close to the groove region. Such dislocations are useful in gettering processes as they do not interfere very much with device operation unlike dislocations which extend through the bulk of the cell. Only a few dislocation etch pits were observed with a dislocation density of 2×10^3 cm⁻² calculated for a 20-frame scan of the sample surface. This is five times lower than the dislocation density at the rear of the wafer. The inhomogenous distribution of dislocations may have affected the counting procedure resulting in this rather low value. As the dislocations reach the rear of the . cell, they may go farther apart from each other.

Figure 5.22. Dislocations at different depths in the cell: A) near the bottom of the groove and B) near the bottom of region similar to Figure 5.21.B. The large holes are where the grooves have crossed over.





Differences in etch pit shape are apparent for the experimental cell in Figure 5.19 and the pilot-line cell (Figures 5.20 to 5.22). The dislocation etch pits for the experimental cell are round and, therefore traverse the sample surface perpendicularly. Those for the pilot-line cells are elliptical or shaped like a teardrop. This difference may be due to the relative orientation of the groove to the crystal facets. The experimental cells were scribed along (110) planes while the pilot-line cells are scribed 45 from these planes. The main reason for this off-axis scribing is to enhance the mechanical strength of the cell. It is well-known that (110) planes are the weakest in . a Si crystal and are used as cleaving planes in microelectronics dicing procedures.

Another difference between dislocations generated in the experimental and pilot-line cell is the distance of the pits from the groove. Figure 5.19 shows the dislocations extending 40 to 50 μ m from the original groove (without Secco etching). The pilot-line cells have dislocations extending up to only 30 μ m from the original groove. This difference may be due to the difference in the laser pulse frequency used for the cells: 4 kHz for Figure 5.18 and 5.19 and 10 kHz for pilot line wafers (Appendix A). This will result in longer thermal diffusion lengths for 4 kHz ($\approx 60\%$ longer). Table speed and pulse peak powers used may have affected the extent of the . dislocations as well, but were not recorded for the cells in Figures 5.18 and 5.19 making comparisons difficult.

The preceding discussions have so far shown that the shape of the EBIC contrast in Figure 5.18 can be explained via preferential diffusion of P along the dislocations observed in Figures 5.20 to 5.22. The observed P diffusion depth of up to 30 μ m (Figure 5.18) is consistent with the 50 μ m extent of some dislocations (Figure 5.19). It is estimated that around 50 dislocations will intersect the P-diffused groove region shown in Figure 5.18. The superposition of P diffusion along them can generate the EBIC junction shape. However, the threadlike features at the fringes of the EBIC image most probably come from other defects. This provides additional evidence for the existence of thermal-wave-induced defects which enhance P diffusion. Self-interstitials, which promote P diffusion, are the most likely defects

generated in this case. Hayafuji et al. (1981) has uncovered the generation pseudoswirl defects using low-intensity laser irradiation of Si. Thermal wave induced defects may be similar to these defects.

5.3.5 Gettering Model for the Laser-Grooved Solar Cell

Figure 5.23 summarises the results of groove characterisation from the previous sections. Starting with an oxidised, lightly P-diffused textured or planar wafer, the laser scribing step introduces damage via laser ablation and thermal wave induced defects. During the scribing process, oxidation-induced precipitates may be gettered via thermal waves. The KOH etch step removes most of the damage caused by laser ablation and defines the shape of the final groove. Thermal wave induced defects may still persist in the region surrounding the groove. When P is diffused heavily into the grooves, it generates stress in the groove resulting in the dislocations originating from the groove and terminating at the cell surface or another dislocation (section 2.1.2). At the same time, P starts diffusing preferentially along these dislocations and where thermal wave induced defects are present. The sintering step then results in further groove stress and dislocations start to multiply. P is driven in farther into the substrate and along defects extending the collecting junction of the cell. The gettering action of dislocations start to take effect and is complemented by P gettering. P diffusion along the defects also ensure their passivation. With the Al at the rear, the sintering step is then the most effective gettering step in the lasergrooved solar cell processing sequence with the simultaneous action of three gettering mechanisms (P, Al and laser damage gettering) acting on the entire cell volume.

5.4 Summary

This chapter has shown that the main defect generating process in the lasergrooved solar cell sequence is the laser grooving procedure. Oxidation-induced haze resulting from furnace contamination has been identified and minimised via TCA precleaning and oxidation procedures. Thermal wave effects during the laser scribing

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Figure 5.23. A summary of groove processing and gettering in the laser-grooved solar cell processing sequence. The sintering step with Al at the rear of the wafer is the most effective gettering step in this sequence combining P, Al and groove damage gettering.

of Si have been uncovered and shown to play a significant role in the final characteristics of the laser groove. Characterisation of the finished grooves have exposed dislocations arising from stress generated during heavy P diffusion and drivein. With this work, gettering mechanisms in laser-grooved cells have been clarified. The sintering step is then identified as the most effective gettering step in the processing sequence. Potential applications for thermal wave effects in the fabrication and characterisation of solar cells and other devices still remain to be explored.

CHAPTER 6

CAST POLYCRYSTALLINE SILICON

6.1 Introduction

Among the polycrystalline Si materials obtained by our laboratory, PESC's fabricated on cast polycrystalline Si (Narayanan, 1989, p. 36) have yielded the best results. Optimisation of P pre-treatment and Al gettering made it possible to attain efficiencies of over 17% on Osaka Titanium substrates. It is believed that differences in substrate quality accounted for the differences in cell performance in the array of materials tested (Narayanan, 1989, pp. 56-61). This conclusion was reached with the observation that the optimal processing conditions for high quality substrates are different to that for low quality substrates. Initial investigations by Yun (1992) on the effects of different grain boundary types on cell output characteristics have, so far, proven inconclusive.

This chapter intends to systematically characterise intrinsic defects in various cast polycrystalline Si materials tested in our laboratory. For such large-grain material, intragrain defects start to influence cell characteristics. The defects to be considered are interstitial oxygen O_i , substitutional carbon C_s , dislocations, grain boundaries and inclusions. Spreadsheet analysis of FTIR spectra (section 4.2.1.1 and Appendix B) was developed to evaluate C_s and O_i concentrations (denoted by $[C_s]$ and $[O_i]$ respectively) in the samples. Annealing experiments show no significant precipitation of O_i occurs for normal processing thermal treatments. An IR microscope (section 4.3.2.2) was developed for evaluating inclusion density. Its image processing capabilities also allows the analysis of dislocation distribution in

Secco-etched samples. Finally, EBIC techniques (section 4.6.2) were developed to evaluate recombination activity arising from dislocations, inclusions and grain boundaries. EBIC contrast due to intragrain dislocations, High Dislocation Density Areas (HDDA's) and inclusions has not been observed so far. Only grain boundaries and dislocations along them seem to be electrically active. EBIC profiles of grain boundaries present evidence for their partial passivation via P diffusion. These profiles are analysed using a model developed by Dimitriadis (1985). EBIC linescans across grain boundaries can also be fitted with this model enabling the evaluation of grain boundary recombination velocity and intragrain diffusion length.

With the development of appropriate characterisation equipment and techniques, an attempt to correlate defect densities with solar cell output parameters \cdot (section 4.6.1) is made. Preliminary results on planar cells fabricated using lasergrooved solar cell processing indicate that low interstitial oxygen concentrations result in higher short circuit current density J_{sc} and cell efficiency η . This is consistent with reported results (section 6.4.3). Dislocation densities show an inverse correlation to $[O_i]$ and, hence, result in higher J_{sc} and η for higher densities. It will be shown that this correlation is not real and that the dislocations are actually neutral as the EBIC studies suggest. $[O_i]$ is then identified as the dominant defect. Correlations between cell output and other defects (C_s and inclusions) can be revealed by using substrates with the same $[O_i]$ but varying $[C_s]$ or inclusion densities.

6.2 Defects Considered in Cast Polycrystalline Si Materials

Table 6.1 gives a summary of the various manufacturers of cast polycrystalline Si indicating how many batches of samples were received from each and sample designations for the work to be carried out in this chapter. Each batch presumably came from different ingots. However, it is suspected that O1 and O2 came from the same batch even though their defect densities varied considerably (see Table 6.2). The rest of this section describes how defects were identified and quantified for each sample to enable comparison between them.

| Manufacturer | Date of receipt | Resistivity | Sample |
|-----------------|--|-------------|-------------|
| | and the second | (Ω cm) | Designation |
| Bayer | 1/92 | 1 | B 1 |
| | 1/92 | 1 | B2 |
| | - (| | |
| Crystal Systems | 2/90 | 1 | С |
| Eurosolare | 10/90 | 1 | I1 |
| | 7/91 | 2 | I2 |
| | | | |
| Osaka | 1988 | 1 | O 1 |
| | 1988 | 1 | O2 |
| | 3/91 | 1 | O3 |
| | 1/92 | 1 | O4 |
| | 5/92 | 1 | 05 |
| | | | |
| Solarex | 11/89 | 0.7 | S 1 |
| | 9/91 | 0.7 | S2 |
| | 9/91 | 0.7 | S 3 |
| XX 7 4 | 1005 | | |
| Wacker | 1985 | 0.5 - 1 | WI |
| | 1985 | 0.5 - 1 | W2 |

Table 6.1. Cast Polycrystalline Substrates received from different manufacturers.

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6.2.1 Carbon and Oxygen

Oxygen precipitation (section 2.2.2) is the main concern for monitoring O_i in CZ-Si. Oxygen precipitates can act as recombination centres (section 3.3.4) or as
gettering sites (section 3.5.1) in the bulk of the Si substrate. For solar cell operation, the gettering action of these precipitates is insignificant compared to the hindrance they cause to carrier generation and collection. For polycrystalline Si, oxygen segregation at dislocations (Sumino, 1986) and grain boundaries (Pizzini et al., 1989) can occur. Pizzini et al. (1989) has reported a correlation between trap states in the grain boundary with oxygen segregation. This implies that O segregation contributes to recombination activity in grain boundaries. The main role of C is to trigger O precipitation (Leroueille, 1981). C also precipitates into SiC in the bulk of the wafer and is the main source for inclusions observed in polycrystalline Si material (section 6.2.4). C also segregates at dislocations (Seiter, 1987) and grain boundaries (Pizzini et al., 1989) and can contribute to recombination processes.

The evaluation of O precipitation normally requires measuring the interstitial oxygen concentration $[O_i]$ in a substrate before and after thermal processing (ASTM F1239-89). The difference between the two values then represent how much oxygen has precipitated during processing. This can also be applied to C to determine any interaction with O precipitation. The procedure for Excel spreadsheet IR spectra analysis for determining $[O_i]$ and $[C_s]$ has been previously explained in section 4.2.1.1 with specific spreadsheet structure described in Appendix B.

Cast polycrystalline Si is well-known to contain substantial concentrations of O_i and C_s due to contamination from materials used during growth processes (section 2.2.1.2). Novel casting techniques like electromagnetic casting (Kaneko et al., 1990) have been aimed at reducing such contamination by replacing the casting mould with an electromagnetic field. Table 6.2 shows a summary of $[C_s]$ and $[O_i]$ measured in the various substrates available in our laboratory. Table 6.2 indicates a rather wide range of O_i and C_s concentrations with no particular correlations being established between them. O4 is an electromagnetically cast substrate but had high C_s and O_i concentrations due to difficulties experienced during growth (Kaneko, 1992). The high concentration of Si_3N_4 inclusions attested to this. It is of interest to note that O1 had C_s and O_i concentrations below detection limits for the method and is

| SAMPLE | Inclusion Density ^a | [O _i] | [C _s] |
|-----------------|--------------------------------------|-------------------|-------------------|
| | (10^{3} cm^{-3}) | (ppma) | (ppma) |
| B1 | 2.4 | 3.0 | 9.7 |
| B2 | 1.1 | 2.9 | 10 |
| | | | |
| С | 1.2 | 6.8 | 9.1 |
| | | | |
| I1 | 1.7 | 9.8 | 13.1 |
| I2 | 0.7 | 4.1 | 14.7 |
| | | | |
| O 1 | <0.3 | <0.5 | <0.5 |
| O2 | 20 | 10.7 | 0.9 |
| O3 | 23 | 2.5 | 11 |
| O4 ^b | 15 (Si ₃ N ₄) | 23.8 | 1.5 |
| | 20 (SiC) | | |
| 05 | <0.4 | 3.3 | 11.6 |
| | | | |
| S 1 | 3.2 | 14.8 | 6.2 |
| S2 | 15.4 | 3.2 | _ c |
| | | | |
| W 1 | 2.0 | 6.9 | _ d |
| W2 | 26 | 1.1 | 10.4 |

 Table 6.2.
 Summary of defects for polycrystalline substrates available.

^a For inclusions having a diameter > 1.3 μ m.

^b Electromagnetically cast.

^c Wafer broken.

^d C peak obscured by free carrier absorption.

practically inclusion-free. The best solar cell result obtained by Narayanan (1989) was obtained on a similar substrate.

To check oxygen precipitation during cell processing, samples C, O1, O2, S1, S2, W1 and W2 were annealed at 900°C for 13 hours under a nitrogen ambient. $[O_i]$ and $[C_s]$ were remeasured after removal of the oxide layer that formed on the surface. No significant changes were observed in $[O_i]$ and $[C_s]$. Subsequent annealing at 1000°C for 9 hours likewise did not result in any change in the $[O_i]$ and $[C_s]$ of the samples. It can then be assumed that no significant precipitation occurred during the thermal treatments. This result is consistent with results obtained by Shimura and Tsuya (1982) for CZ-Si annealed at 1000°C for 16 hours under a dry O₂ ambient. They concluded that O precipitation does not or rarely occurs for $[O_i]$ less than a critical concentration of \approx 14 ppma. At such temperatures, Seiter (1987) has reported reductions in $[O_i]$ for cast polycrystalline Si with $[C_s]$ and $[O_i]$ very close to the solubility limit. He also observed that incoherent grain boundaries act as a sink for O_i in such samples. These results in the prevention of precipitate formation in the vicinity of incoherent grain boundaries.

At very high annealing temperatures (e. g., $T = 1250^{\circ}C$ under dry nitrogen ambient) O precipitates are dissolved resulting in an increase in $[O_i]$ (Pivac, 1990). As-received polycrystalline Si samples with $[O_i]$ initially below the detection limit of room temperature IR spectroscopy have been found to contain significant amounts of $[O_i]$ after such an annealing step. A similar heat treatment has been used by Jastrzebski et al. (1982) to determine total oxygen concentrations in single crystal CZ-Si.

6.2.2 Dislocations

Dislocations in cast polycrystalline Si results from the release of stresses in the crystal due to thermal gradients during its growth. In the various substrates listed in Table 6.1, high dislocation density areas ($>10^7$ cm⁻²) were consistently observed. Figure 6.1A shows an optical micrograph of such an area exposed by a 5-minute

Figure 6.1. A) High dislocation density area on cast polycrystalline exposed by a Secco etch. B) SEM micrograph of a similar area.





Secco etch. The whole area appears dark and counting is impossible. Figure 6.1 B is an SEM micrograph of a similar area. The conical etch pits characteristic of dislocation etch pits (Figure 5.1) are distinct. Counting, however, still remains difficult. In order to account for these areas properly, percent area measurements of the dark regions in optical micrographs were made using statistical and image · processing techniques. The experimental set-up used for this procedure has already been described in section 4.3.2.

For a typical Secco etched wafer, 60 to 70 frames were recorded using a 100^{\times} magnification. For some samples, the pits were smaller for unknown reasons. In this case, higher magnification (200^{\times}) was required. The frames were more or less equally spaced along the wafer surface to avoid overlapping. A random starting point for frame recording ensured that a random sample (Walpole and Myers, 1989, p. 196) of the wafer surface was taken. On playback of the recorded images, proper brightness and contrast threshold levels were chosen for each frame to isolate the dark areas known to consist of dislocations. An internal procedure in the image processing software is then used to calculate the %area covered by the dark region. An average of the %area values over the total number of recorded frames for the sample would then represent how much of the sample is covered by dislocations and grain boundaries and sub-boundaries counted along in this procedure has been compensated for. Table 6.3 (section 6.4.1) compares the distribution of high dislocation density areas (HDDA's) for cast polycrystalline Si substrates made into solar cells.

The tabulated dislocation densities in Table 6.3 are for frames with little or no HDDA and where dislocations were reasonably countable. These dislocations were counted via image processing software using the same threshold settings for HDDA evaluation. To exclude small pits, grain boundaries and other features generating similar contrast to dislocation etch pits, only features with areas greater than 6 μ m² and less than 120 μ m² were considered. This restriction accounts for intragrain etch pits 3 to 12 μ m in diameter. Features were then classified and counted automatically

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and averaged over several frames (usually 40 to 50 frames). Figure 6.2A shows a frame ideal for counting. The processed image after counting is shown in Figure 6.2B. Even with a few overlapping dislocation pits, the counting remains quite accurate (error<10%). In the presence of HDDA, bright regions enclosed by dark areas are mistaken for dislocation etch pits. In frames with little HDDA, this error compensates slightly for the error in counting overlapping dislocation pits.

When correlating dislocations to cell performance, %HDDA and intragrain dislocation density are expected to give a better indication on the effects of dislocations on cell characteristics.

6.2.3 Grain Boundaries

The average grain size for all cast polycrystalline Si substrates examined in this thesis is 4 to 5 mm with some grains achieving lengths of up to 20 mm. Such large grains greatly reduce the detrimental effects of grain boundaries on cell performance (Martinuzzi, 1987) and intragrain defects start to play a significant role in cell operation. Grain boundary recombination will be investigated using EBIC techniques in section 6.3.2.

6.2.4 Inclusions

The minute non-carrier-generating volumes due to inclusions in the bulk of a solar cell usually have little bearing on solar cell operation. A more important effect is the introduction of recombination centres at the interface of the inclusion and the Si substrate (section 3.3.4). Inclusions normally come from impurity precipitation during crystal growth (section 2.2.1.2). They can also come from particle coatings of casting moulds which act as releasing agents for the ingots after casting (Ast et al, 1991). In some instances, inclusions are intentionally added to the melt to relieve stress during crystal growth (Green, 1992). This prevents microcracks from forming in the growing crystal improving its mechanical strength.

Figure 6.2. A) Optical micrograph of isolated dislocation etch pits. B) Image processed frame of the same area with dislocations classified and counted (marked A on micrograph).





It has been discussed in section 2.1 how defects tend to associate with each other. These associations can potentially result in poorer cell performance. Figure 6.3 shows inclusions A and B heavily decorated by dislocations. EDX analysis identified A as a Si_3N_4 inclusion (Figure 6.4) and B as SiC (Figure 6.5). Using a 10 keV electron beam (1.4 µm penetration depth) ensured that the Si and N peaks in Figure 6.4 and the Si and C peaks in Figure 6.5 come only from the inclusion being probed. The EDX spectra at point C only shows Si (Figure 6.6) and is then the normal wafer material. In this particular sample, Si_3N_4 powder was believed to have been used as a releasing agent from the casting mould and was probably carried into the ingot during growth.

In some instances, these particles can be transformed during crystal growth. Figure 6.7 illustrates a Si₃N₄ particle with needle-like structures emanating from it. These structures can be explained by a phase transformation of α -Si₃N₄ to β -Si₃N₄ (Green et al., 1992). Typical Si₃N₄ particles are composed mainly of α -Si₃N₄ grains. Between 1400 and 1500°C (normal Si crystal growth temperature) some of the α -Si₃N₄ grains can be dissolved and precipitated as β -Si₃N₄ (Ghaemi, 1992). The needle-like structures in Figure 6.7 are then a result of β -Si₃N₄ precipitation. This substrate was made using the electromagnetic casting technique in which the Si₃N₄ particles were used as a releasing agent from a graphite pedestal (Kaneko, 1992). Table 6.2 suggests that electromagnetic casting did not reduce [O_i] for this substrate (sample O4). [O_i] for sample O4 is even larger than for the conventionally cast substrates. This result may be linked to the unusually high Si₃N₄ inclusion density in the substrate.

In Figure 6.3 the SiC inclusion was polished together with the Si material and would not have been observed if the dislocations surrounding it were not exposed. Thus, Secco-etching is required to delineate SiC inclusions. Their different etch rate compared to Si and the dislocations decorating them make them stand out (Figure 6.8A). The same is true for Si_3N_4 inclusions (Figure 6.8B). For inclusion densities less than 10^4 cm⁻³, surface scanning of the sample is difficult to perform with very

Figure 6.3. Dislocation decorated Si_3N_4 (A) and SiC (B) inclusions. The EDX spectra for the three points A, B and C are shown in the following figures. Point C is part of the substrate.





Figure 6.4. EDX spectra for point A in Figure 6.3. Si and N are detected, indicating a Si_3N_4 inclusion.

a SiC inclusion. Figure 6.5. EDX spectra for point B in Figure 6.3. Si and C are detected, indicating



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Figure 6.6. EDX spectra for point C in Figure 6.3. Only Si is detected. This indicates that C is part of the Si substrate.

Figure 6.7. Si_3N_4 inclusion showing a hexagonal bulk structure with needle-like structures protruding from it. This structure is explained by a phase transformation of α -Si₃N₄ powder (hexagonal structure) into β -Si₃N₄ (needle-like structures) during crystal growth.



Figure 6.8. SiC (A) and Si_3N_4 (B) inclusions exposed via defect etching. Such inclusions protrude to a certain degree because of their slower etch rate and are normally decorated by dislocations.



few frames showing any inclusions. In addition to this, density measurements cannot be performed. Nevertheless, EDX analysis of the exposed inclusions is possible and elemental composition determined.

A more effective way of looking for inclusions and counting them is via an IR microscope (section 4.3.2). Samples are polished on both sides to minimise scattering and remove confusing surface features which are not related to inclusions. Densitometric measurements can be made by making a depth scan for each frame examined. Figure 6.9 shows an example of a depth scan. Figure 6.9A is an IR image focused near the top surface of a sample. The inclusions appear dark as they absorb or scatter IR radiation. Other inclusions are apparent but are out of focus indicating that they are at a different depth. Figure 6.9B is an IR image focused deeper into the Si material. Inclusions which were out of focus in Figure 6.9A have now come into focus while the focused ones are now out of focus. The inclusions shown here are 10 to 40 μ m in diameter.

Counting inclusions as they come into focus during a depth scan then yields the number of inclusions in the inspected volume. Table 6.2 summarises the average inclusion density for the materials examined in this thesis. Around 30 depth scans were made for each sample with a $100 \times$ magnification. The scans were distributed over a 2.5 cm × 2.5 cm area at the centre of the wafer. These depths scans are easily recorded on a VHS cassette for review specially in high inclusion density samples. Inclusion densities less than 10^3 cm⁻³ are hard to detect with only one inclusion turning up every 7 depth scans for a $100 \times$ magnification and a 300 µm substrate thickness. The O1 and O5 substrates are practically inclusion-free with all frames examined showing no inclusions. Smaller inclusions beyond the resolution of the microscope can, however, still exist. For a $100 \times$ magnification, a 5 µm inclusion appears as a speck ≈1 mm in diameter on a 28 cm TV monitor. Inclusions with diameters less than 1.3 µm are not resolved and, hence, not visible.

Not all of the inclusions counted in Table 6.2 are SiC particles. Some other particles present in materials produced by Bayer probably came from contamination

Figure 6.9. IR depth scan: A) IR image focused near the top surface and B) IR image focused deeper into the substrate. Features out of focus in A) become sharp in B) and vice versa.





during the growth process. Figure 6.10 shows one of these inclusions. The EDX spectra of this inclusion is shown in Figure 6.11. Probable elements fitted to the spectrum are Al, Fe and O. These elements indicate that the inclusion is some form of metal oxide. Only a few such particles were found due to their low density and they yielded effectively the same EDX spectra. The inclusion shown in Figure 6.10 is \approx 30 µm in diameter and is roughly the same size as the SiC inclusions in Figure 6.9.

6.3 EBIC Investigation of Defects

6.3.1 Dislocations and Inclusions

Evidence of recombination activity in finished solar cells attributable to dislocations are shown via EBIC in Figure 6.12. The dark spots are indicative of strong recombination in that area. The feint dark lines running through them are grain boundaries. EBIC probing of grain boundaries will be treated in greater detail in the The recombination area of the dislocation appears larger than next section. dislocation etch pits created by them. This size is dependent on the recombination velocity at the dislocations and the grain diffusion length (see next section). EBIC recombination features have not been observed for intragrain dislocations and HDDA's up to a depth of 13 µm. This observation may have some bearing on the observed correlation between dislocations, J_{sc} and η . It may be attributed to the fact that dislocations are neutral unless decorated by an impurity or precipitate (section 3.3.2). Dislocations along grain boundaries are more susceptible to impurity decoration as the grain boundary can act as an efficient sink for precipitates (Seiter, 1987). Deeper probe depths via STEM-EBIC or LBIC may be more suitable for evaluating the bulk recombination activity for such defects. (Ast et al., 1991).

It is quite possible that the recombination activity observed in Figure 6.12 is due to inclusions. Inclusions are not expected to generate any carriers and would, therefore, yield no EBIC response. The diameter of the recombination area ($\approx 15 \mu m$) is likewise consistent with inclusion diameters observed in section 6.2.4. However,

Figure 6.10. Inclusion in a Bayer substrate after a Secco etch. The fact that dislocations do not appear to decorate the inclusion is indicative that it may not be SiC. The EDX spectra in Figure 6.11 indicates it is some form of metal oxide.





Figure 6.11. EDX spectra for the inclusion in Figure 6.10. Fitting elements to the peaks yield Al, Fe and O indicating that the inclusion is some form of metal oxide.

Figure 6.12. EBIC image of dislocations along grain boundaries. The large dark spots represent strong localised recombination and are probably due to dislocations.



the density of inclusions for such a substrate is not that high to warrant the classification of all such recombination areas as due to inclusions. Moreover, EBIC scanning of cells with known high inclusion densities have not yielded contrast attributable to inclusions.

6.3.2. Grain Boundaries

P pretreatment on grain boundaries have resulted in better performance for polycrystalline Si solar cells (Narayanan et al., 1986). This improvement has been attributed to preferential diffusion of P along grain boundaries and its passivating and gettering qualities. The EBIC technique (section 4.6.2) allows the evaluation of grain boundary recombination activity resulting from P treatments like this. An EBIC depth profile of a polycrystalline laser-grooved solar cell shows increasing grain boundary recombination activity with deeper electron penetration depths (Figures 6.13B to D). Figure 6.13A shows the corresponding cell surface where the grain boundaries have been delineated by surface texturing. A textured surface generates topographic contrast (see Figure 4.20) in EBIC images. Topographic contrast generates a uniform distribution of tiny dark patches over the EBIC images in Figures 6.13B to D. The two dark spots at the top of the EBIC images is due to the shading effect of metal particles on the Si surface visible in Figure 6.13A. In Figures 6.13B to D, the induced current was maintained at a constant value by adjusting the probe current appropriately. The depth of the generated carriers for EBIC can be deduced from Figure 4.17.

At a depth of 2.8 μ m (E=15 keV), the GB features are barely visible (Figure 6.13B). EBIC linescans at E=10 keV (1.4 μ m depth) show no observable drop in induced current where the grain boundaries are expected to be. The diminishing recombination activity of the grain boundary at shallower probing depths can be explained by partial passivation of the grain boundary. As the carrier generation volume penetrates more deeply, more recombination occurs at the active parts of the grain boundary resulting in enhanced EBIC contrast. At E=15 keV, it is believed that

Figure 6.13. EBIC depth profile of grain boundaries: A) SEI of cell surface. B) EBIC image for E=15 keV. C) EBIC image for E=20 keV. D) EBIC image for E=25 keV. The increasing grain boundary recombination activity (features becoming darker and darker) can be explained by partial passivation of grain boundaries via P diffusion. At E=10 keV, grain boundary features disappear with linescans indicating no recombination arising from them. As the grain boundary is probed deeper, more of its active parts become more prominent resulting in increased recombination activity.



the edge of the generation volume is just past the edge of the passivated portion of the grain boundary. The faint grain boundary contrast illustrates this point. This depth is deeper than the cell junction by $\approx 2 \mu m$. The expected junction depth for the cell is <1 µm after drive-in diffusion and is shallower than that for single crystal cells (section 5.3.5) because of the lower processing temperatures (maximum of 880°C) used in its fabrication. Holloway (1982) calculated that for a 40 minute 900°C diffusion, the diffused depth at the grain boundary should be 6 µm deeper than the junction depth. Diffusion depth depends on the surface concentration of P, the temperature at which processing is carried out and the duration of such processing. Moreover, Faughanan et al. (1981) found that not all grain boundaries exhibit enhanced P diffusion.

Figure 6.14 shows an EBIC linescan across two boundaries indicating differences in grain boundary recombination activity. The part of the solar cell scanned is indicated by a bright horizontal line. The dark vertical lines at the sides of the image are due to shading from metal fingers. The central dark line is due to damage caused by scribing the cell (section 5.3.3.3). The magnitude of the inverted spikes in the EBIC linescan indicates how active the recombination centres are. The obvious source for the different spike magnitudes for the grain boundaries is the difference in recombination activity due to a difference in grain boundary structure (section 3.3.3). The dependence of preferential P diffusion and, hence, P passivation depth on grain boundary structure may also have contributed to the observed difference in grain boundary recombination activity. The following discussion will provide a means to interpret such recombination activity with the possibility of extracting information on grain boundary recombination velocities S_{GB} and grain diffusion lengths L.

Dimitriadis, (1985) presents an easy-to-use model for evaluating grain boundary parameters via EBIC (equation 4.18 in section 4.6.2). If I_N is plotted as a function of x, it would then yield the equivalent of an EBIC linescan across the grain boundary. Although no attempt was made to fit actual EBIC linescans with the

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Figure 6.14. EBIC linescan of grain boundaries showing different grain boundary recombination velocities. The sharp peaks indicate short diffusion lengths for the grains surrounding the boundaries. The metal fingers on the cell produce the dark strips running from top to bottom in this micrograph. The bright line across the image indicates the region where the linescan was made.



parameters S_{GB} , r_e , D and L; such a routine would have extracted important parameters for the grain boundary and the grain itself. This can be carried out easily using spreadsheet analysis (Figures 6.15 to 6.17) but would require probing several grain boundaries over the cell area to come up with a meaningful analysis for solar cells. Such a task is reserved for future investigators. Instead, a family of linescan curves will be plotted to understand the nature of the EBIC images previously generated (Figures 6.13 and 6.14).

Figure 6.15 illustrates the calculated variation in the linescans when S_{GB} is varied. The points were calculated via an Excel spreadsheet. For this analysis, D (= $kT\mu_n/q$) was calculated by assuming low injection conditions (μ_n =1350 cm² s⁻¹) on a p-type substrate, L was assumed to be 50 μ m and the electron accelerating voltage . is V_e =25 kV. It can be clearly seen that larger spikes represent higher S_{GB} consistent with the observation made in Figure 6.14. Note that the scribe damage can be approximated as a grain boundary (section 5.3.3.3) with a very high S_{GB} .

Figure 6.16 displays calculated linescans with varying L (25 to 200 µm) for a grain boundary with S_{GB} =80,000 cm s⁻¹. The rate at which EBIC decays towards the grain boundary increases for shorter L. Longer diffusion lengths mean that a generated carrier has a greater chance of reaching the recombination site at the grain boundary. Longer L will then result in wider EBIC features which appear fuzzy while shorter L will give rise to narrower but sharper EBIC features. In Figure 6.14, the sharp drop in the EBIC near the grain boundary is indicative of short diffusion lengths in the grain.

Figure 6.17 shows how probe depth affects the calculated linescan. For V_e =10 kV, the carrier generation radius (1.4 µm) is double the expected junction depth. Emitter contribution to the EBIC is taken into account by considering an effective D, where minority hole and electron mobilities have been averaged out, and an effective L slightly shorter due to the higher doping in the diffused layer. It is interesting to note that the family of curves predict increasing EBIC contrast with increasing probe depth similar to the pattern generated in Figure 6.13. It may be



Figure 6.15. Normalised EBIC response I_N calculated for grain boundaries with varying recombination velocities ($S_{GB} = 10,000$; 20,000; 40,000 and 80,000 cm s⁻¹). V_e =25 kV and L=50 μ m.


Figure 6.16. Normalised EBIC response I_N calculated for grain boundaries at varying probe depths achieved by varying electron accelerating voltages ($V_e = 10, 15, 20, 25 \text{ and } 30 \text{ kV}$). S_{GB} =100,000 cm s⁻¹ and L=50 µm.



Figure 6.17. Normalised EBIC response I_N calculated for grain boundaries with varying intragrain diffusion lengths (L = 25, 50, 100, 150 and 200 μ m). V_e =25 kV and S_{GB} =80,000 cm s⁻¹.

possible then that preferential P did not occur or that prolonged thermal treatments during oxidation, groove diffusion and Al sintering have redistributed the P diffused in the boundaries negating the desired effect. These effects need to be investigated further via EBIC or junction staining techniques on angle-polished cells.

The insufficient diffusion of P along the grooves due to the lower processing temperatures failed to produce groove characteristics similar to that for single crystal laser-grooved cells (section 5.3.4). Dislocations generated by this process are expected to have a lower densities and are obscured by bulk dislocations already present in the material.

6.4 Correlation Between Defects and Solar Cell Performance

6.4.1. Characterisation of Substrates

Table 6.3 gives a summary of the defects and their densities for each substrate before being made into a solar cell following a modified laser-grooved solar cell processing sequence. The samples were alphabetically labelled randomly to provide anonymity for the manufacturers. Substrates 10 cm \times 10 cm were cut into 5 cm wafers and then polished on both sides using chemomechanical polishing procedures (section 4.3.1.1). After removing residual oxides from the wafers, FTIR spectra were acquired for each to evaluate $[O_i]$ and $[C_s]$. Inclusion density measurements were then made by depth scanning with the IR microscope. At this stage, the samples could have been defect-etched, evaluated for dislocation density and HDDA and then repolished for cell fabrication. To save time from the lengthy development of an appropriate density measurement procedure, a wafer cut from the same 10cm \times 10cm substrate was etched and evaluated for dislocation density instead. The counting procedures for dislocations and inclusions have been elaborated on in sections 6.2.2 and 6.2.4.

| SAMPLE | HDDA (%area) | DD (10^4 cm^{-2}) | Inclusion Density ^a (10^3 cm^{-3}) | [O _i] (ppma) | [C _s] |
|------------|-----------------|-----------------------------|---|-----------------------------|-------------------|
| | (/ =====) | | () | (FF) | |
| A 1 | 5.1 | 12 | 2.4 | 3.0 | 9.7 |
| A2 | 6.3 | 46 | 1.1 | 2.9 | 10 |
| В | 5.4 | 8 | 1.3 | 5.3 | 13 |
| C1 | 7.0 | 37 | 23 | 2.6 | 10 |
| C2 | 6.0 | 38 | 20 | 1.4 | 9.6 |
| D | 2.2 | 6 | 3.4 | 10.5 | 5.1 |

 Table 6.3. Defects in cast polycrystalline Si processed into planar laser-grooved solar

 cells (DD=Dislocation Density).

^a For inclusions with diameter > 1.3 μ m.

6.4.2. Solar Cell Fabrication

A pair of wafers from each 10 cm \times 10 cm substrate were set aside after inclusion density evaluation and divided into two groups each consisting of one type of substrate. Each group of wafers were then simultaneously processed into solar cells using a modified version of the laser-grooved solar cell procedure (Appendix A). The modifications consisted of top P diffusion and oxidation being carried out at 840°C and groove diffusion and sintering at 880°C (Yun, 1992). Surface texturing was also bypassed to avoid possible interferences from it in measuring solar cell output.

The first batch of solar cells to be processed performed rather poorly due to precipitate contamination during the polishing step. An RCA1 followed by an RCA2 bath proved insufficient to rid the wafers of these unknown polishing residues. Etching a few μ m off the surface with an HF:HNO₃ mixture resulted in better cell performance. Only the results for the second batch was considered and summarised in Table 6.4. The high reflection loss from planar surfaces explains the low J_{sc} value obtained. The best laser-textured polycrystalline Si solar cells fabricated from the

| SAMPLE | V _{oc} | J_{sc} | FF | η |
|------------|-----------------|------------------------|-------------|------|
| | (mV) | (mA cm ⁻²) | (%) | (%) |
| control | 611 | 28.4 | 78.2 | 13.6 |
| A1 | 596 | 29.0 | 76.6 | 13.2 |
| A2 | 599 | 29.4 | 77.4 | 13.6 |
| В | 588 | 29.2 | 75.4 | 12.9 |
| C 1 | (broken | during | processing) | |
| C2 | 596 | 29.6 | 76.9 | 13.6 |
| D | 599 | 28.1 | 76.7 | 12.9 |

 Table 6.4.
 Solar cell parameters for the planar cells fabricated from substrates in

 Table 6.3.

same materials considered in this experiment using laser-grooved processing have J_{sc} in the 35 to 36 mA/cm2 range and η from 15.7 to 16.6 % (Yun, 1992).

6.4.3. Defects and Solar Cell Performance

Scatter plots of V_{oc} , J_{sc} , FF and η with the various defects listed in Table 6.3 reveal correlations only for J_{sc} and η with $[O_i]$, dislocation density and HDDA. Figure 6.18 shows the scatter plot for J_{sc} and η against $[O_i]$. The observed drop in J_{sc} with increasing $[O_i]$ is in rough agreement with reported results. Doolittle et al (1990) observed that the best cell performance produced on Controlled Directional Solidification (CDS) semicrystalline Si in their study occurred for wafers with minimum $[O_i]$ and maximum $[C_s]$. Hide et al. (1990) concluded that for solar cells fabricated on spin cast Si, better performance is achieved for $[O_i] < 15$ ppma. These reports are consistent with Shimura and Tsuya's (1982) and Seiter's (1987) observation that oxygen precipitation, which can degrade cell performance (section 3.3.4), occurs only for concentrations larger than 14 ppma. A report on the beneficial effects of O_i on Si (Sopori, 1988) likewise proves effective only for $[O_i] < 10$ ppma. In Figure 6.18, it is observed that cell output starts to drop for $[O_i]$ well below the precipitation limit. Although no O precipitation was observed in the experiments carried out in section 6.2.1, it may be that the precipitates have already formed prior to characterisation and the residual $[O_i]$ measured is indicative of the amount of precipitates present. A proper measurement of $[O_i]$ using high temperature treatments (Pivac, 1990) should then be considered for future experiments.

Figures 6.19 and 6.20 show the scatter plots for J_{sc} and η against intragrain dislocation density and HDDA. J_{sc} and η both increase with increasing dislocation density and HDDA. The similar results attained for dislocation density and HDDA indicates a correlation between them (Figure 6.21). Increasing HDDA represents increasing stress in the crystal and it is reasonable to expect that intragrain dislocation densities will likewise increase.

The trend observed for J_{sc} in Figures 6.19 and 6.20 apparently contradicts the theoretical and experimental results of El Ghitani and Martinuzzi (1989a, b). They have shown that dislocation densities greater than 10^3 cm^{-2} cause a decrease in J_{sc} . This decrease becomes more marked for dislocation recombination velocities exceeding 10^4 cm s^{-1} . Attempts to evaluate recombination activity from dislocations and HDDA's in the finished laser-grooved polycrystalline Si cells using EBIC proved unfruitful (see section 6.3.1). This indicates that the dislocations and HDDA's observed in the cells being studied have negligible recombination velocities. They may actually be neutral and the observed correlation may be an artifact of some sort.

Figures 6.22A and B show scatter plots for dislocation density and HDDA against $[O_i]$. A trend showing a decrease in dislocations and HDDA's with increasing $[O_i]$ is discernible. This is expected as O_i can act as a stress-releasing agent similar to inclusions (see section 6.2.4) during crystal growth. This should result in a decrease in dislocation density and HDDA's as $[O_i]$ increases. No clear trend exists between dislocations, HDDA and inclusions. Figure 6.22C shows some correlation between inclusions and $[O_i]$.



Figure 6.18. Scatter plots for $[O_i]$ and A) cell short circuit current density, J_{sc} and B) cell efficiency, η .



Figure 6.19. Scatter plots for dislocation density and A) J_{sc} and B) η .



Figure 6.20. Scatter plots for HDDA and A) J_{sc} and B) η .



Figure 6.21. Scatter plot for HDDA and dislocation density.



Figure 6.22. Scatter plots for $[O_i]$ and A) dislocation density, B) HDDA and C) inclusion density.

From Figure 6.22A and B, if the dislocations and HDDA's were neutral, a correlation between them and J_{sc} and η opposite to the trend observed with $[O_i]$ can still be obtained. This assumption of neutrality is consistent with results reported by Doolittle et al. (1990) and may be due to the fact that they are not decorated by impurities or precipitates.. They reported no correlation between etch pit density and cell performance. More definite trends can be observed if the recombination velocity due to the dislocations are known (El Ghitani and Martinuzzi, 1989a, b). Recombination velocities in dislocations are affected by impurities and precipitates trapped in them. This supports the idea that undecorated dislocations have negligible electrical activity (section 3.3.2)

 $[C_s]$ and inclusion density did not reveal any conclusive trends with device characteristics. This does not necessarily mean that they are neutral but that they are not the dominant defects for the cells under consideration. Minimisation of effects due to $[O_i]$ may reveal trends with other defects. This is an area worth investigating in the future. More data points are likewise needed for a study like this. The problem of characterisation and uniform processing of a large number of large area devices should also be properly addressed.

6.5 Summary

The work carried out in this chapter has seen the development of characterisation techniques for evaluating $[O_i]$, $[C_s]$, dislocation density and inclusion density in cast polycrystalline Si (IR spectra analysis, defect etching, IR and visible microscopy and image processing). EBIC studies revealed recombination contrast for grain boundaries and the dislocations in them. Intragrain dislocations and HDDA's are apparently neutral. Dimitriadis' (1985) model for EBIC linescans across a grain boundary has been shown to yield useful results in the interpretation of recombination contrast observed in grain boundaries. Further potential applications for this technique involve curve-fitting routines which enable the extraction of precise grain boundary recombination velocities and intragrain diffusion lengths. Combined with

ECP techniques (section 4.4), grain boundary passivation may be evaluated effectively (Yasutake et al., 1990).

The establishment of systematic defect density evaluation techniques allowed correlation between defect density and solar cell performance. Preliminary results from solar cells fabricated using a modified laser-grooved solar cell processing sequence indicate that low $[O_i]$ result in higher J_{sc} and η . Trends observed with dislocations may just be an artifact of its inverse correlation to $[O_i]$. They may actually be neutral as EBIC probing has suggested. $[O_i]$ is then the dominant defect for this particular experiment. More cells need to be processed to verify this correlation. A proper measurement of $[O_i]$ should also be considered using high temperature treatments (Pivac, 1990). Further work will involve sorting out the influence of other defects.

CHAPTER 7

SOLUTION-GROWN SILICON

7.1 Introduction

The main reason for exploring Si growth on glass is the economy achieved by the elimination of low yield processing of ingots into wafers and the minimisation of other material used in the final module. More than half the Si is wasted as kerf or cutting loss during wafering (Yoo et al., 1978) and the slices are thicker than the optimal 100 µm thickness (Green, 1987 p.97) because of minimum mechanical strengths required for handling the wafers. The main intention in growing Si sheets \approx 20 µm thick on glass substrates is to minimise such wastage in Si material. With the use of randomised light trapping schemes, the drop in cell performance because of the thinner Si material is not that bad. The required mechanical strength for processing the Si sheet into solar cells is provided by the glass substrate. Lower processing temperatures are, however, required to minimise thermal stresses due to lattice mismatch between the Si material and the glass substrate. The development of low temperature crystal growth and processing techniques further reduce the cost associated with solar cells.. Glass is the usual encapsulant for solar cell modules and is actually a superstrate for Si growth. Better substrates exist in the form of conductive ceramics engineered to accommodate lattice mismatch and high temperature processing (Barnett et al., 1988). Nevertheless, glass is cheaper and more readily available. It also reduces the amount of other materials used in the final module. Satisfactory cell structures incorporating the glass superstrate (illumination from the glass side, junction creation and metallisation from the rear) have been

recently designed and await testing on actual Si on glass material (Taouk, 1992). This chapter involves the characterisation of defects in solution-grown Si being developed at the University of New South Wales in the hope of providing a more effective strategy for the growth of Si on glass.

Liquid Phase Epitaxy involves the growth of a semiconductive layer from a supersaturated melt solution on a similar substrate (Nelson, 1969, US Patent 3,565,702). Figure 7.1 illustrates the slider boat configuration used to grow the epitaxial layers at the UNSW (Lee, 1990). Upon heating the melt at a temperature sufficient to dissolve all the Si in the melt solution, a Si substrate at the same temperature is put into contact with it by pushing the sliding boat. On cooling the melt solution, Si precipitates form and nucleate on the surface of the Si wafer. After growing the desired epilayer thickness, the wafer is pushed away from the melt, cooled down and taken out of the boat. Various surface treatments have been discussed by Lee (1990) in order to improve the nucleation density of Si on the wafer. This enables the growth of a continuous epilayer. Au60wt%Bi was likewise identified as an appropriate melt to achieve solution growth of Si at temperatures <500°C (Lee and Green, 1991).

The characterisation of these grown layers will be dealt with in the next section. Hot probe and four-point probe measurements determine these layers to be n-type with an average resistivity of 0.04 Ω cm. Spreading resistance measurements eventually replaced Capacitance-Voltage (C-V) techniques for dopant profiling as the unexpectedly high dopant concentration in the layers limited the C-V profile depth to <1 μ m. PIXE measurements (section 4.2.2.1) narrowed the choice of the dominant dopant impurity to Bi and arsenic with photoluminescence (PL) measurements (section 4.2.1.2) identifying Bi as the appropriate dopant impurity. High concentrations of Au and Bi were also measured by PIXE indicating the presence of inclusions in the layers. IR images of the epilayer/substrate interface reveal the inclusions. EDX probing of an inclusion exposed at a cleaved edge shows that it is made of melt material (Au and Bi) probably trapped at the interface as the growing

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Figure 7.1. A slider boat set-up for the epitaxial growth of Si via LPE.

crystals impinged on one another. These inclusions generate strong EBIC contrast as they hinder carrier generation in the cell. They also introduce shunting effects as they are located right at the cell junction. This results in large leakage currents which reduces cell V_{oc} and FF (section 4.6.1).

Improved growth of n- and p-type layers was recently achieved using Sn-Sb and Sn-Al melts, with Sb acting as a donor and Al acting as an acceptor impurity in Si (Shi, 1992a, p. 185). EBIC micrographs show the same problem with trapped melts along the epilayer/substrate interface. EBIC investigation of junctions fabricated by growing an n-type layer over a p-type layer shows junctions devoid of strong recombination centres. The weak recombination features observed apparently come from the substrate/LPE-layer interface where inclusions are still expected to be present. This indicates diffusion lengths greater than the lower LPE layer thickness. Efficiencies as high as 11% have been achieved on cells fabricated from similar LPE layers.

The possibility of growing $Si_{1-x}Ge_x$ layers via LPE was demonstrated by Healy et al. (1991). Studies have shown that cell improvements are possible for $x \in [0.1, 0.2]$ (Healy and Green, 1992). Section 7.3 presents results obtained from the characterisation of $Si_{1-x}Ge_x$ alloys using the same techniques as in section 7.2. Alloy composition was determined via EDX and verified against RBS and PIXE measurements. Bandgap reduction was measured by measuring the shift in the Bi nophonon (NP) peak position obtained by PL. A promising result from the PL bandgap reduction measurements is the identification of strain in the dilute Ge alloys (x \approx 0.025). Such layers can find future applications in solar cell efficiency enhancement and superlattice growth. They are the thickest and the largest strained layers reported in the literature to date. Cells fabricated from these layers reveal a greater density of recombination centres which are probably due to dislocations. Secco-etching reveals that this dislocation density increases more than an order of magnitude for x=0.025 and x=0.19.

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The last section covers developments in Si-on-glass growth techniques. Successful growth of Si on glass was recently achieved at the softening temperature of glass. It is believed that growth proceeded via processes similar to rheotaxy (Shi, 1992a, p. 137). EDX probing of an interfacial layer between the glass and Si layer indicates the presence of an AlSiMgO compound from which Si growth may proceed. Secco-etching of the substrates reveal twinning planes similar to that observed for Si on sapphire (Nolder et al., 1965).

7.2 Liquid-Phase Epitaxial (LPE) Si

7.2.1 Growth

LPE Si layers were grown on 30 to 70 Ω cm, <111> p-type Si. The use of Au60wt%Bi solution allowed the growth process to be carried out at very low temperatures (450 to 380°C). The area of the layers was limited by the graphite boat well size of 2.5 cm × 2.5 cm. The layers were typically grown 10 to 15 μ m thick. A more detailed account of the low temperature LPE process can be found in Lee et al. (1990). The inclusion of Bi (see next section) in the grown layer makes it n-type. This results in the formation of a junction between the substrate and the grown layer. Device fabrication for EBIC and solar cell analysis was done with layers grown from Au-Bi melts on heavily doped (0.03 Ω cm) p-type substrates.

The growth of a junction entirely by LPE was achieved by the initial growth of a p-type layer followed by the growth of an n-type layer at a lower temperature range (Shi, 1992a, p. 185). A Ga-Al melt was initially found suitable for the growth of ptype layers. However, junction fabrication required the Ga-Al and Au-Bi melts to be present simultaneously in the furnace. This presented melt cross-contamination problems when sliding the substrate from the Ga-Al melt to the AuBi melt. A better strategy consisted of using a common melt for the growth of the two layers. Sn-based melts where Al was added for p-type layers and Sb for n-type layers resulted in the fabrication of good quality LPE junctions. The higher growth temperatures (500 to 800°C) required for this process was justified with the achievement of Si growth on glass at its softening temperature (section 7.4). The softening temperature for borosilicate glass is 755°C (Paul, 1982, p. 75).

7.2.2 Characterisation

Simple hot probe tests (section 4.5.1) determine the carrier type in the LPE layers. These tests confirm that films grown with Au-Bi and Sn-Sb melts are n-type while those grown with Ga-Al and Sn-Al are p-type. Knowing the carrier type in the layers, their sheet resistivity can be determined with a four-point-probe apparatus (section 4.5.1). Epilayer thickness can then be measured with a Dektak IIA surface profilometer and the resistivity of the layers estimated. These resistivity values can easily be translated into dopant concentrations using ASTM F723-82(87). This conversion may not be that accurate for dopant impurities other than B or P as the size of the impurity can affect carrier mobility in Si. Nevertheless, it provides a rough estimate of the average carrier concentration in the layer. Capacitance-Voltage measurements (section 4.5.2) made on n-type LPE-Si grown from Au-Bi melts give limited dopant concentration profiles because of the unexpectedly high dopant concentrations present in the layer. Figure 7.2 is an example of a dopant profile obtained via C-V measurements. Schottky and ohmic contact patterns were deposited according to section 4.5.2. Although the profile is quite shallow, the measured concentrations are consistent with spreading resistance measurements (Figure 7.3). Spreading resistance became the preferred method in subsequent dopant concentration profile measurements. Phosphorus is, however, assumed to be the dopant impurity in this method and errors due to mobility differences may arise as has been observed for converting resistivities to carrier concentrations using ASTM F723-82(87).

The identity of the dopant impurity in layers grown with Au60wt%Bi remained uncertain for some time. Although Bi is the most likely dopant, the resulting concentration from spreading resistance measurements exceed what the

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Depth (µm)

Figure 7.2. Capacitance-Voltage profile of <111> n-type Au60wt%Bi LPE Si layer. The depth of the profile is severely limited by the dopant concentration of the layer. However, the measured concentrations are consistent with spreading resistance measurements (see Figure 7.3).



Figure 7.3. Spreading resistance profile of a spot bevelled LPE layer similar to the one used for Figure 7.2. The substrate-layer interface is $\approx 15 \,\mu m$ deep. Some errors in the concentration values may occur due to the assumption of a P dopant impurity. Other dopant impurities may yield different mobility values.

| Impurity | Impurity Concentration (ppma) | | | |
|----------|-------------------------------|------|--|--|
| | AB-1 | AB-2 | | |
| As | 11 | 8 | | |
| Au | 1630 | 1990 | | |
| Bi | 3300 | 3970 | | |

 Table 7.1. Impurities in LPE-Si layers (AB-1 and AB-2) grown from Au60wt%Bi

 melts detected by PIXE.

published solid-solubility curve for Bi in Si (Sze, 1981, p. 69) would indicate at the growth temperatures used. At any rate, it has been pointed out by Lee et al. (1990, p. 55) that the published solid-solubility curve for Bi may not be that authoritative. Table 7.1 lists a number of elements identified by PIXE analysis of a typical layer grown from a Au-Bi melt. Although Cr, Fe, Mn and Ni gave readings above the minimum detection limit, they come mainly from beam spray off the chamber walls and sample holders during measurement and are consequently ignored in Table 7.1. Arsenic is detected just above the minimum detection limit during the measurement and in the correct concentration to account for the dopant concentration. It is suspected to be an impurity in the Au-Bi melt. However, PIXE probing of both used and freshly prepared melts yielded better curve fits assuming arsenic is absent from the melts. The peaks appearing to come from arsenic can be accounted for by the random summing of L X-rays from Au and Bi (Hotchkis, 1991). An upper bound for the arsenic concentration is likewise difficult to establish as its K X-rays appear under the L X-rays of Au and Bi. Estimates of this upper bound yield 1500 ppma. Au and Bi are present in large amounts (>1000 ppma) in the LPE samples (Table 7.1) and the arsenic detected may just be an artifact coming from the random summing of AuL and BiL X-rays as described above for the Au-Bi melt. No conclusions about arsenic in the LPE samples can, therefore, be drawn from PIXE measurements. It is to be noted that only a small fraction of the detected Bi in the layers is needed to account for the dopant density in it. Another characterisation technique is then needed to correctly identify the dominant dopant impurity.

Figure 7.4 shows the PL spectrum of a typical LPE-Si layer grown from a Au-Bi melt. The spectrum was obtained at T=9°K, laser power of 40 mW, 1 mm slit width and a resolution of 2 meV (see section 4.2.1.2). A no-phonon (NP) peak at 1.147 eV and a TO-phonon assisted peak at 1.089 eV are visible and consistent with observed peak positions for Bi (Dean et al, 1967). Arsenic would have peaks at 1.149 eV and 1.091 eV. In view of the resolution used, it is possible that the PL peaks are due to arsenic. To test this assumption, the PL spectrum of a phosphorusdoped sample (Figure 4.6) was obtained. The PNP peak in this case is at 1.151 eV while the expected peak position is 1.150 eV. The peak for arsenic should, therefore, be above the expected position of 1.149 eV. The observed NP peak in Figure 7.4 is right at the expected position of 1.147 eV for BiNP. Moreover, a peak at 1.097eV corresponding to the free-exciton TO phonon replica can be discerned from the spectrum. Therefore, Bi is the dopant impurity in the LPE layers and the arsenic peaks in the PIXE spectra are artifacts from random summing of L X-rays as discussed previously. Electron hole drop peaks are not present in the PL spectrum as there were no significant changes in the PL spectra obtained at higher temperatures (Cuthbert, 1970) and lower laser powers (Pokrovskii, 1972).

The large concentrations of Au and Bi in the samples (Table 7.1) are believed to come from melt material trapped at the epilayer-substrate interface as the growing crystals impinged on one another (Possin, 1984, p. 175). The fact that the ratio of the Au and Bi concentrations, when converted to ppm weight (ppmwt), is roughly the same as the melt composition supports this assertion. Inspection under the IR microscope (section 4.3.2.2) reveals contrast consistent with the presence of inclusions (Figure 7.5). Figure 7.5A is a brightfield image of a typical LPE layer grown from a Au-Bi melt. Under the infrared mode of the microscope, dark patches (5 to 30 μ m in diameter) appear at approximately the depth of the interface (Figure



Figure 7.4. Photoluminescence spectra of n-type LPE-Si. The peak at 1.047 eV is identified as the Bi^{NP} peak according to Dean et al. (1967). The peak at 1.089 eV is 58 meV below the NP peak and is, therefore, the TO-phonon replica of Bi^{NP}.

Figure 7.5. A) Brightfield image of LPE-Si surface. B) IR image of A focused at the LPE-Si/Si substrate interface. Well-defined dark patches (5 to 30 μ m in diameter) indicate the presence of inclusions at the interface.



7.5B). Such contrast can be attributed to the presence of inclusions (see Figures 4.10and 6.9 for comparison). EBIC micrographs (Figures 7.6 A and B) likewise suggest their existence. The dark streaks across the cell (Figures 7.6 A) represent recombination centres or non-carrier-generating regions in the cell. A closer look at such regions (Figure 7.6B) reveal well-defined dark patches ($\approx 20 \ \mu m$ in diameter) attributable to such inclusions. Similar features are exposed on a Secco-etched layer (Figures 7.7 A to D). Figures 7.7A and B show streaks quite similar to the dark streaks observed in Figure 7.6A. A closer look at the streaks (Figure 7.7C) reveal holes 5 to 20 µm in size where the inclusions were apparently etched away in the process. The holes are heavily decorated with dislocations as has been observed for inclusions in cast polycrystalline Si (see Figures 6.3 and 6.8). Dislocations are likewise apparent in the unstreaked region (Figure 7.7D) but at much lower densities ($\approx 10^6$ cm⁻² compared to $\approx 10^7$ cm⁻² for Figure 7.7C). The observed distribution of the holes is consistent with the idea that melt is trapped in regions of impinging crystal growth. Surface contaminants (impurities and surface oxides) are believed to enhance this melt-trapping mechanism as they provide nucleation points for the trapped melt (Shi, 1992a, p. 185).

Observation along a cleaved edge of the sample in Figure 7.6 reveals particles along the LPE-Si/Si substrate interface (Figure 7.8). This interface is actually a p-n junction and can be located using EBIC. The bright region 10 μ m from the epilayer surface is the EBIC image of the interface and is in good agreement with the expected epilayer thickness of 10 μ m as measured with a Dektak IIA profilometer. The recessed areas near the interface are believed to have been occupied by inclusions which were removed during the cleaving process. The particle at the bottom of the image ($\approx 2.5 \mu$ m in diameter) is one which was not plucked out during the cleaving process. EDX analysis of the particle (Figure 7.9) identifies it as a Au-Bi compound. This demonstrates beyond doubt that melt material is trapped at the epilayer-substrate interface. The large particle extending from the interface to the top surface of the layer is due to evaporated Ti metal filling a hole or a surface break in the layer. After

Figure 7.6. EBIC image of the LPE-Si/substrate interface. A) Dark streaks representing highly recombinative regions or non-carrier-generating regions near the cell surface. B) A closer look at some of the streaks in A) revealing well-defined dark patches ($\approx 20 \ \mu m$ in diameter) attributable to inclusions.





Figure 7.7. Secco-etched LPE layer grown using Au60wt%Bi. A) Showing regions where melt had collected generating the EBIC contrast in Figure 7.6. B) Showing an enlarged view of A) revealing holes in the layer, C) Showing holes 10 to 30 μ m in diameter in B) heavily decorated by dislocations and D) Showing dislocations on the cleaner area with lower density ($\approx 10^6$ cm⁻²) to that in C) ($\approx 10^7$ cm⁻²).



Figure 7.8. SEI of LPE-Si/Si interface showing particles exposed by cleaving the cell in Figure 7.6. The EBIC image of the interface (bright region) is superimposed to locate the interface at which a p-n junction was formed. The recessed areas near the interface are believed to have been occupied by trapped melt which were removed during the cleaving process. The particle at the bottom of the image ($\approx 2.5 \mu m$ in diameter) is one which was not plucked out during the cleaving process. EDX analysis of the particle (Figure 7.9) identifies it as a Au-Bi compound. The large particle extending from the interface to the top surface of the layer was also occupied by an inclusion but was removed via an aqua regia bath. Consequently, it was filled with evaporated Ti metal used to make the top ohmic contacts.



30-Oct-1993 15:50:06 Execution time = 19 seconds Preset= Elapsed= 100 secs 100 secs 432 counts Disp= 1 Vert= Âu Bi Bi ∬ ||~₁ | Bi || Aull AuBi uAuAu AuBi hellinstylithmushlowithen hauser with BiAu Au 10.110 -> 25737 l3 Range = |4 |5 10.230 keV 12 **7**6 18 1 0.000 Integral Ø -2

are attributed to AuL and BiL X-rays. Figure 7.9. EDX spectra of the particle identified in Figure 7.8. The peaks present

the growth process, residual melt on the layer is etched via an *aqua regia* bath. This cleaning procedure can result in holes where melt material was removed. Some of these holes are filled by Ti during metallisation of the epilayer to provide ohmic contact to the device.

The dislocations in Figure 7.7 terminate at the LPE-Si/Si substrate as has been observed by Shi (1992a, p. 91) on LPE-layers grown from Sn-based solutions. The dislocations in the epilayer are most likely decorated with Au and are then expected to contribute to recombination in the cell given the well-known recombination properties of Au (section 3.3.1). Recombination activity due to dislocations will become more apparent in the discussion of Si_{1-x}Ge_x alloys in the next section. The elimination of such active defects is imperative for satisfactory solar cell operation.

The cell in Figure 7.6 was the best one at that time made from an n-type LPE Si grown from a Au-Bi melt on a heavily doped p-type substrate. It had a low V_{oc} (\approx 300 mV) probably due to junction recombination and shunting (section 4.6.1) brought about by the presence of inclusions at the junction region. Recombination via the decorated dislocations is not apparent in Figure 7.6B.

Similar melt trapping mechanisms have also been observed on p-type LPE layer grown from a Sn-Al melt. PIXE measurement of the Sn concentration and PIGE measurement (section 4.2.2.2) of the Al concentration in an LPE layer grown with Sn10wt%Al have yielded 2500 ppma and 360 ppma respectively. These large concentrations of Sn and Al indicate the presence of inclusions in the epilayer as had large concentration is two orders of magnitude larger than the measured dopant concentration in the epilayer ($\approx 10^{17}$ cm⁻³). Figure 7.10A shows the SEI of the surface of a typical p-type LPE-Si/n-type Si substrate structure (left half) and the EBIC image of the same region (right half). The dark features in the EBIC image indicate the presence of inclusions at the interface.

Figure 7.10B shows an SEI of the surface (left half) and the corresponding EBIC micrograph for the same region (right half) of a cell fabricated by growing an n-

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Figure 7.10. A) SEI (left) of a p-type LPE-Si layer grown from Sn-Al melt on an n-type substrate. The corresponding EBIC image (right) shows strong recombination regions indicating the presence of inclusions at the epilayer-substrate interface. B) SEI (left) of n/p LPE-Si cell grown from Sn-based solutions (Sn-Sb/Sn-Al) on a heavily doped p-type substrate showing the absence of strong recombination areas. The faint dark spots indicate lesser activity from epilayer-substrate inclusions as they are farther away from the junction region.




type LPE layer over a p-type LPE layer on a heavily doped p-type substrate. Snbased solutions were used for both layers. The absence of dark recombination features in the EBIC image indicates that the interface between the two LPE layers is free of inclusions. It is believed that the minimisation of surface impurities and oxides minimised melt trapping at this interface. After the p-type layer was grown, it was immediately put into contact with the second melt solution with minimum exposure to the furnace ambient resulting in minimal surface contamination. The few faint features in Figure 7.10B may be due to LPE-Si/Si substrate interface inclusions. Activity from these inclusions is greatly reduced because they are farther away from the active junction region. Efficiencies up to 8.5% were reported on cells fabricated entirely by solution growth with V_{oc} exceeding 600 mV (Shi et al, 1992a).

The successful creation of a junction is easily verified by the presence of an EBIC signal. EBIC techniques also allow the measurement of the junction depth as already seen in Figure 7.8. A more accurate measurement is possible by locating the peak in an EBIC linescan (Figure 7.11B) obtained at a very slow scan speed across a cleaved section of the cell. This is easily done by superimposing the EBIC linescan to the corresponding region in the SEI of the cleaved section (Figure 7.11 A). The cell in Figure 7.11 is an LPE cell fabricated entirely from Sn-based solutions. The junction depth for this cell is 3 μ m and corresponds to the thickness of the top LPE layer. The bottom LPE layer is expected to be ~10 μ m thick.

The measured junction depth for the cell in Figure 7.11 is too deep. Better cell output can be achieved by bringing the collecting junction as close to the surface as possible (Green, 1986, p. 145). Junction depths less than 1 μ m has recently been achieved on LPE cells similar to the one in Figure 7.11. Such depths are difficult to measure using the EBIC technique as the best resolution obtainable via EBIC is $\approx 1 \mu m$ (section 4.6.2). Fine spreading resistance measurements allow such depths to be measured with a certain degree of accuracy. Figure 7.12 is an example of a fine spreading resistance measurement identifying the junction depth in an LPE cell to be

Figure 7.11. A) SEI of a cleaved section of n/p LPE-Si cell grown from Sn-based solutions on a heavily doped p-type substrate. B) EBIC linescan along the bright horizontal line across the cell junction. By superimposing B) on A), the junction depth can be measured by measuring the distance between the top surface of the cell and the peak of the EBIC linescan. For this cell, the junction is $\approx 3 \mu m$ deep.





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Figure 7.12. Spreading resistance profile showing a junction depth of 0.15 μ m on an LPE-Si junction grown from Sn-based solutions. The open squares (\Box) represent carrier concentrations on the n-type LPE-Si layer while the closed squares (\blacksquare) that on the p-type LPE-Si layer.

around 0.15 μ m. Cell efficiencies up to 11% have been achieved on LPE cells with similar junction depths (Shi, 1992b).

7.3 LPE Si_{1-x}Ge_x

7.3.1 Growth

Si_{1-x}Ge_x layers were grown by adding a small amount of Ge to the Au60wt%Bi solvent (section 7.2.1). The amount of Ge added to the melt was estimated using a quasi-ternary Si-Ge-Au60wt%Bi model (Healy et al., 1991). The layers were typically grown 5 μ m thick with a compositional range 0<x<0.2. A junction for device evaluation was achieved by growing the n-type layer on a heavily doped (0.03 Ω cm) p-type substrate. Si capping layers were grown over the Si_{1-x}Ge_x layers opens up the possibility of superlattice fabrication with low temperature LPE (ibid.).

7.3.2 Characterisation

Table 7.2 lists the alloy composition of several Si_{1-x}Ge_x layers as measured by semi-quantitative EDX analysis. A 5 keV electron beam was used to avoid beam penetration through the epilayer at the same time allowing sufficient excitation of the Si K α and Ge L α X-rays (Kevex Corporation, 1988). Some of these measurements were verified by RBS and PIXE and are also shown in the table. The EDX values are consistently higher than the PIXE and RBS values by 10%. This may be attributed to the difference in probe sizes (\approx 1 µm for EDX compared to \approx 1 mm for RBS and PIXE) and differences in penetration depths (see section 4.2.2). However, it must be kept in mind that the EDX analysis carried out is only semi-quantitative and has a 10% accuracy which may well have explained the above-mentioned discrepancy.

Knowing the alloy composition, the next step involves evaluating the reduction in the Si bandgap as a result of alloying Ge to it. The usual method to measure this reduction in bandgap is via optical absorption measurements (Braunstein

| SAMPLE | Ge content (at%) | | | $\Delta E_g(meV)$ |
|--------------|------------------|------|------|-------------------|
| | EDX | RBS | PIXE | |
| SG- 1 | 2.4 | | | 34 |
| SG-2 | 3.0 | 2.0 | 2.1 | 36 |
| SG-3 | 2.6 | | | 39 |
| SG-4 | 10 | 8.5 | 8.5 | 46 |
| SG-5 | 17 | | | 58 |
| SG-6 | 19 | 17.0 | 16.7 | 66 |
| SG- 7 | 19.5 | | | 73 |

Table 7.2. Alloy composition of $Si_{1-x}Ge_x$ layers grown by low-temperature LPE as determined by EDX analysis. Some values were verified using RBS and PIXE. ΔE_g in the last column is the measured bandgap shifts derived from PL spectra.

et al., 1958). In the past decade, however, PL has become increasingly prominent in evaluating bandgap reductions for Si_{1-x}Ge_x alloys (Mitchard and McGill, 1982; Weber and Alonso, 1989; Dutartre et al, 1991; Terashima et al, 1990; Robbins et al., 1992 and Hansson et al., 1990). Figures 7.13 A to C show the PL spectra (T=9°K) of LPE-grown Si_{1-x}Ge_x for x = 0, 0.025 and 0.19 respectively. The spectra were obtained at a resolution of 2 meV for the Si layer and 5 meV for the Si_{1-x}Ge_x alloys. The peaks in Figure 7.13A have been previously identified in Figure 7.4. The PL peaks observed for Si_{0.975}Ge_{0.025} and Si_{0.81}Ge_{0.19} are separated by 58 meV which is consistent with the observation of a NP peak and its TO phonon replica. Since the Si_{1-x}Ge_x alloys were grown from the same melt with the addition of a small amount of Ge, these peaks should likewise come from Bi-bound excitons. A possible impurity introduced in the layer because of the introduction of Ge is Cu which is specified as having concentrations of 0.05 to 0.1 ppmwt in Ge (ESPI). Cu



Figure 7.13. Photoluminescence spectra for A) LPE-Si, B) $Si_{0.975}Ge_{0.025}$ and C) $Si_{0.81}Ge_{0.19}$. Bandgap reduction due to the alloying process can be measured by comparing NP peaks in B) and C) to that in A).

limits and increases from 2 to 55 ppma with increasing Ge concentrations (2 to 20 at%).

Figures 7.13B and C show the Bi PL peaks noticeably shifted towards lower energies compared to Figure 7.13A. The bandgap reduction ΔE_g due to alloying can be calculated by subtracting the position of the Bi^{NP} peaks in Figure 7.13B and C to the Bi^{NP} peak position in Figure 7.13A. ΔE_g calculations for the samples in Table 7.2 are listed in the last column. The doping concentration for the films ($\approx 10^{17}$ cm⁻³ see Figure 7.3) precludes any heavy doping effects on the PL spectra. Heavy doping creates a similar broadening and shifting of PL peaks due to impurity band effects and band tailing (Schmid et al., 1981). The observation of broad PL peaks in the Si_{1-x}Ge_x alloys has been reported by other workers. Mitchard and McGill (1982) have observed broadening of In-bound exciton peaks in bulk Si_{0.90}Ge_{0.10}. Weber and Alonso (1989) had similar peaks for bulk Si_{0.92}Ge_{0.08}. They also observed a decrease in peak half-widths with increasing Ge content. This effect is not evident in Figure 7.13 due to the broadening effect of the low resolution used. It has been observed though for higher resolution PL spectra.

In calculating ΔE_g , the difference in the exciton binding energy in Si (8.9 meV, Dean et al., 1967) and Ge (1.3 meV, Mayer and Lightowlers, 1979) has to be considered. As the Ge content of the alloy increases, this binding energy moves closer to the Ge binding energy level. Most of this change is expected to occur for x > 0.85 when the alloy becomes more Ge-like, i. e., the <111> conduction band minima become lower than the <100> minima (Braunstein, 1958). A worst case estimate (linear extrapolation) for discrepancies due to this effect is a decrease of 1.5 meV in ΔE_g for x=0.2. The 5 meV resolution presents a more significant source of error in establishing the Bi^{NP} position. A 2 meV difference is easily attributed to this factor.

Figure 7.14 plots the measured ΔE_g in Table 7.2 as a function Ge content. The horizontal bars indicate a 10% uncertainty in the determination of the Ge content from the average and expected average of the EDX and RBS/PIXE values. For



Figure 7.14. A plot of ΔE_g from Table 7.2 (×)against Ge content x of the alloy. The horizontal error bars indicate the uncertainty in the measured Ge content of the samples. Curve fits for unstrained (—) (Weber and Alonso, 1989) and strained layers (---) (People, 1986); and data points from Weber and Alonso (1989) (\blacksquare), Terashima et al. (1990) (+), Dutartre et al. (1991) (\blacklozenge) and Robbins et al. (1992) (Δ) are shown for comparison. All data points were deduced from PL measurements. ΔE_g for Ge-dilute samples in Table 7.1 agree well with the strained-layer curve.

x<0.1, the error bars were fixed for a 0.01 spread. Weber and Alonso's fit for the bandgap variation in unstrained layers (Weber and Alonso, 1989),

$$\Delta E_g = 0.43x - 0.206x^2$$
 [7.1]

is plotted as a solid line (-). The solid squares (\blacksquare) are their data points deduced from PL measurements. Our data show good agreement with Weber and Alonso's data points and curve fit for samples SG-4 to SG-7 considering the error in determining the Ge content in the grown alloys. The dashed curve (---) in Figure 7.14 represents ΔE_g in strained layers deduced from People (1986, Figure 10 p. 1701). The solid diamonds (\blacklozenge) are data points from Dutartre et al. (1991), the triangles (Δ) from Robbins et al. (1992) and the plus signs (+) from Terashima et al. (1990). All the data points were deduced from PL measurements and are in rough agreement with the dashed curve except that the data points from Robbins et al. (1992) are significantly lower (10 to 15 meV less). Note that samples SG-1 to SG-3 give ΔE_g slightly greater than the strained layer curve. Moreover, the trend in ΔE_g for slight differences in the Ge content of these samples follows the curve. These observations indicate that samples SG-1 to SG-3 are strained. The slightly larger values for ΔE_g are hard to account for since the PL spectrum for SG-2 was taken at a resolution of 2 meV. In addition to this, the PL peak positions for SG-1 and SG-3 did not significantly shift at higher resolutions.

Critical thickness as a function of alloy composition for strained $Si_{1-x}Ge_x$ has been calculated by People (1986) using the energy balance and self-energy concept for an isolated dislocation. For x=0.025, this thickness approaches 10µm as can be extrapolated from Figure 3 in People (1986, p. 1698). The 5 µm thicknesses achieved via LPE are well below this critical value. They are the thickest $Si_{1-x}Ge_x$ strained layers reported so far (Chan et al., 1992).

Attempts to expose misfit dislocations from both strained and unstrained layers via defect etching (Powell et al., 1991) were obscured by the already high dislocation densities present in the layers. Figure 7.15A is an SEM micrograph of a Secco etched (2.5 minutes) strained (x=0.025) layer with a dislocation density of 3×10^6 cm⁻² which agrees with the dislocation density observed in inclusion-free regions in Si layers grown with a Au-Bi melt (see Figure 7.7D). Figure 7.15B is a similarly etched unstrained (x=0.19) layer showing dislocation densities exceeding 5×10^7 cm⁻². It is still unclear whether these dislocations are threading dislocations arising from misfit dislocations.

EBIC probing of capped Si_{0.90}Ge_{0.10} layers grown on heavily doped p-type Si and isolated into mesas by wax masking and etching, have revealed recombination contrast which probably arise from the dislocations uncovered in Figure 7.15. Figure 7.16A is an SEM micrograph of a mesa cell. Figure 7.16B shows the EBIC micrograph of the same mesa cell. The bright region surrounding the mesa cell is part . of the p-n junction exposed by an initial etch. A second etch was necessary to satisfactorily isolate the mesa cells from one another. The more interesting feature is the EBIC contrast generated in the mesa cell. A closer look at the dark areas (Figure 7.17) reveal tiny specks (\approx 5 µm in diameter) which can be attributed to dislocations. The density of the specks is \approx 10⁶ cm⁻² which is less than the value expected for x=0.10. However, the growth of the Si capping layer may have affected the density of such dislocations. The recombination activity of the dislocations is most probably due to contamination with Au from the melt. Salih et al. (1985) have observed the gettering of metallic species, including Au, at misfit dislocations.

IR images of a similarly capped $Si_{0.90}Ge_{0.10}$ layer did not show any sign of inclusions. The same is true with $Si_{0.975}Ge_{0.025}$. PIXE analysis, however, still yield a large concentration of Au and Bi in these layers. It is then assumed that the inclusions are too small for detection via the IR microscope (section 4.3.2.2). It is then possible that the specks observed in Figure 7.17 are generated by inclusions. The reason why the inclusions changed in size drastically is still unclear. Inclusions can be directly observed only on higher Ge content layers. Figure 7.18A is a brightfield image of the surface of a $Si_{0.83}Ge_{0.17}$. The corresponding IR image in

Figure 7.15. A) Defect etched $Si_{0.975}Ge_{0.025}$ strained layer showing a dislocation density $\approx 3 \times 10^6$ cm⁻². B) Defect etched $Si_{0.81}Ge_{0.19}$ unstrained layer showing dislocation densities exceeding 5×10^7 cm⁻². It is still unclear whether the dislocations exposed here are threading dislocations from misfit dislocations. The greater dislocation density in the $Si_{0.81}Ge_{0.19}$ layer indicates that this may be so.



Figure 7.16. A) SEI of $Si_{1-x}Ge_x$ mesa cell. B) Recombination or non-generating regions exposed by EBIC.





Figure 7.17. Higher magnification EBIC micrograph of an area in Figure 7.16B revealing dark specks consistent with dislocations observed in Figure 7.15. The density of the specks ($\approx 5 \,\mu$ m in diameter) is $\approx 10^6 \text{ cm}^{-2}$.



Figure 7.18. A) Brightfield image of the surface of a $Si_{0.83}Ge_{017}$ layer. B) IR image of A) revealing inclusions near the epilayer-substrate interface.





Figure 7.18B shows well defined dark patches similar to the ones observed in Figure 7.5 but with a much lower area density ($< 10^4 \text{ cm}^{-2}$).

7.4 Si on Glass

The growth of Si on glass is the ultimate goal of exploring low temperature LPE growth techniques. It was initially thought that the use of glass as a substrate will limit growth temperatures to the strain point of glass, T \approx 500°C (Paul, 1982, p.75). This explains the choice of growth temperatures using Au60wt%Bi melts in section 7.2.1. Recently, the growth of continuous large-grain Si layers on glass was achieved around the softening point of glass (Shi, 1992a, p.150). This raised temperature limits to 800°C and resulted in improved LPE Si solar cells (see section 7.2.2).

Figure 7.19 shows an SEI of a cleaved section of polycrystalline Si on glass. EDX analysis of the crystals at the top (Figure 7.20) reveal only a Si peak. The slight O peak in the spectrum may have resulted from beam spray from adjacent glass materials. The use of high probe currents and the unusual sample geometry easily account for this effect (section 4.3.2.3). The dark strip (indicated by cross hairs) in between the Si grains and the glass substrate is suspected to be a transition layer facilitating the growth of Si on glass. EDX probing of the interface region (Figure 7.21) reveals O, Mg, Al and Si. Si and O are the usual components of glass (Figure 7.22). Al and Mg came from the growth solution. The reaction between Al and Mg and glass may hold the key to the observed Si growth on glass.

Several growth techniques have been explored in growing Si on glass substrates at the UNSW (Shi, 1992a, pp. 137-153). The most promising technique to date is to use Al- and Mg- based melts around the softening temperature of glass (Shi et al., 1992b). Large-grain continuous polycrystalline Si growth occurs under these conditions. Mg and Al in the melt is believed to deplete oxygen from the glass surface creating a Si-rich surface suitable for growth. A Si-rich surface improves wetting between the melt and the substrate and acts as a seeding layer for subsequent Figure 7.19. Cleaved section of a Si on glass sample exposing an interfacial layer (cross hairs) which allows the nucleation and growth of Si crystals.





Figure 7.20. EDX spectra for the Si layer in Figure 7.19. The slight O peak can be due to actual O concentrations in the Si crystals or is an artifact produced by beam spray from adjacent glass material. Large probe currents needed for the measurement and the unusual surface topography easily account for beam spray.



Figure 7.21. EDX spectra for the Si-glass interface in Figure 7.19 indicated by cross hairs. This interfacial layer is consistent with the formation of an AlSiMgO compound from which Si growth may proceed.



Figure 7.22. EDX spectra for the glass substrate in Figure 7.19. Si and O are the main components of glass.

nucleation (ibid.). An alternative growth mechanism is the formation of an AlSiMgO compound from which Si growth proceeds. The observation of the interfacial layer in Figure 7.19 is consistent with this idea. The role of the interfacial layer in Si growth on glass is still being investigated further. This layer can later prove to be a detriment during cell operation if it absorbs visible and near infrared light. IR imaging of Si on glass has been unsuccessful because of the absorbing qualities of the interfacial layer. The optical properties of such a layer needs to be investigated further.

Figure 7.23 is an SEI of a resulting continuous polycrystalline Si layer on glass mentioned above. The grains extend up to 100 μ m in diameter. Figure 7.24 shows a similar layer which has undergone a 3-minute Secco-etch. Twinning is evident (parallel line structures) and has been observed by Nolder et al. (1965) in Si on sapphire. X-ray diffraction shows a predominantly <110> orientation for the crystals (Shi, 1992, p. 162). ECP studies (section 4.3.3) on the individual grains are difficult to carry out because the sample needs to be flat during observation.

7.5 Summary

In this chapter, the characterisation of LPE Si and Si_{1-x}Ge_x layers provided vital information for the development of solution growth techniques. Si layers grown from Au-Bi alloys were shown to be n-type with dopant concentration $\approx 10^{17}$ cm⁻³ near the surface. PIXE measurements presented a choice between arsenic and Bi for the dopant impurity with PL measurements identifying Bi as the dopant impurity. The arsenic peaks in the PIXE spectra were then attributed to random summing of AuL and BiL X-rays. The large concentrations of Au and Bi in the layers were attributed to the presence of trapped melt at the epilayer-substrate interface. IR microscopy, EBIC and EDX analysis positively identified the presence of these inclusions. The growth of an LPE layer over another resulted in an inclusion-free junction as verified by EBIC imaging. This showed that impurities and surface oxides contributed to melt trapping mechanisms which result in the generation of inclusions in the interfacial layer. The use of Sn-based solutions for LPE growth resulted in better layers with

Figure 7.23. SEI of continuous polycrystalline Si layer on glass. The grains can grow up to $100 \ \mu m$ in diameter.



Figure 7.24. Secco-etched Si on glass sample similar to that shown in Figure 7.23. The parallel lines running across the grains are twin boundaries. Such twinning structure has been observed for Si grown on sapphire substrates (Nolder et al., 1965).



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efficiencies reaching 8.5% and V_{oc} exceeding 600mV (Shi et al., 1992a). Further improvements in junction depth resulted in efficiencies up to 11%.

Strain in dilute Ge (x≈0.025) Si_{1-x}Ge_x layers was identified using PL measurements. Their 5 μ m thickness make them the thickest strained layers reported Such thick strained layers find useful applications in thin film cells so far. incorporating a $Si_{1-x}Ge_x$ layer (Healy and Green, 1992). The observation of misfit dislocations was obscured by the already large dislocation density of the layers. It was not clear whether these dislocations were threading dislocations from misfit dislocations themselves. Differences in the measured densities on strained $(3 \times 10^6 \text{ cm}^{-2})$ and unstrained $(>5 \times 10^7 \text{ cm}^{-2})$ layers support this possibility. EBIC analysis of capped $Si_{1-x}Ge_x$ cells showed significant recombination activity arising from such dislocations. The density of the recombination specks in an EBIC micrograph (~10⁶ cm⁻²) roughly corresponded to expected dislocation densities in the layer. Inclusions were not directly observed on capped Si_{0.90}Ge_{0.10} and on strained Si_{0.97}Ge_{0.03} layers although PIXE measurements still indicate the presence of large concentrations of Au and Bi in the layers. It is believed that the size of the inclusions is below the resolution of the IR microscope. Only inclusions in higher Ge content alloys are directly observable and give a similar contrast to inclusions observed on layers grown with Au60wt%Bi melt.

EDX probing of a cleaved section of Si on glass revealed a promising nucleation mechanism for the growth of Si on glass. EDX analysis of an interfacial layer between the glass and Si layer indicated the presence of an AlSiMgO compound from which Si growth proceeds. Such interface layers may, however, interfere with cell operation if they absorb the incoming light through the glass. Further work is needed to evaluate their optical properties. Secco-etching of Si on glass revealed twin structures similar to that observed by Nolder et al. (1965) on Si on sapphire.

CHAPTER 8

CONCLUSION

8.1 Conclusion

In the hope of making photovoltaic energy economically viable, higher solar cell efficiencies should be attained or the cost of the starting solar cell material reduced. The development of the laser-grooved solar cell and the use of cast polycrystalline and solution-grown Si at the University of New South Wales (UNSW) have successfully addressed this problem. However, further improvements in laser-grooved solar cell performance need an understanding of defects generated during cell processing. For low cost materials, inevitable defects generated during crystal growth need to be identified and their impact on solar cell performance evaluated.

In the course of this thesis, a number of characterisation techniques (EBIC, FTIR, IR microscopy and video microscopy) were set-up and used successfully for the first time on novel solar cell materials (solution-grown Si) and novel processing techniques (laser-grooving) developed at the University of New South Wales. Characterisation techniques available at other laboratories (PL, PIXE, RBS) were also successfully adapted and data interpreted for Si material. The main results of this thesis involved the evaluation of extrinsic defects in laser-grooved solar cell processing and intrinsic defects in cast polycrystalline Si and solution-grown Si. Preferential defect etching coupled with microscopy and EBIC techniques proved indispensable in this work.

In Chapter 3, free carrier absorption was shown to have a significant effect on the long wavelength response of solar cells. Light-trapping properties of cells are

expected to be the most severely affected specially under concentrated sunlight. A model for incorporating free carrier absorption into solar cell equations was then proposed. Conflict between theoretical and experimental results for α_{FC} in p-type Si is overcome by using empirically derived values for the wavelength dependence of α_{FC} .

A number of interesting results arose from defect evaluation in laser-grooved solar cell processing (Chapter 5):

- 1) The uncovering of thermal wave effects during laser scribing of Si.
- 2) The discovery of a gettering effect via thermal waves.
- The revelation of damage due to laser-groove processing leading to a specific gettering model for the laser-grooved solar cell.
- The correct identification of oxidation-induced defects previously reported by Chong (1989, pp. 162-189).

In situ photoacoustic (PA) characterisation during laser scribing of Si for groove fabrication and cleaving was identified as an attractive non-destructive technique for controlling or monitoring scribe depth in the mass production of solar cells.

For cast polycrystalline Si (Chapter 6), the variability in intrinsic defects for samples received from different manufacturers were systematically characterised and an attempt to correlate these differences to solar cell performance was made. It was shown that interstitial oxygen concentration showed a strong correlation with cell J_{sc} and η . An EBIC linescan curve-fitting technique for quantifying grain boundary recombination velocity and intragrain diffusion length was suggested. This technique was applied as a first order approximation to evaluate possible electrical effects arising from thermal wave damage (Chapter 5).

The characterisation of solution-grown Si (Chapter 7) mainly involved the characterisation of low-temperature LPE Si (Lee, 1990 and Shi, 1992a)and $Si_{1-x}Ge_x$ layers (Healy et al., 1991) Hot probe measurements led to correct dopant type identification and spreading resistance measurements proved most effective in evaluating dopant carrier concentration profiles. PIXE identified arsenic as a possible

dopant impurity besides Bi in n-type LPE Si grown from Au60wt%Bi melts. Bi was, however, identified positively by PL measurements as the dopant impurity. The arsenic identified in PIXE measurements was attributed to random summing of AuL and BiL X-rays as curve-fitting experiments using Au-Bi melts indicated (Hotchkis, 1991). Inclusions from trapped melt at the epilayer-substrate interface were identified via IR microscopy and EDX analysis on an exposed particle along a cleaved section of the interface. The strong EBIC contrast generated by these inclusions demonstrated the potential harm they can do to cells made out of these layers. The creation of junctions from LPE layers resulted in a cleaner interfaces (Shi et al., 1992a). With the distancing of the inclusions from the active junction region, undesirable electrical effects from these inclusions are diminished as shown by EBIC micrographs of and improved performance from cells fabricated with such junctions.

The potential applications of $Si_{1-x}Ge_x$ alloys in solar cells and superlattice structures made them an ideal material to exploit using a low-temperature LPE process (Healy et al., 1991 and Healy and Green, 1992). Bandgap measurements using PL spectra have identified strain on SiGe alloys with low Ge content (Chan et al., 1992). These layers can be grown with thicknesses sufficient for solar cell applications.

Finally, a nucleation mechanism for Si growth on glass was identified by EDX probing of an interface layer apparent from SEM micrographs of a cleaved section. The presence of O, Mg, Al and Si in the interface layer suggested the formation of an AlSiMgO compound from which Si growth proceeds. The role of this interfacial layer in Si growth on glass is still being studied. Twin planes typical of Si growth on sapphire (Nolder et al., 1965) were observed on Secco-etched Si on glass.

8.2 Original Contributions

The original contributions of the author during the course of this thesis include:

- 1. The development of a model for incorporating free carrier absorption effects in solar cell equations. Rough calculations showed that free carrier absorption affects the long wavelength response of solar cells fabricated on a substrate with a resistivity of 1 Ω cm. The impact of free carrier absorption will be felt most in light trapping schemes.
- 2. The correct identification of oxidation-induced defects in laser-grooved solar cell processing. Etch pits generated by a Secco etch on finished solar cells are S-pits and not dislocation etch pits as previously thought (Chong, 1989, pp. 162-189). S-pits usually come from precipitates. Oxidation of planar surfaces can lead to S-pit generation with densities ≈7×10⁴ cm⁻² being observed. Oxidation of textured surfaces did not lead to the generation of S-pits.
- 3. The observation of thermal wave effects during pulsed laser processing of Si. Laser scribing of oxidised Si wafers reveal a dark band surrounding the scribe using the secondary emission mode of an SEM. The extent of the dark band varies with the laser pulse frequency according to $f^{-1/2}$ and is comparable to thermal diffusion lengths calculated from thermal wave theory.
- 4. The discovery of a gettering effect attributable to thermal waves generated by pulsed-laser processing of Si. Oxidation-induced precipitates surrounding a laser scribe have been gettered during the laser scribing process. The gettered region extends beyond the known heat affected region specified by the laser scriber manufacturer and displays a similar dependence on pulse frequency as the dark bands observed in 3.
- 5. The uncovering of defects induced by laser-groove processing in laser-grooved solar cells. Laser scribing of Si introduce surface recombination centres along the thermal-wave-affected zone. Dislocations are not apparent after laser scribing and it is believed that the recombination centres may be due to unknown point defects.
Dislocations up to 15 μ m away from the groove are initially observed after heavy P diffusion into the grooves. After sintering the heavily diffused grooves, dislocations multiply rapidly and may extend up to 30 μ m away from the groove.

- 6. The presentation of a gettering model suitable for laser-grooved solar cells as a result of the studies carried out on oxidation-induced defects and laser groove characterisation. The diffusion depth of P observed in EBIC images of the final groove is cosistent with preferential P diffusion along the dislocations and other probable thermal wave induced damage.
- 7. The development of spreadsheet analysis of FTIR spectra for the evaluation of $[O_i]$ and $[C_s]$ in single crystal and cast polycrystalline Si. This techniques involved the direct calculation of absorption coefficients from IR transmission spectra. Only a single high resistivity wafer is required as a reference. Free carrier absorption can also be modelled and subtracted. The advent of extended RAM and very fast microprocessors allow spectra analysis in a matter of minutes using commercially available spreadsheet software (Microsoft Excel 4.0).
- The use of video microscopy and image processing software on defect-etched samples for systematic dislocation density evaluation. Random sampling ensures accurate representation of the sample surface.
- The evaluation of cast polycrystalline materials being used at the UNSW. [O_i],
 [C_s], dislocation density and inclusion density have been characterised for the first time in our laboratory and, in some instances, for the manufacturer of the substrates.
- 10. The correlation of defects and solar cell performance for laser-grooved polycrystalline solar cells. This is the first attempt of such a study using the unique solar cell processing technique developed at the UNSW.
- 11. The evaluation of material quality of novel low temperature solution-grown Si being developed at UNSW. This involved determining carrier type and the average carrier concentration using the hot probe and four-point probe, identifying the dopant impurity via PIXE and PL, the evaluation of inclusions via

IR microscopy and EDX analysis, the verification of junction creation and junction depth measurement using EBIC and the evaluation of recombination activity due to defects using EBIC and defect etching.

12. The identification of strain in dilute-Ge Si_{1-x} Ge_x alloys grown using lowtemperature LPE. Strain is detected according to the amount of bandgap reduction occurring for a particular Ge concentration. Bandgap reductions were measured via PL measurements.

8.3 Future Work

The extensive nature of defect characterisation of Si solar cell materials provides a multitude of avenues for further work. Most of the following suggestions have already been made in the text:

- 1. The use of photoacoustic (PA) techniques for *in situ* control of laser scribe depth for solar cell grooving and cleaving. A microphone set-up similar to the one used by Miyazaki and Tanaka (1991) is sufficient for normal laser scribing frequencies currently being used.
- PA characterisation of solar cells (Kessler et al., 1991; Flaisher et al., 1989; Mello et al., 1987 and Faria et al., 1986).
- Identification thermal wave induced defects. This may involve the identification of point defects and their complexes and may require high resolution techniques.
 PA techniques may prove useful in this endeavour as the primary signal source for PA techniques is a thermal wave.
- 4. Further exploitation of thermal wave effects in laser-grooved solar cell processing. Adjustments to laser power, frequency, and table speed need to be explored further. A balance will have to be sought out between the desired thermal wave effect and optimal groove characteristics for optimal cell output. It may well be that thermal wave effects have been optimised in the search of optimal processing conditions (Chong, 1989).

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- Application of thermal wave gettering effects to solar cells and other devices.
 Pulsed laser treatments, scribing and cleaving operations, laser marking and other laser processing steps present opportunities for making use of this effect.
- 6. Extension of defect density and device output correlation studies for cast polycrystalline solar cells. More data points are needed for the initial correlation study done in Chapter 6. Attention must be given to characterisation and uniform processing of a large number of large area cells.
- The use of the EBIC linescan curve-fitting technique to evaluate grain boundary recombination velocities and intragrain diffusion lengths. ECP (section 4.3.3) studies can complement such a study by providing useful information on grain orientation (see Yasutake et al., 1990).
- 8. Further application of current characterisation techniques and development of further techniques for solution grown Si.
- 9. The incorporation of free carrier absorption effects in solar cell simulation software. Empirical parameters can be derived easily from FTIR measurements of the particular substrates being used for solar cell fabrication.

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APPENDIX A

LASER-GROOVED SOLAR CELL PROCESSING SEQUENCE

This section describes the standard laser-grooved solar cell processing sequence for experimental cells (after Chong, 1989, pp. 239-242) and for the Pilot Line (Wu Yan, 1993, private communication, Centre for Photovoltaic Devices and Systems, UNSW). Slight variations in Pilot Line processing are indicated

1) Wafer selection

p-type, <100>, 0.5 Ω cm, as-lapped Si (Pilot Line)

2) Surface Preparation

NaOH or KOH surface texture

RCA1, HF dip, RCA2 cleaning sequence

3) Top Surface Diffusion

Phosphorus solid source under nitrogen ambient

10 minutes at 800°C

20 minutes at 840°C (Pilot Line)

4) Wet Oxidation

300 to 310 nm oxide thickness.

1.5 hours 980°C (Pilot Line).

5) Laser Scribing

Groove depth 50 μm (60 μm Pilot Line). Groove width 20 μm (30 μm Pilot Line) Laser pulse frequency of 4 kHz (10 kHz Pilot Line). Table speed 2 - 3 cm s⁻¹ (3 cm s⁻¹ Pilot Line) Laser power of 4V peak to peak on oscilloscope Laser power set to 40 - 45 % on peak chuck detector (Pilot Line).

6) Groove Cleaning

NaOH etch 12% W/V KOH at 52°C (Pilot Line). RCA2 clean.

7) Groove Diffusion

Phosphorus solid source under nitrogen ambient.

3 hours at 950°C

3 hours at 940°C (Pilot Line).

8) Al Deposition on Rear

Vacuum evaporation.

Thickness of Al $\approx 2 \ \mu m$.

9) High Temperature Sinter

16 hours at 1000°C

14 hours at 980°C (Pilot Line)

10) Metallisation

Initial Ni plating Sinter in nitrogen ambient (370°C). Second Ni plating. Cu plating. Ag plating (Pilot Line).

11) Oxide Thinning for AR coatingBuffered HF dip.Oxide thickness ≈ 110 nm

12) Edge Isolation

Laser scribe rear of cell. Cleave edges.

APPENDIX B

SPREADSHEET ANALYSIS OF FTIR SPECTRA

B.1 FTIR Spectra Manipulation

Spreadsheet analysis of IR spectra was developed because such an analysis was impossible to carry out using Nicolet FTIR 520 software. Such an analysis is essential in evaluating impurities in substrates of varying thicknesses and resistivities.

B.1.1 Data Preparation

- 1 Acquire or recall an IR transmission spectrum at desired resolution and wavenumber range
- 2 If interference fringes are present, smooth the spectrum with the Savitzky-Golay curve-smoothing routine available in the FTIR software
- 3 Save the spectrum data points in ASCII format.
- 4 Convert the file into a format that will fill a column in Excel 4.0

B.1.2 Spreadsheet Manipulation

- 1 Read converted file in Excel 4.0 and format the numbers accordingly.
- 2. Load appropriate Excel 4.0 spreadsheet and linked graphs (see next section) for analysing the IR spectrum
- 'Copy' data from converted file and 'Paste' (see User's Guide Microsoft Excel
 4 0, 1992 for a description of these Excel operations) it in the transmission (T)
 column
- 4 Enter the thickness (x) of the sample.
- 5. If free carrier absorption is observable, adjust the wavelength exponent (b) until the baseline of the spectrum at the impurity peak is as flat as possible The linked graphs should help in this process. In the absence of free carrier

absorption, b is set to 0 to minimise interference from it in the calculation of impurity peak heights.

- 6 Check that the impurity peak position is correct.
- 7 The impurity concentration ([O] or [C]) is given in ppma and cm^{-3}

B.2 Excel 4.0 Spreadsheet Structure

Figure B 1 shows the spreadsheet structure for the evaluation of $[O_i]$ and $[C_s]$ in Si Absolute cell positions are indicated by row and column numbers and relative positions by square brackets (see User's Guide Microsoft Excel 4.0, 1992 for a more detailed description of the Excel 4.0 spreadsheet). Cells can contain alphanumeric data or formulas. Equation 4.4 is seen in the ABSORPTION COEFFICIENT column while Equation 4.5 is in the IMPURITY column. α_{FC} is evaluated empirically assuming $\alpha_{FC} = K \lambda^b$ (section 3.2.1) where K (R3C5 in spreadsheet) is calculated for $\lambda = 5 \ \mu m$ using a wavelength exponent b which gives the best BASELINE fit to the NET spectrum. The linked graphs consist of a line plot of the NET and BASELINE columns against the WAVELENGTH column and a line plot of the IMPURITY column against the WAVELENGTH column (e g., Figures 4.2 and 4.3) Interactive adjustment of the BASELINE is an important feature of this analysis for spectra affected by free carrier absorption. In Excel 4.0 editing a cell which affects the cells used in the graphs brings about an immediate recalculation of the affected cells and updating of the graphs. The best b value can then be obtained by entering b values until the best approximation to the spectrum baseline is achieved Conversion factors from ASTM F1188-88 and ASTM F123-86 are used in determining [O] (R1C8) and [C] (R2C8) respectively The O BASELINE (R3C8) and C BASELINE (R4C8) ensures accurate impurity peak height measurements.

The size of the spreadsheet depends on the resolution and the wavenumber range used in the acquisition of the transmission spectrum. A simple 'Fill Down' operation (User's Guide Microsoft Excel 4.0, 1992) allows the adjustment of the spreadsheet size to fit the spectrum resolution (R4C2) and wavenumber range (R1C2

| | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | C9 |
|----|------------------|------------------------|--------|---|-----------------------------|---------------|--------------------|-----------------------|--------------------|
| R1 | FIRST PT = | 2002.37 | | x (sample thickness) = | 0.0275 | | (0) = | 6.28*(R[238[C-R[2]C) | (RC[-1]/2) 1 E+ 17 |
| R2 | LAST PT - | 397,39 | | b (free carrier absorption wavelength exponent) - | 2.0 | | [C] = | 2*(R[367]C-R[2]C) | (RC[1]/2)*1 E+17 |
| R3 | (NO. PTS.) - 1 = | 416 | | K= | R[4]C[1]/(R[4]C[-4]^R[-1]C) | | O BASELINF = | (R[219]C + R[264]C)/2 | |
| R4 | INCREMENT = | (R[-3]C-R[-2]C)/R[-1]C | | | | | C BASELINE = | (R[369]C + R[370]C]/2 | |
| R6 | | | | | | | | | |
| R6 | WAVELENGTH | WAVENUMBER | Т | ABSORPTION COEFFICIENT | REFERENCE | NET | BASELINE | IMPURITY | |
| R7 | 10000/RC[1] | R[-6]C | 0.5319 | (LN((-0.49 + SQRT(0.2401 + 0.36*RC(-1)^2))/(0.18*RC(-1)))/(-R1C6) | -0.17692 | RC[-2]-RC[-1] | R3C6*(RC(-6)*R2C6) | RC[2] RC[-1] | |
| R8 | 10000/RC[1] | R[-1]C-R4C2 | 0.5319 | (LN((-0.49 + SQRT(0.2401 + 0.36 *RC[-1]^2))/(0.18 *RC[-1]))/(-R1C6) | -0.19756 | RC[-2]-RC[-1] | R3C5*(RC[-6]*R2C5) | RC[-2]-RC[-1] | |
| | • | • | | • | • | | • | | |
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Figure B.1. Excel 4.0 spreadsheet structure for $[O_i]$ and $[C_s]$ analysis in IR spectra of Si. The linked graphs consist of a line plot of the NET and BASELINE columns against the WAVELENGTH column and a line plot of the IMPURITY column against the WAVELENGTH column (e. g., Figures 4.2 and 4.3).

indicates the maximum and R2C2 indicates the minimum). A spectra obtained at a resolution of 1 cm⁻¹ over the wavenumber range 400 to 2000 cm⁻¹ generates a spreadsheet file ≈ 1.1 MB big The advent of extended RAM and high-speed microprocessors, allow IR spectra analysis to be carried out on personal computers at reasonable speeds For an IBM PC compatible 486 computer with 4 MB RAM, spreadsheet analysis of a spectrum taken at the above-mentioned resolution and wavenumber range can be done in a matter of minutes Data preparation (including spectrum-smoothing) takes less time The acquisition and analysis of such a spectrum takes around 10 minutes

APPENDIX C

LIST OF ACRONYMS

- BSD = Back-Scattering Detector
- BSI = Back-Scatter Image
- C-V = Capacitance-Voltage
- DTGS = Deuterated Tri-Glycine Sulfate
- EBIC = Electron Beam Induced Current
- ECP = Electron Channelling Pattern
- EDX = Energy Dispersive X-ray
- FTIR = Fourier Transform Infrared
- HRTEM = High Resolution Transmission Electron Microscope
- I-V = Current-Voltage
- IR = Infrared
- LBIC = Light Beam Induced Current
- NDIC = Nomarski Differential Interference Contrast
- NP = No Phonon
- PA = Photoacoustic
- PESC = Passivated Emitter Solar Cell
- PERL = Passivated Rear Locally-diffused Cell
- PIGE = Proton-Induced Gamma-ray Emission
- PIXE = Proton Induced X-ray Emission
- PL = Photoluminescence
- RBS = Rutherford Back-scattering Spectroscopy
- SEI = Secondary Emission Image
- SEM = Scanning Electron Microscope
- STEM = Scanning Transmission Electron Microscope
- TO = Transverse Optical

APPENDIX D

AUTHOR'S PUBLICATIONS

D.1 Journal Paper

 Chan, B.O., Healy, S A. and Green, M.A., 1992. "Strained Si_{1-x}Ge_x layers grown by low-temperature liquid-phase epitaxy." *Materials Letters* 14, pp 263-267.

D.2 Conference Papers

- Healy, S A, Taouk, M, Chan, B. and Green, M A., 1991 "Enhancement of sub-bandgap absorption in X-Si solar cells by alloying with germanium" *Proceedings of the 10th European Photovoltaic Solar Energy Conference*, Lisbon, Portugal, 8-12 April 1991, pp 73-74
- Shi, Z, Chan, B. and Robinson, S., 1992 "Thin film solar cells by liquid-phase epitaxy." Proceedings of the 30th Annual Conference of the Australian and New Zealand Solar Energy Society, Darwin, Northern Territory, Australia 15-18 July, pp. 339-346.
- 3 Green, M.A.; Chan, B. and Ghaemi, S. (1992), High Efficiency Crystalline and Polycrystalline Silicon Solar Cells, 4th Sunshine Workshop on High Efficiency Silicon Solar Cells, Tokyo, November.

D.3 Reports

 Green, M.A.; Wenham, S.R.; Zhao, J.; Wang, A.; Dai, X.; Milne, A, Taouk, M, Shi, J.; Yun, F.; Chan, B.; Sproul, A.B. and Stevens, A., 1992 "One-sun silicon solar cell research." *Final Report, SANDIA Contract* 66-5863, March

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- 3 Green, M.A; Wenham, S.R; Chan, B., Narayanan, S, Szpitalak, T, Yun, F and Zolper, J (1992), 18% Efficient Polycrystalline Silicon Solar Cell, *Final Technical Report* August, 1992, ERDC Project No 1360.