ABSTRACT

SEN, Indradeep. Correlation of grain-to-grain electrical properties with impurities and defects in solar grade polycrystalline silicon. (Under the guidance of Dr. George Rozgonyi.)

In this study a three pronged diagnostic approach has been adopted for the characterization of active recombination centers in thin film polycrystalline silicon. It comprises structural, chemical and electrical analysis of the various lifetime limiting defects and impurities which are responsible for the variations observed in the electrical activity across different grains.

Preferential defect etching using Wright and Secco etchant solutions provided for the structural analysis. This approach was useful in determining the nature and distribution of the structural defects and how they affect the growth characteristics. The process induced structural changes were also delineated using this approach and successfully correlated with the electrical activity observed in particular regions. The work then focuses on chemical characterization of the impurities and the analytical tools used for this purpose were Fourier Transform Infra-red Spectroscopy (FTIR) and Deep Level Transient Spectroscopy (DLTS). The chemical data were enhanced by Secondary Ion Mass Spectroscopy (SIMS) data from Astropower (AP). The effect of light elements like oxygen, carbon and nitrogen were studied in relation to their concentration, agglomeration and generation of heterogeneous nucleation centers for metallic precipitation in various grains through FTIR studies. DLTS, on the other hand, identified the metallic impurities (Fe, Cr & Al) which are acting as deep traps in the material and quantified their gettering efficiency at the grain-boundaries and extended defects in the
material. The above characterization tools were well complemented by electrical characterization through micro-wave photo-conductance (µ-PCD) decay lifetime mapping and Electron Beam Induced Current (EBIC) techniques. These two techniques facilitated the identification of the electrically active areas in the material while providing images to correlate with the etch pit data.

Through the above complimentary set of characterization tools, it was shown that the electrical activity of a grain is determined by its size and local defect density. Generally, grains less than 100 µm in diameter performed worse than the large ones. A large variation in the gettering and precipitation behavior of individual grains has been demonstrated, typically controlled by the defect clusters or “Black Spots” in the grains. Metal precipitation takes place in the as-grown as well as thermally treated samples. In the as-grown samples, SiO\textsubscript{x} complexes and other micro-defects provide the nucleation sites, whereas the same has been shown to be provided by oxygen and carbon precipitates after thermal treatment. The formation of an impurity free denuded zone occurs along the grain-boundaries (GB) while twin-boundaries act as diffusion barriers for impurities but exhibit no electrical activity, unlike the GB’s. It is also shown that oxygen precipitation after thermal treatment is aided by carbon rather than nitrogen. Furthermore, the presence of SiN inclusions in small grains is discussed in light of increased N-related IR absorption in these regions. Finally, the gettering efficiency of the thermal processes adopted by AP has been characterized by DLTS and µ-PCD measurements and it is shown that the aluminum gettering step is the most effective in this regard and determines the final diffusion length of the material.
Correlation of grain-to-grain electrical properties with impurities and defects in solar grade polycrystalline silicon

By:

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CHAPTER 1
Introduction

1.1 Motivation

The photovoltaic (PV) industry is in the process of identifying newer techniques for PV manufacturing, focused on lower costs, easier processing and higher mechanical yield of solar cells. At present the vast majority of photovoltaic cells are made from silicon due to its abundance in nature and its near ideal energy band-gap for photovoltaic use. In general, cells are classified as either crystalline (sliced from ingots or castings or grown ribbons) or thin film (deposited in thin layers on a low cost substrate). The fabrication of thin film or sheet silicon on cheap substrates is emerging as a major cost-efficient growth technique pioneered by Astropower Inc. In this method the polycrystalline sheet is grown on a low cost electrically conductive ceramic substrate over a belt furnace with the melt being cooled from the top and the bottom [1, 2]. During growth, a nitrogen-based substance on the top encapsulates the melt.

The major disadvantages of using metallurgical grade silicon as the starting material for solar cell fabrication are significantly higher transition metal impurity content and higher density of lattice defects such as grain-boundaries, dislocations and precipitates in the material after growth. Both these factors are responsible for degrading the overall cell conversion efficiency by reducing the minority carrier diffusion length. Also, diffusion length varies from grain-to-grain due to non-uniform distribution of intra-granular defects, which serve as nucleation sites for metal precipitation. The non-homogeneity of intra-granular defects is related to differences in the concentration of
oxygen, carbon and nitrogen within grains and their interactions with point defects during subsequent thermal processing thus giving rise to extended defects and metal precipitation. These extended defects can also be decorated by metallic impurities that then render the defects electrically active. Therefore, the presence of such extended defects decorated with metal near the cell active region can affect the cell parameters substantially.

This work is therefore an attempt to gain a qualitative and quantitative understanding of these dominant recombination centers in the material. It seeks to probe into the gettering of metals at grain-boundaries and oxide/carbide/nitride precipitates in the bulk with the help of various structural, chemical and electrical characterization techniques like DLTS, FTIR, \( \mu \)-PCD, EBIC and wet preferential etching. It will also attempt to study the impact of these recombination active centers on the electrical performance of the solar cell.

1.2 Solar Cell Working

Solar cells fall into the group of opto-electronic devices which convert optical energy (sunlight) into electrical energy. In general, thermally generated carriers within a diffusion length of each side of the junction field diffuse to the depletion region and are swept to the other side by the electric field. This constitutes a reverse electric current (\( I_{th} \)). If the junction is uniformly illuminated by photons \( h\nu > E_g \), the excess electron-hole pairs (EHP) generated also add to this reverse current given by (\( I_{op} \)). Thus the total reverse current with illumination is given by equation 1-1
\[ I = I_{th}(e^{\frac{qV}{KT}} - 1) - I_{op} \]  \[ - - - - - - - - - - - (1-1) \]

A solar cell may be represented by the equivalent circuit shown in Fig. 1.1 consisting of a photon induced current generator \( I_{op} \), a diode, a series resistor \( r_s \) and a shunt resistor \( r_{sh} \). \( R_L \) is

![Equivalent circuit of a solar cell](image)

**Figure 1.1** Equivalent circuit of a solar cell

the external load connected to the cell. A typical current-voltage curve of a solar cell is shown in Fig. 1.2. The open-circuit voltage \( V_{oc} \), short circuit current \( I_{sc} \), and the maximum power point voltage \( V_{max} \) and current \( I_{max} \), are also shown. For Si the voltage \( V_{oc} \) is less than about 1V. The current generated depends upon the illuminated area, but typically \( I_{op} \) is in the 10-100mA range for a junction area of about 1cm\(^2\). However, if many such devices are used to form modules, the resulting power can be significant [3].

The \( V_{oc} \) and \( I_{sc} \) are determined for a given light level by the cell properties. The maximum power delivered to the load occurs when the product \( VI \) is maximum. Referring to these values of voltage and current as \( V_m \) and \( I_m \), we find that the maximum delivered power represented by the area inside the dotted rectangle in Fig. 1.2 is less than the \( V_{oc} I_{sc} \) product. The ratio \( V_m I_m / V_{oc} I_{sc} \) is called the Fill Factor and is a Fig. of merit for solar cell design. The conversion efficiency of a solar cell is represented as the ratio of incident sun power on the cell to the electrical power generated by the cell. It is usually
Figure 1.2  I-V characteristic of a solar cell

determined under standard test conditions of 1,000 W/m² illumination and 25°C. The spectral distribution of the light is expressed in terms of an optical air mass (AM) number. AM0 corresponds to the spectrum in space, AM1 to the spectrum at the earth’s surface when the sun is overhead, AM2 when the sun is 60° off overhead, etc. Cells and modules for terrestrial use are generally measured under AM1 or AM1.5 conditions [4] and typical experimental record conversion efficiencies are 23% for a single crystal silicon cell, 18% for a multicrystalline silicon cell, 13% for an amorphous silicon cell and 35% for a GaAs/GaSb tandem cell under concentrated light [4]. The reasons for such low efficiencies include incomplete absorption of light or dissipation of a part of the photon energy as heat. Not all the solar power can be converted to electricity. Much of the photon flux is less than the silicon band-gap and is not absorbed. High energy photons are strongly absorbed and the resulting ehp’s may recombine at the surface [3]. Various methods have been developed to increase the power absorbed per unit cell area like using anti-reflective coatings, solar concentrator systems etc. Other factors that affect fill factor and conversion efficiency are imperfect junctions, recombination effects within the bulk
and surfaces, and series and shunt resistance effects [2]. Commercial module efficiencies
have been shown to be significantly less than the cell efficiencies quoted above due to
larger area of cell required, loss due to electrical mismatch of the cells and losses due to
gaps between the cells. The highest reported module efficiency for silicon is 20.5% [5].

1.3 Materials for Photovoltaics

There is large variety of silicon based materials and cell structures considered for
solar cell fabrication in order to achieve the ultimate requirements of efficiency, cost,
stability and environmental effects. These materials have either found widespread
application in the industry or are being considered as potential technologies in the near
future. Some of them are listed below [4]:

1) Single Crystal Silicon
2) Cast multicrystalline silicon (also referred to as cast polycrystalline silicon)
3) Thin-film polycrystalline silicon
4) Amorphous silicon
5) Copper indium diselenide
6) Cadmium telluride
7) Gallium arsenide
8) Multi-quantum wells
9) Iron-sulfide and
10) Nano-crystalline (dye sensitized) thin films
Of the above 1) and 2) represent the widely understood and used crystalline silicon technologies, 3) represents the low cost sheet technique commercialized by AstroPower Inc., in early 1990’s and which is the material under study in this work from Chapter 3 onwards, 4) 5) and 6) represent the popular thin film materials used effectively nowadays, 7) and 8) are two distinctly different high efficiency approaches while 9) and 10) are about new “super-low-cost” thin-film options.
CHAPTER 2

Thin-Film Polycrystalline Silicon

The main objective of developing thin polycrystalline silicon solar cells was to derive cost benefits by using thin films and at the same time retaining the high performance obtained from crystalline silicon. This has prompted a lot of research interest in the past decade to develop thin film poly crystalline Si solar cells on low cost substrates. Popular thin film techniques include Si-on-ceramic, Si-on-glass, and silicon growth/deposition on low quality Si substrates etc. [1]. The thin film silicon on ceramic substrates was developed and commercialized by Astropower in early 1990’s and goes by the trademark “Silicon-Film” solar cell technology.

2.1 Astropower Silicon-Film manufacturing process.

AstroPower (AP) produces APx-8 polycrystalline Silicon-Film solar cells as well as single crystal solar cells manufactured from recycled wafers at its Pencader facility, Newark, Delaware. This plant has a capacity to produce 15MW of power per year through its single thread production line (STPL) that has been developed to produce APx-8 solar cells. These advanced solar cells are 20.8 cm on each side and are cut from 110 cm long sheets [6]. The details of the sheet growth process have not yet been disclosed in detail but a generic description of the process revealed that it is grown on a conveyer with the molten silicon being supported on a low cost conducting ceramic substrate. The thickness of the silicon film varies from 30-50 µm[1] over a total sheet thickness
approximately >1mm. During growth the sheet is cooled from the top and the bottom and it is covered by a nitrogen based substance from the top. The sheet pulling speed is 3.1m/min while the sheet growth speed is of the order of 1cm/min. The sheet pulling speed is not equal to the sheet growth speed because in this approach of sheet growth the heat of solidification is removed perpendicular to the sheet pulling direction. The growth speed is therefore comparatively lower which consequently reduces the temperature gradient at the solid-liquid interface, resulting in lesser thermal stress induced material defects [2].

### 2.2 Grain Size and Growth Speed

The requirements for single crystal silicon growth are [2]:

a) relatively pure starting material.

b) a technique for seeding.

c) temperature gradient at the solid-liquid interface should approach zero.

If any of the above requirements are not met, it will result in polycrystalline and/or dendritic growth. Normally, all conventional low cost substrate silicon growth approaches start with a relatively pure starting material in order to minimize defect generation due to constitutional supercooling of impurities. Also these approaches do not employ a preferential seeding procedure thus resulting in polycrystalline material. The temperature gradient at the solid-liquid interface determines the growth speed of this sheet silicon. A steep temperature gradient will thus ensure faster growth rates. The inherent problem with faster growth rates is the introduction of thermal induced stresses.
In the worst case these stresses can lead to sheet deformation [7]. Even if deformation is absent the presence of stress induced structural defects, mostly dislocations, can lead to degradation of electrical properties of the solar cell.

Conventional sheet technologies also suffer from the drawback of low areal generation rate which affects the throughput directly. Areal generation rate \( (\text{d}A/\text{d}t) \) is proportional to the product of growth speed \( (\text{d}x/\text{d}t) \) and the area of the solid-liquid interface (given as \( w \times l \), where \( w \) and \( l \) are the width and length of the solid-liquid interface) and inversely proportional to the effective thickness \( (s) \) of the solar cell as given by equation 2-1

\[
\frac{\text{d}A}{\text{d}t} = \frac{w l (\text{d}x/\text{d}t)}{s} \quad (2-1)
\]

In such growth techniques, the length of the interface is equal to the thickness \( s \) of the solar cell and therefore, \( \text{d}A/\text{d}t \) is essentially equal to the product of \( w \) and growth speed \( \text{d}x/\text{d}t \). Also for these processes, the direction of growth is collinear with the pulling direction and therefore the grains grow long and wide along the direction of sheet motion. However, high areal throughput can be achieved by separating the growth direction from the sheet pulling direction as illustrated in Fig. 2.1. Such a growth technique has been successfully implemented by AP in their Silicon-Film process.

\[\text{Figure 2.1} \quad \text{Schematic diagram of high areal throughput sheet growth process}\]
In the above Fig. the ratio $l/s$ is larger than unity and therefore for the same growth rate as used in conventional technologies, the areal throughput and the pulling speed $V_p$ is higher in this case. Sheet pulling speed $V_p$ is related to the growth speed through equation 2-2

$$V_p = l/s (dx/dt) \quad \text{(2-2)}$$

It has been shown that higher pulling speeds (>10 cm/min) affect the structural and electrical properties of the cell in three distinct ways. Firstly, the material is comprised of columnar grains, typically in the size range of 100 to 1000 µm and the grains are comparable to the sheet thickness. Secondly, in all higher areal speed approaches the heat of solidification is removed perpendicular to the plane of sheet growth and the actual growth rates are reduced. Therefore, the thermal stress induced defects are greatly reduced. Thirdly, the observed minority carrier diffusion lengths are smaller than and decrease with grain size. The conversion efficiencies reported for these high speed materials are in the range of 10-12% indicating that the grain boundaries are not the limiting factor in these mid-sized grain materials and further improvement of diffusion length and efficiencies could be achieved by post growth processes to improve the material properties and device performance [2].

### 2.3 Astropower Solar Cell Manufacturing Process

The advanced APx-8 solar cell process sequence contains 11 discrete operations and no cassette handling steps which makes it a continuous single thread production line. Wafers are transferred between stations in magazines which simplify the process sequence and reduce the amount of handling. The throughput of the line is determined by
the initial sheet formation step which is 3.1m/min. Each of the process steps employed for manufacturing the APx-8 solar cells is described below [6].

**Sheet formation:** The Silicon-Film single thread production line is based on a polycrystalline sheet machine that operates at a sheet generation speed of 3.1m/min. The 110-cm long sheets are cut into five APx-8 wafers and loaded into coinstack magazines for transfer to the impurity gettering system.

**Pre-Diffusion Gettering:** Wafer surface preparation consists of three parts: pre-getter surface cleaning, impurity gettering and pre-diffusion surface etching. The sized wafers are cleaned and the transferred to a high temperature belt furnace for impurity gettering (1100°C in N₂ ambience or 1300°C in air). The gettered wafers are loaded into coinstack magazines for transfer to the surface etch system.

**Surface Etch/Junction Diffusion:** Once the wafers are gettered, they are etched using an in-line caustic etch system and then immediately diffused in a rapid thermal IR belt diffusion furnace. The diffusion temperature and duration is not known accurately. After the diffusion cycle the wafers are quenched at a rate of 1-10°C/min. The diffused wafers are unloaded from the furnace belt and transferred to the junction isolation system in magazines.

**Junction Isolation:** The emitter junction is isolated from the back surface by abrading the diffused layer at the wafer edges (edge isolation). This being a dirty process, the system is purposely kept separate from any other system. The wafers are the transferred to the diffusion oxide etching system.

**Diffusion Oxide Etching/PECVD Anti-reflection (AR) Coating:** The diffusion oxide is removed by etching the wafers in dilute HF solution. This process is performed using a
continuous wet chemical process system. The wafers are immediately transferred to an in-line PECVD system where they are coated with a silicon nitride layer. This process provides the AR coating and also hydrogen passivation as shown by Hezel and Jäger [8]. When this structure is annealed or fired at 500-600°C hydrogen diffuses into silicon [9]. The wafers are shifted to the contact metallization system after this step.

**Contact Metallization:** Front and back contact metallization is based on thick film inks that are printed and “spike” fired using infra-red belt furnaces. The contacts are fired through the SiN AR coating. To reduce ink costs, the back metallization incorporates a co-fired aluminum “field” region outside of the solder tabbing areas. There are three printing operations, two low temperature ink-drying steps, and one high temperature co-fire process as follows:

1. Print Al-Ag bus bars and dry at 250°C
2. Print Al contact (BSF) and dry at 250°C
3. Print Ag gridlines and bus bars and spike fire at 900°C.

The metallized wafers are loaded into coinstack for transfer to the test-and-sort system.

**Test, Sort, Inspection:** Completed solar cells are electrically tested and sorted into power categories. A vision system on the cell tester-sorter system inspects for any manufacturing defects prior to packaging. This eliminates an additional visual final inspection. The tester-sorter system delivers cells in coinstacks.

Immediately after the junction diffusion step the wafers undergo a post diffusion annealing cycle. The temperatures and durations followed during this cycle are given in Table 2.1. This is a very critical step towards the final cell efficiency since it is intended
to getter the lifetime killing metallic impurities at the nucleation sites offered by oxygen precipitates and defects in the bulk.

**Table 2.1** Details of post diffusion anneal procedures used by Astropower.

<table>
<thead>
<tr>
<th>Cycle step</th>
<th>Anneal Temperature (°C)</th>
<th>Duration</th>
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<tbody>
<tr>
<td>1</td>
<td>1060</td>
<td>3 hr</td>
</tr>
<tr>
<td>2</td>
<td>920</td>
<td>3.5 min</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>6 hr</td>
</tr>
<tr>
<td>4</td>
<td>Quenched to room temperature</td>
<td>Rate not known</td>
</tr>
<tr>
<td>5</td>
<td>800</td>
<td>15s</td>
</tr>
<tr>
<td>6</td>
<td>780</td>
<td>15s</td>
</tr>
</tbody>
</table>
CHAPTER 3
Factors Limiting Solar Cell Efficiency

The upper limit on silicon cell efficiency as calculated for one-sun illumination assuming ideal cell structures, complete light trapping properties and highly passivated surface and bulk regions is 33% [5, 10]. More than two-thirds of the total losses in such an ideal cell are attributed to spectral mismatch associated with the different wavelengths of the incoming photons and one band-gap for absorption [4]. Recombination mechanisms intrinsic to indirect band-gap semiconductors like Auger recombination further reduces the maximum efficiency achievable to approximately 29%. The problem of spectral mismatch can be addressed to by using multi-bandgap structures (tandem junctions) with the band-gap decreasing from top to bottom. Limitations to conversion efficiency intrinsic to a material system include $V_{OC}$ and fill factor limitations. $V_{OC}$ can never exceed the built-in potential because if it did the excess majority carriers on the two sides of the junction would reduce the built-in potential and the excess minority carriers in the quasi-neutral regions could no longer be separated. With regards to fill factor, it is seen from Fig. 1.2 that only the area in the rectangle bounded by $V_m$ and $I_m$ contributes to the power delivered to the load. The remaining power between the curve and the rectangle is lost through series and shunt resistances [10]. Other factors like surface and bulk recombination which directly affect $V_{OC}$ and $I_{SC}$ further degrade the efficiency via non-radiative recombination mechanism [11]. This imposes certain quality standards for the silicon material and surface passivation techniques used. Extensive research has been
done to understand and minimize the deleterious effects of bulk defects and surface/grain-boundary recombination in solar grade polycrystalline silicon.

3.1 Global Defect Model for Photovoltaic Silicon

An important area in the study of solar cells is the identification of efficiency limiting defects in the material. These defects which control the electrical properties of the material may be associated with either structural defects (such as grain boundaries dislocations, stacking faults, micro-precipitates) or impurities. Therefore, it is important to find not only the dominant recombination active defects but also to understand their chemical nature and identify the factors which affect their formation and recombination properties [12]. The recombination properties of crystal defects are mainly defined by recombination-active impurities decorating the particular defects, i.e the recombination activity is not an intrinsic defect property [13].

The most common type of crystal defect is the native point defect- vacancy and self-interstitial. Point defects will exist in the crystal in equilibrium at all temperatures above 0K because the presence of such defects minimizes the free energy of the crystal [14]. The interaction of point defects with impurities, substrate dopants and process ambience can be correlated to cell efficiency through specific extended defects (dislocations and stacking faults) and precipitates [15]. An attempt to model this interaction has been made in Fig. 3.1 which shows the global defect model for photovoltaic silicon. At the center of the model lies the ultimate objective of solar cell efficiency or diffusion length. The circle adjoining the innermost circle lists the various methods of PV silicon growth. The numbers against each type of material indicate the
commonly encountered defects in each material. As pointed out above, impurities are the major contributors of electrical activity of defects and are therefore of utmost importance in the study of recombination activity of various defects in solar cells. Thus, the model in Fig. 3.1 highlights them at the top. Impurities have been classified depending on their electrical and chemical activity as metallic (Fe, Cr, Ni, Cu) and non-

Figure 3.1 Global defect model for photovoltaic silicon
metallic (O, C, N) species. The metallic impurities have a stronger impact on the lifetime due to their deeper energy levels in the silicon band-gap. On the other hand, the light non doping impurities like oxygen, carbon and nitrogen involve in a complex interaction with the host silicon lattice and the structural defects which may modify their electrical activity. Normally, oxygen occupies an interstitial position in the silicon lattice after growth and its concentration is of the order of $10^{18}$ cm$^{-3}$. Carbon on the other hand occupies substitutional sites since it can easily replace silicon atoms by virtue of being in the same column in the periodic table as silicon and having a smaller atomic radius as compared to silicon. After thermal processing, formation of SiO$_x$ precipitates takes place depending on the processing temperature. These silicon oxide based precipitates have been used to advantage in IC industry to reduce impurities in the device active regions by a process called internal gettering (IG). However, in photovoltaic materials, since the entire device thickness is used as the active region of the device, these SiO$_x$ precipitates can act as recombination centers for carriers via strain fields created around them. Carbon and nitrogen have been shown to enhance the formation of this internal oxide depending on their concentrations and processing conditions [16, 17].

As shown earlier in section 2.2, the thermal stresses generated due to rapid sheet growth can cause a variety of structural changes in the material. Firstly, these stresses can give rise to most common extended defects like dislocations, stacking faults and grain-boundaries shown in the left half of the inner annular band of Fig. 3.1. Some other extended defects are generated due to interaction of point defects with metallic and non-metallic impurities. Examples of such defects are voids, swirls, precipitates shown in the right half of the inner annular band of Fig. 3.1. Some interesting interactions include the role of oxygen in nucleation of swirl defects which are believed to be condensed supersaturated interstitials [18] and formation of haze or saucer-pit defects due to interaction of self interstitials with metallic impurities [19]. The role of vacancies in the formation of precipitates due to
recombination with interstitials is well known. Recently, Rozgonyi et al. demonstrated the role of V-O complexes in nucleation of the initial silicon oxide and voids in the material [20]. These reactions are represented by the thick arrows relating vacancies with voids and precipitates in Fig. 3.1.

Polycrystalline silicon is characterized by a significantly higher metal content due to the poor quality of semiconductor grade silicon used as a starting material for its growth. This is further aggravated by the faster pulling and solidification rates employed during its growth. The latter factor renders it ineffective to the phenomenon of impurity segregation between the liquid phase and the growing sheet as achieved in CZ or FZ technology [21]. During further processing, there is also the possibility of contamination by metallic impurities most commonly encountered during high temperature furnace treatments. The source of such contaminants is normally the quartz tubes used in diffusion furnaces and other furnace components. Since the Astropower junction diffusion process takes place in belt furnaces which do not employ quartz tubes and it’s a rapid thermal process, the extent of contamination during this step is greatly minimized.

Once within the crystal, impurities in isolation can act as strong recombination centers or can be precipitated at crystallographic defects, with the combined defect acting as an effective recombination site. As mentioned above the recombination properties of extended crystal defects are mainly defined by the metallic impurities decorating the particular defects. Therefore, if defects are present near the junction or in the region within one or two diffusion lengths of the junction, it can result in a sharp decrease in $V_{OC}$ of the device if these defects are decorated with metals. It is therefore absolutely necessary to remove these metallic impurities from the active device regions or render them electrically inactive. This is achieved through appropriate passivation techniques and a phenomenon known as “gettering” highlighted at the bottom of the inner annular ring in Fig. 3.1. The
small red arrows connecting gettering to the various extended defects indicate the possible gettering agents or heterogeneous nucleation centers. When gettering is achieved by means of extended defects present in the bulk, it is termed as *intrinsic gettering* although this term is used primarily for referring to gettering through silicon oxide precipitates in the bulk. Another technique shown in the model employs Al, P diffusion and this method is classified as *extrinsic gettering* mechanism and it is widely used in solar cell processing.

The global defect model for PV silicon presented in Fig. 3.1 therefore suggests a strong relationship between metallic impurities and crystal defects which are responsible for lowering the overall cell efficiency. The remaining of this work will therefore focus on understanding the electrical activity of crystal defects and their impact on cell parameters, methods to minimize the deleterious effects of impurities by means of gettering and finally report the characterization results of these defects and impurities.

### 3.2 Electrical Activity of Extended Defects

As mentioned above polycrystalline silicon is characterized by a lot of extended defects. Therefore, use of poly-Si as a material for solar cells demands a careful study of these defects with respect to their structural and electrical properties. The most common type of extended defect found in poly-silicon is a dislocation and its formation results in two important effects. First, band bending occurs in the vicinity of a dislocation due to the elastic distortions or localized stresses associated with it. Secondly, dangling bonds are created along the core of the dislocation giving rise to deep states in the band-gap [22, 23]. The density of these bonds for dislocations can be more than $10^7 \text{ cm}^{-1}$ but most of them undergo core reconstruction as described later in this sub-section. These dangling bonds contribute towards the intrinsic electrical activity of dislocations and grain-boundaries whereas the
extrinsic properties are associated with their interaction with a variety of other kinds of defects, in particular with impurities which can decorate them and change its properties.[22].

Many models have been proposed by various researchers to account for the electronic properties of dislocations. One such widely used model by Schröter and Labusch predicts that dislocation bands are half-filled in neutral state, see Fig. 3.2(a). This hypothesis can be used to define the electronic behavior of perfect, clean dislocations (having Burgers vector a/2<110> and gliding along {111} planes) in p-type semiconductor wherein it can be assumed that dopant atoms accept electrons from the partially filled band of the dislocation. Thus dislocation behaves as a donor. A space charge region is formed in this case and consists of a positively charged dislocation surrounded by negatively charged acceptor ions as shown in Fig. 3.2(b).

If the free carrier densities p & n are neglected, the radius of a space charge cylinder is given by the following expression:

$$ R = \left( \frac{F(E)}{\Pi C(N_a - N_d)} \right)^{1/2} $$

---

**Figure 3.2** Schematics showing (a) dislocation band models by Schröter and Labusch and (b) space charge region around a positively charged dislocation in a p-type semiconductor.
where \( F(E) \) is the Fermi distribution function, \( C \) is the spacing between dangling bonds and \((N_a - N_d)\) is the net acceptor concentration. The presence of the space charge cylinder creates a potential barrier at the dislocation which can influence the cell parameters like \( I_{SC} \). The existence of space charge cylinders around a dislocation can also reduce the conductivity of the crystal in directions both parallel and normal to the dislocation lines. However, this effect depends on the dislocation density and their distribution [23].

Thus, as shown above, the electrical activity of a/2<110> perfect dislocations are attributed to presence of dangling bonds along the core of the dislocation. These perfect dislocations can dissociate into two Shockley partials (a/6<112>) with orientations which depend on the orientation of the perfect dislocation. This increases the free energy of the dislocation system locally, and the cores of these partials can undergo reconstruction to lower the system free energy and eliminate dangling bonds. Hirsch [24] has found that 30º Shockley partials can be reconstructed in this way. Thus, electrical activity of dissociated Shockley partials can vary with the orientation of the perfect dislocation [23], and in most cases, as pointed above, these partials tend to pair rendering the dislocations electrically inactive due to absence of dangling bonds.

Besides the deep levels associated with dangling bonds, shallow states associated with strain field in the vicinity of the dislocation core also contribute towards their electrical activity. However, the activity can be observed only at low temperatures by Electron Beam Induced Current (EBIC) technique [13].

The extrinsic nature of electrical activity of dislocations and other extended defects arises from recombination-active impurities decorating the particular defects introducing deep levels in the band-gap. The extent of this recombination activity has been quantified in terms of the contrast observed in EBIC. It has been shown by many researchers that the
magnitude of this contrast and its temperature dependence depends on the degree of contamination of the crystal defects [25, 26].

3.2.1 Model to Quantify Recombination Activity of Contaminated Dislocations

A model that combines the effect of shallow intrinsic defect levels discussed above and deep contamination induced centers has recently been proposed by Kveder & Kittler [13, 27] and shown schematically in Fig. 3.3. It shows the band scheme around a dislocation with shallow dislocation bands ($E_{De}$, $E_{Dh}$) related to 1-dimensional dislocation bands induced by dislocation strain fields and deep contamination related levels near the core ($E_M$). The main recombination channels are indicated by arrows. For details of this model, the reader is referred to the article by Kveder et al. in Ref. [27].

Figure 3.3 Model to show charge carrier recombination at dislocations. Recombination at clean dislocations occurs via direct exchange between the 1-dimensional dislocation bands $E_{De}$, $E_{Dh}$ (A). With deep centers $E_M$ present close to the dislocation core, recombination processes involving the deep level take over (B), i.e., $E_D < - > E_M$, and (C), i.e., $E_{C,V} < - > E_M$. 
3.2.2 Electrical activity of other extended defects

The surfaces of intrinsic and extrinsic stacking faults (SF) and coherent twin boundaries are not electrically active since they are coherently bonded to each other by the faulted and un-faulted regions and dangling bonds are not created. However, partials bounding various stacking faults should be electrically active due to the presence of dangling bonds [23, 28]. Extrinsic mechanisms due to segregation of impurities can also render SF’s electrically active [28]. Grain-boundaries, semi and non-coherent precipitates can be treated as assemblage of dislocations or bound by dislocations. Therefore in terms of electrical activity, these kinds of extended defects can be analyzed like dislocations.

3.3 Influence of Defects on Cell Performance

Extended defects are known to influence the performance of solar cells. As the grain-size increases compared to the cell thickness, grain-boundary recombination is no longer a limiting factor for achieving high cell efficiencies. Hence, the dominant effect on the cell performance comes from intra-granular defects. However, GB’s are potential centers of metal precipitation and segregation of oxygen and carbon at GB’s can affect the cell characteristics by providing shunt paths. The effect of these two major classes of extended defects on cell performance will be discussed briefly in this sub-section.

A) Grain-boundaries (GB):

It has been mentioned earlier that GB’s are an assemblage of dislocations and as far as electrical properties are concerned, they can be treated as dislocations. The space-charge
region accompanying GB’s due to accumulation of fixed charges can produce potential barriers. The carrier transport over these barriers can lead to non-ohmic behavior, higher resistivity and degradation of fill factor [2]. In addition GB’s act as effective traps due to segregation of metallic and light impurities like oxygen and carbon thereby providing a mechanism for producing physical shunts across junction regions [29]. This increases the dark reverse current of the junction diode and limits the photo-generated current [30]. The shunting increases as the recombination activity of GB’s increases. This effect has been observed after high temperature treatments like phosphorous diffusion and attributed to segregation of metal and O/C precipitates at GB’s [31]. The geometry of the GB with respect to the junction can also affect the photocurrent. If the GB is horizontal and close to the junction, it can severely reduce the photocurrent since then the carriers will be recombined at the GB before reaching the junction electric field. If the GB is vertical, then carriers lying closer to the GB than to a junction edge will be rendered inactive [29]. Also, major photocurrent and photovoltage losses have been reported from non-planar GBs; planar GB’s have relatively small effect [32].

B) Intra-granular defects

For large grains, intra-granular defects play an important role in determining the solar cell properties. The analysis of intra-grain effects has found dislocations to influence the cell performance the most. For polycrystalline silicon it has been reported that dislocation density is highest in a plane perpendicular to the growth direction. Lowest dislocation densities are observed for dislocations that lie on (110) planes and have {112} growth directions. Simple slip dislocations are seen only in the grains with low dislocation density. These are believed to be the regions of low thermal stresses which follow dislocation generation along [111] slip
planes [32]. However, these conditions are highly dependant on growth and processing conditions and therefore cannot be generalized to poly silicon grown by other techniques.

The first degradation factor due to dislocations comes from their shunting effect which as explained in relation to GB’s, increases the dark current of the diode. This enhancement in the dark current is linearly proportional to the dislocation density and it reduces the $V_{oc}$ and $I_{sc}$ of the cell [32, 33]. Moreover, gettering of metallic and non-metallic impurities at the dislocation introduces deep levels in the band-gap and enhances their recombination activity. This has a direct impact on the diffusion length $L_D$. It has been shown by Kittler, McHugo, Weber and many other researchers that $L_D$ is low in regions with high dislocation density. These bad regions account for low open circuit voltage of the cell and decrease the overall cell performance. The degradation in $L_D$ has been explained by the high binding energies of transition metals to the defects which makes it difficult to remove them by external gettering processes [12]. Other extended defects like stacking faults, twins, precipitates etc. also affect cell characteristics by reducing the $I_{sc}$. 
CHAPTER 4
Gettering and Passivation

4.1 Principles of Gettering

Gettering is a technique whereby impurity concentrations are reduced in the device region of the wafer by localizing them in separate, predefined regions of the wafer. All gettering techniques are based on the fundamental physical principles of non-equilibrium (relaxation) gettering and equilibrium (segregation) gettering. Relaxation gettering requires impurity supersaturation which typically occurs during cooling from high temperatures. Any mobile or supersaturated impurity will precipitate (relax) in regions of the wafer with high concentrations of precipitation sites (like SiO$_x$ precipitates in the bulk). The device or surface region is depleted of oxygen by a prior out-diffusion treatment to create a zone popularly called the denuded zone (DZ). Thus the DZ contains lower concentration of oxygen precipitates and therefore lesser nucleation sites for supersaturated impurities. This difference in precipitation rates creates a dissolved impurity concentration gradient, which causes the diffusion of these impurities away from the device active region into the bulk, towards gettering sites [34]. An example of relaxation gettering could be the internal gettering commonly employed in IC industry. The AstroPower pre-diffusion gettering step done at 1100ºC is believed to create such a DZ near the surface of the wafer. This will facilitate the formation of the solar cell junction on clean silicon minimizing recombination in the diode space-charge region. This process improves $V_{OC}$ and FF of the cell [35].

Segregation gettering is based on a gradient or a discontinuity in the effective impurity solubility. The region of higher solubility acts as a sink for impurities from the
lower solubility region. This is because the electro-chemical potential of a dissolved impurity, for the same dissolved concentration, is lower in the regions with higher equilibrium solubility. The segregation effect can result from (i) a difference in phase, for example between crystalline and liquid silicon during crystal growth; (ii) a difference in material, for example silicon and aluminum layer deposited on the back side of the wafer surface (this method is followed by AP); (iii) a difference of doping levels in different areas of the wafer which results in gettering due to the effect of the Fermi level on the solubility of metals or due to formation of metal-acceptor pairs; and (iv) strain, which may increase or decrease the local solubility of metal impurities (a technique used in proximity gettering). The advantage of segregation gettering over relaxation gettering is that no supersaturation is required. Thus low impurity concentrations are quickly achieved at elevated temperatures where the impurities diffuse quickly, and even small contamination levels can be further reduced by gettering [34]. The commonly accepted model for segregation (extrinsic) gettering is as follows [36, 37]:

1) Extraction of impurities from grain-boundaries, lattice imperfections, clusters, precipitates, etc. to interstitial sites.
2) Fast diffusion of impurities through the crystal.
3) Trapping at gettering sites and

A fourth step consisting of removal of the defected layers can also be added for solar cell processing. In general, high temperatures are needed to enable both the extraction and the diffusion of the impurity. Several surface treatments such as phosphorous in-diffusion, metal film deposition and subsequent annealing, $S_iN_4$ film deposition followed by thermal treatment and mechanically damaging the surface have been shown to provide such sinks [37]. Out of these methods, the first two, namely phosphorous in-diffusion on
the front surface and aluminum alloying to create a back surface field (BSF) have been effectively used in solar cell processing to enhance the diffusion length $L_D$. These two gettering methods will be described in detail in the next sections.

4.2 Phosphorous-diffusion Gettering

Phosphorous gettering is achieved by the emitter diffusion step in solar cell possessing thereby eliminating the requirement of a separate gettering step. The diffusion temperature and the drive-in time are however critical parameters to determine the gettering efficiency. It is particularly suited for substitutional metals whose gettering is limited by diffusion [34]. This technique is only partially explained by segregation gettering and most of the gettering effect is accounted for by injection of silicon self-interstitials from the front surface into the bulk [34, 38]. Phosphorous gettering POCl$_3$ is more efficient than any other P-diffusion treatments as it is an effective way to attain very high P concentration at the surfaces (around $10^{21}$ cm$^{-3}$) [39]. Such a high concentration leads to SiP precipitate formation which create gettering sites and in the process help in injecting silicon self interstitials into the lattice. This results in a non-equilibrium concentration of silicon interstitials in the lattice. In thermal equilibrium the concentration of metal atoms on substitutional sites $M_s$ is far greater than the concentration of metal atoms on interstitial sites $M_i$. Consequently, out-diffusion of metal atoms on substitutional sites occurs by transformation of $M_s$ into $M_i$. The metals are trapped by the combined effects of an increased solubility in heavily n-type doped regions and the trapping of these metal interstitials at the extended defects that grow in the P-diffused region (SiP precipitates) or deeper in the bulk. In thermal equilibrium, the process of
transformation of $M_s$ to $M_i$ can be represented by the reaction where $I$ represents the silicon self interstitials

$$M_i \rightarrow M_s + I$$

The transformation process is self-limiting, by the above reaction, because it produces an undersaturation of $I$. Phosphorous diffusion relieves this limitation by injecting $I$ and driving the equilibrium more towards $M_i$ [10]. Another advantage of phosphorus in poly silicon is its preferential diffusion at crystallographic defects near to the cell surface. This would be expected to result in those defects being engulfed in P-rich regions thus suppressing their electrical activity as minority carrier sinks. Therefore, it is beneficial to employ higher diffusion temperatures and longer drive in times in high dislocation density material [19, 40].

4.3 **Aluminum back-surface field gettering**

Aluminum back surface gettering has become a widely accepted gettering method for thin film silicon solar cell fabrication. As the thickness of solar cells keeps on reducing, back surface field becomes more and more important in order to reduce the back surface recombination velocity and to increase conversion efficiency [41]. Al diffusion creates a $p^+$ layer, which can reflect electrons and avoid recombination at the back surface. This is called the back surface field effect [39]. However, BSF in case of APx-8 process is of no consequence since the wafer thickness is far greater than the diffusion length and any increase in $L_D$ is attributed to segregation of metallic impurities in the $p^+$ regions at the bottom of the wafer. Al gettering occurs by deposition or screen-printing of a thin layer of Al (1µm) on the back side of the wafer followed by heating which forms an Al-Si alloy. The heating (firing) process is carried out well above the
eutectic temperature (577ºC) in order to ensure that Al alloys with Si and melts at this temperature [39]. In the Apx-8 wafers the final spike firing done at 900ºC during the contact metallization step forms the Al-Si alloy which also helps in forming a good ohmic back contact. The solubilities of various metals like Fe, Cu, Ni and Au are orders of magnitude higher in this Al-Si melt than the silicon bulk over a wide temperature range [10]. For example Hieslmair et. al. [42] found that the segregation coefficient of Fe between silicon and Al layer is $10^5 – 10^6$ at temperatures from 750ºC to 950ºC. It has also been shown by Rohatgi et.al. that Al gettering when combined with SiNx co-firing in hydrogen ambience accelerates production of atomic hydrogen which is used for defect passivation [43]. The authors proposed a model explaining this passivation effect. According to them Al-Si alloying, which is known to inject excess vacancies in the silicon lattice, initiates a vacancy enhanced dissociation of molecular hydrogen. Atomic hydrogen thus created migrates towards the defect sites and are retained at these sites providing the passivation effect [39]. This effect could then possibly explain why the silicon nitride AR coating in case of AstroPower wafers is done before the contact metallization step.

Phosphorous and aluminum (P/Al) co-gettering has been found to enhance the gettering effect obtained from these two treatments when done individually. The co-gettering concept involves annealing the P-diffused layer and the Al alloy together in a single high temperature step [37, 39]. The high temperature co-firing treatment during the contact metallization step in the APx-8 process is believed to benefit partially from such a simultaneous P/Al gettering. Work done by various researchers on a comparative study
of separate P and Al gettering and P/Al co-gettering have indicated increase in diffusion length after the latter process for multi-crystalline silicon [39].

4.4 Effectiveness of P-diffusion gettering (PDG) and Al gettering (AlG) in poly-Si

Polycrystalline silicon is a very inhomogeneous material with localized regions of high dislocation density and large impurity and precipitate concentrations. The grain-size and grain-boundary recombination also varies randomly across different grains. It was shown earlier by Bailey et. al. [44] and McHugo et. al. [45] that grains with higher dislocation density resulted in lower diffusion lengths and higher iron precipitation rate than grains with lower dislocation density. The grains with higher concentration of dislocations and micro-defects trap and bind the transition metals inside the grain, whereas a lower defect concentration in good grains allows transition metals to diffuse through the grain on cooling leaving very small concentrations of saturated metals. Experiments with intentional Fe contamination in mc-Si followed by PDG or AlG revealed that Fe is strongly bound to the dislocations in bad grains and this strong binding energy of metals to these defects have been suggested to be the reason for low effectiveness of the above gettering techniques [45]. One of the reasons suggested and experimentally proved by McHugo et. al. was that Fe forms stronger bonds than iron silicides to the defects. X-ray absorption spectra of Fe precipitates in mc-Si showed that the precipitate consisted of neither iron nor iron silicide, but is rather iron oxide or iron silicate. Iron oxides and silicates are much more stable and difficult to dissolve than silicides [46]. A second explanation for the gettering resistance of precipitated Fe was
provided by Plekhanov *et.al.* who observed that if the total amount of Fe precipitated within a grain is higher than its equilibrium solubility at the gettering temperature, then precipitate dissolution will be limited by diffusion of Fe towards sinks [47]. Tan *et.al.* however, proved by simulation and experiments that the response to AlG is indeed poor at temperatures below about 900ºC and for times less than 1hr. Their simulation and experimental results went on to demonstrate that extended high temperature AlG can improve minority carrier diffusion length in these low quality crystal regions and homogenize the electrical properties of mc-Si [48]. The APx-8 high temperature co-firing process is carried out at 900ºC by a spike annealing treatment. This step is therefore very critical for improving the $L_D$ in these wafers. Also by carrying out the contact printing processes at a low temperature of 250ºC helps in minimizing the introduction of metallic contaminants from the IR belt furnace.

PDG has been shown to be affected by oxygen in mc-Si wafers where $[O_i]$ is higher than $6 \times 10^{17}$ cm$^{-3}$. This is due to the formation of oxygen precipitates in the wafer during extended POCl$_3$ diffusion steps. This sets up a competition between internal gettering by oxygen precipitates and external gettering by P-diffused layers [39]. Further, oxygen precipitates are very efficient internal getters and do not reemit metals into the bulk easily when they have a high strain field associated with them [49].

PDG and AlG efficiency has also been shown to be limited by carbon concentration. Mahfoud *et.al.* and Heilsmair *et.al.* observed this effect and tentatively attributed it to an interaction between carbon and iron suppressing the gettering [39].
4.5 Hydrogen Passivation in Solar Cells

Hydrogen passivation is widely used in solar cell processes to passivate dopant atoms, grain-boundaries, intra-granular defects like dislocations, dissolved and precipitated impurities (metallic and non-metallic) or impurity-defect complexes [9]. Hydrogen is introduced in silicon after deposition of a hydrogen rich silicon nitride layer by PECVD method [8] which not only acts as an anti-reflection coating, but also passivates the emitter surface of the cell. When this structure is annealed or fired at 500°C-600°C hydrogen diffuses into silicon. In p-type material it exists in a positive charge state ($\text{H}^+$) and it is a very fast diffuser ($D \sim 10^{-10} \text{cm}^2$/s at RT). Hydrogen diffuses easily through dislocations and grain-boundaries (GB) and modifies the dopant profile close to the surface or passivates the deep level associated with the dislocations and GB’s. The mechanism by which this passivation occurs is not well understood to date, but a H-defect, H-impurity type complex reaction has been ascribed for this behavior [9]. The electrical activity of crystallographic defects attributed to their interaction with various kind defects and impurities is associated with deep level centers [22]. Hydrogen has been shown to have excellent passivating effect on these deep level centers and it also reduces the potential barrier at GB’s and dislocations, improving the cell I-V characteristics [30]. Isolated metallic impurities like Fe, Cu, Cr are passivated and the reduction of their recombination activity can be well controlled by DLTS measurements.

The stability of hydrogen passivation has still remained questionable since recovery of electrical activity of passivated defects has been observed after annealing above 400°C. This has been attributed to the breaking of H-defect bond. For deep level
centers, the passivation has been shown to be more stable than for shallow level hydrogen-dopant complexes. A guide to the experimentally determined values of energy levels in the gap & reactivation energies of various defects/impurities in silicon can be found in Ref. [9]. Due to the relatively low thermal stability of H-passivation, this step is normally taken up as the last thermal processing step in solar cell manufacturing.
CHAPTER 5
Results & Discussion

This chapter will report the results of various structural, chemical and electrical characterization techniques employed for the analysis of as-grown and thermally treated thin film polycrystalline silicon. The preliminary investigation of the grain-structure of the AP sheet material started with optical etch pit studies. Surface studies clearly showed etch pit densities varying from grain-to-grain indicating a large variation of defect distribution, impurity levels and precipitation/gettering activity within each individual grain. This gives rise to variations in the electrical activity across the grains as demonstrated by the \( \mu \)-PCD lifetime map in Fig. 5.1. A cross-sectional image of an as-grown sample, see Fig. 5.2, received with the first batch of samples showed columnar growth of grains was achieved for almost the entire cross-section. However, some grains were seen to terminate very close to the surface. Zhang [50] subsequently verified this in his work on a new batch of samples. High defect density clusters, see “Black Spot” (BS) regions in Fig. 5.1, appeared identical to the surface image indicating that the defects are localized and do not extend along the growth direction.

Our first objective was to identify the various metallic and non-metallic impurities in the as-grown material and correlate it with grain-size and electrical activity. It was also necessary to investigate the effect of light elements like O, C & N on the precipitation/gettering of metallic impurities. Examples of such interesting interactions include dependence of interstitial oxygen concentration on SiO\(_2\) formation, the extent of N and C aided oxygen precipitation, effect of the nitrogen capping layer on Si\(_3\)N\(_4\) formation etc. The results of etch-pit, EBIC, FTIR \( \mu \)-PCD and DLTS studies on
Figure 5.1 μ-PCD Lifetime map of an as-grown 2x2 cm sample with its histogram on the right. The lifetime values outside the dotted rectangle in the map are unreliable due to edge effects produced by the micro-wave probe.

Figure 5.2 Optical etch-pit images of the surface (top) and its corresponding cross-section (bottom) showing a near columnar grain growth mitigated by few horizontal grain-boundaries near the surface.
different sets of as-grown samples obtained from time to time during the course of this study are discussed in the next section which will be followed by a similar analysis of the thermally treated samples.

5.1 Analysis of as-grown sample

The first task was to chemically identify the lifetime limiting metallic impurities in this as-grown material which, as will be shown later, are responsible for the variations in the lifetime observed in Fig. 5.1. For this purpose numerous DLTS studies were undertaken on different sets of samples in order to investigate different properties of metals ranging from GB gettering efficiency to metal-acceptor pairing reactions. Fig. 5.3 shows the DLTS spectra obtained from two different diodes on an as-grown sample. Both spectra are very similar, displaying four prominent peaks. These peaks have been labeled $H1$ through $H4$. Two less pronounced peaks were also observed at 60 and 160 K and are labeled $H5$ and $H6$, respectively. The Arrhenius plots corresponding to the peaks $H1$ through $H4$ are shown in Fig. 5.4. The activation energy $E_A$ (obtained from the slope) and capture cross-section $\sigma$ (obtained from the y-intercept) of each level are summarized in Table 5.1. According to their individual $E_A$, $\sigma$ and $T$ values, these levels have been classified as follows:

**Level $H1$:** This peak has been associated with the well known Fe-B donor-acceptor pair. Although, the published activation energy of 0.1 eV [51] is slightly higher than the measured value, the position of the peak along with its measured
Figure 5.3 DLTS spectra obtained on two different regions of the virgin sample.

Figure 5.4 Arrhenius plot of peaks corresponding to Fig. 5.3(b)

Table 5.1 Activation energies ($E_a$), carrier capture cross-sections ($\sigma$) and trap densities ($N_T$) obtained from the Arrhenius plots in Fig. 5.4, along with the most probable identity for each trap.

<table>
<thead>
<tr>
<th>Level</th>
<th>$H1$</th>
<th>$H2$</th>
<th>$H3$</th>
<th>$H4$</th>
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<tbody>
<tr>
<td>$E_A$ [eV]</td>
<td>0.07±0.01</td>
<td>0.204±0.004</td>
<td>0.27±0.01</td>
<td>0.42±0.04</td>
</tr>
<tr>
<td>$\sigma$ $[\text{cm}^2]$</td>
<td>(2 to 9)$\times10^{-16}$</td>
<td>(2 to 3)$\times10^{-14}$</td>
<td>(2 to 8)$\times10^{-15}$</td>
<td>(3 to 40)$\times10^{-16}$</td>
</tr>
<tr>
<td>$N_T$ $[\text{cm}^{-3}]$</td>
<td>(2 to 6)$\times10^{13}$</td>
<td>(2 to 7)$\times10^{12}$</td>
<td>(3 to 4)$\times10^{12}$</td>
<td>(5 to 6)$\times10^{11}$</td>
</tr>
<tr>
<td>Identity</td>
<td>FeB</td>
<td>FeAl</td>
<td>CrB</td>
<td>Fe$_i$</td>
</tr>
</tbody>
</table>
cross-section within the accuracy limits of the system, supports the classification of the level.

**Level H2:** This level has been attributed to the Fe-Al donor-acceptor pair. This defect has two possible configurations: the Fe-Al pair can lie in the <111> direction (which is the case for this H2 level) or in the <100> direction. The level properties compare well with previous studies [51] and the peak lies within the expected temperature range (roughly 105 K). The formation of Fe-Al pairs is certainly expected, since SIMS measurements at AP revealed the presence of high concentrations of Al ($10^{15}$-$10^{16}$ cm$^{-3}$).

**Level H3:** This level has been attributed to the Cr-B complex. Since interstitial Cr has a donor level close to the conduction band ($E_C - 0.22$ eV), it will always be positively charged, independent of the hole concentrations and temperature. Similar to Fe-B complexing, the opposite charge state of Cr$_i$ facilitates its capture by the immobile B atoms. This is also justified by the detection of Cr ($10^{14}$-$10^{15}$ cm$^{-3}$) by the AP SIMS measurements.

**Level H4:** As is expected with the presence of Fe-acceptor pairs (H1 & H2), interstitial iron (Fe$_i$) is also anticipated. This level produces a DLTS peak near 250K and has been reported to have an activation energy ranging between 0.35 and 0.46 eV. The capture cross-section was also found to vary significantly from $4 \times 10^{-17}$ to $4 \times 10^{-15}$ cm$^2$ in the course of this study.

In addition to the four dominant peaks, two smaller peaks were also observed at roughly 60 and 160 K. Although an Arrhenius plot of the shoulder peak at 60 K was fairly poor, the H5 level has been tentatively attributed to the second Fe-Al pair configuration ($E_A =$
0.13 eV), i.e. Al projected in the <100> direction. The DLTS spectrum of the 160 K peak (H6) is shown in Fig. 5.5(a). The Arrhenius plot of this peak, shown in Fig. 5.5(b), gave activation energy of roughly 0.33 eV and an extremely large capture cross-section of 4×10^{-13} cm^2. At this stage this level has been attributed to either another donor level associated with interstitial Fe, which has an activation energy of 0.30 eV, with an unknown capture cross-section, or to Au, which has an activation energy of 0.35 eV. The details of levels H5 and H6 are summarized in Table 5.2.

![Figure 5.5](image)

**Figure 5.5** DLTS spectrum (a) and corresponding Arrhenius plot (b) of the 160 K peak measured in the as-grown sample.

**Table 5.2** Activation energies (EA), carrier capture cross-sections (σ) and trap densities (NT) for levels H5 and H6, along with the most probable identity for each trap.

<table>
<thead>
<tr>
<th>Level</th>
<th>H5</th>
<th>H6</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA [eV]</td>
<td>~0.1</td>
<td>~0.33</td>
</tr>
<tr>
<td>σ [cm^2]</td>
<td>5×10^{-17}</td>
<td>4×10^{-13}</td>
</tr>
<tr>
<td>NT [cm^3]</td>
<td>~2×10^{12}</td>
<td>~2×10^{12}</td>
</tr>
<tr>
<td>Identity</td>
<td>Fe-Al</td>
<td>Fe-Al or Au?</td>
</tr>
</tbody>
</table>
Figure 5.6 Optical etch-pit images (a) (c) & (e) and room temperature EBIC images (b) & (d) of a medium sized grain with high dislocation density and twins boundaries.
Figure 5.6 shows the etch-pit and EBIC micrographs of a region with medium-sized grains (300-500µm) in the as-grown sample. Fig. 5.6(a), which shows the etch pit distribution under a diode corresponding to the bright region in the EBIC micrograph of Fig. 5.6(b), clearly shows dislocations pits and BS across the entire region. It also shows large twins contained within the grains. The etching contrast observed between the grains includes a dense array of small granular pits, see Figs. 5(c) & (e), typically ascribed to impurity complexes. Note also that the region near the GB’s are devoid of such pits, indicating a contamination free denuded zone (DZ) along the GB’s. The width of this DZ is approximately 10µm on each side of the GB. The EBIC images in Figs. 5.6(b)&(d) also show this DZ with the GB acting as a strong recombination center due to being decorated with metallic impurities and oxygen/carbon precipitates. It is believed that the GB’s are acting as strong gettering sites for metallic as well as non-metallic impurities. However, twins on the other hand are not electrically active, as verified by its absence in the EBIC images, as previously discussed in section 3.2.2.

As seen in Fig. 5.6(c), the region bounded by the GB and the twin is devoid of the small granular etch pits. These etch pits are most likely associated with metal precipitates on small SiO$_x$ complexes with oxygen in interstitial form. Alternatively, they can also be thought of as metal precipitates/agglomerates on grown-in micro-defects as has been observed by McHugo et al. [46] who studied the nature of such precipitates in mc-Si and found them to be iron oxide or iron silicates. The clean region in Fig. 5.6(c) can therefore be concluded to be containing less metallic impurities and this effect can be partially explained by the twin boundary acting as a strong diffusion barrier for these impurities. The EBIC image in Fig. 5.3(b) therefore is brighter (higher collection efficiency) in this
region and the darker regions immediately on the right of the twin boundary suggest decoration of complexes with metallic impurities.

Our hypothesis that the small granular etch pits are related to metal precipitates on SiO\textsubscript{x} complexes or other grown-in micro-defects, has been further verified chemically by microscopic FTIR observations on three different regions of this sample representing different grain sizes and twin distributions. The room temperature FTIR maps for these three regions are shown in Fig. 5.7 with the micro-FTIR spectra shown in 5.7(a) and a wide beam spectrum covering the entire sample shown in 5.7(b). The lower spectrum in Fig. 5.7(b) corresponds to FTIR data after the getter anneal step at 1100°C and will be discussed later in this chapter. As seen from these two figures, oxygen is homogeneously distributed across different regions and the interstitial oxygen concentrations [\textit{O}_i] measured in various grains also agree well with the average [\textit{O}_i] measured by wide beam FTIR. The band of absorption peaks seen from 800 to 1000\textsuperscript{-1} cm\textsuperscript{-1}, though poorly resolved, are nitrogen related, like N-N pairs and N-O complexes as assigned earlier by Stein \textit{et al.}\[52] or due to SiN inclusions which are known to exist in the AP material as verified by Lu through his SEM/EDS studies \[53]. The sharp peak at approximately 605 cm\textsuperscript{-1} seen in Fig. 5.7(b) indicates the presence of a high concentration of substitutional carbon. Carbon and nitrogen are known to affect oxygen precipitation during thermal annealing differently and this behavior will be discussed later in the chapter.

Figure 5.8 shows another region in the same sample with very high dislocation density and a grain-size greater than 1mm. The EBIC image on a diode over this region is shown in Fig. 5.8(b). This grain does not exhibit the granular etch-pits observed in Fig. 5.5. The DLTS spectra corresponding to the diodes in Figs. 5.6 & 5.8 are shown in Figs.
Figure 5.7(a) Micro-FTIR Spectra for the as-grown sample in regions with varying grain sizes. Spectra displaced for clarity.

Figure 5.7(b) Wide beam-FTIR Spectra for the as-grown and gettered sample.
Figure 5.8 Optical etch-pit images (a) (c) & (e) and room temperature EBIC images (b) & (d) of a large grain area with very high dislocation density.
5.9(a) & (b) respectively. The decrease in the amplitude of the H1 peak in Fig. 5.9(a) as compared to Fig. 5.9(b) without any appreciable differences in the FeI levels in both the spectra shows that some of the Fe has precipitated in case of the lower dislocation density sample. The emergence of a large negative peak at around 170K is likely to be related to this precipitation. Also the Fe-Al and Cr-B peaks have overlapped in this case due to the presence of deep levels introduced by the dislocations, as seen from the broad peak from 70K-150K. Another broad peak from 200-300K is attributed to the decoration of extended defects (dislocations) by interstitial Fe.

The effect of extended defects on the transition metal distribution is best exemplified by the DLTS spectrum in Fig. 5.9(b). This region has a very high dislocation density and therefore it can be assumed that either Fe decorates these dislocations in interstitial form or starts to precipitate. A similar spectrum has been previously reported by Mishra et al. [54] wherein the broad peak from 100-250K was found to be due to large oxygen precipitation induced defects. The small H6 peak observed in this case shows that Fe exists in interstitial form and if the negative peak observed in Fig. 5.9(a) is indeed related to Fe precipitation, then the absence of this peak in Fig. 5.9(b) validates the interstitial state of Fe. Also, the concentration of FeB measured in this case is higher ($\sim 10^{13}$ cm$^{-3}$) than that measured ($\sim 3 \times 10^{12}$ cm$^{-3}$) in Fig. 5.9(a) indicating that more Fe is available in this region.

The total dissolved Fe and Cr concentrations have been found to be functions of GB density and intra-granular defect sites available for gettering. Figs. 5.10(a) & (b) show EBIC images on two Schottky diodes having different GB density. Figs. 5.10(c) & (d) show their respective DLTS spectra. The total Fe concentration ($Fe_i + FeB + FeAl$)
Figure 5.9 DLTS Spectrum of an as-grown sample measured with $\tau = 20$ ms. (a) showing a possible Fe precipitation peak at 170K and (b) overlapping of peaks due to decoration of extended defects by transition metal impurities.
clearly decreases with available GB’s from approximately 2E13 cm$^3$ in low GB density diode to around 8E12 cm$^3$ in the high GB density diode. However, the GB density marginally affects the CrB concentration. Thus, the fast diffusing Fe is efficiently gettered by GB’s whereas the less mobile Cr atoms are only slightly gettered. The numbers indicated by arrows to the right of Fig. 5.10(a) indicate the EBIC collection currents from different regions of the diode. It may therefore be beneficial to achieve an optimum grain-size just larger than the diffusion length in order to keep the dissolved Fe concentration low by engineering a GB gettering of most of the Fe. This is especially true in case of thin film solar cell materials wherein the thickness is usually smaller than the grain-size and the final diffusion length obtained from a grain is controlled by the dissolved Fe concentration.

Calculations have been made using the Shockley-Read-Hall recombination theory to correlate the minority carrier recombination lifetime of materials with the deep level trap concentrations. For details of the mathematical analysis of this model, the reader is referred to the text by D.K Schroder [55]. Based on this model, plots of effective lifetime ($\tau_{\text{eff}}$) and diffusion lengths ($L_D$) corresponding to various trap concentrations ($N_T$) of the traps identified in the present material was constructed and shown in Fig. 5.11. It is seen that the $\tau_{\text{eff}}$ and the $L_D$ obtained from a grain is largely limited by the Fe concentration. The traps parameters used for the SRH recombination calculations are shown in Table 5.3.

The SRH lifetimes obtained from the above calculations agree well with the experimental values obtained by Zoth et al. for Fe$_i$ and FeB [56]. The increase in the
Figure 5.10  EBIC images (a) & (b) and corresponding DLTS spectrum (c) & (d) of two regions on different samples with varying grain sizes. The trap concentrations in the DLTS spectra are in cm$^{-3}$.
recombination efficiency of Fe\textsubscript{i} by greater than 10 as compared to Fe-B has been previously reported by Graff [57] and Zoth \textit{et al.} [58]. This matches closely with the

Table 5.3 Parameters used for the SRH recombination calculations. Lifetimes were determined for room temperature and acceptor concentration of $N_A = 10^{15}$ cm\textsuperscript{-3}

<table>
<thead>
<tr>
<th>Trap Parameters</th>
<th>Fe\textsubscript{B}</th>
<th>Fe\textsubscript{Al}</th>
<th>Cr\textsubscript{B}</th>
<th>Fe\textsubscript{i}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level [eV]</td>
<td>$E_V + 0.1$</td>
<td>$E_V + (0.2\pm0.01)$</td>
<td>$E_V + 0.28$</td>
<td>$E_V + (0.38\pm0.01)$</td>
</tr>
<tr>
<td>$\sigma_n$ [cm\textsuperscript{2}]</td>
<td>$6 \times 10^{13}$</td>
<td>$1 \times 10^{13}$ *</td>
<td>$2 \times 10^{14}$ *</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>$\sigma_p$ [cm\textsuperscript{2}]</td>
<td>$2 \times 10^{14}$</td>
<td>$2 \times 10^{14}$</td>
<td>$5 \times 10^{15}$</td>
<td>$7 \times 10^{17}$</td>
</tr>
</tbody>
</table>

* Assumed a $\sigma_n$ value which is an order of magnitude less than $\sigma_p$ in line with minority trap characteristics of Fe-B pair.

numbers derived from our calculations and translates to an increase in the diffusion length of Fe\textsubscript{B} by a factor of almost five over that of Fe\textsubscript{i}. As a matter of fact, this decrease in the diffusion length by a factor of 3 to 5 when Fe\textsubscript{B} is dissociated is often used as a signature for iron in the sample.

The analysis of the as-grown material showed gross variations in the distribution of defects and impurities in different grains. Interactions between these defects and impurities will be an important factor in determining the lifetime of the material after thermal processing. In addition, the effect of carbon and nitrogen on oxygen precipitation and, in turn, the effectiveness of gettering at these oxide precipitates and process induced defects will be a key factor in the study of thermally treated samples in the next section.
Figure 5.11 Dependence of (a) minority carrier SRH lifetime and (b) diffusion length on different types and concentrations of traps.
5.2 Analysis of thermally treated samples

The AP thermal treatment procedure comprises of (i) standard getter anneal at 1100°C (ii) phosphorous diffusion, at 850-900°C, followed by quenching and (iii) a series of temperature cycles as the post-diffusion anneal step (PDA). The details of this last step are given in Table 2.1 in section 2.3. As seen in the as-grown material, the grain-boundaries and dislocations form the prominent impurity gettering centers. The thermal treatment of the as-grown material will therefore initiate numerous defect-impurity reactions, which will in turn govern the minority carrier diffusion length obtained from an individual grain. Since oxygen is present in the material in a supersaturated state (1E18 cm\(^{-3}\)), oxygen precipitates (SiO\(_x\)) are expected to be the dominant nucleation sites for metal-silicide precipitation. Both intra-granular defects and grain-boundaries provide nucleation centers for oxygen precipitation. The efficiency of metal-silicide precipitation is therefore dependent on the distribution of these nucleation sites. Oxygen precipitation has been shown to be affected by impurities like carbon, nitrogen and Fe itself [59]. Therefore, the efficiency of gettering will also depend on the distribution of these impurities in various grains.

5.2.1 Effect of C & N on oxygen precipitation

Fig. 5.12(a) is the µ–PCD lifetime map of the gettered sample showing distinct variations of lifetime across the sample after the 1100°C anneal. The patch marked “X” in the lifetime map is an artifact caused due to polishing of this sample. Structurally,
Figure 5.12  (a) µ–PCD lifetime map of the gettered sample with (b) its histogram and EBIC images (c)-(e) corresponding to the three regions marked ‘A’, ‘B’ and ‘C’ in the lifetime map respectively.

Mean 825 ns
Std. Dev 222 ns
region ‘A’ corresponds to small grains with few BS, region ‘B’ has smaller grains with a high density of BS, while region ‘C’ corresponds to a large grain region with few dislocation pits. The EBIC electrical activity images shown in Fig. 5.12 have been examined chemically using micro-FTIR spectra as shown in Fig. 5.13. Note that there is a reduction in $[O_i]$ after thermal annealing in all three regions when compared with Fig. 5.7(a). Also, the absorption peaks, between 850 to 1000 cm$^{-1}$, related to nitrogen undergo a small change with respect to the as-grown case, which is further confirmed by Fig. 5.7(b) which also shows a reduction in the substitutional carbon concentration at 605 cm$^{-1}$ indicating a carbon enhanced oxide nucleation in this case.

It has been shown earlier by Sun, Yao et al. [16] that in a sample co-doped with carbon and nitrogen, the latter suppresses the effect of carbon on oxygen precipitation provided that the sample is initially annealed at 1100°C. The authors also showed that the FTIR spectrum after annealing is characterized by disappearance of the nitrogen related peaks between 766 cm$^{-1}$ and 1026 cm$^{-1}$ (in this study we see them between 800 to 1000 cm$^{-1}$) and emergence of two characteristic luminescence lines, D1 & D2, originating from the stress induced defects enhanced by the precipitation process. Further, the authors showed that in nitrogen free samples only a marginal decrease in $[O_i]$ is observed mainly due to oxygen out-diffusion. Since our sample has also been annealed at 1100°C and, if we consider that the absorption bands between 800 and 1000 cm$^{-1}$ are indeed related to N, then we can infer that N-enhanced oxide nucleation is not dominant in our samples. The above results indicate that the heterogeneous nucleation centers required for O-precipitation are being provided by bulk defects formed during sheet growth. Since carbon enhances precipitate growth via interacting with Si self interstitials during oxygen
$A \ [O_i] = 3.14E17 \text{ cm}^{-3}$

$B \ [O_i] = 3.14E17 \text{ cm}^{-3}$

$C \ [O_i] = 4.0E17 \text{ cm}^{-3}$

**Figure 5.13(a)**  Micro-FTIR Spectra for the regions A, B & C in the lifetime map in Fig. 5.12

**Figure 5.13(b)**  Micro-FTIR Spectra for the regions A, B & C in the lifetime map in Fig. 5.17
precipitation, we would attribute this decrease in \([O_i]\) to the decrease in \([C_s]\) observed in Fig. 5.7(b). It has been seen [16] that a decrease of \([O_i]\) is accompanied by a decrease in \([C_s]\) and these two processes are quantitatively correlated as \(\Delta[C_s]=\frac{1}{2}\Delta[O_i]\). From our experiments, we calculate \(\Delta[C_s]=1E17\) cm\(^{-3}\) and \(\Delta[O_i]=5E17\) cm\(^{-3}\). The deviation of the experimental values from the above relation suggests that not all the substitutional sites required for oxygen precipitation are being provided by carbon. Other mechanisms that can explain this effect are grain-boundary segregation of oxygen during thermal treatment, as discussed in the next section.

5.2.2 Grain-boundary agglomeration

Oxygen normally segregates as SiO\(_x\) along with carbon at GB’s rendering the GB’s electrically active [60]. Such segregation of O & C around the GB’s is highly favorable from the internal equilibrium point of view as the strain field generated locally by SiO\(_x\) segregation is compensated by the agglomeration of C around it. In the absence of C, the stresses produced by SiO\(_x\) at the GB’s are released by dislocation formation. These dislocations are easily decorated by metallic impurities, thereby increasing the electrical activity of the GB’s. The electrical activities of the GB’s should therefore show large variations depending on the concentrations of carbon and oxygen present, as well as the thermal history of the sample. High and low recombination regions could therefore be either due to different oxygen concentrations alone, or due to the relative degrees of O and C agglomeration. Fig. 5.14 compares the electrical activities of GB’s in an as-grown and thermally treated sample. The inset in Fig. 5.14(b) clearly shows the abrupt change in
**Figure 5.14** EBIC images of (a) as-grown, and (b) thermally-treated samples. Images were obtained under low injection levels.

**Figure 5.15** Wide beam-FTIR Spectra for the diffused and PDA samples
the recombination efficiency of the GB. This effect is more commonly observed in small grains rather than in large grains which can be explained by the low diffusivities of oxygen and carbon. Therefore, the slightly high \([O_i]\) measured in spectrum ‘C’ of Fig. 5.13(a) and spectrum ‘C’ of Fig. 5.13(b), corresponding to large grain regions could also be explained by lesser agglomeration at these GB’s.

5.2.3 Effect of thermal treatment on oxygen precipitation

The post growth treatments followed by AP starts with a step analogous to the three-step internal gettering procedure adopted by the IC industry. The first step high temperature getter anneal produces a near surface denuded zone by removing oxygen and metallic impurities from a surface layer about two microns thick. This facilitates the formation of a junction on clean silicon and minimizes recombination within the diode space charge region [2]. The second step of nucleating O-precipitates in the bulk can prove counter-productive in case of solar cells which use the entire bulk as the device active region. Therefore, any further O-precipitation and growth within the bulk will be detrimental. Hence, a combination of silicon self-diffusion and aluminum gettering from the backside, added to bulk passivation through hydrogenation, is generally used to minimize bulk and GB effects.

Comparing Fig. 5.15 with Fig. 5.7(b), we find that the getter anneal step done at 1100°C is the only step which controls O-precipitation. Fig. 5.15, which shows the wide beam FTIR spectra of the diffused and PDA samples, indicates no change in the oxygen and carbon concentrations with respect to the gettered sample spectrum in Fig. 5.7(b).
Table 5.4 Activation energy ($E_A$), carrier capture cross-section ($\sigma$) and trap density ($N_T$) for $H7$, along with the most probable identity for the trap

<table>
<thead>
<tr>
<th>Level</th>
<th>$H7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_A$ [eV]</td>
<td>$\sim0.20$</td>
</tr>
<tr>
<td>$\sigma$ [cm$^2$]</td>
<td>$\sim3\times10^{-17}$</td>
</tr>
<tr>
<td>$N_T$ [cm$^{-3}$]</td>
<td>(7 to 20)$\times10^{12}$</td>
</tr>
<tr>
<td>Identity</td>
<td>Fe precipitate ?</td>
</tr>
</tbody>
</table>

Figure 5.16 DLTS spectra obtained from two different regions of the PDA sample. The spectra of figures (a) and (b) have been deconvoluted into their five constituent peaks, with the red curve representing the sum of all five blue curves. The Arrhenius plot (c) corresponds to the $H7$ level in (b).
This is in line with the gettering approach outlined above wherein any further oxygen precipitation after the getter anneal step is undesirable. The diffusion and the PDA steps therefore contribute towards metallic impurity gettering only. The aluminum back-surface gettering during the contact printing and co-firing process further reduces the impurity concentrations and determines the final diffusion length obtained from the cell.

### 5.2.4 SiN inclusions

Another interesting observation from the FTIR spectra in Fig. 5.13 is that the N-related IR absorption peaks from 800 to 1000 cm\(^{-1}\) are reduced in large grain regions as compared to small grain regions. We attribute this observation to SiN inclusions which are seen predominantly in small grain regions through SEM/EDS studies by Lu and Zhang [53]. Zhang has also proposed that these inclusions determine the size of the grains during growth process [61]. More TEM studies are required in the future to confirm this preliminary observation.

### 5.2.5 DLTS of thermally treated samples

The dissolved impurity concentration measured after thermal annealing will depend on the solubility limit of the impurity during the last thermal processing temperature, provided sufficient mobility exists for the diffusion to the nucleation sites. Thus, DLTS studies were carried out on the PDA samples, since it is the last thermal process done on the batch of samples used in this study. Unlike the spectra of the as-
grown sample, the peaks of the PDA-samples were not clearly resolved, see Fig. 5.16, with the spectra consisting of a series of overlapping peaks. In addition, the DLTS spectra of two different regions investigated on an annealed sample from the same batch as that of the as-grown sample investigated earlier see Fig. 5.3. Note that Figs. 5.16(a) & (b) clearly have different spectra, with the $H2$ through $H6$ levels significantly overlapping. The only consistent observation is the absence of the $H1$ level (Fe-B pair) and the addition of a peak at roughly 190 K, labeled $H7$. Analysis of the dominant $H7$ level gave an activation energy of roughly 0.20 eV and a small capture cross-section of $3 \times 10^{-17}$ cm$^2$, see Fig. 5.16(c) and Table 5.3. The origin of this level is not entirely certain, but the position of the peak, together with the absence of FeB pairs in the presence of Fe$_i$ concentration are indicators that the level is associated with Fe precipitation or with Fe gettered by oxide or carbide precipitates. This level has previously been measured at roughly 184 K and was assigned an activation energy of 0.23 eV [62].

A slight increase in the hole concentration was also observed via C-V measurements after thermal treatment. The hole concentration for the as-grown sample was measured as $4.5 \times 10^{15}$ cm$^{-3}$ while that for the PDA sample was found to be $5.5 \times 10^{15}$ cm$^{-3}$. This is due to the recovery of electrically active boron pairing with Fe and Al in the as-grown sample. The FeB pairing reaction has been shown to be proportional to [B] and the diffusion coefficient of Fe$_i$ [58]. This was also experimentally verified in this study through samples having different Fe and B concentrations but undergoing the same thermal treatment [63, 64].
The DLTS results clearly show that Fe precipitation after thermal treatment varies across the grains and is possibly determined by grain-size, oxide/carbide precipitates and other extended defect distribution. The lifetime map of a PDA sample (see Fig. 5.17) for which the IR absorption spectra have been measured and shown in Figs. 5.13(b) & 15, also brings out this fact.

### 5.2.6 Gettering efficiencies of annealed samples

The regions marked ‘A’ to ‘C’ in the lifetime map shown in Fig. 5.17 correspond to regions with different grain-sizes and defect distributions in the PDA sample as shown by their respective EBIC images. It shows that there are strong variations in the gettering efficiencies from region-to-region which are controlled by the intra-granular defects in individual grains. It has been shown by McHugo, Weber et al. [46] that lower gettering efficiencies in regions with high density of intra-granular defects (bad grains) are due to the formation of strong metallic precipitates other than silicides at these defects. These precipitates are harder to dissolve and therefore account for the low lifetimes observed in these regions. The blue regions in Fig. 5.17 correspond to high lifetimes (>2 μs) and are relatively clean, large grains whereas, the poor lifetime regions contain appreciable electrically active defect clusters within them.

The mean lifetime measured in the PDA sample (728 ns) is also lower than that measured for the gettered sample (825 ns). This effect could either be due to Fe contamination during the diffusion step or to the re-emission of Fe from bulk precipitates/defects after the spike annealing steps in the PDA cycle. The possibility of
Figure 5.17 (a) μ–PCD lifetime map of the PDA sample with (b) its histogram and EBIC images (c)-(e) corresponding to the three regions marked ‘A’, ‘B’ and ‘C’ in the lifetime map respectively.
contamination is very unlikely since the diffusion is carried out in a relatively contamination-free belt furnace and for a very short duration of time. DLTS measurements on a different set of high resistivity material yielded a dissolved Fe concentration ranging from $1 \text{ to } 3 \times 10^{12} \text{ cm}^{-3}$, which corresponds to the solubility limit of Fe at the final spike anneal temperature of $780^\circ \text{C}$. The dissolved Fe would then stay in solution if the samples are cooled rapidly explaining the lifetime degradation after this step. These results indicate that the final spike anneal steps are intended to release metallic impurities from their nucleation sites and keep them in solution so that they can be easily gettered by the aluminum gettering step that follows PDA in the manufacturing process. The Al gettering takes place during the spike firing of the printed front and back contacts of the cell at $900^\circ \text{C}$. A lifetime map, see Fig. 5.18, of the final solar cell material, after removing the contacts, indeed shows an increased mean lifetime of 2.83 $\mu$ s. Thus, the Al gettering step is very effective in controlling the final diffusion length obtained from the AP material and samples after this stage should be studied in detail for their gettering behaviors.

![Image of lifetime map](image)

**Fig. 5.18**  Lifetime map on a piece of 10 x 10 cm wafer after 30 minute dip in 10% HF
CHAPTER 6

Conclusions & Future Work

6.1 Conclusions

In this study, the grain-to-grain electrical activity variations of the Astropower polycrystalline material was investigated using a broad range of structural, chemical and electrical diagnostic tools. Etch-pit and DLTS studies showed non-uniform distribution of defects and impurities to be responsible for these gross variations. The growth of the polycrystalline grains was shown to be mostly columnar with some grains terminating close to the surface. However, the defects do not follow the growth pattern and show a highly randomized distribution across the entire volume of the material.

Serious deep level impurities like Fe, Cr and Al were identified through DLTS measurements and a correlation was established with the help of EBIC studies between the concentrations of these impurities and the grain size, metal-acceptor pairing reactions and acceptor concentrations. Fe was found to be efficiently gettered by the grain-boundaries whereas the less mobile Cr atoms are only slightly gettered. Calculations based on the SRH model were presented to correlate the effective lifetime of the material with the observed trap concentrations. It was shown that diffusion length obtained from a grain is limited by the dissolved Fe concentration which can be effectively controlled by initiating less harmful FeB pairing reactions. It was also shown that nitrogen related IR absorption is slightly higher in small grains which were attributed to SiN inclusions seen in these grains. FTIR studies also indicated that oxygen precipitation after the getter anneal step is carbon assisted with N playing no significant role. Any subsequent thermal
processing does not induce further O-precipitation, but strongly influences the gettering of metallic impurities at these precipitates.

Thermal treatment has been shown to induce considerable metal precipitation at the intra-granular defects and oxide/carbide precipitates. However, considerable variations in the gettering/precipitation rate were observed arising out of inhomogeneous distribution of nucleation centers across different grains. EBIC and μ-PCD studies clearly demonstrated that small grains with appreciable defect clusters are regions of high recombination. Similarly, agglomeration of O and C at the grain-boundary sites during thermal treatment was shown to control its electrical activity as a result of decoration of the extended defects generated due to oxygen precipitation at these sites. The spike anneal steps during the PDA cycle is believed to dissolve the metal precipitates formed at the extended defects and keep the impurities in solution so that they can be easily gettered by the aluminum gettering step that follows. The Al gettering step has been shown to increase the net effective diffusion length of the material by μ-PCD lifetime maps.

6.2 Future Work

Though this work clearly identified the lifetime limiting factors in the material and studied the relative impact of defects and impurities on its electrical behavior, an absolute analysis of the prominent defects and impurities should be undertaken in order to extract maximum cell performance. As a starting point, minority carrier traps should be identified by DLTS studies of diffused junction or by optical DLTS. Extensive TEM and
SEM/EDS studies should be considered for the structural and chemical characterization of defects and inclusions observed in the material. More importantly, the effect of carbon manifesting in different forms in the material should be studied more closely. The scope of this study was limited to samples till the PDA step only. Therefore, it is necessary to investigate the material after Al gettering in order to understand the impact of thermal processes and defect distribution on the gettering efficiency of each individual grain and correlate it with LBIC maps obtained from AP. Since the samples used for this study were highly non-planar, extensive planarizing operations often removed substantial material from the top surface. In order to study the critical near surface region of the material, it will be necessary to initiate the planarizing operation from the back side keeping the top surface intact.
References