This thesis examines light element impurities and related defects in polycrystalline sheet and RGS (Ribbon Growth on Substrate) ribbon silicon. The interaction dynamics between oxygen, carbon, nitrogen, and intrinsic point defects, as well as the role of grain boundaries (GBs) on oxygen and carbon precipitation have been studied.

Sheet silicon wafers subject to various heat treatments have been studied by infrared microspectroscopy. An interstitial oxygen (Oi) denuded-zone near the top surface is observed in the virgin wafer grown with a more aggressive thermal profile. The Oi denuded zone is sustained as a 250 µm wide precipitate-denuded-zone during annealing, mainly due to the critical role of the initial Oi concentration and quenched-in vacancies on precipitate nucleation. It is found that carbon precipitation is well correlated with that of oxygen. By monitoring the substitutional carbon (Cs) reduction by infrared absorption and the precipitate density by preferential etching, it is concluded that formation of interstitial carbon by trapping silicon self-interstitials is an indispensable step for the observed fast Cs precipitation.

Carbon and oxygen precipitation in four sets of RGS wafers with similar carbon contents and very different oxygen concentrations has been studied. It is found that carbon precipitation in an oxygen containing wafer consists of two distinct steps; namely, an initial rapid oxygen-carbon co-precipitation in the very first hour annealing, followed by slow
precipitation during subsequent prolonged annealing. A high oxygen content enhances carbon precipitation throughout the two steps. It is shown that the formation of interstitial carbon in the presence of excess silicon self-interstitials generated during oxygen precipitation plays an important role in increasing the carbon precipitation rate in the first hour annealing. Because of the absence of interstitial injection during the following slow precipitation process, the enhancement effect of oxygen can only arise from an increase in precipitation sites. It is proposed that the oxygen-carbon co-precipitates formed in the very first hour annealing provide sites for continuous carbon precipitation. This explains why carbon impurities precipitate faster in a high oxygen containing wafer, even after removal of all the interstitial oxygen from the silicon matrix.

The impact of GBs on oxygen precipitation in sheet silicon has been investigated. Infrared microspectroscopy shows nitrogen gettering at GBs, and preferential etching reveals a precipitate-denuded-zone near GBs. The gettering of nitrogen at GBs is likely to be responsible for the denuded-zone formation, considering the enhancement of nitrogen impurities on oxygen precipitation. The impact of GBs on carbon precipitation in RGS ribbons has also been studied. Infrared microspectroscopy indicates a higher remaining $C_s$ concentration in the intra-grain region, while preferential etching reveals a 20 to 30 $\mu$m wide precipitation band near GBs. Assuming that the tensile strain associated with carbon precipitates must be relaxed in order for the precipitation to proceed, it is shown that the precipitation band formation is mainly controlled by diffusion of vacancies from the intra-grain region to GBs.

In summary, a high concentration of $O_i$ is found to precipitate readily in polycrystalline sheet and ribbon silicon, and the precipitation of $C_s$ is mainly controlled by oxygen
precipitation. GBs have a strong impact on both oxygen and carbon precipitation by gettering of nitrogen impurities and by interaction with interstitials and vacancies. It is concluded that a low oxygen content is vital important to prevent extensive oxygen precipitation. On the contrary, a high carbon content (\( \sim 1 \times 10^{18} \text{ cm}^{-3} \)) can be tolerated as long as the initial O\(_1\) concentration is low.
Light element impurities and related defects in polycrystalline silicon for photovoltaic application

By

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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

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Fall 2004

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To my parents
BIOGRAPHY

Jinggang Lu was born in Liaoning Province of P. R. China on February 4th, 1972. He was accepted as an undergraduate student by the department of Metal Physics of the University of Science and Technology, Beijing in August 1989. After graduating from the university, he joined the Anshan Iron and Steel Group Complex as a junior engineer in July 1993. He worked in the X-ray crystallography and electron microscopy group of the company’s technology center, where he performed X-ray diffraction analyses, and was responsible for the maintenance of the Siemens D-500 x-ray diffractometer. In 1998, he left the company and joined the State Key Laboratory of Silicon Materials of Zhejiang University for his graduate study. He studied the process-induced defects in nitrogen-doped silicon under the direction of Prof. Deren Yang. After received his master degree from Zhejiang University, he enrolled at North Carolina State University as a PhD student in 2003, where his research was focused on light element impurities and related defects in polycrystalline silicon.
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INTRODUCTION

World shipment of photovoltaic cells and modules has increased significantly in the past decade. In 2003, the total world shipment reached 744MW, an increase of 32.4% from that of 2002 [1]. Because of its relatively low cost, crystalline silicon continues to be the dominant technology for terrestrial-based photovoltaic applications [2, 3]. In 2002, approximately 90 percent of the world photovoltaic production was based on single and multicrystalline silicon.

The direct growth of ribbon silicon from molten Si has received increased attention in recent years. It has the advantage of not requiring wafering. Also it needs little surface preparation before cell manufacture and produces wafers with a shape suitable for high-density packing. Different ribbon technologies can be classified into two categories, vertical versus horizontal growth. The typical pulling rate of the vertical growth is around 1–2 cm/min in order to control the thermal stress [4], and the low throughput is a disadvantage. The silicon sheets [5] and RGS ribbon [6,7] studied in this thesis are grown in a horizontal configuration. This permits a two orders higher pulling rate than the vertical configuration by decoupling the pulling direction from that of grain growth. Since each grain only needs to grow a distance equal to the sheet thickness, low-cost, impure feedstock can be used without deteriorating the grain structure integrity.

Accompanying these cost-efficiency and high throughput advantages, the grain size of the sheet silicon is small due to the high solidification rate and random nucleation of grains at the substrate, and the impurity concentration is high due to the relative large contact area with refractory materials [8,9]. In particular, a high concentration of oxygen and carbon in the
range of 10 to 50 ppma are usually present in the sheet and RGS ribbon silicon [10,11]. In some cases, particles can be detached from the refractory materials and be incorporated into the sheet silicon as inclusions [12,13]. Although metallic impurities are usually the dominant lifetime killers in the as-grown wafers, extended defects such as oxygen and carbon precipitates, included particles and associated dislocation clusters are found to be the major lifetime limitation factors in the processed wafers [14]. To take advantage of the high throughput sheet and ribbon formation processes, detailed knowledge on the impact of impurities on cell performance is required.

In this thesis, light element impurities and related defects were examined by infrared absorption microspectroscopy, preferential etching/Nomarski optical microscopy, and electron beam induced current. In particular, the interaction dynamics between oxygen, carbon, nitrogen, and intrinsic point defects, as well as the role of grain boundaries on oxygen and carbon precipitation have been studied.
Chapter 1 reviewed oxygen and carbon precipitation in crystalline silicon. In particular, the effect of impurities and point defects on oxygen precipitation, the interaction between oxygen and carbon, the impact of oxygen precipitation on minority carrier lifetime, and the role of oxygen and point defects on carbon precipitation have been examined.

Chapter 2 briefly described the experimental techniques employed in this study.

Chapter 3 studied the oxygen precipitate (OP) denuded zone in sheet silicon. It was found that an O$_i$ denuded zone is generated in the as-grown sheet silicon wafer grown with a more aggressive thermal profile. The O$_i$ denuded zone is sustained as a 250 µm wide precipitate denuded zone after annealing, mainly due to the critical role of the initial O$_i$ concentration on precipitate nucleation. EBIC characterization shows that the lifetime in the denuded zone is significantly improved.

Chapter 4 examined the spatial variation of oxygen and carbon precipitation in four sets of sheet silicon samples grown with different thermal profiles. The complicated oxygen and carbon precipitation behaviors observed in the four sets of samples were clarified by recognizing that oxygen precipitation is controlled by the initial O$_i$ content and quenched-in vacancies, and carbon precipitation is further controlled by oxygen precipitation through the formation of interstitial carbon by trapping silicon self-interstitials (I$_{Si}$).

Chapter 5 examined the infrared absorption spectra of SiC precipitates in crystalline silicon. Comparison between measured and calculated spectra shows that the
triangular-shaped band is likely due to absorptions by small disk-shape precipitates with a range of aspect ratios. Whereas, the rectangular-shaped band arises from both scattering and absorption at relatively larger disk-shape precipitates. It is believed that the impacts of oxygen content and annealing temperature on the size of SiC precipitates are likely related to their critical role on precipitate nucleation.

Chapter 6 investigated the impact of oxygen content and annealing procedure on carbon precipitation in RGS wafers. It is found that carbon precipitation in an oxygen containing wafer consists of two distinct steps; namely, an initial rapid oxygen-carbon co-precipitation in the very first hour annealing, followed by slow precipitation during subsequent prolonged annealing. A high oxygen content enhances carbon precipitation throughout the two steps. It is shown that the formation of interstitial carbon in the presence of excess \( \text{I}_{\text{Si}} \) generated during oxygen precipitation plays an important role in increasing the carbon precipitation rate in the first hour annealing. Because of the absence of interstitial injection during the following slow precipitation process, the enhancement effect of oxygen can only arise from an increase in precipitation sites. It is proposed that the oxygen-carbon co-precipitates formed in the very first hour annealing provide sites for continuous carbon precipitation. This explains why carbon impurities precipitate faster in a high oxygen containing wafer, even after removal of all the interstitial oxygen from the silicon matrix.

Chapter 7 studied the impact of grain boundaries (GBs) on oxygen and carbon precipitation. During the cooling down period of the sheet formation processes, transition metals and nitrogen preferentially precipitated along GBs. After annealing, an oxygen
precipitate denuded zone was formed near GBs, which is likely related to the depletion of nitrogen near GBs. Infrared microspectroscopy showed that the remaining $C_s$ concentration was higher in the intra-grain region than the GB region in the annealed RGS ribbon silicon, and a 20 to 30 µm wide precipitation band near GBs was revealed by preferential etching. It was demonstrated that the precipitation band formation is mainly controlled by diffusion of vacancies from the intra-grain region to GBs.

Chapter 8 examined secondary phase particles in sheet silicon. In particular, their composition, distribution, impact on grain structure morphology and impurity gettering, have been investigated. Chemical reactions between included particles and molten Si are discussed based on a thermodynamic analysis. It is concluded that $\alpha$-Si$_3$N$_4$ particles will transform into oxynitride in the region where the dissolved oxygen exceeds $2.8 \times 10^{17}$ cm$^{-3}$. 
CHAPTER 1. LITERATURE REVIEW

1.1 Oxygen precipitation in crystalline silicon

Oxygen in silicon has been extensively studied in the integrated circuit industry mainly because of the importance of the intrinsic gettering technique for device yield improvement and as a challenging prototype to study solid-state reactions from a fundamental point of view [15]. In Czochralski (Cz) growth process, oxygen is continuously dissolved from the silica crucible into molten silicon. The typical interstitial oxygen (Oi) concentration in Cz wafers is in the range of 10 to 20 ppma, which is supersaturated at common device processing temperatures. As a result, Oi will precipitate into oxygen precipitates during thermal processing. While oxygen precipitates act negatively as minority carrier recombination centers, they can also act beneficially as gettering sites for transition metals [16].

Oxygen in sheet silicon is likely to come from the feedstock, which contains a high content of oxide. In the case of RGS wafers, oxygen might be incorporated into molten silicon from the growth ambient, as well as the feedstock. The Oi concentration in sheet silicon is approximately 20 ppma, and is in the range of 10 to 50 ppma in the RGS ribbon silicon. Precipitation of such a large amount of Oi will severely degrade solar cell performance. It is known that the initial Oi concentration, intrinsic point defects, the presence of carbon and nitrogen can all affect oxygen precipitation. The situation becomes more complicated in sheet silicon where a high concentration of carbon and nitrogen co-exist with grain boundaries. Thus, experimental characterization of the distribution of oxygen, carbon, nitrogen and their complex across the wafer thickness and near GBs via low temperature, infrared microspectroscopy is indispensable to clarify oxygen precipitation in sheet and ribbon silicon, and is helpful to the successful application of these two materials in the solar cell industry.
1.1.1 **Interstitial oxygen in crystalline silicon**

Oxygen incorporated in the silicon wafers mainly exists in the interstitial sites, denoted as O\textsubscript{i}, as revealed by the high-resolution cryogenic infrared absorption measurements [17] and by the small increase in Si lattice parameter compared with FZ Si [18]. O\textsubscript{i} is covalently bonded with two neighboring silicon atoms along the four equivalent <111> directions [19]. Early studies on interstitial oxygen [20] in silicon showed two main absorption features in the middle infrared (519 cm\textsuperscript{-1} and 1136 cm\textsuperscript{-1} at low temperature) and another structure in the far infrared (29 cm\textsuperscript{-1}). The three features were assigned to the three fundamental vibration modes of a puckered Si\textsubscript{2}O molecule, \nu\textsubscript{1} (the 519 cm\textsuperscript{-1} peak), \nu\textsubscript{2} (the 29 cm\textsuperscript{-1} band), and \nu\textsubscript{3} (the 1136 cm\textsuperscript{-1} or 9 \mu m stretching band), see Fig. 1(a).

It was recently shown [21,22] that the puckered image was misleading, a better one being that of a linear Si\textsubscript{3}≡SiO≡Si\textsubscript{3} molecule with dynamic D\textsubscript{3d} symmetry, as shown in Fig. 1(b) for the vibration modes. The assignments were consequently revised: the 519 cm\textsuperscript{-1} peak is not a vibration of the Si\textsubscript{2}O pseudomolecule, but a backbond Si—Si vibration of Eu symmetry of the corresponding D\textsubscript{3d} point group. The stretching mode (\nu\textsubscript{3}) remains essentially unchanged. At room temperature, interstitial oxygen gives rise to the well known 1107 cm\textsuperscript{-1} infrared absorption peak, and its concentration can be conveniently characterized by infrared measurements.

Diffusion of O\textsubscript{i} atoms occurs by atomic jumps from a bond-centered site to one of the six equivalent adjacent sites with a jump distance \( d = (2)^{1/2}a_0/4 = 1.92 \text{ Å} \), where \( a_0 = 5.42 \text{ Å} \) is the lattice spacing of Si. \( D_{\text{OXY}} \) is equal to \( d^2/\tau \), where \( \tau \) is the mean lifetime for a jump to
Fig. 1. Fundamental vibrational modes of the (a) puckered and (b) linear Si$_2$O quasimolecules, together with (c) the illustration of quantum delocalization of oxygen in Si:O$_i$ in the plane perpendicular to the Si-Si axis (Ref. [23]).

Fig. 2. Measured values and the best fit of the (a) diffusivity and (b) solubility of O$_i$ in crystalline silicon (Ref. [24, 31]).
occur. $\tau$ is given by $\tau_0*\exp(E_D/kT)$ at a temperature $T$, where $E_D$ is the activation energy. Thus $D_{\text{OXY}} = D_0 \exp(-E_D/kT)$, with $D_0 = a_0^2/8\tau_0$ [24]. Diffusivities of $O_i$ have been obtained from measurements of single atomic jumps by stress-induced dichroism [25,26], as well as analyses of high temperature in-diffused [27,28] and out-diffused [29] profiles by secondary ion mass spectroscopy (SIMS). After analyzed and fit these data for both low and high temperatures, Mikkelsen [30] showed that $O_i$ diffusion can be described by

$$D_{\text{OXY}} = 0.13 \exp(-2.53 \text{ eV/kT}) \text{ cm}^2 \text{ s}^{-1} \quad (1)$$

for a wide temperature range from 1325 to 350 $^\circ$C, see Fig. 2 (a). Diffusivities at temperatures below 400$^\circ$C can be precisely determined by stress-induced dichroism measurements, and those at temperature above 700$^\circ$C can be well characterized by in- and out-diffusion experiments. Diffusion data in the range of 400 to 700$^\circ$C are not well available because the temperature is too high to perform infrared measurements, while the diffusivity is too small for diffusion measurements. Anomalous enhanced $O_i$ diffusion has been observed in this temperature range [31].

The solubility of oxygen in crystalline silicon had been studied by different techniques. By fitting the experimental results from different groups, Mikkelsen showed that $O_i$ diffusion can be described by

$$C_0 = 9 \times 10^{22} \exp(-1.52 \text{ eV/kT}) \text{ cm}^{-3} \quad (2)$$

Figure 2 (b) gives an overview of the most important experimental results and the line
represents Eq. (2). Note that for temperatures above 1000 °C, the oxygen solubility values determined by different techniques are comparable, while significant differences have been observed at low temperatures.

1.1.2 Precipitate nucleation and growth: effect of impurities and point defects

The first stage of oxygen precipitation in silicon is nucleation, a process leading to the formation of aggregates of a few atoms, the so-called nuclei or precipitate embryos. Nucleation can proceed homogeneously or occur preferentially at crystal defects. Nuclei larger than a critical size will become stable and grow into large precipitates. The nucleation step is more complicated than precipitate growth, which is mainly controlled by O₂ diffusion. In polycrystalline sheet and RGS ribbon silicon, nucleation of oxygen precipitates is not likely to be a homogeneous process considering the readily available heterogeneous nucleation sites, such as dislocations, grain boundaries, and various kinds of C-O and N-O complexes presented in the wafers.

Oxygen precipitation is associated with a large volume expansion, and the resulted strain can be relieved either by absorption of vacancies, by emitting silicon self-interstitials, or by punching out dislocation loops. As a result, the presence of vacancies/interstitials will enhance/suppress oxygen precipitation. That is the reason why oxygen precipitation is suppressed when the wafer is annealed in an oxidation ambient. Voronkov studied oxygen precipitation in wafers with controlled vacancy concentration induced by rapid thermal annealing [32]. It was found that, with the vacancy concentration increased from 5 x 10¹² to 1 x 10¹³ cm⁻¹, the precipitate density increased by one order of magnitude, from 10⁹ to 10¹⁰ cm⁻³. Clearly, a higher vacancy concentration gave rise to a significantly higher precipitate density.
The impact of vacancies on oxygen precipitation is well illustrated by the successful application of Magic Denuded Zone (MDZ) process [33,34]. The first step of MDZ process is to install a vacancy concentration profile by rapid thermal annealing. The vacancy profile is further transformed into an oxygen precipitate profile during subsequent annealing by virtue of the enhancement of vacancies on precipitate nucleation.

The initial $O_i$ supersaturation ratio also has a strong impact on oxygen precipitation [35]. Figures 3 (a) and (b) show the reduction in $O_i$ concentrations in relation to the initial oxygen contents. B- and P-doped Cz (100) oriented silicon wafers from different silicon material vendors have been studied in different laboratories by measuring the difference of $O_i$ concentrations before and after the following two thermal treatments [36]. Test A consisted of a 16h annealing at $1050^\circ$C and test B was the same as test A, but with a 4 h preheating at $750^\circ$C. The solid lines around the data points in the figures represent the $2\sigma$ band in $\Delta O_i$ as calculated from the data of four laboratories. Note that when the initial $O_i$ concentration is below a critical level (15-17 ppma and 13-14 ppma for Test A and B, respectively), there is essentially no oxygen precipitation during annealing. On the other hand, if the initial $O_i$ concentration is 2 ppma higher than the critical level, there will be a significant amount, ~4 to 6 ppma, of $O_i$ precipitated. When the initial $O_i$ concentration is lower than a critical level for precipitate nucleation, nucleation and precipitation will be suppressed. On the other hand, the nucleation rate will be high if the initial $O_i$ concentration is high, which further results in a rapid precipitation. As a result, more $O_i$ eventually remained in the wafer having a lower initial $O_i$ concentration.
The presence of a low concentration of nitrogen significantly enhances oxygen precipitation. By examining the nitrogen doped and nitrogen-free samples after a three-step high-low-high intrinsic gettering process, Shimura [37] found that oxygen precipitation occurred in the oxygen out-diffusion region in the N-doped sample, a clear indication of enhanced oxygen precipitation. Nakai [38] also found that nitrogen doping enhances oxygen precipitation after heat treatment. The oxygen precipitate density in nitrogen-doped crystals after heat treatment does not change regardless of the heat treatment temperature, while the oxygen precipitate density of nitrogen-free crystals decreases as the heat-treatment temperature increases. They pointed out that a high density of grown-in oxygen precipitates might exist in the nitrogen doped as-grown samples.

Aihara [39] examined the thermal stability of oxide precipitate nuclei in Czochralski silicon crystals doped with nitrogen. The wafers were subjected to heat treatments ramping from T °C (T=600–1000) to 1050 °C with a rate of 1.5 °C/min, followed by a successive
annealing at 1050 °C for 4 h. The density of oxide precipitates after the heat treatment was measured by a light scattering topography method. It was found that nitrogen doping only enhances precipitate nucleation at higher temperatures during crystal cooling. The enhanced precipitate nucleation during cooling is considered to be through excess vacancies, which cannot agglomerate because of nitrogen. The fact nitrogen can suppress the formation of vacancy related defects suggests that nitrogen-vacancy reactions, no matter by forming N$_2$-V$_2$ or N$_2$-V [40,41], proceed at a temperature higher than 1100°C, which is the temperature for vacancy aggregation [42]. The presence of nitrogen helps trap vacancies at a higher temperature and further enhances oxygen precipitation.

The presence of substitution carbon was also found to enhance oxygen precipitation. Shimura [43] studied the oxygen precipitation in high carbon CZ wafers by infrared spectroscopy and proposed that carbon enhances oxygen precipitation at annealing temperature below 800 or 850°C by providing heterogeneous nucleation sites, such as [C–Oi] complexes. Hahn [44] studied the effect of carbon on oxygen precipitation and related phenomenon during various furnace and rapid thermal annealing. It was found that carbon enhances oxygen precipitation, and with the increase of carbon content, the precipitates predominantly have a polyhedral shape and are free of bulk stress. It was also found that carbon atoms suppress thermal donor formation during 450°C furnace annealing. The authors suggested that the major role of carbon in silicon wafers is to act as vacancy source, with perhaps a secondary role via a reduction of the Si-SiO$_2$ interface energy.

The opposite volume change associated with oxygen (+) and carbon (-) precipitation favors co-precipitation in an approximate ratio of 2:1. Sun found a direct correlation between the reduction of the substitutional carbon and that of interstitial oxygen for annealing at 750
and 1100 °C by means of FTIR measurements [45]. The correlated change in carbon and oxygen concentrations during annealing was explained by Cs-interstitial interactions. They proposed a two step process consisting of oxygen precipitation and kick-out of Cs by interstitials. In this process, oxygen precipitation controls the generation rate of interstitials, which in turn controls the removal of carbon atoms from their interstitial sites. The authors proposed that carbon enhances oxygen precipitation by providing heterogeneous nucleation sites and by trapping interstitials generated during oxygen precipitation.

1.1.3 Infrared studies of Oi and oxygen precipitates

Dissolved oxygen occupies interstitial sites, and gives rise to a strong absorption peak at 1107 cm\(^{-1}\) at room temperature. The 1107 peak was originally assigned to the antisymmetric stretching mode of the Si\(_2\)O pseudomolecule by Hrostowski and Kaiser [46], and has been used for many years to measure the concentration of O\(_i\) in silicon crystal. This band has a full width at half maximum (FWHM) of 34 cm\(^{-1}\) at room temperature and splits into a serious of features at low temperatures. Figure 4 is a recent high resolution FTIR absorption spectrum [47] obtained at 4.2 K from a sample containing enriched \(^{17}\)Oi and \(^{18}\)Oi. The line-widths are close to 1 cm\(^{-1}\), and two relatively weak satellite features on the low energy side of each line, displaced by 1.9 and 3.8 cm\(^{-1}\), respectively, are due to the vibrations of oxygen atoms bonded to a naturally occurring \(^{28}\)Si (92.3%) atom and a \(^{29}\)Si (4.7% abundance) or \(^{30}\)Si (3.0%) isotope, rather than to two \(^{28}\)Si (92.3%) atoms [48,49].

Oxygen precipitation can be indirectly studied by monitoring the change in O\(_i\) concentration before and after annealing. The ASTM standard F1239 was developed based on this idea to characterize oxygen precipitation in silicon wafers. Oxygen precipitates which
give rise to a broad absorption band can also be directly characterized by FTIR. Under different annealing procedures and impurity contents, the precipitated oxide might have various structures, such as α-quartz, cristobalite, amorphous, and B-doped oxide. It is also known that oxygen precipitates might be composed by SiO_x with x < 2 [50]. Oxide with different stoichiometry compositions and structures will have different dielectric constants, therefore will give rise to various shapes of absorption bands.

Figure 5 shows a series of infrared-absorption spectra of different silicon samples annealed in the temperature range of 600 to 1275°C [51]. In Fig. 5 (a) the broad band centered at about 1085 cm⁻¹, obtained on samples with O_i= 1.4 x 10¹⁸ cm⁻³, C_s=2.2 x 10¹⁶ cm⁻³ and annealed at 600°C for 240 h, is correlated with the presence of needle-shape precipitates. Spectrum (b) shows a less symmetrical broad band centered near 1100 cm⁻¹, which is obtained on sample with O_i= 1.5 x 10¹⁸ cm⁻³, C_s= 10.5 x 10¹⁶ cm⁻³, and annealed at 900°C for 64 h. Spectrum (c) is acquired on a sample contains O_i=1.4 x 10¹⁸ cm⁻³, C_s=6 x 10¹⁶ cm⁻³, and annealed at 900°C for 64 h, and shows a double band with peaks at 1120 and 1225 cm⁻¹. The 1225 cm⁻¹ band can be attributed to disk-shape precipitates, as suggested by Hu [52]. Spectra (d) is from a low carbon CZ sample annealed at 1275°C for 2 h. This spectrum shows the same features as the typical spectrum of amorphous bulk SiO₂ and was found only in Si wafers initially oxygen rich and carbon free. The corresponding TEM image reveals faceted octahedral precipitates in this sample.

Oxygen precipitates of different shapes give rise to infrared absorption bands with different structures. Hu [51] calculated the infrared spectra of silicon wafers with 50 ppm volume of small SiO₂ particles of various shapes using an effective medium theory. He found that disk-shaped precipitates tend to give rise to an absorption band at a high
Fig. 4. FTIR spectrum of a silicon sample (at 4.2 K) containing enhanced concentrations of $^{17}\text{O}$ and $^{18}\text{O}$, showing isotopic shifts of the associated LVMs to lower frequencies compared with that of $^{16}\text{O}$. The two weak satellites on the low energy side of each of the strong absorption lines are due to O atoms located between adjacent $^{29}\text{Si}$–$^{28}\text{Si}$ and $^{30}\text{Si}$–$^{28}\text{Si}$ isotopes, rather than a pair of $^{28}\text{Si}$ isotopes (Ref. [47]).

Fig. 5. Infrared-absorption spectra of different silicon samples annealed in the temperature range 600-1275°C (Ref. [51]).
wavenumber range, while needle-shaped precipitates give rise to an absorption band at a low wavenumber range. Similar approach was used in chapter 5 to calculate the infrared absorption spectra of SiC precipitates of various shapes.

1.1.4 Effect of oxygen precipitation on carrier lifetime

Under a constant level of minority carrier injection, the minority carrier distribution near oxygen precipitates will not vary with time, thus

$$\frac{\partial C}{\partial t} = D \cdot \nabla^2 C + G - \frac{C}{\tau_0}$$

(3)

The boundary conditions are

$$C\big|_{r=\infty} = G \cdot \tau_0$$

(4)

$$S \cdot C\big|_{r=r_0} = D \cdot \frac{\partial C}{\partial r}\big|_{r=r_0}$$

(5)

where, $C$ is the minority carrier concentration, $D$ the diffusivity coefficient of minority carriers, $\tau_0$ the lifetime due to impurities or detects other than precipitates, $G$ the generation rate of minority carriers, $S$ the recombination velocity at the precipitate-Si interface, and $r_0$ the radius of the precipitate. Using spherical coordinates, and let $y = C \cdot r$, equation (3) can be written as

$$\frac{\partial^2 y}{\partial r^2} - \frac{y}{L_0^2} + \frac{G \cdot r}{D} = 0$$

with $L_0^2 = D \cdot \tau_0$. The solution is

$$y = G \cdot \tau_0 \cdot r + A \cdot \exp\left(-\frac{r}{L_0}\right)$$. Thus, $C = G \cdot \tau_0 + A \cdot \frac{r}{r_0} \cdot \exp\left(-\frac{r}{L_0}\right)$

(6)

By Substituting (6) into the boundary conditions (4) and (5) and recognizing $L_0$ is much larger than $r_0$, we have,
\[ C = C_0 \left(1 - \frac{S}{S + \frac{D}{r_0}}\right) \cdot \frac{r_0}{r} \cdot \exp\left(-\frac{r-r_0}{L_0}\right) \]  \hspace{1cm} (7)\\

where, \( C_0 \) is the carrier concentration far from a particle.

Lifetime due to precipitates then equals (again using relation \( 1/L_0<<1/r_0 \)),

\[ \tau_{op} = \frac{C_0}{4\pi \cdot r_0^2 \cdot D \cdot \frac{\partial C}{\partial r} \mid_{r=r_0}} = \frac{1}{4\pi \cdot r_0 \cdot D \cdot n} \cdot \frac{S + D / r_0}{S} \]  \hspace{1cm} (8),

where, \( n \) is the precipitates density. In most practical cases, the size of the precipitates is below 1 \( \mu \text{m} \). Therefore, for P-type materials, \( D/r_0 \) is larger than \( 6 \times 10^5 \) cm/s, which is in general much larger than the effective surface recombination velocity at the Si-precipitate interface. Thus, equation (8) can be simplified as,

\[ \tau_{op} = \frac{1}{4\pi \cdot r_0^2 \cdot S \cdot n} \]  \hspace{1cm} (9).

Note that \( 4\pi \cdot r_0^2 \cdot n \) is just the total surface area \( A \) of the precipitates. Equation (9) implies that if \( S \) is significantly smaller than \( D/r_0 \), then the minority carrier concentration at the Si-precipitate interface will be the same as that far away from the precipitates, and the minority carrier recombination rate is proportional to \( S \cdot A \).

From the symmetry consideration, the concentration gradient at the middle of two adjacent particles should be zero, which cannot be satisfied by equation (7). In fact, we need to calculate the carrier distribution within a spherical cell with a radius \( R \), defined by \( \frac{4}{3} \pi \cdot R^3 = \frac{1}{n} \). Correspondingly, we need to replace the boundary condition (2) by \( \frac{\partial C}{\partial r} \mid_{r=R} = 0 \).
The only difference in the solution is that we need to keep the \( \exp\left(\frac{L}{L_0}\right) \) term in equations (6), which must be dropped off if we use the boundary condition (2) because it diverges at infinity. It is straightforward to calculate the carrier distribution using the new boundary condition. The result from the exact solution was compared with that from equations (9), and it was found that the difference is in general less than 5\% [53]. Considering that the uncertainties involved in the values of D, n, and S are all larger than 5\%, equation (9) is used to calculate the dependence of \( \tau_{op} \) on the precipitate density \( n \). Figure 6 shows the \( \tau_{op} \) verse \( n \) curve for the case \( \Delta O_i = 8 \times 10^{17} \text{ cm}^{-3} \) and two different surface recombination velocities. It is evident that S has a strong impact on lifetime, suggesting that a slight passivation of the precipitates can greatly suppress their recombination activities. Note that for the case of \( S = 1 \times 10^5 \text{ cm/s} \), the precipitate density need to be controlled below \( 1 \times 10^8 \text{ cm}^{-3} \) to make sure \( \tau_{op} \) larger than 8\( \mu \text{s} \).

Hwang and Schroder [54] studied the recombination properties of oxygen precipitated silicon using infrared absorption, TEM, DLTS, and SPV. They found that once interstitial oxygen precipitated in the silicon bulk, the minority carrier recombination lifetime reduced dramatically. TEM results showed that oxygen precipitates were the dominant structure defects, while dislocation loops and stacking faults were seldom observed. It was concluded that oxygen precipitates are mainly responsible for the observed lifetime degradation and that recombination at OPs takes place through Si-precipitate interfacial states. They found that the degree of lifetime degradation is more pronounced in p-Si than in n-Si. It was postulated that the existence of positive fixed charges in OPs, similar to the oxide charges in the oxide near the Si/SiO\(_2\) interface, are responsible for the lifetime difference between n-type and p-type
Fig. 6. Dependence of $\tau_{op}$ on the precipitate density for $S=1 \times 10^5$ and $2 \times 10^4$ cm/s, respectively.

Fig. 7. Schematic band diagram with band bending due to positive fixed charges in OPs which gives rise to (a) a depletion region in p-Si and (b) an accumulation layer around OPs in n-Si (Ref. [54]).
silicon. The positive charges give rise to a depletion region around OPs in p-Si, providing a larger collecting volume for minority carrier electrons, but an accumulation layer in n-Si, acting as a reflecting barrier for minority holes, see Fig. 7.

Based on the fact that oxygen precipitates can act as effective recombination centers, non-destructive methods for the determination of the density of oxygen precipitates in p-type silicon have been evaluated by means of minority carrier diffusion length measurements using surface photovoltage (SPV) and electrolytical Metal Analysis Tool (ELYMAT) methods [55]. P-type, <100> oriented, CZ-grown silicon wafers with O_i in the range of 10 to 17 ppma were annealed at low and high temperatures to facilitate precipitate nucleation and growth. The annealed samples were then examined by SPV and ELYMAT for carrier diffusion length, and by cleave and etching for the precipitate density. Figure 8 shows the relationship between SPV diffusion length and oxygen precipitate density. A good correlation can be observed in the density range of $5 \times 10^6$ to $10^{11}$ cm$^{-3}$. Note that the diffusion length decreased to several microns with the precipitate density approaching $1 \times 10^{11}$ cm$^{-3}$. In the ELYMAT case, again a good correlation was observed between the diffusion length and the precipitate density.

A high O_i concentration in multi-crystalline cast silicon was found to give rise to oxygen precipitates during solar cell processing and to decrease the short-circuit-current of the finished solar cells [56]. Figure 9 shows the variation of FeB and oxygen concentrations together with short circuit current values, measured on solar cells processed with and without hydrogen passivation from a SiN coating, in relation to the ingot position. Note that wafers from the bottom have a higher oxygen concentration, correspondingly give rise to a low short circuit current after solar cell processing, even after H passivation. By noticing that FeB
Fig. 8. SPV diffusion length plotted versus the precipitate density determined with the cleave and etch technique. Nucleation temperature is $650^\circ$C. (Ref. [55]).

Fig. 9. FeB and oxygen concentrations together with Short circuit current value in relation to the ingot position. (Ref. [56]).
concentration increases from 20 to 120 mm position, and its concentration in this region is overall below $2 \times 10^{11}$ cm$^{-3}$, the reduced short circuit current in the region from 20 to 60 mm is most likely due to oxygen precipitation.

Although the detrimental effect of oxygen precipitation on minority carrier lifetime has been well documented, there are only a few reports on defect levels in the band gap caused by oxygen precipitation [57]. While Hwang reported that oxygen precipitates give rise to localized states with energy levels at about $E_V +0.08$ eV, $E_V +0.3$ eV, and $E_C -0.45$ eV, Schmalz [58] reported deep levels at $E_C -0.3$ eV and $E_C -0.4$ eV. Koizuka [59] studied the gap states associated oxygen precipitates in both n- and p-type silicon crystals containing various types of precipitates by DLTS. A gap-state level at about $E_C -0.25$ eV was observed, as well as the previously reported peak at $E_V +0.3$ eV. The facts that the observed distribution of the gap-state density is very similar to that of the well-known Pb center due to dangling bonds of silicon atoms at the Si/SiO$_2$ interface and the gap states could be passivated by hydrogen, as found for the Pb center, suggest that both peaks are likely due to oxygen precipitates themselves, in particularly, defects at the Si-oxide interface.

1.2 Carbon precipitation in crystalline silicon

In modern Czochralski grown silicon used in the semiconductor industry, substitutional carbon ($C_s$) concentrations are in general below the detection limit of infrared measurements. Even for the wafers which indeed contain a small amount of carbon, studies of carbon have mainly focused on its enhancement effect on oxygen precipitation [43-45] and interactions with silicon self-interstitials ($I_{si}$) [60,61]. Carbon precipitation by itself is rarely an important process because of the typically low $C_s$ levels. The situation is very different in polycrystalline sheet and ribbon silicon. The $C_s$ concentration is in the range of 20 to 50 ppma.
in RGS silicon, and is approximately 10 ppma in sheet silicon. The high C\textsubscript{s} supersaturation
degree, plus the presence of a high concentration of O\textsubscript{i} and other structure defects, enhances
carbon precipitation. Considering a high density of carbon precipitates are likely to degrade
the minority carrier lifetime \[62\], an examination of carbon precipitation process in sheet and
RGS silicon is essential for their photovoltaic application.

1.2.1 Substitutional carbon in crystalline silicon

It has been shown \[63\] by differential infrared absorption that carbon occupies a
substitutional site in crystalline silicon. The absorption line of \(^{12}\text{C}\) was located at 605 cm\(^{-1}\) at
room temperature, and was overlapped on the shoulder of the strong lattice absorption band of
crystalline silicon. Corresponding lines were found for \(^{13}\text{C}\) and \(^{14}\text{C}\) at 586 and 570 cm\(^{-1}\),
respectively \[64\]. Triple-crystal X-ray spectroscopy measurements \[65\] confirmed that the
lattice constant of silicon decreases with increasing carbon content, also indicating a
substitutional configuration. Because carbon atoms occupy substitutional sites (denoted as C\textsubscript{s}),
they are not electrical active in crystalline silicon.

The carbon solubility in crystalline silicon wafers was investigated by infrared
absorption in the temperature range of 1150 to 1400\(^{\circ}\)C by Bean and Newman \[66\]. The
samples were first annealed for 100h at 1000\(^{\circ}\)C to reach equilibrium, then heated at a higher
temperature to let the precipitated oxygen and carbon dissolved until reaching their
corresponding solubility levels. The solubility of O\textsubscript{i} was found to be 2 x 10\(^{23}\) exp
\([(-1.65\pm0.15)eV/kT]\) cm\(^{-3}\), which was in reasonable agreement with the value given by
Mikkelsen \[30\]. Thus, it seems that a high carbon concentration does not modify the solubility
of O\textsubscript{i} at high temperature. The solubility of carbon was found to be 9 x 10\(^{24}\) exp
[(-2.3±0.25)\text{eV/kT}] \text{ cm}^{-3}, \text{ see Fig. 10. Endo [67] later confirmed that the uncertainty of the heat of dissolution was within 4%}.

The diffusion coefficient of carbon was measured by Newman and Wakefield [68] by measuring the in-diffusion profiles. Silicon samples were exposed in sealed SiO$_2$ ampoules filled with acetylene enriched with $^{14}$C or $^{14}$CO$_2$. Diffusion was performed in the temperature range of 1050 to 1400°C. The carbon profiles determined by sectioning and counting methods were fitted to an error function complement distribution. The diffusivity of carbon was found to be $1.9 \exp \left(\frac{-3.1\pm0.2}{\text{eV/kT}}\right) \text{ cm}^2/\text{s}, \text{ see Fig. 11. Recent experiments performed by Rollert [69] yielded essentially identical results with an activation energy of } 3.04\pm0.05 \text{ eV, over a more extended temperature range down to } 900^0\text{C}.$

![Fig. 10. An Arrhenius plot of the solubility of Cs in crystalline silicon (Ref. [66]).](image)
1.2.2 Effect of intrinsic point defects and oxygen content on carbon precipitation

Because of the large volume decrease associated with carbon precipitation and the relatively low diffusivity of $C_s$, carbon precipitation is difficult to proceed without the assistant of silicon self-interstitials. Oxygen precipitation is associated with a volume increase. The strain relief of oxygen precipitation may be realized by punching out small dislocation loops, or more probably by emitting silicon self-interstitials. The opposite volume change associated with oxygen (+) and carbon (-) precipitation favors co-precipitation in an approximate ratio of 2:1, as actually observed by Newman [66] and Sun [45]. It was also found that oxygen and carbon tend to co-precipitate at common sites, as revealed by SIMS [70]. Figure 12 illustrates the volume changes and defect reactions during oxygen and carbon precipitation [71].
Hul et al \cite{72} studied oxygen and carbon co-precipitation in Czochralski Si in terms of a diffusion-limited growth model. It was found that, at annealing temperatures below about 1000 °C, the enhancement effect of carbon on oxygen precipitation results primarily from an increase in the precipitate density. They again confirmed that an enhancement of C diffusivity in the presence of excess interstitials plays an important role in increasing the precipitate growth rate.

Silicon carbide precipitates can be directly characterized by infrared spectroscopy. Bean and Newman \cite{66} studied oxygen and carbon precipitation in high carbon CZ wafers by infrared spectroscopy, and found that with the removal of C\textsubscript{a} from the silicon, a asymmetrical broad band at 830 cm\textsuperscript{-1} appeared in the spectra of the annealed samples. They pointed out that the asymmetric band is due to SiC particles having a range of ellipsoidal shapes. The reason that the absorption band of SiC precipitates appeared at a higher wavenumber compared with
that of bulk SiC is that the precipitates are much smaller than the corresponding infrared wavelength (3.5 µm) in silicon matrix. A more symmetric SiC absorption band in the wavenumber of 800 to 950 cm\(^{-1}\) was observed in the 1250\(^{\circ}\)C annealed, low O\(_i\) containing EFG ribbon samples [73]. In all these studies, no specific correlation between the structure of infrared absorption bands and the geometry of SiC particles has been established. Because a characterization of the size and shape of SiC particles is essential for clarifying the nucleation and growth mechanisms of SiC precipitates, as well as for studying their impact on minority carrier lifetime, a quantitative interpretation of the infrared absorption band in terms of the size and shape of SiC particles is presented in chapter 5 by comparing the measured and calculated spectra.
Reference


(1983).


CHAPTER 2. RESEARCH METHODOLOGY

2.1 Introduction

In this thesis, different techniques were employed to characterize the structure, chemical, and electrical properties of light element impurities and related defects in sheet and ribbon silicon. Structurally, the grain structure, precipitate density, and the distribution of particle/dislocations clusters were studied by preferential chemical etching. Chemically, the spatial variation of C<sub>4</sub> and O<sub>1</sub> precipitation was studied by Fourier transform infrared (FTIR) microspectroscopy. The particle composition was characterized by secondary ion mass spectroscopy (SIMS) depth profile and FTIR measurements. The electrical activities of defects were evaluated with electron beam induced current (EBIC) technique. This chapter briefly describes these techniques and experimental procedures employed in this study.

2.2 Preferential chemical etching/Nomarski optical microscopy

Preferential chemical etching coupled with Nomarski optical microscopy allows us to quickly examine defects in a large sample area and with a high sensitivity. Polycrystalline sheet and ribbon silicon wafers are very inhomogeneous materials. We need to examine samples of several centimeters in order to correlate the cell performance with defect profile. Oxygen and carbon precipitates with a size of several tens nanometers and a density typically in the range of 10<sup>9</sup>-10<sup>11</sup> cm<sup>-3</sup> are difficult to study using other techniques, especially when we need to study their distribution within a millimeter large grain or across a thick cross-section. It is therefore not surprising that defect etching is the method of choice for characterizing defects in sheet and ribbon silicon. Complement with EBIC and FTIR microspectroscopy,
preferential etching is useful to determine the origin of the EBIC contrast, and to locate specific region for FTIR studies. Besides these specific virtues, preferential etching allows us to have an overview for what is going on in the sample, therefore provides guidance for further detailed studies.

2.2.1 Preferential etching formulas for crystalline silicon

The basic reactions in the dissolution of a Si surface are an oxidation of the silicon followed by removal of the oxide with HF. Usually, HF is in excess in the etching solution and the oxide is removed as fast as it forms. Thus, the delineation rate will be determined by the difference in oxidation rates between the defective and the surrounding areas. Local stress levels at defects are different from stress levels in the perfect silicon lattice. Since the oxidation rate is sensitive to this difference in stress levels, etch pits or hillocks will form at the defective sites, which can be further identified under a microscope.

Over the past fifty years, different preferential etching formulas have been developed. The commonly employed oxidants are HNO₃, CrO₃, K₂Cr₂O₇, and Cu(NO₃)₂. The fast working Sirtl etch [1] is almost exclusively used as a preferential etch for (111) wafers, and fails to produce pits on (100) planes and planes close to (100) orientation. Mounds are formed on (100) wafer surfaces, resulting in rough surface and loss of detail. The Secco etchant [2] works over a wide range of resistivities for n- and p-type silicon. It produces elliptical shaped dislocation pits on both (100) and (111) surfaces, making orientation determination by etch pits more difficult. The Wright etch [3] also works well for (100) and (111) oriented, n- and p-type silicon. In this system, the silicon is oxidized with HNO₃, CrO₃, and Cu(NO₃)₂. The CrO₃ is considered to be the principal oxidizing species. With the addition of a small amount
of Cu(NO₃)₂ the definition of the defect was enhanced. Besides the improved surface finishing and enhanced defect delineation, another advantage of the Wright etch is that it has long shelf life, about 6 weeks. Compared with the Sirtl etch, the Schimmel [4] and Yang [5] etches have a low concentration of oxidant, which gives rise to a slow etch rate, therefore helps to accentuate the etch rate difference between the defective sites and the surrounding area. They both works well on (111) and (100) planes. The Dash etch [6] yields deep etch pits from dislocations on any surface independent of its crystallographic orientation. It usually needs very long etch times of 4 to 16h. Formulas of commonly used preferential etches are listed in Table 2.1.

**Table 2.1** preferential etchants for crystalline silicon

<table>
<thead>
<tr>
<th>Etch</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sirtl</td>
<td>1 HF (49%) : 1 CrO₃ (5M)</td>
</tr>
<tr>
<td>Secco</td>
<td>2 HF (49%) : 1 K₂Cr₂O₇ (0.15M)</td>
</tr>
<tr>
<td>Wright</td>
<td>2 HF (49%) : 2 CH₃COOH : 1 HNO₃ + 1 CrO₃ (4M) : 2 Cu(NO₃)₂·3H₂O (0.14M)</td>
</tr>
<tr>
<td>Schimmel</td>
<td>2 HF (49%) : 1 CrO₃ (1M)</td>
</tr>
<tr>
<td>Yang</td>
<td>1 HF (49%) : 1 CrO₃ (1.5M)</td>
</tr>
</tbody>
</table>

### 2.2.2 Preferential etching of polycrystalline sheet and ribbon silicon

The Secco, Wright, and Schimmel etches have a low oxidant concentration, which makes them work well on both (100) and (111) surfaces. All three formulas can reliably delineate dislocations in polycrystalline sheet and ribbon silicon which has grains of various orientations. However, delineation of small precipitates is much difficult. In fact, we found
that none of these etches can reliably delineate small precipitates in grains with (100) orientation [7], which is known to etch at a faster rate than (111) plane, therefore has a poor selectivity.

The Secco etch is commonly used in our experiments. Depending on the objective and defect density, the etch time varies from 15 to 60 seconds. The density of precipitates is determined from grains with the highest pit density. These grains are found to be approximately in the (111) orientation by examining the directions of the stacking faults, which are observed in some annealed samples. An etch rate of 1 µm/min was used to calculate the bulk density of the precipitates. A well polished and cleaned surface is crucial important for delineating precipitates because these precipitates normally give rise to very small features. Any artifacts introduced by poor polishing or cleaning might prevent us from successfully characterizing the distribution and density of these small features. Normally, the sample was first boiled in acetone, then cleaned in methanol with ultrasonic agitation. Finally, the sample was rinsed in DI water and dried by compressed nitrogen gas. For some critical experiments which require a high reliability, such as delineation of defects in the specific region after EBIC characterization, samples were further boiled in a piranha solution (concentrated H₂SO₄ and H₂O₂ in 1:1 ratio) after methanol cleaning, and the oxide was then removed in a diluted HF solution. If dislocations and grain structures are the only concerns, polishing and cleaning procedures are not so critical because both Secco and Wright etches give rise to well resolved dislocation etch pits if the etching time is not too short, say no less than 30s.

2.2.3 Nomarski optical microscopy

The resolution of an optical microscope is limited by the diffraction effect. According to
the Raleigh criteria, the smallest distance between two points which can be resolved is \(d = \frac{0.61\lambda}{n \cdot \sin \alpha}\), where \(\lambda\) is the wavelength of light, \(n\) the index of refraction of air (or immersion oil), and \(\alpha\) the divergence angle that the objective lens can accept. The product \(n \cdot \sin \alpha\) is called the numerical aperture (NA). The resolution of the best optical microscope is about 0.2 \(\mu\)m.

**Fig. 1.** Ray diagram of a differential interference contrast (Nomarski) microscope working in the reflection mode. OP, object plane; MO, microscope objective; IP, ray intersection plane; NP, Nomarski prism; BS, beamsplitter; P, polarizer; A, analyzer; T, tube lens; C, image plane (Ref. [9]).

A major breakthrough in optical microscopy is the invention of the differential interference contrast technique by Nomarski [8]. It is the most important method for optical examination of semiconductor surfaces after preferential etching. Figure 1 illustrates the ray diagram of a Nomarski microscope working in the reflection mode [9]. Illumination generated by the light source first passes through a linear polarizer P. The linearly polarized light is then
reflected by a beamsplitter placed at a 45-degree angle to the incident beam. The deflected light waves, which are now traveling along the microscope optical axis, enter a Nomarski prism located above the objective in the microscope nosepiece where they are split up by the Nomarski prism into extraordinary (E) and ordinary (O) rays and sheared according to the geometry of the birefringent prism. The microscope objective focuses sheared orthogonal wavefronts produced by the Nomarski prism onto the object plane or the specimen at two closely separated points. Reflected wavefronts, which experience varying optical path differences as a function of specimen surface topography, are gathered by the objective and focused on the interference plane of the Nomarski prism where they are recombined to eliminate shear. After exiting the Nomarski prism, the wavefronts pass through the beamsplitter, and then encounter the analyzer normally positioned with its transmission axis orthogonal to the axis of the polarizer. Components of the orthogonal wavefronts that are parallel to the analyzer transmission vector are able to pass through, and subsequently undergo interference to generate amplitude fluctuations and form the differential interference contrast image [10]. Formation of the final image is the result of interference between two distinct wavefronts. Note that the contrast of the Nomarski image is controlled by the optical path difference between the orthogonal components. Therefore, the surfaces having the same slope will have the same contrast (or color).

2.3 Fourier transform infrared spectroscopy

Because oxygen, carbon, and nitrogen are less massive than the host silicon atoms, they typically show local vibrational modes and give rise to sharp infrared-absorption peaks. Their corresponding precipitation phases, oxide, carbide and nitride are polar compounds, and give
rise to strong absorption bands in the infrared range. Thus, infrared absorption spectroscopy is an unique and powerful technique in studies these light element impurities and related defects because it can differentiate these light elements in their different states (dissolved, complexes, and precipitates) and characterize their corresponding concentrations with high detection limits, in general below 0.2 ppma at room temperature. In recognizing the technical importance of FTIR, several ASTM standards [11] have been developed to measure the O\text{I} and Cs concentrations, and characterize oxygen precipitation in silicon wafers.

### 2.3.1 Principle of Fourier transform infrared spectroscopy

All our infrared absorption measurements are performed on Fourier transform infrared spectrometer. Compared with dispersive infrared spectroscopy, FTIR spectroscopy has the advantages of high spectral resolution, good signal-to-noise ratios, and the ability to measure a broad region of the spectrum in a short amount of time [12]. The central component of a FTIR spectrometer is a Michelson interferometer, see Fig. 2. A parallel beam of collimated light from a broadband source is directed at a semitransparent beamsplitter. One of the two beams reflects off a movable mirror while the other beam reflects off a fixed mirror. The two beams recombine at the beamsplitter, travel through the sample, and finally impinge upon a detector. The detector signal is proportional to the intensity of the interfered beam and the plot of intensity versus optical path difference in real space is the interferogram. The Fourier transformation of the interferogram gives rise to the spectrum in frequency space, which is usually called the single channel spectrum. In practice, to maximize the signal-to-noise ratio, up to several thousand interferograms are taken and averaged before the Fourier transform is performed.
2.3.2 Equipment setup and experimental procedure

Two sets of FTIR systems are used in this experiment. One is a Digilab FTS-6000 FTIR spectrometer, equipped with an UMA 500 infrared microscope. A broad-band mercury – cadmium – telluride (MCT) detector with a cutoff frequency of 430 cm$^{-1}$ is mounted in the spectrometer bench, and a narrow-band MCT detector with a cutoff frequency of 650 cm$^{-1}$ is mounted in the infrared microscope. The configuration of this micro-FTIR system is schematically shown in Fig. 3.

The O$_i$ absorption peak cannot be well distinguished from the absorption band of oxide precipitates at room temperature due to the band overlapping. With the decrease of the sample temperature, the O$_i$ peak shifts to higher wavenumbers and becomes sharper, while the OP absorption band essentially does not change. Thus, a low temperature setup is needed.
to characterize Oᵢ in oxygen precipitated wafers. Compatible with the UMA 500 IR microscope, a continuous liquid-He cooled micro-cryostat from Oxford Instruments allows us to perform low temperature FTIR microspectroscopy. Samples are usually polished to 250 to 300 µm thick to minimize the infrared beam spreading inside the sample, and to prevent the Oᵢ absorption from saturation at low temperatures. Because of the attenuation of the infrared beam by the small aperture and the two ZnSe windows of the cryostat, plus the use of a thin sample, the S/N level is barely acceptable when the rectangular aperture is adjusted to 250 x 40 µm².

**Fig. 3.** Schematic of the UMA 500 infrared microspectrometer used in this study. The system is a combined FTIR spectrometer and microscope.

Another system is a Bruker 66v/S Fourier transform infrared spectrometer equipped with an IR microscope at the U2A beamline of the National Synchrotron Light Source. Besides the
internal narrow-band MCT detector in the microscope, a bolometer or a B-doped Si detector, both working at liquid He temperatures, can be accommodated in this micro-FTIR system. A switchable internal mirror, designed to intercept the collimated beam just upstream of the system’s conventional mid-IR MCT detector, directs the infrared to an off-axis parabolic mirror that focuses the light into the external detector. A significant advantage of this system is that the synchrotron infrared light source is about 3 orders brighter than the conventional Globar infrared source. Thus, a diffraction limited spatial resolution is achievable and the spectra have a better signals-to-noise ratio. Figure 4 shows the intensity profile of the synchrotron light source measured at the U2A beamline using a 5 µm pinhole. Note that the synchrotron beam flux is concentrated in the center ~10 µm region [13].

**Fig. 4.** 3D intensity profile and the counter of the synchrotron source mapped with a 5 µm pinhole. Note the FWHM is less than 20µm [13].
2.4 Electron beam induced current (EBIC) characterization

The EBIC technique employs a SEM to study the electrical activity of defects under a thin electron-transparent Schottky contact (usually evaporated Al), see Fig. 5. The electron beam generates electron-hole pairs. The minority carriers either recombine at defects or are collected at the Schottky contact. The amplified EBIC current is synchronized with the electron beam scan to generate an image, which is either displayed on a monitor or recorded by a computer. The presence of electronically active defects will enhance minority carrier recombination, thus reduce the EBIC current and give rise to a dark contrast in the EBIC image. In this manner, the electrical activity and distribution of defects is characterized. In our experiments, Al-Schottky diodes were fabricated on chemical-mechanical polished surface for EBIC measurements, which were performed on a scanning electron microscope with a typical accelerating voltage of 20 KV and a beam current of ~0.1 nA.

![Fig. 5. Schematic of EBIC measurement [14]]
Fig. 6. (a) Illustration of the direct EBIC comparison measurement. (b) Directly EBIC comparison image acquired on the as-grown (left half) and 1100°C, 3h annealed (right half) sheet silicon samples.

While EBIC can detect small lifetime variation within one diode, it is difficult to compare the electrical activities of defects in different diodes or samples. The reason is that it is difficult to maintain the exactly same electron beam current when we move the probe from one diode to another. The drift of the electronic system will also make it very difficult to detect small lifetime difference between two diodes. To compare samples after different thermal processes, it is important to measure them within the same diode. A method used in this study is to contact the two samples by a copper wire to form one diode on two samples. First, Al Schottky contacts were fabricated near the sample edges. Then, the two samples were placed side by side and a Cu wire was put between the two adjacent half-circle contacts. We
press the probe on the copper wire to make sure it is well connected to both samples. By this way, one diode was formed on two samples and direct EBIC comparison was performed. Figure 6 (a) and (b) are an illustration of directly EBIC comparison measurements and a direct comparison EBIC image acquired on an as-grown and 1100°C, 3h annealed sheet silicon wafers. Note that the lifetime is dramatically improved during annealing.
Reference


11. Annual Book of ASTM Standards (American Society for Testing and Materials), Philadelphia, PA, 1994, Vol. 10.05, p. F1188 (Oi concentration), F1619 (Oi concentration with polarized radiation incident at the Brewster angle), F1391(Cs concentration), and F1239 (oxygen precipitation).


CHAPTER 3. OXYGEN-PRECIPITATE DENUDED-ZONE IN POLYCRYSTALLINE SHEET SILICON

3.1 Introduction

The direct growth of sheet or ribbon silicon from molten Si has received increased attention in recent years because it is highly suitable for low-cost terrestrial-based solar cells [1]. Three different ribbon or sheet technologies, the edged defined film filled growth (EFG), the string ribbon, and the Silicon-Film, have reached the MW volume production level. The Silicon-Film sheets studied here are grown in a horizontal configuration. This permits a two orders higher pulling rate than the vertical configuration used in EFG and string ribbon technologies by decoupling the pulling direction from that of grain growth [2]. Since each grain only need to grow a distance equal to the sheet thickness, low-cost, impure feedstock can be used without deteriorating the grain structure integrity. Accompanying these cost-efficiency advantages, the impurity concentration is usually high due to the relative large contact area with the substrate and the low cost silicon feedstock used in sheet generation [3, 4]. Thus, detailed knowledge is required on the impact of impurities on cell performance to take advantage of this highly cost-effective growth process.

Of particular importance is the control of oxygen precipitates (OP), which can significantly degrade the minority carrier lifetime. Because the low-cost feedstock usually contains a high content of oxide, the concentration of interstitial oxygen (O_i) in the as-grown wafers usually reaches $10^{18}$ cm$^{-3}$. Once incorporated into the wafer, precipitation of supersaturated O_i is enhanced during annealing because of the presence of readily available impurity and microdefect nucleation centers [3]. The characterization presented in this paper reveals a 250µm wide precipitate denuded zone near the top surface generated through
combined control of the growth and annealing processes. Thus, the detrimental effect of OPs on the minority carrier lifetime is partially eliminated.

A denuded zone near the top surface is usually considered not to be useful for silicon solar cells since the entire wafer thickness is functioning as an active region with respect to light absorption and minority carrier collection. While this is absolutely true for high efficiency solar cells, it is not true for solar cells made from low-cost silicon sheets. Because the minority carrier diffusion length of the sheet silicon is about 50 to 100µm, a high lifetime denuded zone with a width of 250µm will certainly improve the cell performance. Denuded zone formation coupled with internal gettering has been successfully employed in the integrated circuit industry for device yield improvement in the past three decades [5,6]. Such a traditional denuded zone is usually achieved through a three step, high-low-high annealing process, and its width is in general below 20µm, which is too small for significant solar cell efficiency improvement. A 250µm OP denuded zone in sheet silicon is achieved through a combined control of the growth and annealing processes. First, a large Oi denuded zone is installed into the silicon sheet by enhancing SiO evaporation via a more aggressive growth thermal profile. The Oi denuded zone is further sustained as a precipitate denuded zone during the following annealing.

3.2 Experiments

Polycrystalline sheet silicon wafers used in this study were generated at a linear sheet speed of 3.1 meters/min. The wafers were about 800 µm thick and were boron doped to a resistivity of 2 to 3 ohm·cm. A more aggressive growth thermal profile was used to facilitate oxide dissolution and SiO evaporation. The upper region of the polycrystalline silicon sheet
has columnar grains, ranging in size from 200 µm to 2 mm. One-inch square samples cut from an eight-inch wide silicon sheet were annealed in air at 1050°C for 2, 4, 8, and 16 hours, respectively, to study oxygen precipitation in sheet silicon.

The O\textsubscript{i} depth profiles were characterized by cross-sectional Fourier transform infrared (FTIR) microspectroscopy at 4.2K using a Digilab FTS-6000 spectrometer equipped with an UMA 500 infrared microscope and a continuous liquid-He cooled micro-cryostat from Oxford Instruments. Low temperature measurements are required to measure O\textsubscript{i} concentration in annealed samples, due to the need for separating the O\textsubscript{i} peak from the OP bands [7]. A 1.5 mm wide strip was cut from each sample and double-side cross-sectionally polished to 300µm. A thin sample is required to minimize the infrared beam spreading inside the sample, and to prevent the O\textsubscript{i} absorption from saturation at low temperatures. FTIR microspectroscopy was performed on the polished cross-section with a step size of 50 µm and an aperture size of 250 x 40 µm\textsuperscript{2}. The long edge parallel to the wafer surface increased the beam intensity, while the short edge perpendicular to the wafer surface increased the spatial resolution. The spectra resolution is set at 4 cm\textsuperscript{-1} to eliminate interference fringes due to multi-internal reflections.

After cross-sectional FTIR measurements, the distributions of OPs and associated extended defects were also examined by Nomarski optical microscopy following a 30 seconds preferential Secco etch. To verify the impact of OPs on minority carrier lifetime, Al-Schottky diodes were fabricated on polished cross-sections for electron beam induced current (EBIC) measurements, which were performed on a scanning electron microscope at room temperature with an accelerating voltage of 20 KV and a probe current of 0.2 nA.
3.3 Results and Discussion

Figures 1 (a) and (b) are the cross-sectional FTIR spectra of the as-grown and 2h annealed samples. The absorption bands at 850-1050 cm\(^{-1}\) are due to oxynitride particles [8]. Note that the noise level of the spectra is quite high because of the attenuation of the infrared beam by the small aperture and the two ZnSe windows of the cryostat. The thin samples used in this study also increase the background noise level. However, the O\(_i\) absorption peak can still be well resolved because of peak sharpening with decreasing temperature. Note that the intensity of the 1136 cm\(^{-1}\) oxygen peak in the as-grown sample decreases towards the top surface, while the oxide absorption band at 1100 cm\(^{-1}\) appears in the deeper region of the sample, see Fig. 1(a). From the fact that the O\(_i\) denuded zone does not form in wafers grown with a less aggressive thermal profile, it is proposed that SiO evaporation from the Si melt during sheet growth is responsible for the denuded zone formation. After 2 hours annealing at 1050° C, more O\(_i\) remained in the near top surface region, while almost all the interstitial oxygen precipitated in the deeper region, see Fig. 1 (b). Note that the oxide absorption band in the deeper region increased significantly with the precipitation of O\(_i\).

The O\(_i\) concentration was further calculated from the integrated intensity of the 1136 cm\(^{-1}\) absorption peak, using a conversion factor obtained by measuring O\(_i\) concentration of an as-grown, precipitate-free Czochralski wafer at room temperature, and the integrated absorption of the 1136 cm\(^{-1}\) peak of the same sample at 4.2K. Figure 2 plots the calculated O\(_i\) depth profiles of the as-grown and annealed samples. Note that almost all supersaturated oxygen in the deeper region precipitated during a 2h annealing, while a considerable amount of O\(_i\) remained near the top surface region, even after 16h annealing. It is well known that the
Fig. 1. FTIR spectra acquired at 4.2K on the polished cross-sections of (a) as-grown and (b) $1050^\circ$C, 2h annealed sheet silicon samples.
initial O\textsubscript{i} supersaturation ratio has a strong impact on oxygen precipitation in CZ wafers [9]. When the initial O\textsubscript{i} concentration is lower than a critical level for precipitate nucleation, precipitation will be suppressed. On the other hand, the nucleation rate will be high if the initial O\textsubscript{i} concentration is high, which further results in rapid precipitation. As a result, more O\textsubscript{i} is left in the region having a lower initial O\textsubscript{i} concentration. While the initial O\textsubscript{i} concentration is an important factor impacting oxygen precipitation, the fast precipitation in the deeper region might also be related to the nitrogen distribution. Since its segregation factor is smaller than unity, nitrogen will buildup near the back surface region with solidification proceeding from top to bottom. Considering that nitrogen [10,11] can enhance oxygen precipitation, it is believed that the higher contents of N in the deeper region also contribute to the fast oxygen precipitation there.

The distribution of OPs and associated extended defects was also examined by Nomarski optical microscopy following cross-sectional polishing and a 30 seconds preferential Secco etching. No significant difference was detected between the four annealed samples. Figure 3 shows the Nomarski images of the 8h annealed sample. Note that a 250µm wide, well-defined precipitate denuded zone was formed near the top surface, see Fig. 3 (a). Under higher magnification, it is evident that the defects in the deeper region are either isolated OPs or stacking faults (SFs), see Fig. 3 (b). While a high density of SFs was observed in the region shown in Fig. 3, some grains contained only a high density (1x10\textsuperscript{11} cm\textsuperscript{-3}) of OPs. It was also found that the density of OPs in the region with SFs is in general several times lower than the region without SFs. While the generation of self-interstitials during oxygen precipitation makes SF formation thermodynamically favorable, OPs themselves make SF formation kinetically possible by acting as heterogeneous nucleation.
Fig. 2. Depth profiles of \( O_i \) of the as-grown and 1050\(^{0}\)C annealed samples.
Fig. 3. Cross-sectional Nomarski images of the $1050^\circ$C, 8h annealed sample after 30s Secco etching. (a) low magnification image with top surface facing upwards; (b) zoom in of the shadowed region indicated in (a).
sites. With the same amount of $O_i$ precipitated, the higher the OP density, the smaller each precipitate. The suppression of SF formation in the region with a high density of OPs is likely due to the absence of large precipitates, which are needed for SF nucleation.

There are three main limitation factors on diffusion length in the polycrystalline sheet Si; namely, a high density of precipitates, the presence of grain boundaries, and included particles with associated dislocation clusters. Because of the low spatial resolution of diffusion length characterization techniques (below 100 microns in general), it is difficult to isolate the contribution due to oxygen precipitates from those of grain boundaries and dislocation clusters. As a result, we cannot say the diffusion length is improved/degraded because of the denuded zone, even if the measured diffusion length is indeed higher/lower than that in a control wafer. However, the higher spatial resolution of EBIC permits us to study the impact of precipitates on diffusion length without the interference of grain boundaries and dislocation clusters, although we cannot quantitatively determine the diffusion length from the EBIC contrast.

Al-Schottky diodes were fabricated on polished cross-sections for EBIC measurements. Again, the denuded zone was observed in all the annealed samples, except the as-grown one. Two representative EBIC images obtained on the as-grown and 4h annealed samples are shown in Fig. 4. Note that the EBIC contrast is uniform across the cross-sections of the as-grown sample, while a bright contrast with a depth of 200-300µm is formed near the top surface of the 4h annealed sample. Correlated with the FTIR and etching results, the bright contrast near the top-surface region is clearly due to the absence of OPs. The high density of OPs in the deeper region might function as beneficial gettering sites for transition metals,
Fig. 4. Cross sectional EBIC images of the as-grown (a) and 1050°C, 4h annealed (b) samples.

The sample thickness is around 800µm and the top surfaces are facing upwards.
further improving the lifetime of the denuded zone. Because OPs will act as effective recombination sites after decorated by transition metals, and the Fe concentration in the sheet silicon is on the order of \(10^{14}\) to \(10^{16}\) cm\(^{-3}\), the dark EBIC contrast in the deeper region is clearly due to the high density, decorated OPs and SFs.

### 3.4 Conclusion

In summary, an O\(_i\) denuded zone is generated in the as-grown sheet silicon wafer by employing a more aggressive growth thermal profile. The O\(_i\) denuded zone is sustained as a 250 µm wide precipitate denuded zone after annealing, mainly due to the critical role of the initial O\(_i\) concentration on precipitation. EBIC characterization shows that the lifetime in the denuded zone is significantly improved. Considering that the minority carrier diffusion length of current finished solar cells with no denuded zone is around 50-100µm, it is anticipated that a 250 µm thick denuded zone with an increased minority carrier diffusion length will improve solar cell performance.
Reference


CHAPTER 4. SPATIAL VARIATION OF OXYGEN AND CARBON PRECIPITATION IN POLYCRYSTALLINE SHEET SILICON

4.1 Introduction

Sheet silicon wafers studied here are grown in a horizontal configuration, which permits a two order higher pulling rate than the vertical configuration used in EFG and string ribbon technologies by decoupling the pulling direction from that of grain growth [1]. Since each grain only need to grow a distance equal to the sheet thickness, low-cost, impure feedstock can be used without deteriorating the grain structure integrity. Accompanying these cost-efficiency advantages, the impurity concentration is usually high due to the relative large contact area with the substrate and the low cost silicon feedstock used in sheet generation [2, 3]. Thus, detailed knowledge is required on the impact of impurities on cell performance to take advantage of this highly cost-effective growth process. Of particular importance is the control of oxygen precipitates (OP), which can significantly degrade the minority carrier recombination lifetime [4-8]. Because the low-cost feedstock usually contains a high content of oxide, the concentration of interstitial oxygen (O_i) in the as-grown wafers usually reaches $10^{18}$ cm$^{-3}$. Once incorporated into the wafer, precipitation of supersaturated O_i is enhanced during annealing because of the presence of readily available impurity and microdefect nucleation centers [2].

Substitutional carbon (C_S) in crystalline silicon is not electrical active [9], and its concentration in as-grown sheet silicon wafer is around 3 to $5 \times 10^{17}$ cm$^{-3}$. Studies of carbon in Czochralski silicon have been mainly focused on its enhancement effect on oxygen precipitation [10-13] and interactions with silicon self-interstitials (I_{Si}) [14-15]. Carbon
precipitation by itself is rarely an important process because of the typically low $C_S$ levels in silicon wafers. The situation is very different in the polycrystalline sheet silicon, which usually contains a high concentration of $C_S$ and $O_i$. The high supersaturation degree of $C_S$ and the presence of $O_i$ enhance the formation of carbon precipitates [16]. A high density of carbon precipitates will degrade the minority carrier lifetime. Thus, detailed knowledge on carbon precipitation, especially regarding to the effect of oxygen content, is required to improve the performance of solar cells made from sheet silicon.

Optimization of the spatial distribution of precipitates is an important issue for solar cell efficiency improvement considering that minority carrier recombination centers located near the emitter are more detrimental to the short-circuit current, open-circuit voltage, and filling factor than defects located in the deeper region. This is especially true for sheet silicon because the minority carrier diffusion length of the sheet silicon is about 50 to 100µm, and defects located in 200µm or deeper region will have a minor impact on cell efficiency. In this chapter, spatial variation of oxygen and carbon precipitation in relation to thermal annealing process in four sets of sheet silicon wafers were studied. Issues regarding to the precipitate distribution, the impact of quench-in vacancies, and the effect of oxygen content on carbon precipitation have been examined.

4.2 Experiments

Four sets of sheet silicon samples, denoted as #79, 80, 253, and 254, respectively, were grown with different thermal growth profiles at GE Energy. Sample #79 was grown with the most aggressive thermal profile; in other words, the feedstock silicon powder experienced a deeper and longer melting process. Sample #80 was grown with a medium thermal profile,
and samples #253 and 254 were grown with the lowest thermal profiles. One-inch square samples cut from samples # 79 and 80 were annealed in air at 900 and 1200°C for 4h, and at 1050°C for 2, 4, 8, and 16 h, respectively, to study oxygen and carbon precipitation in sheet silicon. Samples #253 and 254 went through a high temperature annealing process performed at about 1100°C for 3 h.

EBIC needs to be performed on a polished surface to eliminate the interference due to surface topography, whereas FTIR measurements need to be performed on an etched surface to locate the area with desired grain structures. Therefore, samples were first characterized by cross-sectional EBIC, followed by preferential etching/Nomarski optical microscopy, and finally examined by FTIR microspectroscopy.

A 1.5 mm wide strip was cut from each sample and double-side cross-sectionally polished to 300µm. A thin sample is required to minimize the infrared beam spreading inside the sample, and to prevent the O₁ absorption from saturation at low temperatures. Al-Schottky diodes were fabricated on polished cross-sections for EBIC measurements, which were performed on a scanning electron microscope at room temperature with an accelerating voltage of 20 KV and a probe current of ~0.1 nA. Direct EBIC comparison of samples after different processing was conducted by wiring of the front contacts by a copper wire.

Following EBIC measurements, the distribution of precipitates and associated extended defects was examined by Nomarski optical microscopy after stripping off the Al contacts in a HCl solution and etched in a Secco solution [17] for 30 sec. Finally, the O₁ depth profiles in the representative large grain regions were characterized by cross-sectional FTIR microspectroscopy at 4.2K using a Digilab FTS-6000 spectrometer equipped with an UMA 500 infrared microscope and a continuous liquid-He cooled micro-cryostat from Oxford.
Instruments. Low temperature measurements are required to measure $O_i$ concentration in annealed samples, due to the need for separating the $O_i$ peak from the OP bands. FTIR microspectroscopy was performed with a step size of 50 µm and an aperture size of 250 x 40 µm$^2$. The long edge parallel to the wafer surface increased the beam intensity, while the short edge perpendicular to the wafer surface increased the spatial resolution. The $O_i$ concentration was calculated from the integrated intensity of the 1136 cm$^{-1}$ absorption peak, using a conversion factor obtained by measuring $O_i$ concentration of an as-grown, precipitate-free Czochralski wafer at room temperature, and the integrated absorption of the 1136 cm$^{-1}$ peak of the same sample at 4.2K.

Because the narrow-band MCT detector of the UMA 500 IR microscope cuts off at ~650 cm$^{-1}$, the $C_s$ absorption peak located at 607 cm$^{-1}$ cannot be resolved. Therefore, $C_s$ profiles were further characterized on a Bruker 66v/S FTIR spectrometer equipped with an IR microscope and a B-doped Si detector working at liquid-He temperatures, at the U2A beamline of the National Synchrotron Light Source. The concentration of $C_s$ was determined from the absorption peak at 607 cm$^{-1}$ using the conversion constant in ASTM methods F1391.

4.3 Results and Discussion

4.3.1 $O_i$ and $C_s$ profiles in the as-grown wafer: impact of growth thermal profile

Figure 1 shows the $O_i$ depth profiles of the as-grown samples. We can see that the $O_i$ concentrations in wafers experienced more aggressive thermal growth profiles were overall lower than those grown with less aggressive thermal profiles. Note that $O_i$ denuded zones with a width of 250 and 100 µm were formed in samples #79 and 80, respectively. No $O_i$ denuded zone was observed in samples #253 and 254. It is known that more than 95% of the oxygen
dissolved from the quartz crucible during Czochralski silicon growth evaporates into the ambient in the form of SiO [18]. From the facts that the O_i denuded zone is deeper in the sample grown with a more aggressive thermal profile, and the denuded zone does not form in wafers grown with less aggressive thermal profiles, it is proposed that SiO evaporation from the Si melt during sheet growth is responsible for the denuded zone formation. Note from Fig. 1(b) that C_s was homogeneously distributed across the wafer thickness, and its concentration, which varied from 3 to 4 x 10^{17} \text{cm}^{-3}, was not dependent on the growth thermal profile. Since its segregation factor is smaller than unity, C will tend to build up near the back surface with solidification proceeding from top to bottom. The measured homogeneous distribution profiles suggest that the solidification rate is so high that the effective segregation factor approaches unity.

The diffusivity of oxygen in molten Si is around 10^{-4} \text{cm}^2/\text{s} [19], therefore the diffusion length in 1 sec is approximately 100\mu m. Since the total melting time will be much longer than one second, it is difficult to explain why the O_i denuded zone is only 100 and 250\mu m wide in samples # 80 and 79. Note that even a layer of Si_3N_4 or solid Si formed on the top surface preventing SiO evaporation, oxygen atoms should still be homogenized in the liquid phase in a short time. Assuming that there are no sources or sinks in the liquid bulk and the surfaces, and the profile starts from a stepwise distribution-the most inhomogeneous distribution, theoretical calculation shows that it only takes about 7 and 2 seconds to homogenize oxygen in a 700 and 350\mu m thick liquid silicon layer, respectively. The difficulty of the simple evaporation-diffusion model is that the distinct denuded zones appeared in samples #79 and 80 require the whole solidification process across the wafer thickness to be
Fig. 1. $O_i$ depth profiles in as-grown wafers.

Fig. 2. $C_s$ depth profiles in as-grown wafers.
finished in a very short time, say less than 2-3 seconds. It is believed that the relative small O_i

denuded zone is likely due to the presence of a high content of oxide in the silicon feedstock.

At the top surface, SiO continuously evaporates from the melt into the ambient; in the molten
Si, oxide particles continuously dissolve and provide oxygen to Si melt. The balance between
oxide dissolution, oxygen diffusion, and SiO evaporation controls the oxygen profile.

For a short melting time, oxide particles are distributed throughout the liquid layer and
the evaporation of SiO can only build up a small oxygen gradient just below the surface.
Because the oxygen concentration near the top surface is lower than the deeper region, oxide
particles will dissolve faster. With the larger oxides become smaller and smaller ones totally
dissolved, the oxygen concentration near the top surface will continuously decreases.

Following the dissolution of oxide, the oxygen denuded zone becomes deeper. In the deeper
region, the dissolution rate is low. With the presence of oxide particles, the oxygen
concentration remains high. It is anticipated that oxygen will be depleted throughout the
whole wafer thickness if the feedstock silicon does not contain oxide particles, such as the
Czochralski grown silicon.

4.3.2 Spatial variation of oxygen and carbon precipitation

(a) Sample #79

Figure 3 shows a cross-sectional EBIC image of the 1050°C, 4h annealed sample #79.
Note that a clearly defined EBIC dark contrast strip appeared at the 300 µm deep region.
Figure 4 is the corresponding Nomarski image of the region marked in Fig. 3. Note that the
EBIC dark contrast strip was well correlated with the presence of a high density of
precipitates. Supposing that 0.5µm materials was removed during a 30 sec Secco etching, the
precipitate density inside the precipitation band can be determined as $\sim 8 \times 10^{10} \text{ cm}^{-3}$ and that outside the band (near the top surface or the deeper regions) is around or below $1 \times 10^{10} \text{ cm}^{-3}$. It was found that the precipitation band in fact appeared in all the annealed samples except the one annealed at $1200^\circ\text{C}$.

The existence of the precipitation band was further verified by FTIR microspectroscopy, which was performed at 4.2K to separate the O$_i$ absorption from that of oxygen precipitates [20]. Figure 5 shows the O$_i$ and C$_s$ depth profiles of the as-grown and $1050^\circ\text{C}$, 4h annealed samples. Correlated with the precipitation band observed by preferential etching and EBIC, a depression in O$_i$ and C$_s$ concentrations was evident in the 300-400 $\mu\text{m}$ depth region. Inside the precipitation band, the O$_i$ concentration decreased by 6 to $7 \times 10^{17}\text{ cm}^{-3}$, and C$_s$ concentration decreased by $\sim 2 \times 10^{17}\text{ cm}^{-3}$. Given the fact that there is a significant amount of both O$_i$ and C$_s$ precipitated inside the precipitation band, we need to determine which process, either oxygen or carbon precipitation, is the controlling one for the precipitation band formation.

According to the theory of Ham [21] on diffusion limited precipitation, the precipitation rate will be proportional to $nr_0$, where $n$ is the precipitate density and $r_0$ the diameter of the precipitates. The precipitate density $n$ inside the band is $\sim 1 \times 10^{11} \text{ cm}^{-3}$, as measured by preferential etching. The largest possible size of these precipitates, or the most favorable condition for C$_s$ precipitation, is realized if we assume that all the $6 \times 10^{17}\text{ cm}^{-3}$ amount of O$_i$ precipitate first and these oxygen precipitates further act as precipitation sites for C$_s$. Under these conditions, the reduction in C$_s$ concentration can be estimated according to the following equation,
Fig. 3. EBIC image of the 1050°C, 4h annealed sample #79 with top surfaces facing upward.

Fig. 4. Corresponding Nomarski images of the region marked in Fig. 3. Note the dark EBIC contrast is well correlated to the precipitate band, outlined by dash lines.
\[ C(t) = C(0) \cdot \exp(-4\pi n D r_0 t) \quad (1) \]

where, \( C(0) = 3.5 \times 10^{17} \text{cm}^{-3} \) is the starting \( C_s \) concentration, \( n = 1 \times 10^{11} \text{cm}^{-3} \) is the precipitate density, \( r_0 = 31 \text{nm} \) is the radius of the precipitates with \( 6 \times 10^{17} \text{cm}^{-3} \) amount of \( O_i \) precipitated, \( D = 5.0 \times 10^{-12} \text{cm}^2/\text{s} \) the diffusivity of \( C_s \) at \( 1050^0 \text{C} \), and \( t \) the annealing time. It turns out that even under these most favorable conditions, \( C_s \) concentration can only decrease to \( 2.6 \times 10^{17} \text{cm}^{-3} \) in a 4 hours annealing at \( 1050^0 \text{C} \). The fact that \( C_s \) concentration in the precipitation band decreased to \( \sim 1.5 \times 10^{17} \text{cm}^{-3} \) suggests that a fast diffusion channel might exist to facilitate the fast \( C_s \) reduction. This situation becomes more obvious in the case of \( 900^0 \text{C} \) annealing, see Fig. 6. Note that \( C_s \) concentration inside the precipitation band decreased by \( \sim 2.3 \times 10^{17} \text{cm}^{-3} \) in a \( 900^0 \text{C}, 4 \) hours annealing. Whereas, according to equation (1), the \( C_s \) reduction will be very small, say less than \( 1 \times 10^{16} \text{cm}^{-3} \), if we assume carbon precipitation is controlled by the diffusion of \( C_s \). Clearly, a fast diffusion channel is needed to account for the observed fast \( C_s \) reduction inside the precipitation band.

It is known that silicon self-interstitials (\( I_{Si} \)) are generated during oxygen precipitation, and interstitial carbon can therefore form through capturing of \( I_{Si} \) by \( C_s \) atoms [9]. The high diffusivity of interstitial carbon allows fast precipitation. Although co-aggregation of oxygen and carbon at common sites has been observed in Czochralski silicon [22], it is hard to tell whether carbon precipitated into distinct SiC precipitates or co-aggregation with oxygen in the highly defective polycrystalline sheet silicon, considering the readily available heterogeneous nucleation sites. The critical step for the fast \( C_s \) reduction is the formation of high diffusivity, interstitial carbon. Since carbon precipitation is mediated by the silicon self-interstitials generated during oxygen precipitation, the formation of the precipitation band must be controlled by the oxygen precipitation process.
Fig. 5. O (a) and Cs (b) depth profiles of as-grown and 1050°C, 4h annealed samples #79.

Fig. 6. O (a) and Cs (b) depth profiles of as-grown and 900°C, 4h annealed samples #79.

Fig. 7. O (a) and Cs (b) depth profiles of as-grown and 1200°C, 4h annealed samples #79.
While Figs 5 (a) and 6 (a) show that almost same amount of O\textsubscript{i} precipitated in the precipitation band and the deeper region, we can see that much less C\textsubscript{s} precipitated in the deeper region than in the precipitation band, see Figs. 5 (b) and 6 (b). I\textsubscript{Si} generated during oxygen precipitation will be consumed either by direct absorption at sinks, such as dislocations and grain boundaries, or by C\textsubscript{s}. The high density of precipitates in the precipitation band provide more carbon precipitation sites, and I\textsubscript{Si} generated inside the band was mainly consumed by the reactions C\textsubscript{s} + I\textsubscript{Si} → C\textsubscript{i} → precipitates. On the contrary, due to the low precipitate density, less carbon precipitated in the deeper region and most of the I\textsubscript{Si} were directly absorbed by dislocations or grain boundaries, instead of by formation and precipitation of C\textsubscript{i}.

With the solidification proceeds from top to bottom, nitrogen tends to buildup near the back surface, instead of in the middle of the wafer. Thus, the precipitation band formation is not likely due to the distribution of carbon or nitrogen which are known to enhance oxygen precipitation [10-13, 23-24]. It is known that the presence of vacancies strongly enhances oxygen precipitation. It will be shown in the later discussion that the cooling rate following solidification is fast enough to quench vacancies inside the sample. The presence of nitrogen will further help to trap vacancies by forming N\textsubscript{2}-V\textsubscript{2} [25] or N\textsubscript{2}-V [26] complexes. It is proposed that the formation of the precipitation band is arisen from the distribution of vacancies and the presence of nitrogen-vacancy complexes, which act as effective nucleation sites for oxygen precipitation.

The O\textsubscript{i} and C\textsubscript{s} depth profiles of the as-grown and 1200\textdegree C, 4h annealed samples #79 are shown in Fig. 7. Note that the O\textsubscript{i} concentration decreased to approximately 4 to 5 x 10\textsuperscript{17} cm\textsuperscript{-3}, corresponding to its solubility level. The C\textsubscript{s} concentration decreased by 0.5 x 10\textsuperscript{17} cm\textsuperscript{-3} over the
whole thickness of the sample. Note that \( C_s \) did not precipitate faster in the deeper region where more \( O_i \) precipitated, indicating that the formation of \( C_i \) is not the control factor effecting carbon precipitation. Even without the formation of \( C_i \), a co-aggregation of carbon and oxygen will result in larger precipitates, which further gives rise to a higher carbon precipitation rate. The fact that the carbon precipitation rates are essentially the same for regions with very different amount of \( O_i \) precipitation, see Fig. 7, suggests that there is neither \( C_i \) formation, nor co-aggregation of oxygen and carbon. It is proposed that carbon atoms are most likely to precipitate into distinct SiC precipitates via \( C_s \) diffusion during 1200\(^{\circ}\)C annealing.

![Diagram of reactions involved in carbon precipitation in sheet silicon.](image)

**Fig. 8.** Illustration of reactions involved in carbon precipitation in sheet silicon.

Note that the \( C_s \) reduction in the precipitation band of the 1050\(^{\circ}\)C annealed sample is not as aggressive as that in the 900\(^{\circ}\)C annealed sample, see Fig. 5(b) and 6(b). Also note that there is no \( C_i \) formation during 1200\(^{\circ}\)C annealing. The reactions involved in carbon precipitation were illustrated in Fig. 8. Note that any factors that facilitate reactions R1, R2, and R4 will enhance carbon precipitation. Clearly, the more \( O_i \) precipitation, the more \( I_{si} \) generated, and therefore the more aggressive is the carbon precipitation. It was also found that for the same amount of oxygen precipitation, carbon precipitation proceeded more
aggressively if the annealing was performed at a lower temperature or the precipitate density was higher. It was proposed that reaction R2 is likely to be an exothermic process, which tends to proceed in the reverse direction at a higher annealing temperature, therefore suppressing carbon precipitation. A higher density of oxygen precipitates will enhance reaction R4 by providing more precipitation sites for C\textsubscript{i}. That is the reason why carbon precipitation was strongly effected by precipitate density.

(b) Sample #80

Figure 9 shows the EBIC and corresponding preferential etching/Nomarski images of a 1050\textdegree C, 4h annealed sample #80. Note a 300 µm wide region with a higher current collection efficiency was observed near the top surface. Nomarski microscopy shows that the bright EBIC contrast is due to suppression of oxygen precipitation near the top surface. The oxygen precipitate density in the deeper region was in the range of 0.8 to 1 x 10\textsuperscript{11} cm\textsuperscript{-3}, and that in the denuded zone was around 1 to 3 x 10\textsuperscript{10} cm\textsuperscript{-3}.

The existence of the precipitate denuded zone was further verified by FTIR microspectroscopy performed on polished cross-sections. Figures 10 (a) and (b) plot the O\textsubscript{i} and C\textsubscript{s} depth profiles of the as-grown and annealed samples. It is interesting to note that, in contrary to the virgin sample, the O\textsubscript{i} concentration in the annealed samples was high at the near top surface regions and low in the deeper regions. We can see that almost all supersaturated oxygen in the deeper region precipitated during a 4h annealing at 900 or 1050\textdegree C, while a considerable amount of O\textsubscript{i} remained near the top surface region. When
Fig. 9. EBIC and corresponding Nomarski images of a processed sample #80-4. Note the dark EBIC contrast is well correlated to the formation of precipitates with a density of 0.8 to 1 x10^{11} \, \text{cm}^{-3}. OPs density in the denuded zone varies from 1 to 3 x10^{10} \, \text{cm}^{-3}.
annealed at $1200^\circ\text{C}$, the O$_i$ concentration decreased to $\sim4\times10^{17}$ cm$^{-3}$, corresponding to its solubility level. Note that the shape of C$_s$ depth profiles in the annealed samples mimics that of O$_i$ profiles. The C$_s$ concentrations in the 900 and 1050$^\circ\text{C}$ annealed samples decreased to $\sim0.5\times10^{17}$ cm$^{-3}$ in the deeper region, and remained at $\sim3\times10^{17}$ cm$^{-3}$ in the near top surface denuded zone.

Based on similar arguments on the formation of the precipitation band in sample #79, it was found that a process only involving the diffusion of C$_s$ cannot account for the fast C$_s$ reduction observed in the deeper region of the 1050$^\circ\text{C}$ annealed sample, not to mention the 900$^\circ\text{C}$ annealed sample. Formation of C$_i$ by capturing I$_{Si}$ is needed to facilitate the fast carbon precipitation. Note that, in the deeper region, O$_i$ and C$_s$ concentrations decreased by $\sim8$ and $3.5\times10^{17}$ cm$^{-3}$, respectively when the samples were annealed at 900 or 1050$^\circ\text{C}$. Given that one I$_{Si}$ is emitted for every two O$_i$ precipitation, the approximately 2:1 precipitation ratio suggests that most of the I$_{Si}$ generated during oxygen precipitation was consumed by the formation and precipitation of C$_i$. This is consistent with the Nomarski microscopy observation, which shows a high density, $\sim1\times10^{11}$ cm$^{-3}$, of precipitates was present in the deeper region, which provide more trapping sites for C$_i$.

If we only examine samples #80, it is straightforward to conclude that the initial O$_i$ concentration is responsible for the formation of the precipitation denuded zone. The precipitation was suppressed in the denuded zone, where the initial O$_i$ concentration is lower than the critical level for precipitate nucleation [27]. The situation becomes complicated when we compare samples #80 with #79. Note that O$_i$ and C$_s$ precipitated more aggressively in the deeper region of sample #80 than in sample #79, although the oxygen and carbon contents in
Fig. 10. $O_i$ and $C_s$ depth profiles of the as-grown and annealed samples #80.

Fig. 11. $O_i$ (a) and $C_s$ (b) depth profiles of the as-grown and annealed samples #253.
the as-grown wafers are similar for the two sets of samples. Clearly, the initial $O_i$ and/or $C_s$ concentrations cannot account for the difference in precipitation rates between sample #80 and #79. It is known that the cooling profile after sheet formation approximately follows an exponential decay based on the thermal mass of the silicon sheet, the carrier substrate, and the insulation system [28]. Since sample #80 was grown with a less aggressive thermal profile compared with sample #79, it is likely that sample #80 also experienced a faster cooling after sheet formation. As will be discussed in Section 4.4.3, a faster cooling rate results in a higher concentration of quench-in vacancies, which might be responsible for a more aggressive $O_i$ and $C_s$ precipitation process.

(c) Sample #253 and 254

Samples #253 and 254 were grown with the lowest thermal profiles. Figure 11 shows the $O_i$ and $C_s$ depth profiles of the as-grown and 1100°C, 3h annealed samples #253. Due to the low growth thermal profile which suppressed SiO evaporation, there was no well-defined $O_i$ denuded zone in the as-grown sample, although the $O_i$ concentration was overall lower near the top surface and higher in the deeper region. The fluctuation observed in the $O_i$ profile suggests a complicated growth process. The $O_i$ concentration in the annealed sample decreased to $\sim 2 \times 10^{17}$ cm$^{-3}$. It is interesting to note that the $O_i$ profile in the annealing sample mirrors that in the as-grown sample, namely, the $O_i$ concentration is lower in the region originally having a higher $O_i$ content. This clearly indicates that a higher initial $O_i$ concentration is an important factor in enhancing oxygen precipitation. Similar with sample #80, carbon precipitation in sample #253 was also controlled by oxygen precipitation. Note that the $C_s$ profile in the annealed sample varies in the same trend as the $O_i$ profile. We can see
that a precipitation band was formed in the 400 to 600 µm depth region. Another interesting feature is that carbon precipitation was totally suppressed, and oxygen precipitation was moderately suppressed near the back surface.

Figure 12 shows the \(O_i\) and \(C_s\) depth profiles of the as-grown and \(1100^\circ\text{C}, 3\text{h}\) annealed samples \#254. Note that there was relatively less variation in the \(O_i\) and \(C_s\) profiles. The carbon and oxygen precipitation in sample \#254 was overall similar with sample \#253. We can see that precipitation near the back surface was also suppressed in sample \#254.

Figure 13 is a direct comparison EBIC image acquired on the cross-sections of the virgin and annealed samples \#253 and 254. Note that for both sample \#253 and 254, the EBIC collection currents of the annealed samples are significantly higher than those corresponding virgin samples. The lifetime of the virgin sample is mainly limited by the high concentration of dissolved transition metals, say interstitial Fe and Fe-B pairs [2]. While a high density of oxygen and carbon precipitates tends to degrade the minority carrier lifetime, they can also beneficially act as precipitation site for transition metals considering that metal precipitates are much less detrimental to the minority carrier lifetime compared with their dissolved counterparts. The beneficial impact of metal precipitation at localized defects overwhelms the detrimental effect of oxygen and carbon precipitation, and the carrier lifetime is therefore improved during annealing.
Fig. 12. O$_i$ (a) and C$_s$ (b) depth profiles of the as-grown and annealed samples #254.

Fig. 13. Direct cross-sectional EBIC comparison of samples #253 and 254. V=virgin; A=annealed.
Well correlated with the $O_i$ and $C_s$ profiles, a dark EBIC contrast strip was present in the 400 to 600 µm depth region in the annealed sample #253 and the EBIC collect current was enhanced near the back surface region of the annealed samples. Figure 14 shows cross-sectional Nomarski images acquired on the annealed sample #253. Note that a high density of precipitates were present in the region with a dark EBIC contrast, see Fig. 14 (b), whereas the precipitate density was lower near back surface region where precipitation was suppressed and a bright EBIC contrast was observed. The fact that the EBIC contrast was well correlated with the precipitate distribution clearly indicates that oxygen and carbon precipitation is one of the most important lifetime limitation factors in the annealed sample. It is worth to point out that, because of the removal of the most detrimental lifetime killer, the dissolved transition metals, from the virgin sample, the overall lifetime was improved although a high density of precipitates have been formed during annealing.

4.3.3 Quench-in vacancy profile in the as-grown sheet silicon wafer

The equilibrium concentration of vacancies $C_{V}^{eq}$ is higher than that of interstitials $C_{I}^{eq}$ in the temperature range of 1000 to 1400°C. The difference between $C_{V}^{eq}$ and $C_{I}^{eq}$ is larger at higher temperatures, and both $C_{V}^{eq}$ and $C_{I}^{eq}$ decrease rapidly with decreasing temperature [29-30]. These features make it possible to quench vacancies in the bulk of the wafer if the cooling rate is fast enough. When the wafer is cooling down from a higher temperature, excess vacancies and interstitials recombine with each other. The decay lifetime of the
Fig. 14. Cross-sectional Nomarski images of annealed sample #253. A low magnification image (a) shows the whole cross-section, and two zoom-in images show a region with high density of precipitates (b) and a precipitates denuded region near the back surface (c).
recombination process ranges from 0.01 to 1 \( \mu \text{s} \) in the temperature range of 1200 to 1400\(^0\)C [31]. Because of the fast recombination and the relative higher \( C_v^{eq} \), vacancies will become the dominant point defects and interstitials will essentially be eliminated in the middle of the wafer. Near the wafer surface, \( C_v \) and \( C_i \) will assume their equilibrium concentrations due to the recombination and/or generation processes at the surface. Thus, vacancies will diffuse from the middle to wafer surfaces and interstitials will diffuse in the opposite directions. If the cooling rate is high, the diffusion flux can only affect the near surface region and vacancies will be frozen inside the deeper region. If the cooling rate is low, vacancies and interstitials will both assume their equilibrium concentrations throughout the wafer thickness. Neglecting the thermodiffusion terms, the vacancy and interstitial profiles evolve according to the following coupled partial differential equations,

\[
\frac{\partial C_v(x,t)}{\partial t} = D_v(T) \frac{\partial^2 C_v(x,t)}{\partial x^2} - k_{rv}(T) \cdot [C_i \cdot C_v - C_{v}^{eq}(T) \cdot C_{v}^{eq}(T)] \tag{2}
\]

\[
\frac{\partial C_i(x,t)}{\partial t} = D_i(T) \frac{\partial^2 C_i(x,t)}{\partial x^2} - k_{iv}(T) \cdot [C_i \cdot C_v - C_{i}^{eq}(T) \cdot C_{i}^{eq}(T)] \tag{3}
\]

where \( C_{i}^{eq}(T), C_{v}^{eq}(T) \) are the equilibrium concentrations of interstitials and vacancies; \( D_i(T), D_v(T) \) are the diffusion coefficients of interstitial and vacancies; \( k_{iv}(T) \) the rate coefficient for the recombination reaction. The boundary conditions are

\[
C_i(0,t) = C_i(d,t) = C_{i}^{eq}(T) \tag{4},
\]

\[
C_v(0,t) = C_v(d,t) = C_{v}^{eq}(T) \tag{5},
\]

where \( d \) is the wafer thickness. The cooling profile was assumed to obey the following equation,

\[
t = \alpha \cdot (1/T - 1/T_M) \tag{6},
\]
where $T_M$ is the melting point of silicon and $t$ the time taken for the wafer cooling down from $T_M$ to $T$. The evolution of the vacancy profile was calculated numerically for three different cooling rates with $\alpha = 5, 3.2, \text{ and } 2 \times 10^5 \text{ (s K)}$, respectively. The diffusion coefficients, equilibrium concentrations and the recombination rate constant of vacancies and interstitials are taken from Ref. [31]:

$$D_i(T) = 0.242 \cdot \exp\left(\frac{-0.937eV}{kT}\right)$$

$$D_v(T) = 0.001 \cdot \exp\left(\frac{-0.457eV}{kT}\right)$$

$$C_i^{eq}(T) = 2.97 \times 10^{21} \exp(1.4 + 0.00385 \cdot T - (3.46 + 3.08 \times 10^{-4} \cdot T)eV / kT)$$

$$C_v^{eq}(T) = 4.97 \times 10^{22} \exp(-3.7 + 0.00353 \cdot T - (2.48 + 2.33 \times 10^{-4} \cdot T)eV / kT)$$

where the temperature $T$ is in unit of Kelvin, the diffusivity in $\text{cm}^2/\text{s}$, and the concentration in $\text{cm}^{-3}$. The simulation starts at $1410 \text{^0C}$ with $C_i$ and $C_v$ assuming their corresponding equilibrium concentrations. This is not the real situation, and we shall show in the later part that the variation of the starting concentration profiles will have little influence on the final vacancy profiles.

The vacancy profiles at $1050 \text{^0C}$ for a $720\mu\text{m}$ thick wafer, together with the corresponding cooling profiles are shown in Fig. 15 (a) and (b). We can see that $C_v$ in the middle of the wafer is on the order of $10^{13} \text{ cm}^{-3}$ when the wafer is cooled down to $250 \text{^0C}$ in 4 to 11 minutes. The critical concentration of vacancies for precipitation enhancement can be achieved with an $1175 \text{^0C}$ rapid thermal processing [30]. According to the solubility data used in our calculation, this gives rise to a critical vacancy concentration of $2.4 \times 10^{13} \text{ cm}^{-3}$, which can be attained by the cooling rate B.

The vacancy profiles at $1050 \text{^0C}$ are given in Fig. 15 (a) to represent the final profiles of
the quench-in vacancies because, below this temperature, the effective vacancy mobility will be rapidly reduced by forming $O_2V$ complexes [32]. The presence of nitrogen will help to trap vacancies at a higher temperature. The fact nitrogen can suppress vacancy aggregation suggests that nitrogen-vacancy reactions, no matter by forming $N_2V_2$ or $N_2V$ [25-26], proceed at a temperature higher than $1100^0C$, which is the temperature for vacancy aggregation [33]. Thus, the profile at $1050^0C$ should be understood as a lower limit of the quench-in vacancy profile. The evolution of vacancy and interstitial profiles in a 720µm thick wafer for the cooling profile B is shown in Fig. 16. We can see that the final trapping temperature has a strong impact on the vacancy concentration. Considering the nitrogen effect, the critical cooling rate will be smaller than that of profile B.

**Fig. 15.** Vacancy profiles (a) at $1050^0C$ for a 720µm thick wafer and the corresponding cooling profiles (b). The values of the cooling rate parameter $\alpha$ are A=5, B=3.2 and C=2 x $10^5$ (s K).
Fig. 16. Evolution of vacancy (a) and interstitial (b) profiles in a 720µm thick wafer for the cooling profile B.

Fig. 17. Two sets of quench-in vacancy profiles in wafers cooling down according to profile B in Fig. 15(b). The dark lines represent profiles calculated exactly from the melting point. The light lines represent profiles calculated from 1300°C and assuming the $C_V$ equals the equilibrium concentration across the wafer thickness.
In all the above calculations, it was assumed that both vacancies and interstitials assume their corresponding equilibrium concentrations at the melting point. This is not true considering that incorporation of point defects into silicon is effected by solidification rate and local temperature gradient. The follow calculation shows that the starting vacancy profile at 1400°C has minor impact on the final quench-in vacancy profile at around 1100°C. Figure 17 shows two sets of vacancy profiles when the wafer is cooling down from different temperatures according to profile B with $\alpha$ equal 3.2 X $10^5$ (s K). The dark lines represent profiles calculated exactly from the melting point. The light lines represent profiles calculated from 1300°C by assuming $C_V$ and $C_i$ equal to their corresponding equilibrium concentrations across the wafer thickness. Note that while the vacancy profiles are very different at 1300°C, they become essentially the same when cooling down to 1100°C. This clearly indicates that the quench-in vacancy profile is essentially decoupled from the detail of the solidification process, and is mainly determined by the cooling rate. This is why we can simply assume $C_i$ and $C_V$ equal their corresponding equilibrium concentrations when we start the simulation from the melting point. In fact, the decoupling feature also makes it easier to engineer the quench-in vacancy profile.

4.3.4 Effect of quench-in vacancies on oxygen precipitation

It is known that the cooling profile after sheet formation approximately follows an exponential decay based on the thermal mass of the silicon sheet, the carrier substrate, and the insulation system. Therefore, the cooling rate is in general higher at high temperatures and lower at low temperatures. The cooling rate after sheet formation is estimated to be located
between profiles A and B in Fig. 15 (b). Sample #79, which was grown with a more aggressive thermal profile, is likely to have experienced a relatively slow cooling rate due to the large thermal mass of the whole system. Therefore sample #79 might have a relatively lower quench-in vacancy concentration. The oxygen precipitate density is controlled by both the initial \(O_i\) concentration and the vacancy profile. The \(O_i\) denuded zone near the top surface and the higher vacancy concentration in the middle of the wafer gave rise to the precipitation band located at 300-400\(\mu\)m depth region. Note that the precipitation band is not located exactly at the middle of the wafer. This is likely due to the fact that more heat was dissipated through the front surface than the back surface with the presence of substrate and supporting system. Therefore, the vacancy profile shifted a little bit towards the front surface.

Sample #80, which was grown with a less aggressive thermal profile, is likely to be cooled down faster than sample #79. The faster cooling rate resulted in a higher concentration of quench-in vacancies, which further gave rise to a high density of oxygen precipitates throughout the region which has a relatively high initial \(O_i\) concentration (except the near top surface \(O_i\) denuded zone). Samples #253 and 254 were grown with the lowest thermal profile. Due to the reduced SiO evaporation, a high concentration of \(O_i\) was present throughout the wafer thickness. The low thermal profile also gave rise to a high concentration of vacancies in the as-grown wafer. The high concentration of \(O_i\) and vacancies together gave rise to the high density of precipitates.

Note that cross-sectional EBIC, preferential etching, and FTIR results revealed a precipitate denuded zone near the back surface. This is likely due to the no symmetric cooling process. The lower cooling rate near the back surface resulted in a lower vacancy concentration, which further suppresses oxygen precipitation there. Note that a similar back
surface denuded zone was also observed in sample #80, see Fig.9(a).

In the magic denuded zone (MDZ) process [29-30], a vacancy concentration profile depleted near the wafer surface is installed into silicon wafers by a rapid thermal annealing process. This profile subsequently controls the distribution of oxygen precipitates. It is interesting to note that vacancies impact oxygen precipitation in sheet silicon in exactly the same manner as in the MDZ process by recognizing that the cooling down period after sheet formation acts just as the rapid thermal annealing step in the MDZ processing.

4.4 Summary and Conclusion

The spatial variation of oxygen and carbon precipitation in four sets of sheet silicon samples grown with different thermal profiles were studied in cross-sectional configuration by preferential etching/Nomarski optical microscopy, EBIC and infrared microspectroscopy. Examination of the as-grown wafers shows that an OІ denuded zone is generated in the sample grown with a more aggressive thermal profile. It is believed that SiO evaporation from the Si melt during sheet growth is responsible for the denuded zone formation. It is also found that the Cs concentration, which varied from 3 to 4 x 10^{17} cm^{-3}, was not dependent on the growth thermal profile.

After annealing at 900 and 1050°C, a precipitation band was generated in the 300-400µm depth region in sample #79 and a ~250µm wide precipitate denuded zone was formed in sample #80. It is proposed that the spatial variation of oxygen precipitation observed in sheet silicon was mainly controlled by the initial OІ and quenched-in vacancy profiles in the as-grown samples. Carbon precipitation was well correlated with oxygen precipitation in all the four sets of samples. Examination of the precipitation rate of Cs by
infrared spectroscopy and the precipitate density by preferential etching indicates that formation of C\textsubscript{i} by capturing of I\textsubscript{Si} generated during oxygen precipitation is a necessary step for the enhanced carbon precipitation.
Reference


28. Based on information provided by Ralf Jonczyk of GE Energy.


CHAPTER 5. INFRARED ABSORPTION OF SIC PRECIPITATES IN CRYSTALLINE SILICON

5.1 Introduction

Substitutional carbon (C_S) in crystalline silicon is not electrical active [1]. Studies of carbon in Czochralski silicon have been mainly focused on its enhancement effect on oxygen precipitation [2-5] and interactions with silicon self-interstitials (I_{Si}) [6-7]. Carbon precipitation by itself is rarely an important process because of the typically low C_S levels in silicon wafers [8]. The situation is very different in polycrystalline ribbon silicon [9], which usually contains a high concentration of C_S, ranging from 0.5 to 2 x 10^{18} cm^{-3}. The high supersaturation degree and the presence of interstitial oxygen (O_i) enhance carbon precipitation. Bean and Newman [10] studied the infrared absorption of SiC precipitates in crystalline Si. They pointed out that the asymmetric broad band at 830 cm^{-1} is due to SiC particles having a range of ellipsoidal shapes. Slightly different SiC absorption bands have also been observed in the low O_i samples [11]. In all these studies, no specific correlation between the structure of IR absorption bands and the geometry of SiC particles has been established. Because a characterization of the size and shape of SiC particles is essential for clarifying the nucleation and growth mechanisms of SiC precipitates, as well as for studying their impact on minority carrier lifetime, a quantitative interpretation of the IR absorption band in terms of the size and shape of SiC particles is presented in this article by comparing the measured and calculated IR spectra.

5.2 Experimental data

Two sets of RGS (Ribbon Growth on Substrate) silicon ribbons, numbered as #133 and
were grown at the Energy Research Center of the Netherlands. The concentrations of $C_S$ and $O_i$ of sample #133 are $1.47 \times 10^{18}$ and $0.7 \times 10^{18}$ cm$^{-3}$, respectively; and those of #92 are $1.43 \times 10^{18}$ and $1.52 \times 10^{18}$ cm$^{-3}$, respectively. Samples were annealed in nitrogen ambient at $920^\circ C$ and $1020^\circ C$ for different times to study carbon precipitation. After dipped in a dilute HF solution, samples were examined on a Digilab FTS-6000 Fourier transform infrared spectrometer. A float-zone silicon wafer was used as a reference to subtract the silicon lattice absorption. Figure 1 shows the IR absorption spectra of virgin and annealed samples. Note that the SiC bands located at 800-930 cm$^{-1}$ can be classified into two types: (I) a asymmetric, triangular-shaped absorption band formed in the $920^\circ C$ annealed, low $O_i$ sample and all the annealed high $O_i$ samples, see Figs. 1 (A1, B2-B3); (II) a symmetric, rectangular-shaped band observed only in the $1020^\circ C$ annealed, low $O_i$ sample, see Figs. 1 (A3). The observed dependence of IR absorptions on the annealing temperature and $O_i$ content is consistent with previous studies. IR absorption of SiC precipitates in the high $O_i$ content, carbon-doped Czochralski Si wafers [3,10] gave raise to similar Type-I band; whereas the Type-II band had been observed in the $1250^\circ C$ annealed, low $O_i$ content polycrystalline Si samples [11]. In the following, we first calculate the IR absorption spectra of SiC particles in various shapes and interpret the measured spectra by comparison with the calculated ones.

### 5.3 Theoretical calculation

SiC particles embedded in a Si matrix will attenuate the intensity of the incident electromagnetic field through absorption and scattering. The phase difference between polarization and external electric field results in the absorption and the electric dipole radiation from the particle gives raise to the scattering. The measured IR absorption
coefficients are in fact extinction coefficients, which arise from both absorption and scattering.

The C\textsubscript{S} concentration in crystalline silicon is in general below 2 x 10\textsuperscript{18} cm\textsuperscript{-3}, which corresponds to a SiC volume ratio of 40 ppmv. Therefore, we can neglect the interaction between adjacent precipitates when calculating the absorption and scattering of the incident light by each precipitate, because the average distance between the adjacent SiC precipitates is at least 30 times larger than the size of each precipitates. A mathematically convenient shape of considerable generality is a spheroid (a\textsubscript{1}=a\textsubscript{2}≠a\textsubscript{3}) which, in various ratios of its axes, encompasses the shape of disk, sphere, and needle, which are the common shapes of precipitates from solid solution [12]. The field inside a spheroid dielectric is uniform if the external field is uniform. For small (compared to the IR wavelength in Si matrix) spheroid shape SiC particles in an external field \( E \) parallel to the axis \( i \) (\( i=1, 2, \) or 3), we have \( P=V\alpha_iE \), with

\[
\alpha_i = \frac{\varepsilon_m}{4\pi L_i \varepsilon_p + (1 - L_i) \varepsilon_m} \left( \varepsilon_p - \varepsilon_m \right), \quad (1)
\]

where \( P \) is the polarization, \( V \) the particle volume, \( \alpha_i \) the polarizability, \( L_i \) the depolarization factor which can be calculated from the axial ratio [13], and \( \varepsilon_p \) and \( \varepsilon_m \) are the dielectric constants of SiC and Si, respectively. The mean energy dissipated in a particle per unit time is

\[
Q = \frac{1}{2} \sum_{i=1}^{3} \alpha_i' \varepsilon_i^2 \omega V \sum_{i=1}^{3} \alpha_i'' \varepsilon_i^2, \quad (2)
\]

where \( \alpha_i'/\omega \) is the imaginary part of the polarizability, and \( \omega \) is the angular frequency of the incident electromagnetic field. The mean energy dissipation \( Q \) needs to be averaged over
particles with different orientations. Since the host Si lattice has cubic symmetry, the orientation of the axis \(a_i\) must possess the same symmetry. In other words, the possibilities for the axis \(a_i\) aligned along any of the 24 equivalent directions of \(<hkl>\) must be the same. Therefore,

\[
\overline{E_i^2} = \frac{1}{24} \sum_{hkl} (hu + kv + lw)^2 E^2 = \frac{1}{3} E^2
\]  

(3)

where \([uvw]\) and \(<hkl>\) are the directional cosines of \(E\) and axis \(a_i\), respectively, and the summation is over the 24 equivalent directions. Note that equation (3) is correct for any direction of \([uvw]\) and family of crystallographically equivalent directions of \(<hkl>\). By substituting equation (3) into (2), we have

\[
\overline{Q} = \frac{1}{2} \omega V \overline{\alpha''} E^2, \quad \overline{\alpha''} = (\alpha''_1 + \alpha''_2 + \alpha''_3)/3.
\]

The absorption cross-section \(\sigma_{abs}\) is given by the ratio of the energy dissipation \(Q\) to the incident energy flux density. The absorption coefficient is

\[
n \sigma_{abs} = 4 \pi \omega \cdot n \cdot V \cdot \overline{\alpha''}/(c \sqrt{\epsilon_m}), \quad \text{where } n \text{ is the particle density.}
\]

The calculated absorption spectra are shown in Fig. 2, together with the measured IR spectra. The dielectric constant of 3C-SiC is taken from Ref. 14. In the wavenumber range near 850 cm\(^{-1}\), the real part of the dielectric constant of silicon equals 11.7 and the imaginary part is neglected because it is approximately \(10^{-3}\) and is about 2 orders smaller than that of SiC. Note that non-spherical particles give raise to two distinct absorption peaks. One peak arises from \(E\) in the \(a_3\) direction, the other from \(E\) in the \(a_1\) and \(a_2\) directions. It is evident that the envelop of the absorption peaks of the oblate spheroid or disk-shape particles is similar to the Type-I band. In fact, absorption above 863 cm\(^{-1}\) can only arise from an oblate spheroid with an axial ratio \(a_1/a_3\) larger than 2. Note also that the Type-I band is not likely arisen from perturbed [O\(_x\)-C\(_y\)] C(3)
centers [15]. The reason is that almost all supersaturated O$_i$ were removed in the first hour
annealing at 920°C, whereas there is only a small change in C$_S$ concentration in such a short
time. In other words, the removal of O$_i$ and C$_S$ from the Si matrix happens at different time
slots during annealing, that means any kind of C-O complexes are not likely to form. What
happened might be that oxygen precipitates formed first and these precipitates further act as
nuclei for carbon precipitation. Another factor preventing the formation of C(3) centers is that
I$_{Si}$, which is needed for interstitial carbon generation, will be depleted with the precipitation
of a high concentration of C$_S$. Therefore, we conclude that the Type-I band is mainly due to
absorption at disk-shape SiC precipitates with a range of axial ratios.

The difference between the Type I and II bands is that absorptions in the high
wavenumber range of the Type-II band are significantly stronger, and further resulting in a
rectangular-shaped band. Note that simply increasing the content of oblate spheroid
precipitates with a large axial ratio cannot produce this kind of change in band shape, since
absorption at ~810 cm$^{-1}$ will increase simultaneously with that at ~920 cm$^{-1}$. It is known that
the power of electric dipole radiation is proportional to the square of the polarization
magnitude. For the case of a small particle, the scattering cross-section is then proportional to
the square of the particle volume, whereas the absorption cross-section is proportional to the
particle volume itself. As a result, it is anticipated that the scattering component is likely to
become more and more important relative to the absorption component with the increasing of
the SiC particle size. The scattering cross-section [16] due to electric dipole radiation is

$$\sigma_{sca} = \frac{8\pi\alpha^2\omega^4V^2}{3c^4}.$$  

Note that for same volume of SiC precipitates, the lower the precipitate density, the larger is each precipitate and the larger the total scattering power by
these particles. The attenuation spectra due to scattering are calculated, see Fig. 3. Note that
the scattering intensity is very small when the particle size is 0.003\(\mu\)m\(^3\). When the particle size is 0.03\(\mu\)m\(^3\), the scattering intensity is significantly larger. We can see that large disk-shape precipitates \((a_1/a_3=8\text{ and } V=0.03\mu\text{m}^2)\) indeed only give rise to strong scattering at \(\sim 920\text{ cm}^{-1}\). We propose that the scattering at the large disk-shape precipitates, plus the absorption component, gives rise to the Type-II band.

The above interpretation is consistent with the understanding on carbon precipitation. It is known that a large volume decrease is associated with carbon precipitation, which occurs only in the presence of a supersaturation of silicon self-interstitials or oxygen \([8]\). The opposite volume change associated with oxygen and carbon precipitation favors co-precipitation in an approximate ratio of 2:1 as has actually been observed \([3]\). Since the C\(_s\) concentration in our samples is not high enough to fully relieve the tensile strain associated with carbon precipitation, a disk-shape SiC precipitate will be favorable in order to minimize the strain energy.

When samples are annealed at 920\(^0\)C, the chemical driving force (the supersaturation degree of carbon) for SiC nucleation is so overwhelmingly large that a high density of precipitates are generated, no matter what the O\(_i\) content. A similarly high density of SiC precipitates can also form in the 1020\(^0\)C annealed, high O\(_i\) sample because oxygen clusters or carbon-oxygen complexes might act as nuclei for SiC precipitates. The insufficient relieve of the tensile stress results in disk-shape precipitates with a range of axial ratios. The absorption at the high density, small disk-shape precipitates gives rise to the triangular-shaped IR band. On the contrary, in the 1020\(^0\)C annealed, low O\(_i\) sample, because of the reduced carbon supersaturation degree at a higher temperature and the absence of oxygen related heterogeneous nucleation sites, the SiC precipitate density is low and the size of the individual
Precipitate is therefore larger. The reduced silicon self interstitial generation in the low O$_i$ sample results in disk-shape precipitates with a higher axial ratio. The scattering at these low density, large, disk-shape precipitates, plus the absorption component, gives rise to the rectangular-shaped IR band.

5.4 Conclusion

In summary, infrared absorption of SiC precipitates in crystalline silicon is studied experimentally and theoretically. Comparison between measured and calculated spectra shows that the triangular-shaped band is due to absorptions by small disk-shape precipitates with a range of axial ratios. Whereas, the rectangular-shaped band arises from both scattering and absorption at relatively larger disk-shape precipitates. It is believed that the impacts of oxygen content and annealing temperature on the size of SiC precipitates are likely related to their critical role on precipitate nucleation.
Reference


Fig. 1. Infrared absorption spectra of virgin and annealed wafers with different oxygen concentrations.
Fig. 2. Calculated absorption component and measured IR spectra. Each calculated spectrum is normalized to 1 ppmv SiC precipitates.

Fig. 3. Calculated extinction coefficient (normalized to 1 ppmv SiC) due to scattering at disk-shape precipitates for two particle sizes and different axial ratios.
CHAPTER 6. EFFECT OF OXYGEN CONTENT ON CARBON PRECIPITATION IN 
RGS RIBBON SILICON

6.1 Introduction

Substitutional carbon (Cs) in crystalline silicon is not electrical active\(^1\). Studies of carbon in Czochralski silicon have mainly focused on its enhancement effect on oxygen precipitation\(^2\)\(^-\)\(^6\) and interactions with silicon self-interstitials (I\(_{Si}\))\(^7\)\(^-\)\(^9\). Carbon precipitation by itself is rarely an important process because of the typically low Cs levels in silicon wafers. The situation is very different in polycrystalline ribbon silicon\(^10\)\(^-\)\(^12\), which usually contains a high concentration of Cs. The high degree of carbon supersaturation enhances carbon precipitation. Considering that a high density of carbon precipitates will degrade the minority carrier lifetime, detailed knowledge on carbon precipitation is required to improve the performance of solar cells made from these high carbon content ribbon silicon.

RGS (ribbon growth on substrate) ribbons\(^13\) studied in this experiment contain a high concentration of Cs and interstitial oxygen (O\(_i\)). Of particular important is the manner in which O\(_i\) influences carbon precipitation. It is known that oxygen precipitation is associated with a volume increase of about 100\%, while carbon precipitation is associated with a similar magnitude of volume decrease. Therefore, co-precipitation of oxygen and carbon in an approximate ratio of 2:1 would be energetically favorable, as actually observed in carbon doped Czochralski silicon\(^3\). It is also known that excess silicon self-interstitials (I\(_{Si}\)), which are generated during oxygen precipitation, play an important role in increasing the carbon precipitate growth rate by forming high diffusivity, interstitial carbon\(^6,11,12,14,15\). Oxygen can also enhance carbon precipitation by providing heterogeneous nucleation sites through various
C-O complexes\textsuperscript{2,16}. Despite all these studies, the exact effects of oxygen on the nucleation and the growth of carbon precipitates are still not clearly understood. In this experiment, carbon precipitation in RGS wafers has been investigated by infrared (IR) spectroscopy. New evidence for the effect of oxygen on carbon precipitation is presented, which probably benefits the understanding of carbon precipitation in polycrystalline ribbon silicon.

6.2 Experiments

Four sets of RGS silicon ribbons with similar carbon concentrations and very different oxygen contents, denoted as \# 92, 133, 149, and 226, respectively, were grown at the Energy Research Center of the Netherlands. The wafer thickness is approximately 300 \( \mu \text{m} \) and the grain size varies between 100 and 500 \( \mu \text{m} \). Table I summarizes the concentrations of Cs and O\(_i\) in the as-grown samples, as determined by infrared absorption measurements. The specimens were annealed in a nitrogen atmosphere at temperatures between 800 and 1020\(^{\circ}\)C for times between 1 and 64h. Because the Cs concentration varies by 1-2 \( \times 10^{17} \) \( \text{cm}^{-3} \) within a large wafer, specimens with a size of 2 x 2.5 mm\(^2\) cut from a small region of the wafer were used in this study in order to minimize the sample-to-sample variation.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>( \text{O}_i \times 10^{18} \text{ cm}^{-3} )</th>
<th>( \text{Cs} \times 10^{18} \text{ cm}^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>92</td>
<td>1.6</td>
<td>1.4</td>
</tr>
<tr>
<td>149</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>133</td>
<td>0.7</td>
<td>1.4</td>
</tr>
<tr>
<td>226</td>
<td>0.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Infrared absorption measurements were performed on a Bruker 66v/S Fourier transform infrared spectrometer equipped with an IR microscope at the U2A beamline of the National Synchrotron Light Source of the Brookhaven National Laboratory. A low oxygen containing float-zone silicon wafer was used as a reference to subtract the silicon lattice absorption. The concentrations of Cs and Oi were determined from the absorption peaks at 607 and 1107 cm\(^{-1}\) using the conversion factors in ASTM methods F1391 and F1188, respectively\(^{17}\).

6.3 Results and Discussion

Figures 1 (a) and (b) show a series of representative IR absorption spectra of samples #92 and 133 after different thermal annealing. Note that, while the two set of samples have similar carbon contents, sample #92 has a significantly higher oxygen content than sample #133. It is evident that essentially all the O\(_i\) in sample #92 has precipitated within one hour annealing at 800\(^{0}\)C and 900\(^{0}\)C; whereas a noticeable O\(_i\) absorption peak is still present in the corresponding 1h annealed sample #133, see Fig. 1(b). The fast O\(_i\) precipitation in the high oxygen containing sample #92 indicates that the O\(_i\) supersaturation degree is a key factor affecting oxide nucleation.

Compared with oxygen precipitation, carbon precipitation is a relatively slow process when annealed at 900\(^{0}\)C or below, see Fig. 1. However, when annealed at 1020\(^{0}\)C, carbon precipitation proceeds much faster, especially in the presence of a high concentration of oxygen. The faster carbon precipitation in the high O\(_i\) containing sample clearly suggests an enhancement effect of O\(_i\) on carbon precipitation. Note that oxygen content also has an impact on the shape of the IR absorption bands located at 800-930 cm\(^{-1}\). By comparing the measured and theoretically calculated infrared spectra\(^{18}\), it has been shown that the triangular-shaped
band observed in the high O\textsubscript{i} wafer is due to absorptions by small disk-shape SiC precipitates with a range of axial ratios. Whereas, the rectangular-shaped band observed in the low O\textsubscript{i} containing wafer arises from both scattering and absorption at relatively larger, disk-shape precipitates.

The observed structural dependence of IR absorption on oxygen content is consistent with previous observations. Similar triangular-shaped IR absorption band has been observed in the high O\textsubscript{i} content, carbon-doped Czochralski Si wafers\textsuperscript{2,3,16,19}, and the rectangular-shaped band has been observed in the 1250\textsuperscript{0}C annealed, low O\textsubscript{i} containing EFG wafers\textsuperscript{10}. Note that the broad infrared absorption bands observed here are not likely arisen from perturbed [O\textsubscript{i}-C\textsubscript{s}] C(3) centers\textsuperscript{2,16} or other C-O complexes\textsuperscript{10}. The reason is that, while almost all supersaturated O\textsubscript{i} has precipitated in the very first hour annealing at 900\textsuperscript{0}C, the broad IR band was generated during the subsequent prolonged annealing, which is accompanied by removal of C\textsubscript{s} from the silicon matrix. Therefore, the broad IR band observed in our samples must be mainly arisen from silicon carbide precipitates, instead of C-O complexes.

The precipitation dynamics of O\textsubscript{i} and C\textsubscript{s} are further examined by plotting the decrease of O\textsubscript{i} and C\textsubscript{s} in samples #92 during 800\textsuperscript{0}C annealing, see Fig. 2 (a). It is evident that, during the very first hour annealing, essentially all the O\textsubscript{i} impurities have precipitated and the C\textsubscript{s} concentration decreased from 14 to 10 x 10\textsuperscript{17} cm\textsuperscript{3}. Note also that there is no further carbon precipitation during prolonged annealing. Carbon precipitation in the early stage of 900\textsuperscript{0}C annealing is similar to that at 800\textsuperscript{0}C. However, after the initial fast precipitation, C\textsubscript{s} continued to precipitate during prolonged 900\textsuperscript{0}C annealing, and its concentration reached 4.7 x 10\textsuperscript{17} cm\textsuperscript{3} after 64h, see Fig. 2 (b).

It is known that interstitials are generated during oxygen precipitation, and interstitial
carbon can therefore form by capturing \( I_{Si} \). The high diffusivity of interstitial carbon allows it to readily precipitate or form complexes with oxygen\(^9\). The opposite volume change associated with oxygen (+) and carbon (-) precipitation also favors co-precipitation in an approximate ratio of 2:1, as observed in Czochralski silicon\(^3\). In sample # 92, the measured co-precipitation ratio of oxygen and carbon is approximately 4:1. Considering that one \( I_{Si} \) is emitted for every two precipitated oxygen atom, a co-precipitation ratio of 4:1 implies that approximately half of the \( I_{Si} \) generated during oxygen precipitation is trapped by \( C_s \) atoms, and the other half is absorbed by grain boundaries or dislocations, which can act as effective sinks for \( I_{Si} \).

Because the annealing was performed in nitrogen ambient and all the \( O_t \) atoms have precipitated in the first hour annealing, there will be no \( I_{Si} \) injection during the subsequent prolonged annealing process. Therefore, carbon precipitation can only proceed via diffusion of substitutional carbon. Figure 2 shows that, without the assistance of \( I_{Si} \), \( C_s \) cannot precipitate at 800\(^0\)C due to the reduced diffusivity of \( C_s \), and can slowly precipitate at 900\(^0\)C. It has been found by several groups\(^{12,14,15}\) that, without \( I_{Si} \) injection, \( C_s \) cannot precipitate at annealing temperatures below ~1000\(^0\)C. Note that both \( C_s \) and \( O_t \) concentrations in our samples are approximately 1.5 x 10\(^{18}\) cm\(^{-3}\), which are much higher than those in the carbon doped CZ and EFG wafers. The reason that \( C_s \) can continuously precipitate in samples #92 at relatively low temperature, say 900\(^0\)C, is that all the \( O_t \) and part of the \( C_s \) atoms co-precipitate in the first hour annealing and these precipitates provide a large amount of sites for further \( C_s \) precipitation.

The reduced \( O_t \) supersaturation degree in sample #133 results in a relatively slow oxygen precipitation. It takes approximately 8 hours for all the \( O_t \) to precipitate at 800\(^0\)C and
900°C, see Fig. 3. Accompanying O\textsubscript{i} precipitation, the C\textsubscript{s} concentration decreases from 14 to 12 x 10\textsuperscript{17} cm\textsuperscript{-3}, and no further precipitation occurs after an additional 32 h annealing at 800°C, see Fig. 3 (a). The large sample-to-sample variation observed in the 900°C annealed samples prevents us from detecting the small C\textsubscript{s} reduction (~ 1 to 2 x 10\textsuperscript{17} cm\textsuperscript{-3}) during oxygen precipitation. However, C\textsubscript{s} reduction during the prolonged annealing process is well resolved. Note that C\textsubscript{s} concentration continuously decreases to 9 x 10\textsuperscript{17} cm\textsuperscript{-3} after 64h annealing at 900°C.

The impact of oxygen content on carbon precipitation is well illustrated by comparing sample #133 and 92. From figures 2 (a) and 3 (a), we can see that precipitation of O\textsubscript{i} by 1.6 and 0.7 x 10\textsuperscript{18} cm\textsuperscript{-3} is accompanied by a decrease of C\textsubscript{s} by 4 and 2 x 10\textsuperscript{17} cm\textsuperscript{-3} in sample #92 and 133, respectively. Because the fast carbon precipitation step is controlled by the formation of interstitial carbon in the presence of excess I\textsubscript{Si} generated during oxygen precipitation, a more aggressive oxygen precipitation process in the high oxygen containing wafer will generate more I\textsubscript{Si}, which further gives rise to a more aggressive carbon precipitation.

Following the fast precipitation in the first hour annealing, the C\textsubscript{s} concentration continuously decreases during the subsequent prolonged annealing at 900°C. As pointed out earlier, carbon precipitation during the prolonged annealing can only proceed via diffusion of C\textsubscript{s} due to the absence of I\textsubscript{Si} injection. It is evident from Figs. 2 (b) and 3 (b) that carbon precipitation proceeds faster in the high oxygen containing sample, even after removal of all the O\textsubscript{i} from the silicon matrix. The correlation between oxygen content and carbon precipitation rate was also observed in the 1020°C annealing process. Figure 4 shows that the higher the O\textsubscript{i} content, the faster the carbon precipitation. In our experiments, it took approximately 30 minutes to heat the sample from 900 to 1020°C. Considering the fast
precipitation observed during 800 and 900°C annealing, oxygen precipitation must have completed during the heating up period. As a result, carbon precipitation during 1020°C annealing must also proceed by Cs diffusion, except for the heating up period.

Now, the question is why does the Cs precipitate faster in a high Oi containing wafer, even after all the Oi has precipitated. Without a fast diffusion channel, the enhancement effect of oxygen can only arise from an increase in precipitation sites. According to the theory of Ham on diffusion limited precipitation\textsuperscript{20}, the precipitation rate is proportional to $n \cdot D$, where $n$ is the precipitate density and $D$ the diameter of the precipitates. Co-precipitation of oxygen and carbon has been clearly identified by secondary ion mass spectroscopy working in a scanning mode for a 1000°C annealed, carbon-doped Czochralski Si sample\textsuperscript{21}. It is proposed that the oxygen-carbon co-precipitates formed in the very first hour annealing provide sites for continuous carbon precipitation during the subsequent prolonged annealing. Therefore, a higher Oi concentration will result in larger precipitates, which will further give rise to a faster Cs precipitation. For the same volume of precipitates (proportional to $n \cdot D^3$), the precipitation rate (proportional to $n \cdot D$) will be higher if the precipitate density $n$ is larger. The second reason for the enhancement effect of oxygen is that the precipitate density is higher in a high Oi containing wafer, considering the higher Oi supersaturation degree and the enhanced precipitate nucleation through various C-O complexes\textsuperscript{2,16,22}.

6.4 Conclusion

The behavior of carbon precipitation in relation to oxygen content in RGS ribbon wafers subject to various heat treatments has been investigated by infrared spectroscopy. It is found that carbon precipitation in an oxygen containing wafer consists of two distinct steps; namely,
an initial rapid oxygen-carbon co-precipitation in the very first hour annealing, followed by slow precipitation during subsequent prolonged annealing. It is also found that a high oxygen content enhances carbon precipitation throughout the two steps.

Based on these experimental results, it is proposed that the formation of interstitial carbon in the presence of excess silicon self-interstitials generated during oxygen precipitation plays an important role in increasing the carbon precipitation rate during the first hour annealing. Because of the absence of interstitial injection during the following slow precipitation process, the enhancement effect of oxygen on carbon precipitation can only arise from an increase in precipitation sites. It is proposed that the oxygen-carbon co-precipitates formed in the very first hour annealing provide sites for continuous carbon precipitation. This explains why C<sub>s</sub> impurities precipitate faster in a high oxygen containing wafer, even after removal of all the O<sub>i</sub> from the silicon matrix.
Reference


Fig. 1. FTIR spectra of samples #92 and 133 after different annealing procedures. Spectra are shift for clarity.

Fig. 2. O_i and Cs concentrations in samples #92 annealed at 800 °C (a) and 900°C (b) for different times.
Fig. 3. O₁ and Cs concentrations in samples #133 annealed at 800 °C (a) and 900 °C (b) for different times.

Fig. 4. Cs concentration in 1020°C annealed samples.
CHAPTER 7. EFFECT OF GRAIN BOUNDARY ON OXYGEN AND CARBON PRECIPITATION

7.1 Introduction

With the solar cell industry growing at about 20% per year and silicon continuing to be the dominant technology, the need for silicon feedstock has moved past the level that can be supported by electronic-grade silicon. One important alternative feedstock is up-graded metallurgical grade silicon, a low-cost limitless supply. Detailed knowledge is required on impurities’ impact on performance to take advantage of this opportunity. The sheet silicon process [1] that generated the samples used in this study uses low-cost Si materials (high in transition metals as well as nitrides, oxides and carbon) and high solidification rates for cost efficient high volume production. As a result of these tradeoffs, the grain size of these wafers is relatively small, ranging from 100µm to 1mm. Thus, grain boundaries (GBs) play a more important role in sheet silicon than in ingot cast silicon, which has significantly larger grain sizes.

Much attention has been paid to grain boundaries in recent years due to their technology importance in solar cell materials and thin film devices. It is known that, they provide heterogeneous gettering sites for transition metals [2-4], oxygen [5], and carbon [6]. There is also a strong interaction among these impurities. For example, carbon [7] and nitrogen [8-10] can enhance oxygen precipitation (OP), as well as iron [11], if its concentration reaches $10^{14}$ cm$^{-3}$. The situation becomes much more complicated in sheet silicon where all of these impurities co-exist with grain boundaries. Clarifying the influence of GBs on the distribution of transition metals and light elements is indispensable for utilizing impure feedstock and
designing effective solar cell processing.

Of particular important is the manner in which oxygen precipitates influence solar cell performance. They can act negatively as minority carrier recombination centers or beneficially as gettering sites for transition metals [12]. The interstitial oxygen in sheet silicon materials is on the order of $10^{18}$ cm$^{-3}$ and will precipitate during solar cell processing. The impact of the GB on oxygen precipitation is twofold. On the one hand, they enhance oxygen precipitation by providing preferential nucleation sites [6]; alternatively, they can suppress oxygen precipitation by gettering nitrogen and carbon, which are known to act as nuclei for oxygen precipitation [7-10]. The effects of grain boundaries on the impurity gettering and oxygen precipitation in polycrystalline sheet silicon materials were examined in this chapter.

Polycrystalline RGS ribbon silicon usually contains a high concentration of carbon on the order of $10^{18}$ cm$^{-3}$. The high degree of carbon supersaturation and the presence of O$_i$ enhance carbon precipitation [13-17]. A high density of carbon precipitates will degrade the minority carrier lifetime by introducing interfacial states into the energy bandgap. Thus, detailed knowledge on carbon precipitation is needed to improve the performance of solar cells made from these high carbon content ribbon silicon. Besides interstitial oxygen, GBs can also have a significant impact on carbon precipitation, considering that they can provide heterogeneous nucleation sites for carbon precipitation and act as sources/sinks for intrinsic point defects [15-17]. The grain size of RGS ribbon silicon is around 100µm, and the relatively small grain size makes GBs an increasingly important factor effecting carbon precipitation. In this chapter, carbon precipitation near GBs will be investigated by infrared microspectroscopy and preferential etching/Nomarski microscopy.
7.2 Experiments

Polycrystalline sheet silicon wafers grown at GE Energy were used in this study. Wafers with a thickness of about 800 µm were boron doped with a resistivity of 2 to 3 ohm·cm. The grain size ranged from 100µm to 1mm. Both as-grown and after solar cell processing wafers were characterized. For the processed wafers, a high temperature annealing of 3 hours at 1060 °C was used in addition to the conventional solar cell processing sequence.

After chem-mechanical polishing, Al-Schottky diodes were simultaneously fabricated on both the as-grown and processed samples for EBIC characterizations. The contacts with a diameter of 1mm gave good I-V characteristics, with leakage currents below 1 µA. EBIC measurements were performed on a scanning electron microscope at room temperature with an accelerating voltage of 20 KV and a probe current of ~0.2 nA.

FTIR measurements with a spatial resolution of 70µm were performed on a Bio-Rad FTS-6000 spectroscope with an infrared microscope to investigate the oxygen precipitation behavior across individual grain boundaries in sheet silicon. A rectangular aperture was used with an IR beam size of 500 x 70 µm. The long edge parallel to the GB increased the beam intensity, while the short edge was kept perpendicular to the GB to increase the spatial resolution. Since individual grains were on the order of several hundred microns across and generally columnar in cross-section, it was possible to ensure that no “buried” GB contributes to an intra-grain FTIR signal by polishing the sample to 300µm. Measurements were then performed on a GB between two relatively large 1mm grains. In order to locating the GB under the infrared microscope, samples were etched in the Secco etchant for 1min after polishing. The spectral resolution was set at 8cm⁻¹ to eliminate fringes due to multiple-internal reflections. The interstitial oxygen concentration [Oi] was measured by the routine wide beam
FTIR at room temperature using a calibration factor of $3.14 \times 10^{17} \text{ cm}^{-2}$ from the intensity of the 1107 cm$^{-1}$ peak. Finally, samples that had been etched in the Secco solution for 1 min were examined under a Nomarski microscope.

RGS ribbons with similar carbon concentrations and very different oxygen contents were grown at the Energy Research Center of the Netherlands. The oxygen and carbon concentrations in the as-grown samples were listed in Table I of chapter VI. Samples were annealed at 900 and 1020°C for different times and examined by Nomarski microscopy after chemical-mechanical polishing and a 30 sec Secco etch. FTIR microspectroscopy was performed on the polished samples to investigate carbon precipitation near grain boundaries. Both virgin and annealed samples were examined on a Bruker 66v/S Fourier transform infrared spectrometer equipped with an IR microscope at the U2A beamline of the National Synchrotron Light Source of the Brookhaven National Laboratory. The size and configuration of the aperture for the intra-grain and GB comparison measurements are shown in Fig. 1. The aperture glass is transparent for visual light, which makes it convenient to locate the interested region. Note the aperture width was approximately 25 µm.

7.3 Experimental results

7.3.1 Impurity Gettering: As-grown Wafer

A room temperature EBIC image of an as-grown sample, see Fig. 2, shows that a higher collection efficiency halo is formed near the grain boundaries and for smaller grains the bright contrast is observed throughout the grain. These halos and bright contrast suggest that the
Fig. 1. Images show the size and configuration of the aperture for intra-grain and GB comparison.

Fig. 2. EBIC image of the as-grown sample.
grain-boundaries are acting as gettering centers, significantly increasing the carrier lifetimes. Since the cooling rate is very high during sheet growth, these effects are most likely due to GB gettering of transition metals with high diffusivities.

Figure 3 is a Nomarski micrograph of an as-grown sample after a 60 seconds Secco etch, which shows that precipitates with a density of $2 \times 10^7$ cm$^{-2}$ formed on the GB. Because only $\sim 1 \mu$m material is removed during the etching, the grain boundaries that spanned about 8-10$\mu$m must be almost parallel to the sample surface. The precipitate density was obtained by directly dividing the number of the precipitates by the GB area. Note also that no precipitates formed on the two parallel twin boundaries in the upper-right hand corner of Fig. 3. This is consistent with the fact that twins, which are present in the sample, are electrically inactive and not visible in the EBIC image.

Deep level transient spectroscopy measurements performed on the same set of as-grown samples [4] revealed four deep levels arising from Fe-B, Fe-Al, Cr-B, and Fe$_i$. The concentrations of the transition metals varied from diode to diode. Since the grain-boundary length in the region below the contact is expected to determine the extent of gettering, the GB density (total GB length / diode area) was measured by EBIC and correlated with the measured impurity concentrations of each contact. It is found that the total Fe concentration decreases strongly with an increase in GB density, whereas the Cr-B concentration only decreases slightly. Based on the DLTS results, it is proposed that the EBIC halo around GBs is likely due to gettering of Fe at boundaries and the etch pits on the boundaries observed by preferential etching/Nomarski microscopy are likely due to Fe precipitates.
**Fig. 3.** Nomarski micrograph of the as-grown sample after 2min Secco etching.

**Fig. 4.** Conventional wide-beam FTIR spectra of as-grown and processed samples.
7.3.2 Impact of GB on oxygen precipitation in sheet silicon

The presence of a series of absorption bands from 850-1100 cm\(^{-1}\) was detected by FTIR in both as-grown and processed samples, see Fig. 4. From their position and the fact that a high concentration of nitrogen is present in these samples, these bands were assigned to silicon oxynitride particles [18]. Depending on the nitrogen to oxygen ratio in the silicon oxynitride, the absorption appears at different wavenumber, from about 850 cm\(^{-1}\) for silicon nitride to 1072 cm\(^{-1}\) for silicon oxide [19]. The IR absorption lines (766 and 963 cm\(^{-1}\)) expected for dissolved nitrogen pairs [20] were not detected in these samples, and is likely due to the sample thickness (700\(\mu\)m), small grain size and high dislocation density.

Note during solar cell processing, interstitial oxygen decreased significantly from 14.4 to 2.2x10\(^{17}\) cm\(^{-3}\), and substitutional carbon decreased moderately from 3.3 to 2.3x10\(^{17}\) cm\(^{-3}\). The only high temperature annealing step in which interstitial oxygen has a significant diffusivity is the 3h, 1060°\(\text{C}\) annealing step. Since almost all the supersaturated oxygen precipitated during the 3h annealing, it appears that oxygen precipitation proceeds much faster in sheet silicon than in the dislocation-free Czochralski silicon used in the IC industry [21-22]. The fast precipitation process is likely related to the quench-in vacancies, see chapter IV, as well as supersaturated nitrogen and substitutional carbon, which are known to enhance precipitate nucleation [7-10].

The Nomarski micrograph of the processed and etched sample, see Fig. 5 (a) clearly shows a well defined precipitate-free denuded zone formed around the GB. At higher magnification, see Fig. 5(b), it is evident that most of the defects are actually stacking faults (SF), generated by self interstitials (I\(_{\text{Si}}\)) injection during the oxygen precipitation.
Fig. 5. Nomarski micrograph of the processed sample after 2min Secco etching. Low magnification image (a) shows the GB denuded zone and the high magnification image (b) taken at the intra-grain region shows that most of the intra-grain defects are stacking faults.
Because the range of the SF denuded zone is about 50µm and the total diffusion length of O$_i$ is only about 7µm during solar cell processing, the distribution of SF evidently arises from some fast-diffusion species. Stacking faults suppression near GBs might be: i) the GB acts as a sink for I$_{Si}$ and results in a locally reduced I$_{Si}$ supersaturation, or ii) The GB getters nitrogen and iron, which can enhance the oxygen precipitation.

To investigate the role of GBs on oxygen and silicon oxynitride precipitation distribution, microscopic FTIR measurements were performed on regions with and without a GB. The microscope FTIR spectra of the processed and as-grown samples are shown in Figs. 6 (a) and (b), respectively, which indicate that for both samples, more silicon oxynitride appears in the GB region. This fact implies that nitrogen preferentially precipitated along the GB during the cooling down period of the wafer growth process. At the melting point, the solubilities of nitrogen in liquid and solid silicon are $6 \times 10^{18}$ and $4.5 \times 10^{15}$ cm$^{-3}$, respectively [23]. Thus, for the high solidification rates in sheet Si growth, the concentration of nitrogen trapped in the crystalline silicon grain will significantly exceed its corresponding solubility. Even with the high cooling rate after solidification, due to its high diffusion coefficient [24], the nitrogen can still move to and preferentially precipitate along GBs, thereby creating a nitrogen-depleted zone near the GB. This is consistent with the fact that we cannot detect the absorption lines due to dissolved nitrogen, and the absorption bands due to silicon oxynitride precipitates in Fig. 6 do not change during processing. This nitrogen depletion zone is a likely cause of the oxygen precipitate/SF denuded zone in Fig. 5, since low concentrations ($10^{14}$ cm$^{-3}$) of nitrogen will enhance oxygen precipitation. Note also that the O$_i$ peak in the microscopic FTIR scan of Fig. 6 is almost uniform across the GB of the as-grown sample, while more oxygen is present as interstitial oxygen in the GB region after solar cell processing.
Fig. 6. Microscopic FTIR spectra of the processed (a) and as-grown (b) samples. The IR beam size was 500 x 70 µm.
It is useful to compare the magic denuded zone (MDZ) formation process [25] in single crystal CZ wafers with that formed near a GB. In this case, the depletion of nitrogen by GB gettering is similar to vacancies to CZ wafers surface. In the MDZ case, a vacancy concentration profile which is depleted near the surface is installed into silicon wafers by a rapid thermal annealing process. This profile subsequently controls the distribution of oxygen precipitates. In case of the GB denuded zone, nitrogen preferentially precipitates on the GB and forms a depletion zone around the GB, thus determining the distribution of oxygen precipitates.

### 7.3.3 Impact of GB on carbon precipitation in RGS ribbon silicon

Since grain boundaries act as sources/sinks of intrinsic point defects, they will have a significant effect on oxygen and carbon precipitation, which are two processes associated with volume increase and decrease, respectively. The grain size of RGS ribbon silicon is relative small, say ~ 100 µm. Therefore, clarifying the role of grain boundaries is important for a better understanding of carbon precipitation in RGS ribbon silicon.

Figure 7 compares two infrared absorption spectra acquired at the intra-grain and GB region of a high oxygen containing as-grown sample. Note that the silicon lattice absorption, which gives rise to the absorption band at 610 to 620 cm\(^{-1}\) with an intensity of approximately 9 cm\(^{-1}\) at room temperature, was not subtracted from the spectra. The absorption peak at 605 cm\(^{-1}\) overlapping on the shoulder of the silicon lattice absorption band is due to substitutional carbon. The \(C\(_s\)\) concentration can be quantitatively estimated by using the lattice absorption
Fig. 7. Infrared absorption spectra of the intra-grain and GB region of an as-grown high oxygen containing sample.

Fig. 8. Infrared absorption spectra of the high oxygen containing samples after 920°C, 64h (a) and 1020°C, 2h annealing (b), respectively.
band as an internal reference. Note from Fig. 7 that the Cs concentration was almost the same for the intra-grain and GB region. This is consistent with the facts that the fast solidification and cooling rate will effectively suppress carbon segregation during solidification, as well as precipitation during cooling down.

The infrared absorption spectra of the annealed high oxygen-containing sample are shown in Fig. 8. Note that the intensity of the carbon absorption peak significantly decreased after a 920°C, 64h annealing. The remaining Cs concentration is higher in the intra-grain region than the GB region. Similar results were also observed in the 1020°C, 2h annealed sample, where a small amount of Cs remained in the intra-grain region and almost all Cs had precipitated near GBs, see Fig. 8 (b). As discussed in chapter 6, the early stage of carbon precipitation in the high oxygen wafer is controlled by the formation of interstitial carbon by capturing I$_{Si}$ generated during oxygen precipitation. The presence of GBs in the high oxygen-containing sample can suppress carbon precipitation near GBs through absorbing I$_{Si}$, which is needed for the formation of high diffusivity C$_i$ and the relief of the tensile strain associated with carbon precipitation. On the other hand, grain boundaries can also provide heterogeneous nucleation sites, therefore enhance carbon precipitation. During the annealing process beyond the very first hour annealing, carbon precipitation is controlled by the diffusion of Cs. Therefore, carbon precipitation is likely to be enhanced with the presence of boundaries which provide more precipitation sites for Cs. Results shown in Fig. 8 indicate that the enhancement effect of providing more precipitation sites overwhelms the suppression effect of absorbing interstitials. Therefore, the presence of GBs overall enhances carbon precipitation.
Fig. 9. Infrared absorption spectra of a low oxygen containing samples annealed at 1020°C for 2h (a) and 4h (b), respectively.

Fig. 10. Nomarski optical micrograph of a 1020°C, 2h annealed, low oxygen containing sample after a 20s Secco etch.
The $O_1$ concentration in the low oxygen sample is $6 \times 10^{17}$ cm$^{-3}$, and there will be around $3 \times 10^{17}$ cm$^{-3}$ of interstitials generated during oxygen precipitation, which is small compared to the $13 \times 10^{17}$ cm$^{-3}$ amount of $C_s$. Therefore, the suppression effect of grain boundaries on carbon precipitation due to trapping of silicon self-interstitials will not be significant. Figure 9 shows the infrared absorption spectra of a low oxygen containing sample annealed at 1020$^0$C for 2h (a) and 4h (b), respectively. Note that the remaining $C_s$ concentration in the intra-grain region was significantly higher than the GB region in the low oxygen containing wafer. By comparing Fig. 8 (b) and Fig. 9 (a), we can see that the remaining $C_s$ concentration was higher in the low oxygen content wafer than in the high oxygen wafer. This is a clearly indication that the presence of oxygen enhances carbon precipitation.

The enhanced carbon precipitation near GBs was further verified by preferential etching, see Fig. 10. Note that a 5 $\mu$m wide precipitate denuded zone was formed adjacent to the GBs, which is likely due to $C_s$ gettering at GBs. Next to the denuded zone, a 20 to 30 $\mu$m wide precipitation band containing a high density of precipitates was observed. Further away from the boundaries or in the center region of each large grains, the precipitate density decreased again by approximately one order compared to that in the precipitation band.

Without vacancy generation or self-interstitial absorption, the large volume decrease associated with carbon precipitation will give rise to a large tensile strain, which will suppress the nucleation and growth of carbon precipitates. The presence of $I_{si}$ enhances silicon carbide nucleation and growth by formation of high diffusivity $C_i$ and by relieving the tensile strain associated with carbon precipitation. Because of the low oxygen content and the nitrogen annealing ambient, the $I_{si}$ will mainly come from grain boundaries or wafer surfaces, or by Frenkel-pair generation at intra-grain regions. With the precipitation of $C_s$, interstitials will be
depleted and vacancies will build up in the middle of large grains. Therefore, vacancies diffuse from the intra-grain region to the grain boundaries, and interstitials diffuse in the opposite directions. The generation/recombination of the vacancies and interstitials in the bulk silicon is a very fast process, which has a lifetime of approximately several milliseconds or smaller at $1020^0\text{C}$ [26]. As a result, the vacancy and the interstitial concentrations will obey the law of mass action, and a depletion of one species will automatically result in an accumulation of the other. Therefore, the distribution profiles of vacancies and interstitials near GBs will be the same whether the strain relief proceeds by emission of vacancies or absorption of self-interstitials.

The distribution profiles of $C_s$, $I$, and $V$ near a grain boundary are schematically illustrated in Fig. 11. At the boundary, interstitials are continuously generated and diffuse into the intra-grain region, and vacancies come from the intra-grain region are absorbed. The effective generation/recombination processes at GBs will keep both $C_i$ and $C_v$ close to their equilibrium concentrations, which are $1.6 \times 10^{11}$ and $1.7 \times 10^{12}$ cm$^{-3}$ at $1020^0\text{C}$, respectively [26]. In the intra-grain region, interstitials are depleted and vacancies are therefore supersaturated. Note that both vacancy and interstitial fluxes contribute to the strain relaxation of carbon precipitation.

For a complete description or modeling of the carbon precipitation process in polycrystalline silicon, detailed knowledge is required regarding to the interfacial energy of silicon carbide precipitates, the dependence of nucleation rates on intrinsic point defects and carbon concentrations, the accommodation of volume mismatch by elastic strain, etc. Because of the uncertainty involved in most of the important parameters, a complete modeling is not
Fig. 11. Schematically illustration of distribution profiles of $C_s$, I, and V near a grain boundary.
likely to give physical insight regarding to the carbon precipitation mechanism. In this paper, we assume that the tensile strain associated with carbon precipitates need to be largely relaxed in order for the precipitation to proceed. It is demonstrated that carbon precipitation in the low oxygen containing ribbon silicon is mainly controlled by the diffusion of supersaturated vacancies from the intra-grain region to grain boundaries.

For a unit area of grain boundaries, an increment $\Delta d$ of the precipitation band width requires

$$[C_s] \cdot \Delta d \quad \text{------------------------(1)}$$

amount of interstitials, where $[C_s]$ is the substitutional carbon concentration. Whereas, the amount of interstitials provided by the in-coming interstitial and the equivalent out-going vacancy fluxes in a time interval $\Delta t$ is

$$\frac{(s-1) \cdot C_v^{eq}}{d} D_v \cdot \Delta t + \frac{1-1/s}{d} \cdot C_i^{eq} D_i \cdot \Delta t \quad \text{------------------------(2)}$$

where, $s$ is the supersaturation degree of vacancies in the region outside the precipitation band; $C_i^{eq}, C_v^{eq}$ are the equilibrium concentrations of interstitials and vacancies; $D_i, D_v$ are the diffusion coefficients of interstitials and vacancies. Note that the law of mass action has been used in formula (2). The supersaturation degree of vacancies is controlled by the balance between the total flux of V and I, and the carbon precipitation rate. Considering the large carbon supersaturation degree, interstitials will be largely depleted; therefore, $s$ is most likely to be significantly larger than unity. As a result, the second term in formula (2) will be much smaller than the first term, which means that the strain relaxation of carbon precipitation is mainly realized by the out-diffusion of vacancies from the intra-grain to the nearby grain boundaries. Vacancies can be generated in the intra-grain region either by directly emission
from carbon precipitates or by Frenkel-pair formation. In the later case, the generated interstitials will be absorbed by carbon precipitates to relieve the tensile strain, while the simultaneously generated vacancies will diffuse to and recombine at the nearby grain boundaries. A full strain relaxation means that formula (1) must equal to (2). Therefore, the relation between the precipitation band width and the annealing time is obtained,

\[ [C_s] \Delta d = \frac{s \cdot C_{eq}^s}{d} D_v \Delta t \]  

---(3)

Note that the second term in formula (2) is neglected, and \( s-1 \) is simplified as \( s \) due to the relatively large \( s \) value. By integrating equation (3), we have

\[ d^2 = \frac{2 \cdot s \cdot C_{eq}^s}{[C_s]} D_v \cdot t \]  

---(4)

By substituting \( t = 7200 \text{ sec}, d=25 \mu m, \ [C_s]=1.3 \times 10^{18} \text{ cm}^{-3}, D_v=1.55 \times 10^{-5} \text{ cm}^2/\text{s}, \) and \( C_{eq}^s = 1.71 \times 10^{12} \text{ cm}^{-3} \) into equation (4), the vacancy supersaturation degree \( s \) can be determined as 200, which is a reasonable value considering the large carbon supersaturation degree.

It is worth to point out that the diffusivities of vacancies and interstitials are on the order of \( 10^{-5} \text{ cm}^2/\text{s} \) at \( 1020^0 \text{C} \), therefore it only needs several seconds for vacancies or interstitials to diffuse through a 100 \( \mu m \) large grain. On the other hand, the precipitation band width was only 20 to 30 \( \mu m \) after two hours annealing. The discrepancy can be resolved by recognizing that the concentrations of vacancies and interstitials are about five orders smaller than the \( C_s \) concentration.

7.4 Summary and Conclusions

In summary, the impact of grain boundaries in the polycrystalline sheet and ribbon
silicon on impurity gettering, oxygen and carbon precipitation have been investigated. It was found that, during the cooling down period of the sheet formation processes, transition metals and nitrogen preferentially precipitated along GBs. While the gettering of transition metals gave rise to the EBIC halo around the GB and the dependence of transition metal concentrations on the GB density, the gettering of nitrogen resulted in a nitrogen depletion zone around the GB, which further gave rise to the oxygen precipitate denuded zone.

Infrared microspectroscopy studies show that the remaining $C_s$ concentration is higher in the intra-grain region than the near GB region in the annealed RGS ribbon silicon. In the 1020°C, 2h annealed low oxygen containing sample, a 20 to 30 µm wide precipitation band near GBs was revealed by preferential etching. Assuming that the tensile strain associated with carbon precipitates must be largely relaxed in order for the precipitation to proceed, it is demonstrated that the precipitation band formation is mainly controlled by the diffusion of vacancies, which were either directly emitted from carbon precipitates or generated via a Frenkel mechanism, from the intra-grain region to GBs.
Reference


CHAPTER 8. PARTICLES IN POLYCRYSTALLINE SHEET SILICON

8.1 Introduction

Crystalline silicon is the most important material for making solar cells. The direct growth of ribbon silicon from molten Si has received increased attention [1] in recent years because it is highly suitable for low-cost terrestrial-based solar cells. In particular, it has: (i) minimum waste of material during sawing; (ii) little surface preparation before cell manufacture, and (iii) a shape suitable for high density packing in solar modules. Accompanying these cost-efficiency advantages, the grain size of the sheet silicon may be small due to the high solidification rate, and the impurity concentration is usually high due to the relative large contact area with refractory materials used as die or substrate, such as graphite or silicon nitride. In some cases, particles can be detached from the refractory materials and be incorporated into the sheet silicon as inclusions. Impurities and secondary phase inclusions can also come from the low cost silicon feedstock used in sheet generation. Although metallic impurities are generally the dominant lifetime killers in as-grown sheet silicon wafers [2], included particles and associated dislocation clusters can also degrade solar cell performance [3,4]. To take advantage of the high throughput production and low-cost feedstock of the sheet formation process, detailed knowledge regarding the impact of impurities on cell performance is required. This chapter experimentally investigates the chemical composition and distribution of these second phase particles together with their impacts on grain structure morphology and impurity gettering, and provides a thermodynamic analysis of the chemical reactions involved in particle formation.

Crucibles, dies, and substrates for the production of solar grade silicon are usually made
from refractory materials such as graphite, carbide and nitride. Considerable effort has been
directed at studying the wetting and erosion behaviors of these refractory materials in molten
Si [5-8]. A final aspect to this study on the reactions involved in nitride and carbide particle
formation is to provide insight into the reactions between refractory materials and molten
silicon.

8.2 Experiments

Polycrystalline sheet silicon wafers used in this study were generated with a linear sheet
speed of 3.1 meters/min at GE Energy. The top surface of the polycrystalline silicon sheet has
columnar grains, ranging in size from 100 µm to 5 mm. The total sheet thickness ranges from
600 to 800 mm. After chem-mechanical polishing, samples were etched in the Secco solution
and examined under a Nomarski optical microscope. To delineate the defects and, at the same
time, not remove the small inclusions, a relative short etching time of 15 seconds was used,
during which a 0.25 micron thickness of silicon was etched off (the etching rate of the Secco
solution is approximately 1 µm/min). Inclusions with a size of 1-3 µm were identified, which
were usually associated with dislocation clusters. The chemical composition of these
inclusions was initially analyzed in a Hitachi 3-3200N scanning electron microscope equipped
with an Oxford-Link X-ray energy dispersive spectroscopy (EDS) system. A relatively low
acceleration voltage of 5-10 kV was used to increase the intensity of the signal from
inclusions by decreasing the penetration depth of the electron beam. Detailed chemical
information was further acquired from SIMS and FTIR measurements. SIMS depth profile
measurements were performed on polished samples with a CAMECA IMS 6F system using a
Cs⁺ primary ion beam current of 400 nA. Based on the initial EDS results, SIMS profiles of
the three light elements of C, N and O were measured. $^{28}\text{Si}^{14}\text{N}$ was used to measure the nitrogen concentration because of its higher yield relative to $^{14}\text{N}$.

The composition variation of secondary phase inclusions and the variation of the interstitial oxygen concentration across the wafer thickness were studied with an infrared microscope attached to a Bio-Rad FTS-6000 FTIR spectrometer. Samples were double-side polished to ~350 µm thick from the cross section direction. Micro-FTIR measurements were made on the polished cross-section with a spectral resolution of 4 cm$^{-1}$ and a step size of 40 µm. A rectangular aperture was used with an infrared beam size of 500 x 50 µm$^2$. The O$_i$ distribution across the sample thickness was determined from the intensity of the 1107 cm$^{-1}$ peak using a calibration factor of 3.14 x 10$^{17}$ cm$^{-2}$.

Aluminum Schottky diodes were fabricated on the as-grown samples after chem-mechanical polishing for EBIC measurements, which were performed on a scanning electron microscope with an accelerating voltage of 20 KV and a probe current of 0.2 nA. EBIC images were acquired at different temperatures between 100 and 295 K.

### 8.3 Experimental results

#### 8.3.1 Composition analysis

Figure 1 is a Nomarski optical micrograph of an as-grown sample after a 15 sec Secco etch, which shows a number of second phase particles surrounded by dislocation clusters. Due to the short etching time, dislocations appeared as small dots instead of well resolved pits. Considering the silicon sheet was grown at 3 meters/min and was cooled down to 400°C in several minutes, these 1-3 µm large particles are believed to have been incorporated into the
Fig. 1. Nomarski image of an as-grown sample after 15s Secco etching and the corresponding SEM-EDS spectra of the particles.
silicon matrix as inclusions rather than by precipitation during cooling. Note the secondary phase inclusions are usually associated with dislocation clusters resulting from thermal expansion/contraction stresses. While the inclusions and dislocation clusters will locally decrease the minority carrier lifetime, they might also provide an overall benefit by providing gettering sites for transition metals. The particles’ compositions were characterized by SEM, and EDS spectra were also shown in Fig. 1. Note that there are basically two kinds of inclusions, which contain primarily carbon or nitrogen.

Due to the small size of the inclusions and the low detection limit of SEM-EDS analysis, the detail composition cannot be acquired by SEM-EDS, therefore, the sample was further characterized by SIMS and FTIR. The SIMS depth profiles of O, N and C were acquired near the top-surface region, see Fig. 2, which shows that most of the inclusions belong to following two types: nitrogen rich with trace oxygen and carbon rich with trace nitrogen. Two cases where O, N and C peaks appeared simultaneously were identified, suggesting the possible existence of inclusions containing all three light elements.

Figure 3 compares the FTIR spectrum from the sheet silicon sample with those from $\alpha$-Si$_3$N$_4$ prepared by different methods [9-12]. The spectrum from Ref. 9 was acquired from $\alpha$-Si$_3$N$_4$ powder. Spectra from Ref. 10 and 11 were taken on $\alpha$-Si$_3$N$_4$ produced by CVD growth plus a high temperature annealing. The sample studied in Ref. 12 was produced by a $^{14}$N$^+$ ion implantation, followed by a 1200°C 3h annealing. In Ref. 10-12, the formation of $\alpha$-Si$_3$N$_4$ was verified by XRD studies. The characteristic absorptions due to $\alpha$-Si$_3$N$_4$ are indicated by dash lines. We can see that while the main features at ~850 cm$^{-1}$ are consistent, the structure of the $\alpha$-Si$_3$N$_4$ varies slightly with different preparation conditions. From the
Fig. 2. SIMS depth profiles of carbon, nitrogen and oxygen acquired from the near top-surface region. Most of the inclusions belong to following two types: nitrogen rich with trace oxygen (N+O) and carbon rich with trace nitrogen (C+N).
Fig. 3. Comparison of the FTIR spectrum from the sheet silicon sample with those from $\alpha$-Si$_3$N$_4$ prepared by different methods reported in literatures.

Fig. 4. Nomarski images of large and small grain regions after 60 sec Secco etching.
similarities between the spectrum from the sheet silicon sample and those from the literatures, we can conclude that $\alpha$-Si$_3$N$_4$ exists in our samples. It has been reported that the absorption of silicon oxynitride appears at different wavenumber depending on the nitrogen to oxygen ratio [13,14], from about 850 cm$^{-1}$ for silicon nitride to 1072 cm$^{-1}$ for silicon oxide. The relative strong absorptions at 900, 950 and 1005 cm$^{-1}$ suggest that silicon oxynitrides with different nitrogen/oxygen ratio exist in our sample. Note the two peaks at 607 and 1107 cm$^{-1}$ are due to substitutional carbon and interstitial oxygen, respectively. Since the SIMS profiles show that the samples contain around 100 ppm volume of carbon rich particles, the absence of a strong absorption due to SiC [15,16] located at 780-810 cm$^{-1}$ indicated that most of the carbon rich particles might be a form of graphite.

**8.3.2 Distribution dynamics**

A comparison of large and small grain regions of an as-grown sample after a 60 sec Secco etch, see Fig. 4, indicates that more particle/ dislocation clusters exist in the small grain regions. Regions with different grain sizes were also examined by FTIR with an infrared beam size of 250 µm in diameter and the spectra are compared in Fig. 5. Consistent with the etching/Nomarski results, the amount of $\alpha$-Si$_3$N$_4$ and SiNO in the small grain regions was twice that of large grain regions. Note that the position and shape of the absorption bands from the large and small grain regions are essentially the same, indicating particles appeared in different regions have similar compositions. It was also found that a region with a higher content of particles usually contains un-melted silicon chips or insufficiently melted regions.
Fig. 5. FTIR spectra of large and small grain regions.

Fig. 6. Cross-sectional Nomarski micrograph of an as-grown sheet silicon sample after 30s Secco etching. The top-surface is facing upwards.
The distribution of particles across the wafer thickness was characterized by preferential etching and infrared microspectroscopy. Figure 6 is a Nomarski image of a large grain region. Note that there are more particle/dislocation clusters in the middle and the deeper regions of the wafer. Similar particle distribution profile was also observed in the small grain region, where the particle density was overall significantly higher than the large columnar grain region. Note that large particle/dislocation clusters, marked by arrows in Fig. 6, were observed near the wafer back surface. Since these large particle/dislocation clusters only appeared in the wafer grown with a more aggressive thermal profile, but not in samples grown with a less aggressive thermal profile, it is proposed that they might be particles detached from the substrate considering that a longer and deeper melting apparently enhances substrate erosion.

The depth distribution of $\alpha$-Si$_3$N$_4$ and SiNO was also characterized by cross-sectional micro-FTIR. The spectra in Fig. 7 are shifted relative to each other for clarity. Consistent with the preferential etching results, there are more oxynitrides (800-1060 cm$^{-1}$) appearing in the middle of the wafer than in the near surface regions. Note that in addition to the overall oxynitride band intensity changing with depth, the detailed structure also changes. We can see that the SiNO bands from the near top-surface region arise almost entirely from $\alpha$-Si$_3$N$_4$. With the increase of the depth, the absorptions at ~900 and 950 cm$^{-1}$ become stronger relative to that at 850 cm$^{-1}$ and some detail structure become less well defined. Considering that the oxynitride absorption will shift to higher wavenumber with increasing oxygen content [13,14], it appears that oxynitrides located at the deeper region contain more oxygen. The oxygen content might vary with different inclusions, resulting in broader absorption bands.
Fig. 7. FTIR spectra from the cross-section sample with a step size of 40µm and an aperture size of 500x50µm.

Fig. 8. Cross-sectional Nomarski images of an as-grown sample with top surfaces facing upwards show large columnar grains(a)-(b), and grain structure breakdown (c)-(d).
The composition variation is likely to be related to the O\textsubscript{i} distribution, see the variation of the interstitial oxygen peak at 1107 cm\textsuperscript{-1} in Fig. 7. Note that an oxygen denuded zone with a dimension of 200 µm was formed near the top-surface. In the deeper region where the oxygen concentration is high, α-Si\textsubscript{3}N\textsubscript{4} reacts with oxygen by forming oxynitride Si\textsubscript{2}N\textsubscript{2}O; while there is no oxynitride formation at the near top surface oxygen-depleted region. It will be shown in Sec 8.5.1 that the formation of oxynitride Si\textsubscript{2}N\textsubscript{2}O is thermodynamically favorable only if the oxygen concentration is higher than 2.8\times10\textsuperscript{17} cm\textsuperscript{-3}.

Both particles and un-melted silicon chips (or the insufficiently-melted-region) prefer to appear in the middle of the wafer and in the small grain regions. The fact that the particle distribution follows the same pattern of silicon chips, which are apparently associated with a low thermal profile, strongly suggests that the growth thermal profile is responsible for the particle distribution. It seems that oxide, nitride, and graphite (or carbide) are continuously dissolved into the molten Si. The small grain region is the insufficiently-melted-region, thus more particles sustain. Because the melting of the silicon powder starts from the top and the bottom, the middle part experiences a shorter melting period at relative lower temperatures, therefore more particles sustain there. The higher density of particles and the smaller grain size are most likely arisen from the same reason, say the localized low growth thermal profile or insufficient melting.

It is known that the segregation coefficients of transition metals, nitrogen, carbon and aluminum are all much smaller that unity. We also know that sufficient small particles can be pushed by the solidification front [17,18]. The presence of included particles and associated high concentration impurities will certainly contribute to the grain structure breakdown by providing heterogeneous nucleation sites for new grains and by increasing the degree of
constitutional supercooling. On the other hand, the trapping of particles and impurities will increase enormously when morphological breakdown occurs, as observed in the small grain regions of sheet silicon and in previous silicon directional solidification studies [19].

### 8.3.3 Impact of secondary phase particles on grain structure morphology

Figure 8 (a)-(d) are the cross-sectional images of an as-grown sample. For both large and small grain regions, there are more particles/ dislocation clusters in the middle of the wafer than near surface regions. In general, the interface starts to breakdown and the grain size shrinks with the increase of particle density. Note that a series of particles, marked by arrows in Fig. 8 (c) and (d), appeared at the interface between the large grain and the subsequently nucleated small grains, indicating that particles are likely to enhance interface breakdown via providing heterogeneous nucleation sites. However, the fact that large columnar grains can be achieved even with the presence of a relative high density particles, see Fig. 8 (b), suggests that some other factors other than particles are playing important roles on grain structure morphology.

The morphology breakdown will happen only if the liquid in front of the solidification front is undercooled, so that new grains might be nucleated. This might be realized by a negative temperature gradient in front the solidification interface or through a constitutional supercooling, see Fig. 9. The criterion for constitutional supercooling is that

\[
\frac{dT}{dx} < m \cdot V \sum_i C_i^0 \left(1 - \frac{k_i}{D_i}\right) \cdot \frac{1}{D_i},
\]

where \(C_i^0\), \(k_i\), \(D_i\) are the concentration, segregation coefficient, and diffusivity of impurity \(i\) in molten Si, respectively; \(V\) the grain growth velocity; \(m\) the slope of the liquid line in the phase diagram [20]. The molten Si in the sheet growth process
can be treated as a dilute solution, and m can be approximated as $m = \frac{T_M^2 \cdot R}{L} = \frac{466}{2} \text{ K/mol}$ fraction, where $T_M$ is the melting point of silicon, R the gas constant, and L the latent heat of melting [21]. Note that only those impurities which have small segregation coefficients can significantly contribute to the constitutional supercooling. For the sheet Si growth, we only need to consider carbon and transition metals. The carbon concentration in the liquid Si is ~ 10 ppma and $k_C = 0.07$; the total concentration of transition metals is around 1 ppma and their segregation coefficient is around 0.001. The diffusivities of different impurities in molten Si are all similar, and are approximately $2 \times 10^{-4} \text{ cm}^2/\text{s}$; the grain growth rate is estimated to be 0.002 cm/s. Substituting these values into the equation, the critical temperature gradient is estimated to be 5 K/cm. Since a negative or small positive temperature gradient at the solidification front is a necessary condition for interface breakdown, it is possible to achieve large columnar grains in the region with a high density of particles, see Fig. 8(b), if we increase the temperature gradient at the solidification front by enhancing the top surface cooling and/or the bottom surface heating.

While the undercooling of molten silicon in front of the solidification front is an indispensable condition for grain structure breakdown, whether new grains indeed form also depends on the nucleation process. The grain size is determined by the ratio of the growth rate verse the nucleation rate. A large growth rate and a small nucleation rate will result in large grains. Depending on the grain orientation and the dislocation density, the growth rate is proportional to $\Delta T^m$, where $m = 1-2$ and $\Delta T$ is the undercooling. The nucleation rate is exponential depending on the undercooling [22]. Therefore, the nucleation rate will increase more significantly than the
Fig. 9. Illustration of the two morphological interface breakdown situations. (a) negative temperature gradient and (b) constitutional supercooling. $T_M$ is the melting point, $T$ is the real temperature profile, and $C$ is the solute concentration profile. The shadowed region in (b) is the undercooling region.
growth rate with an increasing undercooling degree, and severe grain structure breakdown will happen.

The insufficient heating from the bottom side is likely to be one of the dominant reasons for interface breakdown because it decreases the temperature gradient in front of the solidification front or even result in a negative temperature gradient. In the localized insufficient-melted-region, the temperature gradient is more easily becoming negative, further results in interface breakdown and small grains. More particles sustained in this region can further decrease the grain size by providing heterogeneous nucleation sites. Note that particles themselves cannot result in interface breakdown, although they can affect the local temperature profile and increase the extent of the breakdown (the smaller grains).

8.3.4 Transition metal gettering by particles

Figure 10 (a)- (d) are the EBIC images of an as-grown sample at different temperatures, which show a bright contrast halo formed around the inclusion/dislocation clusters. Note that the contrast halo around GBs and the halo around particles have similar dimension and temperature dependent behaviors. Since it has been shown that the contrast halo around the GBs is mainly arisen from Fe gettering [2], the halo around the particles might also be due to Fe gettering. This is supported by the SIMS result done at NREL [4], see Fig. 11, which shows that iron was gettered by carbon-rich particles.

Figure 12 shows the variation of the EBIC collect current versus temperature for the gettered and ungettered regions. The uncertainty of the EBIC current was around 2%, which was determined by measuring the current every 15s for a period of 5 min at the same region. Note that the EBIC currents decrease with the decreasing of temperatures for both gettered
Fig. 10. EBIC images taken at different temperature show the transition metal gettering by particles.

Fig. 11. SIMS depth profiles of C, Al and Fe clearly indicate iron gettering by C-rich particles (Ref. [4]).
and ungettered regions, and with the ungettered region (dark region) decreasing faster.

Interstitial Fe can pair with acceptors to form different complexes. Fe-B pairs formed in B-doped wafers introduce two energy levels in the band gap [23]. One donor level FeB\(^{3+0}\) locates at 0.1eV above the valence band, and one acceptor level FeB\(^{0/-}\) at ~0.25eV below the conduction band, which is the level responsible for the lifetime degradation at room temperature. If the lifetime limitation impurities in the as-grown sample are FeB pairs, then with the temperature decrease, the Fermi level will approach the valence band and the donor level (E\(_V\)+0.1eV) will become more and more active. Due to the electrostatic attraction, the electron capture cross section of the donor level at E\(_V\)+0.1eV should be much larger than that of the acceptor level. It is the activation of this donor level that gives rise to the decrease of the EBIC collect current at low temperatures.

### 8.4 Thermodynamic phase stability analysis

#### 8.4.1 Thermodynamic calculation

Near the nitrogen rich inclusions, carbon will assume its average concentration, which is around 4x10\(^{17}\) cm\(^{-3}\) as determined by FTIR and is lower than its solubility of ~2.8x10\(^{18}\) at the melting point. Thus, we can neglect the effect of carbon when discussing reactions in most parts of the system, except when dealing with SiC formation near graphite particles. The equilibrium phases in the Si(l)-N-O system are \(\alpha\)-Si\(_3\)N\(_4\), Si\(_2\)N\(_2\)O, SiO\(_2\), Si(l) and a gas phase. The reactions involved in this system are summarized in table 8.1.

The equilibrium between Si\(_2\)N\(_2\)O and Si can be determined from reaction (3). When Si\(_2\)N\(_2\)O and Si are in equilibrium and coexist in the system, their activities must be equal to 1. We have
from which the boundary between Si$_2$N$_2$O and Si can be calculated. Here, $P$ is the pressure relative to the 1 atm standard state. Similarly, equilibria between Si / SiO$_2$, Si /$\alpha$-Si$_3$N$_4$, Si$_2$N$_2$O / SiO$_2$, and Si$_2$N$_2$O /$\alpha$-Si$_3$N$_4$ can be determined from reaction (1), (2), (4), and (5), respectively. In this manner, the phase stability diagram at 1685 K was constructed, see Fig. 13. The free energies of formation of SiO$_2$ and $\alpha$-Si$_3$N$_4$ were taken from the JANAF tables [24] and that of Si$_2$N$_2$O was from Hendry [25]. Since the free energies of formation of $\alpha$-Si$_3$N$_4$ and $\beta$-Si$_3$N$_4$ are very close at 1685K, the phase diagrams will be the same by using either $\alpha$ or $\beta$-Si$_3$N$_4$. The reason that $\alpha$-Si$_3$N$_4$ was used in the discussion is that it is the one which is actually detected in our system.

While the phase stability diagram was expressed in the partial pressures of N$_2$ and O$_2$, what we are able to measure and are really concerned about are the concentrations of N and O dissolved in liquid and solid silicon. Since the solubility of nitrogen in liquid silicon is just the concentration of dissolved nitrogen equilibrated with Si$_3$N$_4$, the nitrogen concentration will assume its solubility value at the phase boundary between Si(l) and Si$_3$N$_4$. After the first correlation point is determined, the correlation can be extended to other concentrations from the reaction N$_2$(gas)=2 N (in liquid Si). In exactly the same manner, a correlation between the oxygen concentration and P$_{O2}$ was established. The correspondences between impurity concentrations in the solid Si and the partial pressures were also calculated by using the solubility data in the solid silicon. The O and N concentrations in liquid and solid silicon are shown in the lower-left corner, near the liquid silicon phase region. Since the segregation factor of oxygen is almost unity, the oxygen concentrations in liquid and solid silicon are almost the same, and only the concentration in solid Si is shown in the diagram. Note the
Fig. 12. Temperature dependence of the EBIC collect currents of the gettered and ungettered regions.

Fig. 13. Phase stability diagram of Si-N-O system at 1685 K. The corresponding O and N concentrations in liquid and solid silicon are shown in the lower-left corner, near the liquid silicon phase region.
partial pressures in the diagram are expressed in logarithmic scale while the concentrations of dissolved N and O are in a linear scale. The standard free energies of formation and solubilities used in the calculation are summarized in Table 8.2 and 8.3.

8.4.2 Analysis of the sheet silicon growth system

In the region near $\alpha$-Si$_3$N$_4$ particles located in the deeper region, nitrogen concentration will assume its solubility value and the oxygen concentration was around $1 \times 10^{18}$ cm$^{-3}$, see Fig. 5. This system will be located within the shadowed region #1 in the phase stability diagram and Si$_2$N$_2$O will form through reaction Si$_3$N$_4$+Si+2O $\rightarrow$ 2Si$_2$N$_2$O. In the region near the top-surface, nitrogen will be continuously incorporated into liquid Si from the gas phase and the oxygen concentration is below $2.82 \times 10^{17}$ cm$^{-3}$ (point B in Fig. 13). This system will be located within the shadowed region #2 in the phase stability diagram and $\alpha$-Si$_3$N$_4$ is the stable phase relative to Si$_2$N$_2$O. Thus, $\alpha$-Si$_3$N$_4$ incorporated from the refractory materials will be sustained and new $\alpha$-Si$_3$N$_4$ might form through melting Si-N$_2$ reaction in the near top-surface region. The trace amount of oxygen observed in SIMS might just arise from $\alpha$-Si$_3$N$_4$. It has been shown by Colquhoun [30,31], that $\alpha$-Si$_3$N$_4$ was, in fact, an oxynitride containing up to 2 atomic % oxygen and its composition varies in the range of Si$_{11.4}$N$_{15}$O$_{0.3}$- Si$_{11.5}$N$_{15}$O$_{0.5}$. The above analysis is consistent with the cross-section FTIR results which show that oxynitrides located at the deeper region contain more oxygen than those in the near surface region. In summary, silicon nitride will sustain in the near top-surface region due to the low [O] and
Table 8.1 Equilibrium reaction in Si-N-O system.

<table>
<thead>
<tr>
<th>Reactions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{Si} + \text{O}_2 = \text{SiO}_2 )</td>
</tr>
<tr>
<td>2</td>
<td>( 3\text{Si} + 2\text{N}_2 = \alpha-\text{Si}_3\text{N}_4 )</td>
</tr>
<tr>
<td>3</td>
<td>( 2\text{Si} + \text{N}_2 + 0.5\text{O}_2 = \text{Si}_2\text{N}_2\text{O} )</td>
</tr>
<tr>
<td>4</td>
<td>( 2\text{Si}_2\text{N}_2\text{O} + 3\text{O}_2 = 4\text{SiO}_2 + 2\text{N}_2 )</td>
</tr>
<tr>
<td>5</td>
<td>( 6\text{Si}_2\text{N}_2\text{O} + 2\text{N}_2 = 4\alpha-\text{Si}_3\text{N}_4 + 3\text{O}_2 )</td>
</tr>
</tbody>
</table>

Table 8.2 Standard free energy of formation of condensed phases at 1685K

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta G ) (KJ/mol)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiO}_2 )</td>
<td>613</td>
<td>24</td>
</tr>
<tr>
<td>( \alpha-\text{Si}_3\text{N}_4 )</td>
<td>189</td>
<td>24</td>
</tr>
<tr>
<td>( \text{Si}_2\text{N}_2\text{O} )</td>
<td>434</td>
<td>25</td>
</tr>
<tr>
<td>( \beta-\text{SiC} )</td>
<td>60.2</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 8.3 Solubilities of oxygen, nitrogen and carbon in liquid and solid silicon at 1685K

<table>
<thead>
<tr>
<th>Solubility</th>
<th>Liquid ((\text{cm}^{-3}))</th>
<th>Solid ((\text{cm}^{-3}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>( 3.4\times10^{18} )</td>
<td>( 2.9\times10^{18} )</td>
<td>26,27</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>( 6.0\times10^{18} )</td>
<td>( 4.5\times10^{15} )</td>
<td>30</td>
</tr>
<tr>
<td>Carbon</td>
<td>( 9.1\times10^{18} )</td>
<td>( 2.8\times10^{18} )</td>
<td>27, 29</td>
</tr>
</tbody>
</table>
tend to transform to Si$_2$N$_2$O in the deeper region where [O] is higher than 2.8x10$^{17}$ cm$^{-3}$. Based on the same argument, it is anticipated that an oxygen depleted zone near the top-surface might form through Si$_2$N$_2$O formation, even after a cap layer of Si$_3$N$_4$ is formed on the surface preventing SiO from evaporating.

Thermodynamically, graphite is not a stable phase relative to SiC in the silicon melt. Kinetically, the formation of SiC seems also to be not a problem. Deike [6] has shown that the average thickness of the beta-SiC layer formed in melting Si kept at 1500°C for 10 min is 13 and 7µm for graphite and glassy carbon, respectively. Li’s experiments [5] showed that the thickness of the continuous SiC layer formed on the glassy carbon surface was ~6µm after 1 hour at 1430°C, and they also noted that most of the SiC layer was formed in the first several minutes. Zhou’s results [32] also showed that the thickness of the beta-SiC layer formed on the glassy carbon surface at 1430°C in 10 min is ~4 µm. Although all these analyses show that a ~3µm graphite particle will transform into an SiC particle in minutes, FTIR measurements did not detect the absorption peak due to SiC located at 780-820 cm$^{-1}$. The controversy between the theoretical analysis and FTIR results can be reconciled by proposing that a layer of silicon nitride or oxynitride might form on the C-rich particles near the top-surface or in the deeper regions, respectively. The silicon nitride or oxynitride layer will further prevent the SiC formation. SIMS results indicated that C-rich particles near the top-surface did contain trace amount of nitrogen.

8.5 Conclusions

Secondary phase inclusions in polycrystalline sheet silicon were investigated. The existence of particles with a size of 1-3 µm typically, associated with dislocation clusters was
identified by Nomarski microscopy and SEM. (i) SIMS depth profile measurements indicate that there are mainly two types of inclusions in sheet Si: nitrogen-rich with trace oxygen, and carbon-rich with trace nitrogen. FTIR spectroscopy results show that the nitrogen rich particles are either $\alpha$-Si$_3$N$_4$ or silicon oxynitride. (ii) More particles are located in small grain regions, and in the middle of the wafer cross sections. It is proposed that the small grain size and the high particle content are likely arisen from the localized low thermal profile or insufficient-melting. (iii) Temperature dependent EBIC studies show that, while particle/dislocation clusters detrimentally act as recombination sites for minority carriers, they also beneficially function as gettering sites for transition metals. (iv) Inclusions deeper in the wafer are found to contain more oxygen than those near the top-surface. Chemical reactions between included particles and molten Si are discussed based on a thermodynamic analysis. It is concluded that $\alpha$-Si$_3$N$_4$ particles will transform into oxynitrides in the deeper region where the dissolved oxygen exceeds $2.8\times10^{17}$ cm$^{-3}$, and sustain in the low oxygen containing near top-surface region.
Reference

   Trans. JIM 38, 990 (1997).
SUMMARY

This thesis examines the light-element impurities and related defects in polycrystalline sheet and RGS (Ribbon Growth on Substrate) ribbon silicon. The interaction dynamics between oxygen, carbon, nitrogen, and intrinsic point defects, as well as the role of grain boundaries (GBs) on oxygen and carbon precipitation have been studied.

Sheet silicon wafers subject to various heat treatments have been studied by infrared microspectroscopy. An O$_i$ denuded-zone is observed in the virgin wafer, which is sustained as a 250 µm wide precipitate-denuded-zone during annealing, mainly due to the critical role of the initial O$_i$ concentration and quenched-in vacancies on precipitate nucleation. The carbon precipitation profile is well correlated with that of oxygen. By monitoring the C$_s$ reduction by infrared absorption and the precipitate density by preferential etching, it is concluded that formation of interstitial carbon by trapping silicon self-interstitials is an indispensable step for the observed fast C$_s$ precipitation.

Carbon and oxygen precipitation in four sets of RGS wafers with similar carbon contents and very different oxygen concentrations has been studied. It is found that carbon precipitation in an oxygen containing wafer consists of two distinct steps; namely, an initial rapid oxygen-carbon co-precipitation in the very first hour annealing, followed by slow precipitation during subsequent prolonged annealing. A high oxygen content enhances carbon precipitation throughout the two steps. It is shown that the formation of interstitial carbon in the presence of excess silicon self-interstitials generated during oxygen precipitation plays an important role in increasing the carbon precipitation rate in the first hour annealing. Because of the absence of interstitial injection during the following slow precipitation process, the
enhancement effect of oxygen can only arise from an increase in precipitation sites. It is proposed that the oxygen-carbon co-precipitates formed in the very first hour annealing provide sites for continuous carbon precipitation. This explains why carbon impurities precipitate faster in a high oxygen containing wafer, even after removal of all the interstitial oxygen from the silicon matrix.

The impact of GBs on oxygen precipitation in sheet silicon has been studied. Infrared microspectroscopy shows nitrogen gettering at GBs, and preferential etching reveals a precipitate-denuded-zone near GBs. The gettering of nitrogen at GBs is likely to be responsible for the denuded-zone formation, considering the enhancement of nitrogen impurities on oxygen precipitation. The impact of GBs on carbon precipitation in RGS ribbons is also studied. Infrared microspectroscopy indicates a higher remaining Cs concentration in the intra-grain region, while preferential etching reveals a 20 to 30 µm wide precipitation band near GBs. Assuming that the tensile strain associated with carbon precipitates must be relaxed in order for the precipitation to proceed, it is shown that the precipitation band formation is mainly controlled by diffusion of vacancies from the intra-grain region to GBs.

In summary, a high concentration of Oi is found to precipitate readily in polycrystalline sheet and ribbon silicon, and the precipitation of Cs is mainly controlled by oxygen precipitation. GBs have a strong impact on both oxygen and carbon precipitation by gettering of nitrogen impurities and by interaction with interstitials and vacancies. It is concluded that a low oxygen content is vital important to prevent extensive oxygen precipitation. On the contrary, a high carbon content (~ 1x 10^{18} \text{ cm}^{-3}) can be tolerated, as long as the initial Oi concentration is low.