ABSTRACT

YOON, YOHAN. The Impact of Metallic Impurities on Minority Carrier Lifetime in High Purity N-type Silicon. (Under the direction of Dr. George A. Rozgonyi).

Boron-doped p-type silicon is the industry standard silicon solar cell substrate. However, it has serious limitations: iron boron (Fe-B) pairs and light induced degradation (LID). To suppress LID, the replacement of boron by gallium as a p-type dopant has been proposed. Although this eliminates B-O related defects, gallium-related pairing with iron, oxygen, and carbon can reduce lifetime in this material. In addition resistivity variations are more pronounced in gallium doped ingots, however Continuous-Czochralski (c-Cz) growth technologies are being developed to overcome this problem. In this work lifetime limiting factors and resistivity variations have been investigated in this material. The radial and axial variations of electrically active defects were observed using deep level transient spectroscopy (DLTS) these have been correlated to lifetime and resistivity variations. The DLTS measurements demonstrated that iron-related pairs are responsible for the lifetime variations. Specifically, Fe-Ga pairs were found to be important recombination sites and are more detrimental to lifetime than Fe_i.

Typically n-type silicon has a higher minority carrier lifetime than p-type silicon with similar levels of contamination. That is because n-type silicon is more tolerant to metallic impurities, especially Fe. Also, it has no serious issues in relation to lifetime degradation, such as FeB pairs and light-induced degradation (LID). However, surface passivation of the p⁺ region in p⁺n solar cells is much more problematic than the n⁺p case where silicon nitride provides very effective passivation of the cell. SiO₂ is the most effective passivation for n-
type surfaces, but it does not work well on B-doped surfaces, resulting in inadequate performance. Al₂O₃ passivation layer suggested for B-doped emitters. With this surface passivation layer a 23.2 % conversion efficiency has been achieved. After this discovery n-type silicon is now being seriously considered for photovoltaics. The detrimental effects and electrical properties of transition-metal impurities, e.g., iron, and its complexes, such as FeB, in p-type silicon are well-known. However, in n-type silicon wafers, although there is evidence of greater tolerance, the impact of specific metallic impurities on minority lifetimes is not as well established.

The major contribution of this dissertation is to provide new electrical data relating to metallic impurities in n-type silicon, e.g. activation energy, capture cross sections. The injection-dependent lifetimes of intentionally metal contaminated n-type CZ silicon wafers were investigated using resonant-coupled photoconductance decay (RCPCD) and the quasi-steady-state photoconductance technique (QSSPC). Finally, a direct correlation between minority carrier lifetime and the concentration of specific electrically active metallic impurities was established using DLTS.
The Impact of Metallic Impurities on Minority Carrier Lifetime in High Purity N-type Silicon

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

Materials Science and Engineering

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DEDICATION

With love to my parents and
my lovely wife Seori's devotion
BIOGRAPHY

Yohan Yoon obtained his B.S. degree in Materials Science and Engineering, Seoul National University, Seoul, South Korea in 2007. After graduation, he continued to study for M.S. degree in the Nanodevice Materials Laboratory, Seoul National Univ. and obtained M.S. degree in Materials Science and Engineering in 2009.

While pursuing the M.S. degree, he focused his research on laser annealing of 3% Si steel and inkjet printed Ag films under the guidance of Prof. Young-chang Joo. After his graduate study, he enrolled in the Ph.D. program in Dept. of Materials Science and Engineering at NC State University, Raleigh. He joined as research assistant in Prof. Rozgonyi’s lab and mainly focused on the impact of metallic impurities and light elements on the minority carrier lifetime of silicon for solar cells.
ACKNOWLEDGMENTS

I would like to acknowledge and extend my heartfelt gratitude to the committee members, Dr. George Rozgonyi, Dr. Jerome Cuomo, Dr. Liyou Cao, and Dr. Mehmet C Öztürk for their generous guidance and review of this work. Of the many people who have been enormously helpful in the completion of this dissertation, I am especially thankful to Dr. George Rozgonyi for his help and support in guiding me through to its successful completion. His passion for research showed me how to approach and conduct research, and his teaching throughout the program will play a definite role in leading my future research as well as my own personal life. Also, his feedback and support have helped me achieve numerous insights into my research, and has provided me with new perspectives on research process. I also would like to expand my thanks to my friends in NCSU, especially Dr. Jinwoo Kim. Also I really appreciate church people’s help, especially group Nehemiah. Thanks for all the prayers and well wishes. I am very grateful to the members of research group Dr. Khaled Youssef, Dr. Bijaya Paudyal, Mr. Francois Hautin, Dr. Liya Yu, Dr. Prashant Kulshreshtha, Meirong Shi, and Yixin Yan for their advices and instructions in the lab. Finally, I thank to the God Almighty. Thank God for the bread of my life.

I dedicate this dissertation to my parents, sister, and my wife for their unconditional love and support in every way possible throughout the process of this course, this dissertation and beyond. Without their efforts and prayer, this work would have never been possible. Finally, I am proud to be your father, my adorable daughter, Julee Yoon. Forever will be my love to you. This work was supported by the Silicon Solar Consortium (SiSoC) as part of NSF’s Industry/University Cooperative Research Center (I/UCRC) program.
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1. **Motivation and Background**

1.1 **Limitations of Boron-doped P-type Silicon**

Boron-doped p-type silicon is widely used as the active absorbing region in Si solar cells. However, it has serious limitations in the form of powerful recombination centres, specifically iron boron (Fe-B) pairs and light induced degradation (LID). Iron is one of the major metallic impurities in Si solar cell fabrication. Although the concentration level of iron is initially low (<$10^{11}$ cm$^{-3}$ in conventional Cz Si ingots), it may increase during cell processing up to $10^{13}$ cm$^{-3}$ or even more [1]. Especially in p-type wafers, which is commonly used for photovoltaics, interstitial iron (positively-charged state) reacts with boron to form FeB pairs. FeB pairs as well as interstitial iron are strong recombination centers, which result in the degradation of minority carrier lifetime and consequently in a reduction in solar cell efficiency. In addition, minority carrier lifetime degradation occurs in boron doped p-type Si solar cells. This is caused by a meta-stable defect which can be activated by illumination or minority carrier injection [2]. The origin of this light-induced degradation is attributed to boron-oxygen pairs, since no degradation was observed in gallium doped p-type silicon, float zone (low oxygen) silicon or in n-type silicon [3].

1.1.1. **Iron-Boron (Fe-B) pairs**

The possibility of iron-boron (FeB) pairing was firstly suggested by Collins in 1957. [4] The energy level of (FeB)$^{0+}$ at $E_V + (0.10 \pm 0.01)$ eV was identified by Feichtinger [5], and confirmed by various groups from Hall effect and DLTS studies. [6-8] The identification of this level was supported by studies of the dissociation and association kinetics of the pairs by
Graff and Pieper [9] and by Kimerling et al. [10] Figure 1.1 shows the DLTS peak associated with the FeB pair (H1) and its Arrhenius plot. [11]. FeB pairs are strong recombination centers in spite of their shallow energy level. This is because recombination at low injection levels occurs through the acceptor state at $E_C - 0.29$ eV which is close to the midgap of silicon. [12].

### 1.1.2. Light Induced Degradation (LID)

LID is observed in solar cells fabricated on boron-doped p-type Cz-Si wafers. [13] Figure 1.2 shows the degradation of cell performance (the power output $P_m$, the short-circuit current $I_{sc}$, and the open-circuit voltage $V_{oc}$) after a short period of light illumination. However, the cell performance was recovered by a 200 °C annealing. This degradation was found only in boron-doped p-type silicon which contained oxygen. Figure 1.3 shows the measured carrier lifetimes of of B-, Ga-, and P-doped Cz-Si and B-doped MCz-Si (low oxygen) before and after light soaking. [14] The origin of this degradation has been studied by many researchers. Glunz et al. [15] confirmed the strong correlation between the LID in Cz-Si and the boron and oxygen concentrations. They proposed that $B_iO_i$ pairs were the defect complexes associated with the LID. However, it was shown that the LID recombination center is not close to the energy level of the $B_iO_i$ pair, see Fig. 1.4. [16]. Bourgoin et al. [17] proposed a possible atomic configuration of the boron-oxygen complex where the $B_x$ atom is surrounded by three $O_i$ atoms, see Fig. 1.5. However, this model has not been verified experimentally.
1.2 Gallium-doped P-type Silicon

To suppress LID, the replacement of B by Ga as a p-type dopant has been proposed [18-23]. In spite of the effective elimination of B-O related defects, Ga-related pairing with iron, oxygen, and carbon can also reduce lifetime [20, 23]. In this work we explore this and investigate the resistivity variation and lifetime limiting factors in c-Cz grown Ga-doped Si. The radial and axial variation of electrically active defects were observed in DLTS spectra and correlated to lifetime and resistivity variations. DLTS measurements demonstrated that iron-related pairs are responsible for the variations. Specifically, Fe-Ga pairs were found to be serious recombination sites, which are more detrimental to lifetime than Fe.

1.3 Phosphorus-doped N-type Silicon

Typically n-type silicon has a higher minority carrier lifetime than p-type silicon with similar levels of contamination. That is because n-type silicon is more tolerant to metallic impurities, especially Fe [24]. Also, it has no serious issues in relation to lifetime degradation, such as FeB pairs and light-induced degradation (LID). However, surface passivation of the p⁺ region in p⁺n solar cells is much more problematic than the n⁺p case where silicon nitride provides very effective passivation of the cell. SiO₂ is the most effective passivation for n-type surfaces [25], but it does not work well on B-doped surfaces, resulting in inadequate performance [26-29]. Benick et al. [30] suggested an Al₂O₃ passivation layer for B-doped emitters. With this surface passivation a 23.2 % conversion efficiency has been achieved. After this discovery n-type silicon is now being seriously considered for photovoltaics. The detrimental effects and electrical properties of transition-metal impurities,
e.g., iron, and its complexes, such as FeB, in p-type silicon are well-known. However, in n-type silicon wafers, although there is evidence of greater tolerance, the impact of specific metallic impurities on minority lifetimes is not as well established.

1.4 Metallic Impurities in Silicon Solar Cells

The electrical properties of various metallic impurities, e.g. Fe, Ni, Cu, Mo, have been studied by many researchers. The metallic impurities form electrically active sites, i.e. deep levels, in the silicon bandgap, in general these act as recombination sites and compete for minority carriers with the current generation in the solar cell hence reducing efficiency. Lifetime degradation can occur not only via these deep levels but also through metal precipitates. Therefore, understanding their impact on minority carrier lifetime is very important in silicon solar cells. Fig. 1.6 and 1.7 show a direct correlation between metallic impurity concentrations and relative efficiencies for boron-doped p-type and phosphorus-doped n-type silicon solar cells, respectively. The most appropriate way to characterize the impact of metallic impurities is the minority carrier recombination lifetime. Minority carrier lifetime can be measured using microwave-photoconductance decay (MW-PCD) and quasi-steady-state photoconductance technique (QSSPC).

Fig. 1.8 shows solar cell conversion efficiency as a function of minority carrier lifetime for different types of commercial solar cells. Increasing the minority carrier lifetimes monotonically increases the conversion efficiencies. In this case the solar cell conversion efficiencies are simulated data which was calculated using PC1D, but the effect is confirmed in practice in real solar cells.
Lifetime spectroscopies are based on Shockley-Read-Hall (SRH) recombination [31-32] which is a defect-assisted recombination process between the conduction band and the valence band. Lifetime spectroscopies with different carrier injection levels are important in identifying recombination mechanisms since the total lifetime is the sum of three different recombination processes: Auger, Radiative, and Shockley-Read-Hall recombinations.

The total (bulk) lifetime is determined according to the relationship

\[ \frac{1}{\tau_B} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{Auger}} \]  

(1)

where, \( \tau_{SRH} \) is the Shockley-Read-Hall recombination, \( \tau_{rad} \) the radiative recombination, and \( \tau_{Auger} \) the Auger recombination.

As shown in Fig. 1.9, at low injection levels (LLI) (\( \eta < 1 \)), \( \tau_{rad} \) and \( \tau_{Auger} \) are much longer than \( \tau_{SRH} \). Therefore, bulk lifetime is expressed by

\[ \frac{1}{\tau_B} \approx \frac{1}{\tau_{SRH}} \]  

(2)

So, for the purpose of defect characterization, lifetime at LLI needs to be determined.

Injection dependent lifetime measurements show the impact of metallic impurities on the bulk lifetime, but they have limitations in identifying metallic impurities. Deep level transient spectroscopy (DLTS) has been performed to detect and characterize the metal impurity related deep levels in the silicon bandgap [33].

1.5 Overview of Dissertation

Chapter 2 introduces various techniques employed for this research, including deep level transient spectroscopy (DLTS), micro-wave photoconductance decay (\( \mu \)-PCD) and quasi-
steady-state photoconductance (QSSPC). Also, the basic concept of Shockley-Read-Hall recombination and Injection Dependent Lifetime Spectroscopy (IDLS) are reviewed.

Chapter 3 presents the characteristics of Ga-doped p-type c-Cz silicon. The first section discusses the resistivity variation and lifetime limiting factors of the silicon samples. This is followed by a discussion of the identification of electrically active defects responsible for the lifetime degradation. Finally, the dissociation of the electrically active defects after low temperature annealing is detailed.

Chapter 4 presents a detailed discussion of recombination in mc-Si. This is an essential pre-requisite to engineering effective gettering and passivation and hence to achieving very high efficiency solar cells made from these complex materials.

Chapter 5 presents the impact of nickel contamination on high carrier lifetime n-type crystalline silicon wafers. This was investigated using resonant-coupled photoconductance decay (RCPCD) and quasi-steady-state photoconductance technique (QSSPC). The impact surface recombination velocity (SRV) on apparent lifetime was determined. A direct correlation between minority carrier lifetime and the concentration of electrically active substitutional Ni and Ni silicide precipitate traps measured using deep level transient spectroscopy (DLTS) was established.

Chapter 6 presents injection dependent lifetime spectroscopy (IDLS) technique performed to identify the type and concentration of the defects associated with metal impurities (Cu, Mo) in crystalline silicon wafers. Minority carrier lifetimes in intentionally contaminated silicon wafers using various metal concentrations were measured by a transformer-coupled, radio frequency-based photo conductance measurement tool, GLM™
Concentrations ($N_i$) of electrically active defect states associated with Mo and Cu impurity are determined from measured bulk lifetime at low level injection, using Shockley-Read-Hall, carrier concentrations ($n_1$ and $p_1$), and known activation energy levels ($E_a$) from the literature of the identified metal.

References


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2. Research Methodology

2.1 Introduction

In this thesis, in order to quantify the impact of metal impurities (Fe, Mo, Ni, etc.) in n-type silicon (n-Si) on carrier lifetime and device performance, different techniques were employed. Electrically active defects were evaluated with deep level transient spectroscopy (DLTS) in the range of $10^{-10}$ to $10^{-14}$ cm$^{-3}$ level. Their energy levels, carrier capture cross sections, and densities were measured using DLTS technique. Minority carrier lifetimes were measured via $\mu$-wave photoconductance decay ($\mu$-PCD) and quasi-steady-state photoconductance (QSSPC). A direct correlation between minority carrier lifetime and the concentration of electrically active defects for metal contaminated samples measured using deep level transient spectroscopy (DLTS) was established.

2.2 Deep level Transient Spectroscopy (DLTS)

Deep level transient spectroscopy is an experimental tool for identifying deep energy levels in semiconductor bandgap. The technique was developed by D.V. Lang in 1974. [1] During measurements, a reverse bias is applied to a Schottky diode and a reduced bias is pulsed. The bias can be changed with different applied voltages, selecting the depth of the space charge regions. By reverse biasing, the space charge region is at its widest and depleted of majority carriers. During a pulse, majority carriers fill some deep energy traps in the depletion region. If the diode is held in another reverse bias, the majority carriers are emitted from the traps. The emission is determined by observing capacitance transient change of the diode. The emission rate is temperature dependent, so it can be expressed as
where $\sigma_1$ is the minority-carrier capture cross section, $<v_1>$ mean thermal velocity of minority carriers, $N_{D1}$ the effective density of states in the minority carrier band, $g_1$ the degeneracy of the trap level, $\Delta E$ the energy separation between the trap level and the minority-carrier band.[1] As expressed in equation (2.1), the emission rate is increased with increasing temperature and decreased with decreasing temperature. For this reason, different capacitance decays can be obtained with temperature scan from low temperature (30 K) to room temperature (300 K). A rate window is selected in two points in the different capacitance transients. As shown in Fig. 2.1, the difference of capacitance decay at the rate window ($t_2-t_1$) versus temperature is the DLTS spectrum. The normalized DLTS signal can be defined as

$$S(T) = \frac{[C(t_1)-C(t_2)]}{\Delta C_0}$$

where $\Delta C_0$ is the change of capacitance induced by the pulse at $t = 0$.

2.2.1. Shockley-Read-Hall (SRH) Recombination

The Shockley-Read-Hall recombination was proposed by W Shockley, W T J Read and R N Hall. [2, 3] In the recombination process, electrons in the silicon conduction band are recombined with holes in the valence band through defects in the silicon band gap. This is two step recombination process: (1) electron transition from the conduction band to the defect state (2) hole transition from the valence band to the defect state. Figure 2.3 (a) and (b) show the state before and after the carrier transaction, respectively.
2.2.2. Derivation of SRH Recombination

**Rate of Change of Carrier Concentrations**

The capture rate of electrons \((Cn)\) and holes \((Cp)\) for a defect centre can be expressed as

\[ C_n = \sigma_n \nu_{th} n = C_n n \quad \text{for electrons and} \quad C_p = \sigma_p \nu_{th} p = C_n P \quad \text{for holes} \quad (2.3) \]

where, \(\nu_{th}\) is thermal velocity of the defect centre, \(\sigma_n\) the capture cross sections of electrons, \(\sigma_p\) the capture cross sections of holes.

If \(f_e\) is the probability of emission of electrons in a deep level energy in the CB, \(1-f_e\) is the probability of capture of the electrons. The rate change of electrons and holes can be expressed as

\[ \frac{dn}{dt} = \text{electron emission} - \text{electron capture} = e_n N_i f_e - c_n n N_i (1-f_e) \quad (2.4) \]

\[ \frac{dn}{dt} = \text{hole emission} - \text{hole capture} = e_p N_i (1-f_e) - c_p p N_i f_e \quad (2.5) \]

where, \(e_n\) is the emission rate of electrons, \(e_p\) the emission rate of holes, \(N_i\) number of same energy level defects.

In the equilibrium condition \(dn/dt = 0\) and \(dp/dt = 0\), the expression for \(e_n\) and \(e_p\) can be expressed as

\[ e_n = c_n n \left( \frac{(1-f_e)/f_e}{(1-f_e)} \right) \quad \text{and} \quad e_p = c_p p \left( \frac{f_e/(1-f_e)}{1-f_e} \right) \quad (2.6) \]

**Expression for \(U_{SRH}\) and \(\tau_{SRH}\)**

Applying \(n_1 p_1 = n_i^2\) (intrinsic carrier concentration), and \(f_e\), which is expressed as \((f_e = (c_n n + c_p p_1) / (c_n (n + n_i) + c_p (p + p_1)))\), to equation (2.3) and (2.4), the recombination rate can be expressed as
Both $\tau_n^0$ and $\tau_p^0$ are capture time constants and depend on the capture cross section ($\sigma$), thermal velocity ($v_{th}$) and defect concentrations ($N_t$). Therefore, it can be expressed as:

$$
\tau_n^0 = \frac{1}{N_t \sigma n v_{th}} \quad \text{and} \quad \tau_p^0 = \frac{1}{N_t \sigma_p v_{th}}
$$

(2.8)

The non-equilibrium carrier densities $n$ and $p$ can be replaced by the sum of the carrier densities at thermal equilibrium ($n_0 + p_0$) with the excess carrier densities ($\Delta n$ and $\Delta p$). For negligible trapping effect of the defect level $\Delta n = \Delta p$, hence the SRH lifetime can be expressed as [4]

$$
\tau_{SRH} = \frac{\Delta n}{U_{SRH}} = \frac{\tau_{p0} (n_1 + n_0 + \Delta n) + \tau_{n0} (p_0 + p_1 + \Delta n)}{n_0 + p_0 + \Delta n}
$$

(2.9)

2.3 Microwave Photoconductance Decay (MW-PCD)

Microwave Photoconductance Decay (MW-PCD) is a contactless method for lifetime mapping, which was firstly proposed in 1955. [5] MW-PCD is the most common way of measuring lifetime. The measurements are performed by observing microwave reflection of a laser pulsed sample. The laser pulse can create excess carriers in the sample, and the excess carriers cause the change of microwave reflection. While a periodical laser pulse of light, transient decay of microwave reflection can be observable. The transient decay can be converted to the minority carrier lifetime using some equations.
The lifetimes measured by using MW-PCD are effective lifetime due to surface recombinations. In order to minimize the effect of surface recombinations, minority carrier lifetimes were measured with the samples immersed in an iodine-ethanol solution during the lifetime measurements.

2.4 Injection Dependent Lifetime Spectroscopy (IDLS)

The objective of injection dependent lifetime spectroscopy (IDLS) is to determine electrical properties of deep energy levels responsible for lifetime degradation using the SRH equation. As mentioned in the previous section, the best way for observing the SRH effects is to fit lifetimes as a function of various injection levels, and determine low level injection (LLI). Schmidt et al. [6] performed IDLS to determine $\sigma_p$ of boron-oxygen ($\text{B}_i\text{O}_i$) pairs in boron-doped Czochralski silicon. The concentration of $\text{B}_i\text{O}_i$ pairs increased with increasing light intensity, so lifetime curve was fitted to SRH equation as a function of excess carrier concentration. IDLS also was performed by different researchers. [7]

2.4.1. Quasi-Steady-State Photoconductance (QSSPC)

Quasi-Steady-State Photoconductance is the most common technique for measuring effective lifetimes. [8] This is a convenient technique to approach the steady-state by using light pulse, varying very slowly compared to the minority carrier lifetimes of samples.

In steady-state condition, the generation and recombination rates of electron-hole pairs should be in balance. This can be expressed as current densities.
The total recombination can be expressed as,

\[ J_{\text{ph}} = J_{\text{rec}} \]  \hspace{1cm} (2.10)

where, \( J_{\text{ph}} \) is the average excess minority carrier density, \( W \) sample thickness, \( \tau_{\text{eff}} \) effective minority carrier lifetime.

The photo-generated excess carriers should be in balance (\( \Delta n = \Delta p \)), and \( \Delta n = G_L \tau_{\text{eff}} \) (classic relationship), so the excess photoconductance can be expressed as

\[ \sigma_L = q(\Delta n_{\text{av}} \mu_n + \Delta p_{\text{av}} \mu_p)W = q\Delta n_{\text{av}} (\mu_n + \mu_p)W \]  \hspace{1cm} (2.12)

by (2.11) and (2.12) equations,

\[ \tau_{\text{eff}} = \sigma_L / \{ J_{\text{ph}} (\mu_n + \mu_p) \} \]  \hspace{1cm} (2.13)

In this QSSPC technique, the effective lifetimes can be determined by these equations. Fig. 2.4 and 2.5 show the examples of photoconductance and effective lifetimes.

References


Fig. 2.1 The left-hand side shows the capacitance transient over a range of temperatures, and the right-hand side shows the DLTS signal ($C(t_1) - C(t_2)$) as over the same range of temperatures. [1]
Fig. 2.2 (a) State before carrier transaction (b) state after carrier transaction
Fig. 2.3 IDLS analysis of 1 Ω cm boron-doped silicon. [6]
Fig. 2.4 Raw data from quasi-steady-state photoconductance measurements. The lifetime is proportional to the photoconductance amplitude. [9]
Fig. 2.5 The inverse of effective lifetime vs. minority carrier density for a 345 ns small-grained multi-crystalline silicon sample. [9]
Abstract

Continuous-Czochralski crystal growth has been suggested as a viable technique for the fabrication of photovoltaic Si wafers due to its low resistivity variation of dopants, independent of segregation, compared to conventional Cz. In order to eliminate light induced degradation due to boron-oxygen traps in conventional p-type silicon wafers, gallium doped wafers have been grown by continuous Cz method and investigated using four point probe, deep level transient spectroscopy and microwave-photoconductance decay. Iron-gallium related electrically active defects were identified using DLTS as the main lifetime killers responsible for reduced non-uniform lifetimes in radial and axial positions of the c-Cz silicon ingot.
3.1 Introduction

The significant minority carrier lifetime degradation observed in boron doped p-type Cz Si is mainly caused by two issues: iron-boron (FeB) pair traps and boron-oxygen (B-O) driven light-induced degradation (LID). To suppress LID, the replacement of B by Ga as a p-type dopant has been proposed [1-6]. In spite of the effective elimination of B-O related defects, Ga-related pairing with iron, oxygen, and carbon can also reduce lifetime [3, 6]. Moreover, the resistivity of Ga doped Si ingots, grown using conventional Cz, varies along the growth axis due to the low segregation coefficient (0.08) [7]. Although the varying resistivity of Ga-doped Si can be mitigated with changes in cell processing for fabricating high efficiency solar cells [8], the cost of these changes is not economically viable, making it expensive to utilize traditionally grown crystal [9]. As an alternative, the c-Cz method, in which the crucible is refilled by adding polycrystalline silicon chips has been developed for uniform resistivity. Even though theoretical models and experimental growth of Ga-doped C-Cz Si and Ga segregation for Cz Si co-doped with B [8, 10, 11] have been studied, very limited data is available on the distributions of dopants and defects and their correlations with minority carrier lifetime in axial and radial directions. This paper provides detailed new information on the electrical properties of Ga doped c-Cz Si samples, wherein the resistivities and minority carrier lifetimes in different positions of a Si ingot were correlated with deep energy levels using deep level transient spectroscopy (DLTS). Especially, Ga related defects as lifetime killers have been identified and quantified and their dissociation by low temperature annealing determined.
3.2 Experimental Procedures

Six-inch diameter, Ga-doped (concentration \(\sim 1 \times 10^{15} \text{ cm}^{-3}\), p-type), 3 mm-thick c-Cz Si samples from various positions along the ingot height (38, 730, 888 mm from the seed of the ingot) were selected for lifetime and deep energy level measurements. Samples from the center, middle, and edge of each sample were selected for evaluation of the radial variation of lifetime and deep energy levels. Each sample was mechanically polished and RCA cleaned. Resistivities were measured using 4-point probe (4PP). The as-grown data was collected directly from silicon samples that were cut from the ingot. The post-anneal samples were measured after a heat treatment at 750°C for 30 minutes and quenched in air. Minority carrier lifetimes were measured using the microwave photoconductance decay (MW-PCD) technique with the samples immersed in an iodine-ethanol solution during the lifetime measurements for surface passivation. A Bio-Rad DL8000 DLTS system was used to determine the concentration and trap energy of electrically active defects. Aluminum Schottky diodes under a 3V reverse bias were pulsed for 50 µs at 0 V to obtain DLTS data from 40 K to 298 K. Finally, dissociation of electrically active defects was studied following annealing for 2 min at 250 °C and 300 °C in a vertical tube furnace under Argon (Ar) ambient, followed by slow cooling in air.

3.3 Results and Discussion

3-3-1. Resistivity

Figure 3.1(a) shows resistivities of as-grown and post-anneal samples in radial and axial positions of the Ga-doped c-Cz Si. The as-grown data is the resistivity due to the Ga
dopant and the thermal donors formed during the crystal growth process. The thermal donors, which are due to oxygen, compensate the Ga atoms but are removed from the crystal during the annealing. The post-anneal resistivity is due to the intentional Ga doping only. Figure 3.1(b) more clearly shows the resistivity control of the c-Cz process by comparing the as-grown and post-anneal data from the center of the ingot. The variation of resistivity from seed to tail was around 0.2 $\Omega\cdot$cm (2.1 $\sim$ 1.9 $\Omega\cdot$cm) which is less than 10%. This value is smaller than that of conventional B-doped Cz Si and is much smaller than that of conventional Ga-doped Cz Si [12]. Although the resistivity variation of the post annealed samples is low, Ga concentration variations still exist. Theoretically, in continuous Cz process, almost constant resistivities can be achieved by the process optimization, e.g. the replenishment of polysilicon, the pulling conditions, the experimental apparatus, etc. [13, 14]. According to the theoretical model, the concentrations of impurities at the interface of the melting and solidified Si can be expressed as a function of the dimensionless dilution rate ($\beta$) and the segregation coefficient of the impurity ($k$). Uniform radial and axial distributions of the dopants can be achieved by adjusting $\beta$ according to $k$ [13]. As for the growth of the samples for this study, the axial profile of the resistivity is a good example of what can be produced in a cost-effective production environment. The growth process was changed to introduce a larger radial gradient for this work.

3-3.2 Defect Identification

Figure 3.2 shows DLTS spectra for samples on various radial and axial positions of the c-Cz Si ingot. Four hole traps were labeled as H1, H2, H3 and H4, which have energy
levels of $E_v+0.13$ eV, $E_v+0.23$ eV, $E_v+0.36$ eV, $E_v+0.44$ eV, respectively. Table 3.1 lists the identifications, activation energy levels, the capture cross sections of those hole traps and trap densities.

The hole traps H1 at 80 K and H2 at 120 K are attributed to iron-gallium pairs ($Fe_i$-$Ga_s$) with different charge states. The hole trap H1 corresponds to the metastable $<111>$ configuration and H2 corresponds to the stable $<100>$ configuration, and their transformations are completely reversible [15-18]. H1 and H2 were either observed together or negligible on each sample. There are three possible origins of the hole trap H3: 1) interstitial iron-self-interstitial-silicon complex ($Fe_i$Si$_i$) [19], 2) interstitial iron-vacancy complex ($Fe_i$V) [20, 21], and 3) interstitial-carbon-interstitial-oxygen complex ($C_i$O$_i$) [19-21]. Native point defects such as silicon self-interstitials (Si$_i$) and vacancies (V) usually exist in Cz Si, although neither of their concentrations are high [22, 23]. $C_i$O$_i$ was less likely to dominate in our case since high concentration of interstitial carbon ($C_i$) is required to form $C_i$O$_i$ and the dominant light impurity is substitutional carbon ($C_s$) rather than interstitial carbon ($C_i$) in Cz Si. The identification of H3 was investigated further by dissociation during thermal annealing, see Sec 3-3-3 below. The hole trap H4 is attributed to interstitial iron ($Fe_i$), as a common metallic impurity in Cz Si [18]. The origin of the trap H4 was also confirmed by its annealing behaviors in the later section.

As shown in Fig. 3.2, the compositions of the peaks at different axial position (38, 730, and 880 mm) in the ingot are consistent, however their concentrations change with radial positions (center, middle, and edge). While center samples exhibit all four peaks regardless of their axial positions, samples in the middle only show spectral peaks H3 and
H4, while edge samples have no signal detected above the DLTS detection limit of $1 \times 10^{11}$ cm$^{-3}$. The non-uniform axial distribution of the electrically active defects is attributed to the low segregation coefficient of Fe ($k_0 = (5–7) \times 10^{-6}$) [24, 25] and the effective segregation coefficient which is reported to be smaller than 0.05 [26]). Therefore, iron segregates in both center and bottom areas of the Si ingot. The increase in signal intensity of H2 clearly shows the increase of Fe concentration from seed to tail. Also, Ga segregates at the center areas due to its relatively low segregation coefficient [27]. Also both Fe and Ga evaporate from the melt and their concentrations are low at the edge and middle areas of the crystal. Therefore, Fe-Ga pairs (H1 and H2) are present in the center of the samples regardless of the axial positions, but absent in the middle and edge areas, see Fig. 3.2. The surface of the ingot is a sink for silicon interstitials, so H3 and H4 peaks are absent in the edge areas. Similar to Fe-B pairs, the equilibrium of Fe-Ga pair reaction depends on the temperature and the Ga concentration. The study on Fe-B pair reactions showed that the interstitial fraction ($\frac{[\text{Fe}_i]}{[\text{Fe}]} = \frac{[\text{Fe}_i]}{([\text{Fe}_i]+[\text{FeB}])}$) increased with temperature but decreased with B concentration [28]. Similar behaviors are applicable to Ga-doped samples. Therefore, the total amount of electrically active Fe is the sum of the interstitial Fe concentration and Fe-Ga pairs. The dissociation or association of the Fe-Ga pair will be discussed in the annealing behavior section below.

Minority carrier lifetimes were measured for three samples in the center areas of various axial positions (38, 790, and 880 mm) from the seed. Fig. 3.3 shows the direct correlation between the lifetimes and the concentrations of Fe-Ga defects. The sample at the height of 38mm has the highest lifetime and the lowest concentration of Fe-Ga pairs, and the
sample at 880 mm has the lowest lifetime and the highest concentration of Fe-Ga pairs. This indicates that the concentration of Fe-Ga pairs is more detrimental to minority carrier lifetime than that of Fei. The main reason is the comparatively large electron-capture cross section \( \sigma_n \) (2.5×10\(^{-14}\) cm\(^2\)) of Fe-Ga pairs [6, 29].

### 3-3-3. Annealing Behaviors of The Defects

In order to verify the identity of peak H3 (Fe\(_i\)V / Fe\(_i\)Si\(_i\)) and the thermal stability of Fe-Ga pairs, the middle wafer 880 mm sample was annealed at 250 and 300 °C. The DLTS spectra for the control and the annealed samples are shown in Fig. 3.4. The intensity of H3 (Fe\(_i\)V / Fe\(_i\)Si\(_i\)) decreases significantly while those of H1, H2 and H4 increase during annealing due to the dissociation of Fe\(_i\)V/Fe\(_i\)Si\(_i\) pairs. It is clearly proved that the hole trap H3 is associated with Fe\(_i\)Si\(_i\) pair due to its dissociation temperature (~250 °C) [19]. The interaction between Fe and V is more energetic than that between Fe and Si\(_i\), thus the dissociation temperature of the Fe\(_i\)V pair is comparatively higher (~400 °C) [20, 21]. Furthermore, the relatively high dissociation temperature of the C\(_i\)-O\(_i\) pair (~400 °C) [3] excludes the possible identification of the hole trap H3 as C\(_i\)-O\(_i\) trap level.

The dissociation of the hole trap H3 induces the appearance of the hole traps Fe-Ga pairs (H1 and H2) and Fei pairs (H4). However, the H3 and H4 pairs increase at higher annealing temperature (300 °C) due to the dissociation of Fe-Ga pairs. As mentioned in the discussion on defect composition, the fraction of Fe\(_i\) could be expressed as a function of the temperature and the dopant concentration. Thus, when the annealing temperature increases from 250 to 300 °C, Fe\(_i\)V/Fe\(_i\)Si\(_i\) pairs are further dissociated, and even Fe-Ga bonds also are
broken, contributing to a larger fraction of Fe$_i$ [28]. Moreover, all the changes in the intensities of the peaks confirmed the identification of H4 as Fe$_i$.

### 3.4 Summary

In conclusion, resistivity variation and lifetime limiting factors were investigated in c-Cz grown Ga-doped Si. The resistivity variation of c-CZ wafers showed a relatively good uniformity of dopant distribution compared to conventional CZ wafers. The radial and axial variation of electrically active defects were observed in DLTS spectra and correlated to lifetime and resistivity variations. DLTS measurements demonstrated that iron-related pairs are responsible for the variations. Specifically, Fe-Ga pairs were found to be serious recombination sites, which is more detrimental to lifetime than Fe$_i$. A c-Cz method was found to have potential for fabricating uniformly Ga-doped Si for high performance solar cells, but the issue of iron contamination still needs to be addressed.

### References


Fig. 3.1 (a) Resistivities of (a) as-grown and post-anneal samples in radial and axial positions and (b) as-grown and post-anneal samples in the center of ingot.
Fig. 3.2 DLTS spectra of - scale shift - of samples near the center, the middle and the edge of samples at heights of 38 mm, 730 mm and 880 mm. The spectra were acquired using a reverse bias of 3 V, a pulse voltage of 0 V, a pulse width of $5 \times 10^{-5}$ s, and a period width of 50 ms.
Fig. 3.3 The concentration of Fe-Ga and minority carrier bulk lifetime of the samples of the center of the wafers along a CZ-Si ingot height. The distance is from the seed of the ingot.
Fig. 3.4 DLTS spectra of annealed samples from the middle of the CZ-Si ingot 880 mm from the seed. The samples were annealed at 250 and 300 °C for 2 min. The spectra were acquired using a reverse bias of 3 V, pulse voltage of 0 V, pulse width of $5 \times 10^{-5}$ s, and period width of 50 ms.
Table 3.1 Activation energies (Ea) and carrier capture cross-sections (σ) of four peaks in Fig. 3.1.

<table>
<thead>
<tr>
<th>Identity</th>
<th>H1</th>
<th>H2</th>
<th>H3</th>
<th>H4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe$_i^+$-Ga</td>
<td>Fe$_i^0$-Ga</td>
<td>Fe$^{iV}$/ Fe$_{ii}$</td>
<td>Fe$_i$</td>
</tr>
<tr>
<td>Ea (eV)</td>
<td>0.13</td>
<td>0.23</td>
<td>0.36</td>
<td>0.44</td>
</tr>
<tr>
<td>σ (cm$^2$)</td>
<td>2.5×10$^{-14}$</td>
<td>5.5×10$^{-15}$</td>
<td>3.3×10$^{-16}$</td>
<td>3.8×10$^{-16}$</td>
</tr>
</tbody>
</table>
4. Recombination via Point Defects and Their Complexes in Solar Silicon

Abstract

Electronic grade Czochralski and float zone silicon in the as grown state have a very low concentration of recombination generation centers (typically < $10^{10}$ cm$^{-3}$). Consequently in integrated circuit technologies using such material, electrically active inadvertent impurities and structural defects are rarely detectable. The quest for cheap photovoltaic cells has led to the use of less pure silicon, multi-crystalline material and low cost processing for solar applications. Cells made in this way have significance extrinsic recombination mechanisms. In this chapter we review recombination involving defects and impurities in single crystal and in multi-crystalline solar silicon. Our main techniques for this work are recombination lifetime mapping measurements using microwave detected photo-conductivity decay and variants of Deep Level Transient Spectroscopy. In particular we use Laplace DLTS to distinguish between isolated point defects, small precipitate complexes and decorated extended defects. We compare the behavior of some common metallic contaminants in solar silicon in relation to their effect on carrier lifetime and cell efficiency. Finally, we consider the role of hydrogen passivation in relation to transition metal contaminants, grain boundaries and dislocations. We conclude that recombination via point defects can be significant but in most multi-crystalline material the dominant recombination path is via decorated dislocation clusters within grains with little contribution to the overall recombination from grain boundaries.
4.1 Introduction

The last decade has witnessed a commercial and technological revolution in silicon photovoltaics. The quest for viable renewable energy sources has resulted in many countries establishing policies which provide taxation advantages or feed in tariffs to encourage the take up of renewable energy. This has been remarkably successful and has had the desired effect of stimulating the market enabling successful manufacturers to effect reductions in manufacturing cost. Silicon photovoltaics have benefited from this and progress along the learning curve necessary to achieve economies of scale in manufacture has been very rapid (a learning rate of 20% compared to an industry norm of 10%, i.e. a cost reduction of PV systems by 20% per each doubling of cumulated PV installations).

There are many factors involved in this but innovative cell design, the use of low cost materials and advances in power management electronics have each played a role. At the moment >85% of all installations use wafered silicon cells of multi crystalline or single crystal material. In particular the cost of silicon in the cell, which used to be ~50% of the cell value, has been reduced by using thinner slices and moving away from electronic grade single crystal material grown as Czochralski (Cz) ingots to less pure “solar grade” silicon usually cast in multi-crystalline blocks. Although such material produces cells of lower conversion efficiency than electronic grade silicon, a cost reduction per kWh delivered is achieved because the reduction in efficiency is more than compensated for by the lower price of the silicon.

The term “solar grade silicon” does not have a unique definition it has been used to describe Cz silicon grown from silicon scrap feedstock, block cast multi-crystalline material
with electronic grade feedstock or silicon grown from feedstock that has been produced by refining process less energy hungry and less effective than the electronic grade Siemens process. These include fluidized bed methods and in the extreme improved metallurgical (IMG) silicon. These materials contain very much higher concentrations of metals than electronic grade material and in some cases higher carbon content. This can originate from upgraded metallurgical extraction methods or from casting highly refined silicon in graphite crucibles. Such material contains concentrations of carbon in solution around the equilibrium solubility at the melting point ($3.5 \times 10^{17} \text{cm}^{-3}$) and SiC particles.

In cast multi-crystalline silicon the presence of grain boundaries and dislocations makes the material inhomogeneous in terms of its electronic properties. An example of this inhomogeneity can be seen in Fig 4.1 which shows a variation of 25% in lifetime. Comparison with a map of the grains in this slice shows that the excess recombination is not associated with the grain boundaries but rather with regions within specific grains which we associate with decorated dislocation clusters. A lifetime map of present day state of the art electronic grade single crystal material (Cz or FZ) shows a variation of minority carrier lifetime of ~1% with edge exclusion.

The combination of the structural defects, metal content and precipitates of various sizes make defect reactions extremely complex and the material very difficult to assess by conventional techniques. The pragmatic approach of the solar industry is to measure average properties assigning a single lifetime to the whole slice (~5 inch square). In many cases this works quite well at least in terms of deciding if material is worth processing into cells but
such averaging is not adequate in trying to understand the localized recombination paths and improving the material.

Originally it was thought that grain boundaries acted as important recombination centers in mc-Si but it now seems that this is not often the case. A number of factors have made grain boundaries of little significance in present day mc-Si. The first is that in recent material the grains are very much larger than the diffusion length in equivalent single crystal material and the grain boundaries are mostly parallel to the direction of carrier flow in the cell. In addition grain boundaries in mc-Si are not usually associated with a high density of dangling bonds or large strain field and so are less attractive as sites for rapidly diffusing metals than dislocations. The combination of these factors results in recombination at grain boundaries being a relatively small perturbation in terms of cell efficiency or minority carrier lifetime.

In this chapter, we consider solar silicon in two stages. Firstly we review single crystal materials containing metals including some of our recent measurements which try to resolve discrepancies and which consider small precipitates and their passivation with hydrogen.

In general transition metals, particularly those in the 3d series, are common contaminates in lower grade feedstock. These will act as recombination centers if present in the finished solar cell on specific sites. This provides some in-sight into Cz material grown from impure feedstock as a solar cell material. We then consider multi-crystalline solar silicon with similar contamination and explore the role of grain boundaries, dislocations and precipitates in the minority carrier recombination processes.
This necessitates localized measurements of specific grains and grain boundary regions. In combination with hydrogen passivation this provides us with a basis for understanding some of the efficiency limitations which occur in this very complex material system.

4.2 Metallic Contamination in Single Crystals

4.2.1. Impact on Cell Efficiency: An Overview

There is a vast literature on metals in silicon with an emphasis on the transition metals, some of these publications focus on photovoltaics. An early experiment, known as the Westinghouse study [1,2] added contaminants to a Czochralski melt and pulled small ingots of both n and p-type material (3.3cm diameter grown at 7 cm/hr). Chemical concentrations of impurities in slices cut from the ingots were measured using neuron activation analysis and spark source mass spectrometry.

Concentrations of electrically active defects were measured in some slices using DLTS. Solar cells were fabricated (both n+p and p+n) with and without an antireflection layer and the efficiency measured. In all approximately 200 ingots were grown and processed into solar cells. Although there was no intentional hydrogen passivation the contacts were sintered at 300-550 °C in hydrogen. The efficiency of uncontaminated cells was around 10% with no antireflection layer and 14% with a silicon dioxide antireflection film.

The impact of various impurities is shown in Fig 4.1 in terms of the effect of chemical concentration of metals in the slices cut from the various ingots on the solar cell efficiency for the case of a p-type base. It is important to emphasis that these results convolute many factors apart from the Shockley Read Hall (SRH) properties of the defect state associated
with the metal. Not all the metal will be electrically active in the slice, the n+ layer diffusion will tend to getter metals with high diffusivity and growth of precipitates may occur during cell processing.

DLTS measurements for some of the metals have been published as part of the Westinghouse study and the concentration of specific gap states compared with the chemical concentrations. These are tabulated elsewhere [1] as values of the ratio NT/Nchem. These are specific to the elements concerned but for Cr, V, Ti and Mo are independent of the concentration over the range studied (up to $10^{14}$ cm$^{-3}$) suggesting that precipitation did not occur during ingot cooling for these elements under the conditions used. For example, all of the Mo was present as an electrically active species at EV + 0.3 eV, Ti had a ratio of 0.4 for a defect at Ev + 0.3, Cr 0.23 for a state at Ev + 0.22 eV. Cu and Ni were exceptional in that no electrically active defects could be detected. In the light of what we know today this is not unexpected. In the case of Cu its extremely high diffusivity in p-type would remove it to energetically preferred sites (surface and precipitates) where it might be electrically inactive as a recombination center. It must however be emphasized that some precipitates can act as recombination centers and can also degrade solar cells by acting as current leakage paths (shunts) which affect the IV characteristic of solar cell and reduce its efficiency by the effect on the fill factor.

The phenomena of precipitation will be discussed in more detail later but at this stage we can say that in the Westinghouse experiment over the range of metal concentrations studied the recombination activity impairing the solar cell efficiency associated with the added
impurities was due to metals in solution i.e. the classic point defects which are well characterized in terms of their recombination behavior.

In as grown electronic grade Cz material, without added contaminants the concentration of electrically active defects behaving as recombination centers is vanishingly small. This is a result of high purity feedstock and the low segregation coefficient, $k_{\text{eff}}$, between the solid and the melt in Cz growth. For most of the 3d transition metals $k_{\text{eff}}$ lies between $10^{-8}$ and $10^{-5}$ ($k_{\text{eff}} = \text{impurity concentration in ingot/ impurity concentration in melt}$). This is a great advantage to those companies growing Cz Si from lower purity cost feedstocks as a way of reducing costs.

In our work on single crystal silicon we have also used some material in which metals have been incorporated during Cz and Fz growth but the studies we report here have mostly been done on electronic grade Cz or Fz material into which specific metals have been introduced by diffusion.

4.2.2. Solubility and Diffusivity

The solubility and diffusivity of contaminant metals are central to understanding their effects in solar silicon. In the 3d transition metals diffusion is almost exclusively interstitial over a wide temperature range but there is a systematic increase in both solubility and diffusivity in the 3d series progressing from the light to the heavy elements.

A combination of high concentration and high diffusivity will result in precipitation on cooling either at surfaces and interfaces or at nucleation centers such as dislocations. Copper is the classic example precipitating as lamina usually lying in \{110\} planes.
Copper has a high diffusivity in p-type material even at room temperature is unstable in its interstitial form. A consequence of this is that only a small fraction of copper in silicon is electrically active ($\sim 10^{-4}$) as complexes or as Cu$_x$ [3]. The remainder is present as dislocation decoration or large precipitates (which are not electrically active). The presence of such precipitates can be very detrimental to the finished cell by acting as a shunt across the junction.

At the other extreme of the 3d metals, titanium has a very low solubility and diffusivity. This results in very small or no precipitates and a large part (0.4) of the Ti being electrically active on interstitial sites. It is these phenomena which explain the results of the Westinghouse experiment shown in Figure 4.2 rather than a difference in the recombination properties of the species in solid solution.

Table 4.1 lists solubility and diffusivity data at 1100 °C for the 3d transition metals and for Mo and Au. B and P data are included for comparison. Where available the results of chemical methods are cited in preference to electrical techniques which may only be valid for one configuration or charge state of the species.

### 4.2.3. Recombination Kinetics

Recombination via point defects is usually described by SRH kinetics in which the recombination rate is proportional to the defect concentration and a property of the defect quantified as the minority carrier capture cross section. The dominant factor determining the cross section is the charge state of the defect so that a donor (positively charged) will repel holes but attract electrons. In the case of low level excitation and a near mid gap state in
silicon at room temperature these are the only parameters of importance so the lifetime due to SRH via point defects can be expressed for p-type material as:

\[ \tau_n = \frac{1}{N_T \sigma_n V_{th}} \]  

(1)

where \( V_{th} \) is the thermal velocity, \( N_T \) the defect concentration and \( \sigma_n \) the minority carrier capture cross section.

However, solar cells do not always operate in a low excitation regime. At an intensity of one sun the excess carrier population is below the usual doping level of the base but sufficiently high to necessitate taking into account the possible saturation of some defects. Saturation starts to occur when the majority carrier capture rate is comparable with the minority carrier capture rate. This effect is easily observed in lifetime measurements as shown in Fig. 4.4 which shows lifetime dependencies resulting from different concentrations of boron-oxygen recombination center.

The saturation behavior depends on the ratio of the minority and majority cross sections, on the doping level of the sample and the temperature. It follows that such measurements can be used to determine \( \sigma_n/\sigma_p \) if a single species is dominant. The cases of boron-oxygen [14] and for chromium and cobalt [15] are referred to as examples. The \( \sigma_n/\sigma_p \) parameter may be an aid to identifying the defect species responsible for the lifetime degradation. Such “identification” is only feasible if the cross section ratios of the potential contaminants are known. In some samples surface recombination and trapping in passivating layers can complicate the interpretation of lifetime dependency on excitation density.
The second case where Eq. (1) is too simplistic is where the state is sufficiently near one of the bands energetically for the thermal emission rate to be a significant fraction of capture rate. This thermalization reduces the recombination rate and again it can be used as a tool to determine the parameters of the recombination center [16].

Both these processes are quantified in the detailed SRH formalism which is presented in many standard texts [17] as well as in the original papers. In summary in p-type material a positively charged defect (donor or double donor) will exhibit a large capture cross section for electrons (minority carriers) and hence could be an important recombination centre. However in order to continue to capture minority carriers it must also capture majority carriers. If the defect is doubly positively charged (i.e. a double donor) then the capture of the electrons will be very fast but majority carrier capture will be slow and saturation will be observed at low excitation densities unless the material is heavily doped. In the case of a single donor minority carrier capture will be quite fast but majority carrier capture will be into a neutral center, again saturation will be observed but at a higher excitation density than for the double donor case.

Table 4.2 lists some of the published data on the energy levels of transition metals in silicon. It must be emphasized that this is a selection from a vast amount of data in the literature. Where a review exists comparing differing results this is cited. Specifically excluded are those data inferring capture cross sections from DLTS emission data using detailed balance. Such data can give values which exceed the directly determined values by several orders of magnitude.
Some of the transition metals form complexes with acceptors. In p-type material the best known case is that of FeB. The interstitial iron is positively charged and is coulombically attracted to the negatively charged boron acceptor. The result is that FeB pairs are the room temperature equilibrium state but are dissociated in the presence of minority carriers. This dissociation is used as a test for iron because although both Fe$_i$ and FeB are important recombination centers Fe$_i$ has more impact on the lifetime than FeB at low excitation densities consequently a measure of the change of lifetime on dissociation of the FeB pair has become a standard test for iron contamination in Si within the PV industry. However care must be exercised as at high excitation densities the FeB pair is a more effective recombination centre and so the excitation density affects the [Fe] lifetime relationship and hence the calibration [26,27]. In machines such as the Semilab WT-2000 PV a iron test procedure is built into the operating system so ensuring that the correct test conditions are always used.

The FeB pair is well understood as a complex in silicon but as we progress along the 3d series in the periodic table to the heavier elements with the highest diffusivities the situation becomes much more difficult to predict. In particular Co, Ni and Cu diffuse interstitially but are more likely to form complexes rather than stable interstitial recombination centers or to form a simple pair with an acceptor as is the case with the lighter 3d elements. We discuss this behavior in section 2.5.
4.2.4. Passivation with Hydrogen

A crucial part of solar cell fabrication is the use of anti-reflection films which also incorporate hydrogen. The classic case is silicon nitride deposited by plasma assisted chemical vapor deposition (plasma CVD). Such films contain high concentrations of hydrogen. The exact amount depends on the deposition conditions but 25at% hydrogen is fairly typical for films used in silicon solar cells. Silicon nitride acts as a source of hydrogen during subsequent processing. This dramatically reduces surface recombination but also some hydrogen diffuses into the bulk of the silicon and passivates recombination centers. The details of this process are the subject of debate but what is certain is that the incorporation of hydrogen into solar silicon increases the minority carrier lifetime considerably.

In silicon hydrogen diffuses predominantly interstitially in atomic form. It exists as $H^+$ at a bond center site in p type material and $H^-$ at an interstitial tetrahedral site in n type, the neutral state $H^0$ being metastable. The donor level lies above the acceptor level, with the consequence that monatomic hydrogen behaves as a negative-U defect in silicon. The behavior is reviewed in detail elsewhere [28].

Both the positive and negative ions are very reactive so as the hydrogen ions migrate through the lattice they combine with the unsatisfied bonds of defects and impurities rendering them electrically inactive or in some cases shifting the electronic levels within the gap. The most obvious reaction is with the shallow donors and acceptors forming pairs which are electrically inactive. However the binding is quite weak (e.g. BH 1.28eV & PH 1.2eV). The BH bond is dissociated at low annealing temperatures (~200 °C) freeing the hydrogen to
continue its migration and enabling it to passivate recombination centers. The PH pair is also dissociated in the presence of holes.

In the case of the transition metals, many hydrogen reactions have been reported. In general there is the possibility of binding with several hydrogen ions to form (TM)H\(_n\). The addition of hydrogen shifts the TM energy level in the gap and may render it electrically inactive (passivated).

Only in a relatively few cases is the sequence of reactions clearly documented. In the case of platinum all the three complexes PtH\(_n\) (n=1 to 3) have been unambiguously identified by a combination of DLTS, EPR and LVM [see 28 for a compilation of references]. In the case of AuH and AuH\(_2\) the addition of hydrogen shifts the level in the gap. Figure 4.5 illustrates the small shift observed which is barely detectable in conventional DLTS but can be seen clearly with the Laplace DLTS technique [29]. Annealing at 250 °C removes the hydrogen from the gold resulting in a reduction of the G4 peak and an increase in the Au peak [24]. The reaction is reversible in the presence of free hydrogen. AuH\(_2\) has been seen in the same way [25].

The situation with the predominantly interstitial TMs may follow a similar pattern but seems to be more complex. Many electrically active states have been reported as a result of hydrogenation [see Ref. 30 for citations] but there is a worrying lack of consistency. In some cases passivation has been inferred from a reduction in the total number of electrically active states i.e. the electrically active [TM] prior to passivation is greater than the electrically active [TM]H\(_n\) after passivation. In general reactions with H\(^+\) in p-type Si with the TM interstitial ion in a positively charged state seems highly improbable unless minority carriers
are present e.g. $\text{Ti}_i^+ + e \rightarrow \text{Ti}_i^0$ which can then react with $\text{H}^+$ or $\text{H}_0^+$ [31]. That paper and first-principle studies of hydrogen reactions [32] illustrate very clearly that these are difficult systems to understand in detail.

The situation is even more complex for the heavier 3d metals which diffuse faster and tend to form larger complexes. Although electrically active states have been observed after hydrogenation of Ni or Cu doped Si [33, 34], theoretical studies are not consistent with Ni$_i$H$_n$ or Cu$_i$H$_n$ but may be related to substitutional fractions of Ni or Cu [32, 35, 36]. The emphasis is on the word “may” because at least eleven distinctly different DLTS lines have been reported for nickel hydrogen complexes and many more for the copper hydrogen case.

This leaves us in a very unsatisfactory position because we observe experimentally a substantial improvement in lifetime in mc-Si after hydrogenation but do not understand explicitly what is being passivated (apart from the surface) and more importantly what is not being passivated. Increasing the carrier lifetime in solar silicon is crucial if major improvements in efficiency are to be achieved. Gettering plays a key role in removing the fast diffusing species from the active region of the cell but is less effective for the slower diffusing elements or for fast diffusants trapped in relatively stable configurations. These can be powerful recombination centers where probably the only route to removing them is by passivation.

### 4.3 Defect Complexes and Dislocations

One of the reasons for the problems in understanding the behavior of the heavier 3d transition metals is that their high diffusivity facilitates the formation of complexes. The
highly mobile interstitial migrates through the lattice until it finds an energetically favorable site. This can be bonding with another impurity (the FeB defect already discussed is a classic case), with an intrinsic defect or with itself. These complexes can consist of just two atoms or large precipitates which strain the lattice and act as favorable sites for more mobile impurities. It is often the case on analyzing such defects that more than one element is present so, for example, the strain field in the vicinity of a copper silicide particle could trap nickel or iron.

In general it seems that such accumulations of metals are not very recombination active but can be important in creating leakage paths. Micro-Raman techniques are immensely valuable in mapping the strain field around such precipitates and other extended defects [37]. Early impressions are that much can be learned by comparing lifetime maps with localized strain measurements.

4.3.1. Dislocations and Decoration

The strain field of a dislocation can be a sink for fast diffusing species. This is important because there is now overwhelming evidence that absolutely clean dislocations are not important recombination centers and have little electrical activity but decorated dislocations can degrade lifetime. Early measurements of electrical activity were undertaken on plastically deformed silicon [38]. It now seems that these samples were contaminated with metals from the bending jig and so these early results described decorated dislocations.

Subsequent measurements on the Frank partial dislocations surrounding stacking faults (which could be created in ultra clean conditions) showed that the electrical properties
and recombination activity depended very strongly on the level of decoration. This is the case in both n-type [39] and p-type [40]. The electrically active defects, determined by DLTS, were found to increase in concentration and move deeper in the gap with an increasing concentration of metal concentration, so increasing the recombination activity, until micro-precipitates started to be observed on the dislocation by TEM. At this point the electrical activity diminished rapidly [41].

The concept of dislocation decoration has been embedded into a model describing the observed EBIC contrast [42]. More recently enhancement of recombination behavior by decoration at grain boundaries has been explored using a model system based on misorientated bonded wafers [43]. These observations are of crucial importance in mc-Si which contains grain boundaries, dislocations and an ample supply of TM impurities to effect decoration.

4.3.2. Small Complexes

In addition to these defects which consume considerable numbers of metal atoms there is evidence of small complexes consisting of between three and ten atoms.

Historically photoluminescence (PL) has been very effective in identifying such defects. Recently the topic has advanced rather spectacularly by the use of isotopically pure silicon and the implantation of radioactive isotopes using the ISOLDE facility at CERN. This and earlier work on PL of TMs in silicon has been the subject of an Applied Physics Review [44].
Importantly a number of four and five atom families have been revealed including Cu complexes some of which have been the subject of ab-initio calculations [45].

DLTS peaks associated with extended defects such as decorated dislocations and silicide precipitates are broad with a carrier capture which slow as more carriers are accumulated because the extended defect becomes coulombically repulsive. This is sometimes referred to as logarithmic filling.

In Laplace DLTS the instrumental broadening characteristic of the conventional technique has been eliminated so a perfect point defect gives a delta like function on the emission rate scale. The peaks shown in Figure 4.5 are typical of ideal isolated point defects. Broadening can occur due to field dependence of the emission or to inhomogeneous strain. However Laplace DLTS confers little benefit to the study of extended defects where the broadening is a fundamental physical process and very substantial.

Figure 4.6 compares Laplace DLTS measurement of two samples, both are of hole emission at 190K. The peak at the right of the diagram is from Mo in p-type silicon. This is a classic and well documented defect. The only notable issue is that the peak half width is larger than that normally observed for an ideal point defect. We attribute this to biaxial strain. The measurement was made on lightly doped epitaxial silicon deposited on a highly doped substrate.

In the case of the peak at the left of the diagram the broadening is much more substantial. The measurement was taken of hole emission from n-type material using MCTS [46] with back face illumination.
Based on the complex annealing behavior of Si:NI Indusekhar and Kumar [47] suggested that Ni existed as a complex with a vacancy. We would expect an ideal point defect peak from such a defect and propose that the peak is due to a grouping of Ni atoms bonded in a stable configuration. The peak is reproducible but has unusual capture behavior for both holes and electrons which will be discussed elsewhere.

4.3.3. Boron-Oxygen

Perhaps the complex which has gained most attention in recent years is a defect associated with boron and oxygen. The efficiency of solar cells fabricated from Czochralski boron-doped silicon degrades when excess electrons are created by illumination [14]. In cells fabricated with high quality Cz material and state of the art fabrication the BO defect is now the most important non-radiative recombination route. The defect was thought to be BsO2i which from carrier lifetime spectroscopy appeared as a recombination centre 0.41eV from the conduction band with $\sigma_n/\sigma_p=9.3$ [48, 49].

The basis for the structural assignment was a dependence of the concentration of the assumed recombination center (derived from the lifetime degradation) on $[O_i]^2$ and $[Bs]$. The formation mechanism was suggested to be the migration of the oxygen dimer to Bs via an enhanced diffusion mechanism (the dimer is normally immobile at room temperature). This enhanced diffusion was proposed as being due to a Bourgoin-Corbett mechanism under minority carrier injection [50]. This occurs in other defect systems but necessitates in this case a change in the charge state of the dimer upon capture of a minority carrier i.e. two charge states of the dimer must exist.
Two important studies have subsequently shown that the defect in question is unlikely to be $\text{B}_3\text{O}_2$. Firstly it was observed that in compensated material the degradation depended on the carrier concentration rather than the boron concentration [51]. Secondly a study of the optical absorption spectra of the oxygen dimer showed that only one charge state exists making the Bourgoin-Corbett mechanism impossible in the case of the oxygen dimer [52].

An alternative model has been proposed by Voronkov and Falster in which the defect is $\text{B}_3\text{O}_2$ formed during ingot growth [53]. The defect is then activated by the presence of minority carriers. Several arguments have been put forward against this model including evidence that the defect density is not fixed during cooling [54] and quantitative disagreement with observations in boron compensated n-type material [55]. However in the latter case there is a question as to whether saturated concentrations of the BO complex were attained.

A crucially important dilemma is that despite many attempts no SRH defect has been observed by DLTS or related techniques which fits the observed lifetime degradation behaviour. It is evident that despite an immense amount of data and efforts by many groups throughout the world we do not as yet have a fundamental understanding of boron oxygen degradation in solar cells.

### 4.4 Recombination in Multi-Crystalline Silicon

The situation in mc-Si is very much more complex than in single crystal material. The ingots contain grain boundaries with various degrees of mis-orientation between the grains. The material also contains dislocations and dislocation clusters within the grains. In general
mc-Si often has metallic contamination originating from the crucible material or from the use of less pure feedstock such as improved metallurgical silicon.

Neutron activation analysis has been used by several researchers to determine the level of TMs in mc-Si. Istratov et al [56] found that the dominant metal impurities were Fe (6x10^{14} \text{ cm}^{-3} \text{ to } 1.5x10^{16} \text{ cm}^{-3}), Ni (up to 1.8x10^{15} \text{ cm}^{-3}), Co (1.7x10^{12} \text{ cm}^{-3} \text{ to } 9.7x10^{13} \text{ cm}^{-3}), Mo (6.4x10^{12} \text{ cm}^{-3} \text{ to } 4.6x10^{13} \text{ cm}^{-3}), \text{ and Cr (1.7x10^{12} cm}^{-3} \text{ to 1.8x10^{15} cm}^{-3}).

Macdonald et al [57] looked at metals in different regions of cast ingots. The concentrations of Fe, Co, and Cu are determined by segregation from the liquid which produces high concentrations near the top of the ingot, which can diffuse back into the ingot. Near the bottom, the concentrations are high due to diffusion from the crucible after crystallization has occurred. In general concentrations similar to those above were found with the addition of Cu up to 3x10^{15} \text{ cm}^{-3}. Zn, Cr and Si were more uniformly distributed in the ingot (2x10^{12} \text{ to } 3x10^{13} \text{ cm}^{-3}).

An experiment to examine the effect of specific metals on the electrical behaviour of mc-Si was undertaken by Pizzini et al [58]. In this work Cz ingots were grown from intentionally contaminated feedstocks. Multicrystalline growth occurred because necking the ingot after seeding was omitted. Although the results are complicated the overall conclusion was that the presence of grain boundaries and dislocations did not enhance the detrimental effect of the metallic impurities beyond that expected for a similar metallic concentration in single crystal silicon.

Very recently an experiment analogous to the Westinghouse study was undertaken on cast mc-Si under the EU project “CrystalClear” [59]. The project used material produced by
directional solidification (Bridgeman technique) with ingots 250mm diameter and 110mm height. High purity feedstock and furnace components were used so without added contaminants the material had a lifetime of 60 μs. Solar cells with a p-type base of area 156 cm² were made using a classic industrial process with silicon nitride passivating/anti reflection layer, 185 μm thick with aluminum back surface field. The uncontaminated efficiency was 15.5 %. The effects of Fe, Cr, Ni, Ti and Cu on the efficiency were investigated and the Fe study has been published in considerable detail [60].

A known amount of the impurity was added to the melt and the effect on the cell efficiency determined. In the iron case the electrically active iron content was measured in the slice. In terms of the concentration of impurity added to the melt it was found that 8 ppm wt of Cr, 11 ppm wt of Fe, 0.1 ppm wt of Ti, 13 ppm wt of Ni and 8 ppm wt of Cu are all equivalents in terms of their effect on solar-cell performance giving a degradation of about 2%.

Taking into account the segregation coefficients the rank order is the same as the Westinghouse experiment (the Cu comparison is difficult due to uncertainties regarding the effective segregation coefficient in casting processes) and the absolute concentration added to the melt for a similar degradation is of the same order. This is rather surprising when we consider that the metal distribution would be expected to be non-uniform across the slice and that far fewer atoms might be expected to be in solution due to accumulation at grain boundaries and dislocations.

On the other hand maybe this is offset by localized recombination. Sopori et al have studied such localization in cast mc-Si [e.g. 61] and find that regions with clusters of
dislocations exhibit very high recombination. In cases where the same number of dislocations are spread evenly across the cell, recombination is much reduced. This was attributed to gettering and hydrogenation being much more effective in the case of distributed dislocations. This is consistent with our work on decoration of dislocations.

Our observation is that grain boundaries are not effective recombination centers after hydrogenation even in the presence of metals and presumably after decoration. As discussed previously in the case of large grains it is unlikely that grain boundaries will have much effect on the carrier lifetime simply because the grain size is very much larger than the diffusion length. In addition in the solar cell the minority carrier flux is parallel to the grain boundaries so will not have much effect on the photocurrent.

We have undertaken DLTS studies on solar grade mc-Si with grains in the size range 1 to 15 mm. The technique we have used is shown in Fig. 4.7 where semitransparent Schottky diodes have been deposited on mc-Si. It is possible to see the grain boundaries in the optical micrographs or by mapping the magnitude of the Raman scattering. The lifetime distribution around the diodes can also be seen.

In some slices the DLTS signatures from diodes on grain boundaries are quite different to those relating to defects in the center of the grains. In particular negative DLTS peaks indicating emission of minority carriers are often seen at the grain boundaries [62]. However, in many cases the DLTS spectra from different regions of the same slice show similarities. Figure 4.8 shows the case of a slice containing a broad distribution of dislocation clusters. The peak on the right at around 330K was greatly reduced by hydrogenation and showed the logarithmic filling behavior of an extended defect The family of peaks in the
range 100-150K was essentially unaffected by hydrogenation and had point defect like carrier capture. These defects have all the characteristics of powerful recombination centers.

4.5 Conclusion

Our work and many cases in the literature make it evident that achieving a detailed understanding of recombination in mc-Si will be a major task. In our view this is an essential pre-requisite to engineering effective gettering and passivation and hence to achieving very high efficiency solar cells made from these complex materials.

References


[47] H. Indusekhar and V. Kumar, J. Appl. Phys. 61, 1449 (1987)


Fig. 4.1 Map of the minority carrier lifetime of a silicon nitride passivated multi-crystalline silicon slice taken from near the top of a cast ingot. The low lifetime is due to high concentrations of metallic impurities and dislocations. The map was taken using a Semilab WT-2000 PVN in the μPCD mode with a 0.5mm diameter 904nm laser probe and a background illumination of one sun.
Fig. 4.2 The effect of metallic contaminants on solar cell efficiency. The impurity concentration is that in the slice prior to cell processing. The data are taken from the Westinghouse experiment [1] and re-plotted by Pizzini et al [2].
Fig. 4.3 Solubility (squares) and diffusivity (triangles) of 3d transition metals plotted in the sequence of their atomic number. These physical properties are the primary cause of the sequencing of the 3d metals in Fig. 4.2.
Fig. 4.4 Effect of excitation density on minority carrier lifetime. These data were recorded using a Semilab WT-2000 PVN in which the lifetime is measured using the μPCD technique. A 903 nm LASER is used to create the small carrier perturbation whose decay is measured. A second LASER creates the background excitation density in this case up to 14 suns.
Fig. 4.5 Comparison of Laplace DLTS and conventional DLTS measurements of electron emission form a silicon sample doped with gold and hydrogen [24]. Laplace DLTS clearly distinguishes the gold hydrogen from the gold emission characteristics.
Fig. 4.6 Laplace DLTS of two hole traps observed in silicon. The peak at the right is due to Mo in p-type Si while the peak on the left is associated with Ni in n-type Si and measured with Laplace MCTS. Both peaks are broadened as discussed in the text.
Fig. 4.7 Schottky diodes on a mc-Si wafer showing a) μPCD lifetime map on the original unpassivated slice. b) the same region with semi-transparent diodes deposited and c) an optical micrograph of the diodes.
Fig. 4.8 DLTS spectra of three regions of a mc-Si wafer.
Table 4.1 Solubility and Diffusivity in Silicon

<table>
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<th>Solubility* (atoms/cm$^3$)</th>
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<tr>
<td>Fe</td>
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<td></td>
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* at 1100 °C
Table 4.2 Electrically active states associated with transition metals in silicon

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<th>Notes &amp; reference</th>
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<td>Ev-230</td>
<td></td>
<td>DLTS [20]</td>
</tr>
<tr>
<td>(CrB)⁰⁺⁺</td>
<td>Ev+280</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>see [21]</td>
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<td>Ev-110</td>
<td>σₚ=1.2 x10⁻¹⁴</td>
<td></td>
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<tr>
<td>Feᵢ⁺⁺⁺⁺</td>
<td>Ev+385</td>
<td>σₚ*=8 x10⁻¹⁷</td>
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<tr>
<td></td>
<td></td>
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<tr>
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<td>σₚ=3 x10⁻¹⁵</td>
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</tr>
<tr>
<td>Co</td>
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<td>see [11, 3]</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td>see [3]</td>
</tr>
<tr>
<td>Mo (4d)</td>
<td>Ev+300</td>
<td>σₚ=5.5 x10⁻¹⁶</td>
<td>DLTS [13]</td>
</tr>
<tr>
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<td>Ev+350</td>
<td>σₚ*=1.1 x10⁻¹⁵</td>
<td>MCTS [23]</td>
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<td>Au^{0}</td>
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<td>(AuH)^{0}</td>
<td>E_c-542</td>
<td>σ_n=6 x10^{-17}</td>
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<td>E_c-578</td>
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<td></td>
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* indicates a significant dependence of the capture cross section on temperature …see reference
5. Effect of Nickel Contamination on High Carrier Lifetime N-type Crystalline Silicon

Abstract

The injection-dependent lifetimes of different levels of Ni contaminated n-type CZ silicon wafers were investigated using resonant-coupled photoconductance decay (RCPCD) and quasi-steady-state photoconductance technique (QSSPC). The lifetime degradation of the most heavily contaminated samples was caused by Ni silicide precipitates at the surface of the wafers. The impact on lifetime was determined by surface recombination velocities (SRV). SRV values from RCPCD were comparable to those extracted by the QSSPC technique. A direct correlation between minority carrier lifetime and the concentration of electrically active substitutional Ni and Ni silicide precipitate traps measured using deep level transient spectroscopy (DLTS) was established.
5.1 Introduction

The detrimental effects and electrical properties of transition-metal impurities, e.g., iron, and its complexes, such as FeB, in p-type silicon are well-known [1]. However, in n-type silicon wafers, the impact of specific metallic impurities on minority lifetimes is not as well established. Nickel is one of the main impurities which can contaminate the wafer during solar cell manufacturing process [2]. Due to its high diffusivity, nickel can form precipitates at the wafer surface or decorate existing lattice defects [3-4]. These band-like defects act as recombination centers and decrease the effective lifetime [5]. Surface recombination velocity (SRV) is useful to evaluate the impact of precipitates at the surface of wafers [6]. SRV and injection-level dependent lifetimes have been determined using QSSPC [5, 7] and microwave-detected photoconductance decay (MWPCD) [8-9]. However, for more accurate calculation, the studies about the separation of bulk and surface components of effective lifetimes [10] are still in demand. In this paper, the method for the separation of bulk and surface component of recombination is suggested by RCPCD signal transient and measured SRV are verified against the extracted SRV from QSSPC measurements.

Shockley-Read-Hall (SRH) recombination [11-12] is affected by electrically active impurities or traps. Ni-related electrically active defects [13-14] and precipitates [15] have been measured using DLTS by a number of authors in the past. However, the fraction of electrically active defects of Ni-contaminated samples following a high temperature diffusion is on the order of $10^{-3}$ to $10^{-4}$ that of the total Ni in in the silicon sample [16]. Rapid quenching after a high temperature annealing may slightly increase the ratio [17]. For this reason, Ni-related deep-level impurities have been mostly negligible and ignored in the past.
However, in high purity wafers, even, a small concentration (<10^{12} \text{ cm}^{-3}) of impurities can cause a significant degradation in minority carrier lifetime. In this study, Ni-related electrically active defects in samples with different low levels of Ni-contamination were examined using DLTS, and compared with lifetime data.

5.2. Experimental Procedures

High lifetime (2.9 ms), six inch diameter, 5 \Omega \cdot \text{cm phosphorus doped (9.2 \times 10^{14} \text{ cm}^{-3} \text{ n-type})} 200 \text{ \mu m thick CZ silicon wafers were selected for Ni contamination. For comparison, a control wafer was not contaminated and annealed. The wafers were RCA cleaned before dipping into a Ni-spiked solution (1 mg/ml) at room temperature. A 30 min, 575 \degree \text{C to 770 \degree \text{C drive-in annealing was then performed in a vertical tube furnace under Argon (Ar) ambient, followed by slow cooling in air. Four levels of Ni contamination (labeled N1 to N4) were obtained, see Table 5.1. The total Ni concentrations of the four samples were measured by inductively coupled plasma mass spectrometry (ICP-MS). Note that the Ni concentrations are average values of the 200 \text{ \mu m samples, and only qualitatively reflect the near-surface concentrations where the electrical analyses were performed.}}

To evaluate the surface recombination component of the contaminated samples, N1 to N4 were etched in a 20\% KOH: 80\% H2O solution which removed \sim 5 \text{ \mu m from the surface. Minority carrier lifetimes were measured using QSSPC and RCPCD with the samples immersed in an iodine-ethanol solution during the lifetime measurements for surface passivation. The QSSPC technique determines the minority carrier lifetimes as a function of
excess carrier concentration, $\Delta n$. Injection-dependent lifetime spectroscopy (IDLS) [18] was used in order to probe deeper into the electrical properties of Ni-impurities in Si at various injection levels. The recombination properties of these Ni-contaminated samples were compared at the same injection level, $\eta = \Delta n/N_{\text{dop}}$, where $N_{\text{dop}}$ is the phosphorus doping concentration. Resonant-coupled photoconductance decay (RCPCD), a transient-based technique for obtaining lifetimes from photoconductivity decay curves as a function of time, was used next. A Nd:YAG laser with optical parametric oscillator provides carrier excitation in the form of 3–5 ns pulses of 1000 nm wavelength light. The RCPCD system measures photoconductivity by inductive-coupling of a coil to the wafer using approximately 420 MHz. Finally, a Bio-Rad DL8000 system DLTS was used to determine the concentration and trap energy of electrically active defects in the contaminated samples. Evaporated gold Schottky diode DLTS measurements were carried out at -3 V reverse biased, and pulsed at 3.2 V for 100 µs.

5.3 Results and Discussion

Figure 5.1(a) plots the QSSPC determined room temperature effective lifetime ($\tau_{\text{eff}}$) of four Ni-contaminated plus one uncontaminated reference n-type Si wafer. At the injection level of phosphorus doping density ($9 \times 10^{14}$ cm$^{-3}$), $\eta = 1$, the effective lifetimes of N1, N2 and N3 gradually decreases with increasing Ni concentration and are not greatly different from each other, however, sample N4, which has the highest contamination level, is significantly lower. Note that for the etched samples, see Fig. 5.1(b), the effective lifetime of sample N4-E is noticeably higher than, not only non-etched sample N4, but even other etched
samples N2-E and N3-E. It appears that at the highest Ni contamination level of sample N4 (6.2 \times 10^{13} \text{ cm}^{-3}), localized surface recombination centers are formed, which seriously decrease the lifetime at the sample surface, but apparently are dissolved out during the etching process. It is well known that Ni, particularly interstitial Ni (Ni$_i$) has high diffusivity in silicon (2.5 \times 10^{11} \text{ cm}^2/\text{s at RT}) \[2\]. Majority of dissolved Ni$_i$ diffuses to the sample surface during cooling process in the air after drive-in annealing. Therefore, at the surface Ni concentrations beyond the solid solubility limit are likely to form precipitates \[2\].

The presence of Ni precipitates can be inferred by SRV (cm/s) and extracted from the expression

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{2S}{W}
\] (1)

(\text{where } \tau_b \text{ is the bulk lifetime, } W \text{ the wafer thickness, and } S \text{ the surface recombination velocity})

The SRV values are essential in separating the bulk lifetime as measured by the effective lifetime after the surface etching process. However, the effective lifetime of etched samples may not correspond to the true bulk lifetime since some precipitates or stress induced dislocations may still exist in the bulk after the shallow etching process. Therefore, the separation of surface recombination and bulk recombination is needed and was carried out using RCPCD injection-dependent lifetime data.

Figure 5.2 shows the RCPCD signal as a function of time for the Ni-contaminated samples N1 to N4, the control sample, and etched N4-E sample. Each sample has a transient with two or three different slopes as a result of a varying balance of recombination
mechanisms. The slope of the transient curve has been converted to lifetime by the following equation.

$$\Delta p(t) = \Delta p_0 e^{-t/\tau}$$

(2)

(where \(\tau\) is the lifetime. The lifetime is then obtained by plotting \(\ln[\Delta p(t)]\) versus time and measuring the slope of the plot.)

The initial instantaneous lifetime at \(t = 0\) is [19]

$$\tau_1 = \tau_B/(1+\alpha S \tau_B)$$

(3)

(where \(\tau_B\) is the bulk lifetime and \(\alpha\) the absorption coefficient).

When the initial lifetime is much shorter than the bulk lifetime,

$$\tau_1 = 1/\alpha S$$

(4)

the initial lifetime is dominated by surface recombination.

The bulk lifetime is then determined according to the relationship

$$1/\tau_B = 1/\tau_{SRH} + 1/\tau_{rad} + 1/\tau_{Auger}$$

(5)

where, \(\tau_{SRH}\) is the Shockley-Read-Hall recombination, \(\tau_{rad}\) the radiative recombination, and \(\tau_{Auger}\) the Auger recombination.

At low injection levels (\(\eta < 1\)), \(\tau_{rad}\) and \(\tau_{Auger}\) are much longer than \(\tau_{SRH}\). Therefore, bulk lifetime is expressed by [20]

$$1/\tau_B \approx 1/\tau_{SRH} = (1 + (C/C_{ref})/\tau_{max}$$

(6)

where, \(\tau_{max}\) is the low-injection SRH lifetime (lifetime of a second slope), \(C\) the doping concentration, and \(C_{ref}\) an experimentally determined constant (7 \(\times 10^{15}\) cm\(^{-3}\)).
In this study, \( \tau_B \) is 1.13 \( \tau_{\text{max}} \) from equation (6) and the bulk lifetime component of the control sample, see Fig. 5.2(b) is 2.7 ms, well matched with the 2.9 ms lifetime measured for the silicon ingot before wafer slicing, for which surface recombination is not an issue. This demonstrates that the bulk lifetime corresponds to the second slope in Fig. 5.2.

The strong surface recombination of sample N4 at high injection levels produces a much shorter lifetime, 44 \( \mu \)s, than other contaminated samples, but improved to 310 \( \mu \)s following etching, see Fig. 5.2. This is well matched with the QSSPC data, see Fig. 5.1. Note that the bulk lifetime of N4 (~210 \( \mu \)s) is not accurate, since the second slope is not linear due to the RCPCD signal initially decaying so strongly that the second slope couldn’t be saturated. Thus, the bulk lifetime of N4-E can be used for N4.

Figure 5.3 shows the surface recombination velocity as a function of total Ni concentration using QSSPC and RCPCD. The surface recombination velocities at the fixed injection level of \( \eta=1 \) for QSSPC measurement were extracted by equation (1). Also, \( \tau_B \) and \( \tau_{\text{eff}} \) are replaced by 1.13 \( \times \) \( \tau_{\text{max}} \) and, \( \tau_1 \) respectively, for RCPCD measurement. The surface recombination velocity of RCPCD is comparable to that of QSSPC. Note that SRV values of RCPCD are slightly higher than that of QSSPC since the effect of remaining precipitates at the surface of etched sample can be removed in case of RCPCD.

The lifetime shapes of N3-E and N4-E at a low injection level (\( \eta < 1 \)), which is mostly affected by SRH recombination, are different to those of N1-E and N2-E samples, see Figure 5.1(b). Also, the bulk lifetime of the N4-E is still lower than the bulk lifetime of the control sample, see Figure 5.2(b). It means that some electrically active defects exist in the bulk.
Figure 5.4 shows DLTS spectra for etched Ni contaminated samples. However, non-etched samples couldn’t be measured since shallow polishing is needed to improve the electrical performance of the evaporated Schottky contacts and minimize the leakage current. The electron trap E1 at 45 K is attributed to the substitutional Ni double acceptor [2], and is present in most of the contaminated samples, except for the control sample and the most lightly contaminated sample N1-E which had no signal detected above the DLTS detection limit ($1 \times 10^{11} \text{ cm}^{-3}$). The activation energy and capture cross-sections for E1 are 0.07 eV and $3.22 \times 10^{-18} \text{ cm}^{-2}$, respectively. As the Ni concentration increases, the concentration of trap E1 increased (trap densities of N2-E and N3-E are $3.9 \times 10^{11} \text{ cm}^{-3}$ and $5.4 \times 10^{11} \text{ cm}^{-3}$, respectively), since the substitutional Ni cannot reach the wafer surface and precipitates due to its low diffusivity [2]. However, the concentration of trap E1 for the most heavily contaminated sample N4-E ($1.7 \times 10^{11} \text{ cm}^{-3}$) decreases compared to N2-E and N3-E, and, in addition, exhibits a broad negative peak from 150~250 K. This broad peak was examined with various reverse bias voltages, which change space charge sampling regions and the peak position shift with reverse bias voltage suggests that this peak is due to extended defects, such as Ni precipitates [15] or associated dislocations, since nickel can precipitate locally during cooling due to its low solubility at low temperatures. These precipitates and deep level impurities are responsible for the different recombination properties observed in the bulk (see Fig. 5.2).
5.4 Summary

In conclusion, the impact of Ni on high carrier lifetime is mainly limited to wafer surfaces when the concentration exceeds the certain level. The lifetime degradation can be recovered by a few μm etching, even though substitutional Ni and small Ni precipitates still remain in the bulk and affect effective lifetime. The SRV extracted from RCPCD measurements is very useful in separating surface and bulk recombination mechanisms, allowing the improvement of lifetime by shallow etching to be quantitatively tracked. The distribution of electrically active defects or traps as recombination sites depends on the thermal conditions and diffusivity of metallic impurities. Other transition metals, such as Mo and Ti, which have relatively low diffusivity, tend to form moderate concentrations of interstitial centers at room temperature after high temperature processing. Further studies about the effect of these transition metals (below Group 8 in the periodic table) [21] are continuing.

References


Fig. 5.1 Effective carrier lifetime ($\tau_{\text{eff}}$) as a function of excess carrier concentration ($\Delta n$) for (a) non-etched (b) etched (5 $\mu$m removed both surfaces) n-type CZ samples with various Ni concentrations.
Fig. 5.2 RCPCD signal as a function of time for (a) control (non-contaminated) sample and different level of Ni contaminated samples and (b) the comparison of non-etched N4 sample and etched N4 sample (N4-E).
Fig. 5.3 Surface recombination velocity (SRV) calculated by QSSPC and RCPCD as a function of total Ni concentration at a fixed injection level of $\eta=1$. 
Fig. 5.4 DLTS spectra for (a) a set of surface etched, Ni-contaminated, high lifetime, n-type CZ samples with both sharp, fixed position, Ni positive trap peaks, and (b) one broad negative mobile with various reverse bias voltage from -2V to -7V extended defect peak for etched Sample N4.
Table 5.1 Drive-in annealing temperature and averaged ICP-MS concentrations of Ni-contaminated phosphorus doped to $9.2 \times 10^{14}$, 5 $\Omega$·cm, n-type CZ samples

<table>
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<tr>
<th>Sample Identification</th>
<th>Annealing temperature ($^\circ$C)</th>
<th>Ni concentration measured by ICP-MS ($\times 10^{12}$ cm$^{-3}$)</th>
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<tr>
<td>N1</td>
<td>575</td>
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<td>N2</td>
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<tr>
<td>N3</td>
<td>712</td>
<td>25</td>
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<td>N4</td>
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6. Identification of Metal Impurities in Crystalline Silicon Wafers

Abstract

Injection dependent lifetime spectroscopy (IDLS) was performed to identify the type and concentration of the defects associated with metal impurities in crystalline silicon wafers. Minority carrier lifetimes in intentionally contaminated silicon wafers using various metal concentrations were measured by a transformer-coupled, radio frequency-based photoconductance measurement tool, GLM™ 2000. Lifetimes in the bulk of the silicon wafers were measured at low injection level using a square pulse cycle of light with half period > 10 milliseconds to ensure steady state photoconductance was reached. Analysis of the data using Shockley-Read-Hall theory demonstrates the ratio of capture cross-section of electrically active defect level associated with molybdenum (Mo) and copper (Cu). Concentrations (N_i) of electrically active defect states associated with Mo and Cu impurity are determined from measured bulk lifetime at low level injection, using Shockley-Read-Hall carrier concentrations (n_1 and p_1), and known activation energy levels (E_a) of the identified metal from the literature.
6.1. Introduction

The Silicon photovoltaic (Si-PV) industry can suffer from poor manufacturing control of metal impurities in low cost directionally solidified or cast wafers making up > 85% of the capacity being delivered today. The capability to detect the type and concentrations of impurities in solar wafers helps to qualify vendors, identify point of contamination in the fabrication line and the possible sources of contamination. Lifetime spectroscopy (LS) is a non-destructive measurement and quick analysis technique for metal impurity characterization in silicon photovoltaic (Si-PV) cells [1]. LS determines the measured lifetime dependence on various changes in either injection level or the substrate temperature to extract defect specific parameters in the silicon wafers.

Effective minority carrier lifetime in silicon wafers is often dominated by the surface recombination velocity (SRV) [2] and as such is a poor indicator of quality of the bulk property of the crystal. In this part, the bulk minority carrier lifetime signals were measured by a newly developed photoconductance measurement tool, GLM™ 2000 [3] after surface passivation.

The GLM™2000 is a multi-parameter, transformer-coupled instrument with programmable LED array that measures radio frequency based photo conductance changes in the wafer. Fig. 6.2 depicts the schematic diagram of the photoconductance instrument. GLM™ 2000 has the capability to use near IR LEDs for full penetration of the wafer or a green LED array penetrating near surface [3]. The unique programmable illumination method allows simultaneous determination of transient and true steady state photoconductance
measurements and the capability to control the intensity of light to access ultra-low injection levels (much less than the dopant concentration, \( N_{\text{dop}} \)).

This part explains the procedure for identification and quantification of a dominant metal impurity in silicon wafers by implementing Injection Dependent Lifetime Spectroscopy using the GLMTM 2000. The theory section describes unique simplifications in applying Shockley-Read-Hall (SRH) \([4, 5]\) lifetime expression by leveraging ultra-low level injection (LLI). In the experiment section two case studies utilizing bulk carrier lifetime measurements is described for intentionally metal-contaminated silicon wafers using Mo and Cu impurities. The measurement results, comparison to previous research, and concluding analysis are presented in the result and discussion section.

6.2. Background and Theory

Lifetime spectroscopy is a proven technique for defect characterization in the silicon industry \([1, 6]\) and allows for simplified instrumentation, short measurement cycles, no sample preparation, is nondestructive, and has low cost of ownership. Alternatives for impurity identification in silicon wafers include Deep Level Transient Spectroscopy, (DLTS), and Inductively Coupled Plasma-Mass Spectrometry (ICPMS). In low level injection, \( \Delta n \ll N_{D,A} \), the carrier lifetime in silicon is mostly dominated by the recombination via defect levels, otherwise known as Shockley Read Hall (SRH). \([4, 5]\)

The well-known SRH equation shown in (1) can be simplified for the low light injection condition.
Further simplification of the SRH equation for a p-type Si wafer can be made when the defect energy level \( E_d \) lies in the lower half of the band gap (LBGH). The LBGH approximation can be made when the following assumptions hold true: (A) electron concentration at thermal equilibrium \( n_0 \) in silicon can be neglected in comparison to the holes concentration \( p_0 \) at room temperature \( n_0 << p_0 \), (B) SRH electron concentrations \( n_1 \), are sufficiently less than \( \Delta n \) when \( E_d \) lies in the LBGH [4, 5] and satisfies \( n_1 + n_0 << \Delta n \) as well as for a deep levels \( p_1 << p_0 \) at room temperature, and (C) for low level injection (LLI), \( p_0 >> \Delta n \), \( \Delta n \) can be removed from the denominator and from the second part of the numerator in (1), which can be re-expressed as

\[
\tau_{SRH} = \frac{\Delta n}{U_{SRH}} = \frac{\tau_{p0}(n_1 + n_0 + \Delta n) + \tau_{n0}(p_0 + p_1 + \Delta n)}{n_0 + p_0 + \Delta n}
\]

(1)

Hence for a particular temperature and \( \Delta n \) range, when conditions A, B and C are satisfied, a plot of \( \tau_{SRH}(T) \) versus \( \Delta n \) gives a slope equals to \( \tau_{p0}(T)/p_0(T) \) and an intercept as \( \tau_{n0}(T) \). These measured quantities explicitly determine \( \tau_{p0} \) and \( \tau_{n0} \) and give a characteristic capture cross section ratio \( \sigma_n/\sigma_p \). This ratio uniquely establishes an impurity type and serves as a fingerprint for a metal impurity in the silicon wafer. An analogous approximation can be
made at LLI for different Si-PV use cases such as; p-type Si with defect in upper half of the band gap (UBGH). Simplified SRH equation for n-type Si, when the $E_t$ lies in the LBGH and UBGH can be expressed as

$$
\tau_{SRH}(T) = \tau_{p0}(T) + \frac{\tau_{n0}(T)}{n_0(T)} \times (\Delta n)
$$

(3)

$$
\tau_{SRH}(T) = \tau_{p0}(T) \left[ \frac{n_1(T) + n_0(T)}{n_0(T)} \right] + \frac{\tau_{n0}(T)}{n_0(T)} \times \Delta n
$$

(4)

SRH capture time constants for $\tau_{n0}$ and $\tau_{p0}$ can be determined using (3) with doping density $n_0$ and $n_1(T)$ can be calculated from the known defect energy level [7] for the temperature range as shown in Fig 6.2. Capture cross section ratios are calculated by using (3) and (4) and the thermal velocity for electron and holes [7] as

$$
\sigma_n = \frac{1}{N_t \times v_{thn} \times \tau_{n0}} \quad \text{and} \quad \sigma_p = \frac{1}{N_t \times v_{thp} \times \tau_{p0}}
$$

(5)

where, $N_t$ is the electrically active defect density and $v_{thn}$ and $v_{thp}$ are the thermal velocities of electrons and holes in the silicon. Hence the characteristic ratio $\sigma_n/\sigma_p$ of the recombination center of the defect energy level in the bulk of the silicon wafer can be calculated from the slope and intercepts of the linear fit of the minority carrier lifetime at LLI, when the $E_t$ lies in the LBGH as

$$
\frac{\sigma_n}{\sigma_p} = \frac{\text{Intercept} \times v_{thp}}{\text{Slope} \times v_{thn} \times n_0}
$$

(6)
The assumption \( p_1(T) \) or \( n_1(T) \gg 0.01 \times \Delta n \) becomes invalid as the \( E_t \) goes deeper into the band gap of Silicon and the linear fit of measured lifetime at LLI against excess carrier density no longer prevail at the room temperature. Fig 6.2 presents the minimum temperature required for \( p_1(T) \) or \( n_1(T) \gg 0.0001 \times p_0(T) \) or \( n_0(T) \) for different \( N_{dop} \) and \( E_t \).

6.3. Experimental Procedures

Phosphorus-doped c-Si samples with resistivity measurements of \( 5 \pm 2 \Omega \text{ cm} \) (\( N_{dop} \approx 9.2 \times 10^{14} \text{ cm}^{-3} \)) were used. Sections \((5 \times 5 \text{ cm}^2)\) were cut out of from the large-area wafers \((15.6 \times 15.6 \text{ cm}^2)\) with an average width of 200 microns. The wafers were RCA cleaned before dipping into five different concentrations of metal spiked solutions at room temperature. For Mo-contaminated samples, five wafers were dipped into the spiked solutions of concentrations 0.1, 1, 10, 100, 1000 ppm followed by a drive-in annealing process, 10 hr, 1000 °C in a vertical tube furnace under Argon (Ar) ambient, followed by slow cooling in air. The wafers are labeled as Mo_1 to Mo_5. For Cu-contaminated samples, 2 wafers were dipped into the spiked solutions of 1, 10 ppm with concentrations 1 and 10 ppm followed by a drive-in annealing for 30 min at 900 °C in a similar condition as mentioned above. The wafers are labeled as Cu_1 and Cu_2. Minority carrier lifetimes in the bulk of the metal contaminated Si-wafer and the control Si-wafer (sister wafer without metal contamination) were measured by using a transformer-coupled, radio frequency-based photo conductance (RF-PC) measurement tool, GLM™2000, explained elsewhere [3]. An array of light emitting diodes (LEDs) of 890 nm wavelength of light were used to illuminate the silicon wafers and
partially processed cells for more than 10 ms, to ensure that steady state photoconductance was achieved.

### 6.4 Results and Discussion

The Minority carrier lifetimes in Mo-contaminated wafers were found to be less than the reference wafer by a factor of 3 to 7, which showed the Mo-defects were dominating the recombination centers. Continuous lines are the fitted SRH lifetime with Mo impurity with defect energy level $E_t = E_v + 0.31$ eV [1], $\sigma_p = 6 \times 10^{-16}$ cm$^2$ [8]. Measured injection dependent lifetime at LLI is depicted in Fig 6.3 (a).

The measured injection dependent minority carrier lifetimes of the Mo contaminated Si wafers at low injection level are fitted linearly. Linear fit of the measured lifetime versus excess carrier density data for sample Mo_5 is depicted in Fig 6.3 (b). The characteristic ratio ($\sigma_n/\sigma_p$) is calculated by using (6). Measured slopes and intercepts with calculated $\sigma_n/\sigma_p$ are depicted in Table 6.1. The concentration of electrically active Mo-defect levels in the silicon wafers ($N_t$) is calculated by using the literature value $\sigma_p = 6 \times 10^{-16}$ cm$^2$ [8] and are depicted in Table 6.2. A monotonic increment of impurity concentration on the wafers from Mo_1 to Mo_5 is expected according to the concentrations of Mo-spiked solutions during the contamination.

Measured value of capture cross section ratio is lower than the literature values [1, 8, 9]. The capture mechanism for electrons and holes of Mo defects in silicon follows the excitonic Auger capture (EAC) [10] and has a strong temperature dependent behavior. The difference
in the measured results of $\sigma_n/\sigma_p$ is obvious for the measurements taken at different temperatures.

Cu is incorporated into the silicon lattice in interstitial form, introducing one of three defect energy levels ($E_i$). These defect levels may appear in the form of substitutional Cu or as the Cu-related pairs. The substitutional Cu in the silicon lattice are namely, an accepter ($Cu^{-}$), a donor ($Cu^{+}$) and a double donor ($Cu^{++}$), all of which can act as recombination centers [8, 11]. It is essential to first make sure of the dominance of a particular energy level before performing lifetime spectroscopy for defect characterization. The dominant defect is confirmed as $Cu^{-}$ by analyzing the measured lifetime data with the procedure mentioned elsewhere [12]. The measured lifetime on Cu contaminated were found to be less than an order of magnitude then the reference wafer, which showed the Cu defects were dominating the recombination centers. Continuous lines are the fitted SRH lifetime with $Cu^{-}$ impurity with defect energy level $E_i = E_C - 0.161 \text{ eV}$, $\sigma_n = 1.9 \times 10^{-17} \text{ cm}^2$ [8, 11]. Measured injection dependent lifetime at LLI is depicted in Fig 6.4 (a). The measured injection dependent minority carrier lifetimes of the Cu contaminated Si-wafers at low injection level are fitted linearly. Linear fit of the measured lifetime versus excess carrier density data for sample Cu_1 and Cu_2 are depicted in Fig 6.4 (b). The characteristic ratio ($\sigma_n/\sigma_p$) is calculated by using (4). Measured slopes and intercepts with calculated $\sigma_n/\sigma_p$ are depicted in Table 6-3.

The concentration of electrically active $Cu^{-}$ defect levels in the silicon wafers ($N_i$) is calculated by using the literature value [8, 11] and are depicted in Table 6-4. Calculated impurity concentration on the sample Cu_1 and Cu_2 is consistent with the concentrations of Cu spiked solutions during the contamination.
6.5 Summary

An explicit measurement of $\sigma_u/\sigma_p$ was performed for Mo and Cu-contaminated wafers performed applying IDLS. Electrically active Mo$_i^+$ and Cu$_s^-$ concentrations ($N_t$) were calculated by using the value of $\sigma_p = 6 \times 10^{-16} \text{ cm}^2$ and $\sigma_p = 1.9 \times 10^{-17} \text{ cm}^2$ respectively from the literature. Measured $N_t$ were found in accordance with the impurity concentration on the metal spiked solution prepared for contamination.

References


Characterization in Silicon," Ph D, Engineering and IT, The Australian National University, Canberra, Australia, 2010.


Fig. 6.1 Schematic diagram of GLM™2000 and light annulus on the wafer under test.
Fig. 6.2 Minimum temperature required for $p_1(T)$ or $n_1(T) \gg 0.0001 \times p_0(T)$ or $n_0(T)$ for different $N_{dop}$ and $E_d$. 
Fig. 6.3 (a) Minority carrier lifetime measured in Mo contaminated and reference wafer for various excess carrier densities. Continuous line shows the fitted SRH lifetime with Mo impurity. (b) Linear fit of the measured lifetime versus excess carrier density data for sample Mo_5.
Fig. 6.4 (a) Minority carrier lifetime measured in Cu-contaminated and reference wafer for various excess carrier densities. Continuous line shows the fitted SRH lifetime with Cu impurity (aa). (b) Linear fit of the measured lifetime versus excess carrier density.
Table 6.1 The ratio of electron to hole capture cross-sections for Mo contaminated samples

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>Slope($r_{n0}/n_0$)</th>
<th>Intercepts ($r_{p0}$)</th>
<th>$(\sigma_n/\sigma_p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo_1</td>
<td>$1.25 \times 10^{-13}$</td>
<td>84.55</td>
<td>$0.42 \pm 0.04$</td>
</tr>
<tr>
<td>Mo_2</td>
<td>$1.11 \times 10^{-13}$</td>
<td>79.19</td>
<td>$0.43 \pm 0.04$</td>
</tr>
<tr>
<td>Mo_3</td>
<td>$1.02 \times 10^{-13}$</td>
<td>63.18</td>
<td>$0.45 \pm 0.04$</td>
</tr>
<tr>
<td>Mo_4</td>
<td>$7.56 \times 10^{-14}$</td>
<td>54.12</td>
<td>$0.44 \pm 0.04$</td>
</tr>
<tr>
<td>Mo_5</td>
<td>$6.97 \times 10^{-14}$</td>
<td>49.47</td>
<td>$0.43 \pm 0.04$</td>
</tr>
</tbody>
</table>
Table 6.2 Defect concentrations and electron capture cross-sections for Mo contaminated samples

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>$N_t$ (cm$^{-3}$)</th>
<th>$\sigma_n$ (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo_1</td>
<td>2.55 x 10$^{12}$</td>
<td>2.52 x 10$^{-16}$</td>
</tr>
<tr>
<td>Mo_2</td>
<td>2.75 x 10$^{12}$</td>
<td>2.58 x 10$^{-16}$</td>
</tr>
<tr>
<td>Mo_3</td>
<td>3.25 x 10$^{12}$</td>
<td>2.70 x 10$^{-16}$</td>
</tr>
<tr>
<td>Mo_4</td>
<td>4.00 x 10$^{12}$</td>
<td>2.64 x 10$^{-16}$</td>
</tr>
<tr>
<td>Mo_5</td>
<td>4.32 x 10$^{12}$</td>
<td>2.58 x 10$^{-16}$</td>
</tr>
</tbody>
</table>
Table 6.3 The ratio of electron to hole capture cross-sections for Cu contaminated samples

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>Slope ($\tau_{n_0}/n_0$)</th>
<th>Intercepts ($\tau_{p_0}$)</th>
<th>$\frac{\sigma_n}{\sigma_p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_1</td>
<td>$9.74 \times 10^{-14}$</td>
<td>12.18</td>
<td>$1/526 \pm 50$</td>
</tr>
<tr>
<td>Cu_2</td>
<td>$7.78 \times 10^{-14}$</td>
<td>10.29</td>
<td>$1/538 \pm 50$</td>
</tr>
</tbody>
</table>
Table 6.4 Defect concentrations and hole capture cross-sections for Cu contaminated samples

<table>
<thead>
<tr>
<th>Wafer ID</th>
<th>( N_t \text{ (cm}^{-3}\text{)} )</th>
<th>( \sigma_p \text{ (cm}^2\text{)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu_1</td>
<td>( 4.3 \times 10^{13} )</td>
<td>( 1.02 \times 10^{-14} )</td>
</tr>
<tr>
<td>Cu_2</td>
<td>( 5.2 \times 10^{-13} )</td>
<td>( 1.00 \times 10^{-14} )</td>
</tr>
</tbody>
</table>
7. Summary

N-type silicon has higher minority carrier diffusion length than p-type silicon. That is because n-type silicon is more tolerant to metallic impurities. Also, it has no serious issues for lifetime degradation, such as FeB pairs and light-induced degradation (LID). However, adequate passivation layer had not been assigned to B-doped emitters. Jan Benick et al. suggested Al₂O₃ passivation layer for B-doped emitters. With this surface passivation layer, 23.2% conversion efficiency was achieved. With this successful achievement of passivation layer, n-type silicon has been studying for photovoltaics. The detrimental effects and electrical properties of transition-metal impurities, e.g., iron, and its complexes, such as FeB, in p-type silicon are well-known. However, in n-type silicon wafers, the impact of specific metallic impurities on minority lifetimes is not as well established. In this dissertation, limitations of Ga-doped p-type silicon have been determined and the impact of various metallic impurities on minority carrier lifetime in n-type silicon has been studied.

Resistivity variation and lifetime limiting factors were investigated in c-Cz grown Ga-doped Si. The resistivity variation of c-CZ wafers showed a relatively good uniformity of dopant distribution compared to conventional CZ wafers. However, it is still not ideal. The radial and axial variation of electrically active defects were observed in DLTS spectra and correlated to lifetime and resistivity variations. DLTS measurements demonstrated that iron-related pairs are responsible for the variations. Specifically, Fe-Ga pairs were found to be serious recombination sites, which is more detrimental to lifetime than Fei. A c-Cz method was found to be potential for fabricating uniformly Ga-doped Si for high performance solar cells, but the issue of iron contamination still needed to be addressed.
The impact of Ni on high carrier lifetime is mainly limited to wafer surfaces when the concentration exceeds the certain level. The lifetime degradation can be recovered by a few µm etching, even though substitutional Ni and small Ni precipitates still remain in the bulk and affect effective lifetime. The SRV extracted from RCPCD measurements is very useful in separating surface and bulk recombination mechanisms, allowing the improvement of lifetime by shallow etching to be quantitatively tracked. The distribution of electrically active defects or traps as recombination sites depends on the thermal conditions and diffusivity of metallic impurities.

An explicit measurement of $\sigma_n/\sigma_p$ was performed for Mo and Cu-contaminated wafers performed applying IDLS. Electrically active $\text{Mo}_i^+$ and $\text{Cu}_s^-$ concentrations ($N_i$) were calculated by using the value of $\sigma_p = 6 \times 10^{-16}$ cm$^2$ and $\sigma_p = 1.9 \times 10^{-17}$ cm$^2$ respectively from the literature. Measured $N_i$ were found in accordance with the impurity concentration on the metal spiked solution prepared for contamination.