Evaluation of plasma induced defects on silicon substrate by solar cell fabrication process

Kohei Onishi1, Yutaka Hara1, Tappei Nishihara1, Hiroki Kanai1, Takefumi Kamioka2, Yoshio Ohshita3, and Atsushi Ogura1, 3

1 Meiji University, Kawasaki 214-8571, Japan
2 Toyota Technological Institute, 2-12-1 Tennpaku, Nagoya, Aichi 468-8511, Japan
3 Meiji Renewable Energy Laboratory, Kawasaki 214-8571, Japan

Received May 29, 2020; revised May 25, 2020; accepted June 1, 2020; published online June 17, 2020

1. Introduction

Crystalline silicon solar cells are dominating the solar cells industry due to high efficiency with suppressed fabrication cost.1–3 For example, silicon heterojunction (SHJ) solar cell shows the high voltage and the high conversion efficiency over 25% by adopting the amorphous Si (a-Si) and crystalline silicon heterojunction.4–8 However, these still have a problem of reducing minority carrier lifetime by various crystal defects, such as impurities, precipitates and dislocations, which are inevitably introduced in the fabrication process.9–12 In order to reach the theoretical limitation of cell efficiency, it is important to reduce crystal defects induced during the cell fabrication process and deactivating carrier recombination centers.

A transparent conductive oxide (TCO) film such as indium-tin oxide (ITO) is one of the most important components of SHJ solar cell and inserted between the a-Si layer and the electrodes.13–15 Reactive plasma deposition (RPD) is another deposition technique that is recognized to provide relatively less damage by incident ions than sputtering.16–20

However, the lifetime degradation after ITO deposition through these plasma processes has been a concern. The reason for this deterioration is attributed to the defects formation on the crystalline surface by the plasma process. Such plasma induced defects in the silicon substrate act as carrier recombination centers, therefore deteriorate solar cell performance significantly.16,21–24 On the other hand, the cause of the plasma induced damage in the silicon substrate has not been sufficiently clarified yet. Impurities such as oxygen and carbon are present in the silicon crystal, and it is possible that these impurities and plasma irradiation defects may have a correlation. Therefore, it is necessary to identify and control the cause of damage in order to increase the efficiency of solar cells.

In this study, we evaluated the cause of lifetime degradation in plasma process for solar cell on silicon substrate. In order to investigate the relationship between plasma irradiation defects due to the RPD process and the impurity, samples with different impurity concentrations in which ITO film was deposited by the RPD were used.

2. Experiment

For the evaluation of minority carrier lifetime and irradiation defects, 200 μm thickness n-type single crystal Czochralski silicon (Cz-Si) substrate with different oxygen and carbon concentration were used as shown in Table I. The resistivity and dopant concentration are approximately 3.1 Ω·cm and 1.5 × 1015 cm−3, respectively. Oxygen concentration were measured by Fourier transform infrared (FTIR) absorption spectroscopy and quantitatively evaluated following the protocol set by JEITA. Carbon concentrations were also measured by FTIR and photoluminescence (PL) method.25,26

For the sample preparation, first, the sawing damage on the substrate surfaces was removed about 10 μm on both sides with a HF and HNO3 mixture. Then, the ITO films were deposited approximately 70 nm on the both sides of the silicon substrate by the RPD method. Here, RPD was performed under standard conditions used in actual solar cell fabrication.27 Finally, the ITO layer was removed with HF solution to evaluate the plasma induced damage on the silicon substrate. The purpose of this study is to clarify the damages and types of defects caused by the RPD process. If the ITO layer is deposited on a-Si, Sn diffusion or In precipitation on the substrate may occur, which may make it difficult to clearly evaluate damage on the Si substrate.28 Moreover, it is extremely difficult to clarify the damages on a-Si itself. Therefore, the ITO layer was deposited directly on the substrate.

In order to evaluate the minority carrier lifetime, Sinton WCT120 was used after the quinhydrone methanol passivation treatment. In addition, PL spectroscopy was performed under the excitation of the 532 nm with a beam diameter of approximately 3 nm and the cryostat temperature was set at around 4 K. However, the substrate temperature is considered to be slightly higher because of the distance between the...
cryostat and the measurement sample position. Also, a cooled Indium gallium arsenide (InGaAs) photodiode array was used as the detector. These evaluations were performed after removing the ITO film with an HF solution for evaluating the plasma induced damage on the substrate.

3. Results and discussion

Figure 1 shows minority carrier lifetime before and after RPD process measured at $1.0 \times 10^{15}$ cm$^{-3}$ carrier injection density. In the minority carrier lifetime before RPD treatment (as-grown), we observed the variation in lifetimes, which is probably attributed to the defects related to oxygen and possibly carbon such as point defects. After the RPD process, minority carrier lifetime was greatly reduced. That is, we have shown that plasma irradiation introduces some defects into the silicon substrate and significantly reduces the minority carrier lifetime. Furthermore, the minority carrier lifetime on the silicon substrate after the RPD process was lower with high oxygen and carbon concentration. This suggests that plasma irradiation defects in RPD process have some correlation with impurity carbon and oxygen.

Subsequently, we evaluated the plasma induced defects after RPD process by PL measurement. Here, to evaluate the damage into silicon substrate, the PL measurement was similarly performed on the samples in which the ITO film deposited by RPD method was removed. Figures 2 and 3 shows the PL spectra before and after the RPD process, respectively. The peak due to band edge emission and phonon replica were clearly observed at around 1.1 eV. The peak was observed in the deep level region of 0.79 eV for each sample after the RPD process while it was not observed from the substrate without RPD (as-grown). This suggests that the plasma irradiation induced a deep level emission line. This deep level emission line can be assigned as C-line, which is originated from the radiation-induced defects of the interstitial carbon (Ci) and interstitial oxygen (Oi) complexes (Ci–Oi). That is, it is suggested that the main cause of the lifetime degradation on the silicon substrate is Ci–Oi defects originated by plasma irradiation during the RPD process.

It has been reported that the origin of the Ci–Oi defect is kick out Ci formation caused by electron or energy particle. Although various factors may be considered for the defect formation of the substrate in the plasma process, we presume that electron and ion can contribute to the pushing of Si atoms into the interstitial lattice, and then Ci is kicked out. However, further studies are needed to reveal in detail factors that cause defect formation.

Also, we have confirmed that C-line intensity is closely related to minority carrier lifetime after RPD process. Figure 4 shows that the C-line intensity is high when the lifetime is low. Therefore, there is the possibility that the number of defects introduced by plasma irradiation on silicon substrate differs depending on the impurity concentration, even at the same irradiation energy. From these results, we revealed that in RPD process, Ci–Oi defects are formed by plasma irradiation, resulting in lifetime degradation on Si substrate.

Furthermore, we evaluated the depth profile of irradiated defects in the substrate with step etching by HNO$_3$, CH$_3$COOH and HF mixture (HNO$_3$:CH$_3$COOH:HF = 40:15:1). The etching cycle was repeated with one dipping for 5 s in the solution followed by flowing deionized water. Figure 5 shows the relationship between the C-line intensity and minority carrier lifetime dependence of the etching depth in the sample.

| Oxygen concentration (cm$^{-3}$) | Carbon concentration (cm$^{-3}$) |
|---------------------------------|----------------------------------|
| $2.0 \times 10^{18}$           | $1.3 \times 10^{14}$            |
| $2.0 \times 10^{18}$           | $1.2 \times 10^{15}$            |
| $2.0 \times 10^{18}$           | $4.3 \times 10^{14}$            |
| $2.0 \times 10^{18}$           | $1.2 \times 10^{16}$            |
| $1.3 \times 10^{18}$           | $1.3 \times 10^{14}$            |
| $1.7 \times 10^{18}$           | $1.3 \times 10^{14}$            |
| $2.0 \times 10^{18}$           | $1.3 \times 10^{14}$            |

Fig. 1. (Color online) Relation between Cs/Oi concentration and minority carrier lifetime before and after RPD process with (a) oxygen concentration (b) carbon concentration.
with low carbon \((1.3 \times 10^{14} \text{ cm}^{-3})\) and oxygen \((1.3 \times 10^{18} \text{ cm}^{-3})\). One etching cycle corresponds to approximately 1 nm depth, which was estimated from 1 \(\mu\text{m}\) etching time. From Fig. 5, the minority carrier lifetime was gradually improved by etching, approached to the same value as the as-grown sample. In addition, we have confirmed that the C-line intensity decreases with the improvement of the lifetime on the silicon substrate. Therefore, it is considered that high density recombination centers exist near the surface of the silicon substrate within approximately 100 nm from the surface. Also, it has been clarified that the origin of the defects which cause in the lifetime degradation of the silicon substrate by plasma irradiation is \(\text{C}_i\text{-O}_i\) defects.

We investigated the correlation between the C-line intensity obtained after the RPD process and the minority carrier lifetime. From Fig. 6, the minority carrier lifetime drastically decreased according to the C-line. Here, we assume that the C-line intensity is correlated with the density of \(\text{C}_i\text{-O}_i\) defects. Figure 6 suggested that these are proportional relation. Although correlation coefficient of \(R^2 = 0.93\) proves there is a strong correlation between C-line intensity

![Fig. 2. PL spectra of as-grown sample.](image)

![Fig. 3. PL spectra after RPD process with (a) oxygen concentration of \(2.0 \times 10^{18} \text{ cm}^{-3}\) (b) carbon concentration of \(1.3 \times 10^{14} \text{ cm}^{-3}\).](image)
and $1/\tau$. One may anticipate slight deviation especially in the low C-line intensity region. This may be attributed to the fact that it is usually hard to reproduce low PL intensity completely. The difference of the other defects such as meta impurities, oxygen precipitates, or dangling-bond caused by strain may affect somehow. However, the major origin of the lifetime degradation by the RPD process is most likely attributed to the Ci–Oi defects formation.

The effective minority carrier lifetime is expressed as

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{surface}}} + \frac{1}{\tau_{\text{sub-surface}}} + \frac{1}{\tau_{\text{bulk}}},$$

where, $\tau_{\text{surface}}$, $\tau_{\text{sub-surface}}$ and $\tau_{\text{bulk}}$ is the surface, sub-surface and bulk recombination lifetime, respectively.

From Fig. 5, the high density recombination center exists approximately 100 nm from the Si substrate surface. Therefore, sub-surface recombination is more dominant than bulk: $1/\tau_{\text{sub-surface}} \gg 1/\tau_{\text{bulk}}$ and Eq. (1) can be expressed as

![Figure 4](Color online) Relationship between C-line intensity and minority carrier lifetime.
The minority carrier recombination rate $U_{\text{total}}$ is expressed as

$$U_{\text{total}} = U_{\text{SRH}} + U_{\text{Rad}} + U_{\text{Auger}} + U_{\text{surface}}.$$  \hfill (3)

The total recombination ratio $U_{\text{total}}$ and the SRH recombination ratio $U_{\text{SRH}}$ due to impurities and defects are expressed as

$$U_{\text{total}} = \frac{1}{\tau_{\text{eff}}} \frac{\Delta n}{W},$$  \hfill (4)

where $W$ is the wafer thickness and $\Delta n$ is the excess carrier density.

$$U_{\text{SRH}} = \frac{\nu_{\text{th}} \sigma_n \sigma_p N_t (p n - n_1^2)}{\sigma_n (n + n_1) + \sigma_p (p + p_1)},$$  \hfill (5)

where $\sigma_n$ and $\sigma_p$ are the cross sections of electrons and holes, $\nu_{\text{th}}$ is the thermal velocity of electrons, and $N_t$ is the defect density. Also, $n$ is the electron density, $p$ is the hole density, and $n_1$ and $p_1$ are variables related to the recombination rate depending on the energy $E_t$ of the trap level. That is, the following equation is given from the Eqs. (3)–(5) by using the arbitrary constant $a$ representing the bulk recombination components, and the constant $b$ representing the surface recombination and other recombination components

$$\frac{1}{\tau_{\text{eff}}} = a N_t + b.$$  \hfill (6)

Assuming that $N_{\text{Cl-Oi}}$ is the density of Cl–Oi defects and $N_t = N_{\text{Cl-Oi}}$, Eq. (7) expressed as

$$\frac{1}{\tau_{\text{eff}}} = a N_{\text{Cl-Oi}} + b.$$  \hfill (7)

Equation (7) implies that the inverse lifetime is proportional to the Cl–Oi defect density, and we have experimentally shown that it is correct. Hence, the relation coefficient of the graph was $R^2 = 0.93$ and it can be concluded that the density of Cl–Oi defects and the minority carrier lifetime showed good correlation and the Cl–Oi defects is a dominant carrier recombination center. We can also conclude that the Cl–Oi defects are the SRH recombination centers. The surface defects are usually composed of dangling-bond without termination. Thus, we recognized Cl–Oi defects as bulk defects rather than surface defects. However, Cl–Oi defects are confined in the relatively close to the surface ($\sim$100 nm), which may also affect the small deviation in the low C-line intensity region of Fig. 6.
From these results, we have demonstrated that the plasma process used in solar cells fabrication such as the RPD method originates defects formation in the silicon substrate and reduces the minority carrier lifetime. In addition, PL spectroscopy identity the origin of the irradiation defect was a defect derived from impurity carbon and oxygen, namely a Cl–Oi defect. These defects were stable even after 200 °C 20 min annealing which is simulating the low temperature electrode fabrication process. It is also presumed that this type of defects can be produced through low density a-Si: H layer with several tens nano-meter even in the actual device process. Therefore, it is important to control this type of defect on the silicon substrate during the process to increase the cell efficiency. This should be able to be achieved by reducing O and C impurities and/or plasma damage.

4. Conclusions

Plasma irradiation defects on silicon substrates during the solar cell process were evaluated by minority carrier lifetime and PL spectroscopy. Plasma irradiation introduces some defects into the silicon substrate and significantly reduces the minority carrier lifetime. Therefore, we revealed that the cause of the lifetime degradation on the silicon substrate is Cl–Oi defects originated by plasma irradiation during the RPD process. There was a correlation between these defects and minority carrier lifetime degradation by plasma irradiation. In addition, the etching depth profile showed that these defects were exist at high density on the substrate surface. From the above, the plasma process such as the RPD method in solar cell fabrication may introduces defects that degrade the cell performance to the silicon substrate. Therefore, in order to achieve high efficiency, efforts to control irradiation defects such as Cl–Oi defects are required.

Acknowledgments

This research was conducted with the support of New Energy and Industrial Technology Development Organization. We would like to thank Dr. Michio Tajima, Meiji University, for his advice on the PL characterization.

ORCID iDs

Atsushi Ogura © https://orcid.org/0000-0003-2008-7695

© 2020 The Japan Society of Applied Physics