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Determination of low carbon concentration in Czochralski-grown Si crystals for solar cells by luminescence activation using electron irradiation

Hirotatsu Kiuchi1*, Michio Tajima1*, Fumito Higuchi1, Atsushi Ogura1, Nobuhiro Iida2, Shoji Tachibana2, Isao Masada2, and Eiichi Nishijima2

1Meiji University, Kawasaki 214-8571, Japan
2Tokuyama Corporation, Shunan, Yamaguchi 745-8648, Japan

*E-mail: ce61029@meiji.ac.jp; tajima@meiji.ac.jp

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We attempted the quantification of carbon concentration in Czochralski-grown Si crystals for solar cells by luminescence activation in the concentration range lower than the detection limit of IR absorption spectroscopy. A positive correlation was found between the relative intensity of the C-line and the substitutional carbon (Cs) concentration determined by IR absorption in the low $10^{15}$ cm$^{-3}$ range. The detection limit was estimated to be approximately $5 \times 10^{15}$ cm$^{-3}$. We measured and compared the Cs concentrations in the wafers sliced from ingots grown under different conditions. The variations in Cs concentrations in the respective ingots were consistent with the segregation effect.

**Table I. Specifications of CZ-Si samples.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>[Cs] ($10^{15}$ cm$^{-3}$)</th>
<th>[Cs] by PL ($10^{12}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>3</td>
<td>3.0</td>
</tr>
<tr>
<td>#3</td>
<td>≈1</td>
<td>1.3</td>
</tr>
<tr>
<td>#9</td>
<td>&lt;1 (Lower*)</td>
<td>0.6</td>
</tr>
<tr>
<td>#5</td>
<td>&lt;1 (Lowest*)</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a) Expected from growth condition.

Recently, carbon (C) impurity has attracted attention as one of the factors that degrade the quality of Czochralski-grown Si (CZ-Si) crystals. The detection limit of Fourier transform infrared spectroscopy (FT-IR), which is a typical method for determining substitutional carbon (Cs) concentration, is $2 \times 10^{15}$ cm$^{-3}$. However, solar cells and power devices require crystals with lower C concentrations. Under this circumstance, the luminescence activation method attracts attention, which enables us to quantify Cs by measuring the photoluminescence (PL) of the C-line at 0.790 eV and that of the G-line at 0.969 eV generated by electron irradiation.\(^3,4\) The C- and G-lines originate in the radiation-induced defects of the interstitial carbon and interstitial oxygen complex (C$_i$-O) and Cs and C$_i$ complex (C$_i$-Cs), respectively.\(^5,6\) The determination of extremely low Cs concentrations in floating zone (FZ), magnetic-field-applied Czochralski (MCZ), and epitaxial Si crystals by using the intensity of the G-line as an index has recently been reported.\(^7,8\) In this study, we attempted the quantification of low C concentrations in CZ-Si crystals for solar cells by using the intensity of the C-line as an index.

The relative intensity of the C-line increased with the fluence of the electron irradiation, resulting in the improvement of the detection limit of Cs concentration. We demonstrated the effectiveness of the present PL method by comparing the Cs concentrations in CZ-Si ingots grown under the normal and low C concentration conditions.

The samples used for the present study were n-type (P-doped) CZ-Si wafers for solar cells, as summarized in Table I. Since the intensities of the C- and G-lines are greatly affected by dopant impurity and O$_i$ concentrations, the samples had similar phosphorus (P) and O$_i$ concentrations $[P] \approx 1.5 \times 10^{15}$ cm$^{-3}$, $[O_i] \approx 1.3$–1.4 $\times 10^{18}$ cm$^{-3}$, where the O$_i$ concentration was determined by FT-IR using the conversion factor of 3.14 $\times 10^{17}$ cm$^{-2}$.$^2$ The Cs concentration was measured by FT-IR,\(^1,2\) and it was below the detection limit for samples #9 and #5. The Cs concentration of sample #5 was expected to be lower than that of sample #9, because sample #9 was grown under the normal condition, whereas sample #5 under the low Cs concentration condition. We also measured wafers sliced from n-type CZ-Si ingots A, B, and C with diameters of 150–200 mm, where ingots A and B were grown under the low Cs concentration condition and ingot C under the normal condition. The P and O$_i$ concentrations of the wafers were in the ranges of $(1.2$–6.9)$ \times 10^{15}$ and $(0.9–2.2) \times 10^{18}$ cm$^{-3}$, respectively. We investigated the variation in Cs concentration with the solidified fraction $g$.

The samples were irradiated with 2 MeV electrons with a fluence of $1 \times 10^{15}$ cm$^{-2}$. Higher fluences of $5 \times 10^{15}$ and $1 \times 10^{16}$ cm$^{-2}$ were also tested to examine the fluence dependence. PL spectroscopy was performed at 4.2 $\mathrm{K}$ under the excitation of the 532 nm line of a diode-pumped solid-state laser with a beam diameter of about 2.3 mm and an intensity of about 50 mW on a sample surface. The emission from the sample was dispersed using a monochromator ($f = 0.32$ m) with a 300 groove/mm grating blazed at 1.2 $\mu$m and detected using a cooled InGaAs photodiode array. The measurement conditions were basically in accordance with Japanese Industrial Standard (JIS) H 0615.$^5,6,13$ The spectral response of the measurement system was calibrated using a standard lamp. The intensity axis in the PL spectra was determined to be proportional to the number of photons per unit energy interval.

A typical PL spectral change induced by electron irradiation is shown in Fig. 1 for sample #1. The spectral components appeared only in the near-band-edge region before the irradiation. They were identified as no-phonon (NP)- and transverse-optical (TO)-phonon-assisted lines of bound excitons associated with the dopant P, denoted as $P_{\text{np}}(\text{BE})$ and $P_{\text{TO}}(\text{BE})$, respectively, and a TO-phonon-assisted electron–hole droplet (EHD) line, denoted as $I_{\text{BE}}(\text{EHD})$.$^7,17$ After the irradiation, the C- and G-lines appeared in the deep-level PL region in addition to the near-band-edge emission, as reported previously.\(^7,14\)

The deep-level PL spectra for samples #1, #3, #9, and #5 after the electron irradiation are shown in Fig. 2, where the...
spectra were normalized with respect to the major $P_{\text{TO(BE)}}$ line. The symbol “×8” denotes the amplitude factor with respect to the band-edge region. The G-line was detected for samples #1 and #3, whereas it was below our detection limit for samples #9 and #5. Regarding the intensity of the C-line, a positive correlation was observed between the intensity and the Cs values obtained by FT-IR for samples #1 and #3. The intensity decreased on the order of the expected Cs concentrations for samples #9 and #5. Since the C-line intensity depends on the surface condition of samples and other factors, we used the intensity ratio of the C-line to the $P_{\text{TO(BE)}}$ line as an index, following the JIS method. We estimated the Cs concentration on the basis of the correlation between the C-line intensity $I_c$ and the Cs concentration $[\text{Cs}]$

$$I_c \propto [\text{Cs}]^{0.9},$$

which was reported in Fig. 4 in Ref. 10. We calculated the Cs concentrations of the respective samples using the highest Cs concentration observed in sample #1 as a reference value.

The estimated values are given in “$[\text{Cs}]$ by PL” in Table I. The lowest Cs concentration of $2 \times 10^{14} \text{cm}^{-3}$ was estimated in sample #5.

To estimate the detection limit of the present PL method, we focused on sample #5 with the lowest Cs concentration of $2 \times 10^{14} \text{cm}^{-3}$. The dependence of PL spectra on the electron fluence is shown in Fig. 3. The C-line intensity increased with the electron fluence, suggesting the possible detection of a lower Cs concentration under a higher electron fluence. We tried to improve the S/N ratio of the PL spectra by using a lock-in mode, in which the signal and background were alternately recorded twenty times. The PL spectrum obtained after this procedure for sample #5 irradiated with the electron fluence of $1 \times 10^{16} \text{cm}^{-2}$ is shown in Fig. 4. The S/N ratio was approximately 100, suggesting that a signal with two one-hundredths of this intensity was detectable. This indicates that the detection limit of the Cs concentration is approximately $5 \times 10^{12} \text{cm}^{-3}$. Further improvement of the detection limit seems possible by increasing the electron fluence and data accumulation time.

PL spectra were measured for wafers sliced from CZ-Si ingots A and B grown under the low C concentration condition and ingot C under the normal condition. The intensity ratios of the C- and G-lines to the $P_{\text{TO(BE)}}$ line (C/P and G/P, respectively) are shown in Fig. 5. In each ingot,
In conclusion, we demonstrated that the luminescence activation method is applicable to the quantification of a low Cs concentration of $10^{14}$ cm$^{-3}$ in CZ-Si crystals. The detection limit was estimated to be below $5 \times 10^{13}$ cm$^{-3}$. We measured and compared the Cs concentrations in the ingots grown under different conditions. The variations in Cs concentrations in the respective ingots were consistent with the segregation effect.

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1) JEITA EM-3503 (2002).

![Fig. 5. Comparison of intensity ratios of C- and G-lines to PTO(BE) line in wafers sliced from CZ-Si ingots grown under different conditions: ingots A and B under low C concentration condition and ingot C under normal condition. Cs concentration in right axis is estimated from C/P value.](image-url)