

Quantitative Analysis of Low-level Carbon in Si Using Room-Temperature Photoluminescence after Electron Irradiation

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Abstract

We demonstrate that a broad emission band observed at room temperature near the C-line after electron irradiation is applicable for the C quantification. Despite the thermal instability of radiation-induced defects, the band is stable under the long-term illumination of laser light for the photoluminescence measurement at room temperature. A positive correlation was observed between the C concentration and the intensity ratio of the broad band relative to the band-edge emission in many sets of samples sliced from the same ingots in the concentration range of 2×10^{14} to 4×10^{16} cm⁻³. This allows us to use the intensity ratio of the band as an index for practical quantitative analysis of low-level C in Si.

1. Introduction

Recently, the C quantification lower than 1×10^{15} cm⁻³ in Si crystals has been required for high efficiency solar cells and high-performance power devices. In particular, the determination of a trace amount of C is indispensable for the improvement in the lifetime of wafers for solar cells with high efficiency close to the theoretical limit. However, the targeted C concentration range is below the detection limit of the standardized IR absorption method. Under this circumstance, the photoluminescence (PL) activation method using electron irradiation has attracted considerable attention as a technique for the low-level quantification of C impurities [1]. Until recently, various researchers carried out the determination of C concentration by the PL method using the C-line (0.79 eV) and G-line (0.97 eV), where the measurement was performed at liquid He temperature (4.2 K) in all the cases. The author's group demonstrated that the detection of the C- and G-lines is possible at liquid N temperature (77 K) [2], and that the C concentration is quantified in the same way as at 4.2 K. Recently, the same group has reported that a broad emission band near the C-line (C08-band) is observable even at room temperature and has a very similar origin to the C-line [3].

The purpose of this study was to perform quantitative analysis of low-level C in Si using the C08-band at room temperature. Our concern was the stability of the defects responsible for the C08-band during the PL measurement. We confirmed that the variation of the PL is negligible after long-term laser illumination. Then, we investigated the relationship between the intensity of the C08-band and the C concentration for various Si ingots. We demonstrate that the C08-band is useful for the determination of the C concentration for practical application.

2. Experimental methods

The samples used in this study were approximately 130 pieces of Si crystals grown by Czochralski (CZ), magnetic-field-applied Czochralski (MCZ), and floating-zone (FZ) methods from four different organizations. The C concentration ranges from 2×10^{14} to 4×10^{16} cm⁻³, according to the data given by the suppliers, where the concentration was determined by the IR absorption, secondary ion mass spectrometry, or the PL measurement at 4.2 K. The samples were irradiated with 2 MeV electrons with a fluence of 1×10^{15} cm⁻². PL spectroscopy was performed at room temperature in air ambient under the excitation of the 532 nm line of a diode-pumped solid-state laser with a beam diameter of approximately 2.3 mm and intensity of approximately 190 mW on a sample surface. A typical measurement time for taking one spectrum is 30-60 sec.

3. Results and discussion

Figure 1 shows the PL spectra at room temperature of MCZ-Si wafer with C and O concentrations of 1×10^{15} and 3×10^{17} cm⁻³ (a) before and (b) after electron irradiation. The

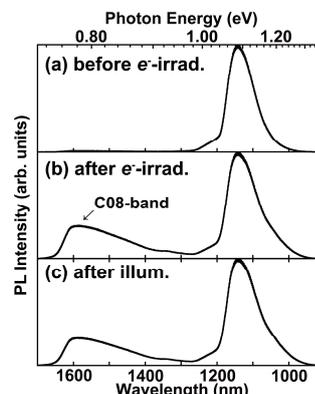


Fig. 1. Room-temperature PL spectra of MCZ-Si with C concentration of 1×10^{15} cm⁻³ (a) before and (b) after 2 MeV *e*-irradiation and (c) after 1 h laser illumination. (Spectral response was not calibrated.)

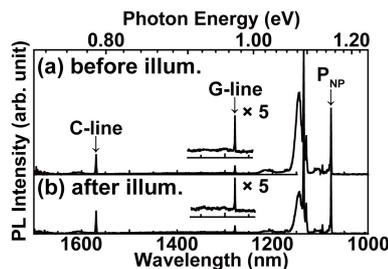


Fig. 2. PL spectra at 4.2 K of MCZ-Si crystals after 2 MeV *e*-irradiation (a) before and (b) after 1 h laser illumination.

electron irradiation induced the C08-band at about 0.8 eV near the C-line.

It has been reported that the radiation-induced defects responsible for the G- and C-lines are annealed out at 250 and 500 °C, respectively [4]. When the PL measurements are carried out at room temperature, radiation-induced defects may disappear by the temperature rise of the sample surface due to long-term illumination of the laser beam. To check this problem, we compared the PL spectra before and after the laser illumination for 1 hour under the same condition as the PL measurement at room temperature. Figure 1(c) is the PL spectrum after 1-hour illumination. There were spectral changes neither between Fig. 1(b) and (c) at room temperature nor between Fig. 2(a) and (b) at 4.2 K. These findings confirm for us that the laser illumination under the present measurement condition does not affect the radiation-induced defects.

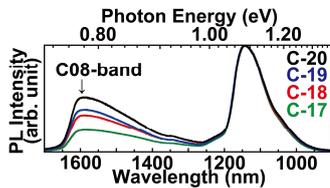


Fig. 3. Normalized PL spectra at room-temperature of Si samples sliced from CZ ingot after 2 MeV e^- -irradiation.

We investigate the variation of the C08-band with the C concentration. Figure 3 shows the PL spectra at room temperature of four samples sliced from different solidified fraction (g) of a CZ ingot, where the intensity was normalized by the band-edge emission. The C concentration varied in the range of $0.2\text{-}2.0 \times 10^{15} \text{ cm}^{-3}$, which was determined by the PL using the intensity ratio of the G-line at 4.2 K [5]. The O and dopant concentrations were within a certain range, since the samples were from the same ingot. The intensity ratio of the C08-band relative to the band-edge emission increased with the C concentration.

The g dependence of the intensity ratio of the C08-band was compared with that of the C- and G-lines at 4.2 and 77 K, as shown in Fig. 4. For all the cases, the intensity ratios increased with g , reflecting the segregation effect. We have already reported a quantitative correlation between the C concentration and the relative intensity of the G-line at 4.2 and 77 K in Ref. 4. The present comparison in Fig. 4 indicates that

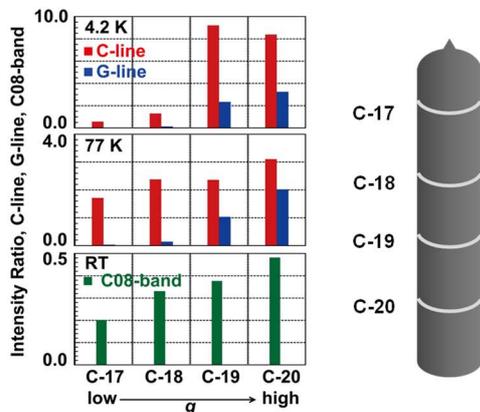


Fig. 4. The g dependences of intensity ratios of C- and G-lines at 4.2 and 77 K and C08-band at room-temperature relative to band-edge emission in wafers sliced from CZ-Si ingot.

the relative intensity of the C08-band shows at least qualitative correlation with the C concentration.

We examined the correlation between the C concentration and the relative intensity of the C08-band for 11 groups of samples, as shown in Fig. 5. The samples in a group were sliced from the same ingots or had nearly the same O and dopant concentrations, and were distinguished by markers. Positive correlations were obtained between the ratio and the concentration for most groups, suggesting the applicability of the C08-band for the C quantification.

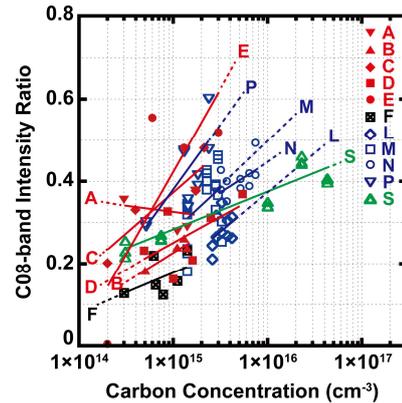


Fig. 5. Relationship between C concentration and intensity ratio of C08-band relative to band-edge emission at 300 K.

4. Conclusions

The C08-band appearing in room-temperature PL after electron irradiation did not show any change by long-term illumination of the laser light for the PL measurement. This eliminates concerns about thermal instability of radiation-induced defects during the room-temperature PL measurement. The intensity ratio of the C08-band has positive correlations with the C concentration in Si crystals sliced from the same ingots and in those having nearly the same O and dopant concentrations. The present results lead us to suggest that the room-temperature PL measurement can be used for the quantitative analysis of low-level C in Si.

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