PHOTOLUMINESCENCE DUE TO OXYGEN PRECIPITATES DISTINGUISHED FROM THE D LINES IN ANNEALED Si

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Abstract. Highly spatially resolved mapping of deep-level photoluminescence in annealed Czochralski-grown Si crystals has revealed for the first time that the D1/D2 lines at low temperatures show the opposite intensity contrast around dislocations with respect to the 0.77 eV band observed commonly at room temperature. The intensity of the D1/D2 lines decreases on the dislocation lines in the same way as the cathodoluminescence image of the D1/D2 lines in a plastically deformed float-zone Si crystal. The 0.77 eV band is renamed D_b band, since the peak shifts parallel to the bandgap with temperature. The positive correlation between the D_b band i... ...d oxygen concentration and the agreement of their distributions lead us to su... ...ssociated with the oxygen precipitation. The increase of the D_b band on ... ...ue to the preferential precipitation of oxygen.

Introduction

Deep-level photoluminescence (PL) lines labeled D1-D4 are kno... ...ratures in deformed float-zone (Fz) Si crystals containing dislocations [1-... ...also been observed in annealed Czochralski(Cz)-grown Si crystals, where s... ...generated from oxygen precipitates [4,5]. The deep-level emission remains at room temperature as the 0.77 eV band [6,7]. The intensity of the 0.77 eV band correlates positively with the precipitated oxygen concentration [7]. It is not clear, however, whether the D1/D2 lines and the 0.77 eV band originate in the generated dislocations or in the oxygen precipitates themselves. We believe that microscopic mappings of these deep-level emissions around dislocations will give us a prominent clue to identify their origins.

The purpose of this paper is to extract the spectral component associated with the oxygen precipitates. We have developed a unique scanning-beam micro PL mapping apparatus, which enables us to measure the spatial variation of weak PL emission in the infrared region at low temperatures. We have distinguished a broad band (called D_b band) from the D lines and ascribed it to the oxygen precipitates.

Experimental Technique

Sample. The sample used for this study was a rapidly cooled and dislocated Cz Si wafer. The oxygen concentration of the ingot was determined to be about 1×10^{18} cm^{-3} with infrared absorption spectroscopy using a conversion factor of 3.14×10^{17} cm^{-2}. The distribution of dislocations was obtained by X-ray topography. The oxygen precipitation process around dislocations in the sample was investigated in detail previously [6]. A wafer was sliced from the ingot parallel to the growth direction, and a small wafer chip with a dislocated area was cut for the measurement. The sample was annealed at 1000°C for 16 h with pre-annealing at 450°C for 64 h, so that a considerable number of oxygen atoms were precipitated. A dislocated Fz wafer was also annealed as a control sample to check the effect of inadvertent contamination with transition metals, since there was a controversy as to the effect of transition metal contamination on the generation of the D lines [8,9].

PL spectroscopy. The PL spectra of the sample were measured in the temperature range between 4.2 and 295 K, using the 647 nm line of a Kr ion laser as an excitation source. Details of the measurement system were described previously [6]. After the spectral response calibration, the

spectra were plotted with the abscissa and the ordinate linearly proportional to the photon energy and the number of photons, respectively.

Microscopic PL mapping. A highly spatially resolved PL mapping on the sample was performed with the newly developed apparatus. The sample was mounted on a temperature-variable cryostat of a He closed-cycle type. The Kr ion laser beam was focused and scanned on the sample surface with a diameter of 10 µm and with a scanning range of 1 mm x 1 mm, using lenses and deflection mirrors. The PL from the sample was collected with an F=1.5 lens system. The working distance of both excitation and collection lens systems was 80 mm, so that a conventional cryostat could be fitted in the apparatus. The collected light was passed through narrow bandpass filters to extract a specific spectral component, and then transferred to a Ge detector with an image size of 3.5 mm. The position of the image on the detector was designed to be nearly unchanged regardless of the scanning position.

Results

Temperature dependence of PL. The PL spectra of the sample were measured at temperatures from 11 to 295 K. Typical spectra are shown in Fig. 1, where their intensities are normalized at their respective peaks. The relative intensity of the peak is shown in brackets in the figure. The D1 and D2 lines were observed at low temperatures, while the 0.77 eV band appeared at room temperature. The effect of the contamination with transition metals can be ruled out in our case, since neither the D lines nor the 0.77 eV band appeared in the dislocated Fz sample which was subjected to the same heat-treatment as the Cz sample. These results are consistent with the previous observation [6].

We will show that the 0.77 eV band at room temperature is not traceable to the D1/D2 lines, contrary to the previous report by the present author and his colleagues [6]. The spectrum at 11 K consists of D1, D2, and possibly D3 lines at 0.81, 0.84, and 0.93 eV, respectively. Beside these lines, a broad background emission at 0.8 - 1.0 eV was observed, which we call tentatively D_a band.

The intensities of the D1/D2 lines decrease with temperature and are buried in the D_a band above 100 K. This is consistent with the previous report [3] that the intensities of D1 - D4 lines are reduced to ≤ 1/100 of the initial value above 100 K. In contrast, the intensity of the D_a band is nearly constant up to 150 K, with no change in spectral shape. This fact indicates that the contribution of the D3 line is very weak in the spectral component at 0.93 eV at low temperatures. In the temperature range between 100 and 180 K the D_a band dominates the deep-level emission spectrum. Above 150 K, the intensity of the deep-level emission band decreases with the peak shifting parallel to the band gap and with the halfwidth narrowing. We interpret that the D_a band is quenched above 150 K and the other emission band called D_b band becomes dominant. The D_b band remains at room temperature as the 0.77 eV band. Since the peak position of the D_b band shifts parallel to the band gap, its peak position at liquid helium temperatures is estimated to be 0.83 eV. The D_b band component is negligible compared with the D1/D2 lines and the D_a band at low temperatures. The distinction between the D_b band and the D_a band will be confirmed in the next section.

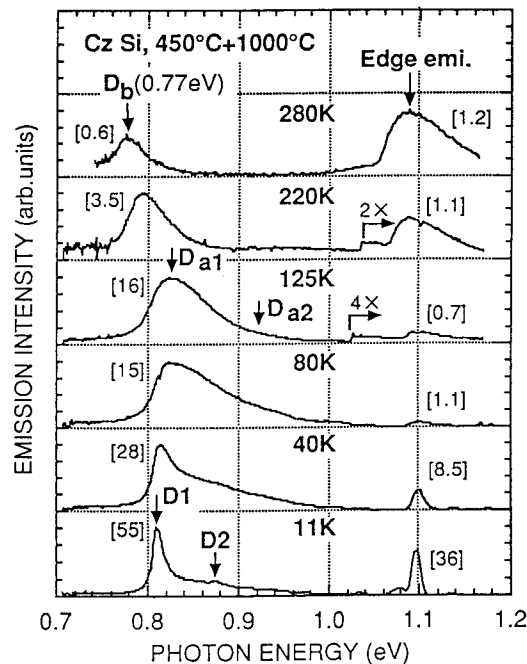**Room-temperature mapping.** The intensity mappings of the 0.77 eV band and the

Fig. 1. Temperature dependence of PL spectra of Cz Si crystal annealed at 1000°C for 16 h with pre-annealing at 450°C for 64 h.

band-edge emission at room temperature are shown in Fig. 2. Whiter gradation indicates higher intensity level. The X-ray topography on the same sample has revealed that slant line patterns correspond with bundles of dislocation lines. The intensity of the 0.77 eV band is raised along the dislocation lines. This core region is surrounded by a low-intensity region (denuded zone). A complementary intensity pattern is observed for the band-edge emission. These intensity patterns are identical with those found previously [6].

Low-temperature mapping. The intensity mappings of the D1, D_a, D2, D3/D_a, and band-

(a) D_b   **(b) Edge emission**
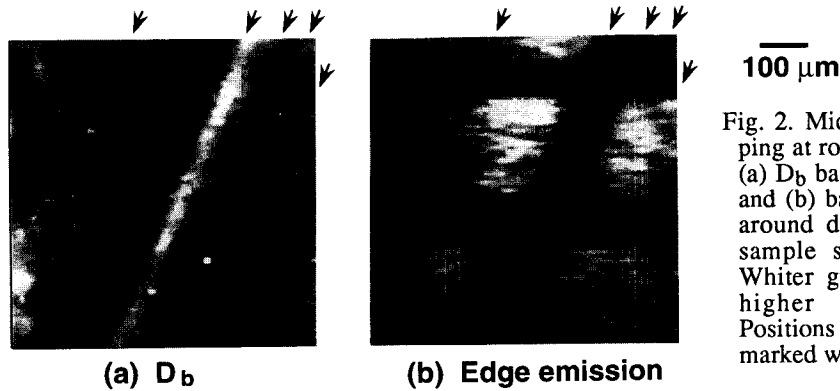
100 μm

Fig. 2. Microscopic PL mapping at room temperature of (a) D_b band (0.77 eV band) and (b) band-edge emission around dislocations in the sample shown in Fig. 1. Whiter gradation indicates higher intensity level. Positions of dislocations are marked with arrows.
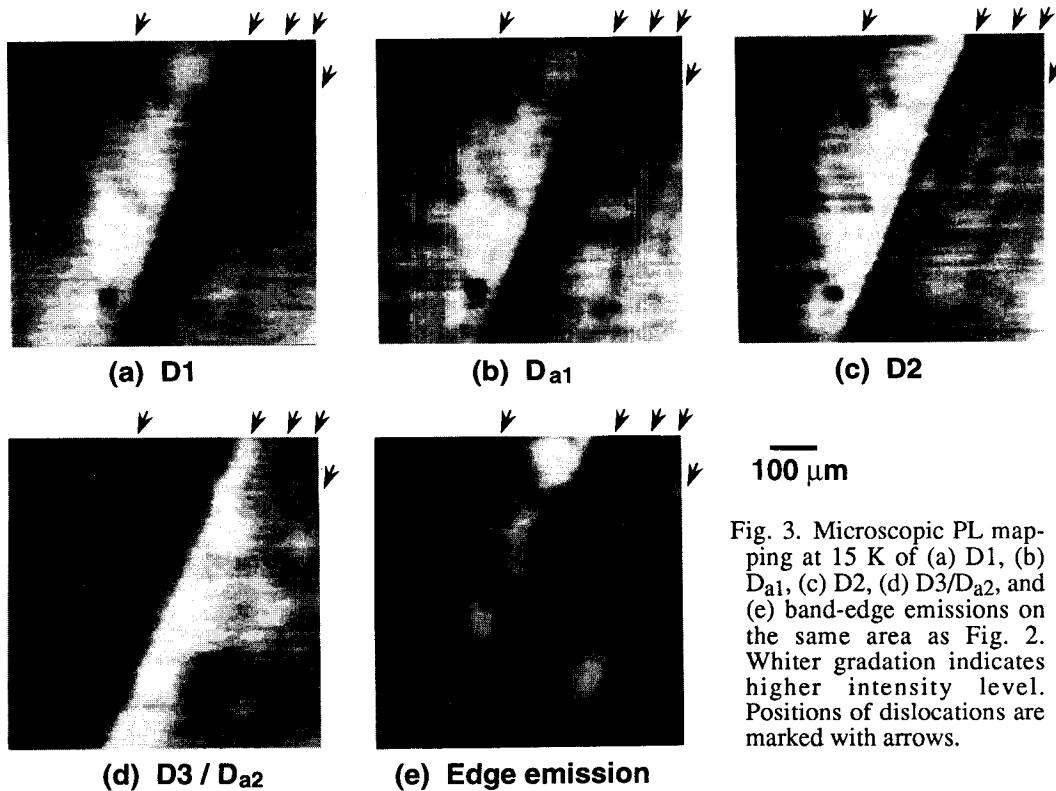

(a) D1   **(b) D_{a1}**   **(c) D2**

(d) D3 / D_{a2}   **(e) Edge emission**

100 μm

Fig. 3. Microscopic PL mapping at 15 K of (a) D1, (b) D_{a1}, (c) D2, (d) D3/D_{a2}, and (e) band-edge emissions on the same area as Fig. 2. Whiter gradation indicates higher intensity level. Positions of dislocations are marked with arrows.

edge emissions at 15K on the same area as Fig 2 are shown in Fig. 3 (a) - (e). The bandpass filters with maximum transmission at 0.81, 0.87, 0.88, 0.93, and 1.09 eV are used to monitor the respective emissions. The intensity patterns for the D1, D_a, D2, and band-edge emissions are essentially the same as Fig. 2 (b), while the pattern for the $D3/D_a$ band is the same as Fig. 2 (a). As described in the preceding section, the D_a band dominates the spectral component at 0.93 eV, and the D3 line contribution is negligible. Therefore, the D_a band in the lower photon energy region (Fig. 3(b)) shows the opposite contrast with respect to that in the higher photon energy region (Fig. 3(d)). This result leads us to suggest that the D_a band actually consists of two different bands: the lower energy band D_{a1} and the higher energy band D_{a2}.

There is a possibility that the intensity patterns for the D_{a1} and D_{a2} bands in Fig. 3 (b) and (d) are affected by the overlapping of the neighboring D1/D2 and D3 lines, respectively. In order to check this intensity mappings were also performed at 125 K, where the D1 - D4 lines are completely quenched. The D_{a1} and D_{a2} bands show the identical pattern as Fig. 3 (b) and (d), respectively. We have, therefore, confirmed that the intensity patterns for the D_{a1} and D_{a2} bands are not affected by the overlapping of the D1 - D3 lines.

It is our interpretation that the spectral change in the deep-level emission around 200 K is due to the switchover of the dominant emission band from the D_{a1} band to the D_b band. This is confirmed by a drastic change in the intensity pattern of the deep-level emission: the pattern is the same as Fig. 3 (b) at T ≤ 180 K, while it switches to a reversal contrast as in Fig. 2 (a) at T ≥ 220 K.

Discussion

The present results clearly show that the origin of the D_b band observed commonly as the 0.77 eV band at room temperature in annealed Cz crystals is different from that of the D1/D2 lines. In addition to the D_b band and the D1 - D4 lines, the D_{a1} and D_{a2} bands are shown to be present in the crystals. The appearance and disappearance of these bands depending on the measurement temperature are schematically summarized in Fig. 4, where the intensity contrast is also indicated.

The D1-D4 lines were reported to be grouped into D1/D2 and D3/D4 lines, according to their similar optical characteristics [3]. The halfwidth of the D1-D4 lines depends on the dislocation density, the method of introduction of dislocations, and the external stress [3]. The D_{a1} and D_{a2} bands underlie the D1/D2 lines and the D3/D4 lines, respectively. The D_{a1} band and the D1/D2 lines have the same intensity pattern, while the D_{a2} band has the opposite pattern. We conclude from these facts that the D_{a1} and D_{a2} bands are correlated with the D1/D2 lines and the D3/D4 lines, respectively. It should be pointed out that the decrease of the D1/D2 line intensity and the increase of the D3/D4 line intensity on the dislocation lines have also been reported in low-temperature cathodoluminescence images of a plastically deformed Fz Si crystal [10].

We believe the D_b band is associated with the oxygen precipitation; this is based on the fact that the intensity of this band correlates positively with the precipitated oxygen concentration [6,7]. A macroscopic intensity pattern of the D_b band is shown [6] to agree with the concentration profile of the precipitated oxygen concentration determined by infrared absorption spectroscopy. However, its microscopic correlation is not necessarily obvious because of the insufficient spatial
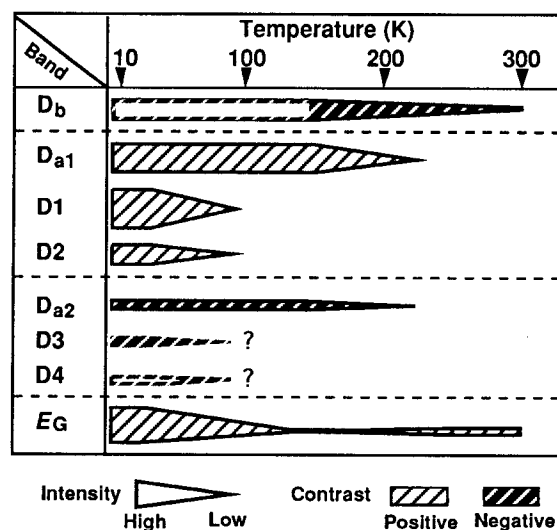

Fig. 4. Schematic chart of intensity variation of D1 - D4, D_b, D_{a1}, D_{a2} and band-edge emissions depending on the measurement temperature. Bar width represents intensity, and bar pattern distinguishes intensity contrast around dislocations.

resolution of infrared absorption spectroscopy. The increase of the D_b band intensity on the dislocation lines indicates the enhancement of the oxygen precipitation on these lines. We believe that this is due to the preferential precipitation of oxygen atoms at the dislocations. A similar effect has been observed in a transmission electron microscopy image around dislocations in an annealed Cz crystal [11].

Conclusions

The opposite intensity contrast around dislocations between the 0.77 eV band observed commonly at room temperature in annealed Cz Si crystals and the D1/D2 lines at low temperatures has revealed for the first time that their origins are different, contrary to the previous assumption. The 0.77 eV band, called D_b band in the present notation, is associated with the oxygen precipitation. The increase of the D_b band on the dislocation lines is due to the preferential precipitation of oxygen. The decrease of the D1/D2 lines on the dislocation lines is consistent with the cathodoluminescence image of a plastically deformed Fz Si crystal. The deep-level PL of annealed Cz Si crystals consists of the D_b band, the D1/D2-related D_{a1} band, and the D3/D4-related D_{a2} band, in addition to the D1-D4 lines. Further analysis of the microscopic distributions of the D_b, D_{a1} and D_{a2} bands and the D1-D4 lines will lead to fundamental understanding of the oxygen precipitation process.

Acknowledgments

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