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Analysis of Intra-Grain Defects in Multicrystalline Silicon Wafers by Photoluminescence Mapping and Spectroscopy

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Highly spatial resolved photoluminescence (PL) characterization of intra-grain defects in recent multicrystalline Si wafers for solar cells was performed. Comparison of band-edge PL intensity mapping with minority carrier lifetime mapping on a whole wafer showed that low PL intensity regions correspond to short lifetime regions. PL microscopic mapping revealed that micron-sized defects are present in these regions. We also confirmed that grain boundaries are not active recombination centers. Low-temperature PL spectra were investigated, and dislocation-related lines, D1–D4, were observed only in the defect areas. We consider that these defects are ascribable to dislocations decorated with heavy metals and responsible for great degradation of lifetime. [DOI: 10.1143/JJAP.45.L641]

KEYWORDS: photoluminescence, PL, mapping, multicrystalline Si, intra-grain, defects, dislocations, D-lines

The photovoltaic industry has recently been requiring high quality multicrystalline Si (mc-Si) wafers to fabricate higher-efficiency solar cells. Reduction of the effects of grain boundaries is important because they act as the active recombination centers and degrade the performance of the cells. So far, the quality of the wafers has been improved by enlarging the grain size. Recent wafers have a large grain size of more than a few cm and an average minority carrier diffusion length of more than 400 µm.[1)] Under these circumstances, the effects of the intra-grain defects on the performance of the wafers have become greater than those of grain boundaries.[2)] Understanding the electrical activity of the defects is essential to the development of high quality mc-Si wafers. Photoluminescence (PL) spectroscopy is a useful technique to detect defects and impurities in semiconductors. Highly spatial resolved PL characterization of the latest mc-Si wafers has been performed by the authors, and the existence of the intra-grain defects in the low minority carrier diffusion length regions has been disclosed.[3)] The purpose of this work was to analyze the origin of these defects.

We investigated the cast mc-Si wafers fabricated by a multi-stage solidification controlling method.[4)] The wafer was boron doped with a resistivity of 2.5 Ω cm, a thickness of 270 µm and a size of $50 \times 50\,\mathrm{mm}^2$. The slicing damage was etched off by the HNO_3/HF solution. The minority carrier lifetime mapping was obtained by microwave photoconductivity decay method. Before the lifetime measurement, the surface was passivated by iodine, and then the passivated layer was etched off. Since the surface passivation was not necessary for PL measurement, we used the non-passivated wafer. For the PL mapping, we used a system which had an accurate and fast X–Y stage with a position-repeatability as high as 0.3 µm and a maximum translation speed of 100 mm/s.[5)] The PL mappings were obtained at room temperature (RT) using the 532 nm line of a Nd:YVO_4 laser as an excitation source. Luminescence light was collected by an objective, passed through a spatial filter and the band-pass filters with the transmission band of 1050–1230 nm, and then detected by a photomultiplier (Hamamatsu R5509-72). First, we took a whole wafer mapping of the intensity of the band-edge emission with a spatial resolution of 100 µm, and then we zoomed in on the areas of interest with resolutions of 1–10 µm. The excitation power of the macroscopic and microscopic mappings was about 10 and 0.1 mW, respectively. PL spectroscopic measurements were performed at liquid helium temperature (4.2 K) under the excitation of the 647 nm line of a Kr^+ laser. The excitation power and laser beam diameter were about 0.55 mW and 1.0 mm, respectively. PL from the samples was transferred to a grating monochromator (Jobin Yvon HR320: $f = 320$ mm, $F = 4.2$) with 600 groove/mm grating blazed at 1.0 µm and detected by a Ge pin diode (North Coast EO-817L) cooled at 77 K. The detected signal was processed with a lock-in technique. The spectral response of the measurement system was calibrated with blackbody radiation.

Figure 1 shows a comparison between the band-edge PL intensity mapping and the minority carrier lifetime mapping on a whole wafer. To remove the effects of the edge reduction, the peripheral region (5 mm) of the sample is not shown. We found that the low PL intensity regions correspond to the short lifetime regions, while the pattern of the grain boundaries hardly correlates with the distribution of the lifetime. The spatial resolution of the PL mapping was ten times higher than that of the lifetime mapping, which enabled us to learn there are dark-line PL patterns in the short lifetime regions. We also confirmed that there are few dark-line patterns in the long lifetime regions.

We zoomed in on the short lifetime regions by PL microscopic mapping technique, as shown in Fig. 2. Various characteristic patterns, such as dark lines, micron-sized dark spots, and a dark loop were observed. Figures 2(a), 2(b), 2(c), and 2(d) is the microscopic mapping on the area marked A, B, C in Fig. 1, and D in Fig. 2(a), respectively. From the optical microscope image, we determined that these patterns do not originate from surface scratches or the grain boundaries. Therefore, we believe these patterns originate from the intra-grain defects. There was a strong resemblance between these patterns and the well-established

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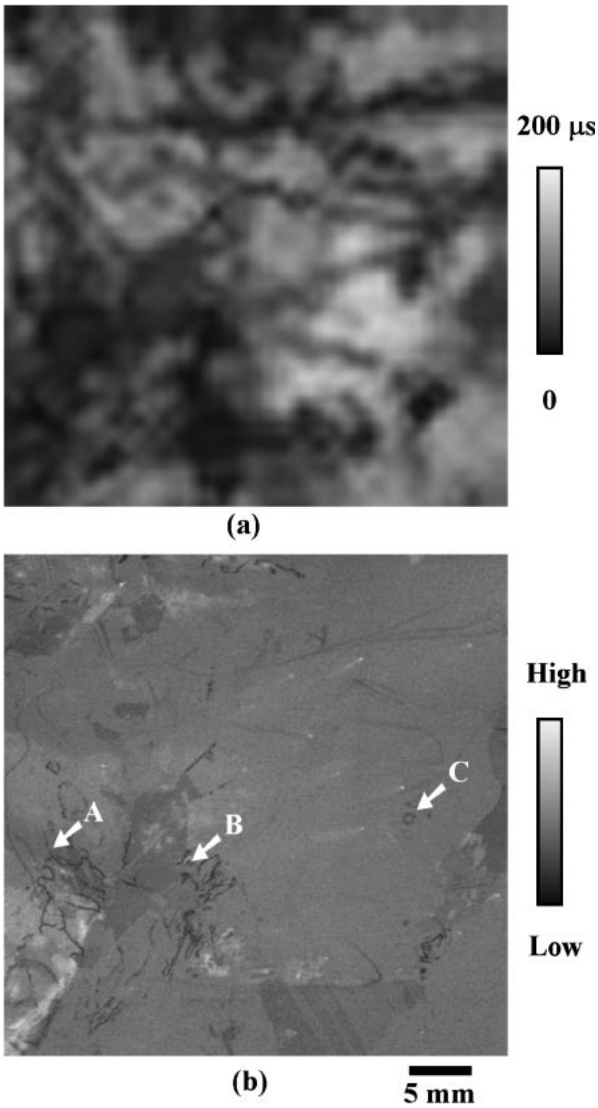

Fig. 1. Comparison between (a) minority carrier lifetime mapping and (b) band-edge PL mapping on a whole wafer. Whiter region indicates long lifetime and high PL intensity region. Spatial resolution of (a) and (b) is 1 mm and 100 μm, respectively.

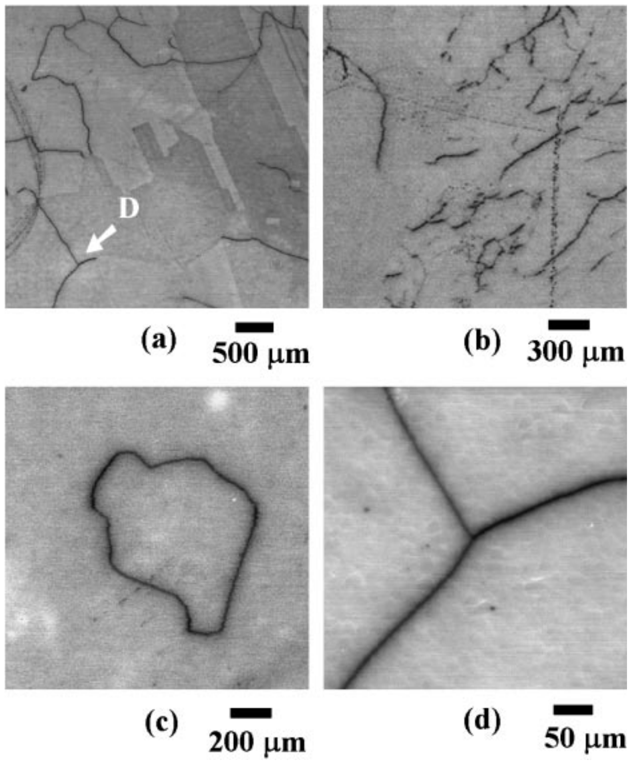

Fig. 2. PL microscopic mappings on short minority carrier lifetime region with higher spatial resolution than 10 μm. (a), (b), (c), and (d) is the identical region shown in A, B, C in Fig. 1 and D in Fig. 2, respectively.

dislocation patterns. We also confirmed that the grain boundaries have not become the active recombination centers. The results suggest that the intra-grain defects observed in the PL mapping as the dark patterns degrade the lifetime to a great extent.

To analyze the origin of the intra-grain defects, we performed low-temperature PL spectroscopic measurement. In Fig. 3, PL spectra from the long and short lifetime regions are presented. The PL spectrum of Figs. 3(a), 3(b), and 3(c) was obtained from the short lifetime region in Figs. 2(c), 2(b), and 2(a), respectively. Figure 3(d) depicts one of the examples of the spectrum taken from the long lifetime regions. The 1.093 eV line marked B_{TO} is the TO-phonon replica of the boron bound exciton. Intensity of B_{TO} from the long lifetime regions was higher than that from the short lifetime regions. In the short lifetime regions, D1–D4 lines which were reported to be due to dislocations[6] were observed besides the band-edge emission. In Fig. 3(a), the D1 and D2 lines broadened and the spectral shape was similar to the spectrum reported by Tarasov *et al.*[7] on mc-Si wafers grown by a edge defined film-fed growth technique. The intensity of the D1 line was extremely low in Fig. 3(b). To our knowledge, there have been no reports on the D-line spectrum missing only the D1 line. Broadband emission around 0.86 eV appeared in Fig. 3(c) in addition to the D1–D4 lines. The origin of the 0.86 eV band has not yet been revealed. The deep-level luminescence from the long lifetime regions was below our detection limit. The sharp line at 1.00 eV in Fig. 3(d) was not the D4 line but the zone-center optical phonon sideband of the two-hole transition in the boron bound exciton.[8] These findings show clearly that the intra-grain defects relate to the dislocations. We also found that the D-line spectral patterns, that is, the variation of the full-width at half-maximum, relative intensities and peak positions of the D-lines, differ depending on the measurement points. The D-line spectral pattern is dependent on the density and the type of dislocations.[6] In addition, the recombination activity of dislocations greatly depends on the metal contamination.[9,10] Arguirov *et al.* suggested that the D1 and D2 lines would be especially influenced by a local condition such as material stress.[11] We believe that the intra-grain defects observed in the PL mapping are dislocations decorated with the heavy metals, and we theorize that the variety of the D-line spectral shape reflects the variation of the dislocation density and the amount of metal contamination.

In summary, from a comparison between the PL intensity mapping and lifetime mapping on a whole wafer, we confirmed that the dark-line PL patterns existed in the short lifetime regions. PL microscopic mapping revealed that micron-sized defects were present in these regions. We also

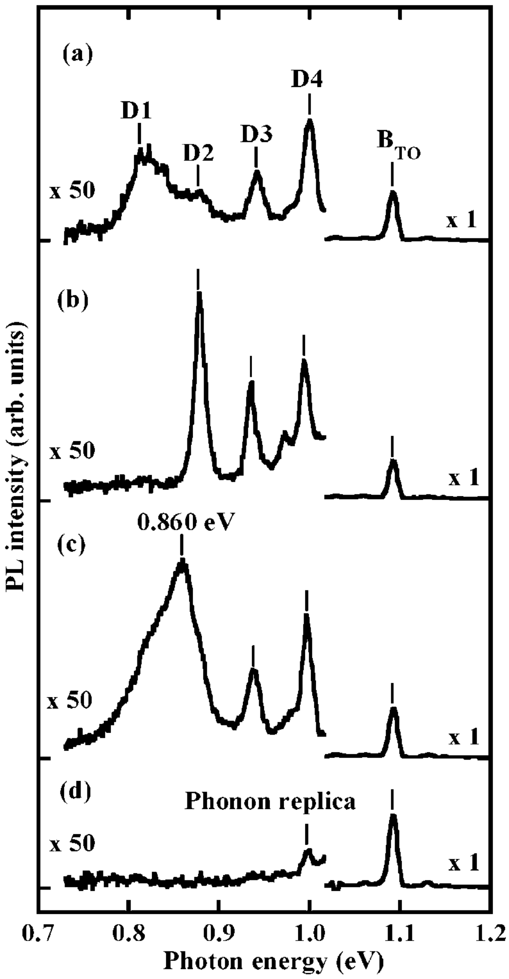

Fig. 3. PL spectra at 4.2 K of (a)–(c) short minority carrier lifetime regions and (d) long lifetime region. Symbol "×50" denotes relative amplitude.

found that the grain boundaries did not primarily degrade the lifetime but the intra-grain defects degrade the lifetime extensively. For low-temperature PL spectroscopic measurement, dislocation-related lines, D1–D4, were observed only in the defect areas. We believe that the dark-line patterns are dislocations decorated with the heavy metals. We are confident that the present results will contribute greatly to the development of high quality mc-Si wafers.

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