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Photoluminescence Analysis of Iron Contamination Effect in Multicrystalline Silicon Wafers for Solar Cells

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We investigated the effect of Fe contamination on the electronic properties of dislocation clusters in relation to oxygen precipitation in multicrystalline silicon (mc-Si). Photoluminescence (PL) spectroscopy and mapping were performed at room and liquid-He temperatures on mc-Si wafers before and after Fe contamination. PL spectra consisted of the band-edge emission, the 0.78-eV emission associated with oxygen precipitates, and the dislocation-related D-lines. The Fe contamination increased the electrically active dislocation clusters. Part of these clusters acted as preferential oxygen precipitation sites, and their electronic properties were not further influenced by the Fe contamination.

Key words: Photoluminescence, multicrystalline silicon, dislocation cluster, iron contamination, oxygen precipitation, D-line

INTRODUCTION

One of the most important electronic parameters specifying the crystalline quality of materials for solar cells is the minority-carrier lifetime. Distribution of the minority-carrier lifetime has been successfully analyzed in multicrystalline Si (mc-Si) by band-edge photoluminescence (PL) mapping[1,2] and imaging,[3,4] with the advantages of high speed and high spatial resolution. Dark lines in PL imaging, corresponding to regions of short lifetime, were identified as being due to dislocation clusters forming small-angle grain boundaries based on the agreement between PL, etch-pit, and electron backscattering diffraction patterns.[5] mc-Si contains a large number of heavy-metal and light-element impurities. Among the heavy-metal impurities, Fe is known as the most detrimental because of the electrical activity of interstitial Fe, Fe-B pairs, and other complexes.[6] Carbon and oxygen are omnipresent impurities, and carbon attracts a great deal of attention in mc-Si because of its formation of harmful SiC. In contrast, less attention has been paid to oxygen, since the oxygen concentration is on the order of 1×10^{17} cm^{-3}, where supersaturation is not expected to occur. However, the appearance of the 0.78-eV band in deep-level PL spectroscopy indicated the occurrence of oxygen precipitation in mc-Si,[7] and SiO_2 precipitates were detected by transmission electron microscopy.[8] This can be explained by the aggregation of oxygen atoms on dislocations followed by rapid pipe diffusion in the dislocations. Impurity decoration and precipitation on dislocations are well-known phenomena and are responsible for the electronic properties of dislocation clusters.[9–11] The purpose of the present study is to investigate the effect of Fe contamination on the electronic properties of dislocation clusters in relation to oxygen precipitation in mc-Si by PL spectroscopy and mapping.

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EXPERIMENTAL PROCEDURES

Samples used for the present measurements were two adjacent wafers with a thickness of 270 μm, sliced from a B-doped mc-Si ingot. The wafers had a resistivity of about 2.5 Ω cm and oxygen and carbon concentrations of about 1×10^{17} cm^{-3} and 1×10^{17} cm^{-3} to 3×10^{17} cm^{-3}, respectively. One of the two wafers was contaminated with Fe by dipping it in an $FeCl_3$ solution, followed by annealing at 800°C for 1 h. The Fe concentration introduced by this process was estimated to be on the order of 1×10^{15} cm^{-3}.[12] PL spectroscopy and mapping were performed under excitation by the 532-nm line of a Nd:YVO_4 laser at room and liquid-He temperatures. The sample was immersed in liquid He in a quartz cryostat for spectroscopy and mounted on a cryostat of He closed-cycle type for mapping. PL mappings were taken by scanning a 10-μm-diameter laser beam over the sample surface. Details of the mapping apparatus for room and liquid-He temperatures were described previously.[13,14] The spatial resolution of the present technique was determined by the volume of the photoexcitation, the diffusion of photoexcited carriers, and the spatial filter of the mapping apparatus, and was estimated to be about a few tens of microns. The resolution became higher at defective areas because of the reduction of the diffusion length there.

RESULTS AND DISCUSSION

PL spectra from the region containing a high density of dislocation clusters consisted of band-to-band (BB) and 0.78-eV emission at room temperature and the B-bound exciton (BE) lines and D-lines at 4.2 K, as shown in Fig. 1. The 0.78-eV band is due to oxygen precipitates[15,16] and is differentiated from the D-lines.[7,17] Although the origin of the D-lines is still under debate, the grouping into D1/D2 lines and D3/D4 lines based on the similarity of their optical properties, the association of D3/D4 lines with inherent properties of dislocations,[18,19] and activation of the D-lines by heavy-metal impurity contamination[20,21] have been pointed out by several researchers. The intensity of the BB and 0.78-eV emissions at room temperature decreased after Fe contamination. In contrast, only the D2 line was reduced greatly at 4.2 K after the contamination, while the other D-lines and BE line did not change substantially.

Intensity mappings of the BB and 0.78-eV emissions at room temperature are shown in Fig. 2. The BB mapping revealed the dislocation clusters as dark lines, as shown in Fig. 2a. The majority of the dark lines appeared as bright lines in 0.78-eV mapping (Fig. 1b). This supports the idea that oxygen impurities precipitate preferentially on dislocation clusters.[7] The Fe contamination reduced the intensities of both BB and 0.78-eV emissions. The dark lines in the BB mapping elongated with increase in their density (Fig. 1c), whereas the intensity pattern of the bright lines in the 0.78-eV mapping was not altered (Fig. 1d).

We obtained intensity mappings for the spectral components of the BE and D1–D4 lines at 15 K in the area marked with a square in Fig. 2, and compared them with the BB and 0.78-eV mappings at room temperature. The mappings are shown in Fig. 3, where the D1 and D3 mappings are omitted, since their patterns were similar to the D2 and D4

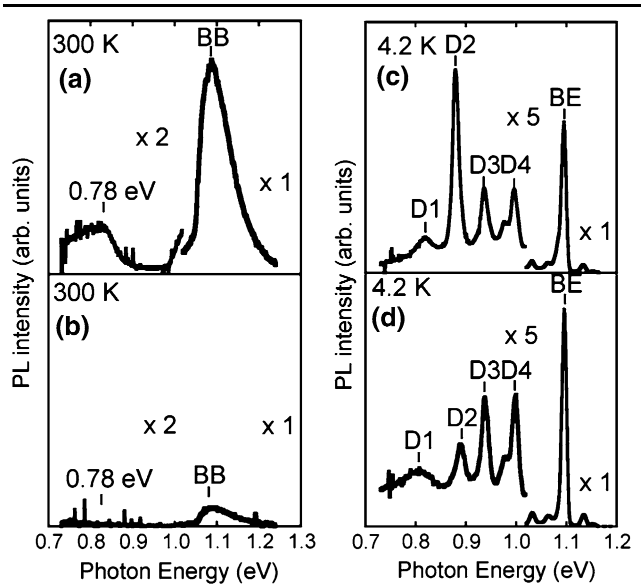

Fig. 1. PL spectra from a highly dislocated region of mc-Si at (a, b) 300 K and (c, d) 4.2 K, before (a, c) and after (b, d) Fe contamination.

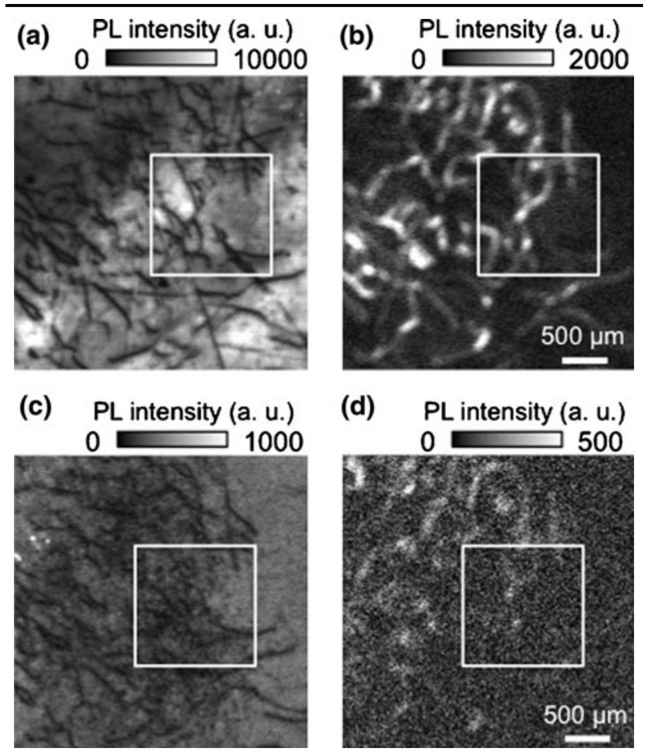

Fig. 2. PL mappings of (a, c) BB and (b, d) 0.78-eV emission from mc-Si wafer at 300 K before (a, b) and after (c, d) Fe contamination. The excitation intensity for (b) and (d) was 100 times higher than that for (a) and (c).

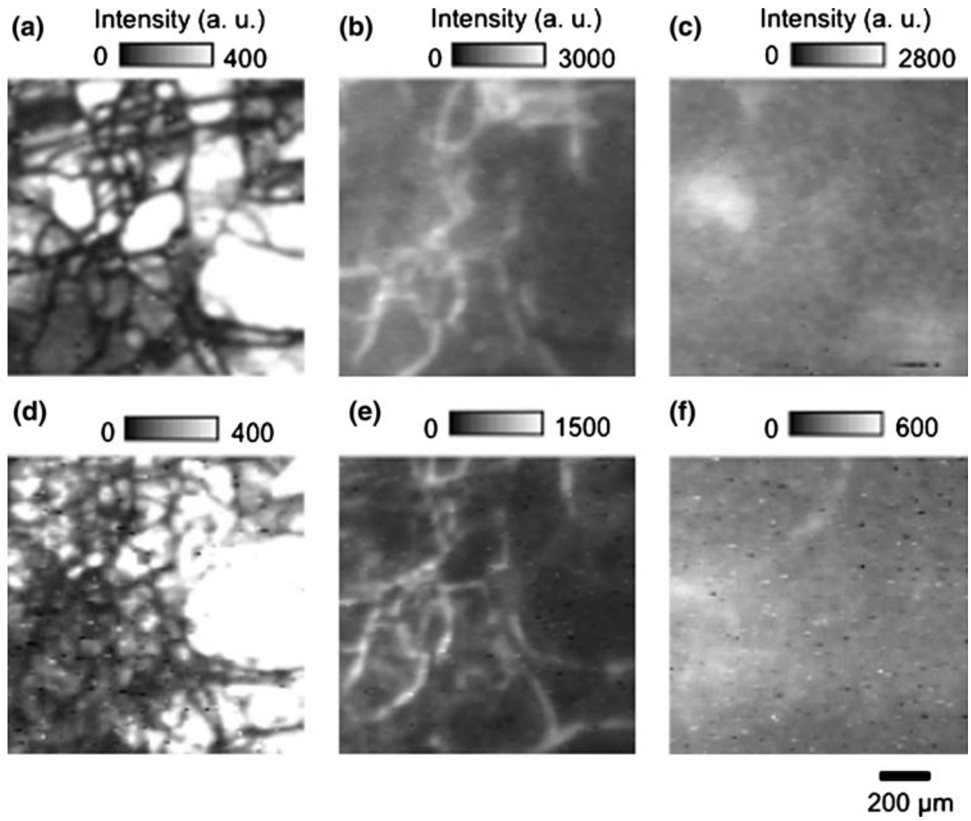

Fig. 3. PL mappings of (a, d) BE, (b, e) D4, and (c, f) D2 line in the area marked with a square in Fig. 2 of mc-Si wafer at 15 K, before (a, b, c) and after (d, e, f) Fe contamination. The excitation intensity condition was the same for (a) to (f).

mappings, respectively. Dark lines appeared in the BE mapping at a higher density than in the BB mapping, where the dark lines in the BB mapping remained in the BE mapping, as shown in Fig. 3a. We believe that the increase of the dark-line density from room temperature to 15 K is due to enhancement of the electrical activity of dislocation-related recombination centers at lower temperature. Part of the dark lines in the BE mapping appeared as bright lines in both D3 and D4 mappings. This could be very clear if the two mappings were superimposed on the computer with a fade-in/fade-out effect. The bright-line pattern looked similar to that of the BB and 0.78-eV mappings; however, substantial differences could be found: Some bright lines in the D4 mapping corresponded neither to any dark line in the BB mapping nor to any bright line in the 0.78-eV mapping (Fig. 3b). D1 and D2 lines showed blurred patterns, as in Fig. 3c, where there was very little correlation of the patterns with the BE and D4 mappings. The Fe contamination caused elongation of both dark and bright lines with increase in their densities, as shown in Fig. 3d and e. Extension of the bright-line pattern in the D4 mapping after the contamination was in striking contrast to the lack of observable change in the 0.78-eV mapping.

The present findings support the idea that the D3/D4 lines are intrinsic to dislocations,[18,19] and that dislocations are electrically activated by heavy-metal contamination.[20,22] They are also consistent with the idea that the 0.78-eV band is associated with oxygen precipitation and has a different origin from the D lines.[7,15,21] We theorize that dislocations are decorated with Fe and oxygen during crystal growth, resulting in the formation of the recombination centers responsible for D-lines at liquid He temperature and those for the 0.78-eV band at room temperature, respectively. The deliberate Fe contamination after the growth activated the dislocations further, but did not change the electronic properties of the oxygen precipitates on the dislocations.

It should be pointed out that the D2 line dominated the deep-level spectrum in the present sample, which was one of the typical types often observed in the highly dislocated region of mc-Si.[2] The other type was the D1-line-dominant spectrum which appeared in the region with lower dislocation density. Samples of the two types showed a striking difference in the pattern of deep-level PL mapping, which we will discuss in a forthcoming paper.

CONCLUSIONS

Dislocation clusters appeared as dark lines in the BB mapping, and the majority of them as bright lines in the 0.78-eV mapping at room temperature.

This indicates that part of the electrically active dislocation clusters acted as preferential oxygen precipitation sites. The Fe contamination increased these electrically active dislocation clusters but did not change the electronic properties of the oxygen precipitates on the clusters. The present results provide useful and important information on the interaction between Fe and oxygen impurities and dislocation clusters in mc-Si.

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