Electronic and structural properties of grain boundaries in electron-irradiated edge-defined film-fed growth silicon

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Electronic and structural properties of grain boundaries in electron-irradiated edge-defined film-fed growth silicon

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Abstract

Edge-defined film-fed growth (EFG) is an economical method of producing multi-crystalline silicon ribbon for solar cells. Such silicon is heavily doped with carbon. After electron irradiation, the dominant defect found in this material is the G centre, which is associated with the C_sC_i defect. In this paper, the techniques of scanning cathodoluminescence and electron backscattered diffraction pattern analysis are used to correlate the luminescence from the G centre with the grain boundary structure in electron-irradiated EFG silicon. A localised enhancement of G centre luminescence is found near twin boundaries at temperatures above 20K, whereas no such enhancement is found near low angle grain boundaries at temperatures up to 80K or at twin boundaries below 20K. This behaviour may be caused by thermal ionisation of excitons from traps at the twin boundaries, and their subsequent capture at G centres.

1. *Introduction*

An economical method of growing crystalline silicon for solar cell production is to produce it in the form of a ribbon, thereby avoiding the cost and wastage involved in slicing a boule. One technique, known as edge-defined film-fed growth (EFG), is to draw silicon from a melt through a slotted graphite die such that it solidifies into a ribbon above the die. An early review of this technique is given in [1]. EFG silicon is heavily doped with carbon from the graphite crucible and die. The performance of solar cells made from this type of Si can be improved by doping the silicon with oxygen by growing it in an atmosphere of argon and carbon monoxide, which may also introduce C into the material. EFG silicon is multi-crystalline, containing extremely elongated grains running parallel to the growth direction. Twin boundaries, regions with a high concentration of microtwins, and low-angle grain boundaries are all found in this material [2]. Despite these many structural defects, the photoluminescence spectrum of EFG silicon is identical to that from electronic grade silicon with the same boron doping, with no significant additional traps for excitons being found in EFG silicon [3]. It is important to study the response of EFG silicon to irradiation, as the growth of detrimental radiation-induced defects may be a factor in the lifetime expectancy of solar cells based on this material. A commonly-found radiation-induced centre in carbon-rich silicon is the G-centre, which has been identified as an interstitial carbon atom trapped at a substitutional carbon atom [4]. Although the G centre has been extensively studied by photoluminescence [5], it has been much less extensively studied by cathodoluminescence, and almost all studies have been made using single-crystal silicon. A decrease in low temperature (10K) CL intensity of the G band at grain boundaries in electron-irradiated silicon has been reported previously [3], but the correlation of the luminescence behaviour with the structure of the boundaries and the temperature dependence of the luminescence have not previously been investigated, to the best of our knowledge.

2. Material and experimental techniques

In this work p-type EFG silicon with a background boron concentration of 6 x 10^{15} cm^{-3}, an oxygen concentration of 8 x 10^{16} cm^{-3} and a carbon concentration of 1 x 10^{18} cm^{-3} was irradiated with 2MeV electrons to a dose of 1 x 10^{17} cm^{-2}. The as-irradiated sample was then studied by photoluminescence (PL), cathodoluminescence (CL) and electron backscattered diffraction (EBSD). The CL studies were performed in a JEOL 840 scanning electron microscope (SEM) equipped with a MonoCL cathodoluminescence system [6] and infrared spectrometer. The signal was collected using a Ge p-i-n detector operating at liquid nitrogen temperatures and analysed using a lock-in amplifier. The accelerating voltage of the SEM was varied between 7 and 30 kV, and the beam current was in the range 1-10 nA. The specimen was mounted on a liquid helium-cooled stage that could hold the temperature stable to ± 1K over a range of 8K to 300K.

EBSD studies were performed in a Philips XL30 field emission gun (FEG) SEM equipped with a state-of-the-art EBSD system and Flamenco software [7]. The specimen was tilted 70° towards the camera in order to optimise collection of the backscattered electrons. The operating voltage was 20 kV and the beam current was 50 nA. The lateral spatial resolution of the system is less than 70nm, and the angular resolution is about 0.1°. The specimen was mapped in a rectangle 272.8 μm along the growth direction and 359.6 μm perpendicular to the growth direction, using steps of 400 nm between points.

3. Results and discussion

3.1 Luminescence studies

Figure 1 is a secondary electron image of the sample illustrating clearly the high number of grain boundaries running parallel to the growth direction. Figure 2 shows the cathodoluminescence spectrum, which was found to be virtually identical to the PL spectrum (not shown), despite the different excitation mechanism. Both the PL and CL spectra are dominated by the emission at 969 meV (1.28 μm) associated with the G centre. Panchromatic CL images (formed using all wavelengths detected by the Ge detector - 1.77 μm to 1.03 μm) are therefore virtually identical with CL images formed using only 1.28 μm radiation. The advantage of using panchromatic images is that no signal is lost during a filtering step, considerably increasing the signal-to-noise ratio. Figs. 3(a) and (b) are panchromatic images of the specimen at 17K and 60K respectively with excitation by a 15kV beam. At temperatures below 20 K, the panchromatic CL images showed uniform luminescence across the specimen except at grain boundaries and surface defects, such as the long diagonal scratch on the specimen visible in Fig. 3, where competing non-radiative recombination mechanisms operate. At temperatures above 20 K, the behaviour was very different – on approaching some boundaries there was an increase in intensity before the abrupt quenching at the boundary. This effect became more pronounced as the temperature increased up to 80 K (the maximum temperature used in these experiments). Most of the boundaries in Fig. 3 (b) demonstrate this enhanced luminescence near to the boundary, but the boundary nearest the bottom of the picture does not. To illustrate this effect more clearly, Fig. 4 is a line scan of the CL intensity from the same region of each image (the region selected is indicated in Fig. 3(a)) with the data scaled to similar average intensities. The panchromatic CL images of this area have been measured at three different beam voltages, 7, 15 and 30 kV, corresponding to penetration depths of approximately 0.7, 2 and 7 µm respectively. Localised enhancement of the CL near certain boundaries above 20 K was observed for all three operating voltages, establishing that this is not a surface-related phenomenon.

It is known that in EFG silicon, carbon can be present, and even increase in concentration, near twin boundaries [8]. The G centres are well-defined molecular structures which therefore cannot exist in the boundaries themselves. Consequently, as we map across the sample there will be a dip in CL intensity from the G centres at the boundaries. The excitation for Fig. 4 was by a 15 kV electron beam, which penetrates to a depth of about 2 µm, and also spreads laterally by about the same amount, giving a minimum spatial resolution of about 2 µm. At low temperature, the beam may create excitons which diffuse through the crystal. The diffusion distance d depends critically on the concentration of traps for the excitons. In similar EFG material, d has been estimated as ~ 6 µm [9]. Consequently, the observation of dips in the signal at 20 K with full widths at half height of ~ 10 µm is reasonable. At 60 K, the reduced exciton lifetime is likely to make the diffusion lengths will be smaller, increasing the spatial resolution, towards the 2 µm limit imposed by the sphere of primary excitation. The dips in the signal on Fig. 4 are therefore sharper for 60 K than for 20 K. The surprising result is the increase in the CL signal near some of the boundaries.

3.2. EBSD studies

To understand why some of the grain boundaries in this sample cause localised enhancement of the luminescence above 20K and others do not, the nature of the grain boundaries was investigated by electron backscattered diffraction (EBSD). EBSD is an SEM-based technique that uses the angular dependence of the backscattered electron signal to extract information about the crystal structure and orientation of the near-surface layer of the specimen. The correlation of the area studied by CL and that investigated by EBSD was, therefore, easily achieved. The data obtained from EBSD were analysed using VMAP [10] to produce pole figures and orientation maps.

Fig. 5 is a relative Euler plot of the EBSD mapping data. Analysis of the EBSD data indicates that the majority of the boundaries in this material are 60°, Σ3 twin boundaries (labelled 1 in Fig. 5), and a few low angle grain boundaries (such as that labelled 2 in Fig. 5) are also present. Upon correlation with the CL data, it is evident that the local enhancement of the luminescence occurs only near the twin boundaries, and not at the low angle grain boundary.

The temperature at which we observe the change in luminescence behaviour is in the range at which thermally-excited transfer of excitons occurs between different optical centres, very close to the temperature at which thermal ionisation of excitons begins to take place [5]. It is therefore possible that above 20 K excitons may be thermally ionised from traps in the twin boundaries, and that these excitons subsequently diffuse away from the boundaries and are captured at G centres nearby. It is entirely reasonable that the nature of the exciton traps in twin and low angle grain boundaries is very different, and that the thermal ionisation of excitons trapped at the low angle grain boundary does not occur. Upon careful examination of the 17 K data presented in Fig. 4, it is also apparent that there are more competing non-radiative recombination centres at the low angle grain boundary, as the G-line luminescence is more strongly quenched at this boundary, with the luminescence at the boundary being only 65% of that in the neighbouring bulk. At the twin boundaries the luminescence is about 80% that of the neighbouring grains.

4. Conclusions

In conclusion, we report the first study correlating the luminescence from the G centre with the grain boundary structure in EFG silicon. We find that the luminescence behaviour of this centre depends on the boundary type, showing local enhancement near twin boundaries at temperatures above 20K. No such enhancement of luminescence is observed at low angle grain boundaries. We suggest that the change in luminescence behaviour at twin boundaries may have an excitonic cause, possibly the thermal ionisation of excitons from traps at these boundaries and their subsequent capture at G centres.

5. Acknowledgement

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Figure Captions

Fig. 1. Secondary electron image of electron-irradiated EFG silicon.

Fig.2. Cathodoluminescence spectrum of electron-irradiated EFG silicon taken at 17K with an accelerating voltage of 15keV.

Fig. 3. Panchromatic CL images taken at 15kV accelerating voltage. (a) was taken at 17 K and (b) at 60 K. Fig. 3(a) also indicates where the line scan shown in Fig.4 was taken.

Fig. 4. Line scans of CL intensity for panchromatic images taken at 17K and 60K along the line indicated in Fig. 3 (a).

Fig. 5. Relative Euler map generated from EBSD data, showing twin and low-angle grain boundaries (labelled 1 and 2 respectively).