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Investigation of Microdefects in Multicrystalline Silicon for Photovoltaic Applications

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ABSTRACT

Electron microscope and X-ray microprobe techniques were applied to study intragranular microdefects in polycrystalline silicon solar cell material (SILSO and BAYSIX), as-grown and intentionally Fe-contaminated. Electron Energy Loss Spectroscopy (EELS) imaging revealed bright contrast in metal diffused samples. High-resolution and analytical electron microscopy identified Fe- and Cu silicide particles in the contaminated SILSO samples whereas in BAYSIX material after Fe diffusion precipitation was only observed at dislocations.

INTRODUCTION

The conversion efficiency of solar cells made up of polycrystalline silicon is not yet comparable to the efficiency of high-quality single crystal silicon [1]. For large-grain material such as edge-defined film fed growth (EFG) or directionally solidified cast silicon to be discussed here, the grain size is of the order of mm^2 to cm^2 so that well-passivated grain boundaries are no longer the main problem. A serious problem, however, is the carrier recombination within the grains.

In polycrystalline silicon the carrier diffusion length is typically shorter than the wafer thickness. Measurements of the spatial distribution of the diffusion length show a grain-to-grain variation by a factor of two to five within a single solar cell [2]. The mapping of the carrier lifetime reveals corresponding variations. Thus the solar cell efficiency might considerably be improved if all grains would be like the best grains.

The detailed structural analysis showed that grains of a high dislocation density (above ca. 10^7 cm^{-2}) generally have a short diffusion length. However, even grains of a low dislocation density exhibit a large variation of their diffusion lengths. Therefore, these variations have to be ascribed to microdefects hitherto unidentified within the grains.

A previous study of the internal gettering in Cz-Si revealed that the precipitation rate of quenched-in interstitial Fe can be used to measure the density of the microdefects acting as nucleation sites to metal precipitation [3]. Detailed investigations of EFG-silicon showed that the precipitation rate of Fe intentionally introduced in different grains scaled well with the carrier diffusion length measured before the Fe contamination: grains of long diffusion lengths consistently showed slow Fe

precipitation, whereas those of short diffusion lengths showed fast Fe precipitation [4]. These observations proved intragranular microdefects to act as nucleation sites to metal precipitation and to influence the lifetime of many grains.
The nature of these microdefects has not yet been identified. Most likely candidates are oxygen or carbon-containing precipitates or agglomerations of native defects. Obviously, these defects are electrically active after metal impurity decoration [5], however, it still is an open question whether these microdefects themselves limit the carrier lifetime and the diffusion length, or whether metal decoration is responsible for the high recombination rate at these defects.
All attempts have failed to detect these microdefects in as-grown material by electron microscopy. Therefore via heat treatment we first introduced additional metal (Fe) contaminants into polysilicon samples before we analysed the latter by conventional, high resolution and analytical electron microscopy.

EXPERIMENTAL

Cast p-type polycrystalline silicon wafers (SILSO and BAYSIX) were characterized by Surface Photovoltage (SPV) measurements to determine the carrier diffusion length. After splitting the samples, Fe was evaporated onto one part, whereas the other part was studied as-grown. Fe diffusion was performed for 1 hour at 1050°C, with the Fe solubility being 10^{15} cm^{-3}. Some BAYSIX samples were Fe-diffused at 1150°C to increase the Fe content. After quenching Fe remained interstitials or formed Fe-B pairs. Annealing at 250°C caused the Fe-B pairs to break up followed by precipitation of mobile interstitial Fe.
Electron microscopy was performed in a JEM 4000 EX high-resolution electron microscope (HREM). Electron energy loss-spectroscopy (EELS) and imaging were performed in an energy selective microscope (ZEISS EM 902) creating an image with electrons of specific energy loss compared with the incoming electron beam. For energy dispersive X-ray spectroscopy (EDXS) a Phillips CM 20 was used. X-ray microanalysis mapping of the as-grown samples was performed at the Lawrence Berkeley Laboratory synchrotron (Advanced Light Source).

RESULTS

In order to identify metal decorated defects, Fe diffused and as-grown samples were used for EELS imaging. Figure 1a shows an EELS image typical of a Fe-diffused sample. Using the selected energy loss of 63 eV ($M_{2,3}$-peak of Fe) Fe-decorated defects are expected to appear in bright contrast. Bright spots similar to those in figure. 1a are easily detectable in all Fe-diffused samples. In as-grown samples such bright contrasts also appear, but not so frequently. Such a decorated defect (small dot at the center marked by an arrow) is shown in figure 1b.
We also investigated these bright contrast features in EELS spot-mode. The spectra did not exhibit the charactristic energy-loss edge of iron or any other element, probably owing to the dominating plasmon peaks of silicon in the low-energy loss range and to the small concentration of impurities. Also EELS images and spectra taken at higher energy losses did not allow these bright contrasts to be identified as Fe containing precipitates. Therefore intentionally Fe contaminated samples were analysed in detail by further electron microscope techniques.
Conventional electron microscope investigations indicated precipitation colonies in the Fe diffused SILSO samples (see figure 2). These colonies are inhomogeneously distributed, sometimes agglomerating at dislocations or in dislocation free areas. The colonies consist of two types of particles, viz. spherical and plate-like. The spherical particles show a distinct Moiré contrast with a stripe distance of about 4 to 5 nm parallel to the Si (220) planes. This value and the distance between the lattice planes revealed by HREM correspond to the values expected for CuSi precipitates.

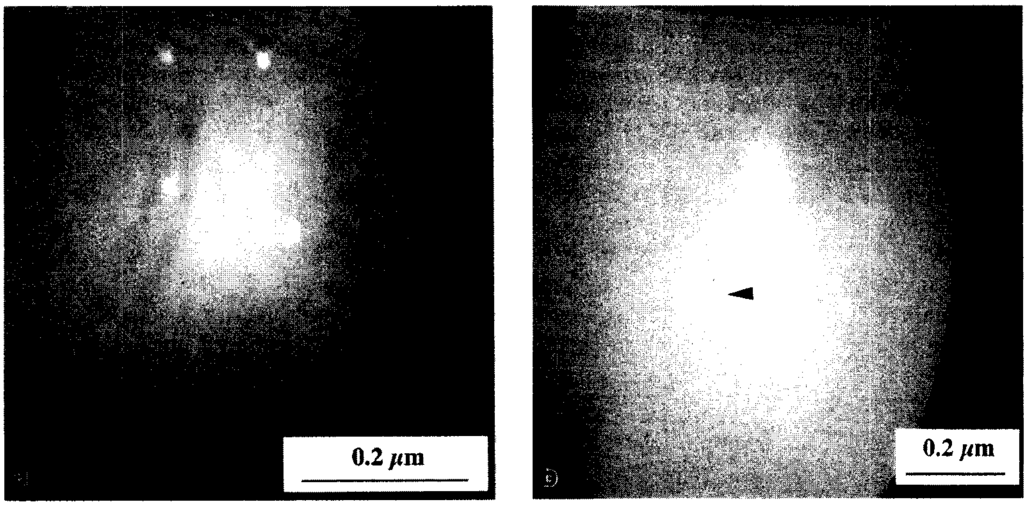

Fig. 1: EELS images of cast polysilicon SILSO samples, Fe-diffused (a) and as-grown (b)

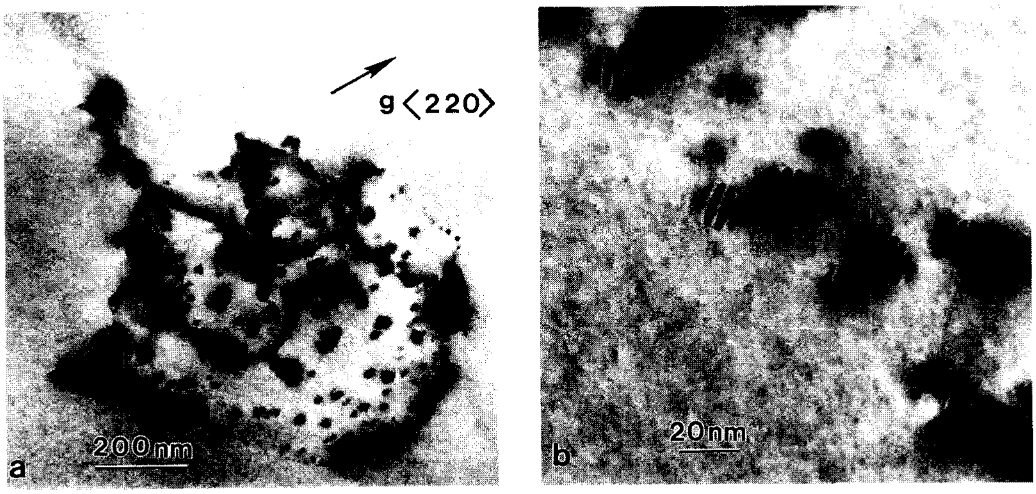

Fig. 2: TEM micrograph of precipitates in Fe-diffused SILSO samples
a) precipitate colony
b) another region at higher magnification, showing CuSi precipitates (by Moiré-fringes) too.

Plate-like precipitates with edges parallel to {111} planes are shown in figure 3. A HREM micrograph of a single particle is presented in figure 4. These particles are often characterized by a twinned structure with respect to the Si matrix which causes Moiré-like stripes at 1.0 nm spacings parallel to the Si (111) planes. The cubic structure of these particles and the lattice plane distance observed of 0.33 nm correspond to the values expected for γ-$FeSi_2$. EDXS point analysis at the site of the precipitates confirms that they contain Cu and Fe.
To clarify at which stage of the process Cu contamination occurs, reference samples of FZ silicon were added to each annealing step. After changing the quartz tube for Fe diffusion there was no Cu

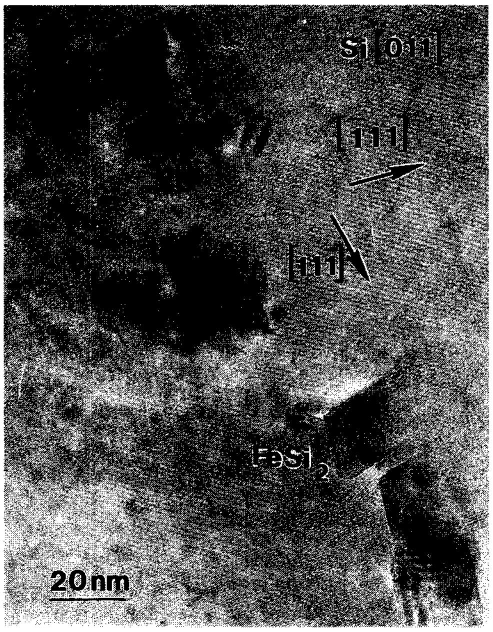

Fig. 3: Platelike precipitates of iron silicide with parallel edges to {111} matrix planes

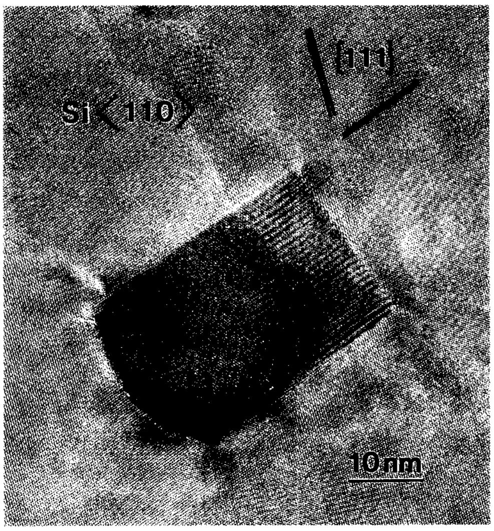

Fig. 4: High resolution micrograph of $FeSi_2$-particle in a SILSO sample, foil orientation is <110>

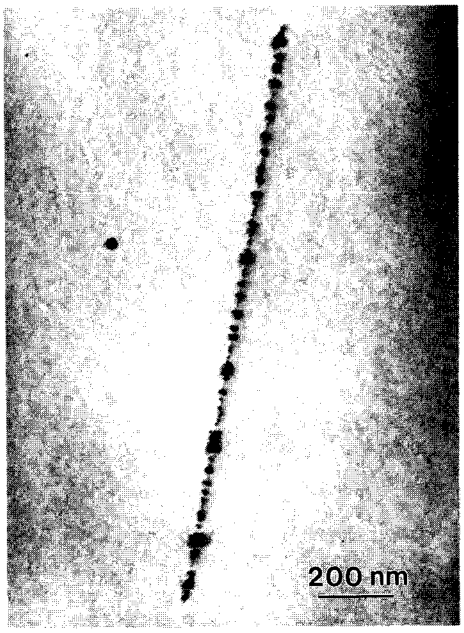

Fig. 5: Dislocation decorated with precipitates in a Fe-diffused BAYSIX sample

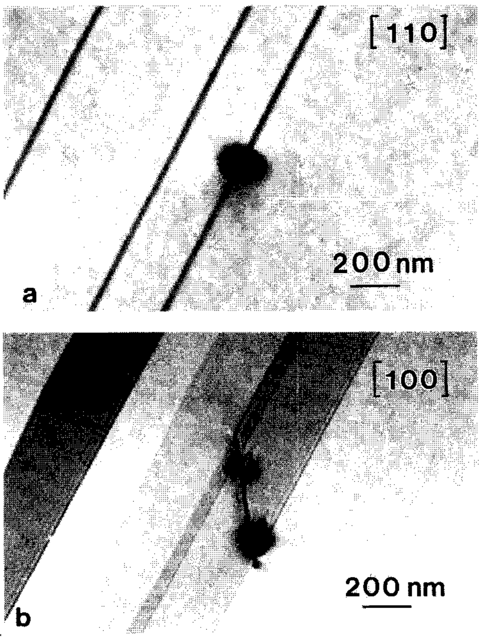

Fig. 6: Dislocation with non-characteristic strain fields in one of three microtwins in a Fe-diffused BAYSIX sample, seen in different orientations

in FZ and other samples. Thus it is concluded that the samples have unintentionally been contaminated by Cu during annealing for Fe diffusion.

The results obtained from the BAYSIX-samples were different. The characterization of the wafers by SPV showed a higher carrier diffusion length, viz. 20 to 40 µm, than in SILSO material, where it typically was 10 to 20 µm. In the upper region of the cast Si-block a diffusion length of nearly 200 µm is attained. These values suggest decisively fewer microdefects in the BAYSIX material than in SILSO silicon. All TEM and HREM investigations have not yet evidenced intragranular Fe precipitates at microdefects in the Fe-diffused BAYSIX samples. Only precipitates at dislocations have been detected as shown in figure 5. The precipitates probably contain Fe, as HREM or EDXS will prove in future.
The situation is similar for dislocations in microtwins quite often found in this material. Figure 6 shows three microtwins with a decorated dislocation lying in one of the microtwin planes. Dislocations with such non-characteristic strain fields occur at 10 to 20 µm spacings. The core of these strain fields have not yet been identified but they seem to contain small precipitates.

First X-ray microanalysis mapping of as-grown SILSO-samples has been performed at the Advanced Light Source (ALS) in Lawrence Berkeley Laboratory. These measurements show clearly the presence of several metal agglomerations like Fe, Co and Cr at specific sample sites (see figure 7a-c). A comparison between the Fe content at such intragranular sites and at a boundary showed a difference in the metal concentration of one order of magnitude(see figure7d).

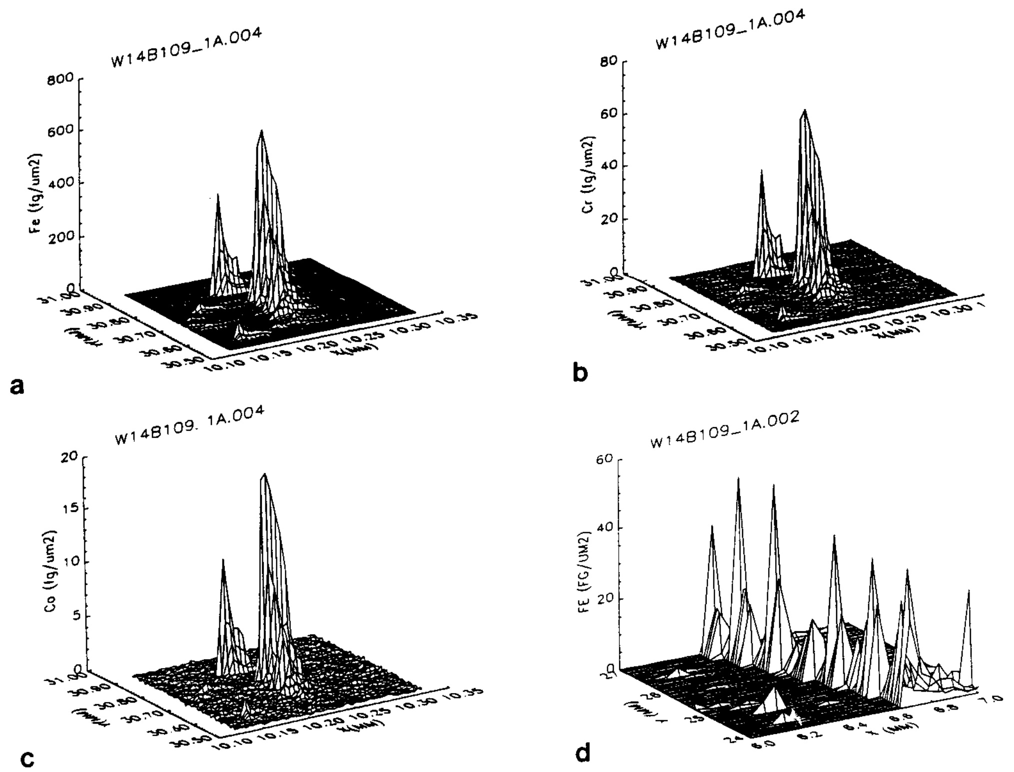

Fig. 7: X-ray microanalysis mapping of as-grown SILSO samples show the presence of Fe, Cr and Co agglomarations at the same sample sites (a-c). The metal concentration at grain boundaries is one order of magnitude smaller than at intragranular sites (d)

SUMMARY AND CONCLUSIONS

The results of this study give evidence for the presence of intragranular defects that act as nucleation sites for metal contamination, although these defects could not yet be directly identified in as-grown samples. Silicide precipitates of CuSi and γ-Fe Si2 were identified after Fe diffusion and subsequent precipitation treatment.

EELS imaging gave further evidence of the existence of metal-decorated particles in this material even in the as-grown state. This was further supported by recent X-ray microanalysis mapping of the same samples performed at the ALS in Lawrence Berkeley Laboratory [6]. These measurements clearly showed the presence of local inhomogeneities decorated with several metals such as Fe, Cr and Co.

In conclusion, intragranular defects in polycrystalline Si were found to act as nucleation sites for metal contaminants. Metal-decorated defects were evidenced to exist already in as-grown material. These findings support the model that metal-decorated microdefects are decisive lifetime killers in as-grown material, but this mechanism still has to be finally confirmed. Further studies will be directed to this question and to the identification of the microscopic nature of these microdefects.

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