IBIC Studies of structural defect activity in different polycrystalline silicon material

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Abstract

In the research of semiconducting materials, the ion beam induced charge collection (IBIC) technique can provide interesting and straightforward information about the different electronic device characteristics. This nuclear microprobe technique was used for the qualitative analysis of the spatial distribution of charge collection efficiency in several types of poly-Si material. We studied the influence of light impurities (oxygen, carbon) on electrical activity of extended defects. It is shown that oxygen segregating close to structural defects influences their electrical activity, while for carbon we did not observe the same effect. We demonstrated that IBIC can be applied to provide spatial information about the position of electrically active defects and its activation during subsequent processing.

Keywords: Silicon; Defects; Oxygen; Grain boundaries; IBIC

1. Introduction

Polycrystalline silicon (poly-Si), which can be produced by different growth techniques, can meet both the low-cost production and high efficiency requirements for solar cells. Since poly-Si wafers are inhomogeneous, various techniques have been considered to track the recombination activity of defects across entire wafers. The electron beam induced current (EBIC) technique in the scanning electron microscope is a well established technique for the characterization of defects in semiconducting materials and devices [1]. More recently, the possibility of making similar observations using a focused beam of high energy light ions has been demonstrated [2–5]. As with the related and more widely known EBIC microscopy, an energetic ion slowing down in a sample creates charge in the form of electron–hole pairs. These may drift from their origin under the influence of an internal electric field or diffuse through field-free regions of the sample. In the case of IBIC microscopy, however, a single MeV ion creates a dense path of electron–hole pairs, displaces sample atoms, and may induce sample atom spallation or fission. In addition to these atomic effects, the major difference between IBIC and EBIC are that an MeV ion will typically reach depths an order of
magnitude deeper in the sample than the electrons used in EBIC and will also undergo relatively minimal sideways scattering. Thus deeply buried structures can be probed with relatively little loss of spatial resolution.

Among different possible applications of IBIC the imaging of charge-transport properties of polysilicon solar cells is particularly interesting where the properties of grain boundaries are of considerable interest and have been previously extensively investigated by electron and optical-based probes. Donolato et al. [6] performed the first IBIC study on solar cells and subsequently presented sophisticated analytical models for the IBIC signal. Grain boundaries and other structural defects are clearly visible in typical IBIC images, which are usually presented as median-energy maps. In a median-energy map, the median charge collected from five or more ions per pixel is displayed as a false colour scale that effectively represents contours of charge-collection efficiency.

It was shown [7,8] that structural defects (such as dislocations, grain boundaries and twins) together with the impurities present in solar grade material directly influence its electrical properties and therefore solar cell performance. Light non-doping impurities like oxygen and carbon are of particular importance because of their complex interaction with structural defects in silicon, which may modify their electrical activity.

Oxygen is found in all types of silicon materials that have been processed in contact with a quartz crucible. The process of oxygen incorporation into Czochralski (CZ) single crystals has been recently reviewed by Borghesi et al. [9]. The float zone (FZ) silicon has very low oxygen content, typically below the detection limit of IR (which is about $5 \times 10^{15}$ atoms cm$^{-3}$), while CZ silicon contains $\sim 10^{18}$ at cm$^{-3}$ of oxygen. The difference in efficiency of solar cells produced on CZ and FZ material is usually 2–3% in favour of FZ cells. This was attributed to the negative impact of oxygen on the electronic characteristics of the material. On the contrary in some multicrystalline materials, like edge-defined film-fed grown (EFG) sheets, oxygen at a certain level (up to $5 \times 10^{17}$ cm$^{-3}$) was found to be beneficial for solar cell properties. Nevertheless, the mechanism responsible for such improvement was not found. It has been shown that the oxygen presence passivates a trap level at 0.35 eV of unknown origin [10] in EFG material. In multicrystalline silicon rich in various kinds of structural defects, oxygen tends to segregate close to structural defects already in the course of material production or during the thermal treatment [11,12].

Using the deep level transient spectroscopy (DLTS) on as-received EFG material, we have shown [13] that the concentration of electrically active traps, with an activation energy of $E_v=0.36$ eV, increases with increasing oxygen content. We also found that temperature treatment might significantly change the electrical activity of such material.

2. Experimental

Two different types of EFG Si sheets for the present study were grown at Mobil Solar Energy Corp. (now ASE Americas Inc.) and at Foteks Ltd (Moscow). All of the samples were boron-doped, with resistivity $2–4 \Omega$-cm and their thicknesses were about 200 $\mu$m. ASE Americas’ EFG samples were grown in an argon atmosphere with or without addition of various amounts of CO$_2$ gas using a graphite die-crucible. FOTEKS’s EFG samples were grown in vacuum using a quartz crucible and a graphite die. The crystalline structure of the latter crystals was demonstrated to be very similar to ASE Americas’ EFG samples [14–16].

IBIC measurements presented here were performed using the nuclear microprobe set-up of the Rudjer Boskovic Institute in Zagreb. The nuclear microprobe consists of the Oxford microbeam quadrupole doublet, a data acquisition and a microbeam control based on a SPECTOR software/hardware system. The measurements were made using the low current irradiation geometry explained in detail elsewhere [17]. The ion beam diameter was about 1 $\mu$m.

All samples were cleaned and slightly etched in buffered HF prior to contact deposition. Aluminium and gold were evaporated through shadow masks on a clean surface to form ohmic (gold) and
Schottky barrier (aluminium) contacts, respectively. Both $I-V$ and $C-V$ measurements were taken to insure the integrity of the diode characteristics. The DLTS spectra were taken with a SULA Technologies spectrometer. The sample temperature was ramped from 80 to 350 K, and spectra were taken at window rates from 0.2 to 50 ms.

IR measurements were performed with a Fourier transform IR (FTIR) spectrometer (Bruker IFS 113v using a Globar source) a KBr beam splitter, and a deuterated triglycerine sulfide detector. Spectra were collected from 5000 to 400 cm$^{-1}$, 4 cm$^{-1}$ resolution, and 512 scans were averaged to improve signal-to-noise ratio. A float zone single crystal silicon wafer was used as a reference to remove multiphonon absorption.

3. Results and discussion

In this study we compared IBIC images on two types of polycrystalline silicon materials grown by a similar method of ribbon pulling (EFG), however, one type was pulled from a graphite container (EFG-A) and another from a silica crucible (EFG-F). Fig. 1 shows the IR spectra for the EFG material grown from the graphite container. The oxygen presence in this material is clearly shown by a broad peak close to 1100 cm$^{-1}$.

Moreover, IR measurements performed on both types of as-received samples have always shown the presence of oxygen in the bulk, but with distinctly different concentrations and different placements in the lattice [18]. Oxygen also demonstrated a strong tendency to segregate close to structural defects already in the phase of crystal pulling [18]. If oxygen in such a case, when decorating structural defects, exhibits also significant influence on the electrical activity of structural defects, we expected the IBIC image to show different charge collection efficiency (CCE) for different parts of the sample, as a function of oxygen presence and particularly close to the grain boundaries. Furthermore, IR results have shown that, besides oxygen, these materials are particularly rich in carbon. It has been also shown that oxygen and carbon, when simultaneously present in the bulk of polycrystalline material, both tend to segregate to grain boundaries affecting therefore the electrical activity [19]. The question also arises, whether carbon alone interacting with structural defects, affects the electrical activity.

The results of IBIC measurements on an as received, carbon-rich and nearly oxygen free EFG sample are shown in Fig. 2. The IBIC image is compared with the optical micrograph (taken at the same spot), indicating that there is no measurable loss of CCE over the measured area of studied sample, which includes several larger structural defects like twin boundaries. This is in good agreement with the other findings with EBIC, indicating that twin boundaries do not show electrical activity. Moreover, this also proves that the carbon presence in the bulk, even to very high supersaturation, does not significantly affect the electrical activity of larger structural defects.

As already mentioned, samples doped with oxygen even before any thermal treatment (as-received, however, with its own thermal history) show that oxygen is not only more or less homogeneously distributed throughout the bulk in the form of isolated interstitial atoms, but also dominantly segregated close to the larger structural defects. Furthermore, to check for a possible distinction between decoration of dislocations in the bulk and grain boundaries, we made diodes on
the grain boundary (examining therefore the grain boundary and its vicinity) and within the grain which is single crystalline but with a very high density of dislocations (up to $10^7 \, \text{cm}^{-2}$). A clear difference in the DLTS signal, shown in Fig. 3, led to the conclusion that the observed oxygen-related defects are predominantly segregated to the larger structural defects like grain boundaries [19]. It has been already shown that, when a dislocated crystal contains impurities in supersaturation, the precipitation of impurities takes place preferentially at dislocations, influencing therefore the mechanical properties of Si [20].

Fig. 4(a) and (b) show IBIC images taken on samples EFG-F grown from a quartz crucible (a) and EFG-A grown from a graphite crucible and intentionally doped with oxygen (b). As shown in the figures most of the grain boundaries existing in the scanned area have enhanced electrical activity i.e. a significantly reduced IBIC signal. Therefore the first impression is that there is no significant difference between the two samples despite their quite different growth conditions.

Recently we reported on a comparative study of the impurity content in both samples grown from graphite and quartz crucibles [18]. It has been shown that samples grown from graphite crucibles contain negligible amounts of interstitial oxygen, and in this case oxygen may be intentionally added during the growth process through an oxidizing atmosphere. On the other hand, samples grown from quartz crucibles contain an apparently negligible amount of interstitial oxygen, too.
However, a certain amount of oxygen is definitely present in the bulk but dispersed in small clusters and therefore it is IR invisible in the as-received samples. Annealing of such samples at intermediate temperatures produces oxygen redistribution, i.e. its precipitation. Nevertheless, the influence of thermal treatment on C content in both types of EFG-Si is almost negligible up to very high temperatures. This is explained with Si-I deficiency in the Si lattice. From our unpublished DLTS results on the effect of thermal annealing on such materials we found that annealing at about 750°C significantly enhances the electrical activity of such polycrystalline material.

Fig. 5 shows the IBIC image of the EFG-A sample annealed at 750°C for two hours in vacuum. As shown in the figure this temperature treatment produced a significant decrease in IBIC response over all the sample area and, particularly, a widening area close to grain boundaries. Nevertheless, some areas still preserve a good IBIC response. Quite contrary to this were the findings on the EFG-F material. The figure of its IBIC

Fig. 5. 3 MeV proton IBIC image of the EFG-A sample annealed at 750°C for two hours in vacuum. Intensity is given in relative units of a grey scale, where whiter area represents enhanced electrical activity of defects. The area shown in the figure is approximately 0.3 mm².
image after annealing at 750°C is not shown since the response was extremely low (barely a few counts scattered over the scanned area). This finding for sample EFG-F is in complete accordance with FTIR analysis of the same material [18]. It has been shown that annealing at this intermediate temperatures cause a significant oxygen precipitation throughout the bulk which, in turn, produces poor electronic quality of the material.

4. Conclusion

IBIC has been used to image the spatial distribution of imperfections in charge collection for different types of EFG and EFG-like poly Si. The poly-Si materials studied were grown under different growth conditions. IR measurements showed that oxygen present in the various materials differs not only in the concentration, but also in the ways it is incorporated in the lattice (isolated interstitial position or precipitated in \( \text{SiO}_x \) form and segregated close to structural defects). We used IBIC to study the influence of incorporated oxygen on electrical behaviour of extended defects present in the material. Our findings support the assumption that oxygen, when segregated close to structural defects, influences the electrical behaviour of the “decorated” extended defect in poly-Si material. Moreover, thermal annealing at intermediate temperatures produces a quite complex response of the material that requires a further study.

References