Impact of Extended Defects on the electrical properties of Solar Grade Multicrystalline Silicon for Solar Cell Application

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Abstract. Aim of this work is to study the electrical properties and the minority charge carrier recombination behaviour of extended defects in multicrystalline silicon (mc-Si) ingots grown from solar grade silicon (SoG-Si) feedstock. The pure metallurgical SoG-Si feedstock has been produced directly by carbothermic reduction of very pure quartz and carbon without subsequent purification processes. This mc SoG-Si is studied by temperature-dependent Electron Beam Induced Current measurements and PhotoLuminescence spectroscopy and the potentiality of the combination of these two techniques in the identification of the defects which limit the quality of the base material is shown. The EBIC mapping technique shows the presence of electrically active grain boundaries at room temperature while dislocations result inactive. Dislocations become active only at temperatures lower than 250K, indicating a moderate level of metal decoration. The most detrimental defects in this material seem to be the grain boundaries and impurities dissolved in the matrix. Furthermore, the PL spectra reveal the presence of oxygen and carbon related complexes. In this work we show that the knowledge about the defect related recombination processes acquired by a combined application of EBIC measurements and PL-spectroscopy is of particular importance to tune the proper solar cell process step to be applied on such material.

Introduction

Nowadays silicon covers, as single- and multicrystalline (mc) Si almost 90% of the photovoltaic (PV) market. Currently the only commercial source for solar grade silicon (SoG-Si) is rejected and no-prime silicon from the semiconductor industry, but at the moment the shortage of Solar grade silicon is leading to high prices and a new supply of SoG-Si at reasonable costs is crucial for the development of the PV-industry.

One of the possible solutions is to produce SoG-Si via a direct metallurgical route, followed by a purification process and by a final casting step to get mc-Si wafers. The material today available is however characterized by a high impurity content and relevant defect concentration (dislocations, precipitates). So the use of this material for solar cell production depends on the possibility of improvement of the electrical quality during the cell process in order to make it compatible in terms of solar cell efficiency.

Furthermore a deep understanding of the chemical physics of defect interactions and of the impurity segregation processes is the basic background needed to develop tools able to adapt the material to PV applications.

The aim of the present work is to show that a combined application of Electron Beam Induced Current (EBIC) technique and Photoluminescence (PL) spectroscopy to study the recombination activity of extended defects in SoG-Si wafers succeed in the identification of the nature of the defects which limit the quality of the base material and therefore the efficiency of the solar cell.

Experimental details

The material studied was made by direct reduction of extra pure quartz and carbon. After tapping from the reduction furnace, the material was cooled down, etched and cleaned with DI water. The

resulting p-type ingot (size: \emptyset 250 x 120 mm², 12kg) was cut into wafers after a single crystallization step.

The local recombination activity of extended defects (dislocations and grain boundaries) was studied by the EBIC technique at room temperature and down to 100 K. The EBIC measurements were carried out with a Vega TS5136 XM Tescan Scanning Electron Microscope (SEM) equipped with an EBIC apparatus. The electron beam excitation was fixed at 25 kV at a beam current kept always below 10 pA. A quantitative analysis of the recombination activity of extended defects was obtained using the EBIC contrast C(T) defined by $C(T) = (I_b - I_g)/I_b$ where I_b and I_g are the EBIC currents in the bulk and at the grain boundary (GB), respectively. For our set-up, the minimum contrast significantly measurable has been estimated to be close to 1 % on as-grown polished samples.

Before the EBIC measurements, the samples were mechanically and then chemically polished with CP4 (HF:HNO₃:CH₃COOH = 3:5:3 in volume ratio). Thereafter, Al Schottky contacts were realized by evaporating the metal under vacuum conditions of about 10^{-8} Pa.

The lifetime was determined using the quasi-steady-state photoconductance technique (QSSPC). The sensing coil of the QSSPC instrument has a diameter of 2 cm and covers an area of approximately 3 cm². In order to reduce the recombination velocity of the charge carriers at the surface the samples were passivated by an iodine ethanol (IE) solution [1]. The measured area always includes some grain boundaries and thus provides a mean value of the recombination in the intra-grain regions and of the extra recombination at the grain boundaries.

In addition, PL-measurements were carried out to get supplementary information on radiative recombination processes occurring under illumination.

The PL spectra were recorded at 14 K with a spectral resolution of 6.6 nm, using an InGaAs detector and a quantum well laser (λ =805 nm) as excitation source.

Finally, the interstitial oxygen $[O]_i$ and substitutional carbon $[C]_s$ content was determined by Fourier Transform InfraRed (FTIR) spectroscopy in the 400-4000 cm⁻¹ range, at room temperature (ASTM, F1391.93 ; ASTM F1188 93a) and the resisistivity maps were collected by the four point probe technique (ASTM F43-93, 1996).

Experimental results and Discussion

The average resistivity value (3.4 Ohm cm) is well suited for PV application, but in each wafer the resistivity presents a highly inhomogeneous distribution ($\pm 1.4 \ \Omega$ cm) (see Fig. 1) due to active grain boundaries.

The FTIR analysis indicates a high concentration of oxygen and carbon of about 25 and 12 ppma, respectively.



Figure 1 A typical resistivity map collected by the four probe method. The measurements were carried out on an area of 3x3 cm², the points were equally distributed.



Figure 2 a) Typical PL spectrum collected at T = 12K and P = 6W/cm2) b) PL spectrum collected after an annealing at 650 °C for 10'.

A typical PL spectrum of these samples, reported in Fig. 2 a), shows in the low energy range the presence of a line at about 0.77, usually labelled P line, together with two signals respectively at about 0.91 and at 0.93 eV (H line) [2, 3]. These lines are related to the presence of C-O complex and nuclei of SiO_x , known as old thermal donors (OTD), in agreement with the high oxygen and carbon concentration measured by FTIR.

As the the P line luminescence should be related to a transition from a thermal Donors (TD-) bound exciton level to a deep level corresponding to the C-O complexes [4, 5], it could be responsible for a decrease of the carrier-lifetime. Moreover, taking into account that the presence of OTD should be avoided in substrates for solar cells, we have carried out a heat treatment at 650 °C for 10' to dissolve these complexes. The PL spectrum collected after the annealing procedure (see Figure 2b) showed the total absence of the P, H lines.

The eventual slight increase in resistivity due to the dissolution of thermal donors are not detectable by resistivity measurements due to the high inhomogeneity of the resistivity values. The lifetime variation after annealing was undetectable by QSSPC but the PL measurements indicate an increase of FE emission as expected.

Furthermore an intense peak at about 1.05 eV is present in both spectra. This peak, according to our experience is a typical PL signature of compensated mc-Si and is probably related to a transition involving dopant levels [6]. However, taking into account the energetic position of this emission, one or two shallow levels should be involved, and the related defects should play, therefore, a negligible role in lifetime losses.

The lifetime obtained by the QSSPC technique, reported in Table 1 is relatively low (1.6 ± 0.1) . As the QSSPC-technique provides only an average value over an area which is very large (3 cm^2) compared e.g. to the grain dimensions, EBIC measurements were carried out to study the spatial distribution of recombination centres in order to identify the defects responsible for the low electrical quality of this material. The room temperature EBIC maps (an example is reported in Figure 3) show the presence of many electrically active GBs, even if not all the GBs in the sample are active. The intra-grain regions seem to be free of active defects (dislocations or precipitates).



Figure 3 Room temperature EBIC image of a selected zone.

However, measurements below room temperature reveal the presence of more defects whose electrical activity increases with decreasing temperature. Fig. 4 compares two EBIC maps collected at room temperature (Fig. 4a) and 100K (Fig. 4b) respectively. In the 100K EBIC map almost all grain boundaries are active. Furthermore, in some grains extended networks of dislocations are visible.

It is well known [7] that the electrical behaviour of defects in EBIC analysis depends on the electrical levels associated to defects. Kveder et al. [7] have proposed that the room temperature recombination activity of dislocations is due to impurities decoration which introduces deep levels in the energy gap. As in our room temperature EBIC maps dislocations are not visible we can conclude that they are only moderately contaminated with impurities (metals) [8]. This can be explained by the fact that the GBs act as sinks for impurities preventing a higher decoration of the dislocations.



Figure 4 EBIC maps at room temperature (a) and 100K (b).

The analysis of the temperature dependence of the EBIC contrast allows the study of the energy levels responsible for the recombination activity of the defects and thus, an estimation of the level of defect contamination.

With this aim, EBIC contrast values (C%) of different grain boundaries and dislocations (indicated in Figure) were collected at different temperatures between 100 and 300 K. The results of the temperature analysis is reported in Fig. 5c.

Compared to literature data, the EBIC contrast values of dislocations at 100K are quite high - we cannot exclude that in our measurements the dark spot visible in the map is due to more than one dislocation.

The temperature-dependence of the EBIC-contrast of the dislocations confirms the presence of deep levels but with a moderate contamination [7, 8].



Figure 5 EBIC maps at RT (a) and at T=90K (b) of a limited zone of Figure . In the map at T=90 K are indicated the defects analysed. In c) are reported the contrasts vs temperature for defects indicated in (b).

Summary

In this work we reported a first study of solar grade silicon obtained directly by carbothermic reduction of very pure quartz and carbon. The results of the electrical characterization have shown that a single directional solidification step seems to be sufficient to reduce the metallic impurity concentration to values compatible with solar application, starting from high grade metallurgic grade silicon.

We have shown by EBIC measurements that the samples studied are characterized by the presence of a high dislocation density, but the dislocations are not electrical active at room temperature and therefore cannot be considered as direct lifetime killer, (even if we can not exclude an effect on mobility and therefore on diffusion length of minority carriers).

The low lifetime values obtained for this material should be related therefore to presence of impurities (most probably metals) dissolved in the matrix. This is confirmed by the higher GBs contrast values at room temperature compared to the C(%) values of GBs in mc-Si made from electronic grade silicon [9] which is probably due to diffusion of metallic impurities towards certain GBs (internal gettering).

Taking into account the well known gettering effect of P-diffusion step on dissolved metals (phosphorus gettering) [9,10], we are, therefore confident that the overall material quality can be improved during solar step process.

However, considering the high density of extended defects, is important to reduce and to control the diffusion of impurities to them, during any thermal solar cell process as it is widely known that extended defects can eventually compete with external gettering process [11].

Furthermore, the presence of carbon and oxygen related complexes showed by PL measurements could be annihilated by proper thermal treatments – similar to those occurring during solar cell processing – neutralizing the influence of these complexes on the minority carrier lifetime

In conclusion, we have shown that defect monitoring by local techniques like EBIC and PL is essential for designing specific defect engineering processes needed for solar grade silicon and that the preparation of a "good" solar grade silicon requires a deep physical-chemical knowledge of a multinary system (Si+ impurities+ defects). The data and information obtained by these analysis are used for an optimisation of a solar cell process for this material which is currently in progress.

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