EXTRACTION OF THE SURFACE RECOMBINATION VELOCITY AND DIFFUSION LENGTH FROM LBIC AND EBIC MEASUREMENTS AT GRAIN BOUNDARIES IN MC SILICON

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ABSTRACT: The surface recombination velocity at grain boundaries as well as the intra-grain diffusion length can be extracted in principle from Light and Electron Beam Induced Current measurements (LBIC and EBIC). This paper focuses on the influence of the grain size and the impact of hydrogen passivation steps during the solar cell process on these parameters. A set of differently treated multicrystalline floatzone (mc FZ) solar cells with different grain sizes (0.2–1 mm) was characterized by LBIC and EBIC measurements. Efficiencies reached on the processed solar cells (up to 16.0%) are the highest reported so far for material with such small grains. Also, the positive effect of hydrogenation can clearly be seen and quantitatively compared by extraction of the surface recombination velocity and the intra-grain diffusion length using a direct fitting procedure. Compared to [1] the describing theoretical model is adapted and extended [2], which allows the modeling of neighboring grains with different diffusion length. The obtained results could be very helpful for evaluation and determination of the efficiency potential of small grained wafer materials.
Keywords: defects, diffusion length, modeling, passivation, silicon solar cell

1 INTRODUCTION

Higher solar cell efficiencies and lower costs are required to make photovoltaics an economically interesting alternative to other electricity generating technologies. An approach to reduce the solar cell costs is the use of low cost silicon material which usually goes along with a high defect density. This limits the efficiency of energy conversion compared to material of high quality, so that different defect passivation steps have to be applied to low cost silicon material during the solar cell process to increase the solar cell efficiency. For this a fundamental knowledge about defect engineering is essential.

Impurities and the individual crystal structure limit the quality of multicrystalline (mc) silicon material. Besides this the grain size itself could be a limiting factor to the solar cell parameters due to a lower effective intra-grain diffusion length for smaller grains compared to larger grains e.g. because of recombination of minority charge carriers at grain boundaries. The influences of impurities, dislocations and extended crystal defects are usually superposed and an extraction of the impact of the grain size on the solar cell parameters is difficult. To minimize the impact of impurities and the interaction between them a very pure and small-grained crystalline material, in this case mc floatzone (FZ) silicon, is used, which allows to separate the influence of grain boundaries.

The comparably clean grain boundaries of mc FZ silicon material can act as a model for the detrimental effect of their recombination activity. In addition the beneficial effect of hydrogenation via firing of a hydrogen-rich PECVD (Plasma-Enhanced Chemical Vapor Deposition) SiN$_x$ layer on the recombination activity of grain boundaries can be studied and evaluated. An appropriate theoretical model allows the extraction of numerical values for the surface recombination velocity of grain boundaries and the intra-grain diffusion length on the basis of experimental EBIC [3] and LBIC [1, 2] data. This enables the quantification of the beneficial effect of hydrogenation on the considered parameters.

Allowing a quantitative comparison of different hydrogen passivation techniques and parameters, this model could be very helpful for evaluation and determination of the efficiency potential for small-grained wafer materials. The model used for determination of surface recombination velocities at grain boundaries in [1] has been extended and is now able to deal with different diffusion lengths in the two neighboring grains [2].
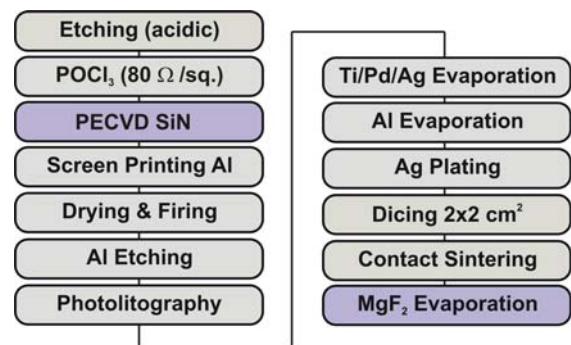
2 CELL PROCESS AND RESULTS

Figure 1: Photolithography based cell process applied to the mc FZ material. Some processing steps (dark colored) are optional and were not applied to all cells.

To demonstrate the material potential and to minimize processing induced defects or limitations a photolithography based laboratory-scale solar cell process was applied to the mc FZ silicon material. Usual block cast mc silicon may suffer from a variety of crystal defects due to the production process (e.g. impurities from the crucible), which complicates the separation of the influence of the grain size alone on the material quality and the solar cell parameters. In contrast to block cast mc silicon, mc FZ wafers were obtained from mc FZ ingots, grown from a mc seed crystal. This process results in a very pure material quality and different

average grain sizes, which rapidly increase at the beginning of the crystal growth process. With grain sizes in the broad range of a few hundred microns to the mm scale, the grain size of mc FZ silicon wafers is comparable to low cost, small grained materials like e.g. RGS (Ribbon Growth on Substrate) silicon.

Figure 1 shows the applied solar cell process which is described in detail in [4]. The achieved solar cell efficiencies of mc FZ silicon material with different grain sizes (0.2 and 1 mm), antireflective coatings and with optional hydrogenation during processing are summarized in table I. Compared to RGS with grain sizes around 0.2 mm and record efficiencies of 14.4% [4], the impurity content of mc FZ silicon is very low which results in higher efficiencies of 16.0% for the larger and 15.5% for the smaller grained solar cells. To our knowledge these are the highest reported efficiencies for mc material with such small grains.

Table I: IV data of mc-FZ solar cells ($2x2$ cm^2) with different grain sizes, antireflective coatings and with optional hydrogenation during processing.

Grain Size [mm]	FF [%]	V_{OC} [mV]	J_{SC} [mA/cm^2]	η [%]
DARC (SiN$_x$ / MgF$_2$)				
0.2	79.6	600	32.4	15.5
1	79.3	599	33.7	16.0
no hydrogenation, no ARC				
1	76.5	551	21.4	9.0

3 CHARACTERIZATION

The processed mc FZ solar cells were characterized by LBIC and EBIC measurements. Figure 2 gives an overview of the gained results which are described in detail in [1].

Summarizing the results it can be found that the recombination activity of grain boundaries varies in a broad range, not only when comparing of different grain boundaries or process treatments but also along a single grain boundary. The variation in recombination activity of grain boundaries ranges from non active up to very detrimental grain boundaries for each investigated solar cell.

In case of the larger grained solar cell two neighboring wafers with an average grain size of 1 mm and an almost identical grain structure were processed with and without a hydrogen passivation via SiN$_x$ firing. Comparing the corresponding LBIC and EBIC measurements (figure 2 B-E), the beneficial effect of hydrogenation obviously results in lower recombination activities of the grain boundaries and higher intra-grain Internal Quantum Efficiency (IQE), which is related to a higher diffusion length. The use of neighboring wafers allows a comparison of each grain boundary with and without hydrogenation and it is found that hydrogen passivation affects the grain boundaries differently. While the recombination activity of some grain boundaries vanishes completely, other grain boundaries are only insignificantly influenced.

In addition, a small grained wafer (0.2 mm, figure 2A) was identically processed compared to the large grained, hydrogen passivated wafer. The LBIC data reveal that the large grained solar cell shows broader areas of a higher IQE.
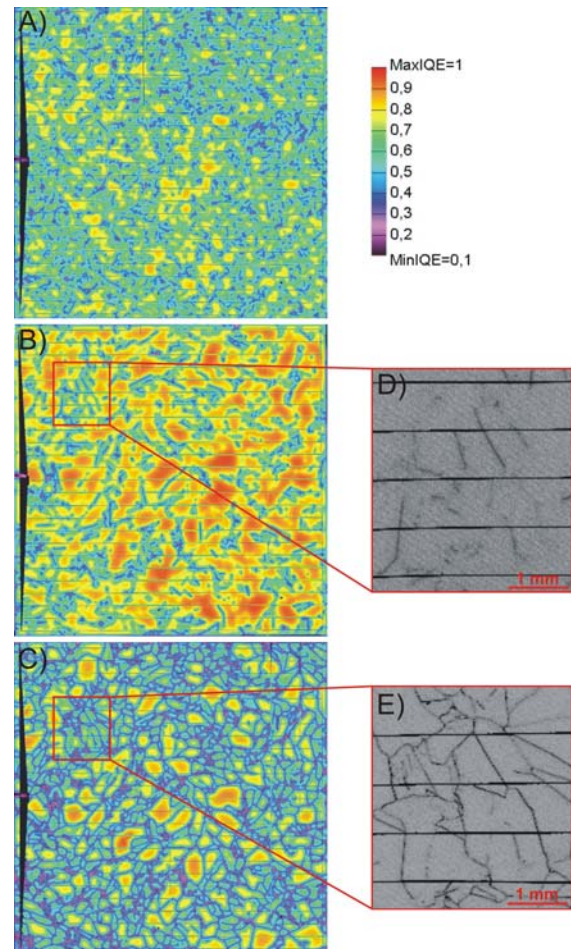

Figure 2: IQE (at 980 nm, left, same scaling for all LBIC measurements) and EBIC contrast at 300 K (right) of mc FZ solar cells with different grain sizes. Grain size of (A) is 0.2 mm, (B) and (C) 1 mm (C is a neighboring wafer to B, but without ARC and thus without hydrogenation via SiN$_x$ firing).

4 MODELING

The surface recombination velocity (SRV) at grain boundaries as well as the diffusion length (L_{diff}) of the minority charge carriers of each adjacent grain can be extracted in principle from EBIC measurements. To assess SRV and L_{diff}, linescans were extracted perpendicular to the grain boundaries and normalized to the plateau level obtained far away from these grain boundaries (so called contrast profiles). The describing theoretical model is based on the solution of the minority carrier continuity equations with suitable boundary conditions [3]. A direct fitting procedure approach allows better accuracy of the extracted values [5]. In [1] the successful implementation of LBIC profiles considering the Gaussian power density profile of our LBIC laser is described. Two symmetrical grain boundaries which were differently affected due to the hydrogenation were exemplary shown. In the following we focus further on

the experimental LBIC data.

Extracted contrast profiles often show asymmetries, which can in principle result from

- different intra-grain diffusion lengths of the neighboring grains,
- the proximity of other grain boundaries,
- decorating impurities along the grain boundary or
- a grain boundary not lying perpendicular to the surface.

Usually these asymmetries cannot be handled by the used theoretical model. Micard et al. [2] describe a model which is able to deal with asymmetries due to different L_{diff} in two neighboring grains in a measured contrast profile. Figure 3 shows the measured LBIC contrast profiles of corresponding grain boundaries of the large grained hydrogenated (red squares) and non hydrogenated (black squares) solar cell. This grain boundary is strongly affected due to hydrogen passivation. The positive effect of hydrogenation differs from grain boundary to grain boundary. The recombination activity of some grain boundaries vanishes completely while other grain boundaries show just a small influence of hydrogenation, like the shown grain boundaries in [1]. A still recombination active but strongly influenced grain boundary like the investigated grain boundary shown in figure 3 is rarely found in our investigated solar cells. Furthermore, a significant asymmetry in the measured contrast profile can be seen, especially in case of the hydrogenated solar cell. At first, a direct fitting procedure assuming the same diffusion length for both grains was applied (blue curve). Comparing the measured data and fitting results for the solar cell with and without hydrogenation, it is obvious that this model cannot fit the measured results correctly. The implementation of different diffusion lengths for both grains leads to a much better accuracy (green curve). The theoretical background, the applicability and a comparison of these fitting approaches are described in detail in [2].
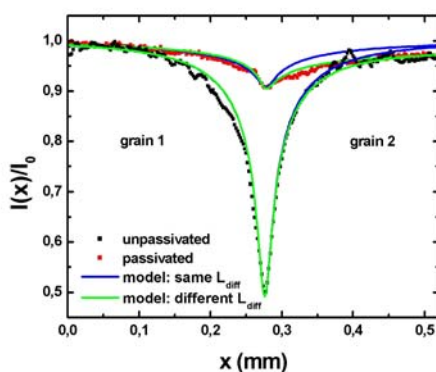

Figure 3: Measured LBIC profiles and fits applying the one (blue curve) and two (green curve) diffusion length model for the large grained cells with and without hydrogenation.

The parameters fitted according to both models show a decrease of the surface recombination velocity at the grain boundary and an increase of the intra-grain diffusion length due to hydrogen passivation. The numerical values are shown in table II.

Table II: Calculated values of the diffusion length and SRV of the grain boundary extracted from LBIC measurements. The results of the one and of the two diffusion length model are compared.

		unpassivated	passivated
same L_{diff} (blue)	L_{diff} [mm]	0.3	0.5
	SRV [cm/s]	$1.1*10^5$	$2.8*10^3$
different L_{diff} (green)	L_{diff1} [mm]	0.3	1.0
	L_{diff2} [mm]	0.2	0.38
	SRV [cm/s]	$1.1*10^5$	$2.3*10^3$

We observe a large discrepancy between the diffusion lengths of the grain 1 for the hydrogenated solar cell between the two models. Indeed, the one diffusion length model has been shown to be erroneous when the diffusion lengths on each side of the grain boundary are different and the grain boundary SRV is small enough to permit significant carrier transport across the grain boundary [6].

If, however, SRV of the grain boundary is high, there is no significant carrier transport across the grain boundary so that each side could be modeled independently using the one diffusion length model as a good approximation, which also results in different diffusion lengths for the adjacent grains. The values in table II were calculated without independent fitting on both sides of the grain boundary, but the results of both models in case of the non hydrogenated grain boundary are still in a comparable range. The two fits of this grain boundary shown in figure 3 are very similar and show a significant difference only in the plateau level for the grain on the right hand side. Due to the low SRV of the hydrogenated grain boundary the discrepancy of the two models is considerably larger in the fits (figure 3) as well as in the calculated values (table II). For this grain boundary the hydrogen passivation reduces the SRV by nearly a factor of 50.

5 SUMMARY

A laboratory-type photolithography based solar cell process was applied to mc FZ silicon wafers with different grain sizes, resulting in efficiencies up to 16.0%. Corresponding crystal structures were investigated by LBIC and EBIC measurements, which show a strong influence of the grain size as well as the applied hydrogenation on intra-grain diffusion length and recombination activity of grain boundaries. The performance of the investigated mc FZ solar cells seems to be limited by the size of the grains. Lower efficiencies of other small grained material like RGS can be explained by additional other intra-grain defects, i.e. impurities, and therefore grain size in general is not the most prominent limiting factor for efficiency in these materials. The application of a fitting procedure to the LBIC contrast profiles at grain boundaries and the extraction of the diffusion length and surface recombination velocity lead to an estimation and quantitative evaluation of the positive effect of hydrogen passivation. The applied model has been extended and can now be also applied to asymmetries in contrast profiles, if these asymmetries are caused by different diffusion lengths of the adjacent grains.

6 OUTLOOK

The presented data will be investigated further in order to find correlations between grain sizes, crystal orientation or other crystal related characteristics and the resulting solar cell parameters. The applied model will be expanded, e.g. taking the influence of another nearby grain boundary into account.

Further the influence of additional passivation by MIRHP (Microwave Induced Remote Hydrogen Plasma) to the recombination activity of the grain boundary will be investigated.

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