MICROSCOPIC ANALYSIS OF THE INFLUENCE OF SOLAR CELL PROCESS STEPS ON THE RECOMBINATION ACTIVITY OF EXTENDED CRYSTAL DEFECTS

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ABSTRACT: Gettering and passivation steps during solar cell processing influence the recombination activity of grain boundaries in silicon wafers. The purpose of this work is to study the influence of different solar cell processing steps on the recombination activity. Neighbouring wafers of intentionally contaminated multicrystalline ingots were differently processed to solar cells or treated with single $POCl_3$-diffusion, hydrogenation or temperature steps. Therefore, the influence of these solar cell processing steps on recombination activity could be evaluated individually by electron beam induced current (EBIC) measurements. Afterwards these wafers were investigated by electron backscatter diffraction (EBSD) measurements to determine the crystal orientations and the crystallographic properties of the grain boundaries. Combined EBIC and EBSD results allow the evaluation of the influence of solar cell processing steps on recombination activity in dependence of several grain boundary types. The gained results might be important for defect engineering and the development of an optimized solar cell process on cost effective and impurity-rich silicon material to reduce the recombination activity at grain boundaries in multicrystalline silicon material.
Keywords: mc Si, grain boundaries, gettering

1 INTRODUCTION

One limiting factor of solar cell efficiency is the recombination activity of extended crystal defects, like grain boundaries and dislocations, which are the dominating defects in block cast multicrystalline silicon. Spatially resolved measurements of the solar cell quality, like for example LBIC (Laser Beam Induced Current) or EBIC, indicate clearly the detrimental effect of grain boundaries on the energy conversion. These measurements show also that the recombination losses vary for different grain boundaries or even along a grain boundary. Amongst others, the tilt angle of the two neighbouring grain orientations and the distribution of impurities along the grain boundary determine the recombination activity of a grain boundary, which can be influenced by different solar cell processing steps. For example, the beneficial effect of hydrogenation via firing of a hydrogen-rich PECVD silicon nitride is discussed e.g. in [1] and [2].

In this work we focus on the recombination activity of grain boundaries after different processing steps in dependence of the angle between the two neighbouring crystal grain orientations. A better understanding of the influence of solar cell processing steps on extended crystal defects and therefore on the material quality is necessary to develop an optimized solar cell process on cost effective and defect-rich silicon material.

2 INVESTIGATED MATERIALS

Besides the impact of crystallographic properties the recombination activity of grain boundaries is also influenced by their decoration with different impurities. Therefore, multicrystalline silicon material was intentionally contaminated with iron and copper which enables the investigation of highly recombination active grain boundaries. These block cast ingots were fabricated within the SolarFocus project [3] by adding Fe and/or Cu in the melt. More details about these materials are described in [4].

Mainly an ingot with 20 ppma Fe and 20 ppma Cu was investigated. Figure 1 shows the iron and copper concentration within the contaminated wafer based on neutron activation analysis (NAA). Additionally some processing steps were also applied to wafers originating from ingots with lower contamination (2 ppma Fe, as well as 2 ppma Fe + 20 ppma Cu). In this work we focus mainly on the influence of crystallographic properties of grain boundaries and less on their contamination degree.

Wafers originating from the top of the ingots were investigated. The comparable grain structure of neighbouring wafers allows the evaluation of the influence of several solar cell processing steps on the recombination activity.
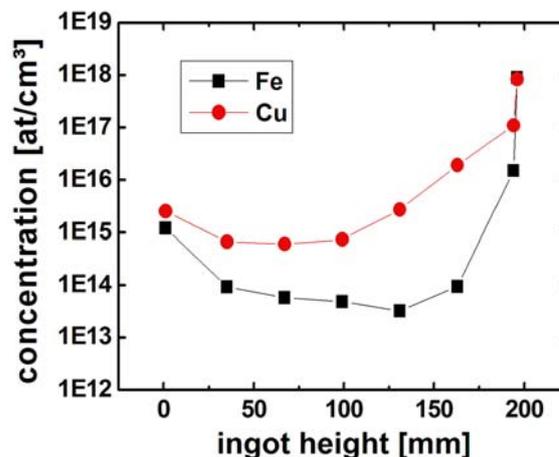
Figure 1: Iron and copper concentration over the ingot height of an ingot intentionally contaminated with 20 ppma Fe and 20 ppma Cu measured by NAA.

3 PROCESSES AND EXPERIMENTAL RESULTS

To study the influence of solar cell processing steps on recombination activity of grain boundaries two sets of samples were investigated by EBIC:

1) Solar cell based experiment (section 3.1)
Neighbouring wafers with comparable grain structure were differently processed to solar cells.
2) Wafer based experiment (section 3.2 and 3.3)
Single solar cell processing steps or only their temperature profile were applied to neighbouring wafers to separate their impact on recombination activity of grain boundaries. Parts of these samples were also investigated by temperature dependent EBIC measurements.

In addition to EBIC, EBSD (Electron BackScatter Diffraction) measurements were performed and lead to information about the crystal orientations and the tilt angle between two neighbouring grains. To describe the orientation of a grain boundary we use the Σ-notation of the coincidence site lattice. Grain boundaries without coincidence relation were indicated as random angle grain boundaries.

3.1 Solar cell based experiment

Four neighbouring wafers originating from the top region of the block cast ingot which was contaminated with 20 ppma Fe and 20 ppma Cu in the melt were differently processed to solar cells.

The applied solar cell processing sequences included a phosphorous diffusion (80 Ω/sq) while an extended temperature treatment (700°C, 1 h) was additionally applied for two samples. Each one of these differently diffused samples was covered with silicon nitride as antireflection coating. The metal front contacts were formed by evaporation through a shadow mask for samples without SiN_x layer, and by photolithography based contact evaporation for cells with SiN_x, which results in another contact structure. A firing step leads to an additional hydrogen passivation for the two samples with hydrogen-rich PECVD silicon nitride layer. Therefore, four differently processed solar cells were obtained:

A) P-diffusion, with SiN_x layer
B) P-diffusion, without SiN_x layer
C) P-diffusion, extended gettering step, with SiN_x
D) P-diffusion, extended gettering step, without SiN_x layer

Further details about the processing and solar cell parameters of these samples are described in [5]. As expected, the influence of hydrogenation can clearly be seen in solar cell parameters while the impact of the extennded gettering step is negligible in solar cell parameters. Also lifetime studies as performed in [6] show that an extended gettering step has nearly no influence on contaminated wafers.

In this work the solar cells described in [5] were investigated by detailed EBIC measurements to determine the influence of these different solar cell process steps on recombination activity. Figure 2 shows exemplarily EBIC measurements of solar cells (C) and (D). To compare the recombination activity of the differently processed solar cells, linescans perpendicular to a grain boundary were extracted and the contrast profile were calculated as defined by Donolato [7]. Afterwards, the metal contacts as well as the emitter and the eventually existing antireflection layer were etched off. Several regions which show different behaviour in their recombination activity due to variations in solar cell processing were additionally investigated by EBSD to

determine the crystal orientation and the coincidence values of the grain boundaries.
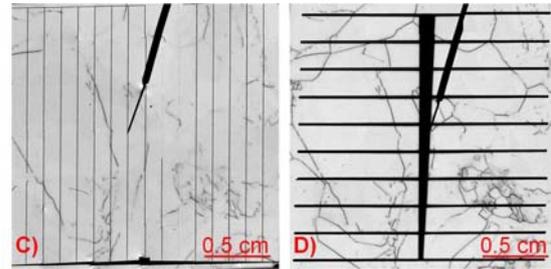
Figure 2: EBIC measurements of solar cells (C) left and (D) right (2x2 cm²). Due to the comparable grain structure of neighbouring wafers, the impact of the additional hydrogenation via firing of a silicon nitride layer on the recombination activity can clearly be seen. The different contact structure is induced by the solar cell process.

Due to the comparable grain structure of the four neighbouring wafers, the impact of the process steps on recombination activity could be determined in dependence of the Σ-value of the grain boundaries. In the following grain boundaries with different Σ-value are discussed separately.

Within the investigated areas only two recombination active grain boundaries with $\Sigma3$ coincidence were found, while all other $\Sigma3$ grain boundaries were non recombination active independently from the applied solar cell process A to D. If a $\Sigma3$ coincidence grain boundary is recombination active, an additional temperature treatment leads to a lower recombination activity (process B compared to D). Therefore, we conclude that impurities were not collected at a highly ordered $\Sigma3$ coincidence grain boundary during this additional temperature step. Also, the recombination activity of the grain boundary is further reduced after a hydrogen passivation due to firing of a hydrogen-rich SiN_x-layer. Compared to grain boundaries with other tilt angles, the recombination activity of these two $\Sigma3$ coincidence grain boundaries remains relatively strong after hydrogenation.

$\Sigma3$ is a very dominating coincidence grain boundary. In an additional experiment we investigated wafers originating from different ingot heights by EBSD. Approximately two third of the grain boundaries found were in $\Sigma3$ coincidence. As already stated, most of these $\Sigma3$ coincidence grain boundaries are not recombination active in the as grown state as well as after processing.

The recombination activity of investigated $\Sigma9$ and $\Sigma13b$ coincidence grain boundaries was enhanced after the additional temperature treatment. Therefore, it seems that grain boundaries in $\Sigma9$- or $\Sigma13b$-configuration provide a getter sink during this process step. $\Sigma9$ and $\Sigma13b$ coincidence grain boundaries of solar cells with additional SiN_x layer (sample A and C) were very well passivated.

Grain boundaries with $\Sigma27a$ and $\Sigma27b$ configuration were also found within the investigated areas. Their recombination activity could be reduced by the extended temperature treatment, while the impact of an applied hydrogenation step differs for this grain boundary type.

While one $\Sigma 27a$ coincidence grain boundary is well passivated, the recombination activity of another is nearly not affected by hydrogenation.

Additionally, several grain boundaries with random angle were found. It seems that their recombination activity is higher for smaller tilt angles. These random angle grain boundaries mostly provide a getter sink during an extended temperature treatment. Hydrogenation via SiN_x firing results in well passivated grain boundaries with very low recombination activity.

While solar cell parameters in [5] and minority charge carrier lifetime studies in [6] exhibit no significant effect of the extended gettering step, the EBIC measurements show a variation in recombination activity for some kind of grain boundaries which provide a getter sink. The beneficial effect of hydrogen passivation via SiN_x firing is obvious in the reduction of recombination activity compared to the samples without SiN_x layer. Also the effectiveness of hydrogenation depends on crystallographic properties.

These results show that besides the decoration of the grain boundary with impurities also the grain boundary properties indicated by their coincidence value have a strong influence on the recombination activity. In a further step, a group of grain boundaries with the same coincidence value should be investigated in dependence of the orientations of adjoining surfaces.

3.2 Wafer based experiment (EBIC measurements at room temperature)

Due to the complexity of the interaction mechanism of grain boundaries, impurities and process steps, single solar cell processing steps were applied to neighbouring wafers. The influence of those processing steps on minority carrier lifetime was already discussed in [6] in dependence of the contamination. In a first approach the same samples as in [6] were used for EBIC measurements within this work. Therefore, the contamination is different from the solar cell based experiment described above. The investigated Si block cast materials were intentionally contaminated with 2 pmma Fe as well as 2 ppma Fe and 20 ppma Cu in the melt.

The following processes were investigated:
a) as-grown
b) firing of a SiN_x layer
c) $POCl_3$ diffusion
d) $POCl_3$ + SiN_x + firing step.

By this procedure processing steps could be evaluated separately regarding their influence on the recombination activity of a grain boundary. In addition EBSD measurements were performed to determine the grain orientations. Fig. 3 shows exemplarily EBIC and EBSD measurements of the iron contaminated wafers after different processing steps. Comparing these samples to wafers originating from the iron and copper contaminated ingot no significant effect due to the different contamination could be observed.

The material quality evaluated by EBIC signal and contrast is differently influenced by processing steps. Regarding the EBIC measurement of the as-grown wafer (Fig. 3a) it is obvious that the recombination activity varies for different grain boundaries or even along a grain boundary. A higher material quality around grain boundaries is observed due to internal gettering effect

during crystal growth. Comparing the EBIC and EBSD measurements it is noticed that $\Sigma 3$ coincidence grain boundaries are mainly not recombination active even in the as-grown wafer.

A phosphorous diffusion leads to a higher material quality especially within a grain due to external gettering (Fig. 3c). Obviously, a hydrogen passivation via firing of a SiN_x layer is only effective after a previous gettering step (compare Fig. 3b and 3d). After a phosphorous diffusion the recombination activity of grain boundaries is diminished by a hydrogen passivation. Regarding grain boundaries with different coincidence values, the results go along with the evaluation in the solar cell based experiment above. Without previous phosphorous gettering the activation of some recombination centers is observed after the deposition and firing of a SiN_x most probably due to clustering of interstitial iron [8]. The evaluation of the EBIC measurements leads to the same results as the studies on the minority charge carrier lifetime [6].
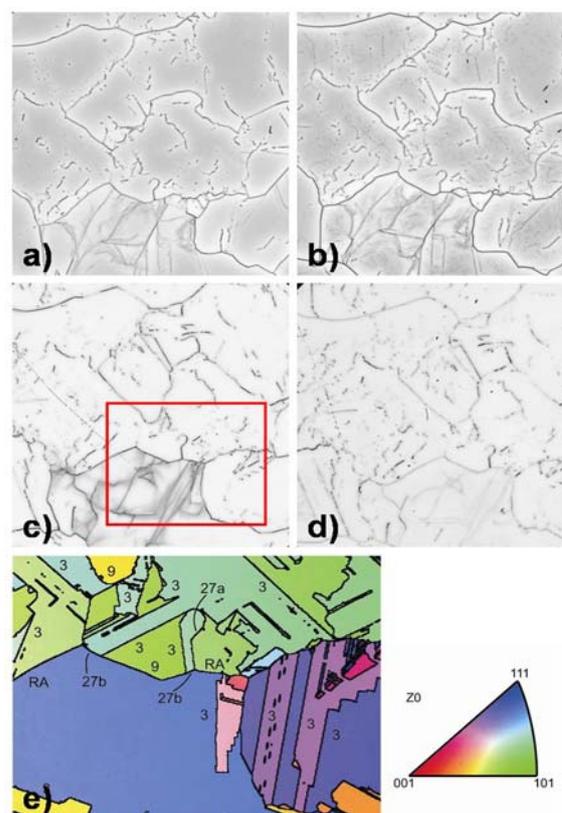
Figure 3: a)-d): EBIC measurements (8.6x8.6 mm²) of iron contaminated wafers (2 ppma) after different process steps: a) as grown, b) SiN_x + firing c) P-diffusion, d) P-diffusion and SiN_x.+ firing
e) EBSD measurement of the indicated area in c).

It is known that also temperature treatments influence the material quality and the distribution of impurities. Therefore, additional processing steps were implemented in a second set of samples to evaluate the impact of the temperature load during processing. For example, $T(POCl_3)$ means that the temperature profile of a phosphorous diffusion was applied but without any phosphorous source, while the wafers were treated only

by the temperature profile of a silicon nitride deposition in case of $T(SiN_x)$. Additionally the firing step after the SiN_x deposition was investigated separately. The processed wafers originate from the top region of the higher contaminated ingot (20 ppma Fe + 20 ppma Cu) like the samples in the solar cell based experiment.

To evaluate the impact of solar cell processing steps, linescans perpendicular to grain boundaries were extracted and compared in detail. The EBIC contrast profile varies even along a single grain boundary within a wafer e.g. due to local stresses and impurities. Due to the complex interaction of local crystal structure, impurities and processing steps these linescans vary strongly for the investigated regions on the differently processed neighbouring wafers, making comparisons between neighbouring wafers difficult.

In the following the influence of those processing steps will be discussed exemplarily in case of a random angle grain boundary. The linescans in Fig. 4 show the recombination activity of corresponding grain boundaries after different processing steps. The variation in linescans due to local in homogeneities overshadows weaker influences of processing steps. The linescans can be separated in two groups: processing sequences which include a firing step result in an enhanced recombination activity at the grain boundary compared to the corresponding wafer treatments without firing. Also other high temperature treatments without external getter sink, like $T(POCl_3)$, leads to a higher EBIC contrast compared to the standard phosphorous diffusion. Due to the missing external getter sink in case of $T(POCl_3)$, the dissolution and redistribution of impurities is mainly driven by internal gettering at grain boundaries which increases their recombination activity.

The influence of those processing steps on the EBIC profile perpendicular to a grain boundary differs for several coincidence values according to the solar cell based experiment and could not be generalized.
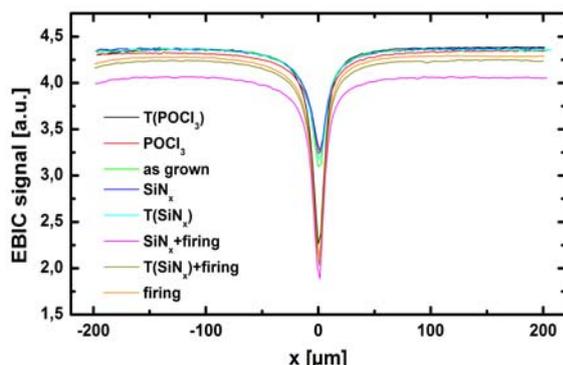

Figure 4: EBIC linescans (room temperature) perpendicular to a random angle grain boundary after different processing steps. The detrimental impact of high temperature treatments (including firing steps and temperature treatments without external getter sink) on the recombination activity of this grain boundary can clearly be seen.

3.3 Low temperature EBIC measurements

EBIC measurements at lower temperatures allow to draw conclusions on the contamination of extended crystal defects like dislocations [9]. This approach could also be used to evaluate the influence of different processing steps on the contamination of grain boundaries by measuring the temperature dependent behaviour of the EBIC contrast as defined in [7].

Fig. 5 shows the EBIC contrast values at different temperatures after several processing steps. The investigated grain boundary is the same as shown in Fig. 4 and discussed above. The behaviour of EBIC contrast values in dependence of temperature has changed for processing sequences with firing step or high temperature treatment without external getter sink indicated by their different gradient in dependence of temperature. Therefore, the impurity content at this grain boundary is strongly influenced by the applied processing steps. If a splitting of the contrast profiles between groups of processing steps is observed, then it is only between the two aforementioned ones.
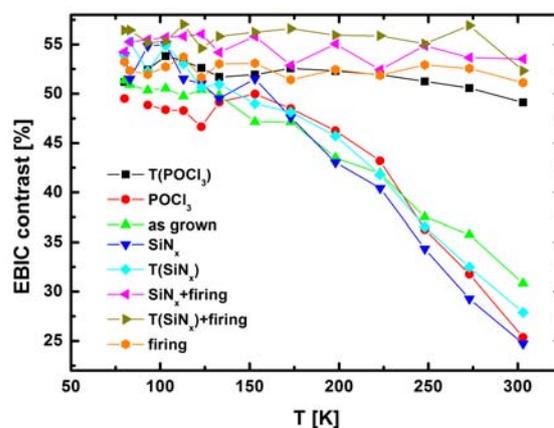
Figure 5: Temperature depending EBIC contrasts of the same grain boundary as in Fig. 4. The different behaviour after processing steps indicates that the content and distribution of impurities change after several processing steps.

4 SUMMARY

Measurements of the recombination activity of grain boundaries and the crystallographic properties were combined to evaluate the impact of different solar cell processing steps on material quality in dependence of different types of grain boundaries.

Process steps like P-gettering and hydrogenation have a strong influence on the recombination activity of grain boundaries as well as the intra-grain material quality. The impact of these process steps cannot be generalized for all grain boundaries and depends on their properties. For example, the impact of solar cell processing steps is related to the angle between the crystal orientations of two adjacent grains. This could be shown for different coincidence values of grain boundaries in the case of applied hydrogenation or variations in gettering steps. In dependence of their coincidence value some grain boundaries provide an internal getter sink during an extended getter step which results in an enhanced recombination activity. Also the effectiveness of hydrogenation is influenced by the coincidence conditions. Grain boundaries were only passivated by firing of a hydrogen-rich SiN_x layer after a previous gettering step. Without such a previous gettering step grain boundaries were not effectively

passivated. Other crystallographic parameters besides the coincidence conditions like the orientation of the adjoining crystal planes at the grain boundary or local stresses were not taken into account so far.

The temperature dependent behaviour of the EBIC contrast can be changed by solar cell processing steps, especially after firing or high temperature steps without external getter sink. Therefore, the impurity content and their distribution at the grain boundary can strongly be influenced by those process sequences.

5   ACKNOWLEDGEMENT

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