EVALUATION OF PROCESSING STEPS REGARDING LIFETIME OF IRON/COPPER CONTAMINATED MC SI WAFERS

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ABSTRACT: It is well known that gettering and passivation steps during solar cell processing enhance the minority charge carrier lifetime (here simply referred to as lifetime) in the silicon wafers. The purpose of this work is to study the influence of different solar cell processing steps on lifetime depending on the impurity level. Therefore neighboring wafers of standard multicrystalline as well as differently contaminated ingots were treated with various $POCl_3$-diffusion and/or hydrogenation steps. The sequence of treatments is varied to check the effect of each processing step individually and to investigate if an individual processing step is less or more effective if another step was applied before. Afterwards these wafers were examined by microwave photoconductance decay measurements (µPCD). 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 detrimental impact of metal impurities on solar cell parameters.
Keywords: mc Si, impurities, gettering

1 INTRODUCTION

The use of cost effective silicon material usually goes along with a higher defect concentration, which influences minority charge carrier lifetime and solar cell parameters. A better understanding of the interaction of impurities with the solar cell processing steps is therefore necessary to develop an optimized solar cell process on cost effective and impurity-rich crystalline silicon material.

In this work we focus on multicrystalline (mc) wafers with different metal impurity content, especially of transition metals iron and copper. In order to reduce their detrimental impact, the influence of phosphorous gettering and hydrogenation as well as different combinations of these processing steps on lifetime will be discussed in particular on a standard mc silicon reference material and on iron and copper contaminated samples.

2 INVESTIGATED MATERIALS

The influence of solar cell processing steps on minority charge carrier lifetime was studied on standard industrial block cast Si material (referred to as standard block cast in the following). Neighboring wafers originating from different ingot heights and therefore with different impurity levels were investigated.

Focusing further on the impurity content, in addition to the standard block cast wafers, wafers from several experimental block cast ingots were also processed.

Table I: Overview of the experimental block cast ingots with additional Fe and Cu contamination in the melt.

Ingot number	Additional metallic impurity
(1) reference	0 ppma Fe + 0 ppma Cu
(2)	2 ppma Fe + 0 ppma Cu
(5)	2 ppma Fe + 20 ppma Cu

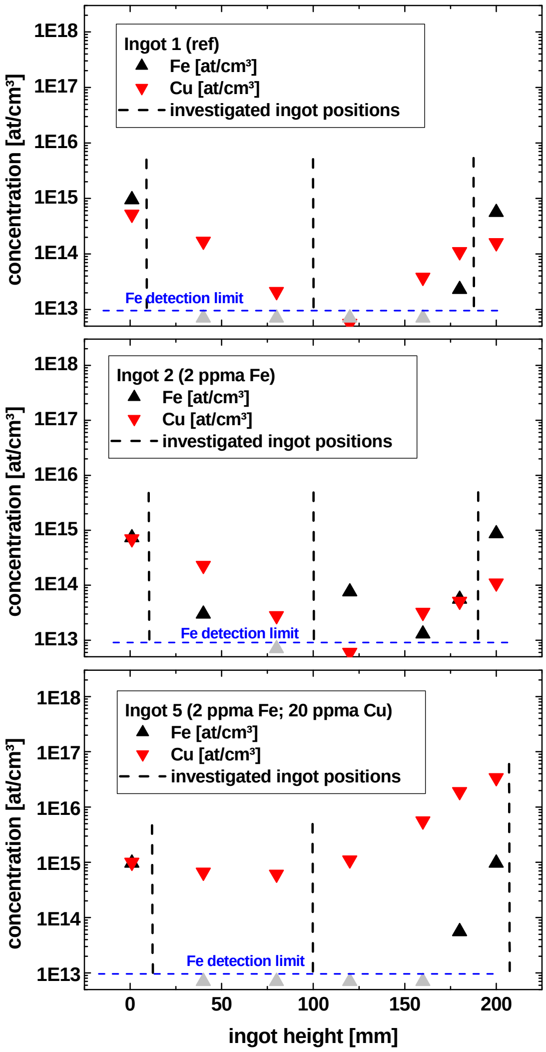

Figure 1: Iron and copper concentration over the ingot height of the experimental reference (1) (top) and the contaminated ingots (2) (middle) and (5) (bottom). Dashed lines indicate the origin of the processed wafers.

These ingots (intentionally contaminated plus one not intentionally contaminated reference ingot) were fabricated within the SolarFocus project [1] by adding Fe and/or Cu in the melt, all other crystallization conditions as well as the used standard feedstock remained constant. More details about these materials are described in [2]. Differently processed solar cells out of these ingots are discussed in [3]. In this work we investigated three ingots with different additional metallic impurity content in the melt (to be consistent with [2] and [3] the same ingot numbering is used, Tab. I). Figure 1 shows the iron and copper concentration within the contaminated wafer based on neutron activating analyses (NAA).

3 PROCESSES AND EXPERIMENTAL RESULTS

3.1 Applied standard processing sequences

Due to the variation of the impurity concentration along the height of the ingot we extracted wafers from three locations along the growth direction (extreme bottom, middle, and extreme top of the ingot). These wafers were cut to 5x5 cm² and a polishing etch was applied to remove the saw damage. To ensure a good comparability between different processing sequences shown in Figure 2, neighboring wafers out of the different ingot heights were processed, while one of these neighboring wafer remains in the as grown state (A). For $POCl_3$-diffusion (80 Ω/sq) an open tube furnace is used while hydrogenation is carried out via firing of a hydrogen-rich double sided PECVD (plasma enhanced chemical vapour deposition) SiN_x layer in a belt furnace. At the end of each processing sequence the SiN_x layer and/or the emitter were removed and the samples have been investigated via spatially resolved µPCD.

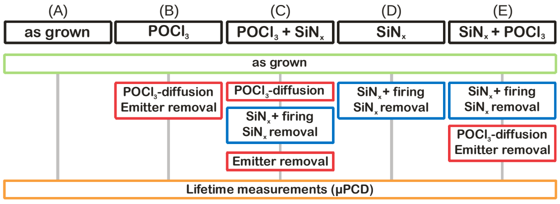

Figure 2: Experimental scheme of the different solar cell processing steps applied to neighboring standard mc Si wafers.

3.2 Standard block cast material

At first we discuss an industrial standard block cast mc Si material as an industrial reference. All process steps shown in Figure 2 were applied to this material. The µPCD results for all three ingot heights are shown in Figure 3 and 4. Comparing the non-processed as grown wafers (A) from different heights in the ingot and therefore with different impurity concentrations, the lifetimes of the middle region of the ingots are, as expected, remarkably higher than in the extreme top (segregation e.g. of metals) or bottom (high oxygen content, crystal defects) (note the different scaling).

The measurements in Figure 3 are monitoring the minority charge carrier lifetime in a standard solar cell process. The beneficial effect of a P-gettering step (B) (80 Ω/sq.) can clearly be seen for all regions of the ingot.

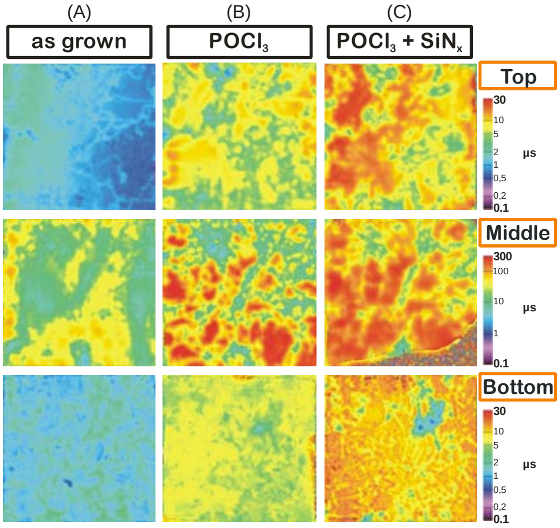

Figure 3: Lifetime maps of differently processed wafers (5x5 cm²) originating from different ingot heights of a standard block cast Si material. Note the different scaling in middle!

In this case a deposition of an additional SiN_x layer plus firing (C) leads to a further enhancement, especially for the wafers from the extreme top and bottom. Comparing process sequence (B) and (C) for wafers originating from the middle of the ingot it is found that regions of lower lifetime after process treatment (B) improve their lifetime due to additional hydrogenation (C) while there is nearly no effect on regions of higher lifetimes.

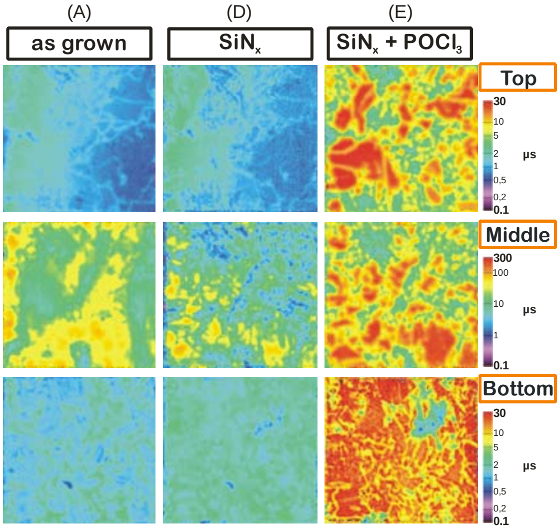

Figure 4: Lifetime maps of wafers (5x5 cm²) focusing on the influence of hydrogenation during processing sequences. Note the different scaling in middle!

Focusing further on the influence of hydrogenation (Figure 4), a SiN_x layer alone (D) (deposited on both sides for all experiments discussed in this paper) shows nearly no positive (top, bottom) or even detrimental (middle) effect on carrier lifetime.

If the fired SiN_x layer was removed and a phosphorous diffusion was added (E), the lifetimes reached for the top and bottom region are higher than in the case of P-gettering alone (B) and partially even higher than in the $POCl_3$ + SiN_x process (Figure 3, (C), bottom). Lifetime measurements of wafers originating from the middle of the ingot show nearly no difference due to process treatment (B) or (E) (Figure 3 and 4).

Due to the high temperature (>800°C) during the subsequent phosphorous gettering in process sequence (E) the hydrogen will diffuse out of wafer. The strong impact of the SiN_x layer in process (E) on defect-rich wafers originating from the bottom of an ingot will be further investigated in the following part.

3.3 Experimental ingots

Focusing on the impact of transition metals on lifetime during solar cell processing, we used neighboring wafers from the extreme bottom, middle, and extreme top of the experimental ingots describe in Table I. These wafers were processed identically to the standard mc Si material (Figure 2). Additionally we included a process treatment (F) T + $POCl_3$: firing (without SiN_x layer) and subsequently a phosphorous diffusion to check for the influence of temperature treatment alone during the firing step. To shield the wafer from contamination of other impurities in the belt furnace the sample was placed between two Czochralski (Cz) wafers during firing.

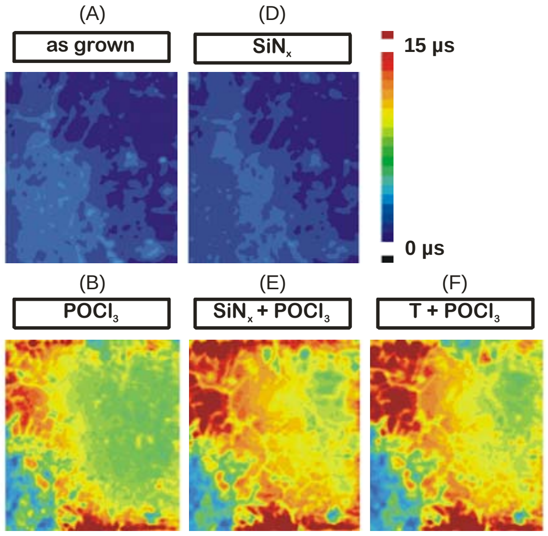

Figure 5: Lifetime measurements of differently treated Fe + Cu contaminated samples (4.5x5 cm²) originating from the bottom of the ingot (5).

Figure 5 shows exemplarily some lifetime measurement results of the iron/copper contaminated wafers originating from the extreme bottom part of the ingot, which were processed as described above. The lifetime measurements show comparable tendencies for all three ingots as discussed for the standard block cast mc Si material. As expected, the lifetimes of the contaminated wafers are lower compared to the standard block cast material shown in Figure 3 and 4. Also the quality of the non-contaminated reference ingot (1) is below the standard industrial block cast material which was discussed in section 3.2. Neutron activating analyses in Figure 1 show a relatively high impurity content also for the non-contaminated reference ingot (1). The impurity concentrations in the top and bottom region of the ingot are comparable to the iron contaminated ingot (2) in Figure 1. Therefore lifetimes of wafers originating from ingot (1) are in the same range as for wafers from the same height of the contaminated ingots (2) or (5).

While a hydrogenation step alone (D) leads to no remarkable effect for all three experimental ingots regardless of the ingot height, the lifetimes increase after phosphorous gettering (B) (shown exemplarily for the bottom of ingot (5) in Figure 5). Comparing the phosphorous diffused wafers (B), (E), and (F) it is found, that there are only small enhancements due to process (E) and (F) for samples out of the top (not shown). For wafers out of the middle of these three special ingots a firing step without SiN_x before $POCl_3$ diffusion (F) leads to the same lifetimes than a phosphorous gettering alone (B), while a previous hydrogenation (E) results in lower lifetimes for all three ingots (again not shown here).

For samples originating from the bottom of the ingot (for example Fe/Cu-ingot (5) in Figure 5) a temperature treatment followed by a phosphorous gettering step (F) results in comparable but still a little bit lower lifetimes than in process (E). It seems that for the defect rich bottom region of the ingot the hydrogen and/or especially the temperature treatment influence the underlying recombination active defects e.g. by restructuring of the defects leading to a more effective phosphorous gettering step afterwards.

3.4 Additional gettering steps

Focusing further on the strong influence of phosphorous gettering, we extended the next experiment by a post-gettering process (G) and two different pre-gettering sequences (H, I). The additional processing steps are also shown in Figure 6. We used a standard industrial $POCl_3$-diffusion as a pre-gettering step (50 Ω/sq), removed this emitter using a polishing etch and added an 80 Ω/sq-diffusion (H) which has also been used for the other gettering steps described above. For process (I) we added an annealing step between the two $POCl_3$-diffusion steps. Analogue to process sequence (F) we realized the annealing step in process (I) by firing the sample between two Cz wafers in a belt furnace. The post-gettering treatment (G) was performed by an extended drive-in step during phosphorous diffusion (700°C, 1 h) and therefore a prolonged temperature treatment of the wafer.

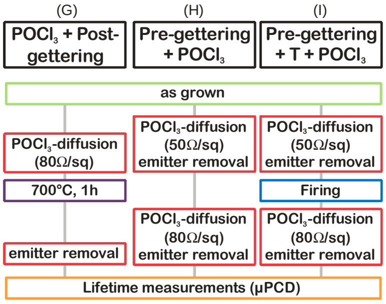

Figure 6: Experimental scheme of additional applied process steps.

These processes were also applied on wafers out of the iron and iron/copper contaminated ingots (2) and (5) as well as on the reference material (1) which was also discussed in section 3.3. As an example, the results of the lifetime measurements of the middle region of the Fe/Cu ingot are shown in Figure 7.

A full solar cell process was also applied to wafers originating from these contaminated ingots. The influence of phosphorous gettering and hydrogenation steps during solar cell processing on solar cell parameters is described and discussed in [3].

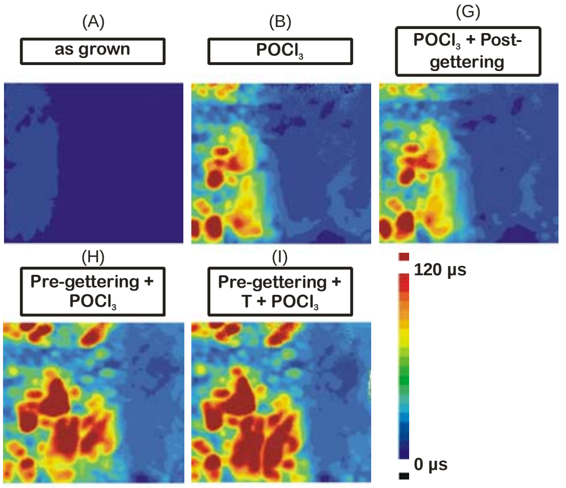

Figure 7: Lifetime measurements of iron/copper contaminated samples (4.5x4 cm²) originating from the middle height of the ingot (5) close to the crucible wall. Different gettering processes were applied.

Comparing the measurement results of the gettered (B) and the post-gettered (G) wafers out of the same ingot height it is found that the post-treatment has nearly no effect on carrier lifetime. Both process treatments result in comparable carrier lifetimes for silicon wafers with the same impurity concentration.

In contrast to the post-gettering process a pre-gettering treatment (H or I) leads to remarkably higher minority carrier lifetimes. Due to a pre-gettering process even highly contaminated wafers of the top region can reach lifetimes which are comparable to usually gettered samples (B) out of the middle of the ingot. The effect of the temperature treatment (simulated firing conditions) between the two diffusions (I) is very small. Generally, it is found that pre-gettering leads to higher intra-grain minority carrier lifetime, while the lifetime of areas around grain boundaries stays in the same range as compared to samples with a single gettering step (B). This is consistent with the operation principle of gettering (internal gettering at extended defects during high temperature steps).

The samples shown in Figure 7 originate from the edge of the Fe/Cu contaminated ingot, which results in lower lifetimes on the right side of the samples. Comparing the pre-gettering processes (H, I) to the phosphorous diffused sample (B) it is generally noticed that the area with higher lifetimes is enlarged due to pre-gettering.

For all wafers out of the bottom of the different contaminated and reference ingots we found regions where minority carrier lifetimes could not be positively influenced by any process treatment and stayed at the level of the as grown wafer (for example at the left bottom of the samples shown in Figure 5). These regions have to be further investigated by microscopic characterisation techniques to reveal the underlying structural defects.

4 SUMMARY

Process steps like P-gettering and hydrogenation have a strong influence on lifetime, especially for contaminated wafers. While hydrogenation via SiN_x firing alone shows nearly no effect, the lifetime enhancement due to P-gettering is remarkable. This can be further increased by a firing step prior to gettering. Also pre-gettering steps lead to higher lifetimes, especially in the grains.

5 OUTLOOK

The processed wafers will be investigated further to find correlations between the resulting lifetimes after different treatments and the impurity concentration and distribution using more advanced characterization techniques.

The recombination activity will be measured via electron beam induced current (EBIC). Synchrotron based analytical techniques have already been and will be further used to analyze the impact of single processing steps on concentration and distribution of metal precipitates in ingot cast mc silicon. First results on the impact of gettering steps on transition metal precipitates will be published in [4].

Further on, the influence of an additional hydrogen passivation using the MIRHP technique (Microwave Induced Remote Hydrogen Plasma) on lifetime will be investigated. Another part of the sample can be used for binding energy mapping as described in [5].

The used μPCD setup allows the mapping of the iron content via light induced dissociation of iron/boron pairs. Such measurements are expected to confirm the results gathered by μPCD.

6 ACKNOWLEDGEMENTS

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