Grain boundary effect on lifetime in high performance multicrystalline silicon during solar cell processing

Krzysztof Adamczyk [*,1], **Rune Søndenå**[2], **Mohammed Mhamdi**[1,3], **Antoine Autruffe**[1], **Gaute Stokkan**[4], **Marisa Di Sabatino**[1]

[1] Department of Materials Science and Engineering, NTNU, NO-7491 Trondheim, Norway
[2] Department of Solar Energy, IFE, NO-2007 Kjeller, Norway
[3] Sintef Materials and Chemistry, NO-0314 Oslo, Norway
[4] Sintef Materials and Chemistry, NO-7465 Trondheim, Norway

* Corresponding author: e-mail krzysztof.adamczyk@ntnu.no

High performance multicrystalline silicon wafers used in solar cell processing have been investigated with focus on quantification of the grain boundary effect on lifetime. The lifetime of a set of 16 wafers from different positions along the ingot and after different process steps – phosphorus gettering, SiNx:H layer deposition and firing - is measured by µPCD and compared with microstructural information from EBSD. This allows for analysis of the behaviour of grain boundaries and their influence on lifetime during solar cell processing. The minority carrier lifetime of HPMC-Si wafers is not increased after the gettering step, but even reduced for some samples. It is shown that the lifetime in areas close to grain boundaries is reduced during the gettering step and this has a stronger effect on the average value than the improvement within the grains. Only wafers after both gettering and hydrogenation show an overall improvement in carrier lifetimes. However, in the regions close to the bottom of the ingot, wafers show lifetime degradation after the hydrogenation process. The results are used to obtain quantitative information on recombination velocity of grain boundaries.

1 Introduction

Multicrystalline silicon (mc-Si) is widely used in the photovoltaic industry, despite the performance limiting defects and impurities that are abundant in this material [1,2]. One route to improve efficiency is to use the so-called high performance multicrystalline silicon (HPMC-Si). The structure of such material is based on reduced grain size and increased number of random grain boundaries, which correlates to an overall reduced dislocation density and a lower number of dislocation clusters [3]. Recombination activity of both grain boundaries and dislocations has been shown to correlate to the level of impurity content in the material [4, 5]. Conventional multicrystalline silicon has been studied extensively in regard to changes in defect recombination activity during solar cell processing [6-8]. Two main process steps affecting this mechanism are phosphorus diffusion gettering and hydrogenation. Gettering has a thermal budget high enough to allow impurity diffusion towards the electrically inactive emitter, but also to dissolve precipitates decorating bulk defects. This leads to a competition between the extraction of harmful, interstitial impurity atoms from the bulk and impurity re-precipitation with a different precipitate distribution, possibly leading to new defect mechanisms [9, 10]. Subsequent contact firing, usually with a hydrogen rich anti-reflection coating present, also requires high temperatures. Even though the firing time is much shorter than the gettering process, it can also affect impurity distribution [9]. During the firing step hydrogen from passivation layers or antireflection coatings is able to diffuse into the bulk and passivate bulk defects, reducing their impact on minority carrier lifetimes [11]. In conventional multicrystalline p-type material the response to these processes varies, depending on process conditions and initial impurity content and distribution. In general, it is assumed that gettering increases the average bulk carrier lifetime in multicrystalline

silicon by removing impurities, while hydrogenation has a positive effect on the recombination strength in crystal defects. There are differences between conventional mc-Si and the HPMC-Si studied in this work, mostly due to different defect distribution. While conventional mc-Si suffers from dislocations multiplicating in relatively large grains, HPMC-Si is characterized by reduced grain size and more random angle grain boundaries, on which dislocations annihilate. These different defect distributions result in different behaviour upon solar cell processing [12]. This work investigates this behaviour in industrially processed wafers.

2 Experimental methods

The material used in this study comes from an ingot solidified, wafered and processed largely in industrial conditions. Sample wafers were taken from 4 different positions in the ingot, at 6, 25, 43 and 62% of relative height. Neighbouring wafers from each position were divided in 4 different groups. The sample groups have been processed as presented in Fig. 1.
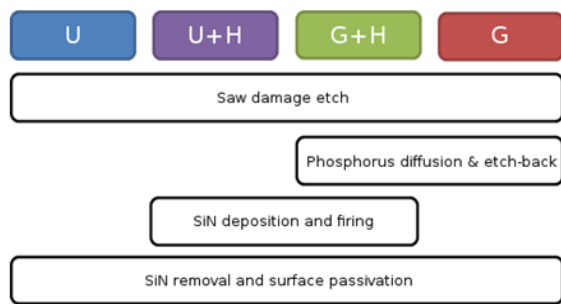
Figure 1 Processing scheme for the experiment. U and G refer to ungettered and gettered, respectively. H represents an additional hydrogenation process, i.e. a simulated contact firing with a SiN-layer present.

State-of-the-art industrial processing was utilized for both high temperature steps. All samples, both gettered and ungettered, are etched for the same amount of time in order to obtain comparable surface properties. After the industrial processing, hydrogenated samples had their SiN layer removed. Prior to minority carrier lifetime measurements the surfaces were electrically passivated by deposition of approximately 40 nm hydrogenated amorphous silicon on both sides, followed by a short anneal [13]. Sample lifetime has been mapped with μPCD (microwave photoconductive decay) on a WT-2000PVN instrument from Semilab. After lifetime measurements, the samples were polished down to 1 μm for Electron Backscatter Diffraction (EBSD), which was performed on Jeol SEM – JSM 840, with Nordif EBSD detector. Grain boundaries have been classified as coincident site lattice (CSL) boundaries vs. random angle grain boundaries according to the Palumbo criterion [14]. Sub grain boundaries with misorientation angle below 5° are not detected.

Carrier lifetimes values in the intra-grain area and on the recombination active grain boundaries have been averaged from plateau and peak values in linescans perpendicular to recombination active grain boundaries.

The lifetime-prediction model, designed in Comsol, is based on Donolato's theory on dislocation recombination strength [15,16]. The model has been designed to fit the predicted lifetime to linescans perpendicular to GBs. Measured intra-grain lifetime (τ_0) has been used to adjust for intra-grain dislocation recombination. The boundary's recombination velocity S was obtained by fitting predicted lifetime values to measured linescans.

3 Results and discussion

EBSD measurements show that wafers along the ingot contain on average 49% CSL $\Sigma 3$ boundaries, and 39% random angle grain boundaries. $\Sigma 9$ and $\Sigma 27$ grain boundaries have also been detected, with average share of 8 and 4%, respectively. Of the two dominating grain boundary orientations $\Sigma 3$ GBs are the least, and random angle grain boundaries are the most recombination active [4]. Therefore the focus here is on random angle grain boundaries.
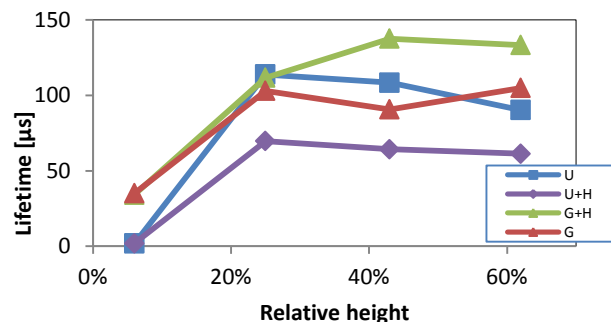

Figure 2 Mean lifetimes of measured HPMC-Si samples.

Mean lifetime values, shown in Fig 2, indicate that for the middle part of the ingot both phosphorus gettering and a subsequent hydrogenation step are required in order to exceed the ungettered lifetime. Both gettering and hydrogenation will, if used separately, deteriorate the wafer electrical performance in the middle of the ingot. This HPMC-Si behaviour is different from the results presented by Karzel et al. for a standard multicrystalline wafer, where gettering resulted in increasing values relative to the ungettered state, but is in agreement with observations by other works on mc-Si [6, 7, 13]. Improvement of lifetime only by gettering is obtained in the bottom of the ingot, at 6% of the ingot height. Impurities dissolved in the lattice are more easily gettered than those in precipitates. The ratio between dissolved and precipitated impurities is higher in bottom wafers, where the total amount of impurities is higher due to in-diffusion from the crucible during cooling of the ingot. In order to distinguish between the random angle GBs in the bottom area and the middle of the ingot,

samples from 6% height are discussed separately from samples from 25, 43 and 62% of height.

3.1 Bottom of ingot

Lifetime images and values in the bottom part of the ingot are presented in Fig. 3 and in Table 1, respectively.
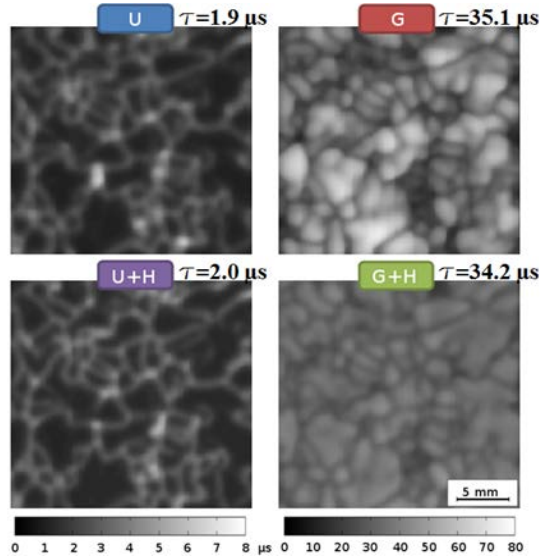
Figure 3 Spatially correlated lifetime maps of neighbouring wafers from about 6% relative height, processed in different routes. Note the different lifetime scales for gettered and ungettered samples. Average lifetime for each map presented on its upper right corner.

Table 1 Lifetime values extracted from samples at 6% height. Both intra-grain and GB lifetime values were extracted from the maps using linescans. IG stands for intra-grain.

| Process	No. of GBs	IG avg [μs]	IG std dev	GBs Avg [μs]	GBs std dev
U+H	65	1.5	0.2	2.5	0.3
U	58	1.4	0.4	2.4	0.5
G+H	58	37.9	2.8	30.8	2.5
G	50	49.4	8.8	33.9	6.5

The ingot fraction rich in impurities is mostly affected by gettering process. In ungettered state, both with and without a hydrogenation process, areas near grain boundaries show higher lifetime values than intra-grain. This is probably because grain boundaries act as precipitation sites while the ingot is cooling after solidification, resulting in denuded zones close to grain boundaries [17]. Lateral carrier diffusion leads to smearing in the images, and only the denuded zones close to grain boundaries are visible, while decreased lifetime values directly at the boundaries are not detected.

Gettering considerably improves the intra-grain lifetime and to a lesser extent lifetime measured at GBs. The intra-grain improvement is varied from grain to grain. Grain boundaries and dislocations are known to reduce the efficiency of the gettering process [18]. Hydrogen defect passivation is not effective in this ingot part. It leads to a slight decrease in both GB and intra-grain lifetime values relative the gettered state. In addition to reducing the intra-grain lifetime, the variation in lifetime between grains is reduced. Passivation of certain defects must be assumed.

3.2 Middle and top of ingot

In the middle of the ingot, where impurity levels are lower, lifetimes in both grains and GBs are higher. The data is presented in Fig. 4 and Table 2.
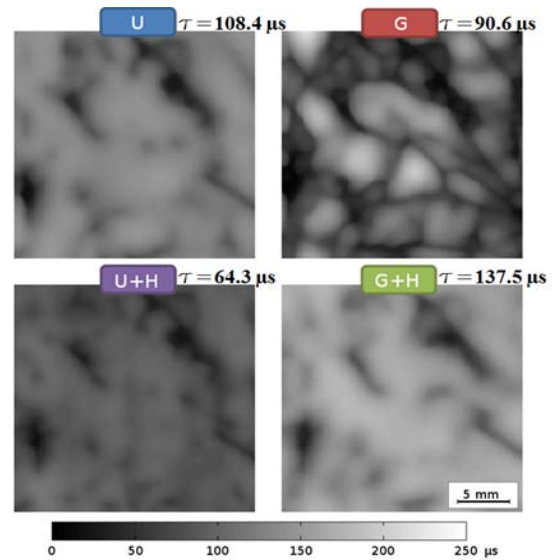
Figure 4 Spatially correlated lifetime maps of neighbouring wafers from about 43% relative height, processed in different routes. Average lifetime for each map presented on its upper right corner.

Table 2 Lifetime values extracted from samples at 25, 43 and 62% heights.

Process	No. of GBs	IG avg [μs]	IG std dev	GBs avg [μs]	GBs std dev
U+H	22	82.3	9.4	65.7	9.5
U	34	134.6	20.0	106.8	17.2
G+H	18	143.1	17.2	113.0	20.2
G	47	159.0	41.0	97.9	25.7

Gettering increases intra-grain lifetimes from the ungettered state in the middle of the ingot by about 8%, but lifetimes measured near GBs deteriorate by 15%. Since the HPMC-Si material contains more GBs than conventional mc-Si, this effect leads to a reduction of average wafer lifetime. This is, however, mitigated by subsequent hydrogenation.

The results show that hydrogenation reduces the lifetime difference between GB and intra-grain areas from ungettered state, but it also deteriorates the mean lifetime of the wafer. When hydrogenation is performed after gettering, the impurity concentration is already reduced in the active wafer part and since passivation reduces GB recombination, this leads to about 15% improvement of mean lifetime for the middle of the ingot.

3.3 Modeling results

Recombination strengths of 10 GBs are calculated using the lifetime prediction model. Linescans from samples from the middle of the ingot were used, and the study was limited to recombination active boundaries. The results are presented in Table 3.

Table 3 Recombination velocities (S) of GBs.

Process	avg S [cm/s]	std dev S [cm/s]
U+H	1106	871
U	816	584
G+H	800	708
G	1413	866

The model predictions are in line with values presented in previous section and show that gettering increases the recombination velocity of grain boundaries, but this effect is then reduced by hydrogenation, which allows full lifetime improvement. When hydrogenation is applied without previous gettering, recombination velocity decreases. Highest recombination velocities are shown after gettering without hydrogenation, but since intra-grain lifetime is also increased by gettering, the average measured GB lifetime is not far from that on ungettered samples. Both hydrogenation and gettering increase recombination velocity when applied without the other. This suggests that the associated heat treatments activate new defects or the precipitate distribution rearranges.

4 Conclusions

Combining microstructural analysis with electrical properties measurements gives good insight into the mechanisms governing wafer performance. We have shown that in the middle section of commercially available ingots both gettering and hydrogenation are needed to achieve lifetime improvement from the ungettered state. The mean lifetime of wafers from the main part of the ingot studied in this work improved by approximately 15%. Gettering alone deteriorates the average wafer lifetime relative to ungettered state, even though intra-grain lifetime is increased, because of the increased recombination activity of random angle grain boundaries after this step. The firing required for hydrogenation used without previous gettering also has a negative effect on mean wafer lifetime.

This is also confirmed by a lifetime prediction model, which shows that the values measured on samples from middle of the ingot can be obtained when the recombination velocity of grain boundaries increases by gettering, and is subsequently reduced by hydrogenation. For samples hydrogenated without gettering the model also predicts increased recombination velocities.

Bottom wafers react differently to processing due to higher impurity content. While hydrogenation has minor effect on such wafers, gettering can enhance their quality considerably, mainly by removing fast diffusing impurities.

References

[1] International Technology Roadmap for Photovoltaic (ITRPV.net) Results 2015, 7th ed., vers. 2, 2016.
[2] L. Arnberg, M. Di Sabatino, E. J. Øvrelid, J. Cryst. Growth, **360**, 56 (2012).
[3] C. W. Lan, W. C. Lan, T. F. Lee, A. Yu, Y. M. Yang, W. C. Hsu, B. Hsu and A. F. Yang, J. Cryst. Growth, **360**, 68 (2012).
[4] J. Chen, T. Sekiguchi, D. Yang, F. Yin, K. Kido and S. Tsurekawa, J.Appl. Phys., **96**, 5490 (2004).
[5] M. I. Bertoni, D. P. Fenning, M. Rinio, V. Rose, M. Holt, J. Maser and T. Buonassisi, Energy Environ. Sci., **4**, 4252 (2011).
[6] M. Rinio, A. Yodyungyong, S. Keipert-Colberg, D. Borchert and A. Montesdeoca-Santana, Phys. Status Solidi A, **208**, 760 (2011).
[7] P. Karzel, M. Ackermann, L. Gröner, C. Reimann, M. Zschorsch, S. Meyer, F. Kiessling, S. Riepe and G. Hahn, J.Appl. Phys., **114**, 244902 (2013) .
[8] H. C. Sio, S. P. Phang, T. Trupke and D. Macdonald, IEEE J. Photovolt., **5**, 1357 (2015).
[9] A. E. Morishige, H. S. Laine, J. Schön, A Haarahiltunen, J. Hofstetter, C. del Cañizo, M. C. Schubert, H. Savin and T. Buonassisi, Appl. Phys. A., **120**, 1357 (2015).
[10] M. S. Wiig , K. Adamczyk, H. Haug, K. E. Ekstrøm, R. Søndenå, Energy. Proc. (2016) (to be published).
[11] B. Sopori, J. Electron. Mater., **31**, 972 (2002).
[12] S. Castellanos, K. E. Ekstrøm, A. Autruffe, M. A. Jensen, A. E. Morishige, J. Hofstetter, P. Yen, B. Lai, G. Stokkan, C. del Canizo, T. Buonassisi, IEEE J. Photovolt. **6** (2016).
[13] R. Søndenå, J. Gjessing, H. Angelskår, Ø. Norseth, S. E. Foss, E. S. Marstein, in: 28th EUPVSEC, Paris, France, 2013.
[14] G. Palumbo, K. T. Aust, E. M. Lehockey, U. Erb, P. Lin, Scr. Mater. **38**, 1685 (1998)
[15] C. Donolato, J. Appl. Phys., **84**, 2656 (1998).
[16] G. Stokkan, S. Riepe, O. Lohne, W. Warta, J. Appl. Phys., **101**, 053515 (1998).
[17] M. Knörlein, A. Autruffe, R. Søndenå, M. Di Sabatino, Energy procedia, **55**, (2014).
[18] A. Bentzen, A. Holt, Mat. Sci. Eng. B, **159-160** (2009).