GETTERING AND PASSIVATION OF ADVANCED HIGH PERFORMANCE MULTICRYSTALLINE SILICON MATERIAL

Christian Fischer, Jeanette Lindroos, Annika Zuschlag, and Giso Hahn
University of Konstanz, Department of Physics, 78457 Konstanz, Germany
christian.fischer@uni-konstanz.de, Tel: +49 7531 884995, Fax: +49 7531 883895

ABSTRACT: High performance multicrystalline (HP mc) silicon material with local effective minority charge carrier lifetime above 1 ms is a promising pathway to increase efficiency in mc silicon solar cells. Critical for the success of the material is the behavior of the material quality during solar cell processing. Phosphorus gettering during emitter formation for example is known to reduce contaminations and thus to enhance carrier lifetime in multicrystalline material. In contrast, also an increase of charge carrier recombination was recently reported for P-gettering in HP mc-Si. Therefore, a detailed analysis of different P-gettering profiles and temperature effects combined with several surface passivations ($SiN_x:H$, AlO_x and iodine-ethanol) is performed to gain further understanding of this phenomenon. Especially changes in τ_{eff} due to different thermal load and in-diffusing hydrogen from $SiN_x:H$ are investigated.
Keywords: Gettering, High Performance Multicrystalline Silicon, Lifetime, Passivation

1 INTRODUCTION

In 2017 the market share of high-performance multicrystalline silicon (HP mc-Si) material already exceeded standard p-type mc silicon [1]. This material is a promising pathway to increase efficiency in solar cells like recently projected for (PERC) passivated emitter rear contact cells [2].

On one hand effective minority charge carrier lifetimes τ_{eff} >1 ms with AlO_x passivation are reported [3], on the other hand changes in recombination activity are observed in HP mc-Si materials during solar cell processing. Phosphorus (P) diffusion is normally known to enhance material quality through gettering effects in mc-Si. A contrary influence of P-gettering was observed on HP mc-Si [4-7]. An increase in recombination was reported after P-gettering especially at grain boundaries [5, 7].

In this study, the influence of different thermal loads with and without presence of P-doping layers on material quality is investigated and effects of $SiN_x:H$ and AlO_x deposition and surface passivation are compared by using wet-chemical iodine-ethanol (IE) passivation.

2 EXPERIMENTAL

156x156 mm^2 B-doped HP mc-Si wafers (~1-1.5 Ωcm) from an advanced crystallization run and mid ingot height were used with defined orientation of each wafer in the block and processed as 50x50 mm^2 samples. A total of 17 samples were processed and measured according to the process sequences shown in Fig. 1.

After wafer cleaning and saw damage removal, P-diffusion gettering was performed with several temperature profiles (samples 4-12). A $POCl_3$-diffusion used for solar cell processes resulting in a 50 $\Omega/\square$ emitter with a peak temperature of about 840 °C was compared to two diffusions with adjusted temperature profiles (Fig. 2). One was performed with an about 30 K elevated peak temperature resulting in a 27 $\Omega/\square$ emitter. The other diffusion with a peak temperature of 840 °C had a slow cool-down ramp before unloading (55 $\Omega/\square$). This should improve precipitation of defects and contaminations.
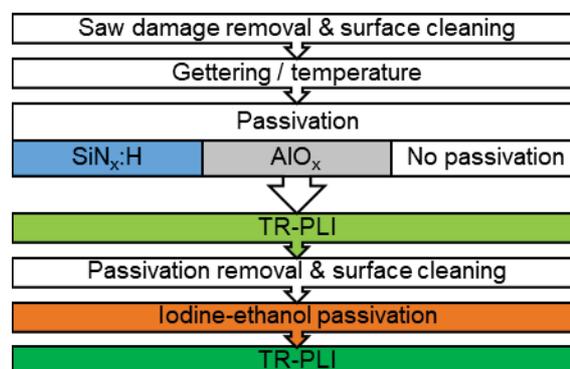

Figure 1: Process sequence of sample preparation and characterization of investigated lifetime samples.

	Passivation	$SiN_x:H$	AlO_x	IE
Gettering				
untreated		1 & 1*	2	3 & 3+
$POCl_3$ gettered	840°C	4	5	6
	870°C	7	8	9
	840°C with CD	10	11	12
Temperature profile $POCl_3$		13 broken	14	15

Figure 2: List of all lifetime samples with P-gettering or temperature step, respectively, on the left side and passivation method in top line. P-gettering at about 840 °C with slow cool-down is labeled with CD. 1* unfired sister wafer. 3+ fired sister wafer.

To distinguish between gettering efficacy and temperature-induced material changes, a set of samples received the temperature profile of P-gettering at T_{peak} 840 °C without PSG(phosphorus-silicate glass)-layer deposition. Effects of surface passivation were investigated with samples 1-3 (Fig. 2). Those samples were passivated without previous gettering or temperature step.

PSG and diffused layers were removed by chemical etching and, as all other samples received thickness relevant etching steps, a similar final wafer thickness was achieved for all samples. One group of samples was passivated with direct plasma-enhanced chemical vapor

deposition (PECVD) SiN_x:H on both sides (deposition temperature 450 °C) and fired in a belt furnace (peak set-temperature 800 °C). One group was passivated with AlO_x from atomic layer deposition (ALD) and annealed at around 400 °C (30 min). The last group was directly wet chemically passivated with IE. τ_{eff} was measured for all samples by time resolved photoluminescence imaging (TR-PLI) [8]. Finally, SiN_x:H and AlO_x passivation were removed and the samples were wet chemical passivated with IE for lifetime measurement. Afterwards, all samples can be compared with similar surface passivation.

Untreated sister wafers not included in the list were CP4 etched and Piranha cleaned. Afterwards the samples were polished and Secco etched [9] for etch pit density analysis.

3 RESULTS AND DISCUSSION

Local lifetimes exceeding 1 ms and a harmonic mean τ_{eff} of 654 µs were observed on the AlO_x passivated sample without gettering as shown in Fig. 3 (sample 2) demonstrating the high potential of the used HP mc-Si material.

τ_{eff} maps of all 5x5 cm² samples passivated with AlO_x are shown in Fig. 3. P-gettering strongly reduces harmonic mean τ_{eff} (Fig. 3: 2 vs 5, 8, 11). As this reduction is also present in ungettered sample 14 with temperature load corresponding to P-diffusion, it is due to detrimental temperature load. The areas remaining on a high lifetime level after temperature treatment benefit from P-gettering and can even surpass $\tau_{eff,max}$ of the ungettered sample. The differences between several P-gettering profiles indicate that a slow cool-down after gettering at high temperatures results in slightly reduced negative effects in highly defected areas on the one hand and on the other hand reduces maximum τ_{eff}.

PECVD SiN_x:H and IE passivation result in lower lifetimes than AlO_x. This is due to better surface passivation of AlO_x. But also a temperature related effect induced by deposition and annealing of AlO_x cannot be excluded. P-gettering reduces drastically lifetimes in AlO_x passivated samples. This effect is also observed in samples with SiN_x:H and IE passivation, but is less pronounced due to a generally lower lifetime level (Fig. 4).

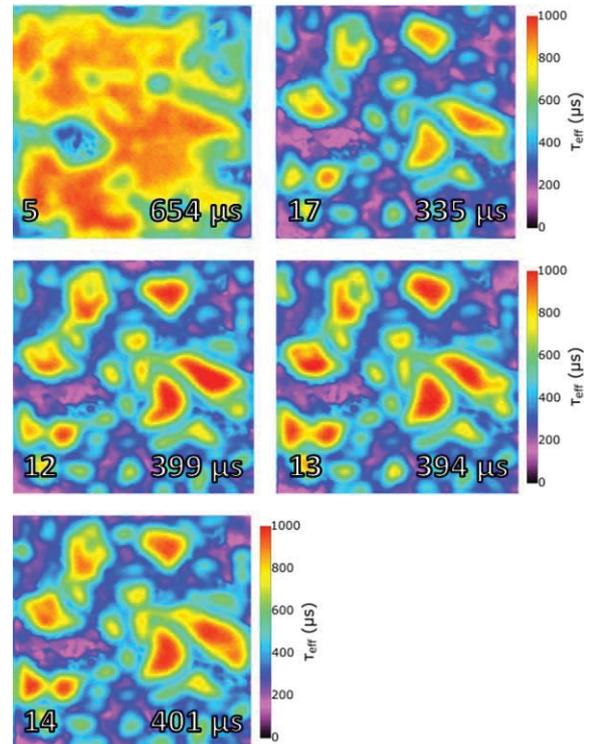**Figure 3:** τ_{eff} maps of the 5x5 cm² samples passivated with AlO_x with sample codes according to Fig. 2 and harm. mean of τ_{eff}. 2: untreated sample, 14: sample with temperature profile of P-gettering without diffusion, 5: sample with P-gettering at 840 °C, 8: sample with P-gettering at 870 °C, 11: sample with P-gettering at 840 °C with slow cool-down ramp.
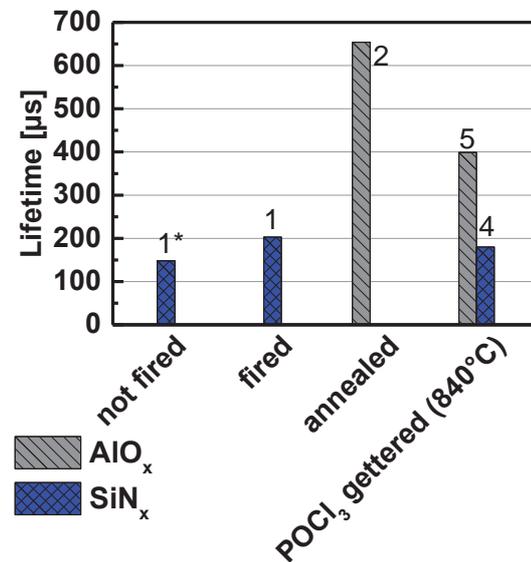

Figure 4: Harmonic mean τ_{eff} based on TR-PLI maps of passivated 5x5 cm² samples.

The final wet-chemical IE passivation after removal of all functional layers allows comparing all samples with similar surface passivation quality. Although general lifetime level is reduced due to limited IE passivation quality in areas with highest τ_{eff}, differences between τ_{eff} values for different sample (Fig. 5) can be attributed to the bulk. This reveals the negative effect of firing, as lifetimes of fired samples are in all cases below unfired samples (e.g., Fig. 6: 3 vs 3+). SiN$_x$:H passivated samples show expected behavior with low passivation quality of the unfired sample 1* (Fig. 6 1 vs. 1*). However, after removal of this layer and IE passivation the opposite behavior is observed (Fig. 6 1 IE vs. 1* IE). Sample 1* with SiN$_x$:H deposition and no firing step shows with IE passivation higher lifetimes than sample 3 without any high temperature or passivation steps. A possible explanation can be in-diffusion of hydrogen during deposition or an internal gettering effect induced by deposition temperature of SiN$_x$:H. This may also explain more homogenous τ_{eff} maps of SiN$_x$:H samples and an improvement in low lifetime areas.
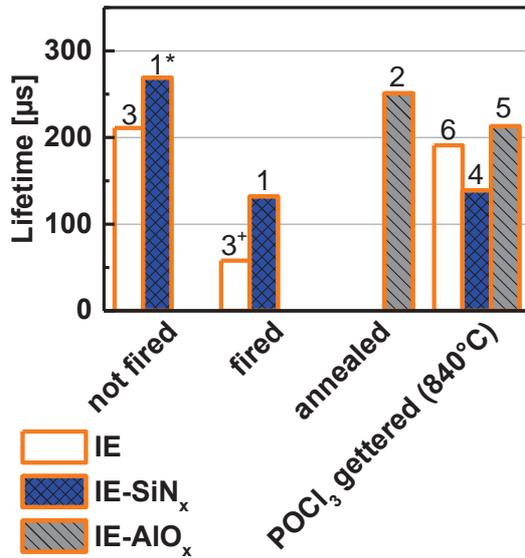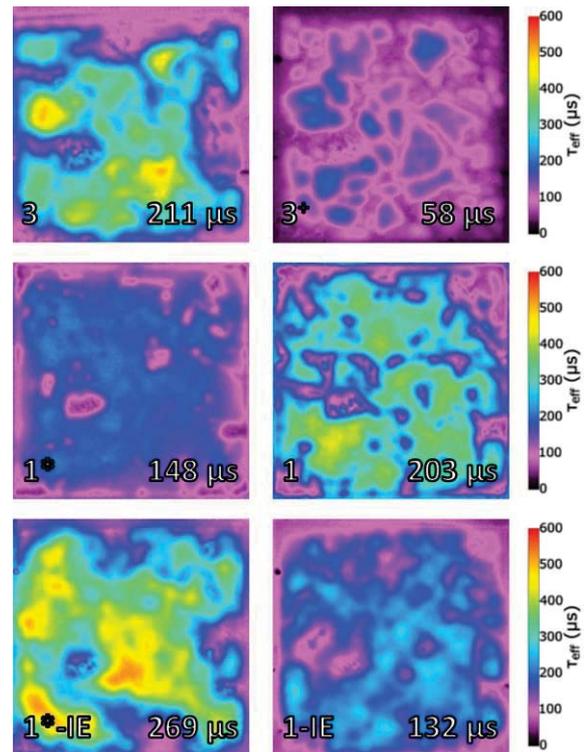

Figure 6: τ_{eff} maps of ungettered 5x5 cm² samples with sample codes according to Fig. 2 and harm. mean of τ_{eff}. 3: ungettered IE passivated, 3*: fired IE passivated, 1*: SiN$_x$:H-layer deposited not fired, 1: SiN$_x$:H-layer deposited and fired, 1*-IE: sample 1* with IE repassivation, and 1-E: sample 1 with IE repassivation.

Figure 5: Harmonic mean τ_{eff}, based on TR-PLI maps of IE passivated 5x5 cm² samples.

In addition to TR-PLI analysis, sister samples were Secco-etched and microscopic pictures show etch-pit density in comparison to material quality as determined by TR-PLI. In Fig. 7 a detail of the TR-PL image of sample 3 with grain boundary overlay is compared with a microscopic picture of the etched region. A high etch-pit density corresponds to a low lifetime region. This could be the effect of dislocations like discussed in [2].
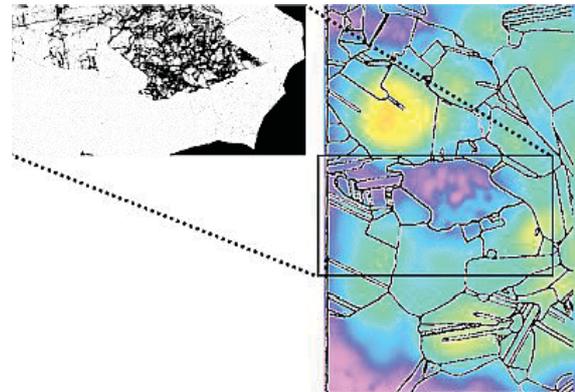

Figure 7: Etch-pit map (left) with corresponding position on a lifetime sample with a grain boundary overlay (right). The wafer broke during processing on right side and black parts in the picture result from missing edges.

4 CONCLUSION

In conclusion, this study gives improved insight in the behavior of high quality HP mc-Si material regarding P-gettering, temperature treatment and different surface passivation processes. Temperature steps above 800 °C are drastically decreasing material quality in most areas. This negative effect cannot be compensated by P-gettering. A slight improvement is observed by SiN_x:H deposition without firing. But altogether prediction of end-of-process material quality remains difficult to predict for HP mc-Si, as not only very high initial τ_{eff} in the as-grown state are important. Instead, final lifetime after process-relevant high temperature steps has to be considered when optimizing the crystallization process.

5 ACKNOWLEDGEMENTS

6 REFERENCES

[1] International Technology Roadmap for Photovoltaic (ITRPV), 2017 Results (Ninth Edition, March 2018)
[2] P. P. Altermatt *et al.*, Solar Energy (2018) DOI: 10.1016/j.solener.2018.01.073
[3] C. Winter, A. Zuschlag, D. Skorka, G. Hahn, AIP Conference Proceedings 1999 (2018) 130020.
[4] K. Adamczyk, R. Søndenå, G. Stokkan, E. Looney, M. Jensen, B. Lai, M. Rinio, M. D. Sabatino, Journal of Applied Physics 123 (2018) 055705.
[5] M. S. Wiig, K. Adamczyk, H. Haug, K. E. Ekstrøm, R. Søndenå, Energy Procedia 92 (2016) 886.
[6] G. Stokkan, D. S. Marisa, R. Søndenå, M. Juel, A. Autruffe, K. Adamczyk, H. V. Skarstad, K. E. Ekstrøm, M. S. Wiig, C. C. You, H. Haug, M. M'Hamdi, Physica Status Solidi A 214 (2017) 1700319.
[7] H. Sio, D. Macdonald, Solar Energy Materials & Solar Cells 144 (2016) 339.
[8] D. Kiliani, G. Micard, B. Steuer, B. Raabe, A. Herguth, G. Hahn, Journal of Applied Physics 110 (2011) 054508.
[9] F. Secco d' Aragona, Journal of the Electrochemical Society 119(7) (1972) 948.