

Al₂O₃ REAR SURFACE PASSIVATION FOR SILICON RIBBON SOLAR CELLS

J. Ebser, J. Junge, T. Lüder, S. Seren, B. Terheiden, G. Hahn
 University of Konstanz, Department of Physics, P.O. Box X916, 78457 Konstanz, Germany
 Jan.Ebser@uni-konstanz.de, Tel.: +49 7531 88 4995, Fax: +49 7531 88 3895

ABSTRACT: In this work the application of an Al₂O₃ surface passivation layer to low-cost multicrystalline silicon ribbon material is investigated. Symmetrical lifetime samples are prepared from adjacent p-doped EFG (Edge-defined Film-fed Growth) wafers and spatially resolved μ PCD (Microwave detected PhotoConductance Decay) measurements are carried out to determine the minority charge carrier lifetime. It is shown that even very thin layers (5 nm) of Al₂O₃ can provide an excellent surface passivation of the mentioned silicon ribbon material. Instead of annealing in N₂ ambience a MIRHP (Microwave Induced Remote Hydrogen Plasma) treatment is applied. This process step allows hydrogen atoms to pass the thin Al₂O₃ layer and to increase lifetime by passivating recombinative defects in the bulk material. In addition to the Al₂O₃ layer, hydrogen-rich silicon nitride (SiN_x:H) is deposited by PECVD (Plasma Enhanced Chemical Vapor Deposition) on top of selected Al₂O₃ samples to increase the mechanical and chemical stability during a subsequent solar cell process. This deposition can replace the necessary Al₂O₃ annealing step leading to a comparable passivation quality. Finally, 2 x 2 cm² solar cells are processed including the Al₂O₃ rear side passivation in a photolithography based high-efficiency process reaching efficiencies above 18% on multicrystalline EFG material [1].

Keywords: Ribbon Silicon, Passivation, Annealing

1 INTRODUCTION

Improving rear surface passivation plays an important role to increase the efficiency of silicon solar cells, especially as wafers get thinner and material quality is further increased. For this purpose Al₂O₃ (aluminum oxide), deposited by ALD (Atomic Layer Deposition), provides excellent long term stable dielectric surface passivation on p-doped silicon due to the field effect of built-in negative charges [2].

Silicon ribbon can be used for solar cell processing to reduce the amount of silicon per watt peak by avoiding silicon loss due to wire sawing. In this work p-doped EFG material [3] produced by SCHOTT Solar is used. As the material quality of these wafers increased during the last years, cell efficiencies of silicon ribbon solar cells approached the range of block cast multicrystalline efficiency values. To optimize silicon consumption per watt peak, wafer thickness will decrease in the future and thus rear side passivation will become more important even for materials with a limited diffusion length.

Dielectric layers – as for example Al₂O₃ – may lead to a much better surface passivation than the standard Al-BSF (Aluminum Back Surface Field) due to passivation of dangling bonds on the Si-surface in combination with the strong field effect passivation. Previous high efficiency approaches for ribbon materials at University of Konstanz featured a passivation via a thermal silicon oxide deposited at temperatures above 800°C [4]. But this high temperature step often proved to reduce the bulk lifetime significantly in defect-rich multicrystalline silicon materials [5, 6]. To overcome this restriction, a deposition of Al₂O₃ at low temperatures of less than 200°C with a subsequent annealing step at about 400°C is applied replacing the oxidation step at temperatures above 800°C.

2 EXPERIMENTAL

To investigate the application of Al₂O₃ on silicon ribbon materials, symmetrical lifetime samples are prepared (Figure 1). Most of the processing steps are

carried out under conditions close to the intended solar cell process [1]: p-doped EFG material with a specific resistivity of about 3 Ω cm is used. The 125x125 mm² wafers are damage etched in a chemical polishing solution. Afterwards a standard POCl₃ emitter diffusion is applied. For the lifetime samples only P-gettering, which takes place during the emitter formation, is of interest at this point because after the P-glass removal the emitter layer is removed in a second chemical polishing etching step as well.

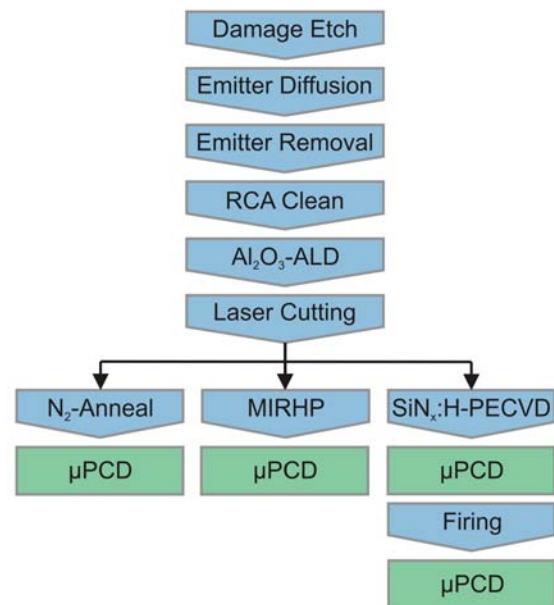


Figure 1: Processing sequence of p-doped 3 Ω cm EFG lifetime samples. Passivation is performed by Al₂O₃, either annealed in N₂ ambience (left branch), after a MIRHP treatment (middle branch), or alternatively with PECVD-SiN_x:H on top of the Al₂O₃ layer (right branch).

Subsequently, the surface is cleaned by RCA cleaning. Then Al₂O₃ is deposited by a commercial FlexAl tool (Oxford Instruments) on both sides of adjacent EFG wafers. Different film thicknesses between

5 and 120 nm are tested. The film thickness is characterized by ellipsometry.

The coated wafers are cut into 2.5 x 5 cm² samples. After activating the passivation by annealing in a tube furnace with N₂ atmosphere at a temperature of about 400°C, spatially resolved μ PCD lifetime measurements are carried out to determine the passivation quality. Instead of the standard annealing in N₂ ambience, a MIRHP treatment [7] at the same temperature (process corresponding to the middle branch of Figure 1) is also possible.

In addition, 75 nm of a hydrogen-rich silicon nitride (SiN_x:H) is deposited by PECVD on both sides of selected Al₂O₃-coated samples to increase the mechanical and chemical stability (right branch of Figure 1). Finally, firing of these samples in a conventional belt furnace at different peak temperatures is performed to investigate the thermal stability of the passivation layer. Furthermore, the firing step is expected to lead to enhanced bulk lifetimes due to hydrogen which is released from the SiN_x:H and diffuses through the Al₂O₃ layer into the bulk where it passivates recombination active defects.

3 RESULTS

Due to its elongated grain structure, crystallites in EFG silicon usually proceed over several sample lengths for the sample size used (2.5 x 5 cm²) and material quality is assumed to be homogeneous for one selected grain. Therefore, adjacent samples allow for a representative investigation of the influence of different Al₂O₃ layers or annealing conditions on the passivation quality.

3.1 Al₂O₃ annealing conditions

The standard Al₂O₃ annealing which activates the passivation is performed in N₂ ambience for 30 min [2] at a temperature of about 400°C.

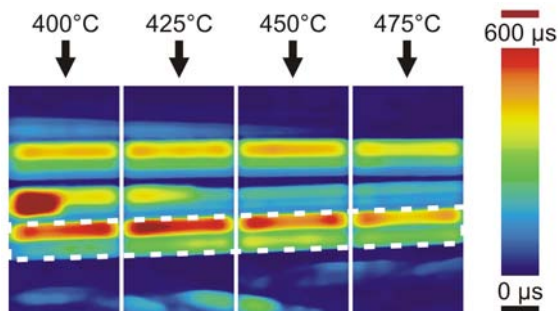


Figure 2: μ PCD-measurements of EFG lifetime samples. The grains of interest proceed over four samples. The samples are passivated by 30 nm Al₂O₃ and annealed at different temperatures between 400°C and 475°C.

For EFG material it is shown that a relatively wide temperature range leads to similar lifetime values (Figure 2). The best grains hereby achieve extraordinary high lifetime values of up to 700 μ s. The optimal annealing temperature appears to be – like for reference samples on FZ material – around 425°C (shown are temperature set-points of the annealing furnace, sample temperature may vary for some degrees, Figure 3). The

presented values for the EFG samples are arithmetic mean values over an area with homogeneous high material quality and elongated grains (marked with dashed lines in Figure 2).

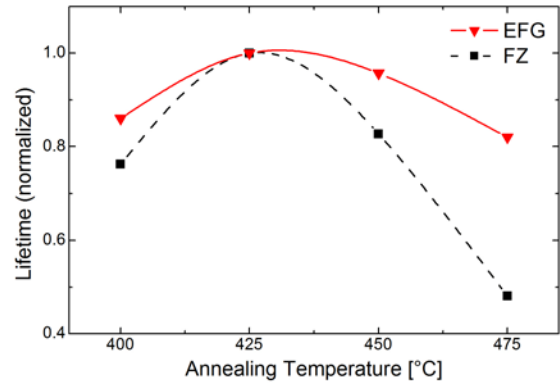


Figure 3: Lifetime values of samples passivated by 30 nm Al₂O₃ and annealed at different temperatures. The optimum annealing temperature appears to be around 425°C.

3.2 Influence of the MIRHP treatment

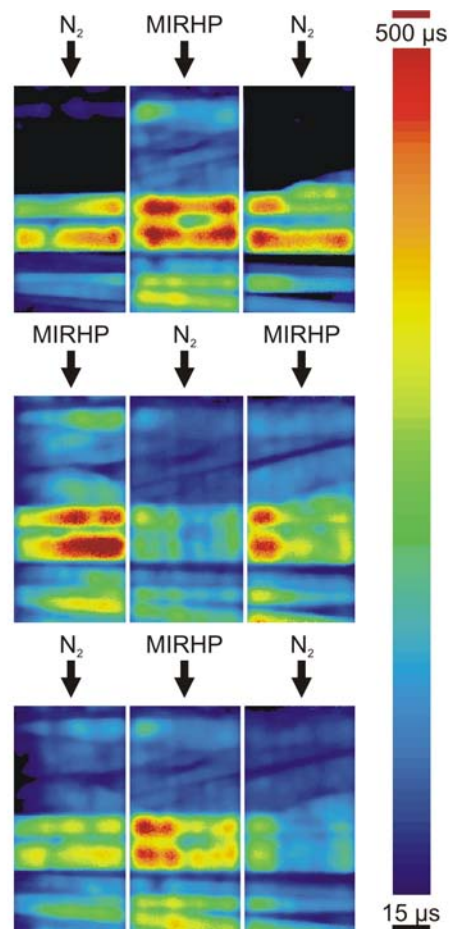


Figure 4: μ PCD-measurements of EFG-Si, 5 nm Al₂O₃ on both sides. The same three samples are shown after subsequent annealing steps, alternately in N₂ atmosphere and MIRHP. A significant increase in minority carrier lifetime in consequence of the hydrogen passivation is observable.

The MIRHP treatment at the same temperature can enhance the measured lifetime significantly (first line of Figure 4) compared to standard annealing conditions (N₂, section 3.1). It is supposed that in-diffused hydrogen is the reason for the improved passivation quality.

This effect is to some extent reversible, as seen in the second and third line of Figure 4. A subsequent MIRHP-anneal after the N₂ anneal leads to an increase in lifetime, while a following second annealing in N₂ ambience seems to lead to out-diffusion of hydrogen again.

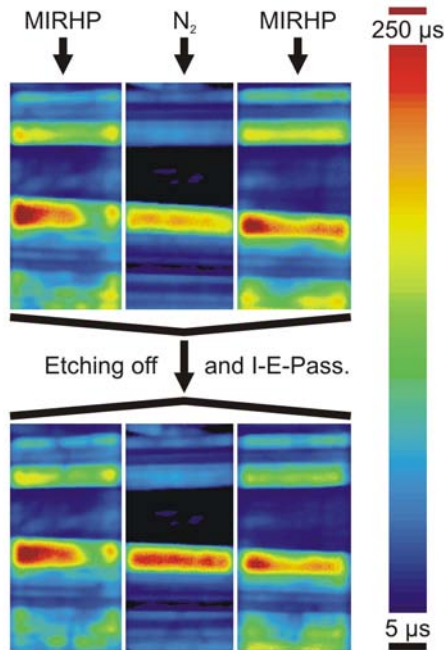


Figure 5: μ PCD-measurements of EFG-Si, 5 nm Al₂O₃ on both sides. The same three samples are shown with Al₂O₃ passivation (top) and after etching off the Al₂O₃ layer and a homogeneous chemical surface passivation by iodine-ethanol (I-E-Pass.) showing improved bulk passivation of the two samples with prior MIRHP treatment (bottom).

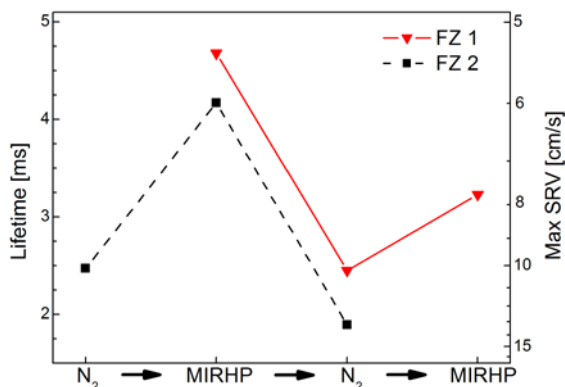


Figure 6: Transient-PCD-measurements of two 2 Ω cm FZ samples, 5 nm Al₂O₃ on both sides. The same samples are shown after annealing steps, alternately in N₂ atmosphere and MIRHP. A significant increase in minority carrier lifetime in consequence of exposure to atomic hydrogen can be seen (experiment comparable to the one shown in Figure 4).

On the one hand the positive effect of the MIRHP treatment is due to passivation of recombination active bulk defects by hydrogen atoms that pass the thin Al₂O₃ layer. This can be demonstrated after etching off the Al₂O₃ layer and a chemical surface passivation by an iodine-ethanol solution (Figure 5).

Figure 6 shows, that on the other hand the MIRHP treatment has a positive influence on the Al₂O₃ surface passivation itself, concerning the layer and/or interface properties. This is observed in a similar experiment using transient-PCD-measurements on FZ reference samples, which are not expected to profit from a hydrogen bulk passivation.

3.3 PECVD-Si_x:H capping layer

It is found that the additional PECVD-Si_x:H deposition at a temperature of about 400°C can replace the Al₂O₃ annealing step (process corresponding to the right branch of Figure 1) and lead to comparable results in surface passivation quality (first line of Figure 7). Samples with 7.5 nm Al₂O₃ and 75 nm Si_x:H reach even higher lifetime values than comparable N₂ annealed samples. On the one hand this is at least partly due to bulk passivation by atomic hydrogen, which can be seen after removal of the passivation layers and subsequent chemical passivation by an iodine-ethanol solution (second line of Figure 7). On the other hand FZ-silicon reference samples which should not benefit from bulk hydrogenation show higher lifetime values after PECVD-Si_x:H as well. This indicates an improvement of the Al₂O₃ layer and/or the Si-Al₂O₃ interface.

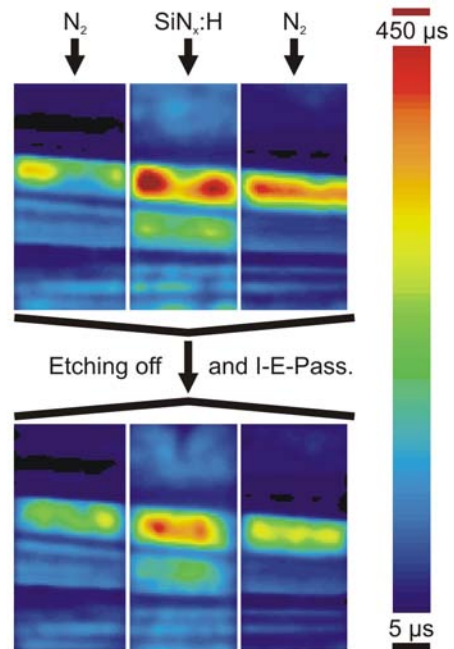


Figure 7: μ PCD-measurements of three adjacent EFG wafers with the same grain structure, passivated by 7.5 nm Al₂O₃. The sample in the middle features an additional protection layer of 75 nm Si_x:H. The higher lifetime values of this sample are also seen after etching off the dielectric passivation layers and a homogeneous chemical surface passivation (I-E-Pass.) suggesting a hydrogen passivation of the bulk during the PECVD of Si_x:H.

Figure 8 shows that firing the samples with the Al_2O_3 - SiN_x :H-stack system in a conventional belt furnace reduces the measured lifetime values significantly. That demonstrates that a decreasing surface passivation quality outweighs the positive effect of the hydrogen passivation by SiN_x :H during the firing step. A clear temperature dependence is observed: the higher the peak temperature the lower the lifetime.

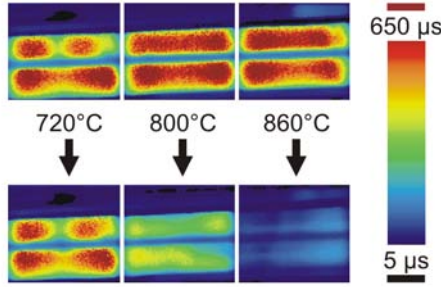


Figure 8: Detail of μPCD -measurements of adjacent EFG-Si-wafers, passivated by 30 nm Al_2O_3 and an additional 75 nm PECVD- SiN_x :H. The upper part shows the lifetime before, the lower part after a firing step at different peak temperatures.

3.4 Solar cells with Al_2O_3 rear surface passivation

To demonstrate the observed promising passivation properties not only on lifetime level but on solar cell level as well, $2 \times 2 \text{ cm}^2$ solar cells on $1 \Omega\text{cm}$ EFG material and $0.5 \Omega\text{cm}$ FZ reference material are processed in a next step. The Al_2O_3 passivation is included in a photolithography based high-efficiency cell process at the University of Konstanz [1] which is specially adapted for defect-rich multicrystalline silicon materials. The rear contact is realized by LFCs (Laser Fired Contacts, [8]).

Hereby, the best EFG samples reached remarkably high efficiencies above 18% [1]. The results of the best EFG solar cell and FZ reference are presented in Table I. The EFG sample features a passivation layer of 10 nm Al_2O_3 and an additional SiN_x :H layer. The FZ solar cell is passivated by 30 nm Al_2O_3 without a capping layer.

Table I: Specifications of the best solar cells including MgF_2 as second antireflexion layer.

Material	FF [%]	j_{sc} [mA/cm^2]	V_{oc} [mV]	η [%]
EFG	78.1	36.9	630	18.1
FZ	79.5	38.3	660	20.1

4 CONCLUSION

It is demonstrated that a rear surface passivation by Al_2O_3 is well applicable to the low-cost multicrystalline silicon ribbon material EFG resulting in high minority charge carrier lifetimes. Instead of a common annealing in N_2 ambience a MIRHP treatment is applied leading to significantly increased lifetime values. On the one hand this process step allows hydrogen atoms to pass the thin Al_2O_3 layer and increase lifetime by passivating recombination active bulk defects. On the other hand the MIRHP treatment has a positive influence on the Al_2O_3

surface passivation itself, concerning the layer and/or interface properties. Similar results are found for an additional PECVD- SiN_x :H layer deposited on top of selected Al_2O_3 samples. Finally, $2 \times 2 \text{ cm}^2$ solar cells are processed including the Al_2O_3 passivation in a photolithography based high-efficiency process reaching efficiencies above 18% on the EFG material [1].

5 ACKNOWLEDGEMENTS

We would like to thank Lisa Rothengaß, Sebastian Joos and Sabine Graf for support during processing and characterization.

The financial support from the BMU projects 0327650H (SolarFocus) and 0325079 is also gratefully acknowledged in particular for the processing equipment.

The content of this publication is the responsibility of the authors.

6 REFERENCES

- [1] J. Junge et al., *Evaluating the efficiency limits of low cost mc Si materials using advanced solar cell processes*, presented at the 25th EU-PVSEC, Valencia, 2010.
- [2] B. Hoex et al., *Ultralow surface recombination of c-Si substrates passivated by plasma-assisted atomic layer deposited Al_2O_3* , Applied Physics Letters 89, 042112, 2006.
- [3] F. Wald, *Crystals: Growth, Properties and Applications* 5, Springer-Verlag, 1981.
- [4] J. Junge et al., *Laser Fired Contacts for High Efficiency Solar Cells based on EFG Material*, 23th EU-PVSEC, Valencia, 1561-1563, 2008.
- [5] M. Stocks et al., *Minority Carrier Lifetimes of Multicrystalline Silicon During Solar Cell Processing*, 14th EU-PVSEC, Barcelona, 770, 1997.
- [6] D. Groetschel et al., *Plasma Texturing and its Influence on Surface Passivation*, 23th EU-PVSEC, Valencia, 1534-1536, 2008.
- [7] M. Spiegel et al., *Detailed Study on Microwave Induced Remote Hydrogen Plasma Passivation of Multicrystalline Silicon*, 13th EU-PVSEC, Nizza, 421-424, 1995.
- [8] E. Schneiderlöchner et al., *Laser-Fired Rear Contacts for Crystalline Silicon Solar Cells*, Progress in Photovoltaics: Research and Applications 10, 29-34, 2002.