Investigation of a PECVD silicon oxide/silicon nitride passivation system concerning process influences

Sinje Keipert-Colberg*[1], Nadine Barkmann[1], Christian Streich[1], Andreas Schütt[2], Dominik Suwito[3], Petra Schäfer[1], Stefan Müller[1], Dietmar Borchert[1]
* Corresponding author, e-mail: sinje.keipert-colberg@ise.fraunhofer.de
[1] Fraunhofer Institute for Solar Energy Systems, Laboratory and Servicecenter Gelsenkirchen, Auf der Reihe 2, 45884 Gelsenkirchen, Germany, phone: +49 209 155 3911, fax: +49 209 12090 93
[2] University Kiel, Chair for General Materials Science, Kaiserstrasse 2, 24143 Kiel, Germany
[3] Formerly at Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2-4, 79110 Freiburg, Germany

ABSTRACT: In this work we investigated the properties of silicon oxide (SiO_y) and silicon nitride (SiN_x) layers deposited by a large area 13.56 MHz PECVD system as well as of the combined SiO-SiN "stack".
The bonding nature of the layers was determined by FTIR spectroscopy. Furthermore, a characterization of the interface trap density as well as of the fixed charges in the different passivating layers was performed by preparing and measuring metal-insulator-semiconductor samples and supplemented by lifetime measurements. We show how temperature steps as well as x-ray and UV-radiation change the layer properties: High energetic radiation leads to a depassivation of the surface deposited with the SiO-SiN stack. The low surface recombination velocity can be fully recovered by an annealing step. In addition, rear side passivated solar cells were fabricated with a SiO-SiN stack as passivation layer and the rear surface recombination velocity of the solar cells was measured by the CELLO technique.
Keywords: surface passivation, silicon oxide, silicon nitride, PECVD, layer characterization

1 INTRODUCTION

In the field of crystalline silicon solar cells the surface passivation of the rear side has gained importance over the last years [1], especially the rear surface passivation of thin multi crystalline silicon solar cells became more and more interesting for industrial implementation [2]. Among the suitable materials for surface passivation, the combination of PECVD silicon oxide and PECVD silicon nitride appears as a promising and industrially feasible candidate [3, 4]. In this paper we present an overview on our experiments on the properties of a SiO-SiN layer stack for rear side passivation of multicrystalline silicon solar cells and their process induced changes.

2 EXPERIMENTAL

Shiny etched float zone 1 Ohm*cm p-type silicon wafers were used to prepare lifetime samples by symmetrical deposition of the passivation layers after wet chemical cleaning ending with an HF-dip as well as samples for electrical and optical characterization. The depositions were performed in a large area 13.56 MHz PECVD system with one deposition chamber and a parallel plate direct plasma reactor. For the SiO_y a mixture of SiH_4 and N_2O was used at a deposition temperature of 300 °C, the mixture for the SiN_x deposition contained SiH_4, NH_3, and H_2 at 425 °C.

For layer characterization different measurement methods have been applied such as FTIR spectroscopy and capacitance voltage measurements. The procedure of the latter method and its sample preparation was described in [5]. The minority carrier lifetime of the passivated samples was measured after subjecting the wafers to a sintering step comparable to contact firing. Microwave photo conductance decay was used for spatially resolved lifetime maps and the Sinton WCT-120 set-up for injection level dependent measurements.

For the experiments concerning degradation by high energy radiation two different approaches were followed: For the x-ray exposure test, the samples were partially covered by a vacuum resistive adhesive tape and subjected to an aluminum metallization by electron beam evaporation. During the evaporation the samples were placed in metallic wafer holders with a several mm thick support structure orientated towards the evaporation chamber. After the evaporation the metalized adhesive tape was removed and spatially resolved lifetime maps were taken. Afterwards the samples were annealed in a sintering furnace in air ambient at a furnace temperature of 360 °C for approx. 9 min.

For the UV degradation, the lifetime samples were placed in a sun simulation set-up with UV rich spectrum (SOL2 by Dr. Hoenle AG) for increasing time periods. After each degradation period the injection dependent lifetime was measured. After more than 60 h of cumulated light exposure the samples were annealed following the procedure described above.

The solar cells were prepared from p-type multicrystalline silicon wafers starting with a saw damage removal in a non-texturing mixture of HNO_3, HF, and DI water. After the inline emitter diffusion the parasitic emitter on the rear side was removed by single sided etching off of several micrometers using an acidic polishing solution. Then the phosphorus glass was removed and the wafers were cleaned. Directly after an additional HF-dip, the cell's rear sides were passivated with 70 nm of PECVD SiO_y and 80 nm of SiN_x. The wafers were then turned and the front sides were deposited with the SiN_x antireflective coating. The rear side point contacts were then established by means of photolithography and wet etching with HF.

Front and rear contacts were then formed by screen printing and firing of silver and aluminum containing paste, respectively.

3 RESULTS

3.1 FTIR measurements

The FTIR spectra of the single layers (see Fig. 1 a) and b)) reveal that not only the SiN_x but also the SiO_y

contains at least some hydrogen as can be seen by the small Si-H (2260 cm^{-1}), the O-H (3650 cm-1) and the N-H peaks (3302 cm^{-1})(wavenumbers taken from [6-9]). The latter vibration furthermore indicates that nitrogen is incorporated in the SiO-layer which can be attributed to the use of N_2O as oxygen source for the PECVD process. The deposited SiO_y is therefore rather a silicon oxynitride with a very low amount of nitrogen. This is consistent with a measured refractive index of ~ 1.51 at 632 nm in comparison to 1.46 for thermal SiO_2.

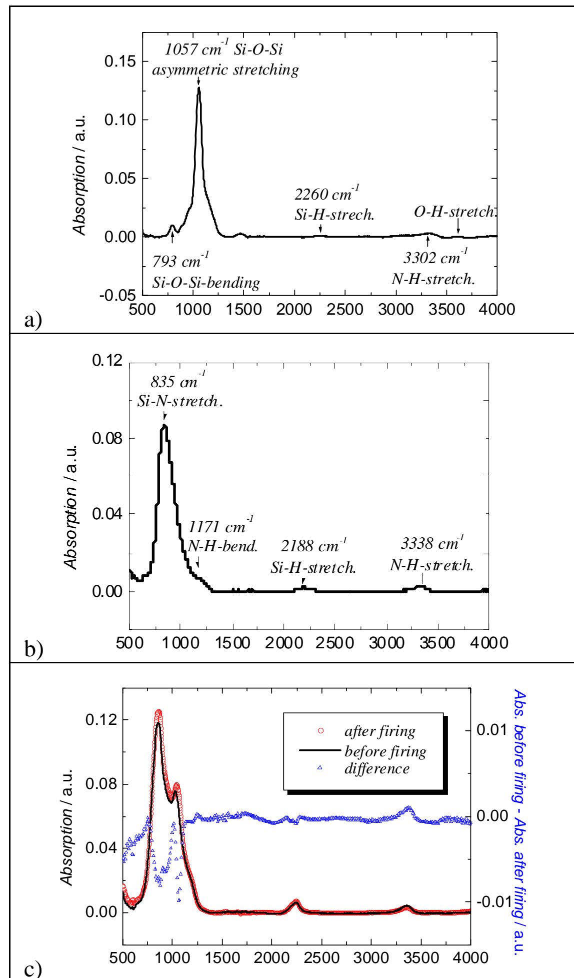

Figure 1: FTIR spectra of a) SiO_y, b) SiN_x, and c) a SiO-SiN-stack system before and after firing

A high temperature step as performed for contact firing reduces the hydrogen related absorption peaks and results in a densification of the layers (confirmed by the increase in height of the Si-N and Si-O stretching peaks after firing, [10]) as can be seen for the SiO-SiN stack before and after firing comparison in Fig. 1 c).

3.2 Capacitance-Voltage measurements

In contrast to thermal SiO_2 or PECVD SiO_x [5] both the SiO-SiN stack and SiN_x can only be measured with our set-up after a high temperature firing step. This treatment drastically reduces the leakage currents impeding the CV measurement. Evaluation of the CV curves reveals a smaller fixed charge density for the SiO-SiN layer stack (~ $6.5 \cdot 10^{11}$ cm^{-2}) in comparison with a single SiN_x layer (~$2.5 \cdot 10^{12}$ cm^{-2}). In the majority half of the bandgap, SiO-SiN also shows a smaller interface defect density (D_{it}) than the SiN_x as can be seen in Fig.2. In addition, the minimum of the SiN_x-D_{it} curve seems to be shifted towards the conduction band edge.

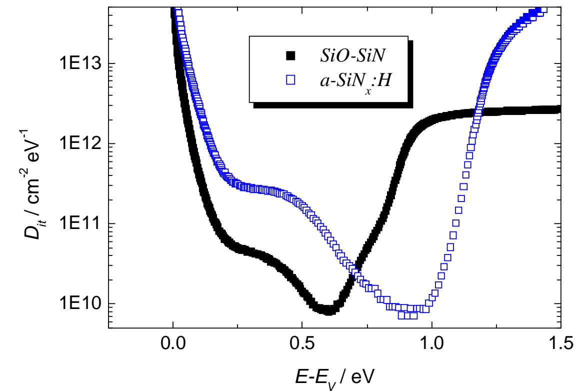

Figure 2: Interface defect density (D_{it}) vs. bandgap position of a SiO-SiN layer stack sample and a SiN_x layer, both deposited on a shiny etched p-type floatzone wafer.

3.3 Lifetime experiments

Fig. 3 shows a comparison of the effective injection dependent lifetime of float zone wafers passivated with 100 nm SiO_y (black symbols), 80 nm SiN_x (blue symbols), and an equally deposited 100 nm SiO_y plus 80 nm SiN_x stack (green symbols) and subjected to a high temperature step.

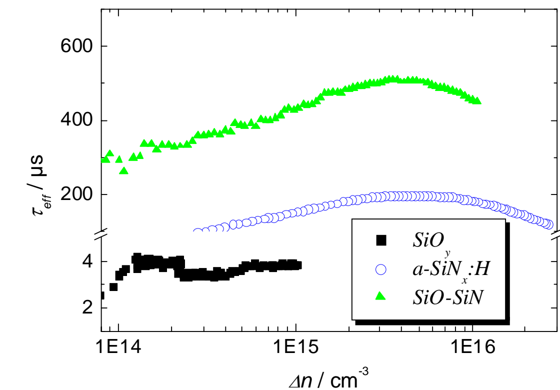

Figure 3: Effective minority carrier lifetime vs. excess minority carrier density for SiO_y, SiN_x, and SiO-SiN after a firing step

In fact, the SiO_y layer shows no passivation at all, no matter if a high temperature treatment was applied or not. Both the SiO-SiN and the SiN_x passivation are temperature stable with the stack passivation performing much better than the SiN_x single layer.

The results of the x-ray exposure are displayed below in Fig. 4. The lifetime map taken directly after the electron beam assisted evaporation reveals a total breakdown of the passivation in the non covered area. In the adhesive tape protected area the lifetimes are only slightly higher whereas the edge regions covered by the metallic sample holder show lifetimes above 100 µs. After annealing, the original lifetime is completely restored on the complete sample. Thus it can be stated that high energy radiation during electron gun based Al evaporation decreases lifetime drastically for SiO-SiN

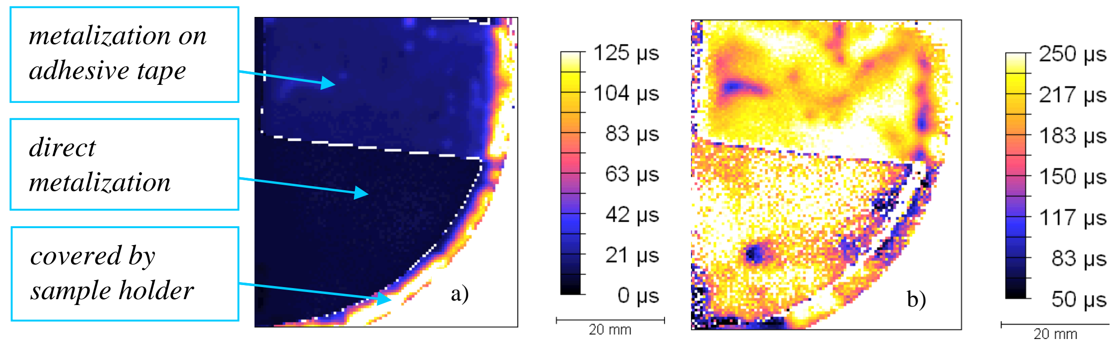

Figure 4: Lifetime maps of a SiO-SiN passivated sample a) after electron gun based Al evaporation and b) after subsequent annealing

stack samples. We also found that SiN_x is almost unaffected by x-ray exposure [5] and that no degradation of the SiO-SiN passivation scheme occurs if thermal evaporation is used. The latter clearly supports the explanation of the radiation induced degradation.

However, degradation of SiO-SiN passivation is also found for UV rich illumination as shown in Fig. 5 where the lifetime evolution during degradation of two different samples is displayed. The two lifetime samples A and B were taken from different deposition campaigns with several months in between. To account for lifetime changes during storage, an additional annealing step as described above was performed prior to the degradation experiment. The slight increase of the lifetime of sample A after the first short degradation period is most probably also due to a temperature effect, as the samples heat up to approx. 60 °C during degradation.

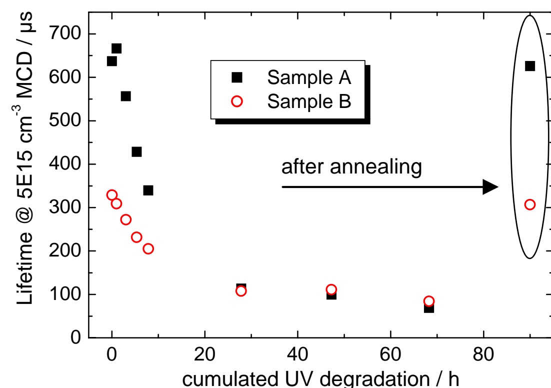

Figure 5: Development of the lifetime of SiO-SiN passivated samples with cumulated exposure time to UV rich illumination. Sample A is passivated by 100 nm SiO_y and 80 nm SiN_x, sample B by 70 nm SiO_y and 80 nm SiN_x.

With elongated degradation the samples seem to reach a saturation level which is identical for both sample A and B. Again, the initial lifetime can be fully recovered by an annealing in air ambient.

Samples with SiN_x only passivation behave slightly differently at exposure to UV rich illumination as can be seen from Fig. 6. We see again a small increase in lifetime with the first short degradation cycle as for the SiO-SiN passivated samples and afterwards the onset of a lifetime decay. However, in an equal time scale of cumulated exposure the measured lifetime does not reach a saturation level and the degradation is found to be not as severe as for the SiO-SiN stack passivation.

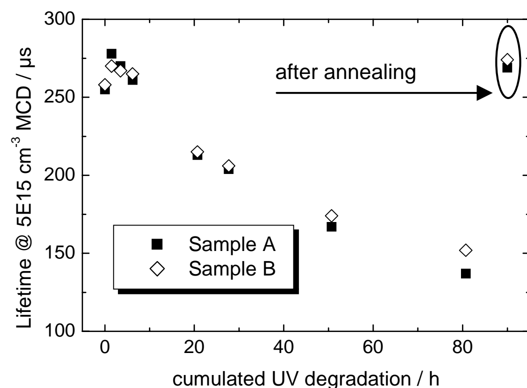

Figure 6: Development of the lifetime of only SiN passivated samples with cumulated exposure time to UV rich illumination. SiN_x thickness was 80 nm for both samples, the degradation was performed after an initial annealing step in air ambient.

The SiN_x passivation can as well be fully recovered after a final annealing step in air ambient

3.4 CELLO investigation

In order to investigate if the good passivation properties of the SiO-SiN stack still hold for solar cell devices and in order to check if differences between conventional and rear side passivated solar cells are not only caused by optical effects due to a better internal rear reflectance of the passivated cells, the solar cells' rear surface recombination (S_{back}) velocity was measured by photoimpedance spectroscopy with the CELLO set-up [11]. Fig. 7 reveals a distinct reduction in S_{back} for the SiO-SiN passivated solar cell with respect to a cell with full coverage back surface field from aluminum screen printing.

The point contacts of the rear side passivated cell are also clearly visible as spots of increased surface recombination velocity in Fig. 7b). The "bare silicon" edges of the solar cells - where for the conventional cell no back surface field was formed and for the passivated cell the passivation layer was removed during the photolithography / etching process - show in both cases a drastically increased recombination velocity.

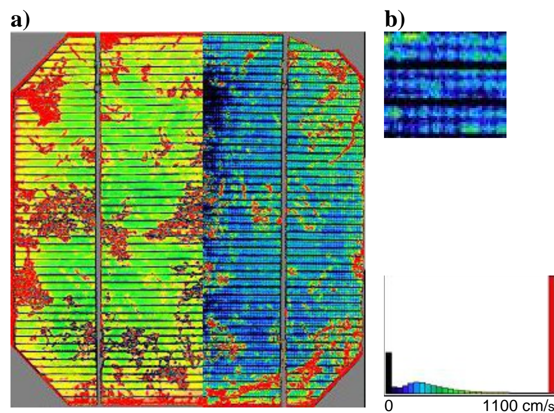

Figure 7: a) Rear surface recombination velocity of a solar cell with conventional rear side metallization (left) and SiO-SiN-rear side passivation plus screen printed metallization (right). b) shows a magnification of S_{back} of the passivated cell with visible contact points.

5 DISCUSSION AND SUMMARY

The PECVD SiO-SiN stack system shows good and high temperature stable passivation properties. In comparison with single SiN_x layers a reduced interface defect density and a reduced fixed charge density are found. The SiO-SiN system shows sensitivity to high energy radiation, however, the X-ray and UV light induced degradation is fully reversible under annealing.

Since the SiN_x-passivation is not as drastically affected by the X-radiation it is plausible that the SiO_y layer is responsible for the lifetime degradation. A similar behaviour was found and explained for SiO_2 for example by [12, 13]. Winokur and Sokoloski [12] could show that the radiation induced defect generation in thermal SiO_2 proceeds via several steps inside the SiO_2 and finally increases the D_{it}. The interface defect is in this case created by proton reactions, with the active species originating from Si-H or Si-O-H bonds. Additionally, Reed and Plummer [13] found that for the annealing of defects in SiO_2 created by X-radiation during electron beam aluminum evaporation no external hydrogen supply during the annealing is needed since hydrogen has already been released inside the material due to the radiation. As our SiO-SiN samples show very similar features we propose an equivalent microscopic process for the PECVD SiO_y deposited on silicon. Since the lifetime of the merely SiO_y passivated samples is so poor the effect can only be observed in SiO-SiN stack passivated wafers.

The fact that originally differently performing lifetime samples show degradation down to a certain and similar “saturation” lifetime level indicates that two different passivation mechanisms are responsible for the overall surface passivation of the SiO-SiN stack in the non degraded state. One of these two mechanisms is then affected by the radiation induced damage. With the explanation above that the radiation induced damage leads to an increase in D_{it} we attribute the loss in lifetime to a loss in chemical passivation, the “saturation lifetime” would in this case be determined by the field effect passivation.

The comparison of the UV degradation of SiO-SiN and SiN_x only passivated lifetime samples revealed some differences in the depassivation over exposure time. It is known for SiN_x that UV illumination leads to a discharge of the so called K^+ centres that are in their positively charged state responsible for the field effect passivation of SiN_x [14, 15]. Schmidt and Aberle [16] stated that these K^+ centres form near the Si-SiN_x interface assisted by a native oxide layer present on the Si surface. Thus it would not be stunning to find that different kinds of defects with different charging/decharging behaviour caused by UV illumination form at the Si-SiO_y, SiO_y-SiN_x, and Si-SiN_x interfaces. Further experiments to gain more insight into this topic are ongoing.

On cell level however, by applying the CELLO technique with its photoimpedance evaluation feature for determining the rear surface recombination velocity we could already show that the SiO-SiN passivation definitely works not only on lifetime samples. Spatially resolved measurements revealed the good passivation properties of SiO-SiN even after point contact formation and Al screen printing. For more information about the current status of the CELLO technique please refer also to the conference contributions BV.2.39 and 2DO.3.3.

6 ACKNOWLEDGEMENTS

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