SiliconPV 2023
Session 4: Silicon Materials
https://doi.or/10........ DOI placeholder (WILL BE FILLED IN BY TIB Open Publishing)

Investigation on the Long-Term Stability of AlO_x/SiN_y:H and SiN_y:H Passivation Layers during Illuminated Annealing at Elevated Temperatures

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Abstract. Most crystalline Si based solar cells, e.g. passivated emitter and rear cells, rely on SiN_y:H and AlO_x/SiN_y:H passivation layers. In this work, the long-term behavior of minority charge carrier lifetime in such symmetrically passivated samples during illuminated annealing at elevated temperatures is investigated by means of photoconductance decay based lifetime measurements, corona charging and capacitance voltage measurements. Thereby, AlO_x layers, which are known to reduce H in-diffusion due to their barrier properties, deposited by atmospheric pressure chemical vapor deposition as well as by atomic layer deposition were considered enabling a comparison of different deposition techniques. The frequently published behavior of the bulk related degradation could be confirmed and the qualitative correlation between maximum defect density and the changing total amount of H in the Si bulk due to the barrier properties of the individual layers dielectric layers could be shown. Furthermore, for the subsequently observed degradation accelerated by a treatment at higher temperatures, literature indicates degradation to be caused by surface related degradation. Investigations on field effect passivation during degradation by means of corona charging and CV measurements showed a large drop in fixed negative charges in the passivation layer stacks.

Keywords: Degradation, Surface passivation, Crystalline silicon

Introduction

Bulk related degradation (BRD) phenomena, such as light- and elevated temperature-induced degradation (LeTID), can reduce bulk minority charge carrier lifetime and thereby affect the efficiency of Si solar cells. However, the effective minority charge carrier lifetime τ_{eff} may suffer from surface related degradation (SRD) as well [1], [2]. Literature indicates that SRD can occur in samples passivated by SiN_y:H and AlO_x/SiN_y:H [2] – both passivation layer systems found in passivated emitter and rear cells (PERC). For both, LeTID and SRD, it is known that properties of the passivation layer can influence the kinetics of LeTID [3] and SRD [4]. In this work, short- and long-term stability of τ_{eff} in samples passivated by SiN_y:H and AlO_x/SiN_y:H during illuminated annealing at elevated temperatures is investigated. AlO_x layers from two different deposition tools, atmospheric pressure chemical vapor deposition (APCVD) and atomic layer deposition (ALD), are considered to check whether different AlO_x layer microstructures have an impact on degradation kinetics as already indicated in a previous study [5].

Experimental

For the degradation experiments ~1 Ωcm B-doped FZ-Si wafers serve as base material. After an HF etching step, 5-18°nm AlO_x is deposited on both sides by two different deposition techniques, APCVD at 590°C and ALD at 300°C, except for reference samples. All samples are then coated on both sides with 75 nm SiN_y:H via plasma-enhanced chemical vapor deposition and subsequently fired at a sample peak firing temperature of $T_{\text{sample,peak}}$ = 800°C. LeTID related degradation and regeneration is carried out at 80°C and 0.9(1) suns. After reaching a maximum in τ_{eff}, indicating that SRD starts to become dominant, treatment temperature is increased to 200°C to accelerate this second degradation. τ_{eff} is determined at room temperature using photoconductance decay (PCD) evaluated at an excess charge carrier density $\Delta n = 0.1\, p_0 \approx 1.5 \cdot 10^{15}$ cm^{-3}, with p_0 being the base doping. From PCD measurements, the lifetime equivalent maximum defect density (Δn → 0) ΔN^*_{leq}, is calculated as described in [6], [7]. Additionally, the surface saturation current density j_0 is determined. The evaluation of j_0 during both, BRD and SRD was performed by the j_0 difference analysis according to [7].

For the investigation of the passivation mechanism during SRD, the alternating PCD measurement and applying of corona charging (CC) are performed at two specific times, directly at the beginning of the temperature treatment at higher temperature ($t_{2,\text{initial}}$) and at the τ_{eff} minimum of SRD ($t_{2,\text{min}}$). In addition, the fixed charge density Q_f in the SiN_y:H and AlO_x/SiN_y:H layers is determined by capacitance voltage (CV) measurements directly after firing and at the τ_{eff} minimum of SRD. For CV measurements, Al was evaporated on one side of the samples followed by production of laser fired contacts (LFC). The evaluation of the CV data is performed according to [8] via the determination of the slope of the $1/C^2$ curve. The H content in the Si bulk is analyzed via resistivity measurements to determine the amount of acceptor-hydrogen pairs according to [9].

Results and Discussion

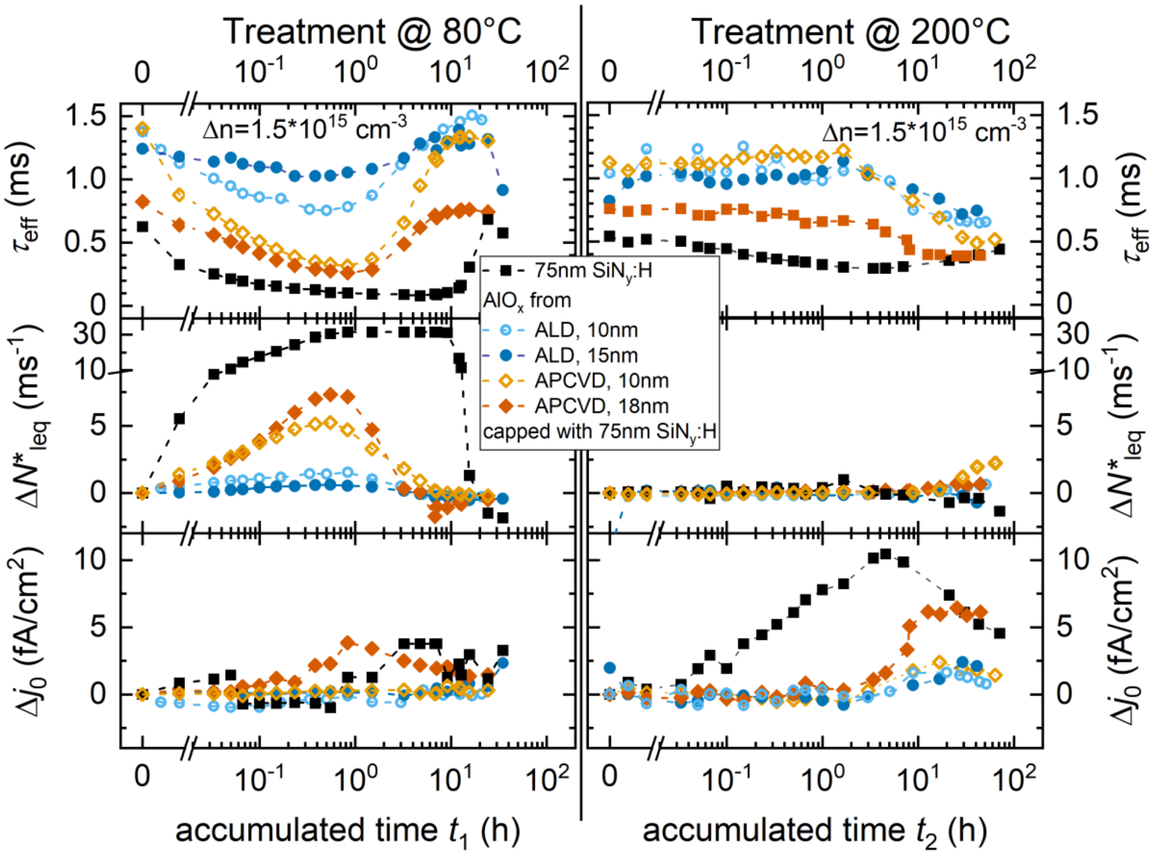

Figure 1. Measured τ_{eff} (top) and resulting ΔN^*_{leq} (middle) and change in j_0 (bottom) compared to initial values versus accumulated time for SiN_y:H and AlO_x/SiN_y:H passivated samples. To trigger degradation and regeneration related to LeTID, samples are first illuminated at 80°C (left) and subsequently at 200°C for accelerated study of SRD (right).

Fig. 1 shows the measured τ_{eff}, the resulting ΔN^*_{leq}, and change in j_0 values for the differently passivated samples. As expected, the progression of τ_{eff} and ΔN^*_{leq} values during illuminated annealing at 80°C shows a degradation and regeneration behavior which can be attributed to the LeTID defect. The occurrence of a BRD is indicated by the fact that j_0 stays nearly constant during degradation. During degradation at 80°C, the samples with AlO_x layer show lower ΔN^*_{leq} values compared to the sample with only SiN_y:H. With LeTID known to scale with the bulk H content, this behavior can be attributed to the barrier properties of the AlO_x layer, known to reduce in-diffusion of H [10], [11]. Indeed, a supplemental study on BH-pair formation confirms this reduced H content, see Fig. 2.

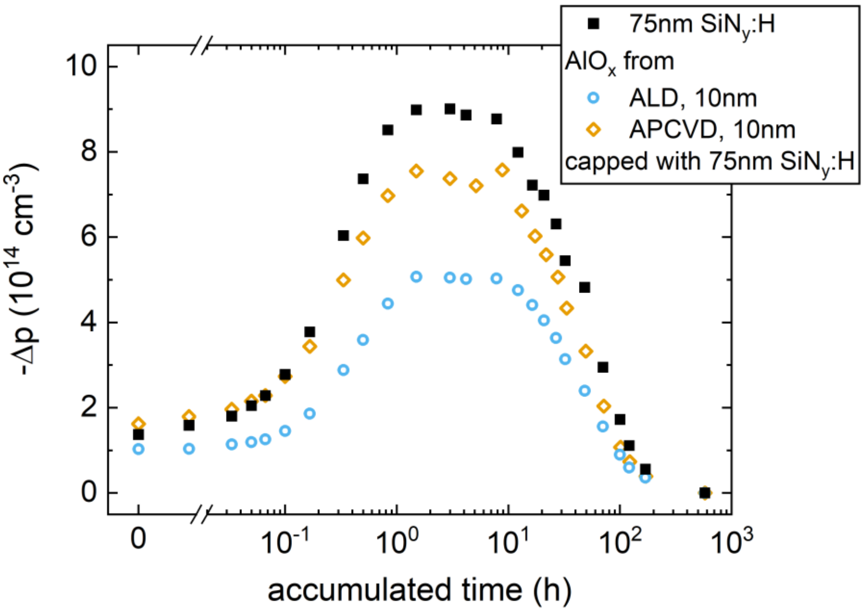

Figure 2. Change in hole concentration $-\Delta p$ versus accumulated time during dark anneal at 220°C for the differently passivated samples (fired).

Compared to ALD AlO_x, APCVD AlO_x shows barrier properties which are not as strong. After switching the treatment temperature to 200°C, the differently passivated samples suffer from a second degradation, whereby the samples with AlO_x/SiN_y:H stacks show a significantly delayed degradation compared to the SiN_y:H reference. The steady increase in j_0 of the SiN_y:H passivated sample suggests that this second degradation is related to surface passivation (SRD). A slight increase in j_0 is also observable for the AlO_x/SiN_y:H stacks but especially for the thinner AlO_x samples only to a very limited extent. Considering ΔN^*_{leq}, especially for the sample group with thinner APCVD AlO_x, it can be observed that something seems to change in the bulk for >20 h. This can also be confirmed in Fig. 3 (right). The injection-resolved lifetime curves show a reverse behavior (lower lifetimes at low injection) for t >20 h, which can undoubtedly be assigned to a BRD. So far, it is not clear what triggers this phenomenon.

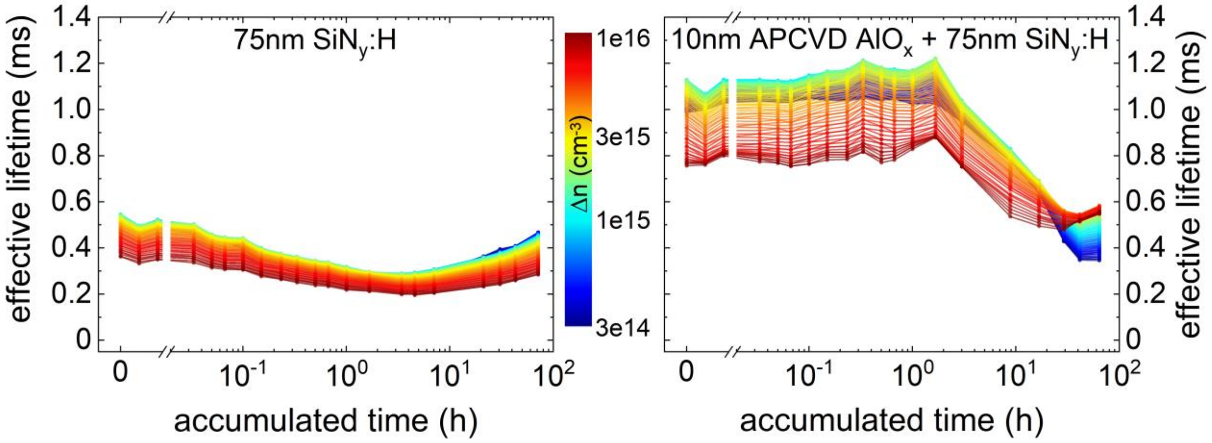

Figure 3. Injection resolved τ_{eff} over accumulated time of the sample with SiN_y:H (left) and of a sample with APCVD AlO_x/SiN_y:H (right) during degradation at 200°C (right).

Focusing on the surface, the behavior during CC of the samples is investigated, presented in Fig. 4, where the measured τ_{eff} is shown depending on charging time. At the beginning of SRD, the respective τ_{eff} minimum of the AlO_x/SiN_y:H stacks is almost at the same level. Compared to the SiN_y:H sample, the samples with AlO_x/SiN_y:H stacks show a higher minimum. However, a different behavior can be observed at the minimum in τ_{eff} of the following treatment at 200°C (Fig. 4, right). The minima of the AlO_x/SiN_y:H stacks are on a similar or even slightly higher level than at $t_{2,\text{initial}}$, but the CC time has decreased tremendously. Conversely, it can be observed for the SiN_y:H sample that the τ_{eff} minimum is slightly decreased and the corona charging time is very similar compared to $t_{2,\text{initial}}$. Note that a rather uncharged surface also leads to the fact that lifetime may not be described by an injection-independent j_0 value. This may explain the drop in j_0 during the second degradation (see Fig. 1, right) for the thinner AlO_x layer stacks.

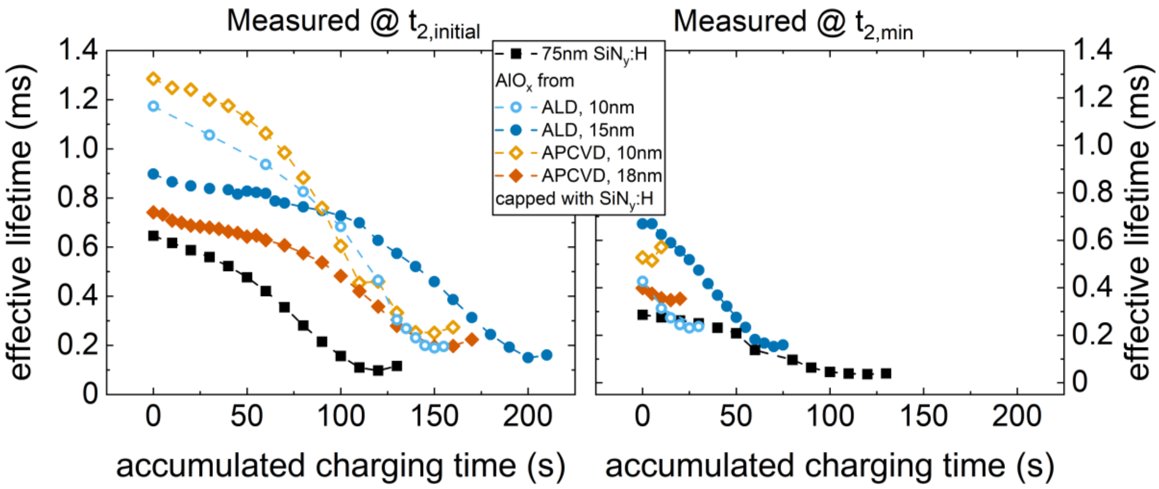

Figure 4. Corona charging time at the τ_{eff} minimum of the different samples with SiN_y:H layer or AlO_x/SiN_y:H layer stacks at the beginning (left) and at the minimum in τ_{eff} of the second degradation at 200°C (right). Negative charging for SiN_y:H, positive charging for AlO_x/SiN_y:H.

Thus, SRD in the SiN_y:H passivated sample could be explained by the decrease in chemical surface passivation quality, whereas the second degradation, between ~1-10 h at 200°C, in AlO_x/SiN_y:H passivated samples, seems to be related to a decrease in field effect passivation. It is remarkable that despite the strongly different extent of initial BRD, both, samples with ALD and APCVD AlO_x layers, show a very similar course during the second degradation.

For a comparison of the CC measurements, the CC duration until reaching the τ_{eff} minimum is shown for the differently passivated samples in Fig. 5 (left). In addition, CV measurements are applied to measure the absolute fixed charge density which is shown in Fig. 5 (right). Samples with AlO_x/SiN_y:H layers show a decline of negative fixed charges during SRD measured by CC as well as by CV. However, the quantitative amount measured by CV cannot be directly compared with the corona charging time, especially for APCVD AlO_x interlayers, which may be due to the differences in the layer microstructure. While the CC time of the SiN_y:H passivated samples does not change significantly during SRD, the CV measurements show that there is a slight increase in positive fixed charge density. There is thus a net decline of negative charge density or net increase of positive charge density during SRD independent of the passivation type. However, which of these is the case cannot be clearly assigned by the CV measurement. This allows the hypothesis to be made that the net fixed charge is involved in the SRD and opens the further question whether the positively charged H species plays a key role in SRD.

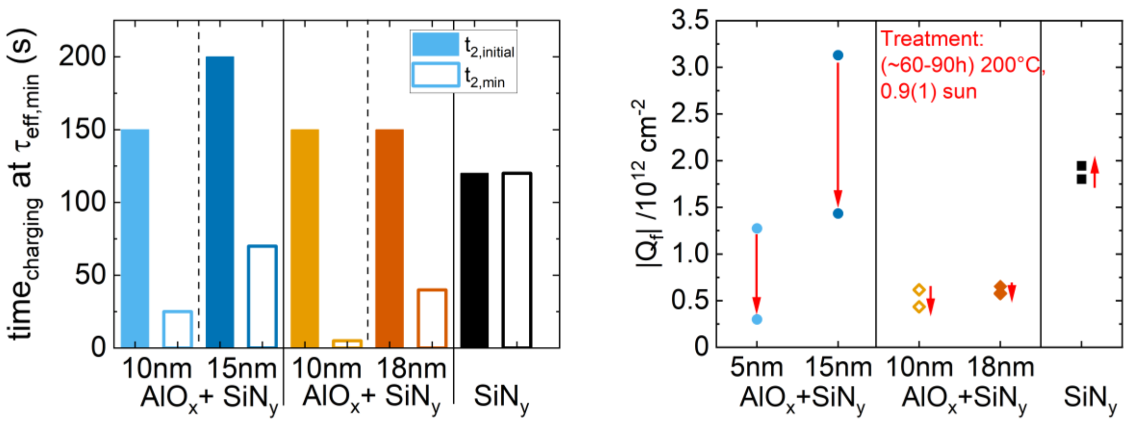

Figure 5. (Left) Corona charging time required to reach the τ_{eff} minimum (in Fig. 4) of the different samples with SiN_y:H layer or AlO_x/SiN_y:H layer stacks at the beginning (filled) and at the minimum of the second degradation (unfilled). (Right) Absolute fixed charge density $|Q_f|$ from CV measurements of the different samples with SiN_y:H layer or AlO_x/SiN_y:H layer stacks directly after firing and after reaching the minimum of the second degradation. Blue colours: ALD AlO_x, orange colours: APCVD AlO_x.

Conclusion

It could be shown that AlO_x layers from ALD and APCVD both serve as a barrier layer for H during firing. Since the ΔN^*_{leq} and $-\Delta p$ values of the ALD AlO_x/SiN_y:H passivated samples are lower than those of the APCVD AlO_x/SiN_y:H passivated samples, it is concluded that the ALD AlO_x layer has a stronger barrier effect and/or is a less effective source of H. This also confirms a correlation between ΔN^*_{leq} and H amount for LeTID. The second degradation for the SiN_y:H passivated samples could be attributed to SRD by the steady increase of j_0 and by the injection resolved lifetime. On the other hand, the AlO_x/SiN_y:H passivated samples with ALD and thin APCVD AlO_x layers show only a slight increase in Δj_0 and in addition the thin APCVD AlO_x layer sample group showed a reverse dependence in the injection-resolved lifetimes for >10 h at 200°C, indicating another and yet unknown BRD effect. From the CC and CV measurements, a decline of negative fixed charges in the AlO_x/SiN_y:H layers could be observed during SRD while in the SiN_y:H layer there is a slight increase in positive fixed charge density.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

F. Geml: conceptualization, project administration, supervision, validation, writing – original draft, writing – review & editing; **M. Mehler:** formal analysis, investigation, validation, visualization, conceptualization, writing – original draft, writing – review & editing; **S. Sanz:** investigation; **A. Herguth:** software, validation, writing – review & editing; **G. Hahn:** funding acquisition, project administration, resources, supervision, writing – review & editing.

Competing interests

The authors declare that they have no competing interests.

Funding

Part of this work was funded by German Federal Ministry for Economic Affairs and Climate Action under contract numbers FKZ 03EE1051C and FKZ 03EE1102C. The content is the responsibility of the authors.

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