

EFFECT OF DIFFERENT AL₂O₃ PASSIVATION LAYERS DEPOSITED BY APCVD AND ALD ON LETID

Melanie Mehler, Fabian Geml, Andreas Schmid, Annika Zuschlag, Giso Hahn
University of Konstanz, Department of Physics
D-78457 Konstanz, Germany

ABSTRACT: In this work the influence of Al₂O₃, acting as a barrier layer for in-diffusion of H from a H-rich dielectric layer, on the strength and kinetics of the LeTID (light- and elevated temperature-induced degradation) phenomenon is investigated. For this purpose, different Al₂O₃ passivating layers deposited by different deposition methods, APCVD (atmospheric pressure chemical vapor deposition) and ALD (atomic layer deposition), are considered. Since the composition and material properties of the Al₂O₃ layers fabricated in the two deposition systems are not exactly the same, the LeTID defect kinetics may differ. In the first experiment, by varying the Al₂O₃ layer thickness, it could be confirmed that on Cz material the Al₂O₃ layers grown by ALD and APCVD function as a barrier layer for H. In the second experiment, the comparison of the different Al₂O₃ layers from APCVD and ALD is considered in more detail. The deposition temperature is varied for the respective methods, but the Al₂O₃ layer thickness of 10 nm remains constant for all samples. To obtain conclusions on the LeTID behavior and the H content in the Si bulk, excess charge carrier lifetime and B-H measurements will be performed on the samples. Besides the Al₂O₃ single layers, Al₂O₃/SiN_y:H stacks are also investigated. The results show that the APCVD Al₂O₃ layer is more permeable to H than the Al₂O₃ layer grown by ALD. Alternatively, the obtained results could also be explained assuming that the APCVD layer contains generally more H in the layer than the ALD Al₂O₃ layer. The findings can help to better understand the origin of LeTID and find new processing sequences that can avoid or minimize the occurrence of LeTID, leading to higher stabilized efficiencies for high efficiency cell concepts.

Keywords: Degradation, Hydrogen, CVD Based Deposition

1 INTRODUCTION

Many high efficiency solar cell concepts such as PERC (passivated emitter and rear cell) are susceptible to degradation issues, reducing the efficiency over time. One of these phenomena is the LeTID (light- and elevated temperature-induced degradation) effect. The mechanism and the root cause of LeTID are not sufficiently understood yet. However, it has been shown that H plays an important role in LeTID [1-2]. The occurrence of LeTID was shown after firing of H-rich dielectric passivation layers such as SiN_y:H [3]. Since Al₂O₃ layers represent a diffusion barrier for atomic H, the H content in the Si bulk can be affected by them [4].

The aim in this work is to investigate different Al₂O₃ barrier layers that can influence the diffusion of H into the Si bulk in order to achieve a positive effect on the LeTID degradation behavior. Besides the variation of the layer thickness and the composition of the passivation layer, the deposition method can influence the LeTID effect. For this, the two different deposition methods APCVD (atmospheric pressure chemical vapor deposition) and ALD (atomic layer deposition) are investigated. In order to draw conclusions about the H content in the Si bulk, the concentration of BH pairs was determined via resistivity measurements.

2 EXPERIMENTAL

2.1 Sample preparation for Al₂O₃ as diffusion barrier

B-doped Cz-Si wafers with a bulk resistivity of ~1 Ωcm serve as base material and were lasered to 5x5 cm². After saw damage removal and cleaning, the samples are gettered using a POCl₃ diffusion. The resulting emitter is removed in an etching step and the samples are cleaned again. Afterwards, the samples are deposited with Al₂O₃ from ALD at 300°C and the thickness of the layer is varied from 10-25 nm. Since the deposition time is different for each layer thickness, the time was adjusted so that the samples have the same temperature

profile. In addition, 75 nm SiN_y:H was deposited on the Al₂O₃ layer. After firing at a temperature of T_{sample,peak}=813°C, samples were degraded at 80°C and at 0.9(1) suns. The effective lifetime τ_{eff} is determined using photoconductance decay (PCD) and evaluated at Δn=0.1·p₀, with p₀ being the doping density. To allow a better comparison of the degradation and regeneration behaviour, the lifetime equivalent defect density ΔN_{leq} is calculated from τ_{eff}.

2.2 Sample preparation for Al₂O₃ from different deposition tools

Again, B-doped Cz-Si (~1 Ωcm) serve as base material. After saw damage removal and cleaning, Al₂O₃ was deposited on the 5x5 cm² samples with two different deposition tools, APCVD and ALD. In addition to change of deposition methods, different deposition temperatures are also considered. With APCVD, Al₂O₃ layers are deposited at 590°C and 690°C, and with ALD at 170°C and 300°C. However, the Al₂O₃ layer thickness of 10 nm is the same for all samples. To investigate the influence of an additional SiN_y:H layer on LeTID and on the H content in the Si bulk, some of the samples were additionally coated on both sides with 75 nm SiN_y:H and fired at a temperature of T_{sample,peak}=813°C. The remaining samples, which are only coated with Al₂O₃, are also fired at the same temperature.

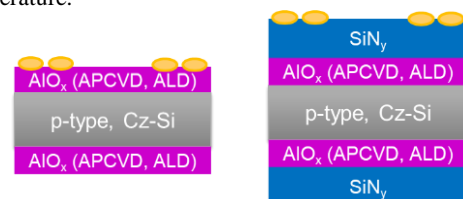


Figure 1: Schematic sample structure for B-H and lifetime measurements on fired samples with Al₂O₃ (left) and fired samples with Al₂O₃/SiN_y stacks (right). Al contacts shown in orange.

For the determination of the BH pairs via resistivity measurement [5], aluminum was deposited on one side of the samples followed by laser fired contacting (LFC), see Fig. 1. For better statistics, two samples were processed for each variation. Analogous to the previous procedure, τ_{eff} is determined using PCD and the samples were degraded at 80°C and at 0.9(1). For the BH measurements the samples were annealed at 220°C in the dark.

3 RESULTS

Fig. 2 shows the resulting ΔN_{leq} of the samples, which are deposited with 0-25 nm thick ALD AlO_x layers and an additional 75 nm thick $\text{SiN}_y\text{:H}$ layer. As expected, the progression of ΔN_{leq} values shows a degradation and regeneration behavior. Within the first hour, ΔN_{leq} increases and reaches the maximum after about 0.5-2 h, followed by a decrease of ΔN_{leq} . It can be seen that the different AlO_x layer thicknesses lead to a decrease in ΔN_{leq} . Compared to the 0 nm thick AlO_x layer, the maximum value of the $\Delta N_{\text{leq,max}}$ decreases from 12 ms^{-1} to below 4 ms^{-1} for the 10 nm thick AlO_x layer. Increasing the layer thickness to 15-25 nm does not lead to a further decrease of ΔN_{leq} . This could be due to a saturation value of AlO_x with regard to H diffusion. These data confirm the results of [6].

The same experiment with variation of AlO_x layer thickness was performed with APCVD. It could be shown that the APCVD AlO_x layers also function as a barrier layer [7].

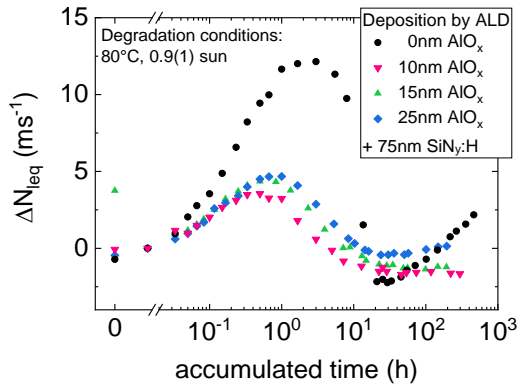


Figure 2: Lifetime equivalent defect density ΔN_{leq} over accumulated time (80°C, 0.9 sun) of AlO_x layers of different thickness with an additional 75 nm $\text{SiN}_y\text{:H}$ layer after firing.

When comparing the different AlO_x layers from the two deposition methods, the layer thickness of 10 nm, which acts as a diffusion barrier (see Fig. 2), is the same for all samples. As mentioned earlier, the determination of the BH pairs is done by resistance measurement, but not every change in resistance can be attributed to the change in BH pairs. Depending on the treatment conditions, thermal donors could occur which can influence the change in resistance [8]. Since one hole is consumed for the formation of BH pairs from H2 in boron-doped silicon [9], the change in hole concentration $-\Delta p$ is given. Thus, $-\Delta p$ includes the change in BH pairs and the possible occurrence of thermal donors.

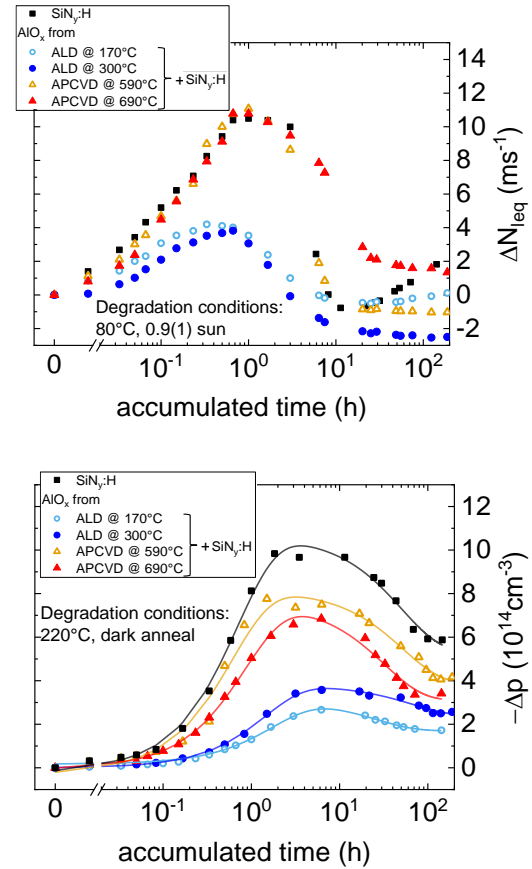


Figure 3: Lifetime equivalent defect density ΔN_{leq} (top) and change in hole concentration $-\Delta p$ with fit (bottom) over accumulated time of AlO_x layers deposited by APCVD and ALD with an additional 75 nm $\text{SiN}_y\text{:H}$ layer after firing.

Fig. 3 shows the defect density ΔN_{leq} and changing hole concentration $-\Delta p$ over treatment time of the fired samples with $\text{AlO}_x/\text{SiN}_y\text{:H}$ layers and $\text{SiN}_y\text{:H}$ layer as reference. The ALD AlO_x layers was deposited at 170°C and 300°C, and the APCVD AlO_x layers at 590°C and 690°C. Also here, the progression of ΔN_{leq} shows a degradation and regeneration behaviour. The maximum of ΔN_{leq} lies for all samples around 1 h and as can be seen, that the maximum of ΔN_{leq} for the APCVD AlO_x layers ($\sim 11 \text{ ms}^{-1}$) and for the $\text{SiN}_y\text{:H}$ reference ($\sim 11 \text{ ms}^{-1}$) is higher than for the ALD layers ($< 4 \text{ ms}^{-1}$). During degradation the $\text{SiN}_y\text{:H}$ reference and the APCVD AlO_x layer have comparable ΔN_{leq} values but differs during regeneration. APCVD AlO_x deposited at 690°C shows a flatter progression of regeneration compare to AlO_x deposited at 590°C and $\text{SiN}_y\text{:H}$ reference. Furthermore, except for the $\text{SiN}_y\text{:H}$ reference and the ALD AlO_x layer deposited at 170°C, the samples do not reach the minimum of ΔN_{leq} within 200 hours.

In the lower graph of Fig. 4 the changing hole concentration $-\Delta p$ is given. As mentioned in the experimental part, for the BH measurements two samples were processed for each variation, but since the data of the two samples is reproducible, only one sample per variation is shown in the graph. In the first hours $-\Delta p$ increases and reaches the maximum after about 2-10 h, afterwards $-\Delta p$ starts to decrease again before $-\Delta p$ starts to rise again after 200 h. Since it can be assumed that this second increase is not caused by the formation of BH pairs but by other

processes in the Cz-Si, e.g. thermal donors, the data are normalized to $t=0$. As can be seen, the maximum of $-\Delta p$ for the APCVD AlO_x layers ($6\text{-}8\cdot 10^{14}\text{ cm}^{-3}$) is higher than for the ALD layers ($<4\cdot 10^{14}\text{ cm}^{-3}$). Together with the results of the defect densities ΔN_{leq} the APCVD layer appears to be more permeable to H diffusion from the $\text{SiN}_x\text{:H}$ layer than the ALD layer. It could also suggest that the APCVD AlO_x layer generally already contains more H than the ALD layer.

To get more insight into the influence of the different AlO_x layers, AlO_x samples with or without additional $\text{SiN}_x\text{:H}$ layer are investigated. Fig. 4 shows the resulting ΔN_{leq} and $-\Delta p$ of the fired samples passivated either with AlO_x only or with $\text{AlO}_x/\text{SiN}_x\text{:H}$. The AlO_x layers are deposited with the ALD at 170°C and 300°C . Since the single APCVD AlO_x layers have a very low effective lifetime ($\tau_{\text{eff}} < 1\ \mu\text{s}$) which affect the degradation behavior, the sample was not further analysed. Also here, the normalization was performed at time $t=0$.

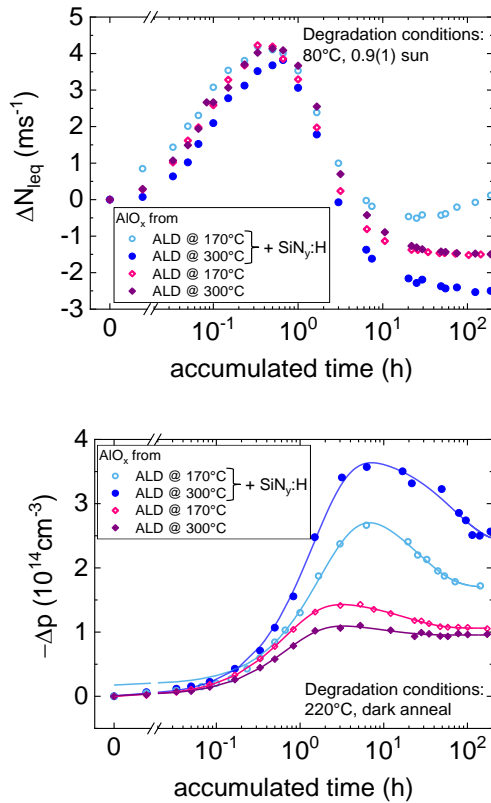


Figure 4: Lifetime equivalent defect density ΔN_{leq} (top) and change in hole concentration $-\Delta p$ (bottom) over accumulated time of single AlO_x and $\text{AlO}_x/\text{SiN}_x\text{:H}$ layers. AlO_x layers deposited with ALD at 170°C and 300°C .

The ALD AlO_x samples with and without $\text{SiN}_x\text{:H}$ show the same defect kinetics. During degradation the deposition temperature does not seem to have any influence on ΔN_{leq} . However, the presence of an additional $\text{SiN}_x\text{:H}$ layer appears to affect the regeneration kinetics. The minimum of ΔN_{leq} is less than 30 hours for AlO_x/C stacks at ALD deposition of 170°C while the minimum is not reached within 200 hours for samples with single AlO_x layer and for $\text{AlO}_x/\text{SiN}_x\text{:H}$ stack at ALD deposition of 300°C . Thus, the deposition temperature seems to have an influence on the regeneration kinetics through the presence of a $\text{SiN}_x\text{:H}$

layer. In the lower graph of Fig. 4 the changing hole concentration $-\Delta p$ is given. As can be seen, the maximum $-\Delta p$ for the $\text{AlO}_x/\text{SiN}_x\text{:H}$ layer ($2\text{-}4\cdot 10^{14}\text{ cm}^{-3}$) is higher than for the single AlO_x layer ($<1.5\cdot 10^{14}\text{ cm}^{-3}$). Thus, as expected, an additional $\text{SiN}_x\text{:H}$ leads to more H in the Si bulk. Therefore, the additional $\text{SiN}_x\text{:H}$ layer leads to a doubling of the hole concentration. The deposition temperature does not appear to have a significant effect on $-\Delta p$.

4 CONCLUSION

Since the ALD AlO_x shows lower defect density ΔN_{leq} and changing hole concentration $-\Delta p$ compared to AlO_x deposited by APCVD, it seems that ALD AlO_x has a stronger barrier effect than APCVD AlO_x . Besides the barrier properties, a general high amount of H in the APCVD AlO_x layer compared to ALD AlO_x can also be an explanation. The influence of different deposition temperatures of ALD or APCVD show no significant influence on the degradation kinetic but on the regeneration kinetic. Also, the samples with and without additional $\text{SiN}_x\text{:H}$ layer show comparable ΔN_{leq} and $-\Delta p$ values during degradation, but differ during regeneration. The influence of the temperature input during deposition is further described in [7]. Due to the thermal donors, the BH measurements on FZ material seem to be more suitable.

5 ACKNOWLEDGEMENT

Part of this work was financially supported by the German Federal Ministry for Economic Affairs and Climate Action (FKZ 03EE1051). The content is the responsibility of the authors.

6 REFERENCES

- [1] M.A. Jensen et al., J. Appl. Phys. 124(8) (2018) 085701.
- [2] K.W. Boer, Solar Cells 16 (1996) 591.
- [3] F. Kersten et al., Energy Procedia 92 (2016) 828-832.
- [4] A.A. Dameron et al., J. Phys. Chem. C 112(12) (2008) 4573-4580.
- [5] A. Herguth, C. Winter, IEEE J. Photovolt. 11(4) (2021) 1059-1068
- [6] A. Schmid, et al., IEEE J. Photovolt. 11(4) (2021) 967-973.
- [7] F. Geml and M. Mehler et al., to be published, 2022.
- [8] C. Winter et al., Phys. Status Solidi A 218(23) (2021) 2100220.
- [9] C. Sah et al., Appl. Phys. Lett. 43 (1983) 204-206.