

SiliconPV: 17-20 April 2011, Freiburg, Germany

Comparison of the thermal stability of single Al_2O_3 layers and $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks for the surface passivation of silicon

Boris Veith^{a,*}, Florian Werner^a, Dimitri Zielke^a, Rolf Brendel^{a,b}, Jan Schmidt^{a,b}

^a*Institute for Solar Energy Research Hamelin (ISFH), Am Ohrberg 1, 31860 Emmerthal, Germany*

^b*Institute of Solid-State Physics, University of Hannover, Appelstrasse 2, 30167 Hannover, Germany*

Abstract

We measure surface recombination velocities (SRVs) below 10 cm/s on low-resistivity (1.4 Ωcm) *p*-type crystalline silicon wafers passivated with plasma-assisted and thermal atomic layer deposited (ALD) aluminium oxide (Al_2O_3) films. Ultrathin Al_2O_3 films (< 5 nm) are particularly relevant for the implementation into solar cells, as the deposition rate of the ALD process is very low compared to e.g. plasma-enhanced chemical vapor deposition (PECVD). Hence, we examine the passivation quality of a stack consisting of an ultrathin Al_2O_3 passivation layer deposited by ALD and a SiN_x capping layer deposited by PECVD. Our experiments show a substantial improvement of the thermal stability during firing at 810°C for the $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks compared to a single Al_2O_3 layer. We report on a ‘regeneration effect’ observed for Al_2O_3 single layers after firing, where the degraded passivation is significantly improved after annealing at 400°C and also by illumination at room temperature using a halogen lamp. Nevertheless, for $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks we measure SRVs < 15 cm/s after firing, whereas for Al_2O_3 single layers the regenerated SRVs are in the range of 10-30 cm/s. $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks are hence ideally suited for the implementation into industrial-type silicon solar cells, although ‘regenerated’ Al_2O_3 single layers should result in a comparable cell performance.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).
Selection and/or peer-review under responsibility of SiliconPV 2011.

Keywords: Silicon; Surface passivation; Aluminum oxide; Solar Cells

1. Introduction

In recent years, aluminum oxide (Al_2O_3) deposited by atomic layer deposition (ALD) has been shown to provide an outstanding level of surface passivation on crystalline silicon [1,2,3] due to its large

* Corresponding author. Tel.: +49-5151-999-635; fax: +49-5151-999-400.
E-mail address: veith@isfh.de.

negative fixed charge density and moderate interface state density. No parasitic shunting was observed on passivated emitter and rear solar cells (PERC) on *p*-type silicon [4] and very high independently confirmed efficiencies of 21.4% were achieved [5]. These lab-type solar cells featured evaporated metal contacts. Industrial-type solar cells however use screen-printing of metal pastes and firing at high temperatures (700-900°C) for the contact formation. Hence, they require a high thermal stability of the surface passivation. In a recent contribution we demonstrated that ultrathin Al₂O₃ layers tend to degrade during firing, but that a hydrogen-containing SiN_x capping layer deposited by PECVD improves the firing stability [6]. In this work we investigate the impact of different firing conditions on the level of surface passivation for various Al₂O₃ layer thicknesses and for Al₂O₃/SiN_x stacks for Al₂O₃ layer grown by plasma-assisted (PA) ALD and by thermal ALD. Our experimental results reveal that Al₂O₃/SiN_x stacks are the ideal choice for the passivation of the rear of screen-printed industrial PERC-type solar cells.

2. Surface passivation: Al₂O₃ vs Al₂O₃/SiN_x stacks

The symmetrical lifetime samples used in this study were fabricated on (100)-oriented 300 μm thick *p*-type float-zone (FZ) silicon wafers of 1.4 Ωcm resistivity with a size of 12.5×12.5 cm². All wafers were RCA-cleaned before surface passivation. Al₂O₃ films were symmetrically deposited on both wafer surfaces in an Oxford Instruments FlexAL™ reactor [7] by PA-ALD at a deposition temperature of 200°C, or by thermal ALD at 260°C, respectively. On some samples SiN_x films with a refractive index of *n* = 2.05 (at 632 nm) and a thickness of 70 nm were deposited on top of the Al₂O₃ in a Roth & Rau SiNA system using plasma-enhanced chemical vapor deposition (PECVD). The effective carrier lifetimes were measured using the photoconductance decay method [8] (Sinton Instruments WCT120).

The initial effective lifetimes measured directly after Al₂O₃ deposition are usually very low (~3 μs for PA-ALD and 20-100 μs for thermal ALD [9]). After deposition of the SiN_x layer we measure a higher effective lifetime, which indicates that the deposition of SiN_x at a deposition temperature of ~400°C for several minutes has an effect similar to a short anneal. Figure 1 shows the effective lifetime τ_{eff} for different post-deposition treatments as a function of Al₂O₃ layer thickness, in (a) for PA-ALD and in (b) for thermal ALD. Without an additional anneal of the PA-ALD-Al₂O₃/SiN_x stacks, no thickness dependence of the effective lifetime is observed for a thickness ≥ 4 nm. After annealing at a temperature of 425°C for 15 min a thickness dependence can be observed showing the best results for PA-ALD-Al₂O₃ layers ≥ 20 nm. The best lifetime results are achieved with annealed PA-ALD-Al₂O₃ single layers,

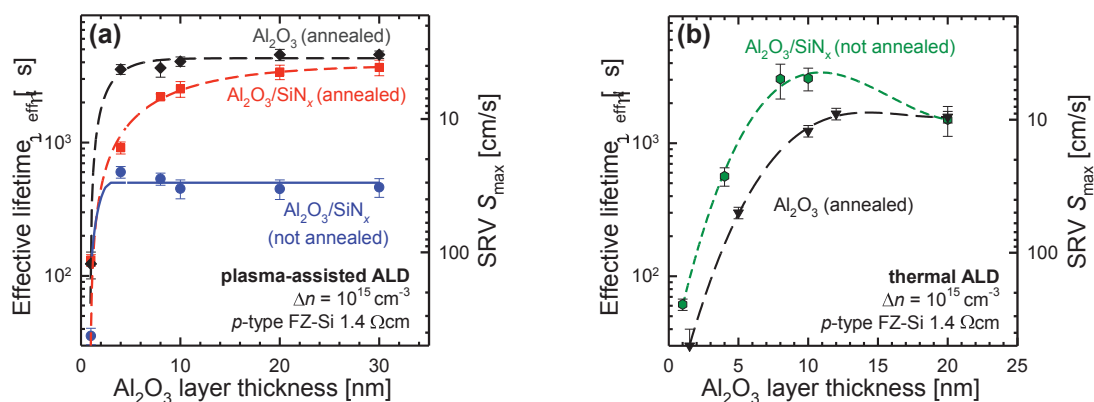


Fig. 1. Measured effective lifetime as a function of Al₂O₃ layer thickness for lifetime samples (a) with PA-ALD-Al₂O₃ layers and (b) with thermal ALD-Al₂O₃ layers with and without SiN_x capping layers. Annealing was performed at 425°C for 15 min. The lines are guides to the eye.

yielding lifetimes between 4 and 5 ms. This lifetime is above the commonly used empirical expression for the intrinsic lifetime limit of 3.1 ms for 1.4 Ωcm p -type silicon [10], showing the nearly perfect passivation quality of the Al_2O_3 layers. Assuming an infinite bulk lifetime, the upper limit of the effective surface recombination velocity (SRV) is $S_{\text{max}} = 4$ cm/s, as calculated using $S_{\text{max}} = W/(2\tau_{\text{eff}})$, where W is the wafer thickness. After deposition of the SiN_x capping layer, the thermal ALD- $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks already show an excellent surface passivation, with effective lifetimes up to $\tau_{\text{eff}} = 3.6$ ms, corresponding to an S_{max} of 4.2 cm/s. This lifetime is higher than the effective lifetime that could be reached with thermal ALD- Al_2O_3 single layers. Hence, for thermal ALD- Al_2O_3 the passivation quality can be significantly improved using SiN_x as capping layer, which might be due to the hydrogenation of interface states.

3. Thermal stability

Firing experiments were performed in an industrial infrared conveyor-belt furnace (Centrotherm Contact Firing Furnace DO-FF-8.600-300). Most of the experiments were performed with a set peak temperature of 860°C and a belt speed of 3 m/min. We also used a recipe with a belt speed of 5.9 m/min and higher set peak temperature of 910°C. These two recipes are typical firing conditions for the production of screen-printed silicon solar cells. When using the ‘slow’ profile the silicon is ~12 s above 600°C compared to ~6 s for the ‘fast’ profile, whereas the peak temperature of the silicon is comparable (~810°C).

Figure 2 shows the effective lifetime after firing for different layer systems using the ‘slow’ profile with 860°C and the ‘fast’ profile with 870°C, 910°C and 950°C as set peak temperatures. It can be seen that for all layer systems the ‘fast’ profile provides the higher lifetimes, with the thicker (20 nm) PA-ALD- Al_2O_3 single layer showing a better firing stability at the maximum set temperature of 950°C. For the PA-ALD- $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks (10 nm Al_2O_3 and 70 nm SiN_x) a peak temperature of 910°C is optimal, resulting in lifetimes up to 5 ms, corresponding to a SRV below 4 cm/s. When using the ‘slow’ profile, the effective lifetime after firing decreases well below 1 ms for both PA-ALD- Al_2O_3 single layers. Hence, the ‘slow’ profile is more detrimental to the single PA-ALD- Al_2O_3 layers compared to the PA-ALD- $\text{Al}_2\text{O}_3/\text{SiN}_x$ stack, which still provides a SRV < 7 cm/s after the ‘slow’ firing. Note that the samples of Fig. 2 and Fig. 3 received no pre-firing anneal at low temperature (~425°C). Annealed samples were examined as well but showed the same effective lifetime after firing as the non-annealed samples.

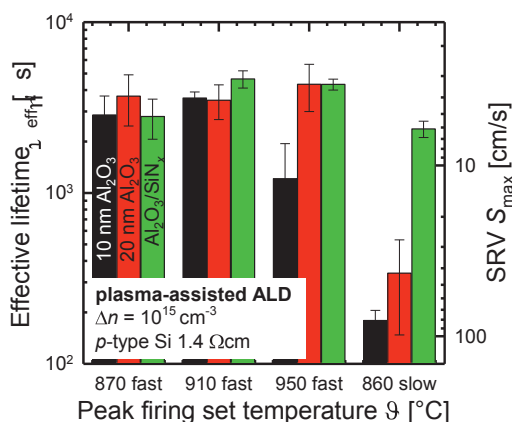


Fig. 2. Measured effective lifetime as a function of firing profile and set peak temperature. Shown are PA-ALD- Al_2O_3 layers with 10 nm and 20 nm thickness and PA-ALD- $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks with 10 nm Al_2O_3 and 70 nm SiN_x . The samples received no pre-firing anneal.

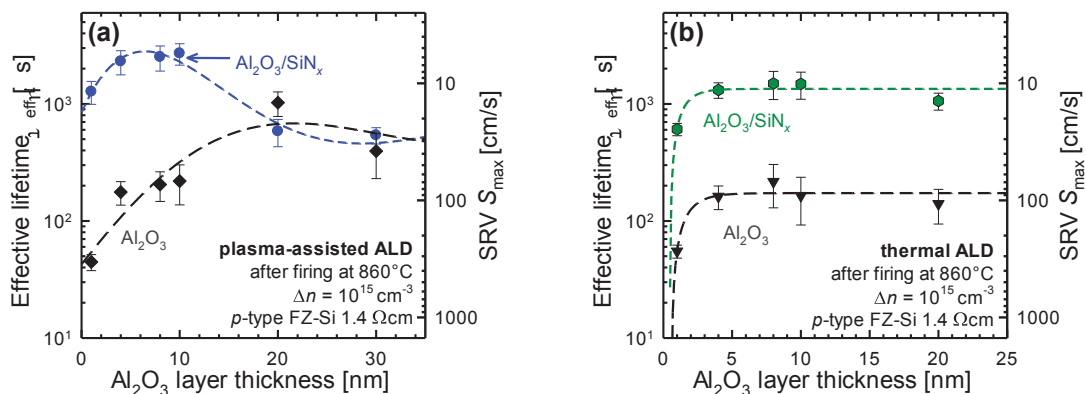


Fig. 3. Measured effective lifetime as a function of Al₂O₃ layer thickness after firing using the ‘slow’ profile with a peak temperature of 860°C. Shown are the results for (a) PA-ALD-Al₂O₃ layers and (b) thermal ALD-Al₂O₃ layers with and without SiN_x capping layer. The samples received no pre-firing anneal. The lines are guides to the eye.

Figure 3 shows the effective lifetime after firing using the ‘slow’ profile for different layer systems as a function of Al₂O₃ layer thickness, in (a) for PA-ALD-Al₂O₃ and in (b) for thermal ALD-Al₂O₃. For PA-ALD-Al₂O₃ single layer < 20 nm a pronounced degradation of the effective lifetime after firing is observed compared to the lifetimes after annealing at 425°C shown in Fig. 1, whereas Al₂O₃/SiN_x stacks with thin Al₂O₃ layers below 20 nm show negligible degradation of the effective lifetime and even an improvement for ultrathin layers ≤ 4 nm. For layers of thickness ≥ 20 nm there is no significant difference between single layers and Al₂O₃/SiN_x stacks. Both PA-ALD-Al₂O₃ [Fig. 3(a)] and thermal ALD-Al₂O₃ [Fig. 3(b)] layers provide almost the same passivation level, with slightly higher effective lifetimes for the PA-ALD-Al₂O₃/SiN_x stacks than for the thermal ALD-Al₂O₃/SiN_x stacks. It is noteworthy that both stack systems with Al₂O₃ layers between 4–10 nm provide lifetimes between 1 and 3 ms after firing, corresponding to a SRV below 11 cm/s. Hence both stacks are well suitable for the application to high-efficiency screen-printed PERC-type solar cells.

4. Regeneration of passivation

We investigate the impact of illumination and annealing on the degraded lifetime after firing using the ‘slow’ profile on samples with a single 10 nm PA-ALD-Al₂O₃ layer. The degraded lifetime of 200 μs after firing can be significantly improved both by annealing at 400°C, which is in good agreement with results published recently by Lüder et al. [11], and by illumination at room temperature. The lifetime improves up to 900 μs after illuminating the samples for 1 hour at 20 mW/cm² using a halogen lamp. The samples that receive a post-firing anneal at 400°C reach a peak in the effective lifetime at 700–800 μs after 15 min. This corresponds to the optimal annealing parameters for the post-deposition anneal, showing that the post-firing anneal has approximately the same time constant as the post-deposition anneal.

The ‘regeneration effect’ was examined in more detail on a batch of samples using only PA-ALD-Al₂O₃ layers. Figure 4(a) shows the measured effective lifetime as a function of illumination time for different illumination intensities. The samples were kept at 80°C during illumination. Samples kept in the dark at 120°C for 60 min as reference did not show a significant change in lifetime over the 60 minutes. The samples that were illuminated showed a steep increase in effective lifetime already after 5 seconds of illumination [Fig. 4(a)]. We fitted the measured data with a double exponential with the fast component

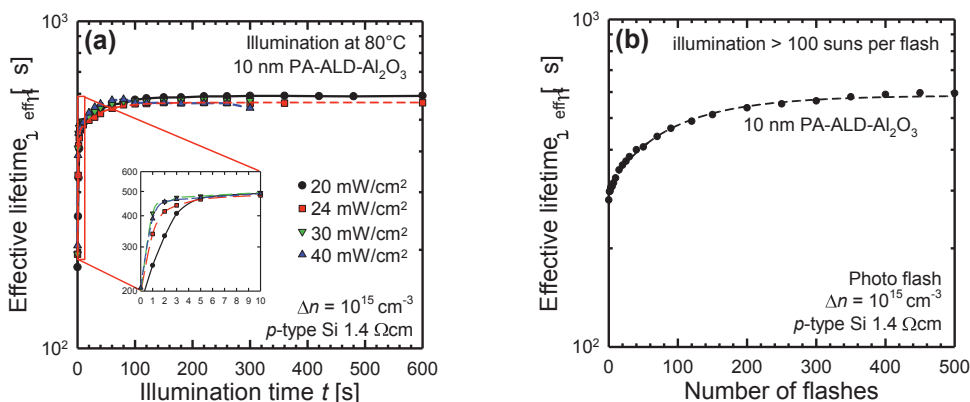


Fig. 4. (a) Measured effective lifetime as a function of illumination time for lifetime samples with a 10 nm PA-ALD-Al₂O₃ layer after firing using the ‘slow’ profile. The lines are fits using a double exponential. (b) Measured effective lifetime as a function of number of photo flashes for a 10 nm PA-ALD-Al₂O₃ layer after firing using the ‘slow’ profile. The line is a guide to the eye.

responsible for the steep lifetime increase during the first minute. The rate of the fast component is denoted R . After firing the samples showed effective lifetimes of around 200 μs and after illumination for 10 min around 600 μs . The inset in Fig. 4(a) shows that the illumination intensity only has an influence during the first 5 seconds. This is attributed to an already high regeneration rate caused by the 80°C substrate temperature [Fig. 5(a)], which was used to keep the samples at a constant temperature. The inset in Fig. 4(a) suggests that the regeneration rate saturates with increasing illumination intensity, but this is probably due to a high measurement uncertainty of the illumination time when illuminating for only 1 second. To further reduce the illumination time intervals, we used a photoflash Quantum Qflash X5d-R for illumination. In Fig. 4(b) the measured effective lifetime is plotted as a function of number of flashes for a sample with 10 nm PA-ALD-Al₂O₃. The sample was placed in a distance of 5 cm from the bulb. The total flash duration is 14 ms with an exponential decay in intensity, but the intensity remains above 100 suns during the entire 14 ms of flash duration. From our experimental data shown in Fig. 4(b) we estimate 6 seconds as illumination time needed to reach a lifetime of around 600 μs .

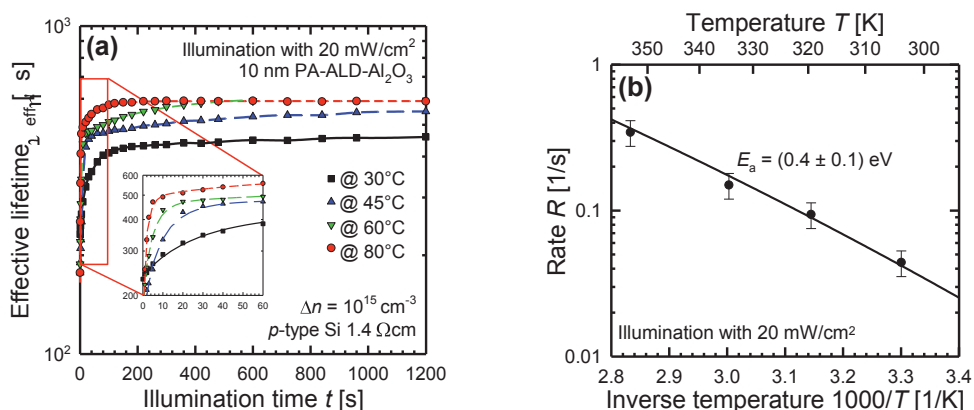


Fig. 5. (a) Measured effective lifetime as a function of illumination time for lifetime samples after firing using the ‘slow’ profile. Samples were illuminated with 20 mW/cm² and the sample temperature was varied. The lines are fits using a double exponential. (b) Regeneration rate as a function of inverse temperature for a 10 nm PA-ALD-Al₂O₃ layer illuminated with 20 mW/cm².

Figure 5(a) shows the effective lifetime as a function of illumination time for different sample temperatures during illumination. All samples were illuminated with 20 mW/cm^2 . The sample at 80°C reaches a lifetime of around $600 \mu\text{s}$ after 10 min, whereas the sample at room temperature reaches a lifetime above $500 \mu\text{s}$ after 40 min of illumination. The inset in Fig. 5(a) shows that the regeneration rate R strongly increases with increasing temperature. In Fig. 5(b) the calculated regeneration rate R as a function of inverse temperature in an Arrhenius plot is shown. We extract an activation energy of $E_a = (0.4 \pm 0.1) \text{ eV}$ for an illumination intensity of 20 mW/cm^2 . Further investigations on the physics of the regeneration process are currently under way in our lab [12].

5. Conclusion

We have shown that the thermal stability of Al_2O_3 single layers is excellent when using a ‘fast’ firing profile with a small thermal budget. The passivation quality is reduced after a ‘slow’ firing process, but can be improved by annealing or by illuminating the samples. Thin ($\leq 10 \text{ nm}$) Al_2O_3 layers show excellent thermal stability for all used firing profiles when a PECVD- SiN_x capping layer is applied. $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks are hence ideally suited for the implementation into industrial-type silicon solar cells.

Acknowledgements

Funding was provided by the State of Lower Saxony and the German Ministry for the Environment, Nature Conservation and Nuclear Safety (BMU) under contract number 0325050 (“ALD”).

References

- [1] Agostinelli G, Delabie A, Vitanov P, Alexieva Z, Dekkers HFW, De Wolf S, Beaucarne G. Very low surface recombination velocities on p -type silicon wafers passivated with a dielectric with fixed negative charge. *Solar Energy Materials & Solar Cells* 2006; **90**:3438-3443
- [2] Hoex B, Heil SBS, Langereis E, van de Sanden MCM, Kessels WMM. Ultralow surface recombination of c -Si substrates passivated by plasma-assisted atomic layer deposited Al_2O_3 . *Applied Physics Letters* 2006; **89**:042112
- [3] Dingemans G, Seguin R, Engelhart P, van de Sanden MCM, Kessels WMM. Silicon surface passivation by ultrathin Al_2O_3 films synthesized by thermal and plasma atomic layer deposition. *Physica Status Solidi Rapid Research Letters* 2010; **4**:10-12
- [4] Schmidt J, Merkle A, Brendel R, Hoex B, van de Sanden MCM, Kessels WMM. Surface Passivation of High-efficiency Silicon Solar Cells by Atomic-layer-deposited Al_2O_3 . *Progress in Photovoltaics: Research and Application* 2008; **16**:461-466
- [5] Schmidt J, Werner F, Veith B, Zielke D, Bock R, Tiba V et al.. Industrially relevant Al_2O_3 deposition techniques for the surface passivation of Si solar cells. *Proceedings of the 25th European Photovoltaic Solar Energy Conference, Valencia, Spain, 2010*, pp. 1130-1133
- [6] Schmidt J, Veith B, Brendel R. Effective surface passivation of crystalline silicon using ultrathin Al_2O_3 films and $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks. *Physica Status Solidi Rapid Research Letters* 2009; **3**:287-289
- [7] Heil SBS, van Hemmen JL, Hodson CJ, Singh N, Klootwijk JH, Roozeboom F et al.. Deposition of TiN and HfO_2 in a commercial 200 mm remote plasma atomic layer deposition reactor. *Journal of Vacuum Technology A* 2007; **25**:1357-1366.
- [8] Kane DE, Swanson RM. Measurement of the emitter saturation current by a contactless photoconductivity decay method. *Proceedings of the 18th IEEE Photovoltaic Specialists Conference, Las Vegas, USA, 1985*, pp. 578-583.
- [9] Schmidt J, Veith B, Werner F, Zielke D, Brendel R. Silicon surface passivation by ultrathin Al_2O_3 films and $\text{Al}_2\text{O}_3/\text{SiN}_x$ stacks. *Proceedings of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, USA, 2010*, pp. 885-890.
- [10] Kerr MJ, Cuevas A. General parameterization of Auger recombination in crystalline silicon. *Journal of Applied Physics* 2002; **91**:2473-2480.
- [11] Lüder T, Raabe B, Terheiden B. Annealing behavior of Al_2O_3 thin films grown on crystalline silicon by atomic layer deposition. *Proceedings of the 25th EU Photovoltaic Solar Energy Conference, Valencia, Spain, 2010*, pp. 2138 - 2140.
- [12] Veith B et al.. in preparation