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

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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$_2$O$_3$) films. Ultrathin Al$_2$O$_3$ 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$_2$O$_3$ 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 Al$_2$O$_3$/SiN$_x$ stacks compared to a single Al$_2$O$_3$ layer. We report on a ‘regeneration effect’ observed for Al$_2$O$_3$ 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 Al$_2$O$_3$/SiN$_x$ stacks we measure SRVs < 15 cm/s after firing, whereas for Al$_2$O$_3$ single layers the regenerated SRVs are in the range of 10-30 cm/s. Al$_2$O$_3$/SiN$_x$ stacks are hence ideally suited for the implementation into industrial-type silicon solar cells, although ‘regenerated’ Al$_2$O$_3$ single layers should result in a comparable cell performance.

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1. Introduction

In recent years, aluminum oxide (Al$_2$O$_3$) 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
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 SiNx 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/SiNx stacks for Al2O3 layer grown by plasma-assisted (PA) ALD and by thermal ALD. Our experimental results reveal that Al2O3/SiNx 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/SiNx 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 Ω·cm 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 SiNx 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 SiNx layer we measure a higher effective lifetime, which indicates that the deposition of SiNx at a deposition temperature of ~400°C for several minutes has an effect similar to a short anneal. Figure 1 shows the effective lifetime \( \tau_{\text{eff}} \) 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/SiNx stacks, no thickness dependence of the effective lifetime is observed for a thickness \( \geq 4 \) 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 \( \geq 20 \) nm. The best lifetime results are achieved with annealed PA-ALD-Al2O3 single layers,
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 $\Omega\text{cm} \ p$-type silicon [10], showing the nearly perfect passivation quality of the Al$_2$O$_3$ layers. Assuming an infinite bulk lifetime, the upper limit of the effective surface recombination velocity (SRV) is $S_{\text{max}} = 4 \ \text{cm/s}$, 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-Al$_2$O$_3$/SiN$_x$ stacks already show an excellent surface passivation, with effective lifetimes up to $\tau_{\text{eff}} = 3.6 \ \text{ms}$, corresponding to an $S_{\text{max}}$ of 4.2 cm/s. This lifetime is higher than the effective lifetime that could be reached with thermal ALD-Al$_2$O$_3$ single layers. Hence, for thermal ALD-Al$_2$O$_3$ 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$_2$O$_3$ single layer showing a better firing stability at the maximum set temperature of 950°C. For the PA-ALD-Al$_2$O$_3$/SiN$_x$ stacks (10 nm Al$_2$O$_3$ 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$_2$O$_3$ single layers. Hence, the ‘slow’ profile is more detrimental to the single PA-ALD-Al$_2$O$_3$ layers compared to the PA-ALD-Al$_2$O$_3$/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$_2$O$_3$ layers with 10 nm and 20 nm thickness and PA-ALD-Al$_2$O$_3$/SiN$_x$ stacks with 10 nm Al$_2$O$_3$ and 70 nm SiN$_x$. The samples received no pre-firing anneal.](image-url)
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.
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 s and after illumination for 10 min around 600 s. 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 s.

![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.](image)

![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.](image)
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/cm². The sample at 80°C reaches a lifetime of around 600 µs after 10 min, whereas the sample at room temperature reaches a lifetime above 500 µs 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 \( E_a = (0.4\pm0.1) \) eV for an illumination intensity of 20 mW/cm². 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 Al₂O₃ 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 (≤ 10 nm) Al₂O₃ layers show excellent thermal stability for all used firing profiles when a PECVD-SiNₓ capping layer is applied. Al₂O₃/SiNₓ stacks are hence ideally suited for the implementation into industrial-type silicon solar cells.

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References

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