Effect of a post-deposition anneal on Al₂O₃/Si interface properties

J. Benick¹, A. Richter¹, T. T. A. Li³, N. E. Grant², K. R. McIntosh², Y. Ren², K. J. Weber², M. Hermle¹, S. W. Glunz¹
¹Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, D-79110 Freiburg, Germany
²Centre for Sustainable Energy Systems, The Australian National University, Canberra, ACT 0200, Australia
³School of Engineering, The Australian National University, Canberra, ACT 0200, Australia

ABSTRACT

While Al₂O₃ has been proven to provide an excellent level of surface passivation on all sorts of p-type doped silicon surfaces, the passivation mechanism of this layer and especially the influence of the post-deposition anneal on the Al₂O₃/Si interface properties is not yet completely understood. A great increase in the surface passivation is observed after a post-deposition anneal, i.e. a post-deposition anneal is mandatory to activate the surface passivation. Thus, the influence of this anneal on the interface properties, density of negative fixed charges \( Q_f \) and density of interface traps \( D_t \), will be investigated and correlated to the measured minority carrier lifetime. In the case of plasma enhanced ALD, \( Q_f \) is already high in the as-deposited state and the annealing process only has a minor effect on \( Q_f \) (\( Q_f \) increases by 20-50 %, depending on the annealing temperature). The \( D_t \) however is strongly reduced by the post-deposition anneal, decreasing by two orders of magnitude. This large reduction in \( D_t \) is a prerequisite for benefiting from the strong field effect induced by the high density of negative charges of the Al₂O₃.

INTRODUCTION

In recent years Al₂O₃ has been proven to be capable of providing an excellent passivation on all sorts of p-type doped surfaces [1, 2]. Especially in photovoltaics this closes a gap, as an effective low-temperature passivation on p-type surfaces was missing in the past. A first application is the reduction of the surface recombination at the rear side of p-type silicon solar cells. For this purpose Al₂O₃ is a promising alternative to thermally grown SiO₂. On p-type PERC solar cells several authors showed that Al₂O₃ is at least as effective for the rear side passivation as thermally grown, annealed SiO₂ [3, 4]. Furthermore the realization of alternative solar cell concepts, e.g. on n-type silicon, might be enabled by the application of Al₂O₃ as well. Due to the effective passivation of the front side boron emitter by Al₂O₃, we were able to realize conversion efficiencies of 23.5% on n-type PERL solar cells. Thus, the properties of the Al₂O₃ passivation using different deposition techniques (ALD, PECVD, rf sputtering) are being investigated by various authors [5-10]. However, the passivation mechanism of Al₂O₃ is not yet completely understood. In general, two different strategies for the passivation of surfaces, i.e. the reduction of the surface recombination, exist: (i) reduction of the interface trap density \( (D_t) \) and (ii) field effect passivation due to fixed charges \( (Q_f) \) within the dielectric passivation layer.

Particularly a very high density of fixed negative charges, \( Q_f \), (up to \(-10^{13} \text{ cm}^{-2}\)) is one of the special characteristics of the Al₂O₃. However, to be able to reach a high level of surface passivation as is reported for Al₂O₃, in addition to an effective field effect passivation, the density of interface traps has to be greatly reduced as well. Indeed, low densities of interface traps, \( D_t \), in the range of \( 8 \times 10^{10} \) to \( 2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1} \) are reported [6, 11]. However, in the as-deposited state, no passivation is provided by the Al₂O₃ at all, regardless of the deposition method. An additional post-deposition anneal is required to activate the surface passivation. In practice the initial carrier lifetime of 1 μs increases to >2 ms after annealing at 425°C (1 Ω cm p-type FZ Si). Thus, substantial changes in the Al₂O₃ layer itself or at the silicon interface occur during the post deposition anneal. The influence of this post-deposition anneal on the Al₂O₃/Si interface properties (density of negative fixed charges \( Q_f \) as well as on the density of interface traps \( D_t \)) is investigated within this work and will be correlated to the measured minority carrier lifetime. A thin (~1–2 nm) layer of SiO₂ is often observed to be present at the silicon interface or to develop during the anneal process [1, 12], i.e. an Al₂O₃/SiO₂-Si interface. In the following, however, the interface will be referred to as Al₂O₃/Si.

EXPERIMENTAL

For the investigation of the Al₂O₃/Si interface properties MIS (metal/insulator/semiconductor) capacitor structures were prepared on shiny etched 1 Ω cm p-type FZ Si(100) substrates with a thickness of 250 μm. \( D_t \) and \( Q_f \) of the MIS samples were determined by high-frequency and quasistatic capacitance-voltage (C-V) measurements [13]. To measure the effective minority carrier lifetime \( (\tau_{\text{eff}}) \), symmetrically coated lifetime samples have been processed on the same substrate material. These samples were characterized by the Quasi Steady State PhotoConductance (QSSPC) method [14]. From these lifetime measurements the maximum effective surface recombination velocity \( S_{\text{eff}} \) was determined by [15]

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{W(2S_{\text{eff}}) + W^2(D_{\pi}^2)}
\]

with \( W \) the wafer thickness and \( D \) the minority charge carrier diffusion constant. Assuming an infinite bulk lifetime \( \tau_{\text{bulk}} \), we therefore determine an upper limit to \( S_{\text{eff}} \). To get some information of a possible change in the layer composition by the annealing process FTIR
measurements have been performed on the symmetrically coated lifetime samples as well.
The dielectric passivation layer $\text{Al}_2\text{O}_3$ (30 nm) was deposited by PE-ALD (OpAL™, Oxford instruments) at a temperature of 180°C. Prior to the $\text{Al}_2\text{O}_3$ deposition the samples were cleaned by a HNO$_3$ etch followed by a short HF (1%) dip. The samples then underwent a 25 min post-deposition anneal on a hotplate in ambient atmosphere at a temperature ranging from 300°C to 550°C. For the MIS structure aluminium dots (700 µm) were thermally evaporated through a shadow mask. Eutectic gallium-indium was used to ensure a good rear side contact of the MIS structure.

**RESULTS AND DISCUSSION**

The measured injection-level-dependent minority carrier lifetime of the lifetime samples which were coated on both sides with $\text{Al}_2\text{O}_3$ in Figure 1 shows an extreme influence of the post deposition anneal on the $\text{Al}_2\text{O}_3$ surface passivation. Whereas in the as-deposited state with a measured lifetime of ~1 µs no passivation at all is provided by the $\text{Al}_2\text{O}_3$, the measured lifetime increases with annealing temperature up to ~2.3 ms, a value close to the Auger-limit [16], at a temperature of ~425°C. For higher annealing temperatures above 425°C the lifetime decreases again. However, this decrease is only small, after annealing at 550°C the lifetime is still well above 1 ms (1.2 ms @ $\Delta n = 10^{15}$ cm$^{-3}$).

![Figure 1 Injection-dependent minority carrier lifetime of the PE-ALD $\text{Al}_2\text{O}_3$ passivated lifetime samples in the as-deposited state as well as after annealing (hotplate) at different temperatures.](image1)

Figure 2 High-frequency (hf) and quasistatic (qs) capacitance-voltage measurements of PE-ALD $\text{Al}_2\text{O}_3$ passivated MIS samples ($1 \Omega \text{ cm p-type FZ}$) after post-deposition anneal (hotplate) at different temperatures.

![Figure 2 High-frequency (hf) and quasistatic (qs) capacitance-voltage measurements of PE-ALD $\text{Al}_2\text{O}_3$ passivated MIS samples (1 $\Omega$ cm p-type FZ) after post-deposition anneal (hotplate) at different temperatures.](image2)

The accumulation and inversion capacitance of all four MIS structures is consistent with the values expected of such samples. The accumulation capacitance assumed equal to the insulator capacitance, is measured to be $C_{\text{insulator}} = 880 \pm 30$ pF, which amounts to the $\text{Al}_2\text{O}_3$ having a dielectric constant of $8.1 \pm 0.3$, as calculated from the area of the metal ($A = 0.0038$ cm$^2$) and the thickness of the $\text{Al}_2\text{O}_3$ ($t_{\text{insulator}} = 30$ nm), from

$$
\varepsilon_i = \frac{C_{\text{insulator}}}{A}. 
$$

While the accumulation and inversion capacitance are similar for all four MIS structures, the C-V curves also exhibit pronounced differences in relation to (i) translation on the X-axis due to charge in the dielectric; (ii) the difference between quasistatic and high frequency curves due to the interface states; and (iii) “stretch-out”, also due to interface states [13].

The fixed charge in the dielectric layer, $Q_f$, can be determined from the flatband voltage, $V_{fb}$, (neglecting the influence of $Q_i$) from the high-frequency C-V curve by

$$
Q_f = (\Phi_{\text{ms}} - V_{fb}) C_{\text{insulator}}
$$

with $\Phi_{\text{ms}}$ being the difference between the metal and silicon work functions, and where $Q_i$ is assumed to reside at the $\text{Al}_2\text{O}_3$/Si interface. The flatband voltage increases from 2.8 V in the as-deposited state up to 4.9 V at an annealing temperature of 425°C, the charge densities are $-6.0 \times 10^{15}$ cm$^{-2}$ and $-9.9 \times 10^{15}$ cm$^{-2}$ respectively. For higher
post-deposition annealing temperatures the shift in the flatband voltage is smaller, and thus \( Q_f \) is comparatively smaller in magnitude as well (see Fig. 3a). A number of methods are available for extracting the density of interface states \( D_i \). One of the more accurate and very common methods for the extraction of \( D_i \) is based on the comparison of the high-frequency and quasistatic C-V curve [Castagne and Vapaille [17]]. The smaller the difference between the two C-V curves, the lower is the density of interface traps. Thus, by regarding the original curves it can be qualitatively stated that the \( D_i \) decreases with increasing temperature of the post-deposition anneal. We have used three different methods to determine \( D_i \): (i) from the high-frequency [18], (ii) from the quasistatic [19] and (iii) from the comparison of high-frequency and quasistatic C-V curves [17]. An overview over the data extracted from the C-V curves (\( Q_i, D_i \) at midgap) as well as the respective minority carrier lifetimes (at \( \Delta n = 10^{15} \text{ cm}^{-3} \)) is shown in Figure 3. As mentioned earlier, up to \( \sim 425^\circ\text{C} \) the density of negative charges increases with increasing temperature of the post-deposition anneal and decreases again for higher temperatures. In general, with a value of \(-6.0 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1} \) at midgap, the \( D_i \) in the as-deposited state is very high. However, by the post deposition annealing this high \( D_i \) can be lowered by approximately two orders of magnitude, to \( \sim 1.3 \times 10^{13} \text{ cm}^{-2} \text{ eV}^{-1} \) at midgap, by annealing at a temperature of \( 500^\circ\text{C} \). The different methods for the extraction of \( D_i \) here result in comparable \( D_i \) values, suggesting a reliable \( D_i \) measurement. Regarding the measured minority carrier lifetime, shown in Fig. 3c, it can be seen that the lifetime varies by orders of magnitude as well. The increase of the minority carrier lifetime with increasing annealing temperature (up to \( 425^\circ\text{C} \)) thus can be related to the improvement of the interface, i.e. the reduction of the density of interface traps. This becomes particularly obvious by the comparison of the samples annealed at \( 300^\circ\text{C} \) and \( 500^\circ\text{C} \). Those samples having a comparable density of negative interface charges \( (Q_{f,300} = -8.2 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1} , \quad Q_{f,500} = -8.3 \times 10^{15} \text{ cm}^{-2} \text{ eV}^{-1} \) respectively, \( Q_{f,500}/Q_{f,300} = 1.02 \), show a pronounced difference in the density of interface traps of more than one order of magnitude \((D_{f,300}/D_{f,500} = 26.0) \). Thus, as the density of fixed charges of these samples is nearly the same and the effective surface recombination velocity is proportional to \( D_i \), the ratio \( S_{eff,300}/S_{eff,500} \) should be the same as \( D_{f,300}/D_{f,500} \). In fact, taking the quotient \( S_{eff,300}/S_{eff,500} \) this results in a value of 22.1, which is close to the value that has been calculated for \( D_{f,300}/D_{f,500} \) (26.0). Thus, it can be stated, that the great improvement of the surface passivation of the Al₂O₃ by a post-deposition anneal is mainly related to the reduction of \( D_i \). A sufficiently low level of \( D_i \) therefore is necessary to benefit from the field effect induced by the negative interface charges. It has already been reported that a density of negative charges in the range of \(-5 \times 10^{12} \text{ cm}^{-2} \) is sufficient for an effective field effect passivation [20, 21]. Higher charge densities therefore only lead to modest improvements of the passivation. This is also confirmed by the samples annealed at \( 425^\circ\text{C} \) and \( 500^\circ\text{C} \), which have almost identical values for \( D_i \). The effect of the different charge densities \((-9.9 \times 10^{12} \text{ cm}^{-2} \) and \(-8.3 \times 10^{12} \text{ cm}^{-2} \) of these samples is only moderate \((2660 \mu s \text{ and } 1460 \mu s \) respectively).

**Figure 3** Charge density \((Q_i)\), interface defect density \((D_i)\) at midgap and effective lifetime \((\tau_{eff})\) of the annealed samples passivated by PE-ALD Al₂O₃. \( Q_i \) and \( D_i \) were extracted from the C-V data, \( \tau_{eff} \) was measured on identically processed lifetime samples (1 Ω cm p-type FZ Si).
These observed significant changes in the interface properties indicate that substantial changes in the physical Al₂O₃/Si interface occur. For non-annealed Al₂O₃ layers, i.e. in the as-deposited state, different observations have been reported. An abrupt interface between Al₂O₃ and Si is reported for Al₂O₃ layers deposited by low pressure MOCVD and thermal ALD [12, 22]. For plasma assisted ALD deposited Al₂O₃ layers however a thin (1.2 nm) interfacial SiO₂ is reported [1], that has been attributed to the exposure of the substrate to the O₂ plasma during the first ALD cycles. An annealing process however leads to the formation of a thin interfacial SiOₓ, independent of the initial interface [1, 12]. The interfacial SiO₂ layer is supposed to play a central role with respect to the Al₂O₃ surface passivation. Johnson et al. [23] and Kimoto et al. [24] have already shown that an interfacial SiO₂ is crucial for the formation of the negative interface charges. Further, SiO₂ is known to effectively reduce the Dₖ at the SiO₂/Si interface [25]. Thus, such a thin interfacial SiO₂ might be responsible for the low Dₖ of the Al₂O₃ passivation after the post-deposition anneal.

The FTIR measurements that were performed on the Al₂O₃ passivated lifetime samples annealed at different temperatures. After annealing the peak related to the asymmetric stretch of the O in Si-O-Si bridging bonds can be observed and increases with increasing annealing temperature.

The FTIR measurements which were performed on the Al₂O₃ passivated lifetime samples with increasing annealing temperature show the evolution of an absorption band at 1060 cm⁻¹. This absorption band is known to originate from the TO mode arising from the asymmetric stretching of O in Si-O-Si in thermally grown amorphous silicon dioxide (a-SiO₂) [26, 27]. Thus, this indicates that for the annealed samples an interfacial SiO₂ layer exists between the Al₂O₃ and the silicon substrate. However for the as-deposited sample this absorption band cannot be observed, indicating a different chemical configuration or even a non-existence of an intermediate SiO₂ layer. Thus, by the correlation to the measured effective lifetime as well as the Dₖ it can be stated that the interfacial SiO₂ plays a central role in the passivation of silicon surfaces by Al₂O₃.

**SUMMARY**

In summary, the Al₂O₃/Si interface properties, Dₖ and Qᵣ have been measured as a function of the temperature of the post-deposition annealing and have been correlated to the majority carrier lifetime. Both, Qᵣ and Dₖ are affected by the post deposition anneal. However, even in the as-deposited state the PE-ALD deposited Al₂O₃ shows a sufficiently high density of negative charges and the impact of the annealing on the charge density is only moderate. From C-V measurements, Qᵣ increases from -6.0×10¹² cm⁻² in the as-deposited state to -9.9×10¹² cm⁻² after annealing at a temperature of 425°C (Qᵣ₄₂₅/Qᵣ₅₅₀ = 1.6). The initially high Dₖ at midgap, however is strongly reduced (two orders of magnitude) with increasing temperature of the post deposition annealing up to 550°C. The minority carrier lifetime at the same time increases from 1µs in the as deposited state to >2 ms after annealing at 425°C. Thus the great improvement of the Al₂O₃ surface passivation by the post deposition annealing is mainly related to the strong improvement of the Dₖ at the Al₂O₃/Si interface. A sufficiently low Dₖ therefore is a prerequisite to benefit from the strong field effect induced by the high density of negative charges of the Al₂O₃. FTIR measurements indicate that a thin interfacial layer of SiO₂ is formed during the annealing process. This interfacial SiO₂ layer is supposed to play a central role with respect to the Al₂O₃ surface passivation and further investigations have to be performed to examine the function of this layer on a microscopic scale.

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**REFERENCES**


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Figure 4 FTIR spectra of the ALD Al₂O₃ passivated samples annealed at different temperatures. After annealing the peak related to the asymmetric stretch of the O in Si-O-Si bridging bonds can be observed and increases with increasing annealing temperature.
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