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Influence of the Oxidant on the Chemical and Field-Effect Passivation of Si by ALD Al₂O₃

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Differences in Si surface passivation by aluminum oxide (Al₂O₃) films synthesized using H₂O and O₃-based thermal atomic layer deposition (ALD) and plasma ALD have been revealed. A low interface defect density of \( D_{it} = 10^{11} \text{eV}^{-1} \text{cm}^{-2} \) was obtained after annealing, independent of the oxidant. This low \( D_{it} \) was found to be vital for the passivation performance. Field-effect passivation was less prominent for H₂O-based ALD Al₂O₃ before and after annealing, whereas for as-deposited ALD films with an O₂ plasma or O₃ as the oxidants, the field-effect passivation was impaired by a very high \( D_{it} \).

Thin films of Al₂O₃ on p- and n-type crystalline silicon (c-Si) yield exceptionally low surface recombination velocities \( (S_{eff}) \), enabling improved c-Si solar cell efficiencies.\(^1\) Since this discovery, Al₂O₃ films have been synthesized mainly by atomic layer deposition (ALD), a method providing extremely uniform films with precise thickness control. Three types of ALD processes have been developed for the deposition of Al₂O₃: a plasma-based process employing an O₂ plasma and two thermal processes with H₂O and with O₃ as oxidant, respectively. No results related to surface passivation have been reported so far where O₂ is the oxidant. For the H₂O-based process, it has recently been demonstrated that a high level of surface passivation can be achieved, comparable to that achieved using plasma ALD.\(^4\) However, distinct differences have also been observed for the Al₂O₃ films synthesized by these two methods. Plasma ALD Al₂O₃ affords no passivation in the as-deposited state and requires annealing to reach low \( S_{eff} \) values. Comparing to the corresponding Al₂O₃ interface was found to exhibit a high fixed negative charge density \( (Q_f > 5 \times 10^{12} \text{cm}^{-2}) \), shielding electrons from the interface and leading to effective field-effect passivation after annealing.\(^2\) In contrast, Al₂O₃ prepared by H₂O-based thermal ALD already provides reasonably low \( S_{eff} \) values in the as-deposited state.\(^4\) Furthermore, it was found that a high level of surface passivation can be maintained for film thicknesses down to 5 nm for plasma ALD, whereas film thicknesses > 10 nm are required for the H₂O-based ALD process.

The question arises as to whether the observed differences in passivation performance between plasma and thermal ALD Al₂O₃ can be understood on the basis of the underlying passivation mechanisms, which, to date, have only partly been uncovered. For plasma ALD Al₂O₃ films, investigations have focused on the presence of field-effect passivation and open questions remain with respect to the importance of the chemical passivation (i.e., reduction of the interface defect density, \( D_{it} \)) and the changes of \( D_{it} \) upon annealing. For state-of-the-art Al₂O₃ synthesized with H₂O-based thermal ALD, the effect of both \( Q_f \) and \( D_{it} \) on the surface passivation performance remains unaddressed. Therefore, in this letter, the chemical passivation and field-effect passivation were studied using capacitance–voltage (C–V) measurements in conjunction with optical second-harmonic generation (SHG) spectroscopy. The latter technique is nonintrusive and probes the electric field at the Si interface directly.\(^9\) The results indicate that during ALD, the oxidant has a significant influence on the surface passivation mechanism. This will be also demonstrated for O₃-Al₂O₃, which is a very relevant alternative oxidant for industrial-scale thermal ALD processes. We will show that in the as-deposited state, the Al₂O₃ films prepared by H₂O-based ALD resulted in a significantly lower \( D_{it} \) compared to those of O₃-based ALD and plasma ALD. For plasma ALD Al₂O₃, the Si/Al₂O₃ interface properties were affected by the plasma process, namely, plasma radiation. After annealing, all three ALD methods resulted in comparable low \( D_{it} \) values, but with a significantly lower \( Q_f \) for Al₂O₃ synthesized by H₂O-based ALD. Although the working principle of Al₂O₃ surface passivation films is often attributed to field-effect passivation, our results underline that the high level of chemical passivation afforded by the Al₂O₃ films is vital to their performance.

The plasma ALD and thermal ALD (H₂O-based, abbreviated “H₂O-ALD”) films were deposited using an Oxford Instruments single wafer reactor. A substrate temperature of \( T_{dep} \approx 200^\circ\text{C} \) was used, which is in the range for optimal passivation performance for the Al₂O₃ films \( (T_{dep} = 150–250^\circ\text{C}) \). The O₃-based ALD process (“O₃-ALD”) was carried out in an industrial-scale ASM batch reactor with the O₃ generated from a N₂–O₂ mixture. The ALD cycle was optimized for surface passivation performance, and the films were deposited within the range \( T_{dep} = 150–200^\circ\text{C} \). For ALD, O₂ is sometimes preferred to H₂O, as it is a stronger oxidizer and easier to remove from the reactor by purging.\(^1\) All Al₂O₃ films had a thickness of \( \sim 30 \text{ nm} \) and were deposited on \( \sim 2.5 \Omega \text{cm} \) p-type c-Si FZ wafers (thickness = \( \sim 280 \mu\text{m} \)).\(^8\) The material properties of the films resulting from the three ALD methods were determined with Rutherford backscattering spectroscopy and elastic recoil detection (RBS), and they are listed in Table I. The films deposited with O₃-ALD exhibited a slightly higher hydrogen content \( ([\text{H}] \sim 5 \text{ atom }%) \) and an O/Al ratio > 1.5, resulting in a slightly lower mass density compared to the other two methods. As the hydrogen content is strongly dependent on the substrate temperature,\(^7\) the higher \([\text{H}]\) for the O₃-ALD films could be related to a slightly lower \( T_{dep} \) in the batch reactor. Infrared absorption measurements have indicated the presence of –OH groups in the material, while some hydrogen could also be incorporated as –CH₃ groups. The carbon content of all ALD films was below the detection limit of \( \sim 5 \text{ atom }% \) of RBS. To evaluate the surface passivation performance of the films, the upper limit of \( S_{eff} \) was determined from the effective lifetime at an injection level of \( \Delta n = 10^{15} \text{ cm}^{-3} \) by assuming an infinite bulk lifetime. The \( S_{eff} \) values before and after the annealing of the films at 400°C (10 min in \( N_2 \)) are given in Table I. In agreement with previous reports,\(^8\) before annealing, H₂O-based thermal ALD led to a higher level of passivation \( (S_{eff} \sim 30 \text{ cm/s}) \) than plasma ALD, whereas after annealing, both methods resulted in Al₂O₃ films that afforded a high level of surface passivation \( (S_{eff} < 5 \text{ cm/s}) \). In the as-deposited state, the O₂-ALD films afforded a low level of passivation (similar to the plasma ALD films). After annealing, excellent surface passivation properties were obtained.
Plasma ALD passivation performance is relatively insensitive to the material. Plasma ALD Al₂O₃ films, the as-deposited and annealed films were an optical model, the SHG response from our Si optical resonances related to the EFISH contribution. The data taking three critical-pointlike resonances into account including the different scales on the vertical axes. The solid lines present a fit to the data. The negative $Q_f$ value of 2 $\pm$ 1 $\times$ 10¹² cm⁻² was obtained for as-deposited H₂O-ALD Al₂O₃, whereas a high negative $Q_f$ value of 2.4 $\times$ 10¹² cm⁻² was extracted for as-deposited plasma ALD Al₂O₃. For O₃-ALD Al₂O₃, even higher $Q_f$ values of 3.4 $\times$ 10¹² cm⁻² were determined for the as-deposited films. After annealing, the negative $Q_f$ increased to 3.6 $\times$ 10¹² cm⁻². A good qualitative agreement therefore exists between the SHG and C–V results, also considering the fact that different samples were prepared for either technique. For the O₃-ALD Al₂O₃ films, $Q_f$ was found to decrease slightly during the annealing treatment in contrast to the other two ALD methods.

**Table I.** Comparison between material and passivation properties of Al₂O₃ prepared by plasma ALD and thermal ALD with H₂O and O₃. Maximum surface recombination velocity, $S_{eff,max}$, interface defect density, $D_{it}$, and fixed negative charge density, $Q_f$, before and after annealing, for $\sim$2.5 Ω cm $p$-type c-Si wafers. The O/Al ratio, mass density, $\rho$, and hydrogen content, [H], are also given for the as-deposited films.

<table>
<thead>
<tr>
<th>Method</th>
<th>$S_{eff,max}$ (cm/s)</th>
<th>$D_{it}$ (eV⁻¹ cm⁻²)</th>
<th>$Q_f$ (cm⁻²)</th>
<th>O/Al ratio</th>
<th>$\rho$ (g cm⁻³)</th>
<th>[H] (atom %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Plasma ALD</strong></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>$3 \times 10^3$</td>
<td>$\sim 10^{13}$</td>
<td>$1-3 \times 10^{12}$</td>
<td>$1.52 \pm 0.10$</td>
<td>$3.1 \pm 0.2$</td>
<td>$2.7 \pm 0.2$</td>
</tr>
<tr>
<td>Annealed</td>
<td>$3.7$</td>
<td>$1 \times 10^{11}$</td>
<td>$5.8 \times 10^{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Annealed</td>
<td>$2.8$</td>
<td>$0.8 \times 10^{11}$</td>
<td>$5.6 \times 10^{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Annealed</td>
<td>$450^\circ$°C</td>
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<tr>
<td><strong>H₂O-ALD</strong></td>
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<tr>
<td>As-deposited</td>
<td>$3.3 \times 10^3$</td>
<td>$\sim 10^{13}$</td>
<td>$1.3 \times 10^{12}$</td>
<td>$1.52 \pm 0.10$</td>
<td>$3.0 \pm 0.2$</td>
<td>$3.6 \pm 0.2$</td>
</tr>
<tr>
<td>Annealed</td>
<td>$4.9$</td>
<td>$1 \times 10^{11}$</td>
<td>$2.4 \times 10^{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Annealed</td>
<td>$350^\circ$°C</td>
<td>$0.4 \times 10^{11}$</td>
<td>$1.3 \times 10^{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td><strong>O₃-ALD</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>As-deposited</td>
<td>$1 \times 10^3$</td>
<td>$\sim 10^{13}$</td>
<td>$5.3 \times 10^{12}$</td>
<td>$1.69 \pm 0.10$</td>
<td>$2.8 \pm 0.2$</td>
<td>$5.0 \pm 0.2$</td>
</tr>
<tr>
<td>Annealed</td>
<td>$6.0$</td>
<td>$1 \times 10^{11}$</td>
<td>$3.4 \times 10^{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

$S_{eff} < 6$ cm/s, comparable to the results for the single wafer reactor. These results were obtained in a batch reactor, thereby demonstrating the industrial feasibility of Al₂O₃ for surface passivation in c-Si photovoltaics. In addition, the results underline that the surface passivation performance is relatively insensitive to the material properties of the as-deposited Al₂O₃ films.

To assess the field-effect passivation of the H₂O-ALD and plasma ALD Al₂O₃ films, the as-deposited and annealed films were measured with SHG and the spectra are displayed in Fig. 1. Note that with SHG spectroscopy in the photon energy range used, the optical resonances related to the $E'_0/E_1$ critical point of silicon are probed in the near surface region, as described elsewhere. With an optical model, the SHG response from our Si/Al₂O₃ samples could be well-fitted with three critical-pointlike resonances: a Si–Si interface contribution (second harmonic photon energy of $\sim 3.3$ eV), an interfacial SiO₂ contribution ($\sim 3.6$ eV), and an electric-field-induced (EFISH) contribution ($\sim 3.4$ eV). The latter is most relevant for this study, as the amplitude of the EFISH contribution scales with the electric field within the Si space charge layer below the interface induced by the $Q_f$ in the Al₂O₃. It is therefore a measure for the field-effect passivation. When considering Fig. 1, it is evident that the SHG intensity shows a marked increase after annealing the Al₂O₃ films, for both plasma ALD (consistent with previous results) and H₂O-ALD. For the annealed samples, the EFISH contribution at $\sim 3.4$ eV was found to dominate the SHG signal. By normalizing the EFISH amplitude, $A_{EFISH}$, to the value for plasma ALD Al₂O₃ after annealing, it was found that $A_{EFISH}$ = 1 (by definition) for plasma ALD Al₂O₃ after annealing and $A_{EFISH}$ = 0.62 $\pm$ 0.13 for thermal ALD Al₂O₃ after annealing. For the as-deposited samples, $A_{EFISH}$ = 0.52 $\pm$ 0.13 for plasma ALD Al₂O₃ and $A_{EFISH}$ = 0.17 $\pm$ 0.13 for H₂O-ALD Al₂O₃ (for this sample the SHG signal was not dominated by the EFISH contribution). The data therefore demonstrate that the level of field-effect passivation is significantly higher for plasma ALD Al₂O₃ compared to H₂O-ALD, before as well as after annealing.

High-frequency and quasistatic C–V measurements on metal–insulator–semiconductor structures were performed to extract the fixed charge density and interface defect density at midgap for films deposited using all three ALD methods. Evaporated Al was used for the metal contacts. When applied, annealing was performed prior to the metallization. As displayed in Table I, a low negative charge density of $Q_f$ = 1.3 $\times$ 10¹³ cm⁻² was obtained for as-deposited H₂O-ALD Al₂O₃, whereas a high negative $Q_f$ value of 2 $\pm$ 1 $\times$ 10¹³ cm⁻² was extracted for as-deposited plasma ALD Al₂O₃. For O₃-ALD Al₂O₃, even higher $Q_f$ values of 5 $\times$ 10¹³ cm⁻² were determined for the as-deposited films. After annealing, the negative $Q_f$ increased to 2.4 $\times$ 10¹² and 5.8 $\times$ 10¹³ cm⁻² for H₂O-ALD and plasma ALD Al₂O₃, respectively. A good qualitative agreement therefore exists between the SHG and C–V results, also considering the fact that different samples were prepared for either technique. For the O₃-ALD Al₂O₃ films, $Q_f$ was found to decrease slightly during the annealing treatment in contrast to the other two ALD methods.

**Figure 1.** (Color online) Second harmonic generation spectra for plasma ALD and thermal ALD (H₂O) Al₂O₃ films before and after annealing. Note the different scales on the vertical axes. The solid lines present a fit to the data taking three critical-pointlike resonances into account including the EFISH contribution.
Both the C–V and the SHG results show that for the H$_2$O-ALD films, the chief effect of annealing was the significant increase of $Q_f$. For the O$_3$ and plasma ALD Al$_2$O$_3$ films, on the other hand, the impact of annealing on the level of chemical passivation was particularly prominent. For the plasma ALD samples, the $D_b$ was initially very high and decreased from an estimated $\sim 10^{13}$ eV$^{-1}$ cm$^{-2}$ to a value of $1 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ after annealing (Table I). A similar trend was observed for the O$_3$-based process. For as-deposited H$_2$O-ALD Al$_2$O$_3$, a low defect density of $3 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ was obtained, which further improved to $10^{11}$ eV$^{-1}$ cm$^{-2}$ during annealing, reaching a level similar to that for plasma and O$_3$-ALD Al$_2$O$_3$. The $D_b$ values of $\sim 10^{11}$ eV$^{-1}$ cm$^{-2}$ are in good agreement with the lowest values for Al$_2$O$_3$ reported in the literature. The additional data in Table I demonstrate that slightly lower $D_b$ values $<10^{11}$ eV$^{-1}$ cm$^{-2}$ can be obtained for H$_2$O-ALD and plasma ALD films by using an annealing temperature of 350 and 450°C (10 min), respectively. To study the chemical passivation in more detail, future research could be directed toward other aspects, such as the energy distribution of the interface states, providing more information than $D_b$ at midgap.

As is evident from the data in Table I and Fig. 1, the reasonable level of surface passivation afforded by as-deposited H$_2$O-ALD Al$_2$O$_3$ can be attributed primarily to the relatively low defect density. On the other hand, for as-deposited O$_3$ and plasma ALD Al$_2$O$_3$, the effect of the high $Q_f$ appears to be nullified by the extremely high $D_b$. From the Shockley–Read–Hall formalism, one would assume that, in principle, a higher $Q_f$ could offset a higher $D_b$ to reach a satisfactorily low level of surface recombination. For example, numerical simulations with the PCD program indicated that a negative $Q_f$ of $10^{12}$ cm$^{-2}$ leads to a reduction of the surface electron density by a factor of 10$^3$ (with a bulk injection level of $N_D = 10^{15}$ cm$^{-3}$) and, therefore, to a drop in surface recombination. In practice, however, $D_b$ values $<10^{11}$ eV$^{-1}$ cm$^{-2}$ appear to be required to effectuate the (field-effect) passivation. The passivation properties of Al$_2$O$_3$ are likely to be intimately related to the properties of the interfacial silica oxide (1–2 nm) present between Si and Al$_2$O$_3$. We have demonstrated experimentally that the O$_2$ plasma process can damage this interfacial oxide region for as-deposited Al$_2$O$_3$ due to the presence of vacuum ultraviolet (VUV) radiation in the O$_2$ plasma. An annealed 30 nm thick Al$_2$O$_3$ film was exposed to an O$_2$ plasma (under the same conditions as those used during plasma ALD) and an exponential decay of the effective lifetime as a function of cumulative plasma exposure time was observed on relevant timescales, as shown in Fig. 2. The degradation can be attributed mainly to photons with an energy of 9.5 eV, as measured by vacuum optical emission spectroscopy (Fig. 2, inset). We have previously shown that UV photons with an energy up to 4.9 eV do not reduce the passivation performance. The effect of VUV radiation during deposition was confirmed by the observation that a reduction of $D_b$ by approximately an order of magnitude (to $D_b \approx 7 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$) could be achieved for as-deposited films by reducing the plasma time in the ALD cycle from 3 to 0.5 s. Accordingly, a significantly higher level of surface passivation, with $S_{eff} < 90$ cm/s, was obtained, which can be attributed to the enhanced chemical passivation. This $S_{eff}$ value is still somewhat higher compared to as-deposited H$_2$O-ALD Al$_2$O$_3$, which exhibits lower $D_b$. In this respect, it is interesting to note that the O$_2$-ALD process, free of VUV radiation, also resulted in high $D_b$ prior to annealing. Such poor interface properties have been reported before for O$_3$-based ALD processes, for example, for ZrO$_2$ films. Apparently also other processes, apart from the plasma radiation, affect the interface properties of the as-deposited films when synthesized by ALD with strong oxidants. We expect that in particular the properties of the interfacial SiO$_2$ layer can be affected. Fortunately, the interface defects created during the ALD processes with an O$_2$ plasma and O$_3$ can be passivated very effectively during annealing, as is evident from the decrease of the values of $D_b$ in Table I. The significant reduction of this defect density during annealing involves the passivation of Si dangling bonds (such as P$_5$-type defects) under influence of hydrogen released from the Al$_2$O$_3$ film.

We would like to point out that the higher $Q_f$ after annealing for plasma ALD Al$_2$O$_3$ when compared to H$_2$O-ALD Al$_2$O$_3$ appears to have no major additional impact on the level of surface passivation obtained for 30 nm thick films. For an increasingly good surface passivation performance, the measured effective lifetime approaches a value dictated by the (intrinsic) recombination in the bulk, and as a consequence, values of $Q_f$ above a certain threshold will not be reflected by a significantly lower $S_{eff,max}$. Nevertheless, for Al$_2$O$_3$ films that exhibit lower $Q_f$, the surface passivation performance is more strongly dependent on the chemical passivation. This may, for instance, explain why the minimum required film thickness is larger for thermal ALD compared to plasma ALD films. In addition, a lower field-effect passivation may have implications for the thermal stability at elevated temperatures. It is furthermore noted that Al$_2$O$_3$ films with higher $Q_f$, for instance synthesized with plasma ALD, could be more suited for the passivation of highly doped $p$-type surfaces as, for example, used in $p^+$ emitters.

In conclusion, we have shown that the mechanisms underlying the Si surface passivation induced by Al$_2$O$_3$ films are significantly affected by the oxidant employed during ALD (H$_2$O, O$_3$, or an O$_2$ plasma). The differences observed in chemical and field-effect passivation for the different ALD processes may have important consequences for specific applications of Al$_2$O$_3$ in solar cells and other optoelectronic devices.

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