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Influence of the Oxidant on the Chemical and Field-Effect Passivation of Si by ALD Al$_2$O$_3$

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Differences in Si surface passivation by aluminum oxide (Al$_2$O$_3$) films synthesized using H$_2$O and O$_3$-based thermal atomic layer deposition (ALD) and plasma ALD have been revealed. A low interface defect density of $D_{it} = \sim 10^{11}$ eV^{-1} 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 H$_2$O-based ALD Al$_2$O$_3$ before and after annealing, whereas for as-deposited ALD films with an O$_2$ plasma or O$_3$ as the oxidants, the field-effect passivation was impaired by a very high D_{it}.
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Thin films of Al$_2$O$_3$ on *p*- and *n*-type crystalline silicon (*c*-Si) yield exceptionally low surface recombination velocities (S_{eff}), enabling improved *c*-Si solar cell efficiencies.[1-6] Since this discovery, Al$_2$O$_3$ films have been synthesized mainly by atomic layer deposition (ALD), a method providing extremely uniform films with precise thickness control.[7] Three types of ALD processes have been developed for the deposition of Al$_2$O$_3$: a plasma-based process employing an O$_2$ plasma and two thermal processes with H$_2$O and with O$_3$ as oxidant, respectively. No results related to surface passivation have been reported so far where O$_3$ is the oxidant. For the H$_2$O-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 Al$_2$O$_3$ films synthesized by these two methods. Plasma ALD Al$_2$O$_3$ affords no passivation in the as-deposited state and requires annealing to reach low S_{eff} values.[1,2,4] The corresponding Al$_2$O$_3$ interface was found to exhibit a high fixed negative charge density ($Q_f > 5 \times 10^{12}$ cm^{-2}), shielding electrons from the interface and leading to effective field-effect passivation after annealing.[1,2,8] In contrast, Al$_2$O$_3$ prepared by H$_2$O-based thermal ALD already provides reasonably low S_{eff} values in the as-deposited state.[4,8] 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 H$_2$O-based ALD process.[4]

The question arises as to whether the observed differences in passivation performance between plasma and thermal ALD Al$_2$O$_3$ can be understood on the basis of the underlying passivation mechanisms, which, to date, have only partly been uncovered. For plasma ALD Al$_2$O$_3$ 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 Al$_2$O$_3$ synthesized with H$_2$O-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.[9-11] The results indicate that during ALD, the oxidant has a significant influence on the surface passivation mechanism. This will be also demonstrated for O$_3$, which is a very relevant alternative oxidant for industrial-scale thermal ALD processes. We

will show that in the as-deposited state, the Al$_2$O$_3$ films prepared by H$_2$O-based ALD resulted in a significantly lower D_{it} compared to those of O$_3$-based ALD and plasma ALD. For plasma ALD Al$_2$O$_3$, the Si/Al$_2$O$_3$ 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 Al$_2$O$_3$ synthesized by H$_2$O-based ALD. Although the working principle of Al$_2$O$_3$ surface passivation films is often attributed to field-effect passivation, our results underline that the high level of chemical passivation afforded by the Al$_2$O$_3$ films is vital to their performance.

The plasma ALD and thermal ALD (H$_2$O-based, abbreviated "H$_2$O-ALD") films were deposited using an Oxford Instruments single wafer reactor. A substrate temperature of $T_{dep} \sim 200°C$ was used, which is in the range for optimal passivation performance for the Al$_2$O$_3$ films (T_{dep} = 150–250°C).[4,8] The O$_3$-based ALD process ("O$_3$-ALD") was carried out in an industrial-scale ASM batch reactor with the O$_3$ generated from a N$_2$–O$_2$ mixture. The ALD cycle was optimized for surface passivation performance, and the films were deposited within the range T_{dep} = 150–200°C. For ALD, O$_3$ is sometimes preferred to H$_2$O, as it is a stronger oxidizer and easier to remove from the reactor by purging.[12] All Al$_2$O$_3$ films had a thickness of ~ 30 nm and were deposited on ~ 2.5 Ω cm *p*-type *c*-Si FZ wafers (thickness = ~ 280 μm).[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 O$_3$-ALD exhibited a slightly higher hydrogen content ([H] ~ 5 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,[8] the higher [H] for the O$_3$-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 –CH$_x$ groups. The carbon content of all ALD films was below the detection limit of ~ 5 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 $\Delta n = 10^{15}$ 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,[4,8] before annealing, H$_2$O-based thermal ALD led to a higher level of passivation (S_{eff} <30 cm/s) than plasma ALD, whereas after annealing, both methods resulted in Al$_2$O$_3$ films that afforded a high level of surface passivation (S_{eff} <5 cm/s). In the as-deposited state, the O$_3$-ALD films afforded a low level of passivation (similar to the plasma ALD films). After annealing, excellent surface passivation properties were obtained

Table I. Comparison between material and passivation properties of Al_2O_3 prepared by plasma ALD and thermal ALD with H_2O and O_3. Maximum surface recombination velocity, $S_{eff,max}$, interface defect density, D_{it}, and fixed negative charge density, Q_f, before and after annealing, for ~2.5 Ω cm p-type c-Si wafers. The O/Al ratio, mass density, ρ, and hydrogen content, [H], are also given for the as-deposited films.

Method	$S_{eff,max}$ (cm/s)	D_{it} (eV^{-1} cm^{-2})	Q_f (cm^{-2})	O/Al ratio	ρ (g cm^{-3})	[H] (atom %)
Plasma ALD						
As-deposited	3×10^3	$\sim 10^{13}$	1–3×10^{12}	1.52 ± 0.10	3.1 ± 0.2	2.7 ± 0.2
Annealed 400°C	3.7	1×10^{11}	5.8×10^{12}	—	—	—
annealed 450°C[a]	2.8	0.8×10^{11}	5.6×10^{12}	—	—	—
H_2O-ALD						
As-deposited	30	3×10^{11}	1.3×10^{11}	1.52 ± 0.10	3.0 ± 0.2	3.6 ± 0.2
Annealed 400°C	4.9	1×10^{11}	2.4×10^{12}	—	—	—
annealed 350°C[a]	4.0	0.4×10^{11}	1.3×10^{12}	—	—	—
O_3-ALD						
As-deposited	1×10^3	$\sim 10^{13}$	5.3×10^{12}	1.69 ± 0.10	2.8 ± 0.2	5.0 ± 0.2
Annealed 400°C	6.0	1×10^{11}	3.4×10^{12}	—	—	—

[a] Data for optimized annealing temperatures.

(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 Al_2O_3 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 Al_2O_3 films.[8]

To assess the field-effect passivation of the H_2O-ALD and plasma ALD Al_2O_3 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.[10,11] With an optical model, the SHG response from our Si/Al_2O_3 samples
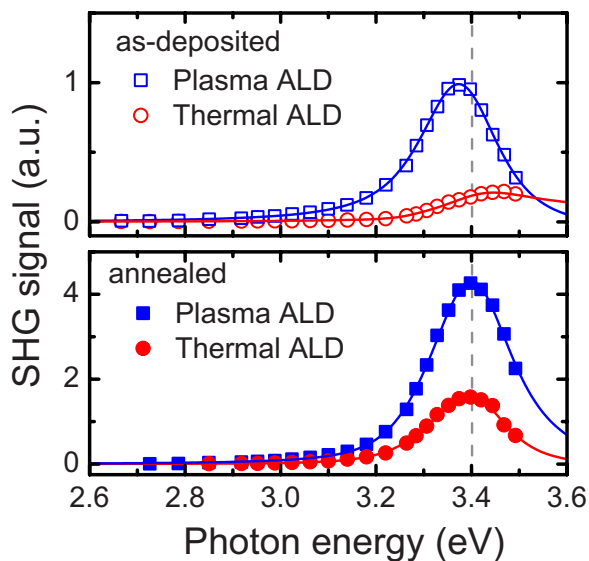

Figure 1. (Color online) Second harmonic generation spectra for plasma ALD and thermal ALD (H_2O) Al_2O_3 films before and after annealing. Note the different scales on the vertical axes. The solid lines present a fit to the data taking three critical-pointlike resonances into account including the EFISH contribution.

could be well-fitted with three critical-pointlike resonances: a Si–Si interface contribution (second harmonic photon energy of ~3.3 eV), an interfacial SiO_x contribution (~ 3.6 eV), and an electric-field-induced (EFISH) contribution (~ 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 Al_2O_3. It is therefore a measure for the field-effect passivation.[10] When considering Fig. 1, it is evident that the SHG intensity shows a marked increase after annealing the Al_2O_3 films, for both plasma ALD (consistent with previous results[10]) and H_2O-ALD. For the annealed samples, the EFISH contribution at ~3.4 eV was found to dominate the SHG signal. By normalizing the EFISH amplitude, A_{EFISH}, to the value for plasma ALD Al_2O_3 after annealing, it was found that A_{EFISH} = 1 (by definition) for plasma ALD Al_2O_3 after annealing and A_{EFISH} = 0.62 ± 0.13 for thermal ALD Al_2O_3 after annealing. For the as-deposited samples, A_{EFISH} = 0.52 ± 0.13 for plasma ALD Al_2O_3 and A_{EFISH} = 0.17 ± 0.13 for H_2O-ALD Al_2O_3 (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 Al_2O_3 compared to H_2O-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 (D_{it})[13] 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 = 1.3×10^{11} cm^{-2} was obtained for as-deposited H_2O-ALD Al_2O_3, whereas a high negative Q_f value of $2 \pm 1 \times 10^{12}$ cm^{-2} was extracted for as-deposited plasma ALD Al_2O_3. For O_3-ALD Al_2O_3, even higher Q_f values of 5×10^{12} cm^{-2} were determined for the as-deposited films. After annealing, the negative Q_f increased to 2.4×10^{12} and 5.8×10^{12} cm^{-2} for H_2O-ALD and plasma ALD Al_2O_3, 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 O_3-ALD Al_2O_3 films, Q_f was found to decrease slightly during the annealing treatment in contrast to the other two ALD methods.

Both the $C-V$ and the SHG results show that for the H_2O-ALD films, the chief effect of annealing was the significant increase of Q_f. For the O_3 and plasma ALD Al_2O_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_{it} was initially very high and decreased from an estimated $\sim 10^{13}$ eV^{-1} cm^{-2} to a value of 1×10^{11} eV^{-1} cm^{-2} after annealing (Table I). A similar trend was observed for the O_3-based process. For as-deposited H_2O-ALD Al_2O_3, a low defect density of 3×10^{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_2O_3. The D_{it} values of $\sim 10^{11}$ eV^{-1} cm^{-2} are in good agreement with the lowest values for Al_2O_3 reported in the literature.[14-16] The additional data in Table I demonstrate that also slightly lower D_{it} values $< 10^{11}$ eV^{-1} cm^{-2} can be obtained for H_2O-ALD and plasma ALD films by using an annealing temperature of 350 and 450°C (10 min), respectively.[4] 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_{it} 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_2O-ALD Al_2O_3 can be attributed primarily to the relatively low defect density. On the other hand, for as-deposited O_3 and plasma ALD Al_2O_3, the effect of the high Q_f appears to be nullified by the extremely high D_{it}. From the Shockley–Read–Hall formalism,[17] one would assume that, in principle, a higher Q_f could offset a higher D_{it} to reach a satisfactorily low level of surface recombination. For example, numerical simulations with the PC1D 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 $\Delta n = \sim 10^{15}$ cm^{-3}) and, therefore, to a drop in surface recombination. In practice, however, D_{it} values $\ll 10^{13}$ eV^{-1} cm^{-2} appear to be required to effectuate the (field-effect) passivation.

The passivation properties of Al_2O_3 are likely to be intimately related to the properties of the interfacial silicon oxide (1–2 nm) present between Si and Al_2O_3.[2] We have demonstrated experimentally that the O_2 plasma process can damage this interfacial oxide region for as-deposited Al_2O_3 due to the presence of vacuum ultraviolet (VUV) radiation in the O_2 plasma. An annealed 30 nm thick Al_2O_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.[18] The effect of VUV radiation *during deposition* was confirmed by the observation that a reduction of D_{it} by approximately an order of magnitude (to $D_{it} \sim 7 \times 10^{11}$ 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.[c] This S_{eff} value is still somewhat higher compared to as-deposited H_2O-ALD Al_2O_3, which exhibits lower D_{it}. In this respect, it is interesting to note that the O_3-ALD process, free of VUV radiation, also resulted in high D_{it} prior to annealing. Such poor interface properties have been reported before for O_3-based ALD processes, for example, for ZrO_2 films.[19] Apparently also other processes, apart from the plasma radiation, affect the interface properties of the as-deposited films when synthesized by
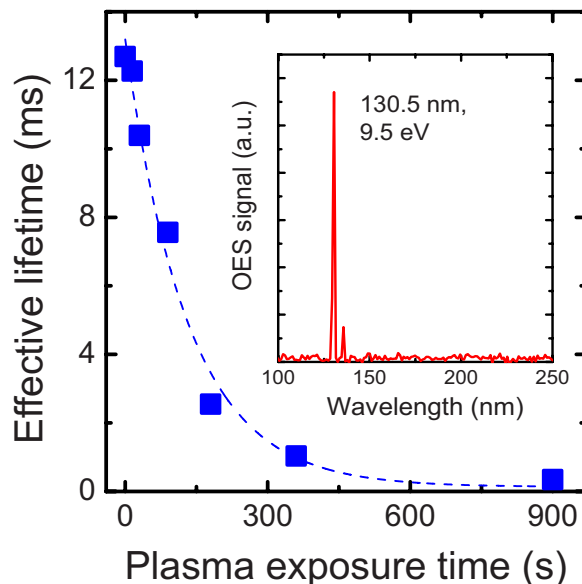

Figure 2. (Color online) Effective lifetime for an *n*-type silicon wafer (3.5 Ω cm resistivity) passivated with plasma ALD Al_2O_3 after annealing, as a function of cumulative plasma exposure time. The dashed line is an exponential fit to the data. The inset shows the O (I), $2p^4$ ^{3}P-3s ^{3}S^o emission at 9.5 eV as measured with optical emission spectroscopy.

ALD with strong oxidants. We expect that in particular the properties of the interfacial SiO_x 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_{it} in Table I. The significant reduction of this defect density during annealing involves the passivation of Si dangling bonds (such as P_b-type defects) under influence of hydrogen released from the Al_2O_3 film.[20]

We would like to point out that the higher Q_f after annealing for plasma ALD Al_2O_3 when compared to H_2O-ALD Al_2O_3 appeared 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_2O_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.[4,11] In addition, a lower field-effect passivation may have implications for the thermal stability at elevated temperatures. It is furthermore noted that Al_2O_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.[1,5]

In conclusion, we have shown that the mechanisms underlying the Si surface passivation induced by Al_2O_3 films are significantly affected by the oxidant employed during ALD (H_2O, 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_2O_3 in solar cells and other optoelectronic devices.

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[c] A reduction of the plasma time to 0.5 s, also led to subsaturated ALD growth with a decrease of the growth-per-cycle from 1.2 to 0.8 Å. The value of Q_f for as-deposited and annealed Al_2O_3 was not significantly affected by the shorter plasma time.

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