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Influence of the Deposition Temperature on the c-Si Surface Passivation by Al₂O₃ Films Synthesized by ALD and PECVD

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The material properties and c-Si surface passivation have been investigated for Al₂O₃ films deposited using thermal and plasma atomic layer deposition (ALD) and plasma-enhanced chemical vapor deposition (PECVD) for temperatures (T_{dep}) between 25 and 400°C. Optimal surface passivation by ALD Al₂O₃ was achieved at $T_{\text{dep}} = 150\text{--}250^\circ\text{C}$ with $S_{\text{eff}} < 3\text{ cm/s}$ for $\sim 2\text{ }\Omega\text{ cm}$ p-type c-Si. PECVD Al₂O₃ provided a comparable high level of passivation for $T_{\text{dep}} = 150\text{--}300^\circ\text{C}$ and contained a high fixed negative charge density of $\sim 6 \times 10^{12}\text{ cm}^{-2}$. Outstanding surface passivation performance was therefore obtained for thermal ALD, plasma ALD, and PECVD for a relatively wide range of Al₂O₃ material properties.

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Al₂O₃ recently emerged as an effective material for the passivation of crystalline silicon (c-Si) surfaces, enabling ultralow surface recombination velocities (S_{eff}) on p-, n-, and p⁺-type c-Si^{1,2} leading to enhanced solar cell efficiencies.³⁻⁵ A combination of chemical passivation (i.e., the reduction of interface defects) and field-effect passivation (i.e., electrostatic shielding of minority charge carriers) provided by a large amount of fixed negative charges located at the c-Si/Al₂O₃ interface is key to the high level of surface passivation achieved. To date, the Al₂O₃ surface passivation films were mostly synthesized by plasma and thermal atomic layer deposition (ALD) at a substrate temperature of $\sim 200^\circ\text{C}$.¹⁻⁸ Very recently, it has been shown that other techniques, such as sputtering and plasma-enhanced chemical vapor deposition (PECVD),⁹⁻¹¹ can also be used to deposit Al₂O₃ surface passivation films. These alternative deposition techniques allow for higher growth rates but generally do not surpass ALD in terms of material and surface passivation quality.

In this article, the influence of the substrate temperature (T_{dep}) during deposition on the Al₂O₃ material properties and the surface passivation performance is addressed for Al₂O₃ films deposited at temperatures in the range of $T_{\text{dep}} = 25\text{--}400^\circ\text{C}$ for thermal and plasma ALD and PECVD. We report that PECVD can be used to deposit Al₂O₃ films that provide a similar level of surface passivation as ALD Al₂O₃ while enabling higher deposition rates. By corona charging experiments, the presence of a high fixed negative charge density in the PECVD Al₂O₃ films is demonstrated.

Experimental

A direct comparison between thermal ALD and plasma ALD was enabled by employing both methods in an Oxford Instruments OpAL ALD reactor (operating pressure $\sim 170\text{ mTorr}$) and in a second reactor, the Oxford Instruments FlexAL (operating pressure $\sim 15\text{ mTorr}$). For both ALD methods, trimethylaluminum [Al(CH₃)₃] was used as the Al precursor in the first half cycle of the ALD process. During the second half cycle, either H₂O or an O₂ plasma was used for thermal and plasma ALD, respectively.⁷ Cycle and purge times were optimized to reach a truly self-limiting ALD process at every T_{dep} . The PECVD process employed a continuous remote O₂/Ar plasma and Al(CH₃)₃ as the Al precursor. Unlike ALD, the deposition rate for PECVD scaled with the Al(CH₃)₃ flow that was introduced into the reactor. The refractive index (at a photon energy of 2 eV) and growth rate were determined by in situ spectroscopic ellipsometry, the atomic Al and O densities were determined by Rutherford backscattering spectroscopy, and the atomic hydrogen density was determined by elastic recoil detection. To

evaluate the level of surface passivation, low resistivity p- and n-type $\sim 275\text{ }\mu\text{m}$ thick float zone (100) c-Si wafers were coated on both sides with Al₂O₃ with a thickness of $\sim 30\text{ nm}$. Before deposition, the wafers were treated with diluted HF (1% in deionized H₂O). The surface passivation was evaluated in the as-deposited state and after a 10 min postdeposition anneal at 400°C in a N₂ environment.⁷ The upper limit of the surface recombination velocity ($S_{\text{eff,max}}$) was determined from the effective lifetime (τ_{eff}), as measured with photoconductance (Sinton WCT 100) at an injection level of 10^{15} cm^{-3} by assuming an infinite bulk lifetime.²

Results and Discussion

The results regarding the substrate temperature variation are shown in Fig. 1-3. The growth rate, refractive index, and surface passivation performance were evaluated for plasma and thermal ALD in Fig. 1 and for PECVD in Fig. 2. The mass density, atomic O/Al ratio, and hydrogen concentration for corresponding Al₂O₃ films are displayed in Fig. 3.

The results for the growth-per-cycle (GPC) as a function of T_{dep} for plasma and thermal ALD (Fig. 1a) agree well for the OpAL and the FlexAL reactors. The higher GPC for plasma ALD compared to thermal ALD, which is observed over the full temperature range but particularly pronounced at low temperatures, has been ascribed to a more efficient surface oxidation by plasma-generated O radicals compared to thermally activated oxidation by H₂O.¹² The decrease in GPC with increasing T_{dep} can be mainly attributed to a decreasing density of OH surface groups due to dehydroxylation reactions.^{12,13} The refractive index (Fig. 1b) increases with deposition temperature, which is directly linked to material densification, as displayed in Fig. 3a. The mass density of the films increased with T_{dep} , saturating at $3.2 \pm 0.2\text{ g/cm}^3$ at a high temperature.

In Fig. 2a and b, the deposition rate and refractive index as a function of substrate temperature are shown for the PECVD process. The values were measured at a fixed location on the various wafers, as a variation in thickness, and refractive index was observed for the PECVD samples due to the nonuniformity of the film caused by the deposition technique. The refractive index and mass density (Fig. 3a) increased with T_{dep} , similar to the ALD case. The refractive index values for PECVD Al₂O₃ are lower than the ones obtained for ALD at the same T_{dep} . The deposition rate, R_{dep} , decreased strongly with increasing T_{dep} , saturating at $\sim 5\text{ nm/min}$ for $T_{\text{dep}} > 200^\circ\text{C}$. The higher R_{dep} at low temperature can be partly attributed to a lower mass density linked to a higher density of hydrogen (mainly incorporated as OH groups) and carbon-related impurities in the films, as revealed by IR absorption analyses. Furthermore, the general trend of R_{dep} as a function of T_{dep} is an indication of a growth process controlled by the adsorption of surface species, as also pre-

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Figure 1. (Color online) (a) GPC, (b) refractive index, n , and (c) maximum surface recombination velocity, $S_{eff,max}$, as a function of substrate temperature for plasma and thermal ALD. The data in (c) correspond to Al_2O_3 deposited on $\sim 2 \Omega \text{ cm}$ p-type c-Si in the OpAL reactor. Open symbols represent as-deposited Al_2O_3 films and closed symbols films after annealing at 400°C . Lines serve as a guide for the eyes.

viously reported for the PECVD of SiO_2 .¹⁴ Dehydroxylation reactions could also play a role, but a more in-depth research is necessary to further elucidate the growth mechanism.

For all three deposition methods, the material densification with increasing T_{dep} can be partly explained by the decreasing hydrogen concentration as evidenced by Fig. 3c. For the same T_{dep} , the hydrogen concentrations of the PECVD Al_2O_3 films were significantly higher than those for the ALD Al_2O_3 films. The O/Al ratio decreased with increasing T_{dep} , as displayed in Fig. 3b, and (nearly) stoichiometric Al_2O_3 films, with O/Al ratios close to 1.5, were obtained at $T_{dep} > 200^\circ\text{C}$.

The level of c-Si surface passivation by ALD-synthesized Al_2O_3 is evaluated in Fig. 1c. The results demonstrate that thermal ALD Al_2O_3 provides a higher level of surface passivation in the as-deposited state (with lowest $S_{eff} < 35 \text{ cm/s}$) than plasma ALD Al_2O_3 .⁷ It is observed that the as-deposited passivation quality increases with T_{dep} for the plasma ALD, whereas a small decrease with increasing T_{dep} is observed for the thermal ALD. After annealing, the surface passivation quality improved significantly,^{7,15} with the best passivation performance obtained at $T_{dep} = 150\text{--}250^\circ\text{C}$ for both ALD methods. Values of $S_{eff,max}$ down to $\sim 3 \text{ cm/s}$ are reached for $\sim 2 \Omega \text{ cm}$ p-type c-Si by both plasma and thermal ALD.

The trend observed for the passivation quality of the as-deposited PECVD Al_2O_3 , shown in Fig. 2c, is similar to the one for plasma ALD Al_2O_3 . Annealing also improved the passivation properties of the PECVD Al_2O_3 films. The annealed films afforded a high level of surface passivation with $S_{eff} < 10 \text{ cm/s}$ for $T_{dep} = 150\text{--}300^\circ\text{C}$. In addition to the data shown in Fig. 2c, exceptionally low S_{eff} values were obtained at $T_{dep} = 200^\circ\text{C}$, for example, $S_{eff} < 2.9 \text{ cm/s}$ (τ_{eff}

Figure 2. (Color online) (a) Deposition rate, R_{dep} , (b) refractive index, n , and (c) maximum surface recombination velocity, $S_{eff,max}$, on $\sim 2 \Omega \text{ cm}$ p-type c-Si as a function of substrate temperature for PECVD Al_2O_3 . Open symbols represent as-deposited Al_2O_3 films and closed symbols films after annealing at 400°C . Lines serve as a guide for the eyes.

$= 4.7 \text{ ms}$) and $S_{eff} < 0.8 \text{ cm/s}$ ($\tau_{eff} = 18 \text{ ms}$) on $2.2 \Omega \text{ cm}$ p-type and $3.5 \Omega \text{ cm}$ n-type c-Si, respectively; and also $S_{eff} < 14 \text{ cm/s}$ ($\tau_{eff} = 1 \text{ ms}$) on $1 \Omega \text{ cm}$ p-type c-Si. The corresponding injection-level-dependent lifetime curves are displayed in Fig. 4. These results were obtained with a deposition rate of $\sim 5 \text{ nm/min}$. Significantly higher deposition rates of $> 30 \text{ nm/min}$ were also feasible while maintaining a good level of surface passivation, as demonstrated by $S_{eff} < 14 \text{ cm/s}$ on $3.5 \Omega \text{ cm}$ n-type c-Si. For comparison, under the present conditions the maximum deposition rate for ALD was $\sim 1.8 \text{ nm/min}$ at $T_{dep} = 200^\circ\text{C}$.

The improvement of the passivation properties of the as-deposited plasma ALD and PECVD Al_2O_3 films with increasing T_{dep} can be explained by an in situ anneal effect at high temperatures. The interfacial oxide (SiO_x) that forms between c-Si and Al_2O_3 is thought to play an essential role in the surface passivation properties of Al_2O_3 .¹⁵ The interface quality and related surface passivation properties improve during plasma ALD and PECVD at high temperatures, which is similar to the effect observed during the post-deposition anneal.^{7,15} For thermal ALD, an in situ anneal effect was not observed, and $S_{eff,max}$ for the as-deposited films even slightly increased with increasing T_{dep} . Apparently, lower temperatures led to improved interface properties for Al_2O_3 deposited by thermal ALD.

The Al_2O_3 material properties are expected to affect both the chemical and field-effect contributions to the surface passivation performance of the films. The fixed negative charge density, Q_f , that increases drastically during annealing,^{15,16} induces the field-effect passivation and is expected to be closely related to the Al_2O_3 structural properties near the interface.¹⁵ As shown in Fig. 5, we have also verified the presence of a high negative Q_f of (6.5 ± 1)

Figure 3. (Color online) (a) Mass density, ρ_{mass} , (b) O/Al ratio, and (c) the H concentration, [H], determined as a function of substrate temperature for as-deposited films. Data are given for plasma and thermal ALD Al_2O_3 films deposited in the OpAL reactor and PECVD Al_2O_3 films. Lines serve as a guide for the eyes.

$\times 10^{12} \text{ cm}^{-2}$ for PECVD Al_2O_3 deposited at $T_{\text{dep}} = 200^\circ\text{C}$ after annealing. Q_f was determined by depositing positive corona charges on a passivated c-Si wafer using a similar approach, as described in Ref. 2. A sharp drop of the level of surface passivation (increase in $S_{\text{eff,max}}$) was observed at the point where the amount of negative fixed charge in the Al_2O_3 was exactly balanced by positive corona charges. In the same way, a negative Q_f of $(5 \pm 1) \times 10^{12} \text{ cm}^{-2}$ for plasma ALD Al_2O_3 was determined. These Q_f values for plasma ALD and PECVD Al_2O_3 are higher than the negative Q_f values reported for microwave PECVD ($Q_f \approx 2 \times 10^{12} \text{ cm}^{-2}$)¹¹ and

Figure 4. (Color online) Injection-level-dependent effective lifetime for n- and p-type c-Si wafers of various resistivities passivated by PECVD Al_2O_3 with $T_{\text{dep}} = 200^\circ\text{C}$ after annealing.

Figure 5. (Color online) Maximum surface recombination velocity $S_{\text{eff,max}}$ as a function of the positive corona charge density Q_{corona} deposited on Al_2O_3 films synthesized by plasma ALD and PECVD ($T_{\text{dep}} = 200^\circ\text{C}$) after annealing. As substrates, $3.5 \Omega \text{ cm}$ n-type c-Si wafers were used.

sputtered Al_2O_3 ($Q_f \approx 3 \times 10^{12} \text{ cm}^{-2}$).⁹ Our measured Q_f values are within the range of the previously reported values of negative Q_f between 5×10^{12} and $13 \times 10^{12} \text{ cm}^{-2}$ for plasma ALD Al_2O_3 .^{2,15,16} For thermal ALD Al_2O_3 preliminary data suggest that after annealing the negative Q_f values are significantly lower.

Comparing the material properties with the passivation performance of Al_2O_3 films, it is apparent that conventional measures for high material quality, such as a high refractive index and mass density, stoichiometry (O/Al ratio ~ 1.5), and low impurity content, do not directly reflect the passivation performance. In fact, a high level of surface passivation was obtained for a relatively wide range of Al_2O_3 material properties, such as a refractive index and hydrogen concentration in the range of 1.55–1.65 and 2–7.5 atom %, respectively. This observation is consistent with the expectation that, ultimately, after annealing, the c-Si/ Al_2O_3 interface properties determine the level of surface passivation and that the Al_2O_3 bulk material properties may deviate from those close to the c-Si interface.^{17,18} During postdeposition annealing, structural modification of the material bulk and interface takes place,^{2,8,18} which improves the surface passivation of c-Si. These structural rearrangements, in conjunction with the importance of the interface properties, might relax the requirements on the Al_2O_3 bulk material properties significantly.

Conclusion

We have studied the influence of the substrate temperature on the material properties and the surface passivation performance of Al_2O_3 films synthesized by plasma and thermal ALD and PECVD. The Al_2O_3 material properties, such as mass density and hydrogen content, were dependent on the deposition technique used, but the resulting surface passivation performance was excellent for plasma and thermal ALD Al_2O_3 at $T_{\text{dep}} = 150$ – 250°C and for PECVD Al_2O_3 at $T_{\text{dep}} = 150$ – 300°C . Consequently, a principal result of this work is that we have demonstrated that PECVD can be used to deposit high quality Al_2O_3 films, resulting in exceptionally low surface recombination velocities and containing a high fixed negative charge density of $\sim 6 \times 10^{12} \text{ cm}^{-2}$. The deposition method of choice for Al_2O_3 therefore depends largely upon the extent to which other relevant factors (such as deposition uniformity, conformality, throughput, and scalability) play a role in the envisaged application of Al_2O_3 .

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