Influence of the deposition temperature on the c-Si Surface passivation by Al2 O3 films synthesized by ALD and PECVD

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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,\textsuperscript{1,2} leading to enhanced solar cell efficiencies.\textsuperscript{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 \(\sim 200^\circ\text{C}\).\textsuperscript{1,4} Very recently, it has been shown that other techniques, such as sputtering and plasma-enhanced chemical vapor deposition (PECVD),\textsuperscript{6} 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 (\(T_{\text{dep}}\)) during deposition on the Al2O3 material properties and the surface passivation performance is addressed for Al2O3 films deposited at the temperatures in the range of \(T_{\text{dep}} = 25-400^\circ\text{C}\) for thermal plasma and PECVD ALD. 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 OppAL ALD reactor (operating pressure \(\sim 170\) mTorr) and in a second reactor, the Oxford Instruments FlexAL (operating pressure \(\sim 15\) 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. Cycle and purge times were optimized to reach a truly self-limiting ALD process at every \(T_{\text{dep}}\). 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 \(\sim 275\) \(\mu\text{m}\) thick float zone (100) c-Si wafers were coated on both sides with Al2O3 with a thickness of \(\sim 30\) 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 \(400^\circ\text{C}\) in a N2 environment.\textsuperscript{7} The upper limit of the surface recombination velocity (\(S_{\text{eff,max}}\)) was determined from the effective lifetime (\(\tau_{\text{eff}}\)), as measured with photocurrent (Sinton WCT 100) at an injection level of \(10^{13}\) \(\text{cm}^{-2}\) by assuming an infinite bulk lifetime.\textsuperscript{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 \(T_{\text{dep}}\) for plasma and thermal ALD (Fig. 1a) agree well for the OppAL 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.\textsuperscript{12} The decrease in GPC with increasing \(T_{\text{dep}}\) can be mainly attributed to a decreasing density of OH surface groups due to dehydroxylation reactions.\textsuperscript{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 \(T_{\text{dep}}\), saturating at \(3.2 \pm 0.2\) 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 \(T_{\text{dep}}\), similar to the ALD case. The refractive index values for PECVD Al2O3 are lower than the ones obtained for ALD at the same \(T_{\text{dep}}\). The deposition rate, \(R_{\text{dep}}\), decreased strongly with increasing \(T_{\text{dep}}\), saturating at \(5\) nm/min for \(T_{\text{dep}} > 200^\circ\text{C}\). The higher \(R_{\text{dep}}\) 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 \(R_{\text{dep}}\) as a function of \(T_{\text{dep}}\) is an indication of a growth process controlled by the adsorption of surface species, as also pre-
were obtained at addition to the data shown in Fig. 2c, exceptionally low
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Figure 1.
As-deposited Al₂O₃ films and closed symbols films after annealing at 400°C. Lines serve as a guide for the eyes.
Figure 2. (Color online) (a) Deposition rate, R /dep (b) refractive index, n, and (c) maximum surface recombination velocity, S eff,max as a function of substrate temperature for PECVD Al₂O₃. Open symbols represent as-deposited Al₂O₃ films and closed symbols films after annealing at 400°C. Lines serve as a guide for the eyes.

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 Al₂O₃ deposited on ~2 Ω cm p-type c-Si in the OpAL reactor. Open symbols represent as-deposited Al₂O₃ films and closed symbols films after annealing at 400°C. Lines serve as a guide for the eyes.

viously reported for the PECVD of SiO₂. 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 /dep can be partly explained by the decreasing hydrogen concentration as evidenced by Fig. 3c. For the same /dep, the hydrogen concentrations of the PECVD Al₂O₃ films were significantly higher than those for the ALD Al₂O₃ films. The O/Al ratio decreased with increasing /dep, as displayed in Fig. 3b, and (nearly) stoichiometric Al₂O₃ films, with O/Al ratios close to 1.5, were obtained at /dep > 200°C.

The level of c-Si surface passivation by ALD-synthesized Al₂O₃ is evaluated in Fig. 1c. The results demonstrate that thermal ALD Al₂O₃ provides a higher level of surface passivation in the as-deposited state (with lowest S eff < 35 cm/s) than plasma ALD Al₂O₃.² It is observed that the as-deposited passivation quality increases with /dep for the plasma ALD, whereas a small decrease with increasing /dep is observed for the thermal ALD. After annealing, the surface passivation quality improved significantly, with the best passivation performance obtained at /dep = 150–250°C for both ALD methods. Values of S eff,max down to ~3 cm/s are reached for ~2 Ω cm p-type c-Si by both plasma and thermal ALD.

The trend observed for the passivation quality of the as-deposited PECVD Al₂O₃, shown in Fig. 2c, is similar to the one for plasma ALD Al₂O₃. Annealing also improved the passivation properties of the PECVD Al₂O₃ films. The annealed films afforded a high level of surface passivation with S eff < 10 cm/s for /dep = 150–300°C. In addition to the data shown in Fig. 2c, exceptionally low S eff values were obtained at /dep = 200°C, for example, S eff < 2.9 cm/s for plasma ALD, which is evaluated in Fig. 1c. The results demonstrate that thermal ALD Al₂O₃ provides a higher level of surface passivation in the as-deposited state (with lowest S eff < 35 cm/s) than plasma ALD Al₂O₃.² It is observed that the as-deposited passivation quality increases with /dep for the plasma ALD, whereas a small decrease with increasing /dep is observed for the thermal ALD. After annealing, the surface passivation quality improved significantly, with the best passivation performance obtained at /dep = 150–250°C for both ALD methods. Values of S eff,max down to ~3 cm/s are reached for ~2 Ω cm p-type c-Si by both plasma and thermal ALD.

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In conclusion, the results presented in this study demonstrate the importance of ALD for the fabrication of high-quality surface passivation layers for c-Si, with potential applications in solar cell technology.
reported for microwave PECVD ALD and PECVD Al₂O₃ are higher than the negative deposited in the OpAL reactor and PECVD Al₂O₃ films. Lines serve as a guide for the eyes.

In the same way, a negative Ref. 2. A sharp drop of the level of surface passivation on a passivated c-Si wafer using a similar approach, as described in S

A function of the positive corona charge density a

Mass density, f values are significantly lower. Comparing the material properties with the passivation performance of Al₂O₃, 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 Al₂O₃ 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/Al₂O₃ interface properties determine the level of surface passivation and that the Al₂O₃ bulk material properties may deviate from those close to the c-Si interface. During postdeposition annealing, structural modification of the material bulk and interface takes place, 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 Al₂O₃ bulk material properties significantly.

Conclusion

We have studied the influence of the substrate temperature on the material properties and the surface passivation performance of Al₂O₃ films synthesized by plasma and thermal ALD and PECVD. The Al₂O₃ 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 Al₂O₃ at T_{dep} = 150–250°C and for PECVD Al₂O₃ at T_{dep} = 200°C after annealing. Consequently, a principal result of this work is that we have demonstrated that PECVD can be used to deposit high quality Al₂O₃ films, resulting in exceptionally low surface recombination velocities and containing a high fixed negative charge density of ∼ 6 × 10^{13} cm⁻². The deposition method of choice for Al₂O₃ therefore depends largely upon the extent to which other relevant factors (such as deposition uniformity, conformity, throughput, and scalability) play a role in the envisaged application of Al₂O₃.

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