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- and n-type c-Si, leading to enhanced solar cell efficiencies. 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 200–400°C. Very recently, it has been shown that other techniques, such as sputtering and plasma-enhanced chemical vapor deposition (PECVD), 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_{dep} = 25–400°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 ~170 mTorr) and in a second reactor, the Oxford Instruments FlexAL (operating pressure ~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_{dep}. The PECVD process employed a continuous operating pressure of 1013 mTorr, saturated at 1015 mTorr. The surface passivation was evaluated in the as-deposited environment. The upper limit of the surface recombination velocity (S_{eff,max}) was determined from the effective lifetime (τ_{eff}), as measured with photocurrent (Sinton WCT 100) at an injection level of 1015 cm−3 by assuming an infinite bulk lifetime.

**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. The decrease in GPC with increasing T_{dep} can be mainly attributed to a decreasing density of OH surface groups due to dehydroxylation reactions. 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 ± 0.2 g/cm3 at a high temperature.

In Fig. 2, 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 ~5 nm/min for T_{dep} > 200°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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viously reported for the PECVD of SiO$_2$. 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$_2$O$_3$ films were significantly higher than those for the ALD Al$_2$O$_3$ films. The O/Al ratio decreased with increasing $T_{dep}$, as displayed in Fig. 3b, and (nearly) stoichiometric Al$_2$O$_3$ films, with O/Al ratios close to 1.5, were obtained at $T_{dep} > 200^\circ$C.

The level of c-Si surface passivation by ALD-synthesized Al$_2$O$_3$ is evaluated in Fig. 1c. The results demonstrate that thermal ALD Al$_2$O$_3$ provides a higher level of surface passivation in the as-deposited state (with lowest $S_{eff} < 35$ cm/s) than plasma ALD Al$_2$O$_3$. 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, with the best passivation performance observed at $T_{dep} = 150$–250$^\circ$C for both ALD methods. Values of $S_{eff,max}$ down to ~3 cm/s are reached for ~2 $\Omega$ cm p-type c-Si by both plasma and thermal ALD.

The trend observed for the passivation quality of the as-deposited PECVD Al$_2$O$_3$, shown in Fig. 2c, is similar to the one for plasma ALD Al$_2$O$_3$. Annealing also improved the passivation properties of the PECVD Al$_2$O$_3$ films. The annealed films afforded a high level of surface passivation with $S_{eff} < 10$ cm/s for $T_{dep} = 150$–300$^\circ$C. In addition to the data shown in Fig. 2c, exceptionally low $S_{eff}$ values were obtained at $T_{dep} = 200^\circ$C, for example, $S_{eff} < 2.9$ cm/s $\tau_{eff} = 4.7$ ms and $S_{eff} < 0.8$ cm/s ($\tau_{eff} = 18$ ms) on 2.2 $\Omega$ cm p-type and 3.5 $\Omega$ cm n-type c-Si, respectively; and also $S_{eff} < 14$ cm/s ($\tau_{eff} = 1$ ms) on 1 $\Omega$ 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 $\sim 5$ nm/min. Significantly higher deposition rates of >30 nm/min were also feasible while maintaining a good level of surface passivation, as demonstrated by $S_{eff} < 14$ cm/s on 3.5 $\Omega$ cm n-type c-Si. For comparison, under the present conditions the maximum deposition rate for ALD was $\sim 1.8$ nm/min at $T_{dep} = 200^\circ$C.

The improvement of the passivation properties of the as-deposited plasma ALD and PECVD Al$_2$O$_3$ 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$_2$O$_3$ is thought to play an essential role in the surface passivation properties of Al$_2$O$_3$. 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. 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$_2$O$_3$ deposited by thermal ALD.

The Al$_2$O$_3$ 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, induces the field-effect passivation and is expected to be closely related to the Al$_2$O$_3$ structural properties near the interface. As shown in Fig. 5, we have also verified the presence of a high negative $Q_f$ of (6.5 ± 1)
reported for microwave PECVD/H20849 ALD and PECVD Al2O3 are higher than the negative
charges. 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
with a function of substrate temperature for
as-deposited films. Data are given for plasma and thermal ALD Al2O3 films. These
Figure 3. (Color online) (a) Mass density, \( \rho_{\text{max}} \), (b) O/Al ratio, and (c) the H
concentration, \([H]\), determined as a function of substrate temperature for
plasma ALD and PECVD Al2O3 films. Lines serve as a
guide for the eyes.

\( \times 10^{12} \text{ cm}^{-2} \) for PECVD Al2O3 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
\( \varepsilon_{\text{eff,max}} \)) was observed at the point where the amount of negative
fixed charge in the Al2O3 was exactly balanced by positive corona charges. In the same way, a negative \( Q_i \) of \( (5 \pm 1) \times 10^{12} \text{ cm}^{-2} \)
for plasma ALD Al2O3 was determined. These \( Q_i \) values for plasma
ALD and PECVD Al2O3 are higher than the negative \( Q_i \) values
reported for microwave PECVD (\( Q_i = 2 \times 10^{12} \text{ cm}^{-2} \) \( \text{11} \) and

\( \times 10^{12} \text{ cm}^{-2} \) for sputtered Al2O3 (\( Q_i = 3 \times 10^{12} \text{ cm}^{-2} \)).\( \text{6} \) Our measured \( Q_i \) values are
within the range of the previously reported values of negative \( Q_i \) between \( 5 \times 10^{12} \) and \( 13 \times 10^{12} \text{ cm}^{-2} \) for plasma ALD
Al2O3.\( \text{2,15,16} \) For thermal ALD Al2O3 preliminary data suggest that
after annealing the negative \( Q_i \) values are significantly lower.

Comparing the material properties with the passivation performance
of Al2O3 films, it is apparent that conventional measures for high
material quality, such as a high refractive index and mass
density, stoichiometry (O/Al ratio \( \approx 1.5 \)), 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.\( \text{7,18} \) During postdeposition annealing, structural modification
of the material bulk and interface takes place,\( \text{2,8} \) which improves the surface passivation of c-Si. These structural rearrange-
ments, 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 \( T_{\text{dep}} = 150–250^\circ \text{C} \) and for PECVD
Al2O3 at \( T_{\text{dep}} = 150–300^\circ \text{C} \). 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 \( \approx 6 \times 10^{13} \text{ cm}^{-2} \). 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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**Figure 3.** (Color online) (a) Mass density, \( \rho_{\text{max}} \), (b) O/Al ratio, and (c) the H
concentration, \([H]\), determined as a function of substrate temperature for
plasma ALD and PECVD Al2O3 films. Lines serve as a
guide for the eyes.

**Figure 4.** (Color online) Injection-level-dependent effective lifetime for
n- and p-type c-Si wafers of various resistivities passivated by PECVD Al2O3
with \( T_{\text{dep}} = 200^\circ \text{C} \) after annealing.

**Figure 5.** (Color online) Maximum surface recombination velocity \( S_{\varepsilon_{\text{eff,max}}} \) as
a function of the positive corona charge density \( Q_{\text{corona}} \) deposited on Al2O3
films synthesized by plasma ALD and PECVD (\( T_{\text{dep}} = 200^\circ \text{C} \)) after
annealing. As substrates, 3.5 \( \Omega \) cm n-type c-Si wafers were used.
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