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COMPARISON BETWEEN ALUMINUM OXIDE SURFACE PASSIVATION FILMS DEPOSITED WITH THERMAL ALD, PLASMA ALD AND PECVD

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ABSTRACT

Surface passivation schemes based on Al_2O_3 have enabled increased efficiencies for silicon solar cells. The key distinguishing factor of Al_2O_3 is the high fixed negative charge density (Q_f = 10^{12}-10^{13} cm^{-2}), which is especially beneficial for *p*- and *p+* type *c*-Si, as it leads to a high level of field-effect passivation. Here we discuss the properties of Al_2O_3 surface passivation films synthesized with plasma atomic layer deposition (ALD), thermal ALD (using H_2O as oxidant) and PECVD. We will show that with all three methods a high level of surface passivation can be obtained for Al_2O_3 deposited at substrate temperatures in the range of 150-250°C. Furthermore, the role of chemical and field-effect passivation will be briefly addressed. It is concluded that the passivation performance of Al_2O_3 is relatively insensitive to variations in structural properties. Al_2O_3 is therefore a very robust solution for silicon surface passivation.

INTRODUCTION

In the past few years, Al_2O_3 films have demonstrated their potential as surface passivation scheme for silicon photovoltaics by enabling ultralow surface recombination velocities [1-5] and enhanced solar cell efficiencies [6,7]. The key differentiator of Al_2O_3 in comparison to other passivation schemes is its high fixed *negative* charge density (10^{12}-10^{13} cm^{-2}) located at the Al_2O_3/Si interface which produces effective field-effect passivation by shielding electrons from the interface. This makes Al_2O_3 especially suited for the passivation of *p*-type silicon and *p+* emitters, while Al_2O_3 is expected to be less suitable for *n*-type (due to parasitic shunting) and *n+* type silicon (yet this still remains to be proven). The thermal stability of Al_2O_3 during firing and the low temperature deposition of the films, are compatible with industrial solar cell processes [8]. Al_2O_3 is transparent (bandgap ~9 eV) and stable under UV illumination [9,10], but the refractive index of ~1.64 makes it less suitable for single layer antireflection coating on the front side as compared to *a*-SiN_x. As a back reflector, however, Al_2O_3 is superior. Also the fact that very thin Al_2O_3 films (down to 5 nm) can be used [5], is another benefit of Al_2O_3 and enables flexibility in the design of surface passivation schemes and stacks. As a consequence of these (unique) properties, Al_2O_3 is now considered as an important candidate for surface passivation in industrial solar cells, either for front and/or rear side passivation. A remaining challenge in this respect, is the development of deposition tools for Al_2O_3 films compatible with the requirements, especially in terms of throughput, of the solar cell industry.

To date, Al_2O_3 surface passivation films have been mainly synthesized with atomic layer deposition (ALD). The ALD growth process is based on self-limiting surface reactions, and therefore allows for film thickness control on the sub-monolayer level as well as excellent uniformity and conformality. A thermal and plasma ALD process for Al_2O_3 using H_2O and an O_2 plasma as oxidants, respectively, have been successfully tested for Si surface passivation. The traditionally low deposition rates of ALD, have been the incentive for testing of alternative deposition methods. It has for instance been shown that other techniques, such as sputtering and plasma enhanced chemical vapour deposition (PECVD) [11-14], can also be used to deposit Al_2O_3 for surface passivation. These methods generally allow for higher deposition rates and are well established in solar cell manufacturing in contrast to the ALD method. It should be noted, however, that the current limitations in terms of growth rate and throughput for lab scale ALD reactors are not fundamental [15]. With the use of batch processes but also with innovative developments, ALD may meet the throughput requirements of the solar cell industry, especially when ultrathin films are considered. Very recently it has for instance been shown that high deposition rates can be achieved with ALD by a reactor design separating the precursor and oxidation steps *spatially* instead of temporarily [16]. When the throughput requirements are met, the benefits of ALD can lead to its introduction in high volume manufacturing of solar cells.

In this contribution, we compare plasma ALD, thermal ALD and PECVD grown Al_2O_3 films in terms of surface passivation and material properties. We will also briefly address the underlying passivation mechanism in terms of chemical passivation (i.e. reduction of interface defect density) and field-effect passivation [17]. The message that we want to convey here is that good surface passivation can be obtained for a large range of Al_2O_3 material properties, which alleviates the requirements on the deposition methods, operating conditions and the reactor tools.

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). For both ALD methods, trimethylaluminum [$Al(CH_3)_3$)] was used as the Al precursor in the first half cycle of the ALD process. During the second half cycle, either H_2O or an O_2 plasma was used for thermal and plasma ALD, respectively [5]. The films were deposited using substrate temperatures ranging from 50°C-400°C [14]. Cycle and purge times were optimized to reach a truly self-limiting ALD process at every T_{dep}. A schematic of the ALD cycles of the two methods are shown in Fig. 1. The PECVD process employed a continuous remote O_2/Ar plasma and $Al(CH_3)_3$ as the Al precursor. Unlike ALD, the deposition rate for PECVD scales with the $Al(CH_3)_3$ flow introduced into the reactor. Rutherford backscattering spectroscopy and elastic recoil detection were used to determine the material properties in terms of atomic composition and mass density. Lifetime spectroscopy (Sinton WCT100) was used to evaluate the passivation performance. Annealing was done in N_2, at 400°C, for 10 minutes. The upper limit of the surface recombination velocity, $S_{eff,max}$, was determined (at an injection level of 1×10^{15} cm^{-3}) by assuming that all recombination takes place at the surfaces.

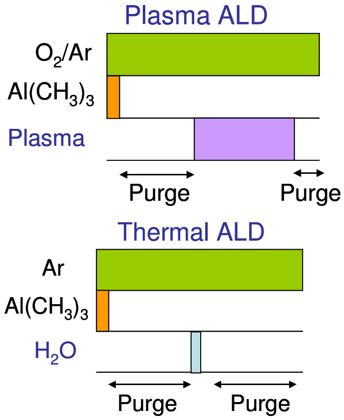

Figure 1. Schematic representation of the plasma ALD and thermal ALD cycle. During 1 cycle, typically ~0.1 nm Al_2O_3 is deposited. By repeating the cycles, the targeted film thickness can be reached with submonolayer growth control.

RESULTS

The maximum surface recombination velocity is plotted as a function of the deposition temperature for plasma and thermal ALD in Figure 2 and for PECVD in Figure 3. Significant differences were observed for as-deposited films. For plasma ALD and PECVD, the as-deposited surface passivation performance was very poor for T_{dep} = 50-200°C. For higher T_{dep}, the S_{eff} values are observed to decrease significantly, which can be explained by an *in-situ* anneal effect. For thermal ALD Al_2O_3, the as-deposited passivation performance was significantly better. After annealing, thermal ALD and plasma ALD afford a similar high level of surface passivation for T_{dep} = 150-250°C. $S_{eff,max}$ values as low as 3 cm/s were obtained on 2 Ω cm *p*-type FZ *c*-Si.

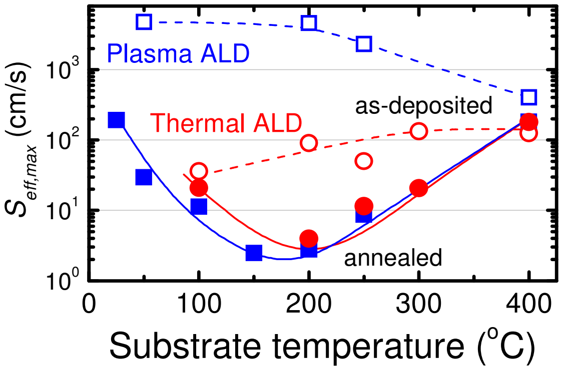

Figure 2. Influence of the deposition temperature on the passivation performance of as-deposited (open symbols) and annealed (closed symbols) Al_2O_3 films synthesized with plasma ALD (squares) and thermal ALD (circles). As substrates, 2 Ω cm *p*-type FZ *c*-Si wafers were used.

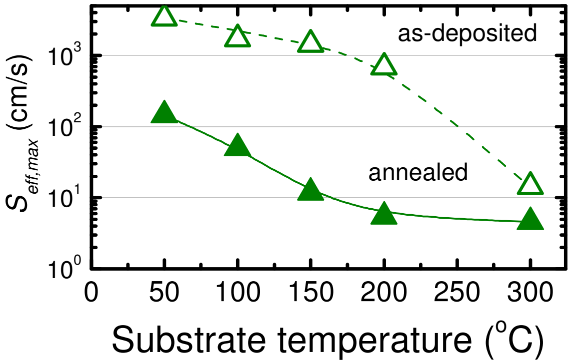

Figure 3. Influence of the deposition temperature on the passivation performance of as-deposited and annealed Al_2O_3 films synthesized with PECVD. As substrates, 2 Ω cm *p*-type FZ *c*-Si wafers were used.

Also PECVD results in a comparable high level of surface passivation for T_{dep} = 150-300°C. Figure 4 shows the injection level dependent effective lifetime for two PECVD Al_2O_3 films, both deposited at T_{dep} = 200°C, using a deposition rate of ~5 and ~18 nm/min. An exceptional high effective lifetime of ~20 ms is measured (at injection level of 5×10^{14} cm^{-3}), for the film deposited at 5 nm/min on 3.5 Ω cm *n*-type *c*-Si. This corresponds to S_{eff} < 1 cm/s, amongst the lowest reported for *c*-Si. With this high level of surface passivation the effective lifetime of the minority carriers is mainly determined by Auger recombination in the Si bulk. The decreasing lifetime at low injection levels for these *n*-type wafers can be attributed to the formation of an inversion layer. This indicates the presence of a significant density of fixed negative charge (Q_f) at the interface, which was confirmed by corona charging experiments that indicated a Q_f value > 6×10^{12} cm^{-2} [14]. For higher deposition rates, R_{dep} = ~18 nm/min, the level of surface passivation is still very good with S_{eff} < 9 cm/s. For comparison, under the present conditions the maximum deposition rate for ALD was ~1.8 nm/min at T_{dep} = 200°C.

For industrial solar cells, it is important to evaluate the stability of the surface passivation upon a high temperature firing process. It was already demonstrated that the ALD films exhibited sufficient thermal stability at temperatures > 800°C [8]. Also the PECVD Al_2O_3 films were sufficiently stable. S_{eff} values < 10 cm/s were measured (for *n*-type wafers 3.5 Ω cm) after a firing process in an industrial belt line furnace (no metal paste was applied). The depassivation of interface defects at elevated temperatures, likely plays a role in the observed decrease of the surface passivation performance.

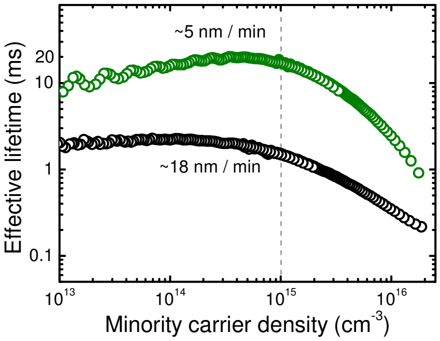

Figure 4. Effective lifetime for Al_2O_3 after annealing, deposited with PECVD at a deposition rate of ~5 and ~18 nm/min.

Table 1 summarizes the material properties of the films deposited with the three methods, for the (optimal) substrate temperature of 200°C. The main difference between plasma and thermal ALD Al_2O_3, is the higher hydrogen concentration for the latter (3.6 at.%). As compared to the ALD films, the mass density of the PECVD Al_2O_3 film is significantly lower and the O/Al ratio of 1.61 indicates an excess of oxygen. Both observations are linked with the incorporation of significant amounts of hydrogen during the PECVD process. The deposition temperature has a significant impact on the structural properties of Al_2O_3, as discussed in detail in Ref. 14. Here we would like to emphasize that the passivation performance after annealing as displayed in Figs. 2 and 3, is rather insensitive to the significant differences in material properties between films deposited with the various deposition techniques and deposited within a broad range of substrate temperatures.

Table 1: Material properties of Al_2O_3 synthesized with PECVD, plasma ALD and thermal ALD at T_{dep} = 200°C.

Deposition process	[O]/[Al]	[H] at.%	ρ_{mass} (g/cm^3)
PECVD (5 nm/min)	1.61	7.5	2.7
Plasma ALD	1.52	2.7	3.1
Thermal ALD	1.52	3.6	3.0

Capacitance-voltage and second harmonic generation experiments were used to study the chemical and field-effect passivation underlying the surface passivation properties [17]. Briefly, the lack of significant surface passivation for as-deposited Al_2O_3 deposited with plasma ALD (and PECVD) was attributed to a very high interface defect density, despite the presence of a significant negative $Q_f > 10^{12}$ cm^{-2}. We have demonstrated that the defective interface can be attributed to plasma induced damage during deposition [17]. After annealing, both plasma and thermal ALD Al_2O_3 exhibited a low interface defect density with D_{it} values of ~10^{11} eV^{-1} cm^{-1} or below. Q_f values were higher for plasma ALD and PECVD ($Q_f > 5\times10^{12}$ cm^{-2}) than for thermal ALD (Q_f ~2×10^{12} cm^{-2}). Chemical passivation therefore plays a more prominent role for the thermal ALD Al_2O_3 films. Taken together, the results show that the chief effect of annealing was the improvement of the chemical passivation for plasma ALD Al_2O_3 films, whereas for thermal ALD, the increase of the field effect passivation was more pronounced [17].

CONCLUSION

Al_2O_3 films deposited with plasma ALD, thermal ALD and PECVD afforded a high level of Si surface passivation, for a relatively broad range of substrate temperatures during deposition. Similar to ALD, the PECVD Al_2O_3 films exhibited a high fixed negative charge density after annealing and a good firing stability. The results demonstrate that the passivation performance is relatively insensitive to the structural properties of bulk Al_2O_3, which makes Al_2O_3 a robust solution for silicon surface passivation in photovoltaics.

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