Crystalline silicon surface passivation by the negative-charge-dielectric Al$_2$O$_3$

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ABSTRACT

In this contribution it will be demonstrated that Al₂O₃ films synthesized by plasma-assisted atomic layer deposition are a very interesting low temperature solution for the passivation of highly and lowly doped p-type c-Si and lightly doped n-type c-Si. From experiments it will be shown that the excellent surface passivation by Al₂O₃ can for a large part be attributed to a high fixed negative charge density in the film on the film-substrate interface. The implications of this high fixed negative charge density on the surface passivation of both n- and p-type c-Si will be addressed.

INTRODUCTION

Surface passivation of crystalline silicon (c-Si) is becoming increasingly important for the performance of c-Si solar cells. Surface passivation is not only requisite for high efficiency solar cells. Surface passivation is, moreover, becoming vital for all solar cells based on c-Si as the cost-driven reduction of the solar cell thickness is increasing the surface-to-volume ratio.

Thin films (typically 20-80 nm) of thermal silicon dioxide (SiO₂), silicon nitride (a-SiNₓ:H) and amorphous silicon (a-Si:H) are currently used for surface passivation of c-Si solar cells in industry. A material that has recently regained interest for the passivation of c-Si is aluminum oxide (Al₂O₃). In the late eighties Al₂O₃ was already applied for c-Si surface passivation in a metal-insulator-semiconductor (MIS) solar cell by Hezel and Jaeger.[1] They demonstrated that Al₂O₃ could provide a reasonable level of surface passivation with an effective surface recombination velocity of ~200 cm/s on 2 Ω cm p-type c-Si. More recently Agostinelli et al. demonstrated that Al₂O₃ grown by atomic layer deposition (ALD) could provide an excellent level of surface passivation on p-type c-Si.[2]

In this contribution we will demonstrate that Al₂O₃ deposited by plasma-assisted ALD[3,4] yields a state-of-the-art level of surface passivation on various c-Si surfaces. Moreover, we will address the c-Si surface passivation mechanism of Al₂O₃ and show that this underlying mechanism makes Al₂O₃ a particularly interesting candidate for the passivation of p-type c-Si with an arbitrary doping level. This also includes the passivation of p-type emitters which has been found challenging so far.

EXPERIMENTAL

Al₂O₃ films with a thickness of 7-30 nm were grown in a commercial (Oxford Instruments, FlexAL) and home-built PA-ALD reactor (ALD-I) at a substrate temperature of 200 °C. The films were prepared by alternating trimethylaluminium (TMA) exposure and a remote O₂ plasma. The film growth was monitored by means of in situ spectroscopic ellipsometry (250-1000 nm range) and revealed a growth rate in the 1.2 Å per cycle range. The surface passivation was tested by depositing identical Al₂O₃ films on both sides of low resistivity c-Si substrates with various doping concentrations and dopant types. The substrates received a standard RCA clean with final HF dip prior to deposition to remove the native oxide. After deposition, the lifetime samples were annealed in a N₂ environment for 30 minutes at 425 °C in a rapid thermal anneal furnace. The effective lifetime \( \tau_{\text{eff}} \) was measured using a lifetime tester (Sinton WCT-100) in both the quasi steady state and transient mode.[5] The level of surface passivation is quantified by the effective surface recombination velocity. Assuming an infinite bulk lifetime, the upper limit of the effective surface recombination velocity \( S_{\text{eff}} \) can be calculated by:

\[
S_{\text{eff}} \leq \frac{W}{2 \cdot \tau_{\text{eff}}}
\]

with \( W \) the substrate thickness.

In Fig. 1 the effective lifetime is shown for low resistivity n-type c-Si passivated by Al₂O₃ films with a thickness of 7-30 nm as determined from photoconductance measurements.[5] Effective lifetimes in excess of 6 ms were measured indicating a surface recombination velocity \( S_{\text{eff,max}} \) of 2 cm/s assuming an infinite bulk lifetime. These values are comparable to the best values published for annealed thermal SiO₂.[6] A 7 nm thick Al₂O₃ still yields a \( S_{\text{eff,max}} \) of 5 cm/s.
Injection level $L_{\text{in}}$ (em-

**Figure 1:** Effective lifetime as a function of the excess carrier density for low resistivity n-type (275 μm, <100>, 1.9 Ω cm) float zone c-Si substrate passivated with a 30, 15 and 7 nm thick Al₂O₃ film.[7]

In Fig. 2 the effective lifetime is shown for a 2 Ω cm p-type wafer passivated by a 10 and 30 nm Al₂O₃ film. Effective lifetimes in excess of 3 ms were measured, corresponding to a $S_{\text{eff, max}}$ of 5 cm/s. In Fig. 3 the combined $S_{\text{eff, max}}$ values are shown for p-type c-Si with various doping concentrations passivated by Al₂O₃. Literature values obtained by thermal SiO₂ (either forming gas annealed or annealed), as deposited a-SiNₓ:H and a-Si:H are included for comparison. The values for a B-doping concentration $> 10^{16}$ cm$^{-3}$ were extracted from the measured emitter saturation current density on B-doped p-type emitters as discussed in detail in a separate publication.[8] The effective surface recombination values for lightly B-doped c-Si were calculated assuming an infinite bulk lifetime and using the best values published in the studies of Kerr et al.[6,9,10] and Dauwe et al.[9]

**Figure 2:** Effective lifetime as a function of the excess carrier density for low resistivity p-type (300 μm, <111>, 2 Ω cm) float zone c-Si substrate passivated with a 30 and 10 nm thick Al₂O₃ film.

**Figure 3:** Upper level of the effective surface recombination velocity as a function of the B-concentration for c-Si wafers passivated by plasma-assisted ALD Al₂O₃, thermal SiO₂, a-SiNₓ:H, and a-Si:H.[6,9,10]

Figure 3 clearly demonstrates that Al₂O₃ provides a state-of-the-art level of surface passivation on p-type c-Si with an arbitrary doping level.

The excellent level of surface passivation by Al₂O₃ was also confirmed by solar cell device performance. Al₂O₃ applied at the rear of p-type c-Si solar cells yielded a maximum efficiency of 20.6%. This work was done in collaboration with the solar cell institute ISFH in Germany and will be presented in a separate contribution at this conference.[11,12] The performance of the Al₂O₃ passivated solar cells was at least equal to the solar cells with an annealed thermal SiO₂ rear surface passivation.[11,12]

c-Si SURFACE PASSIVATION MECHANISM OF Al₂O₃

In Fig. 4 field-effect passivation is simulated for a moderately doped n-type c-Si wafer for both a negative and positive charge density $Q_{\text{effective}}$ at the surface. It can clearly be seen that a high positive or negative $Q_{\text{effective}}$ results in a significant reduction of $S_{\text{eff}}$. For a sufficiently high $Q_{\text{effective}}$ the minority surface carrier density scales with $1/Q^2$ at the c-Si surface; hence the field-effect passivation scales with $Q^2$, irrespective of the polarity of the $Q_{\text{effective}}$.

The surface passivation mechanism of Al₂O₃ is mainly based on field-effect passivation by a high fixed negative charge density $Q_{\text{effective}}$ in the Al₂O₃ film. In Fig. 5 it is demonstrated that a positive corona charge density $Q_{\text{corona}}$ of $1.3 \times 10^{13}$ cm$^{-2}$ at the Al₂O₃ surface is required to cancel the field effect passivation. $Q_{\text{corona}}$ is balancing the negative fixed charge density in a 26 nm Al₂O₃ film, resulting in a maximum in $S_{\text{eff}}$.

Negative fixed charges are routinely reported for Al₂O₃ films deposited on c-Si, irrespective of the deposition technique. The origin of these negative charges is most probably related to the
presence of Al vacancies in the Al2O3 film.[14] It was shown that these vacancies are predominantly present at the c-Si/Al2O3 interface,[15] in excellent agreement with the position of the fixed negative charge density deduced from thickness dependent capacitance voltage measurements by for example Abouaf et al.[16]

A negative Qf is especially beneficial for the passivation of p-type c-Si as the minority carriers, the electrons, are effectively shielded from the c-Si surface. This is clearly apparent from the fact that the negative-charge-dielectric Al2O3 provides a state-of-the-art level of surface passivation even on highly B-doped p-type c-Si surfaces as shown in Fig. 3. The negative sign of the fixed charge also explains the flat injection level dependence of the surface passivation on low resistivity p-type c-Si as shown in Fig. 2 of this proceeding in excellent agreement with the extended Shockley-Read-Hall model.[17] A strong injection level dependence is routinely reported for p-type c-Si passivated by thermal SiO2, a-SiNx:H and a-Si:H.[6,9,10] As the fixed charge density in Al2O3 is typically one order of magnitude higher compared to a-SiNx:H and two orders of magnitude higher compared to thermal SiO2 and a-SiCx, this implies that the field-effect passivation by Al2O3 is 2 - 4 orders of magnitude stronger compared to these types of surface passivation films. This difference in the level of field-effect passivation significantly relaxes the requirements on the interface defect density at the c-Si/Al2O3 interface. However, the relative low $S_{ef}$ at the point where the field-effect passivation is cancelled in Fig. 5 illustrates that the c-Si/Al2O3 interface defect density is also relatively low due to the presence of a thin SiO2-like film between the c-Si and the Al2O3 film as generated during the Al2O3 deposition process.[7]

CONCLUSIONS

It is demonstrated that Al2O3 is an interesting material to obtain a high level of c-Si surface passivation as required for high efficiency solar cells. Al2O3 not only yields a state-of-the-art level of surface passivation on low resistivity n- and p-type c-Si, but its high fixed negative charge density makes it also particularly interesting for the passivation of p-type c-Si with an arbitrary doping level such as highly doped p-type emitters. The field-effect passivation by Al2O3 is orders of magnitude stronger than for passivation layers such as a-SiNx:H and thermal SiO2 and this relaxes the demanding requirements on the electrical interface quality. The excellent level of surface passivation has already been demonstrated by p-type c-Si solar cell devices.

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