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Surface passivation of phosphorus-diffused n^+-type emitters by plasma-assisted atomic-layer deposited Al_2O_3

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In recent years Al_2O_3 has received tremendous interest in the photovoltaic community for the application as surface passivation layer for crystalline silicon. Especially p-type c-Si surfaces are very effectively passivated by Al_2O_3, including p-type emitters, due to the high fixed negative charge in the Al_2O_3 film. In this Letter we show that Al_2O_3 prepared by plasma-assisted atomic layer deposition (ALD) can actually provide a good level of surface passivation for highly doped n-type emitters in the range of 10–100 Ω/sq with implied-V_{oc} values up to 680 mV. For n-type emitters in the range of 100–200 Ω/sq the implied-V_{oc} drops to a value of 600 mV for a 200 Ω/sq emitter, indicating a decreased level of surface passivation. For even lighter doped n-type surfaces the passivation quality increases again to implied-V_{oc} values well above 700 mV. Hence, the results presented here indicate that within a certain doping range, highly doped n- and p-type surfaces can be passivated simultaneously by Al_2O_3.

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Amorphous aluminium oxide (Al_2O_3) films have been shown to provide excellent surface passivation on lightly doped n- and p-type as well as highly doped p^+-type silicon surfaces [1–3]. The underlying mechanism of this high level of surface passivation is related to a high fixed negative charge density (10^{12}–10^{13} cm^{-2}) in the Al_2O_3 film in combination with a low interface defect density in the range of 10^{11} eV^{-1} cm^{-2} [4, 5]. In recent years various deposition technologies have been used for the deposition of Al_2O_3 films with a good level of surface passivation after a post-deposition thermal treatment, including atomic layer deposition (ALD), plasma-enhanced chemical vapour deposition (PECVD) and sputtering [1, 2, 6–9]. This clearly demonstrates the versatility of Al_2O_3 as a surface passivation film.

To this date Al_2O_3 has mainly been considered for the application in p-type passivated emitter rear contact (PERC), p-type Al local back-surface field (Al-LBSF), or n-type passivated emitter and rear local contact (PERL) solar cells due to its excellent passivation properties on p-type silicon surfaces with an arbitrary doping level [10–12]. However, in some solar cell architectures such as all back contact solar cells highly doped p- and n-type surfaces are present at the same side of the silicon substrate. Hence, it is of high interest to investigate the surface passivation performance of Al_2O_3 on n^+-type silicon surfaces, even though the polarity of the fixed charge is not ideal for this kind of surface. In the case of a-SiN_x:H on p^+-type silicon surfaces this results in a very poor passivation due to the positive fixed charges in the dielectric film [2, 13].

In this Letter we investigate the surface passivation of n^+-type silicon surfaces by Al_2O_3 films grown by plasma-assisted ALD. We show that Al_2O_3 can provide a good level of surface passivation for a wide range of n^+-type silicon surfaces which are typically used in all-back-contact solar cell architectures.

The n^+/p/n^+ structures in this study were fabricated by exposing ⟨100⟩ shiny-etched p-type Si wafers (200 Ω cm) with a thickness of 250 μm to $POCl_3$ at a temperature of 850 °C to 1000 °C in a diffusion tube. The sheet resistance

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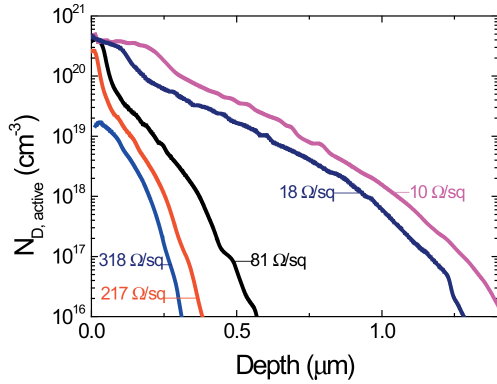

Figure 1 (online colour at: www.pss-rapid.com) Active dopant profile measured by ECV profiling of selected n^+-diffusions investigated in this study. The sheet resistance determined by 4-point probe measurements is indicated in the figure.

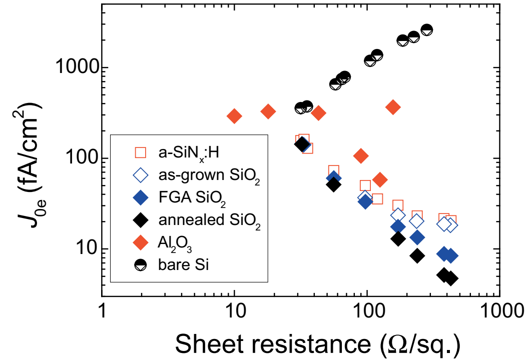

Figure 2 (online colour at: www.pss-rapid.com) Measured J_{0e} values for n^+-type emitters passivated by Al_2O_3 as a function of the sheet resistance (red diamonds). For comparison literature values from Kerr et al. are included as well for n^+-type emitters without passivation (bare Si) and emitters passivated by a-SiN_x:H and thermally grown SiO_2 [19]. It should be noted that the Auger recombination in the n^+-diffusions used in this work and Kerr's work is different which explains part of the difference in J_{0e}.

of the n^+-emitters was determined by 4-point probe measurements and the doping profile was determined by electrochemical capacitance–voltage (ECV) profiling, shown in Fig. 1. The sheet resistance of the n^+-diffusion was varied by changing the temperature and time during the $POCl_3$ diffusion process.

Before deposition the samples received a conventional RCA cleaning with a final dip in diluted HF (1%). An Al_2O_3 film was deposited on each side of the samples by alternating $Al(CH_3)_3$ dosing and O_2 plasma exposure in a remote plasma ALD reactor (Oxford Instruments FlexAL™) at a substrate temperature of 200 °C [14]. 255 ALD cycles of 4 s resulted in 30 nm thick Al_2O_3 films as determined by *in situ* spectroscopic ellipsometry. Subsequently, the samples received a 30 minute anneal at 425 °C in N_2. The passivation quality of the films was quantified by the emitter saturation current-density J_{0e} of the n^+-emitters. The emitter saturation current-density J_{0e} was determined from contactless photo-conductance decay measurements in both the quasi-steady-state and transient mode (Sinton WCT-100) [15] from the relation proposed by Kane and Swanson [16]:

$$\frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{Auger}}} = \frac{1}{\tau_{\text{SRH}}} + 2\,\frac{J_{0e}(N_d + \Delta n)}{q n_i^2 W}\,, \qquad (1)$$

where τ_{eff} is the measured effective excess carrier lifetime of the sample, τ_{Auger} the intrinsic Auger lifetime [17], τ_{SRH} the defect-related bulk lifetime, N_d the base doping level, n_i the intrinsic carrier concentration of c-Si [18], q the elementary charge, Δn the excess carrier density, and W the sample thickness. For some samples the J_{0e} value cannot be extracted from Eq. (1) and the implied-V_{oc} at one sun is used instead. The implied-V_{oc} can be calculated by

$$V_{oc} = (kT/q)\ \ln\,[(\Delta n(N_d + \Delta n)/n_i^2) + 1]\,, \qquad (2)$$

where k is the Boltzmann constant, T the temperature, and q the elementary charge [15].

In Fig. 2 the experimentally extracted J_{0e} values are shown for n^+-type emitters passivated by Al_2O_3 grown by plasma-assisted ALD. For a sheet resistance above 150 Ω/sq the Auger corrected inverse lifetime no longer demonstrated a linear dependence on the excess carrier density. Consequently Eq. (1) could no longer be used to extract J_{0e}. A similar behaviour was observed for p^+-type emitters passivated by the positive charge dielectric a-SiN_x:H [13]. For this reason the implied-V_{oc} values at a light intensity of 1 sun are plotted in Fig. 3. Similar as observed in previous studies [1], the passivation quality of the as-deposited Al_2O_3 films was very poor with e.g. an emitter saturation current density of 1000 fA/cm^2 for a 90 Ω/sq n^+-emitter comparable to the value reported for an unpassivated n^+-emitter as can be seen in Fig. 2. The J_{0e} value reduced to 100 fA/cm^2 after the post-deposition anneal.

From Figs. 2 and 3 we can learn that Al_2O_3 provides a good level of surface passivation on n^+-type surfaces with a moderate sheet resistance up to ~100 Ω/sq. For a higher sheet resistance the passivation quality significantly re-

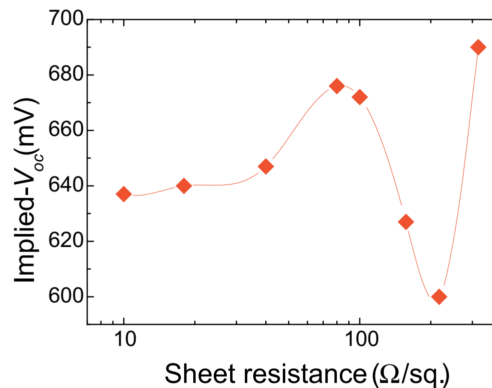

Figure 3 (online colour at: www.pss-rapid.com) Implied-V_{oc} of the $n^+/p/n^+$ lifetime samples passivated by 30 nm Al_2O_3 grown by plasma-assisted ALD. The line serves as guide for the eye.

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duces as apparent from a strong decrease in the implied-V_{oc} in Fig. 3. However, for a sheet resistance of 317 Ω/sq the implied-V_{oc} increases again significantly. This is consistent with the excellent passivation results obtained for lightly doped n-type surfaces passivated by Al_2O_3 films [1]. If we compare the results obtained in this study for Al_2O_3 to results obtained in another study for n^+-type silicon surfaces passivated by thermal SiO_2 and a-SiN_x:H in Fig. 2, we can learn that Al_2O_3 films show a slightly poorer level of surface passivation in the 10–100 Ω/sq. range compared to the best results reported for the other dielectric materials [19]. It should be noted that part of this difference could be related to the *intrinsic* recombination in the emitter e.g. due to Auger recombination, but this is beyond the scope of this Letter [20].

These results can be explained by the fact that Al_2O_3 films grown by plasma-assisted ALD are found to have a very low interface defect density on silicon [5]. Hence, the good passivation for highly P-doped surfaces is ruled by the good chemical passivation by the Al_2O_3 film and the negative fixed charge density in the Al_2O_3 film does not significantly increase the surface recombination as it is unable to significantly increase the minority carrier (hole) concentration at the highly doped surface region. In the range of 10 Ω/sq to 80 Ω/sq the implied-V_{oc} increases due to a reduction of the Auger recombination in the emitter. For lightly doped n^+-type surfaces with a sheet resistance in the range of 100 Ω/sq to 200 Ω/sq the negative charge density increases the minority carrier density and, consequently, the surface recombination rate significantly increases resulting in a significant drop in the implied-V_{oc} of the lifetime samples. For even lighter doped n^+-type surfaces (sheet resistance of 318 Ω/sq) the surface is inverted and the surface minority carrier (in this case electron) concentration is reduced by the negative fixed charge density in the Al_2O_3 film. This is very similar as observed by p^+-type surfaces passivated by the positive-charge dielectric a-SiN_x:H [13].

In conclusion we have shown that Al_2O_3 films can effectively passivate highly doped n^+-type silicon surfaces with a sheet resistance up to 100 Ω/sq. This range is most relevant for industrial application in e.g. all back contact n-type silicon wafer solar cells. The good passivation of n^+-type surfaces by Al_2O_3 can be attributed to chemical passivation by the low interface defect density between the Al_2O_3 film and the c-Si surface. Poor passivation is observed in the 100–200 Ω/sq range and can be attributed to the negative fixed charge density in the Al_2O_3 film. As the fixed charge density and the interface defect density of Al_2O_3 films depend on the deposition technique [4], this poor passivation will occur at a different sheet resistance for the various deposition techniques. It is expected that the poor passivation, e.g., shifts to higher sheet resistances if the negative fixed charge density is lower as in the case of thermal ALD grown Al_2O_3.

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