Excellent passivation of highly doped *p*-type Si surfaces by the negative-charge-dielectric Al_2O_3

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From lifetime measurements, including a direct experimental comparison with thermal SiO_2, *a*-Si:H, and as-deposited *a*-SiN_x:H, it is demonstrated that Al_2O_3 provides an excellent level of surface passivation on highly B-doped *c*-Si with doping concentrations around 10^{19} cm^{-3}. The Al_2O_3 films, synthesized by plasma-assisted atomic layer deposition and with a high fixed negative charge density, limit the emitter saturation current density of B-diffused p^+-emitters to ~10 and ~30 fA/cm^2 on >100 and 54 Ω/sq sheet resistance p^+-emitters, respectively. These results demonstrate that highly doped *p*-type Si surfaces can be passivated as effectively as highly doped *n*-type surfaces. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2784168]

Research within the crystalline silicon (*c*-Si) photovoltaic community is driven by the necessity to decrease the costs per watt peak. As a consequence, the thickness of *c*-Si solar cells is reduced and alternative *c*-Si material and production processes are investigated. Presently, most Si solar cells are fabricated from *p*-type *c*-Si base material. However, the relative insensitivity of *n*-type *c*-Si to various impurities and defects could well result in a switch in the future to predominantly *n*-type base material.[1] The success of these developments will depend, among others, on the level of surface passivation that can be obtained on the surfaces of interest. Especially the passivation of highly doped *p*-type surfaces is of key interest for diffused emitter cells based on *n*-type silicon.

The passivation of highly B-doped *p*-type *c*-Si (for example, a p^+-emitter on a *n*-type Si wafer) is still trailing behind the results obtained on highly doped *n*-type *c*-Si.[2,3] This gap in performance can, at least partly, be explained by the presence of positive built-in charges in the commonly used passivation films such as thermal SiO_2 and as-deposited *a*-SiN_x:H.[2] Recently, Chen *et al.*, however, demonstrated that highly B-doped *p*-type *c*-Si can be effectively passivated by silicon rich *a*-SiN_x:H after prolonged annealing (up to 4 h) yielding an at least equal performance to as-grown thermal SiO_2 for sheet resistances >130 Ω/sq.[4] Furthermore, it was shown that *a*-Si:H can yield a surface passivation of p^+-emitters comparable to forming gas annealed thermal oxide[2] whereas the performance of *a*-SiC_x:H remained significantly poorer.[5]

An appealing approach is to passivate highly doped *p*-type *c*-Si by a dielectric containing a fixed *negative* charge density. In this way, the minority carrier (electron) concentration is effectively reduced at the highly defective surface and consequently the recombination rate is reduced. It is well known that Al_2O_3 can contain a high density of built-in negative charges (up to ~10^{13} elementary charges/cm^2) and Al_2O_3 has recently been shown to provide a state-of-the-art level of surface passivation on moderately doped *p*- and *n*-type *c*-Si.[6,7] In this letter, we show that Al_2O_3 synthesized by plasma-assisted atomic layer deposition (ALD) provides an excellent level of surface passivation on B doped p^+-type emitters with surface concentrations ranging from 5×10^{18} to 3×10^{19} cm^{-3}. From a direct experimental comparison, it is established that Al_2O_3 yields a higher level of surface passivation than forming gas annealed thermal SiO_2, *a*-Si:H, and as-deposited *a*-SiN_x:H applied on the same samples. Moreover, it is demonstrated that highly B-doped *p*-type *c*-Si surfaces can as effectively be passivated as highly doped *n*-type *c*-Si surfaces.

The $p^+/n/p^+$ structures used in this study were prepared at the Australian National University by exposing ⟨100⟩ shiny etched *n*-type *c*-Si (90 and 20 Ω cm) with a thickness of ~260 μm to BBr_3 at $T=895-1010$ °C.[8] After stripping the B containing glass, B diffusion was driven by thermal oxidation at 1050 °C.[8] The sheet resistance of the samples was determined by four-point probe measurements and the doping profile, shown in Fig. 1, was determined by both electrochemical capacitance-voltage (ECV) profiling and secondary ion mass spectrometry (SIMS). The level of surface passivation of thermal SiO_2, *a*-SiN_x:H and *a*-Si:H on these p^+-emitter samples was already reported in a previous study.[2,8] Before deposition a possibly remaining film from previous experiments was stripped off and the samples received a conventional RCA cleaning with a final dip in di-

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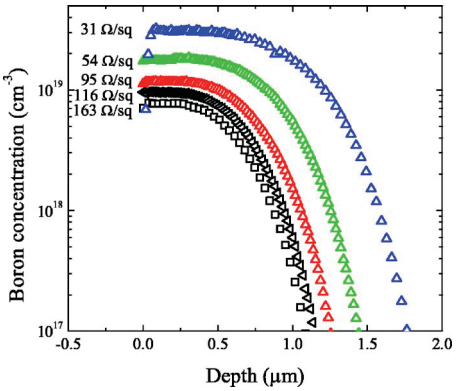

FIG. 1. (Color online) B-doping profiles of the $p^+/n/p^+$ samples with various sheet resistances as determined by ECV profiling and experimentally verified by SIMS measurements (54 and 95 Ω/sq).

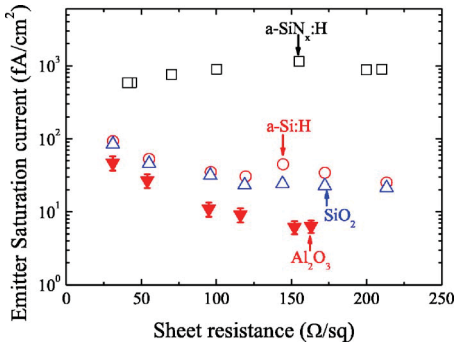

FIG. 3. (Color online) Measured emitter saturation current density J_{0e} as a function of the sheet resistance for B-doped p^+-emitter samples passivated by Al_2O_3, as-deposited a-SiN_x:H, a-Si:H, and forming gas annealed thermal SiO_2.

luted HF (1%). Al_2O_3 films were deposited on both sides 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.[9] 255 ALD cycles of 4 s resulted in 30 nm thick Al_2O_3 as determined by *in situ* spectroscopic ellipsometry. Subsequently, the samples received a 30 min annealing at 425 °C in N_2.[7] The passivation quality of the films was quantified by the emitter saturation current density J_{0e} of the p^+-emitters. The emitter saturation current density J_{0e} was determined from contactless photoconductance decay measurements in both the quasi-steady-state and transient mode (Sinton WCT-100)[10] from the relation proposed by Kane and Swanson [11]

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

where τ_{eff} is the measured effective excess carrier lifetime, τ_{Auger} the intrinsic Auger lifetime,[12] τ_{SRH} the defect-related bulk lifetime, N_d the base doping level, n_i the intrinsic carrier concentration of c-Si,[13] q the elementary charge, Δn the excess carrier density, and W the sample thickness.

In Fig. 2, the Auger-corrected inverse effective lifetimes are shown for samples with various sheet resistances passivated by 30 nm Al_2O_3 films. The curves do not show a strong nonlinear behavior such as in the case of a-SiN_x:H.[8] Consequently Eq. (1) can be used to extract J_{0e} and no alternative quantification such as implied open-circuit voltage has to be used in this case.[14] Nevertheless a small nonlinearity is still observed, possibly explained by minor experimental uncertainties or uncertainty in the empirically determined Auger lifetime at high injection level.[12] Therefore, J_{0e} is determined for a moderate injection level up to 2×10^{16} cm^{-3} where Auger recombination does not dominate. Similar to the results obtained on lightly doped n- and p-type c-Si,[7] the level of surface passivation by Al_2O_3 is dramatically affected by the postdeposition annealing. The emitter saturation current for the 163 Ω/sq sample coated with an as-deposited Al_2O_3 film (not shown) is in the order of ~1.2 $\times10^3$ fA/cm^2, which is comparable to a nonpassivated sample, and is reduced to below 10 fA/cm^2 after a 30 min annealing at 425 °C in N_2. This dramatic improvement in surface passivation is related to changes at the c-Si/Al_2O_3 interface affecting both the amount of built-in negative charge and the interface defect density as will be reported in a separate study.

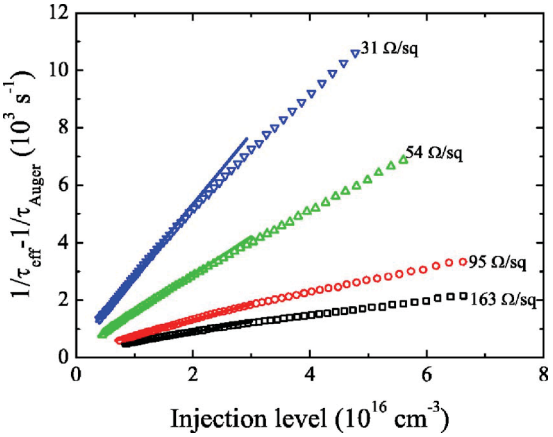

FIG. 2. (Color online) Measured Auger corrected inverse effective lifetime as a function of the injection level for c-Si samples with double sided B-doped p^+-emitter and various sheet resistances passivated on both sides by a 30 nm Al_2O_3 film. The emitter saturation current density is extracted from the linear fit up to 2×10^{16} cm^{-3} by means of Eq. (1).

In Fig. 3, the extracted J_{0e} values are shown as a function of the emitter sheet resistance of p^+-emitters passivated by Al_2O_3 and are compared to earlier published results for thermal SiO_2, a-Si:H and a-SiN_x:H.[2,8] The p^+-emitter samples with SiO_2 were forming gas annealed and those with a-SiN_x:H were as deposited. Clearly, the J_{0e} values obtained for Al_2O_3 are significantly lower for the complete sheet resistance range tested; J_{0e} values below 10 fA/cm^2 are obtained for a sheet resistance >100 Ω/sq and J_{0e} is only ~50 fA/cm^2 for a 31 Ω/sq emitter. The emitter saturation currents on p^+-emitters are even lower than obtained on highest-quality n^+-emitters with a comparable sheet resistance passivated with aluminum annealed thermal SiO_2 or as-deposited a-SiN_x:H.[15] The emitter saturation current density obtained in this study for a 95 Ω/sq emitter would limit the room temperature open circuit voltage of a solar cell to 747 mV by applying the ideal diode law and assuming a short-circuit current of 40 mA/cm^2.[16]

The most fundamental property to compare, however, is the surface recombination velocity at the highly doped B surface which strongly depends on the surface doping concentration. The S_{n0} values were extracted from the experimental J_{0e} values and dopant profiles by numerical modeling using the device simulation package SENTAURUS (Ref. 17) and the physical models established in Refs. 2 and 3 and the

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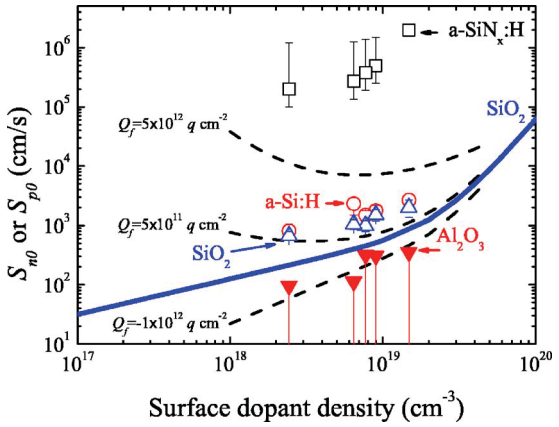

FIG. 4. (Color online) Surface recombination velocity S_{n0} at the B-doped p^+-type c-Si surface as a function of the surface dopant density as determined by ECV measurements. The S_{n0} values were deduced by device simulation using the values in Figs. 1 and 3. The solid blue line indicates the empirical relation obtained for S_{p0} obtained on heavily doped n-type surfaces passivated by aluminum annealed thermal SiO_2 (see Ref. 3). By assuming $S_{p0}=S_{n0}$ this empirical relation is used to simulate the impact of positive and negative built-in charges Q_f on S_{n0} as indicated by the dashed lines.

results are shown in Fig. 4. The experimental errors in both J_{0e} and the dopant profile and the relative strong Auger recombination in these emitters only allowed extraction of the maximum error bounds for the Al_2O_3. For comparison also the S_{n0} values obtained for thermal SiO_2, a-Si:H, and a-SiN_x:H are given as determined on the same sample set.[2] The solid blue line in Fig. 4 shows the empirically determined limit of the surface recombination velocity S_{p0} obtained by aluminum annealed thermal SiO_2 on highly doped n^+-emitters.[3] From Fig. 4 it is evident that the level of surface passivation on highly doped p-type c-Si provided by thermal SiO_2, a-Si:H, and a-SiN_x:H was significantly poorer than what is obtained on highly doped n-type c-Si. Moreover, the S_{n0} values obtained by Al_2O_3 on the highly doped p-type c-Si are well below the best values obtained on highly doped n-type surfaces which indicates that highly doped p-type surfaces can as effectively be passivated as highly doped n-type c-Si. Figure 4 also illustrates that a negative built-in charge is indeed very beneficial for passivating highly doped p-type surfaces compared to the positive built-in charge commonly present in thermal SiO_2 and as-deposited a-SiN_x:H. At the same time the excellent results for B concentrations of $\sim 10^{19}$ cm^{-3} indicate that also the c-Si/Al_2O_3 interface defect density is sufficiently low and/or that the dominant interface defect has a relatively low electron capture cross section.

In summary, we have demonstrated that Al_2O_3 synthesized by plasma-assisted atomic layer deposition shows an excellent level of surface passivation on highly doped p-type c-Si. Consequently, highly doped p-type c-Si can as effectively be passivated as highly doped n-type c-Si allowing maximum freedom in the solar cell design either using p-type or n-type c-Si base material.

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