Excellent passivation of highly doped p-type Si surfaces by the negative-charge-dielectric Al2O3

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(Received 6 July 2007; accepted 21 August 2007; published online 11 September 2007)

From lifetime measurements, including a direct experimental comparison with thermal SiO2, a-Si:H, and as-deposited a-SiNₓ:H, it is demonstrated that Al2O3 provides an excellent level of surface passivation on highly B-doped c-Si with doping concentrations around 10¹⁹ cm⁻³. The Al2O3 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 ~10⁻¹⁰ and ~30 fA/cm² 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 SiO2 and as-deposited a-SiNₓ:H.² Recently, Chen et al., however, demonstrated that highly B-doped p-type c-Si can be effectively passivated by silicon rich a-SiNₓ:H after prolonged annealing (up to 4 h) yielding an at least equal performance to as-grown thermal SiO2 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 SiO2, a-Si:H and as-deposited a-SiNₓ: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 BB₃ at T=895–1010 °C.⁵ After stripping the B containing glass, B diffusion was driven by thermal oxidation at 1050 °C.⁶ 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 SiO2, a-SiNₓ: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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luted HF (1%). Al₂O₃ films were deposited on both sides of the samples by alternating Al(CH₃)₃ dosing and O₂ plasma exposure in a remote plasma ALD reactor (Oxford Instruments FlexAL™) at a substrate temperature of 200 °C. 255 ALD cycles of 4 s resulted in 30 nm thick Al₂O₃ as determined by in situ spectroscopic ellipsometry. Subsequently, the samples received a 30 min annealing at 425 °C in N₂. The passivation quality of the films was quantified by the emitter saturation current density Jₑ of the p⁺-emitters. The emitter saturation current density Jₑ was determined from contactless photoconductance decay measurements in both the quasi-steady-state and transient mode (Sinton WCT-100) from the relation proposed by Kane and Swanson

\[ \frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{Auger}}} = \frac{2J_e(N_d + \Delta n)}{qni^2W}, \]  

where \( \tau_{\text{eff}} \) is the measured effective excess carrier lifetime, \( \tau_{\text{Auger}} \) the intrinsic Auger lifetime, \( N_d \) the base doping level, \( n_i \) the intrinsic carrier concentration of c-Si, \( q \) the elementary charge, \( \Delta n \) 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 Al₂O₃ films. The curves do not show a strong nonlinear behavior such as in the case of a-SiNₓ:H. Consequently, Eq. (1) can be used to extract \( J_e \) and no alternative quantification such as implied open-circuit voltage has to be used in this case. 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. Therefore, \( J_e \) is determined for a moderate injection level up to \( 2 \times 10^{16} \) cm⁻³ where Auger recombination does not dominate. Similar to the results obtained on lightly doped n- and p-type c-Si, the level of surface passivation by Al₂O₃ is dramatically affected by the postdeposition annealing. The emitter saturation current for the 163 Ω/sq sample coated with a as-deposited Al₂O₃ film (not shown) is in the order of \( \sim 1.2 \times 10^3 \) fA/cm², which is comparable to a nonpassivated sample, and is reduced to below 10 fA/cm² after a 30 min annealing at 425 °C in N₂. This dramatic improvement in surface passivation is related to changes at the c-Si/Al₂O₃ interface affecting both the amount of built-in negative charge and the interface defect density as will be reported in a separate study.

In Fig. 3, the extracted \( J_e \) values are shown as a function of the emitter sheet resistance of p⁺-emitters passivated by Al₂O₃ and are compared to earlier published results for thermal SiO₂, a-Si:H and a-SiNₓ:H. The p⁺-emitter samples with SiO₂ were forming gas annealed and those with a-SiNₓ:H were as deposited. Clearly, the \( J_e \) values obtained for Al₂O₃ are significantly lower for the complete sheet resistance range tested; \( J_e \) values below 10 fA/cm² are obtained for a sheet resistance >100 Ω/sq and \( J_e \) is only \( \sim 50 \) fA/cm² 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 SiO₂ or as-deposited a-SiNₓ:H. 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/cm². 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 \( S_n \) values were extracted from the experimental \( J_e \) 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

![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).](image)

![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 Al₂O₃ film. The emitter saturation current density is extracted from the linear fit up to \( 2 \times 10^{10} \) cm⁻³ by means of Eq. (1).](image)

![FIG. 3. (Color online) Measured emitter saturation current density \( J_e \) as a function of the sheet resistance for B-doped p⁺-emitter samples passivated by Al₂O₃, as-deposited a-SiNₓ:H, a-Si:H, and forming gas annealed thermal SiO₂.](image)
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$_2$O$_3$. For comparison also the $S_{p0}$ 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 $S_{p0}$ values obtained by Al$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ 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.

The authors acknowledge the experimental work of M. Kerr and A. Cuevas, and thank W. Keuning, M. J. F. van de Sande, J. F. C. Jansen and J. J. A. Zeebregts for their skillful technical assistance. The Netherlands Technology Foundation STW is acknowledged for their financial support. The work of one of the authors (B.H.) is financially supported by OTB Solar. The research of another author (W.K.) has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences (KNAW).

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17. SENTaurus, Mountain View, CA (www.synopsys.com/products/tdac/tdac.html).