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Citation for published version (APA):

DOI:
10.1063/1.2784168

Document status and date:
Published: 01/01/2007

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

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Excellent passivation of highly doped p-type Si surfaces by the negative-charge-dielectric $\text{Al}_2\text{O}_3$

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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 SiO$_2$, $\alpha$-Si:H, and as-deposited $\alpha$-SiN$_x$:H, it is demonstrated that $\text{Al}_2\text{O}_3$ provides an excellent level of surface passivation on highly B-doped c-Si with doping concentrations around 10$^{19}$ cm$^{-3}$. The $\text{Al}_2\text{O}_3$ 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 $\sim$10 and $\sim$30 fA/cm$^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. 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. 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 $\alpha$-SiN$_x$:H. Recently, Chen et al., however, demonstrated that highly B-doped $p$-type c-Si can be effectively passivated by silicon rich $\alpha$-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. Furthermore, it was shown that $\alpha$-Si:H can yield a surface passivation of $p^+$-emitters comparable to forming gas annealed thermal oxide whereas the performance of $\alpha$-SiN$_x$:H remained significantly poorer.

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 $\text{Al}_2\text{O}_3$ can contain a high density of built-in negative charges (up to $\sim$10$^{13}$ elementary charges/cm$^2$) and $\text{Al}_2\text{O}_3$ has recently been shown to provide a state-of-the-art level of surface passivation on moderately doped $p$- and $n$-type c-Si. In this letter, we show that $\text{Al}_2\text{O}_3$ 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 $\times$ 10$^{18}$ to 3 $\times$ 10$^{19}$ cm$^{-3}$. From a direct experimental comparison, it is established that $\text{Al}_2\text{O}_3$ yields a higher level of surface passivation than forming gas annealed thermal SiO$_2$, $\alpha$-Si:H, and as-deposited $\alpha$-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 $\sim$260 μm to BB$_3$ at $T=895–1010$ °C. After stripping the B containing glass, B diffusion was driven by thermal oxidation at 1050 °C. 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$_2$, $\alpha$-SiN$_x$:H and $\alpha$-Si:H on these $p^+$-emitter samples was already reported in a previous study. 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-
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 \( J_{0e} \) 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) from the relation proposed by Kane and Swanson

\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{Auger}}} + 2J_{0e}(N_d + \Delta n) qn^2 W,
\]

where \( \tau_{\text{eff}} \) is the measured effective excess carrier lifetime, \( \tau_{\text{Auger}} \) the intrinsic Auger lifetime, \( \tau_{\text{SRH}} \) the defect-related bulk 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-SiN\(_x\):H. 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. 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, \( J_{0e} \) is determined for a moderate injection level up to \( 2 \times 10^{16} \text{ cm}^{-3} \) 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 \( \Omega \)/sq sample coated with a as-deposited Al2O3 film (not shown) is in the order of \( \sim 1.2 \times 10^3 \text{ fA/cm}^2 \), 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 \( J_{0e} \) 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-SiN\(_x\):H. \( p^+ \)-emitter samples with SiO2 were forming gas annealed and those with a-SiN\(_x\):H were as deposited. Clearly, the \( J_{0e} \) values obtained for Al2O3 are significantly lower for the complete sheet resistance range tested; \( J_{0e} \) values below 10 fA/cm² are obtained for a sheet resistance >100 \( \Omega \)/sq and \( J_{0e} \) is only \( \sim 50 \text{ fA/cm}^2 \) for a 31 \( \Omega \)/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-SiN\(_x\):H. The emitter saturation current density obtained in this study for a 95 \( \Omega \)/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 \( S_{n0} \) 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
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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