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Effective passivation of Si surfaces by plasma deposited SiO$_x$/a-SiN$_x$::H stacks

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Very low surface recombination velocities $<6$ and $<11$ cm/s were obtained for SiO$_x$/a-SiN$_x$::H stacks synthesized by plasma-enhanced chemical vapor deposition on low resistivity $n$- and $p$-type c-Si, respectively. The stacks induced a constant effective lifetime under low illumination, comparable to Al$_2$O$_3$ on $p$-type Si. Compared to single layer a-SiN$_x$::H, a lower positive fixed charge density was revealed by second-harmonic generation measurements, while field-effect passivation was absent for a reference stack comprising thermally grown SiO$_2$. The results indicate that hydrogenation of interface states played a key role in the passivation and remained effective up to annealing temperatures $>800$ °C. © 2011 American Institute of Physics. [doi:10.1063/1.3595940]

Minimizing the surface recombination of charge carriers is a key issue for high efficiency silicon solar cells. Not all passivation schemes that have been investigated proved to be equally well applicable to $n$- and $p$-type Si surfaces in solar cells. While generally providing a high level of passivation for $p$-type and (diffused) $n$-type Si surfaces, $^{1-5}$ a-SiN$_x$::H films (SiN$_x$, in brief) can lead to compromised solar cell performance when applied on the $p$-type Si base at the rear side. This is related to the presence of an inversion layer below the surface induced by the fixed positive charge density, $Q_f$, present in (nearly) stoichiometric SiN$_x$ (with refractive index, $n$, $\sim$ 1.9–2.2),$^5$ which can lead to current flow between the rear metal contacts. This effect is known as parasitic shunting.$^5$ The positive charges in SiN$_x$ originate from the so-called K centers, which are dangling bonds of Si atoms that are backbonded to three N atoms.$^6$–$^8$ Therefore, Si-rich SiN$_x$ films generally exhibit a lower $Q_f$ than (nearly)stoichiometric N-rich films.$^8$ Consequently, Si-rich SiN$_x$ leads to high sheet resistances or the absence of an inversion layer. However, the chemical and thermal stability of these films may prove insufficient. Alternatively, it has been suggested that the effect of parasitic shunting can be reduced or avoided by the use of a (thin) SiO$_2$ layer between Si and SiN$_x$.$^{9,10}$ SiO$_2$/SiN$_x$ stacks comprising thermally grown SiO$_2$ provide a high level of passivation,$^{11-13}$ with surface recombination velocities $S_{\text{eff}}$ $<10$ cm/s, and have led to enhanced solar cell efficiencies.$^{10}$ In contrast, low-temperature SiO$_x$ synthesized by plasma enhanced chemical vapor deposition (PECVD) in combination with a SiN$_x$ capping layer has not resulted in a comparable high level of passivation yet. For such PECVD SiO$_x$/SiN$_x$ stacks, the lowest value ($S_{\text{eff}}$ $\sim$ 40 cm/s) was reported recently by Hofmann $et$ $al.$$^9$ for low resistivity $p$-type c-Si.

In this letter, a very high level of passivation is reported for PECVD SiO$_x$/SiN$_x$ stacks on low resistivity $c$-Si with $S_{\text{eff}}$ $<6$ cm/s. These stacks comprised SiN$_x$ with a refractive index of 2.05, which is known to be chemically stable during high temperature metallization processes in solar cells. By optical second-harmonic generation (SHG) spectroscopy, it is shown that the positive charge density for the stacks was reduced significantly compared to single layer SiN$_x$. This difference was in line with observations for a comparable stack comprising thermally grown SiO$_2$, which exhibited virtually no field-effect passivation. Furthermore, the thermal stability (up to 850 °C) of the stack was found to be very high, which can be ascribed to effective hydrogenation of the Si/SiO$_x$ interface under influence of the SiN$_x$ layer. The results presented are especially timely because various low-temperature passivation schemes, such as aluminum oxide (Al$_2$O$_3$),$^{14-16}$ are currently under evaluation as replacements for the standard aluminum back surface field in solar cells with thinner Si wafers.

The low-temperature SiO$_x$ ($\sim$ 50 nm) films were synthesized at a rate of $\sim$ 1 nm/s, at a substrate temperature of $\sim$ 300 °C, in a parallel-plate PECVD reactor.$^{17}$ Rutherford backscattering spectroscopy and elastic recoil detection revealed an O/Si ratio of $\sim$ 2.1 and a hydrogen content [H] of $\sim$ 9 at. %. The SiN$_x$ films were deposited by PECVD, using a linear microwave source, at a substrate temperature of $\sim$ 350 °C. Results on “standard” SiN$_x$, films with a refractive index of 2.05 (N/Si ratio=1.15, [H]=9.3 at. %) were compared to Si-rich SiN$_x$ films with a relatively high refractive index of $\sim$ 2.7 (N/Si ratio=0.5, [H]=16.1 at. %). The SiN$_x$ films ($\sim$ 70 nm) were deposited either on top of the PECVD SiO$_x$ or, for comparison, directly on c-Si. As substrates, 3.5 Ω cm $n$-type and 2.2 Ω cm $p$-type floatzone (100) c-Si wafers were used. Prior to deposition, the bare wafers received a short treatment in diluted HF. In addition, the field-effect passivation was compared to a stack comprising 50 nm thermally grown SiO$_2$ (dry oxidation, 950 °C) on $n$-type c-Si. The surface passivation properties were evaluated by measuring the effective lifetime $\tau_{\text{eff}}$ of the minority carriers by the photocurrent decay method (Sinton WCT 100). The upper limit of $S_{\text{eff}}$ was determined from the effective lifetime by assuming an infinite bulk lifetime, i.e., $S_{\text{eff}} < W/2\tau_{\text{eff}}$ where W the wafer thickness of 280 μm and will

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be quoted at an injection level of $5 \times 10^{14} \text{ cm}^{-3}$.

The PECVD SiO$_2$ films did not afford a significant level of surface passivation in the as-deposited state with $S_{\text{eff}} < 500 \text{ cm/s}$.\textsuperscript{17} The surface passivation could be improved somewhat, i.e., to $S_{\text{eff}} < 100 \text{ cm/s}$, by annealing at 400 °C in forming gas (10% H$_2$ in N$_2$). However, the passivation was not stable and degraded over time. The deposition of the SiNx capping films on top of as-deposited SiO$_x$ led to a significantly improved surface passivation, e.g., $S_{\text{eff}} < 27 \text{ cm/s}$ for SiNx with $n=2.05$ on $n$-type Si. This can be related to the incorporation of hydrogen, e.g., from the plasma,\textsuperscript{18} which reduces the interface defect density during “in situ” annealing at the deposition temperature of $\sim 350$ °C. After postdeposition annealing of the SiO$_x$/SiNx stacks at 400 °C (10 min, N$_2$), the surface passivation performance improved even more. A very low $S_{\text{eff}} < 6 \text{ cm/s}$ ($\tau_{\text{eff}}=2.3 \text{ ms}$) and $S_{\text{eff}} < 11 \text{ cm/s}$ ($\tau_{\text{eff}}=1.3 \text{ ms}$) were obtained for $n$- and $p$-type c-Si, respectively (Fig. 1). Compared to single layer SiNx on $n$-type Si, the passivation quality of the stack was only slightly lower. However, on $p$-type Si, the SiO$_x$/SiNx stack was clearly superior to the single layer SiNx. The level of passivation induced by atomic layer deposited (ALD) Al$_2$O$_3$ containing $>5 \times 10^{12} \text{ cm}^{-2}$ negative charges,\textsuperscript{16} was higher, but not substantially so, than that for the stacks, as shown in Fig. 1. For example, $S_{\text{eff}} < 4.5 \text{ cm/s}$ was obtained for Al$_2$O$_3$ on $p$-type Si. Another important observation is related to the injection level dependence of the effective lifetime. Single layer SiNx on $p$-type Si exhibited a very strong injection level dependence [Fig. 1(a)], similar to Al$_2$O$_3$ on $n$-type c-Si [Fig. 1(b)]. The observed decreasing lifetime at low injection levels was attributed to the recombination in the inversion layer that is formed below the Si surface.\textsuperscript{14,19} In sharp contrast, the stacks on $n$- and $p$-type c-Si exhibited a constant effective lifetime at low injection levels which is important for solar cell operation.

SHG spectroscopy was used to investigate the differences in the level of field-effect passivation. SHG allows for contactless probing of the electric field below the Si surface induced by fixed charges in the dielectric.\textsuperscript{20,21} Second-harmonic photons are resonantly generated at an energy of 3.4 eV in the space charge region of Si when the sample is irradiated by laser light of 1.7 eV. This electric-field induced SHG (EFISH) contribution is a measure of the field-effect passivation and can be extracted from the measured data by modeling the spectral dependence taking other contributions to the SHG signal as well as the optical propagation in the film(s) into account.\textsuperscript{20,21} The SHG spectra for single layer SiNx and the corresponding SiO$_x$/SiNx stack are compared in Fig. 2. The spectrum for SiNx is clearly dominated by the EFISH contribution at 3.4 eV, indicating the presence of a significant number of positive charges ($Q_f > 1 \times 10^{12} \text{ cm}^{-2}$, as verified by corona charging experiments). For the stack, the SHG intensity was significantly lower than that of SiNx. From the modeling, we established that the ratio between the EFISH amplitudes (scaling with the square root of the EFISH intensity) of the stack and the single layer SiNx was $\sim 0.6$. As $Q_f$ is approximately proportional to the EFISH amplitude, we can conclude that the stack exhibited a significantly lower level of field-effect passivation. This difference was even more pronounced for a stack comprising thermal SiO$_2$. This stack did not reveal a significant EFISH contribution, indicating that virtually no field-effect passivation was present. We recently reported similar observations for SiO$_2$/Al$_2$O$_3$ stacks.\textsuperscript{17,18} These results in combination with the lifetime data in Fig. 1 suggest that recombination in the inversion layer plays less of a role for the stacks than for single-layer SiNx on $p$-type Si. Regarding solar cells, the lower $Q_f$ for the stacks will lead to the formation of an inversion layer with a higher sheet resistance or to the absence of inversion. The results indicate that the fixed positive charge density depends on whether SiNx is applied directly to $c$-Si or on top of SiO$_2$. Previous studies have indicated that the charge density of SiNx can be manipulated by hole/electron injection into the underlying Si substrate.\textsuperscript{6–8,22} Therefore, the lower $Q_f$ observed for the stacks may be related to the SiO$_2$ interlayer acting as a barrier for the interaction between Si and SiNx. Moreover, the absence of fixed charges in the stack comprising thermal SiO$_2$ might suggest that the positive charges measured for the PECVD
SiO$_2$/$\text{SiN}_x$ stack are present mainly in the SiO$_2$ film rather than in the SiN$_x$ layer.

A high thermal stability of a surface passivation scheme is a prerequisite for application in solar cells with screen-printed contacts. Therefore, the passivation properties of the SiO$_2$/$\text{SiN}_x$ stacks were monitored for increasing annealing temperatures in the range of 400–850 °C and compared to the corresponding single layer SiN$_x$ films (with $n=2.05$ and 2.7). The results are given in Fig. 3 and two main observations can be discerned. First, the stacks exhibited qualitatively a similar trend as the corresponding single layer SiN$_x$. Second, we observe that the stack with SiN$_x$ ($n=2.05$) exhibited a higher thermal stability (>700 °C) compared to that for $n=2.7$. We consider the decrease in passivation at high annealing temperatures to be indicative of the dehydrogenation of the Si/SiO$_2$ interface. The observed differences between Si-rich and N-rich SiN$_x$ capping films are consistent with the fact that the diffusion and release of hydrogen, initially bonded as Si–H and N–H in SiN$_x$, are very sensitive to film composition. Effusion of hydrogen in Si-rich SiN$_x$ was shown to occur at lower temperatures compared to more compact SiN$_x$, which led to a reduced availability of hydrogen at high annealing temperatures. Therefore, the results in Fig. 3 suggest a more effective dehydrogenation of the interface at higher annealing temperatures for N-rich SiN$_x$ than for Si-rich SiN$_x$ capping films.

In summary, the results presented show that a very high level of surface passivation can be achieved by SiO$_2$/$\text{SiN}_x$ stacks synthesized by PECVD at temperatures $<350$ °C, also under low illumination levels. We have experimentally established that these stacks, as well as stacks comprising thermal SiO$_2$, exhibited a significantly reduced field-effect passivation compared to single layer SiN$_x$. It is discussed that the chemical passivation, induced by effective hydrogenation under influence of the SiN$_x$ capping layer, plays a key role in the passivation mechanism and thermal stability of the stacks.

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