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Effective passivation of Si surfaces by plasma deposited $SiO_x/a\text{-}SiN_x:H$ stacks

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Very low surface recombination velocities <6 and <11 cm/s were obtained for $SiO_x/a\text{-}SiN_x:H$ 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_2O_3 on *p*-type Si. Compared to single layer $a\text{-}SiN_x:H$, 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] $a\text{-}SiN_x:H$ 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, $n=\sim 1.9\text{–}2.2$),[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 $S_{eff}<10$ 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 ($S_{eff}\sim 40$ 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 $S_{eff}<6$ 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_2O_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 (~50 nm) films were synthesized at a rate of ~1 nm/s, at a substrate temperature of ~300 °C, in a parallel-plate PECVD reactor.[17] Rutherford backscattering spectroscopy and elastic recoil detection revealed an O/Si ratio of ~2.1 and a hydrogen content [H] of ~9 at. %. The SiN_x films were deposited by PECVD, using a linear microwave source, at a substrate temperature of ~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 ~2.7 (N/Si ratio=0.5, [H]=16.1 at. %). The SiN_x films (~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 τ_{eff} of the minority carriers by the photoconductance decay method (Sinton WCT 100). The upper limit of S_{eff} was determined from the effective lifetime by assuming an infinite bulk lifetime, i.e., $S_{eff}<W/2\tau_{eff}$, with W the wafer thickness of 280 μm and will

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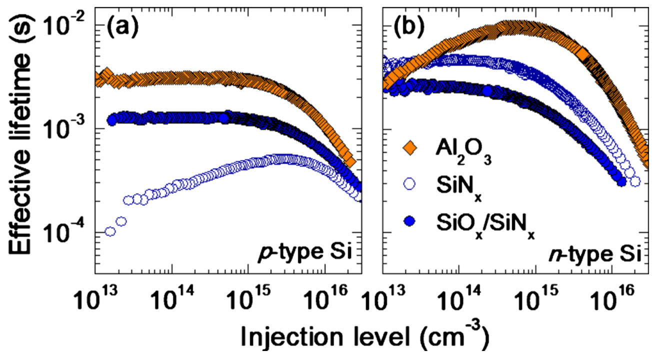

FIG. 1. (Color online) SiO_x/SiN_x stacks (50 nm/70 nm) compared with single layer SiN_x (70 nm) on (a) 2 Ω cm *p*-type *c*-Si and (b) 3.5 Ω cm *n*-type *c*-Si. The refractive index of SiN_x was 2.05. Data for plasma ALD Al_2O_3 (30 nm) are also given. All samples were annealed at 400 °C (10 min, N_2).

be quoted at an injection level of 5×10^{14} cm^{-3}.

The PECVD SiO_x films did not afford a significant level of surface passivation in the as-deposited state with S_{eff} <500 cm/s.[17] The surface passivation could be improved somewhat, i.e., to $S_{eff}<\sim100$ 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 SiN_x capping films on top of as-deposited SiO_x led to a significantly improved surface passivation, e.g., S_{eff} <27 cm/s for SiN_x with $n=2.05$ on *n*-type Si. This can be related to the incorporation of hydrogen, e.g., from the plasma,[18] which reduces the interface defect density during "*in situ* annealing" at the deposition temperature of ~350 °C. After postdeposition annealing of the SiO_x/SiN_x stacks at 400 °C (10 min, N_2), the surface passivation performance improved even more. A very low $S_{eff}<6$ cm/s ($\tau_{eff}=2.3$ ms) and $S_{eff}<11$ cm/s ($\tau_{eff}=1.3$ ms) were obtained for *n*- and *p*-type *c*-Si, respectively (Fig. 1). Compared to single layer SiN_x on *n*-type Si, the passivation quality of the stack was only slightly lower. However, on *p*-type Si, the SiO_x/SiN_x stack was clearly superior to the single layer SiN_x. The level of passivation induced by atomic layer deposited (ALD) Al_2O_3, containing $>5\times10^{12}$ cm^{-2} negative charges,[16] was higher, but not substantially so, than that for the stacks, as shown in Fig. 1. For example, S_{eff} <4.5 cm/s was obtained for Al_2O_3 on *p*-type Si. Another important observation is related to the injection level dependence of the effective lifetime. Single layer SiN_x on *p*-type Si exhibited a very strong injection level dependence [Fig. 1(a)], similar to Al_2O_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.[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.[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

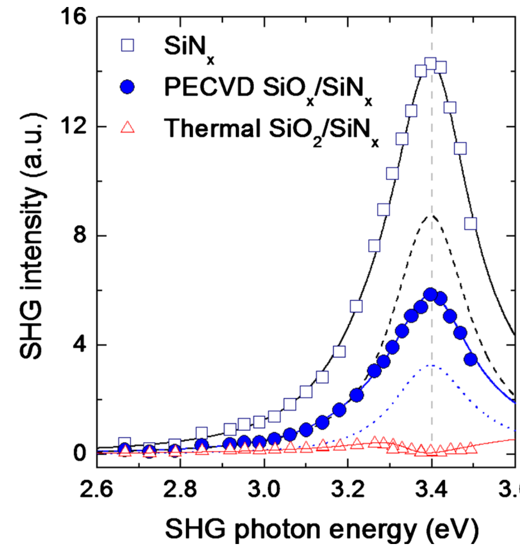

FIG. 2. (Color online) Optical SHG spectra for a SiN_x film, a PECVD SiO_x/SiN_x stack, and a thermal SiO_2/SiN_x stack. Both SiO_2 films had a thickness of 50 nm. The SiN_x ($n=2.05$) thickness was 70 nm. The Si substrates were *n*-type. All samples were annealed at 400 °C (10 min, N_2). The solid lines are fits to the data, taking the various resonances and the optical propagation into account. The dashed line represents the EFISH contribution corresponding to the SiN_x film while the dotted line corresponds to the stack comprising PECVD SiO_x.

modeling the spectral dependence taking other contributions to the SHG signal as well as the optical propagation in the film(s) into account.[20,21] The SHG spectra for single layer SiN_x and the corresponding SiO_x/SiN_x stack are compared in Fig. 2. The spectrum for SiN_x is clearly dominated by the EFISH contribution at 3.4 eV, indicating the presence of a significant number of positive charges ($Q_f>1\times10^{12}$ cm^{-2}, as verified by corona charging experiments). For the stack, the SHG intensity was significantly lower than that of SiN_x. 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 SiN_x was ~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_2O_3 stacks.[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 SiN_x 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 SiN_x is applied directly to *c*-Si or on top of SiO_2. Previous studies have indicated that the charge density of SiN_x can be manipulated by hole/electron injection into the underlying Si substrate.[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 SiN_x. Moreover, the absence of fixed charges in the stack comprising thermal SiO_2 might suggest that the positive charges measured for the PECVD

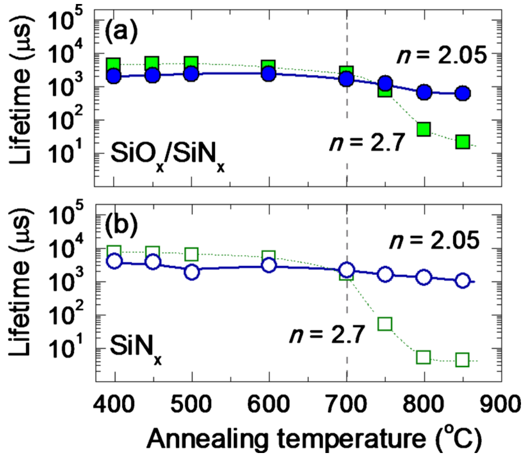

FIG. 3. (Color online) Thermal stability for (a) SiO_x/SiN_x stacks (50 nm/70 nm) and (b) SiN_x layers (70 nm). SiN_x films with two different refractive indices are compared. The Si substrates were n-type. Annealing was done in sequential steps of 1 min, except for the annealing temperatures of 400 °C (10 min) and 850 °C (30 s).

SiO_x/SiN_x stack are present mainly in the SiO_x 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_x/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_x interface.[11,18] 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.[23–25] Effusion of hydrogen in Si-rich SiN_x was shown to occur at lower temperatures compared to more compact SiN_x,[24,25] which led to a reduced availability of hydrogen at high annealing temperatures. Therefore, the results in Fig. 3 suggest a more effective hydrogenation 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_x/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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