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Surface passivation of black silicon phosphorus emitters with atomic layer deposited SiO$_2$/Al$_2$O$_3$ stacks

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Abstract

Black silicon (b-Si) is a promising surface structure for solar cells due to its low reflectance and excellent light trapping properties. While atomic layer deposited (ALD) Al$_2$O$_3$ has been shown to passivate efficiently lightly-doped b-Si surfaces and boron emitters, the negative fixed charge characteristic of Al$_2$O$_3$ thin films makes it unfavorable for the passivation of more commonly used n$^+$ emitters. This work studies the potential of ALD SiO$_2$/Al$_2$O$_3$ stacks for the passivation of b-Si phosphorus emitters fabricated by an industrially viable POCl$_3$ gas phase diffusion process. The stacks have positive charge density ($Q_{\text{tot}} = 5.5 \cdot 10^{11}$ cm$^{-2}$) combined with high quality interface ($D_0 = 2.0 \cdot 10^{11}$ cm$^{-2}$eV$^{-1}$) which is favorable for such heavily-doped n-type surfaces. Indeed, a clear improvement in emitter saturation current density, $J_{\text{sc}}$, is achieved with the stacks compared to bare Al$_2$O$_3$ in both b-Si and planar emitters. However, although the positive charge density in the case of black silicon is even higher ($Q_{\text{tot}} = 2.0 \cdot 10^{12}$ cm$^{-2}$), the measured $J_{\text{sc}}$ is limited by the recombination in the emitter due to heavy doping of the nanostructures. The results thus imply that in order to obtain lower saturation current density on b-Si, careful optimization of the black silicon emitter profile is needed.

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Keywords: black silicon; surface passivation; phosphorus diffusion; atomic layer deposition; SiO$_2$; Al$_2$O$_3$
1. Introduction

Black silicon (b-Si) has been of interest of the photovoltaic community already some time due to its excellent light absorption properties. The difficulties in the surface passivation of b-Si have recently been overcome with atomic layer deposited (ALD) Al$_2$O$_3$ which has been demonstrated both on substrate [1,2] and device level [3,4]. However, there is no proper solution yet presented for the dominating n$^+$ emitter as Al$_2$O$_3$ provides only limited passivation for such emitters due to its negative fixed charge. This problem is enhanced in b-Si since its passivation relies more heavily on the field-effect [5]. Thus, in order to make b-Si a viable option for current PV industry, a conformal thin film with positive fixed charge combined with high quality interface is required.

The negative charge in Al$_2$O$_3$ has been suggested to originate from electron trapping to O interstitials or Al vacancies as they both produce defect states in the lower half of the band gap and can hence be negatively charged [6]. It has been shown earlier that this negative charge formation in Al$_2$O$_3$ can be prevented by introducing a thin dielectric layer, e.g. ALD SiO$_2$, between the Al$_2$O$_3$ thin film and the Si substrate [7]. The SiO$_2$ layer acts as an electron tunnel barrier which efficiently prevents charge injection into the trap sites in Al$_2$O$_3$ [8]. With an interlayer thick enough, the effective total charge density in the SiO$_2$/Al2O$_3$ dielectric stack can be changed to positive due to the fixed and bulk charges in the SiO$_2$ film [7].

The potential of ALD SiO$_2$/Al$_2$O$_3$ stacks on the passivation of n$^+$ emitters has been studied on planar surfaces by van de Loo et al. [9]. With interlayers thicker than 3.6 nm, the authors achieved emitter saturation current densities, $J_{0e}$, as low as 50 fA/cm$^2$. Later they applied the stacks also on nanostructured phosphorus emitters and showed that the implied open-circuit voltage ($i$-$V_{oc}$) was improved from 609 to 640 mV by the introduction of a SiO$_2$ interlayer as compared to bare Al$_2$O$_3$ [10]. However, the reported $i$-$V_{oc}$ values were achieved with black silicon that had underwent an alkaline etch treatment to remove sub-surface defects which decreased the height of the silicon needles to only 246 nm and eventually degraded the optical properties of the structure. Moreover, the emitter was made with ion implantation which is not currently a mainstream process in PV industry [11].

This work studies the effectiveness of the positively charged ALD SiO$_2$/Al$_2$O$_3$ dielectric stack for the passivation of b-Si phosphorus emitters fabricated by an industrially feasible POCl$_3$ gas phase diffusion process. The optical performance of the deep nanostructures is evaluated after the diffusion and subsequent drive-in process steps to see how well the structures withstand these processes. Additionally, the film properties are characterized by interface defect density, $D_{it}$, charge density, $Q_{tot}$ and emitter saturation current density, $J_{0e}$.

2. Experimental details

Black silicon was etched on both sides of p-type CZ wafers (20 Ωcm, 675 μm) by deep reactive ion etching using process parameters reported in [12]. Emitters were formed in a tube furnace by POCl$_3$ diffusion at two different temperatures: 830 and 800 °C (POCL$_{830}$ and POCL$_{800}$, respectively). POCl$_3$ gas was introduced for 20 minutes, followed by a 5 min drive-in in an O$_2$ ambient at the same temperature. Sheet resistance was measured with four-point probe and confirmed later by an inductive coupling based method. The higher diffusion temperature resulted in sheet resistances of 95 and 53 Ω□ and the lower temperature in 225 and 113 Ω□ in planar and b-Si samples, respectively. Profiles of total and electrically active phosphorus concentration were measured from planar samples with secondary ion mass spectrometry (SIMS) and electrochemical capacitance-voltage (ECV) profiling method, respectively. Profiles in b-Si were not measured due to instrumental limitations to measure doping concentration accurately in the case of nanostructured surfaces.

After the phosphosilicate glass (PSG) removal in 5% HF, the samples were passivated with either 22 nm of ALD Al$_2$O$_3$ or a stack of 6.5 nm of plasma-enhanced ALD SiO$_2$ and 30 nm of thermal ALD Al$_2$O$_3$. A commercial Si precursor and O$_2$ plasma were used for SiO$_2$, whereas TMA + H$_2$O process was utilized for Al$_2$O$_3$. All depositions were performed at 200 °C. The passivation was subsequently activated by annealing the samples at 400 °C for 30 min in N$_2$ ambient. The conformality of the ALD films on high aspect ratio nanostructures was confirmed with scanning electron microscopy (SEM, Fig. 1a).

To characterize the passivation quality, emitter saturation current density, $J_{0e}$, was extracted from the measured quasi-steady-state photoconductance (QSSPC) lifetime data at an injection level of 10$^{16}$ cm$^{-3}$. In the extraction, Auger model according to Richter et al. was applied which takes the band gap narrowing into account [13,14]. In
addition, to study the passivation properties more thoroughly, total oxide charge density, $Q_{\text{tot}}$, and interface defect density, $D_{\text{it}}$, were determined from separate lifetime samples processed in the same ALD runs by contactless CV (COCOS) method [15]. Finally, positive corona charge was deposited onto the samples to study the effect of surface charge on the passivation and the resulting $J_0e$. The actual amount of deposited charge was determined by measuring the change in the contact potential difference between a Kelvin probe and the silicon substrate in every deposition step.

3. Results and discussion

Doping profiles measured from the planar reference samples are presented in Fig. 1b. The difference between the total and electrically active phosphorus concentration measured with SIMS and ECV, respectively, in the POCL$_{830}$ profiles near the sample surface indicates the presence of inactive dopants. Moreover, based on the sheet resistance values shown as an inset in Fig. 1b, the enhanced surface area of b-Si results in a larger amount of phosphorus in those emitters. As the silicon needles are covered with phosphosilicate glass on all sides, more phosphorus diffuses into the substrate during the drive-in. Similar observations have also been reported earlier [16, 17]. In this study, the sheet resistance in the nanostructured samples is found to be 1.8–2 times that in the planar counterparts. Thus, a considerably higher amount of phosphorus in the b-Si samples is expected, which indicates that emitter recombination will most likely be limiting the $J_0e$.

Possible effect of the diffusion and thin film deposition processes on the optical properties of b-Si is evaluated by surface reflectance measurements. The reflectance of a b-Si surface after POCl$_3$ diffusion and PSG removal as a function of wavelength, shown in Fig. 1c, proves that the structure retains its excellent optical properties in the diffusion process despite the oxidizing drive-in step. Indeed, the reflectance remains below 1% for almost the whole sun spectrum range. This observation hence promises that diffusion parameters can be tailored to optimize the emitter profile without significant tradeoffs in the low reflectance of black silicon. The deposition of a SiO$_2$/Al$_2$O$_3$ stack slightly increases the reflectance in the wavelength range of 400–1000 nm but enhances the optical properties in the UV region. This change is caused by the interference of light rays reflected from the interfaces of the dual-layer structure and the substrate. The two materials in the stack with refractive indices of 1.47 and 1.62 for ALD SiO$_2$ and Al$_2$O$_3$, respectively, reduce surface reflectance especially in the short wavelength range with the selected film thicknesses, which can be observed also from the relatively low reflectance of the planar reference sample in the UV region. This improvement in combination with the optical properties of b-Si results in the observed flat spectral reflectance in the wavelength range of 300–1000 nm. This low reflectance corresponds to ~98% absorbance.

Fig. 1. a) SEM image of b-Si conformally covered with 6.5 nm of ALD SiO$_2$ + 30 nm of Al$_2$O$_3$. b) Doping profiles of two planar samples measured with ECV. In addition, a SIMS profile of a POCL$_{830}$ diffused sample is presented. The measured sheet resistance values are shown as an inset, including b-Si samples. c) Reflectance of a nanostructured surface after POCl$_3$ diffusion and PSG removal (black solid line), and after subsequent deposition of the stacks. As a reference, reflectance of a planar surface covered with the stacks is shown.
Fig. 2a presents emitter saturation current densities for both planar and b-Si samples with two different emitter profiles, POCL_830 and POCL_800, and two different ALD passivation schemes, bare Al_2O_3 and SiO_2/Al_2O_3 stacks. As hypothesized, the SiO_2/Al_2O_3 stacks provide lower J0e values compared to bare Al_2O_3 in all cases due to the more suitable polarity of the oxide charge (Fig. 2b). Although the absolute value of Qtot is lower in the oxide stack, it outperforms the negatively charged Al_2O_3 in J0e since the doping concentration in the emitter is too high for the negative charges in Al_2O_3 to induce inversion. In addition, approximately three times higher effective charge density was measured from b-Si samples compared to the planar references, which is in agreement with the previously reported results [5]. Better passivation provided by the SiO_2/Al_2O_3 stacks can partly be explained also by the lower mid-gap interface defect density, as presented in Fig. 2b. This reduction in Dn is caused by hydrogen diffusion from the Al_2O_3 film to the Si/SiO_2 interface during post-deposition annealing [18]. Mid-gap Dn is reported only for the planar samples since its extraction from COCOS measurements in the case of b-Si is not yet unambiguously defined. The improvement in J0e is higher in the samples with lower doping concentration (i.e., POCL_800) which can be attributed to a smaller amount of inactive phosphorus and less dominating Auger recombination.

The surface passivation quality, as characterized by Dn and Qtot (Fig. 2b), indicated better J0e values than were measured in the stacked samples. In order to study whether the reason for the rather high J0e values was due to insufficient level of field-effect passivation or emitter recombination, positive corona charge was deposited onto the samples. As shown in Fig. 3, J0e of the Al_2O_3 passivated samples, both planar and b-Si, was reduced substantially by the deposition of positive charge, as expected and previously reported in literature [9]. On the contrary, positive corona charge had barely any impact on the samples passivated with the stacks. Furthermore, J0e saturated to approximately same value for both Al_2O_3 and SiO_2/Al_2O_3 passivated planar samples. Thus, this value can be considered as the J0e limited by Auger and Shockley-Read-Hall (SRH) recombination in the emitter region, the latter caused by defect states introduced by inactive phosphorus [19]. Therefore, lower values could be achieved only by designing the emitter profiles further in order to avoid excessive doping. Similar trends are observed with both POCL_830 and POCL_800 diffusion profiles, the effect of corona charge being more significant in the samples with less doping (i.e., POCL_800) due to less dominating Auger recombination and a smaller amount of inactive phosphorus. The same reason also explains the steeper decrease in the J0e of the planar samples as the b-Si counterparts have higher doping concentration.

![Fig. 2. a) Emitter saturation current density of phosphorus emitter samples passivated with either SiO_2/Al_2O_3 stacks or bare Al_2O_3. b) Total charge and interface defect density after annealing of the dielectric layers obtained with the COCOS method. The values are extracted from separate lifetime samples processed in the same ALD runs with the emitters. The charge of bare Al_2O_3 is negative as indicated by the diagonal stripes. Dn values are determined from the planar samples.](image-url)
Fig. 3. $J_{0e}$ as a function of deposited corona charge density for two different emitter profiles: a) POCL\_830 and b) POCL\_800. Open symbols denote planar and filled symbols b-Si samples. The deposited charge reduces the $J_{0e}$ of the Al$_2$O$_3$ passivated samples considerably, while it has barely any impact on the SiO$_2$/Al$_2$O$_3$ passivated samples. In the samples with lighter doping (i.e., POCL\_800), the effect is more significant. The $J_{0e}$ limited by Auger and SRH recombination caused by inactive phosphorus is higher in the b-Si samples.

In the case of b-Si samples, however, somewhat lower $J_{0e}$ values were obtained with bare Al$_2$O$_3$ than with the stacks by corona charging, as visible in Fig. 3a-b. This could be explained by weaker chemical passivation provided by the stacks on b-Si, opposite to what observed from the planar samples by COCOS method. However, the interface quality in the case of b-Si cannot be directly concluded from the $D_{it}$ values measured from the corresponding planar samples. For instance, rather short ALD precursor pulse and purge steps may provide excellent thin film quality on planar surfaces, but result in an imperfect film on b-Si due to the high aspect ratio of the nanotexture [20]. Thus, the corona charging experiments indicate that the full potential of the SiO$_2$/Al$_2$O$_3$ stacks was not reached on b-Si, but even larger improvement in $J_{0e}$ could be achieved by fine tuning the ALD process parameters for nanostructured surfaces.

The $J_{0e}$ values measured from the planar samples passivated with the stacks are comparable to results reported by Bordihn et al. where the SiO$_2$ interlayers were deposited by PECVD [21]. The authors achieved a $J_{0e}$ of \~200 fA/cm$^2$ in an $n^+$ emitter with a doping profile close to that of POCL\_830. Thus, the electrical properties of SiO$_2$/Al$_2$O$_3$ stacks are not limited to ALD films only, although for b-Si, this deposition method is most likely the only viable option due to the high aspect ratio of the nanostructures. Although direct comparison with results on implanted b-Si emitters is challenging, the performance of the stacks on phosphorus-diffused b-Si emitters is consistent with the implied $V_{oc}$ of 616–640 mV reported by van de Loo [10], the corresponding values being 626 mV and 633 mV in the samples with POCL\_830 and POCL\_800 profiles, respectively.

4. Conclusions

This work studied the potential of ALD SiO$_2$/Al$_2$O$_3$ stacks for b-Si $n^+$ emitter passivation. The positive fixed charge in the stacks resulted in lower emitter saturation current densities compared to bare Al$_2$O$_3$ which is a promising step towards the implementation of b-Si in commercial p-type silicon solar cells. However, the $J_{0e}$ values in b-Si were in general higher than the corresponding planar references, mainly due to recombination in the heavily doped emitter that was not optimized for b-Si. Black silicon emitters suffered from enhanced excessive doping and a large amount of inactive phosphorus resulting in large Auger and SRH recombination which was found by corona charging. These experiments also revealed that the full potential of the stacks was not reached on b-Si, but even higher improvement in $J_{0e}$ could be achieved by fine tuning the diffusion and ALD process parameters for nanostructured surfaces.
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