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Passivation of black silicon boron emitters with atomic layer deposited aluminum oxide

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Keywords black silicon, surface passivation, boron diffusion, aluminum oxide

The nanostructured surface - also called black silicon (b-Si) - is a promising texture for solar cells because of its extremely low reflectance combined with low surface recombination obtained with atomic layer deposited (ALD) thin films. However, the challenges in keeping the excellent optical properties and passivation in further processing have not been addressed before. Here we study especially the applicability of the ALD passivation on highly boron doped emitters that is present in crystalline silicon solar cells. The results show that the nanostructured boron emitters can be passivated efficiently using ALD Al₂O₃ reaching emitter saturation current densities as low as 51 fA/cm². (Removed: However, the nanostructures are known to cause enhanced surface recombination and are physically vulnerable for further processing. In crystalline silicon solar cells, the nanostructures need to survive several processing steps and be well passivated at the end. Emitter saturation current densities of 51 fA/cm² prove that the nanostructured boron emitters can be passivated efficiently using ALD Al₂O₃.) Furthermore, reflectance values less than 0.5 % after processing show that the different process steps are not detrimental for the low reflectance of b-Si.

1 Introduction Black silicon (b-Si) has attracted attention in many research fields, especially in the photovoltaic and photodetector community because of its low surface reflectance of even below 1% over a large wavelength range [1, 2]. However, one major challenge has been the reduction of the increased recombination of charge carriers caused by the large area of the nanostructured surface. This causes poor spectral response especially at short-wavelengths [3]. Black silicon has been mostly applied on p-type cells using both thermal oxidation [4] and PECVD (plasma-enhanced chemical vapor deposition) SiNₓ [5, 6] for the front surface passivation. Especially in the case of SiNx the poor conformality of the PECVD film has resulted in insufficient passivation [5, 6]. The highest obtained efficiency of a p-type black silicon solar cell with thermal oxide as the front surface passivation material is 18.2 % [7].

Reactive ion etching (RIE) process is a well-known method to fabricate black-silicon, although it was originally considered as an undesirable etching result and was used mainly for optimizing the etching parameters to produce vertical sidewalls [8]. Besides RIE, other methods for b-Si fabrication, such as laser texturing [9], metal-catalyzed wet chemical etching [10] or plasma immersion ion implantation [11] have been suggested. Also, the applications for b-Si besides photovoltaics and photodetectors [11] are numerous including microelectromechanical systems (MEMS) [12], ion mobility spectrometers (IMS) [13], terahertz emitters [14], and drug analysis [15]. One interesting aspect of black silicon surfaces is their superhydrophobicity which opens up the possibility to make them self-cleaning [16]. Using RIE for b-Si etching has certain advantages: it is relatively fast and inexpensive and nanostructures can be made without mask layers [2]. In addition, in an RIE the etch rate is independent of crystalline planes which is an issue in wet chemical etching.

In recent years Al₂O₃ has been considered to be one of the most promising silicon surface passivation materials [17-19]. The passivation ability of Al₂O₃ is related to the combination of low defect density and negative fixed charge at the Si/ Al₂O₃ interface. These properties make it promising for passivation of lowly doped n- and p-type as well as highly doped p-type surfaces [20, 21]. Atomic layer deposited (ALD) Al₂O₃ provides the lowest surface recombination velocities compared to Al₂O₃ deposited by other methods such as PECVD or sputtering [22] and because of its conformality [23] we consider ALD as a natural choice for the coating of nanostructured b-Si surfaces.
We have previously shown that b-Si surfaces can be sufficiently passivated with ALD Al₂O₃ and that Al₂O₃ acts as an antireflection coating and reduces the already low reflectance of b-Si even below 1% both in mono- and multicrystalline silicon [24, 25]. The next step is naturally to study the passivation of the emitters by the same method. Moreover, the other black silicon solar cell studies have mainly concentrated on entire cell structures, thereby the emitter formation and its passivation has not been systematically studied before. In this paper, therefore, we focus on two important questions: i) Is the black silicon surface passivation by ALD still efficient after emitter formation? ii) Does the dopant glass removal have an effect on the nanostructures and the reflectance? The changes in the nanostructure after different diffusion processes are investigated by reflectance measurements and scanning electron microscopy (SEM). To estimate the emitter profile both simulations and UV micro Raman Spectroscopy [26] are applied. The passivation quality of Al₂O₃ on boron doped black silicon emitters is evaluated by extracting the emitter saturation current density Jₜ₀ from minority carrier lifetime measurements.

2 Experimental details
Black silicon was fabricated using a maskless cryogenic deep reactive ion etching process (ICP-RIE, Plasmalab System 100, Oxford Instruments) at -120 °C. Both sides of each 4 inch n-type FZ wafer (5 Ωcm, 400 μm) were etched to produce symmetric samples for emitter saturation current measurements. A mixture of SF₆/O₂ was used as the etching gas and their flows were set to 40 sccm and 18 sccm, respectively while the powers of ICP were 200 W and 70 W, respectively. In addition some of the samples went through a 1h drive-in oxidation at 1050 °C after the etch and at 890 °C in order to lower the surface doping and have a deeper emitter profile. Table 1 summarizes the three studied process sequences. The boron silicate glass (BSG) was etched off in 50% HF (2 min) after the diffusion. In samples which had additional drive-in oxidation, the glass was removed before the oxidation (see table 1). (Removed: After the diffusion and especially before the drive-in oxidation the boron silicate glass (BSG) was etched away in 50% HF (2 min.).) Al₂O₃ was deposited on both wafer sides with plasma-assisted ALD (PA-ALD) at 180 °C using Trimethylaluminum (TMA) as the aluminum source. The total cycle time was 7 seconds and 78 cycles led to a layer thickness of around 10 nm. The passivation was activated with a forming gas anneal (FGA) at 425 °C for 25 minutes.

To evaluate the passivation quality the emitter saturation current density Jₜ₀ of the b-Si emitters after the boron diffusion at 910 °C and with Al₂O₃ passivation was extracted from the quasi-steady-state photocurrent measurements (QSSPC, Sinton WCT-120) by using the high injection method [27]. In this method the Jₜ₀ value is estimated from the slope of the linear fit to the curve of the inverse effective lifetime subtracted by the intrinsic bulk lifetime, 1/T_eff-1/T_bulk,intrinsic, as a function of the injection level Δn. Here, the fitting was done around the injection level of 1×10¹⁶ cm⁻³. In the Jₜ₀ calculation an intrinsic carrier concentration n_i of 8.6×10¹⁵ cm⁻³ (25 °C) and a revised Auger parametrization according to Richter et al. [28] were used. Using the one-diode equation and omitting the effect of the recombinance at the rear side and in the base we can estimate a maximum open-circuit voltage V_ Voc,max for the b-Si samples and eventually for a b-Si n-type solar cell:

\[ V_{ Voc,max} = \frac{k_B T}{q} \ln \left( \frac{J_{ Voc}}{J_{ Voc}} + 1 \right) \]

where \( k_B \) is the Boltzmann constant, \( q \) the elementary charge, \( T \) the temperature and \( J_{ Voc} \) the short-circuit current density.

3 Results and discussion
We evaluate the changes in the nanostructures by measuring the reflectance before and after different diffusion processes. In Fig. 1a the b-Si reflectance after the diffusion at 910 °C is compared to the measured reflectance of random pyramids coated with SiO₂/SiNₓ (8 nm/65 nm) as well as inverted pyramids with an Al₂O₃/SiNₓ stack (10 nm/65 nm). The AM1.5G spectrum weighted average reflectances Rₑ were calculated in the wavelength range 300 – 1200 nm. The escape is omitted in the Rₑ calculations as well as in the reflectances shown in the figures by assuming the front surface reflectance to be linear for \( \lambda > 900 \) nm and by extrapolating the measured reflectance. In the short wavelength range the b-Si reflectance is much lower than in the reference samples whereas in the mid-wavelength range the reference samples exhibit slightly smaller reflectance values because of the SiNₓ antireflection coating with near zero reflectance at 600 nm. Rₑ is however smallest in the black silicon sample (~0.7%) even after processing and only with 10 nm Al₂O₃ on the front surface.

In Fig. 1b the reflectance of b-Si surfaces after different diffusion processes as well as in the initial state, i.e directly after etching, is shown. Surprisingly, there are no significant

<table>
<thead>
<tr>
<th>Diffusion temperature &amp; time</th>
<th>BSG etching</th>
<th>Drive-in oxidation</th>
<th>Passivation</th>
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</thead>
<tbody>
<tr>
<td>890 °C, 1 h</td>
<td>50% HF</td>
<td>-</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>910 °C, 1 h</td>
<td>50% HF</td>
<td>-</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>890 °C, 1 h</td>
<td>50% HF</td>
<td>1050 °C</td>
<td>Al₂O₃</td>
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Table 1 The different processing sequences implemented in this study.
changes in the reflectance even in the sample having combination of diffusion and a following drive-in oxidation. The small increase in the reflectance indicates that there can be some changes in the nanostructure. This can be verified by the SEM images in Fig. 2 where the b-Si structure is shown before and after diffusion and drive-in. Indeed, small changes in the nanostructure height and shape can be seen, i.e. the needles become shorter and sharper. The fact that diffusion can be done without causing drastic changes in the reflectance gives more freedom also in the optimization of the emitter profile i.e. if a deeper emitter is needed a drive-in can be applied without losing the good optical properties of black silicon. The small increase in the reflectance indicates that there can be some changes in the nanostructure.

Figure 1 In a) the b-Si reflectance (after diffusion at 910 °C and Al$_2$O$_3$ deposition) and the reflectance from random and inverted pyramids are shown. For passivation and antireflection there is a SiO$_x$/SiNx stack in the random pyramid sample and Al$_2$O$_3$/SiNx stack in the inverted pyramid sample. b) presents the initial b-Si reflectance and the reflectances after different diffusion processes. Al$_2$O$_3$ was deposited on the diffused samples. The escape reflection is removed from the curves and also ignored in the calculation of the spectrum weighted average reflectances (calculated between 300 nm and 1200 nm).

Figure 2 SEM image from a black silicon surface a) before and b) after boron diffusion at 890 °C and the subsequent drive-in oxidation. Boron glass was removed before the drive-in oxidation. With close examination small changes in the nanostructure can be seen. This is coherent with the reflectance results and is caused by the consumption of silicon during the boron glass formation and the drive-in oxidation.

Our simulations with Sentaurus Process [29] indicate that all diffusion processes used in this study lead to a complete doping of the nanostructure i.e. the junction is nearly flat under the surface and only mildly follows the surface structure. This and the final emitter profile naturally depend on the diffusion process. The consumption of silicon during the boron glass formation and the drive-in oxidation was taken into account in the simulations [30]. To investigate whether a homogeneous emitter depth inside the silicon bulk is established, two dimensional doping density measurements on polished cross section cuts using UV micro Raman Spectroscopy [26, 31] was performed. Fig. 3a shows the measured doping density of the 890°C diffused and Fig. 3b the 890°C diffused and oxidized sample within the bulk beneath the needle structure (the sample surface was estimated from the Raman scattering intensity). Both measurements are scaled identically. The doping depth (drop of doping density from the bottom of the needles to below the detection limit of 3·10$^{17}$ cm$^{-3}$ inside the bulk) can be readily estimated to be less than 400 nm for the diffused and 1.5 µm for the oxidized sample. Furthermore it can be seen clearly that in both cases a homogeneous doping profile depth was established. On the right of the measured emitters in Fig. 3a and b the doping profiles simulated with Sentaurus Process are depicted. It can be seen that the doping concentration as well as the emitter depth is predicted well by the Sentaurus Process simulation in comparison to the micro Raman measurement. The smoother drop of the measured doping density can be well understood by a signal smearing due to measuring at the spatial resolution limit. The dashed line depicts the simulated p/n junction, which in both cases is predicted of being developed homogeneously.
Fig. 4 shows the measured inverse effective lifetime and the corresponding emitter saturation current $J_{0e}$ of the most industrially relevant b-Si sample, i.e. after diffusion at 910 °C. $J_{0e}$ value of 51 fA/cm$^2$ prove that an efficient surface passivation can be obtained with an industrial type of emitter. (Removed: The measured inverse effective lifetime and the corresponding emitter saturation current $J_{0e}$ of the b-Si sample after diffusion at 910 °C is shown in Fig. 4. $J_{0e}$ value of 51 fA/cm$^2$ prove that an efficient surface passivation can be obtained with this emitter.) As a reference, $J_{0e}$ values as low as ~11 fA/cm$^2$ have been reached on high efficiency boron emitters and 20–25 fA/cm$^2$ on more industrial type emitters with Al$_2$O$_3$ passivation [32]. These results are for planar surfaces and naturally for textured surfaces the values are higher: for industrial type emitters with random pyramids $J_{0e}$ values of ~45 fA/cm$^2$ are reached when using Al$_2$O$_3$/SiNx stacks for surface passivation [33]. The $V_{oc,max}$ value of 703 mV was calculated with Eq. (1). ($T = 25$ °C, $J_{sc} = 40$ mA/cm$^2$) proving that black silicon with Al$_2$O$_3$ surface passivation could be applied on high-efficiency n-type solar cells. The effective lifetime $\tau_{eff}$ at an injection level of $1 \times 10^{15}$ cm$^{-3}$ is 0.78 ms and the implied open-circuit voltage $V_{oc,impl}$ = 688 mV (at 1 sun), both measured with QSSPC. If a symmetrical structure is assumed (i.e. emitters on both surfaces are taken into account in the calculation $2 \times J_{0e} = fA/cm^2$) the one-diode model gives a maximum open circuit voltage of 686 mV. This is in good agreement with the measured implied $V_{oc}$ value.

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