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Low surface damage dry etched black silicon

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Black silicon (bSi) is promising for integration into silicon solar cell fabrication flow due to its excellent light trapping and low reflectance, and a continuously improving passivation. However, intensive ion bombardment during the reactive ion etching used to fabricate bSi induces surface damage that causes significant recombination. Here, we present a process optimization strategy for bSi, where surface damage is reduced and surface passivation is improved while excellent light trapping and low reflectance are maintained. We demonstrate that reduction of the capacitively coupled plasma power, during reactive ion etching at non-cryogenic temperature (−20°C), preserves the reflectivity below 1% and improves the effective minority carrier lifetime due to reduced ion energy. We investigate the effect of the etching process on the surface morphology, light trapping, reflectance, transmittance, and effective lifetime of bSi. Additional surface passivation using atomic layer deposition of Al2O3 significantly improves the effective lifetime. For n-type wafers, the lifetime reaches 12 ms for polished and 7.5 ms for bSi surfaces. For p-type wafers, the lifetime reaches 800 μs for both polished and bSi surfaces. Published by AIP Publishing.

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I. INTRODUCTION

High-efficiency conventional silicon solar cells are based on surface texturing using wet alkaline etching with a feature size between 5 and 10 μm. This process has been adopted as a standard by the photovoltaic industry because of its cost-efficiency and good light trapping properties.1 However, this surface texturing leads to a reflectivity of approximately 5%–10%, and so single or multilayer antireflective (AR) coatings are applied on top of the microstructures to reduce reflectance to 2%.2 Black Si nanotextured surfaces, which are textured using mask-less RIE, may be a replacement for wet-chemical texturing in silicon solar cell fabrication.3–7 Black Si yields extraordinary low reflectance in an extremely broad spectral range. Thus, an additional AR coating is not required to reduce reflectance.

Black Si can also be fabricated using wet chemical metal assisted catalytic etching (MACE)8,9 and laser ablation (LA),9 and both methods may result in low reflectance (below 1%) surfaces. The MACE process does not cause surface damage, but the use of noble metal catalysts in the process may lead to severe contamination issues that may compromise the effective carrier lifetime. Inherent to the LA process is melting and recrystallization of the silicon surface which may cause a high density of traps for recombination at grain boundaries. Fabrication of black Si using RIE can be achieved at cryogenic10 as well as non-cryogenic conditions.11,12 The cryogenic RIE process may lead to very low surface damage resulting in high effective carrier lifetime; the process is however difficult or costly to industrialize, and for that reason the non-cryogenic RIE process is preferred. In the non-cryogenic RIE process, surface damage due to energetic ion-bombardment causes a reduction of the effective carrier lifetime due to surface or near surface recombination.

Black Si RIE technology also enables reduction of the Si wafer thickness to below 100 μm,7 which avoids use of toxic materials,13 provides easy RIE process optimization through adjustment of plasma parameters, and offers the possibility to texture any Si-based film or wafer, such as multicrystalline,14 cast-mono, kerfless, and diamond-wire sawn Si substrates.

Recent attempts to integrate black Si into solar cell fabrication resulted in promising conversion efficiencies.6,15 The best result was obtained at cryogenic RIE conditions, while the non-cryogenic RIE process gave lower conversion efficiency due to surface defects and surface recombination caused by ion impact damage16 and increased effective surface area. A possible solution is to optimize the plasma texturing process with a focus on reduction of surface recombination as also discussed by Gaudig et al.12 and

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a)Author to whom correspondence should be addressed: makpl@dtu.dk
von Gastrow et al.\textsuperscript{10} The importance of low sub surface plasma damage was also highlighted by Otto et al.\textsuperscript{11} In order to optimize the RIE process, we consider black Si formation consisting of three steps (even though it is a single SF\textsubscript{6}/O\textsubscript{2} plasma process):\textsuperscript{12} (1) isotropic Si etching with fluorine radicals to form volatile SiF\textsubscript{4}; (2) addition of O\textsubscript{2} causes a local masking layer of SiF\textsubscript{6}O\textsubscript{2} to build on the Si surface (mainly on sidewalls); and (3) etching of the SiOF passivation and Si layers. The etching process includes chemical and physical etching (ion-assisted etching).

In this work, we focus on reduction of the ion energy and flux density by controlling the capacitively coupled plasma power during reactive ion etching at non-cryogenic temperature (\(-20\,^\circ\text{C}\)). This leads to reduced surface damage and consequently an improvement in the effective carrier lifetime. To passivate black Si, we deposited Al\textsubscript{2}O\textsubscript{3} on an ultra-thin interlayer of chemically grown native oxide. Finally, the electro-optical properties of the samples such as lifetime and surface recombination velocity (SRV) were investigated. Very high effective lifetime and extremely low surface recombination velocity were demonstrated on both polished and nanotextured silicon surfaces.

II. MATERIALS AND METHODS

A. Materials

The materials used for the experiments were 100 mm diameter Czochralski (CZ) mono-crystalline Si (100) n- and p-type (1.5 \\Omega cm) wafers with thickness 350 \pm 25 \mu m and a bulk lifetime above 2 ms.

B. Fabrication

As an additional reference sample, we used alkaline (KOH/IPA-based) textured Si wafers for optical measurements. The KOH-based texturing process consisted of preparation of a KOH-based solution with 2\% concentration mixed with 7\% isopropyl alcohol (IPA) solution in deionized (DI) water, i.e., 120 ml KOH, 210 ml IPA and 3 l of DI water. The obtained solution was heated to 70 \textdegree C, which was the texturing process temperature. The consistency of the solution was preserved with a magnetic stirring bar. When the solution reached the required temperature, Si wafers were immersed in the solution for 50 min for texturing. After completion of the texturing process, all wafers were post cleaned in the solution of sulfuric acid (98\%) and ammonium persulfate (known as 7-Up), then rinsed in DI water, and spin dried. To create the nanotextured Si surfaces, we used a SPTS Pegasus deep reactive ion etching system (Fig. 1). The setup can produce an ICP using external coils and a CCP using parallel plate internal electrodes with both power systems driven at 13.56 MHz. Each discharge type can be sustained separately or assist each other. In the pure ICP mode, the wafer stage is grounded, so that ions are accelerated towards the wafer in the potential difference given by the plasma potential, which is at most a few tens of volts.\textsuperscript{13} If CCP bias is added, the ion energy can be significantly larger.

Ions are assisting radicals formed in the discharge, thus providing a rather mild etching. The CCP mode builds up a positive sheath above the wafer, due to the large difference in mobility between ions and electrons. This causes a negative DC bias on the substrate holder in the range from tens of volts to above of 100 V, depending on the power and the pressure. Since the ICP discharge can provide much higher plasma density that the CCP discharge,\textsuperscript{16} the simultaneous use of both sources provides very good control of the RIE process such as to reduce or increase the ion energy and/or flux. In this study, we supplied SF\textsubscript{6} (70 sccm) and O\textsubscript{2} (100 sccm) gases while the wafer stage temperature was kept at \(-20\,^\circ\text{C}\). The CCP power was kept low (10 to 50 W) to reduce the kinetic energy of ions while the ICP power was increased from 2500 to maximum 3000 W to create a homogeneous and high-density plasma to enhance the etch rate. The surface aspect ratio of nanostructures was controlled via the chamber pressure which was kept at 38 mTorr to provide the right balance between directionality of the ions and the necessary collisional frequency to produce radical species assisting the etching. As an experimental procedure, the maskless RIE black Si method developed by Jansen et al.\textsuperscript{18} was used. Even though we obtained a homogenous black Si surface with reflectivity below 1\% relying on the process developed by Davidsen et al.,\textsuperscript{6} the effective lifetime at \(10^{15}\, \text{cm}^{-3}\) injection level for p-type Si was below 50 \(\mu\)s for passivated wafers while reference untreated wafers had \(600 \pm 200\, \mu\)s. We started our process optimization based on Gaudig et al.\textsuperscript{12} and Otto et al.\textsuperscript{11,19} The final optimized parameters are shown in Table I. The study includes samples that were RIE textured on one side only as well as samples that were RIE textured on both sides [double side (DS) samples].

C. Sample cleaning and passivation

After the etching process, all samples were cleaned using the standard RCA procedure. To further decrease surface recombination we used a wet chemical RCA cleaning, and subsequently, we applied an Al\textsubscript{2}O\textsubscript{3} passivation layer...
using atomic layer deposition (ALD). Excellent surface passivation is known to be obtained with ALD Al\textsubscript{2}O\textsubscript{3} on planar silicon due to the high fixed negative charge in Al\textsubscript{2}O\textsubscript{3} and the low defect density at the interface between Si and Al\textsubscript{2}O\textsubscript{3}. Subsequently, wafers were coated with 380 cycles of ALD Al\textsubscript{2}O\textsubscript{3} synthesized from trimethyl aluminum (TMA) and H\textsubscript{2}O at 180°C. For reference purposes, two polished wafers (p- and n-type) were also included in the ALD Al\textsubscript{2}O\textsubscript{3} passivation process. The passivation layers were activated by post-deposition annealing in N\textsubscript{2} ambient at 500°C for 5 min.

D. Characterization

The thickness of the Al\textsubscript{2}O\textsubscript{3} layer was measured using ellipsometry (VASE J.A. Woollam Co.) at 5–10 different spots on the samples. The Al\textsubscript{2}O\textsubscript{3} layer had a thickness of 32 ± 1 nm on polished samples. The spectral resolved reflectivity \( R \) and transmittivity \( T \) of the black Si were measured with a Perkin Elmer Lambda 1050 UV/Vis/NIR Spectrophotometer in the wavelength range of 200–1100 nm. The absorptivity \( A \) was calculated from \( A = 1 - R - T \). Surface morphology analysis was done using a scanning electron microscope (SEM) Zeiss Supra 40. The effective minority carrier lifetime \( \tau_{\text{eff}} \) was measured using the microwave detected photoconductivity (MDP) method (Freiburg Instruments). The measurements were done in transient and injection dependent single point modes and the lifetime mapping mode. Lifetimes were also evaluated in the quasi-steady-state photoconductivity (QSSPC) method in an injection dependent mode using a Sinton WCT-120 instrument. The resistivity of the wafers was also obtained using the Sinton WCT-120 instrument.

III. RESULTS AND DISCUSSIONS

A. Fabrication of black Si and optimization for low reflectivity and high lifetime

Before we present the results of the optimization strategy, we will describe the actual black Si RIE process. The black Si nanostructuring process consists of three main steps occurring at low temperature: passivation layer formation, passivation layer etching, and Si etching, which were repeated in discretized time increments until the final process was reached. The nanostructuring process was conducted as illustrated in Fig. 2.

The etching process was set based on previously optimized parameters such as SF\textsubscript{6} and O\textsubscript{2} partial pressures, process temperature, and DC bias voltage measured at the wafer stage. In-depth understanding of black Si formation can be obtained elsewhere, including the experimental analysis of Gaudig \textit{et al.}, Otto \textit{et al.}, and the theoretical model developed by Saab \textit{et al.}. The shapes of these nanostructures were observed by Jansen \textit{et al.} and can be modified depending on the process parameters. The shape can be

\begin{table}[h]
\centering
\caption{RIE process parameters.}
\begin{tabular}{|c|c|c|c|}
\hline
RIE parameters & References 11, 12, and 19 & Reference 6 & This work \\
\hline
SF\textsubscript{6} flow (sccm) & 47 & 37 & 70 \\
O\textsubscript{2} flow (sccm) & 55 & 37 & 100 \\
Pressure (mTorr) & 50 & 24 & 45 \\
CC power (W) & 20 & 100 & 10–70 \\
IC power (W) & 600 & 0 & 3000 \\
Temperature (°C) & 20 & –10 & –20 \\
Max. DC bias (V) & 34 & 41 & 41 \\
\hline
\end{tabular}
\end{table}

FIG. 2. Schematic view of black Si nanostructure formation in SF\textsubscript{6}/O\textsubscript{2} plasma. Initially, random etching of the native oxide (ions and fluorine) roughens the surface. Silicon etching by atomic fluorine enhances the roughness. Regrowth of oxide by atomic oxygen protects the sidewalls of the roughness as etching of silicon proceeds to produce the final black Si surface. All are done automatically in a single mask-less RIE process.
changed from parabolic to randomly distributed etch pits that eventually overlap and leave needle-like Si features in-between in agreement with simulations conducted by Saab et al.\textsuperscript{17} and observation from other studies and in this report (Fig. 3). The aspect ratio of the nanostructures can be controlled via the gas pressure, which determines the directionality of ions. This directionality affects the physical etching component. The shape of nanostructures and their aspect ratio are discussed further in Sec. III B.

The main goals of the black Si optimization process were low reflectivity (below 1%) and improved effective lifetime. The starting process had a reflectivity of 0.5% but a low effective carrier lifetime of 50 $\mu$s. After the process analysis of the etch recipe, we found that the CCP power was too high leading to high DC bias causing ion impact damage which leads to the low effective minority carrier lifetime. By combining the analytical model and the simulation program provided by Saab et al.\textsuperscript{17} with the experimental results (SEM images shown in Fig. 3), we reduced CCP power during etching. This modified etching process resulted in uniform texturing of the wafer surface, i.e., 5%–7% variation in nanostructure height across the 100 mm silicon wafer [Fig. 3(d)]. The measured effective lifetimes are shown in Fig. 4. All the other parameters in this experiment were kept constant. Figure 4 shows that the effective lifetime increased with decreased CCP power, while reflectivity was unaffected except at CCP power below 10 W. Below 10 W, the reflectivity increased rapidly, and at 0 W, the wafer had an almost polished surface morphology. The best trade-off between reflectivity and lifetime is found at 10 W CCP power and a reflectivity of 1% (yellow zone in Fig. 4) results. These experimental parameters were used for the etch time and DS nanotexturing effect studies presented below.

### B. Origin of the optical effects in black Si

#### 1. Black Si morphology

The origin of the optical effects of black Si nanostructures can be understood from morphology studies of the surfaces. Final nanostructures coated with 30 nm ALD Al$_2$O$_3$ are shown in Figs. 5(a)–5(c) as SEM cross-sections, SEM images at 30° tilt, and drawn profile cross-sections. We conducted RIE with 4 min increments starting from the 8 min etch (8, 12, and 16 min) to find the minimum reflectivity of the Si nanostructures in the complete absorption spectral range of Si. For each etch time, the height and pitch of nanostructures varied, and the variation agreed with an etch rate of 30 nm/min; a summary is presented in Table II.

We used drawn profiles to calculate the Si volume fraction as a function of normalized depth as shown in Fig. 6. Since the lateral features are smaller than the wavelength of the incident light, minimal reflection occurs; instead, the incident wave experiences a gradual change in the refractive index that depends on the Si volume fraction. This effect is also known as the effective medium theory or the moth-eye theory.

#### 2. Surface area enhancement

The exact surface area of nanostructures is not known and cannot be measured due to the random nature of the nanostructures. From SEM cross-section images in Fig. 5, we estimated the profile shape and evaluated the surface enhancement factor (SEF) $\gamma$ involved in the nanostructuring process as the ratio of top surface area of the nanostructure $A_{\text{nano}}$ to the projected area $A_{\text{proj}}$

$$\gamma = \frac{A_{\text{nano}}}{A_{\text{proj}}}$$

Obviously, $\gamma$ becomes unity for the reference sample. From the reconstructed surfaces shown in Fig. 5, $\gamma$ increases for higher aspect ratio nanostructures. The height of the nanostructure depends on the etch rate, while $\gamma$ changes from 1 to 7 from planar to high aspect ratio nanostructures (above
12 min etch time). The shape of the nanostructures is more complex as discussed in Sec. II. Hence, we used statistical calculations of Si fraction variation within normalized depth based on the nanostructure shape shown in Fig. 5(a).

3. Si fraction and gradual refractive index

The Si fraction at a certain depth is defined as the integrated cross-sectional area of all protruding Si features that are traversed by a horizontal plane, normalized to the whole cross-section area. The complement presents the fraction of the surrounding air medium. According to Fig. 6, the nanostructures have a shape profile between ideal parabolic and conical shapes. The corresponding Si fraction diagram shows three transition regions between the air medium and silicon.

The top layer (I) is defined as a vanishing small conical Si fraction since it contains only very sharp tips of few nanometers. The second layer (II) depends on the etch time of the samples: for 8 and 12 min samples, the second layer was characterized by the almost linear increase of Si fraction with slight variations in-depth; the 16 min samples have the parabolic Si fraction increase with depth. Such dependency corresponds to the transition across the major structural features of the texture, from the top of the conical or parabolic shapes to the bottom layer.

These layers can act as an effective optical medium because the Si nanostructures are not distinguished from the surrounding medium by light with effective wavelength higher than $\lambda_{Si} = 100\,\text{nm}$, which is equivalent to $\lambda_{air} > 400\,\text{nm}$, since $\lambda_{Si} = \lambda_{air}/n_{Si}$. This is also known as the so-called “zero order effective medium requirement.” The secondary texture features act like a zero order effective medium in the long wavelength region ($>1000\,\text{nm}$) similar to a stack of plain surfaces with an increased effective refractive index and effective diffractive scattering centers in the visible and NIR wavelength region (400–1000 nm). The third layer (III) has the lower increase of Si fraction for all nanostructures shown in Figs. 5 and 6. From SEM images, one can see that this layer contains sharp pits. The pits are separated laterally by a pitch from 180 to 280 nm with the aspect ratio close to one as shown in Table II.

According to Fresnel and Snell laws, the reflectivity, absorptivity, and transmittivity spectra depend on the effective refractive index of Si and air, and cosine of the propagation angle in each media, and it is also valid for nanostructures. The refractive index profile of the nanostructures was calculated using the statistical Si fraction curves shown in Fig. 6. Figure 7 shows the calculated resulting effective refractive index profile for a range of different surface morphologies.

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**TABLE II.** Etch time-dependent black Si nanostructure dimensions.

<table>
<thead>
<tr>
<th>Etch time (min)</th>
<th>Height (nm)</th>
<th>Pitch (nm)</th>
<th>$\text{Al}_2\text{O}_3$ thickness (nm)</th>
<th>SEFa, c</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>280 ± 50</td>
<td>180 ± 20</td>
<td>30 ± 5</td>
<td>3.8</td>
</tr>
<tr>
<td>12</td>
<td>440 ± 70</td>
<td>200 ± 20</td>
<td>30 ± 5</td>
<td>5.4</td>
</tr>
<tr>
<td>16</td>
<td>510 ± 80</td>
<td>250 ± 30</td>
<td>30 ± 5</td>
<td>6.9</td>
</tr>
</tbody>
</table>

*aSurface enhancement factor.*
Southwell defined these gradient index functions and showed the surface enhancement factors. Due to the effective refractive index gradient, there is no abrupt interface between silicon \( (n_{Si\text{pristine}} = 3.4) \) and air \( (n_{air} = 1) \) and Fresnel reflections are strongly reduced.

### 4. Light trapping mechanism in black Si

Due to the variation of shape and size of nanostructures with etch time, we consider two light trapping mechanisms in black Si nanostructures based on the effective medium approximation and diffraction mechanism. Hence, the diffraction mechanism based on Lambertian randomized light trapping is the dominant mechanism according to Yablonovitch.\(^{22,24,25}\) With diffraction, solar radiation is smoothly in-coupled from air to Si leading to nearly zero reflectance. According to Fig. 5 and Table II, the pitch between nanostructures is in the range of 180–280 nm, which is smaller than or similar to the wavelength in the range (200–1100 nm), and then light interferes and forms a transmissivity diffraction pattern behind the nanostructures acting as a diffraction slit. Following Koynov,\(^{22}\) the transmittivity diffraction grid of nanostructures is characterized by an average distance \( \Delta \) between scatters. According to Bragg’s equation, the direction of constructively interfering rays can be defined as 

\[
\Delta n = \frac{\lambda \sin \beta}{D} < \Delta
\]

where \( \Delta n \) is the wavelength of the incident light in air \( \lambda_{air}/n_{Si} \), \( \Delta \) is the effective light wavelength and the scattering angle within the Si layers, respectively. Efficient light trapping occurs for rays that enter the film (scattering angles \( \beta < \pi/2 \) in the direction of the incident beam) and reach the rear Si-air interface under angles \( \beta \) higher than the critical angle for total internal reflection. These assumptions are equivalent to the requirements \( 0 < \sin(\beta) < 1 \) and \( \sin(\beta) > 1/n_{Si} \). By applying these conditions to Bragg’s equation, one could deduce

\[
\lambda_{air}/n_{Si} = \Delta < \lambda_{air}.
\]

Therefore, the efficient light trapping via diffractive scattering depends on the average distance between the scattering centers, i.e., black Si nanostructure peaks. The light absorption enhancement should occur at light wavelengths longer than the absorption edge of the nanostructure layer, i.e., for the typical Si layer with a thickness of \( \sim 1 \mu m \) in the range of \( \lambda_{air} \approx 700–1000 \text{ nm} \). Thus, the best distances between the scattering structures on the surface of Si should be in the range of \( 150 \text{ nm} < \Delta < 1000 \text{ nm} \) according to Eq. (2). Spacing beyond this limit will be inefficient for light trapping by diffractive scattering. Smaller spacing leads to effective medium approximation, while larger spacing (above 1000 nm) leads to geometrical ray optics.\(^{26}\) According to Fig. 5, the spacing between the secondary features of the black Si films (pits and valleys spaced at 180 to 300 nm) matches perfectly the favorable range. Such spacing resulted in rather high scattering angles (above the critical angle) that considerably increase the light path lengths, accounting for the near perfect light trapping effects experimentally shown in the black Si nanostructures and reported in Fig. 8.

### 5. Optical properties of black Si

The spectral resolved reflectivity \( R \) and transmittivity \( T \) of the black Si were measured with a Perkin Elmer Lambda 1050 UV/Vis/NIR Spectrophotometer in the wavelength range of 200–1100 nm. Figure 8 shows the reflectivity, absorptivity, and transmittivity spectra in the wavelength range of 200–1100 nm before \( \text{Al}_2\text{O}_3 \) deposition. The optical spectra change slightly after deposition of the thin \( \text{Al}_2\text{O}_3 \) layer. For comparison, a theoretical Yablonovitch limit\(^{25}\) with the resulting absorptivity

\[
A_{abs} = 1 - \frac{1}{1 + 4n_{Si}^2z_{Si}d}
\]

is also plotted. Here, \( n_{Si} \) is a Si refractive index, \( z_{Si} \) is the absorption coefficient, and \( d \) is the wafer thickness.

Figure 8(a) compares the total reflectance spectra of the polished (100) Si wafer, 8 min, 12 min, 16 min, 20 min, and 16 min DS black Si textured samples with those of KOH-textured samples. The polished reference sample has around 30% reflectivity, while the KOH-textured reference has the much lower average reflectance of \( \sim 8\% \). All black Si (RIE) samples exhibit very low reflectance in the 400–950 nm spectral range. We identify three regions: I (UV), II (visible-NIR), and III (IR) regions. In region I (UV), all samples have a fluctuating reflectivity. These fluctuations are due to Si absorption coefficient fluctuations that agree with the reflectivity peaks. The sample etched for 8 min has a reflectance gradient in the 400–1000 nm range. The reflectivity gradient is analyzed based on the Si nanostructure shape.
fraction, and gradient refractive index shown in Figs. 5, 6, and 7, respectively. The nanostructures etched for 8 min have an average depth of 250–300 nm subject to transition from diffractive scattering to effective media conditions. This transition is especially important at an increased wavelength (above 475 nm) and explains the increasing reflectivity shown in Fig. 8(a) as the red curve. Most nanostructured samples, except those etched for 8 min, approach the Yablonovitch limit, particularly in the range from 450 to 1100 nm. In the case of the 16 min DS samples, low reflectivity is implied by conical nanostructures on both sides of the sample, while the 20 min samples have the lowest reflectivity due to the enhanced surface morphology only at the front surface.

Figure 8(b) illustrates the total transmittivity of the same set of samples. In general, transmittivity decreases for deeper RIE nanostructures. The transmittivity for the sample etched for 8 min is higher than that of the reference polished Si sample. This is also valid for 12 min etched samples that overlap with the polished Si reference. On the other hand, KOH-textured samples have lower transmittivity almost in agreement with the ideal Yablonovitch limit. This effect can be explained by the 54.74° angle of the KOH-etched facets.

The measured absorptivity and theoretical model are shown in Fig. 8(c). The total internal absorptivity was calculated as $A_{\text{total}} = 1 - R - T$. The absorptivity spectra of all nanostructured samples follow similar trends to transmittivity measurements. We compared experimental absorptivity with the theoretical model described in Eq. (3). The highest absorptivity is reported for the 20 min etch and DS 16 min etch. However, the KOH-textured sample has higher absorptivity in the NIR region (red region) due to the front surface facets at an angle of 54.74°. The absorptivity of the textured samples near the absorption edge, i.e., near the band gap of Si, exceeds that of a polished wafer with perfect ARC and provides a light trapping effect due to light scattering at the black Si nanostructures.

C. Electro-optical properties of black Si

1. ALD Al₂O₃ passivation scheme and model of effective lifetime and SRV

The ALD Al₂O₃ passivation scheme provides chemical and enhanced field-effect passivation. These two schemes allow achieving high lifetimes for polished and nanotextured black Si samples. In this study, we investigated the passivation properties on both n- and p-type Si wafers. Al₂O₃ is well known as a relatively high negative charge density dielectric. In the case of n-type wafers, negative surface charges repel majority carriers from the surface, leading to depletion or even inversion. In the case of p-type wafers, the high charge density leads to accumulation at the nanotextured surface; the effect of passivation due to charge was discussed by von Gastrow et al.

The effective lifetime and effective surface recombination velocity $S_{\text{eff}}$ also depend on the surface processing parameters as explained below. If the surface recombination velocity is not too high, the excess hole concentration $p_e$ at the surface may be assumed constant, and thus the surface recombination current magnitude is $I_p = q p_e S_{\text{loc}} A_{\text{nano}}$, where $S_{\text{loc}}$ is the real recombination velocity at the surface which has the real area $A_{\text{nano}}$. This current passes through the projected area $A_{\text{proj}}$ just below the surface, and thus we may define an effective (projected) surface recombination velocity $S_{\text{eff}}$ such that $I_p = q p_e S_{\text{eff}} A_{\text{proj}} = q p_e S_{\text{loc}} A_{\text{nano}}$.

Solving the effective recombination velocity yields

$$S_{\text{eff}} = \frac{A_{\text{nano}}}{A_{\text{proj}}} S_{\text{loc}} = \frac{A_{\text{nano}}}{A_{\text{proj}}} \frac{S_{\text{loc}}}{S_{\text{pol}}} S_{\text{pol}},$$

where $S_{\text{pol}}$ is the surface recombination velocity of a polished silicon surface. Surface modification with bombarding ions increases the defect density $D$, and thus increases the recombination velocity since $S = v_{ih} \sigma D$, where $v_{ih}$ is the thermal velocity of diffusing charges (in Si $\sim 10^7$ cm/s) and $\sigma$ is the capture cross section ($\sim 10^{-15}$ cm²) of the defects.

Since a nanotextured Si surface has a surface area enhancement factor $\gamma$ as discussed in Sec. III B and shown in Eq. (1), we may write

$$S_{\text{eff}} = \frac{A_{\text{nano}} D_{\text{loc}}}{A_{\text{proj}} D_{\text{pol}}} S_{\text{pol}} = \gamma \zeta S_{\text{pol}},$$

where $\zeta$ is the ratio of defect densities, showing that two mechanisms increase the surface recombination velocity. Let us consider the dependency of an effective lifetime on surface recombination on both sides of samples when the bulk
lifetime is assumed as infinitely large. Then, the effective lifetime equation is
\[ \frac{1}{\tau_{\text{eff}}} = \frac{S_{\text{eff}}^n + S_{\text{eff}}^p}{W}. \]

Since we study both SS and DS nanotextured and polished samples, the appropriate equations for each type of samples are presented in Table III.

2. Lifetime and $S_{\text{eff}}$ analysis

Figures 9(a) and 9(b) show the etch time-dependent effective lifetime of n- and p-type samples. The effective lifetime of n- and p-type samples differs by almost an order of magnitude due to different Shockley–Read–Hall and Auger lifetimes of n- and p-type materials; in addition, the electron diffusivity is higher than the hole diffusivity (by a factor of 3), and thus surface recombination has a stronger impact on p-type than on the n-type material.

For polished Si samples, $\tau_{\text{eff}} = 12$ ms for n-type and $\tau_{\text{eff}} = 800$ µs for p-type Si were measured. For nanotextured n-type samples, the best results were for 8 min etch $\tau_{\text{eff}} = 4$ ms and for 16 min SS nanotextured $\tau_{\text{eff}} = 7.5$ ms, while p-type samples obtained $\tau_{\text{eff}} = 400$ µs for 12 min etch and $\tau_{\text{eff}} = 800$ µs for 16 min DS textured samples. Figures 9(c) and 9(d) display the effective minority carrier lifetime as a function of injection level for polished and nanotextured samples on p-type and n-type samples, respectively. The effective SRV $S_{\text{eff}}$ was determined according to Eqs. (9) and (10) and is shown in Fig. 9(b). All n-type samples had extremely low $S_{\text{eff}}$ values below 10 cm/s. The lowest value was for the polished reference samples ($S_{\text{eff}} = 1.5$ cm/s), 8 min etch ($S_{\text{eff}} = 4$ cm/s), and for 16 min SS textured ($S_{\text{eff}} = 3$ cm/s) samples. The best results on p-type samples were obtained on the polished reference ($S_{\text{eff}} = 22$ cm/s) samples, the 12 min etch samples (65 cm/s), and the 16 min DS textured samples ($S_{\text{eff}} = 25$ cm/s). This difference in $\tau_{\text{eff}}$ and $S_{\text{eff}}$ for n- and p-type samples is based on the inversion and depletion mechanism of electrostatic passivation of Si.

TABLE III. Lifetime and SRV relations for single and double side affected surfaces. $D_c$, diffusivity of charge carriers.

<table>
<thead>
<tr>
<th>Surface Type</th>
<th>$S_{\text{eff}}$ Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Si on front side, $S_F \neq S_B$</td>
<td>$\tau_{\text{eff}} = \frac{W}{S_{\text{eff}}} + \frac{4}{D_c} \left( \frac{W}{\pi} \right)^2$ (7) $S_{\text{eff}} = \frac{W}{\tau_{\text{eff}} - \frac{4}{D_c} \left( \frac{W}{\pi} \right)^2}$ (9)</td>
</tr>
<tr>
<td>DS polished or black Si, $S_F = S_B$</td>
<td>$\tau_{\text{eff}} = \frac{W}{S_{\text{eff}}} + \frac{4}{D_c} \left( \frac{W}{\pi} \right)^2$ (8) $S_{\text{eff}} = \frac{W}{\tau_{\text{eff}} - \frac{1}{D_c} \left( \frac{W}{\pi} \right)^2}$ (10)</td>
</tr>
</tbody>
</table>

FIG. 9. Measured effective lifetime (a) and surface recombination velocity (b) at an injection level $\Delta n = 10^{15}$ cm$^{-3}$ and injection dependent effective carrier lifetime for (c) p-type and (d) n-type samples. Note: DS textured samples were prepared by sequential RIE texturing of both sides of the wafer.
induced by ALD of the Al₂O₃ layer. We also achieved excellent passivation results for the DS textured black Si samples, which demonstrates how efficient reduction of the CCP power is in obtaining good black Si surfaces.

The variation of the effective lifetime τ_eff and SRV S_eff with etch time is fairly weak and not quite systematic. For SS-textured bSi p-type samples, the SRV hardly varies with the etch time while the DS-textured sample has a significantly lower SRV. We tentatively attribute the surprisingly improved SRV to the effect of an additional RCA clean (removes some surface damage) done for the DS-textured sample. Also for the SS-textured bSi n-type samples, the SRV hardly varies with etch time while the DS-textured sample has a slightly increased SRV and lower effective lifetime as expected. In conclusion, the variation in surface recombination velocity with etch time is small enough to be attributed to experimental uncertainty and sample variation.

IV. CONCLUSIONS

Low optical reflectivity and excellent passivation quality are key factors for black Si use in photovoltaics. We have demonstrated that both low reflectance and good surface passivation can be obtained if low CCP power in the RIE process at −20°C was used for black Si nanostructuring. We found that lower CCP power (~10 W) reduces surface damage and improves the minority carrier lifetime effectively. The resulting nanostructures led to almost ideal reflectivity below 1% approaching Yablonovich limits in the visible and NIR ranges. With ALD Al₂O₃ passivation films deposited on a native oxide interlayer, we achieved the remarkably high effective lifetime. Polished n-type wafers reached 12 ms while black Si n-type samples reached 7.5 ms when RIE textured for 16 min. Polished p-type wafers reached 800 μs, and the same result was obtained for p-type black Si with double-sided nanotexturing for 16 min. Effective surface recombination velocities below 10 cm/s were obtained, with the lowest value for polished reference samples (1.5 cm/s), while slightly larger values resulted (4 cm/s for 8 min etch and 3 cm/s 16 min etch) on single side nanotextured n-type samples. On p-type samples, higher surface recombination velocities were measured (65 cm/s for 12 min etch and 25 cm/s for 16 min double side nanotextured). These findings show that high effective lifetime values can be obtained on both single- and double-sided nanotextured surfaces. Thus, the use of black Si in the fabrication of high-efficiency Si solar cells is very promising.

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