Defect engineering in black silicon

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Abstract

Black silicon (b-Si), i.e. a nanostructured silicon surface, is currently a subject of great interest within the photovoltaics (PV) community due to its excellent optics. While PV-related b-Si research has mainly focused on the reduction of reflectance and surface recombination, other possible effects of nanostructured surfaces have received less attention. This thesis investigates b-Si from a wider perspective and concentrates on engineering of surface and bulk defects in b-Si solar cells.

The thesis first focuses on b-Si surfaces. It is demonstrated that no trade-offs are required between the optical and electrical properties of wet-chemically fabricated b-Si by the application of atomic-layer-deposited (ALD) aluminum oxide (Al₂O₃) surface passivation. The current mainstream solar cell architectures, however, have a phosphorus-doped emitter on the front, and thus, the negatively-charged Al₂O₃ is non-optimal. This work addresses the issue by using positively-charged ALD SiO₂/Al₂O₃ stacks, which result in reduced recombination at diffused b-Si phosphorus emitter surfaces. In addition to affecting surface passivation, heavy phosphorus doping is shown to accelerate the consumption of silicon in standard cleaning solution, which strongly impacts both electrical and optical properties of b-Si emitters. All these results need to be considered in the design of high-efficiency b-Si solar cells.

The second main theme of the work is engineering of bulk-related phenomena by b-Si. The nanostructures are shown to enhance gettering of detrimental metal impurities. Indeed, intentionally iron-contaminated b-Si wafers have more than three times higher minority carrier lifetime than polished samples after gettering (720 µs vs. 200 µs). In addition to impurity gettering, the impact of b-Si on another important bulk phenomenon, i.e., light-induced degradation (LID), is demonstrated. Black multicrystalline (mc-Si) passivated emitter and rear cells (PERC) show no or only slight degradation under illumination at elevated temperature, while standard acidic-textured equivalents suffer from severe LID. The increased gettering efficiency and reduced LID clearly demonstrate that benefits provided by b-Si are not limited only to the excellent optics.

Finally, dry-etched b-Si is applied to industrial mc-Si PERC solar cells and modules. The fragile nanostructure is demonstrated to remain intact through cell and module fabrication at industrial production lines. Indeed, the prototype modules appear uniformly black after processing without anti-reflection coatings. Furthermore, the b-Si modules are shown to retain their performance until an incidence angle of 60°, whereas the modules with standard acidic-textured cells start to lose their performance already after a 30° tilt. Hence, the results demonstrate that the optical and electrical properties of b-Si can be maintained also at module level.

Keywords black silicon, solar cells, surface passivation, gettering, light-induced degradation
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Musta pii, eli nanokuvioitu pii pinta, on tällä hetkellä aurinkokennoyhteisön suureen mielenkiinnon kohteena erinomaisten optisten ominaisuuksien ansiosta. Aurinkokennoihin liittyvät mustan piin tutkimus onkin aiemmin keskittyntä lähinnä heijastuksen ja pintarekombinaation vähentämiseen, ja nanokuvioituksen muut mahdolliset vaikutukset ovat jääneet vähemmälle huomiolle. Tässä väitöskirjassa laajennetaan mustan piin tutkimusaihetta käsittämään pintojen lisäksi myös ilmiöitä, joihin nanokuvioitun pinta vaikuttaa syvällä piikiekoissa.


Avainsanat musta pii, aurinkokenno, pintaapassivointo, getteronti, valodegradaatio


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Espoo, September 2019,

Toni Pasanen
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This thesis consists of an overview and of the following publications which are referred to in the text by their Roman numerals. (*equal contribution)


Author’s contribution

Publication I: “Chapter 6.6: Black silicon”

The author performed a literature review on the topic and solely prepared the book chapter.

Publication II: “Effect of MACE parameters on electrical and optical properties of ALD passivated black silicon”

The author participated actively in sample processing, measurements and analyzing the results. The author prepared the manuscript.

Publication III: “Surface passivation of black silicon phosphorus emitters with atomic layer deposited SiO$_2$/Al$_2$O$_3$ stacks”

The author planned the experiments, processed the samples, and performed the characterization with the exception of doping profile measurements. The author analyzed the results and prepared the manuscript.

Publication IV: “Impact of standard cleaning on electrical and optical properties of phosphorus-doped black silicon”

The author participated actively in planning the experiments and sample processing. The author performed the characterization with the exception of doping profile measurements, analyzed the results, and prepared the manuscript.
Author's contribution

**Publication V: “Black silicon significantly enhances phosphorus diffusion gettering”**

The author participated actively in planning the experiments and processed and measured the samples. The co-authors performed the intentional iron contamination and the simulations. The author participated actively in analyzing the data and prepared the manuscript.

**Publication VI: “Impact of black silicon on light- and elevated temperature-induced degradation in industrial passivated emitter and rear cells”**

The author participated actively in planning the experiments, textured the wafers with black silicon, and coordinated the processing of the solar cells. The author participated actively in analyzing the data and prepared the manuscript.

**Publication VII: “Industrial applicability of antireflection-coating-free black silicon on PERC solar cells and modules”**

The author participated actively in planning the experiments, developed a black silicon etching process for industrial-sized wafers, textured the wafers with black silicon together with the second author, and coordinated the processing of the solar cells. The author participated in fabrication of the prototype modules and coordinated the module measurements. The author took the SEM images, analyzed the data and prepared the manuscript.
List of abbreviations

Ag silver
AgNO₃ silver nitrate
ALD atomic layer deposition
Al₂O₃ aluminium oxide
AR anti-reflection
Au gold
B boron
b-Si black silicon
CH₃COOH acetic acid
COCOS corona oxide characterization of semiconductors
CV current-voltage
Cz-Si silicon grown by the Czochralski method
DIW deionized water
DRIE deep reactive ion etching
DWS diamond wire-sawn
ECV electrochemical capacitance-voltage
EVA ethylene vinyl acetate
Fe iron
Fz-Si silicon grown by the float-zone method
HF hydrofluoric acid
HNO₃ nitric acid
H₂O water
H₂O₂ hydrogen peroxide
ICP inductively-coupled plasma
IQE internal quantum efficiency
IR infrared
LeTID light- and elevated temperature-induced degradation
List of abbreviations

LID    light-induced degradation
LTA    low temperature annealing
MACE   metal-assisted chemical etching
mc-Si  multicrystalline silicon
N\textsubscript{2}  nitrogen
NH\textsubscript{3}  ammonia
NH\textsubscript{4}OH  ammonium hydroxide
O\textsubscript{2}  oxygen
P      phosphorus
PDG    phosphorus diffusion gettering
PECVD  plasma-enhanced chemical vapor deposition
PERC   passivated emitter and rear cell
PL     photoluminescence
POCl\textsubscript{3}  phosphorus oxychloride
PSG    phosphosilicate glass
PV     photovoltaic
QSSPC  quasi-steady-state photoconductance
RIE    reactive ion etching
SC     standard clean
SDR    saw damage removal
SEM    scanning electron microscope
SF\textsubscript{6}  sulfur hexafluoride
Si     silicon
SIMS   secondary ion mass spectrometry
SiN\textsubscript{x}  silicon nitride
SiO\textsubscript{x}  silicon oxide
SiO\textsubscript{x}F\textsubscript{y}  silicon oxyfluoride
SiO\textsubscript{2}  silicon dioxide
SPV    surface photovoltage
SRH    Shockley-Read-Hall
SRV    surface recombination velocity
UMG-Si upgraded metallurgical-grade silicon
UV     ultraviolet
\mu-PCD microwave-detected photoconductance decay
List of symbols

\begin{itemize}
\item \([\text{AgNO}_3]\) \hspace{1cm} \text{silver nitrate concentration}
\item \(C\) \hspace{1cm} \text{dopant density- and injection-level dependent factor in Eq. 4.1}
\item \(D_{it}\) \hspace{1cm} \text{interface defect density}
\item \([\text{Fe}]\) \hspace{1cm} \text{iron concentration}
\item \(I_{sc}\) \hspace{1cm} \text{short-circuit current}
\item \(J_{0e}\) \hspace{1cm} \text{emitter saturation current density}
\item \(n\) \hspace{1cm} \text{refractive index}
\item \(Q_{tot}\) \hspace{1cm} \text{total charge}
\item \(R_{sh}\) \hspace{1cm} \text{sheet resistance}
\item \(S_f\) \hspace{1cm} \text{ratio of textured surface area to polished surface}
\item \(V_{oc}\) \hspace{1cm} \text{open-circuit voltage}
\item \(\eta(\theta)\) \hspace{1cm} \text{power conversion efficiency}
\item \(\eta'(\theta)\) \hspace{1cm} \text{normalized power conversion efficiency}
\item \(\eta(0^\circ)\) \hspace{1cm} \text{power conversion efficiency at normal incidence}
\item \(\theta\) \hspace{1cm} \text{incidence angle}
\item \(\tau_0\) \hspace{1cm} \text{minority carrier lifetime before Fe-B pair dissociation}
\item \(\tau_1\) \hspace{1cm} \text{minority carrier lifetime after Fe-B pair dissociation}
\end{itemize}
1. Introduction

Silicon solar cells typically have a characteristic blue color, which originates from the so-called anti-reflection (AR) coating that is applied on the front surface of the device. Without such film, the cells would suffer from substantial optical losses and the power conversion efficiency of the device would be very modest. Indeed, combined with a micrometer-scale surface texture, an AR coating reduces the reflectance of the surface from over 30% of a bare silicon (Si) surface down to only ~5% [1]. However, conventional AR coatings function efficiently only at a single wavelength, whereas sunlight consists of a wide spectrum of wavelengths. The fact that the surface appears blue indicates that a portion of the incoming solar radiation, namely the photons with wavelength that we sense as blue color, is reflected from the surface, and hence, is not converted into electric power.

An interesting alternative solution to reduce surface reflectance is nanosstructured black silicon (b-Si). The nanometer-scale surface texture has been studied extensively in recent years due to its ability to efficiently reduce reflectance on a wide wavelength and incidence angle range [2]. Especially, the b-Si nanostructure is more directly compatible with diamond wire-sawn (DWS) multicrystalline silicon (mc-Si) wafers, which have recently replaced slurry-cut wafers [3], than the conventional micrometer-scale techniques. However, the gain obtained from the excellent optics was for a long time cancelled out by increased recombination losses at the b-Si surface due to the large surface area of the nanostructures. The issue is no longer a hindrance for high-efficiency devices due to the advancements in novel surface passivation methods that efficiently reduce surface recombination [2, 4, 5, 6]. Indeed, the potential of b-Si for PV devices has recently been demonstrated as impressive laboratory-scale b-Si solar cell results by several research groups [6, 7, 8, 9].

While PV-related b-Si research has mainly focused on the reduction of reflectance and surface recombination, other possible effects of nanostructured surfaces have received less attention. For instance, the large surface area affects also doping processes [7, 10], and thus, junction formation
Introduction

and impurity gettering capabilities. This could have an interesting impact on the properties of the bulk material in addition to surfaces and provide an opportunity for efficient engineering of bulk defects. Additionally, the optical and electrical properties of wet-chemically fabricated nanostructures have remained compromised due to the application of non-optimal surface passivation techniques for b-Si in industrial production. It has also remained ambiguous, whether dry-etched b-Si is applicable to industrial solar cell and module production lines due to the fragile nature of the nanostructures. Finally, it is still under discussion, how well the beneficial properties of b-Si are maintained at the module level.

This thesis addresses the above questions by engineering of surface and bulk defects in b-Si. First, the thesis briefly covers the physical background for the optical properties of nanostructured surfaces and summarizes the fabrication methods for b-Si, which are discussed in more detail in Publication I. Chapter 3 introduces electrical aspects related to b-Si and concentrates on the engineering of surface-related phenomena. It is first studied, if the trade-off between the optical and electrical properties of b-Si fabricated by metal-assisted chemical etching (MACE) is necessary (Publication II). The effect of fixed charges in the passivation layer (Publication III) and wet-chemical processing (Publication IV) on electrical and optical properties of phosphorus-doped b-Si emitter surfaces is next investigated. In Chapter 4, the focus is shifted towards possible effects of b-Si on bulk properties. First, the gettering performance of b-Si phosphorus emitters is investigated at the material level (Publication V), followed by the engineering of light-induced degradation (LID) in complete b-Si solar cells (Publication VI). Finally, industrial applicability of b-Si is investigated in Chapter 5 (Publication VII).
2. Black silicon - optics and fabrication

2.1 Optical properties

Reflectance losses of silicon solar cells are conventionally reduced by a combination of an AR coating, most commonly silicon nitride (SiN$_x$) deposited by plasma-enhanced chemical vapor deposition (PECVD), and a micrometer-scale texture, which is typically fabricated by a wet-chemical alkaline [11] or acidic-based [12] process depending on the type of the substrate material. The first technique is based on destructive interference of light reflected from the interfaces of the AR coating with either Si or air. Additionally, light rays reflected from the sidewalls of the microtexture have a high probability to encounter the wafer surface again, and hence, have another possibility to be absorbed. However, these methods allow to minimize reflectance efficiently only at a single wavelength (the grey curve in Fig. 2.1) and incidence angle. In solar applications, the reflectance minimum is adjusted to ~600 nm wavelength that is close to the irradiance maximum of the solar spectrum [13], which results in losses in the blue and ultraviolet (UV) wavelength regions.

On the other hand, if the surface texture has dimensions that are small with respect to the wavelength of light, which is the case with b-Si as visible in a scanning electron microscope (SEM) image in Fig. 2.1, the ordinary ray optics are inapplicable. Instead, the nanostructures act as an effective refractive index ($n$) medium, and the refractive index changes gradually from that of air ($n = 1$) to that of Si ($n = 3.4$) [14, 15, 16]. Consequently, incident light encounters no clear interface between air and silicon, which virtually eliminates surface reflectance in a wide wavelength range from deep UV to infrared (IR) (Fig. 2.1). However, tiny nanostructures provide only weak light trapping, since the optically flat surface scatters only little light [17], and hence, the highest absorbance is achieved by a combination of structures with various sizes [18, 19].

In addition to the negligible dependency on wavelength, the reflectance of
b-Si is rather independent of light polarization [20, 21] and incidence angle [6, 21, 22]. Indeed, the reflectance of a bare b-Si surface remains close to zero until a 60° angle and increases only to ~10% at 70° [22]. This feature is very different to standard AR coatings, which can be optimized only for a single incidence angle. The b-Si optics are likely altered in complete solar modules due to the encapsulation material, most commonly ethylene vinyl acetate (EVA), and the front glass [1, 23]. However, the impact of the protecting layers with different b-Si surface morphologies has remained ambiguous. The reduced dependence of reflectance on incidence angle is beneficial also in other applications than solar cells that favor low light reflection, such as photosensors [22].

Black Si has also several other special properties, including superhydrophobicity [24, 25] and large reactive surface area, which are beneficial in e.g. extra-sensitive biological and chemical sensors [26, 27, 28], microfluidics [29], and batteries [30]. The various properties and applications of b-Si are reviewed in more detail in Publication I.

Figure 2.1. Reflectance of b-Si solar cells coated with atomic-layer-deposited (ALD) aluminum oxide (Al₂O₃) and acidic-textured cells with standard SiNₓ AR coating. The solar spectrum-weighted average reflectance between 300 nm and 1000 nm of b-Si and acidic-textured cells is 0.8% and 8.3%, respectively. The inset presents a SEM image of DRIE-fabricated b-Si nanostructure coated conformally with ALD Al₂O₃. Reprinted with permission from T. P. Pasanen, V. Vähänissi, F. Wolny, A. Oehlke, M. Wagner, M. A. Juntunen, I. T. S. Heikkinen, E. Salmi, S. Sneck, H. Vahlman, A. Tolvanen, J. Hyvärinen, and H. Savin. Industrial applicability of antireflection-coating-free black silicon on PERC solar cells and modules. Proceedings of the 35th European Photovoltaic Solar Energy Conference and Exhibition, Brussels, Belgium, pp. 552–556, November 2018. Copyright 2018, WIP Renewable Energies.
2.2 Fabrication methods

Nanostructured surfaces can be fabricated with several different methods, including reactive ion etching (RIE) [5, 31], metal-assisted chemical etching (MACE) [32, 33], laser treatment [34, 35], and electrochemical etching [36, 37]. This thesis focuses on RIE and MACE, since they are the two most promising methods from the industrial perspective [3, 33, 38] and enable more accurate control on the b-Si morphology [31, 39]. The nanostructures are fabricated with MACE in Publication II and with RIE in Publications III–VII. Other methods are briefly summarized in Publication I and covered in review articles [2, 40].

In MACE, etching of silicon in a mixture of hydrofluoric acid (HF) and hydrogen peroxide (H2O2) or another oxidizing agent is catalyzed by noble metals, typically silver (Ag) or gold (Au) [32, 33, 41, 39]. Several different process sequences are commonly used, and the chemistry and physical principles of the processes are discussed comprehensively in review articles [32, 39]. The three-step process that is used in Publication II is briefly summarized here. Another example for a typical MACE process sequence is described in Publication I.

First, a silicon wafer is immersed in a silver nitrate / water (AgNO3/H2O) solution, causing Ag to attach to the Si surface and to develop into nanoparticles. Subsequently, the b-Si nanotexture is formed in a HF/H2O2/H2O solution. The Ag nanoparticles receive electrons from Si, which causes local oxidation of the latter. Simultaneously, the oxide beneath the nanoparticles is removed by HF, and the particles sink into Si creating nanopillars or a porous structure depending on the process conditions. In addition to the concentration of the liquids and etching time, also temperature and illumination heavily affect the final surface morphology [32]. After b-Si formation, the nanostructures are typically polished (i.e., smoothened) in a mixture of HF, nitric acid (HNO3), and H2O to enhance conformality of PECVD SiNx on the surface texture [42, 43, 44]. A drawback of the polishing step is that it simultaneously increases reflectance. Finally, the nanoparticles are commonly removed by e.g. HNO3 either before or after the polishing step in order to prevent the metal from diffusing into the bulk during high-temperature process steps later in the cell process, which could impair bulk lifetime.

While MACE can more easily be adopted to the existing solar cell production lines without the need for large investment to new equipment due to its wet-chemical nature, RIE allows more control on the nanostructure morphology, and hence, enables better optimization of the b-Si properties [31]. Furthermore, unlike MACE, RIE requires no masking or catalyzing layers on the wafer surface, involves no metals, and is a single-step process.

RIE and its extension cryogenic deep RIE (DRIE) are commonly-used dry-etching methods in microfabrication [45]. Silicon is typically etched with
sulfur hexafluoride (SF$_6$) / oxygen (O$_2$) chemistry: SF$_6$ produces fluorine radicals for chemical etching of Si, and a passivating silicon oxyfluoride (SiO$_x$F$_y$) layer forms simultaneously at cryogenic temperatures [46, 47]. The protecting SiO$_x$F$_y$ layer is removed from horizontal surfaces by perpendicular ion bombardment, and etching proceeds anisotropically only in vertical direction [47].

Black Si was originally an unwanted by-product of the RIE process caused by an overly high oxygen content with respect to SF$_6$ (i.e., so-called overpassivation) and was used to optimize the etching parameters [48]. The special properties of b-Si were later realized, and more attention was drawn to optimize the process parameters for the fabrication of b-Si for various applications. The most critical parameters include the SF$_6$/O$_2$ gas flow ratio, pressure, plasma power, and temperature [31]. By tuning the parameters, DRIE enables accurate control on the b-Si morphology, which can be anything between high aspect ratio spikes with nearly vertical sidewalls and more pyramid-shaped structures (examples are shown in Fig. 2.2). The exact physical mechanism for the formation of nanoscale b-Si spikes has remained unresolved. Nevertheless, the nanostructure has been suggested to originate from micromasking of directional etching caused by e.g. dust and native oxide particles that are on the wafer already prior to etching or silicon oxide (SiO$_x$) that redeposits on the surface from the plasma [48].

The RIE b-Si process is often reported to damage the silicon surface, which causes excessive recombination, especially when high plasma power is used [49, 50]. Consequently, the damaged surface layer is removed by a similar wet-chemical polishing step that is used in MACE [51], which simultaneously impairs the excellent optical properties. Nevertheless, the cryogenic DRIE process with an inductively-coupled plasma (ICP) source provides high plasma density without increasing the ion energy at the substrate, which helps to prevent ion bombardment-induced damage [52]. Hence, such process was selected in this thesis. More recently, damage-free processes operating at room temperature have been developed [53, 54].

Figure 2.2. SEM images of DRIE-fabricated b-Si with different morphologies.
3. Engineering of black silicon surfaces

3.1 Optical vs. electrical performance

The surface area of b-Si nanostructures is drastically enlarged compared to flat surfaces, which increases the relative impact of surfaces on charge carrier recombination. Conventionally, surface recombination is reduced, i.e., the surfaces are passivated, by the PECVD SiN<sub>x</sub> AR coating. However, the nanoscale dimensions of b-Si set demanding requirements for the thin film deposition process, and the conformality of PECVD layers on b-Si is in general insufficient to provide efficient surface passivation [55]. Consequently, the issue of increased surface recombination was for a long time hindering the efficiency of b-Si solar cells.

The challenges related to poor conformality have recently been overcome by the application of atomic layer deposition (ALD), which is demonstrated in the SEM image in Fig. 2.1. Indeed, efficient surface passivation of dry-etched needle-shaped b-Si has been achieved using ALD aluminium oxide (Al<sub>2</sub>O<sub>3</sub>) [4, 5], resulting in high-efficiency laboratory-scale b-Si cells [6, 8]. Figure 3.1 demonstrates that DRIE-fabricated b-Si texture with efficient surface passivation can be upscaled to industrial-sized substrates. The presented black 156 × 156 mm<sup>2</sup>-sized mc-Si wafer shows a high effective minority charge carrier recombination lifetime of 250 μs on average. Separate grains are clearly visible in the map, while the boundary between the b-Si and planar areas near the edges cannot be distinguished, which indicates that the lifetime is limited by the bulk and the b-Si surface is indeed efficiently passivated.

Although dry-etched b-Si provides more control on the nanostructure morphology, the PV industry is currently adopting the MACE process for mc-Si wafer texturization due to its more straightforward implementation [3]. However, the MACE-texture has remained non-optimized from the optics perspective, since the nanostructures are typically wet-chemically polished to enable better conformality, and hence, more efficient surface
passivation using the conventional PECVD SiNx [42, 43, 44]. Due to polishing, reflectance of MACE-textured mc-Si wafers remains as high as 15-30 % without AR coatings and a thick SiNx film is required to reduce reflectance to 8-10 % [43, 44]. To improve the optical performance of solar cells with MACE b-Si nanotexture, Publication II studies if the polishing step can be omitted, or at least substantially shortened, by utilizing ALD Al2O3 instead of SiNx. Furthermore, since the effect of MACE parameters on the electrical properties of nanotextured surfaces has earlier been discussed from the SiNx passivation perspective, the application of ALD Al2O3 could enable the possibility to optimize the parameters further to achieve a more efficient combination of reflectance and surface recombination velocity (SRV). Hence, the effect of AgNO3 concentration in AgNO3/H2O solution and the necessity of a separate Ag removal step in HNO3 are also investigated.

Figure 3.2 shows solar spectrum-weighted (AM1.5G) average reflectance of b-Si samples (p-type float-zone (Fz) Si, ~1 Ωcm, 250 μm, (100) orientation) fabricated with the MACE process described in Chapter 2.2. The samples were polished for various times between 0 and 60 s in HF/HNO3/H2O solution and characterized by integrating sphere-based reflectance measurements. Polishing increases reflectance of all samples, as expected,
since it reduces the size of the nanostructures, which was observed by SEM. The increase in reflectance is initially pronounced in the samples fabricated with 0.05 mmol/L AgNO₃ concentration (labelled "low [AgNO₃]"). The lower [AgNO₃] was found by SEM to produce porous structures instead of needle-shaped nanostructures that resulted from the selected higher concentration level (5 mmol/L, labelled "high [AgNO₃]"). Consequently, the different behaviour of reflectance between the two concentration levels (i.e., between the red and black curves in Fig. 3.2) is likely due to faster etching of the nanoporous structure compared to the larger needle-shaped structures on the high [AgNO₃] samples that have less surface area in contact with the chemicals. As the polishing proceeds, the difference between the high and low [AgNO₃] samples diminishes as the nanopores are eventually entirely removed and the surfaces become more similar, which was observed with SEM imaging.

![Figure 3.2.](image)

The samples, from which the Ag nanoparticles were not removed in HNO₃ (labelled “without Ag removal”), show overall slightly higher reflectance than the equivalents with Ag removal. This can be explained by accelerated polishing of the nanostructures in the presence of Ag nanoparticles. Since the relative HF concentration in the polishing solution (HF/HNO₃/H₂O) is low, consumption of the generated holes is reduced at the nanoparticle-Si interface. Consequently, the excess holes diffuse to all silicon surfaces, which results in enhanced oxidation and subsequent etching of the wafer [32, 56, 57].
Since the electrical properties are at least equally important for solar cell operation as the optics, recombination at the nanotextured surfaces after ALD passivation is further investigated. The sample surfaces were passivated with ~22 nm of Al₂O₃ deposited at 200 °C, and the passivation was activated by a subsequent post-deposition annealing at 400 °C for 30 min in nitrogen (N₂) ambient. Figure 3.3 presents the effective minority carrier lifetime of the passivated b-Si samples determined by the quasi-steady-state photoconductance (QSSPC) technique at an injection level of 10¹⁸ cm⁻³, which is a typical condition under one sun illumination. The figure reveals that all samples have a carrier lifetime on the order of hundreds of μs even without polishing, which is sufficiently high for >20 %-efficient passivated emitter and rear cells (PERC) [58, 59, 60].

The AgNO₃ concentration affects the behaviour of carrier lifetime as a function of polishing. In the high [AgNO₃] samples (black curves in Fig. 3.3), polishing has only negligible effect on lifetime, which agrees with earlier observations [61]. The result indicates that the ALD thin film is capable of passivating needle-shaped b-Si efficiently independent of its dimensions and the reduction in nanostructure size by polishing provides no benefit for surface passivation. Hence, a polishing step is not a prerequisite for good electrical properties in MACE b-Si when using ALD. Surface recombination velocity of 30 cm/s is achieved in combination with 3.9 % reflectance without polishing (high [AgNO₃], without Ag removal), which is at the same level with earlier reports [61, 62].

Opposite to wafers treated with the high [AgNO₃] solution, the low
Engineering of black silicon surfaces

[AgNO₃] samples (red curves in Fig. 3.3), which have a more porous surface, show a trend of increasing lifetime as the polishing proceeds. Although the b-Si spikes on the high [AgNO₃] samples can be coated conformally with ALD Al₂O₃ independent of their size, the nanopores are more challenging to passivate due to their extremely large surface area and complex structure. Thus, the removal of the porous layer by polishing enables more efficient surface passivation within the low [AgNO₃] samples. However, the enhanced electrical properties are obtained with the cost of increased reflectance (Fig. 3.2).

High carrier lifetime in the samples that did not experience the Ag removal step indicates that the bulk remained uncontaminated. Hence, the RCA cleaning that was performed prior to ALD likely removed the remaining nanoparticles. Alternatively, the temperature of annealing that was performed after Al₂O₃ deposition (400 °C) may have been insufficiently high to activate silver-related defects and impair carrier lifetime in the bulk [63]. Typical solar cell processes may include steps that have a higher thermal load, such as contact firing, which needs to be considered.

Surprisingly, the b-Si samples, from which the Ag nanoparticles were not removed in HNO₃, show constantly higher lifetime than the samples with Ag removal, despite the potential risk of silver contamination. As discussed earlier, the surface is smoothened more efficiently when the nanoparticles are present during polishing. Hence, it is possible that also the high [AgNO₃] samples have a very thin nanoporous layer at the surface, which is removed by polishing, resulting in reduced SRV. Nevertheless, the lifetime improvement by the exclusion of the Ag removal step is more significant within the low [AgNO₃] samples, where the removal of the nanoporous layer is more critical to efficient surface passivation.

In conclusion, the results demonstrate that a polishing step, which is typically applied after b-Si fabrication by MACE, is not a prerequisite for efficient surface passivation when the PECVD SiNx is replaced with ALD Al₂O₃. Hence, no trade-offs are required between the optical and electrical properties of MACE b-Si by the application of ALD, when the MACE parameters are appropriately selected. For instance, the AgNO₃ concentration should be kept sufficiently high (in the mmol/L range) to prevent formation of porous silicon.

3.2 Passivation of heavily phosphorus-doped surfaces

As demonstrated above, ALD Al₂O₃ has enabled efficient passivation of lightly-doped b-Si surfaces. Together with the high-quality interface that Al₂O₃ forms with Si after post-deposition annealing at around 400 °C [64], one of the main enablers for the efficient passivation is the high density of negative fixed charges (>10¹² cm⁻²) that is incorporated at the Si–Al₂O₃
interface [65, 66]. However, the mainstream solar cell architectures have typically a heavily-doped layer, i.e., an emitter, on the front surface [3], which is illustrated with a schematic cross-section of a PERC structure in Fig. 3.4. Moreover, the emitter is typically doped with a high concentration of n-type dopants, such as phosphorus (P), for which the negative charges in Al₂O₃ are unfavorable. The issue is enhanced on b-Si surfaces, since their passivation relies more heavily on the field-effect [52]. Thus, in order to make b-Si a viable option for the current PV industry, a conformal thin film with positive fixed charge combined with a high-quality interface is required. A possible solution to this issue is studied in Publication III by using positively-charged SiO₂/Al₂O₃ stacks. Such dielectric stack has earlier been reported to prevent negative charge injection into the trap sites in Al₂O₃ [67], and instead, to result in a positive total charge due to the fixed and bulk charges in the SiO₂ film [68, 69].

![Figure 3.4. Schematic cross-section of a p-type passivated emitter and rear cell (PERC).](image)

Black Si was etched on p-type Czochralski (Cz)-Si substrates (~20 Ωcm, 675 μm, (100) orientation) using a DRIE process reported in [5]. Subsequently, phosphorus-doped b-Si and planar emitters were fabricated in a tube furnace by phosphorus oxychloride (POCl₃) diffusion at two different temperatures: 830 and 800 °C (labelled POCL_830 and POCL_800, respectively). POCl₃ gas was introduced for 20 minutes, followed by a 5 min drive-in in an oxygen ambient at the same temperature.

Doping profiles measured from the planar reference samples are presented in Fig. 3.5. Profiles in b-Si were not measured due to instrumental limitations to measure doping concentration accurately in the case of nanostructured surfaces. The difference between the total and electrically-active phosphorus concentration in the POCL_830 profiles near the sample surface, measured with secondary ion mass spectrometry (SIMS) and electrochemical capacitance-voltage (ECV) profiling, respectively, indicates the presence of inactive dopants. Moreover, the sheet resistance in the nanostructured samples is found to be 1.8-2 times smaller that in the planar counterparts (inset in Fig. 3.5), as determined by four-point probe and confirmed later by an inductive coupling-based method. Hence, 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 (PSG) on all sides, more phosphorus diffuses into the substrate.
Figure 3.5. 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 the b-Si samples. Reprinted with permission from T. Pasanen, V. Vähänissi, N. Theut, and H. Savin. Surface passivation of black silicon phosphorus emitters with atomic layer deposited SiO$_2$/Al$_2$O$_3$ stacks. Energy Procedia, 124, pp. 307–312, September 2017. Copyright 2017, The Authors, Published by Elsevier Ltd.

during the drive-in, as reported also before [7, 10].

After 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$_3$ deposited at 200 °C. The passivation was subsequently activated by annealing the samples at 400 °C for 30 min in N$_2$ ambient.

Performance of solar cell emitters is typically characterized with a parameter called emitter saturation current density ($J_{0e}$), which encompasses recombination at the surface and within the heavily-doped emitter region [70]. Figure 3.6a presents $J_{0e}$ for both planar and b-Si samples with the two different emitter profiles and two ALD passivation schemes extracted from QSSPC lifetime data at an injection level of 10$^{16}$ cm$^{-3}$. As hypothesized, the SiO$_2$/Al$_2$O$_3$ stacks provide lower $J_{0e}$ values compared to bare Al$_2$O$_3$ in all cases. This is due to the more suitable polarity of the oxide charge (Fig. 3.6b), as determined from separate lifetime samples processed in the same ALD runs by the contactless CV (corona oxide characterization of semiconductors, COCOS) method [71]. Although the absolute value of the total charge ($Q_{tot}$) is lower in the oxide stack, it outperforms the negatively charged Al$_2$O$_3$ in $J_{0e}$, since the doping concentration in the emitter is too high for the negative charges in Al$_2$O$_3$ to induce inversion. In addition, approximately three times higher effective charge density was measured from the b-Si samples compared to the planar references, which is in agreement with previously reported results [52]. Better passivation provided by the SiO$_2$/Al$_2$O$_3$ stacks can partly be explained also
by the lower mid-gap interface defect density ($D_{it}$) (Fig. 3.6b), which is caused by hydrogen diffusion from the Al$_2$O$_3$ film to the Si/SiO$_2$ interface during post-deposition annealing [72]. The mid-gap $D_{it}$ is reported only for the planar samples, since its extraction from COCOS measurements in the case of b-Si is challenging. The improvement in $J_{0e}$ 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.

![Figure 3.6](image_url)

**Figure 3.6.** a) Emitter saturation current density $J_{0e}$ of phosphorus emitter samples passivated with either SiO$_2$/Al$_2$O$_3$ stacks or bare Al$_2$O$_3$. The Auger model taking the band gap narrowing into account is applied according to Richter et al. [73, 74]. b) Total charge ($Q_{tot}$) and interface defect density ($D_{it}$) of the dielectric layers after annealing obtained with the COCOS method. The charge of bare Al$_2$O$_3$ is negative as indicated by the diagonal stripes. $D_{it}$ values are determined from the planar samples. Reprinted with permission from T. Pasanen, V. Vähänissi, N. Theut, and H. Savin. Surface passivation of black silicon phosphorus emitters with atomic layer deposited SiO$_2$/Al$_2$O$_3$ stacks. Energy Procedia, 124, pp. 307–312, September 2017. Copyright 2017, The Authors, Published by Elsevier Ltd.

The surface passivation quality, as characterized by $Q_{tot}$ and $D_{it}$ (Fig. 3.6b), indicates better $J_{0e}$ values than were measured in the samples passivated with the dielectric stack. Indeed, further corona charging experiments showed that $J_{0e}$ is limited by Auger and Shockley-Read-Hall (SRH) recombination in the emitter region. Moreover, the $J_{0e}$ in b-Si is in general higher than in the corresponding planar references, which is mainly due to recombination in the heavily-doped emitter that was not optimized for b-Si. Hence, the results imply that lower $J_{0e}$ values could be achieved only by careful optimization of the b-Si emitter profiles to avoid excessively high doping. Nevertheless, the reduced $J_{0e}$ in b-Si emitters achieved with the SiO$_2$/Al$_2$O$_3$ stack is a promising step towards the implementation of b-Si in commercial p-type silicon solar cells. Similar results have been published also with implanted b-Si phosphorus emitters [69].
3.3 Impact of wet-chemical processing on emitter properties

In addition to excellent optical properties and efficient surface passivation, high efficiency cell process requires extreme cleanliness of the bulk material, and hence, cleaning of b-Si surfaces is often a critical process step, especially prior to high-temperature processes. While standard clean (SC) 1 solution efficiently removes possible contamination from wafer surfaces, it may cause challenges in b-Si solar cells, since it consumes Si from the wafer surface: ammonium hydroxide (NH4OH) dissolves the thin native oxide on silicon at a slow rate, while H2O2 simultaneously oxidizes the surface at approximately the same rate [75]. Such unintended etching of Si may modify the surface texture and alter the emitter and the optical properties of the surface, affecting the solar cell performance. Moreover, high phosphorus concentration has been reported to accelerate the etching of Si in HF [76], and it remains ambiguous whether the same phenomenon concerns also the SC1 solution. The extent of these issues is inspected in Publication IV.

Black Si emitters were fabricated on boron-doped Cz-Si wafers (3–5 Ωcm, 525 μm, (100) orientation) using the same DRIE parameters and POCL_3 diffusion recipe that were used in Chapter 3.2. Planar wafers (10–15 Ωcm, same thickness and orientation) were included in the same diffusion batch for reference. The diffusion process resulted in lower sheet resistance in the b-Si wafers (47 Ω/□) than in the planar counterparts (74 Ω/□), as expected based on the results presented above. However, the sheet resistance values are slightly lower than those reported in Chapter 3.2. This difference is due to a cleaning step that the previous samples experienced prior to emitter characterization and highlights the need for this study.

A SC1 cleaning solution with a composition of NH4OH : H2O2 : H2O = 1:1:5 was prepared from VLSI grade chemicals in a standard way, i.e., ammonia solution (25 wt% NH3) was mixed with deionized water (DIW), and H2O2 (30 wt%) was poured into the solution after the batch was heated to 80 °C. The b-Si and planar emitter samples were immersed in the fresh solution for times that varied from one minute to an hour.

Figure 3.7 shows the electrically-active phosphorus profiles and the corresponding sheet resistance (Rsh) values of the planar samples prior to any cleanings and after SC1 immersion for various times. The sheet resistance values demonstrate a significant reduction in phosphorus concentration with increasing cleaning time, indicating that the surface is indeed etched by the cleaning chemicals. To estimate the etch rate of heavily phosphorus-doped silicon in the SC1 solution, the ECV profile of the uncleaned sample was truncated near the surface and sheet resistance was calculated for the resulting profile [77] applying a mobility model from Klaassen [78, 79]. The amount of silicon removed by the cleaning was determined to be the
truncation distance that provided the same calculated sheet resistance value as was experimentally measured.

![Figure 3.7](image.png)

**Figure 3.7.** Electrically-active phosphorus profiles of planar samples prior to any cleanings and after 10- or 30-minute cleaning determined by ECV profiling. Corresponding experimentally determined sheet resistance values ($R_{sh}$) are shown in the legend. The profiles of the cleaned samples are offset by the calculated etch depths. Surface regions that were removed by 10-, 30- and 60-minute SC1 cleanings are highlighted. Reprinted with permission from T. P. Pasanen, H. S. Laine, V. Vähänissä, K. Salo, S. Husein, and H. Savin. Impact of standard cleaning on electrical and optical properties of phosphorus-doped black silicon. IEEE Journal of Photovoltaics, 8, pp. 697–702, May 2018. Copyright 2018, IEEE.

Comparison of the experimentally determined $R_{sh}$ and the corresponding values calculated for the truncated profiles imply that 10-, 30-, and 60-minute cleanings consumed $14 \pm 1.5$ nm, $36 \pm 1.3$ nm, and $71 \pm 1.3$ nm from the sample surface, respectively. The removed regions are highlighted in Fig. 3.7. The ECV profiles measured from the cleaned samples and offset by the calculated etch depths fit well to the original phosphorus profile, which supports the calculated Si consumption. The results show that the etch rate of Si was as high as $1.4 \pm 0.3$ nm/min on average during the first ten minutes and then slowed down to $1.2 \pm 0.2$ nm/min for the last 30 min of the 60-minute cleaning due to reduced surface phosphorus concentration. These values are significantly higher than $0.8$ nm/min previously reported for lightly-doped surfaces [80]. The accelerated Si consumption could be explained by the increased Fermi level, which reduces the activation energy required to release a Si atom from the lattice, similar to previously reported for HF [76, 81]. Alternatively, the increased etch rate could be attributed to inactive phosphorus- or lattice mismatch-induced stress in the heavily phosphorus-doped region [76].

The accelerated Si consumption can be assumed to have even stronger impact on b-Si phosphorus emitters and their electrical properties, since the b-Si spikes have a larger surface area in contact with the cleaning solution,
which could increase the volumetric Si consumption. Consequently, Fig. 3.8 compares the sheet resistance of the b-Si and planar emitter samples immersed in SC1 solution as a function of immersion time. As hypothesized, the sheet resistance of the b-Si samples increases with a slightly higher rate compared to planar surfaces, which underscores the need to optimize cleaning procedures particularly in b-Si solar cells. After a 30-minute immersion, corresponding to three standard ten-minute cleanings, which can plausibly be included in a research-scale high-efficiency solar cell process flow, the sheet resistance nearly triples in the b-Si samples. This change would result in increased resistive losses in the emitter and deterioration of Ohmic contacts, resulting in a significantly reduced cell efficiency.

![Figure 3.8. Sheet resistance of b-Si and planar emitter samples after the immersion in SC1 cleaning solution for various times between one minute and one hour. Note the logarithmic y-axis. The lines act as a guide for the eye. Reprinted with permission from T. P. Pasanen, H. S. Laine, V. Vähänissi, K. Salo, S. Husein, and H. Savin. Impact of standard cleaning on electrical and optical properties of phosphorus-doped black silicon. IEEE Journal of Photovoltaics, 8, pp. 697–702, May 2018. Copyright 2018, IEEE.](image)

In addition to electrical properties, surface morphology and the resulting optics are essential parameters for high-efficiency solar cells. Figure 3.9 presents the surface reflectance spectra of the b-Si emitter samples. The reflectance increases considerably with increasing SC1 cleaning time: the solar spectrum-weighted average reflectance increases from 0.9 % to 1.7 % and 3.3 % during a 30-minute and 60-minute cleaning, respectively. Especially, the deterioration of optical properties is pronounced in the ultraviolet range where a 30-minute cleaning doubles and a 60-minute cleaning quintuples the peak reflectance at 280 nm wavelength from 3.7 % to 8.1 % and 18.4 %, respectively. The reflectance of similar b-Si samples without an emitter is also increased by the cleaning, but in a smaller extent due to lower consumption of silicon. Since the smoothing of b-Si surfaces does not promote more efficient surface passivation (Chapter 3.1), the increased reflectance would thus directly impair the short-circuit current, and hence, the performance of high-efficiency b-Si solar cells.
Figure 3.9. Reflectance spectra of b-Si phosphorus emitter samples before and after the immersion in SC1 cleaning solution for various times between 10 and 60 minutes. Reprinted with permission from T. P. Pasanen, H. S. Laine, V. Vähänissi, K. Salo, S. Husein, and H. Savin. Impact of standard cleaning on electrical and optical properties of phosphorus-doped black silicon. IEEE Journal of Photovoltaics, 8, pp. 697–702, May 2018. Copyright 2018, IEEE.

In conclusion, uncontrolled cleaning times may impair both the electrical and optical properties of b-Si solar cells, and hence, process flows of high-efficiency b-Si solar cells should be carefully designed to avoid unintended etching of silicon. Moreover, unintentional etching of highly phosphorus-doped planar and nanotextured silicon can significantly impact theoretical studies seeking to elucidate the impact of different emitter profiles on solar cell performance [82, 83], or e.g., impurity gettering [84, 85, 86]. Therefore, unnecessary cleaning between emitter realization and emitter characterization should be minimized and any HF dips and SC1 cleanings should be carefully reported in such future studies.
4. Engineering of bulk defects by black silicon

4.1 Phosphorus diffusion gettering in black silicon

Although the optical properties of b-Si have been studied rather extensively in recent years, other potential benefits from nanostructured surfaces have received less attention. One topic worth studying is the possible effect of b-Si on gettering of metal impurities, which are deleterious in several applications, including solar cells [87]. In gettering, the impurities are typically relocated to less critical sites within the device. This is often realised via a process referred as phosphorus diffusion gettering (PDG), where impurity segregation to a heavily phosphorus-doped emitter region is driven by the higher solubility of impurities in the heavily-doped silicon compared to the wafer bulk [84, 88, 89, 90]. Interestingly, since the b-Si nanostructures are typically more heavily doped than planar wafers after dopant diffusion, which was discussed in the previous Chapter and reported also in [7, 10], b-Si could enhance PDG via increased segregation.

Publication V investigates this possibility and quantitatively compares the gettering performance of b-Si and planar reference wafers for iron (Fe), the most deleterious metal impurity in p-type silicon [87, 91].

First, p-type Cz-Si wafers (~7 Ωcm, 440 μm, (100) orientation) were intentionally contaminated with iron by immersing them in an iron-spiked NH₄OH : H₂O₂ : H₂O solution. Subsequently, iron was diffused into the wafers by a heat treatment either at 940 °C for 50 min or at 850 °C for 55 min. The temperature determined the resulting bulk iron concentrations, which were 1.7 · 10¹³ cm⁻³ and 3.6 · 10¹⁴ cm⁻³ (labelled "low [Fe]" and "high [Fe]", respectively), as measured with the surface photovoltage (SPV) method. After iron in-diffusion, the surface contamination was removed by etching the wafers in a H₂O : HF : H₂O₂ (24:1:1) solution and by a RCA cleaning. The wafers underwent a wet oxidation process at 1000 °C for 84 min and a photolithography step to enable selective texturing of the front surface and formation of a single-sided emitter. Consequently, b-Si was
etched on half of every wafer (Fig. 4.1) with the same DRIE parameters as used before to make the comparison between the b-Si and planar surfaces reliable and straightforward.

After removing the rest of the front oxide, a phosphorus emitter was formed in the front side of the wafers with the POCL\_830 process. Subsequently, the temperature was ramped down to 600–800 °C with a 4 °C/min rate for a low temperature annealing (LTA) step. The selected LTA parameters and the resulting sheet resistance values for b-Si and planar halves, as determined by four-point probe, are listed in Table 4.1. The annealing times were chosen based on simulations to reach steady state iron concentration throughout the whole wafer [92]. In order to determine the bulk minority carrier lifetime, the heavily-doped layers were removed by wet etching in a mixture of acetic acid (CH\_3COOH), HF, and HNO\_3 for 2 min, which removed approximately 5 μm from each wafer surface. The surfaces were subsequently passivated with 22 nm of ALD Al\_2O\_3 and annealed at 400 °C for 30 min in N\_2 ambient.

Figure 4.1 shows microwave-detected photoconductance decay (μ-PCD) lifetime maps of a low [Fe] wafer without gettering and a corresponding wafer with POCl\_3 diffusion and a LTA at 800 °C for 2 h. The maps have been measured after emitter removal and surface passivation. The carrier lifetime improves significantly by the presence of b-Si during PDG. The lifetime in the b-Si half of the gettered wafer (720 μs) is more than two orders of magnitude higher than in the ungettered wafer (1.9 μs) and more than three times that of the gettered planar half (200 μs), implying a significantly higher cell efficiency potential for the b-Si wafers [93]. Since both halves have been passivated simultaneously with the same process, the lifetime difference is a direct result of differences in the wafer bulk, indicating more efficient gettering in b-Si. Possible remaining surface roughness on the b-Si area after Si etching would be visible only as a reduced effective lifetime in the b-Si half, which indicates that the difference in bulk lifetime may be even higher.

To determine the interstitial iron concentration in the bulk, the lifetime was measured before and after iron-boron (Fe-B) pair dissociation with the QSSPC technique. The iron concentration ([Fe]) was determined from

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time</th>
<th>( R_{sh} (\Omega/\square, \text{b-Si}) )</th>
<th>( R_{sh} (\Omega/\square, \text{planar}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td>2 h</td>
<td>26</td>
<td>42</td>
</tr>
<tr>
<td>750 °C</td>
<td>3.5 h</td>
<td>36</td>
<td>59</td>
</tr>
<tr>
<td>700 °C</td>
<td>5.5 h</td>
<td>44</td>
<td>71</td>
</tr>
<tr>
<td>650 °C</td>
<td>8 h</td>
<td>48</td>
<td>80</td>
</tr>
</tbody>
</table>

Table 4.1. Low-temperature annealing sequences and the resulting sheet resistance in b-Si and planar emitters.
the measured QSSPC data at an injection level around $10^{16}$ cm$^{-3}$ using equation

$$[\text{Fe}] = C \left( \frac{1}{\tau_1} - \frac{1}{\tau_0} \right),$$

where $\tau_0$ and $\tau_1$ are the minority carrier lifetimes before and after Fe-B pair dissociation, respectively, and $C$ is a dopant density- and injection level-dependent factor per an extended model developed by Macdonald et al. [94]. The iron concentrations in the b-Si and planar halves of the gettered sample presented in Fig. 4.1 are $3 \cdot 10^{10}$ cm$^{-3}$ and $2 \cdot 10^{11}$ cm$^{-3}$, respectively. Hence, the increased carrier lifetime in the b-Si half is indeed due to a reduced amount of iron in the bulk caused by enhanced gettering, as hypothesised.

Figure 4.2 presents the iron concentrations in the wafers gettered at different LTA temperatures. The final iron concentrations are below the solid solubility limit at every temperature, which suggests segregation to be the dominant gettering mechanism. Indeed, the observation that the gettering efficiency is rather independent of the initial iron concentration is also characteristic of segregation [87]. Thus, the decreasing trend of iron concentration with reducing LTA temperature can be attributed to the improving Fe segregation efficiency with decreasing temperature due to a larger iron solubility difference between the heavily phosphorus-doped region and the wafer bulk [95]. Furthermore, activation energies calculated from the low [Fe] data are 2.4–2.5 eV for both b-Si and planar samples, which agree well with the previously reported 2.5 eV activation energy for the Fe segregation coefficient [89]. Hence, the explanation for more efficient gettering induced by b-Si is likely the high phosphorus concentration in the b-Si nanostructures (Table 4.1), which enhances the segregation efficiency of Fe.

Additionally, the large surface area or possible structural defects induced by b-Si fabrication [4, 50, 97] may have provided additional gettering
sites by introducing nucleation sites for metal precipitates, as suggested earlier in the case of sacrificial porous silicon layers [98]. Furthermore, the gettering efficiency may have been intensified by iron accumulation at the Al₂O₃/Si interface during post-deposition anneal [99, 100], which, nevertheless, does not dilute the lifetime or iron concentration difference between b-Si and planar samples.

The difference in iron concentration between the b-Si and planar halves is not as evident within the high [Fe] samples as in the low [Fe] samples. As the initial iron concentration in the high [Fe] samples is well above the iron solid solubility limit, iron starts to precipitate in the bulk during the LTA sequence [96]. As bulk precipitation is independent of wafer surfaces, the phenomenon reduces interstitial iron concentration in b-Si and planar samples to a similar degree. Nevertheless, iron segregation is likely dominant also in the high [Fe] samples, since the final iron concentrations are below the solid solubility limits and the difference in gettering efficiency is visible in carrier lifetime.

In conclusion, the results demonstrate that the large surface area of b-Si, which was a considerable barrier for high efficiency b-Si solar cell in the past, can be used as an advantage to enhance gettering of detrimental
metal impurities. Potential benefits of enhanced gettering include the possibility to use lower quality silicon in high-efficiency photovoltaic devices. Indeed, a recent study reports promising b-Si PERC results obtained with inexpensive upgraded metallurgical-grade silicon (UMG-Si) substrates [101].

4.2 Impact of black silicon on light-induced degradation

A natural continuation for the discovery of enhanced gettering in b-Si is to study, what kind of impact the observed phenomenon has on solar cell performance. Impurities or other defects manifest in silicon solar cells e.g. by reducing cell performance under carrier injection by illumination or forward biasing. The detrimental phenomenon is commonly called light-induced degradation (LID) [102]. Attention has lately been attracted to a recently observed type of degradation, i.e., light- and elevated temperature-induced degradation (LeTID), which is the main culprit for efficiency deterioration in today’s mc-Si solar cells [102, 103]. LeTID may result in over 10 % relative efficiency loss in cells with dielectrically-passivated rear side [103, 104, 105], which is a severe issue for the PV industry that is shifting towards PERC cells [3]. Hence, several PV research groups, academic institutions and companies have recently investigated methods to mitigate the detrimental phenomenon, e.g. via dark annealing [106, 107], reduced peak temperature or ramp rates of contact firing [108, 109, 110, 111], application of high-intensity illumination at elevated temperature [112] or PDG of LeTID-causing impurities [113, 114].

Publication VI studies if b-Si has an impact on LeTID. Industrial b-Si solar cells were fabricated following the standard PERC process from mc-Si material, which was known to be prone to LeTID. Standard acidic-textured cells were fabricated in the same batch for reference. Since hydrogen has been suggested to have a major role in the LeTID phenomenon [115, 116, 117], the cells, both b-Si and acidic-textured, were passivated with either ALD Al₂O₃ or PECVD SiNx on the front to study the possible effect of hydrogen content in the film on LeTID. The Al₂O₃-passivated acidic-textured cells were additionally capped with a PECVD SiNx coating to reduce reflectance, while the corresponding b-Si cells were left without additional thin films. The large surface area of b-Si resulted in a heavier emitter in the b-Si wafers (~50 Ω□ vs. ~80 Ω□, as determined by four-point probe), as expected.

Figures 4.3a and 4.3b present the internal quantum efficiency (IQE) spectra of the b-Si and acidic-textured cells with Al₂O₃ or SiNx front surface passivation, respectively, both before and after degradation under 0.5 sun illumination at 75 °C for one week (~160 hours). LeTID is clearly visible in the acidic-textured cell as a reduction in IQE, while the b-Si
cells nearly perfectly retain their initial performance. In particular, the Al₂O₃-passivated b-Si cells show no degradation (Fig. 4.3a), although also they have a hydrogen-rich Al₂O₃/SiNₓ dielectric stack on the rear. Since ALD Al₂O₃ contains only a small amount of hydrogen compared to PECVD SiNₓ [118], the excellent stability of the Al₂O₃-passivated b-Si cells could at least partly be explained by a lower total amount of hydrogen diffusing into the bulk to activate the LeTID-responsible defects [115, 116]. Nevertheless, b-Si cells with SiNₓ front surface passivation also show only slight degradation compared to the acidic-textured equivalents (Fig. 4.3b), and hence, the superiority of the b-Si cells over the acidic-textured equivalents after degradation cannot be attributed to different surface passivation films alone.

The observations from IQE spectra are supported by spatially-resolved photoluminescence (PL) maps. Figure 4.4a shows a photograph of a b-Si PERC solar cell, and Figs. 4.4b and 4.4c present corresponding relative PL maps for b-Si cells passivated with either ALD Al₂O₃ or PECVD SiNₓ, respectively. The maps represent the PL intensity decrease after a one-week degradation normalized to the initial PL intensity, i.e., blue color represents no change in PL intensity, indicating no degradation in the wafer bulk, whereas red color represent the highest decrease in the PL intensity during degradation. Consistent with the IQE spectra in Fig. 4.3a, the Al₂O₃-passivated b-Si cell completely retains its performance under illumination at elevated temperature (Fig. 4.4b). Simultaneously, the edges, which were not subjected to b-Si etching, show a slight degradation. Hence, hydrogen in-diffusion from the SiNₓ film on the rear is enough to activate some amount of LeTID-causing defects in the bulk on areas without b-Si. However, the degradation is more severe with SiNₓ front
passivation (Fig. 4.4c), as expected [115, 116, 119]. Nevertheless, the b-Si area degrades only slightly, while the non-textured edges show significant deterioration. This agrees with the IQE spectra (Fig. 4.3b) and confirms that the reduced degradation in the b-Si cells cannot be explained only by a different amount of hydrogen in the surface passivation layers.

![Image](ALD Al₂O₃ and PECVD SiNx)

**Figure 4.4.** (a) Photograph of a 156 x 156 mm² multicrystalline b-Si PERC solar cell with Al₂O₃ surface passivation. Approximately 5 mm from wafer edges remained without b-Si due to clamping during the b-Si etching process. (b)–(c) PL intensity change during degradation normalized to the initial intensity of (b) an ALD Al₂O₃ or (c) PECVD SiNx-passivated b-Si cell. The same color scale applies to both maps: red color represents a large decrease in the PL intensity indicating strong degradation, while blue color represents stable PL intensity and no degradation. Reproduced with permission from T. P. Pasanen, C. Modanese, V. Vähänissi, H. S. Laine, F. Wolny, A. Oehlke, C. Kusterer, I. T. S. Heikkinen, M. Wagner, and H. Savin. Impact of black silicon on light- and elevated temperature-induced degradation in industrial passivated emitter and rear cells. Progress in Photovoltaics: Research and Applications, 2018, pp. 1–8, December 2018. Copyright 2018, John Wiley & Sons, Ltd.

The lower magnitude of LeTID in b-Si cells is also reflected in cell efficiency. Figure 4.5 compares the evolution of power conversion efficiency of b-Si and acidic-textured cells normalized to the initial efficiency measured throughout a one-week degradation. As expected from the IQE spectra (Fig. 4.3), the efficiencies of both acidic-textured cells decline significantly (nearly 4 %rel) under 0.5 sun illumination at 75 °C. On the other hand, the ALD Al₂O₃-passivated b-Si cells not only retain their performance, but their efficiency even improves by ~1 %rel, which is most likely due to enhanced field-effect passivation induced by increased charge density in the Al₂O₃ thin film [118]. Likewise, the SiNx-passivated b-Si cells are substantially more stable than either of the acidic-textured cells with only 1.5 %rel degradation, consistent with both the IQE spectra and the PL maps. Similar trends are visible also in open-circuit voltage (Voc) and short-circuit current (Isc) of the cells.

The results demonstrate that the amount of LeTID is reduced by the application of b-Si, indicating that the defect responsible for the phenomenon must be in an inactive state or removed in the b-Si cells. The reduced LeTID could at least partly be explained by a heavier phosphorus emitter,
and hence enhanced gettering, in the b-Si cells, although the defect responsible for the degradation is likely another impurity than iron [120, 121] that was studied in Chapter 4.1. Indeed, recent studies suggest that phosphorus or aluminum gettering can suppress LeTID to some extent [113, 114], especially in material with low lifetime [122].

On the other hand, wafer thickness has been reported to have an effect on the magnitude of LeTID [121]. The b-Si cells are indeed slightly thinner (~140 μm) than the acidic-textured cells (~165 μm) or the non-textured edges of the b-Si cells (~155 μm). Nevertheless, closer inspection of the PL data suggests that the magnitude of LeTID in our cells scales rather with surface area than wafer thickness: b-Si cells with the largest surface area (ratio to polished surface $S_f \approx 5-7$ [52, 123]) experience the weakest degradation, followed by acidic-textured cells ($S_f \approx 2$ [124, 125]), and the strongest LeTID is shown at the edges of b-Si cells, which were chemically polished by saw damage removal (SDR).

Another important aspect affecting the magnitude of LeTID is the applied firing process [108, 109, 110, 111]. Although the cells are fired with identical set peak temperature and profile, the actual temperature reached by the wafers may vary due to differences in optics of the front surface or wafer thickness. Indeed, the higher absorbance of b-Si compared to either of the AR-coated acidic-textured surfaces indicates that b-Si cells may reach a higher temperature during firing. Correspondingly, a thinner wafer may heat up more compared to a thicker one due to the smaller
volume of the wafer. Higher firing temperature has been demonstrated to result in stronger degradation [111, 126], although recent results report thinner samples to experience weaker LeTID [121]. Hence, the possible effect of surface texture or wafer thickness on the actual firing temperature experienced by the wafers should be visible only as more intense LeTID in the b-Si cells. Thus, the difference between the b-Si and acidic-textured cells could be even larger if the actual wafer temperatures were exactly identical. Furthermore, since the set peak firing temperature was 880 °C, it is highly unlikely that any of the cells would have experienced a temperature lower than the threshold for LeTID (720-740 °C [126, 127]).

In summary, although the exact mechanism for LeTID mitigation by b-Si remains unresolved, the phenomenon could be contributed by the strong ability of b-Si to getter LeTID-causing impurities. Furthermore, the negligible reflectance of b-Si suggests that the hydrogen-rich SiNx AR coating can be replaced by ALD Al2O3. This promotes efficient suppression of LeTID by reducing the amount of hydrogen diffusing from the dielectric thin film to the bulk, which is suggested to have a major role in the phenomenon [115, 116]. The results indicate that b-Si has a positive impact on LeTID, and hence, benefits provided by b-Si are not limited only to the excellent optical properties, as commonly understood.
5. Industrial applicability of black silicon

Chapter 4 demonstrated that the beneficial properties of b-Si for silicon solar cells are not limited to the excellent optics, but b-Si also enables more efficient control on detrimental metal impurities and makes the cells more stable. The next logical step is to study the applicability of the dry-etched b-Si nanostructures to industrial production and investigate, how well the beneficial properties are maintained at module level.

For that purpose, DRIE-fabricated b-Si nanotexture was applied to industrial mc-Si PERC solar cells and modules in Publication VII. The cells were fabricated at an industrial production line of SolarWorld Industries, and they were processed further into small modules at the solar module factory of Naps Solar Estonia. The b-Si cells were coated with ALD Al₂O₃ on the front. Although the SiO₂/Al₂O₃ stack that was discussed in Chapter 3.2 would have had more suitable charge polarity for phosphorus emitter passivation, the developed process was not available for full-sized (156 x 156 mm²) solar wafers due to equipment limitations.

Visual and SEM inspection after various process steps reveals that the needle-shaped b-Si nanostructure remains intact during cell and module processing, which is not self-evident due to its fragile nature. No visible mechanical damage is caused to the b-Si by inline equipment or wafer grippers, which is an essential finding for the industrialization of the new technology. Indeed, the b-Si cells appear uniformly black after processing even without any AR coatings (reflectance in Fig. 2.1).

Figure 5.1 presents a cross-sectional SEM image of a b-Si module. The modules consist of a white back sheet, a b-Si PERC cell enclosed by EVA on both sides, and a standard PV glass on the front. The strong cover glass was replaced by a plastic in the module that was inspected by SEM to enable cutting of the device. A few micrometer-sized gaps were located at the EVA – b-Si interface, which allowed closer inspection of the nanostructures. The inset in Fig. 5.1 presents a SEM image taken from such gap, showing intact b-Si covered with EVA. Thus, the fragile nanostructure survives the encapsulation process, which is observed also as a deep black appearance of the finished modules (inset in Fig. 5.2).
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The efficiency of the b-Si and acidic-textured cells are 18.8 % and 18.7 %, respectively. Since the standard diffusion parameters designed for acidic-textured surfaces were applied also to b-Si, the nanostructured cells likely suffer from increased emitter losses due to an excessive amount of phosphorus in the heavily-doped layer, as discussed earlier. Moreover, the efficiency of the b-Si cells is partly limited due to the non-optimal charge polarity in ALD Al₂O₃ for phosphorus emitter passivation [66, 69]. Nevertheless, despite the above-mentioned hindrances, the excellent optics and enhanced gettering capabilities of b-Si raise the efficiency of the nanostructured cells to the same level with acidic-textured equivalents. Hence, higher efficiency should be expected from the b-Si cells after further optimization of the emitter diffusion process for high aspect ratio nanostructures and replacement of Al₂O₃ e.g. with the positively-charged SiO₂/Al₂O₃ stack.

The efficiencies of both b-Si and acidic-textured devices are reduced by 2-3 %abs at module level compared to the corresponding cell performance. This reduction can mainly be attributed to two factors. First, the modules have a single side textured cover glass with no AR coating, which increases the reflectance. Moreover, manual tab wire soldering caused additional losses in the metal contacts and the process generated cracks to both acidic-textured and b-Si cells. Consequently, the b-Si modules show ~1 %abs lower efficiency than the acidic-textured equivalents.

Efficiency measured for perpendicular incident light neglects the ability of b-Si to absorb light that arrives at large incidence angles efficiently. Figure 5.2 presents the efficiency of b-Si and acidic-textured PERC modules.
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as a function of light incident angle normalized to that of normal incidence. The reduced amount of solar irradiance arriving to the cell surface with increasing incidence angle is cancelled out in the data by applying the following equation

\[ \eta'(\theta) = \frac{\eta(\theta)}{\eta(0^\circ) \cdot \cos(\theta)} \]  

(5.1)

where \( \theta \) is the incidence angle as defined in the inset of Fig. 5.2, \( \eta(\theta) \) and \( \eta'(\theta) \) are the measured and normalized efficiencies, respectively, and \( \eta(0^\circ) \) is the efficiency at normal incidence. The preliminary results show that the prototype b-Si modules retain their performance until incident angles larger than 60°, whereas the efficiency of acidic-textured modules starts to decrease already after a 30° tilt due to heavily increased reflectance. Furthermore, at an incidence angle of 70°, the efficiency of b-Si modules has reduced only 7 %rel, while that of the acidic-textured equivalents has decreased more than 25 %rel. Hence, the excellent optical properties of b-Si are maintained also at module level.

While the angle-dependencies in Fig. 5.2 agree well with earlier results reported at cell level [6], they slightly contradict with [23]. The latter reports that although dry-etched b-Si modules have the highest annual yield compared to other surface textures, such as alkaline or acidic, the optical benefit from b-Si is reduced at module level. Nevertheless, the
b-Si studied here is deeper (inset in Fig. 2.1) and has lower reflectance (0.8 % vs. 5.4 %) with even weaker wavelength dependence than reported in [23], which could at least partly explain the improved performance at large incidence angles. Indeed, similar b-Si nanostructures fabricated with the same DRIE process parameters have demonstrated [22] slightly lower reflectance at large incidence angles in air compared to the plasma-etched b-Si fabricated on acidic-textured wafers in [23]. Furthermore, the darker appearance of the b-Si prototype panels compared to the acidic-textured equivalents can be observed by eye. Hence, the optical behaviour of dry-etched b-Si seems to depend on the nanostructure morphology especially at module level.

In conclusion, the results demonstrate that dry-etched b-Si is applicable to current PERC production facilities, which is a promising step towards industrial application of the technology. Furthermore, the preliminary results demonstrate that the excellent optics of b-Si are maintained also at module level, at least if the surface morphology is carefully optimized, which promotes increased yearly power production of silicon solar cells. Hence, this work provides promising results for the PV manufacturers to consider in their discussion on whether they should invest in the dry-etched b-Si technology.
6. Conclusions

This thesis examined the effects of nanostructured b-Si surfaces on industrial silicon solar cells. The first part concentrated on surface-related phenomena. First, a trade-off between the optical and electrical properties of MACE-textured b-Si surfaces was discussed. The results demonstrated that a polishing step, which is typically applied as a part of the b-Si fabrication process by MACE to enhance conformality of the surface passivation layer on the nanostructures, is not a prerequisite for efficient surface passivation when ALD Al2O3 is used instead of PECVD SiNx. Thus, the application of ALD Al2O3 enables the possibility to optimize the MACE parameters more extensively in order to produce nanostructures with lower reflectance without increased SRV. However, the current mainstream solar cell architectures have a heavily phosphorus-doped emitter on the front, for which the negative charge in Al2O3 is non-optimal. Hence, a positively-charged ALD SiO2/Al2O3 stack was applied on b-Si phosphorus emitters. The dielectric stack reduced recombination at the nanostructured emitter surfaces, although the \( J_0e \) was found to be limited by the heavy doping in the emitter region, especially in the b-Si samples.

Heavy phosphorus doping was also shown to accelerate the consumption of silicon in SC1 solution. Consequently, wafer cleaning had a strong impact on both electrical and optical properties of b-Si phosphorus emitters. A 30-minute cleaning, corresponding to three standard ten-minute cleanings, nearly tripled the sheet resistance of the b-Si samples and doubled the peak reflectance in the UV. These changes significantly reduce cell efficiency, and therefore, process flows of high-efficiency b-Si solar cells should be carefully designed to avoid unintended etching of silicon.

The focus was then shifted to bulk-related phenomena. Black Si was first demonstrated to enhance gettering of detrimental metal impurities in intentionally iron-contaminated wafers. Indeed, the gettered b-Si wafers showed more than two orders of magnitude higher carrier lifetime than the ungettered reference and more than three times that of the gettered planar wafers. Correspondingly, the presence of b-Si reduced the final iron concentration in the gettered wafers to an approximately one order of
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magnitude lower level compared to planar equivalents due to increased segregation efficiency of Fe, which was caused by a higher phosphorus concentration in the b-Si emitters.

The study on the impact of b-Si on bulk properties was continued at cell level. Interestingly, industrial multicrystalline b-Si PERC cells showed no or only slight degradation under illumination at elevated temperature, while standard acidic-textured cells suffered from severe LeTID. In fact, the results suggested that the magnitude of LeTID scales with surface area of the texture, which had not been reported in literature before. The phenomenon could be contributed by the strong ability of b-Si to getter LeTID-causing impurities, although more fundamental studies on material level would help to understand the physical mechanisms behind LeTID suppression by b-Si more thoroughly. Furthermore, since hydrogen is also likely involved in the LeTID mechanism, b-Si promotes efficient suppression of LeTID via enabling the possibility to replace the hydrogen-rich SiNₓ AR coating with ALD Al₂O₃ due to the negligible reflectance of b-Si.

Finally, DRIE-fabricated b-Si was applied to industrial mc-Si PERC solar cells and modules. Careful inspection after various process steps demonstrated that the fragile nanostructures survived intact through the cell and module fabrication at industrial production lines. Indeed, the prototype modules appeared uniformly black after processing without AR coatings. The b-Si modules retained their performance until an incidence angle of 60°, whereas the modules with standard acidic-textured cells started to lose their performance already after a 30° tilt. This indicates that the excellent optical and electrical properties of b-Si are maintained also at module level, when the nanostructure morphology is optimized.

The results presented in this thesis provide a promising step towards the industrial application of dry-etched b-Si. Furthermore, the thesis demonstrates that unlike commonly understood, the benefits provided by b-Si are not limited only to the excellent optical properties. Instead, b-Si also enhances gettering of detrimental metal impurities and has a positive impact on LeTID.

One of the challenges in the development of the dry-etched b-Si technology is the upscaling of the etching processes to meet the demanding throughput requirement set by the PV industry. Future research questions include understanding the mechanism for reduced LeTID in b-Si solar cells. Moreover, finding the optimum balance between emitter recombination caused by excessive doping in the nanostructures and the benefits provided by the increased amount of dopants, such as enhanced gettering, constitutes one of the challenges to overcome in order to enable cost-efficient industrial b-Si solar cells with high-efficiency.
References


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