RICE UNIVERSITY

Synthesis of black silicon anti-reflection layers for silicon solar cells

by

Yen-Tien Lu

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APPROVED, THESIS COMMITTEE

Andrew R. Barron
Charles W. Duncan, Jr. – Welch Chair of Chemistry and Professor of Material Science and NanoEngineering

Sibani Lisa Biswal
Associate Professor of Chemical and Biomolecular Engineering and Associate Professor of Material Science and NanoEngineering

Rafael Verduzco
Louis Owen Assistant Professor of Chemical and Biomolecular Engineering and Assistant Professor of Material Science and NanoEngineering

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ABSTRACT

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Solar energy is one of the most important renewable energy resources in the world. Among all kinds of solar cells, the fabrication technology of silicon solar cells is relatively mature which makes them more popular in the solar cell market. However, in order to compete with the traditional energy sources, decreasing cost of per watt output seems necessary. Hence, increasing the energy conversion efficiency with an economical approach is an unavoidable issue. One solution is applying anti-reflection layers onto the silicon solar cells to maximize energy conversion efficiency. Recently, black silicon anti-reflection layers have attracted attention because their anti-reflection ability is less confined by the incident light angle and wavelength. In this thesis, two methods, the metal-assisted chemical etching and the contact-assisted chemical etching method, which have potential to economically fabricate large-scale black silicon on silicon solar cells are systematically studied. The complete etching mechanisms of these two methods are also proposed to clearly describe the fabrication process of black silicon.
“Pluck flowers while they’re still in bloom, or you'll carry empty branches in gloom.”

-Du Qiu Niang
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<td>ALD</td>
<td>atomic layer deposition</td>
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<td>AM</td>
<td>air mass</td>
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<td>AR</td>
<td>anti-reflection</td>
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<tr>
<td>ARC</td>
<td>anti-reflection coating</td>
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<td>b-Si</td>
<td>black silicon</td>
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<td>BOE</td>
<td>buffer oxide etchant</td>
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<td>°C</td>
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<td>ca.</td>
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<td>CACE</td>
<td>contact-assisted chemical etching</td>
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<td>CVD</td>
<td>chemical vapor deposition</td>
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<td>eV</td>
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<td>FESEM</td>
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<td>ICP-AES</td>
<td>inductively couple plasma atomic emission spectroscopy</td>
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<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>short-circuit current density</td>
</tr>
<tr>
<td>λ</td>
<td>lamda, wavelength</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
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<tr>
<td>Lpm</td>
<td>liter per minute</td>
</tr>
<tr>
<td>LPD</td>
<td>liquid phase deposition</td>
</tr>
<tr>
<td>MACE</td>
<td>metal-assisted chemical etching</td>
</tr>
<tr>
<td>µL</td>
<td>microliter, $10^{-6}$ L</td>
</tr>
<tr>
<td>µm</td>
<td>micrometer, $10^{-6}$ m</td>
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<tr>
<td>µM</td>
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<tr>
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<td>omega, ohm</td>
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<tr>
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<td>ohms per square</td>
</tr>
<tr>
<td>PSG</td>
<td>phosphosilicate glass</td>
</tr>
<tr>
<td>R</td>
<td>reflectivity</td>
</tr>
<tr>
<td>sccm</td>
<td>standard cubic centimeters per minute</td>
</tr>
<tr>
<td>SE</td>
<td>selective emitter</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SiNW</td>
<td>silicon nanowire</td>
</tr>
<tr>
<td>T</td>
<td>transmittance</td>
</tr>
<tr>
<td>V</td>
<td>volt</td>
</tr>
<tr>
<td>V_{oc}</td>
<td>open-circuit voltage</td>
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Introduction

Solar energy is considered the best potential energy source for the future and has been widely investigated because the solar energy absorbed by the earth’s atmosphere in 1 hour, $4.3 \times 10^{20} \text{ J}$, is more than all the energy consumed in a year by the world, $4.1 \times 10^{20} \text{ J}$. In order to more effectively capture the solar energy, all solar cells are designed to correspond to the properties of the solar radiation spectrum. The solar irradiance spectrum spans a wide range of 100 nm to 1 mm, but most irradiance occurs in the range of 250 to 2500 nm, especially in the visible-light range (400 to 800 nm). This implies that the solar cells should be designed to absorb a certain wavelength range of sunlight to reach the best photoelectron efficiency. The solar irradiance spectrum for air mass 0 (AM 0) is shown in Figure I.1.

The definition of air mass (AM) is the relative path length of solar radiation as it passes through the Earth’s atmosphere compared to the radiation that passes through the zenith point which is defined as AM 1.0. When the sun is closer to the horizon, the solar radiation travels a longer distance through the atmosphere resulting in more absorption and scattering of the radiation, which decreases the power-output ability of solar cells. Figure 1.2 shows the sun position for AM 0, 1.0, 1.5, and 2.0. One important point to note is that most solar cells are measured under condition AM 1.5.

![Figure 1.2. The definition of various air mass (AM) conditions. (Image courtesy of LaserFocusWorld).](image)

In the solar cell industry, commercial solar cells are usually divided into three categories called generations according to materials and working principles. First generation solar cells, or silicon (Si) solar cells, based on crystalline Si wafers are currently the most well developed, widespread, and efficient commercial solar cells. However, due
to the expensive fabrication cost of Si wafers, research is also devoted to develop other cheaper substitutes. Hence, second and third generation solar cells mainly based on thin film semiconductor materials and organic/novel materials, respectively, are also widely studied in order to cut down the cost of per energy output. Unfortunately, the efficiency of current second and third generation solar cells are still not able to compete with the Si solar cells, limiting their popularity in the solar cell market. Figure I.3 shows the best research-cell efficiency for all different kinds of solar cells. Although the best efficiency of different solar cells shown in Figure I.3 is on a lab-scale, it still suggests that the highest efficiency of Si solar cells, 25.6%, will not easily be defeated by the other commercial solar cells in a short time, which allows the Si solar cells to dominate the solar cell industry.

Figure I.3. Energy conversion efficiency of best research solar cell worldwide from 1975 to 2014 for different technologies. Copyright: Best Research-Cell Efficiencies, http://www.nrel.gov/ncpv/, (accessed November 5, 2014). This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.
Another strategy to cut down the cost of energy output of Si solar cells is using economical approaches to maximize the energy conversion efficiency. In the industry, a semiconductor anti-reflection (AR) coating layer is an optical coating which has been widely applied to the Si solar cell surface. The AR coating layer possesses an intermediate refractive index between the air and the Si wafer surface which can effectively suppresses reflectivity on Si wafer surface to absorb more incident photons for improving solar cell efficiency.\textsuperscript{4-10} However, the most significant limitation of the AR coating layer is that it only performs well with a narrow range of incident light angle and wavelength. The working principle of AR coating is based on the concept of quarter-wave coating; hence, once the incident light angle and wavelength change, the function of the AR coating will dramatically decrease.

**Working principle of AR coating layers.** Refractive index and layer thickness of AR coating layer are the most two important factors of concern. For all materials, their refractive indexes usually vary with incident light wavelength, hence, it is difficult to find a specific AR coating material which can match the whole solar spectrum perfectly. However, materials possessing refractive indexes which work well for a certain range of wavelength range for electricity generation still can be found. On the other hand, a quarter-wave coating is commonly used to decide the thickness of AR coating layer. A proper thickness of AR coating layer allows the AR coating layer to produce a destructive interference for more effectively suppressing reflectivity on the Si wafer surfaces. In order to find the thickness of quarter-wave coating, the incident light wavelength and the refractive index value of AR coating layer must be specified in advance, but good performance can usually be achieved for a relatively wide range of wavelengths.

As incident light travels from one medium to another one, a certain ratio of the light is reflected on the interface between two different media. The percentage of the reflected light to the total incident light, or reflectivity, depends on the refractive indexes of the two
media and the incident angle. The value of reflectivity could be calculated from the Fresnel equations. In the case of that the incident light is perpendicular to the interface of the two media, the reflectivity is

\[ R = \left(\frac{n_1 - n_2}{n_1 + n_2}\right)^2 \]  

(I.1)

where \( R \) is the reflectivity, \( n_1 \) and \( n_2 \) is the refractive index of the first and second medium, respectively.

The \( R \) value should be 0% to 100%, and its corresponded transmittance, \( T \), is \((1-R)\) when the light absorption and scattering of the second medium are negligible. Thus, if an incident beam with luminance, \( I \), vertically hits on the interface, luminance of the reflected beam is \( I \cdot R \), and luminance of the transmitted beam is \( I \cdot T \), or \( I \cdot (1-R)\).

For Si solar cells, there is an AR coating layer between the air and the Si wafer, therefore, the luminance of the transmitted beam which arrives the Si wafer is

\[ (I \cdot T_{om}) \cdot T_{ms} = I \cdot (1 - R_{om}) \cdot (1 - R_{ms}) \]  

(I.2)

where \( T_{om} \) and \( R_{om} \) represent the transmittance and reflectivity on the interface of the air and the AR coating layer, respectively; \( T_{ms} \) and \( R_{ms} \) represent the transmittance and reflectivity on the interface of the AR coating layer and the Si wafer, respectively. Figure I.4 shows a schematic of the interfaces of a Si solar cell system with an incident beam.

As the optimum refractive index of the AR coating layer is applied, the total transmittance would be maximized which means the derivative of Eq. I.2 to \( n_m \) should be zero, and the following equation will be obtained

\[ n_m = \sqrt{n_o \cdot n_s} \]  

(I.3)
where \( n_m, n_o, \) and \( n_s \) represents the refractive index of the AR coating layer, the air, and the Si wafer, respectively.

**Figure I.4.** A schematic of the interfaces of a Si solar cell system with an incident beam.

According to Eq. I.3, the optimum value of refractive index for the AR coating layers on Si wafer surfaces should be 1.99 (\( n_s = 3.95 \)) under an incident light with wavelength of 600 nm. However, a practical AR coating also relies on its destructive interference effect to further diminish the light reflectance. The minimum thickness of AR coating layer for occurring destructive interference follows the principle of quarter-wave coating

\[
d = \frac{\lambda}{4 \times n_m} \tag{I.4}
\]

where \( d \) is the optimum thickness of AR coating layer. For \( n_m = 1.99 \), \( d \) is equal to 75 nm under the incident light with wavelength of 600 nm.
As previously mentioned, the real solar spectrum spans many wavelengths; therefore, a proper refractive index value and thickness of AR coating are necessary to fit within the main absorbed range of incident light to maximize the energy conversion efficiency of Si solar cells.

**Fabrication of b-Si by the metal-assisted chemical etching method.** In order to overcome the limitation of conventional AR coating layers, a novel alternate called black silicon (b-Si) has been studied as an AR layer on the Si solar cells. B-Si is a type of porous Si material consisting of nanopores or nanowires on a Si wafer surface, and possesses low reflectivity and correspondingly high absorption of visible light regardless of the incident light angle and wavelength. The numbers or/and sizes of nanopores or nanowires gradually change with the depth on the wafer surface allowing the b-Si structure to possess a gradient change of refractive index between the air and the Si wafer which is more beneficial for suppressing reflectivity. Figure I.5 represents the refractive index of b-Si changing with the depth.

B-Si can be prepared by several different methods mainly including a reactive ion etching method,\textsuperscript{11–17} femtosecond pulse laser method,\textsuperscript{18–23} and metal-catalyzed etching method.\textsuperscript{24–49} The reactive ion etching method and femtosecond pulse laser method are utilized to fabricate needle-shaped and micron-cone structured b-Si, respectively. However, their threadlike structures are usually greater than 10 μm which causes the b-Si structures to be easily destroyed during assembly and limits b-Si applications. Fortunately, the nanopore-type b-Si synthesized by the metal-assisted chemical etching (MACE) method, which can endure higher stress has also been widely studied. This nanopore-type b-Si is easily fabricated on a large-scale since the fabrication process does not require high energy consumption or complicated instruments, making it a potential material for industrial applications.
A typical MACE method used to fabricate b-Si usually consists of two main reactions, which are metal deposition and electroless chemical etching. For the metal deposition, electroless metal deposition is the simplest approach to prepare metal catalysts on a Si wafer surface. It is usually described as a redox process involving spontaneous oxidation of Si atoms to SiO₂ and reduction of novel metal ions, such as gold, silver, and platinum ions, to nanoparticles (NPs) or a nanofilm on the wafer surface. After the metal deposition, the Si wafer is immersed in a Si etchant consisting of hydrofluoric acid and other chemicals. The as-deposited metal catalysts on the Si wafer surfaces can accelerate the etching rate of SiO₂ and dig numerous pits on the wafer surface. With longer etching time, the pits become deeper and larger and ultimately, connect with each other to form b-Si.

The mechanism of the two-step MACE method consisting of electroless metal deposition and electroless chemical etching was first detailed by Peng et al.⁵⁰ They used a HF/AgNO₃ aqueous solution for the electroless Ag deposition and a HF/Fe(NO₃)₃ aqueous solution for the electroless chemical etching on the Si wafer surface, respectively. The fabricated b-Si structures consisted of well-arranged Si nanowires (SiNWs) and showed no significant dependence on the doping type and crystal orientation of the Si wafer. Figure
I.6 shows the morphology of b-Si fabricated by the two-step MACE method from Peng et al.

Figure I.6. (a) SEM image of Ag NPs deposited onto a p-type Si wafer surface in the HF/AgNO₃ solution for 1 min. (b) SEM image of well-aligned SiNW arrays prepared in HF/Fe(NO₃)₃ solution. (c) SEM cross-sectional image of the SiNW arrays shown in (b). Adapted from: Fabrication of Single-Crystalline Silicon Nanowires by Scratching a Silicon Surface with Catalytic Metal Particles, K. Q. Peng, J. J. Hu, Y. J. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee and J. Zhu, Adv. Funct. Mater., 2006, 16, 387. Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

During the stage of electroless metal deposition, first, the Ag⁺ ions in the HF/AgNO₃ solution near the Si surface obtain electrons from the Si surface and nucleate on the Si surface. Since these Ag nuclei are more electronegative than Si, the Ag nuclei attract electrons from Si and become negatively charged. This results in other Ag⁺ ions in the solution attaching to the negatively-charged Ag nuclei to obtain electrons; therefore, the Ag nuclei can gradually grow into larger Ag NPs. At the same time, the Si under the Ag NPs also oxidizes to SiO₂ since it releases electrons to the NPs. HF in the solution then immediately etches the as-formed SiO₂ and produce shallow pits, which can fix Ag NPs on the Si wafer surface. Figure I.7 shows the mechanism of electroless Ag deposition on a Si substrate in a HF/AgNO₃ solution.
While in the electroless chemical etching process, the as-deposited Ag NPs on the Si surface can effectively enhance the etching rate of Si in the HF/Fe(NO₃)₃ etchant because the Ag⁺/Ag couple has a more positive redox potential compared to the Fe³⁺/Fe²⁺ couple. The Fe³⁺ ions function as an oxidizing agent by obtaining electrons from the Ag NPs to be reduced to Fe²⁺ ions and then oxidizing the Si around the Ag NPs to SiO₂. Meanwhile, the HF in the etchant continuously etches the as-formed SiO₂ around the Ag NPs, making the pits deeper and larger. Finally, the collective sinking tracks of the NPs result in a b-Si structure consisting of freestanding SiNW arrays on the Si wafer surface. Figure I.8 shows a schematic illustration for the fabrication process of b-Si consisting of SiNW arrays in the HF/Fe(NO₃)₃ solution. In the two-step MACE method, both electroless metal deposition and electroless chemical etching rely on metal reductions to form Ag NPs on a Si wafer (Ag⁺ to Ag) and SiO₂ around the Ag NPs (Fe³⁺ to Fe²⁺), respectively.

In order to further simplify the fabrication process of b-Si, an one-step MACE method was first proposed by Branz et al.²⁶ In fact, the one-step MACE method was based on the two-step MACE method; however, the electroless metal deposition and the
Figure 1.8. Schematic of cross-sectional and top views of b-Si formation on a Ag-deposited Si wafer surface in the HF/Fe(NO$_3$)$_3$ solution. (a, b) Electrons transfer between Si atoms and Fe$^{3+}$ ions via Ag nanoparticles inducing local oxidation of the Si substrate. (c, d) Etching of the SiO$_2$ and simultaneous pitting at the same position causes the formation of interconnected Si. (e, f) Formation of b-Si consisting of SiNW arrays due to the further sinking of the Ag particles, and longitudinal and lateral etching of bulk Si. Adapted from: Fabrication of Single-Crystalline Silicon Nanowires by Scratching a Silicon Surface with Catalytic Metal Particles, K. Q. Peng, J. J. Hu, Y. J. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee and J. Zhu, Adv. Funct. Mater., 2006, 16, 387. Copyright © 2006 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

electroless chemical etching occur simultaneously on the Si wafer surface, which allows the b-Si fabrication process to be completed in one batch. In the one-step MACE method, HAuCl$_4$ was used as a precursor of Au NP catalysts and added to a HF/H$_2$O$_2$/H$_2$O solution to form the Si etchant. The H$_2$O$_2$ in the etchant reduces Au$^{3+}$ ions to Au NPs on the Si wafer surface and oxidize the Si around the Au NPs to SiO$_2$. Meanwhile, the HF in the etchant etches away the as-formed SiO$_2$ around the Au NPs and produce b-Si consisting of nanopores on the wafer surface. This one-step MACE method fabricates a nanopore-type b-Si structure on the Si wafer surface and successfully suppresses the Si wafer surface
reflectivity to below 2%. Figure I.9 shows a SEM image of the 80-second Si etching in the Si etchant consisting of HAuCl₄/HF/H₂O₂/H₂O which fabricated nanopores with diameter of 5-20 nm and length up to 200 nm.

**Figure I.9.** Cross-sectional SEM image of the Si wafer surface etched in the Si etchant for 80 seconds. The dashed lines indicate extrema of the density-grade depth found by computerized pixel correlation analysis. Inset is a dark-field TEM image of a nanopore and Au NP (indicated by arrow) produced by the HAuCl₄ etchant with a 100 nm scale bar. Reprinted with permission from: H. M. Branz, V. E. Yost, S. Ward, K. M. Jones, B. To and P. Stradins, *Appl. Phys. Lett.*, 2009, **94**, 231121. Copyright 2009, AIP Publishing LLC.

**Selective emitters (SEs) in Si solar cells.** In addition to b-Si AR layers, designs of selective emitters (SEs) also have been applied to the b-Si solar cells in order to further improve efficiency of the Si solar cells. Applying SEs in Si solar cells have two main advantages: an improved quantum response at short wavelengths and a better contact resistance. Consequently, SEs in the solar cells result in more electrons transported to the metal contacts which allows the Si solar cells to possess higher short-circuit current density ($J_{sc}$), higher open-circuit voltage ($V_{oc}$), and better energy conversion efficiency.
structural designs of a conventional Si solar cell and a SE Si solar cell are shown in Figure I.10.

![Figure I.10](image)

**Figure I.10.** Structural designs of a conventional Si solar cell (a) and a Si solar cell with SEs (b).

A conventional Si solar cell uses a p-type Si wafer as a base and an n-type Si layer is later formed on the p-type Si wafer surfaces via phosphorous diffusion. These two different types of Si layers make up a p-n junction which allows electrons and holes to be generated within the junction under illumination. After coating an AR layer on the Si wafer surface, Ag metal contacts are then printed on the wafer surface and annealed under high temperature to penetrate through the AR layer and touch the Si wafer. The generated electrons from the p-n junction interface would transport through the n-type Si layer (the emitter) and are collected by the Ag contacts.

The main difference between the conventional Si solar cells and Si solar cells with selective emitters (SE Si solar cells) is that in the SE Si solar cells, the n-type Si surface under the Ag contacts has a higher doping level compared to that not under the contacts. This situation results in the contact resistance between the wafer surface and the Ag contacts to be significantly reduced and allows electron collection to be more efficient. Besides, compared to the conventional Si solar cells, the doping level and doping depth of
the n-type Si surface which is not under the Ag contacts is lower and shallower. Since the short-wavelength light has lower penetration ability and is mainly absorbed on the top of the wafer surface, the shallower doping depth of n-type Si can reduce the combination of minority carriers generated by the short-wavelength light. This fact makes the minority carriers easier to arrive the p-n junction interface and improves the energy conversion efficiency of solar cell.

A typical fabrication process of conventional Si solar cell basically consists of wafer texturization, phosphorus diffusion, phosphosilicate glass removal, coating of AR layers, metallization of front and rear contacts, and co-firing of metal contacts. First, a p-type Si wafer is texturized in alkaline solutions to form a micro-pyramid structure on the wafer surface which can increase areas of the Si wafer surface to absorb more incident light. The cleaned textured Si wafer is then transported to a furnace and treated with phosphorous diffusion where POCl₃ is used as a phosphorus source. The phosphorus atoms diffuse into the p-type Si wafer and form an n-type Si layer within the top surface of Si wafer, which generates a p-n junction. The depth of p-n junction interface can be controlled by diffusion temperature, diffusion time, concentration of POCl₃, and intrinsic dopant concentration of the Si wafer.

During the phosphorus diffusion, a layer of phosphosilicate glass (PSG) is also formed on the Si wafer surface and can be easily etched by buffer oxide etch (BOE) or dilute HF solutions after the diffusion. The PSG layer needs to be removed since it would increase the contact resistance between the Si wafer and the Ag contacts fabricated in the following step. Next, a thin layer of SiNₓ with optimized thickness is coated on the wafer surface as AR coating by plasma-enhanced chemical vapor deposition. The AR coating provides an intermediate refractive index between the air and the Si wafer and generate destructive interference on the wafer surface to further suppress the reflection on the wafer surface. Sequentially, Ag paste and Al paste are screen-printed on the front side and back side of the Si wafer as metal contacts, respectively. Finally, the metal contacts are co-fired
in a furnace allowing the paste to penetrate through the AR coating layer on the wafer front side and the native oxide layer on the wafer back side.

A good SE production process applied to Si solar cells usually need to take fabrication cost into account. Hence, additional process steps for SE fabrication have to be minimized and the whole SE fabrication process should be able to easily fit into the original production lines of Si solar cells. Recently, in order to fill the above requirements, several techniques of SE fabrication on Si solar cells have been developed including an etch-back emitter, laser doped SE, ion implantation process, screen-printable phosphorous ink and silicon ink. However, these methods still need at least 1-3 extra main steps for fabricating SE Si solar cells compared to the conventional Si solar cell fabrication process. This fact definitely decreases the feasibility of applying SEs into the current fabrication process of Si solar cells and also limits the applications of SE in b-Si solar cells. Figure I.11 shows a process flow comparison of different SE formation approaches.

My researches focus on improving the current fabrication process of b-Si AR layers and b-Si solar cells to further decrease their fabrication costs. I systematically studied utilizing cheaper metal catalysts to substitute Au NP catalysts for fabricating nanopore-type b-Si structures. The work of fabricating b-Si AR layers on Si solar cells via one-step MACE with Ag NP catalysts is presented in Chapter 1, where AgNO$_3$ was used as a precursor of Ag NP catalysts. In addition to Ag NPs, a more economical fabrication process of b-Si via one-step MACE with Cu NP catalysts is introduced in Chapter 2. The Si etchant consisting of Cu(NO$_3$)$_2$/HF/H$_3$PO$_3$/H$_2$O was used to generate Cu NP catalysts and inverted pyramidal nanopores on Si wafer surfaces.

A new fabrication approach of b-Si AR layers called contact-assisted chemical etching (CACE) method is integrated into the fabrication process of Si solar cells with SEs and presented in Chapter 3. The working principle of the CACE method is similar to the MACE method but relies on utilizing the Au contacts on the Si wafer surface to function
as catalysts for fabricating the b-Si AR layer. The CACE method is successfully integrated into the fabrication process of b-Si solar cells with SEs whose step number is comparable to that of the conventional Si solar cell without b-Si. In Chapter 4, a feasible method of liquid phase deposition is introduced to coat semiconductor AR coating layers consisting of SiO$_2$, TiO$_2$, and ZrO$_2$ on a Si wafer surface. The correlation between the chemical concentrations, film thickness, and the refractive index of film are studied.

**Figure I.11.** Process comparison of different formation approaches of SE Si solar cells. Columns filled with red represent new SE steps and columns filled with blue represent conventional solar cell steps.

**References**


Chapter 1

Nanopore-type black silicon anti-reflection layers fabricated by a one-step silver-assisted chemical etching

 Portions of this Chapter are included in Y.-T. Lu and A. R. Barron, Chem. Phy. Phy. Chem., 2013, 15, 9862. A reprint can be found in Appendix B. A full publication list can be found in Appendix A.

Introduction

Solar cells need low surface reflectance to maximize the amount of incident photons absorbed by the semiconductor to convert incident light into electrical energy. In the solar cell industry, the use of an anti-reflection (AR) coating is a popular method to suppress the reflection of solar cell surface by forming destructive interference of incident light. Typical AR coating for silicon (Si) solar cells are SiN$_x$ produced by chemical vapour deposition have a reflectance of about 6% as compared to 40% for a polished Si wafer. However, AR coating are limited in use because it only reduces the reflection for a narrow range of light wavelength and incident angle since its functionality is based on a quarter-wavelength coating.$^{1-4}$ Thus, the lowest reflectivity (and hence highest photon to electron efficiency) of a solar cell will only occur when the incident sunlight is at a particular angle.

A potential replacement for the conventional AR coating, so-called “black silicon” (b-Si), first reported by Jansen et al.$^5$ has attracted attention for Si solar cells.$^6-8$ B-Si is a type of porous Si material whose surface morphology provides a graded refractive index between the Si surface of the device and air, that results in a low reflectivity and a correspondingly high absorption of visible light.$^9$ B-Si has been successfully fabricated by several different methods including reactive ion etching,$^5,10,11$ laser chemical etching,$^{12-14}$ pulsed electrochemical etching,$^4,15$ and fast atom beam etching.$^{16}$ However, these
techniques need either expensive instruments and high energy consumption or complicated fabricating processes, making them unfavorable for industrial applications.

Recently, an economical and efficient approach for industrial b-Si manufacturing called metal-assisted chemical etching (MACE) method has been developed to avoid the above disadvantages. The MACE method includes two steps: metal deposition and electroless chemical etching. In the metal deposition step, a novel metal, such as gold, silver, and platinum is deposited on the Si surface usually as nanoparticles (NPs). The metal NPs attract electrons from the Si surface promoting the oxidation to SiO\(_2\) in the presence of an appropriate oxidant. In the electroless chemical etching step, the as-formed SiO\(_2\) is etched away by HF (as H\(_2\)SiF\(_6\)) and a pit is produced under each NP. As these reactions occur in a continuous process the pits become deeper and ultimately connect with each other, and remaining Si substrate forms b-Si that consists of a Si nanowire (SiNW) structure. Unfortunately, this nanowire structure is very fragile making the incorporation of b-Si into typical fab processes difficult.

A proposed mechanism based on the working principle of galvanic cells thoroughly explains the electroless chemical etching with metal NP deposition on the Si material surface. The mechanism consists of two half-cell reactions: a cathode reaction at the metal NP surface (Eq. 1.1) and an anode reaction occurring at the contact point between the Si and metal NP (Eq. 1.2 and 1.3). The overall reaction is thus as shown in Eq. 1.4. The potential difference between the cathode sites and the anode sites results a net flux of electrons through the metal NPs and accumulation of electrons on the cathode sites. Since the cathode sites can provide more electrons for the reduction of H\(_2\)O\(_2\), the overall reaction (Eq. 1.4) continues resulting in etching of Si under the Ag NPs.

\begin{align*}
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- & \rightleftharpoons 2\text{H}_2\text{O} \\
\text{Si} + 2\text{H}_2\text{O} & \rightleftharpoons \text{SiO}_2 + 4\text{H}^+ + 4\text{e}^- \\
\text{SiO}_2 + 6\text{HF} & \rightleftharpoons \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}
\end{align*}

(1.1) 
(1.2) 
(1.3)
Branz et al. developed a one-step Au-assisted chemical etching method based on the two-step MACE to fabricate nanopore-type b-Si.\textsuperscript{26} During the process of the one-step MACE method, the deposition of Au NPs and the chemical etching of Si occurred simultaneously on the Si wafer surface within the system consisting of HAuCl\textsubscript{4}:HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O, where Au\textsuperscript{3+} ions were reduced to Au NPs on the Si wafer surface. The fabricated nanopore structure possessed diameter of 5-20 nm and length of 200 nm on the wafer surface and suppressed the reflectance of the wafer to below 2\% across a wavelength range of 300-1000 nm.

Unfortunately, some porous Si structures possessing low reflectivity lead to failure in improving energy conversion efficiency of the Si solar cells because their surface area is too high resulting in high charge recombination. To overcome this problem Branz and co-workers demonstrated that a two-step Ag-assisted chemical etching to fabricate nanopores could be followed by a third step, which involves etching using tetramethylammonium hydroxide (TMAH) to shorten the nanopore length.\textsuperscript{27} However, the concentration of Ag is relatively high (1 mM) for Ag deposition and the process takes three distinct steps to accomplish the desired structure. Based on this result we are interested in two challenges: what is the effect of Ag concentration and can the reaction be formed in a one-step process?

Herein, our research focuses on the one-step Ag-assisted chemical etching to fabricate b-Si, since the Ag precursor has lower cost than the Au equivalent and recycling of the Ag is well understood in the (now defunct) film industry. In our study, AgNO\textsubscript{3} was utilized as an Ag NP precursor in a HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O solution to compose of a Si etchant. The H\textsubscript{2}O\textsubscript{2} not only facilitates the Si etching (Eq. 1.4) but also reduces Ag\textsuperscript{+} ions to Ag NPs on the Si wafer (Eq. 1.5).
$$2\text{Ag}^+ + \text{H}_2\text{O}_2 \rightleftharpoons \text{O}_2 + 2\text{H}^+ + 2\text{Ag} \quad (1.5)$$

We are interested in the effects of the Ag ion concentration and the volume ratio of HF:H$_2$O$_2$:H$_2$O on the morphology and reflectivity of the b-Si surface. Compared to other methods, the one-step Ag-assisted chemical etching simplifies the b-Si fabrication process and may cut down the cost of the facilities and energy expenditures, which is beneficial for industrial applications. In addition, unlike SiNW arrays, the nanopore-type b-Si possesses no high-aspect-ratio needle-like structure and is not as fragile as SiNW arrays and can thus better endure the stress during the solar cell assembly.

**Results and Discussion**

**Ag ion concentration of 500 μM.** Using a high Ag ion concentration (500 μM) results in only Ag NPs and shallow pits being formed. However, no nanopores can be observed on the Si wafer surface. Figure 1.1 shows SEM images of Ag NPs formed on the Si wafer surfaces with different HF:H$_2$O$_2$:H$_2$O volume ratios. We propose that no nanopores appear on the wafer surfaces due to the fact that the majority of the surface is covered by the Ag NPs under the high [Ag$^+$] etching conditions. In the Ag-assisted chemical etching method, the HF etches away not only the areas underneath the Ag NPs but also the areas adjacent to the Ag NPs, as may be seen by the images of the Ag NPs sitting inside larger pits (Figure 1.1b and c). As the majority of the wafer surface is covered by Ag NPs, a near isotropic oxidation of Si occurs. This causes different regions of the Si wafer to be subject a similar etching level and no nanopores can be observed on the Si wafers.

It was also observed that the average diameters of the Ag NPs prepared in solutions of different HF:H$_2$O$_2$:H$_2$O ratios increase with time even at the earliest stages of the etch process. After reaching a maximum size at 5 min, the NPs gradually decrease in size. Figure 1.2 shows the average diameters of Ag NPs for different etching time and HF:H$_2$O$_2$:H$_2$O
volume ratios. A reasonable explanation for this effect is that the H$_2$O$_2$ in the Si etchant not
only assists the Ag NP formation but also dissolves the as-formed Ag NPs into Ag ions
(Eq. 1.6). As the H$_2$O$_2$ has been consumed and its concentration is no longer high enough,
the equilibrium is shifted; resulting in the dissolution of the Ag NPs dominates and
decreases the average size of Ag NPs.

$$2\text{Ag} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ag}^+ + 2\text{H}_2\text{O}$$ \hspace{1cm} (1.6)

**Figure 1.1.** SEM images of the Ag NPs on the Si wafer surfaces synthesized by the Si
etchant containing 500 μM [Ag$^+$] with 10 minutes etching and various HF:H$_2$O$_2$:H$_2$O ratios
as (a) 1:5:2 (b) 1:5:5 (c) 1:5:10 (d) 1:5:20.
Another observation is that with the lower [HF] and [H$_2$O$_2$] the average diameter of the Ag NPs is more constant with etching time and the standard deviation in NP diameter also is smaller (Figure 1.2). This indicates that the Ag NPs are smaller with a more monodispersed size, which may be attributed to the fact that a lower [H$_2$O$_2$] leads a slower rate of formation of Ag NPs (Eq. 1.5). The slower growth rate limits the difference in Ag NP size between the earlier-formed NPs and later-formed NPs during the etching process.

Figure 1.3 and Figure 1.4 show SEM images of Ag NPs formed on the Si wafer surfaces with HF:H$_2$O$_2$:H$_2$O as 1:5:5 and 1:5:10 for various etching time, respectively. As can be seen, the Ag NPs formed with the ratio of 1:5:10 show smaller difference in size with etching time. In addition, it implies that in order to fabricate nanopores with more uniform size distribution, relying on the lower [HF] and [H$_2$O$_2$] to form monodispersed Ag NPs is necessary since the nanopores are simply the sinking track of Ag NPs.
Figure 1.3. SEM images of the Ag NPs on the Si wafer surfaces synthesized by the Si etchant containing 500 μM [Ag⁺] with various etching time with HF:H₂O₂:H₂O ratios as 1:5:5. (a) 2 min (b) 5 min (c) 10 min (d) 20 min.

Ag ion concentration of 50 μM. As the Ag ion concentration is reduced to 50 μM, nanopores are observed on the Si wafer surfaces, with the majority of them being macropores (50-1000 nm). The lower [Ag⁺] provides a lower nucleation and growth rate of Ag NPs; therefore, the Si wafer surface is no longer mostly covered by Ag NPs. In other words, the Ag NPs on the wafer surface are better dispersed and are able to nearly unidirectional oxidize the Si under the Ag NPs to SiO₂ which is immediately etched by HF. As long as both of the oxidation and etching continue, the Ag NPs would keep sinking into the wafer surface and increase the nanopore length. Figure 1.5 shows SEM images of the
Figure 1.4. SEM images of the Ag NPs on the Si wafer surfaces synthesized by the Si etchant containing 500 μM [Ag⁺] with various etching time with HF:H₂O₂:H₂O ratios as 1:5:10. (a) 2 min (b) 5 min (c) 10 min (d) 20 min.

morphology of the b-Si synthesized with various etching time and HF:H₂O₂:H₂O ratios. On the Si wafer surface, only few Ag NPs can be observed since most of them have sunk into the bottom of the nanopores. It is important to note that the diameter and length of the nanopores synthesized with lower [HF] and [H₂O₂] are smaller compared to those synthesized with higher [HF] and [H₂O₂] for the same allotted time. This phenomenon is attributed to the lower [H₂O₂] system requiring more time to grow the Ag NPs, which function as the catalysts for Si etching. Thus, the formation of nanopores is delayed, as well as both the nanopore diameter and length are directly affected. For example, as the
etching time reaches 10 min, the maximum nanopore synthesized with the HF:H_{2}O_{2}:H_{2}O ratio of 1:5:2 has dimensions of 230 nm (diameter) and 4.1 μm (length), see Figure 1.5a and b. These are much larger than those synthesized at the same etching time using a ratio of 1:5:20 whose diameter = 140 nm and length = 380 nm (Figure 1.5e and f).

With a concentration of Ag ion is 50 μM, the Si etching time also plays an important role in the structure of the etched surface. Over time the nanopores become larger and longer on the Si wafer surface (Figure 1.5e-h). The growth of nanopores in the vertical direction is not difficult to understand because the Ag NPs continue catalyzing the Si etching under the NPs to increase the nanopore length, as long as the HF and H_{2}O_{2} are sufficient in the etchant.

The growth of nanopore diameter may be attributed to the presence of the dopant within the Si wafer. For the two-step Ag-assisted chemical etching, Zhong et al. proposed that some Ag ions diffuse upward from the pre-deposited Ag NPs at the nanopore bottom and re-nucleate at the defective sites around the dopant along the nanopore sidewalls.\textsuperscript{28} Figure 1.6 shows Zhongs’ schematic illustrations of the formation process of SiNW arrays through a two-step Ag-assisted etching method. The newly formed Ag nuclei trigger new Si etching processes on the nanopore sidewalls and increase the nanopore diameter and the porosity of sidewalls as well. Since the dopant concentration is higher on the wafer surface, the nanopores usually possess larger diameters at their surface end, resulting in an upside down cone shape. In the one-step Ag-assisted chemical etching method, we can infer that the change of nanopore diameter might be more significant than the two-step method since the Ag ions nucleating at the sidewall would come from not only the existed Ag NPs at the nanopore bottoms but also the Ag ions in the Si etchant.

It has been previously shown that the porous etching is related to the dopant type and dopant concentration in the Si wafer. With regard to the doping type, Zhang et al. reported that etching rate of an n-type Si wafer (7-13 Ω) is faster than that of a p-type Si wafer (7-13 Ω).\textsuperscript{29} They also found that this occurs for both (100) and (111) substrates. With regard
Figure 1.5. SEM images of the morphology of b-Si synthesized by the Si etchant containing [Ag+] = 50 μM with various etching time and HF:H2O2:H2O ratios. Top views: (a) 10 min, 1:5:2 (c) 10 min, 1:5:10 (e) 10 min, 1:5:20 (g) 20 min, 1:5:20. Cross views: (b) 10 min, 1:5:2 (d) 10 min, 1:5:10 (f) 10 min, 1:5:20 (h) 20 min, 1:5:20.
Figure 1.6. The Zhongs’ schematic illustrations of the formation process of SiNW arrays through a two-step Ag-assisted etching method from the highly and lightly doped Si wafers. Reprinted with permission from X. Zhong, Y. Qu, Y. C. Lin, L. Liao and X. Duan, ACS Appl. Mater. Interfaces, 2011, 3, 261. Copyright 2011 American Chemical Society.

to the dopant concentration, it was found that the nanopore becomes shorter with increasing dopant concentration. According to SEM studies it is proposed that the Ag NPs at the nanopore bottom can be oxidized by $\text{H}_2\text{O}_2$ to form $\text{Ag}^+$ ions again, which may diffuse and renucleate on the nanopore sidewalls. The higher the dopant concentration the more the Ag clusters are proposed to re-nucleate at the nanopore sidewalls, and then less Ag NPs are left at the nanopore bottom. This results in a slowing of the etching rates along the vertical direction and consequently shorten the nanopore length.

Another observation from the images in Figure 1.5 that seems not able to be well described by the Zhong mechanism is that the number of the nanopores decreases with the etching time (Figure 1.5e-h). We have found that sonication resulted in more uniform size distribution of the nanopores on the Si wafer surfaces. We propose a possible mechanism that explains the decrease in nanopores as a function of etch time that includes the sonication. Figure 1.7 shows a schematic summary for the formation of nanopores on a Si wafer surface through the one-step Ag-assisted chemical etching method with sonication. Initially, numerous Ag NPs with different sizes are deposited on the wafer
surface and fabricate lots of nanopores with different diameter and length (Figure 1.7a). However, there is also a thin layer of fine etched material that is easily removed by sonication during the etching reaction (Figure 1.7b). Thus, the shallow nanopores are removed with the top surface and only larger and longer nanopores are left on the Si wafer. This results in some of the Ag NPs originally at the nanopore bottoms to partially emerge on the surface again and explains why the number of nanopores on the wafer surface significantly decreases with the etching time.

At the same time, the Ag ions in the etchant aggregate on the re-emerged Ag NPs to form larger NPs because the Ag NPs on the wafer surface can transfer negative charges from the Si to the Ag ions for Ag formation; also, the total free energy of the Ag NP surfaces would be effectively decreased (Figure 1.7c). With larger Ag NPs, nanopores with larger diameters are formed since the nanopores are the sinking tracks of Ag NPs. After a certain period of time, the Ag NPs have sunk too deeply to effectively attract the Ag ions. Hence, many newly formed small Ag NPs deposit on the top Si wafer surface instead of on the Ag NPs at the nanopore bottoms (Figure 1.5g and Figure 1.7d). This proposed mechanism explains the observation that the number of nanopores decreases with the etching time; however, for the growth of nanopore diameter, both our mechanism and the Zhong mechanism may need to be taken into consideration.

It is also worth mentioning that as the [HF] and [H₂O₂] in the etchant decrease, the shapes of nanopores change from circles to squares (e.g., Figure 1.5a, c, and e). A possible explanation is that as the [HF] and [H₂O₂] are higher, the Si etching rate is relatively faster, so the Si under the Ag NPs can be easily etched and form the circular nanopores which are projected outlines of the NPs on the Si wafer surface. Nevertheless, when the [HF] and [H₂O₂] decrease, the Si etching rate slows down leading that the SiO₂ formation and the etching processes prefer to occur along the direction of Si-Si bonding because the bonding possesses a higher free energy and is favourable for the chemical reactions. Since the
Figure 1.7. Schematic illustration of the proposed formation process of large nanopores on the surface of the Si wafer during the one-step Ag-assisted chemical etching method with sonication: (a) nanopores are formed on the Si surface, (b) loose fragments are removed by sonication, (c) new Ag NP deposit near existing NPs, and (d) larger Ag NPs are formed and produce nanopores with larger diameters.
network of Si-Si bonding of the (100) Si wafer surface is square, the obtained outlines of
nanopores from the chemical etching are consequently square as well.

**Ag ion concentration of 5 μM.** Further decreasing the [Ag⁺] to 5 μM maintains the
formation of nanopores on the Si wafer surface, but the nanopores have smaller diameters
and shorter lengths compared to those synthesized with the 50 μM [Ag⁺] for the same
etching conditions (see Figure 1.5 and Figure 1.8). For instance, with an etching time of 10
min, the maximum diameter and length of nanopores synthesized with 5 μM [Ag⁺] and
HF:H₂O₂:H₂O ratio of 1:5:2 is 180 nm and 2.4 μm, respectively, versus 230 nm and 4.1
μm for those synthesized with 50 μM [Ag⁺]. The reason is that the lower [Ag⁺] system
needs more time to grow Ag NPs for the Si etching, thus, it delays the formation of
nanopores, as well as effects the size of the nanopores.

In addition, with the slower rate of Ag NP formation, the nanopore size is more
uniform and better controlled since the difference in size between each Ag NP is smaller.
Figure 1.8 shows SEM images of the morphology of the Ag-removed b-Si synthesized by
the Si etchant containing 5 μM Ag ions for 10 minutes etching and various HF:H₂O₂:H₂O
ratios. Similar to the b-Si synthesized with 50 μM [Ag⁺], the nanopore size on the b-Si
synthesized with 5 μM [Ag⁺] decreases as the concentration of HF and H₂O₂ decrease as
well. After 10 minutes etching, the maximum nanopore diameter and length of the b-Si
fabricated with HF:H₂O₂:H₂O ratio of 1:5:20 is only around 70 nm and 90 nm, respectively
(Figure 1.8e and f). This once again shows that [HF] and [H₂O₂] significantly affect on Ag
NP growth that has a direct relation with the nanopore formation.

**Effects of relative HF:H₂O₂ ratios on b-Si surface morphology.** The relative ratio
of HF:H₂O₂ is also an important parameter for nanopore formation of the b-Si. Figure 1.9
shows SEM images of the surface morphology synthesized with 5 μM [Ag⁺] and the
different relative ratios of HF:H₂O₂. From Figure 1.9, it can be seen that the diameters of
**Figure 1.8.** SEM images of the morphology of b-Si samples synthesized by the Si etchant containing 5 μM [Ag⁺] with 10 minutes etching and various HF:H₂O₂:H₂O ratios. Top views: (a) 10 min, 1:5:2 (c) 10 min, 1:5:5 (e) 10 min, 1:5:10 (g) 10 min, 1:5:20. Cross views: (b) 10 min, 1:5:2 (d) 10 min, 1:5:5 (f) 10 min, 1:5:10 (h) 10 min, 1:5:20.
nanopore decrease with the volume portion of H$_2$O$_2$. The lower the H$_2$O$_2$ concentration in the Si etchant the smaller the Ag NPs that are formed, and consequently smaller nanopores. As the HF:H$_2$O$_2$:H$_2$O ratio reaches 5:1:20, almost all the nanopores on the Si wafer surface are mesopores (2-50 nm) and the nanopore size distribution is decently uniform (Figure 1.9g).

The H$_2$O$_2$ in the etchant not only helps the formation of Ag NPs but also assisted the oxidation of Si under the Ag NPs (Eq. 1.5). The SEM image shown in Figure 1.10 is of a sample prepared with 10 minute etching using a solution comprising 5 μM [Ag$^+$] and a ratio of HF:H$_2$O$_2$:H$_2$O = 6:0:20. As can be seen, without H$_2$O$_2$ there only few Ag NPs deposited on the Si wafer, which results in the Si wafer surface with a low-level texturized surface even though [HF] is sufficient to act as an etchant. This image proves that the addition of H$_2$O$_2$ is beneficial for the nanopore formation.

When the relative ratio of HF:H$_2$O$_2$ increases and the overall HF:H$_2$O$_2$:H$_2$O ratio is 3:3:20, the nanopore length reaches its maximum (690 nm) for 10 minute etching time (Figure 1.9d). However, if the relative ratio of HF:H$_2$O$_2$ is further increased, the nanopore length decreases and finally reaches its maximum of 250 nm with a ratio of HF:H$_2$O$_2$:H$_2$O of 5:1:20. A possible explanation of this result is that the equivalent volume ratio of HF:H$_2$O$_2$ (i.e., 3:3:20) can provide sufficient H$_2$O$_2$ for SiO$_2$ formation and sufficient HF for SiO$_2$ etching in order for the reactions to occur simultaneously. If the HF concentration is relatively low (i.e., HF:H$_2$O$_2$:H$_2$O = 1:5:20) the HF in the etchant is not sufficient to immediately remove the as-formed SiO$_2$ under the Ag NPs; conversely when the H$_2$O$_2$ concentration is relatively low (i.e., HF:H$_2$O$_2$:H$_2$O = 5:1:20) the H$_2$O$_2$ in the etchant is not sufficient to immediately oxidize the Si under the Ag NPs into SiO$_2$ for the consequent etching. Both extremes result in a slowing the etch rate and a decrease in the length of the pores.
Figure 1.9. SEM images of the morphology of b-Si synthesized by the Si etchant containing 5 μM [Ag⁺] with 10 minute etching and various HF:H₂O₂:H₂O ratios. Top views: (a) 2:4:20 (c) 3:3:20 (e) 4:2:20 (g) 5:1:20. Cross views: (b) 2:4:20 (d) 3:3:20 (f) 4:2:20 (h) 5:1:20.
Interestingly, the growth of nanopores is limited if the sonication treatment is not utilized during the Si etching. Without sonication, the nanopore length observed is significantly shorter compared to the ones etched with sonication treatment causing no nanopores can be clearly observed from the cross-sectional SEM images. This indicates the growth of nanopore length is suppressed more significantly than the growth of nanopore diameter in the absence of sonication. Furthermore, this result provides strong evidence that the sonication treatment can assist the HF and Ag ions to diffuse into the nanopore, effectively increasing the etching rate.

Effects of b-Si surface morphology on b-Si surface reflectivity. The morphology of b-Si directly affects the anti-reflection (AR) abilities. After the Ag NPs on the Si wafer surface are removed via the Ag etchant (see Experimental), the relative reflectivity of b-Si is measured for the light wavelengths of 300-1000 nm and compared to the cleaned and un-etched Si wafer whose relative reflectivity is set as 100.00%. A plot of the relative reflectivity as a function of wavelength is shown in Figure 1.8. As may be seen the
reflectivity is highly uniform across a wide range of wavelengths, in particular across the solar spectrum. A summary of the relative effective reflectivity for the samples is given in Table 1.1. There is a question as to whether our treatment results in a b-Si surface or simply a textured surface. The shape of our relative reflectivity curves (Figure 1.11) show the same trend and shape (i.e., higher reflectivity at higher wavelength for incomplete b-Si formation) as those reported by Branz et al.,\textsuperscript{26} as well as well-defined porous Si AR layers prepared by other routes.\textsuperscript{30,31}

**Table 1.1. Summary of relative reflectivity data for b-Si samples.**

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Figure 1.11. Plot of relative reflectivity for b-Si formed using $[Ag^+] = 50$ M, with a HF:H$_2$O$_2$:H$_2$O ratio of 1:5:2, and an etching time of 2 min (black), 5 min (blue), 10 min (red), and 20 min (green). The solar spectrum is overlain (yellow).

In order to graphically compare the various catalyst:etch treatments the relative effective reflectivity was categorized into five groups (<5, 5-10, 10-25, 25-50, 50-100). Figure 1.12 shows the relative effective reflectivity of b-Si samples synthesized with different etching conditions. Generally, the relatively reflectivity of all samples decreases with etching time due to the longer nanopores. The longer nanopores provide a slower gradient change of refractive index within the b-Si surface; hence, they can more effectively suppress the reflection on the Si wafer surfaces.

When the Ag ion concentration is 500 μM, all the relative effective reflectivity of sample is above 5% because only shallow pits are formed on the Si surfaces. However, the shallow pits also become deeper with time and make the surface rougher which still suppresses the reflection of wafer surface in a certain level (see Table 1.1). As compared to the b-Si synthesized with $[Ag^+] = 500$ μM, the samples synthesized with $[Ag^+] = 50$ μM show much better AR properties. With 50 μM $[Ag^+]$, the nanopores are formed on the Si
Figure 1.2. Schematic plot of the average relatively reflectivity of b-Si with various [Ag⁺], etching time, and HF:H₂O₂:H₂O ratio as 1:5:Z.

surface and grow with the etching time allowing the b-Si samples to possess extremely low reflectivity. As the HF and H₂O₂ concentrations increase, the formed nanopores become longer which further lowers the reflectivity of the wafer surfaces. For example, the b-Si synthesized with 20 minute etching and the HF:H₂O₂:H₂O ratio of 1:5:2 shows an relative effective reflectivity of 0.17%, which is the lowest of the samples studied. For the b-Si synthesized with the same [Ag⁺] and etching time but different HF:H₂O₂:H₂O ratios, the relative effective reflectivity increases with lower [HF] and [H₂O₂].

The b-Si fabricated with [Ag⁺] = 5 µM effectively decreases the reflection of the Si wafer surface as well. However, the relative effective reflectivity is lower than the ones fabricated with 50 µM [Ag⁺] because of the shorter nanopore length. The relative effective reflectivity also decreases with the etching time, similar to the b-Si fabricated with 50 µM
[Ag⁺]. With etching time of 10 minutes, the relative effective reflectivity increases with increased dilution (i.e., lower [HF] and [H₂O₂]), see Table 1.1. A similar trend is observed for 20 min etching as well.

It was also found that the relative effective reflectivity decreases as the relative ratio of HF:H₂O₂ increases (Figure 1.13). With etching time of 10 minutes, the relative effective reflectivity decreases with increased HF:H₂O₂ ratio (i.e., decreased [H₂O₂]). This indicates that when the nanopores are short, the effect of nanopore length on reflectivity becomes less significant, and the nanopore size uniformity starts to dominate the reflectivity. Typically, a p-n junction interface in a Si solar cell is about 500 nm below the Si wafer top surface. The maximum nanopores length of b-Si synthesized with the 5 μM [Ag⁺] and HF:H₂O₂:H₂O ratio of 5:1:20 is only around 250 nm, this indicates the synthesized b-Si is favorable for the AR layer of Si solar cells. With these extremely short nanopores, the p-n junction interface will not be destroyed by the nanopore structures during the fabrication process of AR layer via the one-step Ag-assisted chemical etching.

![Figure 1.13](image)

**Figure 1.13.** Plot of the average relatively reflectivity of b-Si with 5 μM [Ag⁺] and various etching time and HF:H₂O₂:H₂O ratio as X:Y:20.
Conclusions

The one-step Ag-assisted chemical etching method we used is a simple and economical technique for rapidly synthesizing nanopore-type b-Si. Our results indicate that the b-Si morphology, which directly affects the reflectivity degree, possesses high dependence on the [Ag\(^+\)], the HF:H\(_2\)O\(_2\):H\(_2\)O volume ratio, and the etching time. The lowest relative effective reflectivity of b-Si that we obtained is 0.17% with the HF:H\(_2\)O\(_2\):H\(_2\)O ratio of 1:5:2 and [Ag\(^+\)] = 50 μM. By adjusting the HF:H\(_2\)O\(_2\):H\(_2\)O ratio to 5:1:20, we can even use further lower [Ag\(^+\)], 5 μM, to fabricate the b-Si whose relative effective reflectivity still reaches 2.60%.

Our b-Si structure with smallest nanopore diameter (<30 nm) and shortest nanopore length (<250 nm) are similar to the structures synthesized by Branz et al. using a gold-assisted chemical etching.\(^{26}\) While, the relative effective reflectivity of this structure (2.60%) is not the lowest of our b-Si samples (0.17%), it is comparable to their lowest effective reflectivity for the similar sized features.\(^{26}\)

We propose that the simplicity of the process and low reaction times, along low consumption of Ag precursor will make such a one-step method scalable for industrial applications where process cost and rate are important. Moreover, the nanopore length of b-Si fabricated with 5 μM [Ag\(^+\)] can be controlled to be around 250 nm, which is shorter than a typical p-n junction depth in Si solar cells, and would not interfere with the function of the cell.

A comparison of our b-Si structures to those reported by Branz and co-workers for multi-step processes\(^{27}\) show that both of the b-Si materials have the similar morphology; the nanopore lengths are both under 500 nm and nanopore diameters are both under 100 nm. This implies that our b-Si is also potential to be used in Si solar cells for obtaining high-energy conversion efficiency. However, our fabrication process based on one-step silver-assisted chemical etching is less complicated than the multi-step process, which is based on a two-step silver-assisted chemical etching that still needs the extra third step to
modify the nanopore length. More importantly we have shown the relationship of silver concentration to the morphology of the b-Si, and that the concentration of AgNO$_3$ that we used for Ag NP formation (5 and 50 μM) is much lower than the concentration for the multi-step process (1 mM). This shows our fabrication process of b-Si is simple and economical. Also, the reflectivity of our b-Si is comparable to, or even lower than that of multi-step process, which is between 2-12% depending on TMAH etching time.

**Experimental**

All the reactions were carried out in sealed plasticware at room temperature. AgNO$_3$ (Sigma-Aldrich), HF (48%, Sigma-Aldrich), H$_2$O$_2$ (30%, EMD), and NH$_4$OH (30%, Fisher Scientific) were used as received. Polished single crystalline (100) p-type boron-doped Si wafers (Silicon Quest International), with resistivity of 1-5 Ω-cm, were individually ultrasonically cleaned in acetone and ultra-pure DI water.

The cleaned Si pieces were etched in Si etchants containing HF (48%), H$_2$O$_2$ (30%), and ultra-pure water in different volume ratios with an equal volume of 1000, 100 and 10 μM AgNO$_3$ aqueous solutions with sonication (Table 1.2), giving an overall [Ag$^+$] in the etchant of 500, 50, and 5 μM, respectively. In the text, the volume ratio is given as X:Y:Z corresponding to the volume ratio of HF, H$_2$O$_2$, and H$_2$O in the etchant, respectively. After etching for 2, 5, 10, or 20 min, the as-prepared b-Si samples were rinsed in ultra-pure DI water, and then cleaned by a Ag etchant consisting of NH$_4$OH and H$_2$O$_2$ in a 1:1 volume ratio at room temperature with sonication to remove the Ag NPs on the wafer surface. The Ag-removed samples were immersed in DI water again and dried by canned air.

The morphology and structure of b-Si samples in plane and cross section were characterized by using FEI Quanta 400 high-resolution field emission scanning electron microscope (FESEM). The Ag NP size on the Si wafer surface was characterized by using the image analysis program ImageJ. The reflectivity of b-Si samples was measured by using Ocean Optics HR2000+ high-resolution spectrometer with a Mikropack DH-2000-
BAL deuterium-halogen light source.

Table 1.2. Summary of etch solutions.

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<th>Volume of H$_2$O$_2$ (mL)$^b$</th>
<th>Volume of DI H$_2$O (mL)$^c$</th>
<th>Volume of mixture (mL)$^d$</th>
<th>Volume of AgNO$_3$ (μL)$^c$</th>
<th>Volume of DI H$_2$O (mL)</th>
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$^a$ 48% HF, $^b$ 30% H$_2$O$_2$, $^c$ [AgNO$_3$] = 0.01 M, $^d$ HF+H$_2$O$_2$+H$_2$O.
References

Chapter 2

Anti-reflection layers fabricated by a one-step copper-assisted chemical etching with inverted pyramidal structures intermediate between texturing and nanopore-type black silicon

Portions of this chapter are included in Y.-T. Lu and A. R. Barron, *J. Mater. Chem. A.*, 2014, 2, 12043. A reprint can be found in Appendix C.

**Introduction**

Low surface reflectance of a silicon (Si) solar cell, so as to maximize the amount of incident photons absorbed by the semiconductor to convert the incident light into electrical energy, is key for the efficiency. With a layer thickness matched to the refractive index based on the quarter-wavelength principle, an anti-reflection (AR) coating layer produces a destructive interference of the incident light to lower the reflectivity on the solar cell surface. For Si solar cells AR coatings are generally silicon nitride (SiN$_x$) produced by chemical vapor deposition. The resulting cells have a reflectance of about 6% as compared to 40% for a polished wafer. Another approach has been to texture the crystalline silicon (c-Si) surface with random or ordered patterns, which causes light to scatter into off-normal directions and thereby to increase its travel distance inside the c-Si wafer. The standard wafer texture process uses a potassium hydroxide–isopropyl alcohol (KOH–IPA) solution to form a random pyramid (ca. 10 μm) structure by anisotropic etching of the Si surface. AR thin films are used for both planar and textured Si solar cells; however, the most significant drawback of the AR coating layers is that the AR ability of the layers is limited in a specific range of light incident angle and wavelength.

Black silicon (b-Si) is a surface modification of Si where a nanoscale surface structure is formed through etching and represents a potential replacement for the conventional AR coating. The resulting nanoscale structure provides an extremely low
reflectivity of close to $0\%$.$^7$–$^{10}$ The nanoscale structure may be in the form of inverted nanoscale cones (i.e., with the tip of the cones pointing upward away from the Si surface) or a series of nanoscale pores of varying depths and diameters extending into the surface.$^{10}$ The low reflectance from a b-Si surface is not caused by light trapping since the features are an order of magnitude smaller than the wavelength of light incident on the surface. Instead, a thin layer possessing a gradient change of refractive index eliminates any abrupt interface such that no reflection occurs.$^{11}$–$^{13}$

B-Si has been successfully fabricated via many techniques including laser irradiation, reactive ion etching, plasma etching, electrochemical etching, and metal-assisted chemical etching (MACE).$^{10}$ Among these methods, the MACE method$^{14,15}$ is the most economical and facile since it does not rely on high energy consumption or complicated processes. The MACE method usually includes two steps, metal deposition and electroless chemical etching. The metal, such as gold or silver, deposited on the Si wafer surface can attract electrons from the wafer surface and causes the oxidation of Si to SiO$_2$, which is then etched by HF to form nanopores or nanowires. To further simplify the fabrication process of b-Si, one-step MACE methods based on the two-step MACE method have been developed. In the one-step MACE method, the metal deposition and the electroless chemical etching occur simultaneously, which makes finding proper etching conditions more challenging. Branz et al. first developed a one-step Au-assisted chemical etching method to fabricate nanopore-type b-Si with the etchant consisting of HAuCl$_4$:HF:H$_2$O$_2$:H$_2$O. The Au nanoparticles (NPs) formed on the Si wafer surface accelerated the oxidation rate of Si underneath them.$^{16}$ In our previous research, we utilized a mixture of AgNO$_3$:HF:H$_2$O$_2$:H$_2$O to prepare b-Si via one-step Ag-assisted chemical etching method.$^{17}$ A low relative effective reflectivity, 0.17%, was achieved and the correlation between the b-Si morphology, the [Ag$^+$], the HF: H$_2$O$_2$: H$_2$O volume ratio, and the surface reflectivity was systematically determined.
Developing a lower cost alternative metal precursor for the MACE method to further cut down the fabrication cost of b-Si is attracting attention. In previous studies, copper (Cu) NPs have been utilized for fabricating porous Si with a two-step Cu-assisted etching method. As with other metal catalysts, the Cu has a higher electronegativity than Si (1.9 versus 1.8, respectively) allowing the withdraw of electrons from the vicinity of the Si substrate. In this way, Si is oxidized to SiO$_2$ and etched by HF. However, instead of the desirable nanopores or nanowires only shallow pits were formed on the Si surface limiting the effectiveness of the surface as an AR layer. Based upon our results with the one-step Ag-assisted chemical etching system, we surmise that the reason for the shallow pit morphology may be due to the extremely small size of the deposited Cu NPs and the dissolution of the Cu NPs in the etchant. The size of the Cu NPs is limited since the etchant solutions did not contain a component to reduce Cu$^{2+}$ ions to Cu$^{0}$ and thus increase/maintain the size of the NPs.

In the present study, we report a one-step Cu-assisted chemical etching method using H$_3$PO$_3$ as a reducing agent in the Cu(NO$_3$)$_2$:H$_3$PO$_3$:HF:H$_2$O system to reduce Cu$^{2+}$ ions to Cu NPs on the wafer surface. Furthermore, we have systematically investigated the effects of the [H$_3$PO$_3$], the [Cu$^{2+}$], and the HF:H$_2$O volume ratios on the b-Si morphology with the corresponding reflectivity of the Si wafer surface.

**Results and Discussion**

Previous metal catalyzed chemical etching processes have used a combination of H$_2$O$_2$:HF as the etchant. The function of the H$_2$O$_2$ is to reduce the M$^{m+}$ to M$^{0}$ in the form of a NP. However, in the case of copper, the oxidization potential of H$_2$O$_2$ ($E = -0.695$ V) is too low to reduce the Cu$^{2+}$ ($E = 0.399$ V). This is evidenced from the SEM image of a Si surface exposed to a solution of Cu$^{2+}$ and H$_2$O$_2$, which shows no Cu NPs on the Si wafer substrate. As an alternative to H$_2$O$_2$, phosphorous acid (H$_3$PO$_3$) is used to reduce Cu$^{2+}$ to Cu NPs (Eq. 2.1).
\[
\text{Cu}^{2+} + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Cu}^0 + \text{H}_3\text{PO}_4 + 2\text{H}^+ 
\] (2.1)

Since Cu has a higher electronegativity than Si, the Cu\(^0\) formed on the Si surface attract electrons from Si and become negatively charged. In this way, the Cu\(^{2+}\) ions in the etchant solution would be attracted to the Si surface and obtain electrons from the charged Cu NPs, and then deposit around the Cu NPs. During the Cu NP growth, the Si around Cu is continuously oxidized to SiO\(_2\), which is etched by HF so that nanopores are formed around the Cu NPs. Hence, the size of the Cu NPs and nanopores would keep increasing with time as long as the [Cu\(^{2+}\)] and [HF] are sufficient.

The Cu NPs on the b-Si can be easily removed by being immersed in the copper etchant. Table 2.1 shows a comparison of the atomic concentrations on the b-Si surface before and after Cu removal. With Cu removal treatment, Cu atomic concentration is effectively decreased to less than 0.1% and Si atomic concentration increases to more than 50% since the majority of Si wafer surface appears (Table 2.1).

**Table 2.1.** Summary of atomic concentrations on surface of b-Si samples before and after Cu removal.

<table>
<thead>
<tr>
<th>[Cu(^{2+})] (µM)</th>
<th>[H(_3)PO(_3)] (mM)</th>
<th>HF:H(_2)O</th>
<th>Etching time (hr)</th>
<th>Cu removal</th>
<th>Atomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>10</td>
<td>1:4</td>
<td>8</td>
<td>Before</td>
<td>C (%)    23.77    O (%) 31.08 F (%) 0.62 Si (%) 33.76 P (%) 4.54 Cu (%) 6.22</td>
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<tr>
<td>50</td>
<td>10</td>
<td>1:4</td>
<td>8</td>
<td>After</td>
<td>C (%)    6.09     O (%) 35.35 F (%) 0.23 Si (%) 52.87 P (%) 5.40 Cu (%) 0.05</td>
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<tr>
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<td>8</td>
<td>Before</td>
<td>C (%)    23.53    O (%) 32.72 F (%) 0.42 Si (%) 35.18 P (%) 3.91 Cu (%) 4.23</td>
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<tr>
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<td>1:7</td>
<td>8</td>
<td>After</td>
<td>C (%)    6.03     O (%) 32.53 F (%) 0.23 Si (%) 56.21 P (%) 4.92 Cu (%) 0.09</td>
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<td>8</td>
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<td>C (%)    21.91    O (%) 32.60 F (%) 0.47 Si (%) 37.06 P (%) 4.42 Cu (%) 3.54</td>
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<td>50</td>
<td>10</td>
<td>1:15</td>
<td>8</td>
<td>After</td>
<td>C (%)    5.55     O (%) 36.54 F (%) 0.22 Si (%) 52.99 P (%) 4.67 Cu (%) 0.04</td>
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Effect of [H$_3$PO$_3$]. Based upon our prior work with Ag one-step process,$^{17}$ we chose an initial [Cu$^{2+}$] = 50 μM. At this concentration pores are obtained on the wafer surface; however, the surface morphology and relative reflectivity are significantly affected by the [H$_3$PO$_3$]. Figure 2.1 shows SEM images of b-Si synthesized with Si etchants containing [Cu$^{2+}$] = 50 μM with a HF:H$_2$O volume ratio = 1:7 and various [H$_3$PO$_3$] for 2 hour etching.

As can be seen, no nanopores are formed on the wafer surface in the absence of H$_3$PO$_3$. Instead, a few shallow pits are found on the wafer surface (Figure 2.1a and b), which are not able to effectively suppress the reflection on the Si wafer. Once the [H$_3$PO$_3$] increases to 10 mM, inverted pyramid-like nanopores are formed on the wafer surface with a maximum nanopore length of 670 nm (Figure 2.1c and d). As [H$_3$PO$_3$] is increased to 25 mM the size of the pores increases (Figure 2.1e and f). However, it is interesting that the maximum pore depth is not significantly affected (670 and 580 nm for 10 and 25 mM), respectively (Figure 2.1d and f). Further increasing the [H$_3$PO$_3$] results in a highly textured surface but with only shallow pores (Figure 2.1g and h).

The relative reflectivity for the resulting Si surfaces were measured over a wavelength range from 300 to 1000 nm and compared to a cleaned and un-etched Si wafer whose relative reflectivity is defined as 100% (Table 2.2). The surface prepared using [H$_3$PO$_3$] = 10 mM shows the lowest relative effective reflectivity across the spectrum (Figure 2.2) with an relative effective reflectivity of 10.44% and a minimum of 7.92% at 461 nm.

The increase in [H$_3$PO$_3$] results in an evolution from pits to nanopores to shallow craters (Figure 2.1) with a concomitant decrease then increase in the reflectivity (Figure 2.2). We propose a possible mechanism to explain this trend and Figure 2.3 shows a schematic and the SEM images for the formation of pits, nanopores, and shallow craters on the Si wafer surface with various [H$_3$PO$_3$].
Figure 2.1. Surface and cross-sectional SEM images of b-Si (after removal of the Cu) prepared with etchants containing [Cu$^{2+}$] = 50 µM with a HF:H$_2$O volume ratio = 1:7, 2-hour etching in the absence of H$_3$PO$_3$ (a,b) and with various [H$_3$PO$_3$]: 10 mM (c,d), 25 mM (e,f), and 50 mM (g,h). Scale bars = 1 µm (d, f, and h) and 2 µm (a–c, e, and g).
Table 2.2. Summary of relative reflectivity data for b-Si samples.

<table>
<thead>
<tr>
<th>[Cu²⁺] (µM)</th>
<th>[H₃PO₃] (mM)</th>
<th>HF:H₂O Etching time (hr)</th>
<th>Relative reflectivity @ 300 nm (%)</th>
<th>Relative reflectivity @ 1000 nm (%)</th>
<th>Relative effective reflectivity (%)</th>
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<tbody>
<tr>
<td>500</td>
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Figure 2.2. Plot of relative reflectivity as a function of wavelength (300 to 1000 nm) for b-Si, prepared using \([\text{Cu}^{2+}] = 50 \, \mu\text{M}\) with a HF : H\(_2\)O volume ratio = 1:7 and \([\text{H}_3\text{PO}_3]\) of 0 mM (a), 10 mM (b), 25 mM (c), and 50 mM (d) for 2 hour etching compared to a cleaned and un-etched Si wafer.

In the absence of H\(_3\text{PO}_3\) the formation and growth of Cu NPs would be limited, such that only few and small Cu NPs would be randomly deposited on the Si wafer surface. Figure 2.3a shows the formation of 20–100 nm Cu NPs. The subsequent oxidation/etching of the Si causes the formation of small and shallow pits under the Cu NPs. Because there are no nanopores the reflectivity is still high. Furthermore, the texturing will result in a highly wavelength dependent reflectivity (Figure 2.2) similar to that observed by an unpolished wafer. It is interesting to note that the pores are significantly larger than the deposited Cu NPs. Given that the etching by HF is of the oxidized surface, this suggest that the region of oxidized Si extends at some distance from the Cu NP.
Figure 2.3. Schematic illustration and SEM images of the formation of nanopores and shallow craters on Si wafer surface with various $\left[ \text{H}_3\text{PO}_3 \right]$ via the one-step Cu-assisted chemical etching method. (a) No $\left[ \text{H}_3\text{PO}_3 \right]$, (b) $\left[ \text{H}_3\text{PO}_3 \right] = 10 \text{ mM}$, and (c) $\left[ \text{H}_3\text{PO}_3 \right] = 50 \text{ mM}$. In the SEM images, the Cu NPs have not been removed.

When a low $\left[ \text{H}_3\text{PO}_3 \right]$ (10 mM) is added to the Si etchant, the reduction rate of Cu$^{2+}$ is much faster allowing more Cu NPs to be formed on the wafer (Figure 2.3b). These Cu NPs continuously attract electrons from the wafer then transfer them to the nearby Cu$^{2+}$ ions present in the solution. This results in more Cu$^0$ being deposited around the existing Cu NPs and more Si to be oxidized to SiO$_2$ (Figure 2.3b). Therefore, the size of Cu NPs (40–130 nm) and the diameter of the resulting nanopores (70–400 nm) can keep growing. The taper shape of pyramid-like nanopores provides a gradient refractive index within the b-Si surface, which can effectively suppress the reflection on the wafer surface (Figure 2.2).

At high $\left[ \text{H}_3\text{PO}_3 \right]$ (50 mM) the reduction of Cu$^{2+}$ will be further faster allowing more and larger Cu NPs to be produced on the wafer surface. However, these larger Cu NPs cover the majority of the Si wafer surface (Figure 2.3c). This situation induces overlapping regions of oxidation and accordingly more isotropic Si etching. The result is that only wide and shallow craters form rather than nanopores. Compared to the b-Si fabricated with the
lower $[\text{H}_3\text{PO}_3]$, these shallow craters cause the entire wafer surface to be relatively smoother which weakens the AR ability of Si surface (Figure 2.3).

We conclude therefore that the size of the pores are controlled by $[\text{H}_3\text{PO}_3]$ and the subsequent size of the Cu NPs. This would suggest that the depth of the pores are mainly limited by [HF] and the etching time.

**Effect of etching time.** Figure 2.4 shows SEM images of samples synthesized by using Si etchant containing 50 μM $[\text{Cu}^{2+}]$ for various etching time. When the etching time increases, the nanopores become larger and longer on the Si wafer surface (Figure 2.4a–d). As long as [HF] is sufficient, the Cu NPs can continue catalyzing the Si etching increasing the nanopore length. The sample consisting of deeper nanopores have a slower gradient change of refractive index; therefore, it can more effectively suppress the reflection on the Si wafer surface. For instance, with 50 μM $[\text{Cu}^{2+}]$ and HF:H$_2$O volume ratio = 1:7, the maximum length and relative reflectivity of nanopores synthesized for 2 h etching is 670 nm (Figure 2.4b) and 10.44%, respectively. Once the etching time increases to 8 h, the maximum length of nanopores increases to 1.6 μm (Figure 2.4d) and the relative effective reflectivity drops to 7.77% (Table 2.2).

**Effect of HF:H$_2$O volume ratio.** The relative volume ratio of HF:H$_2$O (i.e., [HF]) also plays an important role in the nanopore formation. With 8 hour etching, compared to the sample prepared with the HF:H$_2$O volume ratio of 1:7, both samples fabricated with the HF:H$_2$O volume ratio as 1:4 and 1:15 have shorter maximum nanopore length and higher relative effective reflectivity, which are 1.4 μm (Figure 2.4f) and 9.97%, and 1.2 μm (Figure 2.4h) and 9.44%, respectively (Figure 2.5). It is easy to see that the b-Si fabricated with HF:H$_2$O = 1:15 has the shortest nanopore length since a lower [HF] leads to a slower Si etching rate on the wafer surface. However, b-Si fabricated with HF:H$_2$O = 1:4 also has slightly shorter nanopores and higher relative effective reflectivity than b-Si
Figure 2.4. SEM images of b-Si synthesized by using Si etchants containing 50 μM [Cu²⁺] and 10 mM [H₃PO₃] for various etching time and HF : H₂O volume ratios: 2 h, 1:7 (a and b); 8 h, 1:7 (c and d), 8 h, 1:4 (e and f); 8 h, 1:15 (g and h). Scale bars = 1 μm (b), 2 μm (a, d, f, and h), and 5 μm (c, e, and g).
fabricated with HF:H₂O = 1:7 since excess of HF molecules etches not only the Si under the Cu NPs but also the Si around the Cu NPs. This situation causes a decrease of difference in height levels between the nanopore bottoms and the wafer surface so that the nanopores have a shorter length. Besides, the HF:H₂O = 1:4 ratio also provides a faster Si etching rate which allows larger nanopores to be formed on the wafer surface. Some of these large nanopores connect with each other and merge into further larger craters, which lowers the nanopore population density. Both the shorter nanopore length and the lower nanopore population density are not favorable for suppressing the reflection of the Si wafer surface, and therefore the b-Si sample fabricated with HF:H₂O volume ratio of 1:4 shows higher reflectivity than that fabricated with a ratio of 1:7 (Figure 2.5 and Table 2.2).

Figure 2.5. Plot of relative reflectivity as a function of wavelength (300 to 1000 nm) of samples synthesized using 50 μM [Cu²⁺] and 10 mM [H₃PO₃] for various etching time and HF : H₂O volume ratios: 2 h, 1:7 (a); 8 h, 1:7 (b), 8 h, 1:4 (c); 8 h, 1:15 (d).
**Effect of [Cu^{2+}].** As may be expected reducing the [Cu^{2+}] to 5 μM results in the nanopore population density to be lower compared to samples prepared with 50 μM [Cu^{2+}]. Figure 2.6 shows SEM images of b-Si synthesized by using Si etchants containing 5 μM [Cu^{2+}] for various etching time and HF:H_{2}O volume ratios. Similar to samples synthesized with 50 μM [Cu^{2+}], the nanopore length increases and the surface reflectivity decreases with etching time. With a HF:H_{2}O volume ratio of 1:7, the maximum nanopore length increases from 470 nm to 1.5 μm (Figure 2.6b and d) as the etching time increases from 2 h to 8 h. This improves the relative effective reflectivity from 55.17% to 22.54% (Table 2.2). With 8 h etching time and HF:H_{2}O ratios as 1:4 and 1:15, b-Si has maximum nanopore lengths and relative effective reflectivity of 1.6 μm (Figure 2.6f) and 39.44%, and 1.3 μm (Figure 2.6h) and 43.37%, respectively. Although the b-Si fabricated with 5 μM and 50 μM [Cu^{2+}] have similar maximum nanopore lengths, the relative effective reflectivity of the former ones are much higher than the latter ones (9.97% for HF : H_{2}O = 1:4, 7.77% for HF:H_{2}O = 1:7, and 9.44% for HF:H_{2}O = 1:15), see Table 2.2. The main reason for these observations is a lower population density and less uniform distribution of nanopores over the Si wafer surface.

Also, comparing the b-Si synthesized with 5 μM [Cu^{2+}] but different HF:H_{2}O volume ratios, the b-Si fabricated with a HF:H_{2}O = 1:7 has a higher nanopore population density (Figure 2.6c) and the lowest relative effective reflectivity (Table 2.2). When the HF:H_{2}O volume ratio is 1:15, the population density of nanopore becomes lower leading to a higher relative reflectivity because the [HF] in the etchant is insufficient; hence, the HF etches fewer areas on the wafer surface (Figure 2.6g). For the HF:H_{2}O volume ratio of 1:4, the [HF] is high enough to more effectively etch the Si wafer and form more nanopores. However, most of the nanopores connect with each other and form larger irregular nanopores, which decreases the nanopore population and is detrimental for the reflectivity (Figure 2.6e).
Figure 2.6. SEM images of b-Si synthesized by using Si etchants containing 5 μM [Cu$^{2+}$] and 10 mM [H$_3$PO$_3$] for various etching time and HF:H$_2$O volume ratios: 2 h, 1:7 (a and b); 8 h, 1:7 (c and d); 8 h, 1:4 (e and f); 8 h, 1:15 (g and h). Scale bars = 1 μm (b), 2 μm (a, d, f, and h), and 5 μm (c, e, and g).
As expected, increasing [Cu$^{2+}$] to 500 μM results in a more porous surface. Figure 2.7 shows SEM images of b-Si synthesized with Si etchants containing 500 μM [Cu$^{2+}$] for various etching time and HF:H$_2$O volume ratios. Compared to the samples synthesized with the lower [Cu$^{2+}$], the b-Si synthesized with 500 μM [Cu$^{2+}$] has a higher nanopore population density, which leads to a lower relative reflectivity. With 500 μM [Cu$^{2+}$] after 8 h etching, all the samples have extremely low relative reflectivity below 5% (Figure 2.8).

Unlike the b-Si prepared with the lower [Cu$^{2+}$], the nanopore size and length of b-Si prepared with 500 μM [Cu$^{2+}$] decrease when the HF:H$_2$O volume ratio decreases. The samples fabricated with HF:H$_2$O ratio = 1:4 has the fastest Si etching rate causing large and long nanopores (Figure 2.7e and f), whose maximum length is around 2.4 μm. Although the nanopores connect with each other at a certain level and merge into larger irregular nanopores due to the faster Si etching rate, the relative effective reflectivity is still low, 3.06%. As the HF:H$_2$O volume ratio decreases to 1:7, the maximum nanopore length decreases to 1.4 μm (Figure 2.7d) and the relative effective reflectivity decreases to 2.72% (Figure 2.8).

Interestingly, the samples synthesized with the lowest [HF], HF:H$_2$O = 1:15, has the shortest nanopore length, 590 nm (Figure 2.7h), and also the lowest relative reflectivity, 0.96%, among all the samples reported herein. This extremely short nanopore length is ideal for AR layer application in Si solar cells since the depth of p–n junction in Si solar cells is usually less than 1 μm. If the nanopore length were longer than the depth of p–n junction, the nanopores would penetrate the junction and result in a short circuit.

**Conditions for optimized reflectivity.** The low relative effective reflectivity of b-Si can be attributed to the uniform distribution of the nanopores and the high nanopore population density. As the [HF] is lower (i.e., HF:H$_2$O = 1:15), the Si etching rate is consequently slower which is beneficial for keeping the nanopores from merging into larger ones so that the surface reflection can be better suppressed. Besides, comparing
Figure 2.7. SEM images of b-Si synthesized by using Si etchants containing 500 μM [Cu$^{2+}$] and 10 mM [H$_3$PO$_3$] for various etching time and HF:H$_2$O volume ratios: 2 h, 1: 7 (a and b); 8 h, 1:7 (c and d); 8 h, 1:4 (e and f); 8 h, 1:15 (g and h). Scale bars = 1 μm (b and h), 2 μm (a and d), 3 μm (f), and 5 μm (c, e, and g).
samples synthesized with HF:H₂O = 1:15 but different [Cu²⁺], it is found that the b-Si prepared with 500 μM has a shorter nanopore length. The possible explanation for this observation might be that samples prepared with a higher [Cu²⁺] have much more Cu NPs on the entire wafer surface; hence, the HF molecules are consumed relatively less on individual NPs resulting in a slower local nanopore growth, or shorter nanopore length.

In order to better compare the relative reflectivity of b-Si prepared with different etching conditions, the relative effective reflectivity is categorized into five groups, which are <5%, 5–10%, 10–25%, 25–50%, and >50%. Figure 2.9 shows the relative effective reflectivity of samples synthesized with different etching conditions. In general, the relative effective reflectivity of all the b-Si decreases with the etching time. The longer nanopores can more effectively suppress the reflectivity on the wafer surface due to the smoother
gradient change of refractive index. When $[\text{Cu}^{2+}] = 5 \, \mu\text{M}$, the relative effective reflectivity of Si wafer is high due to the low nanopore population density on the surface. However, once the $[\text{Cu}^{2+}]$ increases to 50 $\mu\text{M}$, more nanopores appear on the wafer surface and lead to a lower relative effective reflectivity. With 500 $\mu\text{M}$ $[\text{Cu}^{2+}]$, the fabricated b-Si has the highest population density of nanopores on the Si wafer and the most uniform distribution of nanopores on the wafer surface resulting in a relative effective reflectivity below 5%.

**Figure 2.9.** Schematic plot of the relative effective reflectivity of b-Si synthesized with various $[\text{Cu}^{2+}]$, etching time, and HF:H$_2$O volume ratios.

**Effect of PMMA over-layer.** In a Si solar cell with a traditional CN, AR coating the reflectivity is further improved during module formation. Polymethyl methacrylate (PMMA) is a photovoltaic encapsulation material that has a high light transmission, particularly in the region of the spectral response of the solar cell. It also allows for the heat treatment of solar cells during their manufacture and provides a photo-stability extended
over long periods of 20–25 years that PV manufacturers guarantee a minimum of 8% of the initial performance of their modules (Figure 2.10).

![Plot of relative reflectivity for b-Si formed using [Cu$^{2+}$] = 500 μM, with a HF:H$_2$O ratio of 1:15 and an etching time of 8 h before (black) and after (red) PMMA treatment. The solar spectrum is overlain (yellow).](image)

**Figure 2.10.** Plot of relative reflectivity for b-Si formed using [Cu$^{2+}$] = 500 μM, with a HF:H$_2$O ratio of 1:15 and an etching time of 8 h before (black) and after (red) PMMA treatment. The solar spectrum is overlain (yellow).

Table 2.3 shows a comparison of the reflectivity of selected samples with PMMA coating. In each case the reflectivity is decreased by as much as 50% by the addition of a PMMA over-layer. The AR property of b-Si is a function of the graded refractive index change between air ($n = 1.00$) and Si ($n = 3.42$). The addition of PMMA ($n = 1.48$) provides the same gradient but with an additional interface (air/PMMA). In contrast, traditional textured Si surfaces rely on light trapping by internal reflection. Again the additional air/PMMA interface should decrease reflectivity. As may be seen from Figure 2.10, there
is a decrease in relative reflectivity at longer wavelengths; however, a slight increase results across the key region of the solar spectrum.

Table 2.3. Summary of relative reflectivity data for b-Si samples after coating with PMMA.

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<tr>
<th>[Cu\textsuperscript{2+}] (µM)</th>
<th>[H\textsubscript{3}PO\textsubscript{3}] (mM)</th>
<th>HF:H\textsubscript{2}O Etching time (hr)</th>
<th>Relative reflectivity @ 300 nm (%)</th>
<th>Relative reflectivity @ 1000 nm (%)</th>
<th>Relative effective reflectivity (%)</th>
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Pore shape. An observation worth mentioning is the square outline of the pores in the one-step Cu-assisted method. We have previously found that the b-Si fabricated via the one-step Ag-assisted chemical etching method has circular nanopores, which are projections of the Ag NPs on the wafer surface.\textsuperscript{17} The standard reduction potential of Ag\textsuperscript{+} (\(E = 0.799 \text{ V}\)) is much higher than that of Cu\textsuperscript{2+} (\(E = 0.399 \text{ V}\)). As such Ag\textsuperscript{+} ions can more easily obtain electrons from nearby Si substrate to be reduced to Ag NPs that leads to a faster oxidation rate of Si and a faster formation rate of nanopores. This not only explains why fabricating b-Si structures via the MACE method takes minutes with Ag NPs but hours with Cu NPs, but also provides an indication of the significant differences in the nanopore length and shape. Figure 2.11 shows the nanopore shapes fabricated via Ag-assisted chemical etching method and Cu-assisted chemical etching method, respectively.
Figure 2.11. Schematic of nanopore shapes fabricated via Ag-assisted chemical etching method and Cu-assisted chemical etching method on a Si (100) wafer surface.

Since the Ag NPs can easily oxidize the nearby Si substrate, the Si material under the Ag NPs is continuously etched by HF, so the nanopores actually are the sinking track of the Ag NPs on the wafer surface and possess a slightly-taper cylinder shape in the cross-section (Figure 2.11a). On the other hand, due to the lower ability of withdrawing electrons of Cu NPs, the Cu NPs only attract electrons from the Si substrate where is easier oxidized to SiO₂ and etched by HF. On crystalline Si substrates, the Si etching rate is faster along the directions of [100] and [110] rather than [111]. For a Si (100) surface, the etching mainly occurs along the [100] and [110] directions and stops at the {111} planes; hence, the nanopores fabricated with the presence of Cu NPs would have inverted pyramid-like shapes (Figure 2.11b).

Traditional etching processes for texturing Si wafers occur through etching in the [100] direction (Figure 2.12a).²²,²³ As such the resulting structure is that of overlapping pyramids with features generally in the range of 1–5 μm. However, it has been suggested that greater efficiencies of light trapping are obtained by the formation of an inverted pyramid structure such as obtained herein (Figure 12b).¹,²⁴ Inverted pyramid-like structures are observed for plasma texturing with SF₆/O₂ at high radio frequency power.²⁵ However, the resulting inverted structures are poorly overlapping and far from the ideal inverted
pyramid structure that is desirable for light trapping.\textsuperscript{1,24} In contrast, the present one-pot Cu-assisted etch results in a texturing closer to the ideal structure for traditional light trapping.

\textbf{Figure 2.12.} Schematic of comparison of (a) traditional pyramidal texturing of Si surface and (b) the inverted pyramid structure created by the Cu-assisted chemical etching method.

It has been shown that if inverted pyramids are created with a texturing angle between 45° and 60° the spectral response is better than for pyramids.\textsuperscript{24} More importantly the optimum angle is 54°. The measured angles of the inverted pyramids formed by the Cu-assisted chemical etching method is 53.5–58.9° for all the samples (Figure 2.1, 2.4, 2.6 and 2.7), with the majority in the range 53.7–54.9°. In addition, the nano size of the features (<1 \textmu m) means that the low reflectivity may be not due to light trapping, but the presence of a gradient of refractive index associated with traditional b-Si structures.
Finally, the inverted pyramidal structure obtained using the one-pot Cu assisted etch system described herein represents a structural link between traditional texturing and the structural type of b-Si. The nanoscale structure of b-Si may be in the form of inverted nanoscale needles or cones (Figure 2.13a and b) or a series of nanoscale pores of varying depths and diameters extending into the surface.

![Figure 2.13](image)

**Figure 2.13.** Schematic representation of the continuum between b-Si and texturing: (a) needle-shaped surface structure, (b) micro-cones, (c) nanopores, (d) inverted pyramid, and (e) traditional texturing.

**Conclusions**

We have demonstrated a one-step copper-assisted chemical etching method to synthesize inverted pyramid nanopore-type b-Si at room temperature. According to our results, \([\text{H}_3\text{PO}_3], [\text{Cu}^{2+}], \text{HF}:\text{H}_2\text{O}\) volume ratio, and etching time show direct effects on b-
Si morphology and the corresponding reflectivity. We propose that inverted pyramid shapes of the nanopores is due to the lower reduction potential of Cu$^{2+}$, which causes the Si etching to mainly occur along the Si [100] and [110] directions. In order to maintain a higher nanopore population density, a lower [H$_3$PO$_3$] is beneficial for preventing the nanopores from merging to larger and shallow craters. Also, a higher [Cu$^{2+}$] allows more Cu to be more deposited around the existing Cu NPs and increase the nanopore population density. The AR ability and the extremely short nanopores of the b-Si indicate the potential for AR applications in Si solar cells because the nanopore length is shorter than the typical depth of p–n junctions in Si solar cells.

**Experimental**

Samples were fabricated on polished single crystalline (100) p-type boron-doped Si wafers (Silicon Quest International) with resistivity of 1–5 Ω-cm. Cu(NO$_3$)$_2$:3H$_2$O (Sigma-Aldrich), HF (48%, Sigma-Aldrich), H$_3$PO$_3$ (Sigma-Aldrich), H$_2$O$_2$ (30%, EMD), and NH$_4$OH (30%, Fisher Scientific) were used as received.

**B-Si growth.** The Si wafers were cut into small pieces and ultrasonically cleaned in DI H$_2$O, acetone, and DI H$_2$O sequentially. The cleaned Si pieces were ultrasonically etched in Si etchants consisting of a 5 mL mixture of HF (48%) and DI H$_2$O in different volume ratios and Cu(NO$_3$)$_2$ aqueous solution to give an overall [Cu$^{2+}$] in the etchant of 500, 50, and 5 μM, respectively. The final volume of the etchant was adjusted to 10 mL by adding H$_3$PO$_3$ aqueous solutions with various concentrations. Table 2.4 summarizes the various compositions of the etchant solutions investigated. After etching for 2 or 8 hours, the as-prepared b-Si samples were rinsed in DI H$_2$O, and then cleaned with a copper etchant consisting of NH$_4$OH and H$_2$O$_2$ in a 1 : 1 volume ratio at room temperature with sonication to remove the Cu NPs from the wafer surface (Table 2.4). The Cu-removed b-Si samples were immersed in DI H$_2$O and dried by canned air.
A solution of 5% PMMA in toluene was applied on selected b-Si samples. PMMA with average $M_W = 120,000$ was added in toluene and heated at 50 °C for 3 h with stirring to prepare the 5% PMMA solution. The solution was dropped on the b-Si samples with a spinning rate of 2000 rpm for 60 s. The samples were then dried at 100 °C for 20 min to remove the toluene solvent.

**Characterization.** Scanning electron microscopy (SEM) was carried out using FEI Quanta 400 by placing samples on double-sided carbon tape that was fixed to aluminium SEM stubs (used as received). Images were acquired at a typical operating voltage of 20 kV, with a working distance of 10 mm, spot size 3 in Hi-VAC mode. The total reflectance spectra of the b-Si samples were measured with Ocean Optics HR2000+ high-resolution spectrometer with a Mikropack DH-2000-BAL deuterium-halogen light source. The relative reflectivity is measured over the wavelength range 300–1000 nm and compared to a cleaned and un-etched Si wafer whose relative reflectivity is 100%.

**References**

Table 2.4. Summary of etchants.\(^a\)

<table>
<thead>
<tr>
<th>[Cu(^{2+})]</th>
<th>[H(_3)PO(_3)]</th>
<th>HF:H(_2)O</th>
<th>Volume of HF (mL)(^b)</th>
<th>Volume of DI H(_2)O (mL)(^c)</th>
<th>Volume of mixture (mL)</th>
<th>Volume of Cu(NO(_3))(_2) (µL)(^d)</th>
<th>Stock of [H(_3)PO(_3)] (mM)</th>
<th>Volume of stock H(_3)PO(_3) (mL)</th>
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<tr>
<td>500</td>
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<td>1:4</td>
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<td>4.0</td>
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<td>500</td>
<td>22.2</td>
<td>4.5</td>
</tr>
<tr>
<td>500</td>
<td>10</td>
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</tr>
<tr>
<td>500</td>
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<td>1:15</td>
<td>1.0</td>
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<td>5.0</td>
<td>500</td>
<td>22.2</td>
<td>4.5</td>
</tr>
<tr>
<td>50</td>
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<td>1:7</td>
<td>1.0</td>
<td>4.0</td>
<td>5.0</td>
<td>50.0</td>
<td>0</td>
<td>4.95</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>1:4</td>
<td>1.0</td>
<td>7.0</td>
<td>5.0</td>
<td>50.0</td>
<td>20.2</td>
<td>4.95</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>1:7</td>
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<td>7.0</td>
<td>5.0</td>
<td>50.0</td>
<td>20.2</td>
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<tr>
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<td>101</td>
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<td>4.0</td>
<td>5.0</td>
<td>5.0</td>
<td>20.0</td>
<td>5.0</td>
</tr>
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<td>5.0</td>
<td>5.0</td>
<td>20.0</td>
<td>5.0</td>
</tr>
<tr>
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<td>10</td>
<td>1:15</td>
<td>4.0</td>
<td>15.0</td>
<td>5.0</td>
<td>5.0</td>
<td>20.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

\(^a\) Total volume = 10 mL, \(^b\) 48% HF, \(^c\) HF+H\(_2\)O, \(^d\) [Cu(NO\(_3\))\(_2\)] = 0.01 M.


Chapter 3

In-situ fabrication of a self-aligned selective emitter silicon solar cell using the gold top contacts to facilitate the synthesis of a nanostructured black silicon anti-reflective layer instead of an external metal nanoparticle catalyst

Introduction

Improved performance through increased efficiency and/or significantly reducing the cost of manufacture are two keys to solar energy achieving grid parity with energy derived from fossil fuels.\(^1\) One of the requirements for an efficient solar cell is low surface reflectivity to maximize the amount of incident photons absorbed by the cell. In the industry, silicon nitride anti-reflection (AR) coatings based on quarter-wavelength principle are usually deposited on Si wafer surfaces to suppress the surface reflectivity; however, their AR ability is limited since the AR coatings only perform well in a narrow range of light wavelength and incident angles.\(^2\)-\(^6\)

An alternate material called “black Si” (b-Si) consisting of nanopores or nanowires, has been developed because it can overcome the disadvantages of conventional AR coatings. B-Si possesses a gradient change of refractive index between the silicon (Si) wafer surface and air allowing b-Si to more effectively suppress the reflection on the Si solar cell regardless of the changes in the incident angle and wavelength of the light. The techniques for fabricating b-Si includes reactive ion etching,\(^7\)-\(^{13}\) laser irradiation,\(^14\)-\(^{18}\) electrochemical etching,\(^19\)-\(^{22}\) and metal-assisted chemical etching (MACE).\(^{23}\)-\(^{33}\) Among all of these techniques, the MACE method is the most popular because it has lower energy consumption and needs no complicated instruments. Due to these factors, the MACE method has the potential to be more easily introduced into the current production lines of Si solar cells.\(^1\)
The typical MACE method includes two different steps that are deposition of a metal catalyst and electroless chemical etching, respectively. Recently, we have successfully merged the two steps into an one-step reaction in order to further decrease the fabrication cost of b-Si through the use of silver and copper precursors in the Si etchants to produce metal nanoparticle (NP) catalysts. As is common with all MACE systems, the metal NPs catalyze the Si wafer oxidation (to SiO$_2$), which is then etched by the HF (in the etchant) to form porous b-Si structure. Along with Ag and Cu, Au may also be used as the catalyst.

In fact, Branz et al. first fabricated b-Si by using a one-step Au-assisted chemical etching method with a reagent solution consisting of HAuCl$_4$/HF/H$_2$O$_2$/H$_2$O.

Although the MACE method with different metal catalysts for b-Si fabrication has been successfully demonstrated, the step of removing metal catalysts from the Si wafer surface is still unavoidable for all types of the MACE methods. The residual metal catalysts on the solar cell surface can potentially interfere with the cells performance. However, the extra step of metal removal in the b-Si fabrication process not only increase the b-Si fabrication cost but also appears to cause damages to the b-Si structures when the structure is extremely porous.

One important issue with traditional Si solar cells is the need for a lightly doped ($10^{18}$-$10^{19}$ cm$^{-3}$) emitter region for photon collection but a highly doped ($10^{20}$-$10^{21}$ cm$^{-3}$) region for the top contact metallization. One solution is a selective emitter (SE) device, which allows more electrons to be collected by the metal contacts and generate a higher short circuit current density ($J_{sc}$) and a higher open circuit voltage ($V_{oc}$). Several fabrication techniques of SE Si solar cells have been developed including etch-back emitter, laser doped SE, ion implantation process, and screen-printable ink. These methods typically require 1-3 extra main fabrication steps compared to the conventional Si cell fabrication. Recently, Um et al. have shown that b-Si AR layers and SEs can be concurrently formed in Si solar cells by using MACE method with Ag NPs; however, as noted the complete removal of the residual metal catalyst in the MACE process can be
problematic and represents an additional process step.\textsuperscript{24,29,33} Furthermore, the cost of the catalyst must be taken into account when considering the application of b-Si.

In order to obviate the need for the metal removal step, we report the fabrication b-Si on Si solar cell surface without any addition of metal or metal precursor as catalysts. This new approach can be considered as a metal-less MACE process in which the top contact assists the etching of the silicon to create the nano-textured surface. We have designated this new approach as contact-assisted chemical etching (CACE).

\textbf{Results and Discussion}

\textbf{The mechanism of CACE.} The main issue associated with traditional Ag top contacts prepared with a fire-through step is that the Ag contacts easily spall from the Si wafer during Si etching. As part of study into whether b-Si can be successfully fabricated during different steps of a fab process, Au-coated Si wafers were used and subjected to a typical one-step Ag-assisted chemical etching process (AgNO\textsubscript{3}/HF/H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O).\textsuperscript{29} In order to ascertain the influence of the Au metallization, an identical sample was exposed to the same HF/H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O etchant in the absence of AgNO\textsubscript{3}. For these two samples, masks without fingers but with wider busbar were used to better show the etching effect of Au contacts. Figure 3.1 shows optical images of the Au-coated Si solar cells etched with and without addition of AgNO\textsubscript{3}.

As can be seen from Figure 3.1b, the surface of sample etched with AgNO\textsubscript{3} is entirely etched to show a brown color indicating a relatively uniform etching level compared to the sample etched without AgNO\textsubscript{3}. The reason for this is that the Ag precursor in the Si etchant (i.e., AgNO\textsubscript{3}) is reduced to Ag NPs that are uniformly distributed on the Si wafer surface and able to assist the Si etching. However, while b-Si is produced without AgNO\textsubscript{3} in the Si etchant, the wafer only shows significant etching within 4 mm of the Au contact (Figure 3.1a). The etching occurring around the metallization indicates that the pre-deposited Au contacts are having an intimate effect on the Si etching. We note that the etching also occurs
at the wafer edges presumably because the defects resulted from cutting. Figure 3.2 shows SEM images of the etched regions of the Au-coated Si samples etched with and without AgNO₃ shown in Figure 3.1. SEM analysis (Figure 3.2a) shows the etched regions to be consistent with a b-Si structure, although the morphology is slightly different from samples in which either pre-formed or in-situ formed Ag NPs were used as catalysts (Figure 3.2b).

![Figure 3.1](image1.png)

**Figure 3.1.** Images of b-Si after the etching treatment. (a) Au-coated Si solar cell etched with a Si etchant of HF:H₂O₂:H₂O = 3:3:20 for 3 min. (b) Au-coated Si solar cell etched with a Si etchant of HF:H₂O₂:H₂O = 3:3:20 for 3 min with additional 5 µM AgNO₃.

Analysis of the etchant by ICP-AES showed the metals associated with the MACE processes were below the detection limits (Table 3.1). By comparison with our prior work on the Ag catalyzed b-Si,²⁹ we can infer that the Au lines on the wafer surfaces are catalysts for the b-Si formation. An etching mechanism based on the working principle of galvanic cells is proposed to explain the electroless chemical etching with the assistance of Au lines. A schematic illustration of the CACE method for the b-Si formation on the Si wafer surface is shown in Figure 3.3. The Si etching mechanism consists of two half reactions: H₂O₂ reduction and Si oxidation. The H₂O₂ in the etchant is reduced to H₂O at the interface with the Au lines, and the subsequent holes are injected into the wafer regions near the Au lines (hence the distance effect observed). Once the Si regions obtain the holes, the Si is oxidized
Figure 3.2. Surface SEM image of b-Si after the etching treatment. (a) Surface SEM image of the Au-coated Si solar cell etched with an Si etchant of HF:H$_2$O$_2$:H$_2$O=3:3:20 for 3 min (i.e., CACE). (b) Surface SEM image of the Au-coated Si solar cell etched with an Si etchant of HF:H$_2$O$_2$:H$_2$O=3:3:20 for 3 min with additional 5 µM AgNO$_3$ (i.e., MACE).

Table 3.1. Summary of metal impurities in the chemicals (µM).

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Buffer oxide etchant</th>
<th>48% HF</th>
<th>30% H$_2$O$_2$</th>
<th>DI H$_2$O</th>
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</thead>
<tbody>
<tr>
<td>[Cu]</td>
<td>&lt;0.16</td>
<td>&lt;0.31</td>
<td>&lt;0.16</td>
<td>&lt;0.16</td>
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<td>[Ag]</td>
<td>&lt;0.09</td>
<td>&lt;0.19</td>
<td>&lt;0.09</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>[Au]</td>
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<td>&lt;0.10</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

to SiO$_2$ and then etched by the HF to generate a b-Si structure consisting of nanopores (Figure 3.3b). As is observed experimentally there is no etching of the Si regions covered by the Au metallization since this Si does not contact the etchant directly. Furthermore, etching should be limited to a distance from the metal controlled by the hole diffusion through the wafer surface. This corresponds to our observation in Figure 3.1.
Based upon these results, we proposed that it would be possible to concurrently fabricate a self-aligned SE Si solar cell with a patterned b-Si AR layer on the solar cell surface. In such a process, the initial p-type Si wafers are n-doped by phosphorous diffusion
so the wafer surfaces have a higher dopant concentration than the deeper p-n junction region. The metallization followed by non-metal containing etchants would result in the top Si wafer surface being etched away by the etchant, to reveal the deeper Si. The newly emerging bulk Si surface has a lower dopant concentration and would be less conductive compared to the Si regions under the Au lines, which still possess the original high dopant concentration and build up SEs in the cell as shown in Figure 3.3c. As noted in the Introduction, Um et al. have concurrently produced b-Si structure and SE on Si solar cell surfaces but with a different process which involved two extra steps of addition and removal of the metal catalysts.  A comparison of etching mechanism of CACE and MACE with Ag NPs is shown in Figure 3.4.

Figure 3.4. Schematic illustration of the proposed formation process of b-Si structure on the Au-coated Si wafer surface during chemical etching method. (a) The proposed method without additional metal catalyst (i.e., CACE). (b) The method with pre-deposited Ag NP catalysts on the Si wafer surface (i.e., MACE).
Fabrication of a non-etched Si solar cell. Before any Si etching treatment, the Au-coated Si solar cells possess a smooth top surface. Figure 3.5 shows the surface morphology of non-etched Si solar cell. As can be seen in Figure 3.5, no nanopores or porous Si structures are found on the wafer surface either from the top-view or cross-sectional images. In order to understand how an Al$_2$O$_3$ passivation layer on a Si solar cell affects the surface recombination velocity of charge, a passivation layer (22 nm) was deposited on non-etched Au-coated Si solar cell by atomic layer deposition (ALD) first. Table 3.2 shows the properties of non-etched solar cell before and after the ALD passivation treatment. After ALD, the solar cell efficiency slightly increases from 5.41% to 5.88%, and $V_{oc}$ and $J_{sc}$ increase from 0.561 to 0.565 V and 13.2 to 14.1 mA/cm$^2$, respectively. However, the results are not strong enough to prove that the Al$_2$O$_3$ passivation layer indeed suppresses the surface recombination velocity of charge carries for the un-etched solar cell. The higher efficiency of the solar cell might result from the decrease of surface reflectivity, which drops from 0.466 to 0.361 after ALD.

![Figure 3.5](image_url)

**Figure 3.5.** SEM images of non-etched Si solar cell before the ALD passivation treatment: (a) surface SEM image and (b) cross-sectional SEM image.
Table 3.2. Summary of properties for the non-etched Si solar cell.

<table>
<thead>
<tr>
<th>Al₂O₃ layer by ALD</th>
<th>Efficiency (%)</th>
<th>FF</th>
<th>V&lt;sub&gt;oc&lt;/sub&gt; (V)</th>
<th>J&lt;sub&gt;sc&lt;/sub&gt; (mA/cm²)</th>
<th>Reflectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
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<td>0.73</td>
<td>0.561</td>
<td>13.2</td>
<td>0.446</td>
</tr>
<tr>
<td>After</td>
<td>5.88</td>
<td>0.74</td>
<td>0.565</td>
<td>14.1</td>
<td>0.361</td>
</tr>
</tbody>
</table>

A possible reason that the surface reflectivity of solar cell decreases after Al₂O₃ passivation layer is deposited by ALD is that it has an intermediate refractive index (n = 1.8) between that of the air (n = 1.0) and the smooth Si wafer surface (n = 3.5). The intermediate refractive index allows the passivation layer to function like an AR coating layer even though the layer thickness is not thick enough to significantly suppress the reflection on the wafer surface. More observations on the Al₂O₃ passivation layers will be discussed below.

We have investigated the effects of etchant concentrations and the properties of the resulting b-Si solar cells. In order to be easier to discuss, the results are divided into two different categories based on the HF:H₂O₂:H₂O volume ratio in the Si etchants.

**Effects of [HF] and [H₂O₂] on b-Si solar cell fabrication.** By using the Si etchant consisted of the highest [HF] and [H₂O₂], HF:H₂O₂:H₂O = 1:5:2, the fabricated b-Si solar cells possess the longest nanopores among all the samples, which corresponds with our previous work. A higher [H₂O₂] accelerates the oxidation rate of Si to SiO₂, and a higher [HF] increases the etching rate of the as-formed SiO₂; both are beneficial for nanopore growth on the Si wafer surface.

Figure 3.6 shows SEM images of b-Si solar cells fabricated with a HF:H₂O₂:H₂O volume ratio = 1:5:2. After 5 minute etching, the fabricated nanopores, which have maximum diameter around 50 nm and length around 950 nm, can be clearly observed on
the wafer surface (Figure 3.6a and b). It should be mentioned that the top part of the nanopores are very porous, as a consequence the outlines of nanopore tips cannot be clearly seen in the cross-sectional SEM image (Figure 3.6b).

![Surface and cross-sectional SEM images of b-Si solar cells fabricated with a HF:H2O2:H2O volume ratio = 1:5:2 for 5 min (a and b) and 10 min (c and d).](image)

**Figure 3.6.** Surface and cross-sectional SEM images of b-Si solar cells fabricated with a HF:H2O2:H2O volume ratio = 1:5:2 for 5 min (a and b) and 10 min (c and d).

As the etching time increases to 10 minutes, there are more nanopores appearing on the wafer surface and the maximum diameter of nanopores increases to 80 nm (Figure 3.6c). However, this higher density of nanopore population also causes an extremely porous surface that can easily collapse during longer etching times resulting in the shorter nanopores, with maximum length of 750 nm, being left on the Si wafer surface after etching.
(Figure 3.6d). From the cross-sectional SEM image, the wafer surface becomes much rougher and only nanopores with clearer outlines still exist, which indicates that the majority of extremely porous parts of nanopores have collapsed and been removed from the wafer.

In general, using a lower [HF] and [H\textsubscript{2}O\textsubscript{2}] for Si etching, such as the HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O of 1:5:5 and 1:5:20, causes the b-Si structures to have smaller nanopore sizes compared to that etched with the 1:5:2 ratio due to the slower etching rate. Figure 3.7 shows the SEM images of b-Si solar cells etched with the HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O volume ratio = 1:5:5. After etching with the ratio of HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O = 1:5:5 for 3 minutes, small and short nanopores with maximum diameters around 30 nm and length of 240 nm are observed on the wafer surface (Figure 3.7a and b). As the etching time increases to 5 minutes, the nanopores become extremely porous and the maximum nanopore size grows to 60 nm in diameter and 400 nm in maximum length (Figure 3.7c and d). However, the nanopore size is still smaller than that of the b-Si fabricated with the ratio as 1:5:2 with the same etching time (50 nm in diameter and 950 nm in length).

Interestingly, after 10-min etching, the maximum nanopore diameter and length keep increasing to 85 nm and 850 nm, respectively (Figure 3.7e and f), which are slightly larger and longer than the nanopores fabricated with the higher [HF] and [H\textsubscript{2}O\textsubscript{2}], or HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O = 1:5:2. Even though the b-Si structures begin to collapse on the wafer surface, the remaining nanopores are still long enough to make the collapses less significant and the wafer surface relatively smoother. Thus the use of lower [HF] and [H\textsubscript{2}O\textsubscript{2}] can effectively prevent excessively aggressive etching causes the collapse of b-Si structure and shortening of the nanopore length.

The nanopore size in the b-Si decreases further when [HF] and [H\textsubscript{2}O\textsubscript{2}] are lowered. With a ratio of HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O = 1:5:20, the Si etching is significantly suppressed, leading to a low population density of nanopores on the Si wafer surface after 5-min etching.
Figure 3.7. Surface and cross-sectional SEM images of b-Si solar cells fabricated with a HF:H$_2$O$_2$:H$_2$O volume ratio = 1:5:5 for 3 min (a and b), 5 min (c and d), and 10 min (e and f).
Figure 3.8 shows the SEM images of b-Si solar cells fabricated with a HF:H₂O₂:H₂O volume ratio = 1:5:20. As seen in Figure 3.8a and b the maximum nanopore diameter (45 nm) and length (100 nm) are also extremely small. When the etching time is increased to 10 minutes, the maximum nanopore diameter only increases to 70 nm and the maximum nanopore length also only increase to 130 nm (Figure 3.8c and d). Compared to the b-Si fabricated with the ratio of 1:5:2 and 1:5:5, the nanopore growth rate is much slower due to the lower concentrations of HF and H₂O₂ used. Hence, the lack of collapse of nanopores observed on the wafer surface seem to be more obvious since this b-Si has a relatively shorter length.

Figure 3.8. Surface and cross-sectional SEM images of b-Si solar cells fabricated with a HF:H₂O₂:H₂O volume ratio = 1:5:20 for 5 min (a and b) and 10 min (c and d).
The surface morphology of b-Si solar cells has direct effects on AR ability and energy conversion efficiency of solar cells. The working principle of the b-Si AR layers is based on the gradient change of refractive index of b-Si structure on the wafer surface. Table 3.3 shows the summary of properties of all b-Si solar cells reported herein. A plot of the reflectivity of b-Si solar cells fabricated with the etchant ratio of 1:5:Z is shown in Figure 3.9. Unlike the non-etched Si solar cell, the reflectivity of b-Si solar cells increases in different levels after the Al₂O₃ passivation treatment on the wafer surface. A possible reason might be that the ALD layers interfere the original smooth gradient change of refractive index on the wafer surface resulted from the b-Si structures. Another factor would decrease the AR ability of b-Si structures is that the deposited passivation layer does not fully cover the whole b-Si structures; hence, a non-continuous cover is formed on the wafer surface and causes a non-uniform gradient change of refractive index.

**Table 3.3. Summary of properties of b-Si solar cells.**

<table>
<thead>
<tr>
<th>HF:H₂O₂:H₂O in volume</th>
<th>Etching time (min)</th>
<th>Al₂O₃ layer by ALD</th>
<th>Efficiency (%)</th>
<th>FF</th>
<th>V₋₀ (V)</th>
<th>Jₛₑ (mA/cm²)</th>
<th>Reflectivity</th>
</tr>
</thead>
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<tr>
<td>1:5:2</td>
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<td>Before</td>
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<td>0.566</td>
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<td>a</td>
</tr>
<tr>
<td></td>
<td></td>
<td>After</td>
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<td>4.1</td>
<td>0.031</td>
</tr>
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^a Reflectivity not measured.

In general, the b-Si solar cells fabricated with the HF:H₂O₂:H₂O ratio of 1:5:2 has lower reflectivity (Figure 3.9a) compared to that of 1:5:5 (Figure 3.9b) because the former usually has longer nanopores under at the same etching time. The longer nanopore lengths can provide smoother gradient changes of refractive index which more effectively suppresses the reflectivity on the wafer surfaces. However, the uniformity of nanopore distribution on
the wafer surfaces should be also taken into account since a more uniform distribution can also provide a smoother gradient change of refractive index. For example, after 5-min etching, the reflectivity of the solar cell fabricated with the 1:5:2 ratio after ALD, 0.063, is much lower than that of the one fabricated with the 1:5:5 ratio after ALD, 0.234. Although these two solar cells have similar nanopore distribution on the surface (Figure 3.6a and 3.7c), the former one possesses a lower reflectivity due to the much longer nanopores (950 nm versus 400 nm). After etching for 10 minutes, the b-Si solar cell fabricated with the 1:5:5 ratio has a longer nanopore length compared to the cell fabricated with the 1:5:2 ratio (850 nm versus 750 nm), but the reflectivity of both cells are almost the same after ALD (0.050 versus 0.052). This fact can be attributed to the observation that solar cells with short nanopores have a more uniform distribution of them.

Based on the same principle, the reflectivity should decrease with the etching time since the nanopores usually grow longer after longer etching times. This may explain the observation on the solar cells fabricated with the ratio of 1:5:2 and 1:5:5 for various time. However, the solar cells fabricated with the ratio of 1:5:20 shows the opposite trend, which is the surface reflectivity increases with etching time (Figure 3.9c). A possible explanation is that after longer etching, some regions of b-Si structures become extremely porous and collapse like samples etched with the other ratios. Since the nanopore growth rate with the 1:5:20 ratio is much slower compared to the other etchant ratios, the positive effect that the nanopore growth brings, smoothing the gradient change of refractive index, is not able to compensate for the negative effect that the structure collapse brings, destroying the gradient change of refractive index. Hence, the change of refractive index becomes discrete which causes the Si wafer reflectivity to increase with etching time.

The morphology of b-Si has a significant impact on not only the surface reflectivity but also the energy conversion efficiency of the b-Si solar cells. Figure 3.10 shows a plot of the efficiency of b-Si solar cells fabricated with the ratio of 1:5:Z. As can be seen the efficiency of solar cells show a decrease with etching time, even though most of solar cells
Figure 3.9. Plot of reflectivity for Si solar cells fabricated with the HF:H$_2$O$_2$:H$_2$O ratio = 1:5:Z and various times before and after ALD. (a) HF:H$_2$O$_2$:H$_2$O ratio = 1:5:2. (b) HF:H$_2$O$_2$:H$_2$O ratio = 1:5:5. (c) HF:H$_2$O$_2$:H$_2$O ratio = 1:5:20.
have lower reflectivity after longer etching. A reasonable explanation is that the carrier recombination rate is also increased after the longer etching. During the etching, the nanopore length increases with time causing the b-Si to become more porous and increasing the surface areas of the b-Si structure as well. With the larger surface area, more dangling bonds are shown at the wafer surface leading to a higher surface recombination velocity of the carriers and a decrease in the efficiency, regardless of the ALD passivation treatment.

With the Si etchant consisting of HF:H₂O₂:H₂O = 1:5:2, the b-Si solar cells have the highest efficiency after 2-min etching 7.65% after ALD (Figure 3.10a), compared to the two other etchant compositions. This is most likely due to the relatively longer nanopore length. Surprisingly, after 5-min etching, the efficiency decreased to 1.09% after ALD. Although the increase in the nanopore surface area might be one of the factors resulting this situation, the penetration of the p-n junction interface should be considered main reason for this decrease in efficiency. After 5-min etching, the maximum nanopore length reaches 950 nm, which is long enough to damage the p-n junction and directly affect the solar cell functionality. The $V_{oc}$ and $J_{sc}$ drop from 0.566 to 0.434 V and 21.2 to 4.2 mA/cm$^2$ before ALD, respectively, indicating the excessively long nanopores have deteriorated the energy conversion ability of solar cell.

The b-Si solar cells fabricated with the ratio of 1:5:5 shows a slightly different trend of efficiency (Figure 3.10b) compared to the ones fabricated with the ratio of 1:5:2. The solar cell efficiency slightly increases during the early stage of etching and reaches the maximum, 7.35%, after 3-min etching and then starts to decrease. The small increase of efficiency results from the small decrease of reflectivity on the wafer surface. After that stage, due to the increased growth of nanopore length creating larger surface areas, the solar cell efficiency also drops similar to the cells fabricated with the 1:5:2 ratio but with a slower rate. The slower drop of efficiency can be attributed to the lower growth rate of the nanopores. It is reasonable to infer that the nanopores also penetrate the p-n junction
**Figure 3.10.** Plot of efficiency for b-Si solar cells fabricated with the HF:H₂O₂:H₂O ratio=1:5:Z and various etching time before and after ALD. (a) HF:H₂O₂:H₂O ratio = 1:5:2. (b) HF:H₂O₂:H₂O ratio = 1:5:5. (c) HF:H₂O₂:H₂O ratio = 1:5:20.
interface after 10-min etching since the $J_{sc}$ decrease from 18.70 to 8.65 mA/cm$^2$ and the $V_{oc}$ decrease from 0.567 to 0.464 V before ALD. One thing needing to be mentioned is that after 10-min etching, the measured efficiency after ALD is lower than the efficiency before ALD as some parts of the Al back contact fell off the wafer back surface during ALD. This would result in a lowering of the back contact resistance.

Compared to the b-Si solar cells etched with the 1:5:2 and 1:5:5 ratio, the $V_{oc}$ of solar cells fabricated with the 1:5:20 ratio does not dramatically drop with etching (Figure 3.10c). The nanopores are not long enough to penetrate the interface of p-n junction, which can be also seen from the cross-sectional SEM images (Figure 3.8d). However, the efficiency still decreases with etching time because of the significant increase in reflectivity. This fact once again indicates that not only the reflectivity but also the b-Si morphology affects the energy conversion efficiency of b-Si solar cells.

**Effects of HF:H$_2$O$_2$ ratio on b-Si solar cell fabrication.** We have shown that using lower HF and H$_2$O$_2$ concentrations prevents the fabricated nanopores penetrating the p-n junction interface. Hence, the solar cells fabricated with low [HF] and [H$_2$O$_2$] (i.e., HF:H$_2$O$_2$:H$_2$O = X:Y:20) has been systematically investigated in order to better understand how the relative ratio of HF:H$_2$O$_2$ affects the morphology and other properties of b-Si solar cells. Figure 3.11 shows the SEM images of b-Si solar cells etched with various HF:H$_2$O$_2$:H$_2$O volume ratios for 3 minutes. With HF:H$_2$O$_2$:H$_2$O = 2:4:20 and 3-min etching, the fabricated nanopores in the b-Si solar cell have maximum diameter of 40 nm. The maximum nanopore length is only 130 nm (Figure 3.11a and b), which is much shorter than that within the b-Si structure fabricated with the 1:5:5 ratio for 3 minutes (240 nm, Figure 3.7b). This is not surprising since both the [HF] and [H$_2$O$_2$] in the 2:4:20 ratio etch are lower than that using the 1:5:5 ratio. However, even though the etching time is shorter, the nanopore length of b-Si structure fabricated with the 2:4:20 ratio for 3 min-etching (130 nm) is longer than that fabricated with the 1:5:20 ratio for 5 minute (100 nm). This fact
Figure 3.11. Surface and cross-sectional SEM images of b-Si solar cell fabricated for 3 min with a HF:H₂O₂:H₂O volume ratio equal to 2:4:20 (a and b), 3:3:20 (c and d), and 4:2:20 (e and f).
proves that the relative ratio of HF to H$_2$O is indeed related to the b-Si morphology during the etching.

As the HF:H$_2$O$_2$ relative ratio increases to 3:3 (i.e., HF:H$_2$O$_2$:H$_2$O ratio = 3:3:20), the maximum diameter and length of nanopores slightly increase from 40 to 45 nm and 130 to 150 nm, respectively (Figure 3.11c and d). In addition, the number of nanopores on the wafer surface increases and the nanopore distribution is more uniform as well (Figure 3.11c and d). A possible explanation is that the higher HF:H$_2$O$_2$ relative ratio allows more HF molecules in the etchant to immediately etch the as-formed SiO$_2$ on the wafer surface. However, once the HF:H$_2$O$_2$ ratio further increases to 4:2 (the HF:H$_2$O$_2$:H$_2$O ratio = 4:2:20), the nanopore number on the wafer surface starts to decrease rather than continue increasing. The nanopore diameter and length also slightly decrease to 30 and 140 nm, respectively (Figure 3.11e and f) because the lower [H$_2$O$_2$] in the etchant provides a lower oxidization rate of Si, which is not favorable for the nanopore formation even though the HF concentration is higher.

Like the b-Si solar cells fabricated with a HF:H$_2$O$_2$:H$_2$O = 1:5:Z, the etching time also has a significant impacts on the b-Si morphology of Si solar cells fabricated with the HF:H$_2$O$_2$:H$_2$O = X:Y:20. We are more interested in the b-Si solar cells fabricated with the ratio of 3:3:20, as the cells have longest nanopore length and the most uniform nanopore distribution compared to the cells fabricated with other X:Y:20 ratios. SEM images of b-Si fabricated with a HF:H$_2$O$_2$:H$_2$O = 3:3:20 for variant etching time are shown in Figure 3.12 and 3.13.

With 2-min etching, the Si wafer surface shows a high population density of nanopores and these uniformly distributed nanopores have the maximum diameter of 30 nm and length of 130 nm (Figure 3.12a and b). It can also be seen that some non-etched regions of Si wafer surface turn into the small and short Si pillars standing on the wafer surface. After etching for 3 minutes, the small Si pillars disappear and only nanopores exist on the wafer surface leaving a relatively smooth surface (Figure 3.12c and d). The
maximum diameter and length of the fabricated nanopores slightly increase to 45 nm and 150 nm, respectively. From the cross-sectional SEM image, the continuous change of brightness on the b-Si structure indicates that the Si surface porosity changes with depth, or the refractive index of Si changes with depth, which is more beneficial for suppressing reflectivity on the wafer surface (Figure 3.12d).

Figure 3.12. Surface and cross-sectional SEM images of b-Si solar cell fabricated with a HF:H₂O₂:H₂O volume ratio=3:3:20 for 2 min (a and b) and 3 min (c and d).

When the etching time increases from 3 minutes to 5 minutes, the nanopores possess maximum diameter and length of 55 nm and 190 nm, respectively (Figure 3.13a and b). The collapse of the b-Si structure starts being observed and makes the quantity of nanopore
decrease and the wafer surface rugged, which are detrimental for the anti-reflection ability of b-Si structure. As the etching time further increases to 10 minutes, the maximum nanopore diameter and length grow to 70 nm and 220 nm, respectively (Figure 3.13c and d). The Si wafer surface becomes more rugged and the b-Si structure collapses further, which would lead to a higher reflectivity due to the less smooth gradient change of refractive index. When comparing the b-Si solar cells fabricated with the 3:3:20 ratio to those fabricated with the 1:5:20 ratio, it can be found that the former cells possess much longer nanopores (e.g., 190 nm versus 100 nm after 5-min etching). This result indicates that the 3:3:20 ratio indeed provides a higher Si etching rate (a faster nanopore growth rate) compared with other etchant compositions.

Similar to the b-Si solar cells fabricated with the HF:H₂O₂:H₂O = 1:5:Z, the reflectivity of cells fabricated with the X:Y:20 ratios have strong dependence on the b-Si morphology. Nevertheless, the reflectivity of solar cells fabricated with the X:Y:20 ratio are generally higher due to their shorter nanopore lengths. A plot of the reflectivity of b-Si solar cells fabricated with the ratio of X:Y:20 is shown in Figure 3.14. The solar cells fabricated with HF:H₂O₂:H₂O=1:5:Z, the surface reflectivity of solar cells fabricated with the X:Y:20 ratios also increases after the ALD passivation treatment due to the interruption of gradient change of refractive index resulted from the ALD layers. Figure 3.15 shows reflectivity spectra of non-etched solar cells and b-Si solar cells.

As discussed above, the reflectivity of solar cells fabricated with the ratio of 1:5:20 increases with the etching time (Figure 3.14a) because the slow b-Si growth cannot compensate for the negative effect on reflectivity resulted from the collapse of b-Si structures during etching. Unlike the b-Si solar cells fabricated with the ratio of 1:5:20, the cells fabricated with the ratio of 2:4:20, 3:3:20, and 4:2:20 possess a slightly different trend of reflectivity, which slightly decreases with the etching time first and then increases (Figure 3.14b, c, and d). However, the concept used to explain the reflectivity trend of surfaces fabricated with the 1:5:20 ratio can also be used to explain this observation.
Figure 3.13. Surface and cross-sectional SEM images of b-Si solar cell fabricated with a HF:H$_2$O$_2$:H$_2$O volume ratio=3:3:20 for 5 min (a and b) and 10 min (c and d).

During the early stage of etching, only nanopores are produced on the Si wafer surface creating a lower surface reflectivity. After a time, some top parts of b-Si structures become more porous and start to collapse, destroying the gradient change of refractive index and becomes harmful to the goal of suppressing the reflectivity. Although the collapse might increase the reflectivity, as long as the collapse has not yet become too great, the overall reflectivity can continuously decrease and reach the minimum, as the nanopores are continuing to grow. Nevertheless, once the collapse become too significant with the
etching time, the collapse begins to dominate the change of reflectivity leading to an increase in the surface reflectivity.

**Figure 3.14.** Plot of reflectivity for b-Si solar cells fabricated with the HF:H$_2$O$_2$:H$_2$O ratio=X:Y:20 and various time before and after ALD. (a) HF:H$_2$O$_2$:H$_2$O ratio = 1:5:20. (b) HF:H$_2$O$_2$:H$_2$O ratio = 2:4:20. (c) HF:H$_2$O$_2$:H$_2$O ratio = 3:3:20. (d) HF:H$_2$O$_2$:H$_2$O ratio = 4:2:20.

Since the relative ratios of HF to H$_2$O$_2$ in the HF:H$_2$O$_2$:H$_2$O ratios of 2:4:20, 3:3:20, and 4:2:20 are closer to 1 compared to the relative ratio in the 1:5:20 ratio, the nanopore growth rate from the former etchant compositions should be faster than that of the latter composition because HF and H$_2$O$_2$ in the etchants are both sufficient to grow longer
nanopores. Hence, the collapse of b-Si structure of the solar cells fabricated with the former etchant compositions (the 2:4:20, 3:3:20, and 4:2:20 ratios) has less domination on the reflectivity, which allows the solar cell reflectivity to reach the maximum first and then increase. Among all the solar cells fabricated with the ratio of X:Y:20, the cell fabricated with the 3:3:20 ratio possesses the lowest reflectivity after 3-min etching, 12.6%, because of the faster etching rate, or the longer nanopore length.

**Figure 3.15.** Reflectivity spectra of non-etched Si solar cell and b-Si solar cell fabricated with the ratio of 3:3:20 for 3 minutes before and after ALD. (a) non-etched Si solar cell before ALD. (b) non-etched Si solar cell after ALD. (c) HF:H2O2:H2O ratio = 3:3:20 before ALD. (d) HF:H2O2:H2O ratio = 3:3:20 after ALD.

Unlike the b-Si solar cells fabricated with the HF:H2O2:H2O ratios of 1:5:2 and 1:5:5, the cells fabricated with the ratios X:Y:20 show a more stable energy conversion efficiency with the etching time. Also, the V_{oc} does not drop after a longer time as well because of the slower nanopore growth rate. The slower growth rate can prevent the nanopores from
growing too long and destroying the interface of the p-n junctions. A plot of the efficiency of b-Si solar cells etched with the ratio of X:Y:20 is shown in Figure 3.16.

Figure 3.16. Plot of efficiency for b-Si solar cells fabricated with the HF:H_{2}O_{2}:H_{2}O ratio = X:Y:20 and various time before and after ALD. (a) HF:H_{2}O_{2}:H_{2}O ratio = 1:5:20. (b) HF:H_{2}O_{2}:H_{2}O ratio = 2:4:20. (c) HF:H_{2}O_{2}:H_{2}O ratio = 3:3:20. (d) HF:H_{2}O_{2}:H_{2}O ratio = 4:2:20.

As mentioned before, when the etchant with HF:H_{2}O_{2}:H_{2}O ratio as 1:5:20 is used, the solar cell efficiency decreases with etching time because of the higher surface reflectivity resulted from the relatively large collapse of nanopores (Figure 3.16a). For the solar cells fabricated with the ratio of 2:4:20, 3:3:20, and 4:2:20, the solar cell efficiency
increases with the etching time first and then decreases after reaching the maximum (Figure 3.16b, c, and d), which is opposite to the trend of reflectivity. The efficiency increases at the early state of etching because the growing nanopores can effectively suppress the reflectivity by providing a smoother gradient change of refractive index. However, once the collapse of nanopores starts to occur, the gradient charge of refractive index is interrupted which would increase the reflectivity and decrease the efficiency. Nevertheless, the increase in surface area of nanopores after the longer etching might also explain the decreases in efficiency, since the larger surface area would increase the surface recombination velocity.

Among these different etchant compositions, the b-Si solar cells fabricated with the 3:3:20 ratio shows the highest efficiency. The highest efficiency of the solar cell fabricated with 3:3:20 ratio after ALD is 8.99%, which is much higher than that of the 2:4:20 ratio, 8.58%, and that of the 4:2:20 ratio, 6.91%. The reason is that the 3:3:20 ratio can provide a longer nanopore length and a more uniform distribution of nanopores on the wafer surface (Figure 3.11c and d). Both of these two properties are beneficial for improving the AR ability of Si wafer surface.

The high fill factor (FF) of b-Si solar cell also indicates that the Au contacts adhere well to the wafer surface during the early stage of the etching process. Figure 3.17 shows a plot of I-V curves of the non-etched Si solar cells and b-Si solar cells fabricated with the 3:3:20 ratio. Before Si etching, the non-etched Si solar cell has a high FF, 0.73, which is slightly improved to 0.74 after the Al2O3 passivation treatment by ALD. After 3-min etching, the FF of b-Si solar cell becomes higher, which is 0.75 and 0.79 before and after ALD, respectively. Also, the significant improvement of V_{oc} and J_{sc} observed in the I-V curves might again indicate the existence of a SE in the Si solar cell. However, after 5-min and 10-min etching, the FF dramatically decreases to 0.51 and 0.30 after ALD, respectively, and the efficiency also drops to 4.61% and 2.53%, respectively. This result shows that as the etching time increases, the adhesion between the Au contacts and the wafer surface
becomes worse causing a higher resistance between the contact and the wafer, or a lower FF and efficiency of the cells.

**Figure 3.17.** Plot of I-V curves of non-etched Si solar cell and b-Si solar cells fabricated with the HF:H$_2$O$_2$:H$_2$O ratio=3:3:20 and various time before and after ALD. (a) non-etched Si solar cell before ALD. (b) non-etched Si solar cell after ALD. (c) etching for 3 min before ALD. (d) etching for 3 min after ALD. (e) etching for 5 min after ALD. (f) etching for 10 min after ALD.

**Conclusions**

We have demonstrated that b-Si AR layers are easily to be fabricated on Si solar cell surfaces without addition and removal of any metal catalyst. The pre-deposited Au top contacts also function as metal catalysts for Si etching and can adhere well to the solar cell surface during the etching process. The fabricated b-Si solar cells not only decrease the surface reflectivity to absorb more incident light, but also more effectively collect electrons to improve the $V_{oc}$ and $J_{sc}$ of solar cells. The b-Si solar cell fabricated with the etchant
consisting of the HF:H₂O₂:H₂O ratio = 3:3:20 has the 150 nm of b-Si structure AR layer thickness and the highest efficiency among all the samples, 8.99%, after 3-min etching. The SEM analysis, of the b-Si solar cells as a function of etch time indicate that the b-Si structures will collapse after a longer etching time. Correlated with the trends in efficiency and reflectivity, this collapse has a detrimental effect on the reflectivity and energy conversion efficiency.

Since the Au contacts are deposited on the wafer before the b-Si etching, the Au contacts can better adhere to the Si solar cell surface to enhance the energy conversion efficiency of cells by decreasing the contact resistance. The method should be simple enough to be adapted to the current production lines of Si solar cells since there is no complicated step involved in the method. The proposed method here requires less operation steps compared to the current fabrication processes of b-Si solar cells, hence it can be more useful for the Si solar cell industry to further cut down the cost of per watt output. The method is the first demonstration of the concept that a component in an electronic device (the top Au contact metallization) can also function as a catalyst in the chemical fabrication of the device structure is new, and suggests that other combined processes should be investigated.

**Experimental**

4-inch polished single crystalline (100) p-type boron-doped Si wafers (Silicon Quest International), with a bulk resistivity in the range of 1-5 Ω-cm, were used as a bulk Si material of the b-Si solar cells. Isopropyl alcohol (>99.5%, J. T. Baker), PV-381 Aluminum Photovoltaic Metallization Paste (DuPont), buffer oxide etchant (BOE, Transene Company), poly(methyl methacrylate) (PMMA, average M_w~996,000, Sigma-Aldrich), toluene (>99.9%, Sigma-Aldrich), HF (48%, Sigma-Aldrich), H₂O₂ (30%, EMD), and trimethylaluminium (TMA, electronic grade, Sigma-Aldrich) were used as received. Concentrations of metal impurities in the sealed chemicals, which might affect the Si
etching, were characterized by Evans Analytical Group or provided by the chemical companies with ICP-AES. Table 3.1 shows the concentrations of copper, silver, and gold in each chemical.

**Preparation of b-Si solar cells.** In order to generate p-n junctions in Si wafers, emitter diffusion was performed in a horizontal tube diffusion furnace equipped with 8 inch diameter quartz tubes. The wafers were loaded at a rate of 6 in/min into the tube maintained at 700 °C under N$_2$ flow. Once the wafers were fully loaded into the tube, the temperature was then ramped to 970 °C under N$_2$ flow over 20 minutes. The wafers were then held for 5 minutes at 970 °C in a flow of 4 Lpm N$_2$ and 200 sccm O$_2$. A phosphorous dopant was introduced in the tube by bubbling 690 sccm N$_2$ through a volume of POCl$_3$ maintained at 18 °C for 70 minutes. At the end of the 20 minutes phosphorous doping vapour flow step, the POCl$_3$ bubbler flow was turned off and a flow of 7 Lpm N$_2$ and 800 sccm O$_2$ was maintained in the tube for 70 minutes as the drive-in step. The tube was then returned to pure N$_2$ flow and allowed to cool for 10 minutes during a cool-down step prior to unloading the wafers. This yielded an n-type phosphorous diffusion with a very low sheet resistivity of less than 10 Ω/sq.

Following the diffusion, an aluminium mixture composed of isopropyl alcohol and aluminium paste as 1:1 in weight was spread on the back side of the wafers to form back contacts. The wafers were then fired in a rapid thermal process with a peak temperature of 810 °C and cooled down to the room temperature. The final wafers had a heavily doped n-type front emitter and a heavily doped p-type back surface field.

After the Al metallization, the Si wafers were cut into small pieces with 2 x 2 cm$^2$ and rinsed with DI H$_2$O, acetone, and DI H$_2$O sequentially. A 5% PMMA/toluene mixture was spread on the as-formed Al back contact layer as a protection layer and then the wafers were heated to 180 °C for 20 minutes to evaporate the toluene solvent. The PMMA layer could prevent the back contact from being etched by the following phosphosilicate glass
(PSG) removal and the b-Si etching steps. Next, the Si wafers were immersed into the BOE for 3 minutes to remove a light blue layer of PSG that resulted from the previous phosphorous diffusion step on the Si wafer surface.

Sputtering was used to deposit Au lines with thickness of 100 nm on the Si wafers. A stainless steel mask with a designed pattern of one busbar and nine fingers was put on the front side of the Si wafers before the sputtering. Figure 3.18 shows the mask design used for the sputtering. Both the lengths of busbar and fingers were 1.8 cm, and the width of busbar and the fingers were 0.1 cm and 100 µm, respectively. The distance between each finger was 0.2 cm. After sputtering, the wafers were annealed at 180 °C for 1 hour to improve the adhesion of Au lines on the wafers.

![Figure 3.18. The design of mask for sputtering of Au contacts on Si pieces.](image)

The Au-deposited Si pieces were then etched in Si etchants consists of HF (48%), H$_2$O$_2$ (30%), and DI H$_2$O in different HF:H$_2$O$_2$:H$_2$O volume ratios with an equal volume
of DI H\textsubscript{2}O in sealed plasticware at room temperature. In the text, the volume ratio is given as X:Y:Z corresponding to the volume ratio of HF, H\textsubscript{2}O\textsubscript{2}, and H\textsubscript{2}O in the etchant before adding the equal volume of DI H\textsubscript{2}O. There were two categories of etchant compositions investigated in the content, and the HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O volume ratios of these two categories were 1:5:Z and X:Y:20, respectively. The 1:5:Z category included the 1:5:2, 1:5:5, and 1:5:20 series, and the X:Y:20 category included the ratio as 1:5:20, 2:4:20, 3:3:20, and 4:2:20 series (Table 3.4). After etching for the allotted time, the samples were rinsed by DI H\textsubscript{2}O and immersed into toluene to remove the PMMA protection layer on the backside of the Si wafer.

<table>
<thead>
<tr>
<th>HF:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O</th>
<th>Vol. of HF\textsuperscript{a}</th>
<th>Vol. of H\textsubscript{2}O\textsubscript{2}\textsuperscript{b}</th>
<th>Vol. of DI H\textsubscript{2}O</th>
<th>Vol. of mixture\textsuperscript{c}</th>
<th>Vol. of DI H\textsubscript{2}O</th>
<th>Total vol. of etchant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:5:2</td>
<td>2.0 (mL)</td>
<td>10.0 (mL)</td>
<td>4.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>20.0 (mL)</td>
</tr>
<tr>
<td>1:5:5</td>
<td>1.0 (mL)</td>
<td>5.0 (mL)</td>
<td>5.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>20.0 (mL)</td>
</tr>
<tr>
<td>1:5:20</td>
<td>1.0 (mL)</td>
<td>5.0 (mL)</td>
<td>20.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>20.0 (mL)</td>
</tr>
<tr>
<td>2:4:20</td>
<td>1.0 (mL)</td>
<td>2.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>20.0 (mL)</td>
</tr>
<tr>
<td>3:3:20</td>
<td>1.5 (mL)</td>
<td>1.5 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>20.0 (mL)</td>
</tr>
<tr>
<td>4:2:20</td>
<td>2.0 (mL)</td>
<td>1.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>10.0 (mL)</td>
<td>20.0 (mL)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 48\% HF. \textsuperscript{b} 30\% H\textsubscript{2}O\textsubscript{2}. \textsuperscript{c} HF + H\textsubscript{2}O\textsubscript{2} + H\textsubscript{2}O.

In order to maximize the b-Si solar cell efficiency, an Al\textsubscript{2}O\textsubscript{3} passivation layer with thickness of 22 nm was deposited on the solar cell surface by ALD. The precursors of Al\textsubscript{2}O\textsubscript{3} were DI H\textsubscript{2}O and TMA, and the deposition temperature was 200 °C. The wafers
were then annealed at 465 °C for 30 min with atmosphere consisting of 80% N\textsubscript{2} and 20% O\textsubscript{2}. After annealing, the b-Si solar cells were successfully fabricated.

**Characterization.** Scanning electron microscopy (SEM) images were carried out with FEI Quanta 400 by placing samples on double-sided carbon tape that was fixed to aluminium SEM stubs. Images were acquired at a typical operating voltage of 20 kV, with a working distance of 10 mm, spot size 3 in Hi-VAC mode. Before taking SEM images, the samples were cleaned by canned air to remove dust or tiny particles from the wafer surface.

The total reflectance spectra of the b-Si solar cells were measured with Ocean Optics ISP-REF integrating sphere with internal tungsten light source. The integrating sphere was collaborated by a homemade low reflectivity enclosure as a 0% standard and Labsphere SRS-10-010 Reflectance Standard as a 10% standard. The calculated average reflectivity is weighted by the AM1.5 solar spectrum. The average is the integral of the measured reflectivity over the wavelengths from 400 to 1000 nm times the ratio of the solar spectrum at different wavelength divided by the integral of the solar spectrum.

The efficiency of the b-Si solar cells were calculated from the I-V curves detected via Keithley 2420 and 2425 High-Current SourceMeter with an Oriel Model 81190 Solar simulator, including light intensity feedback control. The intensity of incident light was 100 mW/cm\textsuperscript{2}, which was calibrated by an OAI Mono-silicon 2 cm x 2 cm reference cell with a BK7 window. The cell was calibrated through NREL's Device Performance Measurements laboratory. The I-V curve measurement was based on 4-point probes method in order to get more accurate values. The solar cells were fixed on a metal vacuum chuck that also functioned as two of four probes and connected the back contact of solar cells. On the top surface of solar cells, there were two Cu wires connected to the Au busbar as the remaining two probes. One of them only measured the current and another one only measured the voltage to obtain the real voltage at the solar cell surface.
References


Chapter 4

Fabrication of anti-reflection coating layers for silicon solar cells by liquid phase deposition

Introduction

An anti-reflection (AR) coating is a type of optical coating applied on the surface of a material which can suppress reflection and improve light transmission or absorption. Ceramic AR coating layers are widely used on silicon (Si) solar cell surfaces to assist collection of incident photons and enhance energy conversion efficiency. With the AR coating layer, the reflectivity of the Si wafer surface can be effectively decreased from more than 30% to less than 5%. The ceramic AR coatings are usually prepared by chemical vapor deposition method and sol-gel method. However, both methods have drawbacks which limit their industrial applications: for the chemical vapor deposition method, some specific equipment is required for film depositions; for the sol-gel method, repeated coating is needed in order to get desired film thickness. Fortunately, the liquid phase deposition (LPD) method provides a low-cost way to fabricate oxide thin films on Si wafers as AR coating layers for the Si solar cells.

LPD has been investigated for many oxide formation, which include SiO₂, TiO₂, SnO₂, and WO₃. The LPD method involves a substrate immersion in an aqueous solution consisting of a silicon-fluoro or metal-fluoro complex precursor, [MF₄]⁽ⁿ⁻ⁿ⁾, which slowly hydrolyzes to form a ceramic oxide nanofilm on the substrate surface at low temperature (usually 25-50 °C). Fluoride scavengers, such as water, boric acid (H₃BO₃), or aluminum, can be added into the solution to accelerate film growth rate. Many different modifications of the growth conditions have been studied in order to optimize the electronic, optical, or mechanical properties which are related to crystallinity or porosity.

Simply, synthesis of oxides by LPD could be expressed with the following overall equilibrium reaction:
\[
H_{(n-m)}MF_n + (m/2)H_2O \rightleftharpoons MO_{(m/2)} + nHF
\]  

(4.1)

where \( m \) is the charge of the silicon or metal cation, and \( n \) is the number of fluorine atoms. According to Le Chatelier’s principle, equilibrium will be shifted towards the right-hand side to produce more oxide precipitation via either increasing water concentration or decreasing hydrofluoric acid (HF) concentration through addition of water or fluoride scavengers, respectively.

Although Eq. 4.1 can provide some useful information of the oxide film formation, it still cannot explain some observations of the growth of LPD thin films. For example, it cannot explain how elemental fluorine (F) is uniformly distributed within the films due to the incorporation of an intermediate complex during the growing process. Also, the fact that the films tend to form on SiO\(_2\) covered substrates implies that hydroxyl groups (-OH) are necessary on the substrate for deposition to occur.\(^{11}\) In order to better explain these observations, Wei et al. proposed that during the LPD-SiO\(_2\) formation process, the silicon source, hydrofluorosilicic acid (H\(_2\)SiF\(_6\)), is hydrolyzed to form SiO\(_2\), but some partially hydrolyzed Si intermediates (SiF\(_m\)(OH)\(_{4-m}\), \( m<4 \)) are also formed by the reaction:\(^{12}\)

\[
H_2\text{SiF}_6 + (4-m)H_2O \rightleftharpoons \text{SiF}_m(\text{OH})_{4-m} + (6-m)\text{HF}
\]  

(4.2)

The SiF\(_m\)(OH)\(_{4-m}\) intermediate species in the solution reacts with the -F or -OH groups on the substrate surface and form a SiO\(_2\) film. Meanwhile, the formed HF molecules by Eq. 4.2 also continuously react with the -OH groups on the substrate, decreasing the SiO\(_2\) film growth rate simultaneously. Figure 4.1 shows a schematic of LPD-SiO\(_2\) film formation. Koumoto et al. also proposed an analogous mechanism to describe the details of LPD-TiO\(_2\) film formation.\(^{13}\) This model not only effectively demonstrates the existence of residual fluorine in the LPD-films but also shows the importance of -OH groups on the substrate during the film growth.
Effects of ceramic precursor concentration. In a solution with dissolved ceramic precursors, nucleation and nucleus growth will occur either in the solution (homogenous nucleation) or on the substrate surface (heterogeneous nucleation). For LPD, it is vital that the supersaturation ratio is one that can effectively promote heterogeneous nucleation and suppress homogenous nucleation since successful formation of films relies on the former. If the growth solution is highly supersaturated, both kinds of nucleation will occur,
which causes difficulty in the film formation on a Si wafer. Conversely, as the growth solution is lowly supersaturated, both nucleation rates are slow which causes an extremely low film growth rate. Therefore, an intermediate supersaturation ratio, or ceramic precursor concentration, is necessary to allow the film to grow on the substrate with a proper rate through heterogeneous nucleation. Figure 4.2 shows the effect of supersaturation ratio for both kinds of nucleation.

![Desired zone](image)

**Figure 4.2.** Effect of supersaturation for homogeneous and heterogeneous nucleation rates.

**Effects of [H₃BO₃].** In LPD, the purpose of fluorine scavengers in the treatment solution is to remove the F⁻ ions to increase the oxide formation rate. H₃BO₃ is the most widely used fluoride scavenger for the LPD method due to its high solubility in aqueous solutions. H₃BO₃ immediately reacts with F⁻ ions to form more stable BF₄⁻ ions, and thus accelerates the consumption of non-coordinated F⁻ ions by the following process,¹⁰
\[ \text{H}_3\text{BO}_3 + 4\text{HF} \leftrightarrow \text{BF}_4^- + \text{H}_3\text{O}^+ + 2\text{H}_2\text{O} \quad (4.3) \]

By this way, \( \text{H}_3\text{BO}_3 \) can assist the overall equilibrium reaction, Eq. 4.1, shift to the right-hand side for faster oxide formation.

However, an excessively high \([\text{H}_3\text{BO}_3] \) is unfavorable for compact film formation. It would dramatically accelerate the formation rate of oxide, and thus improperly increase the supersaturation ratio in the solution. The supersaturation ratio would be out of the region of heterogeneous nucleation and result in the precipitation in the solution taking over the film formation on the Si wafer surface.\(^{15}\)

**Effects of temperature.** The LPD method has been proven as an endothermic reaction;\(^{16}\) therefore, raising deposition temperature can promote the hydrolysis reaction to increase the supersaturation ratio, which results in a higher nucleation rate with a smaller critical nuclei size.\(^{11}\) When the supersaturation ratio increases and the precursor concentration exceeds a critical concentration nuclei begin to appear. However, because the precursor concentration is still close to the critical concentration, the precursor molecules favorably condense on existing nuclei, growing and forming an oxide film on the Si wafer instead of forming new nuclei. Therefore, a higher deposition temperature is favorable for oxide film growth. This explanation is consistent with Koumoto et al.’s LPD-\( \text{TiO}_2 \) experimental results which show grain size decreasing with increasing temperature of deposition solution.\(^{13}\)

**Effects of calcination.** Calcination is the most common post-treatment after the film growth and is necessary. Calcination not only removes impurities from substrates, such as organic containments and residual F, but also leads to a higher crystalline degree and better morphology of films. When the calcination temperature is below 500 °C, no diffraction peaks could be observed for the LPD-\( \text{TiO}_2 \) thin films because the crystalline size is too
small to be detected.\textsuperscript{16} However, if the calcination temperature is high enough, the crystallite size starts to increase and morphology becomes smoother as well. This change is attributed to the high temperature that allows the atoms to obtain enough energy to break binding energy and begin to rearrange in order to release surface tension by decreasing the total surface area. Moreover, a high calcination temperature can also provide heat energy to evaporate organic and residual F, and thus these impurities are removed from the substrate.\textsuperscript{15,16}

In this chapter, the object is to fabricate an ideal AR coating layer possessing a refractive index close to 1.99 and film thickness near 75 nm on Si wafer surfaces. For 600 nm incident light, the refractive index of compact fumed SiO\textsubscript{2}, ZrO\textsubscript{2}, and TiO\textsubscript{2} materials are 1.46, 2.21, and 2.50, respectively. Hence, if two of these three materials can be well mixed in a suitable ratio, it is possible to obtain a composite material with a desired refractive index. Here, our strategy is using the LPD method to synthesize composite SiO\textsubscript{2}/ZrO\textsubscript{2} and SiO\textsubscript{2}/TiO\textsubscript{2} films which possess the desired refractive index and film thickness by investigating different film growth parameters.

**Results and Discussion**

In the following section, both film thickness and refractive index of the LPD sample can be simultaneously obtained from an ellipsometer with a model fitting. However, one important thing worth mentioning is that the lower detection limit of the ellipsometer of film thickness is around 20 nm. This means that if the measured result of film thickness is less than 20 nm, there might not be a LPD film on the Si wafer surface, and the measured film thickness and refractive index are not reliable. For this reason, the corresponding refractive indices will not be shown when the measured film thickness is less than 20 nm.

**LPD-SiO\textsubscript{2}** Before studying composite films, synthesis of pure SiO\textsubscript{2} films by the LPD method is first conducted to obtain basic growth conditions for the following composite
film reactions. A compact LPD-SiO$_2$ can be simply obtained using H$_2$SiF$_6$ solution without addition of H$_3$BO$_3$. The film thickness and refractive index of LPD-SiO$_2$ film grown for the deposition time of 24 hr at 30 °C have been investigated (Table 4.1). Without addition of H$_3$BO$_3$, the film thickness of samples shows a near positive linear correlation with H$_2$SiF$_6$ concentrations. Their refractive indices are also pretty close to that of fumed SiO$_2$ (1.46), which means the compact SiO$_2$ thin films are successfully formed on the Si wafers.

**Table 4.1. Summary of the LPD-SiO$_2$ growth.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>[H$_2$SiF$_6$] (M)</th>
<th>[H$_3$BO$_3$] (M)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-7</td>
<td>0.2</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>67.2</td>
<td>1.465</td>
</tr>
<tr>
<td>SZ-10</td>
<td>1.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>396.0</td>
<td>1.445</td>
</tr>
<tr>
<td>SZ-1</td>
<td>0.2</td>
<td>0.4</td>
<td>30</td>
<td>24</td>
<td>85.0</td>
<td>1.104</td>
</tr>
</tbody>
</table>

As H$_3$BO$_3$ is added into the growth solution, although the film thickness is effectively increased from 67.2 to 85.0 nm, the refractive index drops from 1.465 to 1.104 (SZ-7 and SZ-1), respectively, which is close to the refractive index of air (1.00). This indicates that the obtained SiO$_2$ film is very porous and contains a substantial amount of air. A possible reason for this porosity is that the excessively fast deposition rate causes the as-formed SiO$_2$ molecules not to have enough time to arrange well with each other, causing a fractal growth of layers that possess higher porosity, and produces many voids which contain air in the film. Therefore, although H$_3$BO$_3$ can increase the film growth rate, it also decreases the refractive index of film as well. Hence, it is concluded that to obtain a compact oxide film by the LPD method, addition of H$_3$BO$_3$ should be avoided if it is not necessary.
**LPD-SiO$_2$/ZrO$_2$.** Like LPD-SiO$_2$ film synthesis, formation of pure ZrO$_2$ thin film by the LPD method is also investigated before synthesis of composite SiO$_2$/ZrO$_2$ films. If a ZrO$_2$ thin film could be successfully fabricated, the conditions of the ZrO$_2$ film growth might be simply adjusted for fabrication of composite SiO$_2$/ZrO$_2$ films. Table 4.2 shows the film thickness and refractive indices of LPD-ZrO$_2$ films grown with different conditions. However, after increasing the [H$_2$ZrF$_6$], increasing the reaction temperature, extending the deposition time or even adding H$_3$BO$_3$ into the growth solutions, there is still no ZrO$_2$ film detected on the Si wafers. This may imply that the LPD method is not an effective approach to synthesize ZrO$_2$ films on the Si wafer surfaces.

**Table 4.2. Summary of the LPD-ZrO$_2$ growth.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>[H$_2$ZrF$_6$] (M)</th>
<th>[H$_3$BO$_3$] (M)</th>
<th>Temp. ($^\circ$C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-8</td>
<td>0.2</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>4.2</td>
<td>--</td>
</tr>
<tr>
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<td>--</td>
</tr>
<tr>
<td>SZ-2</td>
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<td>0.4</td>
<td>30</td>
<td>24</td>
<td>4.4</td>
<td>--</td>
</tr>
<tr>
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<td>0.4</td>
<td>30</td>
<td>72</td>
<td>4.3</td>
<td>--</td>
</tr>
</tbody>
</table>

Since the SiO$_2$ films have been already successfully synthesized by the LPD method, it is worth adding the SiO$_2$ precursor, H$_2$SiF$_6$, into the growth solutions for the ZrO$_2$ films. The well arranged hydrolyzed intermediates of SiO$_2$ in the solution may interact with the intermediates of ZrO$_2$ to form a composite SiO$_2$/ZrO$_2$ film. The existence of H$_2$SiF$_6$ in the solution might be beneficial for the growth of a composite film. Different ratios of H$_2$SiF$_6$/H$_2$ZrF$_6$ have been used in the growth solution without H$_3$BO$_3$ (Table 4.3), but as can be seen, there is still no film growth on the Si wafer surfaces. This might be due to the
formation rate of the film is too slow; therefore, both addition of $\text{H}_3\text{BO}_3$ and a higher reaction temperature are used to accelerate the film deposition rate.

Table 4.3. Summary of the LPD-$\text{SiO}_2$/ZrO$_2$ growth at 30 °C without $\text{H}_3\text{BO}_3$.  

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{H}_2\text{SiF}_6]$ (M)</th>
<th>$[\text{H}_2\text{ZrF}_6]$ (M)</th>
<th>$[\text{H}_3\text{BO}_3]$ (M)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-12</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>8.4</td>
<td>--</td>
</tr>
<tr>
<td>SZ-23</td>
<td>0.5</td>
<td>1.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>12.8</td>
<td>--</td>
</tr>
<tr>
<td>SZ-25</td>
<td>0.5</td>
<td>2.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>9.7</td>
<td>--</td>
</tr>
<tr>
<td>SZ-26</td>
<td>1.0</td>
<td>1.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>10.0</td>
<td>--</td>
</tr>
<tr>
<td>SZ-28</td>
<td>1.0</td>
<td>2.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>13.4</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 4.4 shows the comparison of the film growth with and without $\text{H}_3\text{BO}_3$. Although the addition of $\text{H}_3\text{BO}_3$ can effectively increase the film growth rate to form $\text{SiO}_2$/ZrO$_2$ films on the Si wafers, the refractive indices of these films are still pretty low. One fact that need to be noted is that as the deposition time is increased to 72 hrs (SZ-6), the refractive index of the film is even lower and closer to the refractive index of air compared to that of the film growth with 24 hrs (SZ-3). A possible explanation might be the as-formed HF molecules in the growth solution start to etch the fabricated oxide film and leave voids in the film. Hence, addition of the $\text{H}_3\text{BO}_3$ seems to be an unsuitable approach to aid in forming a compact $\text{SiO}_2$/ZrO$_2$ film on the Si wafer surfaces.

Similar to the addition of $\text{H}_3\text{BO}_3$, increasing the deposition temperature also assists the formation of $\text{SiO}_2$/ZrO$_2$ films on the Si wafers (Table 4.5). Since the LPD reaction is endothermic, it is reasonable that a higher temperature is favorable for film deposition. As the deposition temperature is increased to 50 °C, a composite film is successfully fabricated in 12 hrs (SZ-20). However, the refractive indices of the obtained films are even lower than
that of films obtained by addition of $\text{H}_3\text{BO}_3$. This indicates that increasing deposition temperature is also not an effective way to synthesize compact composite $\text{SiO}_2/\text{ZrO}_2$ film on the Si wafers.

**Table 4.4.** Summary of the LPD-$\text{SiO}_2/\text{ZrO}_2$ growth at 30 °C with $\text{H}_3\text{BO}_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{H}_2\text{SiF}_6]$ (M)</th>
<th>$[\text{H}_2\text{ZrF}_6]$ (M)</th>
<th>$[\text{H}_3\text{BO}_3]$ (M)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-9</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>4.1</td>
<td>--</td>
</tr>
<tr>
<td>SZ-3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>30</td>
<td>24</td>
<td>60.3</td>
<td>1.262</td>
</tr>
<tr>
<td>SZ-6</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
<td>30</td>
<td>72</td>
<td>123.2</td>
<td>1.046</td>
</tr>
</tbody>
</table>

**Table 4.5.** Summary of the LPD-$\text{SiO}_2/\text{ZrO}_2$ growth at different temperatures without $\text{H}_3\text{BO}_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{H}_2\text{SiF}_6]$ (M)</th>
<th>$[\text{H}_2\text{ZrF}_6]$ (M)</th>
<th>$[\text{H}_3\text{BO}_3]$ (M)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>SZ-23</td>
<td>0.5</td>
<td>1.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>12.8</td>
<td>--</td>
</tr>
<tr>
<td>SZ-18</td>
<td>0.5</td>
<td>1.0</td>
<td>0.0</td>
<td>50</td>
<td>3</td>
<td>6.1</td>
<td>--</td>
</tr>
<tr>
<td>SZ-20</td>
<td>0.5</td>
<td>1.0</td>
<td>0.0</td>
<td>50</td>
<td>12</td>
<td>31.7</td>
<td>1.037</td>
</tr>
<tr>
<td>SZ-22</td>
<td>0.5</td>
<td>1.0</td>
<td>0.0</td>
<td>50</td>
<td>24</td>
<td>95.9</td>
<td>1.045</td>
</tr>
</tbody>
</table>

So far, the effects of $[\text{H}_2\text{ZrF}_6]$ and $[\text{H}_3\text{BO}_3]$, deposition temperature, and deposition time on the LPD-$\text{SiO}_2/\text{ZrO}_2$ film growth have been investigated. Nevertheless, there is still no satisfying composite $\text{SiO}_2/\text{ZrO}_2$ film fabricated on the Si wafer surfaces. The highest refractive index of the LPD-$\text{SiO}_2/\text{ZrO}_2$ film is only 1.262 (SZ-3), which is even much lower than that of LPD-$\text{SiO}_2$ (1.465). Therefore, the oxide precursor solution is changed from
H2ZrF6 to H2TiF6 and fabrication of composite LPD-SiO2/TiO2 films is investigated, which
may possess higher refractive indices.

**LPD-SiO2/TiO2.** For synthesizing composite LPD-SiO2/TiO2 films, formation of
TiO2 films is conducted first in order to acquire basic growth conditions for the further
SiO2/TiO2 film growth. However, without the scavenger (H3BO3), even though the
[H2TiF6] is increased from 0.1 to 1.0 M, there is still no TiO2 film detected on the Si wafers
(Table 4.6).

<table>
<thead>
<tr>
<th>Sample</th>
<th>[H2TiF6] (M)</th>
<th>[H3BO3] (M)</th>
<th>Temp. (°C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-1</td>
<td>0.1</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>3.7</td>
<td>--</td>
</tr>
<tr>
<td>ST-3</td>
<td>0.3</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>3.7</td>
<td>--</td>
</tr>
<tr>
<td>ST-5</td>
<td>1.0</td>
<td>0.0</td>
<td>30</td>
<td>24</td>
<td>3.9</td>
<td>--</td>
</tr>
</tbody>
</table>

Fortunately, as a proper ratio of H2TiF6/H3BO3 is applied to the growth solution, the
TiO2 films can successfully grow on the wafers. Table 4.7 shows a summary of the TiO2
film growth by the LPD method with different ratios of H2TiF6/H3BO3. The results show
that when the H2TiF6/H3BO3 is equal to or large than 1 (ST-4 and ST-6), the TiO2 films are
not formed on the Si wafers most likely because the film growth rate cannot be effectively
accelerated. Nevertheless, with the H2TiF6/H3BO3 ratio of 0.1 M/0.3 M, a LPD-TiO2 film
with refractive index of 1.457 is successfully obtained (ST-2). This refractive index is far
smaller than that of compact TiO2 (2.50), which indicates that the obtained TiO2 film is
still pretty porous.
Table 4.7. Summary of the LPD-TiO$_2$ growth with H$_3$BO$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[H$_2$TiF$_6$] (M)</th>
<th>[H$_3$BO$_3$] (M)</th>
<th>Temp. ($^{\circ}$C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-2</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>24</td>
<td>47.1</td>
<td>1.457</td>
</tr>
<tr>
<td>ST-4</td>
<td>0.3</td>
<td>0.3</td>
<td>30</td>
<td>24</td>
<td>3.5</td>
<td>--</td>
</tr>
<tr>
<td>ST-6</td>
<td>1.0</td>
<td>0.3</td>
<td>30</td>
<td>24</td>
<td>3.9</td>
<td>--</td>
</tr>
<tr>
<td>ST-17</td>
<td>0.1</td>
<td>0.6</td>
<td>30</td>
<td>24</td>
<td>92.9</td>
<td>1.283</td>
</tr>
<tr>
<td>ST-18</td>
<td>0.2</td>
<td>0.6</td>
<td>30</td>
<td>24</td>
<td>27.5</td>
<td>1.439</td>
</tr>
</tbody>
</table>

As the [H$_2$TiF$_6$] is kept at 0.1 M but the [H$_3$BO$_3$] is increased to 0.6 M (ST-17), a much thicker film with a lower refractive index is obtained as compared to the one with a [H$_3$BO$_3$] of 0.3 M (ST-2). Although the film synthesized with a H$_2$TiF$_6$/H$_3$BO$_3$ ratio of 0.2 M/0.6 M (ST-18) has a similar refractive index than the film synthesized with a ratio of 0.1 M/0.3 M (ST-2), the film thickness of the former is much thinner. Since the H$_2$TiF$_6$/H$_3$BO$_3$ ratio of 0.1 M/0.3 M provided the highest refraction index (even though it is still not high enough), the following experiments are based on the H$_2$TiF$_6$/H$_3$BO$_3$ ratio of 0.1 M/0.3 M to further study the effects of other growth conditions on the film formation.

Film deposition time also plays an important role in the film thickness and refractive index of LPD-TiO$_2$ films. Table 4.8 shows the TiO$_2$ film growth with different deposition times. With the H$_2$TiF$_6$/H$_3$BO$_3$ ratio of 0.1 M/0.3 M, the films formed on the Si wafers can be detected by the ellipsometer for a deposition time of 24 and 48 hrs but not for 12 hrs. This means that the film formation is still in the nucleation step during the initial 12 hrs. However, if we focus on the films with the deposition time of 24 and 48 hrs, we can find that the refractive index of the film with the deposition time of 48 hrs (ST-15) is lower than that of of the film with the deposition time of 24 hrs (ST-2). Therefore, the deposition time is set as 12 or 24 hrs for the following composite SiO$_2$/TiO$_2$ film formation to obtain...
compact films.

Table 4.8. Summary of the LPD-TiO$_2$ film growth with different deposition times.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{H}_2\text{TiF}_6]$ (M)</th>
<th>$[\text{H}_3\text{BO}_3]$ (M)</th>
<th>Temp. ($^\circ$C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-7</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>3.9</td>
<td>--</td>
</tr>
<tr>
<td>ST-2</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>24</td>
<td>47.1</td>
<td>1.457</td>
</tr>
<tr>
<td>ST-15</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>48</td>
<td>73.3</td>
<td>1.166</td>
</tr>
</tbody>
</table>

From previous results, it has been shown that addition of H$_2$SiF$_6$ can accelerate the deposition time of the composite SiO$_2$/ZrO$_2$ films. For this reason, we can expect that the addition of H$_2$SiF$_6$ in the SiO$_2$/TiO$_2$ film growth solution should also accelerate the deposition rate of SiO$_2$/TiO$_2$ films. Table 4.9 shows a summary of the composite LPD-SiO$_2$/TiO$_2$ film growth with different [H$_2$SiF$_6$].

Table 4.9. Summary of the composite LPD-SiO$_2$/TiO$_2$ film growth with different H$_2$SiF$_6$ concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\text{H}_2\text{SiF}_6]$ (M)</th>
<th>$[\text{H}_2\text{TiF}_6]$ (M)</th>
<th>$[\text{H}_3\text{BO}_3]$ (M)</th>
<th>Temp. ($^\circ$C)</th>
<th>Time (hr)</th>
<th>Thickness (nm)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST-7</td>
<td>0.0</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>3.9</td>
<td>--</td>
</tr>
<tr>
<td>ST-8</td>
<td>0.015</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>4.2</td>
<td>--</td>
</tr>
<tr>
<td>ST-9</td>
<td>0.03</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>4.7</td>
<td>--</td>
</tr>
<tr>
<td>ST-10</td>
<td>0.05</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>5.5</td>
<td>--</td>
</tr>
<tr>
<td>ST-11</td>
<td>0.08</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>20.5</td>
<td>1.175</td>
</tr>
<tr>
<td>ST-12</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>30</td>
<td>12</td>
<td>27.4</td>
<td>1.104</td>
</tr>
</tbody>
</table>
For the deposition time of 12 hrs, only the films with a $\text{H}_2\text{SiF}_6$ concentration of 0.08 and 0.1 M (ST-11 and ST-12, respectively) can effectively form films on the Si wafer surfaces, but the refractive indices of these two films are still extremely low, which are 1.175 and 1.104, respectively. For the other $[\text{H}_2\text{SiF}_6]$, there is no film detected on the Si wafer surfaces. However, if the deposition time can be appropriately increased, it is believed that the composite LPD-SiO$_2$/TiO$_2$ films should appear on the Si wafer surfaces.

**Conclusions**

In this work, different experimental conditions have been shown to grow composite SiO$_2$/ZrO$_2$ and SiO$_2$/TiO$_2$ AR coating layers on the Si wafer surfaces. The two important properties of the AR coating layers, the film thickness and the refractive index, are obtained by an ellipsometer. From the results, both excessively long deposition time and high deposition temperature are found to be unfavorable for formation of compact films even though the film growth rate could be effectively improved. Although the LPD method has difficulty synthesizing compact SiO$_2$/ZrO$_2$ films, compact SiO$_2$/TiO$_2$ films are possible to be fabricated with some adjustments of experimental conditions. If the fabrication of AR coating layers by the LPD method could be successfully developed, this simple process could replace the CVD method for large-scale industrial applications.

**Experimental**

Hexafluorosilicic acid ($\text{H}_2\text{SiF}_6$, 33.5-35.0 wt.%), hexafluorozirconic acid ($\text{H}_2\text{ZrF}_6$, 50 wt.%), hexafluorotitanic acid ($\text{H}_2\text{TiF}_6$, 60 wt.%), hydrochloric acid (HCl, 37%), hydrochloric acid (HCl, 37%), fumed silica (SiO$_2$, 99.8% pure), titanium dioxide (TiO$_2$), and zirconium dioxide (ZrO$_2$) were obtained from Sigma-Aldrich. Acetone (${(\text{CH}_3)_2\text{CO}}$), boric acid (H$_3$BO$_3$), and hydrogen peroxide (H$_2$O$_2$, 30%) were obtained from Fisher. Ammonium hydroxide (NH$_4$OH, 28-30%) was obtained from EMD. All the chemicals were used as received.

All polished single crystalline (100) p-type Si wafers were obtained from Silicon
Quest International. All water was ultra-pure (UP), obtained from a Millipore Milli-Q UV water filtration system. LPD reaction solutions were filtered using Millipore Express PLUS Membranes made of poly(ethersulfone) with 0.1 µm pore sizes.

All the undiluted solutions of $\text{H}_2\text{SiF}_6$, $\text{H}_2\text{TiF}_6$, and $\text{H}_2\text{ZrF}_6$ were saturated by adding excess fumed $\text{SiO}_2$, $\text{TiO}_2$, and $\text{ZrO}_2$, respectively, and stirred overnight under seal before use. The saturated solutions were then filtered and diluted to allotted concentrations for reactions. The Si wafers were cut into 1 x 3 cm$^2$ pieces and ultrasonically cleaned in acetone and UP water for 20 minutes, respectively. All the Si pieces than were cleaned via the RCA method. RCA cleaning of the Si pieces involved a two-step etching process. First, the Si pieces were immersed in the initial etchant (RCA-1), a solution consisting of $\text{NH}_4\text{OH}$: $\text{H}_2\text{O}_2$: $\text{H}_2\text{O}$ in a 1:1:5 volume ratio, with stirring at 80 °C for 10 minutes. After rinsing with UP water, the Si pieces were immersed in a second etchant (RCA-2) consisting of $\text{HCl}$: $\text{H}_2\text{O}_2$: $\text{H}_2\text{O}$ in a 1:1:6 volume ratio, with stirring at 80 °C for another 10 minutes.

The RCA-1 etchant removes organic impurities by undercutting the oxide layer where the impurities adhere. The oxide layer on the Si wafer surface is slowly etched by the $\text{NH}_4\text{OH}$, which dislodges impurity particles from the wafer surface. Organics are removed via oxidative dissolution and metal such as gold, silver, copper, nickel, cobalt and chromium are also dissolved and removed from the surface. Other metal impurities and $\text{NH}_4\text{OH}$ insoluble hydroxides, such as aluminum, magnesium and zinc hydroxide, are removed via the RCA-2 etchant. These RCA cleanings cover the Si pieces with hydrophilic surfaces containing -OH groups which are beneficial for the thin film growth by the LPD method. In contrast, removing the native oxide layer of the silicon pieces via a dilute HF solution leaves a hydrophobic surface containing with hydrogen groups.

The saturated precursor stock solutions are diluted with UP water to desired concentrations. A $\text{H}_3\text{BO}_3$ solution, a fluorine scavenger, was prepared freshly with UP water and well mixed with the precursor solution(s) to form growth solutions. RCA cleaned Si pieces were vertically immersed in the growth solutions. All reactions were performed
in plasticware without stirring in a water bath at either 30 or 50 °C for an allotted time. To prevent vaporization of the growth solutions and introduction of foreign impurities, the plasticware was covered with plastic lids. The as-prepared samples were rinsed in UP water and dried by canned air. The dried LPD samples were then calcinated at 600 °C for 2 hrs under air atmosphere with a heating rate of 10 °C/min. Figure 4.3 is a flow chart for the LPD thin film process. The refractive index and film thickness of as-grown LPD films were measured by an image ellipsometer (Nanofilm EP3) due to its high precision (0.01 nm) and non-destructive measurement.

Figure 4.3. The flow chart for the front-to-end LPD thin film process.
References


Conclusions

In the silicon (Si) solar cell industry, anti-reflection (AR) coating is widely used to suppress the reflection on the solar cell surfaces for maximizing energy conversion efficiency. In this thesis, I have proven that black silicon (b-Si) consisting of nanopores is a potential replacement for the AR coating. I proposed two feasible and economical approaches which are one-step metal-assisted chemical etching (MACE) method and contact-assisted chemical etching method (CACE) to fabricate b-Si AR layers on Si wafer surfaces. Unlike the conventional AR coating, the AR ability of b-Si is not limited by a narrow range of light incident angle and wavelength, which makes b-Si even more promising for industrial applications.

Fabrication of b-Si by the one-step metal-assisted chemical etching (MACE) method with silver and copper nanoparticles were systematically studied in order to simplify the fabrication process of b-Si by the two-step MACE method. The most important advantage of the one-step MACE method is that both metal deposition and electroless chemical etching occur simultaneously, allowing the b-Si to be fabricated in a one-pot reaction at room temperature. The metal nanoparticle catalysts in the MACE method help oxidize Si around the metal nanoparticles to SiO₂ which is immediately etched by HF in the Si etchant to fabricate nanopores on the Si wafer surfaces.

The one-step silver-assisted chemical etching method can fabricate b-Si in minutes with extremely low silver precursor concentrations (< 500 μM). In general, when the nanopores are longer, the reflectivity of the Si wafer surfaces are lower. However, the length of nanopores need to be well controlled to avoid destroying the p-n junction interfaces in the Si solar cells, which are usually about 500 nm deep under the wafer surface. Fabrication of b-Si AR layers on Si wafer surfaces by the one-step copper-assisted chemical etching method was also first reported by us. This new method can cut down the fabrication cost of b-Si since the precursor of copper catalysts, Cu(NO₃)₂, is much cheaper.
than that of silver catalysts, AgNO₃. Compared to the silver-assisted chemical etching method, the copper-assisted chemical etching method needs more time to fabricate nanopores which is usually more than 8 hrs. The fabricated nanopores have an inverted pyramidal shape which is different from the cylindrical nanopores fabricated with the assistance of silver nanoparticles.

Fabrication of b-Si AR layers on Si solar cells by the CACE method was also introduced and a detailed mechanism of the CACE method was proposed to describe the etching process. The working principle of the CACE method is similar to the MACE method but needs no addition and removal of metal catalysts, which keeps the b-Si structures from being destroyed during the metal removal step. The pre-deposited gold contacts with only 100 nm thickness on the front surfaces of Si solar cells can also function as catalysts to effectively fabricate nanopores. Hence, the CACE method can further decrease the fabrication cost of b-Si AR layers on the Si solar cells. Meanwhile, selective emitters which can improve the open-circuit voltage and short-circuit current density of solar cells were concurrently formed within the cells during the etching process. Besides, it was found that an excessively long etching time is detrimental to solar cell efficiency due to the collapse of b-Si structures and penetration of p-n junction interfaces.

The CACE method is easily integrated into the current production line of commercial Si solar cells without many changes. The highest achieved efficiency of the b-Si solar cell fabricated with the CACE method was 8.99%. This efficiency still can be further improved with optimization of the fabrication parameters. For example, if the thickness of gold contacts increases, the contact resistance would decrease leading to a higher fill factor and a higher corresponding efficiency. Also, a better design of the gold contact pattern should be found in order to maximize the solar cell surfaces exposed to the light and collect more generated charge carriers as well. Another factor of concern is the dopant concentration of the Si wafers. The concentration may not only affect the location of p-n junction interface,
but also the etching rate and the b-Si morphology, which all are related to the solar cell efficiency.

In addition to the b-Si fabrication, the liquid phase deposition (LPD) method was also used to deposit ceramic AR coating layers on Si wafers. In the results, compact SiO$_2$ films was successfully synthesized on the wafers and the film thickness was also easily controlled. However, TiO$_2$, ZrO$_2$, and other composite AR coating layers seemed difficult grow on the wafer surfaces. Neither thickness nor refractive index of the films approached the desired target. In order to improve the properties of AR coating layers fabricated by the LPD method, adjusting the growth conditions of films might be worth trying.

In conclusion, my total work has demonstrated that b-Si AR layers were successfully fabricated by the MACE method and CACE method with the assistance of silver, copper, and gold catalysts. The feasibility of the b-Si fabrication methods and the AR ability of fabricated b-Si have proven potential for b-Si AR layers in the solar cell industry. In the near future, I believe we might be able to see the impacts of b-Si on related research fields and technology of b-Si widely used in commercial Si solar cells.
Appendix A

Complete list of published articles


Appendix B

Reprint

Nanopore-type black silicon anti-reflection layers fabricated by a one-step silver-assisted chemical etching

Yen-Tien Lu and Andrew R. Barron

An effective and economical fabrication process for the synthesis of nanopore-type “black silicon”, that significantly decreases reflectivity of silicon wafer surfaces, is reported using a room temperature one-step Ag-assisted chemical etching method. The effects on the surface morphology and the corresponding surface reflectivity of the concentration of the silver catalyst (500, 50, and 5 μM), the HF and H₂O₂ concentration in the silicon etchant, the HF:H₂O₂ ratio, and etching time have been investigated. Lower reflectivity is a balance between sufficient silver catalyst to create large numbers of nanopores on a silicon surface and excessive silver that brings deeply etched channels that would potentially short-circuit a solar cell junction. The lowest relative effective reflectivity (0.17% over a range of 300–1000 nm) occurs with a silver ion concentration of 50 μM, however, with the silver ion concentration decreases to 5 μM surfaces with a lower relative effective reflectivity (2.60%) and a short nanopore length (<250 nm) can be obtained with 10 minute etching time, indicating that this method can be used as a simple (one-pot), low cost (low silver concentration), energy efficient (room temperature), method for the synthesis of anti-reflection layers for silicon-based solar cell applications.

1. Introduction

Solar cells need low surface reflectance to maximize the amount of incident photons absorbed by the semiconductor to convert incident light into electrical energy. In the solar cell industry, the use of an anti-reflection (AR) coating is a popular method to suppress the reflection of solar cell surface by forming destructive interference of incident light. Typical AR coatings for silicon solar cells are SiNx, produced by chemical vapour deposition have a reflectance of about 6% as compared to 40% for a polished silicon wafer. However, AR coatings are limited in use because it only reduces the reflection for a narrow range of light wavelength and incident angle since its functionality is based on a quarter-wavelength coating.1–4 Thus, the lowest reflectivity (and hence highest photon to electron efficiency) of a solar cell will only occur when the incident sunlight is at a particular angle. A potential replacement for the conventional AR coating, so-called “black silicon” (b-Si), first reported by Jansen et al.,5 has attracted attention for Si-based solar cells.6–8 Black silicon is a type of porous silicon whose surface morphology provides a graded refractive index between the silicon surface of the device and air, that results in a low reflectivity and a correspondingly high absorption of visible light.9 Black silicon has been successfully fabricated by several different methods including reactive ion etching,5,10,11 laser chemical etching,12–14 pulsed electrochemical etching,4,15 and fast atom beam etching.16 However, these techniques need either expensive instruments and high energy consumption or complicated fabricating processes, making them unfavorable for industrial applications.

Recently, an economical and efficient approach for industrial b-Si manufacturing called metal-assisted chemical etching method has been developed to avoid the above disadvantages.8,17–20 The metal-assisted chemical etching method includes two steps: metal deposition and electroless chemical etching. In the metal deposition step, a noble metal, such as Au, Ag, and Pt is deposited on the Si surface usually as nanoparticles (NPs).21,22 The metal NPs attract
electrons from the silicon surface promoting the oxidation to SiO$_2$ in the presence of an appropriate oxidant. In the electroless chemical etching step, the as-formed SiO$_2$ is etched away by HF (as H$_2$SiF$_6$) and a pit is produced under each NP. As these reactions occur in a continuous process the pits become deeper and ultimately connect with each other, and remaining Si substrate forms b-Si that consists of a silicon nanowire (Si-NW) structure. Unfortunately, this nanowire structure is very fragile making the incorporation of b-Si into typical fab processes difficult.$^{20}$

A proposed mechanism based on the working principle of galvanic cells thoroughly explains the electroless chemical etching with metal NP deposition on the Si material surface.$^{23}$ The mechanism consists of two half-cell reactions: a cathode reaction at the metal NP surface (eqn (1)) and an anode reaction occurring at the contact point between the Si and metal NP (eqn (2) and (3)).$^{19,22-25}$ The overall reaction is thus as shown in eqn (4).

$$\begin{align*}
H_2O_2 + 2H^+ + 2e^- & \rightleftharpoons 2H_2O \quad (1) \\
Si + 2H_2O & \rightleftharpoons SiO_2 + 4H^+ + 4e^- \quad (2) \\
SiO_2 + 6HF & \rightleftharpoons H_2SiF_6 + 2H_2O \quad (3) \\
Si + 2H_2O_2 + 6HF & \rightleftharpoons H_2SiF_6 + 4H_2O \quad (4)
\end{align*}$$

The potential difference between the cathode sites and the anode sites results a net flux of electrons through the metal NPs and accumulation of electrons on the cathode sites. Since the cathode sites can provide more electrons for the reduction of H$_2$O$_2$, the overall reaction (eqn (4)) continues resulting in etching of Si under the Ag NPs.$^{23}$

Branz et al. developed a one-step Au-assisted chemical etching method based on the two-step metal-assisted chemical etching to fabricate nanopore-type b-Si.$^{26}$ During the process of the one-step method, the deposition of Au NPs and the chemical etching of Si occurred simultaneously on the Si wafer surface within the system consisting of HAuCl$_4$: HF : H$_2$O : H$_2$O$_2$, where Au$^{3+}$ ions were reduced to Au NPs on the Si wafer surface. The fabricated nanopore structure suppressed the reflectance of the wafer to below 2% across a wavelength range of 300–1000 nm.

Unfortunately, some porous Si structures possessing low reflectivity lead to failure in improving energy conversion efficiency of the Si-based solar cells because their surface area is too high resulting in high charge recombination. To overcome this problem Branz and co-workers demonstrated that a two step silver-assisted chemical etching to fabricate nanopores could be followed by a third step, which involves etching using tetramethylammonium hydroxide (TMAH) to shorten the nanopore length.$^{27}$ However, the concentration of silver is relatively high (1 mM) for Ag deposition and the process takes three distinct steps to accomplish the desired structure. Based on this result we are interested in two challenges: what is the effect of silver concentration and can the reaction be formed in a one-step process?

Herein, our research focuses on the one-step Ag-assisted chemical etching to fabricate b-Si, since the Ag precursor has lower cost than the Au equivalent and recycling of the Ag is well understood in the (now defunct) film industry. In our study, AgNO$_3$ was utilized as an Ag NP precursor in a HF : H$_2$O$_2$ : H$_2$O solution to compose of a Si etchant. The H$_2$O$_2$ not only facilitates the Si etching (eqn (4)) but also reduces Ag$^+$ ions to Ag NPs on the Si wafer (eqn (5)).

$$2Ag^+ + H_2O_2 \rightleftharpoons O_2 + 2H^+ + 2Ag \quad (5)$$

We are interested in the effects of the Ag ion concentration and the volume ratio of HF : H$_2$O$_2$ : H$_2$O on the morphology and reflectivity of the b-Si surface. Compared to other methods, the one-step Ag-assisted chemical etching simplifies the b-Si fabrication process and may cut down the cost of the facilities and energy expenditures, which is beneficial for industrial applications. In addition, unlike Si-NW arrays, the nanopore-type b-Si possesses no high-aspect-ratio needle-like structure and is not as fragile as SiNW arrays and can thus better endure the stress during the solar cell assembly.

2. Experimental

All the reactions were carried out in sealed plasticware at room temperature. AgNO$_3$ (Sigma-Aldrich), HF (48%, Sigma-Aldrich), H$_2$O$_2$ (30%, EMD), and NH$_4$OH (30%, Fisher Scientific) were used as received. Polished single crystalline (100) p-type boron-doped Si wafers (Silicon Quest International), with resistivity of 1–5 Ω cm, were individually ultrasonically cleaned in acetone and ultra-pure DI water.

The cleaned Si pieces were etched in Si etchants containing HF (48%), H$_2$O$_2$ (30%), and ultra-pure water in different volume ratios with an equal volume of 1000, 100 and 10 μM AgNO$_3$ aqueous solutions with sonication (Table 1), giving an overall [Ag$^+$] in the etchant of 500, 50, and 5 μM, respectively. In the text, the volume ratio is given as $X:Y:Z$ corresponding to the volume ratio of HF, H$_2$O$_2$, and H$_2$O in the etchant, respectively. After etching for 2, 5, 10, or 20 min, the as-prepared b-Si samples were rinsed in ultra-pure DI water, and then cleaned by a silver etchant consisting of NH$_4$OH and H$_2$O$_2$ in a 1:1 volume ratio at room temperature with sonication to remove the Ag NPs on the wafer surface. The Ag-removed samples were immersed in DI water again and dried by canned air.

The morphology and structure of b-Si samples in plane and cross section were characterized by using FEI Quanta 400 high-resolution field emission scanning electron microscope (FESEM). The Ag NP size on the Si wafer surface was characterized by using the image analysis program ImageJ. The reflectivity of the b-Si surface. Compared to other methods, the one-step Ag-assisted chemical etching simplifies the b-Si fabrication process and may cut down the cost of the facilities and energy expenditures, which is beneficial for industrial applications. In addition, unlike Si-NW arrays, the nanopore-type b-Si possesses no high-aspect-ratio needle-like structure and is not as fragile as SiNW arrays and can thus better endure the stress during the solar cell assembly.

3. Results and discussion

Using a high Ag ion concentration (500 μM) results in only Ag NPs and shallow pits being formed. However, no nanopores can be observed on the Si wafer surface. Fig. 1 shows SEM images of Ag NPs formed on the Si wafer surfaces with different HF : H$_2$O$_2$ : H$_2$O volume ratios. We propose that no nanopores appear on the wafer...
surfaces due to the fact that the majority of the surface is covered by the Ag NPs under the high [Ag⁺] etching conditions. In the Ag-assisted chemical etching method, the HF etches away not only the areas underneath the Ag NPs but also the areas adjacent to the Ag NPs, as may be seen by the images of the Ag NP sitting inside larger pits (Fig. 1b and c). As the majority of the wafer surface is covered by Ag NPs, a near isotropic oxidation of Si occurs. This causes different regions of the Si wafer to be subject to a similar etching level and no nanopores can be observed on the Si wafers.

It was also observed that the average diameters of the Ag NPs prepared in solutions of different HF:H₂O₂:H₂O ratios increase with time even at the earliest stages of the etch process. After reaching a maximum size at 5 min, the NPs gradually decrease in size. Fig. 2 shows the average diameters of Ag NPs for different etching time and HF:H₂O₂:H₂O volume ratios. A reasonable explanation for this effect is that the H₂O₂ in the Si etchant not only assists the Ag NP formation but also dissolves the as-formed Ag NPs into Ag ions (eqn (6)). As the H₂O₂ has been consumed and its concentration is no longer high enough, the equilibrium is shifted; resulting in the dissolution of the Ag NPs dominates and decreases the average size of Ag NPs.

$$2\text{Ag} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightleftharpoons 2\text{Ag}^+ + 2\text{H}_2\text{O}$$  \hspace{1cm} (6)

Another observation is that with the lower [HF] and [H₂O₂] the average diameter of the Ag NPs is more constant with etching time and the standard deviation in NP diameter also is smaller (Fig. 2). This indicates that the Ag NPs are smaller with a more monodispersed size, which may be attributed to the fact that a lower [H₂O₂] leads a slower rate of formation of Ag NPs (eqn (5)). The slower growth rate limits the difference in Ag NP size between the earlier-formed NPs and later-formed NPs during the etching process. In addition, it implies that in order to fabricate nanopores with more uniform size distribution, relying on the lower [HF] and [H₂O₂] to form monodispersed Ag NPs is necessary since the nanopores are simply the sinking track of Ag NPs.

<table>
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<th>[Ag⁺] (μM)</th>
<th>Volume HF (mL)</th>
<th>Volume H₂O₂ (mL)</th>
<th>Volume DI H₂O (mL)</th>
<th>Volume mixture (mL)</th>
<th>Volume AgNO₃ (μL)</th>
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* 48% HF.  
* 30% H₂O₂.  
* [AgNO₃] = 0.01 M.  
* HF + H₂O₂ + H₂O.
As the Ag ion concentration is reduced to 50 μM, nanopores are observed on the Si wafer surfaces, with the majority of them being macropores (50–1000 nm). The lower [Ag⁺] provides a lower nucleation and growth rate of Ag NPs; therefore, the Si wafer surface is no longer mostly covered by Ag NPs. In other words, the Ag NPs on the wafer surface are better dispersed and are able to nearly unidirectional oxidize the Si under the Ag NPs to SiO₂ which is immediately etched by HF. As long as both of the oxidation and etching continue, the Ag NPs would keep sinking into the wafer surface and increase the nanopore length. The growth of nanopore diameter may be attributed to the lower [H₂O₂] system requiring more time to grow the Ag NPs, which function as the catalysts for Si etching. Thus, the formation of nanopores is delayed, as well as both the nanopore diameter and length are directly affected. For example, as the etching time reaches 10 min, the maximum nanopore synthesized with the HF : H₂O₂ : H₂O ratio of 1 : 5 : 2 has dimensions of 230 nm (diameter) and 4.1 μm (length), see Fig. 3a and b. These are much larger than those synthesized at the same etching time using a ratio of 1 : 5 : 20 whose diameter = 140 nm and length = 380 nm (Fig. 3e and f).

With a concentration of silver is 50 μM, the Si etching time also plays an important role in the structure of the etched surface. Over time the nanopores become larger and longer on the Si wafer surface (Fig. 3e–h). The growth of nanopores in the vertical direction is not difficult to understand because the Ag NPs continue catalyzing the Si etching under the NPs to SiO₂ which is immediately etched by HF. As long as both of the oxidation and etching continue, the Ag NPs would keep sinking into the wafer surface and increase the nanopore length. On the Si wafer surface, only few Ag NPs can be observed since most of them have sunk into the bottom of the nanopores. It is important to note that the diameter and length of the nanopores synthesized with lower [HF] and [H₂O₂] are smaller compared to those synthesized with higher [HF] and [H₂O₂] for the same allotted time. This phenomenon is attributed to the lower [H₂O₂] system requiring more time to grow the Ag NPs, which function as the catalysts for Si etching. Thus, the formation of nanopores is delayed, as well as both the nanopore diameter and length are directly affected. For example, as the etching time reaches 10 min, the maximum nanopore synthesized with the HF : H₂O₂ : H₂O ratio of 1 : 5 : 2 has dimensions of 230 nm (diameter) and 4.1 μm (length), see Fig. 3a and b. These are much larger than those synthesized at the same etching time using a ratio of 1 : 5 : 20 whose diameter = 140 nm and length = 380 nm (Fig. 3e and f).

Fig. 3 SEM images of the morphology of b-Si synthesized by the Si etchant containing [Ag⁺] = 50 μM with various etching time and HF : H₂O₂ : H₂O ratios. Top views: (a) 10 min, 1 : 5 : 2, (c) 10 min, 1 : 5 : 10, (e) 10 min, 1 : 5 : 20; (g) 20 min, 1 : 5 : 20. Cross views: (b) 10 min, 1 : 5 : 2, (d) 10 min, 1 : 5 : 10, (f) 10 min, 1 : 5 : 20, (h) 20 min, 1 : 5 : 20. Note: the magnification of each image is chosen for clarity. Scale bars = 1 μm (a, c, f, g, and h), 5 μm (b), 2 μm (d) and 500 nm (e).
uniform size distribution of the nanopores on the Si wafer surfaces. We propose a possible mechanism that explains the decrease in nanopores as a function of etch time that includes the sonication. Fig. 4 shows a schematic summary for the formation of nanopores on a Si wafer surface through the one-step Ag-assisted chemical etching method with sonication. Initially, numerous Ag NPs with different sizes are deposited on the wafer surface and fabricate lots of nanopores with different diameter and length (Fig. 4a). However, there is also a thin layer of fine etched material that is easily removed by sonication during the etching reaction (Fig. 4b). Thus, the shallow nanopores are removed with the top surface and only larger and longer nanopores are left on the Si wafer. This results in some of the Ag NPs originally at the nanopore bottoms to partially emerge on the surface again and explains why the number of nanopores on the wafer surface significantly decreases with the etching time. At the same time, the Ag ions in the etchant aggregate on the re-emerged Ag NPs to form larger NPs because the Ag NPs on the wafer surface can transfer negative charges from the Si to the Ag ions for Ag formation; also, the total free energy of the Ag NP surfaces would be effectively decreased (Fig. 4c). With larger Ag NPs, nanopores with larger diameters are formed since the nanopores are the sinking tracks of Ag NPs. After a certain period of time, the Ag NPs have sunk too deeply to effectively attract the Ag ions. Hence, many newly formed small Ag NPs deposit on the top Si wafer surface instead of on the Ag NPs at the nanopore bottoms (Fig. 3g and 4d). This proposed mechanism explains the observation that the number of nanopores decreases with the etching time; however, for the growth of nanopore diameter, both our mechanism and the Zhong mechanism may need to be taken into consideration.

It is also worth mentioning that as the [HF] and [H$_2$O$_2$] in the etchant decrease, the shapes of nanopores change from circles to squares (e.g., Fig. 3a, c and e). A possible explanation is that as the [HF] and [H$_2$O$_2$] are higher, the Si etching rate is relatively faster, so the Si under the Ag NPs can be easily etched and form the circular nanopores which are projected outlines of the NPs on the Si wafer surface. Nevertheless, when the [HF] and [H$_2$O$_2$] decrease, the Si etching rate slows down leading that the SiO$_2$ formation and the etching processes prefer to occur along the direction of Si–Si bonding because the bonding possesses a higher free energy and is favorable for the chemical reactions. Since the network of Si–Si bonding of the (100) Si wafer surface is square, the obtained outlines of nanopores from the chemical etching are consequently square as well.

Further decreasing the [Ag$^+$] to 5 μM maintains the formation of nanopores on the Si wafer surface, but the nanopores have smaller diameters and shorter lengths compared to those synthesized with the 50 μM [Ag$^+$] for the same etching conditions (see Fig. 3 and 5). For instance, with an etching time of 10 min, the maximum diameter and length of nanopores synthesized with 5 μM [Ag$^+$] and HF:H$_2$O$_2$:H$_2$O ratio of 1:5:2 is 180 nm and 2.4 μm, respectively, versus 230 nm and 4.1 μm for those synthesized with 50 μM [Ag$^+$]. The reason is that the lower [Ag$^+$] system needs more time to grow Ag NPs for the Si etching, thus, it delays the formation of nanopores, as well as effects the size of the nanopores. In addition, with the slower rate of Ag NP formation, the nanopore size is more uniform and better controlled since the difference in size between each Ag NP is smaller. Fig. 5 shows SEM images of the morphology of the Ag-removed b-Si synthesized by the Si etchant containing 5 μM Ag ions for 10 minutes etching and various HF:H$_2$O$_2$:H$_2$O ratios. Similar to the b-Si synthesized with 50 μM [Ag$^+$], the nanopore size on the b-Si synthesized with 5 μM [Ag$^+$] decreases as the concentration of HF and H$_2$O$_2$ decrease as well. After 10 minutes etching, the maximum nanopore diameter and length of the b-Si fabricated with HF:H$_2$O$_2$:H$_2$O ratio of 1:5:20 is only around 70 nm and 90 nm, respectively (Fig. 5e and f). This once again shows that [HF] and [H$_2$O$_2$] significantly effect on Ag NP growth that has a direct relation with the nanopore formation.

The relative ratio of HF:H$_2$O$_2$ is also an important parameter for nanopore formation of the b-Si. Fig. 6 shows SEM images of the surface morphology synthesized with 5 μM [Ag$^+$] and the different relative ratios of HF:H$_2$O$_2$. From Fig. 6, it can be seen that the diameters of nanopore decrease with the volume portion of H$_2$O$_2$. The lower the H$_2$O$_2$ concentration in the Si etchant the smaller the Ag NPs that are formed, and consequently smaller nanopores. As the HF:H$_2$O$_2$:H$_2$O ratio reaches 5:1:20, almost all the nanopores on the Si wafer surface are mesopores (2–50 nm) and the nanopore size distribution is decently uniform (Fig. 6g).
The H$_2$O$_2$ in the etchant not only helps the formation of Ag nanoparticles but also assisted the oxidation of Si under the Ag nanoparticles (eqn (5)). The SEM image shown in Fig. 7 is of a sample prepared with 10 minute etching using a solution comprising 5 μM [Ag$^+$] and a ratio of HF : H$_2$O$_2$ : H$_2$O = 6 : 0 : 20. As we can see, without H$_2$O$_2$ there only few Ag nanoparticles deposited on the Si wafer, which results in the Si wafer surface with a low-level texturized surface. This is despite a concentration of HF being sufficient to act as an etchant. This image proves that the addition of H$_2$O$_2$ is beneficial for the nanopore formation.

When the relative ratio of HF : H$_2$O$_2$ increases and the overall HF : H$_2$O$_2$ : H$_2$O ratio is 3 : 3 : 20, the nanopore length reaches its maximum (690 nm) for 10 minute etching time (Fig. 6d). However, if the relative ratio of HF : H$_2$O$_2$ is further increased, the nanopore length decreases and finally reaches its maximum of 250 nm with a ratio of HF : H$_2$O$_2$ : H$_2$O of 5 : 1 : 20. A possible explanation of this result is that the equivalent volume ratio of HF : H$_2$O$_2$ (i.e., 3 : 3 : 20) can provide sufficient H$_2$O$_2$ for SiO$_2$ formation and sufficient HF for SiO$_2$ etching in order for the reactions to occur simultaneously. If the HF concentration is relatively low (i.e., HF : H$_2$O$_2$ : H$_2$O = 1 : 5 : 20) the HF in the etchant is not sufficient to immediately remove the as-formed SiO$_2$ under the Ag NPs; conversely when the H$_2$O$_2$ concentration is relatively low (i.e., HF : H$_2$O$_2$ : H$_2$O = 5 : 1 : 20) the H$_2$O$_2$ in the etchant is not sufficient to immediately oxidize the Si under the Ag NPs into SiO$_2$ for the consequent etching.

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**Fig. 5** SEM images of the morphology of b-Si samples synthesized by the Si etchant containing 5 μM [Ag$^+$] with 10 minutes etching and various HF : H$_2$O$_2$ : H$_2$O ratios. Top views: (a) 10 min, 1 : 5 : 2, (c) 10 min, 1 : 5 : 10, (e) 10 min, 1 : 5 : 20. Cross views: (b) 10 min, 1 : 5 : 2, (d) 10 min, 1 : 5 : 10, (f) 10 min, 1 : 5 : 20. Note: the magnification of each image is chosen for clarity of the feature of interest. Scale bars = 1 μm (a and d), 3 μm (b), 500 nm (c), and 300 nm (e and f).

**Fig. 6** SEM images of the morphology of b-Si synthesized by the Si etchant containing 5 μM [Ag$^+$] with 10 minute etching and various HF : H$_2$O$_2$ : H$_2$O ratios. Top views: (a) 2 : 4 : 20, (c) 3 : 3 : 20, (e) 4 : 2 : 20, (g) 5 : 1 : 20. Cross views: (b) 2 : 4 : 20, (d) 3 : 3 : 20, (f) 4 : 2 : 20, (h) 5 : 1 : 20. Scale bars = 300 nm.

**Fig. 7** SEM image of the morphology of b-Si surface synthesized by the Si etchant containing 5 μM [Ag$^+$] with 10 minute etching and a HF : H$_2$O$_2$ : H$_2$O = 6 : 0 : 20.
Both extremes result in a slowing the etch rate and a decrease in the length of the pores.

Interestingly, the growth of nanopores is limited if the sonication treatment is not utilized during the Si etching. Without sonication, the nanopore length observed is significantly shorter compared to the ones etched with sonication treatment causing no nanopores can be clearly observed from the cross-sectional SEM images. This indicates the growth of nanopore length is suppressed more significantly than the growth of nanopore diameter in the absence of sonication. Furthermore, this result provides strong evidence that the sonication treatment can assist the HF and Ag ions to diffuse into the nanopore, effectively increasing the etching rate.

The morphology of b-Si directly affects the anti-reflection abilities. After the Ag NPs on the Si wafer surface are removed via the Ag etchant (see Experimental), the relative reflectivity of b-Si is measured for the light wavelengths of 300–1000 nm and compared to the cleaned and un-etched Si wafer whose relative reflectivity is set as 100.00%. A plot of the relative reflectivity as a function of wavelength is shown in Fig. 8. As may be seen the reflectivity is highly uniform across a wide range of wavelengths, in particular across the solar spectrum. A summary of the relative effective reflectivity for the samples is given in Table 2. There is a question as to whether our treatment results in a b-Si surface or simply a textured surface. The shape of our relative reflectivity curves (Fig. 8) show the same trend and shape (i.e., higher reflectivity at higher wavelength for incomplete b-Si formation) as those reported by Branz et al., as well as well defined porous Si anti-reflection layers prepared by other routes.

In order to graphically compare the various catalyst:etch treatments the relative effective reflectivity was categorized into five groups (<5, 5–10, 10–25, 25–50, 50–100). Fig. 9 shows the relative effective reflectivity of b-Si samples synthesized with different etching conditions. Generally, the relative reflectivity of all samples decreases with etching time due to the longer nanopores. The longer nanopores provide a slower gradient change of refractive index within the b-Si surface; hence, they can more effectively suppress the reflection on the Si wafer surfaces.

When the silver concentration is 500 μM, all the relative effective reflectivity of sample is above 5% because only shallow pits are formed on the Si surfaces. However, the shallow pits also become deeper with time and make the surface rougher which still suppresses the reflection of wafer surface in a certain level (see Experimental). As compared to the b-Si synthesized with [Ag⁺] = 500 μM, the samples synthesized with [Ag⁺] = 50 μM show much better AR properties. With 50 μM [Ag⁺], the nanopores become formed on the Si surface and grow with the etching time allowing the b-Si samples to possess extremely low reflectivity. As the HF and H₂O₂ concentrations increase, the formed nanopores become longer which further lowers the reflectivity of the wafer surfaces. For example, the b-Si synthesized with 20 minute etching and the HF:H₂O₂:H₂O ratio of 1:5:2 shows an relative effective reflectivity of 0.17%, which is the lowest of the samples studied. For the b-Si synthesized with the same [Ag⁺] and etching time but different HF:H₂O₂:H₂O ratios, the relative effective reflectivity increases with lower [HF] and [H₂O₂], see Table 2.

The b-Si fabricated with [Ag⁺] = 5 μM effectively decreases the reflection of the Si wafer surface as well. However, the relative effective reflectivity is lower than the ones fabricated with 50 μM [Ag⁺] because of the shorter nanopore length. The relative effective reflectivity also decreases with the etching time, similar to the b-Si fabricated with 50 μM [Ag⁺]. With etching time of 10 minutes, the relative effective reflectivity increases with increased dilution (i.e., lower [HF] and [H₂O₂]), see Table 2. A similar trend is observed for 20 min etching as well.

It was also found that the relative effective reflectivity decreases as the relative ratio of HF:H₂O₂ increases (Fig. 10). With etching time of 10 minutes, the relative effective reflectivity decreases with increased HF:H₂O₂ ratio (i.e., decreased [H₂O₂]). This indicates that when the nanopores are short, the effect of nanopore length on reflectivity becomes less significant, and the nanopore size uniformity starts to dominate the reflectivity. Typically, a p-n junction interface in a Si-based solar cell is about 300 nm below the Si wafer top surface. The maximum nanopore length of b-Si synthesized with the 5 μM [Ag⁺] and HF:H₂O₂:H₂O ratio of 5:1:20 is only around 250 nm, this indicates the synthesized b-Si is favorable for
the anti-reflection layer of Si-based solar cells. With these extremely short nanopores, the p–n junction interface will not be destroyed by the anti-reflection layer of Si-based solar cells. With these extremely short nanopores, the p–n junction interface will not be destroyed by the anti-reflection layer of Si-based solar cells. With these extremely short nanopores, the p–n junction interface will not be destroyed by the anti-reflection layer of Si-based solar cells. With these extremely short nanopores, the p–n junction interface will not be destroyed by the anti-reflection layer of Si-based solar cells.

Table 2 Summary of relative reflectivity data for b-Si samples

<table>
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<tr>
<th>[Ag⁺] (µM)</th>
<th>X : Y : Z (HF : H₂O₂ : H₂O)</th>
<th>Relative reflectivity @ 300.16 nm (%)</th>
<th>Relative reflectivity @ 999.64 nm (%)</th>
<th>Relative effective reflectivity (%)</th>
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<tr>
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<td>1 : 5 : 2</td>
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<td>5.72</td>
<td>21.20</td>
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</tbody>
</table>

4. Conclusion

The one-step Ag-assisted chemical etching method we used is a simple and economical technique for rapidly synthesizing nanopore-type b-Si. Our results indicate that the b-Si morphology, which directly affects the reflectivity degree, possesses high dependence on the [Ag⁺], the HF : H₂O₂ : H₂O volume ratio, and the etching time. The lowest relative effective reflectivity of b-Si that we obtained is 0.17% with the HF : H₂O₂ : H₂O ratio of 1 : 5 : 2 and [Ag⁺] = 50 µM. By adjusting the HF : H₂O₂ : H₂O ratio to 5 : 1 : 20, we can even use further lower [Ag⁺], 5 µM, to fabricate the b-Si whose relative effective reflectivity still reaches 2.60%.

Our b-Si structure with smallest nanopore diameter (<30 nm) and shortest nanopore length (<250 nm) are similar to the structures synthesized by Branz et al. using a gold-assisted chemical etching. While, the relative effective reflectivity of this structure (2.60%) is not the lowest of our b-Si samples (0.17%), it is comparable to their lowest effective reflectivity for the similar sized features.

We propose that the simplicity of the process and low reaction times, along low consumption of silver precursor will make such a one-step method scalable for industrial applications where process cost and rate are important. Moreover, the nanopore length of b-Si fabricated with 5 µM [Ag⁺] can be controlled to be around 250 nm, which is shorter than a typical p–n junction depth in Si-based solar cells, and would not interfere with the function of the cell.

A comparison of our b-Si structures to those reported by Branz and co-workers for multi-step processes25 show that both of the b-Si materials have the similar morphology; the nanopore lengths are both under 500 nm and nanopore diameters are both under 100 nm. This implies that our black Si is also potential to be used in Si-based solar cells for obtaining high-energy conversion efficiency. However, our fabrication process based on one-step silver-assisted chemical etching is less complicated than the multi-step process, which is based on a two-step silver-assisted chemical etching that still needs the extra third step to modify the nanopore length. More importantly we have shown the relationship of silver concentration to the morphology of the b-Si, and that the concentration of AgNO₃ that we used for Ag nanoparticle formation (5 and 50 µM) is much lower than the concentration for the multi-step process (1 mM). This shows our fabrication process of
black Si is simple and economical. Also, the reflectivity of our black Si is comparable to, or even lower than that of multi-step process, which is between 2–12% depending on TMAH etching time.

Acknowledgements

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Notes and references

Appendix C

Reprint

Anti-reflection layers fabricated by a one-step copper-assisted chemical etching with inverted pyramidal structures intermediate between texturing and nanopore-type black silicon

Yen-Tien Lu\textsuperscript{a} and Andrew R. Barron\textsuperscript{†b,c,d}

A new one-step copper-assisted chemical etching technique is reported to more economically prepare nanopore-type anti-reflective layers, which can effectively suppress reflection of Si wafer surfaces for solar cell applications. In contrast to the Au and Ag processes, phosphorous acid (rather than hydrogen peroxide) is utilized as a reducing agent to reduce Cu\textsuperscript{2+} to Cu\textsuperscript{0} nanoparticles. The Cu nanoparticles catalyse the oxidation of Si in the vicinity of the nanoparticles to SiO\textsubscript{2}, which is then etched by HF to form nanopores. The effects of the HF and H\textsubscript{3}PO\textsubscript{3} concentrations, the HF : H\textsubscript{2}O volume ratio, and the etching time on the black silicon morphology with the corresponding Si surface refection have been systematically investigated. The size and shape of the pores are controlled by [Cu\textsuperscript{2+}] and the subsequent size of the NPs as controlled by [H\textsubscript{3}PO\textsubscript{3}], while the depth of the pores are limited by [HF] and the etch time. With [Cu\textsuperscript{2+}] = 500 \textmu M and [H\textsubscript{3}PO\textsubscript{3}] = 10 mM, the fabricated black silicon possesses the lowest relative effective reflectivity, 0.96%, and the shortest nanopore length (590 nm).

1. Introduction

Low surface reflectance of a silicon solar cell, so as to maximize the amount of incident photons absorbed by the semiconductor to convert the incident light into electrical energy, is key for the efficiency. With a layer thickness matched to the refractive index based on the quarter-wavelength principle, an anti-reflection (AR) coating layer produces a destructive interference of the incident light to lower the reflectivity on the solar cell surface. For silicon solar cells AR coatings are generally silicon nitride (Si\textsubscript{3}N\textsubscript{4}) produced by chemical vapour deposition (CVD). The resulting cells have a reflectance of about 6% as compared to 40% for a polished wafer. Another approach has been to texture the crystalline silicon (c-Si) surface with random or ordered patterns,\textsuperscript{1} which causes light to scatter into off-normal directions and thereby to increase its travel distance inside the c-Si wafer. The standard wafer texture process uses a potassium hydroxide–isopropyl alcohol (KOH–IPA) solution to form a random pyramid (ca. 10 \textmu m) structure by anisotropic etching of the silicon surface.\textsuperscript{2} AR thin films are used for both planar and textured solar cells; however, the most significant drawback of the anti-reflection coating layers is that the anti-reflection ability of the layers is limited in a specific range of light incident angle and wavelength.\textsuperscript{3–5}

Black silicon [b-Si] is a surface modification of silicon where a nanopore structure is formed through etching and represents a potential replacement for the conventional AR coating.\textsuperscript{6} The resulting nanopore structure provides an extremely low reflectivity of close to 0%.\textsuperscript{7–9} The nanopore structure may be in the form of inverted nanoscale cones (i.e., with the tip of the cones pointing upward away from the silicon surface) or a series of nanoscale pores of varying depths and diameters extending into the surface.\textsuperscript{10} The low reflectance from a black silicon surface is not caused by light trapping since the features are an order of magnitude smaller than the wavelength of light incident on the surface. Instead, a thin layer possessing a gradient change of refractive index eliminates any abrupt interface such that no reflection occurs.\textsuperscript{11–13}

Black silicon has been successfully fabricated via many techniques including laser irradiation, reactive ion etching, plasma etching, electrochemical etching, and metal-assisted chemical etching.\textsuperscript{10} Among these methods, the metal-assisted chemical etching method\textsuperscript{14,15} is the most economical and facile since it does not rely on high energy consumption or...
complicated processes. The metal-assisted chemical etching method usually includes two steps, metal deposition and electroless chemical etching. The metal (gold or silver) deposited on the Si wafer surface can attract electrons from the wafer surface and causes the oxidation of Si to SiO₂, which is then etched by HF to form nanopores or nanowires. To further simplify the fabrication process of b-Si, one-step metal-assisted chemical etching methods based on the two-step metal-assisted chemical etching have been developed. In the one-step metal-assisted chemical etching method, the metal deposition and the electroless chemical etching occur simultaneously, which makes finding proper etching conditions more challenging. Branz et al. first developed a one-step Au-assisted chemical etching method to fabricate nanopore-type b-Si with the etchant consisting of HAuCl₄–HF–H₂O₂–H₂O. The Au nanoparticles (NPs) formed on the Si wafer surface accelerated the oxidation rate of Si underneath them. In our previous research, we utilized a mixture of AgNO₃–HF–H₂O₂–H₂O to prepare b-Si via one-step Ag-assisted chemical etching method. A low relative effective reflectivity, 0.17%, was achieved and the correlation between the b-Si morphology, the [Ag⁺], the HF : H₂O₂ : H₂O volume ratio, and the surface reflectivity was systematically determined.

Developing a lower cost alternative metal precursor for the metal-assisted chemical etching method to further cut down the fabrication cost of b-Si is attracting attention. In previous studies, Cu NPs have been utilized for fabricating porous Si with a two-step Cu-assisted etching method. As with other metal catalysts, the Cu has a higher electronegativity than Si (1.9 versus 1.8, respectively) allowing the withdraw of electrons from the vicinity of the Si substrate. In this way, Si is oxidized to SiO₂ and etched by HF. However, instead of the desirable nanopores or nanowires only shallow pits were formed on the Si surface limiting the effectiveness of the surface as an AR layer. Based upon our results with the one-step Ag-catalysed system we surmise that the reason for the shallow pit morphology may be due to the extremely small size of the deposited Cu NPs and the dissolution of the Cu NPs in the etchant. The size of the Cu NPs is limited since the etchant solutions did not contain a component to reduce Cu²⁺ ions to Cu⁰ and thus increase/maintain the size of the NPs.

In the present study, we report a one-step Cu-assisted chemical etching method using H₃PO₃ as a reducing agent in the Cu(NO₃)₂–H₃PO₃–HF–H₂O system to reduce Cu²⁺ ions to Cu⁰ NPs on the wafer surface. Furthermore, we have systematically investigated the effects of the [H₃PO₃], the [Cu⁺], and the HF : H₂O volume ratios on the b-Si morphology with the corresponding reflectivity of the Si wafer surface.

2. Experimental

Samples were fabricated on polished single crystalline (100) p-type boron-doped Si wafers (Silicon Quest International) with resistivity of 1–5 Ω cm. Cu(NO₃)₂·3H₂O (Sigma-Aldrich), HF (48%, Sigma-Aldrich), H₃PO₃ (Sigma-Aldrich), H₂O₂ (30%, EMD), and NH₄OH (30%, Fisher Scientific) were used as received.

2.1 b-Si growth

The Si wafers were cut into small pieces and ultrasonically cleaned in DI H₂O, acetone, and DI H₂O sequentially. The cleaned Si pieces were ultrasonically etched in Si etchants consisting of a 5 mL mixture of HF (48%) and DI H₂O in different volume ratios and Cu(NO₃)₂ aqueous solution to give an overall [Cu⁺] in the etchant of 500, 50, and 5 μM, respectively. The final volume of the etchant was adjusted to 10 mL by adding H₃PO₃ aqueous solutions with various concentrations. Table 1 summarises the various compositions of the etchant solutions investigated. After etching for 2 or 8 hours, the as-prepared b-Si samples were rinsed in DI H₂O, and then cleaned with a copper etchant consisting of NH₄OH and H₂O₂ in a 1 : 1 volume ratio at room temperature with sonication to remove the Cu NPs from the wafer surface (Table 2). The Cu-removed b-Si samples were immersed in DI H₂O and dried by canned air.

A solution of 5% PMMA in toluene was applied on selected b-Si samples. PMMA with average Mn = 120 000 was added in toluene and heated at 50 °C for 3 h with stirring to prepare the 5% PMMA solution. The solution was dropped on the b-Si samples with a spinning rate of 2000 rpm for 60 s. The samples were then dried at 100 °C for 20 min to remove the toluene solvent.

2.2 Characterization

Scanning electron microscopy (SEM) was carried out using FEI Quanta 400 by placing samples on double-sided carbon tape that was fixed to aluminium SEM stubs (used as received). Images were acquired at a typical operating voltage of 20 kV, with a working distance of 10 mm, spot size 3 in Hi-VAC mode. The total reflectance spectra of the b-Si samples were measured with Ocean Optics HR2000+ high-resolution spectrometer with a Mikropack DH-2000-BAL deuterium-halogen light source. The relative reflectivity is measured over the wavelength range 300–1000 nm and compared to a cleaned and un-etched Si wafer whose relative reflectivity is 100%.

3. Results and discussion

Previous metal catalysed chemical etching processes have used a combination of H₂O₂–HF as the etchant. The function of the H₂O₂ is to reduce the M⁰ to M⁶ in the form of a nanoparticle. However, in the case of copper, the oxidization potential of H₂O₂ (E = −0.695 V) is too low to reduce the Cu²⁺ (E = 0.399 V). This is evidenced from the SEM image of a silicon surface exposed to a solution of CuCl₂ and H₂O₂, which shows no Cu NPs on the Si wafer substrate. As an alternative to H₂O₂, phosphorous acid (H₃PO₃) is used to reduce Cu²⁺ to Cu NPs (eqn (1)).

\[
\text{Cu}^{2+} + \text{H}_3\text{PO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Cu}^0 + \text{H}_3\text{PO}_4 + 2\text{H}^+ \tag{1}
\]

Since Cu has a higher electronegativity than Si, the Cu⁰ formed on the Si surface attract electrons from Si and become negatively charged. In this way, the Cu²⁺ ions in the etchant solution would be attracted to the Si surface and obtain electrons from the charged Cu NPs, and then deposit around the Cu.
NPs. During the Cu NP growth, the Si around Cu is continuously oxidized to SiO$_2$, which is etched by HF so that nanopores are formed around the Cu NPs. Hence, the size of the Cu NPs and nanopores would keep increasing with time as long as the concentration of Cu$_{2+}$ and HF are sufficient.

The Cu NPs on the b-Si can be easily removed by being immersed in the copper etchant. Table 2 shows a comparison of the atomic concentrations on the b-Si surface before and after Cu removal. With Cu removal treatment, Cu atomic concentration is effectively decreased to less than 0.1% and Si atomic concentration increases to more than 50% since the majority of Si wafer surface appears (Table 2).

### 3.1 Effect of [H$_3$PO$_3$]

Based upon our prior work with Ag one-step process,\textsuperscript{17} we chose an initial [Cu$_{2+}$] = 50 μM. At this concentration pores are obtained on the wafer surface; however, the surface morphology and relative reflectivity are significantly affected by the concentration H$_3$PO$_3$. Fig. 1 shows SEM images of b-Si synthesized with Si etchants containing [Cu$_{2+}$] = 50 μM with a HF : H$_2$O volume ratio = 1 : 7 and various H$_3$PO$_3$ concentrations for 2 hour etching. As can be seen, no nanopores are formed on the wafer surface in the absence of H$_3$PO$_3$. Instead, a few shallow pits are found on the wafer surface (Fig. 1a and b), which are not able to effectively suppress the reflection on the Si wafer. Once the concentration of H$_3$PO$_3$ increases to 10 mM, inverted pyramid-like nanopores are formed on the wafer surface with a maximum nanopore length of 670 nm (Fig. 1c and d). As the concentration of H$_3$PO$_3$ is increased to 25 mM the size of the pores increases (Fig. 1e and f). However, it is interesting that the maximum pore depth is not significantly affected (670 and 580 nm for 10 and 25 mM), respectively (Fig. 1d and f). Further increasing the [H$_3$PO$_3$] results in a highly textured surface but with only shallow pores (Fig. 1g and h).

The relative reflectivity for the resulting surfaces were measured over a wavelength range from 300 to 1000 nm and compared to a cleaned and un-etched Si wafer whose relative reflectivity is defined as 100% (Table 3). The surface prepared using [H$_3$PO$_3$] = 10 mM shows the lowest relative effective reflectivity across the spectrum (Fig. 2) with an average relative effective reflectivity of 10.44% and a minimum of 7.92% at 461 nm.

The increase in [H$_3$PO$_3$] results in an evolution from pits to nanopores to shallow craters (Fig. 1) with a concomitant decrease then increase in the reflectivity (Fig. 2). We propose a possible mechanism to explain this trend and Fig. 3 shows a schematic and the SEM images for the formation of pits, nanopores, and shallow craters on the Si wafer surface with various H$_3$PO$_3$ concentrations.

In the absence of H$_3$PO$_3$ the formation and growth of Cu NPs would be limited, such that only few and small Cu NPs would be

### Table 1 Summary of etch solutions\textsuperscript{a}

<table>
<thead>
<tr>
<th>[Cu$_{2+}$] (μM)</th>
<th>[H$_3$PO$_3$] (mM)</th>
<th>HF : H$_2$O</th>
<th>Volume HF$^b$ (mL)</th>
<th>Volume DI H$_2$O (mL)</th>
<th>Volume of mixture$^c$ (mL)</th>
<th>Volume Cu(NO$_3$)$_2$$^d$ (μL)</th>
<th>Stock [H$_3$PO$_3$] (mM)</th>
<th>Volume stock H$_3$PO$_3$ (mL)</th>
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\textsuperscript{a} Total volume = 10 mL. \textsuperscript{b} 48% HF. \textsuperscript{c} HF + H$_2$O. \textsuperscript{d} [Cu(NO$_3$)$_2$] = 0.01 M.

### Table 2 Summary of atomic concentrations on surface of b-Si samples before and after Cu removal

<table>
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<tr>
<th>[Cu$_{2+}$] (μM)</th>
<th>[H$_3$PO$_3$] (mM)</th>
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them to the nearby Cu\textsuperscript{2+} ions present in the solution. This continuously attract electrons from the wafer then transfer more Cu NPs to be formed on the wafer (Fig. 3b). These Cu NPs of Cu NPs (40 \text{nM} \textit{etchant}, the reduction rate of Cu\textsuperscript{2+} ions is much faster allowing and more Si to be oxidized to SiO\textsubscript{2} (Fig. 3b). Therefore, the size results in more Cu\textsubscript{0} being deposited around the existing Cu NPs. This situation causes a decrease of di\textsuperscript{ference} in height levels between the nanopore bottoms and the wafer surface. However, these larger Cu NPs cover the entire wafer surface to be relatively smoother which weakens the anti-reflection ability of Si surface (Fig. 3). We conclude therefore that the size of the pores are controlled by [H\textsubscript{3}PO\textsubscript{3}] and the subsequent size of the Cu NPs. This would suggest that the depth of the pores are limited by [HF] and the etch time.

### 3.2 Effect of etch time

Fig. 4 shows SEM images of samples synthesized by using Si etchant containing 50 \mu M [Cu\textsuperscript{2+}] for various etching time. When the etching time increases, the nanopores become larger and longer on the Si wafer surface (Fig. 4a–d). As long as [HF] is sufficient, the Cu NPs can continue catalysing the Si etching increasing the nanopore length. The sample consisting of deeper nanopores have a slower gradient change of refractive index; therefore, it can more effectively suppress the reflection on the Si wafer surface. For instance, with 50 \mu M [Cu\textsuperscript{2+}] and HF : H\textsubscript{2}O volume ratio = 1 : 7, the maximum length and relative reflectivity of nanopores synthesized for 2 h etching is 670 nm (Fig. 4b) and 10.44\%, respectively. Once the etching time increases to 8 h, the maximum length of nanopores increases to 1.6 \mu m (Fig. 4d) and the relative effective reflectivity drops to 7.77\% (Table 3).

### 3.3 Effect of HF : H\textsubscript{2}O ratio

The relative volume ratio of HF : H\textsubscript{2}O \textit{(i.e.,} [HF]) also plays an important role in the nanopore formation. With 8 hour etching, compared to the sample prepared with the HF : H\textsubscript{2}O volume ratio of 1 : 7, both samples fabricated with the HF : H\textsubscript{2}O volume ratio as 1 : 4 and 1 : 15 have shorter maximum nanopore length and higher relative effective reflectivity, which are 1.4 \mu m (Fig. 4f) and 9.97\%, and 1.2 \mu m (Fig. 4h) and 9.44\%, respectively (Fig. 5). It is easy to see that the b-Si fabricated with HF : H\textsubscript{2}O = 1 : 15 has the shortest nanopore length since a lower [HF] leads to a slower Si etching rate on the wafer surface. However, b-Si fabricated with HF : H\textsubscript{2}O = 1 : 4 also has slightly shorter nanopores and higher relative effective reflectivity than b-Si fabricated with HF : H\textsubscript{2}O = 1 : 7 since excess of HF molecules etches not only the Si under the Cu NPs but also the Si around the Cu NPs. This situation causes a decrease of difference in height levels between the nanopore bottoms and the wafer surface so that the nanopores have a shorter length. Besides, the HF : H\textsubscript{2}O = 1 : 4 ratio also provides a faster Si etching rate which allows larger nanopores to be formed on the wafer.
surface. Some of these large nanopores connect with each other and merge into further larger craters, which lowers the nanopore population density. Both the shorter nanopore length and the lower nanopore population density are not favourable for suppressing the reflection of the Si wafer surface, and therefore the b-Si sample fabricated with HF : H2O volume ratio of 1 : 4 shows higher reflectivity than that fabricated with a ratio of 1 : 7 (Fig. 5 and Table 3).

3.4 Effect of [Cu²⁺]

As may be expected reducing the [Cu²⁺] to 5 μM results in the nanopore population density to be lower compared to samples prepared with 50 μM [Cu²⁺]. Fig. 6 shows SEM images of b-Si synthesized by using Si etchants containing 5 μM [Cu²⁺] for various etching time and HF : H2O volume ratios. Similar to samples synthesized with 50 μM [Cu²⁺], the nanopore length increases and the surface reflectivity decreases with etching time. With a HF : H2O volume ratio of 1 : 7, the maximum nanopore length increases from 470 nm to 1.5 μm (Fig. 6b and d) as the etching time increases from 2 h to 8 h. This improves the relative effective reflectivity from 55.17% to 22.54% (Table 3). With 8 h etching time and HF : H2O ratios as 1 : 4 and 1 : 7, b-Si has maximum nanopore lengths and relative effective reflectivity of 1.6 μm (Fig. 6f) and 39.44%, and 1.3 μm (Fig. 6h) and 43.37%, respectively. Although the b-Si fabricated with 5 μM and 50 μM [Cu²⁺] have similar maximum nanopore lengths, the relative effective reflectivity of the former ones are much higher than the latter ones (9.97% for HF : H2O = 1 : 4, 7.77% for HF : H2O = 1 : 7, and 9.44% for HF : H2O = 1 : 15), see Table 3. The main reason for these observations is a lower population density and less uniform distribution of nanopores over the Si wafer surface.

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<th>[H₃PO₃] (mM)</th>
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<th>Time (hr)</th>
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Also comparing the b-Si synthesized with 5 μM [Cu^{2+}] but different HF : H_{2}O volume ratios, the b-Si fabricated with a HF : H_{2}O = 1 : 7 has a higher nanopore population density (Fig. 6c) and the lowest relative effective reflectivity (Table 3). When the HF : H_{2}O volume ratio is 1 : 15, the population density of nanopores becomes lower leading to a higher relative reflectivity because the [HF] in the etchant is insufficient; hence, the HF etches fewer areas on the wafer surface (Fig. 6g). For the HF : H_{2}O volume ratio of 1 : 4, the [HF] is high enough to more effectively etch the Si wafer and form more nanopores. However, most of the nanopores connect with each other and form larger irregular nanopores, which decreases the nanopore population and is detrimental for the reflectivity (Fig. 6e).

As expected increasing [Cu^{2+}] to 500 μM results in a more porous surface. Fig. 7 shows SEM images of b-Si synthesized with Si etchants containing 500 μM [Cu^{2+}] for various etching time and HF : H_{2}O volume ratios. Compared to the samples synthesized with the lower [Cu^{2+}], the b-Si synthesized with 500 μM [Cu^{2+}] has a higher nanopore population density, which
leads a lower relative reflectivity. With 500 μM [Cu$^{2+}$] after 8 h etching, all the samples have extremely low relative reflectivity below 5% (Fig. 8).

Unlike the b-Si prepared with the lower [Cu$^{2+}$], the nanopore size and length of b-Si prepared with 500 μM [Cu$^{2+}$] decrease when the HF : H$_2$O volume ratio decreases. The samples fabricated with HF : H$_2$O ratio = 1 : 4 has the fastest Si etching rate causing large and long nanopores (Fig. 7e and f), whose maximum length is around 2.4 μm. Although the nanopores connect with each other at a certain level and merge into larger irregular nanopores due to the faster Si etching rate, the relative effective reflectivity is still low, 3.06%. As the HF : H$_2$O volume ratio decreases to 1 : 7, the maximum nanopore length decreases to 1.4 μm (Fig. 7d) and the relative effective reflectivity decreases to 2.72% (Fig. 8).

Interestingly, the samples synthesized with the lowest [HF], HF : H$_2$O = 1 : 15, has the shortest nanopore length, 590 nm (Fig. 7h), and also the lowest relative reflectivity, 0.96%, among all the samples reported herein. This extremely short nanopore length is ideal for anti-reflection layer application in Si solar cells since the depth of p–n junction in Si solar cells is usually less than 1 μm. If the nanopore length were longer than the depth of p–n junction, the nanopores would penetrate the junction and result in a short circuit.

3.5 Conditions for optimised reflectivity

The low relative effective reflectivity of b-Si can be attributed to the uniform distribution of the nanopores and the high nanopore population density. As the [HF] is lower (i.e., HF : H$_2$O = 1 : 15), the Si etching rate is consequently slower which is beneficial for keeping the nanopores from merging into larger ones so that the surface reflectance can be better suppressed. Besides, comparing samples synthesized with HF : H$_2$O = 1 : 15 but different [Cu$^{2+}$], it is found that the b-Si prepared with 500 μM has a shorter nanopore length. The possible explanation for this observation might be that samples prepared with a higher [Cu$^{2+}$] have much more Cu NPs on the entire wafer surface; hence, the HF molecules are consumed relatively less on individual NPs resulting in a slower local nanopore growth, or shorter nanopore length.

In order to better compare the relative reflectivity of b-Si prepared with different etching conditions, the relative effective reflectivity is categorized into five groups, which are <5%, 5–10%, 10–25%, 25–50%, and >50%. Fig. 9 shows the relative effective reflectivity of samples synthesized with different etching conditions. In general, the relative effective reflectivity of all the b-Si decreases with the etching time. The longer nanopores can more effectively suppress the reflectivity on the wafer surface due to the smoother gradient change of refractive index. When [Cu$^{2+}$] = 5 μM, the relative effective reflectivity of Si wafer is high due to the low nanopore population density on the surface. However, once the [Cu$^{2+}$] increases to 50 μM, more nanopores appear on the wafer surface and lead to a lower relative effective reflectivity. With 500 μM [Cu$^{2+}$], the fabricated b-Si has the highest population density of nanopores on the Si wafer and the most uniform distribution of
nanopores on the wafer surface resulting in a relative effective reflectivity below 5%.

3.6 Effect of PMMA over-layer

In a silicon solar cell with a traditional CNx AR coating the reflectivity is further improved during module formation. Polymethyl methacrylate (PMMA) is a photovoltaic encapsulation material that has a high light transmission, particularly in the region of the spectral response of the solar cell. It also allows for the heat treatment of solar cells during their manufacture and provides a photo-stability extended over long periods of 20-25 years that PV manufacturers guarantee a minimum of 8% of the initial performance of their modules (Fig. 10).

Table 4 shows a comparison of the reflectivity of selected samples with PMMA coating. In each case the reflectivity is decreased by as much as 50% by the addition of a PMMA over-layer. The AR property of b-Si is a function of the graded refractive index change between air ($n = 1$) and silicon ($n = 3.42$). The addition of PMMA ($n = 1.48$) provides the same gradient but with an additional interface (air/PMMA). In contrast, traditional textured silicon surfaces rely on light trapping by internal reflection. Again the additional air/PMMA interface should decrease reflectivity. As may be seen from Fig. 10, there is a decrease in relative reflectivity at longer wavelengths; however, a slight increase results across the key region of the solar spectrum.

3.7 Pore shape

An observation worth mentioning is the square outline of the pores in the one-step Cu-assisted method. We have previously found that the b-Si fabricated via the one-step Ag-assisted chemical etching method has circular nanopores, which are projections of the Ag NPs on the wafer surface.$^{27}$ The standard reduction potential of Ag$^+$ ($E = 0.799 \text{ V}$) is much higher than that of Cu$^{2+}$ ($E = 0.399 \text{ V}$). As such Ag$^+$ ions can more easily obtain electrons from nearby Si to be reduced to Ag NPs that leads to a faster oxidation rate of Si and a faster formation rate of nanopores. This not only explains why the fabrication process of b-Si takes minutes with the Ag-assisted chemical etching method but hours with the Cu-assisted chemical etching method, but also provides an indication of the significant differences in the nanopore length and shape. Fig. 11 shows the nanopore shapes fabricated via Ag-assisted chemical etching method and Cu-assisted chemical etching method, respectively.

Since the Ag NPs can easily oxidize the nearby Si substrate, the Si material under the Ag NPs is continuously etched by HF, so the nanopores actually are the sinking track of the Ag NPs on the wafer surface and possess a slightly-taper cylinder shape in the cross-section (Fig. 11a). On the other hand, due to the lower ability of withdrawing electrons of Cu NPs, the Cu NPs only attract electrons from the Si substrate where is easier oxidized to SiO$_2$ and etched by HF. On crystalline Si substrates, the Si etching rate is faster along the directions of [100] and [110] rather than [111]. For a Si [100] surface, the etching mainly occurs along the [100] and [110] directions and stops at the [111] planes; hence, the nanopores fabricated with the presence of Cu NPs would have inverted pyramid-like shapes (Fig. 11b).

Traditional etching processes for texturing silicon wafers occur through etching in the [100] direction (Fig. 12a).$^{25,23}$ As such the resulting structure is that of overlapping pyramids with features generally in the range of 1–5 μm. However, it has been suggested that greater efficiencies of light trapping are obtained by the formation of an inverted pyramid structure such as obtained herein (Fig. 12b).$^{1,24}$ Inverted pyramid-like structures are observed for plasma texturing with SF$_6$/O$_2$ at high radio frequency power.$^{27}$ However, the resulting inverted structures are poorly overlapping and far from the ideal inverted pyramid structure that is desirable for light trapping.$^{1,24}$ In contrast, the present one-pot Cu-assisted etch results in a texturing closer to the ideal structure for traditional light trapping.

It has been shown that if inverted pyramids are created with a texturing angle between 45° and 60° the spectral response is better than for pyramids.$^{28}$ More importantly the optimum angle is 54.7°. The measured angles of the inverted pyramids formed by the Cu-assisted etch is 53.5–58.9° for all the samples.
(Fig. 1, 4, 6 and 7), with the majority in the range 53.7–54.9°. In addition, the nano size of the features (<1 μm) means that the low reflectivity may be not due to light trapping, but the presence of a gradient of refractive index associated with traditional b-Si structures.

Finally, the inverted pyramidal structure obtained using the one-pot Cu assisted etch system described herein represents a structural link between traditional texturing and the structural type of black silicon. The nanoscale structure of b-Si may be in the form of inverted nanoscale needles or cones (Fig. 13a and b) or a series of nanoscale pores of varying depths and diameters extending into the surface.

4. Conclusions

We have demonstrated a one-step copper-assisted chemical etching method to synthesize inverted pyramid nanopore-type b-Si at room temperature. According to our results, [H₃PO₃], [Cu²⁺], HF : H₂O volume ratio, and etching time show direct effects on b-Si morphology and the corresponding reflectivity. We propose that inverted pyramid shapes of the nanopores is due to the lower reduction potential of Cu²⁺, which causes the Si etching to mainly occur along the Si [100] and [110] directions. In order to maintain a higher nanopore population density, a lower [H₃PO₃] is beneficial for preventing the nanopores from merging to larger and shallow craters. Also, a higher [Cu²⁺] allows more Cu to be more deposited around the existing Cu NPs and increase the nanopore population density. The anti-reflection ability and the extremely short nanopores of the b-Si indicate the potential for anti-reflection applications in Si solar cells because the nanopore length is shorter than the typical depth of p–n junctions in Si solar cells.

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References

Appendix D

Reprint

Review

Fabrication and characteristics of black silicon for solar cell applications: An overview

Chih-Hung Hsu, Jia-Ren Wu, Yen-Tien Lu, Dennis J. Flood, Andrew R. Barron, Lung-Chien Chen

Department of Electro-optical Engineering, National Taipei University of Technology, 1, section 3, Chung-Hsiao E. Rd., Taipei 106, Taiwan
Department of Chemical and Biomolecular Engineering, Rice University, Houston, TX 77005, USA
Natcore Technology, Inc., 87 Maple Avenue, Red Bank, NJ 07701, USA
Department of Chemistry, Rice University, Houston, TX 77005, USA
Department of Materials Science and Nanoengineering, Rice University, Houston, TX 77005, USA
College of Engineering, Swansea University, Singleton Park, Swansea SA2 8PP, Wales, UK

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Abstract
Anti-reflective (AR) coatings are a critical component of a commercially viable solar cell because by lowering reflection from the surface of the cell they enable more light to be absorbed and hence improve the power conversion efficiency of the cell. Silicon solar cells represent > 80% of present commercial cells and the most common AR coating is PECVD silicon nitride; however, recently, black silicon (b-Si) surfaces have been proposed as an alternative. Black silicon is a surface modification of silicon in which a nanoscale surface structure is formed through etching. Due to the continuous change of the refractive index of this structure surfaces with very low reflectivities are observed (~1%). This review summarizes the recent and substantial developments of black silicon for use in solar cells and discusses the advantages and disadvantages of the different methods of fabrication.

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* Corresponding author. Tel.: +886 2 2771 2171; fax: +886 2 8773 3216.
E-mail address: ocean@ntut.edu.tw (L.-C. Chen).
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1. Introduction

A key requirement for an efficient solar cell is a low surface reflectance to maximize the amount of incident photons absorbed by the semiconductor to convert the incident light into electrical energy. The use of an anti-reflection (AR) coating is used to suppress the reflection of the solar cell surface by forming destructive interference of incident light. For silicon solar cells AR coatings are generally silicon nitride ($\text{SiN}_x$) thin films produced by chemical vapor deposition (CVD). The resulting cells have a reflectance of about 6% as compared to 40% for a polished wafer. However, AR coatings are limited in use because it only reduces the reflection for a narrow range of light wavelength and incident angle since its functionality is based on a quarter-wavelength coating. As a potential replacement for the conventional AR coating, so-called “black silicon” (b-Si) was first reported by Jansen et al. [1].

Black silicon is a surface modification of silicon where a nanoscale surface structure is formed through etching. The resulting nanoscale structure (from porous surface to bulk silicon) provides an extremely low reflectivity of close to 0% [2–4]. Because the b-Si surface nano-structure exhibits high absorption over a wide spectral range ($250$–$2500 \text{ nm}$) [4,5] it offers an ideal solution as an AR coating for solar cells [6–9], as well as applications in photodetectors [10], photodiodes [11], and gas sensors [12]. The nanoscale structure may be in the form of inverted nanoscale cones (i.e., with the tip of the cones pointing upward away from the silicon surface) or a series of nanoscale pores of varying depths and diameters extending into the surface. Both types of nanoscale structures are distributed randomly over the silicon surface.

Although originally prepared as a side effect of reactive ion etching [1], b-Si can be prepared by laser irradiation.
metal-assisted chemical etching (MACE) [14], electrochemical etching [15], and plasma dry etching [16]. The object of this review is to provide a survey of the different methods of synthesizing b-Si along with an appreciation of the merits of each method and future goals.

2. Methods of fabricating black silicon (b-Si)

The preparation methods for the fabrication of b-Si may be divided into dry and wet etching. The former involves gaseous reagents while the latter uses solution chemistry. While similar structures can be made by both methods for simplicity of discussion the two methods will be discussed using this general classification.

2.1. Dry etching

As noted above, b-Si was first prepared by reactive-ion etching (RIE) [1], and hence a significant amount of work has been done in the area. The RIE technique includes variations such as inductively coupled plasma reactive ion etching (ICP-RIE) and damage-free reactive ion etching [17]. Generally RIE uses a combination of at least two gases: the first to generate radical species that react with the silicon surface, and a second to passivate the etched surface. Sulfur hexafluoride (SF$_6$) is used to generate fluorine radicals (F$^-$) that react with the silicon to generate volatile silicon tetrafluoride (SiF$_4$), which is removed from the surface. Sometimes SF$_6$ is used in combination with chlorine (Cl$_2$) in which case silicon tetrachloride (SiCl$_4$, $\text{bp} = -67.74\,^\circ\text{C}$) is formed. Oxygen radicals (O$^-$) generated from oxygen react with the fresh surface to passivate the silicon.

Fig. 3. SEM image of the highly uniform tapered needle-like microstructure of b-Si formed with DC-plasma immersion ion implantation (DC-PIII) using SF$_6$/O$_2$. Reprinted from Y. Xia, B. Liu, J. Liu, Z. Shen, C. Li, Sol. Energy 2011; 85: 1574. Copyright (2011), with permission from Elsevier.

Fig. 4. SEM images of the black silicon produced by PIII process with different gas flow ratios: (a) SF$_6$, (b) SF$_6$/O$_2 = 3.5$, (c) SF$_6$/O$_2 = 4.0$, and (d) SF$_6$/O$_2 = 4.5$. Reprinted from Xia Y, Liu B, Zhong S, Li C, J. Electron. Spectrosc. Relat. Phenom. 2012; 184: 589. Copyright (2012), with permission from Elsevier.

sidewalls to prevent further silicon etching [18–20]. Typical gas mixtures include SF₆/O₂, SF₆/Cl₂/O₂, and SF₆/O₂/CH₄. Isotropic, positively and negatively (i.e., reverse) tapered as well as fully vertical walls are achieved by controlling the plasma chemistry, RF power, and pressure [1]. For example, Fig. 1 shows a series of SEM images of the textured silicon surfaces obtained by etching using different SF₆/O₂ gas ratios [18]. Under the conditions studied the lowest reflectance (10.29%) was obtained for the dense needle-like structure when a SF₆/O₂ gas ratio of 2.8 was used (Fig. 1c).

Fig. 7. Top-view SEM images of silicon substrate (left column) with different density of Ag NPs coating and corresponding as-etched silicon for 3 min (right column): (a–a’) raw silicon, (b–b’) 4 s, (c–c’) 8 s, and (d–d’) 12 s. Reprinted from Y. Bi, X. Su, S. Zou, Y. Xin, Z. Dai, J. Huang, X. Wang, L. Zhang, Thin Solid Films 2012; 521: 176. Copyright (2012), with permission from Elsevier.
A higher SF6/O2 gas ratio results in a sparse surface distribution of needles (Fig. 1d), while lower SF6/O2 ratios give large truncated cones (Fig. 1b) or with an excess of oxygen a homogeneous surface (Fig. 1a).

A further variation on RIE is the plasma immersion ion implantation (PIII) process. Like PIE, PIII uses SF6/O2 gas combinations, but as shown in the schematic of the PIII reactor (Fig. 2) a conducting grid is used to divide the chamber into two parts: an upper plasma region and a lower reactive region. The upper part of the chamber confines the plasma and stops the expansion of the ion sheath since the grid repels electrons that are close to it. Therefore, only positive ions diffuse into the lower part through the grid and become implanted into the wafer [21,22]. Typically, after removal of surface damage of the silicon surface with hot NaOH, the reaction gases (SF6/O2) react (as ions and free radicals) with the surface of the silicon substrate; a high negative voltage pulse is applied to cause the injected ions to react with the silicon substrate.

Fig. 3 shows a scanning electron microscopic (SEM) image of b-Si formed by the PIII process [23]. The surface needles that are formed are densely and uniformly distributed with a mean height of approximately 2 μm, resulting in a low reflectance (1.79%) [23]. As with the RIE process, the use of different reactive gas mixtures has a significant effect on the texture and resulting reflectance of b-Si formed by PIII. As an example, Fig. 4 shows SEM images of etched surfaces formed with a range of SF6/O2 ratios [24]. The use of SF6 alone results in large etch craters (several μm across) presumably as a function of the lack of surface passivation. With the addition of oxygen to the reaction gas more nano-textured surface results. As the SF6/O2 gas ratio increases the morphology changes from porous (Fig. 4b) to needle-like (Fig. 4d) [24].

If laser irradiation is employed in place of plasma, then a wider range of chemical reagent may be employed to control the morphology and size of the resulting b-Si. Lasers commonly used for this purpose range from femtosecond to picosecond; however, femtosecond lasers are the most popular for preparing b-Si because the longer pulses result in significantly lower thermal ablation, owing to the melting threshold temperature of silicon [25–29]. The most commonly used laser sources are either Ti:sapphire and Nd:YLF systems [30,31], with a pulse duration of approximately 30 ~ 200 fs, with a repetition rate of 1 kHz. For research purposes, Ti:sapphire laser systems are used with wavelengths of 387, 775, 780, and 800 nm. [30,32,33]. The use of different reaction gases increases the etching rate to form different shapes and structures (e.g., Fig. 5) [5,32]. A comparison of the results using carbon tetrachloride (CCl4) versus 1,1,2-trichloro-1,2,3-tri-fluoroethane (C3Cl3F3) (Fig. 5a and b, respectively) and SF6 versus Cl2 show that the fluorine containing reaction gas produces smaller features than when chlorine is present. This variation may be due to the higher reactivity of the fluorine radical. It is interesting to note that with the use of oxygen not only are the features very small but also the surface is highly textured with oxide (Fig. 5f) [5].

In each of the dry etches discussed so far (RIE, PIII, and laser irradiation) any chemicals are used as specifically as reagents, i.e., they are present for the purpose of a stoichiometric reaction. Also the resulting morphology of the b-Si is controlled by the reaction rates and/or relative reactivity of the reagents. In contrast, the formation of b-Si with plasma etching requires the formation of a barrier layer or etching mask. The etch mask is ordinarily formed from the surface array of silver or gold nanoparticles [16,34], although iron oxide and anode aluminum oxide (AAO) have also been used to prepare mask layers. [35,36]. A schematic of the general approach of plasma etching is shown in Fig. 6. Firstly, a layer of silver nanoparticles (Ag NPs) is deposited as the etching mask. Varying the
sputtering time, power source, thickness, and annealing temperature can control the size and density of Ag NPs. Next, the reaction etching gas is injected into the chamber, and a voltage is applied to the silicon substrate resulting in etching in the areas without the Ag NPs [16]. Finally, the silver is removed from the tops of the pyramids.

As may be expected the density and size of the pyramids formed by plasma etching are controlled by the distribution/concentration and size of the Ag NPs deposited on the surface of the silicon prior to etching. Fig. 7 shows a series of SEM images of silicon substrates that are coated with different densities of Ag NPs (left column) and of corresponding as-etched silicon (right column) [16]. From the relevant images it is possible to see that the resulting b-Si surface structure is directly related to the Ag NP mask. Another critical factor in controlling the b-Si morphology during plasma etching is etching time. Under a given condition for the preparation of Ag NPs, the height of the silicon tips is proportional to etching time (Fig. 8) [16]. The height of the silicon tips increases from 106 to 222 nm as the etching time increases from 6 to 12 min, while etching for 12 min removes almost all of the Ag NPs from the surface of the silicon [16].

2.2. Wet chemical etching

Wet chemical etching for preparing b-Si includes both metal-assisted (metal catalyzed) chemical etching and also
electrochemical etching (see below). Metal-assisted chemical etching (MACE) generally includes electroless metalization of the surface, or deposition of pre-made metal nanoparticles, followed by etching with a solution of containing an oxidant and a complexing agent for silicon [37]. MACE overcomes the disadvantages of dry etch techniques that need either expensive instruments and high energy consumption or complicated fabricating processes, making them unfavorable for industrial applications.

The metal-assisted chemical etching method involves two steps: metal deposition and chemical etching. In the metal deposition step, a metal (such as Ag, Au, or Pt) is deposited on the Si surface as nanoparticles (NPs). The metal NPs attract electrons from the silicon surface promoting, in the presence of an appropriate oxidant, the oxidation to silica (SiO₂). In the chemical etching step, the as-formed silica is removed as H₂SiF₆ by the reaction with HF and a pit is produced under each NP. The pits become deeper and ultimately connect with each other, and the remaining Si substrate forms b-Si. Fig. 9a shows a typical cross section of a MACE-produced black silicon surface and Fig. 9b shows a MACE-produced black silicon surface that has been sealed and passivated by silicon dioxide. The SiO₂ was deposited by a wet chemical deposition technique rather than by thermal oxidation or CVD [38].

A proposed mechanism based on the working principle of galvanic cells thoroughly explains the electroless chemical etching with metal NP deposition on the Si material surface [39]. The mechanism consists of two half-cell reactions: a cathode reaction at the metal NP surface (Eq. (1)) and an anode reaction occurring at the contact point between the Si and metal NP (Eqs. (2) and (3)) [40–42]. The overall reaction is given in Eq. (4). The potential difference between the cathode sites and the anode sites results in a net flux of electrons through the metal NPs and accumulation of electrons on the cathode sites. Since the cathode sites can provide more electrons for the reduction of H₂O₂, the overall reaction (Eq. (4)) continues resulting in etching of Si under the Ag NPs. A one-step Au-assisted chemical etching method has been developed [43], in which the deposition of Au NPs and the etching of Si occurred simultaneously on the wafer surface using HAuCl₄:HF:H₂O₂:H₂O. The fabricated nanopore structure possessed a reflectance below 2% across a wavelength range of 300–1000 nm:

\[
\begin{align*}
    \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- &= 2\text{H}_2\text{O} \\
    \text{Si} + 2\text{H}_2\text{O} &= \text{SiO}_2 + \text{H}_2\text{O} + \text{H}_2\text{O} \\
    \text{SiO}_2 + 6\text{HF} &= 6\text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \\
    \text{Si} + 2\text{H}_2\text{O}_2 + 6\text{HF} &= 6\text{H}_2\text{SiF}_6 + 4\text{H}_2\text{O}
\end{align*}
\]

When a silicon substrate is coated with a metal thin film (such as Au, Pt, Ag or alloy) [44–48] or when it is plated by immersion in liquid (AgNO₃/HF [24], KAuCl₄/HF [50]), metal ions adhere to its surface and, the reactions of different metal species produce a rough surface. Different metallization procedures yield different pore sizes and pore density [51]. Different metallization conditions in AgNO₃ and KAuCl₄ solution yield different results.

The composition of the etching solution (variations of the relative amounts of HF, H₂O₂, H₂O, or EtOH) affects the dissolution of the oxidized silicon. It is an important parameter that affects the formation and morphology of the silicon substrate. Many groups have used solutions with different compositions in metal-assisted chemical etching [52–54]. The etch time is a further variable that needs to be taken into account. For example, Fig. 10 shows various morphologies that are obtained using HF:H₂O₂; H₂O with various etching times [52]. The depth of pores in the silicon substrate is linearly proportional to the etching time and the rate of penetration R₀ of the Ag NPs into the bulk silicon (Eq. (5)) where \( D \) represents the total mass loss of the wafer; \( t \) is the etching time; \( S \) is the wafer area, and \( d \) is the wafer density [52]:

\[
D = \frac{1}{2} \frac{\Delta m}{S \Delta t} \quad R_0 = \frac{D}{t} \tag{5}
\]

The effects on the surface morphology and the corresponding surface reflectance caused by variation of the concentration of (1) the silver catalyst (500, 50, and 5 μM), (2) the HF and H₂O₂ concentration in the silicon etchant, (3) the HF:H₂O₂ ratio, and (4) etching time have been reported [55]. Lower reflectivity is a balance between sufficient silver catalyst to create large numbers of nanopores on a silicon surface and excessive silver that brings deeply etched channels that would potentially short-circuit a solar cell junction. The lowest average reflectance (0.17% over a range of 300–1000 nm) occurs with a silver ion concentration of 50 μM; however, when the silver ion concentration decreases to 5 μM, surfaces with an acceptably low reflectance (2.6%) and a short nanopore length (< 250 nm) can be obtained with 10 min etching time. As is seen from Fig. 11, the ability to control the silver concentration, the etch solution (i.e., HF:H₂O₂:H₂O ratio) and etch time allow for a wide range of reflectance values [55]. The nanopore size would increase with time as long as [HF] and [H₂O₂] are sufficient.

**Fig. 11.** Schematic plot of the average relatively reflectivity of b-Si with various \([\text{Ag}^+]\), etching time, and HF:H₂O₂:H₂O ratio. Reprinted from Y.-T. Lu, A.R. Barron, Phys. Chem. Chem. Phys. 2013; 15: 9862. Copyright (2013), with permission from the Royal Society of Chemistry.
Geng et al. observed a pore structure when he used a solution of HF:H\textsubscript{2}O\textsubscript{2}:EtOH in the volume ratio 1:1:1, as displayed in Fig. 12 [56]. Quasi-ordered silicon micro/nanostructures have been obtained after 12 h of etching, and the dramatic difference between the morphologies of the (100)- and (111)-orientated silicon substrates (Fig. 12a–d and e–h, respectively) appears to reflect both the underlying crystal orientation and complex dynamical processes during etching [56].

The advantage of the electrochemical treatment over chemical etching is the control of the process is by varying the applied current density rather than alteration of the chemical speciation and reaction time. Electrochemical etching involves immersing a silicon substrate in a solvent, and applying a current for reaction. The current provides the equivalent function of the metal nanoparticle (i.e., Au or Ag) and the hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). Commonly used mixed solvent systems include: ethanol/H\textsubscript{2}O/hydrofluoric acid.

Fig. 12. SEM images of p-type silicon substrate subjected to MACE. The top macroporous layers have been removed by dipping in NaOH (1%) for 15 min. The wafers used are (100) p-type silicon substrate for (a)–(d) and (111) p-type silicon substrate for (e)–(h). Reprinted from X. Geng, M. Li, L. Zhao, P.W. Bohn, J. Electron. Mater. 2011; 40: 2480. Copyright (2011), with permission from The Minerals, Metals & Materials Society (TMS).
HF), H₂SO₄/HF, HF/IPA (isopropyl alcohol)/deionized (DI) water, HF/ethanol/CTAC (cetyl trimethylammonium chloride)/DI water, and HF/DMSO (dimethyl sulfoxide) [15,57–61]. The important electrochemical etching parameters include anode current density, electrolyte solvent, and anodization time [57,60]. Several issues that are associated with the production of black silicon are as follows.

Bastide and Lévy-Clément reported that the anodization of a p-type silicon substrate in mixtures of hydrofluoric acid with specific organic solvents (in the present case either ethanol or DMSO) forms a macroporous region of the substrate, which is very efficient in reducing its reflectance [61]. Fig. 13 shows cross-sectional SEM images of (100) p-type silicon substrates with various Si substrate resistivities following electrochemical etching [61]. The nanopore diameter is directly related to the resistivity of the silicon substrate (Fig. 14) [61]. In contrast, Kim and Cho have reported that a range of vastly different morphologies rather than just dimensionally different structures, can be prepared as a function of the silicon resistivity [58]. The surface structure of a (100) p-type silicon substrate with a resistivity ranging from 0.005 to 15 Ω cm results in ‘sponge’, ‘mountain’ and ‘column’-type morphologies (Fig. 15). Interestingly, the sponge-type structure (Fig. 15a and d) had the largest surface area per unit volume [58].

Bastide et al. studied the texturizing of silicon surfaces by electrochemical dissolution [61]. The silicon substrate was dipped in a mixture of HF with a particular organic solvent (DMSO), which caused the formation of a macroporous structure, to reduce the reflectivity. Fig. 16 shows the reflectivity spectra of a (100) grain and a (111) grain, texturized by both the electrochemical method and NaOH wet etching [61].

The use of different anodization current densities results in various vertical arrays of silicon wires and cones [59]. Fig. 17 plots the I–V curve of p-type silicon in the electrolyte solution with the morphological results at each value. In a similar manner, the anodization current density has an effect on the height and surface density of nanoparticles that are fabricated in the transition regime (Fig. 18) [60].

3. Fabrication of solar cells

3.1. Metal-assisted chemical etching

Many groups have applied the MACE process to the fabrication of silicon solar cells [3,62,63]. Srivastava et al. prepared a silicon solar cell with a silver-catalyzed nano-textured surface by the MACE process [3]. A solar cell with the nano-textured surface is formed by (i) the deposition of a thin film consisting of silver nano-islands over a silicon wafer surface by electroless metal deposition; (ii) the immersion of Ag deposited silicon wafer in H₂O₂:HF:DI water in a volume ratio of 1:2:10 to form the nano-texturing surface; (iii) the diffusion of phosphorous diffusion to form an N⁺-emitter; (iv) the formation of a P⁺-back surface by aluminum-alloying, and (v) the fabrication of front and back metal contacts by evaporating a Ti/Ag bi-
layer and then sintering in a process of rapid temperature annealing. Fig. 19 schematically depicts the complete process of nano-texturing a silicon solar cell by this method. Fig. 20 shows a plot of the $I_V$ characteristics of the illuminated control cell formed on a planar surface and on nano-textured silicon solar cells. For this particular growth methodology, the nano-textured silicon solar cell performed best in the 30 s MACE process: the short-circuit current density ($J_{sc}$), the open-circuit voltage ($V_{oc}$), the fill factor (FF), and the efficiency (EEFF) were 28.9 mA/cm$^2$, 0.578 V, 0.71, and 11.7%, respectively [3]. Even higher efficiencies (18.2%) have been obtained using a two-step MACE process [64].

Organic-black silicon hybrid solar cells have also fabricated. Fig. 21 displays the cross-sectional FESEM image of poly(3-hexylthiophene) (P3HT) on a nanoporous silicon substrate [65]. The P3HT film was formed on the surface of the silicon substrate with nanostructures holes by spin coating. However, P3HT clusters with a diameter of approximately 300 nm could not penetrate into the pores in the silicon substrate to form heterojunctions, because the nanopore diameters of NPSS produced by metal-assisted nanolithography was only around 100 nm. Hence the effective contact area between the P3HT and the NPSS was much smaller than the active area of the device. Increasing the soaking time promoted the formation of the heterojunction but the viscosity of the organic solution determined the maximal efficiency. The P3HT/NPSS structure had a short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), maximum output power ($P_m$), fill factor (FF), and efficiency (EEFF), of 5.52 mA/cm$^2$, 0.345 V, 0.42 mW/cm$^2$, 0.222, and 2.82%, respectively, under a 100 W xenon lamp. However, all such samples had a high series resistance and low fill factor [65].
3.2. Plasma immersion ion implantation (PIII)

Black silicon-based solar cells have been fabricated by plasma immersion ion implantation (PIII) processes under various conditions [23,66]. Photograph of a black silicon-based solar cell with a reflectance of 1.79% by the PIII method is shown in Fig. 22 [23]. The black silicon-based solar cell had an efficiency of 15.68% with a fill factor of 0.783. In contrast, the reference cell had an efficiency of 17.5% with a fill factor of 0.78.

Solar cells with a SiN$_x$ coating over b-Si have been reported to have a conversion efficiency of 15.99%. Polished silicon wafers were etched to form b-Si with various texturing conditions of gas flow rate, voltage pulses, and etching time, as presented in Fig. 23. The best photoelectric conversion efficiency of the textured solar cell with a reflectivity of 3.87% was reported to be 15.99%, and that of an acid-textured solar cell was 16.59%, as presented in Fig. 24. Even though these values are similar, the series resistance of the former was higher than that of the latter because the Ag–N–Si complex layer remained on the black silicon surface [66]. The remaining Ag–N–Si complex layer between Si and Ag crystallites caused current transmission with high contact resistance. The
series resistance was much worse than that of the acid-
textured solar cell, owing to worse Ag–Si contact in the 
bottom of the nanohillocks. The conversion efficiency of 
the black silicon solar cell can be further improved by 
removing the Ag–N–Si complex layer.

4. Comparison of synthetic methods for b-Si and solar 
cell efficiency

Table 1 shows a comparison of the lowest reflectivity of 
various b-Si samples made by different methods. We note 
that these comparisons are made with the understanding 
that the reflectance for b-Si is wavelength dependant, and 
these values are those reported by the various authors. 
However, it is worth noting that the blackest, b-Si to date 
has been made by a modified MACE process[67].

Table 2 compares the best-obtained parameters of 
solar cells that were prepared by various processes. The 
PIII method generally had yielded good performance, and 
originally it was thought that this was the better 
approach compared to MACE cells because of an assumed 
leakage current generated by the residual Ag NPs in the 
MACE method. However, recent work has shown that 
MACE cells can be made with equal efficiencies with 
proper attention to passivation and ensuring that the b-Si 
does not etch through the p/n junction. Furthermore, 
Branz et al. have used a two-step MACE to make cells 
with 18.2% efficiency.

5. Contact formation on black silicon solar cells

One issue that has been overcome is making reliable, 
low resistivity, screen printed contacts to black silicon 
solar cells. Most, if not all, laboratory cells made using 
black silicon anti-reflection control technology have used 
evaporated gold metal contacts. This sort of contact is 
straightforward to make and demonstrates excellent 
adhesion and low contact resistance. It is not, however, 
an acceptable contact for commercial solar cell produc-
tion. The challenge of making acceptable screen printed 
contacts has only recently been met [68] using standard, 
commercially available screen-printing pastes for p-on-n 
solar cells. Achieving acceptable contact resistance 
requires careful attention to curing and sintering tem-
peratures, ambient conditions and time at each
temperature. Nonetheless, a commercially acceptable process has been developed and is ready for large-scale solar cell manufacturing.

6. Theoretical basis for the low reflectance of black silicon

Contrary to what is often assumed or said, the low reflectance from a black silicon surface is not caused by light trapping. The features of such a surface whether dry etched pyramids or wet etched pores is at least an order of magnitude smaller than the wavelength of light incident on the surface. The typical situation is 10s of nm for black silicon surface features versus 100s to 1000s of nm for the wavelengths of light absorbed. An acceptable explanation can be found in the effective medium approximation (EMA) put forward by Bruggemann in 1935 [69]. Using the EMA it is possible to show that the index of refraction of a silicon surface with either type of nanoscale structure (pillars or pores) can be considered to vary essentially smoothly with depth for the black silicon surface. The elimination of any abrupt interface means that no reflection can occur, and indeed, average reflectance as low as

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**Fig. 22.** The EL images of the (a) reference and (b) black silicon cell. Reprinted from Y. Xia, B. Liu, J. Liu, Z. Shen, C. Li, Sol. Energy 2011; 85: 1574. Copyright (2011): with permission from Elsevier.


efficiencies comparable to traditional SiN silicon solar cells have been successfully fabricated with further research. Second, b-Si single and multi-crystalline that passivation of the b-Si surface is an important issue for high series resistance, and the increased surface area means nanoporous surface of black silicon substrates can causes makes it ideal as an anti-reflective coating. However, the efficient (efficiency\% \text{to reduce the cost of a solar cell production by 23.5}\% [67].

The adoption of MACE style b-Si processing has the potential an important goal especially as it has been determined that however, making the b-Si process commercially scalable is

selected parameters for b-Si solar cells prepared with various methods.

<table>
<thead>
<tr>
<th>Process method</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$q$ (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MACE (1 step)</td>
<td>0.594</td>
<td>32.3</td>
<td>76.8</td>
<td>14.7</td>
<td>[66]</td>
</tr>
<tr>
<td>MACE (2 step)</td>
<td>0.628</td>
<td>36.45</td>
<td>0.796</td>
<td>18.2</td>
<td>[64]</td>
</tr>
<tr>
<td>PIIE</td>
<td>0.613</td>
<td>34.2</td>
<td>0.776</td>
<td>16.3</td>
<td>[67]</td>
</tr>
</tbody>
</table>

0.3% across the solar input spectrum absorbed by a silicon solar cell have been measured.

7. Conclusions

In summary, the paper has reviewed recent developments concerning black silicon and its solar cell applications. Overcoming the high series resistance effect enables highly efficient (efficiency > 18%) silicon-based solar cells with very low reflectivity (reflectivity < 1%) to be realized. The following conclusions concerning b-Si and its potential use for solar cells can be drawn. First, the low reflectivity (~1%) of b-Si makes it ideal as an anti-reflective coating. However, the nanoporous surface of black silicon substrates can causes high series resistance, and the increased surface area means that passivation of the b-Si surface is an important issue for further research. Second, b-Si single and multi-crystalline silicon solar cells have been successfully fabricated with efficiencies comparable to traditional SiN, AR coated cells; however, making the b-Si process commercially scalable is an important goal especially as it has been determined that the adoption of MACE style b-Si processing has the potential to reduce the cost of a solar cell production by 23.5% [67]. As such b-Si represents a large step towards grid parity between solar cell technology and traditional carbon fuels.

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