Periodic nano/micro-hole array silicon solar cell

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Abstract
In this study, we applied a metal catalyst etching method to fabricate a nano/microhole array on a Si substrate for application in solar cells. In addition, the surface of an undesigned area was etched because of the attachment of metal nanoparticles that is dissociated in a solution. The nano/microhole array exhibited low specular reflectance (<1%) without antireflection coating because of its rough surface. The solar spectrum related total reflection was approximately 9%. A fabricated solar cell with a 40-μm hole spacing exhibited an efficiency of 9.02%. Comparing to the solar cell made by polished Si, the external quantum efficiency for solar cell with 30 s etching time was increased by 16.7%.

Keywords: Metal catalyst; Nano/microhole Si array; Reflectance; Efficiency

Background
Previous studies have reported that nanostructure surfaces can efficiently couple incident light into semiconductors [1-3]. Efficient light harvesting is vital for solar cells [4,5]. In addition to light coupling, efficient carrier transport in a nanowire structure has been suggested to increase the short-circuit current [6-8]. Therefore, several studies on solar cells have employed nanostructures to enhance performance [9-15]. The difficulty in establishing contact in nanostructures limits progress. In one study, a conducting polymer was adopted because it easily filled the space between nanostructures, enabling high efficiency to be achieved [15]. Creating microholes might be an appropriate approach [16]; however, using microholes may cause the advantages of light harvesting to be lost. In this study, we propose a microhole array structure to facilitate fabrication by implementing metal catalyst etching. Inside the hole, we spontaneously produced a nanowire array to achieve low reflectance. The optical reflectance of nano/microhole arrays with various spacings was evaluated. A solar cell was manufactured using this structure to demonstrate the possibility of attaining high efficiency.

Methods
The microhole arrays were implemented using metal-catalyst etching on a (100) p-type Si wafer (1 to 10 Ω cm). The wafer was cleaned using acetone in an ultrasonic bath for 10 min. After the substrate was rinsed with deionized (DI) water, it was immersed in a H2SO4 and H2O2 mixed solution for 10 min at 120°C. The substrate was further rinsed in DI water, blow-dried, and heated to 120°C in an oven. The microhole array pattern was implemented using photolithography. The diameter of holes on the photomask was 10 μm. The spacing between the holes was varied from 10 to 40 μm. To fabricate the microhole array, a Ag pattern was created by using the lift-off process for catalyst etching. The procedure is described as follows: a layer of photoresist (PR) was spin-coated onto the Si substrate. The Si substrate was then exposed to ultraviolet light through a photomask. After development, the PR on top of the Si substrate was patterned using a periodic hole array. A 50-nm-thick Ag was deposited onto the PR-coated Si substrate. A schematic diagram is shown in Figure 1a. After the PR was removed using acetone, a periodic Ag microdisk array with a diameter of 10 μm was obtained, as shown in Figure 1b. Metal-catalyst etching was conducted by immersing this sample into a H2O2/HF-mixed solution. Ag has a higher electron affinity than that of Si; therefore, the electrons in Si tend to accumulate on the surface of Ag. The H2O2 harvests these electrons and becomes H2O, as expressed in chemical reaction (1). The Si, lacking electrons, simultaneously reacts with H2O to form SiO2 and generate electrons, as expressed in chemical reaction (2). The HF then etches the SiO2 from the...
Ag, as expressed in chemical reaction (3). This process consumes no Ag and produces vertical Si patterns.

\[
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{H}^+ + 4e^- \quad (2)
\]

\[
\text{SiO}_2 + 6\text{HF} \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O} \quad (3)
\]

A 10-μm-deep microhole after being etched for 15 min is illustrated in the cross-sectional scanning electron microscopy (SEM) image shown in Figure 1c. As shown in Figure 1c, the diameter of the hole is 10 μm. Inside the hole, Si nanowires were clearly observed. After being etched, the Ag was removed using a HCl/HNO₃ (3:1 (v/v)) mixed solution. The structure was named ‘nano/microhole array.’ The n⁺ emitter in a solar cell was fabricated by spraying H₃PO₄ onto a p-Si wafer and then annealing the sample in a furnace at 900°C for 30 min [17]. The doping concentration of phosphorus was calculated by converting the resistivity of Si into carrier concentration, in which the resistivity of Si was measured by a spreading resistance profiler. By doping concentration profile, the phosphorus diffuse into Si around 0.2 μm. The solar cells were then implemented by depositing top and bottom electrodes. The area of the solar cell was 1.0 cm².

**Results and discussion**

Cross-sectional SEM images of a nano/microhole array at various etching times are shown in Figure 2. The depths of the hole after 0.5, 1, 5, 10, and 15 min were 0.394, 0.6, 2.6, 4.57, and 7.5 μm, respectively. The etching rate was approximately 0.5 μm/min. The specular optical reflectance on nano/microhole arrays with various spacings was measured at a wavelength of 300 to 800 nm. The specular reflectance was well below 1% for all of the samples, as shown in Figure 3a. The occurrence of the step-like reflectance is due to the resolution limit of the measurement, which is 0.1%. The microhole array sample with highest hole density (10-μm-spacing) exhibits lowest reflectance. In addition to the specular reflectance, the textured surface may cause the incident light scattered back to the incident plane, called diffuse reflectance. The total reflectance (R_{tot}) including specular and diffuse reflectance was measured using an integrated sphere, as shown in Figure 3b. The highest R_{tot} was approximately 14% for the 10-μm-spacing sample, whereas that of the 40-μm-spacing sample was 9%. The solar spectrum-related reflectance (R_{sol}) was 12.66%, 12.16%, 11.65%, and 9.21% for the samples with spacings of 10, 20, 30, and 40 μm, respectively. The R_{sol} was determined using the Equation (4):
where $I(\lambda)$ is the wavelength-dependent solar irradiance.

Unexpectedly, the nano/microhole array with a large surface area (40-μm spacing) exhibited a low reflectance. This is not usual because a flat surface will cause specular reflectance only. The higher diffuse reflectance indicates the surface without hole array may not be flat. To prove this assumption, surface picture was taken by plan-view SEM. Figure 4a shows a SEM image of the Si surface. A porous surface was observed on the area that was not covered by Ag. The incoming light was scattered, causing the specular reflectance to be well below 1%. In addition, the porous-like surface scattered less incoming light than did the periodic structure. Therefore, the sample with a spacing of 40 μm exhibited the least reflectance and is suitable for solar cell application. The mechanism that caused the development of the porous-like surface might be the dissociation of Ag in the H$_2$O$_2$/HF solution. During the etching process, Ag atoms can be converted into Ag$^+$ ion by H$_2$O$_2$. The Ag$^+$ ion can be recovered back to Ag by taking electrons from silicon. This ionized and recovered process will lead Ag to diffuse up and renucleate on the undesigned silicon surface to form new etching sites [18]. A schematic diagram of Ag dissociation in the solution during etching is illustrated in Figure 4b. The dissociation of Ag produced a nanowire in the microholes as well as in the undesigned area. The photovoltaic characteristics were measured under a AM 1.5G condition by using a solar simulator (Model XES-40S1, San-Ei Electric Co., Ltd., Osaka, Japan) equipped with an Agilent B2912A 1-V.
meter (Agilent Technologies, Santa Clara, CA, USA). The dark current–voltage of the nano/microhole array solar cell with a hole spacing of 40 μm at various etching times is shown in Figure 5a. No extensive dark current–voltage difference between the samples was observed. The photocurrent-voltage characteristics of the nano/micro-hole array solar cell are shown in Figure 5b. The device labeled ‘polish-Si’ was a reference device for which no nano/microhole array was composed. This device exhibited a 24.6-mA/cm² short-circuit current density (Jsc), 537-mV open circuit voltage (Voc), and 0.7 fill factor (FF). The power conversion efficiency (η) was therefore 9.37%. By using metal-catalyst etching, the short-circuit current increased extensively. After only 0.5 min of etching, the Jsc increased to 29.1 mA/cm²; this increase can be attributed to the reflectance reduction after etching. However, the porous-like surface rendered achieving favorable electrical contact difficult. The high contact resistance caused the FF to be low. Consequently, a low efficiency of 5.59% was obtained. After the etching time was increased to 5 min, the Jsc did not increase. The contact resistance was reduced, possibly because the nano/microhole array provided a large surface area for contact. The Jsc decreased to 25.5 mA/cm² as the etching time was increased to 10 min. This result is discussed in the subsequent paragraph. In a deep hole, the contact resistance substantially decreased. The series resistance reduced to 5.6 Ω, which is near the value of polish-Si. In addition, the FF improved to 0.65 and the efficiency increased to 9.02%. After the etching time was increased further to 15 min, the efficiency decreased to 6.9%. Both Jsc and FF decreased. The decreased FF might be explained by the suddenly increased Rs. The Rs is expected to reduce as the hole-depth increase by the larger contact area. However, the formation of metal contact in this experiment is not by the metal paste, it is approximately 100 nm thick deposited by
thermal evaporator. Therefore, in the deep hole, the metal line might be broken that causes the increased \( R_s \).

Table 1 lists details on the photovoltaic parameters. To explore the unusual trend in the \( J_{sc} \), external quantum efficiency (EQE) was measured. The EQE spectrum for the nano/microhole array solar cells at various etching times is shown in Figure 6a. The EQE for polish-Si was approximately 0.6 at a wide wavelength range and increased to 0.7 at an etching time of 0.5 min. However, the spectrum indicated that the EQE at a short wavelength decreased as the etching time was further increased, possibly because of carrier recombination at porous-like layers. The depth of the porous-like layer increased as the etching time was increased. The absorption of the incident light by the Si can be evaluated using Equation (5):

\[
I(d, \lambda) = I(0, \lambda) \cdot \exp(- \alpha(\lambda) \cdot d)
\]

where \( I(d, \lambda) \) refers to the intensity of light of wavelength \( \lambda \) transmitted into Si at depth \( d \); \( I(0, \lambda) \) refers to the intensity

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Etching time (min) & \( J_{sc} \) (mA/cm\(^2\)) & \( V_{oc} \) (mV) & FF & \( \eta \) (%) & \( R_s \) (\( \Omega \)) & \( R_{sh} \) (\( \Omega \)) \\
\hline
Polish-Si & 24.6 & 537 & 0.71 & 9.37 & 4.4 & 8,620 \\
0.5 & 29.1 & 542 & 0.35 & 5.59 & 14.9 & 271 \\
5 & 29.3 & 542 & 0.47 & 7.40 & 8.7 & 2,272 \\
10 & 25.5 & 544 & 0.65 & 9.02 & 5.6 & 6,667 \\
15 & 22.9 & 534 & 0.56 & 6.90 & 9.5 & 4,237 \\
\hline
\end{tabular}
\caption{The photovoltaic parameters for the nano/microhole array Si solar cell with different etching times}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Etching Time (min) & 0.5 & 1 & 5 & 10 & 15 \\
\hline
Depth (\( \mu \)m) & 0.394 & 0.6 & 3.06 & 5.19 & 7.5 \\
Wavelength (nm) & 450 & 470 & 620 & 690 & 750 \\
\hline
\end{tabular}
\caption{The depth of hole at specific etching time and the corresponding wavelength with the same absorption depth}
\end{table}
of the incident light at wavelength $\lambda$; and $\alpha(\lambda)$ denotes the absorption coefficient of Si at wavelength $\lambda$ in the unit 1/cm [19]. This equation indicated that a large amount of incident light is absorbed at depth $d = 1/\alpha$. This depth was called the absorption depth. The depth of the hole at a specific etching time and the corresponding wavelength at the same absorption depth are listed in Table 2. Because the carriers generated by incident light at the depth of the porous-like layer have a high recombination rate, the EQE at a corresponding wavelength must be reduced. This assumption was explored using a normalized EQE spectrum. Figure 6b shows the normalized EQE for various etching times. The depth corresponding to the wavelength presented in Table 2 fits the reduction point of the EQE satisfactorily. The results indicated that the $J_{SC}$ can be further increased by appropriately passivating the porous-like layer by using methods such as oxidation. If the surface is well passivated, the optimum depth of hole is suggested to be approximately 20 to 25 $\mu$m by taking the light absorption edge of Si is approximately 900 to 950 nm.

Conclusions
In this study, we demonstrated the formation of a nano/microhole array in Si by using a simple metal-catalyst etching method. The specular reflectance of this structure can be as low as 1%. The solar spectrum-related total reflection was approximately 9% for the 40-$\mu$m spacing sample. Efficiency of 9.02% was achieved by using this nano/microhole array without a surface passivation layer.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
ZP conceived of the study and participated in its design and coordination. GRL carried out the experiments on fabrication and SEM/optical measurements of the nano/microhole array and solar cell. DK contributed the mechanism discussion and drafted the partially manuscript. ZP revised the manuscript. All authors read and approved the final manuscript.

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