Effects of Nanostructures Formed by Plasma Etching on the Reflectance of Solar Cells

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We investigated lithography-free plasma etching methods to modify the surface of single-crystalline Si, which is widely used for manufacturing of solar cells. Experiments were performed using SF$_6$/O$_2$ dry etching for the purpose of reducing the reflectivity at the Si surface. Upon inductively-coupled-plasma (ICP) etching in SF$_6$/O$_2$, pillar-shaped nanostructures were formed on the surface, which changed to black. Furthermore, various etching methods and conditions to suppress the reflectivity in a broad spectral range were investigated for optimization of the surface property of the solar cells, i.e., enhancement of the solar cell efficiency. The mechanisms for the reflectivity on different surface have been studied using scanning electron microscope (SEM), atomic force microscope (AFM) and ultraviolet (UV) analysis. According to the analyses, self-assembled nanostructures efficiently reduce the reflectance. Before etching, the reflectance of a Si wafer was ~35 \% in the wavelength range of 600 ~ 1000 nm and >50 \% in the wavelength range of 200 ~ 400 nm, but it decreased to ~3 \% in the wavelength range of 200 ~ 1000 nm after performing SF$_6$/O$_2$ plasma etching. The formation of nanostructure arrays and the related reflectance were also studied as functions of the time, the bias RF-power and the gas mixture, as the condition of the SF$_6$/O$_2$ plasma markedly affects the reflectance of the nanostructure. We were able to identify the best conditions to obtain high-aspect-ratio vertically-aligned Si nanostructures with a low reflectance.

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I. INTRODUCTION

There have been various studies on the reduction of the reflectance by using chemical solutions. The efficiency of single-crystalline silicon solar cells can be increased by using deeply textured surfaces (depth of several \( \mu \)m), which appear black due to a strong reduction of the reflectivity over a broad spectral range [1]. This kind of texturing using an anisotropic KOH etching solution is applicable only to (100)-oriented single-crystalline silicon [2]. Some chemical solutions are, however, expensive and pose difficulty. Moreover, chemical etching is limited in reducing the reflectance in the wavelength range of 200 ~ 400 nm. Recently, photovoltaic cells based on silicon nanowire arrays have been proposed as a promising candidate for solar energy harvesting [3]. Some nanostructure arrays have much lower reflectance and higher absorbance at wavelengths in the solar spectra [4].

To realize a photovoltaic cell of low reflectance, low cost, large area and maskless self-assembly of vertical Si nano-structure arrays, a SF$_6$/O$_2$ plasma was used in this research because it is known to yield deep trenches with high aspect ratio (depth/width >10) and high anisotropy [5, 6]. The observed reflectance is understood to be related to the diffraction effects and the moth-eye effects [7]. We investigated the correlation between the reflectance and nanopillar made under various plasma conditions: time, bias RF-power and gas mixture of SF$_6$/O$_2$.

II. EXPERIMENT DETAILS

The substrate materials were (100) single-crystalline silicon wafers with a thickness of 700 \( \mu \)m. The wafers were cut into pieces of the proper size and put into a beaker. The wafers were cleaned by using ultrasonic bath of de-ionized (DI) water. The wafers are cleaned by ethanol for 10 min and DI water for 10 min to eliminate all the traces of dust and grease left on the surface.

The etching processes were performed in an ICP reactor [8~10]. The electrical power supplied to the plasma
source was up to 1500 W. The DC bias voltage was generated by using an RF power generator that could supply a power up to 500 W to the wafer. The SF$_6$/O$_2$ mixed gas was introduced from the top of the plasma reactor via gas flow controllers, up to gas flows of 100 sccm for both SF$_6$ and O$_2$. Vacuum grease was applied to the back side of the silicon wafer, then, the silicon wafer was placed stably on a chuck. Except for the changing RF bias power, all the experiments were performed at an ICP power of 600 W and a pressure of 30 mTorr.

After etching, the vacuum grease was removed by using isopropyl alcohol (IPA). We measure the reflectance by using a UV spectrometer. There were several modes of reflection: total reflection, $5^\circ$ reflection and $8^\circ$ reflection. In this work, we measured the reflectance by using the $8^\circ$ reflection. The wavelength was detected in the range of 200 nm $\sim$ 2000 nm, although we used the range from 200 nm $\sim$ 1400 nm. We used barium sulfate as a standard material for the total reflection. The etched features are observed using a field emission SEM and AFM.

### III. RESULTS AND DISCUSSION

1. Effects of Wet Etching and Plasma Etching on the Reflectance

Figure 1 shows the reflectance of the samples with the different surface structures resulting from the etching process. Compared to bulk polished Si, the reflectance measurements of the substrate before and after nanopillar formation show a significant reduction in the reflectance in the range of 200 to $\sim$ 1000 nm. Figure 2 (a) shows the SEM image of the sample after the wet etching using the KOH/IPA solution. The pyramidal structure is larger than 2 nm and its surface is flat. Figure 2 (b) shows the vertically-aligned high-aspect-ratio Si nanostructure arrays after etching using SF$_6$/O$_2$ plasma. The sample without etching is at the polished state and its reflectance is high because the reflectance $R$ in this case can be determined by using the following formula when the light enters from material 2 (refractive index $= n_2$) to material 1 (refractive index $= n_1$):

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

In the case of air and silicon, the refractive indexes are 1 and 3.5. From these values, we estimate $R$ to be $\sim$30.25 % in the visible region. At short wavelengths, the refractive index of silicon is $\sim$5.5, so $R$ is very high. At long wavelengths, light is transmitted through the silicon substrate; therefore, the reflectance on the back surface is added to that on the surface. The reflectance of the sample after wet etching is much lower because of the pyramidal structure (Figure 2(a)) due to the higher light trapping effect obtained by the texture treatment of the silicon surface [11].

The sizes of the pyramidal structures are larger than the wavelength of the solar irradiance. The laws of geometrical optics can be applied here, so ray-tracing can be used to determine the angular distribution of the scattered irradiance. There are two paths of incident light: one is the path of the light entering inside the silicon and the other is the path of the light being reflected from the silicon surface. The reflected light penetrates neighboring hills, resulting in a high light trapping effect, as shown in Figure 2(c) [11]. This can be used to explain the lower reflectance [12]. Because the diameters ($\sim$100 nm) of the high-aspect-ratio nanostructure arrays (Figure 2(b)) are comparable to or smaller than the wavelength of incident solar light, the laws of geometrical optics can’t be applied. In the shorter wavelength region...
Fig. 3. (a) Reflectance spectra and (b) roughness of nanostructures for different etching times.

(such as 200 – 400 nm), diffraction effects are expected to occur when the wavelength of the incident light is comparable to that of the periodicity of the surface structure. The incident light is diffracted so the zeroth-order reflection is weakened. When the shorter-wavelength light enters into the nanopillars, the sub-wavelength resonance effects between nanopillars appear. This is the optical antenna effect. As a result, the reflectance here in the wavelength range especially from 200 to 400 nm is much lower than that of the pyramidal structures. In the longer-wavelength region, the reflectance is also decreased. The effects observed here are closely related to that the so-called “moth eye” phenomena reported in the early 1970’s in which sub-wavelength optical structures on the eyes of moths are understood to be responsible for unusual low antireflective properties and are well described by using an effective medium theory [13, 14]. Moth eyes have orderly bumps on their corneas, creating a situation in which most of the light from the sun is absorbed and efficiently utilized, instead of being reflected uselessly. These two effects, which lead to the broadband characteristics of the reduced reflectance, cannot be separated by using a well-defined wavelength boundary. Therefore, a choice of proper plasma condition enables the reflectance of nanopillars to be reduced by controlling the roughness of the surface.

2. Effects of the Plasma-etching Conditions

Figure 3 shows the reflectance and the roughness of the nanostructure arrays as a function of time. The reflectance of the samples decreased with increasing etching time until 150 s. This reveals that the nanostructures formed with increasing etching time more easily absorb light, as the etched structures are different. In the beginning, when only little roughness on the flat surface is developed, the high-aspect-ratio nanostructure arrays are not observed. One of the reasons is the lack of the reaction products (SiFₓ) to form the SiOₓFᵧ passivation layer. With increasing etching time, the surface becomes rougher, but no high-aspect-ratio nanostructure arrays are observed before 37 s. The sample etched for 60 s shows a very low reflectance (~3 %). For the sample etched for 150 s (Figure 4(a)), the roughness of the high-aspect-ratio nanostructure arrays increases dramatically up to 0.30 µm (Figure 3(b)), which causes a lower reflectance. The reflectance of the sample etched for 300 s (Figure 4(b)) is nearly the same as that of the sample etched for 150 s. The roughness of the surface structure, however, decreases slowly when time is increased further.

Fig. 4. AFM images of nanostructures for different etching times: (a) SF₆/O₂ plasma etching for 150 s and (b) SF₆/O₂ plasma etching for 300 s.
Figure 5 shows the reflectance and the roughness of the nanostructure arrays as a function of the bias RF power. When the bias power is not applied to the wafer, the nanostructure arrays do not form (Figure 6) because the ion energy is not sufficient to etch the silicon in the vertical direction and the reflectance of the wafer is \( \approx 20 \% \). An increase in the bias power from 0 to 20 W has a significant effect on the reflectance and the surface of the etched wafer. The reflectance decreases from \( \approx 20 \% \) to 3 \% (Figure 5(a)) and the roughness dramatically increases from 1.77 nm to 352 nm (Figure 5(b)), while the surface structure changes to high-aspect-ratio nanostructure arrays. The reflectances of the samples etched at bias powers in the range from 20 W to 60 W are similar (2.5 \%) because of the presence of the high-aspect-ratio nanostructures. The high-aspect-ratio nanostructures are similar to nanopillars, but the roughness changes with the bias power.

The reflectance of the samples and the roughness of the high-aspect-ratio nanostructure arrays as functions of the \( \text{O}_2/\text{SF}_6 \) ratio are shown in Figure 7. The RF power (600 W), total gas flow (90 sccm), pressure (30 mTorr) and temperature (290 K) were constant for the experiments. The duration of the plasma processing was 150 s. From Figure 7, the general reflectance trends are found to be similar. For \( \text{O}_2/\text{SF}_6 \leq 0.64 \), the nanostructure arrays are not seen and the reflectance from the surface is high. In the range from \( \text{O}_2/\text{SF}_6 = 0.8 \) (Figure 8(a)) to \( \text{O}_2/\text{SF}_6 = 2 \) (Figure 8(b)), high-aspect-ratio nanostructure arrays give rise to a low reflectance, perhaps due
to the comparable extents of ion bombardment and the formation of the SiO$_x$F$_y$ passivation layer. In this case, increasing O$_2$ results in a more gradual decrease in the roughness (Figure 7(b)). With further increases in the oxygen content, the SiO$_x$F$_y$ passivation layer is easier to form. For O$_2$/SF$_6$ $\geq$ 2.6, the nanostructure disappears, but the reflectance becomes high again because a smooth surface is re-generated.

**IV. CONCLUSIONS**

Large-area high-aspect-ratio (>10 : 1) nanostructure arrays were fabricated in an ICP reactor by using a SF$_6$/O$_2$ plasma at a noncryogenic temperature without using any masks [15]. These nanostructure arrays can be used as absorber materials in novel photovoltaic architectures because of the low reflectance of light from the solar cell surface. The diffraction effect and the moth-eye effect were found to explain these phenomena well. The condition of the SF$_6$/O$_2$ plasma markedly affected the preparation and the reflectance of the nanostructures. According to the experiments performed in this work, a bias power of 30 W, an O$_2$/SF$_6$ ratio of 2 and an etching time of 150 s are the best conditions to attain nanostructures with a low reflectance.

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