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Plasma Surface Texturing of Single-Crystal Silicon Using Dielectric Barrier Discharge

Tatsuya Sakoda, Toshiyuki Hamada and Kunihiro Matsukuma
Department of Electrical System and Computer Engineering, Sojo University,
4-22-1 Ikeda, Kumamoto 860-0082, JAPAN, Fax: 81-96-326-3000, e-mail: sakoda@pe.sojo-u.ac.jp

In order to lower the fabrication cost of single-crystalline solar cells with a low light reflection, a plasma surface texturing using a dielectric barrier discharge was performed on wet-textured Si surfaces of pyramid-like shape. After the surface texturing, the surface state and the reflectance were evaluated. The results showed that the dielectric barrier discharge could make fine uneven structures on the entire area of a wet-textured surface of pyramid-like shape. The lowest reflectance profile was obtained at $O_2/(CF_4+O_2)$ ratio of 0.6, where the reflectance was below 5% at wavelengths from 400 to 1000 nm and showed a minimum of 3.2% at 494 nm.

Key words: dielectric barrier discharge, solar cell, reflectance, texture

1. INTRODUCTION

Photovoltaic power generation has attracted much attention from the viewpoint of the prevention of global warming and energy problems. To popularize the photovoltaic solar system widely, a low-cost photovoltaic solar system with high conversion efficiency is strongly required. One approach to realize a low-cost solar cell with high conversion efficiency is a surface texturing technique which reduces the light reflection from surfaces of solar cells. The primary surface texturing technique is wet chemical etching where randomly distributed pyramids due to crystallographic orientations are formed. The required time for the wet process is short and the fabrication cost is relatively low. However, the reflectance is still high, and its value at 800 nm is approximately 10% for single-crystalline silicon substrates.

On the other hand, a plasma texturing technique using a reactive ion etching (RIE) source operating at a low pressure has been examined by Kumaravelu et al.[1]. They performed RIE texturing on an even Si surface covered with a native oxide and formed innumerable rounded pyramids. The surface mean roughness of the textured surface was approximately 500 nm, while the height of the tallest pyramid was 4 μm. The obtained reflectance was less than 1.4% at approximately 800 nm. However, some important cost problems remain. The required time and temperature for Si substrates were 10 min and 173 K, respectively. As mentioned above, in order to popularize photovoltaic solar system widely, it is necessary to realize a low-cost fabrication method in which a vacuum system and a cooling device for Si substrates are not required. Then, we proposed a new plasma surface texturing technique using dielectric barrier discharge (DBD) at an atmospheric pressure[2-4]. DBD formation is achieved by the arrangement of dielectric layers in the discharge gap. A dielectric layer leads to the formation of a large number of short-lived microdischarges whose gas temperature is low even at an atmospheric pressure[2]. Additionally, in the case where helium is introduced as a carrier gas, the discharge becomes more uniform. Helium atoms have metastable states at high energy levels, and the breakdown voltage is low (4 kV/cm). The radial growth process from an electron avalanche to glow discharge formation in DBD in atmospheric pressure helium has been theoretically analyzed by Honda et al.[5]. They suggested that a slow increase in electron density by moderate ionization under a low reduced electric field induces the radial growth of the discharge.

In this study, we added CF_4 and O_2 gases to DBD for which the carrier gas was helium and performed the texture etching. It should be noted that there is a great difference in the texturing methods between RIE by Kumaravelu et al.[1] and DBD. We attempted to etch wet-textured surfaces of pyramid-like shape, while Kumaravelu et al. performed on an even Si surface covered with a native oxide. After the additional surface texturing, the surface state and the reflectance were evaluated.

2. EXPERIMENTS AND METHODS

A schematic diagram of DBD texturing system is shown in Fig. 1. A parallel electrode type was used for generating DBD. Each electrode 70mm in diameter was made of stainless steel and was cooled by passing cooling water at 20℃ through it. For the dielectric material, a quartz glass disk 100 mm in diameter and 1mm thick was used. The quartz disk was arranged below a high-voltage electrode, and the wet-etched Si substrate was placed on a grounded electrode. Although the original cell size was 125 mm×125 mm with a thickness of 220 μm, 45-mm-square specimens were cut for the surface texturing. The discharge gap length between the quartz glass disk and the wet-etched Si substrate was maintained at 1 mm by placing four spacers (2 mm×2 mm) made of quartz glass 1 mm thick on the substrate.

DBD was operated using a pseudosinusoidal wave, of which the maximum voltage and frequency were 4 kV and 8 kHz, respectively. Figure 2 shows a waveform of the discharge voltage. In this study, the discharge voltage was kept at 2.5 kV. The voltage rise time to a maximum value was 5 μs, and the full width at half maximum of a voltage pulse was approximately 10 μs [4]. Discharge voltage and discharge current were monitored using a high voltage probe and a Rogowski coil, respectively. He, CF_4 and O_2, controlled by mass flow controllers, were supplied to the discharge gap. All experiments reported here were made under atmospheric pressure. A flow rate of He was kept at 750 sccm, and a total flow rate of a mixture of CF_4 and O_2 was set at 100 sccm. The $O_2/(CF_4+O_2)$ flow ratio (F_r) was set at 0, 0.2, 0.4, 0.6 and 0.8. The additional surface texturing was performed for 4, 6 and 8 min.

After the additional plasma surface texturing, HF wet cleaning to remove oxides and organic matters was carried out on each textured substrate and then the surface state and the reflectance were evaluated. The measurement of the reflectance on each substrate was performed at the center of the substrate sample over an area of 20 mm×10 mm.

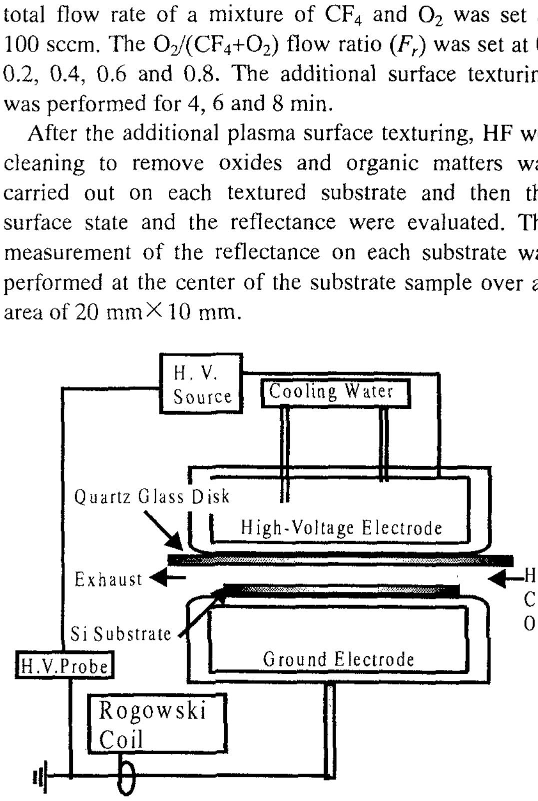


Fig. 1 Schematic diagram of DBD texturing system.

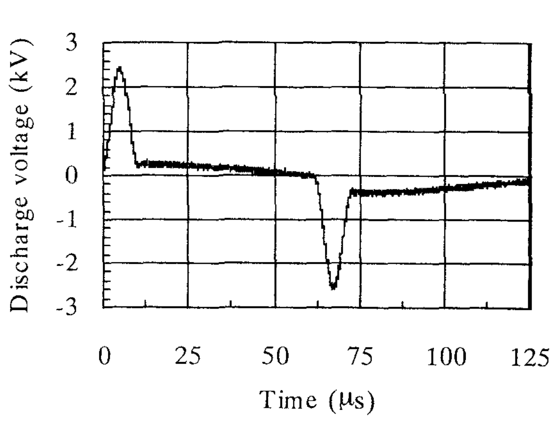


Fig. 2 Waveform of discharge voltage.

3. RESULTS AND DISCUSSIONS

Figure 3 shows the measured reflectance as a function of wavelength. F_r were 0, 0.2, 0.4, 0.6 and 0.8, and each DBD surface texturing was performed for 6 min. For each F_r condition, the discharge power obtained by the integration of the discharge voltage and the discharge current for the period of a pseudosinusoidal wave was approximately 4 W. The temperature on the substrate surface just after the DBD texturing for 6 min was 300 K. From Fig. 3, the reflectance obtained from DBD-treated surfaces decreases in comparison with that from the wet-etched (parent) surface. Except for F_r=0 and 0.8, the reflectance markedly decreases as F_r increases. The lowest reflectance profile is obtained at F_r=0.6, where the reflectance is below 5% at wavelengths from 400 to 1000 nm and shows a minimum of 3.2% at 494 nm. At 600 nm, the reflectances for F_r=0, 0.2, 0.4, 0.6 and 0.8 are 11.5, 5.5, 3.7, 3.7 and 6.9%, respectively.

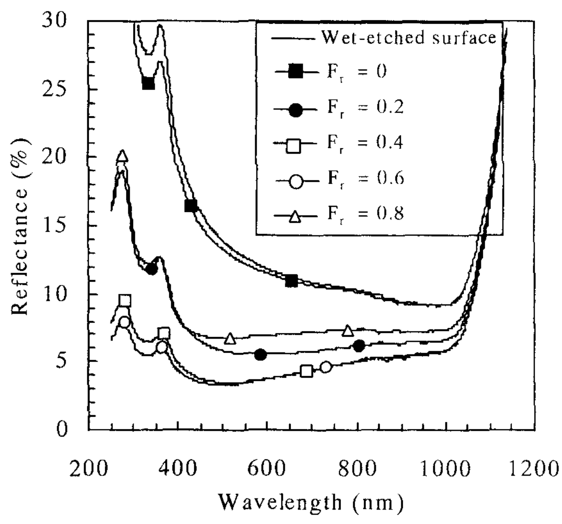
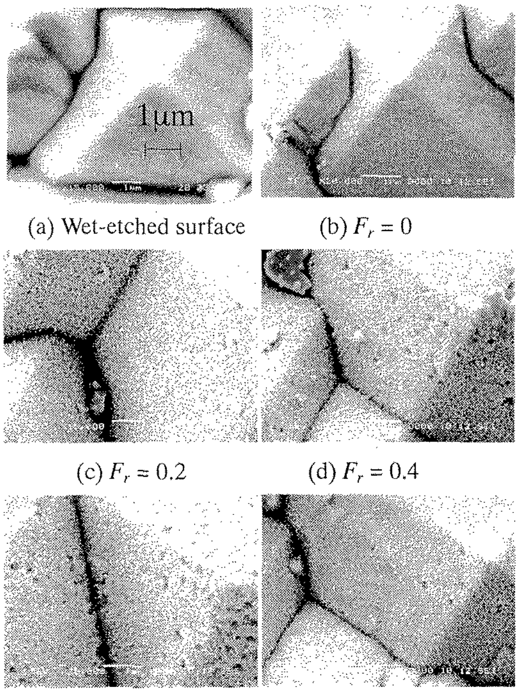


Fig. 3 Reflectance of the wet-etched surface and the DBD-treated surfaces at F_r=0, 0.2, 0.4, 0.6 and 0.8.

Scanning electron microscopy (SEM) images, obtained on the wet-etched surface and the DBD-textured surface at F_r=0, 0.2, 0.4, 0.6 and 0.8 were shown in Fig. 4. It may be seen that each surface of the pyramids fabricated only by wet etching is completely flat. Typical base length and height of the pyramids are approximately 5 μm. When applying DBD to the wet-etched substrate, the pyramid surfaces are etched and the resultant fine uneven structures are formed. However, the surface mean roughness of the surfaces at F_r=0 and 0.8 are much small. For reflectance profiles shown in Fig. 3, the reflectances at F_r=0 and 0.8 are high in comparison with those at F_r=0.2, 0.4, 0.6. Therefore, it seems that the formed uneven structures improve the light trapping effect. For SEM images at F_r=0.2, 0.4, 0.6, the depth of the fine uneven structures increases as F_r increases while the pitch between the fine uneven structures is approximately 100 nm. The depth at F_r=0.6 is approximately 100 nm. Thus, the depth of the fine uneven structures markedly takes part in the decrease of the reflectance which becomes low as the depth increases.

Incidentally, the reflectance obtained by DBD texturing is high in comparison with that by RIE texturing studied by Kumaravelu et al.[1] although there is a great difference in the methods of obtaining surface structures with low reflectance. It is desired to deepen the fine uneven structures.



(a) Wet-etched surface (b) $F_r = 0$

(c) $F_r = 0.2$ (d) $F_r = 0.4$

(e) $F_r = 0.6$ (f) $F_r = 0.8$

Fig. 4 SEM images on (a) the wet-etched surface, the DBD-textured surfaces at (b) F_r=0, (c) F_r=0.2, (d) F_r=0.4, (e) F_r=0.6 and (f) F_r=0.8.

DBD surface treatments at F_r =0.6 were performed for 4 and 8 min. The measured reflectance as a function of wavelength is shown in Fig. 5. It can be seen from this figure that the reflectance doesn't decreases in proportion to DBD texturing time. The reflectance at wavelength above 396 *nm*, obtained on 8 min-treated surface, is higher than that on 4 min-treated surface. At 600 nm, the reflectances for 4 and 8 min are 4.6 and 5.4%, respectively. SEM images obtained on 4 and 8 min-treated surfaces are shown in Fig. 6. For Fig. 6(b), it may be seen that the pitch between the fine uneven structures becomes wider while the depth slightly increases. That is, the reflectance at long-wavelength above 396 nm becomes high as the pitch becomes wider. For F_r=0.6, a reflectance profile on 6 min-textured surface, shown in Fig. 3, is lower than that on 4 min-textured surface, i.e., the lowest profile is obtained on 6 min-textured surface. As mentioned above, the depth and the pitch of fine uneven structures were approximately 100 nm. The average density, which comprises gas and Si, becomes high as the depth becomes larger for the periodic structure due to the fine uneven structures. For long-wavelengths, the wavelength is not short enough to neglect the spatial variation of density in the region of the fine uneven structures. It is probable that the effective reflectance decreases because the in-depth density, i.e., the in-depth refractive index gradually changes in the region of the fine uneven structures. In the case of Fig. 6(b), the pitch between the fine uneven structures is wide. The spatial variation scale of the refractive index against the wavelength is relatively small, and therefore the reflectance at long-wavelength becomes high.

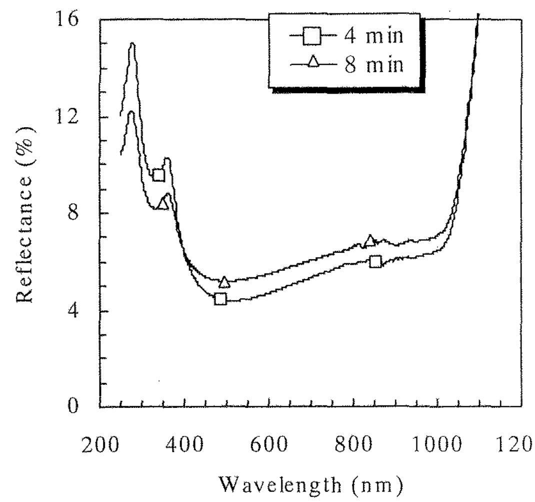
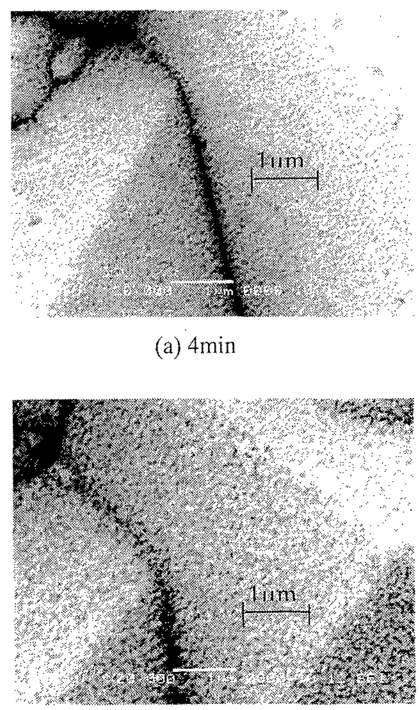


Fig. 5 Reflectance of the DBD-treated surfaces for 4 and 8 min when F_r=0.6.



(a) 4min

(b) 8min

Fig. 6 SEM images on (a) 4 min-textured surface and (b) 8 min-textured surface at F_r=0.6.

The reflectance profile obtained at F_r=0.4, shown in Fig. 3, was the almost same as that at F_r=0.6. Then, at F_r=0.4, DBD surface treatments were performed for 4 and 8 min. Figure 7 shows the measured reflectance as a function of wavelength for the case of F_r=0.4. A reflectance profile for 8 min is lower than that for 4 min and the reflectance at wavelengths from 400 to 1000 nm is only 0.5% higher than that for 6 min. SEM image obtained on 8 min-textured surface was close to that shown in Fig. 4(b). Thus, the reflectance does not decrease in proportion to DBD texturing time, and the tendency of the reflectance variation with DBD texturing time differs in F_r.

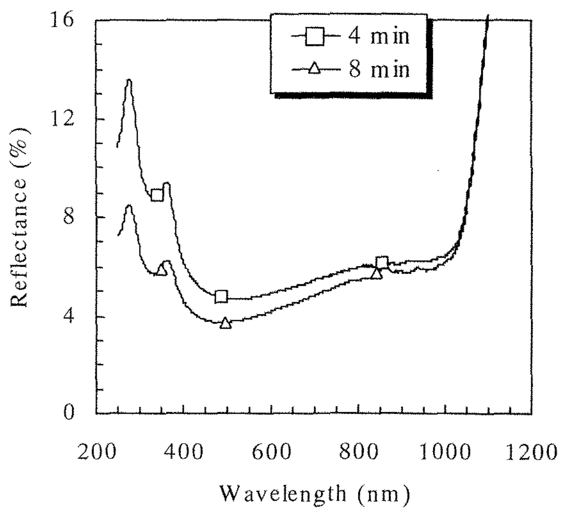


Fig. 7 Reflectance of the DBD-treated surfaces for 4 and 8 min when F_r = 0.4.

The results showed that DBD texturing technique could make fine uneven structures. The similar uneven structure may be formed even using radio-frequency discharge plasmas operating at a low pressure. However, the mean free path of particles in DBD operating at an atmospheric pressure is less than 100 nm and then energy of the produced ion is immediately lost through collisions. As compared with the discharge plasmas operating at a low pressure, the substrate damage due to the ion bombardment is not a serious problem.

This article focused on whether DBD texturing technique was useful to improve the light-trapping effect of single-crystalline Si substrates, and the reflectance and the surface state were measured to investigate the effect of DBD texturing. Characterizations such as current-voltage and conversion efficiency are not yet performed. Incidentally, in this study, DBD texturing was performed only under some discharge conditions. It is necessary to investigate the further optimum discharge condition which can deepen the fine uneven structures. At the same time, DBD texturing should be performed on original 125- or 155-mm-square solar cells, and characterizations such as current-voltage and conversion efficiency should be done. Studies in these directions are now in progress.

5. CONCLUSION

We performed DBD surface texturing on wet-textured single-crystalline Si substrates used for solar cells, where CF_4 and O_2 gases were added to DBD for which the carrier gas was helium. A flow rate of helium was kept at 750 sccm, and a total flow rate of a mixture of CF_4 and O_2 was set at 100 sccm. The lowest reflectance profile was obtained at $O_2/(CF_4+O_2)$ ratio of 0.6, where the reflectance was below 5% at wavelengths from 400 to 1000 nm and showed a minimum of 3.2% at 494 nm. In this case, the pyramid surfaces were etched and the resultant fine uneven structures approximately 100 nm deep and with a pitch of around 100 nm were formed on the entire surfaces of the wet-etched Si substrates. Additionally, the reflectance dropped as the depth of the fine uneven structures increased and became high as the pitch became wider. Thus, it was found that DBD texturing could reduce the reflectance from surfaces of Si substrates in a short time.

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