Optical and electrical properties of porous silicon layer formed on the textured surface by electrochemical etching*

Ou Weiying(欧伟英), Zhao Lei(赵雷), Diao Hongwei(刁宏伟), Zhang Jun(张俊), and Wang Wenjing(王文静)†

Key Laboratory of Solar Thermal Energy and Photovoltaic System, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, China

Abstract: Porous silicon (PS) layers were formed on textured crystalline silicon by electrochemical etching in HF-based electrolyte. Optical and electrical properties of the TMAH textured surfaces with PS formation are studied. Moreover, the influences of the initial structures and the anodizing time on the optical and electrical properties of the surfaces after PS formation are investigated. The results show that the TMAH textured surfaces with PS formation present a dramatic decrease in reflectance. The longer the anodizing time is, the lower the reflectance. Moreover, an initial surface with bigger pyramids achieved lower reflectance in a short wavelength range. A minimum reflectance of 3.86% at 460 nm is achieved for a short anodizing time of 2 min. Furthermore, the reflectance spectrum of the sample, which was etched in 3 vol.% TMAH for 25 min and then anodized for 20 min, is extremely flat and lies between 3.67% and 6.15% in the wavelength range from 400 to 1040 nm. In addition, for a short anodizing time, a slight increase in the effective carrier lifetime is observed. Our results indicate that PS layers formed on a TMAH textured surface for a short anodization treatment can be used as both broadband antireflection coatings and passivation layers for the application in solar cells.

Key words: texture; porous silicon; anti-reflectance coating; solar cell

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1. Introduction

Reducing incident light-reflection losses in crystalline silicon solar cells is one of the key issues for modern photovoltaic technology. Texturing the front surface of a solar cell is an effective way to achieve both a reduction in front surface reflection and an increase in light trapping. It was calculated that the optical length in a medium with a refractive index of n is enhanced by a factor of $4n^2$ when the surface is sufficiently strongly textured[1]. Many techniques have been proposed to texture crystalline silicon in order to achieve better light trapping in solar cells[2−7]. In modern solar cell processing, one of the known technologies to reduce the optical losses is anisotropic alkaline etching of mono-crystalline silicon to form random pyramidal structures on the silicon surface[8]. However, the optical reflectance of such structures is usually over 10% in the wavelength range 300 to 1200 nm. In order to achieve a lower reflectance, antireflection coatings (ARCs) are widely used for mass production of Si solar cells. ARCs are generally fabricated by PECVD technology resulting in an increase in the cost of commercial solar cells[9]. Additionally, the most conventional anisotropic etching solutions are aqueous potassium hydroxide (KOH) and sodium hydroxide (NaOH), which are cost and time efficient but result in potassium and sodium ion contaminations to the solar cell devices[10]. In recent years, tetramethylammonium hydroxide (TMAH) solution was reported to be used for random pyramid texturization on silicon surfaced due to its non-volatile, non-toxic and good anisotropic etching characteristics[11].

Porous silicon (PS), which has been known since 1956, has a lot of advantages in solar cells[12]. PS is a sponge-like material that could be used to enhance light trapping in a cell[13]. Moreover, the effective refractive index of PS is lower than that of bulk silicon and can be variable by the change in porosity, thus it can be used as antireflection coatings for silicon solar cells[14, 15]. Since the first report of the use of porous silicon as an antireflection coating was published in 1982[16], many efforts have been focused on the use of PS as effective ARCs and backside reflectors for silicon solar cells[17−21]. However, few studies were reported with regard to the electrical properties of porous silicon layers formed on a textured silicon surface.

In this paper, the textured surface was achieved by using silicon-dissolved tetramethylammonium hydroxide (TMAH) solutions without the addition of surfactant. Then, PS layers were formed on the textured surface by electrochemical etching in HF-based electrolyte. The aim of this work is to study the optical and electrical properties of porous silicon layers formed on the textured surface.

2. Experimental

P-type solar-grade CZ wafers with {100} orientation, 200 μm thick and 0.5–3 $\Omega\cdot$cm resistivity were used. The wafers were cut into 2 × 1.5 cm^2 samples without any clean process. Firstly, the samples were textured by anisotropic etching in silicon-dissolved TMAH solutions, according to the process detailed in Ref. [22]. Experiments were carried out in a

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† Corresponding author. Email: wjwangwj@126.com
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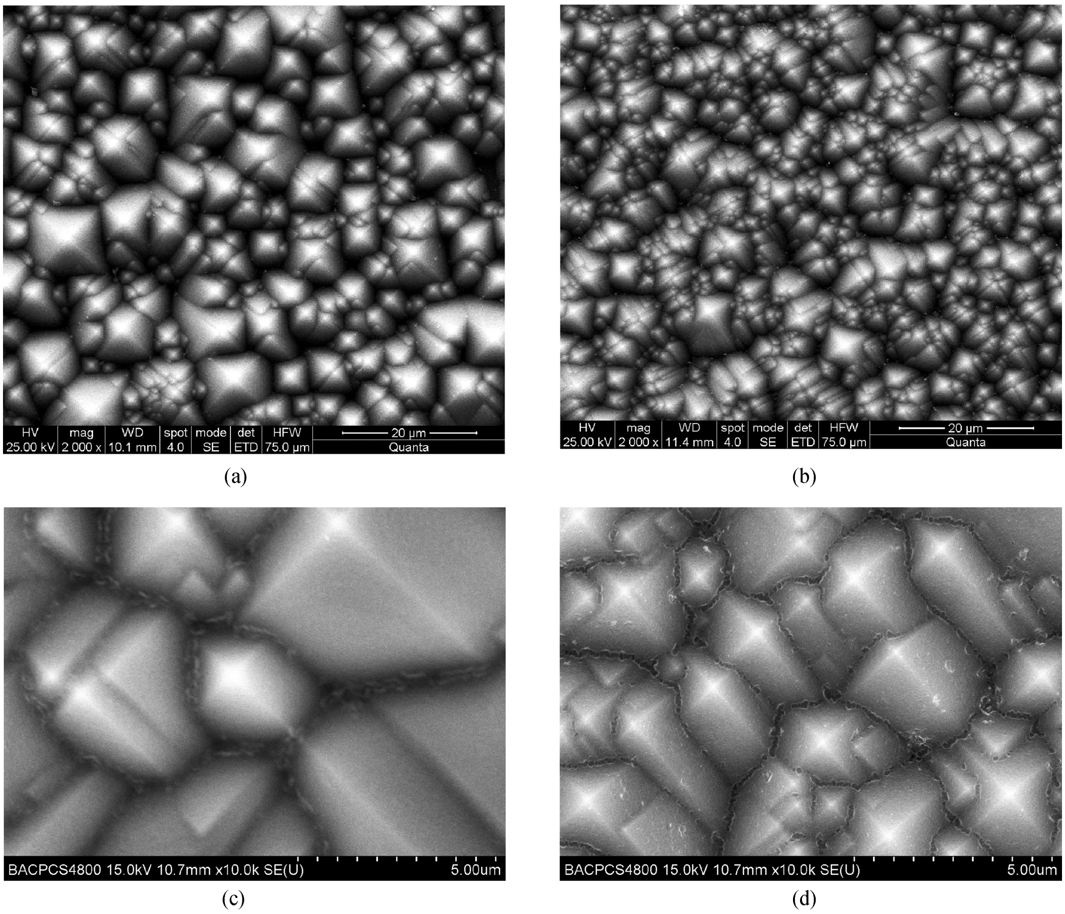

Fig. 1. SEM pictures of the resulting surface morphologies (a, b) before and (c, d) after electrochemical etching for 2 min. The TMAH textured surface was achieved by etching at 80 ℃ for 25 min in solutions of (a, c) 5 vol.% TMAH; (b, d) 3 vol.% TMAH.

Thermostatic Bath covered with a glass vessel in order to limit evaporation of the water. After the texturization processing, the samples were taken out and rinsed in deionized (DI) water. Then the samples were rinsed with acetone and ethanol for 20 min each. Finally, the samples were dried in air for about 10 min.

The PS layers on the textured samples were prepared by electrochemical etching in an electrolyte composed of 6 : 6 : 29 = HF (40%) : DI water : 2-propanol (vol). Etching was performed in a double electrode electrochemical cell. The anodizing time ranged from 2 to 40 min and the applied voltage was 6.5 V. After electrochemical processing, the samples were rinsed first with a solution composed of 1 : 4 = HF (40%) : C_2H_5OH (vol) for more than 10 min to remove surfactant from inside the trenches. Then, the samples were rinsed with ethanol for 10 min. Lastly, the samples were dried with nitrogen.

The surface morphologies of TMAH textured silicon wafers before and after PS formation were analyzed by a scanning electron microscope (SEM). The surface reflectance in the 300–1200 nm range was measured by a UV-VIS-NIR spectrophotometer and the minority-carrier lifetime was measured by microwave photoconductivity decay.

3. Results and discussion

Figure 1 shows the SEM pictures of the resulting surface morphologies before and after electrochemical etching for 2 min. Figures 1(a) and 1(b) show that uniform texturization throughout the surfaces was achieved by etching in both 5 vol.% and 3 vol.% TMAH solutions at 80 ℃ for 25 min. The lower the TMAH concentration, the smaller size of the pyramids. Sponge-like PS was formed on the textured surface with bigger pyramids and mecropore was formed on the textured surface with smaller pyramids, as shown in Figs. 1(c) and 1(d). It was also observed in our experiment processes that the surface showed a deep color after PS formation, and it showed a blue colored porous film when etched for 10 min and blue-violet colored porous film when etched for 20 min.

Figure 2 shows the values of the reflectance of textured surfaces before and after PS formation. Compared to the samples with PS layers, samples before PS formation exhibit very high reflectivity. The larger the size of the pyramids, the higher the reflectance. After the electrochemical processing, porous film was presented on the textured surface of the samples, which results in a dramatic decrease in the effective reflectance. It is noted that the reflective behaviors of the resulting surface depend on the initial surface morphologies. The initial surface with bigger pyramids reduces the reflectance drastically after PS formation in the short wavelength range, and the reflectance is reduced from 36.7% to 16.1% at 300 nm. In contrast, the initial surface with smaller pyramids results in a slight increase in reflectance of 300–330 nm. However, the reflectance of the latter structure decreases quickly with an increase in incident light wavelength, and a minimum reflectance

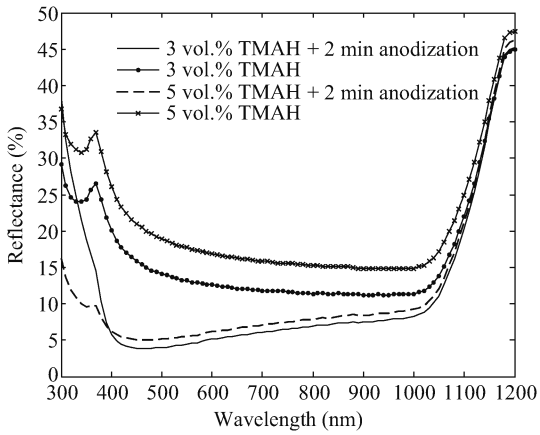

Fig. 2. Comparison reflectance of the TMAH textured surface with and without PS layers. The TMAH textured surface was achieved by etching in different TMAH solutions at 80 ℃ for 25 min.

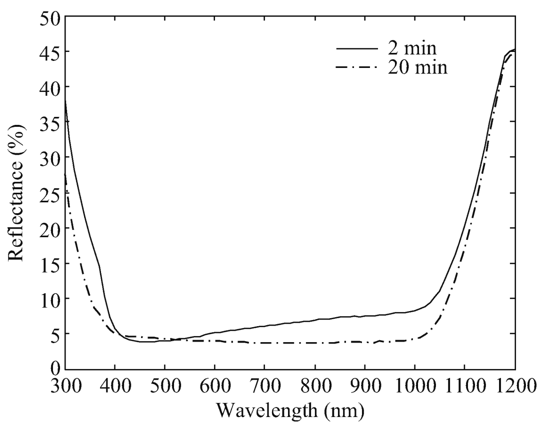

Fig. 3. Influence of anodizing time to the reflectance of the samples after etching in 3 vol.% TMAH solution at 80 ℃ for 25 min.

of 3.86% at 460 nm is achieved for an anodizing time of 2 min.

Figure 3 shows the influence of anodizing time on the reflectance of the surface. Compared to the sample etched for 20 min, the sample with a short anodizing time shows slightly lower values of reflectance in the wavelength range of 400–500 nm. Besides this wavelength range, it is observed that the reflectance is lower with a longer anodizing time for wavelengths in the range of 300–400 nm and 500–1200 nm. Also, for longer anodization, the reflectance spectrum is extremely flat, and the reflectance lies between 3.67% and 6.15% in the wavelength range from 400 to 1040 nm. The results are excellent compared with the reflectance of 4.7% and 7.7% in the same wavelength range for an optimized TiO_2 ARCs[23].

The experimental results can be explained by the character of the PS with a variable index. As mentioned above, the effective refractive index of PS is an intermediate value between air and silicon and can be variable by the change of porosity, thus, different PS morphologies result in different values of refractive index. Pore formation occurs at surface defects or irregularities, therefore, different surface structures may result in different PS morphologies leading to different refractive indices. It is assumed that PS formation on the surface with bigger pyramids achieved a refractive index that was more sensitive to the short wavelength and then led to the reduction of surface reflectance more effectively in this wavelength range. Furthermore, as shown in Figs. 1(c) and 1(d), sponge-like PS was formed on a textured surface with bigger pyramids, which also results in lower reflectance. In addition, the properties of PS also depend on anodization condition, such as current density and anodizing time. For long anodization and a constant applied voltage, it was observed in the experiment that the current changed slightly during the electrochemical processing, which results in graded various refractive index leading to lower reflectance in a whole wavelength range from 400 to 1000 nm.

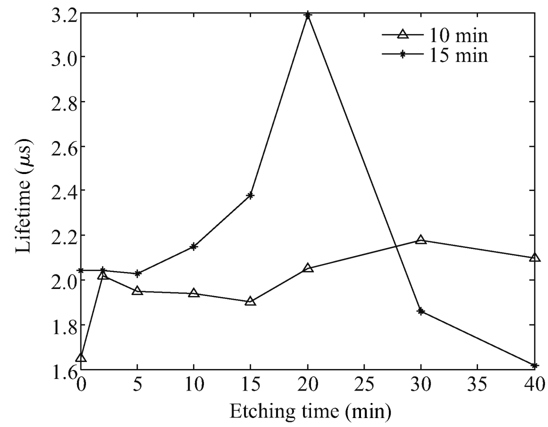

Fig. 4. Influence of anodizing time to effective minority-carrier lifetime of TMAH textured surface after etching in 5 vol.% TMAH solution at 70 ℃ for 10 to 15 min.

The antireflective action alone cannot explain the improvement in cell performance. A good texture must perform well in terms of both electrical and optical properties. In order to study the effects of PS formation on the electrical properties of the samples, the effective minority-carrier lifetime of the samples was measured by a microwave photoconductivity decay technique. Figure 4 shows the influence of anodizing time to effective minority-carrier lifetime of the sample after etching in 5 vol.% TMAH solution at 70 ℃ for 10 to15 min. The influence of anodizing time on the effective lifetime shows different results for different textured conditions. For a shorter texturing time (10 min in our case), the effective lifetime of the sample increases slightly after a short anodizing time and reaches a maximal value for an anodizing time of 30 min, then shows a slight decrease with increasing anodizing time. For a longer texturing time (15 min in our case), the effective lifetime of the sample maintains almost the same value for a shorter anodizing time. However, it increases quickly for an anodizing time larger than 10 min and reaches a maximal value for an anodizing time of 20 min and then decreases quickly with increasing anodizing time. A possible explanation for the observation is the reduction of the surface recombination rate by a large number of Si-hydrides as well as Si-hydroxides formed during PS growth, which would be good for passivation of the Si/PS interface. In addition, a shorter anodizing process can remove the damaged layer from the surface with a shorter texturing time. However, with the increase in anodizing time, the thickness of the porous layer becomes larger, thus it is very difficult to remove surfactant from inside the trenches, which may lead to a decrease in the minority-carrier lifetime.

4. Conclusions

In this paper, we compare the optical and electrical properties of the textured surface with and without PS formation. The results show that both the initial surface morphologies and the anodizing time affect the reflectance and effective lifetime of the resulting surface. The PS layers formation on the textured surface presents a significant decrease in the effective reflectance. Moreover, the reflectance decreases with increasing anodizing time. It is observed that even for a short anodizing time (2 min), a minimum reflectance of 3.86 % at 460 nm is achieved. Furthermore, the reflectance of less than 5 % can be maintained over a broad spectral range from 400 to 1020 nm for the sample etched in 3 vol.% TMAH solution for 25 min and then electrochemical etching for 20 min. Such excellent broadband antireflection is due to the refractive index gradient across the air and silicon. In addition, The PS formation does not significantly affect the minority-carrier lifetime. On the contrary, the minority-carrier lifetime shows a little increase for a short anodizing time. From the obtained results, we can conclude that PS can be used as both broadband antireflection coatings and passivation layers for the application of solar cells.

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