Texturization of mono-crystalline silicon solar cells in TMAH without the addition of surfactant*

Ou Weiying(欧伟英)[1,2,†], Zhang Yao(张瑶)[1], Li Hailing(李海玲)[1], Zhao Lei(赵雷)[1], Zhou Chunlan(周春兰)[1], Diao Hongwei(刁宏伟)[1], Liu Min(刘敏)[1], Lu Weiming(鲁伟明)[1], Zhang Jun(张俊)[1], and Wang Wenjing(王文静)[1]

(1 Laboratory of Solar Cell Technology, Institute of Electrical Engineering, Chinese Academy of Sciences, Beijing 100190, China)
(2 Department of Electronic Engineering, Guilin University of Electronic Technology, Guilin 541004, China)

Abstract: Etching was performed on (100) silicon wafers using silicon-dissolved tetramethylammonium hydroxide (TMAH) solutions without the addition of surfactant. Experiments were carried out in different TMAH concentrations at different temperatures for different etching times. The surface phenomena, etching rates, surface morphology and surface reflectance were analyzed. Experimental results show that the resulting surface covered with uniform pyramids can be realized with a small change in etching rates during the etching process. The etching mechanism is explained based on the experimental results and the theoretical considerations. It is suggested that all the components in the TMAH solutions play important roles in the etching process. Moreover, TMA^+ ions may increase the wettability of the textured surface. A good textured surface can be obtained in conditions where the absorption of OH^-/H_2O is in equilibrium with that of $TMA^+/SiO_2(OH)_2^{2-}$.

Key words: silicon solar cell; texturization; TMAH
DOI: 10.1088/1674-4926/31/10/106002 **PACC:** 4280Y

1. Introduction

Anisotropic etching of silicon to form random pyramids is an important technology for the fabrication of mono-crystalline solar cells[1−4]. Up to now, a mixture of potassium hydroxide (KOH) or sodium hydroxide (NaOH) and isopropyl alcohol (IPA) is the most common etchant for modern silicon photovoltaics[5]. The addition of IPA can improve the wettability of the silicon surface and remove hydrogen bubbles sticking on the silicon wafers, leading to uniformity of pyramids[6]. However, IPA is volatile in a heated etching bath because the boiling point of IPA is around 82 ℃. Therefore, IPA must be constantly added to the solution during the etching process, which results in difficult control and higher consumption of IPA.

In order to reduce or avoid the use of IPA, some researchers have used other etchants, such as potassium carbonate (K_2CO_3) solution, sodium carbonate (Na_2CO_3) solution and tribasic sodium phosphate ($Na_3PO_4{\cdot}12H_2O$) solution, to form random pyramids on the silicon surface[7,8]. Recently, Chu's group reported an approach for texturization on mono-crystalline silicon wafers using NaOH solution without the addition of surfactant. They placed a metal grid with suitable openings on silicon wafers to confine the hydrogen bubbles created during etching[9]. However, the abovementioned etchants all result in metal ion contamination. In recent years, tetramethylammonium hydroxide (TMAH) solution has been reported to be used for random pyramid texturization on the silicon surface due to its non-volatile, non-toxic and good anisotropic etching characteristics[10−12]. Most importantly, TMAH solution presents uncontaminated metal ions[13−15].

In this paper, a texturing process on silicon wafers with silicon-dissolved TMAH solutions without the addition of surfactant has been studied. Experiments were carried out in different TMAH concentration solutions at different temperatures for different etching times. Detailed analyses of the surface phenomena, etching rates, surface morphology and surface reflectance have been carried out. Theoretical analyses of the etching mechanism are described.

2. Experimental

P-type Czochralski silicon wafers with (100) orientation, 200 μm and 0.5–3 $\Omega{\cdot}$cm were used for the etching experiments. Silicon-dissolved TMAH solutions were realized by dissolving a certain amount of silicon in 10 wt.% TMAH solution. The solutions with different TMAH concentrations were prepared by diluting the silicon-dissolved TMAH solutions with deionized water (DIW). Experiments were carried out in a thermostatic bath. The main technical data of the thermostatic bath are: temperature fluctuation: $\leqslant \pm 0.05$ ℃, horizontal temperature uniformity: $\leqslant \pm 0.05$ ℃, vertical temperature uniformity: $\leqslant \pm 0.1$ ℃.

The solutions were held in a glass beaker, and a glass vessel was used to cover the beaker in order to reduce loss of the solutions by evaporation. Wafers were held in a quartz basket.

* Project supported by the National High Technology Research and Development Program of China (No. 2007AA05Z437).
† Corresponding author. Email: ouweiying@mail.iee.ac.cn
Received 12 January 2010, revised manuscript received 14 June 2010

Table 1. Experimental conditions and phenomena in the present study.

Bath No.	Quantity of wafer	TMAH/DIW concentration (vol. %)	Etching time (min)	Temperature (℃)	Surface phenomena
1	6	40/60	10-35	70	Few bubble spots
2	6	20/80	10–35	80	Large amount of bubble spots
3	6	30/70	10–35	80	Few bubble spots
4	6	40/60	10–35	80	No bubble spot
5	6	50/50	10–35	80	No bubble spot
6	6	60/40	10–35	80	No bubble spot

Firstly, the beaker was put in the thermostatic bath, and then the quartz basket was immersed into the beaker after the temperature of the thermostatic bath stabilized. Specially, an agitation of the basket for about 30 s was necessary in order to achieve a uniform wettability of the silicon surface. The experimental conditions are shown in Table 1.

Electronic balance was used to record the weight of the wafer. The average etched rates of the wafers were estimated by the formula $(m_{\text{before}} - m_{\text{later}})h_{\text{thickness}}/t_{\text{etching}}m_{\text{before}}$, where m_{before} is the weight of the wafer before etching, m_{later} is the weight of the wafer after etching, $h_{\text{thickness}}$ is the thickness of the wafer before etching, and t_{etching} is the etching time. The surface reflectance in the 350–1100 nm range was measured using a UV-VIS-NIR spectrophotometer and the surface morphological properties of the textured surface were analyzed using scanning electron microscopy (SEM).

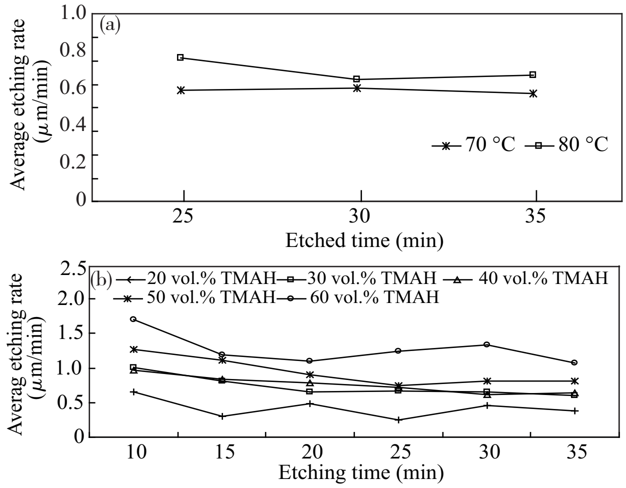


Fig. 1. Average etching rates versus etching time. (a) 40 vol.% TMAH at temperatures of 70 ℃ and 80 ℃. (b) Different TMAH concentrations at a temperature of 80 ℃.

3. Results and discussion

3.1. Surface phenomena

The textured surface is very important in the solar cell industries because a wafer with bubble spots on the surface is not of interest to the purchaser, even if it offers higher efficiency. It is observed that the textured surfaces show bubble spots both in lower TMAH concentration solutions and lower at temperature, as shown in Table 1.

3.2. Etching rate

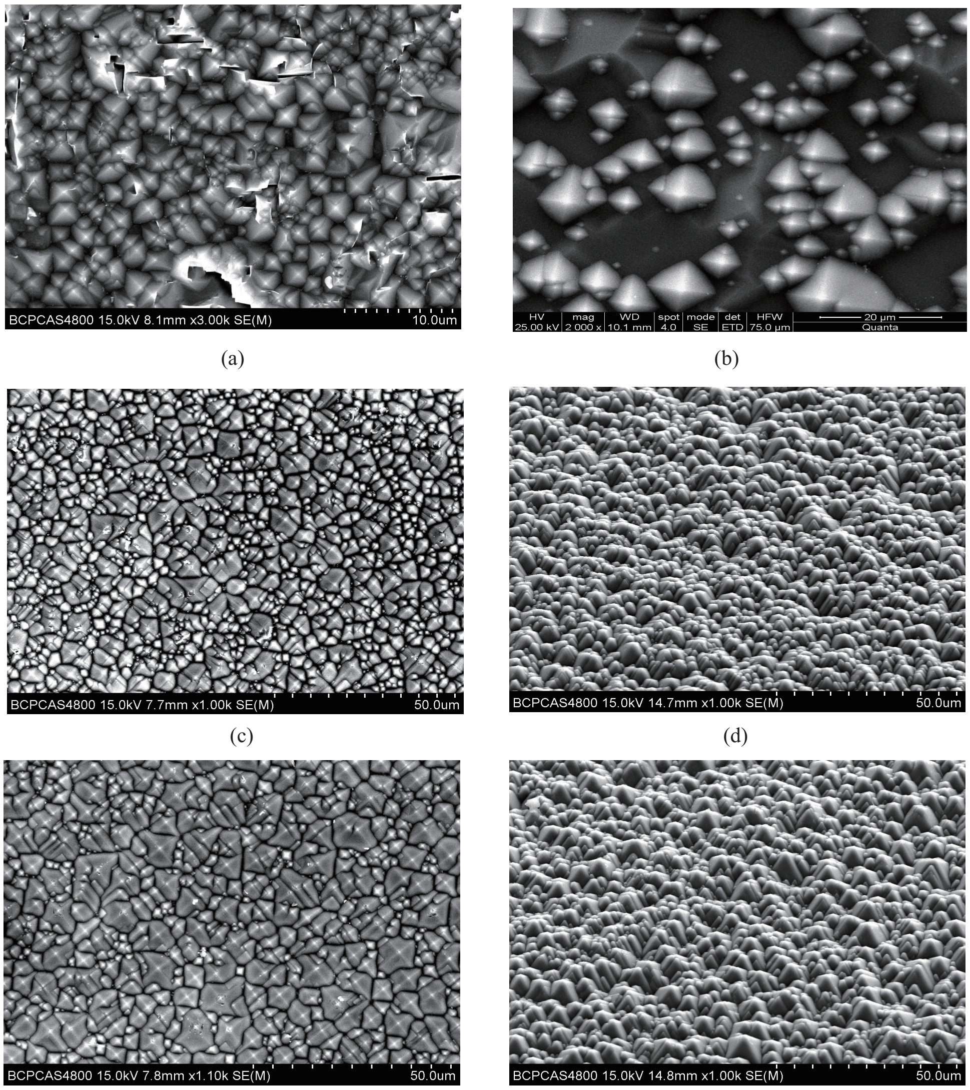
In order to study the stability of the etching process, the changes in the average etching rates with etching time were analyzed, as shown in Fig. 1. Figure 1(a) shows that the average etching rates increase as the etching temperature increases at the same TMAH concentration. Figure 1(b) shows that the average etching rates decrease with decreasing TMAH concentration or increasing etching time. The average etching rates decease slightly at first and then maintain a nearly constant value in medium TMAH concentrations (30 vol.% and 40 vol.% in our case). In comparison to the medium TMAH concentrations, the higher or lower TMAH concentrations result in complicated changes to the etching rates. It has been shown that the average etching rates decrease abruptly at first, then increase slowly and finally decrease slightly in 60 vol.% TMAH solution. The average etching rates fluctuate with time and the amplitude become smaller over longer etching times in 20 vol.% TMAH solution.

3.3. Surface morphology

Since the density, uniformity and size of pyramids are important parameters for the texturization of a silicon solar cell, the morphology of the resulting surface was analyzed using SEM. Figure 2 shows SEM pictures of the resulting surface morphology in different TMAH concentrations. It has been shown that the lower the TMAH concentration, the smaller the pyramids. A little higher or lower TMAH concentrations results in bad surface quality, as shown in Fig. 2 (a). It is observed that the textured surface still shows a damaged layer in 20 vol.% TMAH solution for 30 min. However, the textured surface with insufficient pyramids is found in 60 vol.% TMAH concentration. Compared to the lower or higher TMAH solutions, medium TMAH concentrations result in a good textured surface covered with pyramids. Figures 2(c) and 2(d) show that a textured surface with pyramids sizes around 2–5 μm can be realized in 30 vol.% TMAH. It can be noted that a textured surface with more uniform and slightly larger pyramid around 3–6 μm can be obtained in a slightly higher TMAH concentration (40 vol.% TMAH in our case). The experimental results suggest that a good textured surface with uniform pyramids can be realized with a small change in etching rates.

4. Surface reflectance

Surface reflectance is a key parameter for mono-crystalline solar cells. Figure 3 shows the reflectance of the resulting surfaces at different TMAH concentrations and etching times. Compared to the medium TMAH concentrations, the solutions with highest or lowest TMAH concentrations (60 vol.% or 20 vol.% in our cases), which result in higher reflectance, as shown in Fig. 3(a). The highest reflectance has been observed



(a) (b) (c) (d) (e) (f)

Fig. 2. SEM pictures of the resultingg surface morphology in different TMAH concentrations at a temperature of 80 ℃. (a) 20 vol.% TMAH for 30 min. (b) 60 vol.% TMAH for 15 min. (c), (d) 30 vol.% TMAH for 30 min. (e), (f) 40 vol.% TMAH for 30 min.

at the highest TMAH concentrations due to the lowest density of the pyramids. Figure 3(a) also shows that a slightly higher reflectance was observed in 20% TMAH due to the presence of a damaged layer in the resulting surface. The wafers show similar reflectance for etching times ranging from 15 to 30 min in 30 vol.% and 40 vol.% TMAH solutions. It is noted that the reflectance of the resulting surfaces in 30 vol.% TMAH solution is a little higher than that in 40 vol.% TMAH solution due to the pyramids with smaller sizes on the textured surfaces. A weighted reflectance value of smaller than 13% in the wavelength range from 350 to 1100 nm was successfully achieved with 40 vol.% TMAH solution. It turns out that ensuring a good surface quality results in lower reflectance.

4.1. Discussion

An etching process with a small change in etching rates produces a good textured surface and results in lower reflectance. A further study is required to explain these experimental phenomena. One possible reason is the effects of the etching products in the TMAH solutions. In the TMAH solution, both the OH^- ions and $(CH_3)_4N^+$ (TMA^+) ions appear after the dissociation of TMAH in solution:

$$(CH_3)_4NOH \rightarrow (CH_3)_4N^+ + OH^-. \tag{1}$$

The overall redox reaction is given by

$$Si + 2OH^- + 2H_2O \rightarrow SiO_2(OH)_2^{2-} + 2H_2. \tag{2}$$

The overall etching reaction of silicon in TMAH solution can be given as

$$\begin{aligned} Si + 2(CH_3)_4NOH + 2H_2O \rightarrow\ & 2(CH_3)_4N^+ \\ & + SiO_2(OH)_2^{2-} + 2H_2. \end{aligned} \tag{3}$$

Equation (3) shows that the components of the solutions include TMA^+, $SiO_2(OH)_2^{2-}$, OH^-, H_2O and H_2. The absorption of OH^-/H_2O can enhance the oxidation reaction.

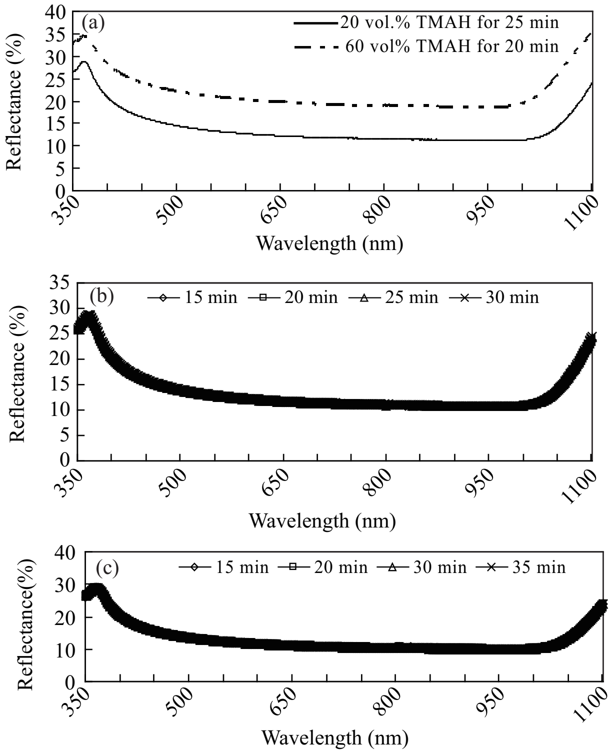


Fig. 3. Textured surface reflectance versus wavelength at 80° for different etching times. (a) 20 vol.% TMAH and 60 vol.% TMAH. (b) 30 vol.% TMAH. (c) 40 vol.% TMAH.

However, the absorption of $TMA^+/SiO_2(OH)_2^{2-}$ slows down the oxidation reaction due to the restriction of the access of OH^-/H_2O.

Reduction in temperature and TMAH concentration enhance the absorption of $TMA^+/SiO_2(OH)_2^{2-}$ and hydrogen bubbles on the etching surface, resulting in lower etching rates. In contrast, an increase in TMAH concentration enhances the access of OH^-/H_2O, leading to higher etching rates. In the initial stages of the experiment, the OH^-/H_2O components are prone to being adsorbed because their higher concentration, leads to higher etching rates at the beginning. However, with increasing etching time, the concentration of the OH^-/H_2O components decreases. Meanwhile, the concentration of $TMA^+/SiO_2(OH)_2^{2-}$ ions increases, leading to more $TMA^+/SiO_2\ (OH)_2^{2-}$ ions absorbed onto the silicon surface, and resulting in a decrease in etching rates. The etching rates maintain a nearly constant value on condition that the absorption of OH^-/H_2O is in equilibrium with that of $TMA^+/SiO_2(OH)_2^{2-}$. With a further decrease in OH^-/H_2O concentration, the etching rates decrease after longer etching times. The above explanations do not always work at both extremely high and low TMAH concentrations. The higher or lower TMAH concentrations result in complicated changes in the etching rates, as mentioned above. Such behavior suggests that TMA^+ ions may increase the wettability of the textured surface, which results in an increase in the etching rates because more water particles take part in the etching process. For extremely low concentrations, the effects of both OH^-/H_2O and TMA^+ ions create instability, resulting in the unstable changes of etching rates.

Adsorption of both the $TMA^+/SiO_2(OH)_2^{2-}$ ions and hydrogen bubbles on the etched surface can help in the formation of pyramids on the P-type ⟨100⟩ surface. At lower TMAH concentrations, it was shown that a large amount of hydrogen bubbles were attached to the etched surfaces, behaving as a mask and therefore restricting the oxidation reaction, leading to a bad textured surface with a damaged layer, even after 30 min etching. However, at higher TMAH concentrations, the rate of absorption of OH^-/H_2O exceeds that of $TMA^+/SiO_2(OH)_2^{2-}$, therefore it is difficult to form pyramids, resulting in insufficient pyramids. Compared to the higher and lower TMAH concentrations, a good textured surface can be realized in medium TMAH concentrations when the absorption of OH^-/H_2O is in equilibrium with that of $TMA^+/SiO_2(OH)_2^{2-}$.

5. Conclusion

In this study, etching experiments were performed on (100) silicon wafers using silicon-dissolved TMAH solutions without the addition of any other surfactant. Based on experimental results and theoretical explanations, it is suggested that the components of the TMAH solutions all play important roles in the etching process. Moreover, TMA^+ ions may increase the wettability of the textured surface and therefore lead to more water particles taking part in the etching process, resulting in an increase in the etching rate both in lower and higher TMAH concentrations. The etching rates maintain a nearly constant value on condition that the absorption of OH^-/H_2O is in equilibrium with that of $TMA^+/SiO_2(OH)_2^{2-}$, which also leads to a good textured surface. An optimized textured surface with uniform pyramids of around 3–6 μm and an average weighted reflectance of 12.8% are achieved in 40 vol.% TMAH concentration at 80 ℃ for 30 min.

References

[1] Wenham S R, Green M A. Silicon solar cell. Progress in photovoltaic research and application, 1996, 4: 3

[2] Green M A. High efficiency silicon cells. SPIE, 1999, 3894: 65

[3] Campbell P, Green M A. Light trapping properties of pyramidally textured surface. J Appl Phys, 1987, 62(2): 243

[4] Rodrfguez J M, Tobias I, Luque A. Random pyramidal texture modeling. Solar Energy Materials & Solar Cells, 1997, 45: 241

[5] Gangopadhyay U, Dhungel S K, Mondal A K, et al. Novel low-cost approach for removal of surface contamination before texturization of commercial monocrystalline silicon solar cells. Solar Energy Materials & Solar Cells, 2007, 91:1147

[6] Kwon S, Yi J, Yoon S, et al. Effects of textured morphology on the short circuit current of single crystalline silicon solar cells: evaluation of alkaline wet-texture processes. Current Appl Phys, 2009, 9: 1310

[7] Gangopadhyay U, Kim K, Dhungel S K, et al. Low-cost texturization of large-area crystalline silicon solar cells using hydrazine mono-hydrate for industrial use. Renewable Energy, 2006, 31: 1906

[8] Gangopadhyay U, Kim K, Kandol A, et al. Role of hydrazine monohydrate during texturization of large-area crystalline silicon solar cell fabrication. Solar Energy Materials & Solar Cells, 2006, 90: 3094

[9] Chu A K, Wang J S, Tsai Z Y, et al. A simple and cost-effective approach for fabricating pyramids on crystalline silicon wafers.

Solar Energy Materials & Solar Cells, 2009, 93: 1276
[10] You J S, Kim D, Huh J Y, et al. Experiments on anisotropic etching of Si in TMAH. Solar Energy Materials & Solar Cells, 2001, 66: 37
[11] Iencinella D, Centurioni E, Rizzoli R, et al. An optimized texturing process for silicon solar cell substrates using TMAH. Solar Energy Materials & Solar Cells, 2005, 87: 725
[12] Papet P, Nichiporuk O, Kaminski A, et al. Pyramidal texturing of silicon solar cell with TMAH chemical anisotropic etching . Solar Energy Materials & Solar Cells, 2006, 90: 2319
[13] Tabata O. pH-controlled TMAH etchants for silicon micromaching. Sensors and Actuators A, 1996, 53: 335
[14] Zubel I, Kramkowska M. The effect of isopropyl alcohol on etching rate and roughness of (100) Si surface etched in KOH and TMAH solutions. Sensors and Actuators A, 2001, 93: 138
[15] Sundaram K B, Vijayakumar A, Subramanian G. Smooth etching of silicon using TMAH and isopropyl alcohol for MEMS applications. Microelectron Eng, 2005, 77: 230