Microstructure evolution during monocrystalline silicon textured in K_3PO_4 and K_2SiO_3 solution

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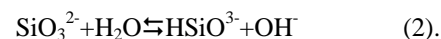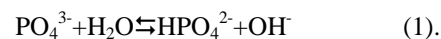Kunming, Yunnan, China
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Abstract—The pyramid construction was formed by different K_3PO_4 concentrations and texturing time. The pyramid microstructure evolution on monocrystalline silicon surface has been studied. We found that the pyramid is approximately 1.3μm in mean size and almost covered the silicon surface with 6wt% K_3PO_4 for 10min. The pyramid mean size is approximately 1.2 μm and uniform with 26wt% K_3PO_4 for 5min. Texturing time has a crucial influence on the pyramid size and K_3PO_4 concentration has a significant influence on the etching rate. With the K_3PO_4 concentration increasing, the pyramid size becomes smaller, and the etching rate reduces. Furthermore, the average reflectivity of silicon surface has also been studied. For the textured silicon surface, the average reflectivity obtained in the optimal etching conditions (6wt% K_3PO_4+ 2wt% K_2SiO_3, 85℃, and 20 min) is close to 11.6%. When texturing time is 5 min, the lowest average reflectivity is about 17.2% with different K_3PO_4 concentrations. This technique provides an alternative way for production high-efficiency silicon solar cells.

Keywords-microstructure; texturization; monocrystalline silicon; Size; reflectivity

I. INTRODUCTION

Texturization of (100)-oriented monocrystalline silicon surface commonly occurs as a result of silicon anisotropic etching in alkaline solutions containing isopropyl alcohol (IPA) as an additive [1-2]. Monocrystalline silicon surface can generate pyramid microstructures in mixture of IPA and alkaline solutions, such as NaOH、KOH [3-6]. The typical texturing temperature is 70~85℃, which is about the boiling point of IPA. For the foregoing reasons, it is difficult to maintain a stable texturing process and to obtain optimal pyramid microstructures [7]. Besides easily evaporates, further disadvantages are that it is a health hazard and an explosive substance [8]. To eliminate isopropyl alcohol, some other solutions be researched, like sodium carbonate (Na_2CO_3), sodium hydrogen carbonate ($NaHCO_3$), tribasic sodium phosphate (Na_3PO_4) 、 tripotassium phosphate (K_3PO_4) [9,10]. Some researchers have reported the texturization with tribasic sodium phosphate (Na_3PO_4) [11]. Na_3PO_4 plays the role of a surface active agent and makes texturization more effective without IPA [11]. We are reporting the use of tripotassium phosphate (K_3PO_4) and Potassium silicate (K_2SiO_3) solution for the texturization on silicon surface [12]. Tribasic tripotassium phosphate and Potassium silicate can hydrolyze in water. The equations are as follow：

$$PO_4^{3-}+H_2O \leftrightarrows HPO_4^{2-}+OH^- \tag{1.}$$

$$SiO_3^{2-}+H_2O \leftrightarrows HSiO_3^-+OH^- \tag{2.}$$

Therefore, in the K_3PO_4 solution, the OH^- is generated and help for forming small pyramids. PO_4^{-3} or its compounds help for forming big pyramids [12]. Moreover, the Na_3PO_4 plays the role of a surface active agent which can decrease the active energy of the texturing reaction and makes texturization of silicon surface more effective [13]. Better still, any additional damage removal step does not require with tripotassium phosphate in the process of texturization [10-15]. In this paper, texturization of monocrystalline silicon wafers with a mixture of potassium phosphate tribasic (K_3PO_4) and potassium silicate (K_2SiO_3) solutions was studied. Meanwhile, the change of pyramid size with etching time, and concentration of K_3PO_4 was also investigated.

II. Experimental Details

Monocrystalline silicon wafers of P-type. <100>oriented and size 1.5cm×1.5cm with resistivity 1-3Ω•cm were used as the etching experiments. Samples were cut from the adjacent wafers. Before etching, wafers were cleaned by the following procedures. The first step was to degrease the samples by cleaning the wafers in ethanol during four minutes of ultrasonic cleaning. The second step the native oxide was removed by immersion of the samples into diluted hydrofluoric acid (4 wt%), for 30 s. The cleaned wafers were took place in a specially designed of the sealing device inside the alkaline mixed solution. Then these samples were etching in different mass ratios of potassium phosphate tribasic (K_3PO_4) and potassium silicate (K_2SiO_3). The different reaction times and reaction temperatures could be controlled. After the etching process the samples were washed into absolute ethanol solution and de-ionized water again, they were dried oven for tests. The total hemispherical reflectance was measured by Shimadzu UV-2600 spectrophotometer (Shimadzu Inc., Japan) equipped with an integrating sphere. The surface morphology was studied with Zeiss EVO MA10 (Carl-Zeiss, Germany) scanning electron microscope (SEM).

III. Results and Discussion

A. Pyramid microstructure evolution under different texturing time

The different pyramid size and etching rate were accomplished by changing the texturing time. All of the pyramid size and etching rate are listed in Table Ⅰ. The morphological properties of the textured surfaces were analyzed using scanning electron microscopy （SEM） as shown in Fig.1. It can be stated that the increase in texturing time (from 10 min to 30min) resulted in the increase of the pyramids size (from 1.28 μm to 3.65 μm) and etching rate (from 87.5% to 93.8%).

TABLE I. DIFFERENT PYRAMID SIZE, ETCHING RATE AND UNIFORMITY OF PYRAMID AFTER TEXTURING (85 ℃，6WT% K_3PO_4 AND 2WT% K_2SiO_3)

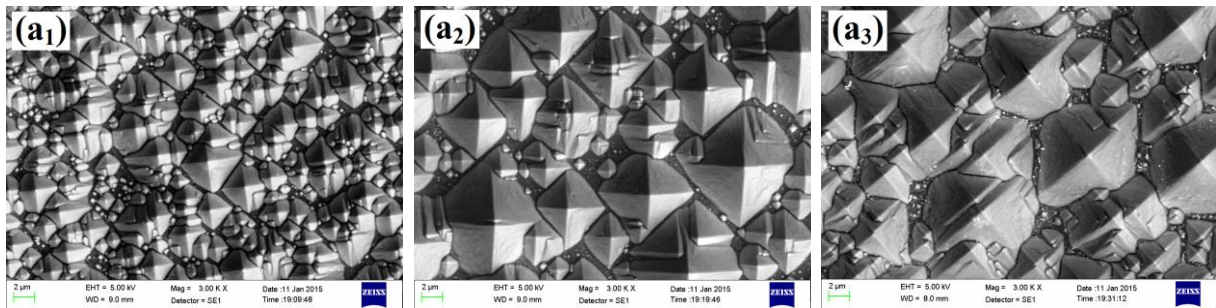| Time	Maximum size (μm)	Mean size (μm)	Etching rate (%)	Uniformity
10min	3.01	1.28	87.5	High
20min	8.59	2.82	90.0	Low
30min	9.19	3.65	93.8	Low

Figure 1. Scanning electron micrographs(SEM) of silicon surface textured 6wt% K_3PO_4 and 2wt% K_2SiO_3 solution with a variation on texturing time at 85℃:a₁=10 min；a₂=20 min；a₃=30 min.

Fig.1(a₁) exhibited the best pyramid pattern, size, etching rate and uniformity with 10 minutes texturing time. Longer etching such as at 30 minutes shows that some of the pyramids were etched off. Fig.1-2 shows that the texturing time and pyramid size have a significant influence on the coefficient of light reflection. Measurements of the average reflectivity were carried out in the spectral range from 350 nm to 900 nm. Fig.2 shows

the results of measurements of light reflection coefficients for the samples obtained in different texturing time. The average reflectivity values were 11.6~15.1% at different texturing time (from 10min to 30min), as can be seen in the Fig.2(b). It can be assumed that the etching time of 20 min can be regarded as optimal. Further increase in etching time will not bring any significant improvement in the reflection coefficient.
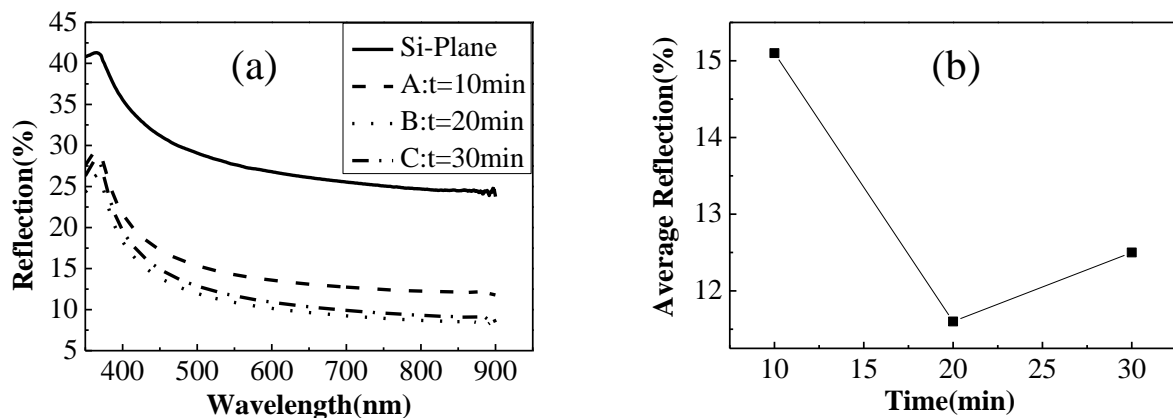

Figure 2. (a)Reflectivity spectra and (b)Average reflectivity of the silicon surface textured 6wt% K_3PO_4 and 2wt% K_2SiO_3 solution with a variation on texturing time at 85℃: A=10 min；B=20 min；C=30 min.

B. Pyramid microstructure evolution in different K_3PO_4 concentration solution

The different pyramid size and etching rate were accomplished by changing the K_3PO_4 concentration and texturing time. All of the pyramid size and etching rate are listed in Table Ⅱ. It can be assumed that the K_3PO_4 concentration (from 30wt% to 4wt%) has a significant influence on etching rate (from 45% to 80.5%) at 5min, but the pyramid size has a little change (from 1.21 μm to 1.68 μm). The optimum pyramid size (1.21 μm) can be noticed at the concentration of wt26% K_3PO_4, and the optimum etching rate (80.5%) at the concentration of wt4% K_3PO_4. With increase of K_3PO_4 concentration, the etching rate significantly reduces at 5min. Table 2 exhibited that the increase in K_3PO_4 concentration(from 26wt% to 34wt%) resulted in the decrease of the pyramid size (from

1.38 μm to 1.05 μm) with 3 minutes time. The texturization of silicon surface has been assessed on the basis of SEM images. SEM images of the textured surfaces are shown in Fig.3-4.

TABLE II. DIFFERENT PYRAMID SIZE, ETCHING RATE AND UNIFORMITY OF PYRAMID AFTER TEXTURING （2WT% K_2SIO_3 AND 85℃）

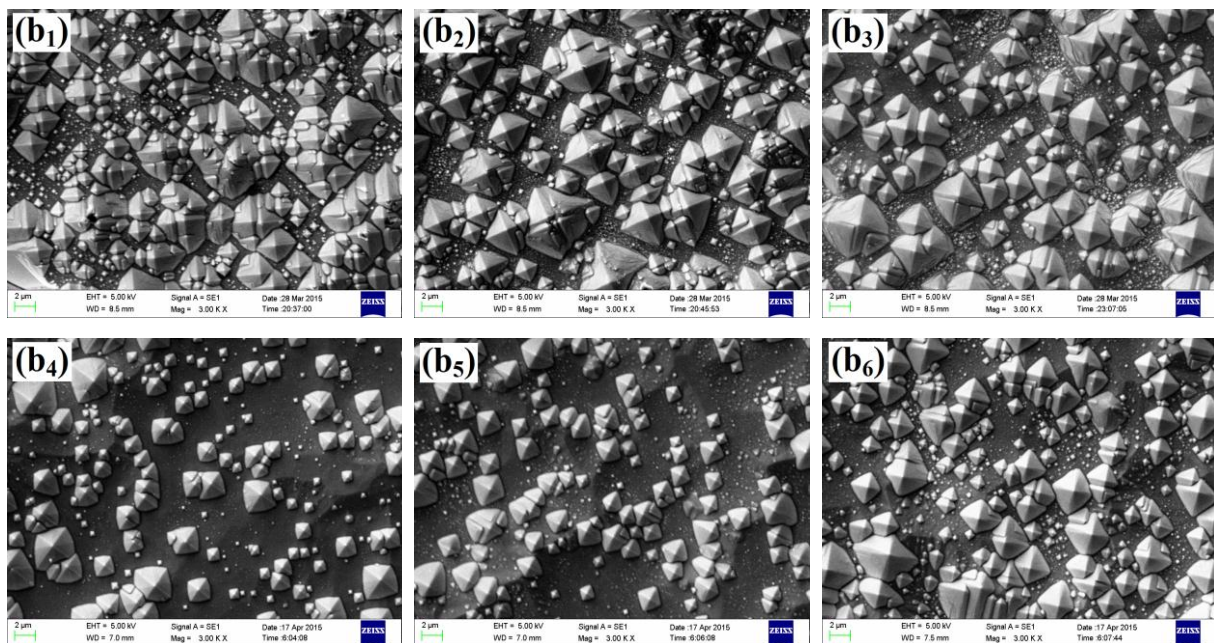| Concentration	Time (min)	Maximum size (μm)	Mean size (μm)	Etching rate (%)	Uniformity
4wt%	5	3.46	1.27	80.5	Regular
8wt%	5	4.81	1.68	80.2	Regular
22wt%	5	4.57	1.54	56.2	Regular
26wt%	5	3.90	1.21	46.5	High
30wt%	5	3.10	1.32	40.0	High
34wt%	5	3.96	1.31	55.7	Regular
26wt%	3	3.06	1.38	35.9	High
30wt%	3	3.52	1.29	28.6	Regular
34wt%	3	2.48	1.05	28.9	High

Figure 3. Scanning electron micrographs (SEM) of silicon surface textured 2wt% K_2SiO_3 and K_3PO_4 solution at 85℃ for 5min :b_1= 4wt% K_3PO_4; b_2= 8wt% K_3PO_4; b_3= 22wt% K_3PO_4; b_4= 26wt% K_3PO_4; b_5= 30wt% K_3PO_4 ;b_6= 34wt% K_3PO_4.
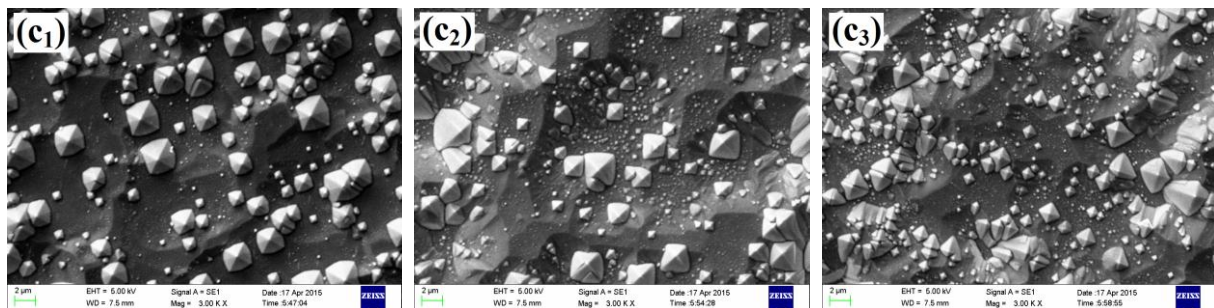

Figure 4. Scanning electron micrographs(SEM) of silicon surface textured 2wt% K_2SiO_3 and K_3PO_4 solution at 85℃ for 3min: c_1= 26wt% K_3PO_4; c_2= 30wt% K_3PO_4 and c_3= 34wt% K_3PO_4.

SEM image (Fig.3-4) shows that the pyramids are discontinuous, the etching rate is low. Some of the silicon surface is not covered by pyramid. This is mainly because the hydrogen bubbles created due to K_3PO_4–Si reaction stick on the silicon surface to impede the formation of

pyramid. During the texturization process it can be seen that some parts of silicon surface are covered by hydrogen bubbles for a long time. Compared to Fig.1, the etching rate reduces, and pyramid size became smaller. The pyramid size is between 0.5 and 3.0 μm with 26wt%

K3PO4. Fig.5 shows the SEM image of textured wafers at 45 ° incidence angle and the distribution of pyramid size when the samples were textured using 30wt% K_3PO_4 for 5 min. The pyramids are 0.5~3.5 μm in size. From to Fig.5(b), pyramids whose size about 0.5-1.5 μm are 70 percent. Fig. 6 shows the averaged reflectance of silicon surface textured in different concentrations of K_3PO_4 solutions. When the concentration of K_3PO_4 solution increases from 8 to 34wt% the averaged reflectance of silicon surface increases from 17 to 25%. The averaged reflectance is high because the etching rate is low.
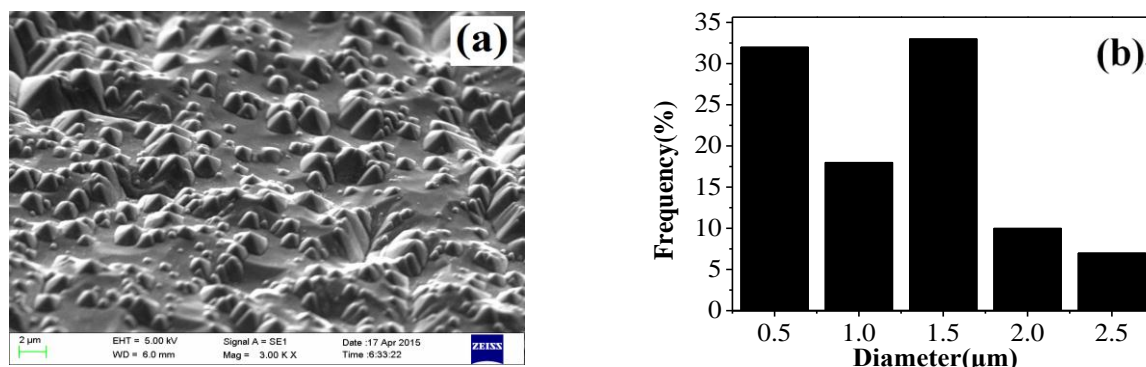

Figure 5.　　　　　(a)Scanning electron micrographs (SEM) of silicon surface and (b)distribution of pyramid size.

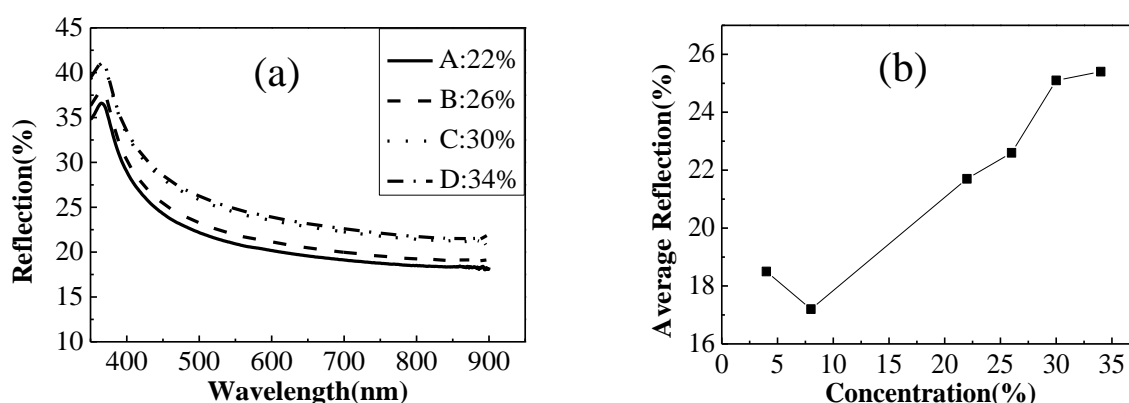Figure 6.　　　　　(a)Reflectivity spectra of silicon surface textured 2wt% K_2SiO_3 and K_3PO_4 solution at 85℃ for 5min: A=22wt% K_3PO_4; B=26wt% K_3PO_4; C= 30wt% K_3PO_4; D= 34wt% K_3PO_4. (b)Average reflectivity of concentration of K_3PO_4 varying from 4wt% to 34wt%.

IV. CONCLUSION

Texturization of monocrystalline silicon surface was formed by different K_3PO_4 concentrations and texturing time. The change of pyramid size with texturing time and K_3PO_4 concentration was investigated. Meanwhile, the etching rate and average reflectivity of silicon surface have also been studied. It is found that the pyramid mean size is approximately 1.3 μm and the etching rate is 87.5% with 6wt% K_3PO_4 for 10 min. The pyramid mean size is approximately 1.2 μm and the etching rate is 46.5% with 26wt% K_3PO_4 for 5min. Texturing time and K_3PO_4 concentration have a crucial influence on the pyramid size and etching rate. The pyramid size becomes bigger with extension of texturing time and the pyramid size becomes smaller with K_3PO_4 concentration increasing. For the textured silicon surface, the average reflectivity is close to 11.6% with 6wt% K_3PO_4 for 20 min. This technique provides an alternative way for the production silicon solar cells.

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