Texturization of Monocrystalline Silicon Wafers with K_3PO_4 /K_2sio_3 Solutions under Different Conditions

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***Abstract*—The pyramid construction was formed with different K_3PO_4 concentrations under different time and temperatures. The pyramid size, density and uniformity on monocrystalline silicon surface have been studied. We found that the K_3PO_4 concentrations and temperature has a crucial influence on pyramid density; the time has a significant influence on pyramid size. With the time increasing (from 5min to 30min), the size varies from 1.2 to 3.7μm. The density varies from 0% to 52.2%, with the temperature increasing (from 30℃ to 90℃). The pyramid size and density obtained in the optimal K_3PO_4 concentrations (30wt% K_3PO_4, 2wt K_2SiO_3, 85℃, and 5 min) are close to 1.3μm and 48.0%. The uniform pyramids are obtained in the optimal temperature (30wt% K_3PO_4, 2wt% K_2SiO_3, 90℃, and 5 min), its biggest size of pyramid is 3.1 μm and mean size is 1.1μm. 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%. This technique provides an alternative way for production high-efficiency silicon solar cells.**

Keywords-monocrystalline silicon; potassium phosphate tribasic; size; reflectivity

I. Introduction

Texturization of (1 0 0)-oriented monocrystalline silicon wafers to form pyramids on silicon surface is an important and effective way to reduce optical reflectivity for solar cells [1-2]. Texturization occurs as a result of silicon anisotropic etching in alkaline solutions, such as sodium hydroxide (NaOH) or potassium hydroxide (KOH) with low hydroxide concentrations [3-4]. Sodium hydroxide (NaOH) or potassium hydroxide (KOH) with isopropyl alcohol (IPA) is generally used in industry for the anisotropic etching of monocrystalline silicon [5]. The IPA performs an indispensable role as a moisturizing and surfactant agent [6]. However, the use of IPA has serious disadvantages because of its toxicity, relatively high cost and low boiling point [7-8]. To eliminate isopropyl alcohol, some researchers used other solutions, like sodium carbonate (Na_2CO_3), sodium hydrogen carbonate ($NaHCO_3$), potassium carbonate (K_2CO_3), potassium hydrogen carbonate ($KHCO_3$), tribasic sodium phosphate (Na_3PO_4), tripotassium phosphate (K_3PO_4) [9-11]. Some researchers have reported the texturization with tribasic sodium phosphate (Na_3PO_4) and found that the Na_3PO_4 plays the role of a surface active agent and makes texturization more effective without IPA [12-13]. We are reporting the use of tripotassium phosphate (K_3PO_4) and Potassium silicate (K_2SiO_3) solution for the texturization on silicon surface in different condition [14-15]. 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 K_3PO_4 and K_2SiO_3 solution, the OH^- is generated and help for forming small pyramids. PO_4^{-3} or its compounds help for forming big pyramids [16]. 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 [17-19]. 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. The change of pyramid size with K_3PO_4 concentration, etching time and temperatures has been investigated. Meanwhile, the change of pyramid density under different conditions also been studied. Finally, we studied the average reflectivity of silicon surface under different conditions.

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 Discussions

A. Pyramid construction *evolution with different K_3PO_4 concentration solutions*

The influence of K_3PO_4 concentration on Pyramid size, density and uniformity was evaluated by varying the K_3PO_4 concentration (from 4wt% to 35wt%). All of the pyramid size, density and uniformity are listed in Table I. The SEM images of the etched surfaces are shown in Figure 1. It can be stated that the increase in K_3PO_4 concentration (from 8% to 25%) resulted in the reduction of the pyramid size (from 1.7μm to 1.2μm) and density (from 80.2% to 46.5%). From to Table I, it can be assumed that the K_3PO_4 concentration (from 4wt% to 35wt%) has a significant influence on density (from 40% to 90.5%) at 5min, but the pyramid size has a little change (from 1.2μm to 1.7μm). The optimum pyramid size (1.2μm) can be noticed at the concentration of wt25% K_3PO_4, and the optimum pyramid density (90.5%) at the concentration of wt4% K_3PO_4.

TABLE I. Pyramid Size, Etching Rate and Uniformity with Different K_3PO_4 Concentration Solutions

Concentration	*Maximum Size (μm)*	*Mean Size (μm)*	*Density (%)*	*Uniformity*
4wt%	3.5	1.4	90.5	Regular
8wt%	4.8	1.7	80.2	Regular
20wt%	4.3	1.5	55.4	Regular
25wt%	3.9	1.2	46.5	High
30wt%	3.1	1.3	48.0	High
35wt%	4.0	1.3	55.7	Regular

Size, etching rate and uniformity of pyramid after texturing （2wt% K_2SiO_3 and different K_3PO_4 concentration at 85℃ for 5min）

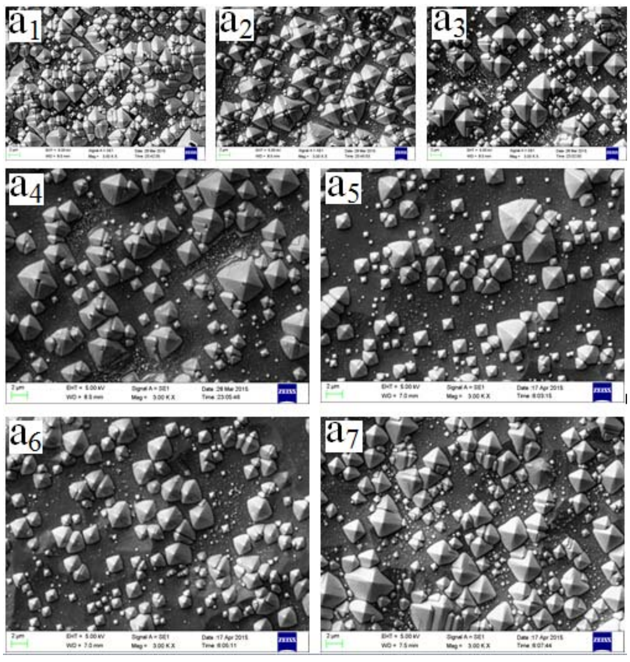

Figure 1. Scanning electron micrographs (SEM) of silicon surface textured 2wt% K_2SiO_3 and K_3PO_4 solution at 85℃ for 5min :a_1= 4wt% K_3PO_4; a_2= 8wt% K_3PO_4; a_3= 20wt% K_3PO_4; a_4= 22wt% K_3PO_4; a_5= 25wt% K_3PO_4; a_6= 30wt% K_3PO_4; a_7= 35wt% K_3PO_4.

The texturization of silicon surface has also been assessed on the basis of SEM images. SEM image (Figure 1) shows that some of the silicon surface is not covered by pyramid with high K_3PO_4 concentration. Figure 2 shows the averaged reflectance of silicon surface textured in different concentrations of K_3PO_4 solutions. Measurements of the average reflectivity were carried out in the spectral range from 350 nm to 900 nm. When the concentration of K_3PO_4 solution increases from 8 to 35wt% the averaged reflectance of silicon surface increases from 15.2 to 25.4%. The averaged reflectance is high because the density is low.

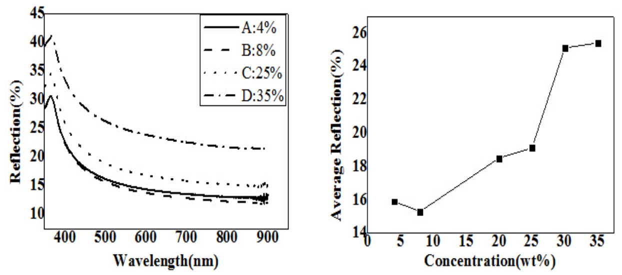

Figure 2. (a) Reflectivity spectra of silicon surface textured 2wt% K_2SiO_3 and K_3PO_4 solution at 85℃ for 5min: A=4wt% K_3PO_4; B=8wt% K_3PO_4; C= 25wt% K_3PO_4; D= 35wt% K_3PO_4. (b) Average reflectivity of concentration of K_3PO_4 varying from 4wt% to 34wt%.

B. Pyramid construction *evolution under different texturing time*

The influence of texturing time on Pyramid size, density and uniformity was studied by changing the time (from 5min to 30min). All of the pyramid size and density are listed in Table II. The morphological properties of the textured surfaces were analyzed using SEM as shown in Figure 3. It can be stated that the increase in texturing time (from 5 min to 30min) resulted in the increase of the pyramids size (from 1.2μm to 3.7μm) and density (from 80.2% to 93.8%). Figure 3 (b_2) exhibited the best pyramid size and uniformity with 10 minutes texturing time. Figure 3 shows that the texturing time has a significant influence on pyramid size. Figure 4 (a) shows the reflectance of silicon surface textured in different texturing-time. Figure 4 (b) shows that the average reflectivity values were 11.6~15.1% at different texturing time (from 5min to 30min), and the optimum average reflectivity (11.6%) can be obtain at etching time of 20 min.

TABLE II. Pyramid Size, Etching Rate and Uniformity Under Different Texturing Time

Time	*Maximum Size (μm)*	*Mean Size (μm)*	*Density (%)*	*Uniformity*
5min	2.9	1.2	80.2	High
10min	3.0	1.3	87.5	High
20min	8.6	2.8	90.0	Low
30min	9.2	3.7	93.8	Low

Size, etching rate and uniformity of pyramid after texturing （2wt% K_2SiO_3 and 6wt%K_3PO_4 for different time at 85℃）

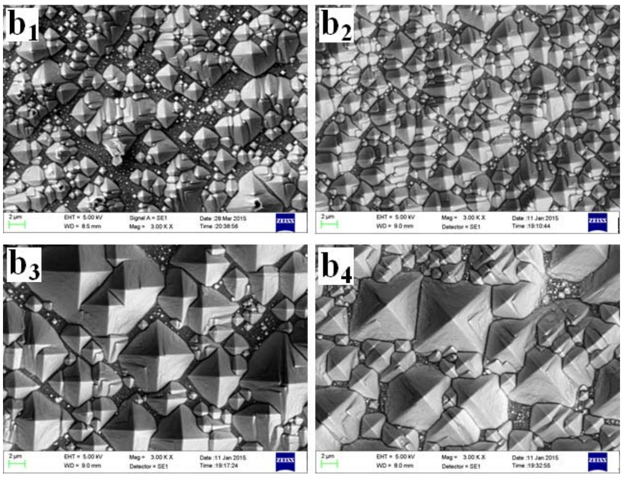

Figure 3. Scanning electron micrographs(SEM) of silicon surface textured 6wt% K_3PO_4 and 2wt% K_2SiO_3 solution with a variation on texturing time at 85℃: b_1=5min; b_2=10 min; b_3=20 min; b_4=30 min.

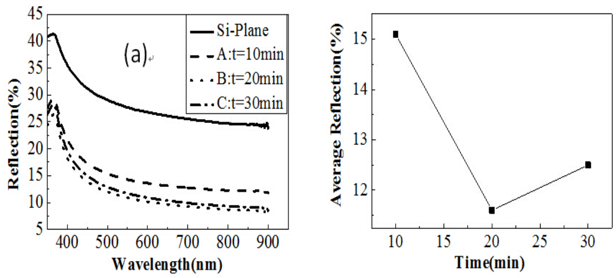

Figure 4. (a) Reflectivity spectra and (b) Average reflectivity of the silicon surface textured 6wt% K_3PO_4 and 2wt% K_2SiO_3 solution with a variation on texturing time at 85℃: A=10 min; B=20 min; C=30 min.

C. *Pyramid construction evolution at different texturing temperatures*

The influence of texturing temperatures on Pyramid size, density and uniformity was evaluated by varying temperatures (from 30℃ to 90℃). From to table III, we have observed that the temperature is very important parameters for texturization. It can be stated that the increase in temperature (from 50℃ to 75℃) resulted in the increase of the density (from 6.9% to 32.2%), but the density reduces (from 32.2% to 22.8%) with temperature increasing (from 75℃ to 90℃).

The scanning electron microscopy (SEM) image (Figure 5) shows that the pyramids are uniform, but the pyramids are discontinuous, the surface coverage is poor. Some of the silicon surface is not covered by pyramid. The size of pyramid varies from 0.9μm to 1.5μm with the temperature variation (from 30℃ to 90℃). It can be assumed that the temperature has a significant influence on density, but the pyramid size hardly varied. The optimum density (32.2%) can be noticed at 80℃， and the most uniform pyramid was formed at 90℃. Figure 6 shows the SEM image of textured wafers at 45° incidence angle and the distribution of pyramid size when the samples were textured at 75℃. The pyramids are uniform; the size of the biggest pyramid is 4.3μm and the mean size of the pyramid is 1.4μm (Figure 2.a). The pyramids are 0.5~4.3μm in size. From to Figure 5 (b), the pyramids whose size about 0.5-1.5μm are 68 percent.

TABLE III. PYRAMID SIZE, ETCHING RATE AND UNIFORMITY AT DIFFERENT TEXTURING TEMPERATURES

Temperature	*Maximum Size (μm)*	*Mean Size (μm)*	*Density (%)*	*Uniformity*
30℃	0	0	0	low
40℃	2.3	0.9	4.5	Regular
50℃	2.4	1.1	6.9	Regular
60℃	3.3	1.2	9.4	Regular
70℃	3.4	1.3	23.0	High
75℃	4.3	1.4	32.2	Regular
80℃	3.3	1.5	29.5	Regular
85℃	3.3	1.3	26.0	Regular
90℃	3.1	1.1	22.8	High

Size, density and uniformity of pyramid after texture with 30wt% K_3PO_4 and 2wt%K_2SiO_3 solution at different temperatures for 5min.

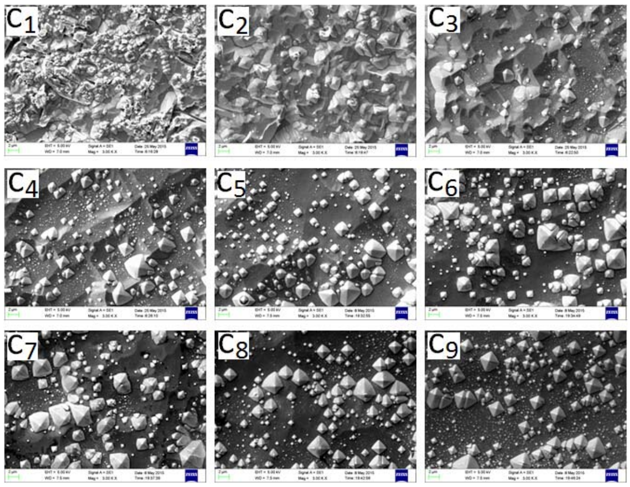

Figure 5. Scanning electron micrographs of silicon wafers textured with 30wt% K_3PO_4 and 2wt% K_2SiO_3 solutions at different temperatures (30℃-90℃) for 5min.c_1=30℃; c_2=40℃;c_3=50℃; c_4=60℃; c_5=70; c_6=75; c_7=80℃; c_8=85℃; c_9=90℃.

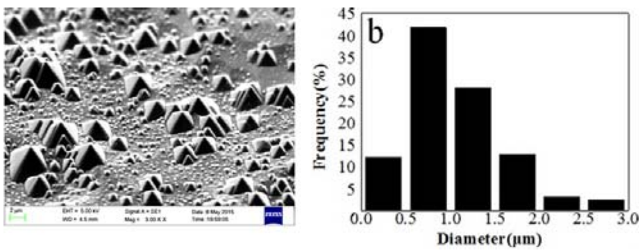

Figure 6. (a)Scanning electron micrographs (SEM) of silicon surface textured at 75℃ and (b) distribution of pyramid size.

IV. CONCLUSION

Texturization of monocrystalline silicon surface was formed by different K_3PO_4 concentrations at different time and temperatures. We have investigated the pyramid size, density and uniformity under different experimental conditions. Meanwhile, the average reflectivity of silicon surface under different conditions has also been studied. We observed that the concentration of Na_3PO_4, texturing time and temperature are very important parameters for texturization. It is found that the Na_3PO_4 concentration and temperature has a crucial influence on density; the time has a significant influence on pyramid size. With the time increasing (from 5min to 30min℃), the size varies from 1.2 to 3.7μm. The density varies from 0% to 52.2%, with the temperature increasing (from 30℃ to 90℃). The pyramid size and density obtained in the optimal K_3PO_4 concentrations (30wt% K_3PO_4, 2wt% K_2SiO_3, 85℃, and 5 min) are close to 1.3μm and 48.0%.The uniform pyramids are obtained in the optimal temperature (30wt% K_3PO_4, 2wt% K_2SiO_3, 90℃, and 5 min), its biggest size of pyramid is 3.1μm， mean size is 1.1μm. 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%. This technique provides an alternative way for production high-efficiency silicon solar cells.

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