Texturization of Monocrystalline Silicon Wafers with K_3PO_4 and K_2SiO_3 Solutions

Rui-Zhi Luo [1, a], Jun-Jun Ma [2,b], Shi-Qing Man [3,c]*, Zheng Jin[4,d],
Ya-Qin Wang [5,e], Qiao-Yun Ye [6,f],Jin -Bao Chen [7,g]

School of Physics and Electronic Information, Yunnan normal university, Kunming, Yunnan, China

[a]email: 1401820876@qq.com, [b]email: 2754127618@qq.com, [c]email: man_shiqing@yahoo.com,
[d]emai: jinzheng620713@sina.com, [e]email: yaqin_w@yeah.net, [f]email: 253438784@qq.com,

[g]email: 1441743141@qq.com

Keywords: monocrystalline silicon; potassium phosphate tribasic; potassium silicate; size; density.

Abstract. The pyramid construction was formed with different K_3PO_4 and K_2SiO_3 concentrations under different temperatures. The pyramid size, density and uniformity on monocrystalline silicon surface have been studied. We found that the temperature has a crucial influence on pyramid density; the K_2SiO_3 concentration has a significant influence on pyramid size and density. With the temperature increasing (from 50°C to 90°C), the density varies from 6.91% to 29.45%. The increase in K_2SiO_3 concentration (from 1wt% to 7wt%) resulted in the reductions of the pyramid size (from 2.37 μm to 1.07 μm) and density (from 88.9 % to 10.5%). The increase in K_3PO_4 concentration (from 26% to 62%) resulted in the reductions of the pyramid size (from 2.48 μm to 1.13 μm) and density (from 77.7 % to 43.9%). the pyramid size and density obtained in the optimal etching conditions (62wt% K_3PO_4, 85°C, and 5 min) are close to 1.13μm and 52.0%. The uniform pyramids are obtained in the conditions (30wt% K3PO4, 2wt% K_2SiO_3, 90°C, and 5 min), its biggest size of pyramid is 3.12 μm and mean size is 1.00 μm. This technique may be probably used in the texturization process for high-efficiency silicon solar cells.

1. Introduction

Anisotropic texturization of monocrystalline has been known for years. The anisotropic etching behavior of monocrystalline silicon used in alkaline solution of sodium hydroxide (NaOH), potassium hydroxide (KOH) or lithium hydroxide (LiOH), isopropyl alcohol (IPA) and deionized water (DIW) was studied [1-2]. In this type of solution IPA performs an indispensable role as a moisturizing and surfactant agent [3]. However, the use of IPA entails serious disadvantages derived from its toxicity and relatively high cost [4]. Moreover, the low boiling point of IPA limits the process temperature, and etching rates also diminish as process temperature is lowered, so longer times are required to complete the surface texturization [5]. As a result of these disadvantages, 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) [6-7]. 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 [8]. 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 [9]. Tribasic tripotassium phosphate and Potassium silicate can hydrolyze in water. The equations are as follow：

$$PO_4^{3-}+H_2O\Delta HPO_4^{2-}+OH^- \quad (1).$$

$$SiO_3^{2-}+H_2O\Delta HSiO^{3-}+OH^- \quad (2).$$

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 [10]. 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 [11]. 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 temperatures, concentration of K_3PO_4 and K_2SiO_3 was also investigated. Finally, we studied the change of pyramid density under different conditions.

2. 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 (4wt%), 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 surface morphology was studied with Zeiss EVO MA10 (Carl-Zeiss, Germany) scanning electron microscope (SEM)

3. Results and discussions

3.1. Influence of temperatures in 30wt% K_3PO_4 and 2wt% K_2SiO_3 solutions for 5 min

Different size pyramid formed by potassium phosphate tribasic (K_3PO_4) and potassium silicate (K_2SiO_3) solution at different concentration, temperature, respectively, was investigated. We have also investigated the density of pyramid on silicon wafers under different experimental conditions. We have observed that the temperature as well as the concentration of solution (Na_3PO_4 and K_2SiO_3) are very important parameters for texturization. Firstly, the influence of texturing temperatures was studied. The different size and density of pyramid were accomplished by changing the texturing temperatures（from 50°C to 90°C）. All of the pyramidsize, density and uniformity are listed in Table 1. 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 temperature (from 50°C to 80°C) resulted in the increase of the density (from 6.91% to 29.45%), but the density reduces (from 29.45% to 22.81%) with temperature increasing (from 80°C to 90°C). The scanning electron microscopy (SEM) image (Fig.1) shows that the pyramids are uniform, but they are discontinuous, the surface coverage is poor. Some of the silicon surface is not covered by pyramid. The size of pyramid varies from 0.95 μm to 1.08 μm with the temperature variation (from 50°C to 90°C).

Table 1. Size, density and uniformity of pyramid after textured with 30wt% K_3PO_4 and 2wt%K_2SiO_3 solution at different temperatures for 5min.

Temperature	Maximum Size(μm)	Mean Size(μm)	Density(%)	Uniformity
50°C	2.42	1.06	6.91	Regular
60°C	2.33	0.95	9.44	Regular
70°C	3.40	0.96	23.00	High
80°C	4.27	1.08	29.45	Regular
85°C	3.27	1.06	26.00	Regular
90°C	3.12	1.00	22.81	High

It can be assumed that the temperature has a significant influence on density, but the pyramid size hardly varied. The optimum density (29.45%) can be noticed at 80°C， and the most uniform pyramid was formed at 90°C. Fig.2 shows the SEM image of textured wafers at 45° incidence angle and the distribution of pyramid size when the samples were textured at 90°C. The pyramids are uniform; the size of the biggest pyramid is 3.12 μm and the mean size of the pyramid is 1.00 μm (Fig.2.a).The pyramids are 0.5~3.12 μm in size. From to Fig.5 (b), the pyramids whose size about 0.5-1.5 μm are 72 percent.

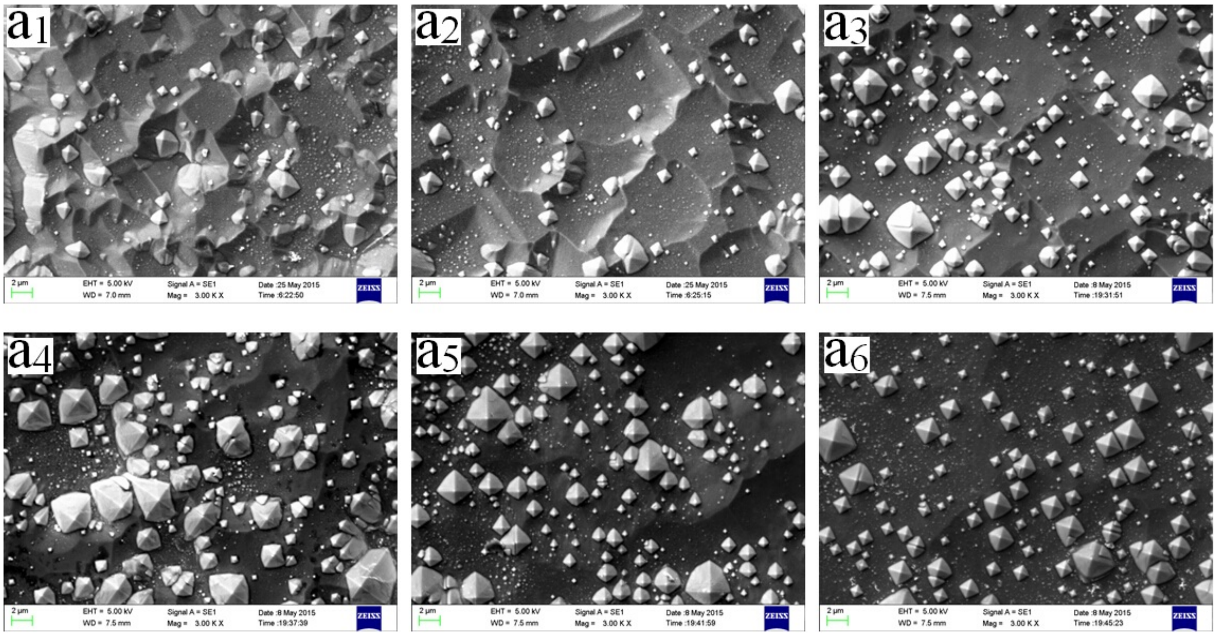

Fig.1. Scanning electron micrographs of silicon wafers textured with 30wt% K_3PO_4 and 2wt% K_2SiO_3 solutions at different temperatures (50°C~90°C) for 5min. a_1=50°C; a_2=60°C; a_3=70°C; a_4=80°C; a_5=85°C; a_6=90°C.

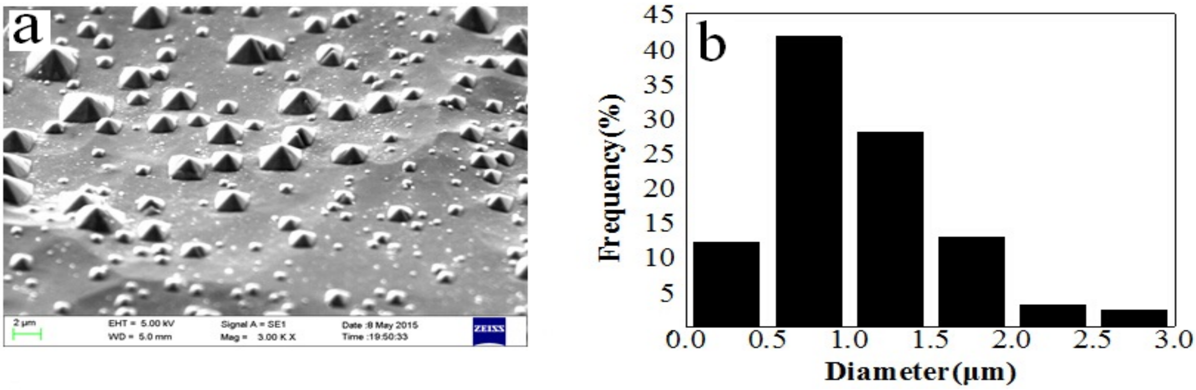

Fig.2. (a)Scanning electron micrographs (SEM) of silicon surface textured at 90°C and (b) distribution of pyramid size.

3.2. Influence of K_2SiO_3 concentration in 30wt% K_3PO_4 solutions for 5 min at75°C

A set of different K_3PO_4/K_2SiO_3 aqueous solutions was prepared, in which K_3PO_4 concentration was kept at 30wt%, while K_2SiO_3 concentration was varied between 1wt% and 7wt%. The influence of K_2SiO_3 concentration was evaluated. From Table 2, it is noticed that there is remarkably different pyramid size and density with different concentration K_2SiO_3. It indicates that the concentration of K_2SiO_3 may has a significant influence on size and density of pyramid (Table 2). The different size and density of pyramid were accomplished by changing K_2SiO_3 concentration. The morphological properties of the textured surfaces were analyzed using scanning electron microscopy （SEM）, as shown in Fig.3. It can be stated that the increase in K_2SiO_3 concentration (from 0wt% to 7wt%) resulted in the reduction of the pyramid size (from 2.37 μm to 1.07 μm) and density (from 88.89% to 10.50%). Moreover, the scanning electron microscopy (SEM) image (Fig.2) shows that the pyramids are no uniformity. When the K_2SiO_3 concentration is 1wt%, most of the silicon surface is covered by pyramid, and when the K_2SiO_3 concentration is 7wt%, most of the silicon surface is not covered by pyramid. Therefore the K_2SiO_3 concentration has a significant influence on the density of pyramid. Fig.4 shows the SEM image of textured wafers at 45° incidence angle and the distribution of pyramid size when the samples were textured with 2wt% K_2SiO_3. The pyramids are uniform; the size of the biggest pyramid is 4.31 μm and the mean size of the pyramid is 1.38 μm. In addition, the density of pyramid is 52.24%. The pyramids are 0.5~4.31 μm in size. From to Fig.5(b), pyramids whose size about 0.5-1.5 μm are 75 percent.

Table 2. Size, density and uniformity of pyramid after texturing (30wt% K_3PO_4, 75°C, 5min).

Concentration	**Maximum Size(μm)**	**Mean Size(μm)**	**Density(%)**	**Uniformity**
0wt%	7.68	2.22	74.23	Low
1wt%	6.46	2.37	88.89	Low
2wt%	4.31	1.38	52.24	Regular
3wt%	4.22	1.25	43.27	Regular
4wt%	4.00	1.50	41.73	Regular
7wt%	3.16	1.07	10.50	Regular

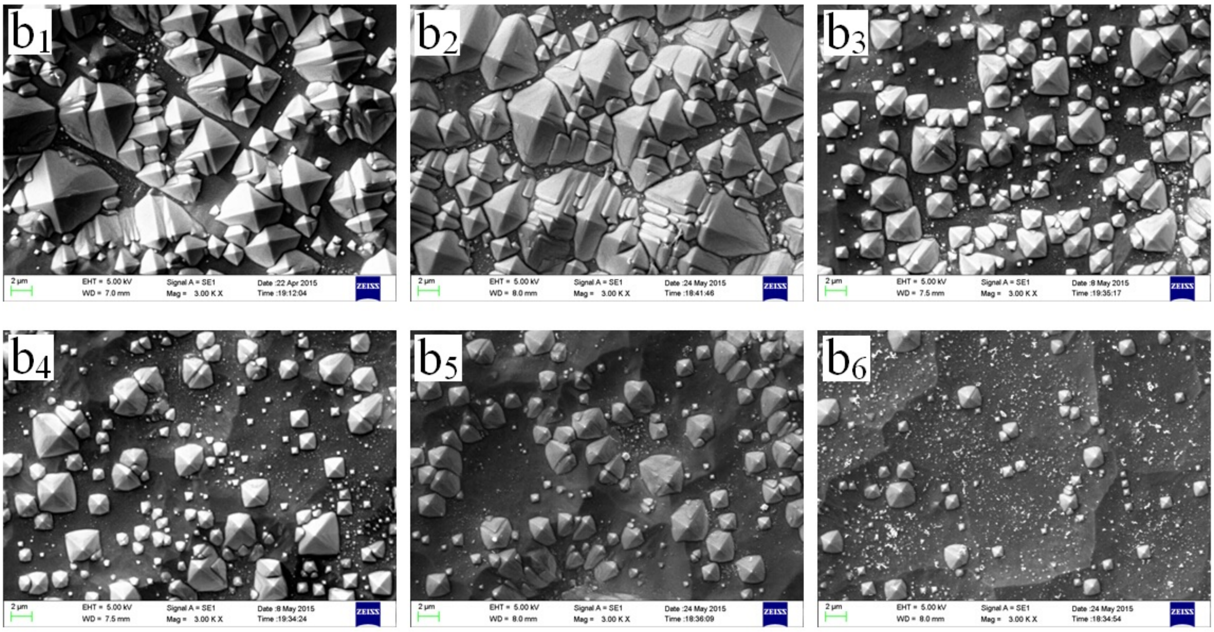

Fig.3.Scanning electron micrographs (SEM) of silicon wafers textured 30wt% K_3PO_4 and K_2SiO_3 solution at 75°C for 5min. b_1=0wt% K_2SiO_3; b_2=1wt% K_2SiO_3; b_3=2wt% K_2SiO_3; b_4=3wt% K_2SiO_3; b_5= 4wt% K_2SiO_3; b_6= 7% K_2SiO_3.

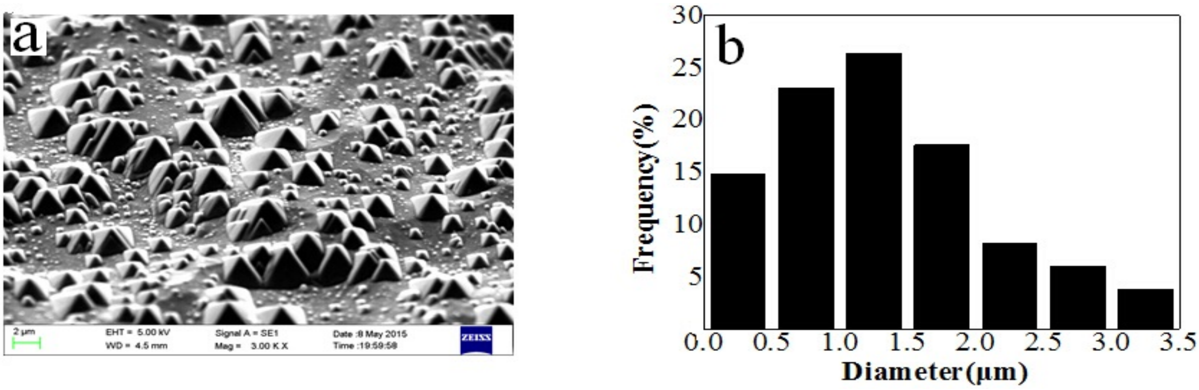

Fig.4. (a)Scanning electron micrographs (SEM) of silicon surface textured with 2wt% K_2SiO_3 and (b) distribution of pyramid size.

3.3 Influence of K_3PO_4 concentration for 5min at 85°C

The influence of K_3PO_4 concentration was evaluated by varying the concentration between 26wt% and 70wt%. The degree of surface texturization has been assessed on the basis of Table 3. SEM images of the etched surfaces are shown in Fig.5. The different size and density of pyramid were accomplished by changing the K_3PO_4 concentration. All of the pyramid size, density and uniformity are listed in Table 3. It can be stated that the increase in K_3PO_4 concentration (from 26% to 62%) resulted in the reduction of the pyramid size (from 2.48 μm to 1.13 μm) , but the pyramid size increases (from 1.13 μm to 1.50 μm) with K_3PO_4 concentration increasing (from 62% to 70%).

Table 3. Size, density and uniformity of pyramid after textured with different K_3PO_4 concentrations at 85°C for 5min.

Concentration	Maximum Size(μm)	Mean Size(μm)	Density(%)	Uniformity
26wt%	7.46	2.48	77.66	Regular
34wt%	4.30	1.72	46.64	Regular
42wt%	4.72	1.55	59.95	Regular
50wt%	3.91	1.43	50.00	High
54wt%	3.09	1.29	54.79	High
58wt%	4.47	1.39	64.60	High
62wt%	3.14	1.13	52.01	High
66wt%	3.26	1.32	48.23	Low
70wt%	3.66	1.50	43.89	Low

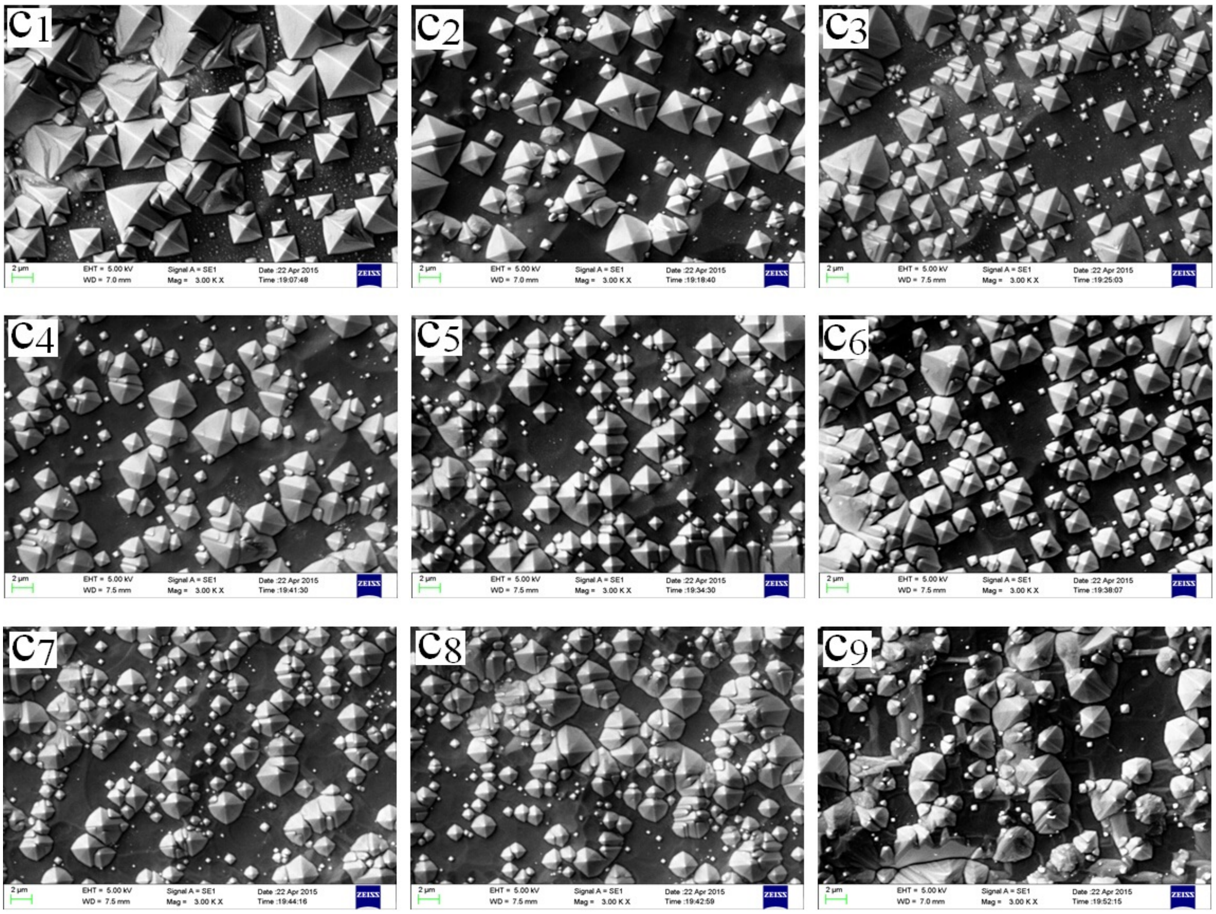

Fig.5.Scanning electron micrographs (SEM) of silicon wafers textured with different K_3PO_4 concentrations at 85°Cfor 5min. c_1=26wt% K_3PO_4; c_2=34wt% K_3PO_4; c_3= 42wt% K_3PO_4; c_4=50wt% K_3PO_4; c_5=54 wt% K_3PO_4; c_6= 58wt% K_3PO_4; c_7= 62wt% K_3PO_4; c_8= 66wt% K3PO4; c_9= 70wt% K_3PO_4.

The pyramids are uniform; density varies from 77.66% to 43.89% with the K_3PO_4 concentration variation. The optimum pyramid size (1.13μm) can be noticed at 62% K_3PO_4. Fig.5 shows the SEM image of textured wafers with 62wt% K_3PO_4 for 5 min. The pyramids are uniform; the size of the biggest pyramid is 3.14 μm and the mean size of the pyramid is 1.13 μm. In addition, the density of pyramid is 52.01%, and the pyramids are 0.5~3.12 μm in size. From to Fig.5(c_7), pyramids whose size about 0.5-1.0 μm are 40 percent.

4. Summary

Texturization of monocrystalline silicon surface was formed by different K_3PO_4 and K_2SiO_3 concentrations at different temperatures. We have investigated the size and density of pyramid under different experimental conditions. Meanwhile, the uniformity of pyramid has also been studied. We observed that the temperature as well as the concentration of solution (Na_3PO_4 and K_2SiO_3) are very important parameters for texturization. It is found that the temperature has a crucial influence on density; the K_2SiO_3 concentration has a significant influence on pyramid size and density. With the temperature increasing (from 50°C to 90°C), the density varies from 6.91% to 29.45%. The increase in K_2SiO_3 concentration (from 1wt% to 7wt%) resulted in the reduction of the pyramid size (from 2.37 μm to 1.07 μm) and density (from 88.9 % to 10.5%). The increase in K_3PO_4 concentration (from 26% to 62%) resulted in the reduction of the pyramid size and density. the pyramid size and density obtained in the optimal etching conditions (62wt% K_3PO_4, 85°C, and 5 min) is close to 1.13μm and 52.0%. The uniform pyramids are obtained in the conditions (30wt% K_3PO_4, 2wt% K_2SiO_3, 90°C, and 5 min). This technique may be probably used in the texturization process for high-efficiency silicon solar cells. This technique provides an alternative way for the production silicon solar cells.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (NSFC) (Grant No.21171072 and Grant No.21361028)

References

[1]. H.Hao.Li, W.F.Liu and A.Liu, J.Solar Energy Materials & Solar Cells 94 (2010) 942–945.
[2]. H.Seidel, L.Csepregi and A.Heuberger, J.Electrochemical Society 137 (11)(1990)3612–3626.
[3]. M. Stefancich, M. Butturi and M. Vincenzi, J.Solar Energy Materials and Solar Cells 69 (2001) 371–379.
[4]. R. Barrio , N.Gonza′lez and J.Ca′rabe, J.J.Gand, J. Materials Science in Semiconductor Processing 16 (2013) 1–9
[5]. X. Zhenquiang, D. Yang and D. Que, J.Solar Energy Materials and Solar Cells 77 (2003) 255–363.
[6]. Z. Xi, D. Yang and W. Dan, J.Renewable Energy 29 (2004) 2101–2107.
[7]. N. Marrero, B. Gonza′lez-Dı′az and R. Guerrero-Lemus, J.Solar Energy Materials and Solar Cells 91 (2007) 1943–1947.
[8]. J.F.Xiao, L.Wang,and X.Q Li, J. Applied Surface Science 257 (2010) 472–475
[9]. D. Iencinella, E. Centurioni and R. Rizzoli, J.Solar Energy Materials and Solar Cells 87 (2005) 725–732.
[10]. P. Papet, O. Nichiporuk and A. Kaminski, J.Solar Energy Materials and Solar Cells 90 (2006) 2319–2328.
[11]. U. Gangopadhyay, K. Kim and S.K. Dhungel, P.K. Basu, J. Yi, Renewable Energy 31 (2006) 1906–1915.