Texturization of Monocrystalline Silicon Wafers with K_2CO_3/K_2SiO_3 Solutions

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Keywords: Monocrystalline silicon; Potassium carbonate; Size; Density.

Abstract. The texturization of monocrystalline silicon wafers using different K_2CO_3 concentrations under different times and temperatures solution has been investigated. In this paper, the pyramid density, size and uniformity on the wafer surface were discussed in different variables. We found that texturing time and temperature have crucial influences on the pyramid density; And the K_2CO_3 concentrations and texturing time have crucial influences on the pyramid size. With the increase in temperature (from 50 ℃ to 90 ℃) resulted in the increase of the size varies from 2.32 to 1.78μm, and the density from 25% to 100 %.With the concentration increasing (from 15wt% to 30wt%), the size varies from 4.63 to 2.49μm, and the density from 95.5% to 86.5 %.With the time increasing (from 5min to 60min), the size varies from 2.18 to 2.92μm, and the density from 44.18% to 100 %. The monocrystalline silicon wafers with micro-structure pyramids can be used for surface-enhanced Raman scattering active substrate in the future research.

1. Introduction

Anisotropic etching of monocrystalline silicon has been known for years and it is a preparation process of silicon devices [1]. By anisotropic etching, monocrystalline silicon wafers surface can form a random distribution of pyramids [2]. Pyramid structure forming a number of internal light trap increase the photo-absorption efficiency, so as to effectively reduce the surface reflectance. The anisotropic etching behavior of monocrystalline silicon using alkaline solution and isopropyl alcohol (IPA), Such as sodium hydroxide (NaOH), potassium hydroxide (KOH) or lithium hydroxide (LiOH), has been studied[3-5]. However, the long-term inhalation of isopropyl alcohol (IPA) is harmful to human. To eliminate isopropyl alcohol, some researchers used other solutions, like sodium carbonate (Na_2CO_3), sodium hydrogen carbonate ($NaHCO_3$), potassium hydrogen carbonate ($KHCO_3$), tribasic sodium phosphate (Na_3PO_4), tripotassium phosphate (K_3PO_4) [6-8]. Although the most common etchants are aqueous solutions of sodium hydroxides or potassium hydroxides with addition of isopropyl alcohol, other groups of researcher reported the texturization with carbonates [9-13]. The advantage of alkali corrosion method is convenient, low cost, but the traditional alkaline corrosion solution is environmentally harmful [14-15]. The texturization of monocrystalline silicon wafer in etching liquid is influenced by many factors [16-17]. In this paper, texturization of monocrystalline silicon wafers with a mixture of potassium carbonate (K_2CO_3) and potassium silicate (K2SiO3) solutions was studied. The change of pyramid size with etching time, temperatures and concentration of K_2CO_3 has been investigated. Meanwhile, the change of pyramid density under different conditions also been studied.

2. Experimental Details

Monocrystalline silicon wafers of P-type. <100> oriented and size 1.7cm×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 five minutes of ultrasonic cleaning. The second step the native oxide was removed by immersion of the samples into diluted hydrofluoric acid (4 wt%), for 60

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_2CO_3) 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 Temperature form 50 ℃ to 90 ℃

The influence of texturing temperatures on pyramid size, density and uniformity was evaluated by varying temperatures (from 50 ℃ to 90 ℃).The pyramid size and density as the change of temperature as shown in Fig.2,From to Table 1, we can clearly observe that the temperature is very important parameters for texturization. It can be stated that the increase in temperature (from 50 ℃ to 60 ℃) resulted in the increase of the density (from 25% to 42.15 %), but the density reduces (from 42.15% to 11.96%) with temperature increasing (from 60 ℃ to 70 ℃).When the temperatures reached 80 ℃, the density gradually increase (from 64.4% to 100%)

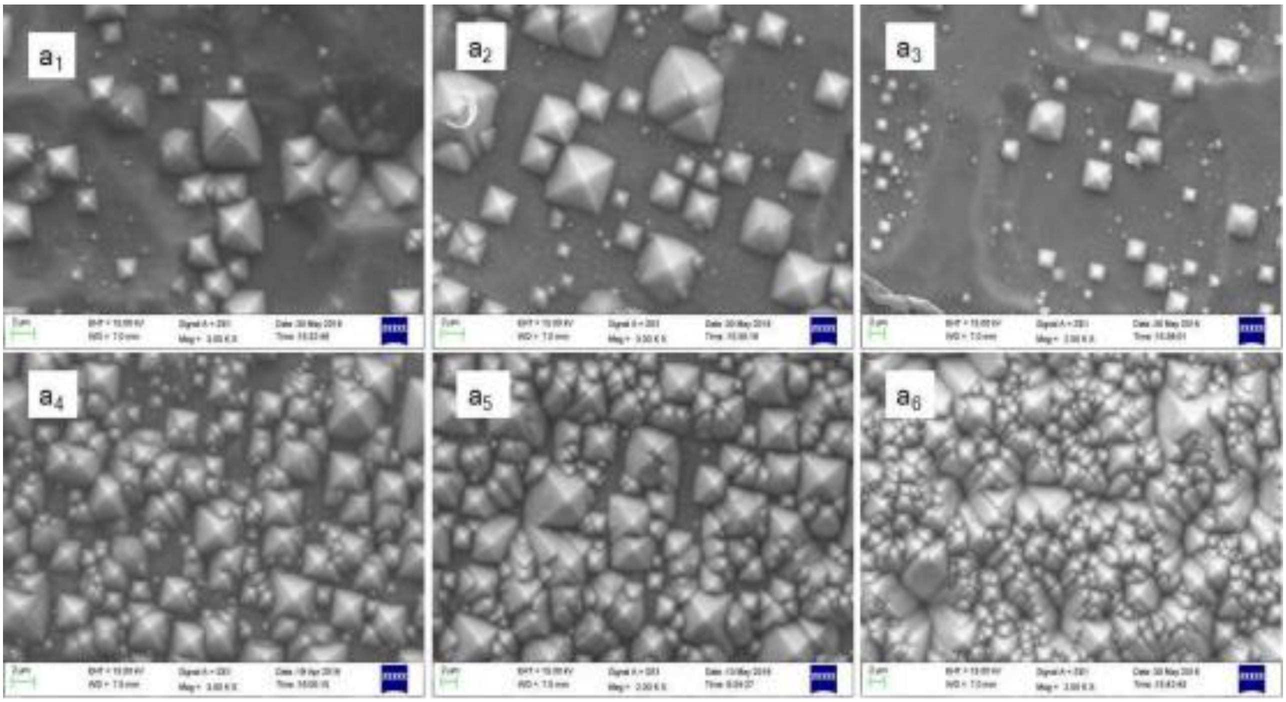

Fig. 1,Scanning electron micrographs (SEM) of silicon surface textured 2wt% K_2SiO_3 and 25wt% K_2CO_3 solutions at different temperatures (50 ℃-90 ℃) for 10min.a_1=50 ℃; a_2=60 ℃;a_3=70 ℃; a_4=80 ℃; a_5=85 ℃; a_6=90 ℃.

Table 1, Size, density and uniformity of pyramid after texture with 25wt% K_2CO_3 and 2wt%K_2SiO_3 solution at different temperatures for 10min.

Temperature	Maximum Size (μm)	Mean Size(μm)	Density(%)	Uniformity
50 ℃	5.14	2.32	25.00	low
60 ℃	6.70	2.55	42.15	low
70 ℃	4.74	1.75	11.96	low
80 ℃	4.62	1.97	64.40	Regular
85 ℃	9.09	3.14	81.20	Regular
90 ℃	4.70	1.78	100	High

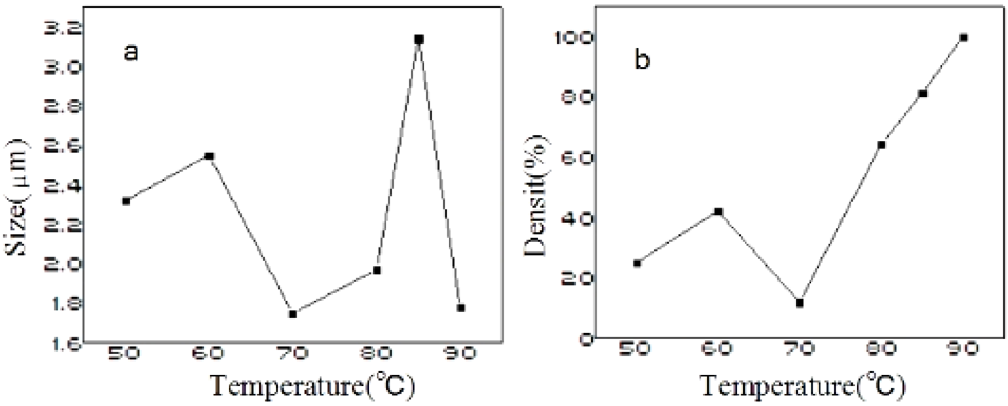

Fig. 2,(a) The pyramid size of variation with temperature (b) Density of variation with temperature.

The morphological properties of the textured surfaces were analyzed using scanning electron microscopy (SEM) as shown in Fig.1. The scanning electron microscopy (SEM) image (Fig.1) shows that the pyramids are nonuniform, and they are discontinuous, the surface coverage is poor. Some of the silicon surface is not covered by pyramid. It can be stated that the increase in temperature (from 50 ℃ to 60 ℃), the pyramid size has little change (from 2.32μm to 2.55μm), the surface coverage is poor. The surface coverage is very low, but the pyramid shape becomes smaller and uniform at 70 ℃. It can be observed that the increasing in temperature (from 80 ℃ to 90 ℃), the pyramid size has big change (from 1.97μm to 1.78μm).The pyramid size increased to 3.14μm because appeared relatively large size of the pyramid , the maximum size is 9.09μm,which is the biggest size in we talk about the different temperatures. The optimum density (81%) can be noticed at 85 ℃, and the most uniform pyramid (1.78μm) was formed at 90 ℃.

3.2 Influence of K_2CO_3 Concentration

The influence of K_2CO_3 concentration was evaluated by varying the concentration between 15 and 30wt%.Under the different concentration of reaction, observing the pyramid of silicon wafer surface size, density, and uniformity. All of the pyramid size, density and uniformity are listed in Table 2, The SEM images of the etched surfaces are shown in Fig.3, From to Table 2, it can be assumed that the K_2CO_3 concentration (from 15wt% to 20wt%) has a little influence on density (from 95.5 to 90.1%) and the pyramid size(from 4.63μm to 5.48μm) at 10min.There are many small pyramid among the big pyramid, the pyramid uniformity is low in silicon wafer surface. But the pyramid size has a clearly change (from 5.48μm to 2.13μm)when the K_2CO_3 concentration (from 20wt% to 25wt%).Pyramid silicon wafer surface coverage become smaller(only86.5%) and the pyramid size has little change when the K_2CO_3 concentration (from 25wt% to 30wt%).The uniformity of the pyramid is better than before. As the concentration was increased, a significant deterioration of surfaces was observed at first sight. The reaction became more vigorous and created many large bubbles that adhered to the surface of the sample. These hydrogen bubbles acted a smack on the surface, inhibiting the texturization reaction. As a result, the surfaces were not uniform and haven't reach the expected results. Fig.4 shows the SEM image of textured wafers at 45 ° incidence angle and the distribution of pyramid size when the samples were textured at 15wt% K_2CO_3. The optimum density (95,5%) of the K_2CO_3 concentration of 15wt%, and the most uniform pyramid(2.13μm) was formed at the K_2CO_3 concentration of 25wt%.

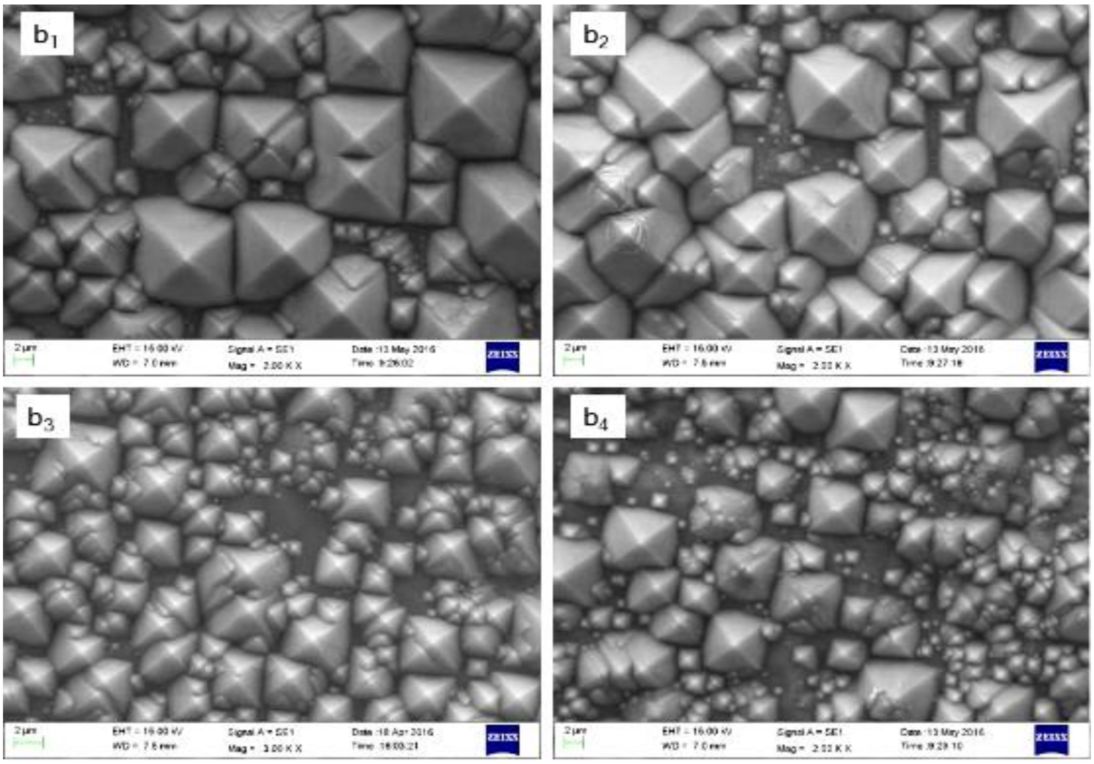

Fig. 3,Scanning electron micrographs (SEM) of silicon surface textured 2wt% K_2SiO_3 and K_2CO_3 solution at 80 ℃ for 10min :b_1= 15wt% K_2CO_3; b_2= 20wt% K_2CO_3; b_3= 25wt% K_2CO_3; b_4= 30wt% K_2CO_3.

Table 2, Size, etching rate and uniformity of pyramid after texturing (2wt% K_2SiO_3 and different K_2CO_3 concentration at 80 ℃ for 10min.

Concentration	Maximum Size (μm)	Mean Size(μm)	Density(%)	Uniformity
15wt%	12.90	4.63	95.5	low
20wt%	12.05	5.48	94.6	low
25wt%	5.73	2.13	90.1	Regular
30wt%	8.35	2.49	86.5	Regular

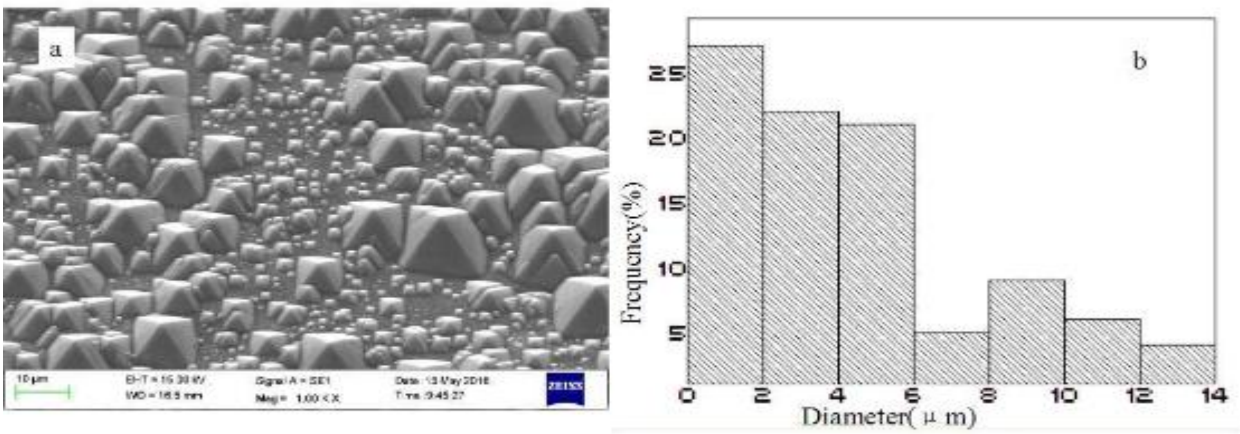

Fig. 4,(a) Scanning electron micrographs (SEM) of 15wt%K_2CO_3 silicon surface and (b) distribution of pyramid size.

3.3 Influence of Texturing Time Form 5min to 60min

The influence of texturing time on Pyramid size, density and uniformity was studied by changing the time (from 5min to 60min).The pyramid size and density as the change of temperature as shown in

Fig.6.The morphological properties of the textured surfaces were analyzed using SEM as shown in Fig.5.And the pyramid size and density are listed in Table 3. It can be stated that the increase in texturing time (from 5 min to 40min) resulted in the increase of the pyramids size (from 2.18μm to 4.05μm) and density (from 44.18% to 100%).As the growth of the time there were obvious changed of the pyramids size and density, and values of the pyramids size and density are increased accordingly. But we need the ideal silicon is large density, pyramids relatively smaller and uniform pyramid. The corrosion Fig.5 (c_1) is obviously less than the other figures. From Fig.5(c_1), we can see that the texturing time too short, silicon surface didn't form enough stuck out of hole. When the reaction time is too long, the pyramid size difference is larger. As time longer, covering the surface of the pyramid number becomes more intense. Although for 60min in texturing time when the pyramid average size is reduced, but it’s largest pyramid size reached a maximum size 14.68μm. It is bad light absorption. Fig.5 (c_2) exhibited the best pyramid size and uniformity with 10 minutes texturing time.

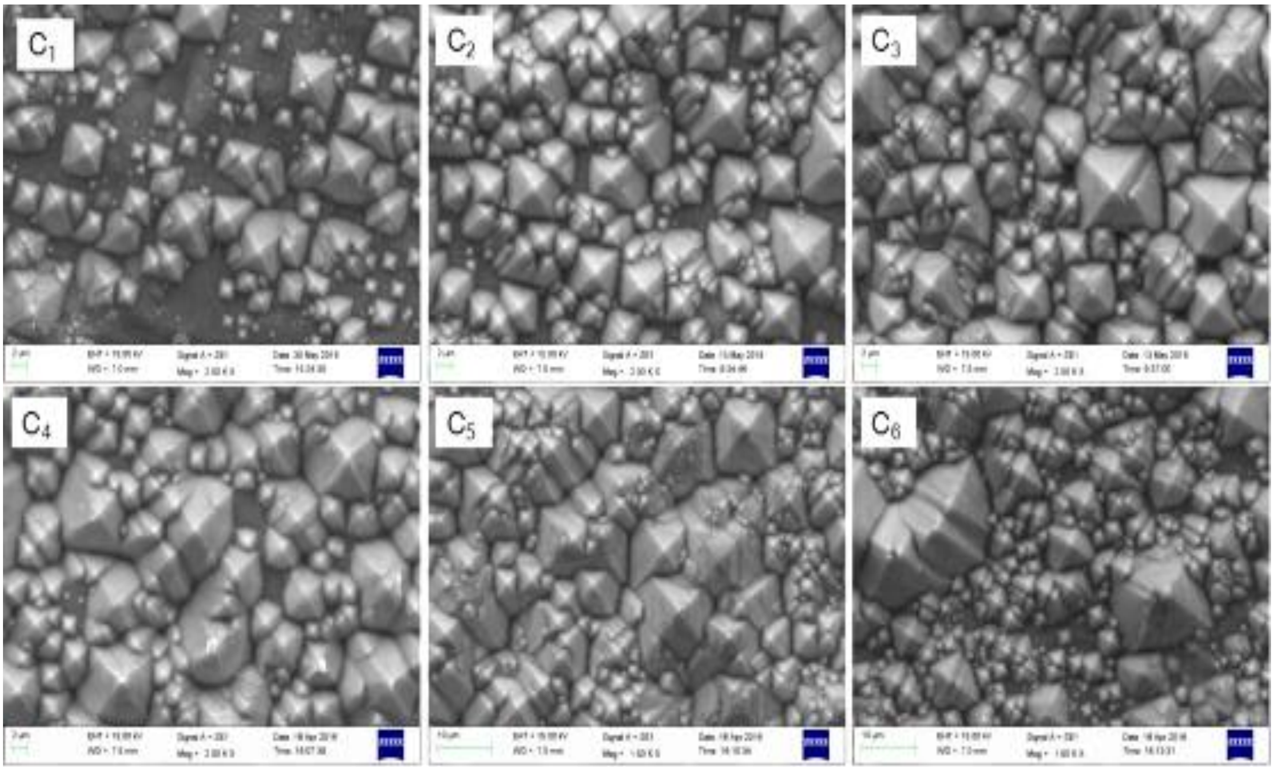

Fig. 5,Scanning electron micrographs (SEM) of silicon surface textured 2wt% K_2SiO_3 and 25wt% K_2CO_3 solution with a variation on texturing time at 85 ℃:c_1=5min;c_2=10 min; c_3=15 min; c_4=20 min; c_5=40 min; c_6=60 min.

Table 3, Size, etching rate and uniformity of pyramid after texturing (2wt% K_2SiO3 and 25wt% K_2CO_3 for different time at 85 ℃).

Time	Maximum Size (μm)	Mean Size (μm)	Density (%)	Uniformity
5min	6.99	2.18	44.18	low
10min	8.15	2.83	92.3	high
15min	10.71	3.38	96.1	Regular
20min	9.88	3.64	93.5	Regular
40min	11.97	4.05	100	Regular
60min	14.68	2.92	100	Regular

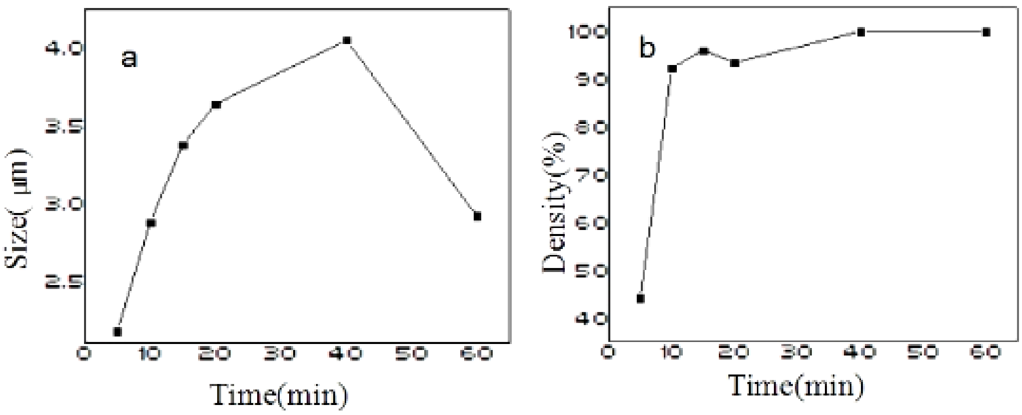

Fig. 6,(a) The pyramid size of variation with time (b) Density of variation with time

Conclusion

In this paper, by changing the reaction of silicon K_2CO_3 concentration and texturing time and temperature, the observed density and coverage of the pyramid, and pyramid size has changed significantly. What we need is a silicon wafer surface pyramid good coverage; pyramid the condition of uniform density and size. And the K_2CO_3 concentrations and texturing time have crucial influences on pyramid density. With the increase in temperature (from 50 ℃ to 90 ℃) resulted in the increase of the density from 25% to 100 %, the size varies from 2.32 to 1.78μm,when 2wt% K_2SiO_3 and 25wt% K_2CO_3 solutions at different temperatures for 10min.The optimum density (81%) can be noticed at 85 ℃, and the most uniform pyramid(1.78μm) was formed at 90 ℃.With the concentration increasing (from 15% to 30%), the size varies from 4.63 to 2.49μm,and the density from 95.5% to 86.5 %,2wt% K_2SiO_3 and K_2CO_3 solution at 80 ℃ for 10min. The optimum density (95.5%) of the K_2CO_3 concentration of 15wt%, and the most uniform pyramid(2.13μm) was formed at the K_2CO_3 concentration of 25wt%.With the time increasing (from 5min to 60min), the size varies from 4.63 to 2.49μm,and the density from 95.5% to 86.5 %,2wt% K_2SiO_3 and 25wt% K_2CO_3 for different time at 85 ℃. The best pyramid size and uniformity with 10 minutes texturing time. This technology can be used for surface-enhanced Raman scattering active substrate, to provide an efficient and beneficial to improve the detection made a feasibility study.

Acknowledgements

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

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