Investigation of Texturization for Monocrystalline Silicon Wafers with NaOH and $Na_2B_4O_7 \cdot 10H_2O$ Solutions

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Abstract. NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions of texturization were investigated and a series of comparative experiments were made by our group. The surface microstructures studied with a scanning electronic microscope (SEM). The different etching time and the different concentration of the solution have a larger effect on the pyramid density and the pyramid size. The SEM pictures showed that the surfaces covered with more perfect uniformly pyramid structures was obtained after texturing with NaOH of 2wt% and $Na_2B_4O_7 \cdot 10H_2O$ of 2wt% solutions at 80℃ and 25min. The pyramid density was 81.8% and the mean size was 1.75 μ m. This result showed the method based on NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions was a promising method for large-scale industrial applications for Raman basal.

1. Introduction

Texturization for monocrystalline silicon solar cells has been widely used with the key of increasing the conversion efficiency [1, 2]. Texturization of the surface of {100} monocrystalline silicon wafer by anisotropic etching is effective to formation of uniformly distributed pyramidal structures on the surface, the structures which geometries allow light to be more easily coupled and efficiently absorbed into the solar cells [3, 4].

Although many researchers claimed to have found more advanced techniques to have better conversion efficiency than anisotropic etching, but most of them become more complex or costly. The most common etching solutions is NaOH/KOH mixed with isopropyl alcohol (IPA) [5-7].As the concentration of IPA is higher than NaOH/KOH solution, on the other hand. As IPA is expensive and easy polluted the environment, Thus, more and more anisotropic etching alkaline solutions has been investigated with the aim to reduce the cost of the etching process [8]. Such as TMAH [9], Na_2SiO_3 [10], Na_2CO_3 and $NaHCO_3$ [11], Na_3PO_4 [12], and so on. In this passage. Texturization for monocrystalline silicon wafers with NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions has been investigated. Using NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions as etchant was successfully carried out. It is also worthy to note the addition of appropriate $Na_2B_4O_7 \cdot 10H_2O$ solution to NaOH solution not only reduced the pyramid size but also obtained a better wafer uniformly pyramid structures. Raman basal need micron-nano-sized structure[13]. Thus. This result showed the method based on NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions was a promising method for large-scale industrial applications for Raman basal.

2. Experimental Method

P-type monocrystalline silicon wafers <100> oriented and size 1.5 cm ×1.5 cm of resistivity 1.0-3.0 Ω/cm was prepared for the etching experiments. The whole 125 mm ×125 mm wafers were cut into small samples.

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Before tuxturization process, the unpolished silicon wafers was immersed in absolute ethanol solution staying 5 min of ultrasonic cleaning and dried in Ovens, the native oxide can be removed from the silicon surfaces by etched in HF solution (about 5wt%) for 30s and immediately rinsed in deionized water, followed by immersed in deionized water staying 5 min of ultrasonic cleaning and dried in ovens. Next, the cleaned samples were reactioned one by one in a special closed plastic container witch the alkaline solutions is inside. Then these samples were etching in different concentration of mixed NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions at 80 and 25min, or varied the etching time of mixed NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions which the concentration were both 2 wt%. After the etching process, the samples were cleaned by absolute ethanol solution and deionized water. Finally, dried the samples for tests.

The surface morphology was studied with Zeiss EVO MA10 (Carl-Zeiss, Germany) scanning electron microscope (SEM).

3. Results and Discussion

Primarily, we fixed the concentration of the etchant $Na_2B_4O_7 \cdot 10H_2O$ solution(2wt%) at 80℃ and etching 25min only varied the concentration of NaOH solution from 1.5wt% to 3wt％, choosing some of the result as an example. As the results shown in table 1. We can found the pyramid density was low when the concentration of the NaOH solution was 1wt %, the density of the pyramid was increased with the concentration of NaOH up to 2wt%(the density was 81.8%, and the mean size was 1.75 μm), the density of the pyramid began to decreased when the concentration was increased to 3wt%(only 21.0%), when the concentration of NaOH was 2wt% we can not only obtained a higher density of pyramid (81.8%) but also make the mean size reduced to 1.75 μm ,thus, the optimum concentration of NaOH was 2wt%.

Table 1 Size, density and uniformity of pyramid after textured with different concentration of NaOH solution and 2wt% $Na_2B_4O_7 \cdot 10H_2O$ solution at 80℃ for 25min.

Concentration (wt %)	Maximum Size(μm)	Mean Size(μm)	Density (%)	Uniformity
1．5	4.84	2.97	35.8	Low
2	5.93	1.75	81.8	Regular
2.5	8.61	2.92	89.5	Regular
3	11.75	3.21	88.6	Low

Fig .1 shows four SEM images of the etching surface with different NaOH concentration and 2 wt% $Na_2B_4O_7 \cdot 10H_2O$ solution for 25min at 80℃. From Fig .1(a, d). It can be seen that when the concentration of NaOH solution is 1.5wt% or 3wt%, we can't get a good result, the Fig .1(b) pyramids were much more smaller than the ones obtained in Fig .1(c) ,but the former's density was only 7.7% lower than the latter.

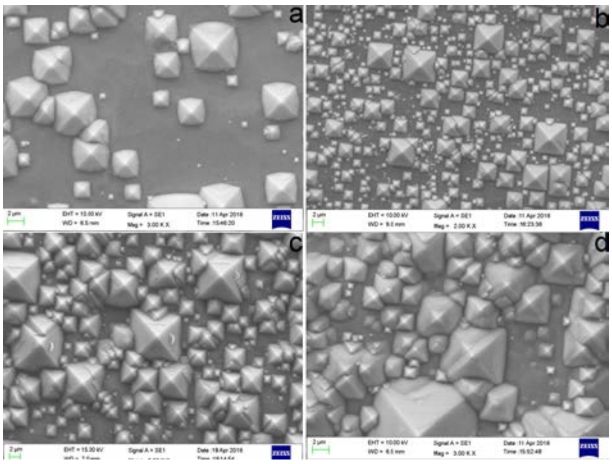

Fig .1 SEM images of silicon wafers textured with different concentration of NaOH solution and 2 wt% $Na_2B_4O_7 \cdot 10H_2O$ solution for 25min at 80℃: a=1.5wt%; b=2wt%; c=2.5wt%; d=3wt%.

Next, we fixed the concentration of the etchant NaOH solution (2wt%) at 80℃ and etching 25min only varied the concentration of $Na_2B_4O_7$ •$10H_2O$ from 1wt% to 2.5wt%, As shown in Table 2 we can found the concentration of $Na_2B_4O_7$ •$10H_2O$ solution has a large effect on the texturing. The pyramid density was find to decreased with the $Na_2B_4O_7$ •$10H_2O$ concentration was increased to 2.5wt%, otherwise, with the concentration of the $Na_2B_4O_7$ •$10H_2O$ solution was 2wt% we can obtained a good pyramid density of 81.8% and the pyramid size was 1.75 μm, but we can't get a good result, when the concentration of $Na_2B_4O_7$ •$10H_2O$ solution was below to 2%.

Table 2 Size, density and uniformity of pyramid after textured with different concentration of $Na_2B_4O_7$ •$10H_2O$ solution and 2wt% NaOH solution at 80℃for 25min.

Concentration (wt %)	Maximum Size(μm)	Mean Size(μm)	Density (%)	Uniformity
1	6.80	3.03	20.8	Regular
1.5	7.09	2.76	75.5	Low
2	5.93	1.75	81.8	Regular
2.5	5.29	2.33	27.6	Low

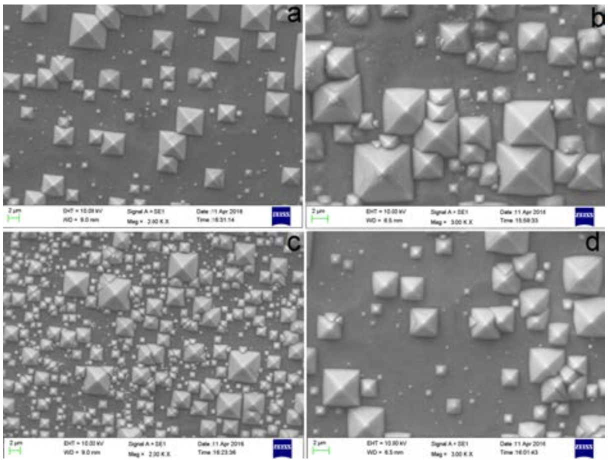

Fig. 2 SEM images of silicon wafers textured with different $Na_2B_4O_7$ •$10H_2O$ solution and 2wt% NaOH solution for 25min at 80 ℃: a=1wt%; b=1.5wt%; c=2wt%; d=2.5wt%.

As we can seen in the Fig .2(a, b and c). The results shown that $Na_2B_4O_7$ •$10H_2O$ added can change the etching rate. As shown in Fig. 2(d) the pyramid was become bigger (2.33 μm) and the density was lower (27.6%).

Finally, we studied the dependence of the pyramid density and the pyramid size at different etching time. According to the former experiments, the concentration of NaOH and $Na_2B_4O_7$ •$10H_2O$ solutions were both of 2wt%, the results as shown in Table 3, it could be found that the density of pyramid improved with the etching time increased to 25 min as we can seen in Fig. 3 (a, b). When the etching time was increased to 30min or 35min, the pyramids began to collapse down as mentioned in Fig. 3(c) and (d). In the same time, we observed that the mean size of the pyramid was 1.75 μm and the pyramid density was 81.8% in Fig. 3(b). Thus. The best pyramidal structures was obtained after texturing with NaOH of 2wt% and $Na_2B_4O_7$ ·$10H_2O$ of 2wt% solutions at 80℃ and 25min.

Table 3 Size, density and uniformity of pyramid after textured with 2wt% $Na_2B_4O_7$ •$10H_2O$ solution and 2wt% NaOH solution at 80℃ for different time.

Time(minute)	Maximum Size(μm)	Mean Size(μm)	Density (%)	Uniformity
20	10.83	4.34	71.6	Low
25	5.93	1.75	81.8	Regular
30	7.38	2.72	18.8	Low
35	9.43	3.76	26.4	Low

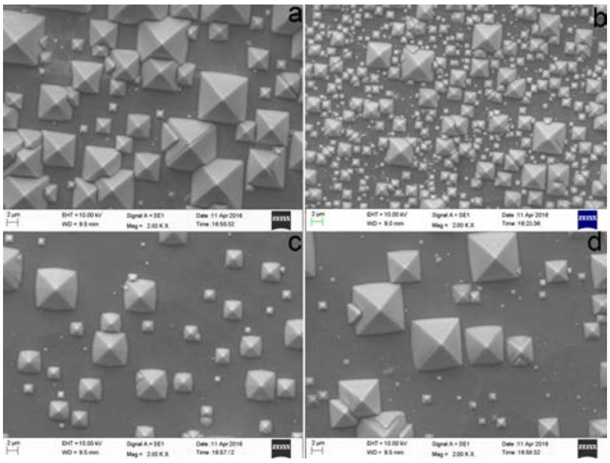

Fig. 3 SEM images of silicon wafers textured with 2wt% $Na_2B_4O_7 \cdot 10H_2O$ solution and 2wt% NaOH solution at 80℃ for different time: a=20 min; b=25 min; c=30 min; d=40 min.

4. Summary

The texturization of monocrystalline silicon wafers using mixed NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions has been studied. It is found that it is possible to improve the surface pyramid density and reduce the pyramid size during varying the concentration of mixed NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions at 80℃ and 25min, or varying the etching time of mixed NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solutions which the concentration were both 2wt%. After experiments, we can found a wonderful and uniform pyramidal texturing surface with the pyramid density was 81.8% and the mean size was 1.75 μ m. This result showed the method based on NaOH and $Na_2B_4O_7 \cdot 10H_2O$ solution was a promising method for large-scal industrial applications for Raman basal.

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