Investigation of Texturization for Monocrystalline Silicon Solar Cells with K_3PO_4/K_2HPO_4 Solutions

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Abstract—The texturization of monocrystalline silicon wafers using a mixture of potassium phosphate tribasic (K_3PO_4) and potassium phosphate dibasic (K_2HPO_4) solutions has been investigated. A series of comparative experiments were made to indicate the dependence of hemispherical surface reflectance on the solution temperature, the etching time, and the concentration of K_3PO_4 and K_2HPO_4. The hemispherical surface reflectance and the surface morphology were measured with a UV-Visible Spectrophotometer and a scanning electronic microscope (SEM), respectively. A wafer with uniform pyramid structures and an average weighted reflectance of 11.27% was obtained after texturing with the mixed solution of 15wt% potassium phosphate tribasic (K_3PO_4) and 1wt% potassium phosphate dibasic (K_2HPO_4) at 85℃ for 15min. our results show that the texturing method based on K_3PO_4/K_2HPO_4 solutions is cost effective, has low pollution and good reproducibility, This method is promising for a large-scale production of crystalline silicon solar cells.

Keywords-Solar cell; Texturing; Monocrystalline silicon; Phosphate; Reflectance

I. INTRODUCTION

The texturization of crystalline silicon solar cells has been widely used with the aim of increasing the conversion efficiency. Anisotropic etching of silicon to form random pyramids is an important technology for the fabrication of mono-crystalline solar cells. The most common etchant is the mixture of sodium hydroxide (NaOH) or potassium hydroxide (KOH) with water and isopropyl alcohol (IPA) [1-5]. In those etch solutions, IPA can help not only to remove hydrogen bubbles but also to promote the formation of big pyramids. However, IPA easily pollutes the workshop and is expensive too. In typical texturing condition, the IPA concentration is higher than the NaOH (or KOH) concentration. Thus, the cost of IPA is dominant in the overall cost of texturing in the commercial NaOH/KOH technique.

As IPA is an expensive chemical product, other solvents are studied to reduce the cost of the process [6-10]. Some researchers have reported the texturization with potassium carbonate (K_2CO_3)[11], sodium carbonate (Na_2CO_3)[12], Sodium silicate (Na_2SiO_3)[13]and sodium phosphate (Na_3PO_4)[14]solutions. These techniques are superior to the conventional method in terms of cost because there is no need of IPA for texturing.

In this paper, texturization of monocrystalline silicon wafers with a mixture of potassium phosphate tribasic (K_3PO_4) and potassium phosphate dibasic (K_2HPO_4) solutions was studied. Meanwhile, the changes of reflectance with etching time, the concentration of K_3PO_4 and K_2HPO_4 and temperature were also investigated.

II. EXPERIMENTAL METHED

Monocrystalline silicon wafers of P-type. <100> oriented and size 1.5cm×1.5cm with resistivity 1-3Ω·cm was used as the etching experiments. Samples were cut from the adjacent wafers. Before etching, wafers were cleaned by the following procedure. 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 wafer 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 phosphate dibasic (K_2HPO_4). The different reaction times and reaction temperatures could be controlled. After the etching process the samples were washed again into absolute ethanol solution and de-ionized water, 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

At first, the dependence of the surface reflectance on solution concentration was investigated. Etching was carried out at 85℃. The reflectance was measured for samples textured using 1wt% K_2HPO_4 solution and different K_3PO_4 concentrations (10wt%, 15wt%, 20wt% and 25wt%) for 25 min at 85℃. The reflectance curves are shown in Fig. 1. The reflectance was found to decrease with increasing K_3PO_4 concentration up to 15wt%. The weighted average reflectance in the range of 400-800nm spectrum range is 12.05%. Fig. 2 show SEM micrographs of monocrystalline silicon wafers textured using 1wt% K_2HPO_4 solution and different K_3PO_4 concentrations (10wt%, 15wt%, 20wt% and 25wt%) for 25 min at 85℃. From the Fig. 2, it can be seen that the texture was excellent. All these mean that this kind of etchant can successfully texture monocrystalline silicon for solar cells. When the K_3PO_4 concentration was increased to 20 wt%, the pyramidal structure began to collapse.

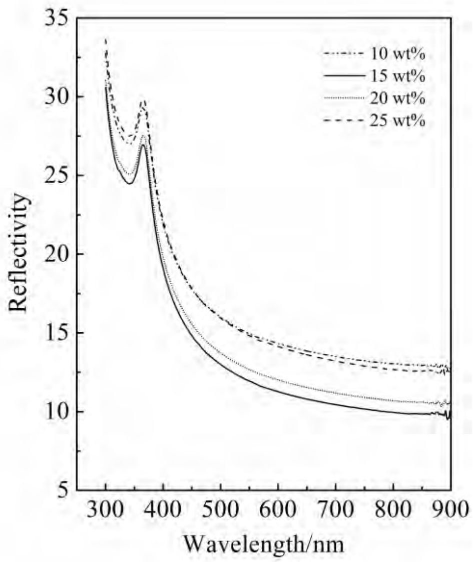

Figure 1. Reflectance curves of monocrystalline silicon wafers textured using 1wt% K_2HPO_4 solution and different K_3PO_4 concentrations for 25 min at 85℃

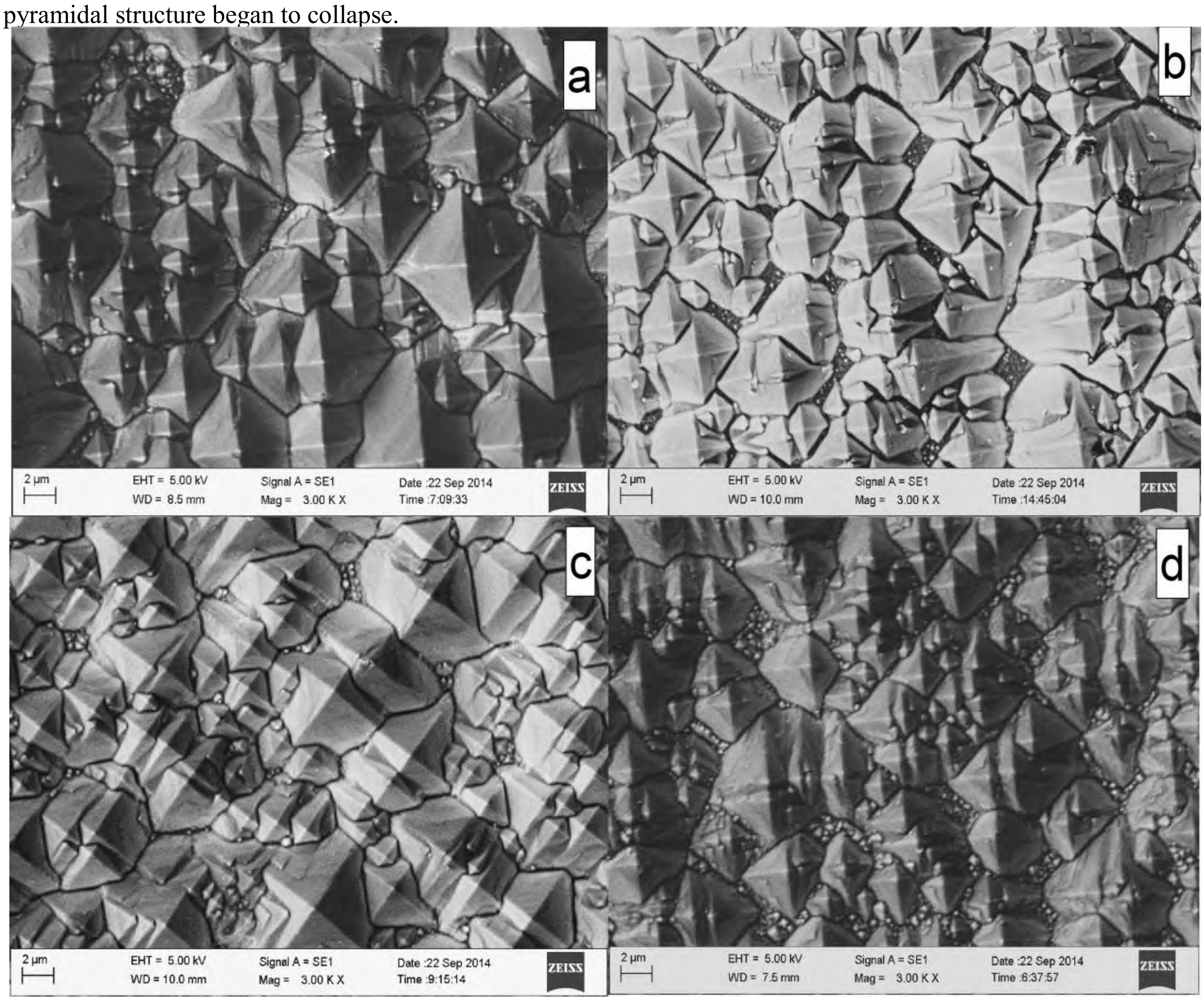

Figure 2. SEM micrographs of monocrystalline silicon wafers textured using 1wt% K_2HPO_4 solution and different K_3PO_4 concentrations for 25 min at 85℃: (a) 10wt%,(b) 1wt%,(c)20 wt%,(d)25 wt%

Next, we investigated the dependence of the surface reflectance on etching time. According to previous studies, the concentration of K_2HPO_4 and K_3PO_4 was fixed at 1wt% and 15wt%, respectively, and the solution temperature fixed at 85℃. Fig. 3 shows the reflectance curve of the monocrystalline silicon surface textured using 1wt% K_2HPO_4 solution and 15 wt% K_3PO_4 at 85℃ for different reaction time. As shown in Fig. 3, at a fixed etching solution and temperature, the reflectance of the textured surfaces decreases with increasing texturing time. A reflectance minimum was observed when the texturing time was increased to 15wt%. The spectrum range of 400-800nm registers the lowest reflectance is 11.27%. With the reaction time increased to 15 min, a homogeneous density of pyramidal structures on the silicon surface can be seen from the micrograph shown in Fig. 4(b). As shown in Fig. 4(c)(d) , the SEM images of the pyramid grows excessively and the quantity of pyramids in unit area decreases, the pyramid structure is over etched and tends to lead to uneven texture surface. In this stage, the continuously increased reaction time would not significantly change the effect of the texture etching. Therefore, the optimal reaction time should be controlled at 15 min.

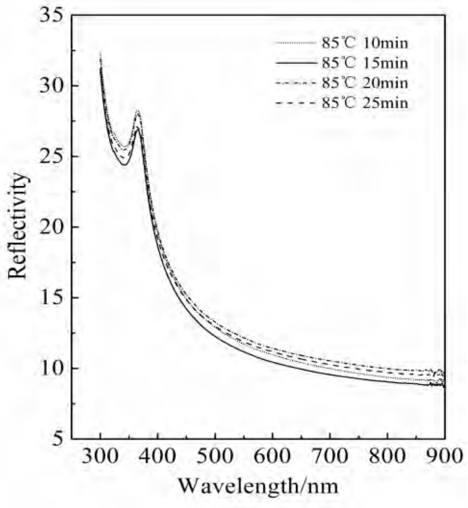

Figure 3. Reflectance curves of monocrystalline silicon wafers textured for different etching time

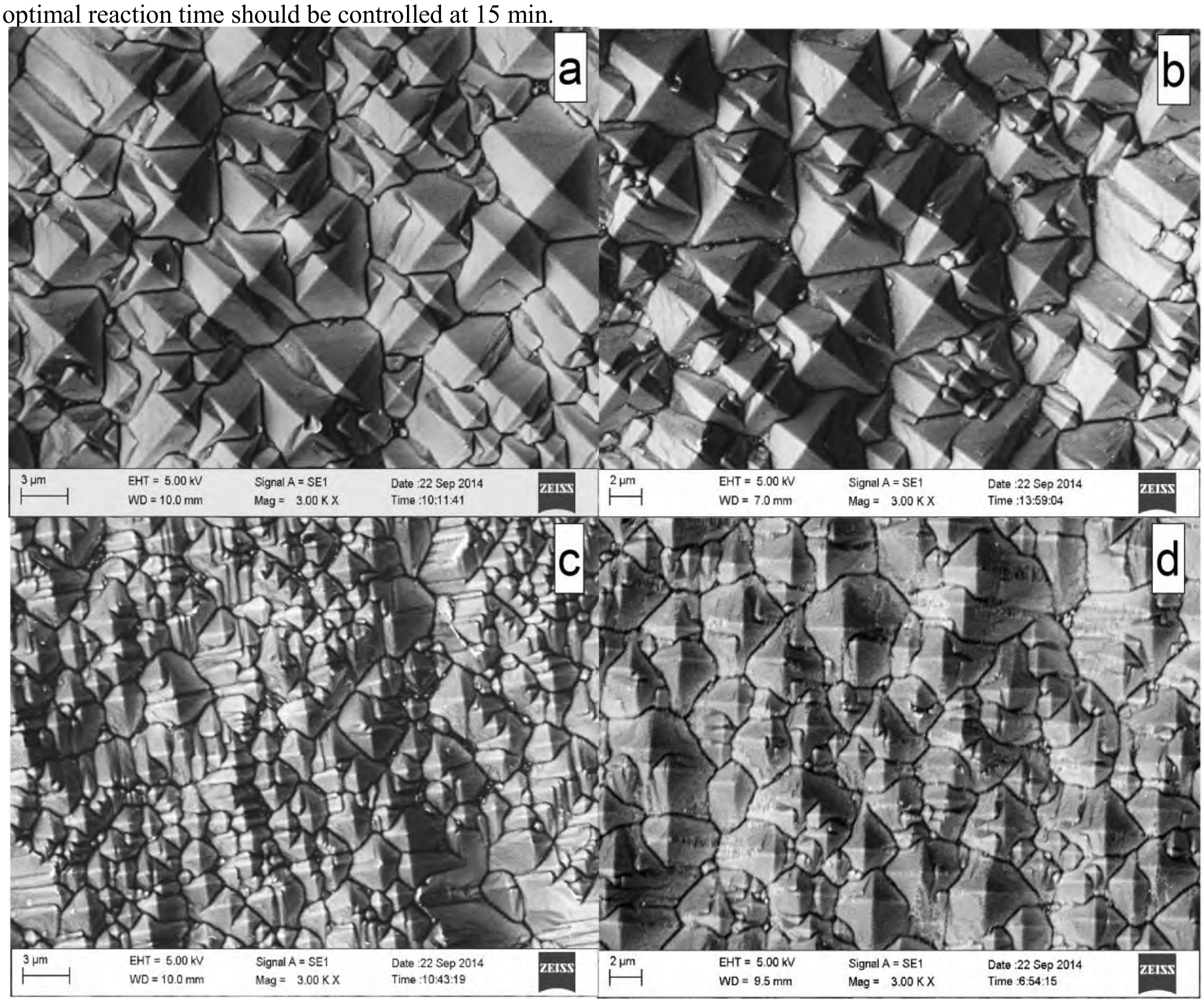

Figure 4. SEM images of monocrystalline silicon wafers textured for different etching time: (a) 10 min,(b)15min,(c)20min,(d)25min

Finally, we investigated the dependence of the surface reflectance of the solution temperature. The concentration of K_2HPO_4 and K_3PO_4 was fixed at 1wt% and 15wt%, respectively, and the etching time was also fixed at 15 min. The experiment was carried out from 75℃ to 90℃. As shown in Fig. 5, the surface reflectance decreased with increasing temperature. Under normal temperatures, alkaline solution could hardly complete the etching reaction on silicon wafers, and proper increase of the reaction temperature could promote the etching reaction better. While the temperature is too high, the surface structure would be over-etched by the alkaline solution and would have decreased ability to absorb the reflected lights and would not obtain ideal reflectance. By experimentally obtained to the optimum temperature is 85℃, and the weighted average reflectance is 11.27%. Fig. 6 is the SEM micrographs of monocrystalline silicon wafers textured at different temperatures. In Fig. 6(c), at 85℃, the pyramid structure and sizes on the silicon surface are much more even compared to those in Fig. 6(d) which textured at 90℃. Thus, the optimal reaction temperature should be 85℃.

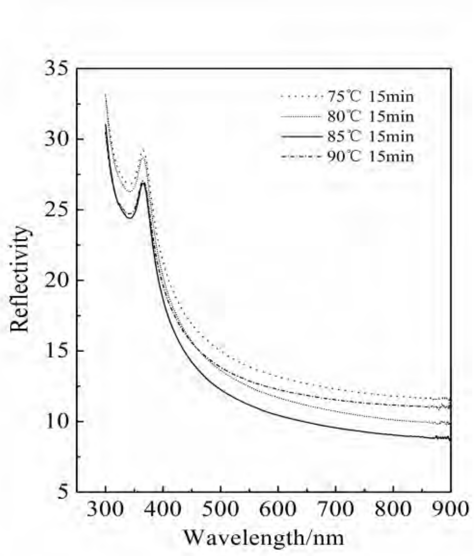

Figure 5. Reflectance curves of monocrystalline silicon wafers textured at different temperatures

IV. CONCLUSION

The texturization of monocrystalline silicon using mixed (K_3PO_4/K_2HPO_4) solutions has been investigated. It is found that it is possible to optimize the reflectance values of the samples by varying the K_3PO_4/K_2HPO_4 concentrations of the solution, the etching time and temperature, thus obtaining low reflectance values comparable to the ones obtained in IPA based solutions. Our optimized process lasted for 15min at 85℃ using a solution containing 15wt% K_3PO_4 and 1wt% K_2HPO_4. After texturing, for monocrystalline silicon wafers, we obtained reliable and uniform pyramidal texturing surfaces with an average weighted reflectance of 11.27%. This novel approach provides an alternative way for the industrial production of high-efficiency solar cells.

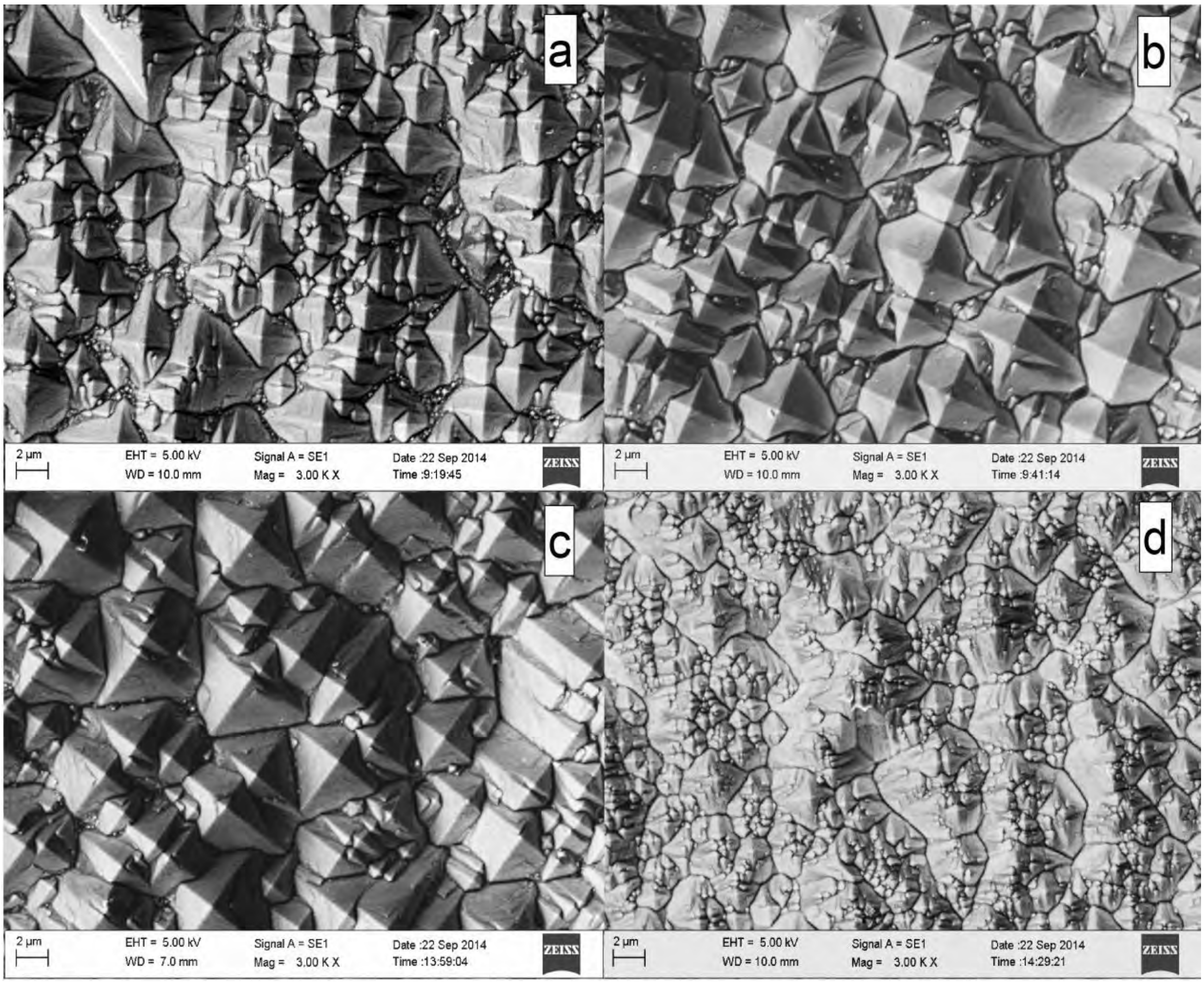

Figure 6. SEM images of monocrystalline silicon wafers textured at different temperatures: (a) 75℃, (b) 80℃, (c) 85℃, (d) 90℃

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