Study on Surface Texturization of Monocrystalline Silicon Wafers with Na_2CO_3 and $NaHCO_3$ Solutions

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Keywords: Surface texturization; Monocrystalline silicon; Reflectivity; Pyramid

Abstract. The surface texturization of monocrystalline silicon wafers based on a mixture of sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) solutions under different conditions have been studied in this work. A series of comparative experiments were made to indicate the dependence of hemispherical surface reflectivity on the Na_2CO_3 concentration, the $NaHCO_3$ concentration and the solution temperature. The results showed that the Na_2CO_3 concentration and the solution temperature have great effects on texture. In addition, the pyramid size and the surface average reflectivity decreased with the addition of $NaHCO_3$. On the basis of our experiments, it is shown that the optimized conditions are 24 wt% Na_2CO_3, 4 wt% $NaHCO_3$, 90 ℃ and 30 min. Under these conditions, uniform pyramids are fabricated and the textured silicon surface exhibits a lower average reflectivity (about 12.34%) in the main range of solar spectrum (400 nm-800 nm). Because this texturization method is economical, nonhazardous and has low pollution, so we feel that it is an attractive alternative for the industrial production.

Introduction

The texturization of silicon surface can remarkably reduce the surface reflectivity to achieve high conversion efficiency. In the case of monocrystalline silicon solar cells, anisotropic chemical etching is used to form pyramidal structure that can collect the reflected light and trap the light inside the cells by internal reflection [1]. Commonly, the etching solutions are a mixture of sodium hydroxide (NaOH) or potassium hydroxide (KOH) with water and isopropyl alcohol (IPA) [2]. In these alkaline solutions, IPA can help not only to remove hydrogen bubbles but also to promote the formation of big pyramids. However, IPA can easily pollute environment and is more expensive than NaOH or KOH. Thus, the cost of IPA is dominant in the overall cost of texturing in this technique. So, reduction in the amount of IPA during texturization of the industrial solar cells fabrication is the most key issue of overall texturization cost reduction approach.

Recently, some groups applied salt solutions to texture monocrystalline silicon solar cells. These solutions are superior to the conventional solutions in terms of cost and environmental protection, because there is no need of IPA for texturing [3]. It is well known that sodium carbonate (Na_2CO_3) and sodium bicarbonate ($NaHCO_3$) can also hydrolyze in water and generate OH^- in order to help for forming small pyramids. Besides, among all the etching solutions, the carbonate and bicarbonate solutions could be considered to be the least harmful, dangerous and expensive [4, 5, 6]. So, it is reasonable to apply Na_2CO_3 and $NaHCO_3$ solutions to texture monocrystalline silicon. In this paper, texturization of monocrystalline silicon with Na_2CO_3 and $NaHCO_3$ solutions was studied. In addition, the changes of reflectivity with different concentration of Na_2CO_3, different concentration of Na_2CO_3 with 4 wt% $NaHCO_3$ and the solution temperature were also studied.

Experiments

Experimental Principle. At first, when the sodium carbonate/sodium bicarbonate powder soluble in water, they will hydrolyze in water as following two steps:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^- \quad (1)$$

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^- \quad (2)$$

Then the anisotropic etching of silicon by alkaline solutions as an oxidation/reduction process, where the oxidation reaction is:

$$Si + 4OH^- \rightarrow Si(OH)_4 + 4e^- \quad (3)$$

The reduction reaction is:

$$4H_2O + 4e^- \rightarrow 4OH^- + 2H_2\uparrow \quad (4)$$

From the four equations above, we know the water has an important role as an active and necessary component. Water provides hydroxide ions that shift the oxidation reaction to the right [7]. Because the process has the autocatalytic character, the hydroxides required for the oxidation are produced in the reduction step [8]. All of these ensure the reaction can proceed smoothly.

Experimental Process. Monocrystalline silicon wafers of P-type <100> orientation with a resistivity of 2 Ω-4 Ω. cm were used for this work [9]. The size of the wafers was quasi-squared 15 mm × 15 mm which cut from the 125 mm × 125 mm. Before texturing, all wafers were handled by the following procedures. The first step was to degrease the samples by cleaning the wafers with the absolute ethanol in the ultrasonic cleaner for 10 minutes. In the next step, the samples were immersed in diluted hydrofluoric acid (HF, 4 wt %) for 1 minute to remove the native oxide and rinsed in deionized water for several times. When all the cleaning work is over, the samples were heated by the drying oven to remove moisture of their surface. Next, the wafers were held vertically in a specially designed device, which is self-made. Then the wafers were etching in different concentration of Na_2CO_3 without $NaHCO_3$ and with 4 wt% $NaHCO_3$ [10]. During the experiments, the reaction temperature and time should be well controlled. When the reaction is over, all the eroded wafers were washed again into the absolute ethanol solution and deionized water for 10 minutes. After that, they were dried in the drying oven for tests. In the end, we obtained the silicon wafers surface reflectivity data by using UV-2600 spectrophotometer (Shimadzu Inc, Japan) equipped with an integrating sphere [11]. In addition, the surface images of monocrystalline silicon wafers were measured by Zeiss EVO MA10 (Carl-Zeiss, Germany) scanning electron microscopy (SEM) [12].

Results and Discussion

Dependence of Reflectivity on the Na_2CO_3 Concentration. The influence of Na_2CO_3 concentration was evaluated by varying the concentration between 16 wt% and 28 wt%. The solution temperature is 90 ℃ and the etching time was carried out at 30 min. As the concentration of Na_2CO_3 was increased, a significant deterioration of surfaces was observed at first sight. Fig. 1 shows the results of measurement of reflectivity and the weighted average reflectivity for the samples obtained in different concentration of Na_2CO_3. It was found that the reflectivity decreased with increasing Na_2CO_3 concentration up to 24 wt%, when the concentration of Na_2CO_3 is over 24 wt%, the reflectivity start to rise. Thus the 24 wt% Na_2CO_3 can be regarded as optimum concentration. We can also see the lowest weighted average reflectivity in the range of 400 nm-800 nm spectrum range is 14.58%. Fig. 2 is the SEM images of wet texturing process variation with different concentration of Na_2CO_3. From the picture, we know using the single reagent of Na_2CO_3 is feasible but not perfect.

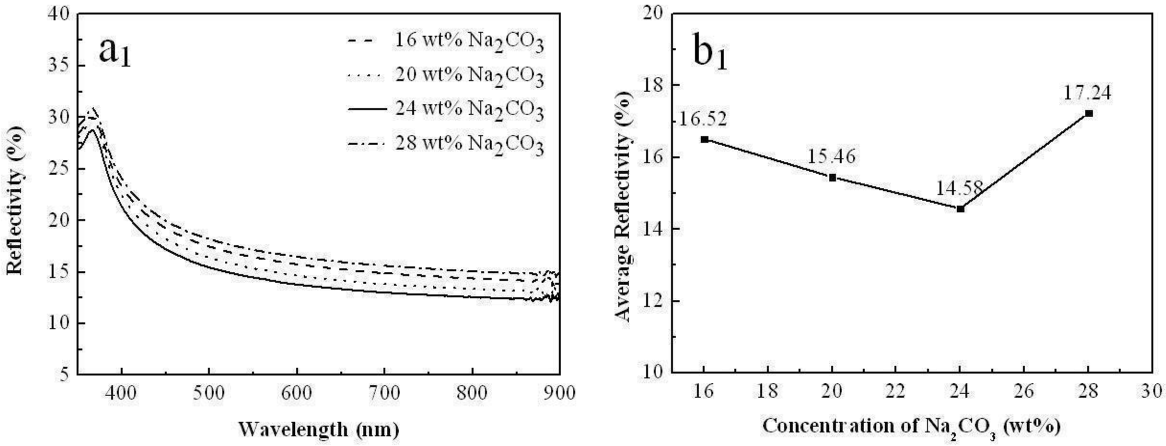

Figure 1. (a_1): The reflectivity of monocrystalline silicon wafers surface textured with different concentration of Na_2CO_3.
(b_1): The average reflectivity of monocrystalline silicon wafers surface textured with different concentration of Na_2CO_3.

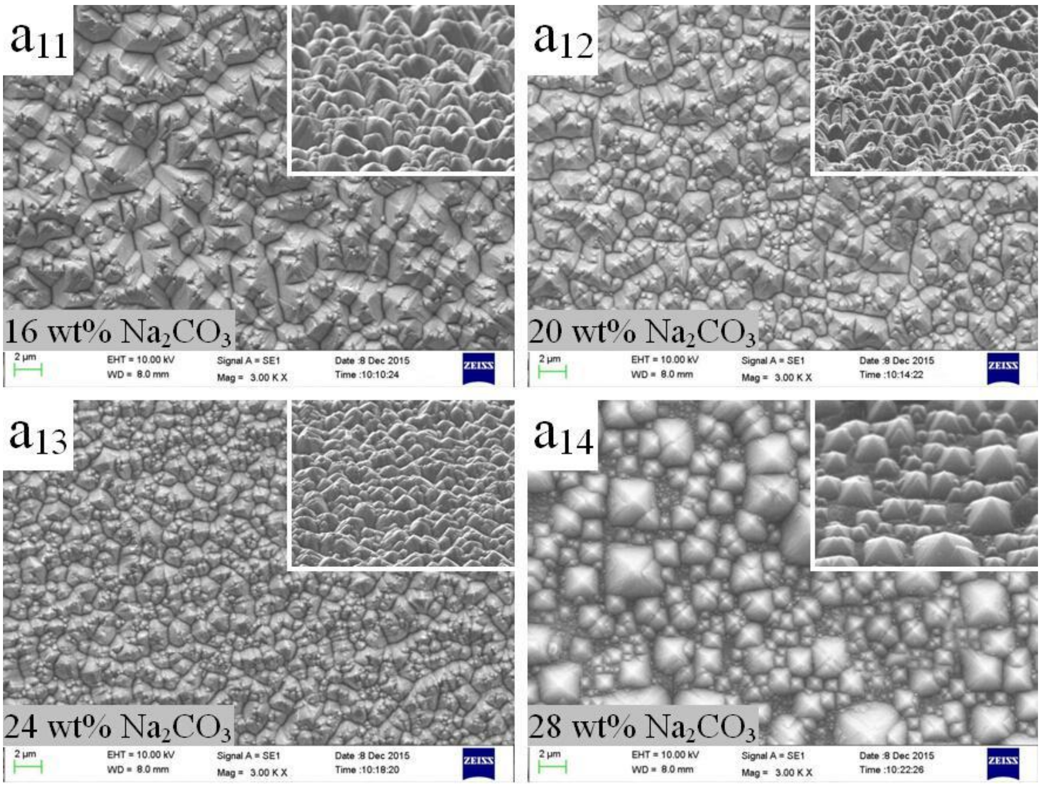

Figure 2. SEM images of monocrystalline silicon wafers surface textured with different concentration of Na_2CO_3: a_{11} (16 wt%), a_{12} (20 wt%), a_{13} (24 wt%), a_{14} (28 wt%).

Now we add 4 wt% $NaHCO_3$, while the concentration of Na_2CO_3 was varied between 16 wt% and 28 wt%. According to the preceding assays, the solution temperature and etching time were maintained at 90 ℃ and 30 min, respectively. Results of the $NaHCO_3$ addition are shown in Fig. 3. It is a comparison of reflectivity curves of silicon wafers textured. It is found that reflectivity is decreased by the addition of $NaHCO_3$ and we obtain a sufficient low weighted average reflectivity, which is 12.34% in the same conditions of texturing. The SEM photographs of texturing are shown in Fig. 4. From the images of SEM study, it could be found that the size of texture becomes smaller by the addition of $NaHCO_3$.

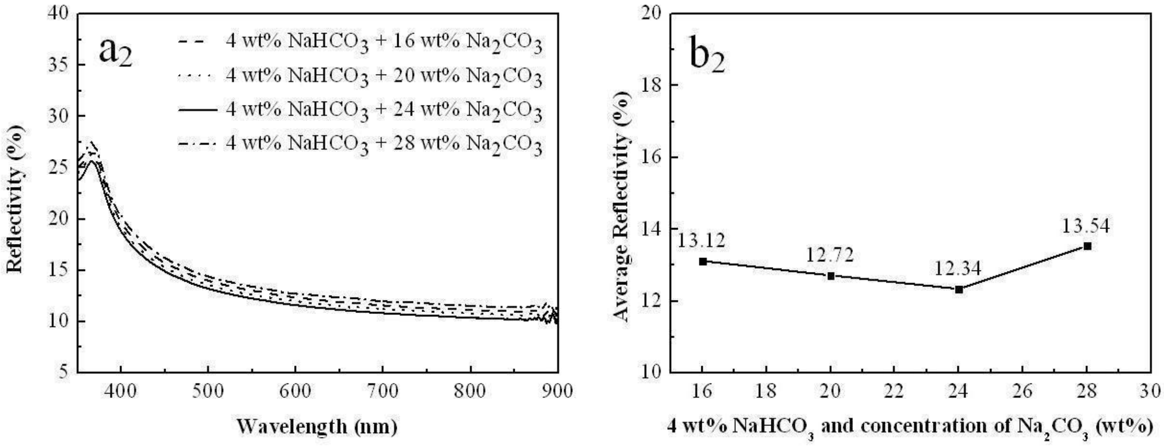

Figure 3. (a_2): The reflectivity of monocrystalline silicon wafers surface textured with 4 wt% $NaHCO_3$ and different concentration of Na_2CO_3.
(b_2): The average reflectivity of monocrystalline silicon wafers surface textured with 4 wt% $NaHCO_3$ and different concentration of Na_2CO_3.

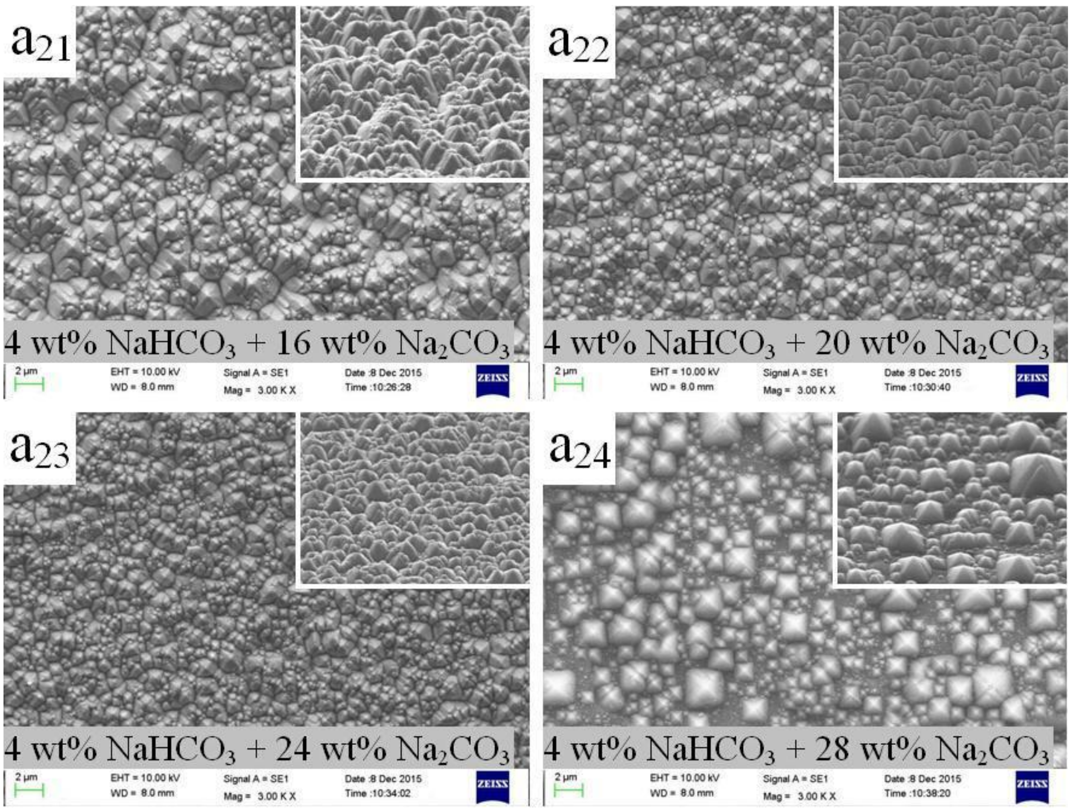

Figure 4. SEM images of monocrystalline silicon wafers surface textured with 4 wt% $NaHCO_3$ and different concentration of Na_2CO_3: a_{21} (16 wt%), a_{22} (20 wt%), a_{23} (24 wt%), a_{24} (28 wt%).

Dependence of Reflectivity on the Solution Temperature. Next, an analysis of reaction temperature of the solutions consisting of 24 wt% Na_2CO_3 and 4 wt% $NaHCO_3$ for 30 min was carried out by varying the temperature from 82 ℃ to 94 ℃. According to the results of experiments, an optimum treatment temperature of 90 ℃ was determined for these conditions. Moreover, a lower temperature was insufficient to texture completely the surfaces, as the solution temperature reaches 90 ℃, the reflectivity changes little. Fig. 5 has proved the results and the weighted average reflectivity is 12.34%. The SEM images of these samples are shown in Fig. 6, which has revealed the process of texturing.

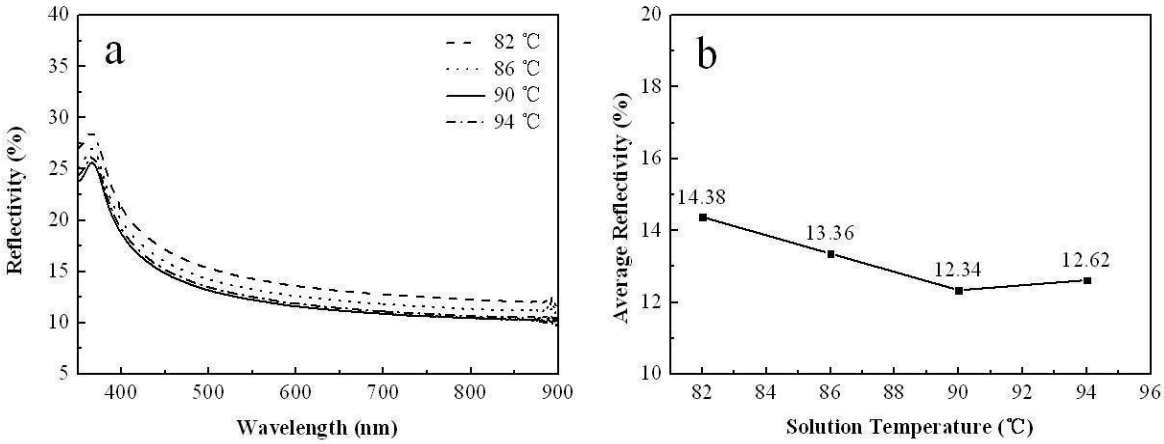

Figure 5. (a): The reflectivity of monocrystalline silicon wafers surface textured at different solution temperature.

(b): The average reflectivity of monocrystalline silicon wafers surface textured at different solution temperature.

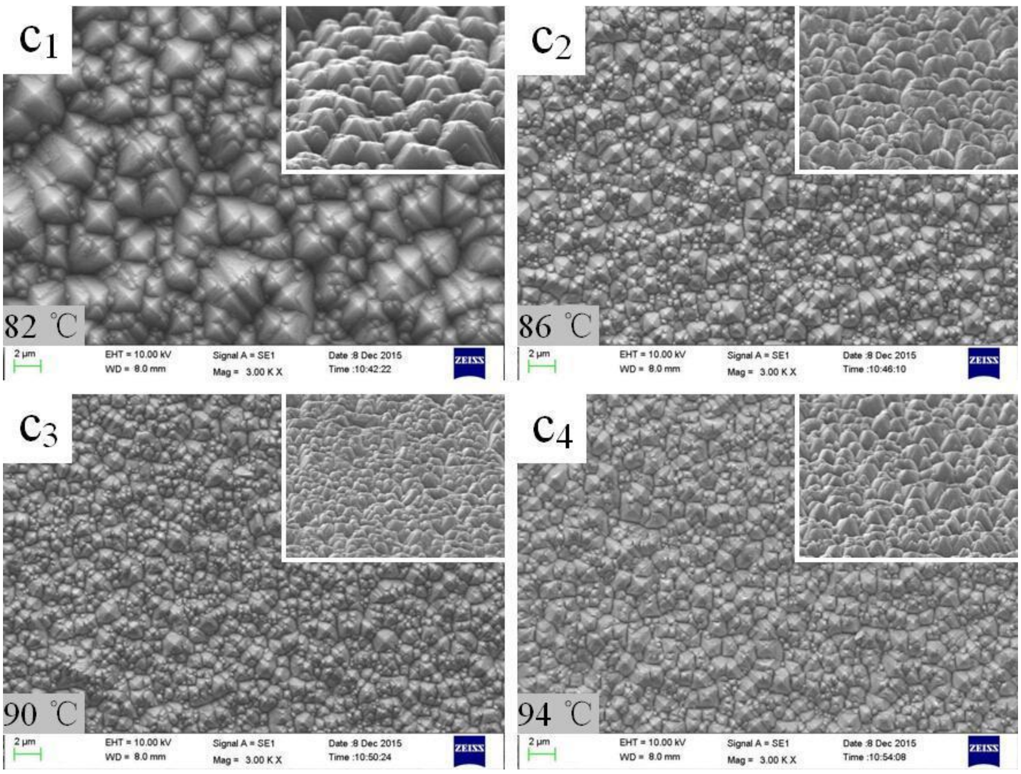

Figure 6. SEM images of monocrystalline silicon wafers surface textured at different solution temperature: c_1 (82 ℃), c_2 (86 ℃), c_3 (90 ℃), c_4 (94 ℃).

Conclusions

In this work, the texturization process of monocrystalline silicon wafers with sodium carbonate and sodium bicarbonate solutions have been studied. From this study, it has been found that it is not possible to completely textured surfaces and obtain a lower reflectivity by using aqueous solutions containing only Na_2CO_3. Moderate amounts of $NaHCO_3$ must be added in order to achieve entirely textured surfaces of higher quality. Thus, it can be considered that HCO_3^- ions perform an important role in moderating etching reactions, which seems to play the same role as IPA. Meanwhile, the effect of solution temperature in this etchant on the texturization has been also studied. The results show that our optimized process lasted for 30 min at 90 ℃ using a solution containing 24 wt% Na_2CO_3 and 4 wt% $NaHCO_3$. After texturing, for monocrystalline silicon wafers, we can obtain reliable and uniform pyramidal texturing surfaces with an average weighted reflectivity of 12.34%. It is hoped that it may lead to an increase in the photon absorption. Therefore, this technique provides an alternative way for the industrial production of high efficient solar cells.

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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