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On the texturization of monocrystalline silicon with sodium carbonate solutions

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Abstract

The texturization of monocrystalline silicon wafers using sodium carbonate solution has been investigated. This etching process has been evaluated in terms of the surface morphology and the reflectance value. The results show that for low concentration of sodium carbonate the increase of texturing time decreases the reflectance value because of the change in morphology from hillocks to pyramidal; on the contrary for intermediate and high concentrations the increase of time has a detrimental effect on texturization because it increases both the pyramid sizes and their non-uniform distribution. However, a good cell performance could be obtained by etching at high concentrations and short times.

Keywords: Monocrystalline silicon; Texturization; Reflectance; Sodium carbonate

1. Introduction

Anisotropic etching of single silicon crystals has been known for years and it is often used in the processing of silicon devices and microstructures (Holmes, 1962). A variety of structures e.g., triangular and rectangular grooves, pyramids, membranes and micro-holes have been made which have found widespread applications in devices. Pyramid formation on the surface of {100} monocrystalline silicon wafers with anisotropic texturing solutions is an important and effective means to reduce reflection losses from the front surface of silicon solar cells.

Anisotropic etchants for silicon are aqueous alkaline solutions where the main component can be either an organic or an inorganic compound (Seidel et al., 1990). The organic compounds, e.g., ethylenediamine and hydrazine, have found less acceptability due to their hazardous nature. Among the inorganic solutions, the most frequently used compounds are KOH and NaOH. Generally, a ternary mixture of KOH or NaOH with water and isopropyl alcohol (IPA) is employed to prepare a suitable surface in single crystalline silicon solar cell fabrication. Although isopropyl alcohol does not participate chemically in the reaction, its presence improves the etching behaviour by decreasing the etch rate.

In general, all aqueous solutions containing hydroxides of other alkali metals, like LiOH and CsOH perform in a similar manner. The most important feature of the anisotropic behaviour of alkaline etchant is the very low etch rate of {111} surface compared to {100} or {110} surfaces. Such strong dependence of etch rates on crystal orientation leads to pyramid formation on {100} silicon surface. The pyramid formation mechanism is currently still under discussion and different hypotheses have been expressed. Declerq et al. (1975) explain the appearance of pyramids from irregularities on the surface of the starting material and the chemical reaction of the etching process is involved with the formation and dissolution of hydrous

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silica. In some cases, this oxide does not dissolve locally fast enough and gives rise to the development of new pyramids. Kendall (1979) proposed that {1 1 1} planes oxidize more rapidly than others and therefore could be covered with a thin oxide layer immediately after immersion into the etchant. Seidel et al. (1990) give basic chemical reactions concerning the etching process. Glembocki et al. (1991) presented a further extension of this model. King and Buck (1991) suppose that the hydrogen bubbles evolving during the etching reaction play an important role. The bubbles stick to the silicon surface and their masking effect results in a lateral etching action of the solution, which is essential for the pyramid formation process. The diameter of the bubbles, their density and the rate of the etching reaction define the geometry of the textured silicon surface. Palik et al. (1983) assume that the anisotropy might be attributable to differences in the activation energies and in backbone geometries on different surfaces. On the other hand, Van Veenendal et al. (2001), in agreement with previous authors, propose that silicate particles adhering to the surface are responsible for the occurrence of the pyramidal protrusion. The hypotheses of these authors are in accordance with several experimental observations reported in the literature but a number of experimental results cannot be easily explained.

Although the most common etchants are aqueous solutions of sodium or potassium hydroxides with the addition of isopropyl alcohol, other groups of researchers reported the texturing with carbonates. Hezel et al. (1989) and Hezel (1990) have studied the influence of surface texturing on the optical, electrical and photovoltaic properties of metal–insulator–semiconductor mono and multicrystalline silicon solar cells; however, these authors gave few details on their texturing conditions with potassium carbonate (K_2CO_3). Chaoui et al. (1997) have presented the results of extensive experiments performed with K_2CO_3 solutions. Following Chaoui's work, Nishimoto and Namba (2000) investigated the texturing using sodium carbonate (Na_2CO_3) and sodium hydrogen carbonate ($NaHCO_3$), two chemicals which are widely used in glass industry. They prove Na_2CO_3 can successfully texture {1 0 0} oriented silicon wafers and the addition of $NaHCO_3$ accelerates the texturing process and the pyramidal size becomes smaller. Nevertheless, when comparing the texturing methods for monocrystalline silicon using KOH/IPA and Na_2CO_3/$NaHCO_3$ solutions, Sparber et al. (2003) observed that the formation of pyramids is different in both etchants. While in KOH/IPA solutions, the pyramids grow homogeneously distributed on overall surface, in the Na_2CO_3/$NaHCO_3$ case the pyramids grow at isolated spots. They say that it was not possible to texture a whole wafer without any blank areas.

Thus, the objective of this work is to investigate if Na_2CO_3 solutions can texture successfully monocrystalline silicon wafers since their use could reduce the texturing cost. Results such as reflection coefficients, surface homogeneity and pyramid size performed with different etching times and concentrations are analyzed.

2. Experimental

The experiments were performed with {1 0 0} oriented monocrystalline Czochralski silicon wafers, provided by ISOFOTON.

Before etching, wafers were cleaned by the following procedure. The first step was to degrease the samples by boiling the wafers in acetone during five minutes and then washed in ethanol. The second step was to remove damage on the surface caused by sawing. This step was carried out in NaOH solution. Afterwards the native oxide was removed by immersion of the samples in diluted hydrofluoric acid (HF, less than 10% wt) and rinsed in deionised water.

The cleaned wafers were held vertically in a specially designed Teflon jig placed inside the alkaline solution for a desired time. The wafers were etched in different solutions of Na_2CO_3 (5%, 15% and 25wt%) and deionised water at 95 °C. The temperature of the solution could be controlled with an accuracy of ±0.2 °C. The wafers were kept in each solution different times: 10, 20, 30 and 40 min. The samples were then washed in flowing deionised water followed by immersing in dilute HF to remove the metallic impurities. Finally, the wafers were washed again in flowing deionised water and they were dried with an air jet.

The surface morphology was studied with a Quanta 200 Scanning Electron Microscope (SEM). The total hemispherical reflectance was measured using an Ocean Optics PC-1000 spectrophotometer equipped with an integrating sphere (Ocean Optics ISP-REF).

3. Results and discussion

The morphology of textured silicon wafers has been investigated evaluating the influence of the duration of texturization process and the concentration of the alkaline solution on the surface reflectance.

Figs. 1 and 2 show the scanning electron microscope (SEM) pictures of silicon surfaces textured with two concentrations, 5 and 25 wt%, of aqueous Na_2CO_3 solutions. In these figures the letters a, b, c, and d indicate the duration of the etching process, being 10, 20, 30 and 40 min, respectively.

As it can be observed, for the Na_2CO_3 solution with a low concentration (5 wt%), a great density of hillocks without a regular arrangement or a uniform size distribution dominates the wafer surface (Fig. 1a and b). Moreover, there are zones, marked with an arrow in Fig. 1a, which looks like sharp grooves in the micrographs but they are in reality extended areas without texturing located between the large size adjacent hillocks. Increasing the texturing time the hillocks grow in size and they become more regular, as Fig. 1c shows, getting a pyramidal shape at 40 min as it can be well observed in Fig. 1d. For this time, the pyramid sizes range between 6 and 1 μm.

For intermediate and high concentrations (15 and 25 wt%) the etching behaviour is different. Surfaces textured

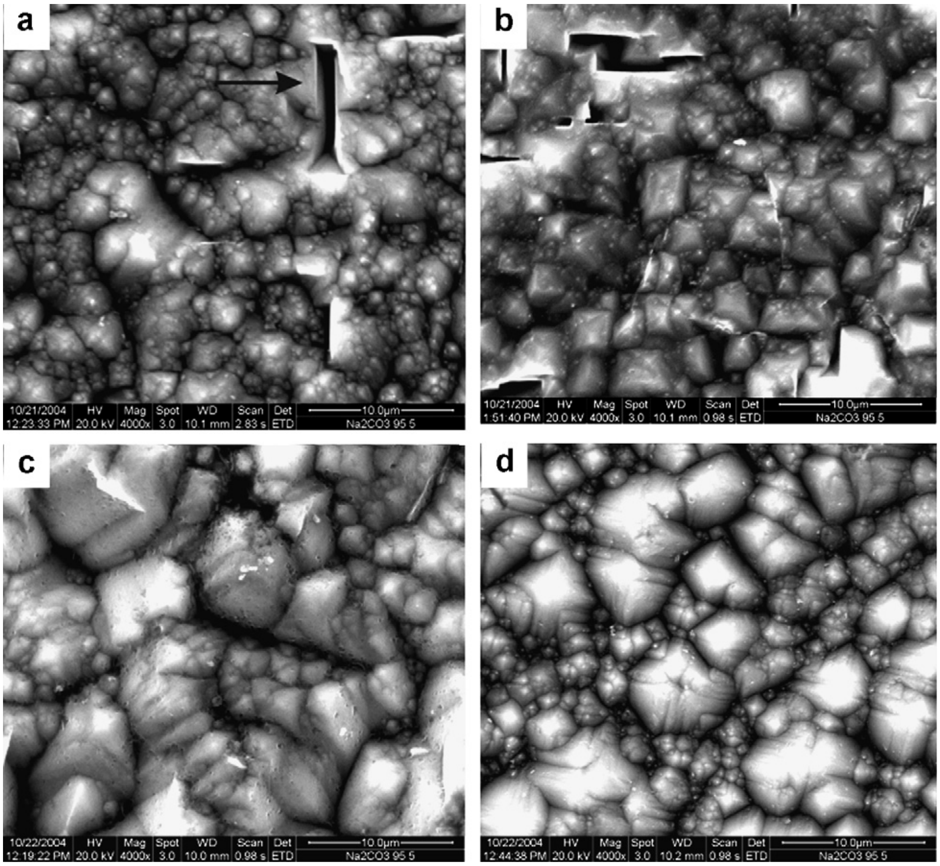

Fig. 1. SEM photographs at 4000× magnification of surface textured of silicon wafer after anisotropic etching in a 5 wt% Na_2CO_3 solution at 95 °C. (a)–(d) correspond to 10, 20, 30 and 40 min of texturization.

during 10 min show a high density of pyramids, a decrease of hillock population and an improvement of the uniformity in the size and shape of pyramids. This can be well observed in Fig. 2a. The average pyramid size corresponding to this etching conditions are between 3.5 and 1 μm.

An increase of etching time for these concentrations has a detrimental effect on texturing. Different phenomena take place. At 20 min (Fig. 2b) the pyramids and hillocks grow in size, the bigger size pyramids reach around 6 μm and it is important to note that this size does not change with a further increase of the etching time. For longer duration of texturization (30 min) the pyramids of medium size develop at expenses of smaller ones leading to an increase in the non-uniformity of the size distribution. Moreover, the small hillocks placed between the great pyramids begin to disappear, at their places deep-holes, like as ‘inverted pyramids’, are generated as can be seen from the micrograph shown in Fig. 2c. This process continues with the etching time and consequently a great density of this kind of structures is generated (Fig. 2d).

According to the results exposed above, it is clear that the solution concentration and the etching time have a strong effect on the texturing process. In this way, the reflectivity of the silicon surface strongly correlates to the pyramidal size and their homogeneity. Thus, the Fig. 3 shows the average reflectance of the textured silicon surfaces as a function of the etching time for the three Na_2CO_3 concentrations used in this work (5%, 15% and 25%). The integration of the reflectance values was carried out over a wavelength interval between 400 and 1100 nm. The reflectance results are a clear manifestation of the change in the pyramidal shape and size with time of texturization. As it can be expected, in the case of low concentrations the average reflectance decreases with the increase of time, due to the change in the pyramidal shape. Nevertheless, for higher concentrations the behaviour is the opposite one. This reflectivity worsening can be explained from two facts. On one hand there is an increment of the pyramids size (from 10 to 20 min of etching time) and, in accordance to Kim and Kim (2004), pyramids should be smaller than 4 μm for the best cell performance. On the other hand, in these conditions, the non-uniformity in the distribution of sizes gets larger with the etching process as it can be observed in Fig. 4, where the difference between the pyramid base width of the bigger and smaller pyramids (Δ) versus the etching times has been represented.

Our results prove, in accordance with those published by Nishimoto and Namba (2000), that silicon wafers successfully texture for high concentrations (25 wt%) and short time (10 min) at 95 °C. However, the reflectivity values given by these authors do not change or slightly improve with the etching time, although the size of their pyramids

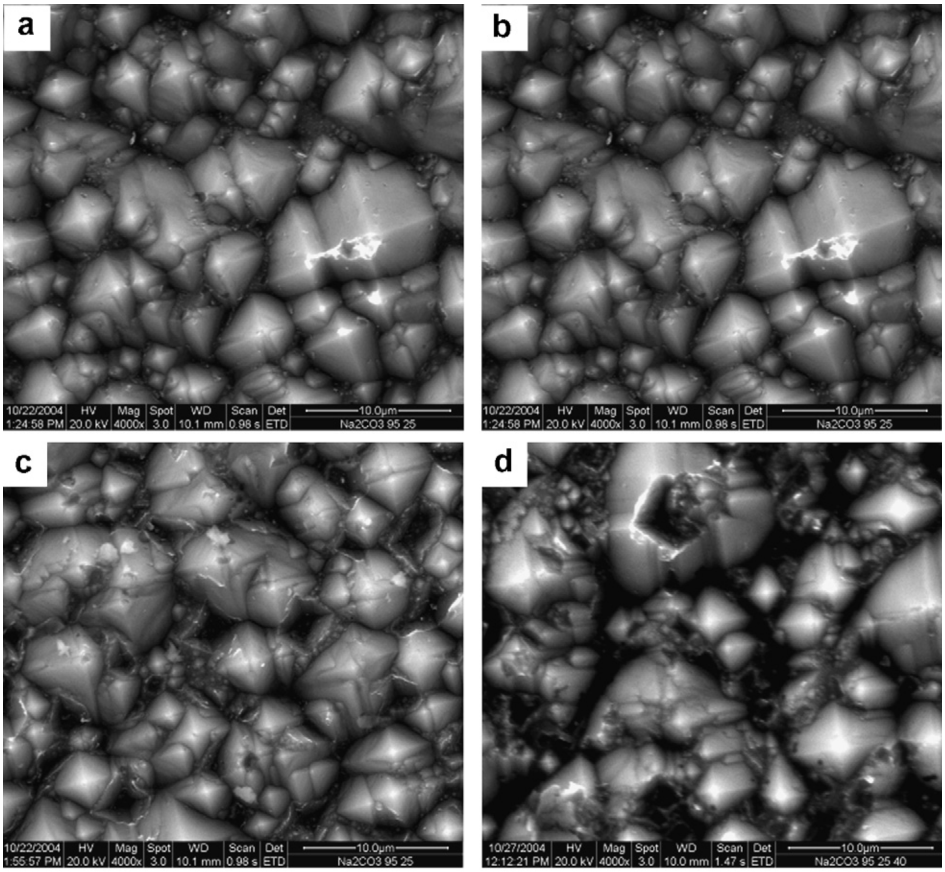

Fig. 2. SEM photographs at 4000× magnification of surface textured of silicon wafer after anisotropic etching in a 25 wt% Na_2CO_3 solution at 95 °C. (a)–(d) correspond to 10, 20, 30 and 40 min of texturization.

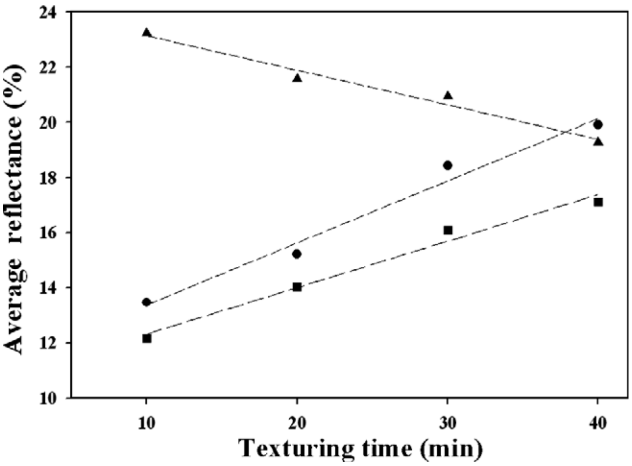

Fig. 3. Average reflectance of silicon wafers as a function of texturing time for different Na_2CO_3 concentrations: (▲) corresponds to 5 wt%, (●) corresponds to 15 wt% and (■) corresponds to 25 wt%.

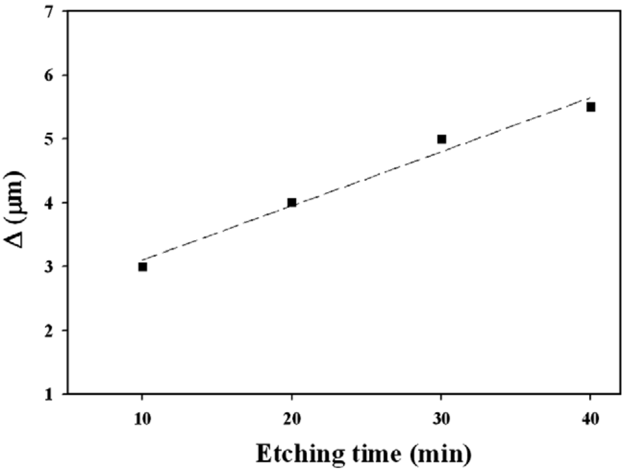

Fig. 4. Difference between the pyramid base width of the bigger and smaller pyramids, Δ, versus the etching time for a 25 wt% Na_2CO_3 concentration at 95 °C.

grow. These observations are not in agreement with our experimental results that prove how the increment and the non-uniform distribution in the pyramid sizes have a detrimental effect in the texturing process and consequently in the reflectivity.

4. Conclusions

The texturization of monocrystalline silicon using sodium carbonate solutions has been investigated. It is shown that the solution concentration and the etch time determine the texture of the silicon surface. For low concentrations, the increase of texturing time reduces the reflectance value due to the change in the morphology from hillocks to pyramids but not so much to get a good cell performance. This can be obtained by etching at high concentrations (25 wt%) for short times (10 min) at 95 °C. On the other hand, for intermediate and high concentrations, the increase of texturing time has a remarkably detrimental effect on the texturization due to an increase in both the sizes of pyramids and their non-uniformity in the distribution.

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