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Texturization of Silicon Wafers for Solar Cells by Anisotropic Etching with Sodium Silicate Solutions

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Abstract. The efficiency of silicon solar cells greatly depends on the texturization of silicon wafers used in their fabrication. Texturization reduces the reflectance of the silicon surface which improves the light trapping ability of the solar cells.

In this study, aqueous Na_2SiO_3 solutions were used as etchants in the texturization of monocrystalline silicon wafers. The main objective was to evaluate the performance of the etchant based on the silicon surface reflectance. The surface morphology and etching rate were also investigated. Results showed that Na_2SiO_3 solutions reduced the surface reflectance of the wafers better than other alkaline etchants. This was brought about by the formation of uniformly distributed pyramidal structures on the surface of the wafer after texturization. The effects of process parameters such as Na_2SiO_3 concentration, solution temperature and etching time on the reflectance were evaluated and optimized by applying ANOVA and Response Surface Method (RSM). The optimum process condition was found to be 6.2 wt% Na_2SiO_3, 80°C and 5 min at which the reflectance of the silicon wafer was reduced to 9.27%. Furthermore, the addition of small amounts of IPA (up to 0.03 wt%) to the Na_2SiO_3 solution reduced the reflectance of the wafer (9.13%) and slightly improved its wettability.

Key words

Anisotropic etching, monocrystalline silicon, reflectance, sodium silicate, texturization

1. Introduction

Texturization of the surface of {100} monocrystalline silicon wafer by anisotropic etching is an effective means that is widely used to reduce surface reflectance and enhance light trapping in silicon solar cells. The etching process leads to the formation of {111} pyramidal structures on the silicon surface which geometries allow light to be more easily coupled into the silicon and efficiently absorbed into the solar cell.

Anisotropic etching employs aqueous alkaline solutions of organic or inorganic compounds. Current practices usually utilize alkaline etchants which are aqueous solutions of NaOH or KOH with isopropyl alcohol (IPA) as surface-active additive. The aqueous alkaline solutions (NaOH or KOH) etch the silicon surface anisotropically, producing uniform pyramid textures, while IPA tends to improve the wettability of the wafer surface [1-2]. These solutions are also preferred due to cost and time efficiency considerations. However, anisotropic etching process works with some disadvantages such as lack of pyramid size control, poor reproducibility and difficulty in controlling the concentration of IPA [3].

While more advanced techniques were claimed to have better performance than anisotropic etching, most of them still remain to be more complex and costly. Thus, significant interest has still been given to the search for novel alternative texturing solutions that are cost-effective. Some of the novel etchants reported in literatures include solutions of NaOH and anhydrous sodium acetate [4], tetramethyl ammoniun hydroxide, TMAH [5], sodium carbonate and sodium bicarbonate [1]. In the present work, we aimed to investigate another etchant, sodium silicate (Na_2SiO_3) solution, for its potential use in the texturization of monocrystalline silicon wafer for solar cell applications. The main objective was to evaluate the performance of the etchant based on the silicon surface reflectance and morphology and the etching rate. The effects of process parameters such as Na_2SiO_3 concentration, solution temperature and etching time on the reflectance were investigated and optimized by applying ANOVA and Response Surface Method (RSM). Furthermore, the effects of the addition of IPA to the Na_2SO_3 solution on the reflectance of the silicon wafer and its wettability were investigated.

2. Experimental

The experiments were performed with p-type {1 0 0} oriented microcrystalline silicon wafers obtained from Sino-American Silicon Products, Inc.

Before etching (texturization), the unpolished silicon wafer was cleaned by immersing it in aqueous HF solution (< 5wt%) for 30 s to remove the native oxides from the silicon surface, followed by rinsing with deionized water and finally dried with nitrogen gas. The etching process was done by immersing the cleaned wafer into the etching solution which was maintained at the desired temperature for a specific etching time. Then, the wafer was immersed in HNO_3 solution (< 10wt%) to remove the adhering etchant solution, followed by rinsing with deionized water and drying using nitrogen gas.

Prior to etching with Na_2SiO_3 solutions, preliminary experiments were first conducted to assess the effectivity of various etchants in reducing the reflectance of the silicon surface. The etchants investigated were aqueous solutions of NaOH (2 wt%), Na_2CO_3 (4.8 wt%), $Na_3PO_4 \cdot 12H_2O$ (14 wt%) and Na_2SiO_3 (5 wt%). From which texturization by aqueous Na_2SiO_3 was found to yield the lowest value of the surface reflectance. The etching of the silicon wafer was then tested using aqueous solutions of Na_2SiO_3 of varied concentrations (2, 4, 6, 8 and 10 wt%) at different solution temperatures (70 – 90)°C and etching times (5 – 25) min. Experiments were also conducted using aqueous Na_2SiO_3 + IPA (0.03, 0.05, 0.1, 0.5 and 1 wt%) solutions.

The surface reflectance was measured using a solar cell surface optical characteristics measurement system (MFS-630) from Yoli Kew Co. Ltd. The surface morphology was analyzed by a Scanning Electron Microscope, SEM (S-4700 type II) from Hitachi Co. Ltd.

3. Results and Discussion

A. Preliminary evaluation of the effectivities of various etchants to reduce surface reflectance

The choice of the etchant Na_2SiO_3 solution was based on the preliminary experiments conducted using a variety of known aqueous alkaline etchants: NaOH (2 wt%), Na_2CO_3 (4.8 wt%), $Na_3PO_4 \cdot 12H_2O$ (14 wt%) and Na_2SiO_3 (5 wt%). The silicon wafers were etched, separately, using these solutions at 80°C for 10 min. The surface reflectances were measured and the morphologies of the etched wafers were determined. Results showed that texturization using aqueous Na_2SiO_3 yield the lowest value of the surface reflectance (Table I) at an etching rate of 0.384 $mg \cdot cm^{-2} \cdot min^{-1}$ that was quite comparable to that of aqueous NaOH. The low reflectance could be explained by the formation of more uniformly sized and shaped pyramids on the surface of silicon wafers etched using the latter as compared to those etched using the other three solutions such as observed in Fig. 1. These findings reveal the potential of aqueous Na_2SiO_3 solutions as promising etchants in the texturization of silicon wafers.

Table I. – Surface reflectance of wafers after anisotropic etching with various etchants for 10 min at 80°C

ETCHANT	REFLECTANCE (%)	ETCHING RATE ($mg \cdot cm^{-2} \cdot min^{-1}$)
NaOH (2 wt%)	15.07 ± 0.16^a	0.348
Na_2CO_3 (4.8 wt%)	14.71 ± 0.23	0.089
$Na_3PO_4 \cdot 12H_2O$ (14 wt%)	10.96 ± 0.10	0.186
Na_2SiO_3 (5 wt%)	10.35 ± 0.30	0.384

[a] Standard deviation of three independent runs.

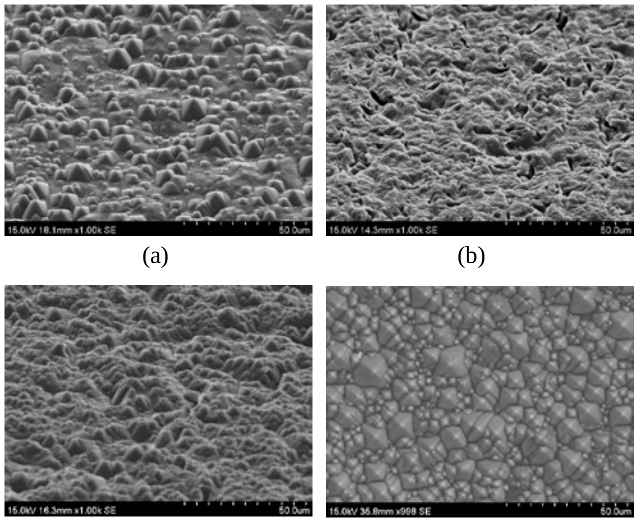

Fig. 1. SEM images of silicon wafers after anisotropic etching for 10 min at 80°C in aqueous solutions of: (a) 2 %wt NaOH; (b) 4.8 wt% Na_2CO_3; (c) 14 wt% $Na_3PO_4 \cdot 12H_2O$; (d) 5 wt% Na_2SiO_3.

B. Optimization of process conditions for wafer texturization using Na_2SiO_3 solutions

Effects of process parameters such as Na_2SiO_3 concentration, solution temperature and etching time on the reflectance of the silicon wafer surface were investigated. Initial evaluation was carried out by etching silicon wafers in different Na_2SiO_3 solutions and varying the solution temperatures and etching times. One-way analysis of variance (ANOVA) was applied as this allowed the evaluation of the effect of each parameter on the reflectance of the wafer. At a level of significance (α) of 0.05, the analysis revealed that the etching temperature had no significant effect on the reflectance with a *P*-value of 1.0 whereas 0.037 and 0.033 were obtained for Na_2SiO_3 concentration and etching time, respectively. From the initial experiments, it was observed that etching at 80°C yield, relatively, the lowest reflectance of the wafer; thus, this temperature was used in the succeeding experiments.

The effects of the Na_2SiO_3 concentration and etching time were evaluated further. The results of the etching experiments are summarized in Table II. It can be observed that no systematic trend was observed pertaining to the effect of varying Na_2SiO_3 concentrations and etching times. Nonetheless, the lowest reflectance (9.35 %) was obtained from texturization by 6 wt% Na_2SiO_3 at 80°C for 5 min while the highest (13.96%) was from texturization by 2 wt% Na_2SiO_3 at 80°C for 15 min.

Using the data presented in Table II, Response Surface Method (RSM) was applied to determine the optimum condition (having the lowest reflectance) for the etching process. By this method, the dependence of the reflectance on both the Na_2SiO_3 concentration and etching time was modeled via quadratic equation of the form

$$\begin{aligned}\text{Reflectance}_{\text{ave}} / \% = 14.64 - 1.812C + 0.116t \\ + 0.142C^2 - 0.002t^2 - 0.005Ct\end{aligned} \quad \textbf{(1)}$$

where C is the concentration of Na_2SiO_3 in wt% and t the etching time in min. A 3D optimization plot (Fig. 2) was then generated from the results of the calculations using Eq. (1).

Table II. – Surface reflectance of wafers after anisotropic etching using various etchants for 10 min at 80°C

ETCHANT	REFLECTANCE (%)	ETCHING RATE ($mg \cdot cm^{-2} \cdot min^{-1}$)
2 wt % Na_2SiO_3		
5	13.32 ± 0.32	0.220
10	13.65 ± 0.34	0.160
15	13.96 ± 0.59	0.137
20	13.02 ± 0.52	0.136
25	12.08 ± 0.18	0.134
4 wt % Na_2SiO_3		
5	12.78 ± 0.50	0.389
10	9.62 ± 0.01	0.328
15	10.40 ± 0.05	0.279
20	10.45 ± 0.36	0.256
25	10.73 ± 0.16	0.244
6 wt % Na_2SiO_3		
5	9.35 ± 0.27	0.477
10	9.47 ± 0.27	0.391
15	9.69 ± 0.09	0.322
20	10.09 ± 0.10	0.300
25	10.43 ± 0.06	0.285
8 wt % Na_2SiO_3		
5	10.68 ± 0.59	0.539
10	10.30 ± 0.22	0.461
15	10.41 ± 0.12	0.379
20	10.48 ± 0.12	0.359
25	10.63 ± 0.12	0.337
10 wt % Na_2SiO_3		
5	11.54 ± 0.68	0.671
10	11.14 ± 0.08	0.572
15	10.48 ± 0.13	0.505
20	10.57 ± 0.15	0.471
25	10.66 ± 0.13	0.441

As shown in Fig. 2, the optimum concentration of Na_2SiO_3 and etching time were at 6.2 wt% and 5 min, respectively. Thus, the optimization of the process variables yield the condition: C = 6.2 wt%, T = 80°C and t = 5 min. This optimum process condition was finally used in the texturization of the silicon wafer. The reflectance of the etched wafer was found to be 9.27%. This low value of the reflectance is a manifestation of the dense, uniformly distributed pyramid structures formed on the surface of the silicon wafers upon texturization. The SEM image of the wafer textured at the optimum condition is shown in Fig. 3.

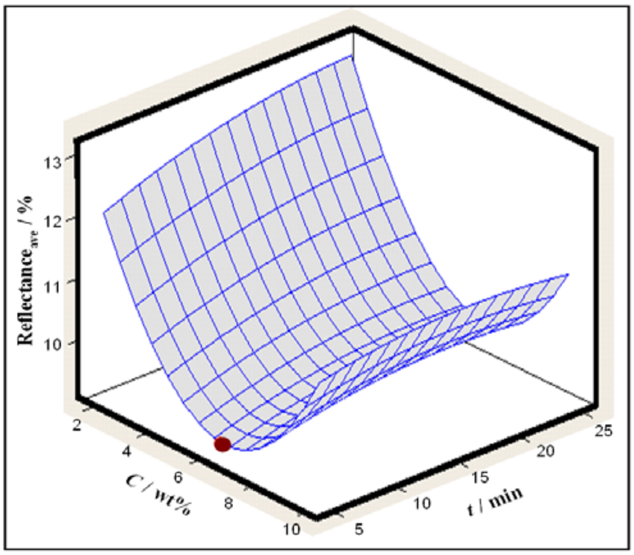

Fig. 2. Reflectance of silicon wafer as a function of Na_2SiO_3 concentration and etching time: red dot represents the optimum condition [as calculated from Eq. (1)].

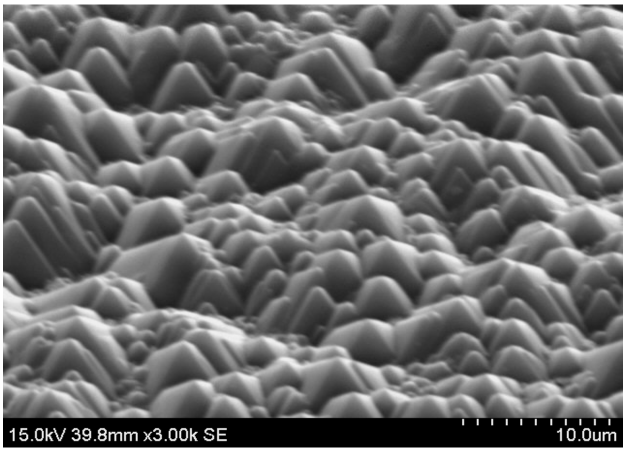

Fig. 3. SEM image of the silicon wafer after anisotropic etching with 6.2 wt% Na_2SiO_3 at 80°C and 5 min.

It is also apparent that the reflectance of the etched wafer is affected by the etching rate. The lowest value of the etching rate obtained was 0.160 $mg \cdot cm^{-2} \cdot min^{-1}$ (textured by 2 wt% Na_2SiO_3 at 80°C for 10 min) while the highest was 0.671 $mg \cdot cm^{-2} \cdot min^{-1}$ (textured by 10 wt% Na_2SiO_3 at 80°C for 5 min). As shown in Fig. 4, generally, low reflectance values were obtained at etching rates 0.3 – 0.5 $mg \cdot cm^{-2} \cdot min^{-1}$. In this range, the reflectance values were less than 11%.

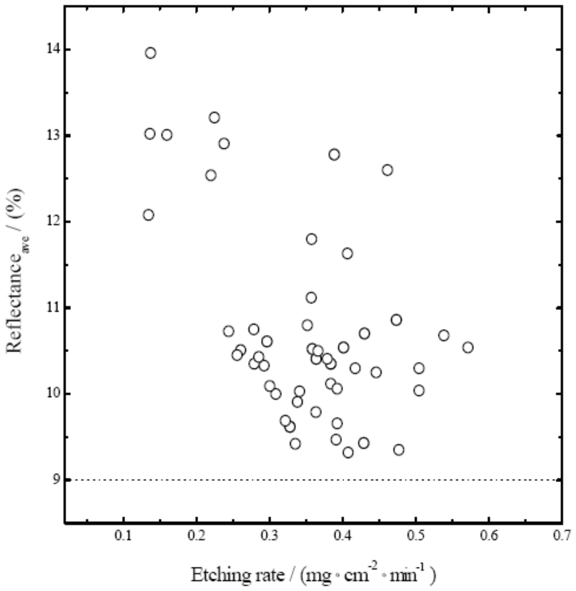

Fig. 4. Reflectance of the textured silicon wafers as a function of etching rate.

C. Addition of IPA to etching solutions

In industrial applications, one problem in the texturization of silicon wafers is the formation of bubbles that adhere on the wafer's surface and inhibiting its texturization. A study reported that the addition of IPA increases the wettability of the silicon surface resulting in the removal of the adhering bubbles [2]. Thus, in this study, we considered the addition of IPA in concentrations (0.03, 0.05, 0.10, 0.50 and 1.0 wt%) to the 6.2% Na_2SiO_3 solution and investigated its effect on the texturization of the silicon wafer. After etching at 80°C and 5 min, the reflectance of the silicon surface was measured and the contact angle was determined via Magic Drop (model 2000) to assess its wettability. The results of the analyses are summarized in Table III along with the etching rates. Results showed that only a small amount of IPA was necessary to improve the reflectance of the silicon surface. Addition of up to 0.03% IPA to the 6 wt% Na_2SiO_3 solution resulted in decreased reflectance of the textured wafer (from 9.27% to 9.13%). However, when added in higher concentrations, IPA increased the reflectance of the silicon surface. It was also apparent that as the concentration of IPA was increased in the solution, the etching rate decreased. These indicate that IPA has detrimental effects on the texturization of silicon wafers using Na_2SiO_3 when used in high concentrations. Nonetheless, the IPA seemed to improve the wettability of the surface as evidenced by the decreasing values of the contact angle as the IPA concentration increased. It is also worthy to note that the addition of IPA to 6.2 wt% Na_2SiO_3 to only up to 0.03 wt% did not significantly improve the wettability of the surface. It can be said that using the Na_2SiO_3 solution without IPA would be a viable choice since IPA also pose some disadvantages in the texturization process.

Table III. – Effects of IPA on the texturization of silicon wafers using 6.2 wt% Na_2SiO_3 + IPA at 80°C and 5 min.

IPA CONC. (wt%)	REFLECTANCE (%)	ETCHING RATE ($mg \cdot cm^{-2} \cdot min^{-1}$)	CONTACT ANGLE (°)
0	9.27 ± 0.27	0.486	38.6
0.03	9.13 ± 0.09	0.461	37.7
0.05	9.58 ± 0.06	0.448	37.3
0.10	10.16 ± 0.13	0.412	36.1
0.50	11.53 ± 0.11	0.373	26.9
1.00	12.13 ± 0.12	0.340	22.5

4. Conclusion

Texturization of monocrystalline silicon wafer for solar cells using aqueous Na_2SiO_3 solutions as etchant was successfully carried out. Results showed that Na_2SiO_3 solutions can reduce the surface reflectance of the wafers better than other alkaline etchants. The effects of process parameters such as Na_2SiO_3 concentration, solution temperature and etching time on the reflectance of the wafer were evaluated and process optimization was carried out. Using one-way ANOVA, the solution temperature was found to have no significant effect on the reflectance. Using RSM, the optimum condition (to obtain the lowest reflectance) for the etching process was determined to be: 6.2 wt % Na_2SiO_3, solution temperature = 80°C and etching time = 5 min where the reflectance of the silicon wafer was reduced to 9.27%. SEM images showed that the texturization of the silicon surface by the Na_2SiO_3 solutions resulted in the formation of uniformly distributed pyramidal structures on the surface of the wafer. Furthermore, the addition of small amounts IPA (up to 0.03 wt%) to the Na_2SiO_3 solution reduced the reflectance of the wafer and slightly increased its wettability.

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