Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Optimization of Chemical Texturing of Silicon Wafers Using Different Concentrations of Sodium Hydroxide in Etching Solution

P. Fallahazad, N. Naderi*, M. J. Eshraghi, A. Massoudi

Department of Ceramic, Materials and Energy Research Center, Karaj, Iran.

PAPER INFO

Paper history:
Received 27 May 2017
Accepted in revised form 12 December 2017

Keywords:
Silicon Pyramid
Nanostructures
Antireflection
Chemical Etching
Surface Texturing

ABSTRACT

Surface texturing is one of the methods that improve the conversion efficiency of silicon-based solar cells by increasing the light trapping. The anisotropic texturing of p-type silicon (100) surface was performed using alkaline etching solution of sodium hydroxide (NaOH) including isopropyl alcohol (IPA) and hydrazine hydrate. The optical properties of etched wafers were investigated using reflectance spectrometer and morphology of surface was studied using scanning electron microscopy (SEM). Influence of NaOH concentration on etched wafers was studied and optimum value of surface reflectance was obtained by applying the best concentration of alkaline solution (NaOH).

1. INTRODUCTION

Surface texturing of silicon wafer is a widely used process in various applications such as solar cell industry and detector applications. The most suggested etchants are sodium hydroxide (NaOH) and potassium hydroxide (KOH) [1]. In 1967, Price used chemical etching of silicon for the first time [2]. His etching solution was composed of potassium hydroxide (KOH), water (H_2O) and isopropyl alcohol (IPA). In 1969, Lee developed this method by applying hydrazine hydrate (N_2H_4) in the etching solution [3]. Hydrazine played the role of oxidant and IPA was a complex agent. In this study, silicon texturing was investigated by applying alkaline anisotropic etching solution consisting of sodium hydroxide (NaOH), isopropyl alcohol (IPA), and hydrazine hydrate. The advantage of alkaline anisotropic etching solution is homogeneous etching of Si (100) substrates. In this report, we have optimized texturing of silicon for trapping the incident light in order to reduce light reflection from silicon surfaces. This technique was used in thin film solar cells to achieve a higher efficiency. The etching process leads to the formation of pyramidal structures with plane orientation of {111} on surface of substrate.
Fig. 1 schematically shows the formation of pyramidal structures.

*Corresponding Author's Email: n.naderi@merc.ac.ir (N. Naderi)

Figure 1. Schematic of silicon surface before and after etching

2. MATERIALS AND METHOD

2.1. Chemical cleaning of silicon

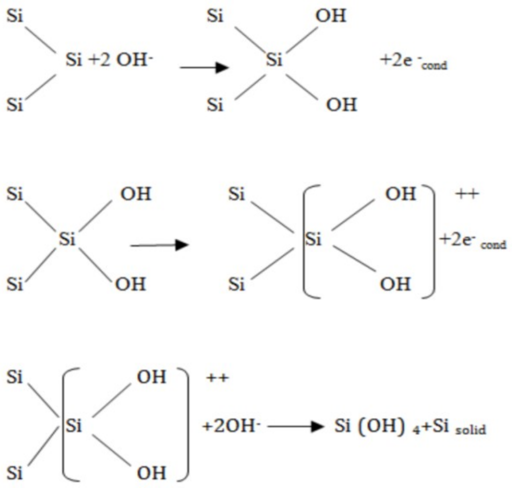
A high-doped p-type silicon (100) wafer with resistivity in range of 1-35 Ωcm was used as the substrate. The experiments were performed on square samples (20 mm × 20 mm) with a thickness of 250 µm. before etching, silicon surface was chemically cleaned using a conventional RCA method to remove the particulate matters on the surface [4]. Adopting the method, the substrates were successively dipped in 1:1:5 (by volume) of NH_4OH:H_2O_2:H_2O for 10 min, 1:50 (by volume) of HF:H_2O for 20 s, and then in 1:1:6 (by volume) of HCl: H_2O_2: H_2O for another 10 min. The samples were then washed with deionized water (DI).

2.2 Chemical etching of silicon

Silicon pyramidal structures were fabricated using a two-step chemical etching process. In the first step, silicon substrates were dipped in a mixture of isopropyl alcohol (C_3H_8O), sodium hydroxide (NaOH, 3wt.%), and hydrazine hydrate (N_2H_4, 3 wt.%) at 85 °C for 1 h. In the second step, the samples were immersed into hydrogen chloride (HCl, 0.1 M) for 24 h at ambient temperature.

3. RESULT AND DISCUSSION

During the texturing process of silicon, hydroxyl ions (OH^-) are bonded to two Si dangling bonds. The Si-OH bond makes the two silicon back bonds weak. Therefore, the silicon hydroxide complex is formed. After this process, the monosilicic acid is formed. The four electrons in the silicon conduction band are transferred to four water molecules.
The details of chemical reactions for etching of silicon are based on the following equations;



$$Si(OH)_4 \longrightarrow SiO_2(OH)_2^{--} + 2H^+$$

$$2H^+ + 2OH^- \longrightarrow 2H_2O$$

The morphology of etched surface is dependent on several parameters such as temperature, concentration solution, etching time, atomic defects and crystallographic orientation of Si wafers. One of the most important parameters is the positions of atoms in Si lattice. Fig. 2 shows different crystal planes of Si described by Miller indices. The density of Si atoms which are in (111) plane is higher than that in (100) plane, therefore (100) planes can be easily dissolved in etchants but (111) planes are more resistive to the etchants and the etch rates of these planes are slower. Therefore, micro-pyramids of silicon are formed by anisotropic etching of silicon wafer with (100) crystal orientation [5-6].
The alkaline etching temperature was 85°C and the NaOH concentration was varied from 1 to 3 wt.% while the IPA and hydrazine concentration was maintained constant.

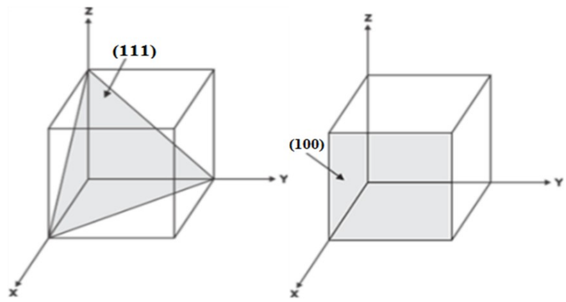


Figure 2. Miller indices and crystal planes in a cubic unit

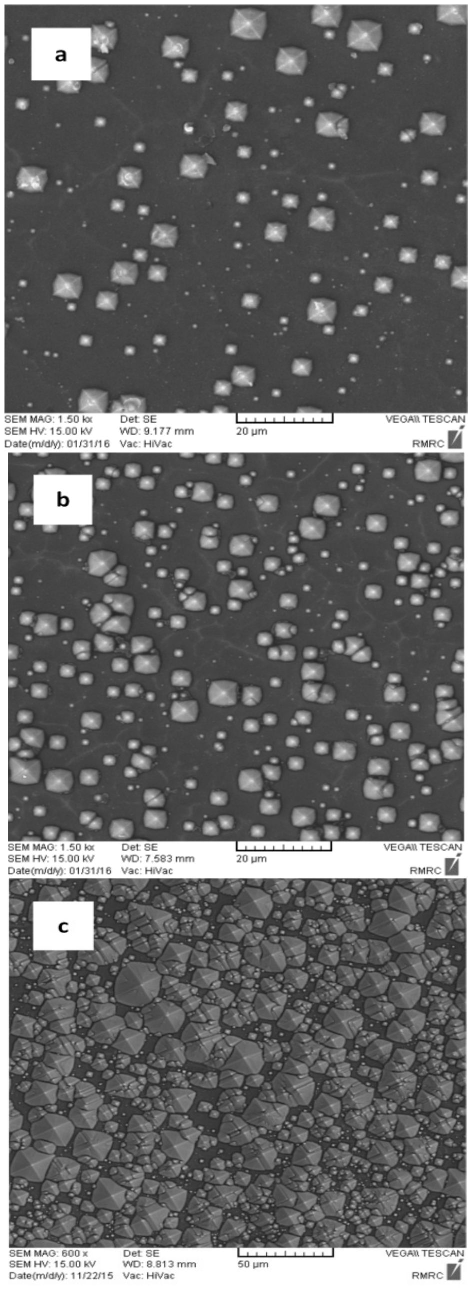


Figure 3. SEM micrographs of silicon micro-pyramids which were etched with different concentrations of a) 1, b) 2, and c) 3wt.% of NaOH

Fig. 3 shows SEM micrographs of silicon wafers etched in a NaOH-IPA solution. Figs. 3(a) and 3(b) show the pyramidal structure of etched Si wafers with 1 and 2 wt.% of NaOH, respectively.

In these figures, small micro-pyramids are visible. However, the whole surface is not covered by pyramids. It is due to the low concentration of etching solution. Fig. 3(c) shows that applying a higher concentration of NaOH (3 wt.%) will improve the size and uniformity of pyramids. For this sample, micro-pyramids covered the whole surface of Si substrate.

The surface optical properties play an important role in solar cell applications. Generally, texturing process reduces the light reflectance of polished silicon.

Fig. 4 shows a comparison between the reflectance curves of silicon wafers which were textured at various concentration.

The spectrum of bare silicon is also shown for comparison. Compared to the bare silicon, the pyramidal textures have relatively low reflectance in visible region. The sample with 3 wt.% of NaOH shows minimum value of reflectance. In higher wavelengths, the difference between reflectance spectra is even larger.

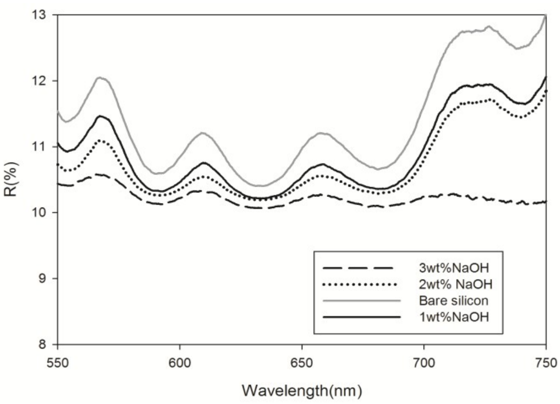


Figure 4. Reflection spectra of the bare silicon surface and the Si pyramidal structures with different concentrations of etching solutions

4. CONCLUSIONS

Silicon micro-pyramidal textures were fabricated by chemical etching process in order to reduce the reflectance spectra of crystalline silicon surface in visible range. The Si pyramids with high uniformity can provide high antireflection properties. Therefore, it can promise potential applications in highly efficient, silicon-based solar cells. In this report, formation of Si micro-pyramidal structures was optimized by applying different concentration of NaOH in etching solution.

5. ACKNOWLEDGMENTS

This work was supported by Materials and Energy Research Center [Grant number: 471394052].

REFERENCES

1. Hylton, J.D., Burgers, A.R., Sinke, W.C. and Energy, E.S., "Light trapping in alkaline texture etched crystalline silicon wafers" ***Proceedings of XVI European Photovoltaic Solar Energy Conference***, (2000).
2. Price, J.B., "Anisotropic Etching of Silicon with KOH", ***Journal of the Electrochemical Society***, Vol. 120, No. 3, (1973).
3. Lee, D.B., "Anisotropic etching of silicon", ***Journal of Applied physics***, Vol. 40, No. 11, (1969), 4569-4574.
4. Naderi, N., Hashim, M.R., &Amran, T.S.T., "Enhanced physical properties of porous silicon for improved hydrogen gas sensing", ***Superlattices and Microstructures***, No. 5, (2012), 626 -634.
5. Bean, K.E., "Anisotropic etching of silicon", ***IEEE Transactions on Electron Devices***, Vol. 25, No. 10, (1978), 1185-1193.
6. Xiang, Z., Liu, C. and Lai, C., "Corrosion of Fresh Porous Silicon in Potassium Hydroxide Solution", ***International Journal of Electrochemical Science,*** Vol. 10, (2015), 3935-3948.