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Texture Etching of Monocrystalline Silicon in Sodium Hypochlorite Solution

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Abstract

Alkaline etching has been widely used in silicon technology and applied for different purposes such as damaged layer removal from silicon surfaces, micro-membrane and complex micro-device fabrication for micro-sensor [1] and for micro-optical elements [2]. In the fabrication of solar cells, silicon wafers are generally etched in an anisotropic alkaline solution. It leads to formation of pyramid structure on the surface of the wafer to reduce the reflection loss from the front surface [3]. Different etching solutions have been reported in the literature to texture the silicon surface. In the case of monocrystalline silicon, mixed alkaline solutions of sodium hydroxide (NaOH) or potassium hydroxide (KOH) with higher concentrations of isopropyl alcohol (IPA) are the most used solutions to texture the silicon surface [4, 5]. Recently, a strong oxidizing reagent NaOCl has been used successfully by several authors to texture the silicon surface [6, 7]. Moreover, NaOCl is cheaper than other etchants and is also largely used in industry. However, the most important inconvenient of NaOCl is its instability, it decomposes in solution. In this work, the effect of the etching parameters such as solution composition, solution temperature on the silicon surface morphology is studied. The surface of etched samples was characterized by Scanning Electron Microscopy (SEM) and Spectrophotometry. The results clearly show a formation of a homogeneous pyramidal structure and an optimal size of pyramids on the silicon surface. The textured silicon surface exhibits a lower average reflectivity (about 9%) in the main range of solar spectrum (500- 1000nm).

Keywords: anisotropic etching/ silicon/ pyramidal structures;

1. Introduction

One of the disadvantages of low cost processing of multicrystalline silicon for solar cells as compared to monocrystalline silicon is the difficulty of successfully texturing wafers or sheets for reduced reflectivity. Monocrystalline wafers, especially (100) oriented wafers, can be easily texture etched by different alkaline etches like KOH or NaOH. As a strong oxidizing reagent, NaOCl, which has some remarkable properties, has been used in industrial production for many years. This etch works anisotropically and leads to the well known random pyramids. The contaminated crystalline silicon wafers can also be submitted to the hot NaOCl solution to remove organic contaminants owing to its oxidizing properties [8]. Moreover, NaOCl is cheaper than other relative etchants. Therefore, it seems that if NaOCl can be used for wafer texturing, the cost of monocrystalline silicon solar cells will be further reduced. Our work does show that NaOCl is a good etchant for silicon surface texturization and no

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problem of instability. Using NaOCl as an etchant a uniform pyramidal structure on the silicon surface can be reached, and the sizes of most pyramids are below 4 μm , which meets the requirement for the best performance [9]. The reflectivity of monocrystalline silicon surface textured with NaOCl is lower than that of silicon surface unetched in the spectrum range of 500-1000 nm.

2. Experimental details

Our experiments were carried out with p-type, 1-10 $\Omega\text{ cm}$, (100) oriented CZ-Si wafers. The texturing process was implemented by two steps. The first step is to remove the adsorbed dust and contamination on silicon surface. It was carried out in acetone; ethanol and deionized water then the native oxide on the wafers was removed by etching in diluted hydrofluoric acid (HF, about 5%). The second step is carried out on a cleaned surface. The wafers were etched in a mixed solution consisting of 5% NaOCl and 10% $\text{CH}_3\text{CH}_2\text{OH}$ at 80°C with an accuracy of $\pm 1^\circ\text{C}$, and the reaction time was set to 5min, 10min, 15min, respectively. Finally, the textured wafers were washed again in flowing deionized water and dried with clean, compressed air.

3. Results and discussion

The etching rate of sodium hypochlorite solution on mono-crystalline silicon (100) surface depends on its concentration [10], and it is a parameter that must be controlled in order to obtain a uniform pyramidal structure and an optimal pyramidal size on the silicon surface, which will affect the surface reflectance [11]. Fig.1 shows the scanning electron microscope (SEM) pictures of silicon surface etched with NaOCl for different times.

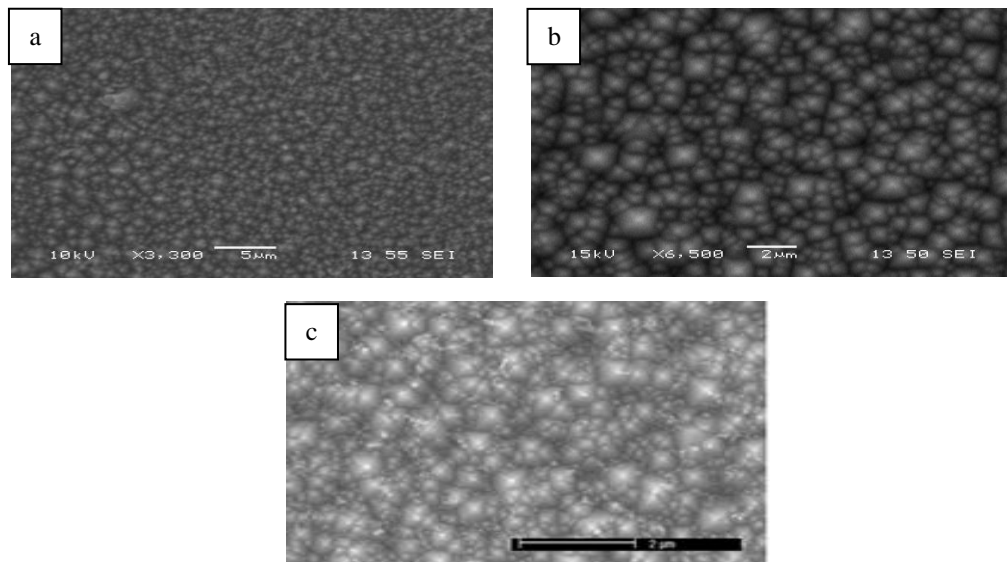


Fig. 1. Surface morphology of silicon wafer textured with NaOCl/ $\text{CH}_3\text{CH}_2\text{OH}$ for (a) 5mn, (b) 15mn, (c) 25mn

It seems that a satisfactory pyramidal structure and an optimal uniformity are reached. It has been noticed that with the reaction time increasing, the size of pyramids gradually becomes bigger and bigger, and the size of the biggest pyramid was still less than $3\mu\text{m}$ when the reaction time was about 15min. Fig.2 shows the relationship between the average size of pyramids and the reaction time.

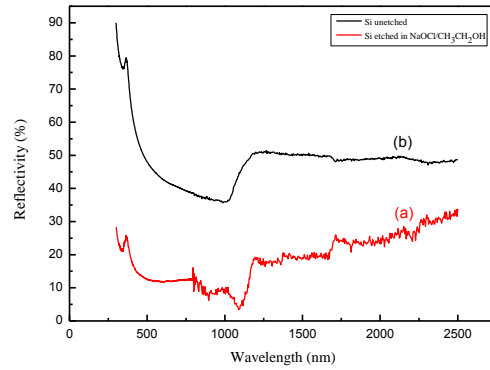


Fig.2. Relationship between the average sizes of pyramids textured with NaOCl /CH₃CH₂OH solution and the reaction time

A comparative study of wafers textured with NaOCl/CH₃CH₂OH solution as well as wafers none textured is also carried out by the reflectivity measurement of silicon surface. Fig. 3. shows the reflectivity of these two wafers in the wavelength range from 500 to 1000 nm. It can be easily calculated from the figure that the average reflectivity is about 9% for the wafers etched with NaOCl/CH₃CH₂OH solution and 35% for the wafers unetched in the main range of solar spectrum, 400-1000 nm. We found that presence, uniformity and size of pyramids are the key factors affecting the reflectivity.

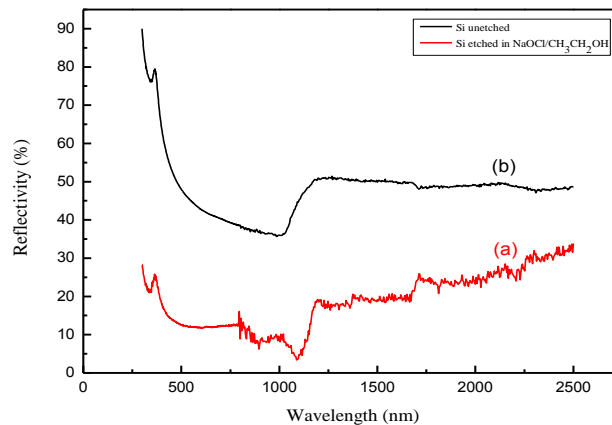


Fig.3. Comparison of the surface reflectance for monocrystalline silicon, (a) textured with NaOCl solution, (b) unetched

4. Conclusion

Anisotropic etching of silicon in inorganic alkaline solution has been studied from the view point of its application in commercial silicon solar cell. For texturisation to form straight pyramids 5% NaOCl solution buffered with ethanol was used. The study of the surface topography and reflection losses for the wafers textured for different durations indicates that the reflectivity is affected by pyramid's size.

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