

Alkali Anisotropic Chemical Etching of P-Silicon Wafer

Marwa Nabil^{1, a}, Hussien. A. Motaweh^{2, b}

¹Advanced Technology and New Materials Research Institute, City for Scientific Research and Technology Applications, New Borg El-Arab City, Alexandria, Egypt.

²Department of Physics, Faculty of Science, Damanhour University, Egypt.

^amarwamoh2000@yahoo.com, ^bprof_motaweh@yahoo.com

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Abstract. The surface chemistry of anisotropic etching of p-type Si-wafer (400) is reviewed and the anisotropic chemical etching of silicon in alkaline solution using wetting agent were discussed. The main factors which affect the production of silicon dioxide layer on crystalline silicon as a result of wet alkali anisotropic chemical etching are the concentration of etching solution (KOH) and wetting agent (n-propanol), temperature (80°C) and time of the etching (4 hr) process. Silicon dioxide layer has found applications in many advanced areas. The synthesized silica layer was systematically characterized by XRD, SEM and FTIR spectroscopy. The XRD results revealed the amorphous nature of silica layer. FTIR spectroscopy confirmed the presence of Si-O in produced samples. SEM confirmed the addition of n-propanol to the KOH solution resulted in an improvement in the etching anisotropy in a smooth etched Si (400) surface.

Introduction

The development of highest efficiency lowest cost solar cells requires surface conditioning steps to maximize the light trapping properties and to reduce the recombination losses on structured interfaces. The texturization of Si surfaces also leads to an increase in surface irregularities that result in an increase in recombination losses. It becomes critical that the damaged surface layers be removed to decrease the micro-roughness. Wet chemical processing is still the standard method used to texturize the wafer surface in solar manufacturing lines [1]. Fundamental etching techniques used in micro fabrication are dry etching (plasma phase) and wet etching (liquid phase). The disadvantages of dry etching are as follows, the gases used in dry etching are quite toxic and corrosive. It requires re-deposition of nonvolatile compounds and it needs specialized and expensive equipment [2].

Wet etching is inexpensive and it has been extensively used for the fabrication of many applications. It is the process of removing a material by using liquid chemicals or etchants from a wafer. The specific patterns are defined by masks on the wafer. Materials that are not protected by the masks are etched away by liquid chemicals. For isotropic wet etching, a mixture of hydrofluoric acid, nitric acid, and acetic acid is the most common etchant solvent for silicon [3]. When the reaction occurs, material is removed laterally at a rate similar to the speed of downward etching. Wet chemical etching is generally isotropic even though a mask is present since the liquid etchant can penetrate underneath the mask [4], as shown in Table 1.

Table 1. Comparison between wet etching and dry etching.

	Wet Etching	Dry Etching
Method	Chemical Solutions	Ion Bombardment or Chemical Reactive
Environment and Equipment	Atmosphere, Bath	Vacuum Chamber
Advantage	1) Low cost, easy to implement 2) High etching rate 3) Good selectivity for most materials.	1) Capable of defining small feature size (<100 nm)
Disadvantage	1) Inadequate for defining feature size < 1µm 2) Leads to some chemical bad effects 3) Wafer Contamination issues	1) High cost, hard to implement 2) low throughput 3) Poor selectivity 4) Potential radiation Damage
Directionality	Isotropic (Except Crystalline Materials)	Anisotropic

Anisotropic wet etching is also known as Orientation Dependent Etching. Liquid etchants etch crystalline materials at different rates depending upon which crystal face is exposed to etchant used. A large difference in the etch rate is there depending on the silicon crystalline plane. When silicon like materials is used, this effect can allow very high anisotropy. The important factor of anisotropy etching includes selectivity, handling and process compatibility and anisotropic. Anisotropic wet etching produces a typical etch rate about 1µm/min.

The etchant KOH (Potassium Hydroxide) is used as an alternative etchant and it is the most used of all hydroxide etches. The wet anisotropic etching of silicon in KOH solution is a key technology for fabricating silicon microstructures [5]. Silicon etching in alkaline solutions has been employed for many years but the mechanism of the process has not been completely recognized yet, especially from the point of view of etching anisotropy, which is associated with various configurations of surface bonds [6].

The objective of this work is to form random pyramid texturing methods using new aqueous solution consisting of potassium hydroxide (KOH)/n-propanol (NPA). Reviewing surface homogeneity, pyramid size and the speed of the texturing process are compared. In this paper we describe a study of the surface morphology of Si etched in 3wt% KOH solutions at 80°C.

Design of the Chip Kick Mechanics

A glass vessel supported with temperature controller and magnetic stirrer was used for the etching process. The cleaned p-type silicon (400) wafers were held vertically in the alkali etching solution. The alkaline compound used in this study is KOH (3 wt%) and n-propanol is used as a wetting agent (15 volume %).

After applying a Teflon mask on one side of Si-wafer, the surface could be etched selectively. The structure and morphology were determined by XRD (X-ray 7000 Shimadzu diffractometer). The shape and random pyramid of texturization process were observed under SEM (Scanning electron microscopy, JEOL (JSM 5300)). And, the formation of chemical bonds for the texturization process of silicon-surface was determined by FTIR (Fourier Transform Infrared Spectrophotometer- Shimadzu FTIR -8400 s, Japan).

Institutions Optimization Design

With the goal to produce homogeneous surfaces which are fully covered with random pyramids of small size and little variation a wide range of different concentrations, etching times and other parameters such as preparation methods were tested. Texturized silicon-surface

was formed in homogeneously mixed KOH with NPA at suitable temperature and certain time of etching.

In the beginning, a hydrogen saturated silicon surface is vertically free from attack by hydroxyl ions in KOH based electrolyte. If a hole reaches the surface, nucleophilic attack on a Si-H bond by a hydroxyl group ion can occur and Si-OH bond is formed. The (Si-OH) bond causes a polarization effect allowing a second hydroxyl group ion to attack and replace the remaining hydrogen bond. Two hydrogen atoms can then combine, injecting an electron into the substrate. The polarization induced by the Si-OH bonds reduces the electron density of remaining Si-Si back bonds making them susceptible to be attacked by KOH in a manner such that the remaining silicon surface atoms are bonded to hydrogen atoms. The silicon tetrahydroxyl molecule reacts with KOH to form highly stable hydroxyl anion. Then, the surface returns to its neutral state until another hole is made available [7].

Test Results

XRD detects the patterns of the p-type Si (400) wafer before and after wet-etching process. Before wet-etching, the crystal structure reveals (400) plane at $2\theta=69.3825^\circ$, which is corresponding to Si-cubic structure (JCPDS Card No.01-027-1402). After 4h of wet-etching process (2wt% KOH, 15 vol% n-propanol), (400) plane appears at $2\theta=68.9806^\circ$ of Si structure (JCPDS Card No.00-027-1402) accompanied with a broad peak in range $2\theta= (19.9083^\circ - 22.8866^\circ)$ corresponds to amorphous silicon dioxide (JCPDS Card No. 00-051-1594), as shown in Fig. 1.

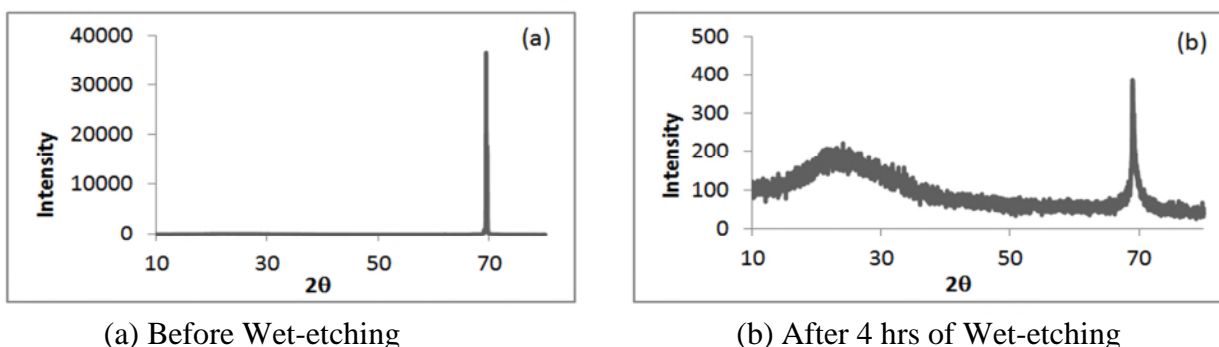


Fig. 1 The experimental results of XRD patterns of Si (400) wafer.

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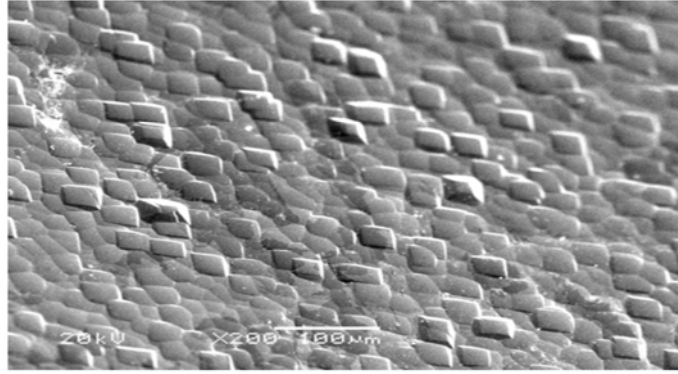


Fig. 2 The experimental results of SEM image of Si (400) wafer; after 4 h of wet etching in (2wt%KOH, 15 vol% n-Propane), T= 80°C.

Then, in case of KOH, the optimum temperature at which the etching process is carried out using this etchant is 80°C. This is because the optimum etching rate with minimum surface roughness is obtained in this condition. The etched silicon surface smoothens with both increase in KOH concentration and bath temperature. Silicon surface roughness degrades with increase in etch duration due to the masking of hydrogen bubbles evolved during etching which significantly contributes to surface roughness.

Potassium hydroxide (KOH) is an alkaline solution, normally used as the etchant for the anisotropic wet process. The former has an excellent uniformity and reproducibility, but not-compatible with an electrical circuits. Generally, the usage of KOH becomes the best choice in the case of that the engineers simply produce the micro-structures onto the Si wafer. The etching rate by KOH strongly depends on the crystallographic orientations of the Si material. The overall chemical etching reaction by alkaline solution is given by, as shown in Eq. 1: [8].



Silicon reacts with water and an OH⁻ ion and produces hydroxide ion and hydrogen gas bubbles. The dependency of the etching rate on the crystallographic orientation said to be the differences of the number of dangling bond at the surfaces. The chemical mechanism behind it is removal of silicon atom in KOH solution takes place in two steps: First, four electrons are affected in bulk silicon, as shown in Eq. 2.

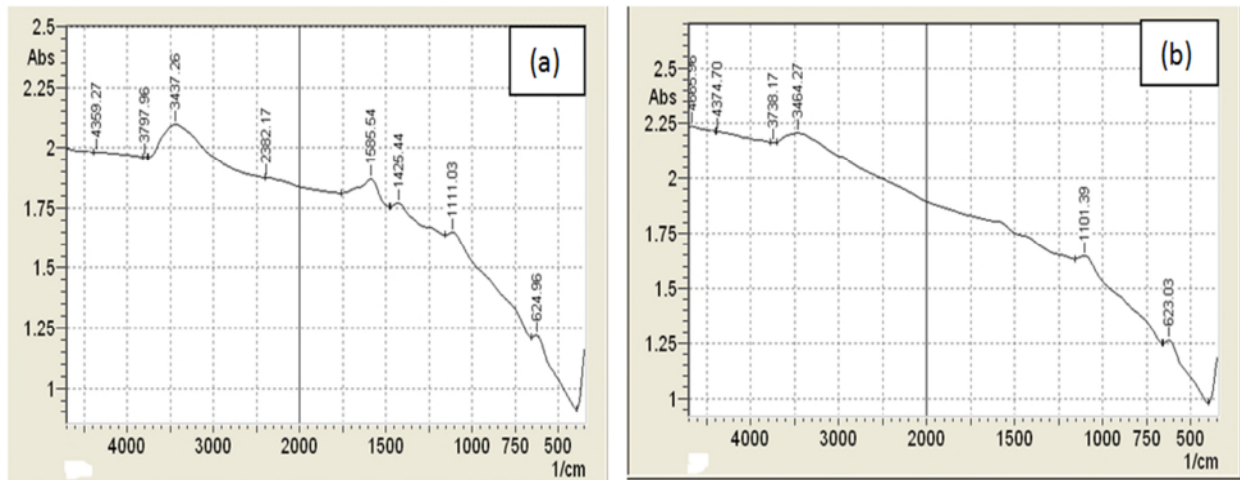


In second step, the electrons are released back into the solution accordingly, as shown in Eq. 3.



Products in first step Si(OH)₄, is supposed to soluble in water. But actually, Si (OH)₄ is decompose into water and silicon-dioxide. The probability of removal of particular silicon atom depends on temperature and microscopic activation energy.

FTIR indicates (Fig. 3) the broad peak at (3000–3700) cm⁻¹, which indicated stretching of O–H bond in SiOH group. Band in region (1000–1200) cm⁻¹ is assigned to Si–O a symmetric stretching in Si–O–Si. Noticeable, disappearing of peaks in region (1400-1600) cm⁻¹, in (b), which corresponds to mix of stretching mode Si–Si and wagging mode Si–H_n (n=1 and 2). So, the best time of etching process is 4h, for formation silica layer on Si-wafer surface.



(a) Before wet-etching process

(b) After 4h of wet-etching process

Fig. 3 The experimental results of FTIR Spectra of Si (400) wafer.

Conclusion

The present work is a study of the preparation of silicon dioxide layers on p-type crystalline silicon wafers (400) and a discussion of the obtained samples. The process of wet alkali anisotropic chemical etching process was monitored as the effect of concentration of alkaline etching solution (KOH), concentration of wetting agent (n-propanol), temperature and time of etching process. XRD spectrum showed amorphous peak of silicon dioxide layer. This particular property might be useful for decreasing the light scattered for optoelectronic devices. Finally, the peculiar hollow structure of the silicon dioxide nano particles could also be useful for trapping or storing molecules. From the FTIR data, it is shown that all samples exhibited characteristic peaks for silicon dioxide.

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