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The morphological study of porous silicon formed by electrochemical anodization method

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Abstract. Due to its good physical and chemical properties, porous silicon (PSi) is very attractive to study. In this research, PSi has been fabricated on n-type Si (100) by the electrochemical anodization method. The electrolyte solution used was a mixture of HF (40%), ethanol (99%) and aquadest with volume ratio of 1:1:2, respectively. It was anodized on Si(100) surface at different current densities of 10 mA/cm^2 and 20 mA/cm^2 with the anodization time at each current density for 10 min, 20 min, and 30 min. The Scanning Electron Microscope (SEM) images showed that the PSi surfaces have inhomogeneous sized pores in the range of 95.00 nm–1.46 μm. The PSi layers with current density and anodization time of 10 mA/cm^2 (10 min), 10mA/cm^2 (20 min), and 20mA/cm^2 (10 min) have spherical shaped pores while the others have some uncommon (cross sectional) shaped pores on surfaces. It is considered that the cross sectional shaped maybe caused by unstable the current during the electrochemical anodization process.

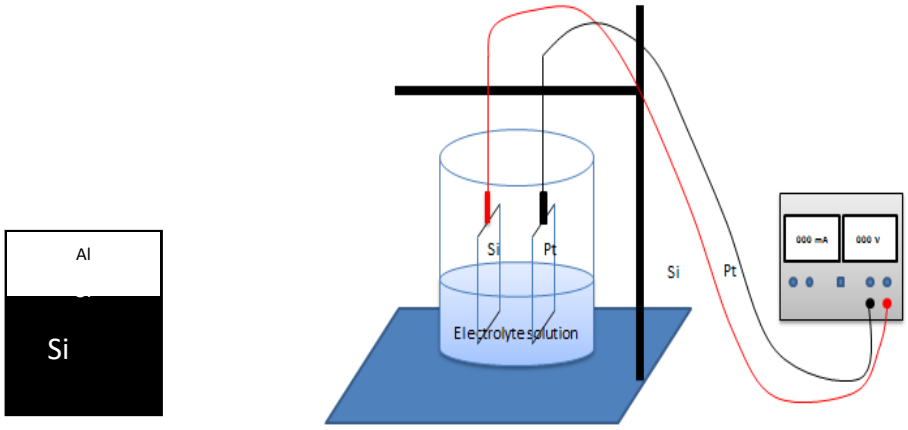
1. Introduction

Porous silicon (PSi) is silicon crystal consisting of voids in the size of nanometer–micrometer on surface [1-2]. PSi remains very attractive to study because it has good physical, chemical, and optical properties that can be applied in technologically electronic devices such as light emitting diodes, waveguides, gas testing devices, chemical and biological sensors, photonic crystal, photovoltaic, etc [1-7].

There are several methods to produce PSi such as electrochemical anodization, focused ion beam, electron beam lithography, metal assisted etching, and rapid thermal annealing [8, 9]. Electrochemical anodization is an easiest way to form porous. Besides, the experimental setup of this method is simply replicable and easy to modify [7]. This method involves two electrodes dipped in hydrofluoric acid (HF) as electrolyte solution while it is supplied by constant current density [3, 10]. In the PSi manufacture, the two electrodes are silicon substrate as the anode and platinum or the other conductive materials resistant to HF as the cathode. The pores formation is affected by some parameters during the electrochemical process such as current density, anodizing time, electrolyte solution and its concentration, and silicon type [7, 11, 12]. Therefore, the electrochemical anodization method remains challenge in formation of PSi.

In this research, the morphological study of porous silicon fabrication has been conducted by electrochemical anodization method. The parameters of the method such as current density and anodization time were varied to investigate their effects on the pore formation. The Scanning Electron Microscopy (SEM) instrument was performed on PSi surfaces to observe the pore shapes.

2. Experimental



(a) (b)

Figure 1. (a) Si substrate with aluminum plaster (b) the experimental setup of electrochemical anodization method

This experiment used n-type Si (100) substrate as an anodized material. It was cut into rectangular shape with size of 1.0×1.5 cm^2. Firstly, the Si samples were cleaned through the RCA cleaning process method. A Si sample was rinsed in NH_4OH: H_2O_2: aquadest solution with volume ratio of 1:1:2 for 5 min at 70ºC-80ºC. Then, it was soaked in aquadest with overflow for 3 min and immersed in 40% HF:aquadest solution with volume ratio of 1:30 for 15 s. Finally, it was dried with Ar gas. The aim of the RCA cleaning process is to remove organic and metallic contaminant, native oxide contaminant and ionic contaminant on layer of commercial silicon wafer [13]. The Si sample was covered by aluminum plaster on 0.5 cm^2 area as shown in Figure 1(a) to make a conductive contact.

The experimental setup as demonstrated by Figure 1(b) was carried out to anodize the Si surface. The Si was placed as anode while the Pt was placed as cathode. They were dipped into electrolyte solution that was a mixture of 40% HF: 99% ethanol: aquadest with volume ratio of 1:1:2. It was then applied in different current densities of 10 mA/cm^2 and 20 mA/cm^2 with the anodizing times of each current density of 10 min, 20 min, and 30 min using DC power supply (SUNSHINE P-3005D). After the anodization process, samples were cleaned in distilled water via ultrasonic cleaner and then dried with Ar gas. The obtained PSi samples were observed by SEM instrument (FEI Quanta 200 FEG).

3. Results and discussion

Figure 2 shows the SEM images of Si surfaces after the electrochemical anodization process at different currents and anodization times. The PSi has been successfully formed on each silicon surfaces. The current density and the anodizing time affect the PSi formation. The pores have inhomogeneous size in the range of 95 nm–1450 nm. Nevertheless, the pores size increases as increasing the current density and the anodizing time. In addition, the PSi layers with current density and anodizing time of 10 mA/cm^2 (10 min), 10mA/cm^2(20 min), and 20mA/cm^2(30 min) have spherical shaped pores, while the others have some uncommon (cross sectional) shaped pores on their

surfaces. It is considered that those inhomogeneous size pores and irregular shaped pores are caused by the unstable current density during the anodization process which is a problem in this experiment.

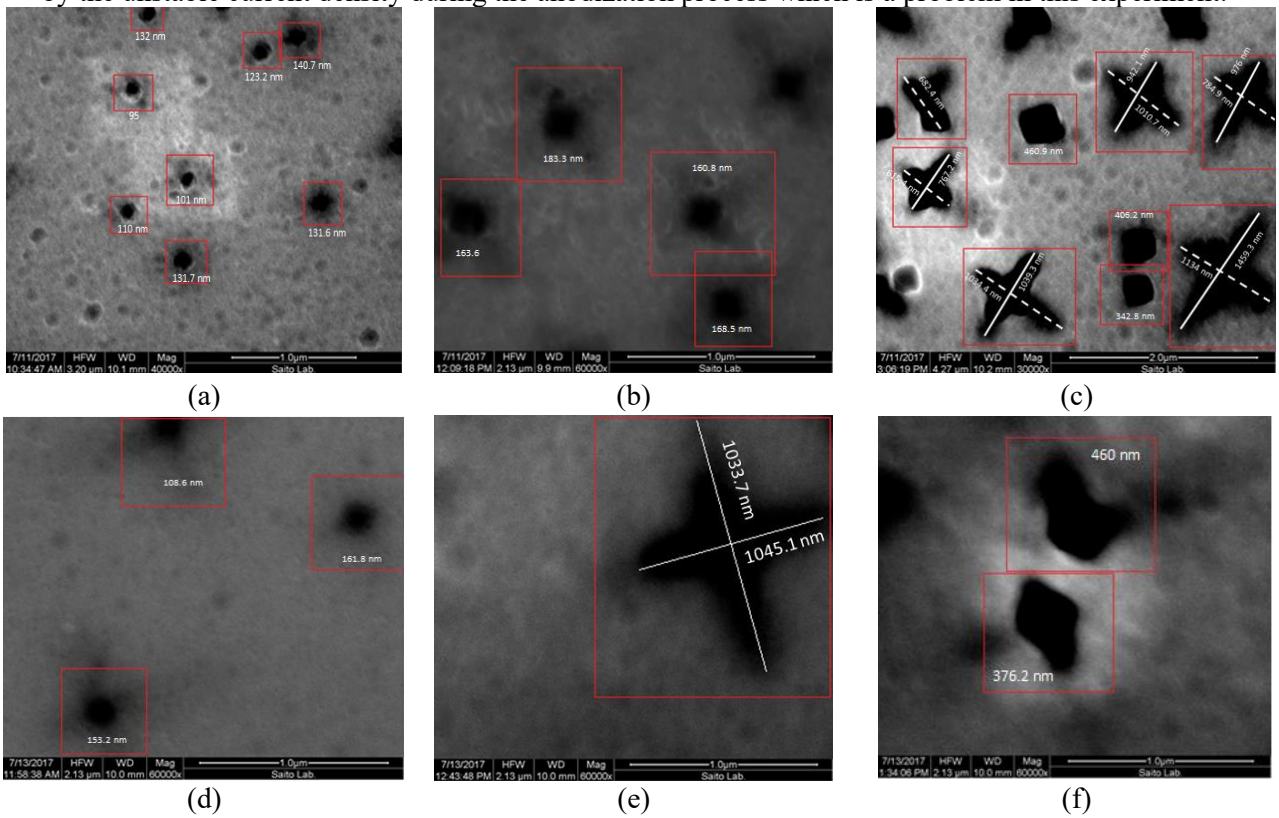


Figure 2. The SEM images of PSi after electrochemical process at various currents and etching times (a) 10 mA/cm^2-10 min (b) 10 mA/cm^2-20 min (c) 10 mA/cm^2-30 min (d) 20 mA/cm^2-10 min (e) 20 mA/cm^2-20 min (f) 20 mA/cm^2-30 min

Furthermore, it is agreed with Burham *et al.* [7] which declares that the unstable current influence on the inhomogeneous size pores and pore structures. Therefore, in the next experiment, we have to make a new DC power supply to control the current density in stable condition during the electrochemical anodization process.

The mechanism of the pores formation has been explained in refs 7, 10, and 13. When the current is in unstable condition, the current increases or decreases at certain current during the electrochemical anodization process, the amount of the holes generated are different. That hole will be attacked by F^- ions thus a pore formed on Si surface. When the currents increase, more holes are attacked by F^- ions to form the pores in larger sizes. While when the currents decrease, less holes are attacked by F^- ions to form the pores in smaller sizes. Therefore, unstable currents will produce inhomogeneous size pores including cross shapes on Si surface

4. Conclusion

PSi has been successfully formed by the electrochemical anodization method on Si(100) surfaces. The pores have inhomogeneous pores size in the range of 95 nm–1450 nm. The PSi structures with current density and anodizing time of 10 mA/cm^2 (10 min), 10mA/cm^2(20 min), and 20mA/cm^2(30 min) have spherical shaped pores, while the others have some irregular shaped pores. It is considered that both inhomogeneous sized and uncommon shaped pore are caused by the unstable current during the electrochemical anodization process. The increase current density and the longer anodizing time tend to make the bigger pore size and the narrower pores distribution. Therefore, it can

be concluded that the parameters of the electrochemical, the current density and the anodizing time, affect the pores formation.

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