Variation of etching time on formation of porous silicon on p-type Si (111) using electrochemical anodization method

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Abstract. Porous silicon (PSi) has been formed on p-type Si (111) substrates using electrochemical anodization method. Silicon surfaces were anodized in HF (40%) dan ethanol (96%) solution with a ratio of 1:1. Anodization time was varied at 6, 8, 10 and 12 min with current density was maintained constant at 80 mA/cm². Platinum foil was as a cathode while silicon was as an anode with a distance of 5 cm. The optical reflectance of the sample was determined using UV-Vis Spectrophotometer and surface morphology was observed using AFM. AFM’s images could determine the depth, width and roughness of PSi. The reflectance of PSi on Si (111) decreased with increasing the etching time. It indicated that many photons were trapped inside the porous. AFM images confirmed that the depth, the width, and the roughness of PSi increased with the increasing of the etching time. It is considered that the etching direction worked in the vertical and horizontal ways.

1. Introduction

Porous silicon (PSi) is a silicon that has a nano or micro porous structure. PSi was first discovered by Uhrl in 1956 who carried out the process of electropolising silicon in a solution of hydrofluoric acid (HF) based at Bell Labs [1]. PSi’s structure on Si wafers layer is formed by etching by electrochemical anodizing containing hydrofluoric acid (HF) and surfactants (predominantly ethanol) [2]. PSi has good physical, chemical, and optical properties that can be utilized for electronic and optical devices, so PSi research is increasing every year [3].

The process of PSi formation by electrochemical anodization is influenced by parameters such as doping of the substrate, current density, HF concentration, and etching time [4]. The physical properties of PSi are determined by diameter, thickness and voids [5]. Porosity, thickness and pore size distribution can be controlled by changing the hydrofluoric acid concentration, current density, anodization length, porous area and the etching time in the electrochemical etching process in the manufacture of PSi [6]. Previous study, Handayani et al. [7] succeeded in forming porous silicon on n-type Si (111) with a resistivity of 1.5-4.5 Ω.cm by using the electrochemical anodizing method with etching solution HF:Ethanol ratio of 1:1, electrode distance of 2.5 cm, current density of 20 mA/cm², and time variations (10, 20, 30 min). The obtained PSi showed an increase in absorbance and pore along with an increase in etching time [7].

In this research, the variation effect of etching time on formation of PSi on p-type Si (111) surfaces using electrochemical anodization method will be conducted. Data obtained in this study include AFM...
images and the reflectance value which is obtained by using a UV-Vis Spectrophotometer. AFM images can be used to find the values of depth, width and roughness of PSi.

2. Experiment

Porous silicon (PSi) is formed on p-type silicon wafers Si (111) substrates which had a resistivity <0.05 Ω·cm in size 1x1.5 cm². The substrate was washed with a solution of NH₄OH: H₂O₂:distilled water using 1:1:5 ratio for 5 min on a hotplate with a temperature at 80ºC. The sample was then washed with distilled water by overflow for 3 min. The sample was cleaned again with a HF solution and distilled water in a ratio of 1:30 by immersing it for 15 s. The sample was washed again with distilled water by overflow for 3 min. The substrate was then dried with N₂ gas sprayed in a position parallel to the sample (not perpendicular). Silicon surfaces were anodized in HF (40%) dan ethanol (96%) solution with a ratio of 1:1 at a current density of 80 mA/cm² for 6, 8, 10, and 12 min. Platinum foil was as a cathode while silicon was as an anode with a distance of 5 cm. PSi was immersed briefly into distilled water and then dried with N₂ gas. These samples were then characterized using a UV-Vis Spectrophotometer to obtain the reflectance values and AFM to get surface morphology of PSi. Furthermore, AFM images could determine the depth, width and roughness of PSi.

3. Results and Discussion

The measurement data of PSi reflectance with UV-Vis Spectroscopy at wavelength 300-600 nm is shown in Figure 1. Every variation of etching time gives different results. The reflectance of PSi decrease with increasing the etching time. For all samples, the reflectance intensity increases at a wavelength of 300-375 nm where the peak intensity occurs at about 375 nm, then it decreases until about 440 nm. Except for sample with etching time for 8 min, the reflectance curves oscillate over 450 nm. It indicated that photons that come in PSi will be reflected with different angles due to the different in the pore depth [5]. It also describes the inhomogeneous pore formed on the surfaces [7].

**Figure 1.** Relationship between wavelength and the reflectance of PSi layer for the etching time of 6 min (purple), 8 min (green), 10 min (blue), and 12 min (red)
AFM’s images are conducted at size 10 μm x 10 μm. Figure 2 shows the surface of PSi at a current density of 80 mA/cm² for 6, 8, 10, and 12 min. In order to determine the roughness value of PSi, a red horizontal line is made on surface with a length of 10 μm. The line profile for each surface can be shown below the PSi morphology for etching time of 6, 8, 10, and 12 min, respectively. Based on the line profile, it is concluded that the PSi is inhomogeneous for all sample. Beside the roughness, the line profile can also determine the width and the depth of PSi.

![AFM images for measurement of porous silicon by horizontal line (10 μm) (a) 6 min (b) 8 min (c) 10 min (d) 12 min](image)

**Figure 2.** AFM images for measurement of porous silicon by horizontal line (10 μm) (a) 6 min (b) 8 min (c) 10 min (d) 12 min

Figure 3 shows the relationship between PSi roughness and etching time. Based on Figure 3, the PSi roughness increases with increasing etching time. This result is similar to reference [8]. The roughness of PSi can be used as an indication of the distribution and the depth of pores. A higher roughness indicates that many pores form on the surface or in other word the pores are well-formed [9].
Figure 3. Roughness of PSi for different the etching times

Figure 4. Pore width and pore depth of PSi for different the etching times

Figure 4 shows the comparison of the depth and the width of PSi at a current density of 80 mA/cm$^2$ for 6, 8, 10, and 12 min. Based on Figure 4, the depth and the width of PSi increases with increasing etching time. The speed of the etching process sideways is faster than inward on the Si surface. The anodization time is proportional to the pore size. A longer anodization process at a stable current would form a thicker layer, because many silicon surfaces were increasingly soluble in HF and ethanol solutions. This affects the absorption of more photons and the reflection of fewer photons in the pore layer [7]. In all four conditions the pore size increased significantly.
4. Conclusions
PSi was successfully made using electrochemical anodization method at a current density of 80 mA/cm² for 6, 8, 10, and 12 min. The reflectance of PSi decreased with increasing the etching time. The reflectance value begins to increase at a wavelength of 300-375 nm, begins to decrease after a wavelength of 375 nm, and at a wavelength of 450-600 nm an anomaly occurs due to the oscillation process at PSi. The speed of the etching process sideways is faster than inward on the Si surface. The results of AFM images show that the value of the depth, the width, and the roughness of PSi increases with increasing etching time. AFM images shows that the pores on the silicon surface is not homogeneous.

Acknowledgements
The authors would like thank Universitas Sebelas Maret for financial support through Penelitian Unggulan Terapan UNS PNBP with contract No. 452/UN27.21/PN/2020.

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