The Effect of Etching Current Density on Porous Silicon Fabricated by Electrochemical Etching Process

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Abstract— Porous silicon (PS) was fabricated using p-type Si with <111> orientation by electrochemical etching process (ECE) at a constant etching time of 20min and different current density of 10-40mA/cm^2. The surface morphology of PS studied by atomic force microscope (AFM) verifies that average diameter and nanostructure are dependent on the etching current density, when the current density increased from 10 to 40mA/cm^2 the average diameter also increased from 29.96 to 45.59nm. The FE-SEM image of the sample prepared at 20min and 10mA/cm^2 shows a homogeneous pattern and confirms the formation of uniform porous structures on the silicon wafer. From XRD pattern, the peak intensity decreased and full-width half maximum (FWHM) increased with increasing current density from 10 to 40 mA/cm^2 and the crystalline size also decreased from 10.8 to 2.5nm. From FTIR spectra of PS at different etching current range from 10 to 40 mA/cm^2, it was found that the transmittance peaks around 997.13 cm^{-1} and 1097.42 cm^{-1} are from Si–O–Si asymmetric stretching modes, which are dependent on the oxidation degree of PS. The transmittance peaks at 624.94-630.68 cm^{-1} Si-H wagging mode bending in (Si$_3$-SiH), and 810.05-813.90 cm^{-1} from Si-F stretching mode. Photoluminescence spectra (PL) showed that the band gap energy increased from 1.610 to 1.638eV when the current density increased from 10 to 40mA/cm^2.

Index Terms— Porous Silicon, Electrochemical Etching, Current Density, XRD, FTIR, AFM, FE-SEM.

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1 Introduction

Porous silicon (PS) is a material formed by anodic dissolution of single crystalline silicon in HF containing solutions [1]. Through anodization in HF solution, Silicon surface will be covered with a brown film. New physical properties appear, when a structure becomes smaller than a characteristic length scale which is of great interest in basic research but also for applications. Nanoscale silicon reducing dimensionality of bulk silicon to nano-scale silicon (PS) leads to appreciable changes in optical, electrical and electronic properties. As a result of these advantages, PS has been widely used in technological applications such as in light-emitting diodes, light testing equipment, photoelectric solar batteries, gas testing devices, microdevices, and biological testing equipment [2]. Several methods are used and developed to fabricate the porous layer such as Photochemical, Electrochemical, Photo-electrochemical, Stain etching processes, and Laser Induced Etching Process [3]. One of the most important methods is electrochemical etching process (ECE). Many parameters that influence on the PS formation process with electrochemical anodization such as substrate doping, current density, HF concentration, and time etching [4, 5].

This paper discusses the effect of current density on the morphological, structural, and optical properties of (111) p-type PS fabricated by electrochemical etching process.

2 EXPERIMENTAL DETAILS

PS layers formed by the electrochemical etching process (ECE) of p-type <111> oriented silicon substrate. The ECE cell was made of Teflon (or any highly acid-resistant polymer) base plate was made of aluminum. A Si wafer cut into a pieces with a square shape at area 1cm^2 and put on the bottom of the cell by using O-ring that allowed the Si surface to be exposed to the homogeneously mixed of HF: ethanol at 1:1 concentration. Si wafers were ultrasonically cleaned in distilled water and acetone, connected to the anode electrode and the Platinum connected to cathode electrode of the power supply as shown in Figure 1. PS samples were fabricated by changing the etching current density with a constant etching time. The prepared samples were characterized by Photoluminescence (PL), Fourier transform infrared transform spectroscopy (FTIR), X-ray diffraction (XRD) and atomic force microscopy (AFM).

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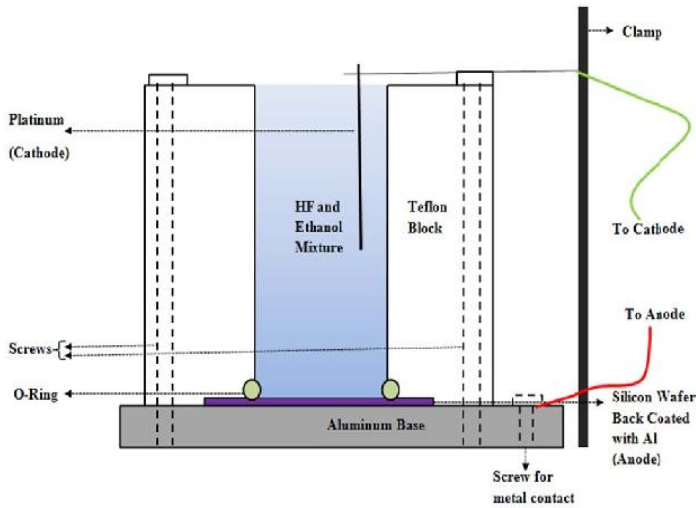
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Figure 1: Setup for the fabrication of porous silicon.

Figure 2: XRD spectra of PS samples a) at 10mA/cm² b) 20mA/cm² c) 30mA/cm² and d) 40mA/cm².

3   RESULTS AND DISCUSSION

Figure 2 shows the XRD spectra of the PS surfaces formed at different etching current densities. A strong peak of PS in 10mA/cm² current density shows a very sharp peak at $2\theta = 27.6°$ and another one, weaker than the former, at $2\theta = 93.9°$. The founded values correspond to (111) and (151) c-Si orientations, respectively. Figure 2b illustrates a shift and a broadened peak for the sample of 20 mA/cm². When the current density increased to 30 and 40 mA/cm² the intensity of peaks becomes very low and broadened peak increased tightly then, a new peaks appears located at $2\theta = 16.2°$, $21.6°$, $34.0°$ which corresponds to 001, 101, 002 orientations respectively represented SiO_2 as shown in Figure 2c and 2d. FWHM was increased from 0.8951 to 3.6250 when the current density increased from 10mA/cm² to 40mA/cm²; these computed results have been compared with the FWHM values of Cu-Kα which have been published by Joint Committee on Power Diffraction Standards (JCPDS) the FWHM of bulk silicon about 0.295.
Crystalline size was calculated by using scherrer equation [6]:

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where K is the Scherrer constant $(1 > K > 0.89)$, λ is the wavelength in nanometers, β is FWHM in radians, and θ is the diffraction angle in radians.

The result shows that the crystalline size decreased from 10.8nm to 2.5nm when the current density increased from 10mA/cm² to 40mA/cm², respectively. In general, when the current density increase the peaks intensity of the PS decreases and crystal size is reduced toward nanometric scale, then a broadening of diffraction peaks is observed and the width of the peak is directly correlated to the size of the nanocrystalline domains [7].
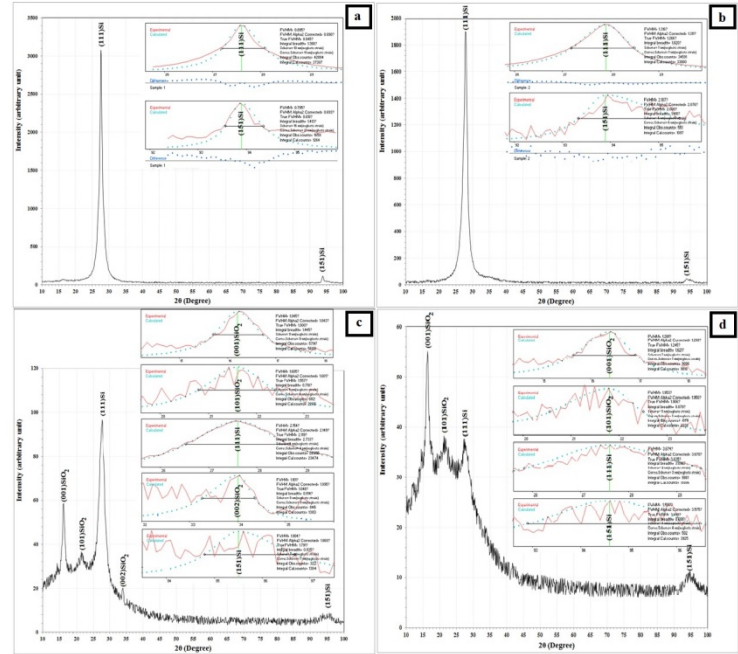
Figure 3 illustrates 3-D images of prepared PS samples showed a sponge-like structure is produced. The change in anodization parameters such as current density cause a big difference in fabricated PS in terms of roughness, thickness, pore's diameter and other properties.

Figure 4 shows the diameter values distribution chart of PS samples in which the irregular and randomly distributed nanocrystalline silicon pillars and voids over the entire surface. Pore diameter generally increases with increasing potential and current density [1]. At low current density, a highly branched, randomly directed and highly interconnected meshwork of pores was obtained. However, increasing in current density orders the small pores to exhibit cylindrical shapes giving rise to larger pore diameter [8].
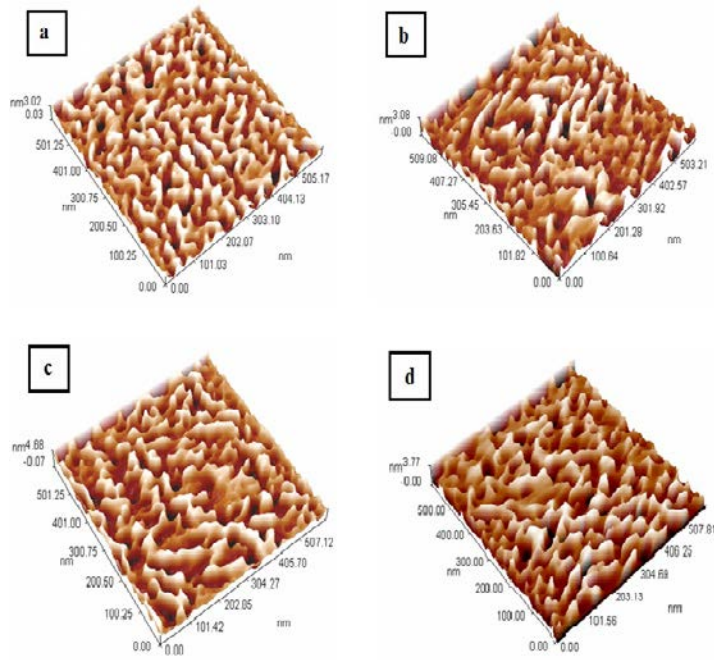
Figure 3: 3-D AFM images of PS a) at 10mA/cm² b) 20mA/cm² c) 30mA/cm² and d) 40mA/cm².
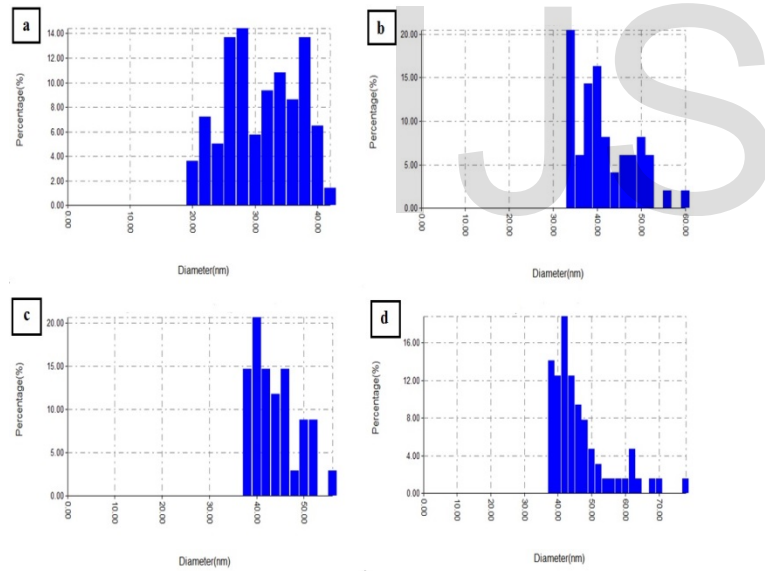

Figure 4: The diameter values distribution chart of PS samples a) at 10mA/cm² b) 20mA/cm² c) 30mA/cm² and d) 40mA/cm².

Table 1 shows the average diameter, average roughness, peak-peak and RMS parameters of the prepared PS samples. It was observed that the higher values of roughness, peak-peak and RMS belong to the sample prepared at current density 30mA/cm².

Figure 5 shows the FTIR spectra of the PS as a function of the transmission. It is clear that there are many distinct peaks with different intensities. The peaks around 997.13 cm^{-1} and 1097.42

Table 1: AFM parameters of the prepared PS samples.

Etching current density (mA/cm²)	Average diameter (nm)	Average roughness (nm)	Peak-peak (nm)	RMS (nm)
10	29.96	0.747	2.99	0.863
20	40.81	0.712	3.07	0.836
30	43.08	1.16	4.75	1.35
40	45.59	0.883	3.77	1.03

cm^{-1} are from Si–O–Si asymmetric stretching modes, which are dependent on the oxidation degree of porous silicon. The transmittance peaks at 624.94-630.68 cm^{-1} Si-H wagging mode bending in (Si$_3$-SiH), and 810.05-813.90 cm^{-1} from Si-F stretching mode. Among the three major surface contaminants, hydrogen is found to exist expectedly and hydrogen related surface states lead to strong PL. The pore surface includes a high density of dangling bonds of Si for original impurities such as hydrogen and fluorine, which are residuals from the electrolyte. Additionally, if the manufactured PS layer is stored in ambient air for a few hours, the surface oxidizes spontaneously [9].
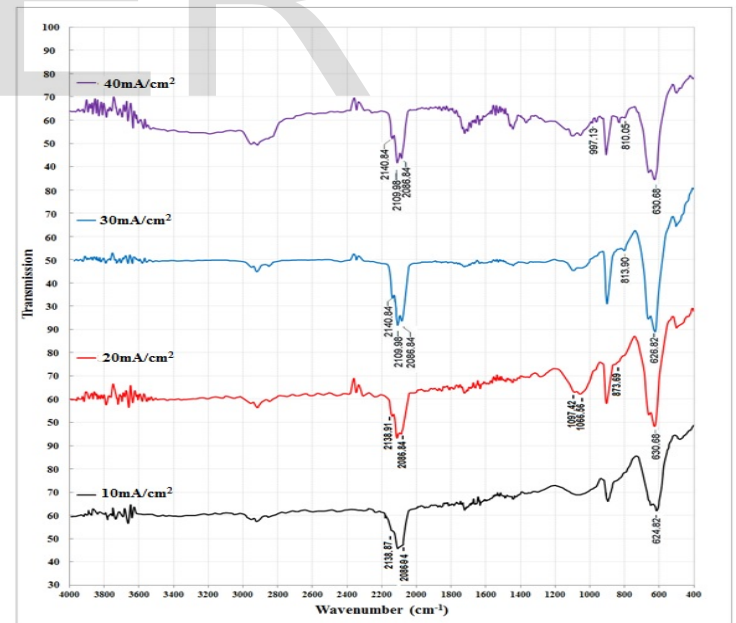

Figure 5: FTIR spectra of the samples p-type etched at a constant time 20 min and different current density.

Figure 6 shows the PL spectra for PS samples. The PL peak position of PS is blue-shifted as a function of the current density as shown in Figure 4.8. According to the quantum confinement model, the peak shift is due to an increase in the energy band gap (Eg) within the porous structure [10]. The result also suggests that the band gap energy increased from 1.610 to 1.638 *eV* when the current density increased from 10 to 40 mA/cm². Figure 7 illustrate the Eg as a function of variation of current density. Increasing in the current density is attributed to the reduction of the Si to nanosize, which favors charge carrier quantum confinement. The probability of recombination of e and h is higher in very small structures (quantum confinement effects), leading to higher emissions. High PL intensity is the result of the conversion of the material band gap conduction from indirect to quasidirect [11]. The quantum dimension of the structure in the sample favors PL shifting toward shorter wavelengths. Other researchers [12] have also found a blue shift of PL peak with increase in the etching current density.
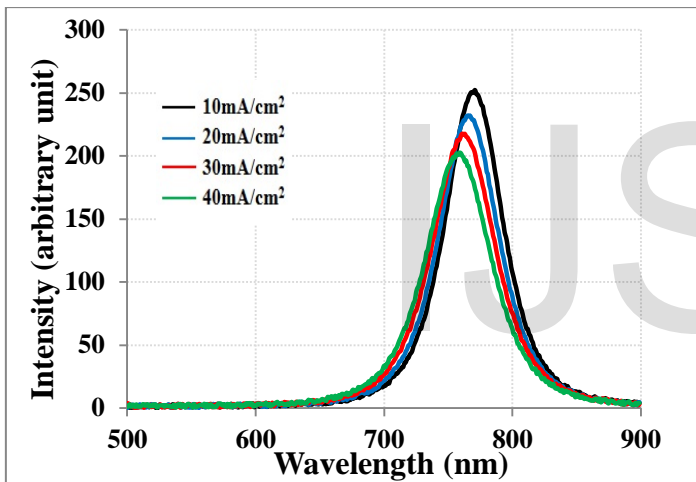
current density 10mA/cm² with time about 20min, it is showed a homogeneous pattern and confirms the formation of uniform porous structures without any cracks on the silicon wafer.
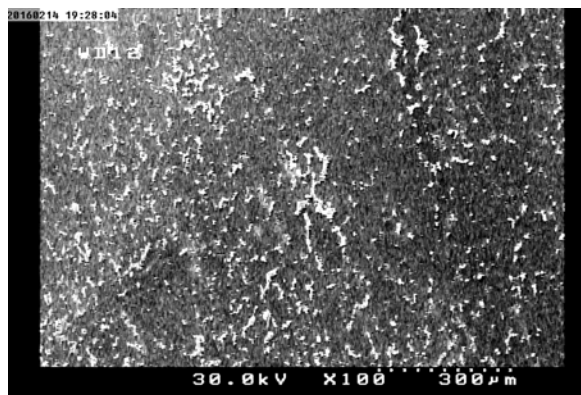

Figure 8: FESEM image of PS sample prepared at 10mA/cm² and 20min.

4 CONCLUSION

ECE mechanism of the PS synthesis, the results of morphological, structural, and optical properties have been investigated. AFM images of PS shows an increment in average diameter with increasing of etching current density. FE-SEM image shows a homogeneous pattern uniform porous structures. XRD pattern of PS shows that increasing of etching current density leads to broadening in diffraction peaks which indicate forming of nanostructure shapes. From FTIR spectra of PS at different etching current density, the peaks appeared from bonding the hydrogen and fluorine from HF solution with the surface of Si. PL measurement indicated the shorter peak wave length of luminescence has caused the increase in the energy band gap (Eg) of the porous structure.

Figure 6: PL spectra of PS etched for 20 min at different current densities.
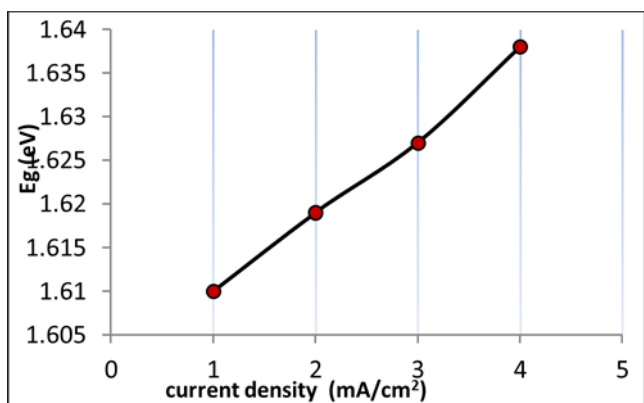
Figure 7: Energy band gap as a function of current

Figure 8 shows the FESEM image of sample prepared at

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