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# Experimental Study of Electrochemically Prepared Porous Silicon as Antireflective Material in Solar Cells

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**Abstract -** *Discovery of Porous silicon has opened a door of research on this material for their wide range of applications such as energy conversion, optoelectronics, microelectronics, bio-technology, micro-optics etc. Porous silicon acts as antireflection coating material therefore; this has been demanded in solar cells to limit the surface reflections. The great advantage of using porous silicon in solar cells is its large surface area and tunability of its properties. In this paper, we present the optical and structural properties of porous silicon using Filmetrics, Fourier Transform Infrared Spectroscopy, UV-VIS reflectance and Field emission scanning electron microscopy.*

***Key Words***: **Porous Silicon, Antireflection Coating, Porosity, Etching, Reflectance.**

## 1.INTRODUCTION

Porous silicon is a semiconductor material composed of silicon structure with network of air voids. A major research on this material was focused after the discovery of quantum confinement effect by Canham in the year 1990 [1].During his experiment, he had observed an emission of light from the silicon wafers during the chemical dissolution. The high surface to volume ratio and tuning of its porosity make this material suitable as an antireflective coating.

Crystalline silicon is the primary material used in solar cells which has high refractive index with a significant portion of solar radiation loss from its surface which leads to in-sufficient electron-hole pair generation and therefore, low-efficiency from the solar cell. Converting silicon into porous silicon acts as a promising material to lower the reflectance off the surface by trapping more photons which are used to generate electron-hole pairs. The refractive index of the host silicon materials can be reduced to a desired level as per the application. The refractive index can be tailored with the porosity of porous silicon by varying the applied current density, HF concentration, etching time and current density. The porous silicon is made by the electrochemical etching or anodization of silicon wafer which is an easy and cost-effective method. This method is a top-down method which employs a platinum electrode as cathode and silicon wafer as anode immersed in a HF concentration that acts as an electrolyte with a constant current source to maintain homogeneous porous layer formation. Porous silicon is having good mechanical robustness, compatibility and reliability that is why have got demanded in various applications like chemical sensors, biological sensors, energy conversion devices, optical memory devices, waveguides etc.[2-6].

In this paper, we present the structural and optical properties of anodized porous silicon for its low-reflection application. The experimental procedure to fabricate porous silicon by anodization cell is presented in Section 2 and characterized results are discussed in Section 3. Section 4, concludes the paper.

## 2. Experimental Procedure

For electrochemical anodization, boron doped silicon substrates p-type of (100) orientation were used. Before electrochemical anodization, the silicon substrates were cleaned to remove the dirt and other possible contaminants. The cleaning process involves the rinsing of silicon substrates in de-ionized water after the separate heating in trichloroethylene, acetone and methanol solutions for 10 minutes at 60°C respectively. After cleaning, the substrates were dried in the presence of nitrogen gas and then used for the anodization.

The electrochemical etching setup used in this experiment is shown in figure 1.It consists of a constant current source CH1100A (USA) and a teflon cell is composed of platinum as cathode and silicon substrate as anode which is depicted in figure 1(a). The electrolyte solution was made up of 1:1:2 of HF:DI:Ethanol where HF and DI are the hydrofluoric acid(48%)and deionized water respectively. The anodization cell was made of teflon material because it is chemically and thermally stable. During anodization, when only HF is used as an electrolyte then hydrogen bubbles are generated which sticks to the surface and leads to a lateral and in-depth in-homogeneity. To overcome problem, ethanol is added to the hydrofluoric acid which is helpful to eliminate the hydrogen bubbles and yields uniform etching.

Two electrode configurations is used for the anodization of silicon substrates as shown in figure 1(b) and the etching was performed at room temperature in the dark. The silicon wafer was placed on 'O' ring to avoid the leakage of electrolyte and to ensure etching on one-side of the silicon substrates.

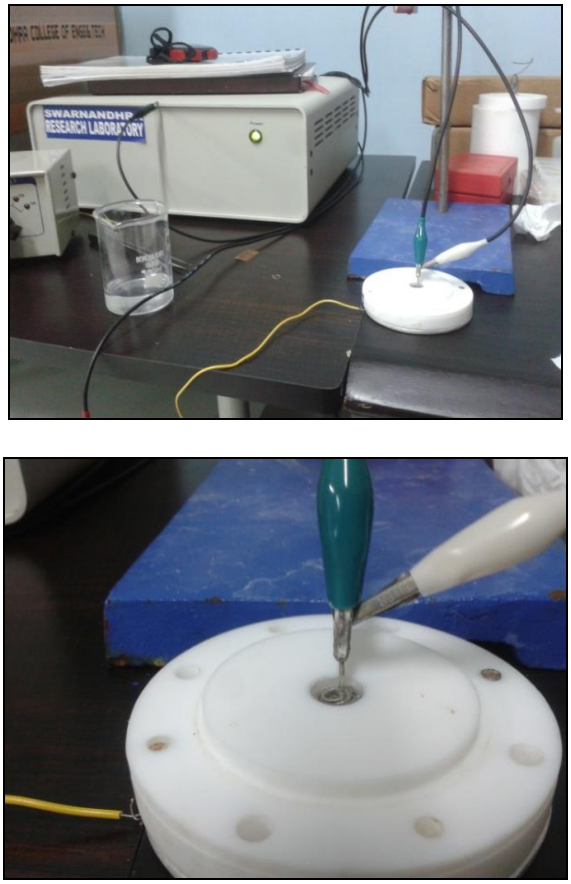


**Fig -1:** Electrochemical etching/anodizaton setup used for the fabrication of porous silicon

Various samples of porous silicon were fabricated with etching time (t) 40, 80, 120, 160, 200 seconds at 30 mA/cm2 current density (J). The digital images of porous silicon samples are shown in figure 2 which shows different colour with the variation in etching time.

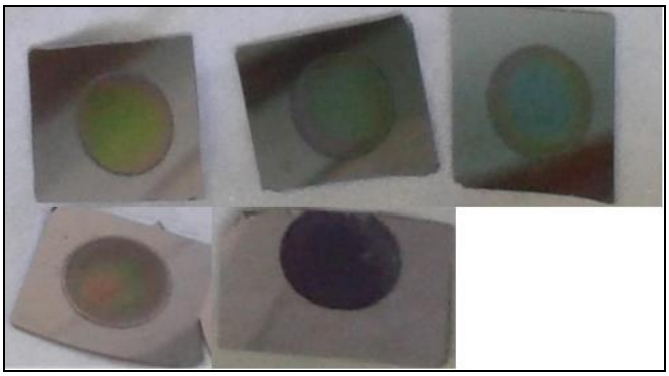

**Fig -2:** Electrochemically fabricated porous silicon samples with various etching time

The as-prepared samples were characterized by using Filmetrics (F20), Fourier Transform Infrared Spectroscopy (Nicolet 370), UV-VIS reflectance (Shimadzu UV1800) and Field emission scanning electron microscopy (ZIESS).

## 3. Result & Discussion

The characteristics of porous silicon such as porosity, thickness and refractive index can be tuned by varying process parameters which include current density, HF concentration, wafer doping and anodization time. Here, we have explored the tuning of porosity, thickness, refractive index by varying the anodization time at constant applied current density. Figure 3 shows the variation in porosity with respect to anodization time.

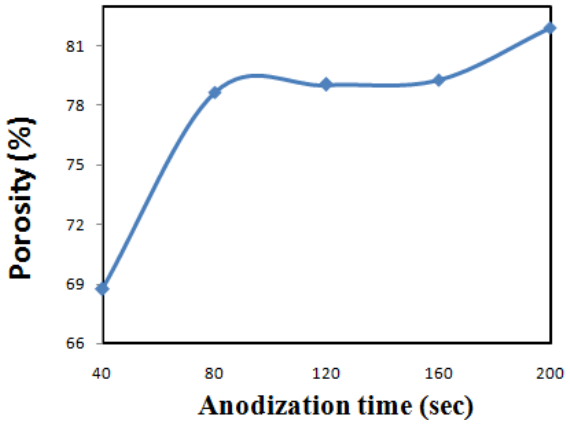


**Fig -3:** Porosity as a function of anodization time

As the etching time increases from 40 to 200 seconds, the porosity is found to be increased from 69 to 82 %. This increase in porosity is due to long time electrochemical etching of silicon in acid containing electrolyte.

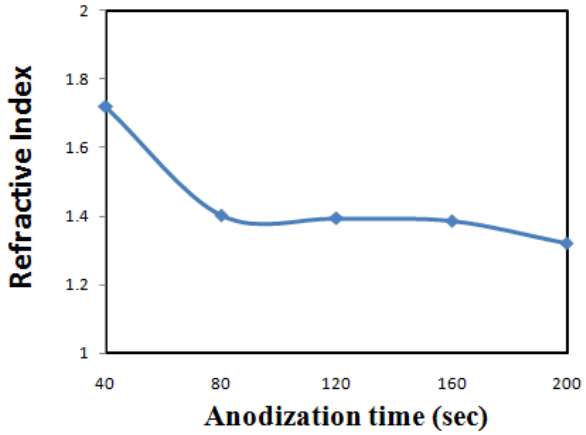


**Fig -4**: Refractive index as a function of anodization time

Figure 4 shows the variation of refractive index with respect to anodization time at fixed current density. As the

anodization time increases from 40 to 200 seconds, the refractive index value decreases from 1.72 to 1.32. This decrease in refractive index is due to an increase in porosity.

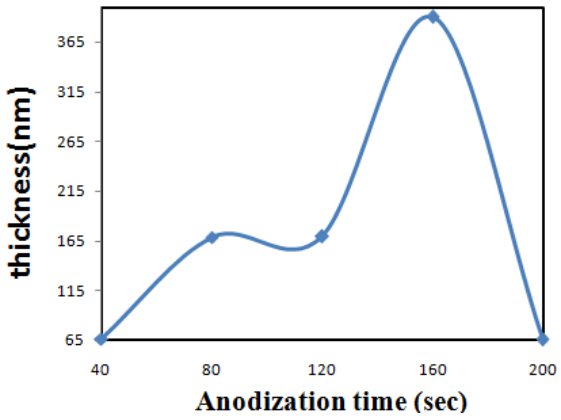


**Fig -5:** Thickness as a function of anodization time

Figure 5 shows the variation in porous silicon thickness with respect to anodization time at fixed current density. As the anodization time increases from 40 to 160 seconds, the thickness value rises from 66.19 to 390.1 nm and at anodization time 200 seconds the thickness is observed to be reduced to 65.71 nm. The similar nature of curve is reported in the literature [7].An increment in the porous silicon thickness can be observed with an increase in etching time. Table I shows the measured values of porosity, refractive index and thickness prepared at constant current density 30 mA/cm $^2$ with different etching time 40,80,120,160 and 200 seconds respectively.

**Table -1:** Obtained values of porous silicon samples

| sample | Electrolyte | Current Density (mA/cm$^2$) | Etching time (sec) | Porosity (%) | Refractive index | thickness (nm) |
|---|---|---|---|---|---|---|
| S1 | 1:1:2 | 30 | 40 | 68.72 | 1.72 | 66.19 |
| S2 | 1:1:2 | 30 | 80 | 78.68 | 1.40 | 168.7 |
| S3 | 1:1:2 | 30 | 120 | 79.04 | 1.39 | 169.3 |
| S4 | 1:1:2 | 30 | 160 | 79.29 | 1.38 | 390.01 |
| S5 | 1:1:2 | 30 | 200 | 81.90 | 1.32 | 65.71 |

With fixed current density, as the anodization time varies the porosity varies which results in variation of reflectance. Figure 6 shows the reflectance of four porous silicon samples prepared at anodization time 80, 120, 160 and 200 seconds. It is observed that with increase in etching time from 80 to 200 seconds, the reflectance value decreases with more oscillations which are due to increased thickness. Our result is agreed with the reported work [7,8].

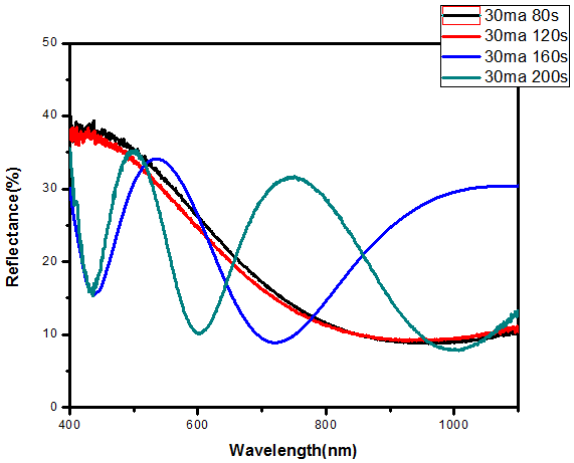


**Fig -6:** Reflectance of porous silicon samples prepared at different anodization time

FTIR absorption spectrum of porous silicon prepared at 30mA/cm$^2$with etching time 160 seconds is shown in figure 7. The molecular structure within the specimen is observed and the absorption peaks of important elements are listed in Table 2.

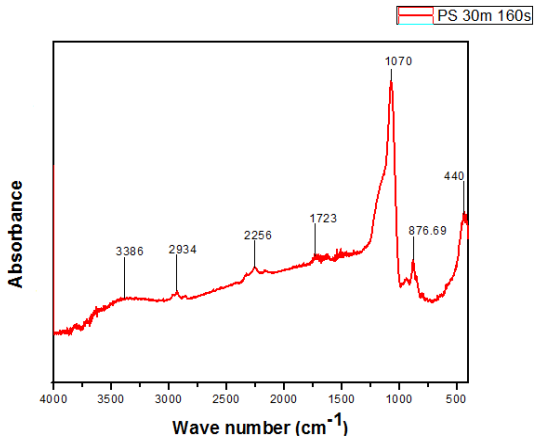


**Fig -7:** FTIR spectra of porous silicon sample prepared at J=30mA/cm2

The presence of Si-Hx groups in porous silicon is confirmed by FTIR analysis and the FTIR peaks are well matched with the reported literature [7,8].

**Table -2:** FTIR absorbance peaks

| Absorption Band (cm$^{-1}$) | Mode | Vibrational mode |
|---|---|---|
| 440 | Si-O-Si | Bending |
| 876.69 | $O_3$ Si-OH | Bending |
| 1070 | Si-OH | Stretching |
| 1723 | C=O | Carbon Oxygen Bond |
| 2256 | C≡C | Alkyne |
| 2934 | $CH_2$ | Asymmetric stretching |
| 3386 | OH | Stretching, water vapour |

Figure 8 shows the Field emission scanning electron microscopy (FESEM) image of porous silicon sample fabricated at current density 30mA/cm$^2$ with etching time 80 seconds. The porous structure is visible with its average pore size 30 nm.

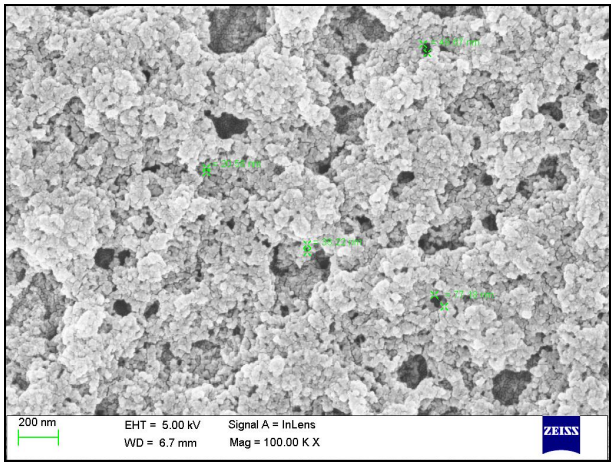


**Fig -8:** Surface morphology of porous silicon by SEM

The diameter of the pores can be obtained by tuning the fabrication parameters and hence, low reflectance can be attained. In this, way porous silicon is useful in solar application as antireflection material to reduce the surface loss of incident light.

## 4. Conclusion

The electrochemical preparation of porous silicon has been presented and characterized. The filmetric measurement showed an increment in the porosity and thickness of the porous silicon with an increase in anodization time while decrement in refractive index with the rise in anodization time. The enhanced anodization time has reduced the reflection as a result of enhanced porosity. FTIR measurement has confirmed the various absorbance peaks corresponding to the porous silicon. The surface morphology (SEM) analysis has also confirmed the rough surface indicating the formed porous structure with about 30 nm pore diameter. As comparis onto silicon-nitride thin film fabricated by chemical vapor deposition, an electrochemical fabrication of porous silicon is easy and cost-effective method. In this way, the fabrication cost of antireflection coating in solar cells can be reduced with porous silicon films.

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