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Structural, Morphological, Chemical and Optical Properties of Porous Silicon Prepared By Electrochemical Etching

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Abstract: In this paper, porous silicon layers was prepared from p-type silicon with orientation (100) by electrochemical etching method , samples were anodized in a solution of 48% HF and 99% C_2H_2OH at 1:1 ratio and study the morphology properties of PSi samples by changing etching time (15, 17 and 20) min for fixed (11.5 mA/ cm^2) current density, and imaged PSi sample in Atomic force microscopy(AFM), which shows the rough silicon surface, with increasing etching process (etching time) porous structure nucleates which leads to an increase in the depth and width (diameter) of surface pits. Consequently, the surface roughness also increases and we found that the porosity of PSi increasing with the increasing etching time. The XRD measurements has confirmed the crystallinity nature of porous silicon. A broad peak of blue emission has also confirmed by photoluminescence (PL) measurements and it has been attributed to SiH_x groups which are confirmed by FTIR spectra. Chemical fictionalization during the electrochemical etching show on surface chemical composition of PSi. From the FTIR analyses showed that the Si dangling bonds of the as-prepared PSi layers have large amount of Hydrogen to form weak Si–H bonds.

Keywords: Porous silicon, X-Ray Diffraction, PL, AFM, and Electrochemical etching method.

1 Introduction

Porous silicon (PSi) consists of a network of nanoscale sized silicon wires and voids which formed when crystalline silicon wafers are etched electrochemically in hydrofluoric acid based electrolyte solution under constant anodization conditions like etching time , current density , HF concentration and Si orientation. Porous silicon structures has good mechanical robustness, chemical stability and compatibility with existing silicon technology therefore has a wide area of potential applications such as waveguides, 1D photonic crystals, chemical sensors, biological sensors, photovoltaic devices etc [1].

Electrochemical is an easy method for porous silicon formation which employs a gold cathode and silicon wafer anode immersed in hydrofluoric acid (HF) electrolyte with constant current source, which is usually implemented to ensure steady tip concentration of HF resulting in a more homogenous porosity layer [2].

The PSi has interesting characteristics such as: low index of refraction, the surface of the PSi being highly textures can enhance light trapping and reduce reflection

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losses of a solar cell, and the tenability of the band gap of PSi may be used to optimize the sunlight absorption [3].

The optical properties of porous silicon (direct gap, low reflectivity, variable refractive index, blue photoluminescence, randomized morphological structure and possibility of band gap engineering) make this material to be a good candidate for photovoltaic applications [4].

The main objective of this paper is to study the effect of etching time on surface changes.

2 Experimental

PSi samples were prepared by electrochemical anodization etching of p-type silicon (100) oriented with a resistivity (10 Ω.cm) at a constant current density (11.5 mA/ cm^2) and the etching times were (15,17 and 20)min and the etching cell made from Teflon because the Teflon not interaction with HF acid, rubber O-ring is used before the upper part of cell. The latter has a central circular of ($1cm^2$) to allow touching the silicon wafer. And the two electrodes are used to apply current across the cell, the lower one is stainless still foil below silicon wafer and the upper one is gold grid connected with the HF solution. For anodization, power supply -305D is used as constant DC current source. With electrolyte solution containing 1:1 ratio of HF (48%): Ethanol (99.99%) respectively.

In case of use of purely aqueous HF solutions, for the formation of PSi formation; hydrogen bubbles stick to the surface and induce lateral and in-depth inhomogeneity. Ethanol is often added to the HF solution to reduce its surface tension, thereby allowing the H_2 gas formed during the reaction to escape, preventing it from sticking to the etching surface and improving the homogeneity of the resulting porous layer.

The structure of porous silicon are studied as shown by XRD-6000 SHIMADZU Japan, FTIR the Fourier Transform Infrared Spectrophotometer (SHIMADZU-8400S) and AFM the atomic force micrographs were taken for porous silicon by a Solver P-47H (Digital Instruments Nanoscope NT-MDT SOLVER P47H-PRO).

3 Results and Discussion

3.1 Structural Properties

Typical diffraction pattern of PSi sample fabricated at current density of (11.5 mA/cm^2) and etching time (15, 17 and 20)min are shown in fig. (1). The X-ray beam is diffracted at specific angular positions with respect to the incident beam depending on the phases of the sample. When 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 [5,6]. One important property of porous silicon is that its skeleton maintains the structure of silicon crystalline after anodization, as shown by X-ray topography studies. It is well known that crystallites size can be estimated from diffraction pattern analysis by measuring the full width at half maximum (FWHM) measurement and applying the Scherrer equation:

$$D=K\lambda/(B\ COS\ \theta_B) \quad (1)$$

Where [7]:-

B: is the FWHM in radians.

K: is the Scherrer constant (1 > K > 0.89).

θ_B: is the diffraction angle in radians.

λ: is the wavelength in nm.

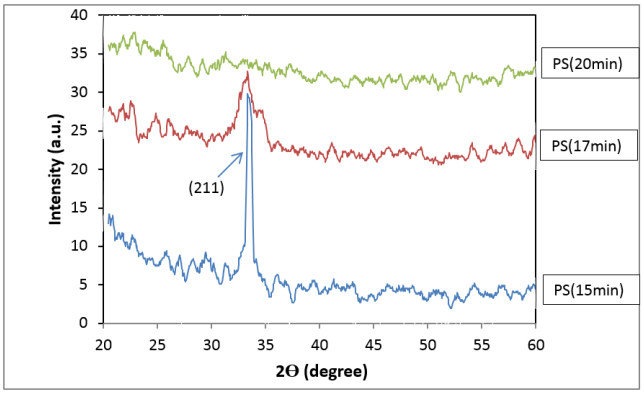


Fig. (1): X-ray diffraction of porous silicon prepared at current density (11.5mA/cm^2) and etching time (15, 17 and 20) min.

The crystallites size obtained for PSi samples are shown in Table (1), when estimated by the Scherrer equation, a significant crystallites size decrease trend can be clearly noted on increasing etching times, these results agree with [4,8]. XRD spectra of PSi showed a broaden peak at 2θ = 33.266° showing the single crystalline nature of the wafer. This peak becomes very broad with varying full width at half maximum (FWHM) for different anodization etching time as shown in Figure (1), which confirms the formation of pores on the crystalline silicon surface. When the etching time is increased from 15 min to 20 min number of pores increased with thicker silicon walls as evident from the broaden nature of the (211) peak. So that, the presence of this peak in all the PSi structures confirms that the cubic structure of the crystalline silicon is retained even after the pore formation [9].

Table 1: Calculated average Grain size, Strain, and Dislocation density for p-PSi for different etching time.

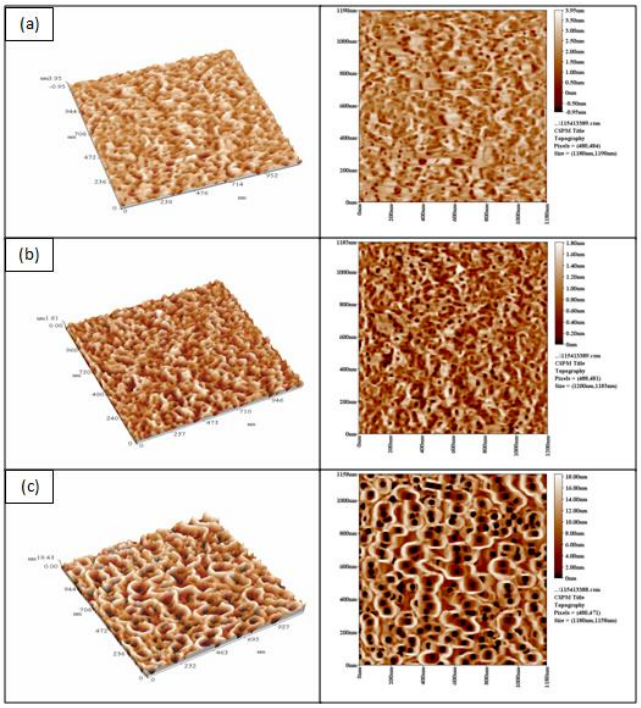
Etching time (min)	2theta (deg)	FWHM (deg)	D (nm)	Strain x10^{-4} Lines^{-2} m^{-4}	Dislocation density x10^{14} Lines m^{-2}
15	33.2	0.172	50.35	7.19	3.94
17	32.9	0.125	69.27	5.23	2.08

20	-	-	-	-	-	20	58.04	4.1	4.93	84.99%

3.2 Morphological Properties

Fig. (2) Shows the morphology of three samples prepared at anodization times of (15, 17 and 20)min, respectively denoted (a), (b) and (c). The effects of varying etching times on PSi at constant etching current density (11.5 mA/cm2) have also been studied. These images show that the PSi has a sponge like structure.

We can note from this figure that the pore width increases with the increasing of etching time. When etching time increases a part of pores coagulate to larger structures. Fig. (2a,b and c) shows relationship between the etching time and pore width, where the value of average pore width increases with increasing of etching time as reported in table (2)[4].



Fig(2): 3D & 2D AFM images (1.5 × 1.5 mm) of PSi samples prepared with etching time of (a) 15min, (b) 17 min and (c) 2 0 min at current density of (11.5 mA/cm^2).

Table (2): The calculated morphology characteristics of PSi samples prepared with different affiliation etching process

Etching time (min)	Diameter Avg. (nm)	Roughness Ave. (nm)	RMS (nm)	Porosity %
15	27.82	0.572	0.712	33.39%
17	30.31	0.302	0.368	64.5%

Porosity can be determined easily by weight measurements. The virgin wafer is first weighed before anodization (m_1), then just after The higher current causes more solving silicon and anodization (m_2) and finally after dissolution of the whole porous layer in a molar NaOH aqueous solution (m_3) [10].

$$\boldsymbol{p(m)\% = \frac{m_1 - m_2}{m_1 - m_3}} \quad (2)$$

As illustrated in table (2), the porosity increase with increasing etching time as shown in fig.(3).The largeness in pore width may be attributed to increase in holes number on surface of silicon electrode with etching time which leads to preferential dissolution of pores, and further the enlargement of the area of each pore leading to reducing the width of the walls that separate pores.

The surface morphology measured by AFM is given in figures(2), which show that the surface of the PSi layer consists of homogeneous and large number of irregularly shaped distributed randomly over the entire surface. We found that the average diameter of pores increase by increasing the etching time from 15 to 20 min, as reported in table (2). These results are in a good agreement with those of other investigations [4,11].

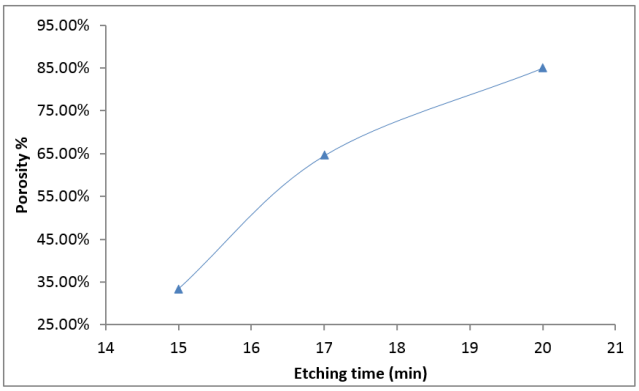


Fig. (3): Porosity as a function of etching time.

3.3 Chemical Composition of PSi Layer

Surface chemical composition of PSi is best probed with Fourier Transform Infrared (FTIR) spectroscopy. FTIR signal in PSi is larger and easier to measure than in bulk Si due to much larger specific area. If the manufactured PSi layer is stored in ambient air for a few hours, the surface oxidizes spontaneously [5]. 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. Fig.(4) shows, the FTIR spectra measured from samples at current density (11.5 mA/cm^2) and etching time (15 , 17 and 20 min), the peaks at around 880 cm^{-1} and

1080 cm^{-1} are from Si–O–Si stretching modes , which are dependent on the oxidation degree of PSi. The transmittance peak at 624.94 cm^{-1}, 2088.99 cm^{-1} and 2113.98 cm^{-1} Si-H bending in (Si_3-SiH), 871.82 cm^{-1} Si-H_2 wagging mode and 644.22 cm^{-1} and 910.4 cm^{-1} Si-H_2 scissor mode

FTIR is powerful technique that can determine the chemical species present in a material. This technique measure the amount of radiation absorbed by the chemical bonds in a material as the radiation wavelength is varied through the infrared region. Specific chemical bonds will absorb the radiation at different frequencies [12].

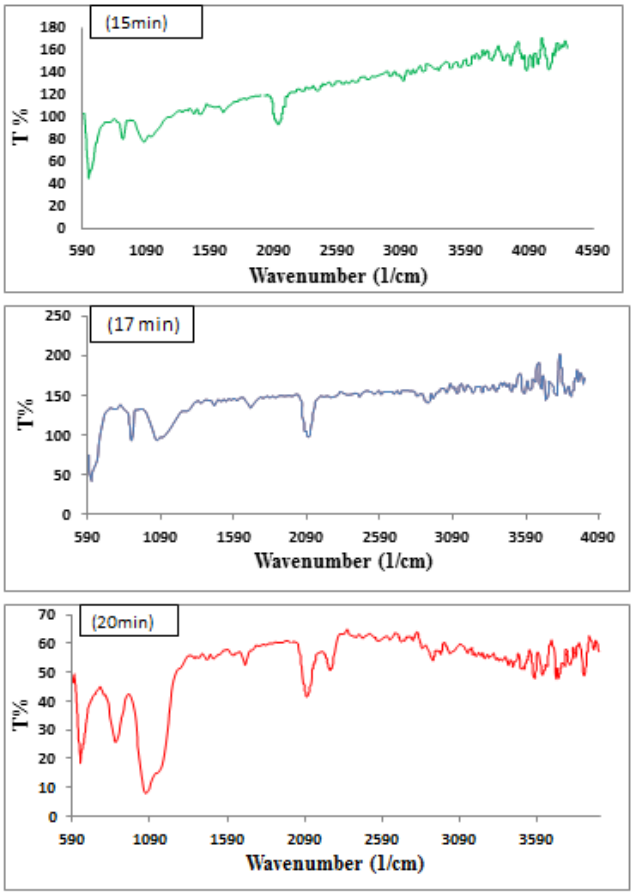


Fig (4): FTIR transmittance spectrum of a PSi layer at (11.5 mA/cm^2) and etching time (15, 17 and 20min).

3.4 Optical properties

3.4.1 Photoluminescence (PL) spectral studies

The photoluminescence (PL) spectra of the p-type PSi formed using different etching times of (15, 17 and 20) min are displayed in fig. (5). It can be seen that room temperature PL in the visible region has been obtained for all the etching times used. The PL intensity maximum has been found to occur at (753, 695.5 and 693.5 nm) for the etching times of (15, 17 and 20) min respectively, indicating that there is a blue shift of the PL maximum with etching time. It is interesting to note that the maximum PL intensity of the PSi sample increases with increasing anodizing time and attains maximum for the anodizing time of (20min). It is highly likely that the increase of the PL intensity is caused by the increase in the total volume of the nanocrystallites on the surface of the PSi [13]. Increasing the etching time to 20 minutes, the pore size is maximum (AFM image); correspondingly the PL intensity is also maximum with a blue shift of the PL peak position. So it can be concluded that as the porosity of PSi increases there is a blue shift of the PL peak position. Such a trend in PL peak position shifting to the blue side, with increasing pore size has been reported earlier [14,15].

The availability of room temperature PL emission in the visible range and a blue shift with porosity of PSi are strong evidences for the quantum confinement effect (QCE) in PSi. According to Chen and Chen [16], when the etching time increases, electrons are confined to a narrower region as a result this 1.78 eV peak is blue shifted [15].

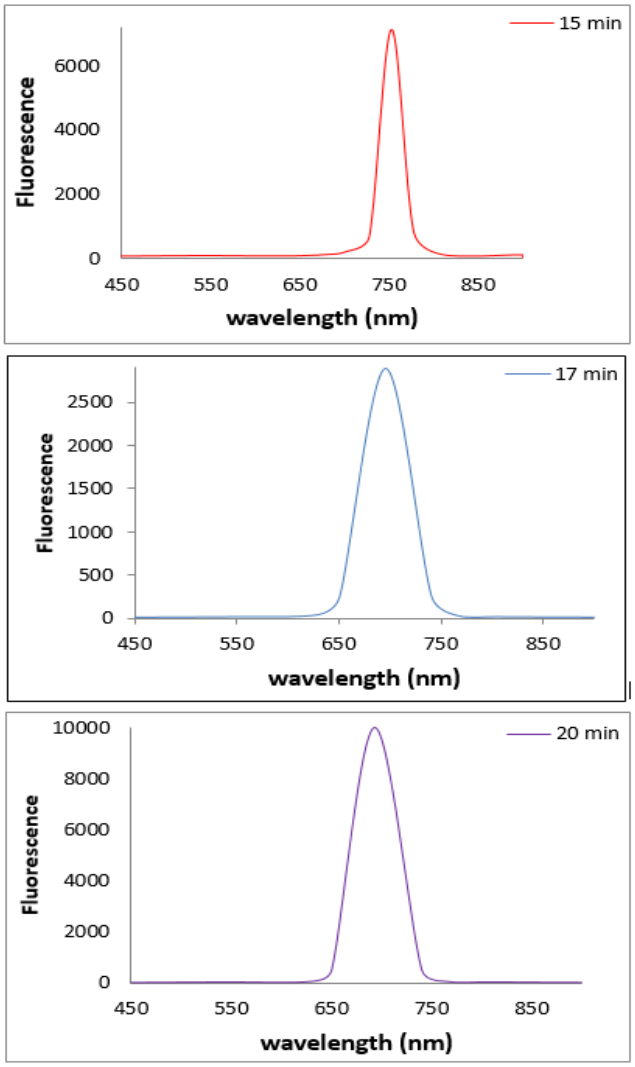


Fig (5): PL spectra of PSi samples prepared at (11.5 mA/cm^2) and etching time (15, 17 and 20min).

4 Conclusion

We found in preparing porous silicon by electrochemical etching for different etching times. It can be concluded that:

1- The XRD properties showed the porous structure and the decrease of the Si nanosized because a broadening of the Si peaks, also a sharp peak which confirmed that the crystalline properties of porous silicon was not disturbed after electrochemical etching process.

2- The AFM investigation shows the rough silicon surface with increasing in etching time orders the small pores to exhibit sponge like giving rise to larger pore diameter and the average pore diameter appears in good agreement with what expected for a mesoporous and macroporous layer. And we also found that when increasing time of etching the porosity of PSi increasing.

3- The surface hydrides on the surface of porous silicon were responsible for the blue band photoluminescence and it has been attributed to SiH_x groups as confirmed by FTIR spectra. A broad peak of blue emission was also confirmed by photoluminescence measurement. The increase of the PL intensity is caused by the increase in the total volume of the nanocrystallites on the surface of the PSi.

4- The FTIR shows that the Si-H_x peaks are observed at the surface of the PSi layer and these chemical species also give raise the PL in PSi.

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