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Influence of Etching time on Refractive index of Nanocrystalline Porous Silicon

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ABSTRACT:-*Porous Silicon (PS) layers produced by electrochemical anodization method of p-type silicon wafer at different etching times. The structural, morphological and optical properties of PS were studied by XRD, SEM and PL analysis. The porosity of the PS layers was determined using the parameters obtained from SEM images by the geometrical method. The refractive index values of the PS layers as a function of porosity were determined by Effective Medium Approximation Methods (EMA). The influence of etching time on porosity and the refractive index of PS, were discussed. SEM images indicate that the pores are surrounded by a thick columnar network of silicon walls. This porous silicon layer can be considered as a sponge like structure. The crystallite sizes of PS nanocrystallites were determined by XRD studies.PL study reveals that there is a prominent emission peak at 776.5 nm. No spectral shift was observed. These results suggest that this nanocrystalline porous silicon could be a potential candidate for optical as well as optoelectronic device applications.*

Keywords: *Porous Silicon; SEM, XRD, PL and EMA*

1. INTROUCTION

Crystalline Silicon (c-Si) has historically been the prevailing material for electronics, spell work in optoelectronics has banked almost exclusively on III - V compound materials such as GaAs and InP. The principal reason for this contradiction is due to the fact that light emission from silicon is visionary because of its indirect band gap structure [1]. The Porous Silicon (PS) has experienced tending both from the experimental as well as the theoretical point of view [2-5]. PS has been examined intensively since the discovery by Canham [1] that even at room temperature PS can emit very promising photoluminescence (PL), in swell contrast to crystalline silicon. PS samples have been prepared by various methods such as electrochemical etching [6], strain etching [7] and laser assisted etching [8] etc., PS can also be formed by an anodic electrochemical etching on single crystalline silicon surface in hydrofluoric acid (HF) mixed solutions [9]. PS can show a large kind of morphologies and particle sizes. In all PS applications, information about the pore size, distribution and surface chemistry and their addiction on the fabrication conditions play a decisive role. Principal parameters such as electrolyte concentration, current density, etching time) that controlling the PS macro pore formation depend on the properties of the silicon substrate wafer type, crystal orientation, doping element and resistivity, etching solution and temperature [10]. The principal intent of the present work is to study the influence of etching time on the physical properties of nanocrystalline PS, especially refractive index.

2. MATERIAL AND METHODS

The Porous Silicon (PS) layers were formed by electrochemical etching of p-type silicon wafers in electrolytes admitting hydrofluoric acid (HF) and ethanol (ratio 1:2). Boron doped p-type silicon wafers (100) orientation having resistivity of 0.5-3.0 ohm-cm and a thickness of 250±0.5µm was used. The constant electrolyte was prepared by mixing HF and ethanol in the ratio of 1:2 and the anodization current density was maintained at 20 mA/cm^2. The electrolyte was taken in a Teflon cell. The cathode of the anodization cell connected to a carbon rod positioned at about 1 cm from the wafer in the electrolyte and the silicon surface itself was the anode. Prior to etching, the samples were placed in the etching solution for 1 min to remove the native oxide. In the present work, the PS layers were formed by constant anodization current density for constant electrolyte concentration and altering etching times. The surface morphology of PS was analyzed using the scanning electron microscope (Philips Model 30XL). The X-ray Diffraction spectra were recorded using Bruker D8 advanced X-ray Diffractometer using CuKα_1 (1.54060 nm) as a source. The PL spectra were recorded using PerkinElmer LS-50B Fluorescence Spectrometer for PS surface.

3. RESULT AND DISCUSSION

3.1 Surface Morphological properties

Fig.1 (a - c) show the top views of the SEM image of our prepared PS samples prepared at anodization etching times of 5 min, 10 min and 15 min, respectively. Fig. 1(a) show that the smaller pores are formed on the silicon surface for etching time 5 min. Further increase etching time 10 min, the pore diameter has increased with a thick columnar network of silicon walls surrounding the pores. When etching time (15 min) increases a part of pores coagulate to larger structures. Fig. 1 (a - c) shows the relationship between the etching time and pore width, where the average pore width increases with increasing of etching time. The pore size distribution is relatively uniform and the columnar walls are thin. The figure clearly indicates the sponge-like structure of PS layer. The average pore diameter was calculated using the following Eq.1 [6,11,12],

$$E(eV) = Eg + \frac{h^2}{8d^2}\left[\frac{1}{m^*_e} + \frac{1}{m^*_h}\right] \quad (1)$$

where E(*eV*) is the energy band gap of PS obtained from the PL peak (Fig. 3). The energy band gap of c-Si is 1.12 eV, h is Planck's constant = 4.13×10^{-15} eVs, d is the diameter of the pore and m^*_e and m^*_h are the electron and hole effective mass, respectively (at 300 K, m^*_e = 0.19 m_o, m^*_h = 0.16 m_o and m_o= 9.109×10^{-31}kg). Average pore diameter of PS is found to be 5.35 nm. The result agrees well with the earlier report on PS layer (6.2 nm) by K.A. Salman et al. [13]. The porosity can be determined easily by a function of geometrical parameters is written [6].

$$P = \left(\frac{\pi}{2} * 1.732\right)\left(\frac{1}{1+\frac{m}{d}}\right)^2 \quad (2)$$

Where, d is the average pore size and m is the distance between pores. Using the above equation, the calculated porosity values are given in Table 1.

Kindly insert Figure 1 and Table 1.

3.2 Structural Properties

The XRD measurement was used to investigate the crystalline size of the PS and to determine the crystalline degree of the etched sample. Fig.2 shows the XRD result for the PS layers at 10 min etching times. The different etching times created different morphologies in the PS layers, this means that the different shapes appeared at the PS layers, which produces different diffraction angles. On the other hand, the different types of porosity caused by the different morphologies of the PS layers were provided to investigate if there is a match between the theoretical part and the experimental part, which will help calculate the grain size [14]. The PS gives a very strong, prominent peak at 2θ = 69.140° (JCPDS Card No. 77-2110) corresponds to the reflection from the (400) set of planes; in addition, it gives a very close weak peak on the higher 2θ side at 2θ = 69.337°. So it can be taken to mean that the wafer used has two different grain sizes. The broadness of the peak is due to the formation of porous silicon and may be attributed to the higher roughness of the sample [15]. On the other hand, to select the best PS layer with optimal etching time as a good substrate for use in the fabrication of devices. Further the narrow peaks with a small value of FWHM can be taken to indicate good crystallinity and large grain size of silicon particles. The grain size for the most dominant peak calculated using the Debye-Scherrer formula [16].

$$D = \left(\frac{0.9\lambda}{\beta\cos\theta}\right) \quad (3)$$

where *D* is crystallite size, λ is X-ray wavelength (0.15406 nm), β is full width at half maximum (FWHM) of peak in radian and θ is Bragg's angle. The average crystallite size was (20.57) for the PS layer at 10 min etching time.

Kindly insert Figure 2.

3.3 Optical Properties

The room temperature photoluminescence (PL) spectra of the PS layers obtained using the anodization times about 5, 10 and 15 min are presented in Fig. 3. It can be seen that the PL in the visible region is obtained at room temperature for three anodization times used. Fig. 3 shows that the maximum PL intensity occurs approximately at 776.5

nm for three samples. It can be noted that when the anodization time increases, the PL intensity gradually increases for the anodization time of 15 min. At the low anodization time of 5 min, the SEM studies show that small pores have been formed on the surface. This is reflected in the PL spectrum by a relatively low PL intensity. When the anodization time of 5, 10 and 15 min is used, uniform pores with a slightly increased diameter are formed (SEM picture) and correspondingly in the PL spectrum there is a rise in the PL emission. When the etching time is further increased to 15 min, maximum sized pores are formed (SEM studies) and this is supported by maximum PL intensity. However, there is no apparent shift in the PL peak position in spite of increasing the porosity to the maximum. The samples exhibit a PL in the red region and there is good room temperature PL emission from the samples. As mentioned earlier, similar results have also been obtained by S. Yaakob et al. [17]. They suggest a hydride-related luminescence in the PS structures in order to explain such results as these results cannot be interpreted in terms of the quantum confinement model.

Kindly insert Figure 3.

4. EFFECTIVE MEDIUM APPROXIMATION (EMA)

The PS is a composite material with a mixture of single crystal silicon (c-Si) and voids. When the void spaces in the host material are much smaller than the wavelength of incident light, the two phase composite materials can be considered as a single effective medium. The widely used method to model the optical properties of composite materials is the effective medium approximation (EMA).

In the two component system of porous silicon (silicon + air), the refractive index is expected to be lower than that of bulk silicon. The Bruggeman [18], Maxwell-Garnett [19] and Looyenga [20] methods are used here to determine the refractive index (n) of porous silicon. These appropriate, effective medium models depend on the porosity and the morphology of the porous silicon.

The expressions (4), (5) and (6) given by Bruggeman, Maxwell-Garnett and Looyenga describe the refractive index as a function of porosity.

$$n_{PS} = 0.5\left[\begin{array}{l} 3P(1-n^2{}_{Si}) + (2n^2{}_{Si}-1) \\ +\left[(3P(1-n^2{}_{Si}) + (2n^2{}_{Si}-1))^2 + 8n^2{}_{Si}\right]^{0.5} \end{array}\right]^{0.5} \quad (4)$$

$$n^{2/3}{}_{PS} = (1-P)n^{2/3}{}_{Si} + Pn^{2/3}{}_{air} \quad (5)$$

$$(1-P)\frac{n^2{}_{Si} - n^2{}_{air}}{n^2{}_{Si} + 2n^2{}_{air}} = \frac{n^2{}_{PS} - n^2{}_{air}}{n^2{}_{PS} + 2n^2{}_{air}} \quad (6)$$

The calculated effective refractive index values are given in Table 2. It shows that the comparison between refractive index values of Bruggeman, Maxwell-Garnett and Looyenga (Effective Medium Approximation methods) linking the porosity to the refractive index. The porosity is gradually increasing, whereas the refractive index decreases. From Table 2, it could be understood that the porosity is tunable which in turn makes refractive index also tunable and because of the control capability of its refractive index, the application of PS as antireflection coating is of atmost importance. The lower refractive index of the nanocrystalline PS layer which includes air pores, silicon networks over bulk Si in view of Optoelectronic and Optical device applications.

Kindly insert Table 2.

5. CONCLUSION

Fabrication and characterization of PS by electrochemical etching under fixed current density and different etching times were studied. Surface Morphological, Structural and Optical properties were strongly dependent on the anodization time. SEM micrographs showed uniform distribution particles in PS with quantum sponge like structure in the thick columnar network of silicon walls. The effective refractive index of PS was calculated by the three different EMA methods. Visible PL were observed for all PS samples and which exhibits a PL band at red region. The XRD and PL studies confirm the presence of silicon nanocrystallites and networks in the PS structure. The observed variation in refractive index and PL emission intensity with respect to anodization etching time show that PS can be a promising candidate to be used as an antireflection layer in solar cells and in intensity varying light emitting diode applications.

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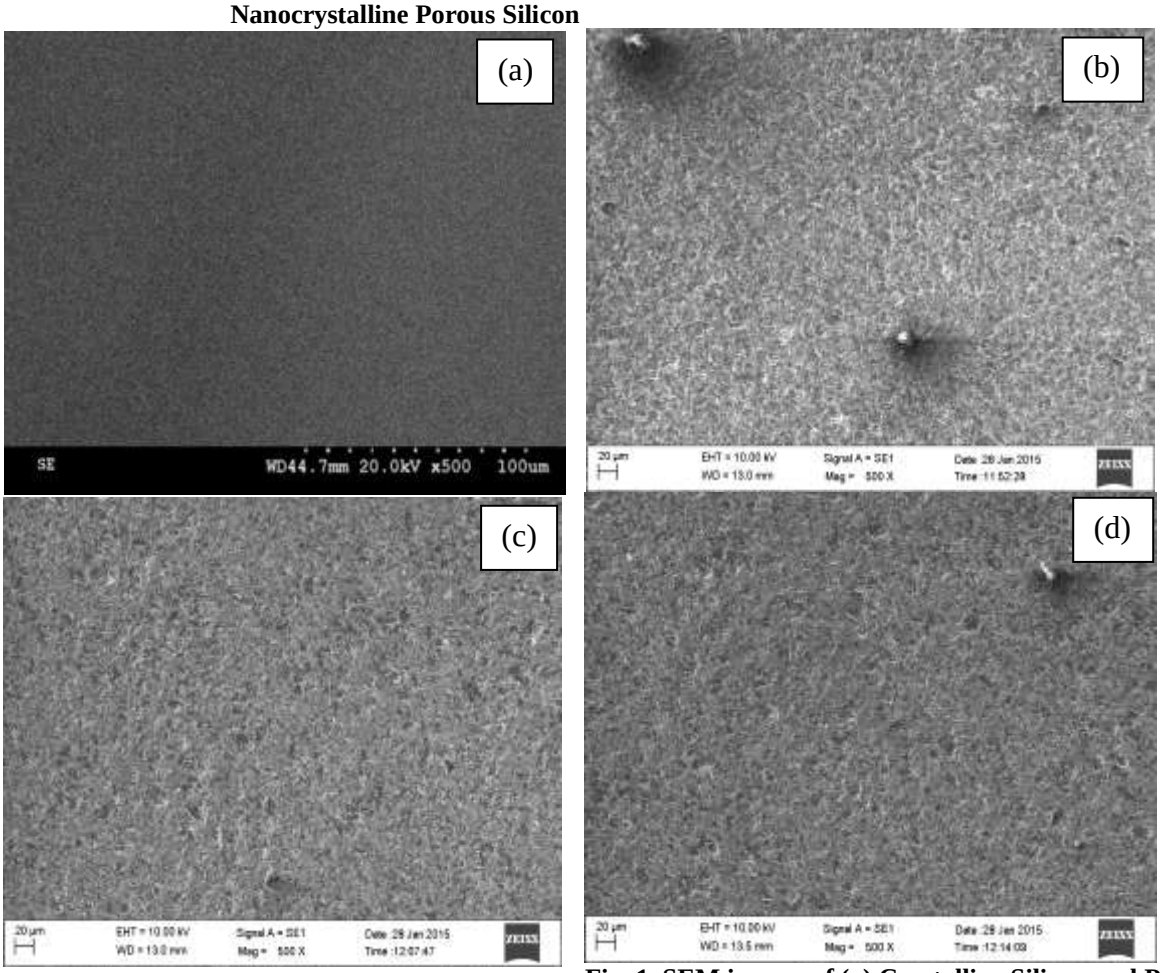

Fig. 1. SEM images of (a) Crystalline Silicon and PS structures formed at anodization etching time of (b) 5 min, (c) 10 min and (d) 15 min.

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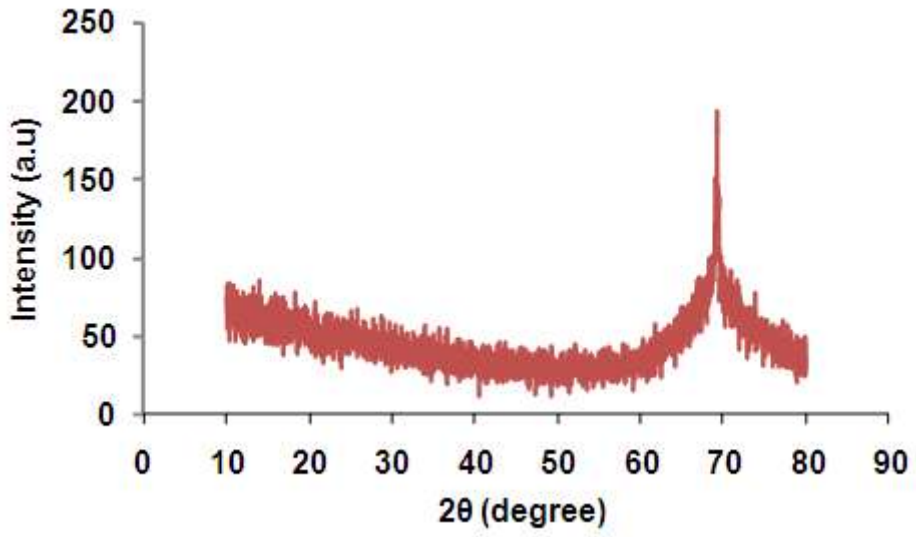

Fig. 2. XRD pattern of Porous Silicon formed at 20 mA/cm^2 for 10 min.

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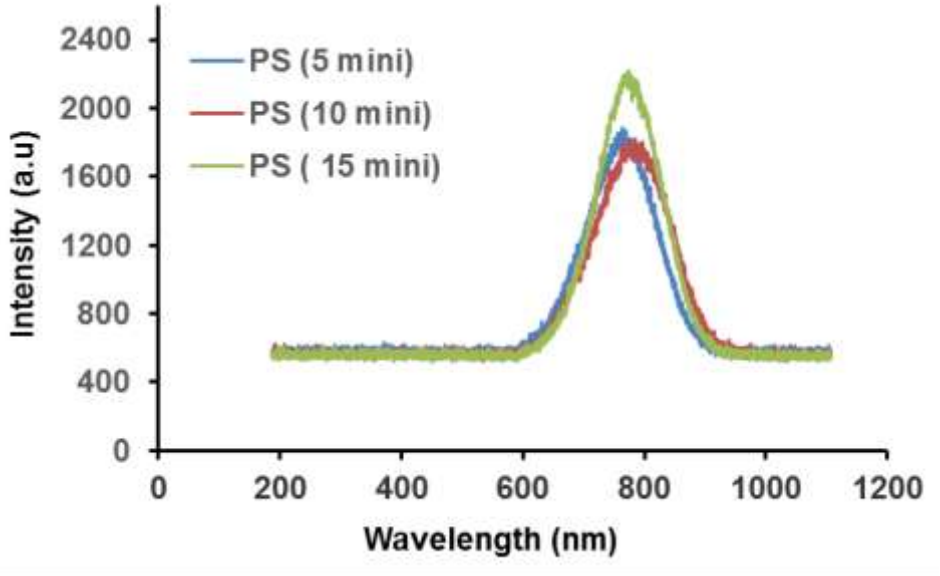

Fig. 3. PL spectra of PS at different anodization times (5, 10 and 15 min.)

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Title of manuscript: Influence of Etching time on Refractive index of Nanocrystalline Porous Silicon

Table 1. Porosity and Pore diameter values of PS for anodization Etching times.

Etching Times (min)	Current density (mA/cm^2)	Porosity (%)	Pore Diameter (nm)
5	20	20	4.95
10		32	5.50
15		45	5.59

Table 2. Calculated values of Porosity and Refractive index values using Effective Medium Approximation methods.

Etching Time (min)	Porosity (%)	Effective Refractive Index (n)		
		Bruggeman Method	Looyenga Method	Maxwell – Garnett Method
5	20	3.22	3.20	3.21
10	32	2.62	2.59	2.60
15	45	2.44	2.40	2.43

