Int. J. Nano Dimens. 6 (3): 315-322, Summer 2015
ISSN: 2008-8868

Contents list available at **IJND**

International Journal of Nano Dimension

Journal homepage: *www.IJND.ir*

Control capability of electrolytic concentration on refractive index and dielectric constant of porous Silicon layers

S. Amirtharajan
P. Jeyaprakash
J. Natarajan
P. Natarajan*

Nanoscience Research Lab, Department of Physics, VHNSN College (Autonomous), Virudhunagar, 626 001, India.

Received 25 August 2014
Received in revised form
15 October 2014
Accepted 20 October 2014

* Corresponding author:
Prithivikumaran Natarajan
Nanoscience Research Lab,
Department of Physics, VHNSN College (Autonomous),
Virudhunagar, 626 001, India.
Tel +919486636535
Fax +914562281338
Email janavi_p@yahoo.com

ABSTRACT

Porous Silicon (PS) samples have been prepared by electrochemical anodization of *p*-type silicon wafer by varying HF concentrations in the electrolytic solution. The structural, surface morphological, optical and surface composition analysis of the prepared samples were done by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Photoluminescence (PL) and Fourier transform infrared (FTIR) spectroscopy studies respectively. The grain sizes of PS were determined by XRD study. The porosity of PS samples was estimated by using the parameters obtained from the SEM images by the geometrical method. The porosity of the samples was found to vary between 11% and 84% due to the variation in HF concentration in the electrolytic solution. The refractive index and dielectric constant values of PS as a function of porosity were determined by Effective Medium Approximation methods. Strong visible emission peak at 498 nm, with no apparent shift with respect to variation in etching parameter, is observed in Photoluminescence study. The surface bonding and their vibration modes of the PS were determined by transmission FTIR spectroscopy.

Keywords: *Porous Silicon; HF concentration; Porosity; Refractive index; Dielectric constant; Photoluminescence.*

INTRODUCTION

Silicon (Si) is a leading semiconductor material in the microelectronic industry. However, due to its indirect band structure, this semiconductor has been considered for a long time as not suitable for optoelectronic applications [1, 2]. Synthesis of Porous Silicon (PS) through electrochemical etching of Si wafer was first reported by Uhlir in 1956 [3]. Canham in 1990 discovered that the electrochemically etched porous silicon can exhibit a very bright photoluminescence (PL) at room temperature, in great contrast to crystalline silicon [1]. PS material has attracted much attention in the optoelectronic industries due to its potential application in the Si-based microelectronics [1, 4].

Porous Silicon generally exhibits a large variety of morphologies and particle size. Principal parameters like HF: ethanol concentration in the electrolytic solution, current density and etching time control the pore formation. The knowledge on the pore size and porosity values of PS samples plays a decisive role in all the applications of PS.

The purpose of this work is to study the control capability of HF concentration in the electrolytic solution on the values of refractive index and dielectric constant of PS samples.

EXPERIMENTAL

Boron doped *p*-type single crystal Si (1 0 0) wafers (0-100Ω cm resistivity) were used in the present study to synthesize porous silicon samples. Porous Silicon was prepared by electrochemical etching of Si wafer for 10 minutes, with a constant current density of 50 mA/cm^2 in an electrolytic solution containing hydrofluoric acid (50% HF) and absolute ethanol (99% C_2H_2OH). The electrochemical etching was done in a Teflon single tank anodizing system, with Si as anode and platinum rod as the cathode. Fixing the concentration of HF in the electrolytic solution as 2.5%, 16.7%, 25%, 33.3% and 37.5% five different PS samples were synthesized.

In the present work the etching current density was chosen as 50 mA/cm^{2}as it has been reported by Pandiarajan *et al*. [5] as the optimized current density to get porous silicon samples with higher porosity.

The X-ray diffraction (XRD) spectra for PS samples were recorded using BrukerD8 advanced X-ray diffractometer using Cu Kα_1 (1.54060 Å) source. The photoluminescence excitation spectra of PS were obtained with a Shimadzu RF 5301 luminescence spectrophotometer, with a pulsed Xenon lamp as the excitation source. To characterize the microstructures of porous silicon the Hitachi S – 3000 N model scanning electron microscope with an accelerating voltage of the electron beam of 30 kV was employed. The Fourier Transform Infra-Red (FTIR) spectra of the samples were recorded using the Shimadzu IR affinity - 1 spectrophotometer. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

XRD analysis

Figure 1 shows the XRD pattern of porous silicon samples prepared on *p*-type silicon wafers keeping concentration of HF as 12.5%, 16.7%, 25%, 33.3% and 37.5% and current density at 50 mA/cm^2.

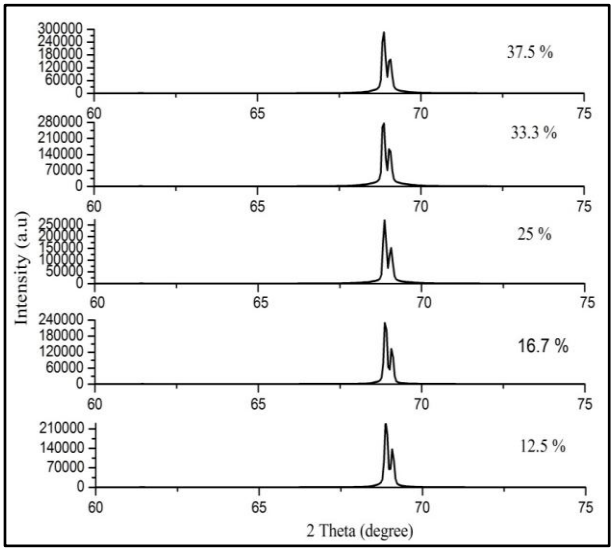

Fig. 1. XRD pattern of porous silicon samples etched with different HF concentrations

The presence of two peaks with 2θ=68.89^o and 69.07^o are observed in the XRD pattern of all the samples. The dominant peak present at 68.89^o corresponds to the reflections from (4 0 0) plane (JCPDS File No. 89-2955) and is due to crystalline Si substrates. Another trivial peak, which occurs at 69.07^o, is due to the porous layer [6]. It is noted that the intensity of all the peaks increases with increase in HF concentration.

The crystallite size (*D*) was estimated using the Debye-Scherer's formula (Equation 1) by substituting the FWHM (β) value obtained from XRD data,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \text{ (nm)} \qquad (1)$$

The calculated grain size values are reported in Table 1.

Table 1. XRD data of porous silicon samples prepared at different HF concentrations.

HF Concentration	2θ	Peak Intensity (a.u)	FWHM	Grain size (nm)
12.5%	68.87°	188660	0.4809	21
16.7%	68.92°	202431	0.3959	25
25%	68.92°	271407	0.3113	32
33.3%	68.87°	276356	0.1186	84
37.5%	68.87°	286286	0.1009	99

It is observed that with an increase in HF concentration the FWHM value decreases and correspondingly grain size value increases.

SEM analysis

A very important characteristic of a porous silicon layer is porosity. The porosity of Porous Silicon (PS) is defined as the quantity of silicon removed during anodization compared with the silicon concentration before anodization evaluated in the same volume. The values of porosity (*P*) of PS sample scan be calculated using the parameters obtained from the SEM images by the geometrical method [7] using the relation,

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

where*d* is the average pore size and m is the distance between pores.

Figures 2a-e show the plane view of SEM images of the PS samples. The SEM image of PS sample etched with 12.5% of HF concentration (Figure 2a) has much wider pores surrounded by Si crystallites. The sample etched with 16.7% of HF has uniform pore distribution with thick columnar network of Si walls, as seen in Figure 2b. In case of sample etched with 25% of HF, the pore size found to decrease (Figure 2c) and the pores are much smaller for the sample etched with 33.3% of HF concentration (Figure 2d). The SEM image of the sample etched with 37.5% HF has large cracks with thin canal like pores all over the surface.

The porosity of all the samples was estimated using Equation 2 and those values are tabulated in Table 2. The porosity was higher (84%) for sample etched with 12.5% HF and is lowest (11%) for 37.5% HF concentration samples.

Buttard *et al.* [6] also observed that an increase in HF concentration decreases the porosity. The EDAX elemental analysis (Figure 2f) shows that the Porous Silicon is composed of Si, O and F elements.

Table 2. Calculated porosity values.

HF Concentration (%)	Porosity (%)
12.5	84
16.7	75
25	71
33.3	20
37.5	11

Refractive index and Dielectric constant of PS samples - Effective medium approximation methods

The Porous Silicon is a complex material with silicon crystal (c- Si) and voids. When the void spaces in the host material are much smaller than the wavelength of an incident light, the two phase complex material can be considered as a single effective medium. The widely used method to study the optical properties of complex materials is the Effective Medium Approximation (EMA). The following expressions (3), (4) and (5) given by Bruggeman [8], Maxwell-Garnett [9] and Looyenga [10]. Effective medium approximation methods are used to find the refractive index of porous silicon samples.

$$n_{PS} = 0.5\left[3P\left(1-n_{Si}^2\right)+\left(2n_{Si}^2-1\right)+\left[\left(3P\left(1-n_{Si}^2\right)+\left(2n_{Si}^2-1\right)\right)+8n_{Si}^2\right]\right]^{0.5} \quad (3)$$

$$\left(1-P\right)\frac{n_{Si}^2-n_{air}^2}{n_{Si}^2+2n_{air}^2} = \frac{n_{PS}^2-n_{air}^2}{n_{PS}^2+2n_{air}^2} \quad (4)$$

and

$$n_{PS}^{\frac{2}{3}} = \left(1-P\right)n_{Si}^{\frac{2}{3}} + Pn_{air}^{\frac{2}{3}} \quad (5)$$

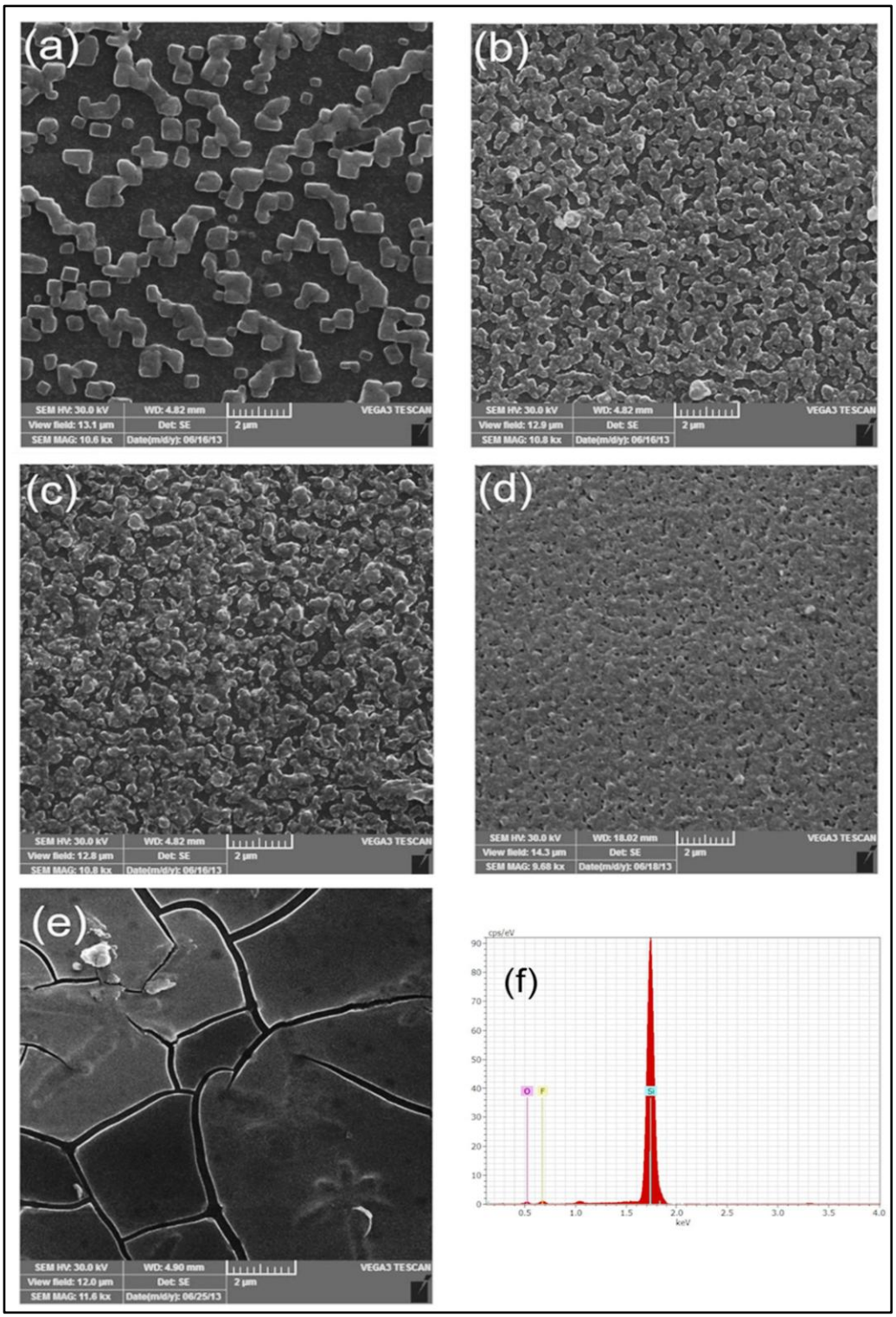

Fig. 2. SEM image of porous silicon surface prepared with (a) 12.5% HF, (b) 16.7% HF, (c) 25% HF, (d) 33.3% HF, (e) 37.5% HF & (f) EDAX spectrum of 25% HF concentration.

These appropriate effective medium models depend on the porosity and the morphology of the porous silicon. The calculated refractive index (n) and dielectric constant (ε) values are given in Tables 3 and 4.

Table 3. Refractive index (n) values calculated using Bruggeman, Looyenga and Maxwell-Garnett Effective medium approximation methods.

Porosity P (%)	Bruggeman method	Looyenga method	Maxwell-Garnett method
11	3.20	3.14	2.82
20	2.98	2.89	2.46
71	1.53	1.60	1.4
75	1.43	1.52	1.32
84	1.24	1.33	1.20

Table 4. Dielectric constant (ε) values calculated using Bruggeman, Looyenga and Maxwell-Garnett Effective medium approximation methods.

Porosity P (%)	Bruggeman method	Looyenga method	Maxwell-Garnett method
11	10.24	9.88	7.97
20	8.86	8.37	6.07
71	2.34	2.59	1.96
75	2.05	2.31	1.73
84	1.54	1.76	1.43

Figure 3a & 3b show the comparative plots of refractive index and dielectric constant values obtained from Bruggeman, Looyenga and Maxwell-Garnett effective medium approximation methods linking the porosity to refractive index and dielectric constant. PS is basically a mixture of silicon and air. So the refractive index (n) of PS is expected to be lower than that of the bulk silicon [11]. It is observed that as the porosity increases the refractive index and dielectric constant decreases. The calculated refractive index values for porosities of 71%, 75% and 84% exactly matches with the reliable results [12, 13].

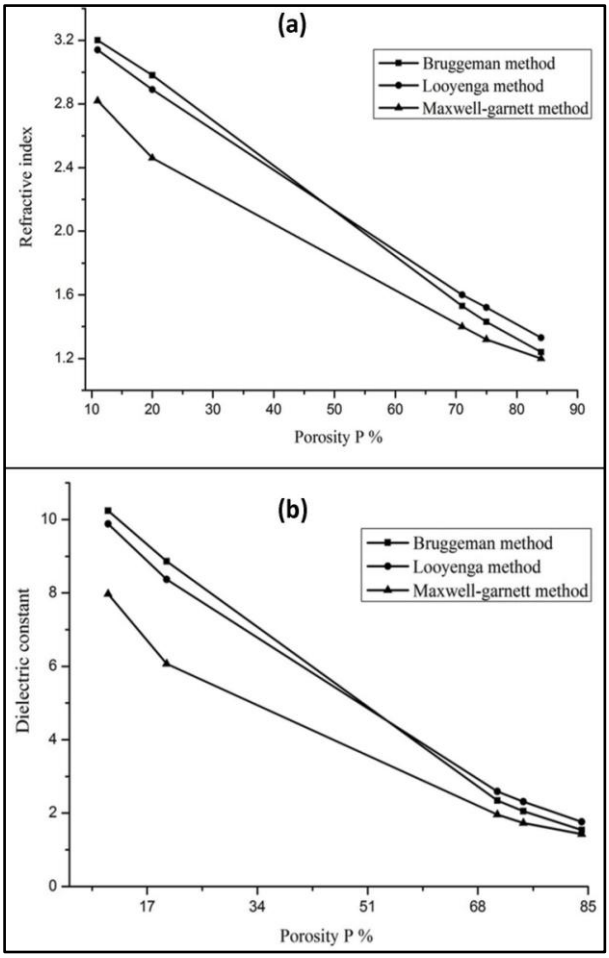

Fig. 3. (a) Comparison plots of porosity *vs* refractive index of porous silicon samples. (b) Comparison plots of porosity *vs* dielectric constant of porous silicon samples.

Photoluminescence analysis

Figure 4 shows the PL spectra recorded at room temperature using an excitation wavelength of 250 nm. It is noted that the PL spectrum has an emission peak at 498 nm in the blue region for all the samples [14, 15]. A strong correlation between the PL intensity and porosity can be observed from the PL spectra. In the present study as the porosity of porous silicon increases, the PL peak intensity increases with no apparent shift in the PL peak position. It has also been reported that high porosity is essential for high visible PL efficiency by O. Bisi *et al.* [11].

FTIR analysis

FTIR spectroscopy gives the information on molecular vibrations; structure, purity and hydrogen bonding present [16]. The optical &

electrical properties strongly depend on the impurity content and surface passivation.

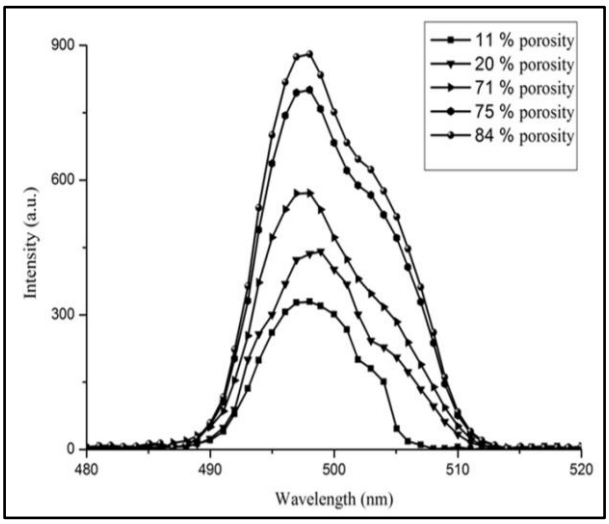

Fig. 4. PL spectra of porous silicon samples with different porosities.

Figure 5 shows the FTIR spectra of porous silicon samples prepared with 12.5%, 16.7%, 25%, 33.3% and 37.5% of HF concentration in the etching solution. The impurity which always found in PS layers is surface passivation hydrogen. FTIR spectra show the presence of Si±H_x group (x=1, 2, 3…. n) in all the PS samples [17, 18].

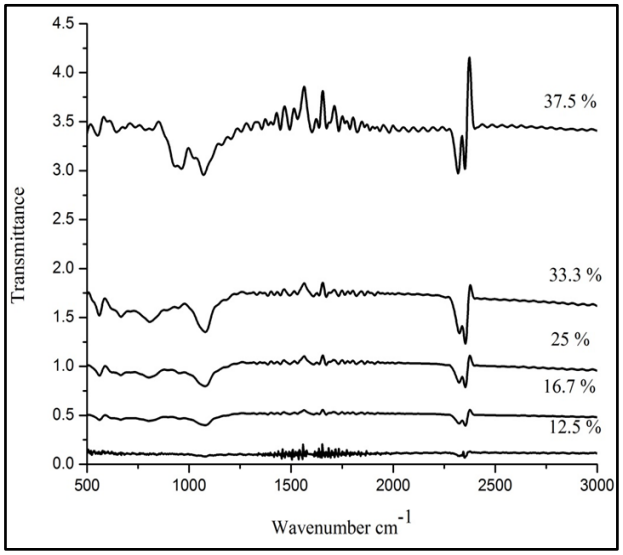

Fig. 5. FTIR spectra of PS samples prepared using different HF concentration.

The observed surface bonding and their corresponding vibration modes are given in Table 5. The peak observed at 450 cm^{-1} is due to Si-O bending and 630 cm^{-1} is owed to Si-H (or) Si-H_2 wagging (or) deformation. The doublet peaks at around 950 $cm^{-1}$are connected to Si-H_2 scissors. The strong transmittance peak is observed at 1000-1200 cm^{-1} and is due to Si-O-Si stretching. The peaks observed in the region 2000-2200 cm^{-1} are assigned to Si-H_x (x=1, 2, 3 … n) bonds.

Table 5. Observed surface bonding in the porous silicon layer.

Wavenumber (cm^{-1})	Bonds	Vibration mode	References
450	Si-O	Bending	[21]
630	Si-H	Wagging	[22]
950	Si-H_2	Scissor	[23]
1160	Si-O-Si	Stretching	[24, 25]
2000-2200	Si-H_x(x=1,2,3…n)	Stretching	[18]
2200-2400	O_3SiH	Stretching	[11]

The presence of hydrogen complexes [Si-$H_{x=1,\ 2,\ 3\ldots\ n}$] are the cause for the occurrence of luminescence in PS samples [19]. Kim *et al.* [20] have pointed out that the role of surface passivation is very important in determining the radiative efficiency of the PS layers. The FTIR transmission peak intensity of SiH_x complexes increases with increase in HF concentration. The results of the present study also indicate that Si-H_x plays a key role in the luminescence properties of PS samples.

CONCLUSIONS

Porous Silicon (PS) has been prepared by electrochemical anodization of *p*-type silicon wafer by varying HF concentrations in the electrolytic solution. The XRD analysis shows that the grain size of the Si crystallites increases with increase in HF concentration. The EDAX elemental analysis reveals that the porous silicon was composed of Si, O and F elements. The porosities of PS samples prepared by varying HF concentration are

determined from SEM images by the geometrical method. The obtained values of porosity found to depend on the concentration of HF in the electrolytic solution. The refractive index (n) and dielectric constant (ε) values were obtained through Effective medium approximation methods using the porosity values. The value of n and ε decreases with increase in porosity value of the PS samples. Visible PL emission peak at 498 nm in the blue region is observed for all the samples. The PL peak intensity increases with increase in porosity and the maximum intensity is observed for sample with 84 % porosity. The FTIR spectra of PS show the presence of Si-H_x bonds and this plays a key role in the variation of PL peak intensity. The present study shows that the porosity of porous silicon is tunable with respect to the HF concentration in the electrolytic solution, which in turn makes the refractive index and dielectric constant also tunable. Thus the control capability of HF concentration over the refractive index of the porous layer makes PS as a potential candidate for tunable antireflection surfaces.

REFERENCES

[1] Canham L. T., (1990), Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers. *Appl. Phys. Lett.* 57: 1046-1048.

[2] Smith R. L., Collins S. D., (1992), Porous silicon formation mechanisms. *J. Appl. Phys.* 71: R1.

[3] Uhlir A., (1956), Electrolytic shaping of germanium and silicon. *J. Bell Syst. Tech.* 35: 333-347.

[4] Canham L. T., Houlton M. R., Leong W. Y., Pickering C., Keen J. M., (1991), Atmospheric impregnation of porous silicon at room temperature. *J. Appl. Phys.* 70: 422-431.

[5] Pandiarajan J., Jeyakumaran N., Natarajan B., Prithivikumaran N., (2013), Influence of current density on refractive index of *p*-type nanocrystalline porous silicon. *Int. J. Nano Dimens.* 3: 207-216.

[6] Buttard D., Bellet D., Baumbach T., (1996), X-ray diffraction investigation of porous silicon superlattices. *Thin Solid Films*. 276: 69-72.

[7] Salcedo W. J., Fernandez F. J. R., Galeazzo E, (1997), Structural Characterization of Photo luminescent Porous Silicon with FTIR Spectroscopy. *Brazilian J. Phys.* 27:158-161.

[8] Bruggeman D. A. G., (1935), Berechnungv Erschiedener physikalischer Konstanten von heterogenen Substanzen. *Ann. Phys. (Leipzig)* 24: 636-679.

[9] Garnett J. C. M., (1904), Colours in metal glasses and in metallic films. *Philos. Trans. R. Soc. London.* 203: 385-420.

[10] Looyenga H., (1965), Dielectric constants of heterogeneous mixtures. *Physica*. 31: 401-406.

[11] Bisi O., Stefano O., Pavesi L., (2000), Porous silicon: a quantum sponge structure for silicon based optoelectronics. *Surf. Sci. Rep.* 38: 111-126.

[12] Theiss W., Hilbrich S., (1997), Refractive index of porous silicon. In Canham L., (Ed.), *Properties of Porous Silicon*. London, United Kingdom:INSPEC. pp: 223-228.

[13] Coyopol A., Diaz-Becerril T., Garcia-Salgado G., Rosendo E., Juarez H., Lopez R., De La Rosa E., Pacio M., Galeazzi R., (2012), Morphological and optical properties of porous silicon annealed in atomichydrogen. *Superficies y Vacio*. 25: 226-230.

[14] Cox T. I., Simons A. J., Loni A., Calcott P. D. J., Canham L. T., Uren M. J., Nash K. J., (1999), Modulation speed of an efficient porous silicon light emitting device. *J. Appl. Phys.* 86: 1999-2764.

[15] Yue Z., Deren Y., Dongsheng L., Minghua J., (2005), Photoluminescence of oxidized porous silicon under UV-light illumination. *Mat. Sci. Engg. B.* 116: 95-98.

[16] Jagmohan A., (2011), Organic Spectroscopy Principles and Applications, Narosa publishing house Pvt. Ltd. Delhi.P. 8.

[17] Prokes S. M., Freitas J. A., Searson P. C., (1992), Microluminescence depth profiles and annealing effects in porous silicon. *Appl. Phys. Lett.* 60: 3295-3297.

[18] Borghesi A., Sassella A., Pivac B., Pavesi L., (1993), Characterization of porous silicon in homogeneities by high spatial resolution infrared spectroscopy. *Solid State Commun.* 87: 1-4.

[19] Hory M. A., Herino R., Lingeon M., Muller F., Gaspard F., Mihalcescu I., Vial J. C., (1995), Fourier transform IR monitoring of porous silicon passivation during post-treatments such as anodic oxidation and contact with organic solvents. *Thin Solid Films*. 225: 200-203.

[20] Kim Y.Y., Lee K.W., Shim S., Yang S. H., Park S. H., Shin H. J., (2003), Photoluminescent Region in a Porous Silicon Layer. *J. Korean Phys. Soc*. 43: 170-173.

[21] Dubey R. S., (2013), Electrochemical Fabrication of Porous Silicon Structures for Solar Cells. *Nanosci. Nanoeng.* 1: 36-40.
[22] Sreejith K., Pillai C. G. S., (2006), IR study on the effect of chloride ion on porous silicon. *Appl. Surf. Sci.* 252: 8399-8403.
[23] Natarajan B., Ramakrishan V., Vasu V., Ramamurthy S., (2006), Structural and Photoluminescence Properties of Porous Silicon: Effect of HF Concentration. *Surf. Review and Lett.* 13: 351-356.
[24] Shao Yuan Li, Wen Hui M., Yang Z., Xiu Hua C., Ming Yu M., Yao Hui X., Zhao D., Xing Hui W., (2013), 3-aminopropyltriethoxysilanes modified porous silicon as a voltammetric sensor for determination of Silver ion. *Int. J. Electrochem. Sci.* 8: 1802-1812.
[25] Acquaroli L. N., Brondino A., Schmidt J. A., Arce R. D., Koropecki R. R., (2009), Infrared study of the oxidation of porous silicon: evidence of surface mode. *Phys. Stat. Sol. C.* 6: 1546-1550.

Cite this article as: S. Amirtharajan *et al.*: Control capability of electrolytic concentration on refractive index and dielectric constant of porous Silicon layers.
Int. J. Nano Dimens.6 (3): 315-322, Summer 2015.