Etching Time Effect on Photoluminescence, Porosity, Surface Morphology and Conductivity of Porous Silicon

Chan Kok Sheng[*]**, Wan M. Khairul Wan Mohamed Zin, Dwight Tham Jern Ee,**
Mohd Ikmar Nizam Mohamad Isa & Mohd Faiz Hassan
School of Fundamental Science, Universiti Malaysia Terengganu,
21030 Kuala Terengganu, Terengganu, Malaysia
[*]e-mel: chankoksheng@umt.edu.my

Abstract

Recently, porous silicon (PS) gains a lot of research interest with its potential applications in optoelectronics, flat panel displays technology, and chemical sensor. In this work, PS was chemically etched on p-type silicon (Si) wafer by hydrofluoric acid (HF) with 40% nitric acid (HNO$_3$) concentration at different etching time. The PS has porosity dependent on etching time in the range (38-60) % that gives orange-red photoluminescence (PL) between 657 nm to 661 nm. The PL intensity increases and the peak wavelength shows slight blue shift as etching time increases. The energy gap obtained are higher than pure Si (1.11eV). Meanwhile, the conductivity of the PS decreases as the porosity and energy gap increase.

Keywords porous silicon, chemical etching, photoluminescence, energy gap, conductivity

INTRODUCTION

Porous silicon (PS) started to gain a lot of interest from the scientific community when the photoluminescence of this material was reported [1]. It is a nanostructured material which introduced nanoporous holes in its structure. Silicon with porous structure was discovered in the 1990's during the electro polishing process of silicon in dilute hydrofluoric solution. Several years later, PS was reported to have a visible photoluminescence at which this important property was pointed out. Besides, PS also demonstrated that it exhibits photoconductivity and photovoltaic properties [2, 3].

Soon after the report of photoluminescence from PS, the possibility for different application of the material was explored. Due to its light emission properties, porous silicon becomes a potential material in the application of optoelectronic, flat panel display technology, and as a chemical sensor. Besides that, porous silicon can be used as a quantum confinement enhancer by anti-reflecting coating on silicon solar cell depending on the charactereristic dimension of the surfaces feature, and also for chemical sensor application, which the effective surface area should be as large as possible [3, 4].

PS is a nanostructured material fabricated by various chemical and electrochemical etching method. Electrochemical etching on silicon (Si) in HF based solution has been commonly used in developing PS, especially in the application of electroluminescence devices. While chemical etching has been another method in forming PS without using external bias which is one of the effective and cost saving methods. The optical property of this material does not only depend on the porosity but also on the structure the porous silicon is formed, different method has been tried and studied. The quantum confinement model have been used to explain the properties of porous silicon, but some evidence suggest that the luminescence properties may not simply be due only to quantum confinement effects [4-6].

In the etching process, the solution used was usually mixture of hydrofluoric acid (HF) and nitric acid with ethanol. Firstly, the silicon surface is oxidized by hole injection from HNO3 and simultaneously its reduction produces NO and water [6, 7]. Then silicon dioxide is etched by a reaction with HF, forming a water soluble complex, H$_2$SiF$_6$ [8]. In past studies, researcher discovered that different etching method and condition in producing PS affect the morphology and photoluminescence [9]. Thus in this study, the porous silicon is first produced by chemical etching using HNO$_3$ as the oxidizing agent at different preparation parameter as compare to other researches. Then the effect of different etching time on the surface morphology, porosity, photoluminescence (PL) and electrical conductivity is studied in detail.

MATERIAL AND METHODS

The silicon wafer used to produce porous silicon is a p-type boron doped silicon wafer with orientation (100), resistivity (0.2 - 0.5) Ω cm and doping concentration ~10^{16}. The reason silicon wafer with orientation (111) is not selected in this research is because will easily break into pie shapes when it is cut. The wafer is cut into the rectangular size with 1.5 ± 0.3 cm^2 by using a precision cutter; model Metkon Micracut 150 and a Polisher; model Metkon Forcipol 2V.

The silicon are then cleaned by the solvent cleaning method to remove oil and organic residue that is on its surface. In the cleaning process, firstly, acetone is poured into a glass beaker and is warmed up by using hot plate at temperature 55 $^{\circ}$C. Then, the silicon are placed into warm acetone bath for 10 min before the samples are removed and placed in the methanol for 5 min. After that, the silicon are removed and rinsed in dionized water (DI water) and are dried by nitrogen gas. The initial weight and thickness of the samples are determined by using the micro balances and digital micrometer.

For the etching process, the solutions were formed with the mixture of HF (48 wt%) and HNO$_3$ (40 wt %) concentrations in 100:1 volume proportion. Then the silicon were dipped into the etchant solution from duration of 5 min to 25 min with interval of 5 min. After etching, the samples were rinsed with distilled water then ethanol and were dried in air [11]. The porosity of the porous silicon is determined gravimetric technique. Porosity is the ratio of the fraction of voids inside the porous layer with the starting silicon. Thus, the porosity is measured by a gravimetric technique that implies the initial weight of the sample and the subsequent weight of the sample after the etching as mention in Equation 1.

$$P = \frac{WT - W2}{WT - W3} \tag{1}$$

Where WT is the theoretically calculated weight of the sample after chemical etching, W2 and W3 are respectively the actual weight of the wafer after the chemical etching and after the porous layer have been removed. The removal of the porous layer is done by dipping the porous silicon in an aqueous solution of 3 wt% potassium hydroxide, KOH in volume for 30 min, where the bulk silicon is not affected.

The morphology properties and surface element of PS were analyzed using the scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) integrated in JEOL JSM-6360LA. SEM is able to produce images of higher resolution compared to optical microscope where it uses electrons (produce from the electron gun) rather than light to form images. The electrical conductivity of the PS surface was measured by using resistivity measurement system with four point probe technique. Besides, the PL of the PS was characterized by photoluminescence spectroscopy system, model JobinYvon HR 800 UV in the range of 500 nm to 800 nm. This system uses a combination of both visible and ultraviolet spectroscopy and particularly useful in the characterization of semiconductor material directly related to the electronic and optical properties of the sample. From the PL spectrum, the energy gap can be determined by Equation (2):

$$E_g = \frac{hc}{\lambda} \tag{2}$$

Where E$_g$ is energy gap of the PS, h is planck constant, c is the speed of the visible light and λ is the peak wavelength (nm) of the PL.

RESULTS AND DISCUSSION

The weight of the sample before and after etching was measured in order to obtain the weight loss of the sample. The porosity of the PS was then determined by gravimetric method. The porosity versus etching time is plotted in Figure 1. It shows that the porosity are linearly increased on the etching time, which is due to the longer contact time of Si with the etchant. The etching rate determined from the gradient of red fitted line is 1.0825 % min^{-1}.

The elemental composition of the PS samples was identified by Energy Dispersive X-ray spectroscopy analysis (EDX) shown in Figure 2. The EDX spectrum shows one similarity that the porous silicon compositions were only consist of two elements namely silicon and oxygen. The first peak and the third peak were the indication of silicon at 0.091 keV and at 1.739 keV, respectively [12]. While the second peak at 0.5249 keV represents the presence of oxygen at the porous silicon surface. Therefore, it can be deduced that the surface of porous silicon contains Si-O and Si-Si bonds [13, 14].

As etching time increases, the void volume increases leading to increase of porosity [15, 16]. Figure 3 shows the SEM images of PS samples prepared with different etching time at magnification of X10000. There were only slight differences on the surface morphology for these samples. Big hillock crystallite structures and small pores population were formed on the PS surface produced at 5 min etching time. The pores size was estimated in range of (50-100) nm and the hillock structure size ~500 nm. At 10 minutes etching time, the PS surface contains small grain structure with the size ~400 nm as shown in Figure 3(a). The small grains are the residue left over from the etched layer of silicon after the chemical etching.
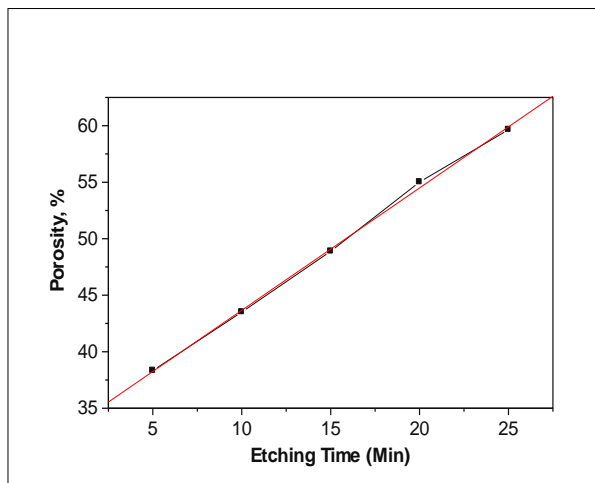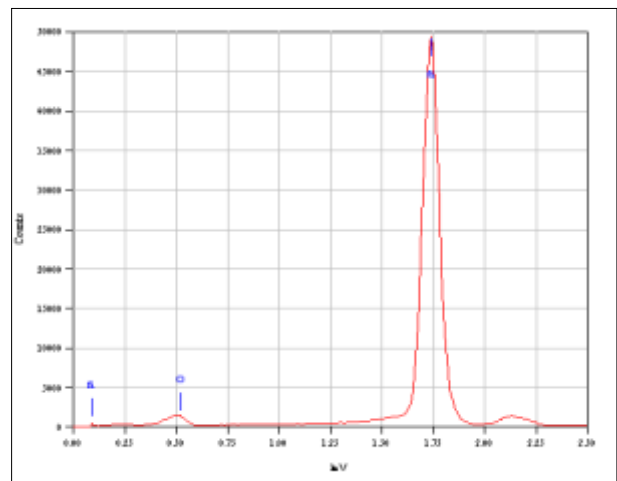

Figure 1 The porosity versus etching time
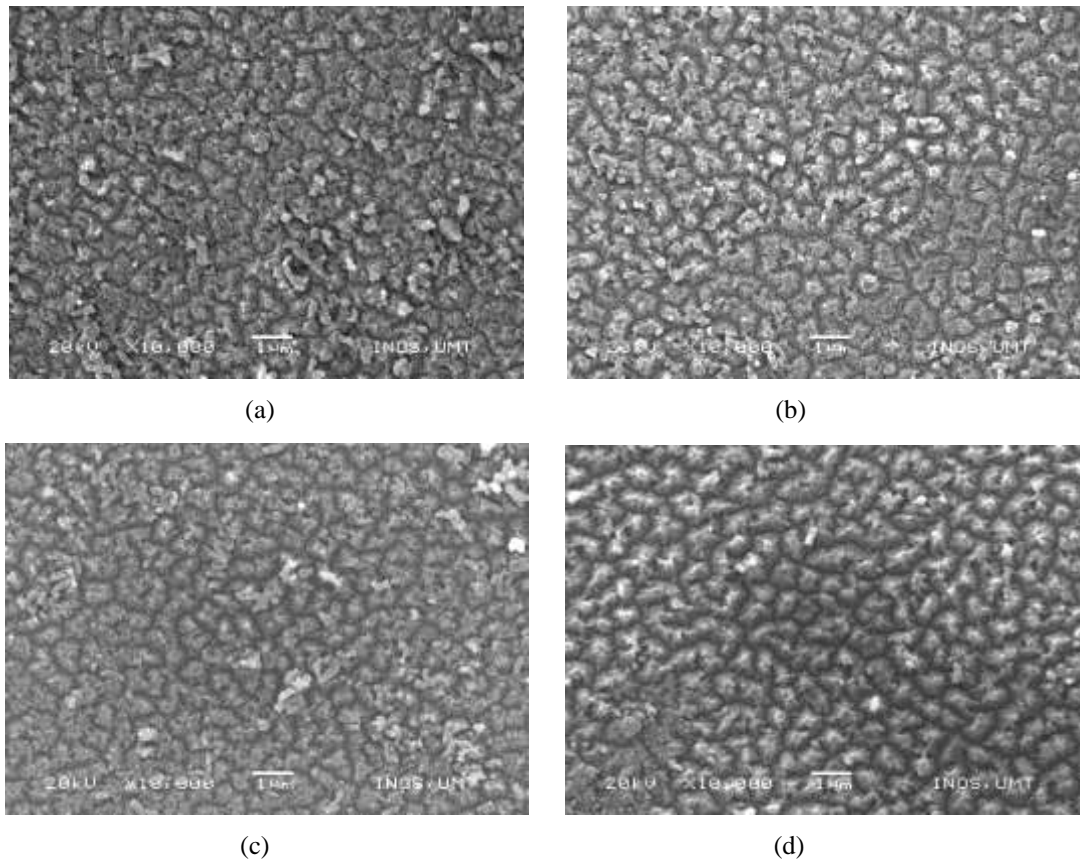

Figure 2 The EDS spectra for PS

Figure 3 SEM images of PS produced at etching time (a) 10 minutes, (b) 15 minutes,
(c) 20 minutes and (d) 25 minutes with magnifications X10000

The grains structures become smaller and lesser in PS at 15 min etching time as depicted in Figure 3(b). Besides, the roughness of surface reduces with wider pores. The surface morphology of PS with 20 min etching time (Figure 3(c)) formed hillock crystallite, slightly more pores and fewer grain structures as compare with those etched at lesser etching time. As shown in Figure 3(d), the surface morphology for PS prepared at 25 min etching time contains more proper formed hillock crystallites and more pores (~100 nm) resulting to higher surface area as compares to others.

The PS was further analyzed by PL spectroscopy and the PL spectrum were Gaussian-like spectrum which almost similar in Vasquez et al. studies [13]. The PL spectrum obtained from the PS at different etching time is shown in Figure 4. The PS are able to illuminate orange-red visible photoluminescence with the PL peak wavelength fall in the range of (657-661) nm.
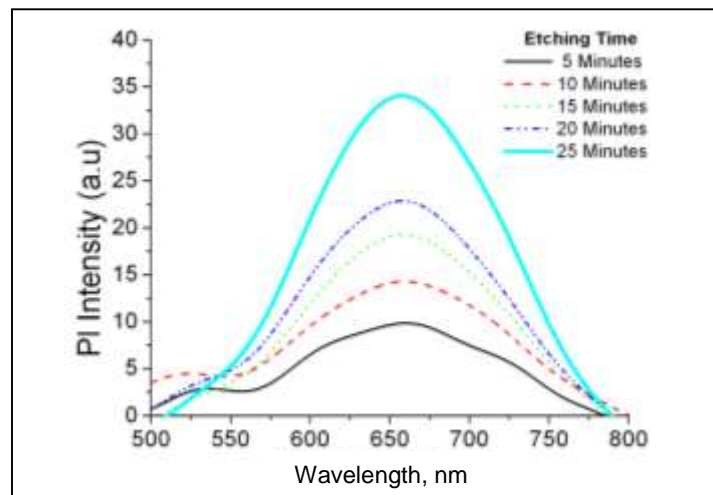
Figure 4 Photoluminescence Spectrum of PS prepare at different etching time

The PL peaks wavelengths plotted in Figure 5(a) shows slight blue shift effect in the range 658 nm to 661 nm as etching time increases. This effect is due to the decrease of the pore population and crystallite structure size as reported by previous researchers [17-20], which consequently resulting in increasing of energy gaps. The shift was small because there were only slight changes on the crystallites and pore size as etching duration varies. The energy gaps of the samples were calculated and plotted in Figure 5(b), where it ranges within (1.9023 - 1.9063) ± 0.0002 eV. The energy gap of PS is higher compare to Si (1.11 eV) and it increases with etching time and porosity, which can be ascribed to quantum confinement effect for silicon nano porous [21-23].

Figure 6(a) depicts that PS porosity and PL peak intensity increases with etching time. These trends were due by the increase of total surface area because high surface area contained more amount of the surface species that illuminate light. Furthermore, the PL peak intensity also shows that it directly proportional with porosity as display in Figure 6(b). There was a sharp increase in PL peak intensity at 25 min etching duration when the porosity only had a slight increased. This phenomenon can be due to the high surface area of the studied sample.
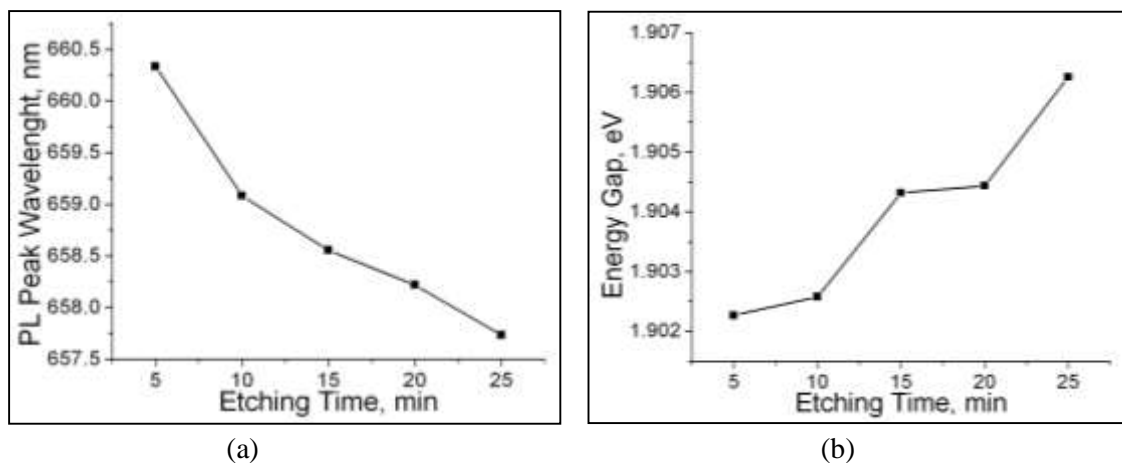

(a)   (b)

Figure 5 Relationship between (a) PL Peak, and (b) Energy Gap with etching time
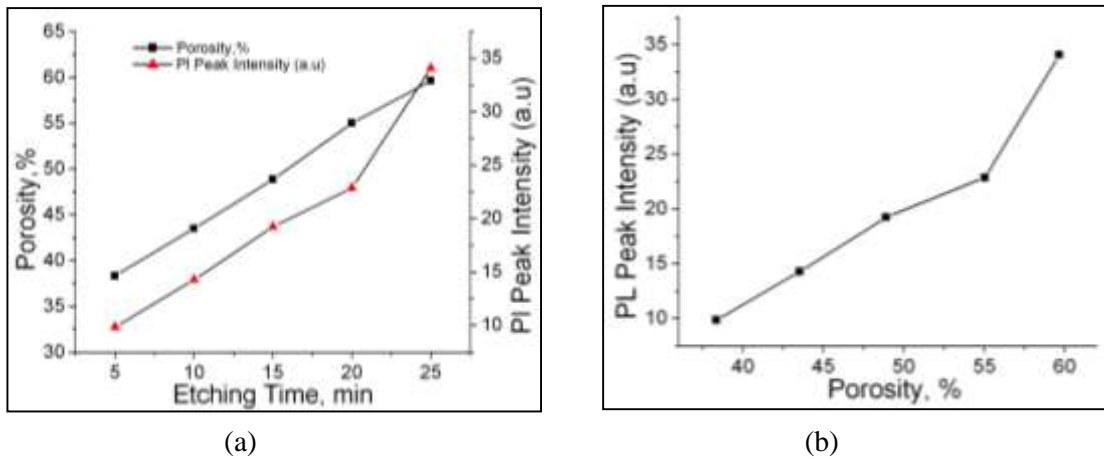
(a) (b)

Figure 6 Relationship between (a) Porosity and PL Peak Intensity with etching time, and
(b) Porosity with PL Peak Intensity

The surface conductivity of PS prepared with different etching time lies in the range of $(3.113 \pm 0.002 \times 10^{-5} - 0.015 \pm 0.001)$ $(\Omega\,cm)^{-1}$. Figure 7(a) shows the conductivity versus porosity for the PS samples. From the figure, the conductivity reduces as porosity and etching time increase. When the porosity increases, some of the carriers at the surface might be etched away and the porous surface with increase surface roughness had reduced the density and mobility of the carriers [24].

Besides, electrical conductivity of semiconductor is also influenced by the energy gap as given in Equation 3

$$\sigma = \sigma_0 \exp(-\frac{E_g}{2kT}) \qquad (3)$$

where σ is electrical conductivity, σ_o is pre-exponential factor, E_g is energy gap. K is Boltzmann constant and T is temperature.
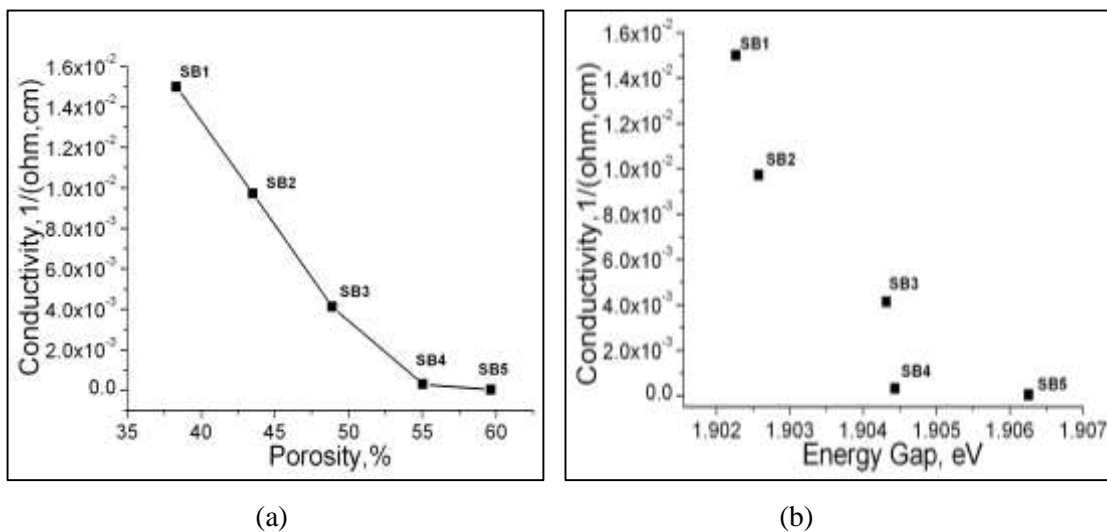

(a) (b)

Figure 7 Relationship between Conductivity with (a) Porosity and (b) Energy gap

From the equation, it shows that the conductivity decreases when the energy gap increases. This is because the minimum energy required to excite an electron from valence band to the conduction band has increased causing less carrier available in the conduction band [25]. This effect can also be evidenced in the plot of

conductivity versus energy gap in Figure 7(b), in which as the energy gap increases, the PS conductivity decreases from 0.015 ± 0.001 $(\Omega \text{ cm})^{-1}$ to $3.113 \pm 0.003 \times 10^{-5}$ $(\Omega \text{ cm})^{-1}$.

CONCLUSION

The PS has been successfully fabricated by chemical etching. The results show that the PL and the electrical conductivity has dependent on etching time and porosity. The porosity is in the range of (38-60) % and increases linearly with etching time. The surface morphology of PS shows that it has crystallites structure surrounded with pores on the surface. The PS able to illuminate orange-red luminescence because of the surface contained species of Si-O bonds as confirmed by EDX analysis. Blue shift effect towards higher energy was observed on PL peak and band gap, which is due to the confinement effect from the reduction of the crystallite size as etching time increases. The conductivity of PS decreases as the etching time, porosity and energy gap increases.

ACKNOWLEDGEMENT

REFERENCES

[1]   Galiy, P.V., Lesiv, T.I., Monastyrskii, L.S., Nenchuk, T.M., Olenych, I.B. 1998. Surface investigations of nanostructured porous silicon. *Thin Solid Films* 318: 113–116.

[2]   Lehmann, V., Gosele, U. 1991. Porous silicon formation: A quantum wire effect. *Applied Physics Letters* 58: 856-858.

[3]   Canham, L.T. 1990. Silicon quantum wire array fabricated by electrochemical and chemical dissolution of wafers. *Applied Physics Letter* 57:1046-1048.

[4]   Saucedo, R.O., Lopez, C.V., Calleja, W., Allred, D.D., Falcony. C. 1999. A rotating electrochemical cell to prepare porous silicon with different surface structures. *Thin Solid Films* 338:100-104.

[5]   Malinovska, D. D., Tzolov, M., Tzenov, N., Nesheva, D. 1997. Electrical, photoelectrical and electroluminescent properties of porous Si–c-Si heterojunctions. *Thin Solid Films* 297: 285-290.

[6]   Fauchet, P.M., Tsybeskov, L., Peng, C., Duttagupta, S.P., von Behren, J., Kostoulas, Y., Vandyshev, J.M.V., Hirschman, K.D. 1995. Light-emitting porous silicon: materials science, properties and device applications. *IEEE Journal of Selected Topics in Quantum Electronics* 1: 1126-1139.

[7]   Kolasinski, K.W. 2003. The mechanism of Si etching in fluoride solutions. Physical Chemistry Chemical Physics 5:1270.

[8]   Kulkarni, M.S. and Erk, H.F. 2000. Acid-Based Etching of Silicon Wafers: Mass-Transfer and Kinetic Effects. *Journal of the Electrochemical Society* 147: 176-188.

[9]   Mortezaali, A., Sani, S.R., Jooni, F.J. 2009. Correlation between Porosity of Porous Silicon and Optoelectronic Properties. *Journal of Non-Oxide Glasses.* 1: 293 – 299.

[10]   Kern, W. 1993. Overview and Evolution of Semiconductor Wafer Contamination and Cleaning Technology. In Handbook of Semiconductor Wafer Cleaning Technology, ed. W. Kern, pp 3-57. Park Ridge, New Jersey: Noyes Publishing.

[11]   Guidoin, R., King, M., Marceau, D., Cardou, A. 1987. Textile arterial prosthesis: Is water permeability equivalent to porosity. *Journal of Biomedical Materials Research* 21: 65-87.

[12]   Thompson, A.C. and Vaughan, D. 2001. X-ray properties of the Element. *Center for X-ray optics advanced light source: X-ray Data Booklet Second edition*. University of California: Lawrence Berkeley National Laboratory

[13]   Vasquez, A.M.A., Rodriguez, G.A., Salgado, G.G., Paredes, G.R., Sierra R.P. 2007. FTIR and photoluminescence studies of porous silicon layers oxidized in controlled water vapor conditions. *Revista Mexicana De Fisica* 53: 431-435

[14]   Malinovska, D. D., Tzolov, M., Tzenov, N., Nesheva, D. 1997. Electrical, photoelectrical and electroluminescent properties of porous Si–c-Si heterojunctions. *Thin Solid Films* 297: 285-290.

[15] Sailor, M.J. and Lee, E.J. 1997. Surface chemistry of Luminescent Silicon Nanocrystallites. *Advanced Material.* 9:783-793

[16] Bhagavannarayana, G., Sharma, S.N., Sharma, R.K., Lakshmikumar, S.T. 2006. A comparison of the properties of porous silicon formed on polished and textured (1 0 0) Si: High resolution XRD and PL. *Materials Chemistry and Physics 97:442–447.*

[17] Berhane, S., Kauslarich, S.M., Nishimura, K., Smith, R.L., Davis, J.E., Lee, H.W.H., Olsin, M.L.S., Chase, L.L. 1993. Investigation of colloidal Si prepared from porous silicon. *Materials Research Society Symposium Proceedings* 298: 99- 102.

[18] Lockwood, D.J., Aers, G.C., Allard, L.B., Bryskieicz, B., Charbonneau, S., Houghton, D.C., McCaffrey, J.P., Wang, A. 1992. Optical properties of porous silicon. *Canadian Journal of Physics* 70:1184-1193.

[19] Takasuka, E. and Kamei, K. 1994. Microstructure of porous silicon and its correlation with photoluminescence. *Applied Physics Letters* 65: 484-486.

[20] Prokes, S., Glembocki, O.J., Bermudez, V.M., Kaplan, R., Friedersdorf, L.E., Searson, P.C. 1992. SiHx excitation: An alternate mechanism for porous Si photoluminescence. *Physical Reviews B* 45:13788-13791

[21] Prokes, S.M. 1993. Study of the luminescence mechanism in porous silicon structures. *Journal of Applied Physics* 73:407.

[22] Stolyarova, S., Cherian, S., Raiteri, R., Zeravik, J., Skladal, P., Nemirovsky, Y. 2008. Composite porous silicon-crystalline silicon cantilevers for enhanced biosensing. *Sensors and Actuators B* 131:509–515.

[23] Nash, K.J., Calcott, P.D.J., Canham, L.T., Needs, R.J. 1995. Spin-orbit interaction, triplet lifetime, and fine-structure splitting of excitons in highly porous silicon. *Physical Reviews B* 51:17698-17707.

[24] Ngan, M.L., Lee, K.C., Cheah, K.W. 2000. Photochemical Etching of Silicon. *Journal of Porous Materials* 7: 41–45.

[25] Anderson, B.L. and Anderson, R.L. 2005. Current Flow in Homogeneous Semiconductor. In *Fundamentals of Semiconductor Devices*, pp111-155.New York: The McGraw-Hill Companies.