Tunable optical properties of porous silicon

F. Alfeel[1], F. Awad[2], and F. Qamar[3]

Received 08/05/2013
Accepted 15/08/2013

ABSTRACT

The optical properties of porous silicon (PS) were studied with the variation of anodization current density and porosity. We've used UV-Vis-NIR Spectrophotometer to measure reflectance R; transmittance T and results were used to calculate tunable optical properties of PS samples. The calculated absorption coefficient decreases with porosity. Refractive index was calculated from Fresnel relation, effective media approximation" Bruggeman theory", and from A. Mortezaali as function of porosity. The optical energy gap was determined experimentally using direct allowed Transition then it was calculated from different models, and results were compared.

Key words: Porous silicon PS, PorosityP%, Absorption coefficient, Refractive index, Energy gap.

[1]PhD., Student, [2] Superviser. [3] Associated Superviser, Department of Physics, Faculty of Sciences, Damascus University, Syria

الخصائص الضوئية القابلة للتوليف في السلكون المسامي

فاتن الفيل[1] و فوزي عوض[2] و فادي قمر[3]

تاريخ الإيداع 2013/05/08
قبل للنشر في 2013/08/15

الملخص

دُرست الخصائص الضوئية للسلكون المسامي PS مع تغيّر كثافة تيار الأنودة للعينات ومع تغيّر المسامية. استخدمنا جهاز قياس الطيف الذي يمسح في أثناء دراسته المجال الطيفي من فوق البنفسجي مروراً بالطيف المرئي حتى تحت الأحمر القريب (UV-VIS-NIR) لقياس الانعكاسية R والنفوذية T، واستخدمت النتائج لحساب الخصائص الضوئية القابلة للتوليف في السلكون المسامي، إذْ وجد أن معامل الامتصاص المحسوب يتناقص بازدياد المسامية. كما حُسبتْ قرينة الانكسار من العلاقات المعروفة مثل علاقة Fresnel ومن تقريب الوسط الفعال "نظرية Bruggeman"، ومن "نظرية A. Mortezaali" كتابع للمسامية. كذلك حُدّدت قيمة ثغرة الطاقة الضوئية تجريبياً من الانتقال المباشر المسموح وباستخدام نماذج حسابية مختلفة وقُورنت النتائج.

الكلمات المفتاحية: السلكون المسامي PS، المسامية P%، معامل الامتصاص، قرينة الانكسار، ثغرة الطاقة.

---

[1] طالبة دكتوراه، [2] الأستاذ المشرف، [3] الأستاذ المشرف المشارك، قسم الفيزياء، كلية العلوم، جامعة دمشق، سورية.

1. Introduction

Low-dimensional materials are found in ever-widening application in many areas of science and Engineering[1]. Porous silicon attracted considerable research interest after their discovery in 1956. Porous silicon is constituted by a nanocrystalline skeleton (quantum sponge) immersed in a network of pores. Variable surface chemistry, or high chemical reactivity properties, along with its easy fabrication and the possibility of producing precisely controlled layered structures make this material adequate for its use in a wide range of fields, such as optics, micro- and optoelectronics, chemical sensing or biomedical applications[2]. In this work samples of PS were prepared using electrochemical etching method [3, 4, 5], and their optical properties were studied.

2. Theory

2.1. Refractive index of porous silicon PS

When structure of silicon changes its optical properties changes, the refractive index of Si according to Fresnel is [6]:

$$n_{si}^{fresnel} = \frac{\sqrt{R_{si}}+1}{\sqrt{R_{si}}-1} \qquad (1)$$

Where R_{si}: reflection of bulk silicon at given wave length, $n_{si}^{fresnel}$ the refraction index of bulk silicon calculated from Fresnel law.

From $n_{si}^{fresnel}$ for Si, the refraction index of porous silicon (for all pore sizes) n_{PS} calculated either from Fresnel relation which becomes:

$$n_{ps} = \frac{1+\sqrt{R_{ps}}}{1-\sqrt{R_{ps}}} \qquad (2)$$

Here R_{ps} is the reflection of porous silicon film. Or from another model, it's Bruggeman effective medium approximation [7]:

$$p\frac{n_{pore}^2 - n_{ps}^2}{n_{pore}^2 + 2n_{ps}^2} + (1-p)\frac{n_{si}^2 - n_{ps}^2}{n_{si}^2 + 2n_{ps}^2} = 0 \qquad (3)$$

n_{PS} is the refraction index of porous silicon, n_{pore} is the refraction index material in pore ($n_{air} \approx 1$). Hence the refractive index of PS is:

$$n_{ps}^{EMA} = 0.5\left[3p(1-n_{si}^2) + (2n_{si}^2 - 1) + ((3p(1-n_{si}^2) + (2n_{si}^2 - 1))^2 + 8n_{si}^2)^{0.5}\right]^{0.5} \quad (4)$$

Where P is the porosity [3].
While another model for refractive index of PS is approximated by A. Mortezaali [8, 11]:

$$n_{ps} = p + (1-p)n_{si} \qquad (5)$$

2.2. Energy band gap of porous silicon PS

The optical energy gap can be calculated using the equation [8]:

$$ahu = A(hu - E_g)^m \; (6)$$

Where A is constant refers to the edge width parameter representing the film quality [8], it defines as:

$$A = \left(\frac{e^2}{n\,\mathrm{C}h^2 m_e^*}\right)\cdot\left(2m_r\right)^{\frac{3}{2}}$$

Where m_e^* effective mass, and m_r reduced mass of charge carries, n the refractive index of the material, C light speed, e electron charge, h blanck's constant [9,10].
Eg is optical energy gap of materials, m determines the type of transition. Here we'll use m=1/2 for direct allowed transition. The value of optical energy gap can be determined by plotting $(ahu)^2$ versus hu, then from the intercept of extrapolation to zero absorption with photon energy axis [8]. The absorption coefficient can be calculated after measuring transmittance T, reflectance R and put them in the relation (7), [12]:

$$a = (1/d)\ln((1-R)/T) \; (7)$$

Ravindra et al. theory has suggested a linear form of n_{PS} as a function of Eg [13]:

$$n_{ps} = a + bE_g \qquad (8)$$

where a = 4.048 and b = -0.62 eV^{-1}. To be inspired by a simple physics of light refraction and dispersion, Ghosh et al. proposed an empirical relation for high frequency as follows[14,15]:

$$n_{ps} = \sqrt{1 + (\frac{a}{E_g + b})^2} \qquad (9)$$

Where $a = 8.2E_g + 134$ eV and $b = 0.225E_g + 2.25$

3. Experimental Method

Porous silicon samples were prepared by electrochemical etching method of p-type cubic silicon wafers (c-Si), (100) orientation, electrochemical dissolution of Si wafers is used: HF-ethanol (measured by volume) aquas with concentration [20%]. The current densities (10... 50) mA/cm^2 was always kept Constant for each sample during etching of PS. Fabricating process done in a normal etching Teflon cell (fig.1). Etching time was 5 min for all samples (Table1). After anodization, PS samples are carefully removed from the bath and cleaned in deionized water. Then the samples were imaged by atomic force microscopy (AFM). The AFM measurements were performed in contact mode (fig.2).

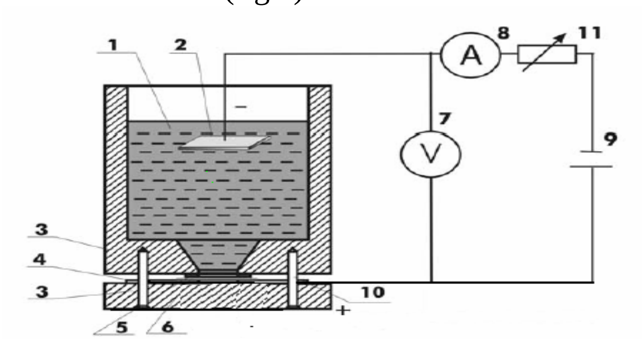

Fig. 1. Iliustration of the experimental setup: a) schematical view, b) crossection of the electrochemical etching cell: 1– electrolyte, 2– copper cathod, 3– electrochemical etching tank (teflon), 4– platinum anode, 5– seal, 6– Si wafer, 7– voltmeter, 8– amperemeter, 9– DC source, 10– grips, 11– rheostat

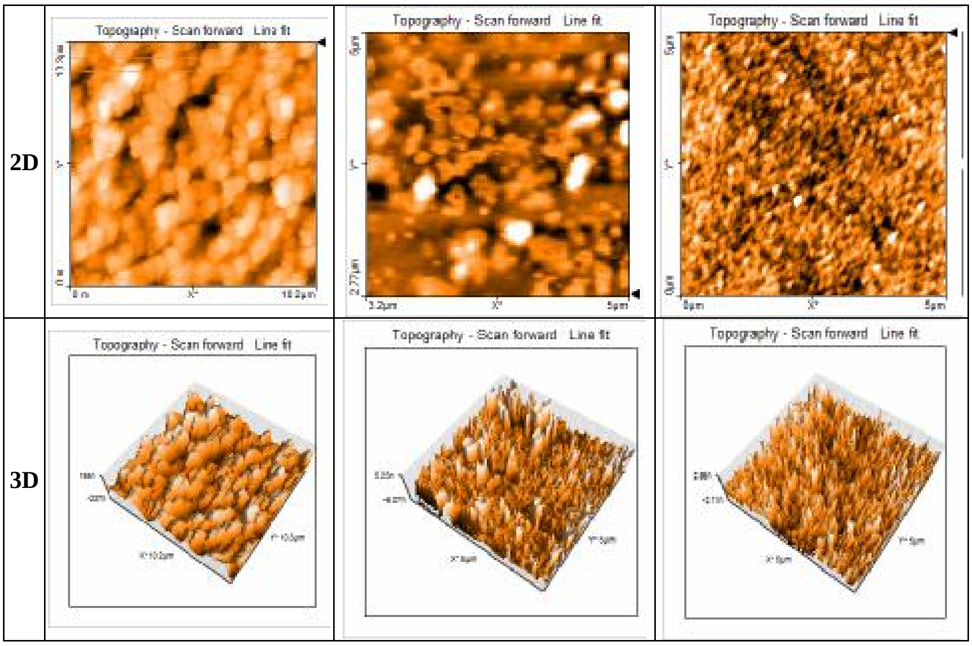

Fig.2. 2D and 3D AFM image of porous silicon samples prepared with etching time of 5 min and current density (20,30,40) mA·cm^{-2}, and HF concentration 20% .

4. Results and Discussion

Fig.3 shows example of spectrum of reflectance R and transmittance T as function of wave length for sample S01, it gives experimental values to find refractive index and absorption coefficient from eq. (2, 7). Then by calculating the refractive index of porous silicon thin film at wavelength=808nm, from equations (4, 5) from our experimental data of porosity we found that the values are approximately the same Fig.4. (Where 808 nm is wave length of laser in our Lab., we choose it to study the tunable optical properties at specific wave length, leaving changing of optical properties with wave length to another search. Our work here is correct to any wave length in visible light range).

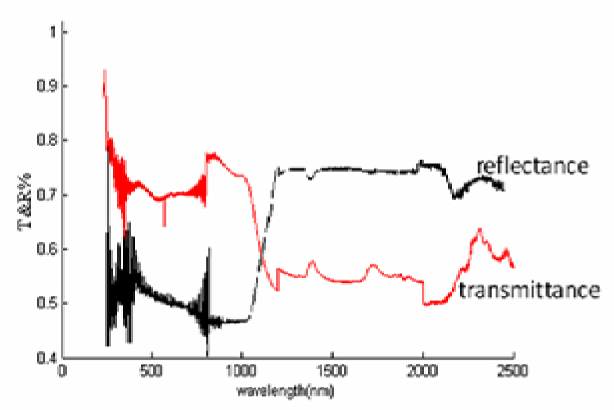

Fig.3 Reflectance and transmittance as function of wave length for sample S01

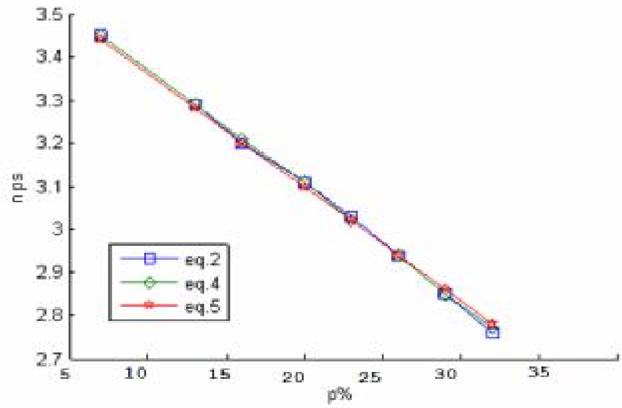

Fig.4. The refractive index of porous silicon film vs. porosity at wavelength = 808nm According to equations (2,4,5) from our experimental data, the values are approximately the same.

It's obvious that the refractive index of PS layer decreases with increasing porosity because light travels faster in air (pores), so more pores means faster light, hence less refractive index. Absorption coefficient decreases in linear manner with increasing porosity, because of the decreasing material in silicon during preparing process (fig.5). So bigger porosity less material and hence smaller absorption coefficient.

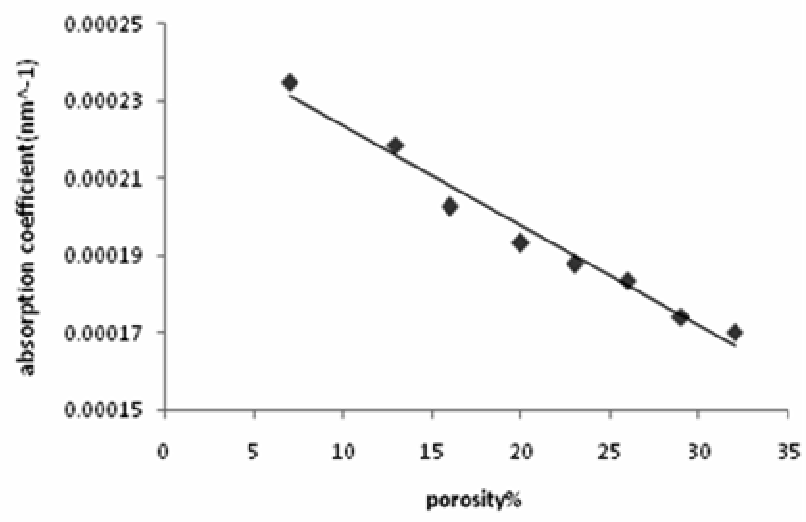

Fig.5. Calculated absorption coefficient vs. porosity

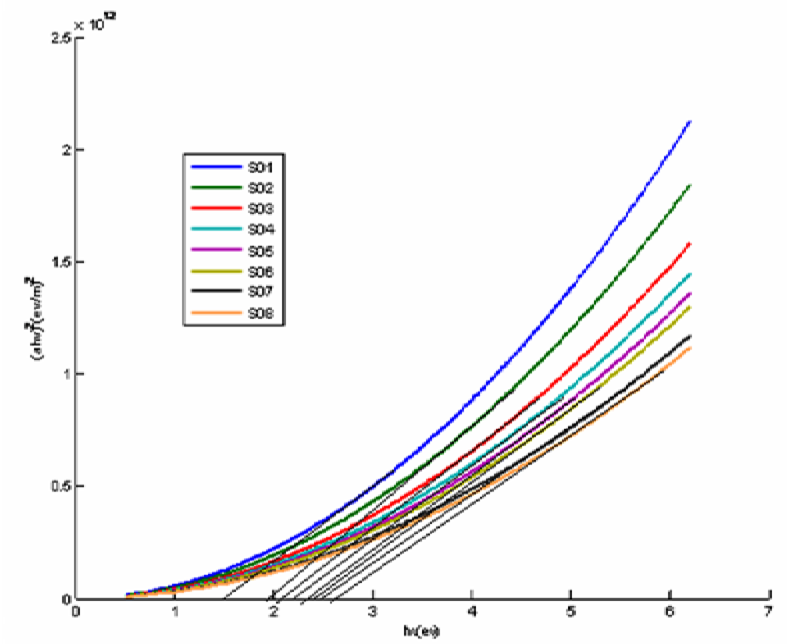

Fig.6. Calculation of energy band gap using $(ahu)^2$ versus (hu) for direct allowed Transition in PS samples with different porosities from eq.(6) .

Energy band gab was calculated using the curve that draws $(ahu)^2$ versus (hu) for direct allowed transition from equation (6) in PS samples with different porosities Fig.6, then it was calculated from equations (8,9 above) the results was drawn in Fig.7

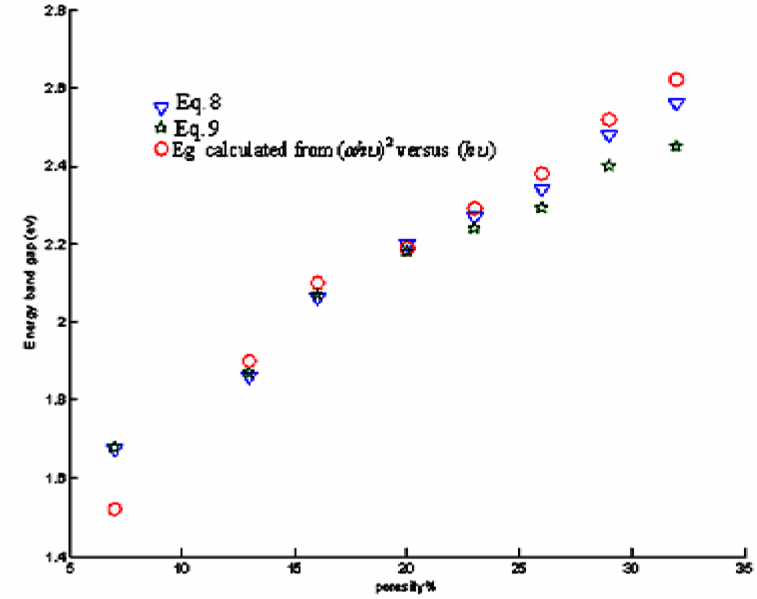

Fig.7. Energy band gap in PS samples versus porosity Calculated from equation (6, 8, 9)

Using three models mentioned above[8,11,12,13], Eg calculated as function of porosity, the result of E_g calculated from $(ahu)^2$ versus (hu) and that from equation (8, 9) was very close, and all give good agreement with experiment. Although it's known that the energy gap is direct in porous silicon from its Luminescent properties [2], the porosity enhances light trapping so we get lower reflectance and more absorbance and that increases PS current and gives better material for solar cell. The relative difference $\frac{\Delta E_g}{E_g}$ is between14% and 33% the reason is the induction method of the curve that I've used.

Table.1. Experimental results for Refractive index and Energy gap for our sample and for Samples from ref.[2]:

Sample	Porosity P%	Refractive index our sample	Refractive index ref.[2]	Energy gap our sample	Energy gap ref. [2]
S01	7	3.44	3.29	1.52	1.22
S02	9	3.29	3.20	1.89	1.37
S03	12	3.2	3.18	2.08	1.4
S04	16	3.11	3.02	2.18	1.66
S05	20	3.02	2.91	2.28	1.84
S06	22	2.95	2.84	2.37	1.95
S07	26	2.86	2.66	2.5	2.24
S08	33	2.77	2.64	2.6	2.16

5. Conclusion

Optical properties of porous silicon such as refractive index and absorption coefficient and energy band gap were studied with changing of porosity. Refractive index and absorption coefficient were determined by effective media approximation" Brugg-eman theory", and by Fresnel relation and by A. Mortezaali. The refractive index decreases with increasing porosity in visible region from 3.4 to 2.75 approximately in three models. Energy band gap was measured using absorption coefficient calculated from transmittance T and reflectance R spectra. Then from drawing $(ahu)^2$ versus (hu) for PS samples with different porosities, (eq.6), for direct allowed transition we can find Eg. Ravindra(eq.8) and Ghosh eq.(9) relations were used in calculating energy gab too. Energy band gap values were almost the same for three models, it increases from 1.5 to 2.7 (ev) with increasing porosity from 7% to 32%. Our work gives known models to be used for porous media such as PS samples, which is better than Si for solar cell because of its lower reflectance and refractive index and higher energy gap, that means higher efficiency solar cell.

REFERENCES

[1] Gan'shina, E. A. Kochneva, M. Yu. and Podgorny, D. A., (2005). Structure and Magneto-Optical Properties of Porous Silicon–Cobalt, Physics of the Solid State, V.l. 47, No. 7, P: 1383–1387.

[2] Torres-Costa, V. Martý´n-Palma, R. J., (2010). Application of a nanostructured porous silicon in the field of optics, J. Mater Sci.V.45, P:2823–2838

[3] Behzad, K. Yunus, W. M. M. and Talib, Z. A., (2012). Effect of Etching Time on Optical and Thermal Properties of p-Type Porous Silicon Prepared by Electrical Anodisation Method, Advances in Optical Technologies, p:1-9

[4] Kim, J. Moon, I. S. Lee, M. J. and Kim, D.W. (2007). Formation of porous silicon by electrochemical etching and application to the silicon solar cell, Journal of ceramic society of Japan, V.115 issue (5) pp. 333-337.

[5] Žvalioniene1, R. J. Grigaliunas, V. Tamulevièius, S. and Guobiene, A., (2003). Fabrication of porous silicon microstructures using electrochemical etching. Materials Science (Medžiagotyra) V.9 No.4, p: 1392-1320.

[6] Edit, A. Korda´s Jouko, K., (2006). Optical properties of porous silicon. Part III: Comparison of experimental and theoretical results, Optical Materials V.28, p: 506–513

[7] Wolf, A. Terheiden, B. and Brendel, R., (2008). Light scattering and diffuse light propagation in sintered porous silicon, J. Appl. Phys.V.104, NO.033106, p:1-16

[8] Mortezaali, A. Sani, S. R. and Jooni, J., (2009). Correlation between Porosity in Porous Silicon and Optoelectronic Properties, Journal of Non-Oxide Glasses, V.1, NO.3, p: 293-299

[9] Mohameda, S. H. Shaaban, E. R., (2010). Investigation of the refractive index and dispersion parameters of tungsten oxynitride thin films, Materials Chemistry and Physics 121,p:249-253

[10] Abkowitz, M, Adachi, S. Adams, A, et al, (2011). Springer hand book of electronic and photonic materials, Springer-Verlag New York,INK

[11] Chan, m. h. So, S. k. and Cheah, K. W., (1996). Optical absorption of free-standing porous silicon films, J.Appl.Phys.V.79 No. (6), P:3273-3275

[12] Tamboli, H. S. Puri, V. and Puri, R. K Patil, R. B. and Luo, M. F., (2011). Comparative study of physical properties of vapors chopped and nonchopped Al_2O_3 thin films, Materials Research Bulletin V.46, p: 815-819.

[13] Ravindra, N.M. Auluck, S. and Srivastava VK., (1979). On the Penn gap in semiconductors. Phys Status Solidi B, V. 93, P: 155–160.

[14] Herve PJ. L., Vandamme L. K. J., (1995). Empirical temperature dependence of the refractive index of semiconductors. J Appl Phys V.77, P:5476–5477.

[15] douri, YAl Ahmed, NM. Bouarissa, n., (2011). Investigated optical and elastic properties of porous silicon: theoretical study, Material and design, V.32, P: 4088-4093