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Optical Properties of ZnO Film on Porous Silicon P-type Substrate

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Abstract

A film of ZnO deposited on two substrates of porous silicon (PS) sample p-type with different porosity, by dip-coating method. The structure of porous silicon substrates was studied using Atomic Force Microscopy (AFM) measurements, then diffuse and specular reflectance were determined by UV-Vis-NIR spectrophotometer before of ZnO film was deposited. The study was repeated again after ZnO film was deposited to see changes in optical and structural properties. The reflection spectrum was used to find the Refractive index, the optical energy gap, and the film thickness. The optical conductivity, and the electrical conductivity were determined.

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Key words: ZnO Zinc Oxide Film, Porous Silicon PS, Porosity P, Refractive Index, Absorption Coefficient, AFM, Surface Roughness, The Optical Conductivity, The Electrical Conductivity, Energy Gap.

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الخصائص الضوئية لغشاء ZnO على ركيزة من السلكون المسامي نوع p–

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الملخص:

رُسب غشاء ZnO على ركيزتين من السلكون المسامي (PS) نوع–p، لهما مساميتين مختلفتين، بطريقة التغشية بالتغميس. ودُرست بنية ركائز السلكون المسامي من خلال قياسات مجهر القوى الذرية (AFM)، ثم قِيست الانعكاسية الانتثارية والانعكاسية المرآتية بمطياف UV–Vis–NIR قبل ترسيب غشاء ZnO . وأُعيدت الدراسة مرة أخرى بعد ترسيب غشاء ZnO لمعرفة تغيرات الخصائص الضوئية والبنيوية. أُستخدم طيف الانعكاسية لإيجاد قيمة قرينة الانكسار وفجوة الطاقة الضوئية. كما حُددت سماكة الغشاء والناقلية الضوئية والناقلية الكهربائية.

الكلمات المفتاحية: غشاء أكسيد الزنك ZnO، السلكون المسامي PS، المساميةP، قرينة الانكسار، معامل الامتصاص، AFM، خشونة السطح، وثغرة الطاقة الضوئية، سماكة الغشاء، الناقلية الضوئية، الناقلية الإلكترونية

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1.Introduction:

Nanostructured porous silicon shows interesting properties, including tunable refractive index, tunable energy gap, low light absorption in the visible, high internal surface, variable surface chemistry, or high chemical reactivity. properties, along with its ease of fabrication and the possibility of producing precisely controlled layered structures make this material adequate for using in a wide range of fields, such as optics, micro- and optoelectronics, chemical sensing or biomedical applications [1,2]. When working on filling the pores of porous silicone by different materials and studying the effect of that on its properties, we noticed that There are few reports concerning ZnO/PS composites. And because during the last few years, zinc oxide has emerged as an important functional oxide material, the sponge-like open structure and large specific surface area of PS make it a convenient material for accommodating ZnO into its pores [3]. In this paper we'll prepare PS film on silicon p-type substrate then ZnO film is deposited on the PS samples. Optical and structural properties were studied before and after ZnO deposition.

2. Experimental Methods

Crystalline silicon (c-Si) wafers, orientation (100), p-type, were electrochemically etched in hydrofluoric acid (HF)and ethanol [20%], at different current densities (45,50) mA/cm^2. The etching time was 5 min, and pores are formed, which is known as porous silicon (PS) layer. The PS layers consist of Si columns and pores or isolated nanocrystalline [4,5,6].

Table 1 fabricating condition of porous silicon samples.

Sample	HF concentration (%)	Current density (mA/cm^2)	Anodization Time (min)
S01	20	45	5
S02	20	50	5

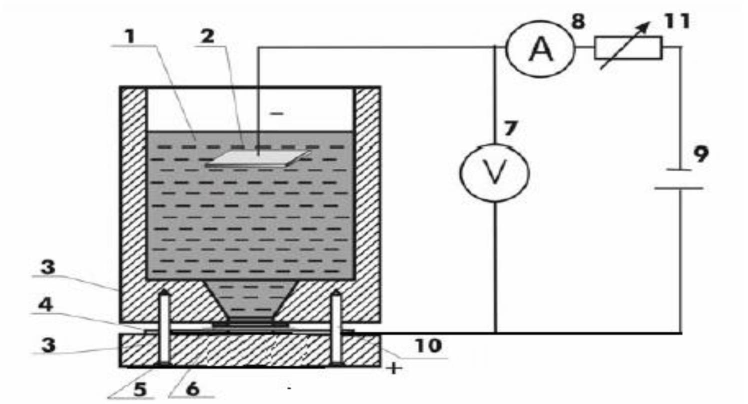

Figure (1) Illustration of the experimental setup:
a) schematically view,
b) cross section of the electrochemical etching cell:
1 – electrolyte, 2 – copper cathod, 3 – electrochemical etching tank (teflon), 4 – platinum anode, 5 – seal, 6 – Si wafer, 7 – voltmeter, 8 – amperemeter, 9 – DC source, 10 – grips, 11 – rheostat [4].

Structure of porous silicon (PS) samples was determined from the Atomic Force Microscopy (AFM) measurements, and the surface mean root square roughness (σ rms) was measured. Specular reflectance was investigated by UV-Vis-NIR spectrophotometer, porosity was studied by a non-destructive method [7]. Before ZnO film was deposited, then the study was repeated again after ZnO deposition.

The precursor solution used was of 0.1M concentration of high purity zinc acetate (Zn $(CH3COO)_2$) prepared in distilled water and stirred continuously for 1 hour at room temperature. This solution is taken in a beaker and the pH was maintained around 8. Another beaker is filled with hot water at a temperature of 90-95°C. The PS substrate was dipped in Zinc acetate solution for fraction of second and then immersed in a hot water solution. This process is repeated 5 times [8].

3. Results and Discussion

3.1 porosity and film thickness

PS porosity “P” is defined as the fraction of void within the PS layer and can be determined easily by weight measurements. The virgin wafer is first weighed before anodization (m_1), then just after anodization (m_2), and finally after the dissolution of the whole porous layer in a molar NaOH aqueous solution (m_3).

$$P(\%) = \frac{m_1 - m_2}{m_1 - m_3} \qquad (1)$$

the removal is made through a dip for some minutes in an aqueous solution of NaOH (3% in volume), which leads to selective removal of PS layer without reacting with the bulk crystalline silicon. But the porosity was studied by a non-destructive method using AFM before ZnO is deposited [7] and for S01 it was 56%, and for S02 it was62%. The porous silicon film thickness L_1 can be determined from the gravimetric measurements:

$$L_1 = \frac{m_1 - m_3}{\rho S} \qquad (2)$$

where ρ is the silicon density and S is the etched surface [9,10]. But since this is destructive method as we need to find (m_3) by dissolution of the whole porous layer in a molar NaOH aqueous solution. The optical properties of bulk materials and thin films that are very important for optoelectronic applications, the properties include absorbance (A), transmittance (T), and reflectance (R), which characterize the interaction of incident radiation with a particular coating of material. These properties are also related to intrinsic properties of films such as coefficient of absorption (α), extinction coefficient (k), refractive index (n). Film thickness L_1 can be calculated from reflectance spectrum by using two adjacent peaks have refractive indexes of n_1 and n_2, and wave lengths λ_1 and λ_2[11], fig. (2):

$$L_1 = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \qquad (3)$$

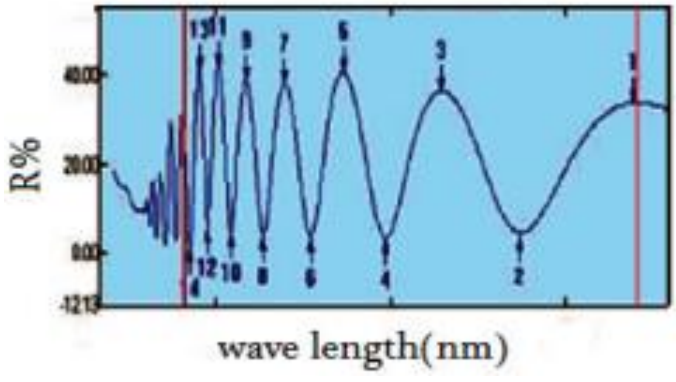

Fig. (2) adjacent peaks in reflectance spectrum

The optical reflection spectrum of PS and ZnO/PS films shown in Figure (3) and Figure (4) for both samples. The values of reflection for PS are less than that of ZnO/PS for both samples except for regions (250-450 nm and 790-1320 nm). So, to decrease reflection we can use a color filter with wavelengths (250-416 nm or 716-1116 nm).

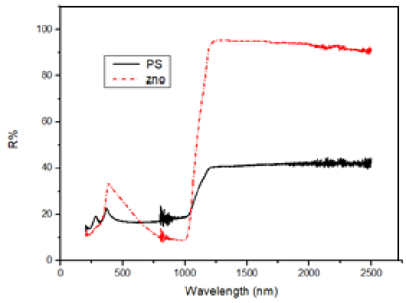

Figure (3) reflection spectrum of PS and Zno/PS for S01

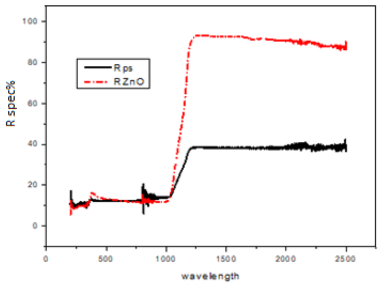

Figure (4) reflection spectrum of PS and Zno/PS film S02

3.2 Refractive index

To calculate the Refractive index of porous silicon film the transmittance spectrum is measured then the refractive index of virgin silicon n_{si} is calculated [7]:

$$n_{si} = \frac{1}{T_{Si}} + \left(\frac{1}{T_{Si}} - 1\right)^{1/2} \qquad (4)$$

Were T_{Si} the transmittance of silicon substrate, n_{si} silicon substrate refractive index. The refractive index of PS (porous silicon film) is calculated from reflectance spectrum before and after ZnO deposition. Refractive index of the film n_1 can be calculated using eq. (5):

$$\mathrm{n_1} = \left(\frac{1+\sqrt{\mathrm{R_f}}}{1-\sqrt{\mathrm{R_f}}}\right) \qquad (5)$$

Where n_1, R_f are film refractive index, film reflectance respectively [2]. PS (porous silicon substrate) refractive index was calculated from the reflectance spectrum for wavelength λ=808nm., it is for S01 is 2.794 and for S02 is 2.363, while for ZnO/PS film it is 1.947 for S01 and 2.176 for S02, due to modified band structure optical Constance different from the bulk values [9], the pores make refractive index of PS less than silicon because of containing air, while filling them with ZnO makes refractive index different and obeys effective medium approximation [3], because it consist of three different mediums (Si,PS,ZnO).

3.3 The absorption coefficient of film:

Practically the optical absorption coefficient which is a function of wavelength can be calculated from the optical absorbance spectra by using the relation $log(\frac{I_0}{I_T}) = 2.303A = \alpha L_1$

where I_0 and I_T are the intensities of the incident and transmitted beams respectively, the optical absorbance A, and L_1 is the film thickness, and absorbance is defined by. $A = log(\frac{I_0}{I_T})$ and $T = 10^{-A}$ [12]. by doing the required substitution we get the absorption coefficient:

$$\alpha = -\frac{1}{L_1} ln(T) \qquad (6)$$

where T is the optical transmittance and L1 is the thickness of the film. After measuring the transmittance and reflectance spectrum for silicon, PS and ZnO/PS the absorption coefficient (α) is obtained using equation (6). [14,13]

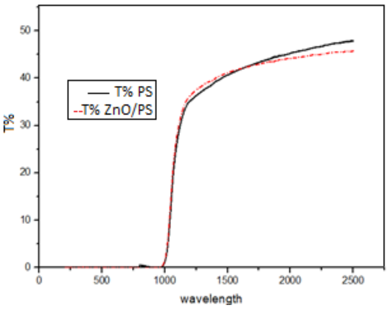

Figure (5) transmittance spectrum of PS substrate and Zno/ps films S01

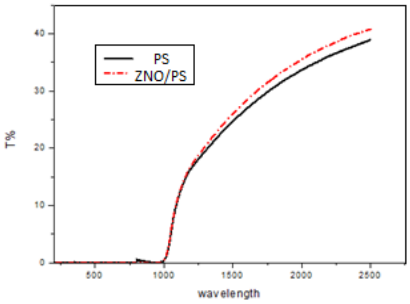

Figure (6) transmittance spectrum of PS substrate and Zno/PS film S02

The transmittance of ZnO/PS and PS is the same except for regions (1000-1750 nm) transmittance of ZnO/PS is higher and (1750-2500 nm) is less for sample S01 fig. (5). The transmittance ZnO/PS sample S02 is the same of PS in range (250-1250 nm) and higher from (1250-2500) fig (6). This change in transmittance is due to the change in band gap of ZnO thin film due to change in crystallite size. ZnO film exhibits high transmittance (>85%) in the visible region, the transmission of ZnO film is high over large wavelengths. This suggests that the produced film indicates a good optical quality due to the low scattering absorption losses [7]. This cause change in absorption coefficient from (11.83 m^{-1}) in PS substrate to (14 m^{-1}) in ZnO/PS in S01, and from (9.9 m^{-1}) in PS substrate to (10.7 m^{-1}) in ZnO/PS for S02.

3.4. Energy band gap:

The optical energy gap of silicon is indirect but after the etching it becomes direct, so we can calculate it using tauc model for PS and ZnO/PS films using equation (7) [3, 13]:

$$\alpha hf = A(hf - E_g)^m \qquad (7)$$

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

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

m_e^*effective mass, and m_r reduced masse of charge carries, n the refractive index of the material, C light speed, e electron charge, h is blanck's constant [10,14]. 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 $(\alpha h\upsilon)^2$ versus $h\upsilon$, then from the intercept of extrapolation to zero absorption with photon energy axis [10,15]. The absorption coefficient (α) is obtained from transmittance spectrum and is used to find energy gap. The optical energy gap can be calculated using equation (7), [3,9,13] for m=1/2 for direct allowed transition. (PS has direct band gab and luminance in ultraviolet fig. (7)), optical energy gab from tauc model is given in fig. (8), and fig. (9)

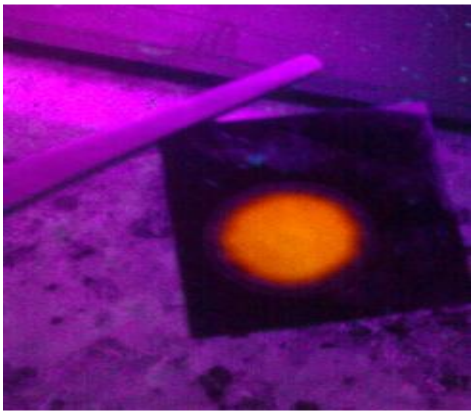

fig. (7) PS luminance in ultraviolet of PS due to change of energy band gab to direct

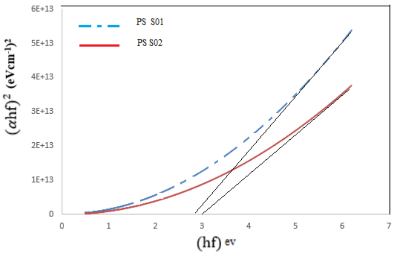

Fig (8) energy band gab of S01 and S02 of PS substrate

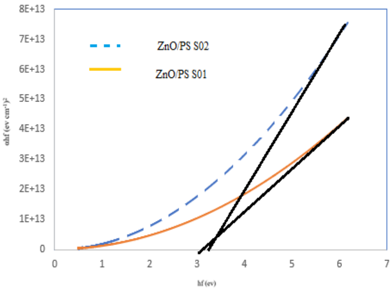

Fig (9) energy band gab of S01 and S02 ZnO/PS

The value of the energy gap of porous silicon is greater than that of bulk silicon due to the presence of pores within its structure and increases as porosity gets larger, when filling pores with ZnO the energy gap still larger of bulk silicon but smaller than ZnO energy gap because of change in medium (effective medium approximation).

Surface roughness plays important role in optical properties such as reflection and absorption, so AFM is used to measure surface roughness of porous silicon substrate and ZnO/PS and study the effect of porosity and ZnO/PS deposition on roughness hence on optical properties for the two samples, fig. (10-1,10-2). &fig.(11-1,11-2)

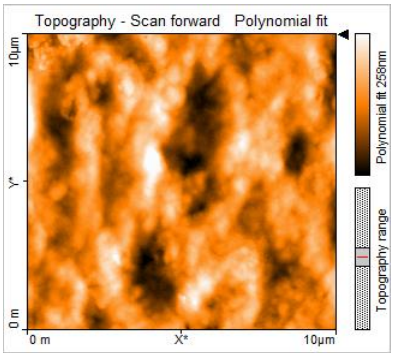

Fig. (10-1) AFM image of porous silicon sample S01 before the film is deposited (the porosity56%)

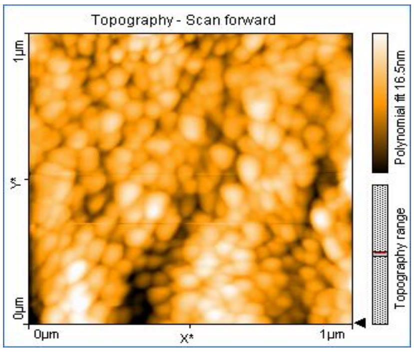

Fig. (10-2) .AFM image of porous silicon sample S01, after ZnO film is deposited (the porosity56%)

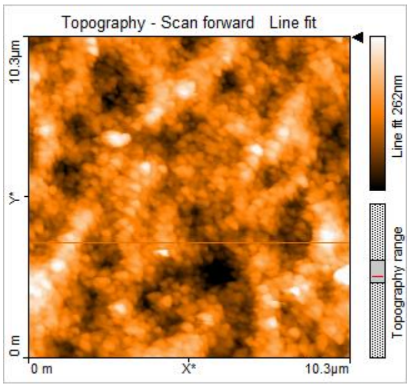

Fig. (11-1) AFM image of PS S02

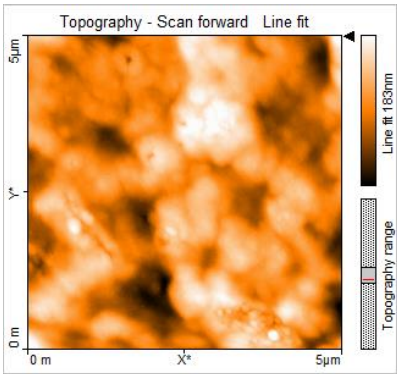

Fig. (11-2) AFM image of ZnO/PS film S02

The surface roughness increases with porosity in porous silicon due to the formation of more pores, so the reflectivity increases and the light capture increases inside these pores, then the zinc oxide film (which has nano-granular structure) is deposited on the porous silicon substrate causing roughness increasing, thus optical properties and optical constant changes due to structure change.

3.5. Optical and Electrical conductivity measurement

The optical conductivity can be calculated using optical constant such as the optical extinction coefficient, from the Shankar and Joseph equation (8) [17]:

$$\sigma_{op} = \frac{\kappa n\, C}{\lambda} \qquad (8)$$

$k$is the optical extinction coefficient $\kappa = \frac{\alpha\lambda}{4\pi}$, n is the optical refractive index of the film, c is the velocity of light, λ is the wavelength of light, and (α) The absorption coefficient.

The electrical conductivity also can be calculated using the Shankar and Joseph equation [17,18]:

$$\sigma_{ec} = \frac{2k\ c\ n}{\alpha} \qquad (9)$$

The optical conductivity and the electrical conductivity both decreasing as porosity increasing due to pores formation and difficulty of electrons and photons moving. After ZnO/PS film formation both optical and electric conductivity are increasing because of ZnO properties.

table (2), all the calculations were done for wavelength λ=808 nm

	S01	S02
Porosity p%	56%	62%
PS refractive index	2.794	2.363
ZnO/PS refractive index	1.947	2.176
PS absorption coefficient (α) $*10^5(m^{-1})$	11.83	9.9
The absorption coefficient (α) of ZnO/PS film $*10^5(m^{-1})$	14	10.7
PS Film thickness µm	44	84
ZnO Film thickness µm	3.08	3.25
ZnO/PS Film thickness µm	47.08	87.25
PS Surface roughness before ZnO (nm) from AFM	35.3	48.79
ZnO/PS Surface roughness (nm) from AFM	60.8	79.85
Band gab energy(ev) of PS	2.7	2.85
Band energy(ev) of ZnO/PS	2.75	3
the optical conductivity PS $(*10^8)\ s^{-1}$	7.9	5.6
the optical conductivity zno/ps $(*10^8)\ s^{-1}$	6.5	5.6
The electrical conductivity(s/m)	107.85	91.21
the electrical conductivity(s/m)	75.15	83.99

Conclusion:

Crystalline silicon (c-Si) wafers p-type, were electrochemically etched in hydrofluoric acid (HF)and ethanol at different current densities, porous silicon (PS) layer formed. Then the PS substrate was dipped in Zincacetate solution. The reflectivity decreases with porosity decreasing before the deposition of ZnO film, and the reflectivity increases after the deposition of ZnO film with porosity. the absorption coefficient decreases with porosity before ZnO, and increases with porosity after ZnO. The film thickness of porous silicon (PS) samples increases with porosity and current density before ZnO deposition and also ZnO film thickness increases with porosity. Surface roughness increases with porosity before and after ZnO is deposition. energy band gab, increases with porosity before and after zno is deposited, that is undesired because it’s the cause of electrical conduction decreasing. The optical conductivity increases after zno deposited, and the electrical conductivity decreases with increasing porosity and thickness, so we have to use the suitable color filter on such film to get the desired reflection and improve optical conductivity.

References:

[1] Gan’shina E. A., Kochneva M. Yu., Podgorny D. A. ,2005,"Structure and Magneto-Optical Properties of Porous Silicon–Cobalt", Physics of the Solid State, Vol. 47, No. 7, pp. 1383–1387.

[2] Alfeel F., Awad F., and Qamar F.,2014,"Tunable optical properties of porous silicon, Damascus University, Science Journal, Syria,Volume IX - Issue 1-2014,p-p: 41-51

[3] Singh1 R. G., Singh2 F., Agarwal3 V, and Mehra1 R M,"2007," Photoluminescence studies of ZnO/porous silicon nanocomposites, J. Phys. D: Appl. Phys. 40 (2007) 3090–3093,

[4] Jarimavičiūtė-Žvalionienė,R., Grigaliūnas, V., Tamulevičius,S., Guobienė, A., (2003), Fabrication of Porous Silicon Microstructures using Electrochemical Etching. Materials Science (MEDŽIAGOTYRA). Vol. 9, No. 4, P:1392-1320

[5] Torres-Costa V., Martý´n-Palma R. J., 2010, " Application of nanostructured porous silicon in the field of optics", J Mater Sci.vo. 45, pp:2823–2838

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

[7] Alfeel F., Awad F., Alghoraibi I., and Qamar F.,2012, " Using AFM to Determine the Porosity in Porous Silicon", Journal of Materials Science and Engineering A 2 (9) (2012) p-p:579-583

[8] Komaraiah D., Radha E., Vijayakumar Y., Sivakumar J., Ramana M. V., Sayanna R.," Optical, Structural and Morphological Properties of Photocatalytic ZnO Thin Films Deposited by Pray Pyrolysis Technique", Modern Research in Catalysis, 2016, 5, p-p130-146

[9] C. PENA, J. TORRES, (2002), "Calculation of Optical Constants in Porous Silicon Thin Films Using Diffused and Specular Reflectance Measurement", Surface Review and Letters, Vol. 9, Nos. 5 & 6, pp. 1821-1825

[10] Canham L., Malvern D., 1997, "Properties of Porous silicon", NSPEC, The Institution of Electrical Engineers, London, United Kingdom, p.18

[11] Ilican S., Caglar M., Caglar Y., 2007," Determination of the thickness and optical constants of transparent indium-doped ZnO thin films by the envelope method", Materials Science-Poland, Vol. 25, No. 3, p-p:4835-4850

[12] Tahir D. A, 2010, "Optical properties of polymer composite PS-PC thin films", Journal of Kirkuk University –Scientific Studies, vol.5, No.2,2010

[13] 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-p:249-253

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

[15] 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-p: 293-299

[16] Martinez L., et al., ZnO-porous silicon nanocomposite for possible memristive device fabrication, Nanoscale Research Letters 2014, vo. 9, Article number 437. (http://www.nanoscalereslett.com/content/9/1/437)

[17] Shankar G., Joseph P.S., YosuvaSuvakin M., and Sebastiyan A., (2013), Optical reflectance, optical refractive index and optical band gap measurements of nonlinear optics for photonic applications, Optics Communications, vo.29, p-p134-139

[18] Alfeel F., Awad F., and Qamar F., (2013),"change of Thermal conductivity, Optical conductivity, and Electric conductivity of porous silicon with porosity", Journal of New Technology and Materials Vol. 03, N°01, p-p: 56-60