Proceeding of First International and the Third Scientific Conference , College of Science - University of Tikrit
17 – 18 Dec. 2018 / (P4)

Promote Scientific Research is Our Way to Serve the Community

Spectroscopic ellipsometry study and variability of optical parameters for blend polymer(PVA:POT)thin films

Raed kadhum[1] , Munaf S. Majeed[1], Kareem K Mohmmad[1], Hussain ali badran[2], Khalid I. Ajeel[2]
[1] *Al-Nahrain Nanorenewable Energy Research center, Al-Nahrain University, Baghdad , Iraq*
[2] *Physics department , College of education for pure science , [2]University of Basrah , Basrah , Iraq*

ARTICLE INFO.

Keywords: Optical parameters; Third-order nonlinear susceptibility; POT; PVA; Electrical and optical conductivity.

Name: Raed kadhum
E-mail:
rrr80kkk@yahoo.com
Tel:

ABSTRACT

The third-order nonlinear susceptibility of blend poly (O-Toluidine-Vinyl Alcohol) were studied as a function of photon energy. The measurement of refractive index (n) and extinction coefficient (k) showed variation in their amount with incident light. In addition, the some optical parameters of the prepared blended polymers were calculated. The optical and electrical conductivity have been measured as a function of photon energy as well as.

Introduction

Thin film fabrication technology is a well-founded materials technology. The request of the desired materials to keep pace with the evolution at twenty-first century, like nanostructured materials and/or handmade super lattices; it is as yet developing on a daily basis. Thin film material technology is both an old and a resent time considered as an important key for material technology studies. Thin film materials and deposition processes with unique properties have been explained in several articles and books. However, there are different technique methods available for thin films fabrication on a single crystal substrate, such as thermal evaporation, spin coating, chemical decomposition, spray pyrolysis and the evaporation of fundamental materials through the radiation of energetic or photons [1, 2]. The studies of the organic conducting polymers started in the last few years for employ in several electronic applications. Especially, the electronic and electrical properties of poly aniline and poly (O-Toluidine) were thoughtful massively [3, 4]. Increasing usage of conducting polymers has quickened studies on polymer applications in recent years. Conducting polymers with long π-conjugated structures have unique properties, such as flexibility, thermal and electrical stability, ease of preparation and immovability [5]. The study of the optical properties for thin films considered as a used tool to understand and explain the behavior of the photonic device applications [6]. In this study of polyvinyl alcohol (PVA) and blend polymers (PVA:POT) are investigated by using UV-visible spectrophotometer (Cary 50 scan VARIAN) and then the optical and electrical conductivity of polymers are calculated. While the optical constants of polymers, such as refraction index (n), extinction coefficient (k) and third-order nonlinear susceptibility determined by using spectroscopic ellipsometry.

Optical studies

The optical constants of prepared polymers (Refractive index (n) and extinction coefficient (k)) are characterized by using Ellipsometry spectroscopy through performing theoretical fitting of the measured ellipsometry data. The Cauchy model has been used to extract the parameters of the polymers in this work. The ration of light velocity in vacuum (C) to it's velocity inside the material (υ) known as refractive index. Depending on the reflectance (R) and extinction coefficient (k) the value of refractive index (n) was determined as following [8,9]:

$$n = \left[\left(\frac{4R}{(R-1)^2}\right) - k^2\right]^{1/2} - \frac{R+1}{R-1} \quad \ldots.(1)$$

Where, the reflectance expressed by the following relation:

$$R = \frac{(n-1)^2+k^2}{(n+1)^2+k^2} \quad \ldots..(2)$$

In general, The extinction coefficient refers to several different measures of the light absorption in a medium. In physics, the extinction coefficient is the imaginary part of the complex index of refractive related to light absorption as well. The imaginary part of complex refractive index (N) which depends on the material type, crystal structure, crystal defects, stress in crystal, and extinction coefficient can be given by the following relations [10-11]:

$N = n - ik$ .....(3)

$k = \alpha\lambda/_{4\pi}$ ......(4)

The reaction between incident light and charges of the material will be happen as result of light energy which absorbed by the material. This process leads to polarize the charges of the material. The polarization usually described by complex dielectric constant (ε) [12].

$\varepsilon = \varepsilon_1 - i\varepsilon_2$ ....(5)

Where, ε_1, ε_2 are the real and imaginary part of the complex dielectric constant respectively.

The dielectric constant in its two parts can be determined by using the following expressions [13,14]:

$\varepsilon = (N)^2$ ....(6)

$\varepsilon_1 = (n^2 - k^2)$ ......(7)

$\varepsilon_2 = (2nk)$ ....(8)

The optical and electrical conductivity is a property of material to conduct the electrical current through it as result of incident light and it depends on the intensity of optical radiation [15]. The optical and electrical conductivity ($\sigma_{opt.}$) ($\sigma_{ele.}$) given by the following relations respectively:

$\sigma_{opt.} = \alpha\, n\, c/4\pi$ ....(9)

$\sigma_{ele.} = 2\lambda\sigma_{opt.}/\alpha$ ....(10)

Where c is the velocity of light.

The refractive index dispersion can be analysed by the single-oscillator model [16].

$(n^2 - 1)^{-1} = \frac{E_o}{E_d} - \frac{1}{E_o E_d}E^2$ .....(11)

Where E_o is the oscillator energy, E the photon energy and E_d is the dispersion energy, which measures the average strength of the interband optical transition. The moments of optical dispersion spectra, M_{-1} and M_{-3}, can be evaluated using the relations [17, 18]:

${E_o}^2 = \frac{M_{-1}}{M_{-3}}$ ....(12)

${E_d}^2 = \frac{{M_{-1}}^3}{M_{-3}}$ ......(13)

The third order nonlinear susceptibility (χ 3) has been calculated from the following equation [19]:

$\chi^{(3)} = A\left\{E_o \frac{E_d}{4\pi({E_o}^2-(h\nu)^2)}\right\}^4 = A/\,(4\pi)^4(n-1)^4$ ..(14)

Where A is constants equal to $1.7\text{x}10^{-10}$.

Experimental

The chemical polymerization method was used to synthesis poly (o-toluidine). The o-toluidine monomer (purchased from Fisher scientific) with molarity concentration of (0.27M) was dissolved in acidic medium of 0.25M hydrochloric acid. The temperature of acidic medium was controlled to be at range of (0-5℃) through ice medium. The ammonium per sulphate (purchased from sigma-Aldrich) with molarity concentration of 0.54M was wisely dropped to the continuously stirred o-toluidine solution as oxidizing agent. The poly (o-toluidine) as greenish-black precipitate was filtered, washed with distilled water , methanol and acetone respectively, and then dried under 60°C. The polymer powder grinded and sieved was then blended with PVA (purchased from sigma-Aldrich) (1:1, 1:2, 2:1 V/V) solution in formic acid and spun into Nano thin films to obtain information about optical parameters.[7].

Results and discussion

Fig. 1 shows behavior of the refractive (n) and extinction coefficient (k) for prepared blend polymers. The refractive index (n) of pure PVA is decreased at a high wavelength while n of blend polymers at different volume ratios (1:1, 1:2, and 2:1 PVA:POT) becomes high at large values of wavelength. The extinction coefficient (k) of pure PVA is decreased at low wavelength values but in case of blend polymer increased. The values of both n and k increased at high and low wavelength relating to the present of POT that also lead to increase in the extinction index value compared with pure PVA. Thus, the large value of refractive index (n) leading to high absorption of incident light by compound of polymers and the changes in value of refractive index with respect to variation of wavelength according to equation (4) [11].

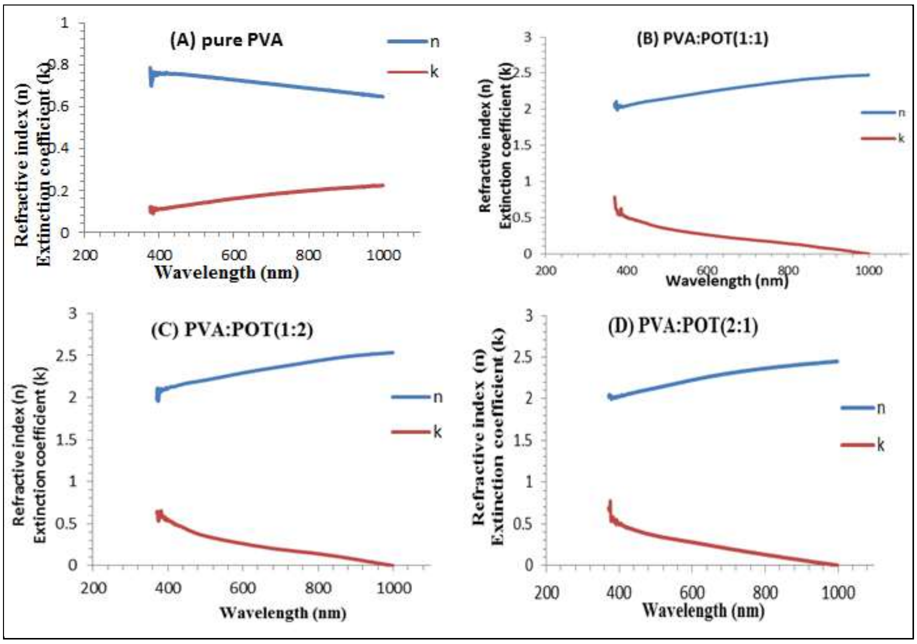

Fig.(1): relation between refractive index (n) / extinction coefficient (k) and wavelength of blend polymers PVA:POT.

The equations (7) and (8) are used to calculate the real and imaginary complex dielectric constant respectively. Real and imaginary part of the complex dielectric constant for the pure PVA is illustrated in fig. 2. The behaviour of real and imaginary dielectric constant approximately same the refractive index because of the value of extinction coefficient is low compare with refractive index value. The real and imaginary part of complex dielectric constant as shown in fig. 3 and 4, are decreased and increased with increasing photon energy respectively.

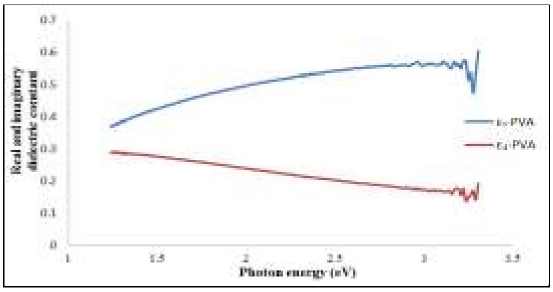

Fig.(2): shows real and imaginary part of complex dielectric constant as function of photon energy for pure PVA.

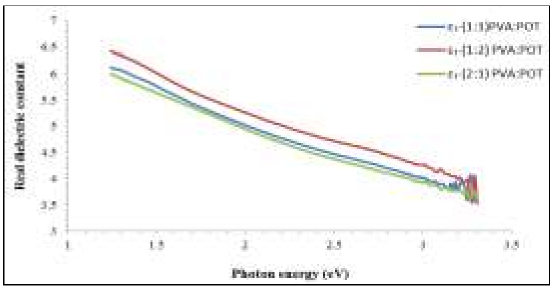

Fig.(3): shows real part of complex dielectric constant as function of photon energy for blend polymers (PVA:POT)

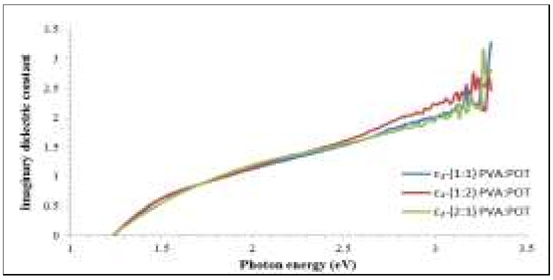

Fig.(4): shows imaginary part of complex dielectric constant as function of photon energy for blend polymers (PVA:POT).

Fig. 5 shows variation of optical conductivity calculated according to equation (9) with photon energy in which the maximum conductivity was recorded at 1.56 eV to be (1.75, 2.12 and 2.5× 10^{14} for (2:1, 1:1 and 1:2 PVA:POT) respectively. The obtained increase in conductivity attributed to present POT as a larger ratio of POT that leads to forming additional charges in polymers. The electrical conductivity decreased with increased photon energy as illustrated in fig. 6. The optical and electrical conductivity of the polymer blend varies with increased amount of POT. Another interesting result is that the optical conductivity exhibit two peaks where the electrical conductivity without peaks. The origin of these two peaks may be refers to optical interband transitions [20].

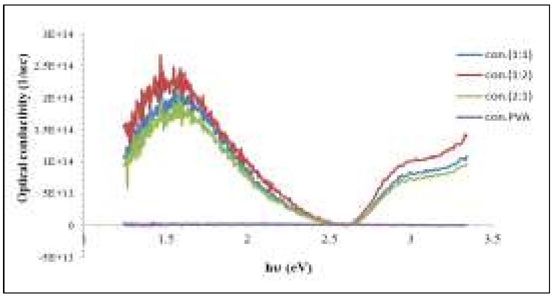

Fig.(5): optical conductivity versus photon energy of blend polymers (PVA:POT).

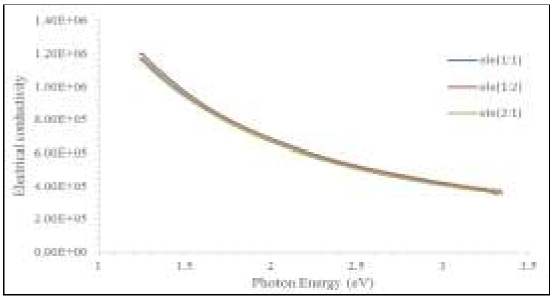

Fig.(6): Electrical conductivity versus photon energy of blend polymers (PVA:POT).

Fig. 7 show the relation between $(n^2 - 1)^{-1}$ and E^2 for the investigated composition. The values of E_d and E_o can be determined from the slope and the intercept. The calculated values of dispersion energy E_d, the oscillator energy E_o are found to be as listed in the table. 1.

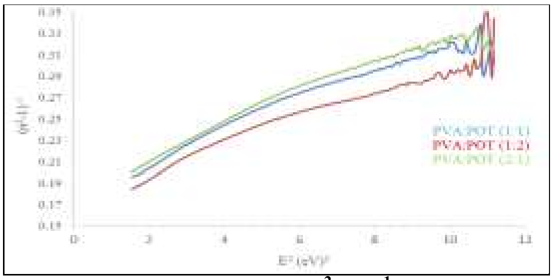

Fig. (7): The relation between $(n^2 - 1)^{-1}$ and E2 of blend polymer (PVA:POT).

Table 1: Optical parameters of blend polymer (PVA:POT).

material	E_o	E_d	M_{-1}	M_{-3}
PVA:POT (1:1)	3.53	19.63	5.56	0.446
PVA:POT (1:2)	3.59	20.98	5.84	0.453
PVA:POT (2:1)	3.50	19.11	5.45	0.443

The fig. 8 shows relation between the third order nonlinear susceptibility as a function of photon energy. The third order nonlinear susceptibility was calculated according to equation 14, and increased with increasing the ratio of POT in blended polymers which gave us a pointer, the POT enhanced the value of third order nonlinear susceptibility. Moreover, its value decreases with increase the incident photon energy.

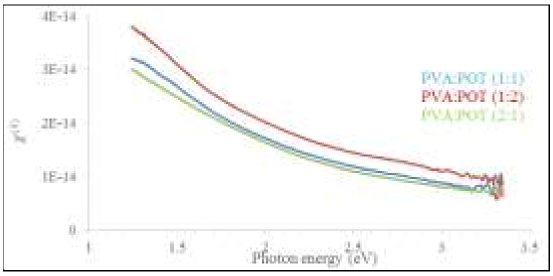

Fig. (8): The relation between the third order nonlinear susceptibility and E of blend polymer (PVA:POT).

Conclusion

In this work, the refractive index (n) and extinction coefficient (k) were characterized by using Ellipsometry spectroscopy through performing theoretical fitting of the measured ellipsometry data. The optical and electrical conductivity of blend polymer (PVA:POT) have been studied. The maximum conductivity was recorded at 1.56 eV to be (1.75, 2.12 and 2.5 for (2:1, 1:1 and 1:2 PVA:POT) respectively. The oscillator energy (E_o) and dispersion energy (E_d) were measured according to single-oscillator model. The moments of optical dispersion spectra, M_{-1} and M_{-3} evaluated as well as. The third order nonlinear susceptibility (χ 3) has been calculated in this work and studied as a function of the photon energy.

References

[1] Seshan, K. (2002). Handbook of thin-film deposition processes and techniques: Principles, Methods, Equipment and Applications. 2nd end., William Andrew publishing Norwich, New York, U.S.A.

[2] Ohring, M. (1992). The Materials Science of Thin Films. United Kingdom Addition published by Academic Press Limited.

[3] Stubb, H.; Punkka, E. and Paloheimo, J. (1993). Electronic and optical properties of conducting polymer thin films. *Science and Engineering*, **10**:85-140.

[4] Kalaivasan, N. and Syed Shafi, S. (2010). Synthesis of Various Polyaniline/Clay Nanocomposites Derived from Aniline and Substituted Aniline Derivatives by Mechanochemical Intercalation Method. *E-Journal of Chemistry,* **7(4)**:1477-1483.

[5] Cabuka, M. and Gündüz, B. (2017). Controlling the optical properties of polyaniline doped by boric acidparticles by changing their doping agent and initiator concentration. *Applied Surface Science*, **7:**

[6] Ahmed, R.M. and El-Bashir, S.M.(2011). Structure and Physical Properties of Polymer Composite Films Doped with Fullerene Nanoparticles. *International Journal of Photoenergy*,: 1-6.

[7] Bonnell, D.; Huey, B. and Carroll, D. (1995). In-Situ Measurement of Electric Fields at Individual Grain Boundaries in TiO2. *Solid State Ionics,* **75**:35.

[8] Majed, M. D. (2012). Preparation of Nanostructured TiO2 Thin Films by Pulsed Laser

Deposition. M.Sc. thesis, College of Science, University of Baghdad.
[9] Sze, S. M. (1981) Physics of Semiconductor Devices. Jon Wiley and Sons, 2nd edu., New York.
[10] Marien, J.; Wagner, T.; Duscher, G.; Koch, A. and Ruhle, M. (2000). Ag, Pt, Pd, Nb Doping (110) TiO2 (Rutile): Growth, Structure, and Chemical Composition of the Interface. *Surface Science*, **446**:219.
[11] Wu, T. and et al. (1993). Effect of noble metal catalyst on titania exhaust gas oxygen sensor. *Sensors and Actuators B*, **13**:41.
[12] Hodgson, J.N. (1970). Optical Absorption and Dispersion in Solids. Chapman & Hall, London.
[13] Khalef, W. K. (2011). Study the Thermoelectric and Characterization of Sn,Zn Thin Films Prepared by Oblique Angle Deposition. Ph.D. thesis, University of Technology.
[14] Borole, D.D.; Kapadi, U.R.; Kumbhar, P.P.; Hundiwale, D.G. (2002). Effect of inorganic dopants (in presence of electrolyte) on the conductivity of polyaniline, poly(o-toluidine) and their copolymer thin films. *Materials Letters*, **57**:844.
[15] Wemple, S.H.; DIDomenico, M. (1971). Behavior of the Electronic Dielectric Constant in Covalent and Ionic. *Material phys*, Rev, **B 3**:1338.
[16] Badran, H.A.; Taha, A.Y.; Abdulkader, A.F.; Emshary, C.A. (2012). Preparation and study of the electrical and optical properties of a new azo dye (4-acetaminophenol – [2-(4-azo)]-4-amino dipheyl sulfone). *J. Ovonic Res.,* **8**:161.
[17] Badran, H.A. (2012). Study on Optical Constants and Refractive Index Dispersion of Neutral red Doped Polymer Film. *Am. J. Appl. Sci.,* **9**:250.
[18] Hemissi, M. and Amardjia-Adnani, H. (2007). Optical and Structural Properties of Titanium Oxide Thin Fils Prepared by Sol-Gel Method. *Digest Journal of Nanomaterials and Biostructures*, **2**:299.
[19] Alfahed, R. K. F. and Ajeel, K. I. (2015). Electrical properties of blend polymers of polyvinyl alcohol/ poly(otoluidine. *IJSBAR,* **23:**173-182.
[20] Farag, A.A.M.; Ashery, A.; Shenashen, M.A. (2012). Optical absorption and spectrophotometric studies on the optical constants and dielectric of poly (o-toluidine) (POT) films grown by spin coating deposition. *Physica B*, **407**:2404.

دراسة المتغيرات البصرية من خلال تحليل اطياف الاليبسومتري لأغشية البوليمرات الممزوجة البولي اورثو تولدين/البولي فنيل الكحول

رائد كاظم فاخب [1] ، مناف صالح مجيد [1] ، كريم خلف محمد [1] ، حسين علي بدران البدران [2] ، خالد ابراهيم عجيل [2]
[1] *مركز بحوث النهرين للطاقة المتجددة النانوية ، جامعة النهرين ، بغداد ، العراق*
[2] *كلية التربية للعلوم الصرفة ، جامعة البصرة ، البصرة ، العراق*

الملخص

تمت في هذه الدراسة حساب بعض الثوابت البصرية للبوليمرات الممزوجة (البولي تولدين/ البولي فنيل الكحول) من خلال تحليل اطياف الالبسومتري، واظهرت الدراسة تباينا في مقدار معامل الانكسار ومعامل الخمود كدالة لطاقة الفوتون، وكذلك تم حساب كلا من التوصيلية البصرية والتوصيلية الكهربائية والتأثرية اللاخطية من الرتبة الثالثة كدالة لطاقة الفوتون. ايضا في هذه الدراسة تم حساب قيم بعض الثوابت البصرية (طاقة الاهتزاز، طاقة التشتت، وزخم اطياف التشتت البصري).