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Effect of Nano Sb_2O_3 on the Dispersive Optical Constants of PMMA Films

Wasan A. Al-Taa'y[1], Mohammed T. Abdul nabi[1], Saad F. Oboudi[2]*, Emad Yousif[3]*

[1]Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq;
[2]Department of Physics, College of Science, University of Al-Nahrain, Baghdad, Iraq;
[3]Department of Chemistry, College of Science, University of Al-Nahrain, Baghdad, Iraq.
**Email: ch@sc.nahrainuniv.edu.iq; emad_yousif@nahrainuniv.edu.iq.*

ABSTRACT: Pure and Antimony Trioxide Sb_2O_3 doped PMMA films were prepared by the casting method. Optical absorption measurements in the wavelength range 200-800 nm were studied by using a computerized UV-Vis spectrophotometer (Shimadzu UV-1601 PC) and these confirmed that PMMA films have a direct band gap that decreases from 5.15 to 4.66 eV as the doping concentration increases to 5wt%. The increase in the density of localized states from 8.9 to 74.5 meV causes an expansion in the Urbach tail and consequently decreases the energy gap. The dispersion of the refractive index was analyzed using the concept of a single oscillator. The values of the single oscillator energy were 32.70, 13.59, 7.06, and 4.58 eV, while the dispersion energy values were 4.36, 49.04, 21.76 and 14.15 eV for the pure, and 3%, 4% and 5% Sb_2O_3 for the doped PMMA films respectively. The single-term Sellmeier were determined, and the average oscillator position was investigated, the value of which decreased with increasing doping concentration. The value of average oscillator strength increased with increasing Sb_2O_3 concentration to 5wt%. Skin depth and optical conductivity could be calculated, and results show a decrease in Skin depth with an increasing impurity percentage, but an increase of optical conductivity with greater impurity

Keywords: PMMA polymer; Optical dispersion parameters.

تأثيرنانو Sb_2O_3 على ثوابت التشتت البصرية لأغشية PMMA

وسن علي الطائي، سعد فرحان العبيدي، محمد طارق عبد النبي وعماد يوسف

الملخص: أغشية PMMA النقية والمشوبة بمادة اكسيد الانتيموان الثلاثيSb_2O_3 حضرت باستخدام تقنية الصب. درست قياسات الامتصاص البصرية ضمن مدى الاطوال الموجية (200-800)nm باستخدام جهاز UV-VIS spectrophotometer (Shimadzu UV-1601 PC). توصلنا في هذا البحث الى أن أغشية PMMA ذات فجوة طاقة مباشرة تنخفض من 5.15 الى 4.66 eV بزيادة تركيز التطعيم الى 5 wt%. الزيادة في المستويات الموضعية من 8.9 الى 74.5 meV تحدث توسيع في ذيول اورباخ وبالتالي انخفاض في فجوة الطاقة. تم تحليل تشتت معامل الانكسار باستخدام مفهوم المذبذب الاحادي. قيم طاقة المذبذب الاحادي هي 32.70, 13.59, 7.09 و 4.58eV, بينما قيم طاقة التشتت 4.36, 49.04, 21.76 و14.1 eV بنسب 0, 3%, 4% و 5% لأغشية PMMA النقية والمشوبة بمادة Sb_2O_3 على التوالي. حسب معدل موقع المذبذب ووجد أن قيمته انخفضت مع زيادة تركيز التطعيم. زادت قيم معدل قوة المذبذب مع تركيز Sb_2O_3 وصولا الى 5wt%. تم حساب عمق الاختراق والتوصيلية البصرية، بينت النتائج حدوث انخفاض في عمق الاختراق مع نسب التشويب بينما تزداد التوصلية البصرية مع هذه النسبة.

الكلمات المفتاحية: بوليمر PMMA ، معاملات التشتت البصرية.

1. Introduction

Films of poly methyl methacrylate (PMMA) as a polymeric waveguide has steadily gained attention for use in optical components and in optoelectronic devices. Recently, some researchers have reported optical components such as an optical switch, a coupler, a splitter and a transceiver [1,2]. Polymeric composites of PMMA are very popular due to their low cost, volume productivity, high strength to weight ratio, noncorrosive properties and simple fabrication methods. They are known for their importance in technical applications [3].

Composites containing two materials with different physical properties often exhibit new properties. The composites can provide improved characteristics that are not obtainable in any of the original components alone; they not only combine the advantageous properties of dopant and polymers but also exhibit many new properties that single-phase materials do not have [4], and they are used in a wide variety of industrial products. A variety of additives are used in the composites to improve these materials' properties, aesthetics, manufacturing processes, and performance.

The structural, optical, and electrical properties of these polymeric materials can be enhanced by incorporation of filler into a polymer matrix, because dispersed filler will enhance various physical properties of the host polymer [5]. In this paper, we report and discuss the optical characterization of PMMA films doped with different concentrations of Sb_2O_3 nanoparticles by UV-Vis spectra.

2. Experimental details

PMMA films doped with different weight concentration (3,4 and 5) wt% of Nano Antimony Trioxide (Sb_2O_3) were prepared by dissolving the dispersed polymer in 100 ml chloroform. Different polymer solutions (volumetric solutions) were cast as films and dried at room temperature for 24 hours. The thickness of the prepared films were measured using an indicating micrometer and found to be in the range of 150 µm. These films were clear, transparent, and free from any noticeable defect and of a light bluish color.

Optical transmittance and absorbance were recorded in the wavelength range 200-800 nm using a computerized UV-Vis spectrophotometer (Shimadzu UV-1601 PC). Optical transmittance and absorbance were reported in order to study the effect of doping on the parameters under investigation.

3. Results and discussion

The study of the optical absorption for the films under investigation, particularly the absorption edge, has proved to be very useful for elucidation of the electronic structure of these materials. The optical absorption spectra of the tested films as a function of dopant concentration are shown in Figure 1. The absorption at higher wavelengths in the visible region is low, but at wavelength 280–380 nm an intense absorption can be seen. Moreover, it can be noticed that the absorbance tends to increase as the doping concentration rises to 5 wt%.

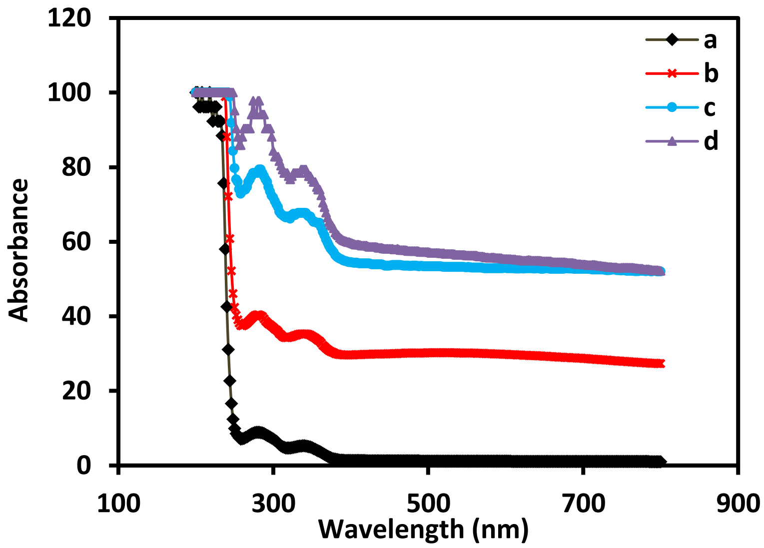

Figure 1. Absorbance of pure and Sb_2O_3 doped PMMA films versus wavelength: eda = is pure PMMA, b = PMMA/3% Sb_2O_3, c = PMMA/4% Sb_2O_3, d = PMMA/5% Sb_2O_3.

The tail of the absorption edge is exponential, indicating the presence of localized states in the energy band gap. The amount of tailing can be predicted to a first approximation by plotting the absorption edge data in terms of an equation originally given by Urbach [6]. The absorption edge gives a measure of the energy band gap and the exponential dependence of the absorption coefficient, in the exponential edge region Urbach rule is expressed as [7,8].

$$\alpha = \alpha^\circ \exp (h\upsilon / E_U) \quad (1)$$

where α is the absorption coefficient, $h\upsilon$ is photon energy, α° is a constant, and E_U is the Urbach energy, which characterizes the slope of the exponential edge. Figure 2 shows Urbach plots of the films. The value of Urbach energy was obtained from the reciprocal gradient of the linear portion of the plot. $\ln\alpha$ vs. $h\upsilon$ is given in Table 1. Urbach energy values change inversely with the optical band gap. The Urbach energy values of the films increases with an increase of doping concentration. The increase of Urbach energy suggests that the atomic structural disorder of doped films is increased by increasing the doping ratio. This behavior can result from increasing the grain size. The size of the grains varies with the doping and influences the value of the optical energy gap; this increase leads to a redistribution of states from band to tail and may be attributed to the improved of crystallinity. As a result, both a decrease in the optical gap and expansion of the Urbach tail take place.

Table 1. The optical parameters.

Sample	E_u (meV)	E_g (eV)	E_d (eV)	E_o (eV)	λ_o nm	$S_o *10^{-5}$ cm^{-2}
pure PMMA	60	5.15	4.36	32.70	254.90	0.26
PMMA/3% Sb_2O_3	83	5.03	49.04	13.59	79.17	57.11
PMMA/4% Sb_2O_3	40	4.82	21.76	7.067	129.18	17.43
PMMA/5% Sb_2O_3	217	4.66	14.15	4.58	378.95	2.66

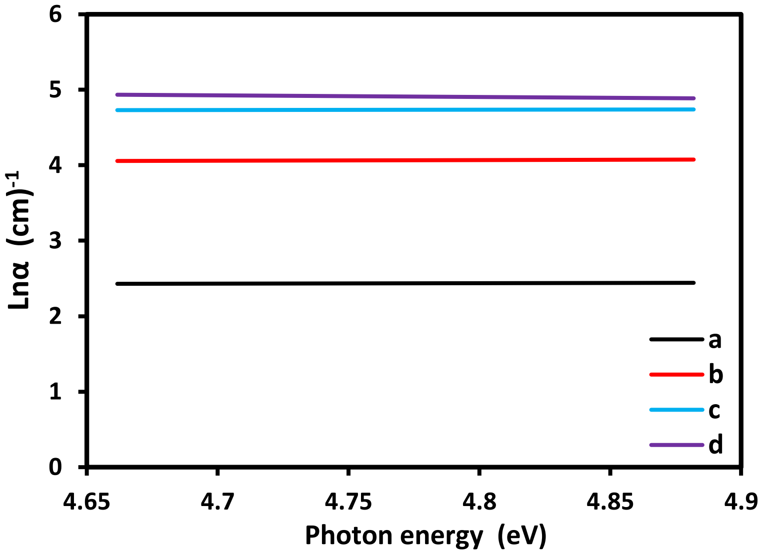

Figure 2. lnα versus photon energy for pure and doped PMMA films: a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3.

According to the inter-band absorption theory, the optical band of the films can be calculated using Tauc's relation [9,10]

$$(\alpha h\upsilon) = A(h\upsilon - Eg)^n \tag{2}$$

where A is a constant, E_g the optical band gap, and n an index which could take different values according to the electronic transition. For allowed direct transitions the coefficient n = 1/2, and for allowed indirect transitions n = 2. The curve $(\alpha h\upsilon)^{1/2}$ for the allowed indirect transition does not present evident linearity; this seems to suggest that PMMA films have a direct band gap.

The extrapolation of the linear part of the curve $(\alpha h\upsilon)^2$ to the energy axis is shown in Figure 3. The direct band-gap energy for the pure PMMA film is 5.15 eV. It can be seen that the energy gap of the films tends to decrease with an increase of Sb_2O_3 concentration; this decrease can be attributed to a decrease in crystallinity disorder of the films. The optical band gap of the PMMA films is obviously affected by defects and by the crystallinity. Such a decrease in the energy gap due to doping was also obtained by other researchers [11-15].

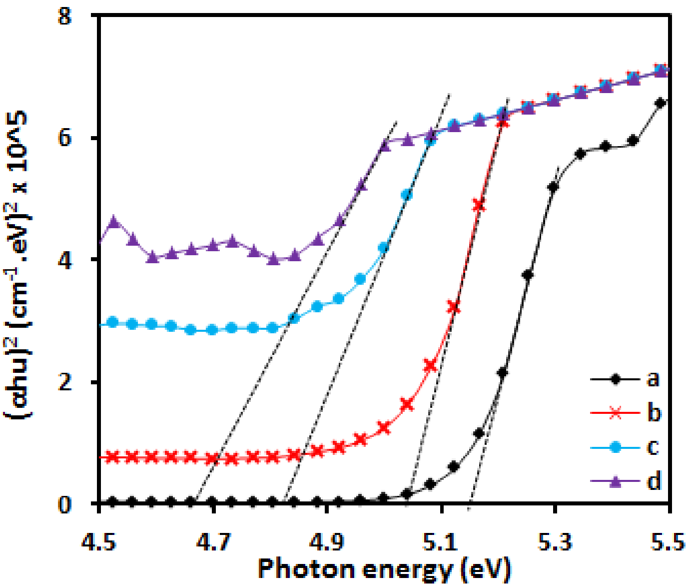

Figure 3. $(\alpha h\upsilon)^2$ versus photon energy for pure and doped PMMA films. a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3.

Wemple and Didomenico [16,17] used a single-oscillator description to define dispersion energy parameters. The refractive index dispersion plays an important role in optical communication and the design of optical devices. Therefore, it is a significant factor. The relation between the refractive index n, and the single oscillator strength is given by the expression:

$$n^2 = 1 + [E_d\, E_o / E_o^2 - (h\upsilon)^2] \quad (3)$$

where E_d and E_o are single oscillator constants, E_o is the energy of the effective dispersion oscillator, and E_d the so-called dispersion energy, which measures the intensity of the inter band optical transitions. The oscillator energy E_o is an average of the optical band gap, and can be obtained from the Wemple–Didomenico model. This model describes the dielectric response for transitions below the optical gap. Experimental verification of Eq. (3) can be obtained by plotting $(n^2-1)^{-1}$ versus $(h\upsilon)^2$, as illustrated in Figure 4, which yields a straight line for normal behavior having the slope $(E_oE_d)^{-1}$ and the intercept with the vertical axis equal to E_o/E_d. E_o and E_d values were determined from the slope, $(E_oE_d)^{-1}$ and intercept (E_o/E_d) on the vertical axis. E_o values decrease as the optical band gap decreases as shown in Table 1. According to the single-oscillator model, the single oscillator parameters E_o and E_d are related to the imaginary part of the complex dielectric constant.

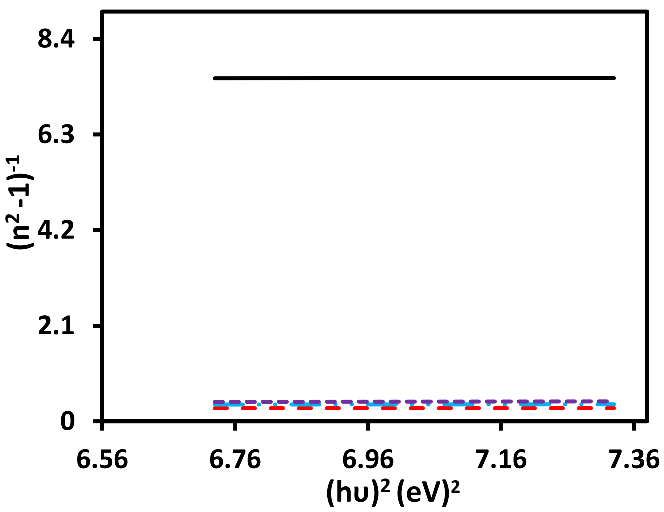

Figure 4. Variation in $(n^2 - 1)^{-1}$ as a function of $(h\upsilon)^2$ for pure and doped PMMA films.: a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3.

The values obtained for the dispersion parameters E_o, E_d, and E_u are listed in Table (1). For the definition of the dependence of the refractive index (n) on the light wavelength (λ), the single-term Sellmeier relation can be used [16]:

$$n^2 (\lambda)^{-1} = S_o\lambda_o^2 / 1 - (\lambda_o/\lambda)^2 \qquad (4)$$

where λ_o is the average oscillator position and S_o is the average oscillator strength. The parameters S_o and λ_o in Eq. (4) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ versus λ^{-2} as shown in Figure 5; the slope of the resulting straight line gives $1/S_o$, and the infinite-wavelength intercept gives $1/ S_o \lambda_o^2$. After doped the average oscillator position values decreased and with increasing doping concentration to 5wt%, the average oscillator strength increased with impurity percentage as shown in Table 1.

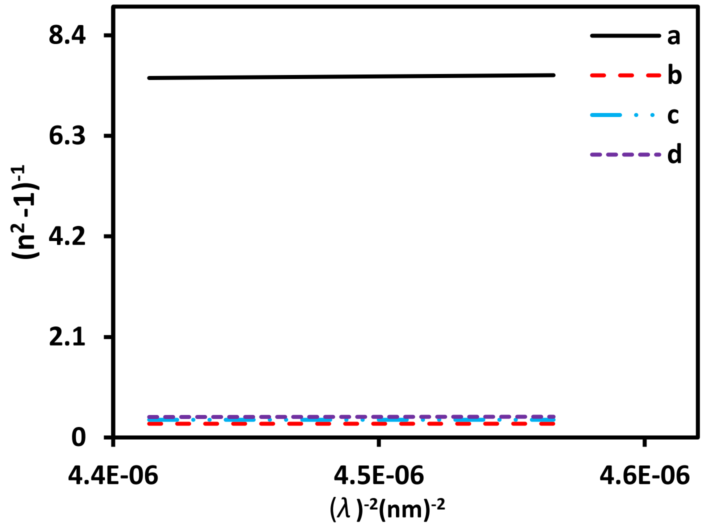

Figure 5. Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for pure and doped PMMA films. a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3.

The skin depth x could be calculated using the following relation [18]:

$$x = \lambda / 2\pi k \qquad (5)$$

Where k is the extinction coefficient. Figure 6 shows the variation of skin depth as a function of wavelength for all films. It is clear from the figure that the skin depth increases as the wavelength increases; this behavior could be seen for all samples (a, b, c and d). However, the skin depth decreases as the Sb_2O_3 concentration increases to 5wt%, which means that the skin depth is transmittance related.

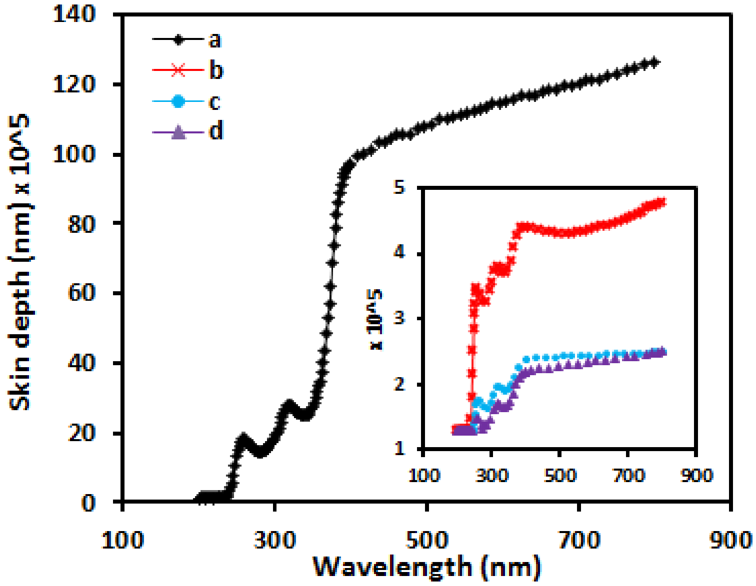

Figure 6. Skin depth versus wavelength for pure and doped PMMA films: a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3.

The optical conductivity σ was calculated using the relation [19]:

$$\sigma = \alpha\, n\, c / 4\pi \quad (6)$$

Where c is the velocity of light. Figure 7 shows the variation of optical conductivity with the wavelength. It can be seen that the optical conductivity for pure film decreases with the increase of wavelength; this decrease is due to the low absorbance of the films in that region. After films are doped, this decrease is gradually changed to the increasing down to percentage of 5wt%. Also, it can be noticed that the optical conductivity increases with an increase in doping concentration. This suggests that the increase in optical conductivity is due to electrons excited by photon energy. The origin of this increase may be attributed to some changes in the structure of the film due to the doping and the charge ordering effect.

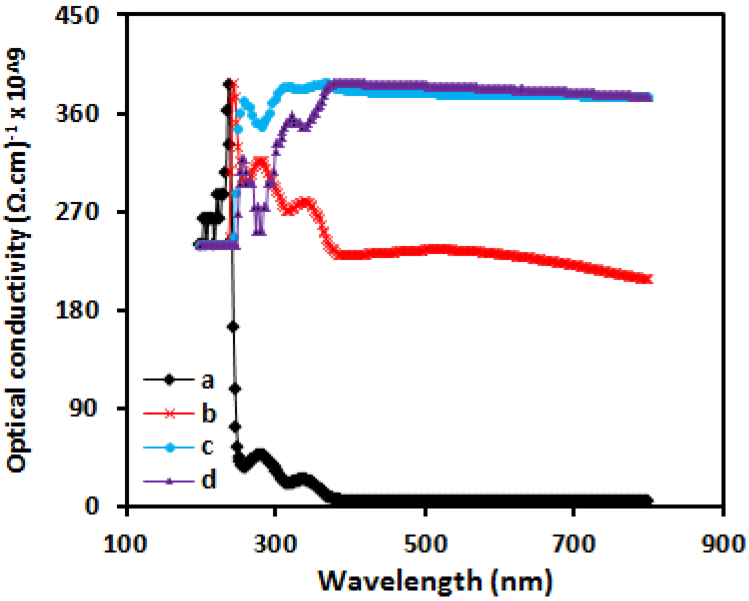

Figure 7. Optical conductivity versus wavelength for pure and doped PMMA films. a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3.

4. Conclusion

Pure and Sb_2O_3 doped PMMA films were successfully prepared by the solution casting method. The optical absorption spectra were calculated and were found to increase progressively after doping with increasing concentrations. The type of optical transition responsible for optical absorption was found to be direct allowed transitions. The energy gap values obtained from the Wemple–Didomenico model were close to those determined from the Tauc model, and were found to decrease with an increase in doping concentration, having the values of 5.15, 5.03, 4.82, and 4.66 eV for the pure PMMA, 3,4, and 5wt% respectively. The optical dispersion parameters were characterized and found to obey the single oscillator model. The single oscillator parameters and the single-term Sellmeier were determined, the change in dispersion and the average oscillator position was investigated and its values decreases with increasing doping concentration to 5wt%. Values of dispersion energy and average oscillator strength increase with the concentration of Sb_2O_3 impurity. Skin depth and optical conductivity could be calculated, with results showing a decrease in skin depth with impurity percentage while optical conductivity increases with increasing impurity.

5. Acknowledgements

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