Effect of Nano Sb$_2$O$_3$ on the Dispersive Optical Constants of PMMA Films

Wasan A Al-Taa'y[1], Saad F Oboudi[2], Hanan Ibraheem[3], Mohammed T Abdul Nabi[1] and 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*

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ABSTRACT

Pure and Antimony Trioxide Sb$_2$O$_3$ doped PMMA Films were prepared by casting method. Optical absorption measurements in the wavelength range (200-800) nm were studied and confirmed that PMMA films have an direct band gap that decreased 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 expanding in the Urbach tail and consequently decreases in 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$_2$O$_3$ doped PMMA films respectively. The single-term Sellmeier were determined, the average oscillator position was investigated and its value decreased with increasing doping concentration. Values of average oscillator strength was increased with Sb$_2$O$_3$ concentration to 5wt%. Skin depth and optical conductivity could be calculates where results show a decreasing in Skin depth with impurity percentage while increasing of optical conductivity with this percentage.

Keywords: PMMA polymer; Optical dispersion parameters

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INTRODUCTION

PMMA as a polymeric waveguide has steadily gained growing attention for use as optical components and in optoelectronics devices. Recently, some researchers 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 and simple fabrication methods. They are known, for their importance in technical applications [3].

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

The structural, optical, and electrical properties of these polymeric materials can be enhanced by incorporation of filler into polymer matrix, because dispersed filler will enhance various physical properties of the host polymer [5].

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In this paper, we report and discuss the optical characterization of the Sb_2O_3 nanoparticles in different concentrations doped PMMA films by UV-VIS spectra.

EXPERIMENTAL DETAILS

Films of poly methyl methacrylate (PMMA) doped with different weight concentration (3, 4 and 5)wt% of Nano Antimony Trioxide (Sb_2O_3) have been prepared by the dispersed polymer dissolve 100 ml chloroform. Different polymer solutions (volumetric solutions) were casted as films, dried at room temperature for 24 hours. Thickness of the prepared films were measured using indicating micrometer, and found to be in the range of 150 μm, these films were clear, transparent, and free from any noticeable defect and showing light bluish color.

Optical transmittance and absorbance were recorded in the wavelength range (200-800) nm using 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.

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 and at wavelength 280–380 nm, an intense absorption can be seen. Moreover, it can be notice that the absorbance tends to increase as the doping concentration rises to 5 wt%.
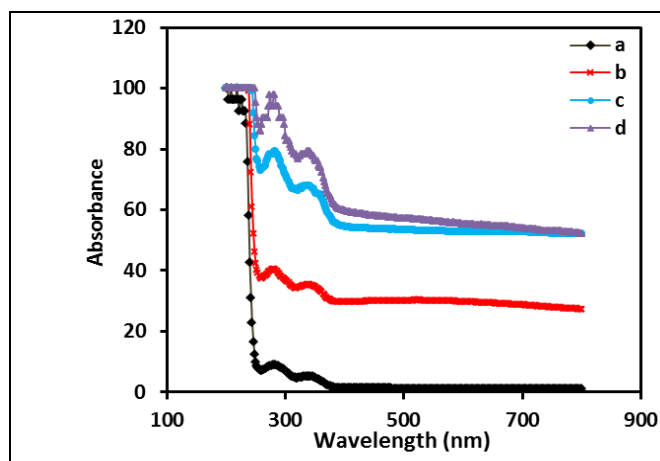
Figure 1: Absorbance of pure and Sb₂O₃ doped PMMA films versus wavelength. Where represent: a is pure PMMA, b is PMMA/3% Sb₂O₃, c is PMMA/4% Sb₂O₃, d is PMMA/5% Sb₂O₃

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, 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. $h\upsilon$ and is given in Table 1. Urbach energy values change inversely with the optical band gap. The Urbach energy values of the films increases with the increasing of doping concentration. The increase of Urbach energy suggests that the atomic structural disorder of doped films increase by increasing the doping ratio. This behavior can result from increasing the grains

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size. The size of the grains varies with the doping and influences the values of optical energy gap, this increase leads to a redistribution of states from band to tail and may be attributed to the improvement of crystallinity. As a result, both a decrease in the optical gap and expanding of the Urbach tail are taken place.
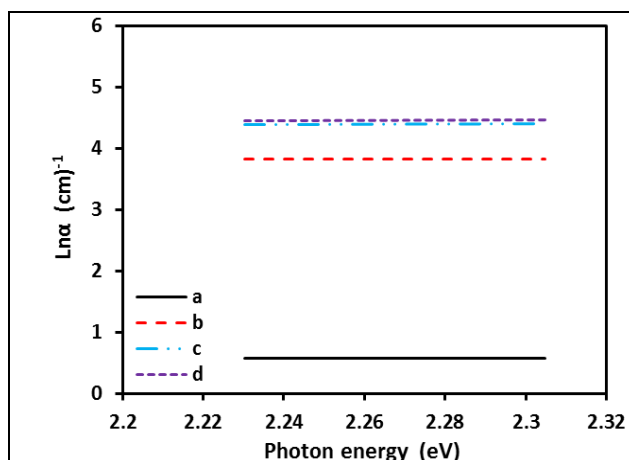

Figure 2: lnα versus photon energy for pure and doped PMMA films. Where represent: a is pure PMMA, b is PMMA/3% Sb₂O₃, c is PMMA/4% Sb₂O₃, d is PMMA/5% Sb₂O₃

According to the inter-band absorption theory, the optical band of the films can be calculated using Tauc's relation [7]:

$$(\alpha h\upsilon) = A(h\upsilon - E_g)^n \quad (2)$$

Where A a constant, E_g the optical band gap and n is 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 curves $(\alpha h\upsilon)^{1/2}$ for the allowed indirect transition does not present evident linearity, this seems to suggest that PMMA films have an 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 equal to 5.15eV. It can be seen that the energy gap of the films is tend to decrease with the increasing of Sb₂O₃ 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 the defects and the crystallinity, such decrease in the energy gap due to doping was also obtained by other researchers [9,10].
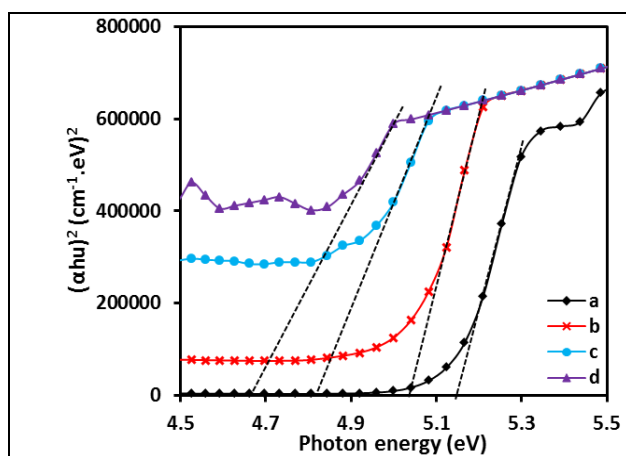

Figure 3: $(\alpha h\upsilon)^2$ versus photon energy for pure and doped PMMA films. Where represent: a is pure PMMA, b is PMMA/3% Sb₂O₃, c is PMMA/4% Sb₂O₃, d is PMMA/5% Sb₂O₃

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Wemple and Didomenico [11-12] use a single-oscillator description to define dispersion energy parameters. The refractive index dispersion plays an important role in the optical communication and designing of the 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, 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, 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 $(n2-1)^{-1}$ versus $(h\upsilon)^2$ as illustrated in Figure 4 which yields a straight line for normal behavior having the slope $(E_o E_d)^{-1}$ and the intercept with the vertical axis equal to E_o/E_d. E_o and E_d values were determined from the slope, $(E_o E_d)^{-1}$ and intercept (E_o/E_d) on the vertical axis. E_o values decreased as the optical band gap decreases as mentioned 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.
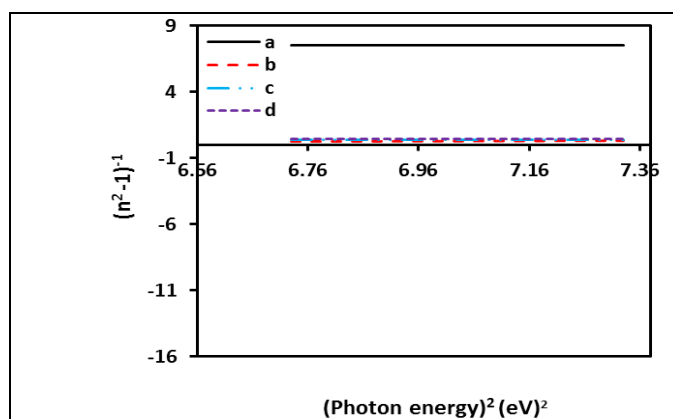

Figure 4: Variation in $(n^2 – 1)^{-1}$ as a function of $(h\upsilon)^2$ for pure and doped PMMA films. Where represent: a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3

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 (Oboudi and etl, 2015) [11]:

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

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 were decreased and with increasing doping concentration to 5wt%, show results that the average oscillator strength increased with impurity percentage as shown in Table 1.

The skin depth x could be calculated using the following relation [13]:
$$x = \lambda / 2\pi k \quad (5)$$
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 increase, this behavior could be seen for all samples (a, b, c and d) also the skin depth decreases as the Sb_2O_3 concentration increases to 5wt%, which means that the skin depth is a transmittance related.
The optical conductivity σ was calculated using the relation [14]:

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

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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 is decreased with the increase of wavelength; this decrease is due to the low absorbance of the films in that region. After doped of films this decreasing is gradually changed to the increasing down to percentage of 5wt%. Also, it can be notice that the optical conductivity increases with the increasing of doping concentration. This suggests that the increase in optical conductivity is due to electrons excited by photon energy. The origin of this increasing may be attributed to some changes in the structure due to the doping and the charge ordering effect.
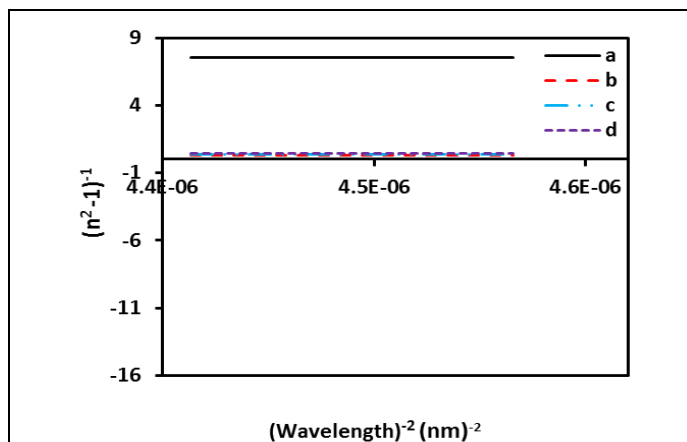

Figure 5: Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^{-2}$ for pure and doped PMMA films. Where represent: a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3

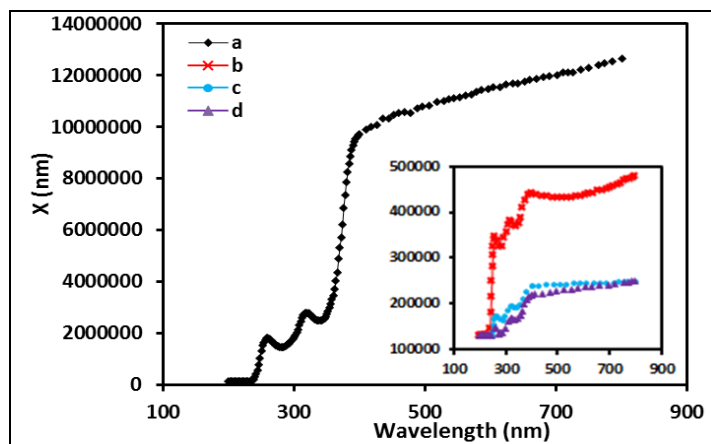**Figure 6: Skin depth versus wavelength for pure and doped PMMA films. Where represent: a is pure PMMA, b is PMMA/3% Sb_2O_3, c is PMMA/4% Sb_2O_3, d is PMMA/5% Sb_2O_3**
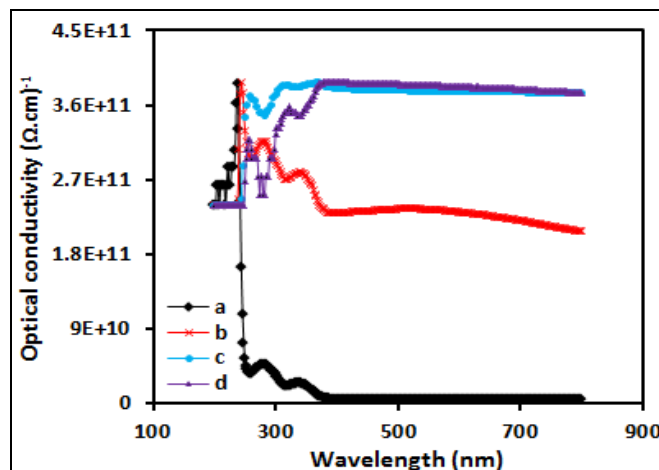
Figure 7: Optical conductivity versus wavelength for pure and doped PMMA films. Where represent: a is pure PMMA, b is PMMA/3% Sb$_2$O$_3$, c is PMMA/4% Sb$_2$O$_3$, d is PMMA/5% Sb$_2$O$_3$

CONCLUSIONS

Pure and Sb$_2$O$_3$ doped PMMA films have been successfully prepared by the solution casting method. The optical absorption spectra were calculated we found increased after doped and with increasing concentration. The type of optical transition responsible for optical absorption was found to be direct allowed transitions. The energy gap values obtained from Wemple–Didomenico model were close to those determined from Tauc model and found to be decreases with the increasing of doping concentration and have 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 be obeyed 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 was increases with concentration of Sb$_2$O$_3$ impurity. Skin depth and optical conductivity could be calculates where results show a decreasing in Skin depth with impurity percentage while increasing of optical conductivity with this percentage.

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