Investigation of the Effects of Fullerene addition and Plasma Exposure on Optical Properties of Polystyrene Films

N. M. Elsayed*, O. F. Farag, M. H. Elghazaly and D. A. Nasrallah

Physics Department, Faculty of Science, Zagazig University, Egypt

Abstract: *In the present study, two different methods of modification (Fullerene addition and plasma exposure) were applied to tune the basic optical properties and optical constants of the polystyrene films with thickness in the range (0.22-0.25 mm). The samples have been investigated via absorbance, transmittance and reflectance spectra, and characterized in the wavelength range 200–900 nm. The optical band gap E_g is found to be decreased after Fullerene addition while it is not changed with plasma exposure. The optical constants (refractive index, extinction coefficient, and real and imaginary parts of the dielectric constant) showed clear changes with Fullerene addition and plasma exposure.*
Keywords: polystyrene/ fullerene/ plasma exposure/ optical constants/ optical band gap/ doping

I. Introduction

In recent years, polymers with different optical properties have been attracted much attentions due to their applications in the sensors, light-emitting diodes and others [1]. The optical study is very interesting because it provides an important information about the absorbance, transmittance and reflectance of the observed polymeric films [2]. The optical absorption and especially the absorption edge present a useful method for the investigation of optically induced transition and for getting information about the band structure, the band tail and the energy gap of the polymeric materials under consideration [3].

The optical properties of polymeric materials can be easily tuned by controlling contents of the different concentrations [1] and by physical surface modification. Physical surface modification by flame, corona treatment, UV, gamma-ray, electron beam irradiations, ion beam, plasma, and laser treatments [4, 5, 6, 7] lead the breakage of covalent bonds, promotion of cross linkages, formation of carbon clusters, liberation of volatile species and in certain cases creation of new chemical bonds [8]. All these processes introduce so-called defects inside the material that are responsible for change in the optical, electrical, mechanical and chemical properties of the material [9].

Polystyrene (PS) is amorphous polymer with bulky side groups. General purposes PS are hard, rigid, and transparent at room temperature and glass like thermoplastic material which can be soften and distort under heat. It is soluble in aromatic hydrocarbon solvents, cyclohexane and chlorinated hydrocarbons [10].

Fullerene (C_{60}) is a widely studied material due to its unique optical, electrical, and chemical properties [11]. It has potential applications in hetero-junction solar cell as well as medical sciences [12]. Incorporation of fullerene and nanotubes into chemical composition of polymers gives one more opportunities for their study and application as composite materials, films, and fibers serving different purposes [13].

Plasma treatment have distinct advantages over other methods, modifications are limited to the surface layer to a depth of typically 0.005 to 0.05 μm without affecting the bulk properties of the polymer [14]. Moreover, it is a rabid and environmentally friendly process [15]. The effect of plasma treatment depends on a verity of parameters such as kind of plasma (DC, radio frequency (RF) or microwave (MW)), the discharge power, the pressure of the gas, as well as exposure time [16].

In the present paper, we study the effects of fullerene addition and DC N_2 plasma on the basic optical properties and optical constants of the polystyrene films.

II. Materials And Methods

1. Samples preparation

The studied samples were prepared by the casting technique. PS of molecular weight 192,000 in the form of grains and Fullerene (C_{60}) of molecular weight 720.64 were supplied by Sigma- Aldrich Company. PS and Fullerene (C_{60}) were dissolved in toluene with purity 99.99 %, the complete dissolution was obtained using a magnetic stirrer at room temperature for half-hour. A mixture of the solution was cast onto a clean glass Petri dish. The whole assembly was placed in a dust free chamber and allowed to evaporate the solvent slowly in air at room temperature for one week. The thickness of the films was in the range of (0.22-0.25 mm), it was determined using micrometer at different places in each film and an average was taken.
The Fullerene content in films prepared in this study are 0, 1×10^{-5}, 5×10^{-5}, 1×10^{-4}, 5×10^{-4} and 1×10^{-3} mol. %.

2. Plasma treatment

Figure (1) represents a schematic diagram of the DC glow discharge setup used for surface treatment of the PS films. The setup consists of a Pyrex tube of (18 cm) long and (13 cm) diameter closed at each end with aluminum plate. Two planes circular stainless steel plates of (5 cm radius) represent the two electrodes are connected to each other with four isolated rods keeping the spacing constant at (7 cm). The two electrodes move axially forward and backward as a unit controlled by a handle outside the tube. The base pressure is attained into the tube at (10^{-3} Torr) by using a rotary pump (Edwards H. vacuum pump, model ED 200) then the N_2 gas is allowed to inter the tube throw a controllable needle valve. Plasma properties were kept constant during the experiment, as the gas pressure was 0.4 Torr, and the discharge power was about 3.5 W. The exposure time was varied from 15 to 120 minutes.

The films were cut to give sample size (1.5 x 2 cm). The samples were supported on a glass rode and put in front of the cathode at the edge of the negative glow.

3. UV-Visible Spectroscopy

Ultra violet and visible (UV/VIS) absorbance, transmittance and reflectance spectra of pristine and plasma treated PS and pristine (PS-C_{60}) films were recorded over a wavelength range 200–900 nm using a Perkin–Elmer Lambda 950 spectrophotometer. The optical absorption and reflectance spectra were analyzed to determine optical constants such as refractive index n, extinction coefficient k, and absorption coefficient α. Analysis of the absorption coefficient was also carried out to determine the optical band gap.
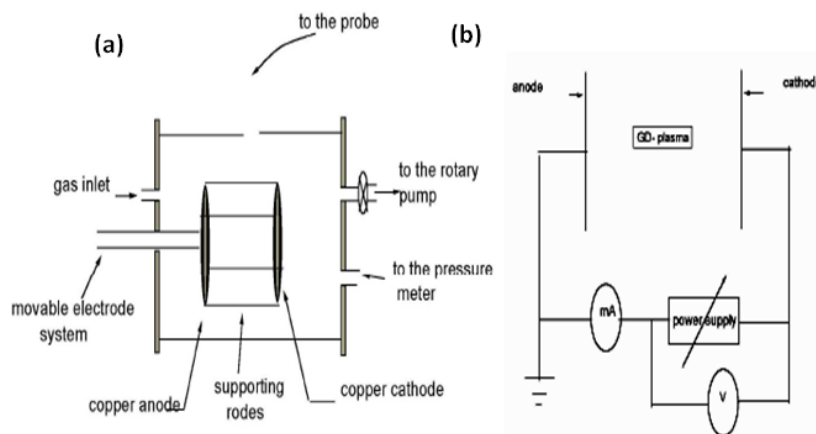

Fig1. A schematic diagram for (a) The experimental equipment and (b) The electrical circuit

III. Results And Discussion

1. Optical absorption spectra

Figure (2.a) shows UV-Visible spectra of the PS films filled with different concentrations of Fullerene (C_{60}). Pure PS exhibit strong absorption over the 200-280 nm range (max 240 nm). The peak at 240 nm can be attributed to the phenyl ring in each repeat unit [17]. On the other hand, Fullerene (C_{60}) exhibit strong absorption peak at 335 nm and two weak-broad bands between 450 and 640 nm which are attributed to the π-π transition and the transition from HOMO to LUMO, respectively [18].

UV-Visible spectra recorded for the plasma treated PS films are displayed in Figure (2.b) for different durations. An increase of absorbance is observed in spectra of samples exposed to plasma, which indicates that absorbing photoproducts (e.g. conjugated double bonds) are present in PS [17].

2. Optical energy gap

The variation of the optical bulk absorption coefficient, α, with wavelength is a unique parameter of the medium. The importance of the absorption coefficient is related to the valuable information that can be obtained, such as the electronic band structure and the optical energy band gap. The absorption coefficient can be estimated from the optical absorption spectrum owing to the following equation [3]:

$$\alpha(\nu) = 2.303\, A / d \qquad (1)$$

where A is the absorbance and d is the film thickness.

Figure (2): The UV-Visible absorption spectra, (a) for PS films filled with different concentrations of C_{60} and (b) for pristine and plasma treated PS films for different durations.
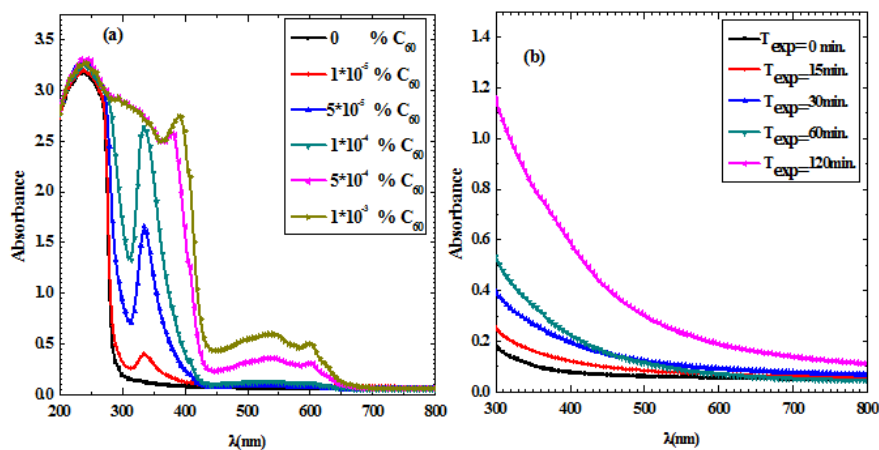
Figure (2): The UV-Visible absorption spectra, (a) for PS films filled with different concentrations of C_{60} and (b) for pristine and plasma treated PS films for different durations.

The relation between the optical energy band gap, absorption coefficient and energy (hν) of the incident photon is given by [19,20]:

$$\alpha h \nu = B (h \nu - E_g)^r \qquad (2)$$

where α is the absorption coefficient, ν is the frequency, h is the Planck's constant, B is a constant, E_g is the optical energy band gap between the valence and the conduction bands and r is the power that characterizes the transition process. Specifically, r can take the values 1/2, 3/2, 2, and 3 for transitions designated as direct allowed, direct forbidden, indirect allowed and indirect forbidden, respectively.

The usual method to determine the optical energy band gap is to plot a graph between $(h\nu\alpha)^{1/r}$ and hν. The best fit of indirect transitions is obtained for r = 2, meanwhile for a direct transition the best fit is obtained for r = 1/2 . The indirect optical energy band gap is determined by plotting $(\alpha h\nu)^{1/2}$ against the photon energy (hν). The extrapolation of the straight parts of the curves to the energy axis (hν) yields the indirect optical energy band gap.

The variation of the absorption coefficient (α) versus photon energy (hν) for pure and doped PS with C_{60} of different concentrations is shown in Figure (3.a). The absorption coefficient of samples increased with increasing C_{60} concentrations in the film. Also, it can be seen that the behavior of (α) is similar to the absorption spectra.

Figure (3.b) shows the absorption coefficient (α) as function of photon energy (hν) for pristine and nitrogen plasma treated PS films at different durations. It is clear from this figure that the values of (α) showed increase with increase in the exposure time. The increase in (α) with increasing the exposure time is attributed to same reasons that were discussed for the increase in the absorbance of UV-Visible spectra.
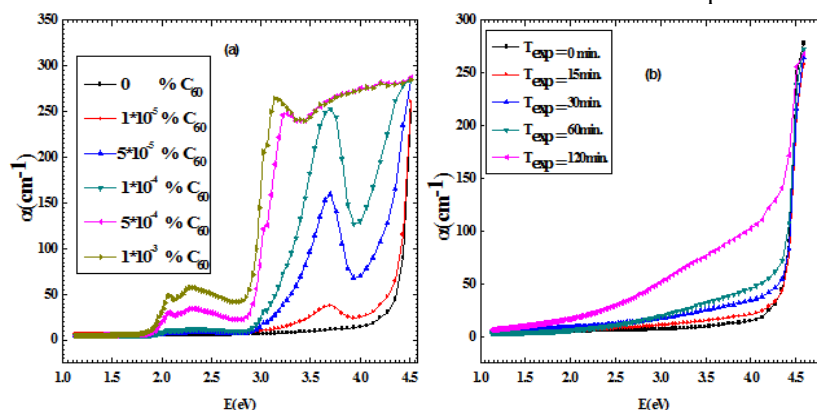

Figure (3): The absorption coefficient as a function of the photon energy, (a) for PS films filled with different concentrations of C_{60} and (b) for pristine and plasma treated PS films for different durations.

Figure (4) displays the C_{60} content dependence of E_g and the results are listed in table 1. It is clear that the values of indirect optical energy band gap are decreased with increasing C_{60} content in PS films. Such behavior is in accordance with those reported previously [21, 22]. The decrease in the optical energy band gap with filling may be explained by increasing the incorporation of C_{60} contents in the polymeric host matrix. This

introduces additional absorption bands in the UV and visible regions of the optical spectra as shown in UV-Visible spectra (fig. 2a).

The values of optical energy band gap for pristine and plasma treated samples are tabulated in Table II. As can be seen the values of indirect optical energy band gap are not changed with the increase in the exposure time. This may be due to low power of the applied plasma [23].
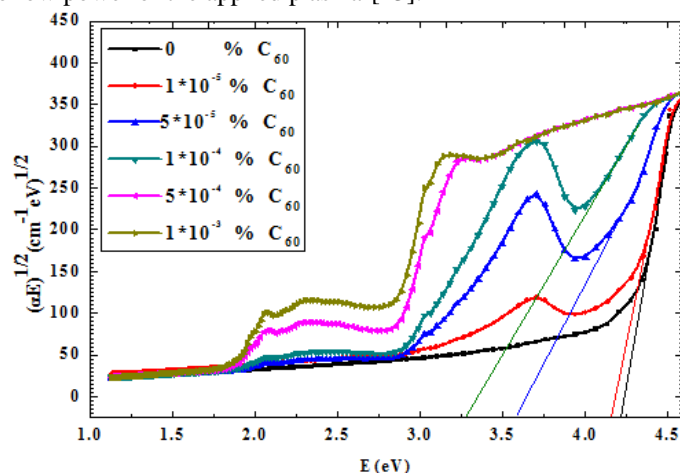

Figure (4): The dependence of $(\alpha \, h\nu)^{1/2}$ on the photon energy for PS films filled with different concentrations of C_{60}.

Table I: Displays the C_{60} content dependence of E_g values of indirect transition.

C_{60} Concentration (mol. %)	E_g (indirect) (eV)
0	4.22
1×10^{-5}	4.14
5×10^{-5}	3.56
1×10^{-4}	3.26
5×10^{-4}	2.42
1×10^{-3}	2.38

Table II: Displays the values of optical energy band gaps for pristine and plasma treated samples.

Exposure Time (min.)	E_g (indirect) (eV)
0	4.22
15	4.22
30	4.22
60	4.22
120	4.22

3. The Refractive index (n)

The index of refraction of a material is the ratio of the velocity of the light in vacuum to that of the specimen. The refractive index of the films was calculated by the following equation [24]:

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (3)$$

where R is the reflectance and k is the extinction coefficient.

The extinction coefficient (k) describes the properties of the material with respect to light of a given wavelength and indicates the absorption changes when the electromagnetic wave propagates through the material. The extinction coefficient (k) was calculated using the following equation [23]:

$$k = \alpha \lambda / 4\pi \qquad (4)$$

where λ is the wavelength and α is the absorption coefficient.

Figure (5.a) shows the refractive index as function of wavelength for pure and doped PS with C_{60} of different concentrations. In this figure, (n) exhibits to decrease with λ for pure and doped films. Also the values of (n) showed increase with increasing C_{60} concentrations. Moreover, (n) increases from 1.45 to 2.45 at $\lambda = 625$

nm (when C_{60} concentration increases from (0 to 1×10^{-3}) mol. %. This is a result of increasing the number of atomic refractions due to the increase of the C_{60} concentrations in the films.

Figure (5.b) shows the refractive index as function of wavelength for pristine and nitrogen plasma treated PS films at different durations. It is clear from this figure, that the refractive index for pristine and nitrogen plasma treated PS films decrease with increasing λ. Also the values of (n) showed increase with the increase in the exposure time. This increase in refractive index with increasing the exposure time may be attributed the etching action of the plasma which increase roughness of film surface.
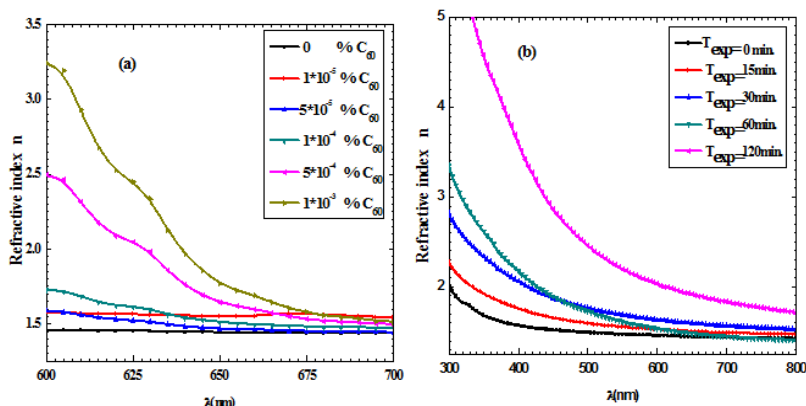

Figure (5): The refractive index as a function of wavelength, (a) for PS films filled with different concentrations of C_{60} and (b) for pristine and plasma treated PS films for different durations.

Figure (6.a) shows the variations of (k) with λ of pure and doped PS with C_{60}. (k) shows an increasing with increasing C_{60} concentration. This increase in the values of (k) can be ascribed to high absorption coefficient [25]. This result indicates that the dopant atoms of C_{60} will modify the structure of PS. C_{60} dopant has increased the absorbance in the visible region.
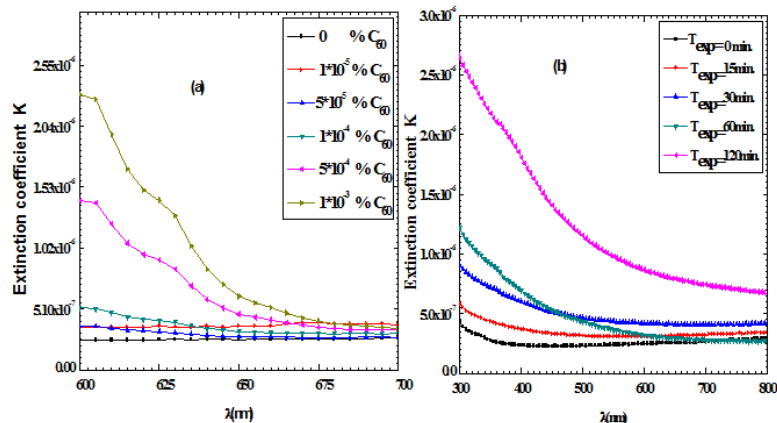

Figure (6): The extinction coefficient as a function of wavelength, (a) for PS films filled with different concentrations of C_{60} and (b) for pristine and plasma treated PS films for different durations.

Figure (6.b) shows (k) as function of wavelength for pristine and nitrogen plasma treated PS films at different durations. It is clear from this figure, that the values of the extinction coefficient showed increase with the increase in the exposure time. The increase in extinction coefficient with increasing the exposure time is attributed to same reason that was discussed for the increase in the absorbance of UV-Visible spectra.

IV.   Complex dielectric function

The complex dielectric constant is defined as the response of the material toward the incident electromagnetic field. The complex dielectric constant of compound ε is divided into two parts real ε_r, and imaginary ε_i. The real and imaginary parts of dielectric constant (ε_r and ε_i) were calculated by the following equations [26, 27]:

$$\varepsilon_r = n^2 - k^2,$$
$$\varepsilon_i = 2nk \qquad (5)$$

Figures (7.a and b) show the real and imaginary parts of dielectric constant (ε_r and ε_i) as function of wavelength for pure and doped PS with C_{60} of different concentrations. From Figures 7a and b it is seen that the real and imaginary parts of the dielectric constant decrease with increasing the wavelength. The real part of the dielectric constant is higher than the imaginary part.
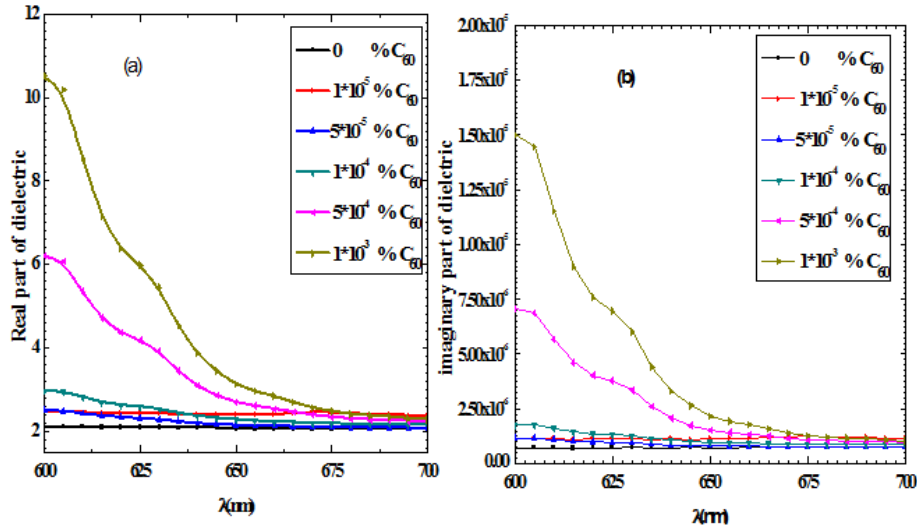

Figure (7): The real part (ε_r) (a) and imaginary part (ε_i) (b) of dielectric constant as a function of wavelength for PS films filled with different concentrations of C_{60}.

Figures (8.a and b) show the real and imaginary parts of dielectric constant (ε_r and ε_i) as function of wavelength for pristine and nitrogen plasma treated PS films at different durations. It is clear from these figures, that (ε_r and ε_i) for pristine and nitrogen plasma treated PS films decrease with increasing λ. Also the values of (ε_r and ε_i) showed increase with the increase in the exposure time.

It is concluded that the variation of ε_r mainly depends on n^2 because of small values of k^2, while ε_i mainly depends on the k values which are related to the variation of absorption coefficients.
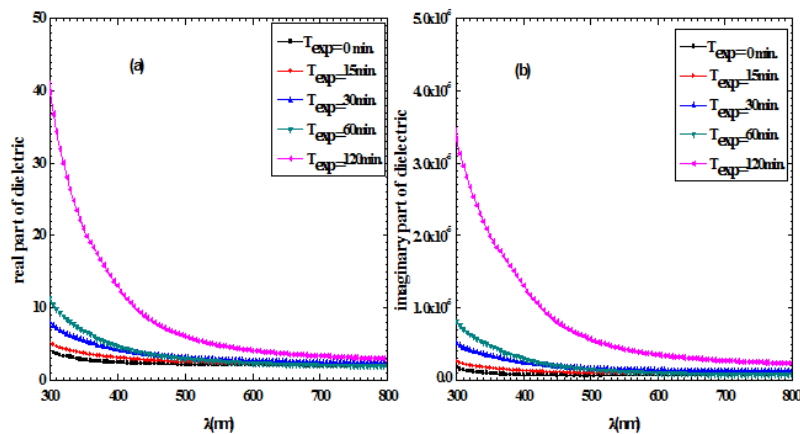

Figure (8): The real part (ε_r) (a) and imaginary part (ε_i) (b) of dielectric constant as a function of wavelength for pristine and plasma treated PS films for different durations.

V. Conclusion

The present study revealed the significant effects of varying Fullerene content and plasma exposure on optical properties of the polystyrene films. From the experimental results we can conclude that:
(1) The values of indirect optical energy band gap are decreased with the increase in the Fullerene content. Meanwhile their values are not changed with the increase in the plasma exposure time.
(2) The Refractive index (n) increases by increasing both Fullerene content and plasma exposure time.

(3) The real and imaginary parts of the dielectric constant were showed clear changes with Fullerene addition and plasma exposure.

References

[1]   Alwan T J, Malaysian Polymer Journal, 2010, 5, 204.
[2]   Deshmukh S H, Burghat D K, Shilaska S N and Deshmukh P T, Indian Journal of Pure & Applied Physics ,2008, 46, 344.
[3]   El-Khodary A, Physica B: Condensed Matter, 2010, 405, 4301.
[4]   Cheung R KY Fu, I T L, Mei Y F, Shek C H, Siu G G, Chu P K, Yang W M, Leng Y X, Huang Y X, Tian X B and Yang S Q, Nuclear Instruments and Methods in Physics Research, 2005, 237, 417.
[5]   Kaczmarek Hand Chaberska H, Applied Surface Science, 2006, 252, 8185.
[6]   Ozdemir M, Yurteri C U and Sadikoglu H, Critical Reviews in Food Science and Nutrition, 1999, 39, 457.
[7]   Zhang W, Chu P K, Zhang J and Jiang Z, Applied Surface Science, 2006, 252, 7884.
[8]   Saravanan S, Anantharaman M R, Venkatachalam S, Avasthi D K, Vacuum, 2007, 82, 56.
[9]   Sharma T, Aggarwal S, Kumar S, Mittal VK, Kalsi PC and Manchanda V K, Journal of Materials Science, 2007, 42, 1127.
[10]   Saeed A A, Ph.D. Thesis, Physics Department, College of Science, Baghdad University, Baghdad, Iraq, (2000).
[11]   Kim JW, Kim KJ, Park S, Jeong K U and Lee M H, Bulletin of the Korean Chemical Society , 2012, 33, 2966.
[12]   Chakraborty C, Malik S, Guenet J M, Macromolecular Symposia, 2011, 303, 56.
[13]   Zhogova K B, Davydov I A, Punin V T, Troitskii B B and Domvachiev G A European Polymer Journal, 2005, 41, 1260.
[14]   Mortazavi S H, Ghoranneviss M and Faryadras S, Journal of Fusion Energy, 2011.
[15]   De Geyter N, Morent R, Leys C, Gengember L and Payen E, Surface & Coatings Technology, 2007, 201,7066,7075.
[16]   Kitova S, Minchev M, and Danev G, Journal of Optoelectronics and Advanced materials, 2005, 7, 249,252.
[17]   Jaleha B, Shayegani Madad M, Farshchi Tabrizi M, Habibi S, Golbedaghi R and Keymanesh MR, Journal of the Iranian Chemical Society ,2011, Soc 8,S161,S168.
[18]   Kumar A, Podhorodecki A, Misiewicz J, Avasthi D K and Pivin J C, Journal of Applied Physics, 2009, 105,024314.
[19]   Tauc J, Amorphous and Liquid Semiconductors, Plenum Press, New York, 1979, pp159
[20]   Mott N and Davis E, Electronic Process in Non-Crystalline Materials, 2nd Edition, University Press, Oxford, 1979.
[21]   Adamopoulos G, Heiser T, Giovanella U, Ould-Saad S, vande Wetering KI, Brochon C, Zorba T, Paraskevopoulos KM and Hadziioannou G, Thin Solid Films, 2006, 511 , 371.
[22]   Ahmed R M and El-Bashir S M, International Journal of Photoenergy, 2011, 801409 ,1.
[23]   Dorranian D, Abedini Z, Hojabri A, Ghoranneviss M, Journal of Non-Oxide Glasses, 2009, 1,217 , 229.
[24]   Dragoman D and Dragoman M, Optical characterization of solids. 1st ed, Springer, Berlin, 2002.
[25]   Hasan B A, Journal of Education College, 2005, 5 (3), 449.
[26]   Seraphin B O, Optical Properties of Solid New Developments, Company, American Elsevier Publishing, New York, 1976.
[27]   Ghanipour M and Dorranian D, Journal of Nanomaterials, 2013,1,10.