Advances in Physics Theories and Applications
ISSN 2224-719X (Paper) ISSN 2225-0638 (Online)
Vol.53, 2016

The surface and volume energy loss of Safranin O thin film prepared by spin coating method

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Abstract

Optical properties of safranin O doped polyvinyle pyrolidone (PVP) thin film prepared by spin coating method on glass substrate at room temperature was investigated .The analysis of the absorption data revealed existence of indirect transition in the optical band gap. The optical constants such as absorbance, transmission, reflection, refractive index, extinction coefficient, real and imaginary parts of dielectric constants, optical and electrical conductivity, dispersion energy E_d and oscillation energy E_0 and the surface, volume energy loss function and electronic interband transition strength have been investigated at film thickness 10 µm over spectral of (300-800) nm.

Keywords: Polymer, Energy gap, Optical constant

1. Introduction

The study of the optical absorption spectra in the solids provides essential information about the band structure and the energy gap in the crystalline and non-crystalline materials [Deshmukh *et al* 2008]. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations while the higher energy part of the spectrum gives knowledge about the electronic states in atom [Abdel Kader *et al* 2004]. Refractive index is an important optical parameter for the design of prisms, windows and optical fibres [Ma *et al* 1993]. The refractive indices of optical materials are considerable importance for applications in integrated optic devices such as switches [Neuman *et al* 1979]. Semi conducting polymeric mixtures take large area in different applications such as heating ,prevention of static electricity accumulation such as preventing dust attraction on electronic device cabinets and electrodes and used for electromagnetic interference shielding of electronic devices and prevention of static electricity hazards in the handling of electronic chips and explosives [Narkis *et al* 1978 ; Carl *et al* 1996]. Many applications require the materials in thin form microscopic defect, which control surface smoothens and coating homogeneity, contribute to the scattering of light and associated degradation of the optical response [Tang 2007]. Similarly, structural disturbance at the atomic level can alter the optical properties through modifications to the complex refractive index of the material [Zhokhavets *et al* 2004].

In this study the Optical properties of safranin O doped polyvinyle pyrolidone (PVP) thin film prepared by spin coating method on glass substrate at room temperature was investigated. The optical constants such as absorbance, transmission, reflection, refractive index, extinction coefficient, real and imaginary parts of dielectric constants, optical and electrical conductivity, dispersion energy E_d and oscillation energy E_0, relaxation time τ and the surface, volume energy loss function and electronic interband transition strength have been investigated

2. Experimental Part

1.5 M (0.315) gm of polymer PVP is first dissolved in Dimethyle Formamide (DMF) with stirred at room temperature for 2 to 4 h 0.2 M (0.351) gm of safranin O dissolved in DMF with stirred at room temperature for 1h, then the dopant was added to the polymer with ratios 30%. The stirred solution was deposited on the substrate cited horizontally to get homogeneous thickness by spin coating method. The important thing before the deposition of films is the careful cleaning of the substrate which cleaned by immersing them in cleaning solution Consists of 10% of potassium dichromate with sulphuric acid for 1h
in ultrasonic path then washed with distilled water and ethanol solvent and acetone solvent. Finally the substrate was dried before use.

2.1 IR Spectra

safranin O doped PVP thin film was identified by FT-IR spectroscopy in the range (4000-600) cm^{-1} as shown in the Fig.1. It is clear from the figure that O-H bending groups appeared at 1292 cm^{-1}. The band corresponding to -N= N was recorded around 1494 cm^{-1}. The C= C of the aromatic ring appeared around 1651 cm^{-1}. The C= O gives band at 1658 $cm^{-1}$and C- H aliphatic gives band at 2953 cm^{-1} .

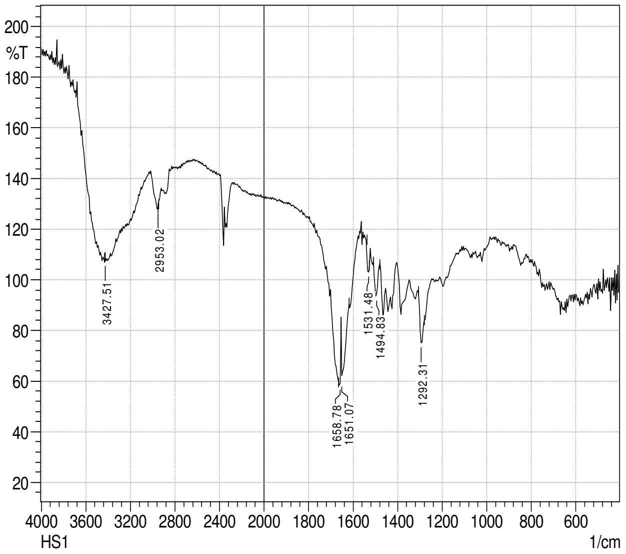

Figure1. IR spectrum of polymer thin film

3. Results and Discussion

A measurement of the spectral absorption, A, and transmittance, T, were recorded using UV-Vis. spectroscopy type CE 3055 in the wavelength (300-800) nm. Fig. 2 shows the relation between absorbance of the film and wavelength. It is clear from the figure that the peak in the curve was appeared at wavelength, λ=610 nm, which represents the transition $\pi \rightarrow \pi^*$.

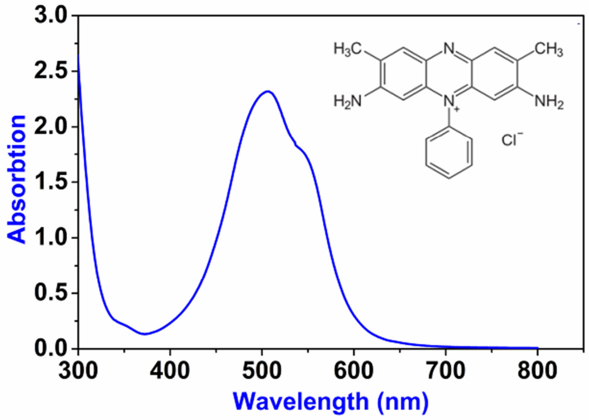

Figure 2. UV–Vis absorption spectrum of thin film. *Inset* shows the chemical structure of safranin O.

The transmittance spectrum in the UV-visible region showed that T was decreased from 60 % to 0 % with increasing of λ from 300-550 nm. It is clear from the figure that is no light transmitted from the film in the wavelength between 550-690 nm, that mean all the light was absorbed by the polymer PVP doped with safranin. At the longer wavelengths (λ >700nm) the polymer became transparent and no light was scattered or absorbed (i.e R+T=1).

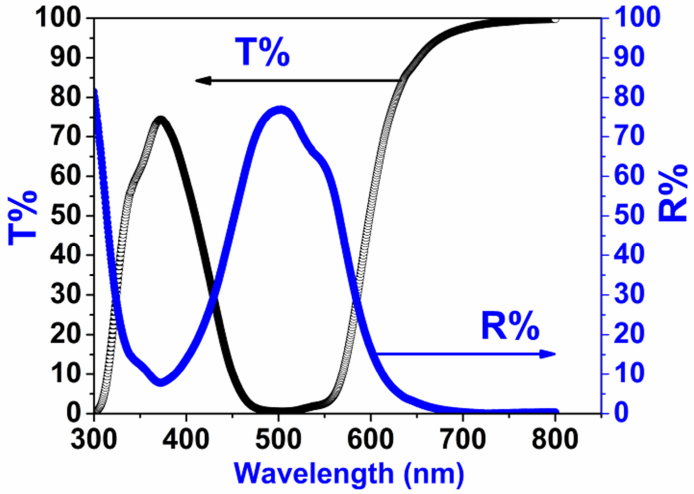

Figure 3. Transmission and Reflectance as a function of wavelength.

The transmission and reflectance spectra of the thin film have been shown in the figure 3. It is clear from the figure that a dramatic increase of R with increasing λ from 300-600 nm and the most reflectance occurs at wavelength around λ=600 nm then R was decreased as λ increased at the range 625-800 nm. The absorption coefficient, α, can be calculated from observed absorbance data using Beer Lamberts' formula (α=2.303A/d) where A is the optical absorbance and d is the thickness of the film [Philip 1985]. Fig. 4 shows the relation between absorption coefficient, α, and photon energy one can observed from the figure that α was increased at low photon energy between 1.8-2.5 eV, moreover one can recognize a peak around 2.5 eV, followed by rapped decrease between 2.5-3.2 eV, then the curve was rocked up at high energies.

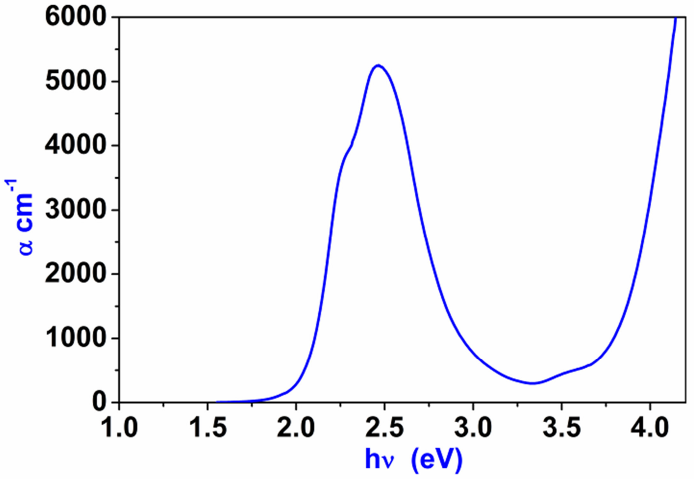

Figure 4. Absorption coefficient as a function of hν

The extinction coefficient can be obtained from the relation ($k = \alpha\lambda / 4\pi$), where λ is the wavelength of the light [Pankove 1971]. The refractive index n can be described by the following relation [Islam *et al* 2009]:

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

Fig.5 shows the dependence of refractive index ,n, and the extinction coefficient k, on the wavelength, it is clear from the figures that the region 300-600 nm the values of n, and k, increases with increasing of wavelength while these values were decreased as wavelength increased in the region (610-800) nm, and the peak occurs around λ=610 nm.

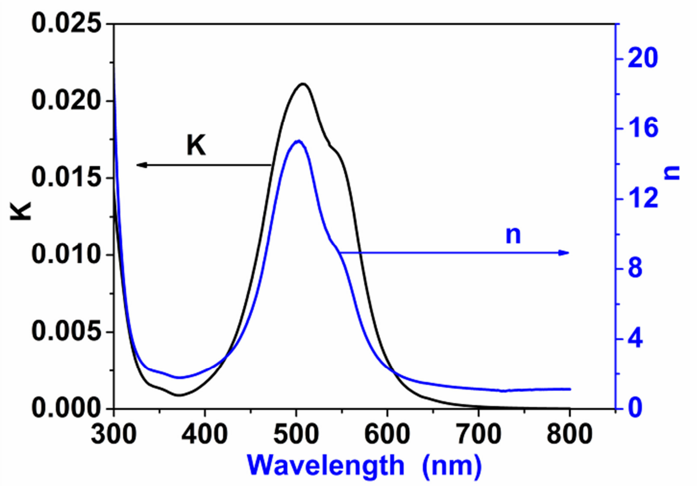

Figure 5. Extinction coefficient and refractive index as a function of wavelength

The absorption coefficient near fundamental absorption edge in both of crystalline and amorphous semiconductors is dependent on the photon energy. For direct transitions the absorption coefficient was taken on the following more general form as a function of photon energy [Tsidilkovsk 1982].

$$\alpha h\nu = A(\alpha h\nu - E_g)^n \qquad 2$$

and for indirect transition

$$\alpha h\nu = B(\alpha h\nu - E_g)^n \qquad 3$$

where υ is the frequency of the incident photon, n is the number which characterizes the optical processes n has the value 1/2 for the direct allowed transition, 3/2 for a forbidden direct allowed transition and 2 for the indirect allowed transition, A and B are constants, and E_g is the optical energy gap. when the straight portion of the graph of $(\alpha h\upsilon)^n$ against hυ is extrapolated to α = 0 the intercept gives the transition band gap [Ezema 2005]. Fig. 6 shows the plot of $(\alpha h\upsilon)^{1/2}$ versus hυ for indirect transition. The indirect energy gap E_g and phonon energy Ep were determined from this curve and given with values of 1.98 eV and 1.74 eV respectively

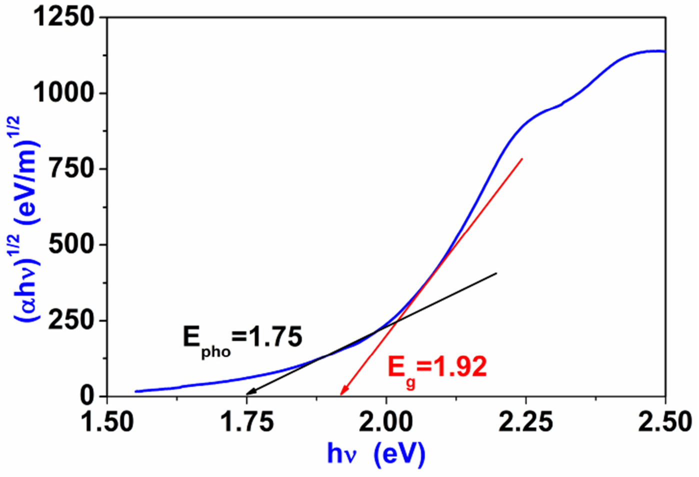

Figure 6. Plot $(\alpha h\upsilon)^{1/2}$ as a function of hν

The real and imaginary parts of dielectric constants were calculated by using equations [Jeon *et al* 2010; Jappor *et al* 2013]:

$$\varepsilon_r = n^2 - k_2 \qquad 4$$

$$\varepsilon_i = 2nk \qquad 5$$

The dependences of ε_r and ε_i on the photon energy as shown in Fig.7. The real and imaginary parts look like the same pattern but the values of the real part are higher than the imaginary part. The relation between the dielectric constant and the photon energy indicates that some interactions between photons and electrons in the films are produced in this energy range. These interactions are observed on the shapes of the real and imaginary parts of the dielectric constant and they cause the formation of peaks in the dielectric spectra which depends on the material type. There was a high peak around 2.5 eV for thin film. The real and imaginary parts of dielectric constant were increased sharply in the high photon energy greater than 3.8 eV, similar behaviour was observed by others [Hussan *et al* 2012].

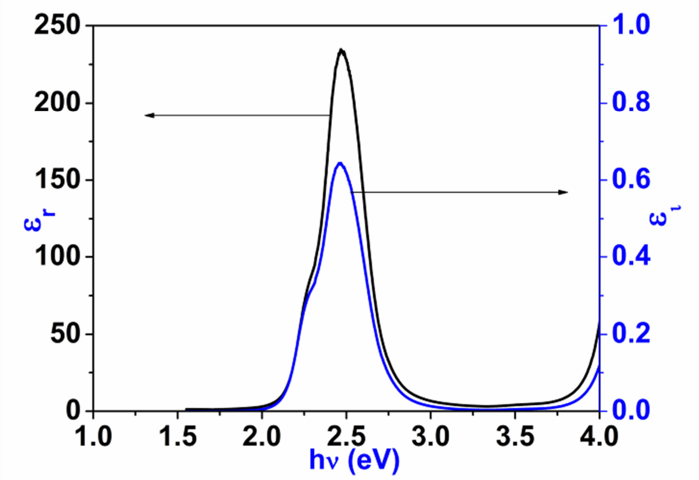

Figure 7. Real and imaginary part of dielectric constant as a function of photon energy.

The dissipation factor tanδ is a measure of loss-rate of power of a mechanical mode, such as an oscillation, in a dissipative system. For example, electric power is lost in all dielectric materials, usually in the form of heat. The dissipation factor tanδ given by [Alla 2012].

$$\tan\delta = \frac{\varepsilon_i}{\varepsilon_r} \qquad 6$$

The variation of dissipation factor of the investigated films with frequency is shown in Fig.8. It is found that the dissipation factor increases with increasing frequency in the absorption region, then there is fluctuation decrease in dissipation factor increasing of frequency.

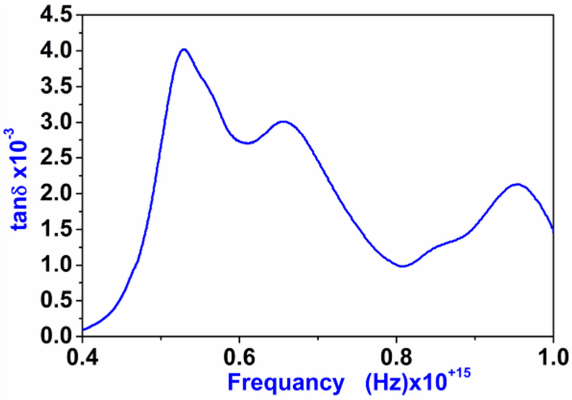

Figure 8. Dependence of dissipation factor tan δ on the Frequency.

Fig. 9 shows the dielectric relaxation time τ as a function of photon energy hν , it is clear from the figure there is a sharp decrease of τ with increasing of photon energy.

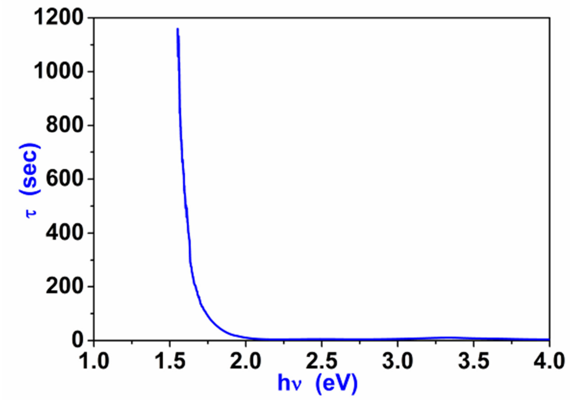

Figure 9. Dielectric relaxation time with photon energy

4. Optical and Electrical Conductivity

The optical and electrical conductivity σ_{opt}, σ_e were calculated depend on absorption coefficient α values as follow [Arquez *et al* 1999 ;Yakuphanoglu *et al* 2005; Hassan 2015]:

$$\sigma_{opt} = \alpha nc/4\pi \quad 7$$

$$\sigma_e = 2\lambda\sigma_{opt}/\alpha \quad 8$$

where c is the velocity of light, α the absorption coefficient and n is a refractive index .

Fig.10 shows the variation of optical conductivity σ_{opt} and electrical conductivity, σ_e as a function of photon energy $h\nu$, one can conclude that the metal inclusion has greatly reduced the dielectric constant and increased the optical conductivity and the peak was recorded around hν=2.5 eV. The increased of optical conductivity at high photon energies is due to the high absorbance of sample thin films and also may be due to the electron excited by photon energy which also caused by hopping of the charge carriers between the localization state [Abdulameer 2011].

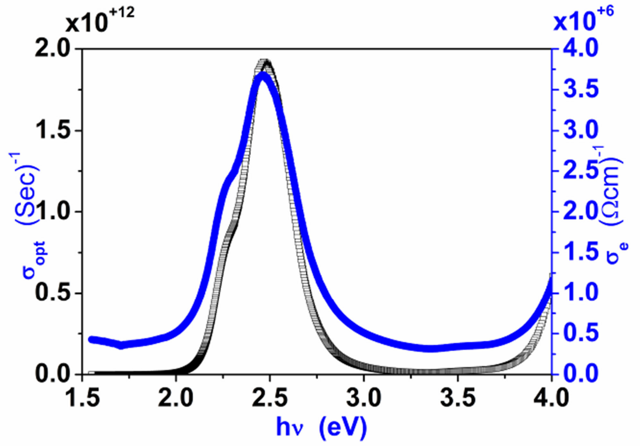

Figure 10. Optical and electrical conductivity as a function of photon energy

Fig.11 shows the variation of lnα as a function of photon energy and the relation given by [Bakr *et al* 2004]:

$$\alpha = \alpha_{\circ} \exp(h\nu / E_u) \quad 9$$

where Eu is the Urbarch energy, it can be evaluated by the reciprocal of the slope yields the magnitude of the Eu and the value was found to be 100 meV.

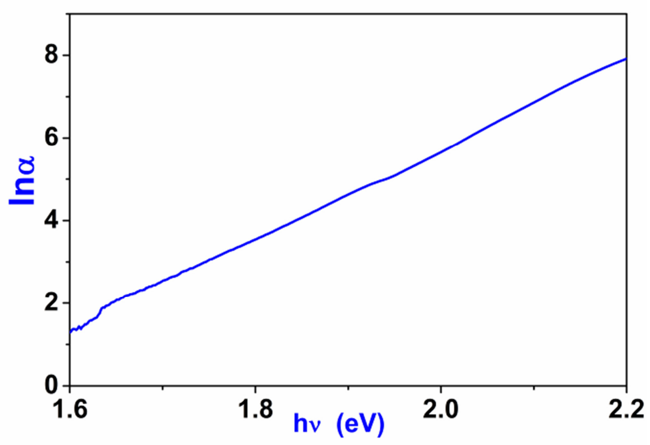

Figure 11. Ln(α) as a function of photon energy

The relation between real part of dielectric constant ε_r and the square of wavelength λ^2 is given by [Osuwa *et al* 2010]:

$$\varepsilon_r = \varepsilon_\infty(1) - B\lambda^2 \qquad 10$$

where $B = e^2N/4\pi^2c^2\varepsilon_0 m^*$, ε_∞ is the lattice dielectric constant or (the high frequency dielectric constant), N is the free charge carrier concentration, ε_0 is the permittivity of free space ($\approx 8.854\times10-12$ F/m), m^* the effective mass of the charge carrier and c the velocity of light. The real part of dielectric constants $\varepsilon_r = n^2$ was calculated at different values of λ. Then, the obtained values of ε_r are plotted as a function of λ^2 as shown in Fig.12. It can observe that the dependence of ε_r on λ^2 is linear at longer wavelengths. The extrapolating the linear part of this dependence to zero wavelength gives the value of $\varepsilon_\infty(1) = 2$ and from the slopes of these lines, values of N/m^* were calculated according to the Equ.10 of the constant B. The obtained value of N/m^* was 1.83×10^{51} $m^{-3}kg$.

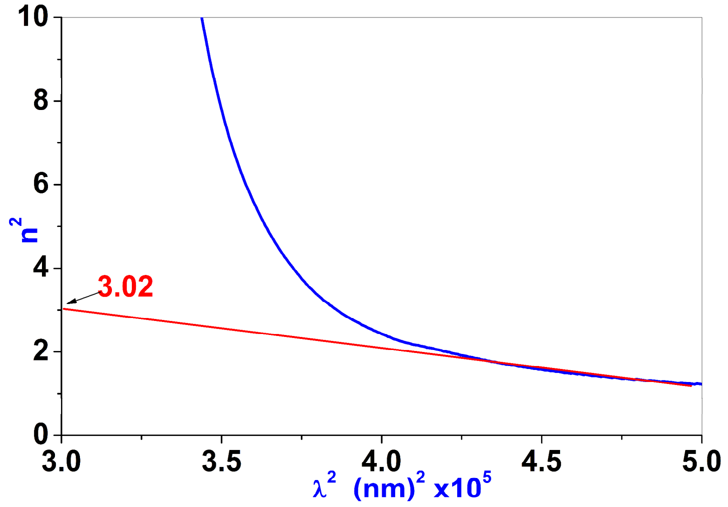

Figure 12. Plot of n^2 as a function of λ^2

Based on the single-oscillator model, Wemple Di-Domenico [Wemple *et al* 1971; Badran *et al* 2011] is a semi-empirical dispersion relation to for determine the refractive index n at photon energy *hν* can be written in the following relation:

$$n^2 = 1 + \frac{E_d E_\circ}{E_\circ^2 - (h\nu)^2} \qquad 11$$

Where $h\nu$ is the photon energy, h is the blank constant , E_0 is the oscillator energy, and E_d is the oscillator strength or dispersion energy. A plot of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ was illustrated in Fig.13. The values of E_d and E_o were obtained from the slope $(E_0E_d)^{-1}$ and the intercept (E_0/E_d) with the vertical axis. Extrapolating the linear part towards long wavelengths, the point of interception with the ordinate at $(h\nu)^2 = 0$ yields the value of the dielectric constant(ε_∞) at higher wavelength. The static refractive index, $n_\circ$ can be calculated using the relation ($n^2= E_d / E_o)+1$. The oscillator strength parameter, F, can be calculated using the following relation:

$$F = E_\circ E_d \qquad 12$$

The values of E_o, E_d ,F and ε_∞ are given in the table 1.

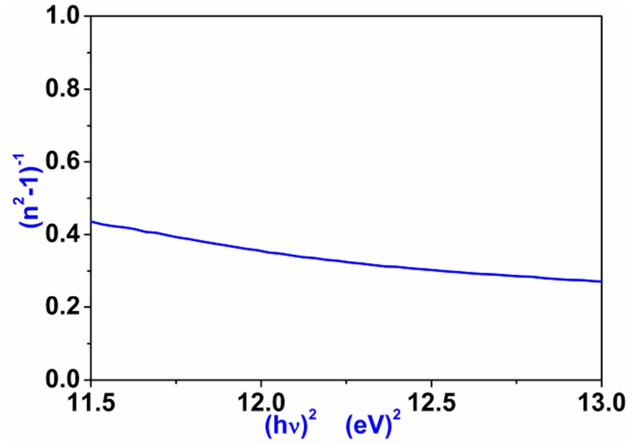

Figure 13. Plot of $(n^2-1)^{-1}$ as a function of $(h\nu)^2$

The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the relationship.

$$E_\circ^2 = \frac{M_{-1}}{M_{-3}} \text{ and } E_d^2 - \frac{M_{-1}^3}{M_{-3}} \qquad 13$$

The M_{-1} and M_{-3} moments were calculated using the above equations and are given in table 1.The properties of the investigated safranin O doped PVP thin film could be treated as a single oscillator at wave length λ_o at high frequency. The high frequency dielectric constant can be calculated by applying the following simple classical dispersion relation [Zeme *et al* 1965]:

$$\frac{n_\circ^2-1}{n^2-1} = 1-\left(\frac{\lambda_\circ}{\lambda}\right)^2 \qquad 14$$

where $n_\circ$ is the refractive index at infinite wavelength $\lambda_\circ$, n the refractive index and λ the wavelength of incident photon. Plotting $(n^2-1)^{-1}$ against λ^{-2} which showed linear part, was shown in the Fig.14

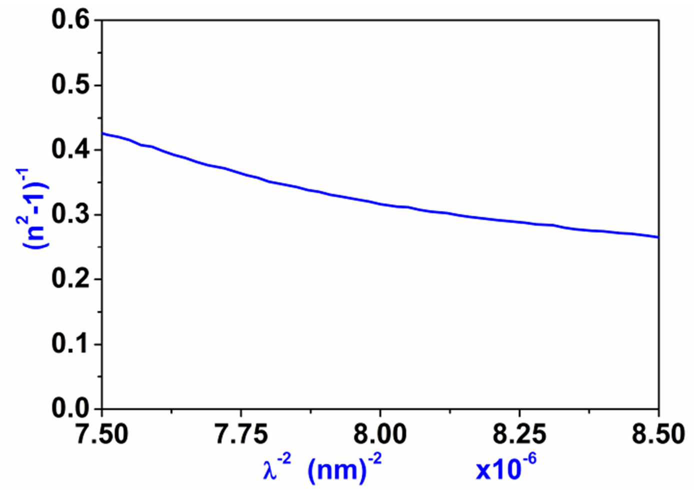

Figure 14 Plot of $(n^2\text{-}1)^{-1}$ as a function of λ^{-2}

The intersection with $(n^2\text{-}1)^{-1}$ axis is $(n_o^2\text{-}1)^{-1}$ and hence n_o^2 at λo equal to $\varepsilon_\infty(2)$ (high frequency dielectric constant). The simple classical dispersion relation can be written as [El-Korashy *et al* 2003]:

$$n^2 - 1 = \frac{S_o \lambda_o^2}{1-(\lambda^2 / \lambda_o^2)} \qquad 15$$

where S_o is the average oscillator strength which is equal to:

$$S_o = \frac{n_o^2 - 1}{\lambda_o^2} \qquad 16$$

The obtained values of S_o and λ_o are given in table 1.

Table 1: The optical parameters of thin film

E_g (eV)	E_{phonon} (eV)	E_u (meV)	M_{-1}	M_{-3} $(eV)^2$	λ_0 (nm)
1.92	1.72	100	2.27	0.72	606
E_0 (eV)	E_d (eV)	F	n_0	$N/m^*(m^{-3}Kg)$	S_0 (m^{-2})
1.77	4.03	7.13	1.91	$1.83x10^{51}$	$7.14x10^{12}$
$\varepsilon_\infty(1) = n^2$	$\varepsilon_\infty(2) = n_0^2$	VELF	SELF	ReJ_{cv} (eV)	ImJ_{cv} (eV)
3.02	3.63	$5.3x10^{-4}$	$3.4x10^{-4}$	$1.61x10^{-5}$	$5.89x10^{-3}$

5. Interband Transition Strength

The complex interband transition strength can be calculated from the real and imaginary parts of the dielectric constant as the following relation [Loughin *et al* 1996]:

$$J_{cv} = J_{cv1} + J_{cv2} = \frac{m_o^2 4\pi^2}{e^2 h^2}\frac{(h\nu)^2}{2}(\varepsilon_r + i\varepsilon_i) \qquad 17$$

where J_{cv1} and J_{cv2} are the real and imaginary part of interband transition strength, e is the charge of electron, m_o is the mass of the electron, the value of pre-factor $4\pi^2 m_o^2 / e^2 h^2 \approx 8.289 \times 10^{-6}$ g cm^{-3} eV^{-2}. It is clear from Equ.17 that the real part of interband transition strength J_{cv1} is proportional to the imaginary part of the dielectric function J_{cv2} is proportional to the real part of the dielectric function. Fig. 15 illustrate the relation between J_{cv1}, J_{cv2} and photon energy respectively. It is clear from the figures that is a dramatic increase in the interband transition strength J_{cv} with increasing of photon energy more than 4eV because the high absorption happens which increases the excitation of the electrons, in addition J_{cv} has significant peak around the photon energy 2.5 eV.

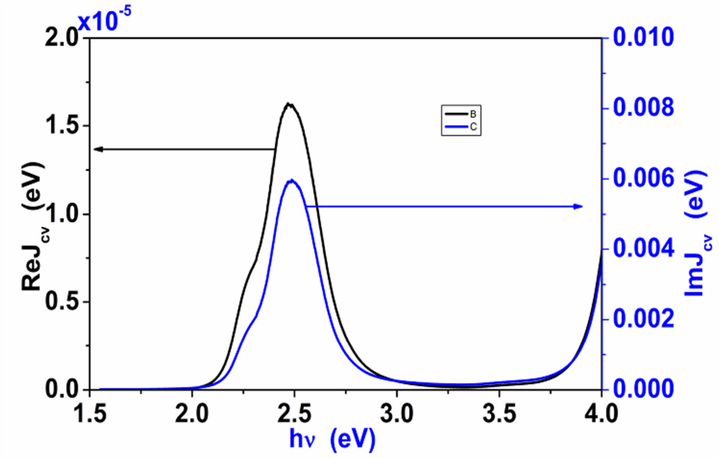

Figure 15. Real and imaginary part of interband transition strength as a function of photon energy.

6. Surface and Volume Energy Loss Function

The surface and volume energy loss functions, *SELF* and *VELF* respectively can be calculating depend on real and imaginary part of dielectric constant as following relations [Ritchie 1957; El-Nahass *et al* 200; Maged 2004]:

$$Surface - Im\left(\frac{1}{1+\varepsilon}\right) = \frac{\varepsilon_i}{(\varepsilon_r+1)^2+\varepsilon_2^2}$$

$$Volume - Im\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon_i}{(\varepsilon_r+\varepsilon_i)^2} \qquad 18$$

It is clear from the Fig. 16 that the peak of volume energy loss function is greater than the peak of surface energy loss function, it is also clear that the peak of *SELF* and *VELF* occurs at 2.042 and 2.084 eV respectively.

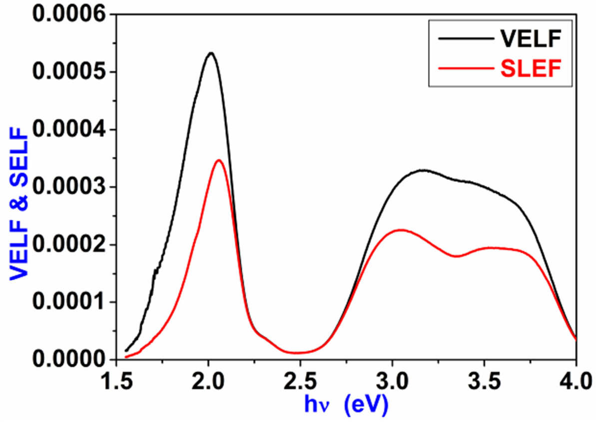

Figure 16. Surface and Volume energy loss as a function of photon energy

Conclusions

In the present investigation, the Optical properties of safranin O doped polyvinyle pyrolidone (PVP) thin film prepared by spin coating method on glass substrate at room temperature were calculated to obtain the optical constants such as absorbance, transmission, reflection, refractive index, long wavelength refractive index n_∞, extinction coefficient, real and imaginary parts of dielectric constants , optical and electrical conductivity ,dispersion energy E_d and oscillation energy $E_\circ$, the oscillator length strength $S_\circ$, the optical moments M_{-1}ans M_{-3}, relaxation time, τ and the surface, volume energy loss function and electronic interband transition strength. The type of optical transition that responsible for optical absorption was indirect transition with energy gap E_g =1.92 eV and phonon energy E_{phonon}=1.72 eV. The dissipation factor $\tan\delta$ and optical conductivity σ_{opt} as well as electrical conductivity σ_e were increased with photon energy.

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