Influence of Thickness on Dispersion Parameters of Silver Nitrate Doped Poly (Vinyl Alcohol)

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ABSTRACT
Poly (vinyl alcohol) doped AgNO₃ films with different thicknesses were prepared by casting method. The thickness of the prepared films were 10, 20, 30 and 40 µm. Absorption spectra have been recorded in order to study the effect of increasing thickness on some optical constants. This study reveals that the absorbance and absorption coefficient have affect by increasing the film thickness.

The single–oscillator parameters were determined and its value decreases from 4.67eV to 3.9eV by increasing thickness from 10 to 40µm. The optical energy gap decreased from 2.33 eV to 1.95 eV.

INTRODUCTION
Polymeric materials have attracted scientific and technological researchers because of their widespread applications. This is mainly due to the light weight, good mechanical strength, and optical properties, which make them multifunctional materials. Moreover, PVA is traditionally considered as an excellent host material for composites [1-5]. Recently, polymer blends and composites have been subjects of interest for both theoretical and experimental studies because of certain physical and chemical properties needed for specific applications that may be obtained by blending [6]. It has been observed that polymer blending has a significant effect on the physical properties, including optical, thermal,
and electrical properties. These changes in physical properties depend on the chemical nature of the guest material and the way in which it interacts with the host polymer. The doping of transition metals to polymeric networks is of considerable interest for scientific and technological purposes [7-9]. The nature of interaction between metal ions and polymer molecules is usually approached by different techniques. In fact, PVA:Ag is one of many compounds used in our laboratory to investigate the effect of various dopants on the physical properties. Hence, in this work, it is planned to study the effect of thickness on some characteristics, including the energy gap and band tail of Ag-doped poly (vinyl alcohol) (PVA) films.

**MATERIALS AND METHODS**

Poly (vinyl alcohol) with molecular weight 10000 g/mol, supplied by (BDH chemicals, England) with high purity were used as basic polymeric materials in this work., the aqueous solution of this polymer were prepared by dissolving PVA with different weight in a mixed of deionized water and ethanol and thoroughly stirred using a magnetic stirrer for about one hour at room temperature until PVA was completely soluble. AgNO$_3$ solution was prepared by dissolving the salt in redistilled water. 5% concentrated of AgNO$_3$ were mixed with PVA matrix. The solution was poured into flat glass plate dishes. Homogenous films were obtained after drying in an oven for 24 hours at 313K. The thickness of the produced films was in the range of 10, 20, 30 and 40 µm. The absorbance and transmittance measurements were carried out using a Shimadzu UV/VIS-160A double bean spectrophotometer in the wavelength range (300-1100) nm.

**RESULTS AND DISCUSSION**

The absorbance spectra of the prepared films are shown in figures (1). Where we can use these spectra to determine optical band gap and optical constants of the films, we can see from this figure that the absorption edge has been slightly changed with the increasing of the film thickness.
The investigation of the spectrum of the absorption coefficient near the fundamental edge was calculated using the following relation\cite{10}:

\[ \alpha = \frac{2.303A}{d} \]  

(1)

Which provides us with valuable information about the energy band structure of the material and is shown in Fig. (2).

Fig. -1: Absorbance versus wavelength for the PVA:Ag films.

Fig. -2: Absorption coefficient versus wavelength.
E\text{g} \text{ values are given in Table 1. It is seen that } E\text{g} \text{ values change with the increasing of film thickness. The width of the localized states available in the optical band gap of the PVA:Ag films affects the optical band gap structure and optical transitions and it is called as Urbach tail, which is related directly to a similar exponential tail for the density of states of either one of the two band edges [10]. The Urbach tail of the films can be determined by the following relation [11]:}

\[
\alpha = \alpha_0 \exp \left( \frac{E}{E_u} \right) \quad \text{(1)}
\]

Where E is the photon energy, \( \alpha_0 \) is constant and \( E_u \) is the Urbach energy which refers the width of the exponential absorption edge. The obtained \( E_u \) values are given in Table 1. Urbach energy values of the films increase with increasing Ag content. The \( E_u \) values change inversely with optical band gaps of the films. The decrease in \( E_g \) is attributed to the creation of levels at the energy gap. This creation leads to a redistribution of states, from band to tail, thus allows for a greater number of possible bands to tail and tail to tail transitions [12]. As a result, both a decrease in the optical gap and a broadening of the Urbach tail occurred.

The refractive index is a significant factor in optical communication and in designing devices for spectral dispersion and the refractive index dispersion data below the interband absorption edge are important for technological applications of the optical materials, because, the dispersion energy is related to the optical transition strengths and optical conductivity. Thus, in order to analyze the refractive index dispersion of the films, we used the single-oscillator model, developed by DiDomenico and Wemple [13]. The refractive index is expressed as follows [13]:

\[
\frac{n^2 - 1}{n^2 + 2} = \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad \text{(2)}
\]

Where \( n \) is the refractive index, and \( E_o \) is the single-oscillator energy for electronic transitions and \( E_d \) is the dispersion energy which is a measure of the strength of interband optical transitions. This model describes the dielectric response for transitions below the optical gap. Plotting \( (n^2 - 1)^{-1} \) vs. \( (h\nu)^2 \) allows us to determine the oscillator parameters. \( E_o \) and \( E_d \) values were calculated from the slope and intercept on the vertical axis of \( (n^2 - 1)^{-1} \) vs. \( (h\nu)^2 \) plot, as shown in Fig. 3. The obtained \( E_o \) and \( E_d \) values suggest that the single-oscillator model is valid for PVA:Ag films. The \( E_o \) values were found to decreases with the increasing of the film thickness.
The $(n^2 - 1)^{-1}$ vs. $\lambda^{-2}$ was plotted to obtain the high frequency dielectric constant value of PVA:Ag films. The single-oscillator parameters $E_o$ and $E_d$ is related to the imaginary part of dielectric constant. The $\varepsilon_i$ parameter includes the desired response information about electronic and optical properties of the optical material. Thus, the fact that the moments of the $\varepsilon_i$ spectrum are determined is very important for the optical applications of the optical material studied.

Fig. -3: Variation in $(n^2 - 1)^{-1}$ as a function of $(hv)^2$ of PVA:Ag films

Fig. -4: Variation in $(n^2 - 1)^{-1}$ as a function of $(\lambda)^2$ of PVA:Ag films
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The $M_1$ and $M_3$ moments of the optical spectrum can be obtained from the following relations [14]:

$$E_o^2 = \frac{M_1}{M_3}, \quad E_d^2 = \frac{M_3}{M_1} \quad \ldots \ldots \ldots (3)$$

The values obtained for the dispersion parameters $E_o$, $E_d$, $M_1$ and $M_3$ are listed in Table (1). For the definition of the dependence of the refractive index $n$ on the light wavelength ($\lambda$), the single-term Sellmeier relation can be used [14]:

$$n^2(\lambda) - 1 = S_0, \lambda_0^2 / 1 - (\lambda_o/\lambda)^2 \quad \ldots \ldots (4)$$

Where $\lambda_0$ is the average oscillator position and $S_0$ is the average oscillator strength. The parameters $S_0$ and $\lambda_0$ in Eq. (4) can be obtained experimentally by plotting $(n^2 - 1)^{-1}$ vs. $\lambda^{-2}$. From Figure 4, the slope of the resulting straight line gives $1/S_0$, and the infinite-wavelength intercept gives $1/S_0 \lambda_0^2$.

<table>
<thead>
<tr>
<th>Thickness $\mu$m</th>
<th>$E_o$ (eV)</th>
<th>$E_d$ (eV)</th>
<th>$E_\infty$ (eV)</th>
<th>$n(\infty)$</th>
<th>$\varepsilon_\infty$</th>
<th>$S_0 \times 10^{13}$ m$^{-2}$</th>
<th>$\lambda$ nm</th>
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<tr>
<td>10</td>
<td>4.67</td>
<td>13.36</td>
<td>2.33</td>
<td>1.96</td>
<td>3.84</td>
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<td>13.60</td>
<td>2.04</td>
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<tr>
<td>40</td>
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<td>13.47</td>
<td>1.95</td>
<td>2.11</td>
<td>4.45</td>
<td>5.2</td>
<td>253</td>
</tr>
</tbody>
</table>

**Table -1 : The Optical Parameters**

We can conclude

The single–oscillator parameters were determined. The change in dispersion was investigated with the increasing of the film thickness. The optical energy gap decreased from 2.33 to 1.95 eV. Analysis revealed that the type of transition is allowed direct one.

REFERENCES


