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Determination the energy gap for polyvinyl alcohol films using copper acetate as additive

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Abstract

This study is to characterize the optical properties of PVA doped copper acetate salt. Thin films of PVA doped with copper acetate were prepared using solution casting method. The optical absorption spectra of synthesized thin films were recorded at room temperature over a wavelength range of ١٩٠-١١00 nm using UV-VIS double beam spectrometer. From the spectral data the optical constants such as energy band gap (both allowed and forbidden), Urbach's energy, refractive index and extinction coefficient were determined. The variation of energy band gap on doping is explained on the basis of incorporation of charge transfer complexes by the dopant. The optical studies have led to a variety of interesting thin film optical phenomenon, which have thrown considerable light on the band structure of solids and phonic states.

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تحديد فجوة الطاقة لبوليمر PVA بشكل غشاء رقيق والمطعم بملح خلات النحاس

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الخلاصة

هذه دراسة لخصائص الخواص البصرية لبوليمر **PVA** المطعم بملح خلات النحاس. حضرت الاغشية الرقيقة بطريقة الصب. وتم قياس اطياف الامتصاص لهذه الاغشية بدرجة حرارة الغرفة وبطول موجي من ١٩٠ الى ١١٠٠ نانومتر بواسطة جهاز قياس المطيافية ثم حسبت منها الثوابت البصرية مثل طاقة الفجوة للانتقالات المباشرة المسموحة والممنوعة وطاقة اورباخ ومعامل الانكسار ومعامل الاخماد. ان الاختلاف الذي ظهر في فجواة الطاقة البصرية وضح اساسيات الاندماج لمركبات الشحنة المنتقلة بواسطة التطعيم. وان دراسة خواص الامتصاص ادت الى مجموعة مختلفة ومشوقة من الظواهر البصرية للاغشية الرقيقة التي القت الضوء على البنية التركيبية للمواد الصلبة وحالة الصوت.

1. Introduction

The study of materials as thin films is one of the most suitable means to know many of their physical and chemical properties, which are difficult to obtain in their natural materials [Ali, (1996), Reggiani et al. (1997)]. So the thin films technology is one of the most important technologies that contributed to the development and study of semiconductors and gave a clear idea of many physical properties and chemical properties [Najem,(2016)].

The solid material becomes thin film when it is prepared as the thin layers by physical methods or chemical or electrochemical reactions and because it have small thickness and easy configuration, so it is deposited on other materials used as sedimentation bases. The base type depends on the nature of use and study such as glass, quartz, silicon and aluminum [Saeed (2009)].

Thin films are importance of use in large fields such as optics for the manufacture of normal mirrors, high reflectivity, electromagnetic radiation detectors, integrated circuit manufacturing, resistors, capacitors and thin connections, they also contributed to the development in the field of digital computing and space research and in the manufacture of solar cells [Umaidi, (2011)].

Polymers are known to be insulating materials, but this fact has changed after the discovery by Heeger, MacDiarmid, and Shirakawa, who have developed the possibility of transforming polymers into electrical conductor via doped it with chlorination, bromine or iodine will make it highly conductive. This discovery offers promising prospects for the application of this phenomenon in various fields of science and technology [Al-Taa'y, (2014)].

Poly (vinyl alcohol) (PVA) is one of the most important polymeric materials as it has manyapplications in industry and is of relatively low cost [Krumova et al. (2000)].

copper acetate salt $Cu_2(CH3COO)_4$ is a chemical compound characterized by high thermal and electrical conductivity which is very absorbent to moisture and uses copper acetate salt in the manufacture of oil paints and pigments and is also used in the preparation of antifungals in addition to being used as an incentive in some organic industries [Mohamed, (2015)].

In this paper, the synthesis of PVA doped with copper acetate thin films using casting method was reported and an investigation is undertaken on the optical properties of these films, with a focus on concentration effects on the values of energy gap, the Urbach's energy and refractive index of the films.

2. Experimental Part

Thin films of PVA doped with $Cu_2(CH3COO)_4$were prepared by dissolved 0.674gm of PVA in 20ml of distilled water, where the mixture was placed in a water bath, then the solution stirred for 2–3 hours, anddissolved 0.2gm of $Cu_2(CH3COO)_4$salt in 10ml of distilled water, than stirring for 30 minutes. The polymer solution was mixed with $Cu_2(CH3COO)_4$salt solution by proportions (5:1, 5:2, 5:3, and 5:4)ml and then cast onto class substrate and evaporated slowly at room temperature for 24 hours to dry.

Thin films thickness was measured using the optical interferometer method employing He-Ne laser 0.632μm, and found to (0.247, 0.247, 0.237 and 0.224)μm respectively for all samples.

The absorbance spectra were recorded using UV-VIS double beam spectrometer in the wavelength optical a range 190-900 nm, the measurements were carried out at room temperature.

Absorption coefficient (α)calculatedusing equation (1) [Han et al. (2008)]:

$$\alpha = \frac{2.303A}{t} \quad (1)$$

The energy band gaps of direct allowed and forbidden transitions of these films were calculated with the help of the absorption spectra. To determinate the energy band gap, $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{2/3}$are plotted versus (photon energy) using the relation (2) [Yadav et al. (2007)].

$$\alpha h\upsilon = B(h\upsilon - E_g)^r \quad (2)$$

whereE_g : the band-gap energy.

h : blank constant.

B: constant

υ: frequency.

The absorption coefficient near the band edge for noncrystalline materials shows an exponential dependence on the photon energy which follows the Urbach's formula (3) [El-Badry et al. (2009)]:

$$\alpha = \alpha^o e^{(h\upsilon/E_u)} \quad (3)$$

Where α^o is a constant

E_u is Urbach's energy

The Extinction Coefficient k is directly proportional to the absorption coefficient as see in relation (4)[Baker and Dyer (1993)]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

The refractive index (n) can be determined from the reflectance (R) using the relation (5) [Ashour et al. (2006)]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (5)$$

3. Result and dissection

The absorption spectra of PVA doped with different volume ratio of$Cu_2(CH_3COO)_4$thin films are shown in Figure (1).

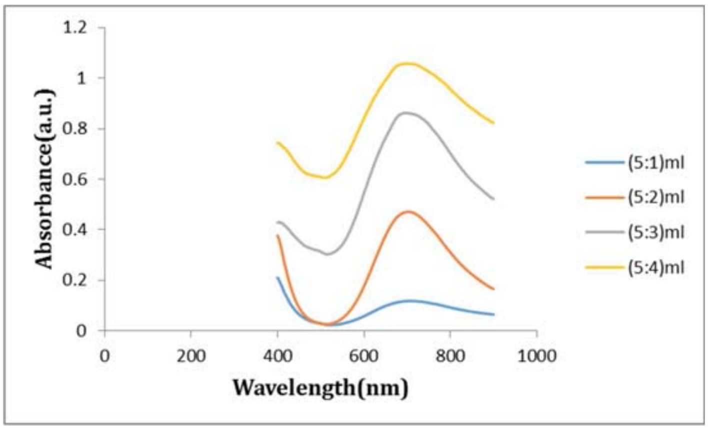

Figure 1. Absorbance versus wavelength(nm) forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

The absorption peaks located of the prepared samples could see at about (708, 702, 698 and 696)nm corresponding to the (5:1, 5:2, 5:3, 5:4)ml respectively. These peaks have light blue shift with the increase of salt concentration. It is found the absorbance increasing with add salt that behavior as in figure (1), which means the salt enhancement the PVA polymer thin films absorbance, this attributed that when adding salt to PVA solutions these molecules fills the vacancies between polymer chains.

The relation of absorption coefficient as a function of incident photon energyfor PVA doped with $Cu_2(CH3COO)_4$thin films isshown in figure (2)

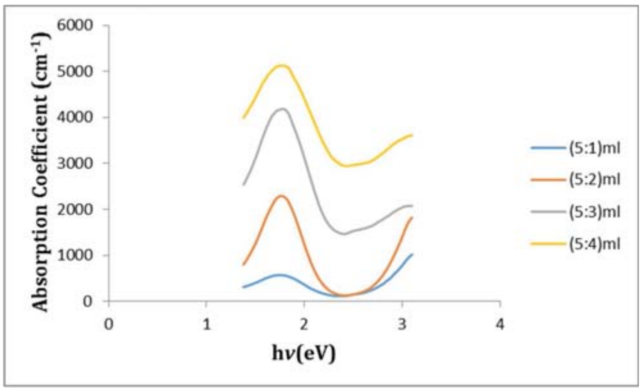

Figure 2. Absorption coefficient versus the photon energy forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

Figure(2) shows the value of absorption coefficient ($\alpha < 10^4$ cm^{-1}) which leads to increasing the probability of occurrence direct transitions. From the same figure one could notice an increasing in absorption coefficient when added $Cu_2(CH3COO)_4$. This is due to the formation of localized levels near the edge of connection that means this increasing could be attributed to the changes in the particle size distribution function of formed thin films.

The optical band gaps were evaluated from $(\alpha h\upsilon)^2$ and $(\alpha h\upsilon)^{2/3}$vs (photon energy) plots as shown infigures. (3,4) and the allowed and forbidden direct transition energies were determined by extrapolating the linear portion of the curves to zero absorption and listed in table (1).

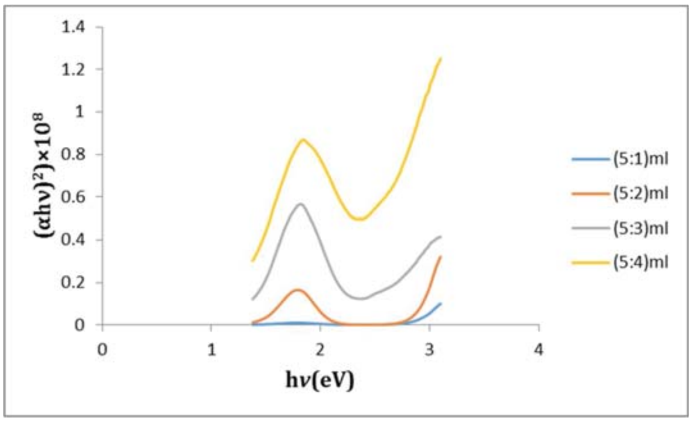

Figure 3. Relationship between $(\alpha h\nu)^2$ and the photon energy forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

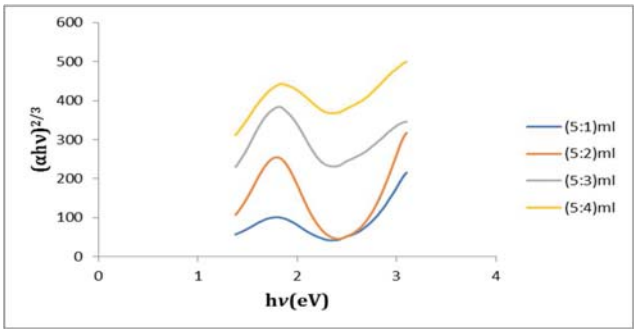

Figure 4. Relationship between $(\alpha h\nu)^{2/3}$ and the photon energy forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

The origin ofthe Urbach's energy (E_u) is considered as thermal vibrations in the lattice [Migahed and Zidan(2006)].Figure 5 show the logarithm of the absorption coefficient as a function of the photon energy for PVA doped with different volume ratio of$Cu_2(CH3COO)_4$thin films. The values of the Urbach's energy (E_u) were calculated by taking the reciprocal of the slopes of the linear portion in the lower photon energy region of these curves and listed in table (1).

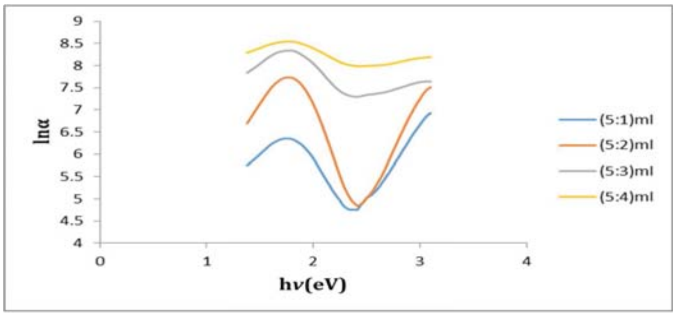

Figure 5. Relationship between (lnα) and the photon energy forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

Table1.the values of energy gap and Urbach's energy for PVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

Samples	The energy band gaps		Urbach's energy (eV)
	Allowed electronic transitions (E_g) eV	Forbidden electronic transitions (E_g) eV	
(5:1)ml	2.85	2.55	293.37
(5:2) ml	2.85	2.59	356.39
(5:3) ml	2.37	1.37	714.61
(5:4) ml	2.16	1.02	995.69

From table (1)one can see that the values of energy gap are decrease with the increasing of the weight percentage of the added (Copper acetate). This is attributed to the creation of onsite levels in the energy gap, the transition in this case is conducted in two stages that involve the transition of electron from the valence band to the local levels and to the conduction band as a result of increasing the added weight percentage. This behavior is attributed to the fact that composites are of heterogeneous type (i.e. the electronic conduction depends on added impurities) this is agree with[Abdallh et al. (2013)].

The decrease in the Urbach's energy in case of PVA doped with $Cu_2(CH3COO)_4$ may be due to the decrease in the crystalline nature of the polymer as shown in table (1) this agree with [Zaki, (2008)].

Extinction coefficient (k) is calculated by using equation (4). The change of the extinction coefficient for PVA doped with $Cu_2(CH3COO)_4$films with different concentrations as a function of the photon energy is shown in figure (6).

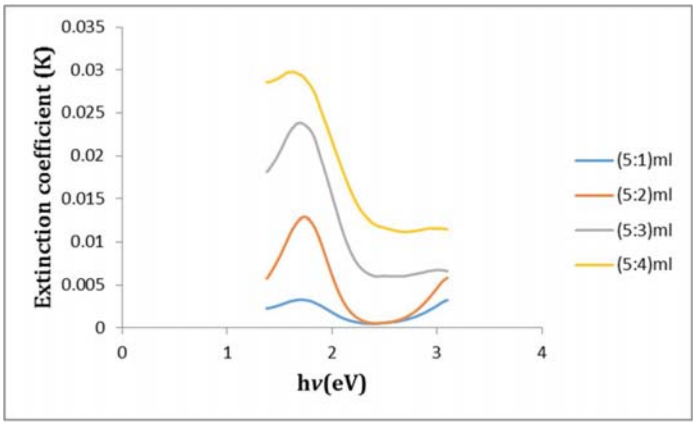

Figure 6. Extinctioncoefficient versus photon energy forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

It can be noticed that the extinction coefficient has lowering values at low concentration, but it increases with increasing the molar percentage of the added (Copper acetate). This is attributed to increased absorption coefficient with increased percentage of added (Copper acetate).

The refractive index (n) is calculated from equation (5). Figure (7) which shows the change of refractive index for PVA doped with $Cu_2(CH3COO)_4$ films with different molar of (Copper acetate) salts as a function of the photon energy.

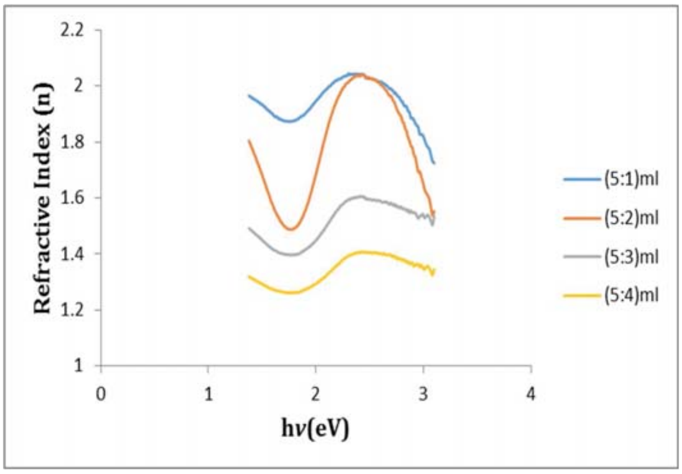

Figure 7.Refractive index versus photon energy forPVA doped with different volume ratio of$Cu_2(CH_3COO)_4$

From figure (7) the refractive index decreases with increasing the weight percentage of the added (Copper acetate). The reason for this result is decrease of the number of free electrons this is agreed with [Alwash. (2010)].

4. Conclusion

In this study the polymer thin films of PVA doped Copper acetate are synthesized using Solution casting technique.

Prepared thin films have high values of absorption coefficient for the wavelength, it is increased when add copper acetate. Absorption and extinction coefficients of PVA thin films increase as film doped with copper acetate. The direct allowed energy gap of PVA doped copper acetate thin films were (2.85–2.16 eV), and forbidden energy gap was (2.55–1.02 eV). This means the copper acetate decreasing the energy gap of PVA.The Urbach's energy increases with the increase of copper acetate consternation. From enhancements for, absorption and electronic transitions for optical properties of PVA thin films prepared can be using it as benefactor of solar cells after adding copper acetate.

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