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Effect of annealing temperature on the optical properties of DCM-PVC doped with TiO_2 nanoparticales thin films

Shymaa K. Hussian
Physics Department, Science College, Al-Muthanna University, Iraq,
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Abstract

Poly (vinyl chloride) (PVC) blended with DCM laser dye co-doped with TiO_2 nanoparticles thin films were prepared using cast method. The TiO_2 nanoparticles was synthesized using sol-gel technique. It was observed from result that the allowed direct electronic transitions energy gap was decreased from 2.08 to 1.94 eV as the temperature increasing from 25-70°C while the allowed indirect electronic transition energy gap increasing from 1.98 to 2.09 eV as the temperature increasing with the same range . The optical properties of final samples such as absorbance, absorption coefficient, refractive index and the optical conductivity of the prepared thin films were studied under the effect of annealing temperature changes.

1.Introduction

A polymer of a particular group is characterized by the molecular weight of the monomer unit [1,2]. A “thin film” is a layer of material having thickness of the order of few nanometers[3]. Polymer thin film technology has made tremendous advancement in the last decade because of the range of technological applications that include coatings, lithography, organic light emitting diodes, sensors and electrochemical cells [4].

Polymers are widely used in electrical and electronic applications. In early works, polymers have been used as insulators because of their high resistivity and dielectric properties. Polymer-based insulators are used in electrical equipment to separate electrical conductors without passing current through themselves. The insulator applications of polymers include printed circuit boards, wire encapsulants, corrosion protective electronic devices, and cable sheathing materials [5]. Polymers have several advantages, such as easy processing, low cost, flexibility, high strength, and good mechanical properties. In the microelectronic fabrication industry, polymers are used in the photolithography process [6]. In recent year polymer increasing applications in electronic industry for preparing different devices. since they are having good photovoltaic characterizations, they are also used for solar cell applications [7].

Polymer blending is the simplest, most well-known technique in polymer engineering for creating new solid materials with more enhanced properties than homopolymers. Polymer blending with other polymer materials or small molecules such asanthracene, pyrene, or pyridine has been performed .Polymer materials have also been mixed with other salts or hybridized with other inorganic/nanoparticle materials to modify the optical and electrical properties of the polymer system[8,9]. All these techniques affect the optical properties of polymers. This work is aimed to understand the fundamental optical properties of PVC polymer blended with TiO_2 nanoparticales as inorganic material and DCM laser dye as organic molecule.

TiO_2 nanoparticales are so far used in many technological applications as a photocatalyst, photovoltaic material, gas sensor, optical coating, structural ceramic, electrical circuit varistor, biocompatible material for bone implants, and spacer material for magnetic spin valve systems etc. [10].

Two effects of TiO_2 are commonly known; first the high refracting index and the associated effect of light scattering [11], and second the degradation effect on polymer matrices [12].

The formation of charge transfer complexes between the polymer host matrix and the dopant are observed. polymer blends and by doping them, the thermal, electrical, dielectric, mechanical and optical properties can be better achieved. The attention of researchers has drawn to study effect of doping because the optical properties of polymers can be tailored to a specific requirement by the addition of suitable dopant materials.

poly(vinyl chloride) (PVC) is an ideal material, because it is highly insulating, tough, flexible, and resistant to both acidic and alkaline solutions[13],poly(vinyl chloride) (PVC) was chosen as the host polymer matrix, because of its wide range of applications, low cost, chemical stability, biocompatibility and sterilizability [14,15].

This research presents experimental results of effects of thermal annealing on the some optical properties of DCM-PVC doped with titanium dioxide nanoparticles thin film using casting method.

2.Experimental methods

Titanium dioxide nanoparticles were prepared using sol-gel method with 10 ml titanium alkoxide), as the raw material, mixed with 40 ml 2-propanol in a dry atmosphere. This mixture was then added dropwise into another mixture consisting of 10 ml water and 10 ml 2-propanol, in order to investigate the effect of pH upon the sample properties, hydrochloric acid or ammonium hydroxide was added, which adjusted the acidity-alkalinity of the gel the value of pH3. A yellowish transparent gel was formed after one hour stirring, the obtained gel then dried at $105C^o$ for several hours until it turned into a yellow block crystal. Calcinations of the synthesized materials were carried out at 500ºC for six hours in a furnace.

To prepare DCM dye solution, firstly dissolving 0.0225 gm in 15 ml of THF solvent and stirrer about 30 minutes to obtain homogenous solution , Polyvinyl chloride was used as a host polymeric material in this work, the aqueous solution of this polymer were prepared by dissolving 3 gm of PVC in 50ml THF and thoroughly stirred using a magnetic stirrer for about two hour until PVC was completely dissolved. To synthesis the final thin films, 1ml DCM solution mixed with 5ml PVC solution and stirrer about 10 minutes to get homogenies solution. Then 2.648×1020 particle densities of obtained TiO_2 nanoparticles was suspended in THF solvent and added to the mixture of DCM-PVC after that by use then cast method can be casting on glass substrate at room temperature. To study the temperature effect on the optical properties of the films, different temperatures 25, 40, 55, 70 C^o were used to drying samples.

Thickness of the prepared thin films was measured using the optical interferometer method employing He-Ne laser 0.632 μm with incident angle 45° .

This method depends on the interference of the laser beam reflected from thin film surface and then substrate, the films thickness (d) can be calculated using the following formula [16]:

$$d = \frac{\lambda}{2} \frac{\Delta x}{x} \quad (1)$$

Absorption and reflectance spectra of the final thin films were recorded using UV-VIS double beam Spectrophotometer type (SHIMADZU)(UV-1650) in the wavelength rang (190-1100)nm.

From the absorbance data, the absorption coefficient (α) was calculated in the fundamental absorption region using Lambert law [17]:

$$\alpha = \frac{2.303}{d} A \quad (2)$$

Where A the optical absorbance and d the film thickness.

Extinction coefficient (k) of prepared films was calculated by using the relation[18]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

Where λ is the wavelength of the incident photon.

From the reflectance data, the refractive index (n) was calculated by using the following relationship [19]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \quad (4)$$

The optical conductivity (σ) can be calculated from the relation [20]:

$$\sigma = \frac{\alpha n c}{4\pi} \quad (5)$$

Where c is the velocity of light.

The real and imaginary complex dielectric constant can be expressed by equations (6, 7) respectively [11] [16]:

$$\varepsilon_r = n^2 - k^2 \quad (6)$$

$$\varepsilon_i = 2nk \quad (7)$$

The nature of transition (direct or indirect) is determined by using the relation[21,22]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^r \quad (8)$$

Where hυ is the photon energy, E_g the band gap energy, A constant depended on type of material and (r) exponential constant, For allowed direct transition, r = 1/2 and for indirect transition, r =3/ 2.

3.Results and Discussion:

The absorption spectra for PVC doping with DCM and TiO_2 nanoparticles thin films at different annealing temperatures (25,40,55 and 70)C$^{\circ}$ as shown in figure(1).It is obviously that the absorption increases as the wavelength increases for all samples within rang (300-500)nm ,while the absorption decrease for wavelength above of 600nm, also one can see that the absorption edge has been changed (increasing) with increasing annealing temperatures.

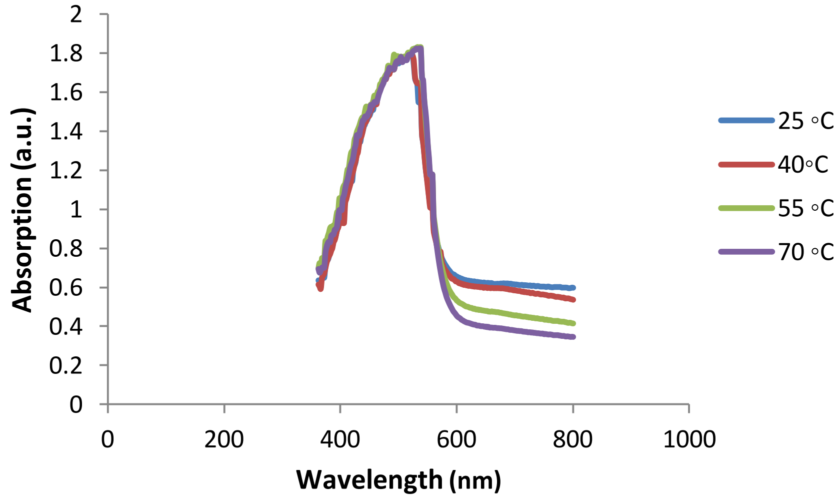

Figure (1) Absorbance for DCM-PVC doped with TiO_2 nanoparticles thin films at different annealing temperatures

Figure(2) shows the absorption coefficient for PVC doping with DCM and TiO_2 nanoparticles thin films at different annealing temperatures which determined from equation(2).The absorption coefficients of these films increase sharply in the UV range ,and then decreased gradually because its inversely proportional to the transmittance. The absorption coefficient is increasing as annealing temperatures increasing.

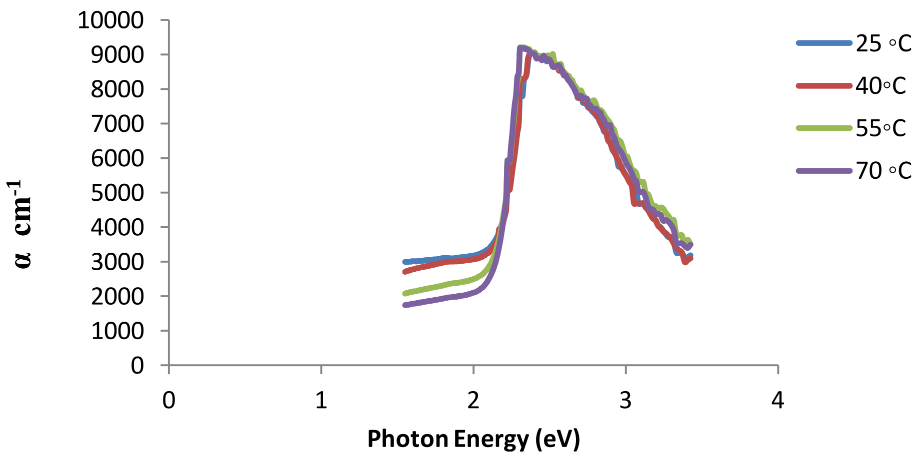

Figure (2) Absorption coefficient for DCM-PVC doped with TiO_2 nanoparticles thin films at different annealing temperatures

Extinction coefficient was calculated using the equation(3),the extinction coefficient for PVC doping with DCM and TiO_2 nanoparticles thin films at different annealing temperatures were shown in fig(3).It is clear that the extinction coefficient increase rapidly in the UV range and then decreased ,all the curves have the same behavior which increasing with annealing temperatures increasing.

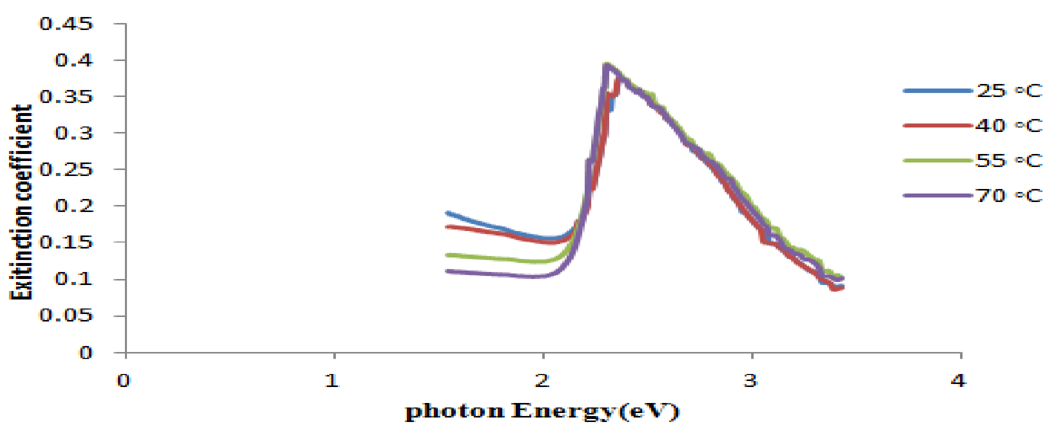

Figure (3) Extinction coefficient against the photon energy (eV)

Figure (4) shows the reflectance spectra for all films at different annealing temperatures ,it is clear that reflectance decrease with increasing the photon energy (UV region) but wavelength equal to (550) nm which represent the center of the visible wavelength is rang increase as the photon energy increase, also it can be seen from the figure that the reflectance decrease slightly with increase the annealing temperatures.

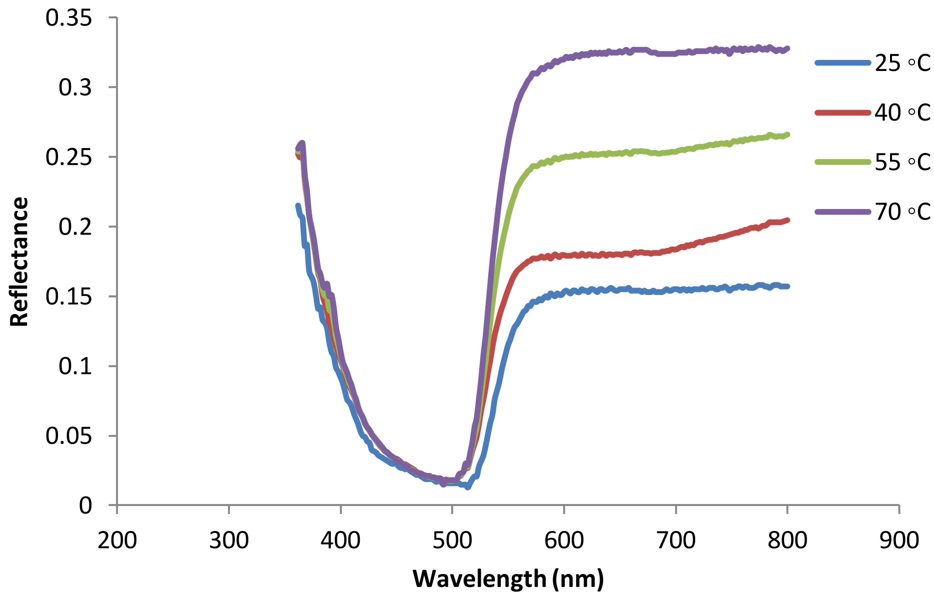

Figure (4) Reflectance for DCM-PVC doped with TiO_2 nanoparticles thin films at different annealing temperatures

The refractive index of PVC doping with DCM and TiO_2 nanoparticles thin films at different annealing temperatures were determined from equation(4).Figure (5) shown the variation refractive index of these films as a function of the photon energy ,the values of the refractive index decreases slightly with increasing the photon energy in the UV and the beginning of visible region ,also one can observed from the figure the refractive index increasing with increasing annealing temperatures.

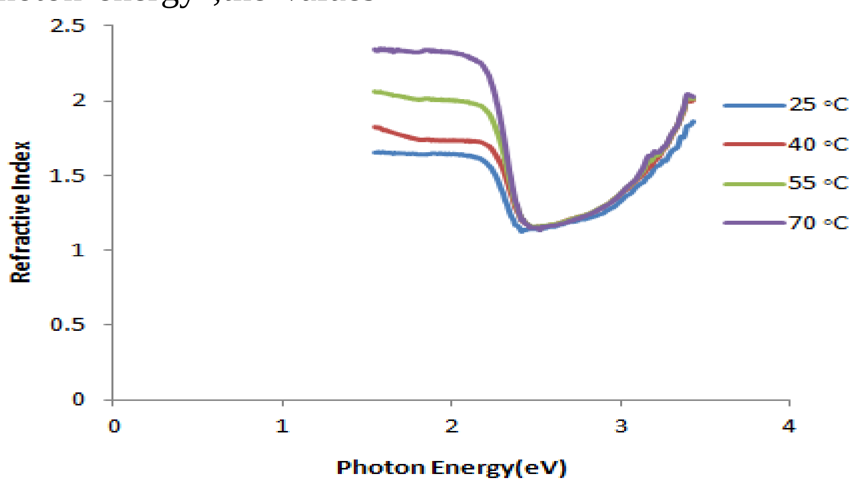

Figure (5) Refractive Index for DCM-PVC doped with TiO_2 nanoparticles thin films at different annealing temperatures

Figure(6) shows the variation of optical conductivity for DCM-PVC doped with TiO_2 nanoparticles as a function of photon energy at different annealing temperatures which calculated using equation(5) .It is clear that the optical conductivity increase with increase annealing temperature for all samples.

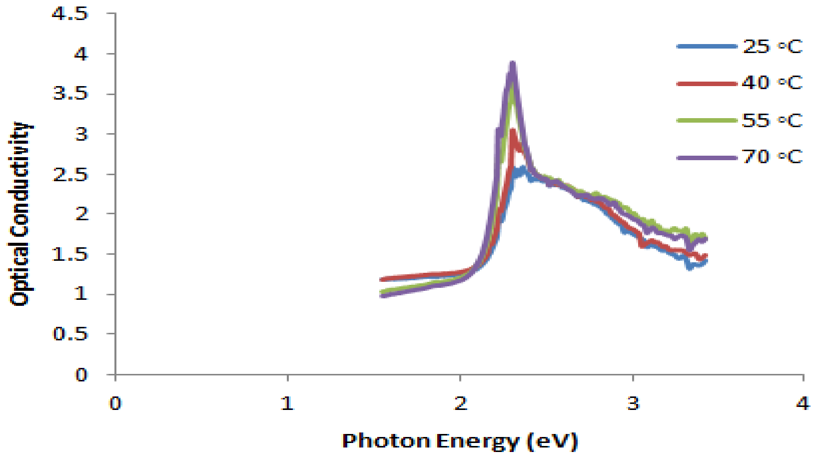

Figure (6) Optical conductivity as a function of the photon energy.

Real (ε_r) and imaginary (ε_i) parts were calculated using equations (6 and 7), and figures (7 and 8) indicate the plot of both (ε_r) and (ε_i) versus photon energy.

The real and imaginary parts of dielectric constant follow the same pattern as the refractive index and extinction coefficient resplendence of (ε_r) on refractive index and (ε_i) on the value of extinction coefficient and the value of real part are higher than the imaginary parts.

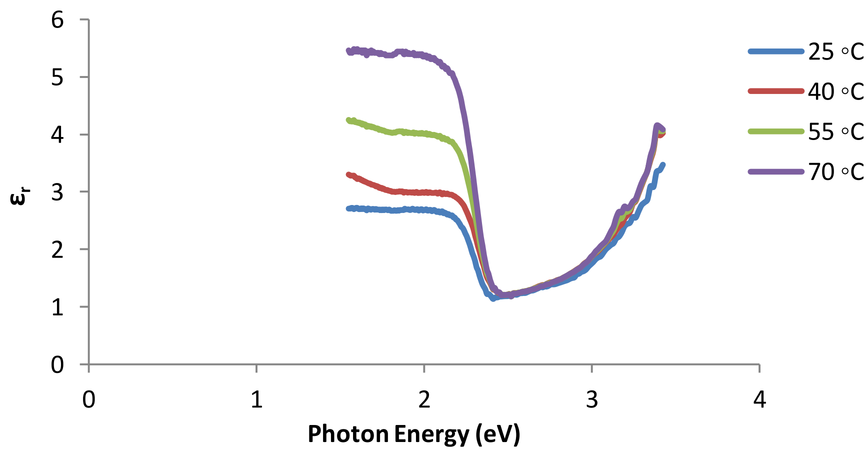

Figure (7) Real part dielectric constant versus the photon energy.

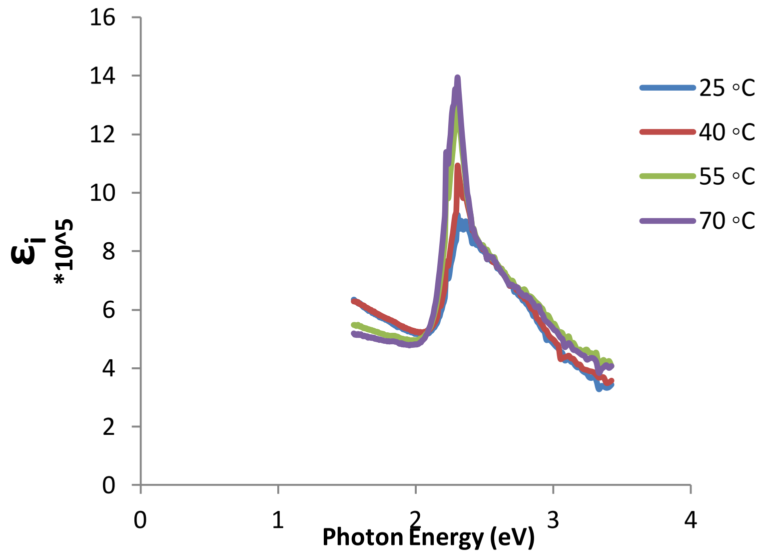

Figure (8) Imaginary part of dielectric constant versus the photon energy.

The variation of $(\alpha h\nu)^2$ as the incident photon energy ($h\nu$) of DCM-PVC doped with TiO_2 nanoparticles thin films at different annealing temperatures was shown in figure (9). The optical band gap was determined by extrapolating the linear portion of this plot at $(\alpha h\nu)^2=0$ which indicates that the direct allowed transition. The energy gap value depends on the films deposition condition and its preparation method [23].

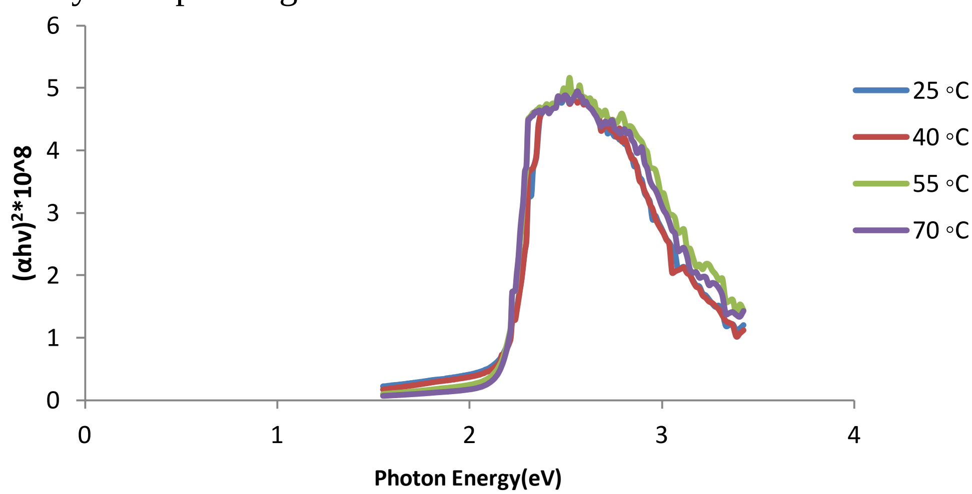

Figure (9) Relationship between $(\alpha h\nu)^2$ and photon energy (eV).

Figure (10) shows the variation of $(\alpha h\nu)^{1/2}$ with photon energy , which used to estimate the indirect energy gap and the phonon energy with helping of equation (8).

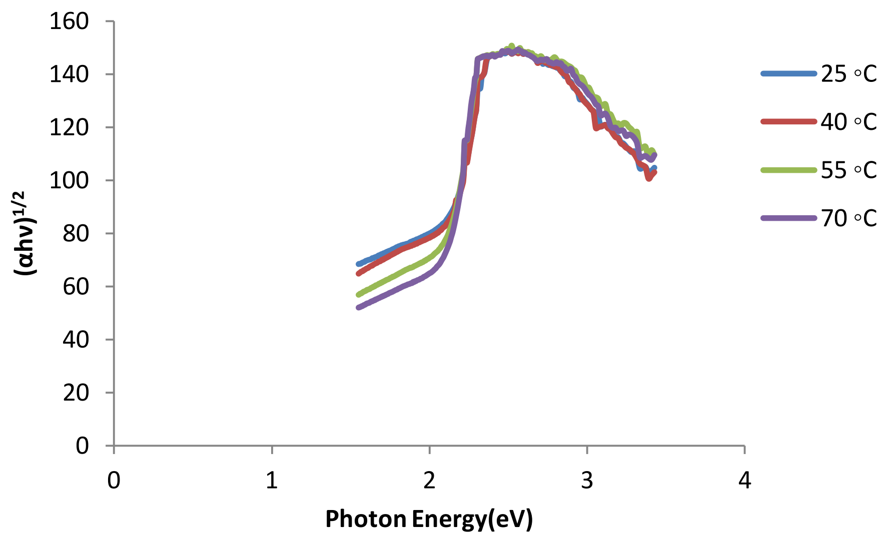

Figure (10) Relationship between $(\alpha h\nu)^{1/2}$ and photon energy (eV).

The energy gap values for direct and indirect for all thin films at different annealing temperatures are summarized in table (1).

Table (1) Electronic transitions energy gap (eV) for PVC doped with DCM thin films.

Temperature(°C)	Allowed direct band gap (eV)	Allowed indirect band gap (eV)
25	2.08	1.98
40	204	2.01
55	1.98	2.03
70	1.94	2.09

From table (1), it observed that allowed direct band gap will decrease from (eV) with increasing the annealing temperatures from (25-70 °C). This decreasing may be attributed to increasing in the density of local energy levels with increasing the annealing temperature between the covalent and valance bands. While in indirect electronic transition, one can see that the allowed indirect band gap was increasing with increasing the annealing temperature for all samples.

CONCLUSION

The effect of annealing temperature on the optical properties of DCM-PVC doped with TiO_2 nanoparticles thin films synthesized using cast method was studied. The band gap of these films in case of direct electronic transitions are decreasing as the annealing temperature increases, but in case of in direct electronic transitions its vice versa. The increasing in annealing temperature causes different effects on the optical properties of the prepared samples, such that the absorption, absorption coefficient, extinction coefficient, and the , imaginary part of dielectric constant and the optical conductivity of prepared thin films are increase as the annealing temperature increasing. While the reflectance, refractive index and real part of dielectric constant are decrease as the annealing temperature increasing.

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تأثير التلدين على الخواص البصرية لاغشية DCM-PVC الرقيقة المشوبة بجسيمات ثاني اوكسيد التيتانيوم TiO_2 النانوية

شيماء كريم حسين

الخلاصة:

مّزج بوليمر بولي كلوريد الفينيل(PVC) مع صبغة (DCM) الليزرية ومع جسيمات ثاني اوكسيد التيتانيوم (TiO_2) النانوية وحضرت الأغشية باستعمال طريقة الصب، اما جسيمات TiO_2 فقد تم تحضيرها بأستعمال تقنية sol-gel. لوحظ من النتائج للانتقالات الالكترونية المباشرة أن فجوة الطاقة قلت من 2.08 eV إلى 1.94 eV مع زيادة درجة حرارة التلدين من $25^{\circ}C$ الى $70^{\circ}C$ بينما كانت فجوة الطاقة للانتقالات الالكترونية غير المباشرة ازدادت من 1.98 eV إلى 2.09 eV بزيادة درجة الحرارة بنفس المدى. الخواص البصرية للنماذج النهائية مثل الامتصاصية، معامل الامتصاص،معامل الانكسار والتوصيلية البصرية للأغشية المحضرة درست تحت تأثير درجة حرارة التلدين.