A study of the characterization of CdS/PMMA nanocomposite thin film

Iftikhar M. Ali, Awattif A. Mohammed, Awras H. Ajil

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

E-mail: awras.alrikaby@gmail.com

Abstract

Nanocomposites of polymer material based on CdS as filler material and poly methyl methacrylate (PMMA) as host matrix have been fabricated by chemical spray pyrolysis method on glass substrate. CdS particles synthesized by co-precipitation route using cadimium chloride and thioacetamide as starting materials and ammonium hydroxide as precipitating agent. The structure is examined by X-ray diffraction (XRD), the resultant film has amorphous structure. The optical energy gap is found to be (4.5, 4.06) eV before and after CdS addition, respectively. Electrical activation energy for CdS/PMMA has two regions with values of 0.079 and 0.433 eV.

Key words

Nanocomposites, Nanoparticles, Cadmium Sulfide, PMMA, Optical Properties, Electrical Properties.

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دراسة خصائص الغشاء الرقيق للمتراكب CdS/PMMA

افتخار محمود علي، عواطف عذاب محمد، اوراس حميد عاجل

قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تم تصنيع المركب النانوي المتكون من المادة البوليمرية PMMA كمادة مضيفة والمركب كبريتيد الكادميوم كمادة تطعيمية بطريقة الرش الكيميائي على ارضية من الزجاج. حضر ت دقائق كبريتيد الكادميوم بطريقة الترسيب المزدوج باستخدام كلوريد الكادميوم والثايواسيتمايد كمواد اولية وهيدروكسيد الامونيوم كعامل مرسب. تم فحص التركيب بواسطة حيود الاشعة السينية وكان للغشاء المحضر تركيب عشوائي. كانت قيم فجوة الطاقة البصرية 4.5 و4.06 الكترون فولت قبل وبعد اضافة كبريتيد الكادميوم على التوالي. وكان لطاقة التنشيط الكهربائية للمتراكب CdS/PMMA منطقتان بقيم 0.079 و 0.433 الكترون فولت.

Introduction

The study of polymer nano-composites (PNC) is a fast growing area of research. The fabrication of polymer nano-composites (PNC) is an integral aspect of polymer nanotechnology. These PNC are composed of two main parts, filler and host matrix. The inorganic particles, having at least one dimension less than 100 nm, are acted as filler and these particles dispersed in polymer, which acts as host matrix. Recently, many efforts have been devoted to the synthesis of polymer nano-composite materials due to their synergistic and hybrid properties [1]. The properties of polymer nano-composite (PNC) mainly depend upon filler material and host matrix. The PNC's show almost all properties of their parent materials together with some additional properties like chemical stability, improved moldability etc.

These polymer nanocomposites (PNC's) are better than conventional composites because conventional composites require high content of filler. But PNC's achieve the same properties with a much smaller amount of filler and producing materials of lower density and higher moldability.

The functions of PNC's depend upon filler phase. In the present study (CdS) nanoparticles were used as filler material. CdS has cubic structure. The polymer nano-composite materials containing semiconductor as filler attract much attention due to their promising engineering applications like sensor technology [2, 3]. In the present paper we synthesized CdS nanoparticles and impregnated them in poly methyl methacrylate (PMMA) matrix. The films were prepared by spray pyrolysis. The aim of this work is to investigate the optical and electrical behavior of polymer nanocomposites.

Experimental part

1. Synthesis of CdS nanoparticles

CdS nanoparticles were synthesized by co-precipitation method. First, $CdCl_2$ and thioacetamide (TAA) at 0.1 M for both materials were dissolved separately in distilled water, with vigorous stirring for 30min. Then they were mixed together and stirred with vigorous stirring for 1hour. Finally NH_4OH was added drop wise with stirring for 30min. Afterward, the resulting yallow suspension was further stirred for 30 min. Then the reactor was cooled up to room temperature. The resulting precipitate was filtered and washed several times with water. Finally it was dried in an oven at 80 ^oC.

2. Synthesis of CdS/PMMA composite thin film

In order to disperse CdS particles in polymer matrix (PMMA), we used solvent evaporation method. As the second step of fabrication of composite material we dissolved 500 mg PMMA in DCM and left the sealed vial overnight. Afterward, the mixture was sonicated for 30 min. When all PMMA dissolved completely, 50 mg CdS filler particles were added in the solution and sonicated the suspension for further 45min. In the last step, this solution was sprayed on glass substrate.

3. Characterization of CdS/PMMA composite thin film

X-ray powder diffraction (XRD) data were taken by X-ray diffractometer (SHIMADZU-XRD 6000) using Cu-Ka radiation (λ=1.54056 Å) at room temperature. The optical absorbance and transmittance spectra were measured using UV/ Visible SP – 8001 spectrophotometer over the range 190–1000 nm to calculate the optical energy gap and optical constants. The energy gap was calculated by using Tauc's relation [4] $\{\alpha h\boldsymbol{\nu}=A(h\boldsymbol{\nu}-\boldsymbol{Eg})^{\boldsymbol{m}}\}$ where A is a constant, which is different for different material, α is the absorption coefficient, h$\boldsymbol{\nu}$ is the energy of incident photon, E_g is the band gap energy. The optical constant such as the extinction coefficient, which is related to the exponential decay of the wave as it passes through the medium, that defined as [5] $\{k = \alpha\lambda/4\pi\}$. Also, the refractive index is determined by using the formula [6]

$$n = \left(\left((4R/(R-1)^2) - k^2 \right)^{1/2} - ((R+1)/(R-1)) \right)$$

where R is the reflectance, and can be expressed by the relation [7]:

$$R = ((n-1)^2 + k^2/(n+1)^2 + k^2)$$

The real (ε_r) and imaginary (ε_i) parts of the dielectric constant of thin films are determined by using equations: [8]

$\{ (n\text{-}ik)^2 = \varepsilon_r - i\varepsilon_i \}$, where $\{\varepsilon_r = n^2 - k^2\}$ and $\{\varepsilon_i = 2nk\}$.

The electrical resistance has been measured as a function of temperature for CdS/PMMA film in the range (298 – 483) K. The measurements is done by using sensitive digital electrometer type Keithley (616) and electrical

oven. The activation energies (E_{a1} and E_{a2}) in these two regions were calculated by using relation

$\{Ln\sigma = Ln\ \sigma_o\ (-E_a / k_B T)\}$

where the conductivity (σ) of the films is calculated by using the following equation:

$$\{\sigma = L/(R.A)\}$$

where L is the distance between electrodes and A is the cross section area. From determination of the slope we can find the activation energy $\{E_a = k_B$. slope$\}$.

Result and discussion

1. XRD analysis

The XRD pattern of nano CdS, exhibits the characteristic peaks for crystalline CdS of hexagonal wurtzite structure. This crystal structure of CdS disappeared due to the presence of PMMA because of the small amount of CdS that well dispersed in the polymer host. The diffraction peaks in XRD patterns of nano CdS has been indexed to the hexagonally wurtzite structured CdS which are consistent with the standard values for CdS given in JCPDS file (80-006). X-ray diffraction of prepared CdS is illustrated in Fig. 1.

X-ray diffraction result of polymer nano composite materials shows that there is amorphous structure because of the high quantity of polymer in the thin film.

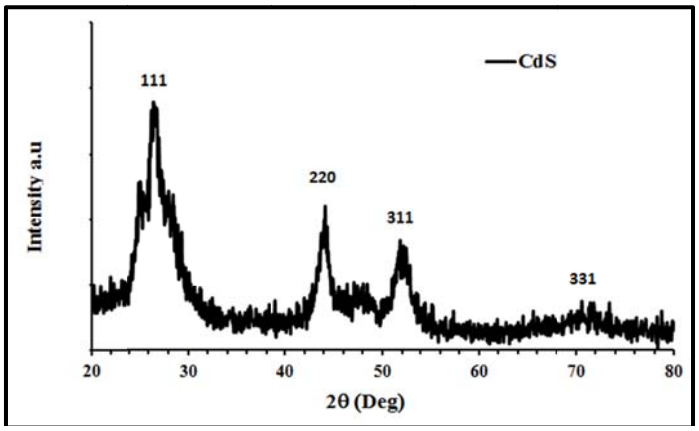

Fig. 1: XRD spectrum of CdS powder.

2. Optical properties

2.1 Absorption and band gap determination for CdS/PMMA film

The UV-Vis absorption spectrum Fig. 2 of the synthesized CdS/PMMA has been recorded to measure its band-gap. CdS/PMMA has good absorption for light within the range of wavelength 190-330 nm and this peak position reflects the band gap of the nanocomposite. The peak of the spectrum corresponds to the fundamental absorption edges in CdS/PMMA, this fundamental absorption, which corresponds to electron excitation from the valence band to conduction band, can be used to determine the nature and value of the optical band gap of the prepared CdS/PMMA. The maximum absorption edge for the sample is observed at 280 nm assigned to the optical transition of the first excitonic state of CdS/PMMA composite and its narrow shape is an evidence of the very small size of the dispersed particles.

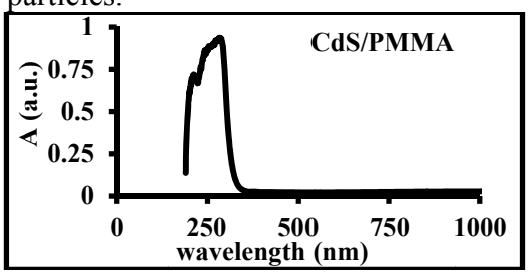

Fig. 2: UV-Vis absorption spectra of CdS/PMMA thin film.

2.2 The transmittance spectra of CdS/PMMA thin films

Fig.3 represents the transmission spectrum of CdS/PMMA composite. The spectrum is recorded in the range of 190-1100 nm at room temperature. High transmission is appeared from 360 nm till 1100 nm and it is more than 80%.

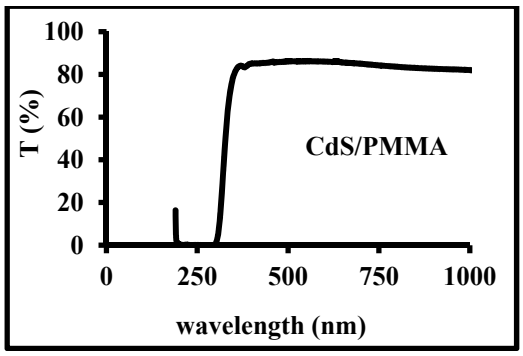

Fig. 3: Transmission spectrum of CdS/PMMA thin film.

2.3 The optical energy gap

CdS/PMMA has direct band gap material where the exponent m value equals to ½ that indicates the type of transition. The linear part of the graph was extrapolated to $\{(\alpha h\nu)^{1/m} \sim 0\}$ to determine the bandgap. From Fig.4, it has been determined that the optical band gap of CdS/PMMA is 4.5 and 4.06 eV without and with CdS nanoparticles.

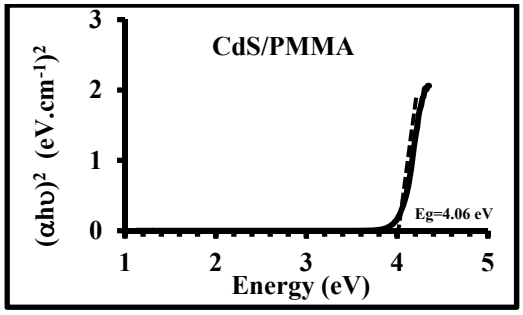

Fig. 4: Tauc plot of CdS/PMMA thin film.

2.4 Optical constants

a) Extinction coefficient

It is clear from the equation mentioned before that (k) depends on (α) and has a similar behavior to it. Fig. 5 illustrate the variation of the extinction coefficient of CdS/PMMA film with the wavelength.

It can be noted that (k) increases highly at the absorption edge region. This increase is attributed to the increase of the absorption coefficient due to the direct electronic transitions. The extinction coefficient later reaches its maximum value at the high absorption region corresponding to the increment in the photon's energy and the increase in the absorption coefficient with the decrease in the wavelength.

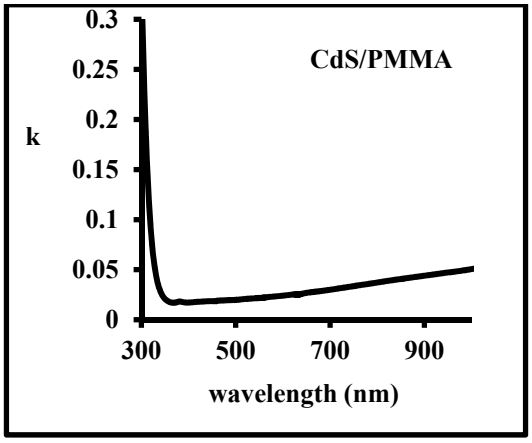

Fig. 5: Extinction coefficient as a function of wavelength for CdS/PMMA thin film.

b) Refractive Index

It is necessary to give attention to the refractive index (n) in order to complete the fundamental study of the optical properties and the optical behavior of the material. The variation of the refractive index as a function of the wavelength for CdS/PMMA thin film is illustrated in Fig. 6. It is clear from the figure that the refractive index decreases with the increase in the wavelength of the incident photon. which intern causing an increment in the compactness of the films which intern reduces the speed of light in the material of the thin film and then leads to an increase in the refractive index according to the relation: {v =c / n}

where (v) is the velocity of propagation, and (c) is light velocity.

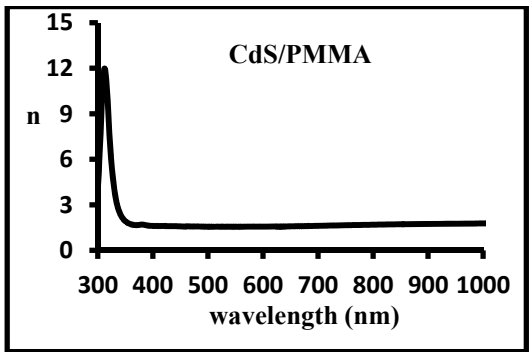

Fig. 6: The variation of the refractive index as a function of the wavelength for CdS/PMMA thin film.

c) Dielectric constant

The real part of the dielectric constant (ε_r) depends mainly on the value of (n^2), because of the smaller values of (k^2) comparison with (n^2), whereas the imaginary part of the dielectric constant (ε_i) depends mainly on the (k) values which are related to the variations of the absorption coefficient. Figs. 7 and 8 illustrate the variation of the real part of the dielectric constant as a function of the wavelength for CdS/PMMA thin film.

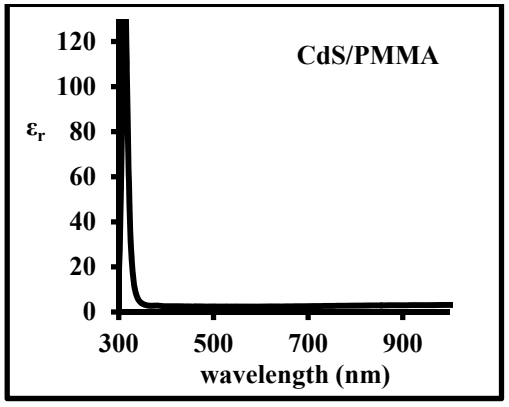

Fig. 7: The variation of the real part of the dielectric constant as a function of the wavelength for CdS/PMMA thin film.

The variation of the imaginary part of the dielectric constant as a function of the wavelength for CdS/PMMA thin film is illustrated in Fig. 8.

The optical properties parameters including absorption coefficient and optical constants which include refractive index, extinction coefficient, real and imaginary parts of the dielectric constant at the wavelength which is equal to 550 nm for CdS/PMMA thin film deposited by chemical spray pyrolysis method on a glass substrate at 100°*C* with thickness about (100) nm are listed in Table 1.

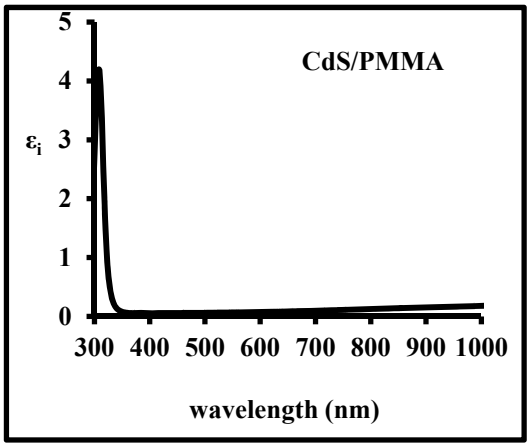

Fig. 8: The variation of the imaginary part of the dielectric constant as a function of the wavelength for CdS/PMMA thin film.

3. The electrical properties of CdS/PMMA thin film

The electrical properties of CdS/PMMA thin Film deposited by chemical spray pyrolysis method on a glass substrate with thickness about (100) nm are studied. These properties include the D.C. conductivity from which the transport mechanism of the charge carriers can be estimated.

Table 1: The optical parameters for CdS/PMMA thin film at (λ=550) nm.

Nanocomposite	T %	α (cm^{-1})	k	n	ε_r	ε_i
CdS/PMMA	86.27	6350	0.021	1.557	2.425	0.067

3.1 D.C. conductivity of CdS/PMMA thin film

The (d.c) conductivity ($\sigma_{d.c}$) for CdS/PMMA film is studied as a function of (1000/T) with the range of (298-483) K, is shown in Fig. 9. It can be deduced from this figure that there is an increase in conductivity with the increase in the temperature that prove the semiconductor behavior for CdS/PMMA nanocomposite. As well as, it can be observed two separated regions throughout the heating temperature range, the first region is at low temperature and the second region is at higher temperature, indicating different conduction mechanisms dominating at specific temperature intervals [9].

These two conduction mechanisms mean that the conductivity is non-linear with temperature. The first activation energy (Ea_1) occurs at low temperatures, in which the conduction mechanism is due to charge carriers' transport (hopping) to localized states near the conduction band [10,11], in this temperature region (298-363) K. The second activation energy (E_{a2}) occurs at high temperatures, in which the conduction mechanism is attributed to the thermal excitation of charge carriers from grain boundaries to neutral region of the grains [10]. It is specifically due to carriers excited into the extended states beyond the mobility edge [9]. In this temperature region (363-483)K, the variation of (ln σ) with (1000/T) is pronounced and increases sharply with high activation energies relative to first activation energies, as shown in the Fig. 9 and Table 2.

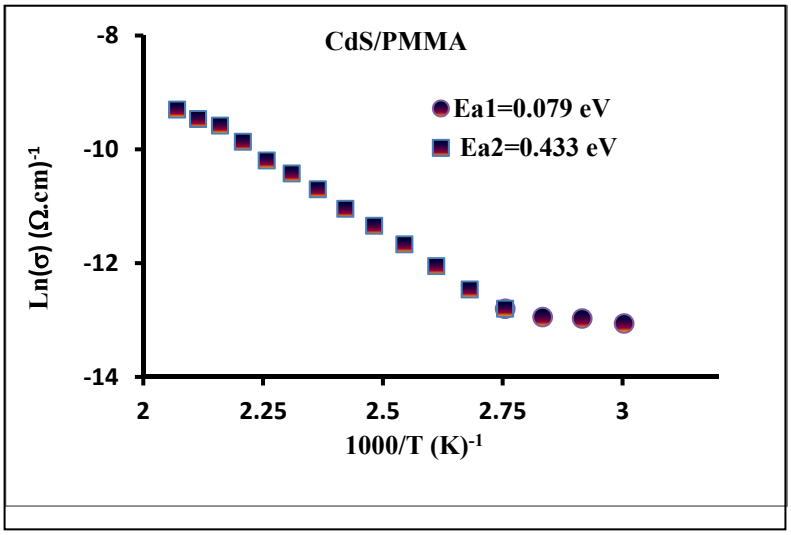

Fig. 9: Ln(σ) versus 1000/T for CdS/PMMA thin film.

Table 2: D.C. Conductivity Parameters for CdS/PMMA thin film.

Sample	E_{a1}(eV) Temp. Range(298-363)K	E_{a2}(eV) Temp. Range(363-483)K	$\sigma_{D.C}$ at R.T$(\Omega cm)^{-1}$
CdS/PMMA	0.079	0.433	3.35E-07

Conclusions

CdS/PMMA nanocomposite has been successfully synthesized via chemical spray pyrolysis method. The XRD results indicate that the composite is in amorphous phase. The optical transition in the CdS/PMMA films is observed to allow direct transition. The refractive index, and extinction coefficient and dielectric constant (real and imaginary parts) decrease with the increasing of wavelength in the UV-Vis-NIR range. There are two transport mechanisms of the charge carrier of the d.c conductivity at temperature range (298-473) K.

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