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Structural and optical properties of CdIn2S4:Cu thin film prepared by chemical spray pyrolysis

Alaa A. Al-jubory
University of Anbar - College of education for pure science
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Abstract

Cadmium indium sulfide (CdIn2S4) thin films were deposited by chemical spray pyrolysis technique on the glass substrate ,and doping by Cu= 1%,3%.5% . The films structure were analyzed by XRD . All the patterns of thin films prepared are polycrystalline .The optical properties are studied by UV-VIS spectrophotometer ,the absorption coefficient was calculated ,its value was more than 104 that supports the direct transition ,the energy gap found between 2.6 eV to 2.85 eV dependent on the ratio of Cu in the thin film. And finally the optical constants such as refractive index ,extinction coefficient, real and imaginary dielectrics were investigated.

Keywords : Structural , optical properties ,CdIn2S4:Cu thin film ,by chemical spray pyrolysis

Introduction

Cadmium indium sulfide ($CdIn_2S_4$) is the semiconducting ternary chalcogenide of the type A^{II}-B_2^{III}-C_4^{IV}. The band gap of the n-type semiconducting $CdIn_2S_4$ at room temperature is 2.62 eV with direct transition .The advantages of using the compound in the form of a film are multiple, for instance, photocatalyst recovery and reactivation are easy to implement, an external bias can be applied to improve the photoelectrolytic process, and gas separation is straightforward[1-5]. Thin films of $CdIn_2Se_4$ and $CdIn_2S_4$ have been obtained by vacuum evaporation, chemical bath deposition technique and spray pyrolysis technique. The attempts have already been made to prepare photoactive $CdIn_2S_4$ thin films by simple and low-cost chemical spray pyrolysis technique . The optical and structural properties of chemically deposited nanocrystalline $CdIn_2S_4$ thin films have been studied by A.V. Kokate et al [6-7].

Experimental

$CdIn_2S_4$ thin films were prepared by chemical spray pyrolysis deposited on micro glass slides which were first cleaned with detergent water and then dipped in acetone. Spray solutions were prepared by mixing 0.1 M aqueous solution of $CdCl_2$, $In(NO_3)_3$, $Cu(NO_3)$,and Thiourea $CS(NH_2)_2$,which were then mixed in a certain amount of solution for each experiment by a magnetic stirrer. Automated spray solution is transferred on the hot substrate kept at the normalized deposition temperature of 300 ±10 ºC with the help of carrier gas. Filtered air is used as carrier gas, the flow rate of which is normalized to ~3ml/min. To avoid excessive cooling of substrate, spraying was achieved in periods of about 10 sec followed by a 15sec waiting period . To deposit films of uniform thickness the distance between the substrate and spray nozzle was kept at 50cm.

Thickness measurement of the films has been carried out using optical method thickness was found to be 400 ±20nm

To determine the nature of the growth and structural characteristics of the prepared thin films, an X-ray diffraction (XRD) obtained for diffract meter type Philips pw. 1840 with target Cu-K**α**. A UV-VIS spectrophotometer type Jenway 6800 UV/VIS was used to measure the absorbance and transmittance in the wavelength range 200-1100nm, and from these measurements, the optical parameters were calculated.

Result and dissection

1- X-ray diffractions

XRD patterns of $CdIn_2S_4$ thin films with doping by Cu are shown in Fig.1 .All the patterns of thin films prepared are polycrystalline with peak (2θ)=(27.2725), (27.0257) and (26.5816) corresponding to (hkl) = (311) . The observed d values of XRD reflections were compared with standard d values taken from (JCPDS) data file No. (27-0060), as given in table 1. The value of 2θ decrease from 27.2725 without doping to 26.5816 with doping with 3%Cu . The thin films of $CdIn_2S_4$ have spinal cubic crystal structure with lattice parameters a= 10.38 Å .

2- Optical Studies

The optical absorption of the films has been studied in the range (200- 1100 nm). The variation of optical density with wavelength is analyzed to find out the nature of transition , for different films were used to calculate the absorption coefficient (α) using the equation [8].

where t is the film thickness

$$= \frac{.}{\quad} \ldots\ldots\ldots\ldots$$

The variation of the absorption coefficient (α) as a function of wavelength (λ) for the different films is shown in Fig.2. It is clear that the value of the absorption coefficient (α) decreases with increase in the wavelength . The value absorption coefficient is of the order of $10^4 cm^{-1}$, that supports the direct band gap nature of the semiconductors[9].

The optical band gap E_g of thin films prepared was calculated by using the following formula [10].

$$= (\quad - \quad) \ldots\ldots$$

where A is constant , hυ is the incident photon energy , and m is a factor whose value dependent on the nature of band transition , $= - \quad -$ for direct allowed and direct forbidden transition [10] . The variation of ( ) versus hυ for the prepared thin films are illustrated in Fig.3. It is clear that the value of E_g increases from 2.6 eV for $CdIn_2S_4$ with increasing ratio of Cu in the films to 2.85 eV as shown in table 1.

The extinction coefficient(k) have been calculated by using the following formula[11]

$$= \frac{\quad}{\quad} \ldots\ldots\ldots\ldots\ldots$$

Fig. 4 show the spectral dependence of extinction coefficient (k) for $CdIn_2S_4$ thin films . The value of extinction coefficient (k) decreases with increase in the wavelength and it also decreases with increasing Cu concentration in the films. The electron affinity has been correlated with the optical band gap , However it is difficult to assign electron affinity value for any semiconducting alloy, as we know, the electron affinity is related to the electronegativity as suggested by Shamshad et al.[11].

The refractive index (n) of thin films can be calculated from their reflectance and transmittance spectra using simple approximations relation [12].

$$= \frac{+}{-} + \frac{\quad}{(\; - \;)} - \quad \ldots\ldots$$

The refractive index is one of the foundation properties of an optical material , because it is closely related to the electronic polarization of ions and the local field inside materials [10]. The calculated n values of $CdIn_2S_4$ thin films are shown in Fig. 5. It can be seen that n increases as wavelength increases.

The increase in the refractive index may be correlated with the increase in the transmittance and the decrease in the absorption coefficient. The increase in the value of the refractive index with increasing wavelength shows normal dispersion behavior of the material [13]. The refractive index for prepared thin films varied from 1.1 to 2.6.

The complex dielectric constant is given by the relation[13].

$$= \quad + \quad = (\quad + \quad) \ldots\ldots$$

.

where the real part, is the normal dielectric constant that shows how much it will slow down the speed of the light in the material, and the imaginary part, , represents the absorption of light associated with the free carriers[13].

Fig. 6 and 7 shows the plot of the real and the imaginary dielectric constant versus the wavelength for $CdIn_2S_4$ thin film deposited. It is clearly shown that for $CdIn_2S_4$ thin films , the value of first increases with increases of wavelength and remains the same for values . The real and imaginary parts of the dielectric constant provides information about the electronic band structure .

Conclusions

$CdIn_2S_4$ thin films have been deposited by chemical spray pyrolysis technique ,the XRD show that the thin films have polycrystalline phases , the optical band gap calculated between (2.6 to 2.85 eV) for thin films prepared , the extinction coefficient value increased in the visible region with increase wavelength , the films have refractive index equal 2.6 . All thin films prepared show the best optical properties to be used for optoelectronic application .

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Table (1) Comparison of experimental 2θ -values with JCPDS data

Sample	*hkl*	*2θ*	2θ JCPDS	*dÅ*	$E_g(eV)$
$CdIn_2S_4$	[311]	27.2725	27.249	3.26735	2.6
$CdIn_2S_4$:1%Cu	[311]	27.0257	27.249	3.29662	2.65
$CdIn_2S_4$:3%Cu	[311]	26.5816	27.249	3.35068	2.78
$CdIn_2S_4$:5%Cu	----	----	----	----	2.85

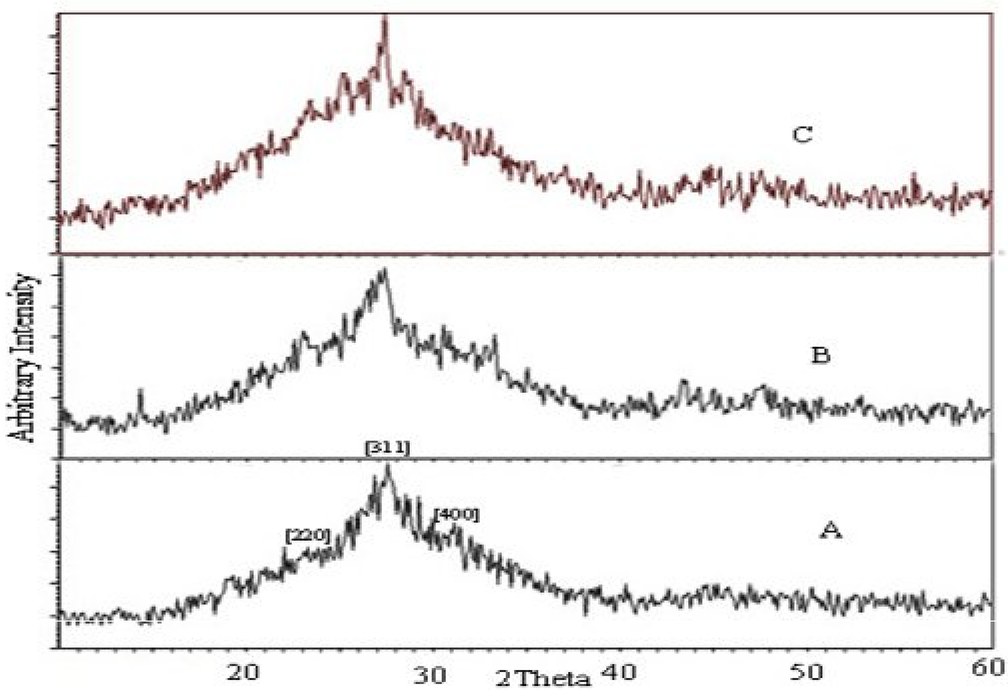

Fig. (1) The XRD pattern of CdIn2S4 thin films(A)without doping, (B)doping 1%Cu,(C)doping 3%Cu

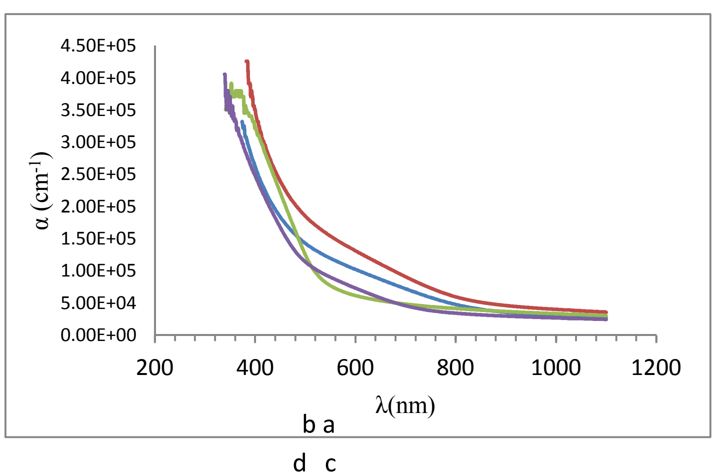

Fig.(2) the varietion of absorbtion coefficient (α)with wavelength (λ) for thin films prepared (a) CdIn2S4 , (b) CdIn2S4:1%Cu,(c) CdIn2S4:3%Cu, (d)CdIn2S4:5%Cu

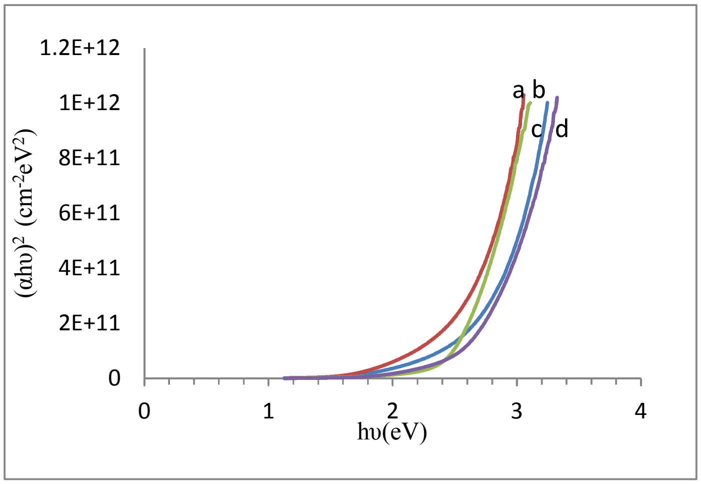

Fig (3) the optical energy gap (Eg) value for thin films prepared (a) CdIn2S4, (b) CdIn2S4:1%Cu, (c)CdIn2S4:3%Cu,(d) CdIn2S4:5%Cu

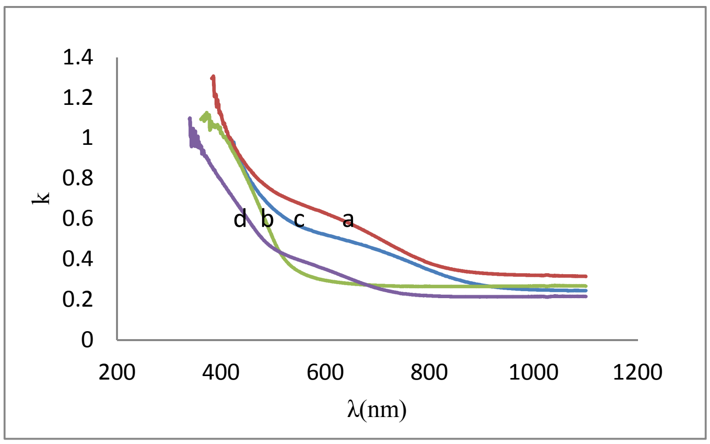

Fig.(4) The varietion of extenction coeficient (k) with wavelength (λ) for thin films prepared (a) CdIn2S4, (b) CdIn2S4:1%Cu, (c)CdIn2S4:3%Cu,(d) CdIn2S4:5%Cu

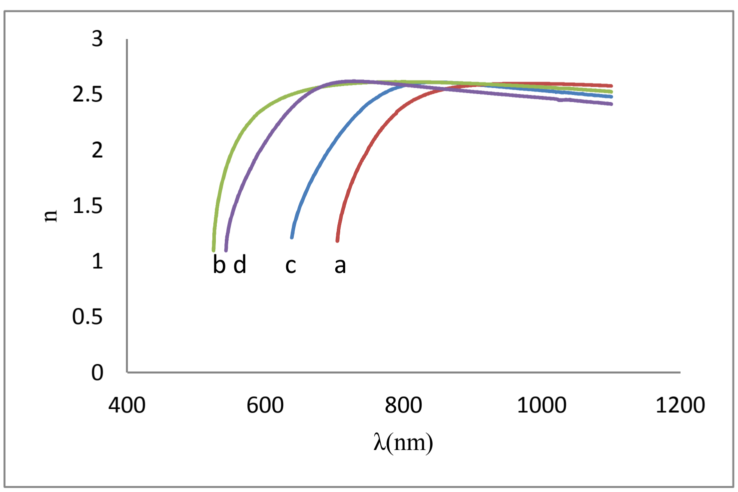

Fig.(5) The varietion of refractive index (n) with wavelength (λ) for thin films prepared (a) CdIn2S4, (b) CdIn2S4:1%Cu, (c)CdIn2S4:3%Cu,(d) CdIn2S4:5%Cu

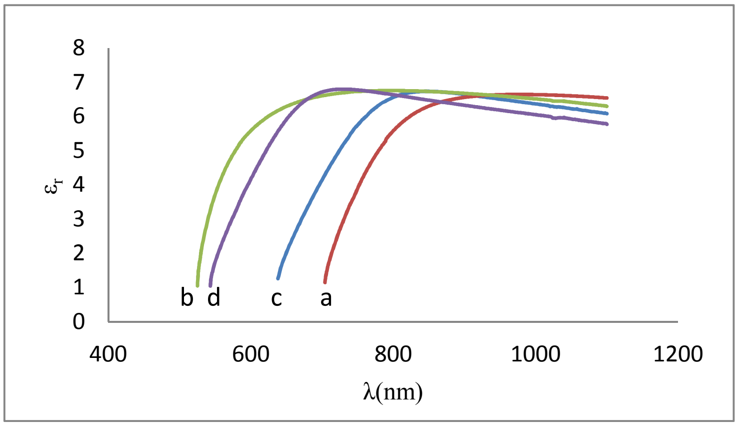

Fig.(6) The varietion of real dielectric constant with wavelength (λ) for thin films prepared (a) CdIn2S4, (b) CdIn2S4:1%Cu, (c)CdIn2S4:3%Cu,(d) CdIn2S4:5%Cu

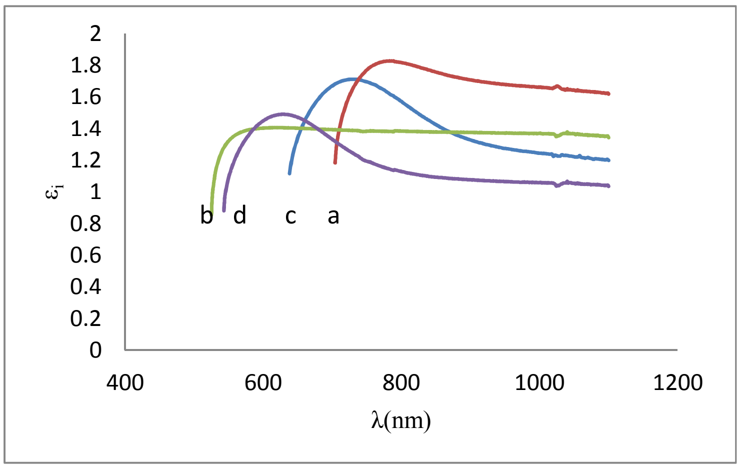

Fig.(7) The variation of imaginary dielectric constant with wavelength (λ) for thin films prepared (a) CdIn2S4, (b) CdIn2S4:1%Cu, (c)CdIn2S4:3%Cu,(d) CdIn2S4:5%Cu

الخواص التركيبيه والبصريه للغشاء الرقيق CdIn2S4:Cu المحضر بطريقه الرش الكيميائي الحراري

علاء احمد الجبوري
E-mail: diehe_1975@yahoo.com

الخلاصه

استخدمت طريقه الرش الكيميائي الحراري لتحضير اغشيه CdIn2S4 الرقيقه على قواعد زجاجيه , وتم تطعيمها بالنحاس لقيم Cu=1%,3%,5% , حيث تم دراسه الخواص التركيبيه لها باستخدام حيود الاشعه السينيه. واظهرت ان جميع الاغشيه المحضرة هي ذات تركيب بلوري متعدد , وكذلك تم دراسه الخواص البصريه وذلك من حساب الامتصاصيه بالنسبه للطول الموجي باستخدام مطياف UV-VIS ومنه تم حساب معامل الامتصاص حيث ظهرت قيمته اكبر من 410 اي ان الانتقال هو انتقال مباشر وكذلك تم حساب فجوة الطاقه البصريه وكانت تتراوح من 2.6eV للغشاء CdIn2S4 قبل التطعيم الى 2.85eV للغشاء CdIn2S4:5%Cu . وتم حساب الثوابت البصريه الاخرى (معامل الانكسار , معامل الخمود وثابت العزل الحقيقي والخيالي) للاغشيه المحضره.