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Structural and optical properties of Cd0.7 Zn0.3S:Pb Nanocrystalline thin films deposited by chemical bath technique.

Jamal. F. Mohammad **Alaa A. AL- Jubory** **Mahir N. Thameel** **Qayes. A. Abbas**

University of Anbar, College of education for pure Sciences.

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ABSTRACT

Nanocrystalline Cd0.7 Zn0.3S:Pb thin films were deposited on glass substrates by chemical bath technique (CBD) at 80±2ºC from an aqueous bath containing cadmium chloride, zinc chloride , thiourea and doped lead chloride in the presence of ammonia solution . Structural properties of the obtained films were studied by X-ray diffraction analysis. The structural parameters such as crystallite size have been evaluated. .The absorption spectra are recorded in the wavelength range 200 - 1100 nm which show Optical spectroscopy results of the films indicated that the optical band gap value decreased from 2.95 to 2.1 eV with the increasing of Pb doping. And finally the optical constants such as refractive index, extinction coefficient, real and imaginary dielectrics were investigated.

Introduction

Nanocrystalline semiconductors of group II-VI have potential applications in many technical fields, including photoluminescence, solar cells and photovoltaic applications [1].

The ternary compound Cadmium Zinc Sulphide ($Cd_xZn_{1-x}S$) have been mostly extensively investigated as important candidate for wide band gap material[2,3].

$Cd_xZn_{1-x}S$ alloy compounds have attracted technological interest because the energy gap can be tuned and the lattice parameters can be varied[4]. $Cd_xZn_{1-x}S$ compound has a band gap between CdS (2.42 eV) and ZnS (3.66 eV) and the value of the band gap depends onto Cd an Zn ratio [5].

Addition of Zn to the most widely used CdS buffer layer material enhances the electronic and optical properties of optoelectronic devices[6]. In solar cell systems, where CdS films have been demonstrated to be effective, the replacement of CdS with the higher band gap $Cd_xZn_{1-x}S$ alloys has led to a decrease in window absorption loss and an increase in the short circuit current [7,8].

The ternary n-type $Cd_xZn_{1-x}S$ compounds have been used as a window layer to form heterojunction solar cell with different p-type materials such as Si, Cu_xS, $CuInSe_2$, $CuGaSe_2$, $Cu(In,Ga)Se_2$ (CIGS) and CdTe [9]. In this work, nanocrystalline **$Cd_{0.7}Zn_{0.3}S$:Pb** thin films were deposited on glass substrates by chemical bath technique (CBD) at 80±2ºC.

Experimental

$Cd_{0.7}$ $Zn_{0.3}S$:Pb thin films were deposited on glass slides using the CBD technique. A bath containing 0.1 M solutions of lead nitrate, cadmium chloride , zinc chloride , and thiourea was developed, and the pH of the solution was adjusted to 10 by addition of NH_4OH. Glass slides were cleaned using liquid detergent in an ultrasonic bath, dipped into a chromic acid bath for 2 h at room temperature, washed

* Corresponding author at: University of Anbar, College of education for pure Sciences. E-mail address:

with distilled water and acetone, and then dried. The glass substrates were immersed vertically in the reaction vessel, and the bath was set to the desired temperature. Deposition was carried out at 70 °C for 120 min, and the slides were left in the bath for 24 h at room temperature. The deposited films were then washed with distilled water and dried in air. The crystallinity phase and orientation of the $Cd_{0.7}$ $Zn_{0.3}S$:Pb films were determined by XRD using a Philips PW 1840 instrument with a Cu-Kα target. A UV-Vis spectrophotometer (Jenway 6800) was used to measure the absorbance and transmittance of the films in the wavelength (λ) range from 300 nm to1100 nm; optical parameters were calculated from these measurements.

Result and discussion

X-ray diffractions

XRD patterns of $Cd_{0.7}$ $Zn_{0.3}S$ thin films with doping by Pb are shown in Fig.1 .All the patterns of thin films prepared are polycrystalline with peak (2θ)=(26.3826) corresponding to (hkl) = (0 0 2) as given in table 1. The value of 2θ increase from 26.3826 without doping to 26.98327 with doping with 5%Pb . The grain size was calculated from (0 0 2) peaks of XRD pattern by using Scherrer formula [10]. The grain size is varied in the range 3–7 nm. The variation of grain size is not linear with the composition.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where k=0.94, λ is the wavelength of X-ray, b is the full width at half the peak maximum in radians and θ is Bragg's angle.

Table 1: XRD patterns of $Cd_{0.7}$ $Zn_{0.3}S$ thin films with doping by Pb

No.	Sampale	2θ	hkl	P.S. (nm)
a	$Cd_{0.7}Zn_{0.3}S$	26.3826	0 0 2	3
b	$Cd_{0.7}Zn_{0.3}S$:1%Pb	26.6808	0 0 2	7
c	$Cd_{0.7}Zn_{0.3}S$:3%Pb	26.9441	0 0 2	4
d	$Cd_{0.7}Zn_{0.3}S$:5%Pb	26.98327	0 0 2	4

Optical Studies

The optical absorption of the films has been studied in the range (300- 1100 nm). Absorption coefficient associated with the strong absorption region of the films was calculated from absorbance (A) and the film thickness (t) using the relation [11].

$$\alpha = \frac{2.303A}{t} \quad \ldots\ldots\ldots\ldots\ldots 2$$

where t is the film thickness.

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. The optical band gap E_g of thin films prepared was calculated by using the following formula [11].

$$\alpha h\upsilon = A(h\upsilon - Eg)^m \ldots\ldots\ldots\ldots \mathbf{3}$$

where A is constant , hυ is the incident photon energy , and m is a factor whose value dependent on the nature of band transition ,m=(1/2) or (3/2) for direct allowed and direct forbidden transition. From fig.3. It is clear that the value of E_g decreases from 2.95eV for $Cd_{0.7}Zn_{0.3}S$ thin film to 2.1 eV for $Cd_{0.7}Zn_{0.3}S$:5%Pb due to increasing in film thickness as shown in table 2.

Table 2: Varying of Eg for Cd0.7Zn0.3S thin films.

No.	Sampale	E_g (eV)
a	$Cd_{0.7}Zn_{0.3}S$	2.9
b	$Cd_{0.7}Zn_{0.3}S$:1%Pb	2.49
c	$Cd_{0.7}Zn_{0.3}S$:3%Pb	2.195
d	$Cd_{0.7}Zn_{0.3}S$:5%Pb	2.1

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

$$k = \frac{a\lambda}{4\pi} \ldots\ldots\ldots\ldots 4$$

Fig.4 show the spectral dependence of extinction coefficient (k) for $Cd_{0.7}Zn_{0.3}S$ thin films . The value of extinction coefficient (k) decreases with increase in the wavelength . The refractive index (n) of thin films can be calculated from their reflectance and transmittance spectra using simple approximations relation [12].

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - K^2\right]^{\frac{1}{2}} \dots\dots 5$$

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. It can be seen that n increases as wavelength increases as shown in fig. 5.

Real and imaginary parts of dielectric constants were determined using the following equations [11].

$$\varepsilon_1 = n^2 - k^2 \quad \dots\dots 6$$
$$\varepsilon_2 = 2nk \quad \dots\dots 7$$

Where ε_1 and ε_2 is the real and imaginary dielectric constant respectively .The plots of (ε_1) and (ε_2) of thin films are illustrated in figures (6 and 7) respectively , from fig.6 the variation of ε_1 is follow the refractive index.

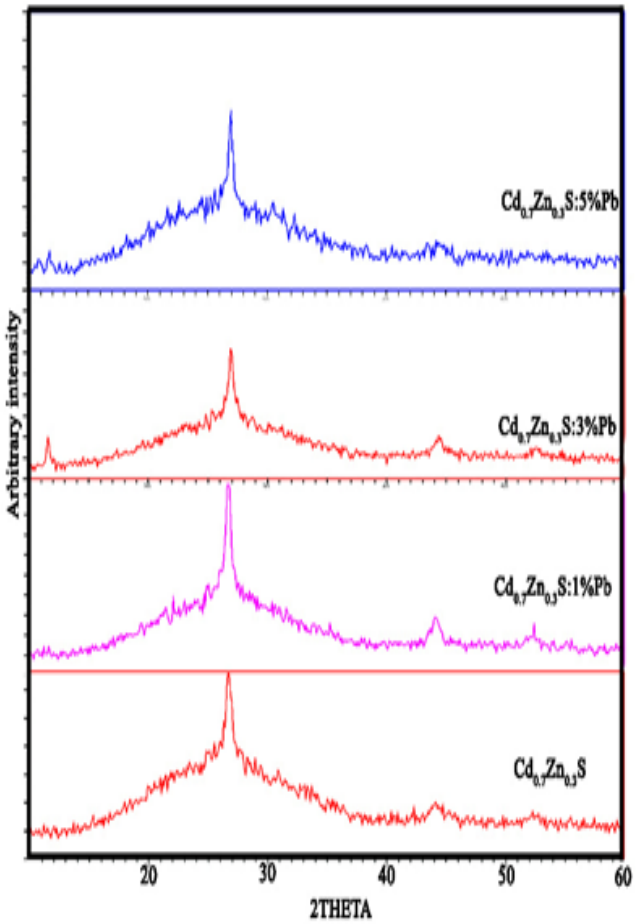

Fig. (1) The XRD pattern of thin films prepared

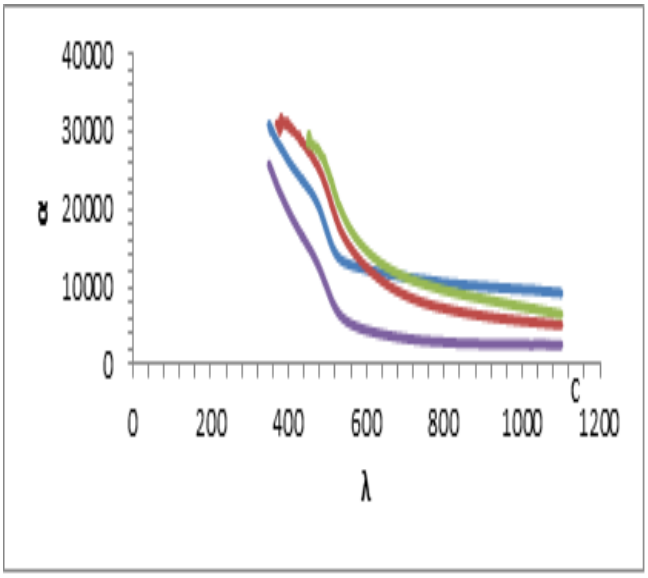

Fig.(2) the varietion of absorbtion coefficient (α)with wavelength (λ) for thin films prepared (a) Cd0.7Zn0.3S , (b) Cd0.7Zn0.3S:1%Pb,(c) Cd0.7Zn0.3S:3%Pb (d) Cd0.7Zn0.3S:5%Pb

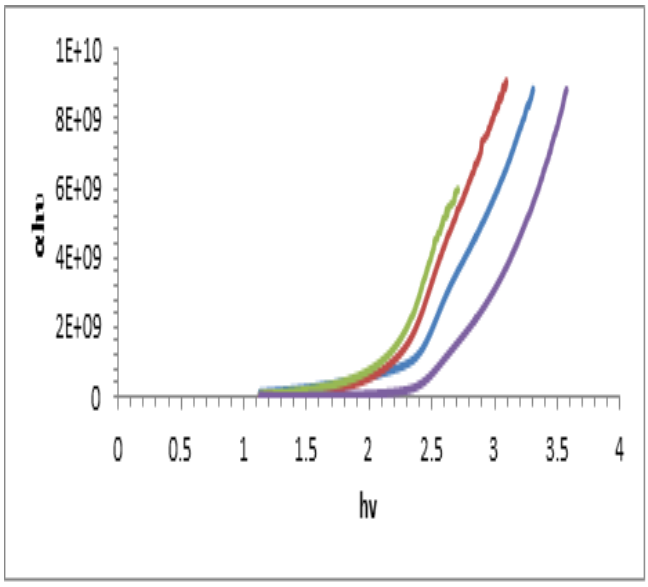

Fig (3) the optical energy gap (Eg) value for thin films prepared (a) Cd0.7Zn0.3S, (b) Cd0.7Zn0.3S:1%Pb,(c) Cd0.7Zn0.3S:3%Pb, (d) Cd0.7Zn0.3S:5%Pb

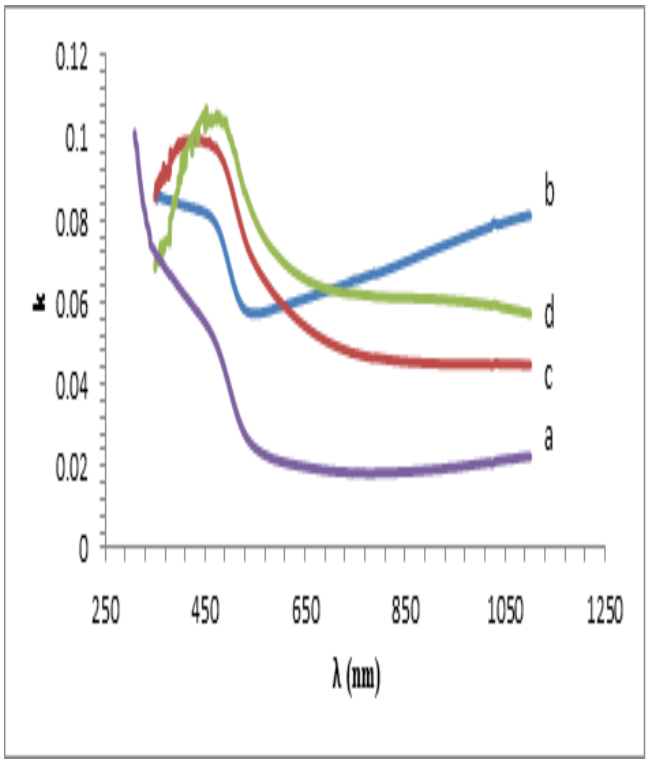

Fig.(4) The varietion of extenction coeficient (k) with wavelength (λ) for thin films prepared (a) Cd0.7Zn0.3S , (b) Cd0.7Zn0.3S:1%Pb,(c) Cd0.7Zn0.3S:3%Pb, (d) Cd0.7Zn0.3S:5%Pb

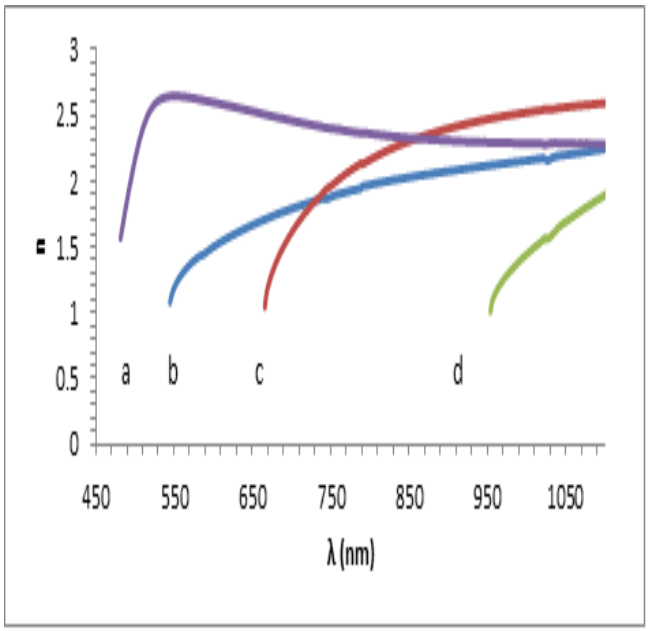

Fig.(5) The varietion of refractive index (n) with wavelength (λ) for thin films prepared (a) Cd0.7Zn0.3S , (b) Cd0.7Zn0.3S:1%Pb,(c) Cd0.7Zn0.3S:3%Pb, (d) Cd0.7Zn0.3S:5%Pb

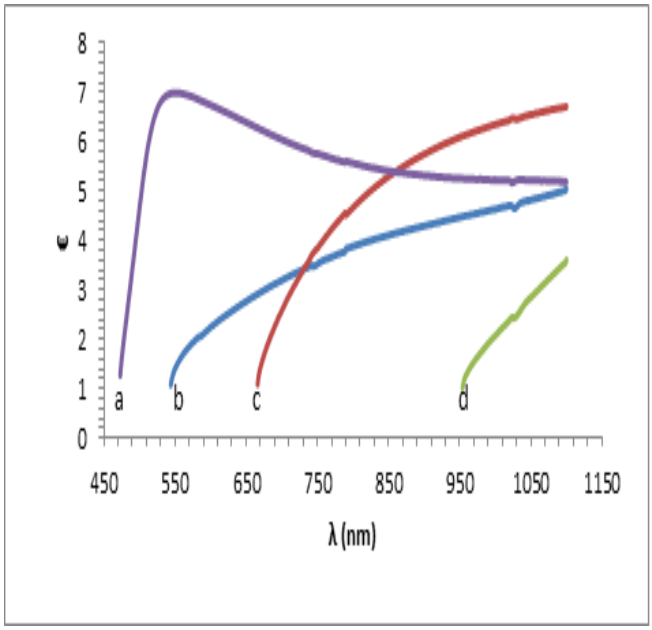

Fig.(6) The varietion of real dielectric constant with wavelength (λ) for thin films prepared (a) Cd0.7Zn0.3S , (b) Cd0.7Zn0.3S:1%Pb,(c) Cd0.7Zn0.3S:3%Pb, (d) Cd0.7Zn0.3S:5%Pb

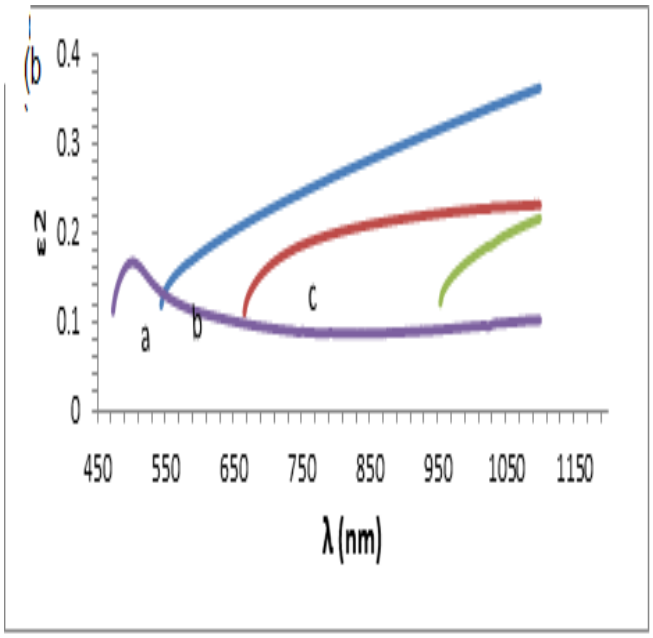

Fig.(7) The variation of imaginary dielectric constant with wavelength (λ) for thin films prepared (a) Cd0.7Zn0.3S , (b) Cd0.7Zn0.3S:1%Pb,(c) Cd0.7Zn0.3S:3%Pb, (d) Cd0.7Zn0.3S:5%Pb

Conclusion

$Cd_{1-x}Zn_xS$ films were deposited on glass substrate at a temperature of 80±2°C and a pH=10 doping with Pb at different concentration by using chemical bath deposition technique (CBD). The prepared films were homogenous and good adherent to the substrate. CBD is useful for deposition of nanocrystalline thin films for solar cells application. It has been observed that good quality films can be prepared by CBD method. The structure of the thin films is hexagonal, which has very strong preferential orientation along the (002) plane. Optical energy bandgap characteristics have been studied.

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Cd0.7 Zn0.3S:Pb الخصائص التركيبية والبصرية لأغشية المركب ذات التركيب النانوي المحضرة بتقنية الحوض الكيميائي

جمال فاضل محمد علاء أحمد دايح ماهر نوري ثميل قيس عبدالله عباس

الخلاصة

تم ترسيب الأغشية الرقيقة ذات التركيب النانوي للمركب الثلاثي المطعم بالرصاص Cd0.7 Zn0.3S:Pb على أرضيات زجاجية بتقنية الحوض الكيميائي عند درجة حرارة ٨٠ سيليزية باستخدام كل من كلوريد الكادميوم، كلوريد الخارصين والثايوريا والمطعم بكلوريد الرصاص مع استخدام محلول الأمونيا. الخصائص التركيبية للأغشية المحضرة تم دراستها باستخدام حيود الأشعة السينية ومن خلالها تم حساب الحجم الحبيبي، أما الخصائص البصرية مثل معامل الامتصاص، معامل الانكسار، معامل الخمود وثابت العزل الكهربائي فتمت دراستها ضمن المدى الطيفي ٢٠٠- ١١٠٠ نانومتر حيث أظهرت النتائج إن فجوة الطاقة البصرية للأغشية المحضرة تتناقص من ٢,٩٥ الى ٢,١ إلكترون فولت مع زيادة نسبة التشويب بالرصاص.