P- ISSN 1991-8941 E-ISSN 2706-6703 Journal of University of Anbar for Pure Science (JUAPS) Open Access
2009,(3), (3) :59-68

The effect of Cd substitution in PbS thin film on the optical properties

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ARTICLE INFO

Received: 19 / 5 /2022
Accepted: 28 / 5 /2022
Available online: 14/6/2012
DOI: 10.37652/juaps.2009.15541

Keywords:
Cd substitution ,
PbS thin film ,
optical properties.

ABSTRACT

Thin films of CdxPb1-x S were prepared by chemical spray pyrolysis with (x=0.6, 0.7, 0.8, 0.9, 1).The optical properties of prepared thin films were studied by UV-VIS spectrophotomer . From the measurement of absorption and transmission, the optical parameters and the optical energy gap (Eg) were calculated. The optical energy gap (Eg) was increased with increasing the value of Cd from 1.2 eV when x=0.6 to 2.4 eV when x=1. The maximum value of refractive index (n) is equal to 2.5 and the maximum value of extinction coefficient is varied between 0.2 to 0.45 depending on the value of x. The film with x=0.7 was doped by Ag in the ratio 1%,3% and 5% . The film after dopping have a direct energy gap also and the value of Eg were increased with increasing (Ag) ratio, these values increased from 1.2 eV for absent Ag to 1.74 eV for 5% Ag.

Introduction

Metal chalcogenides (sulfides, tellurides and selenides) are of great importance for researchers because they are potential candidates for optoelectronic applications such as photodetectors, solar cells, thin film transistors etc[1-3]. Chalcogenide glassy semiconductors have several useful properties that show a continuous change in physical properties with change in chemical composition. Chemical bonds determine the structures and all the properties of a body in any state of aggregation[4]. CdS nanocrystalline thin films belonging to the cadmium chalcogenide family[5]. It have (Eg = 2.4 eV) and hexagonal structure there make it to use as window material together with several semiconductors[1,5]. Lead sulfide (PbS) is a semiconducting chalcogenide with a direct bandgap of 0.41 eV and has a cubic structure. PbS thin films are widely used in IR detectors [6].

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Many techniques have been reported for the deposition of chalcogenide thin films. These include evaporation, sputtering, chemical bath deposition, spray pyrolysis, metal organic chemical vapour deposition molecular beam epitaxy (MBE) technique, electro-deposition, photochemical deposition etc[1-7]. Among the various thin film deposition technique, spray pyrolysis is one of the principle method used to produce a large area and uniform coating [8]. Due to their optical, electrical and photoelectrical properties, PbS and CdS thin films have a large spectrum of applications in optoelectronics, chemistry (as tempera- ture , gas or humidity sensors or catalysts) or as solar control coatings etc[6,9]. In this study, we prepared a thin film of CdxPb1-x S and discussed its optical properties.

Experimental

Cd substitution in PbS thin films, were prepared using the chemical spray pyrolysis method. The films deposited on micro glass slides which were first, cleaned with distilled water, and then dipping in acetone. spray solution are prepared by mixing ,0.1 M aqueous solution of Pb(NO3)2 , 0.1 M CdCl2 , 0.1 M thiourea CS(NH2)2, and 0.1 M Ag(NO3) for dopping. Then mixed the amount of solution for each experiment by a magnetic stirrer. We used air for spraying the solution on a square slide glass at a temperature 300 oC. The film thickness was measurement by optical method. The UV-VIS spectrophoto- meters type HITACHI was used to measure the absorptance and transmittance and then from these measurements, the optical parameters were calculated.

Result and discussion

The absorption coefficient (α) of the CdxPb1-x S thin film were found from the following relation [11]

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

Where A is the absorbance and t is the film thickness. Fig. (1) show the plot of α vs. λ for films of x = 0.6-1 , this figure obtained that the value of α > 104cm-1 for all films , this means that the transition must corresponding to a direct electronic transition [8], and the properties of this state are important since they are responsible for electrical conduction . Also fig. (1) shows that the absorption coefficient edge of the film depends on the value of x, where at x ≥ 0.8, α edge is appears and it shifted towered long wavelength with increasing x. But when x<0.8 no there is edge for α in the spectrum and it is in a NIR wavelength , this is agree with which found by Popescu [10] ,that at mixed PbS and CdS thin films when Pb content is high determined important changes in the NIR spectrum and we found that α decreased almost linearly with the increasing of wavelength (λ).

The optical energy gap (Eg) has been calculated by the relation [5].

$$(\alpha hv)^2 = A\left(hv - E_g\right) \ldots\ldots\ldots\ldots\ldots\ldots \quad 2$$

Where A is a constant .

By plotting $(\alpha hv)^2$ vs hv as shown in fig. (2) and by extrapolating the straight line portion of the curve to intercept the energy axis , the value of the energy gap has been calculated [5] .

Fig. (2) obtained that when x increasing Eg was decreased because at x =1 , the compound is CdS having Eg = 2.4 eV [1] , while when x = 0 , the compound is PbS having Eg = 0.41 eV [6] . The values of Eg of the prepared thin films are ranged from $\{1.2 - 2.4\ eV\}$ as shown in table (1). The value of Eg for these set films are given good semiconductor candidate to use for absorbing the visible light to use in an optoelectronic devices.

Table (1) values of E_g at different x for Cd_xPb_{1-x} S thin film

x	0.6	0.7	0.8	0.9	1
E_g (eV)	1.2	1.45	2.22	2.33	2.44

Variation of extinction coefficient (k) as a function of wavelength are shown in fig. (3) which found from following equation [11] .

$$k = \frac{\alpha\lambda}{4\pi} \ldots\ldots\ldots\ldots\ldots\ldots 3$$

It is observed that the spectrum shape of k as the same shape of α. The maximum and the minimum value of k is depend on the x value, to give a maximum value of 0.44 at x = 1 and a minimum value of 0.08 at x = 0.6. The extinction coefficient is directly related to the absorption of light.

Fig. (4) shows variation in refractive index (n) as a function of wavelength . n was found from the following relation [11] .

$$n = \frac{1+R}{1-R} + [\frac{4R}{(1-R)^2} - K^2]^{1/2} \ldots\ldots 4$$

Where R is the reflectivity.

Fig. (5) shows the variation of the real dielectric constant (ε_1) with wavelength of CdxPb1-x S thin film which calculated from the relation [11].

$$\varepsilon_1 = n^2 - k^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots..5$$

Where the real dielectric (ε_1) is the normal dielectric constant. From fig.(5) the variation of ε_1 is depend on the x value and follow the refractive index shape . The maximum value of ε_1 is about 5.5 while the minimum value is about 2.5.

The imaginary dielectric constant (ε_2) vs λ was shown in fig. (6). this value calculated from the relation [11].

ε2 = 2nk……………6

ε2 represent the absorption associated with free carriers [1]. As shown in fig. (6). the shape of ε2 is the same as ε1 this means that the refractive index was dominated in these behavior and the effect of free carrier absorption is small.

The film of Cd0.7Pb0.3S was doped by Ag element in order to found desirable optical band gap in this range of x. Fig.(7) shows α vs. λ with 1,3,5 wt% Ag , from this figure the value of α > 104 cm-1 so the film is also a direct electronic transition type , and α give a better properties after dopping by Ag .

The optical energy gap of Cd0.7Pb0.3S thin film which doped by Ag was shown in fig. (8). From this figure and by comparison between undoped film and doped film, one observe that the Eg of doped film was increased from 1.45 eV for undoped film to reach 1.74 eV for film doped with 5 wt % Ag. This increases in Eg may be related to substitute Ag atom instead of Cd or Pb atoms and may became an acceptor atoms which may be decrease the local states in the band gap, then increase the energy gap. According to Table (1), the value of Eg = 1.45 eV when x=0.7 while Eg = 2.22 eV when x =0.8, so this gap between them can be increased gradually by doping with Ag element. As shown in Table 2 .

Table (2) E_g value for $Cd_{0.7}Pb_{0.3}S$ thin film doped with Ag.

Ag Wt%	0	1	3	5
E_g (eV)	1.45	1.68	1.71	1.74

The extinction coefficient (k) of the doped film was increased with wavelength in the range λ > 600 nm as shown in fig. (9) this means the absorption of doped film in this region was higher than that undoped film. The refractive index (n) of doped film was shown in fig. (10). this obtain that the value of (n) in the visible region have nearly the same value of undoped film and decrease with wavelength also .This means that may be the structure of the film does not change with doping. The maximum value of n equal 2.55 which is in the range of chalcogenide films [1].

Figure (11) and (12) obtained the real ε1 and imaginary ε2 dielectric respectively for doped thin film by Ag. The comparession between graph of doped and undoped films, shows the behaviors are different due to dopping. The ε1 values are in general decreased with λ for dopent thin film, but its maximum value dos not dopend on Ag content linearly.

Conclusion

Cd_xPb_{1-x} S thin films have been prepared by spray pyrolysis method. The optical properties obtained that the films has good properties for optoelectronic applications .The optical energy gap of direct transition changed from 1.2 eV to 2.44 eV with x= 0.6 to x= 1 respectively. The dopping by Ag element increases the energy gap and give a good optical property parameters for the $Cd_{0.7}Pb_{0.3}S$ thin film. While ε2 values increases with λ in general for dopent thin films .This means that absorption associated with free carriers increases with dopent by Ag metal.

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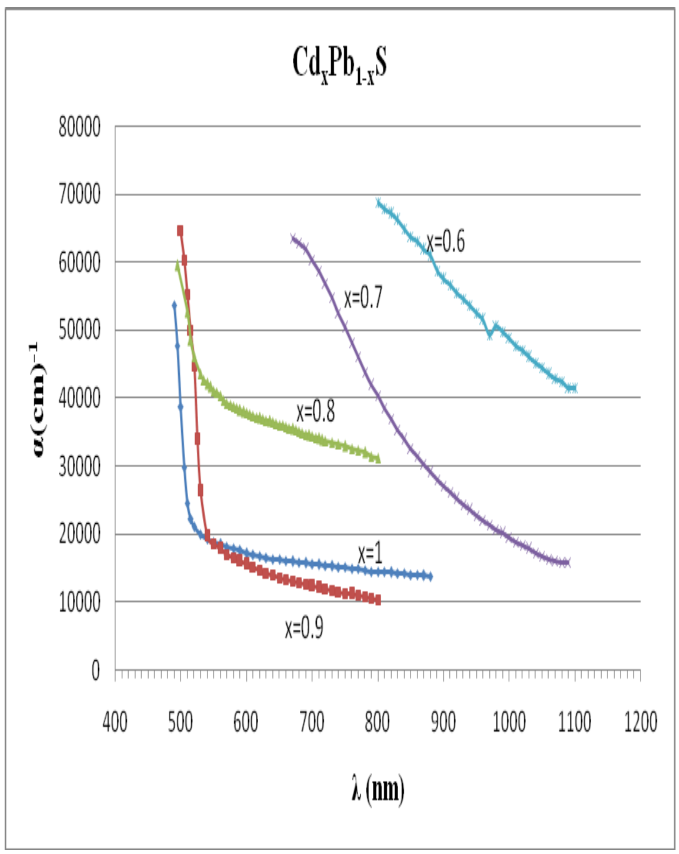

Fig. (1) plot of absorption coefficient vs. wavelength for prepared thin films.

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2009,(3), (3) :59-68

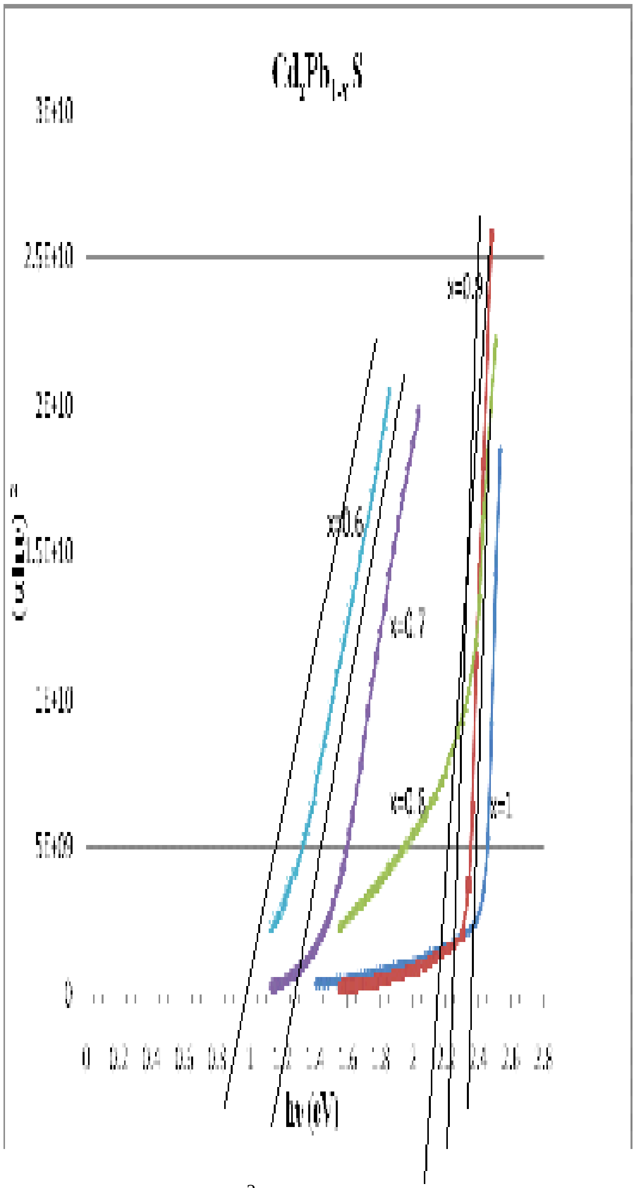

Fig. (2) plot of $(\alpha h\nu)^2$ vs. hν for prepared thin films.

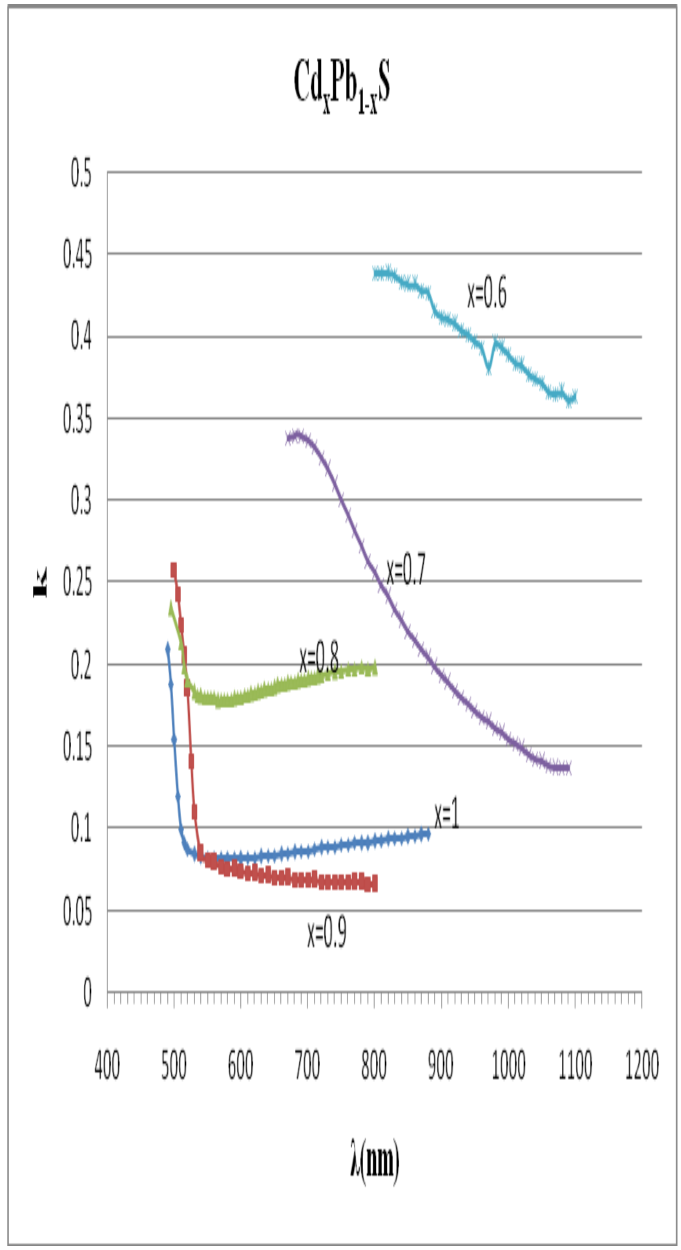

Fig. (3) plot of extinction coefficient vs. wavelength for prepared thin films .

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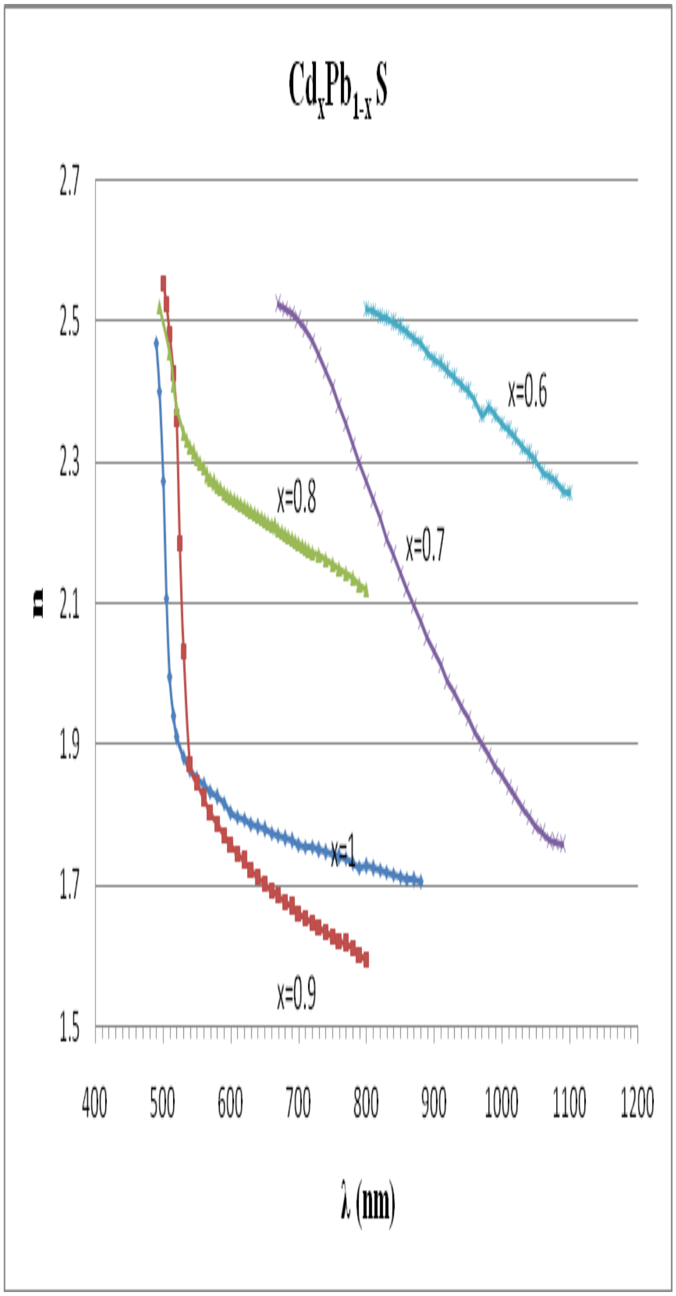

Fig. (4) plot of refractive index vs. wavelength for prepared thin films.

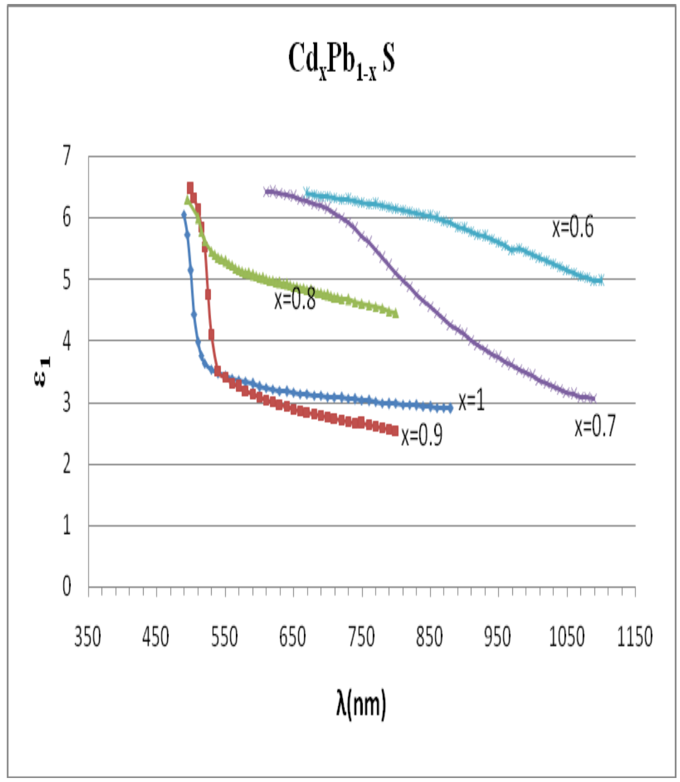

Fig. (5) real dielectric constant vs. wavelength for prepared thin films.

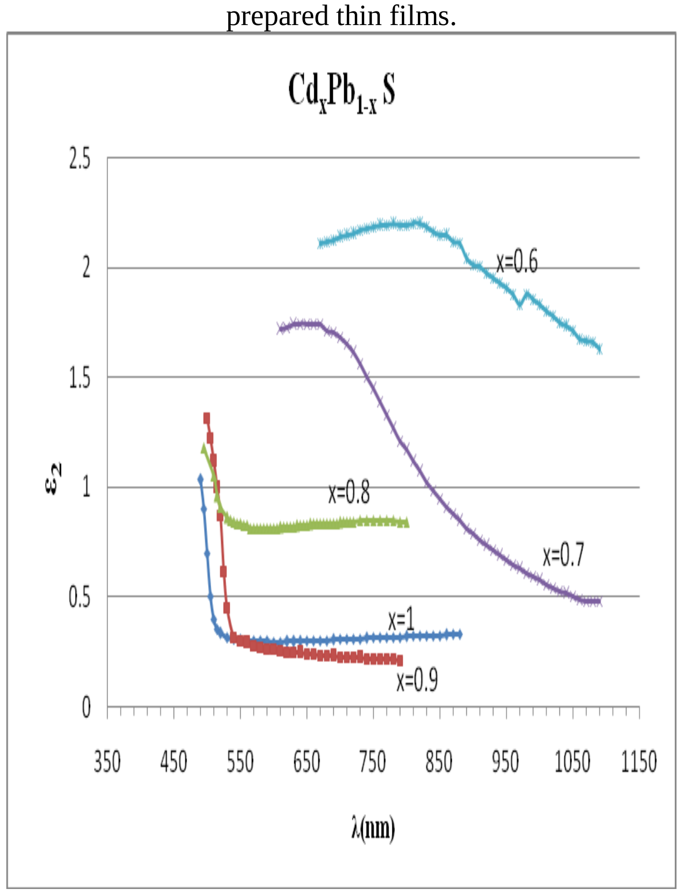

Fig. (6) imaging dielectric constant vs. wavelength for prepared thin films.

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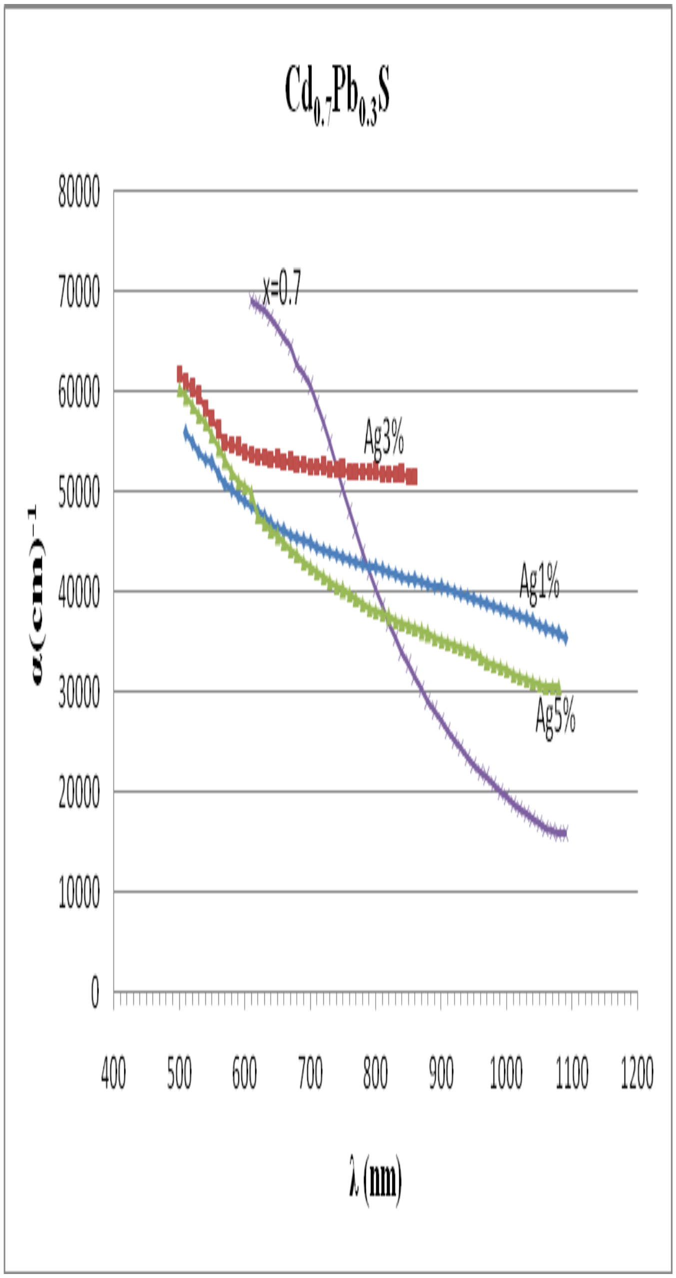

Fig. (7) plot of absorption coefficient vs. wavelength with Ag dopping at x=0.7

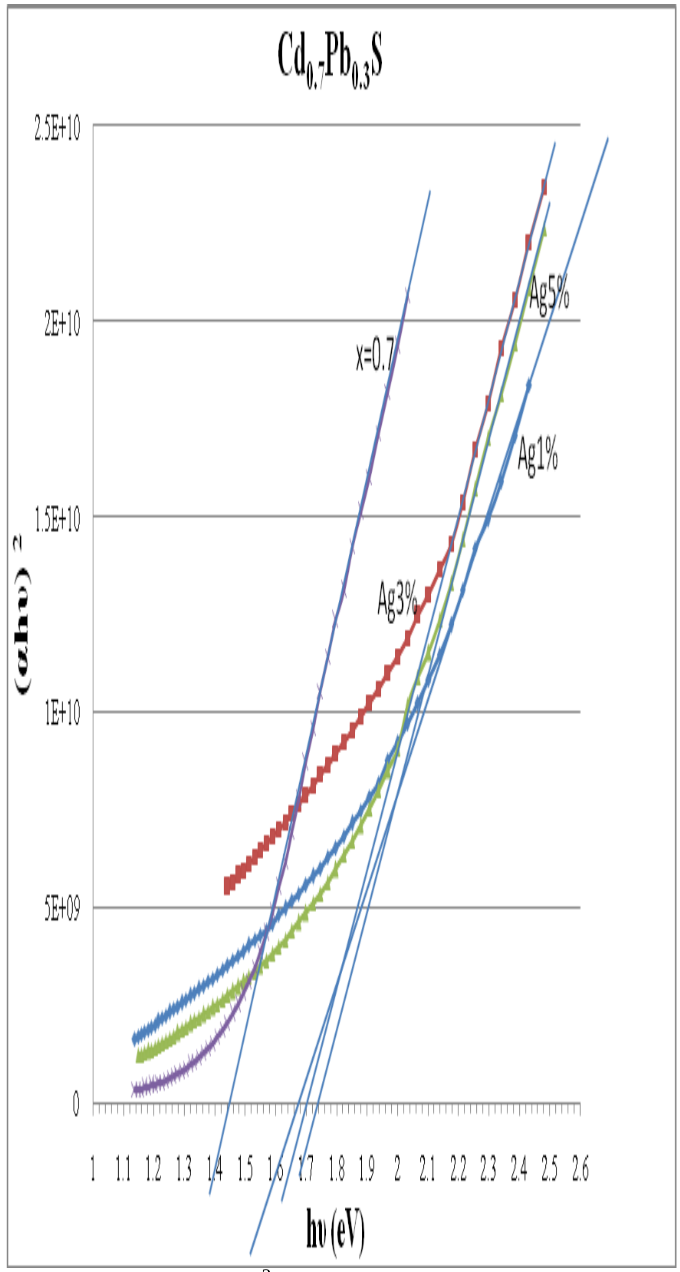

Fig. (8) plot of $(\alpha h\nu)^2$ vs. hν with Ag dopping at x=0.7

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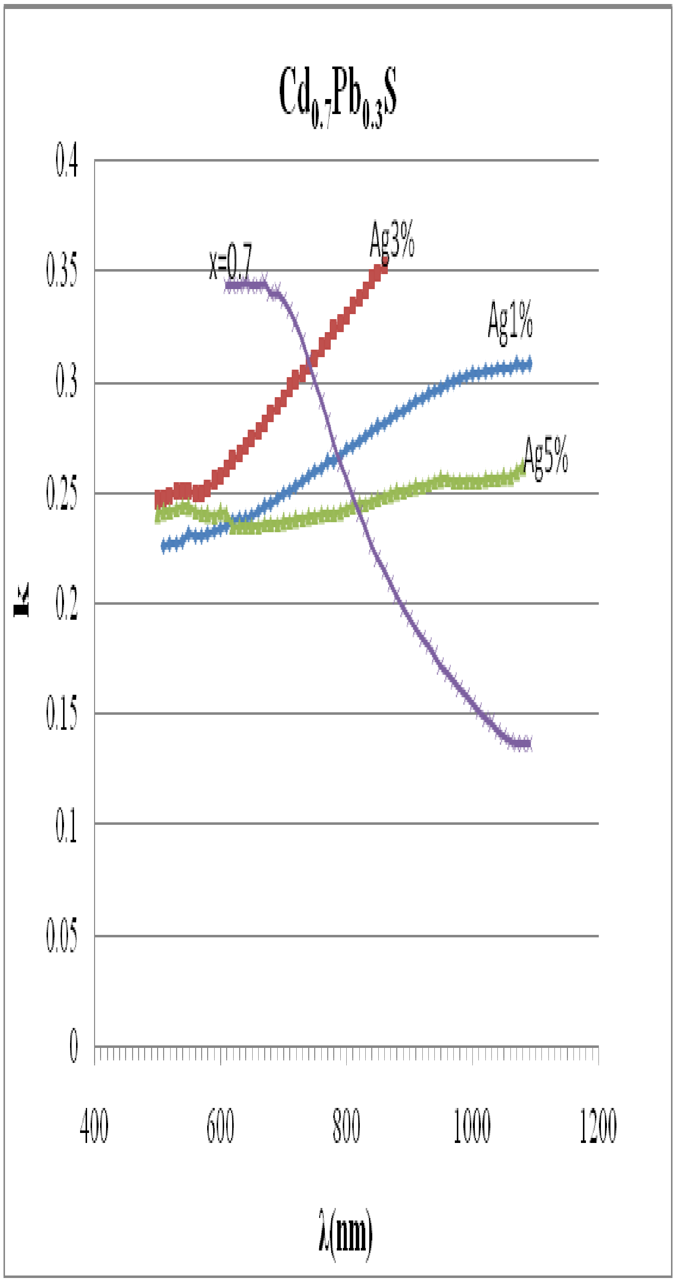

Fig. (9) extinction coefficient vs. wavelength with Ag dopping at x=0.7

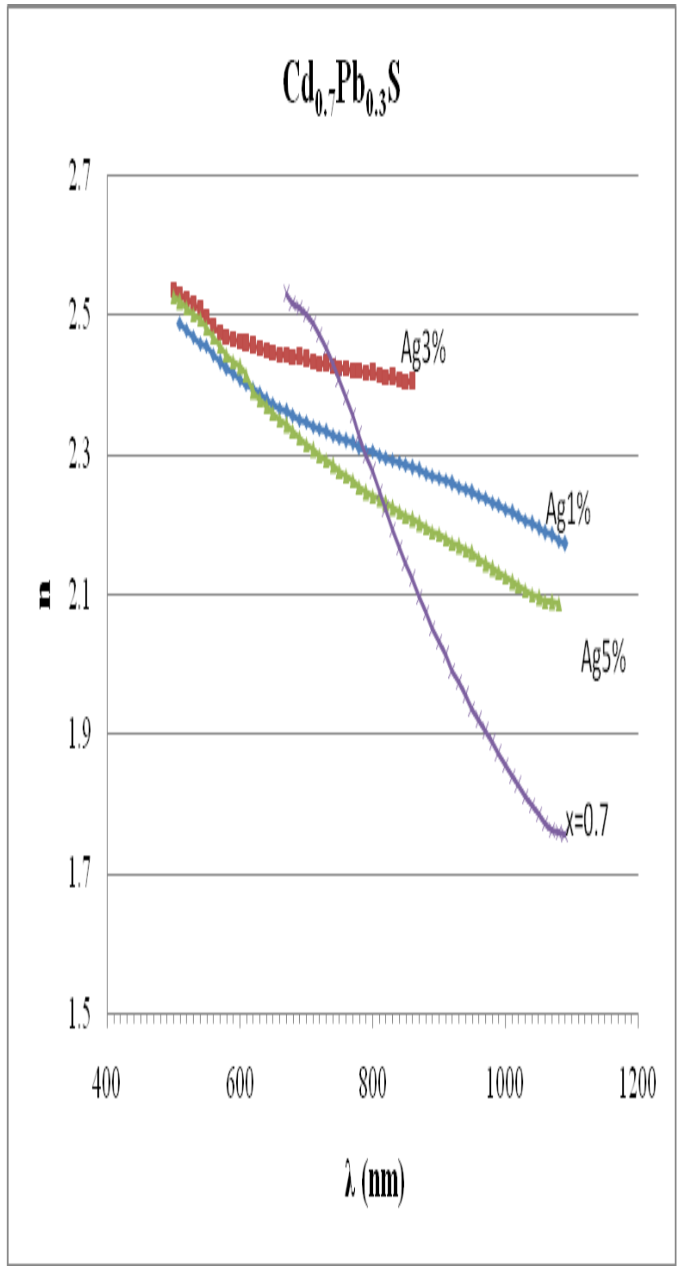

Fig. (10) refractive index vs. wavelength with Ag dopping at x=0.7

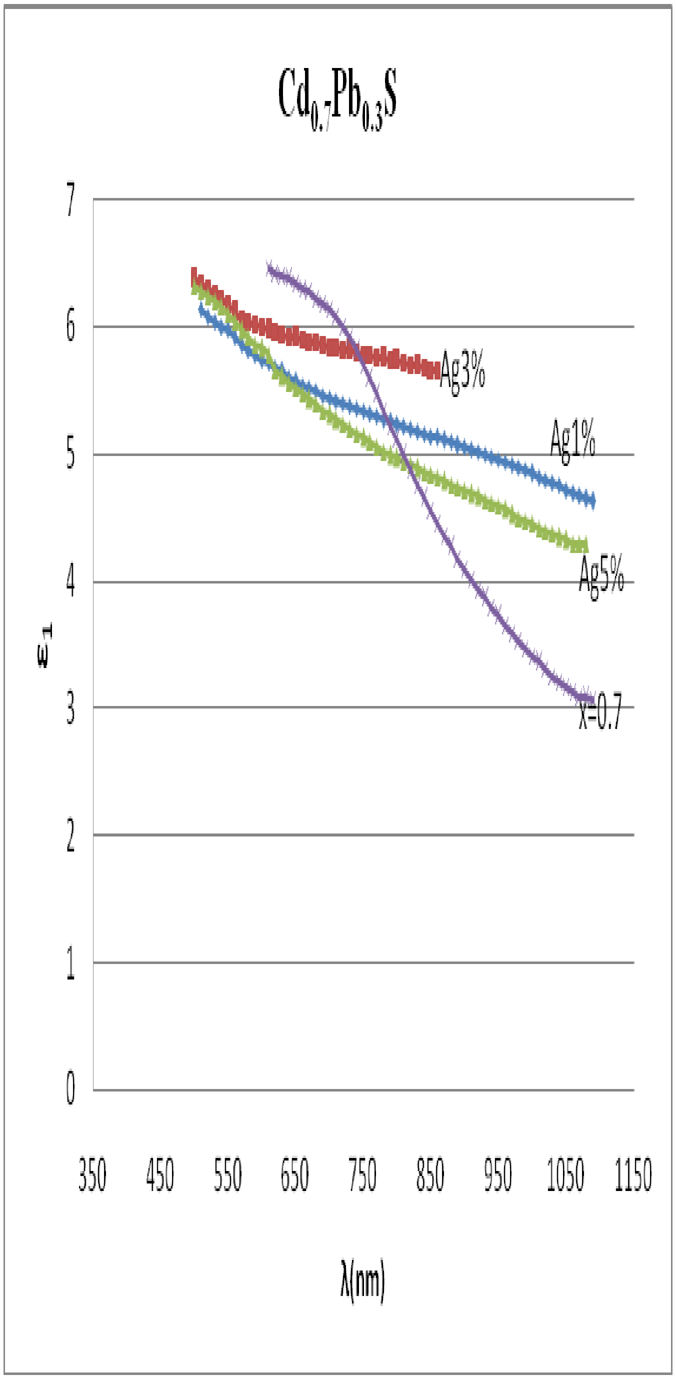

Fig. (11) real dielectric constant (ε_1)vs. wavelength for Ag dopping at x=0.7

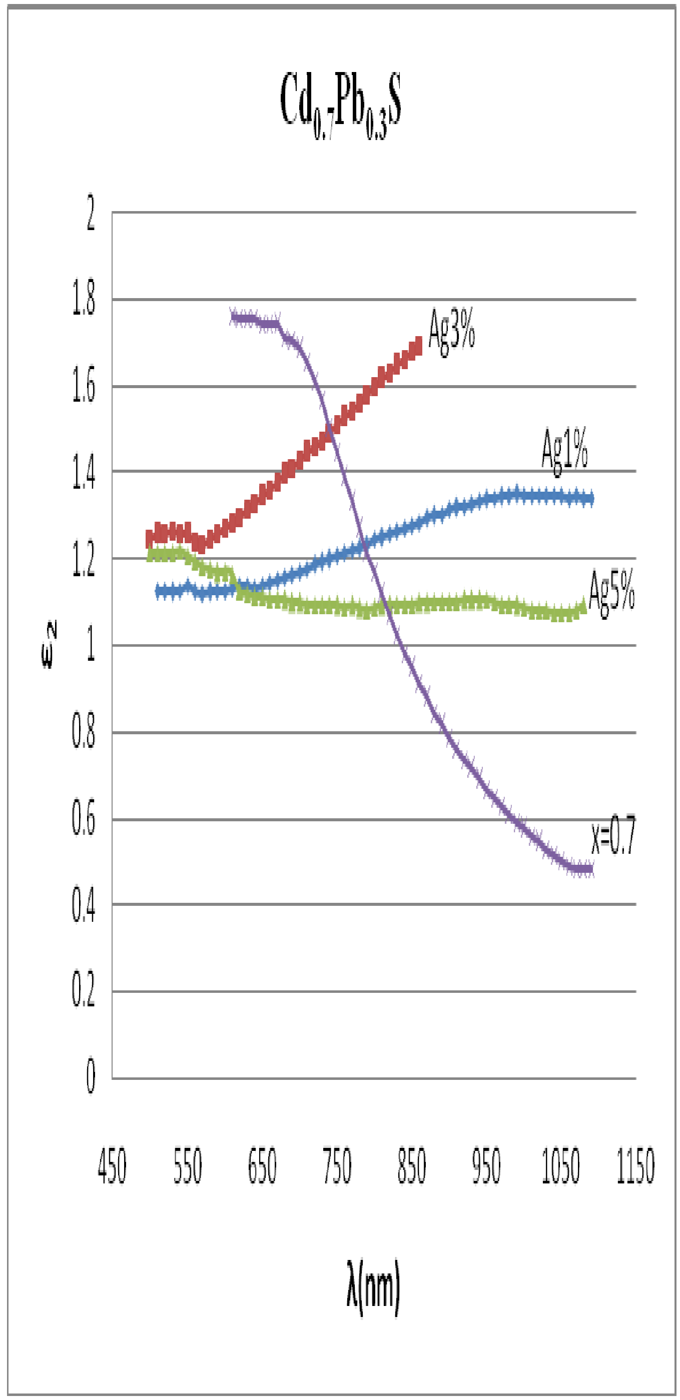

Fig. (12) imaginary dielectric constant (ε_2) vs. wavelength for Ag dopping at x=0.7

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2009,(3), (3) :59-68

تأثير استبدال الكادميوم Cd على الخواص البصرية للغشاء الرقيق PbS

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الخلاصة

تم تحضير اغشية رقيقة من CdxPb1-xS بطريقة الرش الكيميائي الحراري لقيم x = 0.6,0.7,0.8,0.9,1 . وقد درست الخواص البصرية للاغشية المحضرة باستخدام مطياف UV-VIS. من قياسات طيف الامتصاصية والنفاذية تم حساب الثوابت البصرية وفجوة الطاقة البصرية Eg. حيث كانت قيمة فجوة الطاقة البصرية تزداد بزيادة نسبة الكادميوم Cd من 1.2 eVعندما x=0.6 الى 2.44 عندما x=1. وقد وجد ان اعلى قيمة لمعامل الانكسار (n) تساوي 2.5 ، وكذلك فان قيمة معامل الخمود k تتغير بين 0.2 الى 0.45 معتمدة على قيمة x . تم تطعيم الغشاء عند قيمة x = 0.7 بعنصر الفضة وبنسب 1,3,5wt%. وقد وجد ان الغشاء بعد تطعيمه يمتلك فجوة طاقة مباشرة تزداد بزيادة نسبة الفضة هذا القيمة تزداد من 1.2 eV في حالة غياب الفضة الى 1.74 eV عندما تكون نسبة الفضة 5%.