

The Effect of doping on the optical properties of CdS thin films prepared by spray pyrolysis

ADNAN M. AL-SAEEDI

Physics Department, College Science, Karbala University, Iraq

Abstract:

In this search , Cadmium sulphide (CdS) thin films were prepared by the chemical spray pyrolysis technique , films of (CdS) have been prepared as pure and doped by Copper (Cu) with different ratio (2%,4%).The films were deposited on glass slide from aqueous solutions cadmium chloride – $CdCl_2 \cdot 2H_2O$, thiourea - $SC(NH_2)_2$ with molar ratio (0.05) at substrate temperature ($300^{\circ}C$). The topographic properties of the surface thin films which are prepared by reflective optical microscope. As a consequence, the optical parameters of the films were determined by using spectrometer type (SHEMATZU), The optical properties were studied for range of wave length (300-1100nm).Transmission were (89%-83%), this ratio is depended on thickness and doping ratio of the films, where as transmission proportion reversely with increasing doping .The absorption coefficient is determined and correlated with the photon energy in order to estimate the direct transition energy band gap. Direct band gap values of 2.1 -2.6 eV were obtained.The refractive index and Extinction coefficient is reported on depending on the ratio of doping and was obtained from transmission spectra.From this reason ,the films doping can be useful to prepare CdS photovoltaic (solar cells).

الخلاصة:

في هذا البحث ، حضرت أغشية رقيقة من مركب (CdS) النقي والمشاب بالنحاس بنسبة (2%,4%) بطريقة الرش الكيميائي الحراري. هذا الغشاء رسب على قواعد من الزجاج من محاليل كلوريد الكاديوم والثايوريا بمولارية (0.05) وبدرجة حرارة ($300^{\circ}C$). تم فحص طوبوغرافية السطح للأغشية المحضرة بوساطة المجهر الضوئي العاكس وظهر أنها تملك أنتظامية جيدة ، أما بالنسبة للخواص البصرية فقد شخصت من خلال دراسة طيف النفاذية باستخدام المطياف نوع (SHEMATZU) ولأطوال موجية تراوحت (300-1100)nm ، حيث تبين أن الأغشية تمتلك نفاذية عالية جدا بحدود (89%-83%) حيث كان السمك (900 nm) وأن عملية الأشابة قد أدت الى نقصان نفاذيتها مما يؤهلها للاستخدام في تصنيع النباتات (الخلايا الشمسية) ، كذلك تم تعيين قيمة فجوة الطاقة البصرية ولوحظ انها تتناقص مع زيادة نسبة الاشابة من (2.6 eV) الى (2.1 eV). أخيرا تم حساب الثوابت البصرية معامل (الامتصاص ، الانكسار، الخمود) وظهر أنها تتناسب طرديا مع زيادة نسبة الاشابة مما يعني ان الاشابة قد أدت الى تحسين خواص هذا الغشاء.

Introduction:

Cadmium sulphide(CdS) is a yellow compound and can be found in the nature as the mineral greenokite , (CdS) thin films are regarded as one of the most promising materials for heterojunction thin film solar cells. Wide band gap ($E_g=2.42$ eV) has been used as the window material together with several semiconductors such as CdTe, Cu_2S [1].However, due to the high cost of this material, studies were developed towards polycrystalline compound semiconductors and particularly thin polycrystalline films.In recent years,there has been a rapid development in the field of II–VI semiconductors for their use in solar cells , Cadmium sulphide belonging to the II–VI group is the most widely used material for CdS/CdTe and CdS/ Cu_2S heterojunction solar cells. It is because of the fact that CdS has intermediate energy band gap, reasonable conversion efficiency, stability and low cost [2]. Avariety of deposition techniques have been used to grow CdS films of desirable optical, electrical and structural properties, a few of them being chemical deposition [3], physical vapour deposition [4], spray pyrolysis [5], electro deposition [6] etc. each of the above listed techniques has produced sulphur deficient films. Spray pyrolysis although it is expensive, requires the use of sophisticated materials for large areas of deposition, now gives good quality semiconductors which permit the fabrication of solar cells with satisfactory efficiency [7] .The use of thin film polycrystalline semiconductors has attracted much Interest in an expanding variety of applications in various electronic and optoelectronic devices [8] . The technological interest in polycrystalline based devices is mainly caused by their very low production costs. Thin films now

occupy a prominent place in basic research and solid state technology. Cadmium sulphide (CdS) is a very useful optoelectronic [9], The thin films of CdS are of considerable interest for their efficient use in the fabrication of solar cells [10]. The aim of this work is to study the effect of the ratio doping on the optical properties of the CdS (pure & doping) films obtained by spray pyrolysis

Experimental procedure:

The spray pyrolysis technique is a simple technology in which an ionic solution containing the constituent elements of a compound in the form of soluble salts is sprayed onto over-heated substrates using a stream of clean, dry air. The apparatus used for our sprayed process is diagrammed in Fig.1. The spray apparatus was enclosed in a chamber. The substrate temperature was measured using a chromel-allumel thermocouple placed in good thermal contact with the substrate surface. The substrate temperature has a great influence on the deposition process [11] . In this technique, a mist of a spray solution was driven to the surface of a heated substrate where apyrolytic reaction takes place, leaving a solid film plus some volatile compounds. $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ were used to supply Cd and Cu, respectively while thiourea $(\text{NH}_2)_2\text{CS}$, was used to provide sulphur for the CdS:Cu thin films, all substances used were analytical grade reagents [12] .

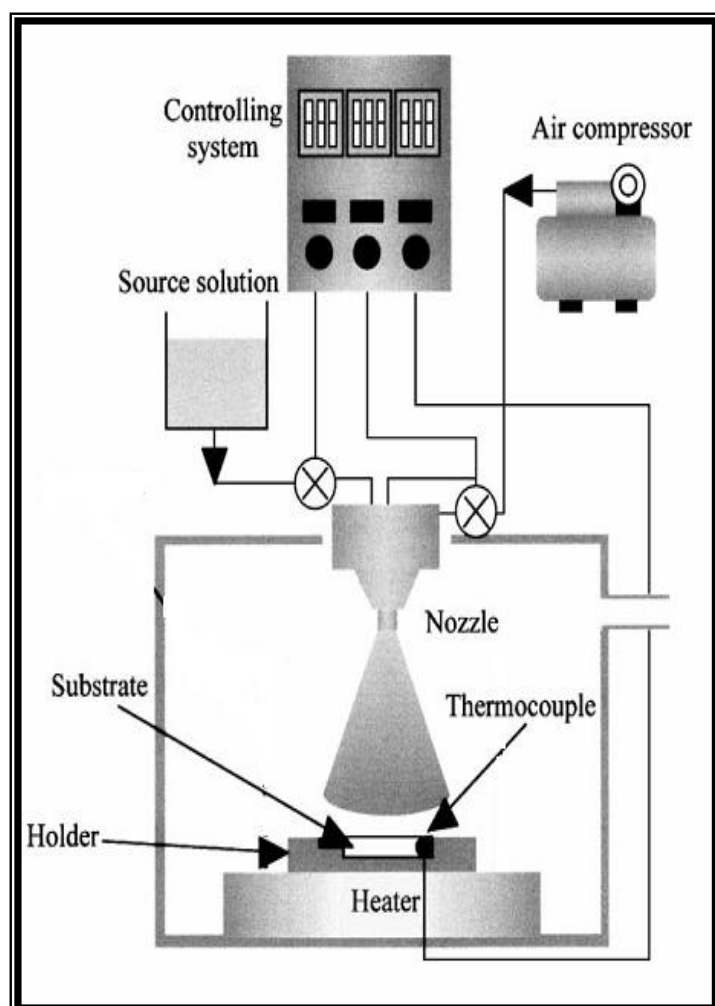


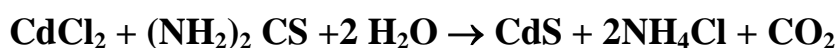
Fig.(1): Schematic representation of a spray pyrolysis deposition (SPD) apparatus[11].

To be controlled during the spraying process to obtain with a good morphology and a homogenous structure:

- 1- The precursor's composition.

- 2- The surface temperature.
- 3- The spraying sequences.
- 4- Drops dimensions.

In the process, the spray rate, the size of the sprayed particles and the spray pattern are strongly influenced by the geometry of the spray nozzle used. Standard commercial glass slides (75×25×1 mm³) were used as substrates. The usual cleaning of the glass slides were first carried out. The solution is sprayed (from a reservoir) by means of the carrier gas, incidently to the substrate.[13] The gas dry air used as a carrier gas flow rate was (5 L·min⁻¹). The spraying time vary between (3) seconds .The CdS thin films were prepared by taking similar mole ratios a (0.05 M) aqueous solution of thiourea and (0.05 M) aqueous solution of cadmium chloride as starting solutions. Also Suitable copper salts for spraying solutions doping are copper chloride CuCl₂·H₂O, in this search a molar ratio of 0.05 was used too . (where concentration solution stands for one part of cadmium chloride and one part of thiourea). The solutions were mixed thoroughly and the final solution was sprayed onto heated substrates kept at temperature ranging from (300±10) °C. Chromel–alumel thermocouple fixed on a dummy substrate holder was used to monitor the temperature of the substrates. When the solution is sprayed the following reaction takes place at the surface of the heated substrate:[14]



The major preparatory parameters in the spray pyrolytic process are substrate temperature, the concentration and the mole rates of starting solutions. In this present work , the films were grown at air temperature; the spray rate was (20-25 cc/min) and the distance between the spray nozzle and the substrate was (30 cm).The thickness of the films were determined by using a weight differential method. The films were deposited on clean glass slides whom mass was previously determined. After the deposition the substrates it was again weighted, determining the quantity of deposited CdS.

Measuring the surface of the deposited film, taking account of CdS specific weight of the film, thickness was determined using the relation:

$$t = \frac{\Delta m}{\rho_{(CdS)} A} \dots\dots\dots(1)$$

where (A) is the surface area of the film (cm²), (Δm) is the weight differential of deposited cadmium sulfide after and before deposition, and (ρ) is the the density of the bulk material of CdS [13] . After deposition, the films were cooled fast to room temperature. the thickness of the film was established by weight differential. The transmittance of the thin films were measured in the wavelength range of (λ=300–1100)nm by using a double beam Shimadzu UV - (PC) spectrophotometer with respect to a piece of glass of the same kind of the substrates. For such band to band transitions the dependence of absorption coefficient a versus photon energy is given by the relations [1]:

$$(\alpha h\nu)^2 = B (h\nu - E_g)^{1/2} \dots\dots\dots(2)$$

where (B) is a parameter independent of (hν) (h) is the planck constant and(ν)is the frequency also (E_g) is the optical band gap energy.

As well as the values of (E_g) calculated from the cutoff wavelength(λ) according to the relation:

$$E_g = h\nu = \frac{hc}{\lambda_{Cutoff}} \dots\dots\dots(3)$$

As well as the absorption coefficient(α) calculated from

the the relation: [12]

$$\alpha = (1/t) \ln(1/T) \dots \dots \dots (4)$$

where (t) is the thickness of film.

The extinction coefficient (k) as a function of wavelength (λ) and absorption coefficient (α) were given by the relation: [15]

$$k = \text{extinction coefficient } t = \frac{\alpha \lambda}{4\pi} \dots \dots \dots (5)$$

index(n) and reflectance(R) for semiconductors is: [15]

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \dots \dots \dots (6)$$

The relationship between refractive

Result and discussion:

The topographic properties of the films were characterized by reflective optical microscope, where shown in figure (2) all films have uniform surface. Optical properties of CdS thin films are also influenced by the deposition conditions. Measured values of transmittance (T) spectra of the film as a function of wavelength (λ) are shown in figure (3), in the UV-Vis spectral range (300-1100)nm of the film with the optimal thickness of (900) nm where film thickness decreased with increased substrate temperature , it shows a transmittance of (83%-89%) . Fig.(3) displays the transmittance curves of CdS(pure) and (CdS:Cu) thin films. As the figure shows, the transmittance is larger than (89)% which is good for solar cell applications. A good optical transparency of about (89)% and (83)% in the visible region is observed for all CdS pure and doping thin films. Figure (3) shows some rise and fall in the transmittance spectra of thin film deposited with substrate temperature (300) °C. below (400)nm there is a sharp fall in the transmittance of the films. The higher transmittance for a higher deposition substrate temperature and the sharp increase of transmittance at the band edge are attributed to the good crystalline owing to small concentration of structural defects The band gap energy was estimated from the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ which is shown in Fig(5), where (α) is the absorption coefficient, (h) is Planck's constant and (ν) is the frequency of the radiation. A linear fit was established in the linear region, where a direct optical transition was assumed, The values of the optical band gap energies obtained from the linear fit in Fig.(5). the CdS is a material with a direct band gap ranging of (2.1-2.6) eV .

So there is a table(1) .

For optical transmission spectra :

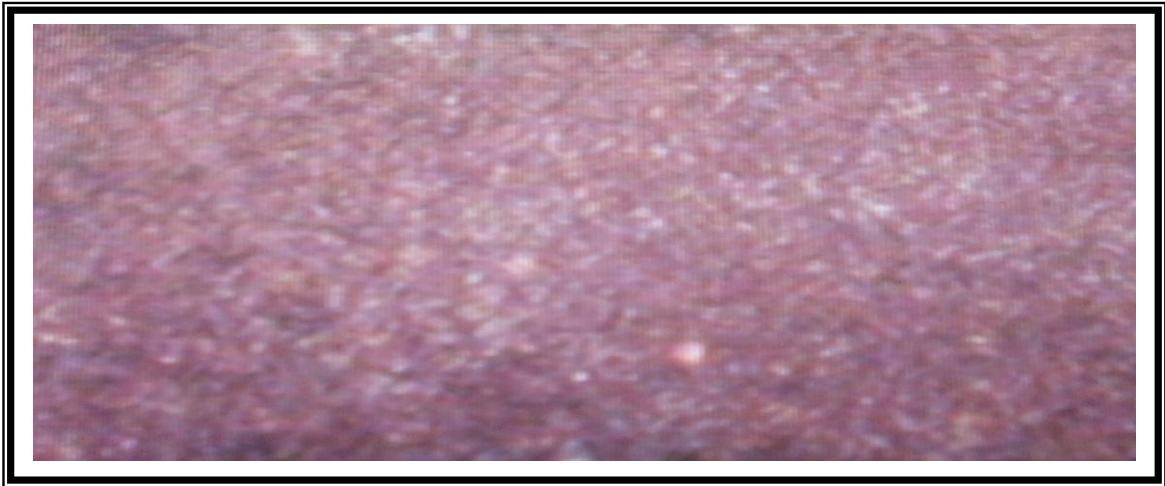
Table(1):values of energy gap

No.	Compound	E_g (eV)
1	CdS (Pure)	2.6
2	CdS (2% Cu)	2.25
3	CdS (4% Cu)	2.1

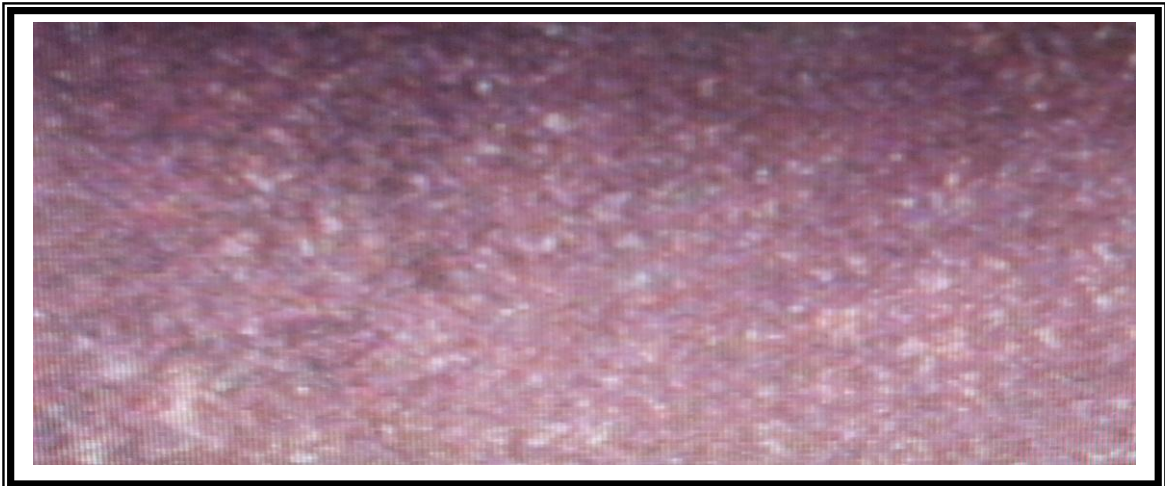
The absorption coefficient(α) versus wavelength (λ) curve is shown in Figure (4) . Extinction coefficient (k) and the refractive index (n) versus wavelength (λ) spectra is shown in Figure (7).the visible range, where(n) and (k) are approximately increases with increasing doping ratio. The increased extinction coefficient at the wavelengths below (400) nm is due to the high absorbance of CdS thin films in that region. For that, the refractive index (n) versus wavelength (λ) curve is shown in Figure (6) .



CdS-PURE x400



CdS-2%Cu x400



CdS-4%Cu x400

Fig.(2): Surface morphology of (CdS) thin film deposited for pure & doping

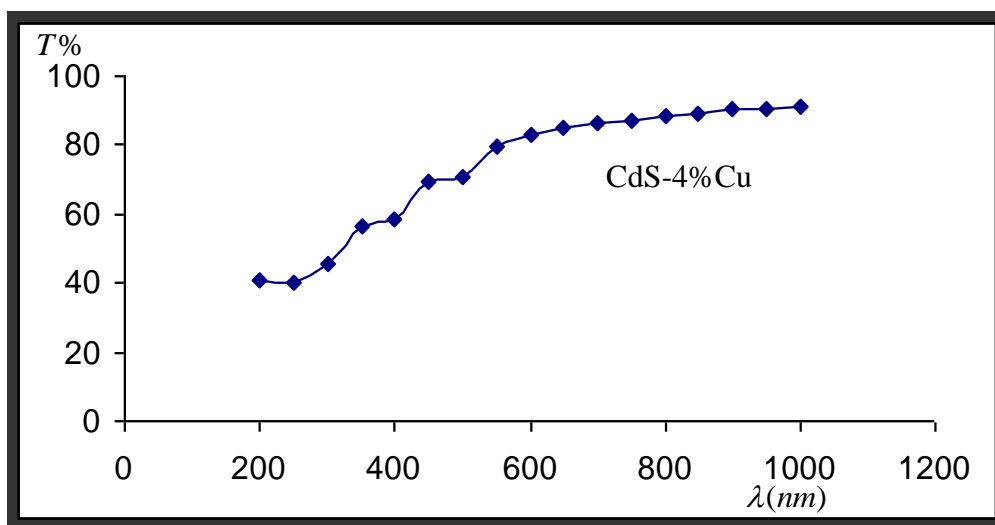
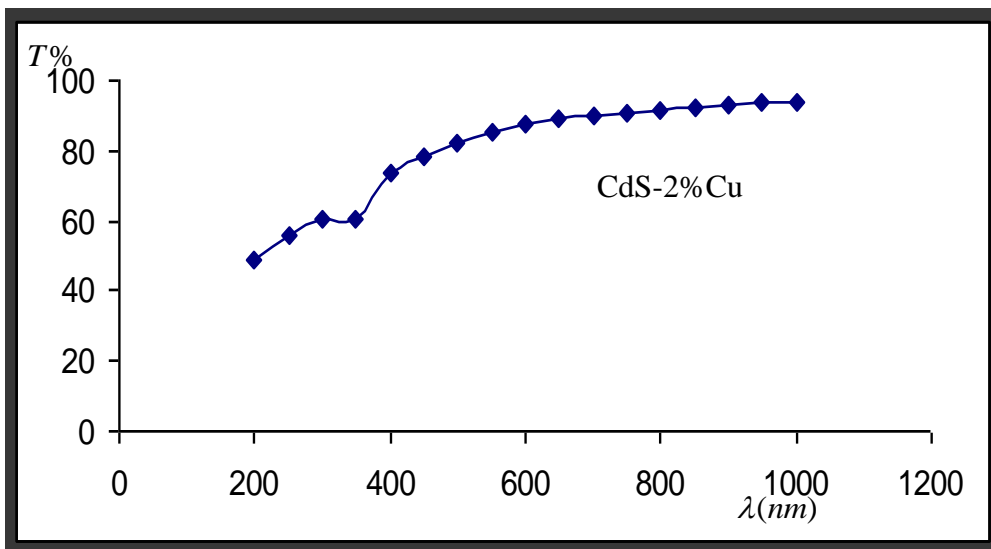
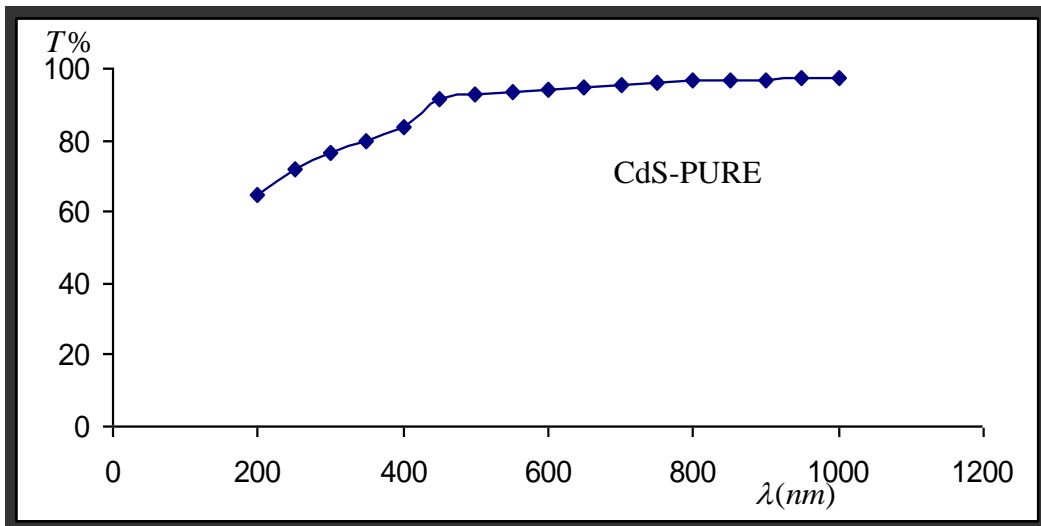


Fig.(3): Transmittance of CdS and two CdS:Cu thin films of thickness about (900nm) deposited at $T=300^{\circ}\text{C}$

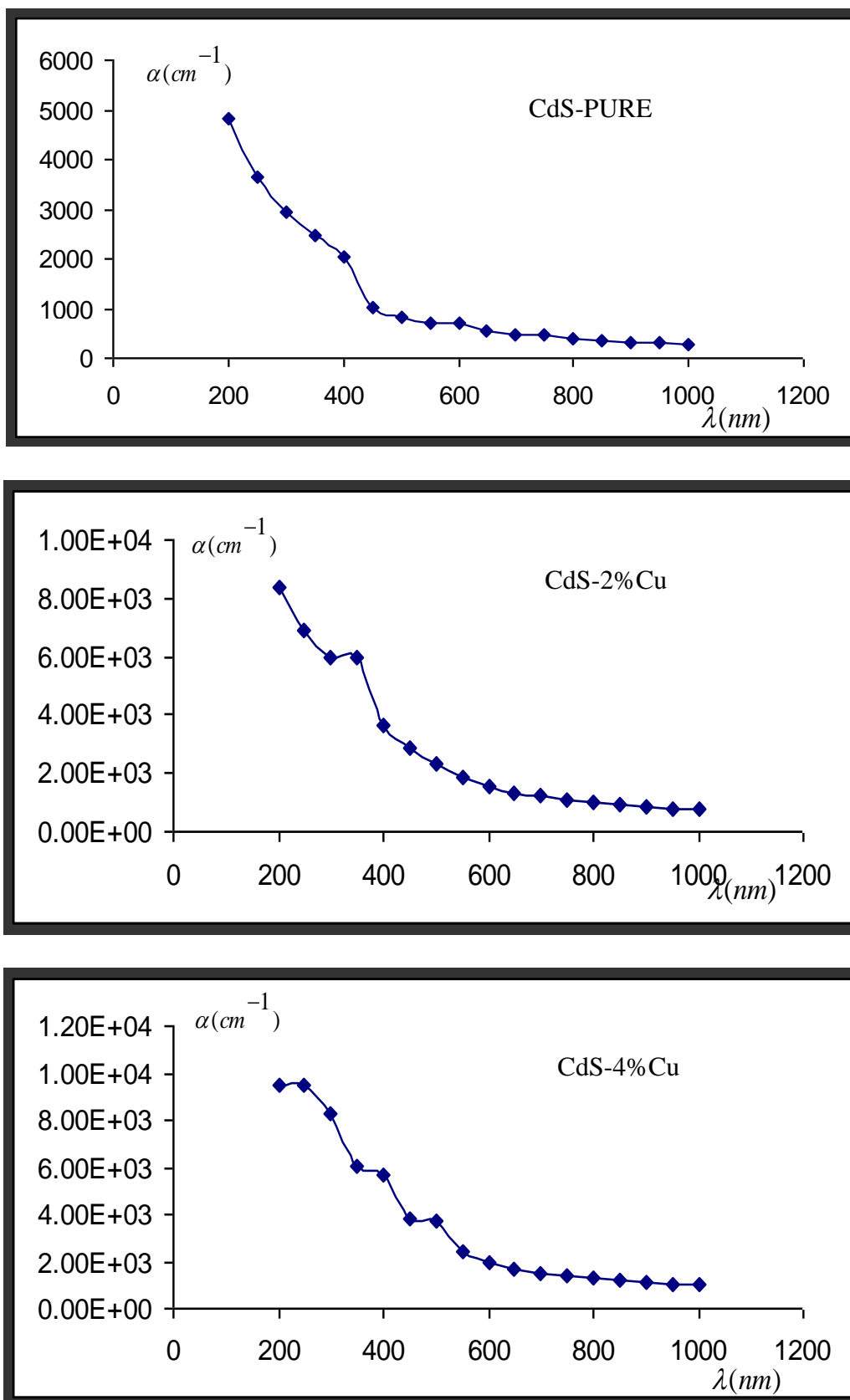


Fig.(4): absorption coefficient of CdS and two CdS:Cu thin films versus (λ) of thickness about (900nm) deposited at $T=300^{\circ}\text{C}$

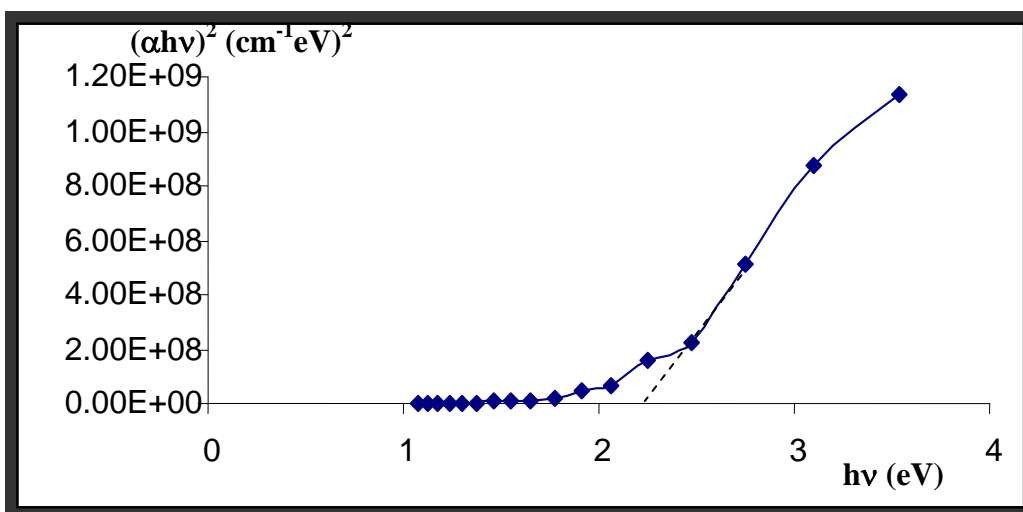
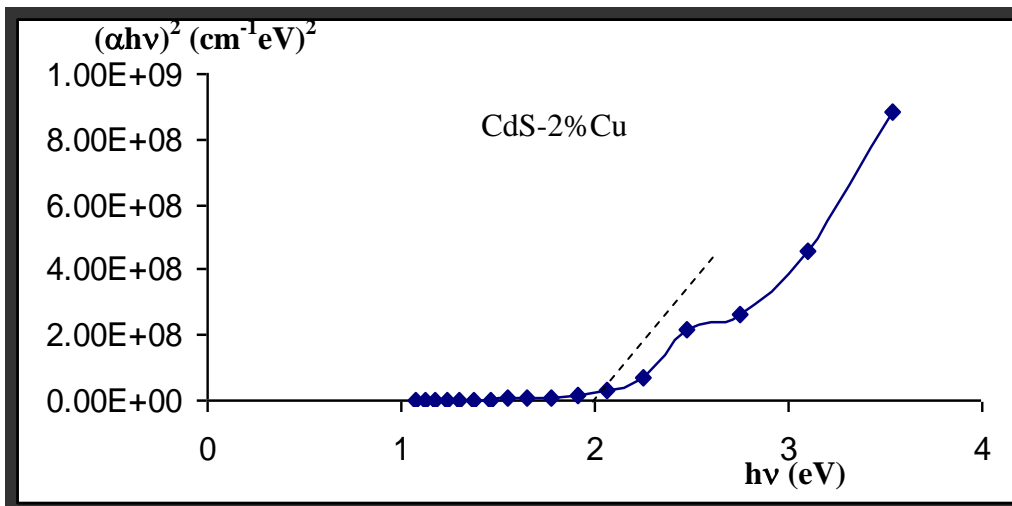
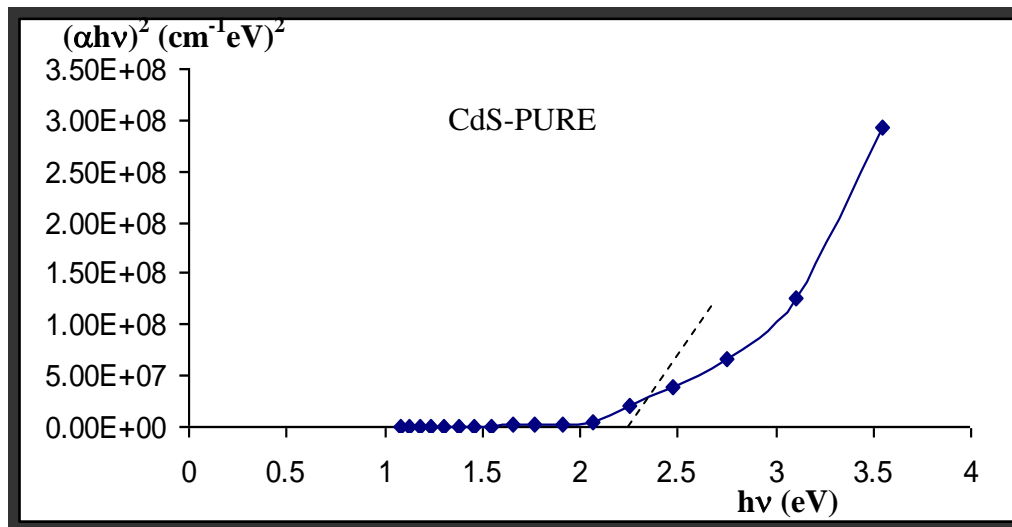


Fig. (5): The plot and linear fit for the films of transmittance shown in Fig.2

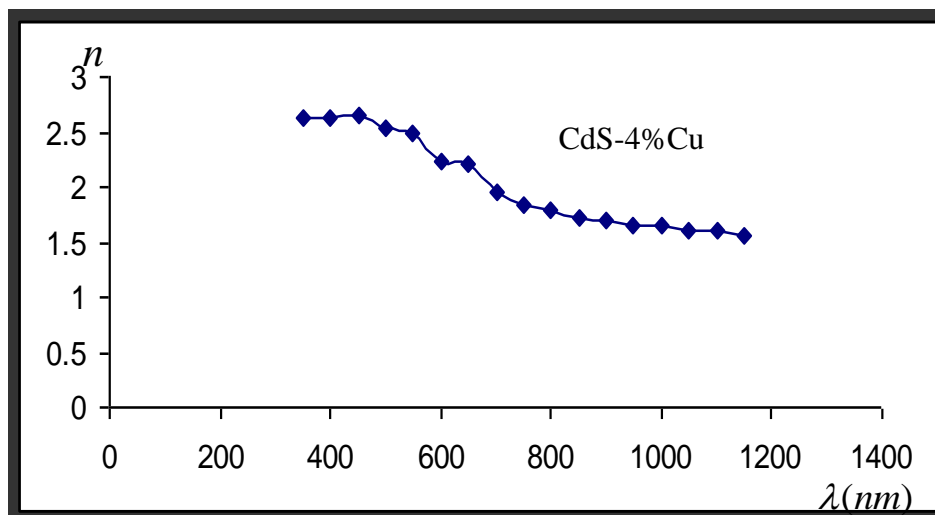
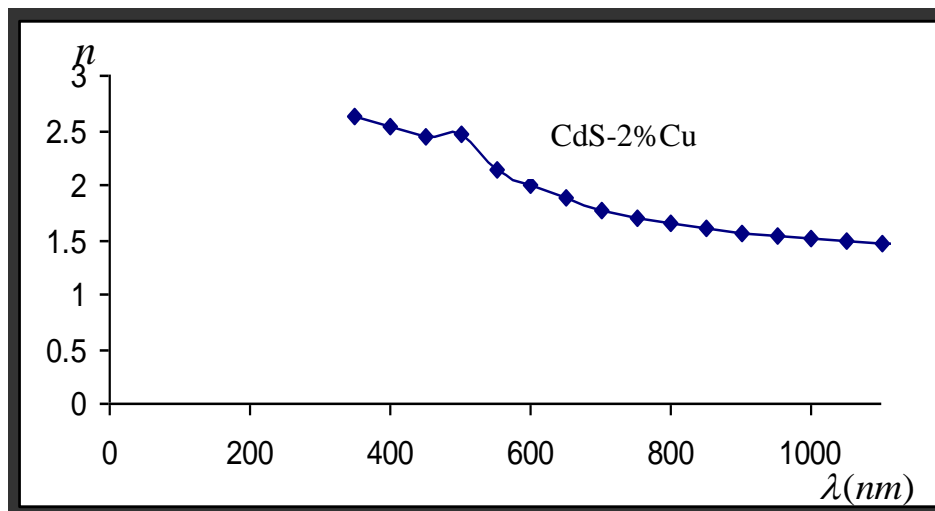
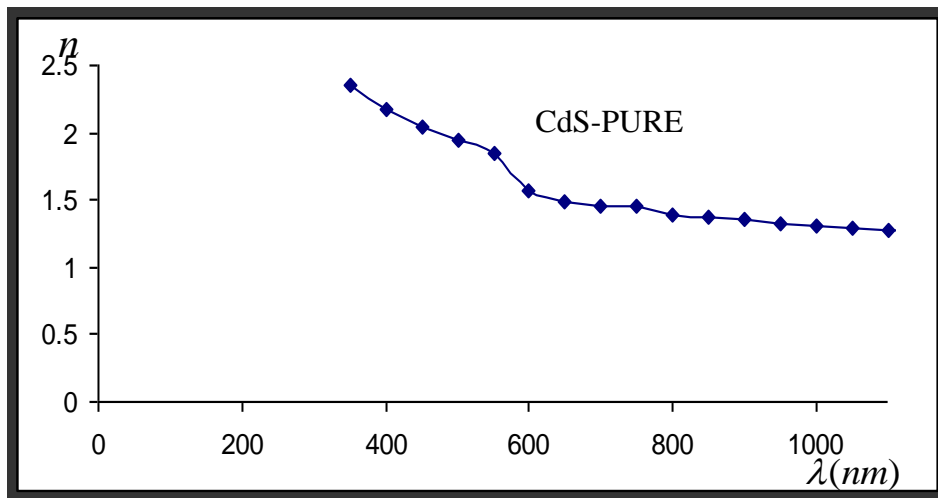


Fig. (6). refractive index (n) of CdS and two CdS:Cu thin films versus (λ) of thickness about (900nm) deposited at $T=300^{\circ}\text{C}$

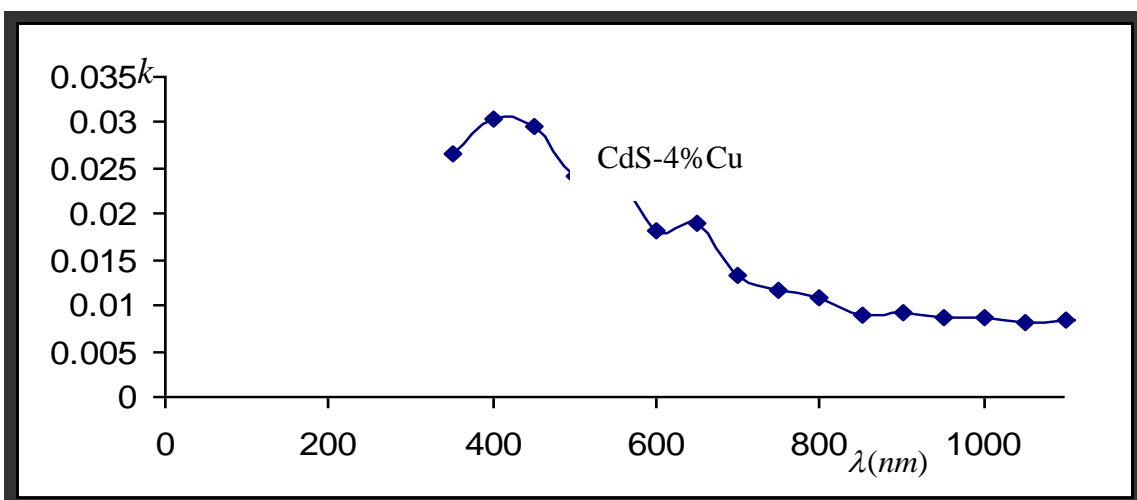
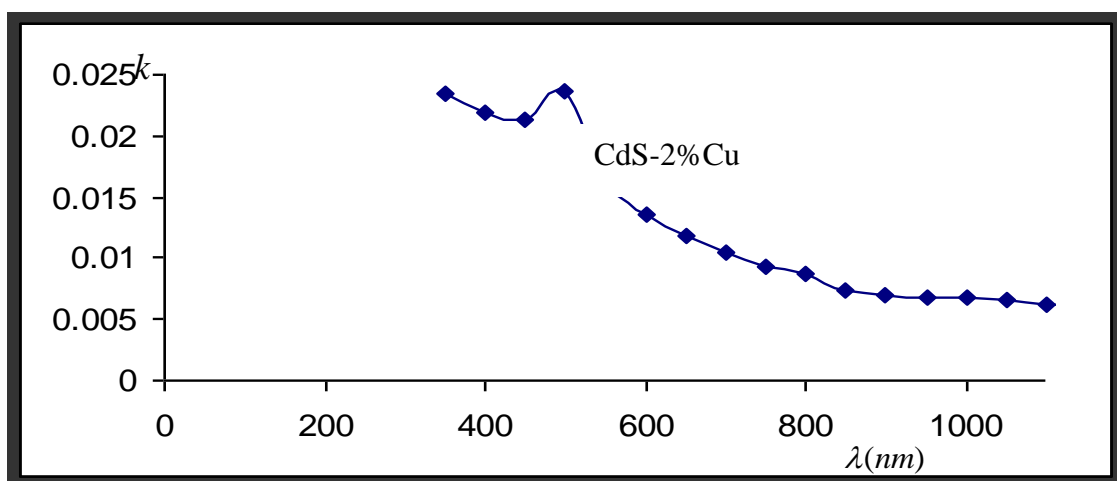
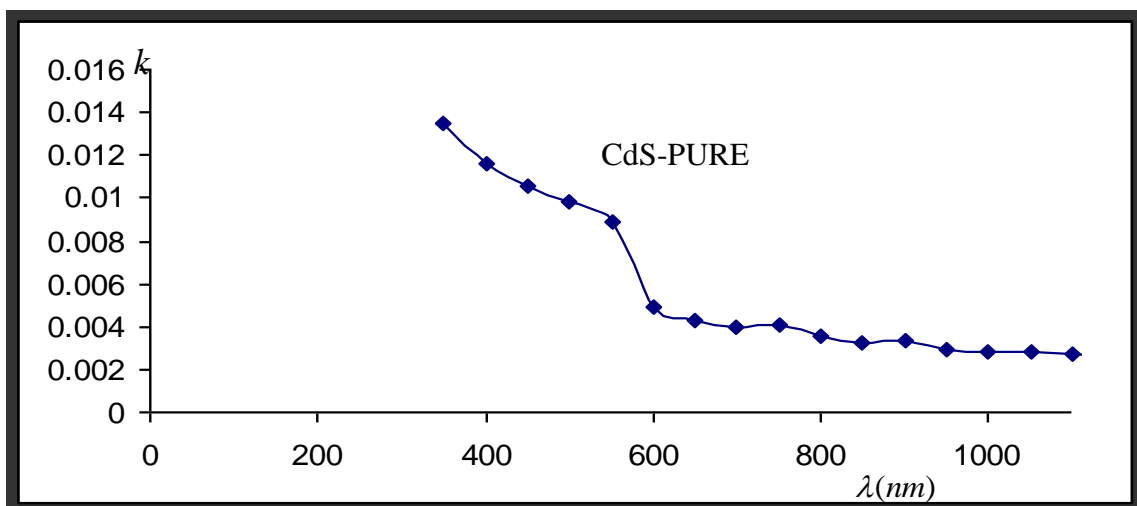


Fig. (7). Extinction coefficient (k) of CdS and two CdS:Cu thin films versus (λ) of thickness about (900nm) deposited at $T=300^{\circ}C$

Conclusions :

We have successfully grown (CdS:Cu) thin films by chemical spray pyrolysis technique, the doping was carried out by adding different relative volumes of the aqueous solution containing (2%,4%).

CdS film were fabricated by using a solution of cadmium chloride and thiourea. The film were deposited onto glass substrates at the selected temperatures of 300C⁰. Substrate temperatures during deposition were found to have influenced the topographic of the film. It was also noticed that film thickness decreased with increased substrate temperature. The film had a high enough long wavelength optical transmission for solar cell application, with a transmittance of about (83-89%) at wavelength beyond the absorption edge for the optimum film thickness obtained. Extinction coefficient, refractive index, and optical absorption coefficient were calculated from optical transmittance and optical absorption values. The film have good optical quality properties and are well suited for solar cell applications. The film exhibited a direct transition in the range (2.6-2.1)eV. These results suggest that the method of spray pyrolysis for the deposition of CdS thin films should be further investigated for application towards the fabrication of solar cells.

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