

Study Some Physical Properties of Cobalt Doped CdS Thin Films

Prepared By CSP Method

Abeer Ghalib Hadi¹, Rana Talib Saihood¹, Raghad Hamdan Mohsin¹,
Sami Salman Chiad^{3*}, Nadir Fadhil Habubi²

¹ Ministry of Education/ General Directorate of Education in Baghdad Governorate/
Rusafa second, Iraq.

² Department of Physics, College of Education, Mustansiriyah University, Iraq.

³ Department of Engineering of Refrigeration and Air Conditioning Technologies,
Alnuhba University College, Iraq.

Abstract

In this paper, structural, morphological and optical of pure CdS and CdS:Co thin films with various cobalt concentrations were synthesized by the Chemicle spray pyrolysis (CSP) method. Hexagonal structure of CdS nanostructures with (020) preferred orientation is detected by XRD. According to morphological analysis, the doped films have homogeneously dispersed spherical grains with an average particle size of 42 nm. The optical parameters are estimated using transmittance and absorption spectra at 300-900 nm. Experimental results showed that when cobalt content increased, the band gap decreased as in

Key words: CSP, CdS: Co, XRD, AFM and Optical properties.

Introduction:

Thin film is solid material when it is built up as a thin layer on a solid support called substrate[1] Thin films are prepared by physical & chemical process also it can be prepared by electrochemical reactions. Physical process like (Sputtering) & (Thermal Evaporation).

Chemicle process like Plasma Enhanced Chemical Vapor Deposition (PECVD) [2].

CdS belong to II – IV semiconductor with a bandgap of 2.42 eV that has been investigated for different optoelectronic applications especially as a window material to fabricate solar cells [3,4]. The hexagonal (wurtzite) structure is the typical phase of CdS crystal when compared to the cubic (zinc blende) phase [5, 6]. So, their reported parameters apply to the hexagonal modification [8-10]. Doping of CdS with metals such as Ni, Sb, Ce, Co etc., has gotten a lot of interest since it suggests a unique way to include electrical and optical characteristics in a single material. [11-14]. Preparation of CdS thin films is obtained utilizing diverse techniques, including vacuum evaporation [16,17], CBD [18, 19], space sublimation (CS) [20], CSP [21, 22], sol-gel [23], dip coating [24], and PLD [25]. Each method creates films

with unique characteristics that need be tailored to specific purposes. The present work deals with the deposition of CdS thin films by CSP at 400°C b temperatures. Many Parameters to be considered important for Spray Pyrolysis such as type of source chemical, (b) Air pressure, (c) deposition spray rate, (d) substrate temperature, (e) nozzle to substrate distance (f) spray time and repeated spray cycles etc .

Material and Methods

Undoped CdS and CdS: Co films were deposited via SPT. 0.1M of Cd [C₄H₆CdO₄] and 0.1M of [CH₄N₂S] to get CdS. The cobalt doping employed was (CoCl₃) resolved by redistilled water, and drops of HCl joined the solution to get it clear. The glass base is preserved at 400 °C. The favorite parameters are: base to spout distance was 28 cm, spraying rate was 4 mL/min, spraying time was 10 followed by 1.5 min to stop extravagant cooling and the carrier gas was Nitrogen. The Gravimetric method was used to, and their values were in the area of 310 ± 25 nm. Transmittance is registered via a double deam spectrophotometer (Shimadzu Japan) in the wavelength range of (300-900) nm. XRD is employed to obtain film structure. Film morphology was determined by AFM (AA3000 SPM).

Result and Discussion

XRD studies

Fig.1 offers XRD pattern plots of pure and cobalt doped CdS prepared using the CSP method at 400 °C. The distinguish diffraction peaks intensities at 2θ values 31.67°, 36.82° 57.82° and 63.27° are indexed as (110), (020), (012) and (130) planes corresponding to that of hexagonal CdS and indicating polycrystalline nature of all prepared film. The strong peak matching to (020) plane of cubic CdS demonstrates main growth along this direction. However, because the metals were in such tiny quantities, no distinct peaks matching them were detected. With increasing cobalt concentration, the intensity decreases gradually and the peak shifts to lower diffraction angle revealing an increase in lattice parameter [26]. Also as cobalt content increases, characteristic diffraction peaks at 2θ = 31.67°, 36.82° 57.82° and 63.27° start decreasing. From the ICDD card no. 43-0985 database, these diffraction angles were found to be related to (101), (102), (103) planes of hexagonal CdS. This may be due to stabilized hexagonal phase in CdS by cobalt doping. Further, one can easily note a slight shift towards a smaller 2θ value for Co doped CdS in comparison to pure one since the ionic radius of cobalt (0.74Å) is smaller than that of Cd (0.96 Å) suggesting that the doped cobalt atoms can

replace the Cd atoms. Using Scherrer's formula [27], the crystalline size (D) has been determined as follows:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

For the undoped CdS film, D values is found to be 17 nm then increased slightly with cobalt content, a maximum value of D was about 19.47nm at doping concentration of 3%.

The calculated structural parameter, dislocation density (δ) [28], is presented in Table 1.

$$\delta = \frac{1}{D^2} \quad (2)$$

The calculated structural parameter micro-strain (ε) [29], is presented in Table 1.

$$\varepsilon = \frac{\beta \cos\theta}{4} \quad (3)$$

micro-strain is decreased by cobalt content. Fig. 2 shows the crystallite size, FWHM, ε and the dislocations with dopants in cobalt different concentrations. The decrease in ε led to a decrease in FWHM and the increase in D . Decreasing ε led to an increment in lattice parameters and this decrease in ε is attributed to the narrowing of diffraction peaks [30].

Table 1. structure parameter of the films.

Specimen	2 θ ($^{\circ}$)	(hkl) Plane	FWHM ($^{\circ}$)	Optical bandgap (eV)	crystallite size (nm)	Dislocations density (\times 10^{14}) (lines/m ²)	Strain ($\times 10^{-4}$)
Pure CdS	36.82	020	0.49	2.85	17.09	34.23	20.28
CdS: 1% Co	36.78	020	0.46	2.81	18.20	30.18	19.04
CdS: 3% Co	36.72	020	0.43	2.76	19.47	26.57	17.80

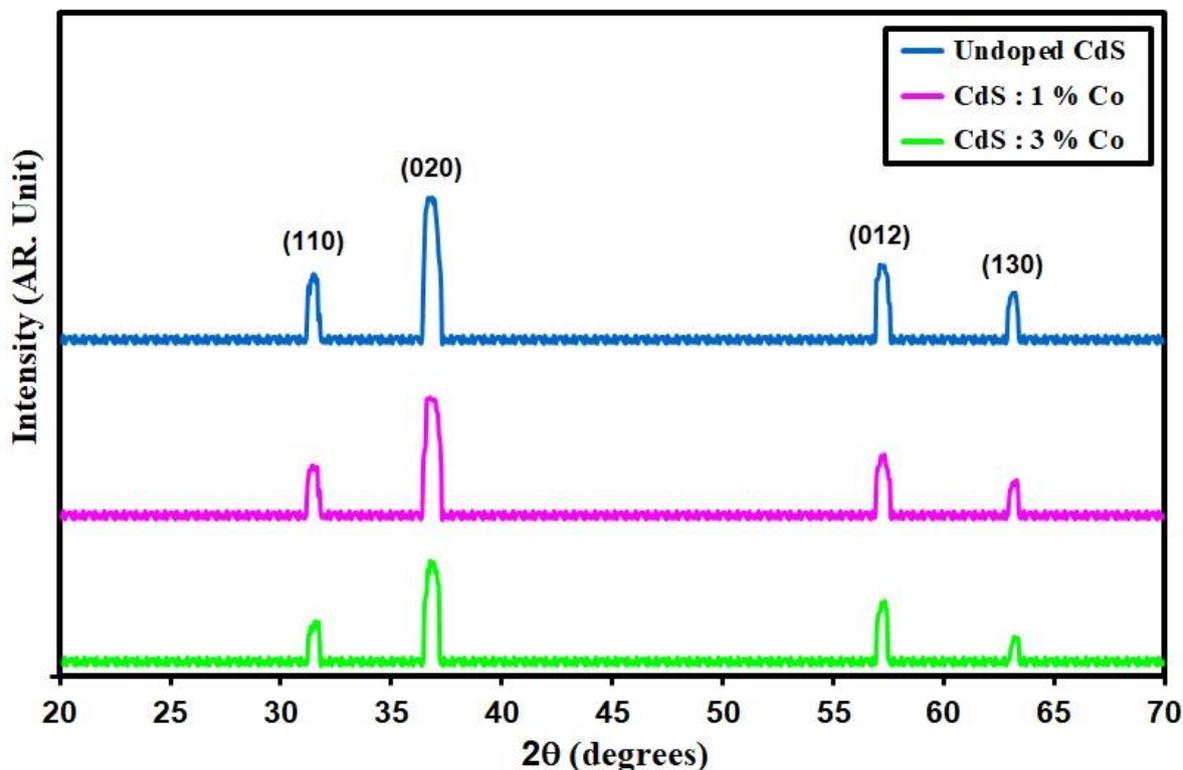


Fig. 1. XRD spectra of the films.

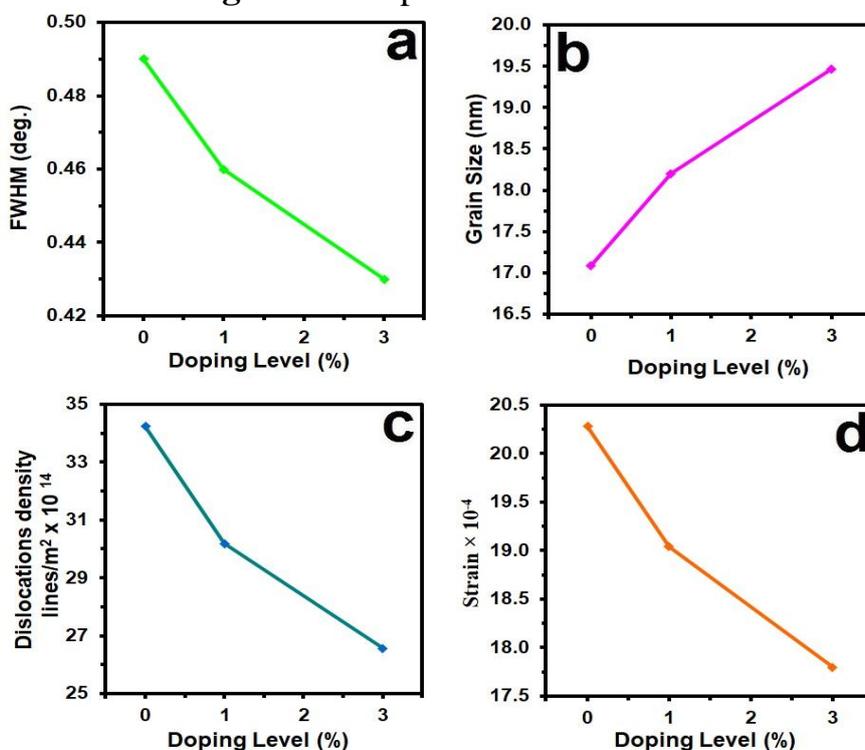


Fig. 2. X-ray parameter of pure and Co-doped CdS films.

AFM Analysis

The topographical features were evaluated using AFM. The 3D and AFM pictures of the films with a scanning area of 76*76 nm are shown in Figure 3. The particles are equally sized and oriented in all directions at random. The deposits' average surface roughness (R_a) and average particle sizes P_{av} values are offered in Table 2. The CdS particles were dispersed randomly on the films' surfaces, which were homogenous. All of the surfaces appear to be densely packed with grains of different sizes and shapes. The entire films surface is composed of nanostructure particles, along with a few pin holes. R_a of CdS (0, 1 and 3 at % Co) are found to be 8.71, 4.91 and 3.29 nm respectively. The root mean squares RMS of CdS:Co films show a decrement as matched to undoped CdS film. The average Particle size values is 48.28 nm at undoped and reduced to 36.17 nm with the increase in cobalt content from 0 to 3% [15].

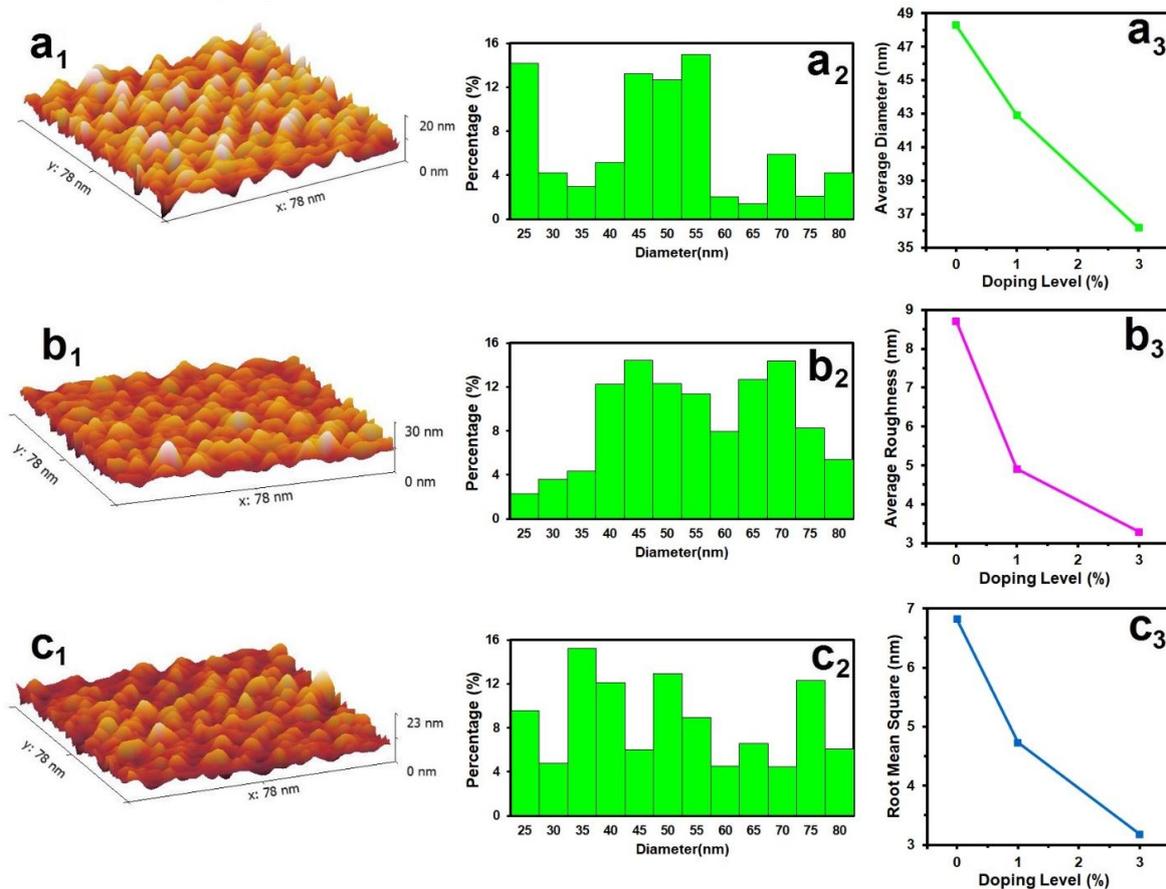


Fig.3. AFM analysis of prepared CdS films.

Table 2. AFM parameter values of the films.

Samples	P_{av} nm	R_a (nm)	RMS (nm)
Pure CdS	48.28	8.71	6.82
CdS: 1% Co	42.90	4.91	4.37
CdS: 3% Co	36.17	3.29	3.18

(UV-Vis) spectroscopy

Fig.4 demonstrates the transmittance (T) of CdS: Co thin films. One can note that all films display 80-85% transmission in the wavelength area of 550–900 nm. T values were decreased after doping with cobalt. However, the lowest value was for CdS: Co (3 at.%), identical behavior was observed for the literature [30]. The absorption coefficient α can be derived from T values for different film thickness d based on the Lambert's equation [31]:

$$\alpha = \frac{\ln 1/T}{d} \quad (4)$$

The behavior of α versus photon energy $h\nu$ was presented in Fig. 5. The absorption coefficient is decreased via increasing cobalt content. The variation of the α against $h\nu$ has the form of [32]:

$$ah\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (5)$$

where E_g is the optical band gap. Fig. 6 shows the plot of $ah\nu^2$ vs. $h\nu$. A clear decrease in E_g values from 2.85 to 2.76 eV can be noticed with increasing cobalt content from 0 to 3%. This trend is clarified with sp-d exchange interactions between band electrons in CdS and localized d electrons of Co^{2+} [33].

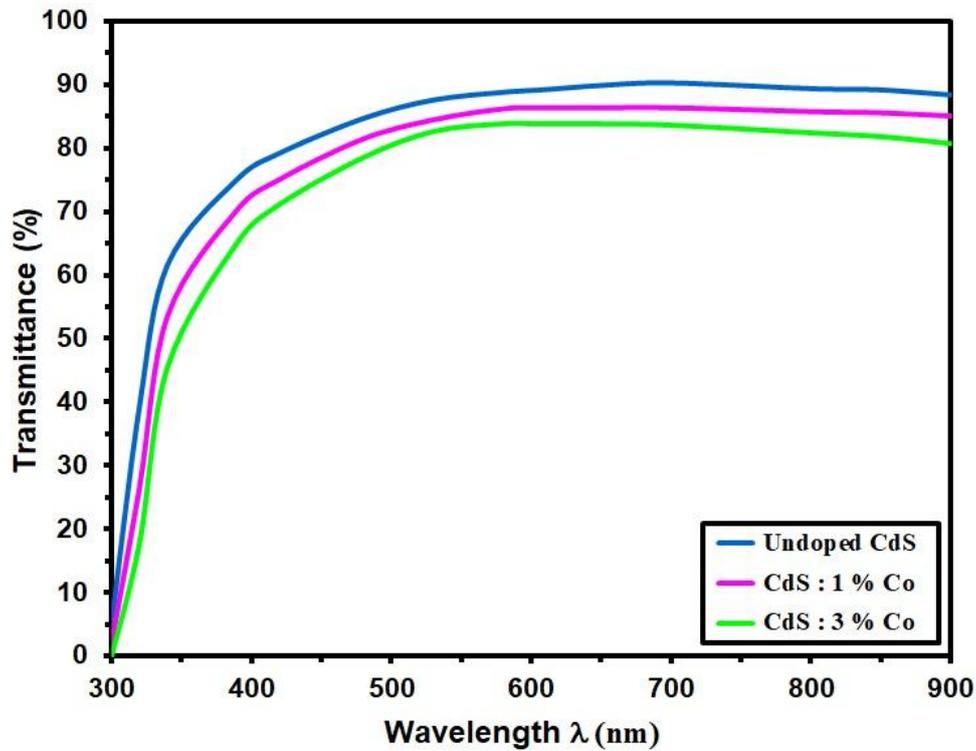


Fig.4. Transmittance of the films.

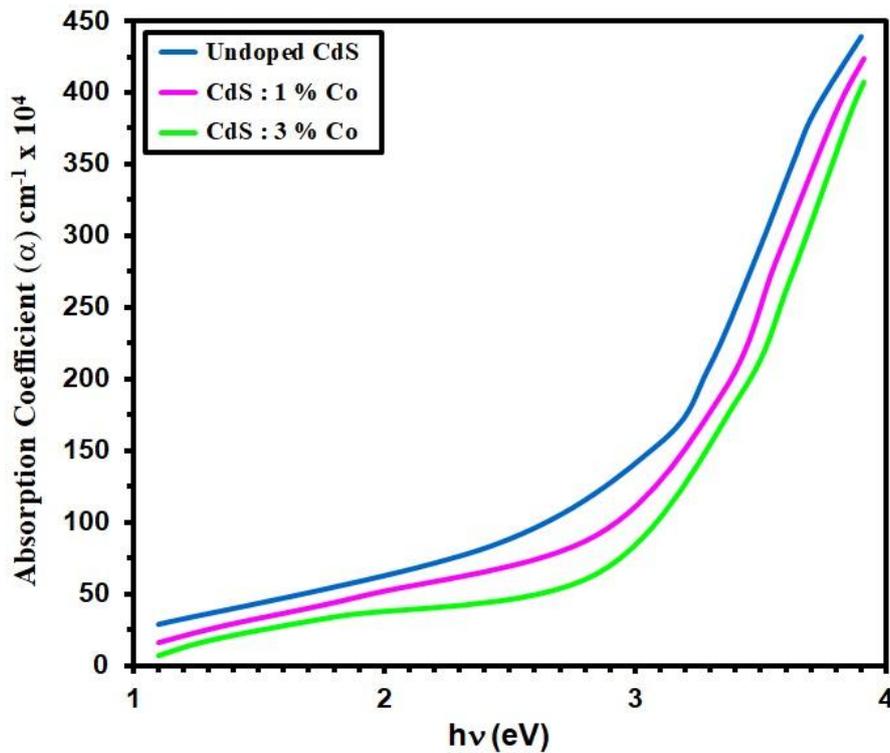


Fig. 5. The absorption coefficient of the films.

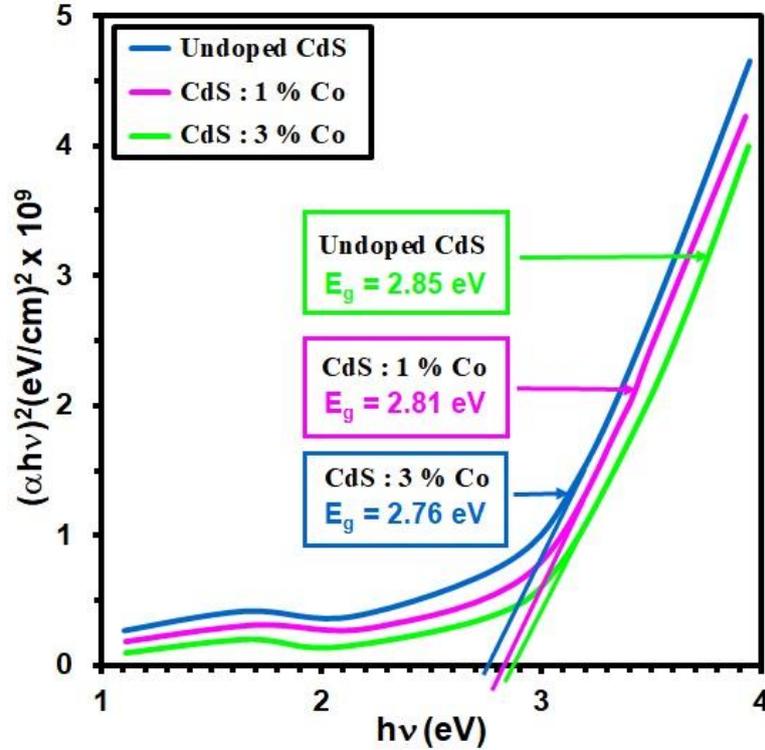


Fig. 6. The optical band gap of the films .

The refractive index (n_o), and extinction coefficient (k_o) via wavelength was calculated by using following equations [34, 35]

$$R = \frac{(n_o - 1)^2}{(n_o + 1)^2} \quad (6)$$

Where R is the reflectance which can be calculated by the following simple equation [36]:

$$A + T + R = 1 \quad (7)$$

$$k_o = \frac{\alpha \lambda}{4\pi} \quad (8)$$

Fig. (7) shows the refractive index (n_o) values, it is found to be increased by increasing the cobalt doping content and may be related to the increase in film polarization. Also (n_o) values increase with increase doping may be assigned to higher packing density [36]. Also the peak values of (n_o) fluctuate in the range of 3.27 to 3.07. Finally, the dependence of extinction coefficient (k_o) on wavelength is represented in Fig. 8. One can see that films have similar behavior of refractive index increase with cobalt concentration increases.

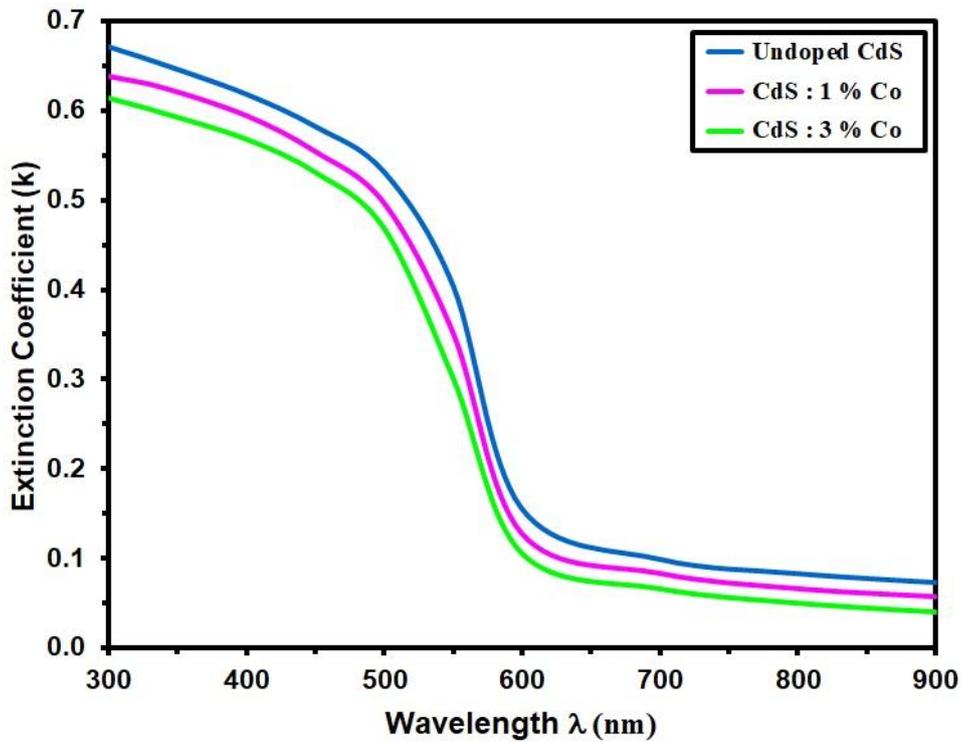


Fig. 7. k_0 values of the films.

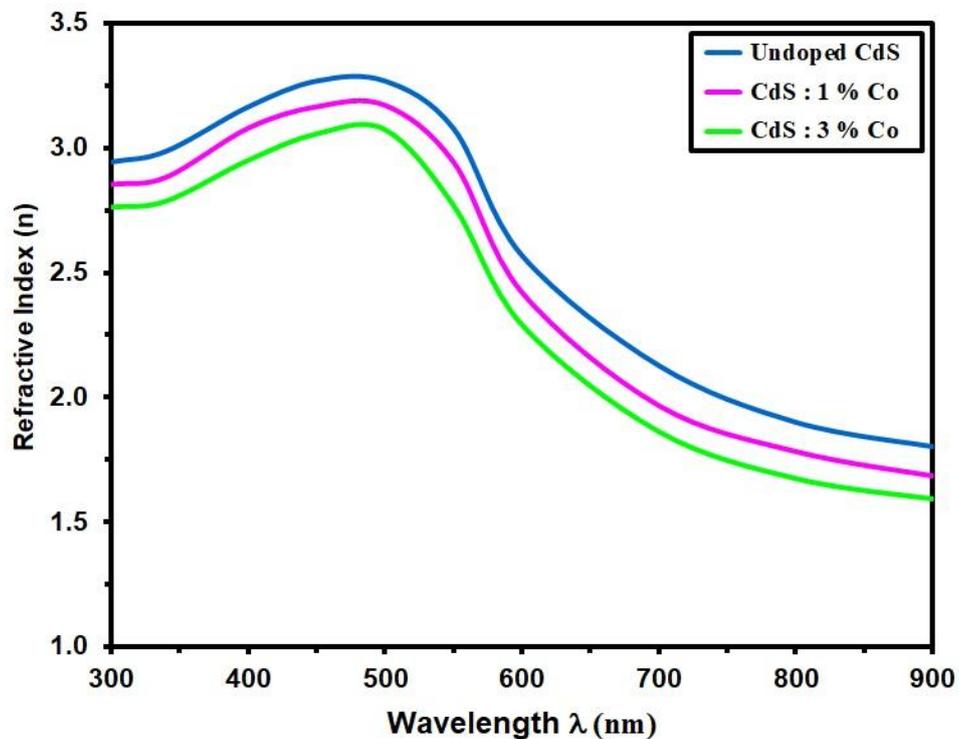


Fig. 8. (n_0) values of the films.

Conclusions

The Chemical pyrolysis method was used to produce cobalt doped cadmium sulfide thin films over a glass substrate with a different cobalt content. X-ray patterns revealed that all films have a hexagonal structure with a preferred orientation of (020). Cobalt doping in CdS caused a slight shift in the (020) peak location, due to the difference in ionic radii of Cd and cobalt. The AFM pictures of the film surfaces showed that cobalt doping reduced the average particle size. Optical investigations indicated that when cobalt content increases, the optical band gap of films reduces

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دراسة الخصائص البصرية لأغشية كبريتيد الكادميوم الرقيقة المشوب
بالكوبلت والمحضرة بطريقة التحلل الكيميائي الحراري

عبيد غالب هادي¹، رنا طالب صيهود¹، رغد حمدان محسن¹، سامي سلمان جواد²،
نادر فاضل حبوبي³

¹وزارة التربية، المديرية العامة للتربية في محافظة بغداد، الرصافة الثانية، العراق.

²قسم الفيزياء، كلية التربية، الجامعة المستنصرية، العراق.

³قسم هندسة تقنيات التبريد والتكييف، كلية النخبة الجامعة، العراق

مستخلص البحث:

في هذا البحث تم دراسة الخواص التركيبية والمورفولوجية والبصرية لأغشية كبريتيد الكادميوم النقية والمشوبة بالكوبلت بتراكيز مختلفة باستخدام طريقة التحلل الكيميائي الحراري. كشف حيود الأشعة السينية بان الاغشية المحضرة ذات التراكيب النانوية ذات تركيب سداسي مع اتجاه سائد (020). وفقا للتحليلات المورفولوجية فان الاغشية المحضرة كانت متجانسة وتظهر حبيبات دائرية وبمعدل حجم جسيمي مقداره 42 نانومتر. حسب الثوابت البصرية وباستخدام أطيف النفاذية والامتصاصية وبالأطوال الموجية (300- 900) نانومتر. اثبتت النتائج العملية بانه عند زيادة شائبة الكوبلت فان فجوة الطاقة تقل

الكلمات المفتاحية: CSP, CdS: Co, XRD, AFM and Optical properties