Study the structural and optical properties of pure and Aluminum doped CdS thin films prepared by chemical bath deposition method

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Abstract

This research deals with the preparation of pure and Aluminum doped CdS thin films by chemical bath deposition method, with a thickness of (450±20) nm and preparation temperature of (75°C). The results of XRD showed that the films had a polycrystalline hexagonal structure. The preferred orientation was along (002) plane. The average c rystallite size increasing with increasing of dopant concentration. The results of (AFM) showed that the roughness and (RMS) value were increased with doping. Results of (SEM) showed that the films were uniformly distributed and homogenous. The optical properties were studied by recording the absorption and transmittance spectra of the wavelength range (300-1100) nm, it was found that absorbance increased and transmittance decreased with increasing doping. It was also found that the absorption coefficient increased with increasing of dopant concentration , optical energy gap found of pure and Aluminum doped CdS thin films with different percentages of (0 , 2.5, 5 , 7.5)%were(2.89 , 2.85 , 2.79 , 2.81)eV respectively.

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Keywords: Structural properties, Optical properties, CdS Thin films , Doping, Chemical bath deposition.

دراسة الخصائص التركيبية والبصرية لأغشية كبريتيد الكادميوم النقية والمشوبةبالالمنيوم المحضرة بطريقة الترسيب بالحمام الكيميائي .

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الخلاصة

يتناول هذا البحث تحضير اغشية كبريتيد الكادميوم CdS النقيةوالمشوبة بالالمنيوم بطريقة الترسيب بالحمام الكيميائي وبسمك (450±20)nm و درجة حرارة التحضير (75°C) . ومن خلال تحليل حيود الاشعة السينية ظهرت الاغشية ذات تركيب متعدد التبلور ذي الطور السداسي ، والاتجاه المفضل للنمو هو (002) . ووجد ان الحجم الحبيبي يزداد بزيادة نسب التشويب . وأوضحت نتائج فحوصات (AFM) ان معدل الخشونة و قيمة معدل الجذر التربيعي (RMS) تزداد بالتشويب . وبينت نتائج (SEM) ان الاغشية ذات توزيع منتظم ومتجانس . وتمت دراسة الخواص البصرية من خلال تسجيل طيف الامتصاصية والنفاذية لمدى الاطوال الموجية من (300-1100)nm وجد ان الامتصاصية تزداد والنفاذية تقل بزيادة نسب التشويب وكذلك وجد أن معامل الامتصاص يزداد بزيادة نسب التشويب وفجوة الطاقة لاغشية كبريتيد الكادميوم المشوبة بالألمنيوم لنسب حجمية (0 , 2.5 , 5 , 7.5)% كانت (2.89 , 2.85 , 2.79 , 2.81)eV على التوالي .

كلمات مفتاحية: خواص تركيبية، خواص بصرية ،اغشية CdS،تشويب،الترسيب بالحمام الكيميائي.

1. Introduction

The term thin films is called a layer or a number of layers of materials that does not exceed one micrometer [1,2] . The study of the properties of the material in the form of thin films have attracted the attention of physicists since the second half of the seventeenth century where many important research has been conducted in this field ,at the beginning of the 19th century, working this thin films development resulted many semiconductors were used in the preparation of thin films such as selenium and silicon [3,4] . The cadmium sulfide CdS is interest to researchers , its semiconductor material of the elements of the group (II-VI) in the periodic table , the crystalline structure of this material is the cube (Zinc blende) or Hexagonal (Wurtzite)[5] .The unit cell is of a type centered faces[6] . Cadmium sulphide films have a direct energy gap at 2.42eV [7], when the wavelength is 520nm in the green color zone of the visible spectrum. This means that the film is absorbed at the green and blue wavelengths while long wavelengths (yellow and red) will be transmitted. The CdS crystal possesses the yellowish color of the orange [3,8].The most important applications are its use in solar cells and photovoltaic reagents, It is easy to prepare, inexpensive and highly stable [9,10] .

2. Experimental Details

In the present work, CdS nanostructure synthesized by (CBD) which were deposited on glass substrate with dimensions (7.62×2.54×0.1)cm there were washed with detergent, and again rinsed in acetone before the deposition of the films, then the substrates were heated in hot air oven for about 15min at a temperature of 50 °C . The weight of substrate and the films were calculated by using digital balance Sensitive 10^{-4}g .

The CdS films were prepared using aqueous solutions of cadmium acetate $Cd(CH_3COO)_2$(0.025 M), thiourea $(NH2)_2CS$(0.05 M), and ammonia NH_3 (25%) .Al doped CdS films were deposited by adding Aluminum sulphate $Al_2(SO_4)_3.16H_2O$(0.025 M) with percentage (0 , 2.5 , 5 , 7.5)%. In this modality the chemical bath solution is stirred mean while glass substrates are immersed vertically into the bath.Both solution is maintained at 75 °C, pH 9.5, and the thickness of the films is 450nm.

Samples were tested with X-ray diffraction type (SHIMADZU Japan XRD 6000) to identify the crystal structure of the prepared films, the crystallite size (D) was calculated using the following equation [11]:

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

Where k=0.94 λ: wavelength, *B*: Full Width at Half Maximum.

Calculation of the lattice constants for hexagonal structure (a, c) according to the following equation [12]

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{(h^2 + hk + k^2)}{a^2}\right) + \frac{l^2}{c^2} \quad \ldots \quad 2$$

Where d isdistance between crystalline levels, (hkl) miller indices .The analysis of the surface topography of the samples by using scanning electron microscope device (SEM) type (manufacturer: FEL, Quanta 450), Surface morphology was analyzed by Atomic force microscope (AFM) device of the type (SPM AA3000 /Angstrom Advanced Inc.). Optical spectrums of the thin films were recorded by (UV-Visible 1800 spectra photometer). The optical absorption and transmittance spectra were analyzed to determine the optical constants such as absorption coefficient (α) according to the following equation [13] .

$$\alpha = 2.303\frac{A}{t} \quad \ldots \quad 3$$

Where A is the absorption, t is film thickness, the optical band gap E_g was calculated by the following relation [11] .

$$\alpha h\upsilon = B\,(h\upsilon - E_g)^r \quad \ldots \quad 4$$

Where hυ is Photon energy, B Constant depends on the nature of the material and r is value depends on the nature of the transition .

3. Results and Discussion

3.1 Structural properties

XRD is a suitable method for the determination of crystal structural and crystallite size. The Fig1a,b,c,d. show the XRD pattern of CdS, CdS:Al with percentage (2.5 , 5 , 7.5)%and compares the results with (JCPDS card No. 41-1049).From the pattern, it is clear that the films are polycrystalline in nature .All peaks from the diffraction patterns were found to be characteristic for pure and Aluminum doped CdS thin films suggesting that incorporation of Al in the films does not imply changes in the crystal structure of CdS . The films exhibit five peaks related to (100), (002), (101), (110) and (112) plane of hexagonal phase and show preferential orientation of (002) plane As shown in table 1 [14,15] .

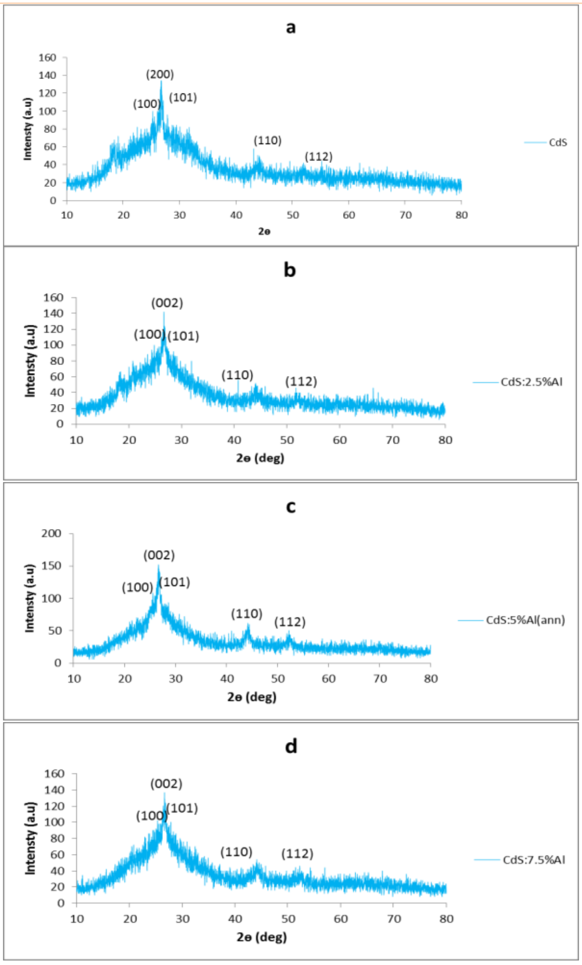

Fig1: XRDpattern of deposited CdS:Al for a:CdS b:CdS:2.5%Al c:CdS: 5%Al d:CdS:7.5%Al

Tab1. XRD result of CdS and CdS:Al

No.	Material	2Θ(deg)	d(Å) Observed	FWHM(deg)	(hkl)	D_{av}(nm)	a (Å)	c(Å)
1	CdS	25.34 26.75 27.84 44.12 52.1	3.51 3.32 3.2 2.05 1.75	0.58 0.82 0.68 0.66 0.4	(100) (002) (101) (110) (112)	10.39	4.05	6.64
2	CdS:Al 2.5%	25.35 26.63 28.4844.1 0 51.72	3.51 3.34 3.13 2.05 1.76	0.92 1.02 0.72 0.78 0.32	(100) (002) (101) (110) (112)	8.35	4.05	6.68
3	CdS:Al 5%	25.15 26.72 28.48 44.07 52.26	3.53 3.33 3.13 2.05 1.74	0.8 0.96 0.52 0.84 0.76	(100) (002) (101) (110) (112)	8.88	4.07	6.66
4	CdS:Al 7.5%	25.57 26.64 28.56 44.13 52.38	3.48 3.34 3.12 2.05 1.74	1.20 0.925 0.36 0.72 0.16	(100) (002) (101) (110) (112)	9.21	4.01	6.68

Fig2. Shows the scanning electron microscope of pure and Aluminum doped CdS films prepared on glass substrate. The samples have homogeneous surface distribution and free spaces and from the observation of the images as in Fig. 2a and

2b the films after the doping reduce the defects, This result corresponds to an increase in granularity calculated from XRD results [16, 17].

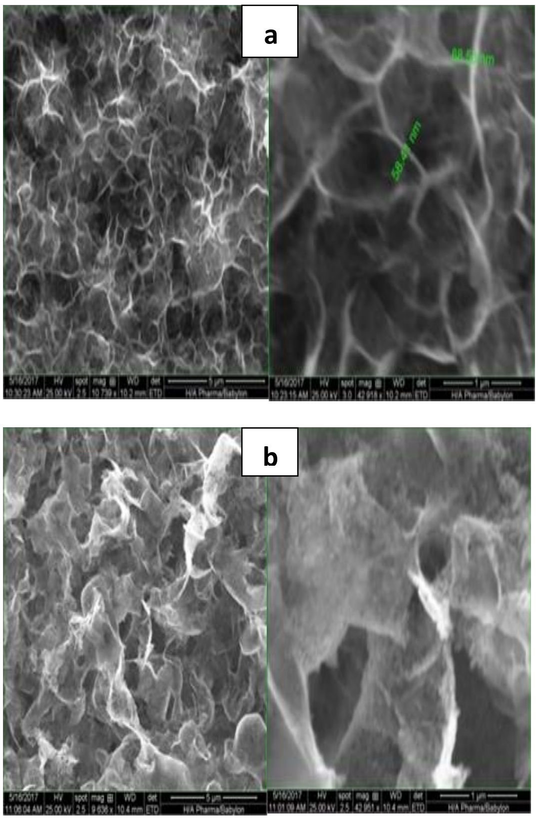

Fig2. SEM images of a:CdS b: CdS:7.5%Al

Fig3. Shows AFM measurement technique offers digital images which allow quantitative measurements of surface features such as root mean square (RMS) or average roughness R Shown in the tab2. When taking two images with dimensions 2D, 3D it can be seen that the films are distributed regularly in the form of small granules connected without spaces between them. Fig3. Shows curved volumetric distribution for crystalline granules where difference with aluminum doping ratio [18, 19].

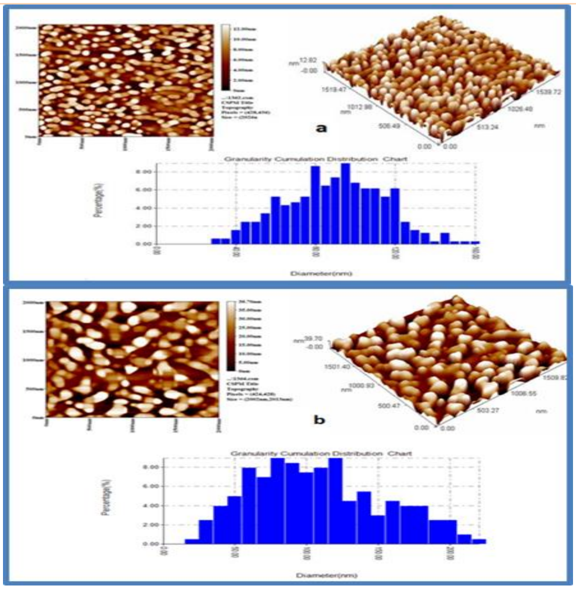

Fig3. AFM images of a:CdS b: CdS:7.5%Al

Tab2. AFM result of CdS and CdS:Al

Materials	*RMS (nm)*	*R (nm)*
CdS	*3.37*	*2.8*
CdS:7.5%Al	*11.4*	*9.87*

3.2 Optical Properties

The spectrum of Transmittance and Absorbance was recorded for the pure and Aluminum doped CdS films with percentages (0, 2.5, 5, 7.5) % within the wavelengths of the range from (300 –1100) nm .Fig4a. Shows the transmittance as a function of the wavelength of pure and Aluminum doped CdS film, where it can be observed an increase in transmittance by increasing the wavelength. It was also observed that the transmittance decreased by increasing doping, we also observe a clear increase in transmittance at wavelength (500 ± 20) nm and these results are concordant with researches [20, 21]. Fig4b. Shows that the absorbance as a function of the wavelength of pure and Aluminum doped CdS films, where observe the absorption values decrease by increasing the wavelength. It can be seen increasing with increasing doping, also fig4b. shows that the absorption edge shifts towards the longer wavelength for CdS:Al compared to CdS thin film [22] .

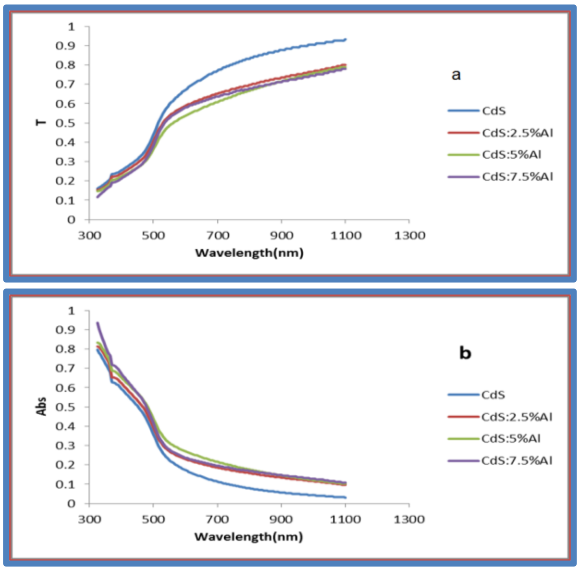

Fig4. a optical transmittance and b theoptical absorption curves of CdS and CdS:(2.5,5,7.5)%Al

Fig5. Shows the absorption coefficient as a function of the energy photon ($h\upsilon$) , it can be seenthat the films have a high absorption coefficient ($\alpha > 10^4 cm^{-1}$) this indicates direct electronic transitions [23] . The absorption coefficient increases by increasing the photon energy and is a quick increase in the range of (2.35 - 2.55) eV,it can be seen observe that the absorption coefficient increases slightly by increasing the doping and that the absorption edge shift towards the low energies this is because new localized levels have been formed that permeate the fundamental levels that absorb the low energy photons and this leads to an increase in the absorption coefficient values [24].

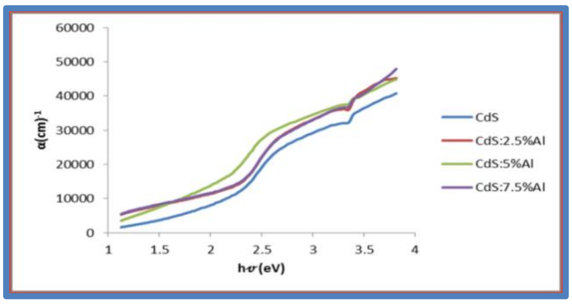

Fig5: Absorption coefficient of CdS and CdS:(2.5,5,7.5)%Al

Fig6. shows the value of the optical energy band gap for allowed direct transition calculated by using relation (4) by selecting the perfect linear part, which is determined by extrapolating the linear portion of the curves until they intercept the photon energy axis at $(\alpha h\upsilon)^2=0$. Its value for different ratios of Aluminum doped CdS thin films are decreased to (2.89, 2.85, 2.79, 2.81) eV for (0, 2.5, 5, 7.5 %) of Aluminum doping ratios respectively. The higher value of the E_g compared with that of the bulk energy gap of 2.42 eV, indicates the formation of nanostructure and presence of quantum confinement effects in the prepared films [25, 26]. The decreases in Eg may be due to the replacement of larger number of substitutional or interstitial Cadmium ions by Aluminum ions, this is because new localized levels have been formed that permeate the fundamental levels [19,27] .

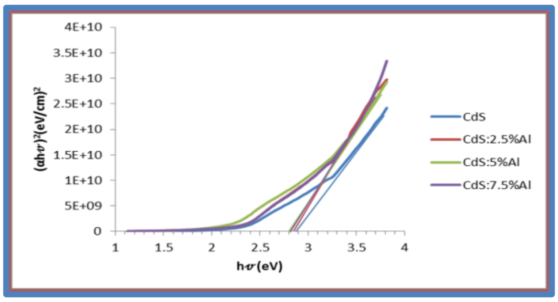

Fig 6: The Energy Gap for the Allowed Direct Transition $(\alpha h\upsilon)^2$ as a Function of Photon Energy CdS and CdS:(2.5,5,7.5)%Al

4. Conclusions

1. Chemical bath deposition method is an easy and inexpensive to prepare cadmium sulfide films.
2. XRD studies of pure and Aluminum doped CdS films indicated the formation of nanocrystalline with polycrystalline hexagonal phase.
3. The surface topography of (SEM), the films were found to be uniformly homogenous and distributed.
4. The high optical transmittance in wavelength region(T > 500 nm) ,its advantageous features of CdS thin films that works as filters, and antireflection coating to improve solar cell efficiency .

5. Films have a high absorption coefficient which gives indication that the electronic transitions is direct transitions, The optical gap decrease with increasing doping ratio from (2.89 - 2.79 eV).

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