Annealing temperature effect on the structural and optical properties of thermally deposited nanocrystalline CdS thin films

R. A. Abdullah[1], M. F.A. Alias[2], M. A. Razooqi[1],

A. A. Al-Douri [3], A. A. Alnajjar[3].

[1] Dept. of Physics, College of Science, University of Tikreet, Iraq.
[2] Dept. of Physics, College of Science, University of Baghdad, Iraq.
[3] Applied Physics Department, Sciences College, University of Sharjah, UAE.

Abstract

A nanocrystalline CdS thin film with 100 nm thickness has been prepared by thermal evaporation technique on glass substrate with substrate temperature of about 423 K. The films annealed under vacuum at different annealing temperature 473, 523 and 573 K. The X-ray diffraction studies show that CdS thin films have a hexagonal polycrystalline structure with preferred orientation at (002) direction. Our investigation showed the grain size of thin films increased from 9.1 to 18.9 nm with increasing the annealing temperature. The optical measurements showed that CdS thin films have direct energy band gap, which decreases with increasing the annealing temperature within the range 3.2- 2.85 eV. The absorbance edge is blue shifted. The absorption coefficient for CdS films decreases with increasing the annealing temperature. The optical constant for the films such as refractive index, extinction coefficient, real and imaginary part of dielectric constant were observed to decrease with increasing the annealing temperature. The particle size calculated from absorption spectrum has increased from 4.74 to 8.38 nm with increasing the annealing temperature.

تأثير درجة حرارة التلدين على الخواص التركيبية والبصرية لاغشية كبريتيد الكادميوم النانوية المرسبة حرارياً

رشا عباس عبد الله[1] وميسون فيصل احمد الياس[2] ومحمدعبد الوهاب رزوقي[1] وعلاء احمد الدوري[3] وعبد الله عبدالعزيز النجار[3]

[1]قسم الفيزياء- كلية العلوم-جامعة تكريت ـ العراق
[2]قسم الفيزياء كلية العلوم،جامعة بغداد،العراق
[3]قسم الفيزياء التطبيقية- كلية العلوم-جامعةالشارقة ـ الامارات العربية المتحدة

الخلاصة

تم تحضير أغشية كبريتيد الكادميوم النانوية بسمك 100 نانومتر بواسطة التبخير الحراري على ارضيات زجاجية بدرجة حرارة اساس 423 درجة حرارة مطلقة. تم تلدين الاغشية المحضرة بدرجات حرارية مختلفة (473 و 523 و 573 درجة حرارة مطلقة). تم فحص تركيب الاغشية بتقنية حيود الاشعة السينية، حيث اظهرت النتائج امتلاك الاغشية تركيب سداسي متعدد التبلور باتجاهية مثلى(002). اوضحت النتائج بأن الحجم الحبيبي قد ازداد من 9.1 الى 18.9 نانومتر مع تزايد درجة حرارة التلدين. اوضحت القياسات البصرية ان اغشية كبريتيد الكادميوم ذات فجوة طاقة مباشرة، والتي تقل بزيادة درجة حرارة التلدين ضمن المدى 3.2 الى 2.85 الكترون فولت. تعاني حافة الامتصاص من ازاحة نحو الازرق. يقل معامل الامتصاص مع زيادة درجة حرارة التلدين ان الثوابت البصرية مثل معامل الانكسار و ثابت الخمود و ثوابت العزل بجزئيها جميعها قد قلت مع زيادة درجة حرارة التلدين. تم حساب الحجم الحبيبي من طيف الامتصاص ، وقد وجد انه يزداد من 4.74 الى 8.38 نانومتر بزيادة درجة حرارة التلدين.

Introduction

Cadmium sulfide (CdS) is an important metal chalcogenides for researchers because they are potential candidates for optoelectronic applications [1]. Polycrystalline CdS thin films are widely used as window material in several heterojunction solar cells for their favorable optical properties [2, 3]. CdS has suitable band gap, high absorption coefficient and considerable energy conversion efficiency [4]. With the recent development of nanoscience and nanotechnology attention has also been given attracted by nanostructured materials. Because of the huge surface-to-volume ratio of nanoparticles and the high porosity of nanoparticle layers and assemblies, a large number of analyte molecules can be adsorbed by a nanoparticle and within a nanoparticle structure in a very short time [5, 6]. CdS nanoparticles have low refractive index compared to the bulk due to the quantum confinement effect. The quantum size effect is theoretically classified into two types: one is the exciton confinement effect and the other is the independent confinement effect of electron and hole [5]. Many techniques have been reported for the deposition of CdS thin film, such as metal organic chemical vapor deposition, molecular beam epitaxial technique [2], laser ablation, close space sublimation, electrochemical deposition technique [3], screen printing, photochemical deposition [4], brush plating, pulsed laser deposition, successive ionic layer adsorption, reaction [5], evaporation, sputtering, chemical bath deposition, spray pyrolysis [7]. In this article CdS nanocrystalline thin layers have been prepared by thermal evaporation technique and the effect of annealing temperature on the structural and optical properties of nanocrystalline CdS thin films have been investigated.

Experimental Work

Corning glass slides used as a substrates, which are cleaned with method in reference [8]. CdS thin films of 100 nm thickness, using weighting method, were prepared by thermal evaporation technique using CdS of 99.999% purity under pressure about 10^{-6} mbar and at substrate temperature of 423K. The distance between the molybdenum boat and the substrate was 20 cm. The deposition rate of CdS films were about 0.16nm/sec. The samples have been annealed in vacuum oven at different annealing temperatures (T_a=473, 523 and 573) K for 60 min. The structure of CdS films have been examined by using XRD with Cuk$_\alpha$ wavelength 1.5405 Å, the scanning angle has varied in the range (20-60) ° with speed 2 cm/min, current 25 mA and voltage 40 kV. The optical properties of prepared films were studied by using UV/VIS. Centra 5 Spectrometer from the absorbance spectra 200nm to 800nm range.

Results and Discussion

1. Structural characteristics

Figure 1 illustrates the XRD spectra for the as prepared and annealed thin CdS films at 473, 523 and 573 K. The spectra of CdS films are compared with ASTM cards of CdS structure, and indicated a polycrystalline structure of pure hexagonal phase. This result is in agreement with Hur et al [9], Shashan and Odhia [10] and Olivia et al [11]. The XRD spectrum for the as deposited film shows strong reflection at (002) plane and very low intensity peaks at (103) and (004). However after annealing the samples at 473, 523 and 573 K, the XRD patterns showed one significant peak, but one expected an improvement in crystallinity, albeit significant decrease as well as in the intensity for all planes,

as well as decreasing in FHWM, means increasing the grain size, which indicates that the process of grain formation is thermally activated [5].The XRD spectrum of the films showed a slight shifting towards a higher diffraction angle. If there is lattice construction caused by narrowing the crystalline size [12], this improvement may be attributed to recrystallization of the films structure, by the enhancement of the re-arrangement of Cd and S atoms in the film crystallites [2, 13].
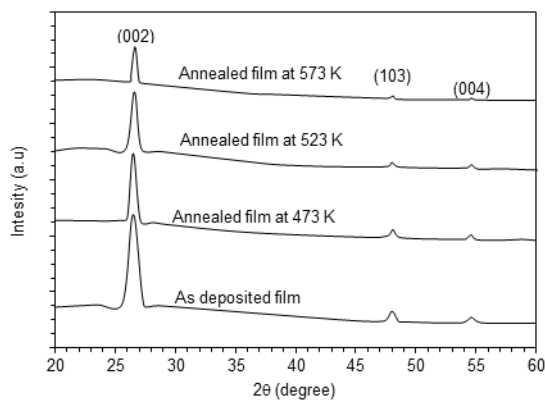
Fig. 1 The XRD spectra for the as deposited and annealed CdS thin films at various T_a.

The lattice constants of CdS powder were a=0.3564 nm and c=0.6717 nm, our result is in good agreement with Thambidurai et al [5] and Haider et al [14]. The grain size dimensions (D_{XRD}) is calculated from Debye Scherer relation [4]:

$$D = k\lambda / \beta \cos\theta \qquad (1)$$

where k is the shape factor, which is approximately 0.9 and β is the line broadening of pure diffraction profile on 2θ in radius and equal to the full width at half maximum intensity (FWHM) of the peak. The CdS grain size has been calculated for (002) plane, which is increased with increase the annealing temperature from 9.1 to 18.9 nm as tabulated in Table 1. Similar results have been found by Sanap and Pawar [4] and Hur et al [9].

The micro strain (S), dislocation density (δ) (defined as the length of dislocation lines per unit area) and numbers of crystallites per unit area (N) have been calculated using the following relations [15] and their values are given in the Table 1.

$$S = \beta \cos\theta/4 \qquad (2)$$
$$\delta = 1/D^2 \qquad (3)$$
$$N = t/D^3 \qquad (4)$$

where t is the thickness of the film. It is interesting to note that the annealing temperature decreases the dislocation density, the number of crystallites per unit area and the strain in the films. Similar results have been found by Bakiyaraj et al [15] and Asogwa [16].

2. Optical characteristics

The absorbance spectra of CdS thin films for as prepared and the annealed films are shown in figure 2. It can be observed that the absorption edge shift toward the shorter wavelengths (blue shift) with increasing the annealing temperature and also with respect to the bulk material (E_g = 2.42 eV), indicating quantum confinement effect in the nonaparticles. Similar results have found by Akintunde [17].
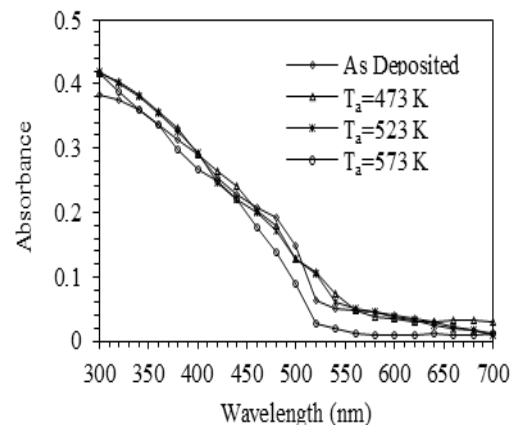
Fig. 2 The absorbance spectra for as the deposited and annealed CdS thin films at various T_a.

It is well known that for semiconductor particles with radius less than bulk Boher exciton radius, there is a blue

shift in the absorption edge due to the quantum size effect [5]. The absorption coefficient (α) can calculated from the relation [18]:

$$\alpha = 1/t \ln(1/T) \qquad (5)$$

where T is the transmittance. One can observe from figure 2 that CdS films exhibits a strong absorption of photons at the short wavelength region within the range 300-540 nm. In the strong absorption region, the absorption coefficient takes higher value within the range $(0.922\text{-}0.110) \times 10^4 \text{cm}^{-1}$. The values of the absorption coefficient are tabulated in Table 1 and nearly agreement with the results of Metİn and Esen [8]. Then after this region the absorption coefficient is slightly decreased with increasing of the wavelength. On the other hand, the value of The absorption coefficient for CdS films at 480 nm wavelength has decreased slightly with increasing the annealing temperatures by factor of 1.4 from $0.446 \times 10^4 \text{cm}^{-1}$ to $0.316 \times 10^4 \text{cm}^{-1}$, this slightly decreasing may be due to structural improvement. The optical energy gap (E_g) has calculating using the following relation [17]:

$$\alpha = A(h\nu - E_g)^r / h\nu \qquad (6)$$

where A is constant, hν is the photon energy and r is constant equal to 1/2 for allowed direct transition. The values of energy gap estimated from the extrapolation to zero absorption in this equation. Figure (3a-d) showed the variation of $(\alpha h\nu)^2$ with photon energy for CdS thin film annealed at various annealing temperature. The variation of E_g with the annealing temperature is tabulated in Table 1. The direct optical energy gaps of CdS films were estimated to lie in the range 3.20-2.85 eV for the as prepared and annealed films at 473, 523 and 573 K. Saikia et al [3], Shashan and Oudhia [10], Haider et al [14], and Heo et al [19] have found direct band gap of thin CdS films. The energy band gap is slightly

decreased with increasing the annealing temperature.

Our results are nearly in agreement with Vavalakar [1], Thambiduria [5] and Aknituned [17]. The decreasing of E_g with increasing annealing temperature is probably due to annealing effect which may change density of crystalline defect [20]. Here the CdS thin films have energy gap larger than the bulk semiconductor (2.42 eV), Chanchiang the geometry of the surface of quantum dot also change the energy band due the small size of dot and the effect of quantum confinement. Our values of energy gap are nearly agreement with Saikia et al [3].
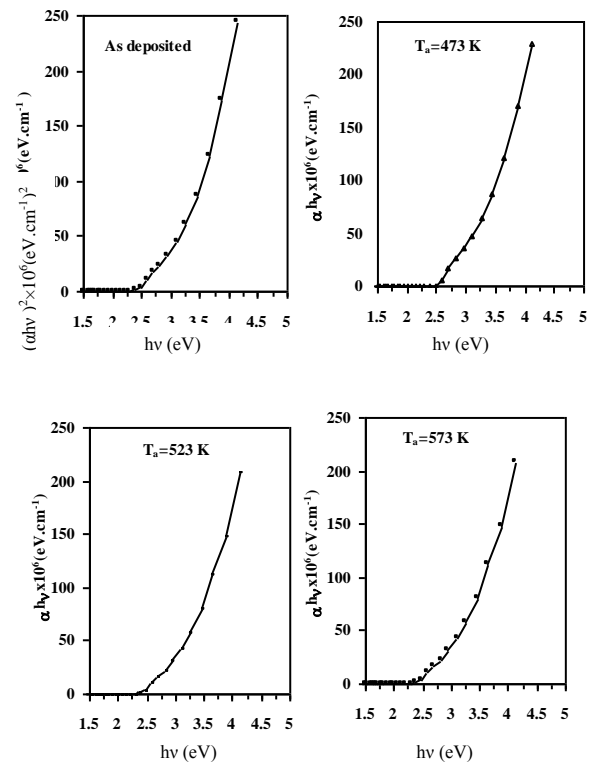
Fig. 3 The plot of $(\alpha h\nu)^2$ vs hυ for as deposited CdS thin films and annealed at various T_a.

The size of the nanoparticles has been calculated using the blue shift of the band gap caused by quantum confinement, and using the effective mass approximation method as the following relation [3, 5]:

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$$E_{gn} - E_{gb} = h^2\pi^2/2MR^2 \qquad (7)$$

where E_{gn} and E_{gb} are the energy gaps of the prepared films and the bulk material respectively. h is Plank's constant, M the translation mass($M = m_e^* + m_h^*$) and R is the particle size. The particle size is found to lie in the range 4.74- 6.38 nm. The values of refractive Index (n), extinction coefficient (k) and dielectric constant (real (ε_r) and imaginary (ε_i) parts) can be calculated from the following equations [21]:

$$n = [(4R/(R-1)^2) - k^2]^{1/2} - [(R+1)/(R-1)] \quad (8)$$

$$k = \alpha\lambda/4\pi \qquad (9)$$

$$n^2 - k^2 = \varepsilon_r \qquad (10)$$

$$2nk = \varepsilon_i \qquad (11)$$

where R is the reflectance and λ is the wavelength of the light. The values of refractive Index (n), extinction coefficient (k) and dielectric constant (ε) for CdS films at 480 nm wavelengths with different annealing temperatures are tabulated in Table 1. It can see that they decreases with increasing annealing temperature, similar data has been observed by Cook and Christy [22] and Tepamtla et al [23]. The variation of real and imaginary part of dielectric constant respectively for CdS films respectively at different annealing temperatures.

The behavior of ε_r is similar to refractive index because of the smaller value of k^2 comparison to n^2, while ε_i depends mainly on the k values, which is related to the variation of absorption coefficient.

For CdS films, it is found that both ε_r and ε_i decreased with increasing Annealing temperature, these results nearly agrees with Cook and Christy [22].

Table 1 Absorption coefficient, E_g, S, δ, N, D, n,k, ε_r and ε_i of CdS thin films at absorption edge.

Sample	$\alpha\times10^4$ cm^{-1}	E_g eV	$S\times10^{-4}$	$\delta\times10^{16}$ Lines/m^2	$N\times10^{18}$ m^{-2}
R.T.	0.44	3.2	19.1	42.20	28.13
473K	0.41	3.0	14.0	37.62	25.08
523K	0.39	2.9	12.3	33.10	22.07
573K	0.31	2.8	9.12	31.33	20.89

Sample	D_{XRD} nm	D_{uv-vis} nm	n	k	ε_r	ε_i
R.T.	9.1	4.74	2.37	0.017	5.64	0.08
473K	12.4	5.32	2.32	0.016	5.41	0.07
523K	14.1	6.04	2.29	0.015	5.26	0.06
573K	18.9	6.38	2.15	0.012	4.63	0.05

Conclusions

CdS films are polycrystalline with pure hexagonal structure. The crystalline orientation and relative intensity were affected by annealing process and which resulted in a strong peak at (002) direction. The grain size increased from 9.1 nm to 18.9 nm with increasing the annealing temperature. The annealing temperature decreases the dislocation density, the number of crystallites per unit area and the strain in the films. The absorption spectra for CdS films found to shift the peak of the absorption edge to the shorter wavelength compared to the as prepared films for all films with increasing annealing temperature due to the quantum confinement effect. The absorption coefficient of CdS films decreases with increasing annealing temperatures. It is found that the optical energy gap has direct transitions and decreased with increasing the annealing temperature. The particle size calculating using the absorption spectrum increased from 4.74 nm to 6.38 nm with increasing the annealing temperature. The refractive index, extinction coefficient and the dielectric constants for CdS films were found to decrease with increasing annealing temperature.

References

[1] S. A. Vanalakar, S. S. Mali, M. P. Suryavanshi and P. S. Patil: Journal of Nanomaterials and Biostructures. 5(2010) no. 4, 805/810.

[2] A. I. Khudiar, S. M. Zulfequar and Z. H. Khan, Chalcogenide Letters, 7 (2010) no. 5, 291/298.

[3] D. Saikia, P. K. Gogoi and P. K. Saikia: Chalcogenide Letters. 7 (2010) no. 5, 317/324.

[4] V. B. Sanap and B. H. Pawar: Chalcogenide Letters. 6 (2009) no. 8, 415/419.

[5] M. Thambidurai, N. Murugan, N. Muthukumarasamy, S. Agilan, S. Vasantha and R. Balasundaraprabhu: J. Mater. Sci. Technol. 26 (2010) no. 3, 193/199.

[6] D. Nesheva, Z. Aneva, S. Reynolds, C. Main and A. G. Fitzgerald: Journal of Optoelectronics and Advanced Materials. 8 (2007) no. 6, 2120/2125

[7] S.J. Ikhmayies and R. N. Ahmad-Bitar: American Journal of Applied Science. 5 (2008) no. 9, 1141/1143.

[8] H. Metİn and R.Esen, Erciyes :Üniversitesi Fen Bilimleri Entitüsü Dergisi. 19 (2003) no. 1-2, 96/102.

[9] S. Hur, E. Kim, J. Lee, G. Kim and S. yoon: J. Vac. Sci. Technol. B. 26 (2008) no. 4, 1334/1337.

[10] S. Shashan and A. Oudhia, Indian :journal of pure and applied physics. 47 (2009) 60/65.

[11] A. I. oliva, R. Castro- Rodriguez, O. Solis-Canto, V. Sosa, P. Quintana and J. L. Pena: Applied Surface Science. 205 (2003) 56/64.

[12] S. N. Sahu and K.K. Nanda Nanostructures Semiconductors : physics and applications, PINSA. 67 (2001) no. 1, 103/130.

[13] M.Zambuto: Semiconductor Device (McGraw-Hill Book Company, USA, (1989).

[14] A. J. Haider, A.M. Mousa and S. M. H. Al-Jawad: journal of semiconductor technology and science. 8 (2008) no. 4, 326/331.

[15] G. Bakiyaraj, N. Gopalakrishanan and R. Dhanasekaran: Chalcogenide Letters. 8 (2011) no. 7, 419/ 426.

[16] P.U. Asogwa: Chalcogenide Letters. 8 (2011) no. 3, 199/206.

[17] J.A.Akintunde: Phys.Stat. Sol. A. 179 (2000) 363/371.

[18] D. A. Newmen: Semiconductor Physics and Devices(Richard D. IRWIN, INC., USA (1992).

[19] J.Heo, H. Thn, R.Lee, Y.Han and D. Kim: Solar Energy Materials and Solar Cells. 75 (2003) 193/203.

[20] N. Mott and E. Davis: Electronic Process in Non-Crystalline Materials (Oxford University Press, 2nd ed. (1980).

[21] T.S.Moss: Semiconductor Opto-electronics(Butter Worths Sci. publishing, London (1973).

[22] R.K.Cook and R.W Christy: J.App.Phys. 51 (1980) no. 1, 658/672.

[23] C.S. Tepamtla, A.M.P. Gonzalez and I.V.Arreola: Revista Mexicana De Fisica. 54 (2008) no. 2, 112/117.