Structural, electrical and optical properties of CdS thin films and the effect of annealing on photoconductivity

Haidar Jwad Abdul-Ameer Al-Rehamey

Al-Manssor Teacherś Training Institute, Ministry of Education, Baghdad, Iraq

E-mail: haydarjwad2@yahoo.com

Abstract

Cadmium sulfide (CdS) thin films with n-type semiconductor characteristics were prepared by flash evaporating method on glass substrates. Some films were annealed at 250 ºC for 1hr in air. The thicknesses of the films was estimated to be 0.5µ by the spectrometer measurement. Structural, morphological, electrical, optical and photoconductivity properties of CdS films have been investigated by X-ray diffraction, AFM, the Hall effect, optical transmittance spectra and photoconductivity analysis, respectively. X-ray diffraction (XRD) pattern shows that CdS films are in the stable hexagonal crystalline structure. Using Debye Scherrerś formula, the average grain size for the samples was found to be 26 nm. The transmittance of the samples was determined from optical trasmittance spectra. It is observed that the direct band gap energy for as deposited and annealed films are (2.55, 2.45) eV, respectively. The effect of annealing at 250 ºC for 1hr in air on optical and photoconductivity of films under various intensity of illuminations (43.81 and 115.12) mW/cm^2 was studied. The dark and photocurrents of the annealed films were found to be greater than that of as deposited.

Key words

CdS thin films, structural properties, optical properties, Hall mobility, photosensitivity.

Article info.

Received: Sept. 2014
Accepted: Nov. 2014
Published: Dec. 2014

الخواص التركيبية والكهربائية والبصرية لأغشية CdS الرقيقة وتأثير التلدين على التوصيلية الضوئية

حيدر جواد عبد الأمير الرهيمي

معهد أعداد المعلمين في المنصور, وزارة التربية, بغداد, العراق

الخلاصة

حضرت أغشيه رقيقه من مادة كبريتات الكادميوم (CdS) التي تمتلك مميزات اشباه الموصلات من النوع n بطريقة التبخير الحراري الوميضي على أرضيات زجاجية. بعض الأغشية سخنت لدرجة 250 ºC في الهواء لمدة ساعة واحده. قيس سمك الأغشية بواسطة المطياف ووجد أنه يساوي 0.5µ. درست الخواص التركيبية و الكهربائية و البصرية و التوصيلية الضوئية لأغشية CdS بواسطة حيود الأشعة السينية و مجهر القوه الذرية و تأثير هول و طيف النفاذية و تحليلات التوصيلية الضوئية على التوالي. أظهرت بيانات حيود الأشعة السينية أن لأغشية الـ CdS تركيب بلوري سداسي مستقر, و قد تم حساب معدل حجم الحبيبات البلورية بأستخدام معادلة ديباي شرر و وجد أنها تساوي 26 nm. حددت نفاذية العينات من القياسات الطيفية، لوحظ أن فجوة الطاقة المباشرة للأغشية غير الملدنة و الملدنه تساوي eV (2.55 ,2.45) على التوالي. تم دراسة تأثير تسخين الأغشية لدرجة 250 ºC لمدة ساعة واحده في الهواء على الخواص البصرية و التوصيلية الضوئية للأغشية لشدات ضوئية مختلفة mW/cm^2 (43.81,115.12). لقد وجد أن تيارات الظلام و الضوء للأغشية الملدنة اكبر من الأغشية الغير ملدنة.

Introduction

Cadmium sulfide (CdS) material has attracted much attention due to itś application in optical-electro devices, such as solar cells and light emitting diodes. Owing to the wide band gap of about 2.4~2.5 eV. CdS polycrystalline thin films are widely used as the window material in hetero junction solar cells. CdS can crystallize in hexagonal (h) wurtzite and cubic (c) zinc blende structures, in which the hexagonal structure is more stable than the cubic structure. Since sulphur is a volatile element, CdS is prone to generate lattice defect during fabrication procedures. For CdS, interstitial Cd atoms and S vacancies act as donors, and Cd vacancies and interstitial S atoms behave like acceptors.
These native defects introduce trapping states into the energy gap, which can significantly influence the optical-electric properties of CdS material [1,2].

CdS is a nonstoichiometric n-type semiconductor with direct band gap energy. In order to allow most of the optically excited electrons to pass through the film, the densities of trapping and recombination centers have to be relatively low. A low resistivity and a high photosensitivity are required for photoconductive-sensor applications.

The band gap of CdS is in the range of visible light so the photosensivity of CdS film in this range very high [3,4].

CdS polycrystalline films have been grown by a variety of film deposition techniques such as thermal evaporation [5], sputtering [6], pulsed laser deposition [7], and chemical bath deposition (CBD) [8]; in each of these methods polycrystalline, uniform and hard films are obtained, and their electrical properties are very sensitive to the method of preparation [9].

In this work CdS thin films were prepared by mean of the flash thermal evaporation technique. Structural, morphological, optical, electrical properties and photoconductivity of CdS films as deposited and annealed films in air for 1hr at 250 ^oC were investigated.

Experimental

CdS thin films were prepared using flash thermal evaporation of CdS powder of 99.999% which was obtained from (Merck Company, Germany) in a residual pressure of 10^{-5} Torr. Films were deposited on glass substrates which were ultrasonically and chemically cleaned. Some films were annealed at 250 ^oC for 1hr in air. The thickness of the films was measured using a (Black CXR-SR-25 spectrometer).

The crystal structure of the films was characterized by the X-ray diffraction (XRD) measurement using (XRD-6000 Shimadzu) diffractometer at a scanning rate of 5^o per minute between 20 – 60^o. The source used throughout this study was Cu,K_α(λ=1.5406 Å) operated at 30 mA and 40 kV. The average grain size was obtained from a Debye-Scherrer formula [7], D=0.9λ/ßcosθ, in which D is the average grain size, λ is the X-ray wavelength, and ß is the full-width at half-maxima (FWHM) in radians and θ is the diffraction angle. The surface morphology of the films was examined by atomic force microscopy (AFM) (SPM-AA 300, Angestrom Advanced Inc., USA). The electrodes of films used for photoconductivity measurement were achieved by thermal evaporation of Al grid through a mask on front surface of the prepared films. Ohmic contacts were made on the grid by indium.

The carrier concentration and Hall mobility of CdS films were investigated by Hall measurement (ECOPIA HMS-3000). Optical absorbance and transmittance were performed over the wave-length range 330-900 nm using UV visible spectrometer (Shimadzu UV-1800). The photoconductivity of as deposited and annealed films was obtained. The photoconductivity of the films was measured by white light from a Halogen lamp and precision multimeter (FIUKE 8846A 6-1/2 DIGIT). The intensity of the incident light on the sample was measured by photometer. The dark and photo currents against an applied voltage (1-10V) at power intensity (43.81 and 115.12) mW/cm^2 were obtained.

Results and discussion

Fig.1 shows the XRD pattern of CdS film deposited on glass substrates. Diffraction peak with the Bragg angle 2θ=26.7 was due to the (002) reflection in this hexagonal phase of CdS films, and this is agree with the literature [10]. The thickness of the films were determined to be 0.5µ.The average grain size of the CdS was estimated to be 26 nm by using Debye-Scherrerś formula and it is nearly agrees with Sung-Gi [11]. Fig.2 and Fig.3 show two and three dimensional AFM micrograph of the CdS thin films as deposited and annealed, respectively. The images show well defined particle like features with granular morphology and indicate the presence of small crystalline grains. The images also reveal a homogeneous formation of films without any cracks and is continuous with very well connected grains. Table 1 shows the values of average roughness and root mean square surface roughness (RMS) of as deposited and annealed films, our results are nearly agree with Hasoon et. al. [12]. From the Hall effect measurement we determined that the CdS film exhibits a negative Hall coefficient (n-type), has a carrier concentration equal 2×10^{15} cm^{-3} and mobility 8 cm^2/Vs . Similar studies of these parameters are reported by others [13, 14].

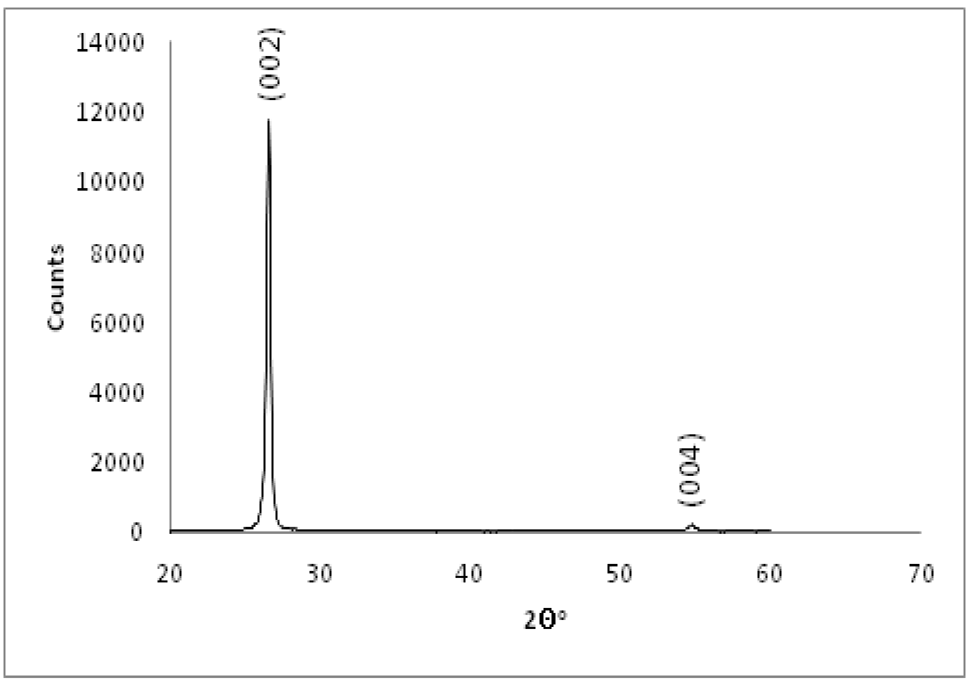
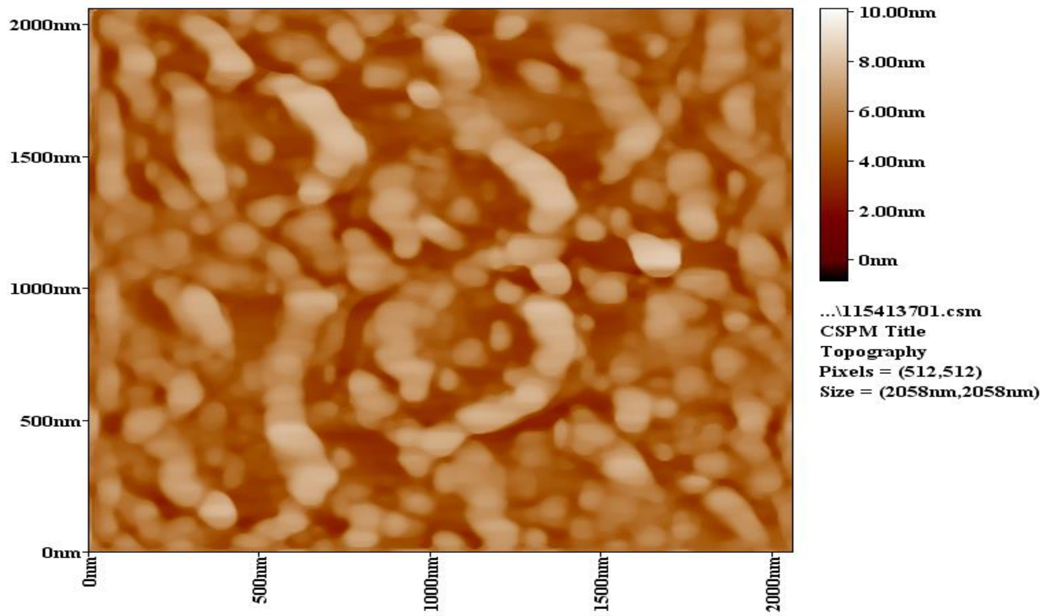
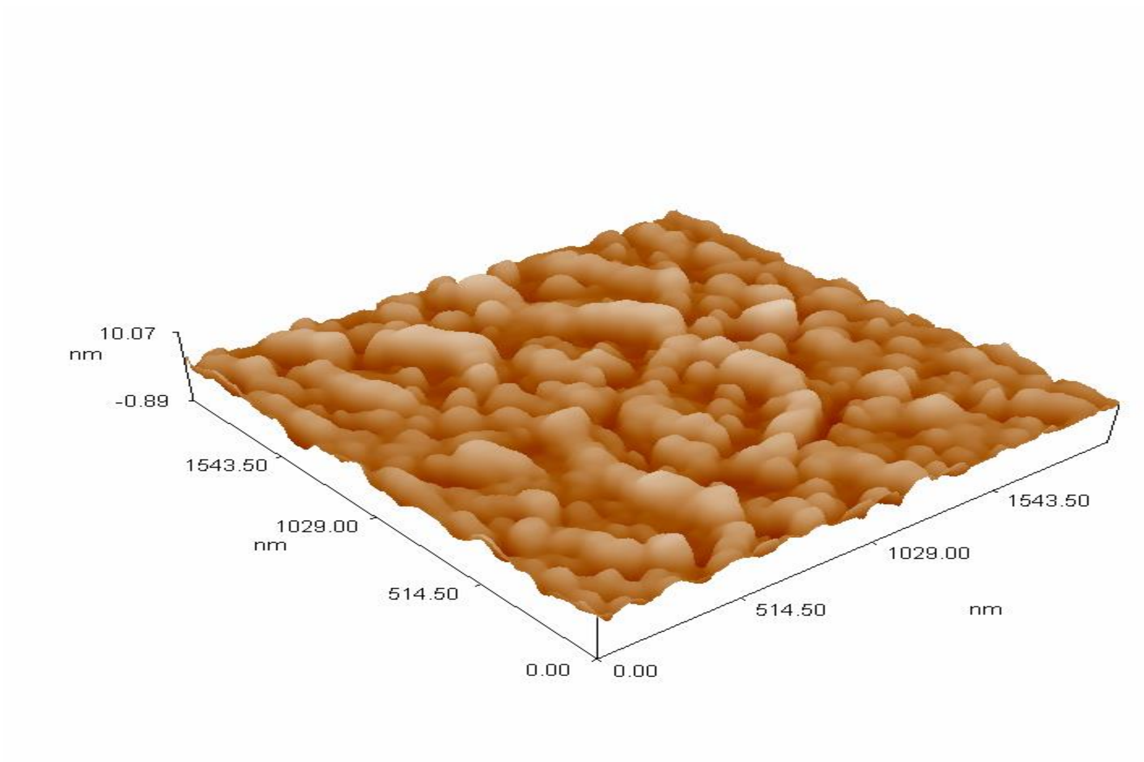


Fig.1: The XRD pattern of CdS thin films.

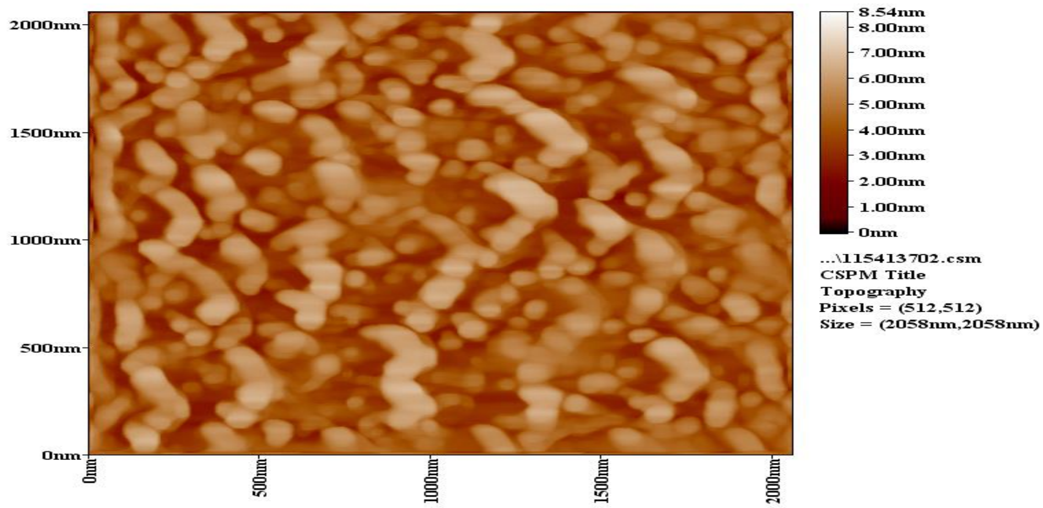


A

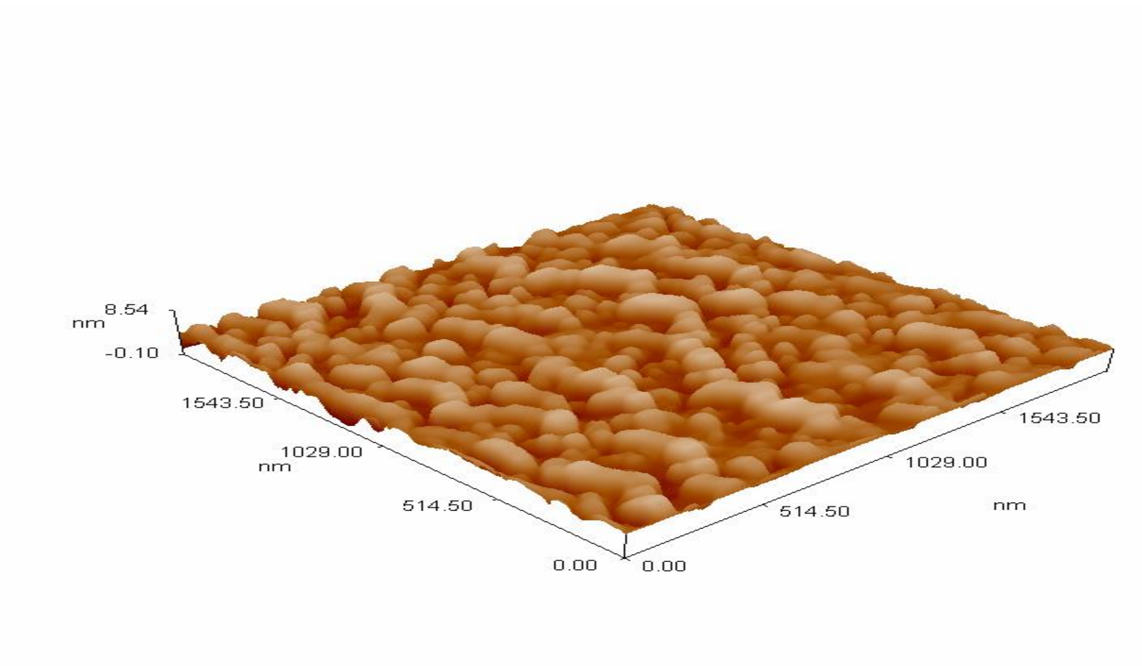


B

Fig. 2: AFM images (A) 2D (B) 3D of as deposited CdS fillm.



A



B

Fig.3: AFM images (A) 2D (B) 3D of annealed CdS film.

Table 1:The values of average roughness and root mean square surface roughness of as deposited and annealed CdS thin films.

	Average Roughness (nm)	Root Mean Square Surface Roughness (RMS) (nm)
As deposited	1	1.19
Annealed	0.853	1.01

Fig.4 and Fig.5 depict the optical absorptance and transmittance spectra of the as deposited and annealed CdS films in the range of 330 nm to 900 nm. It is clear from these figures that the spectral characterization is affected by annealing. It is obvious that the transmittance decreases with annealing because oxegen atoms are introduced in the film so more states will be available for the photons to be absorbed. The films have the transmittance more than 80% at wavelengths longer than the absorption edge. The optical band gap can be obtained by extra plotting the linear portion of the plot $(\alpha h\nu)^2$ versus hν. The direct band gap value of as deposited and annealed films have been obtained from the plot $(\alpha h\nu)^2$ versus hν as shown in the Fig.6 and are found to be (2.55, 2.45) eV ,respectively. Table 2 illustrates the values of direct optical energy gap and the optical constants [refractive index (n), extinction coefficient (k), the real part (ε_r) and the imaginary part (ε_i) of dielectric constant]. Our results are similar to that obtained by Ashour[13] , Moss [15] and Sivaraman [16]. The photoconductivity of the as deposited and annealed films has been determined. The current-voltage characteristics of the films were measured under darkness and illumination. Table 3 shows the dark and photo currents against the applied voltage of the as deposited and annealed films. Fig.7 and Fig.8 show the photocurrent against the applied voltage of the as deposited and annealed films under illumination at power intensity of 43.81 mW/cm^2 and 115.12 mW/cm^2, respectively. The currents of the annealed films were found to be greater than that of the as deposited. The average gain was estimated to be 10.71. The effect of heat treatment in air is to introduce oxygen atoms in the lattice of the CdS films, thereby producing acceptor levels. This behavior is in agreement with Buragohain and Barua [17].

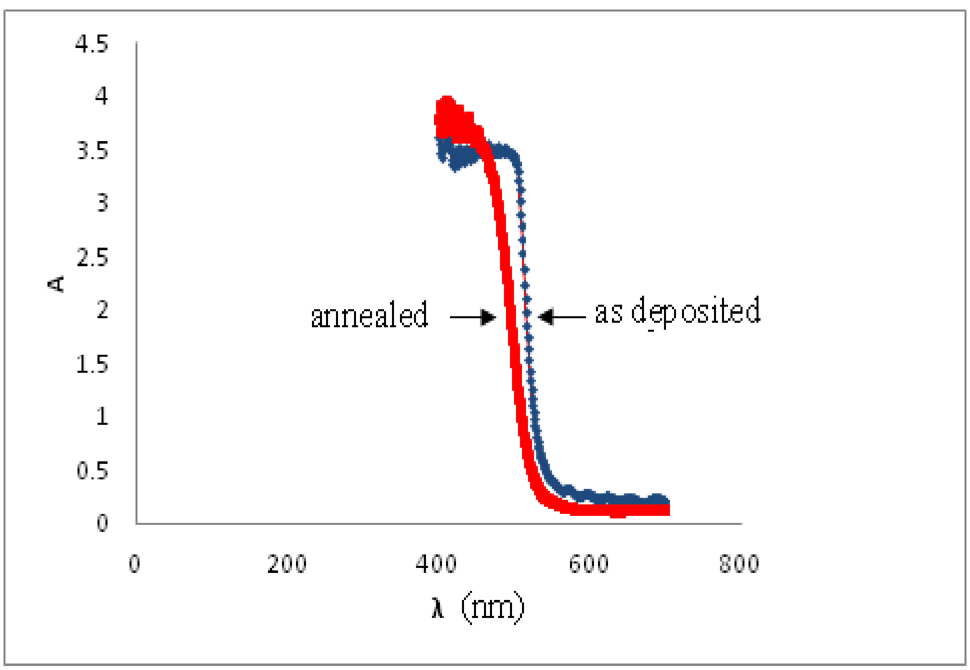


Fig.4: The absorption spectra of as deposited and annealed CdS thin films.

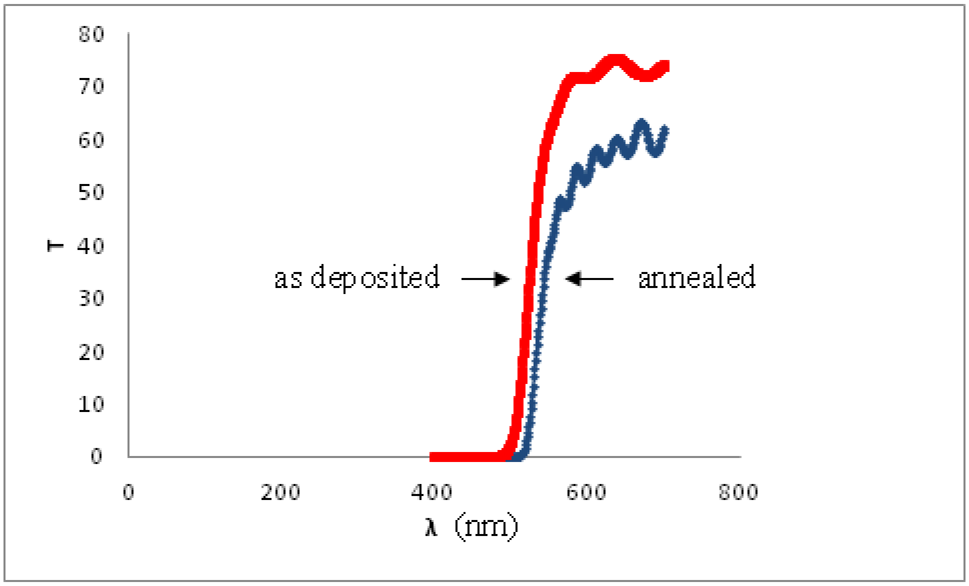


Fig.5: The transmission spectra of as deposited and annealed CdS thin films.

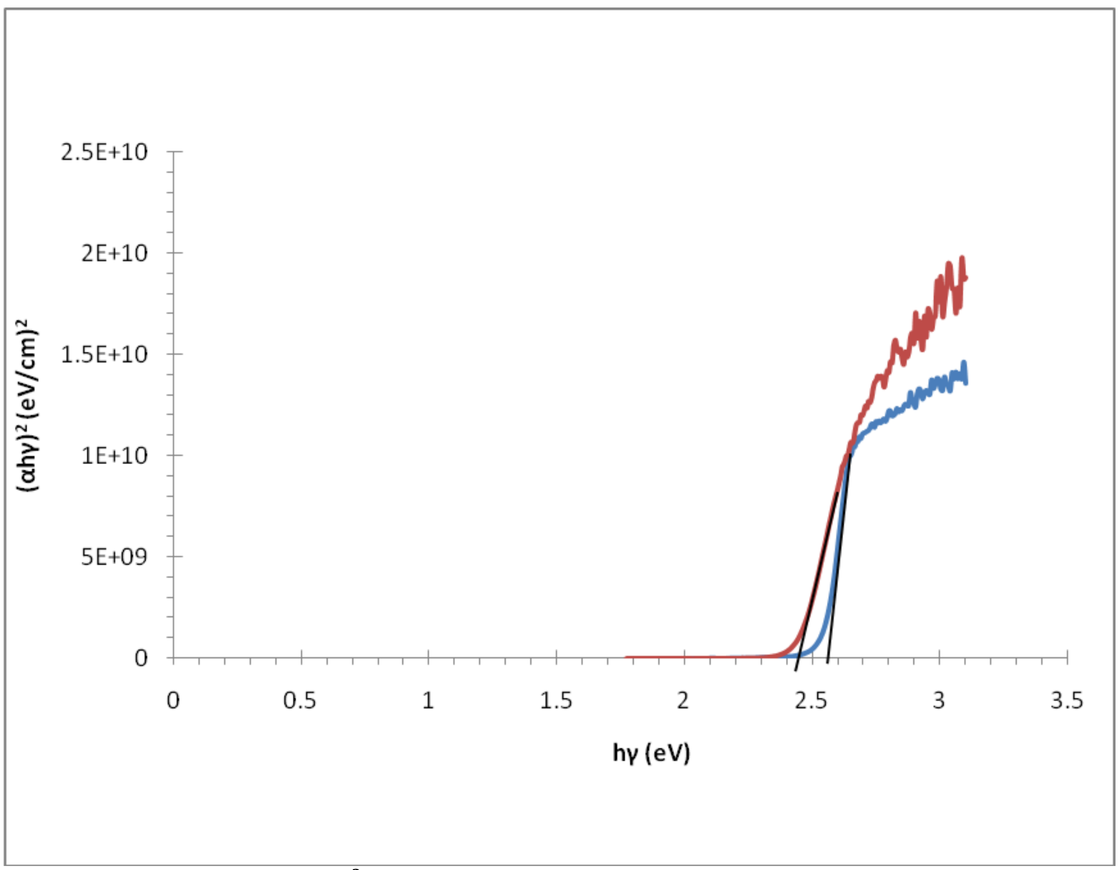


Fig.6: A plot of $(\alpha h\nu)^2$ versus hν of as deposited and annealed CdS thin films.

Table 2:The values of optical energy gap and optical constants of as deposited and annealed CdS films.

	E_g (eV)	n	k	ε_r	ε_i
As deposited	2.55	3.635	0.021	13.213	o.154
Annealed	2.45	2.560	0.010	6.554	0.054

Table 3: The dark and photocurrents against applied voltage of the as deposited and annealed films.

V (volt)	As deposited film			Annealed film		
	I_dx10^{-8} Amp.	I_{ph}x10^{-8} Amp. Under power intensity 43.81 mW/cm^2	I_{ph}x10^{-8} Amp. Under power intensity 115.12 mW/cm^2	I_dx10^{-8} Amp.	I_{ph}x10^{-8} Amp. Under power intensity 43.81 mW/cm^2	I_{ph}x10^{-8} Amp. Under power intensity 115.12 mW/cm^2
1	1.2	5	5	123	169	470
2	1.8	10.9	11	188	330	1020
3	2.6	23	24	226	470	1470
4	3.6	41	48	337	680	2150
5	4.5	54	78	689	970	2870
6	6.2	70	120	860	1100	3550
7	7.2	90	180	990	1300	4380
8	8.4	119	240	1040	1660	5090
9	9	130	270	1180	1800	5630
10	12.2	160	390	1180	2000	6320

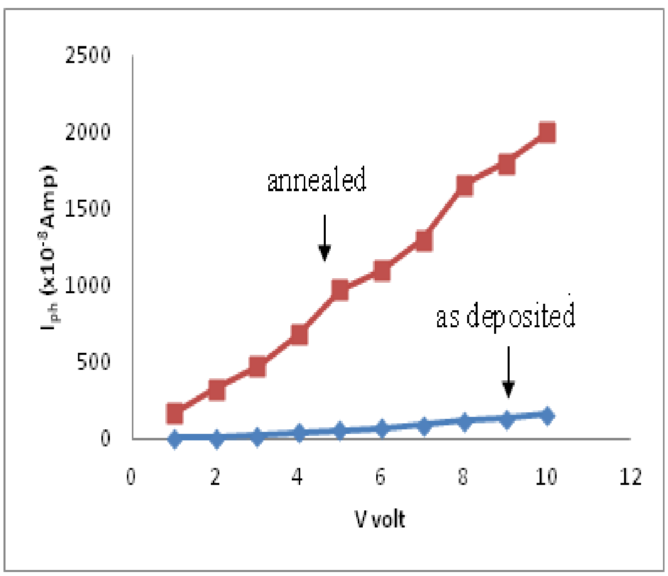


Fig.7: Photo current versus applied voltage of as deposited and annealed CdS thin films under illumination at power intensity 43.8 mW/cm^2.

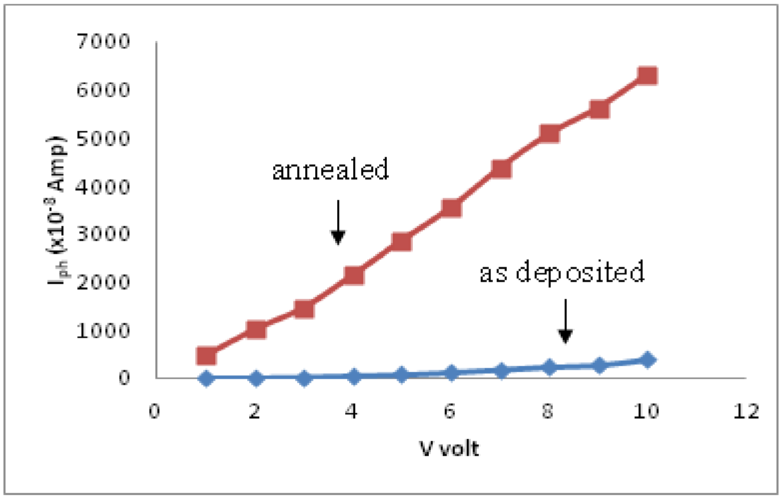


Fig.8: Photo current versus applied voltage of as deposited and annealed CdS thin films under illumination at power intensity 115.1 mW/cm^2.

Conclusions

CdS films with a thickness of 0.5µ were fabricated on glass substrates by flash evaporating method. Some films were annealed at 250 ^{o}C for 1hr in air. Films were investigated by XRD, AFM, Hall effect, optical transmittance spectra and photoconductivity. Based on the above results, the following conclusions can be drawn:

1. The CdS films have a hexagonal (wurtzite) structure and the preferred orientation is (002). The grain size is found to be 26 nm.
2. The average roughness and root mean square surface roughness decrease with annealing.
3. Hall coefficient is negative (n-type), carrier concentration and Hall mobility are 2×10^{15} cm^{-3} and 8 cm^2/ V.s, respectively.
4. The film exhibits an optical absorption edge at 500 nm.
5. The dark and photocurrents of annealed films are greater than those of as deposited films.

Referances

[1] S. K. Das and G. C. Morris, J. Appl. Phys., 73, 782 (1993).

[2] S. Wagner, J. Appl. Phys., 45 (1974) 246.

[3] D. P. Amalnerkar, Mater. Chem. Phys., 60 (1999) 1

[4] P. K. Nair, J. Campos, and M.T. S. Nair, Semicond. Sci. Technol., 3 (1988) 134.

[5] M. Agata, H. Kurase, S. Hayashi and K. Yamamoto Solid State Commun, 76 (1990) 1061.

[6] C. T. Tsai, D. S. Chuu, G. L. Chen and S. L. Yang J. Appl. Phys., 79 (1996) 9105.

[7] G. Perna, V. Capozzi, M. Ambrico, V. Augelli, T. Ligonzo, A. Minafra, L. Schiavulli and M. Pallara Thin Solid Films 453 (2004) 187.

[8] A. E. Abken, D. P. Halliday and K. Durose J. Appl. Phys. 105 (2009) 064515.

[9] C. S. Tepantlán, A. M. P. González and I. V. Arreola, Revista Mexicana de Fisica, 54, 2 (2008)112-117.

[10] Y. H. Sun, Y. J. Ge, W. W. Li, D. J. Huang, F. Chen, L. Y. Shang, P. X. Yang and J. H. Chu, Journal of Physics: Conference Series , 276 (2011) 012187.

[11] S.-G. Hur, E.-T. Kim, j.-H. Lee, G.-H. Kim and S. G. Yoon, J. Vac. Sci. Technol. B 26 (2008) 4.

[12] S. A. Hasoon, I. M. Ibrahim, R. M. S. Al-Haddad and S. S. Mahmood,

International Journal of Current Engineering and Technology, 4 (2014) 2.
[13] A. Ashour, Journal of Optoelectronics and Advanced Materials, 8, 4 (2006) 1447-1451.
[14] J. I. Wilson, J. Woods, J. Phys. Chem. Solids 34 (1973) 171.
[15] T. S. Moss "Optical Properties of Semiconductors", Academic Press, New York, 214 (1959).
[16] T. Sivaraman, V. S. Nagarethinam and A. R. Balu, Research Journal of Material Sciences, 2, 2 (2014) 6-15.
[17] M. Buragohain and K. Barua, Indian J. Phys., 59A, (1985) 178-184.