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INFLUENCE OF ANNEALING ON STRUCTURAL AND OPTICAL PROPERTIES OF CdS THIN FILMS DEVELOPED BY CHEMICAL ROUTE

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Cadmium Sulphide (CdS) is II-VI semiconducting material.CdSnanocrystalline film can be developed by chemical bath deposition usingnon aqueous medium. It is used for solar cells, optoelectronic devices, light emitting diodes, etc. The influence of annealing on solid state and optical properties of the films were studied by XRD, FESEM, EDS, AFM, UV-VIS, PL. The average grain size of as deposited and annealed CdS films are estimated to be 34nm and 48nm using Scherrer's formula. Compositional analysis indicates the presence of Cd, S and Mo.

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*Keywords:*Nanocrystalline, solar cell, ethyleneglycol, XRD, etc.

1. Introduction

In past two decades, group II-VI semiconductor thin film have more attentation by research community due to their wide applications in the field of solid-state solar cells, optical coatings, optoelectronic devices, light emitting diodes, etc. CdS, CdTe,CdSe, etc. are the binary II-VI semiconducting material of the cadmium based chalcogenide family and have more interest due to their use in photoconductive devices and solar cells [1-3]. Among these materials, Cadmium Sulphide (CdS) is the member of II-VI compound. It is n-type semiconducting material and has energy bandgap of 2.42eV [4,5]. The efficiency of solar cells reduces because low energy bandgap of CdS window layer absorbs the blue portion of the solar spectrum [6-8].CdS thin films have been prepared by various techniques including chemical bath deposition [9-12], Vacuum evaporation[13,14], sputtering [15], CVD [16,17],electrodeposition[18,19], etc. Among these deposition techniques, CBD is simple, low cost and easy coating of large surface area deposition of material. NanocrystallineCdS thin films can be prepared by CBD in non aqueous medium. Non aqueous bath offer greater flexibility for deposition of materials sources, higher working temperature ranges, uniform deposits, free from ubiquitous hydrogen evolution reaction [20].

In this paper, we have reported that the effect of annealing on the prepared CdS thin films deposited on molybdenum substrate by CBD in non aqueous medium. The as deposited as well as annealed CdS films were developed and were investigated by XRD, FESEM, EDS, AFM, UV-VIS spectrophotometer and PL spectrophotometer.

2. Experimental procedure

The electrolyte was prepared by using AR grade 0.2M $CdCl_2$ dissolved in 40ml of ethyleneglycol. The electrolyte was continuously stirred for two hours and temperature maintained at 160^0C. The molybdenum substrate having dimension 1.5cm×1cm×0.1cm was dipped into the

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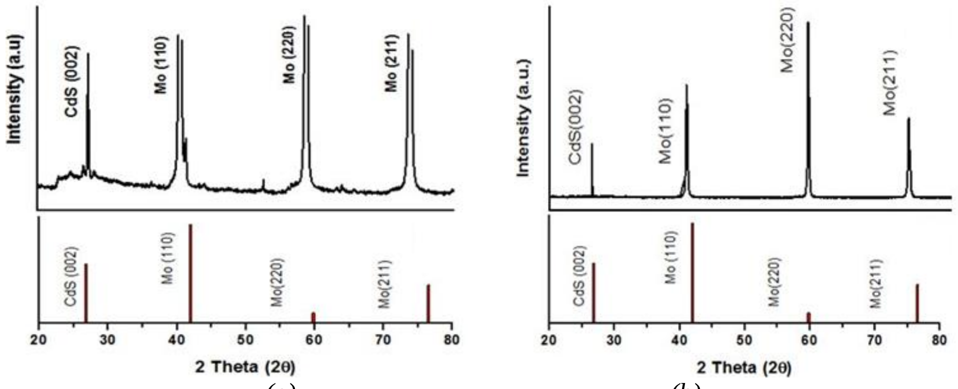
electrolyte with the help of rigid support and 0.4M thiourea was introduced into the electrolyte. The electrolyte was again stirred and deposited for 15 minutes on the molybdenum substrate. After the deposition the films were washed with distilled water for 15 seconds to remove counter ions and organic impurities. The as deposited CdS films deposited on molybdenum substrate were physically stable and identify good adhesion. The prepared as-deposited CdSnanocrystalline film was annealed at 400^0C in air.

The crystallographic structure of as deposited and annealed CdSnanocrystalline films were analysed by Bruker AXS Diffractometer model D8 with CuK_α radiation with wavelength 1.54A°. The average grain size of as deposited and annealed CdS films were obtained byusing Debey-Scherrer's formula. Surface morphology and elemental analysis of both films were carried out by using Field Emission Scanning Electron Microscope, model Quanta 200F, FEI Netherland. Optical property was measured by UV-visible spectrophotometer, model Lambda-25 Perkin-Elmer with wavelength range of 300nm-900nm. Surface roughness of as deposited and annealed CdS films were determined using Atomic Force Microscope, model Nanosurf EZ2, Switzerland. PL studies of both films were carried out by using spectrophotometer, model-RF 5301PC, Shimadzu with wavelength 300nm-800nm.

3. Results and Discussions

3.1. Structural analysis of as deposited and annealed CdS films

The as deposited CdS films deposited on molybdenum substrate are physically stable and shows good adhesion. Figure 1(a) and (b) shows XRD pattern of as deposited and annealed CdS thin films are carried out in the range of 20^0-80^0 with scan rate of 3^0 per minute. It is observed that as deposited CdSnanocrystalline thin films indicate the peak at $2\theta = 26.76^0$ with (002) diffraction planes of crystalline hexagonal CdS structure.



(a) *(b)*

Fig.1 XRD spectra of as deposited CdS films. Fig.1(b): XRD spectra of annealed CdSfilms.

Reflections due to molybdenum substrate, the subsequent peaks are attributed to scattering from (110), (220) and (211) planes. Figure 1(b) shows the X-ray diffraction peak of CdS annealed films at 400^0C. The observed crystalline hexagonal peak (002) is more intense as compared to as deposited film.

The crystallite size of as deposited and annealed CdS thin films are calculated using Scherrer's formula**:**

The crystallite Size $D = K\lambda/\beta \cos\theta$

Where, K= Constant equal to 0.94,

λ = Wavelength of X-ray (=1.54A°),

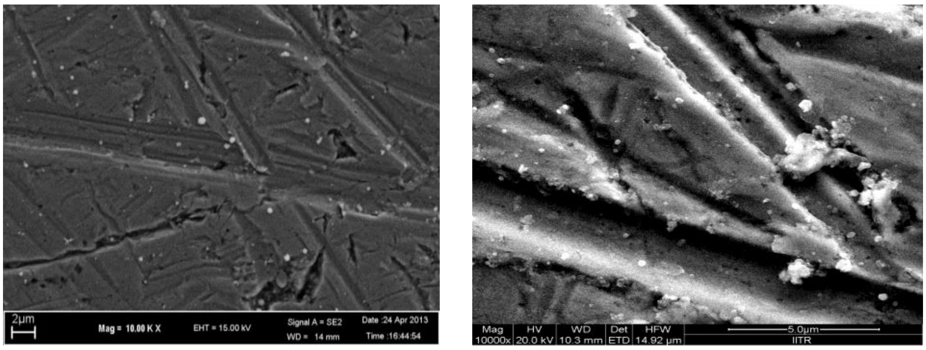
β = Full width at half maxima of (002) peak in radian,

θ = Diffracted angle.

The calculated crystallite size of as deposited and annealed CdSnanocrystalline thin films are 34nm [20] and 48nm respectively. The increase in average grain size due to annealing clearly indicates the complete structural transformation to hexagonal with improved crystallinity. The increase in grain size confirms the reduction in grain boundaries. The reduction in grain boundaries again decrease the trapping the carriers and improves performance of the device.

3.2. Surface morphology studies of as deposited and annealed CdS films

Fig. 2(a) and (b) shows surface morphology of as deposited and annealed CdSnanocrystalline films using FESEM. The magnification of the photograph is fixed at 10000X. The microstructure of as deposited film indicates that the surface is uniform, homogenous, grains are distinct and in single state throughout the analysed area. The surface of the film is without any void, pinholes, crackes, etc. However, annealed at 400^{0}C, the grains are distinct and formation of cluster on the film surface which indicates the improved crystalline nature of CdS films. Due to annealing, recrystallization process intensified and form cluster to minimize the defect.

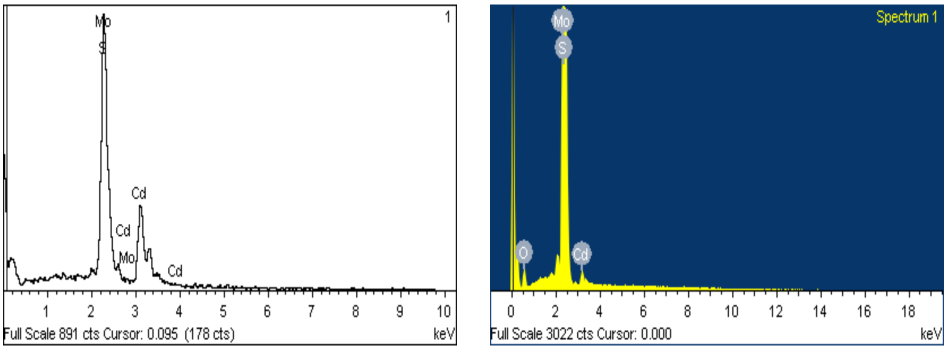


(a) *(b)*

Fig.2 FESEM photograph ofCdS film: (a) as deposited, (b) annealead

3.3. Energy dispersive spectroscopy analysis of as deposited and annealed CdS films

Fig 3(a) and (b) shows EDS spectra of as deposited and annealed CdS film respectively. The EDS spectra of CdS film confirms the elemental peaks of Cadmium (Cd), Sulphur (S) and Molybdenum (Mo).



(a) *(b)*

Fig.3 EDS spectra ofCdS films: (a) as deposited, (b) annealead

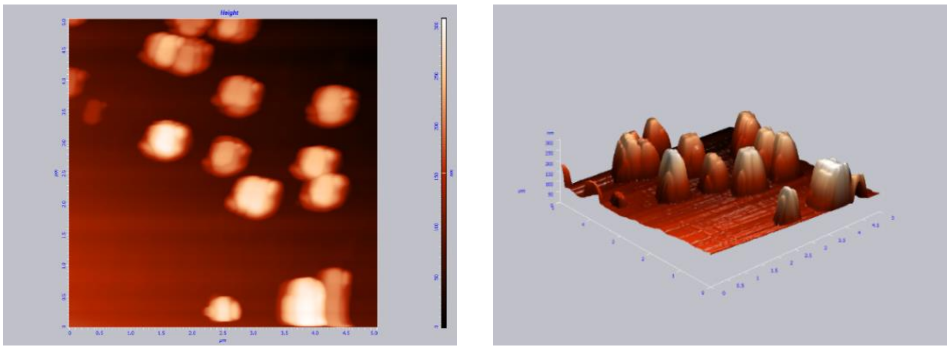
Table 1: Atomic and weight percentages of as deposited and annealedCdS films.

Elements	Atomic percentage		Weight percentage	
	As deposited	Annealed	As deposited	Annealed
Cd	29.11	2.32	39.23	4.33
S	27.13	3.67	10.43	1.96
Mo	43.76	51.62	50.34	82.42
O	-	42.39	-	11.29

It clearly shows that the sulphur peaks overlap with the molybdenum substrate. The atomic percentage and weight percentage of Cd, S and Mo are given in Table 1. It is observed that as deposited CdS film, the ratio of atomic percentage of Cd and S is observed to be nearly equal to 1.0 [20]. After annealing, the ratio of S and Cd is to be 1.58 [21]. We conclude that due to annealing cadmium rich sample changes to sulphur rich as evident from atomic percentage.

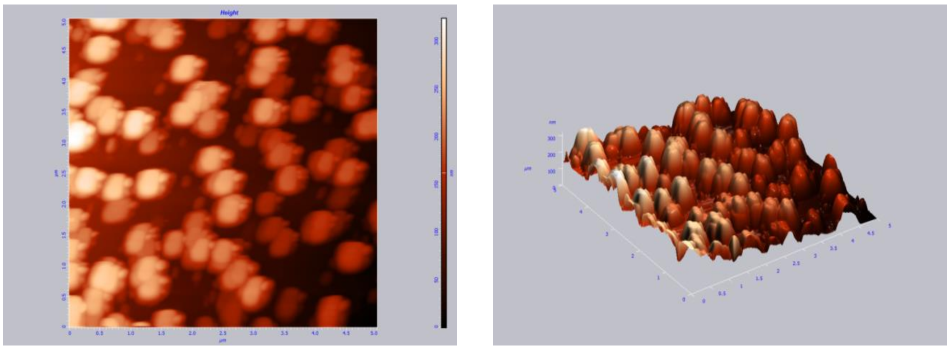
3.4. Surface roughness studies of as deposited and annealed CdS films

From figure 4(a), (b) and 5(a), (b) are the AFM photographs of as deposited and annealed CdS films in two dimension and three dimension respectively. The scan area is 5µm×5µm. The surface texture parameters such as root mean square (RMS) surface roughness, grain size and surface morphology of the films are studied.



(a) *(b)*

Fig 4 AFM image of as deposited CdS films in (a)2D and (b) 3D.



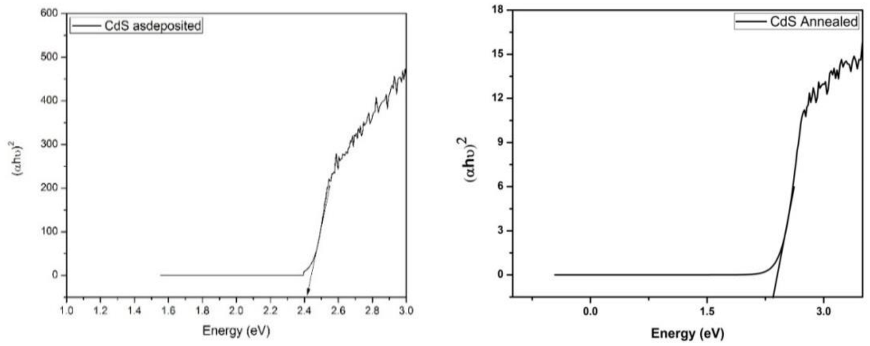
(a) *(b)*

Fig.5 AFM image of annealedCdS films in (a)2D and (b) 3D.

The as deposited CdS films are observed to have smaller grains, uniform grain size and randomly oriented. The RMS roughness is estimated to be 92nm. But annealed at 400^0C, films are smooth, crystallinity increases and roughness decreases to 74nm. The decrease in surface roughness is considered to be due to increase in the crystallite size and reduction in grain boundaries [22].

3.5. Optical properties of as deposited and annealed CdS films

The optical properties of the film gives information regarding development of optical devices. Optical energy bandgap of semiconductor is an important parameter to construct a photovoltaic, photoelectrochemical solar cells.



(a) *(b)*

Fig.6 $(\alpha hv)^2$ versus energy graph ofCdS films: (a) as deposited, (b) annealead

We know that CdS is considered as direct bandgap n-type semiconductors.The direct bandgap material the bandgap can be obtained by following relation [23]:

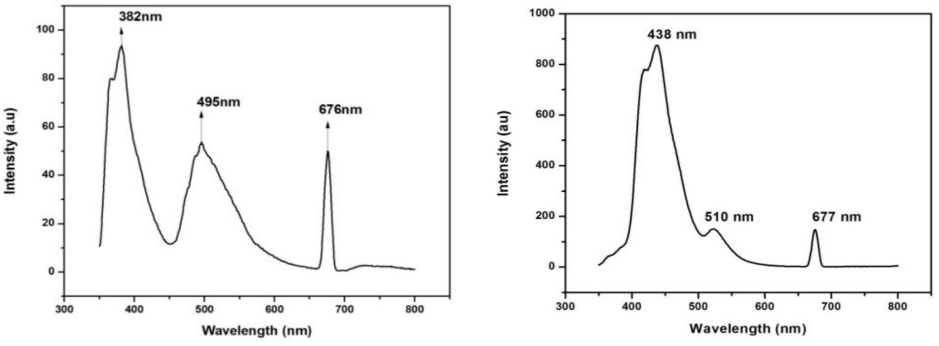
$$\alpha h\nu = A (h\nu - E_g)^{1/2}$$

'α' is the absorption coefficient,
'h' is the Planck's constant,
'ν' be the incident light frequency,
'A' is a constant,
'E_g' is the energy bandgap.

Fig. 6(a) and (b) shows optical absorption spectra of CdSnanocrystalline thin films in as deposited and annealed case which is plot of $(\alpha h\nu)^2 v_s h\nu$and bandgap (E_g) of CdS films is obtained by extrapolation of the straight line to $(\alpha h\nu)^2 = 0$. The energy bandgap is found to be 2.40eV[20] in as deposited case and 2.30 eV[21] in annealed case. Decrease in bandgap would be attributed to the phase transition from cubic to hexagonal [24,25] and can improve crystallinity of the film.

3.6. Photoluminescence studies of as deposited and annealed CdS films

The photoluminescence analysis are carried out for as deposited and annealed CdS film. Fig. 7(a) and (b) shows the photoluminescence spectra of as deposited and annealed CdSnanocrystalline thin films



(a) *(b)*

Fig.7 PL spectra of CdS film: (a) as deposited, (b) annealead

As evident from figure, as deposited CdS thin film have three distinct bands at 382nm, 495nm and 676nm respectively. Sharp emission intensity at 382nm depends on the lower sulphur content. Centered band at 495nm indicates the formation of CdS nanoparticle in as deposited film [26]. The photoluminescence spectra of annealed CdS film, it is at 438nm, 510nm and 677nm respectively. We conclude that there are different bands for CdS films before and after annealing at 400^0C.

4. Conclusions

The CdSnanocrystalline thin film is deposited by using cadmium chloride and thiourea over molybdenum substrate by CBD using non aqueous medium. The structural, morphological, elemental and optical properties of theCdS films have been carried out.

The XRD spectra of as deposited and annealed films show the (002) plane with average grain size 34 nm and 48 nm respectively. Energy Dispersive Spectroscopy (EDS) spectra shows the clear peaks of Cadmium (Cd), Sulphur(S) and Molybdenum (Mo). The energy bandgap of the films are observed to be 2.40eV and 2.30eV.

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