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CdS Thin Films Fabricated by a Simplified Spray Technique Using Cadmium Acetate As Cationic Precursor

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Abstract

Cubic cadmium sulfide thin films with (1 1 1) orientation were prepared by a simplified spray technique using cadmium acetate and thiourea salts as sources for Cd and S respectively. The films were characterized by X-ray diffraction, scanning electron microscopy, optical absorption spectroscopy and two point probe techniques. The crystallite size was found to be equal to 82 nm. Microstructural parameters such as strain, dislocation density and number of crystallites were calculated. The lattice parameter value was found to be equal to 5.810 Å. EDAX spectrum reveals that the film contains excess cadmium with sulfur deficiency. The optical measurement shows the presence of direct transition with energy band gap of 2.38 eV. The film exhibits a maximum transmittance of nearly equal to 85 %. The refractive index at λ = 700 nm was found to be equal to 2.6. Refractive value decreases with increase in wavelength confirming that the films exhibit optical refractive dispersion. The electrical resistivity value was found to be equal to 1.013 x 10^2 *ohm-cm.*

Keywords

X-ray diffraction; Optical absorption; Energy band gap; Refractive dispersion;

1. Introduction

Cadmium sulfide (CdS) is a wide band gap semiconductor extensively studied under various configurations: bulk material [1], thin films [2] and nanostructures as nanowires [3], etc. It is an important II – VI group chalcogenide semiconductor due to its direct band gap transition with band gap energy of 2.42eV at room temperature and unique, electrical, optical and photoconductive properties. Because of its intermediate band gap, high absorption coefficient, low resistivity and easy ohmic contact, it has found potential applications [4- 6]. It is known to be the most convenient partner for heterojunction realization of p - type CdTe and $CuInSe_2$ solar cells [7, 8]. Polycrystalline thin film solar cells with efficiencies of 14 – 16% have been made with CdS as the window layer and CdTe [6] or $CuInSe_2$ as the absorber layers. Various techniques have been used to make CdS films, such as vacuum evaporation [9], sputtering [10], electro deposition [11], spray pyrolysis [12], chemical bath deposition (CBD) [13], and ion layer gas reaction (ILGAR) [14].Among these techniques, spray pyrolysis technique is a simple and easily scalable method to prepare CdS thin films over large area at low cost. Doped films can also be prepared in a facile way by merely adding doping element to the spray solution [15]. Even though the conventional spray pyrolysis technique is simple, it requires high substrate temperature and compressed carrier gas. Considering these factors, a further simplified spray procedure using perfume atomizer is employed in the present work to deposit CdS films. This simplified version of spray technique has several advantages over the conventional spray method [16]. Different cadmium sources have been used in the fabrication of CdS thin films, such as cadmium sulfate [17], cadmium acetate [18], cadmium iodide/nitrate [19, 20] and cadmium chloride [21]. The effect of Cd source on the film properties has drawn attention for some time. The present study represents the preparation of CdS thin film by the simplified spray technique using cadmium acetate, [$Cd(CH_3COO)_2$] which has a stability constant of 2.19 as Cd source and thiourea $SC(NH_2)_2$ as S source and the subsequent characterization of the as-deposited sample by XRD, SEM, UV – Vis – NIR spectrophotometer and two point probe techniques.

2. Experimental details

CdS thin films were fabricated by the simplified spray technique using 50 ml aqueous solution containing a mixture of cadmium acetate, 0.05 M (cadmium source) and thiourea, 0.05 M (sulfur source). Commercial glass slides with dimensions (76mm x 25mm x 1.4mm) used as substrates were cleaned in acetone and soap solution ultrasonically. The starting solution is sprayed intermittently on preheated substrates using a perfume atomizer. Each spray cycle has a spray and a 2sec wait so that the desired temperature is maintained throughout the deposition process. When the solution was sprayed over the hot substrates kept at 400ºC, pyrolytic decomposition of the solution takes place and dark yellow colored films of CdS are formed. The structural characterization of the film was carried out by Xray diffractometer (PANalytical – PW 340/60 X^1 pert PRO) with CuKα radiation. The optical transmittance of the films was studied by using a perkin Elmer UV – Vis – NIR double beam spectrometer. Electrical studies were performed using two point probe method. The thickness of the CdS film measured by profilometer (Surftest SJ – 301) was found to be equal to 347 nm.

The crystallite size was determined using the Scherer formula

$$D = \frac{0.94\lambda}{\beta \cos\theta}$$

where β is the full width at half maximum (FWHM in radians) of the peak corrected for instrumental broadening, and θ is the Bragg's angle.

3. Results and discussion

3.1 Structural studies

The XRD pattern of the CdS film deposited by the simplified spray technique is shown in Fig. 1. The film was cubic with a main (1 1 1) reflection and four other peaks (2 2 0), (3 1 1), (2 2 2) and (4 0 0) peaks that confirmed the cubic nature of the film (JCPDS Card No. 42 – 1411). The whole XRD spectrum exhibit a broad peak situated in the low diffraction angles; this feature is a characteristic of the amorphous nature of the film. This suggests that the film is formed with a small crystallite embedded in an amorphous tissue [22]. The strong orientational growth of the film along the (1 1 1) plane is consistent with the results reported earlier for spray deposited CdS films [23, 24]. The crystallite size of the CdS film estimated using the Scherrer formula was found to be equal to 82 nm. The lattice constant ‘a’ of the cubic structure of CdS film is calculated using the formula:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

The value of ‘a’ is found to be equal to 5.810 Å which exactly matches with the standard value (5.818 Å - JCPDS Card No. 42 – 1411).

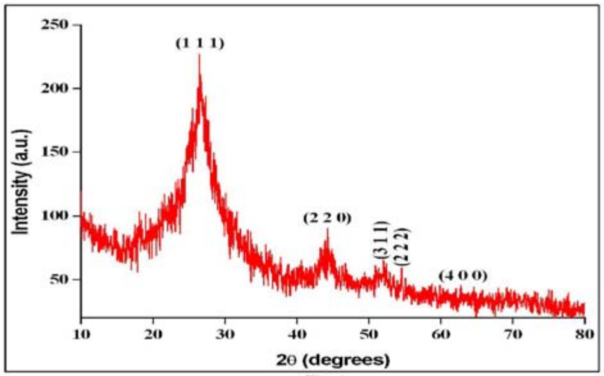

Fig. 1

Figure1
XRD pattern of CdS thin film fabricated by the simplified spray technique.

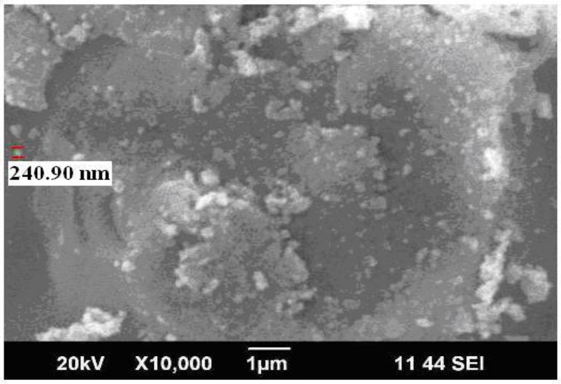

Fig. 2

Figure 2
SEM image of the CdS film fabricated using cadmium acetate as cationic precursor.

3.2 Surface morphological studies

The SEM image of the CdS thin film fabricated by the simplified spray technique using cadmium acetate precursor salt as the source for Cd at 400ºC is shown in Fig. 2. The SEM image depicts island growth on the film surface. The island formation may be attributed to rapid nucleation which takes place due to the high deposition temperature adopted in this work. Spherically shaped grains with size equal to 241 nm were observed randomly scattered throughout the surface. Fig. 3 shows the EDAX spectrum of the as deposited sample. It shows that the film contains elements Cd and S as deposited components and S/Cd atomic ratio equal to 0.82 confirming the fact that the deposited film has excess cadmium ions and this strongly favours the low resistivity value (Section 3.4) obtained in this work. Some peaks correspond to the impurity elements such as Si, Na and Al were observed in the spectrum which may be attributed to the chemical component of the glass substrate.

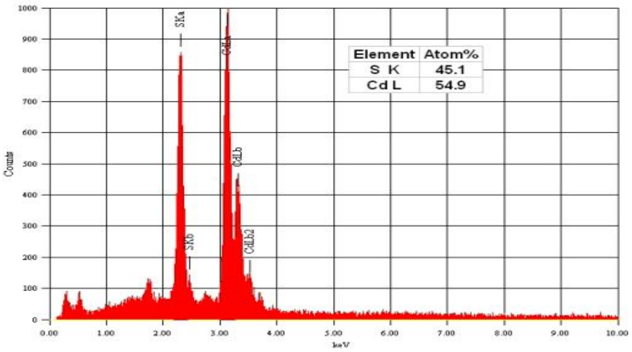

Fig. 3

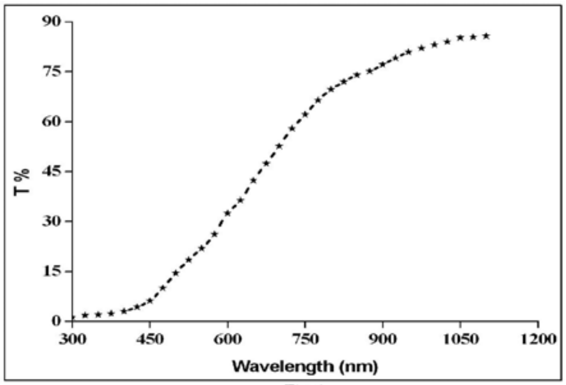

Fig. 4

Figure 3
EDX spectrum of the CdS film.

Figure 4
Transmittance spectra of the CdS film.

3.3 UV-Vis-NIR spectroscopy studies

The optical transparency of the CdS film fabricated by the simplified spray technique is shown in Fig. 4. The percentage transmittance takes very low values in low wavelength region ($\lambda < 500$ nm) which is the spectral region of edge absorption. In this region the incoming photons have sufficient energy to excite electrons from the valence band to conduction band and thus these photons are absorbed within the material to decrease the transmittance. The maximum transmission was found to be equal to 85 %. The optical absorption coefficient (α) is evaluated using Lambert's law [25]:

$$\ln\left(\frac{I_0}{I}\right) = 2.303A = \alpha t$$

where I_0 and I are the intensities of the incident and the transmitted light, respectively, A is the optical absorbance, and t is the film thickness. Fig. 5 shows the optical absorption coefficient α as a function of photon energy hγ for the as deposited CdS film. As CdS is a direct band gap semiconductor, the absorption coefficient and the band gap energy E_g has the form as follows:

$$\alpha h\gamma = k(h\gamma - E_g)^{\frac{1}{2}}$$

where k is a constant related to the effective masses associated with the bands. E_g can be obtained from the graph of $(\alpha h\gamma)^2$ versus hγ, by extrapolating the linear portion of the plot to $\alpha = 0$. The inset of Fig. 5 is $(\alpha h\gamma)^2$ versus hγ curve of the as deposited CdS film, showing an energy band gap equal to 2.38 eV which is slightly smaller than the value of 2.42 eV for single crystal. The value of E_g obtained here exactly matches with the value reported earlier [26]. The decrease of band gap energy is possibly due to structural defects present in the cubic CdS thin film prepared by this simplified spray technique. The formation of localized states with energies at the boundaries of the energy gap is one of the effects of the structural disorder on the electronic structure of amorphous materials. The absorption coefficients of the thin film samples show a tail for sub-band gap photon energy. In the exponential edge region, the coefficient α is well described by the exponential law:

$$\alpha = \alpha_0 \exp \frac{h\gamma}{E_U}$$

known as Urbach law [27]. Here α_0 is a constant, E_U is Urbach energy which characterizes the slope of the exponential edge region and is width of the band tails of the localized states. The Urbach tail of the absorption edge is usually ascribed to the optical electronic transitions between the excited states and the near edge localized states. The values of E_U calculated from the graph plotted between ln(α) and photon energy (hγ) was found to be equal to 0.85 eV and the presence of Urbach tail suggests there exists some disorder which results in deviation of the bond length and angle from the standard value in the coated CdS film. The value of E_U obtained is high compared to the value obtained by Jaber et. al [28] for chemical bath deposited CdS thin film. From the XRD analysis, it is evident that the film is compared with micro crystallites embedded in amorphous phase. This amorphous phase is the origin of the disorder measured in the film network. Optical parameters namely refractive index 'n' and extinction coefficient 'k', have been determined from the transmittance and reflectance measurements using the relation [29, 30]:

$$n = \frac{1+R}{1-R} \pm \left[\left(\frac{R+1}{R-1} \right)^2 - (1-k^2) \right]^{\frac{1}{2}} \qquad (6)$$

where $k = \frac{\alpha\lambda}{4\pi}$ is the extinction coefficient, and λ is the incident light wavelength.

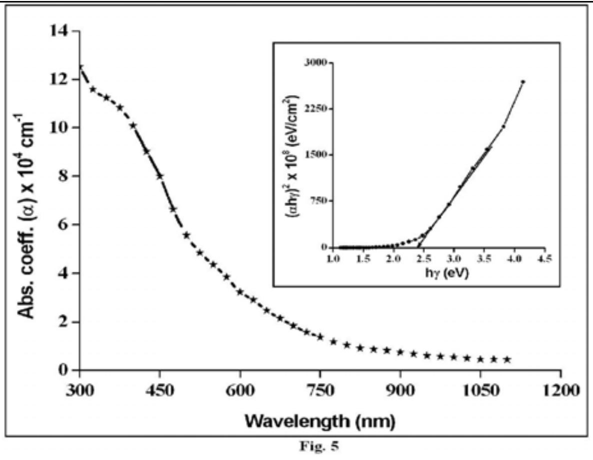

Fig. 5

Figure 5 Variation of absorption coefficient with wavelength and (αhγ) vs hγ graph.

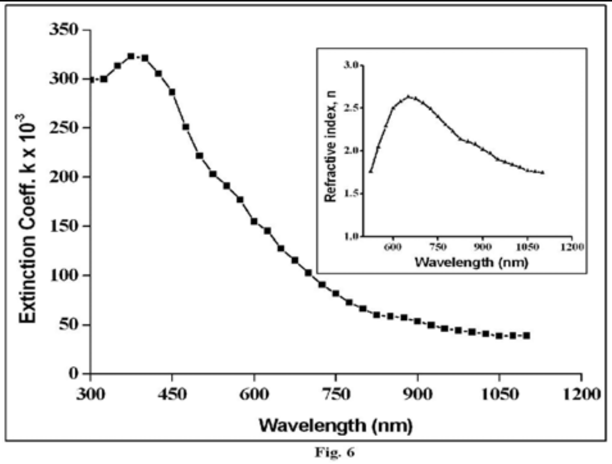

Fig. 6

Figure 6 Variation of extinction coefficient and refractive index with wavelength of the CdS thin film.

The variation of extinction coefficient with wavelength is shown in Fig 6, while the variation of refractive index 'n' with wavelength is shown in the inset of Fig. 6. The behaviour of refractive index has a higher value at very low wavelength (strong absorption). This is due to the quality between the frequency of incident electromagnetic radiation and the plasma frequency. Therefore, there is an anomalous dispersion of refractive index in the region of the plasma frequency. Maximum value of refractive index (n = 2.6) was observed at $\lambda = 700$ nm below which absorption increases. Above 700 nm, the refractive index value decreases reaching the lowest value of 1.8 at $\lambda > 900$ nm. The changes in the refractive index indicated that some interactions take place between photon and electrons in the film.

The polarisability of any solid is proportional to its dielectric constant. The real and imaginary part of complex dielectric constant is expressed as [29]:

$$\varepsilon_r = n^2 - k^2$$

$$\varepsilon_i = 2nk$$

Where ε_r and ε_i are the real and imaginary parts of the dielectric constants respectively. The variation of ε_r and ε_i with wavelength of the as deposited CdS films are shown in Fig.7. The real and imaginary parts of the dielectric constants show similar trend with photon energy which indicates that some interactions between photons and electrons in the films are produced in this energy range. The imaginary part of dielectric constant is directly related to the density of states within the forbidden gap of semiconductor materials.

3.4 Electrical studies

The resistivity of the CdS film fabricated by the simplified spray technique was determined by the two point probe method. Fig 8 shows the variation of resistivity with temperature of the as deposited sample. The resistivity value decreases with increase in temperature indicating the semiconducting nature of the film. The average resistivity of the film in the temperature range 323 K – 358 K was found to be equal to 1.013×10^2 ohm–cm. Khallaf et al. [31] obtained a resistivity of 3.38×10^2 ohm-cm for chemical bath deposited CdS thin film with a thickness of 90 nm deposited using cadmium acetate as cationic precursor. The resistivity value obtained here is very low than the literature values [32, 33] in which the CdS thin films were prepared by conventional spray pyrolysis technique even though the thickness of the film is 347 nm. This may be due to the presence of excess content of Cd which means that either interstitial Cd ions or sulfur vacancies may exist in the film, acting as donors and resulting in an increased carrier concentration with a consequent decrease in the resistivity. The low resistivity value obtained is best suited for optoelectronic applications [34]. The activation energy E_a of film has been determined from the slope of the graph between log ρ versus reciprocal of temperature using the eqn:

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)$$

where ρ is resistivity of the thin film sample, k is Boltzmann constant. The activation energy was found to equal to be 0.207 eV. The value of activation energy obtained exactly matches with the results obtained earlier [35].

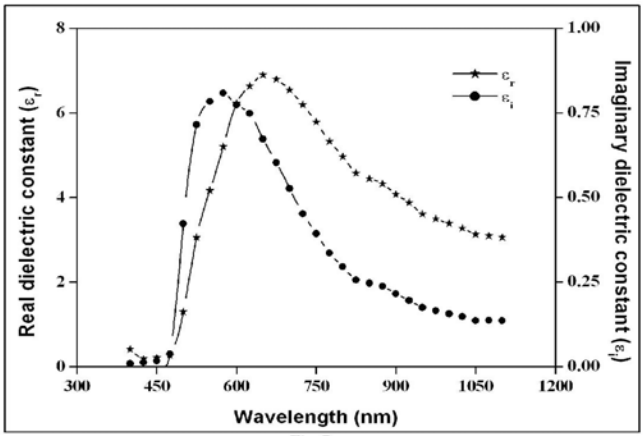

Fig. 7

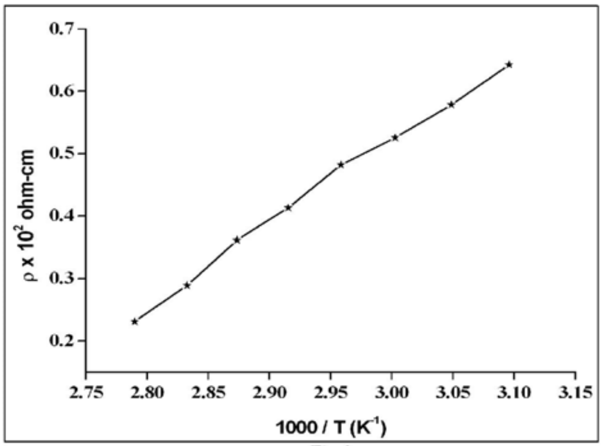

Fig. 8

Figure 7 Variation of real and imaginary dielectric constant with wavelength.

Figure 8 Electrical resistivity variation with temperature of the CdS film.

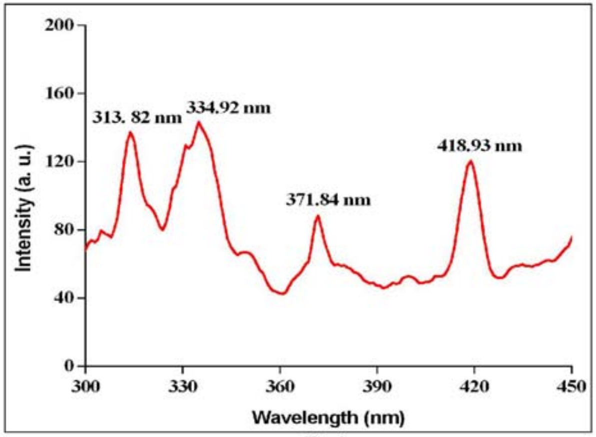

Fig. 9

Figure 9 Photoluminescence spectrum of the CdS thin film.

3.5 PL studies

The room temperature photoluminescence spectrum of the CdS film fabricated at 400ºC is shown in Fig. 9 after excitation at 335 nm. Emission peaks were observed at 314 nm, 335 nm, 372 nm and 419 nm respectively. The peak at 314 nm may be attributed to the transitions due to excitons at higher energy levels. Maleki et al. [36] observed a peak at 340 nm in CdS nanoparticles through 220 nm excitation wavelength, which was related to higher level transitions in CdS crystallites. According to them this kind of band edge luminescence is caused by recombination of excitons and/or shallowly trapped electron-hole pairs. The above discussion holds good for the peak observed at 335 nm in this work. The peak observed at 372 nm may be attributed to a higher level excitonic emission caused to quantum confinement. This fact is well supported by the obtained value of crystallite size (82 nm) from the XRD analysis. Devi et al. [37] reported a peak at 376 nm in nanocrystalline CdS strongly favoring quantum confinement. The peak located at 418.93 nm is due to an exciton bound to a donor level.

4. Conclusion

The as deposited CdS film shows a cubic phase with (1 1 1) orientation. Crystallite size was found to be equal to 82 nm. The optical band determined from the transmittance spectra was found to be equal to 2.38 eV. Urbach energy of 0.85 eV obtained confirms the disorderliness existing in the film. The real and imaginary parts of the dielectric constants show similar trend with photon energy. The electrical resistivity value obtained (1.013 x 10^2 ohm-cm) is best suited for opto electronic applications.

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