STUDIES ON STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF CADMIUM SULPHIDE THIN FILMS

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Cadmium sulphide (CdS) thin films were synthesized by chemical bath deposition (CBD) method. The XRD, SEM, AFM, UV-Visible absorption spectrum, dielectric studies and photoconductivity measurements were used to characterize the CdS films. The X-ray diffraction (XRD) analysis showed that the prepared CdS films were polycrystalline with cubic structure. The crystallite size was determined from the broadenings of corresponding X-ray diffraction peaks by using Debye Scherrer's formula. Scanning Electron Microscopy (SEM) and atomic force microscopy (AFM) revealed that the grains were uniformly distributed over the surface of the substrate for the CdS films. The optical properties were studied using the UV-Visible absorption spectrum. Optical constants such as band gap, refractive index, extinction coefficient and electric susceptibility were determined from UV-Visible absorption spectrum. The dielectric studies of CdS thin films were studied for different frequencies and different temperatures. The temperature dependent conductivity study confirmed the semiconducting nature of the films. The activation energy of the CdS films was calculated. Photoconductivity measurements were carried out in order to ascertain the positive photoconductivity of the CdS thin films.

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1. Introduction

Nowadays nanocrystalline materials are used to convert solar energy into electricity. In nanomaterials the quantum dots increase the efficiency of solar energy conversion through multi-excitons generation. Nanocrystalline semiconducting materials have been used in electronic, optoelectronic and solar energy conversion devices. The use of thin film polycrystalline semiconductors has created much interest in an expanding variety of applications in various electronic and optoelectronic devices. The technological interest in polycrystalline based devices is mainly caused by their low production cost [1].Among the II-VI semiconductors, CdS polycrystalline thin film is a representative material with many applications such as large area electronic devices and solar cells; it has a wide direct band gap (2.42 eV) and so it has been used as a window material together with several semiconductors such as CdTe,Cu_2S and CuInSe [2]. Also the interest in CdS thin films stems from its piezoelectric properties and potential laser applications [3,4]. Cadmium sulphide (CdS), a wide energy gap semiconductor, has emerged as an important material due to its applications in photovoltaic cell as window layers, optical filters and multilayer light emitting diodes, photo detectors, thin film field effect transistors, gas sensors and transparent conducting semiconductor for optoelectronic devices. In chemical methods, the deposition parameters such as pH, temperature, concentration of the solution and deposition time

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influence the formation of nanocrystalline thin films and crystallite size, which in turn modifies the bandgap of the material. The chemical bath deposition (CBD) method appears to be a relatively simple method to prepare homogenous films with controlled composition [5]. In particular CBD is widely used for achieving good-quality CdS thin films [6] .The CBD method gives poor crystalline quality of CdS layers in comparison with other deposition techniques but the films which are deposited by this method give the best photoconductivity and morphological properties such as roughness and pinhole density as compared with the films processed by other techniques [7]. In this paper, the preparation and the deposition of CdS thin films onto microscope glass slides by CBD method is discussed. The results yielded by the investigation of the structural, morphological, optical and electrical properties of the as-prepared CdS thin films are also presented.

2. Experimental procedure

The CdS thin films were deposited from a solution of cadmium nitrate and thiourea in an alkaline solution of ammonia and distilled water. Commercial glass slides used as substrates were cleaned in acetone ultrasonically. The glass slides were kept vertically in a closed beaker. In a beaker containing distilled water, cadmium nitrate was added and then liquid Ammonia was added to it. The mixture was then stirred for a particular time and thiourea was added to it. The process of stirring was continued. Glass substrate was mounted vertically on the beaker containing the solution. After the deposition was complete, the substrates were removed from the bath and were allowed to dry in air. The dried samples were rinsed with acetone and finally dried in a hot oven. The resultant films were homogeneous and well adhered to the substrate with mirror like surface. The deposited good quality CdS thin films were then subjected to characterization studies. The XRD pattern of the CdS thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα, with a diffraction angle between 0° and 80°. Scanning Electron Microscopy (SEM) studies were carried out on JEOL, JSM- 67001. The optical absorption spectrum of the CdS thin films was taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 300 – 800 nm. The dielectric properties of the CdS thin films were analyzed using a HIOKI 3532-50 LCR HITESTER over the frequency range 50Hz-5MHz. Photoconductivity measurements were carried out at room temperature by connecting in series with a picoammeter (Keithley 480) and a dc power supply.

3. Results and discussion

3.1 Structural characterization

In order to determine the size and to study the structural properties of the synthesized CdS thin films, the powder XRD analysis was performed. Structural identification of CdS films was carried out with X-ray diffraction in the range of angle 2θ lying between 0º and 80º. Fig.1 shows the XRD patterns for CdS thin films, which are nanocrystalline in nature. The observed broad hump in XRD pattern is due to amorphous glass substrate. The well-defined (111), (220), (311), and (420) peaks were observed in the XRD patterns. The (111) peak corresponds to the phase of polycrystalline structure of CdS. The strong and sharp diffraction peaks indicate the formation of well crystallized sample. It can be seen that the major peak (111) is dominating the other peaks. The structure of CdS deposited was predominantly cubic and reasonably crystalline. The XRD results revealed that the deposited CdS thin films were polycrystalline in nature with cubic structure having (111) plane as the preferred growth. The average nano-crystalline size (D) was calculated using the Debye-Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the X-ray wavelength (CuK_α), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The average crystallite size was calculated from X-ray line broadening peak and Debye-Scherrer equation and it was found to be about 15.3 nm.

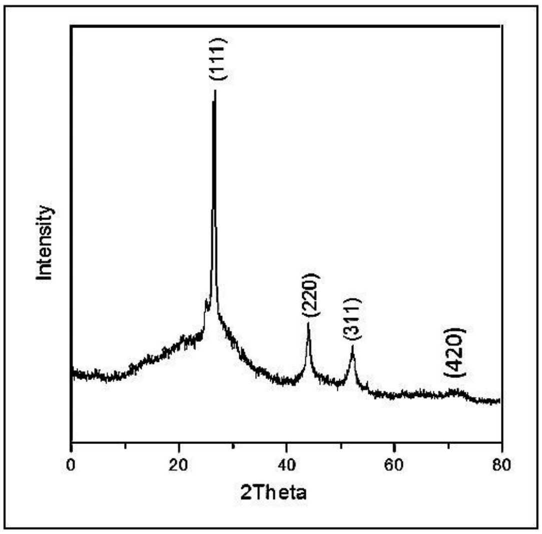

Fig.1.XRD spectrum of CdS thin films

3.2 Surface morphology

Scanning electron microscope (SEM) was used for the morphological study of CdS thin films. Fig.2 shows the SEM images of the CdS thin films. The CdS thin films formed were highly agglomerated. In this image the spherical shape of the CdS nanoparticles deposited was confirmed. The spherical shaped particles having a mean crystallite size of ~ 15 nm were visible through the SEM analysis. Fig.3 shows the AFM images of the CdS films. It is observed from the surface image that the particles are uniformly distributed on the surface of the film. From the 2D image, it is seen that the grains of CdS form large clusters looking like a cauliflower.

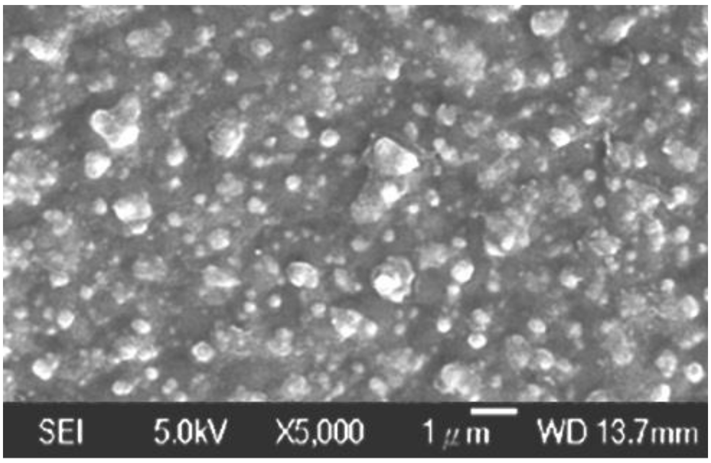

Fig.2 SEM micrograph of chemical bath deposition of CdS thin film

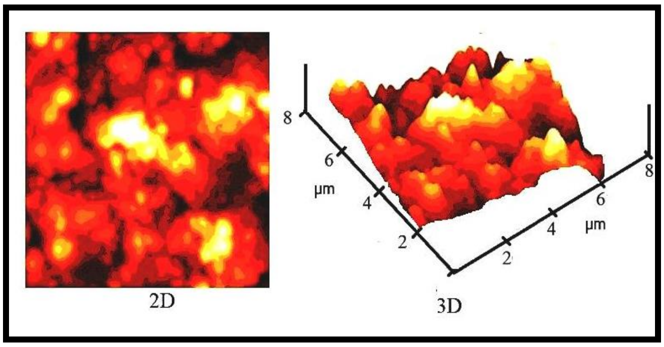

Fig.3 AFM images of CdS thin films

3.3 Optical Properties

The study of optical properties of CdS thin films has special significance in the world of science, technology and industry for the development of new optical devices. Optical absorption study of materials provides useful information to analyze some features concerning the band structure of materials. The optical band gap energy of the semiconductor is an important parameter that plays a major role in the construction of photovoltaic cells. In the present work the optical properties of the CdS deposited on glass substrate were studied from the absorption spectrum in the wavelength ranging from 300 to 800 nm. The variation of absorbance (α) with wavelength (nm) for CdS thin film is shown in Fig.4 (a). The sharp absorption edge observed confirms the good optical band edge property of the CdS thin film. The fundamental absorption, which corresponds to electron excitation from the valance band to the conduction band, can be used to determine the nature and value of the optical band gap. The optical absorption coefficient (α) was calculated from transmittance using the following relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \tag{2}$$

where T is the transmittance and d is the thickness of the films. The films under study have an absorption coefficient (α) obeying the following relation for high photon energies (hν)

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \tag{3}$$

The nature of transition is determined by using the relation,

$$\alpha h\nu = A(h\nu - E_g)^n \tag{4}$$

Where A is constant, hυ is photon energy and E_g is the optical band gap. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Fig..4 (b), where α is the optical absorption coefficient and hυ is the photon energy. E_g was evaluated using the extrapolation of the linear portion of the curve to photon energy axis for zero absorption coefficients; the intercept of the curve i.e., the optical band gap of CdS thin film was estimated and found to be 2.40 eV.

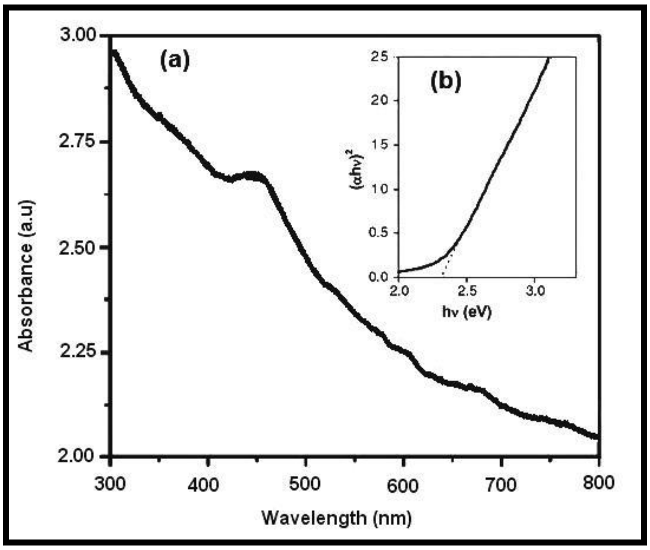

Fig. 4 (a) Absorption spectrum of CdS thin films (b) Plot of (αhv)^2 vs photon energy

3.3.1 Determination of Optical Constants

Two of the most important optical properties, viz., refractive index (n) and the extinction coefficient (K) are generally called optical constants. The amount of light that transmits through the thin film material depends on the amount of the reflection and the absorption that take place along the light path. The optical constants such as the refractive index (n), the real dielectric constant (ε_r) and the imaginary part of dielectric constant (ε_i) were determined .The extinction coefficient (K) could be obtained from the following equation,

$$K = \frac{\lambda\alpha}{4\pi} \tag{5}$$

The extinction coefficient (K) was found to be 2.3 x 10^6 at λ =800 nm. The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \tag{6}$$

Reflectance (R) in terms of absorption coefficient could be obtained from the above equation. Hence,

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)} \tag{7}$$

Refractive index (n) can be determined from the reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{8}$$

The refractive index (n) was found to be 2.15 at λ =800 nm. The high refractive index makes CdS film suitable for use in optoelectronic devices.From the optical constants, electric susceptibility (χ_c) could be calculated according to the following relation

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{9}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \tag{10}$$

where ε_0 is the permittivity of free space. The value of electric susceptibility (χ_c) was 3.62 at λ=800 nm. Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense.The real part of the dielectric constant (ε_r) and the imaginary part of the dielectric constant (ε_i) could be calculated from the following relations

$$\varepsilon_r = n^2 - k^2 \tag{11}$$

$$\varepsilon_i = 2nk \tag{12}$$

The value of real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) at λ=800 nm were estimated to be 3.125 and 0.0042, respectively. The lower value of the dielectric constant and the positive value of the material enable the occurrence of induced polarization due to intense incident light radiation.

3.4 Dielectric Properties

The dielectric constant and the dielectric loss of the CdS thin flims were studied at different temperatures in the frequency region of 50 Hz to 5 MHz. The dielectric constant was measured as a function of the frequency at different temperatures as shown in Fig.5. It is observed (Fig.5) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. This also indicates that the value of the dielectric constant increases with an increase in the temperature. The net polarization present in the material is due to ionic, electronic, dipolar and space charge polarizations [8]. The large value of the dielectric constant is due to the fact that CdS thin flims act as a nanodipole under electric fields. The dielectric loss studied as a function of frequency at different temperatures is shown in Fig.6. These curves suggest that the dielectric loss is largely dependent on the frequency of the applied field, similar to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency at almost all temperatures, but appears to achieve saturation in the higher frequency range at all the temperatures [9, 10]. In the low frequency region, high energy loss is observed, which may be due to the dielectric polarization, space-charge and rotation-direction polarization occurring in the low frequency range [11].

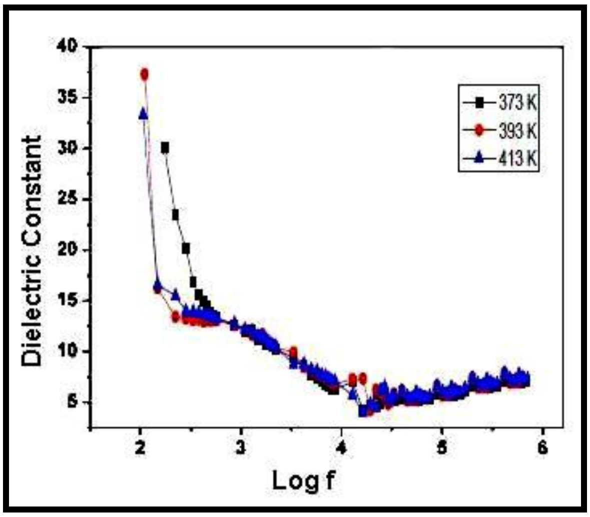

Fig.5 Variation of dielectric constant with log frequency

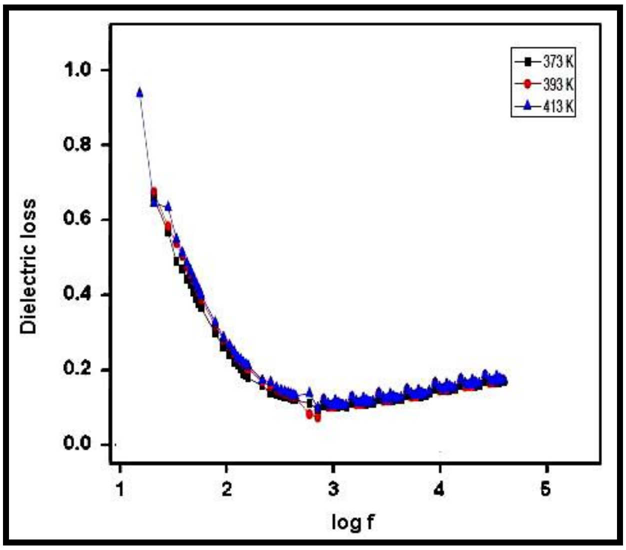

Fig. 6 Variation of dielectric loss with log frequency

3.5 Electrical properties

The variation of current with temperature for CdS thin films is shown in Fig.7. The plot indicates the exponential behavior of the temperature dependent current confirming the semiconducting nature of the CdS thin films. The $\ln\sigma_{dc}$ versus 1000/kT plot is shown in Fig.8. The activation energy was calculated for CdS thin films. The activation energy of the CdS thin films was found to be 0.53 eV. The traps which are present in the CdS thin films may be filled by excitation at low temperature and may be emptied by raising the temperature upon thermal activation [12]. The charge carriers thus excited from the traps may adopt a hopping mechanism to cross the potential barrier and hence produce enhanced current.

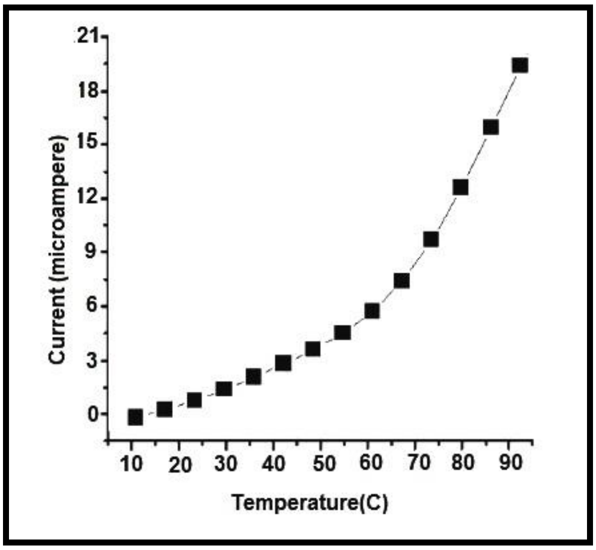

Fig.7. Temperature dependent conductivity of CdS thin films

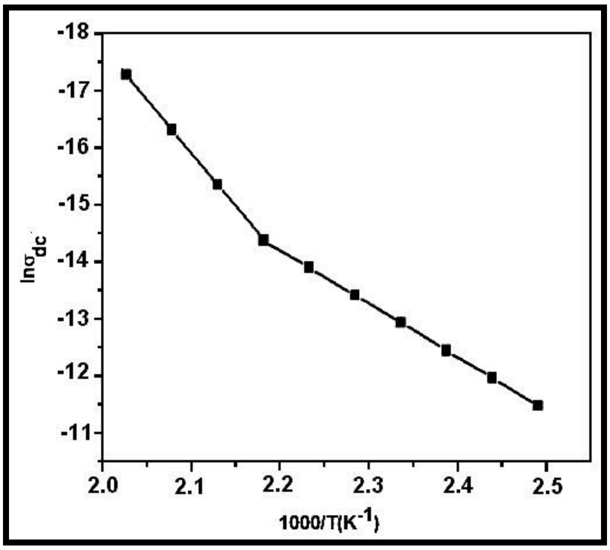

Fig.8 ln I (vs) 1/kT graph of CdS thin films

3.6 Photoconductivity Studies

Photoconductivity is a useful tool to study the properties of semiconductors. Field dependent dark and photoconductivity plot of CdS thin films is shown in Fig.9. It is observed that both the dark and the photo currents increase linearly with the applied electric field with the dark current being less than the photo current which is termed positive photoconductivity. The plot indicates a linear increase of current in the dark and visible light illuminated thin films cases with an increase in applied field depicting the ohmic nature of the contacts [13]. The low values of the dark current and the insignificant rise in photocurrent upon the visible light illumination are as expected. But the photocurrent is found to be more than the dark current. Hence, it can be said that the material exhibits positive photo conductivity. This is caused by the generation of mobile charge carriers caused by the absorption of photons. This is because of an increase in the number of charge carriers or their life time in the presence of radiation.The positive photoconductivity of the films may be due to the increase in the number of charge carriers to reveal the conducting nature of the material. The dark current is less than the photocurrent, signifying positive photoconductivity nature confirmed by the reported results [13, 14].

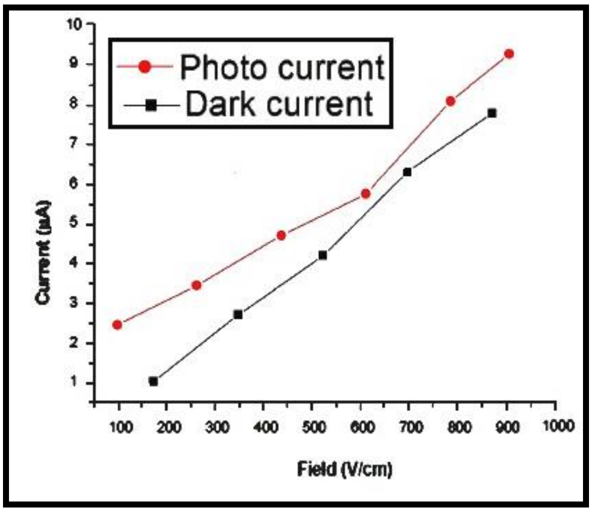

Fig.9 Photoconductivity study of CdS Thin films

4. Conclusion

The CdS thin film was successfully deposited on glass substrate using chemical bath deposition (CBD) technique. The XRD studies showed that the films prepared were in nanocrystalline range; also diffraction peaks were found. The surface morphology of the CdS thin films was characterized using scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM).The UV-Visible absorbance spectrum showed excellent transmission in the entire visible region. The band gap, refractive index, extinction coefficient and electrical susceptibility were calculated to analyze the optical property. The dielectric constant and the dielectric loss of the CdS thin films were measured for different frequencies and temperatures. The temperature dependent conductivity indicated the exponential behavior of the temperature dependent current confirming the semiconducting nature of the thin films. The activation energy of the CdS films was calculated and it was found to be 0.53 eV. The photoconductivity study ascertained the positive photoconductivity nature of the CdS thin films.

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