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STRUCTURAL, SURFACE MORPHOLOGY, OPTICAL AND ELECTRICAL INVESTIGATION OF CdSe THIN FILMS

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Cadmium Selenide (CdSe) thin films were synthesized by chemical bath deposition (CBD) method. The XRD, SEM, UV-Visible absorption spectrum, dielectric studies and photoconductivity measurements were used to characterize the CdSe films. The X-ray diffraction (XRD) is used to examine the structure of CdSe thin film. The surface morphology of the film was analyzed using Scanning Electron Microscopy (SEM) and Atomic Force Microscope (AFM).The optical properties were studied using the UV-Visible absorption spectrum. Optical constants such as band gap, refractive index, reflectance, extinction coefficient and electric susceptibility were determined from UV-Visible absorption spectrum. The dielectric studies of CdSe thin films were studied in the different frequency and different temperatures. In addition, the plasma energy of the valence electron, Penn gap or average energy gap, the Fermi energy and electronic polarizability of the CdSe thin films have been also determined. The AC electrical conductivity measurements reveal that the conduction depends on both the frequency and the temperatures. The temperature dependent conductivity study confirmed the semiconducting nature of the films. Photoconductivity measurements are carried out in order to reveal the positive photoconductivity of the CdSe Thin films.

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1. Introduction

Cadmium selenide is one of the II-VI materials which have been extensively considered by researchers due to their various applications such as photovoltaic applications, solar cells, thin film transistors, sensors, lasers, photoconductors, gamma ray detectors [1-3], and photoelectrochemical cells [4] because of having high efficiency of radiative recombination, high absorption coefficient, high photosensitivity, direct band gap matching to a wide spectrum of wavelengths from ultraviolet to infrared regions [5] and quantum size effect [6]. The nanocrystalline semiconductor belongs to the state of matter in the transition region between molecules and solids. Their physicochemical properties are found to be strongly size dependent.The CdSe thin films weresynthesized by different methods such as vacuum and non-vacuum film deposition methods, including vacuum evaporation and co-evoparation, molecular beam deposition, laser ablation, electrochemical deposition, spray pyrolysis and chemical bath deposition [7-13]. In the present investigation, we report the synthesis and characterization of CdSe thin films. The CdSe thin films have been characterized by X-ray diffraction analysis,

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scanning electron microscopy (SEM), atomic force microscope (AFM), UV analysis, dielectric studies and Photoconductivity measurement.

2. Experimental Procedure

CBD method was broadly used to deposit films of many different semiconductor materials. CBD has proven over the years to be the simplest method offered for this purpose, the typical components of a CBD system are a container for the solution bath, the solution itself made up of common chemical reactive salts, the substrate where the deposition of the film is going to take place, a device to control the stirring process and temperature, sometimes a water bath is included to ensure an homogeneous temperature. In the present work, CdSe thin films were prepared on commercial microscopic glass slide. The reaction mixture was prepared by adding ammonia solution in 0.1 M of cadmium acetate till a pH of 10 is attained. The deposition bath consists of a solution of (0.5 M) cadmium acetateammonia, (4 ml) sodium selenosulphate solution and deionized water to make a total volume of 50 ml under continuous gentle stirring using magnetic stirrer. The deposition has been carried out at temperature 70°C and the growth time was 5 h. A glass substrate was placed vertically inside the vessel with the help of a suitably designed substrate holder. After a time period, the glass slide was removed from the bath and cleaned with deionized water and dried in the hot oven. The resultant films are homogeneous and well adhered to the substrate with mirror like surface. The deposited good quality CdSe thin films were subjected to characterization studies. The XRD pattern of the CdSe thin films was recorded by using a powder X-ray diffractometer (Schimadzu model: XRD 6000 using CuKα (λ=0.154 nm) radiation, with a diffraction angle between 20° to 80°. The crystallite size was determined from the broadenings of corresponding X-ray spectrum peaks by using Debye Scherrer's formula. Scanning Electron Microscopy (SEM) studies were carried out on JEOL, JSM- 67001. The optical absorption spectrum of the CdSe thin films has been taken by using the VARIAN CARY MODEL 5000 spectrophotometer in the wavelength range of 300 – 1000 nm. The dielectric properties of the CdSe 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 it in series with a picoammeter (Keithley 480) and a dc power supply.

3. Results and discussion

3.1. X-ray diffraction Analysis

The phase composition and structure of the film were studied by X-ray diffraction analysis. The XRD patterns of CdSe thin films are shown in Fig.1. The strong and sharp diffraction peaks indicate the formation of well crystallized CdSe thin films. It can be seen that the major peak (111) is strongly dominating the other peaks.The well defined peaks are observed in the XRD pattern. The XRD results reveal that the deposited CdSe thin films are 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 (CuKα radiation and equals to 0.154 nm), θ is the Bragg diffraction angle, and β is the FWHM of the XRD peak appearing at the diffraction angle θ. The average crystalline size is calculated from X-ray line broadening peak and Debye-Scherrer equation to be about 18.6 nm.

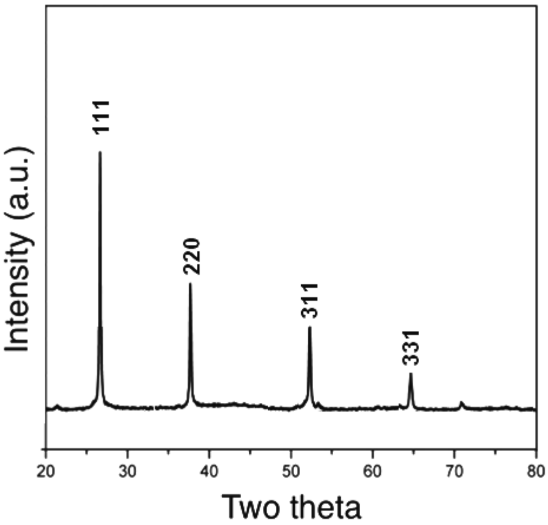

Fig.1.XRD spectrum of CdSe thin films

3.2. Surface Analysis

Scanning Electron Microscope (SEM) is very helpful to study the surface morphology of films. SEM images gives information of the surface structure and roughness. SEM image was obtained for CdSe thin film deposited on glass substrate in order to study thin film surface. Fig.2 shows the SEM images of the CdSe thin films.It can be observed that CdSe thin films are homogeneous and uniformly spread on the substrates. The film shows smooth and uniform crack free surface with spherical-shaped grains spread all over. The surface morphology of the film was analyzed by atomic force microscopy. Fig 3 (A) and (B) show the atomic force microscope image of the CdSe thin 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 CdSe particles are found to exist in spindle shape. The highly elliptical structure of the grains has size distributed on the surface of the film.

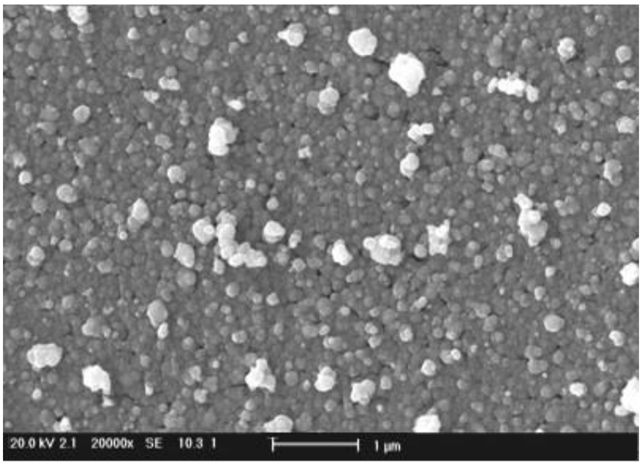

Fig.2. SEM Image of the CdSe thin films

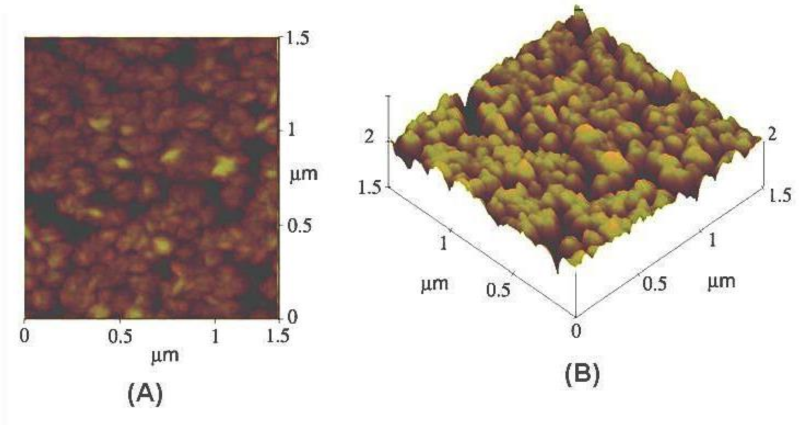

Fig.3 AFM images of CdSe thin film (A) 2 dimension (2D) and (B) 3 dimension (3D)

3.3. Optical studies

Optical investigations of films reveal that there is a band to band direct transition. The absorption data were analyzed using the classical relation for near edge optical absorption of semiconductors. The optical absorption spectrum of CdSe films has been recorded in the wavelength region 300 – 1000 nm and it is shown in Fig.4 (a). It is important to note that CdSe films were very much transparent in the visible region. The dependence of optical absorption coefficient on photon energy helps to analyze the band structure and type of transition of electrons.

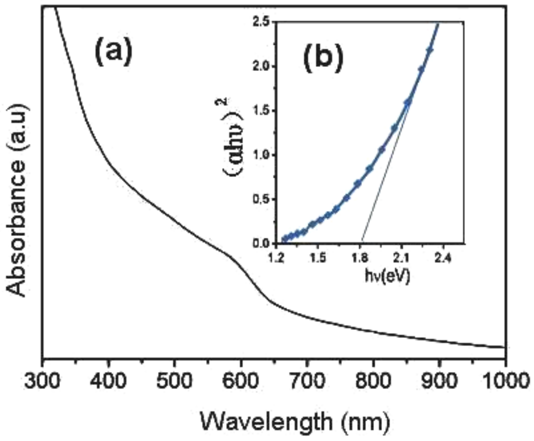

Fig.4. (a) UV-Vis absorbance spectrum ofCdSe films (b) Plot of (αhν)^2 Vs photon energy

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 has an absorption coefficient (α) obeying the following relation for high photon energies (hν)

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{3}$$

where E_g is the optical band gap of the films and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Fig.4 (b). E_g is evaluated using the extrapolation of the linear part. Using Tauc's plot, the energy gap (Eg) was calculated as 1.80 eV. The bandgap value is higher when compared to the bulk value (1.7 eV).

3.3.1 Determination of Optical Constants

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

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

The extinction coefficient (K) was found to be 1.53 x 10^{-7} at λ =1000 nm. The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \tag{5}$$

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

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)} \tag{6}$$

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

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \tag{7}$$

The refractive index (n) was found to be 2.32 at λ =1000 nm. The high refractive index makes CdSe film suitable for use in optoelectronic devices.From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{8}$$

Hence,

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

where ε_0 is the permittivity of free space. The value of electric susceptibility (χ_c) is 4.3824 at λ=1000 nm. Since electrical susceptibility is greater than 1, the material can be easily polarized when the incident light is more intense.The real part dielectric constant (ε_r) and imaginary part dielectric constant (ε_i) can be calculated from the following relations

$$\varepsilon_r = n^2 - k^2 \tag{10}$$

$$\varepsilon_i = 2nk \tag{11}$$

The value of real dielectric constant (ε_r) and imaginary dielectric constant (ε_i) at λ=1000 nm were estimated at 4.673 and 11.5206 x 10^{-5}, respectively. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

3.4 Dielectric Studies

The XRD patters of thin films contain only one strong peak suggesting the evident disordered nature of the film, the same is also confirmed from the SEM. Structural information of thin films suggests simple or multifaceted defects such as defect centres, micro voids, imperfections, cracks, etc that may be present in the films. These defects play very significant role in transport phenomena, as these defects initiate the defect states like shallow and deep states which may act as donor or acceptors. Such type of states affect the transport phenomena in thin films to a great extent by acting as traps and recombination centres for carriers. These states may also pilot to the probable formation of dipoles, which are answerable for the dielectric behavior. Transport of charge carriers between these sites, hop from a donor to an acceptor state. As a result, each pair of sites forms a dipole and contributes to distributed dielectric relaxation. The dielectric constant and the dielectric loss of the CdSe thin films have been studied the frequency region 50 Hz–5 MHz. The dielectric constant was analyzed as a function of the frequency at different temperatures as shown in Fig.5, while the corresponding dielectric loss is shown in Fig.6. The curve reveals that the dielectric constant decreases with increase in frequency and then reaches almost a constant value in the high frequency region [14]. This also indicates that the value of the dielectric constant increases with an increase in the temperatures. The huge value dielectric constant at low frequencies can be attributed to the lower electrostatic binding strength, arising due to the space charge polarization near the grain boundary interfaces. Due to the application of an electric field, the space charges are stimulated and dipole moments are produced and are called as space-charge polarization. Besides to this, these dipole moments are rotated by the field applied ensuing in rotation polarization which is also contributing to the high values. Whenever there is an increase in the temperature, more dipoles are produced and the value increases [15]. In the high frequency region, the charge carriers might have in progress to move and dielectric constant falls to a low value before the field reversal occurs. Fig.6 shows the variation of dielectric loss with respect to the frequency for various temperatures. These curves show that the dielectric loss is dependent on the frequency of the applied field, comparable to that of the dielectric constant. The dielectric loss decreases with an increase in the frequency at almost all temperatures, but appears to attain saturation in the higher frequency range at all the temperatures [16, 17].

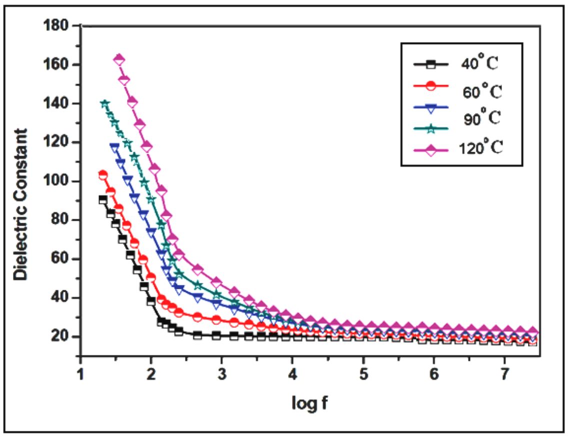

Fig.5. Dielectric constant of CdSe thin films

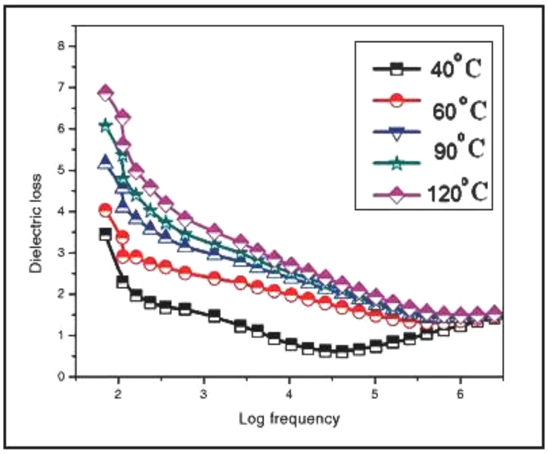

Fig.6. Dielectric loss of CdSe thin films

In the proposed relation, only one parameter viz, the high frequency dielectric constant is required as input, to evaluate electronic properties like valence electron plasma energy, average energy gap or Penn gap, Fermi energy and electronic polarizability of the CdSe thin films. The theoretical calculations show that the high frequency dielectric constant is explicitly dependent on the valence electron Plasma energy, an average energy gap referred to as the Penn gap and Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy [18], the Penn gap is determined. The following relation [19] is used to calculate the valence electron plasma energy, $\hbar\omega_p$

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \tag{12}$$

According to the Penn model [20], the average energy gap for the CdSe thin films is given by

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \tag{13}$$

where $\hbar\omega_P$ is the valence electron plasmon energy and the Fermi energy [19] given by

$$E_F = 0.2948(\hbar\omega_P)^{4/3} \tag{14}$$

Then, the electronic polarizability α, using a relation [21, 22],

$$\alpha = \left[\frac{(\hbar\omega_P)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{15}$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{16}$$

The Clausius-Mossotti relation,

$$\alpha = \frac{3}{4}\frac{M}{\pi N_a \rho}\left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right] \tag{17}$$

The following empirical relationship is also used to calculate polarizability (α),

$$\alpha = \left[1 - \frac{\sqrt{E_g}}{4.06}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{18}$$

where E_g is the bandgap value determined through the UV absorption spectrum. The high frequency dielectric constant of the materials is a very important parameter for calculating the physical or electronic properties of materials [16]. All the above parameters as estimated are shown in Table 1.

Table.1 Electronic parameters of the CdSe thin films

Parameters	**Value**
Plasma energy ($h\omega_p$)	16.657 eV
Penn gap (E_p)	2.15 eV
Fermi Energy (E_F)	12.423 eV
Electronic polarizability (using the Penn analysis)	9.162×10^{-24} cm^3
Electronic polarizability (using the Clausius-Mossotti relation)	9.253×10^{-24} cm^3
Electronic polarizability (using bandgap)	9.028×10^{-24} cm^3

3.4.1 A.C conductivity (σ_{ac}) studies

The ac conductivity (σ_{ac}) has been calculated for the CdSethin films from the following formula

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan\delta \tag{19}$$

Where ε_o is the vacuum dielectric constant (8.85×10^{-12} farad/m), ε_r is the relative dielectric constant and ω is the angular frequency $\omega = 2\pi\nu$ of the applied field. Fig.7 shows the variation of ac conductivity with various frequencies and temperatures. It is seen that the value of ac conductivity increases with increase in frequency. The activation energy of the CdSe thin films found to be 0.182 eV. Fig.8, show the temperature dependent conductivity of CdSe thin films. The plot indicates the exponential behavior of temperature dependent current confirming the semiconducting nature of the material [23].

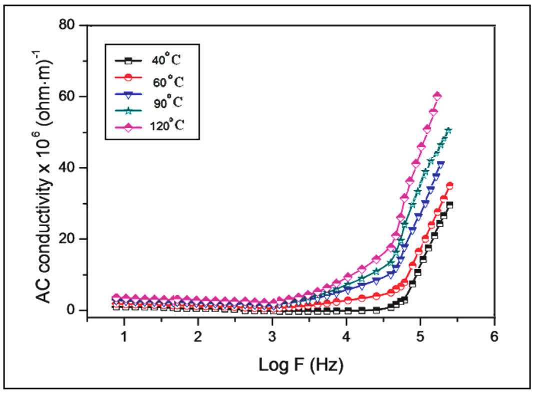

Fig.7. Variation of ac conductivity with frequency at various temperatures

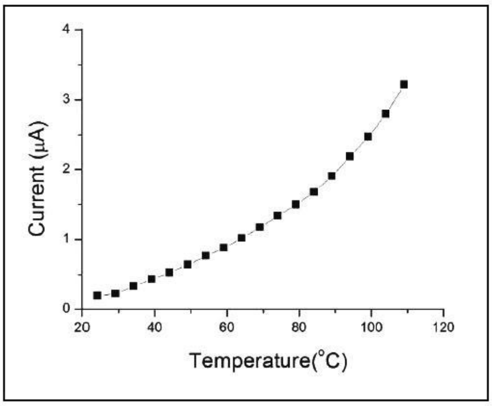

Fig.8. Temperature dependent conductivity of CdSe Thin films

3.5 Photoconductivity Studies

The dc input to the CdSe thin films was increased from 0 to 250 volts in steps and the corresponding dark current was noted from the electrometer. For determining the photocurrent, the CdSe thin films was illuminated with an incandescent light bulb and the corresponding photocurrents were measured. The variation of photocurrent (I_p) and dark current (I_d) with applied field are shown in Fig.9. The plots indicate an increase of current in the dark and visible light illuminated with an increase in applied field depicting the ohmic nature of the contacts [24]. The low values of dark current and 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 photoconductivity. 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 [25].The increase in mobile charge carriers during positive photoconductivity can be explained using the stockman model [26].

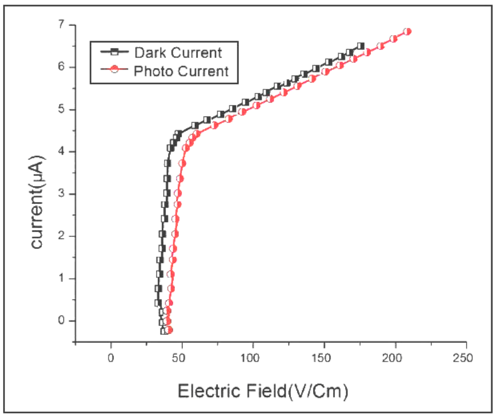

Fig.9 Photoconductivity study of CdSe Thin films

4. Conclusion

The CdSe thin films were prepared by chemical bath deposition technique. Structural and morphology properties of CdSe thin films were investigated by XRD, SEM and AFM methods. The XRD studies show that, well crystallized of CdSe thin films. The morphology of the CdSe thin films have been analyzed by using SEM as well as AFM images.The UV-Visible absorbance spectrum shows 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 dielectric loss of the CdSe thin films are measured in the different frequency and temperatures. In addition, the plasma energy of the valence electron, Penn gap or average energy gap, the Fermi energy and electronic polarizability of the CdSe thin films have been also determined. AC electrical conductivity was found to increase with an increase in the temperatures and frequency. Temperature dependent conductivity indicates the exponential behavior of temperature dependent current confirming the semiconducting nature of the thin films. The photoconductivity study ascertains the positive photoconductivity nature of the CdSe Thin films.

References

[1] K. R.Murali,V. Swaminathan, D. C. Triverdi, Solar Energy Mater.Solar Cells **113,** 81 (2004)
[2] A.S. Khomane, P.P. Hankare, J. Alloys Comp, **489,** 605 (2010).
[3] A.A.Yadav, M.A. Barote , E.U.Masumdar,Mater. Chem. Phys. **121,** 53 (2010)
[4] U.Farva , C.Park, Sol. Energ. Mat. Sol. Cells.**94,** 303 (2010).
[5] D.S. Sutrave, G.S. Shahane, B.B. Patel, L.P. Deshmukh,Mater. Chem. Phys. **65,**298 (2000).
[6] C.B.Murray, C.R. Kagan, M.G. Bawendi, Science. **270,**1335 (1995).
[7] T. Gruszeckix, B. Holmstrom, Solar Energy Materials and Solar Cells.**227,** 31 (1993).
[8] J. Reicman, M. A. Russak, J. Appl. Phys. **53,** 708 (1982).
[9] M. Hyugaji, T. Miura,Jpn. J. Appl. Phys. **24,** 1575(1985).
[10] G. Perna, V. Capozzi, M. Ambrico, J. Appl. Phys. **83,** 3337(1998).
[11] K. C. Mandal, O. Savadogo, J. Mater. Sci. **27,** 4355(1992).
[12] C. J. Liu, J. H. Wang, Appl. Phys. Lett. **36,** 852 (1980).
[13] R. A. Boudreau, D. R. Rauh, J. Electrochem. Soc,**130,** 513 (1983).
[14] S. Suresh, C. Arunseshan,ApplNanosci,**4,** 179 (2014).
[15] Sagadevan Suresh, ApplNanosc.**4,** 325 (2014).
[16] SSagadevan, A Shanmuga Sundaram,Chalcogenide Letters.**11,**159 (2014).
[17] S.Suresh, Journal of Non-Oxide Glasses.**6,**47 (2014).
[18]RavindraNM,Bharadwaj RP, Sunil Kumar K, Srivastava VK, Infrared Phys.**21,** 369 (1981).
[19] Kumar V, Sastry BSR, J. Phys. Chem. Solids, **66,** 99 (2005).
[20] Penn DR, Phys. Rev. **128,** 2093 (1962).
[21] Ravindra NM, Srivastava VK, Infrared Phys. **20,** 399 (1980).
[22]Reddy RR, NazeerAhammed Y, Ravi Kumar M, J. Phys. Chem. Solids **56,** 825 (1995)
[23] F. P. Xavier; G J Goldsmith, Bull. Mat. Sci, **18,** 283 (1995).
[24] L. Armelao; D. Barreca; M. Bertapelle; G. Bottaro; C. Sada; E. Tondello, Thin Solid Films, **442,** 48 (2003).
[25] R. H. Bube, Photoconductivity of solids, (Wiley Interscience, New York, 1981).
[26] N. V. Joshi, Photoconductivity (Marcel Dekker, New York, 1990).