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SOME STRUCTURAL, ELECTRICAL AND OPTICAL PROPERTIES OF VACUUM EVAPORATED CdS THIN FILMS

K. YILMAZ*
Pamukkale University, Science and Arts Faculty, Physics Dept., Kınıklı-Denizli Turkey 20020

In this work, some structural, electrical and optical properties of thermally evaporated CdS thin films with different deposition parameters were investigated. The stoichiometric films that have thicknesses around 2 μm were found to be in a polycrystalline state of hexagonal form with a preferred direction of crystallization in (002) plane. The current transport mechanisms of the films have been studied as a function of temperature over the temperature range 100-430 K. Temperature dependent conductivity data indicated that thermionic emmission and Mott's variable range hopping are the dominant transport mechanisms above and below 200 K, respectively. Scattering mechanisms over the specified temperature range were also studied and it was found that neutral impurity scattering was dominant in the low temperature region while ionized impurity scattering takes place in the high temperature region. The absorption spectra showed that the optical band gap of the films were around 2.4 eV which makes these low resistive films suitable as a window layer for solar cell applications.

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1. Introduction

Cadmium-Sulfide is a member of II-VI family and generally crystallizes in the hexagonal wurtzite form which can be considered as two interpenetrating hexagonal close-packed lattices. Cadmium-Sulfide is widely used in literature as a wide band gap (2.42 eV) window layer for the heterojunction structures. Window layer must be a wide gap material because almost all the absorption should occur within the depletion layer of the narrow gap material. In this sense, CdS is an appropriate material as a window layer for the p-n heterojunction structure over the useful part of solar spectrum since it passes a large fraction of the solar radiation incident on its surface. Furthermore, its resistivity can easily be reduced by intentional doping which results in decreasing the sheet and the contact resistances of the cell so that the depletion layer width in the absorber semiconductor is extended. CdS is one of the most extensively investigated semiconductors in thin film form and a large variety of deposition techniques have been used to obtain solar cells using CdS layers. These deposition techniques include thermal evaporation [1], spray pyrolysis [2], sputtering [3], MBE [4], VPE [5], CVD and chemical deposition [6]. The structural and electrical properties of the CdS thin films strongly depend on the deposition techniques and the substrate temperatures [8]. Evaporated CdS thin films prepared for the solar cell applications usually have resistivities in the range of $1\text{-}10^3$ (Ω.cm) and carrier concentrations in the range of 10^{16} to 10^{18} cm^{-3} [1]. The films are always n-type with a polycrystalline form and the conductivity is dominated by the deviation from stoichiometry which results from the S vacancies or Cd excess. Mobilities are in the range of 0.1-10 ($cm^2V^{-1}\,s^{-1}$) [9]. It has been observed that CdS films grown at higher rates indicate higher carrier concentration and the carrier concentration is found to increase with an

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* Corresponding author: kyilmaz@pau.edu.tr

increase in film thickness which results in a corresponding decrease in resistivity [7]. This work mainly focuses on the conduction and scattering mechanisms of vacuum evaporated CdS thin films, which could be used as a window layer in solar cell applications.

2. Experimental Details

The CdS thin films were deposited onto tin-oxide (TO) coated glass substrates by thermal evaporation technique in a Varian NCR 836 oil diffusion vacuum system. The lowest pressure obtainable with the system is around 10^{-7} Torr. A quartz crucible wound with molybdenum wire was used to evaporate the source. The tube was shielded with a molybdenum cylinder to localize the heat in the source. Pt/Pt-13%Rh thermocouple were placed in contact with the powder to measure the temperature of the source and controlled by Elimko-4000 temperature controller. The substrate heater was made of an aluminum block containing chrome-nickel heating wires insulated by pyrex glass tubes inside the block. The substrate temperature was measured by a copper-constantan thermocouple. CdS powder which was 99.99% pure and had a particle size around 0.3 mm was placed in the quartz crucible as a source material. When the vacuum of around 10^{-6} Torr was obtained, the source and the substrates were started to heat up gradually to the required temperature values. The temperature of the substrate was kept around 200 ^{o}C until the source heated up to the melting temperature of CdS which was around 700 ^{o}C. The deposition time was about 15-20 minutes. The approximate deposition rates for different deposition cycles were in the range of 0.01-0.1 μm/min. Indium contacts were evaporated on CdS thin films to carry out the electrical and optical measurements. The metallic evaporations were achieved by using a Nanotech evaporator system by which the lowest attainable pressure with this system is 10^{-6} Torr through a diffusion pump. Structural analyses of the films were carried out by using JSM-6400 scanning electron microscope (SEM) equipped with energy dispersive X-ray facility (EDXA) and Rigaku Miniflex X-ray diffractometer (XRD). Electrical properties of both films and the devices were carried out using Keithley 220 constant current source and Keithley 619 electrometer. Temperature dependent current-voltage characteristics were done by Janis liquid nitrogen VPF series crysostat. The Hall Effect measurements of the films were carried out by the same system except a constant magnetic field of 0.97 T applied parallel to the c-axis (perpendicular to the film surface) using Walker Magnion model FCC-4D magnet. Optical properties were studied by means of transmission-absorption and spectral response measurements. The transmission-absorption measurements were done by a double beam Perkin-Elmer UV/VIS lambda 2S spectrometer. Spectral response analyses were performed by using an Oriel MS 257 monochromator together with HP 4140 picoammeter/dc voltage source. The thicknesses of the films were measured by DEKTAK 3030ST profilometer for different regions of the films and it was observed that the thickness over the whole surface was almost unchanged.

3. Results and Discussion

CdS thin films have been deposited onto hot soda lime glass by using CdS powder by thermal evaporation technique. SEM and EDXA analysis indicated that the films are composed of Cd and S and no other impurities found in the structure. The XRD spectra, as shown in figure1, exhibits a sharp peak at 2θ equal to 26.44^{o} which corresponds to (002) plane of hexagonal CdS. This result indicates that the film is in a polycrystalline state with a preferred direction of crystallization in (002) plane which is consistent with previous works done by Parlak and Ramesh et.al. [10,15]. A broader and much less weaker peak is also observed in the plane of (004) plane at 2θ equal to 54.52^{o}.

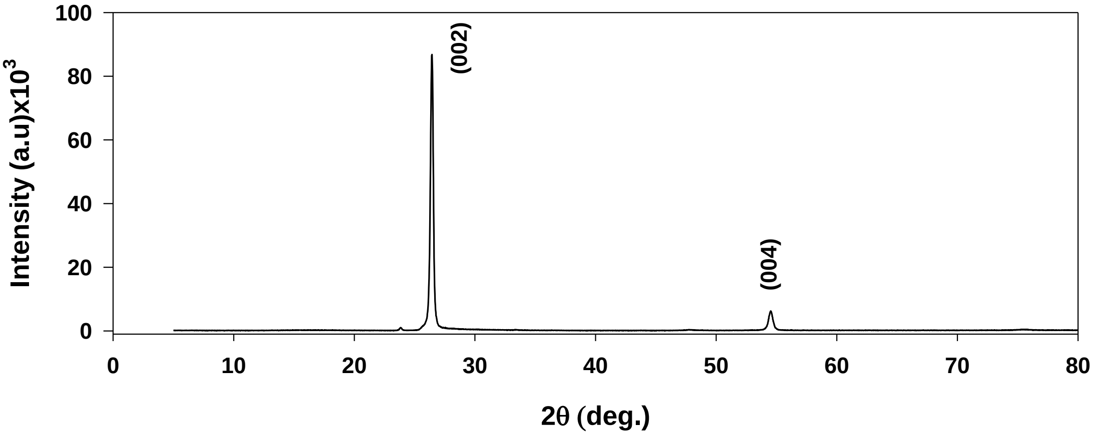

Fig. 1: XRD pattern of CdS thin film

The temperature dependent electrical conductivity and the Hall Effect measurements were carried out for as-grown CdS thin films in the range of 100-430 K. The measurements were done by evaporation of In ohmic contacts onto the six-arm bridge CdS films with thicknesses in between 2.1-2.6 μm. The room temperature conductivities for these films were found to be around 1 $(\Omega cm)^{-1}$ which is in agreement with the result given in a previous work [1]. All the deposited CdS films exhibit n-type conductivity due to sulphur vacancies or cadmium excess, which was determined by the sign of Hall coefficient and the hot probe technique. Temperature dependent conductivity measurements indicated that the conductivity of the CdS films increases exponentially with increasing temperature as illustrated in the figure 2.

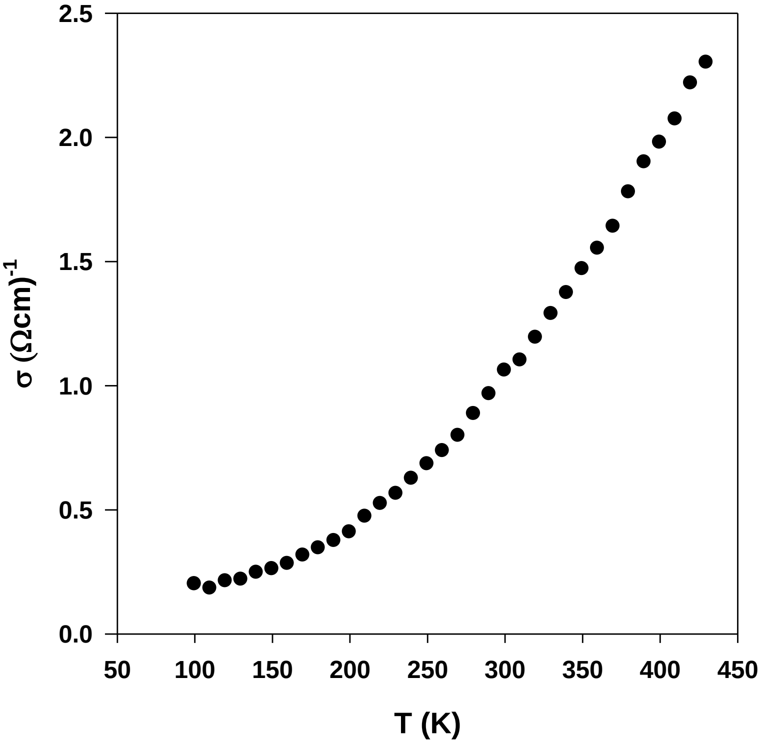

Fig. 2: The variation of conductivity with temperature for a typical CdS thin film

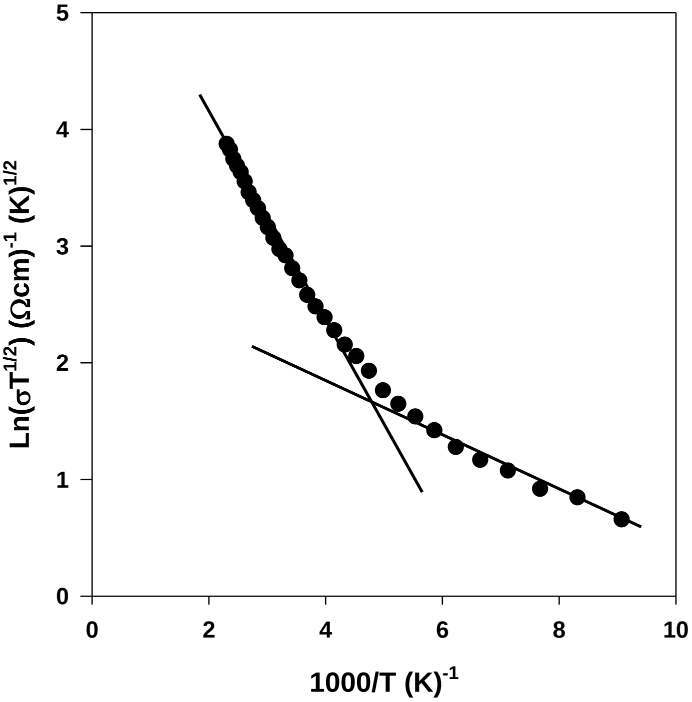

Fig. 3: The variation of the conductivity with inverse temperature in the range of 100-430 K.

The conductivity data for the CdS thin films was analyzed by the grain boundary model proposed by Seto [11]. In order to determine the dominant conduction mechanism; the conductivity-temperature dependence is plotted as Ln($\sigma T^{1/2}$) -1000/T, seen in the figure3. Two linear regions with activation energies of 77 meV and 11 meV were found corresponding to high and low temperature regions, respectively. The analysis of conductivity data indicates that the dominant conduction mechanism above 200 K is the thermionic emission of the carriers over the grain boundary. The activation energy in this region is larger than kT. However, the low activation energy in the 100-200 K temperature range rules out the possibility of thermionic emission over the grain boundary. Thus, Mott's hopping conduction mechanism, expressed as Eq.1, may be the dominant conduction mechanism in this region since the carriers do not have enough energy to surmount the grain boundary potential.

$$\sigma\sqrt{T} = \sigma_0 \exp\left(-\frac{T_0}{T}\right)^{\frac{1}{4}} \tag{1}$$

where T_0 is the degree of disorder and σ_0 is the pre-exponential factor defined as,

$$T_0 = \frac{\lambda\alpha^3}{kN(E_F)} \tag{2}$$

and

$$\sigma_0 = e^2 R^2 \nu_{ph} N(E_F) \tag{3}$$

respectively. Here, α is the inverse of the localization length, $N(E_F)$ is the density of localized states at the Fermi level, λ is a dimensionless constant and ν_{ph} is the phonon frequency which is typically around 10^{12} Hz.

The Mott's parameters are calculated by using the slope and the intercept values of figure 4 and it was found that in between 100 and 200 K conduction is dominated by the variable range hopping (VRH) since the requirement for VRH is satisfied as $\alpha R>1$ and $W>kT$, where R is the average hopping distance and W is the hopping energy. Therefore, the conduction in this low temperature region occurs by hopping of the charge carriers from the filled trap states to the empty trap states.

Annealing effect was also investigated for the sample annealed at 100 ^{o}C for 20 minutes through temperature dependent conductivity and Hall effect measurements but no significant change were observed for the room temperature electrical conductivity of the annealed CdS thin film with activation energies of 78 meV and 9 meV in the high and low temperature regions, respectively.

The Mott's parameters found in the temperature range of 100-200 K for two as-grown CdS thin films grown with different deposition parameters were given in table 1, at an average temperature of 145 K.

Table 1. Mott's parameters of two as-grown CdS films.

T_{source} (^{o}C)	T_{subs} (^{o}C)	T_o (K)	α (cm^{-1})	N(E_F) (cm^{-3}eV^{-1})	R (cm)	W (meV)	αR	kT (meV)
725	213	$2.2\text{x}10^5$	$5.2\text{x}10^7$	$1.1\text{x}10^{23}$	$4.7\text{x}10^{-8}$	21	2.5	13
700	232	$7.1\text{x}10^6$	$1.5\text{x}10^9$	$7.9\text{x}10^{25}$	$4.0\text{x}10^{-9}$	49	5.8	13

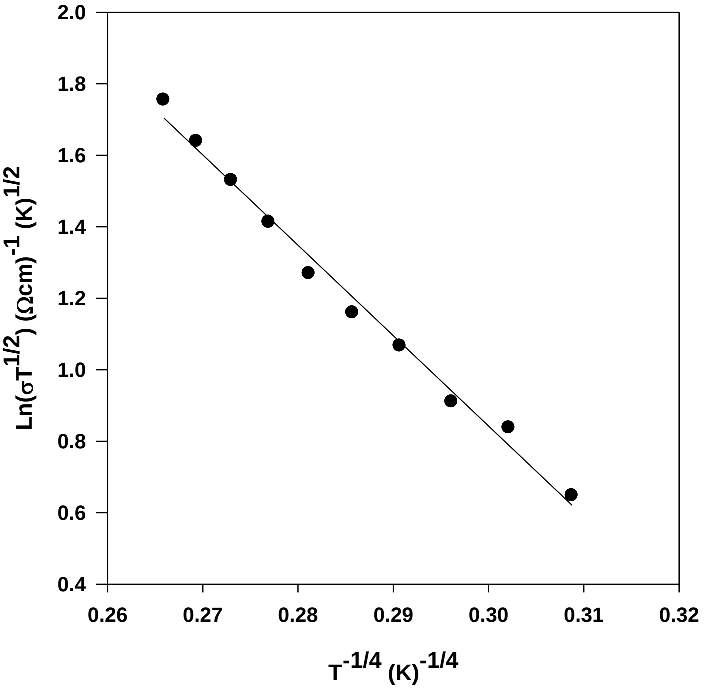

Fig. 4: The Ln($\sigma T^{1/2}$)-$T^{1/4}$ variation in the temperature range of 100-200 K

The carrier concentration and Hall mobility of the CdS thin films were investigated by the Hall Effect measurements. Room temperature electron concentrations of the films were found to be in the range of $1.4\text{x}10^{16}$-$3.4\text{x}10^{18}$ cm^{-3} depending on the substrate temperature which confirms earlier works [1,15,16]. The variation of electron concentration with inverse temperature in the temperature range of 150-420 K for a typical CdS film is illustrated in figure 5, which shows that the carrier concentration increases exponentially with the absolute temperature in the high temperature region where thermionic emission is the dominant conduction mechanism. However, in the low temperature region in between 100-200 K, temperature dependence of the carrier concentration is weak.

The room temperature Hall mobility of the films were found in between 3.1-3.5 $cm^2/V.s$ that is in well agreement with the previous studies [9,10]. The temperature dependence of the mobility data was analyzed according to the thermionic emission model proposed by Petritz [14] and later extended by Seto [11]. In this model the effective mobility can be expressed as;

$$\mu = \mu_0 T^{-\frac{1}{2}} \exp\left(-\frac{q\phi_b}{kT}\right) \tag{4}$$

where ϕ_b is the barrier height at the grain boundary. The $\mathrm{Ln}(\mu T^{1/2})$-1000/T variation of a typical sample is given in figure 6. It indicates that the mobility increases as the absolute temperature increases. The grain boundary height (ϕ_b) was found to be 98 meV and 14 meV above and below 200 K, respectively. The barrier height in the high temperature region is larger than kT which verifies that thermionic emission is the dominant conduction mechanism in this region.

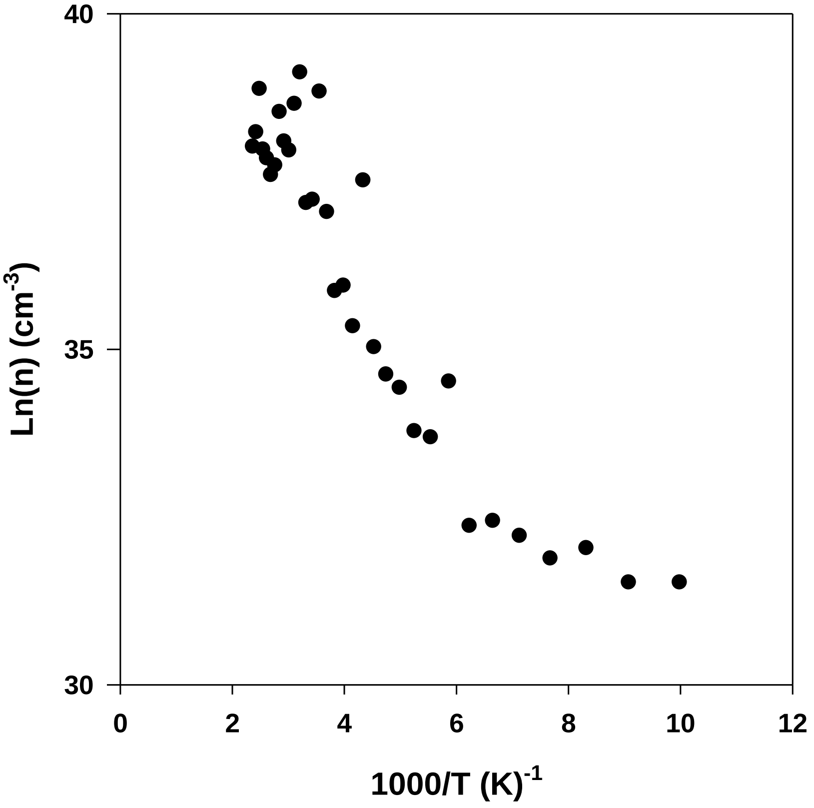

Fig. 5: The variation of electron concentration of a typical CdS thin film.

In order to determine the existent scattering mechanisms; Log(μ)-Log(T) variation in fig. 7 was considered, as the increase in mobility with temperature satisfies the relation $\mu \propto T^n$. The value of the exponent *n* determines the dominant scattering mechanism at each temperature range.

Fig. 7 shows that in the low temperature region the mobility variation is almost temperature independent. The anomalous variation of mobility in this region reveals that the neutral impurity scattering is dominant. However, in the high temperature region above 220 K the linear variation fits to $\mu \propto T^{5/2}$ relation which indicates that ionized impurity scattering is the dominant scattering mechanism. Thus, it can be concluded that scattering of carriers by impurities takes place over the whole temperature range studied and ionization of impurities increases with increasing absolute temperature.

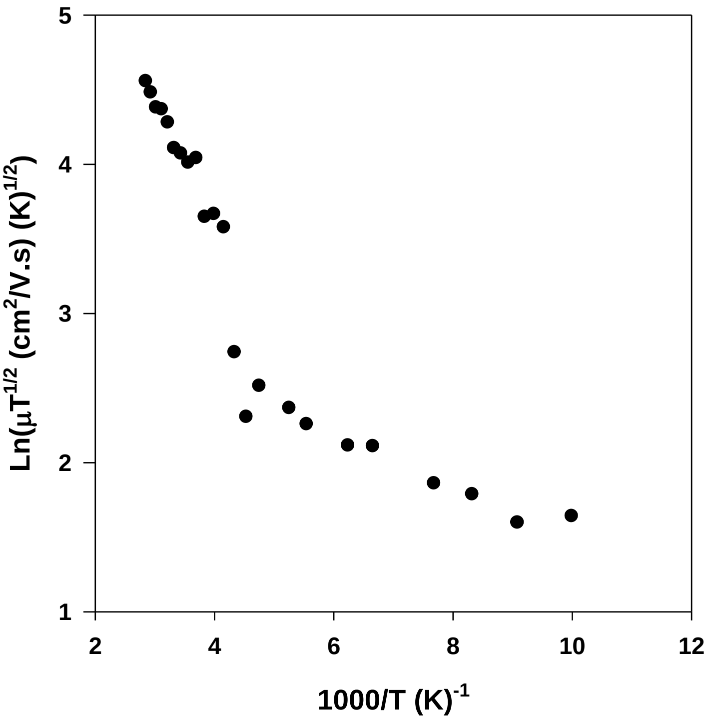

Fig. 6: The variation of mobility with inverse temperature

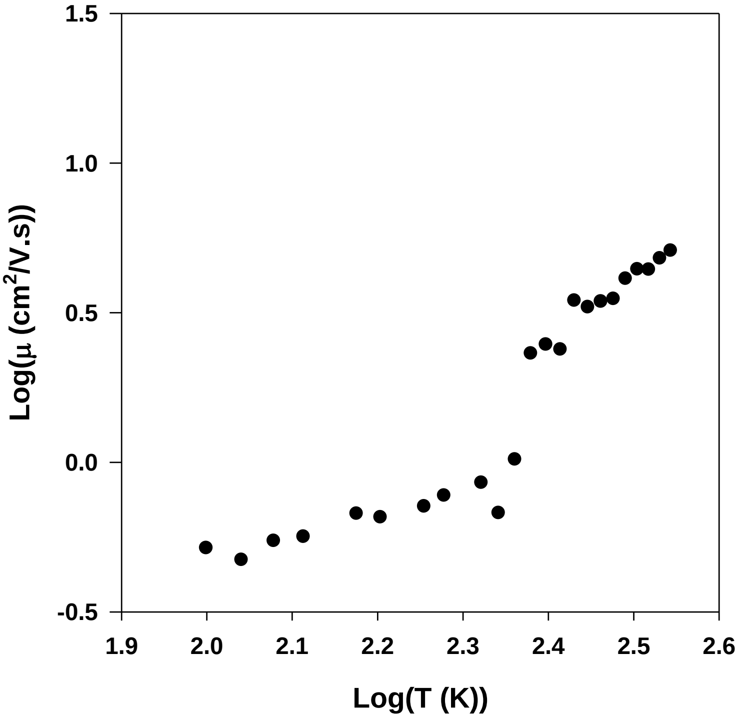

Fig. 7: Log(μ)-Log(T) variation for a typical CdS thin film

Mobility variation with temperature did not change for the annealed sample at 100 ^{o}C for 20 minutes. However, room temperature mobility value decreased from 3.5 to 1.8 cm^2/V.s with annealing whereas the carrier concentration slightly increased from 1.9x10^{18} to 3.4x10^{18} cm^{-3}. Therefore, at high temperatures the contribution of the intergrain ionized impurity scattering to the effective mobility increases with absolute temperature.

The transmission spectrum of a typical CdS thin film measured in the spectral range of 1.1-2.9 eV. Using the transmission data, absorption coefficients at room temperature were calculated by Eq.5 in the specified energy range. The absorption coefficients at room temperature were found to be $1.4x10^3$-$3.8x10^4$ cm^{-1} for the minimum and maximum photon energies, respectively. Figure 8 represents the variation of absorption coefficient with respect to incident photon energy.

$$\alpha = \frac{1}{d}\ln\left(\frac{1}{T}\right) = \frac{1}{d}\ln\left(\frac{I_0}{I}\right) \qquad (5)$$

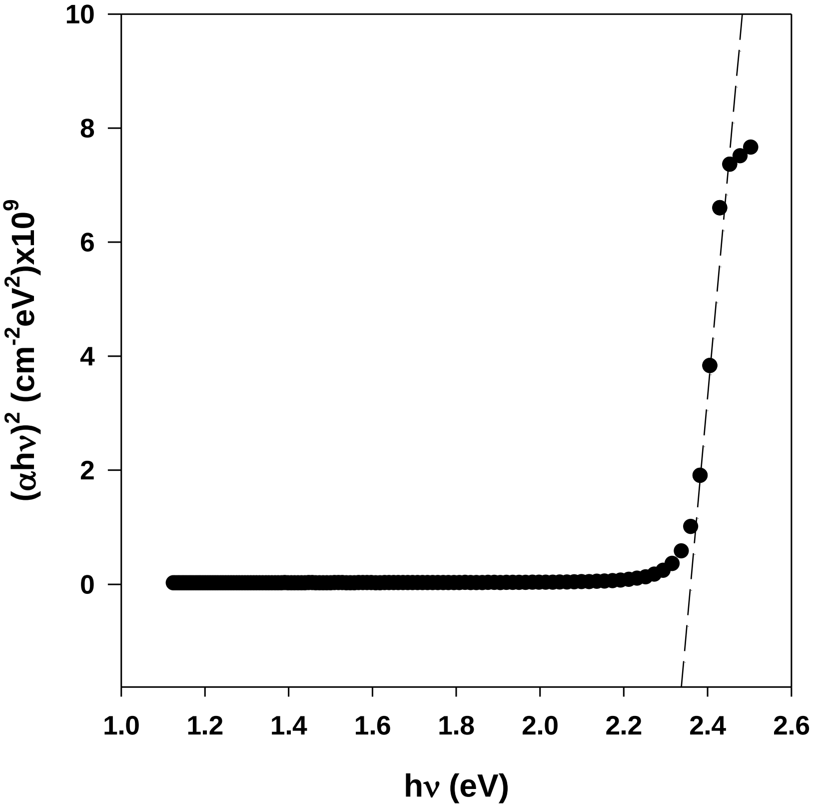

Fig. 8: The variation of absorption coefficient with photon energy for a typical CdS thin film

As seen from figure 8, the film is almost transparent up to 2.31 eV of photon energy and from that point absorption of the photons increases sharply with photon energy in which region the absorption takes place through direct interband transition and extrapolation of the

linear variation gives the optical band gap of about 2.36 eV for a typical polycrystalline CdS film with thickness of 2.64 μm. This result is in well agreement with the previous works done in literature [12,13,15].

4. Conclusion

We have investigated structural, optical and temperature dependent electrical properties of vacuum evaporated CdS polycrystalline thin films. The results have indicated that conduction of the films dominated by two mechanisms above and below 200K, which are thermionic emission over the grain boundaries and variable range hopping. We also found that neutral impurity and ionized impurity scattering mechanisms were effective over low and high temperature regions, respectively. Absorption spectra showed that the band gap of the films were around 2.4 eV which indicated that these low resistive polycrystalline thin films could be used as a window layer in heterojunction applications.

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