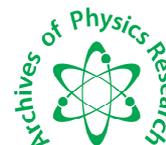




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pH dependent structural, optical and electrical properties of chemically deposited CdS thin films

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ABSTRACT

CdS thin films were prepared by chemical bath deposition technique (CBD) onto the glass substrate at 65 °C. In order to study the effect of pH on structural, optical and electrical properties of thin films. AR grade cadmium sulphate, thiourea use as starting precursor for preparation of thin films, while triethylamine (TEA) used as complexing agent. As prepared thin films were studied using different analytical technique XRD, SEM, EDAX and UV-spectroscopy to known crystal structure, surface morphology, elemental composition and optical band gap energy. It was observed that as pH of the films significantly effect on films thickness, crystallite size, grain size band gap energy and activation energy of prepared thin films of CdS. The result are discussed and interpreted.

Keywords: CdS thin films; chemical bath deposition technique, TEP, electrical conductivity

INTRODUCTION

Now day's current interest in the creation of semiconducting thin films on surfaces by a variety of self-organizing techniques have focused on their application in photoconducting and molecular electronics. Such semiconducting thin films exhibit novel electrical, mechanical, chemical and optical properties [1]. CdS thin films belong to wide direct band gap semiconductors and their energy band gaps is 3.42 eV [2]. Difference in their band gap widths is also found to be very effective way to slow the recombination of electron-hole pairs. Such property consequently increases photo catalytic activity in solar cell applications [3-6].

In recent years, high priority has been given to develop low-cost deposition technique to deposit CdS thin films [7]. Though various deposition techniques such as electrodeposition, screen printing, sputtering , spray pyrolysis [8-11] have been reported, chemical bath deposition (CBD) method has attracted much attention since it is conformed as a simple and promising technique to obtain device quality films. CBD is a simple which is also used to deposited the semiconductor on photovoltaic device. The CBD method appears suitable for large area industrial process because it is the least expensive and a low temperature method. Another advantage of the CBD technique is its ability to deposit very thin films (50 nm) in a conformal manner on a rough substrate surface. The rate of growth in CBD is controllable by pH, temperature, time of dipping and the relative concentrations of the reactants in the bath solution [12].

CdS thin films are important materials, due to their wide applicability in photoluminescence, transparent, semiconductors, photo catalysts, piezoelectricity, UV light emitting devices, varistors and optical devices [13-16]. In this work, CdS thin films were prepared by chemical bath deposition technique. Crystal structured and surface morphology properties were studied using X-ray diffractogram (XRD) and scanning electron microscope (SEM).

Elemental composition was studied using energy dispersive spectrophotometer (EDAX). Optical property was investigated using UV-Spectroscopy. Electrical conductivity measured by two probe method. Thermoelectric power set up (TEP) used to determine type of material.

MATERIALS AND METHODS

This method allows the deposition of very thin films, of the order of a few nanometers and it is an easy and inexpensive chemical bath deposition technique. The physical properties of the chemical deposition of CdS films are dependent upon the growth parameters such as the bath temperature, the relative concentrations of the various reactants in the solution the pH value and the type of substrate. The chemical bath deposition technique was used to deposit the thin films of cadmium sulphide on glass substrate. The starting materials used were cadmium sulphate and thiourea (Made: Sd-fine 99.99% purified). Triethanolamine (TEA) was used as a complexing agent. Ammonia solutions were used to adjust pH of the reaction mixture. In order to obtain good quality of thin films, following parameter were adjust such as deposition time, temperature of deposition. pH of the solution is varied (9 to 10.5) by addition of liquid ammonia drop in the prepared solution. The optimum value of time, temperature and pH were tabulated in Table 1. as the prepared CdS thin films samples were annealed at 200 °C for 10 min. and referred as sample S1, S2, S3 and S4 respectively.

Table 1. Optimum parameter to obtain nanocrystalline CdS thin films

Deposition parameter	Optimum value / item
Deposition time	80 min.
pH	9, 9.5, 10 and 10.5
Concentration of precursor Cadmium sulphate, Thiourea	0.1 M
Solvent	Deionized water
Deposition temperature	65 °C

2.1. Effect of pH on growth of CdS thin films

The variation of pH during the growth is important in the structural film quality and was observed experimentally. It was found that, for low pH the Cd⁺⁺ ion concentration in solution is more due to less complexation of Cd⁺⁺ ions and the homogeneous process takes place at slow rate resulting in a lower thickness. At high pH the Cd⁺⁺ ion concentration is less due to higher complexation but S⁻ ion concentration is more that gives higher deposition rate [17].

RESULTS

3.1. Thickness Measurement of thin films

The film thickness was measured by a weight difference method [18] in which weight of the sample, area and densities were considered. The thickness, sample weight and sample area are related as:

$$t = M/A.\rho \text{ ----- (1)}$$

Where, M is the weight of the sample in gm,

A the area of the sample in cm²

and ρ the materials density in gm cm⁻³.

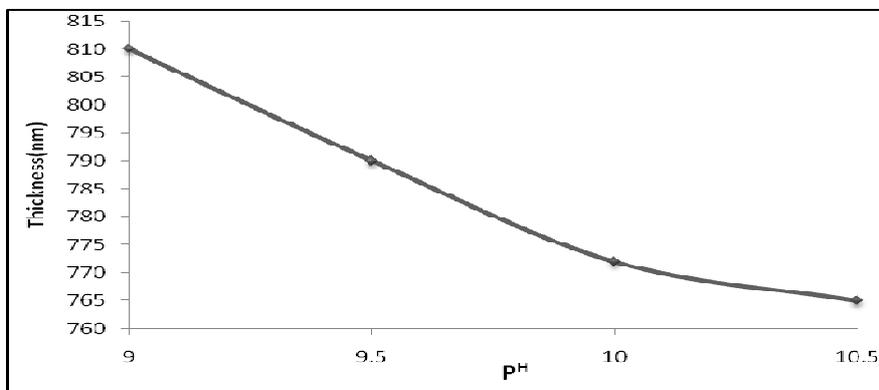


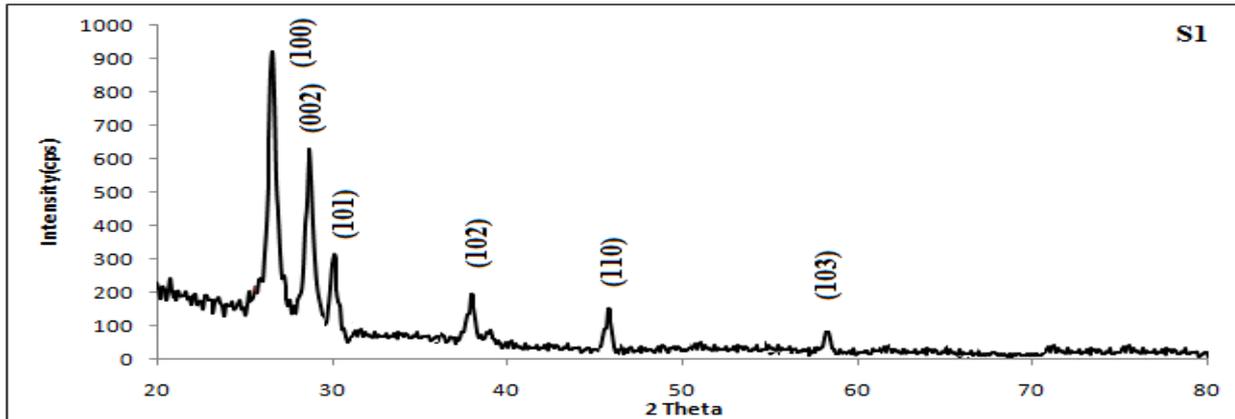
Fig. 1: Thickness of the CdS thin films deposited at different pH values for a constant deposition time of 80 min.

Fig. 1 shows the variation of the thickness for the CdS films as a function of pH value of the reaction mixture for a constant deposition time of 80 min. It was clearly seen from figure 1 that the thickness of the deposited films decreased from 810 to 765 nm with increase in pH values. The bath temperature can be effectively used to control the rate of CdS formation.

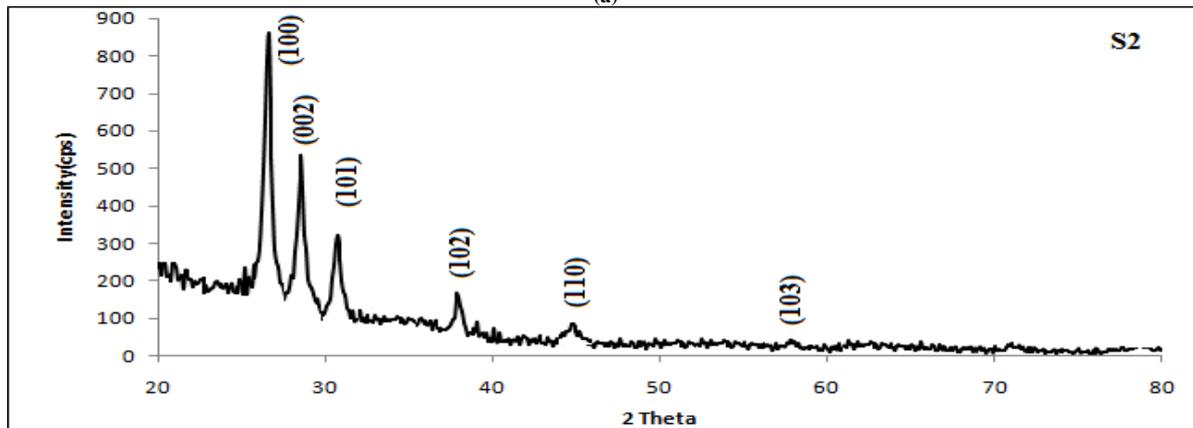
3.2. Structural properties

3.2.1. X-ray diffraction:

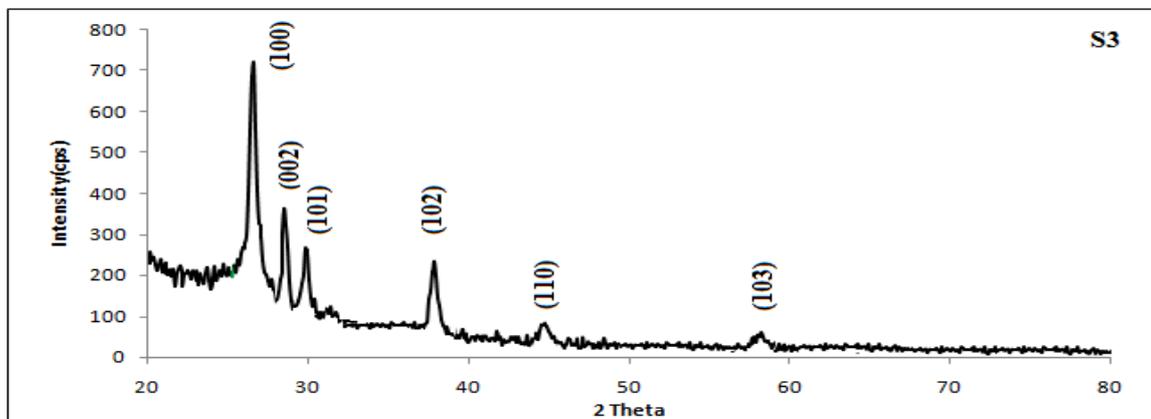
The structures of the film was analyzed with X-ray diffractogram ((Miniflex Model, Rigaku, Japan) using $\text{CuK}\alpha$ radiation with a wavelength of 1.542 Å.



(a)



(b)



(c)

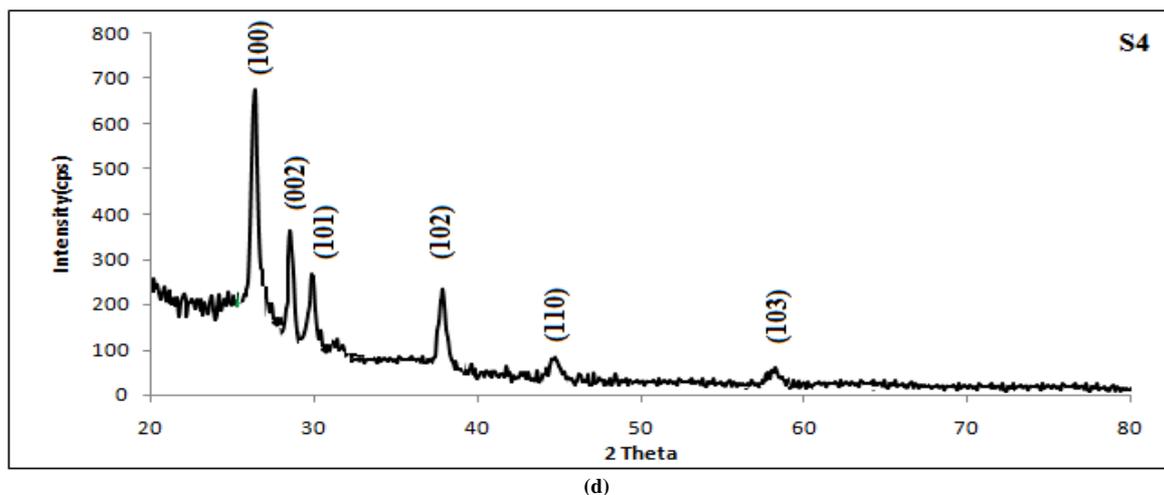


Fig. 2: (a), (b), (c) and (d) shows X-ray diffractogram of CdS thin films.

The structural characterization is very important in explaining structural, microstructural and electrical properties of CdS thin films. The X-ray diffraction patterns were recorded from 20 to 80° as shown in Fig. 2 (a) – (d).

The XRD results show that all the films were nanocrystalline in nature with cubic phase of CdS. It is observed from Fig. 2 (a), (b), (c) and (d). The observed peaks (100), (002), (101), (102), (110) and (103) are match with standard JCPDS data of CdS [19]. The intensity of (100) plane decreases with increasing film p^H of CdS thin films, similarly result were observed by A. Kariper et al [20].

The average crystallite size of CdS thin film samples were calculated by using the Scherrer formula,

$$D = 0.9\lambda/\beta\cos\theta \text{ ----- (2)}$$

Where, D = Average crystallite size

λ = X-ray wavelength (1.542 Å)

β = FWHM of the peak

θ = Diffraction peak position.

The average crystallite size was presented in Table 2.

Table 2: XRD parameters observed for samples S1, S2, S3 and S4.

hkl plane	2θ degree	d values				FWHM				Crystallite size			
		S1	S2	S3	S4	S1	S2	S3	S4	S1	S2	S3	S4
100	26.59	3.33	3.324	3.324	3.324	0.996	0.998	1.100	1.123	23	21	19	17
002	31.79	2.620	2.621	2.621	2.611	0.656	0.658	0.660	0.665	36	34	30	28
101	34.46	2.402	2.401	2.401	2.401	1.437	1.439	1.439	1.442	37	36	19	16
102	36.29	1.789	1.790	1.790	1.790	0.557	0.559	0.561	0.567	35	34	32	29
110	37.96	1.502	1.503	1.504	1.50	1.336	1.335	1.340	1.342	26	24	21	18
103	56.62	1.211	1.210	1.210	1.21	0.413	0.411	0.417	0.421	37	36	33	31

Table 2 shows the XRD parameters observed for samples S1, S2, S3 and S4 such as 'd' values, full width at half maximum values of the films and average grain size with the variation of composition of P^H in CdS thin films (S1 to S4). The FWHM value increases as decreasing in thickness indicating a better crystallinity of the films [21]. Also Fig. 2 shows crystallinity decreases from S1 to S4. This means that the crystallinity becomes better in higher for sample (S4). The average crystallite size decreases with increase in P^H and represented in Table 2.

3.3. Microstructure Study

3.3.1. Scanning electron microscope

The surface morphology of the prepared film was analyzed using a field emission scanning electron microscope coupled with energy dispersive X-ray analysis (EDAX) (SEM, JEOL. JED 6300).

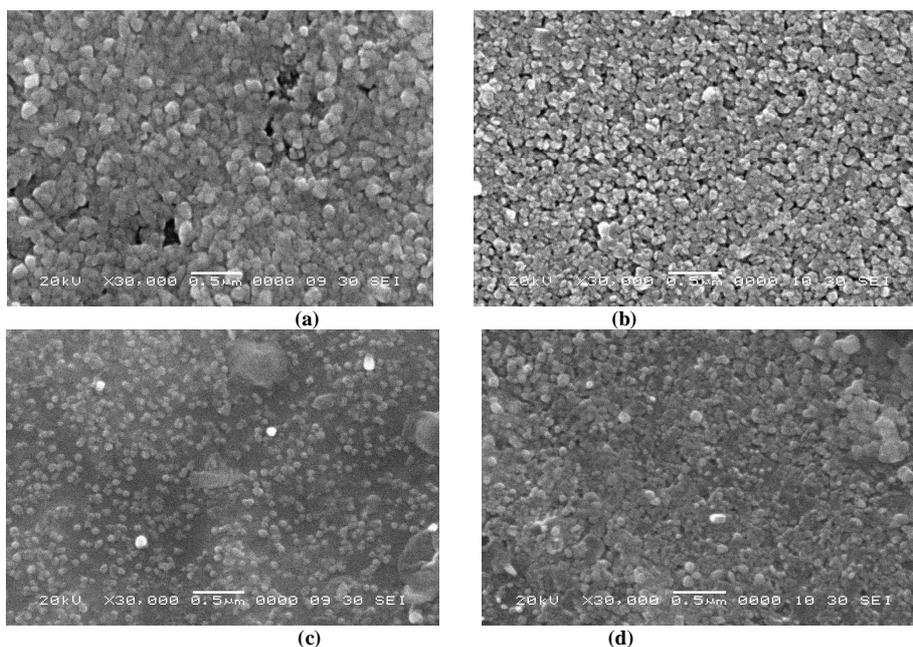


Fig.3. SEM images of CdS thin film sample S1, S2, S3 and S4

SEM imaged of CdS thin films were represented in Fig.3. Scanning electron microscope resolve nanoparticle associated with the film even at high magnification of “20E+3” Fig 3(a) (b) (c) and (d) shows the spherical formation of the particle for CdS thin film. In fig. 3(a) shows agglomerations of the grains. Grain size was tabulated in table 3.

3.4 Quantitative elemental analysis (EDAX)

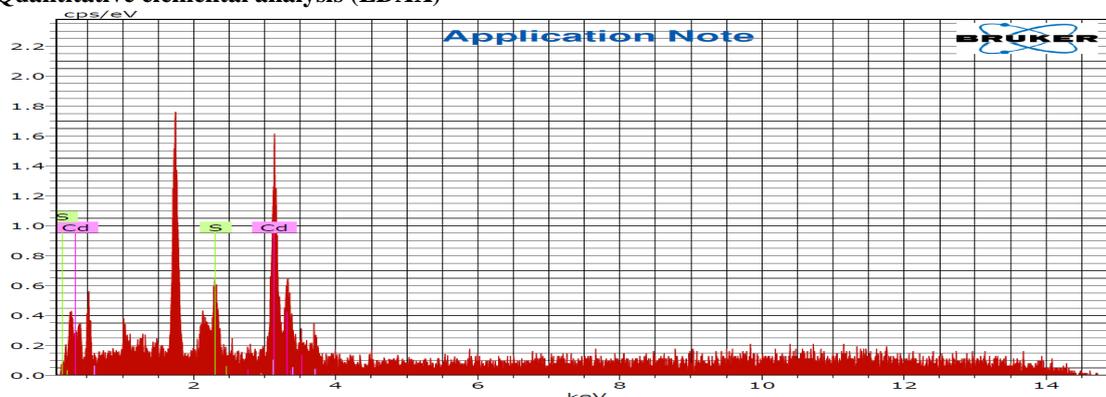


Fig. 4 EDAX of CdS thin film film sample (S3)

The quantitative elemental composition of CdS thin film were analyzed using an energy dispersive spectrometer. Fig.4 shows as the prepared CdS thin film was nonstoichiometric in nature.

Table 3. Quantative elemental analysis as prepared CdS thin films

Element	Observed							
	S1		S2		S3		S4	
	wt %	at %	wt %	at %	wt %	at %	wt %	at %
S	33.60	40.56	34.37	65.81	28.23	43.40	26.23	45.40
Cd	66.40	59.44	65.63	34.19	71.77	56.60	73.77	54.60
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 3 indicate that the formation of CdS thin films. It shows nonstoichiometric formation.

3.5. Optical properties using UV-spectroscopy

The optical absorbances of the films were measured using UV-visible-2450 spectrophotometer at room temperature.

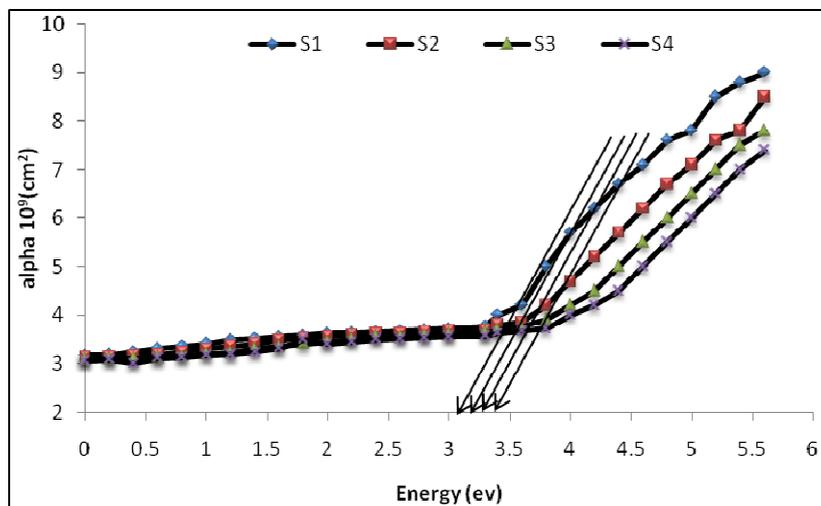


Fig. 5. Plot of the $(\alpha h\nu)^2$ vs photon energy ($h\nu$) for samples S1, S2, S3 and S4.

Optical characterization of thin films gives information about other physical properties, e.g. band gap energy and band structure and optically active defects etc. The effect of p^H on the optical absorbance and the band gap (E_g) values of the CdS thin films have been studied.

The optical gap (E_g) of the film can be obtained by plotting $(\alpha h\nu)^2$ vs $h\nu$ and extrapolating the straight line portion of this plot to the energy axis. The photon energy at the point where $(\alpha h\nu)^2$ is zero is E_g . Table 4 gives the optical band gap values obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $h\nu$ to $\alpha = 0$. These plots are given in Fig. 5 for the films S1, S2, S3 and S4. It is seen that the slight decreases in the optical band gap of the films with the increasing film thickness can be attributed to the increase in the grain size. Another reason could be the improving crystallinity with increasing grain size. This means that the p^H also affects the band gap of the film.

Table 4: Measurement of p^H of thin film, film thickness, crystallite size, grain size and optical band gap energy

Sample No.	p^H	Thickness (nm)	Average crystallite from XRD (nm)	Average grain size from SEM (nm)	Optical band gap from UV-VIS (eV)
S1	9	810	17	39	3.20
S2	9.5	788	19	36	3.31
S3	10	776	21	33	3.36
S4	10.5	765	23	27	3.44

The values of the film p^H are given in Table 4. It is also clear from table 4, that crystalline size, grain size goes on decreasing with increase in p^H of the thin films, while optical band gap energy increases for thin films samples S1, S2, S3 and S4. This may be due to the improvement in the crystallinity with increase in p^H which leads to minimum imperfection. It is seen that the slightly increase in the optical band gap energy of the films with increasing film in p^H can be attributed to the decrease in the crystalline and grain size. Another reason could be improving crystallinity with decreasing grain size. This means that the in p^H also affects the band gap of the film, The result suggests the band gap energy of thin films does not depend significantly on the p^H [22].

3.6. Electrical properties

3.6. 1. Thermoelectric power measurements:

The p -type or n -type semiconductivity of CdS thin films was confirmed by measuring the thermoelectric power of the thin film samples. The thermoelectric power (TEP) was measured as a function of temperature in the range between 320 and 400 K. For CdS material, conduction electrons originate from ionized defects such as oxygen vacancies, rendering n -type conductivity. The variation of the thermo emf with temperature difference for all the samples is

shown in Fig. 6. TEP increases with increase in temperature for all the samples. CdS thin films were observed to be the *n*-type material.

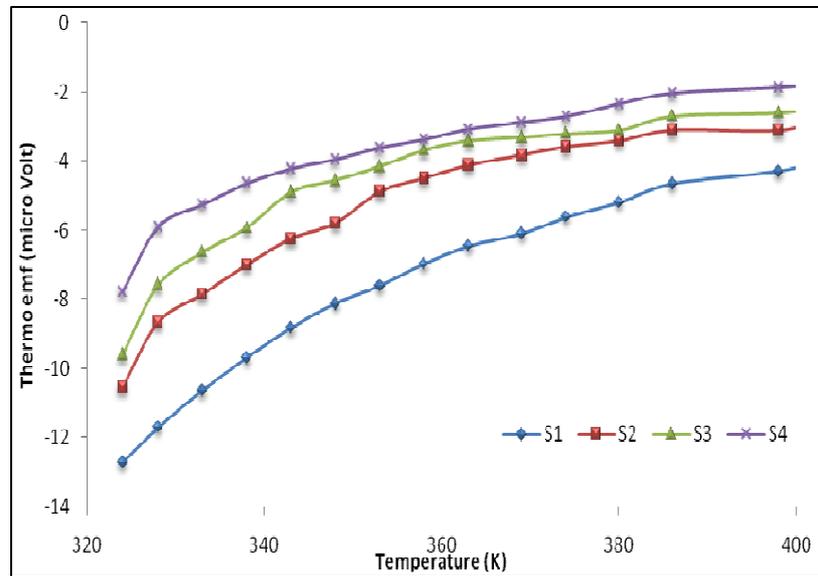


Fig.6.Variation of the thermo emf with temperature

3.6.2. Electrical conductivity

Fig.7 shows the variation of log (σ) with operating temperature. The conductivity of each sample is observed to be increasing with an increase in temperature. The increase in conductivity with increase in temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of CdS thin films.

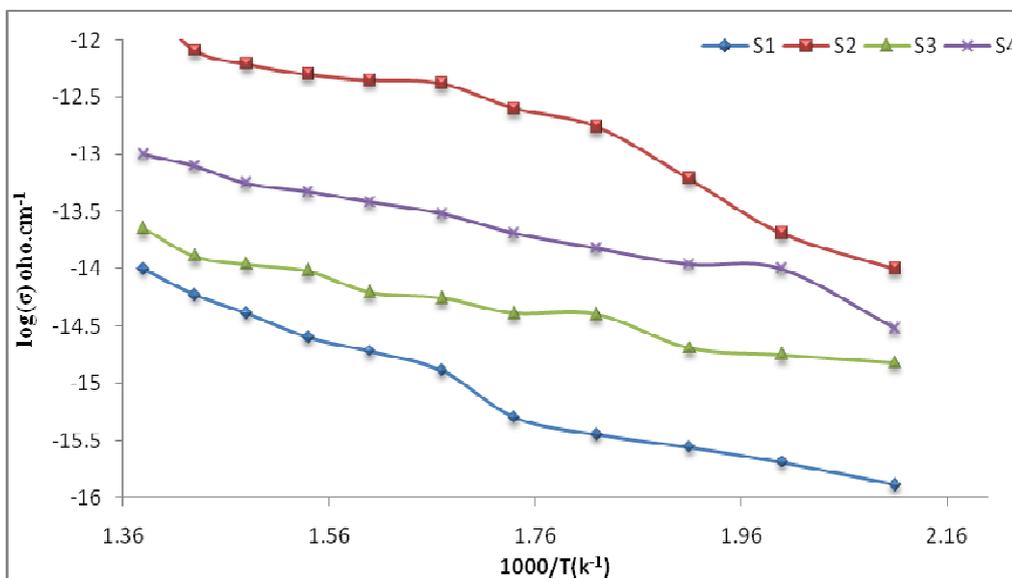


Fig. 7. Temperature dependence of the conductivity of CdS

It is reported [23, 24] that there is a variation of activation energy with thickness. The activation energy calculated from the slopes of line for sample S1, S2, S3 and S4. As films thickness goes on decreasing activation energy

increases, there is variation of activation energy with thickness presented in Table 5. The conductivity studies on films show that all the films exhibit two activation energy at different temperature regions.

Conductivity was given by relation

$$\sigma = \sigma_0 \exp \left(- \frac{E}{kT} \right) \text{----- (2)}$$

Where, σ = conductivity
 σ_0 = conductivity constant
 k = Boltzmann constant
 T = Temperature.

Table 5: Measurement of film thickness with activation energy

Sample No.	Thickness (nm)	Activation energy (E) Δ	
		30 °C	150 °C
S1	810	0.21 eV	0.33 eV
S2	788	0.23 eV	0.36 eV
S3	776	0.27 eV	0.37 eV
S4	765	0.33 eV	0.40 eV

It is observed from the Fig. 8 that as the thickness of the films decreases, activation energy goes on increasing. The increase in activation energy may be due to the change in structural parameters, improvement in crystalline and grain size [25].

CONCLUSION

The deposition conditions are optimized to obtain CdS thin films. The structural investigation using XRD reveals that formation of CdS thin films. Our study have shown that as pH of the film goes on increases, decreasing crystallite size, grain size with increase in optical band gap energy with activation energy. Microstructural properties confirm that the as-prepared CdS thin films were nanocrystalline in nature. The elemental analysis conferred that as prepared CdS thin films were nonstoichiometric in nature. Electrical conductivity increases with increase temperature of the CdS thin films, indicating semiconducting nature. TEP measurement indicates that as prepared CdS thin films are n type.

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