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Behavioral change in Optical and Electrical property of Cd Chalcogenide films containing Te, Se deposited by Thermal and Electron beam evaporation

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ABSTRACT

Cadmium Chalcogenide material has emerged as a promising semiconductor because of its potential applications in the field of electronics and technology. Ternary films of Cd Te Se were coated on glass substrate by thermal and electron beam evaporation. Optical characterization such as Transmittance (T%) and Reflectance (R%) data's were collected. Samples were subjected to thermal analysis like DSC, DTA and TGA to find the composition and the stability. Some of the samples deposited by electron beam evaporation were annealed at temperatures 200° C and 400° C. For the annealed films ($Cd_{0.6}Te_{0.2}Se_{0.2}$ & $Cd_{0.7}Te_{0.2}Se_{0.1}$) % of R and % of T has changed to comparable R&T and finally to T%. These values reveal the antireflection behavior of the coating. Refractive index 'n' of the films deposited by thermal evaporation is very high. This can be explained due to thickness variation or due to density of state. The absorption spectra of the annealed sample gave very broad band absorption characteristics (absence of absorption peak) having potential to yield a broad band antireflection. Optical energy band gap has varied from1.3 eV to 2.65 eV for the various compositions of CdTeSe. The electrical resistivities of few ternary films have been carried out using four probe techniques. It is surprising that samples answer for both +TCR and –TCR, (Temperature co efficient of Resistance) and change occurring at and around 368°K which happens to be the inversion/Transition temperature. Whereas, the other sample answering for both +TCR and –TCR, change occurs at 378°K. Materials with appropriate composition selected for the present study have exhibited both ohmic and semiconducting nature as well as both R%, comparable R% & T%, finally T%. Above points justify the major role played by Se and Te content in the investigated films. The present study signifies the behavioral changes in optical and electrical properties exhibited by Cd Chalcogenide films. Further studies to know the exact inversion/transition temperature is under investigation.

Keywords: Thermal evaporation, Electron beam evaporation, Transmittance, Reflectance, Eg, Resistivity.

PACS: 77.80e, 77.22Ej, 77.84-s

INTRODUCTION

Cd Chalcogenide [for the composition $Cd_yTe_{x-y}Se_{1-x}$ & $CdTe_{1-x}Se_x$] ternary thin films, alloys of the binary compound semiconductors CdSe and CdTe are being investigated largely in recent years due to their unique properties including high photo sensitivity to electromagnetic radiation, almost 100% quantum yield to radiative recombination and their ability to form solid solutions[1].

Cd Chalcogenide find extensive application in solar cells [2], photo conductors [3], solar control applications [4]etc., The main advantage of these thin films is, its crystal structure and tailoring of direct band gap ranging from 1.35 eV to 1.75 eV [5] by changing the concentration of selenium and tellurium, so that solar energy can be effectively harnessed for maximum conversion to electrical energy. Chalcogenide films are contrary to oxide films, transparent in the near- or mid–infrared region of the spectrum (~0.8 – 12 µm), and they can be used for applications in these region. The refractive index of Chalcogenides is larger in near- and mid-infrared region (typically from 2.2 – 2.9) [6]; Chalcogenides can match with high Refractive index materials such as Si, GaAs, ZnSe, InSb and others.

Cd Chalcogenide films containing Te, Se have been deposited by several techniques. Among the various techniques in use [7, 8], thermal evaporation [9] and electron beam evaporation [10] has gained importance because of their simple technique in which quality thin films can be prepared. In the present study, to tune the properties of the films to the requirement, various compositions of Cd, Te, Se having the formula $Cd_yTe_{x-y}Se_{1-x}$ and $CdTe_{1-x}Se_x$ have been deposited. Films have been characterized optically, electrically and topographically. Many of the films with the composition $0 \leq x \leq 1$, $0 \leq y \leq 1$ have been deposited by vacuum thermal evaporation(T.E). Other films have been deposited by electron beam evaporation (E.B). In this case, before depositing the films, to make sure of the desired composition of the compounds, thermal analysis such as TGA, DTA & DSC have been carried out. Compositional dependence of Eg in Cadmium Chalcogenide $Cd_yTe_{x-y}Se_{1-x}$ film has been investigated through optical characterization[11]. Some of the samples have been annealed at 200°C and 400°C. Effects of annealing on optical property have been analyzed. [12, 13]. Electrical and topographical characterization of $CdTe_{1-x}Se_x$ thin films have been investigated using Four probe method and AFM. Samples have exhibited both semiconducting and ohmic nature (–TCR & +TCR).

MATERIALS AND METHODS

Commercially available glass and quartz slides were used as substrates. Substrates were first washed with chromic acid, next cleaned with detergent, rinsed with acetone and finally cleaned with double distilled water before use. Elements Cd, Te, Se were procured in pure form from Aldrich and are used for depositing film. Thin films of CdTeSe deposited on glass and quartz substrates by thermal vapor deposition technique at vacuum of $\approx 10^{-5}$ torr, using 'HIND HIVAC 12A4' equipment. Tantalum boat sources were used for the evaporation of stochiometric powder of the CdTeSe ternary compound. Also, thin films of $Cd_y\,Te_{x-y}\,Se_{1-x}$ were deposited on glass and quartz substrates by electron beam evaporation technique at vacuum of $\approx 10^{-5}$ torr, using 'HINDIVAC 12A4D' & 'EBG-PS-3K' gun powder supply equipment. UV-VIS-IR studies were carried out using Micro pack DH-2000 equipment. The transmission spectra in the region 180 nm to 1100 nm has been collected and optical parameters α, K, n and Eg have been evaluated. Structural analysis has been carried out by XRD & EDAX and topography by AFM. Stylus method has been used to determine the thickness of the films. The electrical resistivity of $CdTe_{1-x}Se_x$ thin films is obtained by four probe technique.

RESULTS AND DISCUSSION

3.1 XRD & AFM

X-ray diffraction (XRD) is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. For all the combinations of Cd Te Se samples (given in Table-3.1) XRD has been taken. XRD confirms (ascertains) the amorphous nature of the sample except $CdTe_{0.3}Se_{0.7}$ and $CdTe_{0.5}Se_{0.5}$. Amorphousity has increased with increasing Chalcogenide content. Typical X-ray diffraction pattern of the $CdTe_{0.3}Se_{0.7}$ & $CdTe_{0.5}Se_{0.5}$ films are given in fig-3.1(a) and fig-3.1(b) and $Cd_{0.7}Te_{0.2}Se_{0.1}$ & $Cd_{0.6}Te_{0.2}Se_{0.2}$ are given in fig3.1(c) and 3.1(d). Slight shift in 2θ values have been noticed.

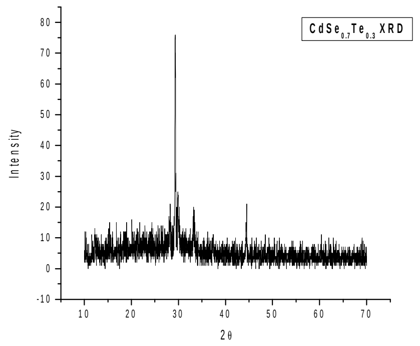


fig-3.1(a)XRD pattern of $CdTe_{0.3}Se_{0.7}$

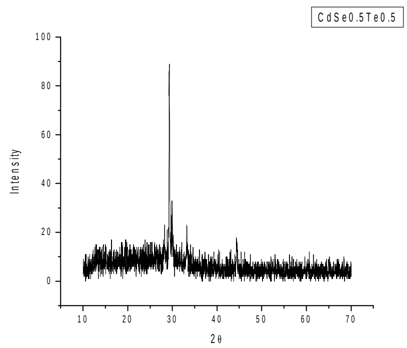


fig-3.1(b) XRD pattern of $CdTe_{0.5}Se_{0.5}$

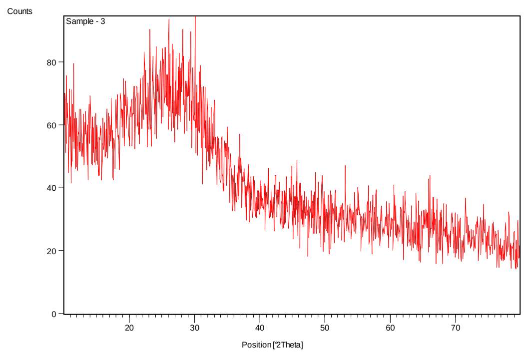


fig-3.1(c) XRD pattern of $Cd_{0.7}Te_{0.2}Se_{0.1}$

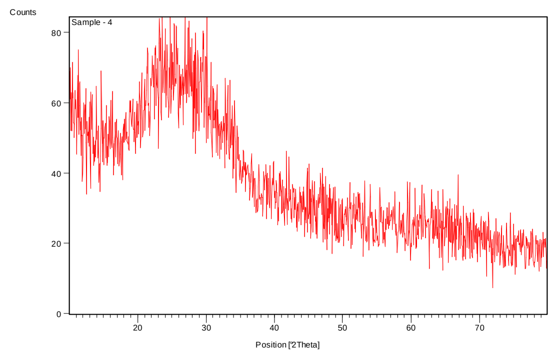


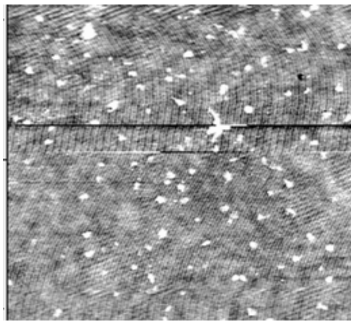
fig-3.1(d) XRD pattern of $Cd_{0.6}Te_{0.2}Se_{0.2}$

The sample, its composition and method of preparation are shown in Table 3.1

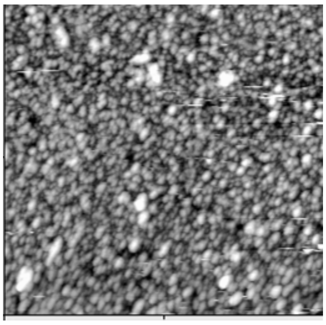
Table 3.1

Sample No	**Composition & Method of preparation**	**Sample No**	**Composition & Method of preparation**
1	$Cd_{0.8}Te_{0.1}Se_{0.1}$(T.E)	7	$Cd_{0.6}Te_{0.2}Se_{0.2}$(E.B)
2	$Cd_{0.7}Te_{0.1}Se_{0.2}$(T.E)	8	$Cd_{0.7}Te_{0.2}Se_{0.1}$(E.B)
3	$Cd_{0.7}Te_{0.2}Se_{0.1}$(T.E)	9	$Cd_{0.8}Te_{0.1}Se_{0.1}$(E.B)
4	$Cd_{0.6}Te_{0.2}Se_{0.2}$(T.E)	10	$CdTe_{0.3}Se_{0.7}$(T.E)
5	$Cd_{0.6}Te_{0.3}Se_{0.1}$(T.E)	11	$CdTe_{0.5}Se_{0.5}$(T.E)
6	$Cd_{0.5}Te_{0.4}Se_{0.1}$(T.E)		

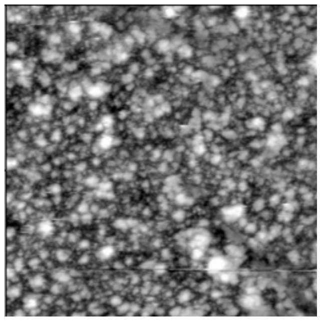
The surface topography of the films is investigated by Atomic Force Microscopy. The $CdSe_xTe_{1-x}$ films appear to be more or less homogeneous. Fig.3.1 (e, f and g) shows the atomic force micrographs of $CdSe_xTe_{1-x}$. From the figures one can observe that by increasing the selenium content in the films, the grains of the deposited films are getting larger and begin to agglomerate and coalesce forming thereby clusters [14].



AFM pattern3.1(e) $CdSe_{07}Te_{0.3}$



AFM pattern3.1(f) $CdSe_{0.8}Te_{0.2}$



AFM pattern3.1(g) $CdSe_{0.9}Te_{0.1}$

3.2 Stylus – Thickness measurement:

Thickness of the thin film is the most significant parameter, which plays important role in the properties of the thin film. Stylus method is a promising method to determine the thickness. The effect of applying a rounded stylus to thin metallic films on glass substrates has been investigated using diamond and steel styli with tip radii of approximately 25 μm and loadings of up to 230 g. In many applications, particularly in the case of the interference filters, an antireflection coating etc., the success of the fabrication depends only on the deposition of specific thickness of the film. The thickness of the films was estimated to be approximately 290 nm to 790 nm using the stylus surface profile-meter. Measurements have been done at two or three places. The values obtained confirm the uniformity of the film.

3.3 TGA, DTA and DSC Analysis:

While depositing the films, to ensure the desired composition x of the compound, TGA, DTA, and DSC studies have been carried out.

TGA analysis provides a quantitative measurement of any weight changes associated with thermally induced transitions.

In DTA, the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature. The DTA peaks for the samples are between 494^0C & 514^0C.

In DSC, the sample and reference materials are subjected to a precisely programmed temperature change. When a thermal transition occurs in the sample, thermal energy is added to either the sample or the reference in order to maintain both the sample and reference at the same temperature.

OPTICAL MEASUREMENTS:

Transmission spectra in the region 180 – 1100 nm has been collected using Micro pack DH-2000 equipment. The T% were used to evaluate the optical parameters such as α, k, n, and Eg. From Transmittance spectra, the absorption coefficient 'α' has been evaluated using the formula

$$\alpha = \frac{2.303}{t} \log\left[\frac{1}{T}\right] \text{ ------------ } (3.4.1)$$

Where 't' is the thickness of the film and 'T' is the transmittance percentage.

The value of absorption coefficient (α) provides valuable information about the inter band transition and hence the energy band structure of the materials.

Extinction coefficient 'K' has been evaluated using the formula

$$K = \frac{\lambda\alpha}{4\pi} \text{ --------- } (3.4.2)$$

where 'λ' is the wavelength and 'α' is the absorption coefficient.

Refractive index 'n' has been evaluated using the formula

$$n = \frac{\lambda\ \alpha}{4\pi k R} \text{ ---------- } (3.4.3)$$

where 'R' is the reflectance percentage.

Plots of **(a)** T% vs λ **(b)** $(\alpha h\gamma)^2$ vs Eg are shown in fig 3.4 (a) & (b).

Optical band gap energy has been evaluated from the Tauc's plot of $(\alpha h\gamma)^2$ vs hυ .

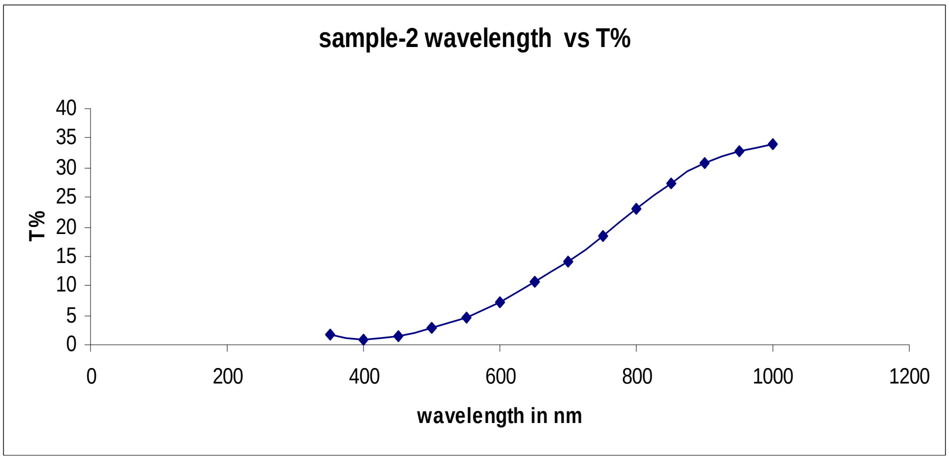


Fig 3.4(a)

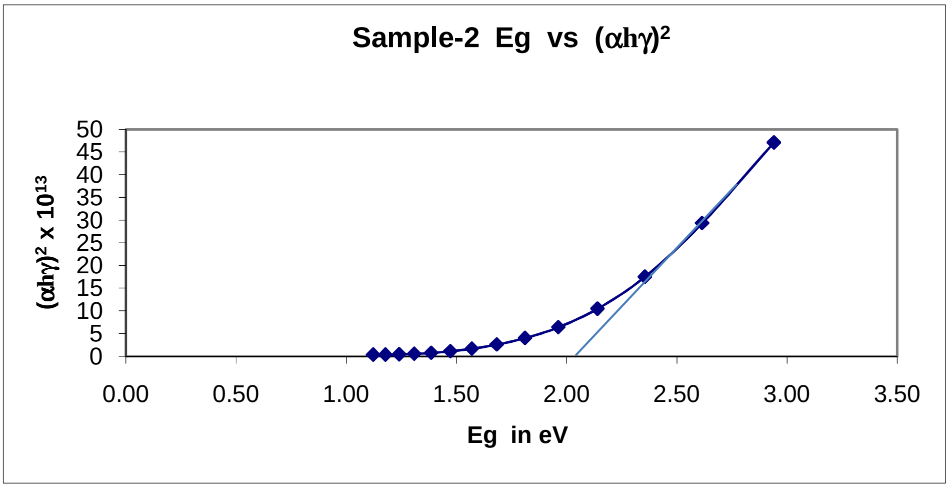


Fig 3.4 (b)

Optical band gap Vs the composition of Cd in CdTeSe film

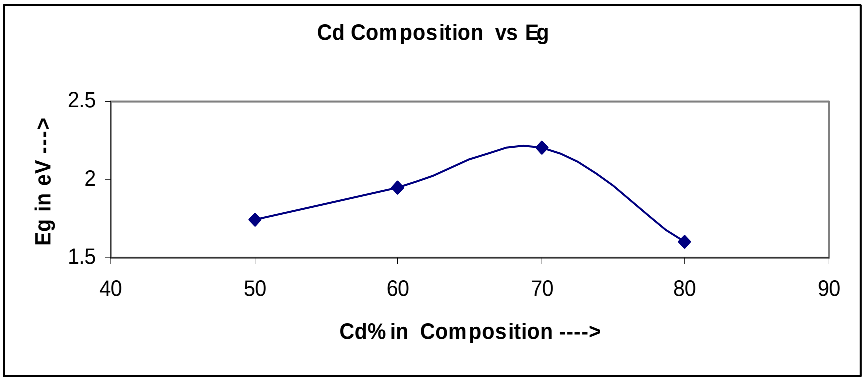


Fig3.4(c)

Variation of Eg with composition is shown in fig 3.4(c). Eg has increased with increase in Cd up to 70% and has answered for decrease in Eg for Cd > 70%. Similar change or turning point is observed even in electrical properties.

Annealing Studies:
A sample answering for complete reflection changes to comparable(R & T) for annealing at 200°C. Finally it changes to complete T% for 400°C annealing shown in fig 3.5(a).

When 'T' and ' R' are comparable, absorption coefficient has been evaluated using the formula [14] $\alpha = \frac{2.303}{t}\log\left[\frac{(1-R)^2}{T}\right]$

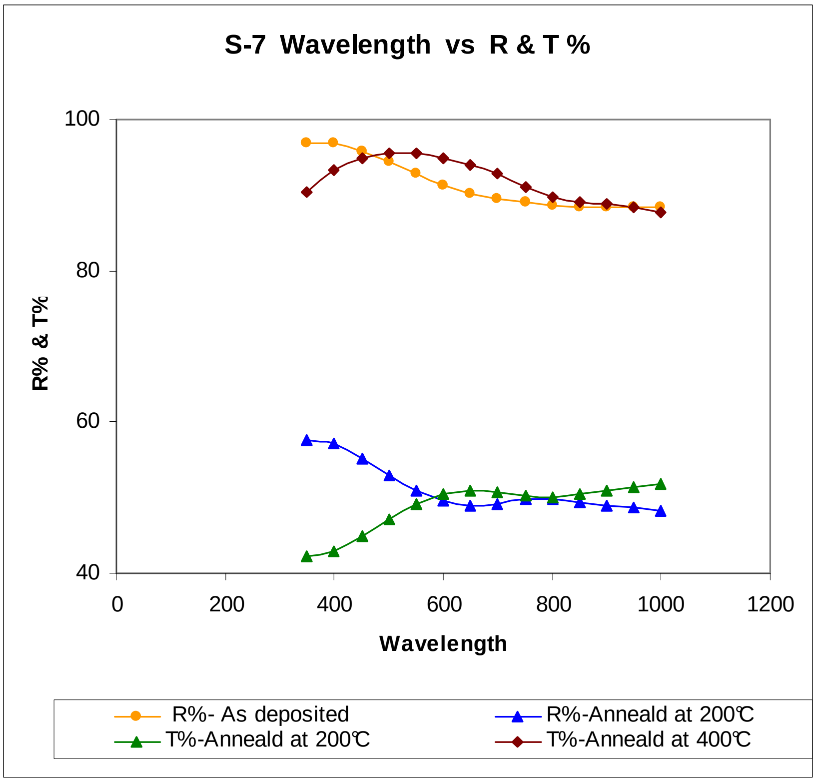


Fig 3.5(a)

Effects of annealing on the optical property of the films are really surprising. Annealing of the films has resulted in drastic change in R & T%. A good reflecting film has changed to comparable R & T and finally to a film with good T%.

Another effect of annealing is drastic change in Eg has also been noticed. Annealing the sample S-7, Eg has decreased from 1.95 (S-8:1.8) to 1.75(1.3) for 200°C, where as for 400°C annealing, Eg has increased to 2.65(2.6). Band gap variation with annealing is shown in Table 3.5(1). The plots of band gap vs temperature is shown in Fig 3.5(b) and (c) for S-7 and S-8 respectively.

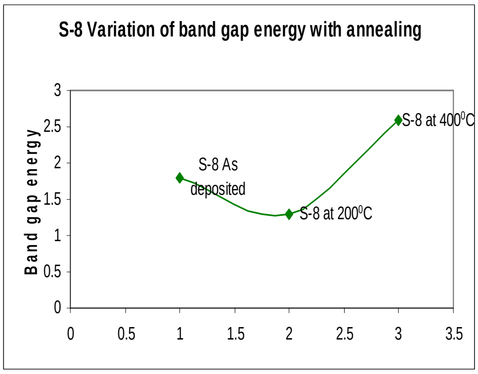


Fig 3.5(b)

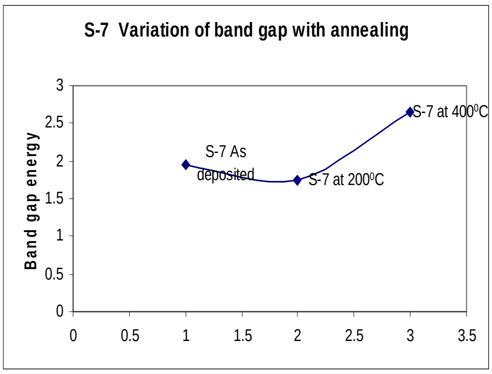


fig 3.5(c)

Table 3.5(1)

Optical Band gap in eV				
sample	**Composition**	**As Deposited**	**Annealed at 200^0C**	**Annealed at 400^0C**
S-7	$Cd_{0.6}Te_{0.2}Se_{0.2}$	1.95	1.75	2.65
S-8	$Cd_{0.7}Te_{0.2}Se_{0.1}$	1.8	1.3	2.6

Resistivity:

The electrical resistivity of $CdTe_{1-x}Se_x$ thin films is determined by four probe method. Fig 3.6 (a) and fig 3.6 (b) shows the variation of the resistivity of Cd $Te_{0.5}Se_{0.5}$ and Cd $Te_{0.4}Se_{0.6}$ films.

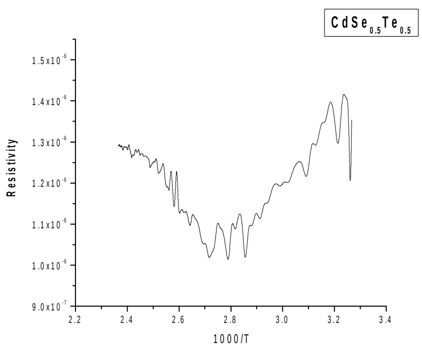


fig 3.6(a)

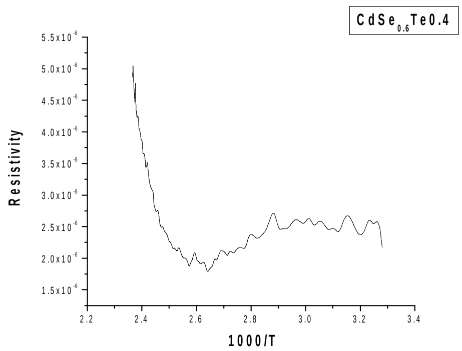


fig 3.6(b)

In case of Cd $Te_{0.5}Se_{0.5}$ film, the resistivity has decreased from 1.414 x 10^{-6} Ωm to 1.02 x 10^{-6} Ωm in the temperature range 309^0K to 368^0K, indicating a negative temperature coefficient. In the same film, the resistivity has increased from 1.02 x 10^{-6} Ωm to 1.2 x 10^{-6} Ωm in the temperature range 368^0K to 416^0K. This behavior reveals ohmic nature or positive temperature coefficient. The temperature (368^0K) at which resistivity is changing its nature reveals the inversion temperature. Whereas in case of Cd $Te_{0.4}Se_{0.6}$ film, the resistivity has decreased from 2.666 x 10^{-6} Ωm to 1.8 x 10^{-6} Ωm in the temperature range 319^0K to 378^0K indicating a negative temperature coefficient / semiconducting nature. For the same film the resistivity has increased from 1.88 x 10^{-6} Ωm to 5.06 x 10^{-6} Ωm in the temperature range 378^0K to 428^0K. This behavior reveals ohmic nature / positive temperature coefficient (+TCR). In this case, the inversion temperature is 378^0K.

The resistivity and the inversion temperature of the films are increasing with increase in the semiconducting selenium content. These materials exhibit both ohmic nature and semiconducting nature. This justifies the major role played by selenium content in the above investigated films.

CONCLUSION

1.Cd Chalcogenide films prepared by thermal evaporation as well as by electron beam evaporation
2.All the films were amorphous except Cd $Te_{0.5}Se_{0.5}$ and Cd $Te_{0.4}Se_{0.6}$.
3.Annealing has changed the reflectance to R+T & then T indicating anti reflective nature.
4.Eg has increased with increase in Cd composition up to 70% and later it has decreased.

5.Electrical measurement has revealed both semiconducting and conducting nature.
6.Inversion temperature or temperature at which behavioral change has taken place is found to be 368^0K for the Cd $Te_{0.5}Se_{0.5}$ film and 378^0K for the Cd $Te_{0.4}Se_{0.6}$ film.
7.The present investigation confirms the behavioral change of CdTeSe films both in electrical and optical property.
8.Further work is in progress to know the exact inversion temperature.

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