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Influence of Thermal Annealing on $Se_{75}Te_{22}Cd_3$ Thin Film for Optical Data Storage

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Abstract

The present work describes the influence of thermal annealing in $Se_{75}Te_{22}Cd_3$ thin film. The bulk alloy of $Se_{75}Te_{22}Cd_3$ was prepared by melt quenching method. The amorphous and glassy texture of the sample was verified by Differential Scanning Calorimetry (DSC) technique. Using thermal evaporation method, thin film of $Se_{75}Te_{22}Cd_3$ alloy was deposited on glass substrate. For the study of influence of thermal annealing, films were annealed for 2 hours at two different temperatures 338 K and 348 K which is in between glass transition (T_g) and crystallization temperature (T_c) of the prepared sample. The X-Ray diffraction measurement was done for both as-prepared and annealed films for phase transformation studies. It confirms the amorphous texture of as-prepared film and crystalline texture of annealed films. From optical measurement the nature of optical transition was found to be indirect in nature. The absorption coefficient (α) and extinction coefficient (k) increases with increasing the incident photon energy and annealing temperature, while the optical band gap decreases with annealing temperature. For electrical studies dc-conductivity measurement was done at different temperature in the range 298 K to 428 K. From the dc-conductivity we found that the dc-conductivity increases with temperature and annealing temperature. The activation energy (ΔE_c) decreases as annealing temperature increases. The outcome of these studies enables us that we can use this material in optical data storage.

Keywords: Chalcogenide, optical band gap, thin films, XRD, dc-conductivity.

1. Introduction

In recent era of technological developments, chalcogenide thin films have made great attention in the form of advanced material because of having special structural, thermal, optical and electrical properties. Chalcogenides can be used in solar cell, optoelectronic

devices, UV lasing diodes, optoelectronic devices, phase change memory, photoelectronic and sensor for infrared radiation [1-3]. The thermal processes are very important in inducing crystallization in chalcogenide films. Due to thermal annealing below crystallization temperature, the amorphous phase changes to crystalline phase. It has much importance for the determination of different parameters, mechanism of crystal growth, nucleation during crystallization and is useful for determining their possible applications in various optoelectronic devices.

Keeping in view of the importance of these studies several authors have been studied different parameters during the phase transformation in chalcogenide thin films. Al-Agel et al. [4] have been studied structural and optical changes in Ga-Se-Te thin film during thermal annealing. Xiao et al. [5] have been studied the fast crystallization of Mg- doped SbTe for phase change memory. Ali et al. [6] have been made a review on advances of thin film materials for solar cell applications. Selvan et al. [7] have studied the properties of Cl-doped ternery CeZnS thin films. Our aim is to study the effect of annealing on different properties of $Se_{75}Te_{22}Cd_3$ chalcogenide thin films and find the possibility of using this films for optical data storage.

2. Experimental Details

By using melt quenching technique bulk $Se_{75}Te_{22}Cd_3$ alloy was synthesized. The constituent element Se, Te and Cd with 5N purity were weighted with their atomic percentage and placed in quartz ampoule. The ampoule was sealed under high vacuum of the order of 10^{-5} Torr. The sealed ampoule was heated in the microprocessor based furnace at temperature 1273 K for 12 hours under constant shaking so that the mixture becomes fully homogenous. After that the ampoule was quenched in to the frizzed-cooled water. For the confirmation of the texture of the prepared alloy Differential Scanning Calorimeter (Model DSC plus, Rehometric Scientific Company, UK) was performed at the heating rate 10 K/min. Thin film of $Se_{75}Te_{22}Cd_3$ was prepared by thermal evaporation method on glass substrates at a pressure of 10^{-5} Torr. For the study of influence of thermal annealing thin films were annealed at two temperatures 338 and 348 K which lies in between glass transition and crystallization temperature of the sample for two hours. The structural studies were done by the Regaku X-ray diffract meter Ultima IV. A JASCO, UV/VIS/NIR computerized spectrophotometer was used for optical absorption study in the wavelength range 400-1100 nm. For the measurement of dc-conductivity, the thin films with pre deposited electrode were placed in a special type of sample holder and throughout the experiment the vacuum was of the order of 10^{-3} Torr in the

sample holder. By applying a constant voltage (1.5 V) on the sample the corresponding current was noted with the help of a Keithley electrometer at different temperature.

3. Results and Discussions

3.1 Structural studies

The glassy nature of prepared alloy was verified by non-isothermal Differential Scanning Calorimeter (DSC) measurements shown in Fig. 1. The endothermic and exothermic peaks are sharp and have single value, which verify the amorphous as well as glassy nature of the prepared sample. The XRD graph of as-prepared and annealed thin films of $Se_{75}Te_{22}Cd_3$ glass is shown in the Fig.2. In XRD measurement, the angle of scan was from 10^0 to 80^0 with scanning speed of 2^0/min. From XRD study it is clear that the as-prepared film has amorphous texture as having no structural sharp peaks where as the annealed films have crystalline nature due to several structural peaks.
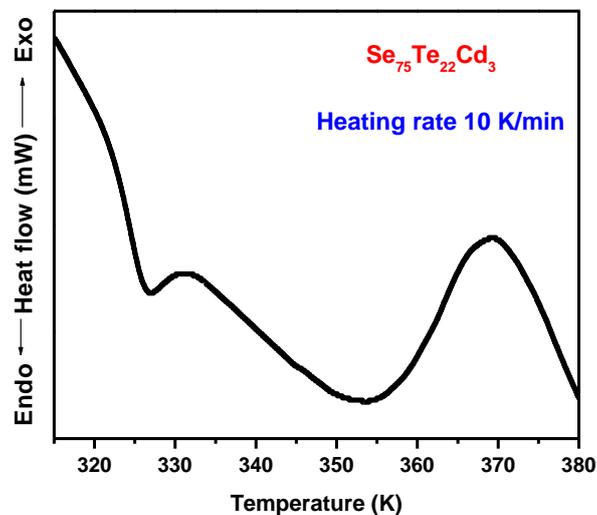

Fig.1 Non-isothermal DSC thermogram.

The crystallized peaks intensity increases as annealing temperature increases this shows that crystallization is higher at higher annealing temperature.
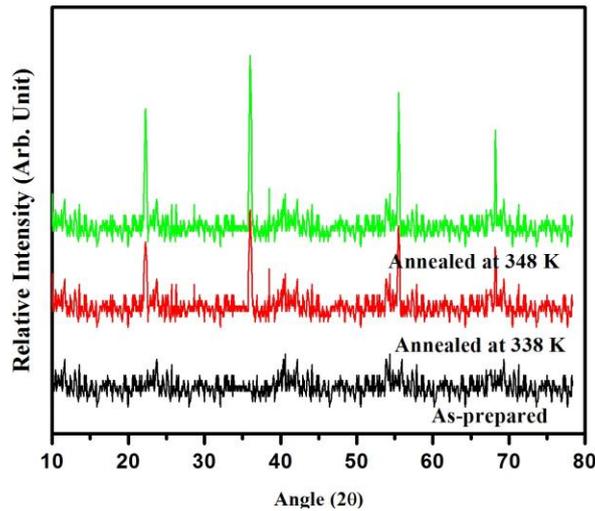
Fig.2 X-ray pattern of $Se_{75}Te_{22}Cd_3$ chalcogenide films.

3.2 Optical Studies

For optical characterization the optical absorbance was measured as a function of wavelength ranging from 400-1100 nm. From the absorption data the absorption coefficient (α) can be calculated by using the relation [8-9]

$$\alpha = \text{Absorbance / film thickness} \qquad (1)$$

Fig.3 shows variation in absorption coefficient (α) with photon energy (hv). It is clear from this graph that for both as-prepared and annealed films the absorption coefficient (α) increases by increasing photon energy and annealing temperature. The value of α is in the range of $10^4 cm^{-1}$ which agrees with others workers [10-11].The measured value of absorption coefficient at wavelength 750 nm is given in the Table 1.
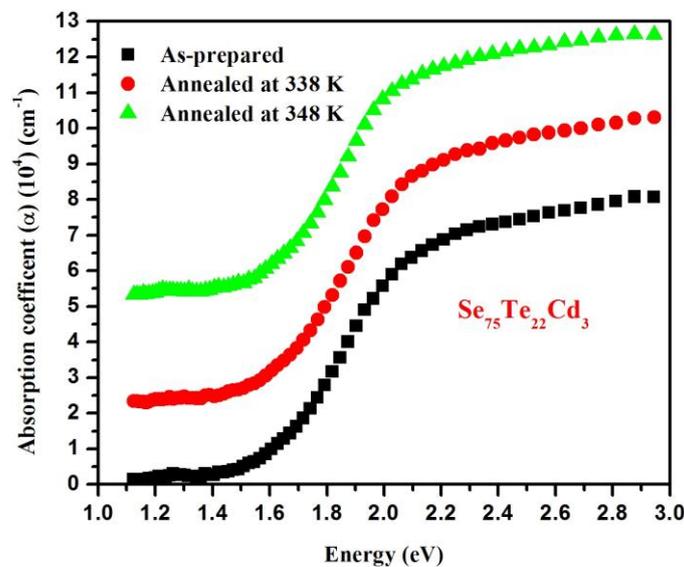

Fig.3 Absorption coefficient (α) with photon energy.

An exponential law is followed by the absorption edge nearly in all amorphous and crystalline thin films which is given as [8]

$$(\alpha h\nu)^{1/n} = B(h\nu - E_g) \qquad (2)$$

Here ν is the incident beam frequency, E_g is optical band gap, B is a constant and n is an exponent. The value of n may be 1/2, 3/2, 2 and 3. These values are defined as n=1/2 denote allowed direct transition, n=3/2 is for forbidden direct transition, n=2 will give allowed indirect transition and n=3 denoted the forbidden indirect transition [12].
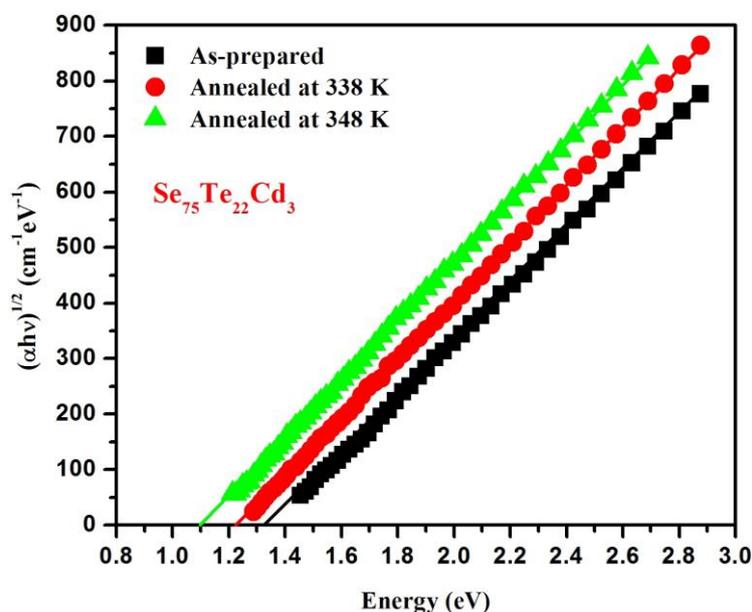

Fig.4 $(\alpha h\nu)^{1/2}$ with photon energy (hν).

For $Se_{75}Te_{22}Cd_3$ glass the value of n is found to be 2 this indicates indirect transition. Fig. 4 shows the variation of $(\alpha h\nu)^{1/2}$ with photon energy (hν). On extrapolating linear portions in the graph to intersect with energy axis we have calculated the optical band gap. The calculated values of optical band gap are tabulated in the Table 1. From this table it is clear that optical band gap decreases as annealing temperature increases. This can be explained as during the deposition of chalcogenide films, dangling bond with some saturated bonds are produced. They cause the formation of some defects in the films. Such defects produce localized states in chalcogenide films. During thermal annealing above glass transition temperature of the chalcogenide films, some of the weaker bonds break due to enough vibrational energy and introducing some translational degree of freedom to the system. Consequently, crystallization via nucleation and growth becomes possible and depends on the annealing temperature. The thermal annealing causes the crystallization in the films and thermally transformed crystalline phase increases with annealing temperature. Thus the major change in optical band gap by doing thermal annealing could be attributed to the thermally induced crystalline phase. The extinction coefficient (k) of as-prepared and annealed films can be determine by using the relation

$$k= (\alpha\lambda)/ (4\pi) \qquad\qquad\qquad (3)$$

Where λ is the wavelength of incident radiation. The variation of extinction coefficient (k) with photon energy is shown in Fig.5.
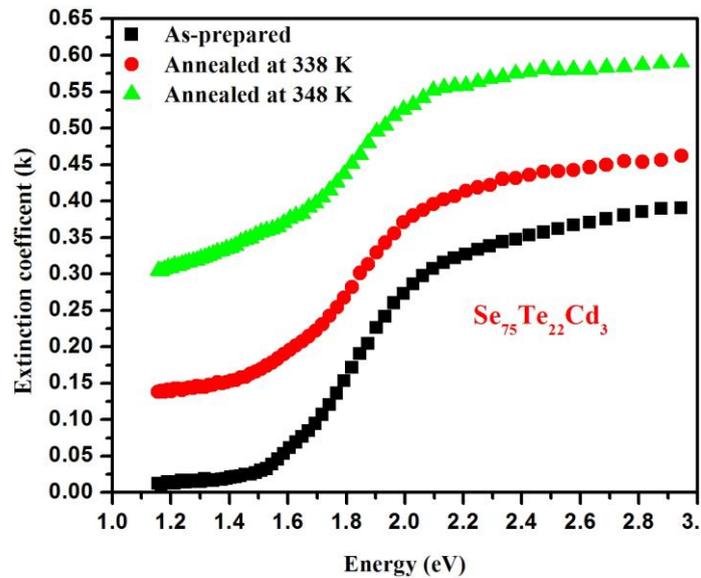

Fig. 5 Extinction coefficient (k) with photon energy.

It is clear from the graph that the extinction coefficient (k) increases as photon energy and annealing temperature increases. The calculated values of excitation coefficient (k) are given in the Table 1. It is clear from the table that the extinction coefficient (k) increases with the increase in annealing temperature. The chalcogenide film always contains unsaturated bonds or defect which is the main reason for the existence of localized states. Due to annealing below the crystallization temperature saturated bonds produces which reduces unsaturated bonds or defect with localized states in bond structure which is responsible for the increase in the value of k as annealing temperature increases.

3.3 Electrical Studies

The dc conductivity measurements of $Se_{75}Te_{22}Cd_3$ chalcogenide films were performed in the step of 5K in the temperature range from 298 K to 428K.

The dc-conductivity is given as

$$\sigma_{dc} = \sigma_0 \exp(-\Delta E_c/KT) \qquad\qquad\qquad (4)$$

Where σ_0 is the pre-exponential factor, ΔE_c represents activation energy and K is Boltzmann constant.

Equation (4) can also be written as

$$\ln \sigma_{dc} = \ln (-\Delta E_c/KT) \qquad\qquad\qquad (5)$$

or, $\qquad\qquad \ln \sigma_{dc} = -(\Delta E_c/1000K)(1000/T) + \ln \sigma_0 \qquad\qquad (6)$

The variation of ln σ_{dc} with 1000/K for $Se_{75}Te_{22}Cd_3$ is shown in Fig.6. From the figure it is clear that dc conductivity increases for as-prepared and annealed films with the temperature which confirms the semiconducting nature of the prepared film. The value of the activation energy (ΔE_c) can be calculated from the slope of the graph by using the relation

$$\Delta E_c = 1000 \text{ K x Slope of straight line} \qquad (7)$$

The calculated value of ΔE_c is given in the Table 1. It is clear from the table that the activation energy reduces with increasing annealing temperature. The calculated value of the activation energy (ΔE_c) suggests that conduction occurs because of hoping of charge carriers in tails states and activation energy decreases due to Fermi level shifting.
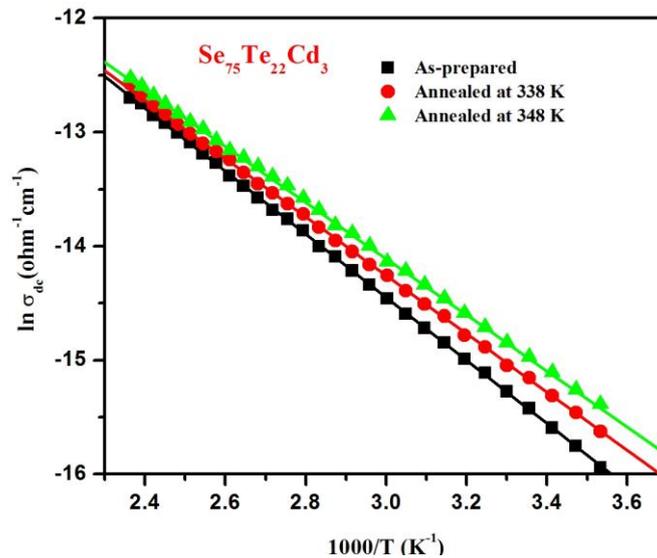

Fig.6 ln σ_{dc} with 1000/K for $Se_{75}Te_{22}Cd_3$ films

4. Conclusions

Our aim was concentrated on to study the influence of thermal annealing in $Se_{75}Te_{22}Cd_3$ chalcogenide thin film. The DSC measurement indicates that the nature of the prepared alloy is amorphous as well as glassy. By thermal annealing the thin film undergoes thermo-structural phase transformation from amorphous to crystalline phase. The transformed phase was verified by the XRD measurements. The optical absorption measurement shows that the optical absorption is due to indirect transition. The absorption and extinction coefficients increases with photon energy and annealing temperature while optical band gap decreases as annealing temperature increases. The decrease in optical band gap is due to the reduction of unsaturated bond after annealing and due to thermally induced crystalline phase. From dc-conductivity measurements it was observed that the dc-conductivity increases with temperature which shows the semiconducting nature of the prepared alloy. The activation energy reduces with the increase in annealing temperature. The calculated value of the

activation energy (ΔE_c) suggests that hoping of charge carriers is responsible conduction in tails states and the activation energy decreases because fermi level changes.

5. Acknowledgement

6. References

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Table-1

Optical and electrical parameters in $Se_{75}Te_{22}Cd_3$ chalcogenide thin films

Optical parameters			
$Se_{75}Te_{22}Cd_3$	Optical band gap (E_g) (eV)	(α) $(10^4$ cm$^{-1})$ at λ= 750 nm	(k) (10^{-3}) at λ= 750 nm
As-prepared	1.32	1.27	7.63
Annealed at 338 K	1.21	3.47	20.75
Annealed at 348 K	1.10	6.47	38.23
Electrical parameters			
$Se_{75}Te_{22}Cd_3$	σ_{dc} $(\Omega^{-1}cm^{-1})$ (10^{-9})	σ_0 $(\Omega^{-1}cm^{-1})$ (10^{-6})	Activation energy ΔE_c (eV)
As-prepared	1.52	4.02	0.24
Annealed at 338 K	1.79	2.48	0.22
Annealed at 348 K	1.93	1.89	0.21