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Structural and optical properties of In doped Se–Te phase-change thin films: A material for optical data storage

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ABSTRACT

$Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, & 9) bulk glasses were obtained by melt quench technique. Thin films of thickness 400 nm were prepared by thermal evaporation technique at a base pressure of 10^{-6} Torr onto well cleaned glass substrate. a-$Se_{75-x}Te_{25}In_x$ thin films were annealed at different temperatures for 2 h. As prepared and annealed films were characterized by X-ray diffraction and UV–Vis spectroscopy. The X-ray diffraction results show that the as-prepared films are of amorphous nature while it shows some polycrystalline structure in amorphous phases after annealing. The optical absorption spectra of these films were measured in the wavelength range 400–1100 nm in order to derive the extinction and absorption coefficient of these films. It was found that the mechanism of optical absorption follows the rule of allowed non-direct transition. The optical band gap of as prepared and annealed films as a function of photon energy has been studied. The optical band gap is found to decrease with increase in annealing temperature in the present glassy system. It happens due to crystallization of amorphous films. The decrease in optical band gap due to annealing is an interesting behavior for a material to be used in optical storage. The optical band gap has been observed to decrease with the increase of In content in Se–Te glassy system.

1. Introduction

Chalcogenide glasses have received great attention in the last decades because of their important applications in optical devices. The probable reasons are their unique properties and the advantages of producing them by means of thin film processes, which do not limit their size and make them adoptable to integration with other solid state technologies. Thin films of chalcogenide glasses are having relatively high atomic mass and weak bond strength resulting in low characteristic phonon energies. Thus, these are highly transparent in mid to far infra-red region. They are used in IR window and optical devices [1].

Amorphous selenium binary alloys with tellurium have been widely studied due to their great storage capacity, fast to access information and electro photographic applications such as photoreceptors in photocopying and laser printing [2,3].

Annealing crystallizes the amorphous layer which changes the optical parameters of chalcogenide thin film. The two states of amorphous and crystalline phases are considered the two bit binary storage data and could be detected optically. Se–Te based chalcogenide alloys are commercially used in optical memory devices such as re-writable Digital Versatile Discs (DVD) and are supposed to be leading candidates for the next generation electronic non volatile memories. The information in these materials is stored as property contrast (reflectivity in optical memory and resistance in electronic memory) between the crystalline and amorphous phase [4].

Se-based chalcogenide glasses have high transparency in the broad middle and far IR regions as well as strong non linear properties [5]. Also selenium based glasses have advantage of low thermal conductivity, low melting point and exceptional stability, allowing for the formation of glasses while doping with various other elements [6,7]. Tellurium on the other hand provides properties which are required now a days in cutting edge technologies based on chalcogenide glasses [8]. These properties mainly include transmittance in the far infra-red region which is used in optical fiber and IR optics [9,10] and ultrafast crystallization which is used in phase change optical data storage devices [11–14]. Though Se-based chalcogenide glasses have tremendous applications in variety of domain, however, thermal instability leading to crystallization is found to be one of the draw backs of these alloys. Many researchers have made attempt to improve the stability of Se–Te by addition of a third element such as (Ga, Ge, Bi, Zn, Sb, etc.).

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Alloying gives higher sensitivity, higher crystallization temperature and smaller aging effects [15–18]. We have chosen In as an additive element in amorphous Se–Te alloy. The addition of third element (In) may expands the glass forming area and also can create compositional and configurationally disorder system with respect to binary alloys which will be useful in understanding the structural and optical properties of Se–Te–In system. Moreover it is observed that the addition of the third element helps in getting cross-linked structure and crystallization temperature of the binary alloy [16,19,20].

The lattice perfection and energy band gap of material play a major role in the preparation of device for a particular wavelength, which can be modified by dopants. The effect of In incorporation on the optical properties of Se–Te matrix has already been studied [21].

Keeping in view the importance of these materials specially in optical data storage a lot of research work is concentrated on Se-based chalcogenide thin films. Various efforts have been made to develop Se-based rewritable optical memories. Since mechanism of recording memories is an optically, thermally or electronically induced reversible phase transition between amorphous to crystalline state and vice versa in thin films [22,23]. However, thermal processes are known to be important in inducing crystallization in semiconducting chalcogenide glasses [24,25]. Though several researchers have studied the effect of thermal annealing on structural and optical properties of chalcogenide glasses [26–31], however very little attention has been paid to study In doped Se–Te chalcogenide glasses.

The aim of the present work is to investigate the structural and optical properties of thermally annealed Se–Te–In thin films. Effective optical band gap during thermal annealing of Se–Te–In films has been determined.

2. Experimental details

Glassy alloys of $Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, & 9) were prepared by using melt quench technique. The exact proportions of high purity (99.999%) Se, Te and In elements, in accordance with their atomic percentages, were weighed using an electronic balance (LIBROR, AEG-120) with the least count of 10^{-4} gm. The material was then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampule (length ~5 cm and internal diameter ~8 mm). The ampule containing material was heated to 800 °C and was held at that temperature for 12 h. The temperature of the furnace was raised slowly at a rate of 3–4 °C/min. During heating, the ampule was constantly rocked, by rotating a ceramic rod to which the ampule was tucked away in the furnace. This was done to obtain homogeneous glassy alloy. After rocking for about 12 h, the obtained melt was rapidly quenched in ice-cooled water. The quenched sample was then taken out by breaking the quartz ampule. Thin films of glassy alloys of a-$Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, & 9) of thickness 400 nm were prepared by vacuum evaporation technique, in which the substrate was kept at room temperature at a base pressure of 10^{-6} Torr using a molybdenum boat. The films were kept inside the deposition chamber for 24 h to achieve the metastable equilibrium as suggested by Abkowitz [33]. The thickness of the film was measured using a single crystal thickness monitor. The XRD patterns of the as prepared and annealed films were recorded with the help of X-ray diffractometer (XPERT-PRO) using Cu Kα radiation (λ = 1.54 Å)with a scanning angle (2θ) from 20° to 90°. A scan speed of 2° per minute and a chart speed of 1 cm/min were maintained. The tube was operated at 45 kV and 35 mA. To determine the crystallization temperatures differential scanning calorimetric (DSC) measurements were carried out on powdered samples of $Se_{75-x}Te_{25}In_x$ under pure N_2 atmosphere using Mettler Toledo Star instrument (Model No. DSC-200PC). Thin films of glassy alloys of $Se_{75-x}Te_{25}In_x$ were annealed for 2 h in a specially designed sample holder under a vacuum of 10^{-2} Pa at three different temperatures (353 K, 373 K and 393 K) which are below the crystallization temperature of the samples. The normal incidence absorption spectra of $Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, & 9) thin films have been taken by a double beam UV–VIS–NIR computer controlled spectrophotometer (ECIL-Hyderabad, India, Model No. 5704 SS) in the wave length range 400–1100 nm at room temperature conditions.

3. Results and discussion

3.1. Structure

A typical DSC thermogram of a-$Se_{69}Te_{25}In_6$ at a particular heating rate of 10 K min^{-1} is shown in Fig. 1. Similar thermograms were obtained for other heating rates at 5, 15, 20 K min^{-1} also (results not shown here). It is evident from Fig. 1 that each thermogram shows two distinct peaks corresponding to glass transition (T_g) and peak crystallization temperature (T_c). Glass transition, onset crystallization (T_x) and peak crystallization temperatures for a-$Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, 9) have been determined and listed in Table 1.

The glassy nature of the alloys was ascertained by X-ray diffraction (XRD) technique. The XRD patterns of $Se_{69}Te_{25}In_6$ alloy in as prepared and annealed form is shown in Fig. 2. Absence of any sharp structural peak in XRD pattern of as prepared $Se_{69}Te_{25}In_6$ alloy confirms the glassy nature of the sample. Similar XRD patterns were obtained for the other glassy alloys (results not shown here).

X-ray diffraction data reveals that as prepared sample is amorphous in nature. The X-ray peaks continue to grow with increasing value of annealing temperature. It is evident that there is formation of polycrystalline phase in amorphous phase after annealing. The mechanism of crystallization can, however, not be ascertained from the present measurements.

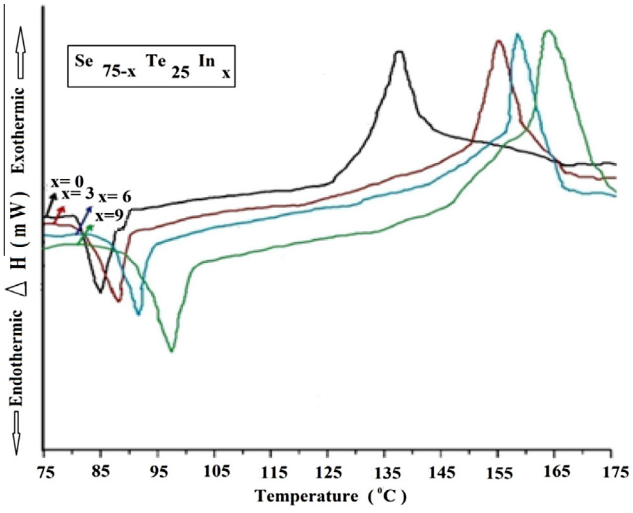

Fig. 1. DSC thermograms for glassy $Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, 9) alloys at heating rate of 10 K/min.

Table 1
Glass transition (T_g), onset crystallization (T_x) and crystallization temperatures (T_c) for glassy $Se_{75-x}Te_{25}In_x$ (x = 0, 3, 6, 9) alloys.

Sr. No.	Samples	T_g (°C)	T_x (°C)	T_c (°C)	ΔT (°C) = ($T_x - T_g$)
1	$Se_{75}Te_{25}$	85	127	137	42
2	$Se_{72}Te_{25}In_3$	89	150	155	61
3	$Se_{69}Te_{25}In_6$	92	155	158	63
4	$Se_{66}Te_{25}In_9$	98	162	166	64