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Photo-induced Amorphous to Crystalline Phase Transformation in $Se_{80}In_5Te_9Sb_3$ Chalcogenide Thin Films

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Abstract

Chalcogenide glasses are interesting materials due to their infrared transmitting properties and photo-induced effects exhibited by them. Bulk samples of $Se_{80}In_5Te_9Sb_3$ alloy was prepared by melt quenching technique. The glassy nature of was verified by non-isothermal DSC measurements. Thin films of $Se_{80}In_5Te_9Sb_3$ alloy with thickness 400 nm were deposited on glass substrate by thermal evaporation technique. The photo-induced crystallization in $Se_{80}In_5Te_9Sb_3$ thin films was done by exposing to light (using 2000 W tungsten lamp) at various illumination times. In the illumination process the ambient temperature was fixed at 375 K which is carefully chosen from DSC thermograms. X-ray diffraction, Field Emission Scanning Electron Microscope (FESEM) and optical measurements were used to characterize as-prepared and photo-induced thin films. The photo-induced crystallization is found to be associated with the change in structure. The detailed study of optical absorption data indicates that the optical absorption is indirect. The observed optical band gap becomes lesser while the absorption and the extinction coefficients tend to increase with increasing illumination time. The lowering of optical band gap is described on the process of photoinduced crystallization.

Keywords: Chalcogenide Glasses, Thin Films, X-ray diffraction, Photo-induced Crystallization, Optical Band Gap

1. Introduction

The considerable interest of research workers in chalcogenide glasses is due to the possibility of their various applications in different fields of electronics, based on the fact that they combine the characteristic features of the disordered systems. They are attracting extensive attention due to their practical and potential uses in the civil, medical and military areas, especially in the fields of infrared optics, opto-electronics, photonics, semiconductor and so on. These glasses have truthfully appeared to be of numerous purpose materials which can be employed in the fabrication of several important technological devices such as infra-red detector, electronic switches, optical recording media, etc. A significant amount of efforts have been made for the development of new erasable optical storage media based on chalcogenide glasses. . The use of thin chalcogenide glass films is also expanding in technology because of their ability of transition from disordered to more organized states. These thin films are being employed in high-resolution display devices and high-density data storage systems. Thin films of these glasses are recently used in photocatalytic sensitization [1], photosensors [2–3], memory switching [4], PCM [5], photoelectronic devices [6-7], and fiber communication devices[8–9]. The rapid growth in information technology has created a demand for advanced and efficient materials for storage devices, which investigate their optical and phase-change properties. Chalcogenide materials are particularly promising due to their phase transition in a controlled way between amorphous and crystalline states, characteristic that is critical for optical memory purposes. A systematic investigation of photo-induced phenomena in chalcogenide thin films has been developed. The work on crystallization phenomena by light illumination in chalcogenide thin films has been done by various researchers [10-17]. The chalcogenide thin films [18-21] with appreciable proportions of selenium exhibit a

variety of changes on illumination. These changes may be reversible or irreversible. The understanding of photon interaction in chalcogenide films is a crucial point to understand the fundamental working and its application in technology.

This research work presents the photo-induced crystallization on the structural and optical properties of $Se_{80}In_5Te_9Sb_3$ thin films. Selenium (Se) is used as a main constituent in this composition due to its exclusive and unique characteristics. Selenium has the property to convert light to electrical energy and variable conductance with illuminated light intensity. These properties are used to design photocells, solar cells and photocopiers. But unfortunately, Se alone is less sensitive, shorter lifetime, thermally unstable and mediocre thermal, electrical and optical properties. Many renowned active researchers have been customized metallic supplements to Selenium and explored their various thermal parameters as well as activation energies for discovering about chalcogenide composite systems having a sufficient temperature window for many applications such as fiber drawing and as such multi-component systems which show low crystallization propensity. It is well known that assured additives are used to enhance the properties of Se especially the use of Se-In, Se-Te, Se-Ge etc. binary alloys have enhanced properties like more hardness, conductance, sensitivity and small ageing effect as compared to pure Se. We have alloyed Se with Indium (In), Tellurium (Te) and Bismuth (Sb). Indium (In) doped chalcogenide glasses have been fascinated much attention for utilizing in solar cell. Tellurium (Te) has versatility as metalloid, high corrosion and heat resistance. It enhances the solar cell efficiency for electricity generation. The doping of Sb makes the synthesized glass rigid and expands the applications domain of synthesized glasses also.

2. Experimental

Melt-quenching technique was used to prepare bulk $Se_{80}In_5Te_9Sb_3$ chalcogenide glass. An extremely pure (99.999% purity) Se, In, Te and Sb in their suitable quantity/percentage were weighted and sealed in quartz ampoule under high vacuum ($\approx 10^{-6}$ Torr) using a molecular turbo pump. This ampoule was placed in a microprocessor-controlled electric furnace, which operated in four steps. In the first step, the temperature was maintained at 673 K for 2 hours; in the second step, it was raised to 873 K for 2 hours; in the third step, it was set to 973 K for 3 hours; and finally, in the fourth step, the temperature was increased to 1023 K for 3 hours. The ampoule was continuously shacked for proper homogeneousness of the melted elements. After that, the ampoule was quenched in ice-cooled water. The samples were collected by breaking the ampoules and grinded in fine powder form. The non-isothermal DSC measurements using Model DSC plus, Rheometric Scientific Company, UK were performed at rates of heating 5, 10, 15, 20 and 25 K min^{-1} to confirm glassy as well as amorphous nature of the synthesized sample. Thin films of $Se_{80}In_5Te_9Sb_3$ glass with thickness 300 nm were prepared on ultrasonically cleaned glass substrates using thermal coating unit (vacuum of 10^{-6} Torr). Thin films of $Se_{80}In_5Te_9Sb_3$ glass were exposed by 2000 W tungsten lamp for various illumination times 240 and 360 min. In this process the film temperature was fixed at 375 K chosen from DSC thermo-grams. X-ray diffraction (XRD), UV/VIS/NIR spectrophotometer and Field Emission Scanning Electron Microscope (FESEM) were used to study the photoinduced crystallization in $Se_{80}In_5Te_9Sb_3$ thin films.

3. Results and discussion

3.1: Structural Studies

The non-isothermal DSC thermograms of $Se_{80}In_5Te_9Sb_3$ glass was scanned at constant heating rate 5, 10, 15, 20 and 25 K $min^{-1}$is shown in Fig. 1. From these figures the glass transition temperature (T_g) and crystallization temperature (T_c) were observed. The selection of temperature 375 K during the illumination is between T_g and T_c.

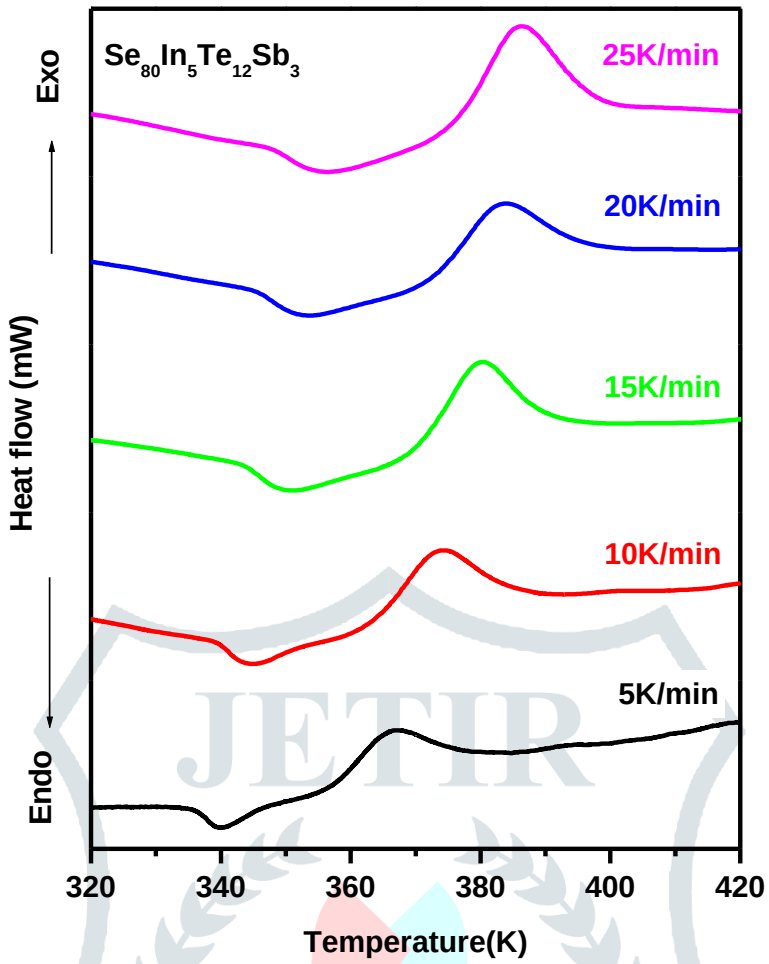

Figure 1: DSC trace for $Se_{80}In_5Te_9Sb_3$ chalcogenide glass at different heating rates

The EDS spectrum was conducted to verify the presence of the desired elements in quaternary $Se_{80}In_5Te_9Sb_3$ chalcogenide glasses. Fig. 2 displays the EDS spectrum and elemental mapping for $Se_{80}In_5Te_{12}Sb_3$ glass, confirming the target elements within the samples. The spectra results confirm the accurate stoichiometry, and EDS mapping highlights the presence of Se, In, Te and Sb in the synthesized chalcogenide glasses with a good distribution of these elements across the samples.

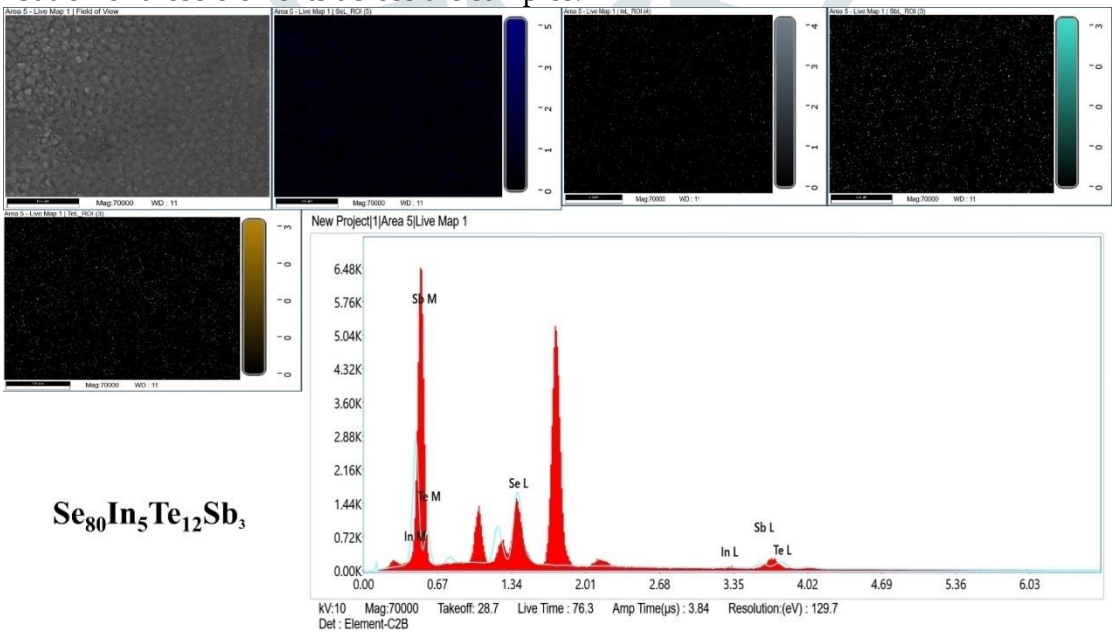

Fig. 2: EDS spectrum and elemental mapping $Se_{80}In_5Te_{12}Sb_3$ chalcogenide glass.

The structural changes during photo-crystallization of as-prepared and illuminated thin films of $Se_{80}In_5Te_9Sb_3$ glass was studied by HRXRD at room temperature. The angle of scan was from 10^0 to 70^0

with Cu target as X-ray source having wavelength l891.54178 Å. The speed of scanning was 2^0/min with a chart speed 1 cm/min. Fig. 3 shows the HRXRD pattern of as-prepared and illuminated thin films.

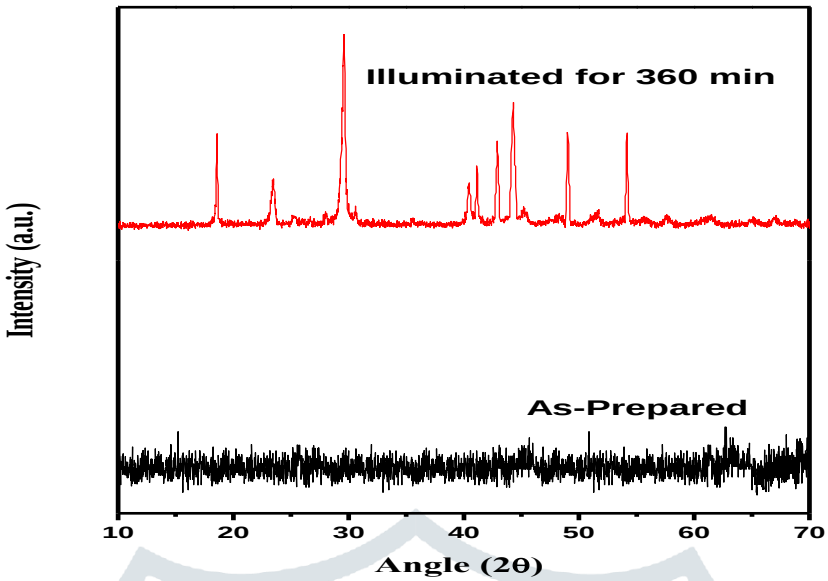

Figure 3: HRXRD pattern of $Se_{80}In_5Te_9Sb_3$ chalcogenide thin films: As-Prepared and illuminated for 360 min.

The nonappearance of any sharp peak in as-prepared thin film indicates the amorphous structure, and the presence of several intense peaks in illuminated film indicates the photo-crystallization behavior of the film.

The surface morphology of as-prepared and illuminated thin films of $Se_{80}In_5Te_9Sb_3$ glass was examined by FESEM.

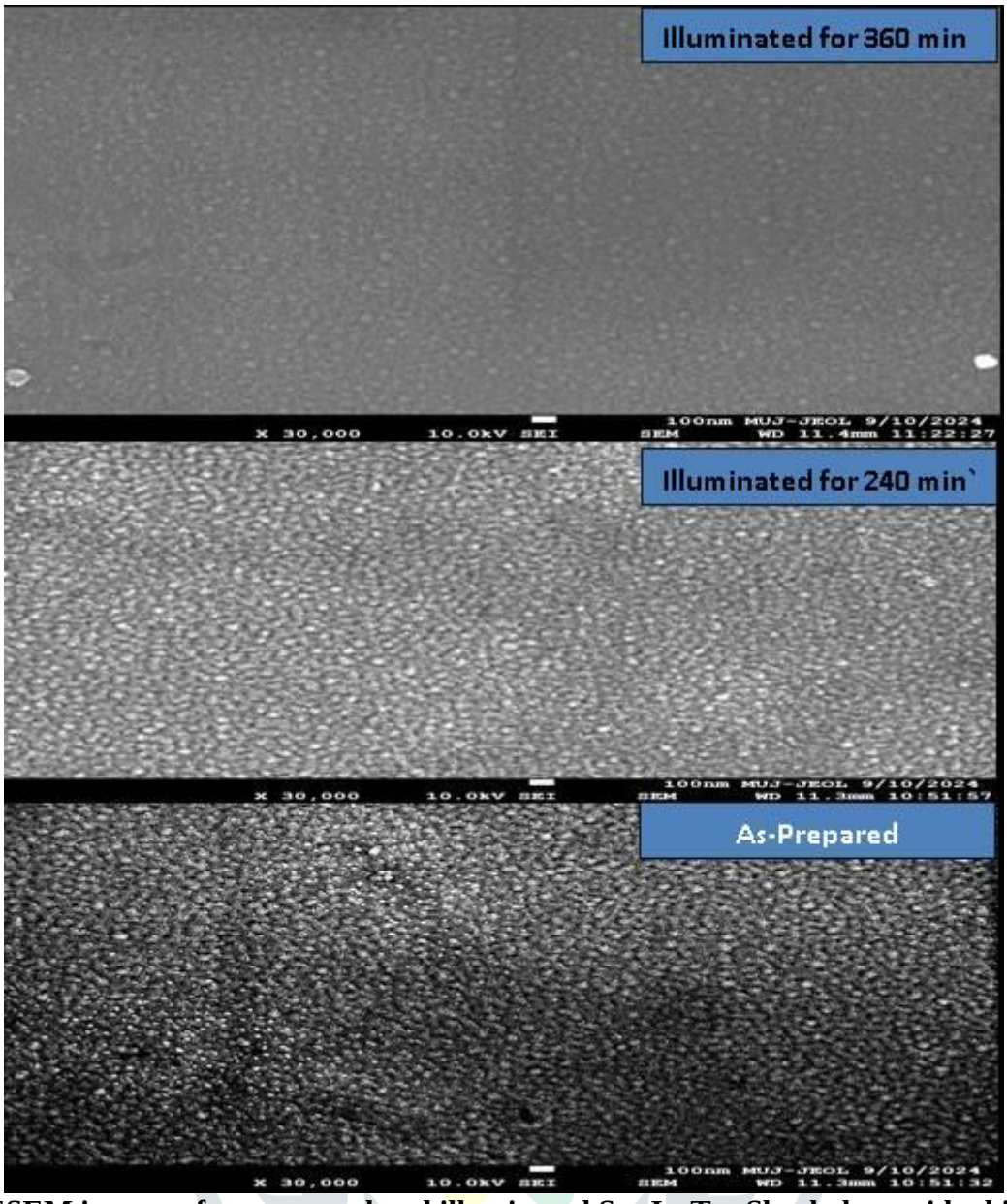

Fig. 4: FESEM images of as-prepared and illuminated $Se_{80}In_5Te_{12}Sb_3$ chalcogenide thin films at different illumination times.

Fig. 4 represents the surface morphology of the as-prepared and photo-crystallized thin film at different exposure times. It is observed from FESEM that the surface morphology of the film changes with illumination that also confirms the photo-crystallization of the as-prepared thin film.

3.2: Optical Studies

The optical studies in chalcogenide glasses have found application in switching elements and in integrated circuits. The most significant optical parameters are absorption coefficient and optical band gap (E_g) and therefore the precise study of these constants is remarkably significant. The optical absorption of as-prepared and illuminated thin films of $Se_{80}In_5Te_9Sb_3$ glass has been measured from 500 nm to 900 nm wavelength as a function of photon energy$(h\nu)$. The optical absorption coefficient (α) is evaluated by using the following relation [22-25],

$$\alpha = Optical\ Density\ (Absorbance)/\ thickness\ of\ the\ film. \quad (1)$$

It is observed that the value of α becomes larger with advanced value of photon energy. The calculated values of α for as-prepared and illuminated thin films with various illumination times for $Se_{80}In_5Te_9Sb_3$ films are shown in Table 1. It is also found that value of α increases with increasing illumination time.

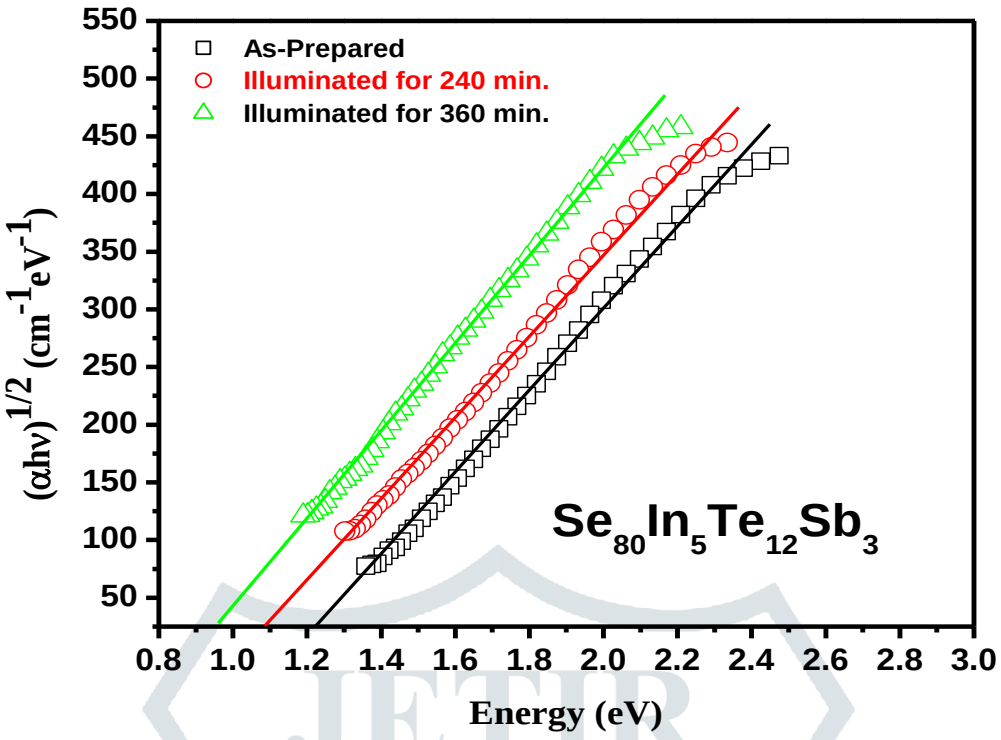

Fig. 5: $(\alpha h\nu)^{1/2}$ against photon energy ($h\nu$) of $Se_{80}In_5Te_9Sb_3$ chalcogenide thin films: as-prepared and illuminated film for 240 and 360 min.

The absorption edges in amorphous semiconductors correlate with the threshold for charge transition among highest nearly filled and lowest nearly empty band. From the inter band absorption theory, the optical band gap of a material in the form of film is determined from the relation [26-30]

$$(\alpha h\nu)^{1/m} = B\left(h\nu - E_g\right) \quad (3)$$

Where B is a constant and m is an exponent. The $Se_{80}In_5Te_9Sb_3$ thin film follows the role of non-direct transition. For such type of transition the value of m is taken as 2. Fig. 5 represents the variation of $(\alpha h\nu)^{1/2}$ with $h\nu$ for virgin and illuminated films of $Se_{80}In_5Te_9Sb_3$ glass. The observed values of E_g are shown in Table 1.

Table 1

Optical parameters in thermally evaporated $Se_{80}In_5Te_9Sb_3$ chalcogenide thin films: As-prepared and illuminated films.

Optical parameters	As-Prepared	Illuminated film for 240 min.	Illuminated Film for 360 min.
Absorption coefficient (α) (cm^{-1}) at 490 nm (10^3)	47.65	68.79	85.46
Optical Band Gap (E_g)***(eV)***	1.23	1.11	0.93

It is observed from the table that as the time of illumination increases E_g becomes lesser. Since the optical absorption depends upon the ordering of short range and the defects associated with amorphous material, the lowering of E_g with time of illumination is due to two most important reasons. Firstly, the reduction in disorder in the atomic bonding between the neighbors and consequently decrease of the density of tail states adjacent to the band edge and secondly the amorphous–crystalline transformations. At the constant ambient temperature 348 K (in between the glass transition and crystallization temperature of $Se_{80}In_5Te_9Sb_3$ glass), during the process of illumination enough vibrational energy is available to break the weaker bonds and introducing few transnational degrees of freedom in the material. On this account, crystallization via nucleation and growth becomes possible which depends upon the time of illumination.

4. Conclusion

This paper reports the structural and optical properties of $Se_{80}In_5Te_9Sb_3$ thin films during photo crystallization. From the analysis of optical absorption spectra, we have found that the mechanism of absorption is due to indirect transitions. The photo crystallization in $Se_{80}In_5Te_9Sb_3$is associated with the change in optical band gap. Observed values of optical band gap are found to decrease from 1.23 to 0.93 eV as the time of illumination increases from 0 to 360 min. This behavior is attributed to the production of surface dangling bonds around the formed crystallites during the process of crystallization i.e. the transformation of phase from amorphous to crystalline state. The HRXRD studies of $Se_{80}In_5Te_9Sb_3$ films show that the as-prepared films are in amorphous phase while the illuminated films are in crystalline phase. This phase transformation due to illumination indicates that the$Se_{80}In_5Te_9Sb_3$ thin films are promising materials for optical recording. An understanding of photo crystallization occurrence in $Se_{80}In_5Te_9Sb_3$ films is very important for advanced applications based on the amorphous to crystallization phase change.

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