Photo induced effects on the optical properties of As$_{20}$Sb$_{20}$S$_{60}$ thin films

Ramakanta Naik$^1$, E. M. Vinod$^2$, Sanjit Parida$^2$, R. Ganesan$^2$ and K.S.Sangunni$^2$

$^1$Department of Physics, Utkal University, Bhubaneswar, 751004, India
$^2$ Department of Physics, Indian Institute of Science, Bangalore, 560012, India

E-mail: ramakanta.naik@gmail.com

Abstract. The thermally evaporated As$_{20}$Sb$_{20}$S$_{60}$ amorphous film of 800 nm thickness was subjected to light exposure for photo induced studies. The as-prepared and illuminated thin films were studied by X-ray diffraction, Fourier Transform Infrared Spectroscopy and X-ray Photoelectron Spectroscopy and Raman spectroscopy. The optical band gap was reduced due to photo induced effects along with the increase in disorder. These optical properties changes are due to the change of homopolar bond densities. The core level peak shifting in XPS spectra and Raman shift supports the optical changes happening in the film due to light exposure.

1. Introduction

Chalcogenide glasses are one of the most widely known families of amorphous materials and have been studied for several decades, because of their interesting fundamental properties and wide range of applications [1]. They have been explored as promising candidates for optical memories, gratings, switching devices, acusto-optic devices, holography, and xerography and information storage media [2, 3]. Arsenic sulfide (As$_2$S$_3$) is the most studied chalcogenide glass and has applications in infrared optics and optical coatings because of its excellent IR transmission, large glass forming tendency, and resistance to moisture and chemicals [4]. Studies on thin films of Sb$_2$S$_3$ are attracting wide attention, for their special applications as a target material for television cameras, microwave devices, switching devices and various opto-electronic devices. Even though As and Sb belong to the same group of the periodic table, As$_2$S$_3$ and Sb$_2$S$_3$ do not display the same glass forming tendency. However, addition of As$_2$S$_3$ to Sb$_2$S$_3$ enhances the glass forming ability of the latter and glasses in the mixed As-Sb-S system can be formed [5].

Photo induced changes in amorphous chalcogenides are an object of systematic investigations with a view to better understanding the mechanisms of the phenomena taking place in them as well as their practical applications. It is well established that chalcogenide glasses undergo structural changes under the action of external influences such as laser, neutron, electron and gamma irradiation [6-8]. The knowledge of the optical properties of thin films is very important in many scientific, technological and industrial applications of thin films such as photo-conductivity, solar energy, photography, and numerous other applications. The present communication reports the effect of laser irradiation on optical properties of amorphous thin films of As$_{20}$Sb$_{20}$S$_{60}$.

$^1$ To whom any correspondence should be addressed.
2. Experimental
Bulk glass of $\text{As}_{20}\text{Sb}_{20}\text{S}_{60}$ was prepared by melt quenching technique. Thin films were prepared by thermal evaporation method at a base pressure of $1 \times 10^{-5}$ Torr from the prepared bulk glass onto the glass substrates. During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain the films of uniform thickness. The thicknesses of the films were around 800 nm. The amorphous state of the film was checked by X-ray (Philips, Cu Kα, $\lambda = 1.54 \text{ Å}$) Diffractometer (XRD). To study the photo induced changes, we irradiated the film at room temperature by a diode pumped solid state laser (DPSS) of wavelength 532 nm with a power of 40 mW. The optical absorption spectra of the as-prepared and illuminated films were taken by using the Fourier Transform Infrared (FTIR) spectrometer (Bruker Optics (IFS66v/S)) in the visible wavelength range of 400-1200 nm at room temperature. The X-ray Photoelectron Spectroscopy (XPS) core level spectra were obtained with Al Kα X-rays (1486.6 eV) at a base pressure of $\sim 10^{-9}$ Torr in Multilab 2000 Thermo Scientific UK instrument. The C 1s line from adventitious carbon on the surface has been widely used for charge referencing [9] and the BE of the reference C 1s line was set as 284.6 eV. The room temperature Raman spectra were recorded in the 180° backscattering geometry, using a 532 nm excitation from a diode pumped frequency doubled Nd–YAG solid state laser and a custom built Raman spectrometer equipped with SPEX TRIAX 550 monochromator and a liquid nitrogen cooled CCD. Laser power at the sample was $\sim 15$ mW and a typical spectrum acquisition took $\sim 1$-2 min.

![Figure 1. XRD patterns of the As$_{20}$Sb$_{20}$S$_{60}$ thin films.](image1)

![Figure 2. Transmission spectra (inset- $\alpha$ change) of the As$_{20}$Sb$_{20}$S$_{60}$ thin films.](image2)

3. Results and Discussion
Figure 1 shows the X-ray diffraction patterns for the As$_{20}$Sb$_{20}$S$_{60}$ thin films. The absence of the diffraction lines in the X-ray patterns indicates that the films have amorphous structures. Transmission spectra corresponding to the amorphous As$_{20}$Sb$_{20}$S$_{60}$ thin films are plotted in figure 2, which shows a clear difference between the as-prepared and the illuminated films. The absorption coefficient ($\alpha$) for the studied films were calculated [10] from the transmittance T and reflectance R using the equation

$$\alpha = \frac{1}{d} \ln \left( \frac{1-R^2}{T} \right)$$

where d is the thickness of the film and T is the transmission and R is the reflectivity of the film. The absorption coefficient increases with illumination which is shown in fig.2 inset. According to Tauc’s relation [11] for the allowed non-direct transition, the photon energy dependence of the absorption coefficient can be described by

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

where B is a parameter that depends on the transition probability and $E_g$ is the optical energy gap. The optical band gaps of the as-prepared and the illuminated films are found to be 1.93 eV and 1.87 eV.
respectively. So, photo induced optical band gap change was observed due to light illumination on the as-prepared film. It can be suggested that the photo induced changes are caused by chemical bond redistribution [12] according to the equation

\[ 2(M - S) \rightleftharpoons M - M + S - S \]  

where M stands for As or Sb, S is for sulfur and dash denotes a chemical bond. Films in the virgin state contain a large density of homopolar bonds due to dissociation of the glass in the course of evaporation and quenching of the vapor on the substrate. There is a high degree of disorder in these films; the atoms are partly statistically distributed, and M-S chemical-bond formation is not fully preferred. Thus exposures of As$_{20}$Sb$_{20}$S$_{60}$ thin films can shift the equilibrium in both directions depending on the conditions of thin film preparation and/or the conditions of light exposure. In case of illumination, the homopolar bond density increases causing more disorder which can be seen from the $B_{1/2}$ values. The $B_{1/2}$ values for as-prepared and illuminated films are 581 and 551 cm$^{-1/2}$eV$^{1/2}$ respectively. The $B_{1/2}$ for illuminated film is less than the as-prepared film which indicates the presence of more no of homopolar bonds due to disorder.

A typical XPS spectrum of As$_{20}$Sb$_{20}$S$_{60}$ film contains many photoelectrons and Auger peaks of As, S and Sb. But, we have considered only the core peaks such as As 3d, Sb 4d and S 2p for the present study. The XPS spectra of the as-prepared and illuminated film for As 3d core level is shown in figure (3a). From the spectra of As 3d peak, it is found that due to illumination, the peak is shifting towards the lower BE due to the formation of As-As homopolar bonds. The As 3d peak position for as-prepared and illuminated films are at 43.01 and 42.73 eVs respectively. This is in accordance with the reduction in optical band gap of the as-prepared film due to photo induced process. The peak position of Sb 4d core level spectra (figure 3a) for as-prepared and illuminated films are at 33.91 and 33.55 eVs respectively. It is found that the peak is shifting towards the lower BE due to the formation of more Sb-Sb homopolar bonds. The S 2p spectra of the as-prepared and illuminated films are shown in Fig. 3b. The S 2p peak position for as-prepared and illuminated films are at 161.72 and 161.91 eVs respectively. The peak shifts towards higher BE shows the formation of S-S homopolar bonds due to illumination as the electro negativity of S (2.58) is more than that of Sb (2.02).

![Figure 3a. As 3d and Sb 4d of As$_{20}$Sb$_{20}$S$_{60}$ thin film.](image1)

![Figure 3b. S2p core level spectra of As$_{20}$Sb$_{20}$S$_{60}$ thin film.](image2)

Direct evidence of structural changes in As$_{20}$Sb$_{20}$S$_{60}$ thin films caused by illumination was obtained from Raman Spectra as shown in figure 4. According to the molecular model [13], each Sb atom in the As-Sb-S ternary glasses is covalently bonded to three S atoms in a pyramidal unit (Sb-S$_3$), and As atoms are covalently bonded to three S atoms in a pyramidal unit (As-S$_3$). The basic structural units As$_3$, Sb$_3$, and S$_3$ are interconnected through bridging S atoms. The coupling between the basic structural groups via S atoms is assumed to be weak, and the vibrational modes are separated into SbS$_3$ and AsS$_3$ like vibration in As-S$_3$ (S$_2$) As-As (S$_2$) and the AsS$_3$ mode is superimposed in that band.
Figure 4. Raman spectra of As$_{20}$Sb$_{20}$S$_{60}$ thin film.

The peak at 113 cm$^{-1}$ and 215 cm$^{-1}$ of the as-prepared film corresponds to S-S vibrational modes respectively. The illumination of the as-prepared film causes the increase in homopolar bond density due to which there is shift in the peak position of the various vibrational modes and new peaks at 142 and 180 cm$^{-1}$ are created.

4. Conclusions

In conclusion, thermally-evaporated amorphous thin films undergo structural transformations when exposed to band gap illumination (photo-structural transformations). Photo induced changes of optical transmissivity, optical band gap, $B^{1/2}$ value; XPS core level peaks and Raman spectra change are observed. The optical band gap is decreased due to illumination. Photo induced changes can be assigned to chemical bond redistribution.

Acknowledgements

The authors thank DST for using the National Facility for Optical Spectrometry at Department of Physics and Surface Science facility, IISc for XPS measurement.

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