

Effect of laser irradiation on the optical properties of $\text{As}_{40}\text{Sb}_{15}\text{Se}_{45}$ chalcogenide thin films

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Abstract. The exposure with band gap light of thermally evaporated $\text{As}_{40}\text{Sb}_{15}\text{Se}_{45}$ amorphous film of 800 nm thickness, were found to be accompanied by optical changes. 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]. The light illumination of amorphous chalcogenides involves, in most cases, changes in their electronic transport and optical properties, as well as modifications in their local structure [2]. In short, photosensitive chalcogenide glasses are of crucial importance in designing high dense optical holograms and high bit rate optical waveguides. The photo induced effects in amorphous chalcogenides have been extensively studied, partly as an interesting subject for fundamental research in the field of disordered materials and partly due to potential application of these effects in optoelectronics (photo resists, optical memories, optoelectronic circuits, etc.) [3,4]. Among that, photo induced effects such as photo bleaching and photo darkening are among the most explored properties of chalcogenide thin films because of the high potential in a variety of applications in information storage, photonics, opto electronics, opto mechanical transducers, etc [5,6]. Due to the presence of localized states in the gap, photo induced effects are very predominant in such type of materials. The presence of lone pair electrons at the valence band and the structural flexibility associated with the glassy network is mainly responsible for this type of changes. The lone-pair character of the valence tails leads to very rich behavior under the influence of light [7]. The illumination by band gap light of many amorphous chalcogenides changes their internal and/or surface structure and the optical absorption edge will have a red or blue shift. Photo induced changes of optical transmittivity and reflectivity, index of refraction, changes of reactivity, rates of diffusion and inter-diffusion, viscosity and the state (phase) have been observed in many materials. The study of the optical absorption

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spectra in chalcogenide glasses provides essential information about the band structure and the energy band gap. The optical band gap of the material plays a major role in the preparation of the device for a particular wavelength. So, the decrease in optical band gap by laser irradiation known as photo darkening is very useful in device making. The present communication reports the effect of laser irradiation on optical properties of amorphous thin films of $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$.

2. Experimental

Thin films of $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ were prepared by thermal evaporation method at a base pressure of 1×10^{-5} Torr from the prepared bulk glass onto the glass substrates. The thicknesses of the films were around 800 nm. The amorphous state of the film was checked by X-ray (Philips, $\text{CuK}\alpha$, $\lambda=1.54 \text{ \AA}$) Diffractometer (XRD). To study the photo induced changes, we irradiated the film at room temperature by a diode pumped solid state laser 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 Mg $\text{K}\alpha$ X-rays (1253.6 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 [8] 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.

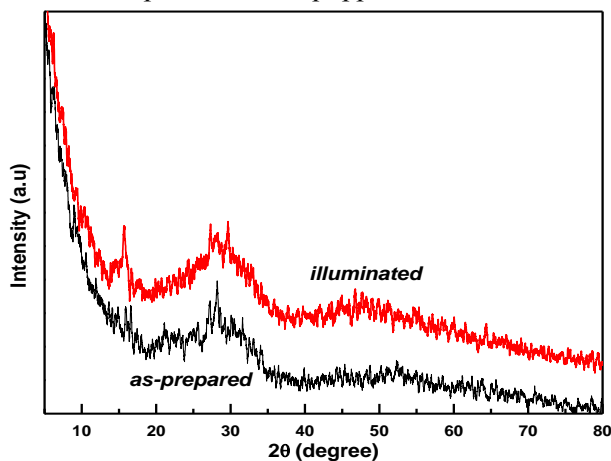


Figure 1. XRD patterns of the $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin films

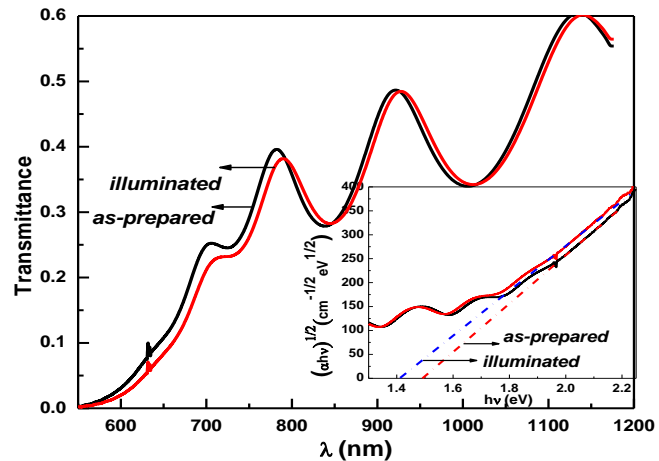


Figure 2. Transmission spectra (inset- E_g change) of the $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin films.

3. Results and Discussion

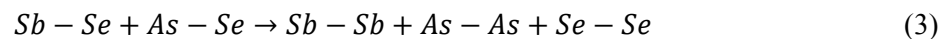
Figure 1 shows the X-ray diffraction patterns for the $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin films. The absence of the diffraction lines in the X-ray patterns indicates that the films have amorphous structures. Transmission spectra corresponding to the amorphous $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin films are plotted in figure 2, which shows a clear difference between the as-prepared and the illuminated films. The absorption coefficient (α) for the studied films were calculated [9] from the transmittance T and reflectance R using the equation

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

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. According to Tauc's relation [10] for the allowed non-direct transition, the photon energy dependence of the absorption coefficient can be described by

$$(\alpha hv)^{1/2} = B^{1/2}(hv - E_g) \quad (2)$$

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 1.49 ± 0.001 eV and 1.41 ± 0.002 eV respectively (figure 2, inset). So, photo induced optical band gap change was observed due to light illumination on the as-prepared film. Since, the optical absorption depends on short-range order in the amorphous states and defects associated with it, the decrease in optical band gap may be explained on the basis of “density of state model” proposed by Mott and Davis and on the basis of change in nature of films due to chemical disorderness [11]. The decrease in optical band gap (E_g) with laser irradiation can be attributed to the reduction in the density of tail states adjacent to the band edge. The $B^{1/2}$ values for as-prepared and illuminated films are 510 ± 4 and 468 ± 2 $\text{cm}^{-1/2}\text{eV}^{1/2}$ 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. It is known that the Urbach edge is a useful parameter to evaluate the degree of disorder. The value of E_e for as-prepared and illuminated $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ films is 198 meV and 231 meV respectively. The Urbach energy E_e of the illuminated film is more than that of as-prepared film which indicates the increase in disorder after illumination. The lower values of $B^{1/2}$ and higher values of E_e of the illuminated film over the as-prepared film clearly indicate that the illuminated film is more disordered (chemically) than the as-prepared film, i.e., the creation of homopolar bonds after photo induced process which is well supported in XPS analysis. The increase in homopolar bond because of micro structural disorderness in the films occurs by photo reaction like



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 (figure 3a inset), the position for as-prepared and illuminated films are at 42.81 and 42.59 eVs respectively. This decrease of 0.22 eV binding energy is in accordance with the reduction in optical band gap of the as-prepared film due to creation of more As-As homopolar bonds as a result of photo induced process as observed for other films also [12]. Similarly, the peak position of Sb 4d core level spectra (figure 3a) is shifting towards the lower BE (34.44 eV to 33.72 eV) due to the formation of more Sb-Sb homopolar bonds. The Se 3d spectra of the as-prepared (54.24 eV) and illuminated (54.54 eV) films are shown in figure 3b. The peak shifts towards higher BE shows the formation of Se-Se homopolar bonds due to illumination as the electro negativity of Se (2.55) is more than that of Sb (2.02).

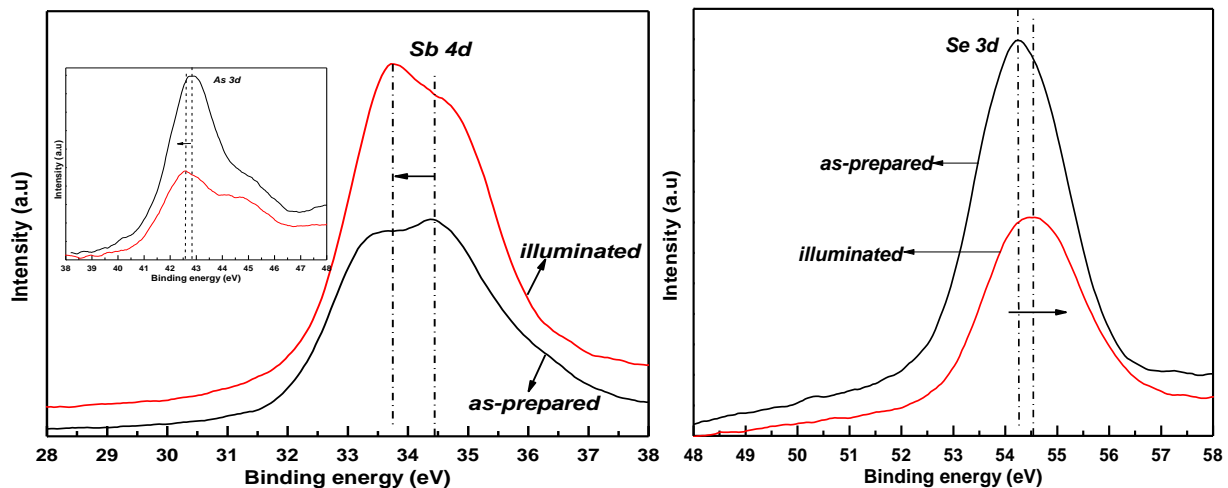


Figure 3a. As 3d and Sb 4d of $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin film. **Figure 3b.** Se 3d core level spectra of $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin film.

Direct evidence of structural changes in $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ 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-Se ternary glasses is covalently bonded to three Se atoms in a pyramidal unit (SbSe_3), and As atoms are covalently bonded to three Se atoms in a pyramidal unit (AsSe_3). The basic structural units AsSe_3 and SbSe_3 are interconnected through bridging Se atoms. The coupling between the basic

structural groups via Se atoms is assumed to be weak, and the vibrational modes are separated into SbSe_3 and AsSe_3 like vibration in As-Se_3 , (Se_2) As-As (Se_2) and the AsSe_3 mode is superimposed in that band at 331cm^{-1} .

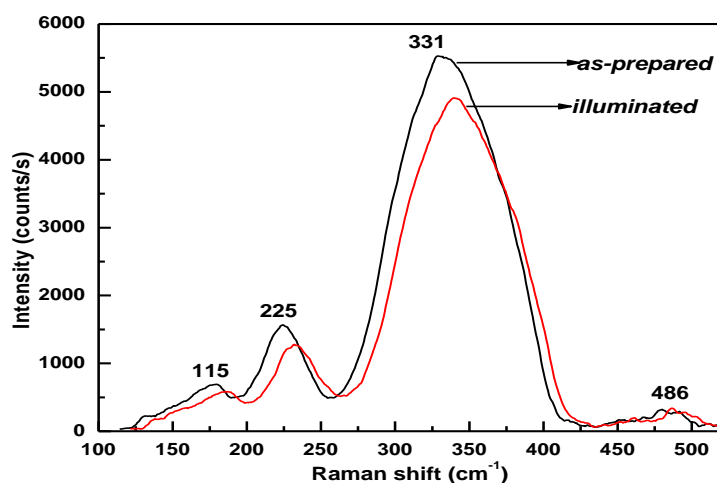


Figure 4. Raman spectra of $\text{As}_{40}\text{Se}_{45}\text{Sb}_{15}$ thin film.

The peak at 115 cm^{-1} and 225 cm^{-1} of the as-prepared film corresponds to Se-Se 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.

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.

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