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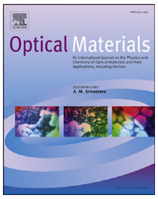

Band gap tuning in $As_{40}Se_{53}Sb_{07}$ thin films by 532 nm laser irradiation: An optical investigation by spectroscopic techniques

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The chalcogenide thin films belongs to a special category of important materials due to the unique IR transparency and light induced linear and non linear optical properties change. The optical band gap tuning in thermally evaporated $As_{40}Se_{53}Sb_{07}$ chalcogenide thin film is being probed under the influence of 532 nm laser illumination. The gradual decrease in transmission and red shift of optical absorption edge with illumination at different time scale is recorded by Fourier transmission infrared spectroscopy. The simultaneous increase in refractive index and absorption coefficient of the illuminated film makes the material as useful candidate for optical switching. The dispersion of refractive index is being analyzed by using Wemple–DiDomenico (WDD) single oscillator model and static refractive index (n_0) has also been reported. The exponential decrease of optical band gap with time is attributed to the increase in density of localized states and vacancies. The entire mechanism is explained by the microscopic model in which heteropolar bonds are converted to homopolar ones by the absorption of high energy photons investigated by X-ray photoelectron spectra. The amorphous nature of the studied films was revealed from X-ray diffraction and composition of the film was determined from energy dispersive X-ray analysis. The surface morphology was determined from the scanning electron microscopy. The optical change in absorption coefficient, refractive index, band gap by influence in laser irradiation in such materials may be suitable for optical disc(memory) application for optical time division switch.

1. Introduction

Chalcogenide glasses are the specific class of amorphous semiconducting materials that contain one or more chalcogen element (S, Se, Te) which makes covalent bonds with the network formers like As, Sb, Ge, Bi etc. The low phonon energy due to high atomic masses in these elements extends the transmission range into infrared region making it a suitable candidate for application in medical imaging, telecommunication, bio sensing, infrared photonics, infrared waveguides, optical fibers [1–4]. The high refractive index, large nonlinearities, low linear and nonlinear loss, high values of absorption coefficient, photosensitivity, intrinsic large dipole moment, tunable band gap makes them potential candidates for applications in high-efficiency fiber amplifiers, grating and ultrafast optical switching devices, optical recording devices, optoelectronics, optical memory devices, optical amplifier, optical integrated circuits, phase change recording purpose, solar cell etc. [5–10]. Another interesting property they exhibit that they show structural, optical properties change under the influence of radiations such as ion irradiation, laser illumination, μs light pulse, e-beam, ϒ radiation etc. with below or above band gap energy [11–15]. The degree and nature of change in such optical parameters like transmittance, absorption power, refractive index, optical band gap, extinction coefficient etc. under laser light irradiation are selectively used in various optical devices such as switches in optical domains [16–18]. The irradiation of these materials with high energy particles or light results bond breaking and bond rearrangement that modifies the local structure which brings subtle effects such as shifts in the absorption edge (photo-bleaching and photo-darkening) [19,20]. The structural flexibility such as low coordination number and presence of lone-pair [LP] p states in their valence bands favors the light-induced changes in such chalcogenide materials [21,22]. The laser induced excited carriers get localized in disordered and defective structure undergo strong

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electron–lattice interaction leading to photo darkening (decrease in optical band gap) [23,24]. The top surface of the valence band which is formed by the LP electrons is broadened due to increase in LP-LP interactions. The kinetics of such change is explained using the photon assisted site switching model (PASS) [25], where a percolative growth of photon assisted site switched chalcogenide clusters of high energy states is predicted with the absorption of light. However, most of the studies were carried out before and after laser illumination which lacks the information regarding the kinetic of optical change with time scale.

On the material selection point of view, Se based chalcogenide amorphous materials draw great attention due to its high glass forming ability and plays a good host matrix for the investigation of chalcogenide glasses in the bulk and thin film forms. However due to its short lifetime and low sensitivity, the film containing only Se is not a useful component for device fabrication. But the alloys containing Se as one of its component overcome the limitation and brings high sensitivity and crystallization [26,27]. The properties like glass transition temperature, optical energy gap, thermal diffusivity, elastic behavior and electrical conductivity of ternary Sb–As–Se bulk system have been measured and analyzed by different workers in the last few years [28–30]. However, the different characteristic properties in thin film form is not extensively investigated except few [31–33].

In the present report we have carried out in situ measurement of the optical properties of $As_{40}Se_{53}Sb_{07}$ film by Fourier Transfer Infrared Spectrometer (FTIR) in the 500–1200 nm spectral range. The optical transmission in many previous experiments of such kind of films were recorded before and after illumination, and hence information about the type of changes in the film structure was missing during photo induced effect. An accurate value of absorption coefficient, optical band gap and refractive index of semiconducting films is essential for the design and analysis of various optical and optoelectronic devices [34]. The refractive index was determined from the transmission data by the well-known Swanepoel method [35]. The analysis of the absorption coefficient was also carried out to determine the optical band gap E_g and the nature of the transitions. The X-ray photoelectron spectroscopy (XPS) measurements show the photo induced bond breaking and rearrangement in the film which supports the optical changes. The chemical composition of the as-prepared film was checked by the Energy dispersive X-ray analysis (EDX) and the surface morphology by Scanning electron microscopy (SEM).

2. Experimental procedures

2.1. Sample preparation

$As_{40}Se_{53}Sb_{07}$ bulk sample was prepared by conventional melt quenching method by using As, Sb and Se (99.995% pure from Sigma Aldrich) which were weighed according to their atomic percentage and sealed in a quartz ampoule in a vacuum of $\sim 10^{-5}$ Torr. The sealed ampoule was kept inside a slow rotating furnace at 1000 °C for 24 h to make the melt homogeneous. The bulk sample was obtained by quenching the ampoule in ice cooled water within fraction of time to avoid crystallization. Thin films of $As_{40}Se_{53}Sb_{07}$ (800 nm thick) was prepared by thermal evaporation process by using Hind High vacuum coating unit (HIND-HIVAC Model 12A4D) on glass substrates at a base pressure of $\sim 5 \times 10^{-5}$ Torr from the prepared bulk sample. The substrate temperature was maintained at room temperature and the rate of deposition was fixed at 5 nm/s during the deposition process. In order to get homogeneous and uniform film, the substrates were rotated slowly.

2.2. Characterizations

The amorphous nature of the prepared films were checked by X-ray (Philips type 1710 with Cu as target and Ni as filter, $\lambda = 1.5418$ Å) Diffractometer (XRD). The presence of elements in the as deposited films was checked by energy dispersive X-ray spectrometer (EDX) with an attachment facility of scanning electron microscope (SEM). The scan were taken at an accelerating voltage of 20 kV with 40 mA emission current with sample exposure of 1 cm^2 size at 2×10^{-7} Torr pressure. The experimental set up for the in situ measurement by FTIR spectrometer is described elsewhere [36]. The sample was illuminated with diode pumped solid state laser (DPSS) of wavelength 532 nm with energy 2.34 eV and the intensity was 35 mW. The transmission spectra from sample was probed using white light in the wavelength regime 400–1200 nm. The pump beam was expanded using a beam expander to encompass an area that was larger than the probe beam, so that an area of uniform light intensity was examined. The two beams were directed such that they crossed each other at the sample with the laser spot completely overlapping the probe light spot from the spectrometer. Note that the increase in temperature (~7 K) at the illuminated spot was calculated according to the procedure outlined in Ref. [25]. The observed changes in the film is due to laser induced effect and not due to thermal as this small temperature rise is not enough to induce any change [37–39]. The reflection loss was less in comparison to the high absorption value at the band gap region. We have determined the refractive index n and absorption coefficient α from the transmission spectrum using Swanepoel's method [35]. To study the formation of new bonds and kinetic of bond formation due to photo induced effect, we have done the XPS measurement which is a very useful surface analytical technique. This method determines the chemical state and local environment of an atom. The XPS core level and valence band spectra were obtained with monochromatic Mg K_α X-rays (1253.6 eV) at a vacuum of 10^{-9} Torr in Multilab 2000 Thermo Scientific UK instrument. The recorded data consisted of survey scans over the entire binding energy (BE) and selected scans over the core level peaks of interest. The energy increment of 1eV was used for collecting the survey spectra and 0.05 eV for the case of core level spectra. The recorded data were averaged over five scans. The data were taken at different regions to check the reproducibility of the measurements. The charging effect can change the BE of the electrons from sample to sample for insulators such as glasses. Therefore, the measurement of the absolute BE of electrons from a specified energy level is not reliable. The C 1s line from either adventitious carbon or intentionally added graphite powder on the surface has been widely used for charge referencing [40]. The adventitious carbon was used as a reference and the BE of the reference C 1s line was set as 284.6 eV. A calibration factor was calculated from the difference between the measured C 1s BE and the reference value 284.6 eV for each sample [41]. The original BE data were corrected according to the calibration factor. All the measurements were done at room temperature (300 K).

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction spectra of as-prepared and illuminated $As_{40}Se_{53}Sb_{07}$ thin films at ambient temperature are presented in Fig. 1. From the XRD plot, it is found that there is no structural change due to the laser irradiation. The absence of sharp peaks confirms the amorphous structure of all the films under investigation. The XRD spectra are quiet similar in nature, so that it is very difficult to make any differences between the films. There was a