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# Laser induced Bi diffusion in $As_{40}S_{60}$ thin films and the optical properties change probed by FTIR and XPS

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ABSTRACT

Amorphous chalcogenide semiconducting materials are playing a pivotal role in modern technology. Such type of materials are very sensitive to electromagnetic radiations which is useful for infrared optics. In the present report, Bi doped in $As_{40}S_{60}$ thin films ($As_{40}S_{60}$, $Bi_{06}As_{40}S_{54}$) of 800 nm thickness were prepared by thermal evaporation method. The $Bi_{06}As_{40}S_{54}$ thin film is subjected to laser irradiation for photo induced study. The X-ray diffraction study reveals no structural change due to laser irradiation. The optical parameters are affected by both Bi addition and laser irradiation which brings a change in the transmitivity and absorption coefficient. The indirect optical band gap is found to be increased by 0.08 eV with laser irradiation with the decrease in disorderness. The Tauc parameter and Urbach energy which measures the degree of disorderness changes with Bi doping and irradiation. The refractive index is modified by the illumination process which is useful for optical applications. The optical property change is well supported by the X-ray photoelectron core level spectra.

## 1. Introduction

Chalcogenide amorphous compounds possess peculiar interesting properties which makes them useful in significant commercial applications [1–3]. The compound generally contains at least one chalcogen elements (S, Se and Te) and elements from other IV, V groups. These materials generally have low phonon energy, high refractive index, wide transmission range, high nonlinear optical property, low band gap (1–3 eV) etc. These materials are commercially used for optical memories, gratings, switching devices, fiber optics, optoelectronics, lithography, xerography, etc [4–7]. The optical switching elements are manufactured from these alloys due to the presence of high non linearity [8]. The less expensive technical devices in the field of optoelectronics are fabricated from these materials. The optical, electrical and thermal properties have found various applications in modern technology. Their characteristic properties such as electronic-excitation phenomena, photo induced phenomena etc. will invite more possibilities in technology sector in the immediate future.

In order to understand the mechanism and the practical applications of photo-induced changes in amorphous materials, various investigation have been done and also going on [9,10]. It is well established that chalcogenide glasses undergo structural changes under the action of external light sources such as laser, neutron, electron and gamma irradiation [11,12]. The light affects the short, medium, and long-range order materials. However, the presence of localized state in the mobility gap as well as various defects in chalcogenide materials affects the optical properties in large extent [13]. The presence of lone-pairs in the valence tails and low coordination number of the chalcogens leads to very rich behavior under the influence of light [14]. We know that the valence band is formed by the interaction of the lone pair orbits in chalcogenide glasses, and the conduction band is formed by the anti-bonding orbitals. Therefore, the lone pair electrons play an important role in the photo induced phenomena by band gap light illumination [15]. These create different metastable states which changes the optical, electrical parameters in the films. The changes could be reversible or non-reversible depending on the composition, structure, or type of excitation. The photo-induced effects in chalcogenide glasses changes the optical constants such as shifts in the absorption edge (i.e., photo darkening or photo-bleaching), transmission, refractive index etc. [16,17]. The photo induced effects in $As_{40}S_{20}Se_{40}$ films shows photo darkening effect upon light illumination which changes the optical dispersion and absorption

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property [18]. Photo structural transformation was observed due to band gap illumination on $As_{40}S_{40}Se_{20}$ films with the photo oxidation process [19]. The photo structural transformation in amorphous $As_2S_3$ system is being explained as a coordination defect formation and annihilation process [20]. The photo induced effect in As–S system doped with Sb shows a decrease in optical band gap [21] where as Ge doped As–S system shows photo bleaching upon laser irradiation [22]. Photo-bleaching due to ϒ irradiation on Ge-As-Se film is discussed in light of the structural aspects and configurational-coordinate model [23]. The study on $As_{50}Se_{50}$ at wavelength of 632 nm revealed the nucleation and gradual growth of micrometer size pyramids that grow with laser irradiation affects the surface morphology [24]. The study was carried out before and after illumination which lacks the information regarding the kinetic of band gap change in $As_{50}Se_{50}$ film. So, the mechanism of photo induced process is different according to the materials and various source of irradiation.

The reversible photo structural changes are more effective in the amorphous chalcogenides with small local atomic density. So, the optical properties change due to photo induced effect is strongly seen in thin films [25]. The optical properties of thin films are very important in many scientific, technological, and industrial applications such as photo-conductivity, solar energy, photography, and various other applications. The important observations such as optical absorption spectra in chalcogenide glasses provides essential information about the band structure and the energy band gap. The useful parameters like optical band gap and refractive index are utilized for fabrication of micro-optical elements, optical waveguides, photonic band gap structures, diffractive optical elements, ultra-fast optical switches, etc., which are important parts of integrated optics/photonics [26].

For the wide application point of view, we have taken the system of interest as Bi–As–S. Arsenic trisulphide ($As_{40}S_{60}$) 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 [27]. The ternary Bi–As–S glasses are formed by adding Bi atoms in the As–S binary system. The corresponding substitution does not alter drastically the basic structure of glass, since both As and Bi are isovalent elements.

The physical aging effect is prominent in chalcogenide materials as studied by various authors [28,29]. The phenomenon of physical aging in chalcogenide glasses has attracted a substantial attention because of new prospects for chalcogenide based optoelectronics [30]. The analysis by various study indicates that physical aging may have a significant effect on the physicochemical properties of chalcogenides [31]. Exposure to strongly absorbed light with a photon energy above the optical band gap of the chalcogenides or to weakly absorbed, below band gap light may also accelerate the physical aging of chalcogenides [32,33]. The microstructural mechanism of this effect is assumed to involve relaxation of the mechanical stress generated in the surface layer of the material by prolonged excitation with above band gap light [33]. Chalcogenide materials are also known to be photosensitive, as well as sensitive to oxygen and humidity and all these phenomena leading to changes in optical properties and film morphology. Consequently, the optical property control of chalcogenides thin films, which is necessary for technological applications, requires a better understanding of their glass network structure and the assessment of a natural aging effect on their optical and morphological characteristics which could be detrimental for a variety of applications [34]. Therefore we have done the various study within a very short period of time after preparing the samples. That is why we predict that the aging effect is not affected the studied films.

The present communication reports the various optical properties change due to Bi addition into $As_{40}S_{60}$ matrix to form $Bi_{06}As_{40}S_{54}$ and the effect of laser irradiation on $Bi_{06}As_{40}S_{54}$ thin film. The optical properties such as optical band gap, Tauc parameter, Urbach energy have been derived from transmission spectra, at normal incidence, in the 500–1200 nm spectral range by the well-known Swanepoel method [35]. Analysis of the absorption coefficient was carried out to determine the optical band gap $E_g$ and the nature of the transitions. X-ray photoelectron spectroscopy (XPS) was carried out to support the optical changes.

## 2. Experimental procedure

Bulk glass of $As_{40}S_{60}$ and $Bi_{06}As_{40}S_{54}$ was prepared by melt quenching technique by taking As, S and Bi (99.995% pure). The chemicals were weighed according to their atomic percentage and was sealed in a quartz ampoule in a vacuum of ~$10^{-5}$ Torr. The sealed ampoule was kept inside a rotating furnace at 1000 °C for 36 h to make the melt homogeneous. The bulk glass was obtained by quenching the ampoule in ice cooled water. 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 elemental composition of the prepared films was checked by energy dispersive X-ray analysis (EDAX) in Sirion XL 40 in which EDAX is attached. The scan was done at 20 kV with 40 μA emission current exposing a sample of 1 $cm^2$ size at $2 \times 10^{-7}$ Torr pressure. The estimated average precision was less than 5% in atomic fraction in each element (Table 1).

The amorphous state of the film was checked by X-ray (Philips, $CuK_\alpha$, $\lambda = 1.54$ Å) Diffractometer (XRD). The absence of sharp peaks confirmed the amorphous nature of the prepared films. To study the photo induced phenomena, we have 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 film was mounted on a sample holder and the laser light was focused into 2 mm wide spot. The increase in temperature at the illuminated spot was calculated according to the procedure described elsewhere [36] and was estimated to be 6 K. This small increment in temperature is not more enough to induce any of the observed phenomena due to local heat. Hence, the observed changes are not due to thermal effect but mainly due to photo induced effects [37]. The optical transmission spectra of the as-prepared and irradiated films were taken by the Fourier Transform Infrared (FTIR) spectrometer (Bruker Optics (IFS66v/S)) in the visible wavelength range 500–1200 nm. The measurement was done inside the sample chamber of the spectrometer in dark condition. The reflection loss was not that much as compared to the high absorption in the band gap region.

XPS analysis will give the information about the new bonds formed between the components due to photo induced effect. Since, XPS is a surface analytical technique; most of the signals will come from the top 70–100 $A^0$. XPS measurements were first made on the as-prepared samples and then for the illuminated samples. The XPS core level and valence band spectra were obtained with monochromatic Al $K_\alpha$ X-rays (1486.6 eV) at a vacuum of $1.33 \times 10^{-7}$ Pa using the Multilab 2000 Thermo Scientific UK instrument. The XPS data consisted of survey scans over the entire binding energy (BE) and selected scans over the core level peaks of interest. An energy increment of 1 eV was used for recording the survey spectra and 0.05 eV for the case of core level spectra. The core level peaks were recorded by sweeping the retarding field and using the constant pass energy of 30 eV. Data were averaged by