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Photo-induced optical changes in $Ge_xAs_{40}Se_{60-x}$ thin films

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Abstract: Ge-As-Se chalcogenide thin films show a wide range of photosensitivity, which is utilized for the fabrication of micro-optical elements for integrated optics. The photosensitivity of $Ge_xAs_{40}Se_{60-x}$ (x=0, 15) chalcogenide thin films for UV light was presented. For that purpose, the bulk samples of $Ge_xAs_{40}Se_{60-x}$ (x=0, 15) chalcogenide glasses were prepared using conventional melt quenching technique, and thin films were prepared using thermal evaporation technique. These thin films were exposed to UV light for two hours. Amorphous natures of bulk samples and thin films were verified by XRD and chemical compositions were verified by EDX measurements. The thicknesses of the thin films were measured using a thickness profilometer. Linear optical analysis of these thin films was done using transmission spectra in wavelength range of 300−900 nm. Optical bandgap was determined by first peak of transmission derivative as well as extrapolation of Tauc's plot. R^2 analysis was done using R software to ensure that the material is indirect bandgap material. It is observed that two hours UV exposure causes photo-darkening along with photo-expansion in $As_{40}Se_{60}$ thin films, while photo-bleaching and photo-densification for $Ge_{15}As_{40}Se_{45}$ thin films. However, the amounts of photo-induced optical changes for $Ge_{15}As_{40}Se_{45}$ thin films are smaller than those for $As_{40}Se_{60}$ thin films. The changes in optical absorption, bandgap and thickness are understood based on the bonding rearrangement caused by UV exposure.

Key words: chalcogenide glasses; thin films; optical properties; photo-induced effect; optical band gap; UV exposure; *R* software

1 Introduction

Chalcogenide thin films are IR transparent, highly nonlinear, low phonon energy materials, hence being frequently used for integrated optics and photonics[1−3]. These thin films contain one or more chalcogen elements, i.e. S, Se and Te. Photosensitivity is one of the interesting properties of these films, which can be used to optimize the optical parameters based on the requirement of an application such as micro-optical fabrication[4−5]. Photo-darkening (red shift in optical bandgap), photo-bleaching (blue shift in optical bandgap), photo-refraction (change in refractive index), photo-densification (reduction in thickness), photo-expansion (increase in thickness), photo-dissolution (change in resistance to alkali solvent) are some interesting photo-induced phenomena shown by chalcogenide thin films[6−7]. In general, the addition of As enhances photo-darkening[8−9], while addition of Ge enhance photo-bleaching[10−11] in chalcogenide thin films.

In the present study, As-Se based thin films are taken as a base sample because of its highly nonlinear properties[12], photosensitivity and high refractive index[8−9, 11−13]. Addition of Ge in As-Se based samples increases the structural rigidity and nonlinearity of the system[14−15]. Hence, these samples are also very useful for the fabrication of nonlinear optical components such as ultra-fast optical switching etc[15−17]. Previous studies on the photosensitivity of chalcogenide thin films show that the changes in optical parameters depend on the frequency range, intensity and time of photo exposure of incident radiation[8−13]. Photo-induced linear optical changes for $Ge_xAs_{45-x}Se_{55}$ (where x=0, 10, 22, 33) thin films were investigated under laser illumination for wavelength of 660 nm and intensity of 150 mW/cm^2 in the past by YANG et al[11], where it was observed that photo-darkening, photo-bleaching or photo-stability depending on Ge/As ratio. Hence, they proposed Ge/As ratio of 0.286 ($Ge_{10}As_{35}Se_{55}$) for the photo-stable glass applications. The effect of 10 min UV exposure (λ=365 nm, intensity=3.5 mW/cm^2 and λ= 436 nm, intensity=12.5 mW/cm^2) on the base sample ($As_{40}Se_{60}$, Ge/As ratio of 0) of $Ge_xAs_{40}Se_{60-x}$ thin films on

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optical properties has already been investigated by CHAUHAN et al[8], which reports photo-darkening and photo- refraction in the base sample. The present study reports the effect of two-hour UV exposure (λ=365 nm, intensity=3.5 mW/cm^2 and λ=436 nm, intensity=12.5 mW/cm^2) on some optical properties (α, k and E_g) and thickness of $Ge_xAs_{40}Se_{60-x}$ (x=0, 15) thin films, and investigates the photosensitivity of Ge-As-Se thin films under UV exposure with different Ge/As ratios.

2 Experimental

Bulk $Ge_xAs_{40}Se_{60-x}$ (where x=0, 15) glasses were prepared by conventional melt quenching technique. For that purpose, all three corresponding elements (purity of As, Se, Ge 99.999%) were weighted according to their atomic percentages, and then sealed in quartz ampoules at base pressure of 1.33 MPa. These sealed ampoules were kept inside a furnace, and heated up to 950 °C at the rate of 3−4 °C/min to prepare the melt. To achieve a homogeneous melt, these ampoules were frequently rocked for 10 h at 950 °C and then quenched in ice water. Thermal evaporation technique was used to prepare amorphous thin films of glassy alloys onto cleaned glass substrates at room temperature inside a coating system (HIND−HIVAC Model 12A 4D−T) at a base pressure of about 1.33×10^{-4} Pa. The deposition rate was about 10 nm/s. To produce uniform films, the substrates were rotated with a frequency of about 5 Hz. The films were exposed for 2 h using Hg lamp through an optical arrangement, which is sensitive for two wavelengths (λ=365 nm, intensity=3.5 mW/cm^2 and λ=436 nm, intensity=12.5 mW/cm^2). The thickness of the films was measured by the thickness profilometer (Tencore Instrument, Model Alpha Step 100). Amorphous natures of bulk samples and thin films were verified using X-ray diffraction measurements (Thermo Electron Corporation, Model ARL X'TRA) with Cu K_α radiation and a scan rate of 3(°)/min. For compositional analysis, EDX measurements were performed at different spots along with the diameter of bulk samples and thin films. EDX measurements were performed using an EDX detector attached with scanning electron microscope (SEI Model Quanta−200). The optical transmissions of thin films were measured using a double beam UV/VIS/NIR computerized spectrophotometer (Hitachi, Model U−3310) in wavelength range of 300−900 nm.

3 Results and discussion

Structural analysis of the bulk samples and thin films was performed using XRD measurements. The XRD patterns of the thin films are shown in Fig.1, where no prominent peaks are observed even for the exposed films, which verifies that UV exposure does not cause crystallization in $Ge_xAs_{40}Se_{60-x}$ (where x=0, 15) thin films, and their amorphous natures are retained.

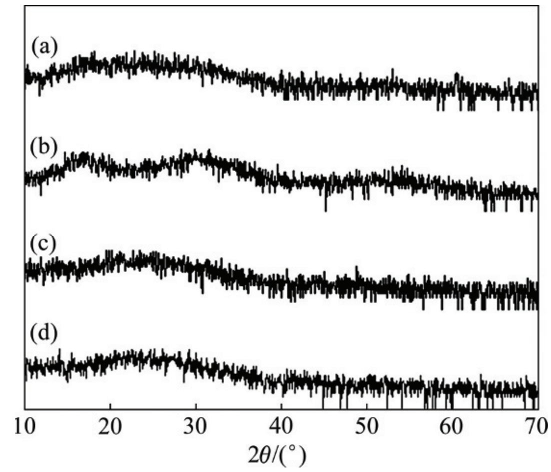

Fig.1 XRD patterns of unexposed and exposed $Ge_xAs_{40}Se_{60-x}$ thin films at room temperature: (a) $As_{40}Se_{60}$[8]; (b) $As_{40}Se_{60}$, exposed; (c) $Ge_{15}As_{40}Se_{45}$; (d) $Ge_{15}As_{40}Se_{45}$, exposed

Compositional analysis of bulk samples and thin films was performed using EDX measurements. The observed chemical compositions of $As_{40}Se_{60}$ thin films by EDX measurements is $As_{40.16}Se_{59.84}$[8], which is close to that of the bulk glass. Fig.2 shows the EDX plot and chemical composition of $Ge_{15}As_{40}Se_{45}$ thin film. Observed chemical compositions of the thin film was $Ge_{11.11}As_{42.51}Se_{46.38}$, which shows that the thin film is deficient in Ge component, and it shows over-stoichiometry in As and Se components. This is due to the difference in melting points of Ge (937 °C), As (817 °C) and Se (217 °C).

In the present study, the linear optical constants are determined using transmission spectra. Transmission plot for $Ge_xAs_{40}Se_{60-x}$ (x=0, 15) thin films are shown in Fig.3.

Element	w/%	x/%	K
Ge	10.54	11.11	0.126 3
As	41.61	42.51	0.420 9
Se	47.85	46.38	0.469 1
Total	100.00	100.00	

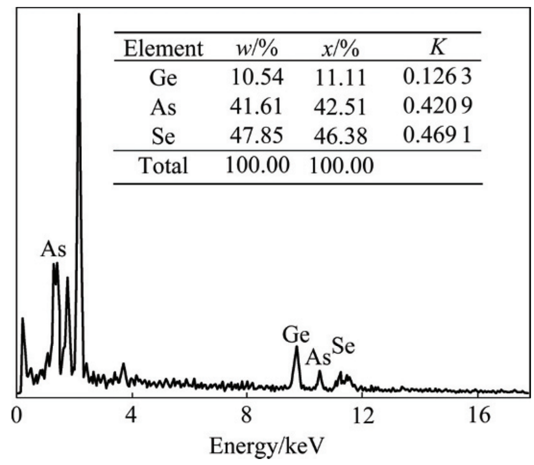

Fig.2 Energy dispersive X-ray spectroscopy (EDX) of $Ge_{15}As_{40}Se_{45}$ thin film