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Evolution of structural disorder in amorphous GeSeS thin films by thickness variation

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ABSTRACT

Amorphous GeSeS thin films are deposited for five different thicknesses using thermal evaporation technique and their microstructures are analyzed. The oscillations obtained in the optical transmittance spectra are resulted from the interference between the air-film and film-substrate interfaces. The observed decrease in the optical band gap with increase in the thickness of the film is associated with the change in the bonds formed in the structure of the network. Structural disorder like unsaturated bonds (dangling bonds) are studied by means of Tauc parameter ($B^{1/2}$), Urbach energy (E_U), and thermal diffusivity. The formation of heteropolar bonds become enormous for higher thickness of GeSeS thin films. From Raman spectra the bonds associated with symmetric stretching and tetrahedral units are discussed. Phonon–phonon scattering is the dominating mechanism which determines the phonon mean free path and hence the measured variation in thermal diffusivity.

1. Introduction

In recent years, Ge-based chalcogenide glasses have received a lot of attention because of its potential use in various solid-state, optical and electrical devices. Specifically, the threshold voltage and memory switching behaviour, and the infrared transmission of many of these glasses make them potential materials for use in memory devices and fiber optics [1,2]. Multi-component glasses are found to be more useful for many of these applications [3]. Many binary and ternary chalcogenide glassy systems such as GeSe [4], Ge–S [5], Ge–Se–Ag [6], Ge–Se–In [7], and Ge–Se–Te [8], are studied in detail to know the structural disorder and optical properties. The ternary chalcogenide alloys are necessary to get relatively stable glassy alloy and leads to enlarge their domain of applications. To get over the shortcomings of Ge-based chalcogenides, we looked into the structural modification of the alloys by the addition of chalcogenide elements like selenium (Se) and sulphur (S). Se is one of the attractive choices to use as an additive material owing to its flexible amorphous structure and a variety of possible applications in optoelectronics and solar cells [9]. However, the addition of S into Ge-Se matrix has not been well explored yet. It is expected that the addition of sulphur would modify the Ge-Se structure and produce significant changes in the phase change properties. Eutectic alloys such as GeS_2 [10] $GeSe_{1.5}S_{0.5}$ [11] shows electrical switching, but the time required for crystallization due to phase change is still unclear. Therefore, a stoichiometric study of GeSeS (keeping the same ratio) would be useful to understand its structural and bonding behaviours. Chalcogenide elements such as sulphur and selenium usually have twofold coordination while the addition of network formers such as germanium having four-fold coordination in Ge–Se–S system establishes cross-linking between the chains to form a stable tetragonal structure [12]. The present study aims to tune the thickness of the film to control the disorder and stability characteristics of Ge-Se-S thin films. The thickness variation of the Ge-Se-S system is reflected on different properties such as the glass forming region, Raman spectra, photo-acoustics and the optical properties. Thermal diffusivity of chalcogenides has been widely studied in the past years [13–15] and is very sensitive to the structure of solids. In fact, thermal diffusivity in glassy materials is connected to the vibrations of the atoms in the network around their equilibrium position and the structural changes are expected to influence the heat diffusion process.

In this paper GeSeS is made into compositional order and the thickness dependent structural disorder in these amorphous thin films is reported.

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2. Experimental procedure

2.1. GeSeS sample synthesis

Bulks of GeSeS was prepared by melt-quenching technique. High purity Ge, Se and S (99.999% HiMedia, India) elements were weighed in appropriate ratios into clean quartz ampoules. They were, evacuated and sealed under vacuum of 10^{-5} Torr. The ampoules were put into a rotating type electric furnace and heated up to 1000 °C with a heating rate of 100 °C/h, and kept at that temperature for 36 h. To ensure the homogeneity of the molten materials the ampoules were rotated for 12 h. Immediately after taking the ampoule out from the furnace they quenched into ice-cold water mixed with NaOH. The ampoule was then broken and the synthesized bulk GeSeS was taken out. The calorimetric measurements for these bulk GeSeS samples were carried out using a calibrated differential scanning calorimeter (DSC 200 PC, PHOX, NETZSCH) at a uniform heating rate of 10 K $\min^{-1}$ and in dry N_2 atmosphere. Thin films were formed using a conventional vacuum deposition unit (HINDHIVAC 12A4D). The bulks of GeSeS were put in a molybdenum boat under a vacuum of 2×10^{-5} Torr. The boat was then heated to the melting point of the material, which was evaporated and deposited on a clean glass substrate at a rate of 5 Å/s. The thickness of the films were controlled by a quartz crystal thickness monitor attached to evaporation chamber. Different depositions were carried out to produce five films of different thicknesses 110, 200, 454, 619 and 710 nm. The thicknesses were also confirmed using the surface roughness tester (SJ-210, MITUTOYO). The substrates were kept at a distance of 10 cm vertically above the source. During each deposition, the bulk material, taken in the boat were completely evaporated at a uniform rate so that no residual alloy remains from a previous deposition. It's worth to mention here that each time fresh pieces of the alloy were used for the deposition of different thickness films. This procedure is necessary to ensure homogeneity and to avoid preferential evaporation of the components, the volatile sulphur and selenium.

2.2. Characterization methods

The elemental compositions of these glasses were analyzed using a high-resolution scanning electron microscope (SEM-FEI Quanta FEG 200) equipped with an energy dispersive X-ray (EDX) analysis facility. The X-ray diffraction (XRD) patterns for the films were carried out using an X-ray diffractometer (PANalytical X'Pert Pro MPD) with Ni filtered Cu radiation. The optical transmittance was measured in the wavelength range 300–1100 nm using a computerised double beam UV–vis-NIR spectrophotometer (Techcomp model 2301). The photo-acoustic (PA) effect and the thermal diffusivity of GeSeS thin films were measured by using a photo-acoustic spectrometer which comprises of a mechanically modulated Xenon lamp of 450 W (Horiba Jobin Yvon, USA) as the source, a monochromator (Horiba Jobin Yvon, USA), a carbon black anodized sample cell having a electret mike and a lock-in amplifier (Stanford Research, USA) for signal detection. The complete description of the photo-acoustic spectrometer used in the present work and the details regarding the measurements of thermal diffusivity is reported in the literature [16,17]. Raman spectra were recorded at room temperature using a Fourier transform Raman spectrometer (Horiba Jobin Yvon, model HR800UV) having He–Ne laser with wavelength of $\lambda = 632$ nm as excitation source, and an output power of 2 mW to avoid laser-induced damage in thin films. All measurements were repeated at different locations on the film in order to check the reproducibility, and the error is found to be ±2%.

3. Results

3.1. DSC and structural properties

Fig. 1 shows DSC thermogram for GeSeS powder sample prepared by the melt quenching technique. The glass transition (T_g) temperature is observed at 77 °C with two crystallization exotherms (T_{C1} and T_{C2}) at 415 °C and 546 °C respectively [18]. Fig. 2 shows the XRD pattern of films of different thicknesses which indicates their amorphous nature as evidenced from the absence of sharp peaks in the XRD pattern. A broad hump in the 2θ range of 20 to 40° may be attributed to the glassy network of the film as well due to the glass substrate [19]. EDX result is given in Fig. 3 and it reveals that generally the films prepared using vacuum evaporation technique are found to be nearly stoichiometric in nature. However, lower thickness films (110 and 200 nm) are found to be slightly selenium rich.

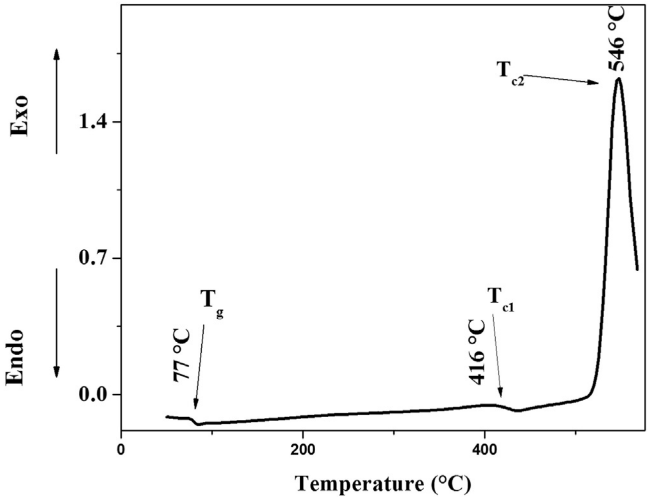

Fig. 1. DSC thermogram for GeSeS powder sample.

3.2. Optical properties

Fig. 4 shows the optical transmittance spectra for all films. In that, the lower thickness film of 110 nm shows almost linear transmittance with two maxima. The thickness of the films can be calculated using the swanepoel method [20] which uses the upper and lower bounding of the maxima and minima present in the optical transmittance spectrum from the relation:

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \tag{1}$$

Since the difference in refractive index is negligible in the wavelength range away from the absorption edge (where the maxima and

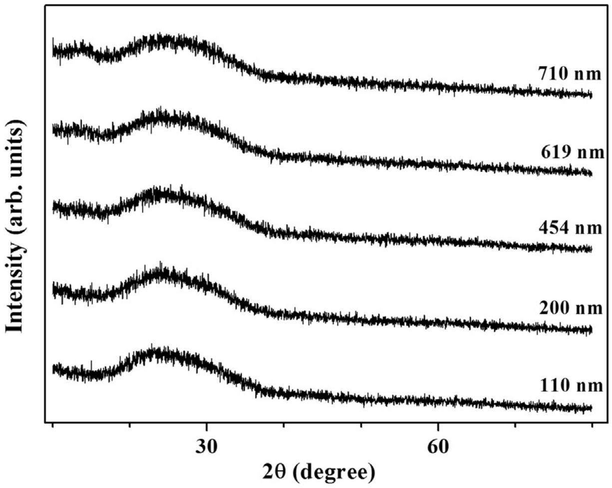

Fig. 2. XRD patterns of GeSeS thin films of various thicknesses.