



Evolution of structural disorder using Raman spectra and Urbach energy in $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films



R.T. Ananth Kumar^a, P. Chithra Lekha^b, C. Sanjeeviraja^c, D. Pathinettam Padiyan^{a,*}

^a Department of Physics, Manonmaniam Sundaranar University, Tirunelveli 627012, Tamil Nadu, India

^b Department of Physics, Pondicherry University, Puducherry 605014, India

^c Department of Physics, Alagappa Chettiar College of Engineering & Technology, Karaikudi, Tamil Nadu, India

ARTICLE INFO

Article history:

Received 3 April 2014

Received in revised form 1 August 2014

Available online 6 September 2014

Keywords:

Chalcogenides;

Vapor deposition;

Raman spectroscopy;

Acoustical properties;

Defects

ABSTRACT

We report thickness dependent structural and optical properties of $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films prepared by vacuum evaporation. From Urbach energy the structural disorder is addressed on the basis of band tailing due to creation of localized energy states. The obtained decrease in band gap and Urbach energy with increase in film thickness is linked to the increase in crystallinity and structural order. Raman spectra also supports the observed change in crystallinity with thickness. The lower thickness samples possess homopolar bonds such as Ge–Ge, Se–Se and S–S while in higher thickness film heteropolar GeSe_2S_2 structural units are formed. These findings suggest that the prepared $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films show an increase in the proportion of edge-sharing tetrahedral units with thickness. The effect of thermo elastic bending on $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films is studied from photo-acoustics and phonon–phonon scattering is found to be the dominating scattering mechanism.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Research in chalcogenide material is continuing due to their wide technological applications and an understanding of physical properties is still required in this area due to their strong dependence on disordered structure [1]. Currently, chalcogenide thin films are being used for the development of optoelectronic devices. Materials prepared from thin films have potential applications in amplifying or generating of optical signal, holography, optical memories, electrical switching and other optoelectronic applications [2]. Many binary and ternary chalcogenide glassy systems such as GeSe, GeS [3], Ge–S [4], Ge–Se [1], Ge–Se–Ag [5], Ge–Se–In [6], and Ge–Sb–Se [7], are studied in detail to know the structural disorder and optical properties. Although extensive research has been carried out on ternary compounds, yet there are no reports available on Ge–Se–S as a composition in thin film form. Chalcogenide elements such as sulfur and selenium usually have two-fold 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 [8]. The outermost electronic configuration of Ge is $(4s)^2(4p)^2$, Se is $(4s)^2(4p)^4$ and that of S is $(3s)^2(3p)^4$. In Se and S atoms, the two 4s and 3s electrons are low in energy and they do not participate in bonding. Two electrons among four p and three p electrons are used to form covalent bond with other two atoms and hence, Se and S

atoms make two-fold coordination. The remaining two p electrons do not participate in bonding and form a pair called “lone-pair electrons” [9]. Hence it is proposed to study the structural and optical properties of a new ternary composition of $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films so that it is possible to understand the formation mechanism.

The previous works reported that non-crystalline GeSe_2 is composed of the corner-sharing $\text{GeSe}_{4/2}$ tetrahedra (CST) and edgesharing $\text{Ge}_2\text{Se}_{8/2}$ bi-tetrahedra (EST) with some wrong bonds [10]. Photo-induced crystallization process in amorphous GeSe_2 thin films is studied by Matsuda et al. [11]. Pan et al. reported that the density of Se–Se bonds gets decreased by increasing the annealing temperature in GeSe_2 thin films [12]. Knotek et al. reported that the photodarkening increases the film disorder for GeS_2 and Ge–As–S thin films. Chalcogenide glasses of ternary Ge–In–Se systems are well known as infrared transmitting materials, which offer infrared transparency, high refractive index and low optical losses permit their developments as infrared optical materials [13,14]. Vinod et al. using Urbach energy studied the low temperature disorder in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ thin films and found that the disorder increases as the temperature increased [15].

The present study aims to tune the thickness of the film to control the disorder and to study the effect of thickness on the structural and optical properties of thermally evaporated $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films. The thickness control of thin films optimally adjusts important parameters such as crystallinity, band gap, and refractive index, which are important for the performance of a device. Therefore, the study of the variation of thickness is aimed to provide a deep insight about the mechanism of disorder and defect formation in the chalcogenide glass composition $\text{GeSe}_{0.5}\text{S}_{1.5}$ from a fundamental point of view.

* Corresponding author. Tel.: +91 9442063155; fax: +91 4622334363.
E-mail address: dppadiyan@msuniv.ac.in (D. Pathinettam Padiyan).

2. Experiment

Bulk $\text{GeSe}_{0.5}\text{S}_{1.5}$ sample has been prepared by melt quenching technique. High purity elements of Ge, Se and S (99.999% HiMedia, India) were taken in the stoichiometric ratio into clean quartz ampoules, evacuated and sealed under the vacuum of 10^{-3} Torr. The sealed ampoules were put into electric furnace and heated up to 1000 °C at 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 and quenched in ice cold water. The ampoule was then broken, synthesized bulk $\text{GeSe}_{0.5}\text{S}_{1.5}$ powder were taken out and used for film preparation. Thin films of $\text{GeSe}_{0.5}\text{S}_{1.5}$ were deposited by vacuum deposition technique on cleaned glass substrates at room temperature at a vacuum of 2×10^{-5} Torr by the evaporation of the bulk alloy using a resistively heated molybdenum boat at a rate of 5 Å/s in a conventional vacuum deposition unit (HINDHIVAC 12A4D) attached with a quartz crystal thickness monitor. The substrates were kept at a distance of 10 cm vertically above the source. Thin films were deposited for five different thicknesses and during each deposition, the bulk material taken in the boat was completely evaporated at the same rate so that no residual alloy would remain 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 due to preferential evaporation of the volatile sulfur and selenium. The thickness of the films is measured using the surface roughness tester (SJ-210, MITUTOYO) and found to be 122, 297, 420, 590 and 710 nm.

The chemical composition of the films was studied using scanning electron microscopy equipped with an energy-dispersive X-ray analyzer (EDAX, ESEM Quanta 200, FEI). The X-ray diffraction patterns (XRD) were recorded using a Panalytical powder X-ray diffractometer with $\text{CuK}\alpha$ (1.5406 \AA) radiation at a step size of 0.017° and step time of 3.175 s. The optical transmittance has been measured in the wavelength range 300–1100 nm using a computerized double beam UV–visible spectrophotometer (Techcomp model 2301). The Raman spectra were recorded at room temperature in a Fourier transform Raman spectrometer (Horiba Jobin Yuov, model HR800UV) using He–Ne laser ($\lambda = 632 \text{ nm}$) as the excitation source having an output power of 2 mW to avoid laser-induced damage in the samples. The photo-acoustic (PA) effect has been used for measuring the thermal diffusivity of $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films using a Xe lamp of 450 W (Horiba Jobin Yvon, USA) as the source. The description of photo-acoustic spectrometer used and the details regarding the measurements of thermal diffusivity were given in the literature [16,17]. All the measurements were repeated at different positions of the thin films in order to check the reproducibility and the error was about $\pm 2\%$.

3. Results

The XRD patterns recorded for $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films of five different thicknesses are shown in Fig. 1. The lower thickness film of 122 nm is found to be amorphous in nature. The film of thickness 297 nm shows a peak at 25.94° and as the thickness increases more peaks are observed. For 710 nm thick film more number of X-ray peaks are observed and it does not match with neither GeSe_2 nor GeS_2 the end members. Hence, to identify the structure, XRD measurements were repeated with a larger scan time of 142.11 s and shown in Fig. 1(e). Peak indexing and peak fitting were done with the help of CMPR [18] and the refined 2θ positions were given as input to the auto indexing program NTREOR [19]. The solution with the best figure of merit, indexed all peaks in an orthorhombic system with $a = 18.0531(4) \text{ \AA}$, $b = 8.6395(2) \text{ \AA}$ and $c = 4.7709(1) \text{ \AA}$. Cell volume is $744.11(2) \times 10^6 \text{ pm}^3$, the figure of merit (FOM) is 72.0 and the mean 2θ difference ($2\theta_{\text{calc}} - 2\theta_{\text{obs}}$) is 0.02055. This results are also further confirmed with the DICVOL [20] algorithms. EDAX results are given in Table 1 and it reveals that all the films prepared using vacuum evaporation technique are found to be

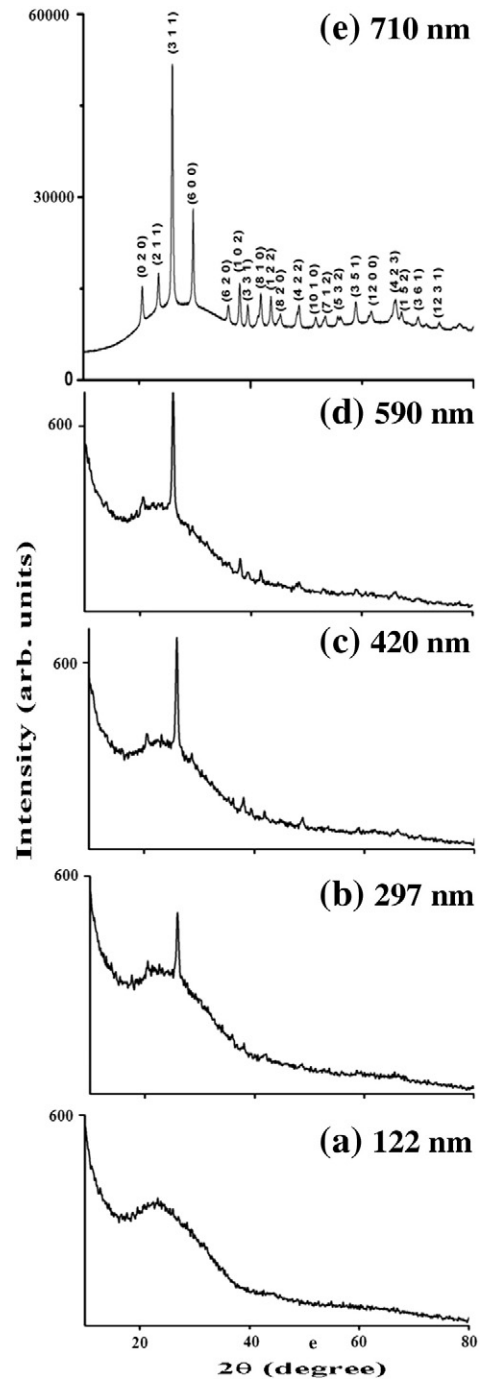


Fig. 1. X-ray diffraction pattern of $\text{GeSe}_{0.5}\text{S}_{1.5}$ thin films of thickness (a) 122 nm, (b) 297 nm, (c) 420 nm, (d) 590 nm and (e) 710 nm.

Table 1

The atomic percentage ratio of Ge, Se and S obtained from energy dispersive X-ray analysis.

Film thickness (nm)	Atomic% (obtained)		
	Ge	Se	S
122	28.59	19.18	52.23
297	33.26	20.51	46.23
420	34.12	17.64	48.24
590	32.22	16.76	51.02
710	33.12	16.76	50.12

Download English Version:

<https://daneshyari.com/en/article/1480966>

Download Persian Version:

<https://daneshyari.com/article/1480966>

[Daneshyari.com](https://daneshyari.com)