Materials Science in Semiconductor Processing 38 (2015) 209–217

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

The influence of the substitution of Se for Sn on the thermal, optical and dispersion properties of $Ge_{14}Se_{86-x}Sn_x$ thin films

H. Mahfoz Kotb [a,b,*], Farid M. Abdel-Rahim [c,d,e]

[a] Physics Department, Faculty of Science, King Faisal University, PO Box 400, Al-Hassa 31982, Saudi Arabia
[b] Physics Department, Faculty of Science, Assiut University, PO 71516, Assiut, Egypt
[c] Physics Department, Faculty of Science & Arts Khulais, King Abdulaziz University, Jeddah, Saudi Arabia
[d] Physics Department, Faculty of Science & Arts Khulais, University of Jeddah, Saudi Arabia
[e] Physics Department, Faculty of Science, Al Azhar University, Assiut Branch, Assiut, Egypt

ARTICLE INFO

Available online 14 May 2015

Keywords:
Ge–Se–Sn
Vacuum deposition
Absorption
Dispersion properties

ABSTRACT

Bulk glasses of $Ge_{14}Se_{86-x}Sn_x$ ($x=0$, 6, 10 and 22) were prepared by melt-quench technique. Glass transition temperature (T_g) and thermal stability of the bulk samples were found to decrease with Sn content. Thin films of $Ge_{14}Se_{86-x}Sn_x$ were deposited onto chemically cleaned glass substrates by thermal evaporation. X-ray diffraction (XRD) patterns of the as-prepared films confirmed its amorphous nature except for the film with $x=22$ at% which is polycrystalline. These results have been supported by scanning electron microscopy (SEM) and atomic force microscope (AFM) investigations. Transmittance and reflectance spectra of the as-prepared films were measured at normal incidence in the wavelength range of 350–2500 nm. Refractive index and the film thickness were determined from optical transmittance data using Swanepoel's envelope method. It was found that the refractive index dispersion data obeys the single oscillator Wemple and DiDomenico model from which the dispersion parameters were determined as a function of alloy composition. Analysis of the spectral behavior of the absorption coefficient revealed an allowed indirect optical band gap in the investigated films. The optical band gap was found to decrease along with a corresponding increase in the refractive index with the incorporation of Sn. These results have been discussed on bases of the chemical bond approach, electronegativity difference of the atoms, cohesive energy and heat of atomization.

1. Introduction

Since the 60s of the last century till now, chalcogenide semiconducting glasses have been extensively studied due to their potential applications in areas of optical recording media, optical fibers, memory devices, xerography, infrared lenses, photolithography, solar cells and laser diodes [1–6]. One of the useful chalcogenide glasses for many technological applications is the Ge–Se system and its base alloys [7–10]. Ge–Se system is known to be covalently bonded chalcogenide glass having a wide glass forming region [11,12]. The study of the influence of metallic impurities on the electrical, optical and structural properties of these chalcogenide glasses is of important concern with respect to their applications. Many researchers [13–24] have studied the effect of Sn addition, keeping a fixed Se content, on the properties of Ge–Se system. Mikrut et al. [21] reported a decrease of the optical band gap from 2.11 eV to 1.65 eV as Sn concentration increases from $x=0$ to $x=0.6$ in $Ge_{1-x}Sn_xSe_2$ thin films. The same trend for the

* Corresponding author at: Physics Department, Faculty of Science, King Faisal University, PO Box 400, Al-Hassa 31982, Saudi Arabia. Tel.: +966 3 5800000; fax: +966 3 5886437.
E-mail addresses: hkotb@kfu.edu.sa (H.M. Kotb), hmkscience@yahoo.com (F.M. Abdel-Rahim).

http://dx.doi.org/10.1016/j.mssp.2015.04.032
1369-8001/

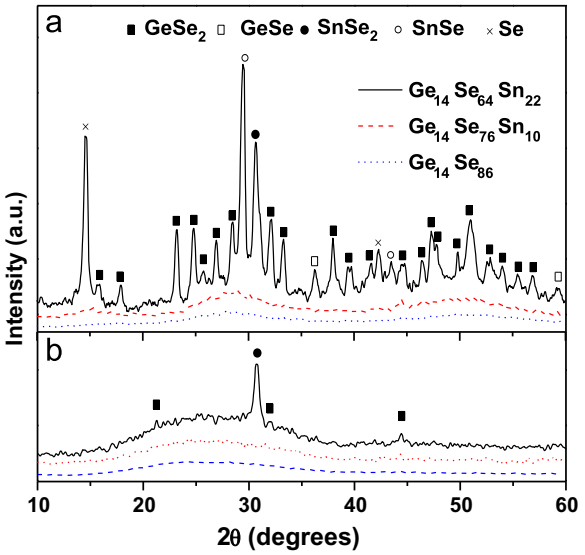

Fig. 1. XRD patterns of as-prepared: (a) bulk and (b) thin films of $Ge_{14}Se_{86-x}Sn_x$ ($x=0$, 10 and 22 at%) samples.

evolution of E_g with Sn content was cited by other researches [18,22]. Fadel et al. [18] indicated that both direct and indirect transitions are active in $Ge_{1-x}Sn_xSe_3$ ($x \leq 0.6$) thin films. Nevertheless, Thakur et al. [22] revealed an indirect optical transition in such system. Recently, Sharma et al. [24] have studied the effect of partial replacement of Se by Ge on the optical and thermal properties of relatively thick (430–577 nm) films of $Ge_xSn_{10}Se_{90-x}$ ($14 \leq x \leq 26$). They reported an increase in the allowed indirect optical band gap from 1.14 eV to 1.30 eV with increasing Ge content. To the authors' best knowledge; there are no explicit results available in the literature on the effect of incorporation of Sn on the expense of Se on the properties of Ge–Se–Sn system. Thus, in the present study we investigate the thermal, structural, and optical properties of $Ge_{14}Se_{86-x}Sn_x$ ($x=0$, 6, 10 and 22) chalcogenide glasses. The sample compositions of interest, $Ge_{14}Se_{86-x}Sn_x$ ($x=0$, 6, 10 and 22), were chosen to cover a wide range of compositions in the Ge–Se–Sn system [20]. Besides, all the studied compositions are Se rich in order to minimize crystallization and phase separation during preparation [25].

2. Experimental

Glassy alloys of $Ge_{14}Se_{86-x}Sn_x$ ($x=0$, 6, 10 and 22) were prepared in the bulk form by the conventional melt quench technique. High purity (5 N) materials were weighted according to their atomic percentages, and then sealed in quartz ampoule under a vacuum of $\sim 10^{-5}$ Torr. The sealed ampoules were heated up to 975 °C and held at this temperature for 14 h. The ampoules were rotated and shacked throughout this period to ensure the homogeneity of the glassy alloy. Quenching of the ampoules was done on ice+water mixture. Thin films of $Ge_{14}Se_{86-x}Sn_x$ were deposited onto chemically cleaned glass substrates kept at room temperature by thermal evaporation technique using a high vacuum coating unit (E306, Edwards Co., UK). During the deposition process (at normal incidence), the substrates were suitably rotated in order to obtain films of uniform thickness. The thickness of the films was measured by a mechanical profilometer (KLA Tencor P-15) and found to be ~300 nm. The structure and phases of the films were analyzed using X-ray diffractometer (XRD) Philips type PW 1710 with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). The surface morphology of the as-prepared films was examined with a Veeco NanoScope III MultiMode atomic force microscope (AFM) in tapping mode with a silicon cantilever. The chemical composition of films was studied by using the standard Energy Dispersive analysis of X-ray (EDX) technique which is attached to a scanning electron microscopy (SEM), Jeol (JSM)-T200 type. Differential thermal calorimetery (DSC) measurements were carried out using a Shimadzu DSC-60 instrument with an accuracy of ± 0.1 K, under dry nitrogen supplied at a rate of 35 ml/min. The optical transmittance (T) and reflectance (R) for the as-prepared films have been measured in the wavelength range 350–2500 nm using double beam spectrophotometer (UV/VIS Lamda 750). The absorption coefficient at different wavelengths was calculated from T and R, and then the optical band gap has been calculated using Tauc plots. The measured transmittance spectra were used to calculate the optical constants using the envelope method, which is detailed elsewhere [26,27].

3. Results and discussion

3.1. Structural characterization: XRD, EDX, AFM

Structural analysis of $Ge_{14}Se_{86-x}Sn_x$ samples showed that the as-prepared bulk alloys and their as-prepared thin films have an amorphous nature except for the sample with $x=22$ at% which is a polycrystalline (or partially crystalline) in both the bulk and thin film forms. As representative examples, the XRD patterns of samples $Ge_{14}Se_{86}$, $Ge_{14}Se_{76}Sn_{10}$ and $Ge_{14}Se_{64}Sn_{22}$ are given in Fig. 1.

Fig. 2 shows the EDX spectrum of the as-prepared $Ge_{14}Se_{80}Sn_6$ and $Ge_{14}Se_{64}Sn_{22}$ thin film as representative examples. The average atomic percentages of Ge:Se:Sn for the different samples agreed with their nominal values to within 0.7 at%.

The SEM images of $Ge_{14}Se_{76}Sn_{10}$ and $Ge_{14}Se_{64}Sn_{22}$ bulk samples are shown in Fig. 3. The growth of crystallites is clearly seen in Fig. 3(b) for the $Ge_{14}Se_{64}Sn_{22}$ bulk glass which is consistent with the XRD results.

The 3D AFM images of the as-prepared films are given in Fig. 4. The surface of the as-prepared thin films is almost smooth with root-mean-square (RMS) peak to peak value of 0.26 nm, 0.45 nm and 0.97 nm for the $Ge_{14}Se_{86}$, $Ge_{14}Se_{76}Sn_{10}$ and $Ge_{14}Se_{64}Sn_{22}$ thin films, respectively. The comparatively higher surface roughness of $Ge_{14}Se_{64}Sn_{22}$ thin film is due to its polycrystalline nature as approved previously by XRD analysis.

3.2. Physical properties: Cohesive energy (C.E.), coordination number $\langle r \rangle$, heat of atomization (H_s)

Cohesive energy (C.E.), i.e. the stabilization energy of an infinitely large cluster of the material per atom, was