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Influence of compositional variation on the optical and morphological properties of Ge–Sb–Se films for optoelectronics application

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ABSTRACT

Thin films of $Ge_xSb_{40-x}Se_{60}$ (x = 15, 20, 25, 27, 32 and 35 at.%) were deposited on quartz by vacuum thermal evaporation of the pre-synthesized parental glasses powders. By spectroscopic ellipsometry the complex refractive index values are determined in the 0.20–33 µm spectral range. The optical band gap and single oscillator energies are established as a function of the Ge content and average coordination number Z. In the (0.85–3.5) µm spectral range the $Ge_xSb_{40-x}Se_{60}$ films possess about 80% transmission. Infrared ellipsometric and Raman studies identified Se–Se and Ge–Ge homopolar bonds, oxygen and hydrogen related impurity bonds and heteropolar Ge–Se and Sb–Se chemical bonds. Neutron- and X-ray Diffraction data coupled with Reverse Monte Carlo simulations support the optical results reproducing the Ge–Se and Sb–Se cell units and cross-linked Ge–Ge bonds. Atomic force microscopic imaging confirmed smooth surfaces with low RMS roughness values (< 2.3 nm) and continuous structure of grains of (16–22) nm diameters. All the considered material parameters show peculiarities in the compositional dependences around 27 at.% Ge, corresponding to average coordination number Z = 2.67, testifying structural phase transition at high Ge content in the $Ge_xSb_{40-x}Se_{60}$ films.

1. Introduction

In recent years a great deal of interest has been devoted to the investigation of chalcogenide ternary Ge–Sb–Se glasses. They are promising materials for infrared optical fibers application due to their low optical loss, high refractive index, high transparency in the middle infrared region, and good thermal, mechanical and chemical properties [1,2]. Addition of Sb to the Ge–Se system strengthens the material by generating stable Sb–Se bonds and cross-linkages between the chains of Ge–Se and Sb–Se structural units [3]. Due to the strong influence of Ge/Sb ratio and, hence the structural arrangement on the physical properties of these glasses, during the last decade the optical, electronic and microstructure properties of Ge–Sb–Se glasses with compositions in broad ranges have been intensively investigated [4–17]. Despite of extended studies, the compositional dependence of optical properties of Ge–Sb–Se system is still of interest, especially for improvement of the transmission in the middle infrared spectral region.

As it is mentioned above, the physical properties strongly depend on the structural arrangement of glasses [18,19]. It has been suggested that by varying the chemical composition the glassy network undergoes structural changes reflected in a threshold transition in the physical parameters of the chalcogenide material. It has been theoretically predicted that a structural transformation from floppy to rigid glassy network occurs around the average coordination number, Z, of covalent bonds per atom $Z = 2.4$ [20]. Tanaka [21] has later predicted that structural transition from layered structure to three-dimensional (3D) network can exist around $Z = 2.67$. The nature of such a critical point or threshold may be topological or chemical. A chemical threshold can exist only in stoichiometric composition. By varying the glassy composition and moving away from stoichiometry, the topological threshold can be revealed. That is why the compositional dependence of the structure and physical properties of the ternary Ge–Sb–Se system is still of interest, especially when they are considered in term of coordination number Z. One of the main questions remains how the glassy

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composition affects the structure and optical properties of thin chalcogenide films from the Ge—Sb—Se system.

In our earlier optical studies of Ge—Sb—Se glasses [22], we have chosen glass compositions along with a pseudobinary line $(Ge_2Se_3)_x(Sb_2Se_3)_{1-x}$ of this system with non-stoichiometric elements (denoted also as $Ge_xSb_{40-x}Se_{60}$). By this way, we could separate the topological threshold from the chemical one and prove experimentally its existence around $Z = 2.67$ by studying the compositional dependence of the optical constants of the bulk glasses [22]. The latter were examined in a narrow spectral range (400–820) nm by spectroscopic ellipsometry (SE).

In this paper we present results on the optical and vibrational properties of $Ge_xSb_{40-x}Se_{60}$ compositions extending our ellipsometric studies on thin films from parent materials in a wide light spectrum from near ultraviolet to middle infrared (IR) range. In addition, we applied Raman spectroscopy in the IR terahertz region and, thus we could identify and assign not only the impurity chemical bonds from the IR spectroscopic ellipsometry (IRSE) but the basic chemical bonds from the Raman data analysis. To support the optical results, we also present some relevant results of the basic chemical bonds and their parameters, additionally evaluated from the data, obtained by neutron- and X-ray diffraction (ND and XRD) methods. Changes in the surface morphology were evidenced by Atomic Force Microscopy (AFM), proving that variation in the chemical composition of the films leads to different grains arrangements at the surface and, accordingly, different roughness values. The results are discussed in term of average coordination number Z. We would like to notice that several studies of Ge—Sb—Se system have been performed so far, but the compositional ranges in these reports either do not cover our chosen compositions [3,4,10–13,16] and/or they are related to bulk glasses [5–7,11]. From this point of view, our comprehensive investigations of the structure, optical, vibrational and morphological properties of the $Ge_xSb_{40-x}Se_{60}$ films would contribute to better understanding the threshold behaviors of Ge—Sb—Se thin films and would expand the compositional range of Ge—Sb—Se system for potential applications in optical devices, such as optical sensors, infrared-transmitting lens, etc.

2. Experimental details

The $Ge_xSb_{40-x}Se_{60}$ glasses with x = 15, 20, 25, 27, 32 and 35 at.% were prepared from elements of 99,999% purity. Appropriate quantities from elements were sealed into quartz ampoules after evacuation down to a pressure of 10^{-3} Pa. The bulk glasses were synthesized by the conventional melt-quenching method in a rotary furnace at 950 °C and after homogenization for 24 h, the melts were quenched in air.

Part of the synthesized glasses was powdered serving as parent material for film preparation. The films with nominal compositions of $Ge_xSb_{40-x}Se_{60}$ were prepared by vacuum thermal evaporation onto quartz substrates at a chamber residual pressure of 10^{-4} Pa. The thickness of the films was controlled around 1.5 µm in situ by MIKI FFV quartz sensor device.

The influence of the glassy composition on the optical constants of the films was studied by SE measurements carried out on two distinct ellipsometers (J.A. Woollam Co. Inc.) aiming to cover a wide spectral range from UV to middle-IR [(0.193–33) µm]. In the UV-Near IR spectral range, the complementary SE measurements were performed on an apparatus, working in (193–1700) nm wavelengths region and at different angles of incidence within 50° and 70°. The SE measurements in middle-IR (IRSE) were performed in the 300–4000 cm^{-1} [(33–2.5) µm] spectral range and at angles of incidence of 50 and 70° with a resolution of 16 cm^{-1} and 20 scans. The accuracy of the n value in IR is within ± 0.05. The transmission spectra were obtained directly by the IRSE measurements done at zero angle of incidence.

At the SE data analysis, the wavelength λ function of the ellipsometric angles $\Psi(\lambda)$ and $\Delta(\lambda)$ were simulated by considering the samples as a two-layer optical system [substrate/1st layer (film)/2nd layer (surface roughness)] and using General Oscillator mathematical models of corresponding software (data acquisition and analysis supplied by J.A. Woollam Co. Inc.). In the SE fitting procedures of both types of measurements, the surface roughness was considered as a mixture of 50% material (film) and 50% voids (air) and was modeled by applying the Bruggemann's effective medium approximation theory [23].

From the spectroscopic ellipsometry data analysis the optical constants, namely the refractive index n and extinction coefficient k were calculated in the whole spectral range of (0.193–33) µm. By analyzing the n and k dispersion data in a proper spectral range, further we obtained the optical band gap energy E_g, oscillation energies E_0 and E_d. Considering the IRSE dispersion spectra of the quantities ε_2 and Im $(-1/\varepsilon)$ being representatives for absorption and dielectric loss in the material respectively, we identified the IR active vibrational modes attributed to impurity atoms and complexes in the chalcogenide films.

In order to detect the vibrational bands related to the basic chemical bonds in the glassy network, we also carried out Fourier Transform Raman (FT-Raman) measurements with a Bruker Vertex 70 spectrometer equipped with a RAM II module using a Nd: YAG laser (1064 nm) with variable power (1–500 mW) and LN_2 cooled Ge detector. The FT-Raman spectra were studied in far infrared region 50–350 cm^{-1} performing 512 scans with 4 cm^{-1} resolution and at a laser power of 500 mW. From several spectra recorded for each sample, the one with the most intense peaks was considered for data interpretation.

The basic Ge—Se and Sb—Se chemical bonds configurations in the parent glassy materials were demonstrated by neutron- (ND) and high-energy X-ray (XRD) diffraction measurements and applying the Reverse Monte Carlo (RMC) technique, which permits to reproduce the experimental data of a highly disordered structure. The ND and XRD measurements and RMC simulations are described in detail elsewhere [24]. Here we just intend to show some relevant details, additionally evaluated from the data given in [24]. In order to see better the chemical bonding, we showed the Bravais-cell models exemplified for the smallest ($Ge_{15}Sb_{25}Se_{60}$) and largest ($Ge_{35}Sb_5Se_{60}$) Ge contents in the studied glasses. The three-dimensional (3D) atomic-scale structural models of these samples were built with the use of RMC modeling based on diffraction data using the last configuration from both samples. Here we used the software package RMC^{++} [25].

In order to evaluate the morphology and the roughness of the Ge—Sb—Se films AFM measurements were performed in air, in non-contact mode, on XE100 apparatus from Park Systems. Sharp AFM tips (NCLR) from Nanosensors™ were used for image scanning. XEI program (v. 1.8.0 from Park Systems) was applied for image processing related to displaying and roughness estimation.

3. Results and discussion

3.1. UV-near infrared spectroscopic ellipsometry

From the ellipsometric data analysis in the UV–visible-near IR spectral range, the optical constants n and k, optical band gap energy E_g and film thickness were determined. By applying a General Oscillator model involving Lorentz and Gaussian oscillators, good fits of the $\psi(\lambda)$ and $\Delta(\lambda)$ spectra were achieved. This is illustrated in Fig. 1, where the experimental and best fit data is exemplified for the $Ge_{35}Sb_5Se_{60}$ film. The mean square error for the best fit is below 10.

The dispersion curves of the refractive index n and extinction coefficient k obtained from the best fit are presented in Fig. 2(a) and (b). For both quantities, a tendency to decrease the values is observed with increasing the Ge content and, correspondingly, decreasing the Sb content at a constant Se amount. The refractive indices of the films coincide with those for the bulk parent materials [22] in the corresponding (400–820) nm range. Although this range is comparatively narrow, the similar n values suggest that the real film composition is the same or close to that of parent glasses.

Above 800 nm, the extinction coefficient values became negligible