Surface topography and optical properties of Ge-Sb(As)-S-Te thin films by atomic-force microscopy and variable angle spectroscopic ellipsometry

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Abstract. Thin films were evaporated from powdered GeₓSb(As)₄₀ₓS₅₀Te₁₀ (x=10, 20 and 27) glassy materials and their optical properties and surface morphology were studied by spectroscopic ellipsometry, performed in the UV-VIS-NIR range, and AFM imaging. For both kinds of quaternary systems, the optical constants (n and k) values decreased with increasing the Ge content in the films, their values being smaller for the GeₓAs₄₀₋ₓS₅₀Te₁₀ compositions. All films were transparent (k = 0) above 800 nm. The optical band gap energy increased with the Ge content; its value was larger for the GeₓAs₄₀₋ₓS₅₀Te₁₀ compositions. The AMF images revealed surfaces which are cracks-free and fully covered with uniformly distributed grains having particular structure depending on the film composition. For all the evaporated films, the average mean square (RMS) roughness did not exceed 5 nm, giving evidence for sufficiently high smoothness.

1. Introduction
The ternary Ge-Sb-S and Ge-As-S glasses with nonstoichiometric compositions have been the subject of intensive studies and their properties are well established. The introduction of a small amount of Te into these glasses alters the glassy structure and optical properties. An important advantage of tellurium-containing glasses is that due to the heavier mass of Te the transmission in the infrared region is shifted toward the longer wavelengths. Therefore, telluride glasses and thin films from quaternary systems are potential candidates for integrated optics due to their high refractive index and photosensitivity, as well as their transparency in the infrared spectral region. For optical device application, the homogeneous surface morphology and small roughness are very important in order to reduce to minimum the optical loss by light scattering and the optical transmission deterioration. While a large number of papers have dealt with thin films from ternary glasses [1-3], there have been few reports in the literature concerning the structure and properties of thin films prepared from quaternary glasses Ge-Sb(As)-S-Te [4-6].

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In this paper we present results concerning the effect of the glass composition on the optical properties and surface morphology of Ge_{x}Sb(As)_{40-x}S_{50}Te_{10} chalcogenide thin films evaporated from the powdered parent glassy material. As tools, spectroscopic ellipsometry (SE) and atomic-force microscopy (AFM) were applied [7-10].

2. Experimental details

The bulk glasses with composition of Ge_{x}Sb(As)_{40-x}S_{50}Te_{10} (x=10, 20, 27 atomic percent) were prepared by the conventional melt-quenching method from 5N purity elements. The syntheses were performed in evacuated quartz ampoules (residual pressure of 10^{-3} Pa) using a rotary furnace. The ampoules were heated up to 950°C and were kept at this temperature for 24 h while rotating the furnace so that the melt be homogenized. After 24 hours, the ampoules were pulled out from the furnace and were quenched in air. The materials thus obtained were powdered.

The films were deposited on glass substrates by vacuum evaporation of powdered parent glassy materials. The thickness of the films was measured by a quartz microbalance during evaporation and determined more precisely from the SE data analysis.

The ellipsometric measurements were performed on a Variable Angle Spectroscopic Ellipsometer (VASE) (J.A.WoollamCo.) within the wavelength region of 250–1700 nm and at different incidence angles varying from 50° to 70°. The optical parameters, refractive index n, extinction coefficient k, absorption coefficient α, optical band gap energy $E_{og}$, and the thicknesses of the films were evaluated from the SE data analysis. The film thickness and the optical constants were obtained with an accuracy of ±0.2 nm and ±0.005, respectively. In the SE data simulation, a two-layer optical model was used as the actual surface roughness was included in the second top-layer with a composition of 50% film and 50% voids. In the spectral range of 400-1700 nm, where the films were expected to be transparent, the optical constants were determined using Cauchy’s equation. Below 400 nm, general oscillator approximation was applied to obtain the optical parameters. An iterative least-squares method was used for minimizing the difference (mean square error) between the experimental data and the theoretical one.

The surface morphology of the films was studied by recording AFM images in intermittent contact mode (Easy Scan2 from Nanosurf) using sharp tips (NCLR type) with a radius of curvature of less than 10 nm (typically 7 nm).

3. Results and discussion

The dispersion curves of the refractive index n and extinction coefficient k for the compositions studied are presented in figure 1. The common feature is that the n and k values of the Ge_{x}Sb(As)_{40-x}S_{50}Te_{10} and Ge_{x}As(Se)_{40-x}S_{50}Te_{10} (x=10, 20, 27) compositions. Inset in (a) presents the n($\lambda$=500 nm) and $E_{og}$ values vs. As(Sb) at. %.

Figure 1. Dispersion curves of the refractive index n (a) and extinction coefficient k (b) of films with Ge_{x}Sb(As)_{40-x}S_{50}Te_{10} and Ge_{x}As(Se)_{40-x}S_{50}Te_{10}(x=10, 20, 27) compositions. Inset in (a) presents the n(\lambda=500 nm) and $E_{og}$ values vs. As(Sb) at. %.
compositions are larger than those for Ge$_{x}$As$_{40-x}$S$_{50}$Te$_{10}$ ones. For both compositions, the $n$ and $k$ values tend to decrease as the Ge content increases. For all films, the $k$ values approach zero above 800 nm indicating good transparency in the spectral range of 800-1700 nm.

The results from the SE data simulations, namely, the thickness of each sub-layer and the refractive index $n$ taken at $\lambda = 500$ nm of the chalcogenide films studied are presented in table 1. As is seen, a surface layer of considerable thickness representing the surface roughness is obtained, it is thicker for the Ge$_{x}$Sb$_{40-x}$S$_{50}$Te$_{10}$ compositions. The thickness of this top-layer is in good correlation with the peak-to-valley values obtained from the corresponding AFM image analysis, for the Sb-series of films, but exhibits some discrepancies for the As-based series due to the presence of superficial larger grains.

| Glassy composition | Thickness of 1st layer $[\text{nm}]$ | Thickness of 2nd layer (roughness) $[\text{nm}]$ | $n$ at $\lambda = 500$ nm | $E_{og}$ [eV] |
|--------------------|--------------------------------------|-----------------------------------------------|-------------------------|--------------|
| Ge$_{10}$As$_{30}$S$_{50}$Te$_{10}$ | 1557.94 | 6.62 | 2.84 | 1.69 |
| Ge$_{20}$As$_{20}$S$_{50}$Te$_{10}$ | 1887.67 | 10.38 | 2.82 | 1.72 |
| Ge$_{27}$As$_{13}$S$_{50}$Te$_{10}$ | 1546.82 | 8.91 | 2.79 | 1.80 |
| Ge$_{10}$Sb$_{30}$S$_{50}$Te$_{10}$ | 1433.60 | 14.70 | 3.38 | 1.54 |
| Ge$_{20}$Sb$_{20}$S$_{50}$Te$_{10}$ | 1385.67 | 19.90 | 3.16 | 1.65 |
| Ge$_{27}$Sb$_{13}$S$_{50}$Te$_{10}$ | 1341.78 | 27.33 | 3.08 | 1.72 |

Figure 2. 2D AFM images (shaded map) at the scale of (8$\mu$m×8$\mu$m) showing the topography of the Ge$_{x}$Sb$_{40-x}$S$_{50}$Te$_{10}$ and Ge$_{x}$As$_{40-x}$S$_{50}$Te$_{10}$ ($x=10, 20, 27$) films; the corresponding composition and root mean square (RMS) roughness values are presented below each image.
The optical band gap energy $E_{og}$ was derived from the absorption coefficient $\alpha$ values ($\alpha=4\pi k/\lambda$) by constructing $(\alpha h \nu)^{1/2}$ versus photon energy ($h \nu$) Tauc plots for indirect transitions (inset in figure 1b). The linear part of the Tauc plot was extrapolated to $\alpha = 0$; the intersection with the energy axis gave the optical bandgaps $E_{og}$ of the films. The $E_{og}$ values are also presented in table 1. One can see that Ge$_{x}$Sb$_{40-x}$S$_{50}$Te$_{10}$ compositions possess band gap energies lower that those for Ge$_{x}$As$_{40-x}$S$_{50}$Te$_{10}$ compositions (inset in figure 1a). For both kinds of compositions, the $E_{og}$ values increase with increasing the Ge content in the film.

Figure 2 presents the 2-dimensional topographic AFM images taken from a 8$\mu$m×8$\mu$m scanning area for the quaternary chalcogenide films, for both series with Ge$_{x}$Sb$_{40-x}$S$_{50}$Te$_{10}$ (first row) and, respectively with Ge$_{x}$As$_{40-x}$S$_{50}$Te$_{10}$ (second row), together with their corresponding root-mean-square (RMS) roughness values. As can be seen, no major defects on the surface are visible at the investigated scale. The films with Sb-containing compositions exhibit smoother surfaces as compared to those with As-containing compositions. Larger grains are formed on the surface of films with Ge$_{x}$As$_{40-x}$S$_{50}$Te$_{10}$ compositions, the biggest size grains being on the surface of the film with 20 at. % As content.

Conclusions
Quaternary chalcogenides films with continuous, homogeneous, smooth and cracks-free surface were deposited by evaporation on glass substrate. The optical constants values ($n$ and $k$) were determined by analyzing the SE data. They show a tendency to decrease as the Ge content increases for both chalcogenide systems. The films are transparent in the infrared spectral range starting from ~700 nm. The transmittance values are within 80-85 %. The optical band gap energy values of the Ge-Sb-S-Te system are lower in comparison with those for the Ge-As-S-Te system.

The AFM images revealed films surface fully covered with uniformly distributed grains and having particular structure depending on the film composition. For all films evaporated, the average roughness does not exceed 5 nm, giving evidence for a sufficiently low roughness.

Acknowledgements
The financial support of Romania-Bulgaria Inter-academic exchange program is gratefully acknowledged.

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