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Large (GeTe):(Sb₂Te₃) ratio phase change memory thin films

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ABSTRACT

Phase change memory thin films from Ge-Sb-Te system with large (GeTe):(Sb₂Te₃) ratio have been deposited via UV pulsed laser deposition technique. The studied compositions were Ge₆Sb₂Te₉, Ge₈Sb₂Te₁₁, Ge₁₀Sb₂Te₁₃, and Ge₁₂Sb₂Te₁₅. Physico-chemical properties of the Ge-Sb-Te thin films, based on the scanning electron microscopy with energy-dispersive X-ray analysis, X-ray diffraction and reflectometry, atomic force microscopy, optical reflectivity, sheet resistance temperature dependences, and variable angle spectroscopic ellipsometry measurements, were studied in order to assess the effect of chemical composition of the deposited layers. All the obtained data confirm the importance of GeTe content in (GeTe)_{1-x}(Sb₂Te₃)_x thin films.

Keywords: chalcogenides, thin films, Ge-Sb-Te, phase change memory materials

1. INTRODUCTION

During the last few decades, the thin films from Ge-Sb-Te or Ag-In-Sb-Te system have been in focus of research of many scientists¹⁻⁷. The main reason is the fact that these materials are able to transform quickly and reversibly between amorphous and crystalline phases as described first by Ovshinsky⁸. Phase transition can be reversibly switched by varying the electric field or temperature when heating is performed using a laser pulse in optical recording applications⁷. The unique characteristics of phase change memory materials from Ge-Sb-Te system are based on huge optical reflectivity or electrical conductivity changes proceeding upon phase transition⁹.

Optimization of employed materials has led to the development of three generation of optical products. Apart from compact disk (CD), digital versatile disks (DVD), Blu-ray disk (BD) or high-definition digital versatile disks (HD DVD) were developed². A material commonly used in early optical discs was Ge₂Sb₂Te₅, where the ratio (GeTe):(Sb₂Te₃) ~ 2:1. Other particular composition from Ge-Sb-Te system is Ge₈Sb₂Te₁₁. Here, (GeTe):(Sb₂Te₃) ratio ~ 8:1. This material is used for the BD. The reasons for the application of Ge₈Sb₂Te₁₁ are fast encoding rate, high stability of the amorphous phase, and also high optical contrast between crystalline and amorphous states in the blue-violet spectral region¹⁰⁻¹⁵.

For the fabrication of Ge-Sb-Te thin films, magnetron sputtering^{1, 16, 17}, thermal evaporation^{18, 19}, chemical vapor deposition^{20, 21} or also atomic layer deposition²² can be used. Apart from mentioned techniques, pulsed laser deposition (PLD) is a suitable deposition method for the thin films growth too. Advantages of PLD concern mainly its simplicity, easy process control, high deposition rate, and often stoichiometric transfer of the material to the films²³⁻²⁵. Our group already reported applicability of PLD for fabrication of different chalcogenide thin films²⁶⁻²⁹.

The aim of this work is to combine PLD as an advanced technique for thin films growth with the fabrication of an important class of inorganic materials represented through (GeTe)_{1-x}(Sb₂Te₃)_x layers with different, but high proportion of GeTe. Indeed in this paper, Ge-Sb-Te thin films with different (GeTe):(Sb₂Te₃) ratio, specifically 6:1, 8:1, 10:1, and 12:1, i.e. Ge₆Sb₂Te₉, Ge₈Sb₂Te₁₁, Ge₁₀Sb₂Te₁₃, and Ge₁₂Sb₂Te₁₅ layers, were fabricated by PLD. Their characterization in as-deposited state (amorphous phase) and crystalline state (after annealing) is performed on the basis of atomic force microscopy (AFM), scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and reflectometry (XRR), electrical resistivity, and variable angle spectroscopic ellipsometry (VASE) data.

2. METHODOLOGY

2.1 Fabrication of samples

Amorphous thin layers were fabricated using polycrystalline chalcogenide targets with nominal composition of $\text{Ge}_6\text{Sb}_2\text{Te}_9$, $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, and $\text{Ge}_{12}\text{Sb}_2\text{Te}_{15}$, i.e., $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$, where $x = 0.14, 0.11, 0.09$ and 0.077 . The polycrystalline targets were prepared by the melt quenching method with high-purity elements (Ge, Sb, and Te of 5N purity) in evacuated and sealed silica ampoules while the melting was done at a temperature of 960°C .

For the fabrication of amorphous thin films, the PLD technique was used employing a KrF excimer laser with parameters specified below: wavelength of 248 nm, output energy of 300 ± 3 mJ per pulse, pulse duration of 30 ns, repetition rate of 20 Hz, energy fluence on the target $\sim 2.6 \text{ J cm}^{-2}$, and the number of laser pulses 6000-7200. The laser beam was incident on the target under an angle of $\sim 45^\circ$. Amorphous thin films were deposited in a vacuum chamber (background pressure $< 4.2 \times 10^{-4}$ Pa). The substrates used for PLD (chemically cleaned microscope glass slides, Si wafers) were positioned parallel to the target surface at target to substrate distance of 5 cm. Both the target and the substrates were rotated in off-axis geometry in order to avoid damage to the target and to improve the thickness homogeneity of the films, respectively. To study the effect of annealing, as-deposited films were annealed in inert atmosphere (pure argon) at the temperature of 300°C (above crystallization temperatures) for 120 min and then slowly cooled down to room temperature.

2.2 Characterization of structure, morphology, and chemical composition

XRD experiments were performed on a PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano geometry, equipped with an Anton Paar HTK 1200 oven chamber, X'Celerator detector and using $\text{Co K}\alpha$ radiation. Patterns within the $10^\circ \leq 2\theta \leq 75^\circ$ range were collected in 47 minutes at constant temperatures, starting at room temperature and up to 400°C with steps of 10 or 5°C . Dried He atmosphere was used to prevent oxidation of the samples and a $1^\circ\text{C}/\text{min}$ heating rate was applied between steps. XRR measurements were performed at room temperature within as-deposited thin films, later on the annealed samples after the high-temperature XRD. A Bruker D8 Discover diffractometer with a horizontal goniometer and a $1/4$ -circle Eulerian cradle was used - $\text{Cu K}\alpha$ radiation, Göbel mirror and LynxEye detector in a 0D-mode.

Atomic force microscopy (Solver NEXT, NT-MDT) was used to study topography of Ge-Sb-Te thin films within typical scanned area $10 \mu\text{m} \times 10 \mu\text{m}$ (or $5 \mu\text{m} \times 5 \mu\text{m}$) in a semicontact mode.

The surface of the GST films and their chemical composition were studied using scanning electron microscopy (SEM, JEOL JSM 6400) linked with energy-dispersive x-ray analyzer.

2.3 Characterization of electrical and optical properties

Two variable angle spectroscopic ellipsometers (J. A. Woollam Co., Inc., Lincoln, NE, USA) were employed for the optical characterization of studied materials: first ellipsometer with automatic rotating analyzer for the spectral range 300 nm - $2.3 \mu\text{m}$ (UV-NIR), measuring 100 revolutions with wavelengths steps of 20 nm at selected angles of incidence (50° , 60° , and 70°); second ellipsometer with rotating compensator for 1.7- $20 \mu\text{m}$ range using angles of incidence as above, 50 scans, 15 spectra per revolution, resolution of 16 cm^{-1} . For the analysis of VASE data in broad measured spectral region (300 nm - $20 \mu\text{m}$), we used Cody-Lorentz (CL) model which includes the correct band edge function, weak Urbach absorption tail description as well as Lorentz oscillator function³⁰; this model is appropriate for the description of amorphous chalcogenides optical functions^{26, 31}. Drude-type contribution for free carriers was added to the CL model for crystallized samples.

Simultaneous optical reflectivity (R) and sheet resistance (R_s) temperature dependences measurements (at the heating rate of 2°C min^{-1}) were realized with a homemade setup employing 650 nm laser diode and using aluminum layer reflectivity as a standard ($R_{Al} \sim 100\%$). Sheet resistance measurements were carried out using a four-point probe based on van der Pauw method³².

3. RESULTS AND DISCUSSION

Thin films fabricated by PLD were amorphous and homogeneous as confirmed by optical or electron microscopy and XRD patterns. The SEM and AFM data showed smooth surface of thin films, without cracks and corrugations, indicating high quality of the fabricated layers. For all amorphous thin films, root mean square (RMS) roughness values determined by AFM were typically found to be lower than ~0.7 nm. Consequently, roughness determined by AFM for crystallized layers was comparable or slightly larger (0.7-0.9 nm).

EDX analysis shows that - in comparison with the nominal composition - the as-deposited films are slightly overstoichiometric in Ge content (4-6 at.%), while Sb content is preserved very well (overstoichiometry of <1 at.%) and Te deficit is present for all the layers (<7 at.%). The tellurium deficiency could be caused by higher volatility of the element in comparison with Ge or Sb. The error limit of the used EDX method is ± 1 at.%.

Room temperature XRD patterns confirm amorphous state of the deposited Ge-Sb-Te layers. The amorphous films start to crystallize at around 165 °C and do not change approximately up to 315°C. When indexing patterns measured at 260 °C as an example, cubic symmetry fits experimental data well. At higher temperatures, diffraction peaks of the thin films move slightly towards lower angles which is consistent with the thermal expansion of the cubic unit cell. Above 315 °C, for three of the Ge-richest samples – $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, and $\text{Ge}_{12}\text{Sb}_2\text{Te}_{15}$, one can observe changes in XRD data, which are consistent with a presence of traces of cubic Ge. This finding could be connected with observed overstoichiometry of Ge in the deposited films.

The crystallization of Ge-Sb-Te films was also evaluated on the basis of temperature dependences of thin films' sheet resistance. The crystallization of the amorphous $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$ PLD films was identified in the region of ~164-172 °C for as indicated by abrupt decrease of sheet resistance and more precisely determined as peak temperatures of $d(\ln R_s)/d(1/T)$ first derivatives. The crystallization temperatures are only slightly dependent on decreasing content of Sb_2Te_3 in the films and are in very good agreement with temperature dependent XRD data. Simultaneous reflectivity measurements at 650 nm show an abrupt increase of reflectivity on crystallization; it grows with increasing content of GeTe in the layers reaching saturated values of ~40-45% larger in crystalline state in comparison with the amorphous ones.

The VASE experimental data were analyzed using a three layer model of optical functions: (i) the substrate (float glass slides), (ii) the chalcogenide thin film, and (iii) the surface roughness layer. To describe the optical response of the chalcogenide layers in the whole measured spectral region, CL model was exploited. For the crystallized thin films, Drude-type contribution was added to the CL model. The surface layer was defined by the effective medium approximation (thin film material mixed with 50% voids). The suitability of the CL model for the analysis of VASE data was confirmed by low values of mean square error of the fitting procedure ($\text{MSE} < 2.8$).

Resulting best fit optical functions, i.e. refractive index and extinction coefficient spectral dependences of amorphous as well as crystalline GST thin films are shown in Figs. 1 and 2. Consequently, optical band gap values were extracted from VASE data employing CL model. Other data resulting from the application of CL model for the analysis of VASE data (thickness ratios between crystalline and amorphous state, thickness nonuniformity values, surface roughnesses, and optical contrast defined as $\Delta n + i\Delta k \approx n, k(\text{crystalline}) - n, k(\text{amorphous})$ at the wavelength of ~400 nm (~3.1 eV)) were evaluated as well.

In studied compositional region, the refractive index and extinction coefficient spectral data are not very dependent of chemical composition, especially in case of amorphous layers (Figs. 1, 2). In crystallized films, one can easily observe an increase of extinction coefficient for energies below ~0.4 eV, which is an indication of lower resistivity of the layers. Optical band gap values show independence on chemical composition; they correlate very well with data measured on GeTe (0.59 eV) and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (0.63 eV) PLD films taking into account error limits in determination of band gap (± 0.01 eV). On crystallization, band gap values of studied Ge-Sb-Te thin films decrease of about 0.2 eV in accordance with previously reported results for $\text{Ge}_2\text{Sb}_2\text{Te}_5$.^{17, 33}

The thickness of all the as-deposited samples under study, as determined by VASE data analysis, was in the range of ~150-200 nm. Contrary, the thickness of annealed layers was ~10-12% lower in comparison with the thicknesses of amorphous layers. The decrease of the thickness upon crystallization of amorphous Ge-Sb-Te films is perfectly coherent with value observed for GeTe PLD films (12.5%) reported earlier.²⁶

The values of optical contrast $\Delta n + i\Delta k$ at 400 nm, which is important for Blu-ray disc technology, for the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ and GeTe films prepared by pulsed laser deposition are of $-1.13+i0.98$ and $-1.98+i1.45$, respectively²⁶. Optical contrast values reported here lie between mentioned values in accordance with the chemical composition of the films. It is evident that larger content of GeTe in GST layers leads to higher value of optical contrast. We note that optical contrast values calculated for $\text{Ge}_6\text{Sb}_2\text{Te}_9$ and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ PLD thin films are in good agreement with the ones published by Yamada.⁶

The thickness ratios (crystallized/amorphous) and densities of as-deposited as well as crystallized GST thin films were extracted from XRR data. One can conclude that upon crystallization, the thicknesses of the films decrease of $\sim 9\text{-}11\%$ in excellent agreement with the values obtained using VASE. The densities of the films increase of $\sim 5\text{-}11\%$ on crystallization. Observed density increase agrees well with XRR data published for Ge-Sb-Te films such as $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($\sim 6\%$ increase),³⁴ $\text{Ge}_4\text{Sb}_1\text{Te}_5$ ($\sim 9\%$ increase),³⁵ and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ ($\sim 9\%$ increase)¹¹ prepared by DC magnetron sputtering.

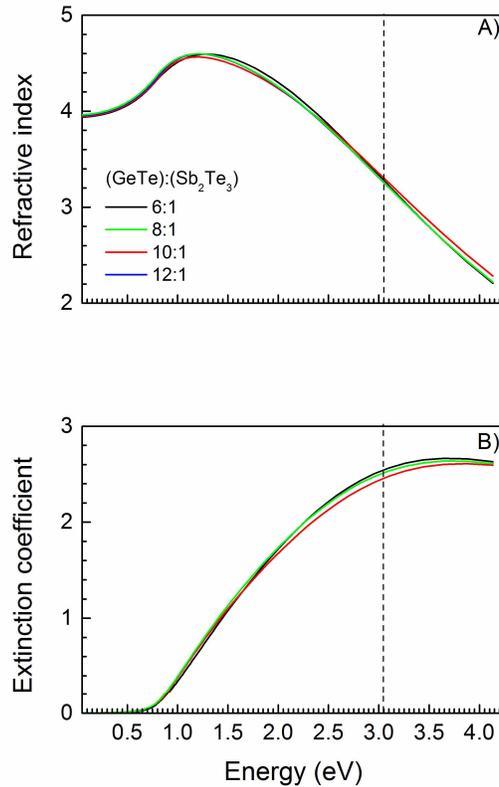


Figure 1. Optical functions of amorphous PLD $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$ thin films: A) spectral dependences of refractive indices, B) spectral dependences of extinction coefficients. Vertical dashed lines represent wavelength of 405 nm used in BD technology.

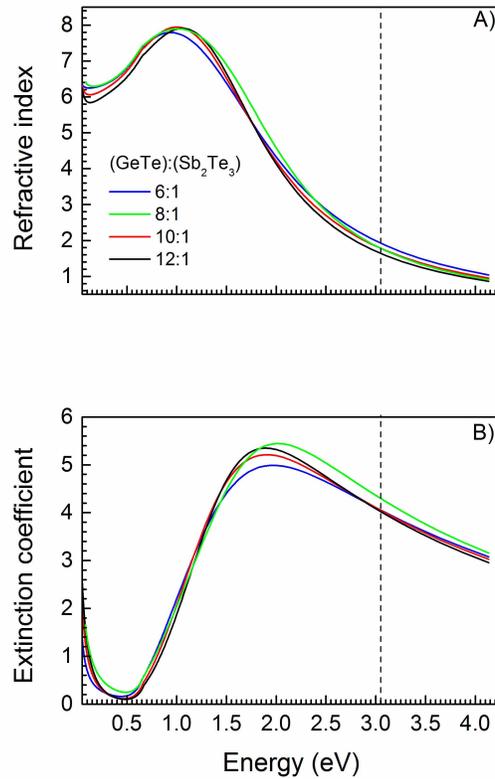


Figure 2. Optical functions of crystallized PLD $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$ thin films: A) spectral dependences of refractive indices, B) spectral dependences of extinction coefficients. Vertical dashed lines represent wavelength of 405 nm used in BD technology.

4. CONCLUSIONS

$(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$ amorphous thin films with high content of GeTe ($\text{Ge}_6\text{Sb}_2\text{Te}_9$, $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, $\text{Ge}_{10}\text{Sb}_2\text{Te}_{13}$, and $\text{Ge}_{12}\text{Sb}_2\text{Te}_{15}$) were fabricated by the pulsed laser deposition. The high quality of the layers is confirmed by SEM and AFM observations. On annealing, the amorphous films undergo phase change to cubic symmetry layers, as deduced from temperature dependent XRD patterns. Optical functions and electrical resistance of the films change drastically upon crystallization of the films, leading to large optical (up to ~ 0.21 at 405 nm reflectivity contrast) and electrical (almost 6 orders of magnitude sheet resistance decrease) differences between amorphous and crystalline phases. Optical band gap values (~ 0.6 and ~ 0.4 eV for amorphous and crystalline films, respectively) are almost independent of GeTe content. Increase of thicknesses, densities, and roughnesses of the layers arising due to the crystallization accompany huge changes of optical and electrical properties. All the obtained data confirm the importance of GeTe content in $(\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x$ thin films.

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