Effect of bismuth ion implantation on the crystallization temperature of the amorphous $Ge_2Sb_2Te_5$ thin films

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Abstract. Bismuth doped $Ge_2Sb_2Te_5$ thin films were prepared by magnetron sputtering of $Ge_2Sb_2Te_5$ target with following ion implantation of Bi. Thin film compositions and elemental distribution across the film thicknesses were determined. An amorphous state of the as-deposited undoped and Bi-doped $Ge_2Sb_2Te_5$ thin films was confirmed by X-ray diffraction. Temperature dependencies of the resistivity for Bi-doped $Ge_2Sb_2Te_5$ thin films were measured. Two resistivity drops due to the crystallization and transformation from the cubic to hexagonal structure were determined. Decreases of the onset temperatures for the first and second transitions from 169.3 to 120.3 °C and from 188.0 to 153.0 °C with the increase of Bi concentration were found. It was shown, that the resistivity of the amorphous films sufficiently decreases with Bi concentration, while the variation of resistivity for the crystallized state is much smaller.

1. Introduction

Phase change memory (PCM) is one of the most perspective candidates for the next generation of non-volatile memory devices [1]. Moreover, PCM pretends to become in future universal memory joining advantages of non-volatile memories and high-speed random access memories.

Currently, chalcogenide semiconductors on the quasi-binary line GeTe-Sb_2Te_3 are considered to be most promising programmable materials for application in the phase change memories [2-5]. The most widely investigated and commonly used among them is $Ge_2Sb_2Te_5$ (GST225) compound due to the complex of properties.

Despite of a recent progress in PCM technology improvement of the PCM characteristics is still required, and some material properties must be optimized. One of the problems is connected with the need of decreasing the data processing time of PCM to the level comparable with that of the random access memory (~10–50 ns) [6]. For this reason, it is necessary to optimize the crystallization parameter of the PCM material.

Effective methods for controlling PCM parameters by varying the PCM material properties are required. Doping and modification of the structural matrix by dopants are used as one of the effective methods for controlling different properties of the materials. However, modification of the chalcogenide glass characteristics is complex problem due to their low sensitivity to doping, and adequate impurities must be found. Previously [7-9] we have shown that doping by Bi have significant impact on the thermal, electrical and optical properties and crystallization kinetics of GST225. Bismuth is one of the elements that can change the type of conductivity in GST225 [10,11]. In addition, the use of Bi doping of Ge-Sb-Te allows lowering RESET current [12].

Selection of the dopant is based on the following assumptions. Bi is isomorphous with Sb, which must lead to the replacement doping mechanism with minimum deformations and mechanical stresses. Presence of cation vacancies in the structure of GST225 with concentration of 10-20 % [13] will benefit this mechanism. In this case formation of weaker Bi-Te bonds than Sb-Te will modify thermal properties and crystallization kinetics of GST225 [14].

Doped GST225 thin films can be obtained using such methods as thermal evaporation in vacuum, magnetron sputtering, ion implantation. Up to now most studies are focused on the incorporation of different impurities into the phase change materials using thermal evaporation in vacuum of the synthesized material, magnetron co-sputtering and reactive magnetron sputtering techniques [11, 15]. Thin films fabricated by thermal evaporation have problems with reproducibility of composition, while magnetron sputtering needs new target for each new material. Ion implantation is less implemented [2, 11, 16, 17], but this method is very good tool for precise controlling the depth and amount of the implanted ions by adjusting the incident energy level and dose [18]. In addition, ion implantation method is compatible with Si technology and current integrated circuit fabrication, and can be used on large areas and for large scale production.

So, the aim of this work was study of the effect of bismuth ion implantation on the crystallization temperature of amorphous GST225 thin films.

2. Methods

Thin films were prepared by DC magnetron sputtering of monolithic polycrystalline $Ge_2Sb_2Te_5$ target at room temperature. The pressure of Ar during the process was $5 \cdot 10^{-3}$ Torr, the sputtering power was 100 W. Silicon and oxidized Si substrates were used. The thicknesses of thin films were controlled by the atomic force microscopy (NT-MDT Solver Pro), and were ~30 nm.

Ion implantation of bismuth was carried out in "Raduga" ion implanter with the ion energy of 80 keV. The beam accelerating voltage was calculated by using the SRIM code in order to implant ions on the required depth taking into account the measured charge state compositions. We used 96, 250 and 560 $\mu C/cm^2$ doses for the Bi ion implantation into GST225 samples.

Thin film compositions and elemental distribution across the film thicknesses were determined by Auger electron spectroscopy (AES, Physical Electronics PHI-670xi) and Time-of-Flight secondary ion mass (TOF-SIMS, IonTOF ToF.SIMS 5) spectrometry. Combination of X-ray diffraction (XRD, Rigaku SmartLab) and transmission electron microscope (TEM, FEI Titan 80–300) was used to determine evolution of the structure of investigated films.

The samples for measurement of resistivity temperature dependencies were prepared as planar structures ($Si//SiO_2/TiN/W/Bi$-doped GST225), the distance between W electrodes was 1.3 mm. Annealing of the experimental structures was performed using Linkam HFS600E-PB4 up to 400 °C with heating rate of 1 °C/min. Resistivity measurements were performed with using of Agilent E3647A DC Power Supply and Keithley 6485 picoammeter. Ar flow through the camera during measurements prevented the oxidation of GST225.

3. Results and discussion

Results of the Auger spectrometry for the undoped GST225 are presented in figure 1, a. The composition of the undoped film is close to $Ge_2Sb_2Te_5$ and has uniform elemental distribution along the film thickness. The Bi concentration was obtained only for the thin films after implantation with "maximum"

dose, which is connected with the resolution of the used spectrometer. The "maximum" implantation dose provides the average bismuth concentration in GST225 film of 5.7 at. % Bi. The forms of the bismuth distribution for all investigated samples were obtained by TOF-SIMS (figure 1, b). Results have shown that the Bi profile of samples has a distribution characteristic for the ion implantation, the peak position of Bi profile was determined near 7.5 nm. The increase of bismuth ion dose during implantation allows increasing the intensity of the peak of Bi distribution. So, the four types of samples with different Bi concentrations were formed using different implantation doses and will be called by us as the "undoped", "minimum", "medium" and "maximum".
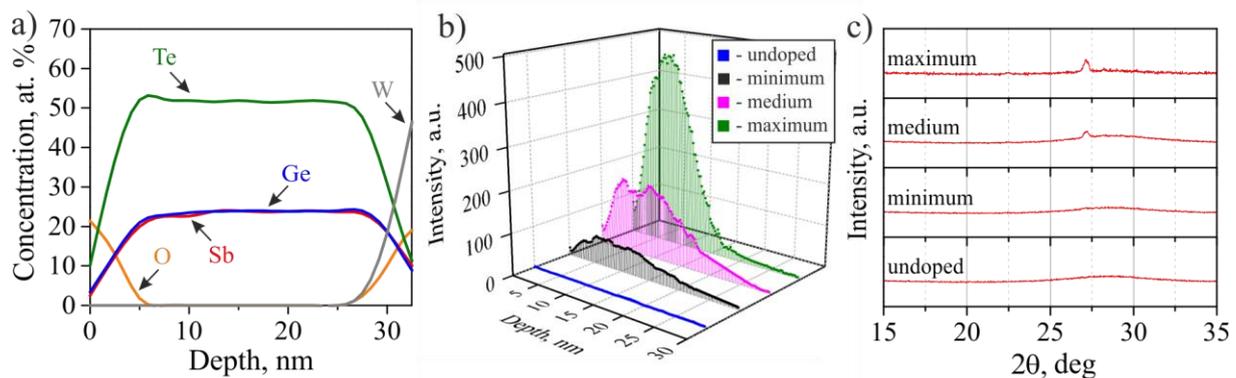

Figure 1. (a) Elemental distribution along the undoped GST225 thin film thickness according to Auger spectrometry. **(b)** Bismuth distribution according to TOF-SIMS and **(c)** X-ray diffraction patterns for the amorphous Bi-doped thin films.

An amorphous state of the as-deposited undoped and Bi-doped GST225 thin films was confirmed by the existence of broad halo with a maximum near $2\Theta \approx 27^0$ on the XRD patterns (figure 1(c)). The appearance of the peak with the background of amorphous halo for the "medium" and "maximum" samples is due to the small particles of the pure bismuth, which fell onto the film surfaces from the ion source.

Temperature dependencies of resistivity for Bi-doped GST225 thin films are presented in figure 2(a). The following features characteristic of the chalcogenide films can be distinguished for the determined dependencies. First, all investigated amorphous thin films have an exponential dependence of resistivity on temperature, which indicates an activation character of conductivity. Second, sharp drops of the resistivities for as-deposited films are observed in the range from 130 to 170 °C and is caused by the crystallization and formation of the metastable cubic state. Third, smoother decrease of resistivity near 300 °C shown in the insert of figure 2(a) was obtained for all investigated thin films excepted for the sample with the "maximum" implantation dose. This decrease can be explained by a transformation from the cubic to hexagonal structure, which is confirmed by the HRTEM measurements (figure 2(b)). It should be noted, that the results of TOF-SIMS (figure 2(c)) showed that annealing up to 180 °C did not cause noticeable redistribution of the elements. However, as can be seen from the figure annealing at 400 °C (above the temperature of the second transition) lead to the sufficient smoothing of Bi distribution.
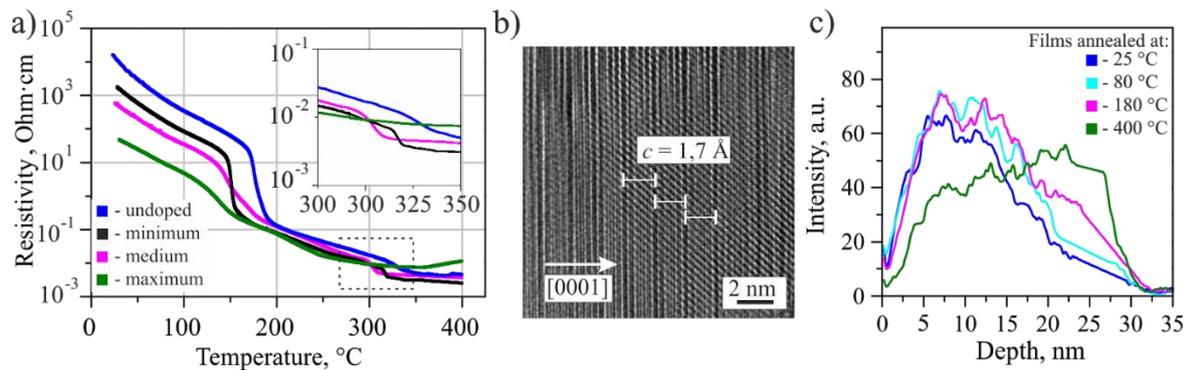
Figure 2. (a) Temperature dependencies of resistivity for Bi-doped GST225 thin films. **(b)** HRTEM image of the GST225 thin film after annealing at 400 °C. **(c)** Influence of the annealing temperature on the bismuth distribution along the thickness of the sample with minimally investigated Bi concentration ("minimum").

Parameters obtained from resistivity temperature dependencies are summarized in table 1, where T_{on1}, T_{end1}, T_{on2}, T_{end2} are onset and endset temperatures for the first and second transitions, respectively; E_a is the conductivity activation energy for amorphous films; ρ_a and ρ_c are resistivities for films in amorphous and crystalline states, which were determined at temperatures of 30 and 400 °C, respectively.

Table 1. Parameters obtained from the temperature dependencies of resistivity for Bi-doped GST225 thin films.

Dose	T_{on1}, °C	T_{end1}, °C	E_a, eV	ρ_a, $\Omega \cdot$ cm	ρ_c, $\Omega \cdot$ cm	ρ_a/ρ_c	T_{on2}, °C	T_{end2}, °C
Undoped	169.3	188.0	0.44	$1.0 \cdot 10^4$	$4.4 \cdot 10^{-3}$	$2.3 \cdot 10^6$	317.4	340.2
Minimum	147.4	155.3	0.40	$1.6 \cdot 10^3$	$2.5 \cdot 10^{-3}$	$6.4 \cdot 10^5$	315.0	319.5
Medium	132.2	175.1	0.37	$4.8 \cdot 10^2$	$3.6 \cdot 10^{-3}$	$1.3 \cdot 10^5$	302.6	308.9
Maximum	120.3	153.0	0.33	$4.7 \cdot 10^1$	$1.1 \cdot 10^{-2}$	$4.3 \cdot 10^3$	-	-

The resistivity of the amorphous films sufficiently decreases with Bi concentration, while the variation of resistivity for crystallized state is much smaller. This leads to a decrease in electrical contrast between amorphous and crystalline states, which may have a negative effect on the possible number of levels in the multilevel cells. However, bismuth ion implantation reduces the conductivity activation energy for as-deposited GST225 thin films, which can be due to the decrease of the mobility gap or redistribution of the localized states density. Also, determined onset temperatures of the first and second transitions decrease from 169.3 to 120.3 °C and from 188.0 to 153.0 °C with the increase of Bi concentration, respectively. The reason for this shift can be the formation of the Bi-Te bonds with lower binding energy (232 kJ/mol) compared with that of Sb-Te (277 kJ/mol) [19]. So, some characteristics of the devices based on the GST225 thin films can be improved by the bismuth ion implantation.

4. Conclusions

The influence of bismuth ion implantation on the resistivity temperature dependence of the GST225 thin films was investigated. Two resistivity drops due to the crystallization and transformation from the cubic to hexagonal structure were determined. Bismuth ion implantation into the GST225 thin films leads to the decrease of the onset temperatures for those transitions. Annealing at a temperature above the temperature of the phase transition into hexagonal structure leads to the sufficient smoothing of Bi distribution. In addition, it was shown that bismuth concentration effects on the resistivity of amorphous and crystalline states and electrical contrast of the GST225 thin film.

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