Influence of the Composition on the Thermoelectric and Electro-physical Properties of Ge-Sb-Te Thin Films for Phase Change Memory Application

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Influence of the composition variation along the quasi-binary line $GeTe-Sb_2Te_3$ on the thermoelectric and electro-physical properties of thin films was investigated. GST amorphous thin films have high Seebeck coefficients, which drops nearly on the order of magnitude after the crystallization. Temperature dependences of the resistivities were studied, and it was determined that crystallization temperature increases with moving along the quasi-binary line $GeTe-Sb_2Te_3$ from $GeSb_4Te_7$ to $GeSb_2Te_4$, and then to $Ge_2Sb_2Te_5$, while the phase transition temperature range decreases. Current-voltage characteristics of amorphous thin films have three voltage ranges with different dependencies due to the different mechanisms of charge carrier transport.

Keywords: Phase change memory, Ge-Sb-Te, quasi-binary line $GeTe-Sb_2Te_3$, Seebeck coefficient, Electrophysical properties.

1. INTRODUCTION

Last decade non-volatile phase change memory (PCM) devices are actively developed [1]. The writing and erasing operations in PCM devices are based on the reversible phase transitions between amorphous and crystalline states, and must be accompanied by the abrupt changes in optical and/or electrical properties.

PCM materials must have unique combination of properties. Some of the properties seem to be contradictory and quite difficult to be achieved. For this reason only few materials are actually useful for PCM application. The most promising programming materials are considered to be chalcogenide semiconductors on the quasi-binary line $GeTe-Sb_2Te_3$ [1-4]. Three compounds exist on this quasi-binary line: $Ge_2Sb_2Te_5$ (GST225), $GeSb_2Te_4$ (GST124), and $GeSb_4Te_7$ (GST147). As was shown by N.Yamada and coauthors [2] thermal properties and crystallization rate of GST materials sufficiently depend on the position on the quasi-binary line $GeTe-Sb_2Te_3$, which is important for PCM application.

These PCM materials are tellurium-based semiconductors and belong to the class of thermoelectric materials. They have extremely low thermal conductivities [5-7], high Seebeck coefficient [8], electrical conductivity, and so high thermoelectric properties, which stimulates interest also for thermoelectric application.

PCM cells experience multiple cycling with large current and temperature variations. In this case peculiarities of PCM materials can provide high thermoelectric effects, which can significantly influence the performance of the cell including programming current and reliability.

So, precise knowledge of thermoelectric properties for PCM materials is very important for the development of cell design. In addition, interplay of the thermoelectric and electro-physical properties must be taken into account.

However, the knowledge of thermoelectric and electro-physical properties and their correlation for the thin films of chalcogenide semiconductors on the quasi-binary line $GeTe-Sb_2Te_3$ is insufficient. The problem is complicated by the strong dependence of the Seebeck coefficient and electrical conductivity on the composition and position on the quasi-binary line, phase content, processing conditions, heat treatment and thermal history.

So, the aim of this work was investigation of the thermoelectric and electro-physical properties for the thin films of chalcogenide semiconductors on the quasi-binary line $GeTe-Sb_2Te_3$.

2. EXPERIMENT

The initial chalcogenide semiconductors GST147, GST124 and GST225 were synthesized with using of the mixture of elements with 99.99 % purity by the method described in [9].

Thin films were prepared by thermal evaporation in vacuum of the synthesized GSTs. Substrate temperature during the deposition did not exceed 50 °C.

Rutherford backscattering (RBS, $E_d = 1.0$ and $E_a = 2.7$ MeV at 135° scattering angle) was used for the analysis of thin film composition. Overlapping of the peaks on the spectra due to the neighbor position of Sb and Te in the Periodic table allowed to determine only ratios Ge/(Sb + Te), which were close to the theoretical values for all investigated compounds.

The polycrystalline and amorphous structures of the synthesized materials and as-deposited films, respectively, were checked by X-ray diffraction (XRD, Rigaku D/MAX, Cu Kα $\lambda = 0.15481$ nm). Annealing of thin films

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at temperatures higher than 150 °C is accompanied by the crystallization of the films.

Atomic force microscopy (NT-MDT SolverPro), scanning electron microscopy (Carl Zeiss NVision 40), optical microscopy (Carl Zeiss Axiovert 40 MAC) and surface profiler (Alpha Step) were used to investigate morphology of thin films. The thicknesses of films were detected with using of atomic force microscope (AFM), and were in the range from 100 to 150 nm.

According to the SEM data, it was found that as-deposited films had uniform surface morphologies. In addition, atomic-force microscopy indicated sharp modification of morphology after the heating. As-deposited films had island-like structure and annealing above 150 °C led to the increase of mean height of the islands nearly on the order of magnitude.

The set-up on the basis of multimeter HP 34401A-01 and power supply Agilent E3674 (fig. 1) was used for the investigation of thermopower and determination of the type of conductivity for investigated films. Samples containing Al electrodes and deposited upon them investigated thin films were fabricated on pyroceramics substrates. The distances between electrodes were 5 mm, and temperature gradient was 5 °C.
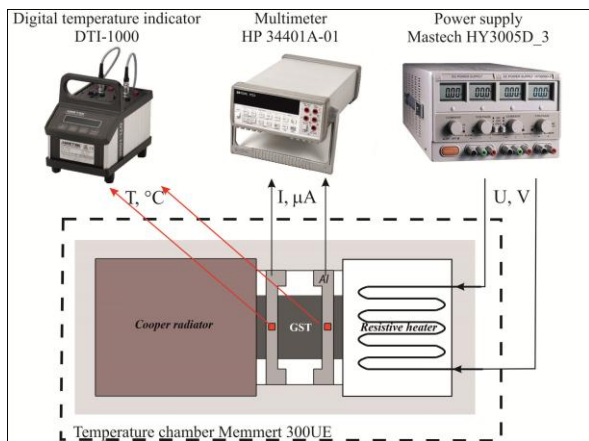
**Fig. 1** – Set-up for thermopower measurements

The research system on the basis of KEITHLEY 6486 and a voltage control unit NI6008 was used for the DC measurements. Current-voltage characteristics (CVC) of samples were obtained for the biases from 0.1 to 10 V at the room temperature. This research system was used also for the investigation of temperature dependencies of the resistivity of amorphous GST147, GST124 and GST225 thin films, which was measured from room temperature to 300 °C at heating rate of 1 °C/min for the bias of 0.7 V. For this purpose planar structures containing Al electrodes with fixed interelectrode distances, and deposited upon them GST thin film were fabricated on oxidized c-Si substrates. The GST thin films were covered with SiO_x layer by electron beam evaporation.

3. RESULTS AND DISCUSSION

Figures 2 and 3 present dependencies of Seebeck coefficient and resistances, respectively, for the films of GST147, GST124, and GST225 on annealing temperature. Samples were annealed in the temperature range

from room temperature to 300 °C during 30 min in air.

As can be seen from the figure three temperature ranges are clearly distinguished on the dependencies, which correlates with the results of the measurements of the resistivity's temperature dependencies for GST225, GST124, and GST147 thin films (fig. 4).
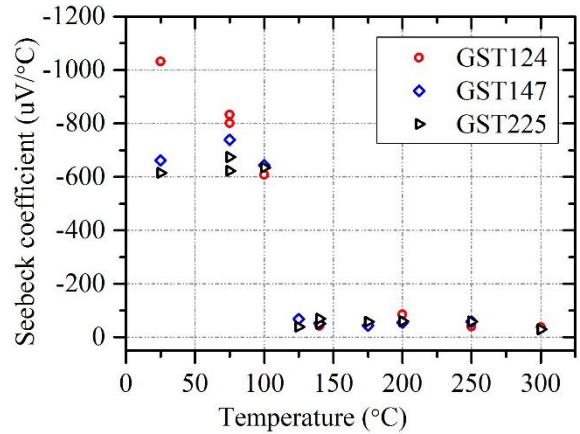
Fig. 2 – Dependencies of Seebeck coefficient on annealing temperature for investigated thin films

From room temperature up to 100 °C thin films have high Seebeck coefficient in the range from – 600 to – 1000 μV/°C. In the temperature range 100-150 °C drop of Seebeck coefficient is observed, which is due to the crystallization of the films. Following increase of the annealing temperature leads to the moderate decrease of the Seebeck coefficient. The drop of Seebeck coefficient due to the crystallization of the films correlates with the drop of resistance measured for these samples (fig. 3).

Measurements of thermoelectric power carried out for investigated thin films, showed that GSTs has a negative values of thermoelectric power, indicating on the dominating p-type conductivity. The negative sign of thermoelectric power and the resulting value of the Seebeck coefficient for the amorphous thin films is consistent with the data of [10].
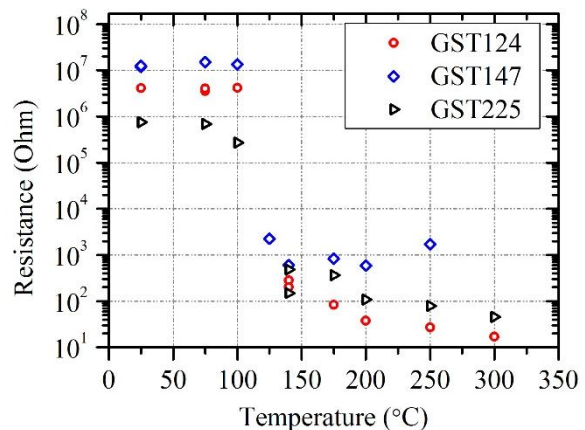
Fig. 3 – Dependencies of resistance on annealing temperature for investigated thin films

The temperature dependencies of resistivities for GST225, GST124, and GST147 thin films are shown in fig. 4. The results of the analysis of the resistivity tem-

perature dependencies are presented in the Table 1, where T_x and T_y are the onset and endset temperatures of the phase transition, $\Delta T_n = T_x - T_y$, ρ_a and ρ_c are resistivities at 20 and 250 °C, respectively.
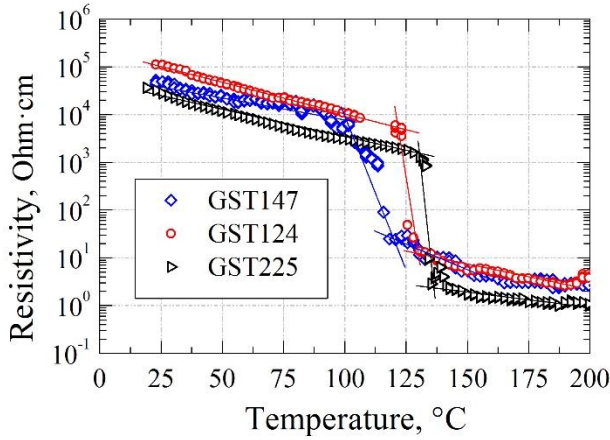
Fig. 4 – Temperature dependences of the resistivities for investigated thin films

The resistivity measurements showed that crystallization is accompanied by the drastic decrease of resistivity (see fig. 4). This sharp drop correlated with results of XRD and AFM investigations and data of optical measurements obtained earlier by ellipsometry [11]. Ratio of the resistivities of amorphous and crystalline states exceeds 10^4 (see Table 1), which is important for the reliable work of PCM.

Table 1 – Characteristics of thin film on the basis of compounds on the pseudobinary line Sb_2Te_3-GeTe

| Com-pounds	$T_x - T_y$, °C	ΔT_n, °C	ρ_a, Ohm·cm	ρ_c, Ohm·cm	ρ_a/ρ_c
	$\rho \sim T$				
GST147	100-118	18	$4,9\cdot10^4$	2.6	$1.9\cdot10^4$
GST124	122-128	6	$1\cdot10^5$	3.8	$2.6\cdot10^4$
GST225	132-139	7	$2.8\cdot10^4$	1.0	$2.8\cdot10^4$

Determined onset crystallization temperature (T_x) adequately correlates with the temperature found earlier by differential scanning calorimetry [12]. Obtained results shows that T_x increases with moving along the quasi-binary line GeTe-Sb_2Te_3 from GST147 to GST124, and then to GST225, while the phase transition temperature range ΔT_n decreases. This result can be explained by the decrease of the concentration of weaker chemical bonds Sb-Te compared with stronger chemical bonds Ge-Te, and correlates with the data of [2].
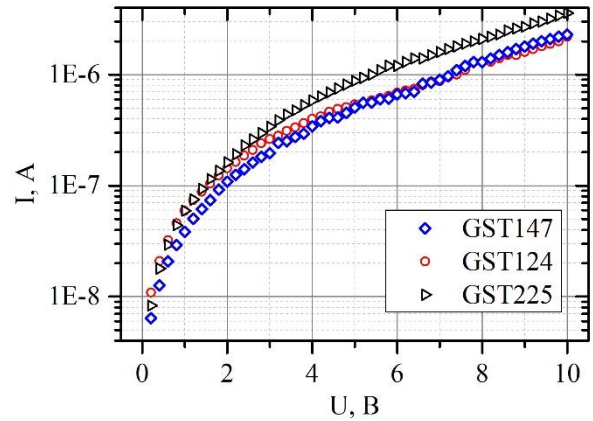
Current-voltage characteristics (CVC) for thin amorphous films of investigated materials at room temperature and at heating are presented in fig. 5 and 6. Characteristics for all compositions at room temperature are close enough. Three voltage ranges with different current-voltage dependencies can be seen for CVC indicating on the different mechanisms of charge carrier transport.

It was found that at low electric field intensity ($E < 10^3$ V/cm) Ohmic dependencies are characteristic for all investigated compounds. CVCs in the middle electric field intensity range ($10^3 < E < 10^4$ V/cm) has power dependences, which is typical for space charge

limited current.
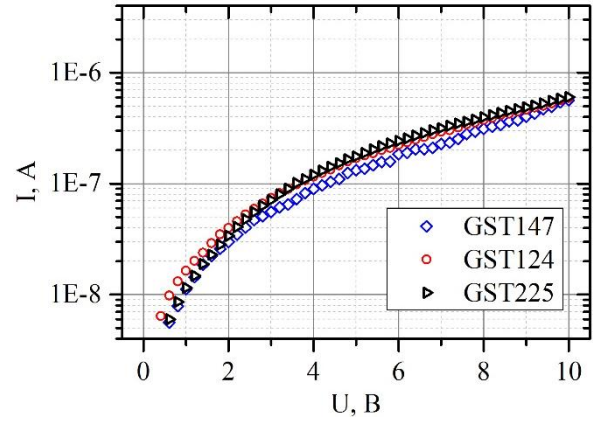
Fig. 5 – Current-voltage characteristics for the amorphous films at room temperature

Fig. 6 – Current-voltage characteristics for the amorphous films at heating

Nonlinear dependences at high electric field intensity ($E > 10^4$ V/cm) can be due to the Poole-Frenkel effect, space-charge limited current, field-induced delocalization of tail states [13]. However, further investigations are needed to clarify transport mechanism in this range.

4. CONCLUSION

So, influence of the composition variation along the quasi-binary line GeTe-Sb_2Te_3 on the thermoelectric and electro-physical properties of thin films was investigated.

GST amorphous thin films have high Seebeck coefficients in the range of -600 to -1000 µV/°C, which drops nearly on the order of magnitude after the crystallization.

Temperature dependences of the resistivities were studied, and it was determined that crystallization temperature increases with moving along the quasi-binary line GeTe-Sb_2Te_3 from $GeSb_4Te_7$ to $GeSb_2Te_4$, and then to $Ge_2Sb_2Te_5$, while the phase transition temperature range decreases. Ratio of the resistivities of amorphous and crystalline states exceeds 10^3.

Current-voltage characteristics of amorphous thin films have three voltage ranges with different dependencies due to the different mechanisms of charge carrier transport. Ohmic dependencies and space charge

limited current determines current-voltage characteristics in the low ($E < 10^3$ V/cm) and middle ($10^3 < E < 10^4$ V/cm) electric field intensity ranges, respectively.

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