Electrophysical properties of phase change memory materials on the pseudo-binary line GeTe-Sb$_2$Te$_3$

A O Yakubov*, D Y Terekhov*, A A Sherchenkov*, S A Kozyuhhin**, P I Lazarenko*, A V Babich* S P Timoshenkov*, D G Gromov* and A S Shuliatyev*

*Moscow State Institute of Electronic Technology (Technical University), 124498 Zelenograd, Russia
**Kurnakov Institute of General and Inorganic Chemistry, RAS, 119991 Moscow, Russia
E-mail: aa_sherchenkov@rambler.ru

Abstract. The temperature dependences of the resistivity and current-voltage characteristics of amorphous thin films on the basis of GeSb$_4$Te$_7$, GeSb$_2$Te$_4$, and Ge$_2$Sb$_2$Te$_5$ perspective for the phase change memory application were investigated. It was revealed that two-channel conduction mechanism with the transport of charge carriers by the localized states in the valence band tail and delocalized states of the valence band is characteristic feature of these materials.

1. Introduction

New generation of non-volatile memory is actively developed now. One of the most promising is phase change memory (PCM) due to the superior rate, durability and radiation resistance in comparison with the most widespread flash memory [1,2].

Two main types of PCM memory devices exist now - optical and electrical phase-change memories. The work of both types of devices is based on rapid reversible amorphous-to-crystalline phase-change processes, which can be initiated by laser or electrical pulses. PCM materials in amorphous and crystalline states have very different optical and electrical properties, and are attributed as “zero” and “unit” logical states. The electrical data storage is based on the large difference in resistivities of amorphous and crystalline phases.

Three compounds exist on this pseudo-binary line: Ge$_2$Sb$_2$Te$_5$ (GST225), GeSb$_2$Te$_4$ (GST124), and GeSb$_4$Te$_7$ (GST147). The most promising among them is considered to be GST225 due to the complex properties.

Despite the successful commercial application of GST materials in optical storage devices, many fundamental and important practical issues related to the electrophysical properties of thin films, are not fully understood. For example, discussions of the possible charge carrier transport mechanisms in Ge-Sb-Te thin films are continued till now [4-7]. Understanding of the transport mechanisms is necessary for controlling the physical properties of programmable materials, and development of effective methods for improving and optimization of phase change memory technology. Therefore, the aim of the work was to study the influence of the composition variation of thin films along the pseudo-binary line GeTe-Sb$_2$Te$_3$ on the temperature dependences of the resistivities, current - voltage characteristics, and energy diagrams.
2. Experimental
The initial GeSb$_7$Te$_7$, GeSb$_4$Te$_4$, and Ge$_2$Sb$_2$Te$_5$ were synthesized with using of quenching technique originally described in [7] and later modified by us. Thin films were prepared by thermal evaporation in vacuum of the synthesized materials in the "explosive" mode. Residual pressure in the chamber was $10^3$ Pa, substrate temperature did not exceed 50 °C. As-deposited films were amorphous, which was confirmed by X-ray diffraction (XRD).

Compositions of thin films were investigated by Rutherford backscattering (RBS) according to the procedure described in detail in (Ed = 1.0, Eα = 2.7 MeV, φ = 135 °). Overlapping of the peaks on the spectra was observed due to the neighbor position of antimony and tellurium in the Periodic table and their close atomic masses, which made impossible quantitative analysis. Therefore, ratios Ge/(Sb + Te) were determined, which for all investigated compounds were close to the theoretical values (Table 1).

Table 1. Results of RBS measurements

| Composition | Ge/(Sb+Te)  | Experimental | Theoretical |
|-------------|-------------|--------------|-------------|
| GST147      | 1/(10.7 ± 0.4) | 1/11         |             |
| GST124      | 1/(6.1 ± 0.2)  | 1/6          |             |
| GST225      | 1/(3.4 ± 0.1)  | 1/3.5        |             |

For the investigation of electrophysical characteristics planar structures were prepared. For this purpose aluminum electrodes were fabricated on the oxidized silicon substrates with interelectrode distance of 7 mm. Amorphous chalcogenide thin film coated further by the protective SiO$_x$ layer was deposited above the interelectrode gap. Geometrical parameters of electrodes were determined by optical microscope (Carl Zeiss Axiocert 40 MAC) and scanning electron microscope (Carl Zeiss VIsion 40). The thickness of the investigated chalcogenide films were controlled by atomic-force microscope (AFM NT-MDT SolverPro) and ranged from 60 to 80 nm.

The electrical characteristics of thin films were studied on a special stand, which included two-electrode circuit based on the voltage control unit NI6008 and picoammeter KEITHLEY 6486. The temperature dependences of the resistivities of thin films were measured at the voltage of 0.7 V (E = $10^3$ V/cm) in the temperature range from room temperature to 200 °C at a heating rate of 1 °C/min. Current-voltage characteristics (CVC) were investigated in the range of 0.1 – 10 V with the increment of 0.1 V, and from room temperature to 70 °C with the increment of 10 °C. The temperature gradient in the plane of the sample did not exceed 1 °C.

Investigations of the thermal properties of thin films were carried out on a differential scanning calorimeter (DSC-50 Shimadzu). Initial samples were thin films deposited on silicon wafers. Films were removed from the substrates by the sapphire scraper and pressed into aluminum crucibles. Measurements were carried out at heating rate of 10 °C/min in an inert atmosphere of nitrogen.

3. Results and discussion
Analysis of the temperature dependences of the resistivities (Figure 1) allowed to distinguish for all the investigated compounds three ranges with the similar temperature dependencies of the resistivities (designated as I, II, and III).

Range I (from room temperature to T = 120 °C) with the exponential temperature dependence.

Range II (from 100 to 140 °C) with a sharp drop in the resistivities of thin films on the several orders of magnitude.

DSC studies of GeSb$_7$Te$_7$, GeSb$_4$Te$_4$, and Ge$_2$Sb$_2$Te$_5$ thin films showed that in this temperature range, the appearance of the exothermic peak is observed, which is caused by phase transition from the amorphous to the crystalline state.
It can be seen that the onset temperature of the exothermic peak is close to the beginning of the resistivity drop ($T_x$), defined as the intersection of approximating lines. Measurements by XRD, as well showed that the observed drop of the resistivity and exothermic peak corresponds to the phase transition from the amorphous phase to the rock salt cubic structure NaCl (fcc).

Range III. For temperatures $T > T_y$ (where $T_y$ is the endset temperature of the resistivity drop) exponential temperature dependences of the resistivities are observed for GST thin films. However, the values of the resistivities are lower than in the range I, which is characteristic for chalcogenide films in the crystalline state [2].

The results of the analysis of the temperature dependence of the resistivity, DSC curves and literature data are presented in the Table 2, where $T_x$ and $T_y$ are the onset and endset temperatures of the phase transition, $\Delta T_n = T_x - T_y$, $\rho_a$ and $\rho_c$ are resistivities at 20 and 250 °C, respectively.

| Compounds  | $T_x$-$T_y$, °C | $\Delta T_n$, °C | $T_x$, °C | $\rho_a$, Ohm·cm | $\rho_c$, Ohm·cm | $\rho_a/\rho_c$ |
|------------|----------------|-----------------|-----------|-----------------|-----------------|----------------|
| GST147     | 100 - 118      | 18              | 115       | 123             | 4.9·10^4        | 2.6            |
| GST124     | 122 - 128      | 6               | 118       | 131             | 1·10^4          | 3.8            |
| GST225     | 132 - 139      | 7               | 136       | 142             | 2.8·10^4        | 1.0            |

The data presented in Table 2 and Figure 1 shows that with the variation of (GeTe)$_n$Sb$_2$Te$_3$$_m$ from $n$:$m = 1:2$ (GST147) to $1:1$ (GST124) and further to $2:1$ (GST225), i.e. with the increasing of GeTe content, onset temperature of the phase transition increases, while the phase transition temperature range $\Delta T_n$ decreases. Slight difference between the onset crystallization temperatures determined by resistivity measurements, DSC data, and data presented in [3] can be explained by the difference in heating rates during measurements. Decrease of the crystallization temperature with the increase of Sb$_2$Te$_3$ while moving from GST225 to GST147, is due to the increase of the concentration of weaker chemical bonds Sb-Te ($277.5$ kJ/mol) compared with stronger chemical bonds Ge-Te ($402$ kJ/mol), which coincides with the data of [3].

CVC measurements showed that there are three characteristic regions with different current-voltage dependencies: for weak ($E < 10^3$ V/cm), middle ($10^3$ V/cm $< E < 10^4$ V/cm) and strong ($E > 10^4$ V/cm) electric fields. Figure 2 shows the current-voltage characteristics of GST225 thin film at different temperatures. The presence of different current-voltage characteristics is due to the dominating of different charge carrier transport mechanisms [7].
Amorphous thin films of the materials studied have nearly exponential temperature dependences of the resistivities in the temperature range from room temperature to 100°C (Figure 1). Such dependencies indicates on the activation nature of conductivity, which is characteristic for chalcogenide glassy semiconductors. In this case, the temperature dependence of the conductivity is described by the following expression:

$$\sigma = \sigma_0 \exp \left( \frac{E_a}{kT} \right),$$

where $\sigma_0$ is pre-exponential factor, $E_a$ is activation energy of the conductivity, $k$ is Boltzmann constant.

Analysis of the dependencies $\sigma = f(1/kT)$ with using of the expression (1) allowed to estimate activation energies of the conductivity, which are consistent with the literature data. Energy parameters for investigated thin films are shown in Table 3, where $E_g$ is the width of the optical gap, $E_0$ is Urbach energy. Widths of the optical gap and Urbach energy are taken from , the error is ± 0.01 eV.

**Table 3. Energy parameters of GST thin films**

| Material   | $E_g$, eV | $E_g/2$, eV | $E_a$, eV | $E_0$, eV | $\sigma_0$, Ohm$^{-1}$·cm$^{-1}$ |
|------------|-----------|-------------|-----------|-----------|----------------------------------|
| GeSb$_2$Te$_7$ | 0.50      | 0.25        | 0.22      | 0.09      | 0.1                              |
| GeSb$_2$Te$_4$ | 0.54      | 0.27        | 0.28      | 0.08      | 1.0                              |
| Ge$_2$Sb$_2$Te$_5$ | 0.61      | 0.30        | 0.29      | 0.13      | 2.2                              |

When analyzing electrical conductivity, we used the Mott - Davis (MD) model of the energy bands. Characteristic features of this model are narrow tails of the localized states at the edges of the valence band and the conduction band, which are spreading in the mobility gap, and the boundary energies separating the localized states from delocalized in bands. The Fermi level in the MD model is fixed near the middle of the mobility gap by the localized states due to the defects. With using of the MD model, and taking into account experimental results, the energy band diagrams for amorphous GST thin films were designed (Figure 3).

Analysis of the diagrams revealed that the obtained values of the activation energies for conductivity are close to the middle of the mobility gap ($E_g/2$), except for GST124. For this composition activation energy is slightly higher $E_g/2$. Measurements of thermoelectric power carried out for investigated thin films, showed that GST has a negative value of thermoelectric power, indicating on the dominating p-type conductivity. The negative sign of thermoelectric power and the resulting value of the Seebeck coefficient (0.5 mV/K) for the amorphous GST225 thin film. Increase of the conductivity activation energy with the transition from GST147 to GST225 (i.e. in the direction from Sb$_2$Te$_3$ to GeTe on the pseudo-binary line) is due to the variation of the optical gap width and density of states in it. Decrease of the optical gap width is caused by the decrease of the conduction band bottom due to the broadening of the antibonding states band and increase of its population with the increase of the concentration of SbTe$_{3/2}$ structural units with weaker chemical bonds.
The spectral dependencies of the absorption coefficient for amorphous GST225, GST124 and GST147 thin films exist ranges with the exponential dependencies, which indicates on the presence of band tails in the mobility gap, and is caused by optical transitions with exponentially distributed states on the band tails. Maximum width of the band tail have GST225 thin films ($E_0 = 0.13$ eV). The values of $E_0$ for thin films of GST124 (0,08 eV) and GST147 (0,09 eV) are close. The obtained values of Urbach parameter indicates that thin films of GST124 and GST147 have less disordered structure in comparison with GST225.

As noted earlier, the activation energies of conductivities for all compositions are close to the middle of the mobility gap. This allows to suggest that significant contribution to the conductivity is caused by the transport of the charge carriers by delocalized states of the valence band. However, it is noted that for most disordered semiconductors with charge carrier’s transport by the delocalized states pre-exponential factor $\sigma_0$ must be in the range from $10$ to $10^3$ Ohm$^{-1}$ cm$^{-1}$. Obtained values of $\sigma_0$ for investigated GST materials are significantly less. Therefore, we used a two-channel conduction model proposed by Nagels. According to the model transport of the charge carriers by the localized states of the valence band tail and by the delocalized of state of the valence band can simultaneously contribute to the p-type conductivity of the chalcogenide glassy semiconductors:

$$\sigma = \sigma_0 \exp[-(E_F-E_0)/kT] + \sigma_{0h} \exp[-(E_F-E_0 + W)/kT].$$

(2)

where the first term corresponds to the transport of the charge carriers by the delocalized of state, and second – to the hopping transport by the localized states of the valence band tail ($W$ is the energy required for hopping). The possibility of using the two-channel model was demonstrated by Van der Plas, Buba and Nagels for the description of the previous generation of PCM materials on the basis of Ge$_x$Te$_{1-x}$ and Si-Te-As-Ge (STAG). We used equation (2) for the description of the obtained dependences of the conductivity on $1/kT$. For the modeling parameters $\sigma_0$, $\sigma_{0h}$ and $W$ were varied, obtained value of the conduction activation energy was used as $E_G$, while $E_F$ and $E_0$ were obtained from the optical transmission spectra measurements (see Table 3).

Figure 4 present the temperature dependences of the conductivities, which show that the results of modeling and experimental data coincide.

Figure 3. Energy diagrams for Ge-Sb-Te thin films: a – GST147; b - GST124; c - GST225.
It should be noted, however, that the use of the equation (2) for fitting the temperature dependence of the conductivity does not allow strictly determine parameters $\sigma_0$, $\sigma_0h$ and $W$. Only possible ranges of these parameters can be estimated, which are shown in Table 4.

Nagels et al gave following values for the pre-exponential factors: $\sigma_0' = 3000 \text{Ohm}^{-1}\cdot\text{cm}^{-1}$ and $\sigma_0h = 90 \text{Ohm}^{-1}\cdot\text{cm}^{-1}$. Our results showed that the values of these parameters obtained with using of two-channel model (see. Table 4) differs from those of the work. However, it should be noted that the difference between estimated value of $\sigma_0'$ and $\sigma_0h$ constitutes several orders of magnitude, which correlates with the data of. This result is also consistent with the MD model, where sharp drop of the carrier’s mobility at the energy separating delocalized and localized states of the valence band is assumed. The difference in the values of pre-exponential factors can be explained by the peculiarities of the physico-chemical properties of GST materials. For example, the GST thin film has an extremely high rate, stability and reproducibility of switching from amorphous to crystalline states under the influence of electric pulses [1-3].

### Table 4. Energy parameters for thin films on the basis of compounds on the pseudo-binary line Sb$_2$Te$_3$ – GeTe

| Compound | Variable values | Fixed values |
|----------|-----------------|--------------|
|          | $\sigma_0'$, Ohm$^{-1}\cdot$cm$^{-1}$ | $\sigma_0h$, Ohm$^{-1}\cdot$cm$^{-1}$ | $W$, eV | $E_g$, eV | $E_g/2$, eV | $E_f$, eV | $E_0$, eV |
| GST147   | 0.08 ± 0.12     | 0.0008 ± 0.0012 | 0.005 ± 0.015 | 0.50 | 0.25 | 0.22 | 0.09 |
| GST124   | 0.45 ± 0.60     | 0.0045 ± 0.0060 | 0.005 ± 0.015 | 0.54 | 0.27 | 0.28 | 0.08 |
| GST225   | 2.0 ± 3.0       | 0.01 ± 0.02     | 0.005 ± 0.015 | 0.61 | 0.30 | 0.29 | 0.13 |

Thus, the experimental results obtained for GST thin films can be described by the two-channel conductivity model. However, additional measurements of the temperature dependences of theromoelectric power and estimation of the Hall mobility of charge carriers are necessary for strict determination of the model parameters.

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