Electrophysical properties of PCM-materials in crystalline and amorphous states

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Abstract. The temperature dependences of the resistivity, thermopower, and Nernst coefficient were experimentally investigated on the samples of phase change materials with a composition of $Ge_{0.15}Sb_{0.85}$ in both the amorphous and crystalline states. It was observed that the crystalline state is characterized by a metallic type of the thermopower temperature dependences, while the resistivity increases slightly with decreasing temperature and the Nernst coefficient has a positive value and demonstrates the complicated temperature dependence. The conductivity in the amorphous state has an activated character with two different activation energies in low and high temperature ranges; the temperature of the transition between these ranges corresponds to the point of a change of thermopower sign. The results obtained point to a need to take into account a contribution of two types of carriers in the conduction process in both phase states.

1. Introduction

Phase change materials (PCMs) are the materials that exist in at least two structurally different solid phases, namely, in the amorphous and crystalline states. Usually, the amorphous and crystalline phases demonstrate very different optical and electrical properties originated from a large difference in the crystalline structure. This can be used in technological applications for storing information, if it is possible to change repeatedly the state of a material between the two phases and both phases are stable at operating temperatures. Nonvolatile memory electrical devices based on PCMs cause now an increasing interest, in particular as a possible alternative to the standard silicon flash memory [1,2].

A potential possibility to use PCMs for practical applications in fields of optical memory cells and phase-change recording was indicated a long time ago [3], but its realization was hampered due to the fact that the previously known PCMs were characterized by a rather slow crystallization speed. However, an interest to this class of materials increased greatly after discovering fast switching alloys based on the pseudobinary line between GeTe and Sb_2Te_3 [4]. As a result, at present the compounds of this family ($Ge_2Sb_2Te_5$, $GeSb_2Te_4$, GeTe, Sb_2Te_3 and others) are considered as the most promising materials for applications in the field of information storage. Moreover, PCMs have already been successfully used to create rewritable DVD and Blu-ray discs [1], as well as a prototype of a multi-layer memory cell based on the $Ge_2Sb_2Te_5$ compound [5].

In contrast to wide development of applications, the mechanism of a rapid phase change, especially crystallization from the amorphous phase, is still not fully understood in spite of a lot of investigations using different techniques (see, for example, [1, 6–8]). As a result, there is no consensus on the fundamental properties and parameters of the charge-carrier system. The questions on mechanisms of modification of those parameters under different kinds of influence, the possible ways of their

purposeful variations are still under discussion. The main reason for this situation is a complicated or unusual energy structure of these materials differing essentially from that of "classical" materials. This circumstance prevents using the well-known models of the energy spectrum as a tool for an analysis of the experimental results on the electron transport. On the other hand, understanding of the transport properties and how they can be affected by different treatments of materials, the degree of disordering, electron-phonon and electron-electron interactions are the problems of fundamental importance for further progress in applications of the considered materials. Nevertheless, the experimental data on the transport coefficients behavior in PCMs are fragmentary; moreover, some of these coefficients have not been investigated yet.

For the above reasons, this work is devoted to the experimental study of the transport coefficients (the resistivity, thermopower, Nernst coefficient) on the $Ge_{0.15}Sb_{0.85}$ samples in both the amorphous and crystalline states.

1. Experiment

The $Ge_{0.15}Sb_{0.85}$ samples were obtained by the magnetron spattering, the samples size was approximately 10×10 mm^2. They were grown in an amorphous phase on the Si/SiO_2 substrate and then crystallized by a slow heating in one case or by a fast heating (at a rate of about 1° C/sec.) in the second case to test the reproducibility of the results. The sample thicknesses were 60 and 600 nm. The sample surface topology was studied by a Dimension 3100 (Veeco) AFM in the semi-contact mode at room temperature using the RTESP probes with the curvature radius of 10 nm.

The temperature dependences of resistivity, ρ, were measured by the van der Pauw method that allowed us to solve the problem of an arbitrary shape of the samples. The thermopower, *S*, was measured by the differential method relative to the copper electrodes and then calculated by correcting for the absolute thermopower of copper. The temperature difference between two edges of the sample was about 2 K. The Nernst coefficient, *Q*, was measured in the constant reversible magnetic field of 1.8 T in a home-made cryostat. In order to suppress spurious voltage, the Nernst signal was calculated as a half-sum of signals measured at different field directions. The temperature difference applied to the sample was about 10 K. All the transport coefficients were investigated in the temperature range of $T = 77–300$ K.

2. Results and discussion

To characterize the sample quality the AFM studies were carried out. Surface topologies for 60 nm $Ge_{0.15}Sb_{0.85}$ samples in the amorphous and crystalline states are shown in figure 1. All the samples have a granular structure with a particle size varying from 10 to 40 nm. The crystalline samples are characterized by a more uniform particle size than the samples of the amorphous phase. At the same time, the surface of all the samples is quite smooth; the surface irregularity is within limits of 10 nm. In the crystalline phase the height variation is a little less than in the amorphous samples for both the thicknesses investigated. Thus, all the sintered samples were of a high quality.

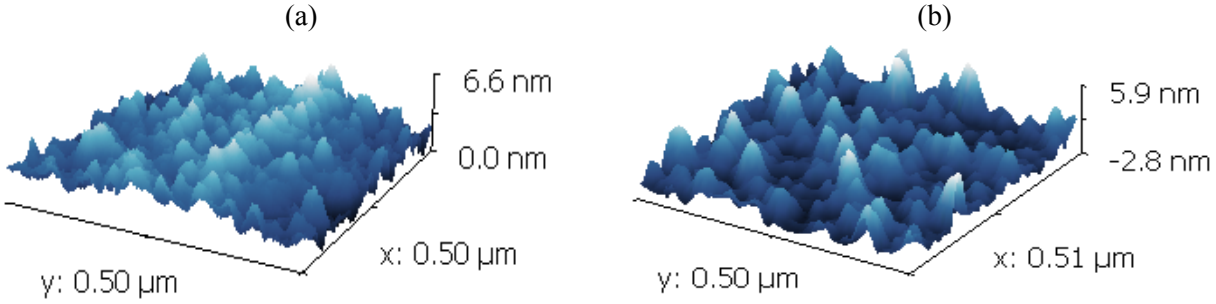

Figure 1. Surface topology of $Ge_{0.15}Sb_{0.85}$ samples (thickness of 60 nm) in crystalline (a) and amorphous (b) states.

The resistivity temperature dependences for the samples of 600 nm thickness are shown in figure 2. These dependences for each sample were measured twice in the van der Pauw configuration, and the resistivity values were calculated taking into account the correction factor determined by the deference between the values obtained by repeating measurements after changing the configuration of contacts [9].

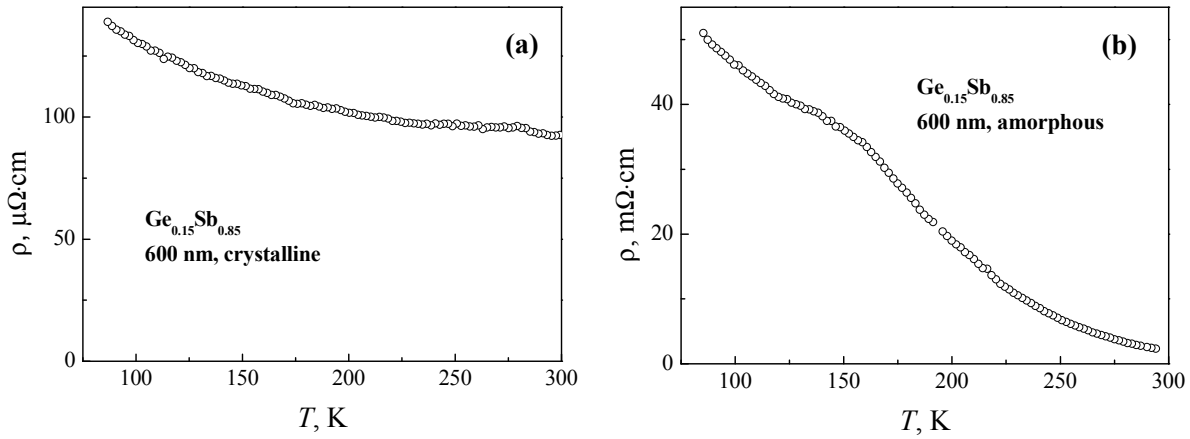

Figure 2. Resistivity vs temperature for the 600 nm thickness $Ge_{0.15}Sb_{0.85}$ samples in crystalline (a) and amorphous (b) states.

The absolute values of resistivity at $T = 300$ K for the samples of the amorphous state were found to be 25–30 times higher than for the crystalline samples. As for the temperature dependence, in the crystalline state the resistivity increases with decreasing temperature but rather slightly (for the sample of 600 nm thickness the resistivity increases by 36 % when temperature decreases from 300 K to 100 K, see figure 2(a)). In the amorphous phase we have observed a strong rise of the resistivity with decreasing temperature (see figure 2 (b)) that indicates an activation type of the conduction process to be realized in this sample state.

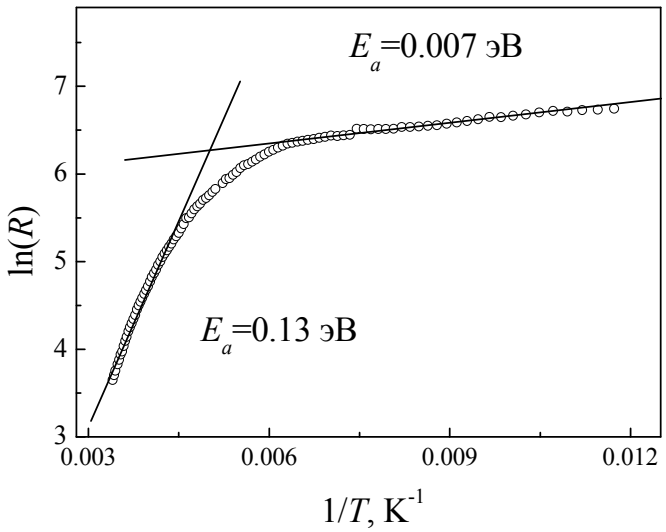

Figure 3. Temperature dependence of the resistivity for the 600 nm thickness amorphous $Ge_{0.15}Sb_{0.85}$ sample in Arrhenius coordinates.

To determine the quantitative characteristics we have plotted the $\rho(T)$ dependence for the amorphous samples in Arrhenius coordinates (see figure 3). The presented data clearly indicate that

the conduction process in different temperature ranges is characterized by the two different activation energies, E_a. At high temperatures ($T > 200$ K) the $\rho(T)$ dependence corresponds to $E_a = 0.13$ eV, while at low temperatures ($T < 150$ K) $E_a = 0.007$ eV.

Figure 4 shows the temperature dependences of the thermopower for the amorphous and crystalline samples of 60 nm thickness. In the crystalline state the absolute values of the thermopower are extremely small (about 4–5 μV/K at $T = 300$ K); the $S(T)$ dependence is of a metallic type, i.e. thermopower decreases linearly with decreasing temperature. In the amorphous state the S values are also quite small (they do not exceed 120 μV/K), while the temperature dependence of the thermopower has a complicated character demonstrating a transition from positive values at $T = 130$–300 K to negative ones at $T < 125$ K. Note, that the temperature of a transition to negative thermopower values is close to that of slope change for the $\rho(T)$ (see figure 2(b)).

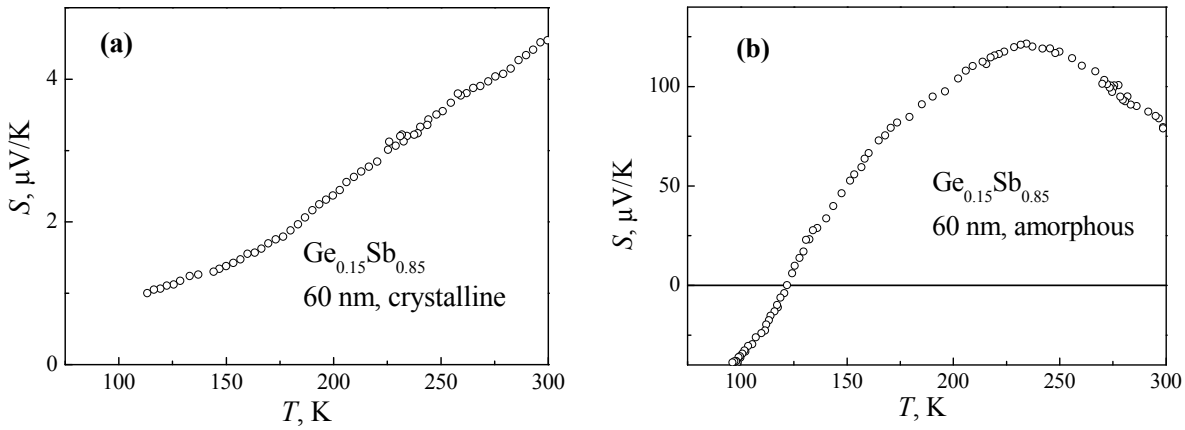

Figure 4. Thermopower vs temperature for the 60 nm thickness $Ge_{0.15}Sb_{0.85}$ samples in crystalline (a) and amorphous (b) states.

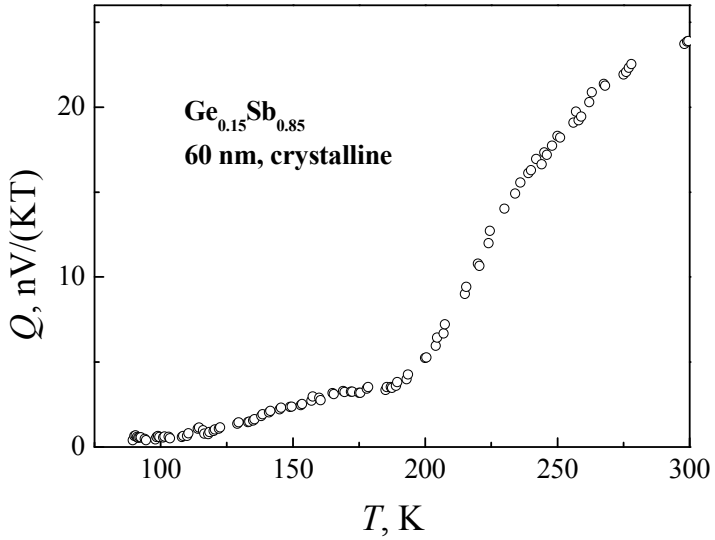

Figure 5. Nernst coefficient vs temperature for the 60 nm thickness crystalline $Ge_{0.15}Sb_{0.85}$ sample.

For the crystalline sample of 60 nm thickness we have also measured the temperature dependence of the Nernst coefficient. Note, that to the extent of our knowledge no data on this coefficient behavior in PCMs of the studied composition have been published to date. The results obtained are shown in figure 5. The Nernst coefficient at $T = 300$ K is positive and equal to about 25 nV/(KT). The $Q(T)$

dependence has two different regions. As temperature decreases down to 200 K the Q value falls sharply, at lower temperatures it decreases much slighter. At $T < 100$ K the Q values become extremely low (about 0.5 nV/(KT)).

Let us discuss briefly the results obtained. As for the amorphous state, it is obvious that to describe the conduction process one should take into account a contribution of two types of carriers. According to the resistivity and thermopower data at low temperatures the main charge carriers are electrons characterized by an activation energy of $E_a = 0.007$ eV, while at high temperatures (above 150–200 K) they are holes with an activation energy of $E_a = 0.13$ eV. The data on the crystalline state are rather contradictive. The type of the thermopower temperature dependence and very small absolute values of it give evidence of a strong degeneracy of the electron gas. On the other hand, the $\rho(T)$ dependence is not a metallic-like. As for the Nernst data obtained, in case of one type of charge carriers they can be explained only by a change in a dominant scattering mechanism with decreasing temperature. However, the resistivity and thermopower data testify against such an assumption. Thus, we believe the results obtained for three transport coefficients to be evidence that the existence of two types of charge carriers is characteristic of both the amorphous and crystalline states of PCMs.

3. Conclusion

Thus, by the method of magnetron sputtering we have sintered the high quality thin film samples of the $Ge_{0.15}Sb_{0.85}$ composition with thicknesses of 60 and 600 nm. We have studied experimentally the temperature dependences of the resistivity and thermopower for both the amorphous and crystalline states, as well as the Nernst coefficient for the crystalline state. The crystalline state is characterized by a metallic-like thermopower temperature dependence, while the resistivity increases with decreasing temperature and the Nernst coefficient having small positive absolute values demonstrates a rather complicated temperature dependence. In the amorphous state the conductivity has an activated character with different activation energies at low and high temperatures; the thermopower has positive values at high temperatures, but negative ones below $T = 125$ K. The qualitative analysis of the results obtained indicates that describing the conduction process in both the amorphous and crystalline states requires taking into account a contribution of charge carriers of different types.

Acknowledgments

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References

[1] Wuttig M and Yamada N 2007 *Nature Materials* **6** 824
[2] Raoux S, Wełnic W and Ielmini D 2010 *Chemical Reviews* **110** 240
[3] Ovshinsky S R 1968 *Physical Review Letters* **22** 1450
[4] Yamada N, Ohno E, Akahira N, Nishiuchi K, Nagata K and Takao M 1987 *Japanese Journal of Applied Physics* **26-4** 61
[5] Chen Y C 2009 *Phase Change Materials: Science and Application**s*** ed S Raoux and M Wuttig (New York: Springer) pp 331–354
[6] Kimura S, Tanaka Y, Kohara S and Takata M 2012 *Materials Science and Technology* ed S D Hutagalung (Rijeka: InTech) pp 259–275
[7] Lencer D, Salinga M and Wuttig M 2011 *Advanced Materials* **23** 2030
[8] Redaelli A, Pirovano A, Benvenuti A and Lacaita A L 2008 *Journal of Applied Physics* **103** 111101
[9] van der Pauw L J 195*8 Philips Research Reports* **13** 1