Local Structure of Amorphous and Crystalline Ge$_2$Sb$_2$Te$_5$ Films

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Abstract—It is shown using Mössbauer spectroscopy on $^{119}$Sn, $^{121}$Sb, and $^{125}$Te isotopes that the local structure of germanium atoms changes during crystallization of amorphous Ge$_2$Sb$_2$Te$_5$ films (tetrahedral symmetry changes to the octahedral one), whereas the environment of antimony and tellurium atoms remains the same (the environment of antimony atoms it close to that in the Sb$_2$Te$_3$ compound).

Keywords: phase memory, Ge$_2$Sb$_2$Te$_5$, Mössbauer spectroscopy.

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Modern phase-memory technology is mainly based on the use of films of Ge$_2$Sb$_2$Te$_5$-type compounds, the crystalline and amorphous states of which are characterized by high optical contrast. Therefore, these materials can be used for erasable optical disks. It is believed that the aforementioned properties of Ge$_2$Sb$_2$Te$_5$ films are due to structural features of amorphous and crystalline phases. In particular, a possible model explaining the mechanism of fast reversible transition from the crystalline to amorphous state for Ge$_2$Sb$_2$Te$_5$ films was proposed in [1]. This model is based on the assumption that the transition under consideration is accompanied by a change in the coordination state of germanium atoms, while the local environments of tellurium and antimony atoms remain the same. Obviously, this statement requires independent experimental confirmation.

Mössbauer spectroscopy is an efficient method for studying local structural transformations in solids during their amorphization, which makes it possible to identify unambiguously changes in the valence and coordination states of a Mössbauer probe [2, 3]. A fundamental requirement to the Mössbauer probe used in these studies is its a priori localization in a specific site of the crystal lattice or a structural network of an amorphous material.

The purpose of this Letter was to study the local structure of crystalline and amorphous Ge$_2$Sb$_2$Te$_5$ films on $^{125}$Te, $^{121}$Sb, and $^{119}$Sn isotopes (obviously, $^{125}$Te and $^{121}$Sb probes occupy tellurium and antimony sites, and the isovalent substitution of impurity tin atoms for germanium atoms in the structure of glassy and crystalline germanium tellurides was reliably established [2, 3]). Crystalline and amorphous Ge$_{1.5}$Te$_{8.5}$ films have also been investigated for comparison.

X-ray amorphous Ge$_2$Sb$_2$Te$_5$, Ge$_{1.5}$Te$_{8.5}$, Ge$_{1.95}$Sn$_{0.05}$Sb$_2$Te$_5$, and Ge$_{1.45}$Sn$_{0.05}$Te$_{8.5}$ films were obtained by dc magnetron sputtering of a polycrystalline target of the corresponding composition in nitrogen. The Ge$_{1.95}$Sn$_{0.05}$Sb$_2$Te$_5$ and Ge$_{1.45}$Sn$_{0.05}$Te$_{8.5}$ films were obtained using $^{119}$Sn isotope with enrichment of 92%. The amorphous films were crystallized at temperatures of 150°C for Ge$_2$Sb$_2$Te$_5$ and Ge$_{1.95}$Sn$_{0.05}$Sb$_2$Te$_5$ and 250°C for Ge$_{1.5}$Te$_{8.5}$ and Ge$_{1.45}$Sn$_{0.05}$Te$_{8.5}$.

The Mössbauer spectra of $^{119}$Sn, $^{121}$Sb, and $^{125}$Te were recorded on a CM4201 TerLab spectrometer at 80 K with sources of Ca$^{119m}$SnO$_3$, Ca$^{121}$SnO$_3$, and Zn$^{125m}$Te. The instrumental widths of the spectral lines ($\Gamma_{\text{instr}}$) for the $^{119}$Sn, $^{121}$Sb, and $^{125}$Te spectra were 0.79(2), 2.35(6), and 6.20(6) mm/s, respectively. The isomer shifts (ISs) of the $^{119}$Sn, $^{121}$Sb, and $^{125}$Te spectra are given with respect to CaSnO$_3$, InSb, and ZnTe absorbents, respectively. Typical spectra are shown in Figs. 1–3.

The spectra of impurity $^{119}$Sn atoms in the amorphous films (Fig. 1) are single broadened lines ($\Gamma \sim 1.25–1.36$ mm/s). This broadening is explained by the absence of the long-range order and is a characteristic feature of Mössbauer spectra of disordered structures.

The $^{119}$Sn spectra of the amorphous films exhibit isomer shifts (IS $\sim 2.01–2.05$ mm/s), which are typical of the $^{119}$Sn spectra of tetravalent tin Sn-IV com-
Based on the values of isomer shifts of the $^{119}$Sn spectra, one can conclude that tin atoms and germanium atoms (for which the former substitute) in amorphous Ge$_2$Sb$_2$Te$_5$ and Ge$_{1.5}$Te$_{8.5}$ films form a chemical-bonding system close to the $sp^3$ tetrahedral one. The proximity of the isomer shifts of the spectra of amorphous Ge$_2$Sb$_2$Te$_5$ and Ge$_{1.5}$Te$_{8.5}$ materials indicates that, in the structural network of amorphous Ge$_2$Sb$_2$Te$_5$, germanium atoms are bound only with tellurium atoms.

The $^{119}$Sn spectra of the crystalline films exhibit isomer shifts $IS \sim 3.49-3.53$ mm/s. These values almost coincide with the isomer shift of the $^{119}$Sn spectrum of the compound of divalent tin Sn$^{2+}$ and tellurium (SnTe; $IS = 3.55(2)$ mm/s), in which an octahedral chemical-bonding system is implemented.

Therefore, crystallization of amorphous films does not change the chemical nature of atoms in the local environment of germanium atoms; however, their coordination number changes from four to six, with their valence state also changing. Note that similar results were obtained in [2] for crystallization of bulk Ge–Te glasses (and confirmed later in [3]) and Ge–As–Te glasses.

The fact that the spectral widths of crystalline films are much larger than $G_{exp}$ indicates that tin in their composition does not form SnTe compound with the NaCl-type lattice. Apparently, tin enters the composition of Ge$_{1-x}$Sn$_x$Te solid solutions (in the Ge$_{1.5}$Te$_{8.5}$ films) or fcc phase (in the Ge$_2$Sb$_2$Te$_5$ films [4]) with rhombohedrally distorted NaCl-type lattices, the Mössbauer spectra of which are broadened due to unresolved quadrupole splitting.

The $^{121}$Sb spectra of the crystalline and amorphous Ge$_2$Sb$_2$Te$_5$ films and the spectrum of Sb$_2$Te$_3$ polycrystals (Fig. 2) are single, somewhat broadened lines (the maximum broadening is observed for the amorphous...
The amorphous Ge\textsubscript{1.5}Te\textsubscript{8.5} film induces the formation of a two-phase mixture of elemental tellurium and germanium telluride, which can be seen in the spectral structure (a superposition of two components related to the aforementioned phases) (Fig. 3). The spectrum of the crystalline Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} film can be described by a single poorly resolved quadrupole doublet (Fig. 3), the parameters of which (IS = 0.30(6) mm/s, QS = 4.30(8) mm/s, and G = 5.52(8) mm/s) correspond to divalent tellurium. In other words, crystallization of the amorphous Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} film does not induce its separation into several phases, and the structures of the nearest environment of tellurium atoms in the amorphous and crystalline films remain close.

Thus, we experimentally confirmed the conclusion drawn in [1] that the phase transition from the amorphous to crystalline state in Ge\textsubscript{2}Sb\textsubscript{2}Te\textsubscript{5} films is accompanied by a change in the coordination state of germanium atoms, whereas the local environments of tellurium and antimony atoms remain the same. One should also take into account that this transition is accompanied by a change in the germanium valence state.

CONFLICT OF INTEREST
The authors declare that they have no conflict of interest.

REFERENCES
1. A. V. Kolobov, P. Fons, A. I. Frenkel, A. L. Ankudinov, J. Tominaga, and T. Uruga, Nat. Mater. 3, 703 (2004).
2. L. N. Seregina, F. S. Nasredinov, B. T. Melekh, Z. V. Maslova, E. Yu. Turaev, and P. P. Seregin, Fiz. Khim. Stekla 3, 328 (1977).
3. M. Micoulaut, K. Gunasekera, S. Ravindren, and P. Boolchand, Phys. Rev. B 90, 094207 (2014).
4. C. Hu, Z. Yang, C. Bi, H. Peng, L. Ma, C. Zhang, Z. Gu, and J. Zhu, Acta Mater. 188, 121 (2020).

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