

# Mössbauer Studies of the Local Surrounding of Atoms in Amorphous and Crystalline Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> Films

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## Mini Review

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## ABSTRACT

The local environment of atoms in crystalline and amorphous films Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> was determined by method of Mössbauer spectroscopy with the <sup>119</sup>Sn, <sup>121</sup>Sb and <sup>125</sup>Te isotopes. The current stage of phase memory (FP) research based on chalcogenide semiconductors is associated with the use of incongruently melting compounds in the Ge-Sb-Te system lying on the GeTe-Sb<sub>2</sub>Te<sub>3</sub> quasi-binary section line, and the composition of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> is of the greatest interest.

Quartz

## INTRODUCTION

An important property of the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  film compound is its ability to rapid and reversible transitions between crystalline and amorphous states under the action of low-energy influences, and one of the tasks to improve the technology of FP is related to the study of the crystallization process of amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films. It is obvious that it is fundamentally important to obtain information about the local structure of the amorphous film.

Crystal structures of the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  alloys were studied in detail [1-4]. As for their amorphous modifications, many studies have been conducted to determine the structure of the short-range order in them [5-8], however, a comparison of all experimental data shows that these structures are still the subject of discussion [1,2,8]. In particular, there are obvious contradictions in the interpretation of experimental results obtained in the study of amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films by X-ray Absorption Fine-structure Spectroscopy (XAFS) [5-7]. This indicates the need to use additional experimental methods that are sensitive to minor changes in the local structure and in the population of the electron shells of atoms during the transition from the amorphous to the crystalline state.

Mössbauer spectroscopy is an effective method for studying structural rearrangements in solids. An important requirement for the Mössbauer probe used for such studies is its a priori localization in a specific node of the crystal lattice or structural grid of an amorphous material. This requirement can be fulfilled by studying the local structure of crystalline and amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films by absorption Mössbauer spectroscopy with the  $^{125}\text{Te}$ ,  $^{121}\text{Sb}$  and  $^{119}\text{Sn}$  isotopes.

In our work [9], the absorption and emission techniques described above were used to study structural rearrangements in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films. This allowed us to obtain information about structural rearrangements in the local environment of Ge, Sb and Te atoms during the crystallization of amorphous material.

## LITERATURE REVIEW

Neodymium  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  and  $\text{Ge}_{1.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_5$  compounds were synthesized from elemental substances in quartz ampoules evacuated to  $10^{-3}$  mm Hg at  $1050^\circ\text{C}$ . X-ray amorphous films were obtained by magnetron sputtering of polycrystalline targets of similar composition at constant current in a nitrogen atmosphere on a silicon substrate. To obtain the  $\text{Ge}_{1.95}\text{Sn}_{0.05}\text{Sb}_2\text{Te}_5$  films, the  $^{119}\text{Sn}$  isotope with an enrichment of 92% was used. The thickness of the films ranged from 40 to 120 microns. Crystallization of amorphous films was carried out at a temperature of  $310^\circ\text{C}$  (with the formation of the hcp phase).

The  $^{119\text{m}}\text{Sn}$  Mössbauer source based on the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  crystalline films were prepared by diffusion of the  $^{119}\text{Sb}$  or  $^{119\text{m}}\text{Te}$  isotopes into an amorphous film at a temperature of  $310^\circ\text{C}$  for 10 hours. The Mössbauer spectra were measured at 80 K.

The  $\text{Ca}^{119\text{m}}\text{SnO}_3$ ,  $\text{Ca}^{121}\text{SnO}_3$  and  $\text{Zn}^{125\text{m}}\text{Te}$  sources were used for measuring the absorption spectra of  $^{119}\text{Sn}$ ,  $^{121}\text{Sb}$  and  $^{125}\text{Te}$ , respectively. Isomeric Shifts (IS) of the  $^{119}\text{Sn}$ ,  $^{121}\text{Sb}$  and  $^{125}\text{Te}$  spectra are given relative to the spectra of the  $\text{CaSnO}_3$ ,  $\text{InSb}$  and  $\text{ZnTe}$  absorbers, respectively. The composition of amorphous and crystalline films was controlled by X-ray fluorescence analysis.

### Absorption Mössbauer spectroscopy data

The spectra of the  $^{119}\text{Sn}$  impurity atoms of amorphous and polycrystalline plates are single widened lines (line width at half-height  $G \sim 1.15\text{--}1.35$  mm/s).

The spectra of the  $^{119}\text{Sn}$  amorphous films have an isomer shift of  $IS = 2.06(3)$  mm/s. These values are typical for isomeric shifts in the spectra of impurity atoms of tin in a  $\text{Ge}_{1.5}\text{Te}_{8.5}$  glassy alloy and compounds of tetravalent tin with a tetrahedral system of chemical bonds [10]. Based on the values of the isomeric shifts of the  $^{119}\text{Sn}$  spectra, it is concluded that tin atoms and germanium atoms replaced by them in the structural grid of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films form a tetrahedral system of  $sp^3$  chemical bonds. Since germanium atoms can have only tellurium atoms in their local surroundings in the structural grid of the amorphous  $\text{Ge}_{1.5}\text{Te}_{8.5}$ , the proximity of isomeric shifts of all the studied amorphous films indicates that germanium atoms are connected only with tellurium atoms in the structural grid of the amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  film.

A characteristic feature of the spectra of  $^{119}\text{Sn}$  impurity atoms in the amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films is their broadening. Two reasons for broadening are considered. Firstly, possible distortions of the angles between the bonds of tin atoms with atoms in its immediate environment should lead to a broadening of the spectrum due to unresolved quadrupole splitting. The second reason for the broadening of the spectra is the fluctuations in the lengths of the Ge-Te bonds while maintaining tetrahedral bond angles. This will lead to a broadening of the spectrum due to an inhomogeneous isomeric shift.

The spectra of the  $^{119}\text{Sn}$  polycrystalline films have an isomer shift of  $IS = 3.53(3)$  mm/s. This value is close to the isomeric shift of the spectrum of compounds of divalent hexocoordinated tin with tellurium ( $IS = 3.55(3)$  mm/s). Consequently, the crystallization of films does not lead to a change in the chemical nature of atoms in the local environment of germanium (tin), but the valence state of germanium (tin) changes. The width of the spectra of the polycrystalline films is significantly larger than the approximate width of the spectral line of  $^{119}\text{Sn}$ . This indicates that in the polycrystalline phases, tin does not form an SnTe compound (a crystal lattice of the NaCl type), but is part of the fcc and hcp phases, for which the Mössbauer spectra are broadened due to unresolved quadrupole splitting.

The  $^{121}\text{Sb}$  spectra of the crystalline and amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films, as well as the spectrum of the  $\text{Sb}_2\text{Te}_3$  polycrystalline compound, are single somewhat widened lines (the maximum broadening is observed for an amorphous film  $G \sim 5.1$  mm/s), whose isomeric shifts ( $IS \sim 5.1\text{--}5.4$  mm/s) are typical for the spectra of the  $^{121}\text{Sb}$  trivalent compounds of antimony. Since the crystallization of the amorphous film does not lead to a significant change in the parameters of the spectra of  $^{121}\text{Sb}$ , and also considering that these parameters are close to the parameters of the spectrum of the  $\text{Sb}_2\text{Te}_3$  compound, it should be concluded that the local structure of the antimony atoms in all the studied materials is approximate.

The spectrum of the  $^{125}\text{Te}$  amorphous films is a quadrupole doublet (quadrupole splitting  $QS = 4.42(8)$  mm/s), whose isomeric shifts ( $IS \sim 0.35(6)$  mm/s) are typical for the Mossbauer spectra of divalent tellurium compounds. The spectrum of the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  crystalline film can be described by a single poorly resolved quadrupole doublet with  $IS = 0.30(6)$  mm/s,  $QS = 4.30(8)$  mm/s and  $G = 6.52(8)$  mm/s parameters corresponding to the divalent

tellurium. At the same time, the immediate environment of tellurium atoms in amorphous and crystalline films remains unchanged.

### Emission Mössbauer spectroscopy data

In the process of the diffusion doping of the amorphous  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  films with the  $^{119}\text{Sb}$  and  $^{119\text{m}}\text{Te}$  impurity atoms at a temperature of  $\sim 300^\circ\text{C}$ , the films crystallize to form the hcp phase.

In the case of parent  $^{119}\text{Sb}$  atoms, the spectrum is a single broadened line ( $G=1.32(2)$  mm/s), whose isomeric shift ( $IS=3.47(2)$  mm/s) corresponds to divalent tin  $\text{Sn}^{2+}$ . The spectrum of the  $^{119\text{m}}\text{Sn}$  impurity atoms formed after the radioactive decay of the parent  $^{119}\text{Sb}$  atoms in the antimony nodes of the  $\text{Sb}_2\text{Te}_3$  crystal lattice has similar parameters, and it can be concluded that in both cases tellurium atoms are located in the local environment of the  $^{119\text{m}}\text{Sn}^{2+}$  atoms. This is consistent with the hcp data of the structure of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  crystal films, which is based on a 9-layer trigonal packing of atoms-Te-Sb-Te-Ge-Te-Ge-Te-Sb, so that tellurium atoms are located in the local environment of antimony atoms.

## DISCUSSION AND CONCLUSION

In the case of parent  $^{119\text{m}}\text{Te}$  atoms, the spectrum is an overlap of two broadened lines ( $G=1.41\text{-}1.46$  mm/s). A more intense line with an isomeric shift of  $IS=2.42(2)$  mm/s, lying in the region of isomeric shifts of the spectra of intermetallic tin compounds, corresponds to the  $^{119\text{m}}\text{Sn}^0$  centers formed after the decay of the parent  $^{119\text{m}}\text{Te}$  atoms in the tellurium nodes. The less intense line ( $IS=3.51(2)$  mm/s) corresponds to the  $^{119\text{m}}\text{Sn}^{2+}$  centers formed after the decay of the parent  $^{119\text{m}}\text{Te}$  atoms, which shifted from tellurium nodes to antimony, germanium or tellurium nodes due to the recoil energy accompanying the radioactive decay of the tellurium isotope. The large width of these lines is explained either by a set of possible atoms (antimony, germanium, tellurium) in the local environment of tellurium nodes, or by a similar set of nodes into which the daughter atom  $^{119}\text{Sb}$  is displaced. The spectra of the  $^{119\text{m}}\text{Sn}$  impurity atoms formed after the radioactive decay of the parent  $^{119\text{m}}\text{Te}$  atoms in the tellurium nodes of the  $\text{Sb}_2\text{Te}_3$  crystal lattice have a similar structure, and it can be concluded that in many cases only tellurium atoms are in the local environment of the  $^{119\text{m}}\text{Sn}^{2+}$  atoms.

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