

High-Speed Phase Change in GeTe-Sb₂Te₃ Pseudobinary Compound, a Superior DVD-RAM Material

In a rewritable phase-change optical disk such as a DVD-RAM (digital versatile disc - random access memory), information is recorded using the change in optical property, such as reflectivity or transmissivity, that results from the phase transformation of the material between the crystal (erase) and amorphous (record) states. Currently, the best-known phase-change material is the GeTe(1-x)-Sb₂Te₃(x) pseudobinary compound, in which the reversible structural change can be induced in a very brief time of 10 ns. The crystallization speed of this compound is very fast, which contributes to the shortening of the erasing time, and extremely high-speed rewriting can be realized. To clarify this high-speed phase-change mechanism, the crystal and amorphous structures of this pseudobinary compound has been studied for several years by powder diffraction, extended X-ray absorption fine structure (EXAFS), and grazing incidence X-ray scattering (GIXS) measurements using synchrotron radiation at beamlines **BL02B2** and **BL19B2**.

X-ray diffraction measurements revealed that this compound crystallizes into a single phase with a simple NaCl-type structure (*Fm* $\bar{3}$ *m*) as the metastable state, upon laser annealing (erasing operation) over a wide composition range of GeTe from 100 mol% to at least 50 mol% (Fig. 1). Te occupies the 4(a) sites (Cl sites) and Ge and Sb locate randomly at the 4(b) sites (Na sites) [1].

EXAFS measurements of the amorphous compound ($x = 0, 1/7, 1/5, 1/3, \text{ and } 1/2$) showed that Ge, Sb, and Te are about four-, three-, and two-fold coordinated, respectively, and these coordination numbers were almost constant and independent of the pseudobinary

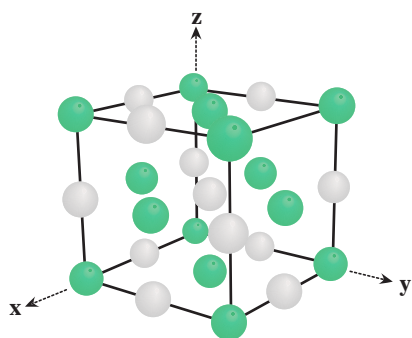


Fig. 1. The crystal structure of laser-crystallized GeTe-Sb₂Te₃ metastable phase shown schematically in perspective. Green circles show atomic positions for Te. Gray circles show those for Ge or Sb. The lattice constant, a , is about 6 Å.

composition (x). In addition, the amorphous compound had a specific coordination feature. The analyzed coordination numbers ($n(x)$) of Ge, Sb, and Te to each other are shown in Fig. 2. From this figure, the following relations can be derived. (i) Te-Te pairs are rarely present in this pseudobinary amorphous compound. In other words, Te is surrounded by only Ge or Sb. (ii) Sb bonds more easily to Te than to Ge or Sb. For example, it is estimated that when one Sb atom is doped into amorphous GeTe ($x = 0$), the Sb atom, which is three-fold coordinated, is surrounded by about two Te atoms but by only one Ge. (iii) Ge bonds to the three kinds of atoms with almost equal probabilities. These suggest that two kinds of atomic pairs, Ge-Te and Sb-Te, exist in this pseudobinary amorphous

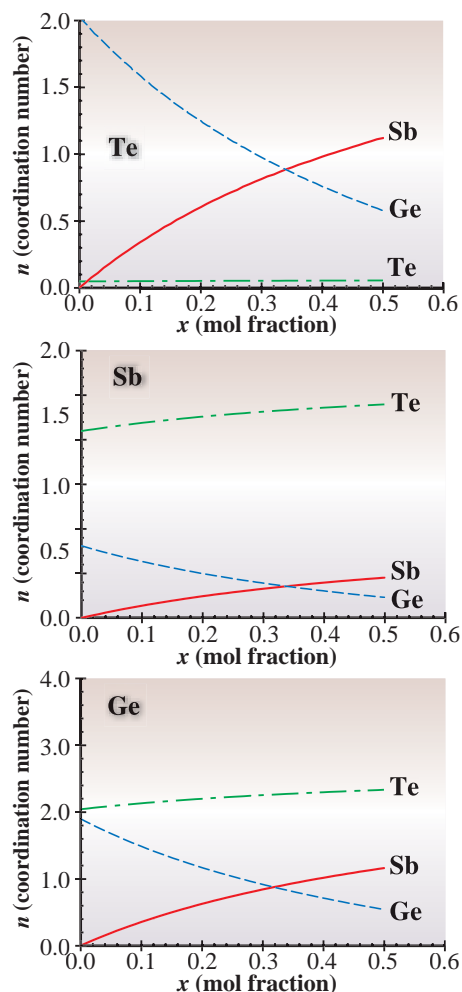


Fig. 2. Determined coordination numbers of the atoms surrounding Te (top), Sb (middle) and Ge (bottom). n and x in the figures indicate coordination number and mol fraction of Sb₂Te₃ in the GeTe-Sb₂Te₃ pseudobinary system, respectively.

compound to a greater extent than if they were coordinated completely at random. These two pairs constitute the structural frame in the crystal phase of this compound; as seen in Fig. 1, only two kinds of bond pairs, Ge-Te and Sb-Te, exist in it. It is consequently presumed that this amorphous compound already has atomic arrangements with the characteristics seen in its crystalline state. When thermal energy is added to the amorphous (recording) mark by laser irradiation, these pairs act as crystallization nuclei and trigger the arrangement of atoms into an NaCl-type structure.

Figure 3 shows the electron radial distribution functions (RDF) for GeSb_2Te_4 ($x=1/2$) and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($1/3$) amorphous films, which were derived by using the GIXS intensities up to the wave number of about 12 \AA^{-1} . The patterns of these RDFs are very similar to each other and clearly indicate a medium-range order; in the patterns we can see three distinct peaks indicating atomic pair distributions at the distances of $r = 2.8, 4.2,$ and 6.2 \AA . Figure 4 shows the RDF calculated for the crystal structure of GeSb_2Te_4 (indicated by bars) with that observed for its amorphous state. It can be seen that the positions and the amplitudes of the three RDF peaks of the amorphous phase are near those of the 1st ($r = 3 \text{ \AA}$ and $\text{CN} = 6$), 2nd (4.2 \AA and 12) and 5th (6.7 \AA and 24) atomic pairs in the crystalline phase. Here, CN means the number of atoms at the i th coordination shell in the crystal (see Fig. 1). It was, however, difficult to find the peaks corresponding to the radial distances of the 3rd (5.2 \AA and 8) and 4th (6.0 \AA and 6) atomic pairs in the crystalline phase. We then divided the RDF of the amorphous film into six single Gaussian peaks (shown by dashed curves in Fig. 4) by least squares fitting. The synthesized curve (thin solid curve) showed good

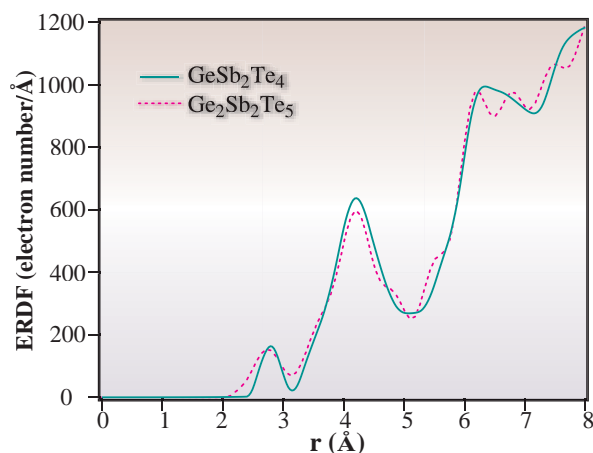


Fig. 3. The electron radial distribution functions (RDFs) of the amorphous films of GeSb_2Te_4 (solid line) and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (dashed line).

agreement with the observed RDF profile. The third observed peak consists of three single peaks at $r = 5.7, 6.2$ and 6.9 \AA , which are presumed to correspond to the 3rd, 4th and 5th atomic pairs of the crystal structure. These results suggest that the local structure of this pseudobinary amorphous compound bears the structural characteristics of its crystalline phase to a large extent [3].

We have seen that the crystal and amorphous phases of the $\text{GeTe-Sb}_2\text{Te}_3$ pseudo-binary phase-change material have very similar atomic arrangements to each other over a wide composition range. It is believed that when an amorphous mark is given energy by laser irradiation to erase a record, this structural similarity between the two phases enables the phase change to occur with only a slight atomic movement, which results in rapid phase transformation.

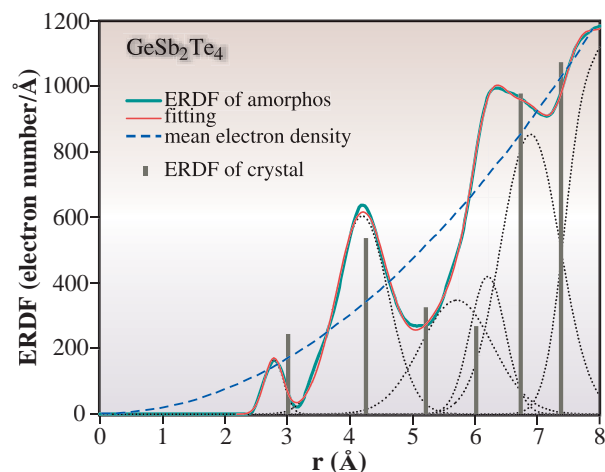


Fig. 4. The electron radial distribution function (RDF) of the amorphous film of GeSb_2Te_4 (indicated by thick line). The bars indicate the calculated RDF of the crystal structure of GeSb_2Te_4 .

Toshiyuki Matsunaga^a, Noboru Yamada^b and Masugu Sato^c

- (a) Characterization Technology Group, Matsushita Technoresearch, Inc.
- (b) Storage Media Systems Development Center, Matsushita Electric Industrial Co.
- (c) SPring-8 / JASRI

E-mail: matsunaga.toshiyuki@jp.panasonic.com

References

- [1] T. Matsunaga and N. Yamada: Jpn. J. Appl. Phys. **41** (2002) 1674.
- [2] T. Matsunaga, N. Yamada and M. Sato: submitted in Phys. Rev. B
- [3] M. Sato *et al.*: 2003 MRS Fall Meeting Proc. (Boston in USA, 2003).