Structural investigation for a-AIST clarify the difference between the two types of contrastive phase-change mechanisms

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ABSTRACT

Nowadays the most common phase-change materials are $GeTe-Sb_2Te_3$ pseudobinary compounds and Sb-Te binary compounds with small amounts of In, Ag and/or Ge. These materials possess sufficiently fast recrystallization speed; however, recrystallization in the two materials is strikingly different, although their crystal structures are very similar to each other. We have already determined the structure of the former amorphous pseudobinary materials and also scrutinized this time the latter amorphous structure by using a combination of advanced syhnchrotron radiation x-ray measurements and massive reverse Monte Carlo / density functional - molecular dynamics simulation; which clarified relationship between amorphous structure and phase-change behavior and difference in mechanism of the high-speed phase change between the two kinds of materials. It was found in the former pseudobinary materials that the recrystallization begins all at once from uncountable crystalline fragments embedded in the amorphous mark; whereas in the latter materials it starts from the rim of the mark and moves toward its center through bond interchanges in the atomic network. (Key words: Ge-Sb-Te, Ag-In-Sb-Te, DFT, RMC, amorphous, crystal, phase change)

1. INTRODUCTION

Phase change (PC) recording is now extensively used for high-density non-volatile memories [1]. Since 1970s, various materials have been proposed for the purpose, and nowadays we have obtained two superior materials of GeTe-Sb₂Te₃ (GST) [2] and Sb-Te based alloys such as AIST (Ag-In-Sb-Te quadruple compounds) [3]. These compounds possess two indispensable features for data storage; i.e., high endurance of the amorphous phase and high-speed PC from the amorphous to the crystalline phase. Their recrystallization speeds are sufficiently fast; however, their PC processes are strikingly different; although their crystal structures are very similar to each other (they have octahedral coordination structures formed by the *p*-*p* bonding [4], [5], [6]). It is well known that in the former group recrystallization proceeds mainly by way of nucleation inside the marks, in the latter group by way of crystal growth from the rim [6]. There have been numerous studies on amorphous GST (a-GST); on the other hand, little is known about the structures of amorphous AIST (a-AIST). In order to clarify difference, we analyse the structure of the AIST amorphous phase using a combination of advanced synchrotron radiation x-ray measurements and massive reverse Monte Carlo (RMC) / density functional (DF)-molecular dynamics (MD) simulation. We believe that this investigation will give us an important clue to develop new PC materials for the next generation.

2. EXPERIMENTS

The Ag _{3.5}In_{3.8}Sb_{75.0}Te_{17.7} powder specimens for the XRD experiments were made by laminating a 5-nm-thick ZnS–SiO₂ film on a glass disc (diameter 120 mm) and sputtering to form a recording film of thickness 200–500 nm. The specimen was removed from the glass substrate using a spatula, and its composition was studied using inductively coupled plasma atomic emission spectrometry. We performed diffraction experiments using the BL02B2 bending-magnet beamline of SPring-8, run by the Japan Synchrotron Radiation Research Institute [7]. The beam energy was about 29.5 keV. Intensity

data were collected using a Debye-Scherrer camera with a 287 mm radius. An imaging plate with a pixel area of 100 μ m² was used as the detector; by reading it for a pixel area of 50 mm², intensity data in steps of 0.01° were obtained. The experiments at low and high temperatures were conducted by blowing N₂ gas at a specified temperature onto the capillary.

The specimens for the EXAFS experiments were made by laminating a Kapton film of 25 μ m thickness overlaid on a glass disc with a diameter of 120 mm, followed by sputtering to form the recording films of thickness 300 nm. XRD measurements confirmed that the films were amorphous. The Kapton film sheets were peeled from the glass discs and cut into 10 mm squares, which were then stacked to form the specimens. The EXAFS measurements were carried out at the BL14B2, another bending-magnet beamline of SPring-8. The incident X-ray beam was monochromatized by a Si double-crystal monochromator with (111) net planes. Contamination with higher harmonics in the incident beam was removed by rhodium-coated mirrors located downstream of the monochromator. Vertical focusing of the incident beam at the sample was performed by slightly bending the mirrors. EXAFS data of Ag, In, Sb and Te K edges were collected in transmission mode. The backscattering amplitudes and the mean free paths used for the EXAFS analyses were obtained from FEFF [8] calculations. The coordination numbers *N* and bond lengths *r* were determined by least-squares fitting using the Rigaku REX2000 software [9]. The analysis was simplified by assuming that each absorbing atom was surrounded by Sb atoms alone.

The XRD experiments for the RMC analysis were carried out at room temperature at the SPring-8 high-energy XRD beamline BL04B2 [10] using a two-axis diffractometer dedicated to glass, liquid and amorphous materials. The incident X-ray energy was 61.5 keV. The diffraction patterns of the powder sample in a thin-walled (10 μ m) tube of 0.5 mm diameter (supplier: GLAS Müller, 13503 Berlin, Germany) and an empty tube were measured in transmission geometry. The intensity of incident X-rays was monitored by an ionization chamber filled with Ar gas, and the scattered X-rays were detected by a Ge detector. A vacuum chamber was used to suppress the air scattering around the sample, and the data collected were corrected using a standard program [10].

3. RESULTS

XRD and EXAFS analyses

X-ray diffraction patterns of the amorphous Ag _{3.5}In_{3.8}Sb_{75.0}Te_{17.7} taken at from RT to 506 K are shown in Fig. 1, which clearly demonstrates the amorphous phase is stable up to about 397 K (125°C). Above 415 K or more, Bragg peaks showing the formation of the crystalline phase (an A7-type structure) emerged in the halo pattern of the amorphous phase. However, the patterns obtained below 397 K are almost the same irrespective of temperature; this strongly suggests that the atomic configuration in this amorphous material remains unchanged not depending on temperature up to the transition temperature to the crystalline phase. Our EXAFS measurements performed at various temperatures revealed that the a-AIST preserves its atomic configuration against rise in temperature. We analyzed the local structures in this amorphous material at several temperatures from 10 K to 300 K by EXAFS method under the assumption that the four kinds of constituent atoms are all surrounded only by Sb atoms, because Sb is the main element of this material (and besides, atomic numbers of these four atoms are very close to each other, which makes it very difficult to distinguish these atoms in the x-ray analyses). The structural parameters, coordination number N, bond length r, Debye-Waller factor B etc. were obtained by least squares curve fitting [8]. The graphs in Fig. 2 show the temperature dependence of these structural parameters derived by the EXAFS method; as seen in these graphs, coordination numbers and bond lengths remain almost unchanged with the increase of temperature. The temperature dependences of the Debye-Waller factors (in the figure, those are shown by transformed into B.), which represent the



Fig. 1. Synchrotron X-ray diffraction patterns for a Ag $_{3.5}In_{3.8}Sb_{75.0}Te_{17.7}$ powder specimen taken at from RT to 693 K.

dynamic and static shifts (fluctuation) their equilibrium positions, gradually increase with temperature raise; however, their slopes are fairy gentle, which is remarkable when compared with those for the crystalline phase [5]. It is suggest from these results that the atomic configuration and the bond lengths remain almost unchanged without depending on temperature. In addition, it has been revealed that the dependence of the atomic fluctuation on temperature is considerably small. These thermal behaviors elucidate



Fig. 2. Temperature dependences of the coordination numbers N, bond lengths r, and temperature factors (the atomic displacement parameters) B for the amorphous Ag_{3.5} In_{3.8} Sb_{75.0} Te_{17.7}.

that the structure of amorphous phase is stable enough probably even at the high temperatures below the transition temperature; in other words, such a structural feature (stability), probably given by the strong covalent bondings of the atoms, is presumed to enable this amorphous material to retain its phase for a sufficiently long time, especially around room temperature. As shown below, RMC/DF-MD analysis revealed in fact that Sb atoms have 3 (short) +3 (long) coordination structures both in the crystalline and amorphous phases; however, in the latter phase, the bond length of the former is

Table 1 Local structure of a-AIST determined by EXAFS at 26 K and DF / MD calculations. *N*, coordination number; *r*, nearest-neighbour bond length; N_{bond} , chemical coordination number. Theoretical values from RMC-refined DF geometry ($N_{\text{DF-MD}}$ and $r_{\text{DF-MD}}$) and chemical bond-order analysis. The N_{bond} values of c-AIST are given in parentheses.

Atom (i)	Ν	r (Å)	N _{DF/MD}	$r_{DF/MD}(Å)$	N_{bond}
Ag	3.3 ± 0.5	2.768 ± 0.006	4.4	2.80 ± 0.05	1.9 (2.0)
In	4.3 ± 0.6	2.826 ± 0.006	3.1	2.85 ± 0.05	2.5 (2.9)
Sb	3.7 ± 0.3	2.872 ± 0.006	3.3	2.85 ± 0.05	3.1 (3.2)
Te	2.4 ± 0.4	2.827 ± 0.006	2.5	2.85±0.05	2.5 (2.6)

considerably shorter than that in the crystalline phase, which corresponds well to typical Sb-Sb covalent bond length. We can therefore regard the number coordination of Sb as approximately three, which satisfies the 8-N rule [11]. This bonding nature has also been observed in the amorphous GST [12], [13]; which is therefore considered to be a major reason that the amorphous phases of these phase-change materials show a sufficient endurance at room temperature.

RMC/DF-MD analysis

As it is well known, MD is a computer simulation of physical movements of atoms and molecules, and DF theory is currently a very useful, another computational analysis method for examining structural, electronic, and dynamical properties in materials science. The combination of these two methods, MD simulation based on DF makes it possible for us to study dynamical processes such as structural transformations of covalently bonded materials as well as chemical reactions in condensed matters. On the other hand, RMC simulation is also very useful to experimentally examine amorphous structures [10]. However, it is ordinary difficult for us to analyze the actual structure of an amorphous material from only one dimensional diffraction data. Besides that, the presence of four elements in AIST and the dominance of two (Sb, Te) with similar atomic numbers make it further difficult to determine the local structure by XRD alone. We then this time scrutinized the amorphous structure by using the combination of (DF) -MD and RMC simulations to reproduce X-ray diffraction (XRD), and furthermore, hard X-ray photoelectron spectroscopy (HXPS) data [6].

The determined structure is shown in Fig. 3 together with that of GST225 (Ge₂Sb₂Te₅). These results agree with those found in the EXAFS analyses. Table 1 also gives values for the RMC/DF-MD geometry on the basis of the partial pair distribution functions and bond-order analysis [6]. The coordination numbers obtained from EXAFS measurements for Sb and Te (3.7 ± 0.3 and 2.4 ± 0.4 , respectively) agree well with the calculated values. The EXAFS measurements indicate that there are only small differences between the bond lengths, with Ag bonds being slightly shorter (2.77 Å). This is consistent with the RMC/DF-MD results, where the bond lengths are near 2.85 ± 0.05 Å for most pair distribution functions. As

mentioned above, the coordination number of Sb approximately satisfies the 8-N rule [11]; however, it connects with other three at longer distance. We stress that Sb atoms in the amorphous phase have 3+3 coordination structures as well as in the crystalline phase as seen in Fig. 3(b).

Figure 4 shows the structure factors S(Q) of AIST and GST obtained using XRD. The crystalline forms of both have sharp Bragg peaks (red lines), and the amorphous forms (black lines) have typical halo patterns. However, oscillations up to the maximum Q value in a-AIST indicate a structure with well defined short-range order. Fourier transformation of the S(Q) leads to the total correlation functions T(r) for c-GST and c-AIST (Fig. 2b), which are very similar beyond 4 Å. Small differences between the two crystalline forms are found at shorter distances, for example the double peak in c-AIST (2.93 Å and 3.30 Å) and a single peak in c-GST (2.97 Å). The T(r) for the amorphous materials, however, are significantly different: the first peak in a-AIST (2.86 Å) is only slightly shorter than that found in c-AIST (2.93 Å), whereas the first peak in a-GST (2.79 Å) is much shorter than that in c-GST (2.97 Å). We note also that the shoulder on the second peak in a-AIST (3.5 Å, arrowed) is near that observed in the crystalline form (3.30



Fig. 3 (a) Section of 460-atom DF-MD model of a-GST (24 Å \times 24 Å \times 12 Å). Ge, red; Sb, blue; Te, yellow; large cavity, pink. (b) Section of 640-atom DF-MD model of -AIST (24 Å \times 24 Å \times 12 Å). Ag, silver; In, magenta; Sb, blue; Te, yellow. A large cavity is present among the atomic arrangement in the a-GST structure. Enlarged configuration (left bottom figure) shows that a-GST has many structural units (ABAB-squares) with alternating Te and Ge (or Sb) atoms. We can observe even a fragment of NaCl lattice. On the other hand, few cavities are observed in the a-AIST structure on the right.

Å). The pronounced difference between the diffraction patterns of the two materials is strong evidence that they crystallize differently. The atomic motion and/or diffusion accompanying the PC are larger in GST than in AIST, where the PC is accompanied by small changes in bond lengths.

4. DISCUSSION

Phase change in GST materials

It is well known that the most commonly used recording material is GeTe-Sb₂Te₃ pseudobinary compound. A recording film made of this material can be switched rapidly and reversibly between the crystalline phase and the amorphous phase by a brief laser irradiation (several tens of nanoseconds). This pseudobinary compound maintains the same NaCl-type structure



Fig. 4. HXRD data for AIST and GST, and atomic configurations of a-AIST and a-GST. (a) Structure factors S(Q) and (b) total correlation functions T(r) of AIST and GST. Red line, experimental data of crystalline phase; black line, experimental data of amorphous phase; blue line, DF-RMC model of a-AIST. The DF-RMC and experimental results are practically indistinguishable.

(space group: $Fm\overline{3}m$) over a wide range of compositions from 100 % of GeTe to at least $(GeTe)_1(Sb_2Te_3)_2$ (namely, $Ge_1Sb_4Te_7$) when subjected to instantaneous heating by laser irradiation followed by equally rapid cooling (see Fig. 3(a)) [4]. In this structure, the Cl:4a site is (almost) completely occupied by Te atoms, whereas the Na:4b site is randomly occupied by Ge and Sb atoms and vacancies. When the chemical formula of the pseudobinary compound is expressed as $(GeTe)_x$ - $(Sb_2Te_3)_{1-x}$; $(0 \le x \le 1)$, the ratio of the vacancy continuously changes according to (1-x)/(3-2x). The atoms in the crystals are orthogonally connected with six adjacent atoms (or vacancies) by p-p bonding; the atomic network of this structure consists of fourfold and sixfold rings. The atomic arrangement of the amorphous phase can be geometrically obtained by minute shifting of the atoms in random directions almost without bond interchanges found in the phase change of AIST (this is shown below), which means that, when an amorphous

GST is given energy by laser irradiation (or ohmic heating) and then instantaneously cooled, the atomic migration distance is so short that the solid instantaneously crystallizes into this type of highly symmetric (spatially isotropic) structure similar to that of the amorphous phase.



Fig. 5. The central atom with three short (red) and three long (dashed) bonds crosses the center of the distorted octahedron, interchanging a short and a long bond. Green: resultant vector of short bonds. The bonding electrons are excited by laser light (hv) to cause an interchange of bonding electrons, for example, between the two bonds pointed by the yellow arch, which moves the atoms in the amorphous phase to form locally crystalline atomic configurations; the local crystalline atomic networks finally form resonant bonding between periodic short and long bonds, which leads to the crystalline A7 network. The grey sticks (lower right) correspond to the red bonds (upper right). Atom colors as in Fig. 3(b).

Many structural investigations have been dedicated to the GST amorphous materials. Coordination numbers for three constituent atoms approximately follow the 8-N rule, largely different from those of the crystalline phase; for instance, those of a-GST225 are ca 3.7, 3.0, and 2.6 around Ge, Sb, and Te atoms respectively. These approximately satisfy the 8-N rule, showing the characteristics of covalent bonds often observed in calcogenide amorphous materials. The bond lengths are also shorter than in the crystalline phase. The atomic configuration is maintained almost unchanged up to the transition temperature to the crystalline phase [12], [13]. It has been considered that such a strong covalent bonding nature gives these amorphous materials sufficient endurance, namely, long-term data preservation. These GST materials contain three kinds of atoms, Ge, Sb, and Te; which means that, if these atoms connect with each other with equal probability in their amorphous structures, six kinds of atomic pairs should be found at the ratio provided by a random covalent network model. It has been revealed, however, that these amorphous materials comprise a large number of Ge-Te and Sb-Te atomic pairs beyond the above estimation (Note that the crystalline phase is formed by these two pairs as well). In a-GST225, 40% of the rings are fourfold or sixfold and a considerable amount of the relict GeTe₄ tetrahedra and SbTe₃ pyramids whose bond angles are distributed around 90° as same as those of the crystalline phase [14], [15]; we can find even NaCl-type crystalline fragments in the amorphous atomic network as seen in Fig. 3(a). Once sufficient heat energy is supplied to the amorphous material; however, those

crystalline fragments act as first nuclei to crystallize their surroundings all at once. We presume that this is the rapid phase-change mechanism of the GST materials. However, in addition to these countless nuclei, a large number of huge voids (see Fig. 3(a)) are present in the amorphous phase, which impedes smooth crystal growth. As a result, the texture of the crystallization-completed amorphous mark shows a mosaic pattern inlaid by a large number of tiny crystallites with 10 - 20 nm diameters. In addition, amorphous and crystalline GST materials have considerably low thermal conductivities, meaning that these materials can locally heat up at once by laser irradiation or ohmic heating [13]. This feature is very favorable to cause rapid PC. Major element in the GST materials is Te; its coordination number in the amorphous phase is approximately two. This means that the Te atoms have to also form other bonds in addition to these existing ones by the transformation to the crystalline phase.

Phase change in AIST materials

Laser-annealed Ag_{3.5} In_{3.8} Sb_{75.0} Te_{17.7} crystallizes into an A7 structure, as do As, Sb and Bi [16]. The A7 structure is shown in Fig. 5(b); four constituent atoms randomly occupy the 6(c) site of space group $R\overline{3}m$ [5]. As seen in Fig. 3 there are three shorter interatomic distances (shown by gray thick line) and three longers between the central atom and its six neighbors. This crystal can be described as a Jahn-Teller deformed structure to stabilize the electronic structure showing a semi-metallic feature [17], which can be regarded almost as a semiconductor. However, as mentioned above, the atoms in the crystal are quasi-orthogonally connected with adjacent six atoms (3+3 octahedron) by *p*-*p* bonding as well as a NaCl-type GST crystal; the atomic network of this structure consists of fourfold and sixfold rings. The densities of states (DOS) of both crystals are very similar to each other. Green arrows in the Fig. 5 show resultant vectors of short bonds,

which are parallel to each other and arranged along the *c*-axis direction. The structure (bond lengths and angles) and chemical coordination numbers obtained by the RMC/DF-MD simulation lead to the local environment around Sb atoms shown in Fig. 5. Both a-AIST (left panel) and c-AIST (right panel) resemble a (distorted) 3 + 3 octahedron.

In the amorphous state, interatomic distance between the central atom and three shorter coordination atoms is considerably shorter than in the crystalline state; they are connected to each other by a stronger covalent force than those in the crystal to form isolated molecule by themselves. These molecules formed by the short bonds are flexibly connected by vertices or edges; a spatially periodic arrangement is not necessarily required of them. For this reason, the green arrows are randomly oriented as seen in the left bottom panel of Fig. 5. However, once sufficient heat energy is given to the amorphous material, it causes interchange of one bond in a 3+3 coordination octahedron to rearrange, parallel neighboring two vectors. This rearrangement swiftly propagates from neighbor to neighbor forming the crystalline preferred orientation to acquire a periodic atomic arrangement, which finally shows needle-like crystallization texture from the rim toward the center of the mark (The crystalline phase is more opaque to the visible light; it is presumed that the crystallization materials, few voids to retard smooth crystal growth were found in the amorphous AIST. We presume that small number of elements, Ag and In play an important role to form simple and spatially isotropic crystalline phase, which is an A7-type structure; for it is considered that atomic arrangements of the amorphous phase can be transformed into that crystalline phase through minimal atomic shifts [18].

5. SUMMARY

According to the bond-interchange model, crystallization of a-AIST can be recognized as a rapid succession of diffusionless events where the 3 + 3 octahedra are aligned along the crystalline *c* axis imposed by the surrounding crystal (see Fig. 5). Heating or photon excitation causes the octahedra to align near the matrix boundary, and blade- or needle-like crystallites can grow along the laser- scanning direction, as often observed in Sb-based PC materials. The lack of cavities and chemical alternation in a-AIST favor smooth crystal growth. On the other hand, in the latter material, GST, high-speed phase change begins from uncountable crystalline fragments embedded in the amorphous network all at once. In the former material, Sb atoms are generally surrounded by Sb atoms of the same kind (with the same coordinate bonding nature); whereas in the latter material, neighboring atom of Sb is almost always Te. This is presumed to be one major reason that the former materials can take place such a bond-interchange phase transition.

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