Understanding of the fine stability of amorphous Ge$_2$Sb$_2$Te$_5$
by structural analyses

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ABSTRACT

Optical recording disks are now extensively used as rewritable nonvolatile high-density memory storage media, particularly for home-use videodisc recorders. The most commonly used materials for optical recording today are GeTe-Sb$_2$Te$_3$ pseudobinary compounds. These compounds have a superior ability to hold data at room temperature for extended periods and they allow high rewrite speeds; therefore, alloys in this system are used not only for rewritable optical recording materials but also recently for non-volatile electronic memories. We investigated the structure of amorphous Ge$_2$Sb$_2$Te$_5$ film by performing extended x-ray absorption fine structure (EXAFS) and high-energy x-ray diffraction (XRD) measurements to reveal the stability of the amorphous phase. The results of the EXAFS measurements showed that the three constituent atoms, Ge, Sb, and Te, hold their coordination structures irrespective of measurement temperature up to the transition temperature of around 413–423 K to the crystalline phase. In addition, the XRD measurements showed that the diffraction patterns remained almost unchanged except at the transition temperature. These results demonstrate that this amorphous Ge$_2$Sb$_2$Te$_5$ film robustly holds its atomic configuration to resist transformation to the metastable NaCl-type crystalline phase at around room temperature. Such structural stability is expected to give this amorphous material sufficient endurance to provide long-term data preservation.

Key words: phase-change memory, Ge$_2$Sb$_2$Te$_5$, XRD, EXAFS, local structure, temperature dependence, endurance
1. INTRODUCTION

In phase-change optical disks, large-capacity data can be recorded by forming high-density amorphous marks on the recording film. The most widely used type of recording material for optical disks today is GeTe-Sb₂Te₃ (GST) pseudobinary materials [1]. These GST materials are used not only for optical recording but also in research and development for non-volatile electric memories, as evidenced by the vigorous activity in this field. This is because the GST materials have three characteristics essential for these memories: (1) records can be rewritten very fast, (2) records can be rewritten up to about 10⁴ times, and (3) records can be retained stably for extended periods of about 30 years. The first and third characteristics are the two extremes, apparently incompatible with each other; however, these GST materials possess both of them, showing superior capabilities for high-speed rewritable and non-volatile memories. It is presumed that the first feature is acquired by the topological similarity in atomic configuration [2] and by a structural feature specific to these crystalline phases [3]. However, for the third characteristic, which is assumed to be strongly related to the atomic configuration and the bond nature of the amorphous phase, the relationship between its structural feature and stability (long-term data preservation/endurance against data extinction has not yet been sufficiently studied. Here, we scrutinized the amorphous Ge₂Sb₂Te₅ film to examine the atomic configuration of the amorphous phase and its temperature dependence by performing the XRD (x-ray diffraction) and EXAFS (extended x-ray absorption fine structure) measurements and analyses, revealing the reason why the amorphous GST retains its phase for a sufficiently long time.

2. EXPERIMENTS

An amorphous Ge₂Sb₂Te₅ thin film with a thickness of approximately 300 nm was formed by sputtering on a glass disk 120 mm in diameter. To prepare the experimental specimen for x-ray diffraction, its powder was then packed into a quartz capillary tube with an internal diameter of 0.3 mm. Both ends of the capillary were closed to prevent contact with the atmosphere. We performed diffraction experiments using the BL02B2 beamline at the Japan Synchrotron Radiation Research Institute [4]. 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 µm² was used as the detector; by reading the imaging plate for a pixel area of 50 mm², intensity data in steps of 0.01° were obtained. Experiments at low and high temperatures were conducted by blowing N₂ gas at a specified temperature onto the capillary.

Another amorphous Ge₂Sb₂Te₅ thin film with a thickness of approximately 300 nm was made for the EXAFS experiments by sputtering on an organic film sheet that was laminated on a glass disk with a diameter of 120 mm. It had been confirmed in advance using x-ray diffraction that the formed film was in an amorphous state. The organic film sheet was peeled off from the glass disk and cut into square pieces about 10 mm in size; appropriate numbers of sheet were then stacked to form a measurement specimen. The EXAFS measurements were carried out at the BL01B1 beamline of the Japan Synchrotron Radiation Research Institute (SPRING-8). The incident x-ray beam was monochromatized by a Si double-crystal monochromator. The net planes of the monochromator were (111). Contamination with higher harmonics in the incident beam was removed by Rh-coated mirrors. EXAFS data of Ge, Sb and Te K-edges were collected in transmission mode. Experiments at low and high temperatures were conducted using a He gas circulation cryostat and an electric furnace. The mean free paths, backscattering amplitudes, and phase shifts were obtained by the FEFF [5] calculations. The Debye temperatures used for the calculations were estimated by performing powder diffraction experiments and Rietveld analyses using appropriate crystalline specimens.

3. RESULTS & DISCUSSION

We show below the XRD and EXAFS measurement results, which reveal that the amorphous Ge₂Sb₂Te₅ robustly holds its atomic configuration with no dependence on temperature.
1. XRD

The x-ray diffraction patterns of the amorphous Ge$_2$Sb$_2$Te$_5$ taken from 90 K to 418 K are shown in Fig. 1, and these clearly demonstrate that the amorphous phase is stable up to about 413 K. Above 413 K, Bragg peaks showing the formation of the crystalline phase (a metastable NaCl-type structure) emerged in the halo pattern of the amorphous phase. However, the patterns obtained below 413 K are almost the same irrespective of temperature; this strongly suggests that the atomic configuration in this amorphous material remains unchanged regardless of temperature. We performed RMC analysis to reveal the atomic configuration in this material at room temperature, which showed a considerable amount of relict GeTe$_4$ tetrahedra and SbTe$_3$ pyramids, whose bond angles are the same as those of the crystal phase [2]. However, the coordination numbers are different from those in the crystalline phase, at 3.7, 3.0, and 2.6 around Ge, Sb, and Te atoms, respectively; these findings show the bond characteristics seen in calcogenide amorphous materials. The bond lengths are also shorter than in the crystalline phase. The above x-ray diffraction measurement results indicate that this atomic configuration analyzed at room temperature is maintained almost unchanged up to the transition temperature to the crystalline phase.

2. EXAFS

Our EXAFS measurements performed at various temperatures revealed that the amorphous Ge$_2$Sb$_2$Te$_5$ defends its atomic configuration against a rise in temperature. The presence of Ge$_2$Sb$_2$Te$_5$ in GeTe-Sb$_2$Te$_3$ pseudobinary compounds is historically important, and it was fabricated first in phase-change optical disks in the early 1990’s. Consequently, many investigations have been conducted on this compound [6]. In EXAFS analyses of them, Paesler et al.’s results [7] are, as shown in Table I, approximately consistent with those of our RMC analysis. We then analyzed the local structures in the amorphous Ge$_2$Sb$_2$Te$_5$ from 10 K to 403 K by the EXAFS method under the assumptions that there were only three kinds of atomic pairs (Ge-Ge, Ge-Te, and Sb-Te) in the matrix and that two kinds of bonds with different interatomic distances are present in the Sb-Te pairs. The structural parameters, $m$, $R$, $B$, etc. were obtained by least squares curve fitting. The analytical software employed was Rigaku REX2000 [8].

Table I presents a summary of the coordination numbers and bond lengths. As indicated in this table, our analysis results showed good accordance with those derived by Paesler et al. The coordination numbers obtained are slightly different from those expected by the 8-$N$ rule. (It is generally believed that in a covalent amorphous state, the IV ($N = 4$) group elements such as Ge, the V ($N = 5$) such as Sb, and the VI ($N = 6$) such as Te have four-, three-, and two-fold coordination, respectively. [9]) However, these EXAFS results approximately coincide with our previous [2] and Paesler et al.’s results; furthermore, they satisfy $n_{\text{Ge-Te}} = n_{\text{Te-Ge}}$ and $n_{\text{Sb-Te}} = n_{\text{Te-Sb}}$ to a good extent, as shown in Table I. The deviation in coordination number from the 8-$N$ rule is also found in the DFT (density functional theory) calculation results by Akola and Jones [10]. The bond lengths obtained also show a good agreement with those derived by our previous work, Paesler et al., and Kolobov et al., [11]. These coordination numbers and bond lengths seen in Table I were nearly constant from 10 K through 403 K. The conditions, $n_{\text{Ge-Te}} = n_{\text{Te-Ge}}$ and $n_{\text{Sb-Te}} = n_{\text{Te-Sb}}$, which should necessarily be satisfied, were held at all of the measurement temperatures as well.

Figure 2 shows the temperature dependence of the Debye–Waller factors (here, transformed into $B$), which represent the dynamic and static shifts (fluctuation) from their equilibrium positions. As can be seen in this figure, $B$s gradually increase with temperature; however, their slopes are fairly gentle, which is remarkable when compared with those for the crystalline phase. We learned above that the atomic configuration and the bond lengths remain almost unchanged, with no dependence on temperature. In addition, it has been revealed that the dependence of the atomic fluctuation on temperature is very small. These two findings mean that the structure of the amorphous phase is stable enough even in the high temperatures below the transition temperature, which is presumed to enable this amorphous material to retain its structure for a sufficiently long time, especially around room temperature or lower. This structural feature of the amorphous phase is probably due to the strong covalent bonding of the atoms.
4. CONCLUSION

We carried out XRD and EXAFS measurements and analyses to examine the atomic configuration of the amorphous phase and its temperature dependence. These analyses revealed that the amorphous Ge$_2$Sb$_2$Te$_5$ robustly holds its atomic configuration almost irrespective of temperature. This is presumed to be the major reason why this amorphous material retains its structure for extended periods of about 30 years around room temperature. However, this material can be rapidly switched to the crystalline phase by instantaneously supplying sufficiently large heat energy. These chalcogenide GST compounds have superior abilities to hold data at room temperature for extended periods and to provide high rewrite speeds; consequently, they are very useful for industry and very interesting for science.

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REFERENCES


Biographies

Dr. Toshiyuki Matsunaga received his Ph.D. in physics for his work on crystal structures, phase transitions, and bonding natures in intermetallic compounds in 1986 from Hiroshima University in Japan. Since joining Matsushita Electric Industrial in 1984, he has developed new electronic devices by analyzing a large number of materials by such surface analysis methods as SEM, XMA, AES, SIMS, and TPD. Since 1996, he has been involved in optical disc R and D, concentrating on basic transition phenomenon research in phase-change recording materials.

Table of his education information

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Figure 1. X-ray diffraction patterns for amorphous Ge$_2$Sb$_2$Te$_5$ taken from 90 K to 418 K (left figure). The amorphous state is maintained up to 403 K; however, Bragg peaks of the metastable NaCl-type crystalline phase can be seen in the diffraction patterns at 413 K and 418 K. Total correlation functions $T(r)$ of 90 K, 300 K, and 408 K are shown in the right figure.
Table I. Local structure for amorphous Ge$_2$Sb$_2$Te$_5$ determined by EXAFS. The symbols $m$, $R$, and $n$ represent coordination number, nearest neighbor bond length, and number of atomic pairs, respectively, and the suffixes $i$ and $j$ indicate the atom species. The numbers of atomic pairs, which can be obtained by $NC_i m_{ij}/(1+\delta_{ij})$, are indicated in terms of a single molecule ($N$ is the number of atoms in the matrix. $NC_{Ge}$, $NC_{Sb}$, and $NC_{Te}$ are 2, 2, and 5, respectively; $C_i$ represents respective atomic concentration. $\delta_{ij}$ is Kronecker’s delta). In the curve fitting analysis for the Te absorption atom, the following three constraints were assumed: 1) $m_{Te(e)-Sb}/m_{Te-Sb} = m_{Sb-Te(e)}/m_{Sb-Te}$, 2) $R_{Te-Sb} = R_{Sb-Te}$, and 3) $R_{Te(e)-Sb} = R_{Sb-Te(e)}$. Paesler et al. attribute Sb-Te(e) with a shorter bond length to the Sb$^–$-Te$^+$ bond.

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Figure 2. Temperature dependences of temperature factors (atomic displacement parameters) $B$ for the amorphous and crystalline (metastable) Ge$_2$Sb$_2$Te$_5$. $B$s for the Na (□) and Cl (○) sites in the Ge$_2$Sb$_2$Te$_5$ metastable crystal obtained by Rietveld analyses, which were performed assuming the NaCl-type cubic structure [12]. The two solid lines in the figure were obtained by least squares fitting to Rietveld analysis results for each site. Those for Ge (●), Sb (×), and Te (○) in the amorphous phase were obtained by the curve fitting method in the EXAFS analysis.