Structure Analysis of δ-phase in Sb-Te Alloys by HRTEM*1

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The crystal structure of δ-phase in the Sb-Te binary system was investigated by high-resolution transmission electron microscopy. The observed high-resolution images could be described by a simple rhombohedral structure with the lattice displacement wave (LDW). The wavelength of LDW was slightly longer than double the (111) plane in the rhombohedral structure, and increased slightly with increasing Te concentration.

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1. Introduction

Ag-In-Sb-Te alloys that are based on the binary Sb-Te system are used as recording materials in optical discs such as CD-RW and DVD+RW.1,2) These types of optical discs make use of the difference between the refractive indices of amorphous and crystalline phases. The amorphous phase has a lower reflectance than the crystalline phase. In order to understand the reason for the difference in the refractive indices, information about the structures of the amorphous and crystalline phase is indispensable. In spite of investigations that have used Extend X-ray Absorption Fine Structure and X-ray diffraction techniques,3,4) the detailed crystal structure of Sb-Te and Ag-In-Sb-Te alloys is still not established. The purpose of the present study is to investigate the crystal structure of sputter-deposited Sb75Te25 thin films on polycarbonate substrates by transmission electron microscopy (TEM). In order to investigate the influence of fabrication on the crystal structure, TEM observations were also made of specimens prepared by conventional melting and grinding.

2. Experimental Procedure

A thin film of Sb75Te25 with a thickness of 20 nm was sputter-deposited onto a polycarbonate substrate. The thin film and substrate assembly was cut into approximately 4 mm × 4 mm squares. A Cu grid mesh of 3 mm in diameter was glued onto the square sample and then immersed in dichloromethane diluted with ethanol to dissolve the polycarbonate substrate.

TEM observations were also carried out on specimens prepared by melting raw materials in an electric furnace. The compositions of the prepared alloys were Sb75Te18, Sb75Te25 and Sb85Te73, which are compositions found in the δ-phase field of the Sb-Te phase diagram.5) The raw materials were encapsulated in an evacuated quartz tube and melted at 1000°C for 1 hour. The specimens were annealed in evacuated quartz tubes at 500°C for 1 hour. The specimens were embedded in an epoxy resin and later sectioned using a microtome unit used for preparation of TEM specimens. The sectioned thin sheets were placed on Cu grid meshes and then fixed by carbon vapor deposition on the meshes.

Microstructures and diffraction patterns of the thin-film and powder specimens were observed by two different transmission electron microscopes (Philips Technai 30 and JEOL JEM-100CX). High-resolution TEM (HRTEM) images of the thin-film specimens were obtained using a JEOL JEM-4000EX. The HRTEM images and diffraction patterns observed in the present study were compared with those calculated using simulation software (MacTempas).

3. Results

Figures 1(a) and (b) show a bright field image and corresponding diffraction pattern observed in the Sb75Te25 thin film. Fig. 1(c) shows a simulated diffraction pattern using MacTempas taken from the [100]H direction for pure Sb with the α-As (arsenic) structure. The subscript H denotes that the index is represented by the hexagonal unit cell. The split spots indicated by the arrows in Fig. 1(b) correspond to the 003H diffraction spot in Fig. 1(c). These diffraction spots are at a distance of 2.45 and 2.91 nm−1 from the 000 spot. The midpoint of these spots is nearly equal to the inverse of the 003H plane spacing in pure Sb. The other split spots in Fig. 1(b) correspond to the diffraction spots for which the reflection indices, hkl, satisfy the condition l = 2n + 1. Aside from the observation that the specific spots are split, Fig. 1(b) is in good agreement with Fig. 1(c).

Figures 2(a), (b) and (c) show diffraction patterns observed in the Sb75Te25 thin film, taken from directions different to Fig. 1(b). Figures 2(d), (e) and (f) show simulated diffraction patterns corresponding to Figs. 2(a), (b) and (c), respectively. Any pair of split spots in Figs. 2(a) and (b) was found to correspond to a spot with an odd l index in Figs. 2(d) and (e), respectively. There are no split spots in Fig. 2(c) since the spots in Fig. 2(c) correspond to the spots with even l index in Fig. 2(f). Figures 2(a), (b) and (c) as well as Fig. 1(b)
correspond to the structure of pure Sb except for splitting of the specific spots.

Figure 3 shows a typical HRTEM image of the Sb$_{75}$Te$_{25}$ thin film taken from the same direction as shown in Fig. 1(b). Corresponding to the strong diffraction spots around the 000 spot in Fig. 1(b), three different kinds of lattice fringes can be observed in Fig. 3. A characteristic feature of Fig. 3 is the observation of two kinds of band-like regions approximately parallel to the (006)$_H$ plane, indicated as Regions (A) and (B) in Fig. 3. In Region (A), lattice fringes change their contrast every two atomic layers, whereas lattice fringes in Region (B) exhibit uniform contrast. Region (A') and (B') have the same lattice fringes feature as Region (A) and (B), respectively. Obviously, the band-like region that links (A) and (A') is not parallel to the (006)$_H$ lattice fringes although the boundaries of Regions A and B (A' and B') are not clear. This discrepancy is caused by the fact that the split spots in Fig. 1(b) deviate from the straight line that links the 000 and 006 diffraction spots in Fig. 1(b).
In order to investigate whether the characteristic crystal structure as described above was caused by the fabrication route for the thin film, some specimens for TEM observations were also prepared by the conventional method. Figures 4(a), (b) and (c) show the electron diffraction patterns obtained from the powder specimens of Sb$_{82}$Te$_{18}$, Sb$_{75}$Te$_{25}$, Sb$_{63}$Te$_{37}$, respectively. The characteristic split spots were also observed in these specimens. In addition, Fig. 4 and Fig. 1(b) show that while the distance of splitting is not influenced by the fabrication route, it is influenced by the concentration of Te. Figure 5 shows the ratio of $k$ to $g_{006}$ as a function of the concentration of Te, where $k$ and $g_{006}$ denote the scattering vector of the split spot and the reciprocal lattice vector of the 006$_H$ spot, respectively. The value of $k/g_{006}$ seems to change continuously as a function of the concentration of Te and cannot be represented by a simple integer ratio.

Figure 6(a) shows the diffraction pattern taken from the same direction as Fig. 1(b), and Figs. 6(b) and (c) are obtained by tilting the specimen by a few degrees around the lines (m) and (n) in Fig. 6(a), respectively. Since the split spots in Fig. 6(b) are still seen around 003$_H$ under the systematic diffraction condition, these split spots are not ghost-formed due to the effect of double diffraction. In Fig. 6(c) the weak spots of 2$k$, as indicated by the arrows, can also be seen to be free of double diffraction effects. This demonstrates that these spots are also intrinsic diffraction spots.

### 4. Discussion

Regarding the binary Sb-Te system, the crystal structures of Sb$_{1-x}$Te$_x$, SbTe and Sb$_2$Te$_3$ can be found in the literature.$^6$ The structures of Sb$_{1-x}$Te$_x$, SbTe and Sb$_2$Te$_3$ are based on the As, BiSe and Bi$_2$Te$_3$ crystal structures, respectively. The diffraction patterns observed in Fig. 1(b) and Fig. 2 cannot be explained by these structures. As described in the previous section, the diffraction patterns of the $\delta$-phase in the Sb-Te binary system are analogous to those of pure Sb with the As structure. Thus, the structure of $\delta$-phase will be considered here based on the As structure. As seen in Fig. 7, the As structure is formed by extending a
simple cubic structure along the [111] direction, followed by alternate displacing of the (111) planes to the controversial [111] direction. The rhombohedral unit cell in Fig. 7 can be transformed into the hexagonal unit cell shown in Fig. 8(a). Owing to the alternate displacing in Fig. 8(a), the super lattice reflections appear at $g_{006}/2$ as shown in Fig. 1(c), where $g_{006}$ is the reciprocal lattice vector corresponding to the (006)$_H$ plane; that is, the (111) plane of the distorted simple cubic structure. In Fig. 8(a), the alternate displacements can be regarded as displacement of the atom at $R_i$ to $R_i + u(R_i)$, where $u(R_i)$ is given by the following equation,

$$u(R_i) = u_0 \cos(2\pi k \cdot R_i).$$  

In eq. (1), $u_0$ and $k$ denote the polarization and wave vector of the lattice displacement wave (LDW), respectively. In the case of pure Sb, $u_0$ is $\sim 0.02 \times [001]_H$ and $k$ is $g_{006}/2$.

The similarity between the diffraction patterns of pure Sb and Sb-Te phases leads to the idea that the Sb-Te phases have a rhombohedral structure modified by the LDW as described in eq. (1). The value of $|k|/|G_{006}|$ is less than 0.5 in Sb-Te although it is 0.5 in pure Sb.

Figure 8(b) shows the model structure of Sb-Te. In this model, 7 wavelengths are equal to 15 atomic layers of the (000)$_H$ plane, that is, $7\lambda = 15d_{006}$. This means that $|k|/|G_{006}| = 7/15$ in reciprocal space. The value of $7/15$ ($= 0.467$) is approximately equal to the observed value shown in Fig. 5. Each atomic plane is shifted to the [001]$_H$ direction in the period of $\lambda$ in the present model. Consequently, in the model, two kinds of region exist, (A) and (B), which are characterized by an alternate atomic displacement similar to the As structure and approximately even atomic spacing, respectively.

Figures 9(a) and (b) show the relationship between the atomic configuration and the corresponding high-resolution image in the [100]$_H$ direction, which are simulated under the same conditions as the experiment. Region (A), which has the As-like structure, displays alternate bright and dark lattice fringes every two atomic layers. On the other hand, Region (B), which has nearly even atomic spacing, displays the simple lattice fringe. These band-like regions are observed to alternate in the [001]$_H$ direction. The simulated high-resolution image is able to reproduce the characteristic features of the observed images shown in Fig. 3. The simulated diffraction pattern (Fig. 9(c)) also reproduces the experimental result shown in Fig. 1(b). The agreement between these results shows that the model structure can be a good approximation of the structure of Sb-Te binary system.

As shown in Fig. 6(b), the split spots are seen in the
systematic diffraction condition. This means that the direction of $u_0$ in eq. (1) has a parallel component to $k$ as in the As structure. In addition, the extra split spots are also seen at $2k$ in Fig. 6(c). This suggests that the origin of the split spots may be caused by the modulation of atom positions rather than by the modulation of charge density. These experimental results support the model shown in Fig. 8(b).

Finally, it should be noted that the wave vector $k$ of LDW changes continuously depending on the concentration of Te. This implies that the formation of LDW is related to the number of the valence electrons of the Sb-Te alloys. Since the Fermi surface changes with the number of the valence electrons, the Fermi surface may play an important role in the formation of LDW. In fact, the formation of LDW can produce the energy gap at the wave vector $k$ of LDW in reciprocal space. If the Fermi surface exists near the corresponding position, the electronic states are expected to decrease.

5. Conclusions

(1) The HRTEM images and diffraction patterns showed that the LDW is formed in the $\delta$-phase of the Sb-Te binary system.

(2) The wave vector of the LDW, $k$, is approximately parallel to the reciprocal lattice vector of $g_{006}$, and $|k|/|g_{006}|$ continuously changes as a function of the Te concentration. This result implies that the Fermi surface plays an important role in the formation of the LDW.

REFERENCES