Variation of Microstructure and Electrical Conductivity of Amorphous AgInSbTe and SbTe Films during Crystallization

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Two kinds of chalcogenide films with similar Sb/Te atomic ratios, AgInSbTe (AIST) and SbTe (ST) were deposited on alkali-free glass using the RF sputtering method. The microstructure characteristics of both ST and AIST films were demonstrated to correlate with the electrical properties. TEM observation and GI-XRD profiles revealed that the structures of as-deposited AIST and ST films were amorphous characteristics. The sheet resistance of the as-deposited AIST films was twice as high as that of ST films and the effect of Ag and In additives was proposed. After annealing at 523 K for 1 h, the sheet resistance of both chalcogenide films decreased by four orders of magnitude due to crystallizations and the sheet resistance of crystallized AIST film was still twice as large as that of crystallized ST film. DSC measurement was used to determine the crystallization temperature of AIST films as 476 K and that of ST films as 445 K. The activation energies of crystallization were determined using Kissinger’s method, and 0.94 eV and 0.84 eV were obtained for AIST and ST films, respectively. TEM observations showed that AgSbTe2 phase exists in the AIST film after heat treatment in addition to δ-Sb phase. No indium compounds were discovered in the AIST film by the energy dispersive spectroscopy (EDS) and XRD measurements. [doi:10.2320/matertrans.48.610]

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1. Introduction

Thin chalcopyrite films such as Ge-Sb-Te and Ag-In-Sb-Te have been used as the recording layer in optical recordable discs. A characteristic of these films is that they are able to be quickly and reversibly transformed from an amorphous state to a crystalline state. The optical contrast and the electric properties corresponding to the change of structures are expected to be significantly different.1–3) Ovonic Unified Memory (OUM) is a kind of nonvolatile memory that utilizes such reversible characteristics in a GeSbTe chalcogenide alloy material. Such a technology can satisfy the requirements for non-volatile memory because both the amorphous and polycrystalline structures are stable at room temperature.2–5) In practical applications, OUM exhibits a high/low resistance ratio of about 10–100, depending on its programmed states, film structures and material properties.4,5) A key physical property for OUM applications is the sheet resistance with dependence on different crystalline structures.

The thermoelectric power and electrical resistivity of crystalline SbTe films have been studied. The sheet resistivity and Seebeck coefficient of SbTe films can change with the crystalline state6) and the appearance of the second phase.7) The SbTe films were also reported to have the potential for the fabrication of chalcogenide nonvolatile memory by using the focus ion beam method.5) However, there are few evidences reported on the relationship between microstructure characteristics and its corresponding electrical properties. The structural change of as-deposited SbTe film caused by post-heat-treatment is investigated in terms of crystallization temperature and thus, activation energy in the present study.6–13) Besides, previous studies have reported that SbTe films with Ag and In additives have a higher crystallization temperature and better stability than the SbTe binary system.14) Hence, this study aims to investigate the electrical properties for both SbTe and AgInSbTe films in association with the microstructural characteristics before and after heat treatment. The differences between SbTe and AgInSbTe films were discussed.

2. Experimental Procedure

Alkali-free glass sheets in 0.7 mm thickness were degreased and ultrasonically cleaned in acetone, and then were dried with clean compressed air. A 13.56 MHz RF sputtering system was adopted to deposit films on glass substrates in this study, and the substrate-to-target distance was fixed at 52 mm. The coater was pre-pumped to a pressure of less than 0.006 Pa. The sputtering pressure was controlled within 0.06 Pa with Ar flow. In the first part of the experiment, AIST films in different thickness were obtained by changing the sputtering duration at a sputtering power of 200 W. Film thicknesses and sheet resistance were measured by α-step equipment and a four-point-probe method, respectively. The variation in sheet resistance with film thickness was analyzed.

In the next part of the experiment, the same sputtering parameters, 100 W sputtering power and 60 s sputtering duration were used to deposit AIST and ST films using two separate targets. The film thickness was recognized as approximate 150 nm and the thickness difference between ST and AIST specimens was less than 10% due to the similar deposition rate. The chemical compositions were analyzed by inductively coupled-plasma spectroscopy and recognized similar Sb/Te atomic ratio for AIST and ST films (shown in Table 1). A differential scanning calorimeter (DSC) was used to analyze the thermal behavior of the AIST and ST films with five heating rates 0.083, 0.17, 0.25, 0.33, 0.50 Ks−1 from room temperature to 673 K. According to Kissinger’s method, the activation energy can be derived from eq. (1) by assuming that the crystallization rate reaches the maximum value in the transformation process.15,16)
from the slope of the straight line. 15) becomes thinner. 19,20) The size effect describes an inverse to bulk scatterings, and therefore the mobile electrons are mobile in the surface. The theory takes into account surface scatterings in addition to bulk scatterings. 17–20) However, a classical size-effect theory is also recognized in Fig. 2(b). The intercept of the straight line was obtained by plotting ln(α/T²) versus 1/T. The activation energy of crystallization was calculated from the slope of the straight line. 15)

ST and AIST films were isothermally annealed at different temperatures for 1 h and were naturally cooled down in the furnace. After heat treatment, the sheet resistance data could be plotted with the parameter against annealing temperatures and the transition temperatures for sheet resistance reduction could be recognized for ST and AIST films. The crystalline structures of specimens were analyzed using a Grazing-Incident X-ray Diffractometer (GI-XRD), and the microstructural feature was also observed by transmission electron microscopy (TEM). Morphologies, chemical compositions, lattice images and Fast Fourier Transform (FFT) images were analyzed to examine the relationship between electrical conductivity and extension of crystallization in ST and AIST films.

3. Results and Discussion

3.1 The relationship between sheet resistance and film thickness

From X-ray diffraction profiles of AIST films deposited at different durations as shown in Fig. 1, the broadened patterns which appear at low diffraction angles prove that all specimens possess amorphous structures even though the sputtering duration is as long as 600 s. It is a well-known phenomenon that for most amorphous materials the sheet resistance will actually be higher than the polycrystalline films. 17) However, a classical size-effect theory is also considered in this investigation quantitatively to confirm that it tends to decrease with increasing film thickness. 17–20) The theory takes into account surface scatterings in addition to bulk scatterings, and therefore the mobile electrons are scattered by the surface structure when film thickness becomes thinner. 10,20) The size effect describes an inverse relationship between sheet resistivity ρₚ and film thickness t as eq. (2).

\[
\rho_p = \rho_0 \left[ 1 + \frac{3}{8} \left( \frac{C_0}{T} \right) \right]
\]

where \( \rho_0 \) is the bulk resistivity, \( C_0 \) is a material constant related to the electron mean free path and the fraction of electrons incident on the surface that are scattered. 10) The plot of sheet resistivity versus film thickness is shown in Fig. 2(a), where the sheet resistivity has a inverse function of film thickness. Also, a linear relationship between ln(\( \rho_p \)) and ln(t⁻¹) is recognized in Fig. 2(b). The intercept of the regressive plot, corresponding to infinite thickness, represents the bulk resistivity of amorphous AIST as 3.11 × 10⁵ Ω·cm.

The variation in the sheet resistance resulting from film thickness must be clarified because crystallization of amorphous films must be taken into account in addition to the contribution due to the size effect. According to the eq. (2), the maximum variation in the sheet resistivity could be approximately 5% if the variation in film thickness can be controlled within 10%. However, it is reasonable that the thickness effect is assumed to be negligible in the next electrical resistance measurements through crystallization because the film thickness has been controlled to be the same.

3.2 Crystallization characteristics of AIST and ST films

DSC analysis of the AIST and ST films at the heating rate of 0.17 Ks⁻¹ are shown in Fig. 3. Exothermic peaks appeared at 476 K in the AIST curve and at 445 K in the ST curve, representing the crystallization temperatures of AIST and ST films. This result is compatible with other studies 21,22) but the crystallization temperature of ST film is found to be lower than that for AIST film in the present experiment. In addition, the XRD profiles of ST and AIST films after annealing at 523 K (as shown in Fig. 5) indicate that the peaks correspond with the crystallization of δ-Sb phase. The plots are obtained with Kissinger’s method of eq. (1), as shown in Fig. 4. The activation energies of crystallization for AIST and ST films were obtained as 0.94 eV and 0.84 eV, respectively. The higher crystallization temperature of AIST films indicates that the addition of the elements of Ag and In improved the stability of the amorphous structure of SbTe films. 23) However, the crystallization activation energies of ST and AIST films are fairly similar, which reveals that the crystallization rate is slightly affected by Ag and In additives.

Table 1 Chemical compositions of two kinds of chalcogenide films deposited using the same sputtering parameters.

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>In</th>
<th>Sb</th>
<th>Te</th>
</tr>
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<tbody>
<tr>
<td>AgInSbTe</td>
<td>3.4 at%</td>
<td>5.2 at%</td>
<td>60.8 at%</td>
<td>30.6 at%</td>
</tr>
<tr>
<td>SbTe</td>
<td>—</td>
<td>—</td>
<td>68.9 at%</td>
<td>31.1 at%</td>
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</table>
3.3 Electrical properties of AIST and ST films

Isothermal annealing was adopted to demonstrate the change in the electrical properties associated with the variation of microstructure. Figure 5 shows that the sheet resistance decreases with an increase of annealing temperature for AIST and ST films, where the sheet resistance of as-deposited film is $3 \times 10^4$ times larger than the film after annealing at 533 K. Furthermore, the sheet resistance of the amorphous AIST film (as-deposited) is approximately twice as high as that of the amorphous ST film and the ratio is maintained for specimens annealed at different temperatures. The transition temperature from a high resistive state (amorphous state) to a low one (crystalline state) is about 423 K for AIST film and 413 K for ST film. Hence, it seems that the higher sheet resistance of as-deposited AIST film is attributed to Ag and In addition.

Figure 6 shows the GI-XRD spectra of the AIST and ST films before and after crystallization, where the broad halo peak at low diffraction angles reveals that the structures of as-deposited specimens are amorphous. The profiles of ST and AIST films after annealing at various temperatures are also shown in Fig. 6(a) and 6(b). The ST film remains amorphous structure at the annealing temperatures below 403 K. Once the annealing temperature rises above 413 K, the $\delta$-Sb phase appears and the crystallinity significantly increases with an increase in annealing temperature. The same phenomenon is occurred in AIST films but the initial crystallization temperature is 20 K higher than ST films. In Fig. 6(a), there is only the $\delta$-Sb phase existing in the crystallized ST films after heat
treatment. The same phase is recognized in the crystallized AIST film as shown in Fig. 6(b). However, some previous studies have reported that AgSbTe_2 phase can precipitate in the SbTe film with silver additives after annealing at a temperature above 423 K. Based on the experimental data, the crystalline structure of AgSbTe_2 is cubic and that of δ-Sb phase is rhombohedral, and the lattice parameters of both phases are similar. Consequently, the diffracted peaks of δ-Sb phase are not easy to distinguish from those of AgSbTe_2 phase. Another literature has also reported that the In atoms can substitute for Sb sites as a solid solution if the In content is less than 5 at%. According to the results shown in Fig. 6(b), it shows a good agreement with the mentions that no indium compound is found. In summary, AgSbTe_2 and δ-Sb phases are expected to be formed in AIST film after annealing at 523 K in this study and it is obvious that the drastic change of sheet resistance from a high value to a low value is due to crystallization of amorphous films, as shown in Figs. 5 and 6.

The electronic transportations in chalcogenide glass is different from the amorphous semiconductors, which is generally attributed to changes occurring in the concentration of so-called valence alternation pairs. The chalcogenide alloy in the polycrystalline state shows a drastic increase in free electron density, which gives rise to a difference in resistivity and reflectivity. That is the reason why the sheet resistance of AIST films can show a drastic decrease from the amorphous to crystalline state. So far, there were two chalcogenide films utilizing such electrical property in OUM applications: (1) Ge-Sb-Te ternary alloy system, in which the sheet resistivity of amorphous film is around 10^3–10^4 times compared to that of crystalline one. (2) Sb-Te binary alloy system, in which the sheet resistivity of amorphous film is around 30 times higher than that of crystalline one. In the present study, the sheet resistance of amorphous AIST film is around 10^4 times compared to that of crystalline film, the value of which is close to the ternary alloy system. Larger difference of sheet resistance between amorphous and crystalline states can be positive to the OUM application because more programmed states (various resistive states) can be achieved for higher capacity of memory device.

3.4 TEM observation of microstructure

TEM observations were carried out for the as-deposited...
AIST and ST films as shown in Fig. 7, where a random atomic modular patterns and selected area diffraction (SAD) patterns refer the as-deposited films to amorphous state. Fine crystallites (black contrast) are observed in the images of the films after annealing at 523 K as shown in Fig. 8, and the AIST film seems to have a larger amount of crystallites than the ST film. In order to identify this crystalline phase, the Fast Fourier Transformation (FFT) diffraction patterns using high resolution lattice images were investigated. The FFT pattern of the crystallite denoted D in Fig. 9(a) is shown in Fig. 9(b), which reveals that the crystallite D is $\delta$-Sb phase with a zone axis $[121]$ ($d_{(012)} = 0.31$ nm) and rhombohedral structure. The size of a single $\delta$-Sb crystallite in the crystallized ST film is estimated to be larger than 20 nm. A partial amorphous structure could still remain in the crystallized ST film, as denoted A in Fig. 9(a). The images of Fig. 8(b) shows that the AIST film after heat treatment possesses a similar morphology with the crystallized ST film but the size of the crystallites is smaller. In addition to the amorphous and $\delta$-Sb phases, a secondary crystallite, denoted T, is also observed in Fig. 10(a). The FFT diffraction pattern as shown in Fig. 10(b) shows the structure of the AgSbTe$_2$ phase with a cubic structure of a zone axis [100] ($d_{(200)} = 0.303$ nm). It is worth noting that a discontinuous interface boundary exists between the adjacent $\delta$-Sb crystallites and this may indicate that each crystalline $\delta$-Sb can nucleate and grow independently. The nucleation and growth of $\delta$-Sb phase can be easy because the literature has reported that there is little volume fraction change associated with the formation of a nucleus for crystallization, and less strain and surface energy need to be overcome when a nucleus grows from the amorphous matrix. The crystallization rates of amorphous AIST...
and ST films can be expected to be small and be close to each other because the same major phase ($\delta$-Sb) is formed. The similar activation energy obtained in Fig. 4 shows a good agreement with this.

The crystallization of amorphous chalcogenide films has been proven by other researchers to be a process involving nucleation and growth. The secondary phase precipitated in the early stage can be expected to enhance the heterogeneous nucleation but the higher crystallization temperature of the AIST film reveals that crystallization may be more difficult for the movement of Ag and In atoms in the amorphous matrix. It is believed that the formation of a small amount of AgSbTe$_2$ phase slightly affected the activation energy and thus, crystallization rate of the amorphous AIST film.

TEM observation and GI-XRD analysis showed that no indium compounds precipitated in the crystallized AIST films. EDS analysis as shown in Fig. 11 reveals that the In element dissolves in the amorphous and crystalline areas. Previous study has reported that In atoms usually substitute for Sb sites in the lattice of the SbTe material. Furthermore, the higher content of Ag element in the crystalline areas, as shown in Table 2 corresponds to the existence of AgSbTe$_2$ crystallites in the crystalline areas, which agrees with the identification from the diffraction pattern.

Several factors have been proven to affect the sheet resistance, such as size effect, grain boundary effect and additives. The size effect has been proven to be a negligible factor in this study. The average grain size of two crystalline films can be derived by Scherrer’s formula, where 15.4 nm
and 11.4 nm were obtained for ST and AIST films, respectively. The mobile electron scattering by the grain boundary is also correlated to the mean free path, which is affected by the grain size. Consequently, the estimated difference of the sheet resistivity resulted from the grain effect can be small because the difference of average grain size is small between ST and AIST films.

The influence of additives on the higher resistance of amorphous and crystalline AIST films than ST films can be mainly from the In element. This phenomenon can be explained by the reduction of the mobility of carriers after increasing the In concentration for In$_2$Te$_3$-Sb$_2$Te$_3$ solid solution, which is because In atoms occupy the lattice position of Sb and concentration of antisite defects is reduced. Concerning of the effect of Ag, the addition of Ag was reported to change the local bonding structure from amorphous to crystalline state, which results in a higher energy needed for crystallization. It means that the amorphous state will be thermally stabilized by the existence of Ag. However, the appearance of the AgSbTe$_2$ phase in the crystalline AIST films did not further change the sheet resistance as compared with the crystalline ST films, which indicates the minor effect of the AgSbTe$_2$ phase on the electrical resistivity.

4. Conclusions

The structures of the as-deposited AIST and ST films are a single amorphous state and their sheet resistances show an extremely high value. The sheet resistance of the as-deposited films is sensitive to film thickness and decreases with increasing film thickness. The sheet resistance of SbTe films with Ag and In additives is twice as high as that of SbTe films before and after crystallization. For AIST films, the sheet resistance ratio of a high resistive state to a low one is approximately $3 \times 10^4$, which results from a drastic decrease in sheet resistance due to crystallization. The difference in the sheet resistance of the AIST film can be high enough to be used in OUM fabrication.

After annealing at 523 K, $\delta$-Sb phase was formed in the crystallized SbTe films, while AgbSbTe$_2$ and $\delta$-Sb phases were formed in the crystalline AIST film. No indium compound was precipitated in the AIST films with 5.2 at% In content after crystallization, while the additives can cause a higher sheet resistance for the films after crystallization. The precipitation of secondary AgSbTe$_2$ phases in AIST film resulted in the production of fine $\delta$-Sb phases.

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REFERENCES