Activation Energy of AgInSbTe Film through Isothermal Sheet Resistance Measurements

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RF sputtering was used to deposit AgInSbTe (AIST) films on silicon substrates. The as-deposited amorphous films were crystallized at temperatures above 413 K and the sheet resistance change was used to characterize the degree of crystallization and the associate activation energy in this study. The sheet resistance of amorphous films quickly decreased when the crystallization was initiated and reached a steady lower value with the IOC index of around 0.7, which means 70% crystallization. The kinetics of sheet resistance change was researched isothermally in an argon atmosphere and compared to the results of DSC measurement with constant heating rates. It was found that activation energy, 0.82 eV, obtained from isothermal sheet resistance measurement was rather close to that, 0.92 eV, obtained from DSC measurement. The Avrami exponent was determined to be 1.1−1.4 in isothermal sheet resistance measurement. A lower Avrami exponent implied that impingement effects possibly resulted in the sheet resistance decreasing with about 78% crystallization of amorphous films. [doi:10.2320/matertrans.48.258]

1. Introduction

Chalcogenide refers to alloys containing at least one Group VI element such as the alloys of GeSbTe, SbTe and AgInSbTe.1–3) By using a focused laser beam irradiating a tiny zone or electrical current at different pulses, chalcogenide films can be reversibly changed between amorphous and crystalline states. This phase change technology has been successfully applied in optical data storage.4–5) Recently, researchers have been trying to develop a new function of the chalcogenide phase change material, non-volatile memory.2,8,9) Two stable structural states of chalcogenide alloys, the amorphous state and polycrystalline state show a significant difference in sheet resistance. Information therefore can be recorded and erased in the memory cell through resistive heating. Although it is a common phenomenon that most amorphous materials possess higher resistance, the stability of amorphous chalcogenide films and their faster switching speed still attract much attention. Sb2Te3 or GeSbTe materials were used to fabricate chalcogenide memory recently and the literatures reported that the crystallization degree can be programmed to have different resistance states.3,10)

The crystallization activation energies of such chalcogenide films are conventionally measured by differential scanning calorimetry (DSC).5,11,12) The constant heating rates are used to perform DSC measurements to obtain the crystallization activation energy by Kissinger’s method. However, the Avrami exponent cannot be obtained from Kissinger’s method because the equation of Kissinger’s method is derived regardless of reaction order.13) A measurement of optical properties is interpreted in terms of Johnson-Mehl-Avrami kinetics for crystallization of amorphous GeTe films by isothermal heating.14) Time- and temperature-dependent changes in optical properties indeed provide a method to study the crystallization of optical active amorphous films. However, there are few reports on the kinetics of sheet resistance change of chalcogenide films and the relationship with the crystallization behavior. It is important to understand the difference between kinetics of sheet resistance change and those of crystallization during the development of chalcogenide memory. Since crystallization-dependent changes in sheet resistance are usual for chalcogenide films, an alternative method by measuring the sheet resistant variation with time is probably applicable to study the crystallization kinetics of amorphous AgInSbTe films. Apparatus has been developed to perform isothermal sheet resistance measurements to obtain the crystallization activation energy and the Avrami exponent, which is subsequently compared with the results of DSC measurement. The crystallization incorporation with sheet resistance changes in AIST films and the corresponding kinetics are discussed in this study.

2. Experimental Method

AIST films were deposited on 0.8 mm thick polycrystalline silicon substrates by the RF-sputtering method. The wafers were pre-cleaned and thermally oxidized to form a 1000 nm SiO2 layer as an electric isolator from deposited films. A 13.56 MHz RF power supply was connected to an target of Ag-In-Sb-Te alloy to provide 200 W sputtering power in a coater which was pre-pumped down to less than 6.67 × 10−3 Pa. The sputtering pressure was maintained at 0.533 Pa by argon gas flow. Film thicknesses (276 ± 16.5 nm) were checked within five analyzed specimens by the α-step method. Film compositions were measured by inductively coupled plasma spectroscopy (ICP) and found to be as follows: Ag 3.08 at%, In 4.89 at%, Sb 59.2 at% and Te 29.6 at%.

A differential scanning calorimeter (DSC) was used to analyze the thermal properties of the AIST films. 3 mg of as-deposited films were scratched from the specimens and sealed in an aluminum crucible. The DSC measurement was
scanned at different heating rates of 5, 10, 15, 20, 30 Kmin\(^{-1}\) from 298 to 723 K in argon atmosphere to prevent oxidation. The as-deposited AIST films were heated in argon atmosphere at four selected temperatures, 413, 433, 453 and 523 K. The heating rate was approximated as 50 Kmin\(^{-1}\) and the heating duration for the four annealing temperatures was one hour after which the specimens were left to cool down naturally. The crystalline structures of the annealed films were checked by Grazing-Incidence Diffraction (GI-XRD) using a Multipurpose X-Ray Thin-Film Diffractometer. The diffractometer was operated at an incident angle of 1\(^{\circ}\) with Cu radiation (\(\lambda = 0.1542 \text{ nm}\)). The sheet resistance at room temperature of the specimens after post-heat-treatment was measured using the standard four-point-probe method.\(^{15}\)

New apparatus was designed to perform isothermal sheet resistance measurements \textit{in situ} at different temperatures. Four tiny probes with the tip diameter smaller than 0.1 mm were placed on the specimen and pressured by a loaded-spring to ensure ohmic contact between probes and specimens. A fixed current (2 mA) was injected through two outside probes from a DC power supply. The apparatus was installed in a sealed chamber and heated in an Ar atmosphere. The temperature was controlled by a PID controller to maintain a temperature deviation within 3 K. The sheet resistance was obtained \textit{in situ} by recording the voltages between two inside probes with a multi-meter during isothermal annealing. Three specimens were selected to be quenched by interrupting annealing and blowing argon gas to preserve the crystalline state at designated heating durations. Transmission electron microscopy (TEM) was adopted to analyze the microstructure of the quenched specimens to check the degree of crystallization.

3. Results and Discussion

3.1 Characteristics of AIST films

The GI-XRD pattern as shown in Fig. 1 reveals that the structure of the as-deposited AIST film was amorphous. The pattern for the specimen after annealing at 413 K also show amorphous-like diffraction peaks at low diffraction angles. After annealing at the temperatures above 433 K, the major phase \(\delta\)-Sb was observed and the highest peak was referred to (021) of \(\delta\)-Sb phase. The \(\delta\)-Sb phase typically had a rhombohedral structure.\(^{16,17}\) Some studies have reported that AgSbTe\(_2\) can also form in the AIST film after heat treatment, however its minor content was too small to be clearly identified in the GI-XRD patterns in Fig. 1.

The crystallization degree of the specimens was determined by using the IOC index defined as eq. (1),\(^{16}\)

\[ IOC = \frac{I_{\text{specimen}}}{I_0} \]  

where \(I_{\text{specimen}}\) is the main peak intensity of crystalline phase in each specimen and \(I_0\) is the main peak intensity of the crystalline phase in the standard specimen which is annealed at 523 K. The IOC index of the standard specimen is defined as 1.0 and specimens with higher IOC index yield better degree of crystallinity. The IOC index can represent the relative crystallization degree of the specimens because the deposition conditions of all specimens, substrates and the post heat treatments are the same.\(^{16}\) Figure 2 shows the variation in IOC indices with the annealing temperatures. The IOC indices of the film after annealing at 433 K did not increase significantly (only from 0.1 to 0.15) in comparison with the as-deposited film. After annealing at temperatures higher than 433 K, the IOC indices increased dramatically to about 0.7~0.8. The main contribution to the increase in the
IOC indices came from the crystallization of δ-Sb phase from the amorphous matrix according to GI-XRD patterns.

3.2 Electrical properties of AIST films

The GI-XRD pattern had confirmed that the as-deposited AIST film had an amorphous structure. The higher sheet resistance of amorphous materials is a well-known phenomenon although the details of the mechanism are still not clear.3,17,18) The initial sheet resistance of the amorphous AIST films was \( 1.5 \times 10^6 \) Ω while that of the polycrystalline films was 43 Ω after annealing at 523 K. The amorphous film transformed to a polycrystalline state after heat treatment, and the sheet resistance consequently decreased. Figure 3 shows the variation in sheet resistance with increasing the annealing temperatures. The transition temperature from a high to low resistance state was observed at 433 K. The sheet resistance transition temperature was consistent with IOC transition temperature as shown in Fig. 2. Much literature has explained that defects of annealing, grain growth, recrystallization, or elimination of remained amorphous materials can contribute to the resistance reduction (or electric conductivity). These effects may also be factors leading to the higher electric conductivity of crystallized chalcogenides.17–22) The additives of Ag and In have also been proven to increase the activation energy of crystallization.5,23,24) Consequently, the activation energy of δ-Sb crystallization can be affected by the following factors: rearrangement of the Sb atoms, diffusion in a short range and the additive atom as an obstacle to the movement of the Sb or Te atoms.

3.3 The activation energy obtained by DSC

Figure 4 shows the results of DSC measurement at the five heating rates of 5, 10, 15, 20, and 30 Kmin\(^{-1}\). There is only one exothermic peak corresponding to the crystallization temperature of amorphous AIST film at each heating rate. For example, the crystallization temperature was 465 K when the heating rate was 10 Kmin\(^{-1}\), as shown in Fig. 4. According to GI-XRD analysis, the exothermic peak should be subject to the crystallization of δ-Sb phase. Besides, the crystallization temperature increased with the heating rate as shown in Fig. 4 and the activation energy of the δ-Sb crystallization was determined to be 0.92 eV using Kissinger’s method. The activation energy of crystallization for δ-Sb phase can attribute to the movement of Sb and Te atoms in a short range and the rearrangements in the crystalline structures because the lattice site is occupied by all the constituent elements at random.20–22) The additives of Ag and In have also been proven to increase the activation energy of crystallization.5,23,24) Consequently, the activation energy of δ-Sb crystallization can be affected by the following factors: rearrangement of the Sb atoms, diffusion in a short range and the additive atom as an obstacle to the movement of the Sb or Te atoms.

3.4 Isothermal sheet resistance measurement

Since the sheet resistance of AIST films has been proven to change with the crystallization degree or IOC indices, the crystallization rate can be evaluated through monitoring the variation in sheet resistance during the isothermal heat treatment. This method, isothermal sheet resistance measurement, was the first time to be adopted to represent the crystallization kinetics of amorphous AIST film in this study. Figure 5 shows a curve of AIST film obtained by an isothermal sheet resistance measurement performed at 433 K. The total heating duration was about 1200 s and the corresponding temperature profile in the heating duration is shown as a broken line in Fig. 5. The three stages were as follows: Stage I, II and III are defined in Fig. 5. In the first stage (Stage I), the temperature was still rising and had not reached 433 K yet. The dramatic decrease of sheet resistance with increasing temperature corresponds to the negative temperature coefficient of resistance (TCR) of amorphous AIST film in Stage I. The sheet resistance could be reversed if annealing was interrupted and the specimen temperature returned to the room temperature. This phenomenon indicates that a thermal activation mechanism of mobile carriers from valence band is responsible for the change of sheet resistance in Stage I. When the annealing duration exceeds 100 s, the temperature profile (broken line) changes its slope.
to a lower value and the heating rate slows down. Meanwhile the change of the sheet resistance curve becomes flat. When the annealing duration exceeds 400 s, δ-Sb phase starts crystallizing significantly in Stage II. Most of the crystallization would occur in this stage. A secondary sheet resistance transient was subsequently observed when the annealing duration was 750 s. Afterward the sheet resistance curve becomes stable again in Stage III. The crystallization might carry on, but the rate would be slow. Three specimens A, B and C were quenched after different durations denoted in Stage I, II and III respectively. A TEM image of the as-deposited film reveals an amorphous structure as shown in Fig. 6. The selected-area electron-diffraction pattern (SADP) in Fig. 6 displays the featureless morphology and diffuse ring pattern that is characteristic of an amorphous material. Figure 7 shows the SADPs of three quenched specimens. An amorphous feature of specimen A reveals that crystallization had not occurred in the early period of Stage I. The SADP of specimen B shows crystalline structures formed in the specimen but the retaining diffused nature of the diffraction rings indicates the crystal size is small. The disappearance of the diffuse ring pattern indicates an improvement in crystallinity for specimen C. Figure 8 shows the TEM images of specimen C quenched after sheet resistance transient. A lot of crystallites, denoted O, had formed in the film but some amorphous areas, denoted A, still retained. The d spacing calculated with the high resolution images referred the crystallite to δ-Sb phase as shown in Fig. 8(b). TEM observations ensured the crystallization of δ-Sb was associated with sheet resistance transient in Stage II.

3.5 Activation energy and Avrami exponent for isothermal crystallization

For further analysis, the local curve of Stage II in Fig. 5 was re-plotted in Fig. 9. The sigmoid feature shown in Fig. 9 can be incorporated into the Johnson-Mehl-Avrami formalism. The transformed volume fraction of AIST film is correlated to the change in isothermal sheet resistance. Isothermal sheet resistance measurements were repeated at annealing temperatures of 423, 433 and 443 K to obtain three JMA curves as shown in Fig. 10. The duration of 50% sheet resistance change (\(t_1/2\)) for each annealing temperature was determined by the method described in Fig. 9 and listed in Table 1.

A quantitative description of the isothermal crystallization kinetics of amorphous solids is able to be made using the classical JMA formalism. The classical JMA formalism can be presented as eq. (2), where F is the volume fraction transformed (equivalent to the fraction of sheet resistance change) at time t, k is the rate constant, and n is the Avrami exponent.

\[
F = 1 - \exp(-kt^n)
\]  

(2)
Equation (2) can be represented as eq. (3) by taking nature logarithm,
\[ \ln(1 - F)^{-1} = \ln k + n \ln t \]  
(3)
In a condition of 50% volume transformed, \( F = 1/2 \) is introduced to eq. (3) and derives eq. (4), where \( k \) is the rate constant which is mainly affected by the annealing temperature and the activation energy.
\[ \ln 2 = \ln k + n \ln(t^{1/2}) \]  
(4)
The rate constant \( k \) can often be represented in Arrhenius form with an activation energy \( Q \):26,27)
\[ k = k_0 \exp(-Q/RT) \]  
(5)
Equation (4) and (5) can be combined as eq. (6),
\[ C - n \ln t^{1/2} = -\frac{Q}{R} \frac{1}{T} \]  
(6)
where \( C \) is a constant related to \( k_0 \) and \( R \) is the gas constant. The activation energy \( Q \) of crystallization can be obtained through regressive plots of \( \ln(t^{1/2}) \) versus \( 1/T \). However the \( Q \) still depends on the Avrami exponent \( n \). The Avrami exponents at annealing temperatures of 423, 433 and 443 K are shown in Fig. 11(a). The slope of each straight line was subjected to the Avrami exponents of each isothermal
The Avrami exponent $n$ which characterizes crystallization behavior can only be determined by isothermal measurements and cannot be obtained through DSC measurement because the equation from Kissinger’s method is derived with regardless of reaction order.\(^\text{13}\) The Avrami exponent typically depends on the dimensions associated with crystal growth and the time dependence of nucleation.\(^\text{14,25,26}\) Theoretical analysis suggests that $n = 2.0 \sim 3.0$ if transformation occurs in a thin sheet of solid material, in which the average dimensions of a transformed region will be much larger in planar surface than in thickness on account of the “thin” nature.\(^\text{27}\) However the Avrami exponent was only $n = 1.1 \sim 1.4$ in this study.

In fact, many anomalous Avrami exponents have been observed in the crystallization processes of various metallic glasses and anomalous exponents can be caused by various reasons such as, (i) different mechanisms controlling the crystallization process, (ii) a time dependent nucleation rate, (iii) possibility of simultaneous grain growth of the crystallized region during crystallization, and (iv) impingement effect, which is important especially at the final stage of crystallization if the anisotropy of the crystals is sufficient high.\(^\text{25,27–30}\) Some experiments and mathematical simulations have been done for local and average Avrami exponents in the crystallization process of various amorphous alloys but not for AIST films.\(^\text{25,29,31}\) A theoretical Avrami exponent $n$ is suggested to be 1.5 for transformations with parabolic growth and the volume transformation rate for spherical growth in the absence of impingement (free growth) can be obtained with the assumption of a random distribution of pre-existing nuclei or constant nucleation rate.\(^\text{26}\)

Figure 12 shows the schematic representation of the crystallization when the isothermal sheet resistance of the amorphous AIST films was measured. The sheet resistance can be an “express” of electron conductivity of all components ($\delta$-Sb crystallites) within an AIST film. Naturally the sheet resistance of the amorphous area is much higher than that of the crystallite ($\sim 3000$ times). Consequently, the sheet resistance of the film can be high when the crystallites are small and few. Once the crystallites grow and make contact with each other, the sheet resistance decreases dramatically due to the high current paths being connected. A simple calculation for the maximum volume percentage of the crystallites while in contact with each other was obtained as the isothermal sheet resistance measurement (0.82 eV) was similar to the result using DSC measurement (0.92 eV).

The main difference between DSC measurement and isothermal sheet resistance measurement is the heating manner, that of DSC measurement was performed at a constant heating rate while isothermal measurement was performed at a fixed temperature. For DSC measurement, the maximum exothermic energy correlated to the maximum crystallization rate is used to obtain the activation energy using Kissinger’s method. However, the duration was as a result of most crystallites forming in amorphous films while the maximum variation in the sheet resistance occurred in isothermal sheet resistance measurement. This indicates that the sheet resistance change was able to be used as a physical parameter, like the exothermic peak in DSC measurement, to calculate the relative kinetics of crystallization.

### Table 1 The durations of $t^{1/2}$ obtained at the annealing temperatures in isothermal sheet resistance measurement.

<table>
<thead>
<tr>
<th>Annealing temperature, (K)</th>
<th>$t^{1/2}$ (s)</th>
</tr>
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<tbody>
<tr>
<td>423</td>
<td>895</td>
</tr>
<tr>
<td>433</td>
<td>750</td>
</tr>
<tr>
<td>443</td>
<td>410</td>
</tr>
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Fig. 11 The regressive plots of Avrami exponent and activation energy for AIST film. (a) $\ln(\ln(1-F)^{-1})$ versus $\ln(t)$ for different annealing temperatures. The slope of each straight line represents the Avrami exponent $n$. (b) $n[\ln(t^{1/2})]$ versus the inverse of annealing temperature. The slope of the straight line was subjected to $Q/R$, where $Q$ is activation energy and $R$ is gas constant.

The range of $n$ value was from 1.1 to 1.4 within the isothermal annealing temperatures from 423 to 443 K. Another regressive line for calculating activation energy using eq. (6) was subsequently plotted with different annealing temperatures as shown in Fig. 11(b). The slope of $Q/R$, gives an activation energy of 0.82 eV when adopting average $n = 1.25$. The activation energy obtained by the
propose an Avrami exponent of significantly slow, the free-growth-like crystallization could (Fig. 9) and hence, before the changing rate becomes the highest changing rate of sheet resistance in the present study (Fig. 12). The Avrami exponent is derived from the assumed contact of each crystallite is responsible for the dramatic decrease of sheet resistance. The increase of high current paths accelerates the decrease of sheet resistance (Fig. 12). The Avrami exponent is derived from the assumed highest changing rate of sheet resistance in the present study (Fig. 9) and hence, before the changing rate becomes significantly slow, the free-growth-like crystallization could propose an Avrami exponent of 1.1~1.4 in AIST film. When the high current paths are well established, which corresponds to the maximum volume percentage of the crystallites, the sheet resistance reaches a stable low-resistance state.

4. Conclusion

Ag-In-Sb-Te alloy deposited on silicon substrate form an amorphous or poor crystallized structure by using RF-sputtering. The high sheet resistance of such as-deposited films changes from an amorphous state to a crystalline state. The major phase δ-Sb forms in the crystallized AIST films when the annealing temperature is above 433 K.

The activation energy obtained using the isothermal sheet resistance measurement is 0.82 eV and is similar to that obtained by DSC. The Avrami exponent was found to be $n = 1.1~1.4$ by isothermal sheet resistance measurement and this number is slightly smaller than 2.0~3.0 for typical transformation in thin films. It is suggested that impingement effects were the cause of the smaller Avrami exponent in isothermal sheet resistance measurement.

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REFERENCES