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Role of crystallized phases in sheet resistance of amorphous AgInSbTe chalcogenide film

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AgInSbTe film was deposited on alkali-free glass using the radio-frequency sputtering method. Variations in sheet resistance with annealing temperatures were accompanied by the crystallization of amorphous films. Grazing-incidence X-ray diffractometer and transmission electron microscopy observations indicated amorphous characteristics for as-deposited films and the crystallized δ-Sb and $AgSbTe_2$ phases for annealed films. The transition temperature of sheet resistance is around 150–160 °C, which is lower than the crystallization temperature obtained by differential scanning calorimetry.

Keywords: Chalcogenide films; Amorphous; Crystallization; Sheet resistance

Sb–Te binary compound alloying of Ag/In (AIST) produces better cycling stability of the amorphous phase and acquires the ability to crystallize sensitively [1–3]. Other than its use in optical recordable discs, the phenomenon resulting in the crystallization accompanies a change in electrical conductivity for most chalcogenide materials. Several articles have reported that GeSbTe and SbTe films can be successfully used to integrate ovonic unified memory (OUM), which is a kind of non-volatile memory that utilizes reversible amorphous–crystalline characteristics [4–7]. In practical applications, OUM exhibits a high/low resistance ratio of about 10–100, depending on its programmed states, film structures and material properties [6,7]. AIST films are expected to be used in OUM chips.

In the last decade, many researchers have concentrated on optical properties and alloys with a focus on disc performance. It was postulated that the reversible transformation of amorphous-to-polycrystalline phases might be correlated with optical applications [1–3, 9–11]. One study investigated the crystallization of glass through in situ capacitance measurement and found that the size of nanocrystallites after an abrupt change in capacitance was in the range of 10 nm [12]. The nano-sized crystallites and related structures of the crystallized AIST film may make it difficult to recognize the effects of the crystalline phases on the electrical properties. This investigation aims to clarify the electrical properties of AIST films in relation to the critical crystallization temperature, the activation energy of crystallization and its microstructures.

AgInSbTe (AIST) films were prepared using a conventional radio-frequency magnetron sputtering technique with 100 W sputtering power and 60 s sputtering duration. The chemical composition was Ag 3.4 at.%, In 5.2 at.%, Sb 60.8 at.% and 30.6 at.%. Differential scanning calorimetry (DSC) measurements were scanned at heating rates of 5, 10, 15, 20 and 30 °C min^{-1} using Kissinger's methods [13] to ascertain that the crystallization temperature and activation energy of crystallization. In addition, the films were isothermally annealed at a temperature range of 100–200 °C for 1 h before the furnace was cooled in vacuum.

The sheet resistances were measured using a four-point-probe method at room temperature. The crystalline phase and its temperature dependency were investigated by grazing-incidence X-ray diffractometry (GI-XRD) using Cu K_α radiation. The index of crystallinity (IOC) was defined as $(I_c/I_0) \times 100\%$, where I_c was the intensity of the highest peak in the XRD pattern of the specimen and I_0 was the intensity of the highest peak in the XRD pattern of the standard specimen which was annealed at 250 °C for 1 h [14]. In addition, the average crystal size was estimated with the highest XRD diffraction peak according to Scherrer's formula [15]. The microstructural features of the films before and after

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isothermal annealing at 250 °C for 1 h were investigated by transmission electron microscopy (TEM). The lattice images and fast Fourier transform (FFT) diffraction patterns were analyzed to provide the correlation with the electrical-crystallization and crystalline phases for AIST films.

Figure 1a shows that the sheet resistances of AIST films decreased drastically as the annealing temperatures were increased, the difference from the high resistive state (as-deposited) being about 30,000 times that of the low one resistive state (250 °C annealed). However, the critical transition temperature from the high to the low resistive state was found to be 150–160 °C. The GI-XRD spectra data after annealing the specimens from 140 to 180 °C are shown in Figure 1b, and the presence of δ-Sb phase and the degree of crystallization tend to increases significantly as the temperature is raised up to 150 °C, which corresponds with the above-mentioned critical transition temperature. The plot of the average crystal size in Figure 1a shows the crystallite grows to around 15 nm after annealing at 250 °C.

From DSC measurements with five different heating rates, as shown in Figure 2, the exothermic peak as depicted in each curve corresponds with the crystallization temperature of the δ-Sb phase. The crystallization temperature is 198 °C at the heating rate of 10 °C min^{-1} and the peak temperature tends to increase with the heating rate. However, the apparent activation energies for the crystallization of δ-Sb phase can consequently be determined by Kissinger's method to be 0.94 eV, which is higher than for the SbTe film (0.84 eV) [16].

Normally, the diffraction peaks of the δ-Sb and $AgSbTe_2$ phases will overlap each other [1,2,8,17,18]; therefore the presence of the $AgSbTe_2$ phase is not easy to identify through XRD measurement, as shown in Figure 1. To clarify the effect of Ag alloying, TEM evidence should be acquired to ensure the presence of $AgSbTe_2$, which has a cubic structure. The crystalline structure of $AgSbTe_2$ actually differs from the δ-Sb phase, which has a rhombohedral structure [17,18]. Based on the XRD evidence, no indium compound is found in the crystallized AIST films because In atoms tend to substitute the atomic sites of Sb as a solid solute element when the content is less than 5 at.% [2,11,19].

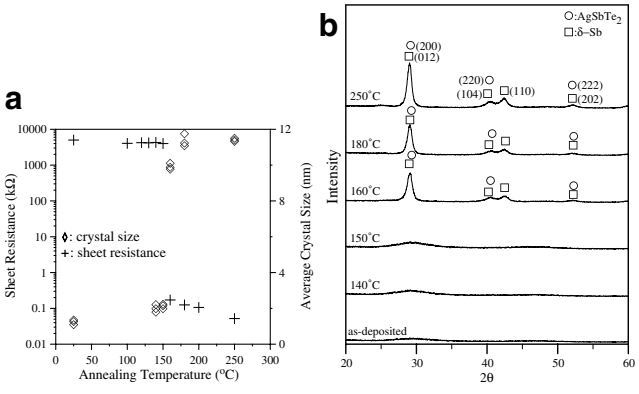

Figure 1. (a) The variations in sheet resistances and average crystal size with annealing temperatures; (b) GI-XRD patterns of AIST films after isothermal annealing at various temperatures for 1 h.

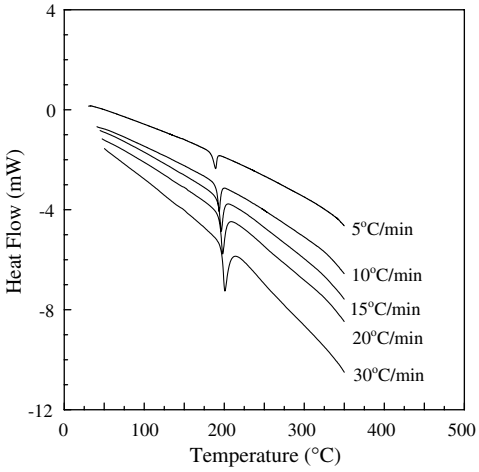

Figure 2. DSC measurement for as-deposited AIST films which were scanned at different heating rates of 5, 10, 15, 20 and 30 °C min^{-1}.

A TEM observation for the as-deposited AIST film is shown in Figure 3a, in which a disordered atomic arrangement and the selected area diffraction (SAD) pattern indicate its amorphous structure. The specimen after annealing reveals a fair amount of microcrystalline areas (black contrast areas), as shown in Figure 3b. EDS analysis of points A and B indicated in Figure 3b are shown in Figure 3c and d, where the point A was the area containing more crystallites than point B. The quantitative result reveals that Ag and In can dissolve in both the amorphous and the crystalline area. However, the higher Ag content (6.7 at.%) in area A as compared with area B (5.3 at.%) may be attributed to the existence of $AgSbTe_2$. The SAD pattern is shown in Figure 4a, and the diffraction rings reveal the polycrys-

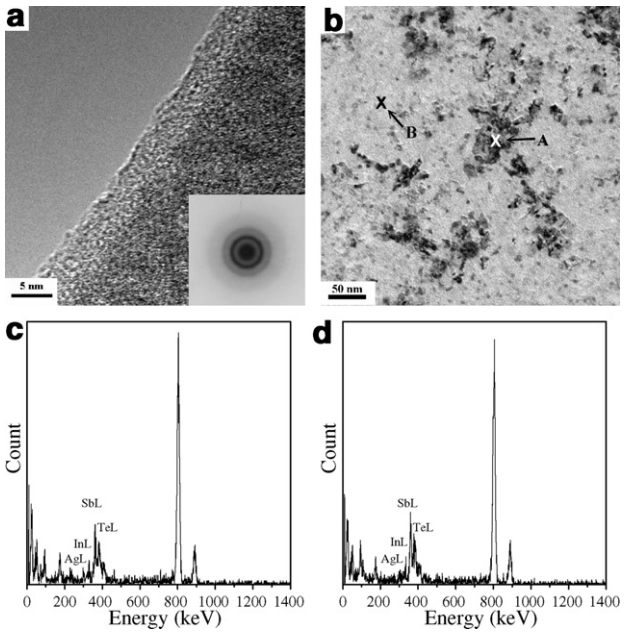

Figure 3. TEM observations on AIST films. (a) The image of as-deposited AIST film; (b) the image of the AIST film after annealing at 250 °C for 1 h; (c) EDS analysis of point A and (d) EDS analysis of point B.