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Microstructure evolution and crystallography of the phase-change material TiSbTe films annealed *in situ*

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ABSTRACT

In this work, the morphology, crystallization process and crystal structure of the phase-change material TiSbTe (TST) alloy have been successfully established, which is essential for applying this alloy in phase-change memory. Specifically, atomic force microscopy (AFM) was employed to characterize the as-deposited and post-annealed thin films, and transmission electron microscopy (TEM) analyses of the films annealed *in situ* were used in combination with selected-area electron diffraction (SAED) and radial distribution function (RDF) analyses to investigate the structural evolution from the amorphous phase to the polycrystalline phase. Moreover, the presence of structures with medium-range order in amorphous TST, which is beneficial for high-speed crystallization, was indicated by the structure factors *S(Q)*s. The crystallization temperature was determined to be approximately 170 °C, and the grain size varied from several to dozens of nanometers. As the temperature increased, particularly above 200 °C, the first single peak of the *rG(r)* curves transformed into double shoulder peaks due to the increasing impact of the Ti–Te bonds. In general, the majority of Ti atoms were doped into the SbTe lattice and tended to form structural defects, whereas the remainder of the Ti atoms aggregated, leading to the appearance of $TiTe_2$ phase separation, as confirmed by the SAED patterns, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images and corresponding energy-dispersive X-ray (EDX) mappings.

1. Introduction

The explosive growth of the market for portable electronic devices, such as smart phones, tablet computers and others, has led to intense interest in non-volatile memory (NVM) technologies in the semiconductor industry. Phase-change memory (PCM), which utilizes the large optical or electrical property contrast between the crystalline and amorphous phases of information storage materials, has been considered to be a promising candidate for future NVM devices [1,2]. Over the past several decades, considerable efforts have been undertaken to develop faster and denser phase-change materials [3–7], which can be primarily divided into two major groups. The first group consists of the quasi-binary GeTe-Sb_2Te_3 alloys, particularly $Ge_2Sb_2Te_5$ [8,9]. The second group is represented by Sb–Te binary alloys, which are typically adjusted by doping. Recently, Zhu et al. [10–12] have reported that PCM cells based on the TiSbTe (Ti as a dopant) alloy show a much faster Set operation speed and lower Reset power compared with the popular candidate $Ge_2Sb_2Te_5$. These authors have argued that Ti-centered octahedral atomic motifs are present in both the crystalline and amorphous phases and play an important role in phase transitions by helping to avoid substantial atomic rearrangement. This provides a promising alternative for the development of high-speed, low-power PCM. Note that dopants can be classified into two types according to their bonding characteristics with host atoms: the interstitial [13,14] and substitutional types [14,15]. Dopants can also segregate at grain boundaries [16,17]. However, the role of the Ti dopant and the mechanism by which the dopants are

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accommodated in the matrix in TST have not yet been completely confirmed. Although it has been found that the crystallization process is closely correlated with both the storage rate and data thermal stability, the inherent mechanism is still unclear [12,18]. Thus, a detailed study of the structural evolution upon thermal annealing from the amorphous to the polycrystalline phase would be meaningful to uncover the aforementioned mysteries of these materials.

In the present work, the surface morphology, phase and simulated images of the TST film were obtained using atomic force microscopy (AFM). Transmission electron microscopy (TEM) analyses of the morphology of the film annealed *in situ* were conducted in combination with electron diffraction and radial distribution function (RDF) analyses [19–24] to investigate the structural evolution from the amorphous phase to the polycrystalline phase as a function of the annealing temperature. The crystal structure and defects in the polycrystalline state were further investigated using an advanced Cs-corrected scanning transmission electron microscope (STEM) equipped with a super energy-dispersive X-ray (EDX) spectrometer.

2. Experimental methods and details

2.1. Sample preparation and characterization

An amorphous TiSbTe (a-TST) film was deposited on a SiO_2/Si (100) substrate using the radio frequency (RF) co-sputtering method with Sb_2Te_3 and pure Ti targets at a working pressure of 2×10^{-4} Pa at room temperature. The Ti content and the sample thickness were controlled by the RF power and deposition time. The thickness of the TST film was ~220 nm. The composition was determined to be $Ti_{6.4}Sb_{44}Te_{49.6}$ by energy-dispersive X-ray (EDX) spectroscopy. The surface morphology, phase and simulated images of the samples were recorded by atomic force microscopy (AFM, Pico Scan TM2500) using the tapping mode. The cross-sectional sample for TEM observations was prepared using the focused ion beam (FIB, FEI Helios NanoLab 600i) lift-off technique, and the Pt foil thickness was approximately 300 nm. The FIB process parameters were optimized to minimize possible damage.

2.2. Electron microscopy

The *in situ* annealing experiments were performed using a JEOL-2010 TEM with a Gatan 652 double-tilt heating holder. The annealing temperature was varied from room temperature to 300 °C. The annealing temperatures were 160 °C, 170 °C, 180 °C, 200 °C, 250 °C and 300 °C, with a holding time of 10 min at each temperature. The selected-area electron diffraction (SAED) patterns were recorded using a Gatan 782 CCD camera. The atomic structures and defects of crystalline TiSbTe (c-TST) annealed at 300 °C were examined using HAADF and EDX mappings on a FEI Titan Chemi-STEM electron microscope equipped with a Cs-corrected probe and Super-X detector operating at 200 kV.

2.3. Radial distribution function (RDF)

The radial distribution function is the primary means for obtaining experimental structural information of disordered materials and the polycrystalline phase [19–24] and was used in this work as a structural probe to study the structural evolution of the amorphous phase and the details of the crystallization process. The structure factors *S(Q)s* were obtained from the SAED patterns according to diffraction theory [25], and then the *RDFs* (referred to here as *rG(r)*) were determined.

3. Results and discussion

3.1. AFM study

The morphology of phase-change materials is closely related to the crystallization process, and maintaining morphological stability is important for high cycling of the read and write processes. Fig. 1 shows the surface morphologies (a_m, b_m, c_m, and d_m) and phases (a_p, b_p, c_p, and d_p) of the samples, and the corresponding simulated images are shown in Fig. S1. The dimensions of the scanned areas were 2 μm for (a) and (c) and 0.5 μm for (b) and (d). As shown in Fig. 1(a_m-b_p), the surface of the as-deposited film was quite smooth. The morphologies of the crystal grains are clearly apparent in Fig. 1(c_m-d_p), which were generated after the annealing treatment at 300 °C. As shown in Fig. 1(d_m) and (d_p), the crystal grains were uniformly distributed. The grain size can be estimated to be dozens of nanometers. The AFM cross-sectional profiles and root mean square (RMS) surface roughness values of the samples are shown in Fig. S1 (in the supplementary materials). As is known, the RMS value of $Ge_2Sb_2Te_5$ increased after annealing [26]. Surprisingly, however, the surface roughness of the crystallized TST film became even smaller than that of the as-deposited film, implying that the grains were closely compacted and that the crystallization process was very different from that of $Ge_2Sb_2Te_5$. These results suggested that TST maintained high morphological stability after crystallization, which is beneficial for high cycling of SET and RESET operations.

3.2. In situ annealing

The thermal stability and crystallization behaviors of the TST thin film were investigated through *in situ* annealing experiments using TEM in the temperature range of 25–300 °C with a heating rate of 10 °C/min and holding for 10 min at the different annealing temperatures. Fig. 2 presents the TEM images of the TST film crystallization process, and the corresponding SAED patterns at the different temperatures are shown in the right upper corner (specifically, Fig. 2(h) corresponds to Fig. 2(g) for annealing at 300 °C). The uniform contrast and the SAED patterns shown in Fig. 2(a) and (b) confirmed that the initial as-deposited film was amorphous and did not crystallize even at 160 °C. In fact, the crystallization temperature (T_c) was approximately 170 °C because several crystallites appeared in the amorphous matrix at this temperature in the images shown in Fig. 2(c), which is consistent with previous reports [11,27]. Similar to our AFM results described above, the grain size was estimated to be dozens of nanometers for the samples shown in Fig. 2(e–g). Through a careful analysis, most of the diffraction spots in all SAED patterns above T_c could be indexed to an $R\bar{3}$ m structure similar to the trigonal structure of Sb_2Te_3 [28], but unfortunately, the possibility of a slight phase separation of $TiTe_2$ ($P\bar{3}$ m1, a = 3.777, c = 6.498 [29]) was observed in the corresponding diffraction spots for c-TST, particularly at 300 °C, as indicated by the arrows in Fig. 2(h).

3.3. Radial distribution function (RDF)

In the above section, the crystallization process of TST film was qualitatively explored via *in situ* TEM observations. Another method, *RDF*, which is the primary experimental method for obtaining structural information from electron diffraction, was subsequently used as a structural probe to investigate the structural evolution during crystallization [23] and was applied to obtain quantitative (or semi-quantitative) results. The *S(Q)*s and *RDF*s (in the form of *rG(r)*) were obtained from the corresponding SAED patterns (in Fig. 2). The results are presented in Fig. 3, with more