Ti_xSb_2Te Thin Films for Phase Change Memory Applications *

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Sb_2Te films with different Ti contents (Ti_xSb_2Te) are derived via the target-attachment method by using the magnetron sputtering technique. The effects of the Ti content on the phase change characteristics and the microstructures are investigated by x-ray diffraction, x-ray photoelectron spectroscopy, scanning electron microscopy and atom force microcopy. Resistance-temperature measurements are carried out to reveal the enhanced crystallization temperature of Ti_xSb_2Te films, indicating a better thermal stability in such films. Both the activation energy and the temperature for 10 y data retention increase with increasing the concentration of Ti. It indicates that the crystallization of the amorphous Sb_2Te film could be suppressed by the introduction of Ti. The improvement of crystallization temperature and the thermal stability of the amorphous Sb_2Te film results from the introduction of Ti in Sb-Te bond that decreases the binding energy of Sb 4d and Te 4d.

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Phase change memory (PCM) has a broad application prospect in the semiconductor market, due to its excellent characteristics including its faster, lower cost, denser, and lower power-consumption characteristic as compared with other non-volatile memories. The reversible phase transition between the amorphous (OFF state-logic 0) and the crystalline (ON state-logic 1) states, which is controlled by electrical pulses, is the key feature of PCM. The stored data 0 and 1 are identified by a large resistance ratio. With numerous advantages, phase change materials are most commonly studied for the next generation of nonvolatile memory.[1,2] $Ge_2Sb_2Te_5$ (GST) sets a significant status in PCM studies due to its prominent electronic character among various chalcogenide compounds. However, its low crystallization temperature (about 150℃),[3] and poor thermal stability (85℃ for 10 y)[4,5] has restricted the widespread application of GST-based PCM. Recently, various efforts have been made in pursuit of improved phase change materials.[6,7] Sb-Te binary alloys were proposed as new phase change materials, showing a higher crystallization speed due to the growth-dominated crystallization mechanism. However, some key issues relating to the crystallization temperature and data retention ability remain to be solved before it could be a suitable PCM. Introduction of foreign elements in Sb–Te binary alloys might overcome such imperfection for PCM applications.

The introduction of Ti into Sb_2Te films has been proposed to improve the thermal stability and power consumption. The co-sputtered $Ti_{0.33}Sb_2Te$ was reported to possess high crystallization temperature and good data retention.[8] Since different doping contents will lead to the change in phase change characteristics, the impact of Ti content introduced into the Sb_2Te films should be understood. In this work, the Ti-content determined microstructures and characteristics of Ti_xSb_2Te ($x = 0.16$, 0.27 and 0.64) are studied.

Electrical properties and microstructures of pristine Sb_2Te and Ti_xSb_2Te layers are respectively investigated. The 300-nm-thick films are deposited on Si and SiO_2/Si substrates by using a magnetron sputtering system at room temperature. The background pressure and Ar gas pressure were 7.0×10^{-4} Pa and 0.25 Pa, respectively. The introduction of Ti into the Sb_2Te film was realized via the target-attachment method,[9] where the doping concentration was determined by the amounts of Ti foils (purity: 99.99%) placed on the Sb_2Te target. The rf sputtering power for the Ti_xSb_2Te target was 60 W. The thickness of the films was measured by a scanning electron microscope (SEM). The film composition is determined by using an energy dispersive spectrometer (EDS) technique. The resistance variation of the as-deposited films on SiO_2/Si substrates during the heating process is measured *in situ* at a heating rate of 30℃/min. Thermal stability of the amorphous films was studied via time-dependent resistance measurements at various isothermal annealing temperatures. The as-deposited films are transformed to crystalline films by using a

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rapid thermal annealing (RTA) process under a nitrogen atmosphere at 250℃ for 10 min. The as-deposited and crystal structures of Ti_xSb_2Te films were investigated by x-ray diffraction (XRD) with a Cu Kα source (Rigaku, ultima Ⅲ). The element binding situation of crystalline Ti_xSb_2Te films was confirmed by x-ray photoelectron spectroscopy (XPS) measurement with an Al Kα x-ray source. SEM and atomic force microscope (AFM) studies were carried out to observe the morphology and microstructure.

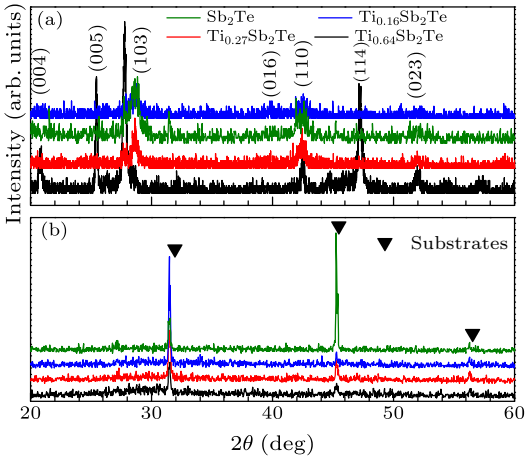


Fig. 1. X-ray diffraction spectra of the as-deposited and annealed Ti_xSb_2Te films.

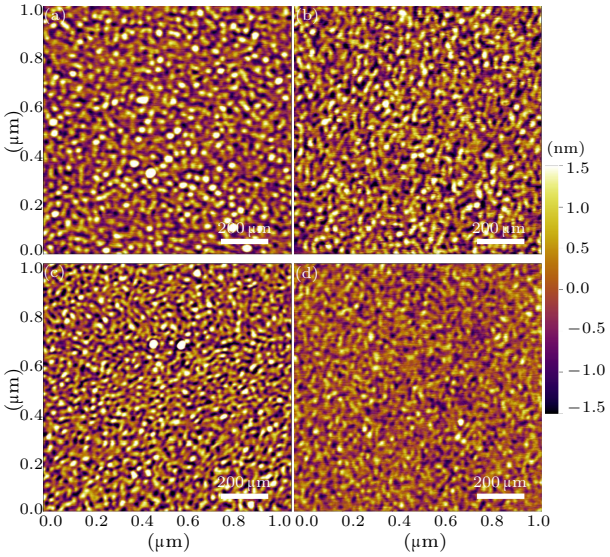


Fig. 2. AFM images of as-deposited (a) Sb_2Te, (b) $Ti_{0.16}Sb_2Te$, (c) $Ti_{0.27}Sb_2Te$ and (d) $Ti_{0.64}Sb_2Te$ films.

Figure 1 shows the XRD patterns of the as-deposited and annealed Ti_xSb_2Te films. The as-deposited films are amorphous in nature. After the films annealed at 250℃ for 10 min, Sb_2Te crystalline phase with some hexagonal diffraction peaks is observed. Some diffraction peaks disappear as more and more Ti is introduced into the Sb_2Te films. However, no new phase was found in these $Ti_{0.16}Sb_2Te$, $Ti_{0.27}Sb_2Te$ and $Ti_{0.64}Sb_2Te$ films. The foreign element Ti might inhibit the crystalline process of Sb_2Te, resulting in the change of diffraction peaks.

AFM images of as-deposited Ti_xSb_2Te films are shown in Fig. 2. The higher the Ti content is, the smoother the surface is. The annealed films (Fig. 3) show the same manner as the amorphous ones, where the surface roughness also decreases as more Ti is introduced. The films will be smoother with the increasing Ti content, no matter whether the films are amorphous or crystalline. SEM images of Sb_2Te, $Ti_{0.16}Sb_2Te$, $Ti_{0.27}Sb_2Te$ and $Ti_{0.64}Sb_2Te$ films annealed at 250℃ for 10 min confirm the AFM results, as shown in Fig. 4. The grain size of Ti_xSb_2Te film decreases clearly with increasing Ti concentration. Ti may serve as a barrier to block the Sb_2Te crystal growth. The smaller grain size may induce more grain boundaries, which could cause the increase of the resistance of crystalline Sb_2Te films. It will be confirmed by the following resistance results.

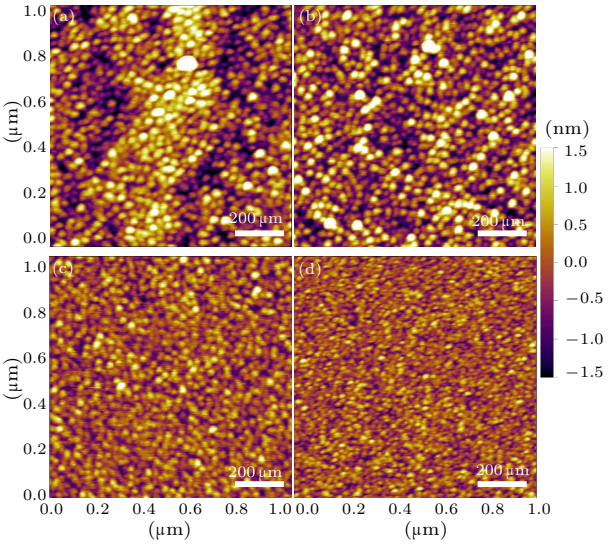


Fig. 3. AFM images of (a) Sb_2Te, (b) $Ti_{0.16}Sb_2Te$, (c) $Ti_{0.27}Sb_2Te$ and (d) $Ti_{0.64}Sb_2Te$ films annealed at 250℃ for 10 min.

The resistance and data retention of Ti_xSb_2Te films were measured by Keithley 2400 source-measure unit. A dc voltage of 0.1 V was used for the reading operation. Figure 5 shows the temperature dependence of the resistance for Ti_xSb_2Te films. The resistance of the as-deposited Sb_2Te film is $8.2 \times 10^5\,\Omega$ at room temperature, and then falls slowly with the increasing temperature. When the film turns into crystallization, the resistance remains to be about 50 Ω. The curve suffers a sudden drop at around 139℃, the so-called crystallization temperature T_c, which is consistent with the result of research reported earlier.[8] After the addition of Ti, the resistances of both as-deposited (R_a) and crystalline (R_c) films increase obviously, so does the T_c of phase change films. The T_c temperatures of $Ti_{0.16}Sb_2Te$, $Ti_{0.27}Sb_2Te$, $Ti_{0.64}Sb_2Te$ films

increase up to 153, 159 and 174℃, respectively. The higher T_c means that the thermal stability of the amorphous state will be prominently improved. The increase of R_c implies that the power consumption of crystalline phase decreases.

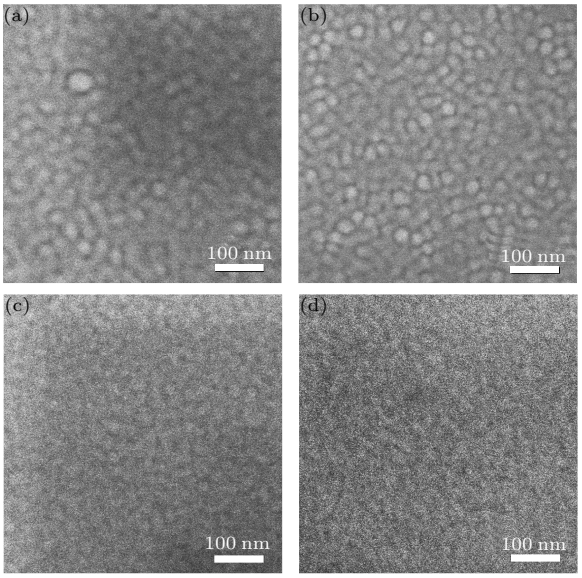


Fig. 4. SEM micrographs of (a) Sb_2Te, (b) $Ti_{0.16}Sb_2Te$, (c) $Ti_{0.27}Sb_2Te$ and (d) $Ti_{0.64}Sb_2Te$ films annealed at 250℃ for 10 min.

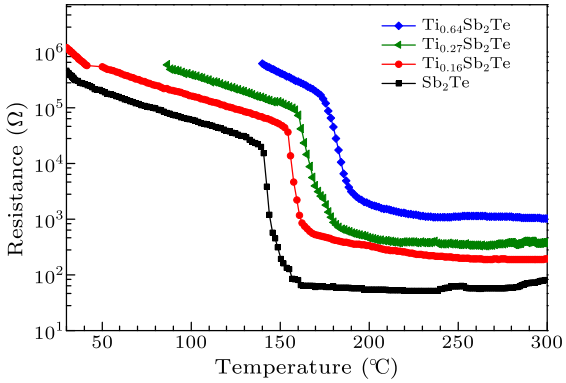


Fig. 5. The temperature dependence of resistance for Ti_xSb_2Te films.

Figure 6(a) shows the 10-year data retention property of Ti_xSb_2Te films. The temperature for the 10-year retention is evaluated according to the change of the characteristic time with the elevated surrounding temperature. The characteristic time is determined by using a certain crystalline resistance that is half of the initial resistance during an isothermal process.[10] The data retention temperature of Sb_2Te, $Ti_{0.16}Sb_2Te$, $Ti_{0.27}Sb_2Te$ and $Ti_{0.64}Sb_2Te$ films for 10 y is 57, 88, 97 and 120℃, respectively. The data retention temperature of the GST film for 10 y is only 83℃.[11] The activation energy E_a was calculated with the Arrhenius equation[12]

$$t = \tau \exp(E_a/k_B T), \qquad (1)$$

where t, τ and k_B are the characteristic time, a proportional time constant and Boltzmann's constant, respectively. In Fig. 6(b), the activation energies E_a of Sb_2Te, $Ti_{0.16}Sb_2Te$, $Ti_{0.27}Sb_2Te$ and $Ti_{0.64}Sb_2Te$ are about 1.91, 2.80, 2.97, and 4.01 eV, respectively, comparable with 2.67 eV for GST.[11] This means that with the increase in the Ti content, the data retention of Sb_2Te obtains outstanding improvement.

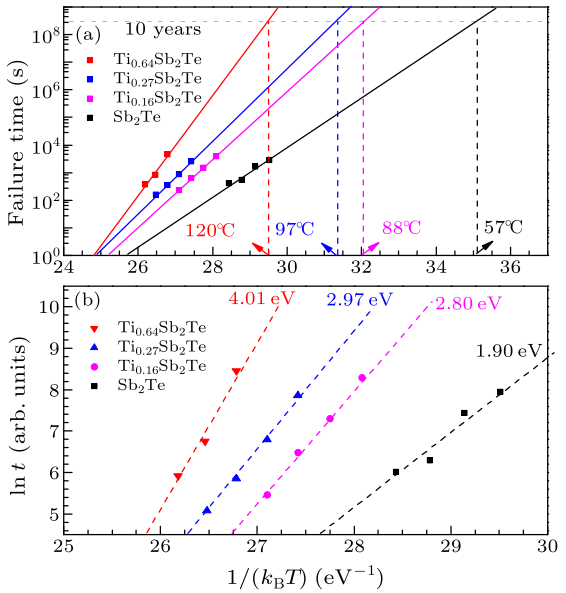


Fig. 6. (a) Arrhenius extrapolation of 10-year of data retention for Ti_xSb_2Te films; (b) the activation energy E_a for Ti_xSb_2Te films.

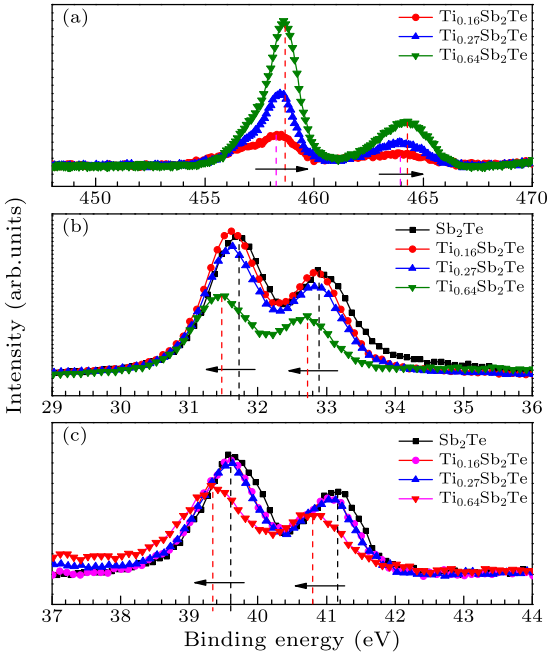


Fig. 7. XPS spectra of Sb_2Te and Ti_xSb_2Te films annealed at 250℃.

To further study the effect of the Ti content on the changes of the chemical bonding state of elements in the Sb_2Te films, XPS spectra were also employed to re-

veal the binding status of the components in all types of samples. Figure 7 shows the XPS spectra of Ti 2p, Sb 4d and Te 4d for Sb_2Te and Ti_xSb_2Te films. The obtained binding energies of Sb $4d_{5/2}$, Sb $4d_{3/2}$, Te $4d_{5/2}$ and Te $4d_{3/2}$ main peaks are found to be 31.70, 32.86, 39.63 and 41.18 eV for Sb_2Te; 31.62, 32.83, 39.63 and 41.06 eV for $Ti_{0.16}Sb_2Te$; 31.62, 32.83, 39.63 and 41.06 eV for $Ti_{0.27}Sb_2Te$; 31.47, 32.72, 39.33 and 40.80 eV for $Ti_{0.64}Sb_2Te$, respectively. It is obvious that the peak positions of Sb 4d and Te 4d all shift to a lower binding energy after Ti is introduced. It indicates that the higher the Ti content, the lower the binding energies of Sb 4d and Te 4d. Simultaneously, as more Ti atoms are incorporated, the binding energy of Ti increases. This implies that Ti atoms bond to Sb and Te atoms forming Ti–Sb and Ti–Te bonds. The binding energy of an element is determined by the electro-negativity of the element that it bonds with.[13] Since the smaller electro-negativity of Ti (1.54) than those of Sb (2.05) and Te (2.1), the binding energy values of Sb and Te decrease as expected once Ti bonds with Sb and Te elements.[8] The change in binding energy indicates that the Sb and Te atoms in Sb-Te bonds are partially replaced by Ti atoms, which are responsible for the improvement of the phase change characteristics in Ti doped Sb_2Te films.

In summary, the effects of the Ti content on both the microstructures and the phase change characteristics of Ti_xSb_2Te films have been investigated. The incorporation of Ti enhances the crystallization temperature and the thermal stability of amorphous Sb_2Te. The activation energy for crystallization increases from 1.90 to 4.01 eV, and the temperature for 10 y data retention increases from 57 to 120℃ as the concentration of Ti increases. Sb and Te in Sb–Te bonds are partially replaced by Ti to decrease the binding energy of Sb 4d and Te 4d, which is responsible for the improvement of crystallization temperature and the thermal stability of the amorphous Sb_2Te film.

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