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Study on the phase change material Cr-doped Sb_3Te_1 for application in phase change memory

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ABSTRACT

The characteristics of Cr-doped Sb_3Te_1 materials were investigated for application in phase change memory (PCM). The crystalline temperature and activation energy of films increase with the increasing content of Cr doping. The X-ray diffraction and X-ray photoelectron spectra methods were applied to analyze the crystal structure and chemical bonding character. It can be found that there are no new lattice structures appearing, and Cr element bonds with Te and Sb during the crystalline process. The size of grains decreases after doping Cr into Sb_3Te_1 by the analysis of transmission electron microscopy images, which indicates that the grains are localized in infinitesimal area by Cr atoms. The endurance of PCM cell keeps 3×10^4 cycles by applying SET operation pulse 1 V/100 ns and RESET operation pulse 2 V/30 ns with the resistance ratio of two orders of magnitude, which reveals good endurance performance and low power consumption. $Cr_{0.37}Sb_3Te_1$ material is a potential candidate for application in PCM.

1. Introduction

In the past decades, phase change memory (PCM) as a rapidly emerging technology has been regarded as the next generation nonvolatile memories, due to its high density, low power consumption, good endurance, fast programming capability, and fabrication compatibility with complementary metal–oxide–semiconductor (CMOS) [1–3]. PCM was proposed by S. Ovshinsky in the 1960s, it relies on the electrical properties of phase change materials changing [4]. The lattice structure of the material is altered by Joule heating, which leads to the transition of the electrical resistance between the amorphous state (RESET state) and crystalline state (SET state) [5]. The characteristics of phase change materials have deep influence on the performance of PCM, thus many phase change materials are studied. $Ge_2Sb_2Te_5$ (GST) is widely utilized in PCM because of good crystallization speed and thermal stability, but low crystallization temperature (T_c) and inferior data retention make it not meet the demand of high thermal stable and high speed PCM [6–10].

However, Sb-rich phase change materials have drawn much attention because of the characteristic of fast transition speed. Sb-rich phase change materials have growth-dominant crystallization behavior, which leads to fast crystallization speed and poor amorphous stability related to the awful material data retention. Many efforts have been done to improve the performance of Sb-rich materials, for instance, adding Si, Al, O and W into Sb-rich materials, which can effectively improve the thermal stability and material grain uniformity [11–14]. In this study, Cr element is doped into the phase change material Sb_3Te_1, $Cr_xSb_3Te_1$ materials were characterized with thermal stability, crystalline structure, and electrical performance, achieving a best composition $Cr_{0.37}Sb_3Te_1$ with better thermal stability and greater grain uniformity.

2. Experiments

The Sb_3Te_1 films were prepared on Si/SiO_2 (100) substrates with Sb_3Te_1 target by radio frequency (RF) magnetron power sputtering at 20 W, $Cr_xSb_3Te_1$ films were deposited on Si/SiO_2 (100) substrates by RF magnetron power co-sputtering with Cr target at 5 W, 7 W, 10 W, 15 W and Sb_3Te_1 target at 20 W related to $Cr_{0.09}Sb_3Te_1$, $Cr_{0.37}Sb_3Te_1$, $Cr_{0.48}Sb_3Te_1$ and $Cr_{0.95}Sb_3Te_1$ respectively. The composition of $Cr_xSb_3Te_1$ films was measured by energy dispersive spectroscopy (EDS). The sheet resistance as a function of the temperature (R–T) was measured in a vacuum chamber with a heating rate of 40 °C/min. The annealed 200 nm crystallization films were characterized with the lattice information by X-ray diffraction (XRD). The X-ray photoelectron spectra (XPS) were applied to analyze the chemical bonding characteristics. The microstructures were observed with high resolution transmission electron microscopy (HRTEM), bright field transmission electron microscopy (BFTEM)

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and selected area electron diffraction (SAED) through transmission electron microscopy (TEM). T-shaped PCM devices were fabricated by 0.13 μm CMOS technology. The 50 nm thick PCM layer was deposited on bottom tungsten heating electrode with a diameter of 190 nm, and 20 nm TiN and 300 nm Al films as the top electrodes. The resistance–voltage (R–V) curves and current–voltage (I–V) curves of PCM cells were measured by a Keithley 2400 m digital sourcemeter, and an arbitrary waveform pulse generator Tektronix AWG 5002B.

3. Results and discussions

Fig. 1(a) shows the results of R–T tests, which are fulfilled in a vacuum chamber to characterize sheet resistance of films as a function of temperature. It can be seen that the sheet resistance decreases with increasing temperature, and drops sharply at T_c. The T_c of Sb_3Te_1 is 145.51 °C, and gets larger with increasing doping Cr content (182.51 °C for $Cr_{0.09}Sb_3Te_1$, 206.49 °C for $Cr_{0.37}Sb_3Te_1$, 232.42 °C for $Cr_{0.48}Sb_3Te_1$ and 263.92 °C for $Cr_{0.95}Sb_3Te_1$). The doping Cr increases the T_c of films, and improves the thermal stability to achieve better data retention. The data retentions of films are shown in Fig. 1(b), which is characterized by extrapolating the isothermal Arrhenius equation: $t = \tau\exp(E_a/k_BT)$, where t is the time of failure and τ is a proportional time coefficient. The failure time t is defined as the time when resistance decreases half of its initial value at the specific temperature (T) as shown in the inset of Fig. 1(b). According to the fitting curves, the temperature of 10 years lifetime and activation energy of crystallization (E_a) were calculated to be 59.5 °C and 2.43 eV for Sb_3Te_1, 97.3 °C and 2.97 eV for $Cr_{0.09}Sb_3Te_1$, 125.2 °C and 3.40 eV for $Cr_{0.37}Sb_3Te_1$, 138 °C and 3.46 eV for $Cr_{0.48}Sb_3Te_1$, and 167.6 °C and 3.82 eV for $Cr_{0.95}Sb_3Te_1$. The temperature of 10 years lifetime and E_a of films ascend with the increasing content of doping Cr, which shows better thermal ability. The 125.2 °C data retention of $Cr_{0.37}Sb_3Te_1$ can meet more applications in high thermal PCM.

The crystal structures were characterized by XRD method to analyze the lattice information after Cr doping. The Sb_3Te_1 and $Cr_{0.37}Sb_3Te_1$ films with a thickness of 200 nm were annealed at 250 °C and 300 °C in N_2 atmosphere for 5 min respectively, and the lattice information is shown in Fig. 2(a) and (b). The diffraction peaks of Sb_3Te_1 are similar to Sb_2Te_1 without separated Sb [15]. After Cr doping, $Cr_{0.37}Sb_3Te_1$ films have no peaks corresponding to Cr metal or Cr-containing compound being observed in Fig. 2(b). It can be seen that no more new peaks can be found with the increasing doping Cr content in Fig. 2(c), but some peaks cannot be observed again, which reveals that the main crystal structure was not changed and some grains were refined.

In order to analyze the impacts of doping Cr, XPS were carried out to investigate the chemical bonding features of Sb_3Te_1 and $Cr_{0.37}Sb_3Te_1$ films in crystalline state. Each sample was annealed at 300 °C in N_2 atmosphere for 5 min, and etched for 240 s to remove O element by Ar^+ sputtering. The XPS spectra of Te3d, Sb3d, Te4d and Sb4d are shown in Fig. 3(a), (b), (c) and (d), respectively. The electronegativity of Cr, Sb and Te element is 1.66, 2.05 and 2.1 respectively [16], so the Cr–Te bond is stronger than Sb–Te. After adding Cr into Sb_3Te_1, Sb is replaced by Cr, which is inclined to bond with Te, resulting in forming more Cr–Te and additional Sb–Sb bonds. Hence, the binding energy of Te3d and Te4d shifts to lower value when more Cr–Te bonds are formed as shown in Fig. 3(a) and (c). It also can be observed that the binding energies of Sb3d and Sb4d decrease as shown in Fig. 3(b) and (d) due to more Sb being replaced by Cr forming more Sb–Sb bonds. Moreover, Cr–Te bond has larger bond energy than Sb–Te bond, which suggests that it needs more energy to destroy Cr–Te bond, leading to a better thermal stability. The TEM was conducted to figure out the microstructures of the crystalline films deposited on the carbon membrane substrate, as shown in Fig. 4. All samples were annealed at 300 °C in N_2 atmosphere for 5 min. First, the crystalline Sb_3Te_1, $Cr_{0.09}Sb_3Te_1$ and $Cr_{0.37}Sb_3Te_1$ thin films were characterized through TEM BF image and the corresponding SAED was shown in Fig. 4(a), (b) and (c). It can be seen that the average grain size decreases by doping Cr into Sb_3Te_1 based on TEM BF images. The corresponding SAED images with the selected range show that the crystalline grain sizes of Sb_3Te_1 and $Cr_{0.09}Sb_3Te_1$ films are at least 1 μm as shown in Fig. 4(a) and (b), revealing that they have the tendency of growth-dominant crystallization. However, the SAED patterns of $Cr_{0.37}Sb_3Te_1$ films exhibit polycrystalline rings, which imply that films have many crystalline grains. This indicates that the crystallization behavior has changed from growth-dominant to nucleation-dominant by doping Cr into Sb_3Te_1. From the HRTEM images of Sb_3Te_1, $Cr_{0.09}Sb_3Te_1$ and $Cr_{0.37}Sb_3Te_1$ films, atomic arrangements and uniform grains can be seen on the surface. Only one or two crystal orientation can be found.

The T-shaped PCM devices based on $Cr_{0.37}Sb_3Te_1$ film were fabricated by 0.13 μm CMOS technology. The relations between the cell electronic resistance and the corresponding SET and RESET operations, and endurance were applied to assess the performance of PCM cells. The various resistance–voltage curves and the measured I–V curve of PCM cell based on $Cr_{0.37}Sb_3Te_1$ film are shown in Fig. 5(a). The voltages for SET and RESET operations change from 0.5 V to 0.8 V and 1.1 V to 1.5 V with the various pulse changed from 100 ns to 40 ns respectively. It can be seen that larger voltages are applied to PCM cell when shorter pulses are applied as shown in Fig. 5(a), which suggests that PCM cells need more energy for phase transition with shorter pulse. As shown in the inset of Fig. 5(a), the PCM device exhibited a threshold switching to the crystalline phase when the current reaches 3.6 μA. Fig. 5(b) shows the endurance characteristics of the PCM cell with $Cr_{0.37}Sb_3Te_1$ film. The endurance of PCM with $Cr_{0.37}Sb_3Te_1$ film keeps 3×10^4 cycles with SET

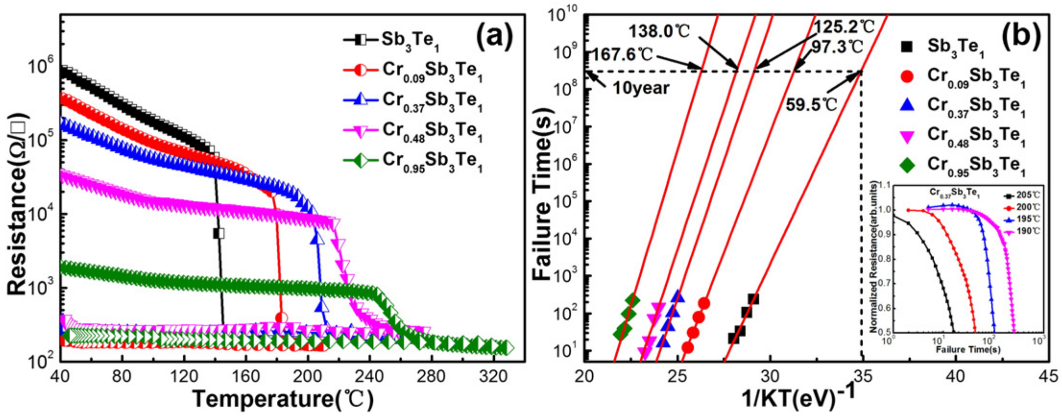

Fig. 1. (a) Sheet resistance of Sb_3Te_1, $Cr_{0.09}Sb_3Te_1$, $Cr_{0.37}Sb_3Te_1$, $Cr_{0.48}Sb_3Te_1$ and $Cr_{0.95}Sb_3Te_1$ films as a function of the temperature with the heating rate of 40 °C/min; (b) Arrhenius fitting plots of Sb_3Te_1, $Cr_{0.09}Sb_3Te_1$, $Cr_{0.37}Sb_3Te_1$, $Cr_{0.48}Sb_3Te_1$ and $Cr_{0.95}Sb_3Te_1$ films for evaluating data retention and activation energy of crystallization; inset is the isothermal plots with the change of resistance as the time for $Cr_{0.37}Sb_3Te_1$ films.