Pt-Sb$_2$Te as high speed phase-change materials with excellent thermal stability

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Abstract

Phase change memory (PCM) has been regarded as one of the most promising candidates for the next-generation nonvolatile memory. In this paper, we propose PtSb$_2$Te (PST) phase change material for phase change memory. The doping of Pt improves the crystallization temperature and Ten-year data-retention temperature of Sb$_2$Te to 180 °C, 192 °C, 204 °C, and 117 °C, 123 °C, 137 °C, and refines the grain to about 10 nm. At the same time, the density change of Sb$_2$Te film after phase transition is reduced to 4.19% due to the addition of Pt. There are no other new phases formed in PST film except hexagonal Sb$_2$Te phase. For PST-based phase change memory cell, only 10 ns electrical pulse is required to complete the reversible operation with a Reset voltage lower than 4.3 V. At the same time, the number of cycle operations of the memory cell exceeds 10$^5$ and it has a lower resistance drift coefficient as 0.019.

1. Introduction

Phase change memory (PCM), as a new type of nonvolatile random access memory (NRA) based on chalcogenides, has the characteristics of excellent nonvolatile, high scalability and fast programming speed [1]. The key of PCM technology is to realize rapid and reversible phase change between amorphous state (high resistance) and crystalline state (low resistance) in phase change materials [2]. Among the widely explored phase change materials, Sb–Te binary alloy has received considerable attention due to its high crystallization rate which is attributed to the growth-dominated crystallization mechanism [3]. However, due to the disadvantages of low crystallization temperature, poor data retention ability and large grain size, Sb–Te binary alloys are not suitable for PCM application without doping modification [4].

In order to solve this problem, many materials doped with transition metal elements have been found, such as Ti–Sb–Te [5] and Sc–Sb–Te [6]. However, Ti and Sc are easy to oxidize in the air, so they are difficult to apply in practice. As we all know, platinum group metals have the advantages of strong oxidation resistance and high thermal stability. At the same time, in the published results, the phase transition time decreases as the Sb/Te ratio increases [7]. Therefore, in order to achieve higher thermal stability and fast setting speed at the same time, in this paper, we propose PtSb$_2$Te as a new phase change memory material.

2. Experiment

80 nm Sb$_2$Te and PtSb$_2$Te films were deposited by the co-sputtering of Pt target and Sb$_2$Te target on SiO$_2$/Si substrates by a RF sputtering system at room temperature. Energy dispersive spectroscopy (EDS) measurements were implemented to measure the elemental composition of films, which are Pt$_{0.14}$Sb$_2$Te, Pt$_{0.21}$Sb$_2$Te, and Pt$_{0.26}$Sb$_2$Te, respectively. The film thickness was measured by scanning electron microscopy (SEM) which was controlled by the sputtering time. The relationship between the resistance of the film and the temperature (R–T)
3. Results and discussion

The variation curve of sheet resistance (\(R_s\)) with temperature (\(R-T\)) of \(\text{Sb}_2\text{Te}\) and \(\text{PtSb}_2\text{Te}\) thin films are shown in figure 1(a). The initial states of all films are amorphous, which are high resistance state. Then \(R_s\) of various films decreases slowly as the temperature rises, while the temperature is close to the crystallization temperature (\(T_c\)), the film resistance suddenly drops, indicating that the films change from the amorphous state with high resistance to the crystallized state with low resistance. The \(T_c\) of \(\text{Sb}_2\text{Te}\), \(\text{Pt}_{0.14}\text{Sb}_2\text{Te}\), \(\text{Pt}_{0.21}\text{Sb}_2\text{Te}\), \(\text{Pt}_{0.26}\text{Sb}_2\text{Te}\) are 150 °C, 180 °C, 192 °C, 204 °C, respectively, which means that the thermal stability of \(\text{Sb}_2\text{Te}\) films is significantly improved with the addition of Pt. It is worth pointing out that crystalline \(R_s\) of \(\text{PtSb}_2\text{Te}\) is increased. The higher crystalline \(R_s\) implies that a lower power is required to achieve the phase transition in the PCM. Although the amorphous \(R_s\) of \(\text{PtSb}_2\text{Te}\) is decreased, it still has enough margins to distinguish the high-resistance state and the low-resistance state. Figure 1(b) presents the data retention capability of \(\text{Sb}_2\text{Te}\) and \(\text{PtSb}_2\text{Te}\) films. The failure time is defined as the time when the sheet resistance falls into half of its original value under isothermal annealing temperature. Ten-year data-retention temperature can be estimated by fitting the Arrhenius equation:

\[
    t = \tau e^{E_a/kT}
\]

where \(t\) is time, \(\tau\) is a constant, \(E_a\) is crystal activation energy, \(k\) is Boltzmann constant, \(T\) is temperature.\(^{[8]}\)

With the Pt content increasing, the estimated ten-year data-retention temperature increases significantly from 55 °C to 117 °C, 123 °C, 137 °C, manifesting the better data retention of \(\text{Sb}_2\text{Te}\) by Pt doping.

The structures of \(\text{Sb}_2\text{Te}\) and \(\text{PtSb}_2\text{Te}\) thin films were investigated by XRD. Figure 2 shows the XRD results of \(\text{Sb}_2\text{Te}\) and \(\text{PtSb}_2\text{Te}\) films. No diffraction peak appears in all the deposited films, indicating that both \(\text{Sb}_2\text{Te}\) and \(\text{PtSb}_2\text{Te}\) films are in amorphous state. Diffraction peaks of hexagonal phase are observed in \(\text{Sb}_2\text{Te}\) and \(\text{PtSb}_2\text{Te}\) films annealed at 230 °C. Compared with \(\text{Sb}_2\text{Te}\) films, the diffraction peak intensity of \(\text{PtSb}_2\text{Te}\) films is reduced. The broad diffraction peaks indicate that the crystalline process of \(\text{Sb}_2\text{Te}\) is inhibited remarkably by the addition of Pt. In addition, the (0 0 4), (0 0 5), (1 1 4) diffraction peaks disappear and the (1 0 3), (1 1 0) diffraction peaks appear because of the addition of Pt. The change of diffraction peak indicates that the addition of Pt can change the crystal growth orientation of \(\text{Sb}_2\text{Te}\). No new phases appear in the \(\text{PtSb}_2\text{Te}\) films excepting the hexagonal structure of \(\text{Sb}_2\text{Te}\) (JCPDS No. 80-1722), shows good uniformity of materials.
where $\alpha_m$ is the incident angle corresponding to the XRR curve, $\lambda$ is the wavelength of Cu K\(\alpha\) spectral line (0.154 nm), $d$ is the thickness of the film, the $m$ represents the order of reflection and the $\Delta m$ should be 1/2 for Sb$_2$Te/Si film [10]. Then the density change of the film can be expressed as the formula:

$$\Delta \rho = \frac{\alpha_m^2 - \alpha_{m+1}^2}{\alpha_{m+1}^2},$$

where $\alpha_m^2$ and $\alpha_{m+1}^2$ are critical angle of amorphous and crystalline films, respectively. The density change of Pt$_{0.21}$Sb$_2$Te film (4.19%) is significantly less than Sb$_2$Te film (5.68%). Therefore, Pt doping significantly decreases the density change between the Sb$_2$Te crystalline state and amorphous state. Small density change can prevent the film from falling off from the surrounding material, thus improving the reliability of the device and prolonging the life of the device [11].

We further revealed the binding state of Sb$_2$Te and Pt$_{0.21}$Sb$_2$Te by XPS, as shown in figures 4(a) and (b). We find that the peaks of Sb element and Te element shift to higher binding energies. Numerous experiments have proved that when element C replaces element B in bonding with element A, if the electronegativity of element C is greater than that of element B, then the binding energy of element A increases [12]. Since the electronegativity of Pt(2.2) is higher than that of Sb(2.05) and Te(2.12), the binding energy of Sb and Te increases, and electronegativity difference ($\Delta S$) of Pt-Te and Pt-Sb is bigger than Sb-Te, the larger the $\Delta S$ between the two atoms, the higher the probability of nucleation, so Pt bonds with both Sb and Te. The structure of Sb$_2$Te is nine layers (Te-Sb-Te-Sb-Sb-Sb-Te-Sb-Te) according to published results [13]. When Pt atom enters Sb$_2$Te, it may substitute Sb atom which will bond with Te and Sb atom simultaneously. The doping of Pt will produce more grain boundaries, which will significantly inhibit the subsequent crystal growth. This may be the reason why the grain size decreases after doping Pt [14].

We obtained more structural information of phase change materials by TEM. Sb$_2$Te and Pt$_{0.21}$Sb$_2$Te films are annealed at 230 °C. According to the bright field transmission electron microscope image in figure 5(a), it can be found that the grain size of Sb$_2$Te thin film is several hundred nanometers. However, after the addition of Pt, it can be seen from figure 5(b) that the grain size is significantly reduced to about 10 nm. By measuring the spacing of lattice fringes, the crystal orientations of Sb$_2$Te and Pt$_{0.21}$Sb$_2$Te films in figures 5(c) (e) are (1 1 4) and (1 0 3), respectively, which are consistent with the XRD test results. It shows that the film still has a hexagonal structure of Sb$_2$Te after Pt doping, and the crystal grain can be refined, which could also be confirmed by the
SAED patterns in figures 5(d) (f). On the one hand, grain refinement increases the scattering probability at the grain boundary, which leads to the increase of film resistance. On the other hand, it can also increase the specific surface area, which is conducive to releasing the stress caused by volume change in the phase transition process and improving the stability of the device [15].

Pt$_{0.21}$Sb$_2$Te thin film based on PCM cell was prepared in order to investigate the device properties of PtSb$_2$Te phase change materials. Figure 6(a) shows the resistance-voltage (R-V) curves for the PCM cell with different pulse widths. The Set and Reset voltages of Pt$_{0.21}$Sb$_2$Te based PCM cells are 2.1 and 4.3 V (with 10 ns pulse width), which are lower than that in Sb$_2$Te film based PCM cells reported in the published work (2.2 and 5.2 V for set and reset with 40 ns pulse width) [16]. This means that the addition of Pt will effectively reduce the required voltage of the device. On the other hand, speed of operation is another important factor in PCM...
application, which is almost determined by crystallization rate. As can be seen from figure 6(b), the higher the voltage, the lower the required $t_{\text{Set}}$. It is worth noting that only a voltage of 1.6 V is needed to complete the Set transition for a 6 ns pulse which is the fastest ever recorded in multiple tests. This test process is the maximum speed of multiple tests, and the voltage will be lower than the R-V test result. This experimental result confirms that the phase change memory device cell based on Pt$_{0.21}$Sb$_2$Te film has a very fast operating speed. Figure 6(c) shows the fatigue cycle test result of the PCM device based on Pt$_{0.21}$Sb$_2$Te film. Under the repeated action of such Set (500 ns/0.8 V) and Reset (300 ns/2.1 V) electric pulses, the device cycle operation times can reach more than $10^5$, indicating that it has good durability. The structural relaxation caused by phase change materials will affect the stability of the device [17]. Therefore, we explored the resistance change curve of the Pt$_{0.21}$Sb$_2$Te phase change memory device Set and Reset over time, as shown in figure 6(d). The resistance drifts can be described by a power-law equation:

$$R(t) = R_0 \left( \frac{t}{t_0} \right)^\nu$$

Where $R_0$ is initial resistance, $t_0$ is initial time, and $\nu$ is drift coefficient [18]. As can be seen from the figure, for the device in the set state, the resistance is very stable over time and the drift coefficient is close to zero. The drift.
The thermal stability, microstructure and device performances of PST are systematically investigated. The addition of Pt can significantly improve the crystallization temperature and data retention of Sb$_2$Te, and reduce the density change after the films phase transition. XRD and TEM results demonstrate that the addition of Pt enables grain refinement and hexagonal Sb$_2$Te is the only phase exists in the crystalline PST. Meanwhile, PST-based PCM device shows excellent reversible phase change ability, good fatigue property and fast crystallization speed as short as 6 ns.

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