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Phase transformation in Mg–Sb_3Te thin films*

Li Jun-Jian(李军建)[a], Wang Guo-Xiang(王国祥)[b], Chen Yi-Min(陈益敏)[a], Shen Xiang(沈 祥)[b]†, Nie Qiu-Hua(聂秋华)[a], Lü Ye-Gang(吕业刚)[a], Dai Shi-Xun(戴世勋)[b], and Xu Tie-Feng(徐铁锋)[b]

[a] *Faculty of Information Science and Engineering, Ningbo University, Ningbo* 315211, *China*

[b] *Laboratory of Infrared Material and Devices, The Advanced Technology Research Institute, Ningbo University, Ningbo* 315211, *China*

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Mg-doped Sb_3Te films are proposed to improve the performance of phase-change memory (PCM). We prepare Mg-doped Sb_3Te films and investigate their crystallization behaviors, structural, optical and electrical properties. We find that Mg-doping can increase the crystallization temperature, enhance the activation energy, and improve the 10-year data retention of Sb_3Te. Especially $Mg_{25.19}(Sb_3Te)_{74.81}$ shows higher T_c ($\sim$ 190 °C) and larger E_a ($\sim$ 3.49 eV), which results in a better data retention maintaining for 10 yr at $\sim$ 112 °C. Moreover R_a/R_c value is also improved. These excellent properties make Mg–Sb–Te material a promising candidate for the phase-change memory (PCM).

Keywords: phase change memory, data retention, Mg–Sb–Te, thermal stability

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1. Introduction

Phase change memory (PCM) has attracted increasing attention, and it is a promising candidate for next generation non-volatile memory[1–3] due to its amazing properties, such as high-speed, high-density, low power consumption, long life cycle, and scalability.[4–6]

Currently, $Ge_2Sb_2Te_5$ film is often used as a phase-change memory (PCM) active layer due to its outstanding electronic performance and thermal stability.[7] However, the problems such as high RESET current and poor stability remain to be solved. During the past few years, in order to solve the problems, great efforts based on doping other elements into Sb–Te binary system, such as N,[8] Al,[9] In,[10] Bi,[11] Ti,[12] and Si,[13] have been made to explore new phase change materials with high thermal stabilities for commercial applications. Our research group has also developed a phase change material Mg–GST films for PCM.[14] The results show that they have good thermal stabilities, rapid phase transitions and high crystalline resistances. However little attention has been paid to the effect of Mg element on the Sb_3Te film. Here in this paper, Mg-doped Sb_3Te films with different Mg concentrations are prepared, and the effects of Mg doping on crystallization characteristics, thermal stabilities, and electrical resistances of Mg–Sb–Te films are systematically studied so as to explore the best composition for PCM applications.

2. Experiment

Thickness values of as-deposited Mg–Sb_3Te films on quartz and SiO_2/Si (100) substrates were all 200 nm under co-sputtering of Mg and Sb_3Te targets. The background pressure was evacuated to 2×10^{-4} Pa, and the sputtering Ar pressure was 0.35 Pa. The sputtering power for Sb_3Te target was fixed at RF 70 W while that for Mg was varied from DC 7 W to DC 13 W. And a pure Sb_3Te film was also prepared for comparison. The concentrations of Mg dopant in the Mg-doped Sb_3Te films, measured by energy dispersive spectroscopy (EDS), were identified to be 12.14 at.%, 15.09 at.%, and 25.19 at.% respectively. The structures of as-deposited and annealed Sb_3Te and Mg-doped Sb_3Te thin films were examined by X-ray diffraction (XRD). The optical band gaps of the films were measured using UV-VIS-NIR spectrophotometer. *In situ* temperature-dependent and time-dependent resistances at various isothermal annealing temperatures were measured in a vacuum chamber.

3. Results and discussion

Figure 1 shows the temperature-dependent sheet resistances of Sb_3Te and Mg-doped Sb_3Te films. The sheet resistance of the as-deposited film increases with increasing Mg content at room temperature. But the sheet resistances of all films decreases with temperature increasing up to their respective crystallization temperature (T_c), which is determined by the minimum of the derivative of *in situ* R–T curve. By raising the Mg content, the T_c of Mg–Sb–Te film can be fur-

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†Corresponding author. E-mail: shenxiang@nbu.edu.cn

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ther increased. T_c values of the films $Mg_{12.14}(Sb_3Te)_{87.86}$, $Mg_{15.09}(Sb_3Te)_{84.91}$, and $Mg_{25.19}(Sb_3Te)_{74.81}$ are 179.5 °C, 184.8 °C, and 190.0 °C respectively, All of them are higher than T_c value of Sb_3Te (135 °C), indicating outstanding amorphous stability of these new materials. Our results show that the increase of Mg content can effectively raise T_c. Excellent amorphous stabilities of these MgSbTe materials can be expected.

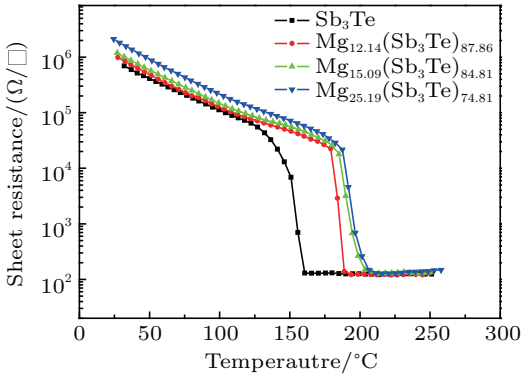


Fig. 1. (color online) Variations of sheet resistance with temperature for Sb_3Te and Mg-Sb_3Te films.

Figure 2 shows the curve of R_a/R_c resistance ratio of MgSbTe film versus Mg content (R_a denotes the sheet resistance at room temperature, and R_c the sheet resistance at 250 °C). It indicates that when the Mg content increases from 12.14 at.% to 25.19 at.%, R_a/R_c values are 7315, 8840, and 16350 respectively, higher than the value 5250 of undoped Sb_3Te. It means that the Mg–Sb_3Te material will have a good switching ratio.

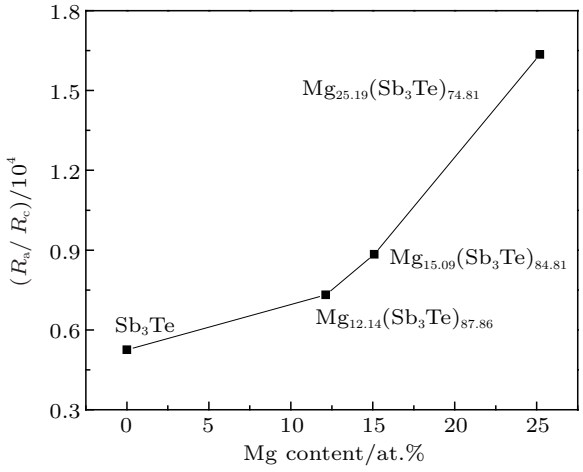


Fig. 2. Variation of R_a/R_c resistance ratio of MgSbTe film with Mg content.

Figure 3 shows the X-ray diffraction (XRD) patterns of the $Mg_x(Sb_3Te)_{100-x}$ thin films annealed at different temperatures for 3 min in Ar atmosphere. According to Figs. 3(a)–3(c), it can be easily found that no crystallization peaks are observed in the as-deposited $Mg_x(Sb_3Te)_{100-x}$ films, indicating that they have an amorphous nature each. Moreover, the amorphous phase can be stabilized at the annealing temperature up to 150 °C. After annealing at 200 °C, the $Mg_x(Sb_3Te)_{100-x}$ thin films each have crystallized into an Sb_2Te phase. Each diffraction peak can be indexed according to the PDF card (JCPDS NO. 80-1722). The crystallization peaks become stronger with annealing temperature increasing. On the other hand, with increasing Mg content, there are found to be no changes in the main peaks in the patterns, which further indicates that when Mg atoms are doped into Sb_3Te, the lattice structure remains unchanged.[15] Moreover, all the peaks are suppressed and broadened after Mg doping from the XRD patterns, implying that crystalline grains become smaller.

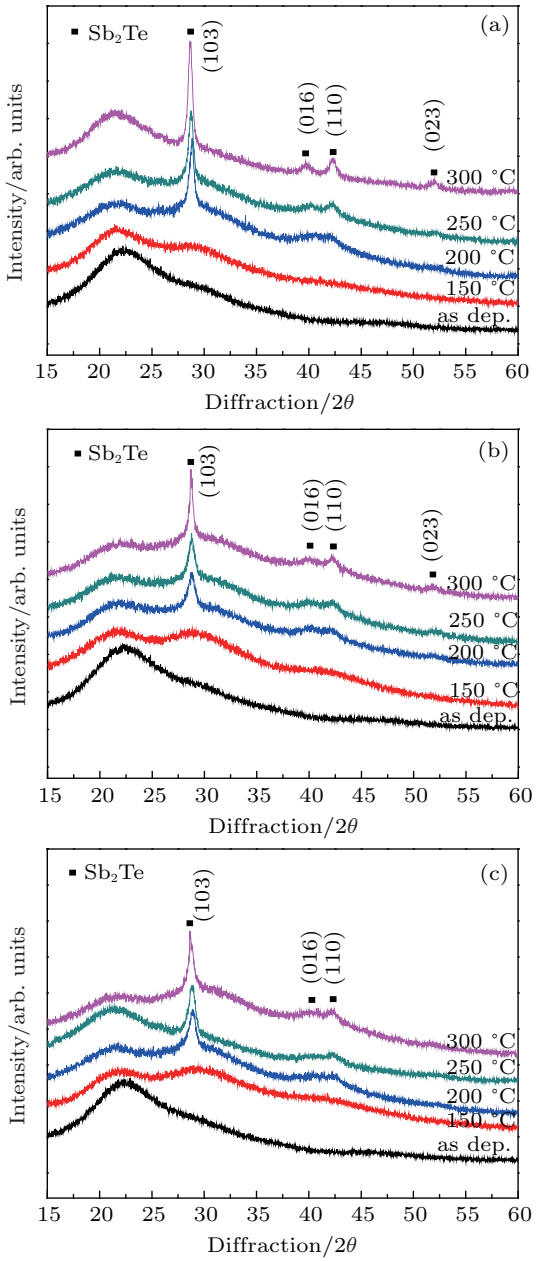


Fig. 3. (color online) XRD patterns of Mg-doped Sb_3Te films annealed at different temperatures for 3 min in Ar atmosphere for (a) $Mg_{12.14}(Sb_3Te)_{87.86}$, (b) $Mg_{15.09}(Sb_3Te)_{84.91}$, and (c) $Mg_{25.19}(Sb_3Te)_{74.81}$ films.

In order to reduce the threshold current, the phase change material needs a large optical band-gap.[16] The optical band-gaps of amorphous films are measured by UV-VIS-NIR spectra, and the results are shown in Fig. 4. The band gap can be obtained using the equation $ah\nu = B(h\nu - E_g)^2$, where a, ν, B, and E_g are the absorption coefficient, incident light frequency, constant, and band gap, respectively. As shown in Fig. 4, the value of $(ah\nu)^{1/2}$ varies almost linearly with the value of $h\nu$, demonstrating that $MgSb_3Te$ is an indirect band gap semiconductor. The optical band gap values of amorphous $Mg_{12.14}(Sb_3Te)_{87.86}$, $Mg_{15.09}(Sb_3Te)_{84.91}$, and $Mg_{25.19}(Sb_3Te)_{74.81}$ films are 0.443 eV, 0.478 eV, and 0.493 eV, respectively. All of them are slightly larger than that of Sb_3Te ($\sim$ 0.432 eV). With the Mg content increasing, the optical band gap becomes larger.

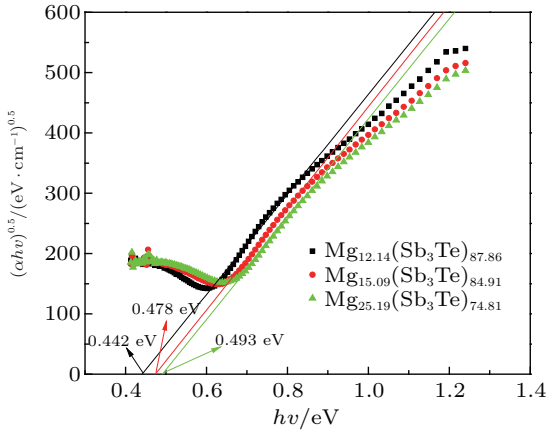


Fig. 4. (color online) Relationships between $(ah\nu)^{1/2}$ and $h\nu$ for as-deposited $Mg_{12.14}(Sb_3Te)_{87.86}$, $Mg_{15.09}(Sb_3Te)_{84.91}$, and $Mg_{25.19}(Sb_3Te)_{74.81}$ films.

Figure 5 shows the diagrams of the resistance versus time at various isothermal annealing temperatures for (a) $Mg_{12.14}(Sb_3Te)_{87.86}$, (b) $Mg_{15.09}(Sb_3Te)_{84.91}$, and (c) $Mg_{25.19}(Sb_3Te)_{74.81}$ films. And the data retention durations of the amorphous materials can be calculated by isothermal change in resistance as shown in Fig. 5(d). The maximum temperature for 10-year data retention performance can be evaluated on the basis of the Arrhenius equation[17]

$$\ln(t) = E_a/kT - \ln(\tau), \tag{1}$$

where t is failure-time, τ a proportional time constant, k the Boltzmann's constant, and T the isothermal temperature. The failure time t is defined as the time when the sheet resistance reduces to half of its initial magnitude at a specific isothermal temperature (T). It is observed that the temperatures corresponding to 10-year data retention durations are 104 °C, 106 °C, and 112 °C and the activation energies are 3.29 eV, 3.39 eV, and 3.49 eV for $Mg_{12.14}(Sb_3Te)_{87.86}$, $Mg_{15.09}(Sb_3Te)_{84.91}$, and $Mg_{25.19}(Sb_3Te)_{74.81}$ films respectively. It shows that the temperature increases with the Mg content increasing. Compared with the conventional phase-change material $Ge_2Sb_2Te_5$ (88 °C, 2.96 eV), Mg–Sb–Te films exhibit good thermal stability. Therefore, the Mg–Sb_3Te-based PCM should store information longer and more stably.

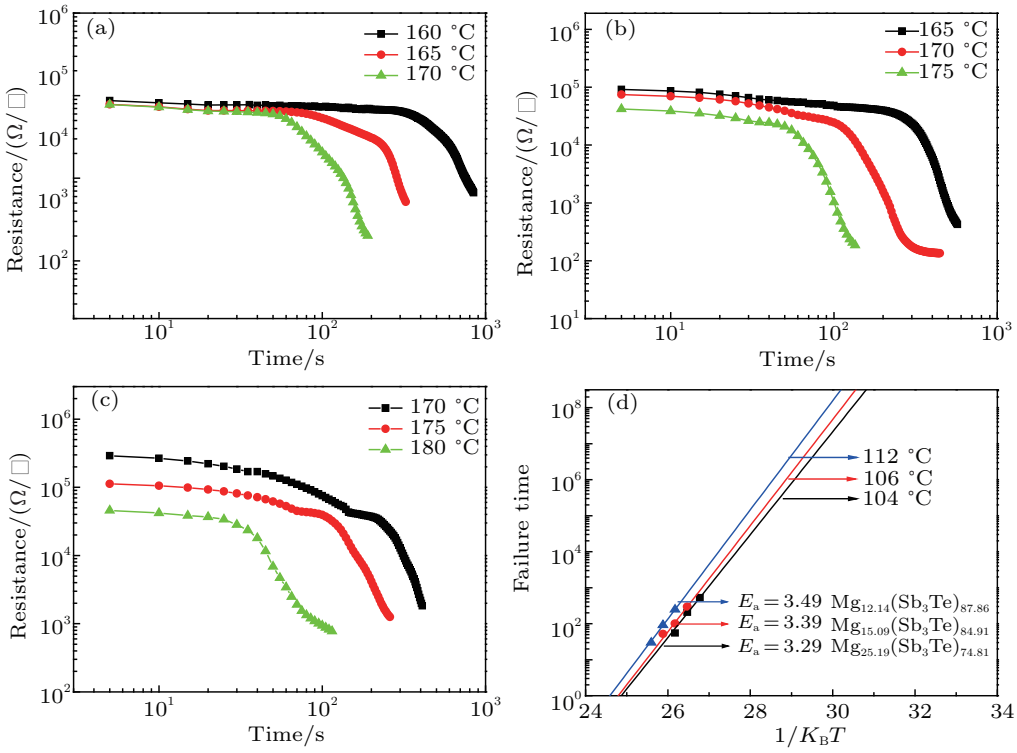


Fig. 5. (color online) plots of resistance versus time at various isothermal annealing temperatures for (a) $Mg_{12.14}(Sb_3Te)_{87.86}$, (b) $Mg_{15.09}(Sb_3Te)_{84.91}$, (c) $Mg_{25.19}(Sb_3Te)_{74.81}$ films, and (d) the Arrhenius plots for amorphous $Mg_{12.14}(Sb_3Te)_{87.86}$, $Mg_{15.09}(Sb_3Te)_{84.91}$, and $Mg_{25.19}(Sb_3Te)_{74.81}$ films.

4. Conclusions

The properties of Mg doped Sb–Te materials have been investigated in detail. Good performances can be achieved with the addition of Mg, including good data retention, high crystallization temperature, large activation energy, single crystalline phase, and wide optical band-gap. In particular, $Mg_{25.19}(Sb_3Te)_{74.81}$ shows higher T_c ($\sim$190 °C) and larger E_a ($\sim$ 3.49 eV), which results in a better data retention duration of 10 years at $\sim$112 °C. Owning to its good thermal stability, rapid phase transition, and stable phase, $Mg_{25.19}(Sb_3Te)_{74.81}$ film can be used for phase change memory.

References

[1] Wuttig M and Yamada N 2007 *Nat. Mater.* **6** 824
[2] Wong H S P, Raoux S, Kim S, Liang J L, Reifenberg J P, Rajen-dran B, Asheghi M and Goodson K E 2010 *Proc. IEEE* **98** 2201
[3] Wuttig M and Steimer C 2007 *Appl. Phys. A: Mater. Sci. Process.* **87** 411
[4] Lankhorst M H R, Ketelaars B and Wolters R A M 2005 *Nat. Mater.* **4** 347
[5] Privitera S, Rimini E and Zonca R 2004 *Appl. Phys. Lett.* **85** 3044
[6] Yamada N, Ohno E, Nishiuchi K, Akahira N and Takao M 1991 *J. Appl. Phys.* **69** 2849
[7] Liu B, Song Z T, Zhang T, Feng S L and Chen B 2004 *Chin. Phys.* **13** 1947
[8] Cheng L M, Wu L C, Song Z T, Rao F, Peng C, Yao D N and Liu B 2012 *Mater. Lett.* **71** 98
[9] Seo J H, Song K H and Lee H Y 2010 *J. Appl. Phys.* **108** 064515
[10] Wang K, Steimer C, Wamwangi D, Ziegler S and Wuttig M 2005 2005 *Appl. Phys. A* **80** 1611
[11] Wang K, Wamwangi D, Ziegler S, Steimer C and Wuttig M 2004 *J. Appl. Phys.* **96** 5557
[12] Wei S J, Zhu H F, Chen K, Xu D, Li J, Gan F X, Zhang X, Xia Y J and Li G H 2011 *Appl. Phys. Lett.* **98** 231910
[13] Zhang T, Song Z T, Liu B, Liu W L, Feng S L and Chen B 2007 *Chin. Phys.* **16** 2475
[14] Fu J, Shen X, Nie Q H, Wang G X, Wu L C, Dai S X, Xu T F and Wang R P 2013 *Appl. Surf. Sci.* **264** 269
[15] Feng W, Zhang T, Liu C L, Song Z T, Wu L C, Liu B, Feng S L and Chen B 2008 *Appl. Surf. Sci.* **254** 2281
[16] Welnic W, Pamungkas A, Detemple R, Steimer C, Blugel S and Wuttig M 2006 *Nat. Mater.* **5** 56
[17] Wuttig M and Steimer C 2007 *Appl. Phys. A* **87** 411