Tunable Phase-Change Performance of Sb-Te-Se Film for Phase Change Memory

Yadong Ma,a,b Yegang Lu,a,b,c,d Zengguang Li,a,b Xiang Shen,b,d Guoxiang Wang,b,d Yongxin Liu,b,d and Shixun Dai,b,d

Faculty of Electrical Engineering and Computer Science, Ningbo University, Zhejiang, 315211, People’s Republic of China
Key Laboratory of Photoelectric Materials and Devices of Zhejiang Province, Ningbo, 315211, People’s Republic of China
State Key Laboratory of Functional Materials for Informatics, Laboratory of Nanotechnology, Shanghai Institute of Micro-system and Information Technology, Chinese Academy of Sciences, Shanghai 200050, People’s Republic of China
Laboratory of Infrared Material and Devices, The Advanced Technology Research Institute, Ningbo University, Zhejiang 315211, People’s Republic of China

In this paper, the phase change characteristics of Sb-Te-Se films were systematically studied by in-situ resistance-temperature measurement, X-ray diffraction (XRD), Raman scattering spectroscopy, X-ray photoelectron spectra (XPS), and Transmission electron microscopy (TEM). For preferred Sb56Te24Se20 and Sb55Te22Se23 films, the temperature for 10-year data retention can be up to 93.1 and 102.6°C, which are higher than that of Ge2Sb2Te5 (GST, 82°C). Both amorphous and crystalline resistivities increase with Se content. The resistance ratios between two states maintain almost 4 orders of magnitude. The microstructure of annealed Sb-Te-Se films exhibits uniform distribution of crystallized phases with rhombohedral Sb2SeTe2 and hexagonal Sb. The improvement in thermal stability of Sb-Te-Se films results from the atomic arrangements and consequently the complex cross bond system.

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.009160jss] All rights reserved.

Manuscript submitted October 30, 2015; revised manuscript received December 15, 2015. Published December 31, 2015.

Demand for mass storage has been increasing owing to explosive growth of information in recent days. To meet this demand, phase change memory (PCM) is proposed and considered as one of the most promising next-generation non-volatile memories because of its superior scaling, fast speed, and low power consumption.1–3 Its performance depends on phase change materials with the high resistance contrast between amorphous and crystalline states. Normally, electrical pulse with high intensity and short width is employed to heat up the phase change materials over its melting point. And the fast quenching leads the material to an amorphous state (high resistance RESET state). Medium pulse intensity for longer time is used to induce the amorphous materials into crystalline states (low resistance SET state) if Joule heating is above its crystallization temperature and below the melting point. Low current with essentially no Joule heating can distinguish the resistance states.

Recently, great efforts have been made to explore novel chalcogenide materials and optimize the phase change characteristics in order to improve the device properties of PCM. Among many phase change materials, Ge2Sb2Te5 (GST) has attracted a great deal of attention due to its good overall performance. However, the low crystallization temperature (~160°C) and relatively slow crystallization should be addressed for further practical applications.4–6 Sb2Te material possesses high crystallization speed and relatively low-melting point, while the drawback of the low crystallization temperature impedes its application for phase change memory.6–9 In fact, much research has been performed by doping various elements such as Zn,10 N,11 W,12 Al,13 Cr,14 into Sb-Te to improve its material properties for PCM. On the other hand, it is reported that Sb-Se material has the advantages of large on/off resistance ratio, low melting point and high crystallization temperature.15,16 It is expected that the combination of SbTe with Sb-Se has advantages of the high speed, low power consumption and long archival life for PCM. Indeed, Sb60Te31Se9 exhibits the 10-years data retention at 87°C, and the device can be operated under the pulse as short as 10 ns.17 Very recently, Sb57Te26Se17 was proposed for PCM due to its brilliant thermal stability.18 In fact, the phase change properties such as thermal stability, crystallization speed, and amorphous/crystalline resistivities can be substantially tailored by the change in composition of Sb-Te-Se ternary system. Nevertheless, the effect of Sb-Te-Se composition on its thermal stability, electrical properties, crystalline structure and bond environments is still unclear. It is necessary for us to investigate the phase change behavior of Sb-Te-Se with different compositions before its practical application for PCM. In this paper, four samples with different Se contents were proposed to insightfully elucidate the effect of dopants on the phase structural and chemical bonds from amorphous to crystalline states. The results can serve as a guide to optimize the phase change properties of Sb-Te-Se materials.

Sb-Te-Se films were deposited on SiO2/Si substrates by co-sputtering Sb2Te and SbSe3 targets at room temperature. The background and sputtering pressures were 2.7 × 10−4 and 0.3 Pa, respectively. The Radio Frequency (RF) power on the Sb2Te target was fixed to be 40 W, and the direct current power of Sb2Se3 target to be 5, 10, 15 and 20 W respectively. The corresponding compositions of the deposited films measured by energy dispersive spectroscopy (EDS) were Sb60Te31Se9, Sb57Te26Se17, Sb56Te24Se20 and Sb55Te22Se23. The sheet resistance of as-deposited films as a function of temperature(R-T) was measured by four-point probe method. The crystal structure of the films annealed at different temperature was measured by X-ray diffraction (XRD) with Cu Kα radiation measurement in the 2θ range from 20° to 60°. Raman scattering spectroscopy and X-ray photoelectron spectra (XPS) were employed to study the chemical bonding feature of films. The microstructure of the films was measured by transmission electron microscopy (TEM).

Fig. 1a shows the sheet resistance as a function of temperature(R-T) with a heating rate of 10°C/minute. Upon heating, a continuous decrease in the resistance is observed for all the films due to the heat active carrier for hopping conduction.19 And then an abrupt drop in resistance occurs when the temperature reaches their respective crystallization temperature (Tc), which is determined by the minimum of the first derivative of R-T. With increasing Se content, Tc raises from 150°C for Sb60Te31Se9 to 180°C for Sb55Te22Se23. Both amorphous and crystalline resistivities increase with Se content, which is favorable for low power consumption. It is also shown that the resistance ratios between the two states maintain at least 4 orders of magnitude, which helps to enhancing the operation reliability of the device. The thermal stability was measured by fitting the data with Arrhenius equation 

\[ t = \tau \cdot \exp \left( \frac{E_a}{K_bT} \right), \]

where t and τ is the time to failure and a proportional time constant, respectively. The time to failure is defined

E-mail: lvyegang@nbu.edu.cn
as the time which the film resistance reaches half of its initial value at the specific temperature. The Arrhenius plot of thermal stability for the as-deposited amorphous Sb-Te-Se films is shown in Fig. 1b. The temperatures for 10-year data retention of Sb60Te31Se9, Sb57Te26Se17, Sb56Te24Se20 and Sb55Te22Se23 films are 75.4, 84.1, 93.1 and 102.6 °C, respectively. The composition of Sb60Te31Se9 is unsuitable for PCM device due to relatively poor thermal stability. Other compositions in this study have a better thermal stability than Ge2Sb2Te5 (82 °C). It indicates that the increase of Se content can significantly improve the archival life of the amorphous Sb-Te-Se films.

Fig. 2 shows XRD patterns of the Sb-Te-Se films annealed at different temperatures. There are no crystallization peaks for the as-deposited films, suggesting its nature of the amorphous state. With increasing annealing temperature, the characteristic peak is observed only for Sb60Te31Se9 film at 150 °C. And the crystallization peaks don’t appear until the annealing temperature increases to 200 °C for other compositions, as shown in Fig. 2. It indicates that the crystallization temperature of the studied films ranges from 150 to 200 °C, which is in good agreement with R-T results. For Sb60Te31Se9 and Sb56Te24Se20 films, with increasing annealing temperature to 300 °C, rhombohedra Sb2SeTe2 and hexagonal Sb phase can be found and the positions of diffraction peaks do not change which indicates that no further phase transition happens. It is reasonable that the incorporation of Sb2Se3 into Sb2Te leads to the change in bond configuration as a result of atomic rearrangement, which will be confirmed by Raman and XPS measurements later. The complex cross bond system contributes to the increase of the crystallization temperature.

Since phase separation (Sb2SeTe2 and Sb) occurred in Sb56Te24Se20 and Sb55Te22Se23 films, it is necessary to clarify the bond vibrations of both samples using Raman measurement. Fig. 3 shows Raman spectra of Sb60Te31Se9 and Sb55Te22Se23 films annealed at different temperatures. For as-deposited and 150 °C annealed films, it is shown that a broad peak in the range from 100 cm⁻¹ to 180 cm⁻¹ which is related to the vibration of amorphous Sb-Te bonds. And the broad band located at around 190 cm⁻¹ corresponds to the heteropolar Sb-Se bond vibrations in the SbSe3/2-pyramids. The spectra with...
Figure 3. Raman spectra of (a) Sb$_{56}$Te$_{24}$Se$_{20}$ and (b) Sb$_{55}$Te$_{22}$Se$_{23}$ films at different annealing temperature.

Figure 4. XPS spectra for Sb$_{55}$Te$_{22}$Se$_{23}$ film: (a) Se 3d, (b) Sb 3d, and (c) Te 3d.

The feature of broad band suggest that the as-deposited films are in amorphous states, which is consistent with the R-T and XRD results. The broad peak at 150 cm$^{-1}$ is divided into three different sharp peaks located at around 114, 141 and 172 cm$^{-1}$, when both samples were annealed at 200°C. Meanwhile, the broad band at 190 cm$^{-1}$ disappears, suggesting part of Sb-Se bond broken in Sb$_2$Se$_3$-pyramids. It is interesting that the peak at 167 cm$^{-1}$ shifts to high wave number with further increasing annealing temperature for both compositions, as shown in Fig. 3. It is reasonable that Se atoms in Sb$_2$Se$_3$ enter into Sb-Te and form chemical bonds with Te.$^{27}$ Thus, rhombohedra Sb$_2$Se$_3$ and hexagonal Sb phase can be found in XRD patterns. The bond recombination accounts for the enhancing crystallization temperature for Sb-Te-Se films with higher Se concentration.$^{28}$ It is shown that Sb$_{55}$Te$_{22}$Se$_{23}$ can serve as the representative of Sb-Te-Se material, and we will further discuss its bond environment and microstructures in next section.

X-ray photoelectron spectra (XPS) of Se 3d, Sb 3d and Te 3d for the Sb$_{55}$Te$_{22}$Se$_{23}$ film were investigated to analyze the chemical bonding features. The binding energy of 53.8 eV in Fig. 4a, which is lower than that of Se-Se homopolar binding energy of pure Se,$^{29}$ are related to Se 3d of Sb-Se for Sb$_{55}$Te$_{22}$Se$_{23}$. After incorporation of Sb$_2$Se$_3$ into Sb$_2$Te, the binding energy of both Sb 3d and Te 3d shifts to high value for Sb$_{55}$Te$_{22}$Se$_{23}$ compared with Sb$_2$Te, as shown in Figs. 4b and 4c. It has been reported that the binding energy of an element increases with increasing electronegativity of the neighboring bonding atom.$^{30}$ The electronegativities of Se, Sb and Te are 2.55, 2.05 and 2.1 respectively.$^{31}$ It indicates that the addition of Sb$_2$Se$_3$ into Sb$_2$Te suffers from atomic reconfiguration and eventually changes the bonding state, which is consistent with Raman results.

The microstructures of crystalline Sb$_{55}$Te$_{22}$Se$_{23}$ film deposited on carbon membrane substrate are studied by TEM. Fig. 5a shows the TEM image of the film annealed at 250°C for 3 min. The incoherent elastic scattering (Rutherford scattering) of electrons leads the dark and bright contrast in the TEM image.$^{35}$ The black particles which are crystallized after annealing with a size of several tens of nanometers are uniformly distributed in the film. The selected area electron diffraction (SAED) pattern in Fig. 5b indicates the rhombohedra Sb$_2$Se$_3$.
and Sb phase, which is in agreement with XRD results. The embedded structure of Sb$_5$Te$_4$ and Sb phases is also confirmed by the high-resolution TEM (HRTEM) images, as shown in Figs. 5c and 5d. Phase separation may lead to the deterioration of the endurance and reliability of the device due to the non-uniform composition in programing region as a result of facility in element migrating or void formation, especially in 10 nm node. However, the phase separation of Sb from the composition may help to improve phase change speed. Sb is characterized by an explosive crystallization which is a thermal process with the heat that is released at the crystallization front serving to drive the crystallization of the surrounding amorphous region further. Sb crystallization may serve as a template for subsequent crystallization to reduce the crystallization time.

In summary, phase change characteristics of Sb-Te-Se with different compositions are systematically investigated. The crystallization temperature, the 10-year data retention, and resistivities of both amorphous and crystalline states increase with increasing Se content. The selected composition Sb$_5$Te$_2$:Se$_{23}$ exhibits higher crystallization temperature (about 180 °C), better data retention (102.6 °C), and relative large crystalline resistivity, which can effectively reduce the write current. The bonding recombination of incorporation of Sb$_2$Te into Sb$_5$Te$_4$ accounts for the improved thermal stability of Sb-Te. The embedded phases of Sb$_5$Te$_4$ and Sb show the uniform distribution in Sb-Te-Se film. With large resistance ratio and good thermal stability performance, Sb-Te-Se material is considered to be a promising phase change material for PCM.

Acknowledgments

This work is supported by National Science Foundation of China (grant Nos. 61301417, 61377061), Ningbo municipal Natural Science Foundation of China (grant No. 2014A610121), Natural Science Foundation of Zhejiang Province (grant No. LQ15F040002), Open Fund of Zhejiang Provincial Key Academic Project (first level, No. xk11530) and sponsored by K. C. Wong Magna Fund in Ningbo University.

References

1. M. H. R. Lankhorst, B. Ketelaars, and R. A. M. Wolters, Nature Materials, 4(4), 347 (2005).
2. J. Tomforde, W. Bensch, L. Kienle, V. Doppel, P. Merkelbach, and M. Wuttig, Chemistry of Materials, 23(17), 3871 (2011).
3. E. R. Meinders and M. H. Lankhorst, Japanese journal of applied physics, 42(2S), 809 (2003).
4. X. Zhou, L. Wu, Z. Song, F. Rao, M. Zhu, C. Peng, D. Yao, S. Song, B. Liu, and S. Feng, Applied Physics Letters, 101(14), 142104 (2012).
5. I. Friedrich, V. Weidenhof, W. Njorge, P. Franz, and M. Wuttig, Journal of Applied Physics, 87(9), 4130 (2000).
6. L. van Pieterse, M. H. R. Lankhorst, M. van Schijndel, A. E. T. Kuiper, and J. H. J. Roosen, Journal of Applied Physics, 97(8), 083520 (2005).
7. M. S. Younm, Y. T. Kim, Y. H. Kim, and M. Y. Song, Physica Status Solidi a-Applications and Materials Science, 205(7), 1636 (2008).
8. Y. Gu, S. Song, Z. Song, S. Bai, Y. Cheng, Z. Zhang, B. Liu, and S. Feng, Applied Physics Letters, 102(10), 103110 (2013).
9. M. Zhu, L. Wu, Z. Song, F. Rao, D. Cai, C. Peng, X. Zhou, K. Ren, S. Song, and S. Feng, Applied Physics Letters, 100(12), 122101 (2012).
10. G. Wang, X. Shen, Q. Nie, R. P. Wang, L. Wu, Y. Lu, S. Dai, T. Xu, and Y. Chen, Applied Physics Letters, 103(3), 031914 (2013).
11. M. Zhu, L. Wu, F. Rao, Z. Song, X. Li, C. Peng, X. Zhou, K. Ren, D. Yao, and S. Feng, Journal of Alloys and Compounds, 509(41), 10105 (2011).
12. C. Peng, L. Wu, F. Rao, Z. Song, P. Yang, H. Song, K. Ren, X. Zhou, M. Zhu, B. Liu, and J. Chu, Applied Physics Letters, 101(12), 122108 (2012).
13. F. Wei, L. Wang, T. Kong, L. Shi, R. Huang, J. Zhang, and G. Cheng, Applied Physics Letters, 103(18), 183108 (2013).
14. Q. Wang, B. Liu, Y. Xia, Z. Zhang, X. Ji, S. Song, Z. Song, W. Xi, D. Yao, S. Lv, and S. Feng, Journal of Materials Science: Materials in Electronics, 26(6), 4163 (2015).
15. K. Kolev and M. Wutte, Applied Physics A, 52(3), 192 (1991).
16. M. J. Kang, S. Y. Choi, D. Wamwangi, F. C. M. M. Wuttig, and M. Wuttig, Journal of Applied Physics, 98(11), 041904 (2005).
17. L. Wu, M. Zhu, Z. Song, S. Lv, X. Zhou, C. Peng, F. Rao, S. Song, B. Liu, and S. Feng, Journal of Non-Crystalline Solids, 358(17), 2409 (2012).
18. L. Chen, S. Song, Z. Song, L. Li, Y. Zheng, Q. Zheng, X. Zhang, X. Zhu, and H. Shao, Applied Surface Science, 327, 603 (2015).
19. M. Wang, Y. Li, X. Shen, G. Wang, J. Li, S. Dai, S. Song, and Z. Song, CrystEngComm, 17(26), 4871 (2015).
20. D. Lencer, M. Saliga, and M. Wuttig, Advanced Materials, 23(18), 2030 (2011).
21. F. Wei, L. Wang, T. Kong, L. Shi, R. Huang, J. Zhang, and G. Cheng, Applied Physics Letters, 103(18), 183108 (2013).
22. D. Trichés, S. Souza, C. Peffo, J. De Lima, T. Grandi, and R. De Biasi, Journal of Alloys and Compounds, 585(2), 762 (2014).
23. A. Diab, M. Wakkad, E. K. Shokr, and W. S. Mohamed, Optik-International Journal for Light and Electron Optical, 126(19), 1855 (2015).
24. P. Nemeck, A. Moreac, V. Nazabal, M. Pavlista, J. Prkryl, and M. Frumar, Journal of Applied Physics, 106(10) (2009).
25. Y. Lu, T. Song, X. Shen, Z. Song, G. Wang, and S. Dai, Thin Solid Films, 589, 215 (2015).
26. A. B. Adam, Journal of King Saud University - Science, 21(2), 93 (2009).
27. L. Xueai, S. Zhimei, S. Zhiting, R. Feng, W. Liangcai, and L. Wei, Solid State Sciences, 1(1), 131 (2009).
28. E.-B. Lee, B.-K. Ju, and Y.-T. Kim, Microelectronic Engineering, 86(7-9), 1950 (2009).
29. Y. Yin, H. Sone, and S. Hosaka, Japanese journal of applied physics, 44(8R), 6208 (2005).
30. A. R. Ranatta and I. Chambouleyron, Physical Review B, 53(7), 3833 (1996).
31. M. Zhu, L. Wu, Z. Song, F. Rao, D. Cai, C. Peng, X. Zhou, K. Ren, S. Song, B. Liu, and S. Feng, Applied Physics Letters, 100(12) (2012).
32. X. Zhou, L. Wu, Z. Song, F. Rao, K. Ren, C. Peng, S. Song, B. Liu, L. Xu, and S. Feng, Applied Physics Letters, 103(7), 072114 (2013).
33. Y. Lu, S. Song, Z. Song, F. Rao, L. Wu, M. Zhu, B. Liu, and D. Yao, Applied Physics Letters, 100(19), 193114 (2012).
34. Y. Lu, S. Song, X. Shen, G. Wang, L. Wu, Z. Song, B. Song, B. Liu, and S. Dai, Journal of Alloys and Compounds, 586, 669 (2014).