Materials Letters 243 (2019) 153–156

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Stability enhancement of the metastable cubic Sb_2Te_3 in supperlattice-like films

Yongjin Chen [a], Xuepeng Wang [b], Qing Zhang [a], Qingsong Deng [a], Xianbin Li [b,*], Bin Zhang [c,*], Ze Zhang [a,d], Xiaodong Han [a,*]

[a] Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100124, China
[b] State Key Laboratory on Integrated Optoelectronics, Jilin University, Changchun 130012, China
[c] Analytical and Testing Center, Chongqing University, Chongqing 401331, China
[d] Center of Electron Microscopy and State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China

ARTICLE INFO

Article history:
Received 23 January 2019
Received in revised form 1 February 2019
Accepted 5 February 2019
Available online 13 February 2019

Keywords:
Interfaces
Multilayer structure
Metastable
Electron microscopy

ABSTRACT

We fabricated the amorphous GeTe/cubic Sb_2Te_3 supperlattice-like structure films by the radio frequency sputtering, and demonstrated the stability of *cubic* Sb_2Te_3 could be strengthened. The competition between interface energy and phase transformation energy resulted in the thermodynamical stability at the nanoscale. The presented design approach opens the doors for the stabilization of metastable phase, and sheds new insights into the role of interfaces in materials synthesis.

1. Introduction

Metastable phases are ubiquitous and commonly observed during materials synthesis, which could exhibit greater functionality and serve as an opportunity from the perspective of materials design [1]. The chalcogenide pseudo-binary GeTe-Sb_2Te_3 (GST) utilize the reversible switching between the metastable amorphous (*a*) state and metastable face centered cubic (*fcc*) crystalline states and distinguish the significantly different electrical resistance, which have been widely used as the next generation non-volatile storage memory materials [2,3]. It will boost the dynamic speed and simultaneously reduce the thermal stability when the composition approach the Sb_2Te_3 end. Moreover, GST also has a stable close-packed hexagonal (*h*) phase. A recent study reported that Sb_2Te_3 also possess a metastable *fcc* structure [4], which easily switched from *fcc*-state to *h*-state due to its extreme proneness of phase transition with vacancy ordering evolution as it has a high content of intrinsic vacancies (1/3) on the cationic sublattice. As a classic theme in diverse regimes of material-based science and technology, it is a daunting task to prevent thermodynamic transformations to lower energy states from higher energy states of metastable materials [1,5–7]. Doping has always been a useful method to stabilize the metastable phase. The thermal stability of amorphous state and preserved high-speed crystallization in Sb_2Te_3 system has been improved by Sc doping [7]. In addition, multilayered heterostructure [1] and nanoscale stablizaition [5,6] were another routes for stabling the metastable phases. The barrier/capping layers, especially in nanoscale, could introduce new interface and confine the grain size. To the best of our knowledge, information of the properties and microstructures of *fcc*-Sb_2Te_3 in the superlattice-like systems are still lacking, especially the effect of the interface.

In this work, we designed a new alternately separated *a*-GeTe and *fcc*-Sb_2Te_3 layered superlattice-like (SL) structures, which improved the thermal stability of metastable Sb_2Te_3. It should be noted that the SL structure is not only different from the interfacial phase-change memory (iPCM) [8], but also from the superlattice-like structures, which composed of *a*-GeTe and *h*-Sb_2Te_3 [2,9]. We carried out various electron microscopy techniques to investigate both the *fcc*-Sb_2Te_3 thermal stability and the interface microstructure.

2. Materials and methods

GeTe, Sb_2Te_3 and superlattice-like films were deposited using the radio frequency sputtering method. For transmission electron

* Corresponding authors.
E-mail addresses: lixianbin@jlu.edu.cn (X. Li), welon5337@126.com (B. Zhang), xdhan@bjut.edu.cn (X. Han).

https://doi.org/10.1016/j.matlet.2019.02.042
0167-577X/

microscope (TEM) investigations the cross-section samples were made using a focused ion beam (FIB) instrument and Ar low-energy ion beam milling. Pt layers were used to protect the surface. To prevent degradation in ambient air, we started TEM investigations immediately after preparing the samples. A Cs-corrected FEI Titan G2 80-300 microscope equipped with a super detector for energy dispersive X-ray spectrometry (EDX) was used for the TEM investigations.

3. Results and discussion

Sb_2Te_3 possesses three states, including the metastable *a*-state, metastable *fcc*-Sb_2Te_3 and the stable *h*-Sb_2Te_3 phase shown in Fig. 1a. The as-deposited Sb_2Te_3 films had a higher sheet resistance at room temperature (Fig. 1b), and maintained the *fcc*-phase below ~120 °C and transform to the *h*-phase above ~130 °C with a sudden drop of resistance. Furthermore, the TEM images of Sb_2Te_3 film at different temperatures during the *in-situ* heating process were shown in Fig. 1c. The *fcc*-state presented uniformly distributed small crystal grains indicate a nucleation-dominant behavior, while a growth-dominant case with quite large crystals appeared in *h*-state. The crystallization temperature of *a*-GeTe is above 200 °C as shown in Fig. 1b, and compatible with Sb_2Te_3 sputtering processes. The *a*-GeTe was used as barrier layers and created the layered superlattice-like structures with extremely thin alternating layers of *a*-GeTe and *fcc*-Sb_2Te_3. According to the previous study [10], the interphase boundary energy would act as a barrier upon *fcc*-to-*h* phase transition while the surface energy and Gibbs free energy represent the positive momentums. By decreasing the film thickness, the interphase boundary energy will increase due to the pretty small average *fcc*-grain size, however the surface energy will increase at the same time. The nucleation and growth start at the atomic and nanoscale, the recently thermodynamic data have led to the general conclusion that metastable polymorphs as micrometer-sized or larger crystals can often be thermodynamically stabilized at the nanoscale resulting from the competition between surface energy and the energetics of phase transformation [11]. It trigger there might be a reversal of relative phase stability in nanoscale superlatttice-like films, which present new interface and confined nanoscale structure.

We further made a thorough TEM investigations of the SL structure. To elucidate the interfaces, TEM bright-field (BF) and aberration-corrected scanning transmission electron microscopy (STEM) high-angle annular dark field (HAADF) with x-ray energy disperse spectroscopy (EDS) mappings techniques were performed to get spatially resolved information about the morphology and structure of the interfaces. The TEM image of the cross-section sample of as-deposited SL film was presented in Fig. 2a, showing several nanometers thick and spatially sandwich separated layer structure. The high magnification HAADF image with element mappings in Fig. 2b produces contrast interpretable by atomic

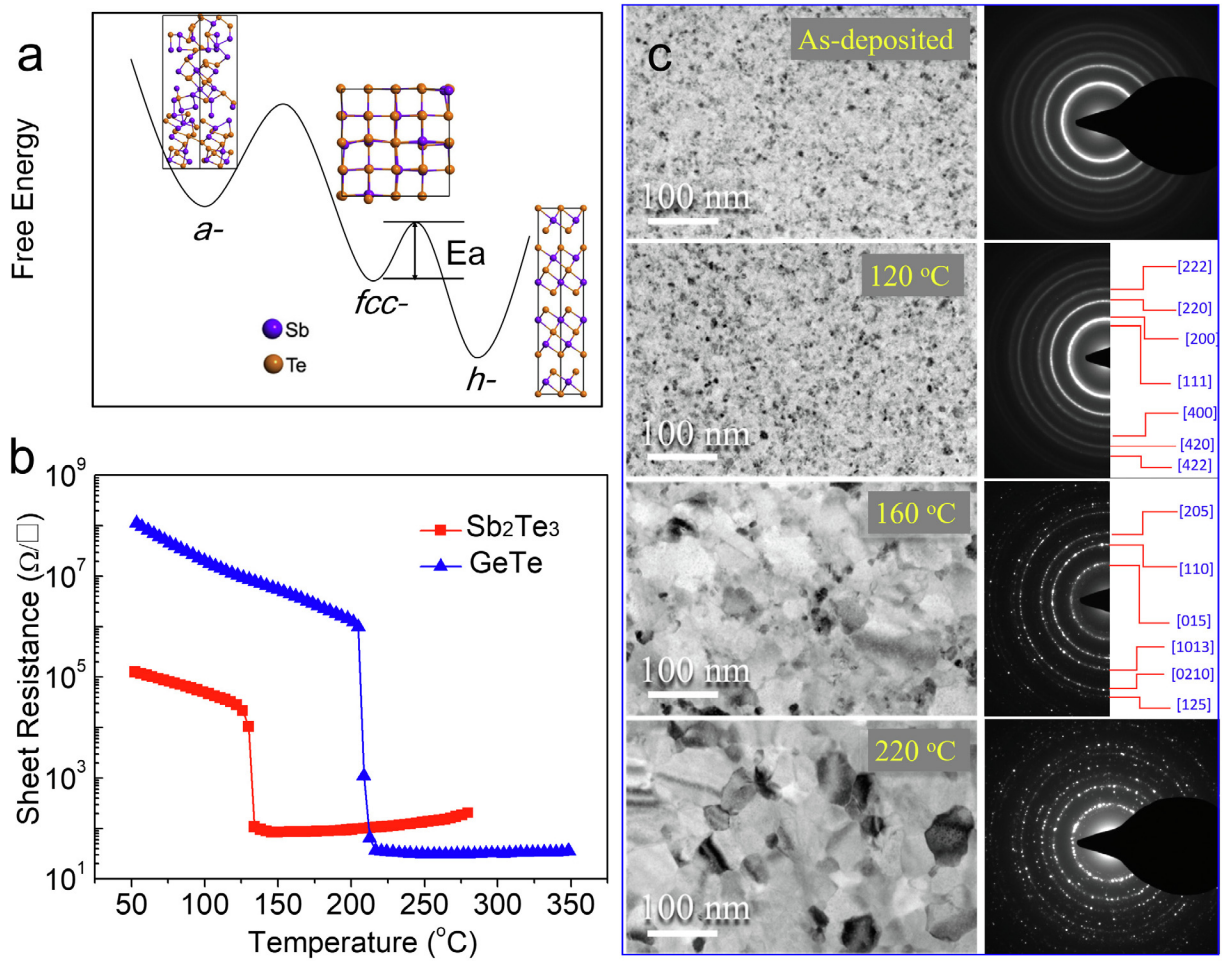

Fig. 1. The structure and thermal stability of Sb_2Te_3. (a) The models and free energy schematic of Sb_2Te_3 amorphous (*a*-), cubic (*fcc*-) and hexagonal (*h*-) states. (b) The sheet resistance as a function of annealing temperature. (c) The *in situ* TEM-BF images and electron diffraction patterns of the Sb_2Te_3 film at different temperatures during the *in situ* heating process.

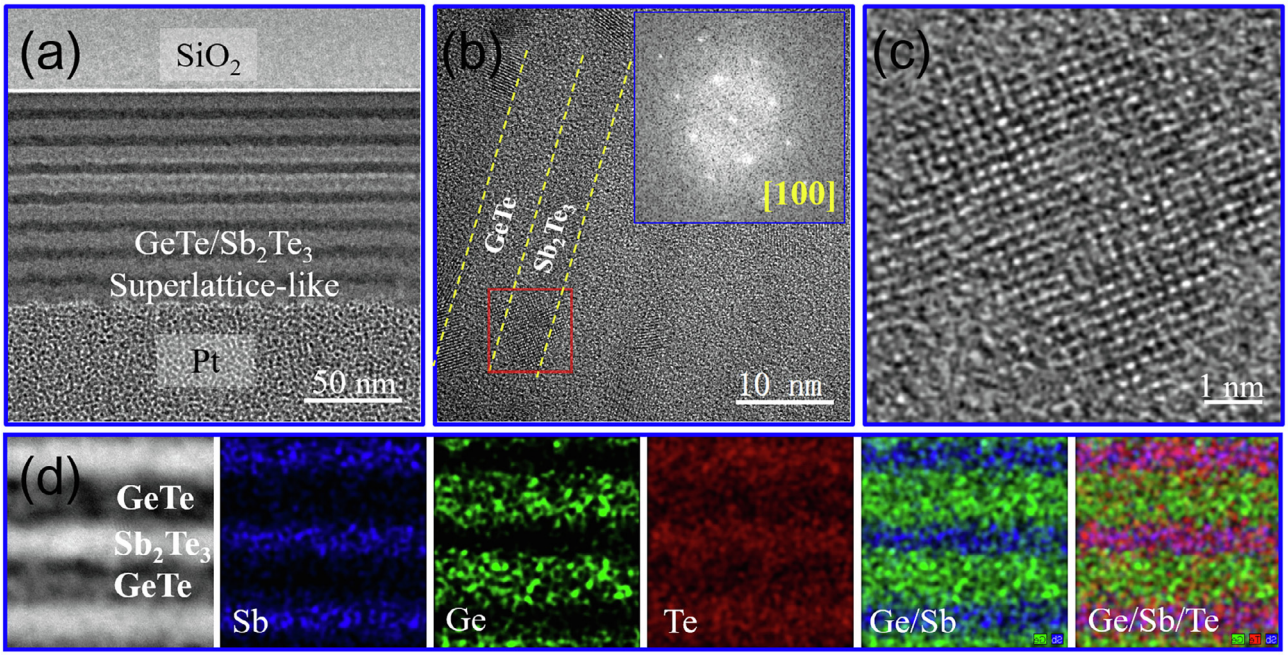

Fig. 2. The cross-section sample of the as-deposited GeTe/Sb_2Te_3 (7 nm/6 nm) superlattice-like film characterized by TEM and EDS mappings. (a) The low magnification TEM observation. (b) The HAADF-STEM image with EDS mappings. (c) The high magnification image of *fcc*-Sb_2Te_3 with FFT of [1 0 0] -orientated grain and the enlarged view in (d).

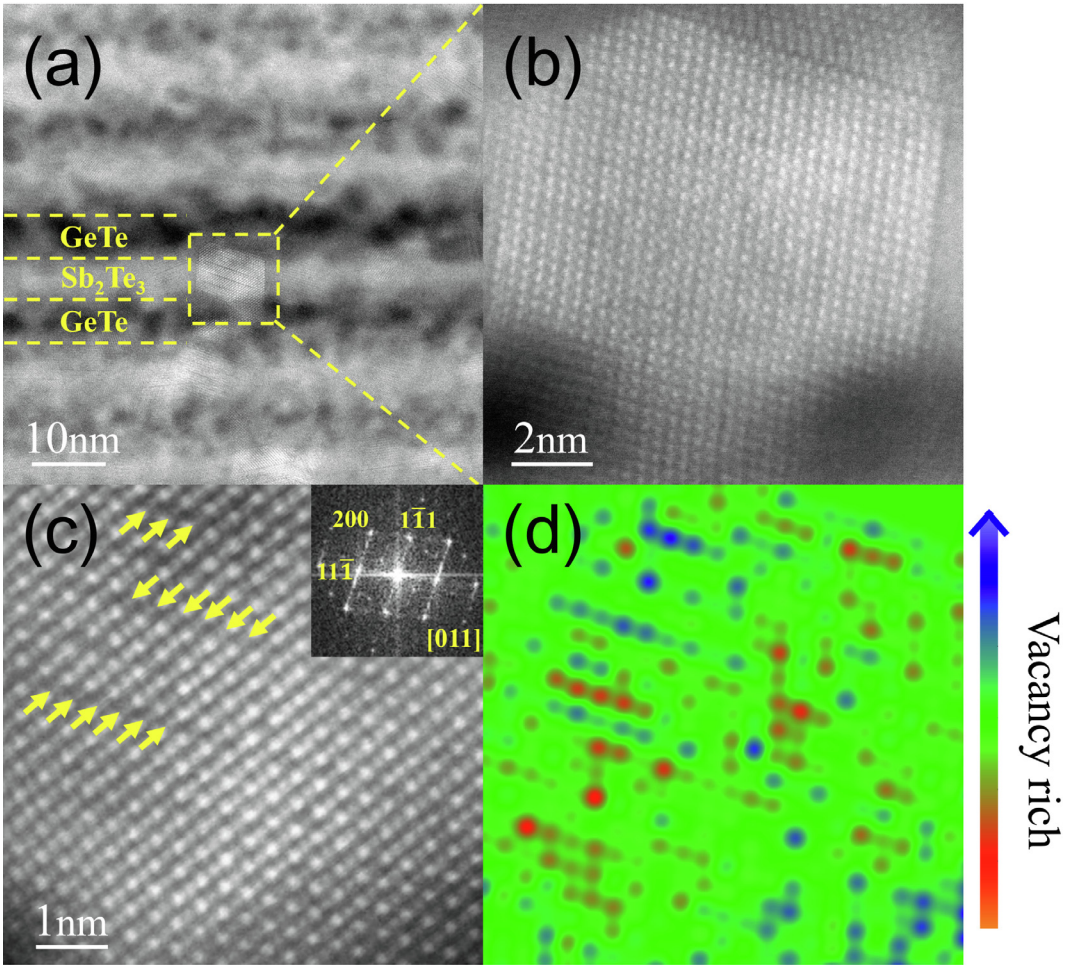

Fig. 3. The thermal stability of GeTe/Sb_2Te_3 superlattice-like film. (a) The Low-magnification STEM-HAADF image after post-annealed at 180 °C for 1 min. (b) The enlarged image of Sb_2Te_3 grain corresponds to the dashed rectangle region in (a). (c) Atomic-scale HAADF image of Sb_2Te_3 structure with the corresponding FFT inset. (d) The corresponding normalized intensity mapping with color bar for Sb/Vacancy sites in (c), reflecting the vacancy fluctuation.

number (also called Z contrast), the interfaces of each component were clearly visible. The high resolution TEM (HRTEM) in Fig. 3c revealed that GeTe was *a*-state, and the fast Fourier Transformation (FFT) and the enlarged view of HRTEM in Fig. 3d show that Sb_2Te_3 kept *fcc*-state.

Furthermore, the cross-section sample of as-deposited SL film was heated *in situ* at 180 °C for 1 min, and vacancy ordered gaps were observed in the Sb_2Te_3 layer by the low magnification HAADF in Fig. 3a and b. The *fcc*-Sb_2Te_3 with clear vacancy-rich layers along the [0 1 1] direction was further identified by the atomic scale HAADF in Fig. 3c. The corresponding normalized intensity mapping, which has been successfully used in the study of vacancy evolution [12,13], reflected the fluctuation distribution of vacancies. The vacancies become locally ordered upon annealing, and decreased the driving force of *fcc-to-h* phase transformation due to the reduced free energy. The SL structure would make the interface boundary energy to be the transforming barriers of *fcc*-Sb_2Te_3, thus the *fcc-to-h* transition can be postponed to higher temperature.

It is worth pointing out that the atoms diffusion and interfacial reaction between GeTe and Sb_2Te_3 films is inevitable. The diffusion-controlled penetration is controlled by the grain boundary wetting phase transition and takes place in a wide variety of materials like Al-based alloys [14], cemented carbides [15] and NdFeB hard magnets [16], which lead to the enhancement of configurational entropy and consequently enhanced the stabilization of the high symmetry cubic phase of Sb_2Te_3 at elevated temperatures. This is similar to the phenomenon which extra elements stabilizes high symmetry phases owing to the enhancement of entropy in high entropy alloys.

4. Conclusion

In summary, the presented supperlattice-like interface design approach sheds new insights into the stabilization of the metastable phase, and opens the doors for precisely identifying the phase-transition intermediates and understanding the transition process. The annealing results show the thermal stability of *fcc*-Sb_2Te_3 is strengthened, the interfaces play an important role for the performance of *fcc*-Sb_2Te_3. This build a deeper understanding of how interfaces influence structure during materials synthesis. Future studies will focus on further reducing the film thickness, confining Sb_2Te_3 in all three dimensions and designing new confinement materials.

Declaration of interest

None.

Acknowledgments

X. D. Han thanks the support from National Key R&D Program of China (2017YFB0305501) and National Natural Science Foundation of China (NSFC) (Grants No. 11327901, No. 51471008). X. B. Li acknowledges the support from National Natural Science Foundation of China (NSFC) (Grants No. 11874171, No. 61775077). B. Zhang thanks the Fundamental Research Funds for the Central Universities of China (Grant No. 0903005203553).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.02.042.

References

[1] S. Sanna, V. Esposito, J.W. Andreasen, J. Hjelm, W. Zhang, T. Kasama, et al., Enhancement of the chemical stability in confined delta-Bi2O3, Nature Mater. 14 (2015) 500–504.
[2] T.C. Chong, L.P. Shi, X.Q. Wei, R. Zhao, H.K. Lee, P. Yang, et al., Crystalline amorphous semiconductor superlattice, Phys. Rev. Lett. 100 (2008) 136101.
[3] H.F. Hamann, M. O'Boyle, Y.C. Martin, M. Rooks, H.K. Wickramasinghe, Ultra-high-density phase-change storage and memory, Nature Mater. 5 (2006) 383–387.
[4] Y. Zheng, M. Xia, Y. Cheng, et al., Direct observation of metastable face-centered cubic Sb2Te3 crystal, Nano Res. 9 (2016) 3453–3462.
[5] S.S. Satyajit Shukla, Rashmi Vij, Sri Bandyopadhyay, Zia Rahman, Effect of nanocrystallite morphology on the metastable tetragonal phase stabilization in zirconia, Nano Lett. 2 (2002) 989–993.
[6] R.B. Soriano, I.U. Arachchige, C.D. Malliakas, J. Wu, M.G. Kanatzidis, Nanoscale stabilization of new phases in the PbTe-Sb2Te3 system: Pb(m)Sb(2n)Te(m+3n) nanocrystals, J. Am. Chem. Soc. 135 (2013) 768–774.
[7] F. Rao, K. Ding, Y. Zhou, Y. Zheng, M. Xia, S. Lv, et al., Reducing the stochasticity of crystal nucleation to enable subnanosecond memory writing, Science 358 (2017) 1423–1427.
[8] R.E. Simpson, P. Fons, A.V. Kolobov, T. Fukaya, M. Krbal, T. Yagi, et al., Interfacial phase-change memory, Nature Nanotechnol. 6 (2011) 501–505.
[9] T.C. Chong, L.P. Shi, R. Zhao, P.K. Tan, J.M. Li, H.K. Lee, et al., Phase change random access memory cell with superlattice-like structure, Appl. Phys. Lett. 88 (2006) 122114.
[10] Y. Zheng, Y. Cheng, R. Huang, R. Qi, F. Rao, K. Ding, et al., Surface energy driven cubic-to-hexagonal grain growth of Ge2Sb2Te5 thin film, Sci. Rep. 7 (2017) 5915.
[11] A. Navrotsky, L. Mazeina, J. Majzlan, Size-driven structural and thermodynamic complexity in iron oxides, Science 319 (2008) 1635–1638.
[12] B. Zhang, W. Zhang, Z.J. Shen, Y.J. Chen, J.X. Li, S.B. Zhang, et al., Element-resolved atomic structure imaging of rocksalt Ge2Sb2Te5 phase-change material, Appl. Phys. Lett. 108 (2016) 191902.
[13] B. Zhang, X.P. Wang, Z.J. Shen, X.B. Li, C.S. Wang, Y.J. Chen, et al., Vacancy structures and melting behavior in rock-salt GeSbTe, Sci. Rep. 6 (2016) 25453.
[14] E.V. Ageev, R.A. Latypov, E.V. Ageeva, Investigation into the properties of electroerosive powders and hard alloy fabricated from them by isostatic pressing and sintering, Russ. J. Non-Ferrous Metals 56 (2015) 52–62.
[15] B.B. Straumal, I. Konyashin, B. Ries, A.B. Straumal, A.A. Mazilkin, K.I. Kolesnikova, et al., Pseudopartial wetting of WC/WC grain boundaries in cemented carbides, Mater. Lett. 147 (2015) 105–108.
[16] B.B. Straumal, A.A. Mazilkin, S.G. Protasova, G. Schütz, A.B. Straumal, B. Baretzky, Observation of pseudopartial grain boundary wetting in the NdFeB-based alloy, J. Mater. Eng. Perform. 25 (2016) 3303–3309.