Phase stability and electronic structure of $Si_2Sb_2Te_5$ phase-change material

Baisheng Sa [a], Nahihua Miao [a], Jian Zhou [a], Zhitang Song [b], Zhimei Sun [a,*], Rajeev Ahuja [c]

[a] Department of Materials Science and Engineering, College of Materials, Xiamen University, 361005 Xiamen, People's Republic of China
[b] State Key Laboratory of Functional Materials for Informatics, Laboratory of Nanotechnology, Shanghai Institute of Micro-System and Information Technology, Chinese Academy of Sciences, 200050 Shanghai, People's Republic of China
[c] Department of Physics and Materials Science, Condensed Matter Theory Group, Uppsala University, Box 530, 75121 Uppsala, Sweden

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ABSTRACT

On the basis of an *ab initio* computational study, the present work provide a full understanding on the atomic arrangements, phase stability as well as electronic structure of $Si_2Sb_2Te_5$, a newly synthesized phase-change material. The results show that $Si_2Sb_2Te_5$ tends to decompose into $Si_1Sb_2Te_4$ or $Si_1Sb_4Te_7$ or Sb_2Te_3, therefore, a nano-composite containing $Si_1Sb_2Te_4$, $Si_1Sb_4Te_7$ and Sb_2Te_3 may be self-generated from $Si_2Sb_2Te_5$. Hence $Si_2Sb_2Te_5$ based nano-composite is the real structure when $Si_2Sb_2Te_5$ is used in electronic memory applications. The present results agree well with the recent experimental work.

1. Introduction

Phase change (PC) materials exhibited gigantic capability of information storage in optical disc devices, such as DVD-RAM and Blue-ray Disc. Additionally, non-volatile phase change random access memory (PCRAM) using PC materials as record media are widely recognized as the next-generation data storage products [1]. In the past decade, Ge–Sb–Te (GST) alloys as leading candidates for PC materials have been extensively studied [2–6]. However, for practical applications of GST in PCRAM, it is still necessary to reduce its power consumption and increase its phase change speed. Therefore, searching new PC materials or tuning the properties of GST to meet the above criteria is hot topic in phase change community. Recently, Si–Sb–Te (SST) ternary alloys were reported as new PC materials, which show low power consumption, rapid phase transition and good data retention [7–12]. Among these alloys, $Si_2Sb_2Te_5$ possesses outstanding electrical properties when used in electronic memory applications [7–9]. However, in early work, self-extrusion of Te nanowire was found in $Si_2Sb_2Te_5$ films at room temperature [10]. And complex Sb_2Te_3 rich SST nanostructures were also reported during the annealing process [11]. According to these results, $Si_2Sb_2Te_5$ might exhibit low structure stability and tends to separate to complex nano-compounds. Very recently, nano-composite structure was found in O-doped $Si_2Sb_2Te_5$ [12].

However, a clear understanding of the basic properties of $Si_2Sb_2Te_5$ has not yet been achieved. Neither the crystal structure nor the electronic structure is clear. Moreover, the analysis of the complex nanostructured SST which was found in $Si_2Sb_2Te_5$ during

annealing has not been discussed, and the drive force for its phase separation is still unclear. The purpose of the present work is to study the phase stability and electronic structure of $Si_2Sb_2Te_5$ and to analyze its phase separation behavior. Based on the present results, we proposed that $Si_2Sb_2Te_5$ is a metastable compound and complex nano-composite could be self-generated from it.

2. Computational details

Our *ab initio* total energy and electronic structure calculation methods are based on density functional theory (DFT) using the VASP [13] code in conjunction with projector augmented wave (PAW) potentials within the generalized-gradient approximations of Perdew–Burke–Ernzerhof (GGA–PBE) [14]. The valence electron configurations for Si, Sb and Te were $3s^23p^2$, $5s^25p^3$ and $5s^25p^4$, respectively. For all the calculations we used tetrahedron method with Blöchl corrections [15], automatically generated $7 \times 7 \times 5$ k-points with Gamma symmetry. The relaxation convergence for both ions and electrons were 1×10^{-5} and 1×10^{-6} eV, respectively. All structures were represented in conventional hexagonal supercells.

3. Results and discussion

We started from hexagonal $Si_2Sb_2Te_5$ which was found by Zhang et al. [11]. Since no detailed structure information has been reported, we suppose that hexagonal $Si_2Sb_2Te_5$ crystallizes in the similar structure as stable $Ge_2Sb_2Te_5$ [3] as Si and Ge are in the same column in the periodic table. Similar to $Ge_2Sb_2Te_5$, $Si_2Sb_2Te_5$ consists of 9 layers in one unit cell with a space group of $P\bar{3}m1$.

* Corresponding author. Tel.: +86 592 2182617; fax: +86 592 2186664.
E-mail addresses: zhmsun2@yahoo.com, zmsun@xmu.edu.cn (Z. Sun).

Table 1

The calculated cohesive energy and equilibrium lattice parameters of different compounds.

Structure	Cohesive energy (eV/atom)	Atom layers per cell	Lattice parameters	
			a (Å)	c (Å)
$Si_2Sb_2Te_5$	−3.8372	9	4.221	17.481
$Si_1Sb_2Te_4$	−3.7752	21	4.256	42.221
$Si_1Sb_4Te_7$	−3.7270	12	4.289	24.562
Si	−5.4200	12	3.868	18.932
Te	−3.1406	9	4.496	17.894
Sb2Te3	−3.6614	15	4.335	31.217

Table 2

Atomic positions for hexagonal $Si_2Sb_2Te_5$.

Atom	Site	x	y	z
Te1	1a	0.0000	0.0000	0.0000
Si	2d	0.6667	0.3333	0.0947
Te2	2d	0.3333	0.6667	0.1858
Sb	2c	0.0000	0.0000	0.3057
Te3	2d	0.6667	0.3333	0.4059

Fig. 1. Partial density of states for hexagonal $Si_2Sb_2Te_5$ with $E_F=0$. Solid black and dashed red lines designate s and p states, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The calculated lattice parameters and cohesive energy of $Ge_2Sb_2Te_5$ are presented in Table 1 and the atomic positions are given in Table 2. Since there is no structure information available, we cannot make a direct comparison. While compared with $Ge_2Sb_2Te_5$ [3], the lattice parameters of $Si_2Sb_2Te_5$ are very close. This is understandable since Si is right above Ge in the periodic table.

We have calculated the elastic constants to reveal the mechanical stability of $Si_2Sb_2Te_5$. It is known that, for hexagonal crystals there are five independent elastic constants, referred to as C_{11}, C_{12}, C_{13}, C_{33} and C_{44}. The requirement of mechanical stability for hexagonal crystals leads to the following restrictions on the elastic constants:

$$C_{11} > 0, \quad C_{11} > |C_{12}|, \quad C_{44} > 0, \quad (C_{11}+C_{12}) \times C_{33}-2C_{13}^2 > 0 \quad (1)$$

The calculated values of C_{11}, C_{12}, C_{13}, C_{33} and C_{44} for hexagonal $Si_2Sb_2Te_5$ are 86.0, 16.0, 31.7, 74.4 and 50.5 GPa, respectively. The whole sets of C_{ij} obey all the conditions of Eq. (1) well. The calculated shear anisotropic factor (A) of $Si_2Sb_2Te_5$ is 2.08 using the following equation:

$$A = \frac{4C_{44}}{C_{11}+C_{33}-2C_{13}} \quad (2)$$

For an isotropic crystal, A is equal to 1, while any value smaller or larger than 1 indicates anisotropy [16]. The present result shows a very high degree of anisotropic character of $Si_2Sb_2Te_5$.

In order to further understand the properties of $Si_2Sb_2Te_5$, we study partial density of states and the electronic band structure, as given in Figs. 1 and 2, respectively. Note that $Si_2Sb_2Te_5$ is a narrow band gap p-type semiconductor with Fermi level (E_F) located right above the valence band which is similar to $Ge_2Sb_2Te_5$. This is in agreement with former studies [7,8]. As Fig. 1 illustrated, the lower lying energy states are dominated by the s states, while the valence states are predominated by the p states showing a p–p hybridized covalent bonding character in $Si_2Sb_2Te_5$. In addition, in the energy range from −2 eV to the Fermi level, it is dominated by both p and s states of Si and Sb atoms which is similar to that of $Ge_2Sb_2Te_5$ [6]. Fig. 2 exhibits the degeneracy of energy level in the same energy range.
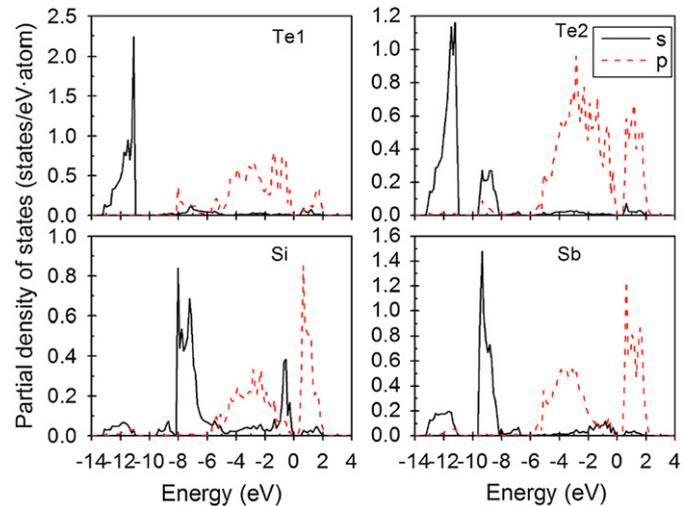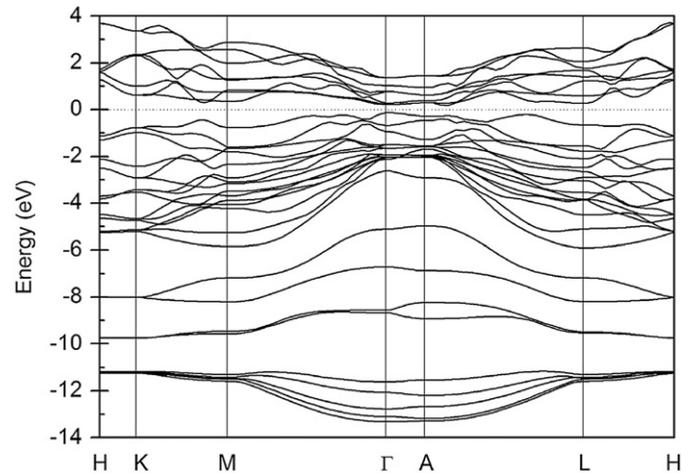

Fig. 2. Electronic band structure for hexagonal $Si_2Sb_2Te_5$ with $E_F=0$.

To explore the driving force for the separation of $Si_2Sb_2Te_5$, we calculated the formation energy by the following equation:

$$E_{formation} = \frac{\sum E_{cohesive,products} - \sum E_{cohesive,reactants}}{N_{atoms}} \quad (3)$$

The separation of $Si_2Sb_2Te_5$ mentioned by Cheng et al. [10] is

$$Si_2Sb_2Te_5 \rightarrow 2Si + 2Te + Sb_2Te_3 \quad (4)$$

The calculated cohesive energy of $Si_2Sb_2Te_5$, Si, Te and Sb_2Te_3 are shown in Table 1. According to Eq. (3), the formation energy of reaction (4) is −24.8 meV/atom. Therefore, $Si_2Sb_2Te_5$ is not energetically stable and will separate into Sb_2Te_3, Si and Te in the ground state. However, a more complex SST nanostructure containing more phases than Sb_2Te_3, Si and Te was found during annealing by Zhang et al. [11]. Hence we suggested that $Si_2Sb_2Te_5$ may be a metastable material, and it could separate to more phase other than Sb_2Te_3, Si and Te. Herein we proposed two new Si–Sb–Te alloys: $Si_1Sb_2Te_4$ and $Si_1Sb_4Te_7$ likewise $Ge_1Sb_2Te_4$ and $Ge_1Sb_4Te_7$ in GST family which has been widely studied. We also assume $Si_1Sb_2Te_4$ and $Si_1Sb_4Te_7$ crystalline is the same structure as that of $Ge_1Sb_2Te_4$ and $Ge_1Sb_4Te_7$, respectively. The calculated cohesive energy and equilibrium lattice parameters for $Si_1Sb_2Te_4$

and $Si_1Sb_4Te_7$ are also listed in Table 1. The separations from $Si_2Sb_2Te_5$ to them are as follows:

$$Si_2Sb_2Te_5 \rightarrow Si + Te + Si_1Sb_2Te_4 \tag{5}$$

$$2Si_2Sb_2Te_5 \rightarrow 3Si + 3Te + Si_1Sb_4Te_7 \tag{6}$$

The formation energies of reactions (5) and (6) we obtained using Eq. (3) are -13.0 and -18.4 meV/atom. This suggests that $Si_2Sb_2Te_5$ will also separate to $Si_1Sb_2Te_4$ and $Si_1Sb_4Te_7$, and the energy required for these two processes is less than that of $Si_2Sb_2Te_5$. This confirms our above assumption.

It is obvious now that the energy instability of $Si_2Sb_2Te_5$ drives its phase separation. Although Sb_2Te_3 is the most stable separation product, $Si_1Sb_2Te_4$ and $Si_1Sb_4Te_7$ exhibit similar crystal parameters to $Si_2Sb_2Te_5$ which would be generated easily. Therefore, we suggest that $Si_1Sb_2Te_4$, $Si_1Sb_4Te_7$ and Sb_2Te_3 coexist in the complex Sb_2Te_3 rich SST nanostructured materials obtained by Zhang et al. [11]. They could be self-generated mixing with minor separation products Si and Te in nano-dimension. This nano-composite might be the real structure when $Si_2Sb_2Te_5$ is used in electronic memory applications. This kind of nano-composite structure could be self-generated from all SST materials and play an important role in the phase change processes.

4. Conclusions

To conclude, we studied the stability and phase separation of $Si_2Sb_2Te_5$ using *ab initio* methods. Based on our calculations and analysis, we obtained the basis information for $Si_2Sb_2Te_5$. We found that the energy instability is the driving force for the phase separation of $Si_2Sb_2Te_5$. A complex nano-composite consisting of $Si_1Sb_2Te_4$, $Si_1Sb_4Te_7$, Sb_2Te_3, Si and Te can be self-generated. We expect that our study provide a fundamental understanding on these SST materials.

References

[1] M. Wuttig, N. Yamada, Nat. Mater. 6 (2007) 824.
[2] S.-H. Lee, Y. Jung, R. Agarwal, Nat. Nano 2 (2007) 626.
[3] Z. Sun, J. Zhou, R. Ahuja, Phys. Rev. Lett. 96 (2006) 55507.
[4] Z. Sun, J. Zhou, R. Ahuja, Phys. Rev. Lett. 98 (2007) 55505.
[5] Z. Sun, J. Zhou, A. Blomqvist, B. Johansson, R. Ahuja, Phys. Rev. Lett. 102 (2009) 075504.
[6] Z. Sun, S. Kyrsta, D. Music, R. Ahuja, J.M. Schneider, Solid State Commun. 143 (2007) 240.
[7] T. Zhang, Z. Song, B. Liu, S. Feng, B. Chen, Solid-State Electron. 51 (2007) 950.
[8] T. Zhang, Z. Song, F. Rao, G. Feng, B. Liu, S. Feng, B. Chen, Jpn. J. Appl. Phys. 46 (Part 2) (2007) 247.
[9] T. Zhang, Z. Song, M. Sun, B. Liu, S. Feng, B. Chen, Appl. Phys. A 90 (2008) 451.
[10] Y. Cheng, X.D. Han, X.Q. Liu, K. Zheng, Z. Zhang, T. Zhang, Z.T. Song, B. Liu, S.L. Feng, Appl. Phys. Lett. 93 (2008) 183113.
[11] T. Zhang, Y. Cheng, Z. Song, B. Liu, S. Feng, X. Han, Z. Zhang, B. Chen, Scr. Mater. 58 (2008) 977.
[12] T. Zhang, Z. Song, B. Liu, F. Wang, S. Feng, J. Nanosci. Nanotechnol. 9 (2009) 1090.
[13] J. Hafner, J. Comput. Chem. 29 (2008) 2044.
[14] J.P. Perdew, K. Burke, Y. Wang, Phys. Rev. B 54 (1996) 16533.
[15] P.E. Blöchl, Phys. Rev. B 50 (1994) 17953.
[16] Z. Sun, S. Li, R. Ahuja, J.M. Schneider, Solid State Commun. 129 (2004) 589.