Ab initio study on hexagonal Ge2Sb2Te5- A phase-change material for nonvolatile memories

4 authors:

Zhimei Sun
Beihang University (BUAA)
157 PUBLICATIONS 3,648 CITATIONS

SEE PROFILE

Pan Yuanchun
Xiamen University
5 PUBLICATIONS 35 CITATIONS

SEE PROFILE

Baisheng Sa
Fuzhou University
40 PUBLICATIONS 282 CITATIONS

SEE PROFILE

Jian Zhou
Beihang University (BUAA)
71 PUBLICATIONS 850 CITATIONS

SEE PROFILE

Ab initio study on hexagonal Ge$_2$Sb$_2$Te$_5$-a phase-change material for nonvolatile memories

Zhimei Sun[a], Yuanchun Pan, Baisheng Sa and Jian Zhou

Department of Materials Science and Engineering, College of Materials,
Xiamen University, Xiamen 361005, China

[a] zmsun@xmu.edu.cn; zhmsun2@yahoo.com; Tel: +86-592-2182617; Fax: +86-592-2186664

Abstract. On the basis of *ab initio* total energy calculations, we have performed an extensive study on the stacking sequence and random occupation of Ge and Sb to make the same layer in stable hexagonal Ge$_2$Sb$_2$Te$_5$ (*h*-GST), an excellent candidate for phase change random memory applications. The results demonstrate that the atomic arrangements have great effects on lattice parameter c and electronic properties of *h*-GST. *h*-GST changes from semiconductor to metallic behavior as varying the atomic sequence.

Introduction

Pseudo-binary mGeTe-nSb$_2$Te$_3$ alloys are important phase-change materials used as record media for optical data storage, and are currently investigated for applications in phase-change random access memory which is considered as the most promising next-generation memory device [1]. Among the GeSbTe alloys, Ge$_2$Sb$_2$Te$_5$ (GST) exhibits the best performance in terms of speed and stability in the data storage process. Even though quite some experimental [2-4] and theoretical [5-9] studies have been conducted, the atomic arrangement in the high temperature stable trigonal or hexagonal (*h*)-GST phase is still in discrepancy. The stable high temperature GST crystallizes in a hexagonal phase with a space group of $P\bar{3}m1$. Experimentally, three stackings have been proposed for *h*-GST [2-4]. Base on transmission electron microscope examinations, Petrov *et al*. [2] and Kooi and De Hosson [3] proposed the stackings of Te-Sb-Te-Ge-Te-Te-Ge-Te-Sb- (Sb$_2$Ge$_2$Te$_5$) and Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge (Ge$_2$Sb$_2$Te$_5$), respectively, where Ge and Sb exchanges their positions. On the basis of the X-ray diffraction analysis, Matsunaga *et al*. proposed a model of random occupation of Sb and Ge at the same layer [4]. It is obvious that there exists great discrepancy in the experimental results. Therefore, researchers resort to *ab initio* calculations to understand the structure. In an early work by means of *ab initio* calculations, we have showed that the *Kooi-De Hosson* model is more stable than the *Petrov* model [5]. However, we should note the small difference in the calculated cohesive energies between the two stackings [5]. Recently, other *ab initio* calculations support either *Kooi-De Hosson* stacking or both *Kooi-De Hosson* and *Matsunaga* stackings [6-8]. However, it has also been shown that the *Petrov* model fits the measurements better in terms of the calculated absorption coefficients [6], while the *Matsunaga* model agrees better with experiments in terms of the calculated Raman spectrum [7]. Furthermore, all of the available work on amorphous structure of GST is obtained by directly melt-quenching the metastable cubic GST. The atomic arrangement of GST melt-quenched directly from stable hexagonal phase is unkown.

In this work, on the basis of *ab initio* and *ab initio* molecular dynamics simulations, we have shed light on the above issues.

Calculation Details

The calculations were performed using a plane-wave pseudo-potential method within the generalized gradient approximation (GGA) adopting the Perdew-Burke-Ernzerhof (PBE) exchange correlation potentials which are implemented in the CASTEP code [10,11]. The GGA-PBE potentials have been

investigated to properly describe the weak bonding between the Te and Te layers in $Ge_3Sb_2Te_6$ [12]. An energy cut-off of 500 eV and $11\times11\times5$ k-points mesh generated by Monkhorst-Pack method were used [13]. The interactions of electrons with ion cores were represented by the norm-conserving pseudo-potentials [14]. For comparison, some calculations were performed using the projector augmented wave (PAW) methods as implemented in the VASP code [15]. The crystal structures were fully optimized in terms of volume and internal atomic coordinates. The convergence criteria for the optimizations were the difference in total energy within 1×10^{-6} eV atom^{-1} and the stress at each volume below 0.1 kbar. The random occupation of Ge, Sb and Te atoms was achieved by the method of virtual crystal approximation (VCA) [16].

Results and Discussion

The atomic arrangements of stable GST and the effects on electronic structures. The calculated results for the three above mentioned stackings in Table 1, wherein two stoichiometries have been considered for the *Matsunaga* model, i.e., $(Ge_{0.56}Sb_{0.44})_2(Ge_{0.44}Sb_{0.56})_2Te_5$ (phase C) and $(Ge_{0.5}Sb_{0.5})_2(Ge_{0.5}Sb_{0.5})_2Te_5$ (phase D). Note that the *Kooi-De Hosson* stacking (phase A) is energetically most stable, which agrees with previous works [5-7]. However, the energy difference between A and B (the *Petrov* stacking) is negligible, therefore, phase B may also be candidate for *h*-GST. The calculated lattice parameters for the four phases are in fairly good agreement with previous works [3-6]. We have noted the scattering in the reported calculated lattice parameters for *h*-GST, which is due to the used different methods or potentials. For example, for phase A, with PAW GGA-PBE potentials as implemented in the VASP code, we obtained lattice parameters of a = 4.296 Å and c = 17.550 Å. While by PAW GGA-91 potentials, the lattice parameters were a = 4.295 Å and c = 16.977 Å [5]. Nevertheless, the structure features are generally preserved once similar methods are used. The splitting character of the Ge-Te bond lengths agrees with previous work, i.e., almost identical Ge-Te bond lengths in phase A and distinguished longer and shorter Ge-Te bonds in phase B [4-6].

Table 1 The calculated relative energies ΔE_c with respect to phase A (in meV/atom), lattice parameters (Å) and bond lengths (Å) for *h*-GST. A: Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge-; B: Te-Sb-Te-Ge-Te-Te-Ge-Te-Sb-; C: $(Ge_{0.56}Sb_{0.44})_2(Ge_{0.44}Sb_{0.56})_2Te_5$; D: $(Ge_{0.5}Sb_{0.5})_2(Ge_{0.5}Sb_{0.5})_2Te_5$;

	Phases			
	A	B	C	D
ΔE_c	0	6	644	653
a	4.157 (4.25)[a]	4.120	4.160 (4.225)[b]	4.157
c	17.281 (18.27)[a]	18.265	17.676 (17.239)[b]	17.755
V_0	28.73	29.83	29.43	29.53
	Bond length (Å)			
Ge-Te	2.89, 2.92	2.74, 3.10	2.85~3.14 (2.90 ~ 3.20)[b]	2.84~3.14
Sb-Te	2.93, 3.11	2.95, 3.09		
Te-Te	4.17	4.76	4.35 (3.75)[b]	4.39
	Free internal parameters z			
Te1:1(a) site	0 (0)[a]	0 (0)[a]	0 (0)[a]	0
Ge (Sb):2(d)	0.0963	0.1084	0.1025 (0.1061)[a]	0.1030
Te2: 2(d)	0.1896	0.2036	0.1961 (0.2065)[a]	0.1966
Sb (Ge): 2(c)	0.3041	0.3124	0.3103 (0.3265)[a]	0.3108
Te3: 2(d)	0.4014	0.3871	0.3974 (0.4173)[a]	0.3964

a: Ref. 3;   b: Ref. 4

The calculated band structure reveals quite different electronic behavior for the four *h*-GST phases. Although accurate band gap can not be obtained by present DFT methods, the trend is preserved. As shown in Fig. 1, structures A, C and D are semiconductors with small direct band gaps of 0.115, 0.217 and 0.221 eV, respectively, while phase B shows a metallic behavior. The results suggest that exchanging Ge and Sb will change the materials from a narrow band gap semiconductor to a metal. Experimentally, an optical gap of ~0.5 eV has been measured for *h*-GST, however, the temperature dependence of the conductivity reveals a metallic character [17]. The calculated band structures for phases A and B are consistent with previous *ab initio* calculations [6].
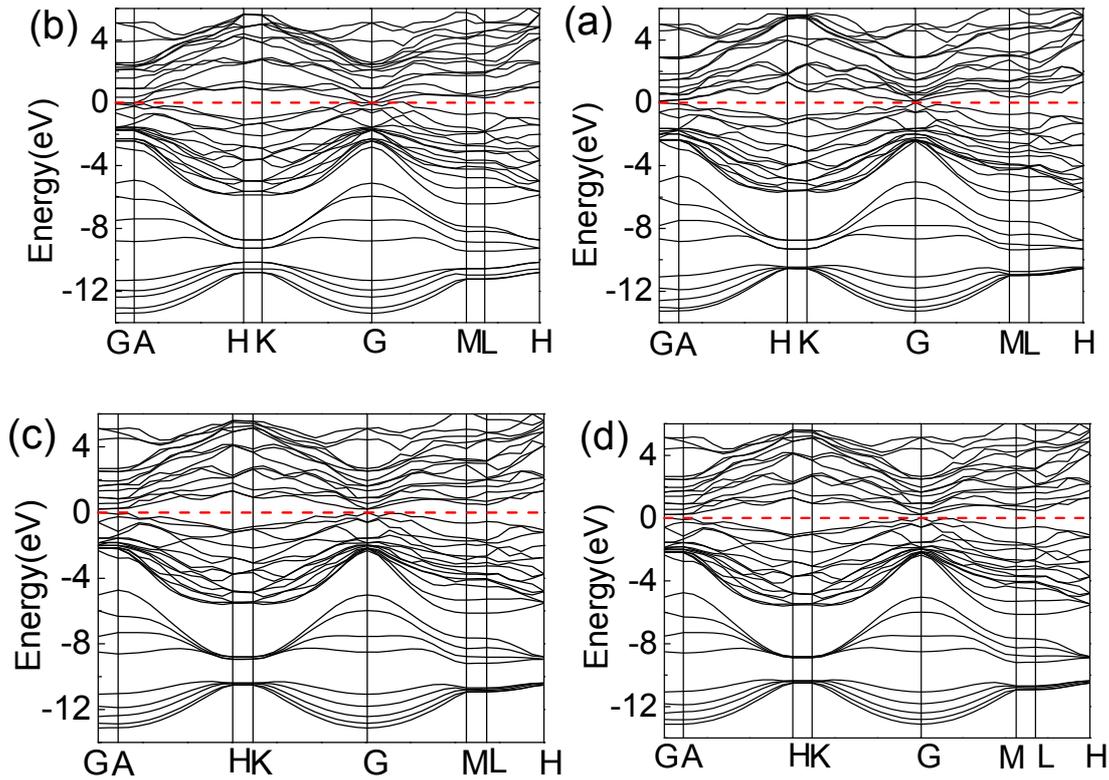
Fig. 1 The calculated band structure for phases (a) A, (b) B, (c) C and (d) D.

Further analysis on the electron density difference shed light on the chemical bonding characters for the four types of *h*-GST alloys. Fig. 2 shows the electron density difference field projected on the (110) plane for phases A, B, C and D. The electron density difference is calculated with respect to a linear combination of the atomic densities, which illustrates the changes in the electron distribution due to formation of chemical bonds in the system. As seen in fig. 2(a), the covalent bond between Te^1 and Ge is slightly weaker than that between Ge and Te^2, while the Te^2-Sb^1 covalent bond is much weaker than that of the Sb^2-Te^3 covalent bond. Furthermore, lone pairs of electrons or nonbonding electrons positioned around Te^3 facing the intrinsic vacancy layer as well as the very weak bonding between Te^3 layers are clearly seen. As Ge and Sb exchange positions, the splitting of both Ge-Te bonds and Sb-Te bonds is obvious (Fig.2b). This is highlighted by weak Te^1-Sb and strong Sb-Te^2 covalent bonds, and by the very weak Te^2-Ge^1 and strong Ge^2-Te^3 covalent bonds. Similar to phase A, lone pairs of electrons at around Te^3 and weak Te^3-Te^3 bond are also observed in phase B. The features of electrons density difference in phase C and D are generally similar, showing a rather strong anisotropic character. The covalent Ge/Sb-Te bond decreases in the sequence of Ge/Sb^2-Te^3 > Ge/Sb^1-Te^2 > Ge/Sb^1-Te^1 > Ge/Sb^3-Te^2. Similar to phase A and B, lone pairs of electrons were also identified to be around Te^3, however, the chemical bonding between Te^3 layers is stronger than that in phase A which is consistent with the corresponding Te-Te bond lengths as shown in Table 1.
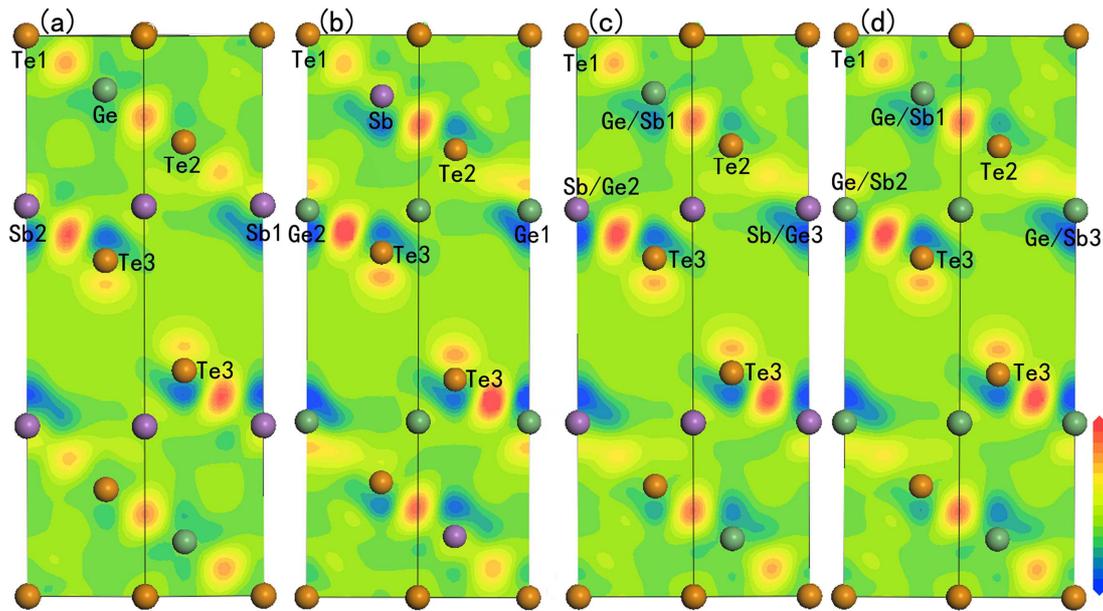
Fig. 2 The calculated electron density difference field projected on the (110) plane for phases
(a) A, (b) B, (c) C and (d) D. The scale is from -0.06 (blue) to 0.08 (red).

Summary

On the basis of *ab initio* total energy calculations, we have performed an extensive study on the stacking sequence and randomly occupation of Ge and Sb to make the same layer for stable *h*-GST. The results demonstrate that the stacking sequences and random occupation of Ge and Sb have great effect on the structure properties, especially electronic properties. Furthermore, from the energy point of view, the proposed models by both Petrov *et al*. and Kooi-De Hosson might also be candidate structures for stable *h*-GST even though the Kooi-De Hosson structure is energetically most stable. While the random occupation of Ge and Sb making the same layer proposed by Matsunaga *et al*. is energetically less favorable. The present results may unravel the diversity of the reported properties for stable *h*-GST and hence contribute to understanding the phase change mechanism for phase change materials.

References

[1] S. Raoux, W. Welnic and D. Lelmini, Chem. Rev. 110, 240 (2010).

[2] I. I. Petrov, R. M. Imamov, Z. G. Pinsker, Phys. Cryst. 13, 339 (1968).

[3] B. J. J. Kooi, T. M. De Hosson, J. Appl. Phys. 92, 3584 (2002).

[4] T. Matsunaga, N. Yamada and Y. Kubota, Acta Cryst. B 60, 685 (2004).

[5] Z. M. Sun, J. Zhou, R. Ahuja, Phys. Rev. Lett. 96, 055507 (2006).

[6] G. Lee and S.-H. Jhi, Phys. Rev. B 77, 153201 (2008).

[7] G. C. Sosso, S. Caravati, C. Gatti, S. Assoni and M. Bernasconi, J. Phys. Condens. Matter. 21, 245401 (2009).

[8] Z. M. Sun, S. Kyrstab, D. Musicb, R. Ahuja, J. M. Schneider, Solid State Commu. 143, 240 (2007).

[9] J. L. F. Da Silva, A. Walsh and H. Lee, Phys. Rev. B 78, 224111 (2008)._

[10] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, J. D. Joannopoulos, Rev. Mod. Phys. 64, 1045 (1992).

[11] J. Perdew, K. Burke, M. Ernzhofer, Phys Rev Lett 77, 3865 (1996).

[12] B. S. Sa, N. Miao, J. Zhou, Z. M. Sun, R. Ahuja, Phys. Chem. Chem. Phys.12, 1585(2010).

[13] H. J. Monkhorst, J. D. Pack, Phys. Rev. B 16, 1748 (1977).

[14] D. R. Hamann, M. Schluter, C. Chiang. Phys. Rev. Lett. 43, 1494 (1979).

[15] G. Kresse, J. Hafner, Phys. Rev. B 47, 558 (1993).

[16] L. Bellaiche, D. Vanderbilt, Phys. Rev. B 61, 7877 (2000).

[17] B. S. Lee, J. R. Abelsona, S. G. Bishop, D. H. Kang, B. k. Cheong and K. B. Kim, J. Appl. Phys. 97, 093509 (2005).

Ab Initio Study on Hexagonal
Ge$_2$Sb$_2$Te$_5$-A Phase-Change Material for
Nonvolatile Memories