Structure of Phase Change Materials for Data Storage

Zhimei Sun,[1,*] Jian Zhou,[2] and Rajeev Ahuja[1,3]

[1]Condensed Matter Theory Group, Department of Physics, Uppsala University, Box 530, SE-751 21 Uppsala, Sweden
[2]Materials Chemistry, Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden
[3]Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

(Received 17 October 2005; published 9 February 2006)

Phase change materials based on chalcogenide alloys play an important role in optical and electrical memory devices. Both applications rely on the reversible phase transition of these alloys between amorphous and metastable cubic states. However, their atomic arrangements are not yet clear, which results in the unknown phase change mechanism of the utilization. Here using *ab initio* calculations we have determined the atomic arrangements. The results show that the metastable structure consists of special repeated units possessing rocksalt symmetry, whereas the so-called vacancy positions are highly ordered and layered and just result from the cubic symmetry. Finally, the fast and reversible phase change comes from the intrinsic similarity in the structures of the amorphous and metastable states.

DOI: 10.1103/PhysRevLett.96.055507 PACS numbers: 61.50.Ah, 61.72.Ji, 64.70.Kb, 71.15.Mb

Back in the 1960s, Ovshinsky put forth an idea of memory switch based on changes in the properties of amorphous and crystalline phases of multicomponent chalcogenides [1]. Using this idea, the commercialized optical disc products and the digital versatile disc random access memory (DVD-RAM) became true [2]. Phase change materials based on the Ge-Sb-Te system have been extensively studied and found to be suitable for optical and electrical memories [3–15]. Among these alloys, $Ge_2Sb_2Te_5$ (GST) exhibits the best performance when used in DVD-RAM in terms of speed and stability. GST demonstrates high thermal stability at room temperature, high crystallization rate at high temperatures (can be crystallized by a less than 50 ns laser heating pulse), and extremely good reversibility between amorphous and crystalline phases (more than 10^5 cycles). However, the paradoxical situation is that the structure changes behind the utilized transition are unknown yet. GST has two crystalline states, metastable cubic and stable hexagonal. The hexagonal structure is a high temperature phase, while the reversible transformation between cubic and amorphous is used for memory storage. Yamada *et al.* [6] and Nonaka *et al.* [11] assumed a rocksalt structure of the metastable phase that the 4(a) sites are fully occupied by Te atoms and Ge, Sb atoms randomly occupy the 4(b) site with 20% vacancies. In a very recent study, Park *et al.* [16] proposed an ordered atomic arrangement at 4(b) site based on high-resolution transmission electron microscopy analysis. The authors suggested that Ge and Sb atoms tend to position themselves on specific planes. The stable hexagonal GST consists of 9 layers in one unit cell with a space group of $P\bar{3}m1$. In a very early work, Petrov *et al.* [17] proposed an atomic stacking sequence of Te-Sb-Te-Ge-Te-Te-Ge-Te-Sb-. Later, in 2002, Kooi and De Hosson [18] proposed a stacking sequence of Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge- with Sb and Ge atoms exchange their positions. Very recently, Matsunaga *et al.* [19] suggested that Sb and Ge should randomly occupy the same layer with the stacking sequence of Te-Sb/Ge-Te-Sb/Ge-Te-Te-Sb/Ge-Te-Sb/Ge-.

The fact that cubic GST can be easily transformed to a hexagonal structure indicates that no large atomic rearrangement occurs in this transformation process. Therefore the atomic arrangement of the cubic GST should have some intrinsic relation with that of its hexagonal structure. *Ab initio* total energy calculations based on density functional theory (DFT) provides us a very accurate way to study phase stability of different atomic arrangements. In this report we used the VASP code [20,21], in conjunction with projector augmented wave potentials within the generalized-gradient approximations (GGA) [22] to give a picture for the atomic arrangements of the GST crystalline states. Pseudopotentials with electronic configurations of Ge $4s^24p^2$, Sb $5s^25p^3$, and Te $5s^25p^4$ were used. All atoms were relaxed until the forces on them were less than 10 meV/Å. The relaxation convergence for ions was 1×10^{-4} eV and it was 1×10^{-5} eV for electronic relaxations. KPOINTS of $5 \times 5 \times 5$ are automatically generated with Gamma symmetry; the tetrahedron method with Blöchl corrections were used for the total energy calculations [23].

We started from the hexagonal structure for which the three above mentioned possible atomic arrangements have been considered. The calculated results are given in Table I. It is seen that atomic stacking (a), Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge-, possesses the lowest total energy and should be the most stable configuration. When comparing the optimized atomic positions of the three configurations with those of the experiments (given in Table II), we see that the values of configuration (a) are in very good

TABLE I. The calculated total energy, lattice parameters, and bond length for the hexagonal structure of $Ge_2Sb_2Te_5$ with various stacking.

Atomic arrangement	E_0 (eV/atom)	a_0 (Å)	c_0 (Å)	Te-Ge bond length (Å)	Te-Sb bond length (Å)	Te-Te bond length (Å)
[a]	−3.787	4.295	16.977	3.00, 3.02	3.06, 3.21	3.51
[b]	−3.767	4.270	17.172	2.87, 3.16	3.07, 3.20	3.54
[c]	−3.785	$a_0 = 4.294$ $b_0 = 4.290$	17.176	2.89−3.23	2.96−3.26	3.54−3.65

[a] Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge- stacking.

[b] Te-Sb-Te-Ge-Te-Te-Ge-Te-Sb- stacking.

[c] Ge and Sb mixed in the same layer as Te-Sb/Ge-Te-Sb/Ge-Te-Te-Sb/Ge-Te-Sb/Ge-. After optimization, the final structure is a slightly triclinic distorted hexagonal structure with $\alpha = 89.99°$, $\beta = 89.92°$, and $\gamma = 120.05°$.

agreement with the experiments. Therefore we can conclude that the stacking of hexagonal GST is the configuration (a) that agrees with the model of Kooi and De Hosson [18].

To study the atomic and vacancy arrangements of cubic GST, we rebuilt the cubic structure in terms of hexagonal stacking based on the (111) planes along the [111] direction. Supercells consisting of 27 atoms with 3 vacancy positions, and 108 atoms with 12 vacancies, have been used in the present studies. The following stacking sequences along the [111] direction for cubic GST have been considered: (a) -Te-Ge-Te-Sb-Te-v-Te-Sb-Te-Ge-; (b) -Te-Sb-Te-Ge-Te-v-Te-Ge-Te-Sb-; (c) -Te-Ge-Te-Sb-Te-Ge-Te-v-Te-Sb-; (d) -Te-Ge/Sb-Te-Ge/Sb-Te-v-Te-Ge/Sb-Te-Ge/Sb- [herein Ge and Sb are mixed in the same (111) layer]; (e) -Te-Ge/v-Te-Sb/v-Te-Ge/v-Te-Sb/v-Te- (herein Ge and Sb atoms are layered along [111] but mixed with vacancies). The "v" represents one vacancy layer or vacancy positions. For atomic arrangements (a) to (c), the vacancies occupy the same (111) plane and are layered along [111]. The calculated total energy and lattice parameters are presented in Table III. Quite interestingly, the atomic arrangement of the lowest total energy of cubic GST coincides with the most stable hexagonal configuration. The calculated lattice parameter for this cubic configuration is $a = 6.054$ Å, about 0.4% higher than the experimental value 6.02 Å [16] that is within the GGA overestimated error. Using the local-density approximation method, we got $a = 6.018$ Å, which is in perfect agreement with the experimental value. Therefore we conclude that cubic GST is a highly ordered structure whose stacking sequence along [111] is the same as its stable hexagonal counterpart.

The present results indicate that metastable GST does not have a cubic structure. It rather consists of two well-defined highly ordered three-dimensional repeat units: -Te-Ge-Te-Sb-Te- (I) and -Te-Sb-Te-Ge- (II). These two three-dimensional repeat units are bonded alternatively in space consistent with a rocksalt structure. Within every unit, the bonding is strong, while the Te-Te bond between the two units is quite weak. The configuration indicates the vacancy positions are highly ordered and layered along the [111] direction, and they are intrinsic to the structure. Experimentally, doping In [24], Sb [25], or Ge [26] in metastable GST resulted in phase separation or the extra elements accumulated at grain boundaries, which confirms the intrinsic character of the vacancies. Therefore we can conclude that the highly ordered "va-

TABLE II. Atomic positions for stable hexagonal GST of various stacking.

Atom	Site	x	y	z	z (Ref.)
Tel	1(a)	$0^{a,b}$ 0.004^c	$0^{a,b}$ 0.009^c	$0^{a,b}$ -0.003^c	
Ge (Sb), Ge/Sb	2(d)	2/3	1/3	0.102^a, 0.119^b, 0.110^c	(0.106)[17,18] (0.1061)[19]
Te2	2(d)	1/3	2/3	0.209^a, 0.225^b, 0.208^c	(0.212)[17,18] (0.2065)[19]
Sb (Ge), Ge/Sb	2(c)	0 0.003	0 −0.001	0.321^a, 0.340^b 0.328^c	(0.317)[17,18] (0.3265)[19]
Te3	2(d)	2/3	1/3	0.427^a, 0.426^b, 0.426^c	(0.421)[17,18] (0.4173)[19]

[a] Te-Ge-Te-Sb-Te-Te-Sb-Te-Ge- stacking.

[b] Te-Sb-Te-Ge-Te-Te-Ge-Te-Sb- stacking.

[c] Ge and Sb mixed in the same layer as Te-Sb/Ge-Te-Sb/Ge-Te-Te-Sb/Ge-Te-Sb/Ge-. After optimization, the final structure is a slightly triclinic distorted hexagonal structure with $\alpha = 89.99°$, $\beta = 89.92°$, and $\gamma = 120.05°$.

TABLE III. The calculated total energy, lattice parameters, and bond length for the metastable cubic $Ge_2Sb_2Te_5$ with various stacking.

Atomic arrangement	E_0 (eV/atom)	a_0 (Å)	Te-Ge bond length (Å)	Te-Sb bond length (Å)
[a]	−3.797	6.054	2.99, 3.03	3.02, 3.21
[b]	−3.779	6.020	2.84, 3.25	3.03, 3.20
[c]	−3.767	6.046	2.83–3.23	3.00–3.30
[d]	−3.789	Monoclinic ($\beta = 103.1°$)	2.78–3.30	2.86–3.37
[e]	−3.784	Monoclinic ($\beta = 114.3°$)	2.88–3.27	2.92–3.34

[a] -Te-Ge-Te-Sb-Te-v-Te-Sb-Te-Ge- stacking.
[b] -Te-Sb-Te-Ge-Te-v-Te-Ge-Te-Sb- stacking.
[c] -Te-Ge-Te-Sb-Te-Ge-Te-v-Te-Sb- stacking.
[d] -Te-Ge/Sb-Te-Ge/Sb-Te-v-Te-Ge/Sb-Te-Ge/Sb-, wherein Ge and Sb atoms are mixed in the same layer. In (a) to (d) v represents a vacancy layer.
[e] -Te-Ge/v-Te-Sb/v-Te-Ge/v-Te-Sb/v-Te-, Ge, and Sb atoms are layer along [111] but mixed with vacancies.

cancies'' come from the structure symmetry. It seems impossible to tune the properties of GST by solid solution at the ''vacancy'' sites.

Before we come to the phase transformation between metastable and stable hexagonal GST, we first compared the corresponding bond lengths of the two structures for configuration (a) as given in Tables I and III. Note that there are shorter and longer bond lengths for both Te-Ge and Te-Sb bonds. The Te-Ge (or Sb) bond lengths of metastable GST are very close to those of the corresponding hexagonal GST. This indicates that as metastable GST transformed into hexagonal GST, the corresponding bond lengths are generally conserved and no large atomic rearrangement should occur. In Fig. 1, we illustrate the atomic stacking sequences for both metastable GST and the hexagonal structure. It is obvious that the lower part, block I of Fig. 1(a), is quite similar to the corresponding hexagonal one [Fig. 1(b)], only the upper parts differ. By slipping block II of metastable GST along [210], we will get the same structure as hexagonal GST. Therefore, the phase transformation between the two crystalline is not a diffusion-controlled process but rather a movement of block II in certain directions.

As for the amorphous GST, the fast and reversible phase change between amorphous and crystalline states indicates that the local amorphous structure should be similar to the crystalline state. In this way, only small atomic rearrangement is necessary for the phase transformation. Here we propose that the local structure of amorphous GST also consists of two repeat units similar to the metastable state. However, the bonding within every units of amorphous GST is even stronger, while the bonding between Te-Te planes of different units is nearly negligible. The reversible phase change between amorphous and crystalline states could be fulfilled by the movement of Te planes. This proposal agrees with the recent simulations that the amorphous spot collapse is assisted by the motion of certain crystal facets [27].

In summary, we demonstrated that metastable GST consists of two well-defined three-dimensional repeat units: -Te-Ge-Te-Sb-Te- (I) and -Te-Sb-Te-Ge- (II). They are bonded alternatively in space possessing a rocksalt symmetry. The vacancies are highly ordered and layered and just result from the rock salt symmetry. Therefore it seems impossible to tune the properties of GST by doping on the vacancy positions. The phase change from cubic to hexagonal is the movement of unit II in the [210] direction. We proposed that the local structure of amorphous GST should be quite similar to its crystalline except that the bonding between Te and Te layers of different units is nearly negligible. The fast reversible phase change could be fulfilled by the movement of Te planes. The above theory can be applied to all the other phase change materials in the Ge-Sb-Te system. We hope our results can provide a fundamental understanding of these technologically im-

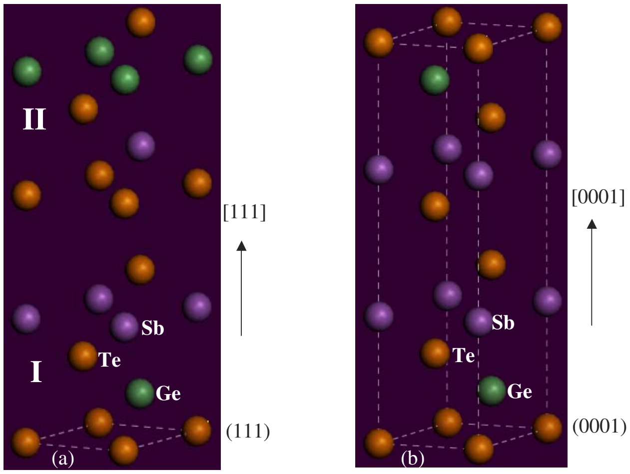

FIG. 1 (color online). (a) Atomic arrangement for metastable $Ge_2Sb_2Te_5$ built based on (111) planes along the [111] direction. (b) Stable crystal structure of hexagonal $Ge_2Sb_2Te_5$.

portant materials and also be beneficial to their commercial applications.

We acknowledge support from the Swedish Research Council (VR), SIDA, and STINT.

---

*To whom correspondence should be addressed. Electronic address: zhimei.sun@fysik.uu.se

[1] S. R. Ovshinsky, Phys. Rev. Lett. **21**, 1450 (1968).
[2] T. Ohta, J. Optoelectron. Adv. Mater. **3**, 609 (2001).
[3] A. V. Kolobov, P. Fons, A. I. Frenkel, A. L. Ankudinov, J. Tominaga, and T. Uruga, Nat. Mater. **3**, 703 (2004).
[4] M. H. R. Lankhorst, B. W. S. M. M. Ketelaars, and R. A. M. Wolters, Nat. Mater. **4**, 347 (2005).
[5] M. Wuttig, Nat. Mater. **4**, 265 (2005).
[6] N. Yamada, E. Ohno, K. Nishiuchi, N. Akahira, and M. Takao, J. Appl. Phys. **69**, 2849 (1991).
[7] N. Ohshima, J. Appl. Phys. **79**, 8357 (1996).
[8] H. J. Borg and R. van Woudenberg, J. Magn. Magn. Mater. **193**, 519 (1999).
[9] V. Weidenhof, I. Friedrich, S. Ziegler, and M. Wuttig, J. Appl. Phys. **86**, 5879 (1999).
[10] T. H. Jeong, M. R. Kim, H. Seo, S. J. Kim, and S. Y. Kim, J. Appl. Phys. **86**, 774 (1999).
[11] T. Nonaka, G. Ohbayashi, Y. Toriumi, Y. Mori, and H. Hashimoto, Thin Solid Films **370**, 258 (2000).
[12] I. Friedrich, V. Weidenhof, W. Njoroge, P. Franz, and M. Wuttig, J. Appl. Phys. **87**, 4130 (2000).
[13] V. Weidenhof, I. Friedrich, S. Ziegler, and M. Wuttig, J. Appl. Phys. **89**, 3168 (2001).
[14] G.-F. Zhou, Mater. Sci. Eng. A **304–306**, 73 (2001).
[15] B. S. Lee, J. R. Abelson, S. G. Bishop, D.-H. Kang, B. Cheong, and K.-B. Kim, J. Appl. Phys. **97**, 093509 (2005).
[16] Y. J. Park, J. Y. Lee, M. S. Youm, Y. T. Kim, and H. S. Lee, J. Appl. Phys. **97**, 093506 (2005).
[17] I. I. Petrov, R. M. Imamov, and Z. G. Pinsker, Sov. Phys. Crystallogr. **13**, 339 (1968).
[18] B. J. J. Kooi and T. M. De Hosson, J. Appl. Phys. **92**, 3584 (2002).
[19] T. Matsunaga, N. Yamada, and Y. Kabota, Acta Crystallogr. Sect. B **60**, 685 (2004).
[20] G. Kresse and J. Hafner, Phys. Rev. B **48**, 13 115 (1993).
[21] G. Kresse and J. Hafner, Phys. Rev. B **49**, 14 251 (1994).
[22] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
[23] P. E. Blöchl, Phys. Rev. B **50**, 17 953 (1994).
[24] K. Wang, C. Steimer, D. Wamwangi, S. Ziegler, and M. Wuttig, Appl. Phys. A **80**, 1611 (2005).
[25] N. Yamada and T. Matsunaga, J. Appl. Phys. **88**, 7020 (2000).
[26] S. Privitera, E. Rimini, C. Bongiorno, A. Pirovano, and R. Bez, J. Appl. Phys. **94**, 4409 (2003).
[27] K. Kohary, V. M. Burlakov, and D. G. Pettifor, Phys. Rev. B **71**, 235309 (2005).