

Atomic and electronic structures of amorphous GST

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ABSTRACT

Despite the commercial applications of chalcogenide-based alloy for the memory devices, the understanding about these materials have not been accomplished deeply because of their complex atomic and electronic structures. In this study, we examine the building block model for the atomic structure of amorphous GST firstly, and then we investigate a pressure effect on the amorphous GST, which is supposed to occur in confined PRAM cell. It is found that the building block model gives an atomic structure which is comparable with experimental data. On the other hand, the study of pressure effect shows that the energy gap and electronic structure near band edge are critically dependent on the simulation volume.

Key words: amorphous, GST, building block, phase change, PRAM, resistance drift

1. INTRODUCTION

High performance and large capacity non-volatile memory (NVM) devices become crucial to the development of the multimedia technology in recent years and the phase change random access memory (PRAM) is supposed to be one of the most promising candidates for the future NVM [1,2]. The $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ pseudo-binary system, usually abbreviated as GST, has been known to satisfy material requirements for the PRAM [3-5]. Although GST materials are already in use for the rewritable CD and DVD and their commercial application to the random access memory is expected in the near future as well, neither the local structure of the material nor the change in the structure during the phase transition is well established. Recently, many extended x-ray absorption fine structure (EXAFS) experiments shows more precise information about the local structure of amorphous GST [6-9].

In this study we investigate atomic and electronic structure of amorphous GST based on the EXAFS results. From the EXAFS experiments, it is known that the local structures change during the phase change. The local structures of amorphous GST seem to satisfy 8-N rule [6,9], which means that each bonding make closed *s* and *p* atomic shell. Furthermore there is a EXAFS experiment which shows the local structure of amorphous GST is robust for various $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ series [8]. From these experimental remarks, we propose building blocks which can be structural unit for the phase change. Moreover we extend building block model to explain rapid phase change between amorphous and crystalline phase. In addition, we study the pressure effect on the amorphous GST. This is motivated by the observation that the GST material is tightly confined within a PRAM cell. Since the volume of amorphous GST is expanded by 6.5%, the pressure effect can play an important role during the phase change. The effect of the confining pressure on the atomic and electronic structures of amorphous GST will be discussed.

2. COMPUTATION METHOD

In order to obtain the proper atomic structures for the amorphous GST, we perform the first-principles density functional theory (DFT) calculation. Electronic density in Kohn-Sham equation is expanded by plain wave basis and PBE-GGA functional is employed for the exchange-correlation functional. Norm-conserving pseudopotential or projector-augmented wave pseudopotential are used. In the first-principles molecular dynamics (FPMD) calculation, the temperature is controlled by velocity rescaling. The computations in this work are performed by Quantum-espresso or Vienna atomic simulation packages.

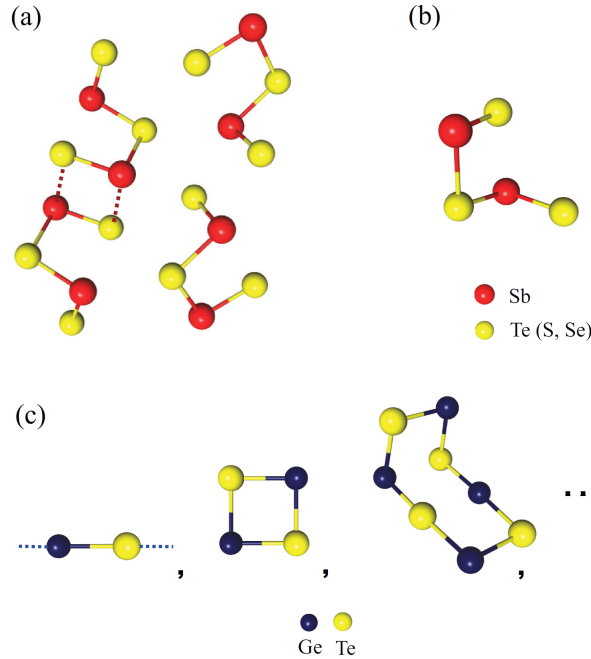


Fig. 1 (a) Unit cell of the stibnite structure. Yellow dots indicate S,Se or Te atoms and the red ones Sb atoms. (b) A subunit of the stibnite structure in (a), which is our proposed building block of Sb_2Te_3 . (c) Proposed structural building blocks of GeTe. Blue dots are Ge atoms and yellow ones Te atoms.

3. BUILDING BLOCK MODEL

In order to explain our structural model, we first introduce the smallest (primary) building blocks. The crystalline $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ obtained during the phase-change device operation is known to have the cubic (rocksalt) structure [10]. In decomposing and analyzing the structure in terms of building blocks, it is natural to consider unit cells of the crystalline GeTe and the crystalline Sb_2Te_3 . We examine Sb_2Te_3 first. The crystalline Sb_2Te_3 turns out to have a hexagonal (Tetradymite) structure and hence not suitable for the starting point to construct the building block of the GST. It is noted that the chalcogenides Sb_2Se_3 (Antimonelite) and Sb_2S_3 (Metastibnite) have the stibnite structure whose local structure resembles the cubic structure [11,12]; the stibnite unit cell consists of four subunits whose shape fits to the simple cubic lattice. Figure 1 (a) shows the unit cell of the stibnite structure and its subunit comprising five strongly-bonded atoms which may be regarded as a part of the rocksalt structure. The local structure of the amorphous Sb-Te compound is also observed to be rocksalt-like [13]. Thus the stibnite-like Sb_2Te_3 subunit in Fig. 1 (b) is a good candidate for the building block of the GST structure which may exist persistently in both crystalline (rocksalt) and amorphous phases. On the other hand, since the crystalline GeTe itself has a cubic (rocksalt) structure, the unit cell (Ge-Te) is a natural building block as shown in the first part of Fig. 1 (c). However, when we study the phase transition to the amorphous phase later, it is necessary to know how the smallest GeTe units are connected to each other. In other words, we need some structural information on a larger scale because the simple GeTe unit, if it were

isolated, would have too many dangling bonds. We note that many chalcogenide compounds (alloys with at least one group VI element S, Se or Te) like to form a chain-like structure [14]. We propose that the multiple units of GeTe tend to form a chain-like structure in the amorphous phase as exemplified in Fig. 1 (c). This chain-like (not necessarily linear) structure is immediately adapted to the rocksalt structure because Ge and Te atoms alternate in the chain as in the rocksalt structure.

Now we construct a secondary building block by attaching the GeTe unit(s) into the stibnite Sb_2Te_3 unit(s). A secondary building block (or, a secondary structural motif) is defined to be a small assembly of primary building blocks which rotates as a whole, while retaining its overall shape, during the phase change. In the case of GeSb_2Te_4 ,

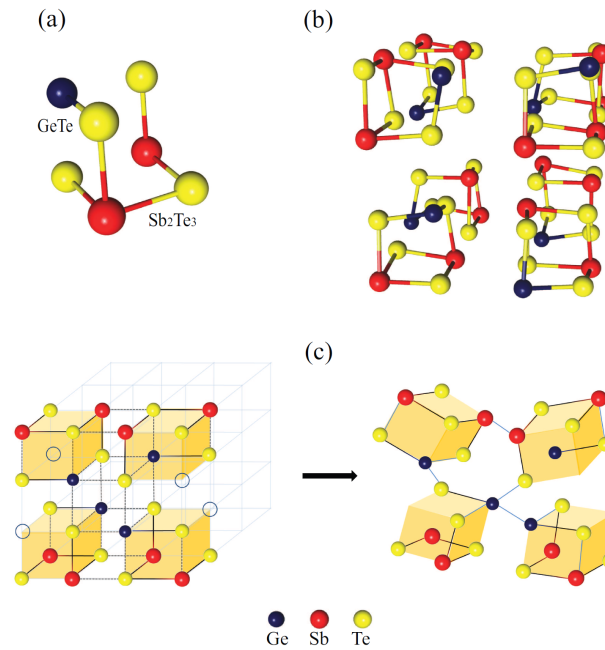


Fig. 2 (a) A secondary building block of GeSb_2Te_4 consisting of one GeTe and one Sb_2Te_3 unit. (b) The supercell used in the simulation which accommodates 8 secondary building blocks in (a). (c) An example of rotated secondary building blocks in the cubic supercell. Only 4 out of 8 secondary building blocks are shown for visual clarity. Blue, red, and yellow dots represent Ge, Sb, and Te atoms, respectively.

the shape of the secondary building block is chosen to be a cube (with one vacancy site) as shown in Fig. 2 (a). This is the smallest secondary block in GeSb_2Te_4 and there could be other kinds of them [15]. The secondary building block is not necessarily unique for given n and m . However, the number of different kinds of secondary building blocks must be very small, if not one, because their size and shape should be adequate for an easy rotation inside the bulk material. Vacancies provide additional room and freedom for the movement of the structural unit. In the present work, we focus on GeSb_2Te_4 because of its simplicity from the building block point of view. The crystalline structure accommodates 8 secondary building blocks of GeSb_2Te_4 in the $4 \times 4 \times 4$ cubic atomic sites (Fig. 2 (b)). To mimic the amorphous structure, each secondary building block in the cube is rotated randomly (Fig. 2 (c)). In this model, crystallization from the amorphous phase is explained by re-orientation of secondary building blocks. This quite simple change of structure can be considered as an origin of fast phase change of GST.

In order to check applicability of model structure, we perform structural relaxation by using first-principles total energy minimization calculation. As a result, we could confirm that the building block model structure well agree with experimental results in bond length and coordination number of GeSb_2Te_4 . The results are summarized in Table 1.

	Bond length (Å)		CN		
	Ge-Te	Sb-Te	Ge	Sb	Te
crystal.(Expt.)	2.83 ¹	2.91 ¹			
crystal.(Calc.)	2.85	2.96	3.0(6)	3.2(6)	2.4(4.5)
amorph.(Expt.)	2.61 ²	2.85 ²	3.91 ²	3.12 ²	1.98 ²
amorph.(Calc.)	2.74	2.90	3.58	3.17	2.41

Table 1 Bond length and coordination number (CN) of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ obtained from energy minimization calculations. [1] A. V. Kolobov *et al.*, (2004). [2] P. Jòvànri, *et al.* (2008)

	Bond length (Å)			CN		
	Ge-Te	Sb-Te	Te-Te	Ge	Sb	Te
0.0%	2.81	2.95	4.09	3.79	2.93	2.44
3.0%	2.81	2.93	4.14	3.68	2.88	2.40
6.5%	2.79	2.92	4.16	3.60	2.89	2.35
10.0%	2.77	2.91	4.17	3.60	2.91	2.34
20.0%	2.79	2.88	4.23	3.45	2.84	2.31
Ideal glass	2.68	2.87	4.30	3.95	2.87	2.02
Crystal	2.96	3.03	4.33	3.60	2.92	2.64

Table 2 Bond length and coordination number (CN) of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ obtained from the simulation of melt-quenching by molecular dynamics. Bond length and coordination number are calculated from partial pair correlation function. Bond length come from the top of 1st peak of partial PCF, and the coordination number calculated by integration of PCFs up to 3.1 Å.

4. PRESSURE EFFECT IN PRAM CELL

Now, we are going to investigate the effect of pressure on the atomic and electronic structures of amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$, which is a material of choice in the optical and electric storages. This work was motivated by the observation that the phase change in the PRAM occurs within a tightly confined cell structure. The original volume is set to that of the crystalline structure, therefore the amorphous structure is significantly compressed depending on the amorphous portion. To figure out the pressure effect in PRAM cell, first-principles calculations are performed based on the density functional calculation. The amorphous structure is obtained by a usual melt-quench process, and supercell volume dependence of atomic and electronic structure is studied.

In Table 2, the bond length and the coordination number of melt-quench results are summarized in each volume. The bond length gets shorter as increasing volume but does not show significant change. On the other hand, the analysis on the coordination number indicates that the 8-N rule is satisfied better in larger volume. Therefore, by comparing with ideal glass and crystalline GST, it is shown that increasing volume results in higher covalent bonds. The volume dependence of electronic structure is also investigated. Here we focus on the energy gap and the number of in-gap states. By fitting the density of states with analytical functions for typical semiconductor materials, it was found that the energy gap increase monotonically as increasing volume of cell. Moreover the amount of localized in-gap state is found to decrease as increasing the cell volume.

5. CONCLUSION

In conclusion, we investigated the atomic and electronic structure of GST with first-principles density functional theory. Firstly, we proposed a structural model for the amorphous $(\text{GeTe})_n(\text{Sb}_2\text{Te}_3)_m$ based on three-dimensional building blocks. In our model, the phase change between the amorphous and the crystalline structure is explained by the reorientation of the secondary building blocks and their relaxation. Calculated equilibrium volumes and bond lengths using *ab initio* computational methods are comparable with experimental data, and the CN's of the amorphous phase are shown to satisfy the 8-N rule. Secondly, we showed volume-dependence of atomic and electronic structure of amorphous GST. As increasing volume, or decreasing the density of systems, the atomic configuration resembles the ideal glass structure. For the electronic structure, the energy gap increases and the number of localized in-gap states decreases.

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Biographies

Professor Seungwu Han was born in 1971. He received his B.S. (1993), M.S. (1995), and Ph.D. (2000) degrees from department of physics at Seoul National University in Korea. He spent the postdoctoral period in 2001-2004 at Princeton Materials Institute in Princeton University. Since 2004, he is holding the professor position in department of physics at Ewha Womans University.

His research expertise is the first-principles calculation of the electronic structures. During the Ph.D. course, he has contributed greatly to the quantum-mechanical calculation of the field emission current from the nanostructures.

When in Princeton, he applied the first-principles methods to study the radiation damage of metal alloys. After coming back to Korea, he has been interested mostly in the electronic materials to be used in DRAM and non-volatile memory. He proposed a model to explain the mechanism of the resistance-switching memory. Recently, he has been applying the first-principles molecular dynamics simulations to study the phase-change phenomena of chalcogenide materials.