Atomic structures and topological insulating property of meta-stable Ge-Sb-Te compounds

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ABSTRACT

Ge-Sb-Te (GST) alloys have extremely fast atomic rearrangements between amorphous and crystalline structure and, in association, drastic changes in electrical conductivity and optical reflectivity. Despite extensive research in both measurements and calculations, underlying mechanisms for the fast phase transition and detailed atomic structures during the transition are still unknown. Recently, new aspects of electronic interactions such as metal-insulator transition or topological insulating property rather than stochastic processes presumably responsible for atomic movements are proposed to understand the behavior of GST alloys. Using first-principles calculations, we study possible pathways of metastable FCC GST to acquire topological insulating property upon atomic exchange of cations, Ge and Sb. Also, starting from the Kooi–De Hosson sequence, we propose the atomic structure of metastable GST that stabilizes energetically the FCC structure.

Key words: topological insulator, phase change materials, GST compounds, first-principles

1. INTRODUCTION

Phage change materials (PCMs) comprised of Ge, Sb, and Te exhibit drastic changes in electrical conductivity and optical reflectivity and have been sought as materials for non-volatile memory devices (*1, 2*). Thermal control of optical and electronic properties by electrical currents is the key process in the memory devices. Short but large electrical current pulses followed by rapid quenching turn PCMs into (amorphous) reset state whereas longer pulses with low electric current produce the (crystalline) set state.

However, the mechanism of the fast phase change in atomic structures is still unclear despite extensive research in both measurements and calculations. While several models of atomic migration during the transition have been proposed (*3*), one interesting observation is the similarity in short range ordering between amorphous and crystalline phases. This implies that the phase change in GST compounds may have a rather deep origin associated with electronic interactions instead of stochastic thermal processes. Topological insulating properties and the metal-insulator transitions are the examples of such understanding as recently proposed (*4*,*5*).

Here we describe the evolution of topological insulating characteristics and the atomic structures of metastable FCC GST compounds. Topology of materials' electronic structures refers to a nature that is resilient to the local, atomistic deformations (*6-8*), but it can change abruptly at a certain point of such deformations. Since the surface or interface states of topological insulators can affect the electrical transport and consequent Joule heating, study of the change in topological insulating properties and atomic migration in GST compounds can provide an interesting frame to understand the structural and electronic properties of the compounds. In previous studies, we showed that hexagonal GST contains interface states driven by topological insulating phase of Sb_2Te_3 (Fig. 1) and that GST alloys in the hexagonal structure exhibit a rich phase diagram of topological – non-topological insulating phase transitions (*4*).

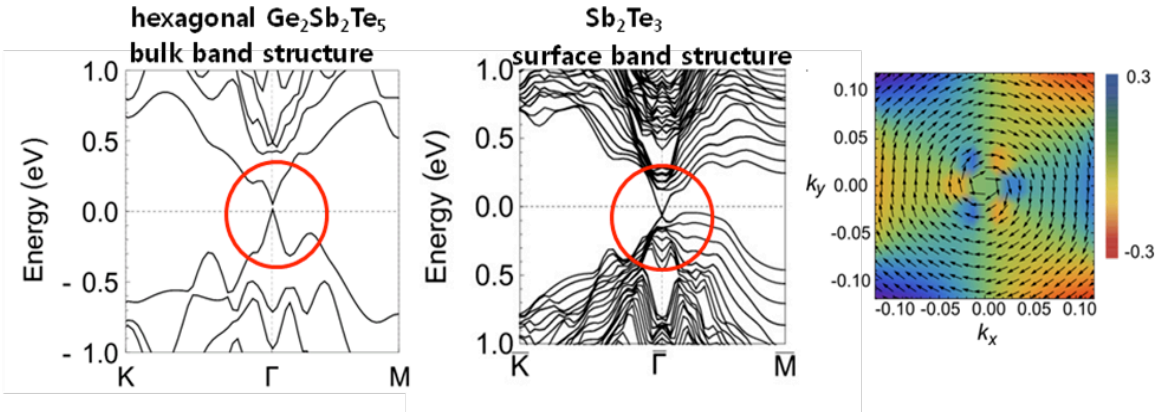

Figure 1 The electronic structure of bulk GST225 and Sb_2Te_3 film near the Fermi level. The special *k* points for Sb_2Te_3 band structure are along 2D Brillouin zone which is a projection of bulk 3D Brillouin zone into the film surface. We observe that they look very similar, particularly the parts within the circles in red. On the right, the helical spin structure of the states inside the red circles is shown. The arrow is the spin direction in the *xy*-plane of 2D Brillouin zone and the color denotes the *z*-component of the spin. The spin in the *xy*-plane is perpendicular to the momentum (k_x,k_y), the essential feature of the helical states. Combined with the linear dispersion in energy, the states in the red circle and electrons occupying them are called the Dirac cone and the massless Dirac fermions.

In this presentation, we discuss the role of topological insulating property of GST compounds in metastable crystalline phases. We discuss how the electronic property of GST can be associated with surface or interface states that originate from topological insulating phases.

2. COMPUTATIONAL

Calculations for crystalline GSTs were performed using first-principles methods based on pseudopotential density functional theory as implemented in the Vienna ab initio simulation package (*9*). Electron exchange-correlation is treated within the scheme of the generalized gradient approximation including SOC. The projector-augmented wave potentials as supplied by the simulation package were used for atomic pseudopotentials. We employed a cutoff energy of 400 eV and the atomic relaxation was carried out until the total energy converges within 0.1 meV. Calculations on rock-salt structure are carried out, maintaining the cubic symmetry while exploiting two representative hexagonal sequences, KH and Petrov sequences along the (111) direction (*10*). The sequences can be interchanged if Ge and Sb layers are switched along the (111) direction. Figure 2 shows the starting atomic structure to investigate possible meta-stable FCC GST. The adjacent layer to Te is Sb in KH sequence and Ge in Petrov sequence. Previous first-principles calculations show that KH sequence is more stable than Petrov or mixed sequences (*4*, *11*). We calculated the total energy for atomic migration to find the minimum energy (energetically favorable) states.

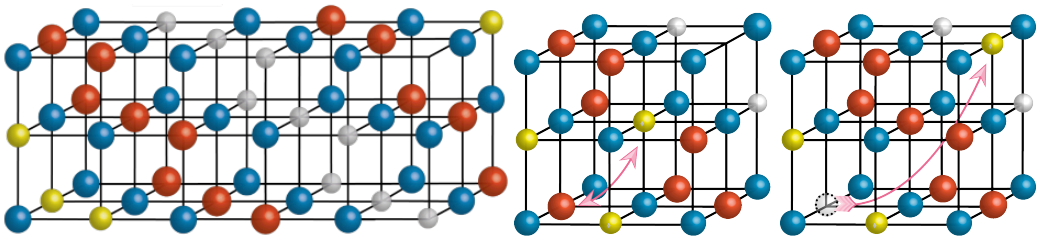

Figure 2 Left, the starting atomic model to emulate metastable FCC GST with KH sequence along the (111) direction (the direction of the short-period superlattice): spheres in yellow, Ge; in purple,

Sb; in blue Te. Vacancies represented by white spheres form ordered layers at initial stages. The Petrov sequence is obtained by switching Ge and Sb layers. Center/right, disorders, Ge<->Sb switching and Ge/Sb->Vacancy migration.

3. RESULTS & DISCUSSION

First we calculated the electronic structure of the GST compounds in Fig. 2. They show significantly different electronic structures near the Fermi level; KH sequence has a direct band gap of 0.26 eV at Γ point whereas Petrov sequence an indirect band gap of about 0.06 eV. While modification by disorders should be considered, KH sequence seems fit experimental observations of the bang gap of 0.3 eV just before the transition into hexagonal structure (*12*).

We believe that KH sequence-like structures are dominant in GST compounds during the transition between meta-stable FCC and more-ordered structures. But in reality (and also for more rigorous checkup), mixed structures of KH and Petrov sequences should not be ruled out. Figure 3 shows calculated electronic band structures upon exchange of Ge and Sb atoms that emulates the structural transition from KH to Petrov sequences. It is found that the valence bands move upward upon the exchange and, when half of Ge atoms are swapped with Sb, the band inversion occurs at Γ point and GST becomes topological insulator. This behavior of the band inversion gives an interesting implication that GST in meta-stable FCC structures may possess different electronic properties, in particular with respect to the topological insulating property. It is reasonable physical intuition to believe that the electronic property goes in parallel with the atomic ordering (in particular, the long-range ordering). But this may not be true for the topological insulating property. If meta-stable GST can possess different topological insulating properties, dissipationless conducting channels may exist at grain boundaries, governing the heat and electrical conduction. Also FCC GST having multi-level states may be designed by controlling the mixing rate.

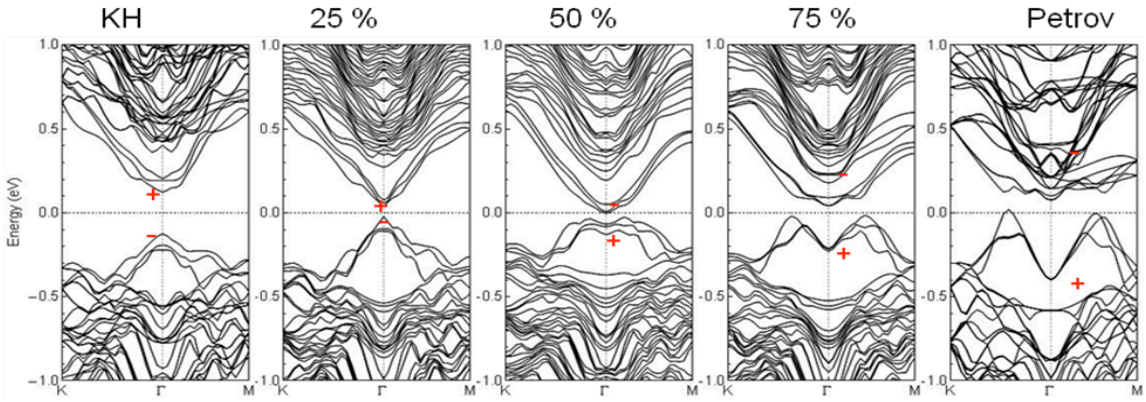

Figure 3 Calculated band structures of GST225 in FCC-like structure as depicted in Fig. 2 upon exchange of Ge and Sb atoms. The signs (in red) at the valence band top and the conduction band bottom indicate the parity of the states. Starting from the KH sequence, the compound experience a continuous transition to the Petrov sequence. The band inversion (the parity reversal) occurs at an exchange rate of about 50% and GST225 becomes topological insulator.

A next question is what possible atomic structures are for meta-stable GST considering all Ge, Sb, and vacancies that occupy one sublattice of the rock-salt structure without the long-range order. To address this issue, we investigated the structural stability of GST compounds for three different types of disorders; the migration of Sb or Ge atoms into vacancy sites and the interchange of Sb and Ge (Sb->V, Ge->V, Ge<->Sb). The relative energy of GST compounds was calculated up to a disorder ratio of 20 %. Our calculations show that Sb->V migration is unstable but Ge->V migration at 2% disorder ratio is more stable than the starting KH sequence (Fig. 2). Ge<->Sb exchange stabilizes GST compounds until 20% mixing rate. Being small and thus easy to migrate at low temperatures, Ge

migration is central to the process of hexagonal - FCC phase change. Our calculations indicate that meta-stable structure may be formed by a substantial amount (a few tens percentage) of Ge-Sb interchange and by a small amount of Ge migration into vacancy sites. If thermal energy (entropy in particular) is considered, Ge(Sb)->V ratio may go up higher. We will discuss the energetics associated with the increase in disorders [Ge(Sb)->V] and the change in the band structures. We also calculated the change in the lattice constant upon the increase of the disorders. The lattice constant is the most sensitive to Sb->V migration while much less sensitive to Ge->V. The shrink in the lattice constant at elevating temperatures is thus attributed to the ordering of Sb atoms. Combining the behaviors in the atomic migration and the lattice constant, we will propose a pathway of the structural transition from cubic to hexagonal structures and related changes in the electronic structures. More details and related figures will be presented at the conference.

4. CONCLUSION

We studied the topological insulating property and the atomic structure of metastable FCC GST compounds using first-principles calculations. Upon the exchange of Ge and Sb atoms, we showed that GST in FCC-like structure experiences a transition in the topological insulating property. We also investigated the energetics of atomic disorders that may occur in the hexagonal-cubic transition, the behavior of the lattice constants, and consequent changes in electronic structures upon atomic disorders.

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Biographies

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