

# Calculation of interfacial energy for design of phase change materials

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## Abstract

**As theoretical approach to design an engineered phase change material, Bi-doped InSbTe (Bi-IST), we have quantitatively calculated how interfacial energy affects the kinetic reactions among amorphous, nucleation, intermediate, and crystallization during the phase transition of Bi-IST. As a result, it is found that the phase transition occurs at lower energy barrier through the heterogeneous nucleation of crystalline InTe on the interface of crystalline InSb owing to amorphous Bi dopants.**

## 1. Introduction

Phase-change random access memory (PCRAM) has been investigated as a next-generation device. The PCRAM stores signals delivered by reversible phase change process between crystalline and amorphous phases. PCRAM will be applied to various field such as embedded memory, neuromorphic system, and 3D cross memory with fast set and reset speeds, long retention, and good endurance.

Despite these advantages, to secure the stability of phase transition process for reliable operation of PCRAM, the fast transition from metastable to stable crystalline phases is essential. The stable phase can prevent element segregation and phase separation during repeatedly reversible phase transition. For the PCRAM, GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudo-binary system has been popularly used, and other Te-based PCMs such as InSb-InTe pseudo-binary systems are suggested to improve the performance of PCRAM [1-2]. In the case of GST along with GeTe-Sb<sub>2</sub>Te<sub>3</sub> pseudo-binary system, the crystalline phases are divided into two, metastable and stable phases, and the metastable crystalline phase has been dominantly used as a crystalline phase for state '1'. However, greater stability of PCMs is now demanded since the metastable crystalline phase causes serious problems, which trigger resistance drift and cell failure during countless operations. For this reason, doping method has been chosen to solve and improve phase transition system and characteristics of PCMs such as endurance, retention, and switching speed [3-4].

A lot of dopants in GST and IST materials have been researched in terms of electrical characteristics, crystal structure, chemical bonding, change of phase transition temperatures, and so on. In our previous works [5], the set and the reset switching speeds of PCRAM fabricated with the Bi-doped IST, and Bi<sub>5.5</sub>(In<sub>3</sub>SbTe<sub>2</sub>)<sub>94.5</sub> is clearly faster than those of the devices fabricated with pure IST and GST.

To use such novel material, control of phase transition

process is vital. Reliability of the material is one of the most considered factors to apply to real industry. For this reason, the phase transitions of IST and Bi-IST are discussed with the effect of interfaces induced by dopant clusters through comparison between IST and Bi-IST materials in the metastable intermediate phases. The phase transition processes are divided into three steps from amorphous to stable crystalline phases, in this study, two steps for stable transition are discussed with interfacial energy induced by amorphous clusters of dopants. The difference of phase transition processes in IST and Bi-IST is thoroughly explained with the effect of formation of interfacial energy with dopant on reduction of energy barrier and change of total Gibbs free energy with bulk energy and TΔS term for phase transition. It will be applied to design for noble PCMs.

## 2. Experimental

Density functional theory (DFT) calculations are performed using Vienna Ab initio Simulation Package (VASP) code. For the DFT calculations on IST, InSb, and InTe as well as Bi-doped IST, InSb, and InTe, the plane-wave basis set is expanded to a cutoff energy of 400.00 eV and the fully relaxed IST supercell model consisting of 64 atoms is used and the average dimension is 12.540 Å. The 4 × 4 × 4 and 2 × 2 × 2 k-point grids generated by the Monkhorst-Pack scheme [6], and the projector-augmented waves (PAW) and the generalized gradient approximation (GGA) are used for the calculation of formation energy corresponding to unit cells and supercells of InSb and InTe that are produced as intermediate phases during the phase transition from amorphous to crystalline IST. The supercells of InSb and InTe consist of 64 and 128 atoms, respectively, with stoichiometry of In:Sb and In:Te. The ionic relaxations of supercells were done using the conjugate-gradient method. The force convergence criterion was set to 0.02eV/Å along all directions. Since the formation energy will be changed by Bi-doping, the formation energy difference (ΔE<sub>f</sub>) between InSb and Bi-doped InSb or between InTe and Bi-doped InTe is calculated by the following equation:

$$\Delta E_f = E[\text{InSb:Bi (or InTe:Bi)}] - [E\{\text{InSb (or InTe)}\} + E_{\text{Solid}}^{\text{Bi}}],$$

where  $E[\text{InSb:Bi (or InTe:Bi)}]$  is the total energy of the Bi-doped InSb or InTe supercell,  $E\{\text{InSb (or InTe)}\}$  is the total energy of the defect-free InSb or InTe,  $E_{\text{Solid}}^{\text{Bi}}$  is the chemical potential of Bi atom. In addition, the calculated values of heats of formation are nearly similar with the experimental results of the previous literatures, InSb (0.35 eV/f.u.) and

InTe (0.74 – 1.00 eV/f.u. Since DFT calculations in this work are mainly used to obtain the energetic parameters for bond formations and breaking, we examined the validity of our computation by comparing the theoretical and experimental heats of formation. To determine the difference in Gibbs free energy for phase transition from the intermediate phases to crystalline IST and Bi-IST, the bulk energies of IST and Bi-IST are calculated by the equations of  $\{E(IST) - E(InSb) - E(InTe)\}/64$  and  $\{E(Bi-IST) - E(InSb) - E(InTe) - E(a-Bi)\}/64$ , respectively.

### 3. Results and discussion

Figure 1 shows that the schematic of heterogeneous nucleation for crystalline InTe with or without amorphous Bi atoms on the interface of crystalline InSb.

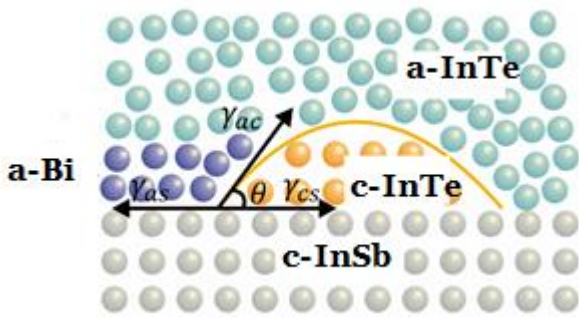


Figure 1. Heterogeneous nucleation of crystalline InTe on the interface of crystalline InSb. Amorphous Bi atoms are involved into the nucleation of InTe on the violet color region.

When Bi is added for the crystallization of InTe, the crystallization of InTe is faster than that of InTe without Bi atoms. The result was already published by our previous work [5] in terms of experimental analysis. To determine quantitatively how interfacial reactions affect the kinetic behaviors among 4 different phases consisted of crystalline InSb, amorphous InTe, crystalline InTe, and amorphous Bi, the interfacial energy per unit area is calculated by equation (1) for five different combinations of the interface between each two phases:

$$\gamma_{as} = \gamma_{cs} + \gamma_{ac} \cos \theta \quad (1),$$

where the subscript, a, s, and c mean the amorphous phase, the substrate for heterogeneous nucleation, and the crystalline phase, respectively.  $\gamma_{as}$ ,  $\gamma_{sc}$ , and  $\gamma_{ac}$  are the interfacial energies per unit area for five different interfaces between a-InTe (or a-Bi)/c-InSb, c-InTe/c-InSb, and a-InTe (or a-Bi)/c-InTe. With the equation (1), the heterogeneous nucleation can be explained with the classical model for energy barrier [7]. The energy barrier for heterogeneous nucleation of crystalline InTe ( $\Delta G_c \equiv \Delta G_c^{het}$ ) can be expressed as equation (2):

$$\Delta G_c^{het} = \Delta G_c \cdot f(\theta), \quad f(\theta) = \left[ \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4} \right] \quad (2),$$

where  $\Delta G_c$  is the energy barrier for the homogeneous nucleation of InTe without Bi, and  $\theta$  is the wetting angle between amorphous and crystalline InTe grown on the InSb surface. The interfacial energies of c-InTe/c-InSb, a-InTe/c-InSb, a-InTe/c-InTe, a-Bi/c-InTe, and a-Bi/c-InSb are 10, 27, 33, 29, and 28 meV/Å<sup>2</sup>. From the equation (2), if the energy barrier

for homogeneous nucleation is 1, the energy barrier for heterogeneous nucleation ( $\Delta G_c^{het}$ ) can be determined by the function of wetting ( $f(\theta)$ ) and the value will be 0.148 without dopant. However, this energy barrier for heterogeneous nucleation is reduced to 0.0943 by adding Bi dopant. This calculation clearly suggests that energy barrier could be dominantly reduced from 0.148 to 0.0943 by the interfacial reaction with amorphous Bi. Therefore, adding Bi dopant in IST material improves crystallization speed for InTe in the intermediate process.

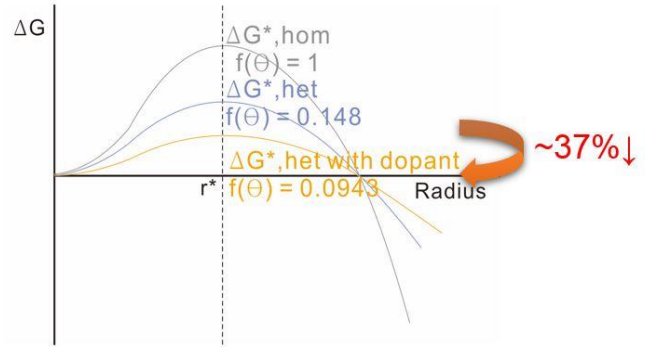


Figure 2. Comparison of energy barrier for homogeneous nucleation and heterogeneous nucleation of crystalline InTe on the interface of crystalline InSb.

### 4. Conclusion

We have explained the effect of interfacial energy induced by Bi dopant on phase transition of IST. But, it is generally useful to understand the effect of dopant in the complicated ternary phase transition process from metastable to stable phases in the view point of the interfacial reactions. In crystalline InSb and amorphous InTe phases, InTe phase is relatively easy crystallized with reduction of energy barrier by amorphous Bi clusters. The phase transition is easily performed by the heterogeneous crystal nucleation with amorphous Bi clusters. This theoretical approach to calculate interfacial energy for stable phase transition will be very helpful to design stable phase change materials.

### 5. Acknowledgements

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