

# What is the Origin of Activation Energy in Phase-Change Film?

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Activation energy is one of the basic parameters used to estimate the physical and chemical features of optical and electrical phase-change (PC) films. However, its origin has not been discussed well because of insufficient understanding of the amorphous structures. In this paper, we reveal the origin of the activation energy using a GeSbTe-superlattice model and *ab-initio* local density approximation (LDA) calculations. The simulated energy required for transition from amorphous to crystal formation in a 9-atomic system was 2.34 eV; This is in good agreement with experimentally reported values. © 2009 The Japan Society of Applied Physics

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## 1. Introduction

Chalcogenide phase-change materials are highly attractive, not only for optical data storage, but also for the next generation solid-state memories. Among them,  $\text{Ge}_x\text{Sb}_y\text{Te}_{1-x-y}$  and Sb-rich Te with or without additives are the most important alloys. High-speed switching, long-term durability at high-temperature and high read-write cyclability are requirement for both types of memories. In optimizing such physical requirements, thermo-physical constants and parameters in the materials are highly important. "Activation energy",  $E_a$ , is one of the intrinsic and especially important parameters related to chemical reaction or transition speed. It has been applied to the understanding of phase-change mechanisms for the last 40 years and several experimental methods such as Kissinger's plot have been used to evaluate it.<sup>1,2)</sup>  $E_a$  of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  has been reported by many groups with different deposition conditions for the last 20 years, and almost all values are scattered between 2.2 and 2.6 eV as summarized in Table I.<sup>3-10)</sup> Although  $E_a$  converges to a meaningful average, unfortunately, until now, nobody has given the exact answer nor the origin of 2.2–2.6 eV. Here we have one question: if a random model of the amorphous structure were true, should not  $E_a$  depend on the level of randomness and give a much bigger deviation around the average? As a result, the energy would take a stronger correlation with the film fabrication condition, rather than with the composition ratio. Reconsidering  $E_a$  from a perspective of physics to chemistry, the definition becomes much clearer. In chemistry,  $E_a$  is determined as an energy difference between an initial state of starting molecules and a *complex molecule*, which is an intermediate state with a higher energy to lead a final state (*product*).<sup>11)</sup> But, it should be noticed that the Gibbs free-energy of formation is only determined by the difference between the initial and the final states: not by  $E_a$ . For example, the formation energy of water (vapor) is only the difference from  $\Delta G_f = G_f(\text{H}_2\text{O})_{\text{gas}} - G_f(\text{H}_2) - G_f(\text{O}_2)$ . However, the gas mixture of  $\text{O}_2$  and  $\text{H}_2$  cannot produce  $\text{H}_2\text{O}$  as they are without some triggers (spark or catalysis), of which the energy is defined as  $E_a$ .

In this paper, based applying the Kolobov model for Ge-switching between octahedral and tetrahedral coordination to a superlattice of a  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  phase-change alloy, which is composed of two main components: a  $\text{Ge}_2\text{Te}_2$  layer unit

**Table I.** Activated energies of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  alloys reported in literature.

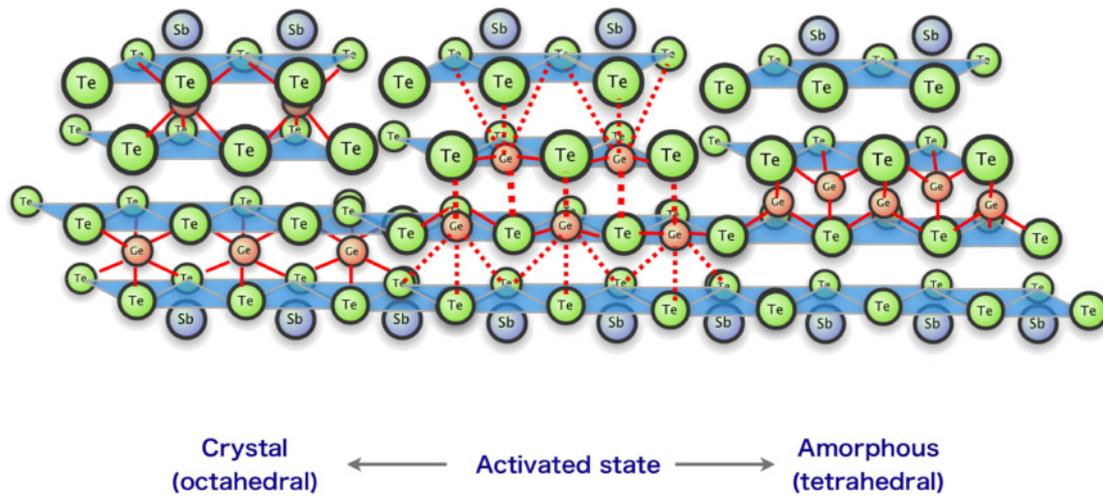
Reference	Evaluated $E_a$ for GST(225) (eV)	Sample preparation	Method
3	2.23	Scratched single film powder	DSC
4	2.26	Scratched single film powder	DSC
5	$2.24 \pm 0.11$	Scratched single film powder	DSC
6	2.3	Scratched single film powder	DSC
7	$2.9 \pm 0.5$	Scratched single film powder	TEM?
8	2.5	Sandwiched film on glass	Optical transition
9	$2.29 \pm 0.09$	Single film on glass	Optical transition
10	2.6	Unknown	Unknown

and another  $\text{Sb}_2\text{Te}_3$  layer unit, we theoretically estimate  $E_a$  by first-principle quantum chemical simulation.<sup>12,13)</sup>

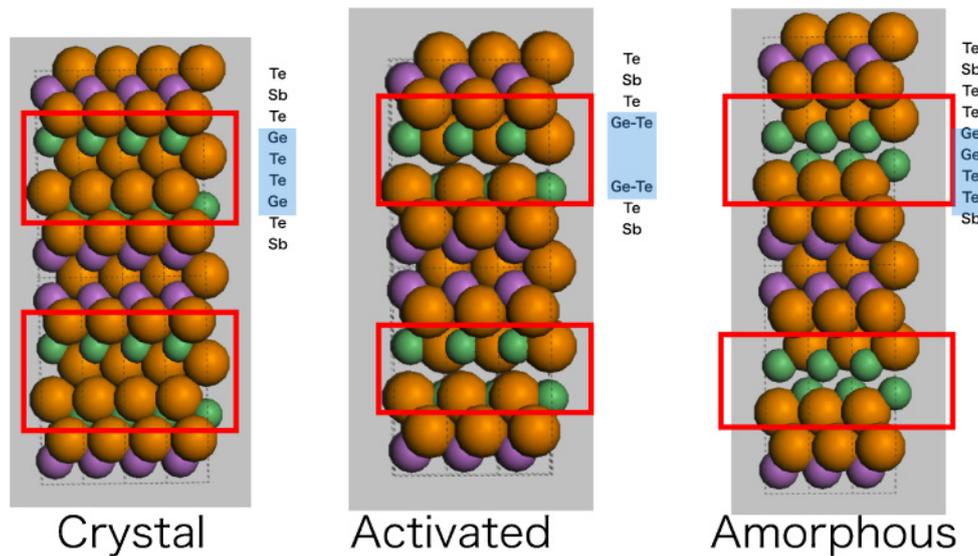
## 2. Model of Activation State

As already reported, it was clear that the index change of refraction in  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  is theoretically reproduced by the exchange of Ge and Te layers between two states:  $[-(\text{Te}-\text{Sb}-\text{Te}-\text{Sb}-\text{Te})-(\text{Te}-\text{Ge}-\text{Ge}-\text{Te})]_n$  in the *amorphous* and  $[-(\text{Te}-\text{Sb}-\text{Te}-\text{Sb}-\text{Te})-(\text{Ge}-\text{Te}-\text{Te}-\text{Ge})]_n$  in the *crystal*.<sup>12,13)</sup> Both have A-7 like structures but the volume of the amorphous structure is slightly larger than the crystal. This is due to the generation of a small space or an imaginary layer for charge-balance between the two *Ge* layers. To generate the transition between the two states, the *Ge* and *Te* layers must diffuse into their respective layers mutually. It is known that both states have an energy minimum and take a stable state respectively and it is thought that the superimposed state of the layers must be a transition state or a *complex molecule* with an associated  $E_a$  for the phase transition. The reaction is depicted in Fig. 1. It should be noticed that in the transition the first *Ge* layer moves downwards and superimposes on the second *Te* layer, while the second *Ge* layer moves upwards and superimposes on the third *Te* layer. The first *Ge* layer makes new bonds with the third *Te* layer, and the second *Ge* layer oppositely makes further new bonds with the second *Te* layer.

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**Fig. 1.** (Color online) Three phases of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> super-lattice structures. Left: crystal state composed of Ge octahedral coordination (six bonds), Center: activated state, and Right: amorphous state composed of Ge tetrahedral coordination (four bonds).



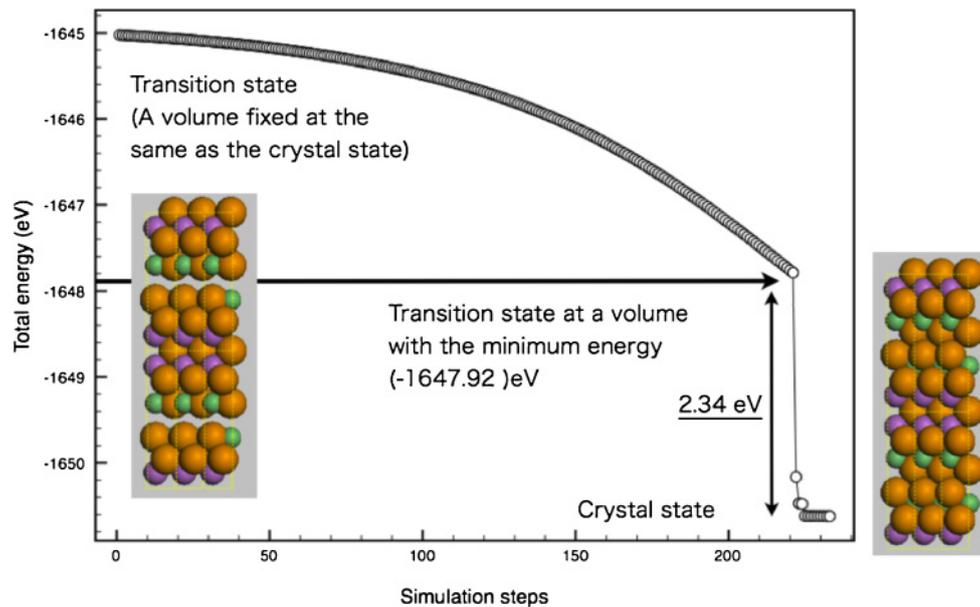
**Fig. 2.** (Color online) Three computer models for crystal (left), activated (center), and amorphous (right) states. Big, middle and small balls are Te, Sb, and Ge, respectively.

### 3. Local Density Approximation Simulation for Activation Energy

We estimated three different super-lattice models as shown in Fig. 2. All simulations were carried out using a local density approximation (LDA) method with plane wave basis sets as Schrödinger wave functions. Ultrasoft pseudopotentials were employed in each atom. Spin polarization was neglected. The triginal primitive cells with nine atoms (two Ge, two Sb, and five Te atoms, respectively) were picked up. The valence electrons in the s- and p-orbitals: 4s<sup>2</sup> 4p<sup>2</sup> for Ge, 5s<sup>2</sup> 5p<sup>3</sup> for Sb and 5s<sup>2</sup> 5p<sup>4</sup> for Te were adapted in the basis set, but d-electrons were not included. The self-consistent total energies were obtained using a density-mixing scheme in connection with a conjugated gradient technique. The total energy was calculated to take into account the relaxation of the lattice constants and internal atomic positions in the amorphous and crystal structure, while the relaxation of internal atomic positions was constrained in the

transition structure in some cases. Atomic positions were optimized by means of the quasi-Newton method within the Broyden–Fletcher–Goldfarb–Shanno scheme. The forces on each atom were relaxed to less than 0.01 eV/Å.<sup>12)</sup>

The calculated total energy in the crystal model was -1650.62 eV with a cell volume of 256.13 Å<sup>3</sup>, while that in the amorphous model was -1650.26 eV and 261.21 Å<sup>3</sup> for nine atoms (two Ge, two Sb, and five Te). The difference of the energies was just 0.37 eV (40.6 meV/atom), which was very close to 36 meV/atom calculated in the transition between distorted cubic and a spinel amorphous model of a Ge<sub>1</sub>Sb<sub>2</sub>Te<sub>4</sub> system.<sup>14)</sup> The volume change between the two states was about 2%. In contrast, the total energy and the volume calculated in the transition model were -1647.92 eV and 285.33 Å<sup>3</sup> at the free-volume condition of the lattice parameters. The volume was +11.4 and +9.4% as large as the crystal and amorphous ones, respectively. Interestingly, the energy difference between the transient state and the amorphous state for the one molecular cell of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>



**Fig. 3.** (Color online) Energy transition from the activated state into the crystalline structure. After the activated energy obtained, the energy state was recalculated under free-lattice and free-atomic position.

(nine atomic system in our simulations) was just 2.34 eV, which was in good agreement with ones reported experimentally. On the other hand, the total energy in the transition state for a fixed volume to the crystal model was  $-1645.06$  eV, which was about 3 eV higher than that of the free-volume condition. Interestingly, once the cell size limit is removed during the simulation, first the volume increases by about 10% and then suddenly Ge atoms transit towards the crystal positions as shown in Fig. 3. According to the results, it is probable that the  $E_a$  experimentally reported with as-deposited films of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  systems is the *Ge-Te* layer exchange energy used to produce the crystalline state. This induces a large reflection or refractive index change. Although some data take a large deviations from 2.34 eV, they were measured not with powders, but with a film deposited on a substrate or a film sandwiched by dielectric layers. In such cases, the interface between the layers and with a substrate may induce a large stress by the volume reduction of phase-change film due to the crystallization. Such a case can also increase or decrease the transition temperature.<sup>2,12</sup> Therefore, our theoretical value of 2.34 eV is in good agreement with data obtained from the powders. Lang *et al.* recently estimated  $E_a$  from a cubic structure (distorted NaCl) based on the Kolobov model by LDA based molecular dynamics at 400 and 500 K.<sup>15</sup> They concluded that  $E_a$  is 0 eV, which is very strange against many experimental data. This is because a (*NVT: a state with fixed atom number, volume and temperature*) ensemble average was picked up in their molecular dynamics and a small volume change was neglected during the phase transition. In this meaning, we can conclude that the volume change during the phase transition is a driving force of a Ge atom flip-flop.

#### 4. Conclusions

We estimated the activation energy of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  based on the Kolobov model by first principle computer simulation. A

calculated value for the exchange of *Ge-Te* layers was 2.34 eV, which was very much compatible to ones reported experimentally. According to these results, the activation energy from GeSbTe amorphous to crystal or *vice versa* is probably attributed to a transition state whereby the exchange of Ge and Te layers occurs in the film.

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