The origin of activation energy in phase-change materials

J. Tominaga, T. Shima, R. Simpson, M. Kuwahara, P. Fons, and A. Kolobov

Center for Applied Near-Field Optics Research (CAN-FOR)
National Institute of Advanced Industrial Science and Technology (AIST)
Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, Ibaraki, 305-8562, Japan
J-tominaga@aist.go.jp

ABSTRACT

Recently, the theoretical analysis of phase-change switching and the structures have been revealed. Among them, the mechanism and structure of GeSbTe are on the hottest topics. To crystallize as-deposited amorphous or re-amorphized phase to crystal phase, it needs "activation energy, ***Ea***" which has been estimated by Kissinger-plot. ***Ea*** obtained from powders are usually reported around 2.3 eV in $Ge_2Sb_2Te_5$ alloy. However, no theoretical work has been reported to evaluate the value. In this paper, we first calculated activation energy of $Ge_2Sb_2Te_5$ by local density approximation (LDA) by the hexagonal model based on Kolobov switching model. It was found that ***Ea*** is 2.34 eV, which is attributed to threshold energy of a Ge atom penetrating a plane consisted of three Te atoms.

Key words: GeSbTe, activation energy, local spin density approximation.

1. INTRODUCTION

Activation energy ***Ea*** is one of the most fundamentally chemical parameters to estimate chemical reaction and to determine a route in many chemical processes. It was first introduced into chemical reaction by one of the founders of chemical physics, Svante August Arrhenius. He introduced a chemical reaction rate k, which is a function of ***Ea***, *R*, and *T*: $k = A \exp(-Ea/RT)$. Hence R and T are gas constant and absolute temperature, and A is called *frequency factor*. An activation state is usually a transition state in chemical reaction between an initial and terminal product [1]. Therefore, a transition state or complex must be generated in a moment.

On the other hand, activation energy used in phase-change transition is somewhat different from the original theory of activation energy. In Avrami theory (JMA model), k corresponds to a temperature dependence rate of crystallization. Therefore, the meaning of Ea in JMA model should not be limited to a nucleation model itself, which is related to a balance of a Gibbs free energy formation of crystal nuclei in surrounding liquid phase, but should be attributed to more fundamental transition state of something generated in the quasi-thermo-equivalent system. Table-1 summarized several Ea values of $Ge_2Sb_2Te_5$ alloy reported in journals up to now [2-9]. Although the data were obtained at different laboratories and by different ways and conditions, almost data were scattered around 2.3 eV. It means that a ***universal transition state*** is hidden in the crystallization in prior to nucleation and growth.

Table-1 $Ge_2Sb_2Te_5$ alloy's Ea reported in journals

Reported journals	Experimental Ea
Yamada et al. : J. Appl. Phys. 69 (1991)	2.23 for GST225
Seo et al. Jpn. J.Appl. Phys. 39 (2000)	2.26 for GST225
Friedrich et al. J. Appl. Phys. 87 (2000)	2.24 ±0.11 for GST225-cubic
Park et al. Jpn. J.Appl. Phys. 38 (1999)	2.3 for GST225
Privitera et al. J. Appl. Phys. 84 (2004)	2.9 ±0.5 for GST225
Men et al.: Jpn. J.Appl. Phys. 40 (2001)	2.5 for GST225
Morales-Sanchez et al.: Thin Solid Films 471 (2004)	2.29 ±0.09 for GST225-cubic
Lacaita: Solid State Electronics 50 (2005)	2.6 for GST225

In this work, we examined the ***transition state*** attributed to Ea by local spin density approximation (LSDA) using a hexagonal model of $Ge_2Sb_2Te_5$ alloy.

2. MODEL AND SIMULATION

Let's consider a Kolobov model of transition in a GeSbTe system [10]. As shown in Figure 1, the crystal has a Ge atom with an octahedral coordination in fcc-Te lattice, while the amorphous has a Ge atom with a tetrahedral one.

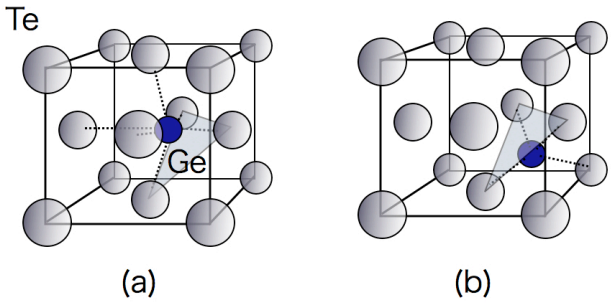


Figure 1 Kolobov phase-change model of Ge flip-flop. (a) crystal and (b) amorphous.

It should be kept in mind that a Ge atom must once penetrate a triangle plane made of three Te atoms in transition. In Kolobov model, therefore, the plane consisting of one Ge atom and three Te atoms is probably thought to be a transition state or a molecular complex in chemical reaction. In order to understand the transition state, the coordination of the other Sb atoms and Ge atoms should be considered [11]. Figure 2 depicts three states in hexagonal phase: crystal, transition state and amorphous.

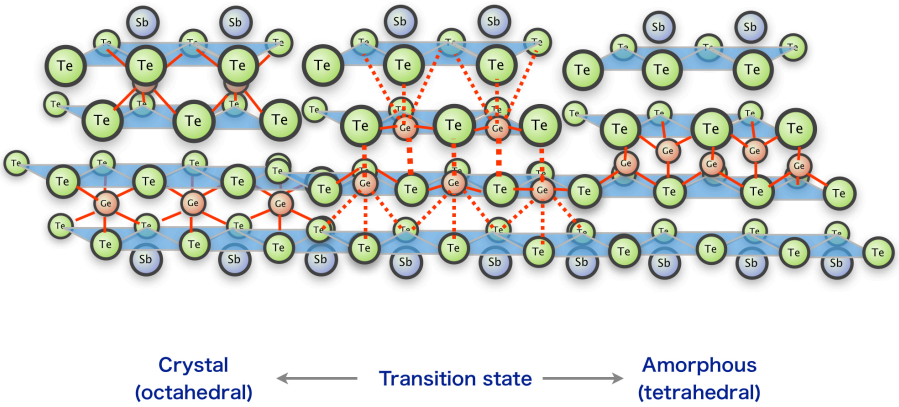


Figure 2 The movement of Ge atoms between crystal and amorphous through a transition state in hexagonal phase.

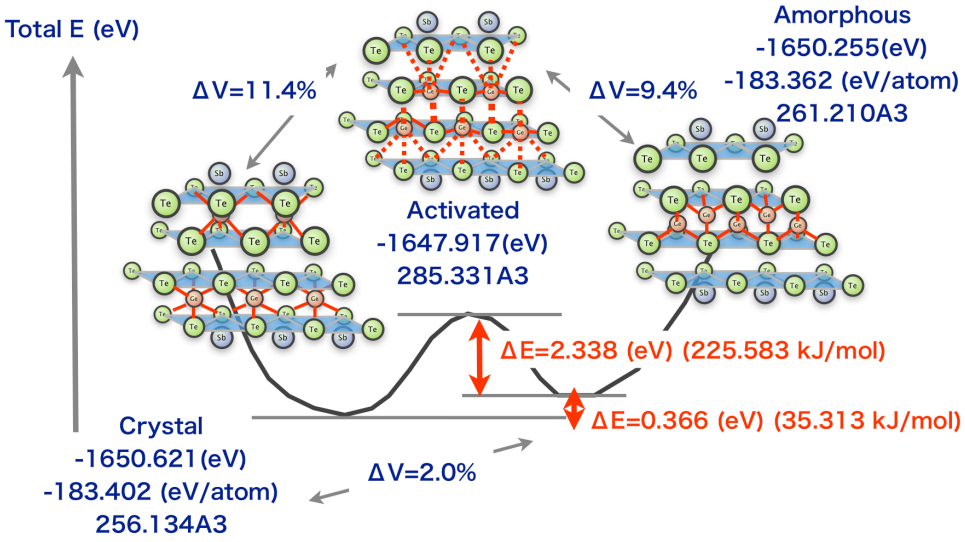
In crystal, Ge atoms hold 6 bonds with surrounding Te atoms (left), while Ge atoms hold four bonds with Te atoms (right). Hence, Ge positions take an edge shearing connection each other. In the middle, transition state, Ge atoms sandwiched between top two Te layers come down, while Ge atoms sandwiched by bottom two Te layers go up. Both atoms top and bottom however must penetrate Te planes. The energy to make the transition state must be the activation energy.

Under the assumption, we made three different computer models shown in Figure 2, and calculated the total energies in each condition by local density approximation (LDA). Hence, we considered a volume-free transition and

its locked condition in the crystal. The cut-off energy of 230 eV, and ultra-soft potentials were used in LSDA. The number of the unit cell was made of 9 atoms: two Ge, two Sb and five Te atoms in a hexagonal primitive cell. 7×7×1 *k* points were calculated to estimate the electronic structures. The simulation step was carried out by the energy deviation < 5×10^{-6} eV/atom, and by Hellmann-Feynman force < 1×10^{-2} eV/A.

3. RESULTS & DISCUSSION

In Figure 3, each total-energy (Et), volume (V) and the differences (ΔE & ΔV) among the states was superimposed on the transition models.



Et in the crystal was –-1650.621 eV, while Et in the amorphous was –1650.255 eV. The deviation of both was 0.366 eV, which was very close to a reference one [12]. The volume change between the amorphous and crystal was 2.0% in the hexagonal phase. However, at the transition state, the activation energy was increased by –183.102 eV/atom. In addition, the volume was increased by 9.4% to the amorphous and 11.4% to the crystal. The energy change between the amorphous and the transition state was amazingly 2.338 eV per one $Ge_2Sb_2Te_5$ unit, which was very close to experimental values listed in Table 1. Our own experimental data from the re-amorphized film by laser to the crystal was 2.33±0.04 eV [13].

4. CONCLUSION

We first estimated activation energy Ea of $Ge_2Sb_2Te_5$ alloy theoretically by LDA method. The simulated result showed Ea=. 2.338 eV, which was in good agreement with 2.33±0.04 eV experimentally measured from the re-amorphized film. It was theoretically revealed that activation energy is attribute to a transition state consisting of one Ge atom and three Te atoms.

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Biographies

I was born in 1959 in Japan. I got my Ph.D .in material science from Cranfield Institute of Technology, UK (Cranfield University) in 1991. For more than 20 years, I have been involved in data storage research, especially in phase-change re-writable disk and ultra-high density optical data storage using optical near-field. I have been the director of center for Applied Near-Field Optics Research (CAN-FOR) in National Institute of Advanced Industrial Science and Technology (AIST) since 2003.