Thermal Properties of Atomically Controlled [GeTe/Sb_2Te_3] Superlattice.

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GeSbTe ternary alloy is a very attractive material not only for rewritable DVD (DVD-RAM) but also realizing solid state PCRAM. Recently, the study of the switching mechanism between the amorphous and the crystal has rapidly increased experimentally and theoretically. Now, the role of the flip-flop transition of a Ge atom in the distorted sc unit cell becomes the center of the discussion. Turning our focus to a much wider region beyond the cell, it is found that GeSbTe has a superlattice consisting of two sublayers: Sb_2Te_3 and GeTe. Based on this model, we fabricated the superlattice and estimated the thermal properties by differential scanning calorimetry (DSC). In this paper, we discuss the proof of the Ge-switch based on the thermo transition data.

1. Introduction

GeSbTe is one of the attractive materials to realize PCRAM. The ternary alloy, especially, on the tie line connecting GeTe and Sb_2Te_3 is the most promising and reliable composition for the objectives because of its high-speed switching and superb read-write cyclability. The alloy was first discovered and developed by Yamada *et al*. in the late 1980s, and the physical and chemical properties have been analyzed mainly in their laboratory for more than 20 years [1,2]. In the late 1990s, the first commercialized product was shipped to the market as rewritable optical disk (PD) and followed by DVD-RAM. Thanks to them, many researchers including us have recently been attracted to the alloy and its more detailed analysis, especially, what is *amorphous* in the system. In 2004, we posted a paper to *Nature Materials* with the title "*Understanding the phase-change mechanism of rewritable optical media,*" which created a great sensation to the researchers *what is the amorphous* [3]. At *E*PCOS06*, on the other hand, a group of DSI Singapore proposed a PCRAM with superlattice consisting of GeSb/Sb_2Te_3 sublayers [4]. They showed a cross sectional view taken by transmission electron microscope in which the superlattice was preserved even after 10^5 read-write cycles. *The E*PCOS06 award winner's paper* was very attractive and woke us up again *what is the switching mechanism to induce a great change on optical constants and on electrical conductivity.* A theoretical paper published in *Nature materials* from professor Wuttig's group of Aachen in Germany in 2006 supported "*the new amorphous model,*" and concluded that the amorphous has a similar structure *to spinel*, resulting in *Ge flip-flop transition* between tetrahedral and octahedral [5].

In this paper, we fabricate a superlattice of GeSbTe based on *the new model*, and reconsider the switching mechanism through the thermal properties.

2. Superlattice fabrication

Thin films consisting of a superlattice of GeTe/Sb_2Te_3 were fabricated by a helicon-wave RF magnetron sputtering method. The system has three independent 2-inch targets

(pure Ge, Sb, and Te) above which a helicon type antenna was fixed to stabilize RF plasma. The distance from the targets to the substrate station was 200 mm. Therefore, no hot plasma contacts a sample surface. A piece of an Al sheet was used as a substrate. In prior to experiment, the layer deposition rates were estimated on a glass substrate by a step profiler (DekTak[3]). The compositions of GeTe and Sb_2Te_3 were determined, comparing the thermal histories by differential scanning calorimetry (DSC, DSC 2910, TA Instruments) with the binary phase diagrams: Ge-Te and Sb-Te. We found that Ge (100W) and Te (13 W) are required to fabricate GeTe(1:1), while Sb (13 W) and Te (13 W) for SbTe(2:3), respectively.

Our fabricated superlattice consisting of Sb_2Te_3 and GeTe is based on t*he new model*. Figure 1 shows projected sheets of $Ge_2Sb_2Te_5$ in cystal (a) and amorphous (b). In the crystal (a), Te (grey), Gb (blue) and Ge (red) are arranged in lattice with some vacancies (20%) to conserve the total charge balance. Each atomic position has an offset from the lattice point. In amorphous, in contrast, Ge atoms in diagonal moves towards the vacancy point to make a pair, as a result the positive charges are pushed out to the original Ge positions (b).

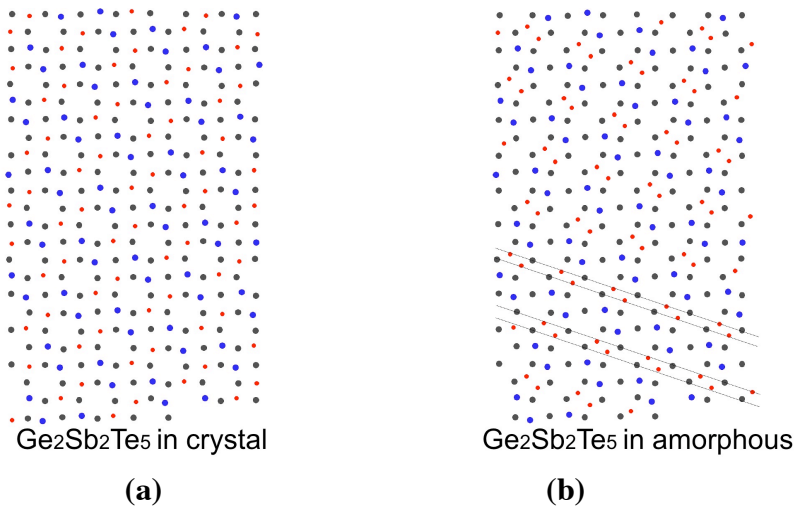

Figure 1 Plane-projected $Ge_2Sb_2Te_5$ model. Crystal (a) and amorphous (b).

As shown in Figure 2, when we superimpose these two sheets, it is clearly understood that $Ge_2Sb_2Te_5$ is made of a stack of $[GeTe/Sb_2Te_3]_n$, where Ge atoms diffuse forwards or backwards to the interface of the layers. This is the switching in *the new switching model*, which must be the ultimate stack of the PCRAM proposed by DSI in *E*PCOS06*.

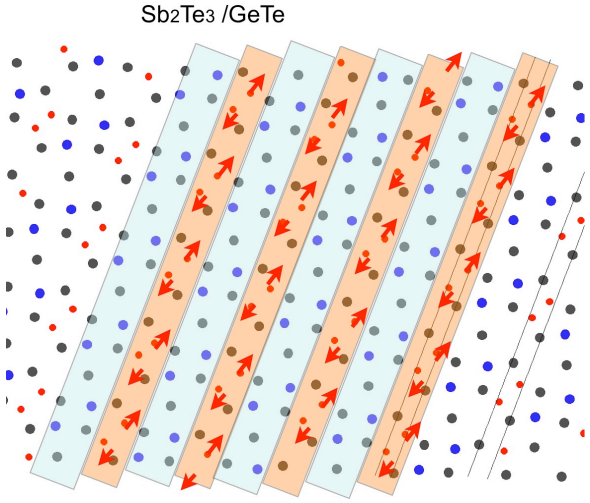

Figure 2 Superimposed images of two projected sheets. Ge atoms (with arrows) in GeTe layers move forwards and backwards to the interface with Sb_2Te_3 layers.

3. Results and Discussion

Figure 3 shows example DSC data for $[GeTe(5A)/Sb_2Te_3(5A)]_{n=20}$ and $[GeTe(5A)/Sb_2Te_3(10A)]_{n=20}$, The total compositions correspond to $Ge_1Sb_2Te_4$ and $Ge_1Sb_4Te_7$, respectively.

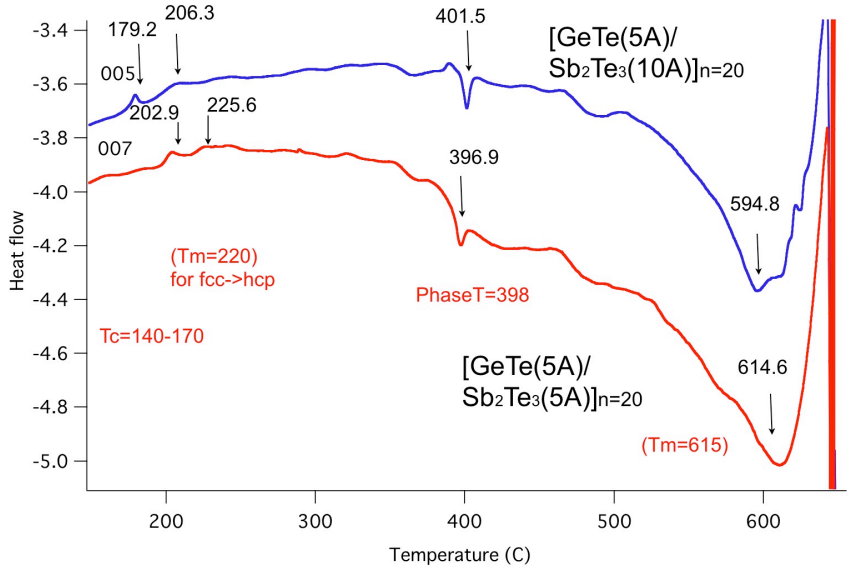

Figure 3 DSC charts of $[GeTe(5A)/Sb_2Te_3(5A)]_{n=20}$ and $[GeTe(5A)/Sb_2Te_3(10A)]_{n=20}$

The melting point of superlattice $Ge_1Sb_2Te_4$ appeared at 614.6ºC against the bulk reference at 605-615ºC. That of superlattice $Ge_1Sb_4Te_7$ showed 594.8ºC against the reference at 593 ºC. According to the good agreement with the bulks, the compositions were probably close to the bulk ones. At low temperature region, we found two transitions: one at 179.2ºC and 202.9ºC, and another at 206.3 ºC and 225.6ºC. However, no large crystallization peak from

as-deposited amorphous in both superlattices. In Sb_2Te_3, a sharp transition of the first transition appeared at 94.2ºC, but no other clear peak was allowed by 451ºC. In GeTe, on the other hand, it showed a large and sharp transition was observed at 181.1ºC, which increased by 256ºC against Te reducing. According to the results, the transition temperature of the superlattices at around 206.3~225.6 ºC are attributed to the GeTe sublayers, and its crystallization under the interface stress. In contrast, the other transitions at 179.2ºC and 202.9ºC were probably due to Sb_2Te_3. As shown in Figure 4, the transition temperature showed a great decrease against the layer thickness. The other remarkable transition was an endothermic peak, which appeared in very narrow temperature range at 396-401ºC, which did little depend on the layer thickness.

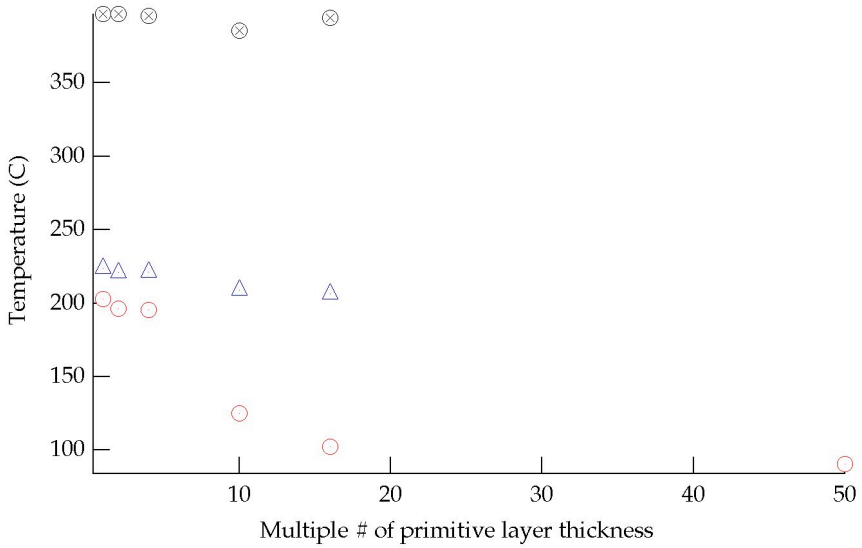

Figure 4 Transition temperatures vs. primitive layer thickness of $Ge_1Sb_2Te_4$

However, each sublayer had no transition temperature at around 400ºC. One of the reasonable explanations is that the composition shift of Ge_1Te_1 to "Te-rich Ge" of the GeTe sublayer. A Te-rich Ge phase may show endothermic peaks at around 388~405ºC from the phase-diagram. The small melting in Figure 3 is probably induced by Ge switch due to producing a rigid crystal form at the interfaces, resulting in a Te-rich composition left. Based on this assumption, it is thought that *the new amorphous transition* occurs at around 400ºC, where the alloy probably conserves the solid phase itself (but a little soft).

4. Conclusions

We fabricated novel superlattices based on the new model, and the Ge switching was confirmed as a heat flow in DSC. We found a small heat absorption due to a composition change of GeTe layers towards Te-rich phase at 395-405ºC before melting.

References:

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