

Theoretical and Experimental Studies on Superlattice $\text{Ge}_2\text{Sb}_2\text{Te}_5$

Junji Tominaga*, Alexander Kolobov, Robert Simpson, and Paul Fons

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 305-8562, Japan
j-tominaga@aist.go.jp

Introduction

Phase change materials, especially Ge-Sb-Te alloys are the promising materials for next non-volatile solid state memory: phase-change random access memory (PCRAM). Since the invention of the alloys in the late 80s^[1], a large amount of research and development has been carried out in order to elucidate the stable switching mechanism, improve life time, cyclability and high-temperature endurance. Although the success of the R&D was first applied to rewritable optical disks, power disk (PD) and DVD-RAM, the switching properties are unsatisfactorily transferred to PCRAM from the point of view of the cyclability and the energy dissipated in comparison with the other competitors. So far, many works have been carried out to improve the cyclability in optical data storage as well as PCRAM. An easy method was to dope a metallic element to a Ge-Sb-Te alloy system, such as Cu or Ag, which prevent the crystalline phase from forming large grains. In contrast, reacting small proportion (< 5 at.%) of relatively light elements, such as N_2 or O_2 was also effective^[2]. Although these supplements made the cyclability a little longer, which is satisfied with the goal of DVD-RAM ($> 10^5 \sim 10^6$), it is still too far from the goal of PCRAM ($> 10^{12} \sim 10^{15}$).

Another method to improve the cyclability without any dopant is to divide a phase change film into each composite element or an alloy of sub-layers, and to reconstruct as a multilayer^[3]. The method was able to increase the Ag-In-Sb-Te (AIST) disk's cyclability from 3,000 to more than 40,000. In optical storage industry, it is unrealistic because such multilayered phase-change films increase a disk production cost. In solid state PCRAM, however, a multilayered phase-change film still has potential since many memory tips are born from one big Si wafer by one parallel deposition, while each optical disk is deposited in series. Chong *et al.* first reported a PCRAM with such a structure: a superlattice-like Ge-Sb-Te film^[4]. Each layer thickness was limited into the thickness of the phase-transition limit reported by Raoux *et al.*^[5]. The internal stress generated between each layer increased the transition temperature from 160°C to more than 230°C^[6]. Therefore, it is important in multilayer fabrication to control the residual stress, although the stress is only one of the driving factors to switch the phase-change film.

In this paper, we discuss on real superlattice Ge-Sb-Te films and simulated models based on the Kolobov switch.

Experimental

Since E*PCOS07, Zermatt in Switzerland, we have reported real superlattice Ge-Sb-Te^[6,7]. Our focus was on fabricating atomic scale superlattices consisting of a stack $[\text{GeTe}/\text{Sb}_2\text{Te}_3]_n$. Hence, n is the repetition number of the stack. In E*PCOS07, we designed the lattice to become a cubic one after annealing. As we reported, the crystallization temperature $T_{C(\text{Sb}_2\text{Te}_3)}$ rose from 90-100°C to 203°C when the Sb_2Te_3 layer becomes thinner to the mono layer. On the other and, $T_{C(\text{GeTe})}$ also rose from $\sim 200^\circ\text{C}$ to 226°C. However, the first small endothermic peak, T_{endo} appears at 396-402°C, which did not depend on the thicknesses. The results show that both sub-layers are put under tensile stresses large or small before crystallization. After the phase transition, the multilayer is further forced

under a stronger tensile condition against the substrate. Therefore, the endothermic peak, which probably corresponds to the melting point of Te-rich GeTe phase, does not shift because the volume expansion to melt is energetically more favorable in the system.

According to the results, a perfect superlattice must be fabricated at a temperature between $T_{C(\text{GeTe})}$ and T_{endo} , otherwise internal stresses generated during the deposition produces dislocations or multi-crystals.

Figure 1 shows a high-resolution TEM view of the superlattice deposited on a Si (100) surface. On a natural SiO_2 layer, the superlattice could be deposited by helicon-wave magnetron sputtering system [6]. The superlattice almost has a [111] face normal to the surface as a cubic lattice: The c-axis [0001] in hcp is normal to the surface.

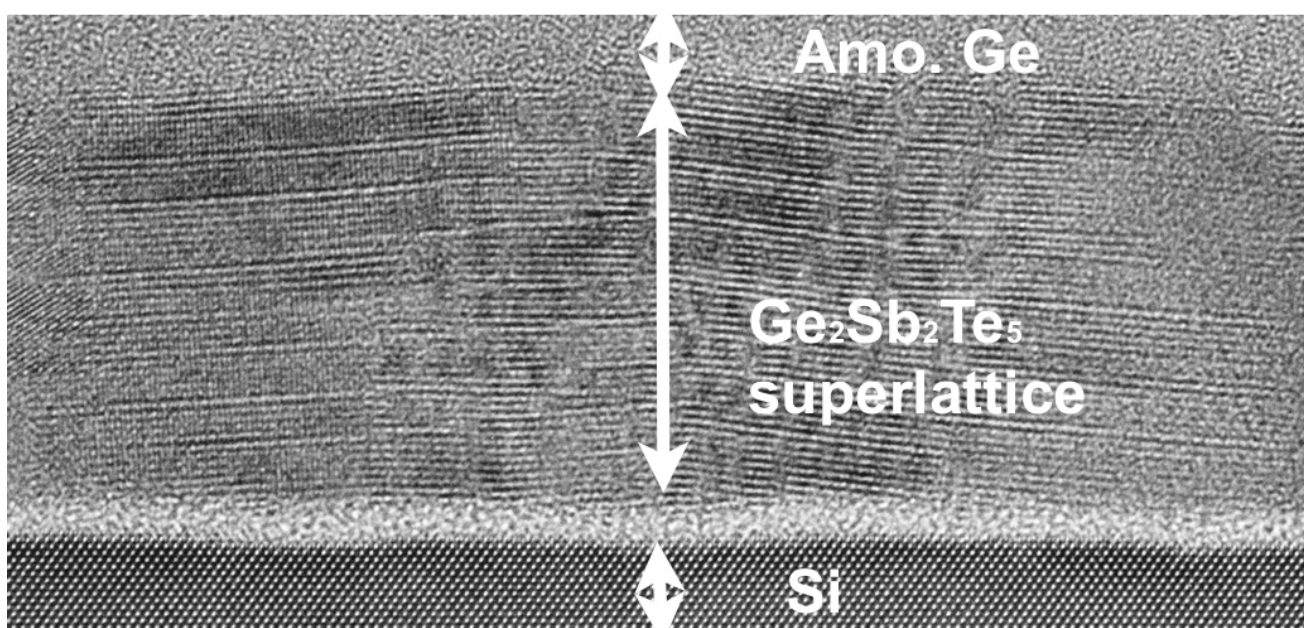


Figure 1 TEM cross sectional view of superlattice $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($[(\text{Ge}_2\text{Te}_2)_1/(\text{Sb}_2\text{Te}_3)_1]_n$)

Molecular dynamics of superlattice $[(\text{Ge}_2\text{Te}_2)/(\text{Sb}_2\text{Te}_3)]_n$

Our superlattice structure was discussed in E*PCOS08 to explain the origin of the activation energy based on the Kolobov model [8]. If the Kolobov switch works in the cubic lattice, it probably does in the hcp lattice. In computer simulation using local density approximation (LDA), the volume change between the two states: $[\text{Sb}_2\text{Te}_3/\text{Ge-Te Te-Ge}]_n$ and $[\text{Sb}_2\text{Te}_3/\text{Te-Ge Ge-Te}]_n$ is only 1%: the former has six-coordinated Ge atoms and the latter has four-coordinated ones. This small volume change between the states is far smaller than that observed in the cubic phase. Thus, a significant improvement in cyclability is likely due to suppression of stress induced fracturing, hence increasing the cell life time. To confirm the switching properties in the LDA computer simulation, we examined the ratio of 4-coordinated Ge atoms to the total Ge ones at a specific condition, using 108 atoms (24 Ge, 24 Sb, and 60 Te). We selected a NVT ensemble (a system with constant atom number, cell volume and temperature) and calculated by 5-ps steps. The volume of the 4-fold coordinated Ge state was set to 102% of the volume of the 6-fold coordinated Ge state, and the simulation was performed at 600K, 900K, 1000K, and 1500K.

Figure 3(a) shows the ratio of 4-fold Ge atoms in each state. Only 4% of Ge atoms takes 4-fold coordinations in the 6-fold Ge state at 600K, while the ratio increases by 33% in the 4-fold Ge state. Interestingly, the ratio in the 6-fold Ge state steeply increases between 900K and 1000K (T_m of bulk Ge₂Sb₂Te₅ ~930K). On the other hand, the ratio is almost constant at 33% by the temperature region and then increases by 63% at 1500K in the 4-fold Ge state. The results are reasonable in comparison with experimental data that the amorphous has 4-fold Ge atoms [9]. The total energy dependence on temperature is also interesting in both states. The energy drop per a Ge₂Sb₂Te₅ molecule is shown in Figure 3(b). At the melting point of the bulk Ge₂Sb₂Te₅, the energy change (we discussed as activation energy in E*PCOS08) are around 2.1-2.6 eV in both states, while it suddenly drops to less than 1.5 eV at 1000K. Therefore, as one would expect, the Ge atoms can move easily above the melting point.

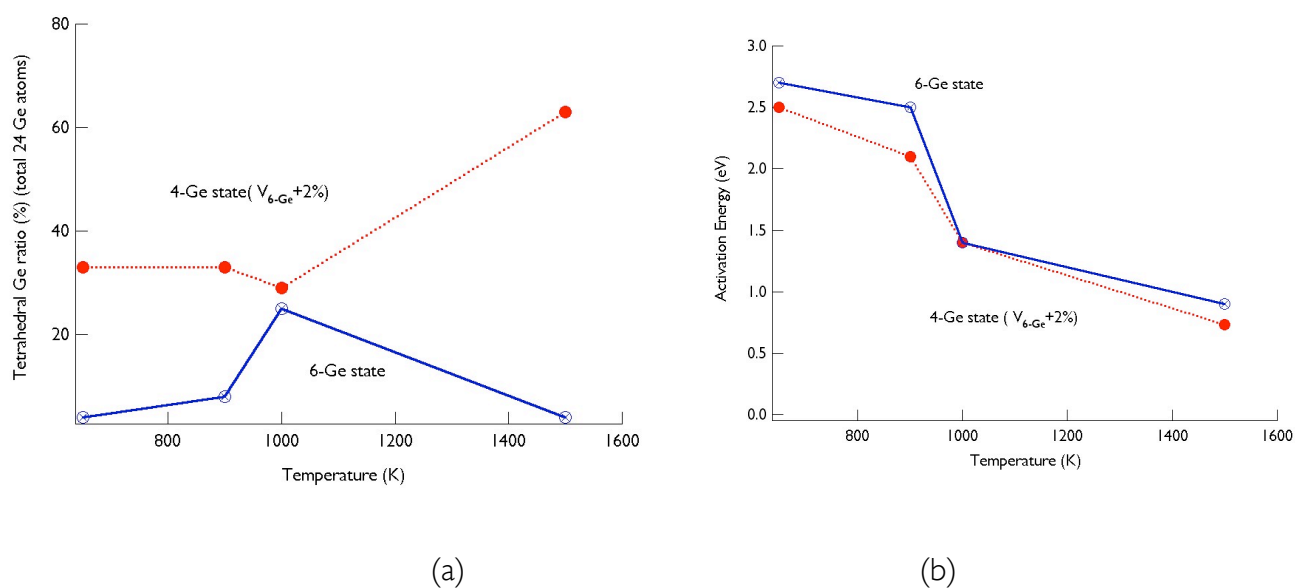


Figure 3 (a) Ratio of 4-coordinated Ge atoms to the total (24 Ge atoms) , (b) the total energy change before and after the simulations

Conclusion

According to the simulations, we can expect that our superlattice [(Ge₂Te₂)/(Sb₂Te₃)]_n can work well as a switching device as well as a single cubic film of Ge₂Sb₂Te₅.

References:

1. N.Yamada *et al.* *J.Appl. Phys.* **69** (1991) 2850
2. R. Kojima *et al.* *Proc. SPIE* **3401** (1998) 14
3. J.Tominaga *et al.* *Jpn.J.Appl. Phys.* **36** (1997) 3598.
4. T. C. Chong *et al.* *Appl. Phys. Lett.* **88** (2006) 122114.
5. S. Raoux *et al.* *Technical digest E*PCOS07*, Zermatt, Switzerland, 2007.
6. J.Tominaga *et al.* *Jpn.J.Appl. Phys.* **47** (2008) 5763.
7. J.Tominaga *et al.* *Technical digest E*PCOS07*, Zermatt, Switzerland, 2007.
8. J.Tominaga *et al.* *Technical digest E*PCOS08*, Praha, Czech Republic, 2008.
9. A. Kolobov *et al.* *Nature Mater.* **3** (2004) 703.