

# Engineering Meta-materials for Future Phase-Change Memory

\*Junji TOMINAGA, Robert SIMPSON, Paul FONS and Alexander KOLOBOV

Functional Phase-Change Device Group (FunPC), Nanodevice Innovation Research Center (NIRC), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 4, 1-1-1 Higashi, Tsukuba, 305-8562, Japan

## Abstract

Phase-change materials have already been installed as a recording film in rewritable optical storages: DVD-RAM, -RW, and Blu-ray. GeSbTe alloys have still been the best materials in the optical storage media as well as phase-change nonvolatile solid state memories. The alloys are pseudo-binaries composed of GeTe and Sb<sub>2</sub>Te<sub>3</sub> compounds. Up to now, the phase-change films have usually been deposited as a single composite layer by physical deposition techniques, and all the physical & chemical properties reported are of the films. In the requirements of faster switching speeds, longer cyclabilities, and more reliabilities in the amorphous and crystalline states, the fine control and advancement of the alloys are now urgent issues, especially in nonvolatile solid state memory using the phase-change mechanism. From the requirement, our group has engaged in fabricating atomically controlled phase-change film (now we call “Phase-Change Meta-material, PCMM”) of GeSbTe, based on the first principle computer simulation since 2007. PCMM is unlike a “superlattice-like” film reported by DSI Singapore [1], is fabricated as a crystal at a high temperature under a strongly oriented crystalline growth condition. Here we report the computer models and real films fabricated based on the simulations, and compared the electrical properties on a real PCRAM device with the same composition single film.

**Keywords:** phase-change film, Ge-Sb-Te, nonvolatile solid-state memory, PCRAM

## 1. Introduction

Phase-change solid state memory (PCRAM) has recently attracted a great attention as a new class memory on the point of view of energy saving and green technology. The switching mechanism is the same as that in DVD-RAM, except for the difference of a method to introduce input energy: laser pulse or electrical pulse current. In both cases, energy is required for melting and crystallization from an amorphous state. As suspected, however, the input energy especially for *Reset* (crystal to amorphous switching) is relatively higher than that of competitors like MRAM and ReRAM unfortunately. The high energy for *Reset* has been one of the fatal issues to be overcome and to win the competition with the other memories. Is it possible to decrease the switching energy in phase-change memory? The answer is probably yes on the point of view of thermodynamics. Once succeeded in reducing *entropy* due to phase-change, the switching energy can greatly be decreased.

According to our hexagonal model [2, 3], the Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> alloy may be thought of as alternately layered sheets of Ge<sub>2</sub>Te<sub>2</sub> and Sb<sub>2</sub>Te<sub>3</sub>. We simulated both the crystalline [Ge-6 fold coordination] and amorphous [Ge-4 fold coordination] structures consisting of [-Te-Sb-Te-Sb-Te-Ge-Te-*v*-Te-Ge-]<sub>n</sub> and [-Te-Sb-Te-Sb-Te-Te-Ge-*v*-Ge-Te-]<sub>n</sub> stacks respectively using ab-initio density functional computation: where *v* is an imaginary (vacancy) layer. The refractive indices of these modelled structure was then compared with those experimentally measured. We have previously shown that two hexagonal structures are bistable with an energy difference of 40.6 meV/atom according to local density approximations (LDA) simulation. The former has a cell volume of 256.13 Å<sup>3</sup>, while the latter has a volume of 261.21 Å<sup>3</sup>; the difference is 2.0%, which is smaller than that of the NaCl-like random composite material: 6-7% [4]. The lattice parameter *c* of the P3-m crystal with 6-fold Ge atoms is 17.786 Å, while that with 4-fold Ge atoms is 18.255 Å. Thus, the volume change during the phase transition is a result of the *c* parameter shortening, and the activation energy of 2.4 eV is dissipated by the Ge flip-flop transition [5]. The refractive indices experimentally measured and theoretically calculated are consistent with each other for the crystalline, 6-fold coordinated, Ge atoms over the visible spectral range. Moreover, the imaginary index of the crystal with 4-fold Ge atoms was approximately half that of the crystal with 6-fold Ge atoms; comparable with experimentally observed reflectivity changes in digital versatile disc random access memory (DVD-RAM) using the same, Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, composition although the material was poly-crystalline. During crystallization, the Ge and Te atoms change position with each other along the *c*-axis, resulting in the change from 4- to 6- fold, Te bonded, Ge atoms and vice versa in the amorphisation process. In the switching procedure, it should be noticed that the Sb<sub>2</sub>Te<sub>3</sub> blocks are unchanged and serve as a skeleton for the whole structure. This model is similar to the host-guest phenomena in intercalation chemistry. Thus, Sb<sub>2</sub>Te<sub>3</sub> layers are the host, while Ge<sub>2</sub>Te<sub>2</sub> layers are the guest. The host layers hold the reactions or transitions of the guest molecules sandwiched between them. Several hexagonal models have been reported [6,7], however, none of them are based on the aforementioned Ge-flipping transition. Realizing the above atomic layer structure can greatly save entropy in the phase-change, resulting in reducing the input energy to PCRAM.

## 2. Entropy due to Phase Change

Using a phase-change meta-material (PC-MM) structure enables the phase-transition at a lower power than using a single film of a PC alloy because of the suppression of the entropy dissipated in the switching cycle: *Set* (amorphous to crystal switching) and *Reset* (crystal to amorphous switching). In thermodynamics, the input electrical energy must be

transferred into the internal energy of the cell ( $\Delta E$ ), the work for the phase-change ( $W_{pc}$ ), and the entropy part of the total energy ( $T\Delta S$ ).  $T\Delta S$  can be roughly estimated using the *Sackur-Tetrode* equation for an independent atomic canonical ensemble system [8]. Although the equation is for an ideal gas system and for a regular solution, it may give the upper limit to an entropy of a real system including covalent bonds.

The partition function  $q$  is given by the average free space in a lattice volume,  $V$ .

$$q = 1/9 \cdot \{2\pi M / (h^2 \beta)\}^{3/2} V \quad (1)$$

Where  $M$  is the atomic (molecular) weight,  $\beta=1/kT$ ,  $h$  is *Plank's* constant and  $k$  is the *Boltzman* constant. The total partition function for the canonical ensemble  $Q$  is given by:

$$Q = q^N / n_1! / n_2! / n_3!, \quad N = n_1 + n_2 + n_3 \quad (2)$$

$N$  is the total number of atoms in the ensemble, and  $n_{1,2,3}$  are the partial numbers of independent atoms. Using equations (1) and (2) at 300°C and assuming a phase changed volume forms a hemispherical dome with a 75-nm diameter. In addition, ignoring the energy to heat a heat element (rod) contacted to a phase-change layer. In actual devices, a heat element is inevitable to heat up a phase-change film by the melting temperature.

Applying equations (1) and (2) to a ternary condition, for the case of using a single film of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ,  $T\Delta S_{\text{single}}$  is estimated to be  $4.20 \times 10^{-12}$  J. On the other hand, the dome requires  $5.20 \times 10^{-14}$  J as internal energy gain  $\Delta E$ , assuming the heat capacity  $C_{p(\text{GeSbTe})}$  to be 0.25 J/g/K, a value measured in our laboratory. Therefore, almost 99% of the energy is wasted or released in the form of entropy in the case of a conventional device. Hence,  $W_{pc}$  is assumed to be the activation energy of 2.34 eV, which corresponds to  $1.53 \times 10^{-13}$  J [3]. By modifying the *Sackur-Tetrode* equation for the *PC-MM* structure, the entropies of multilayer structures and *PC-MM* cells can be estimated. Assuming a superlattice-like structure and the *PC-MM* cells that can be divided into 10-stacked layers with equal thickness, in the superlattice-like cell, Ge, Te and Sb atoms are allowed to move freely in three dimensions within each layer. For this structure, the entropy energy  $T\Delta S_{\text{superlattice-like}}$  is reduced to  $4.26 \times 10^{-13}$  J, which is ~11% of  $T\Delta S_{\text{single}}$ . In the *PC-MM* cell, on the other hand, the Ge and Te atoms in the GeTe layers are limited to movement in one dimension (along the *c*-axis) based on the Ge flip-flop model; the motion of Te and Sb atoms in  $\text{Sb}_2\text{Te}_3$  layers are fixed [2,3]. Leading to the change of the superscript 3/2 into 1/2 in equation (1), the estimated entropy energy  $T\Delta S_{\text{MM}}$  is  $4.53 \times 10^{-14}$  J, and is decreased by ~1% of  $T\Delta S_{\text{single}}$ . That is, using of the *PC-MM* film allows for a 90% energy saving for the *Set* operation in comparison to a conventional PCRAM device. As the partition function in the calculations reduces logarithmically with the number of stacked layers, our simple calculations can reproduce well trend in the experimental results. For the *Reset* operation, the same calculation is applicable (see Table 1). In conclusion, use of a *PC-MM* film allows the input energy to be transferred more efficiently to cell heating  $\Delta E$  and  $W_{pc}$  by depressing  $T\Delta S$ . Conversely speaking, currently released PCRAM devices only use one or two percent energy from the input energy. All the computer simulations reported in PCRAM have only dealt with an equation of heat diffusion, and estimated temperature profiles in the memory cell. However, such a large entropy dissipation of the input energy was not discussed so far. Once based on the entropy suppression, the priority of our *PC-MM* structure is soon understood.

### 3. PC-MM Design & Fabrication

It is very much intriguing to actually fabricate, to realize, and to estimate the device characteristics of the *PC-MM* structures:  $[-\text{Te-Sb-Te-Sb-Te-Ge-Te-}v\text{-Te-Ge-}]_n$  and  $[-\text{Te-Sb-Te-Sb-Te-Te-Ge-}v\text{-Ge-Te-}]_n$ . Our thermal analysis study of  $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)]_n$  stacks showed a strong crystallization temperature dependence on the  $\text{Sb}_2\text{Te}_3$  layer thickness [12]. The  $\text{Sb}_2\text{Te}_3$  crystallization temperature,  $T_{c(\text{Sb}_2\text{Te}_3)}$ , rose from 90-100°C to 203°C, as the  $\text{Sb}_2\text{Te}_3$  layer became thinner and approached that of a monolayer. On the other hand, the GeTe crystallisation temperature,  $T_{c(\text{GeTe})}$ , marginally decreased from 226°C to 208°C as a function of thickness between 0.5 nm and 5.0 nm. Further, the first small endothermic peak, indicating a melting or amorphisation event,  $T_{\text{endo}}$ , was independent of layer thicknesses and occurred at  $399 \pm 3$  °C. The results show that both sub-layers are put under increasing tensile stresses as the layer thickness is reduced. After the phase transition, the multilayer is further exposed by a stronger tensile stress against the substrate. Therefore, the endothermic peak which, most likely, corresponds to the melting point of the Te-rich GeTe phase, does not change due to the energetically favourable volume expansion of the melt. According to these results, the ideal *PC-MM* must be fabricated at a temperature between  $T_{c(\text{GeTe})}$  and  $T_{\text{endo}}$ , otherwise internal stresses generated during the deposition produces dislocations or a multi-crystalline film. Figure 1 shows a large high resolution transmission electron microscope (TEM) image of the  $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)]_{20}$  *PC-MM* (corresponding to  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  composite alloy) deposited upon a Si (100) surface. The *PC-MM* was deposited by a helicon-wave magnetron sputtering system at 250°C. A very smooth and laminar film was obtained with few defects. The electron diffraction showed a strongly 111 oriented structure normal to the substrate surface.

### 3. Device Performances

Until now the *PC-MM* device characteristics have not been compared against those of a device based on a single composite  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  film. Chong *et al.* Reported the characteristics of superlattice-like phase-change films, which were deposited at room temperature with layer thicknesses between 4 nm and 20 nm [1,9]. The films composed of

randomly-oriented, superlattice-like fragments, high-temperature annealing at 200°C for 5 min, except for small periodic cycles [1].

We prepared base devices consisting of a TiN heating rod with a diameter ranging from 50-nm to 75-nm. The thickness of the MM film was fixed at 35 nm, and was capped by a 40-nm thick TiN electrode. Three different PC-MMs: [(GeTe)<sub>4</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>2</sub>]<sub>10</sub> and [(GeTe)<sub>2</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>4</sub>]<sub>8</sub>, and a composite single layer of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> as a reference were prepared. The resistance-current (R-I) and cycling characteristics of the three devices are summarized in Table 2. In addition, a FFT image of electron diffraction pattern observed just above the heater element was similar to a spot pattern simulated from the PC-MM of [(GeTe)<sub>2</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>4</sub>]<sub>8</sub> model with Ge-4 coordinations, after a cycle test terminated at Reset condition. The *Set* and *Reset* pulse lengths were fixed at 500 ns and 100 ns, respectively. Comparing the ratio of the switching energy required for the [(GeTe)<sub>2</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>4</sub>]<sub>8</sub> device with that of the Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> single-layer device, one finds only 0.25 and 0.34 of the energy is used for setting and resetting respectively, assuming the switching speed was constant in each device. The reset energies in Table 2 are reasonable values in comparison with Table 1, although the internal energy gain from the heater element is underestimated. However, a more interesting matter is that the reset energy becomes smaller as the (GeTe) block thickness is thinner. If the GeTe layer is thick, Ge flip-flop switch has more degrees of freedom in three dimensions based on our entropy model, tending to the same value of the superlattice-like or finally the composite film. The device results using the MM films provide a strong evidence that the Ge flip-flop switch is realized in a PCRAM device and a substantial energy saving is possible as a result. PC-MM will probably revolutionise the phase-change memory device in the near future, with high-speed and low power switching performances beyond any other nonvolatile memory devices.

## 5. Summary

We have succeeded in fabricating PC-MM films composed of [(GeTe)<sub>2</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>1</sub>]<sub>20</sub>, [(GeTe)<sub>4</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>2</sub>]<sub>10</sub> and [(GeTe)<sub>2</sub>/(Sb<sub>2</sub>Te<sub>3</sub>)<sub>4</sub>]<sub>8</sub> blocks and confirmed the device characteristics. Calculations have also shown that a significant switching energy saving can be achieved by suppressing entropy, using PC-MM films. We argue that the PC-MM device is no longer operated by the commonly accepted mechanism depending on amorphous to crystal phase transition, but by a Ge flip-flop switch intercalated between Sb<sub>2</sub>Te<sub>3</sub> blocks without any melting transition.

## Acknowledgement

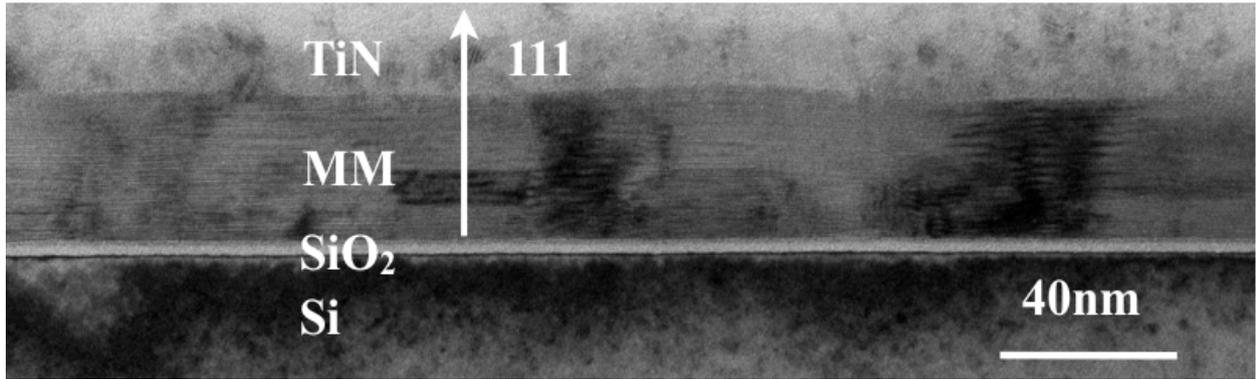
The work was supported by a project :“Research and Development of Nanoelectronic Device Technology” of NEDO.

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**Table 1** Switching energy required in *Set* & *Reset*, and entropy dissipations in the processes. In the model, the internal energy gains of a heater element and of a crystal area surrounding the hemispherical dome (a diameter of 75-nm) were both ignored.

PC film structure	$T\Delta S$ (Set at 300°C) (J)	Total energy required in ideal Set (J) $\Delta H_{Set} = \Delta E + W_{dc} + T\Delta S$	$T\Delta S$ (Reset at 1000°C) (J)	Total energy required in ideal Reset (J) $\Delta H_{Reset} = \Delta E + W_{dc} + T\Delta S$
Single film	$4.20 \times 10^{-12}$	$4.41 \times 10^{-12}$	$9.40 \times 10^{-12}$	$9.81 \times 10^{-12}$
superlattice-like [1]	$4.26 \times 10^{-13}$	$6.31 \times 10^{-13}$	$9.55 \times 10^{-13}$	$1.37 \times 10^{-12}$
PC-MM	$4.53 \times 10^{-14}$	$2.50 \times 10^{-13}$	$1.02 \times 10^{-13}$	$5.15 \times 10^{-13}$



**Figure 1** PC-MM film composed of  $[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_1]_{20}$  blocks deposited on Si wafer at a stress-free condition

**Table 2** Device properties of three devices operated at 100 ns for Set and 500 ns for Reset.

	Set (V)	Reset(V)	$I_{set}$ at $10^6$ cycle (mA)	$I_{reset}$ (mA) at $10^6$ cycle	Reset energy (J)
$\text{Ge}_2\text{Sb}_2\text{Te}_5$ composite	3.0	6.0	0.30	1.25	$7.5 \times 10^{-10}$
$[(\text{GeTe})_4/(\text{Sb}_2\text{Te}_3)_2]_{10}$	2.5	5.0	0.15	0.90	$4.5 \times 10^{-10}$
$[(\text{GeTe})_2/(\text{Sb}_2\text{Te}_3)_4]_8$	1.5	3.5	0.15	0.73	$2.6 \times 10^{-10}$