Phase Change Meta-material and Device Characteristics

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***Green-IT* has now been recognised as an influencing factor in the prevention of global warming and consequently non-volatile solid state memories, especially Magneto-Resistive Random Access Memory (MRAM) and Phase-Change Random Access Memory (PCRAM) have attracted much attention due to their inherent energy efficiency. Current PCRAM technology suffers, however, from the need for a larger switching energy in comparison with MRAM. We demonstrate that by employing a superlattice of GeTe and Sb_2Te_3 in a PCRAM device enables a substantial reduction in the *Set & Reset* energies compared with current PCRAMs devices yet still retains the desirable memory characteristics. It has been confirmed that the superlattice switching is not characterized by a crystallisation and melting process in contrast to conventional phase change memories but by a Ge flip-flop switch intercalated between Sb_2Te_3 blocks in this novel meta-material structure.**

1. Introduction

Phase-change random access memory (PCRAM), magneto-resistive random access memory (MRAM) and ferroelectric random access memory (FeRAM) are the leading candidates for future non-volatile solid state memory technologies. In PCRAM, up to a three orders of magnitude difference in the electrical resistivity between the amorphous and crystalline states is invoked as a binary bit [1]. Injecting a high current (~1.5 mA) with a short pulse (<100 ns) changes the state of the cell from crystalline to amorphous (reset state) with a high resistivity (~MΩ), while injecting a low current (~0.8 mA) pulse, longer in length (~500 ns) returns the state to its crystalline form. Until now, a large number of studies have concentrated on improving the switching speed, endurance and the relatively low cyclability through not only phase-change material optimisation, but also improvements in the device structure [2-4]. Germanium-Antimony-Tellurium (Ge-Sb-Te) ternary alloys have been widely studied and consequently the specific composition $Ge_2Sb_2Te_5$ was developed [5]; it is often acknowledged as the leading core recording material. The structure of the composite alloy is known to consist of a GeTe-Sb_2Te_3 pseudo-binary phase which has a rocksalt structure [4, 5]. Experimental and theoretical investigations of the crystalline and amorphous GST structures were initiated by Kolobov *et al.* in 2004 who first explained the origin of the fast and stable switching phenomenon was first proposed. In the Kolobov model, Ge atoms have 6-fold bonds with neighboring Te atoms in the cubic phase while in the amorphous, Ge atoms have 4-fold bonds. The phase transition is typified by the Ge atoms moving towards the corner Te atom located at (a)-site in the NaCl-*like* block [6-10]. Due to the transition, which is likely to be more favorable with respect to the Gibbs free energy above the melting point, the pseudo-binary phase is split into a liquid mixture of GeTe and Sb_2Te_3 [5]. Elliot *et al.* demonstrated and reproduced the melting and cooling of $Ge_2Sb_2Te_5$ using *ab-initio* molecular dynamics [11]. They reported that *in silico* Ge 4-fold rings with bond angles of 90° (not 109°) were still found in the liquid, but the number increased when the holding temperature was 100K below the melting point. Despite these contributed works, the reasons why GeTe-Sb_2Te_3 pseudo-binary compositions provide us with useful and attractive physical properties are still veiled.

Apart from the cubic block of $Ge_2Sb_2Te_5$, the situation becomes much simpler and more realistic in industrial applications. According to the Kolobov model, the alloy may be thought of as alternately layered sheets of Ge_2Te_2 and Sb_2Te_3 [12-15]. 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-]n and [-Te-Sb-Te-Sb-Te-Te-Ge-*v*-Ge-Te-]n stacks respectively using ab-initio density functional computation: where *v* is an imaginary layer. The refractive indices of these modelled structure was then compared with those experimentally measured [12,14].

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) sumulation. The former has a cell volume of 256.13 Å³, while the latter has a volume of 261.21 Å³; the difference is 2.0%, which is smaller than that of the NaCl-*like* random composite material: 6-7% [15]. 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 [13]. 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, $Ge_2Sb_2Te_5$, 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. The Sb_2Te_3 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_2Te_3 layers are the host, while Ge_2Te_2 layers are the guest. We name this intercalated phase-change film *PC-Metamaterial* (PC-MM) hereafter. The host layers hold the reactions or transitions of the guest molecules sandwiched between them. Several hexagonal models have been reported [14, 15], however, none of them are based on the aforementioned Ge-flipping transition.

2. Switching Performance by Entropy Suppression

Using a 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* and *Reset*. In thermodynamics, the input electrical energy must be transfered into the internal energy of the cell (ΔE), the work for the phase-change (W_{pc}), and the entropy part of the total energy ($T\Delta S$). $T\Delta S$ can be estimated using the *Sackur-Tetrode* equation for an independent atomic canonical ensemble system [16]. The partition function q is given by the average free space in a lattice volume, V.

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

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:

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

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. For example, for the case of using a single film of $Ge_2Sb_2Te_5$, $T\Delta S_{single}$ is estimated to be 4.20×10^{-12} J. On the other hand, the dome requires 5.20×10^{-14} J as internal energy gain ΔE, assuming the heat capacity $C_{p(GeSbTe)}$ 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 1.53×10^{-13} J [13]. By modifying the *Sackur-Tetrode* equation for the PC-MM structure, the entropies of multilayer structures [17] 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 $T\Delta S_{superlattice-like}$ is reduced to 4.26×10^{-13} J, which is ~11% of $T\Delta S_{single}$. 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 Sb_2Te_3 layers are fixed [12, 13]. Leading to the change of the superscript *3/2* into *1/2* in equation (1), the estimated entropy energy $T\Delta S_{MM}$ is 4.53×10^{-14} J, and is decreased by ~1% of $T\Delta S_{single}$. 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 transfered more efficiently to cell heating ΔE and W_{pc} by depressing $T\Delta S$.

Table 1 Switching energy required in *Set & Reset*, and entropy dissipations in the processes. <u>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.</u>

PC film structure	$T\Delta S$ (Set at 300°C) (J)	Total energy required in ideal Set (J) $\Delta H_{Set}=\Delta E+W_{pc}+T\Delta S$	$T\Delta S$ (Reset at 1000°C) (J)	Total energy required in ideal Reset (J) $\Delta H_{Reset}=\Delta E+W_{pc}+T\Delta S$
Single film	4.20×10^{-12}	<u>4.41×10^{-12}</u>	9.40×10^{-12}	<u>9.81×10^{-12}</u>
superlattice-like [17]	4.26×10^{-13}	6.31×10^{-13}	9.55×10^{-13}	1.37×10^{-12}
PC-MM	4.53×10^{-14}	<u>2.50×10^{-13}</u>	1.02×10^{-13}	<u>5.15×10^{-13}</u>

3. MM Design &Fabrication

It is very much intriguing to actually fabricate, to realize, and to estimate the devise characteristics of the PC-MM structures: [-Te-Sb-Te-Sb-Te-Ge-Te-*v*-Te-Ge-]$_n$ and [-Te-Sb-Te-Sb-Te-Te-Ge-*v*-Ge-Te-]$_n$. Our thermal analysis study of [(GeTe)$_2$/(Sb$_2$Te$_3$)$_1$]$_n$ stacks showed a strong crystallization temperature dependence on the Sb$_2$Te$_3$ layer thickness[12]. The Sb$_2$Te$_3$ crystallization temperature, $T_{c(Sb2Te3)}$, rose from 90-100°C to 203°C, as the Sb$_2$Te$_3$ layer became thinner and approached that of a monolayer. On the other hand, the GeTe crystallisation temperature, $T_{c(GeTe)}$, 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_{endo}, was independent of layer thicknesses and occurred at 399 ± 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 $T_{c(GeTe)}$ and T_{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 [(GeTe)$_2$/(Sb$_2$Te$_3$)$_1$]$_{20}$ PC-MM (corresponding to Ge$_2$Sb$_2$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 [12]. 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.
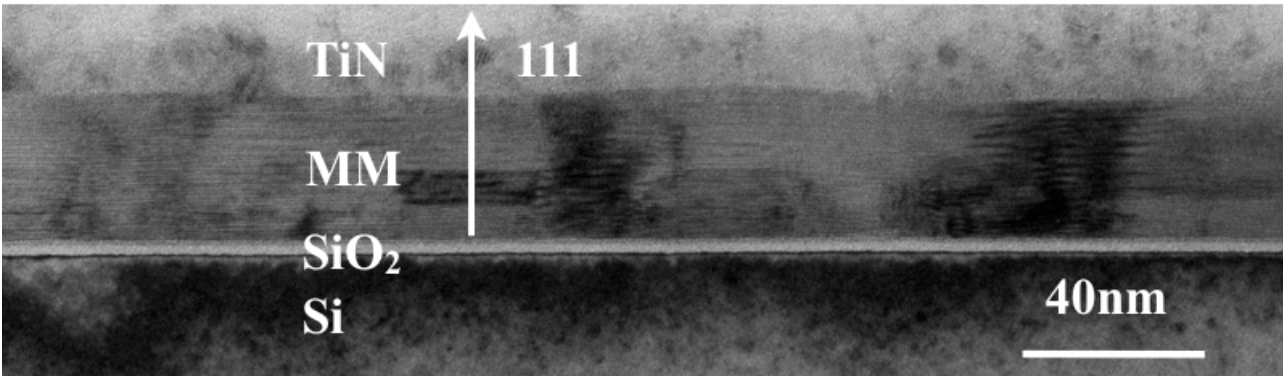

Figure 1 MM film composed of [(GeTe)$_2$/(Sb$_2$Te$_3$)$_1$]$_{20}$ blocks deposited on Si wafer at a stress-free condition

3. Device Performances

Until now the PC-MM device characteristics have not been compared against those of a device based on a single composite $Ge_2Sb_2Te_5$ 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 [17, 18]. The films composed of randomly-oriented, superlattice-*like* fragments, high-temperature annealing at 200^oC for 5 min, except for small periodic cycles [17].

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: $[(GeTe)_4/(Sb_2Te_3)_2]_{10}$ and $[(GeTe)_2/(Sb_2Te_3)_4]_8$, and a composite single layer of $Ge_2Sb_2Te_5$ as a reference were prepared. The resistance-current (R-I) and cycling characteristics of the three devices are summarized in Table 2. 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 $[(GeTe)_2/(Sb_2Te_3)_4]_8$ device with that of the $Ge_2Sb_2Te_5$ 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.

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)
$Ge_2Sb_2Te_5$ composite	3.0	6.0	0.30	1.25	7.5×10^{-12}
$[(GeTe)_4/(Sb_2Te_3)_2]_{10}$	2.5	5.0	0.15	0.90	4.5×10^{-12}
$[(GeTe)_2/(Sb_2Te_3)_4]_8$	1.5	3.5	0.15	0.73	2.6×10^{-12}

4. Summary

We have succeeded in fabricating PC-MM films composed of $[(GeTe)_2/(Sb_2Te_3)_1]_{20}$, $[(GeTe)_4/(Sb_2Te_3)_2]_{10}$ and $[(GeTe)_2/(Sb_2Te_3)_4]_8$ 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_2Te_3 blocks without any melting transition.

Acknowledgement

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