

## Electrical-field induced giant magnetoresistivity in (non-magnetic) phase change films

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Phase-change GeTe/Sb<sub>2</sub>Te<sub>3</sub> multilayered structures, in which the atomic motion at the layer interfaces is limited to one dimension, have been shown to require substantially lower switching energies when compared to monolithic alloys of the same average composition. Here, we report that in the GeTe/Sb<sub>2</sub>Te<sub>3</sub> superlattice, an extraordinarily large magnetoresistance of  $\Delta R/R > 2000\%$  can be induced by application of an electrical field at temperatures exceeding 400 K. This finding paves the way for development of conceptually new memory devices that combine the merits of both phase-change and magnetic data storage. © 2011 American Institute of Physics.

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Magnetoresistance (MR) is one of the pillars of spin-electronics and is widely applied not only in hard disk storage but also in nonvolatile solid state memory such as magnetic random access memory (MRAM). MRAM uses the tunnel magnetoresistance (TMR) of a magnetic tunnel junction consisting of ferromagnetic layers interspaced with an insulating layer such as Al<sub>2</sub>O<sub>3</sub>. The use of TMR is essential in down scaling MRAM structures to achieve storage densities beyond 1 Gbit/in<sup>2</sup>. (Ref. 1) Although TMR devices in hard disk applications use Al<sub>2</sub>O<sub>3</sub> as the insulating layer, recent research has demonstrated that use of a thin MgO spacer layer can lead to a drastic improvement of magnetoresistance with  $\Delta R/R > 1000\%$  at 5 K and 500% at room temperature.<sup>2,3</sup> Thermal issues related to spin-current injection, however, present significant challenges to further scaling due to thermal drift effects resulting in smaller achievable  $\Delta R/R$ .

At the same time, phase-change random access memory (PCRAM) is gaining momentum as the likely candidate technology for the next generation of nonvolatile data storage. PCRAM devices encode data as structural changes in a thin film of a (usually) tellurium-based material. In particular, the stoichiometric compositions along the GeTe/Sb<sub>2</sub>Te<sub>3</sub> pseudo-binary tie-line are of great technological interest. Switching between the disordered and crystalline structural states is typically achieved through Joule heating.<sup>4</sup> Figure 1 (upper panel) shows schematic representations of the two switching states in a typical PCRAM device: in the *reset* state, a high-resistance amorphous hemispherical dome covering the bottom electrode forms due to the application of a relatively high current pulse and subsequent melt-quench; in the conductive *set* state, the dome reverts to the low-resistance crystalline state by application of a relatively low current and long duration pulse. The large property changes observed in the phase-change memory (PCM) between the ordered and disordered phases have been ascribed to a change in the nature of the bonding.<sup>4-6</sup> For Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>, this involves a

change between delocalized resonant bonding in the ordered phase and localized covalent bonding in the amorphous phase. While the disordered phase is normally obtained by quenching the molten phase, in a recent report, multilayered GeTe/Sb<sub>2</sub>Te<sub>3</sub> structures, referred to as interfacial phase-change memory (*i*PCM), were found to lead to a similar change in bonding properties via a solid-solid phase transition.<sup>7</sup> In the *i*PCM structure, the confinement of the switching process to interfaces reduces entropic losses resulting in an order of magnitude improvement in energy consumption.<sup>7</sup> The *i*PCM structure remains crystalline in both low-resistance (Fig. 1, lower panel) and high-resistance states and the property contrast is due to a change in the coordination number of Ge atoms.<sup>7</sup>

Since Ge-Sb-Te alloys do not have a magnetic moment, until now magnetism was not thought to play a role in switching dynamics or electrical properties. At the same time, one of the end points (Sb<sub>2</sub>Te<sub>3</sub>) is a topological insulator<sup>8</sup> and Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> has also been predicted to be a topological insulator for certain layer sequences.<sup>9</sup> It may be expected, therefore, that application of a magnetic field might affect material properties, especially for the GeTe/Sb<sub>2</sub>Te<sub>3</sub> layered *i*PCM phase as application of an external magnetic field is expected to further contribute to the Rashba effect induced splitting in spin states.<sup>10</sup> We suspect that the topological insulating state in the *i*PCM devices does not occur only at the surface but is also present at all interfaces greatly magnifying the magneto-resistance effect and at the same time, reducing the effects of surface contamination that would otherwise make fabrication of a device impractical.

*i*PCM devices with the [(GeTe)<sub>2</sub>(Sb<sub>2</sub>Te<sub>3</sub>)<sub>4</sub>]<sub>18</sub> structure were grown on 50 nm TiN heater rod arrays prefabricated on a Si substrate. Prior to film deposition, a 5-nm thick Sb<sub>2</sub>Te<sub>3</sub> film was initially deposited to ensure strong pseudo-cubic  $\langle 111 \rangle$  orientation of subsequent layers. Each layer of GeTe and Sb<sub>2</sub>Te<sub>3</sub> was formed by a helicon-wave sputtering system with the 2 in. targets. Due to the long target-substrate sputtering distance of 200 mm, atomically controlled layers could be fabricated by automatically opening and closing shutters

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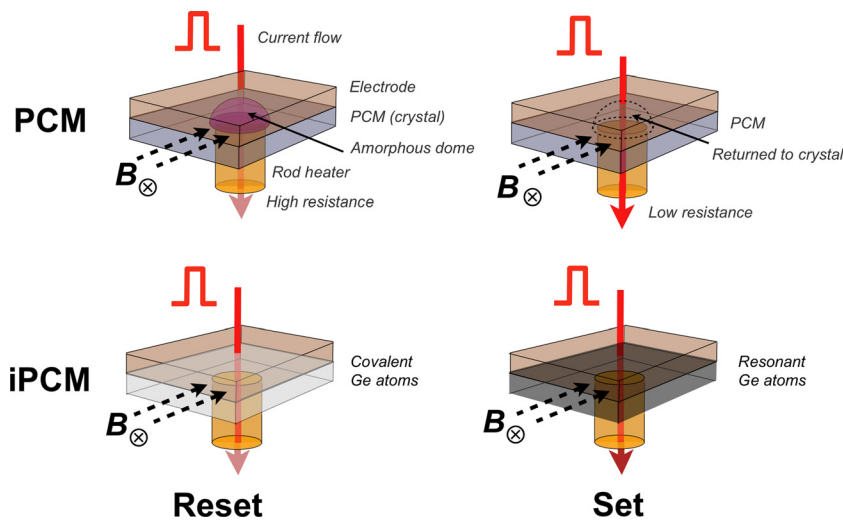


FIG. 1. (Color online) *Reset* (left) and *Set* (right) states of PCRAM (top) and *iPCM* (bottom) devices. The cylindrical heater acts to heat the PCM film. In PCRAM, upon melting and subsequent quenching, a hemispherical amorphous high-resistance dome is formed above the heater (*reset* state). Heating the dome above the crystallization temperature with a relatively low current and long duration pulse reverts its structure to that of the low-resistance crystalline phase (*set* state). In the *iPCM*, on the other hand, the transition between two crystalline states with different bonding characteristics (resonant and covalent in the *set* and *reset* states, accordingly) at interfaces is responsible for the property contrast.

in front of the targets and of the substrate station. The layer deposition temperature was fixed at 520 K, taking into account the crystallization temperature (500 K) of GeTe. The thicknesses of the layers in the *iPCM* structure were 0.4 nm for GeTe and 1.0 nm for Sb<sub>2</sub>Te<sub>3</sub>. A cross sectional image of the device by high-resolution TEM has been published by Tominaga *et al.*<sup>11</sup>

Figure 2 compares the switching behavior of a composite Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> device and an identical composition *iPCM* device with the [(GeTe)<sub>2</sub>(Sb<sub>2</sub>Te<sub>3</sub>)<sub>4</sub>]<sub>8</sub> *iPCM* structure. As expected for a non-magnetic material, the electrical switching properties of a PCRAM device based on a composite Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> alloy were insensitive to the application of a magnetic field of 0.1 T (Fig. 2(a)). The current (I)-voltage (V) characteristics the *iPCM* device, however, showed a strong dependence on a magnetic field (Fig. 2(b)) applied in-plane. Prior to the application of a magnetic field, the *iPCM* device characteristics were similar to those of the composite Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> device with switching from the *reset* to the *set* state occurring at 0.85 V and 0.01 mA, (Joule heat released under such conditions corresponds to temperatures ca. 430 K).<sup>12</sup> Upon application of a magnetic field (0.1 T), however, the threshold voltage increased to 2.0 V (corresponding to temperatures ca. 570 K<sup>12</sup>) and the slope of the I-V curve changed. The effect of the magnetic field was completely reversible. It should be

noted that the I-V curve for the *iPCM* (Fig. 2(b)) at voltages above  $V_{set}$  has reproducible deviations from the expected straight-line behavior observed for the composite material that are reminiscent of the quantum spin Hall effect.

Figure 3 shows resistance (R)—current (I) plots corresponding to the measurements shown in Fig. 2. To characterize the phase-change behavior, R-I plots are typically measured between switching pulses at a constant voltage of 0.5 V during an I-V curve measurement. The composite Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub>-based PCRAM device showed essentially indistinguishable U- or W-shape curves with switching occurring in a resistance range between 4 MΩ and 40 KΩ both with and without a magnetic field. On the other hand, the resistivity of the *iPCM* device in the presence of a magnetic field did not show any change remaining pinned at around 4 MΩ, while the two curves for the case without a magnetic field (before and after) clearly showed a nonvolatile memory switch between 4 MΩ and 200 KΩ. It is clear from this result that not only the application of a magnetic field results in a significant increase in the threshold voltage but also modifies the response of the phase change device from that of a memory cell to that of a threshold switch (that reverts to its original stage once the voltage is decreased).<sup>13</sup> The magneto-resistance over the voltage range of 1 to 2 V reaches the value of  $\Delta R/R \gtrsim 2000\%$ . Alternatively, the observed effect

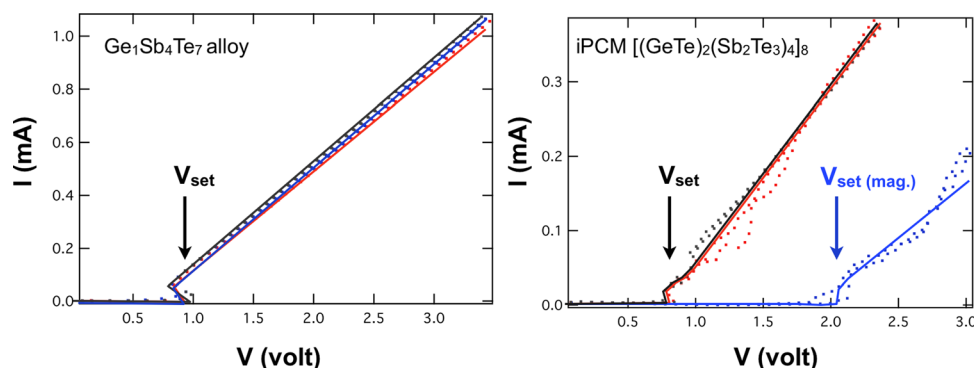


FIG. 2. (Color online) Current-Voltage characteristics of a PCRAM device fabricated using composite Ge<sub>1</sub>Sb<sub>4</sub>Te<sub>7</sub> (left) and an identical composition *iPCM* device (right). As the voltage reaches the threshold value of  $V_{set}$ , the device switches into the low-resistance state. Device characteristics prior to application of a magnetic field, with an external magnetic field of 0.1 T applied, and after removal of the field are shown. The composite device (left) did not show any change among the three states, while the *iPCM* device (right) clearly showed a voltage shift under the magnetic field, indicated as  $V_{set(mag.)}$ . A sequence of 300 ns pulses was used for the measurements. Two scans for each state are shown to demonstrate reproducibility. Dots are experimental data and solid lines are guides for the eye.

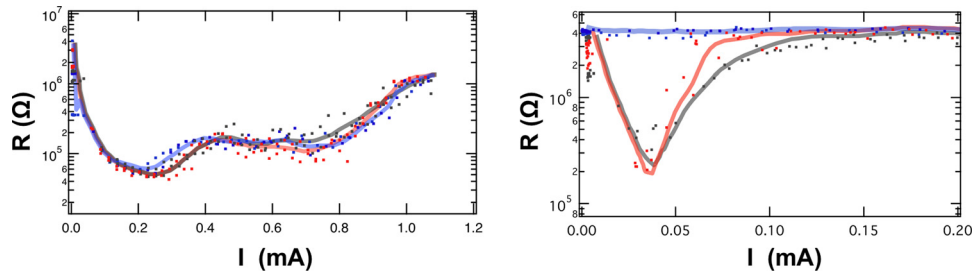


FIG. 3. (Color online) Resistance ( $R$ )-Current ( $I$ ) plots of a PCRAM device (left) and an  $i$ PCM device (right) measured at 0.5 eV. Device characteristics prior to application of a magnetic field, with an external magnetic field of 0.1 T applied, and after removal of the field are shown. The composite device did not show any change among the three states, while the  $i$ PCM device showed a high resistance under the magnetic field (upper line). Two scans for each state are shown to demonstrate reproducibility

may be interpreted as a magnetic-field induced stabilization of the high-resistance (amorphous) phase. This result also demonstrates that the use of a magnetic field can serve to “write protect” an  $i$ PCM device.

It is speculated that the unusually large electrical field-induced magnetoresistance in the  $i$ PCM device arises from a spin current resulting from the topological insulating nature of the multilayered structure where the role of interfaces is enhanced due to its multilayered nature. In topological insulators, the bulk is a conventional insulator. However, time-reversal symmetry-protected conducting states exist on the surface (at interfaces) which are resistant to scattering due to the locking of spin to the propagation direction and destructive quantum mechanical interference. The coupling of the spin to the momentum in the absence of a magnetic field originates from quantum mechanical spin-orbit coupling (SOC), which is larger for heavier elements. This coupling in conjunction with the topological features of the band structure, specifically the band inversion at  $k=0$ , leads to predictions of metallic behavior on the  $\langle 111 \rangle$  surface even in the absence of a magnetic field for materials such as  $\text{Sb}_2\text{Te}_3$ ,  $\text{Bi}_2\text{Te}_3$ ,<sup>14</sup> and leads to up and down spin current channels flowing along surface edges. A similar magnetoresistance effect was observed at ca. 4 K and  $B=3.0$  T, in the layered organic superconductor (bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF),  $(\text{BEDT}-\text{TTF})_2\text{I}_3$ ) with iodine intercalated between the layers, a material that exhibits topological insulator properties.<sup>15</sup>

All electron calculations using the LO-LAPW code Wien2K<sup>16</sup> demonstrated that the electronic structure of  $i$ PCM is typical of a metal if SOC is neglected but changes drastically, (exhibiting Dirac cone-like behavior at  $k=0$  and inversion symmetry in the presence of SOC. These results suggest that the  $i$ PCM structure can act as a topological insulator due to the presence of a strong Rashba effect. For the  $i$ PCM structures reported here, calculations show a Rashba effect induced spin-splitting of more than 200 meV, a value six times greater than that expected from thermal fluctuations at room temperature. These results strongly suggest that the topological nature of the structure is preserved at higher temperatures.

The observed strong magnetic response of  $i$ PCM at temperatures exceeding room temperature paves the way for

designing conceptually novel memory materials with the combined merits of phase-change and magnetic memories. The observed effect may also serve as the basis for a new type of magnetic sensor that can operate at high temperatures. Such a device would match well the requirements for the thermally assisted magnetic heads being proposed now in the literature.<sup>17</sup>

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