Re-amorphization of GeSbTe alloys not through a melt-quenching process

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Received August 10, 2018; accepted November 1, 2018; published online November 26, 2018

Ge–Sb–Te (GST) alloys are one of the most successful chalcogenides used in rewritable optical discs and electric non-volatile memories. In these materials the structural phase transition between amorphous and crystalline states is used for recording. Here, we report that a melt-quenching method is not necessarily the only way to form a high-resistance phase. We found that amorphous-like grains with high resistance are formed in the GST crystal film by holding it at above the crystallization temperature under an external magnetic field, followed by cooling accompanied with pulse current injection. The treatment may open new route for ultra-low current switching phase change memory.

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Chalcogenides, especially, Ge–Sb–Te (GST) alloys are widely used materials in rewritable phase-change optical discs and electric non-volatile memory. Since the discovery in the late 1960s, these alloys have been studied for nearly 40 years.1–4) Now, the alloys are used as recording films in digital versatile disc random access memory and blue-ray discs, and also are used as a recording material in phase-change non-volatile memory (PRAM).5–7) The recording principle relies on the phase transition (change) between an amorphous state and a crystalline state, which is accompanied by a large change in refractive index and electric resistance.8–14) To form an amorphous mark in optical discs or bit in PRAM, a recording area is heated to the melting point (∼900 K), followed by rapid cooling down to below the crystallization temperature (∼430 K).15) When the cooling rate is slow (<∼5 K ns−1), the molten region returns to the crystal state.16) In phase-change devices, the melting process needs a relatively large-energy, which has long been a big issue in PRAM. One solution is to use nanotechnology to make the switching volume as small as possible.12,17,18) Using this method, PRAM called “Optane” was shipped to the market by Intel and Micron Technology in 2017.19) The second solution is to adopt a superlattice (SL) structure consisting of a layered GeTe/Sb2Te3 stack and to suppress the entropy energy loss in the phase transition by confining the Ge atom motion in one dimension.20–22) By this method, approximately 90% or more of the input energy is saved.20) Furthermore, it was newly found that non-doped GeTe/Sb2Te3 SLs are sensitive to a magnetic field and show a large magnetoresistance at room temperature.23,24) Though the origin of the magnetic property is not well understood, it is considered to be related to the topological features of the SL electronic band structure, when the SL consists of normal insulator (GeTe) and topological insulator (Sb2Te3).23–25) In contrast, the GST alloy is considered to be a normal insulator, and is, therefore, insensitive to magnetic fields. What is the difference between the alloy and the SL? If the alloy is made of poly-crystals, microscopically it may somewhat be sensitive to the magnetic field.

In this letter, we show that a polycrystalline Ge2Sb2Te5 (GST225) film is partially re-amorphized when the as-deposited film is once annealed at more than the crystallization temperature and then cooled accompanied with electric pulse injections under a magnetic field.

A 20 nm thick GST225 alloy film was fabricated on a 3" sapphire substrate by rf-magnetron sputtering from an alloy target at room temperature. The growth was carried out at a pressure of 0.5 Pa of Ar gas flowing at a rate of 10 sccm, and a power of 20 W. Top and bottom tungsten electrodes, 40 nm in thickness, were also fabricated by sputtering on a sapphire substrate using a metal stencil mask (80 μm width), where the top electrode was deposited with the mask rotated at 90° with respect to the bottom one. Finally, the GST film was removed by Ar-bombardment except for the region of the top electrode. Thus, the sample had several cross point devices with a size of 80 μm. The cross section of the stacked layers taken by a transmission electron microscope is shown in Fig. 1. To avoid noise from a snake path, one cross-point device was separated out and fixed to a Hall test bar. The thermal annealing and cooling were carried out in He gas using a Hall measurement system (Lake Shore Corp. HMS 8400 Series) equipped with an external electromagnet. The sample was heated to 470 K, held for 2 or 4 h, and then cooled down to room temperature in a magnetic field of 0.5 T normal to the film surface. We called the treatment as thermal annealing under magnetic field (TAUM). The resistance change was monitored using current pulses of 100 μA with time duration of a few tens milliseconds every 3 K. For the Kelvin force measurements, the samples were prepared with bottom electrodes only, and we used a permanent Co magnet with a Curie temperature of ∼1000 K. The magnet was placed above the sample during a TAUM treatment and removed for the Kelvin force measurements. It created a magnetic flux density of 0.2–0.3 T at the sample position as measured by a Hall probe gaussmeter (Lake Shore Corp.).

An electric resistance change of the cross point sample device in a normal annealing cycle without a magnetic field (called TA treatment) is shown in Fig. 2. A typical resistance curve in which it starts from a high-resistance in the as-deposited amorphous state, and terminates to a low resistance in the crystalline state was observed. The electric transition occurred at a temperature of 400–420 K. The features of the resistance–temperature curve are in good agreement with those reported in the literature.1,12,26,27) It is recognized that...
once a GST alloy film is annealed and crystallized the low resistance state is never returned to a high resistance state without a melting process. Though, photo-assisted amorphization without melting has been reported.28)

On the other hand, the resistance–temperature curve is somewhat changed under a magnetic field. Figure 3 shows the cooling curves after the TAUM treatment for 2 and 4 h. After the two hour treatment, the resistance was further lowered to 4 kΩ, whereas after the 4 h it was increased up to 10 kΩ. Especially, it steeply increased at a temperature around 370 K, which was near the crystallization temperature. The behavior is unusual because the GST film resistance normally decreases with annealing time. To elucidate the origin of the high resistance, we analyzed the films at the different TAUM treatment times using the selective area electron diffraction. It is worth mentioning that the only amorphous GST phase or only a special phase of the SL can take a high resistance.20,21,29,30) Therefore, as a reference, we used the SAED spots on the main streak lines those appeared in the [(GeTe)2(Sb2Te3)]n SL. As shown in Fig. 4, there were fewer diffraction spots observed in the film after 4 h TAUM than that after 2 h TAUM. In addition, it was confirmed that amorphous-like area spread over the GST film in Fig. 4.

Here, the polycrystalline GST225 film after the 4 h TAUM was amorphized but was not transformed into a SL. The effect of annealing in a magnetic field was confirmed in separate measurement where a conductive probe of an atomic force microscope (CAFM) was used as a top electrode. The measurements were performed in a vacuum chamber filled with argon gas to avoid the film degradation.29–31) In the AFM contact mode, the temperature dependence of the resistance was similar to that of cross point devices, (Fig. 5) though, the AFM resistance was smaller. At 300–400 K, a negative slope in the resistance–temperature dependence was observed with a thermal coefficient of resistance of ($-10 \pm 2 \times 10^{-3}$ K$^{-1}$ for the as-grown film, and ($-9 \pm 1 \times 10^{-3}$ K$^{-1}$ for the annealed films after the TAUM treatment for 4 h. Moreover, for the three examined samples, a ratio between resistance values at 370 and 300 K was in a range of 0.43–0.62 after the TAUM treatment for more than 3 h. The ratio was always larger than one after the TA treatment. The ratio difference agrees with different temperature dependence of GST devices in SET and RESET states.32) This indicates the different carrier transport mechanism in TAUM- and TA-treated GST225 films, and similar carrier-activation transport in amorphous and the TAUM-treated films.

A steep increase in resistance at about 440 K for TA and ∼430 K for TAUM treatments was observed for both cross-point device and CAFM samples as seen in Figs. 3 and 5.
We note that slight increase in the SET resistance at $\sim 450 \text{ K}$ has been observed for memory devices with a GST SL. Thus, the resistance increase is likely related with internal transformation of the crystal grains in the polycrystalline GST$_{225}$ film at high temperature and applied voltage, and it was modified by the TAUM treatment.

Substantial differences were observed in Fig. 6 in the surface morphology and the electric potential variations of annealed films as measured in a non-contact Kelvin force mode (KFM). The as-grown film had a hill-to-valley height of 0.8 nm (a root-mean-square roughness of 0.11 nm) that is common for amorphous films. Both annealed films had corrugated surfaces with a hill-to-valley height of $\sim 7$ nm (a root-mean-square roughness of $\sim 0.80$ nm). The surface morphology indicates growth of small crystal grains with a grain size of 20–50 nm during the treatment.

The KFM voltage was uniform in the amorphous film. Both annealed GST$_{225}$ films showed the presence of two kinds of grains. Grains of type A (blue in Fig. 6) have a low work function corresponding to release with easy the carriers to the probe electrode, thus, they have relatively high conductance. Grains of type B (yellow and red in Fig. 6) have a high work function and relatively low conductance. At room temperature ($\sim 300 \text{ K}$) the grain-to-grain KFM voltage varies by $\sim 130 \text{ mV}$ for TAUM and more than 200 mV for TA treatments, indicating the better uniformity of the GST$_{225}$ film after the TAUM treatment for 4 h.
With temperature increases, the relative KFM voltage increases and peaks at 360 K for the TAUM sample, while it gradually decreased for the TA sample (Fig. 7). The increase in the KFM voltage corresponds to a shift of the Fermi energy, lowering the resistance of the GST225 film after the TAUM treatment. The change in the KFM voltage coincides with the resistance slope change at 360–370 K in Figs. 5 and 3 for the TAUM treated films. An upward shift of the KFM voltage at 300–400 K has been reported for [(GeTe)$_2$/[Sb$_2$Te$_3$])$_4$ SLs and attributed to shift of the Fermi energy reflecting the band gap opening at elevated temperature. Likewise, the decrease in the KFM voltage with increasing temperature after the TA treatment resulted in increase in the resistance.

The TAUM treatment of polycrystalline GST225 films for 4 h causes formation of an amorphous-like film with atomic disorder within the constituting layers as seen in diffraction data in Fig. 4 while the surface morphology of the films remains. The partial amorphization is accompanied with increase in the resistance by 3–5 times. Here, the partial amorphization is created by a combination of different factors. An uniaxial strain of ~200 MPa is introduced by the volume change after the phase transition from amorphous to crystalline phases as observed in 80 nm thick GST225 films above ~440 K. As crystalline GST225 films includes grains with a hexagonal crystal symmetry similar to that in GST SL grains, there exists an internal biaxial strain by the lattice mismatch ~1% between GeTe and Sb$_2$Te$_3$ layers in the hexagonal crystal grains. The biaxial strain is added to the uniaxial strain by the volume change, thus, contributing to atomic disorder in Ge–Te–Ge–Te bond network and lowering the melting temperature of GeTe. Thermal diffusion and strain cause displacement of Ge atoms creating vacancies. In fact, vacancies are common intrinsic defects in bulk GeTe crystals. Such defects possess small magnetic moments owing to unpaired orbital of a Ge atom adjacent to the vacancy. Vacancy-related magnetism has been reported in 2D systems. Therefore, the atomic disorder is boosted through a force created by interaction of such defects with the external magnetic field at elevated temperature. Moreover, electric-field-induced migration of Ge atoms is likely to occur in our case during the sample cooling under voltage pulses during resistance measurements, increasing the disorder in GeTe layers and creating a high-resistance state. Partial amorphization of GST225 nanocrystals in magnetic field can take place at a temperature lower than the crystallization temperature of the whole film, leading to the amorphous-like high-resistance state.

Furthermore, on cooling the GST225 alloy single crystals with a mixture of GeTe and Sb$_2$Te$_3$ layers are formed. GST225 single crystals with a size of 20–50 nm may occasionally possess a structure similar to that of a GST SL with a periodic sequence of two GeTe and one Sb$_2$Te$_3$ blocks. Such SL crystals have demonstrated a strong magneto-resistance and magnetooptical response about 400 K. If each of such nanocrystals has a small magnetic moment which is aligned towards the direction of the external magnetic field (i.e. normal to the surface), a phase transition from low-resistance state to high-resistance state may become possible. Such magnetic moment may arise from (i) electron exchange coupling along the stacking direction and (ii) imbalance of population of spin-polarized bands under lattice strain. Hybridization across adjacent topological layers may create a set of one-dimensional topological states with different chiral symmetry as reported for Bi$_2$Se$_3$-based heterostructures, where response to magnetic field arises from the broken time-reversal symmetry. Further, spin-ordered states and ferromagnetism at room temperature in non-magnetic material systems such as Cu/C$_6$0 multi-layers has been demonstrated owing to hybridization between orbitals at adjacent interfaces in metal-molecule multilayers. Besides, spontaneous spin-polarization and enormous pseudo-magnetic field (up to 300 Tesla) have been reported experimentally in graphene under local uniaxial stretching owing to the population imbalance between the spin-polarized valleys when the spin-valley degeneracy in the Dirac semimetal was lifted in external magnetic field. Therefore, in our films some of strained crystal grains with certain stacking of GeTe and Sb$_2$Te$_3$ layers are susceptible to magnetic field, and converted to the high-resistance state under TAUM treatment.

In conclusion, we demonstrated partial amorphization of GST225 films annealed at 470 K under moderate magnetic field of 0.2–0.5 T. The partial amorphization was observed as disappearance of long range order, increase in the transverse resistance and shift of the Fermi energy after TAUM treatment for more than 3 h. The results suggest new way to create an amorphous-like disordered state with a high resistance under the presence of magnetic field. Such field-assisted manipulation of matter opens novel processing routes to obtain materials with unique functionalities.

Acknowledgement The work was supported by grant no. JPMJCR14F1 of the Japan Science and Technology Agency (JST/CREST).

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