

Understanding phase and chemical transitions in Ge-rich GeSbTe based phase change memory: a (S)TEM tribute

Sijia RAN¹, Minh-Anh LUONG¹, Eloïse RAHIER¹, Elisa PETRONI², Daniel BENOIT³, Alain CLAVERIE¹

¹CEMES-CNRS and University of Toulouse, Toulouse, France, ²STMicroelectronics, Agrate Brianza, Italy, ³STMicroelectronics, Crolles, France

Background incl. aims

Phase change memory (PCM) has demonstrated potentials to become the mainstream of the non-volatile memory technique at 28 nm node and below and is promising for applications in future computing hierarchy [1]. The data storage of PCM relies on the reversible phase transition of its active material, which exhibits distinct electrical resistances between crystalline (high conductivity, logic “1”) and amorphous (low conductivity, logic “0”) states. To meet high-temperature data retention requirements, compositionally optimized Ge-rich GeSbTe (GGST) alloys are used by the industry for fabricating PCM for embedded applications [2]. While being the key for the improved thermal stability, GGST alloys undergo chemical phase separation during thermal annealing [3]. The crystallized GGST has been found to be a “composite” material, resulting from the formation of multiple crystalline phases, such as GeTe, Ge, GST-225, and Sb₂, at different crystallization stages [4].

In PCM cells, GGST alloys experience different kinds of thermal cycles after deposition. In particular, to allow for the switching between 2 logic states, the GGST layer is locally heated by Joule heating generated by applied current pulses, which provide adequate temperatures either to melt-quench or to crystallize it. Owing to the off-stoichiometry nature of the as-deposited GGST, these heating processes may result in different microstructures and elemental distributions within the cell.

While understanding the evolution of GGST materials is critical for building up the physics behind the functionality of such devices, experimental observations are challenging due to the confinement of the active material to the nanometer scale in integrated PCM. We have thus worked at developing a methodology combining various (scanning) transmission electron microscopy ((S)TEM) techniques to identify grains of different phases that define the cells’ microstructure and the structural and chemical transitions that affect them during electrical programming.

Methods

The studied devices were integrated PCM with a “wall architecture”. The cell consists of a GGST active layer of a few tens of nanometers thick, which is deposited on top of the heater and encapsulated by a metallic top electrode. Extremely thin (<30 nm) TEM lamellas were prepared using focused-ion beam (FIB) from cells after electrical programming. The active region of PCM is a dome which can be amorphous (RESET state, see Fig. a) or crystalline. TEM samples were characterized by various (S)TEM-based techniques: dark-field (DF) and high-resolution (HR) imaging to access crystallographic information, and high-angle annular dark-field (HAADF) imaging and electron-energy loss spectroscopy (EELS) for chemical mapping. In-situ TEM heating was conducted on cells in RESET state under DF imaging conditions using a furnace-type holder. Results were cross-compared with samples after ex-situ baking.

Results

Fig. b shows a typical (S)TEM analysis of the GGST cell for a region near the heater. The cell was programmed by a forming pulse, which is used to activate the material by melting it

followed by slow cooling during which the melt recrystallizes [5]. The STEM HAADF image and associated EELS maps show chemical segregation near the heater: the material is separated into an outer Ge-rich region surrounding a core made of a Sb-rich (left) and a Te-rich (right) regions. TEM HR images of 2 regions in the core show quite similar crystalline lattices. However, when compared using geometric phase analysis (GPA), the corresponding “strain” map indicates the lattice spacing in the Sb-rich region is ~4% larger than found in the Te-rich region. A clear interface is seen which matches with the boundary evidenced in chemical maps. In the SAED pattern, diffraction spots from 2 sets of slightly different lattices are found and show a good match with rhombohedral Sb (ZA 441) and face-center-cubic GST (ZA 111), respectively. By selecting the spot arising from one or the other, DF images of Sb and GST grains can be obtained separately. This demonstrates our ability to identify and distinguish main crystalline phases (Ge, GST, and Sb₂) in GGST cells using combined chemical and crystallographic analysis.

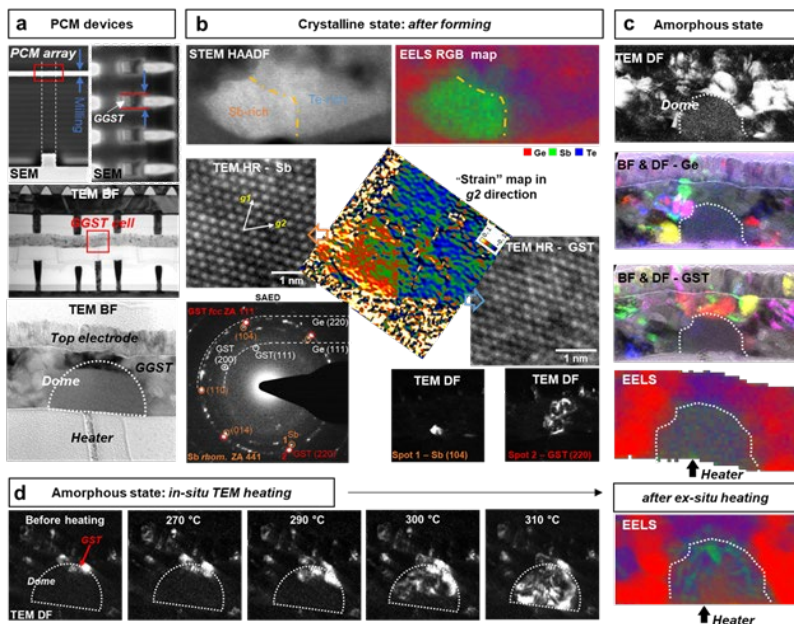
Fig. c shows a GGST cell after being programmed by a melt-quench pulse (RESET). An amorphous dome can be evidenced in the BF and DF images. Beyond that, composite “BF & DF” images can be generated by superimposing the BF and several different DF images of either the Ge or the GST phase. A very peculiar characteristic of the polycrystalline region surrounding the dome is evidenced by DF images and the EELS map: Ge crystals preferentially accumulate at the lateral sides of the dome while GST grains are mainly located above it. The thermal stability of PCM, notably of their RESET state, is a key factor for device reliability. Fig. d shows a GGST cell programmed to the RESET state and subjected to annealing in-situ in the TEM. DF imaging shows a GST crystal located above the amorphous dome. When heating to temperatures at which RESET resistance decreases (250 to 300 °C), DF images show that this grain progressively regrows by epitaxy into the amorphous region until it occupies almost the entire dome. EELS maps of the RESET state and after partial-crystallization (by ex-situ annealing) show that while the amorphous dome is initially chemically homogeneous, phase separation is observed after recrystallization (Fig. c and d): Sb segregates inside the crystallized region while the remaining amorphous material becomes more enriched in Ge.

Conclusion

In this work, we have set up a (S)TEM-based methodology to study complicated phase and chemical transitions that occur when programming GGST-based PCM cells. By combining chemical and crystallographic analyses, grain distributions of crystalline phases formed during programming can be revealed. A specific polycrystalline environment, involving two Ge “walls” and a “roof” of GST grains, has been identified. Using in-situ and ex-situ TEM, the thermal recrystallization behavior of the amorphous dome has been revealed: the growth of GST crystals from top of the dome is the mechanism dominating the crystallization. Further chemical analysis has evidenced the phase separation inside the dome, which limits the crystallization process.

Such complete (S)TEM-based analysis provides important experimental results for setting up physical models describing electrical conduction in PCM cells and to guide the process optimization.

Graphic:



Keywords:

phase-change-memory, chalcogenide, in-situ TEM, crystallization

Reference:

[1] P. Cappelletti, et al. J. Phys. D: Appl. Phys. 53 (2020) 193002.
 [2] F. Arnaud, et al. 2020 IEDM (2020) 24.2.1-24.2.4.
 [3] E. Rahier, et al. ACS Appl. Electron. Mater. 4 (2022) 2682-2688.
 [4] E. Rahier, et al. Phys. Status Solidi – Rapid Res. Lett. (2023) 2200450.
 [5] S. Ran and E. Petroni, et al. “Phase transitions and chemical segregation in Ge-rich GeSbTe based phase-change memory cells (tentative)”, in preparation.