Crystallization investigations of Ge-rich GST cells using *in situ* thermal pulses coupled with STEM-EDX and HR-TEM analyses

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Phase Change Materials composed of ternary alloys, commonly $Ge_2Sb_2Te_5$ (GST), are considered to replace classical non-volatile memories in various applications. The growing interest in this technology is related to the significant difference in physical properties between the amorphous and crystalline phases, which allows for easy modification and reading of the memory state, coupled with a fast-switching capacity of the order of ns. Typical crystallization temperature for GST is in the range of 150-170°C, a temperature too low for data retention in automotive applications. To address this limitation, Ge-rich GST (GGST) alloy with a crystallization temperature of 350°C was developed [1]. This material crystallizes incongruently, and ramp annealing at low heating rates [2] show the presence of crystallized Ge and GST.
In order to investigate the phase separation in conditions closer to the working conditions of memories (i.e. ns timescale), rapid heating experiments are performed by applying brief thermal pulses of 0.3s to GGST amorphous confined nanostructures, *in situ* in TEM/STEM microscopes. STEM-EDX analyses have been performed after each thermal pulse to follow the evolution of the spatial distribution of Ge, Sb and Te as a function of the temperature, within the cell. While the Sb concentration remains quite homogeneous regardless of temperature, inhomogeneities in Ge and Te compositions are evidenced from 320°C on (Fig. 1A and 1B). A local increase in Te content is observed in the periphery of the cell, close to the interface with the surrounding capping layer and in the underlayer (UL). A Ge enrichment of the UL occurs as the temperature increases, accompanied by a Te depletion in the same area. This depletion is correlated with a Te enrichment right above the UL, in the bottom part of the GGST cell. The quantification of Te-rich regions yields a Te/Sb ratio of 0.37, very close to the expected value of 0.4 for GST. A deeper analysis of the elemental maps was made by extracting the composition from every pixel and plotting the Sb/Te, Sb/Ge and Te/Ge ratios. The composition tends to evolve into two opposite directions: Ge enrichment suggesting the formation of Ge grains, and Te-rich regions suggesting the formation of GST when compared to the theoretical ratios. The first crystallization events are observed at 350°C during *in situ* HRTEM experiments. HRTEM analysis after heating at 400°C reveals a complete crystallization of the various investigated cells. The Fast Fourier transforms calculated from HRTEM images were generated and combined with radial integration profiles to identify the different crystalline phases in presence (Fig. 1D). The analysis of the diffraction peaks reveals the presence of the Ge cubic and the GST metastable cubic phases. GST reflections appear at 390°C, highlighting two crystallization temperatures: 350°C for Ge, and 390°C for GST. These temperatures indicate that Te-Ge interdiffusion starts before the crystallization of the first Ge grains. By selecting all the reflections of each phase in the Fourier spectra of the experimental HRTEM images, numerical dark field images are produced, which allow mapping the various crystallized phases, and evidencing the crystallization of the Ge and GST nanograins mainly in the bottom part of the cell (Fig. 1C). *In situ* 4D-STEM analysis coupled with STEM-EDX acquisition are in development to perform both structural and chemical investigations simultaneously. These results, together with synchrotron XRD performed *in situ* during thin films crystallization [3], allow for a complete picture of the crystallization pathways of this Ge-rich GST alloy including elemental separation, crystallization and ordering of different phases, as well as texture in relation with various interfaces.

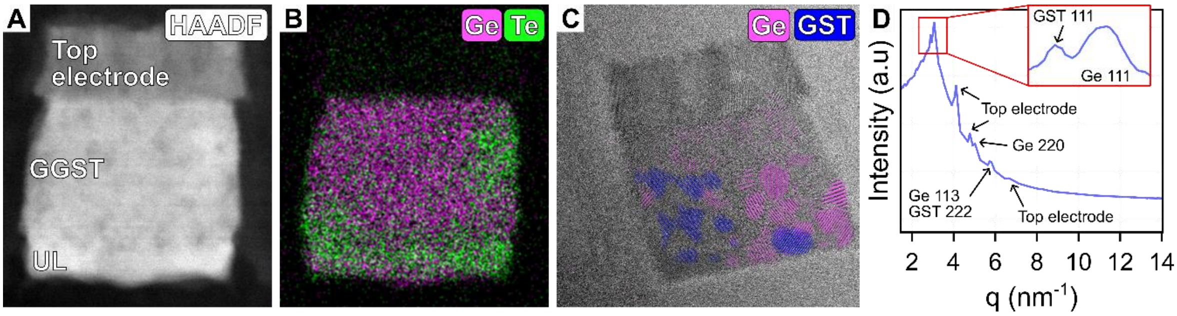

Fig. 1 (A) STEM-HAADF image of a representative GGST cell with (B) its elemental map showing Ge, Sb and Te after a thermal pulse at 380°C. (C) HRTEM image of another GGST cell heated at 400°C, showing evidence of Ge and GST cubic phases inside the cell. (D) Radial integration profile of the corresponding FFT of (C) used to identify the different phases.

References

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