Identification of the phases resulting from the thermal crystallization of Ge-rich GeSbTe alloys using EELS

Dr. Minh Anh Luong[1], Dr. Eloïse Rahier[1], Dr. Sijia Ran[1], Dr. Alain Claverie[1]
[1]CEMES-CNRS and University of Toulouse, 29 Rue Jeanne Marvig, 31055 Toulouse, France

Background incl. aims
Among many phase change materials, Ge-rich GeSbTe (GGST) alloys are of considerable interest due to their high thermal stability, a specification required for the next generation of embedded digital memories. This stability results from the fact that these alloys do not crystallize congruently but experience phase separation and finally form a polycrystalline material in which small grains of Ge and of several GeSbTe (GST) cubic phases coexist [1-3]. As all these phases, which have different chemical compositions, have almost the same lattice parameters, they cannot be differentiated by X-ray diffraction. On the other hand, as the grains are much smaller than the thickness of the lamella, the compositions measured by energy-dispersive X-ray spectroscopy (EDX) or electron energy loss spectroscopy (EELS) in the transmission electron microscope result from the overlapping of many small grains and do not give access to their individual stoichiometry (Figure 1). Herein, we report an efficient method to deduce the stoichiometry of the different phases of the grains which overlap by exploiting “pixel by pixel” EELS data and by extracting their characteristic Sb/Te ratio. Using this method, we show that the crystallization of the GST phase proceeds through the initial formation of cubic GeTe and its progressive enrichment in Sb during thermal annealing, ultimately leading to the formation of the well-known stable GST-225 phase.

Methods
A 100 nm-thick GGST layer was deposited by physical vapor deposition (PVD) onto a naturally oxidized 300 mm Si(100) wafer and covered by a 20 nm-thick TiN cap layer. The samples were annealed in a conventional furnace under nitrogen flux. Cross-sectional specimens were prepared by focus ion beam (FIB) technique operating with a 30 keV Ga ion beam and finally polished and cleaned at 2 keV–3 pA. High-angle annular dark-field (HAADF)-STEM and dual-EELS data were acquired on a probe corrected ARM JEM JEOL 200F microscope, operated at 200 kV. The convergence and collection angles for EELS were 29.6 and 75.9 mrad, respectively. The quantification process was carried out through the following steps: 1) the zero-loss spectrum is used to subtract the background and plural scattering signals caused by the specimen thickness, 2) high-loss elemental peaks are fitted using the Hartree-Slater model, after exclusion of the ELNES edges (about 50eV width) and 3), the Ge, Sb and Te ratios are normalized and the result obtained at each pixel is plotted in a ternary diagram for visualization.

Results
Figure 2 shows HAADF STEM images and corresponding plotted Sb/Te ratio for GGST samples, annealed at different temperatures and time durations. After 320°C/8h annealing, when the first GeSbTe cubic phase forms, the compositional data points spread along an almost horizontal line (Sb/Te = 0.05). The alignment of the pixels on such a horizontal line indicates that the compositions which are measured result from the superposition of pure Ge and almost pure GeTe grains in varying proportions, depending on the overall composition of the layer and statistical fluctuations. The vertical shift of this horizontal line upwards reflects the homogeneous distribution of Sb in the material and should be interpreted as being due to the presence of a third highly dispersed "phase" containing all the Sb. When annealing for longer times or at higher temperatures (320°C/16h, 400°C/30min and 400°C/3h), the Sb/Te ratio characteristic of the GST phase which is formed slowly and progressively increases, from 0.05 (horizontal line) to 0.4, the signature of the well-known stable GST-225 phase. In the meantime, the horizontal shift due to dispersed Sb decreases. This shows that Sb, which was

initially diluted in the matrix, progressively incorporates into the GeTe crystals during annealing (by substitution, necessarily on Ge sites). Moreover, some pixels point toward Sb-rich GST phases. Complementary TEM analysis shows these phases have the hexagonal structure, the most common being Sb2Te3. Pure Sb2 lamellas can also be identified by HAADF STEM imaging and EELS mapping, as shown in Figure 1.

Conclusions

We have thoroughly investigated the phases resulting from the thermal crystallization a GGST alloy using advanced transmission electron microscopy based techniques. While X-ray diffraction cannot differentiate the various phases found in the polycrystalline material due to their "close" lattice parameters, the careful analysis of the Sb/Te ratio obtained from pixelated EELS data gives access to the stoichiometry of the GST phases in the samples. Based on such analysis, we demonstrate that the thermal crystallization of GGST alloys proceeds through the initial formation of GeTe and Sb-poor GST grains which get progressively enriched in Sb during annealing until forming GST-326 (Sb/Te=0.33) and GST-225 (Sb/Te=0.4) grains. Moreover, excess of Sb and Te can be accommodated within Sb2 lamellas and Sb2Te3 hexagonal grains.

Graphic:

Figure 1

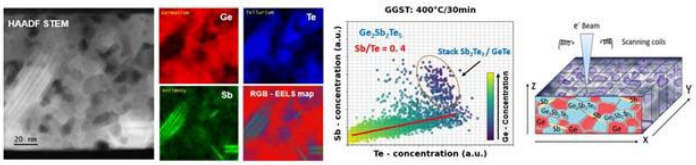
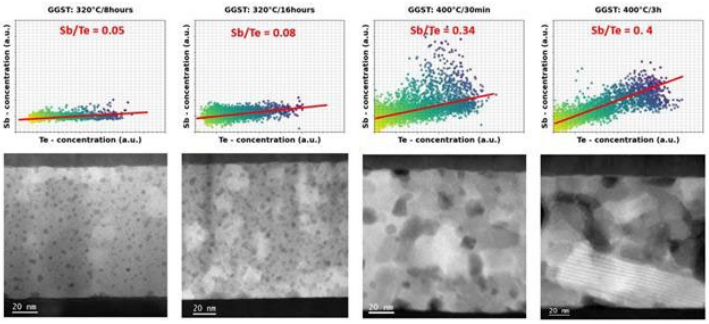


Figure 2



Keywords:

PCMs, GeSbTe, crystallization, EELS, TEM

Reference:

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