ESRF	**Experiment title:** On the influence of confinement geometries on the phase separation and crystallization behavior in a mixed GeSbTe amorphous alloy: combining in-situ XRF and XRD studies	**Experiment number**: IN-849 IRT Nanoelec
Beamline: ID16b	**Date of experiment**: Nov 27th to 29th, 2021	**Date of report**: 24 February 2022
Shifts:	**Local contact(s)**: Jaime Segura Ruiz	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists)

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Report:

The aim of this IRT beamtime was to deliver a proof of concept for studying the distribution of Ge, Sb and Te and their segregation in a ternary Ge-Sb-Te phase change material (PCM) during *in situ* thermal annealing by means of X-ray fluorescence (XRF) nano-mappings at the ID16B beamline. As the title of the proposal mentions, a mirror experiment involving *in situ* X-ray diffraction mapping is planned. It should be performed at ID13 beamline in July 2022. In the following the main takeaways concerning sample preparation and experiment setup and our achievements are discussed.

Sample preparation: Specimens were prepared on micro-heaters developed at ID13 [1]. The prepared micro-heaters were mounted on a specially prepared stage at the beamline (figure 1a). The specimens themselves were cleaved from big wafers (prepared by STMicroelectronics) and thinned down by mechanical grinding and polishing down to a thickness between 40 and 10 µm. Each specimen (maximum size of 30x30x10 µm) was cut and placed onto a single micro-heater with a FIB (focused ion beam) microscope. Some other specimens were also prepared by placing pieces of a crushed, thinned wafer by hand on the chip under a light-microscope.

We learned in the course of this experiment that the best results are obtained with the thinnest and smallest samples. This guarantees the thermal homogeneity and the stability (too big samples tend to jump away from the heater's membrane during transport or after. The heater is vertical during the experiment). Four specimens could be mapped *in situ* during heat treatment. As a backup, a number of samples that were previously studied *in situ* at DiffAbs beamline (Soleil synchrotron) with broad beam X-ray diffraction were placed on a conventional sample holder (mm-sized specimens) and measured *ex-situ* at different spots.

Analyses and proof of concept: In the following we focus on one successful *in situ* measurement that very nicely shows the segregation over time while increasing temperature. The specimen was one of the last ones that were investigated. After a set of initial trials with other samples to get acquainted with the setup, this measurement finally went smoothly. In contrast to other samples, the discussed specimen did not fall off the micro-heater. This is rationalized by a good adhesion of the specimen to the chip owing to the specimen being only 10 µm thin and of optimal remaining specimen dimensions (was prepared by the FIB-routine). The specimen was very homogeneous and all acquired know-how was used for data recording. Instrumental parameters and map sizes are given in the figure's legend.

Data extraction was performed via a custom python routine that includes the fabio reader library. Figure 2a shows the *Ge-distribution* in the monitored area before heating started. Figure 2b shows the same area after segregation started. Figure 2c shows the dynamic ranges (maximum intensity minus minimum intensity of all maps over the course of the experiment). This simple scalar yields an information about the

status of the reaction. This shows that it is in principle possible to follow the segregation of the element distribution by XRF maps *in situ*.

<u>*Conclusions*</u>: this IRT beam time was successful and we could demonstrate the feasibility of the *in situ* monitoring by XRF of elemental segregation during the crystallization of a Phase Change Material. This beamtime has allowed for a clear identification of the most important challenges to overcome for the experiment to be successful. They are listed below:

- handling of samples and micro-heaters is crucial – it was learnt that sample preparation must be well conducted and planned. Very thin samples should be prepared in a FIB (focused ion beam) microscope and directly placed on the heater. Small specimens are more likely to remain on the heater during transport and mounting. Furthermore, timely prepared samples can be checked for homogeneity and documented in an SEM beforehand.
- A heater that is suited for larger specimens could be available for future experiments (must be adapted and tested). This could decrease costs and complexity of such experiments.
- For future experiments an online monitoring of segregation would be extremely helpful. Automation e.g. by visualizing the evolution of the maps' dynamic ranges (fig2 c) could be envisaged and potentially helpful.

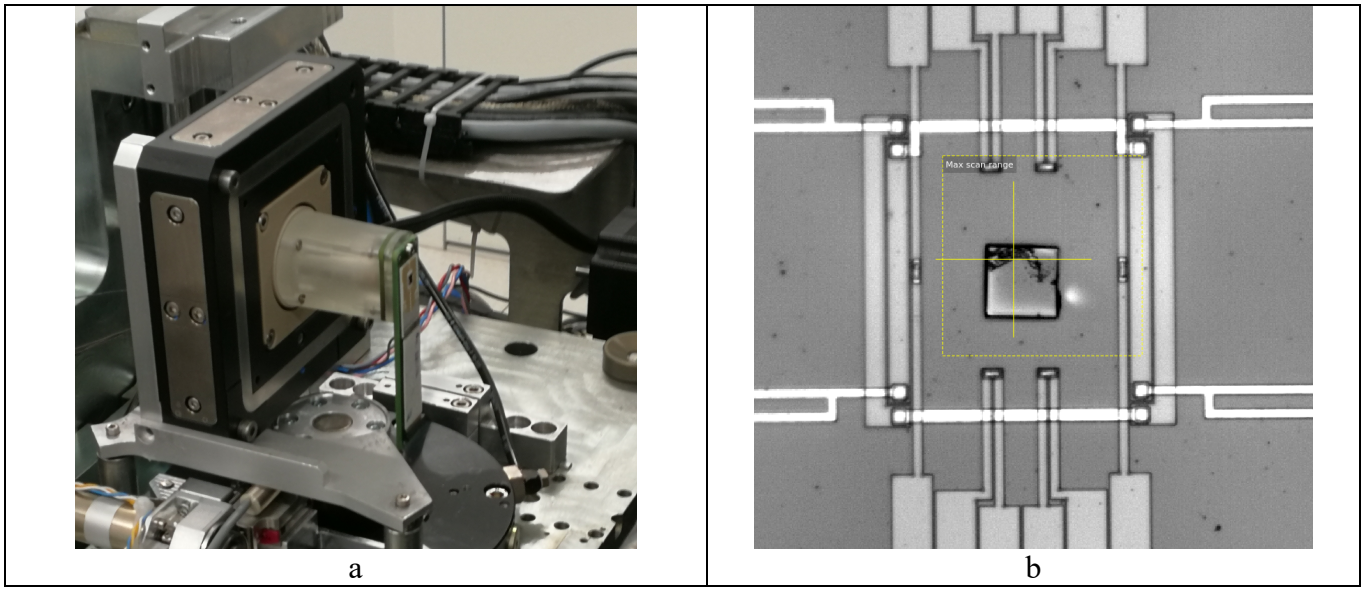

Figure 1: a) device to mount micro-heaters at the beamline; b) camera image of micrometers sized sample on mounted micro-heater.

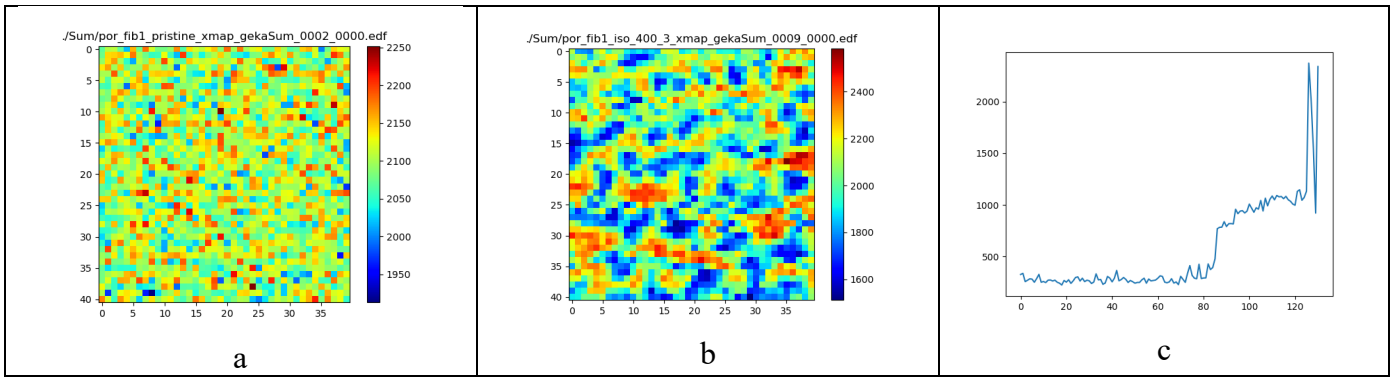

Figure 2: XRF-maps of an FIB prepared sample recorded in situ a) before, b) after the oset of the segregation process. c) gives an overview over the evolution of the dynamic range of each map along the experiment. The maps were acquired with a beam size HxV 68 x 55 um2 and an energy E=33 keV with a flux of 10^11 ph/s. The maps are 2 µm x 2 µm in size and were recorded with a step size of 50 nm and an acquisition time of 30 ms per pixel.

<u>*References:*</u>

[1] M. Rosenthal et al., J Synch Rad vol. 21, 1, 223-8 (2014).