



**Experiment title: “study of crystallization mechanisms of metastable amorphous GeTe and GeSb<sub>6</sub> thin films used in phase change random access memory (PCRAM)”**

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MA-814

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BM02

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## **Report: Proposal summary**

The concept of Phase Change Random Access Memory (PCRAM) attracts great interest in order to overcome limitations of classical floating gate non volatile memories when critical dimensions are below 45nm. PCRAM uses the reversible phase change between the crystalline and the amorphous state of specific materials, such as Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> (in short GST). The crystalline phase of GST has a low resistivity and the amorphous GST has a high resistivity, which corresponds respectively to “0” and “1” bits. In PCRAM cells the reversible switching between these two states is achieved by applying a short and high current pulse to induce the transition from the crystalline to the amorphous state (reset process where the material is molten and then vitrified) and a relatively long and low current pulse for switching from the amorphous to the crystalline state (set process). When aiming at obtaining a high retention time, i.e. a high thermal stability of the amorphous phase, as well as a high cyclability, one has to optimise the crystallisation kinetics.

In phase change materials, a better understanding of the phase change mechanisms is mandatory. Ge<sub>0.5</sub>Te<sub>0.5</sub> and GeSb<sub>6</sub> have shown promising results with respect to crystallisation speed, crystallisation temperature and/or retention time. Ge-Te and Ge-Sb are complementary model systems: looking at their equilibrium phase diagrams, a Ge<sub>5</sub>Te<sub>5</sub> crystalline phase exists whereas no stable crystalline phase exists in the binary Ge-Sb system (GeSb<sub>6</sub> is the eutectic composition). On one hand, Ge-Te is known to belong to the family of phase-change materials whose crystallisation process is nucleation-dominated. On the other hand, Ge-Sb shows a growth-dominated behaviour. Moreover, previous studies have shown that in GeSb<sub>6</sub>, the Sb crystallisation is only observed above 240°C, accompanied by a marked increase of the optical reflectivity and a drop in electrical resistance, and that fcc Ge precipitates above 350°C, with a second small increase of the reflectivity.

*MA-814 experiment* aimed to study the different crystallisation stages: size and chemical nature of the nuclei and the following structural evolutions (texture, lattice parameter, stoichiometry) at different stages of thermal annealing: 10 nm, 30 nm and 150 nm thick Ge<sub>5</sub>Te<sub>5</sub> and GeSb<sub>6</sub> amorphous thin films were deposited on a silicon wafer by PVD and submitted to different thermal annealing processes ex situ before performing X-ray diffraction. About 50 samples were studied .

## Experiment & results:

$4.10^{11}$  photon/s of 10.5 keV were focalised on the center of D2AM diffractometer (0.125 mmV x0.3 mmH). When using a “dd”~95 mm (distance from the sample to the 2D detector), the angular range,  $\Delta 2\Theta \sim 37^\circ$ , is sufficient to determine the texturation with a single image. A 475 mm dd distance ( $\Delta 2\Theta \sim 7.5^\circ$ ) gives a sufficient resolution for studying profile shapes and peak positions. Finally, the accessible q-range allows detecting diffraction peaks at high Miller indices to investigate the nature of the phases, lattice parameters, texturation, diffraction domain sizes and hopefully micro-strains. The sample was in an evacuated cell in order to minimize the empty cell background and the 2D detector was the CCD Princeton@ camera (16 bits dynamics & 1340x1300 pixels of  $50 \times 50 \mu\text{m}^2$ ). When possible, we used the symmetric  $\Theta-2\Theta$  geometry in reflection, but, in the thinnest films, or for samples at early stages of crystallisation, one had to use a grazing geometry.

As an example of the conducted experiments, some results obtained on  $\text{GeSb}_6$  films are reported in Figures 2 and 3 . The samples were studied after the thermal treatments presented in figure 1. Figure 2 shows the 2D diffraction images obtained for 2 film thicknesses (150 nm and 30 nm). First, it is demonstrated that using this setup, films as thin as 30 nm can be analysed. Second, clear evolutions as a function of film thickness and thermal treatment are observed. As expected, Ge crystallisation (311 Ge peak at  $40.56^\circ$ ) has occurred in the samples annealed at  $T_2$ . Besides a strong Sb texture (strong 012 & 024 peaks) is observed . Ge lines are absent in samples annealed at  $T_1$ , but the Sb texture is already present. Several lines cannot be indexed and may correspond to an unknown metastable phase. The weaker signal in the 30nm thick sample has similar shape as the one in the 150nm thick sample. The variations of peak shapes before and after anneal suggest large grain growth during the .

The complete analysis of the images obtained for various film thicknesses, different annealing processes (about 40 such images, plus about an equivalent number for the sample-detector distance of 475 mm) is in progress, focusing on the width, displacement and asymmetry of the rings of known phases and also on attempts to determine new metastable phases.

Concerning GeTe samples, depending on annealing conditions, both the stable R3m GeTe and the metastable fcc “NaCl” like GeTe phase ( $a=0.605$  nm) are observed as well as lines of an unknown phase.

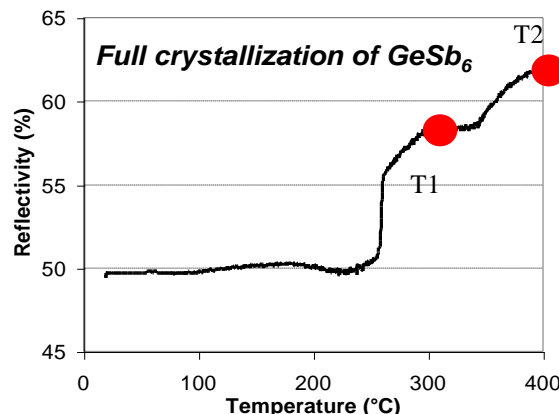


Figure 1: Temperature dependence of the reflectivity of  $\text{GeSb}_6$  film annealed at a constant heating rate ( $10^\circ\text{C}/\text{mn}$ ).

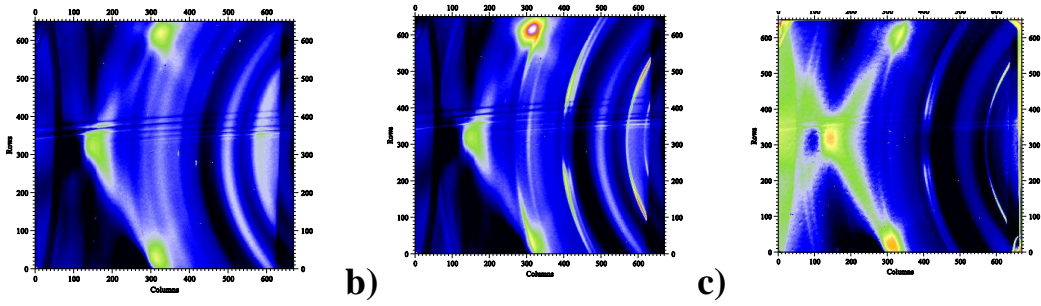


Figure 2: 2D images in symmetrical conditions with the detector centered at  $2\theta=36.5^\circ$  for  $\text{GeSb}_6$  films . (a) 150 nm thick film after the first crystallisation after heating at  $T_1$  ; (b) 150 nm thick film in the fully crystallised state after heating at  $T_2$  ; (c) 30 nm thick fully crystallised film after heating at  $T_2$ . The sample-detector distance was  $\sim 95$  mm. The three strong maxima correspond to the tails of the Bragg peaks of the Si wafer).

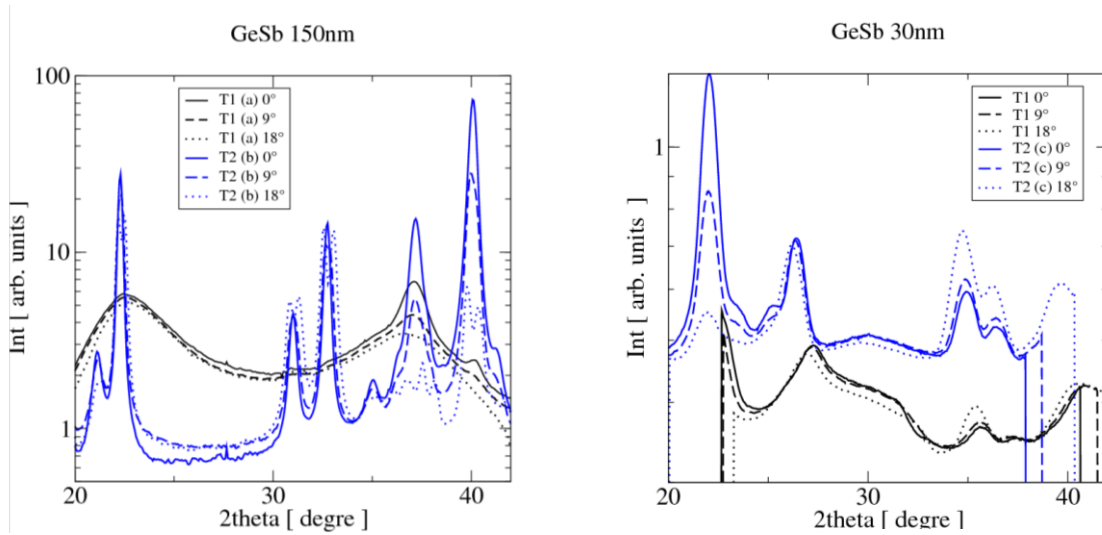


Figure 3: Azimuthal averages in 9 degrees sectors (— centered, ---  $+9^\circ$ , ...  $\pm 18^\circ$ ) defined with respect to the horizontal symmetry for previous samples.