ESRF	**Experiment title: "Size and interface effects in the crystallization of phase change materials nanometric clusters and thin films "**	**Experiment number**: 02-02 800
Beamline: BM02	**Date of experiment**: from: 10/31/12 11/05/12	**Date of report**: 02/14/2014
Shifts: 15	**Local contact(s)**: Nathalie BOUDET	*Received at ESRF:*

Names and affiliations of applicants:

Françoise Hippert (Grenoble-INP & CNRS);

Robert Morel, Ariel Brenac (CEA/INAC); Giada Ghezzi; Frédéric Fillot; Pierre Noé (CEA/LETI)

Proposal summary:

Phase change materials can switch reversibly between crystalline and amorphous phases. The large difference in their optical and electrical properties in the two phases is the basis for optical recording and PC-RAM. One question that arises, notably for the PC-RAM design, is the scalability of these properties. The amorphous to crystalline phase transition shows finite size effects in thin films with an increase in the transition temperature, but results with clusters are less clear. Based results from a previous run with $Ge_2Sb_2Te_5$ clusters [1] we performed, in this study, in situ annealing and X-ray diffraction at grazing incidence measurements in order to observe the phase transition in 5 nm GeTe clusters made by gas-aggregation technique, as well as in GeTe thin films in Al_2O_3. The choice of Al_2O_3 for capping material results from our previous finding that, with $Ge_2Sb_2Te_5$ clusters, it induces large strain in the crystallized clusters without significant change in the transition temperature. In addition to this, samples with Ta-capped GeTe have been measured, to determine which effect this material used for electrodes in real devices has on the phase change properties.

Experiment:

The X-ray photon energy for this run was 18.239 keV (lambda = 0.0679775 nm) and diffraction spectra of the samples were recorded with a Princeton CCD 2D detector with 1340 x 1300 pixels. The detector position was choosen such that the 2θ angular span was from 8.5° up to 26°, with a 4° fixed angle of incidence relative to the substrate plane. Samples used in this run consist in 1) Trilayers with 20 nm or 5 nm GeTe thin film sandwiched between two 20 nm Ta or Al_2O_3 thin films; 2) Granular thin films with 5 nm of GeTe clusters embedded in Ta or Al_2O_3; 3) Bare Si substrates and substrates covered with Ta or Al_2O_3, for background signal measurement.

A first batch of 29 measurements was made at room temperature. Part of these samples had been previously annealed at temperatures ranging from 250°C to 400°C. This first group constitutes the so-called ex situ samples.
For a second group of 4 samples the diffraction spectra were recorded as a function of the temperature—from 170°C up to 370°C—using an Anton-Paar DHS900 furnace with a PEEK dome. These samples constitute the so called in situ samples.

Results:

Ta-covered GeTe : A change in the Ta texture is observed in annealed *vs* as-deposited films, which is not observed with pure Ta film. The tantalum is in its tetragonal phase, with a slight dilatation of the lattice parameter. Given that with our geometry the diffraction vectors are not perpendicular with the thin film surface, the full texture analysis is not possible.

With Ta with 20 nm GeTe thin film, faint GeTe crystalline diffraction lines appear at 325°C (close to the reported bulk transition temperature) but with 5 nm thin film or with clusters it is unfortunately not possible to extract the GeTe signal from the background.

Al2O3-covered GeTe : The measurements with both ex situ and in situ samples allowed to observe the crystallization in GeTe thin films and clusters, visible from the growth of three GeTe reflexion lines. With ex situ measurement the peak position can be determined rather precisely and is found to be very similar for thin films and clusters, which indicates that the GeTe clusters are not significantly strained by the almumina matrix. However, due to the fact that each measurement is made with a different sample, the background signal amplitude and the location of the spurious Kikuchi lines on the 2D images differ and the peaks amplitude could not be assessed from image substraction.

Regarding the in situ measurements, the GeTe diffraction lines are nearly masked by the very intense additional diffracted signal from the furnace peek dome. As a consequence the peak position analysis as a function of temperature is very difficult if not impossible. It was nevertheless possible to assess that the phase transition in clusters starts at a temperature close to that of the films, with a more gradual crystallization (Fig. 1 and 2).

In conclusion this run confirms that it is possible to observe the amorphous-crystalline phase transition in 5 nm clusters, using X-ray diffraction, and that the crystallization temperature of clusters is close to that of thin films. On the other hand the structural evolution of the clusters as they crystallize and their final state could not be measured because the assignment of the GeTe peak position is not precise enough. Regarding the two types of experiment that we undertook, measuring ex situ annealed samples might be more profitable than the in situ annealing measurement using the Anton-Paar furnace, most of all because in the former case the signal/noise ratio is higher and the background signal is flatter. In a future run we plan to look more closely at the clusters structure using a thinner or amorphous substrate, or screening the Kikuchi signal using an absorbing intermediate layer (for instance by depositing a thin HfO_2 amorphous layer underneath the clusters layers).

[1] G. E. Ghezzi *et al.*, APL **101**, 233113 (2012).

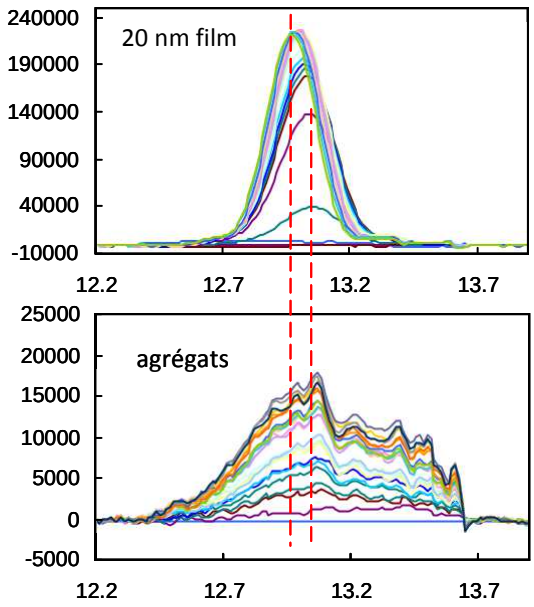

Fig. 1. Temperature variation of the GeTe [012] diffraction peak. From the lower to the upper curve, temperature vary from 200°C to 400°C measured in situ. Upper panel : 20 nm GeTe thin film in alumina ; Lower panel : GeTe clusters in alumina.

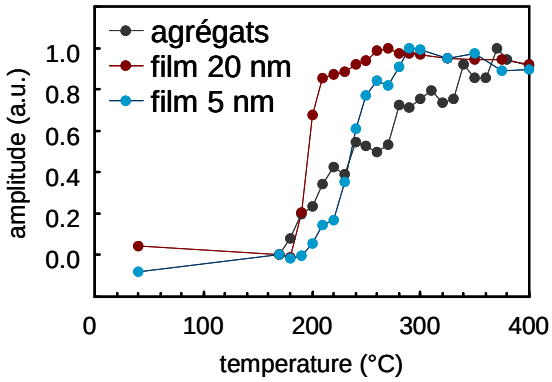

Fig. 2. Relative amplitude of the GeTe [012] diffraction peak as a function of temperature for cGeTe clusters, 230 nm film and 5 nm film in alumina. The onset in the rise indicates the start of the amorphous to crystalline phase transition.