ESRF	**Experiment title: "Study of crystallization of nano-sized clusters of phase change materials"**	**Experiment number**: 02-02 789
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Shifts: 6	**Local contact(s)**: Nathalie BOUDET, Jean-François BERAR	*Received at ESRF:*

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Proposal summary:

Phase change materials (PCM) are excellent candidates for use in non volatile memories due to the large difference between the resistivity of their amorphous and crystalline states. Confining the phase change material has a strong impact on the crystallization mechanism. For thin films it has been demonstrated that the crystallization temperature increases when reducing the thickness of the film under 10nm. Studying thin films offers the possibility of investigating confinement in one dimension only. In order to understand the effect of confinement in three dimensions nano sized clusters of Phase Change Material are required. We succeeded in depositing Ge2Sb2Te5 (GST) clusters with 5 nm diameter using gas-condensation technique and their deposition under UHV, followed by encapsulation with sputtered Al_2O_3 to prevent sintering or oxidation. The aim of the experiment was to study the crystallization of such clusters as part of a more general work aiming at determining the effect of nano size dimensions on phase transition in new materials candidate for PCRAMs, in the framework of an accepted RTRA Nanoscience Foundation project (Percevall).

Experiment:

The incident X-ray energy has been chosen equal to 17.8 keV and the 2D detector was the CCD Princeton@ camera (16 bits dynamics & 1340x1300 pixels of 50x50 μm^2). The 2θ range has been chosen between 8° and 25°. We have measured GST clusters as well as a GST thin film (10 nm) to be used as a reference. For the thin film three successive layers has been deposited: 10 nm Al_2O_3, 10 nm GST, and a 10 nm Al_2O_3 capping layer. For the clusters the same total amounts of Al_2O_3 and GST are deposited, but in order to avoid coalescence effects between clusters during further thermal processing, a multilayer structure is adopted. After a 6 nm Al_2O_3 layer, 4 GST layers, each of equivalent thickness 2.5 nm, are deposited, separated by 3 nm thick Al_2O_3 layers. Finally a 6 nm layer of Al_2O_3 provides the capping. Moreover, one sample of Al_2O_3 alone has been measured in order to subtract accuratly the signal of the substrate. We first measured as-deposited clusters and thin film as well as samples annealed ex situ at 200°C, 300°C and 400°C, in order to determine the crystalline phase and estimate the crystalllization temperature. Then we performed X-Ray diffraction experiments during in situ annealing on GST clusters and film with the intent of obtaining information on the kinetics of the crystallization and a more precise determination of the crystallization temperature. We used a Anton Paar DHS900 furnace equipped with a PEEK plastic dome. For each sample the temperature has been raised by steps of 10°C each 10 minutes and two measurements were performed for each temperature step.

Results:

Examples of images obtained with the CCD camera are reported in Figure 1. We used a dedicated program developped by Jean-François Bérar in order to obtain the value of the scattered intensity as a function of 2θ from the 2D images. We obtained a clear signature of the crystalline phase for the samples annealed ex situ while the measurements performed on the as deposited samples present no Bragg peaks. The results are reported in Figure 2. The position of the Bragg peaks is the same for the film and the clusters and corresponds to the cubic GST phase. These results have been accepted for an oral presentation at the MRS Spring 2012 conference. Analysis of in situ diffraction experiments is in progress. The data treatment is made difficult by the presence of very high peaks due to the furnace dome. The position of these peaks is temperature dependent. The first qualitative results indicate that clusters crystallize at a temperature higher than the one of the corresponding thin film.

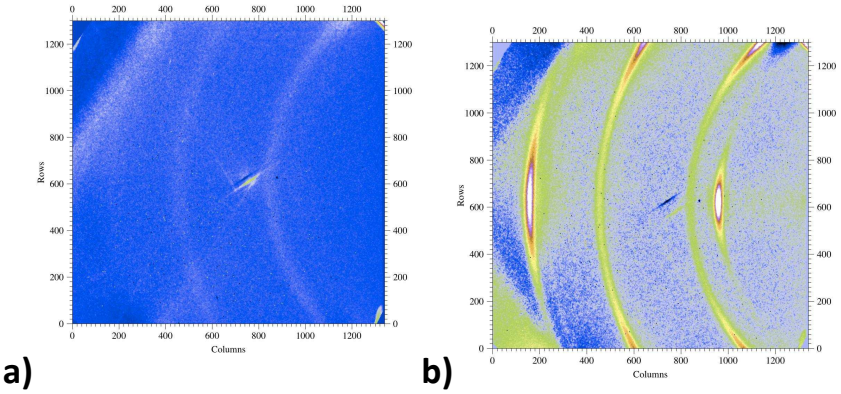

Figure 1: *2D images of GST clusters (a) and thin films (b) annealed at 200°C ex-situ. The image of Al_2O_3 substrate has been subtracted. The diffraction pattern of the film is highly textured.*

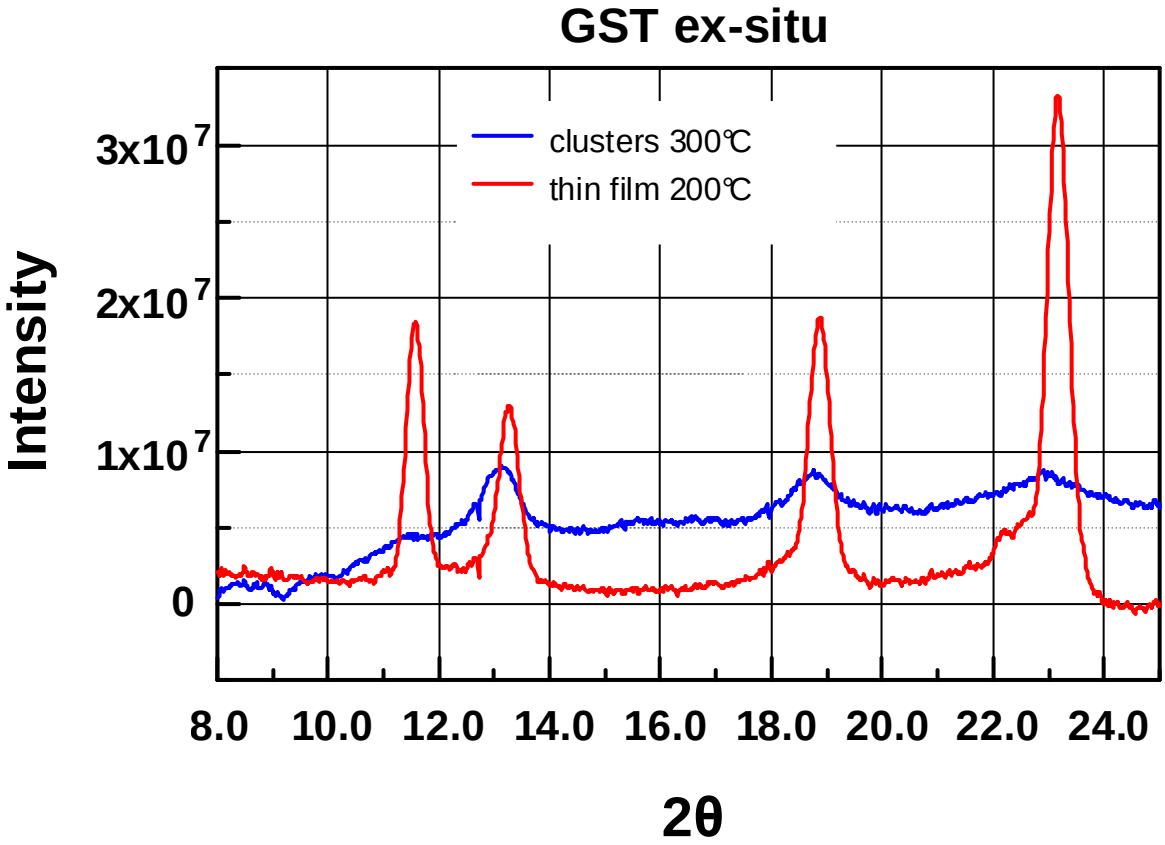

Figure 2: *XRD results for clusters and thin films of GST annealed ex-situ.*