ESRF	**Experiment title:** Crystallisation process in GaSb phase change materials : a combined DSC and quick-EXAFS experiment	**Experiment number**: HC 766
Beamline: BM 23	**Date of experiment**: from: 16/07/2013 to: 22/07/2013	**Date of report**: 26/08/2013
Shifts: 18	**Local contact(s)**: Olivier MATHON	*Received at ESRF:*

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Report:

The aim of the realized experiment was to obtain a deeper understanding of the crystallization process in Ga_xSb_{100-x} amorphous alloys by combining simultaneously EXAFS and DSC acquisition. Those chalcogen-free alloys are seen as potentially good candidates for phase change random access memory (PCRAM) applications. It was recently reported that $Ga_{50}Sb_{50}$ alloy possesses a high crystallization speed and a high crystallization temperature as compared to other candidates such as GeSb [1] or Te-based ternary alloy [2]. Interestingly, stoichiometric GaSb is also characterized by an inverse optical contrast [4] compared to typical PCMs. Finally, for Sb rich compositions ($0.5<x<0.8$) Ga_xSb_{100-x} alloys can show both negative and positive reflectivity contrast upon crystallization (depending on the temperature) which could be advantageously used for multi-bit storage.

Amorphous films of $Ga_{100-x}Sb_x$ were co-deposited by DC magnetron sputtering from nominally stoichiometric GaSb and Sb targets in an argon atmosphere (IBM). The films whose thicknesses were around 100nm, were deposited on photoresist covered Si substrates of 8 inches. The lift-off of the film was realized by disolving the photoresist layer in acetone. The as-obtained flakes were afterward rinced several time with ethanol in order to eliminate the polymer. This procedure, in spite of being time consuming, presents two advantages : i) it avoids any scraping of the sample that be dangerous considering the chemical nature of the alloys and ii) it allows working with films having low thicknesses (100nm to be compared with 1-2 μm for scraping procedure) which ensure the homogeneity of the as-deposited layer. The quantity of sample necessary to obtain a edge-jump around 1 was afterward gently diluted with ~100 mg of boron nitride in a hermetic vessel using a vibrationnary mill. The obtained mixture was then pressed to a pellet. Considering the low quantity of sample we had to make some compromises to be able to study all the samples at the 2 edge. We worked with around 9 mg at the Ga K-edge and around 18 mg at the Sb K-edge except for the $Ga_{30}Sb_{70}$ sample for which we had to work at Sb K-edge with only 10mg.

In order to perform the simultaneous DSC and quick EXAFS acquisition, the BM23 beamline was equipped with the IM2NP calorimeter and 1 shift was devoted to the commissioning of the calorimeter and the calibration of the calorimeter on the beamline. During the given time we studied four compositions (x=50, 30, 20, 12) at Ga K-edge and Sb K-edge using an heating ramp of 2°C/min. With such a heating ramp the phase transition are occurring over 20°C which is well adapted to the time resolution we could reach in QEXAFS. Indeed the acquisition time for a full EXAFS spectrum was equal to 79 seconds the Ga edge and

94s at the Sb edge. The last shifts were dedicated to measurements in fluorescence mode, at the 2 edges, for 2 samples $Ga_{30}Sb_{70}$ and $Ga_{12}Sb_{88}$. The aim of these measurements was to compare the EXAFS signal for two sample configurations: thin film and powder mixed with BN.

We present below our preliminary results for the data obtained for the sample $Ga_{12}Sb_{88}$. As shown in Fig.1, the DSC signal exhibit two exothermic effects located around 447 K and 547 K with respective enthalpy of 25 J/g and 7 J/g. These exothermic effects are characteristic of a transition toward a more ordered system and thus can be assigned to two crystallization events. This kind of two-step crystallization suggests a phase separation tendency, which agrees with the recent results in literature [3].

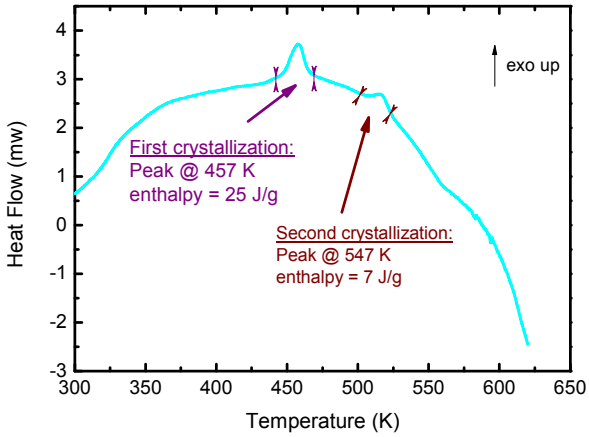

Fig. 1: DSC temperature scan performed at 2°C/min

Data extraction of the EXAFS oscillations for the Sb edge is given in Fig 2. as a function of the temperature. One can observe two clear changes in the frequencies and amplitude of the oscillation. The synchronization with the DSC reveals that those changes are occurring exactly at the temperature of the two exothermic peak in DSC. This suggests that the 2 crystallization events involve Sb atoms.

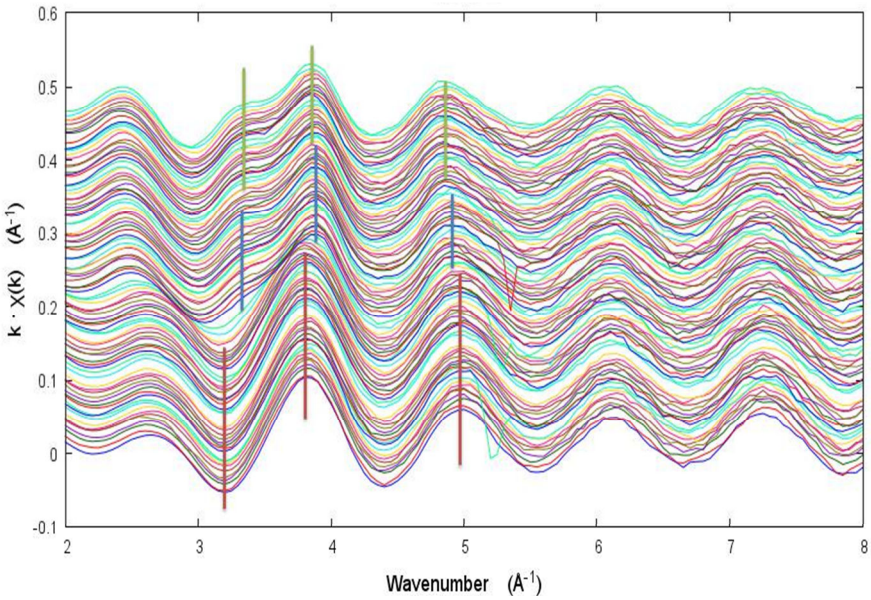

Fig. 2: EXAFS oscillations at the Sb edge

The EXAFS oscillations extracted for the Ga edge are represented in Fig. 3. Interestingly, only one sudden change is observed and it corresponds exactly to the second crystallization peak.

These preliminary results suggest that the first crystallization concerns only Sb atoms while in the second event, both atoms are involved. Considering the phase diagram, we can propose that a pure Sb phase crystallizes around 457 K while a GaSb phase is formed 547 K. A detailed EXAFS modeling will be performed to obtain the variation of the distances, neighbors and Debye-Waller factors.

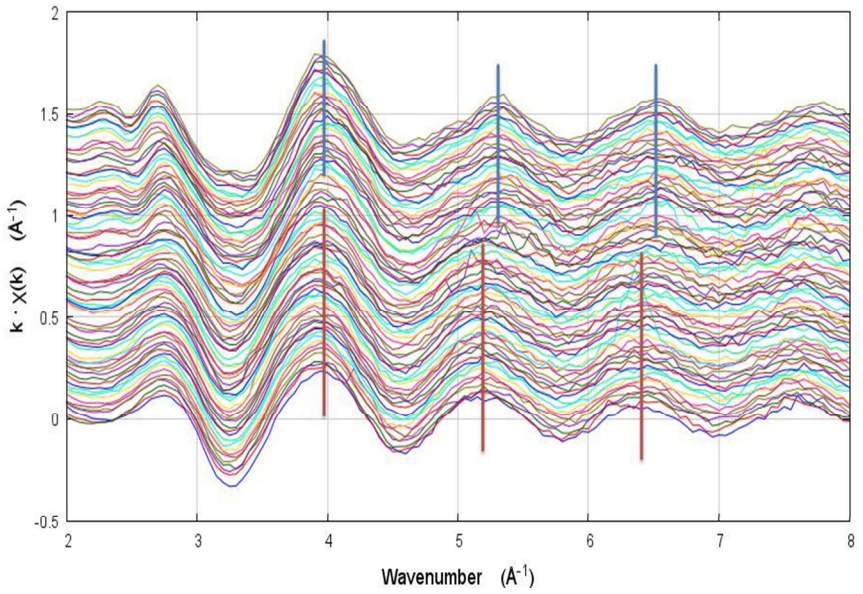

Fig. 3: EXAFS oscillations at the Ga edge

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[2] Lencer, D., Salinga, M. & Wuttig, M. (2011). Adv. Mater. 23, 2030–2058.
[3] S. Raoux, A.K. König, H.-Y. Cheng, D. Garbin, R.W. Cheek, J.L. Jordan-Sweet, and M. Wuttig, Physica Status Solidi (B) **249**, 1999–2004 (2012)