ESRF	**Experiment title:** *Correlated changes in physical properties upon crystallization in phase-change materials using simultaneous in-situ x-ray diffraction, x-ray reflectivity and sheet resistance.*	**Experiment number**: **MA1794**
Beamline: BM20	**Date of experiment**: from: 27 february 2013 to: 04 march 2013	**Date of report**: 11 august 2013
Shifts: 15	**Local contact(s)**: Carsten Baehtz	*Received at ESRF:*

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Report:

1. Introduction

Phase-change materials (PCM) are some of the most promising materials for data-storage applications. They are already used in rewriteable optical data storage (DVD, Blue ray) and offer a great potential for emerging phase-change non-volatile random access memories (PCRAM)[1–3].

The aim of this experiment was to study **the changes in structural and electrical properties of phase change material thin films** (Ga_xSb_{1-x} and GeTe) **by combining simultaneous *in-situ* measurements of x-ray reflectivity (XRR), x-ray diffraction (XRD) and sheet resistance (Rs) during thermal annealing**. Our goal was to obtain **direct correlations between electrical and microstructural changes during the amorphous-to-crystalline phase transition**, with a peculiar attention turned towards the film stoichiometry.

The **Ga_xSb_{1-x} system** has been recently proposed as a new PCM family: it could be advantageously used for PCRAM applications because it exhibits higher crystallization temperature (improving data retention in amorphous state) with a still high crystallization speed[4]. Moreover, depending on the composition, and contrary to most other PCM alloys, it can **show both negative or positive optical contrast upon crystallization** depending on the temperature thus enabling potential multibit storage capabilities.

2. Experimental method

Thin films of $Ga_{1-x}Sb_x$ ($0.5 < x < 0.9$) were co-deposited by DC magnetron sputtering from nominally stoichiometric GaSb and Sb targets in an argon atmosphere in IBM-Yorktown USA. 60 nm thick films were deposited on 500 nm thick SiO_2 layer thermally grown on Si (001) substrate for *in situ* structural and electrical measurements. Simultaneous *in situ* XRD, XRR and Rs measurements were performed on the BM20B-Rosendorf beamline, using an incident photon energy of 11.7 keV and the IM2NP dedicated vacuum chamber (10^{-5} mbar) equipped with a heating stage and an aligned 4-point probe sheet resistance set-up[5,6]. A dedicated adaptive element was built to mount the IM2NP chamber on the BM20 diffractometer by the BM20 technical group. XRD, XRR and Rs measurements were simultaneously performed during annealing with a constant heating rate of 2°C/min, from room temperature up to 350°C. XRD patterns were recorded in grazing incidence (θ = 1°) using a 1D Mythen detector. XRR patterns were also recorded using the 1D-Mythen detector using θ-2θ scans.

3. Results

First, **5 compositions of $Ga_{1-x}Sb_x$ in thin films were characterized** (x= 0.55 ; 0.7 ; 0.76 ; 0.87 ; 0.92) during slow ramp annealing (**2°C/min**) up to 350°C. The composition of the layers was determined before and after the experiments by Rutherford Backscattering Spectrometry (RBS). **The experiment was successful for all the samples**: by combing *in-situ* characterization techniques to study the phase transitions, **we obtained direct correlations between electrical and microstructural changes in the $Ga_{1-x}Sb_x$ alloy**, that exhibit either positive or negative or both optical contrasts upon crystallization, depending on the composition.

An example is shown in Figs. 1 and 2, that show the results obtained for **the stoichiometric GaSb** compound[7]. **For this composition**, we have demonstrated that, upon crystallization, **GaSb thin films exhibit an unusual behaviour with increasing thickness and concomitant decreasing mass density**, while its electrical resistance drops as commonly observed in phase change materials. Furthermore, beyond GaSb amorphous-to-crystalline phase transition, **an elemental segregation and a separate crystallization of a pure Sb phase** was evidenced.

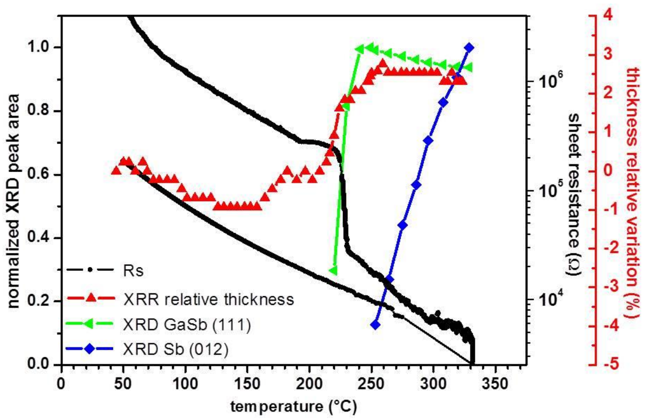

FIG. 2. Temperature-dependent evolution of structural and electrical parameters upon annealing extracted from simultaneously performed XRR, XRD and Rs experiments. For XRD data the normalized integrated intensity of both the GaSb (111) and Sb(012) diffraction peaks are plotted. For XRR data, the thickness relative variation deduced from FFT analysis is plotted.

The characterization of all of the five $Ga_{1-x}Sb_x$ compositions upon crystallization using these combined and *in situ* techniques, allow us to deduce their behaviour during the phase transition. **Moreover, for 3 compositions we also characterized the same layers deposited on Si(100) substrate and with /without capping layer**: therefore **we obtained a complete characterization with any influence of the substrate and/or any evaporation effect upon annealing** being measured.

We thus deduced very nice **correlations between electrical, optical and mass density changes** upon crystallization: **all of these parameters are shown to be dependent on the $Ga_{1-x}Sb_x$ thin film composition**.

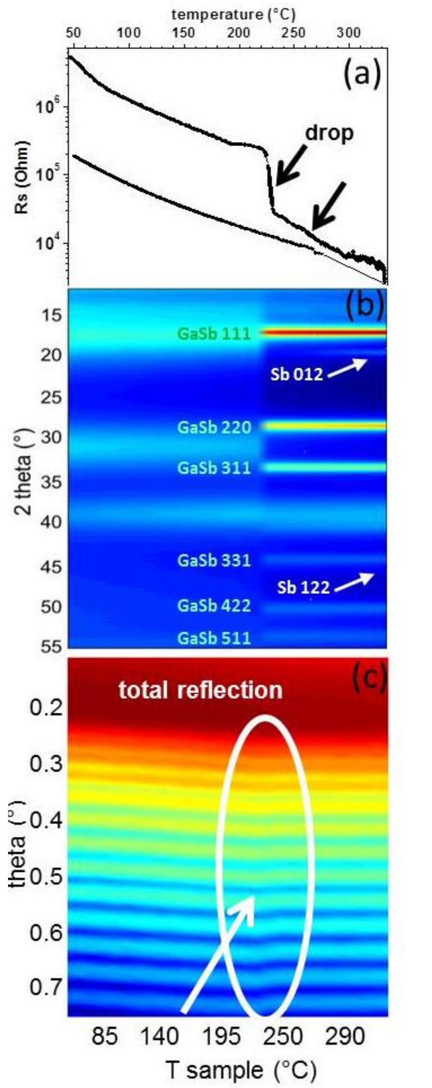

FIG. 1. Combined in situ Rs, XRD and XRR performed simultaneously during the thermal annealing of a 60 nm thick GaSb layer. (a) Sheet resistance, (b) XRD patterns, (c) XRR patterns (2D view).

Moreover, we also correlated the mass density change occurring in these materials during the phase transition (measured by *in situ* XRR) **with the optical contrast measured by stating laser testing on the same layers** in IBM-Yorktown. **The results** show very nice correlations and **allowed to point out a very interesting composition for PCRAM application** because of its small mass density change in spite of its high electrical contrast[8].

<u>Finally, the last day was devoted to a test-experiment</u>: by moving the Mythen detector close to the *in situ* chamber (d = 24 cm), we tried to perform **kinetics measurements by recording both Rs and XRD during fast ramp annealing (<u>1°C/s</u>)**. **Three of the compositions** (Ga/Sb 1:1, Ga/Sb 3:7, and Ga/Sb 8:92) **were successfully analysed using this two combined and time resolved techniques**. An example is shown in Fig. 3 in case of the stoichiometric Ga/Sb compound. This figure shows especially that the separate Sb crystallization is very difficult to detect with such a high annealing rate[9].

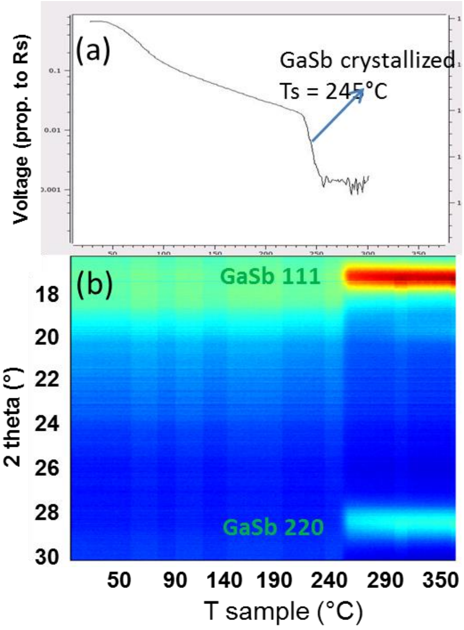

FIG. 3. *Combined and time resolved Rs and XRD performed simultaneously during rapid thermal annealing (1°C/s))of a 60 nm thick GaSb layer. (a) Voltage measured for Rs, (b) XRD patterns.*

<u>4. Conclusion</u>

During this 15 shift-beamtime **we succesfully mounted and aligned the IM2NP *in situ* chamber on the BM20 diffractometer** (about 1.7 shift). Then **we used 10 shifts to completely characterize 5 thin films of $Ga_{1-x}Sb_x$ with various compositions, capped and uncapped, during 2°C/min ramp annealing, and using combined XRD, XRR and Rs measurements**. Especially, we also characterized the same layers on Si(100) substrates (instead of SiO_2 substrate), and the same layer capped with a protective layer to test any effect of the substrate nature and of any layer evaporation.

Finally, **we choose to use the 3 last shifts to test time resolved XRD combined to time resolved Rs during fast annealing ramp (1°C/s) on the same layers** (instead of switching to GeTe layers). Using this geometry (Mythen detector close to the *in situ* chamber), **we successfully characterize 3 of the $Ga_{1-x}Sb_x$ compositions with combined time resolved XRD and Rs upon crystallization**. The results allow comparing the effect of the ramp annealing on the crystallization temperature and kinetics.

<u>5. Dessimenation of the results</u>

Following the beamtime, the analyzed results are beeing dessimenated:

[1] "*The crystallization behavior of GaSb alloy studied by combined in situ x-ray scattering and electrical measurements*", M. Putero, T. Ouled-Khachroum, M.-V. Coulet, C. Muller, C. Baehtz and S. Raoux, **poster accepted** to the **E\PCOS 2013 conference** (European Symposium on Phase Change and Ovonic Science), Berlin, Sept. 9-10.

[2] "*Phase transition in stoichiometric GaSb thin films: anomalous density change and phase segregation*", M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz and S. Raoux, (2013) **Applied Physics Letters**, *submitted*.

[3] "*Unusual crystallization behavior in Ga-Sb phase change alloys*", M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz and S. Raoux, (2013) **Applied Physics Letters Materials**, *submitted*.

[4] "*Phase transition in GaSb alloys: from phase segregation to mass density change*", M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz and S. Raoux, (2013) **Journal of Applied Physics**, *in preparation*.

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[9] M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz, and S. Raoux, J. of Appl. Phys. **in preparation**, (2013).