ESRF	**Experiment title:** *Combined in-situ x-ray diffraction, x-ray reflectivity and sheet resistance as a tool to uncover phase-change materials with no mass density change upon crystallization.*	**Experiment number**: **MA2161**
Beamline: BM20	**Date of experiment**: from: 02 April 2014 to: 08 April 2014	**Date of report**: 26 august 2014
Shifts: 18	**Local contact(s)**: Carsten Baehtz	*Received at ESRF:*

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Report:

1. Introduction

Phase-change materials (PCM) are promising materials for data-storage applications. They are already used in rewriteable optical data storage (DVD, Blue ray) and offer a great potential for non-volatile **phase-change random access memories** (PCRAM)[1–3]. In this technology, the storage mechanism relies on a rapid and reversible **transition between the amorphous and crystalline states**. Upon crystallization, PCM exhibit **structural and electrical changes**: the **mass density**, the **optical reflectivity** and the **electrical resistivity** usually reveal a **steep variation**. Nevertheless, the crystallization is generally accompanied by a **large change in mass density**[4] that leads to voids formation with a **subsequent degradation of PCRAM cells reliability**[5]. Recently, Ga-Sb alloys[6] were shown to undergo an inverse mass density change, *i.e.* an amorphous phase denser than the crystalline one. **Our previous results obtained on BM20**[6–9] (MA1794 – Mars 2013)[10] **we succeeded** in studying several compositions of the **Ga-Sb**[7] phase diagram. By tuning the composition from Ga_9Sb_{91} to $Ga_{45}Sb_{55}$ the change in mass density upon crystallization changes from an increase in mass density which is typical for phase change materials to a decrease in mass density. In particular, we found a specific composition that has **no mass density change**[9] at all but still strong electrical contrast and high crystallization temperature[7,11]. However, a tendency toward phase separation was systematically observed upon crystallization which could be problematic for future application.

The aim of this proposal was thus to **study the effect of Ge, Te, and Si addition to Ga-Sb alloys** with the final goal of finding a **PCM suitable for PCRAM technology and with no mass density change** upon crystallization. This was done by performing **simultaneously *in situ* x-ray diffraction (XRD), x-ray reflectivity (XRR) and sheet resistance measurements (Rs) upon crystallisation.**

2. Experimental method

50 nm thick Si-GaSb , Ge-GaSb and Te-GaSb thin films were deposited by DC and RF magnetron sputtering on 500 nm thick SiO_2 layer thermally grown on Si (001) substrate at IBM-Yorktown (New-York, USA). A

second set of the same layers was capped by 10 nm thick SiO_2 layer to repeat and compare the measurements eliminating any potential element evaporation. Various compositions were elaborated depending on the alloy element: 1 composition for Te-doped GaSb, 2 different compositions for Si-doped GaSb and 3 different composition for Ge-GaSb. This means 6 different compositions, capped and uncapped samples, thus 12 different samples were elaborated.

Simultaneous *in situ* XRD, XRR and Rs measurements were performed on the BM20B-Rosendorf beamline, using an incident photon energy of 11.56 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[12,13]. A dedicated adaptive element was used 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 500°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. Rs measurements were performed using IM2NP current source (Keithley 6220) and nano-voltmeter (Keithley 2182A), both connected to the spec interface.

3. Results

The 6 compositions of Si, Ge and Te-doped GaSb thin films were characterized during ramp annealing (**2°C/min**) up to 500°C. We first performed the experiment on uncapped samples, and then repeat the same annealing ramp on the capped layers. Even if some experiments had to be repeated due to beam shut down and/or Rs failure, **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 Si, Ge, and Te-doped GaSb alloys**, that exhibit either positive or negative or both optical contrasts upon crystallization, depending on the doping element and concentration.

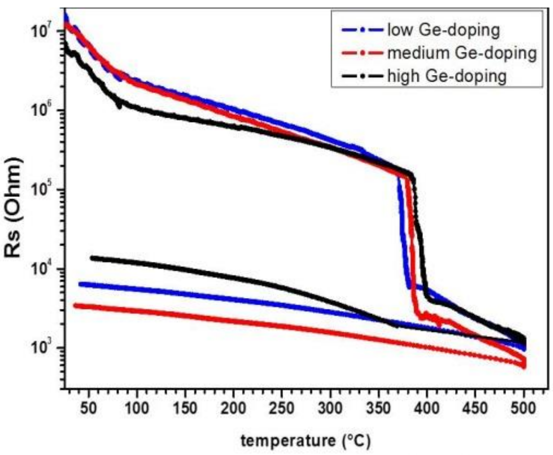

Figure 1: Sheet resistance for Ge doped Ga-Sb alloys as a function of temperature (ramp 2°C/min) and subsequent cooling to room temperature.

An example is shown in case of Ge-doping in Figs. 1-3: these figures show the results obtained for **the three levels of Ge-doped GaSb** alloy (so called "low", "medium" and "high"). Fig.1 shows a comparison of the Rs measurement upon annealing according to the Ge doping level. The samples are initially in a highly resistive amorphous state with a resistance decreasing with temperature as a typical insulator. At the crystallization temperature (T_x) the resistance drops suddenly and as the samples are cooled down they remain in the low resistance state. Compared to undoped GaSb layer[11], the addition of Ge increases both the crystallization temperature allowing a more stable amorphous phase and the electrical contrast. *In situ* XRD patterns reveal the crystallization behavior of the various Ge-doped alloys and confirm that the layers are amorphous after deposition and crystallize at their Ge doping-dependent T_x. Fig.2 shows temperature-dependent *in situ* XRD patterns measured on medium Ge-doped sample. At T_x, three broad diffraction lines appear that are attributed to crystalline GaSb and Ge phases, indicating the onset of the crystallization. This temperature matches well the one deduced from Rs measurement. At about T_x+10°C and for capped layers, all doping concentrations showed that these broad peaks are followed by sharper diffraction lines associated with cubic GaSb, rhombohedral Sb and cubic Ge phases. This feature clearly indicates of segregation of the three materials. Unsurprisingly, Ge peak intensity increases with Ge content. For uncapped layers, the appearance of the three broad peaks is followed by the layer evaporation for all Ge-doping levels, clearly detectable in the *in situ* XRR an Rs measurements: actually, *in situ* XRR patterns recorded simultaneously confirm the layer evaporation for all the uncapped samples, with an enlarged effect for higher Ge content due to the higher T_x, very close to the evaporation temperature.

Capped samples allowed measuring the mass density change upon crystallization: it is found that by Ge-doping the negative variation (decrease of the density) remains upon crystallization; for the lowest Ge-doping the mass density change is small enough to be within the fit error percentage.

Fig. 2 and 3 shows the *in situ* XRD and XRR for the medium and low Ge doped capped samples. **For this doping element**, the results show 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.

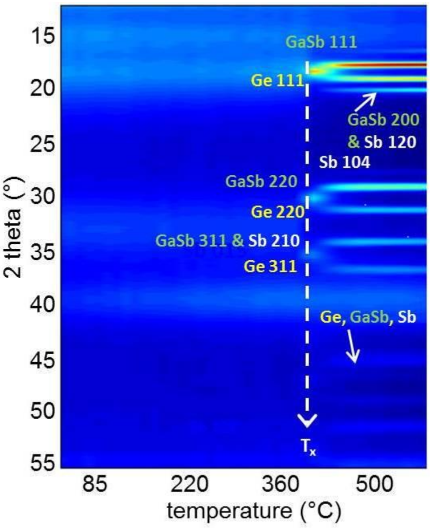

Figure 2: *in situ* XRD (λ=1.074 Å) on medium Ge-doped GaSb (SiO_2 capped).

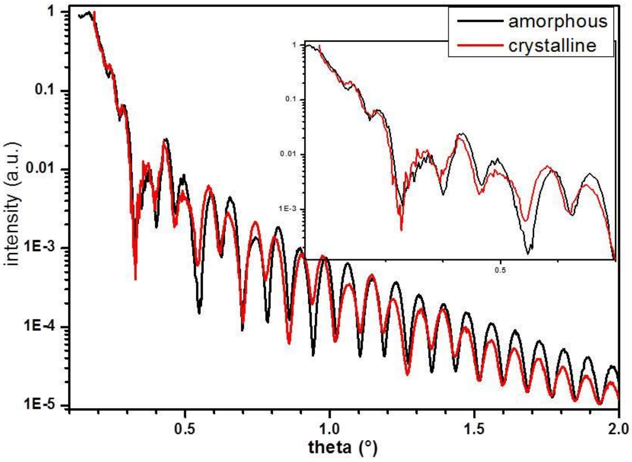

Figure 3: XRR (λ=1.074 Å) before and after annealing of low Ge-dopped GaSb layer (SiO_2 capped). The inset is a zoom on the total reflection edge.

For **Si-doping layers**, the results show that the addition of Si keep the r**elative change in mass density negative**, even if it allows to **reduce it absolute variation to about 2%**. Addition of Si also **increases the crystallization temperature** of about 40°C to 70°C depending on the doping level.

For **Te-doping**, the results show that the addition of Te **switches the relative change in mass density from negative to positive (about +2.4%)** and that no evaporation occurs. The low addition of Te does not change the crystallization temperature.

4. Conclusion

During this 18 shift-beamtime **we succesfully mounted and aligned the IM2NP *in situ* chamber on the BM20 diffractometer** (about 1.5 shift). Then we used the other shifts to **completely characterize 6 different Ga-Sb thin films doped with Si, Te and Ge alloy elements. We also characterized the same layers capped with a SiO_2 thin top layer** to test any effect of GaSb **layer evaporation** during the ramp annealing. All sample were characterized during 2°C/min ramp annealing, and using **combined XRD, XRR and Rs measurements**.

The results allowed **comparing the effect of each alloy element** and **doping level** on the **crystallization temperature**, on the **mass density change** and the **electrical contrast upon crystallization**. Such results are important for both **PCRAM applications** and the **understanding of phase transition** in Ga-Sb alloys.

5. Dessimenation of the results

Following the beamtime, the analyzed results are beeing dessimenated:

[1] "*Effect of Ge doping on GaSb phase transition*", M. Putero, M.-V. Coulet, C. Muller, C. Baehtz, S. Raoux and H.-Y. Cheng, **oral talk accepted** to the **E\PCOS 2014 conference** (European Symposium on Phase Change and Ovonic Science), Marseille, Sept. 7-9.

[2] "*Phase transition in Ga-Sb alloys: phase segregation and effect of doping elements*", M. Putero, M.-V. Coulet, C. Muller, C. Baehtz, S. Raoux and H.-Y. Cheng, **invited talk** to the **MRS-Spring meeting 2015**, symposium Y "**Phase-Change Materials for Data Storage, Cognitive Processing and Photonics Application**", April 6th - 10th San Francisco, USA.

[3] "*Effect of Ge doping on GaSb phase transition*", M. Putero, M.-V. Coulet, C. Muller, C. Baehtz S. Raoux and H.-Y. Cheng, (2014) **Applied Physics Letters**, *in preparation*.

[4] "*Influence of Ge, Te and Si doping on GaSb alloy phase transition for PCRAM applications* ", M. Putero, M.-V. Coulet, C. Muller, C. Baehtz S. Raoux and H.-Y. Cheng, (2014) **Journal of Applied Physics**, *in preparation*.

REFERENCES

[1] M. Wuttig and N. Yamada, Nat. Mater. **6**, 824 (2007).
[2] M. Gill, T. Lowrey, and J. Park, Proceeding IEEE Int. Solid State Circuits Conf. **1**, 458 (2002).
[3] S. Raoux, W. Wełnic, and D. Ielmini, Chem. Rev. **110**, 240 (2010).
[4] Y. Saito, Y. Sutou, and J. Koike, Appl. Phys. Lett. **102**, 051910 (2013).
[5] C.-F. Chen, A. Schrott, M.H. Lee, S. Raoux, Y.H. Shih, M. Breitwisch, F.H. Baumann, E.K. Lai, T.M. Shaw, P. Flaitz, R. Cheek, E.A. Joseph, S.H. Chen, B. Rajendran, H.L. Lung, and C. Lam, in *2009 IEEE Int. Mem. Work.* (IEEE, 2009), pp. 1–2.
[6] M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz, and S. Raoux, Appl. Phys. Lett. **103**, 231912 (2013).
[7] M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz, and S. Raoux, APL Mater. **1**, 062101 (2013).
[8] M. Cherki, "Les puces électroniques flirtent avec leurs limites", Le Figaro.fr 20 avril (2014) http://www.lefigaro.fr/sciences/2014/04/20/01008-20140420ARTFIG00169-les-puces-electroniques-flirtent-avec-leurs-limites.php.
[9] C. Day, "A phase-change alloy that crystallizes without shrinking" Physics update, Physics Today (dec. 2013) http://scitation.aip.org/content/aip/magazine/physicstoday/news/10.1063/PT.5.7031 .
[10] M. Putero, T. Ouled-Khachroum, M.-V. Coulet, C. Muller, and S. Raoux, *ESRF MA1794 Report - Correlated Changes in Physical Properties upon Crystallization in Phase-Change Materials Using Simultaneous in-Situ X-Ray Diffraction, X-Ray Reflectivity and Sheet Resistance.* (2013).
[11] M. Putero, M.-V. Coulet, T. Ouled-Khachroum, C. Muller, C. Baehtz, and S. Raoux, Appl. Phys. Lett. **submitted**, (2013).
[12] M. Putero, T. Ouled-Khachroum, M.-V. Coulet, D. Deleruyelle, E. Ziegler, and C. Muller, J. Appl. Crystallogr. **44**, 858 (2011).
[13] M. Putero, B. Duployer, I. Blum, T. Ouled-Khachroum, M.-V. Coulet, C. Perrin, E. Ziegler, C. Muller, and D. Mangelinck, Thin Solid Films **541**, 21 (2013).