ESRF	**Experiment title:** Coupled GISAXS and GIXRD experiments on Conductive Bridging Random Access Memory	**Experiment number**: MA-1563
Beamline: BM02	**Date of experiment**: from: Sept. 13rd, 2012 to: Sept. 17th, 2012	**Date of report**: July 22nd, 2014 *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Mireille Maret*	

Names and affiliations of applicants (* indicates experimentalists):

V. Jousseaume*, E. Souchier*, P. Gergaud*, CEA, LETI

Report:

Framework of the Project :

One of the promising technologies under development for next generation non-volatile memory is the (CBRAM) which utilizes the reversible switching of an electro-resistive dielectric between two conductive states as means of storing logical data. Devices using this technology are usually composed of a thin film of silver doped chalcogenide sandwiched between a silver anode and an inert cathode. The most promising solid electrolyte consists of a thin amorphous film of GeS_2 with a thin Ag layer subsequently dissolved using a photodissolution process. On bulk materials, previous studies have shown that, depending of the ratio of the concentration of Ag, the incorporation of Ag in GeS_2 leads to the formation of Ag_2S nanospheres (with radius ranging from 2 nm to several nanometers – the mean nanospheres distance can be estimated to few tens of nm) which would be responsible for ionic conduction in the electrolyte. The same studies on thin films are scarce and the influence of these Ag-based nanophases (if any) on the diffusion of Ag ions are not clearly understood. Previous XRD lab experiments do not exhibit such crystalline nanospheres, either because the phases are amorphous or because of the weak diffraction peak of such small clusters. Finally, CBRAM device suffers from data retention issues supposed to be due to the early dissolution of the conductive path in some devices. To overcome this problem, the incorporation of "dopants" in the chalcogenide matrix of GeS_2 is under study. The impact of these doping on the Ag photodissolution and on the formation of Ag_2S nanophases remains unknown. Furthermore, we do not understand yet what is precisely causing the improvements of data retention. The objective of the experiment was to investigate the presence of Ag based nanophases in GeS based matrixes.

Experimental method and strategy :

Grazing Incidence Small Angle X-Ray Scattering (GISAXS) was performed on BM02 using a 2D detector. This technique is well adapted for studying heterogeneities in thin layers grown on opaque substrates, and can detect eventual shape anisotropies. Grazing Incidence X-Ray Diffraction (GIXRD) is also a surface sensitive technique for determining the crystalline structure of nanocrystals contained in a thin film supported on single crystal substrates. First we have performed GIXRD in order to assess the presence of nano-crystallites in the films. Then, in order to understand the effect of preparation conditions, Ag concentration and dopants in the obtained structures, GISAXS measurements were performed on a large number of samples.

Results :

Figure 1 shows typical GIXRD result obtained on a thin sample of GeS_2 with Ag after photodissolution. The presence of Ag-based nanocrystallites was not demonstrated during the experiments. Figure 2a and 2b show typical GiSAXS results obtained on standard GeS_2 thin films on silicon and GeS_2 whith photodissolved Ag. A signal is observed in the pristine film which can be attributed to the amorphous signature of the material. The GiSAXS patern after Ag photodissolution is slighlty more scattered indicating a structural change (even weak) in the material. The Guinier plot can be done in order to deduce mean nanophase diameters (see Fig. 3a) even if the presence of a these Ag-based nanoparticules is not evident.
The different samples investigated during this experiment show similar behaviors (GeS_2 + different Ag concentration, after different thermal annealing at temperature in the range 250°C - 600°C). The Sb-doped GeS samples presnet also a similar behavior in comparison to GeS_2 samples. Finaly, it is interesting to notice the presence of a band in the Sb-doped GeS sample which is still not fully understund (see Fig. 3b).

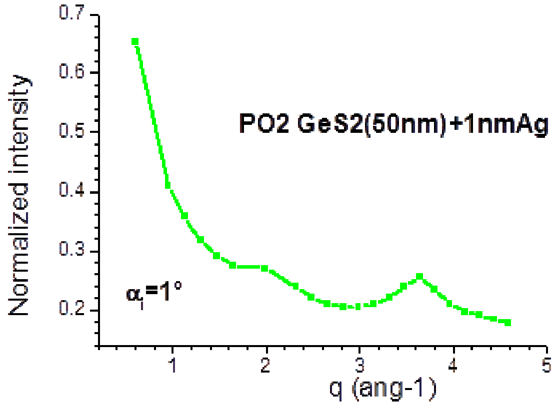

Fig. 1. GIXRD obtained on GeS_2 + 1 nm Ag (after photodissolution).

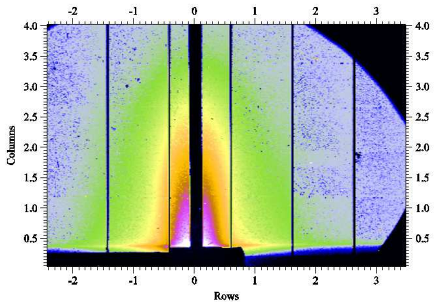

Fig 2a. GiSAXS obtained on GeS_2 thin film (50 nm) at α=0.25°.

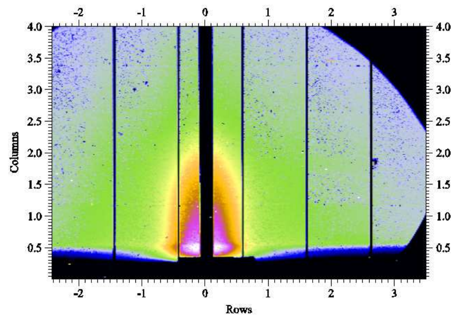

Fig 2b. GiSAXS obtained on GeS_2 (50 nm) + Ag (5 nm) at α=0.25°.

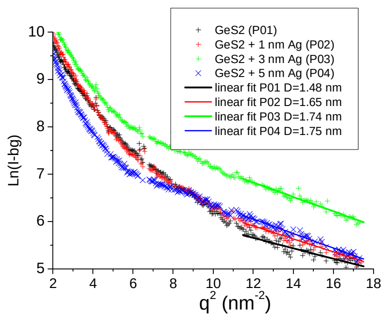

Fig 3a. Guinier plot for different Ag concentrations in GeS2.

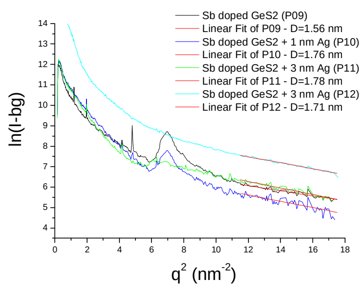

Fig 3b. Guinier plot for different Ag concentrations in Sb doped GeS.