

## Experiment Report Form



**Experiment title: Study of the local environment of Ag<sup>+</sup> ions in Ag-Ge-S glasses thin films for Conductive Bridging RAM devices**

**Experiment number:**  
MA-1571b

<b>Beamline:</b>	<b>Date of experiment:</b> from: 18/02/2013 to: 25/02/2013	<b>Date of report:</b> 06/2013
<b>Shifts: 17</b>	<b>Local contact(s): F. D'ACAPITO</b>	<i>Received at ESRF:</i>
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### Report:

X-ray Absorption Spectroscopy measurements have been carried out at the GILDA-CRG beamline of ESRF on an experimental station dedicated to RefLEXAFS experiments. The monochromator was equipped with a pair of Si(311) crystals and was run in dynamically focusing mode. Harmonic rejection was achieved by using a pair of Pt coated mirrors with a cutoff energy of 30 keV. The full beam dimensions on the sample position were about 0.2 mm (vert)\*2 mm (hor) and a further reduction of the vertical dimension to 50µm was achieved with a slit. The sample was mounted on a stage permitting a precise alignment in total rejection conditions; the incoming beam was read by an ion chamber filled with Ar gas and the rejected beam was detected in a similar way. The fluorescence from the sample was collected by using a 12 elements array of High Purity Ge diodes with an energy resolution of about 400 eV in the energy region of interest (the Ag-K emission line at 22100 eV). Each sample was aligned on the beam and successively RefLEXAFS spectra at 3 different angles were acquired, collecting both the rejected beam and the fluorescence from the layer (See Fig. 1.). The 3 angles define different probing zones of the sample: the **Surface** (collected at 0.06 deg with the extinction length of the probe beam estimated at 40 Å), the **Layer** (collected at 0.15 deg with the probe beam shining the whole Ge(Ag)S layer) and the **Deep** collected at 0.32 deg with the probe beam penetrating also into the **W** bottom electrode layer. A preliminary calibration of the ion chambers response in the whole energy range covered by the EXAFS spectra permitted an absolute calibration of the reflectivity. Note that in all cases the beam footprint was shorter than the samples.

The data in fluorescence mode were analyzed via standard methods with the ATHENA and ARTEMIS codes respectively for data extraction and quantitative fit. RefLEXAFS data were analyzed by using the CARD code. In all cases the theoretical EXAFS paths were generated with the Fefit8 code. Clusters from metallic Ag and Ag<sub>2</sub>S were used as starting structures and the structural model used for the data fit consisted in a balanced mix of these two phases. Metallic Ag was taken into account with 4 coordination shells (totally 5 scattering paths) whereas for the sulphide only the first shell was considered. Free fit parameters were the relative amount metal/sulphide, the Ag-S bond length and Debye-Waller factor (DWF), the overall metallic Ag lattice parameter. For the dynamic part of the metal it has been used the first shell Ag-Ag DWF and a Debye model (with a single free Debye temperature) for the other shells in order

to reduce the number of free parameters. The coordination numbers were fixed to the crystallographic values for the metal and to 2.3 S for the sulphide phase following a fit on a pure sulphide phase sample.

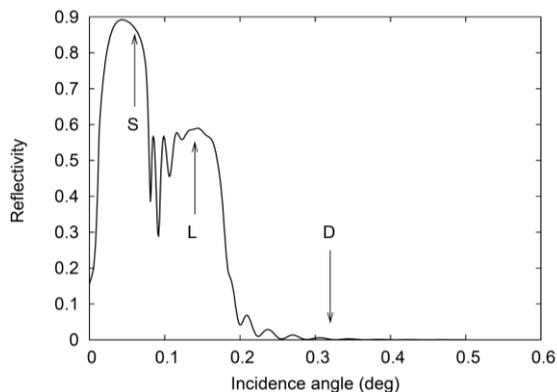


Figure 1: Reflectivity curve collected on sample p15cb3 at 25600 eV. The arrows mark the collection angles for RefEXAFS data: 0.06 deg for the Surface, 0.15 deg for the Layer and 0.32 deg for the Deep parts of the sample.

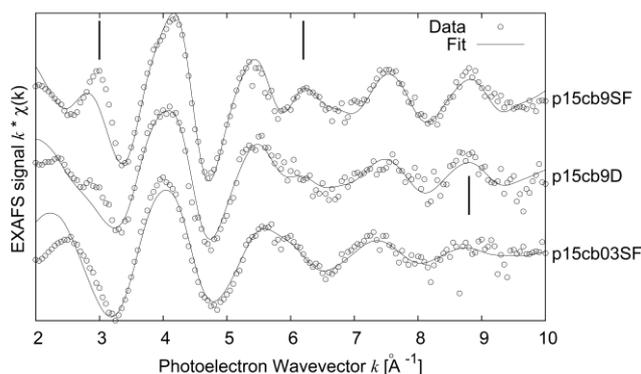


Figure 2: EXAFS spectra of 3 prototypical samples (switched p15cb09 in S and D collection mode and the non-switched p15cb03 in S mode) with the best fit curves. The vertical lines mark the features that grow for increasing Ag-metal content.

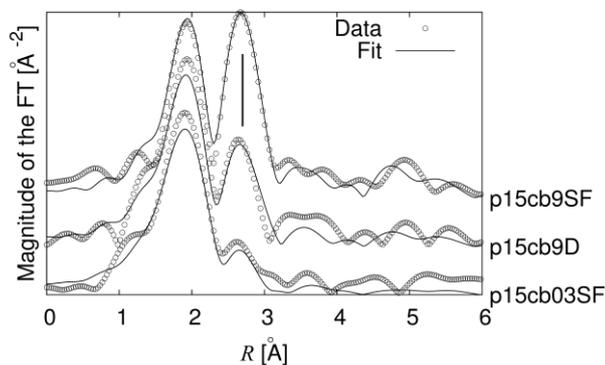


Figure 3: Fourier Transforms of the spectra presented in Fig. 2 with the related best fit curves. The transforms were carried out in the interval  $k=[2.6-9.5] \text{ \AA}^{-1}$  and the fit was carried out in R space on  $k^2$  weighted spectra in the interval  $R=[1.5-5.8] \text{ \AA}$ . The vertical line marks the position of the Ag-Ag bond that decreases for decreasing metal content.

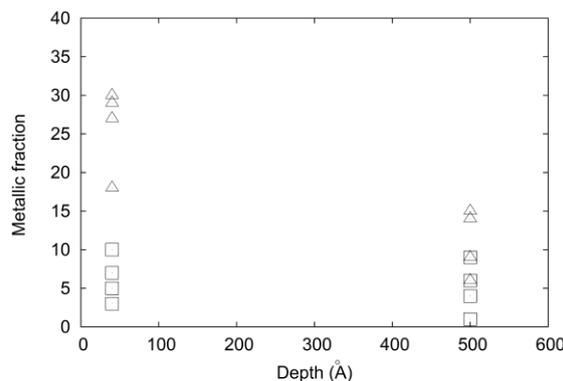


Figure 4: Metallic fraction values detected at the different sampling regions for the switched (triangles) and non-switched (squares) samples.

In all the studied cases the fits of the reflectivity curves yielded similar results (errors are about 10 % of the value) with a 500 Å Ge(Ag)S layer with composition between  $\text{Ge}_{0.75}\text{Ag}_{0.50}\text{S}_{1.75}$  and  $\text{Ge}_{0.88}\text{Ag}_{0.24}\text{S}_{1.88}$  and a roughness of 15-20 Å. The EXAFS data of 3 prototypical samples are shown in Fig.2 whereas the related Fourier Transforms are shown in Fig. 3. The principal difference is the intensity of the peak in the FT (Fig.3) at 2.7 Å that corresponds to the Ag-Ag bond related to the metallic phase. Correspondingly, further features are visible in the EXAFS spectra (Fig.2) that grow with the metallic fraction. A general behavior, confirmed also by the other samples, is that the metal content is higher for spectra in S mode respect to the D mode and that the switched samples contain the highest amount of metal. An example of results of the quantitative EXAFS analysis is shown in Tab. 1:

Sample	Met. Frac. (%)	$R_{\text{Ag-S}}(\text{Å})$	$\sigma_{\text{Ag-S}}^2(\text{Å}^2)$	$R_{\text{Ag-Ag}}(\text{Å})$	$\sigma_{\text{Ag-Ag}}^2(\text{Å}^2)$
p15cb09-SF	30(4)	2.48(2)	0.016(2)	2.86(3)	0.013(2)
p15cb09-SR	30(10)	2.48(2)	0.012(4)	2.89(3)	0.011(4)
p15cb09-L	15(2)	2.50(2)	0.016(2)	2.85(2)	0.012(3)
p15cb09-D	14(2)	2.49(2)	0.016(2)	2.86(3)	0.011(2)

Table 1: Results of the quantitative analysis of the EXAFS data on the p15cb09 (switched) sample collected in S, L and D modes. After S the suffixes F and R denote respectively data in Fluorescence or Reflectivity modes.

In general on all the samples it is detected an Ag-S bond at about 2.50 Å and an Ag-Ag bond at about 2.89 Å. Tentative to reproduce this bond with an Ag-Ge contribution yielded to unphysical results and were abandoned. Fig. 4 collects the data for the Metallic Fraction parameter for samples -15 and p16 in the switched and non-switched forms.

The FT shown in Fig. 3 exhibit 2 main coordination shells for Ag that were identified by the quantitative analysis as Ag-S and Ag-Ag. The Ag-S bond is at 2.50 Å and this is in agreement with what is found in the  $\text{Ag}_2\text{S}$  Acanthite mineral that present distances in the range 2.5-2.6 Å. Also the Bond Valence Method applied to the  $\text{Ag}^+\text{S}^{2-}$  pair foresees a distance of 2.52 Å for a 3 coordinated metal. The slightly lower value found here (2.3 S atoms) can be ascribed to inaccuracies of the amplitude of the EXAFS paths. This reveals the presence of Ag in the  $\text{GeS}_2$  matrix coordinated with 3 S atoms. The possible second Ag-Ge shell is not revealed reasonably due to structural disorder. On

the other hand an Ag-Ag bond is revealed that is related to the metallic phase of silver. Considered the observed distance (2.85-2.90 Å) this is due to a metallic phase ( $R_{Ag-Ag} = 2.88 \text{ \AA}$ ) and not to an  $Ag_2S$  phase which exhibits Ag-Ag distances well above 3 Å. The two phases are in competition as the metallic phase growth happens with a decreasing of the Ag-S phase. The amount of metal observed as a function of the switching state or the depth is of particular interest for the comprehension of the working principles of this device. Fig. 4 clearly shows that samples that never underwent switch have a lower metal content (about 0-15 %) whereas the switched ones have a higher value. Moreover, the surface data show a higher metal content when compared with the data coming from the entire layer. From these considerations it is possible to derive that the switching process involves formation of metallic Ag and that the formation of this phase is initiated at the Ag electrode.