ESRF	**Experiment title:** Determination of the structure of binary and ternary sulfides for photovoltaic applications	**Experiment number**: SI-2501
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Shifts: 9	**Local contact(s)**: Francesco Carla'	*Received at ESRF:*

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Report:

The main purpose of the experiment was the structural characterisation of CuS, $Cu_xZn_yS_z$ and $Cu_xSn_yS_z$ semiconductor thin films suitable for applications in the solar cell production. Samples were prepared by Electrochemical Atomic Layer Deposition (EC-ALD) on Ag(111). Such method allows to deposit, by electrochemical layer by layer growth, ultrathin films with good control the stoichiometry.

In previous experiments we observed that electronic properties of CuS based multinary semiconductors can be tuned by adding an heteroelement (Zn or Sn) to the CuS structure and changing the ratio between Cu and the heteroelement. This behaviour cannot be completely explained with the structural model available for this class of compounds. The experiment aimed to a complete structural investigation on thin films with different composition in order to develop a model capable to match with band gap and compositional data.

X-ray reflectivity analysis for $Cu_xZn_yS_z$ samples is strongly limited by the high surface roughness. The intensity of the reflected beam in fact decreases quite rapidly due to the complex morphology of the substrate (fig 1). The presence of a powderish phase was observed in the in-plane powder diffraction pattern (fig. 2). Nevertheless a more ordered structure was identified in the extended reflectivity curve where the presence of Bragg peaks indicates a film with a well defined order along the normal to the surface (fig 3).

A further analysis clearly revealed the presence of an epitaxial structure with hexagonal symmetry, the same kind of structure was found in all the CuS based samples investigated.

So far the preliminary analysis of the data shows an high structural complexity of the films deposited on Ag(111). As a matter of facts morphology, chemical composition, structure and stacking sequence suggest that the electrodeposition process is characterised by numerous re-organization steps.

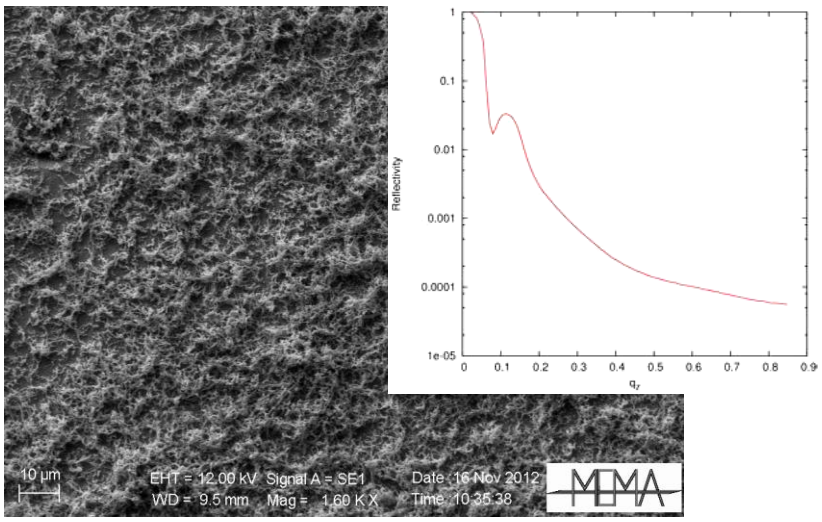

Fig. 1 SEM image of $Cu_xZn_yS_z$ films obtained with secondary electron with a 6500x magnification and XRR curve of the same sample. The fast decrease in XRR signal is due to the presence of sub-micrometric whiskers on the surface.

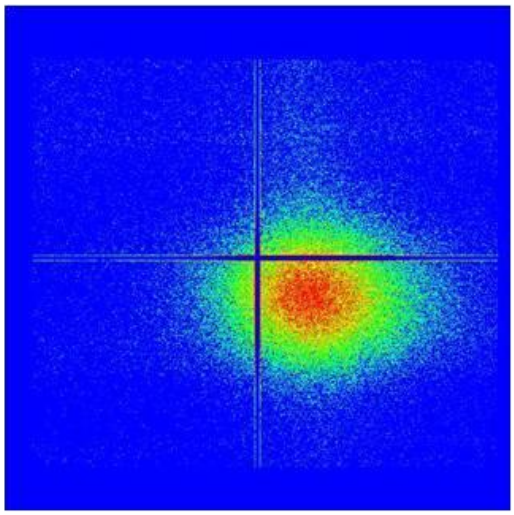

Fig.2 Extended reflectivity: a Bragg peak from the film structure is visible at (0 0 2.22), indicating the presence of an ordered structure in the $Cu_xZn_yS_z$ film along the normal to the surface plane.

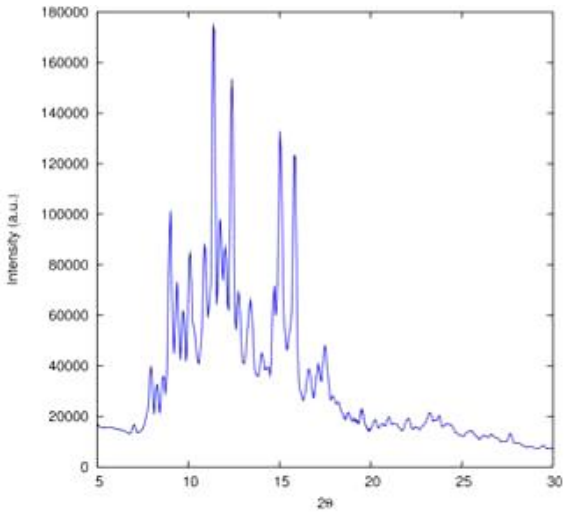

Fig. 3 $Cu_xZn_yS_z$ "in-plane" powder diffraction pattern measured with (E=24KeV).

In conclusion, SXRD and XRR analysis allowed to investigate the structural properties of the samples, moreover structural analysis suggested that a very interesting and complex growth mechanism is taking place at the interface. We are planning to perform an in-situ electrodeposition experiment to further investigate the mechanism of the film growth, whiskers formation and re-organization phenomena during the layer by layer electrodeposition.