ESRF	**Experiment title:** Structural evolution of "Kesterite-like" compound	**Experiment number**: MA-2082
Beamline: ID03	**Date of experiment**: from: 16/07/2014 to: 22/07/2014	**Date of report**: 1/08/2014
Shifts: 6	**Local contact(s)**: Francesco Carlà	*Received at ESRF:*

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Report:

The main purpose of the experiment was the investigation of the growth mechanism of CuS thin films, promising materials for solar-cell production.

Samples were prepared in situ by Electrochemical Atomic Layer Deposition (EC-ALD) on Ag(111) substrate. EC-ALD method allows to grow, layer by layer, thin films of semiconductor compounds with good control on thickness and stoichiometry. The experiment was done using the ID03 flow cell setup (represented in figure 1), already used in the previous experiment MA-1716. The only difference respect that experiment was the thickness of the cell wall. In fact, in order to reduce the intensity of the diffraction peaks due to the peek constituting the cell, the walls of the cell used in this experiment was thinner.

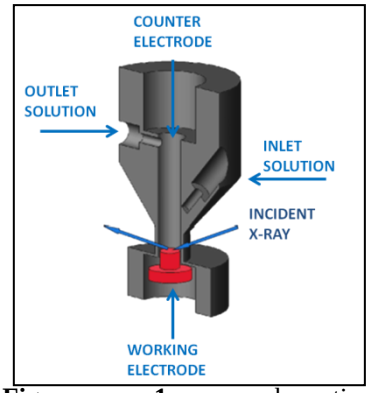

Figure 1: schematic representation of electrochemical flow cell used for the experiment

In previous ex-situ and in-situ study (experiment SI-2501 and MA-1716) the presence of an epitaxial structure with hexagonal symmetry and an high structural complexity of the film deposited on Ag(111) for CuS has been revealed. During the 6 shifts, CuS films were grown twice on Ag (111) substrate, alternating Under Potential Deposition (UPD) of sulphur and copper in order to obtain Ag/S/(Cu/S)n sample, with n from 1 to 60.

The 1st time we have grown the film, we monitored the film growth by following the evolution of the Bragg peak from the film, performing H-K scan at L = 2.1, around the H-K position 0.67-0.79 and H scan at L = 2.1, K = 0.

We performed these scan after every deposition cycle in the first 20 deposition cylcles. In addition, we measured the change in the reflectivity signal (XRR) every five deposition cycles. From the 21th cycle then on, we monitored the evolution of film Bragg every 5 cycles.

No shifts in the Bragg peak position was observed during the film growth indicating an homogeneous growth process starting from the first layers. The intensity of the Bragg peak start to be appreciable from the 15th deposition cycle, suggesting that the material crystallize with low symmetry and a huge elementary cell. After 20 deposition cycles and at the end of the growth we mapped a slice of reciprocal space at L= 0.2 and 2, as shown in figure 2.

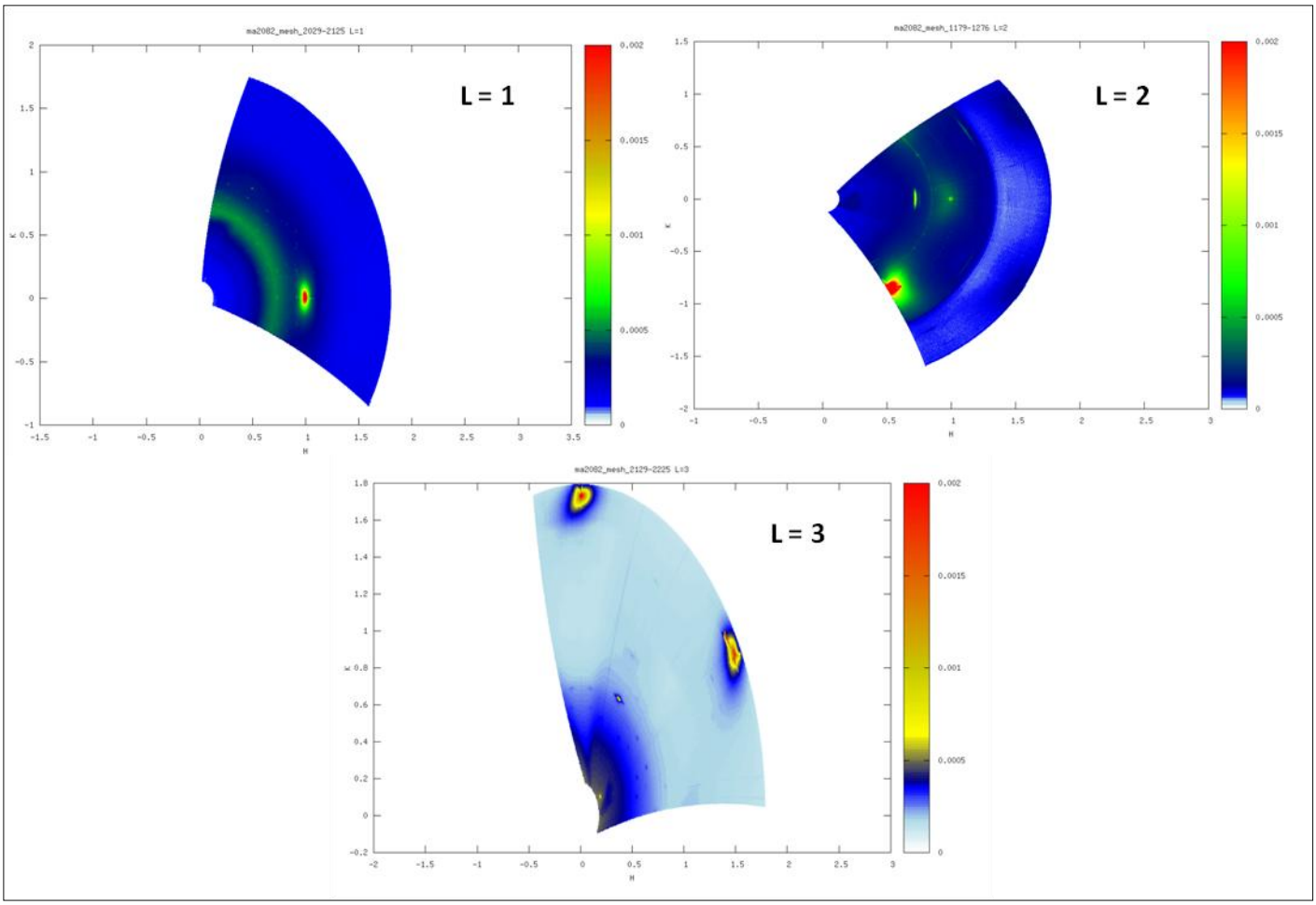

Figure 2: Mapping of some reciprocal space slices at different L position.

Once completed the in-situ characterization, we took off the potential applied to the work electrode, we moved it out from the cell and we repeated the film characterizarion ex-situ, to evaluate possible differences structures, already revealed in the ex-situ experiment SI-2501 . Thus, we repeatead the same H-K and L scan and we mapped the reciprocal space in the same positions. The obtained maps and scan must must be refined an integrate, but we noticed a change in the structure of the film and new signals belonging to different structures appeared.

In the 3 remaining shifts, we started a new growth of CuS film in order to refine and deepen signal from other Bragg peak found in the first growth. At the end of the growth we mapped the reciprocal space at many L positions. Once finished again the in situ characterization, we took off the potential applied to the work electrode, and we performed a time scan to follow change in the Bragg peak position: H = 0.73, K = 0.73, L = 2.1. After few seconds, the signal intensity of this Bragg peak decreased and another Bragg peak appears, in the same position of the ex-situ Bragg peak.

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.