ESRF	**Experiment title:** In-Situ Surface X-Ray Diffraction Investigation of CuxSnyS Grown by ElectroChemical Atomic Layer Epitaxy	**Experiment number**: MA-1716
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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 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.

In previous ex-situ study (experiment SI-2501) the presence of an epitaxial structure with hexagonal symmetry and an high structural complexity of the film deposited on Ag(111) both for CuS, CuSnS and CuZnS films. This experiment attempted to understand the growth mechanism of the film and to investigate possible re-organization steps during the deposition cycles.

CuS films were grown 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 120.

The growth of the film was monitored by following the evolution of a film Bragg peak at H = 0.73, K = 0.73, L = 0.2, as shown in figure 1, measuring the change in the reflectivity signal and monitoring the presence of powder diffraction rings. A complete set of diffraction rod from the film was measured after every deposition cycles stat the end of the deposition (120 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. However, in the first deposition cycles valuable differences from the Ag(111) substrate can be observed.

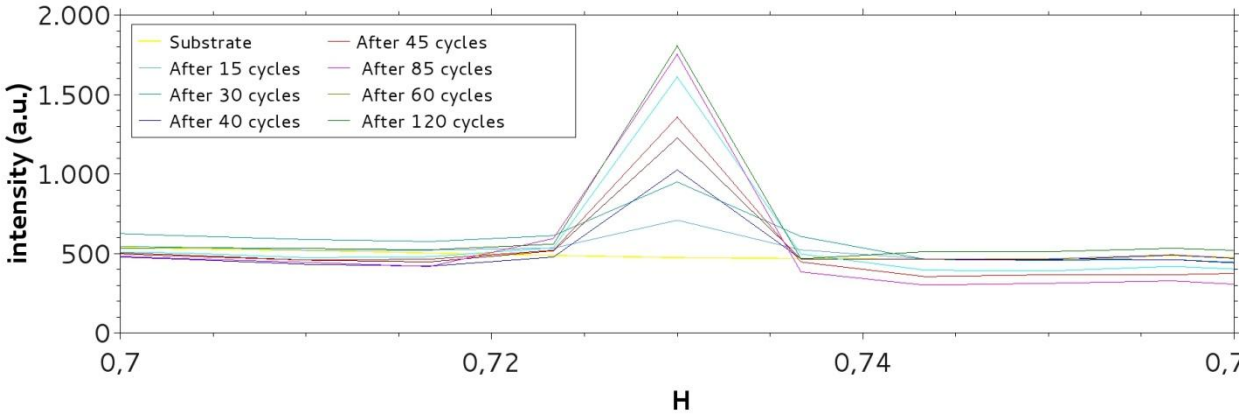

Figure 1: Evolution of the film observing the increasing of the intensity of the Bragg peak with the increasing of cycle number for the position H=0.73, K= 0.73, L=0.2.

Rod signal coming from the film cannot be observed. This can be due to the limited capacity of copper to scatter, to the high background from the solution, or to the roughness of the film. For the same reasons, also X-ray reflectivity analysis was strongly limited.

Once checked the position of the peaks, we performed a peak refinement in order to characterize Crystal Truncation Rods of the material. Because of the complicate structure of the material, the measurement of CuS structure took a lot of time, and there was not more time to measure the ternary compound. In conclusion, SXRD analysis allowed to investigate the structural properties of the samples and we can assume that the film structure is probably one derived from chalcocite.