EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

	Experiment title: Structural evolution of "Kesterite-like" compound	**Experiment number**: MA-2251
Beamline: ID03	**Date of experiment**: from: 26/11/2014 to: 3/12/2014	**Date of report**:
Shifts: 20	**Local contact(s)**: Jakub DRNEC	*Received at ESRF:*

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Report:

The experiment focused on the growth process of $Cu_xZn_yS_z$ compounds on Ag (111) and on the characterisation of the structure of the deposited thin film. The samples were prepared in-situ by Electrochemical Atomic Layer Deposition (E-ALD), and characterised by Surface X-ray Diffraction (SXRD) and X-ray reflectivity (XRR). The use of the electrochemical flow cell developed at the ID03 made possible to monitor the structural changes in the film during the layer-by-layer growth process. The goals of the experiment were:

- ✓ identification of the first appearance of a crystalline structure
- ✓ determination of the crystal structure of the thin film
- ✓ variation of the lattice parameters during the film growth
- ✓ assessment of the phase composition of the film
- ✓ assessment of the long range order arrangement of Cu and Zn in the deposit.

The experiment was performed in the hutch EH1 of the ID03 beamline, using the six circle diffractometer equipped with the ID03 electrochemical flow cell setup (represented in figure 1), already used in our previous experiment MA-2082. In the previous ex-situ study (experiment SI-2501) the presence of an epitaxial structure

with pseudohexagonal symmetry and an high morphological complexity (presence of nanowhiskers) of the film deposited on Ag(111) for $Cu_xZn_yS_z$, has been revealed.
The $Cu_xZn_yS_z$ film was deposited according to the sequence S-(Cu-S-Zn-S)n, with n from 1 to 60, alternating the Under Potential Deposition (UPD) of sulphur, copper and Zinc.

The experimental set up included the Maxipix detector mounted on the diffractometer arm and a Pilatus 300k-w detector used for fast acquisition of in-plane powder diffraction pattern (covering a 2θ range between 10 and 20 with one single images at the energy of 24 KeV).

The film growth was monitored acquiring one map with the Pilatus detector after each deposition cycle (n=1,60). Every 15 cycles, a set of control scans wes recorded: l and h=k scans to monitor the growth of the copper sulfide and an azimuthal scan to monitor the growth of Zn sulfide phase. Moreover, a specular reflectivity and an in plane powder pattern were measured to monitor the appearance of the nanowhiskers.

The experiment resulted successful in obtaining a suitable film with the chosen sequence. At the end of the synthesis a full set of measurements was performed:

- ✓ XRR
- ✓ in-plane powder pattern
- ✓ h, k, l scan over the lattice positions of the CuxS
- ✓ h, k, l scan over the lattice positions of the ZnS
- ✓ h, k maps at l values relevant for the CuS structure.

We are able to conclude that Bragg reflections of Cu_xS_y can be observed after the deposition of 15 cycles. Two different Cu_xS_y structures were, measured, one epitaxial to the Ag (111) surface and the other completely random (feasibly attributed to the nanowhiskers). The two Cu_xS_y species differ by crystal structure and, probably, by stoichiometry. Conversely, reflections due to epitaxial ZnS are not detected, suggesting that this element occurs either dispersed in the Cu_xS_y phases or is deposited with an amorphous structure. Furthermore we observed a reversible re-arrangement of the film structure when the potential applied to the cell is switched off. In fact, as observed in previous experiment MA-2082 the Cu_xS_y Bragg reflection at (0.73, 0.73, 2.1) (substrate coordinates) is losing intensity when the cell is left at open circuit while another signal at a slightly different (h, k, l) position is apperaring. This process seems to be reversible, because if the potential control is switched on, the previous peak appears again.

The growth process of a sample with different Cu/Zn ratio was also investigated.
For the second sample, the deposition sequence was Cu:Zn=1:9, in contrast with the samples with higher Cu concentration, ZnS Bragg reflections were observed after 3 deposition cycles. The obtained film was then investigated ex situ. The 1:9 film appears largely different from the 1:1 film, consisting of epitaxial hexagonal ZnS, disordered powders of ZnS and disordered powders of Cu_xS_y, furthermore changes in the crystal structure are observed respect to the in-situ observation, as already seen in the Cu_xS_y and in the Cu:Zn 1:1 sample.

For the last sample, the deposition sequence was Cu:Zn=1:5, in this case, intermediate results were obtained, by evidencing the presence of epitaxial and disordered Cu_xS_y and ZnS. The results evidence the presence of a complex nanostructured material.

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.

a **b**

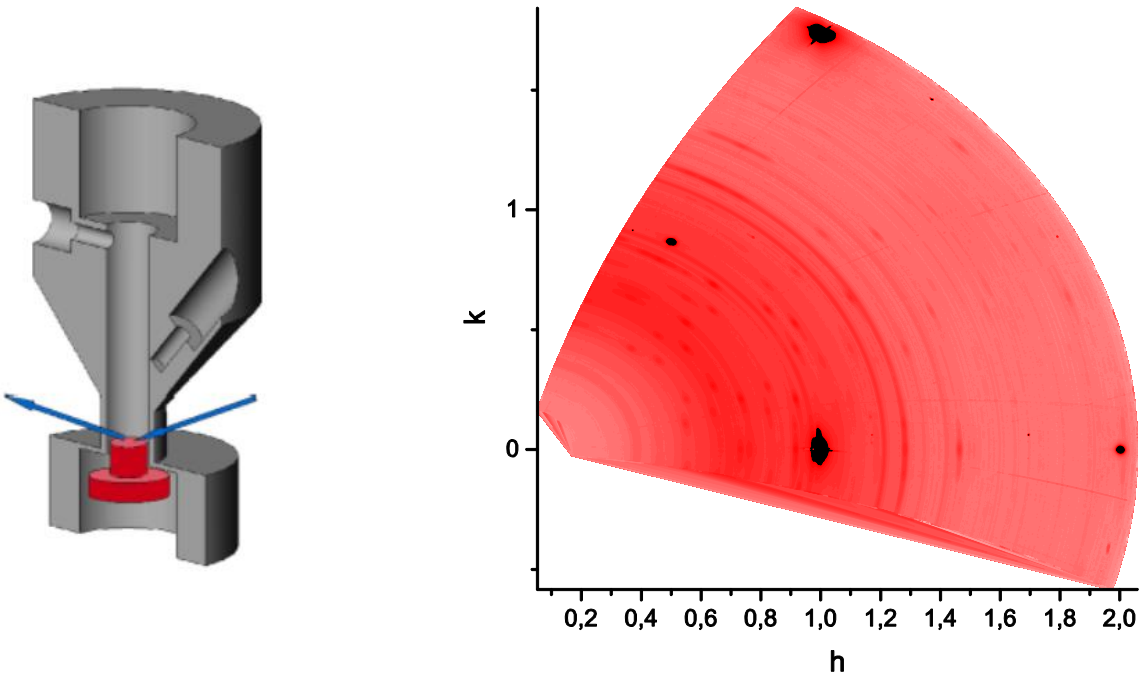

Figura 1 Electrochemistry cell setup for the in-situ experiments (a), an example of a map in the reciprocal space, map of the 1:1 sample at l=1.05 (b)