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ESRF

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.

ESRF	**Experiment title:** Structural evolution during electrodeposition of P and N semiconductors	**Experiment number**: MA2636
Beamline:	**Date of experiment**: from: 24/02/2016 to: 01/03/2016	**Date of report**: 01/03/16
Shifts: 18	**Local contact(s)**: Francesco Carlà	*Received at ESRF:*

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Report:

Aims

The aim of the present proposal was the in-operando characterization of the growth process and structure of p-n junctions of thin films semiconductors obtained by means of Electrochemical Atomic Layer Deposition (E-ALD). The present experiment represents the first attempt to characterise a p-n junction grown by E-ALD. The structural analysis of the films has been carried out both ex situ and in-situ by Surface X-ray Diffraction and X-ray reflectivity.

Methods (1): experimental set up

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 experiments MA-2082 and MA-2251.

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).

Methods (2): samples

Two different kind of samples were considered in the experiment: *ex situ* and *in situ* films. The ex situ films were realised in the Electrochemical Lab at ESRF, using the electrochemical flow cell setup. Two samples were realised in this set up: CdS over CuxS (hereafter labelled as CdS/CuS) and CdS over CuxZnyS (hereafter labelled as CdS/CuS). Samples were realised according to the E-ALD procedure, i.e. alternating the underpotential depositions of the considered elements, assembling layer-by-layer the junction. Equal number of deposition cycles (40) were used for both the p and n layers.

Methods (3): in situ measurements

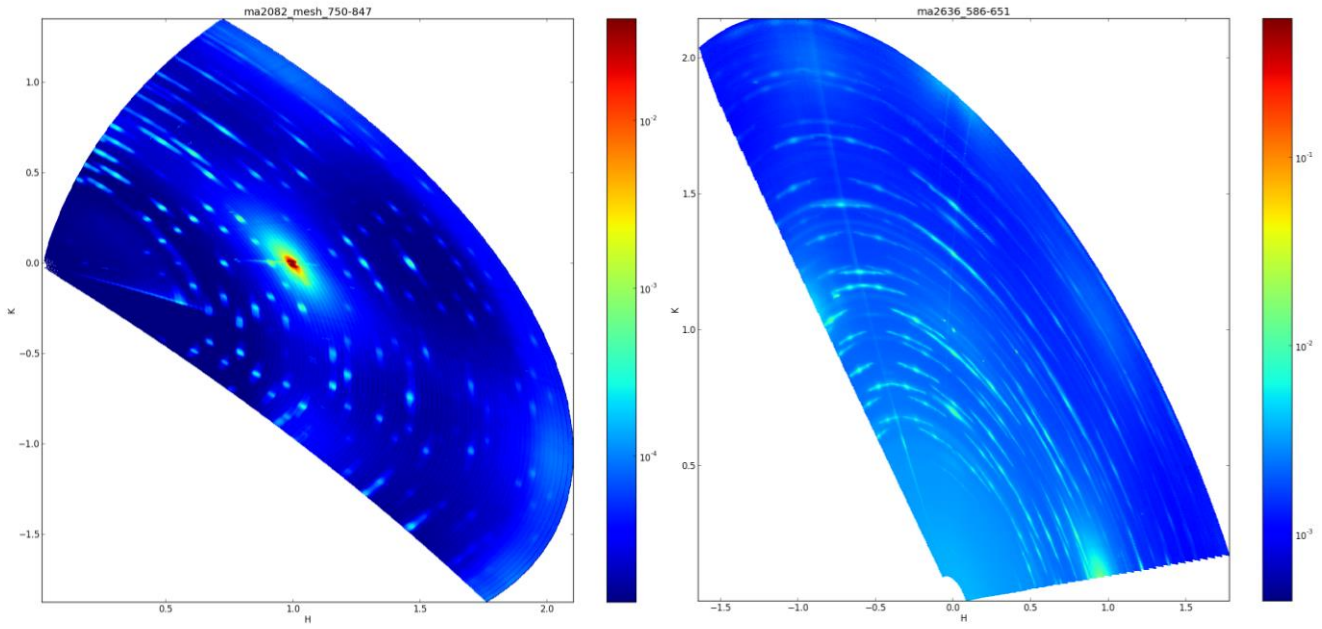
In situ measurements were also realised in the electrochemical flow cell setup, located in the hutch, with the flow cell mounted on the diffractometer. As in our previous experiments we got an exhaustive characterisation of the p layers (CuS and CuZnS), we deposited this layer without intermediate

characterisation. After the 40 cycles of deposition were realised, we performed a fast characterisation to verify the quality of the layer, and we moved to the deposition of the n layer, alternating synthesis and characterisation. In particular, we performed:

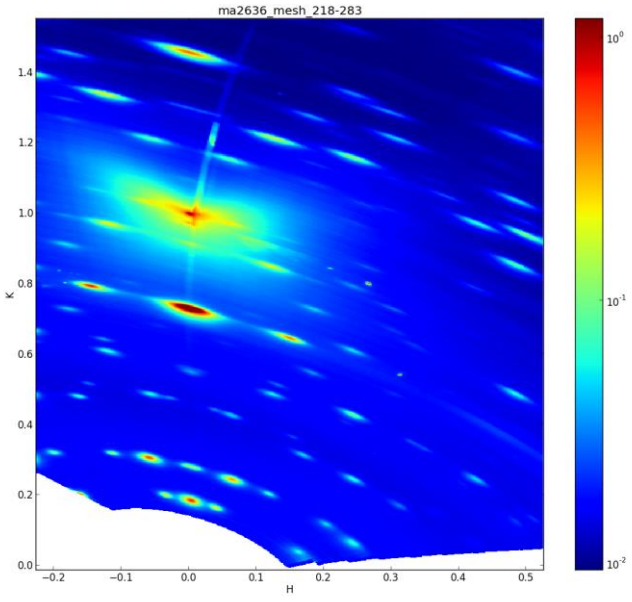
- XRR before starting the E-ALD of the p layer
- XRR after ending the E-ALD of the p layer
- l and (h, k) scans on two different Bragg reflections of the CuS phase (every 10 E-ALD cycles of the n layer)
- l and (h, k) scans on two different Bragg reflections of the CdS phase (every 10 E-ALD cycles of the n layer)
- XRR afte ending the E-ALD of the n layer
- X-ray diffraction maps at several relevant l quotes of the obtained junction.

Preliminary Results

Exemplar h-k X-ray maps of the two ex situ samples are shown in the Figure 1. As it can be noticed, the two samples reveal a complex composite structure, consisting of at least two phases. In both samples, Cd was identified as own phase, well crystallized and well oriented. Cu_2S and Cu_xZn_yS revealed the already studied crystal structure of Cu_2S, whereas a further additional phase was found, whose lattice parameters are not compatible with already known structure of the considered binary and ternary systems. It is noteworhty to mention that the roughness of the p layer surface, which was found relatively low in the previous experiments, is increased after the 40 E-ALD cycles of CdS over it.



Coming to the in situ results, we decided to start investigating the CdS/CuS film, because in this system the ex situ sample appeared slightly less complex. We focussed, in fact, at a first attempt, to reduce the complexity of the E-ALD procedure in the in operando characterisation. Preliminary h-k X-ray maps are shown in the following figure.



An attempt of analysis of the growth process from a crystallographic point of view has been attempted, in fact 3 Bragg peaks has been observed on the plane and out of the plane. Figure 3 shows one of this peak, out of the plane the normalized signal deacreases over the whole deposition of CdS on top of Cu_2S. On the plane, the signal seem to be constant, deeper analysis is needed in order to understand possible mistakes about these considerations.

a b

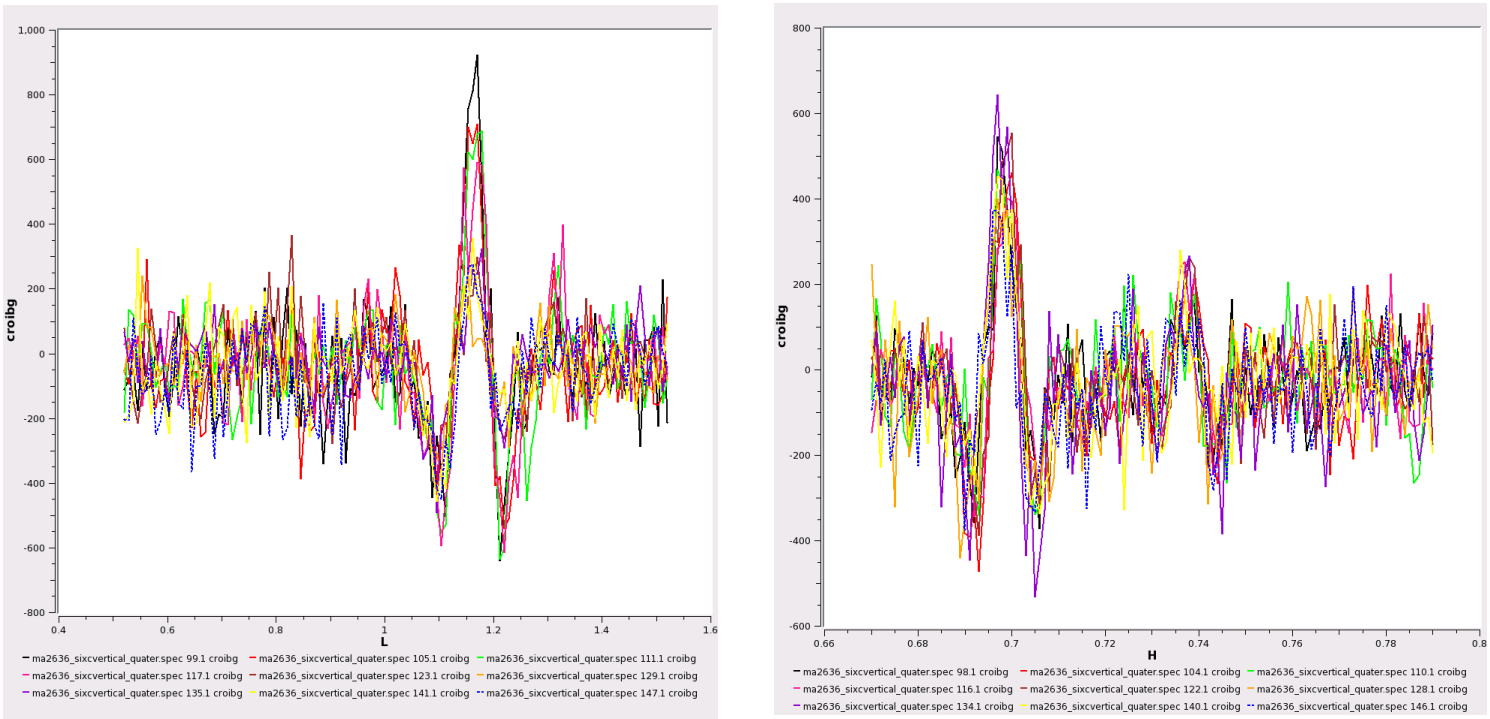


Figure 2: (a) l scan and (b) h=k scan on the peak (0.7 0.7 1.15)

The Bragg peaks we considered are broader very little coherence respect to what expected, in particular we cannot be sure of the formation of two different phase very closely related in h,k since the peak expected at 0.73 is not clearly defined. In conclusion, we performed several h-k maps at different l for the ex-situ

experiments (CdS/Cu_2S, CdS/Cu_xZn_yS and Cu_xS/CdS) and for the in-situ experiments (CdS/Cu_2S and CdS/Cu_xZn_yS). For the CdS/Cu_2S apparently, we found two different pattern on the ex-situ h-k maps very close in l, involving also a spatial disorder as shown by the Bragg rings not detected during the ex-situ experiment on Cu_2S (MA2082). For the CdS/Cu_xZn_yS apparently, we found three different pattern on the ex-situ h-k maps very close in l. Thus, the results doesn't allow the full interpretation of the structure or of the growth process while giving a crucial insight on the materials analyzed by SXRD.

Exploiting the results of this experiment we can define the best possible condition for the structural analysis of such composite thin films.

Further SXRD experiments will be necessary to get a deeper description of the underlying mechanism of the growth.