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 using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now 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:** Investigation of the crystallography and stoichiometry depth profile of metal oxide-semiconductor Schottky barriers by HAXPES in combination with Surface X-ray diffraction	**Experiment number**: HE-3354
Beamline: BM25B	**Date of experiment**: from: 16/07/10 to: 23/07/10	**Date of report**: 2/28/2011
Shifts: 18	**Local contact(s)**: Juan Rubio-Zuazo	*Received at ESRF:*

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Aim of the experiment

Primary aim of this experiment was to determine the oxidational state of noble metal films, which were deposited in oxidizing environment. The oxidational state in the vicinity of the interface of the thin films to the ZnO-substrate was of special interest. Furthermore, the determination of the crystallography by surface X-ray diffraction was set to the agenda of experiment HE-3354.

Sample description:

For the experiment HE-3354, ten different thin films were prepared on previously annealed hydrothermally-grown oxygen-terminated c-ZnO substrates (purchased from Crystec). Subsequently, films were deposited using DC magnetron sputtering of Cu, Ag, Au, Pd and Pt. For each metal, one film was deposited in argon atmosphere and one film in a mixed argon/oxygen –atmosphere. The deposition conditions were adapted, such that the thickness of the all thin films was about 5 nm.

Measurement conditions:

Generally, all measurements could be comfortably performed and the local contacts supported the work satisfactorily. Unfortunately, during the experiment on 6 am of the 18th of august, a failure of the detector screen occurred, which made it-despite of the encouraged

work of our local contacts-impossible to measure between the occurrence of the failure and noon of the next day. Nevertheless, all first priority measurements could be completed, as the measurement duration was adapted to the remaining time-with the consequence of reduced signal to noise ratio.

Obtained Results:

For each sample, the zinc $L_2 2p_{1/2}$-level was measured. Furthermore, for each metal at least two core levels were measured. Finally, the oxygen K 1s level was measured in all samples. By adjusting the spectral position of the zinc $L_2 2p_{1/2}$-level to its theoretical value-under the assumption that its energy remains constant -the exact beam energy was determined and all other spectra were adjusted accordingly. Please note that all samples were processed on ZnO single crystals of one batch and of one cut, which supports the latter assumption of constant zinc $L_2 2p_{1/2}$ energy. Nevertheless, the fact that the zinc $L_2 2p_{1/2}$-level, which stems from the substrate, was measureable for all applied beam energies indicates that the deposited film thickness was in all cases too small. Additionally, calculations of the inelastic mean free path (IMFP) of the used metals support this, yielding for all occurring kinetic energies to IMFP values close to or above the deposited film thickness [2]. The real IMFP can be expected to be even larger than the theoretical values, as the films, deposited at room temperature, include most likely voids and other open-volume defects. Thus the measured signal always represents an average over the entire film thickness.

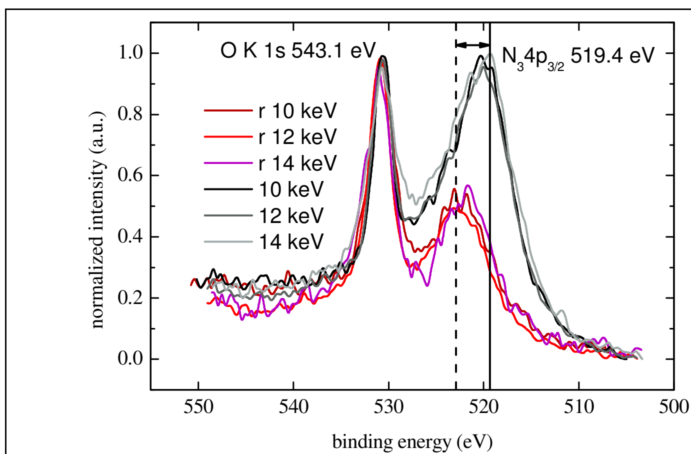

Figure 1: Spectra of the O K1s and the Pt $N_3 4p_{3/2}$ core level for the intentionally oxidized (reddish lines) and the metallic (grayish lines) Pt thin films. The solid line indicates the theoretical position of the $N_3 4p_{3/2}$ level [1]; the dashed line and the arrow indicate the chemical shift of the oxidized thin films with respect to the theoretical value and the metallic films. The spectra are normalized to [0, 1] for comparison.

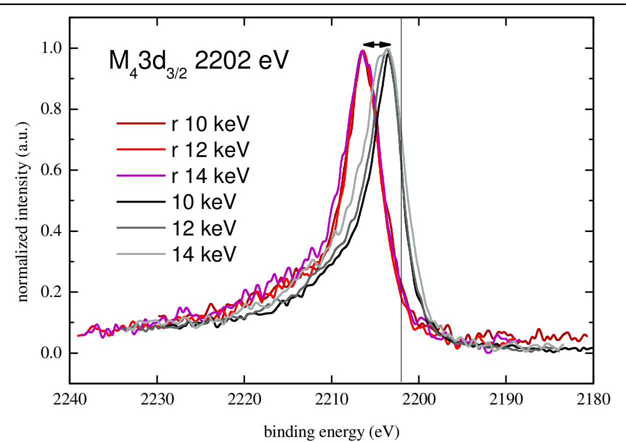

Figure 2: Spectra of the Pt $M_4 3d_{3/2}$ core level for intentionally oxidized (reddish lines) and the metallic (grayish lines) layers. The solid line indicates the theoretical position of the $M_4 3d_{3/2}$ [1]. The arrow indicates the chemical shift of the oxidized thin films with respect to the metallic films. The spectra are normalized to [0, 1] for comparison.

Selected spectra of Pt and Au are exemplarily depicted in figure 1-4. For both metals, at least some spectra permit to distinguish between the films deposited in oxidizing and inert conditions. But within the noise level of the obtained data, there are no obvious differences between the spectral position and the line shape of the films deposited under oxidizing and in

inert conditions for the different beam energies. Yet, there is no possibility to deduce from these data whether the oxidational state varies with the film thickness or not, as all spectra probed the entire film. In case of the other metals, no significant and reproducible differences between the oxidized and the metallic film were observed.

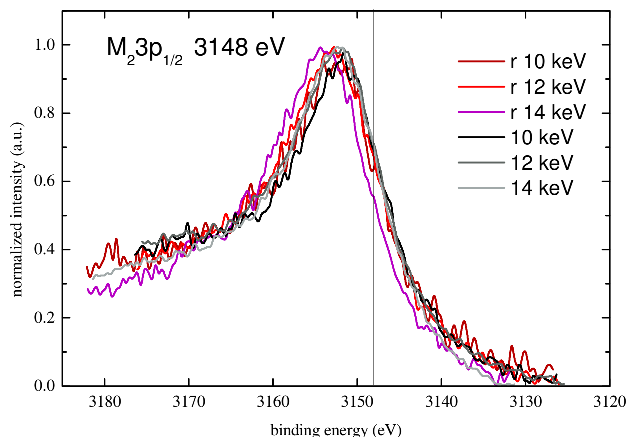

Figure 3: Spectra of the Au $M_2 3p_{1/2}$ core level for the intentionally "oxidized" (reddish lines) and the metallic (grayish lines) Au thin films. The solid line indicates the theoretical position of the $M_2 3p_{1/2}$ level [1].The spectra are normalized to [0, 1] for comparison.

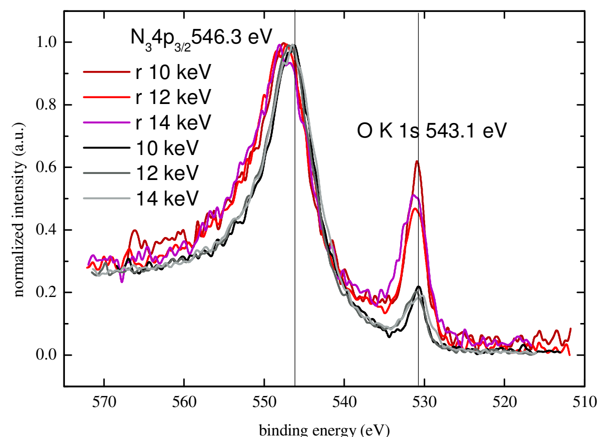

Figure 4: Spectra of the Au $N_3 4p_{3/2}$ and the O K 1s core level for intentionally oxidized (reddish lines) and the metallic (grayish lines) layers. The solid line indicates the theoretical position of the $N_3 4p_{3/2}$ level and the mean detected position of the O K 1s level [1]. The spectra are normalized to [0, 1] for comparison.

Conclusion

In summary, two materials with systematic differences between the films deposited in inert and in oxidizing conditions were identified. For both systems, it is necessary to carry out further investigations with increased film thickness and a higher number of beam energies in order to resolve the depth profile of the oxidational state in vicinity of the interface to the substrate.

References:

[1] X-RAY DATA BOOKLET http://xdb.lbl.gov/

[2] NIST Electron Inelastic-Mean-Free-Path Database: Version 1.2 http://www.nist.gov/srd/nist71.cfm