ESRF	**Experiment title: In situ study of the effect of the polarity of Zn(0001) substrates on the growth of ZnO nanowires by Chemical Bath Deposition**	**Experiment number**: MA 1890
Beamline: BM02	**Date of experiment**: from: 27/11/2013 to: 03/12/2013	**Date of report**: 27/02/2014
Shifts: 18	**Local contact(s)**: Hubert Renevier	*Received at ESRF:*

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Report:

In this experiment we aimed to investigate, *in-situ*, the influence of the ZnO surface polarity on the nucleation stage of ZnO nanowires by chemical bath deposition CBD. For this purpose, we designed and built a suitable PEEK growth cell that gives, via a 90 µm thick PEEK window, a complete access to the sample surface with no in-plane angular limitations and an angular range up to 28° out-of-plane. The growth cell has been successfully installed on the κ-goniometer at BM02 (figure 1).

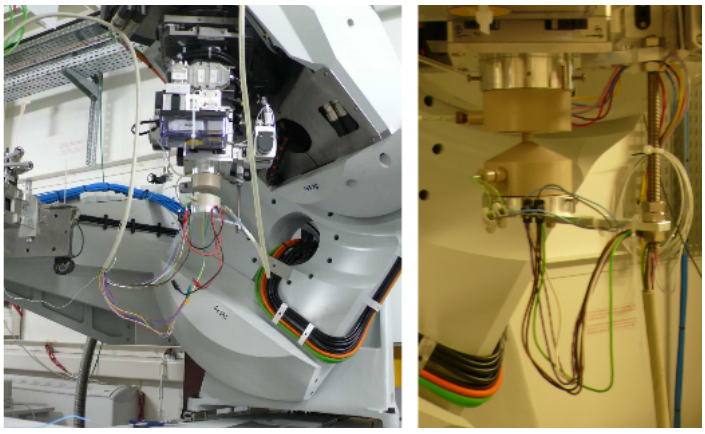

Figure 1.: two pictures of the PEEK growth cell mounted on the κ-head of the BM02 goniometer at the measurement position

As one can see from figure 1, the need to keep the sample up-side-down to avoid ZnO precipitation on the substrate surface, during the chemical reaction, forced the experiment in an unusual configuration where the angle χ is at -90°, η (incidence angle) and δ (out-of-plane scattering angle) are negative while ν (in-plane scattering angle) is positive, together with a φ rotation that occurred in the same direction as ν and the angle μ fixed [1, 2]. Several attempts have been made to make the diffractometer work in *hkl* mode, according to reference [3] no clear reason seems to prevent the pseudo-horizontal scheme to work if a reset of the χ motor to 90° is used. Unfortunately this was not the case as the rotation of the azimuthal angle φ was still in the opposite direction with respect to the **spec** calculations. Therefore

it was not possible to perform any *hklscan* nor *CTRscan* as we planned to do, as described in the proposal. Moreover no GISAXS was available.
So, we focused our work on the growth of ZnO nanowires (NWs) on O-terminated ZnO (0001) single crystal substrates, exploiting the in-plane form factor of the NWs that cause a lengthening of the substrate Bragg peak. Figure 2 shows the φ–rocking scans of the 110 and the 100 reflections at 20 keV.

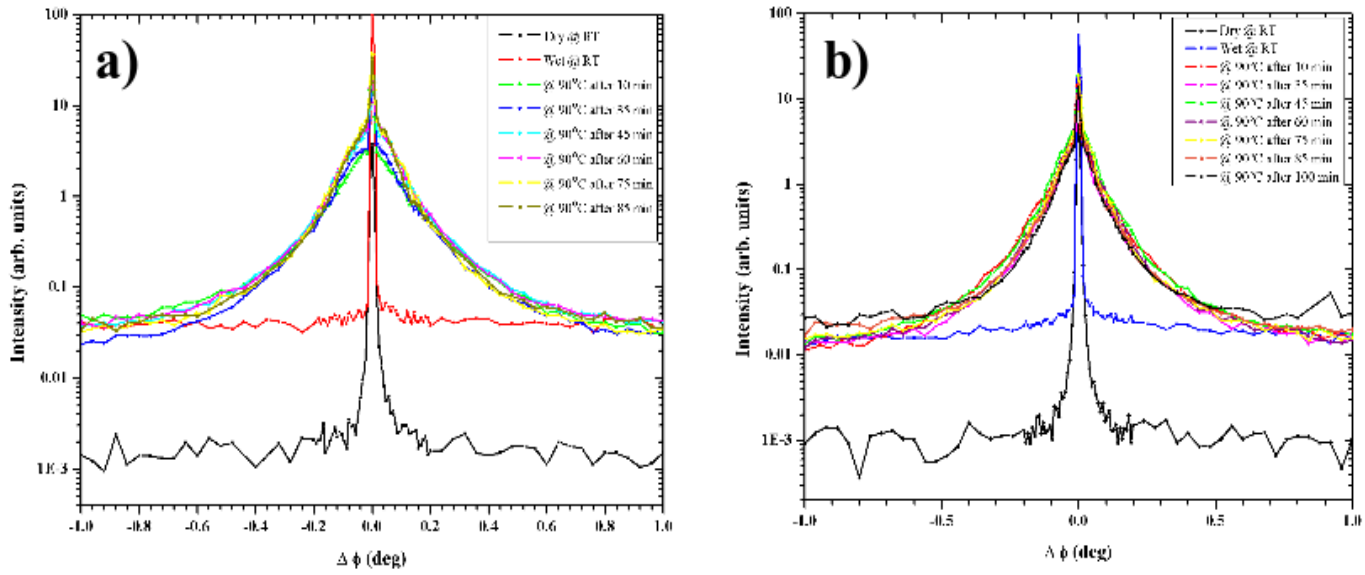

Figure 2.: φ-rocking scans of the 100 (a) and 110 (b) Bragg reflections

The insertion of the aqueous solution (equimolar Zn Nitrate ($Zn(NO_3)_2$) and hexamethylenetetramine (HMTA)) at room temperature caused an increase of the diffused background of about one order of magnitude. Once the targeted growth temperature was reached (about 90°C), and the sample realigned, an important increase of the peak FWHM was detected along both directions. As growth proceeded, no strong change was detected in the shape of the 110 peak (FWHM decreasing from 0,103° to 0,119°). On the contrary, the FWHM of the 100 reflection narrowed constantly showing an increase of the average NW diameter from about 115 nm to approximatively 150 nm.

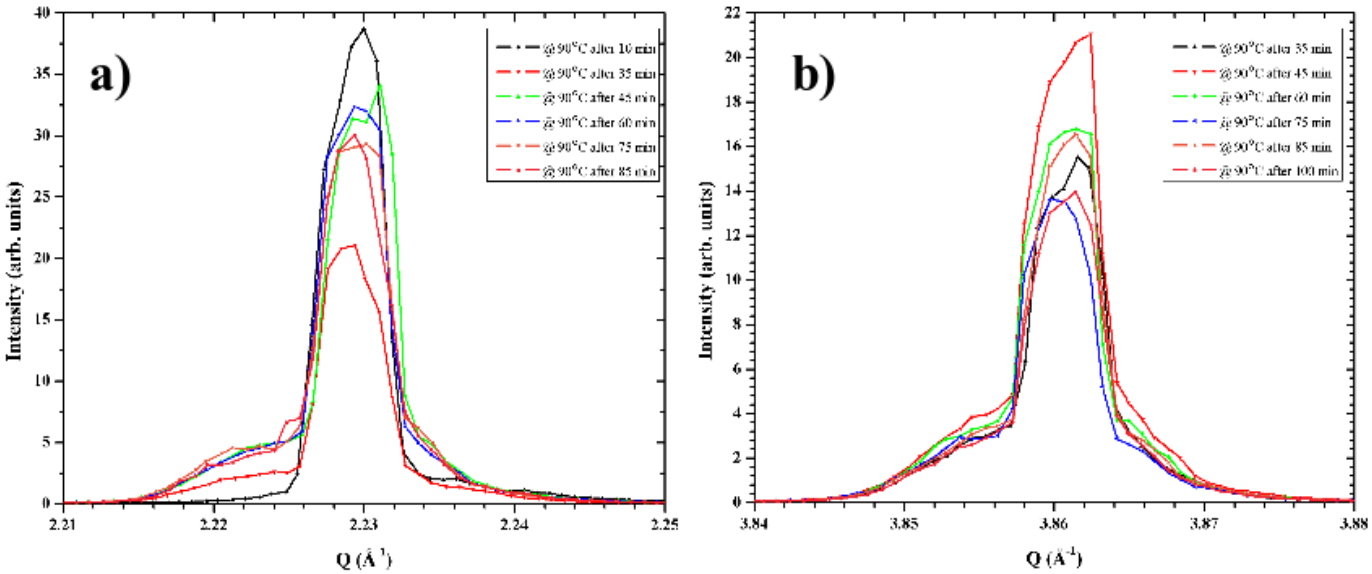

Figure 3.: Radial scans around the (100) (a) and (110) (b) Bragg reflections

In figure 3 radial scans around the 100 and the 110 Bragg peaks are reported. For both reflections we observed a small shift to lower ***Q*** of the NW lattice parameters with respect to the substrate.
The data obtained in this first beam-time about the investigation of the nucleation steps of ZnO NWs by CBD are very preliminary but valuable because scarce and allow us to validate the PEEK cell design and to confirm the possibility to deeply investigate the ZnO surface modifications during CBD.

Reference:

[1] You, H. (1999). J. Appl. Cryst. 32, 614-623.
[2] Thorkildsen, G., Mathiesen, R. H. & Larsen, H. B. (1999). J. Appl. Cryst. 32, 943-950.
[3] http://www.certif.com/spec_help/psic.html