	Experiment title: Local environment of Ga doped vertically aligned wurtzite ZnO nanowires probed by XNLD	**Experiment number**: HC-4600
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Shifts: 18	**Local contact(s)**: Fabrice Wilhelm	*Received at ESRF:*

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Report:

The aim of this project was to probe the local structure and environment around the Ga atoms incorporated in vertically aligned wurtzite ZnO nanowires (NWs) grown by chemical bath deposition (CBD). In as-grown ZnO NWs samples, we believed that Ga predominately substitutes Zn atoms (i.e. GaZn). However, in postdeposition annealed under oxygen atmosphere samples, a partial conversion of GaZn into GaZn−VZn complexes can take place (VZn represents zinc vacancies) based on temperature-dependent Raman spectra. This conversion was further related to a significant relaxation of the strain level in the ZnO NWs as observed by XRD. Though, it was not clear if GaZn and/or their partial conversion in annealed samples are the only mechanisms taking place during the doping or if we have additionally the formation of another crystallographic phase such as α-Ga_2O_3.

To this end, we have used x-ray natural linear dichroism (XNLD) to probe the local environment of the Zn and Ga atoms. We have investigated as-grown and post-annelead ZnO nanowires doped samples with [Ga(NO3)3]/[Zn(NO3)2] ratio values varying from 0 to 10 % for a given pH0 of 10.9. XNLD expereriemts were performed at the Zn and Ga K-edge. We used a diamond quarter wave plate to convert the incoming circularly polarized x-ray beam to horizontal or vertical linearly polarized ones. The x-ray absoprtion spectra were collected using both total electron yield (TEY) and total fluoresence yield (TFY) mode. The TEY detection was important to be measured at the Zn K-edge because it is known not to suffer from self-absorption effects and therefore a direct comparison between the different samples could be made. To record high quality XNLD at the Ga K-edge was rather challenging due to its low concentration and because its K-edge is lying above the Zn K-edge.

The XNLD at the Zn K-edge was shown to be the same for all the samples, as-grown and postdeposition annelead (figure 1 left). This illustrates frist that the wurtzite ZnO NWs are very well aligned with their c-axis being perpendicular to the substrate. Second, the postdeoposition annealing under O_2 atmosphere does not destroy the local wurtzite environment around the Zn atoms. Indeed the spectral shape and intensity of the XNLD signal is as large as for pure ZnO single crystal.

We have then measured the XNLD at the Ga K-edge (figure 1 right). We can first notice a sizeable XNLD at the Ga K-edge for the as-grown sample that is similar in shape and intensity in comparison to the Zn K-edge. This means that Ga atoms are well incorporated in the crytsal lattice and do not form Ga clusters. Moreover, from the XNLD spectral shape, we can deduce that Ga atoms are in substitution with Zn atoms. However, for the post annealed sample, we can first observe that the isotropic XANES is more intense and that the XNLD signal is clearly different. At this stage, we can conclude that the local environement of the Ga atoms is more oxidic in the first coordination shell and consequently may break the wurtzite symmetry. To further interpret our results, we are actually confronting our experimental results to simulations done with the FDMNES code and considering relaxed crystal structure including different type of vacancies and protonation calculated from the VASP code.

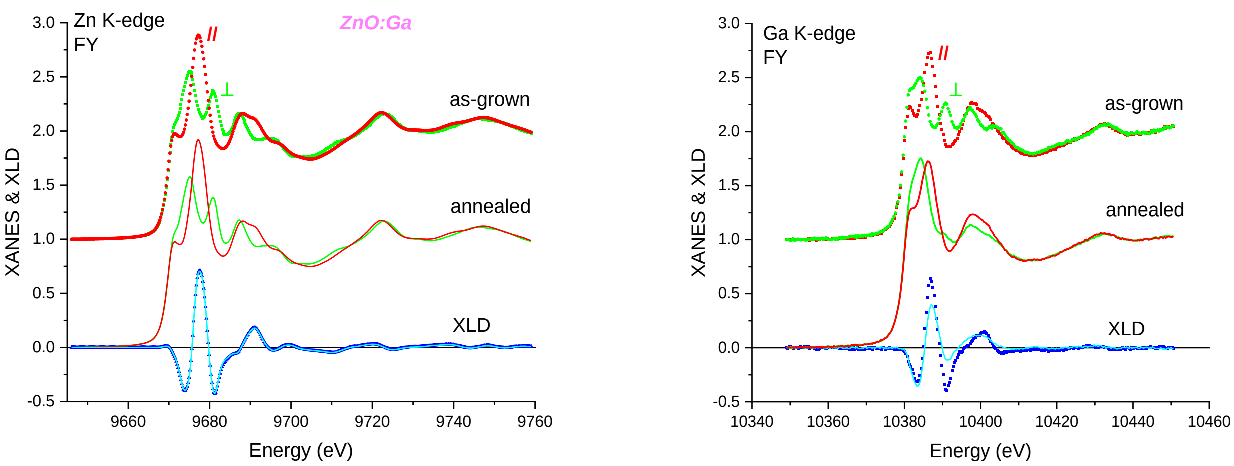

Figure 1: (left) Zn K-edge and (right) Ga K-edge XANES and XLD of as-grown (dotted line) and postdepostion annealed (full line) ZnO NWS doped with Ga for a ration of [Ga(NO3)3]/[Zn(NO3)2] equal to 2.5%. // and ⊥ symbols indicates that the linearly polarized x-ray beam E is parallel and perpendicular to the substrate (c-axis of the wurtzite NWs being perpendicular to the substrate).

Additionnaly, we have also studied ZnO NWs codoped with Ga and Al as grown and postdeposition annealed samples with various Ga/Al ratio. Using XNLD at the Ga K-edge, we found that co-doping with Al atoms indenpendantly of the Al/Ga ratio does hardly affect the local environment of the Ga atoms. The XNLD at the Ga K-edge was found to be similar as for ZnO NWs doped with Ga for the as-grown and postdeposition annealed samples. The data have been analysed and a scientific publication is currently under preparation.