ESRF	**Experiment title:** Structure and stoichiometry of individual Cobald and Europium doped ZnO nanowires	**Experiment number**: HC-871
Beamline: ID13	**Date of experiment**: from: 20. April 2013 to: 23. April 2013 5. July 2013 9. July 2013	**Date of report**: 30. Aug. 2013
Shifts: 18	**Local contact(s)**: Dr. Manfred Burghammer (Dr. Gema Martinez-Criado)	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Prof. Dr. Carsten Ronning* / Dr. Claudia Schnohr*

Friedrich-Schiller-Universität Jena, Institut für Festkörperphysik,
Max-Wien-Platz 1, 07743 Jena, Germany

Report:

The shifts have been split up into two beam times with 6 and 12 shifts taking place in April and July 2013, respectively. This was due to the fact that our group had first to gain experience on the sample geometry and measurements conditions. The second beam time was then performed under highly improved conditions, especially concerning the sample preparation performed in advance at the University of Jena. Whereas thin SiN-membranes were used to support the nanowires for X-Ray investigation at the first beam time, during the second beam time we used thin carbon based TEM grids as substrates, which allowed both the X-Ray examination at ESRF and high-resolution SEM at U Jena of the same implanted nanowires. The latter is an important prerequisite for the targeted research (see proposal), as the diameter of individual nanowire had to be determined, too.

We investigated several Co-implanted ZnO nanowires with varying concentrations (see table 1 below), but we switched at the second beam time to Mn-implanted nanowires. This was due to the failure of the implantation system at U Jena not providing a high enough Co^+ ion beam. A high current Mn^+ ion beam is much easier to realize. This change has no effect on the goal of the proposal, as only the mass of the implanted ion is crucial for this study. ^{55}Mn and ^{59}Co are of similar mass and result into similar sputtering yields. Furthermore the XRF Mn signal was easier to detect, while the XRF Co signal was close to the Zn nanowire and Cu background signals. As suggested by the reviewer of our proposal, we skipped the investigations with high mass rare earth ions (m > 150 amu) implanted into ZnO nanowires. However, such a comparison to the low mass investigations is still very desirable and will be further pursued in the future.

Table 1: *Investigated ZnO nanowire samples during the HC871 experiment.*

nanowire morphology	implanted species	ion energy, angle, temperature	rotated, annealed	concentration [at.%]; ion fluence	# Nanowires investigated
random	$^{59}Co^{+}$	60-300 keV, RT	no, yes	4 ; 6.20e16	4 (XRF)
random	$^{59}Co^{+}$	60-300 keV, RT	no, yes	8 ;1.24e17	4 (XRF, XRD)
aligned	$^{55}Mn^{+}$	175 keV, 45°, RT	yes, no	0,01 ; 2.38e14 cm^{-2}	2 (XRF)
aligned	$^{55}Mn^{+}$	175 keV, 45°, RT	yes, no	0,1 ; 2.38e15 cm^{-2}	2 (XRF)
aligned	$^{55}Mn^{+}$	175 keV, 45°, RT	yes, no	1 ; 2.38e16 cm^{-2}	2 (XRF)
aligned	$^{55}Mn^{+}$	175 keV, 45°, RT	yes, no	2 ; 43.76e16 cm^{-2}	1 (XRF)
aligned	$^{55}Mn^{+}$	175 keV, 45°, RT	yes, no	4 ; 9.53e16 cm^{-2}	2 (XRF)
aligned	$^{55}Mn^{+}$	175 keV, 45°, RT	yes, no	8 ; 1.91e17 cm^{-2}	3 (XRF)

As we proposed, we investigated the incorporation probability of dopant atoms by ion implantation into nanowires. Due to the 3D structure a deviation compared to a flat surface can be simulated by means of different MC-algorithms, such as TRIM or *iradina*. This was performed as a function of ion implantation concentration and diameter of the nanowires. Figure 1 shows, as one example, an XRF-element mapping of a nanowires, which was implanted with Co to a nominal concentration of 8 at%; however, in a random direction. Thus, the average concentration does not match to the simulations and amounts to only 1.2 at%; however, small inclusions show up to 2.8 at% Co where the nanowire is thinner. Those inclusions were also investigated by nano-XRD, which indicates the formation of secondary phases within the ZnO nanowire matrix.

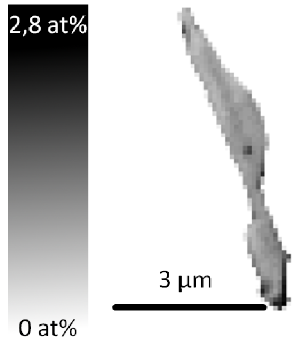

Figure 1: *XRF elemental mapping taken at ID-13 at ESRF in April 2013 of one single ZnO nanowire, which was implanted with Co ions to a nominal concentration of 8 at.% (and has a funny morphology).*

In general we obtained the following results, which will be published in future, but are briefly summarized already here (note that the data taken in July 2013 are still being analyzed):

- Implantation into random nanowires (Co samples):
  - concentration far below simulated results of both *iradina* and TRIM.
  - large local variation due to random orientation/clustering.
- Aligned nanowires during implantation (Mn samples):
  - concentration matches almost *iradina* simulated results, but not TRIM.
  - low local variation, possible concentration gradients along nanowires due to thickness variations.

Further results, which are not listed above, are displayed in detail in the following manuscripts. As soon as we have a full citation, we will add them to the ESRF on-line library.

- **Local lattice distortions in Co-implanted ZnO nanowires**, *M. H. Chu, G. Martínez-Criado, J. Segura-Ruiz, S. Geburt, C. Ronning*, Appl. Phys. Lett. (2013), submitted
- **Intense intra-3d-luminescence and waveguiding properties of Co-doped ZnO nanowires**, *S. Geburt, R. Röder, U. Kaiser, L. Chen, M.H. Chu, J. Segura-Ruiz, G. Martínez-Criado, W. Heimbrodt, C. Ronning*, phys. stat. sol. RRL (2013), accepted, DOI: 10.1002/pssr.201307230
- **Structural order in single Co-implanted ZnO nanowires**, *M. H. Chu, G. Martínez-Criado, J. Segura-Ruiz, S. Geburt, C. Ronning*, phys. stat. sol. A (2013), submitted