ESRF	**Experiment title:** **X-ray absorption spectroscopy in nanowires with electrical detection**	**Experiment number**: HC-2521
Beamline: ID-16B	**Date of experiment**: from: July 6, 2016 to: July 11, 2016	**Date of report**:
Shifts: 12	**Local contact(s)**: Damien Solomon	*Received at ESRF:*

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Report:

The aim of the beamtime was to demonstrate electrically detected X-ray absorption spectroscopy as a new method for investigating nanostructures. To this end, we fabricated samples with electrically contacted single GaInP semiconductor nanowires, as well as a sample holder which fit the sample stage at ID-16B (Fig. 1A-B) [1]. The nanowires have highly *n*-doped ends, with an undoped and highly resistive middle segment. We connected a voltage source and a sensitive current amplifier to the sample holder, and aligned the device in the X-ray nanofocus (about 90 nm diameter). Two X-ray fluorescence (XRF) detectors were used simultaneously and put as close as possible to the sample.

First, 2D raster scans were collected (Fig. 1C) with a constant bias voltage. The Au XRF signal comes from the contacts, and the Ga XRF signal from the nanowire, as expected. The X-ray beam induced conductance (XBIC) signal is only generated in the central segment, since this segment dominates the resistance and therefore has a high electric field. Typical currents were in the pA range. The absorbed X-rays excites non-equilibrium electron-hole pairs which contribute to the conductivity, as shown in previous experiments [2]. The spatial resolution is similar to the beam size.

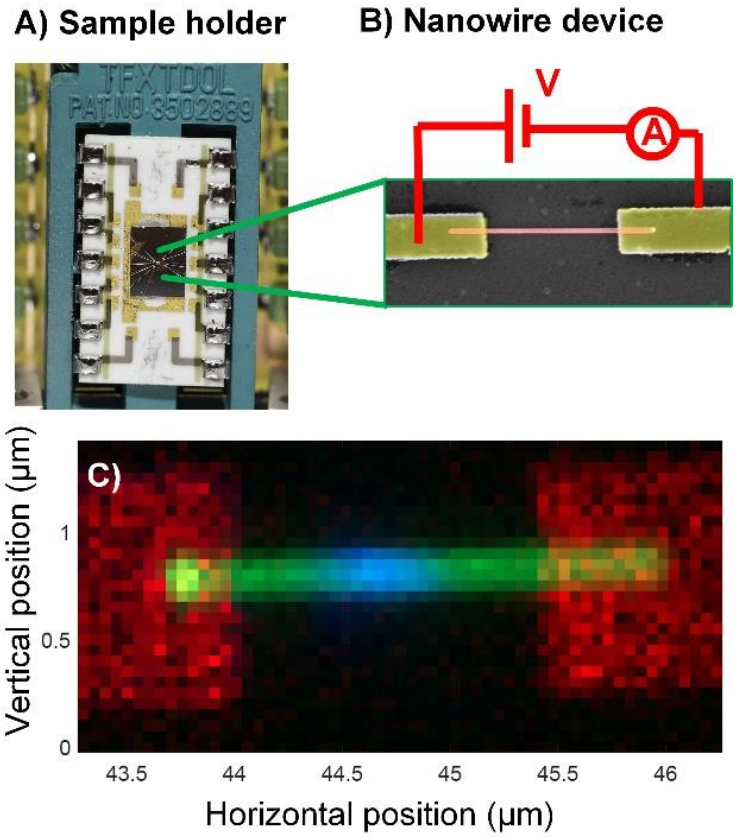

Fig. 1 *A) Sample holder for in operando measurements of nanostructures. B) False-colored SEM shows a nanowire contacted at both ends. C) False-colored image of X-ray induced current (blue) in a electrically biased GaInP nanowire, Au XRF (red) and Ga XRF (green). Step size 50 nm, dwell time 1 s.*

These results show how X-rays can be used to probe the electronic properties of nanodevices with high spatial resolution. Similar measurements can be done with an electron beam, but X-rays have other properties that can be exploited. One of them is the ability to use a monochromatic beam to excite specific elements near an X-ray absorption edge. We performed such energy-resolved measurements around the Ga K-edge, using ID-16B's unique ability to energy scan with a stable nanofocus. We could simultaneously collect

spectra using XBIC and traditional XRF, which was the goal of the beamtime, and observed a clear enhancement of the XBIC signal as the energy crossed the edge. The data needs further analysis, which was not completed within the short time since the beamtime, but the XRF and XBIC showed qualitative similarity.

In a second set of experiments we investigated Zn-doped nanowires using XRF. Zn is used for *p*-doping III-V semiconductors, and control of the level and spatial distribution of doping is crucial for the performance of e.g. solar cells. Unfortunately, characterization of Zn-doping is notoriously difficult in nanostructures, since the concentration is only on the order of 10^{-5} to 10^{-3}. Electrical measurements of Hall-type usually fail since it is very difficult to make ohmic contacts. Electron beam methods fail since they generate too high background signal, but XRF has shown promising results [3].

We investigated two types of nanowires: *p-i-n* doped InP nanowires, which were grown for solar cell applications, and *p*-doped GaInP nanowires, which had nominally homogenous composition. Both nanowires were grown using a Au seed particle, which was still present at the tip.

In the InP nanowires, we successfully detected Zn at the base of the nanowire (Fig. 2 A,B). Note that we used a monochromatic beam ($dE/E \sim 10^{-4}$), since this was required for the XBIC measurements, although a pink beam ($dE/E \sim 10^{-2}$) should give around 100 times stronger signal. It has previously not been possible to measure the Zn doping in such nanowires. We suspected that the Zn doping would give a strong memory effect, extending the p- doping throughout the i-region, but doesn't seem to be the case.

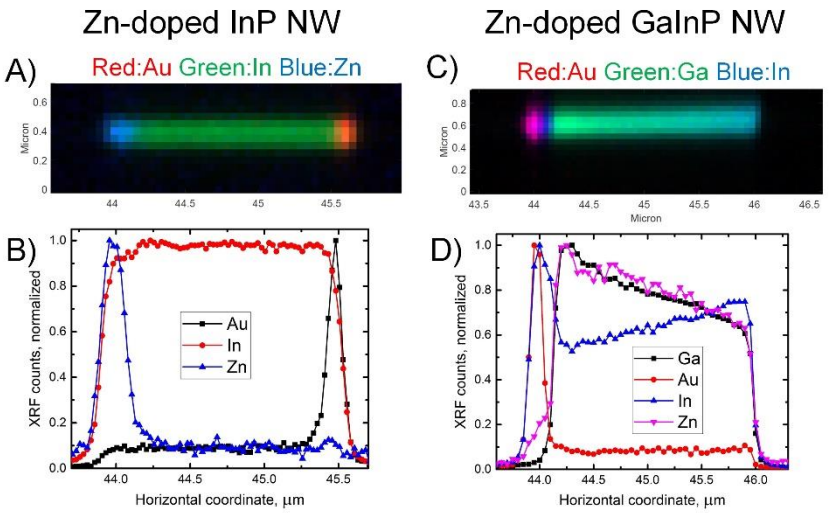

Fig. 2 XRF of single nanowires *A) 2D map of p-i-n doped InP nanowire. B) Line scan. C) 2D map of Zn-doped GaInP nanowire, D) Line scan. All XRF data were normalized.*

In the GaInP nanowire, we found that the Ga concentration increased towards the top, while the In concentration reduced (Fig. 2 C,D). This has previously been observed using electron beam methods. However, here we were also able to measure the Zn concentration. The line scan shows that the Zn concentration is closely correlated with the Ga concentration. The measurements also show that the Zn concentration was significantly higher in the GaInP nanowires than in the InP nanowires. Further analysis is needed to remove background signals and quantify the absolute Zn concentrations.

In conclusion, we showed that spectroscopic XBIC-measurements can be used to investigate individual nanostructures. The XBIC signal gives information about local electronic properties, and with the latest X-ray optics the spatial resolution could be pushed below 10 nm [4]. Compared with electron beams, X-rays have a number of interesting additional opportunities, such as long penetration depths for investigation of complete devices, and time-resolved measurements using the synchrotron pulses.

[1] J Wallentin, M Osterhoff, T Salditt: *In operando X-ray diffraction reveals electrically induced strain and bending in single nanowire device* Adv. Mater. **28** (9) (2016) (http://dx.doi.org/10.1002/adma.201504188)

[2] J Wallentin, M Osterhoff, RN Wilke, et al.: *Hard X-ray detection using a single 100 nm-diameter nanowire* Nano Lett. **14** (12) (2014) (http://dx.doi.org/10.1021/nl5040545)

[3] J Segura-Ruiz, G Martínez-Criado, MH Chu, S Geburt, C Ronning: *Nano-X-ray Absorption Spectroscopy of Single Co-Implanted ZnO Nanowires* Nano Lett. **11** (12) (2011) (http://dx.doi.org/10.1021/nl202799e)

[4] F Döring, AL Robisch, C Eberl, et al.: *Sub-5 nm hard x-ray point focusing by a combined Kirkpatrick-Baez mirror and multilayer zone plate* Opt. Express **21** (16) (2013) (http://dx.doi.org/10.1364/OE.21.019311)