Coherent X-ray nanodiffraction on single GaAs nanowires

J. Gulden[1], **S. O. Mariager**[2], **A. P. Mancuso**[1,†], **O. M. Yefanov**[1], **J. Baltser**[2], **P. Krogstrup**[2], **J. Patommel**[3], **M. Burghammer**[4], **R. Feidenhans'l**[*,2], and **I. A. Vartanyants**[**,1]

[1] Deutsches Electronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany
[2] Nano-Science Center, Niels Bohr Institute, Universitetsparken 5, 2100 København, Denmark
[3] Institute of Structural Physics, Technische Universität Dresden, 01062 Dresden, Germany
[4] European Synchrotron Radiation Facility (ESRF), BP 220, 38043 Grenoble Cedex, France

[*] Corresponding authors: e-mail robert@fys.ku.dk, Phone: +45 35 32 03 97, Fax: +45 35 32 50 16
[**] e-mail ivan.vartaniants@desy.de, Phone: +49 40 8998 2653, Fax: +49 40 8998 4475

[†] Present address: European XFEL GmbH, Albert-Einstein-Ring 19, 22761 Hamburg, Germany

Coherent X-ray nanodiffraction was applied to investigate single GaAs nanowires. Using the nanofocus hard X-ray setup at ID13 of the ESRF, the diffraction signal from isolated nanowires was measured. The diffraction patterns were recorded for different rotations of the sample. These diffraction patterns were then combined to yield three-dimensional information around a wurtzite [101] Bragg peak.

1 Introduction In recent years it has been demonstrated that a new class of solid-state materials – one-dimensional (1D) crystals in the form of nanowires, nanotrees, and nanoflakes – can be synthesized by a range of well-established techniques for growing semiconductor materials [1]. A special focus has been on "bottom up" techniques, where the growth of the nanostructures is promoted by the presence of ultra fine catalyst particles, which act as nanoscale "melting pots" [2]. At elevated temperatures an alloy is formed, consisting of the molten metal particle and semiconductor atoms supplied from a dilute gas. When this alloy is saturated a fine crystalline wire grows epitaxially between particle and substrate. Pursuing this growth at low pressure leads to a forest of micrometer long, uniform, and essentially 1D nanowires. The details of the growth process are, however, still debated. For example, if the catalyst melts during the growth and how the constituents arrive at the growth interface, by diffusion through the catalyst or along the interface [3]. Understanding the growth process is pivotal in the effort to better control of the nanostructure properties', namely, morphology, structure, and purity, which are essential to fabricate nanowires for practical applications, such as biosensing [4], solar cells [5], batteries [6], and future computing devices. In order to understand the growth, strong characterization tools for both ensembles and single wires are required. To this end, this paper addresses the possibility of single nanowire X-ray diffraction experiments. On a broader scale the structure of objects on the nanoscale determines the physical properties of macroscopic materials, which is why it is increasingly important to investigate the structure of nanoscale objects. X-ray scattering gives access to local chemical, elemental, and structural information and provides an ideal tool to investigate matter on the nanoscale.

For many years, the most common nanowire catalyst material has been Au due to its unique ability to promote the nanowire growth. The incorporation of Au, which may create deep levels acting as recombination centers, hence degrading the electronic properties of the material, is still ambiguous [7, 8]. Formation of Au free GaAs nanowires grown by MBE has recently been demonstrated with a thin deposited layer of SiO_2 on Si or GaAs substrates [9, 10], where the obvious advantage is the absence of Au and particularly low C environment. The detailed atomic structure depends critically on the choice of composition and growth parameters, which makes it possible to tailor the structural phase along the typical (111) crystal growth direction, switching between the two possible structures, the

cubic zincblende (ZB) and the hexagonal wurtzite (WZ) phase. In this way phase perfect wires were recently obtained by using specific growth parameters [11].

The structure of III–V nanowires is, however, usually complicated and contains extended domains with mixed WZ or ZB structure, both regular and twinned, as well as numerous stacking faults. Even a regular super lattice stacking of nanoregions of regular and twin structure has been found [12, 13]. In the case of the pure liquid Ga-assisted GaAs nanowires it is known that the wires naturally change the structure from ZB to WZ during growth [14] which makes the situation more complicated.

The combination of the often complicated nanowire structure, and the influence of the structure on the nanowires physical properties suggest the use of both new and well-proven characterization methods. To this end the structure of III–V nanowires has been extensively investigated by transmission electron microscopy (TEM) on single wires and X-ray scattering on the full forest of epitaxial wires or flakes [1, 5, 12, 15, 16]. As such X-rays have proven to be a powerful tool to measure ensemble average properties of entire forests of nanowires. With this technique it is possible to identify the various structures by crystal truncation scans. The shape of the individual Bragg reflections, in addition, defines the external shape of the nanowires [12]. To extend this kind of experiment to single nanowires, or more generally to nanoobjects, an X-ray setup with a nanofocus is required [17], an option which only exists due to recent achievements in the field. The very small focal size opens the possibility to illuminate a single nanowire within an assembly. In addition, the high degree of coherence in the focus of such a beam opens the possibility to effectively apply coherent X-ray diffractive imaging (CXDI) to investigate the structure of a single nanowire.

CXDI is based on the idea that if a finite object is illuminated coherently and its corresponding far-field diffraction pattern is measured and sampled sufficiently, then this diffraction pattern can be inverted uniquely using iterative phase retrieval methods [18]. After its first experimental demonstration [19], CXDI was applied effectively to image different samples and materials (for reviews see Refs. [20, 21]). This method was also successfully implemented for imaging crystalline materials by a local fine scan of the reciprocal space in the vicinity of a chosen Bragg peak from the sample. By inverting this three-dimensional (3D) distribution of the diffracted intensity, the shape and strain field inside a crystalline lead particle was obtained with 40 nm resolution [22] (see for review Ref. [23]).

In this paper, we present the results of a coherent diffraction experiment on a single GaAs nanowire, which besides the relevance to nanowire science, will serve as an ideal test object for coherent nanodiffraction imaging with high-spatial resolution.

2 Experiment The experiment was performed at the nanofocusing beamline ID13 of the European Synchrotron
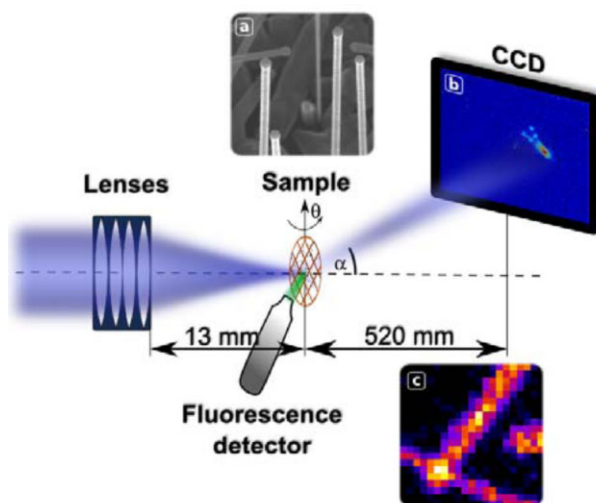

Figure 1 (online color at: www.pss-a.com) Schematic view of the experimental setup. (a) SEM image of GaAs nanowires with a Ga droplet at the tip. (b) Diffraction pattern recorded at an angle of $\alpha = 11.3°$. (c) Fluorescence map of the scanned region.

Radiation Facility (ESRF) with an X-ray energy of 15.25 keV. The diffraction geometry of the experiment is shown schematically in Fig. 1.

The GaAs nanowires were grown on a Si (111) substrate by molecular beam epitaxy. The conventional Au catalyst particles, were substituted with a Ga droplet. Typical dimensions of the nanowires in our sample were 120–140 nm in diameter and 7–8 μm in length.

The GaAs nanowires were mounted on a TEM grid and positioned at the focal plane of two cylindrical Si compound refractive lenses [17]. These were aligned perpendicular to each other, each focusing the beam in one dimension, and producing a 150×150 nm^2 focus, that is just bigger than the nanowire diameter. The focus position was 13 mm behind the last lens [24]. The sample position was adjusted by a set of piezo stages. In addition, the sample could be rotated around both axes perpendicular to the incoming beam direction. Especially important was the rotation around the vertical axis which was scanned to sample the diffracted intensity in a 3D volume around a Bragg peak.

A fluorescence detector was positioned close to the sample perpendicular to the beam. It was used to locate a single wire on the TEM grid, by mapping the combined fluorescence signal of Ga and As. In Fig. 1c a fluorescence map with a step size of 100 nm is shown. Three isolated GaAs nanowires can be resolved in this image. The coherent diffraction signal was recorded by a single photon counting, noise free MAXIPIX detector with 256×256 pixels. Each pixel has an area of 55×55 μm^2. The detector was positioned 520 mm downstream from the sample to record the forward scattering signal. A 1.5 mm wide beamstop was used to prevent damage to the detector from the direct beam. For the measurements of the Bragg peaks the detector was moved away from the optical axis. At an angle of $\alpha = 11.3°$

Phys. Status Solidi A **208**, No. 11 (2011)

Original
___
Paper

2497

the [101] WZ Bragg peak was accessible. An example of a diffraction pattern measured in this geometry is shown in Fig. 1b.

3 Results and discussion In the first step several isolated nanowires were investigated in the forward scattering geometry. In addition to single wires, more dense regions were illuminated, in which several wires were simultaneously in the focus of the X-ray beam. Unfortunately, due to the relatively large beamstop, no significant scattering signal was measured. Increasing the exposure time, to increase the scattering signal, was limited by radiation damage of the sample. It appears that damage occurred to the supporting film before the nanowires were damaged, and this reduced the stability of the setup.

In the next step, single nanowires were measured in the diffraction geometry where the detector is offset from the optical axis which has an additional advantage that there is no scattering from the direct beam and no beamstop is needed. We measured the diffraction signal around a WZ [101] Bragg peak for different angles θ of sample rotation, covering a range of 3° with a step size of 0.05° (Fig. 2). During the scan the diffraction signal drastically changed depending on the angle of rotation. The Bragg peak was observed over a range of 3°, in which the position of Bragg peak on the detector changed.

The different positions of the Bragg peak in the detector correspond to different scattering vectors and is the sign of a crystal truncation rod (CTR) originating from the center of the Bragg peak. This gives rise to an elongated shape of the Bragg peak (Fig. 2). The intensity distribution in reciprocal space is given by a Fourier transform of the crystal shape function, and any sharp truncation of the crystal gives rise to a streak of scattering that is the CTR along the surface normal in reciprocal space. At the angles closest to the center of the peak additional CTRs, originating from the center of the peak but emanating in various directions in reciprocal space, can be seen (Fig. 2c–e).

Each diffraction pattern represents a cut through 3D reciprocal space. By combining these slices the full 3D information around the Bragg peak can be obtained. The result reveals a complicated structure, which can be seen when plotting an isosurface of the scattered 3D intensity (Fig. 3). The elongation of the peak is the CTR of the nanowire and is a clear sign of stacking faults or twin planes along the growth direction of the wire. The fringes along the rod in reciprocal space also occur due to the coherent interference from the size of investigated features. The smaller CTRs, which form a weak six-armed star arise from the nanowire's side facets and show the hexagonal shape of the nanowire. The existence of several such stars confirms that we measured the diffraction from several independent domains in the nanowire, which have the same facet structure (Fig. 3). Due to the slight phase difference of two WZ domains separated by a single twin plane, the scattering from such two domains is slightly separated in reciprocal space. The three hexagonal stars correspond to the three possible WZ stacking sequences, and the fact that they are all roughly equal in magnitude show that the WZ domains are significantly smaller than the X-ray focus size, and randomly distributed.

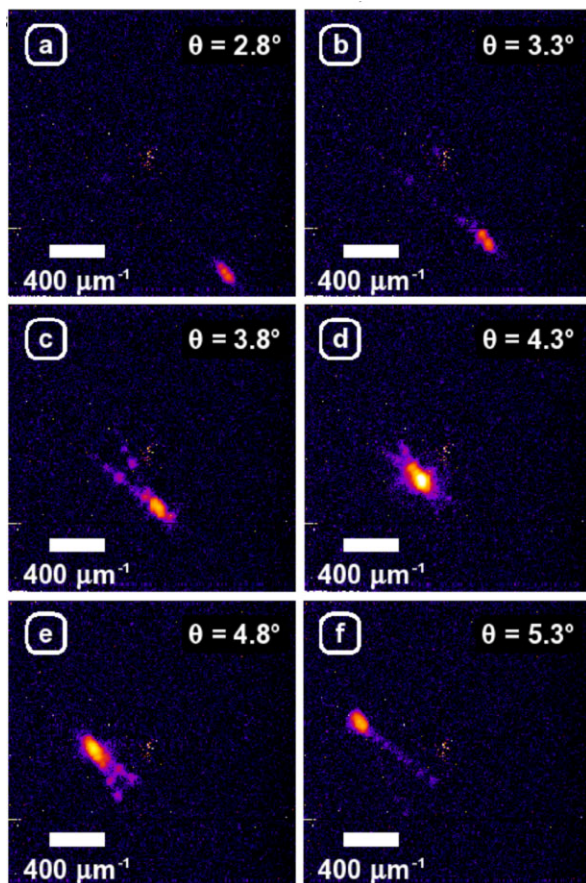The measurements were repeated on different locations along the nanowire that extends in one dimension much

Figure 2 (online color at: www.pss-a.com) Diffraction patterns measured at different angles of sample rotation, shown on a logarithmic scale.
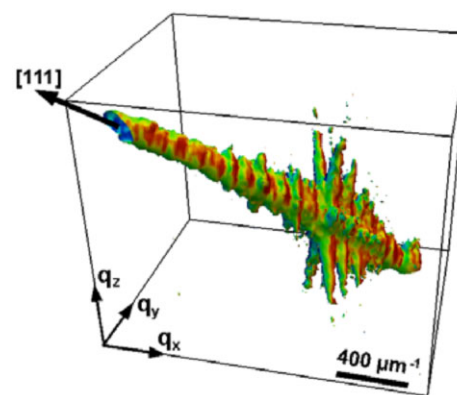

Figure 3 (online color at: www.pss-a.com) A 3D isosurface of the scattered intensity in the vicinity of the Bragg peak in reciprocal space combined of 60 diffraction patterns.

longer than the size of the beam. The overall structure of the Bragg peak remained independent of the position on the wire. The hexagonal CTRs, however, were observed only on the measurement position closest to the tip of the wire, which indicates that the long nanowire only has extended WZ domains with well-defined facet structures at the tip.

Due to instabilities during the measurements the contrast in the images and the number of available fringes was not sufficient to reconstruct the recorded diffraction patterns with conventional iterative phase retrieval methods. This has previously been performed for shorter, thicker, and/or more uniform nanowires [25–27], though the results are limited to obtaining the shape of the wire. A complicated structure like the one studied here, with the existence of several independent domains has not yet been reconstructed successfully.

4 Summary and outlook We used the hard X-ray nanobeam scanning X-ray microscope at ID 13 of the ESRF to perform a coherent diffraction experiment on single GaAs nanowires. Diffraction patterns in the vicinity of a Bragg peak were measured locally in a small region of a selected nanowire and the origin of the different features were explained. It appears clear that the road towards anything but forward scattering is to use nanowires fixed on a substrate, which allows much easier handling and orientation as well as greater stability. With further development of the method CXDI can possibly provide high-resolution images of the complicated nanowire structure.

References

[1] J. Johansson, L. S. Karlsson, C. P. T. Svensson, T. Mårtensson, B. A. Wacaser, K. Deppert, L. Samuelson, and W. Seifert, Nature Mater. **5**, 574 (2006).

[2] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).

[3] P. Krogstrup, J. Yamasaki, C. B. Sørensen, E. Johnson, J. B. Wagner, R. Pennington, M. Aagesen, N. Tanaka, and J. Nygård, Nano Lett. **9**(11), 3689 (2009).

[4] T. Berthing, C. B. Sörensen, J. Nygaard, and K. L. Martinez, J. Nanoneurosci. **1**, 3 (2009).

[5] M. Aagesen, E. Johnson, C. B. Sørensen, S. O. Mariager, R. Feidenhans'l, E. Spiecker, J. Nygård, and P. E. Lindelof, Nature Nanotechnol. **2**, 761 (2007).

[6] C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, Nature Nanotechnol. **3**, 31 (2008).

[7] D. E. Perea, J. E. Allen, S. J. May, B. W. Wessels, D. N. Seidman, and L. J. Lauhon, Nano Lett. **6**, 181 (2006).

[8] J. E. Allen, E. R. Hemesath, D. E. Perea, J. L. Lensch-Falk, Z. Y. Li, F. Yin, M. H. Gass, P. Wang, A. L. Bleloch, R. E. Palmer, and L. J. Lauhon, Nature Nanotechnol. **3**, 168 (2008).

[9] A. Fontcuberta i Morral, C. Colombo, G. Abstreiter, J. Arbiol, and J. R. Morante, Appl. Phys. Lett. **92**, 063112 (2008).

[10] C. Colombo, D. Spirkoska, M. Frimmer, G. Abstreiter, and A. Fontcuberta i Morral, Phys. Rev. B **77**, 155326 (2008).

[11] H. J. Joyce, J. Wong-Leung, Q. Gao, H. H. Tan, and C. Jagadish, Nano Lett. **10**(3), 908 (2010).

[12] S. O. Mariager, R. Feidenhans'l et al., Appl. Phys. Lett. **91**, 083106 (2007).

[13] J. Johansson, B. A. Wacaser, K. A. Dick, and W. Seifert, Nanotechnology **17**, 355 (2006).

[14] D. Spirkoska, J. Arbiol, A. Gustafsson, S. Conesa-Boj, F. Glas, I. Zardo, M. Heigoldt, M. H. Gass, A. L. Bleloch, S. Estrade, M. Kaniber, J. Rossler, F. Peiro, J. R. Morante, G. Abstreiter, L. Samuelson, A. Fontecuberta, and I. Morral, Phys. Rev. B **80**, 245325 (2009).

[15] S. O. Mariager, S. L. Lauridsen, A. Dohn et al., J. Appl. Cryst. **42**, 369 (2009).

[16] V. Chamard, J. Stangl, S. Labat, B. Mandl, R. T. Lechner, and T. H. Metzger, J. Appl. Cryst. **41**, 272 (2008).

[17] C. G. Schroer, O. Kurapova, J. Patommel, P. Boye, J. Feldkamp, B. Lengeler, M. Burghammer, C. Riekel, L. Vincze, A. van der Hart, and M. Küchler, Appl. Phys. Lett. **87**, 124103 (2005).

[18] J. R. Fienup, Appl. Opt. **21**(15), 2758 (1982).

[19] J. Miao, P. Charalambous, J. Kirz, and D. Sayre, Nature **400**, 342 (1999).

[20] K. A. Nugent, Adv. Phys. **59**, 1 (2010).

[21] A. P. Mancuso, O. M. Yefanov, and I. A. Vartanyants, J. Biotechnol. **149**, 229 (2010).

[22] M. A. Pfeiffer, G. J. Williams, I. A. Vartanyants, R. Harder, and I. K. Robinson, Nature **442**, 63 (2006).

[23] I. K. Robinson and R. Harder, Nature Mater. **8**, 291 (2009).

[24] A. Schropp et al., Appl. Phys. Lett. **96**, 091102 (2010).

[25] V. Favre-Nicolin, J. Eymery, R. Koester, and P. Gentile, Phys. Rev. B **79**, 195401 (2009).

[26] A. Diaz C. Mocuta, J. Stangl et al., Phys. Rev. B **79**, 125324 (2009).

[27] A. Biermanns, A. Davydok, H. Paetzelt et al., J. Synchrotron Radiat. **16**, 796 (2009).