Supporting Information: Three-dimensional composition and electric potential mapping of III-V core-multishell nanowires by correlative STEM and holographic tomography

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I. Correction of cupping artefact in the STEM tomogram

The reconstruction of a tilt series of “raw” STEM intensities, ignoring the non-linear relation between STEM intensity and projected effective density (Eq. (2) of main text), may lead to so-called cupping artefacts in the STEM tomogram. These artefacts are visible as amplifications of the tomogram intensities at the object surface, and become more pronounced with higher thickness and atomic number. To avoid them, the STEM intensities need to be converted into mass thickness maps before tomographic reconstruction. The latter provides quantitative tomograms, in which the signal is given by the effective density, i.e., the attenuation coefficient $\mu_a$. Figure 1 illustrates the procedure which we applied for this purpose.

![Figure 1](image)

**Figure 1.** Procedure for the correction of the cupping artefact exemplified on a slice of the Au NP catalyst. 1. Back-projection (BP) of the STEM sinogram (missing tilt range is filled here with symmetrically equivalent projections of the experimentally available tilt range to avoid missing wedge artefacts.) yields the tomogram $I_{\text{Tomo}}$ that shows characteristic cupping artefacts on the object surface. 2. Thresholding the object provides its shape where its interior is set to unity. 3. Forward projection leads to the projected thickness sinogram $t(x, \theta)$. 4. Calculation of STEM sinograms $I_{\text{STEM}}$ from $t(x, \theta)$ while varying the parameters initial intensity $I_0$ and mean free path length $\lambda_a$. 5a-c. Back-projection of the three STEM sinograms yield “simulated” tomograms $I_{\text{Tomo-Sim}}$ with slightly different height of the cupping artefacts depending on the choice of $I_0$ and $\lambda_a$. 6. Comparison of line profiles of simulated and experimental tomograms reveals, 7, the best match for $I_0 = 69200$ and $\lambda_a = 80 \text{ nm}$. 8. Computation of the mass thickness sinogram $\mu_a t(x, \theta)$ from the original STEM sinogram by inserting $I_0 = 69200$ in the displayed equation. 9. Back-projection finally yields the tomogram of the Au-NP whose signal is represented by the attenuation coefficient $\mu_a$ for gold. The cupping artefacts are removed.

It should be mentioned here that the initial intensity $I_0$ can also be measured directly by an HAADF detector scan, *e.g.*, described in Refs. 1, 2. In our case, we did not perform the HAADF detector scan afterwards, because, as obtained by this procedure, the value of $I_0 = 69200$ exceeds the 2-byte integer range of the HAADF detector software. Thus, the intensity values would be clipped numerically to 65536. Just reducing the contrast setting for the HAADF detector scan is however critical, because the relation between collected STEM intensity and contrast setting is not linear as demonstrated in Ref. 2.
II. **Correction of global contrast variations and its influence on tomograms**

The idea behind this approach is that the sum (integral) of the projection values (mass thickness, projected potential) must not depend on the projection angle if calculated over the same area. Thus, any deviation of it must be caused by non-projective imaging artefacts such as diffraction contrast, noise, etc. In order to reduce the influence of these deviations on the reconstructed tomograms, we treated the projections of both mass thickness (STEM) and projected potentials (EH) in the following way (Figure 2):

*Figure 2. Procedure for correction of global contrast variations and its influence on the tomogram.* The contrast variations in the raw sinograms (tilt series) with respect to their mean value, i.e., average over all projections, are computed and normalized by this mean value. The resulting normalized contrast variations for each projection number (tilt angle) are inverted (building the reciprocal) and multiplied with each line of the raw sinograms to obtain a “corrected” version. For comparison, we reconstructed tomograms and observed that they do not deviate much at a first glance. However, the difference between corrected and raw tomogram shows that in specific directions the back-projected data may be modulated depending on the corresponding variations in the projections, whereas the mean value of the tomogram is not altered.
III. Finite support approach for missing wedge correction at low spatial frequencies in the tomogram

The tomographic reconstructions suffer from the limited tilt range of the tilt series (ca. ±70° instead of a complete tilt range of ±90°) which leads to so-called missing wedge artefacts in the tomogram. To correct the latter for at least very low spatial frequencies, we developed and used a finite support approach as illustrated in Figure 3.

Figure 3. Finite support approach for missing wedge correction at low spatial frequencies in the tomogram. The procedure is demonstrated on the example of a cross-section model of the GA-AGA core-multishell nanowire: Its forward projection taking the experimental tilt range yields the sinogram of the model. The tomogram of the model is obtained from the sinogram after W-SIRT reconstruction using the same parameters as for the experimental tilt data. It shows a too high signal (bright regions) in the center and at the upper and lower edge of the object. The next step is thresholding the tomogram to reveal the outer shape of the cross-section and setting the interior to unity. Then, the shape is projected in forward direction and reconstructed again. The result of this operation is used as divisor to normalize the raw tomogram, finally yielding a corrected tomogram. The line profiles quantitatively support the improvement after this correction step. The application of this method on the experimental STEM data also reveal a significant improvement especially in direction of the missing wedge (right panel).
IV. Histogram analysis of 3D data

Figure 4 and Figure 5 depict the histogram data of the NW tomograms, in which peak position and peak width (FWHM) provide reliable measures of mean and deviation.

Figure 4. Histograms of the 3D attenuation coefficient of the GaAs/AlGaAs NW reconstructed by STEM tomography. The histogram peaks for the gold catalyst at $\mu_a = 12.32 \, \mu\text{m}^{-1}$ and GaAs at $\mu_a = 2.42 \, \mu\text{m}^{-1}$ are used to relate them to their atomic number $Z$ according to Eq. (4) of the main text. The cross-sections show regions where the histograms are computed from.

Figure 5. Histograms of the 3D electrostatic potential of the GaAs/AlGaAs NW reconstructed by STEM tomography. The histogram peaks for the gold catalyst at $V = 26.0 \, V$ and GaAs at $V = 13.0 \, V$ are used to correlate them with mean inner potentials according to Eq. (6) of the main text. The cross-sections show regions where the histograms are computed from.
V. Negative charging of GaAs/AlGaAs core-multishell NW during holographic tilt series acquisition

We encountered the problem that the electrostatic 3D potential reconstructed by EHT is reduced in comparison to the expected mean inner potential values for GaAs. The likely source for this offset is the negative charging of the NW, which can be seen as phase gradient in vacuum close to the NW (Figure 6). Such a negative charge can be generated by secondary electrons emitted from nearby surfaces (e.g., TEM grid, carbon foil) illuminated by the extended elliptic electron beam employed in off-axis holography.

Figure 6. Negative charging of GaAs/AlGaAs core-multishell NW. (a) Low magnification TEM image of the NW showing its surroundings and how the NW is contacted to the holey carbon support. (b) Phase image with amplified contrast between $-0.5 \text{ rad}$ and $1.0 \text{ rad}$ to visualize the phase modulations in vacuum. (c) Line profile along the line scan in (b) revealing a phase gradient of $1.8 \text{ mrad/nm}$.
VI. Statistical analysis of GaAs quantum well tube thickness

In order to quantify the GaAs quantum well tube (QWT) thickness variations in greater detail, we perform a statistical analysis on the STEM tomogram (MIP representation) of the NW trunc region. The width in axial (z-direction) of the analyzed region is about $545 \text{ nm}$ consisting of 280 slices of $1.95 \text{ nm}$ width. At each slice (Figure 7a), GaAs core and QWT are segmented by applying a threshold of $12.9 \text{ V}$ (corresponding to $5\%$ Al content). To account for noise and limited resolution of the experimental data, nearest neighbour pixels of pixels which belong to core and QWT were also included to the latter, if they are higher than $12.6 \text{ V}$ (corresponding to $20\%$ Al content). The resulting segmented slice is shown in Figure 7b, and a line profiles according to line scans (red arrows) in (a) and (b) illustrating which values are included to core and QWT are shown in Figure 7c. In a next step, a polar transformation is applied to the the segmented slice, and the GaAs core is removed in the resulting polar transform (Figure 7d). This representation allows to integrate (project) in r-direction to obtain the thickness of the QWT as a function of the azimuthal direction $\varphi$ in $1^\circ$ steps (Figure 7e). This procedure (a-e) is repeated for 280 slices, and the results are displayed in (Figure 7f). Finally, a histogram is calculated from (f) to reveal the thickness variations of the QWT (Figure 7g).

The thickness variations show a relatively broad peak between 7 and 12 nm, whereas the FWHMs are at 4 and 14 nm. The highest peak at 0 nm can mainly be attributed to missing wedge artefacts. The major problem of such kind of analysis is the quite arbitrary choice, which Al concentration is acceptable to define the QWT.

Figure 7. Statistical analysis of QWT thickness. (a) Cross-section of the GaAs-AlGaAs core-multishell NW. (b) Segmented GaAs core and QWT. (c) Line profiles according to line scans (red arrows) in (a) and (b). (d) Polar transform of (b). (e) Integral (projection) of (d) in r-direction yielding QWT thickness as a function of $\varphi$. (f) QWT thickness as a function of $\varphi$ greyscale maps for 280 slices (vertical direction). (g) Thickness variations of QWT obtained from histogram calculation of (g).
VII. Influence of missing wedge artefacts on histogram analysis

The determination of the Al concentration within the AlGaAs shells of the NW was performed using histogram analysis. In order to investigate the influence of missing wedge artefacts on the histogram analysis, we applied the tomographic reconstruction steps used for the experimental data on a cross-section model (Figure 8). As a result, the histogram peak broadens about ±7% but stays at the same position, i.e., at $c_{Al} = 0.33$. This supports that the peak observed at a higher Al concentration, i.e., at $c_{Al} = 0.41$ in the experimental data is not altered by reconstruction artefacts. It should be noted that the histogram of the model (plotted gray in f) contains extra values besides 0.33 stemming from interpolation effects at the interfaces and surface. Moreover, the peak at 0.33 is much higher as shown in the histogram (25686 counts instead of the 2200 counts displayed). Hence, the influence of interpolation on the histogram is relatively small.

Figure 8. Influence of the tomographic reconstruction artefacts on the histogram analysis for the determination of Al concentration. a) Model of GaAs-AlGaAs core-shell cross-section. b) Tomographic reconstruction of the model using the same parameters (e.g., tilt range, W-SIRT iterations) as in the experiment. c-e) Slices through the experimental STEM tomogram at three different positions of the NW trunk: 220 nm (c), 390 nm (d), and 560 nm (e) distant from the GaAs core tip. The black regions in the interior of the NW cross-section represent masks, which are applied on the data to omit the GaAs core and QWT from the histogram analysis. f) Histograms of (a-e) and of the entire NW trunk as presented in the main paper. There is a significant shift between experimentally observed (c-f) and the nominal concentration (a,b) used in the model.
VIII. Comparison of experimental and simulated potentials along cross-sections

In order to gain further insight into the NW composition and properties, we numerically solved the pertinent drift-diffusion equations for characteristic regions of the NW, namely the Au-GaAs interface at the tip, the vacuum-AlGaAs surface in the tapered region and the trunc cross-section. In order to keep computation times low, we worked in a simplified 1D setting as implemented in the ddc_1D package. In case of the trunc cross-section the latter corresponds to a "rolled out" version of the different layers, yielding a good approximation of the cylindric NW, if the extension of eventual space charge regions is small compared to the radius of the surfaces. This condition is generally well justified in case of the trunc with some deviations only expected at the slightly doped core region. At the tapered region and in particular the Au interface the 3D structure of the drift-diffusion potentials is more complex requiring more care when approximated by a 1D model as described in the main text. For instance, the larger extension of the space charge region at the surface of the NW in the tapered region compared to the trunc can be ascribed to the increased curvature of the surface in the tapered region. Fig. 9(e) show the geometry of the simulated cross-section including the AlGaAs-GaAs core-shell structure including the GaAs QW and the GaAs protection layer at the surface. As indicated in the main text, the AlGaAs is n-doped with \( N_D = 1 \times 10^{17} \text{ cm}^{-3} \) and the GaAs p-doped with \( N_A = 7 \times 10^{14} \text{ cm}^{-3} \), as determined by independent measurements. The width of the different layers has been adapted to average values obtained from the tomograms. Inline with the observed fringing fields, the surface has been charged negatively, pinning the Fermi-level approximately 0.4 eV into the conduction band. With these boundary conditions a potential slope as depicted in the Fig. 9(f) is computed. In particular the surface regions correspond well with experimental linescans taken perpendicular to different facets of the NW trunc (suffering differently from missing wedge artifacts). Also the coordinates of the inflection points at the QWs agree well with the experiment. The deviation at the core are ascribed to the previously noted 3D effect and systematic errors in the experimentally reconstructed potential (i.e., the tomographic reconstruction), which are suited to artificially pronounce the core region in the range of 0.2 eV.

Figure 9. Comparison of experimental and simulated potentials along cross-sections. (a) Volume rendering of GaAs-AlGaAs core-shell NW with blue box indicating where the average cross-section is obtained. (b) Cross-section of EH tomogram. (c) Cross-section of STEM tomogram. (d) Difference (=space charge) potential calculated from (b) and (c). (e) 1D Simulation of band structure of the cross-section. (f) Comparison of experimental potential profiles (1-3) in (d) and simulation corresponding to (e).
1. Lebeau, J. M.; Stemmer, S. “Experimental quantification of annular dark-field images in scanning transmission electron microscopy.” Ultramicroscopy 2008, 108, (12), 1653-8.

2. Rosenauer, A.; Gries, K.; Muller, K.; Pretorius, A.; Schowalter, M.; Avramescu, A.; Engl, K.; Lutgen, S. “Measurement of specimen thickness and composition in Al(x)Ga(1-x)N/GaN using high-angle annular dark field images.” Ultramicroscopy 2009, 109, (9), 1171-82.

3. Wu, Y.-R.; Shivaraman R.; Wang, K.-C.; Speck, J. S., “Analyzing the physical properties of InGaN multiple quantum well light emitting diodes from nano scale structure”, Applied Physics Letters 2012, 101 (8), 083505.