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Three-Dimensional Characterization of Core/Shell Nitride Nanowires

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Introduction

Recent advances in nanotechnology have challenged electron microscopy to become more quantitative in determining the composition, size, shape, and electronic properties of individual nanostructures. Traditional techniques in scanning transmission electron microscopy (STEM) have been developed to obtain two dimensional projected atomic structures, but to truly understand the effect of size and shape on the properties of nanomaterials, the three dimensional structure must be determined. This is now possible for inorganic materials using STEM tomography. Here we illustrate this technique by applying it to the study of GaN/AlN core/shell nanowires. GaN-based nanowires are important building blocks for a variety of different nanodevices, such as LEDs, lasers, and transistors. As a majority of nanowires in the literature are being grown by the vapor-liquid-solid (VLS) method, it is important to characterize and understand the properties of these nanowires, and their morphology with respect to the catalyst size, shape, and position on the nanowire. The three-dimensional technique of STEM tomography is therefore ideal for this study.

Techniques

The electron tomography for this work was performed on a 200keV JEOL 2010F STEM/TEM microscope at Sandia National Laboratories, CA, and one experiment was performed on the FEI Tecnai at the University of Cambridge. For the study of inorganic materials, Z-contrast imaging in the STEM is the most appropriate imaging mode for the acquisition of the tilt series, as it can circumvent the problems of unwanted Fresnel and diffraction contrast due to the nature of the incoherent scattering process (which is not true for conventional TEM imaging). Figure 1 shows a schematic of how Z-contrast (STEM) images are formed. The probe is focused and scanned across the specimen, and the scattered electrons are collected at high angles on the high angle annular dark field (HAADF) detector. The scattering is proportional to the square of the atomic number of the species being observed, and is hence called Z-contrast imaging.

Electron tomography is performed by acquiring Z-contrast images through a tilt range of typically -70° to +70° (the higher the better). Anywhere between 100-160 images usually constitute one tilt series. Once the 2-D projections are acquired (figure 2(a)), the reconstruction is achieved, in simple terms, by smearing out the projection back into an object space at the angle of the original projection. Using a sufficient number of projections from different angles, the superposition of all the backprojected 'rays' will return the original object (figure 2(b)), and this object can then be viewed in 360° using a visualization software.

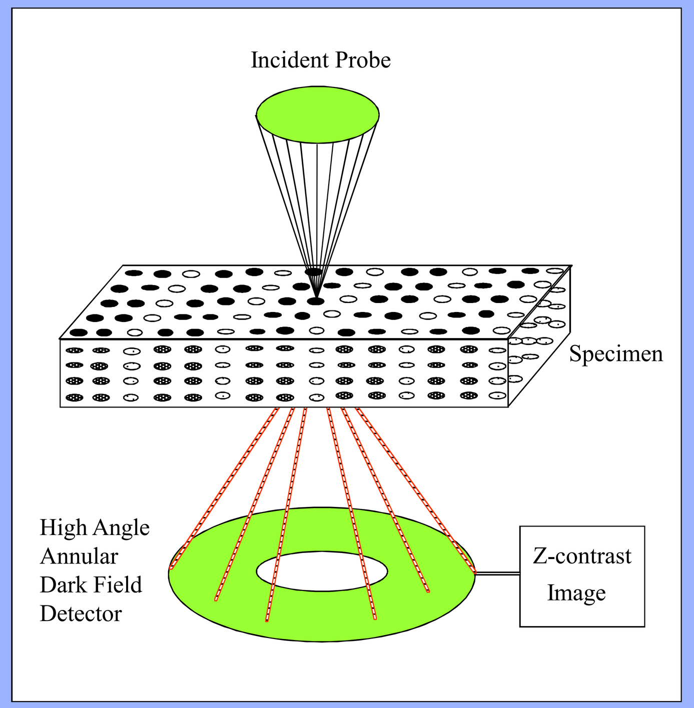


Figure 1: Schematic of Z-contrast imaging. The electron beam is focused on the surface of the specimen and scanned. The scattered electrons are collected on the high angle annular dark field detector.

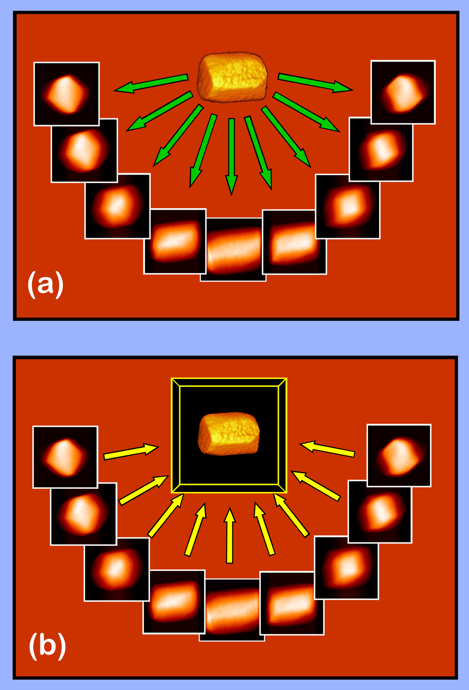
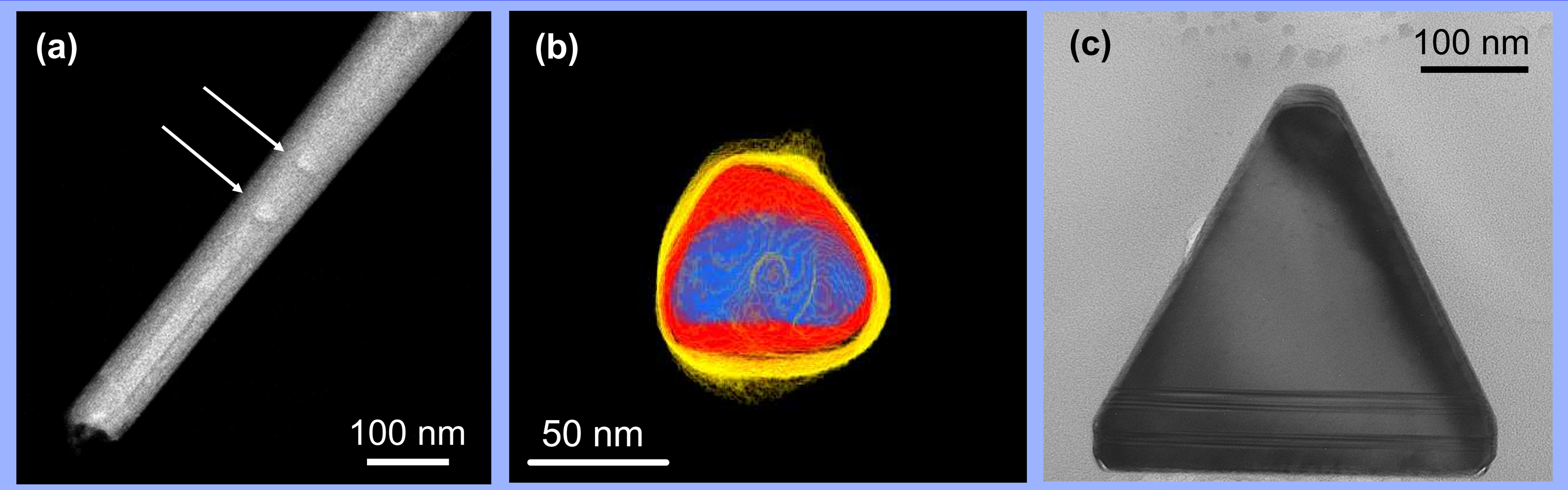
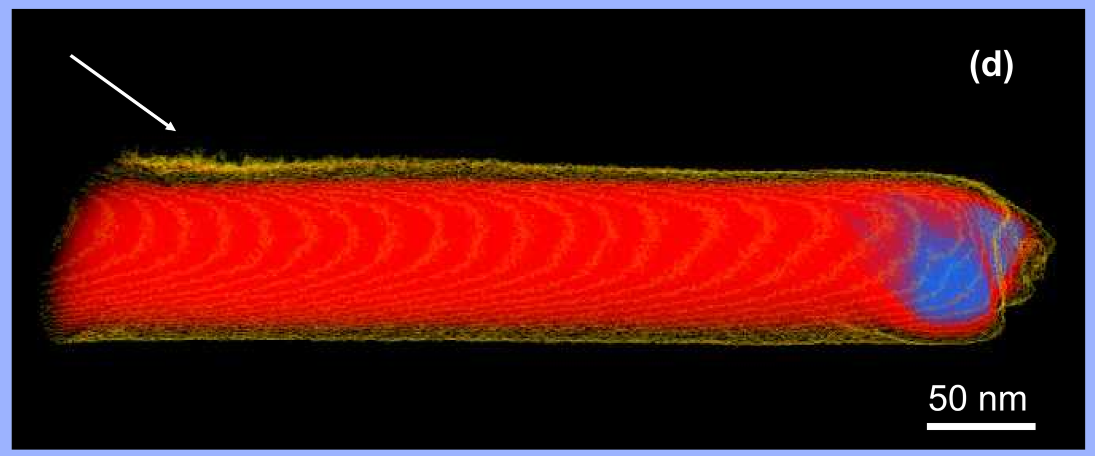


Figure 2: Schematic of a reconstruction by backprojection. (a) An object is sampled by projection of images from different angles in the microscope (Z-contrast images in this case), then (b) reconstructed by backprojecting into the object space. With a sufficient number of projections from different angles, the original object can be reconstructed.

GaN/AlN core/shell nanowire #1: Catalyst in-line with nanowire





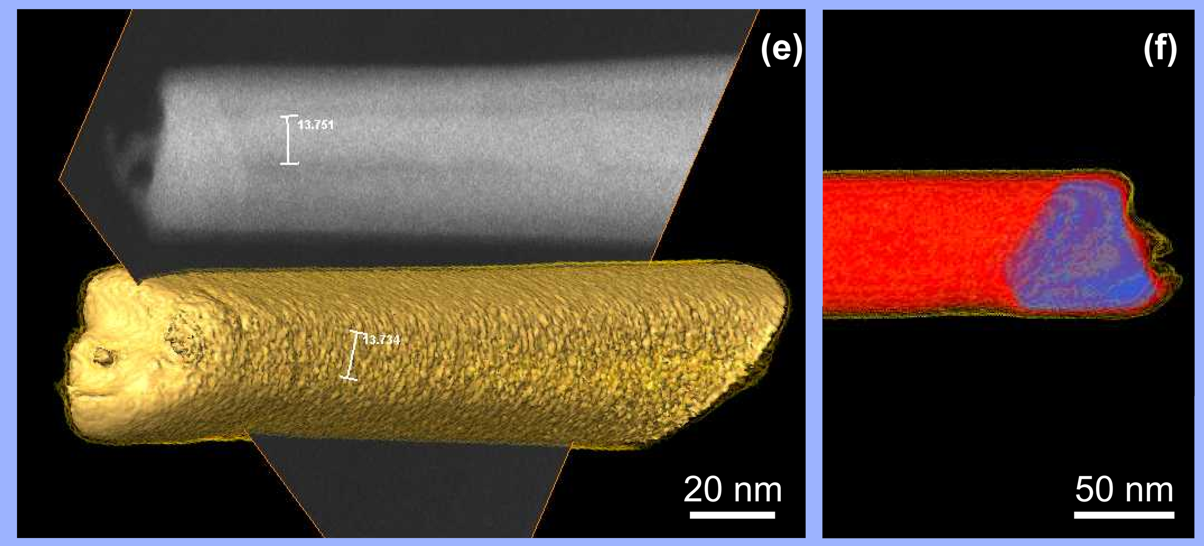


Figure 3: GaN/AlN nanowire (NW) with catalyst in-line and embedded in NW. Yellow, red, and blue represent AlN, GaN, and the Ni catalyst nanoparticle respectively. (a) is one of 153 Z-contrast images in a tilt series showing a bright line of contrast in the center as well as some defects as indicated by the arrows. (b) is an end-on reconstruction showing the cross section is triangular, and compared to the cross sectional TEM image in (c). (d) shows that the defects seen in (a) are actually surface notches. (e) shows that the bright stripe is an additional facet that is created during non-ideal growth. (f) shows the catalyst particle is very well faceted. (b,d,f are volume renders and e is a surface render of the reconstruction).

GaN/AlN core/shell nanowire #2: Catalyst on side of nanowire

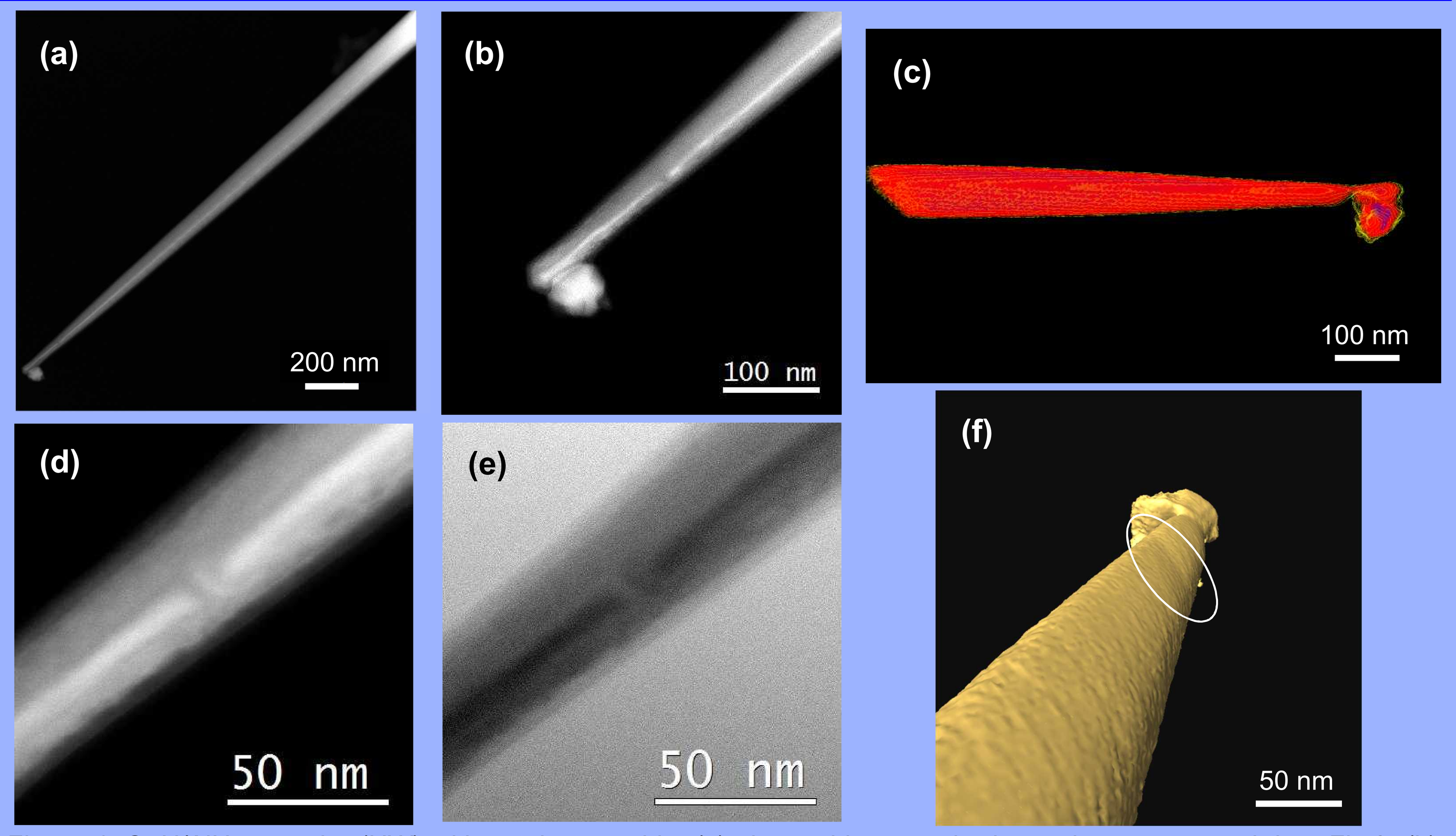
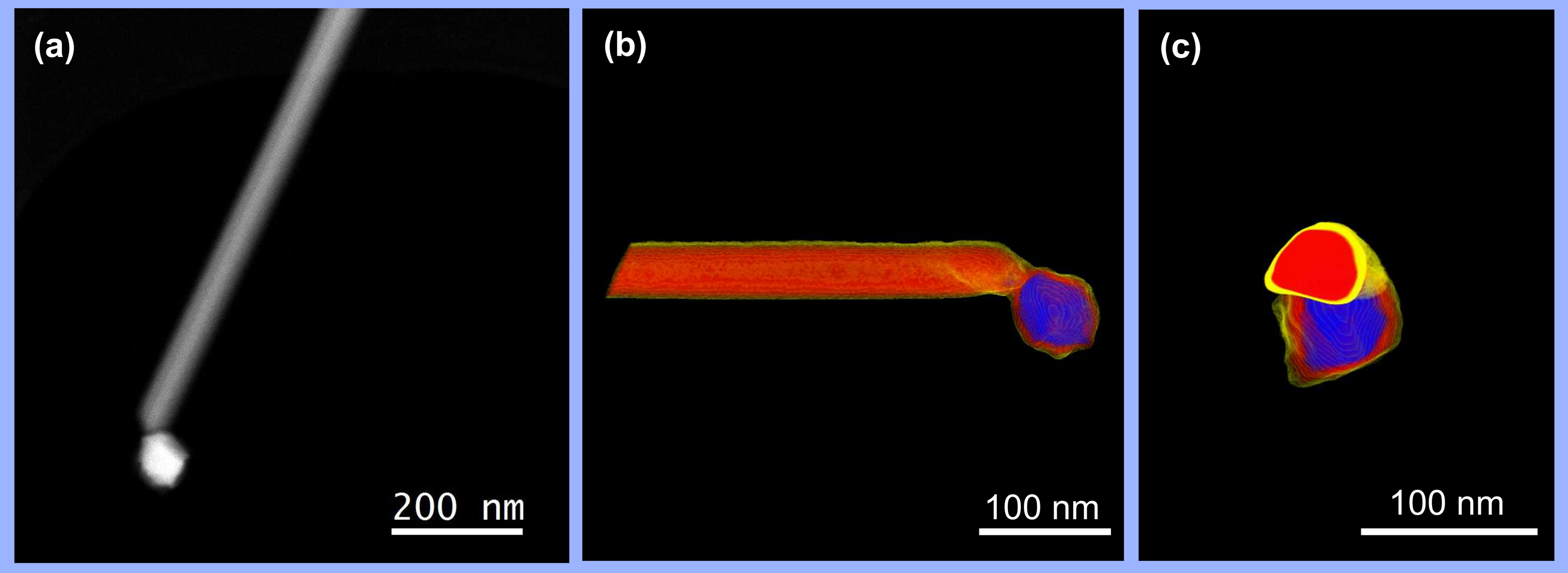
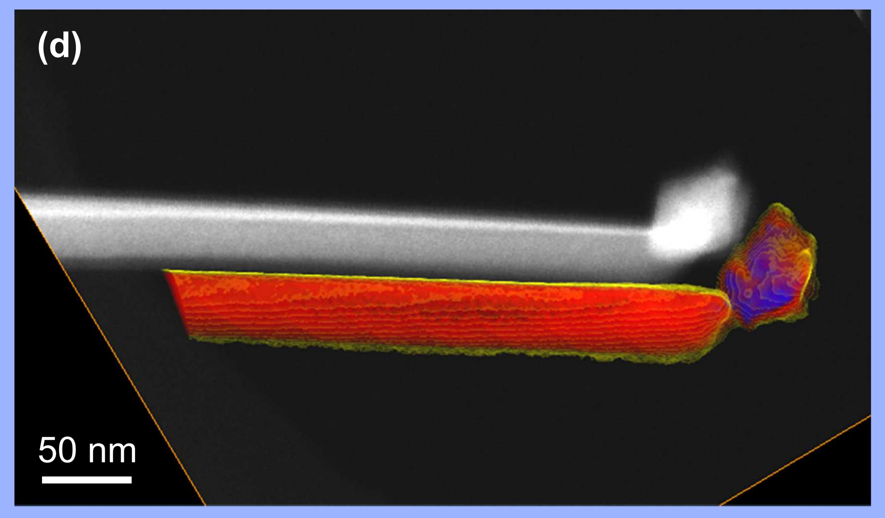


Figure 4: GaN/AlN nanowire (NW) with catalyst on side. (a) shows this nanowire is much more tapered than Fig.3. (b) shows the white "stripe" is very thin, but there is still one defect. (c) is an overall volume-rendered reconstruction of the NW. (d) and (e) are DF/BF STEM images showing the thin AlN shell and the defect at higher magnification, and (f) is a surface-render of the reconstruction that shows the defect is again a surface notch (highlighted by the white oval).

GaN/AlN core/shell nanowire #3: Catalyst off-axis with nanowire





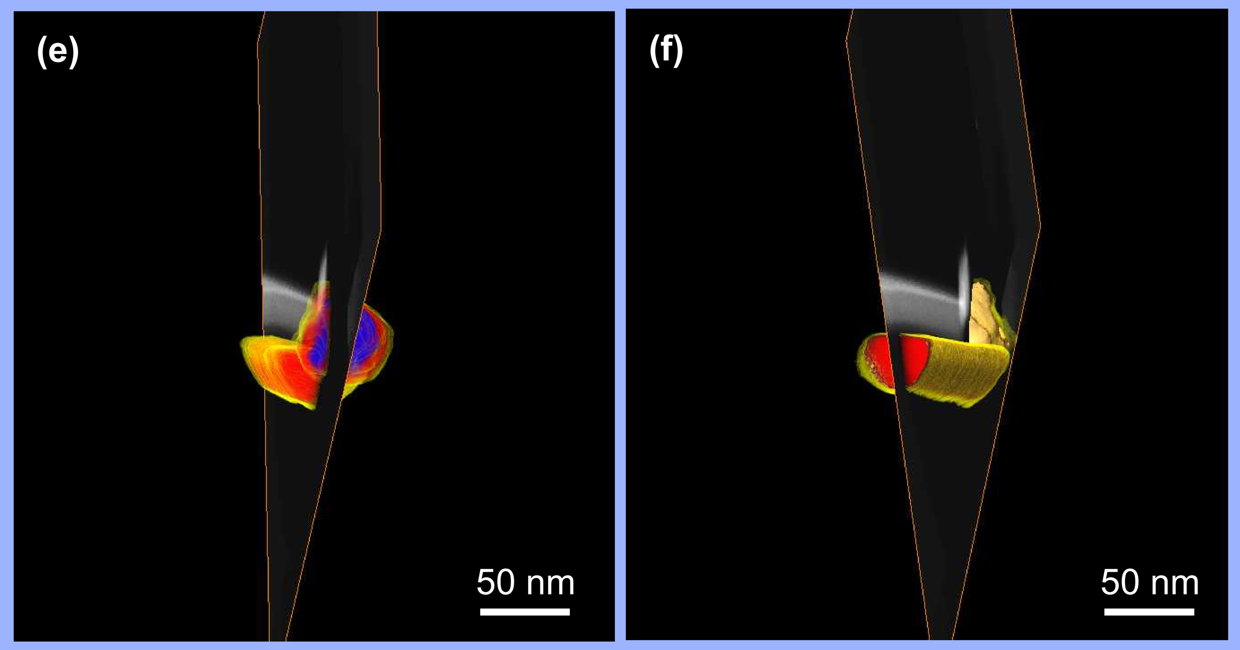


Figure 5: GaN/AlN nanowire (NW) with catalyst off axis. The catalyst is connected to the NW at one particular facet. Again, yellow, red, and blue represent AlN, GaN, and the Ni catalyst nanoparticle respectively. (a) is one Z-contrast image from the tilt series. (b) and (c) are reconstructions showing the Ni particle off-axis in 3-D and that the nanowire is triangular with one edge "sharper" than the other two. This edge appears as the bright line in the comparison of image to reconstruction in (d). This edge is further verified to be the cause of the bright line in the Z-contrast images by comparing the image to the reconstruction at different orientations, as shown in (e) and (f). This nanowire does not show any of the surface defects seen in the other two catalyst particle positions and suggests that this particle orientation is the best for VLS growth. All figures here show volume-rendered reconstructions, and (f) is a volume + surface render to provide an additional view.

Conclusions

- •Catalyst nanoparticle is found to be in one of three positions: in-line with the nanowire, outside of nanowire on the side, or outside of nanowire at tip at a particular facet.
- •Nanowire "defects" are actually surface notches, something we could only identify by doing 3-D tomography. The white "stripe" of nanowire #1 is an extra facet created during non-ideal growth.
- •Catalyst is faceted in 3-D, and not always round. Nanowire diameter is not equivalent to catalyst tip, unless embedded.
- •Nanowire cross section is not exactly triangular close to the catalyst tip, but evolves to become triangular further away from tip.
- •Size, shape, and orientation of catalyst particle appears to affect the growth of the nanowire and the presence of surface notches, and hence may affect the nanowire's transport properties.

Acknowledgements

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