ESRF	**Experiment title:** In-situ investigation of interdiffusion and stress evolution of core-shell nanorods studied by anomalous coherent diffraction	**Experiment number**: SI-2228
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Report:

During this beamtime, we continued our study of the relationship between stresses and interdiffusion in core-shell nanostructures by anomalous coherent diffraction imaging (last experiment: HS-4033). The 3D strain field and the electronic density inside such objects can be analyzed by inversion of the coherent diffraction patterns around Bragg peaks. Information on the elemental distribution can also be deduced from differences in the diffraction patterns recorded using different wavelengths (anomalous diffraction). The combination of the two methods allows for the simultaneous characterization of the strain fields and compositional gradients in-situ for instance during annealing experiments.

We investigated Ag/Au core-shell nanorods prepared by physical vapor deposition [1]. Before the experiment, single Ag/Au nanorods with diameters of ~200 nm were selected from their growth substrate and glued on Mo TEM grids with Pt in a combined SEM/FIB instrument. As previous experiments revealed that plastic deformation can be introduced in the rods during FIB preparation (exhibited by so-called 'barcode diffraction patterns' indicative of the presence of deformation faults), an improved preparation strategy avoiding plastic deformation of the rods by a pull-out to remove the rods from their growth substrate was successfully adopted for the current experiments.

For the anomalous measurements, the beam energy was adjusted either to the Au L_{III} edge (11.92 keV) or below (11.80 keV). The KB system was used for beam focusing. The beam size was relatively large even after repeated alignment (~40 µm (H) x ~8 µm (V)). A multichannel fluorescence detector was employed to locate the nanorod in the beam using the Au fluorescence signal. The initially used heating stage with a Be dome (from ID01), set under vacuum for all measurements to avoid beam damage, had to be replaced by another stage (Anton Paar DHS-900 with a polymer dome) from BM32, as the Be dome was unluckily contaminated with Ge (with the same peak position in fluorescence as Au).

To find a 111 reflection (the (111) planes are parallel to the <110> rod axis), the Maxipix detector was placed close to the sample for covering a large solid angle. After successfully aligning the rod in diffraction condition, the detector distance was increased to ~1 m for better resolution.

Coherent patterns from in total 5 different nanorods were recorded; some had not much intensity, or the 2D or 3D patterns (measured as 2D detector images during rotating the rod around the rod axis) were very complex. One nanorod with clear fringes and oscillations was selected for more detailed measurements (3D patterns at and below the Au edge) in the as-prepared state and eventual in-situ annealing.

Highly fluctuating intensities were detected in timescans (without any distinct frequency; no changes when turning off the vacuum pumps to reduce mechanical vibrations). The beam presumably leads to local heating

and therefore bending of the nanorod (i.e. the diffraction condition is no more fulfilled). Removing the fast shutter ameliorates the behavior, but could not fully resolve the problem.

Successive 3D patterns revealed that the nanorod was modified by the exposure to the X-ray beam at room temperature. The splitting of the diffraction spot increases and the two parts elongate vertically (see Fig. 1). The formation of a C-overlayer (only rough vacuum can be reached in the chamber), as revealed by TEM investigations after the experiment, probably induced significant stresses and bending within the nanorod. During in-situ annealing of this nanorod, 3D diffraction patterns were recorded (after realignment to account for the thermal expansion of the setup) at subsequent temperature steps up to 400 °C, and after cooling down.

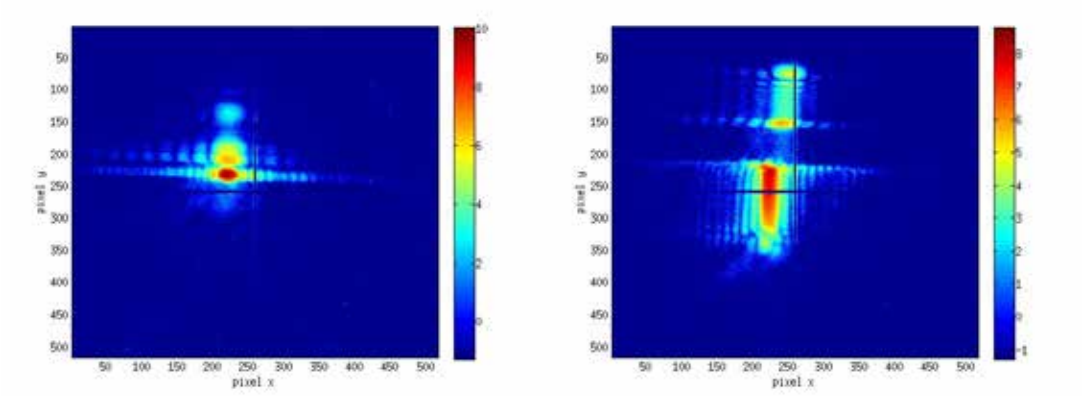

Fig. 1. Detector images (logarithmic intensities) at the maxima of the rocking curves below the Au L_{III} edge, left: at the beginning of the measurements, right: after measuring ~14 hours at room temperature.

In the 2D sections perpendicular to the rod axis (i.e. corresponding to rather homogeneous parts of the nanorod, see Fig. 2), the streaks clearly indicate the facetted cross-section of the nanorod. The asymmetry of the patterns is caused by an inhomogeneous strain field. In the upper part of the images, the oscillations along the streaks have a small periodicity leading to an average lateral size of the rod of ~ 200 nm. Two frequencies clearly overlap on some streaks as expected for a difference between core and shell thicknesses. The lower part of the images exhibits a much larger periodicity along the streaks, indicating a smaller diameter (~ 100 nm) of the corresponding part of the nanorod. A core-shell character is not evident here.

The 2D sections are suitable for the inversion by phase retrieval algorithms (evaluation under progress). Besides the cross-sectional shape and the strain field, this detailed analysis can also reveal the additional information on diffusion from the measurements at two different energies, which is not obvious from qualitative inspection of the patterns.

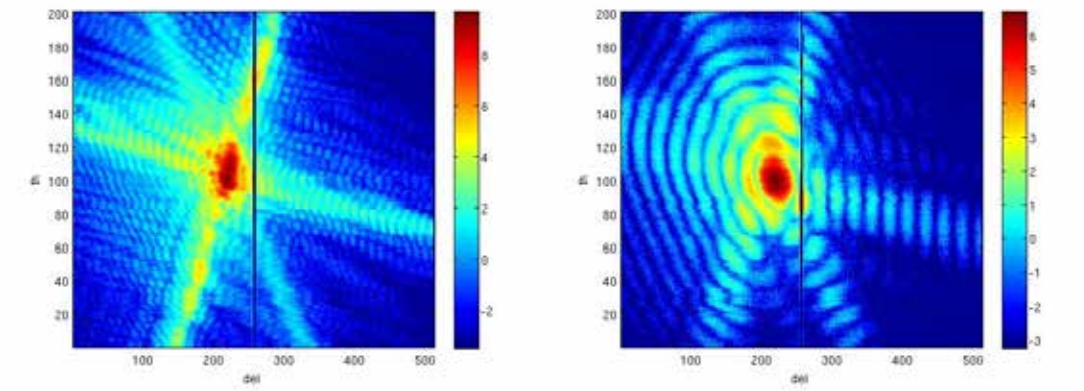

Fig. 2. Sections of the diffraction patterns perpendicular to the nanorod axis below the Au L_{III} edge at the beginning of the measurements, left: lower part , right: upper part of the diffraction spot.

In conclusion, it was demonstrated that core-shell nanorods can be successfully investigated by anomalous coherent diffraction measurements using a dedicated preparation procedure for a deformation-free fixation of the rods on TEM grids and locating the rods with a fluorescence detector. Future experiments have to address the suppression of the formation of the radiation induced C-overlayer by measuring in UHV or using a protective gas atmosphere free of hydrocarbons.

References:

[1] G. Richter *et al.*, Nano Letters 9, 3048 (2009).