Type of presentation: Invited

MS-1-IN-5776 Morphology and inner structure of anisotropic nanoparticles studied by advanced TEM and FIB techniques

Spiecker E.[1], Butz B.[1], Winter B.[1], Niekiel F.[1], Vieweg B.[1]

[1]Center for Nanoanalysis and Electron Microscopy (CENEM), Universität Erlangen-Nürnberg, Erlangen, German

Email of the presenting author: Erdmann.Spiecker@ww.uni-erlangen.de

Extensive research in nanoscience is currently devoted to the synthesis and characterization of complex and anisotropic nanoparticles (NP), with particular focus on low-symmetry NP, patchy structures as well as hybrid particle assemblies. Anisotropy and increased complexity provide additional degrees of freedom for tailoring the physical and chemical properties, making such NP ideal candidates for enhanced chemical, catalytic, and optical applications. In this contribution, microscopic studies of anisotropic and complex NP are presented which illustrate the importance of combining advanced TEM and FIB techniques for comprehensive characterization.

Ge/Si patchy NP formed by gas phase synthesis in a two-stage hot wall reactor [1,2] have been studied by combining HAADF-STEM, STEM-EELS and HRTEM, as illustrated in Fig. 1. The microscopic investigations focused on two key questions, namely the accommodation of misfit (~ 4 %) by defect formation and possible interdiffusion, addressed by HRTEM and STEM/EELS, respectively. Another experimental aspect is the oxidation of the particle surface which could be suppressed by transfer via glove box and vacuum transfer holder.

PbSe quantum dots grown on single wall carbon nanotube (SWCNT) bundles for optoelectronic applications [3] have been studied by combining electron tomography and HRTEM at 80 kV. During wet-chemical synthesis the PbSe NP grow around the SWCNT bundles as revealed by the tomogram in Fig. 2a. In combination with HRTEM contributing crystallographic information (Fig. 2b) a 3D atomistic model is derived (Fig. 2c). By comparison of experimental and simulated HRTEM images the 3D model of the PbSe NP can be further refined.

Ag nanorods formed by wet chemical synthesis [4] are used to illustrate a new FIB method [5] which enables site and orientation specific cross-sectioning of anisotropic NP (Fig. 3). By employing a shadow geometry (Fig. 3b) in which a Si substrate protects the NP from the Ga+ ion beam no protection layer has to be deposited on the NP. Inspection of the NP during milling enables precise positioning of the final cross section. In the case of the Ag nanorod, HRTEM of the final cross section nicely reveals the characteristic five-fold twin structure with additional defects indicating partial strain relaxation (Fig. 3c).

[1] Körmer et al., Crystal Growth & Design 12 (2012), 1330.
[2] Mehringer et al., Journal of Aerosol Science 67 (2013), 119.
[3] Schornbaum et al., Chemistry of Materials, 25 (2013), 2663.
[4] Damm et al., Small 7 (2011), 147.
[5] Vieweg et al., Ultramicroscopy, 113 (2012), 165.
[6] http://www.gmp.ww.uni-erlangen.de/nanoSCULPT.php

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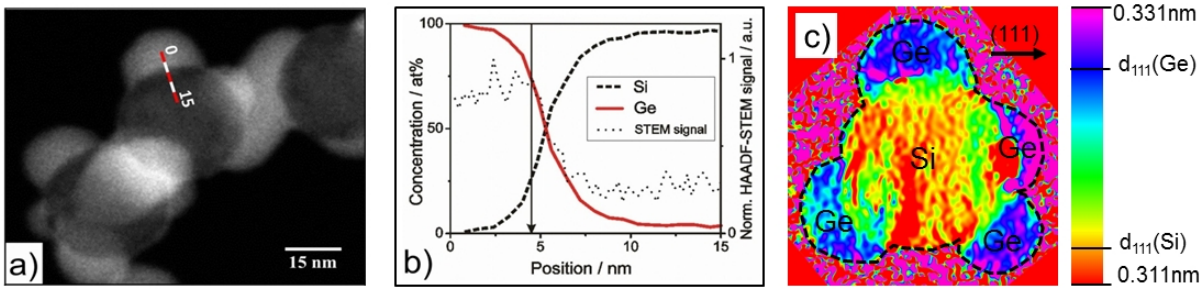

Fig. 1: TEM study of Ge/Si patchy NP produced by gas phase synthesis [2]. a) HAADF-STEM image of aggregated NP with Si cores (dark) and Ge islands (bright). b) Concentration profiles across an interface (line in a)) from EELS line scan. c) Map of (111) lattice plane spacing derived from a HRTEM image (not shown) by geometric phase analysis.

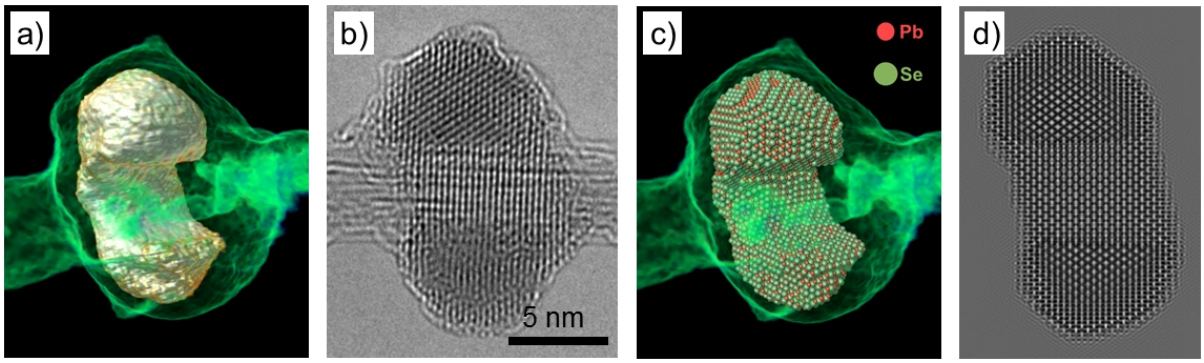

Fig. 2: Morphology and atomic structure of PbSe NP grown on SWCNT bundle [3]. a) Tomogram of PbSe NP. b) HRTEM image of the same NP in [011] zone axis. c) Atomistic model obtained by filling the 3D volume with the PbSe structure in correct crystallographic orientation derived from HRTEM. d) HRTEM image simulation based on atomistic model.

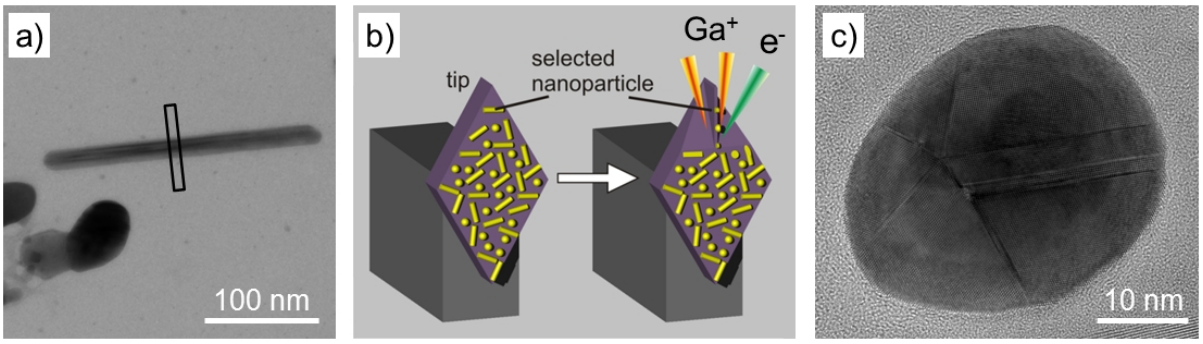

Fig. 3: FIB technique for site and orientation specific sectioning of anisotropic NP [5]. a) TEM image of Ag nanorod with desired cross section indicated by black rectangle. b) Shadow-FIB geometry used for cross-sectioning without protection layer. c) HRTEM image of nanorod cross section showing the characteristic five-fold twin structure.