Z-Contrast Electron Tomography of Embedded Nanocrystals

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OUTLINE

Applications based on well organised nanocrystals embedded in crystalline matrices are the target in different new fields of nanoscience (e.g. [1]). The nanocrystals have to be characterized close to the atomic level to understand and modify their:

- formation process,
- small-size properties,
- size and shape dependent properties [1, 2].

To calculate properties of new nanoobjects correctly, 3D-information on size and shape is essential [2].

As precipitates usually differ from the matrix by elemental content, Z-contrast tomography is well suited. Thanks to the principle of reciprocity, Z-contrast tomography already successfully realized in a STEM (HAADF-STEM-Tomography [3], [4]) should be obtainable in a conventional TEM, and should give, in principle, the same resolution. As conventional TEMs are still wider spread than FEG-TEM/STEM machines, a Z-contrast tomography technique applicable in a conventional TEM is very desirable.

Here we report on:

- the test and application of High Angle Centered Dark Field (HACDF) [5] Electron Tomography and on the comparison to HAADF-STEM-Tomography. As example we use ErSi2 nanocrystals embedded in SiC. (For application to catalyst please see our poster MS2#19)
- the new insight into the nanocrystal formation process of ErSi2 nanocrystals embedded in SiC obtained from electron tomography and 3D-reconstruction compared to 2D–imaging [6, 7].

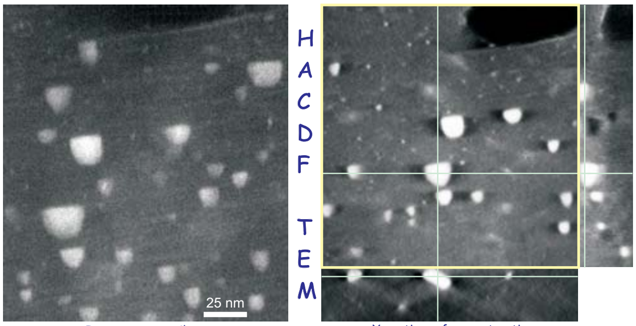
1. E. L. Wolf, Nanophysics and Nanotechnology An Introduction to Modern Concepts in Nanoscience Wiley-Vch 2004
2. Bechstedt, F., Fissel, A, Furthmüller, J. U. Kaiser, H.-Ch. Weissker, W. Wesch, Quantum structures in SiC, Appl. Surf. Science 212-213 (2003) 820-825
3. P.A. Midgley, M. Weyland, 3D electron microscopy in the physical sciences: the development of Z-contrast and EFTEM tomography, Ultramicroscopy 96 (2003) 413–431
4. C. Kübel et al., Microscopy and Microanalysis, 2005, 11(5), in print
5. U. Kaiser, A Chuvilin, Enhanced compositional contrast in imaging of nanoprecipitates buried in a defective crystal using a conventional TEM, Microscopy and Microanalysis (2003), 9(1), 36-41
6. U. Kaiser, D. A. Muller, J. L. Grazul, A. Chuvilin, M. Kawasaki, From atoms to embedded nanocrystals: Direct observation of defect mediated cluster formation, Nature Materials, I (2002) 102-105
7. U. Kaiser, J. Biskupek, K. Gärtner, Faulted GeSi and Si nanocrystals buried in hexagonal SiC Phil. Mag. Lett, (2003) 83, 4, 253-263

HACDF-Method

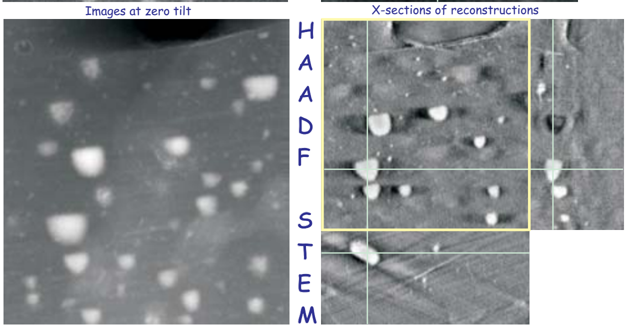
Within the centred objective aperture thermal diffuse scattered electron are collected at the optical axis of the TEM (imaging conditions are the same as for HRTEM) [5].

Comparison of HACDF-TEM and HAADF-STEM Tomography

example: $ErSi_2$ nanocrystals embedded in 4H-SiC created after high dose and high temperature Er ion implantation and high temperature annealing
Ch. Schubert, U. Kaiser, A. Hedler, W. Wesch, T. Gorelik, U. Glatzel, J. Kräußlich, B. Wunderlich, G. Heß, K. Goetz, Nanocrystal formation in SiC by Ge ion implantation and subsequent thermal annealing, Journal of Applied Physics 91/3 (2002) 1520-1524

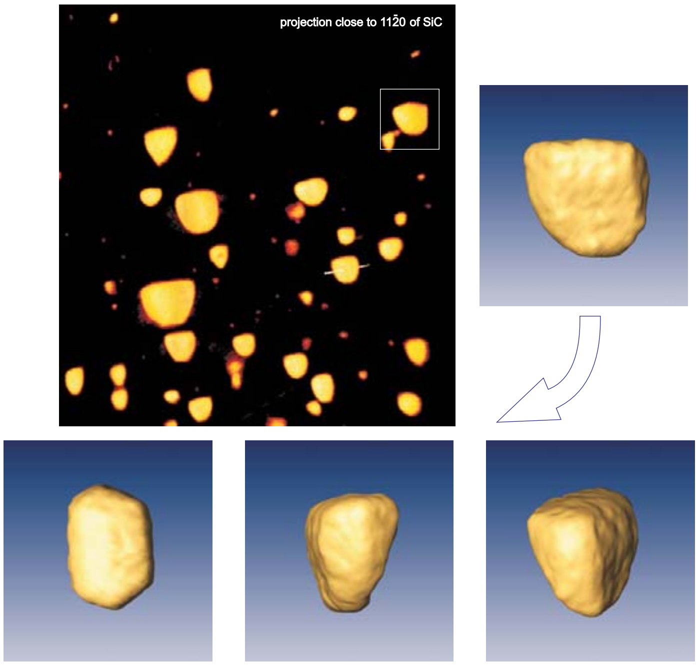


Images at zero tilt — X-sections of reconstructions

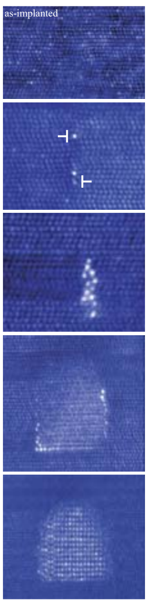


As can be seen: Reconstructed nanocrystals obtained by Z-Contrast TEM and -STEM Electron Tomography give about the same result. The methods do not differ significantly in resolution.

HACDF-TEM Tomography visualised in 3D.
The different faces of 20 nm crystal are clearly revealed.



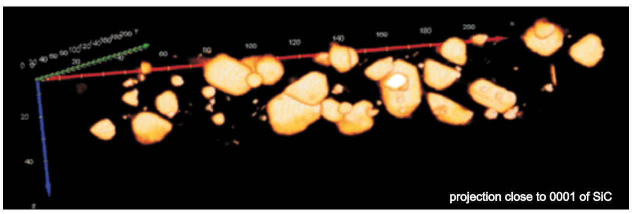
Z-Contrast Electron Tomography: New insight into the nanocrystal formation process.



What we knew from 2D-HAADF-STEM inspection of the sample (see the left row of figures)

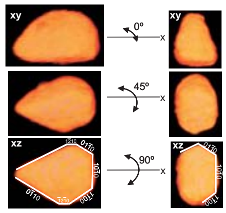
1. ErSi2 nanocrystals are of hill-like shape; no relationship between nanocrystal faces and matrix faces were revealed.
2. The chemical reaction between Er (foreign atoms) and Si (of the matrix) was suggested to be the origin of the hill-like shape of the ErSi2 nanocrystals.
3. ErSi2 NCs form from a single foreign atom column, nucleated at a matrix defect (interstitial loop) over a state of 2D-Er-defects. However, the role of the interstitial loops in the diffusion mechanism is not clear so far.

U. Kaiser, D. A. Muller, J. L. Grazul, A. Chuvilin and M. Kawasaki: From atoms to embedded nanocrystals: Direct observation of defect mediated cluster formation Nature Materials, I (2002) 102-105

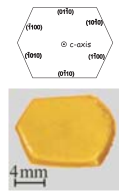


What we learn after Z-Contrast Electron Tomography inspection?

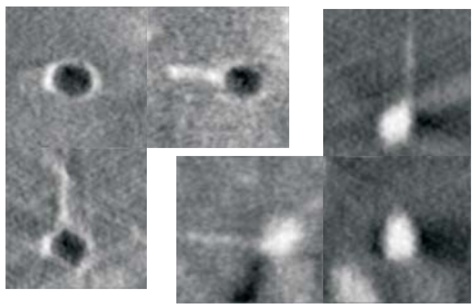
1. The nanocrystals are well facetted in 11-20 projection (not hill-like shaped!!)
2. In 0001 projection the nanocrystal show very pronounced facets. These facets are those of the basal 0001 SiC plane (see the SiC crystal). We conclude that it is the SiC matrix which determines the facets of the NC.
3. Bright stripes could be imaged, which originate from cores of dislocations containing Er atoms. These stripes are connected to the nanocrystals, indicating that dislocation cores serve as preferable diffusion paths for foreign atoms.



Two crystals, reconstructed from electron micrographs



Optical photograph of a bulk SiC crystal



Stripes attached to nanovoid and nanocrystal - X-sections of tomographic reconstruction.