Transmission Electron Microscopy II – High Resolution

Nicola Pinna

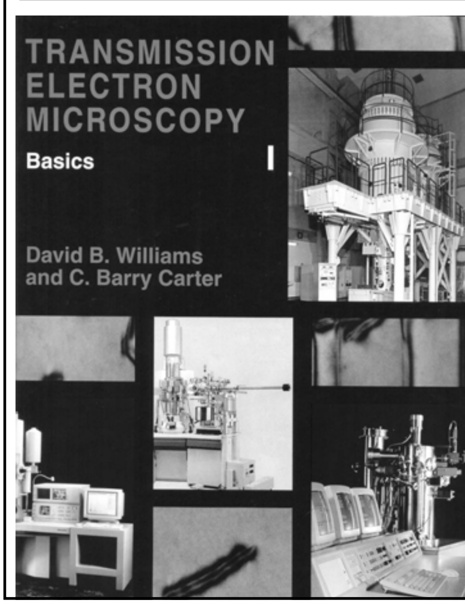
Department of Chemistry, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal.

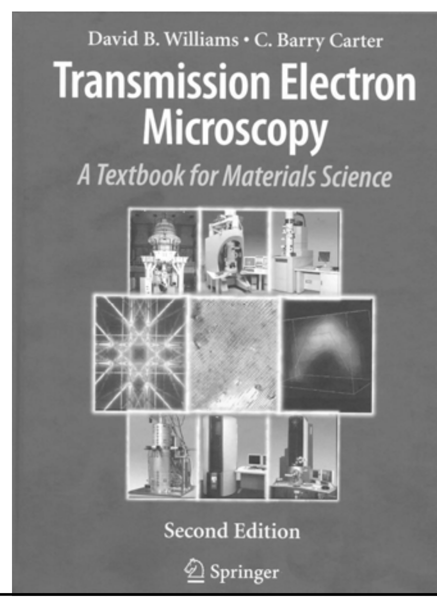
School of Chemical and Biological Engineering, College of Engineering, Seoul National University (SNU), Seoul 151-744, Korea

E-mail: pinna@ua.pt - pinna@snu.ac.kr

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

Literature





Phase-Contrast Images

High resolution transmission electron microscopy (HRTEM) is one of the most powerful tools used for the characterization of nanomaterials. The most important contrast mechanism for high resolution electron microscopy is phase-contrast

If the specimen is suitably thin for HRTEM, i.e. less than about 50 nm, the interaction of the electron beam with the inner potential of the specimen predominantly causes phase shifts of parts of the electron wave front

A phase contrast image requires the selection of more than one beam (direct + diffracted)

Two beams can interfere to give an image with a periodicity related to $|\Delta \mathbf{g}|^{-1}$. Since one beam is the direct beam, $|\Delta \mathbf{g}|^{-1}$ is just d the interplanar spacing corresponding to ***g***

If the beam is aligned parallel to a low-index zone axis, fringes running in different direction are observed. These fringes correspond to an array of spots in the diffraction pattern

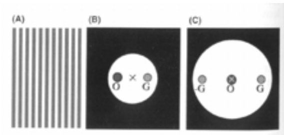


FIGURE 23.1. (A) Schematic tilted-beam 111 lattice fringes in Si formed using the O and G beams symmetrically displaced relative to the optic axis; **g** is normal to the fringes. (B) Ideal diffraction geometry to produce tilted-beam fringes. (C) On-axis, three-beam geometry.

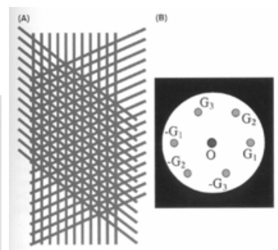


FIGURE 23.2. (A) Schematic many-beam image showing crossing lattice fringes and (B) the diffraction pattern.

The trouble is that the fringes look so like atomic planes that we can be easily misled into thinking that they are atomic planes.

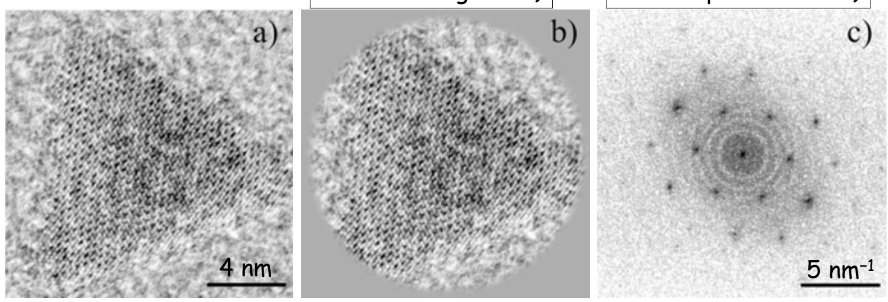
Lattice fringes are not direct images of the structure, but just give you information on lattice spacing and orientation

The image interpretation in HRTEM is not straight forward. This is because in addition to the interaction of the electron beam with the specimen, also the effect of the imaging process by imperfect electron lenses has to be considered. The way how the microscope transfers waves with different relative phase shifts down through the column is defined by the so called contrast transfer function.

It depends on the performance of the objective lens (spherical aberration), the acceleration voltage and the focus conditions. Further, chromatic aberrations, focal and energy spread of the beam and instabilities in the high tension and objective lens current play a role in the contrast formation.
Assistance in the interpretation of HRTEM images is provided by image processing and image simulation.

Extracting lattice distances

Masked Image of a) Power Spectrum of b)



Power Spectrum can be obtained by calculating the discrete Fourier transform of the HRTEM image and corresponds to a "computer-generated DP"

$$d_{hlk} = \frac{N_{pix-image} * P_{size}}{N_{pix}}$$

$N_{pix-image}$: N° of pixels along the quadratic frame (128, 256, 512 ...) of the image

P_{size} : Pixel size in the HR image

N_{pix} : N° of pixel between the origin and the reflection hkl studied

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos
SEOUL NATIONAL UNIVERSITY

Phase Determination

The PS always show pairs of reflections hkl and h k l which are lying diametrical opposite around the origin. The plane distances and angles extracted from the PS have to be compared to plane spacings and angles of known structures.

This approach leads to a clear identification of a particle if it is crystallized in a known structure and does not present complicated defects.

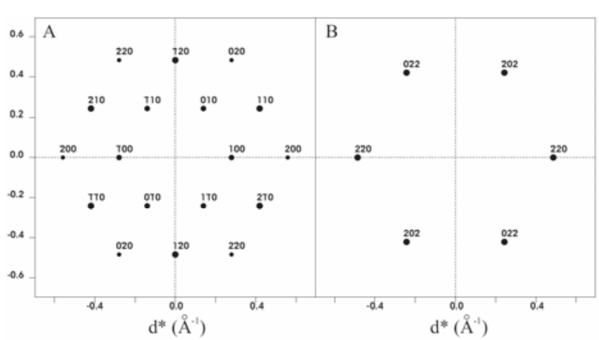
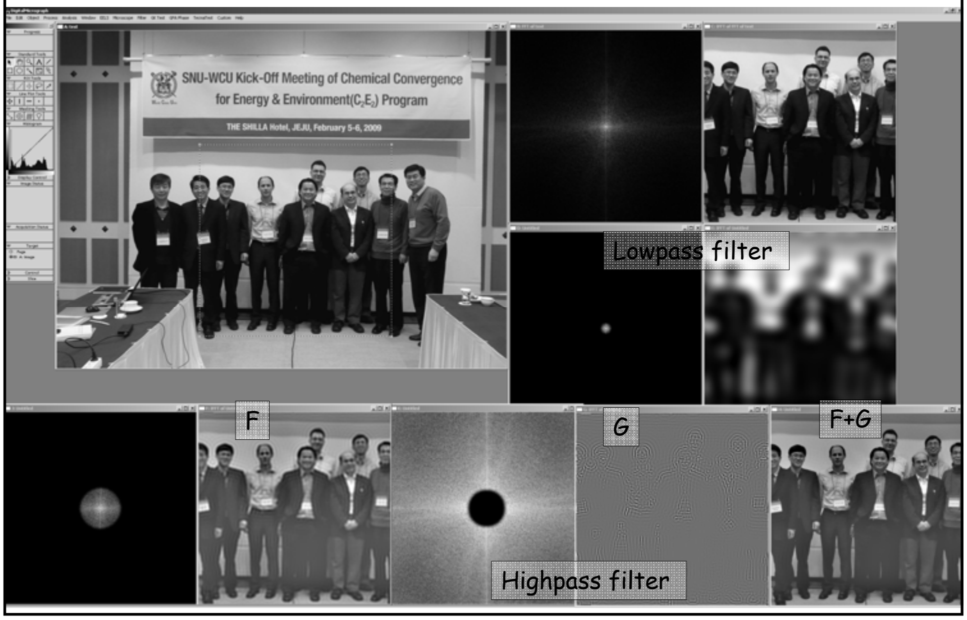


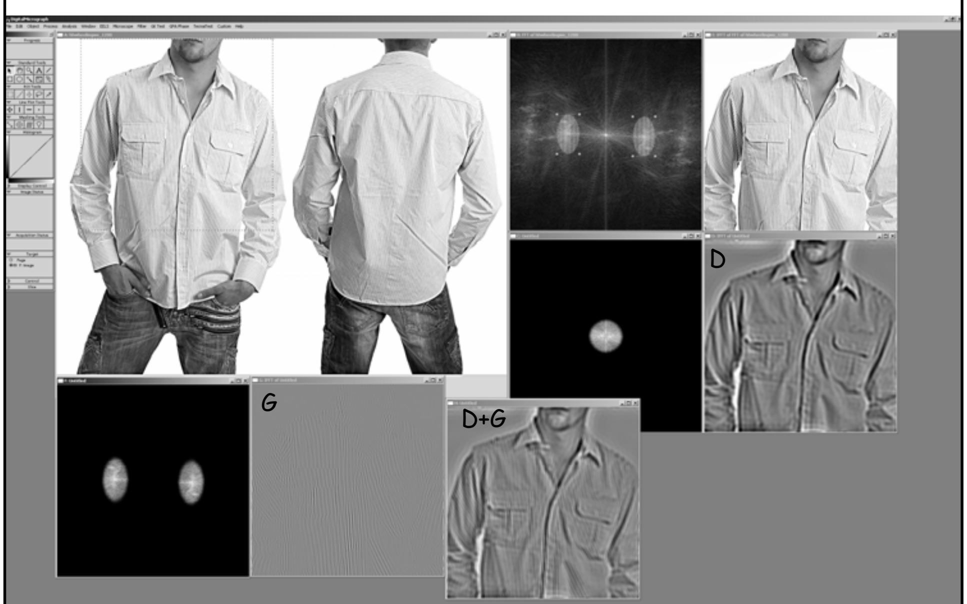
Figure 9: single crystal diffraction calculated for the CdS wurtzite structure aligned along the [001] axis (A) and the CdS zinc blende structure aligned along the [111] axis (B)

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

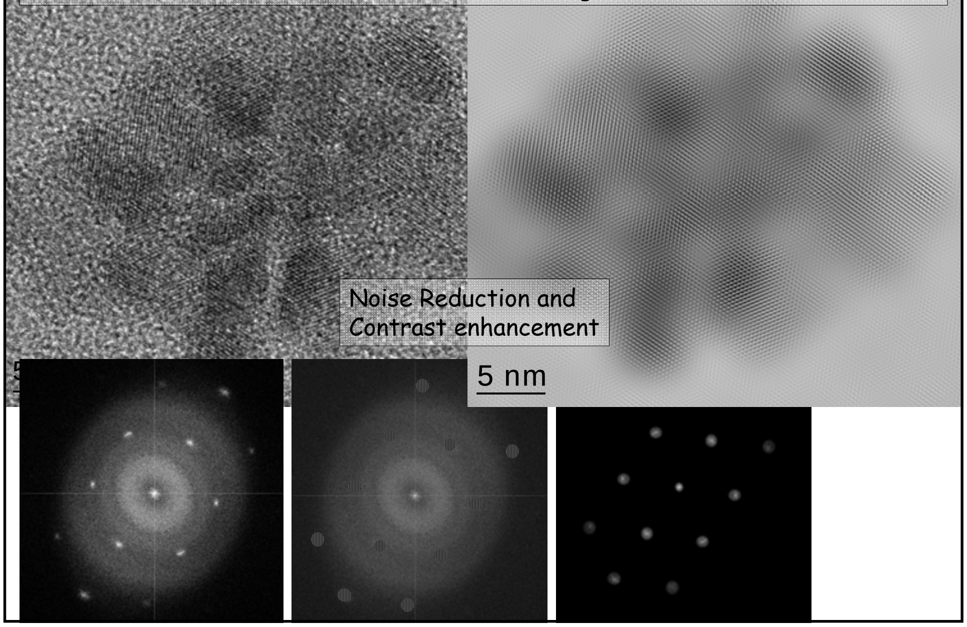
Image Processing



universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

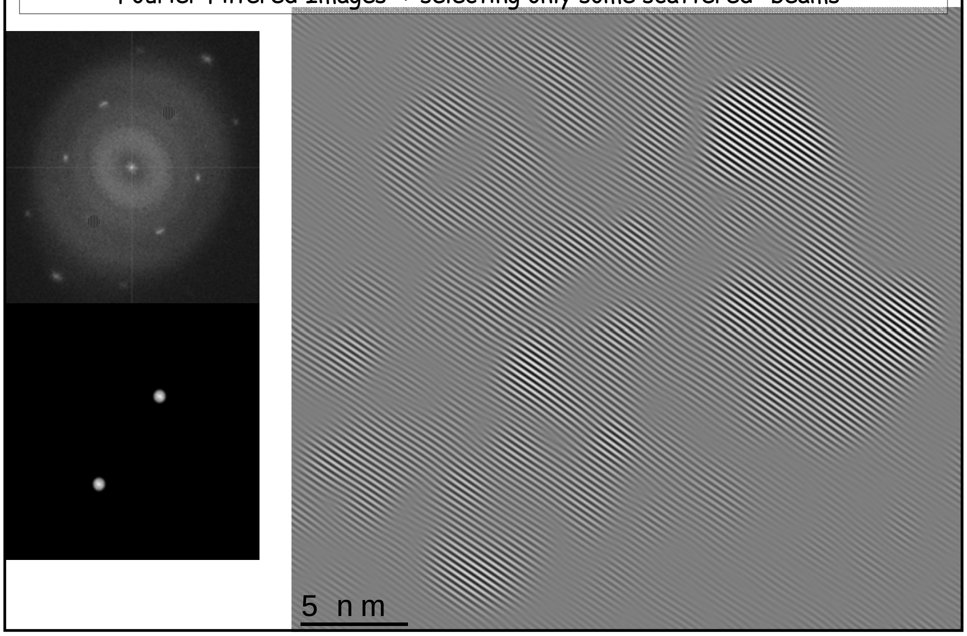


Fourier Filtered Images

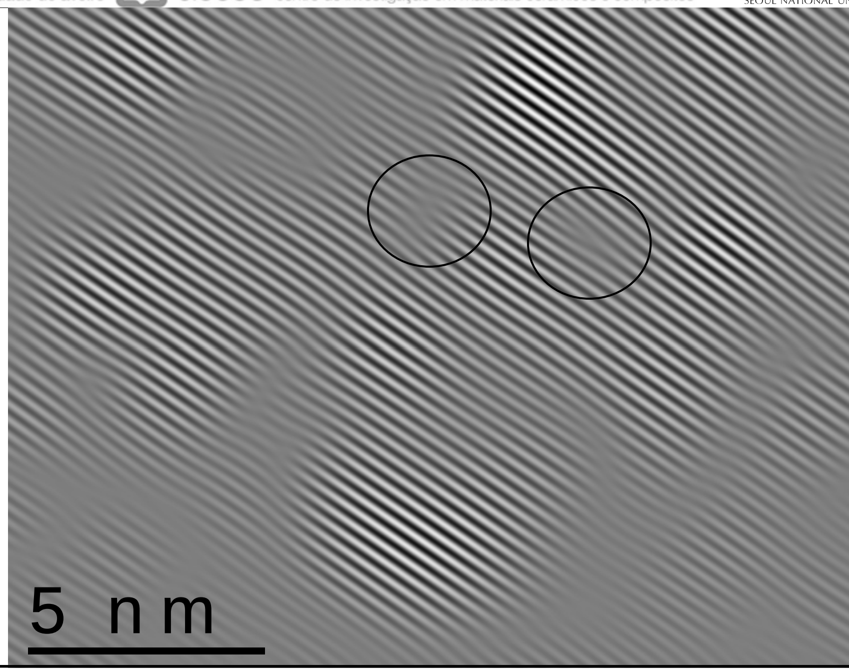


universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

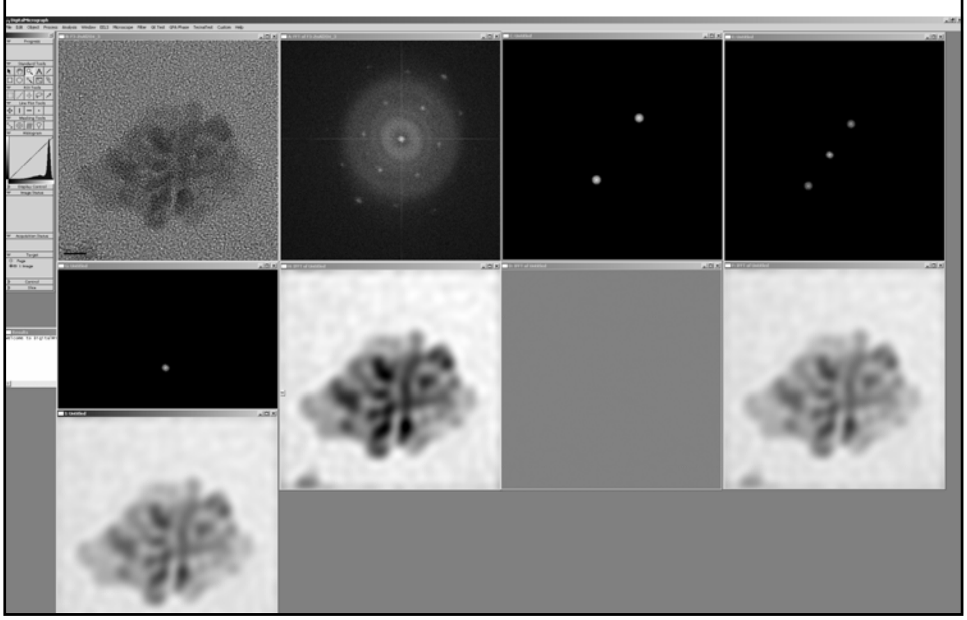
Fourier Filtered Images -> selecting only some scattered “beams”



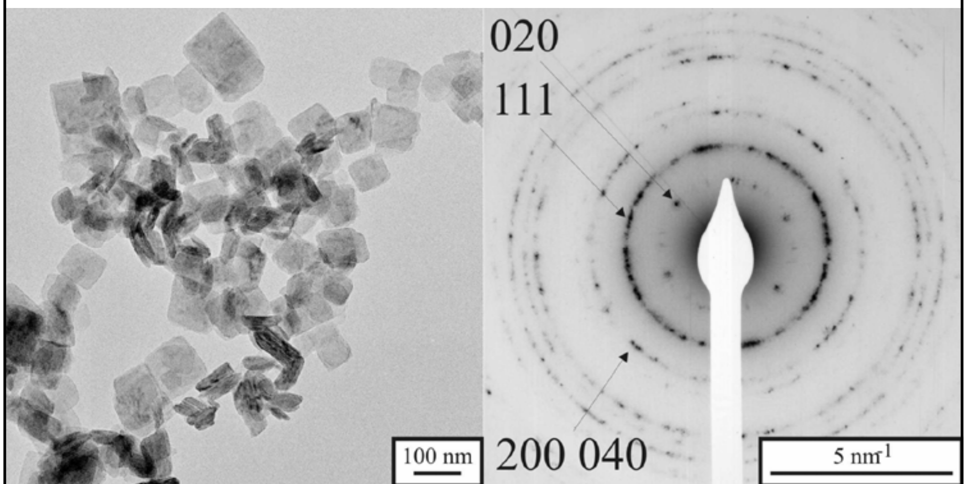
universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY



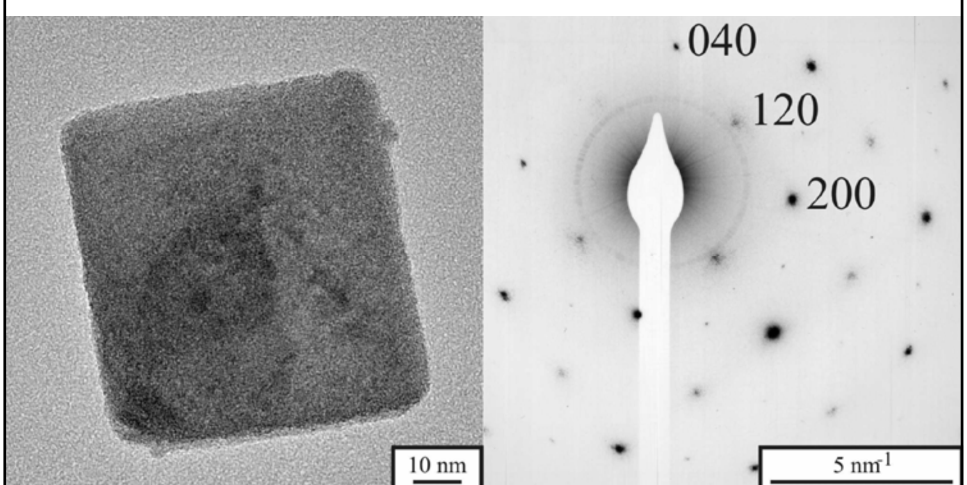
universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

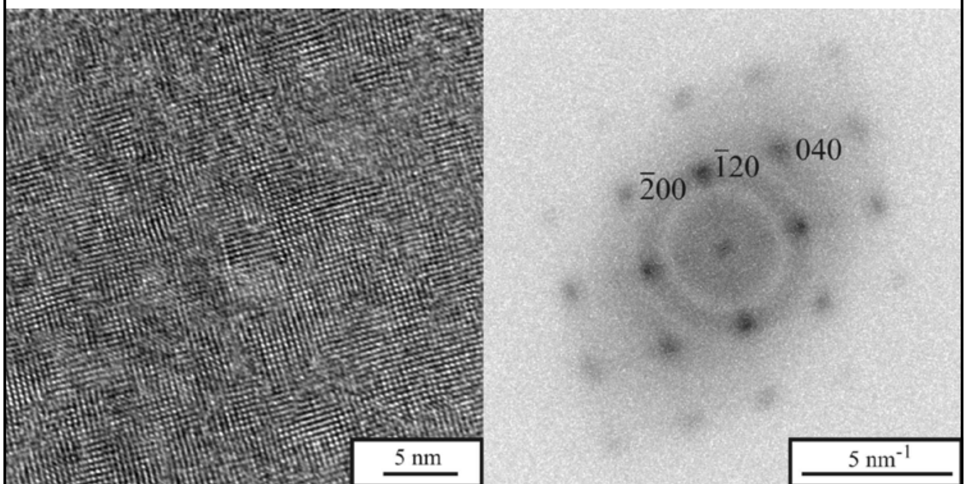


Tungstite nanoplatelets

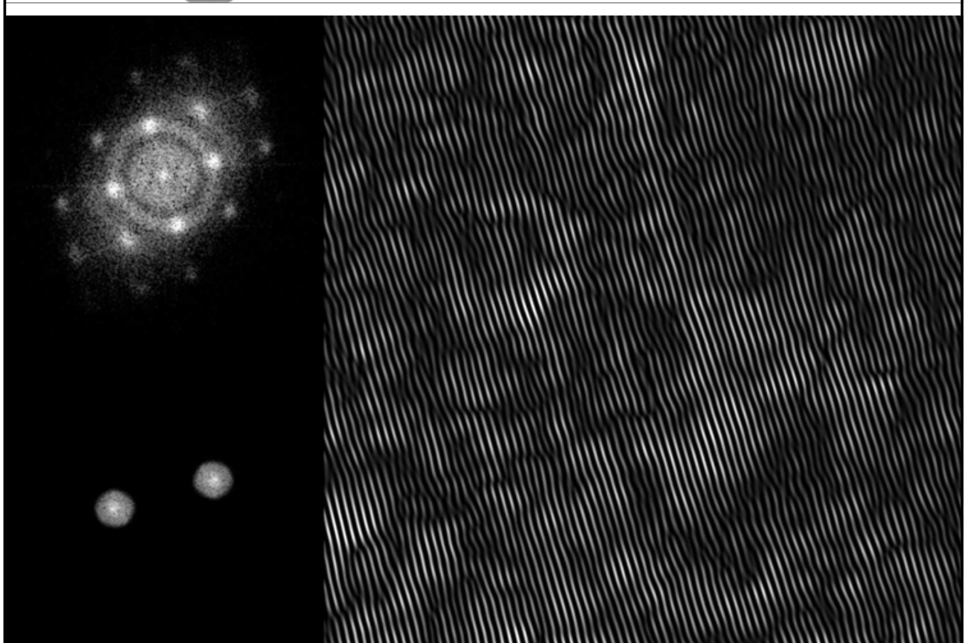


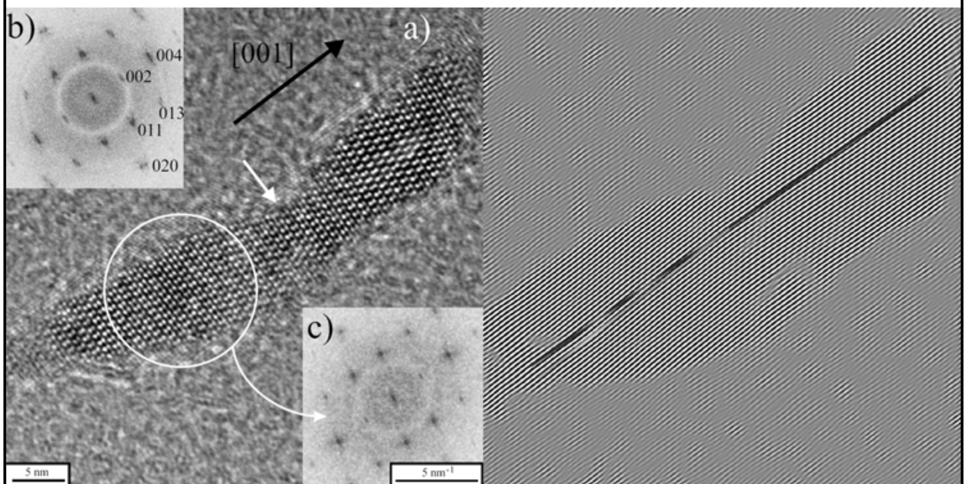
universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY





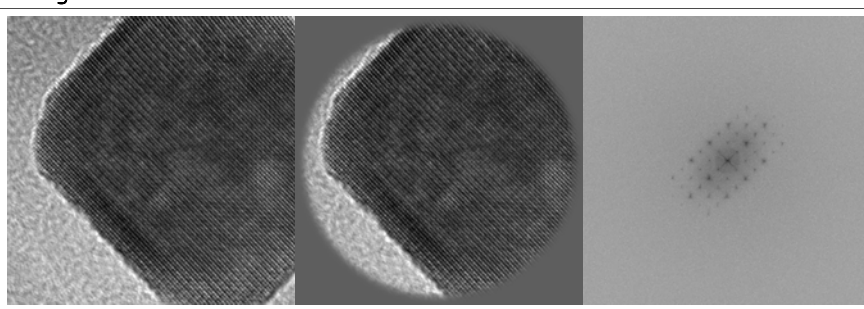
universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY





Exercise (In_2O_3 nanocubes)

Frame size 1024x1024 pixels^2 – Pixel size=0.0226 nm
-> image size 23.14 x 23.14 nm^2

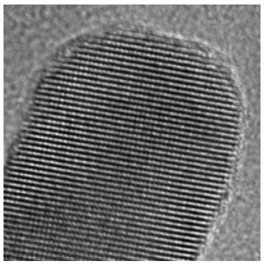


1 - Try to measure the d_{hkl} using scionimage software from the power spectrum with the macro distributed.

2 – Compare the d_{hkl} measured from the power spectrum to the ones of the In_2O_3 cubic structure (JCPDS card N° 6-416)

http://www.scioncorp.com/pages/download_now.asp

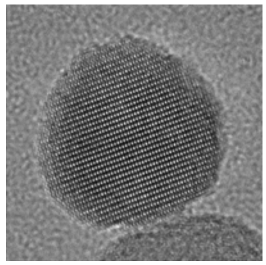
Additional exercises



Ta_2O_5 768x768 pixels^2

Pixel size=0.0226 nm

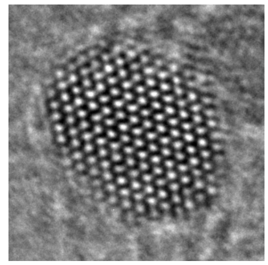
Adv. Mater. 2004, 16, 2196



Fe_3O_4 1024x1024 pixels^2

Pixel size=0.0226 nm

Chem. Mater. 2005, 17, 3044



HfO_2 288x288 pixels^2

Pixel size=0.0226 nm

Adv. Mater. 2004, 16, 2196

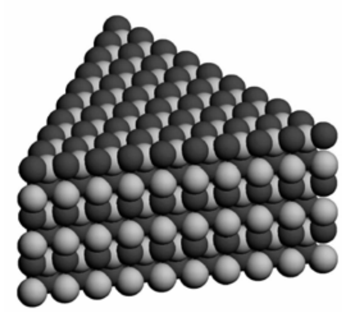
universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

HRTEM Simulations

Computer simulation of the HRTEM images on the basis of the structure of model particles with the multislice technique:

1. The construction of one or more atomic models of the nanocrystals
2. The calculation of the HRTEM image of these models
3. The calculation of the PS of the calculated HRTEM image
4. The comparison of the HRTEM images and the PS calculated with the data obtained from the experimental HRTEM

Example: CdS wurtzite



Electrons are assumed to scatter only in a forward direction with small diffraction angles. With this approximation the crystal can be divided in sub-slices with a thickness z perpendicular to the incident beam.

1. The crystal is divided in slices perpendicular to the electron beam

2. The electrostatic potential V (x, y) with in-plane coordinates x,y of the sliced crystal or supercell is projected for each slice of the included atoms onto its exit surface

3. On the basis of V_P (x, y) the amplitude of the electron wave function is calculated

4. Calculate the propagation of the electron wave through all the slices

J.W. Cowley, A.F. Moodie, Acta Cryst. 10, 609, 1957

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

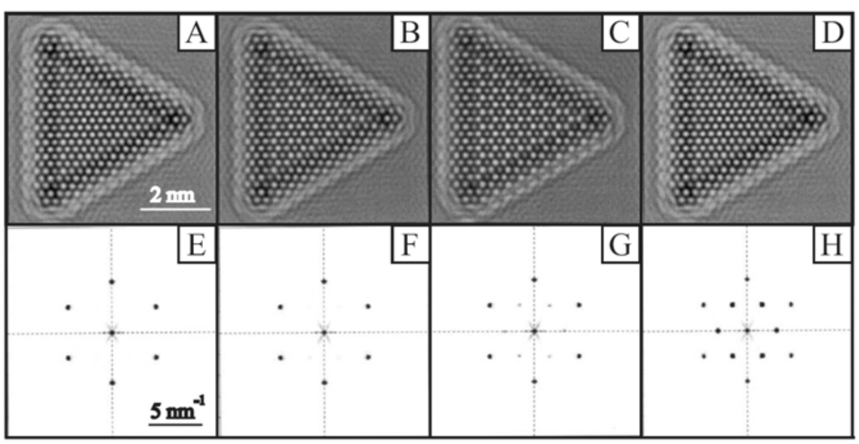


Figure 11: Calculated HRTEM image of CdS triangular shaped nanocrystal of four different structures: (A) zinc blende; (B) zinc blende with incomplete stacking sequence; (C) wurtzite with 1 stacking fault; (D) wurtzite. (E-H) PS of these images, respectively. Adapted with permission from *Langmuir* **2001**, *17*, 7892

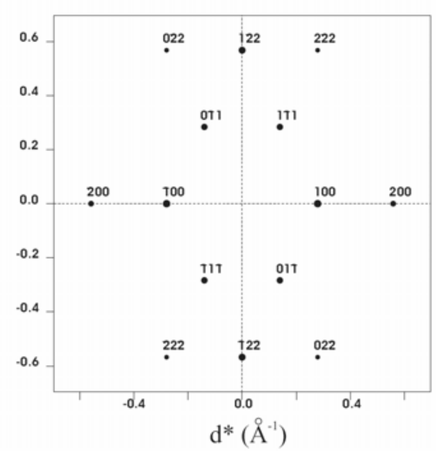


Figure 12: single crystal diffraction calculated for the CdS wurtzite structure aligned along the [011] axis

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos
SEOUL NATIONAL UNIVERSITY

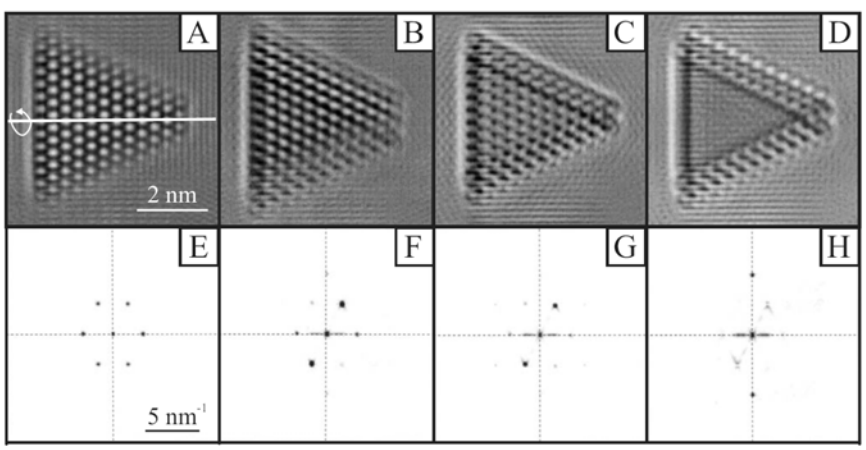


Figure 13: Calculated HRTEM image of CdS triangular shaped nanocrystal of four different structures tilted of 31.6°: (A) wurtzite; (B) wurtzite with 1 stacking fault; (C) zinc blende with incomplete stacking sequence; (D) zinc blende. (E-H) PS of these images, respectively. The tilt axes are reportend on the figure (white line)

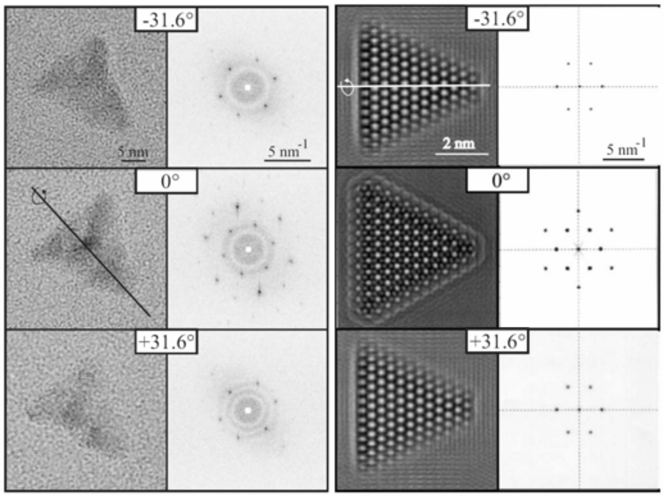


Figure 14: Left: Experimental HRTEM images of CdS triangular shaped nanocrystal tilted by -31.6°, 0°, and +31.6° and the respective PS. Right: Calculated HRTEM images of CdS triangular shaped nanocrystal tilted by -31.6°, 0°, and +31.6° and their respective PS.
The tilt axes are reportend on the figures (black and white line respectively). Reproduced with permission from *Langmuir* **2001**, *17*, 7892

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

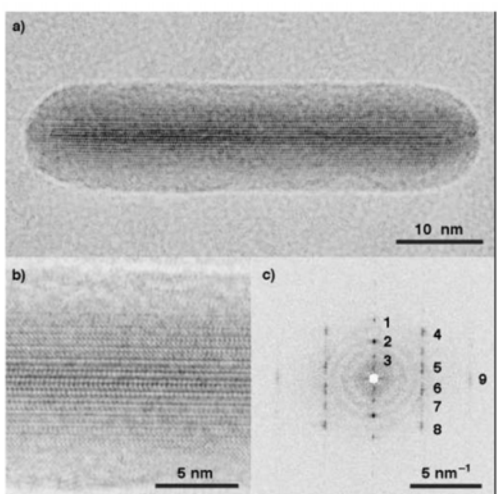


Figure 27: High resolution images from a particle showing a) a truncated decahedron structure, b) the central section of the rod, and c) its power spectrum. Reproduced with permission from *Chem. Phys. Chem.* **2000**, *1*, 140

PHYSICAL REVIEW B VOLUME 61, NUMBER 7 15 FEBRUARY 2000-I

Structural investigations of copper nanorods by high-resolution TEM

I. Lisiecki and A. Filankembo
Université Paris VI, U.P.M.C. Laboratoire SRSI, Boite Postal 52, 4 Place Jussieu, F-75005 Paris, France and CEA-Saclay, DSM-DRECAN-SCM, F-91191, Gif-sur-Yvette, France

H. Sack-Kongehl and K. Weiss
Fritz-Haber-Institut der MPG, Abteilung AC, Faradayweg 4-6, D14195 Berlin, Germany

M.-P. Pileni
Université Paris VI, U.P.M.C. Laboratoire SRSI, Boite Postal 52, 4 Place Jussieu, F-75005 Paris, France and CEA-Saclay, DSM-DRECAN-SCM, F-91191, Gif-sur-Yvette, France

J. Urban*
Fritz-Haber-Institut der MPG, Abteilung AC, Faradayweg 4-6, D14195 Berlin, Germany

(Received 1 March 1999; revised manuscript received 22 July 1999)

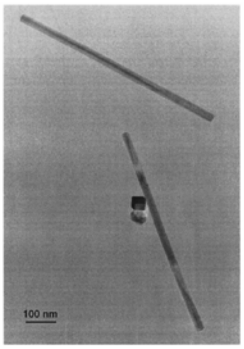


FIG. 1. Overview electron micrograph Cu rods with an electron optical magnification of 57 000×.

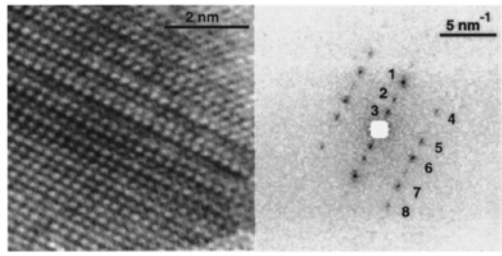


FIG. 2. Detail of a copper rod. The right image represents the PS. The reflection spots are labeled from 1 to 8 with lattice parameters: $d_1=0.211$ nm, $d_2=0.332$ nm, $d_3=0.566$ nm, $d_4=d_7=0.184$ nm, $d_5=d_6=0.252$ nm, and $d_8=0.148$ nm. The angle between planes represented by reflections 5 and 6 is 27°.

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

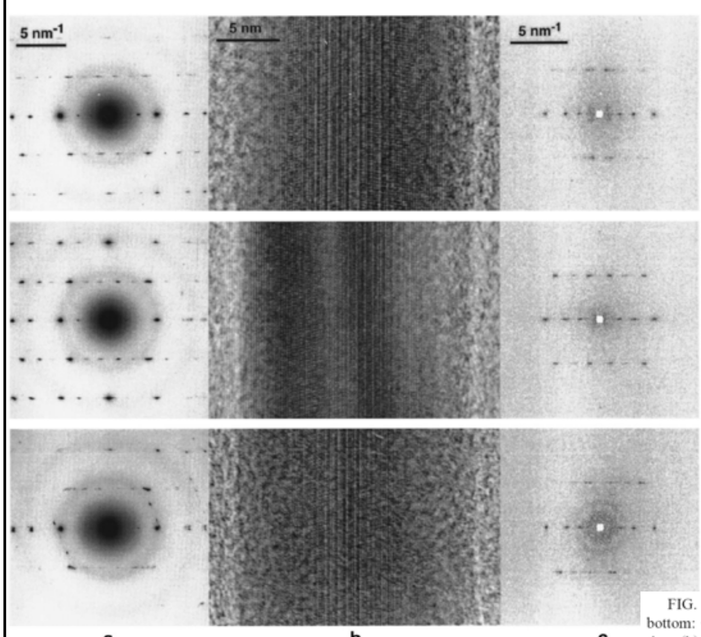


FIG. 3. Tilt series of sample 1: From top to bottom: +36°, 0°, and −36°. (a) Electron diffraction. (b) HRTEM image. (c) PS.

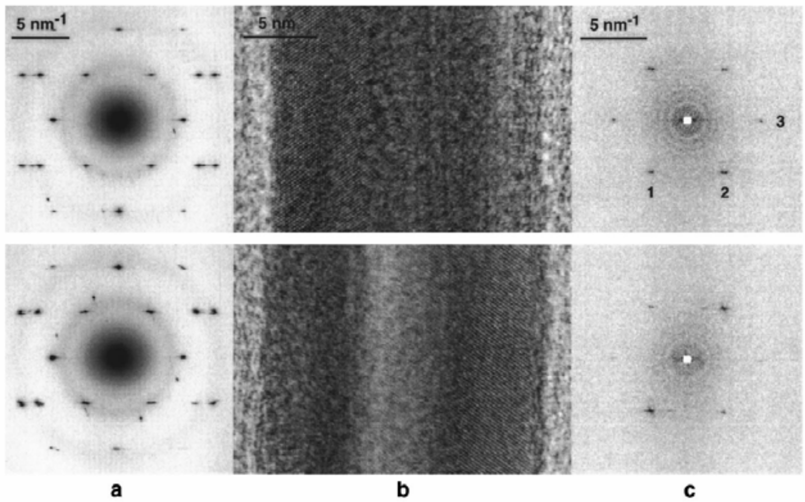


FIG. 4. Tilt series of sample 1: From top to bottom: $+18°$ and $-18°$, (a) Electron diffraction. (b) HRTEM image. (c) PS. Three pairs of reflections in the PS are labeled by 1, 2, and 3. $d_1 = 0.206$ nm, $d_2 = 0.207$ nm, and $d_3 = 0.179$ nm. The angle between d_1 and d_2 is 71.5°.

universidade de aveiro ciceco centro de investigação em materiais cerâmicos e compósitos SEOUL NATIONAL UNIVERSITY

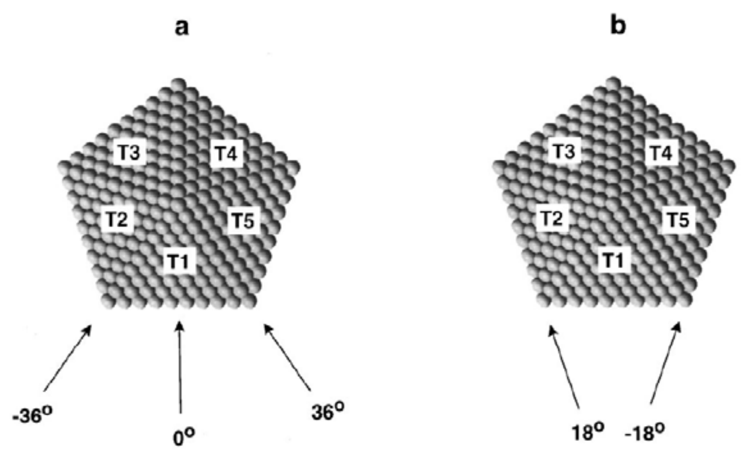


FIG. 7. Decahedral model particle viewed along the fivefold axis. The deformed subunits are labeled $T1,...,T5$. The arrows indicate the directions of the electron beam by tilting the model: (a) 0° and ±36°. (b) ±18°.

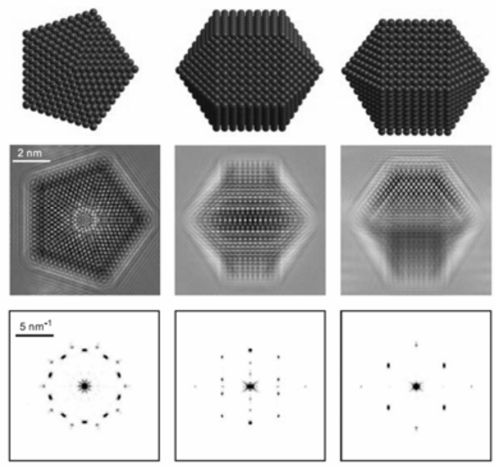


Figure 28: Models, calculated images and PS for truncated decahedral particles for three different orientations. From left to right: fivefold axis, in [001] direction and in a [1-10] directions [parallel to a (001) plane], i.e., 0° and 18°, perpendicular to the fivefold axis for the latter two. Reproduced with permission from *Phys. Rev. B* **2000**, *61*, 4968