2009 spring

Microstructural Characterization of Materials

06. 03. 2009

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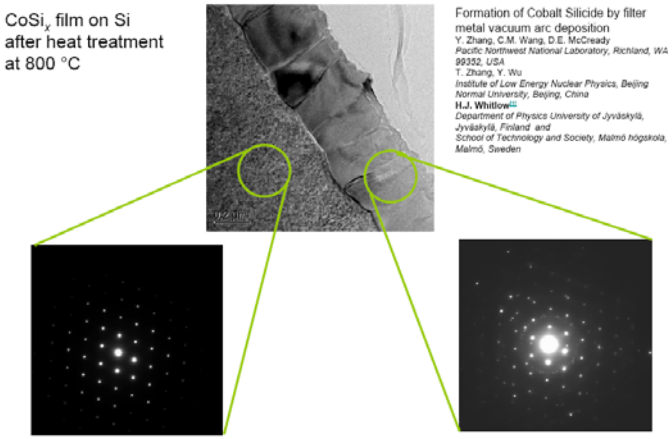
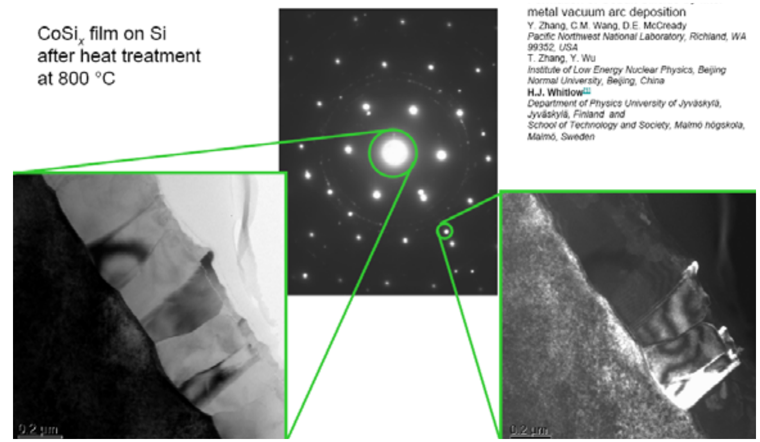
Content for previous class

Selected area diffraction ⟷ **Dark field image**





Analysis for Ring pattern and Spot pattern

kikuchi pattern

Mechanisms of image formation: contrast

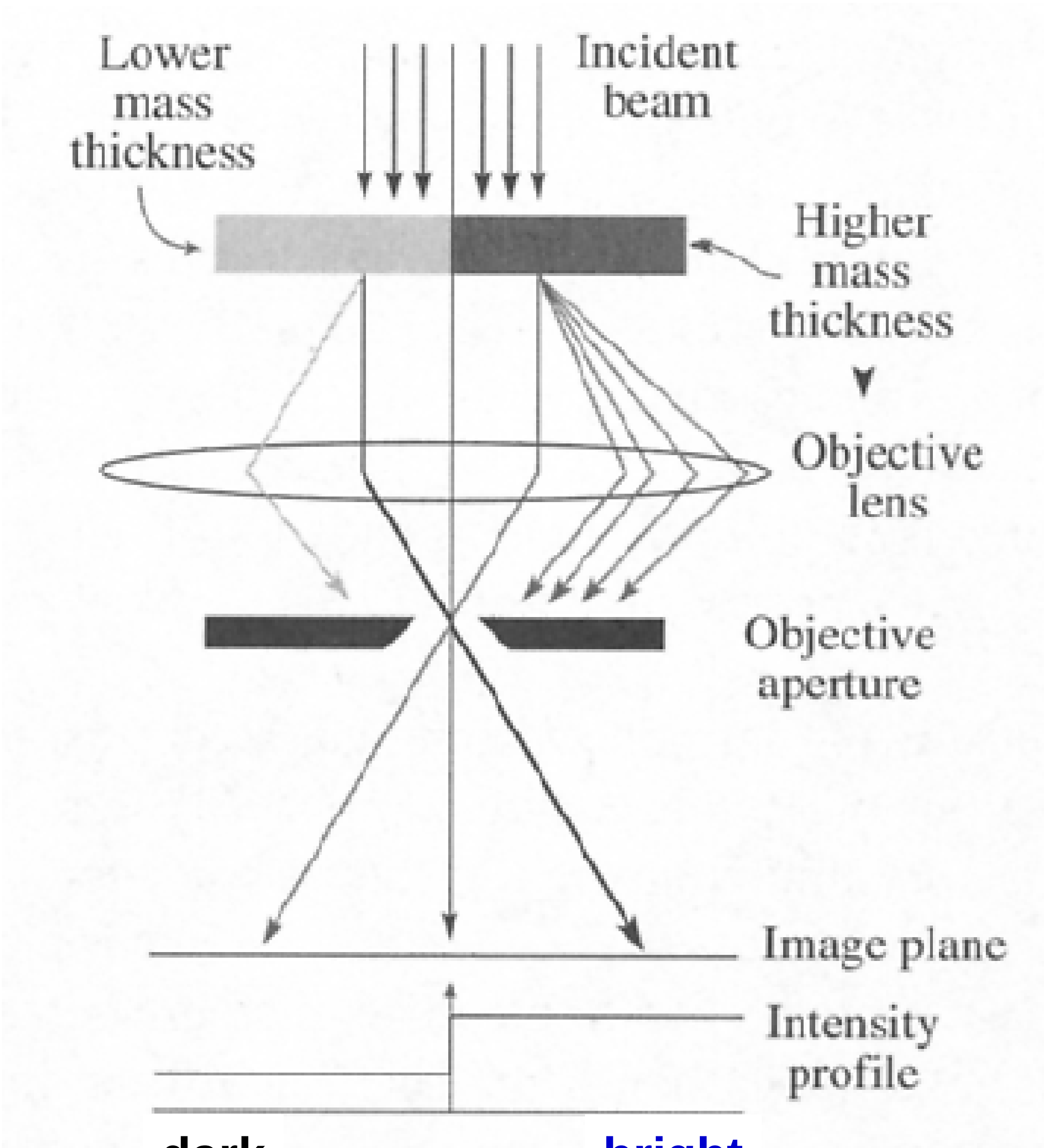
Mass-thickness contrast

Diffraction contrast
(major image formation mechanisms)

Phase contrast
(high resolution image of crystal lattice)

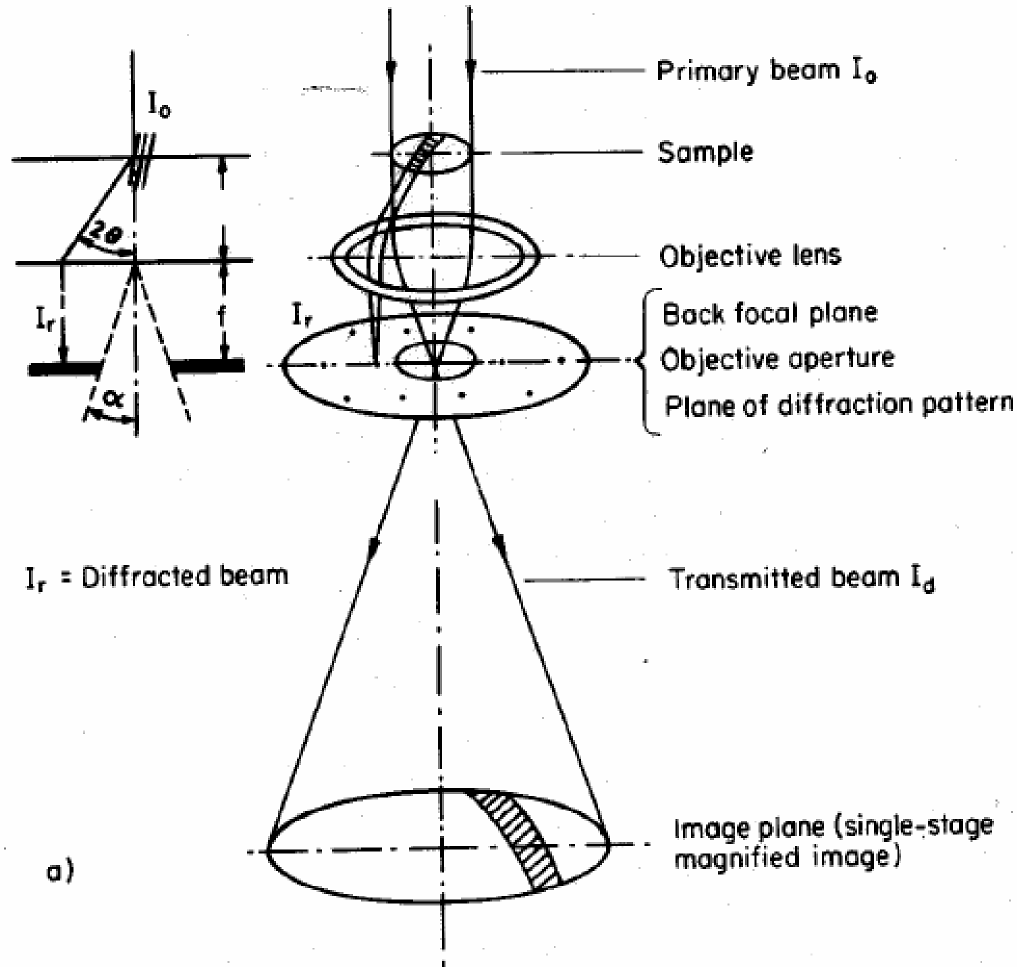
Z contrast imaging
(Dark field-STEM)

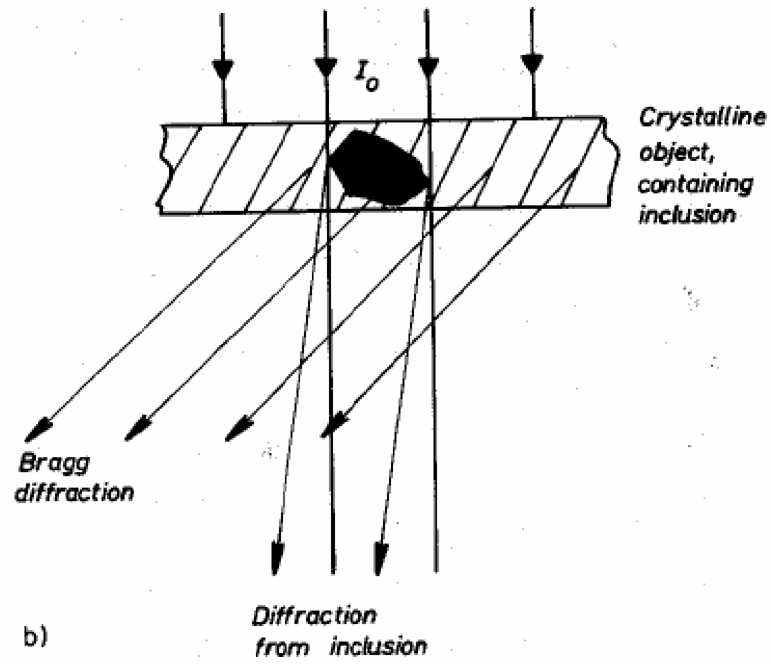
Mass-thickness contrast



dark **bright**

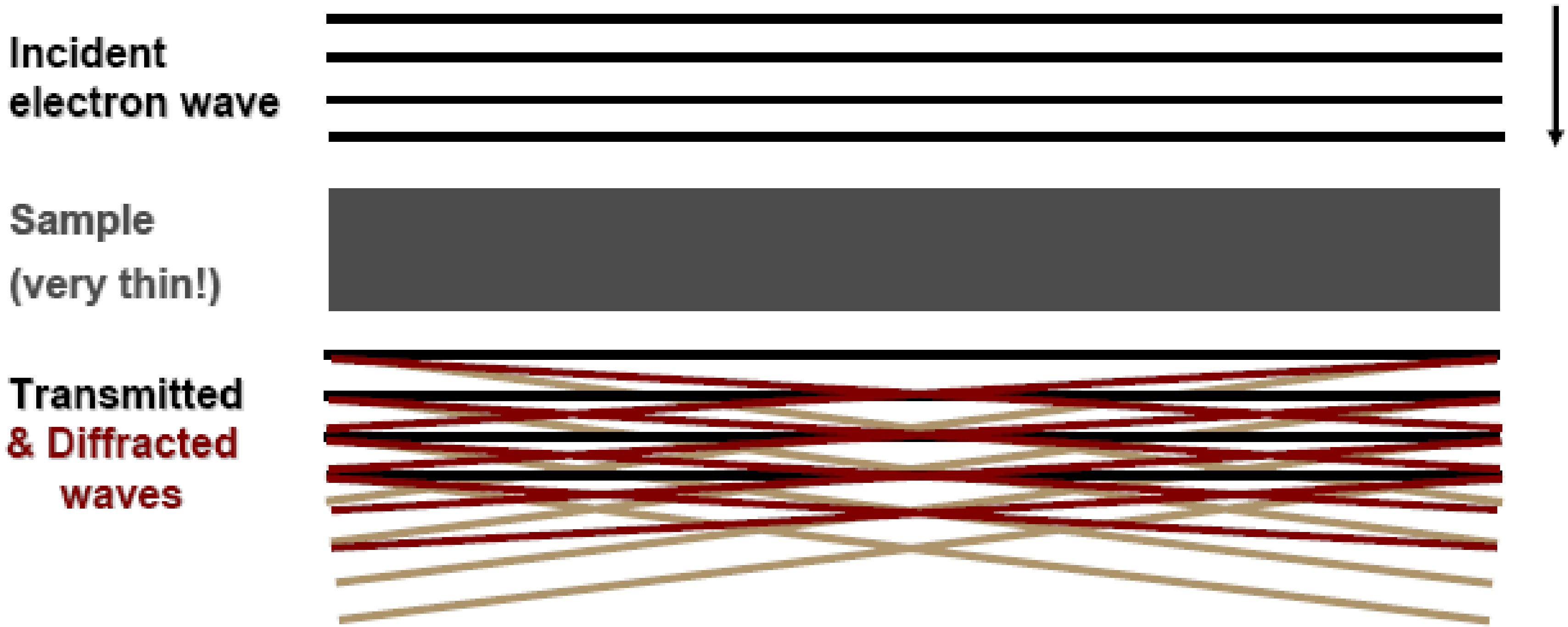
Diffraction contrast (major image formation mechanisms)





When the Intensity I_r is removed from the primary beam I_o by the Bragg reflection, the image of the respective sample area appears dark.

High-resolution EM
general idea



Transmitted & diffracted waves each have a different phase

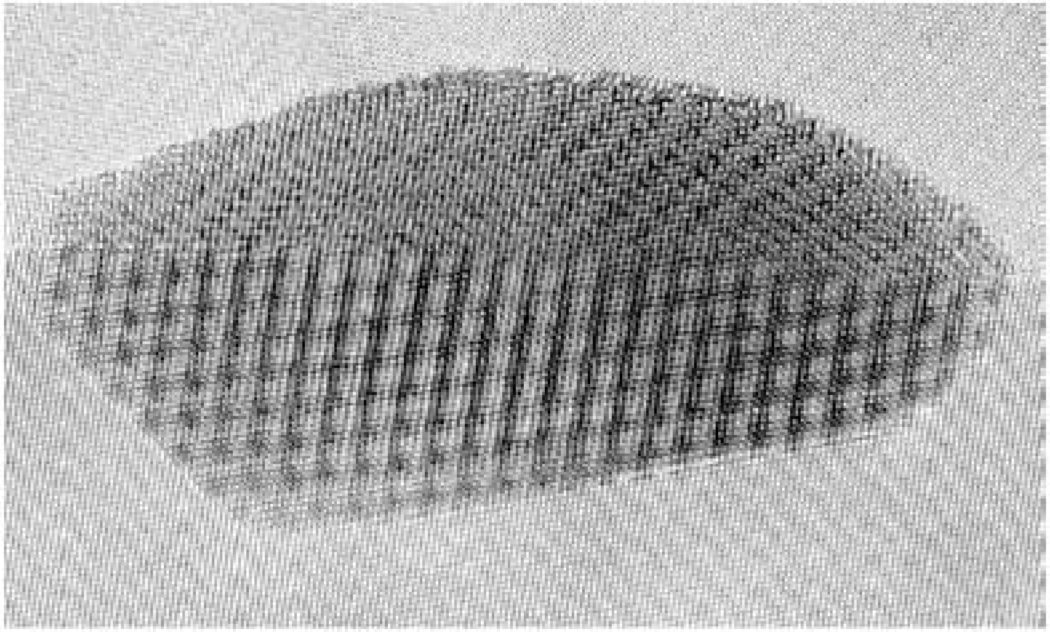
Result is an interference pattern - our 'phase contrast' or HREM image

Phase contrast

(high resolution image of crystal lattice)

Atomic column images at resolutions from 0.7Å and above

Results from interference of transmitted and diffracted electron waves



High resolution micrograph of a precipitate at a high angle grain boundary in aluminum

High-resolution imaging

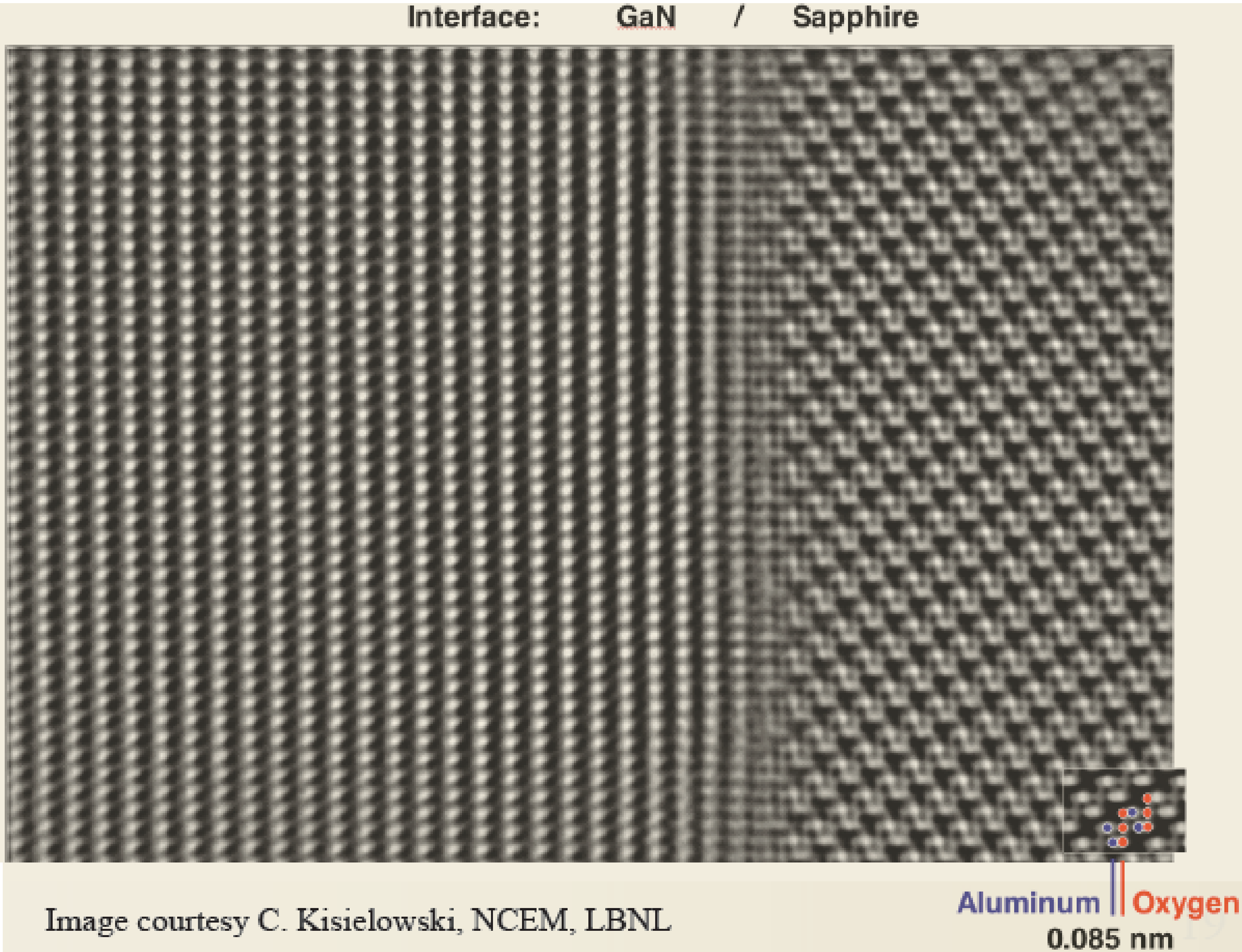
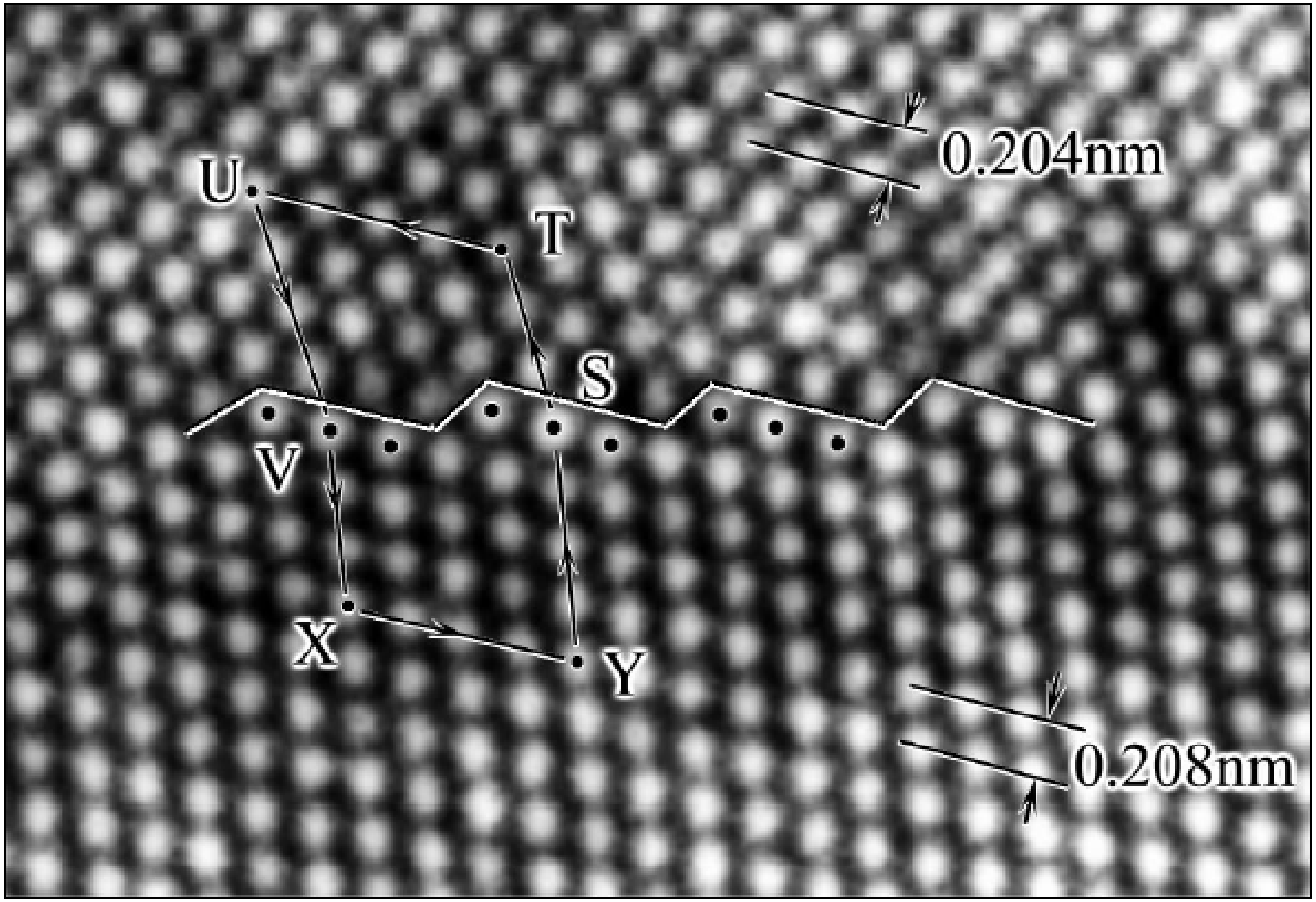


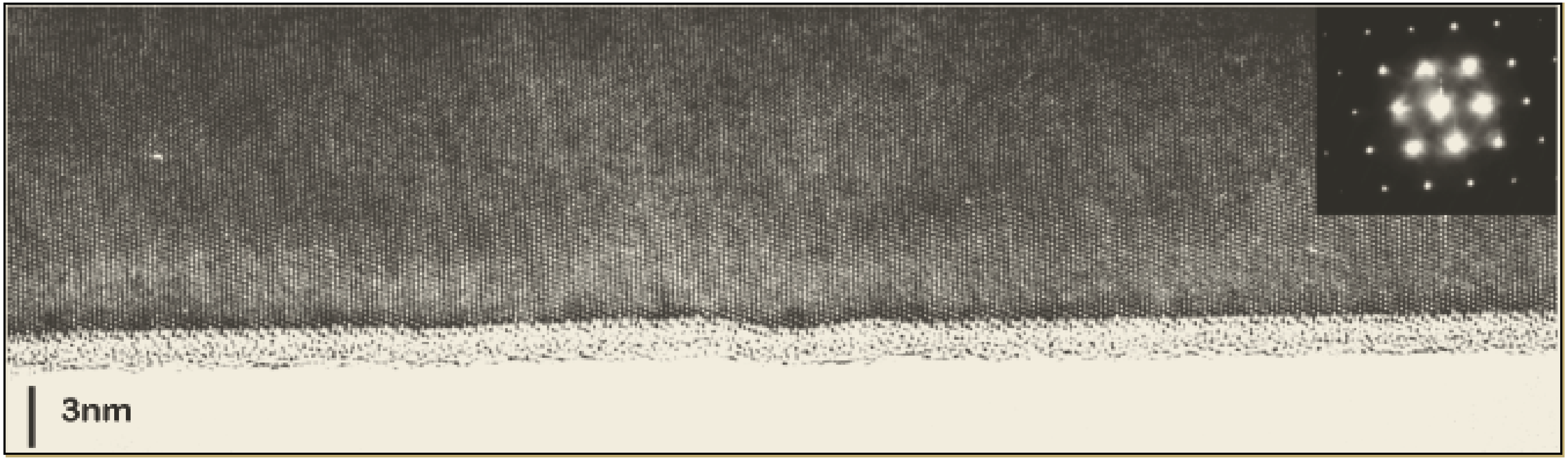
Image courtesy C. Kisielowski, NCEM, LBNL

High-Resolution TEM



Lattice parameters, grain misorientation, burgers vectors are all measurable.

High-resolution imaging



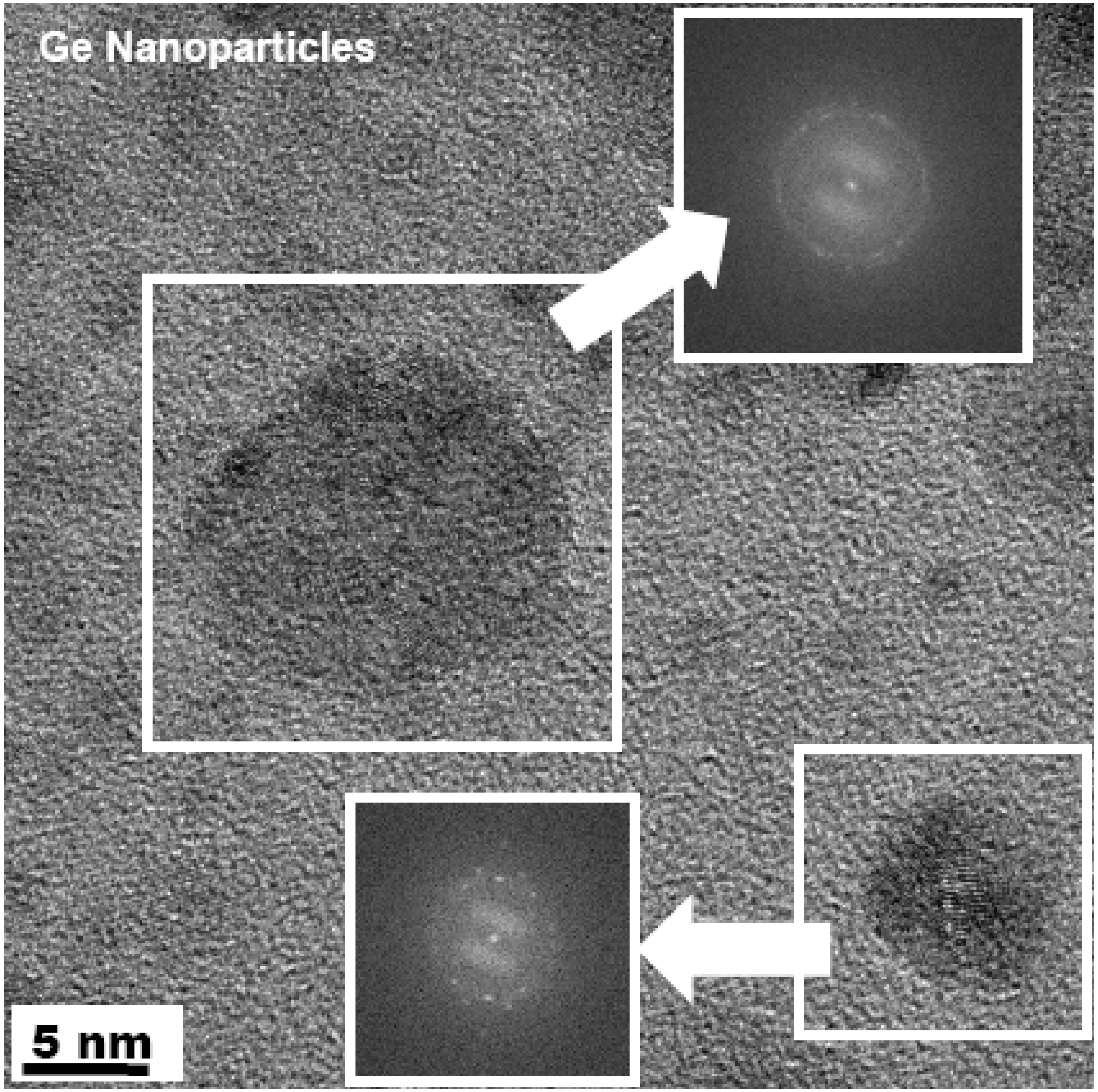
Often high-resolution imaging is used in nanoscience to show 'single crystalline' nature of nanostructures

In fact, electron diffraction is superior for this (though less visually appealing)

High-resolution imaging

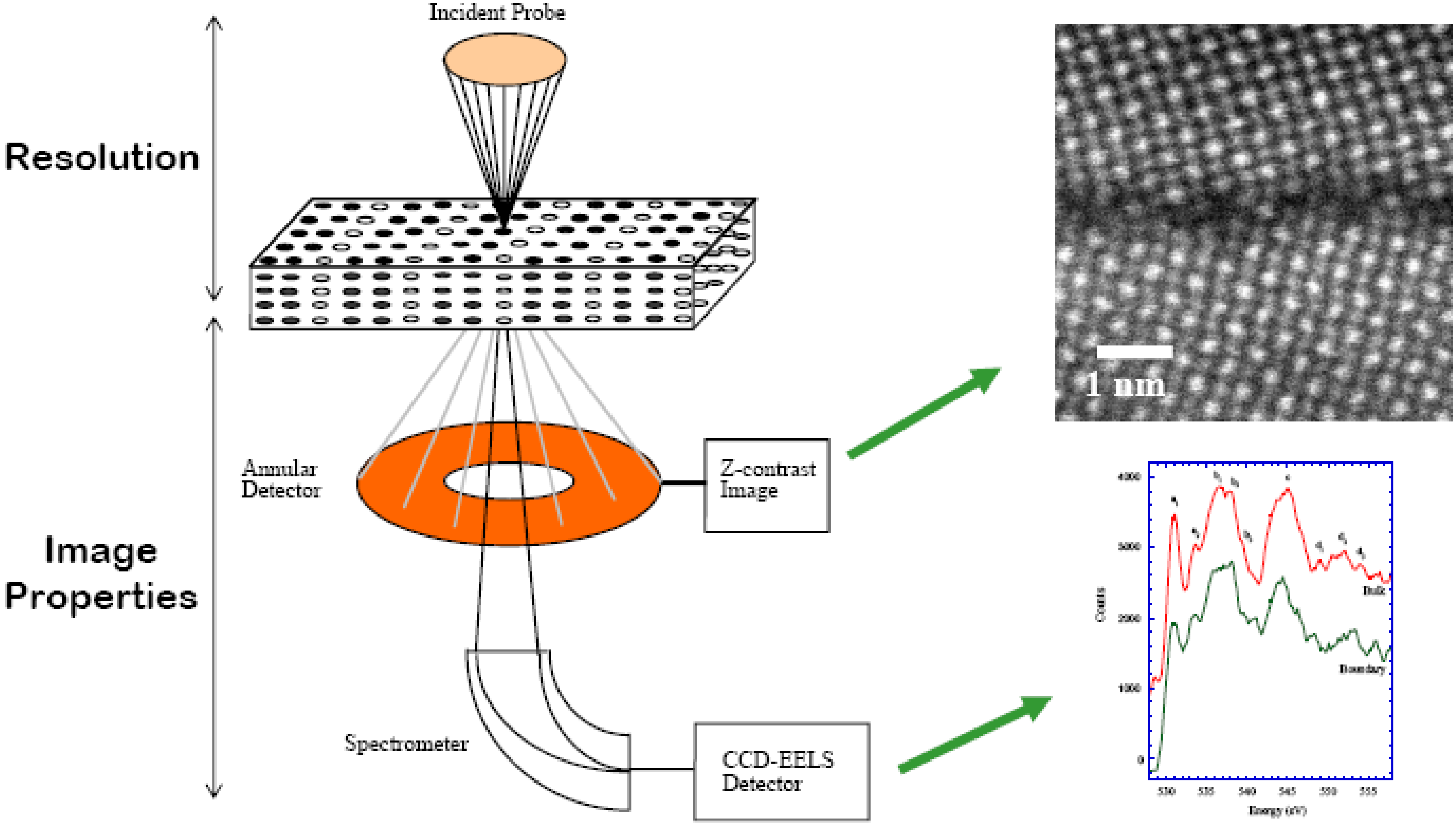
- But, can be only way to characterize some nanomaterials
- Can computationally extract diffraction information from HREM images
- Would never get this directly
  - Scattering is too weak at this size scale

Fast Fourier Transformation



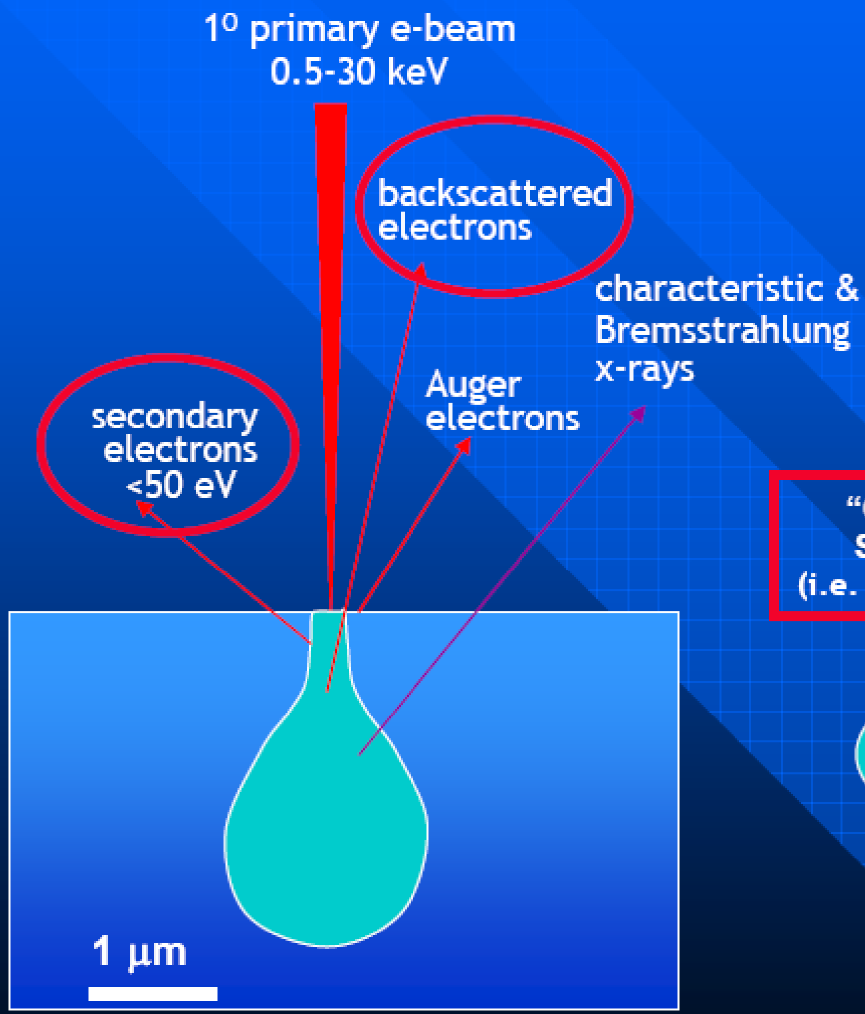
Scanning transmission electron microscopy (STEM)

STEM

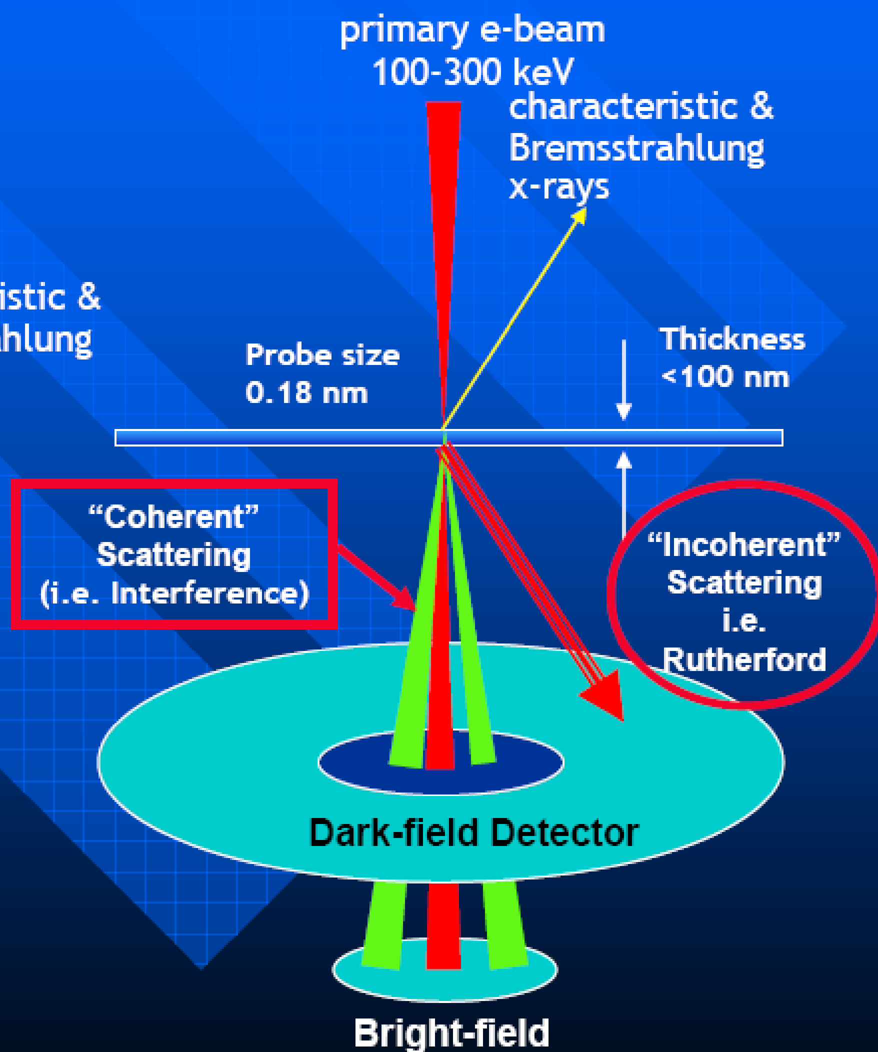

Resolution
Image Properties
Incident Probe
Annular Detector
Z-contrast Image
Spectrometer
CCD-EELS Detector
1 nm

SEM vs STEM

Scanning electron microscopy (SEM)

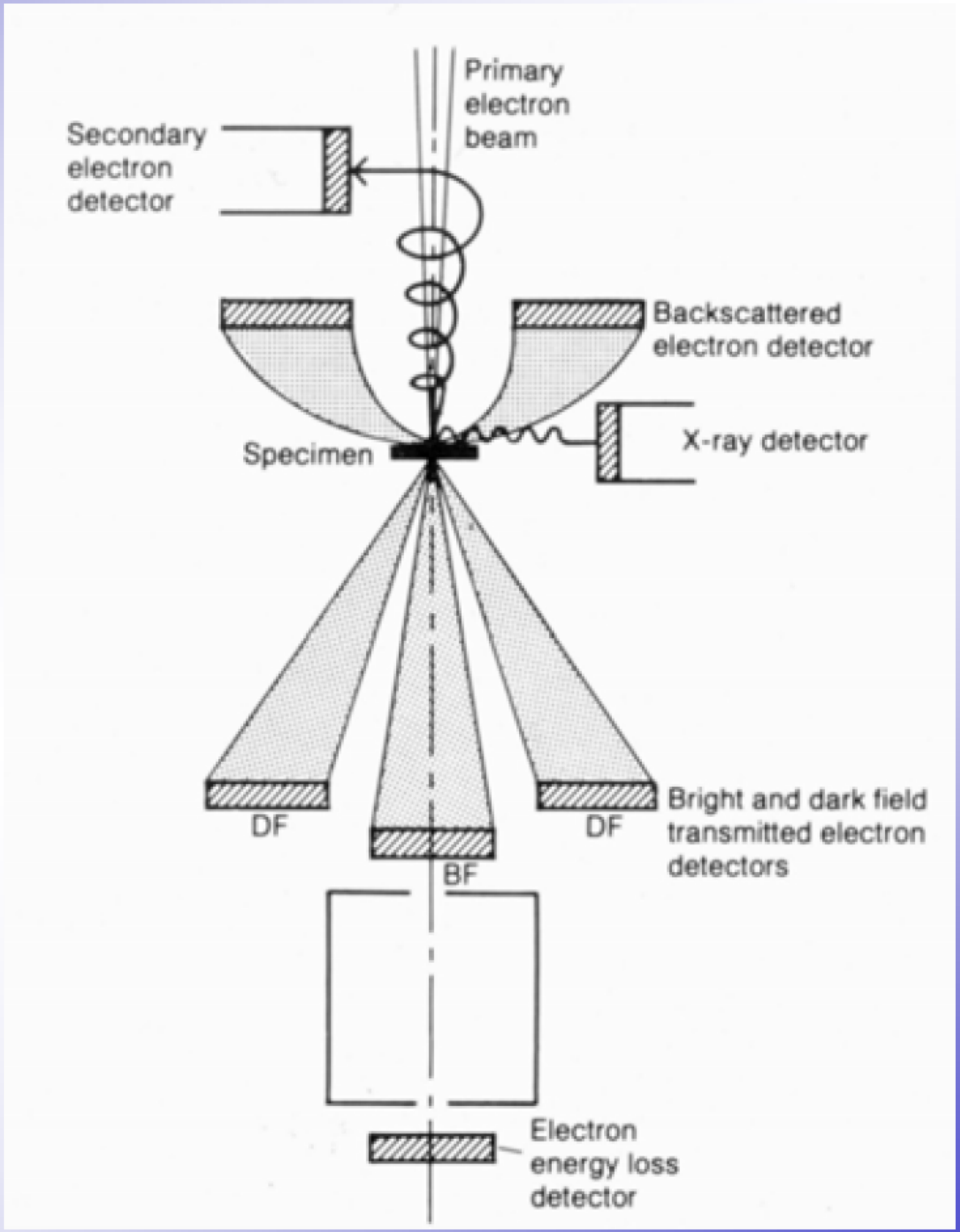


Scanning transmission electron microscopy (STEM)



Detectors in S(T)EM

- Secondary Electrons
- Backscattered Electrons
- X-rays
- EELS
- Bright field
- Dark field
- (Absorbed current)

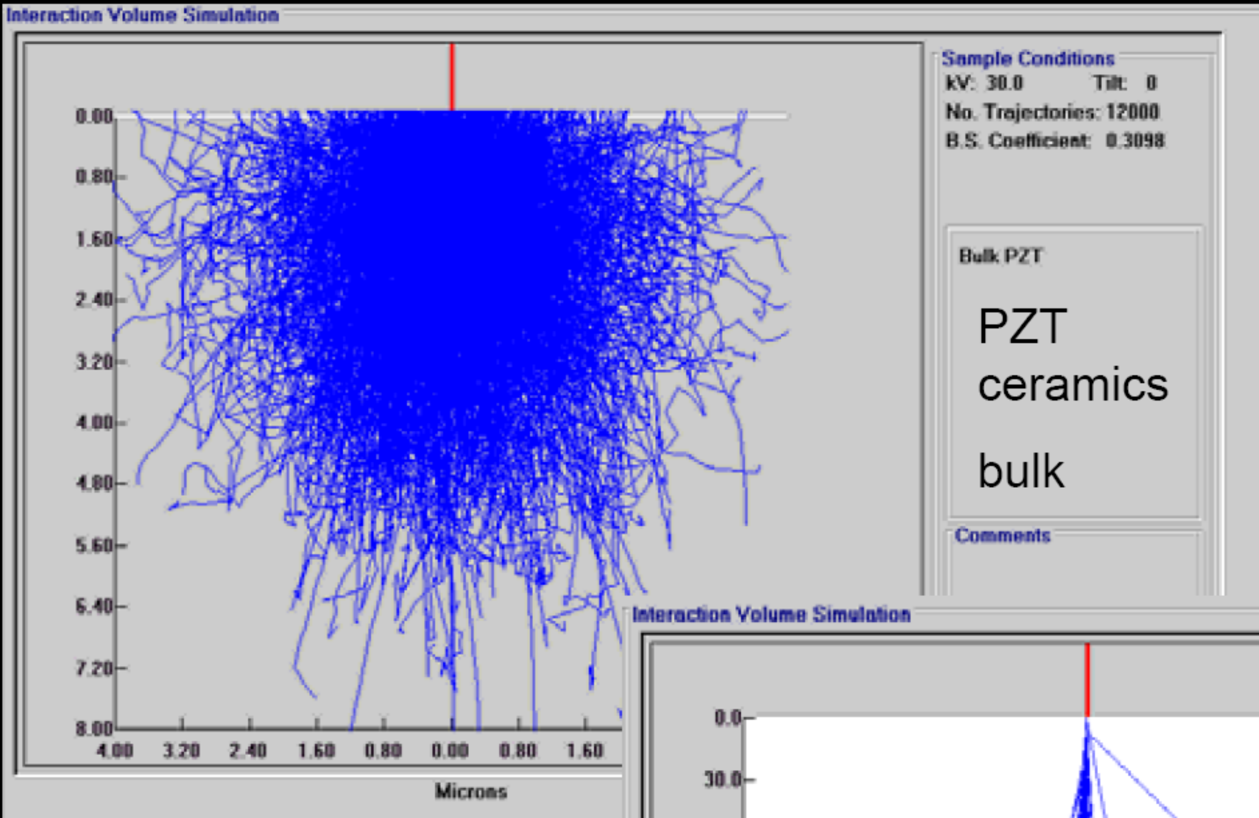


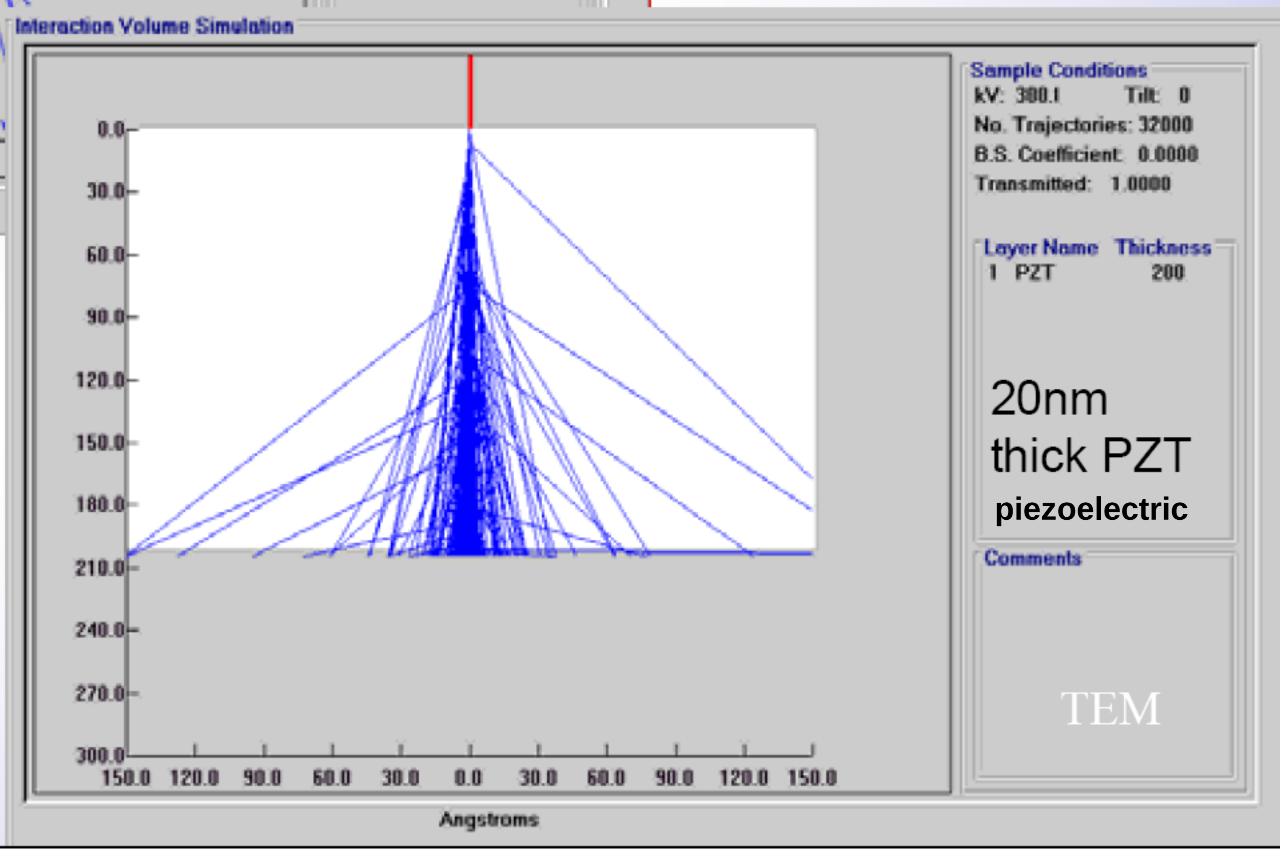
Interaction volume

SEM (30KeV), bulk

versus

TEM (300KeV), thin film





Small interaction volume -> high spatial resolution for EDX Analysis!

Advantages and disadvantages of Scanning Beam Microscopy SEM,TEM <-> STEM

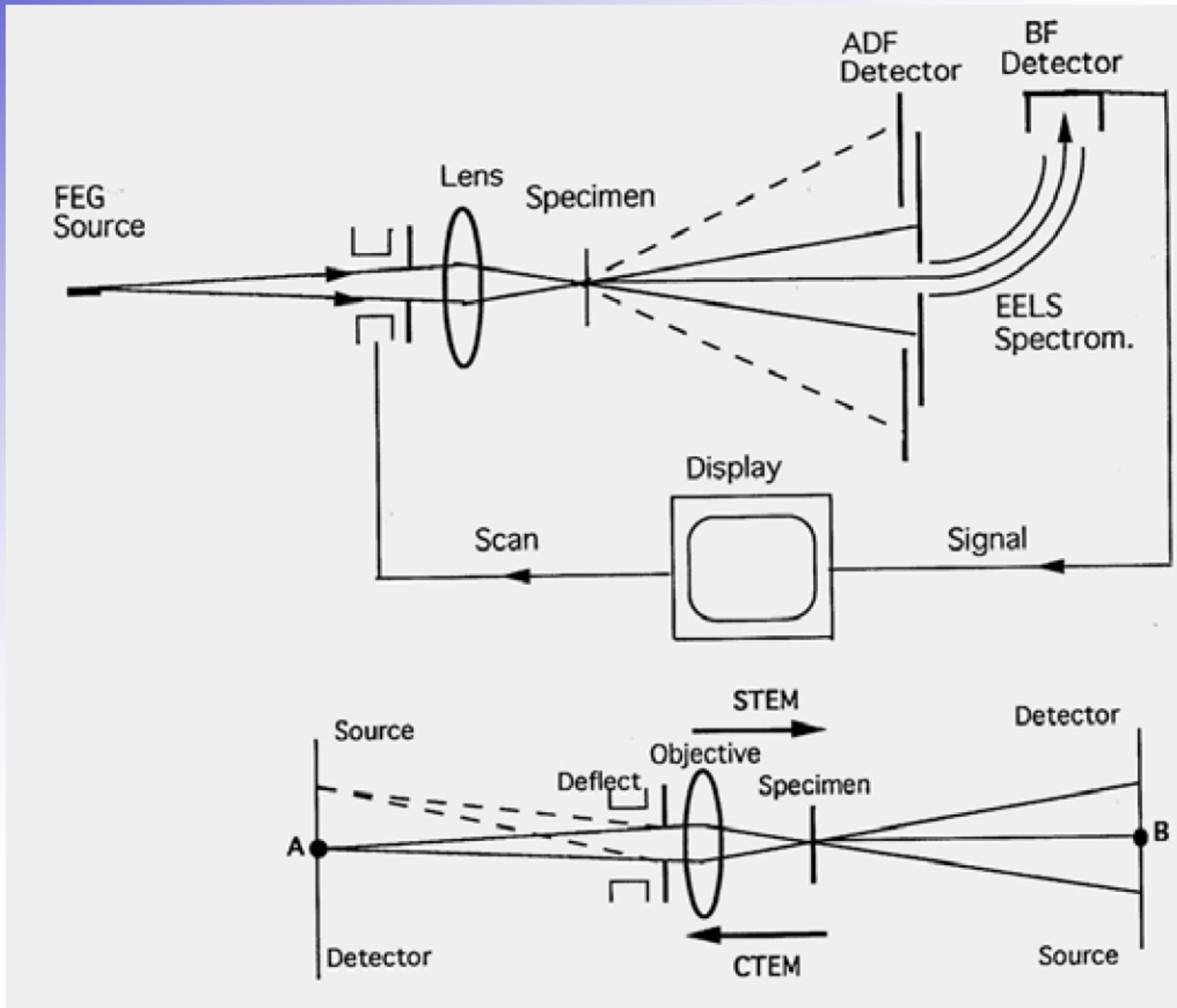
Advantages

- Parallel detection of different signals
- Easy positioning of the beam (EDX, EELS)
- Small interaction volume, High energy (EDX)

Disadvantages

- Longer acquisition times (line by line)
- Image distortions (deflection coils)
- More complicated alignment procedure
- More expensive…

Principle



ADF Detector
BF Detector
FEG Source
Lens
Specimen
EELS Spectrom.
Display
Scan
Signal
STEM
Source
Detector
Objective
Deflect
Specimen
A
B
Detector
Source
CTEM

Reciprocity

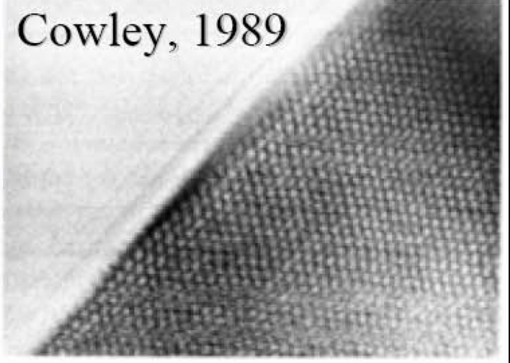
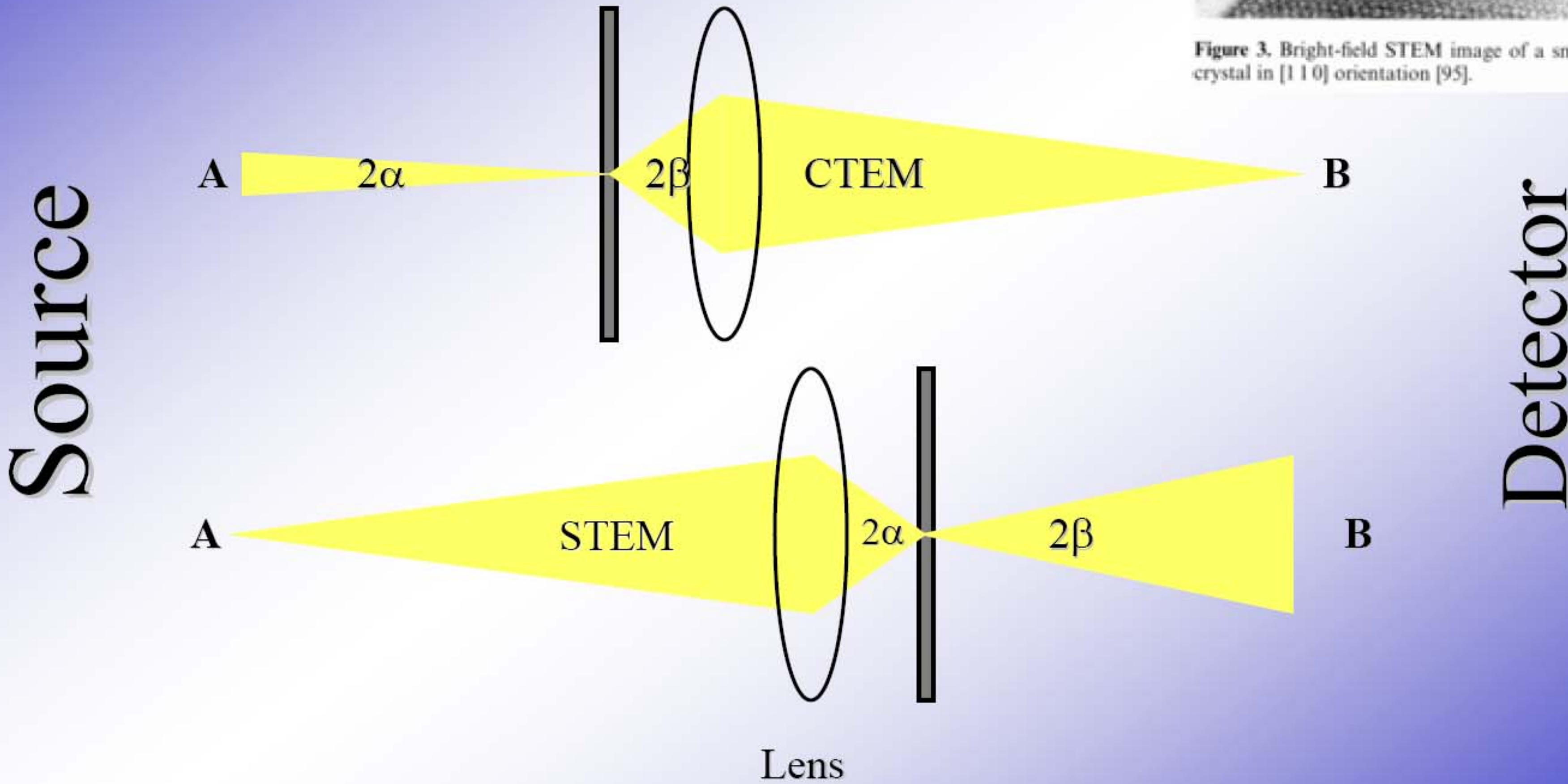
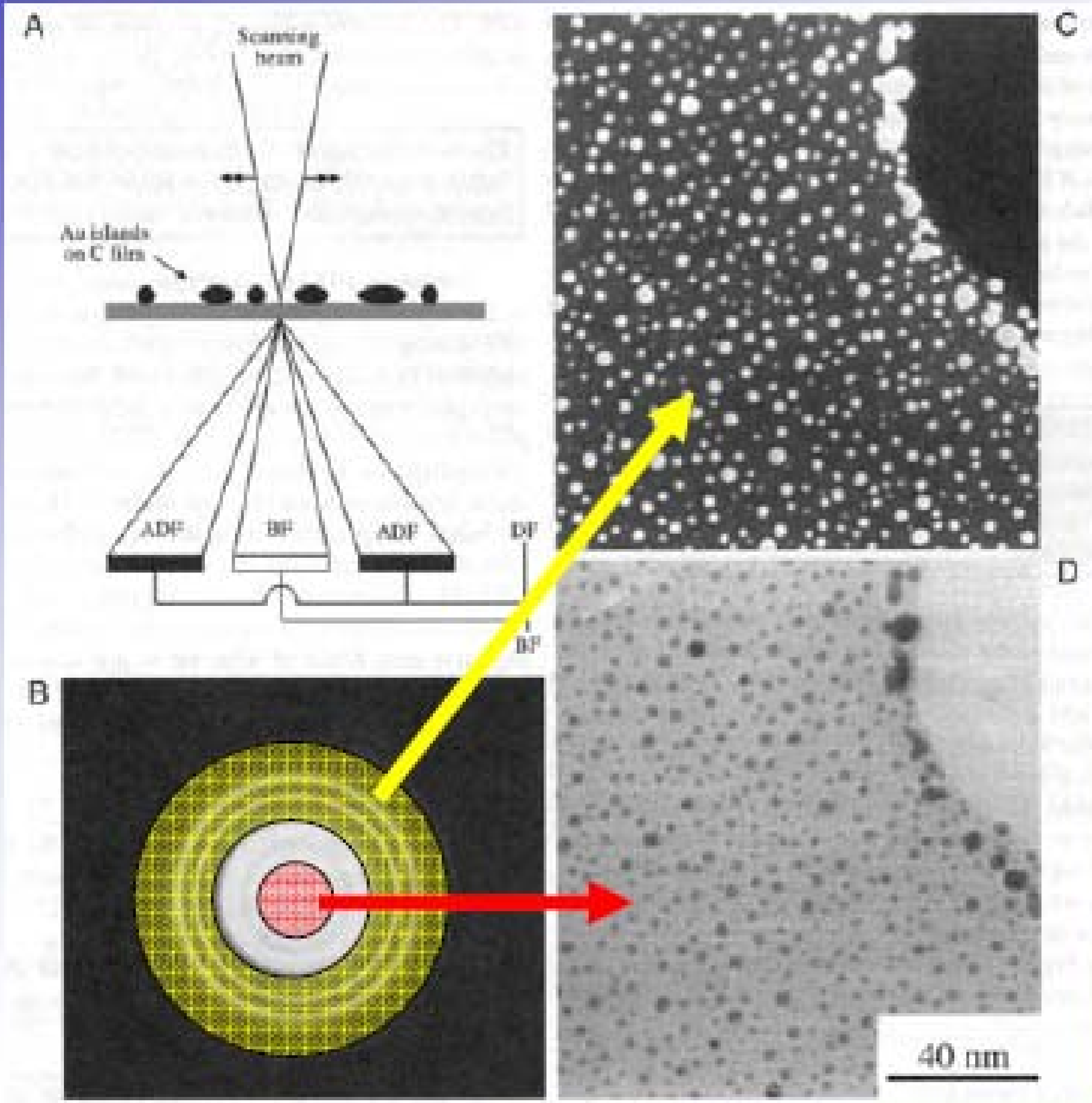


Figure 3. Bright-field STEM image of a small MgO crystal in [1 1 0] orientation [95].



Cowley (1969): for the same lenses, apertures and system dimension the image contrast must be the same for CTEM and STEM

Au particles on a C film



STEM ADF:

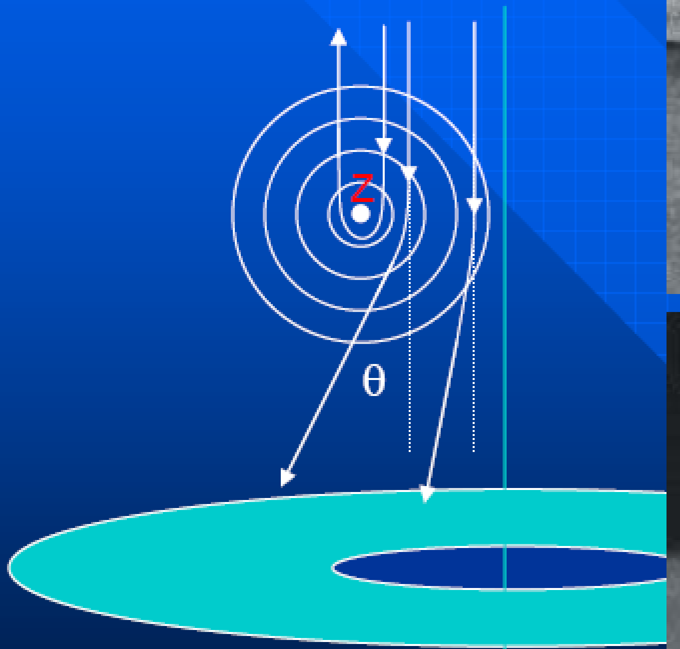
Area of the annular DF detector is much bigger than the objective aperture in CTEM DF imaging
-> much stronger signal

STEM BF:

Similar to CTEM BF image

TEM vs STEM

1. **STEM imaging gives better contrast**
2. **STEM images show Z-contrast**

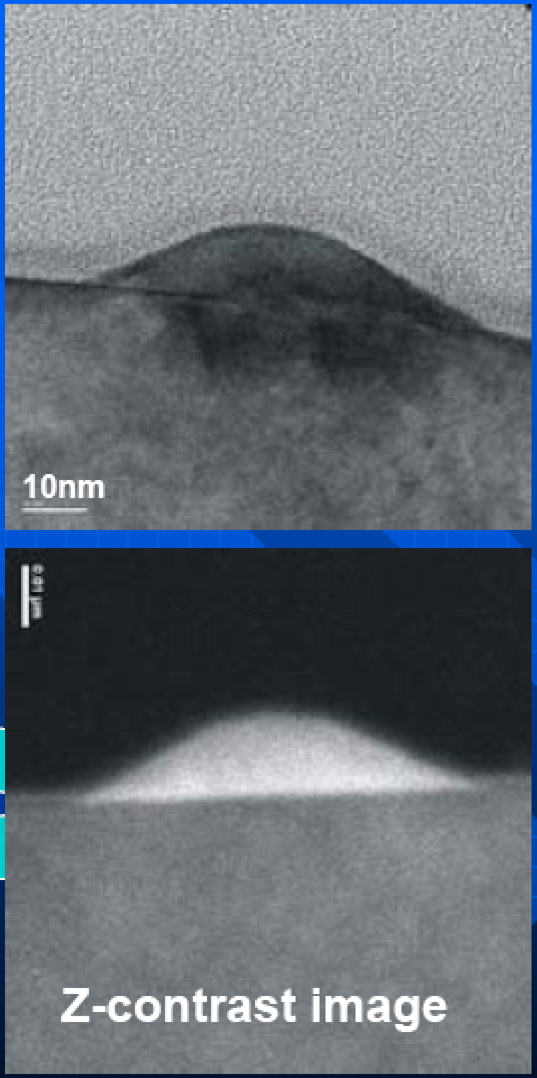


Annular dark-field (ADF) detector

$I \propto Z^2$

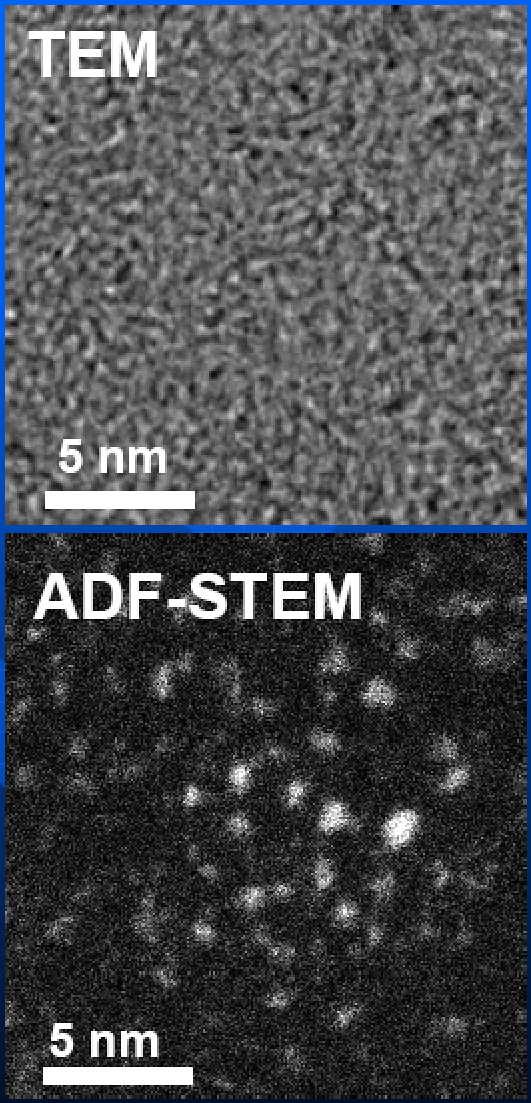
Z-contrast imaging

Ge quantum dots on Si substrate



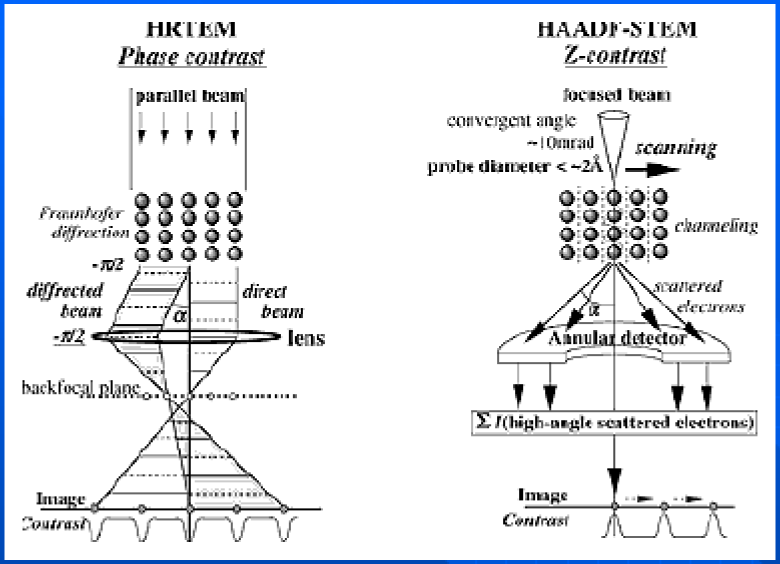
J.G. Wen

Ir nanoparticles



L. Long

HRTEM vs STEM

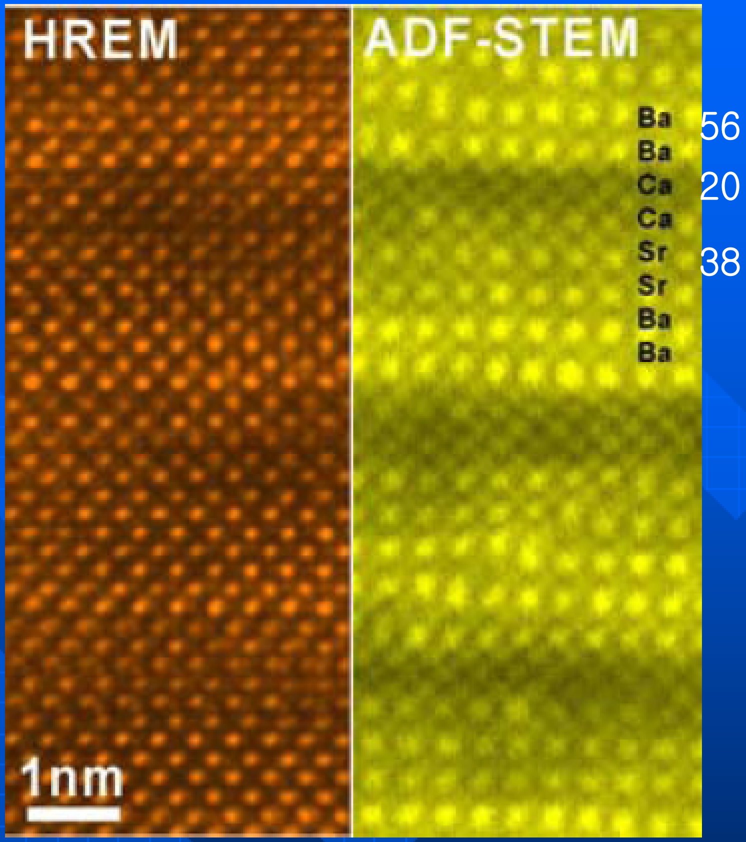


1. Contrast

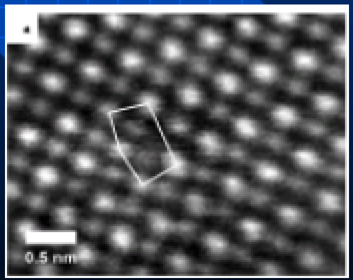
- High-resolution TEM (HRTEM) image is a phase contrast image (indirect image). The contrast depends on defocus.
- STEM image is a direct atomic column image (average Z-contrast in the column).

2. Delocalization Effect

- High-resolution TEM image from FEG has delocalization effect.
- STEM image has no such an effect.



$BaTiO_3/SrTiO_3/CaTiO_3$ superlattice J.G. Wen



From Pennycook's group

Types of STEM images

Bright-field

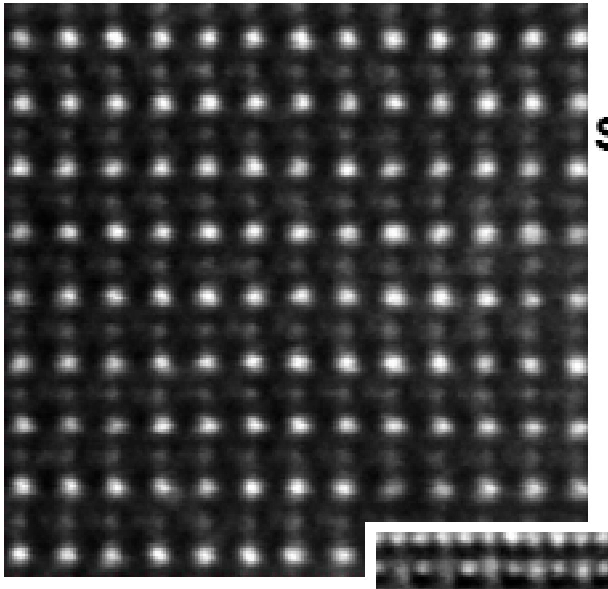
- Collect central beam with a small collection angle

Low-angle annular dark field

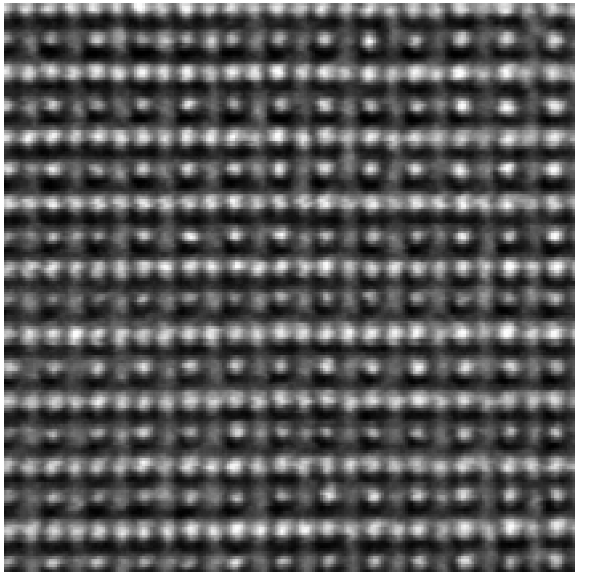
- Collection angle of 25 - 50 milliradians (mrad)

High-angle annular dark field

- Collection angle of 50 - 250 mrad
- Largely phonon scatter (TDS)



Coherent BF-STEM image of $SrTiO_3$ <110>

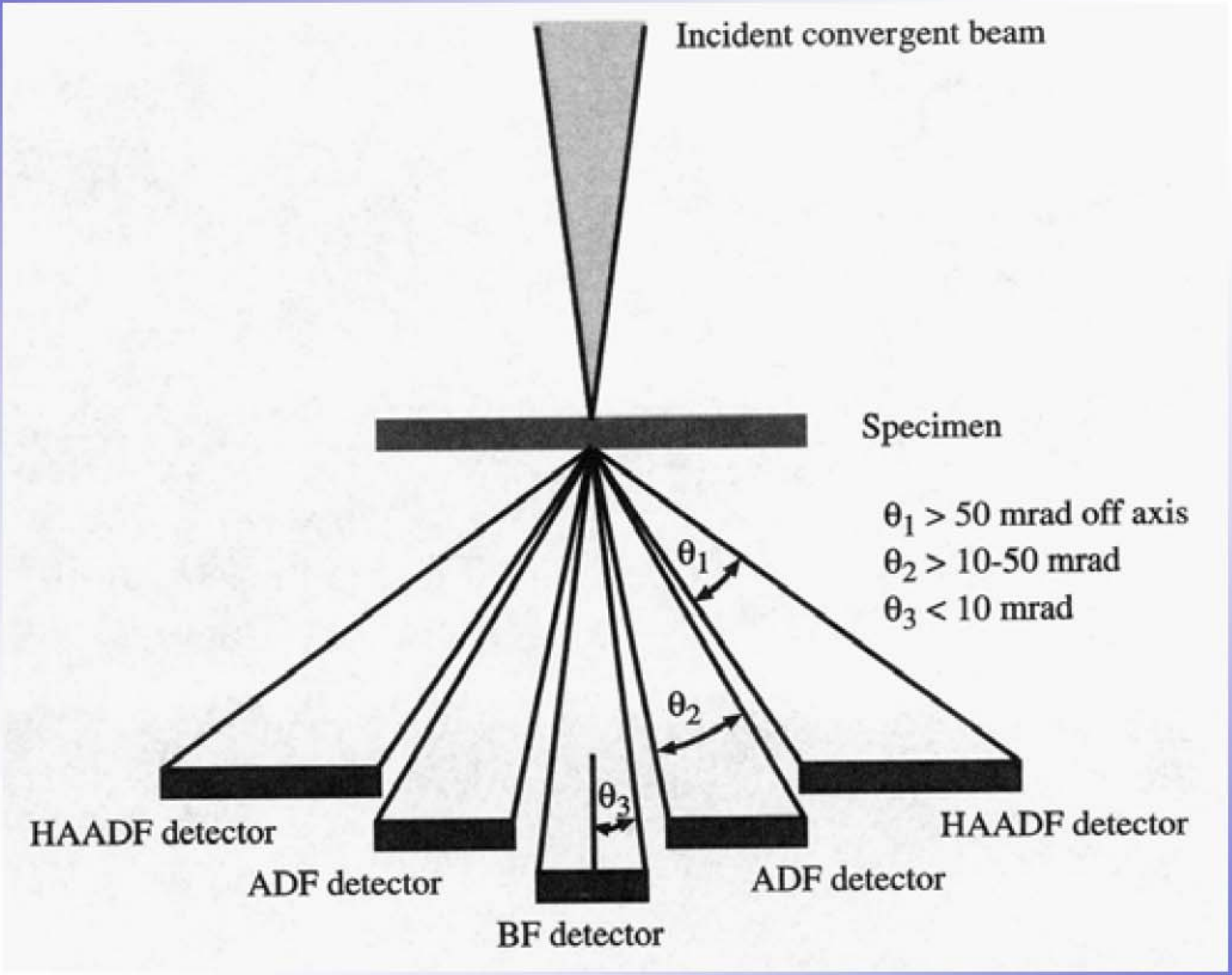


HAADF-STEM

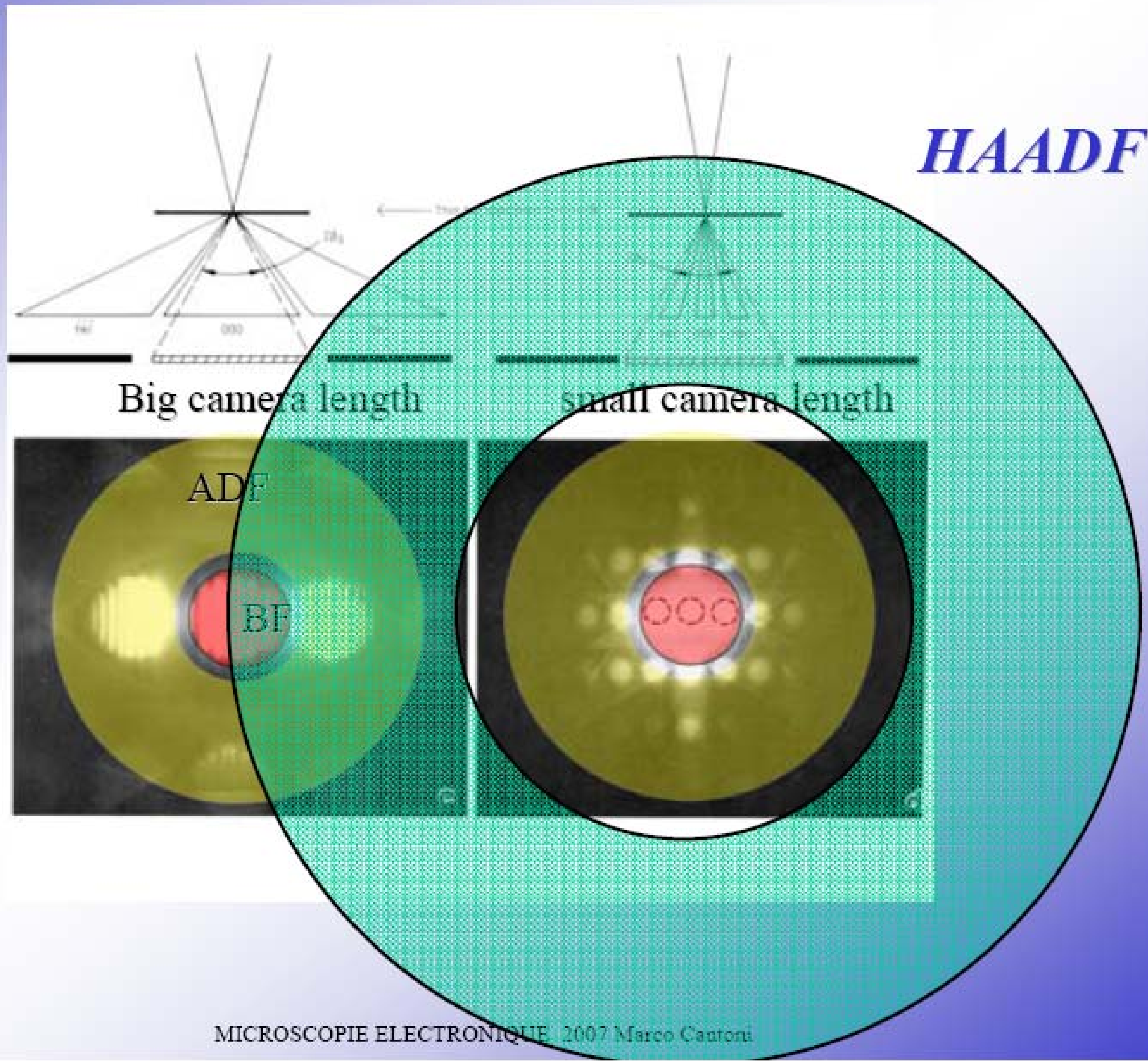
High Angle Annular Dark Field z-contrast

- Ultramicroscopy 30 (1989) 58-69
- North-Holland, Amsterdam
- **Z-CONTRAST STEM FOR MATERIALS SCIENCE**
- S.J. PENNYCOOK

- Ultramicroscopy 37 (1991) 14-38;
- North-Holland
- **High-resolution Z-contrast imaging of crystals**
- S.J. Pennycook and D.E. Jesson


Incident convergent beam
Specimen
θ1 > 50 mrad off axis
θ2 > 10-50 mrad
θ3 < 10 mrad
θ1
θ2
θ3
HAADF detector
ADF detector
BF detector
ADF detector
HAADF detector

High Angle Annular Dark field detector



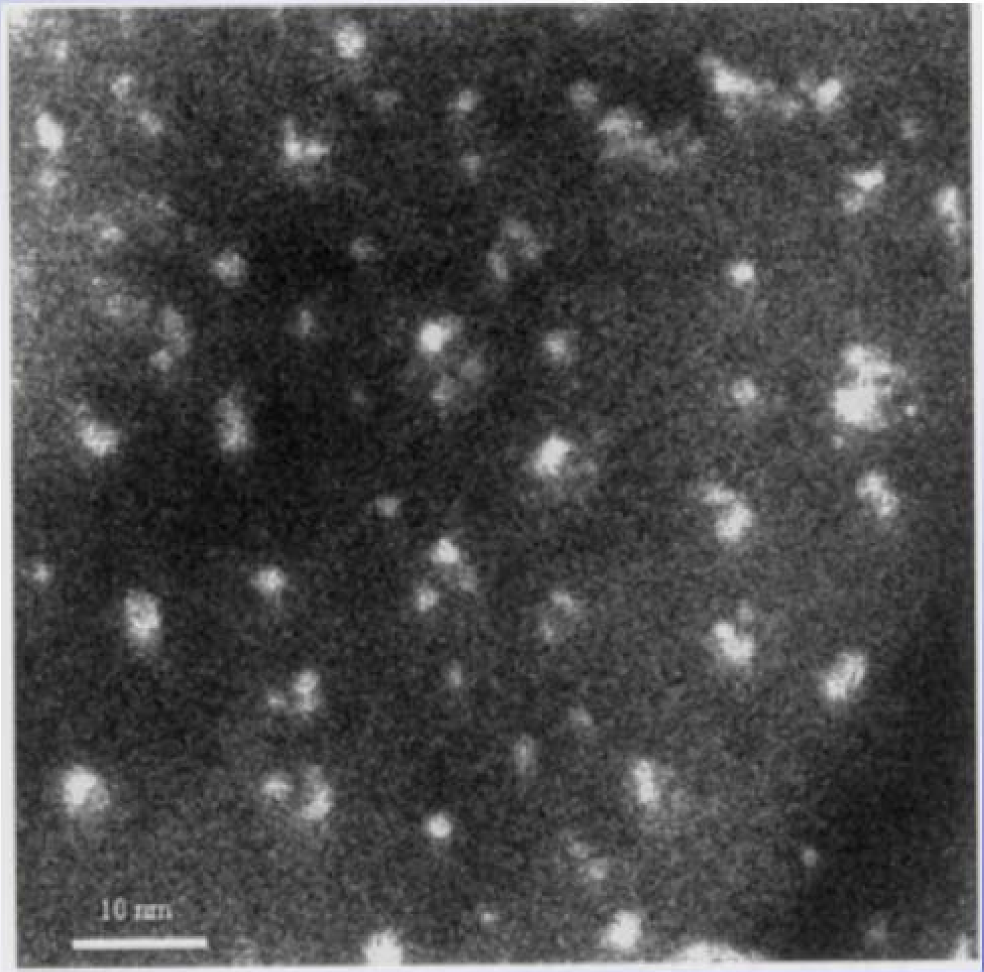
High angle incoherent scattering

- The annular DF detector is placed beyond the **bragg-scattered** electrons…
- Small camera length and large diameter of the detectors inner diameter

The image is formed by high angle incoherently scattered electrons -> Rutherford scattering at the nucleus of the atoms

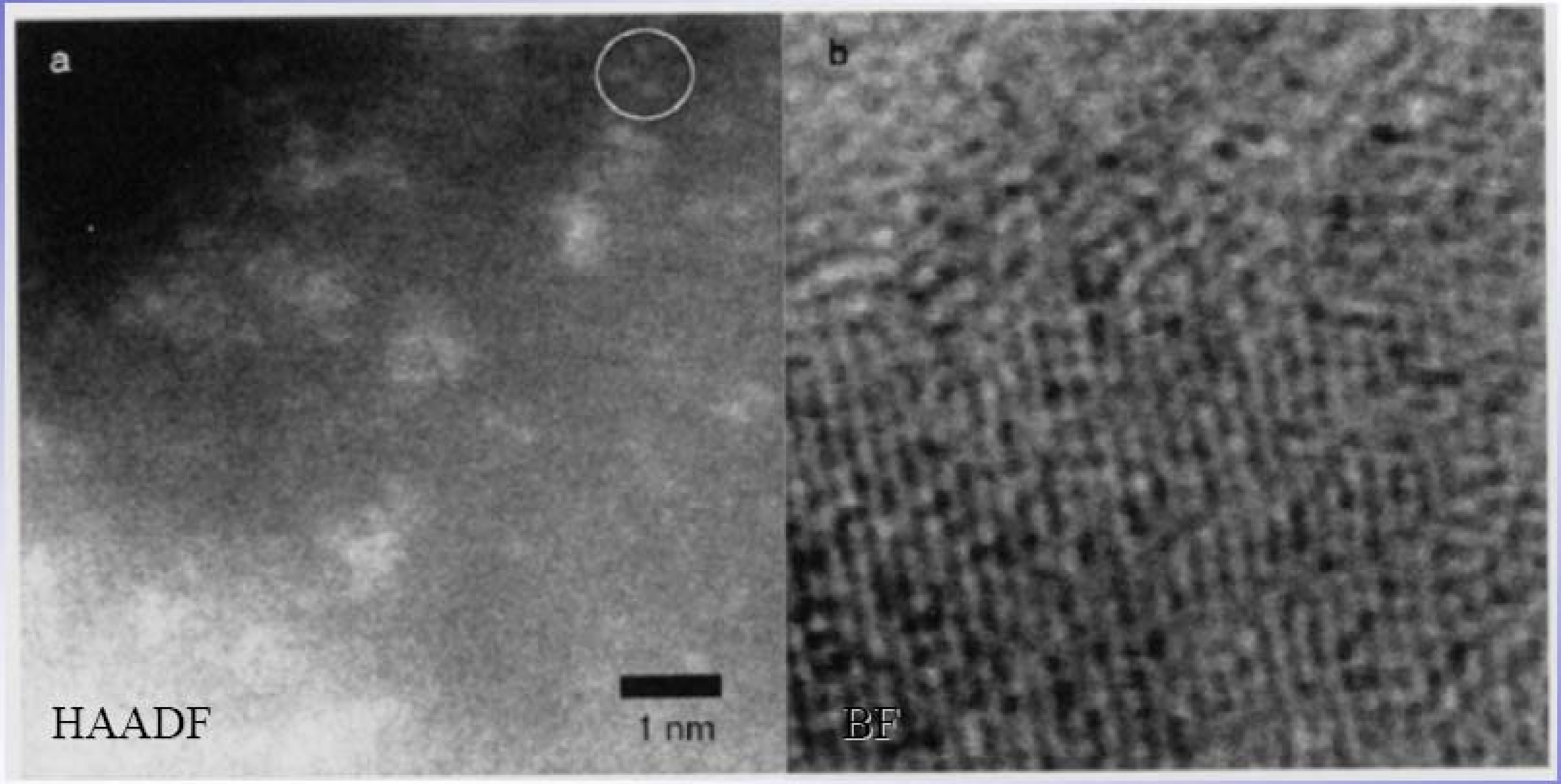
$\sigma \sim z^2$

Z-Contrast



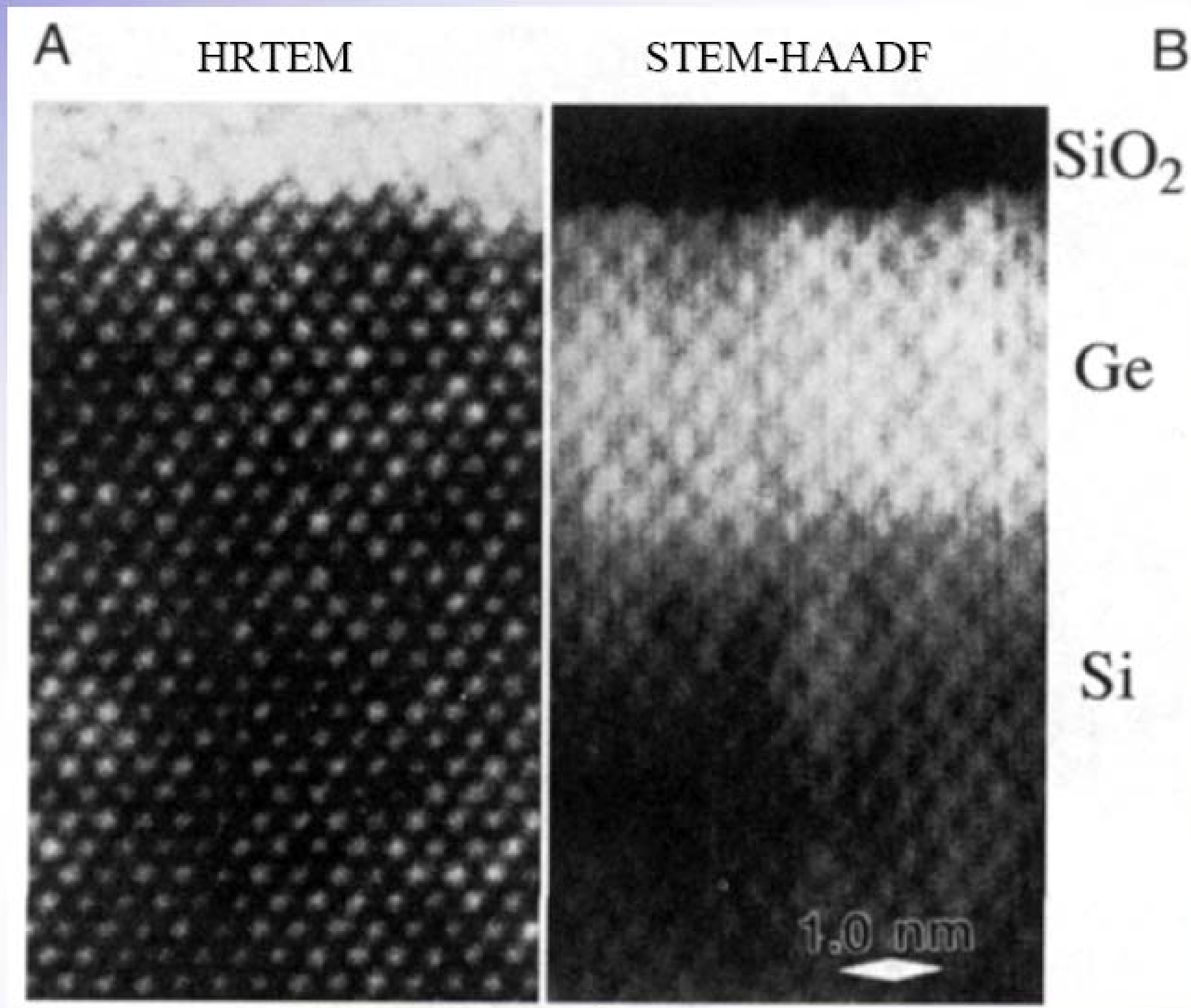
Si nano-crystals in SiO_2 formed by implantation

HAADF <-> HRTEM



- Pt catalyst on Al_2O_3
- Pt particles become visible in the HAADF image

HRTEM <-> STEM HAADF



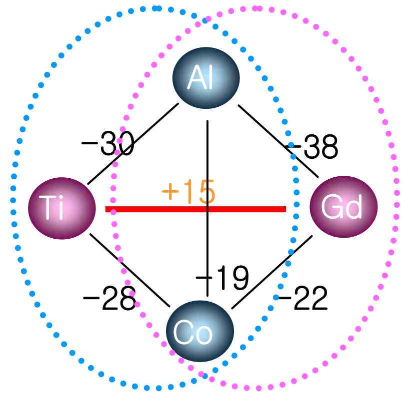
32

14

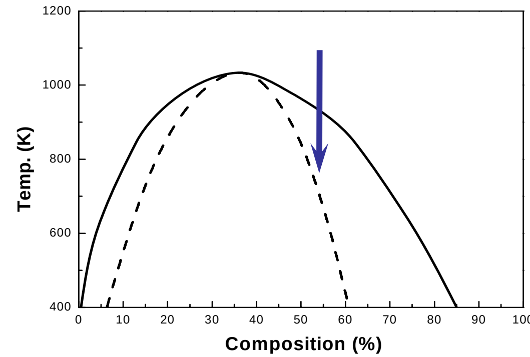
Phase separation

1) Droplet structure

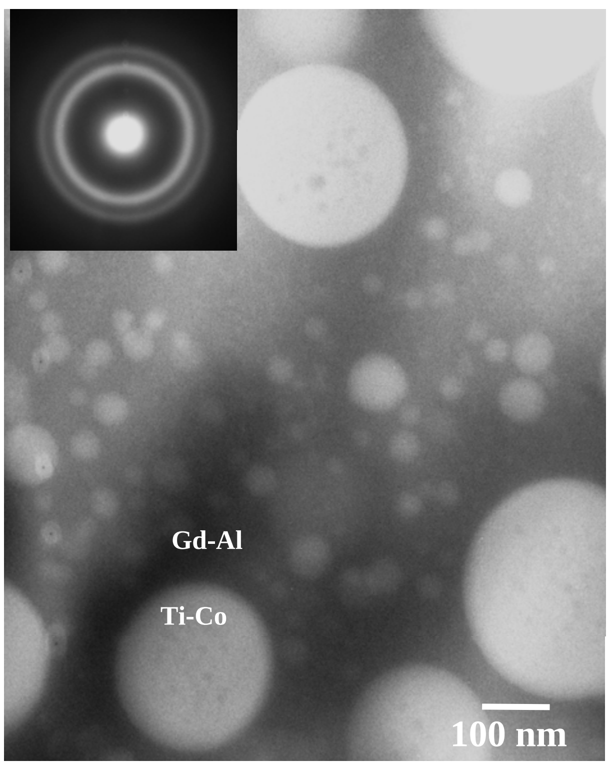
in Gd-Ti-Al-(Co, Ni, Cu) alloy system



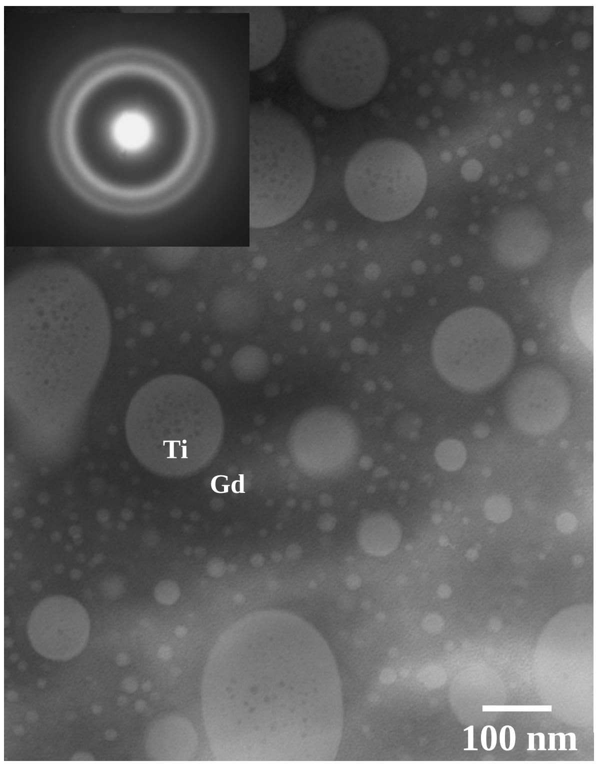
*** unpublished (2006)**



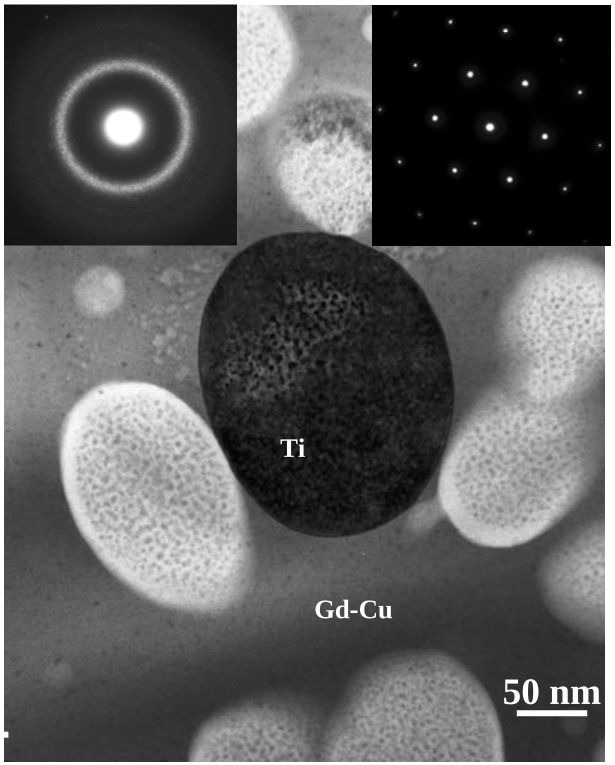
$Gd_{30}Ti_{25}Al_{25}Co_{20}$



$Gd_{30}Ti_{25}Al_{25}Ni_{20}$



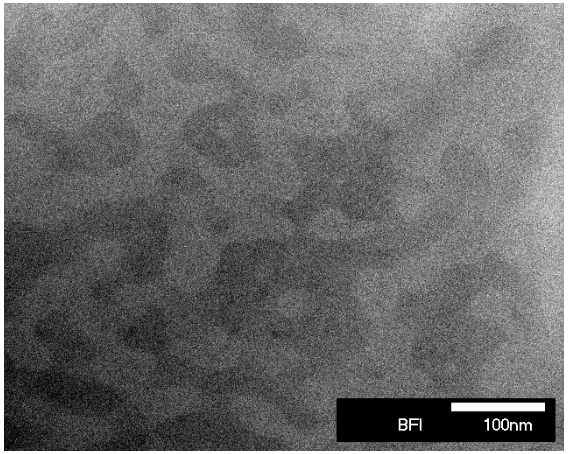
$Gd_{30}Ti_{25}Al_{25}Cu_{20}$

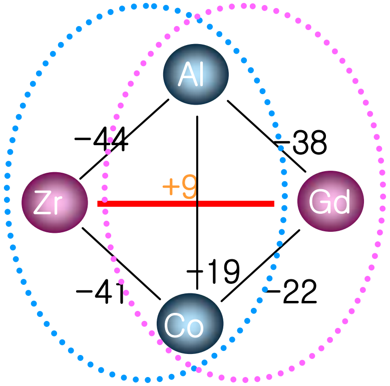


Phase separation

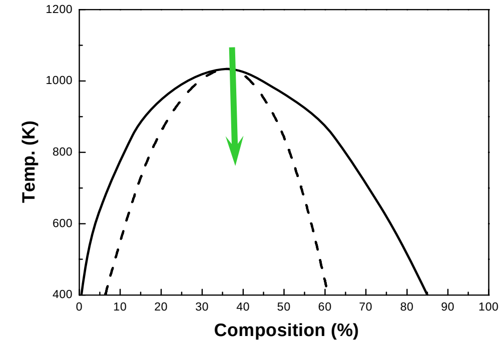
2) Interconnected structure

in Gd-Zr-Al-(Co, Ni, Cu) alloy system

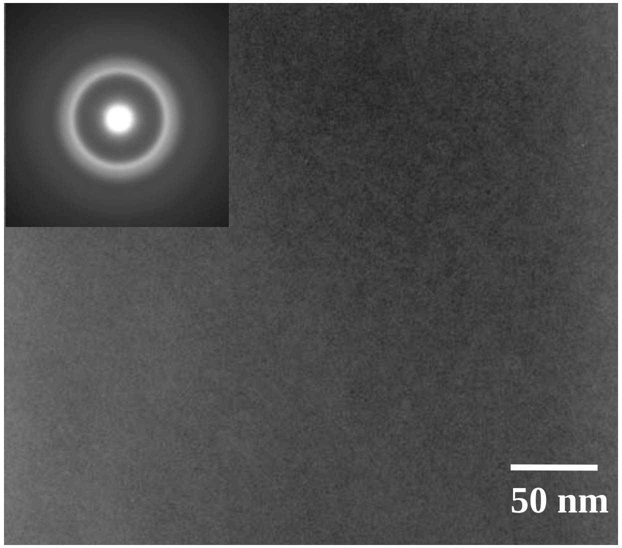




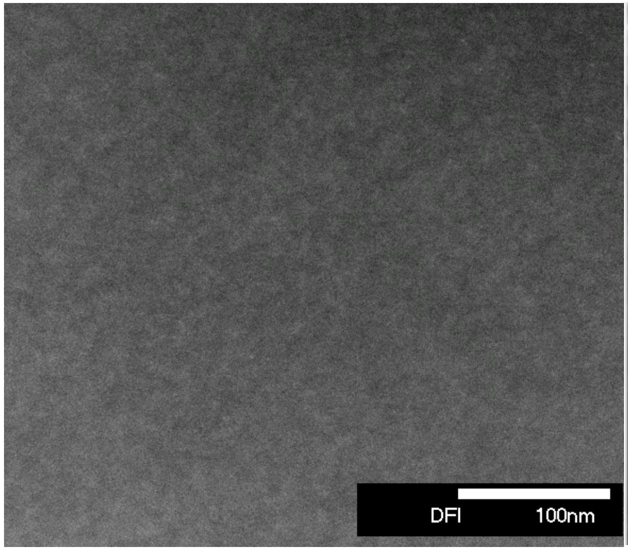
* unpublished (2006)



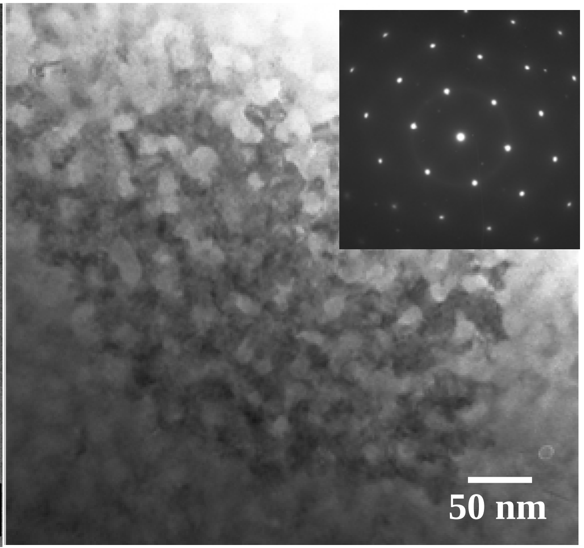
$Gd_{30}Zr_{25}Al_{25}Co_{20}$



$Gd_{30}Zr_{25}Al_{25}Ni_{20}$



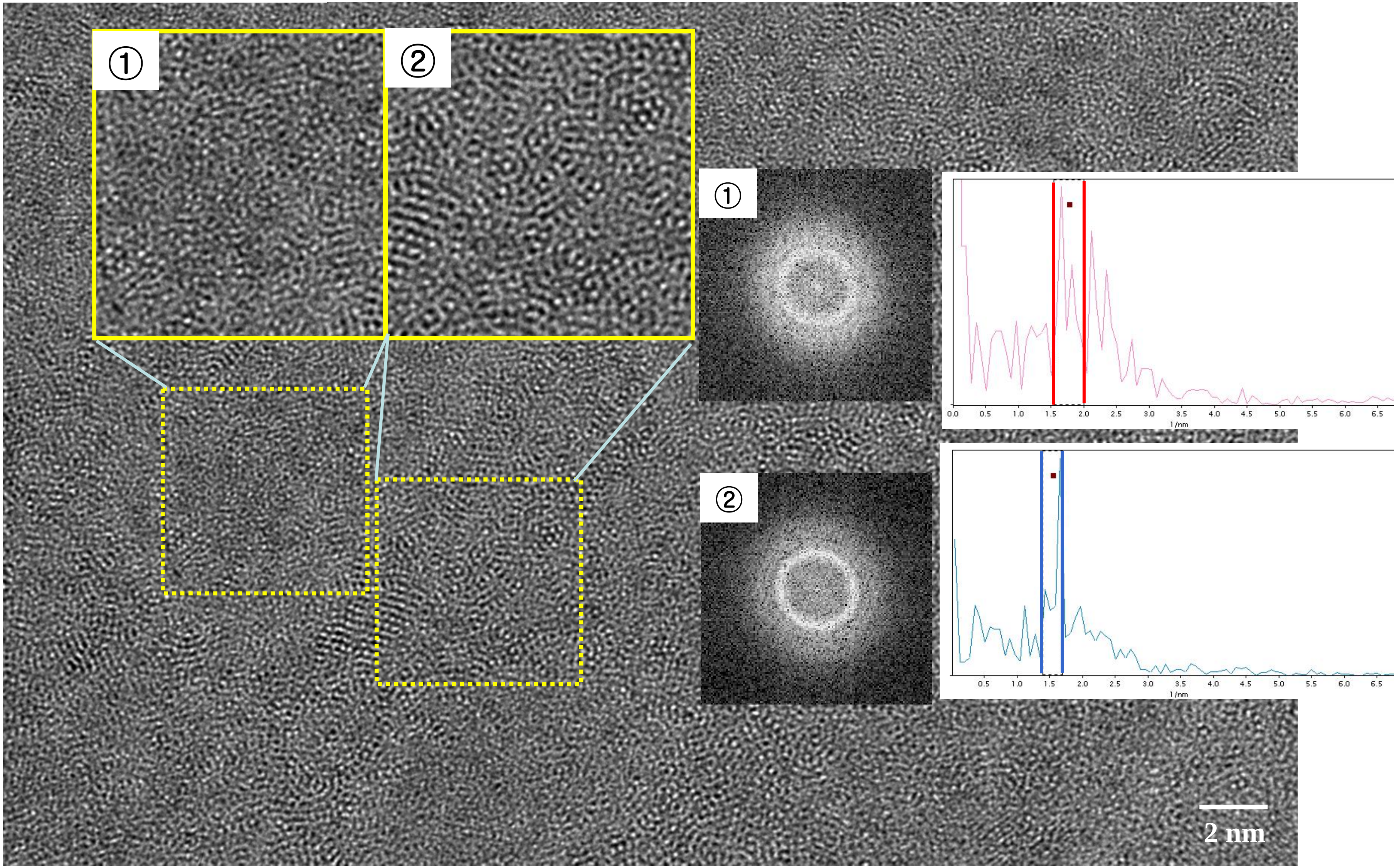
$Gd_{30}Zr_{25}Al_{25}Cu_{20}$



Nano scale (<3 mm) interconnected Phase separation

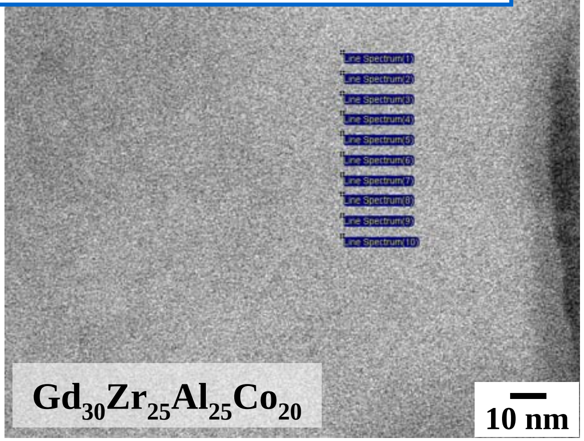
$Gd_{30}Zr_{25}Al_{25}Co_{20}$

* unpublished (2008)

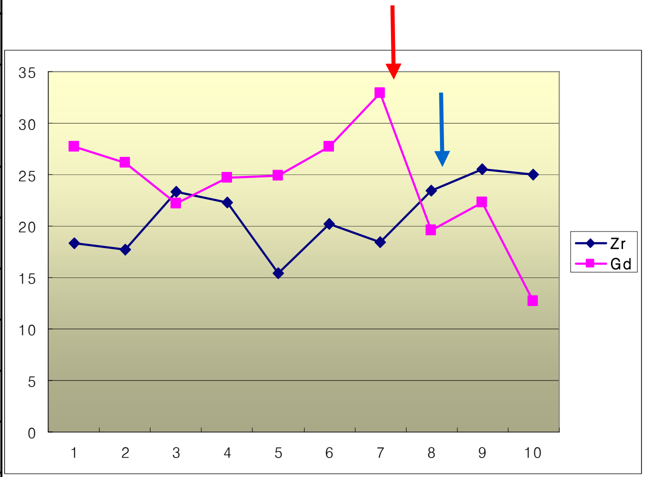


Chemical fluctuation - EDS

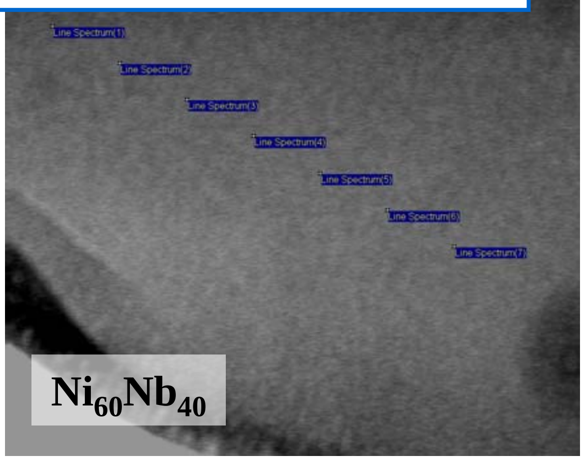
Beam size : 0.7 nm
Distance between spots : ~ 5 nm



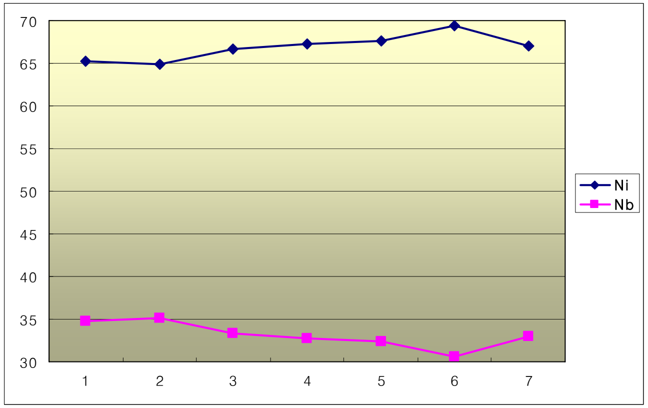
Spectrum	Al	Co	Zr	Gd
Spectrum(1)	23.16	30.79	18.34	27.70
Spectrum(2)	22.74	33.40	17.74	26.12
Spectrum(3)	24.15	30.38	23.29	22.18
Spectrum(4)	21.48	31.52	22.31	24.69
Spectrum(5)	22.45	37.20	15.46	24.89
Spectrum(6)	27.20	24.83	20.24	27.74
Spectrum(7)	23.67	24.90	18.47	32.96
Spectrum(8)	22.47	34.47	23.44	19.62
Spectrum(9)	26.01	26.16	25.50	22.33
Spectrum(10)	17.90	44.35	25.05	12.70



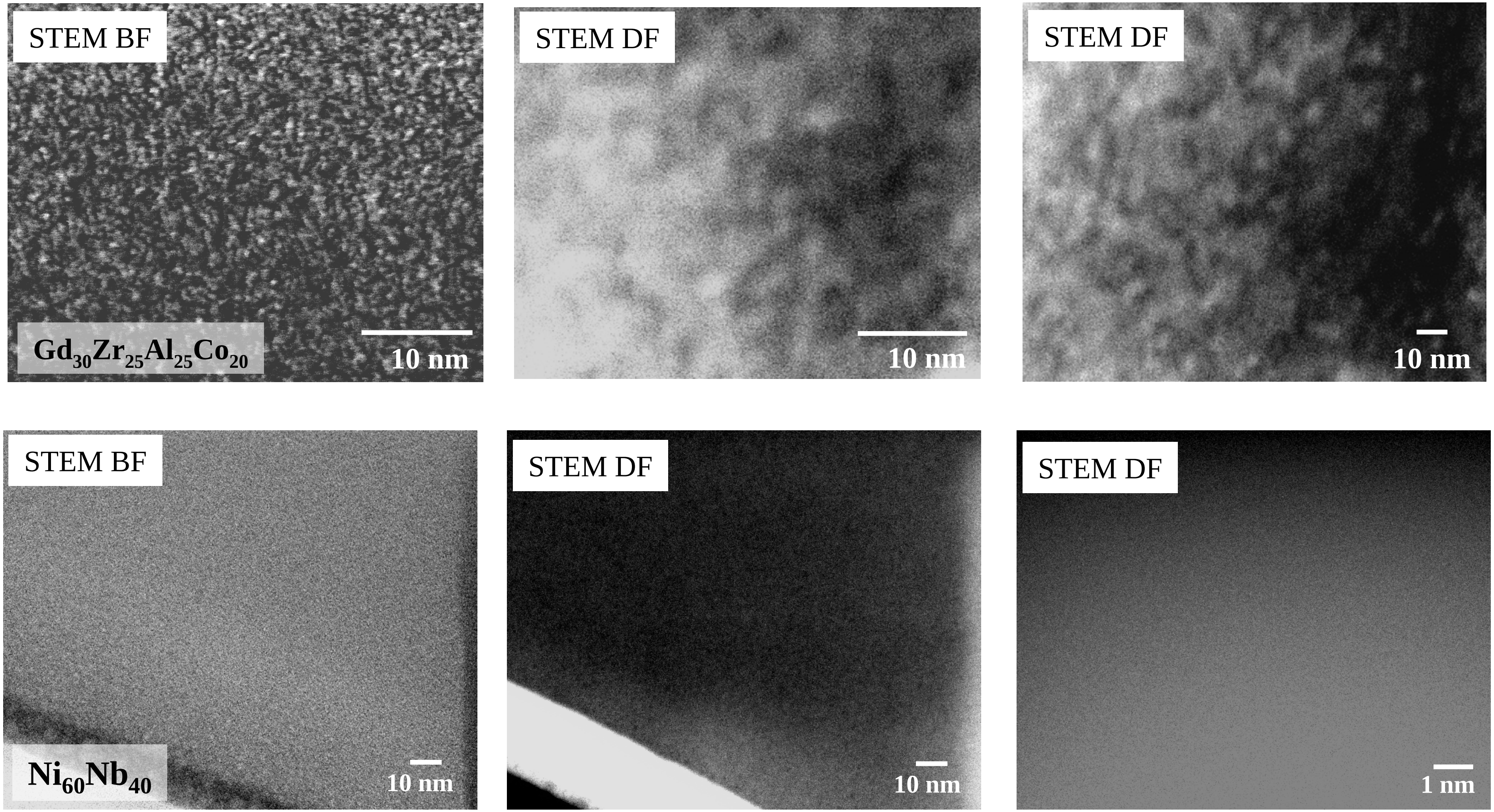
Beam size : 0.7 nm
Distance between spots : ~ 15 nm



Spectrum	Ni	Nb
Spectrum(1)	65.22	34.78
Spectrum(2)	64.84	35.16
Spectrum(3)	66.66	33.34
Spectrum(4)	67.23	32.77
Spectrum(5)	67.57	32.43
Spectrum(6)	69.42	30.58
Spectrum(7)	66.98	33.02



Chemical fluctuation – Z contrast



- **nm scale contrast fluctuation in Z contrast image**
  ⇒ early stage in spinodal decomposition

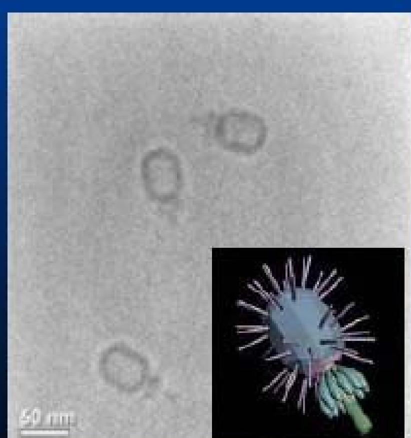
What can you do with a TEM?

In-situ capabilities

1. Heating (hot stage 1000°C)
2. Cooling (liquid N_2)
3. Tensile-stage
4. MEMS tensile stage
5. Universal MEMS holder
6. Wet-cell
7. Nanomanipulator
8. Environmental holder
9. Applied voltage to sample

10. Cryo transfer holder

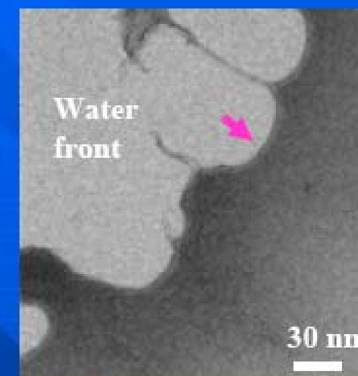
N. Schmit

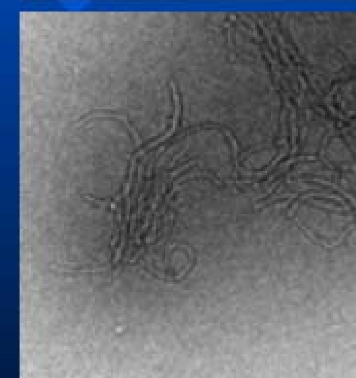


In-situ holders

All developed at CMM

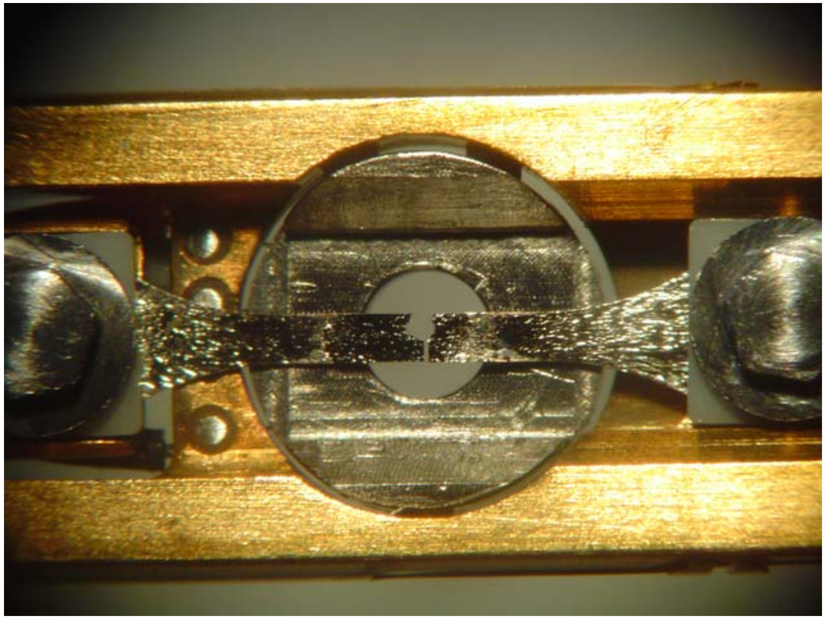
CNT in water

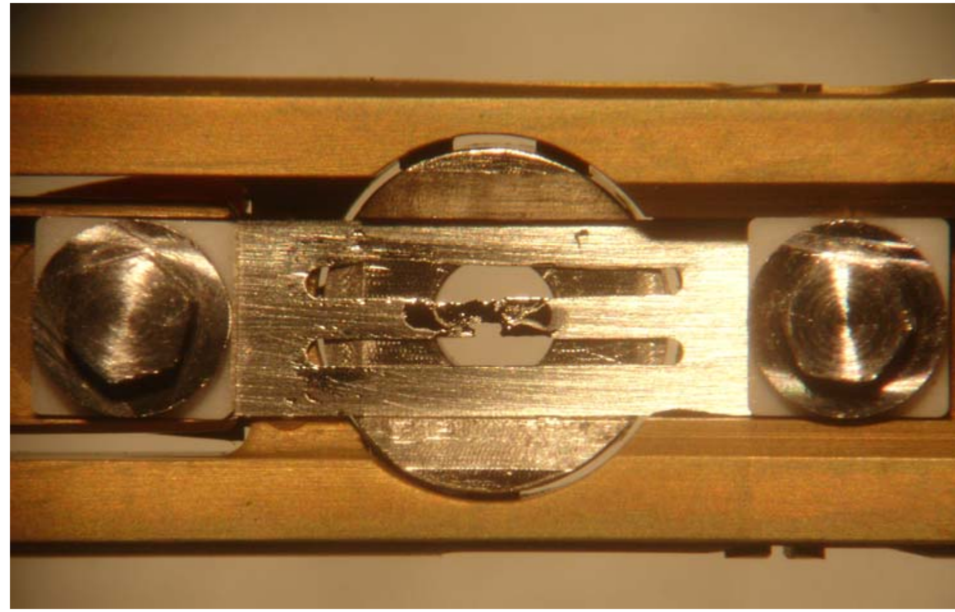


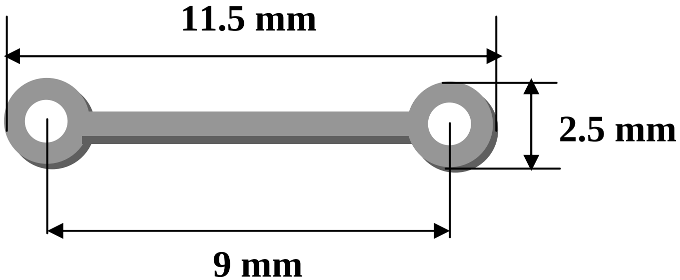


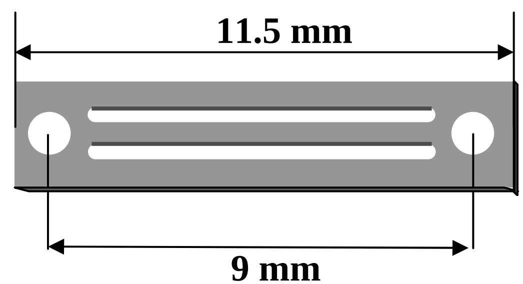
J.G. Wen

EXAMPLE: Preparation of specimen for in-situ tensile test





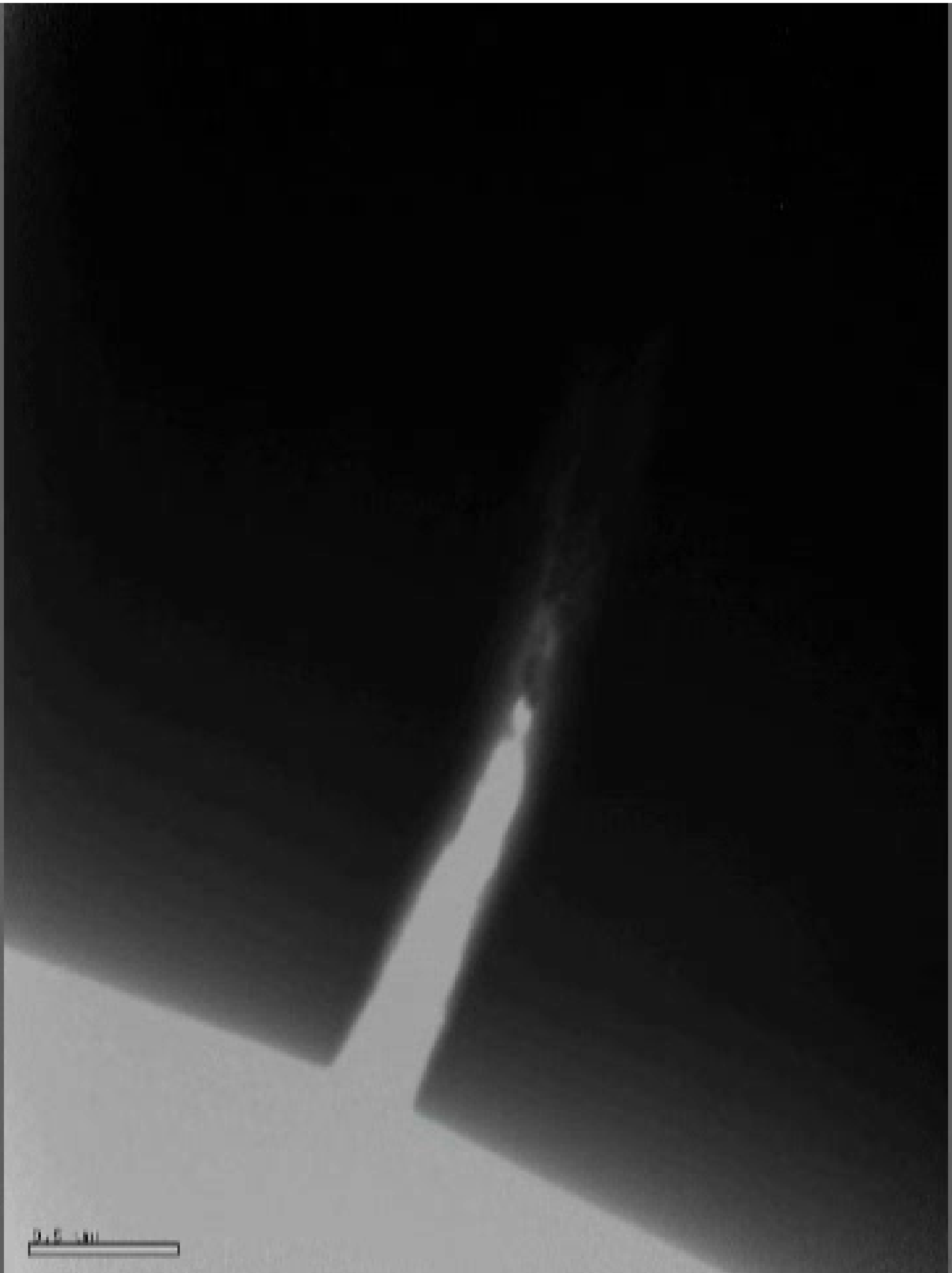




시편 종류 : $Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$ ribbon monolithic / crystallization of 4 %
시편 두께 : 60 ㎛
Thinning method : jet polishing (No ion-milling)
Strain interval = 1.0 ㎛/s ~ 0.1 ㎛/s
Strain at fracture = 290 ㎛

in-situ tensile test

$Ti_{40}Zr_{29}Cu_9Ni_8Be_{14}$



H.J. Chang et al. Unpublished. (2008)

Captured images