Transmission Electron Microscopy: a complement to X-rays and Neutrons

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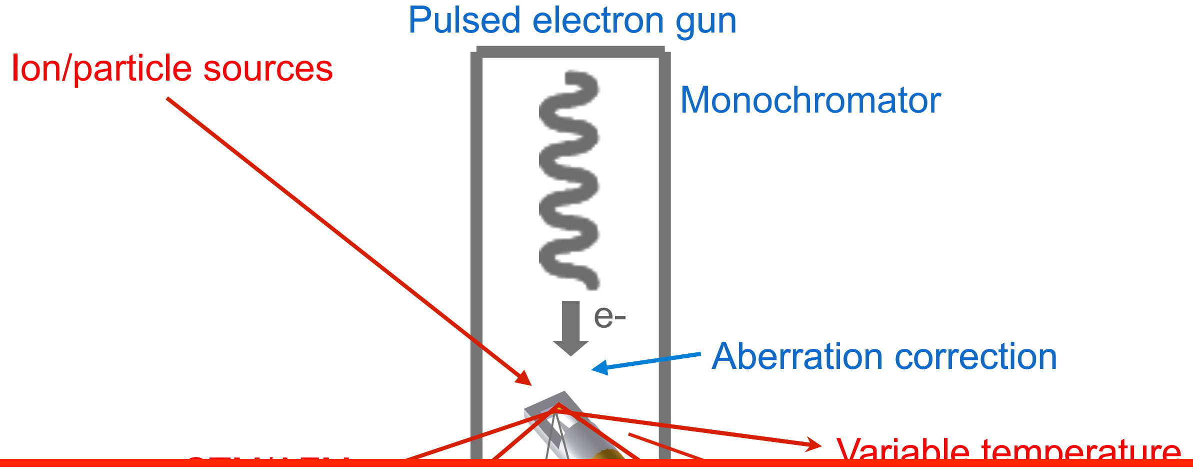
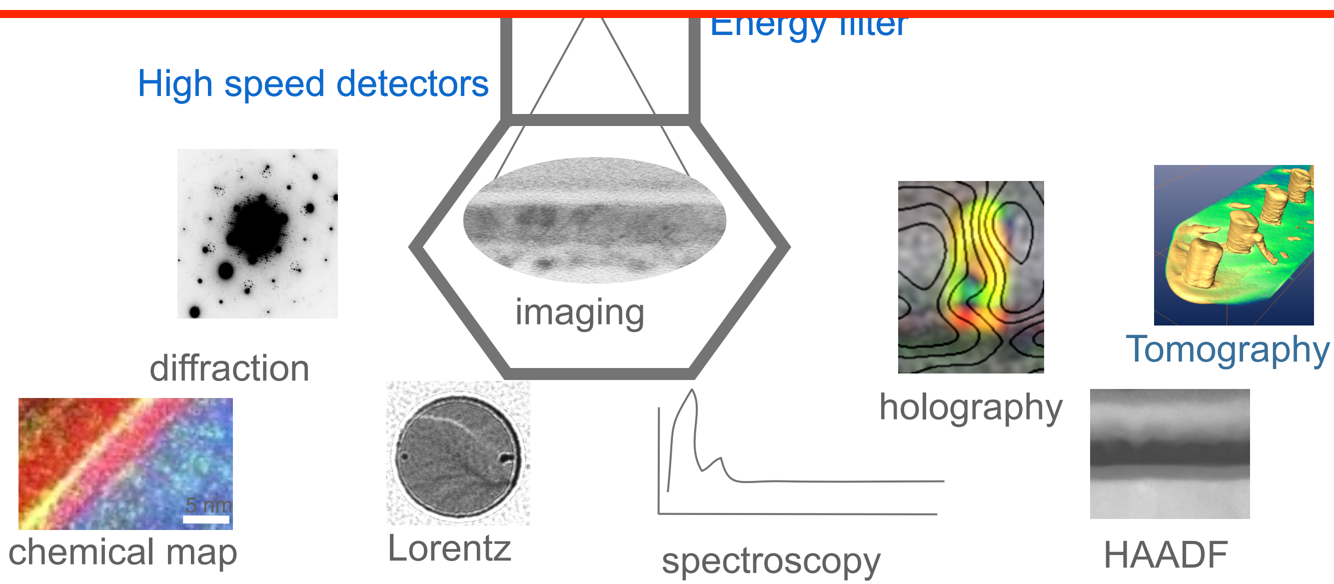
Materials Science and Engineering Dept, Northwestern Univ.

What can we do with TEM??



Need more than one instrument so that capabilities are not compromised

Design "electron optical beam lines" dedicated to specific applications

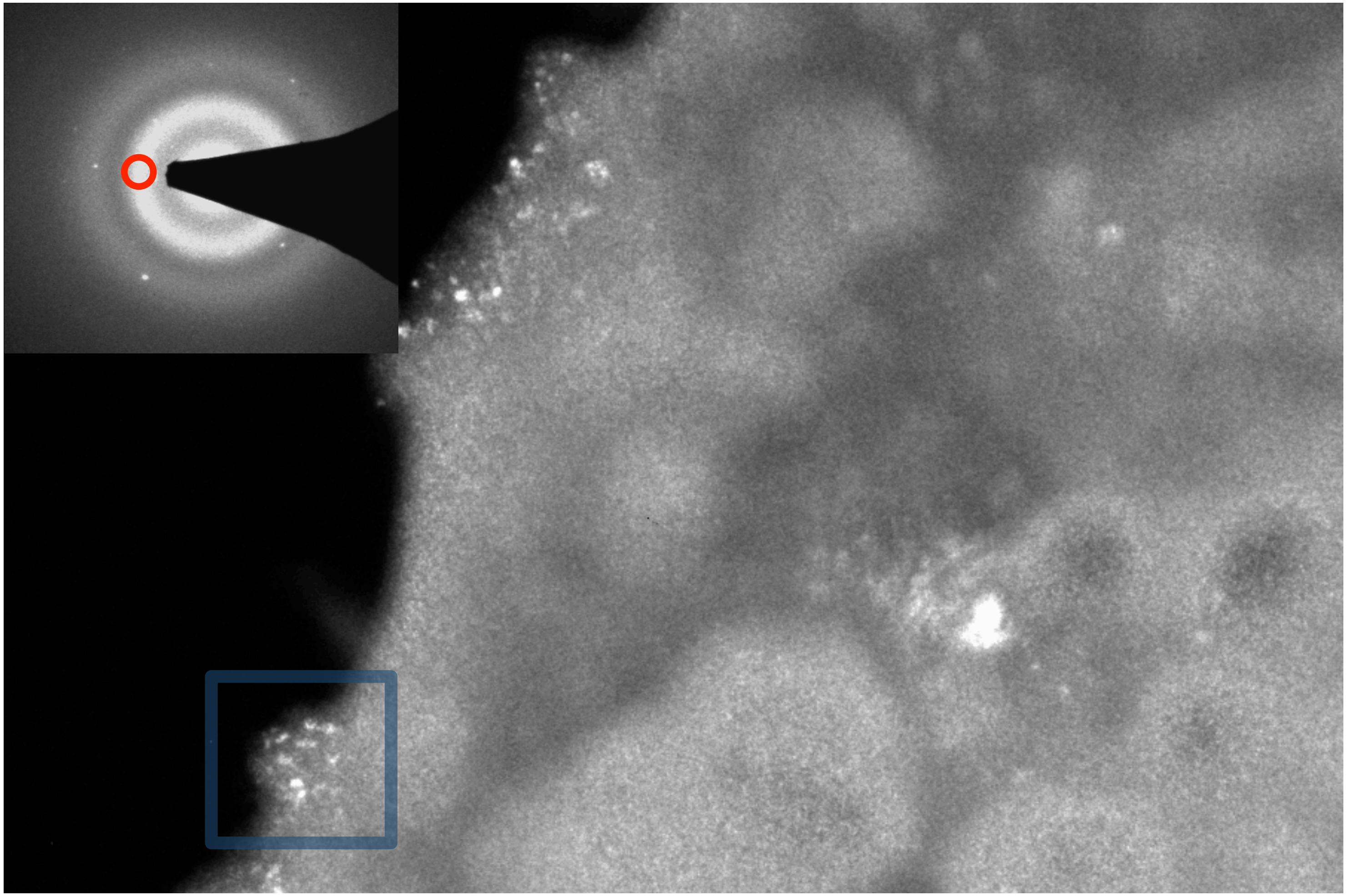


Imaging and diffraction: 2D and 3D Structure

Origin of image contrast in TEM

- Mass contrast
  - Absorption differences for different materials
- Diffraction Contrast
  - Contrast depends critically on diffraction conditions
- Phase Contrast
  - Contrast depends on phase shift of electrons passing through sample
  - High resolution electron microscopy – weak phase object approximation
    - $\Psi = e^{i\sigma V(r)} \approx 1 + i\sigma V(\mathbf{r})$
  - Lorentz microscopy
  - Electron Holography
- High-angle annular dark field (HAADF) imaging
  - Also known as scanning TEM (STEM) contrast
  - A function of atomic number

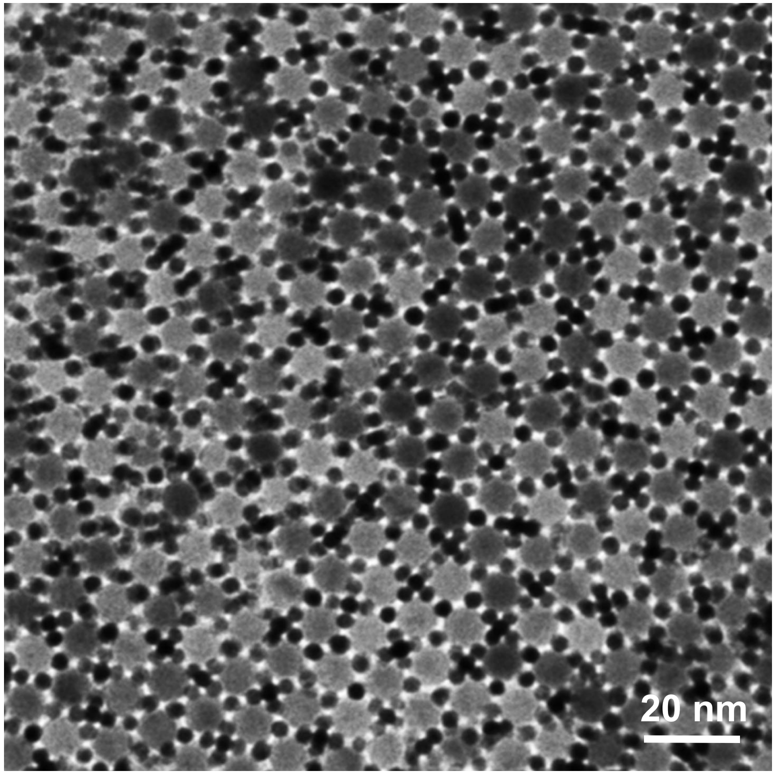
Partially-crystallized ZBLAN glass

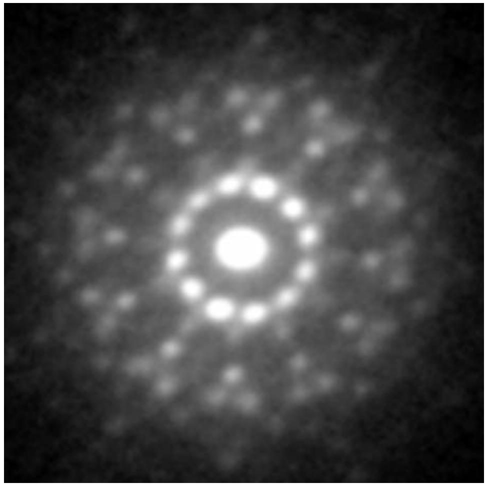


- Insert aperture to select defined region of the diffraction pattern. Contrast in image comes only from electrons diffracting within aperture

Image courtesy of Carlos Alvarez and Yuzi Liu

Au/Fe_3O_4 nanoparticle superlattice

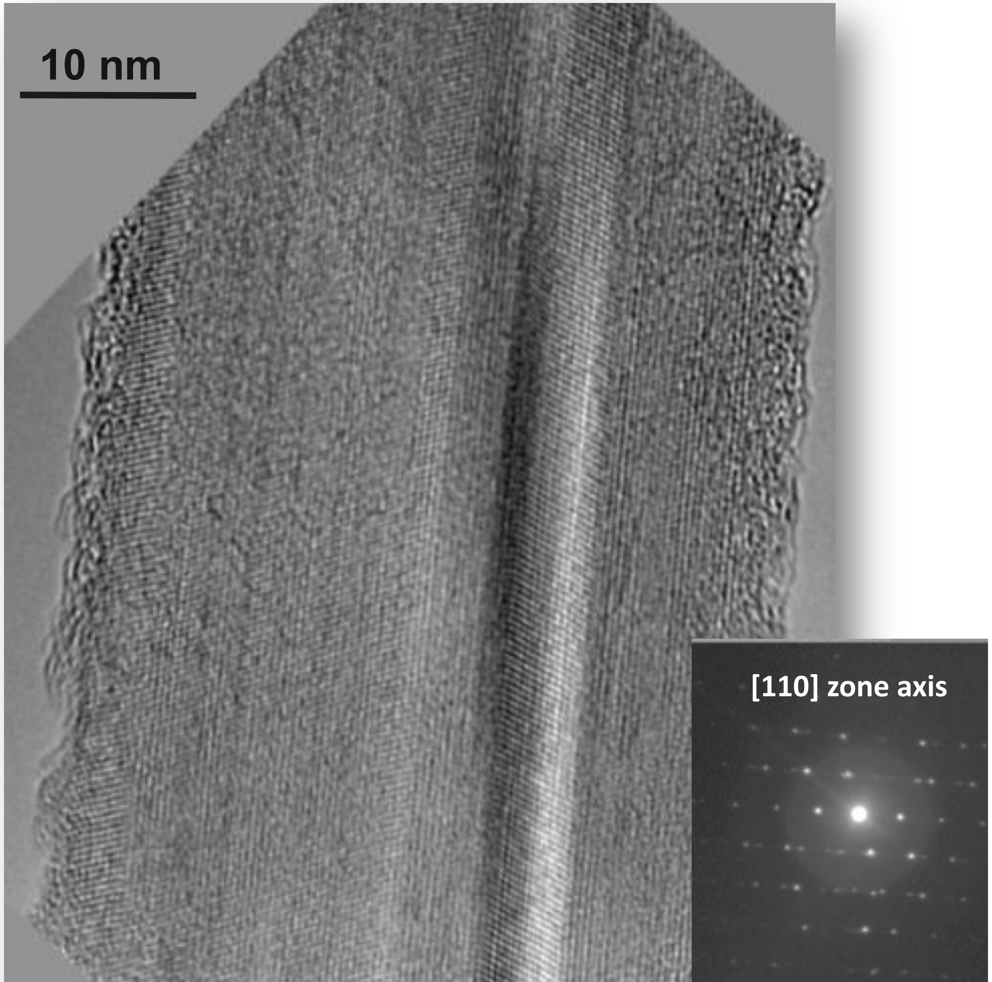


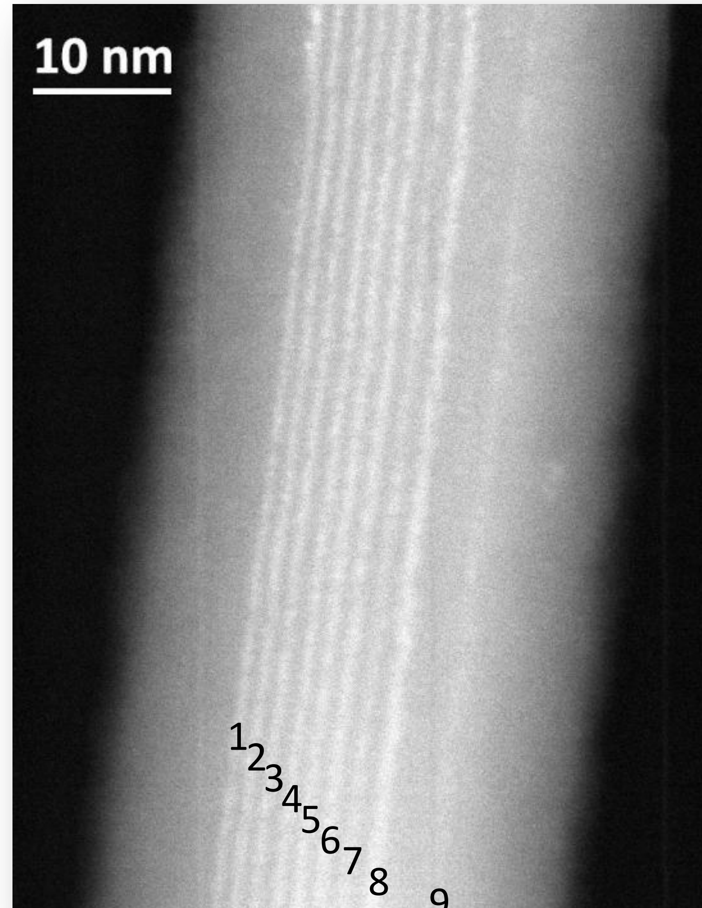


- Nanocrystals self-assemble to form quasicrystal structure

D.V. Talapin, E.V. Shevchenko, M. I. Bodnarchuk, X. C. Ye, J. Chen, and C.B. Murray, Nature **461**, 964 (2009).

Defective Si nanowire grown using Au catalyst

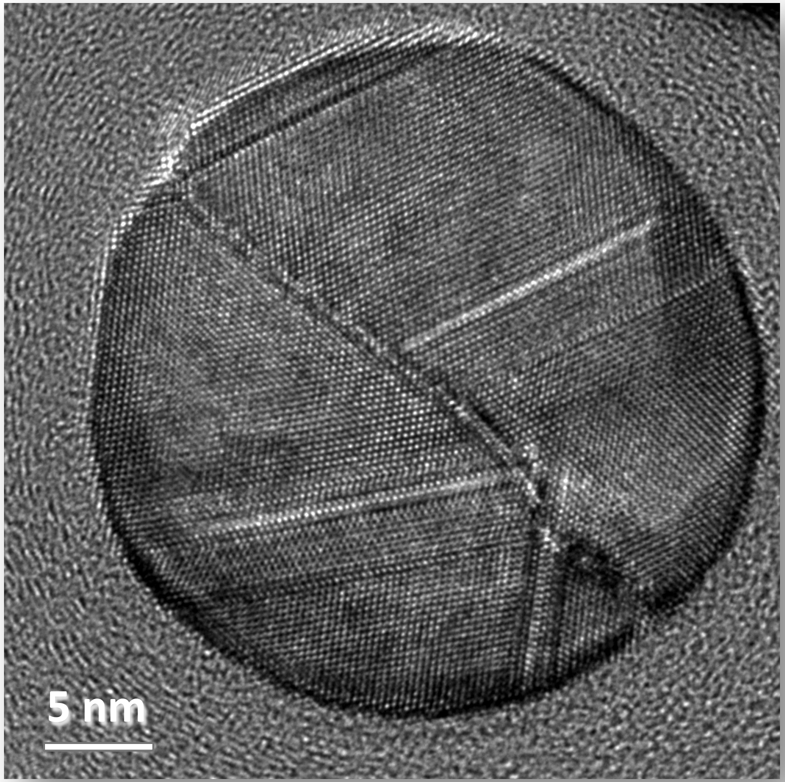


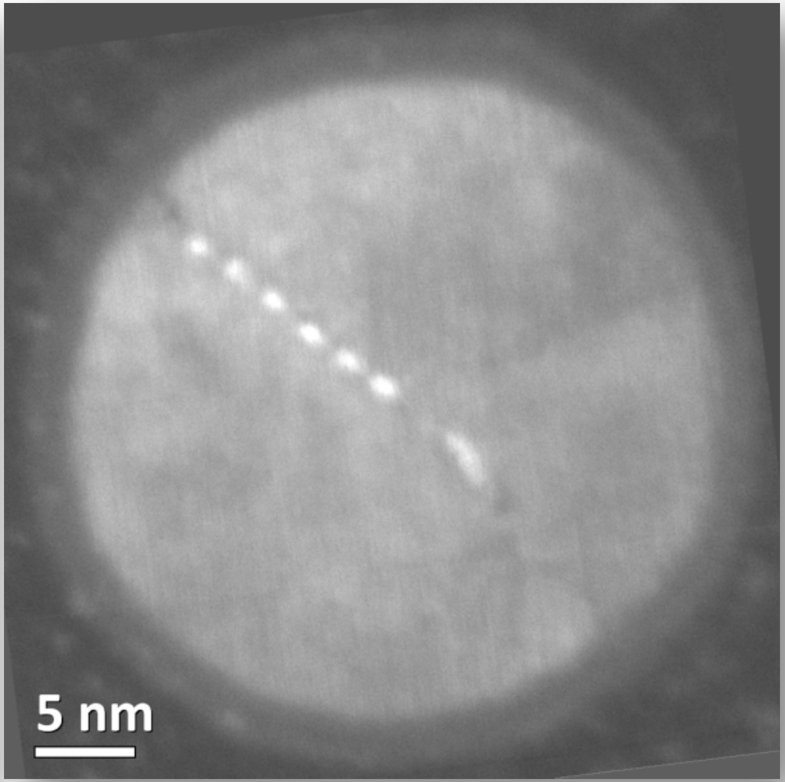


- Nanowire has a [110] growth direction
- Nine lines of high atomic number atoms can be seen using HAADF
- Atomic lines appear with an ordered arrangement

Courtesy of E Hemesath and L Lauhon, Northwestern University.

Gold atoms at a grain boundary

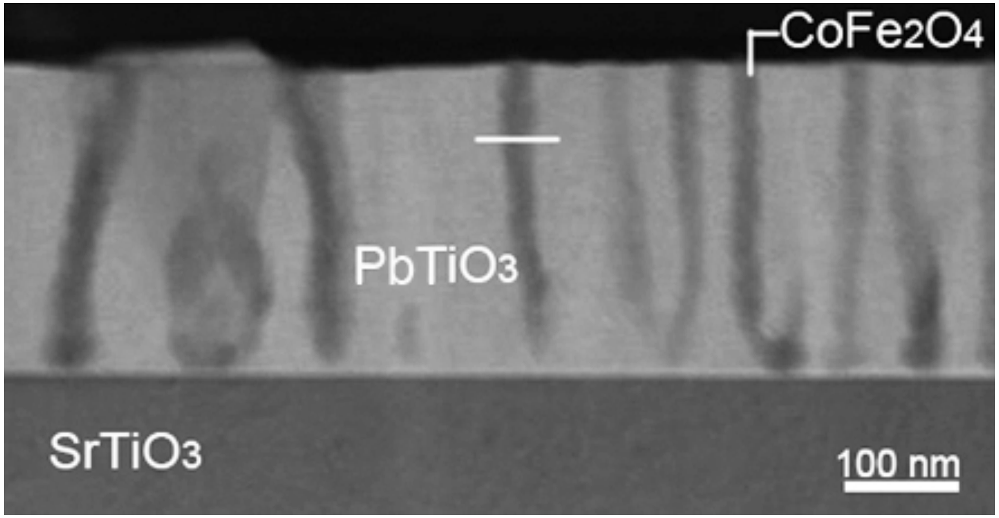




- Bicrystalline nanowire with an asymmetric [110] tilt boundary
- ~13° misorientation
- Axial twin planes are present in both crystals
- Array of Au columns at the grain boundary

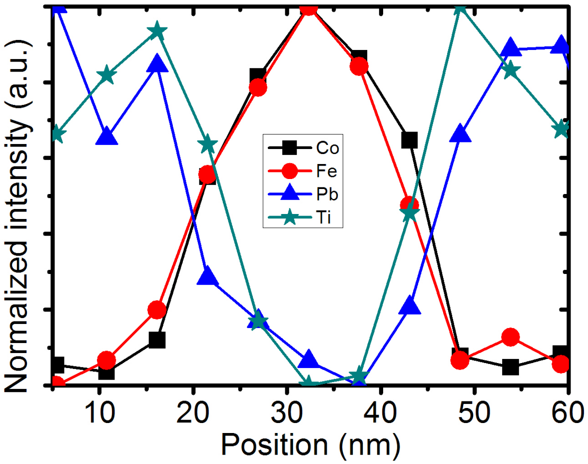
Courtesy of E Hemesath and L Lauhon, Northwestern University.
Cross-section sample prepared by D Schreiber and P Adusumilli

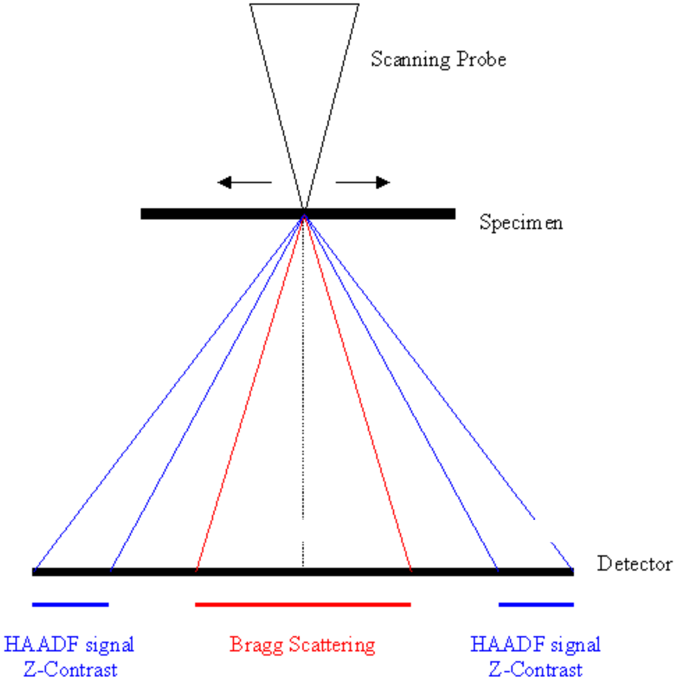
$CoFe_2O_4/PbTiO_3$ nanocomposite



STEM HAADF image

Mengchun Pan, Yuzi Liu and Guoren Bai

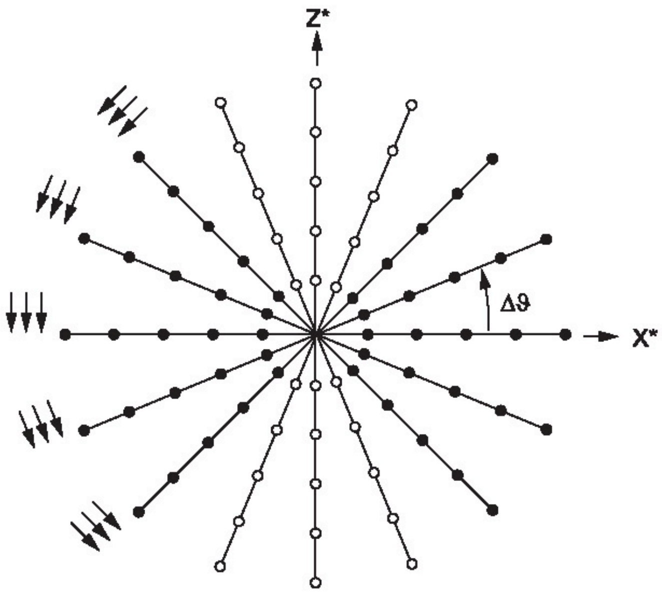




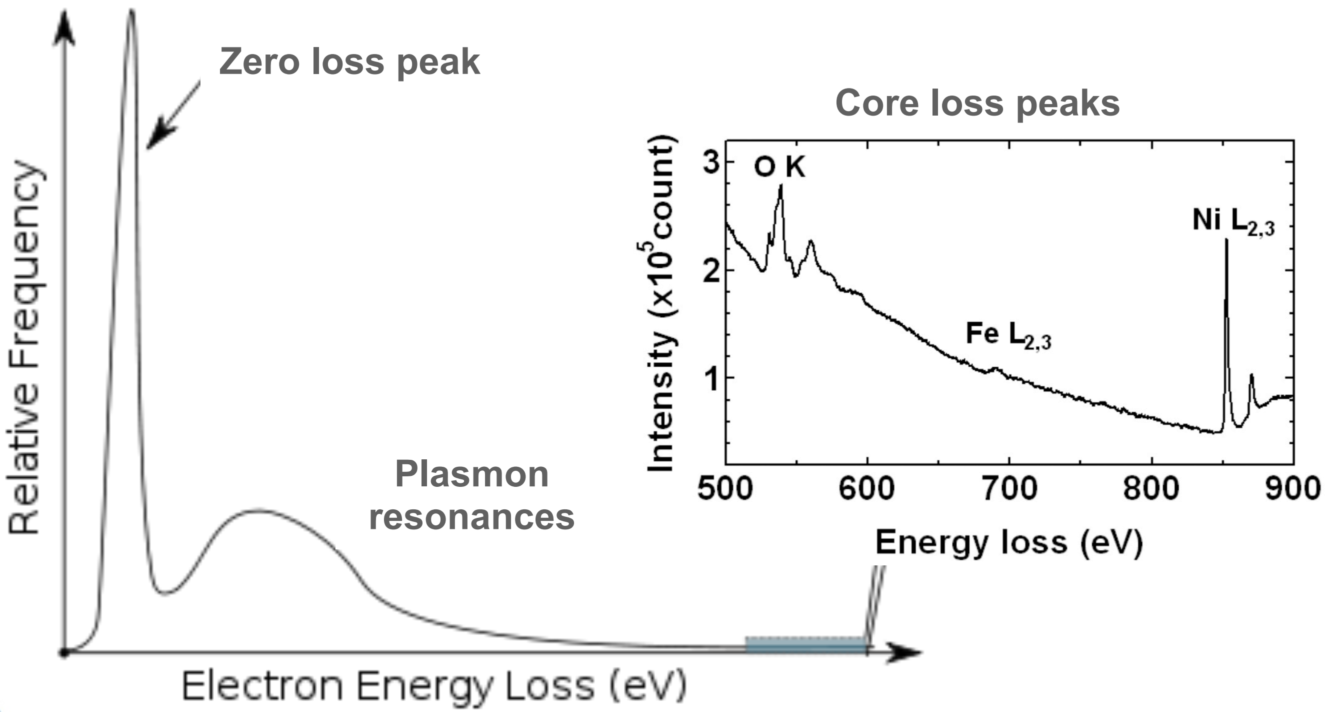
HAADF detects inelastically-scattered electrons

Electron tomography

- It is often the case that a two-dimensional view is not enough
- Three-dimensions is better!!
- Collect images over a large range of tilt angles
- Reconstruct using one of various methods to form 3D image of sample

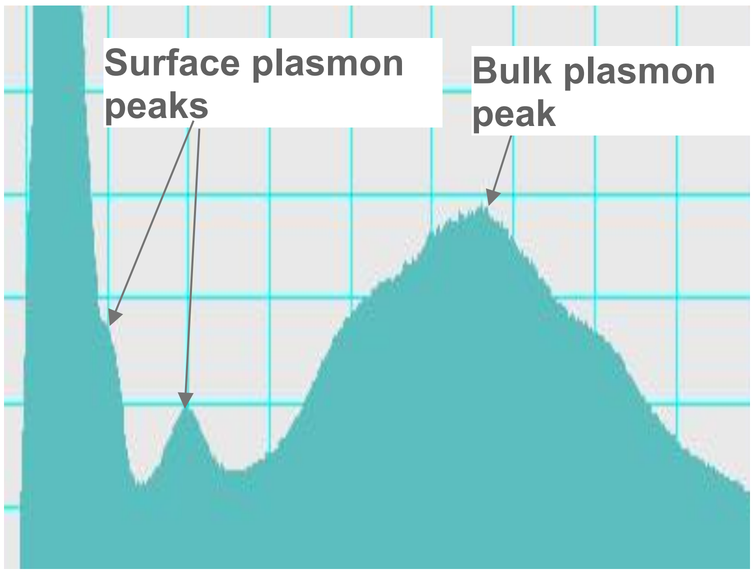


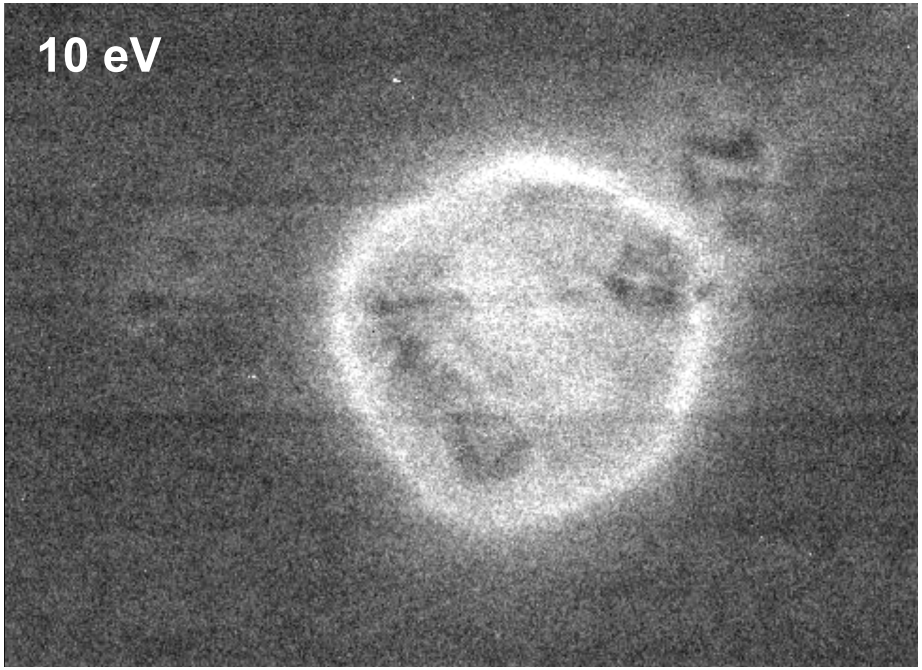
EELS and EFTEM



Core-shell nanoparticles

- 20 nm diameter Fe_3O_4 core with Ag shell
- Successive images are at energy loss shown on image
- Spatial extent of surface plasmon is clearly visible around Ag shell

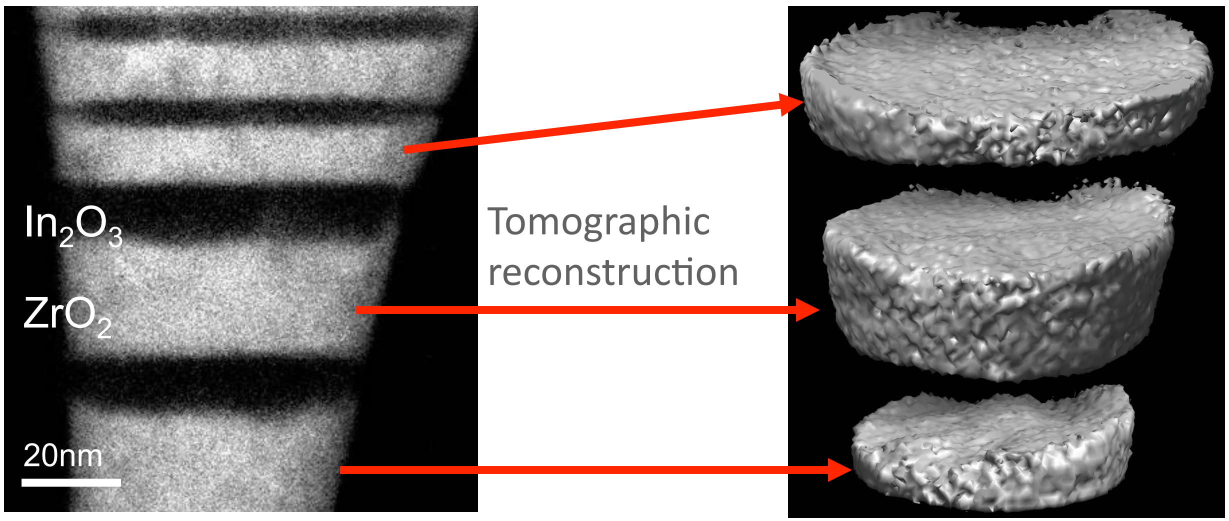




Collaboration with Sara Majetich and Alex Eggeman,
Carnegie Mellon University

Interface structure of ZrO_2/In_2O_3 Multilayer Films

- 3D elemental map derived from energy-filtered images of an interface
- 3D characterization of the interfaces of a In_2O_3 / ZrO_2 multilayer
  - ZrO_2 on In_2O_3: Rough interface on a nanometer scale
  - In_2O_3 on ZrO_2: Sharp interface with a step of one unit cell



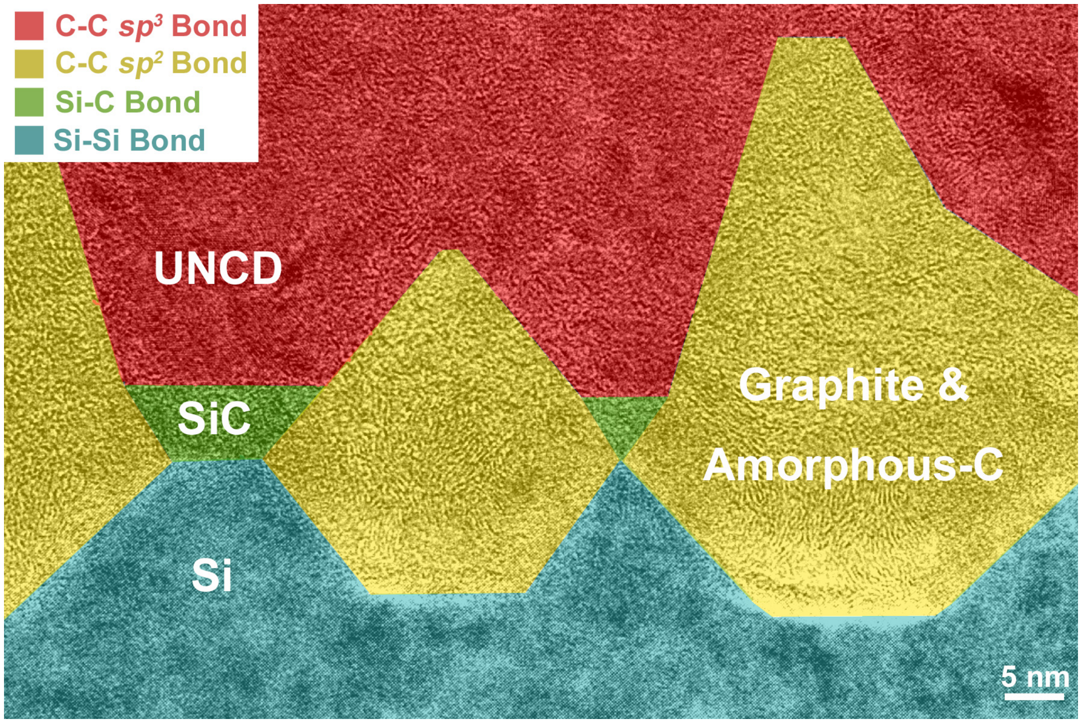
2D Zr Elemental Map

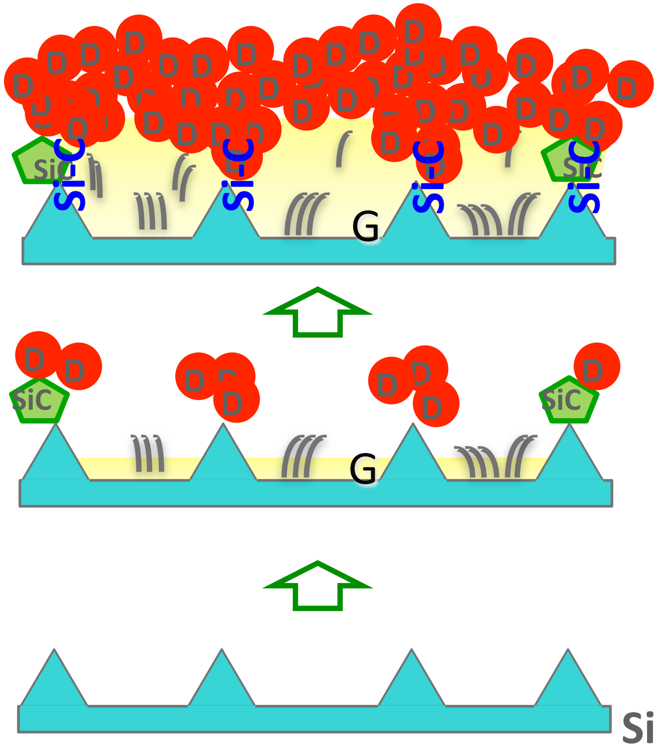
3D elemental map of Zr

Xiaoyan Zhong, Bernd Kabius, Jeff Eastman, Dillon Fong

Nucleation of ultrananocrystalline diamond films on Si

◆ EFTEM mapping using C K edge identified inhomogenous distribution of graphite, amorphous C and SiC at ultrananocrystalline diamond (UNCD)/Si interfaces and led to proposed mechanism for nucleation of UNCD films on Si



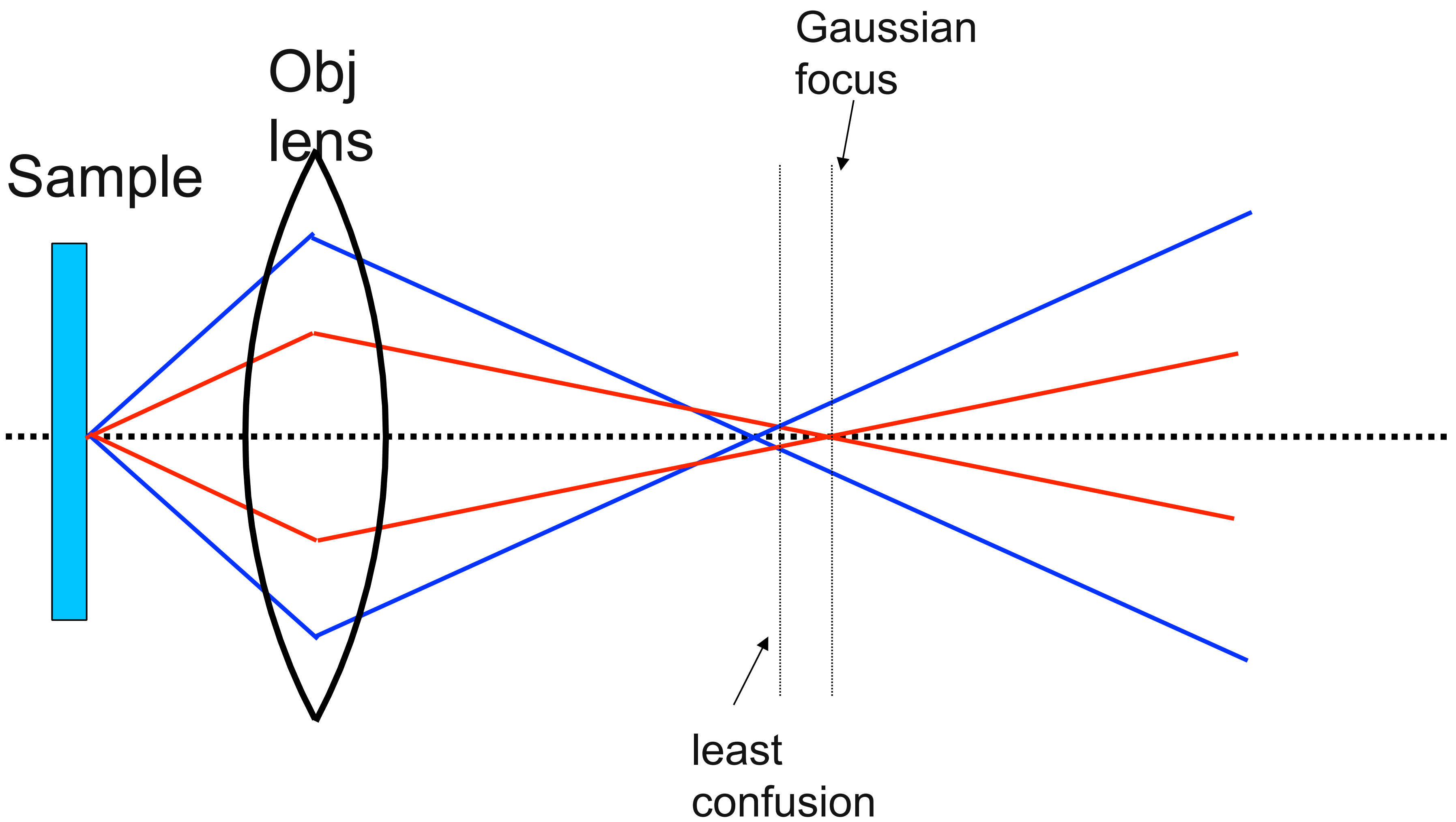


Xiaoyan Zhong, Bernd Kabius,

Y.C. Chen, X. Y. Zhong et al.
Appl. Phys. Lett. 92, 133113 (2008)

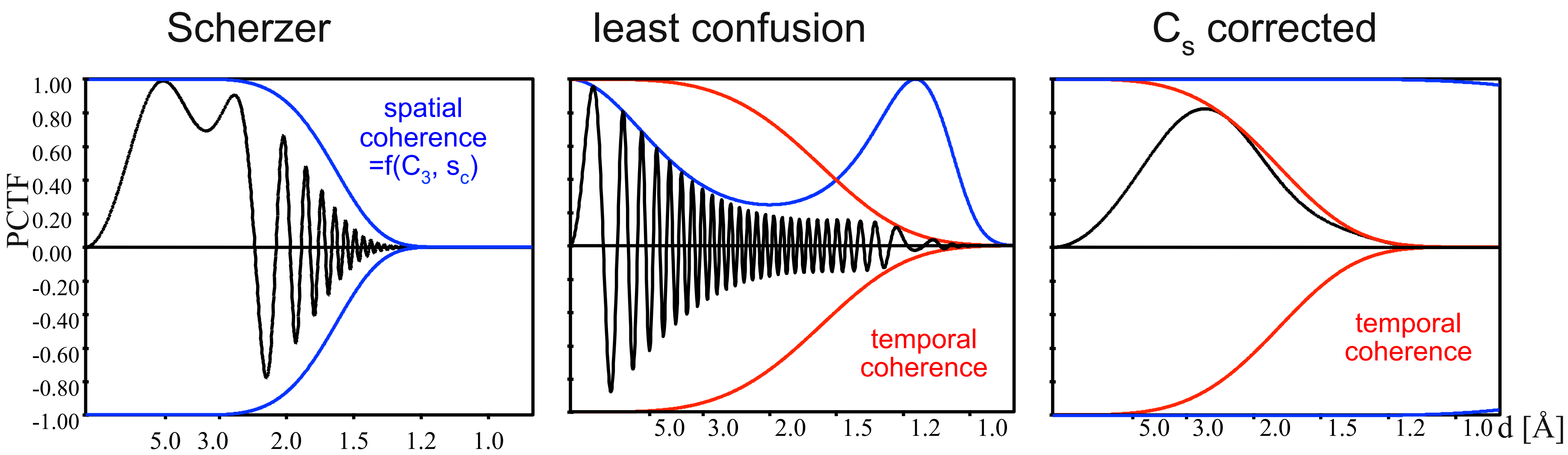
Aberration-correction

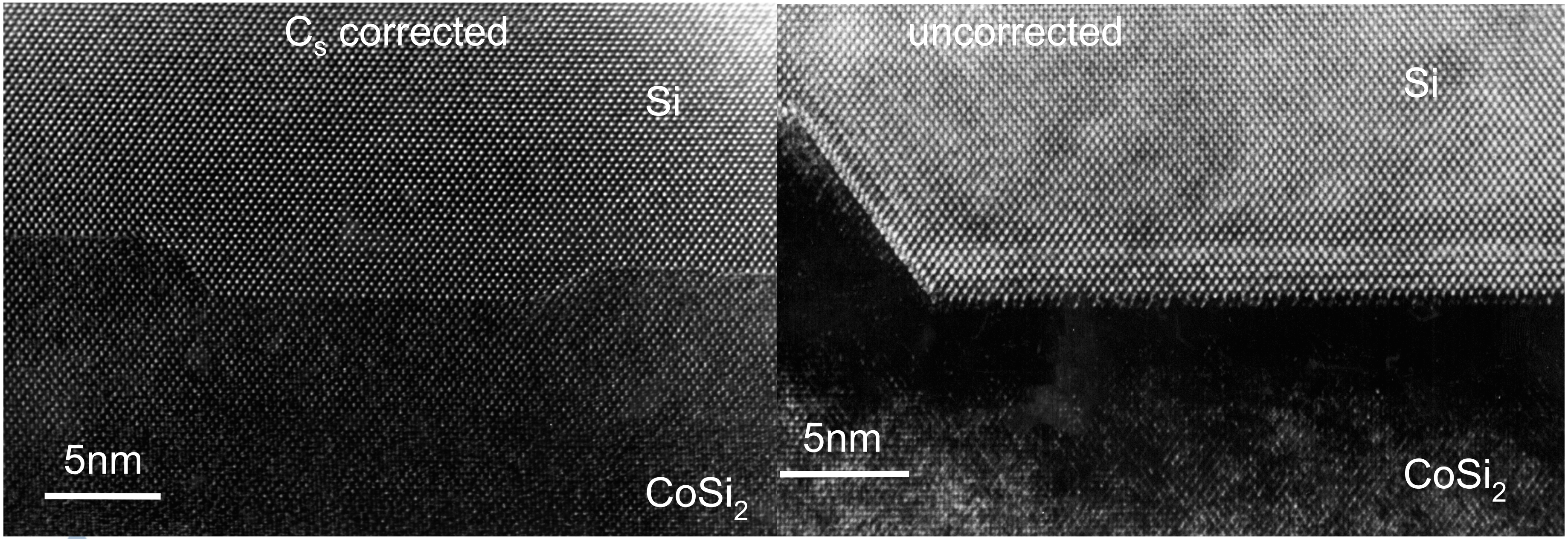
Spherical Aberration: C_s



Slide courtesy of Bernd Kabius

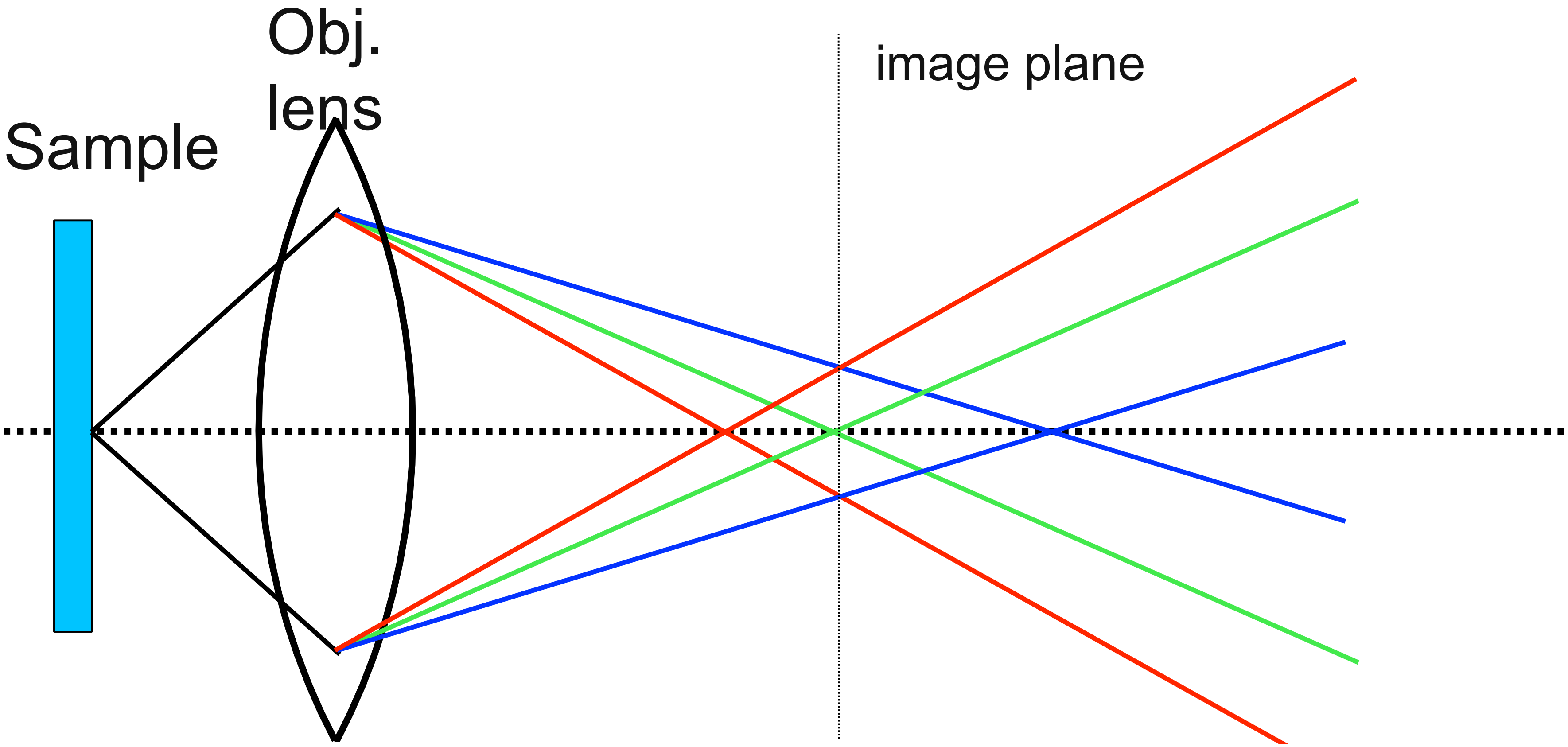
C_s correction





Slide courtesy of Bernd Kabius

Chromatic aberration: C_c

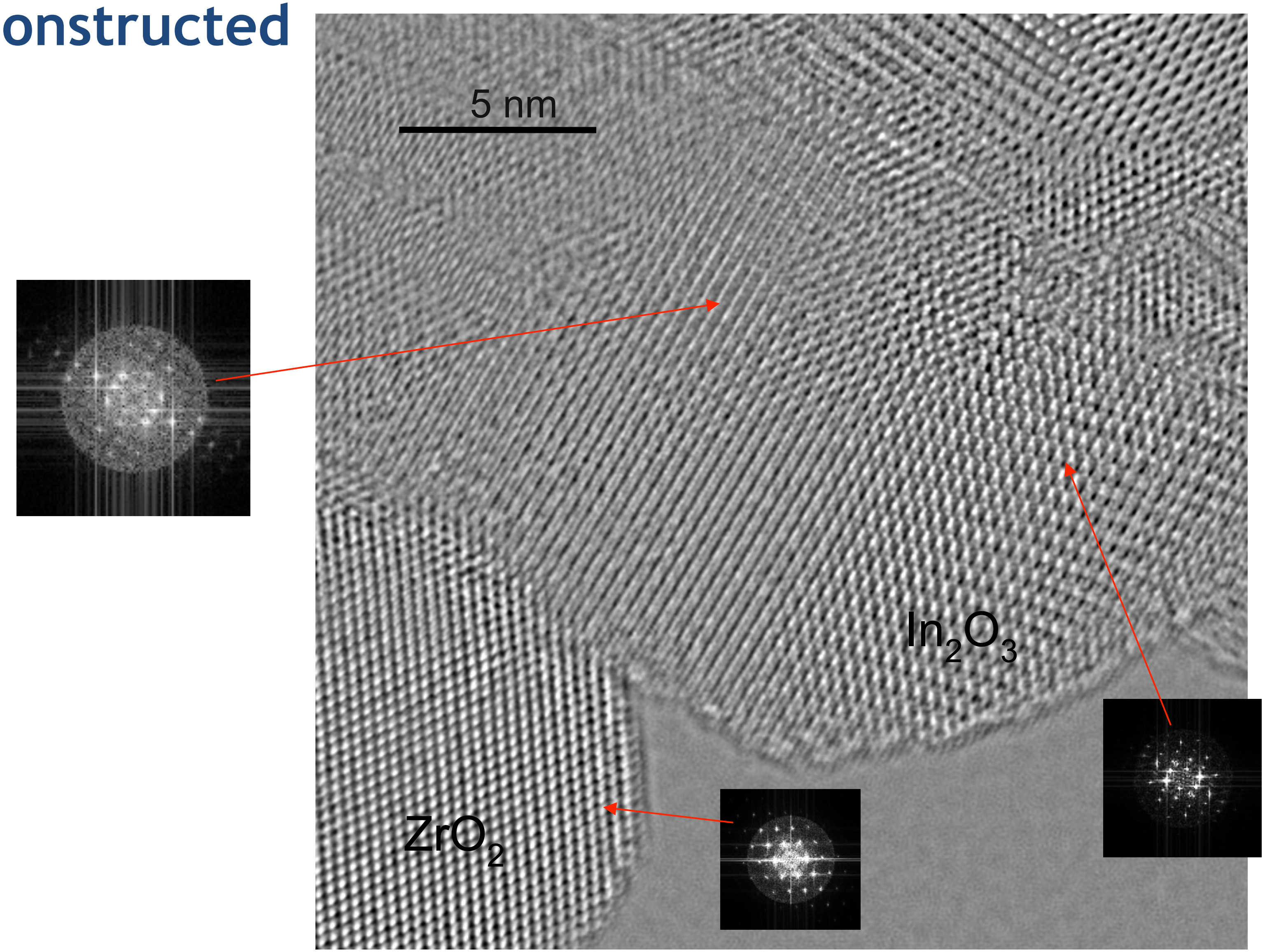


$$E_t = \exp\left[\frac{-(0.5\,\pi\,\lambda\,d_s)^2 * q^4}{1.0 + (\pi\,\lambda\,s_c\,d_s)^2}\right]$$

$$d_s = \sqrt{\left(d_s^Q \frac{2\,\Delta I_Q}{I_Q}\right)^2 + \left(d_E^Q \frac{\Delta E_Q}{E_Q}\right)^2 + \left(C_c \sqrt{\left(\frac{\Delta E}{E}\right)^2 + \left(\frac{\Delta H}{H}\right)^2 + \left(\frac{2\,\Delta I}{I}\right)^2}\right)^2}$$

Slide courtesy of Bernd Kabius

ZrO_2 / In_2O_3 on YSZ: C_c corrected, 80kV
Phase reconstructed



Slide courtesy of Bernd Kabius

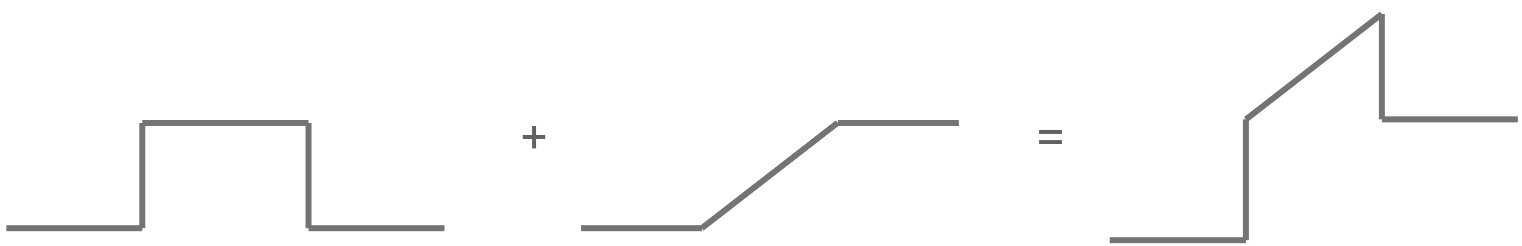
Imaging Electric and Magnetic Fields

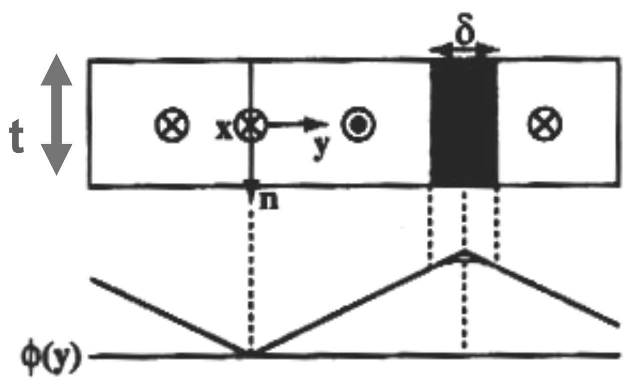
Making use of phase shift to image fields

The phase ϕ of an electron wave (wavelength λ) is modified when passing through a sample in the presence of electromagnetic potentials V and A ($B = \nabla\times A$)

$$\phi = \frac{\pi}{\lambda E_t}\int_L V(r_\perp, z)dz - \frac{e}{\hbar}\int_L A(r_\perp, z)dz$$

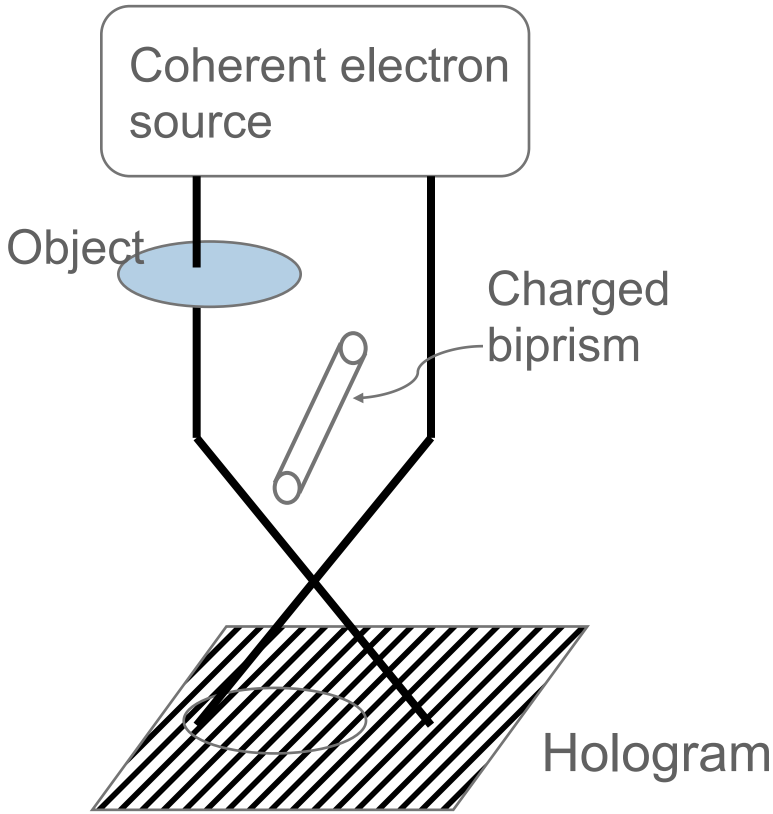
E_t – total energy of the beam electrons; z – coordinate along the optic axis; $r_\perp$- radial coordinate in the sample plane

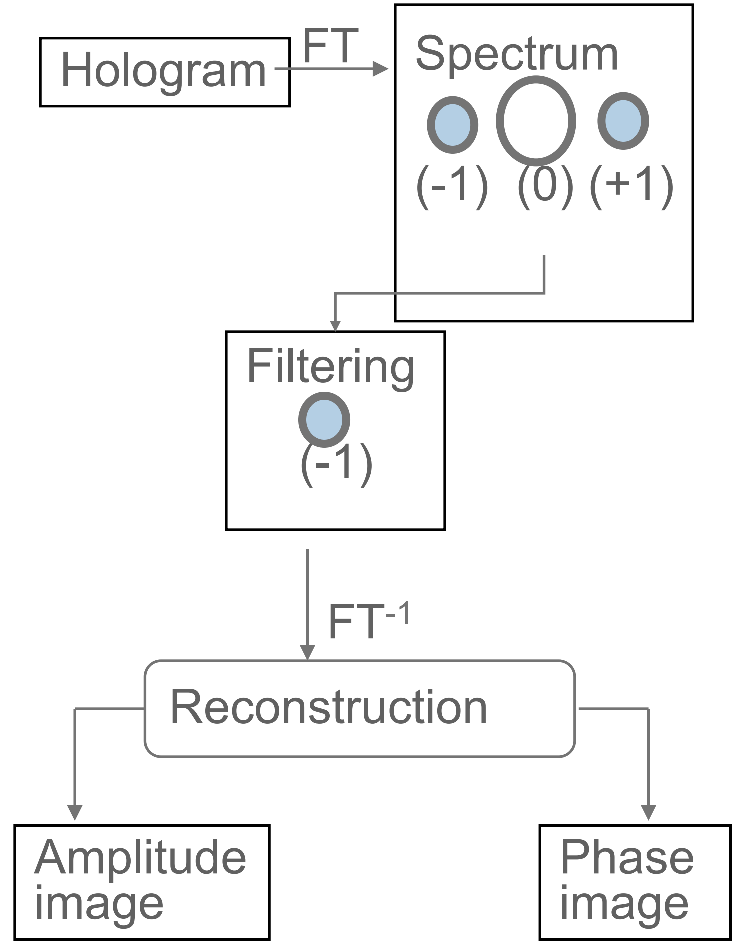




$$\boxed{\nabla\phi = \frac{e}{\hbar} B_\perp t\hat{e}}$$

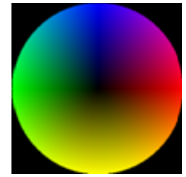
Electron holography

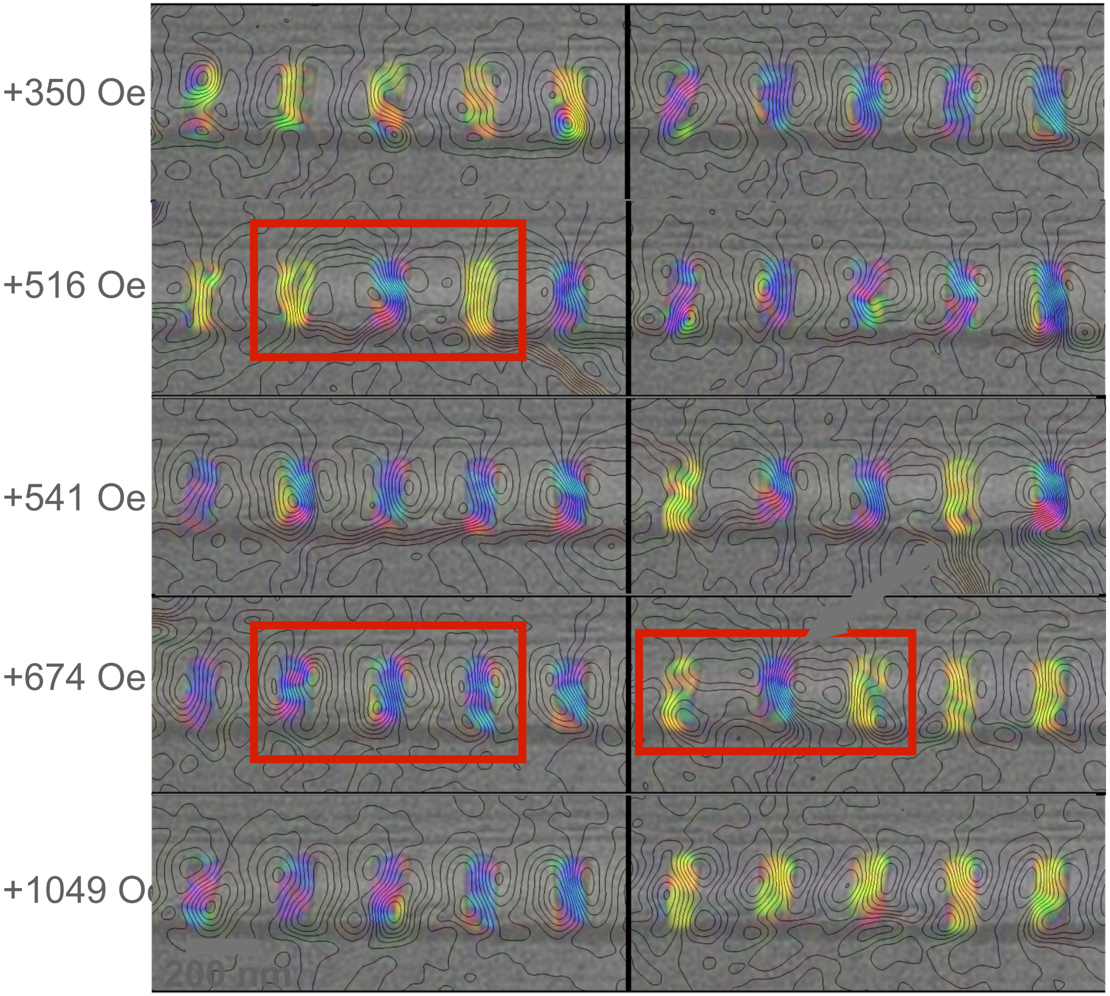




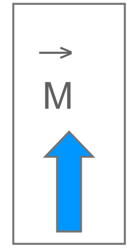
- adjacent interference fringes are separated by a flux quantum, h/*e*
- Images are non-trivial to interpret

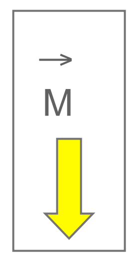
Ni pillars

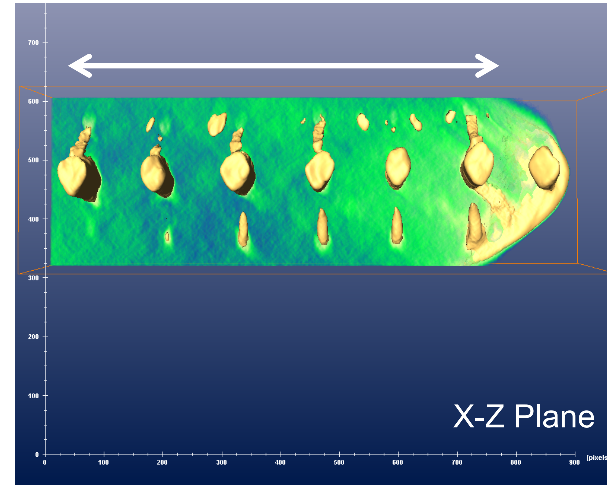


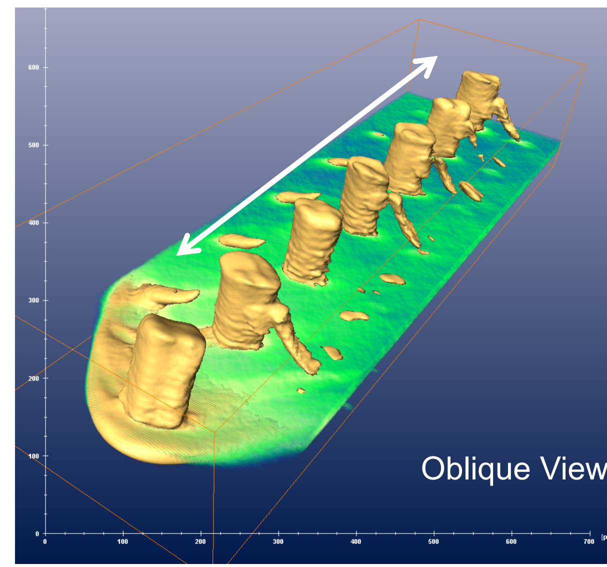


Remanent state magnetic induction maps for Ni pillars after application of different applied fields



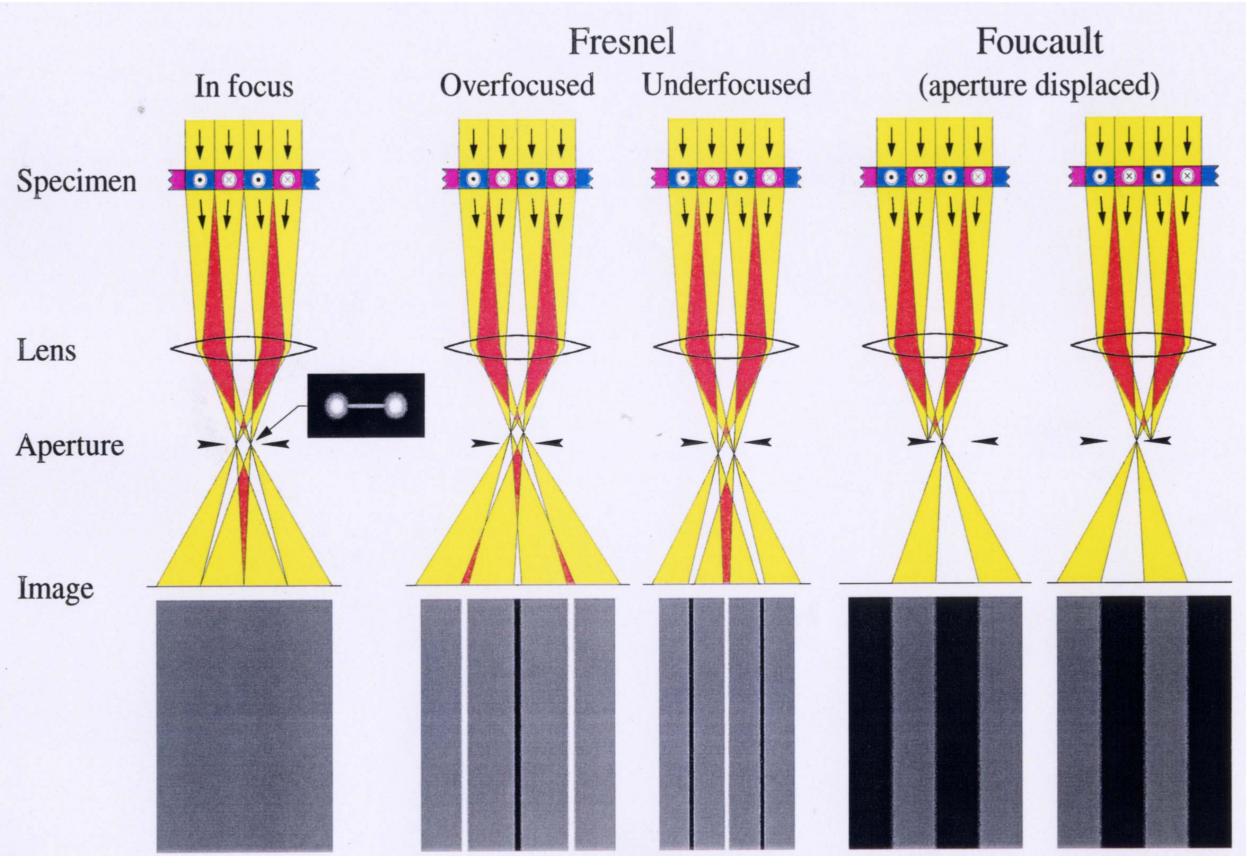


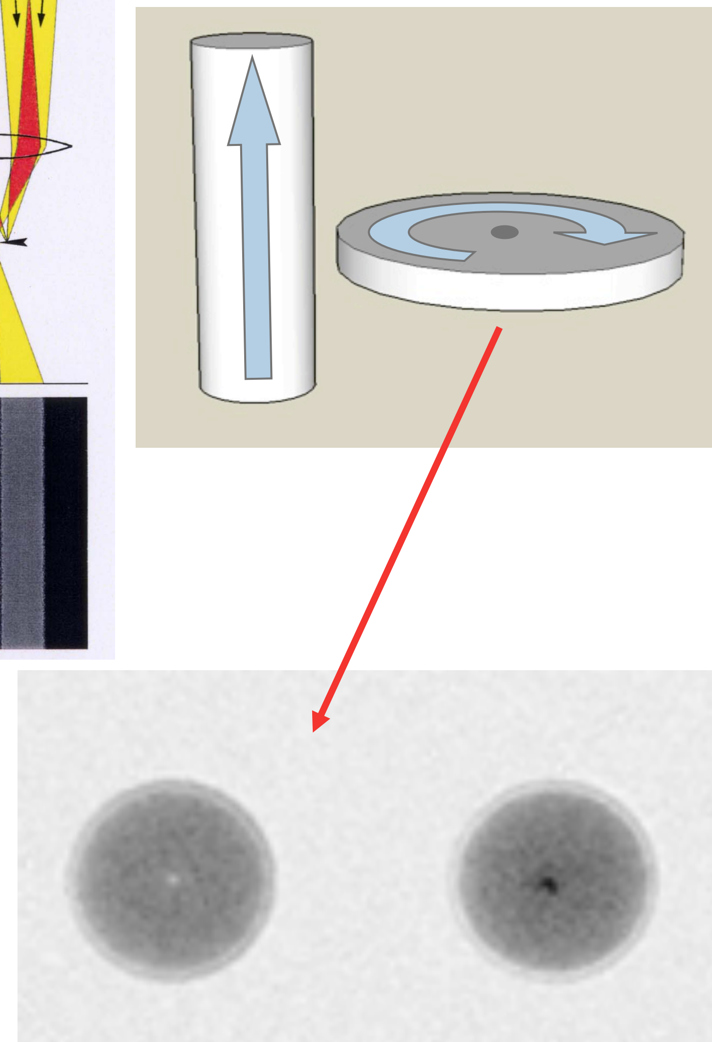




Bromwich et al., Nanotechnology **17**, 4367 (2006)

Lorentz TEM

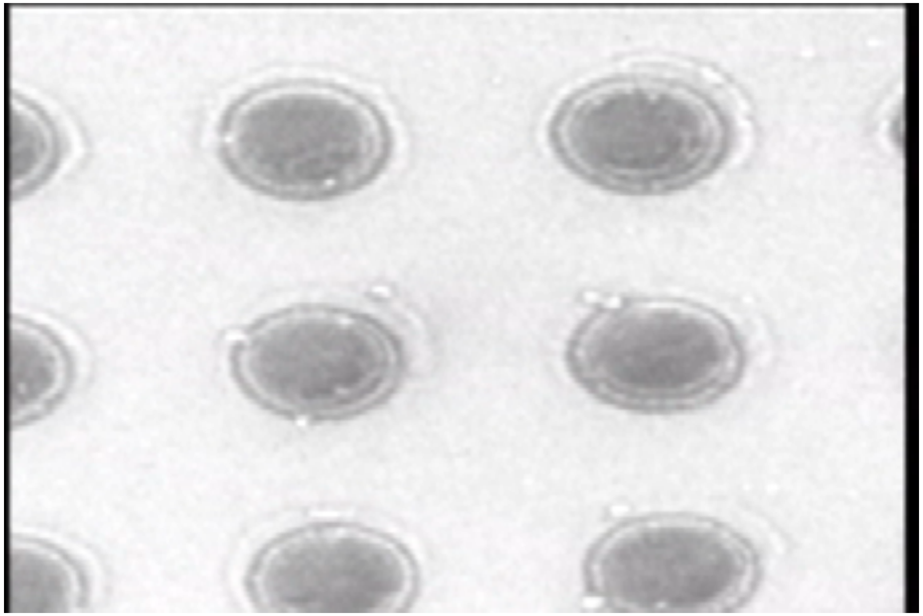




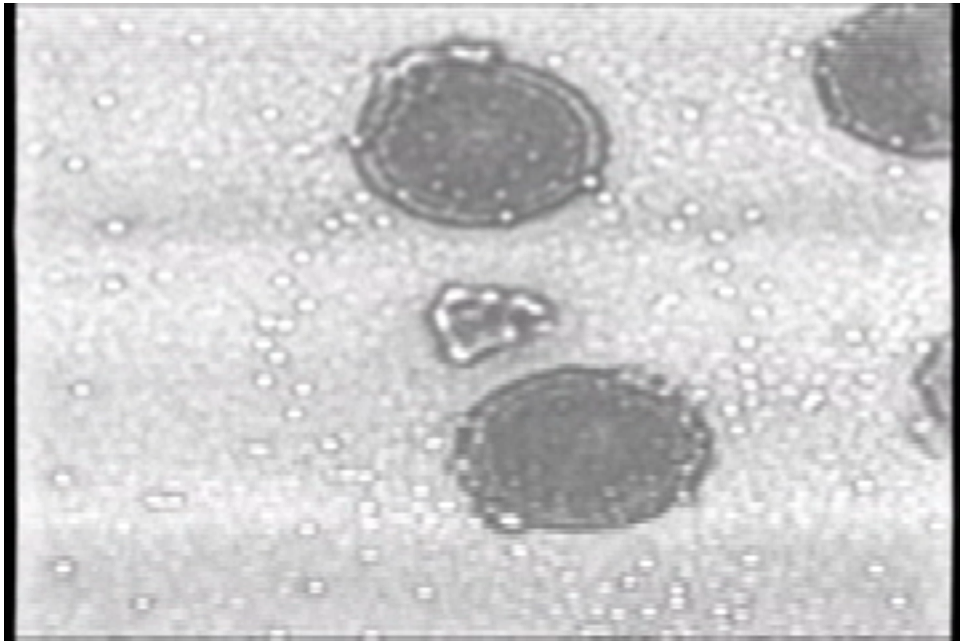
- Field applied in-situ:
  - Using magnetizing coils in a sample holder
  - By tilting sample into lens field

- Time resolution not good: can image time-averaged behavior

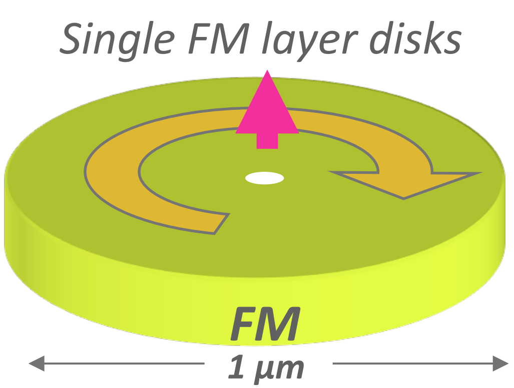
Reversal mechanisms in NiFe and NiFe/IrMn disks

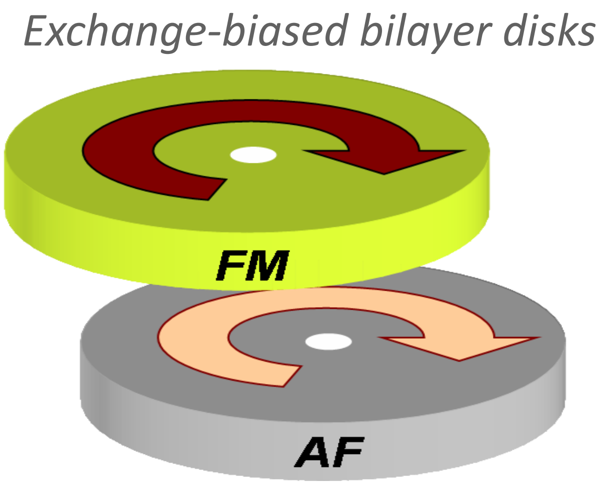


Single layer NiFe disk



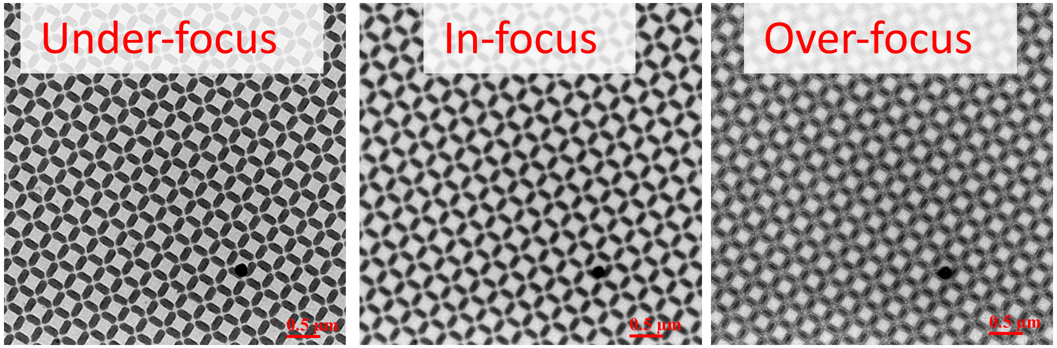
Bilayer NiFe/IrMn disk





M. Tanase et al., PRB 79, 014436 (2009)

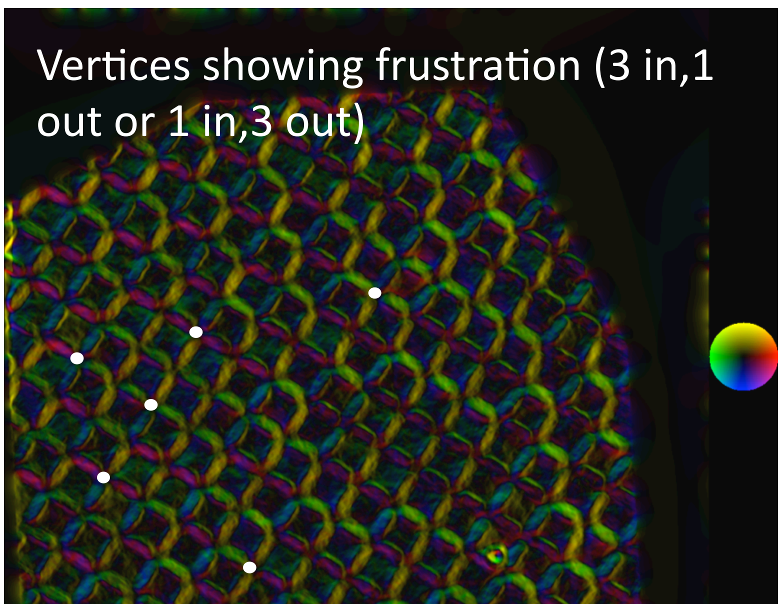
Spin ice structure

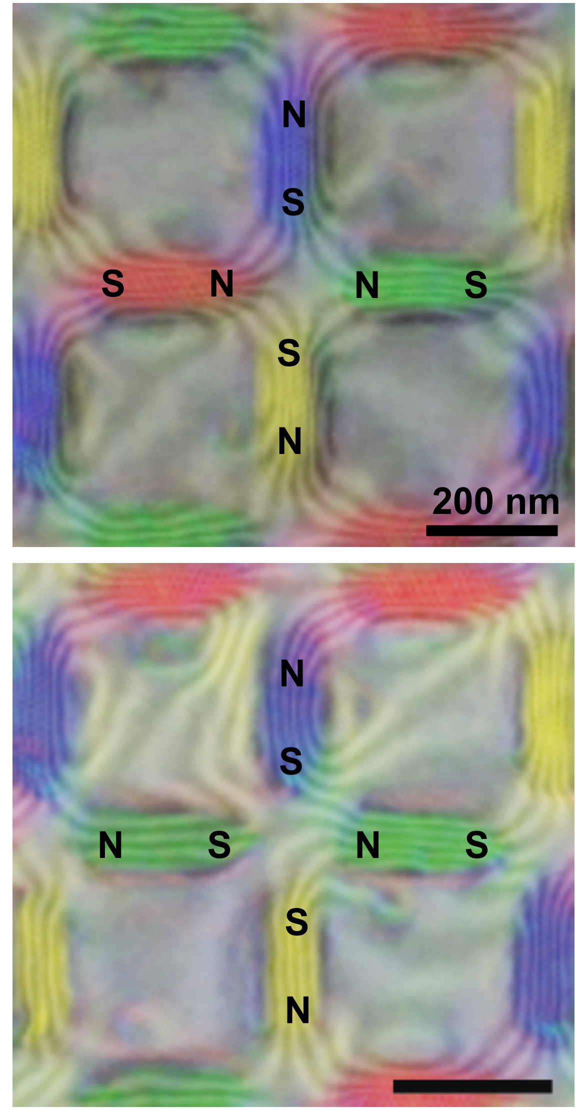


Array of NiFe stadia: 200 nm long

"Transport of Intensity" equation

$$\nabla_{\perp} \cdot \left[I(r_{\perp}, z) \nabla_{\perp} \phi(r_{\perp}, z) \right] = -k \partial_z I(r_{\perp}, z)$$

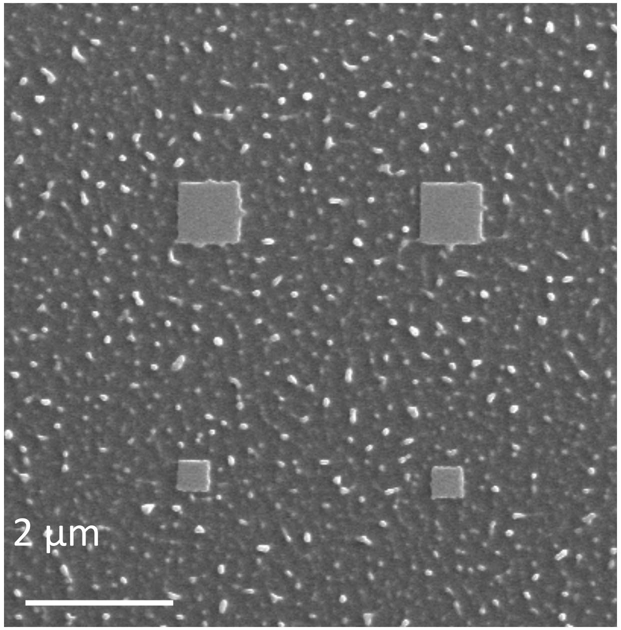




Images showing standard vertex obeying spin ice rule (L) and vertex showing emergent magnetic monopole (R)

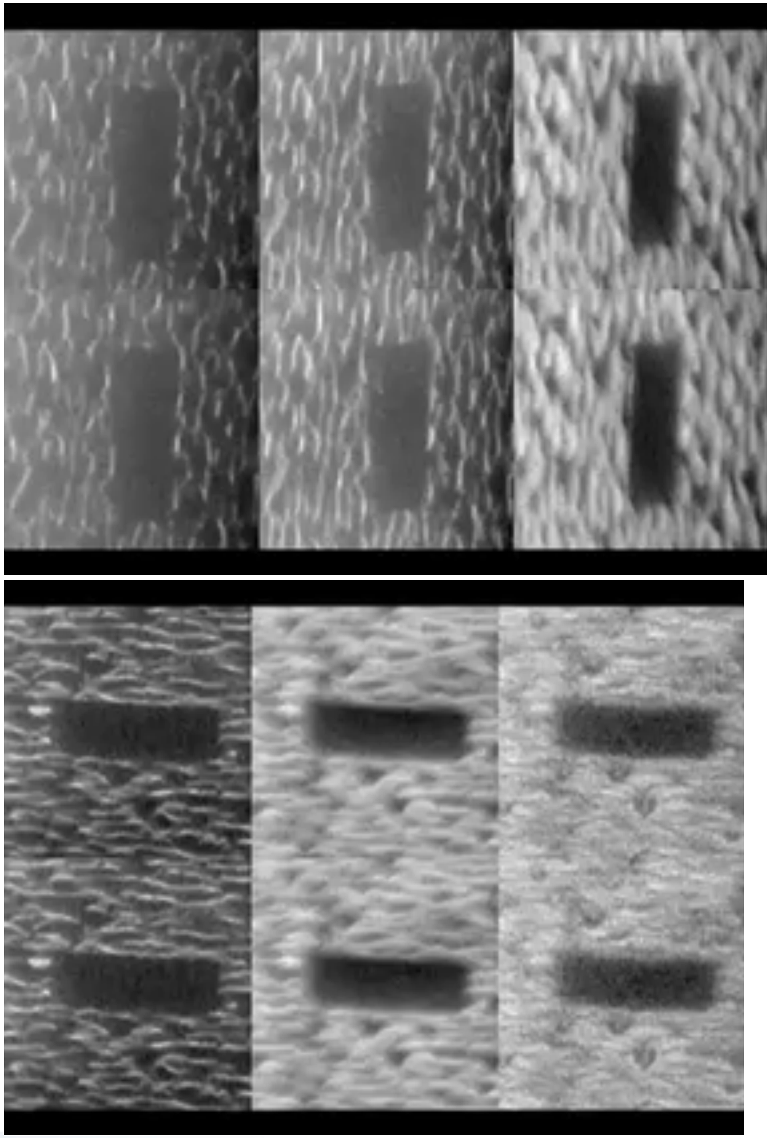
C Phatak et al., Phys. Rev. B 83, 174431 (2011)

Vector field tomography of Permalloy square

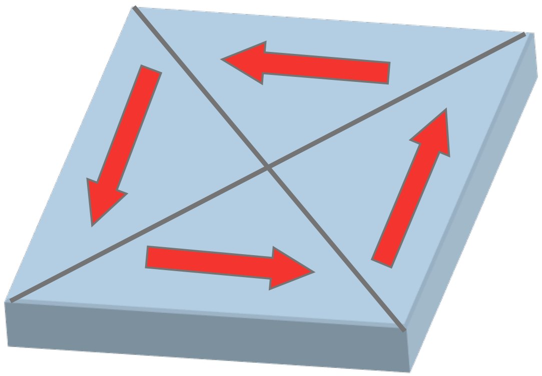


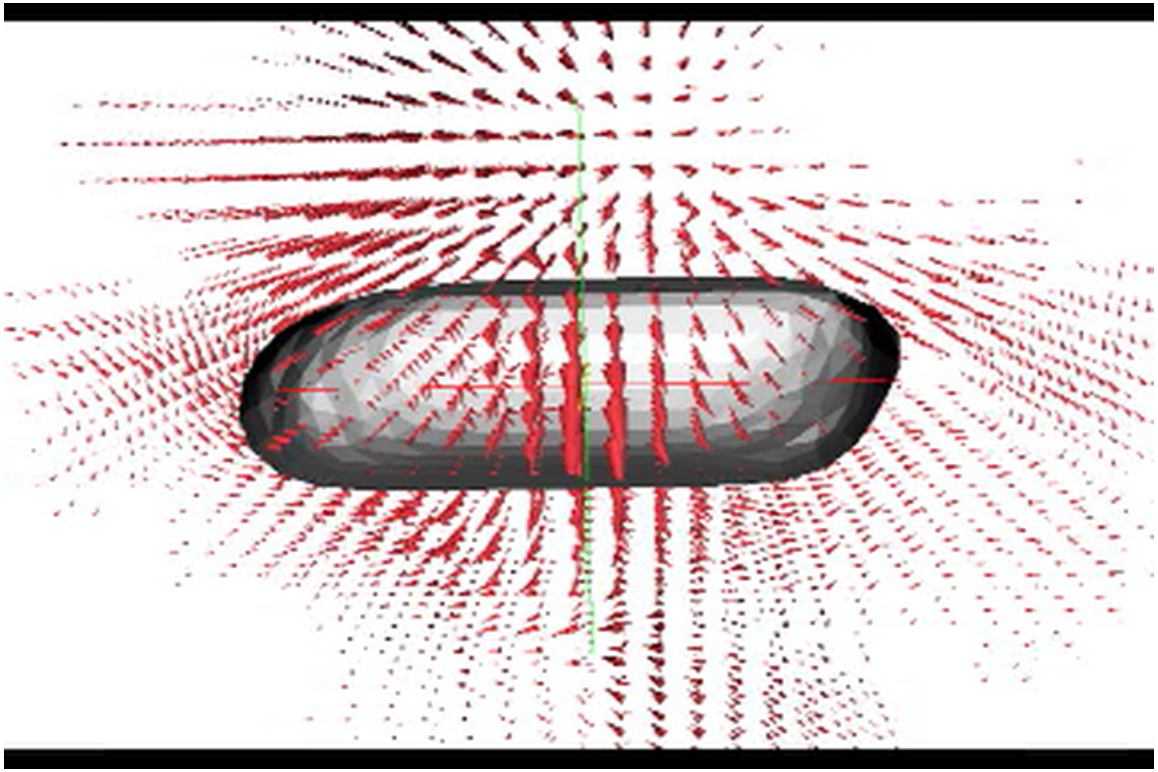
- Structures patterned using direct FIB milling of $Cr/Ni_{80}Fe_{20}$ film deposited on SiO membrane

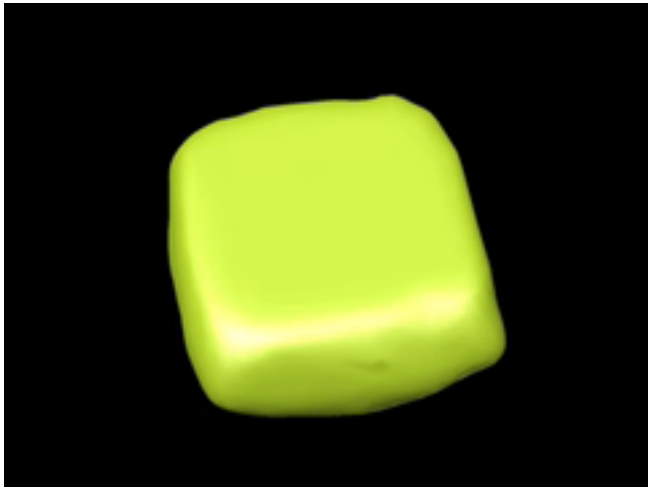
- Record four tomography tilt series, with three images at each angle
  - x; x/flipped; y; y/flipped



Scalar and vector tomography reconstructions





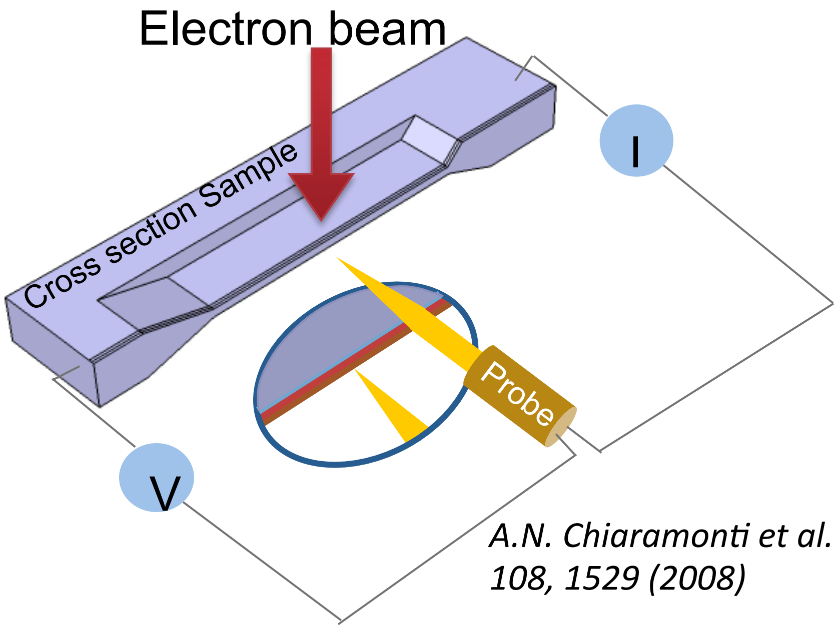


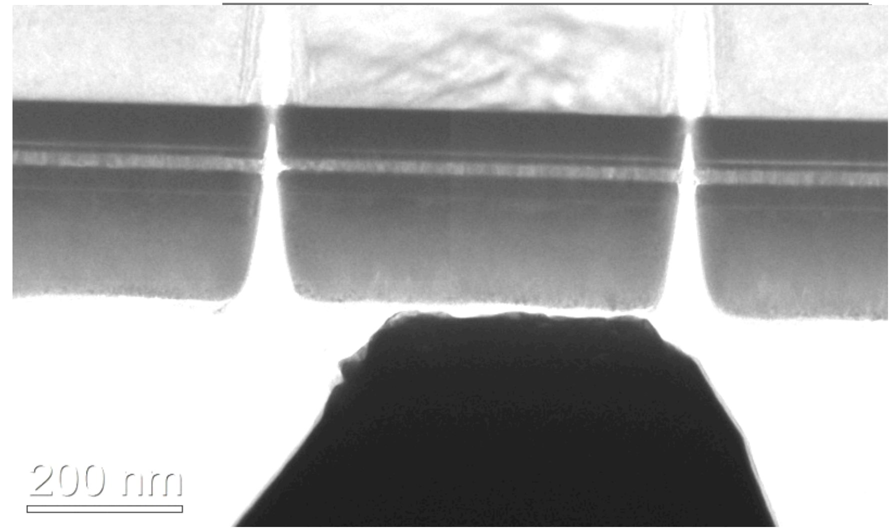
- Use Transport of Intensity Equation formalism to reconstruct scalar and magnetic vector potentials

C D Phatak, A K Petford-Long and M De Graef, PRL **104**, 253901 (2010).

Measuring local transport behavior

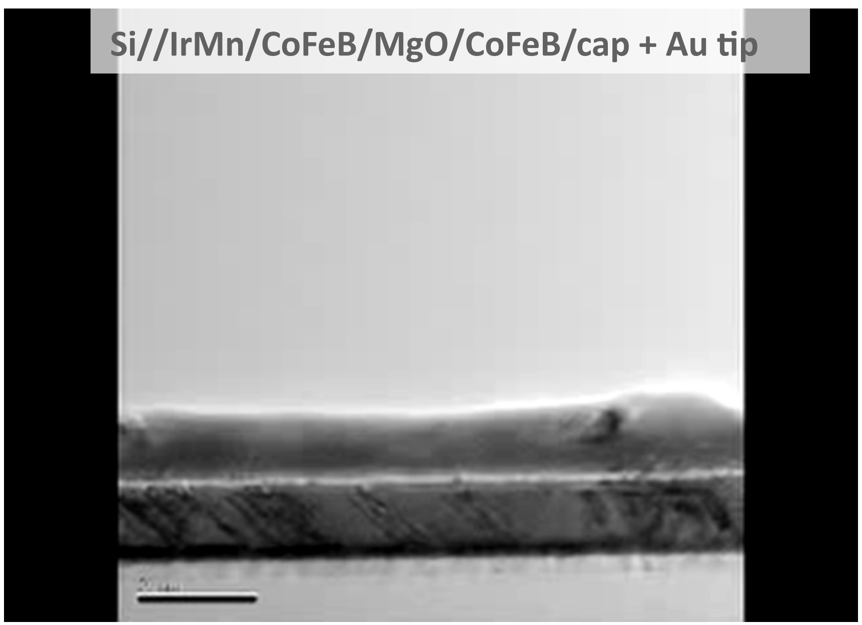
Local Transport Behavior

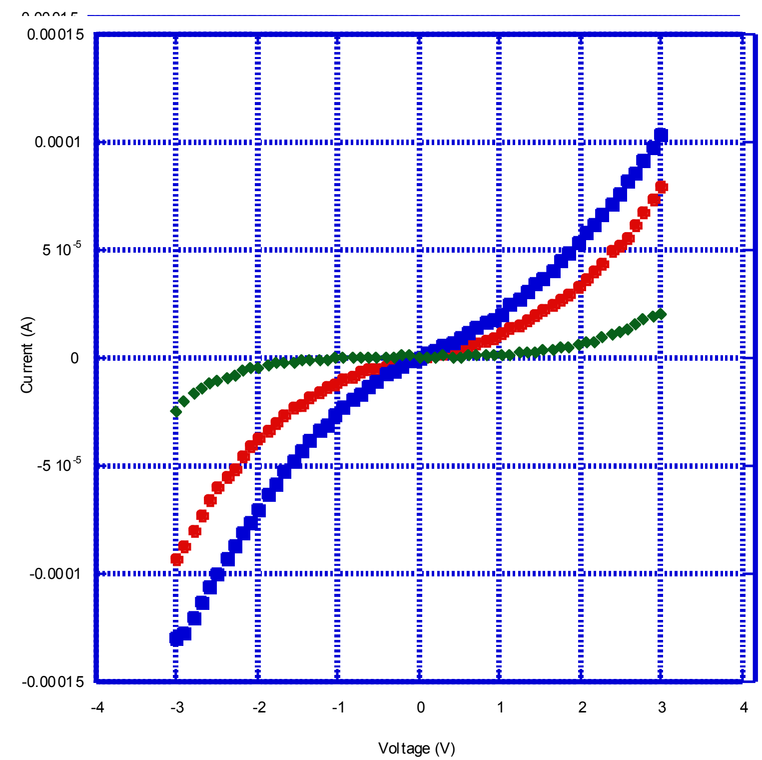




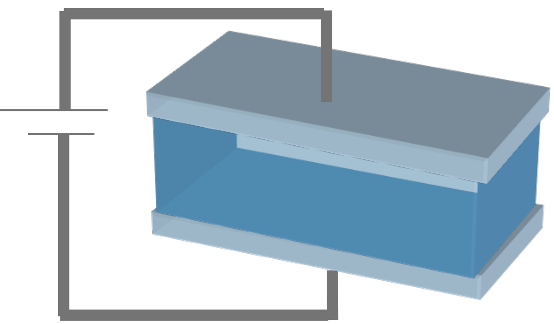
A.N. Chiaramonti et al. Ultramicrosc. 108, 1529 (2008)

Hummingbird Nanobiasing holder



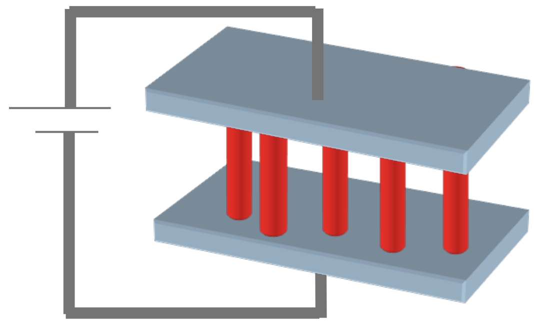


Electroforming NiO by Pt Migration



OFF state: high resistance

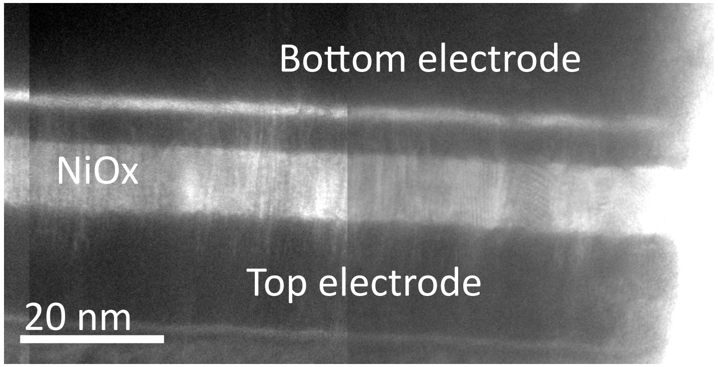
Uniform current flow



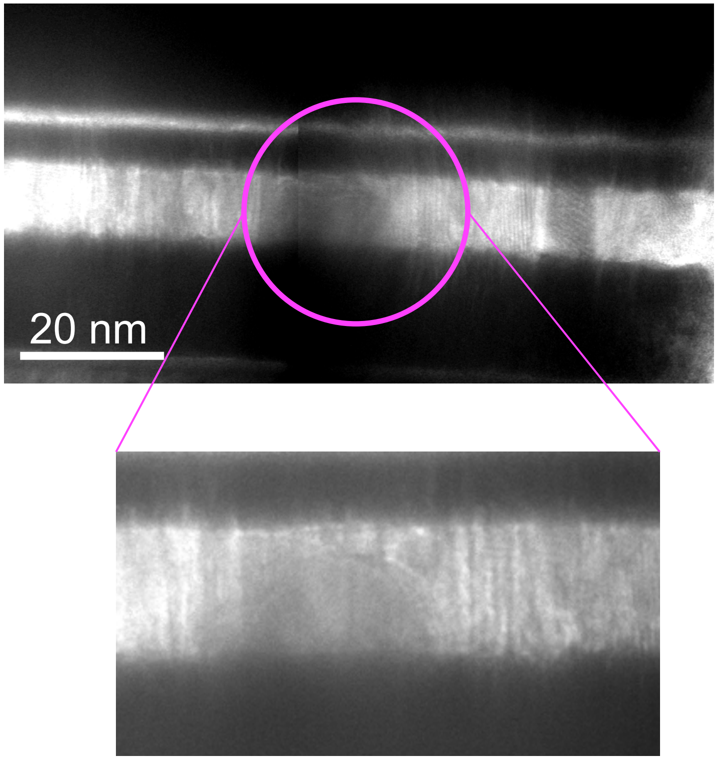
ON state: low resistance

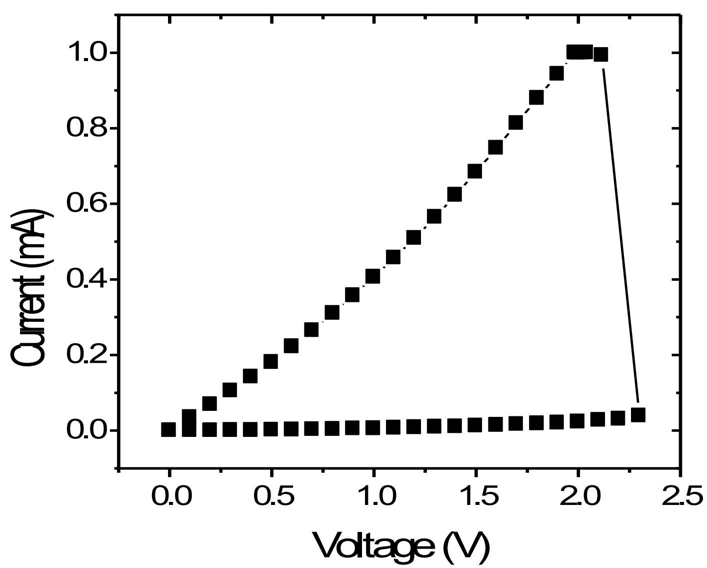
Current flow along metallic filaments

Before forming



After forming

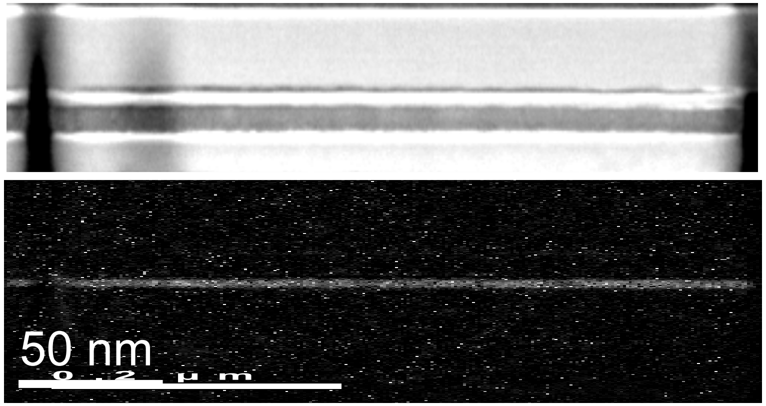




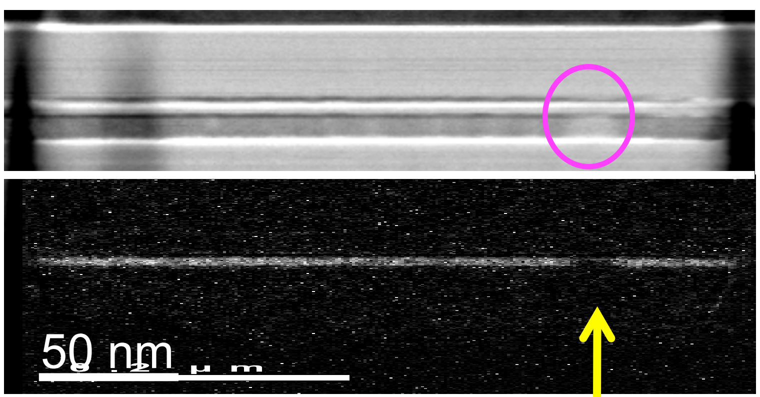
Ken D' Aquila and Yuzi Liu

Electroforming by Pt Migration

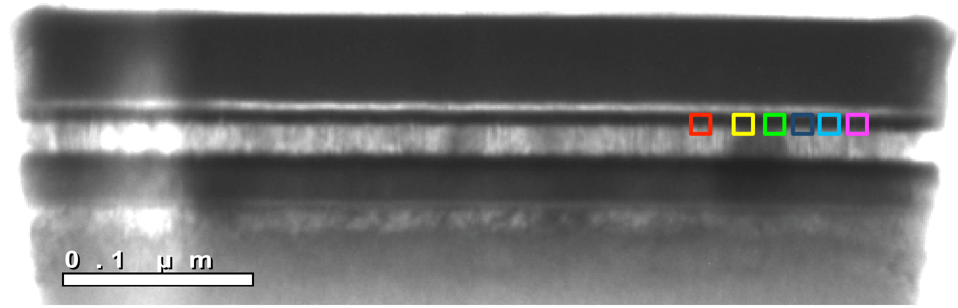
HAADF image (top) and Ni mapping (bottom) before electroforming

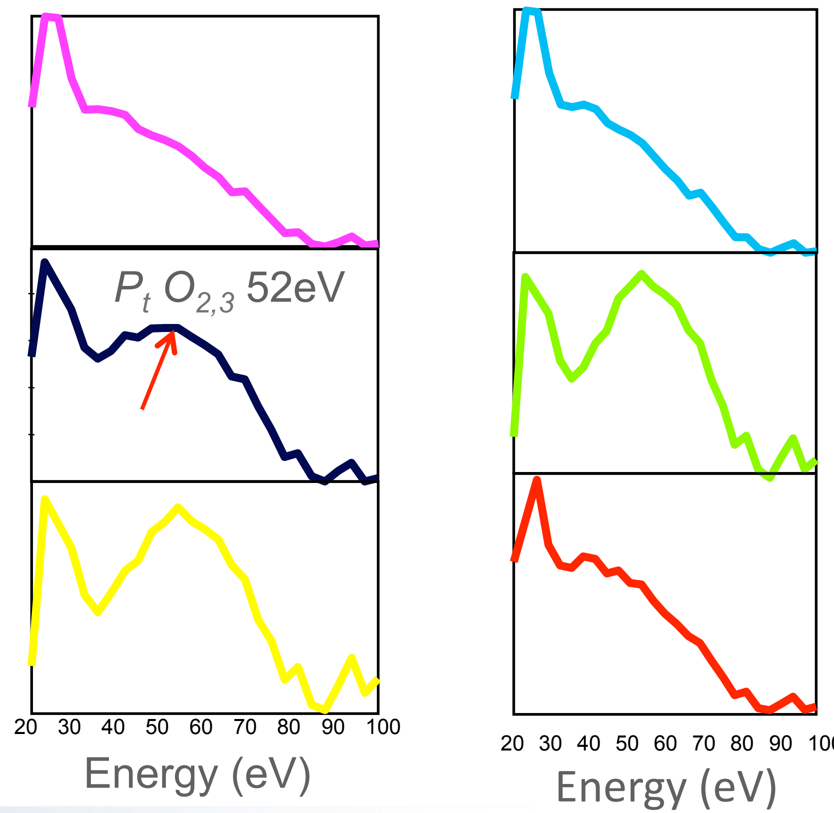


HAADF image (top) and Ni mapping (bottom) after electroforming



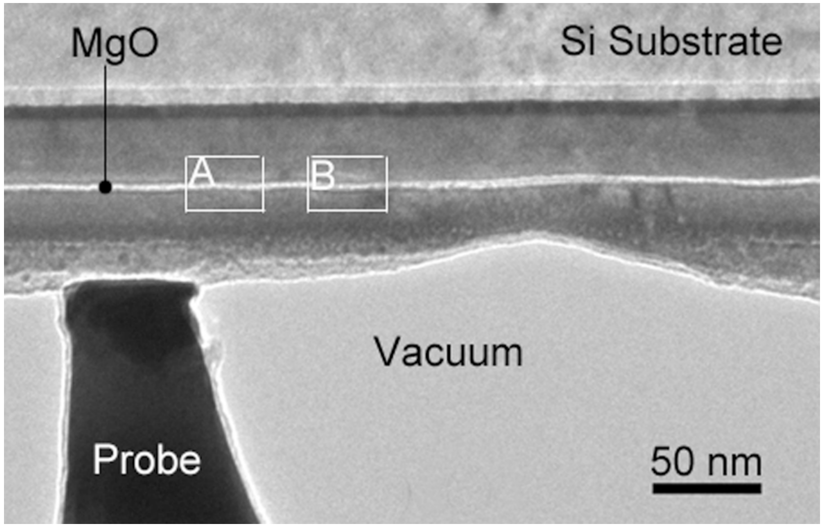
First spectrum image across Pt $O_{2,3}$ edge (Stack from 20 eV−100 eV, step: 3 eV)



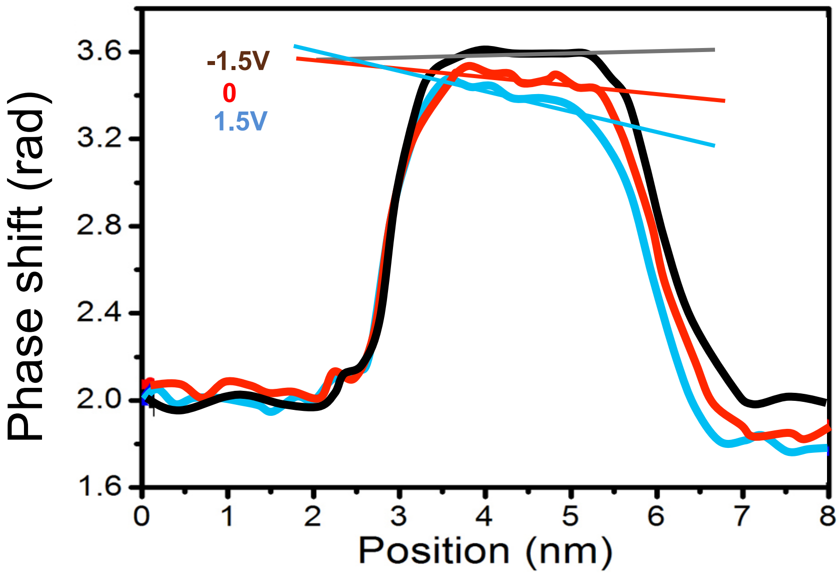


Ken D' Aquila and Yuzi Liu

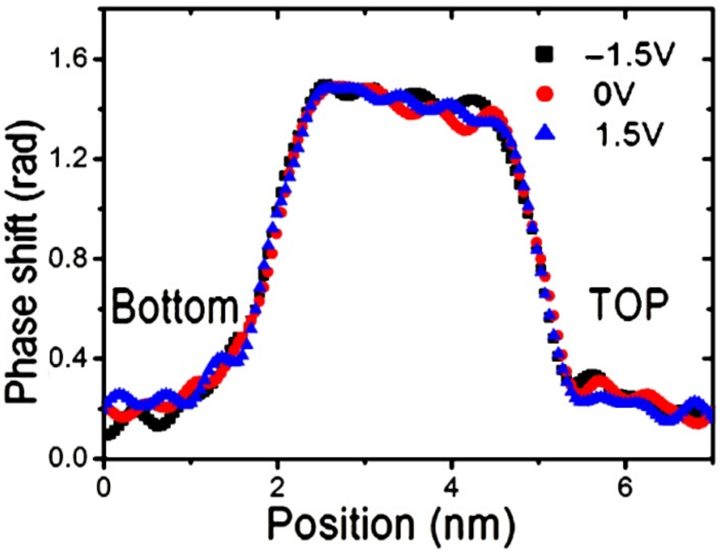
Effect of Probe Position on Barrier Shape



Under Au contact



Away from Au contact



- Phase shift profile across the barrier is related to tunnel barrier shape & height
- The effective barrier width and asymmetry increase with increasing applied voltage from −1.5V to 1.5V
- "Control" curves recorded away from contact do not show this effect implying limited current spreading in electrode

Y. Liu et al., Phys. Rev. B 83, 165413 (2011)

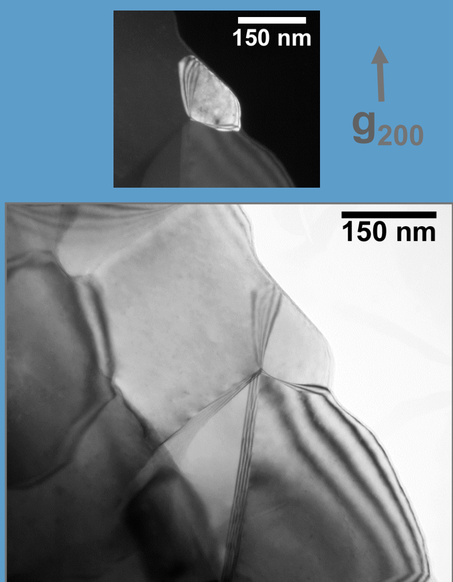
Mechanical Testing

Advantages of *in situ* mechanical testing

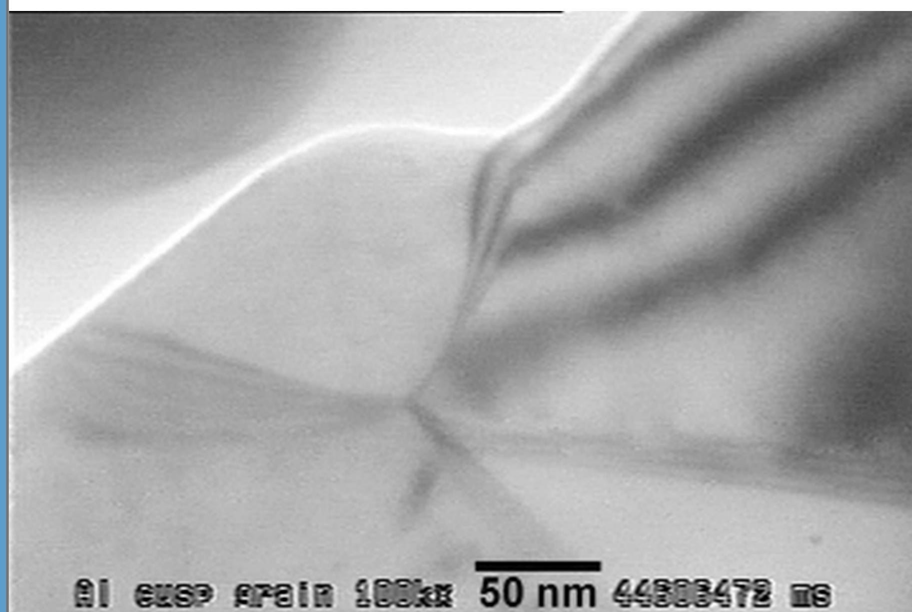
Slide courtesy of Andy Minor, NCEM, LBL

(1) Dynamics- when a before and after image just doesn't do . . . .

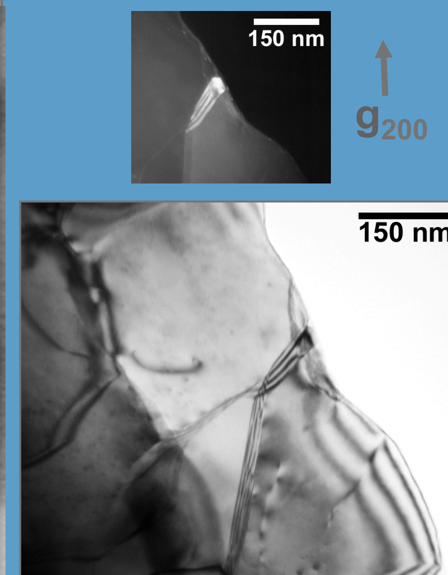
Before



During



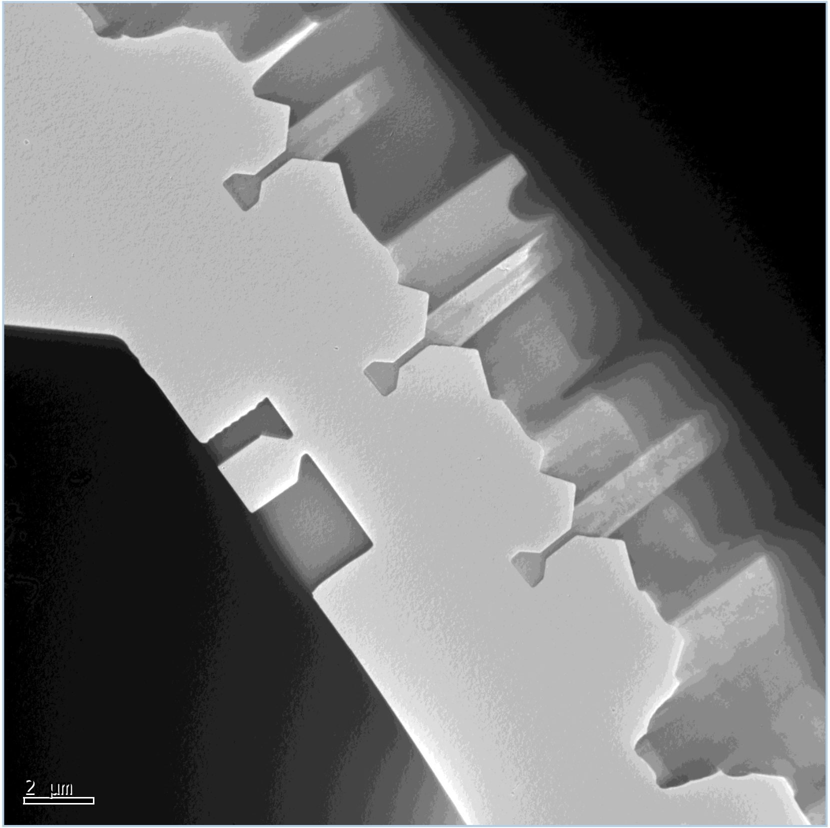
After

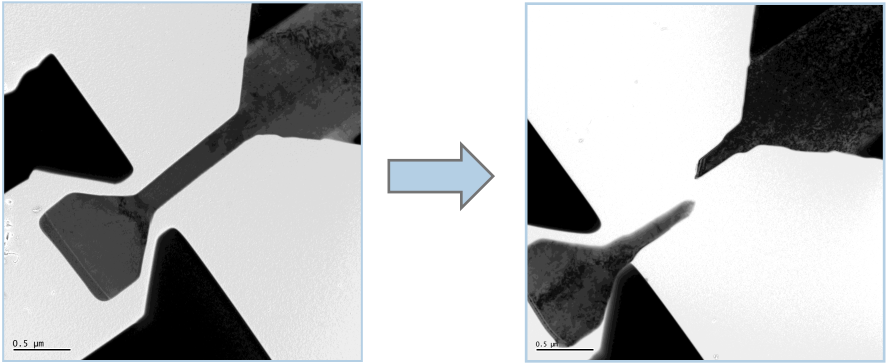


M. Jin, A. Minor, et al, Acta Mat 2004

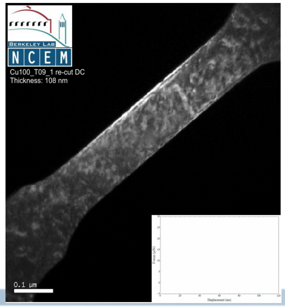
Quantitative in situ TEM tensile testing

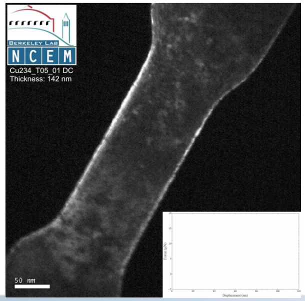
Slide courtesy of Andy Minor, NCEM, LBL





FIB structuring of tensile samples allows for:
- Protective Pt deposition
- Compensate for the taper
    - (~3° or less, in one dimension only)
- Vary surface to volume ratio (sheet vs. wire)
- Well defined and variable gauge length



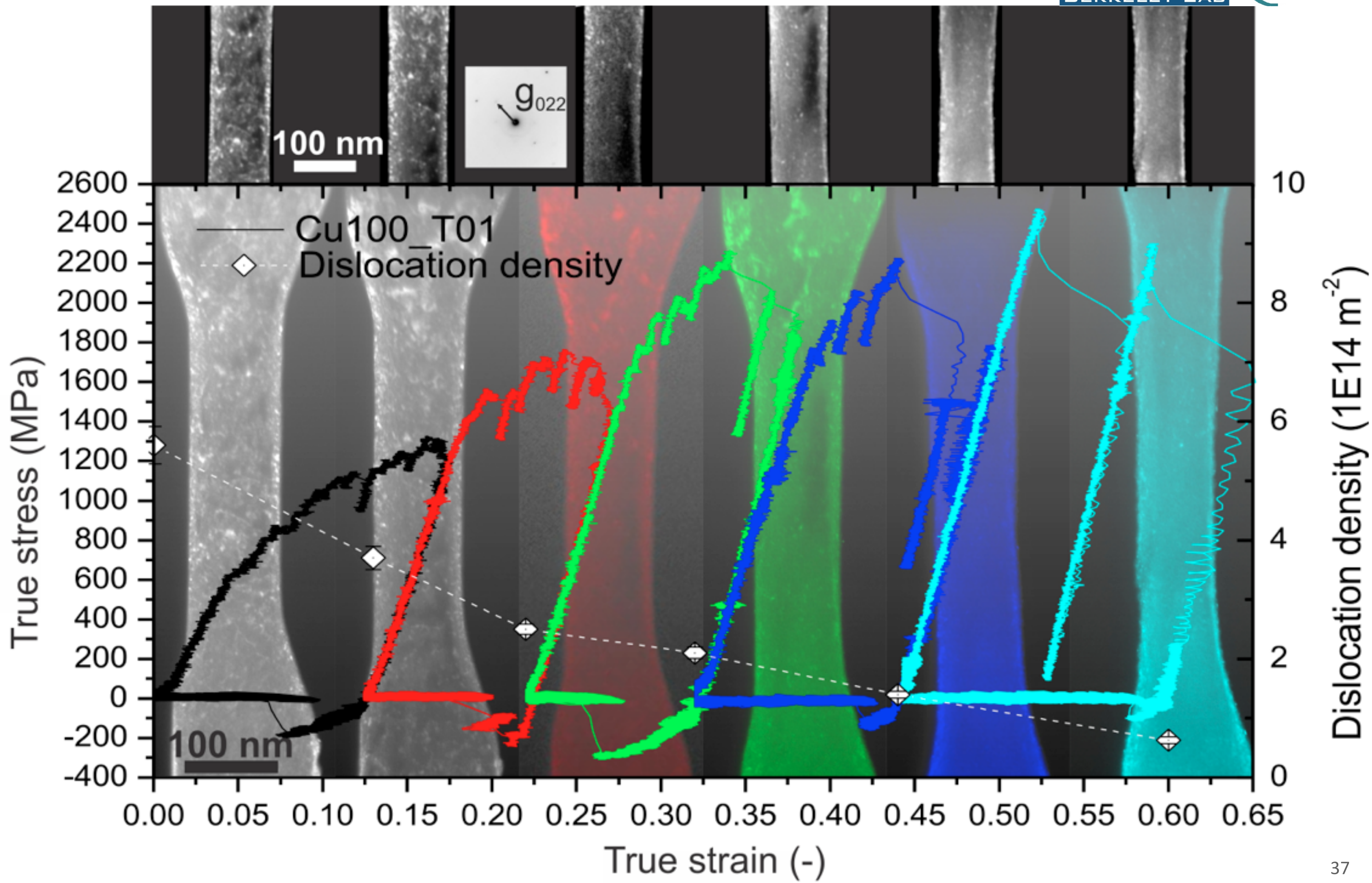


Typical dimensions:
Width: 200 nm
Length: 1000 nm
Thickness: 100 – 200 nm

-D. Kiener & A.M. Minor, submitted

Strength correlated to defects

Slide courtesy of Andy Minor, NCEM, LBL



Comparison: X-rays with (S)TEM

- TEM has higher spatial resolution (down to 0.1 nm or less with aberration correction
-
- BUT: sample thickness is limited to 100-200 nm for most materials
  - Use of chromatic aberration correction greatly increases sample thickness that can be analyzed e.g. 1 μm for biological sample WITH high spatial resolution
- High energy electron beam (100-400 keV) can easily damage biological samples
  - X-rays also give rise to damage…. Would need to compare beam intensities
- FEGTEM in micro(nano)diffraction mode produces largest signal from smallest volume of material
  - Field-emission source is brighter than a synchrotron and the elastic scattering cross-section is very large
  - Probes down to ~0.1 nm can be achieved

CNM: a DOE user facility for nanoscience research

State-of-the-art scientific user facility at Argonne National Laboratory for the development and use of techniques for synthesis, fabrication, characterization and theory of materials at the nanoscale

Goals:

- A productive and satisfied user community
- High impact staff science
- Supporting the DOE BES mission in fundamental research and energy

http://www.cnm.anl.gov