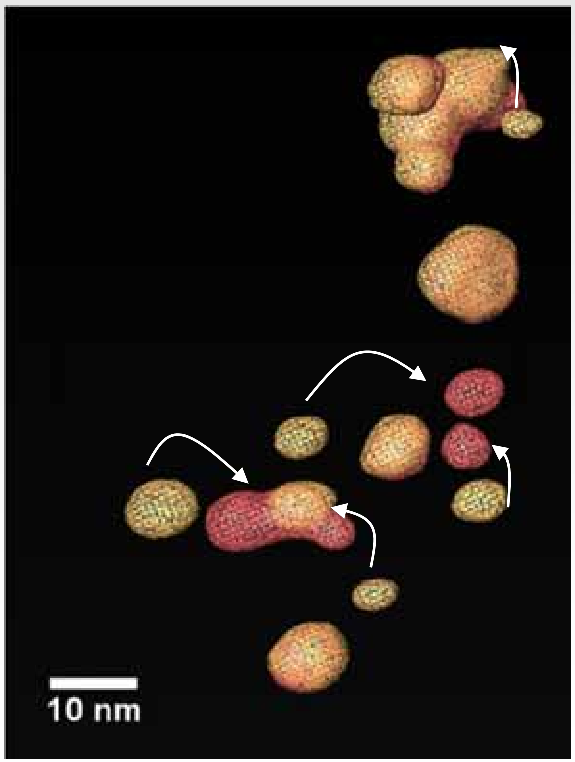
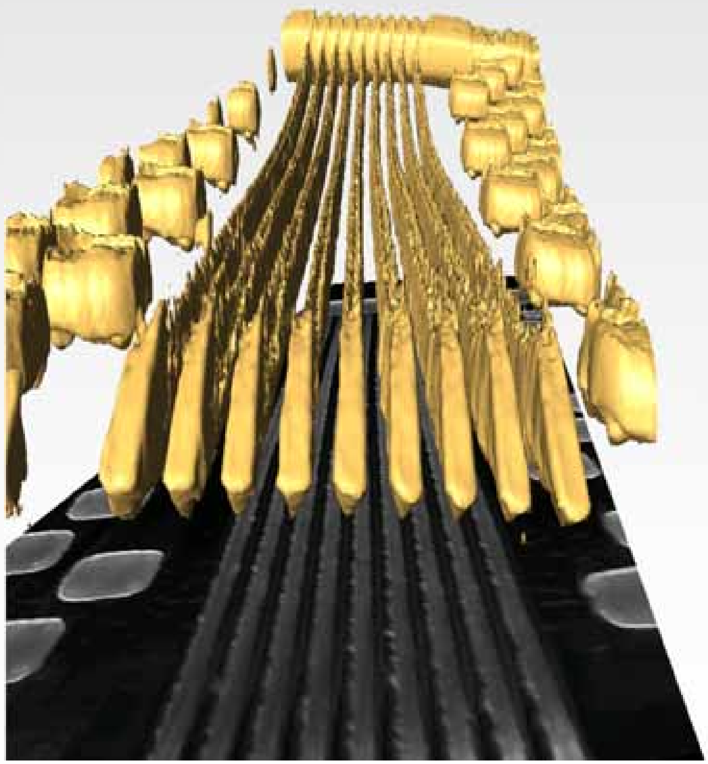
3D and Atomic-resolution Imaging with Coherent Electron Nanobeams - Opportunities and Challenges for X-rays

David A. Muller

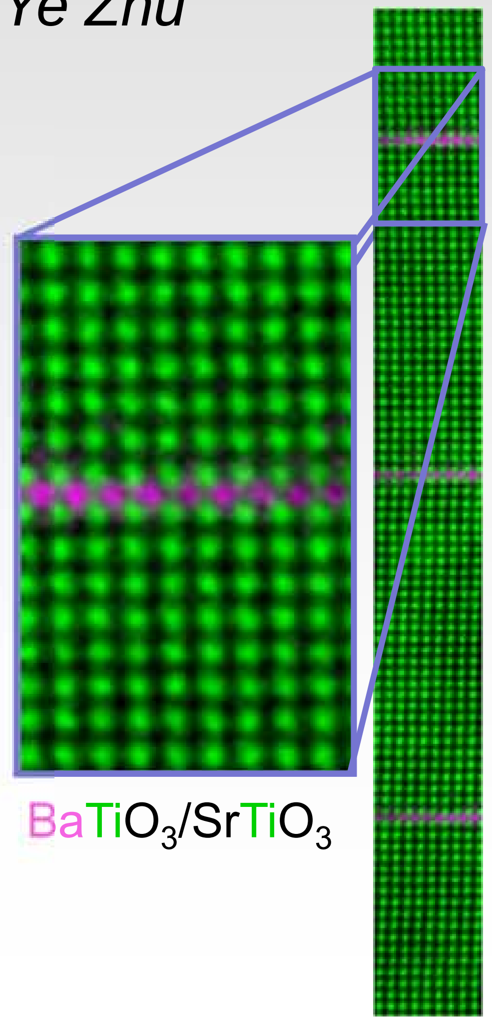
Lena Fitting Kourkoutis, Megan Holtz, Robert Hovden, Qingyun Mao, Julia Mundy, Yingchao Yu, Huolin L. Xin, Ye Zhu



Pt-Co Fuel Cell Catalysts coalescence in 3D

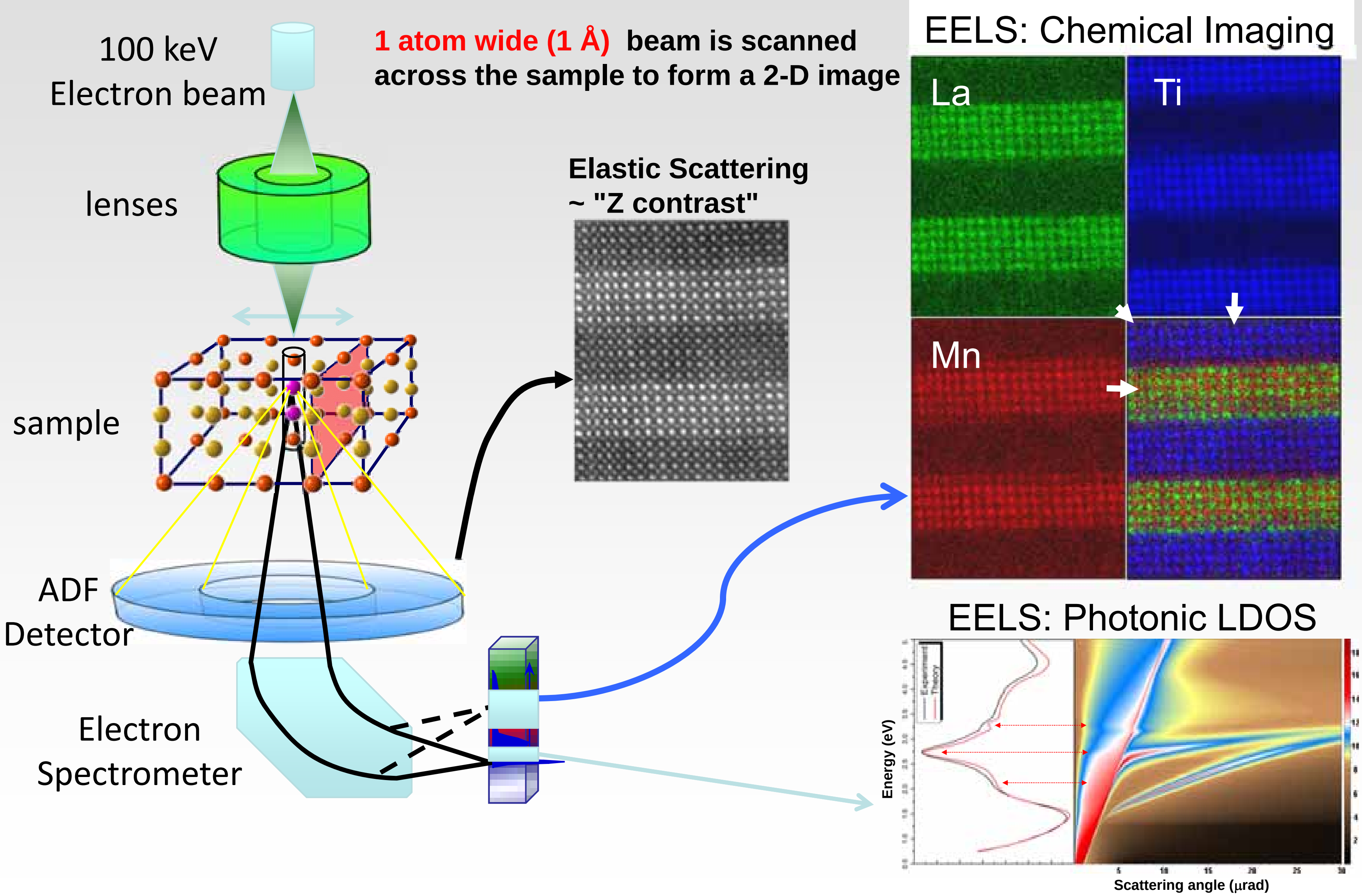


Integrated Circuits



$BaTiO_3/SrTiO_3$

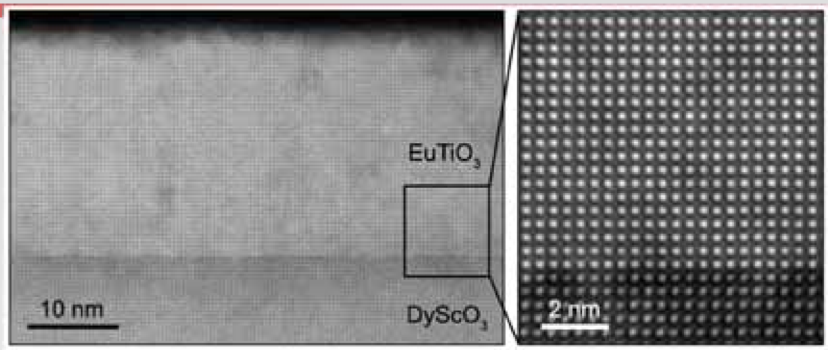
Scanning Transmission Electron Microscopy

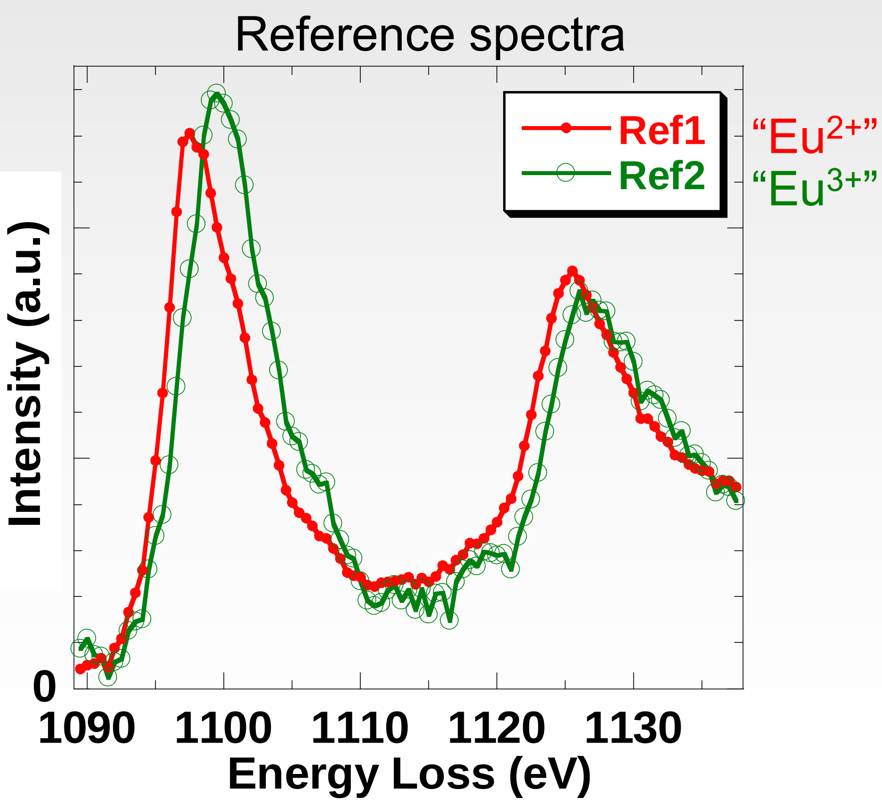


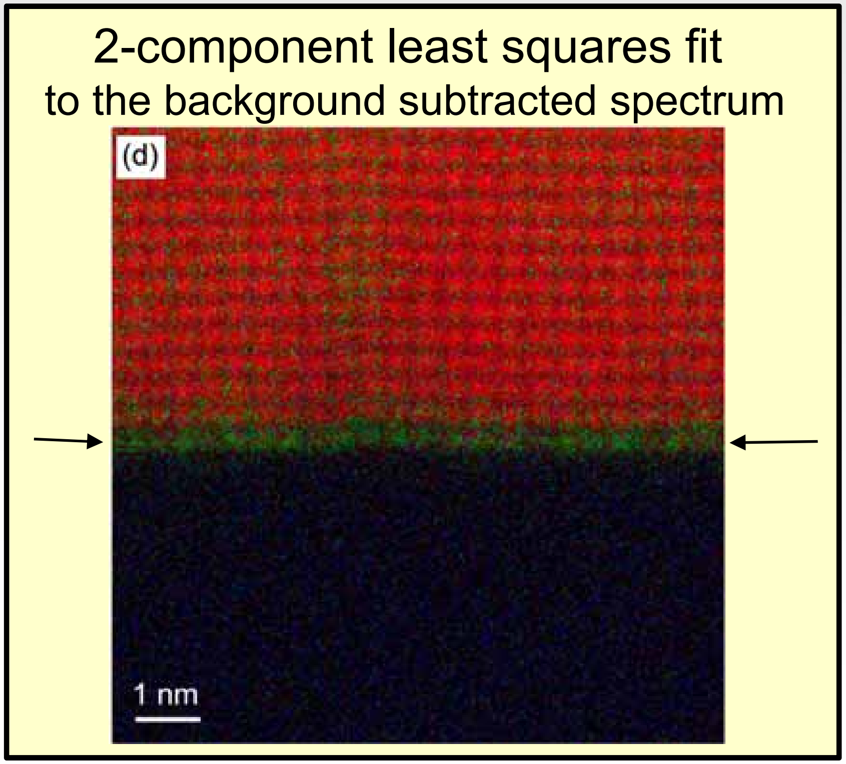
Muller, Kourkoutis, Murfitt, Song, Hwang, Silcox, Dellby, Krivanek, *Science* **319**, 1073 (2008).

2D imaging of electronic structure

$EuTiO_3$ on $DyScO_3$ (Lee, Schlom, *Nature* ***466***, 954 (2010))

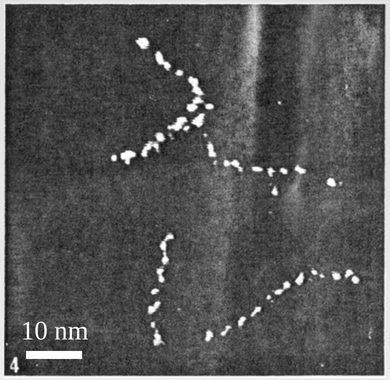






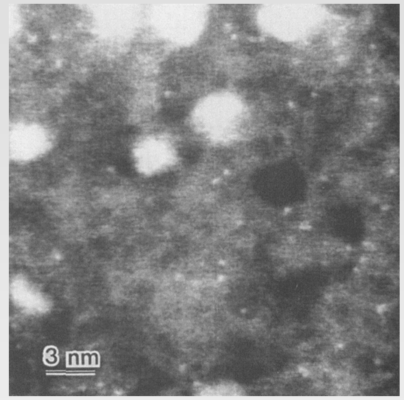
Increased Eu valence in one atomic layer at the interface

Single Atom Imaging: Catalysis and Dopants



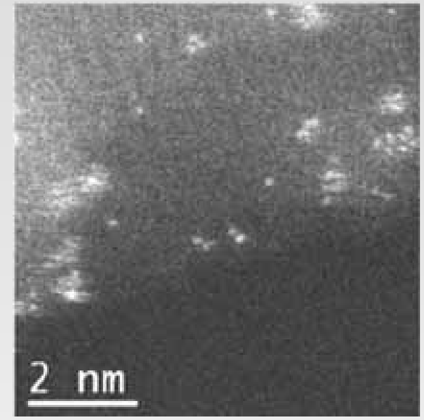
Th on a-C

Crewe *et al*., Science **168**, 1338 (1970)



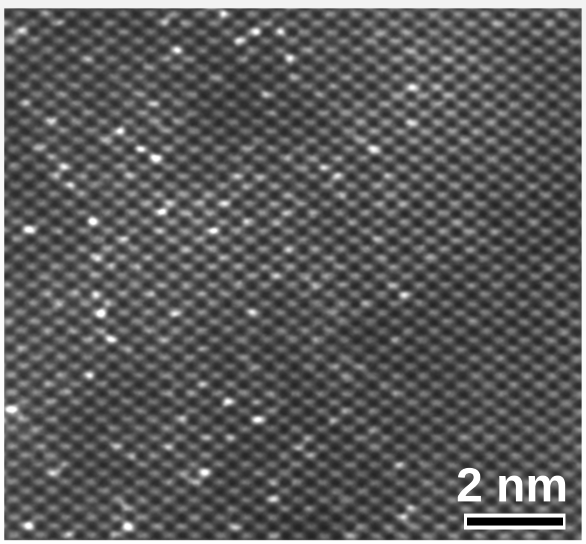
U on a-C

Treacy & Rice, J. Microscopy **156**, 211 (1989)



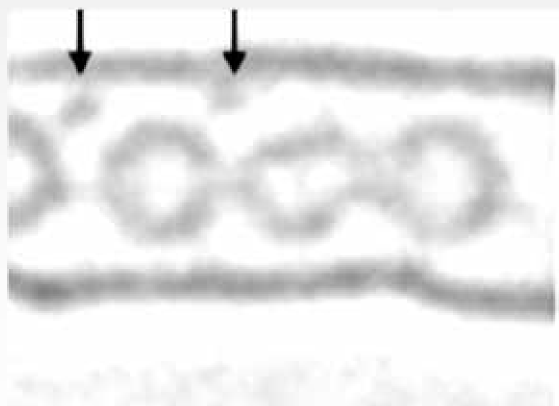
Pt on a-Al_2O_3

Blom et al, *Microsc. Microanal.* **12**, 483, 2006



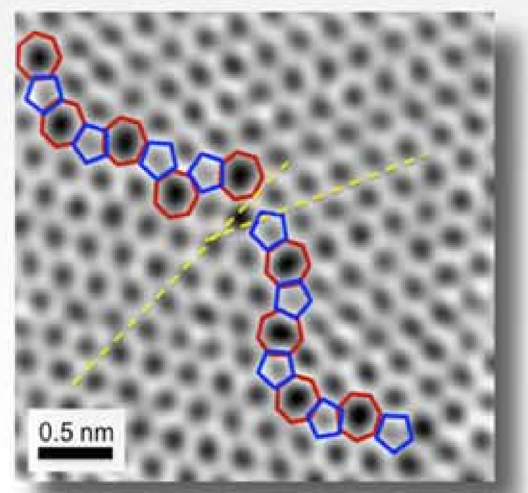
Sb in Si

Voyles *et al*., Nature **416** 826 (2002)



K-doped C_{60} peapods

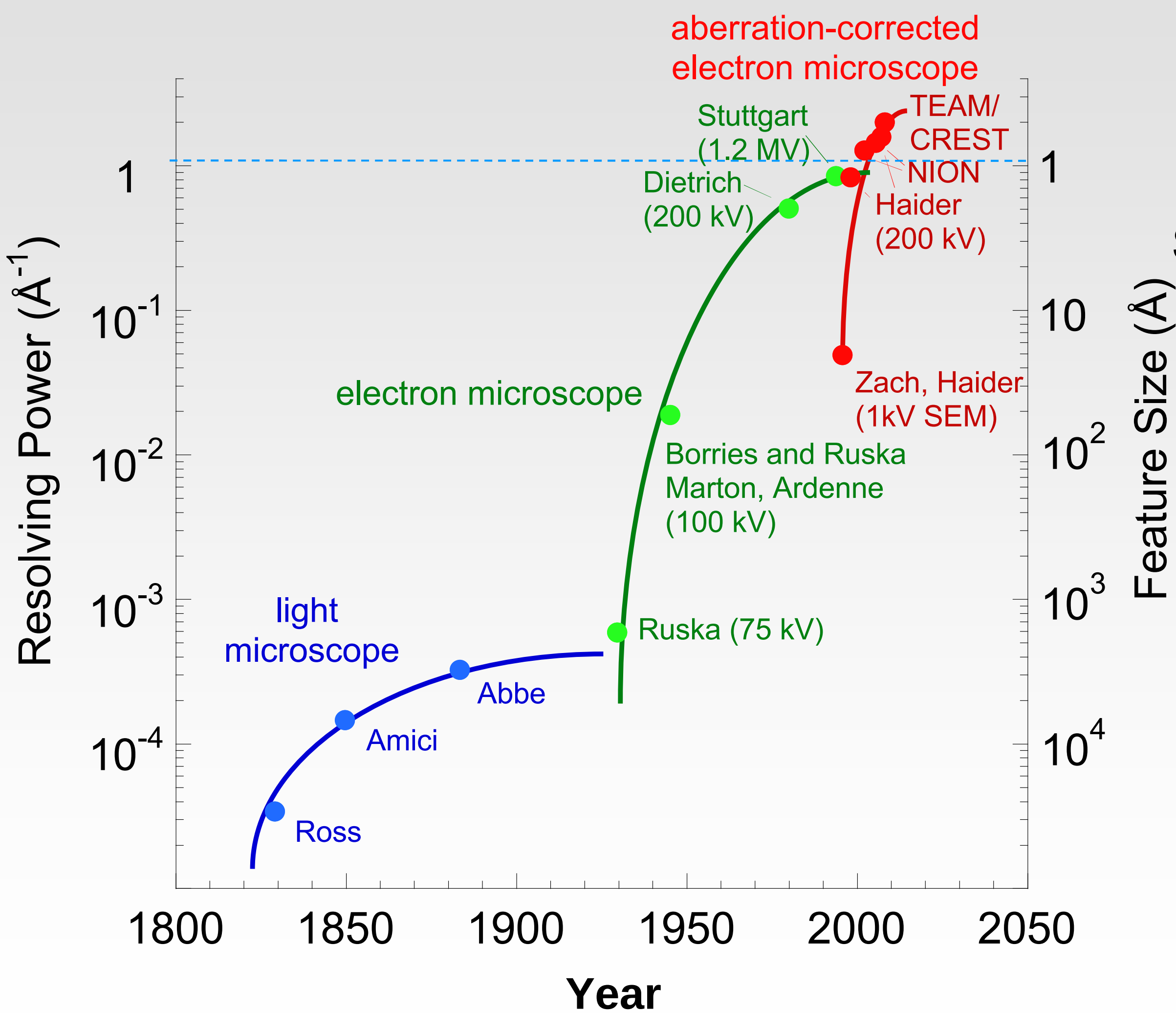
Guan *et al*., PRL **94**, 045502 (2005)



Graphene Grain Boundaries

Huang et al, *Nature* **469**, 389 (2011)

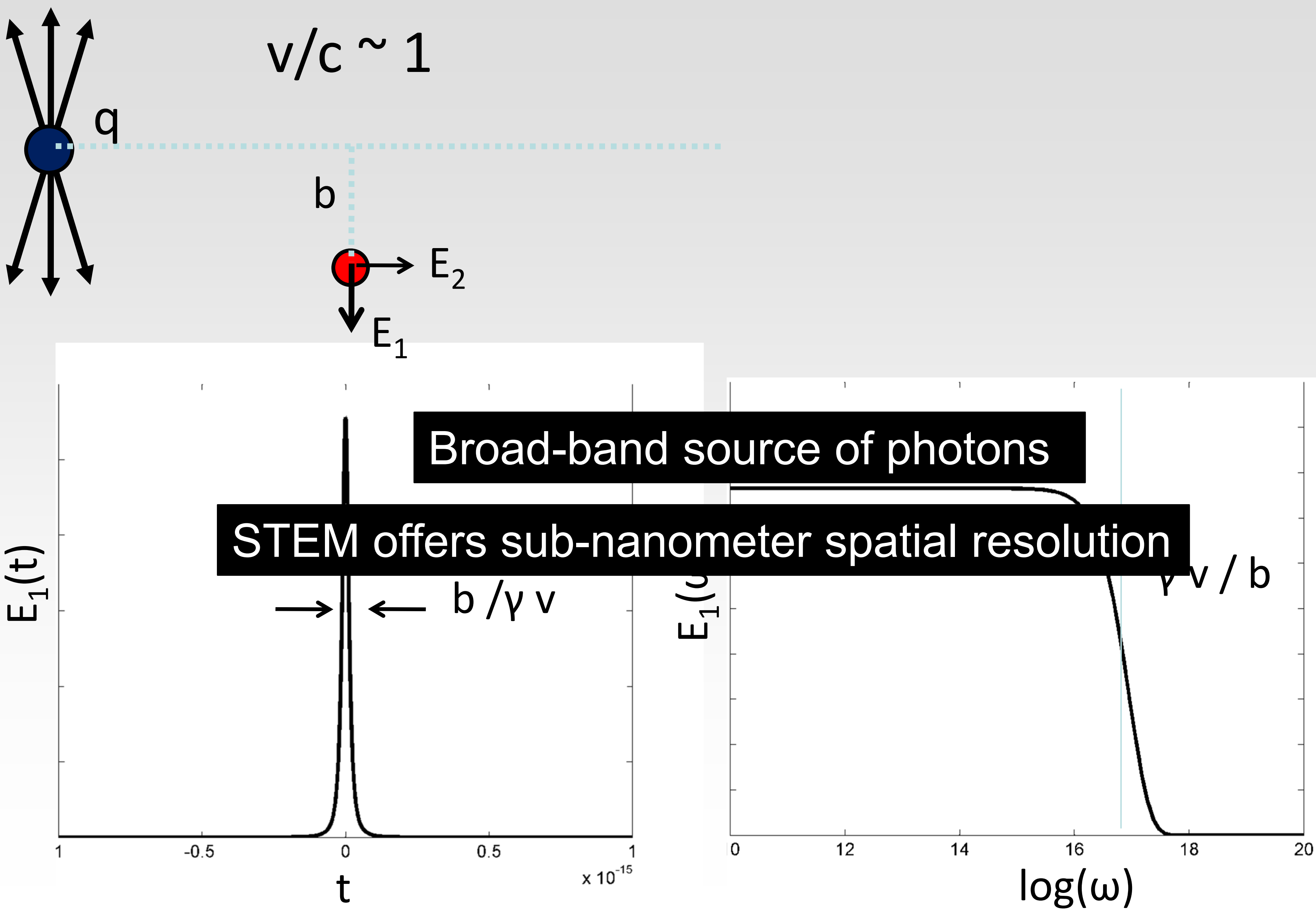
Hardware Advances in Microscopy



Corrected optics have enabled practical Sub-Angstrom resolution

Muller, Nature Materials, (2009), Adapted from Rose (2009)

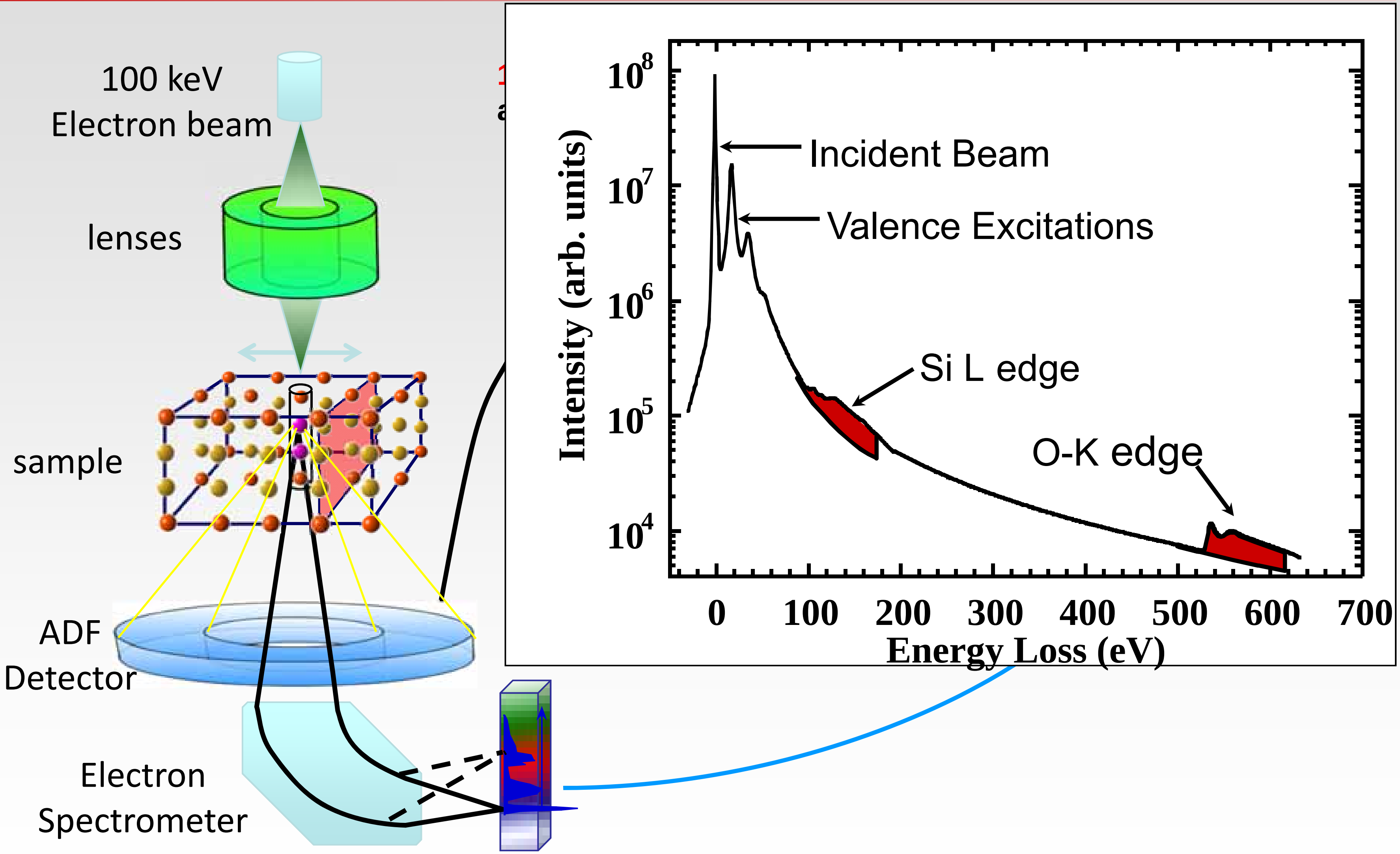
Relativistic Charge as a Virtual Light Source



Broad-band source of photons

STEM offers sub-nanometer spatial resolution

Scanning Transmission Electron Microscopy

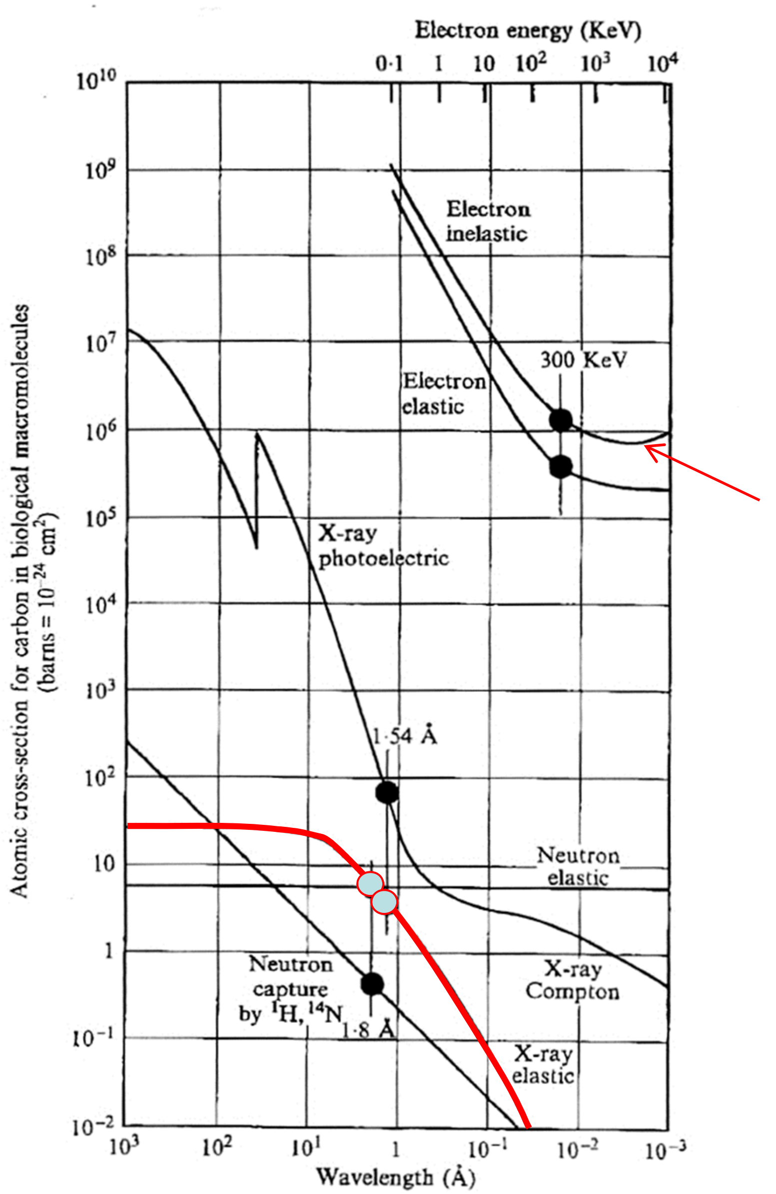


Single atom Sensitivity:

ADF: P. Voyles, D. Muller, J. Grazul, P. Citrin, H. Gossmann, *Nature* **416** 826 (2002)
EELS: U. Kaiser, D. Muller, J. Grazul, M. Kawasaki, *Nature Materials*, **1** 102 (2002)

How Bad is Radiation Damage?

R. Henderson, Quarterly Reviews of Biophysics 28 (1995) 171-193.

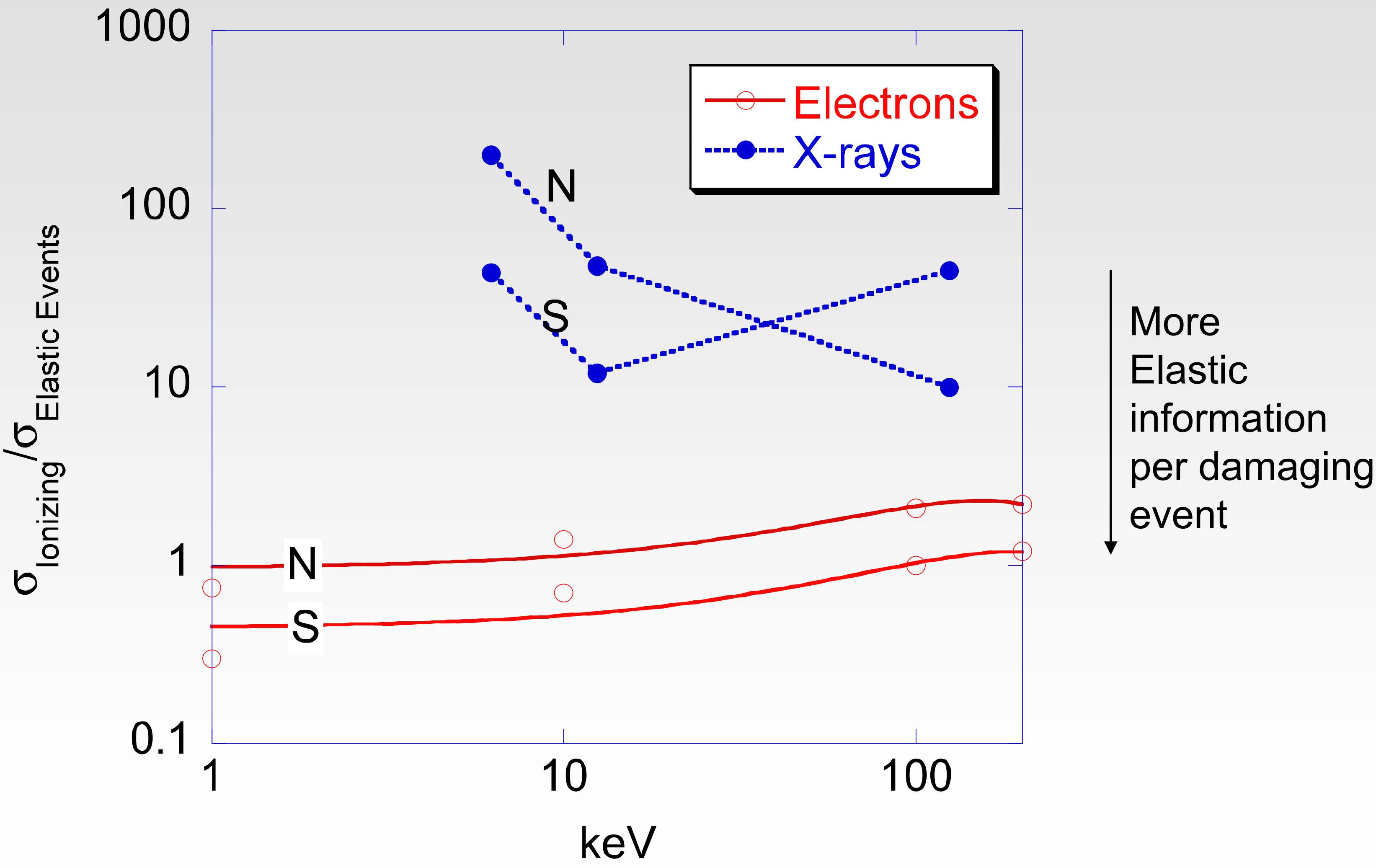


It's not the cross-section, but

How many damaging events per useful imaging event?

Least Damage:
Elastic imaging - Electrons wins
Inelastic imaging - Soft X-rays win

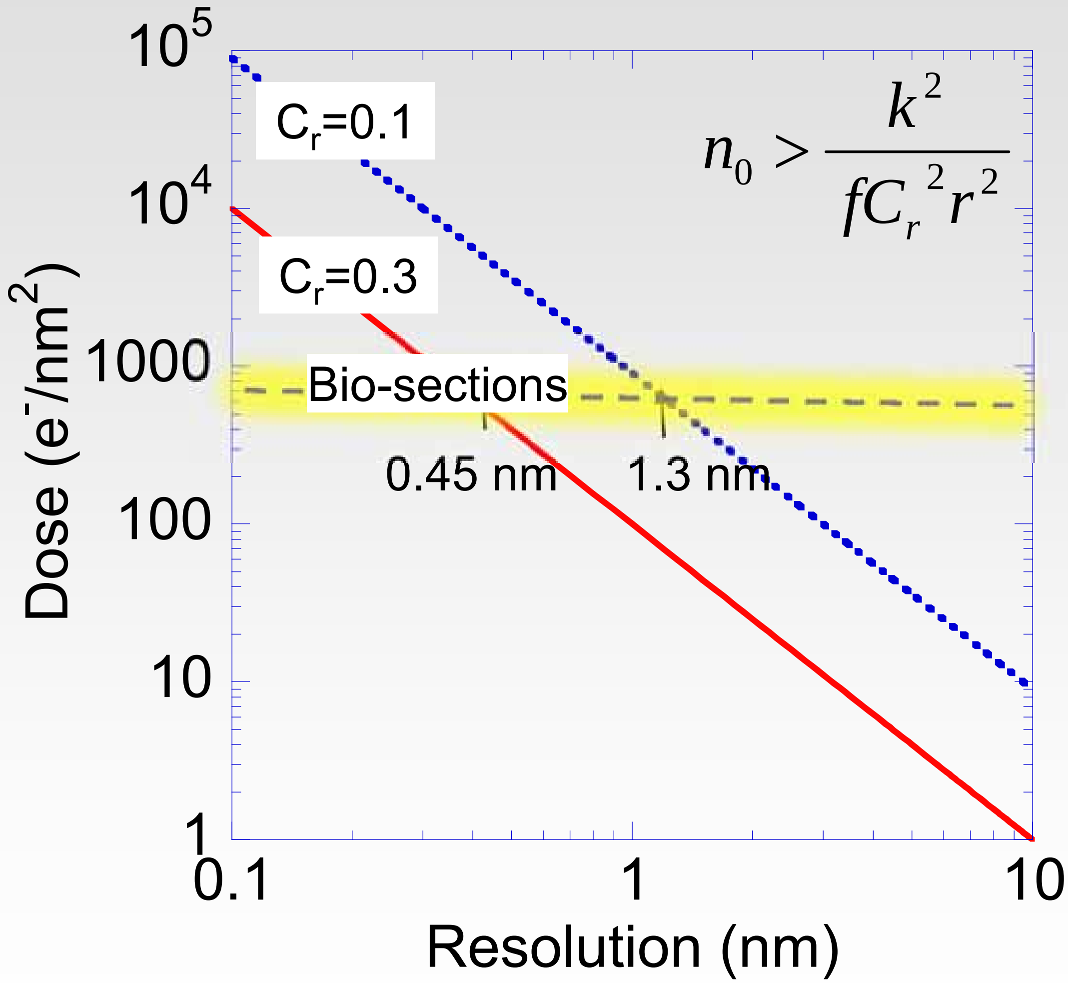
Radiation Damage as a Fundamental limit



Data from Breedlove and Trammell, Science 170 (1970) 1310-1313

For electrons σ_i / σ_e ~ln (E)

Dose Required for 2D-Imaging



$$n_0 > \frac{k^2}{f C_r^2 r^2}$$

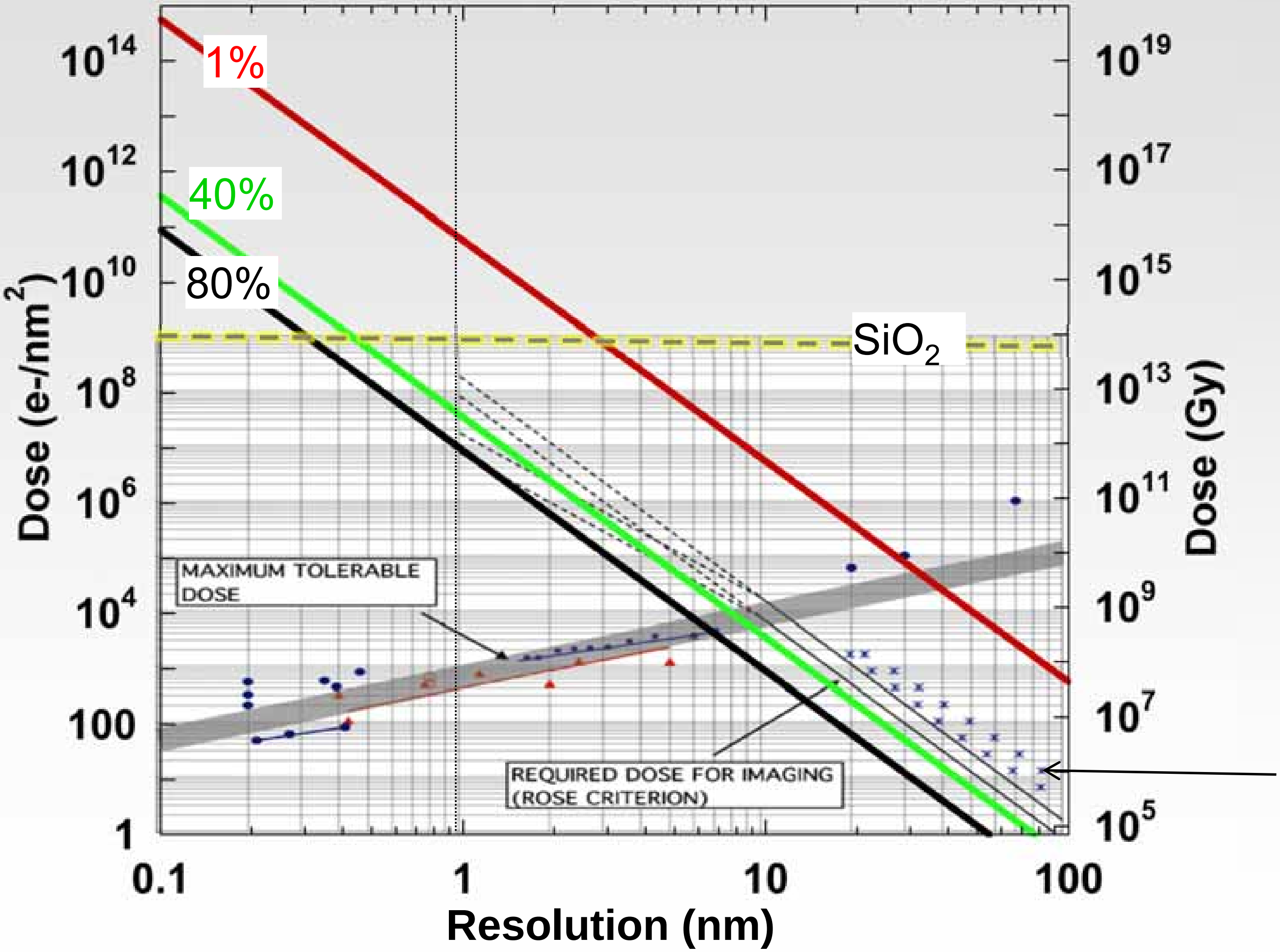
Resolution 〈 1/(Dose)$^{1/2}$

Resolution 〈 1/(Contrast)

It's almost impossible to do atomic-resolution phase contrast imaging with biological samples (except by averaging over many similar molecules)!

Dose Required for 3-D Reconstructions is high

B. F. McEwen et al, Journal of Structural Biology **138** 47–57 (2002)
Saxberg & Saxton, W.O., Ultramicroscopy **6**, 85–90 (1981)
M.R. Howells et al, J. Electron Spec. Rel. Phenom. **170** 4 (2009)

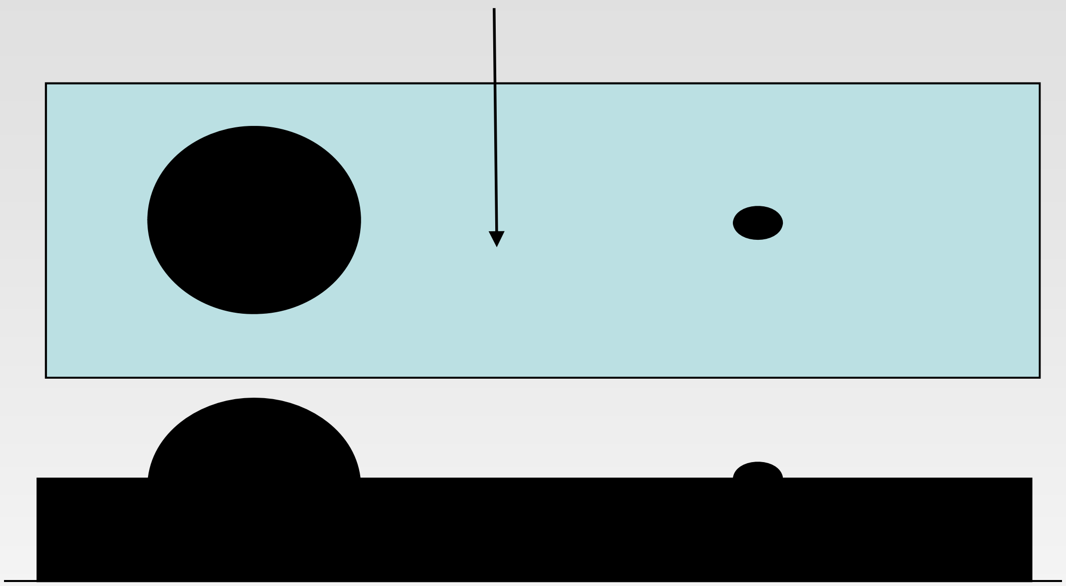


r 〈 1/(Dose)$^{1/4}$

r 〈 1/(Contrast)$^{1/2}$

Dose-limited resolution for oxides is ~0.2-2 nm and ~3-10 nm for polymers

High Resolution= Thin Sections



Small features have low contrast (and for a fixed dose we trade 2D resolution for contrast)

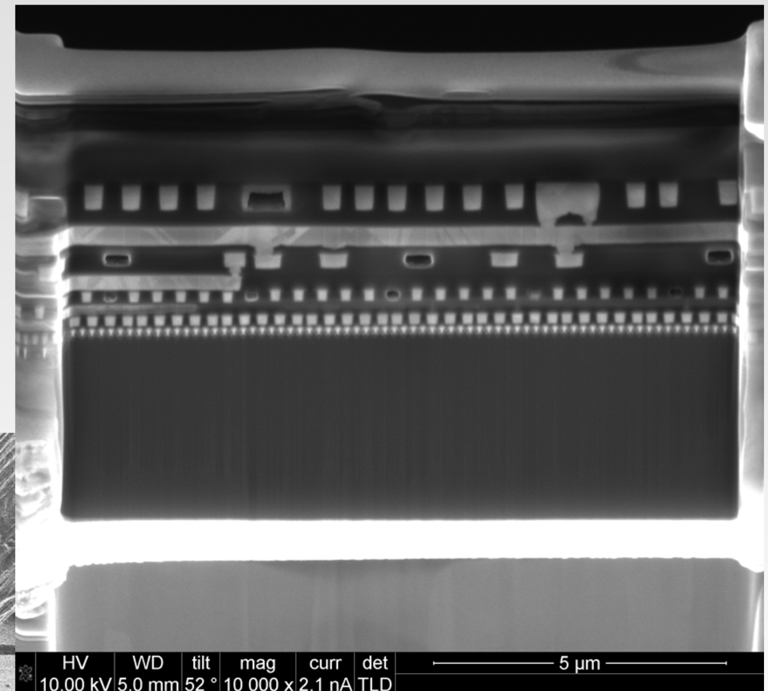
Resolution 〈 Sample Thickness

➡ Need to make thin samples (true for x-rays as well as electrons)

(unless we have a fluorescence detection method & there is only 1 object)

Site-Specific Focused Ion Beam

"high-k": Xeon X3220, 2.5 GHz, Quad Core



Thin-section
Mounted for TEM

Liftout

Transmission electron microtomography without the "missing wedge" for quantitative structural analysis

Noboru Kawase[a], Mitsuro Kato[a], Hideo Nishioka[b], Hiroshi Jinnai[c,*]

Ultramicroscopy, **107** (2007) p8

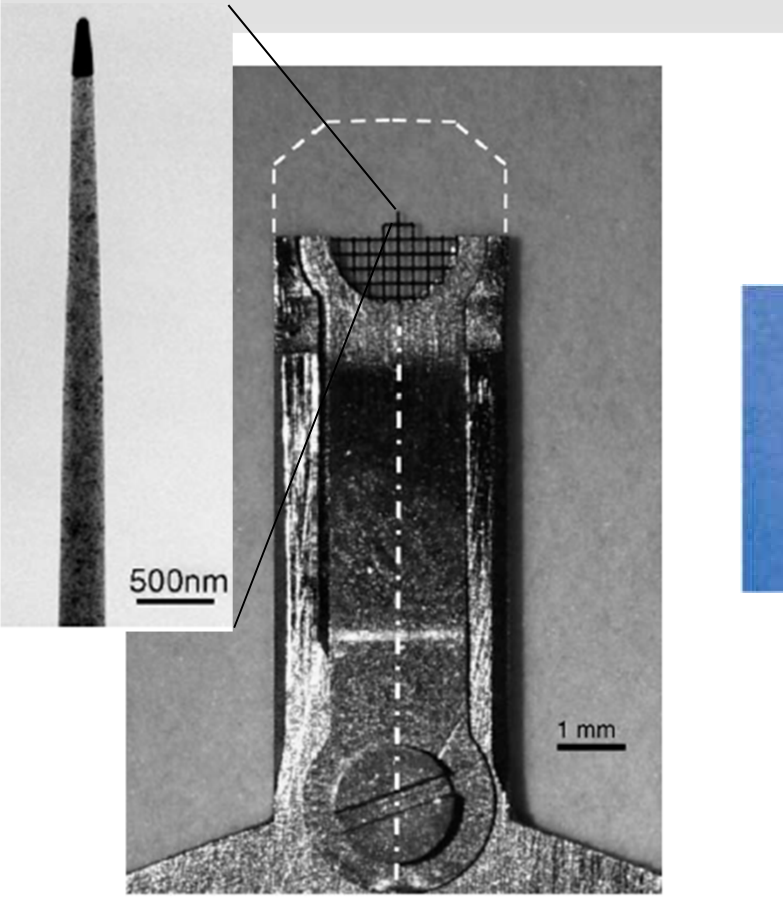
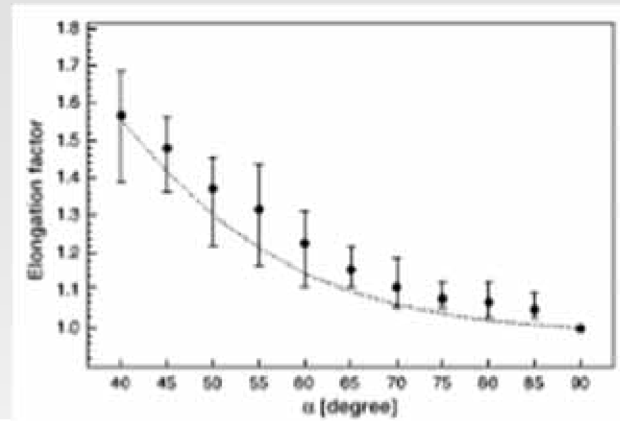
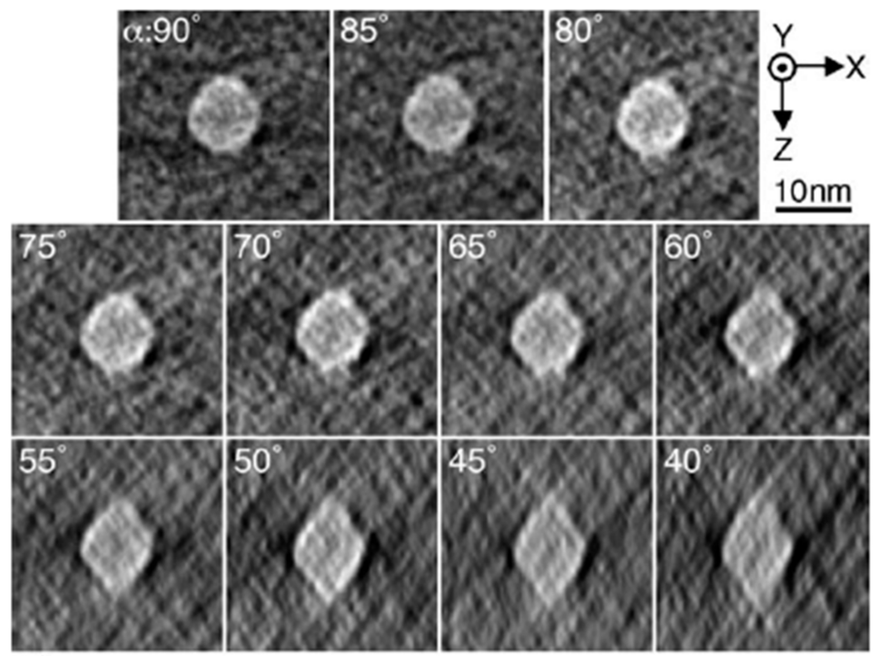
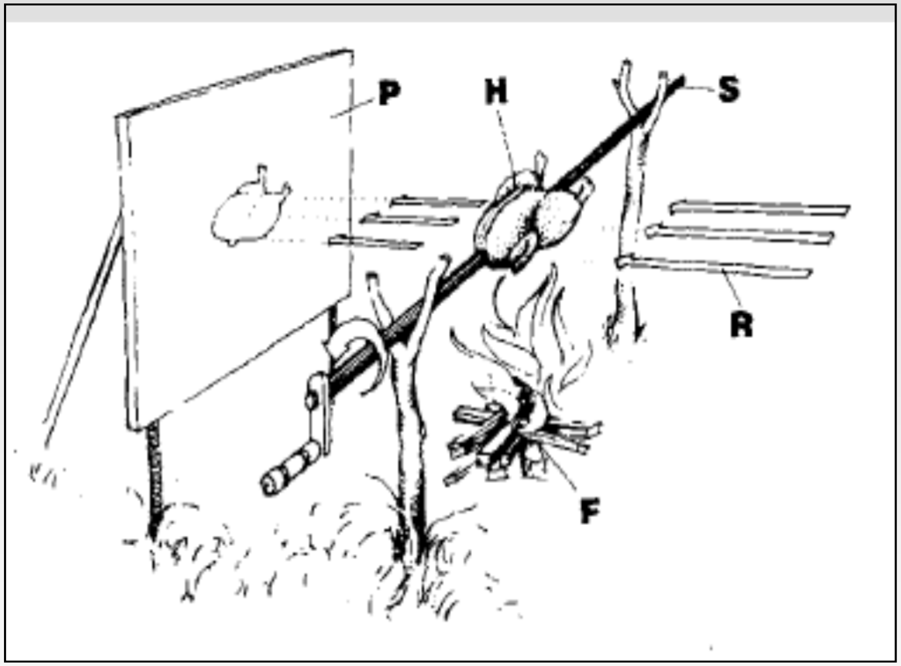


Fig. 2. A modified JEM2200FS specimen holder allowing ±90° tilt. The original profile is marked by the dashed line.

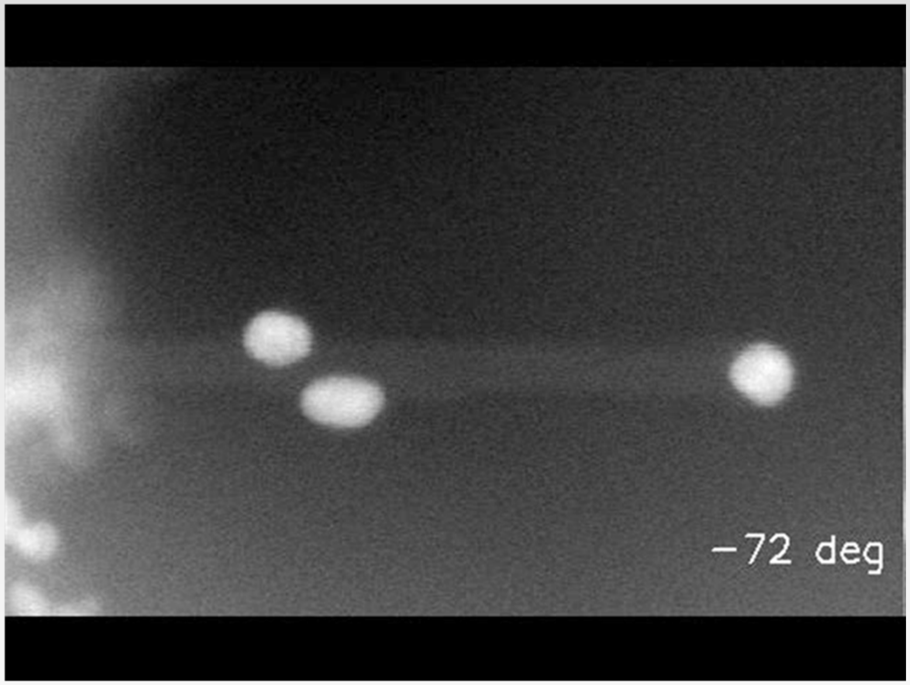




Electron Tomography – Experiment

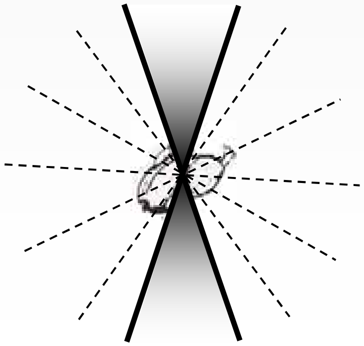


Walter Hoppe, *Angew. Chem. Int. Ed. Engl.* ***22*** *(1983) 456-485*

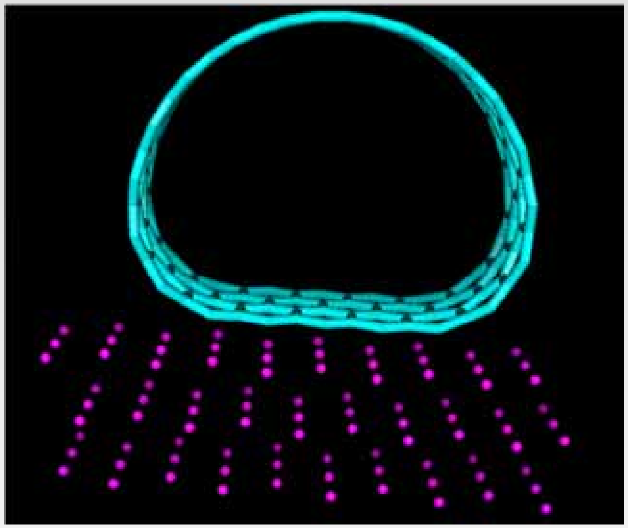


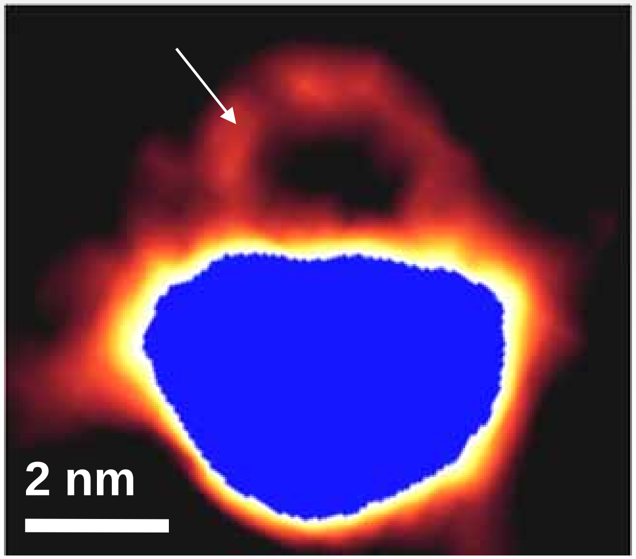
Field of View : 127 nm

3D resolution function
along X, *dx* ~ 0.2-1 nm
along Y, dy ~ >1 nm
along Z, *dz* ~ >1 nm
(due to limited tilt range and finite number of projection images)

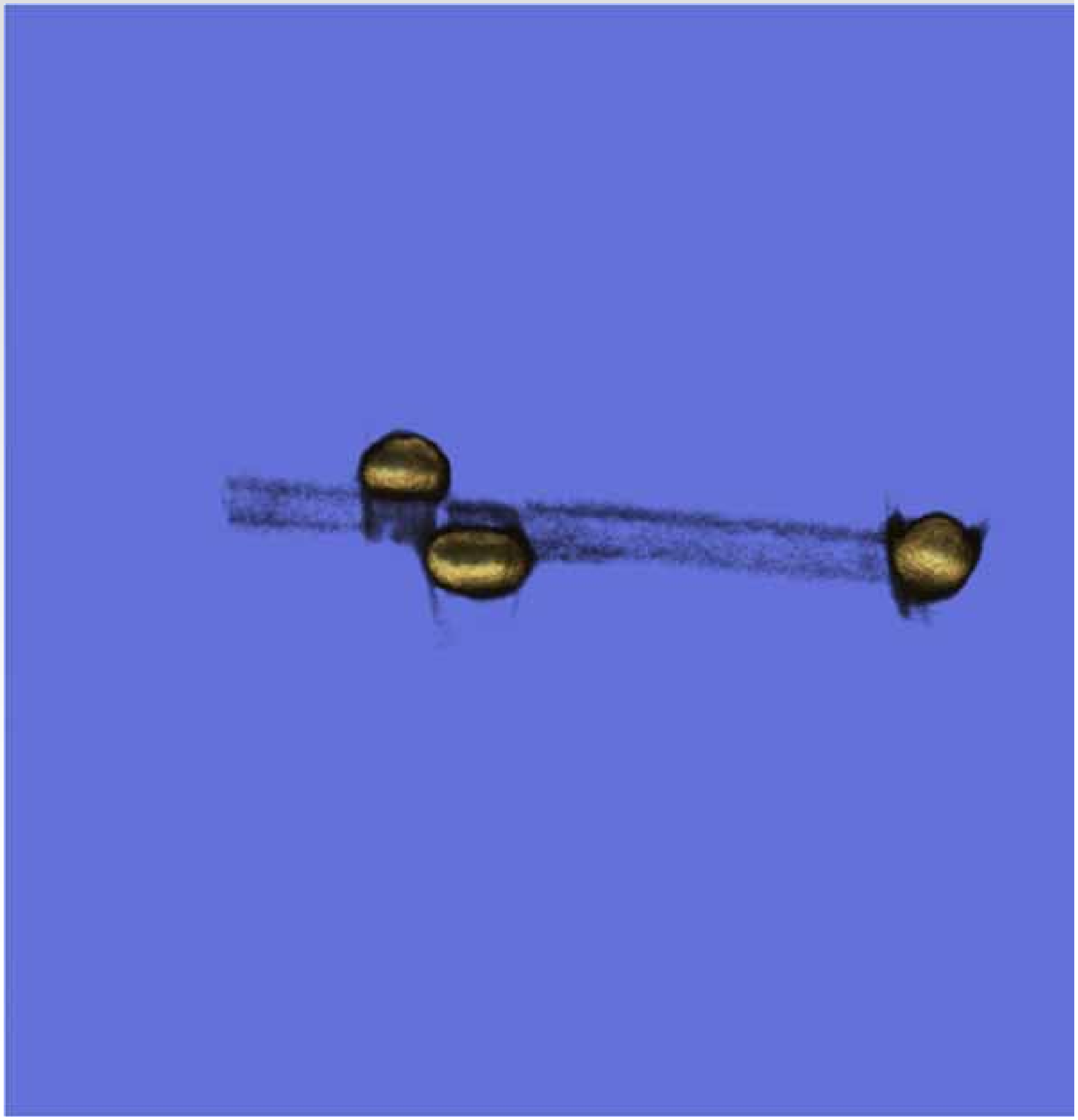


Three-Dimensional Imaging at the Nanoscale: How Metal Contacts Form on a Carbon Nanotube



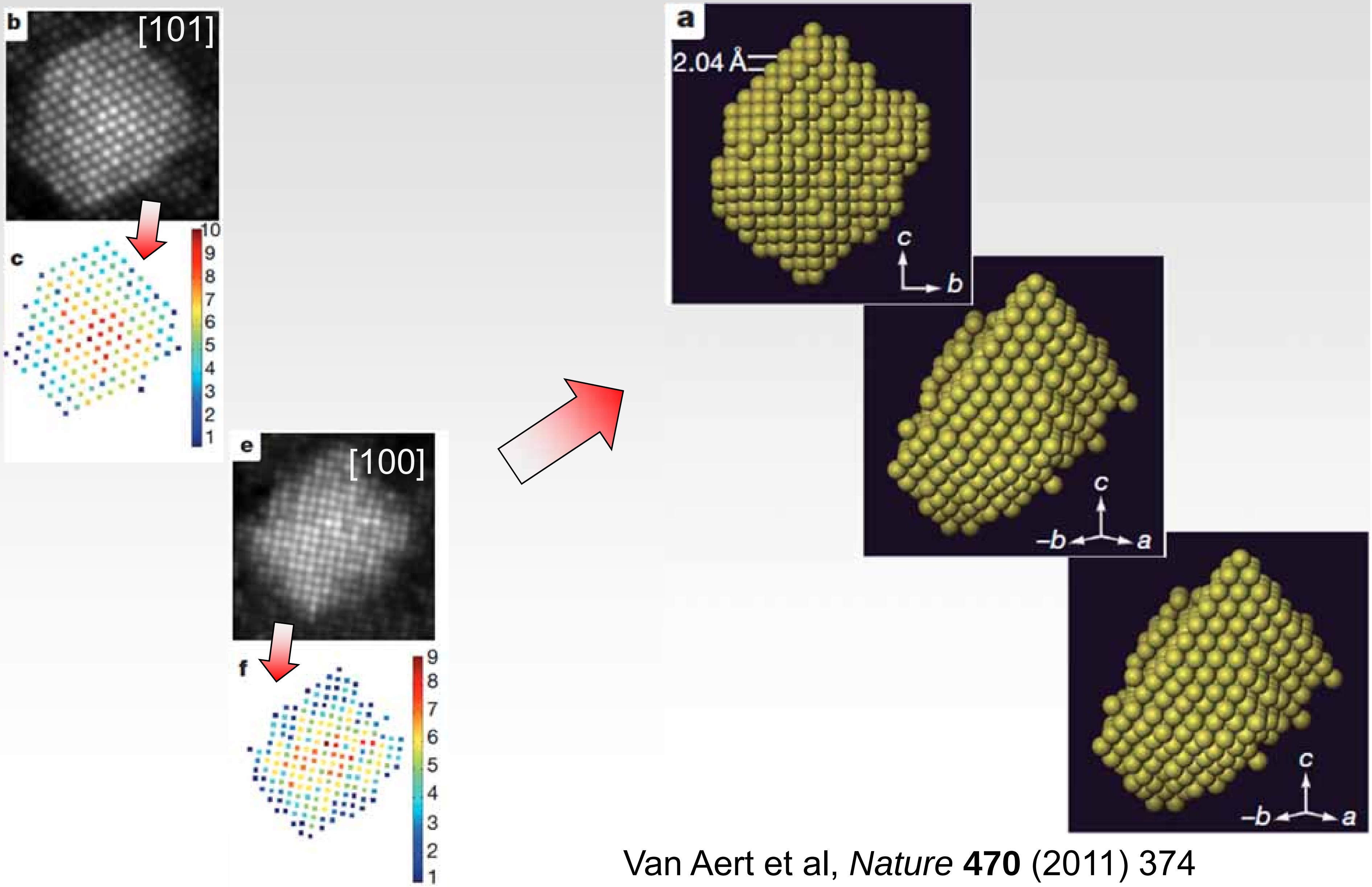


Nano Letters **7** 3770 -3773 (2007)



Discrete Tomography at Atomic Resolution?

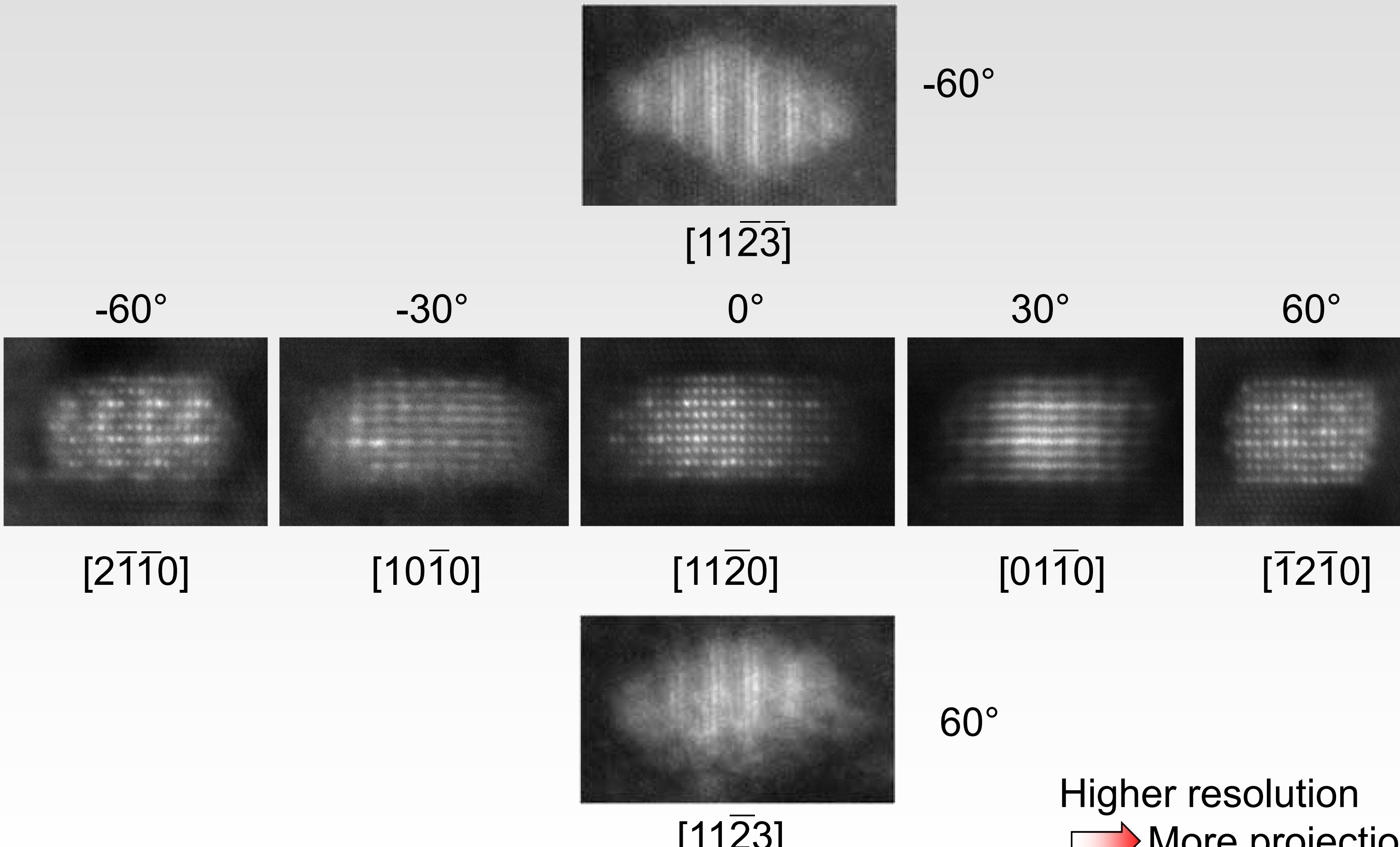
Discretize a small set of atomic-resolution zone-axis projections



Van Aert et al, *Nature* **470** (2011) 374

Discrete Tomography at Atomic Resolution?

Discretize a small set of atomic-resolution zone-axis projections



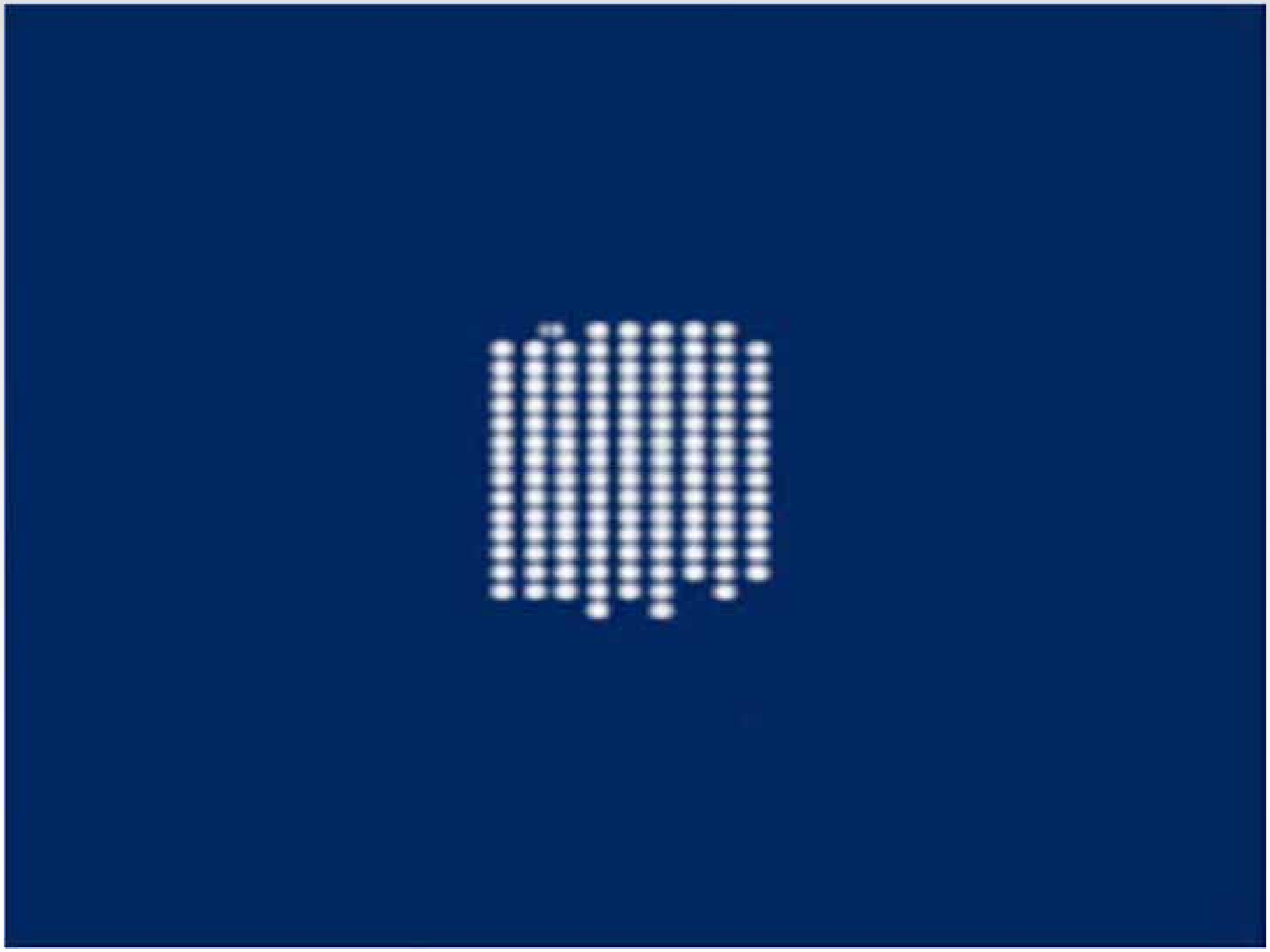
Higher resolution
→ More projections

See also Jinschek et al, *Ultramicroscopy* **108** (2008) 589

Discrete Tomography at Atomic Resolution?

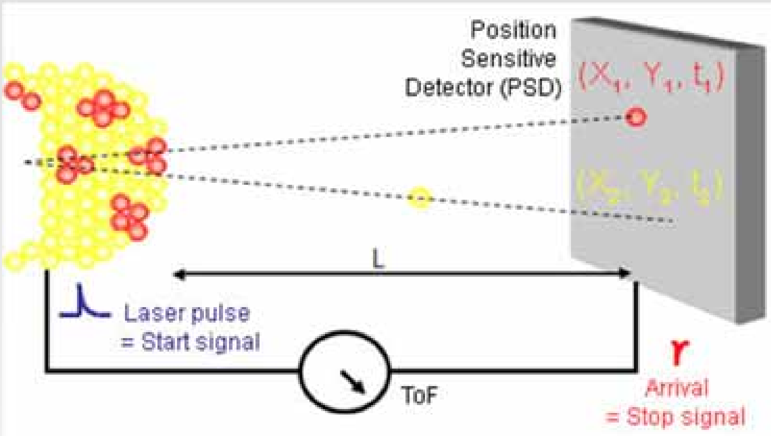
Digitize a small set of atomic-resolution zone-axis projections

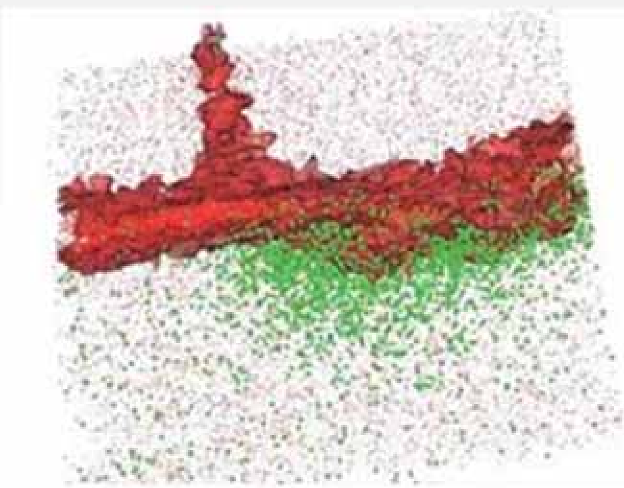
Er in Si



Uniqueness?

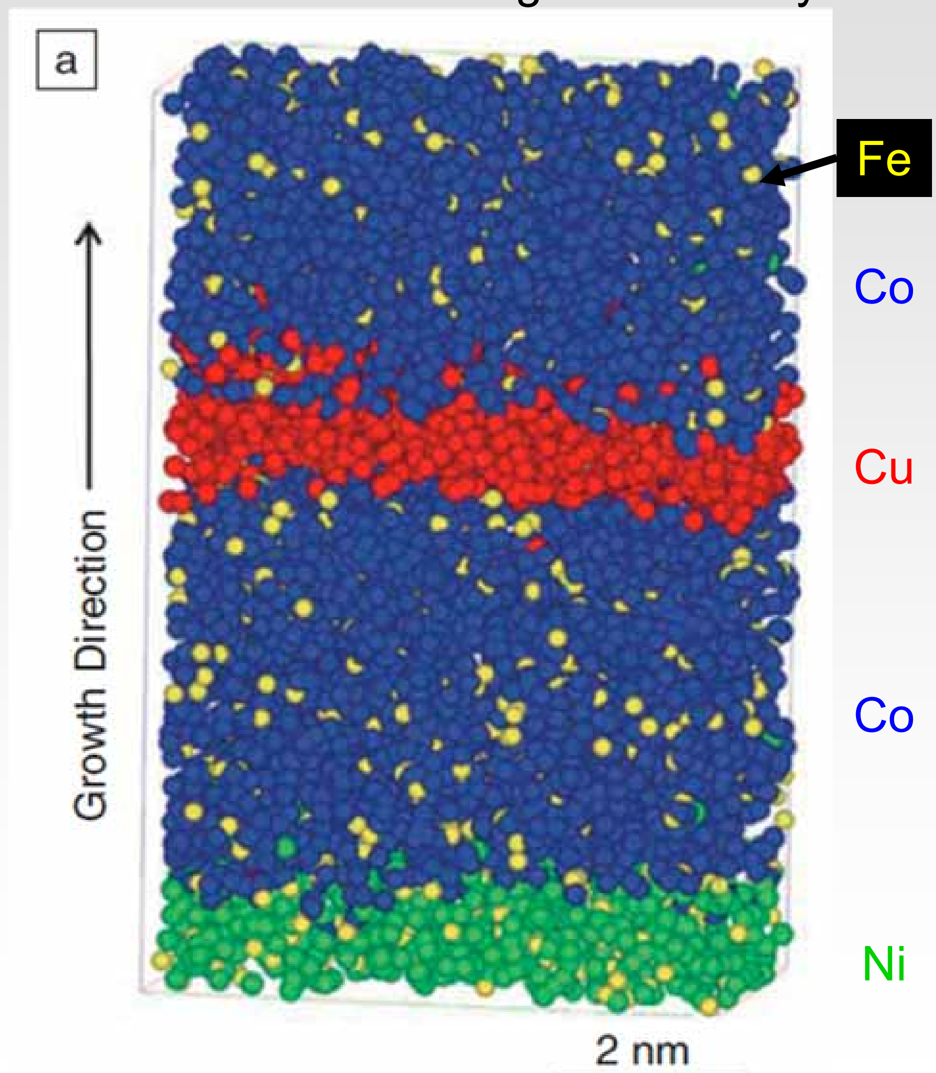
Atom-Probe Tomography:
3D Composition at Sub-nanometer Resolution
(~0.5 nm resolution, 50-60% of atoms detected)





LEAP Si Analysis: ~100nm FOV, 3D image of real dopant distribution (Arsenic atoms in green) in ultra shallow junction specimen.

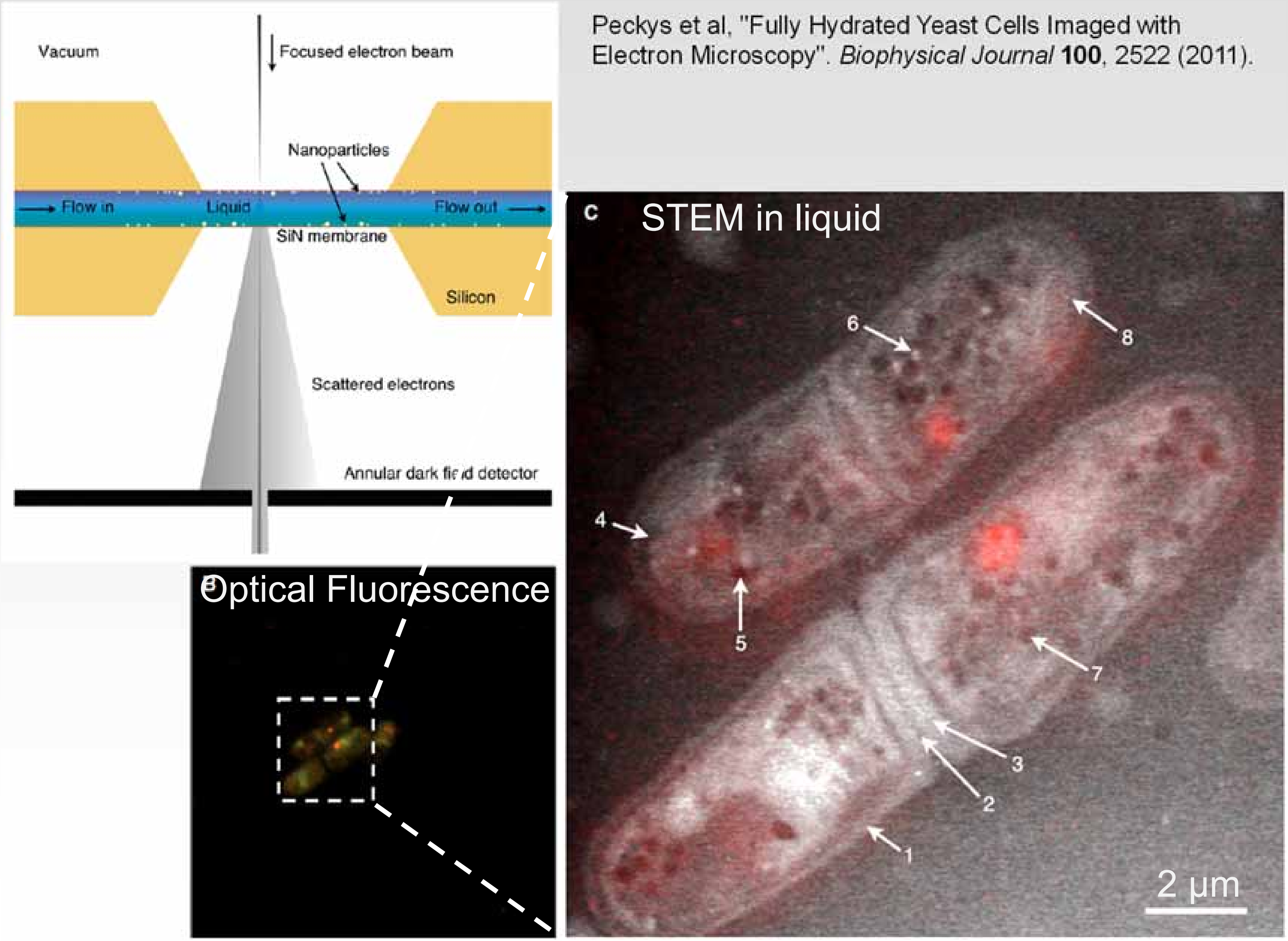
CoFe/Cu/CoFe Magnetic Multilayer



X.W. Zhou et al, *Acta Mater*. **49**, 4005 (2001)

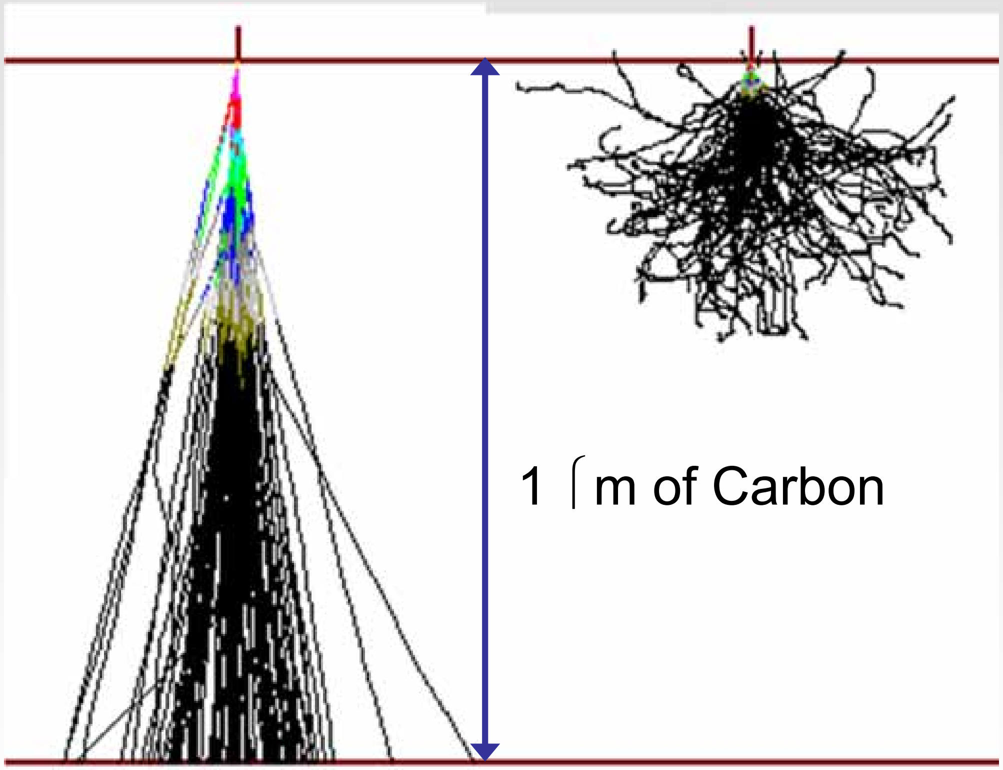
TEM in Liquids

Peckys et al, "Fully Hydrated Yeast Cells Imaged with Electron Microscopy". *Biophysical Journal* **100**, 2522 (2011).



Electrons go a Long Way

E_0=200 keV E_0=20 keV

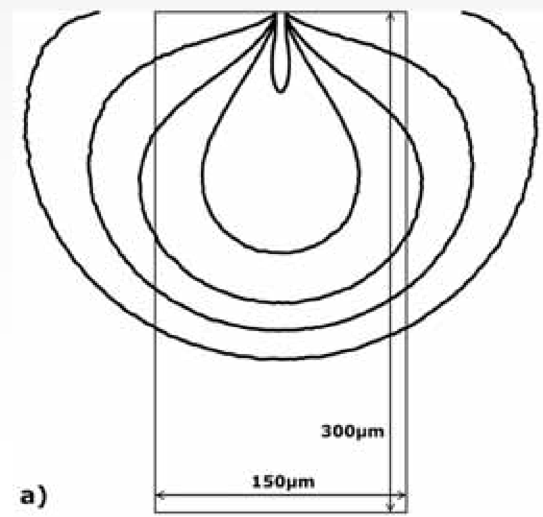


Electron Range (in μm):

$$R \approx \frac{0.064}{\rho} E_0^{1.5 \pm 0.3}$$

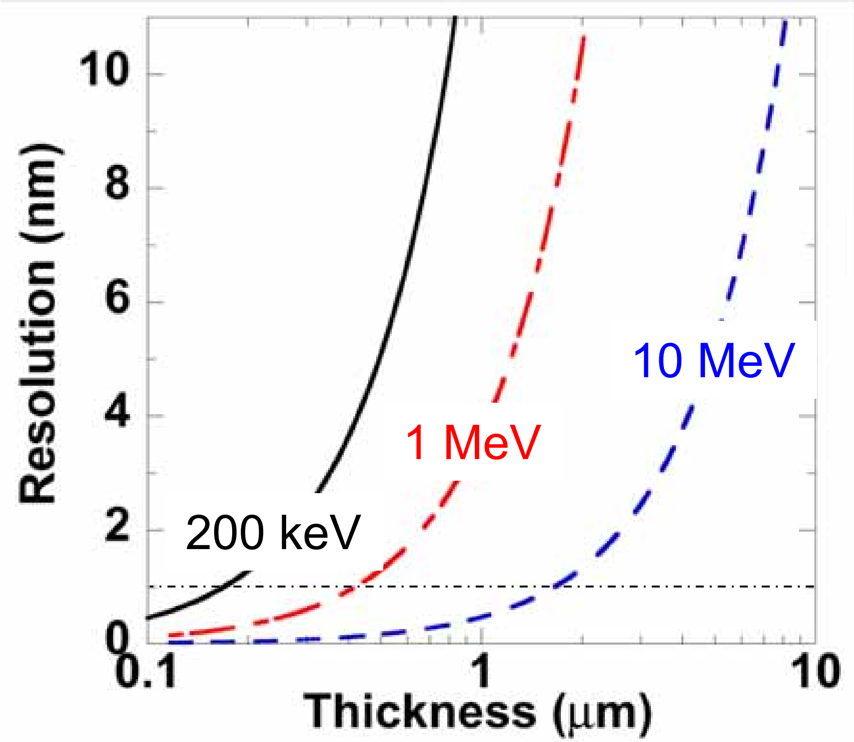
(density ρ in g/cm^3, E_0 in keV)

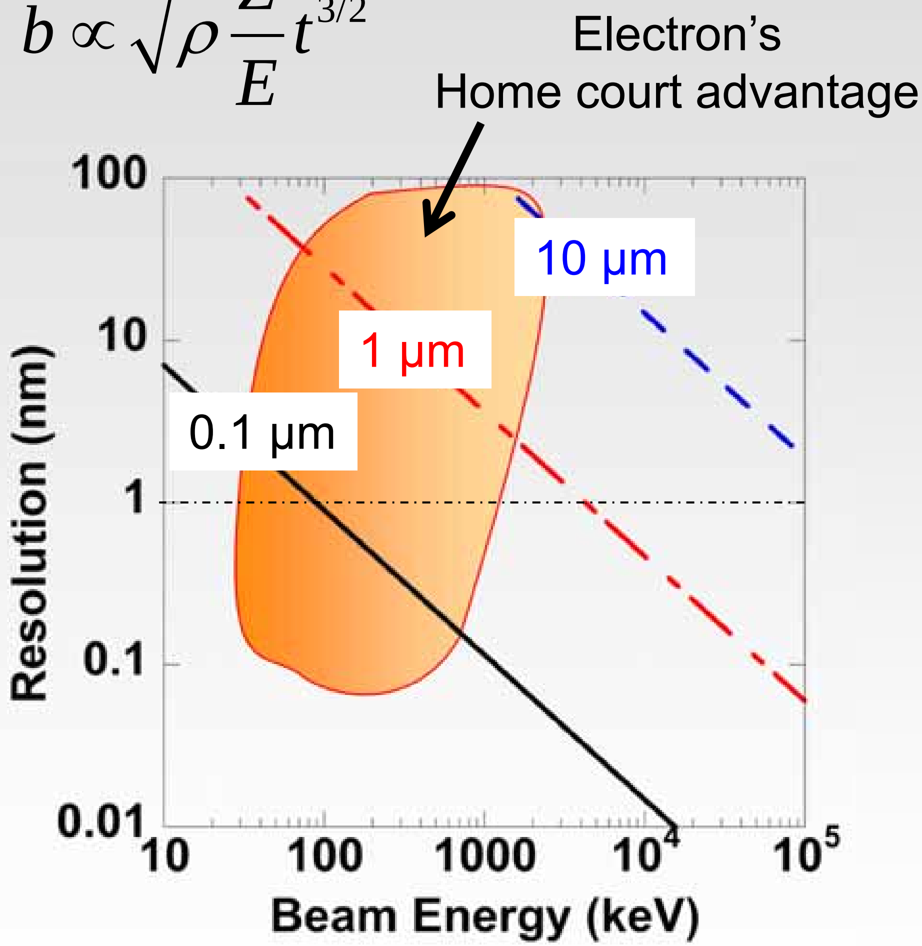
R~ 150 μm at 200 keV
in silicon



Beam Spreading (in Water)

Beam Spreading $b \propto \sqrt{\rho}\frac{Z}{E}t^{3/2}$





By changing the collection angle, can trade off
a linear improvement in resolution (~ x 2)
for an exponential drop in signal

Appl. Phys. Lett. **88** 243116 (2006)

Why not build an electron beamline?

(you have all the pieces already…)

Resolution Limits

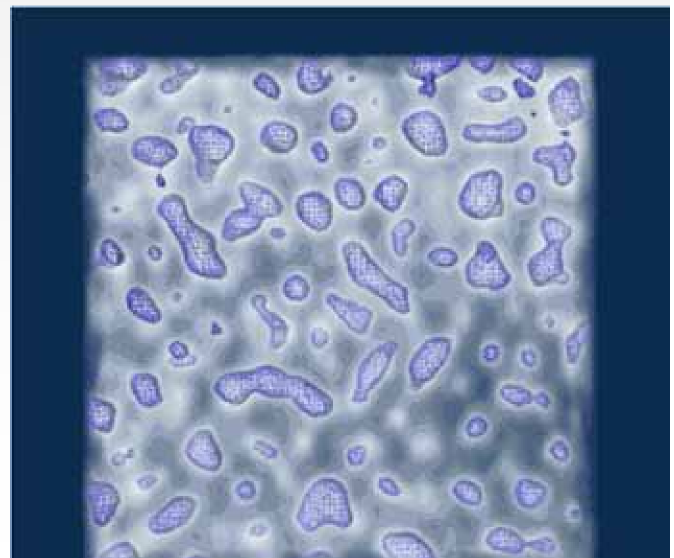
- Electron optics: Higher brightness, Ultrafast, 1 nm spot @ 1 μm
- Radiation Damage limits the imaging of UV-sensitive materials (~10x better for electrons)

Tomography

- Quantitative measurements of 3D objects
  - -1-3 nm resolution at 0.1-1 ⌠m thick
  - - 10 nm for 10-20 microns @ MeV
  - -Atomic resolution may be possible in inorganics

EELS Imaging (not time-resolved)

- 2D Chemical information at the atomic scale
- 3D may be possible at the nanometer scale



Plasmon Map of Si in SiO_2

Kavli Institute at Cornell

Outlook