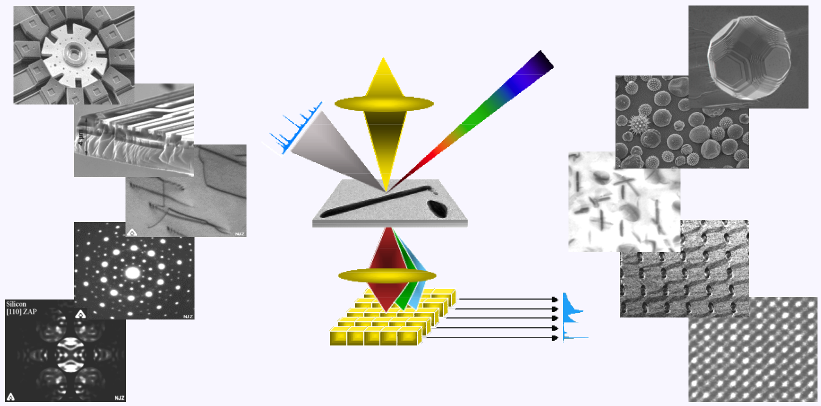
Pushing the Limits of AEM:
Where are we now and where are we going?



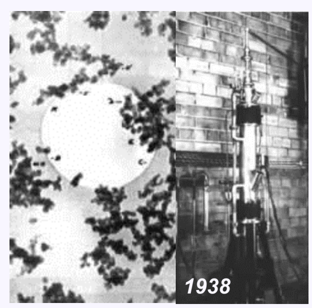
Nestor J. Zaluzec
zaluzec@aaem.amc.anl.gov
zaluzec@microscopy.com

Thanks to….

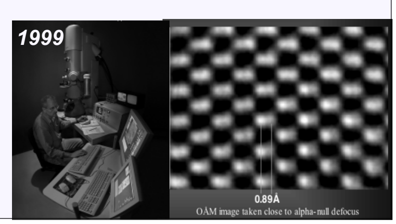
Australian Microscopy and Microanalysis Society

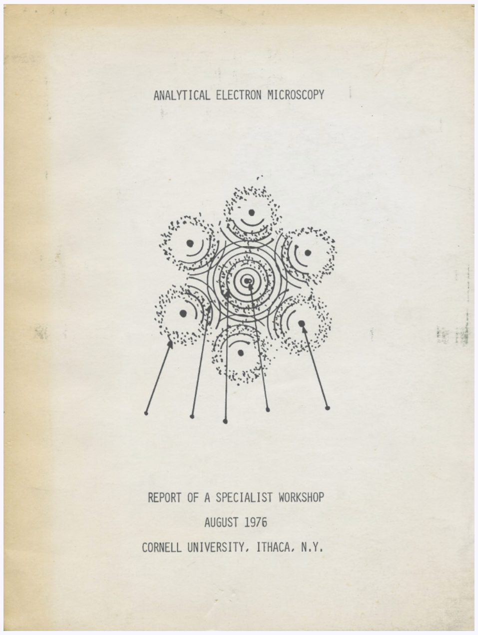
University of Technology Sydney

A Historical Time Line in Electron Optical Instrumentation



1897 JJ Thompson - Discovery of the Electron
1926 H. Bush Magnetic/Electric Fields as Lenses
1929 E. Ruska PhD Thesis Magnetic lenses
1931 Knoll and Ruska 1st EM built
1932 Davisson and Calbrick - Electrostatic Lenses
1934 Driest & Muller - EM surpases LM
1939 von Borries & Ruska - 1st Commerical EM
~ 10 nm resolution
1945 ~ 1.0 nm resolution (Multiple Organizations)
1965 ~ 0.2 nm resolution (Multiple Organizations)
1968 A. Crewe - U.of Chicago - Scanning Transmission Electron Microscope
~ 0.3 nm resolution probe - practical Field Emission Gun
1986 Ruska etal - Nobel Prize
1999 < 0.1 nm resolution achieved (OÅM)
2009 0.05 nm resolution (TEAM project)



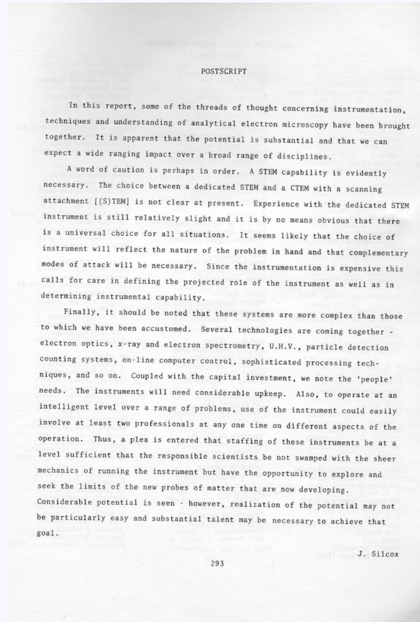


ANALYTICAL ELECTRON MICROSCOPY

REPORT OF A SPECIALIST WORKSHOP

AUGUST 1976

CORNELL UNIVERSITY, ITHACA, N.Y.



POSTSCRIPT

In this report, some of the threads of thought concerning instrumentation, techniques and understanding of analytical electron microscopy have been brought together. It is apparent that the potential is substantial and that we can expect a wide ranging impact over a broad range of disciplines.

A word of caution is perhaps in order. A STEM capability is evidently necessary. The choice between a dedicated STEM and a CTEM with a scanning attachment [(S)TEM] is not clear at present. Experience with the dedicated STEM instrument is still relatively slight and it is by no means obvious that there is a universal choice for all situations. It seems likely that the choice of instrument will reflect the nature of the problem in hand and that complementary modes of attack will be necessary. Since the instrumentation is expensive this calls for care in defining the projected role of the instrument as well as in determining instrumental capability.

Finally, it should be noted that these systems are more complex than those to which we have been accustomed. Several technologies are coming together - electron optics, x-ray and electron spectrometry, U.H.V., particle detection counting systems, on-line computer control, sophisticated processing techniques, and so on. Coupled with the capital investment, we note the 'people' needs. The instruments will need considerable upkeep. Also, to operate at an intelligent level over a range of problems, use of the instrument could easily involve at least two professionals at any one time on different aspects of the operation. Thus, a plea is entered that staffing of these instruments be at a level sufficient that the responsible scientists be not swamped with the sheer mechanics of running the instrument but have the opportunity to explore and seek the limits of the new probes of matter that are now developing. Considerable potential is seen - however, realization of the potential may not be particularly easy and substantial talent may be necessary to achieve that goal.

J. Silcox

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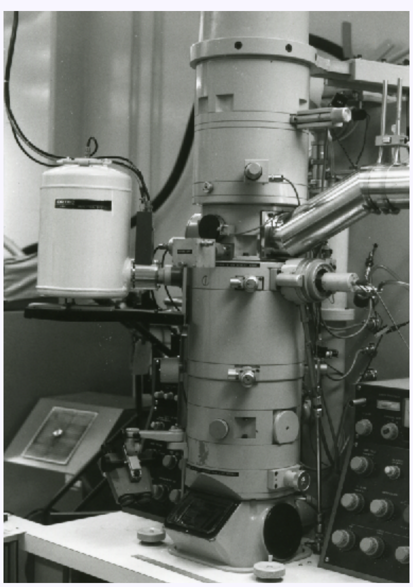
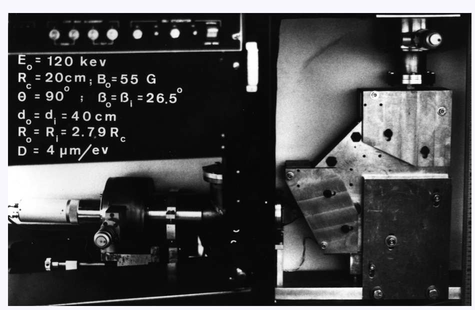
Back in the "Good Old Days"

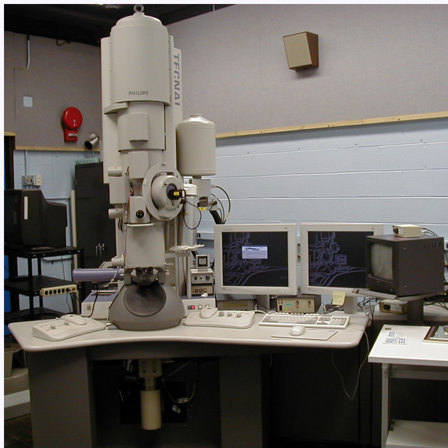


~1975 UIUC



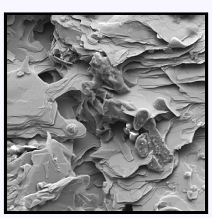
~1978 ORNL

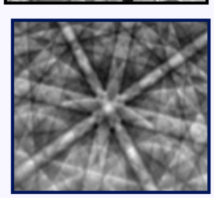
Not so long ago



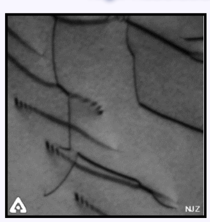
Traditional Analytical Electron Microscopy

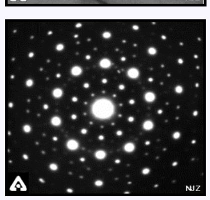
SEM
Scanning Electron Microscopy

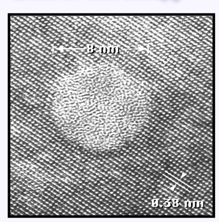


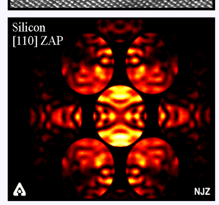


TEM - STEM - HREM
Transmission - Scanning Transmission - High Resolution Electron Microscopy

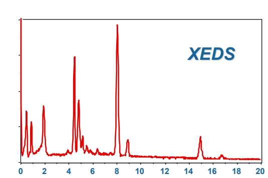


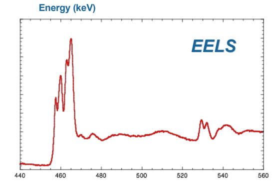






AEM
Analytical Electron Microscopy



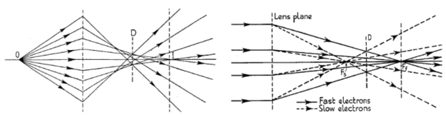


Morphology, Crystallography, Elemental , Chemical , Electronic Structure

What are the limitations in EM ?

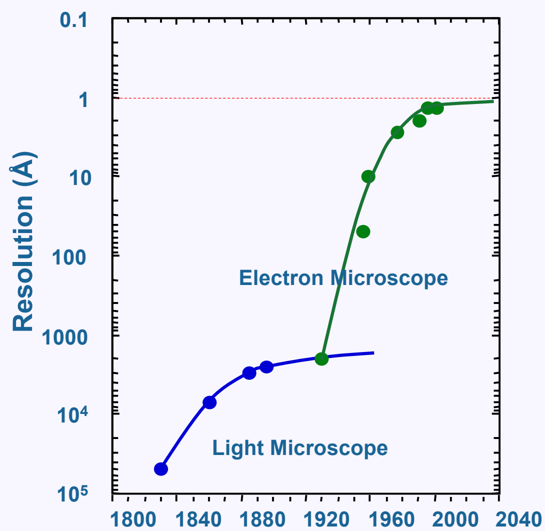
Aberrations

- Spherical
- Chromatic



$$r_{sph} = C_s \beta^3 \qquad r_{chr} = C_c \frac{\Delta E}{E} \beta$$

The source and solution to "resolution limitations" has been known for nearly 50 years



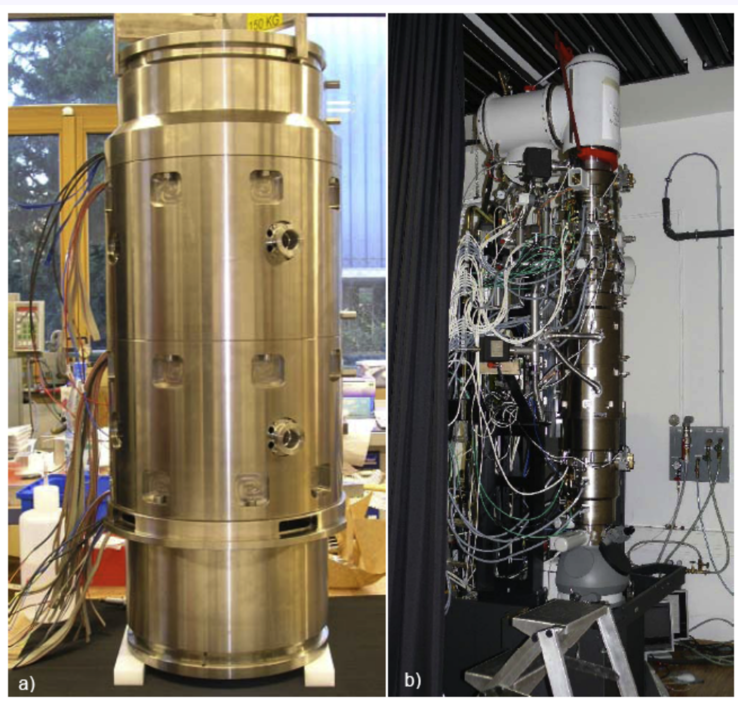
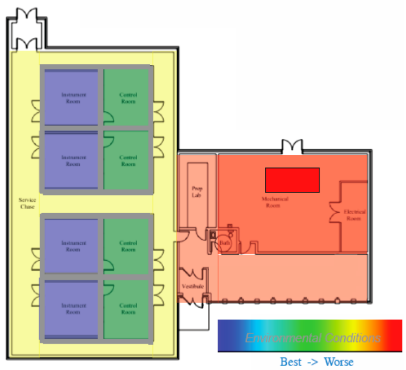
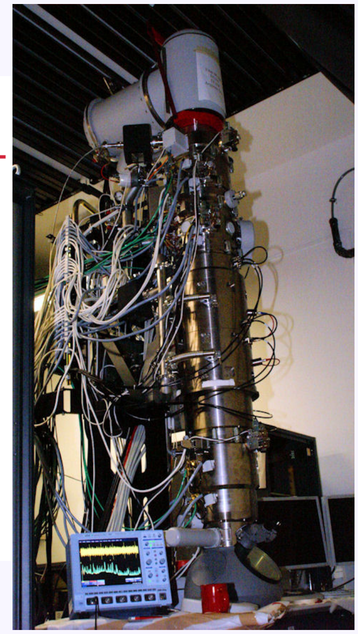


Fig. 1: *a) The Cc/Cs-corrector (C-COR) after construction showing the total length (83 cm) without filter boxes and vacuum lines and b) the Titan with the C-COR incorporated.*

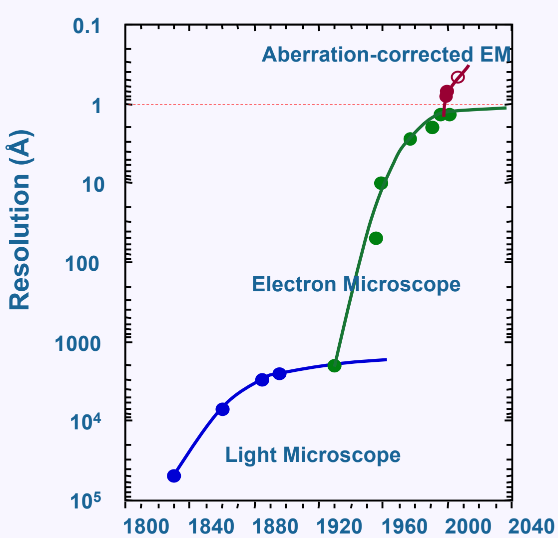
The Sub-Ångstrom Microscopy and Microanalysis Laboratory (SAMM)

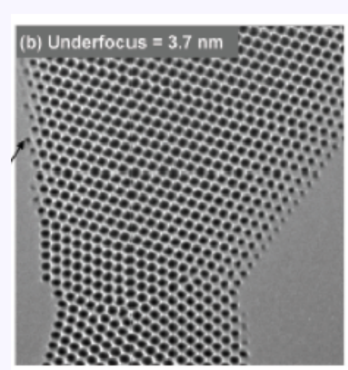


- four new state-of-the-art research laboratories to meet the needs of next generation instrumentation
- isolated slabs for instruments and support equipment
- room within a room concept



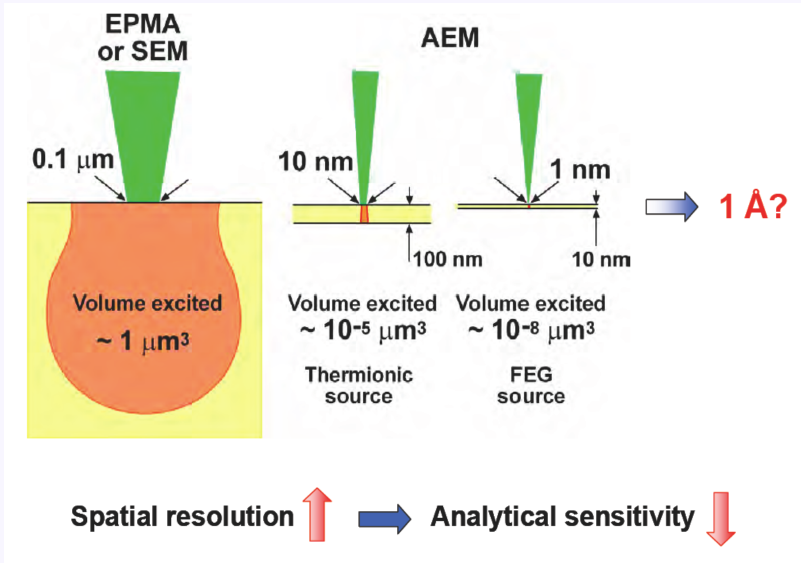
DoE TEAM Project





US DoE TEAM 0.5

Aberration Corrected Instruments



Williams & Carter

Probe - Current - Brightness Equations

Probe Size = Quadratic Sum of

Geometric + Aberrated Discs of least "least confusion"*.

$$d_p^{\,2} = d_o^{\,2} + d_d^{\,2} + d_s^{\,2} + d_c^{\,2}$$

d_o = geometric source size $= \dfrac{2}{\pi\alpha}\sqrt{\dfrac{I_p}{\beta}}$

d_d = diffraction aberration limit $= \dfrac{1.22\lambda}{\alpha}$

d_s = spherical aberration limit $= 0.5\, C_S \alpha_o^3$

d_c = chromatic aberration limit $= C_C \alpha_o \left(\dfrac{\Delta V}{V} + \dfrac{2\Delta I}{I}\right)$

*This is an approximation and is only strictily true for Gaussian shaped distributions

Probe Size Variation with C_s , C_c and α

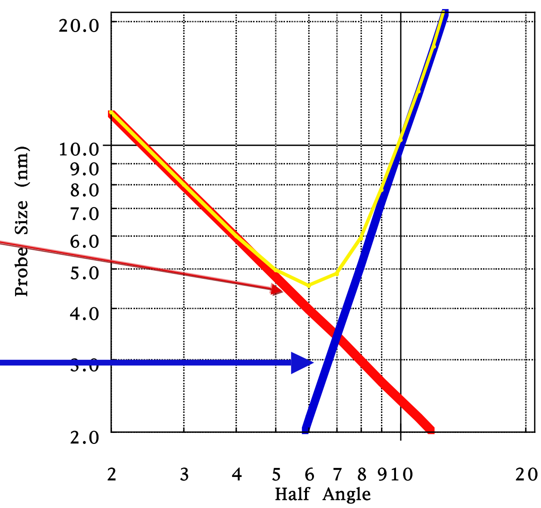
$$d_p^{\,2} = d_o^{\,2} + d_d^{\,2} + d_s^{\,2} + d_c^{\,2}$$

$$\frac{2}{\pi\alpha}\sqrt{\frac{I_p}{\beta}}$$

$$\frac{1.22\lambda}{\alpha}$$

$$0.5\ C_S\alpha_o^3$$

$$C_C\alpha_o\left(\frac{\Delta V}{V}+\frac{2\Delta I}{I}\right)$$



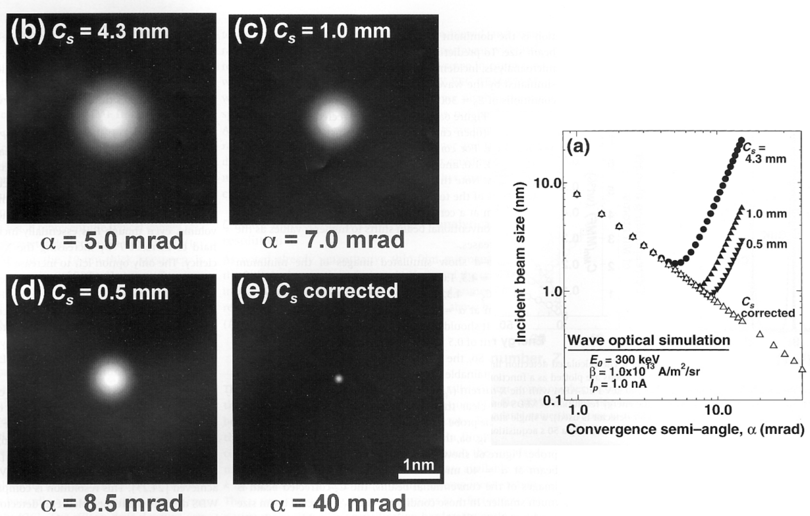
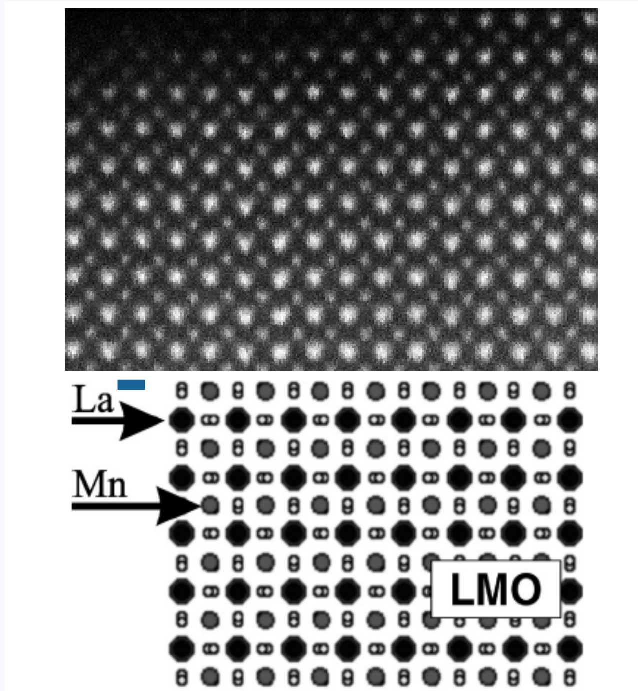


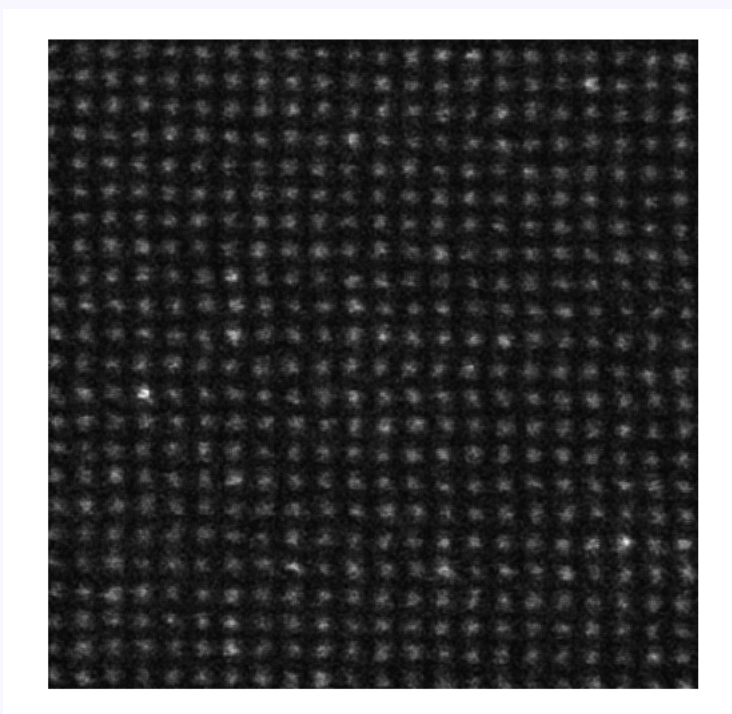
Fig. 6 (a) The simulated probe size (90%) with a beam current of 1 nA in conventional (C_s = 4.3, 1.0, and 0.5 mm) and C_s-corrected FEG-microscopes at 300 keV, plotted against probe convergence semi-angle. When a C_s corrector is used, the probe size is reduced significantly. Simulated probe images at α = 5 mrad with C_s = 4.3 mm (b), at α = 7 mrad with C_s = 1.0 mm (c), at α = 8.5 mrad with C_s = 0.5 mm (d), and at α = 40 mrad with a C_s corrector (e). The beam size approaches 2 Å with the C_s corrector at a beam current of 1.0 nA.

Williams, Papworth, Watanabe
JEM 51 S 113-126 (2002)

$LaMnO_3$



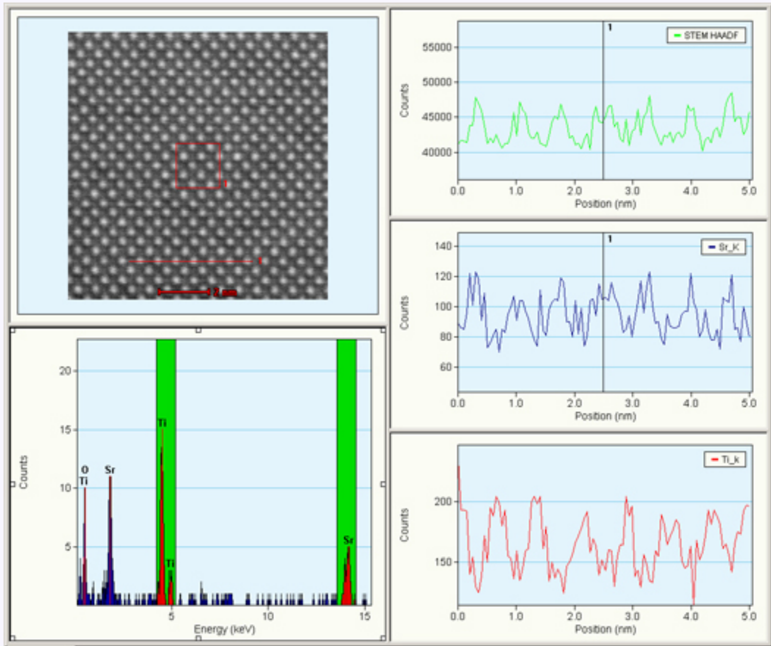
10/06/2009



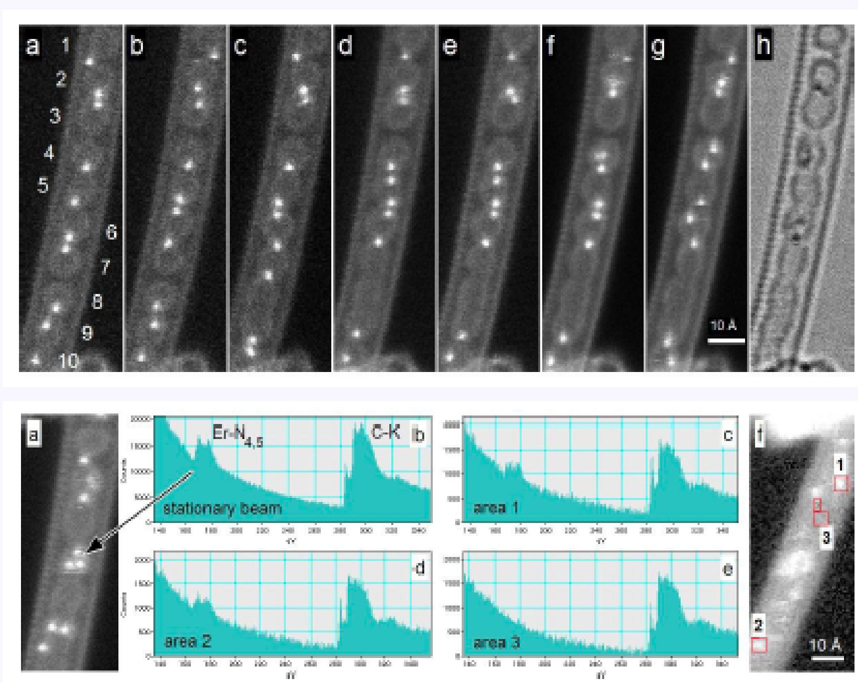
As
Doped
Si

Y. Oshima etal
MM2009

What are the Limits ?

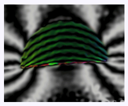
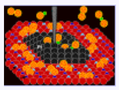
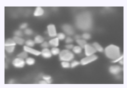
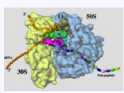
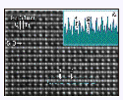


Dmitri Klenov B.Freitag,FEI

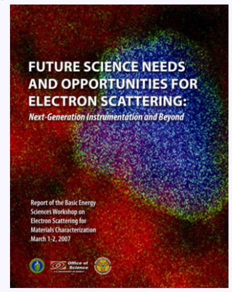


Krivanek etal 2010

Today's Research Opportunities using Microscopy & Microanalysis

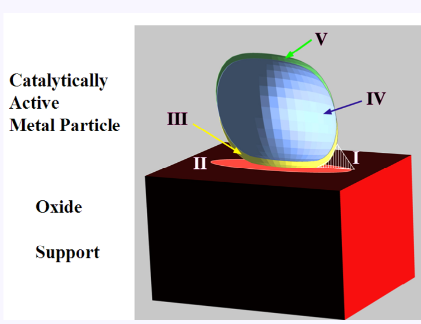
- *High Performance Materials: Understanding the Nanoscale Origin of Macroscopic Properties.*
- *Understanding Individual Atoms, Point Defects and Dopants*
- *Interfaces at Arbitrary Orientations*
- *Crystals Interacting with Liquids, Vapors, Soft Materials*
- *Mapping Fields In and Around Matter*
- *Small Particles – Large Impact*
- *Materials in Extreme Environments: The Behavior of Matter Far from Equilibrium*

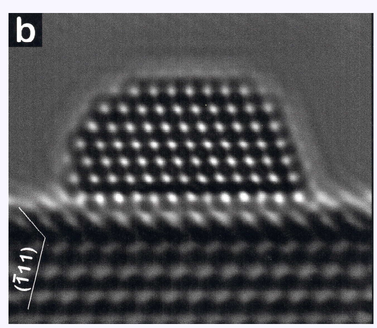


Challenges

Quantitative, Atomic Level , In-situ, Real Time

NanoMaterials
Small Particles – Large Impact





Catalysis
Where is the active site ??
How do we find it??

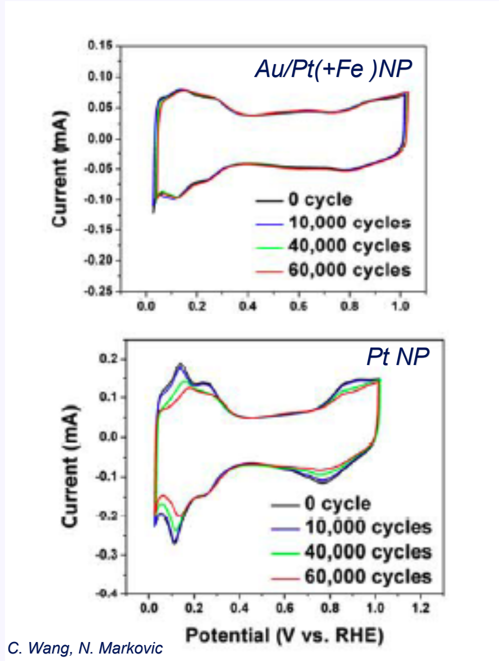
In Fuel Cell Technology Pt is a heavily used catalyst for large scale applications

Pt catalysts at the oxygen reduction cathode become unstable due to acidic envrionments

The oxygen potential of Pt catalysts can also be improved by incorporating Au.

The addition of transition metal (Fe, Co, Ni) alloying elements to Pt can significantly Improve the catalyst stability.

Nanoparticle structures are synthesized by epitaxially coating Au NPs with Pt (+Fe) using a series of chemical reduction and preciptation steps from RT to 200^o C.

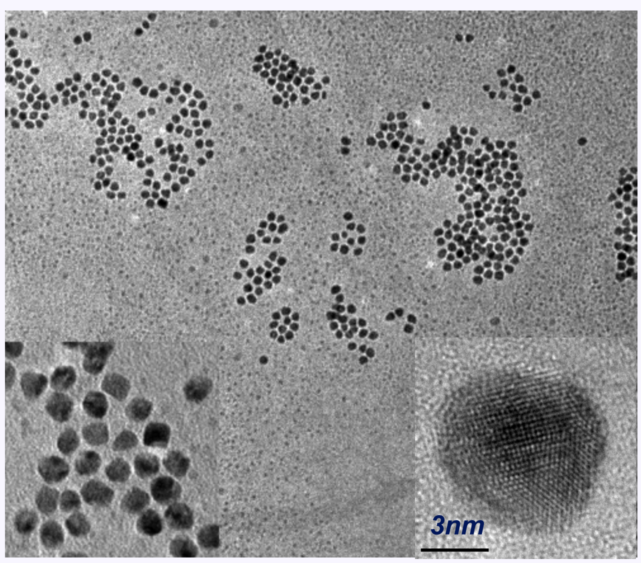


C. Wang, N. Markovic

NP Electrochemical Stability Tests 60 kcycles

Functionality Required is Influenced by the Science `

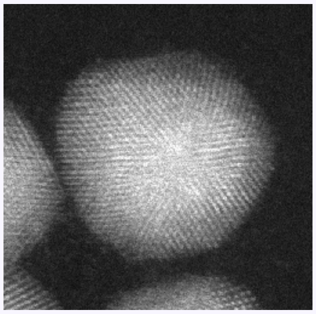
Pt (+Fe)/Au Catalyst Particles for Fuel Cell Applications



Wang, Markovic , Zaluzec

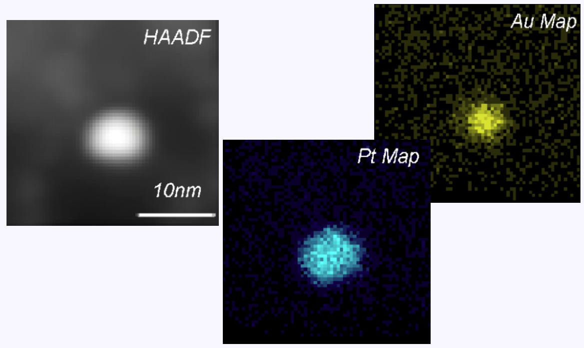
Why AEM?

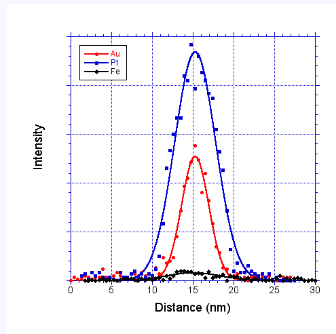
Because imaging is not always sufficient!



Atomic Resolution HAADF Image Of Pt/Au Nanoparticle (NP)

Where is the Pt, Au, Fe?





Experimental AEM XEDS Maps & Line Profiles of 10 nm NP demonstrating Au Core with Pt Shell

Minimium Detectable Mass

$$\mathrm{MDM} \sim \frac{k}{P_x I_o \tau} = \frac{k^*}{P_x J_o d_o^2 \tau}$$

Minimum Mass Fraction

$$\mathrm{MMF} \sim \frac{k}{\sqrt{[P_x (\frac{P}{B})_x I_o \tau]}} = \frac{k^*}{\sqrt{[P_x (\frac{P}{B})_x J_o d_o^2 \tau]}}$$

k, k^* = Constants

P_x = Characteristic Signal from element X

$(P/B)_x$ = Peak to Background ratio for element X

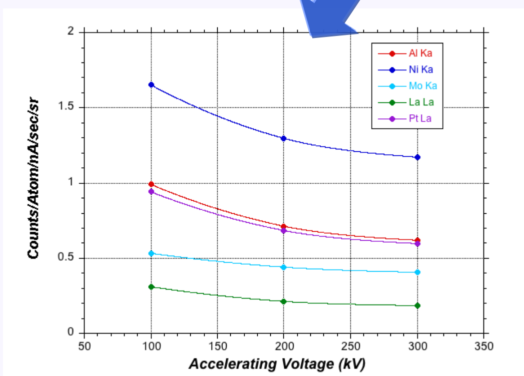
I_o = Incident electron flux

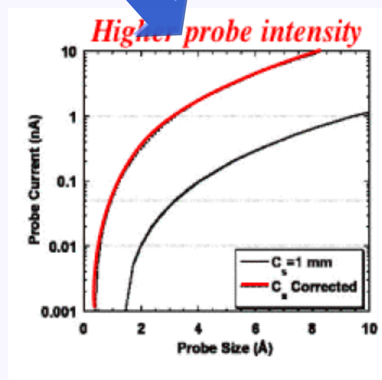
J_o = Incident electron current density

d_o = Probe diameter

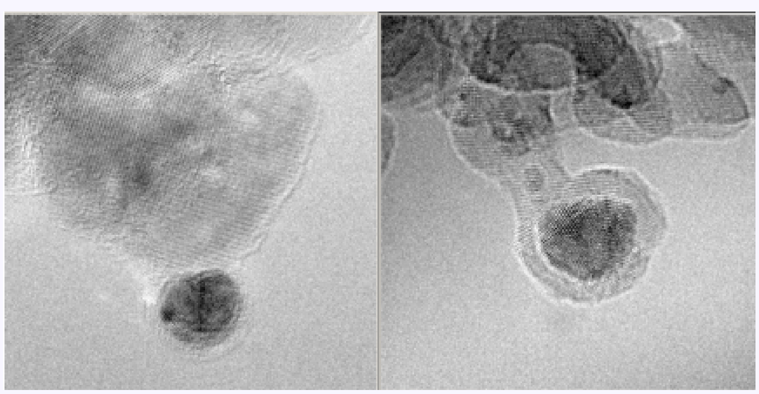
τ = Analysis time

$$I_A^{K\alpha} = \left[\sigma_A^K(E_o)\,\omega_A^K\,\Gamma_A^{K\alpha}\right]\bullet\left(\cancel{C_A\frac{N_o\rho\, t}{W_A}}\right)\bullet(\eta)\bullet\left(\varepsilon_A^{K\alpha}\Omega\right)$$

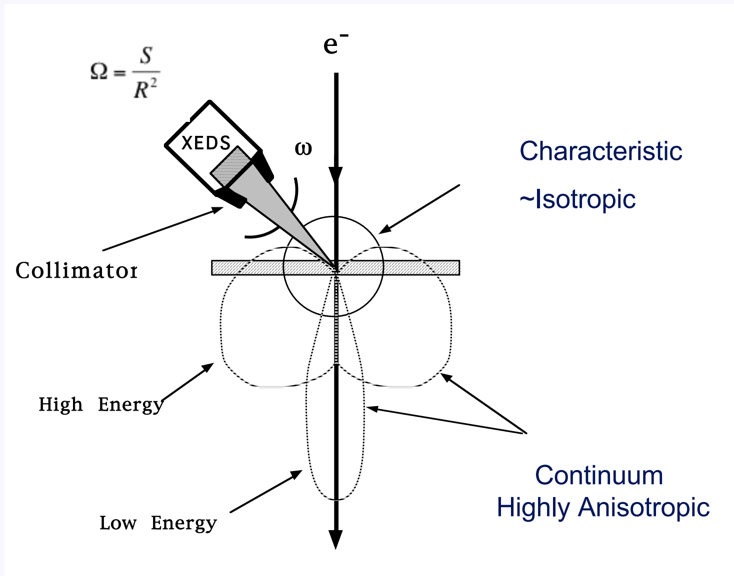




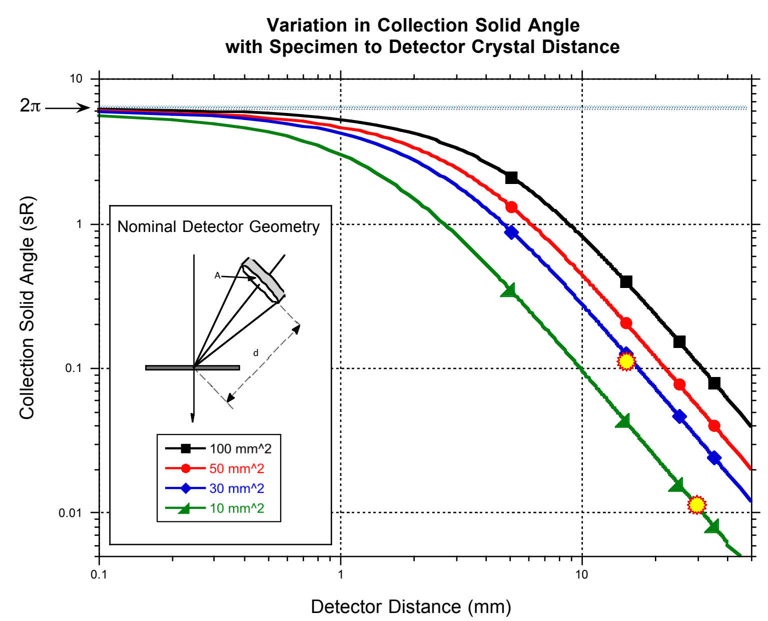
Nanoparticles can "damage" under high energy electron beams



Detector/Specimen Geometry



The Detector Collection Efficiency in Today's Instruments is at Best Mediocre

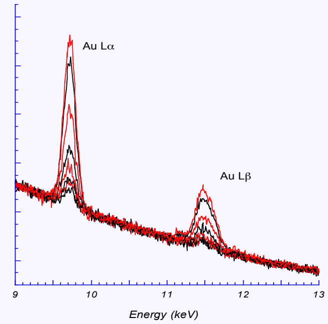


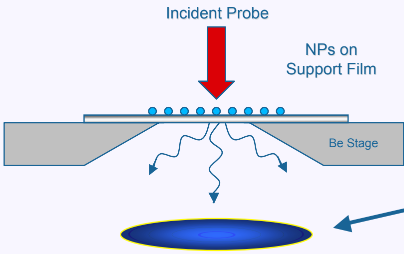
100%

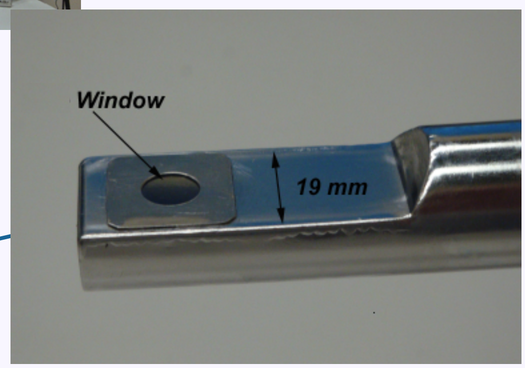
1.6%

0.16%

The transmission geometry is being tested on the ANL ESEM

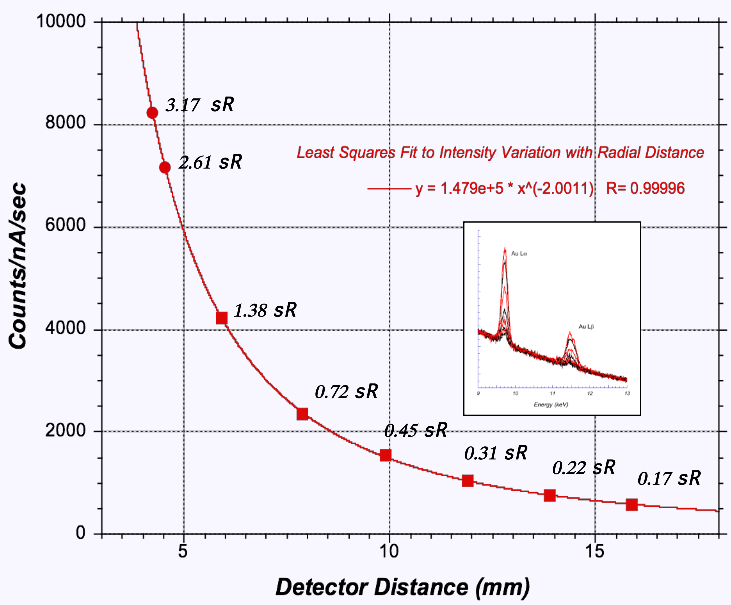




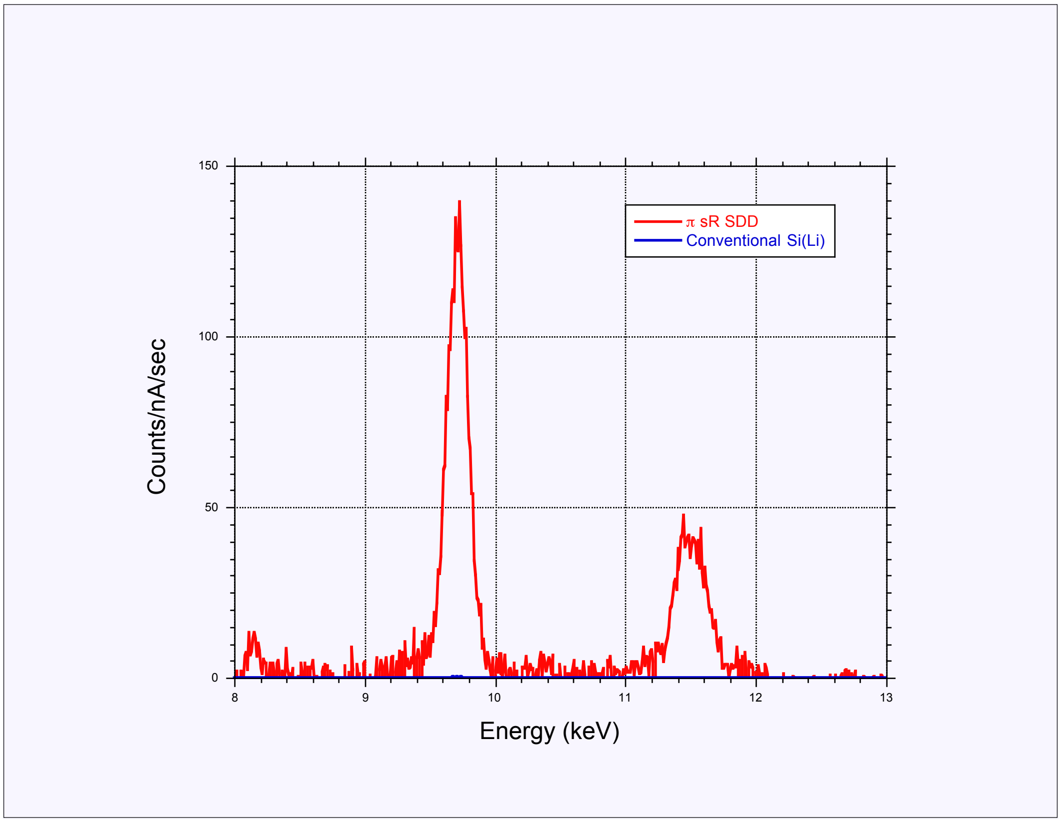


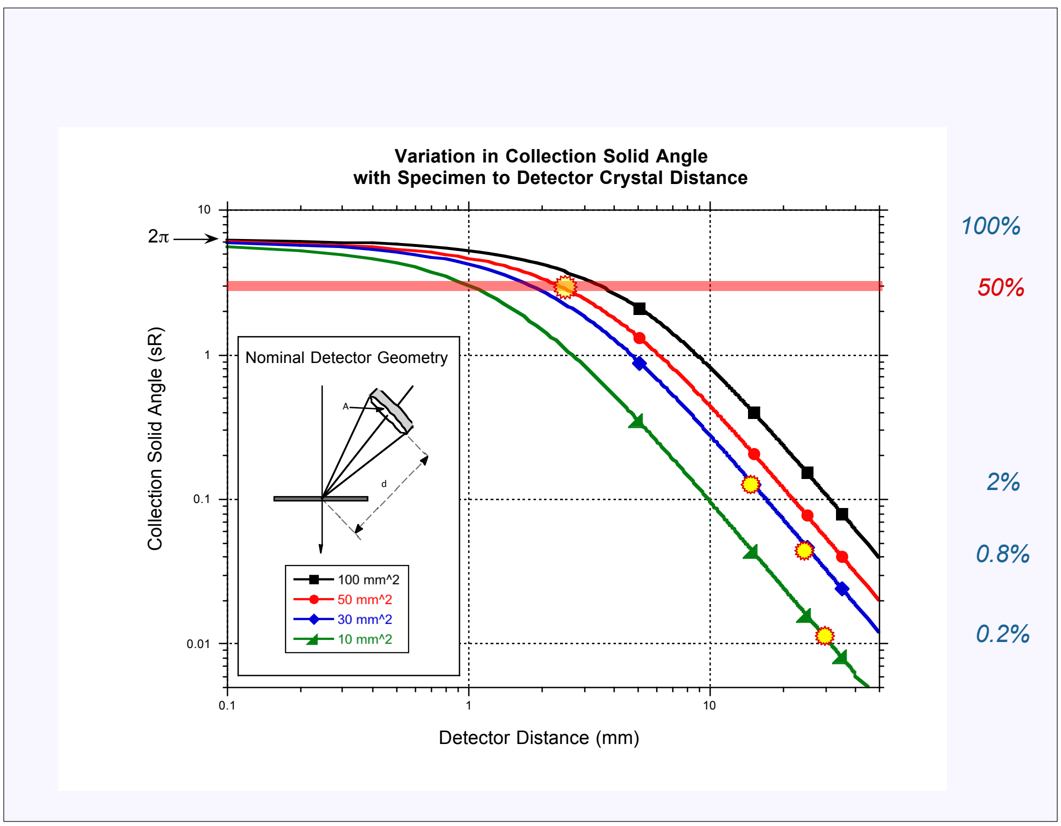
Transmission XD system

Experimental Variation of Intensity with Distance



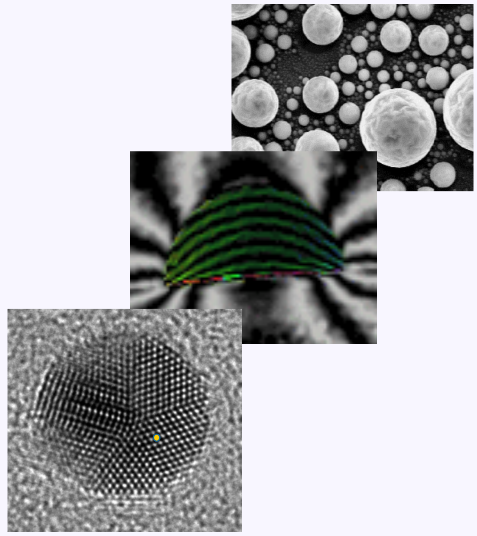
Numerical Values at each data point are the achieved solid angle


Counts/nA/sec
150
100
50
0
8
9
10
11
12
13
Energy (keV)
π sR SDD
Conventional Si(Li)

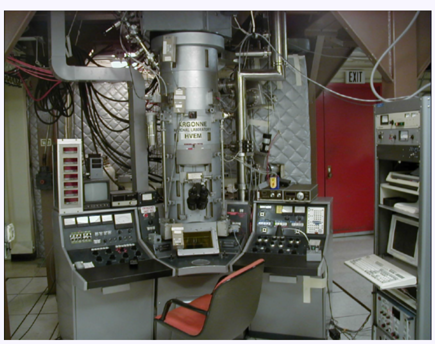

Variation in Collection Solid Angle
with Specimen to Detector Crystal Distance
2π
10
1
0.1
0.01
Collection Solid Angle (sR)
Nominal Detector Geometry
A
d
100 mm^2
50 mm^2
30 mm^2
10 mm^2
0.1
1
10
Detector Distance (mm)
100%
50%
2%
0.8%
0.2%

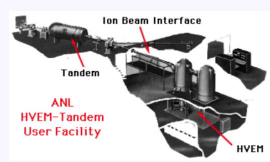
Observation of the State of a material during Dynamic conditions

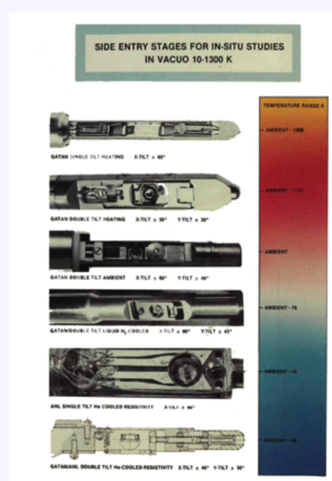
- *State*
  - *Morphology*
  - *Crystallography*
  - *Elemental/Chemical Constituents*
  - *Bonding/Electronic State*
- *Dynamic Conditions*
  - *Temporal*
  - *Temperature*
  - *Stress/Strain/Mechanical Deformation*
  - *Vacuum/Gaseous/Liquid Environment*
  - *EM Fields*
  - *Irradiation Environment*
    - *Charged Particles*
    - *Photons*



ANL has a Long History in In-situ Experimentation in the EM

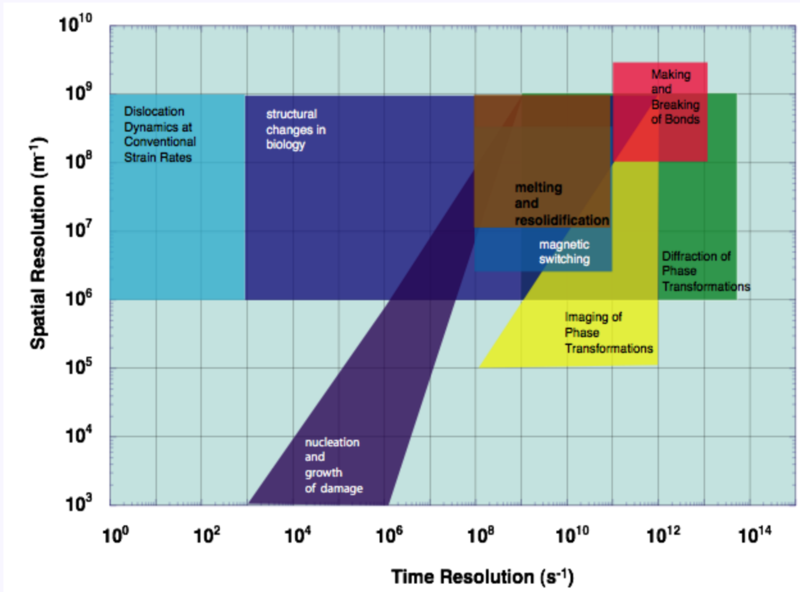






Decommissioned Fall 2001

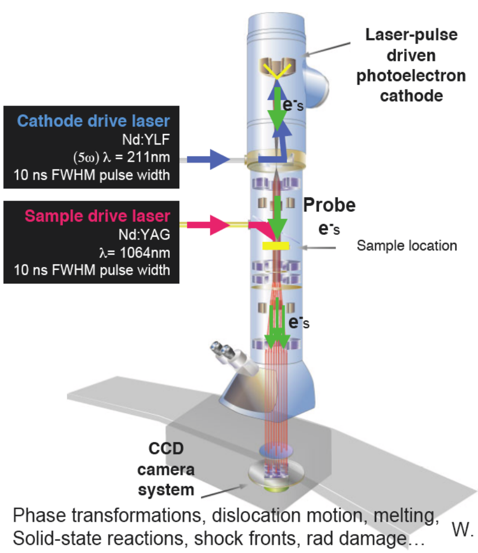
Ultra High Speed Imaging



Courtesy of N. Browning UC Davis

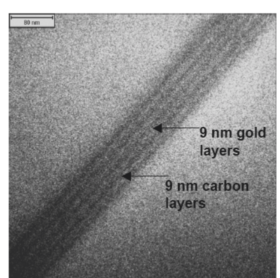
Overview of LLNL Dynamic TEM (DTEM)

Aim: to image transient phenomena to understand reaction pathways, kinetics, esp in solid state.



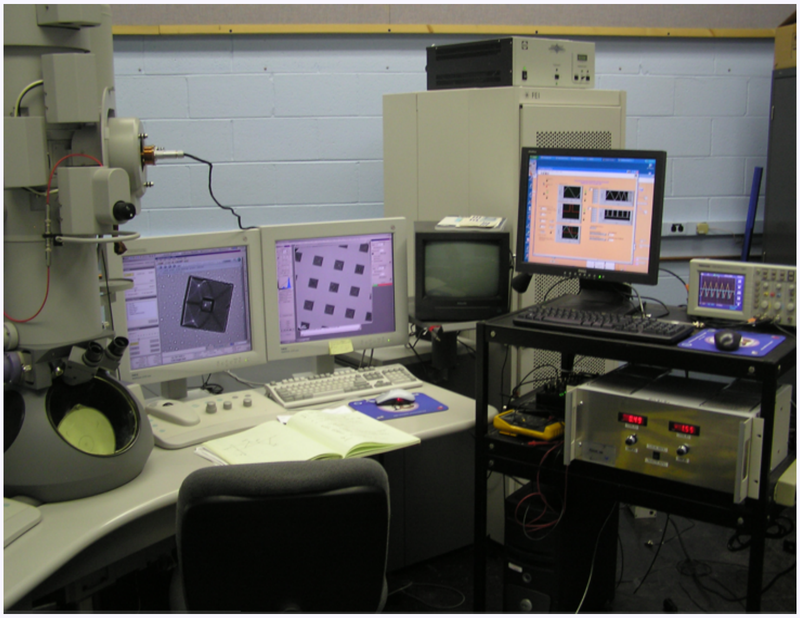
Phase transformations, dislocation motion, melting, Solid-state reactions, shock fronts, rad damage…

- Laser-driven photocathode electron source
- Nanosecond-scale *in situ* TEM
- Gun and optics developments underway

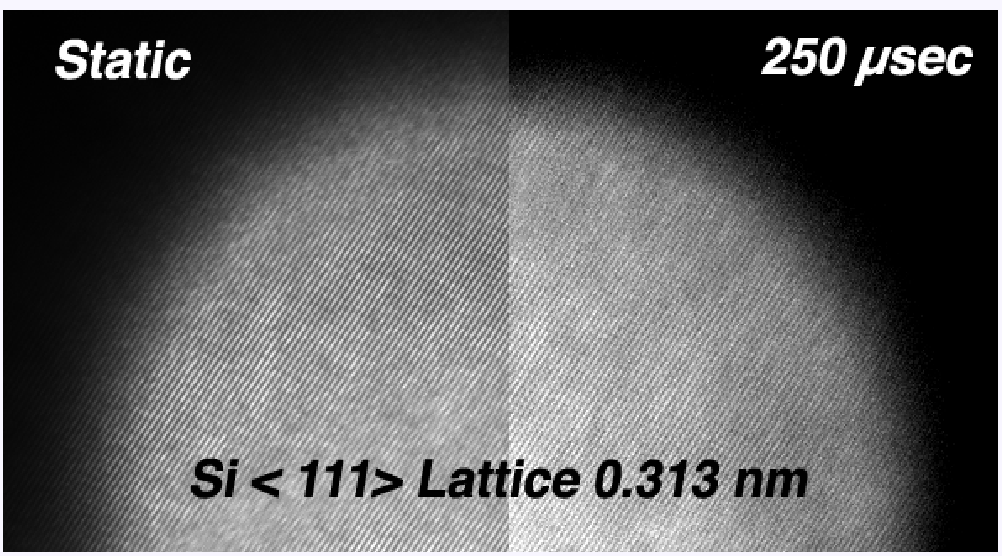


Single-Shot 15 ns DTEM Image

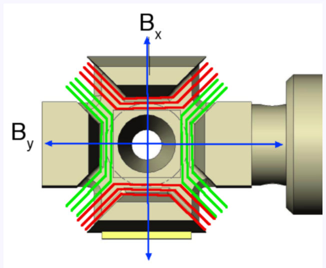
W. King, G,Campbell, N.Browning, B. Reed….

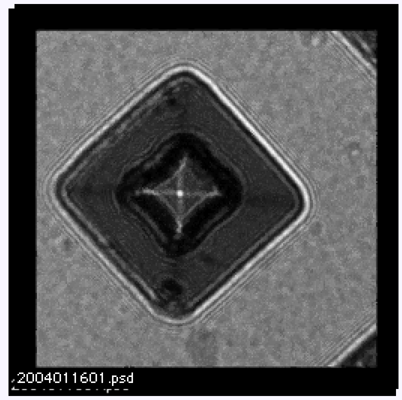


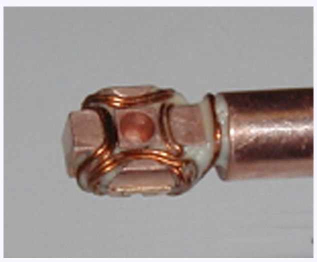
Not so High Speed Imaging

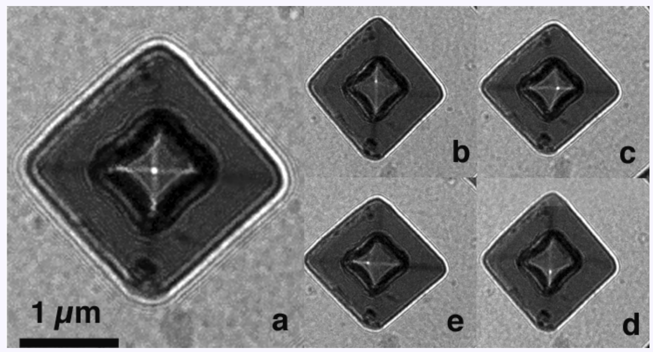


Observing Controlled Vortex and Domain Motion





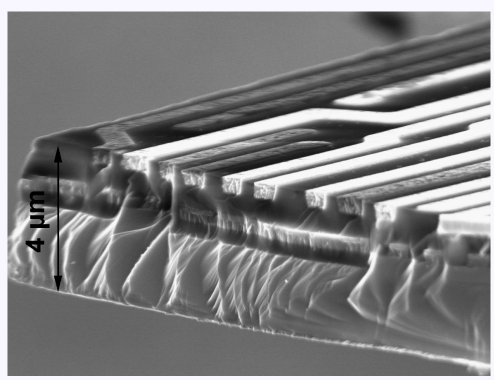




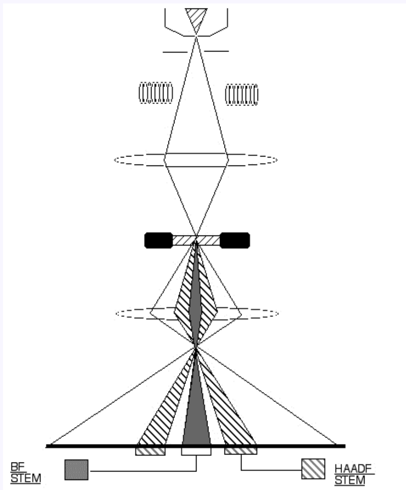
Ultra High Convergence & Large Gaps

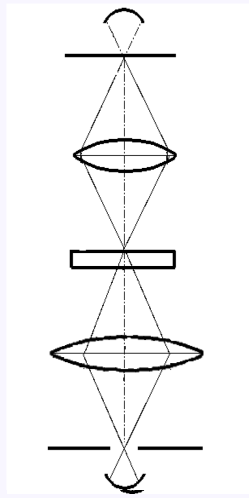
Additional Challenges in Materials Science

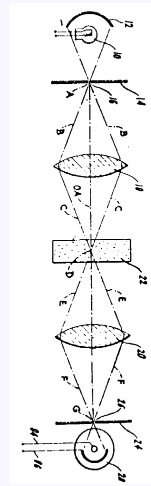
- **Optically Opaque Layers**
- **Thick Specimens**
- **Variable Compositions**
- **Visualizing Buried Layers**
- **“Resolution” at Depth**



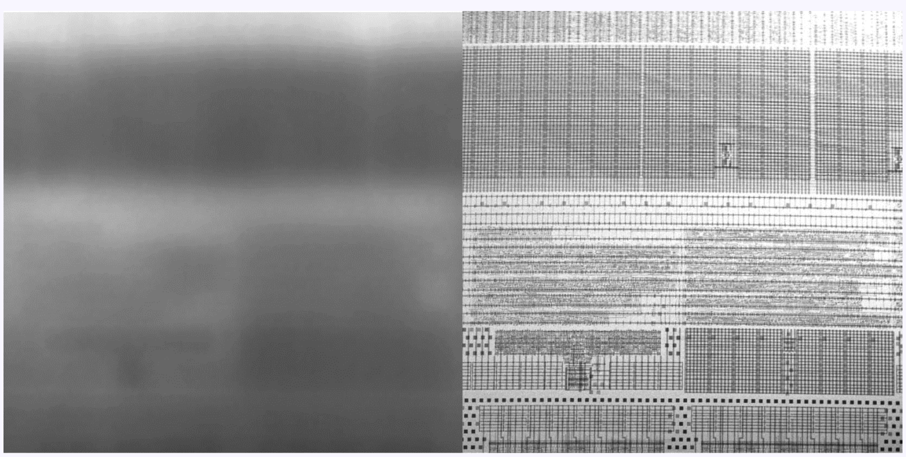
Scanning Confocal Electron Microscopy





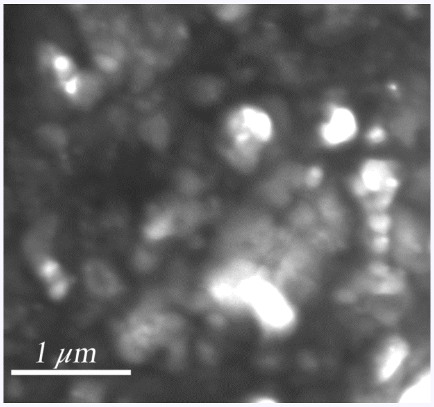


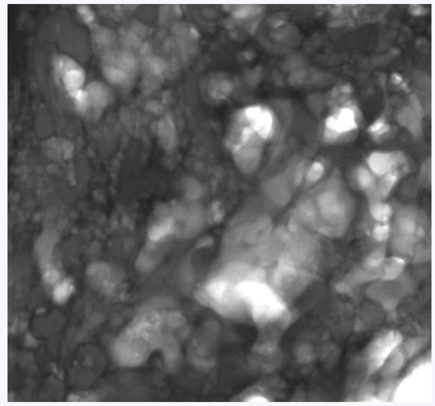
Comparison TEM/SCEM
Semiconductor Specimen



TEM *SCEM*

Comparison of TEM/SCEM imaging
5 μm thick X-section of hair medulla





TEM

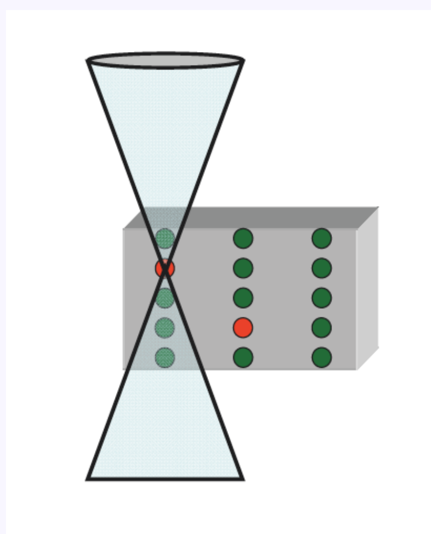
SCEM

P. Hallegot & N. J. Zaluzec
Scanning Confocal Electron Microscopy of Thick Biological Materials
Microscopy & Microanalysis 2004, Savannah Ga

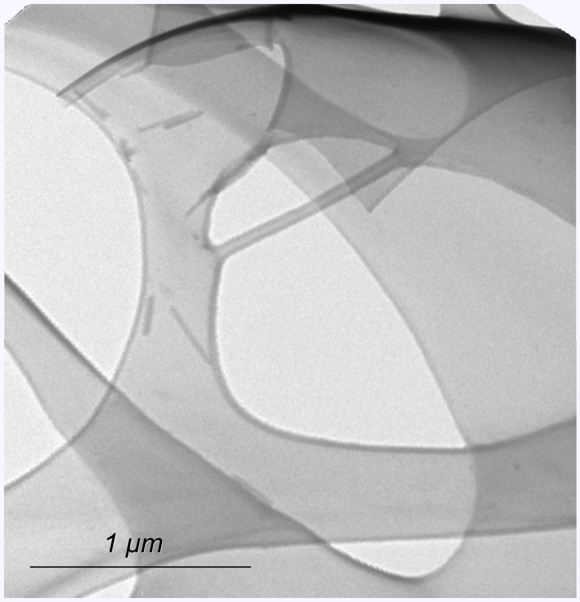
Scanning Confocal Electron Microscopy
Depth Profiling

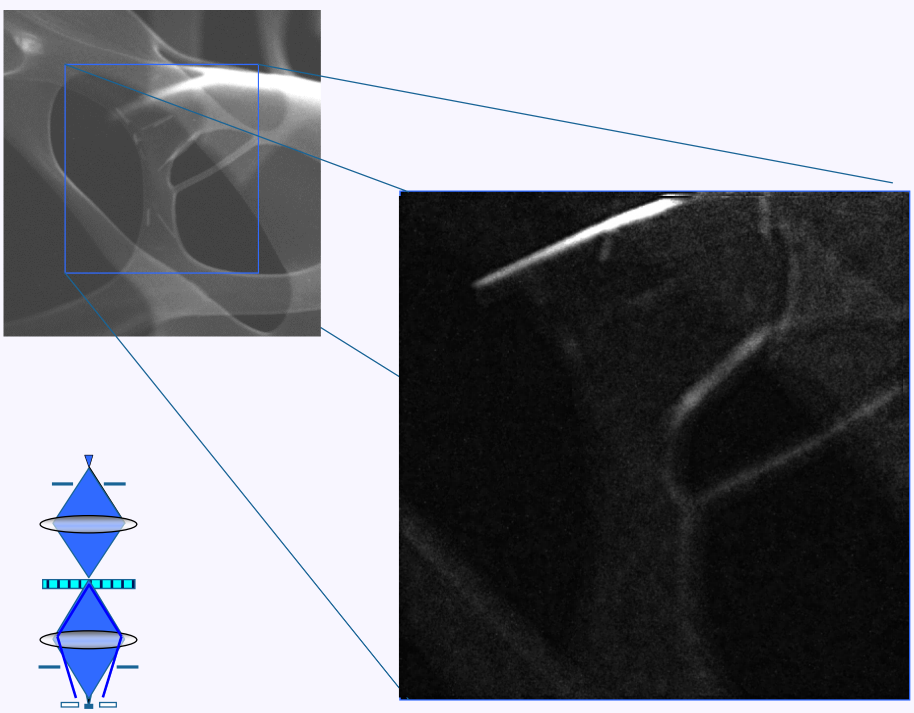
Aberration-correction allows for larger probe-forming aperture angles.As aperture angle increases, probe width decreases. Moreover "depth of focus"decreases, and even more rapidly.

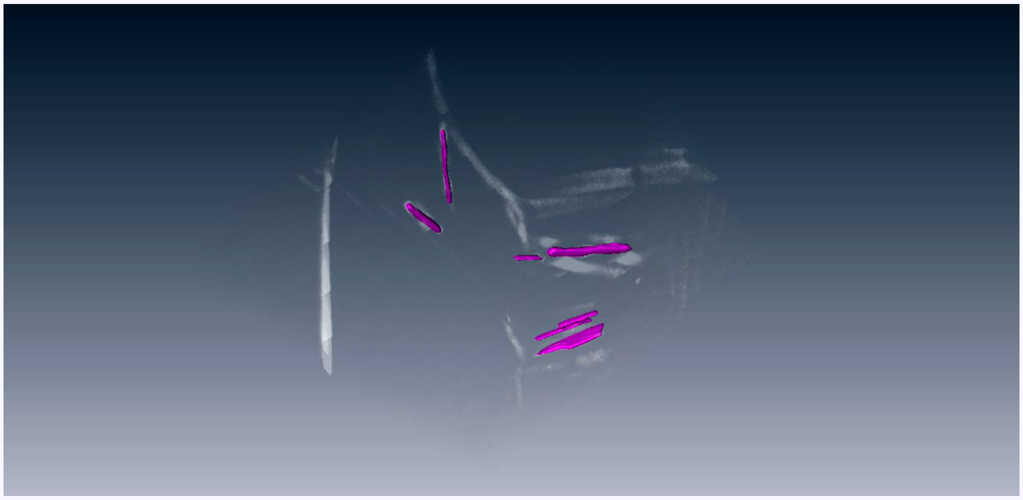
By varying defocus, in additional to usual 2D raster scan, could now scan in 3D.Can still measure several signals simultaneously.



Conventional BF TEM of SCEM Test Specimen #2
Ag Nano Wire on SiO Holey Film







Inelastic (Electron/Photon) Scattering Spectroscopies

	Type

Electron Energy Loss Spectroscopy (EELS),
  EXtended Energy Loss Fine Structure (EXELFS),
  Energy Loss Near Edge Fine Structure (ELNES),
Auger Electron Spectroscopy (AES),
	$e^- \Rightarrow e^-$

X-ray Emission Spectroscopy (XES),
  X-ray Energy Dispersive Spectroscopy (XEDS),
  Wavelength Dispersive Spectroscopy (WDS),
Cathodoluminescence (CL)
	$e^- \Rightarrow \lambda$

X-ray Photoelectron Spectroscopy (XPS), *X-ray Photoelectron Microscopy (XPM),* *Ultraviolet Photoelectron Spectroscopy (UPS),*	$\lambda \Rightarrow e^-$

X-ray Absorption Spectroscopy (XAS),
  EXtended X-ray Absorption Fine Structure (EXAFS),
  X-ray Absorption Near Edge Fine Structure (XANES)
X-Ray Fluorescence (XRF).
	$\lambda \Rightarrow \lambda$

PhotoLuminescence (PL)	

Plasmonic Fields & Radiative Transfer in Nanostructures

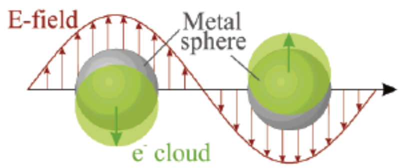


Figure 1. Schematic of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei.

When a small metallic nanoparticles are irradiated by light or electrons, the oscillating electric field causes the conduction electrons to oscillate coherently.

The oscillation frequency is determined by four factors:

- the density of electrons,
- the effective electron mass,
- shape and size of the charge distribution.

The collective oscillation of the electrons is called the dipole plasmon resonance of the particle and is manifest both in photon and electron spectroscopy.

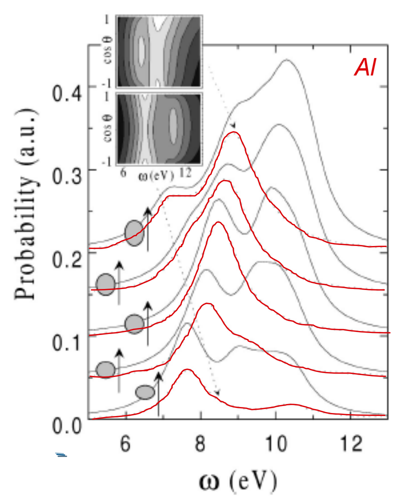


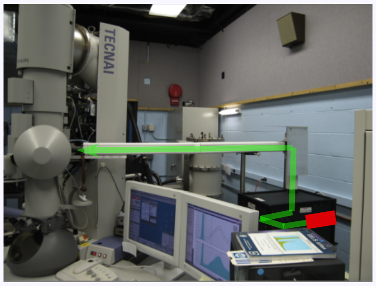
FIG. 4. Loss probability (solid curves) and photon-emission probability (broken curves, multiplied by a factor of 3) for a 100-keV electron passing at a distance of 1 nm from the surface of a Al cylindrical ellipsoid. The electron moves parallel to the axis of symmetry, along which the semiaxis of the ellipsoid takes different values (b = 14, 12, 10, 8, and 6 nm from top to bottom; see insets). The other semiaxis is 10 nm in all cases. Consecutive curves have been shifted 0.05 a.u. upwards to improve readability. The angular distribution of photon-emission probability is shown in the insets for the extreme cases of b = 6 nm and b = 14 nm.

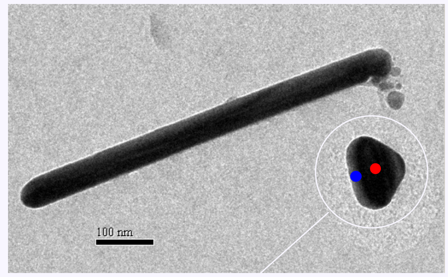
F. Abajo & A. Howie PRL 80 23, 5180 (1998)

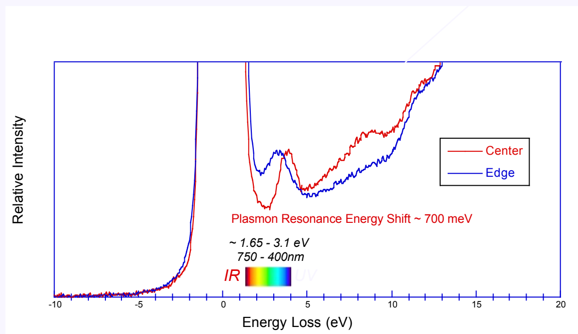
Optical Properties of Metal Nanoparticles

Influenced by Size, Shape, Local EM Fields & Dielectric Environment

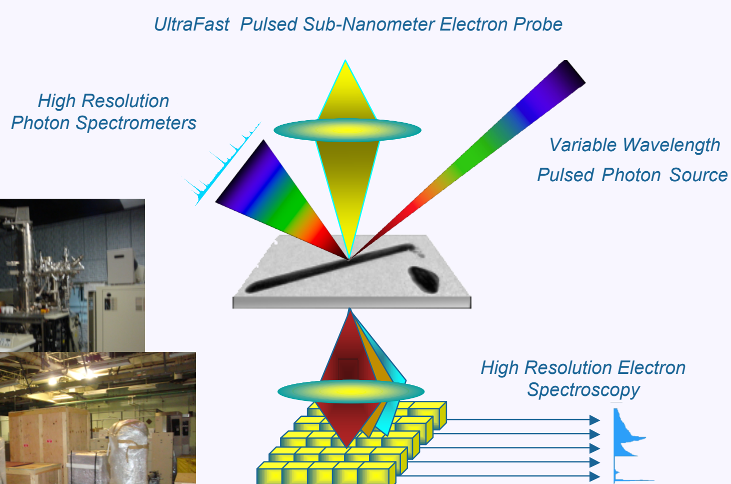
Plasmon resonances due to local electromagnetic fields will affect light scattering properties, these can be temporally probed by optical excitation of plasmons.



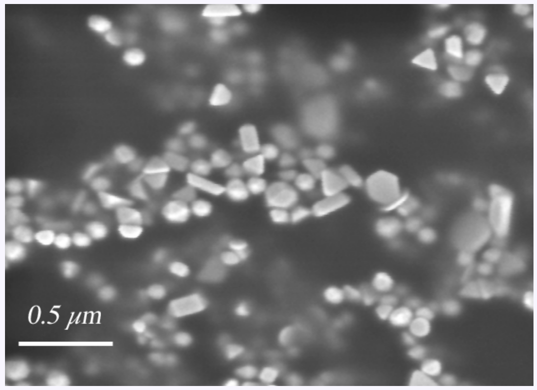




Integrating Spectroscopy & Time-Synchronized Characterization



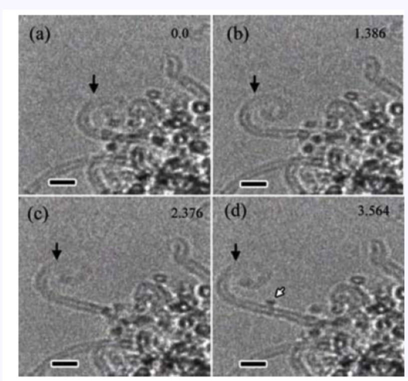
In-situ Liquid/Gaseous



Au Multifaceted Particles

Firestone etal 2005

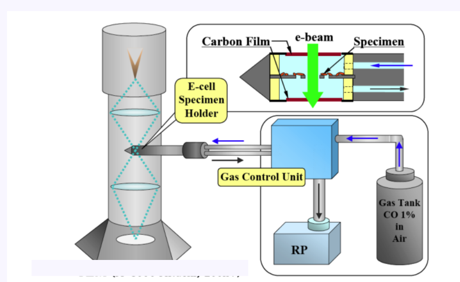
Current Generation Environmental Cell TEM



In-Situ TEM Studies of Carbon Nanotube Growth By Catalytic Decomposition of Acetylene

R. Sharma[1*], G.H. Du[1], P. Rez[2] and M. M. J. Treacy[2]

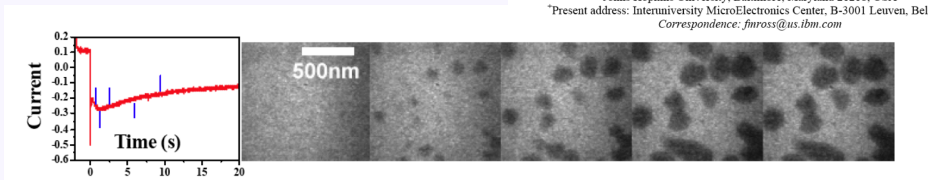
[1]Center for Solid State Science, Arizona State University, Tempe, AZ 85287
[2]Dept. of Physics and Astronomy, Arizona State University, Tempe, AZ 85287
**Correspondence: Renu.Sharma@asu.edu*

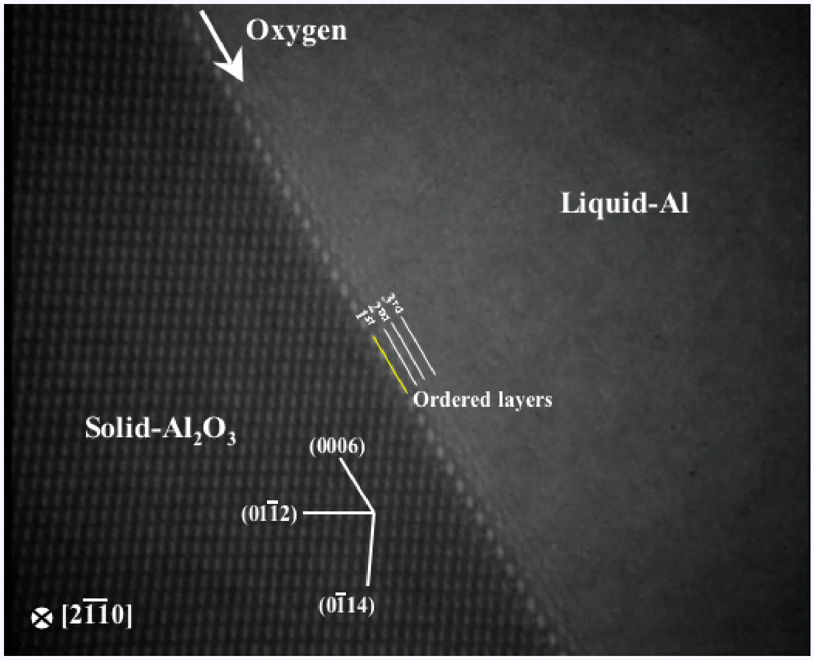


***In situ* Microscopy of Electrochemical Reactions**

F. M. Ross, A. Radisic[*+], P. Vereecken[+], J. B. Hannon, and P. C. Searson[*]

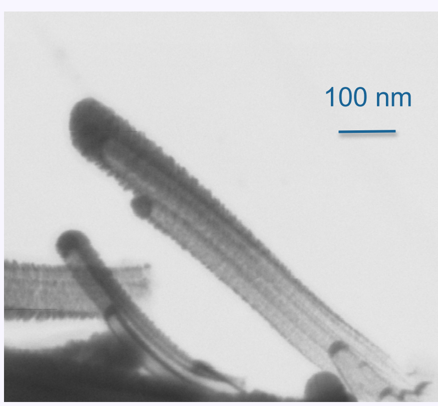
IBM T. J. Watson Research Center
1101 Kitchawan Road, Yorktown Heights, New York 10598, USA
[*]Department of Materials Science and Engineering
Johns Hopkins University, Baltimore, Maryland 21218, USA
[+]Present address: Interuniversity MicroElectronics Center, B-3001 Leuven, Belgium
Correspondence: fmross@us.ibm.com

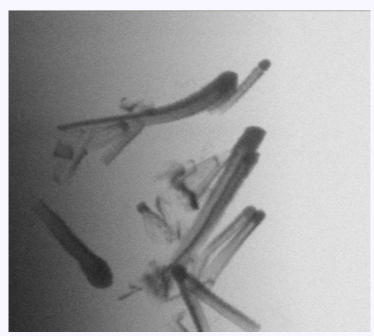


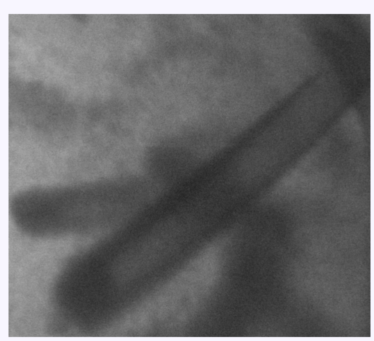


HREM image of the interface between solid Al_2O_3 and liquid Al. (M. Ruehle)

"STEM" of Catalysts in Water







What will the needs be in the future?

Gaseous Environment:

- ***Resolution 0.1 nm***
- ***Pressure up to 320 Torr***
- ***Temp to 800 ^{o}C***

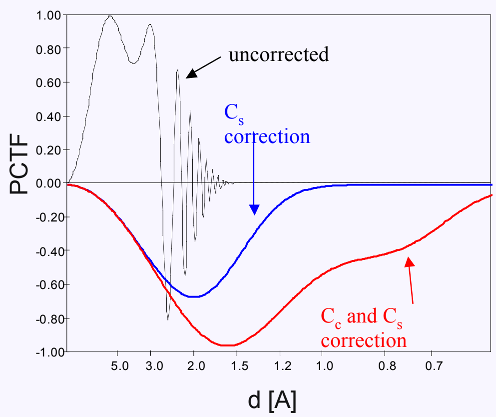
Fluidic Environment:

- ***Resolution < 1 nm***
- ***Fully immersed materials in flowing liquid***
- ***Temp to 200 ^{o}C***

Functionality Required
In-situ environments permitting observation of processes under conditions which replicate real world/real time conditions (temperature, pressure, atmosphere, EM fields, fluids) with minimal loss of image and/or spectral resolution.
Detectors which enhance by more than an order of magnitude the temporal, spatial, and/or collection efficiency of existing technologies for electrons, photons, and/or x-rays.
Higher temporal resolution instruments for dynamic studies with a continuous range of operating conditions from microseconds to femtoseconds.
Sources having higher brightnesses, temporal resolution, and polarization
Electron-optical configurations designed to study complex interactions of nanoscale objects under multiple excitation processes (photons, fields, ….)
Virtualized instruments which are operating in connection with experimental tools allowing real time data quantitative analysis or simulation and community software tools for routine and robust data analysis.

The next step: aberration correction for in situ capability

Effect of aberration correction for optics optimized for "in situ" (large gap)



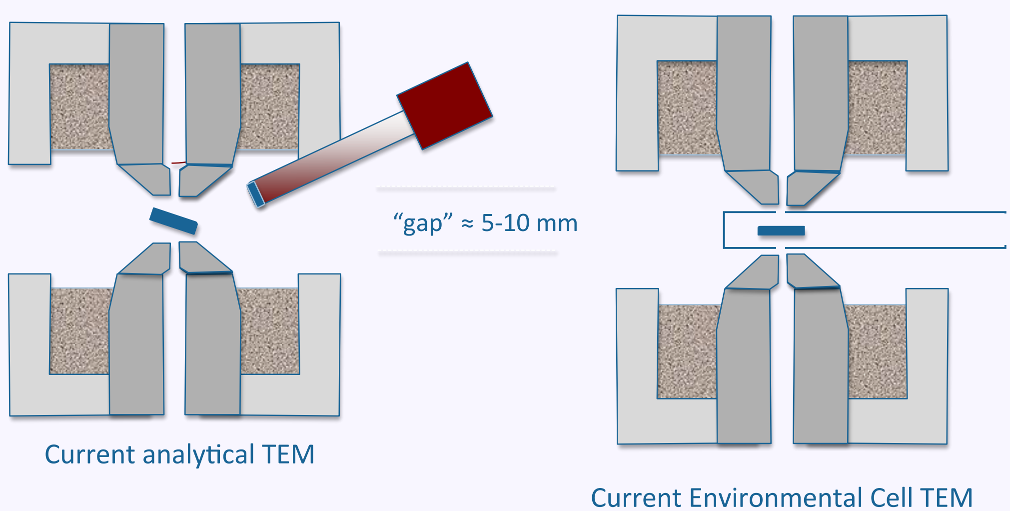
ANL is proposing to build and operate the next-generation TEAM optimized for in situ capability:

the *in situ* TEAM (*i* TEAM)

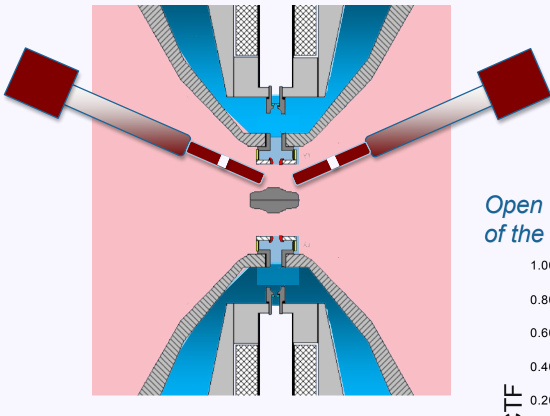
Builds on:
- successful development of Cc
- expertise in aberration correction
- user facility operation
- science partners
- user and community interest

Influence of pole piece "gap" on current microscopy capabilities

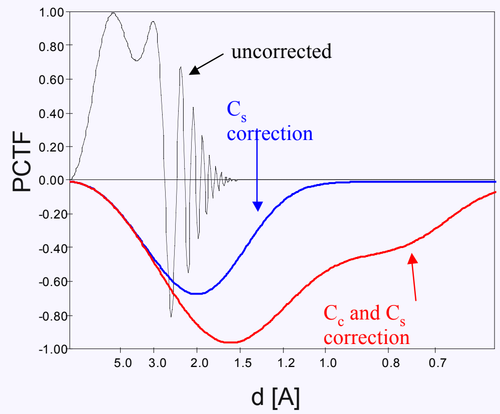
- In most microscopes, the gap is kept small to minimize the deleterious effect of aberrations – especially chromatic aberrations …



iTEAM an In-Situ Analytical NanoLaboratory

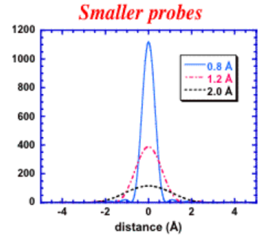


Open up the "Gap" but use AC to recover some of the resolution

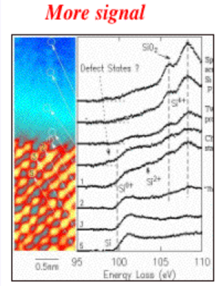


What does aberration correction buy us?

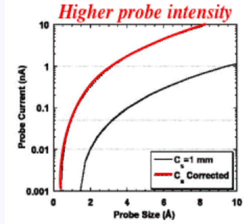
Smaller probes



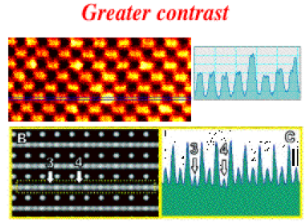
More signal



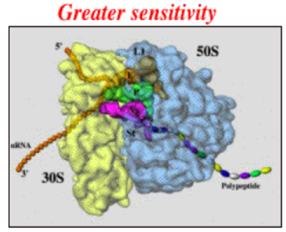
Higher probe intensity



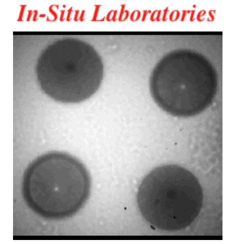
Greater contrast

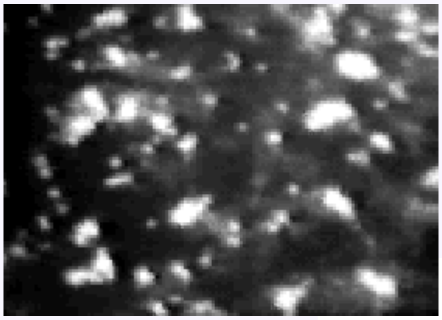


Greater sensitivity



In-Situ Laboratories





Crew etal 1969

Thanks
Questions?