SAND2014-4679C

State-of-the-art Analytical Electron Microscopy: 100 times better than before

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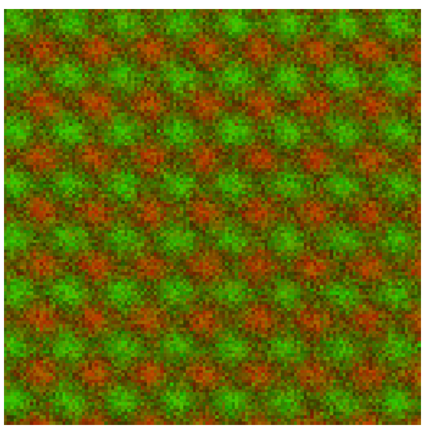
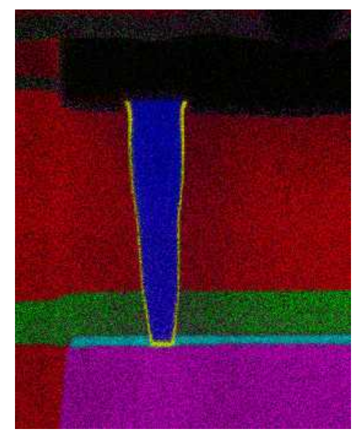


- Atomic-resolution x-ray microanalysis
  - Brighter sources
  - Probe correction
  - Efficient x-ray detectors
- Future applications



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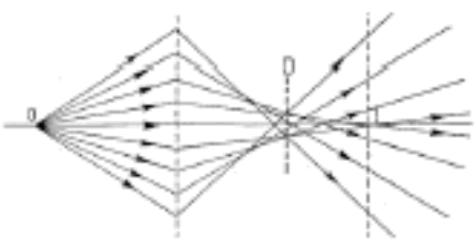
A new paradigm in x-ray microanalysis

- For almost 30 years we have been stuck at about the same point
- Other approaches to high-resolution TEM
  - MeV TEMs (decrease λ), holography (recovers phase and amplitude of the exit wave), focal series exit wave reconstruction, small focal length objective lenses (reduces C_s)
  - In STEM, Cold FEG which gives small source size
- What’s changed?
  - Silicon-drift detectors which perform better in all ways than Si(Li) and can be flexibly integrated into the column (-20ºC operation)
  - In the past 10 years, aberration correctors coupled with more stable microscope designs
- Simultaneous imaging and x-ray microanalysis at atomic resolution

Motivation of Aberration Correction

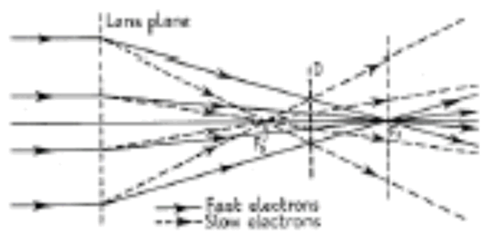
Aberrations

- Spherical

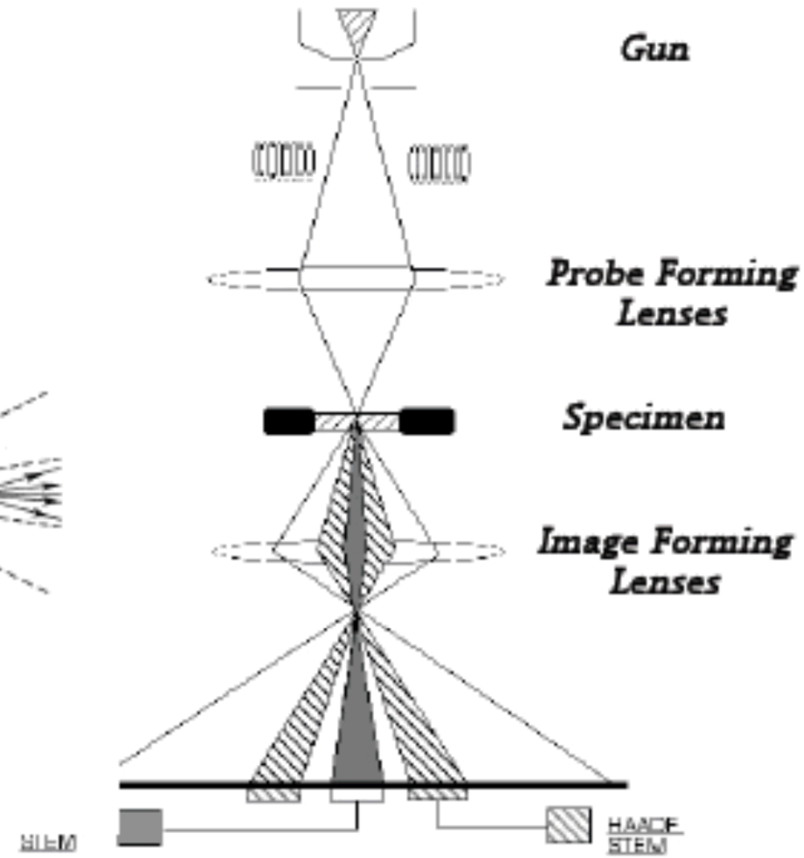


$$r_{sph} = C_s \beta^3$$

- Chromatic



$$r_{chr} = C_c \frac{\Delta E}{E} \beta$$



Courtesy Nestor Zaluzec, ANL

Sherzer's Theorum

O. Scherzer, *Z. Phys.* **101** (1936) 593

- Electromagnetic lenses with rotational symmetry
  - Suffer unavoidably from chromatic and spherical aberration, Cs is ~1/2 focal length of the objective lens (immersion geometry) ~1-3 mm

Dodecapole lens used in the DCOR can correct Cs because rotational symmetry has been broken

http://ceos-gmbh.de/FAQ/hexapole.html

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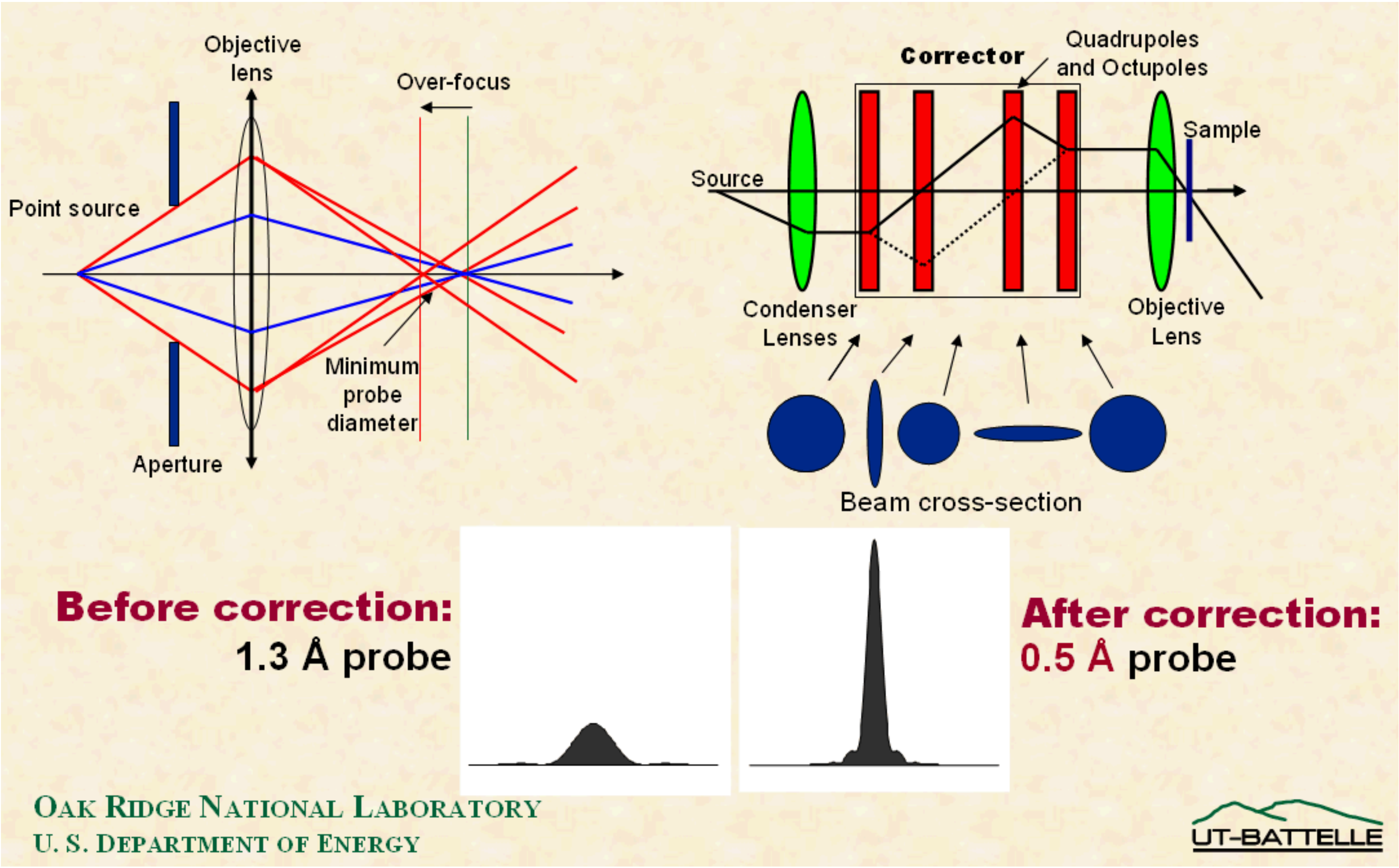
Aberration Correction in practice

http://www.ornl.gov/~grg/BES_sym/talks/Pennycook.ppt#386,9,2002: NION builds successful STEM aberration corrector



2002 Nion probe corrector, slide from Pennycook, ORNL

Extra non-rotationally symmetric lenses allow correction of Cs and higher order aberrations as well

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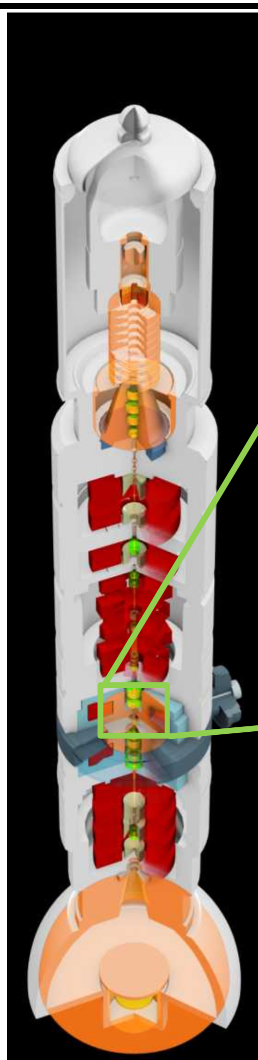
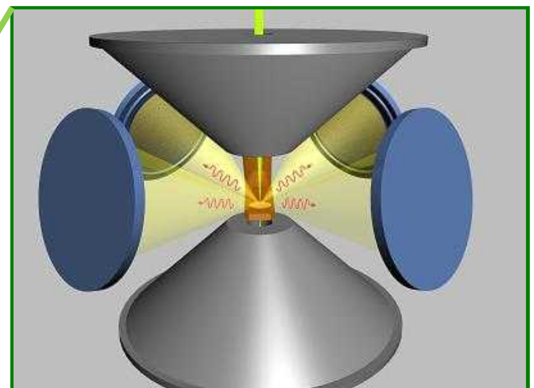
Atomic resolution x-ray microanalysis

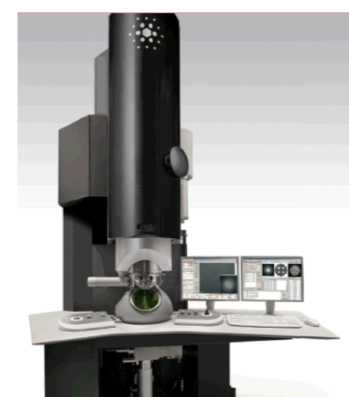




Critical elements for atomic resolution x-ray microanalysis

- High brightness gun
  - X-FEG
- Probe corrector (CEOS-DCOR)
  - 0.08nm @ 200kV
  - 0.12nm @ 80kV
- Efficient x-ray detector(s)
  - SuperX, SDD array

All of these elements have been integrated on the FEI Titan ChemiSTEM-P (200kV)
SNL has the first one



New Shottky emitter technology

- New Shottky emitter with the brightness of a cold FEG

- FEI X-FEG brightness increased to ~ 10^8 A/sr/m^2/ V
  - ~2 x 10^9 A/cm^2/sr @ 200 kV
  - Comparable to a cold FEG but more stable over time
  - 0.8eV energy spread

- Probe current (w/o corrector)
  - 0.5 nA in 0.3 nm diameter
  - **Increased by 5x** relative to regular Schottky FEG

- Probe current (with DCOR probe corrector)
  - 200 kV, 1.3 nA in 0.2 nm diameter probe
  - 80 kV, 0.5 nA in 0.2 nm diameter probe

Detector Efficiency: Arrays

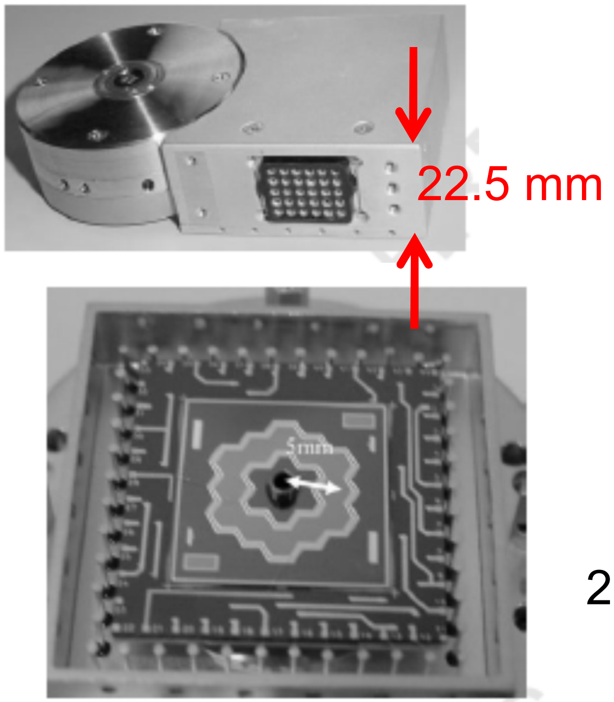
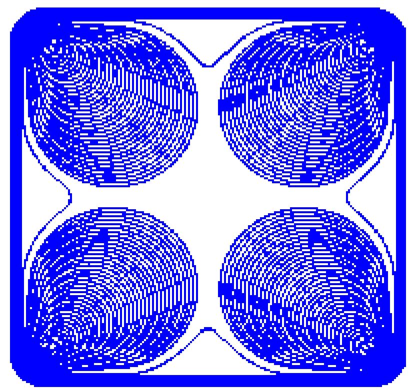
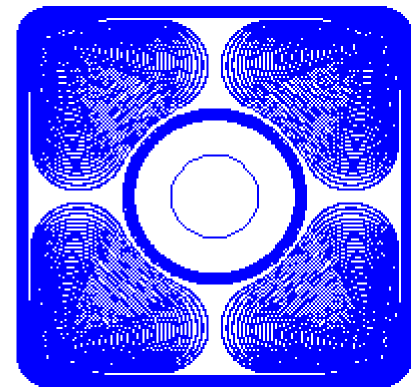


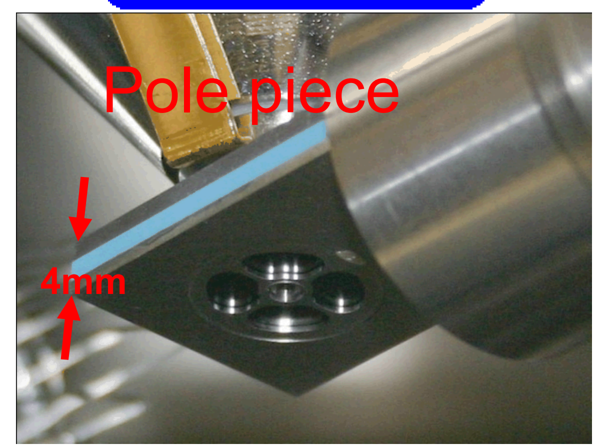
Figure 2. The Ketek 12-element annular SDD chip mounted in its package. The tantalum ion collimator that protects the SDD from scattered protons can be seen protruding through a hole in the center of the chip.

2005 Ketech/Custom imp.
2^{nd}-3^{rd} generation annular
(1.1 sr)



2005 pnSensor/Roentec
4-5^{th} generation
conventional
(40 mm^2, 0.06 sr)





2007 pnSensor/Bruker
5^{th} generation annular at
SNL(60 mm^2, 1.1 sr)

B. L. Doyle, D. S. Walsh, P. G. Kotula, P. Rossi, T. Schülein and M. Rohde, “An annular Si drift detector μPIXE system using AXSIA analysis,” *X-Ray Spectrom.* (2005) 34

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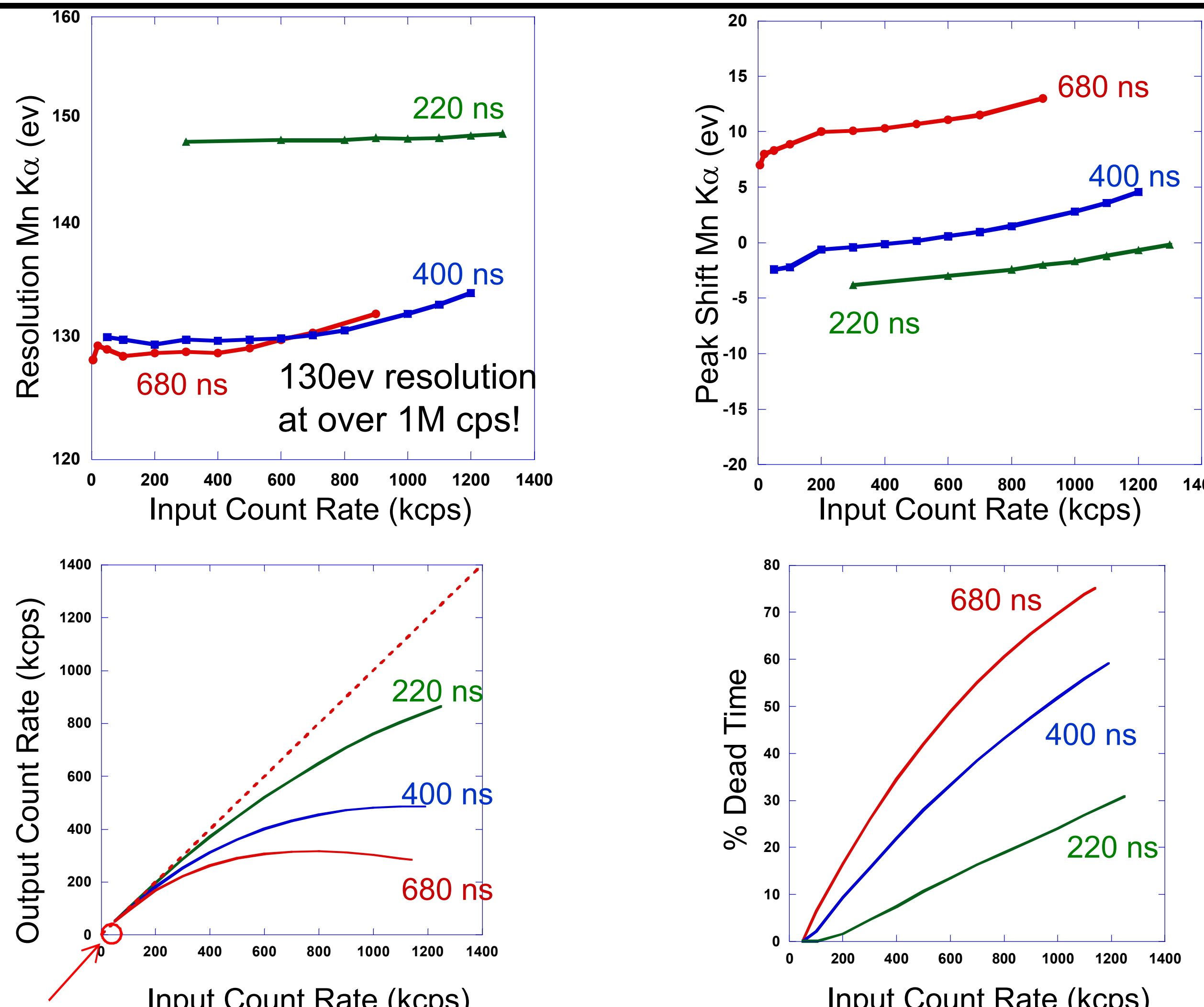
5th generation SDD-array performance

SEM data from 4-detectors summed



Si(Li) performance area at 180eV FWHM Mn-Kα

Performance superior in every way to Si(Li)

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SuperX^{TM}: Large solid angle silicon drift detector array provides more flexible AEM integration

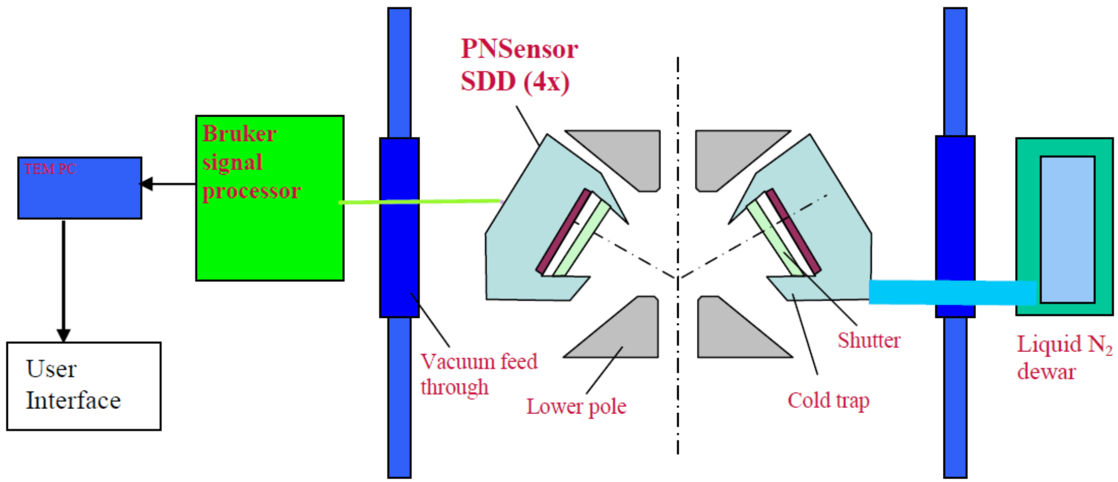
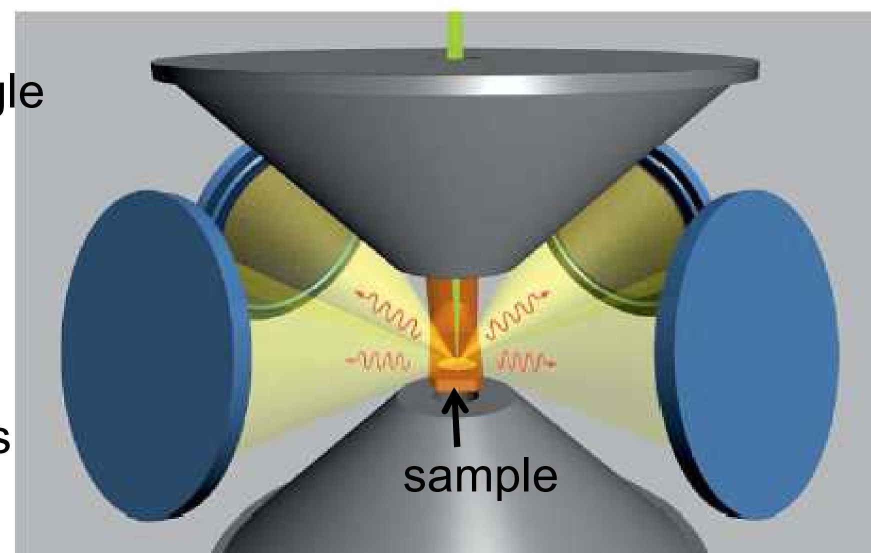


Figure 1. Schematic of Super-X detector

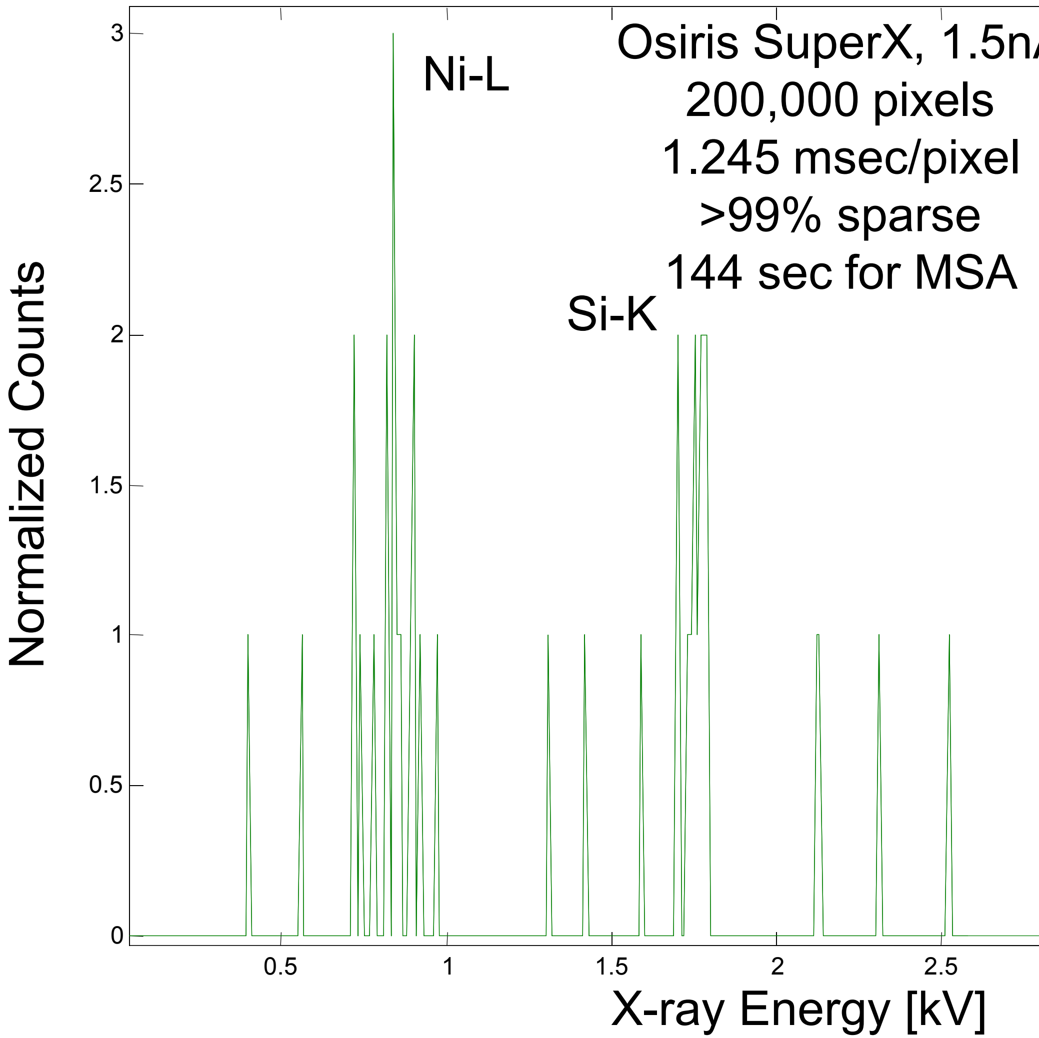
Conceived by FEI with collaboration from Bruker and pnSensor

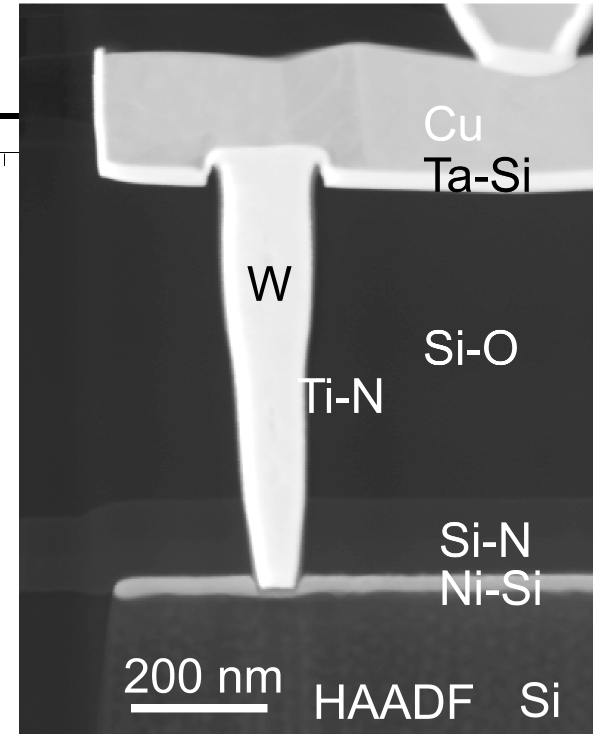
Revolutionary change in AEM-EDS

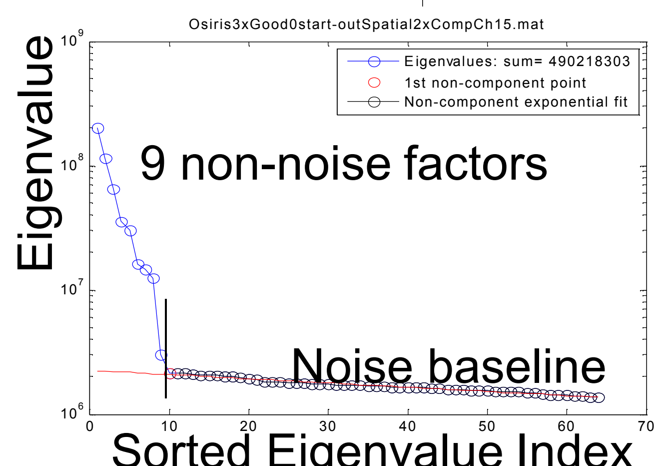
- 4-30mm^2 (120mm^2) SDDs with large solid angle
  - 0.9 sr (Osiris-uncorrected)
  - 0.7 sr (Titan-probe corrected)
  - State-of-the-art SDDs
  - Windowless & pnWindow…good light-element performance (C, N, O previously)
  - High-throughput…10 μsec instantaneous dwell times, multiple pass, drift correction



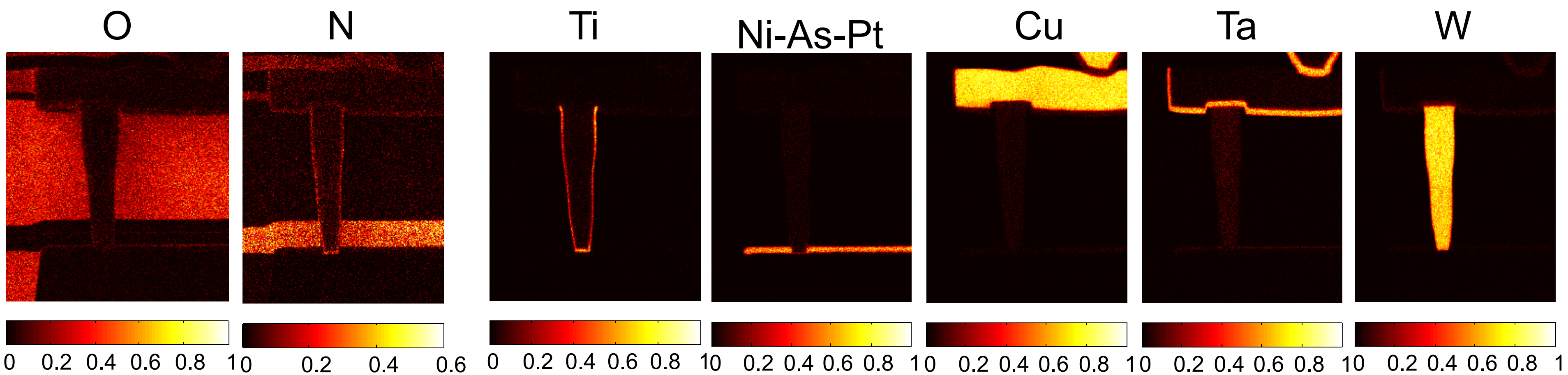
Raw spectrum from the CMOS spectral image

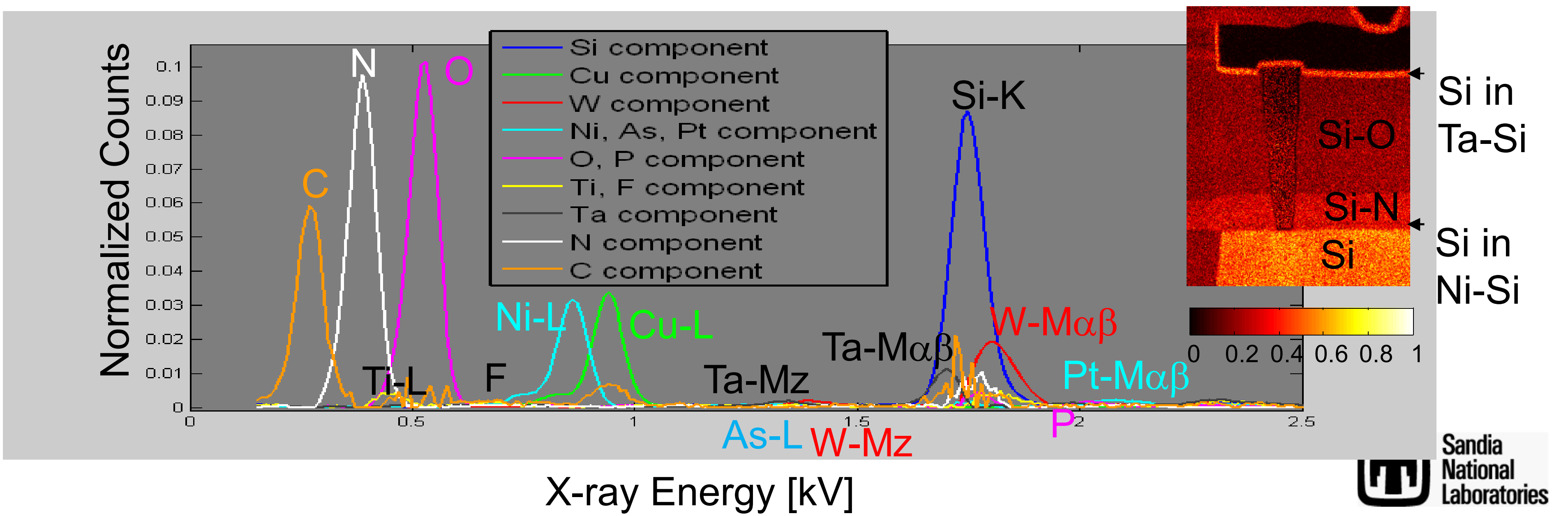






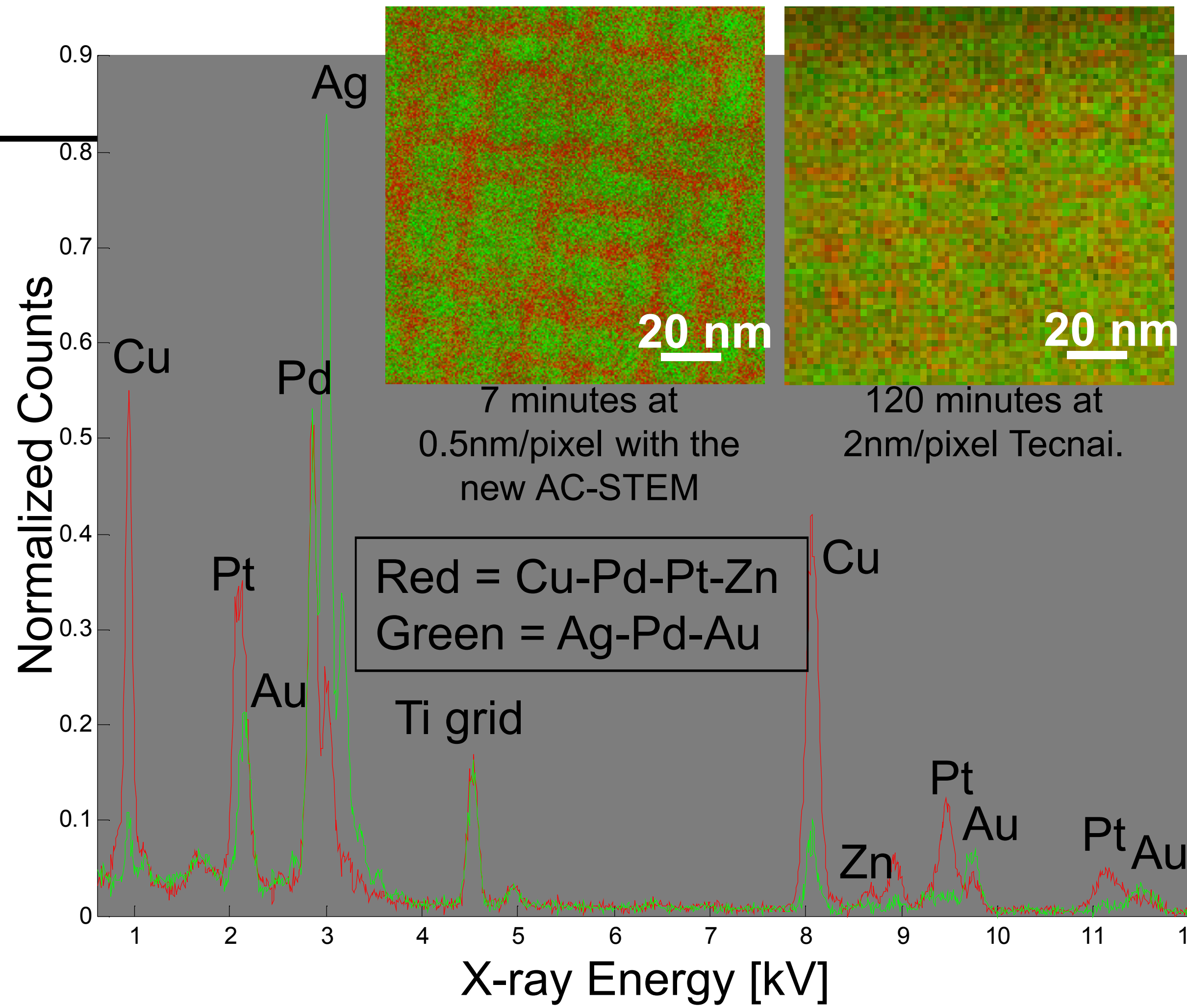
Spectral-Domain Simplicity
Best Spectral or Elemental 'Contrast'





Medium end analysis
Sub-nm microanalysis of electrical contact materials

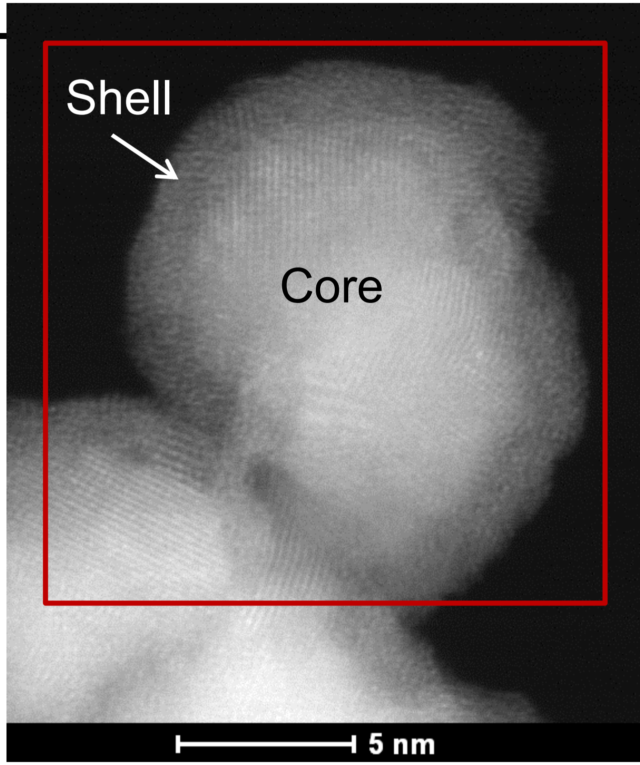
Paliney 7, electrical contact material nanometer-scale spinodal decomposition.



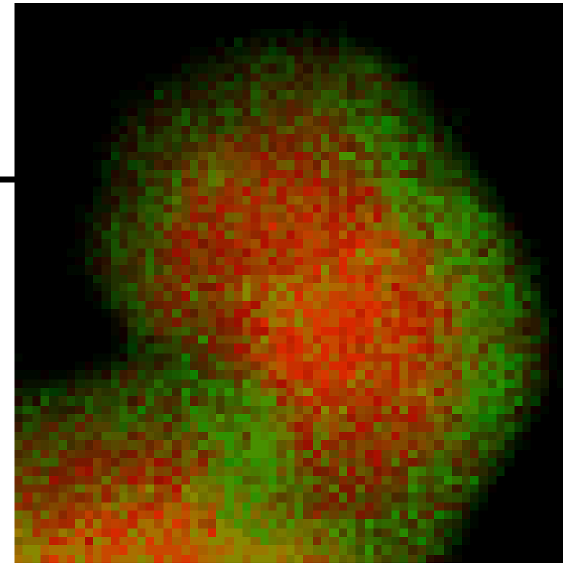
The analytical power of the AC-STEM is *at least* **70x** better than the older analytical microscope at Sandia.

D.F. Susan, Z. Ghanbari, P.G. Kotula, J.R. Michael & M.A. Rodriguez, (2014) *Metall and Mat Trans A*
DOI 10.1007/s11661-014-2334-x

Medium end, characterization of hydrogen isotope storage materials

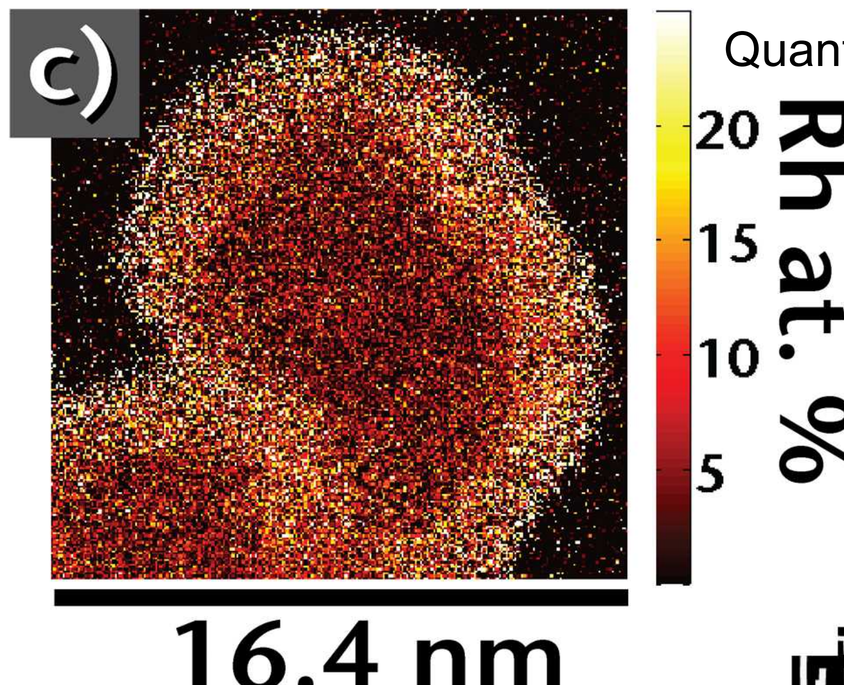


HAADF image



MSA results
Red = Pd-rich core
Green = Rh- and O-rich shell

Quantification

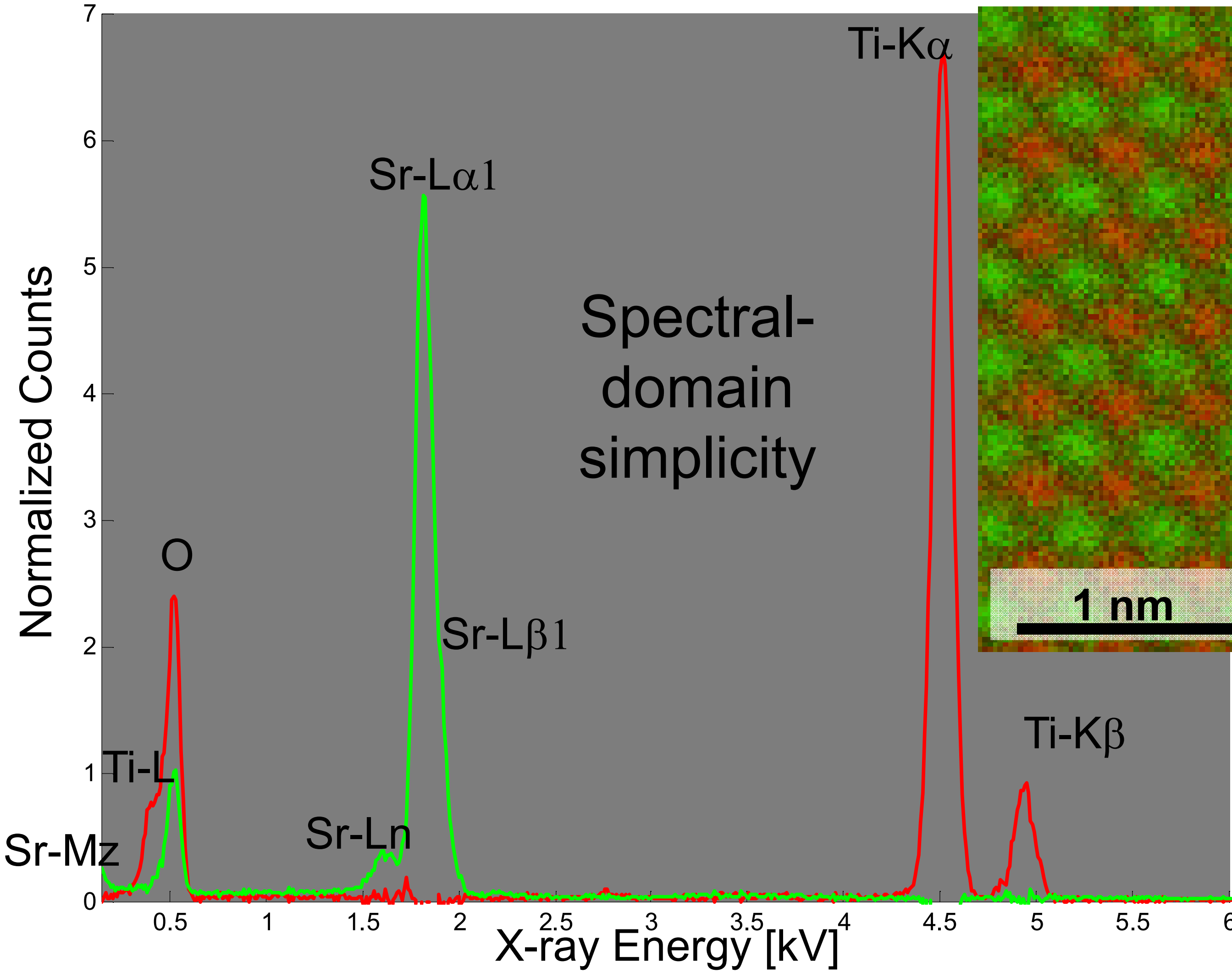


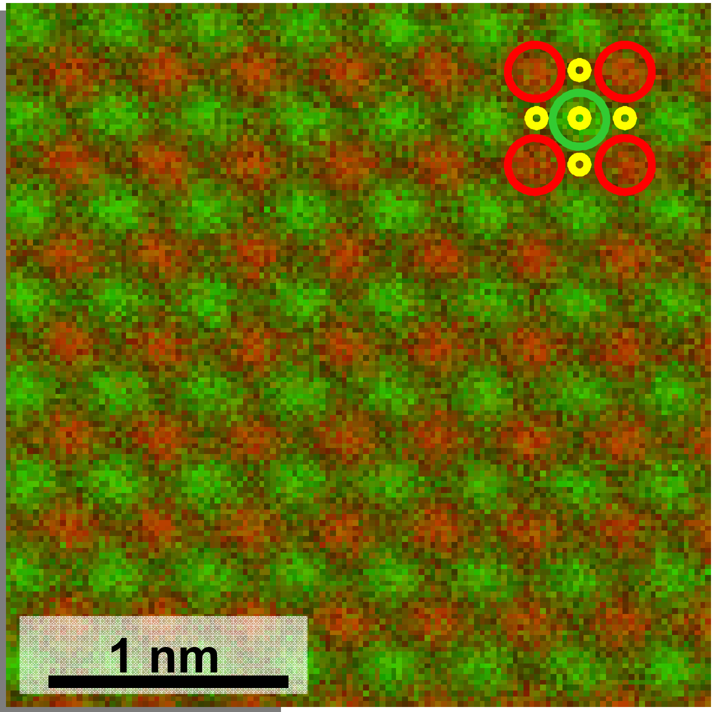
Robinson et al., *J. Mater. Chem.*, 2012, **22**, 14013

Data courtesy Dmitri Klenov, FEI Company

SrTiO3 [100]

MSA-processed spectral image of $SrTiO_3$ with no *a priori* information





Red = Ti columns
Green = Sr columns

Sr-K lines not shown but correlate with Sr-L

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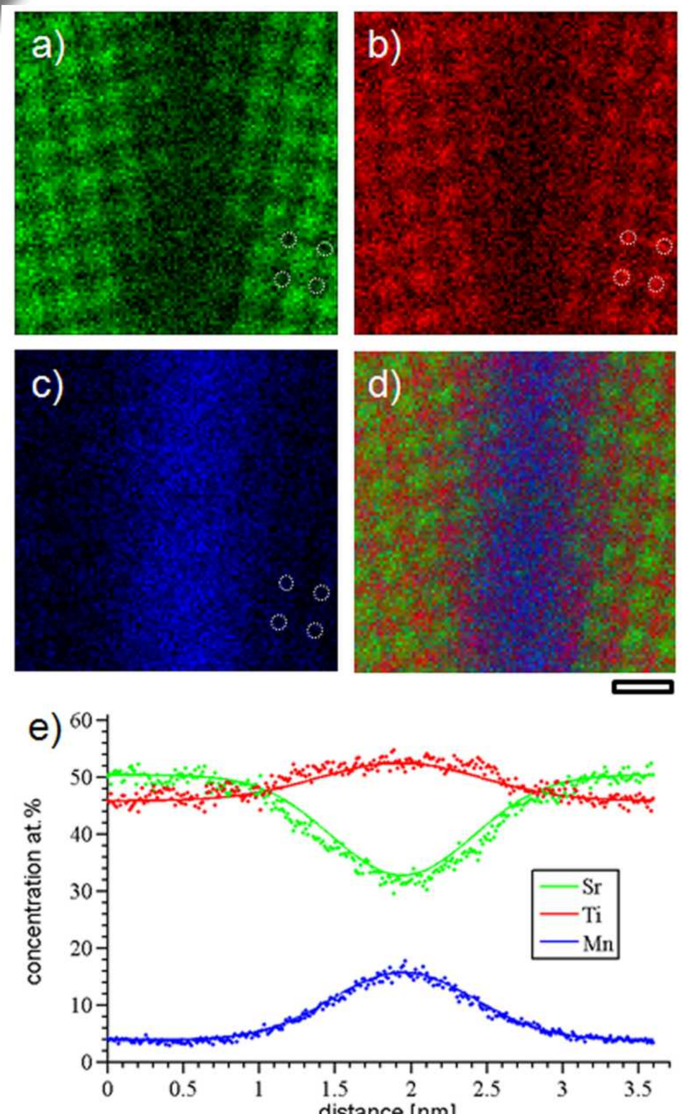
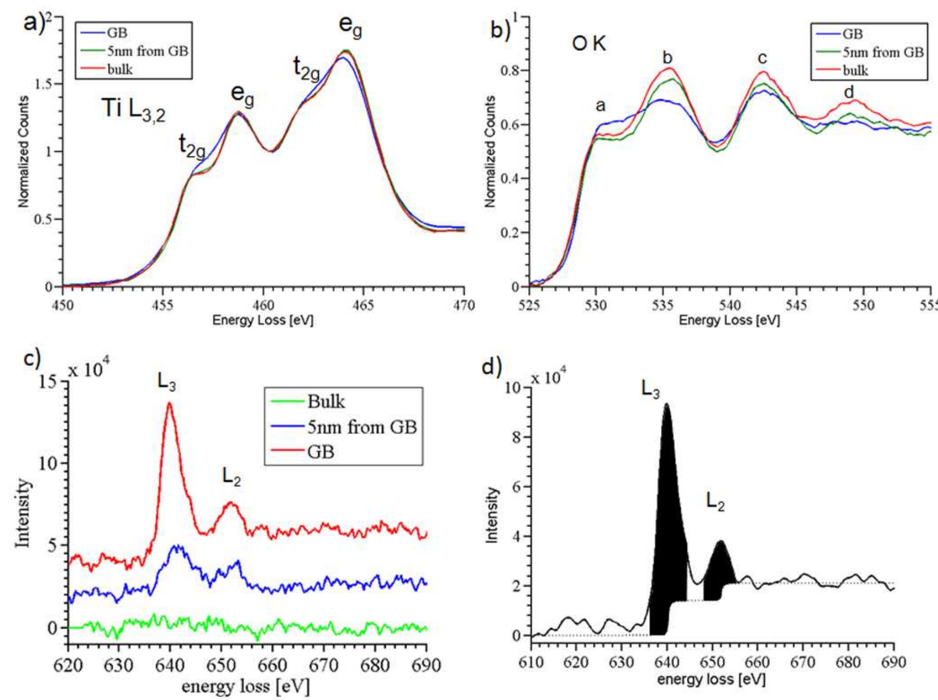
Analysis of Mn-doped STO Σ=13 Boundaries

∑13 (510)/[001]

Quantitative EDS and EELS





FWTM enrichment at the boundary less than 2nm

Mn^{+2} at boundary

Mn^{+4} in bulk near boundary (subsitutional with Ti)

Hao Yang, Paul G. Kotula, Yukio Sato, Yuichi Ikuhara, Nigel D. Browning. “Segregation of Mn^{2+} Dopants as Interstitials in $SrTiO_3$ Grain Boundaries,” Submitted to APL (2013).

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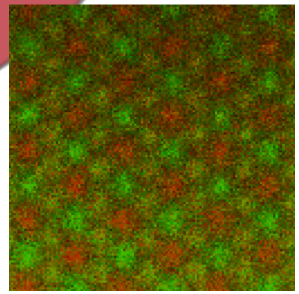
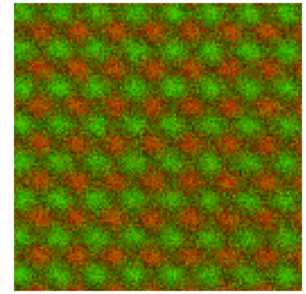
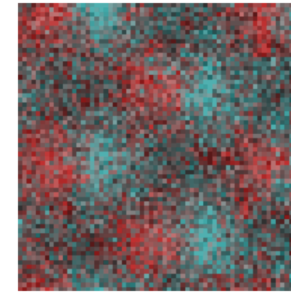


Conclusions





- AEM is undergoing a renaissance with correctors, SDDs, novel diffraction techniques, and better sources.
- Atomic resolution EDS will become more common than EELS. Easier, more elements accessible, esp. heavy ones, more readily quantified
- Novel detector geometries for AEM improve sensitivity and throughput.
- MSA methods are very useful for simplifying the analysis of large, complex data sets (only very simple ones shown today!)
  - Importance of Poisson normalization
  - Factor rotation, spatially or spectrally simple viewpoints
  - Unbiased analysis powerful for materials science, etc. Needle in the haystack….single atoms….
- Quantitative analysis pushed to smaller volumes
  - Understanding the spectrum is critical…every bump matters!
  - Potential for 1000 ppm sensitivity at 0.2 nm?
  - 100 ppm sensitivity at 1 nm?

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