Promises and Challenges of Atomic Scale Tomography

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Collaborators and Sponsors

- David Diercks, Rita Kirchhofer, Adam Stokes, George Burton, Corinne Packard – *Colorado School of Mines*
- Harvey Guthrey, Mowafak Al-Jassim, David Ginley – *National Renewable Energy Laboratory, Golden, CO*
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- Andrew Breen, Anna Ceguerra, Julie Cairney, Simon Ringer – *University of Sydney*
- Tom Kelly – *Cameca Instruments*
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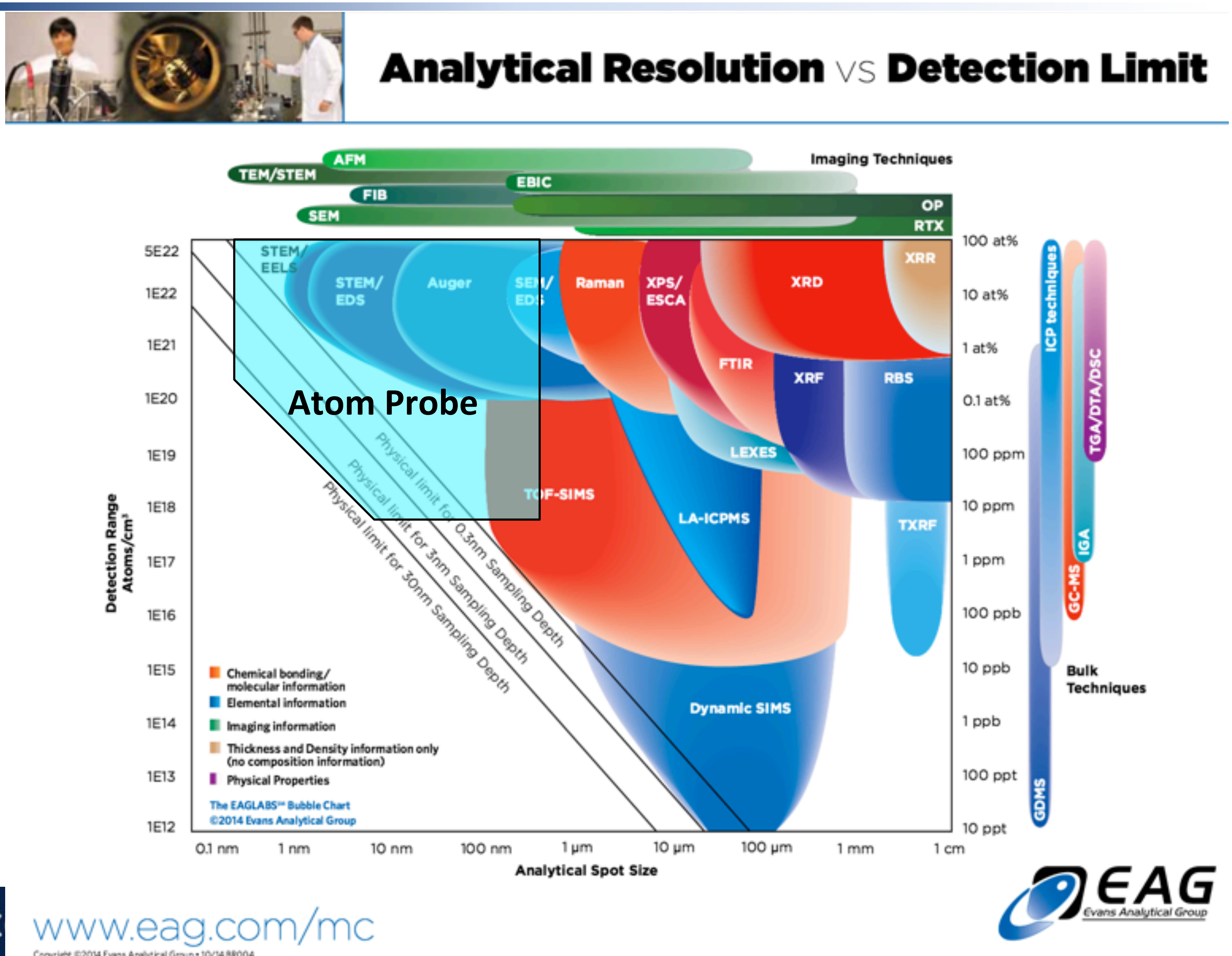
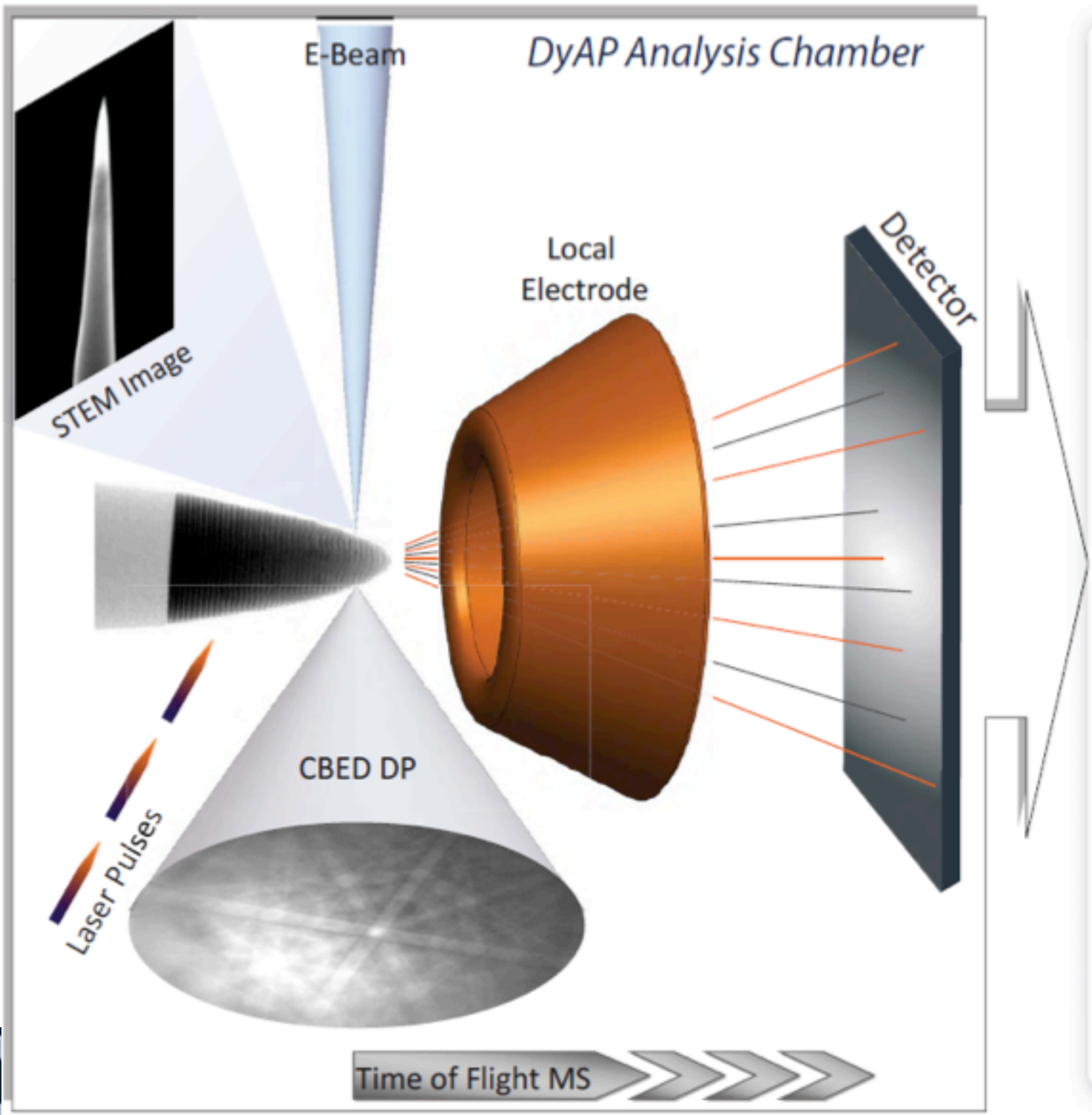
Atomic Scale Tomography (AST)

- AST: determine location and identity of all (?) atoms <u>in 3-D</u>
- Why do we want to do this?
  - *Directly relate structure to properties!*
  - First principles understanding of materials
- Materials of Interest
  - PV (Si, CdTe, CIGS, CZTS, GaAs, OPV, MOIP)
  - Oxide ion conductors
  - Ferroelectrics and Dielectrics
  - Solid State Quantum Computation
  - Semiconductor devices (CMOS, RRAM, FRAM)

AST – How to Get There?

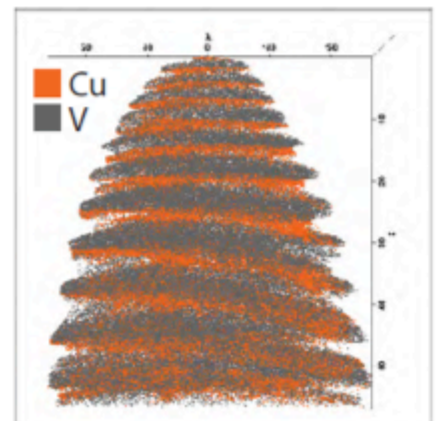


Atom Probe Tomography (APT) Basics



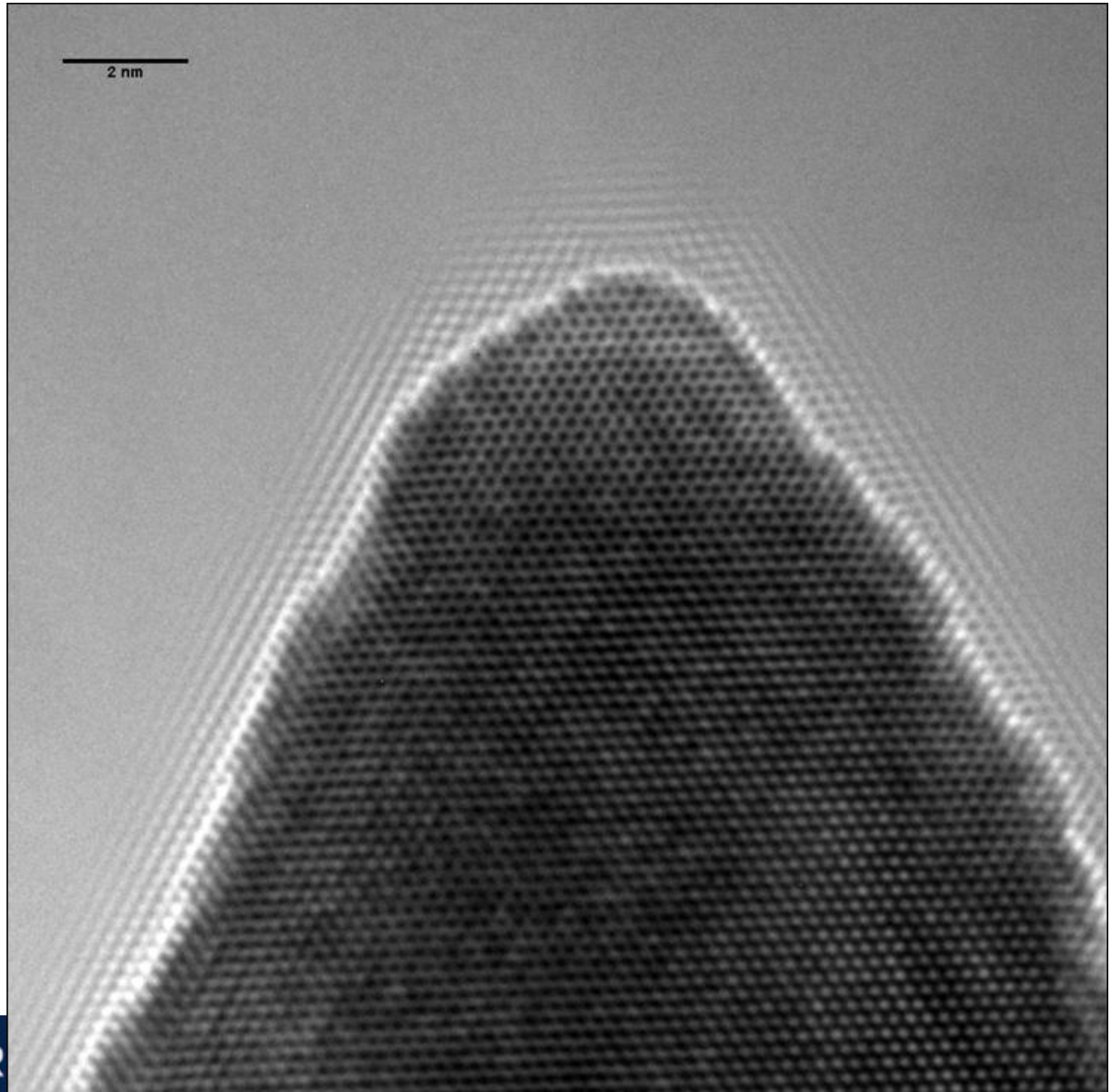
3D Reconstruction

Specimen reconstruction from the ions collected



- Position (x,y) of atoms determined by detector.
- Timed evaporation events used to determine the z-position of the ions:
- Use Local Electrode fields in combination with laser pulses (ns time resolution).

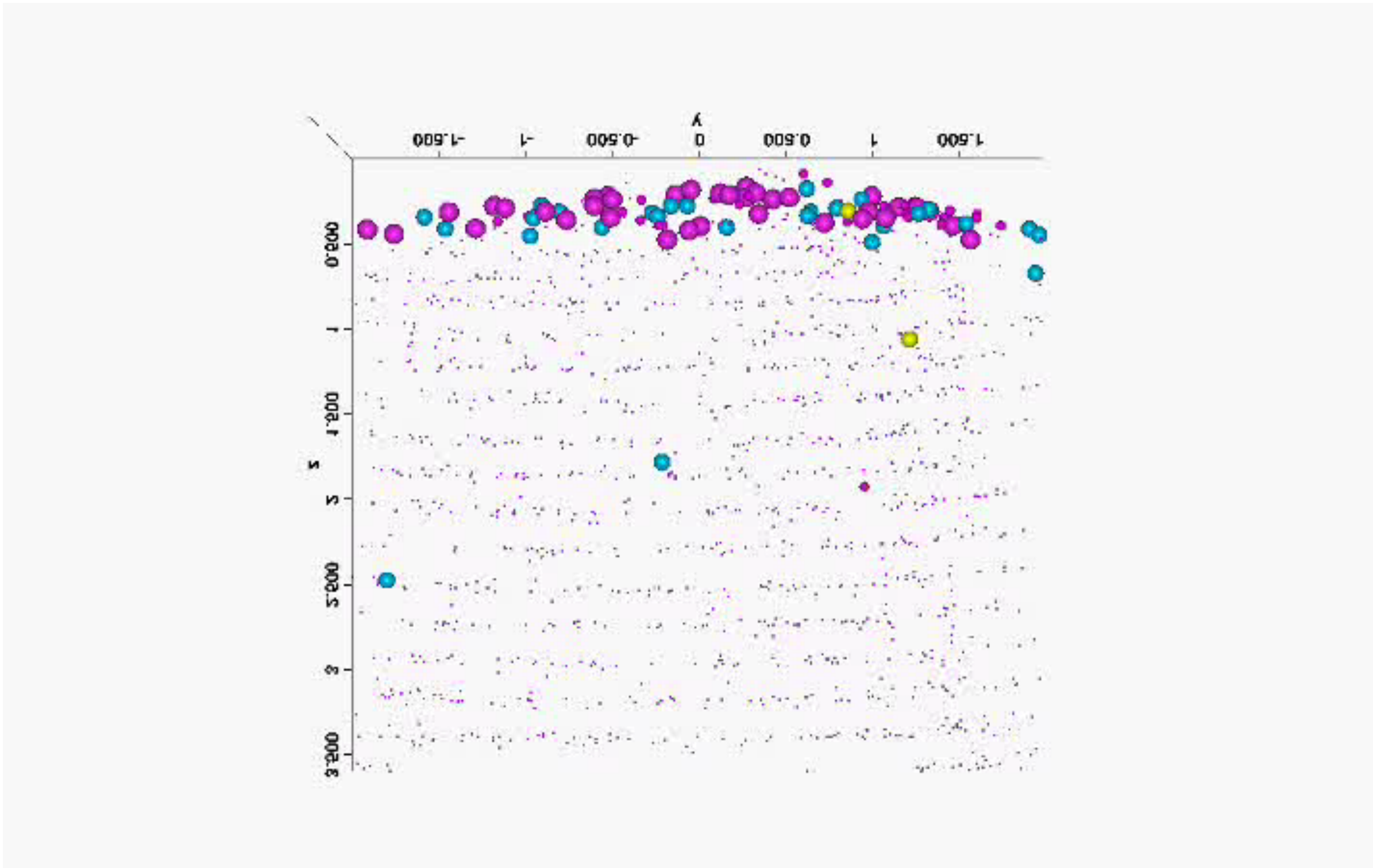
HRTEM of Cylindrical Specimen



COLOR

W Atom Probe Reconstruction

W –
W-O –
O –
Ga –



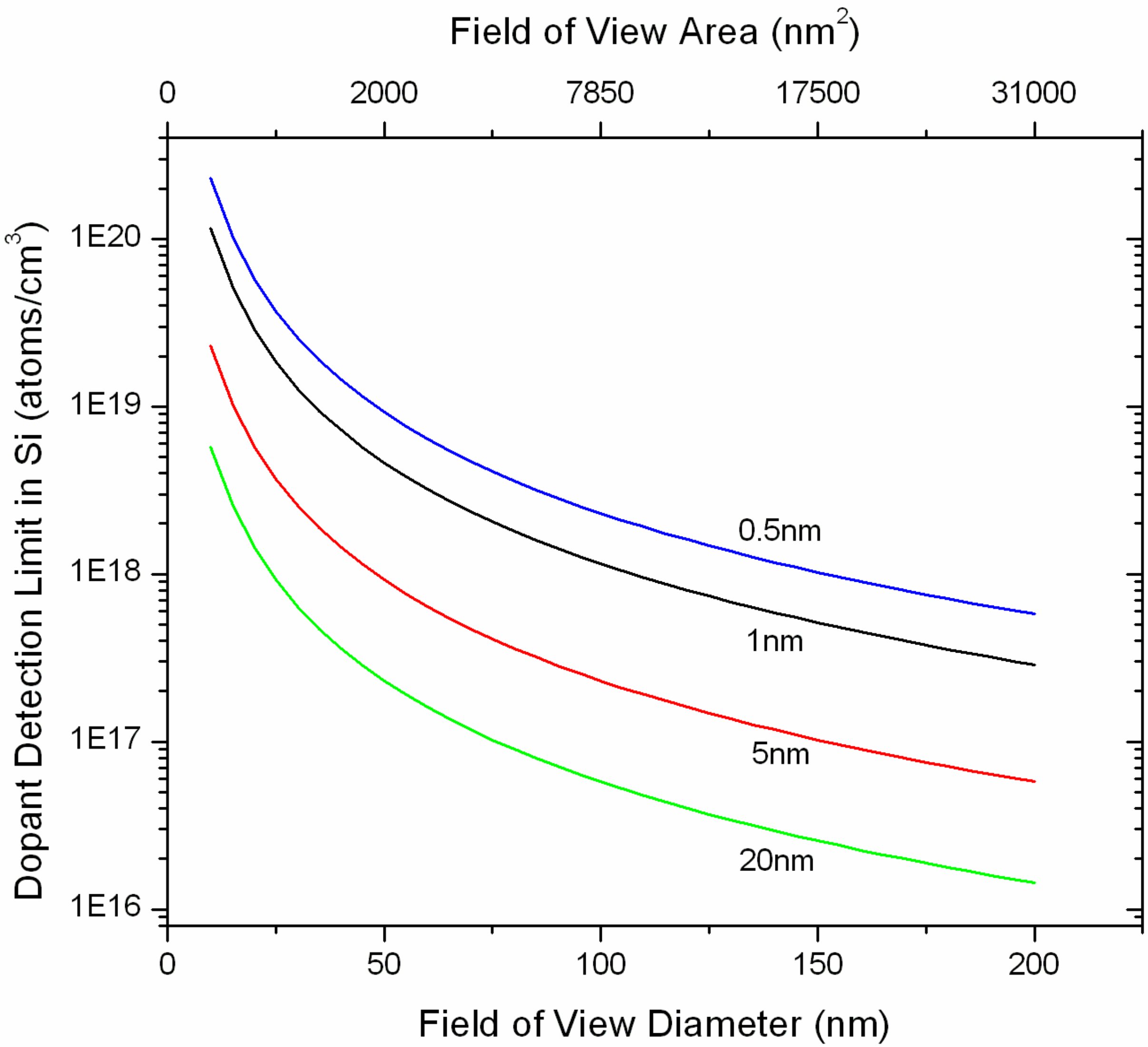
Atomic resolution in Z-direction, not in X-Y
Small field of view

Atom Probe Detectability Limits

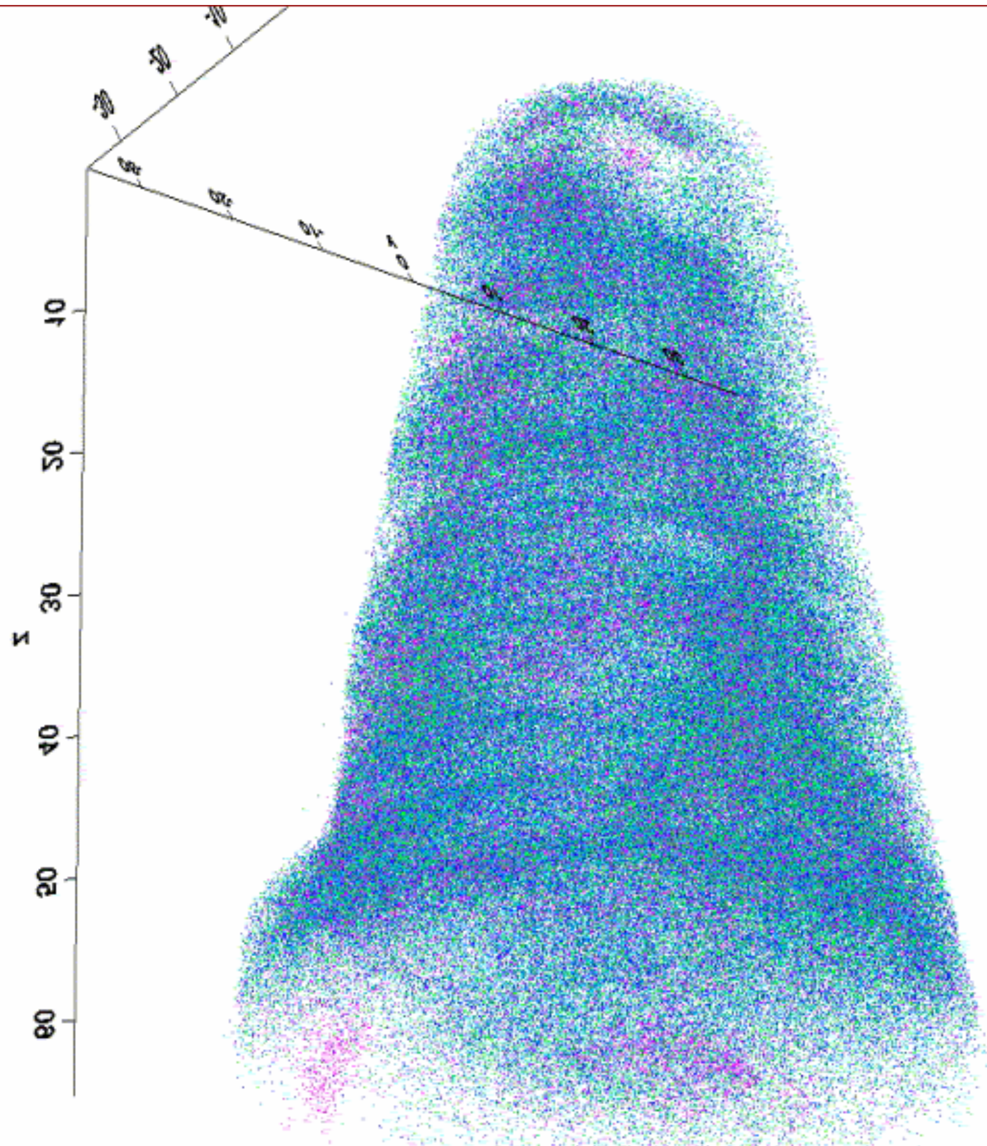
- Are there atoms in the field of view?
  - 100 nm diameter FOV is ~100,000 atoms / surface
- Can we detect each atom?
  - MCP / cross-wire delay line detector has ~57% collection efficiency
  - We then capture ~57,000 atoms / surface
  - Can theoretically detect one atom count above the background, or 10^{17} to 10^{18} atoms/cm^3

B. P. Gorman, A. G. Norman, Y. Yan, "Atom Probe Analysis of Semiconductor Photovoltaics", *Microscopy and Microanalysis*, **13** (6), 493-502 (2007).

APT Detectability Limits



APT Example - $LiCoO_x$



< 0.5 nm spatial resolution in 3-D

<10 ppm chemical resolution down to Li (sometimes H)

0.25 amu isotopic resolution

- Metallic Li particles present after 200 electrochemical cycles

- Most likely precipitate to voids and cracks during charging

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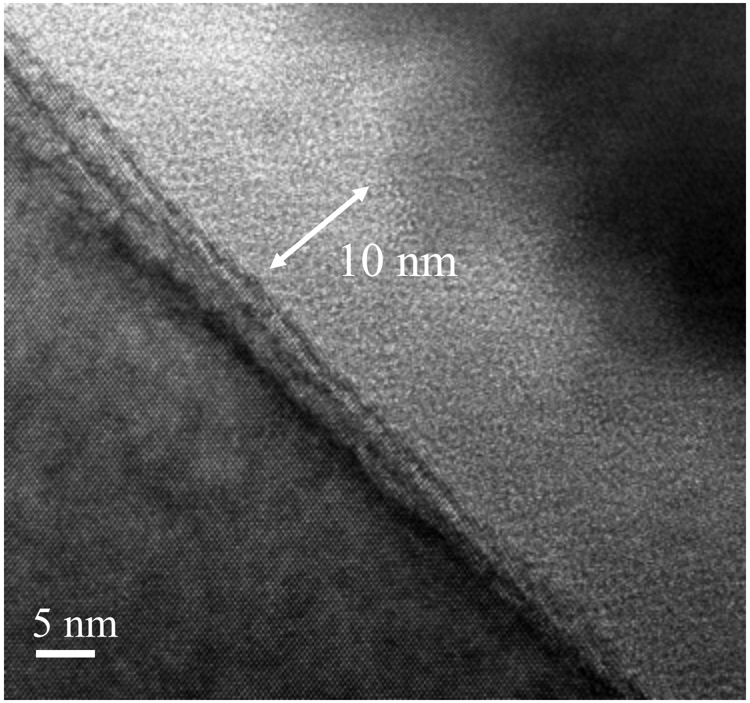
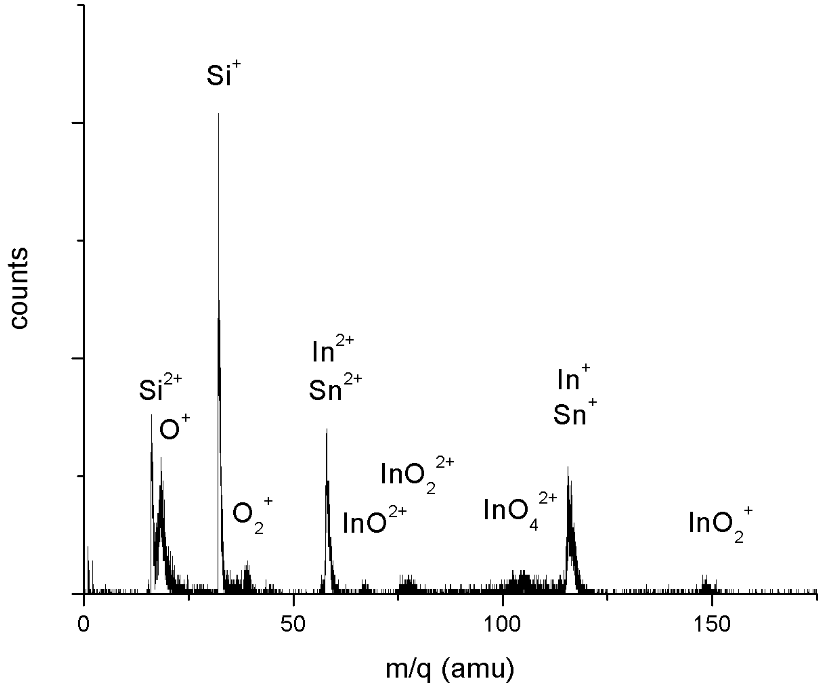
APT OF PHOTOVOLTAICS – Si AND CIGS

APT – Si Heterojunction Cell





- Laser Pulsed APT used to collect ions through the ITO / a-Si / c-Si interfaces
- Dopant profiling across the interfaces allows for calculation of junction depletion widths

B. P. Gorman, A. G. Norman, Y. Yan, "Atom Probe Analysis of Semiconductor Photovoltaics", *Microscopy and Microanalysis*, **13** (6), 493-502 (2007).

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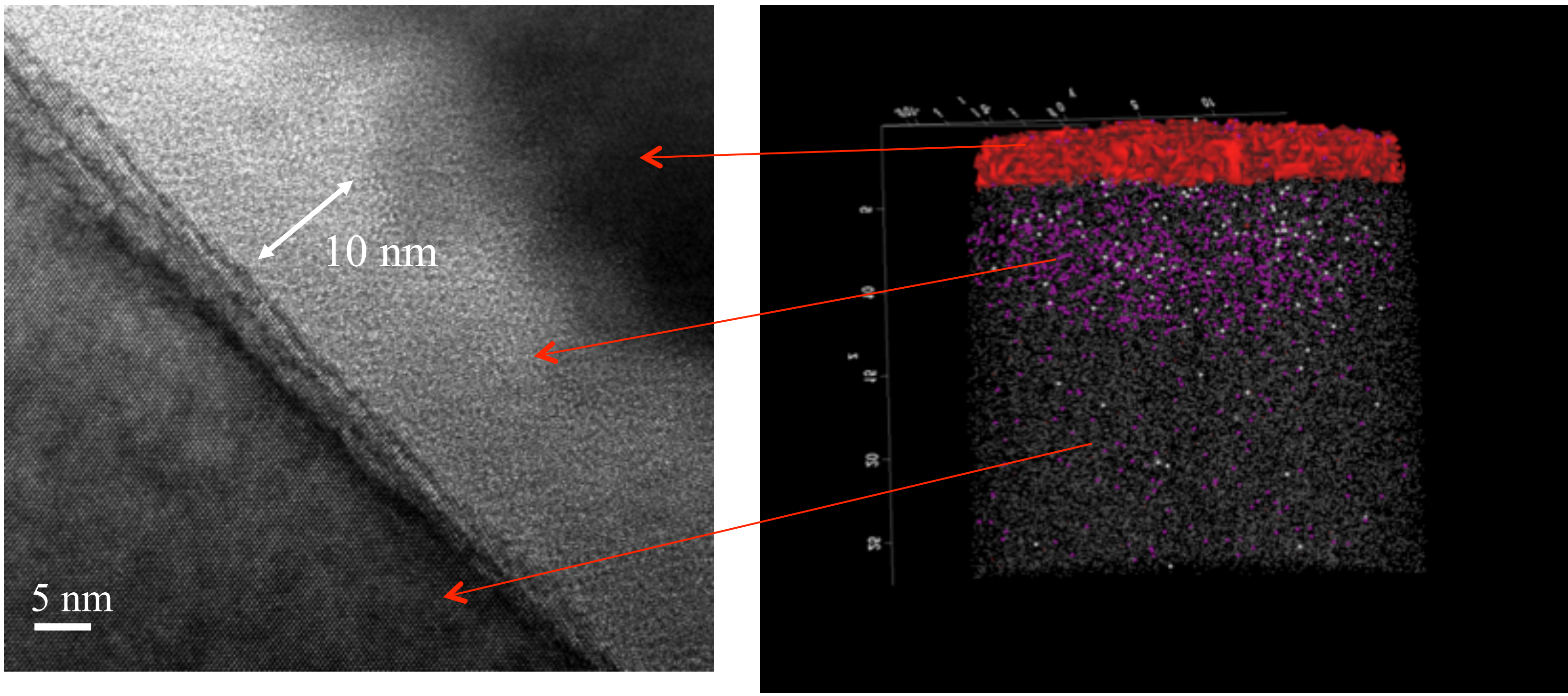
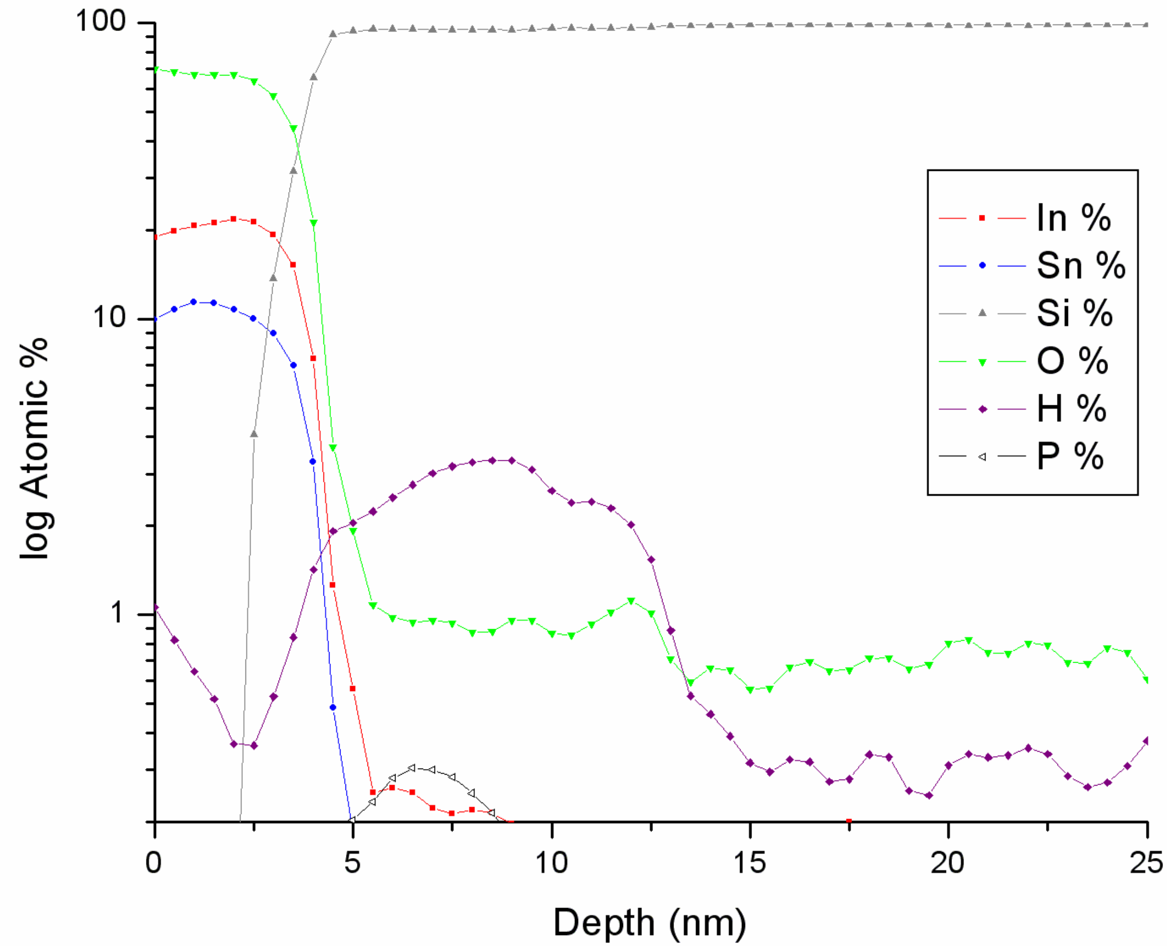
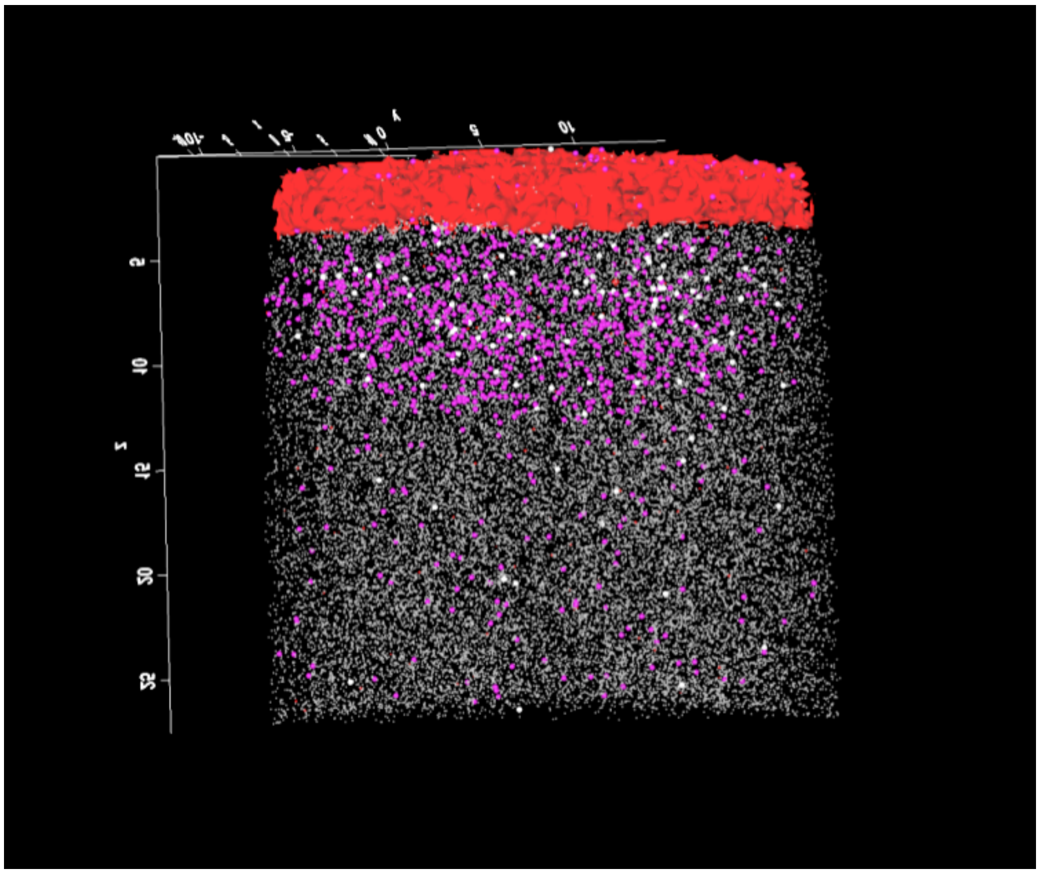


APT – Si Heterojunction Cell



APT- Photovoltaics

- Quantification of extrinsic dopant locations and relate to electronic properties



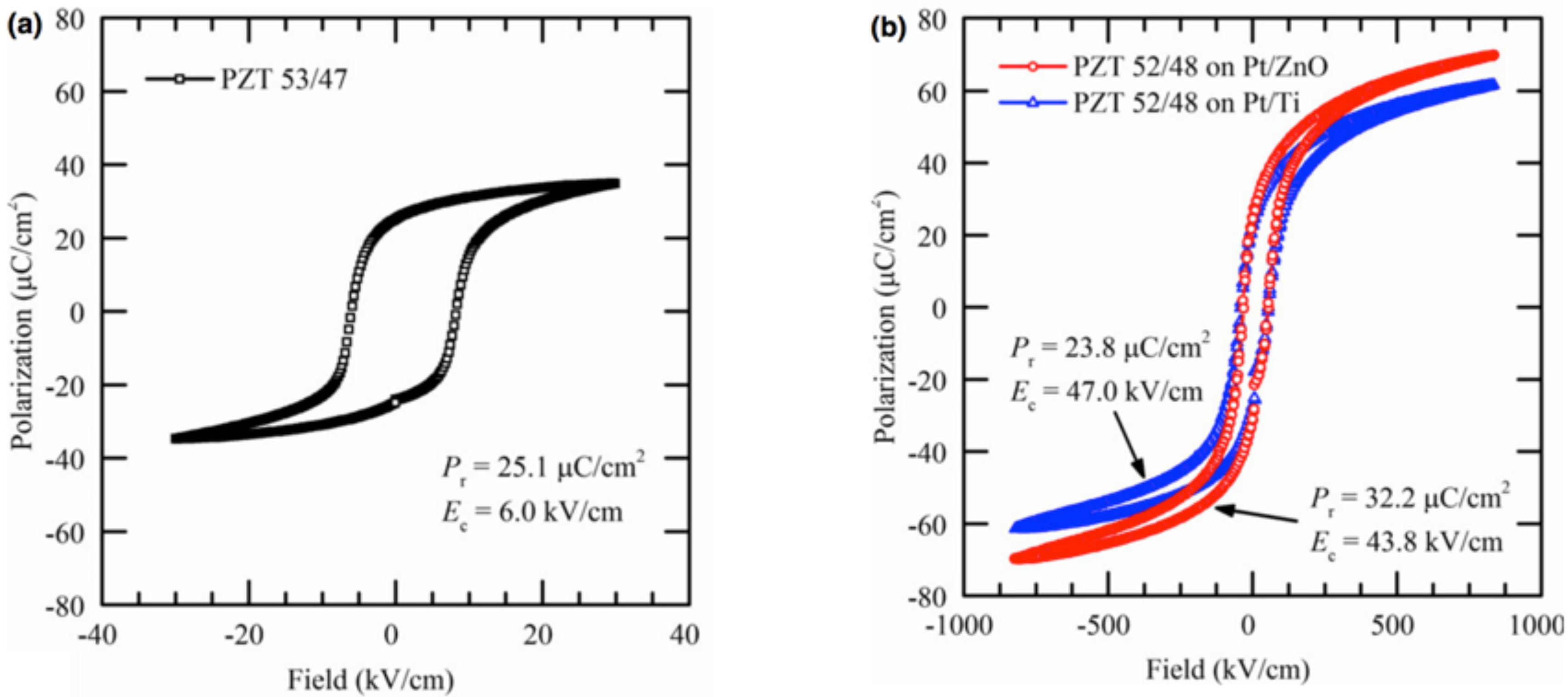
$$qV_{bi} = k_B T \cdot \ln\left(\frac{N_A N_D}{n_i^{2}}\right)$$

$$W = \sqrt{\frac{2\varepsilon_s \varepsilon_o}{qN_D}\left|-V_{bi}\right|}$$

APT OF FERROELECTRICS - PZT

Ferroelectric Properties of PZT

- Bulk vs. thin film PZT polarization curves
- Strong differences in coercive fields – nanostructural origins?

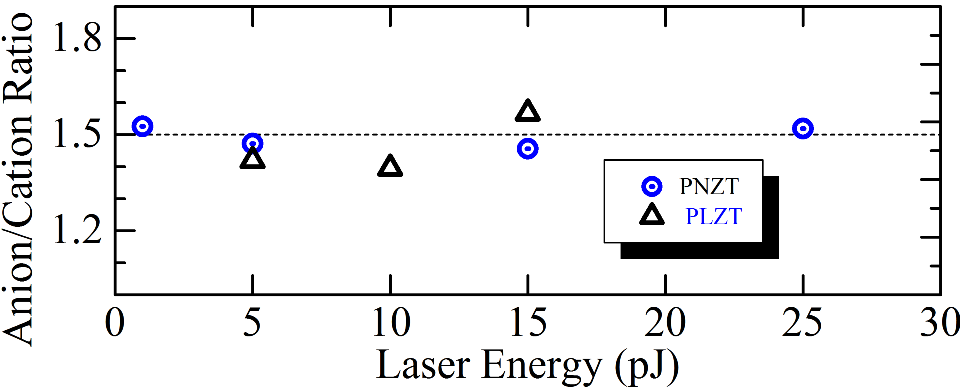


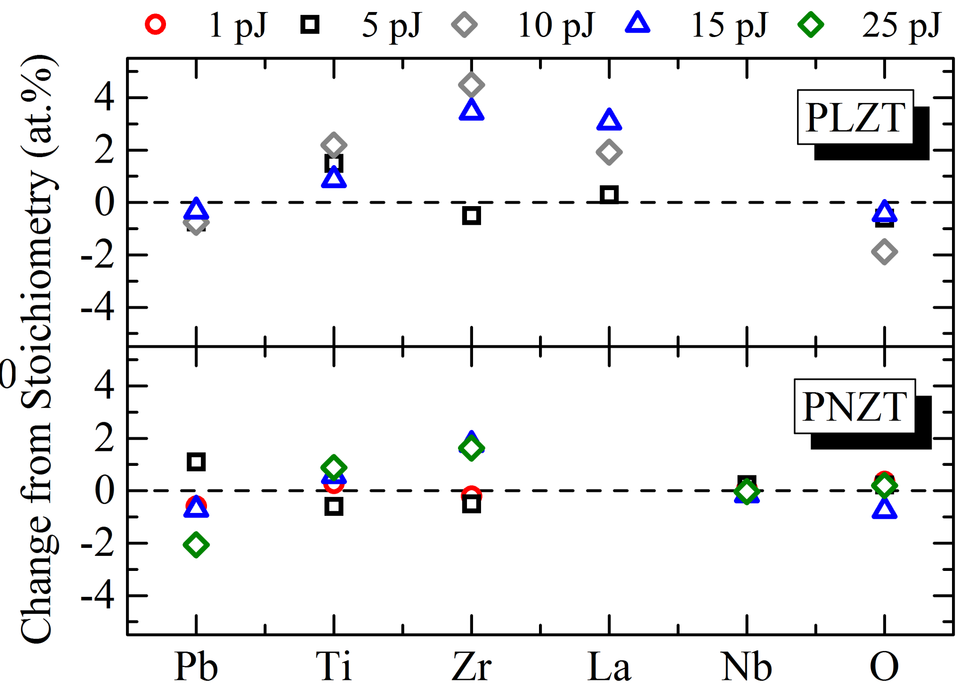
Materials

Material	Composition	Type	Substrate
PZT 53/47	$Pb_1Zr_{0.53}Ti_{0.47}O_3$	Bulk	-
PZT 52/48	$Pb_1Zr_{0.52}Ti_{0.48}O_3$	Thin Film	$Pt/Ti/SiO_2$
PZT 52/48	$Pb_1Zr_{0.52}Ti_{0.48}O_3$	Thin Film	$Pt/ZnO/SiO_2$
PLZT	$Pb_{0.88}La_{0.12}Zr_{0.70}Ti_{0.30}O_3$	Bulk	-
PNZT	$Pb_{0.976}Nb_{0.024}Zr_{0.52}Ti_{0.48}O_3$	Bulk	-

Kirchhofer, Rita; Diercks, David R; Gorman, Brian P; Ihlefeld, Jon F; Kotula, Paul G; Shelton, Christopher T; Brennecka, Geoff L; "Quantifying Compositional Homogeneity in Pb (Zr, Ti) O3 Using Atom Probe Tomography", *Journal of the American Ceramic Society*, **97**, p. 2677-2697 (2014).

Composition Measurements

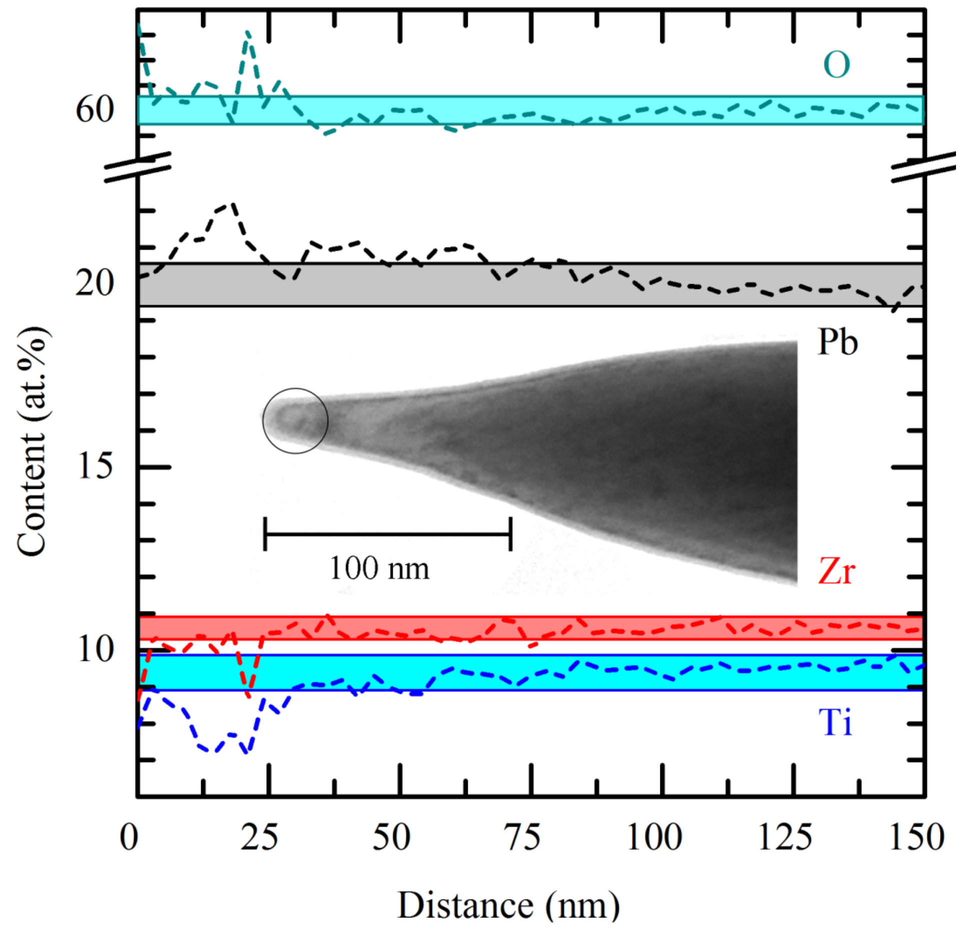




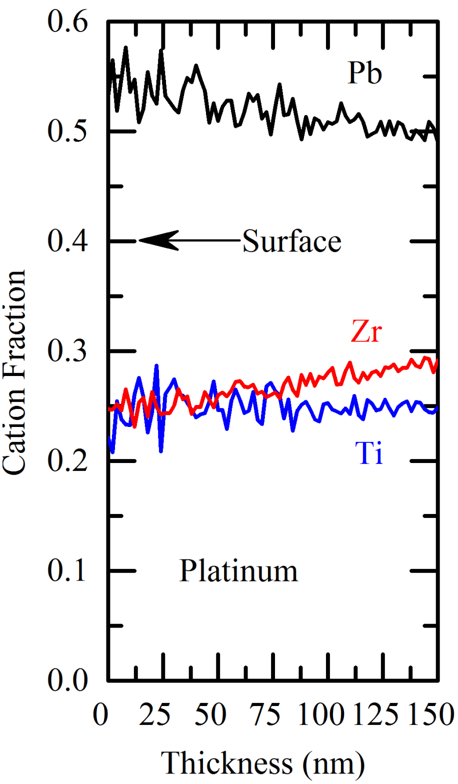
- Oxygen stoichiometry
  - Optimize the anion/cation ratio
- Cation composition not always optimized by ratio
  - Preferential evaporation of species

Composition Profiles

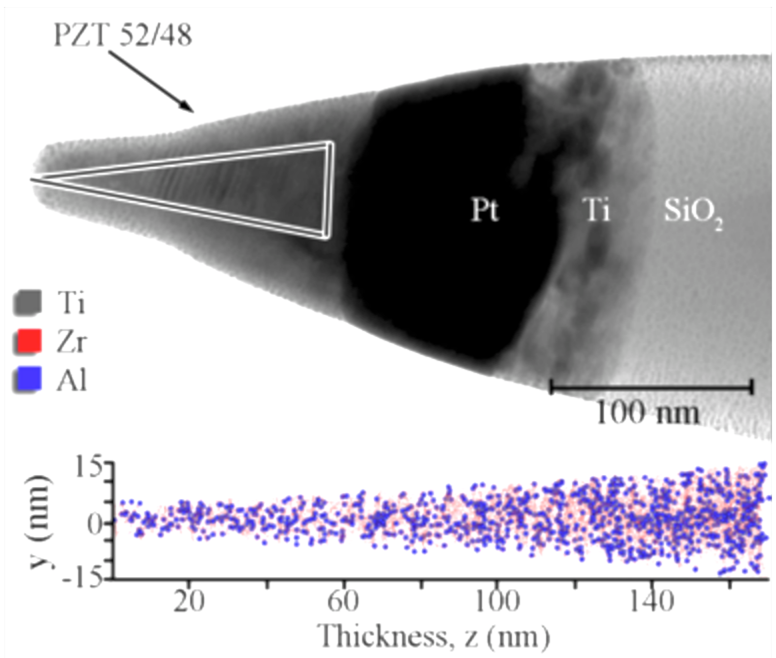
- Compo profiling at sub-nm scale
  - Quantitative O content
  - See relative changes in composition
    - Even when stoichiometry is not exact
- Can correlate to TEM data



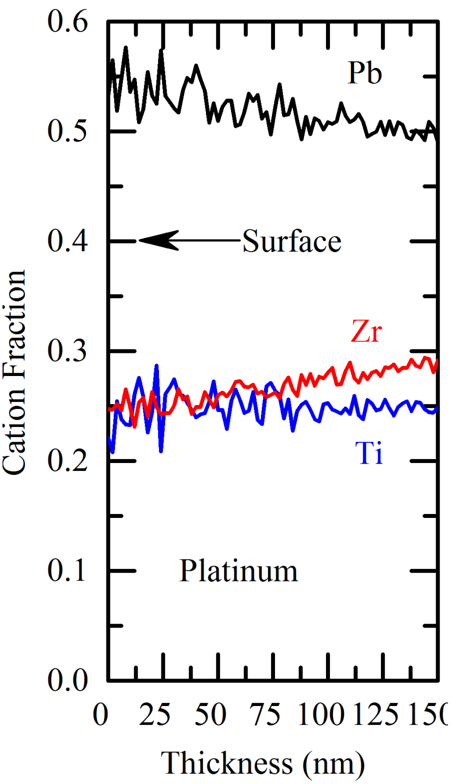
Composition Profiles



- Not only 1D
  - **2D profiles** possible with <1nm resolution
- Correlate to STEM EDS data



Composition Profiles



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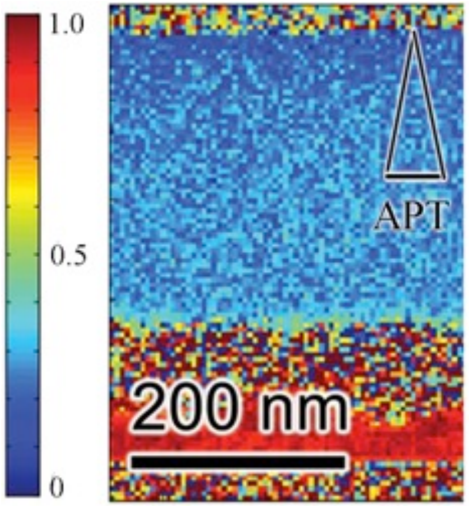
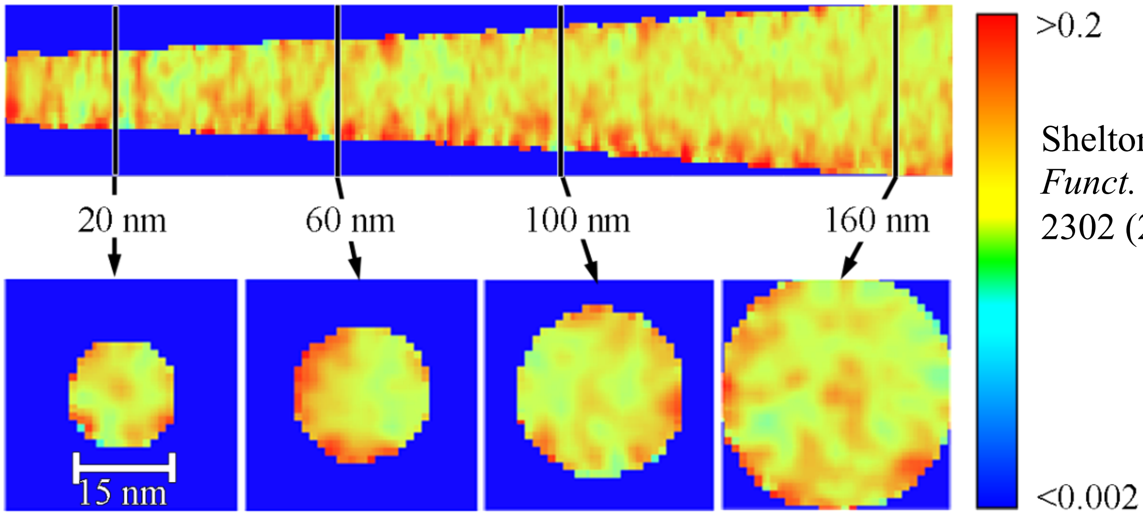
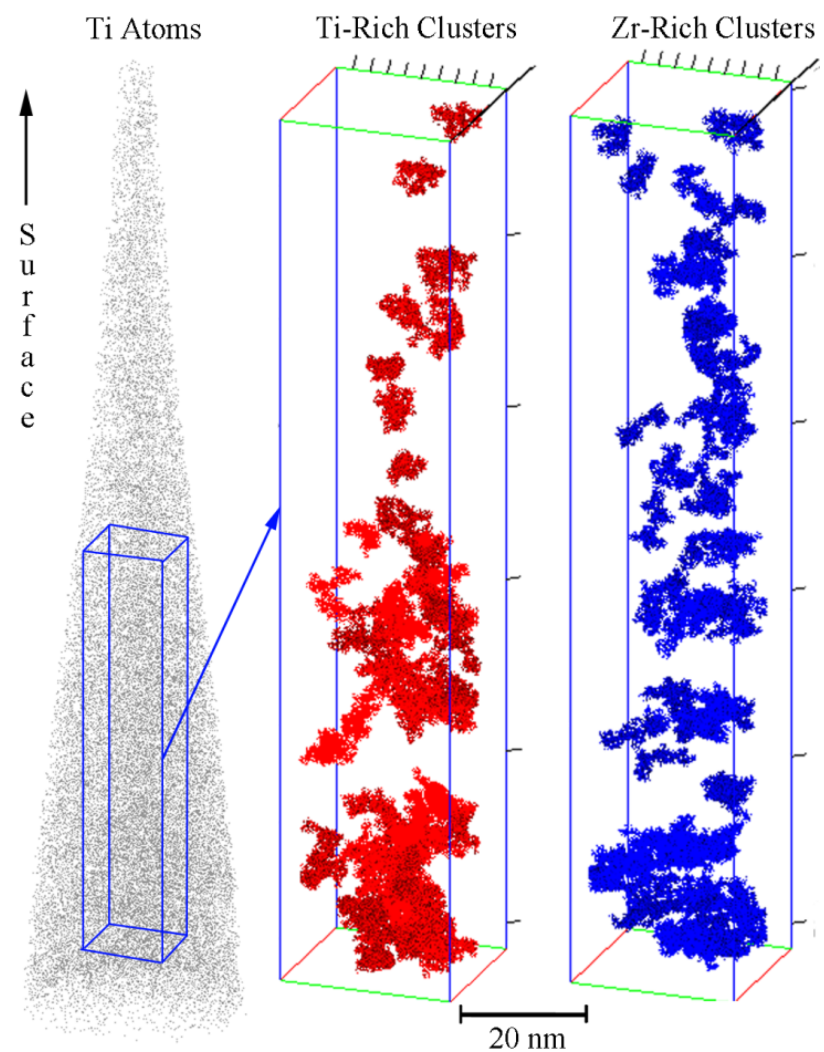




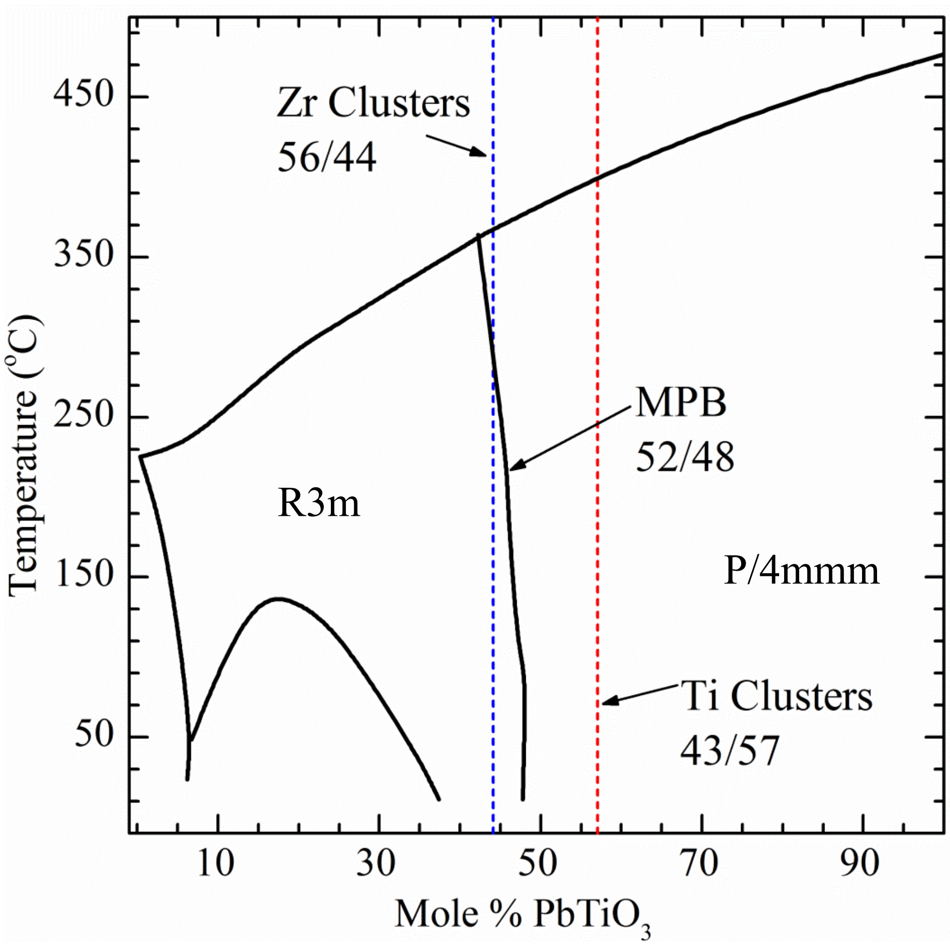
Shelton, C. T. *et al*. *Adv. Funct. Mater.* **22,** 2295–2302 (2012).

Cluster Analysis – Bulk PZT

- Found B-site cation clustering in PZT 53/47
  - Obtain correct reconstruction
  - Able to discern ion locations
- May explain performance of PZT near MPB



Cluster Analysis on PZT



- Found cluster composition on either side of the MPB
  - Cluster size 5 – 10 nm
  - Too small to have proved with TEM
- Correlates to changes in crystal structure
  - Domain wall mobility response

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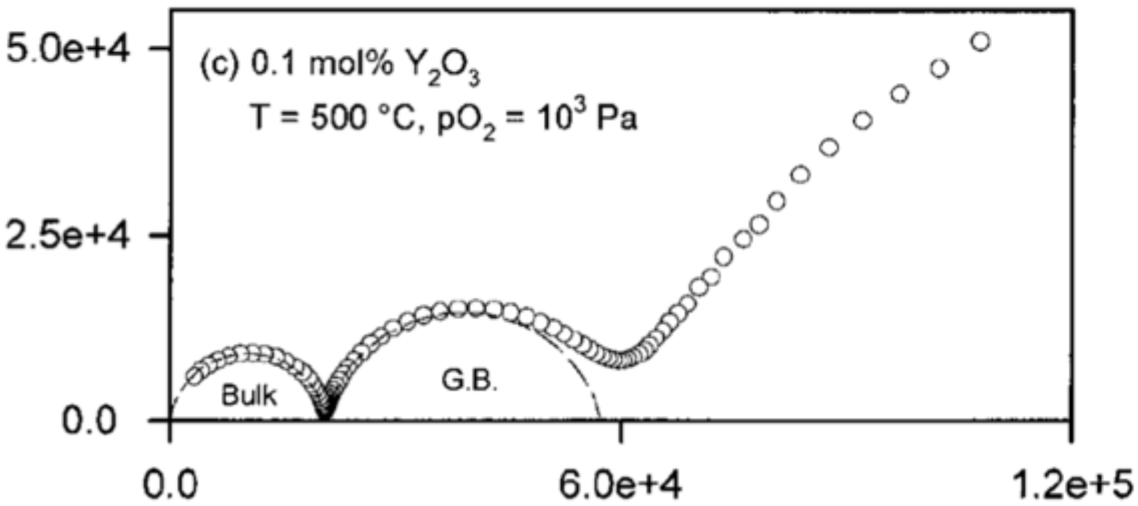
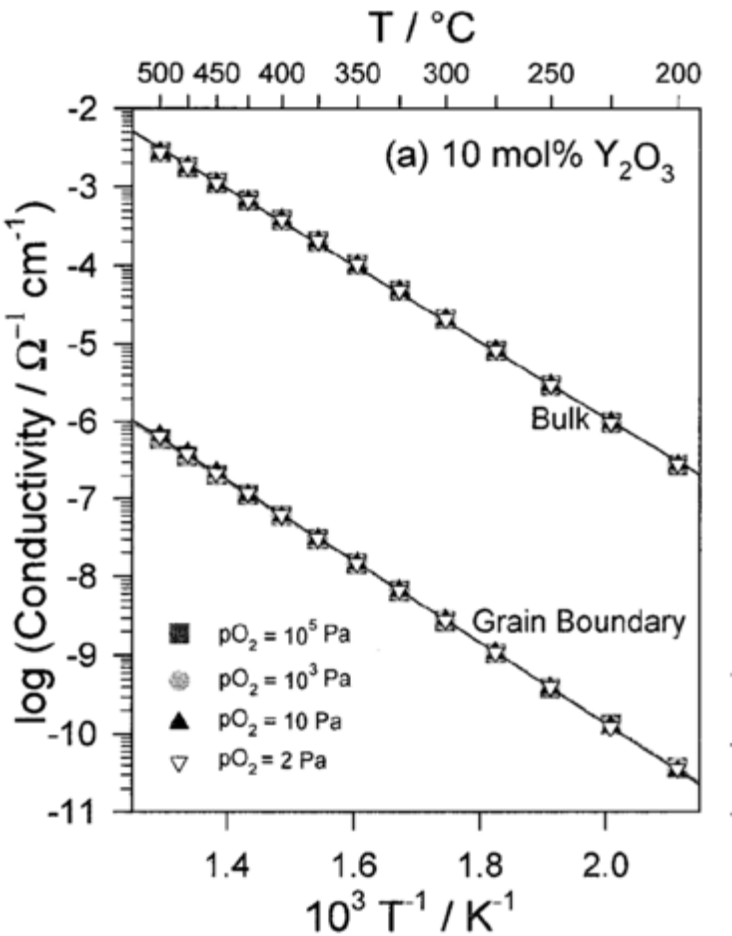
David R. Diercks, Jianhua Tong, Huayang Zhu, Robert Kee, George Baure, Juan C. Nino, Ryan O'Hayre, Brian P. Gorman, "Quantification of 3-D Space Charge Effects at Individual Oxide Grain Boundaries by Atom Probe Tomography", *Journal of Materials Chemistry A*, available online March 2016.

APT OF OXYGEN ION CONDUCTORS – Nd:CeO_2

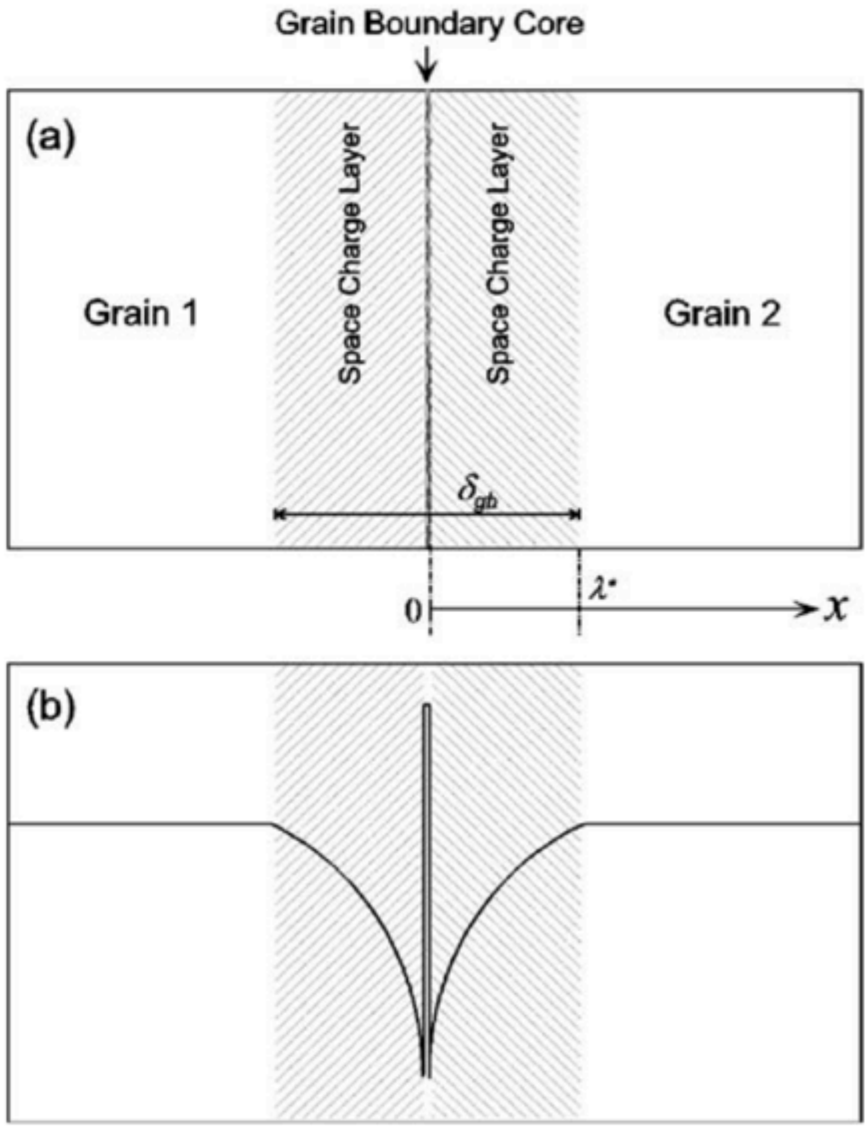
Space Charge Limited Conductivity

- Determine grain boundary vs. bulk conductivities using EIS
- GB typically orders of magnitude less conductive than bulk





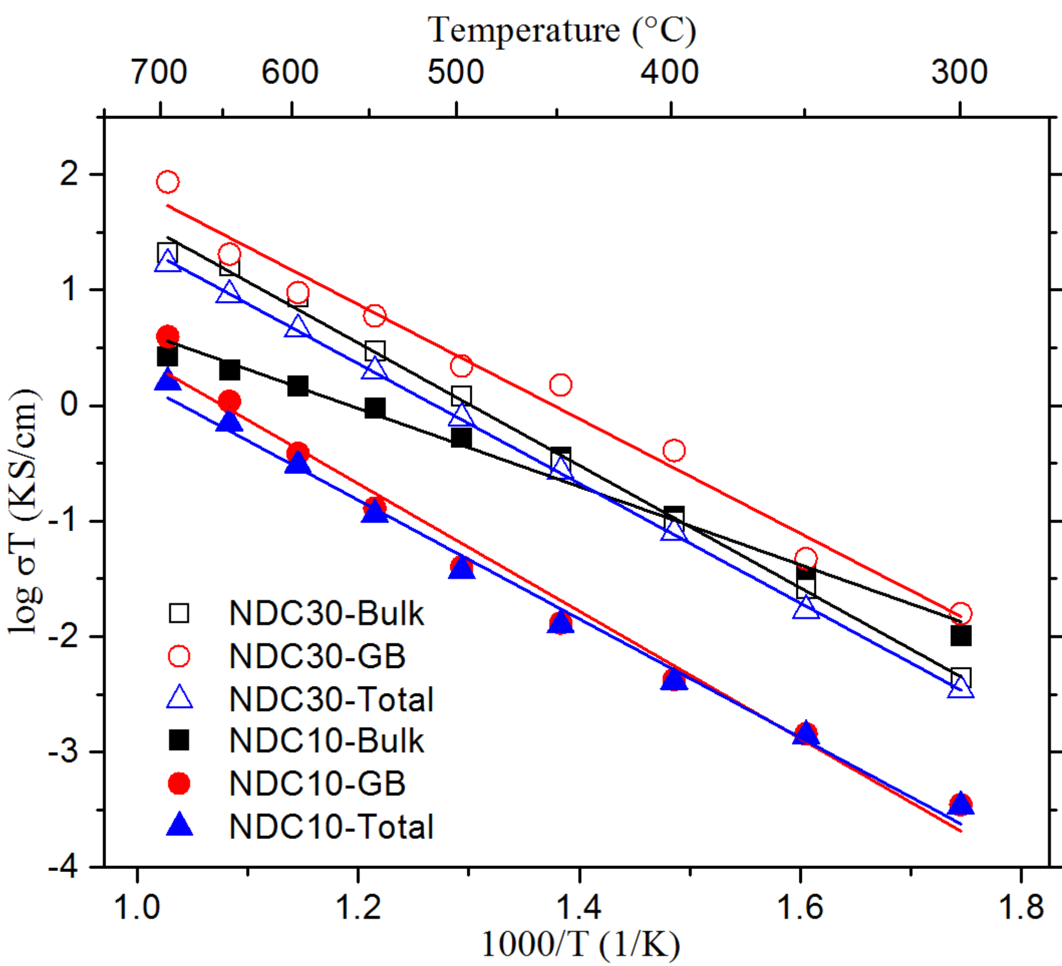
Space Charge Limited Conductivity



Nd-doped CeO_2

- Two compositions of $Ce_{1-x}Nd_xO_{2-\delta}$
  - x = 0.1 (NDC10) – typical of electrolytes in SOFCs
  - x = 0.3 (NDC30) – near disorder-order phase transformation
- GB conductivity is lower than bulk
- Why?

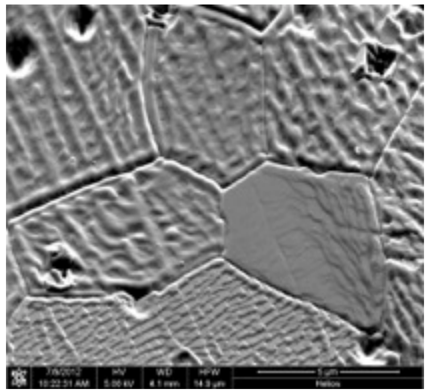
$$\sigma_{spgb} = \frac{\tau_{bulk}}{\tau_{gb}} \sigma_{bulk}$$



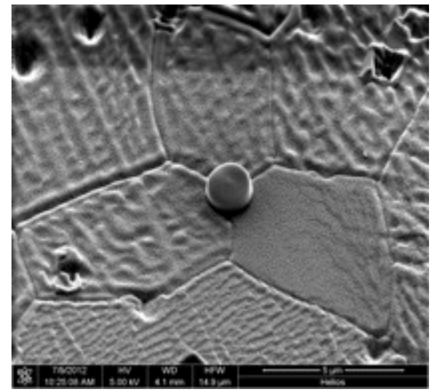
FIB Site-specific Specimen Preparation – Example Data

Site-specific specimen preparation can target electrically interesting areas

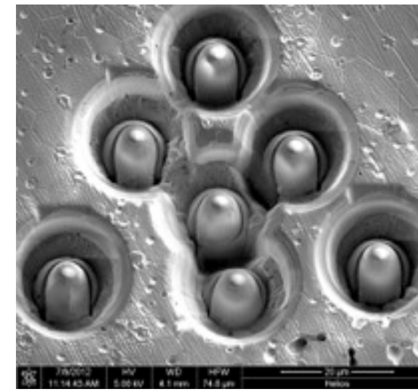
Current FIB capabilities can utilize EBIC, conductive AFM, NSOM for indentifying ROI



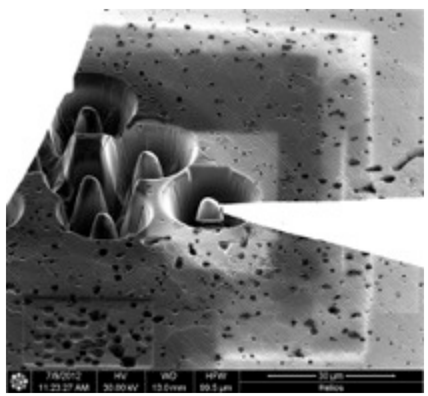
1. SEM imaging of GBs (CeO2)



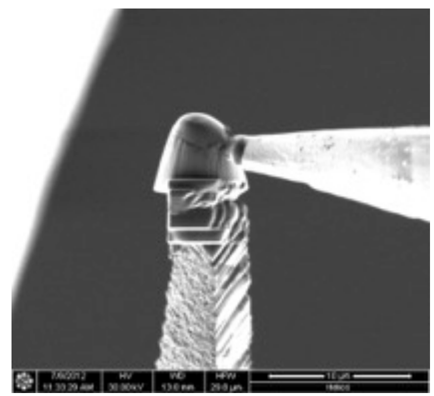
2. Pt deposition to mark ROIs



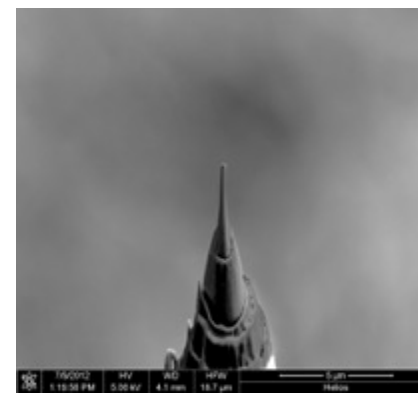
3. FIB milling of ROIs



4. in-situ manipulation from bulk

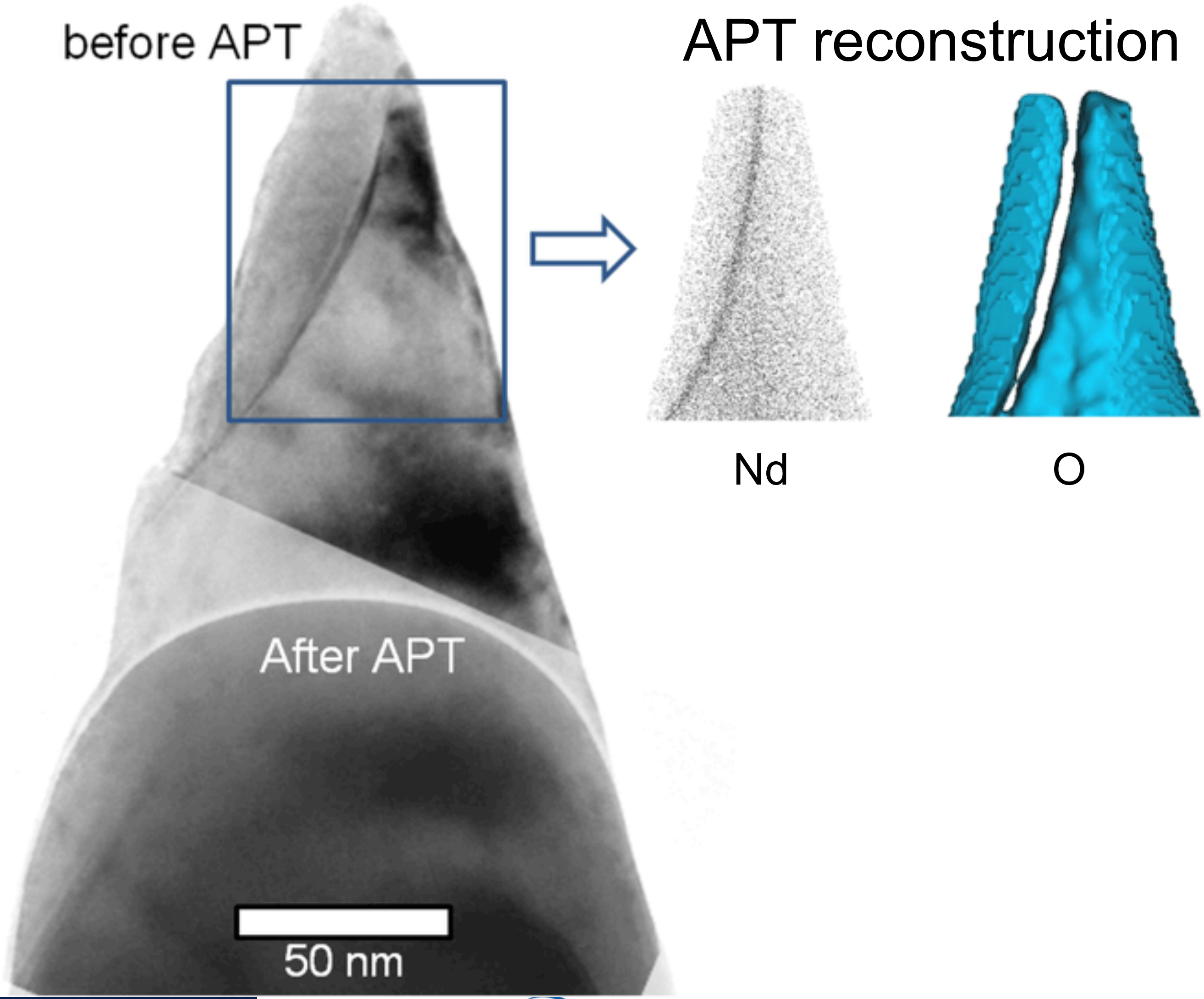


5. in-situ manipulation to TEM grid post

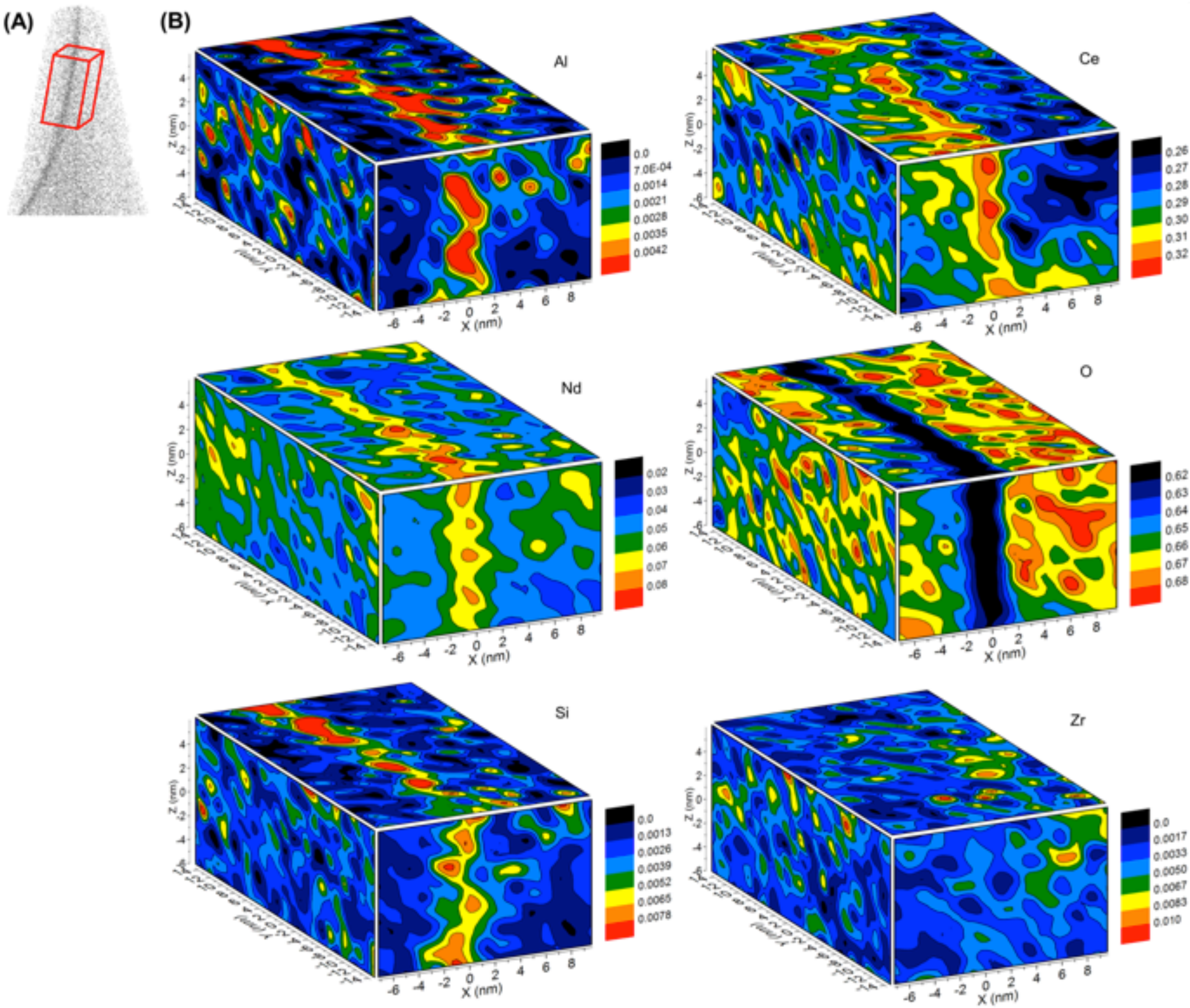


6. Final FIB shaping of specimen

Nd-doped CeO_2 – NDC10



Nd-doped CeO_2 – NDC10

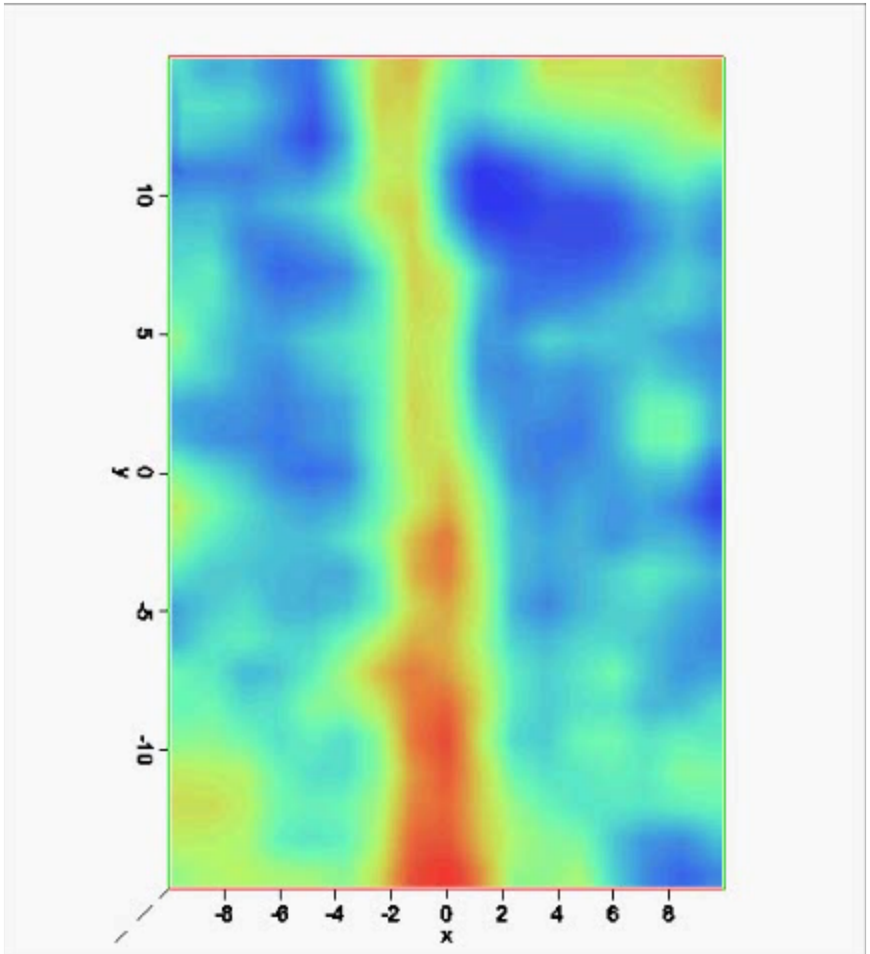


$$\sigma_{spgb} = \frac{L}{AR_{gb}} \frac{g}{G}$$

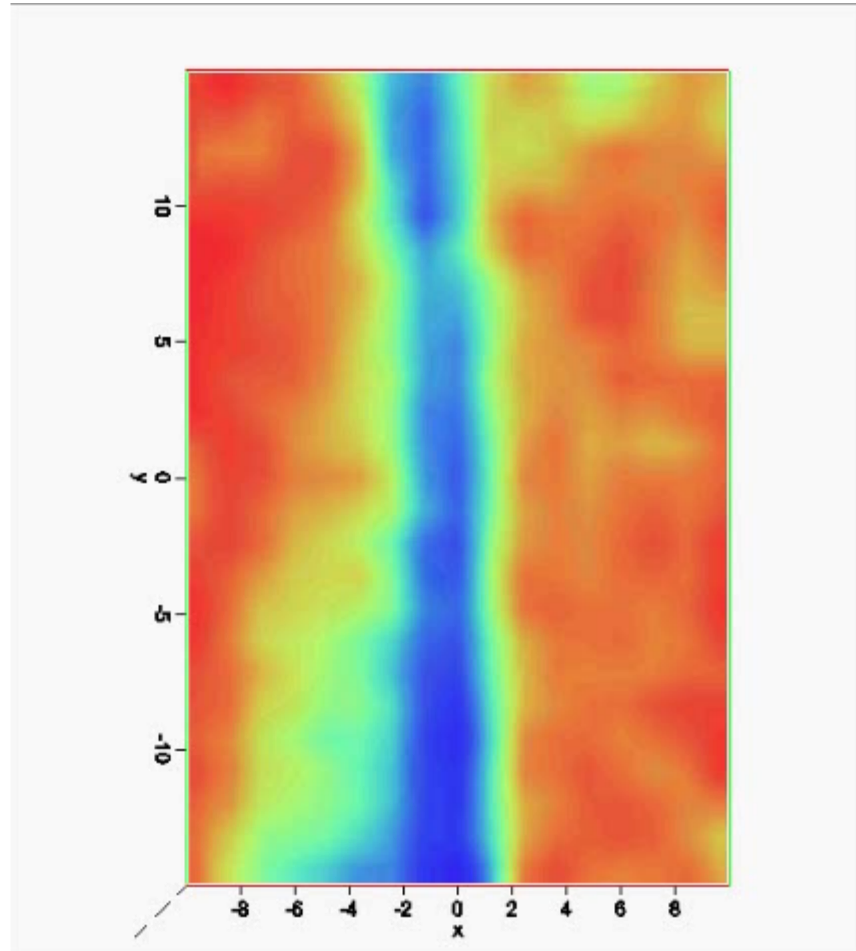
Quantify grain boundary width

Use to quantify EIS conductivity data

Nd-doped CeO_2 – NDC10



Nd



O

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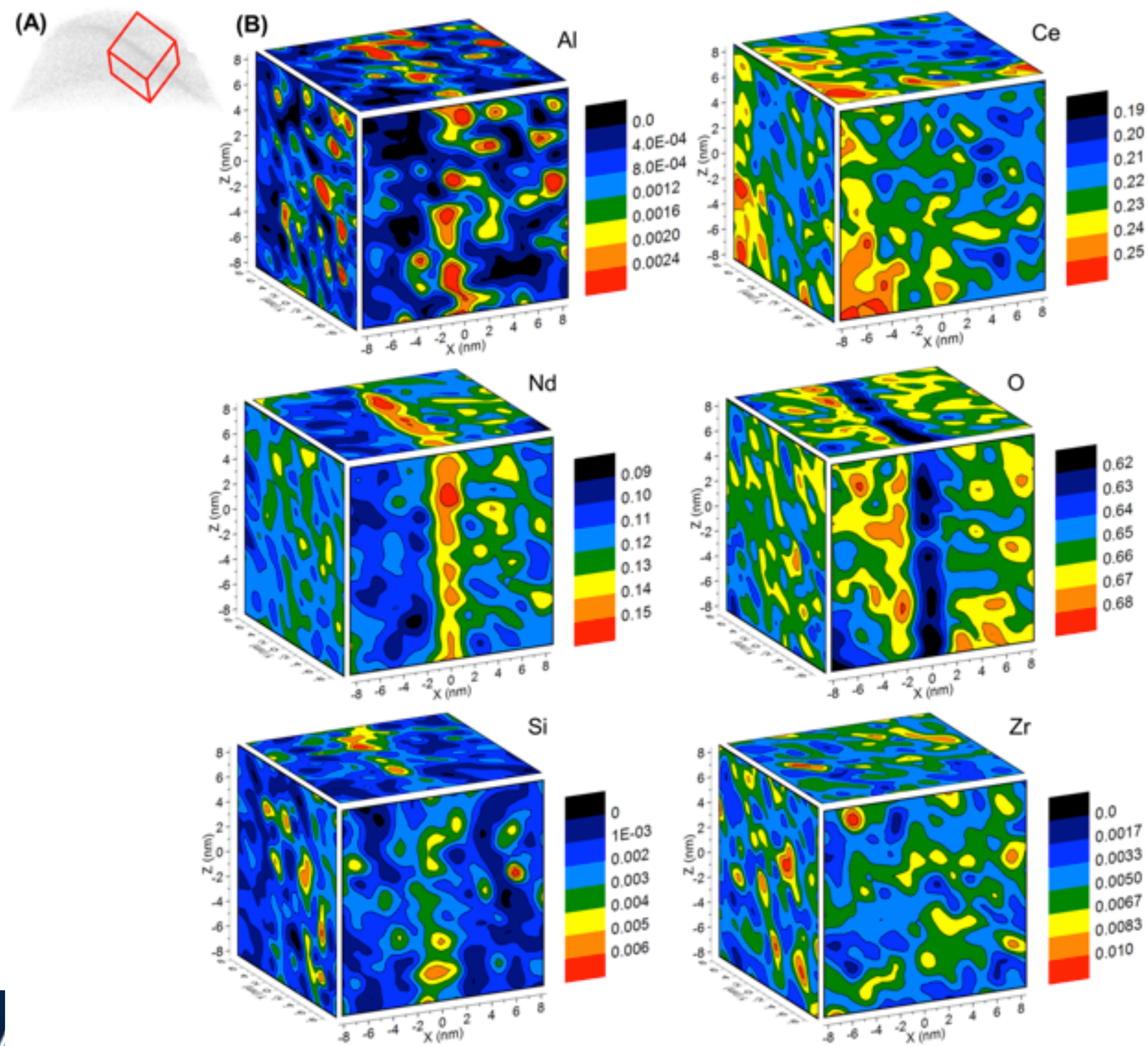
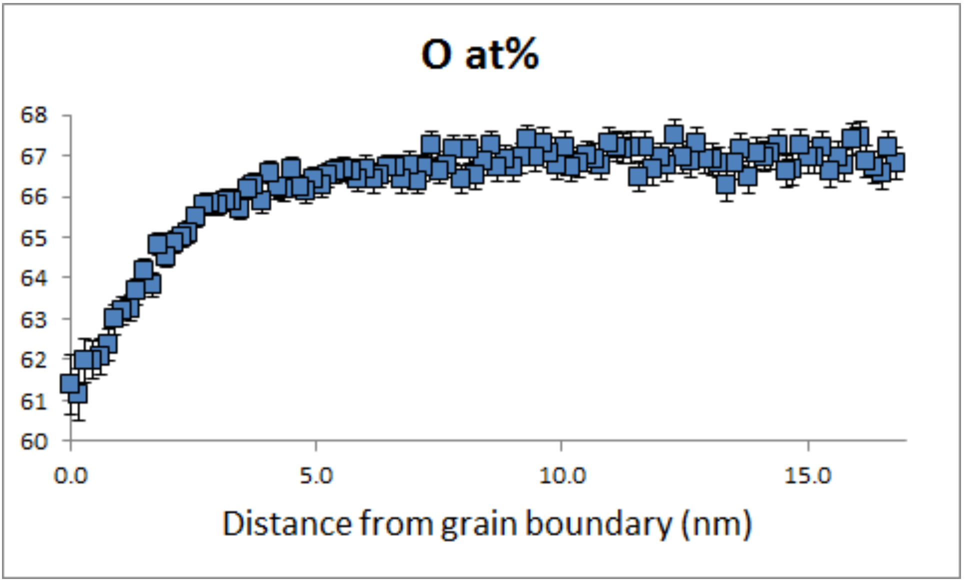
Nd-doped CeO_2 – NDC30

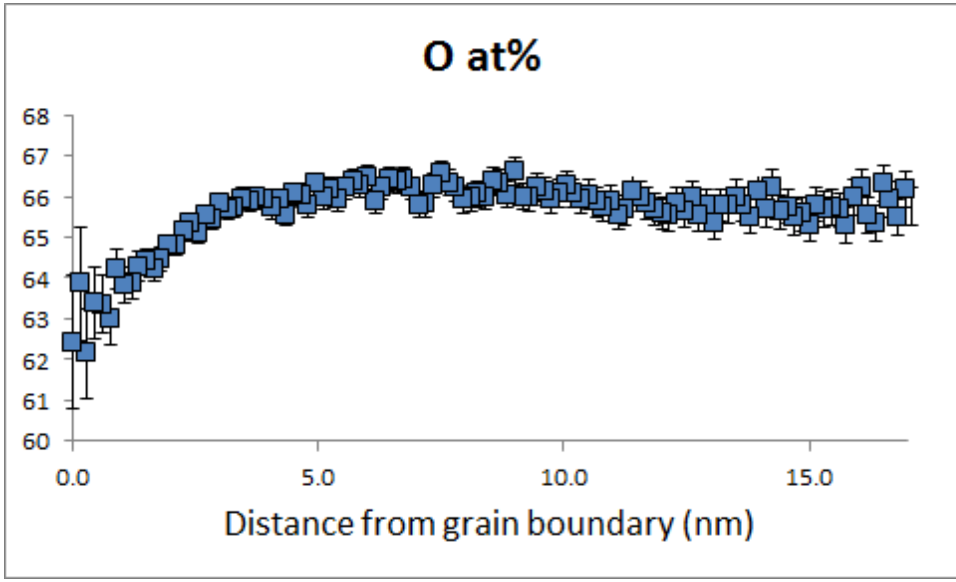


Comparison of 10 and 30 at% Nd:CeO2

- O profiles

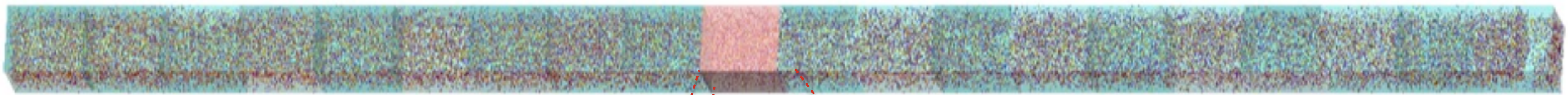


10 at%

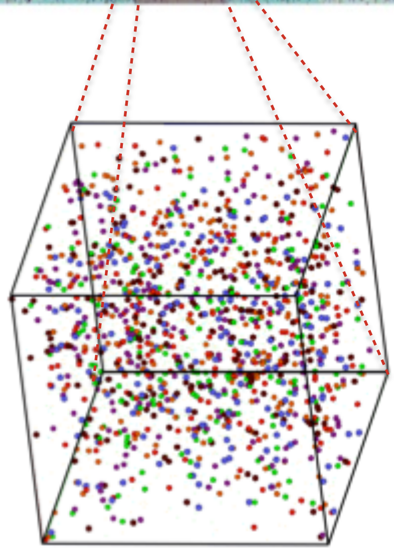


30 at%

Nd-doped CeO_2 – Potential



Need to turn 3-D composition into 3-D charge density



O: 2-
Ce: 3+, 4+
Nd: 3+
Al: 3+
Si: 4+
Zr: 4+

Calculate charge density from # of ions in each volume

$$\rho = \rho_{other} + F(2[V_O^{\bullet\bullet}] - [Ce'_{Ce}]).$$

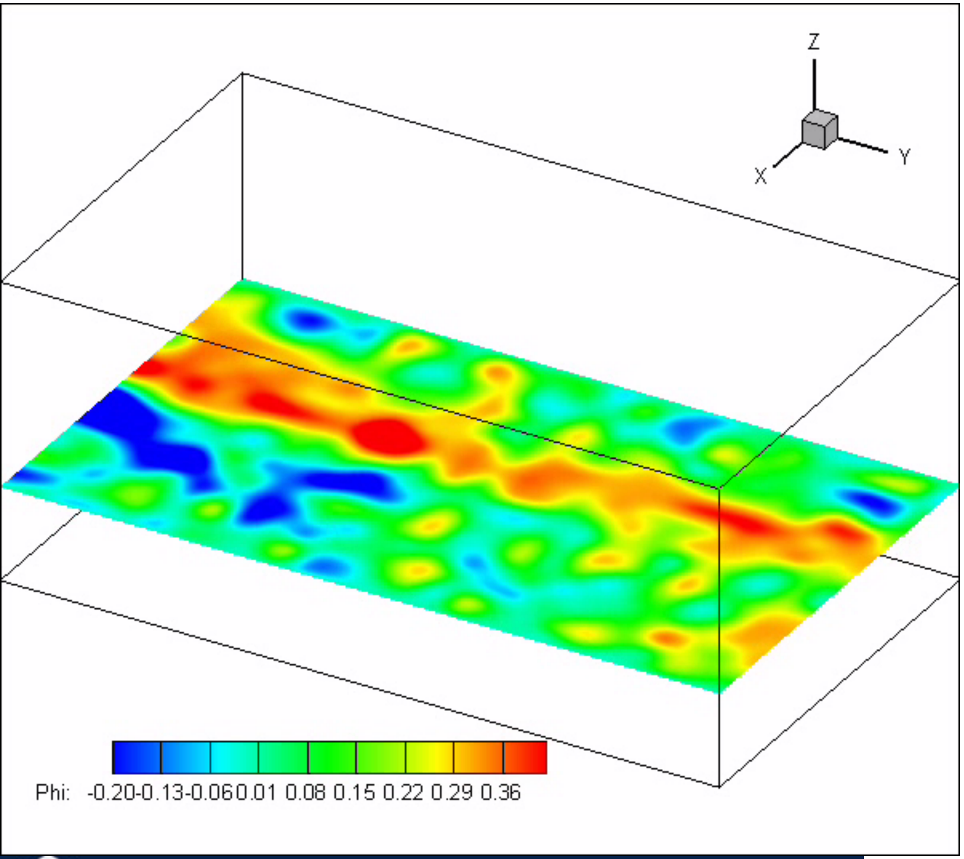
Use Poisson equation to determine field at each volume in 3-D

$$\nabla \cdot \epsilon_0 \epsilon_r \nabla \phi = -\rho$$

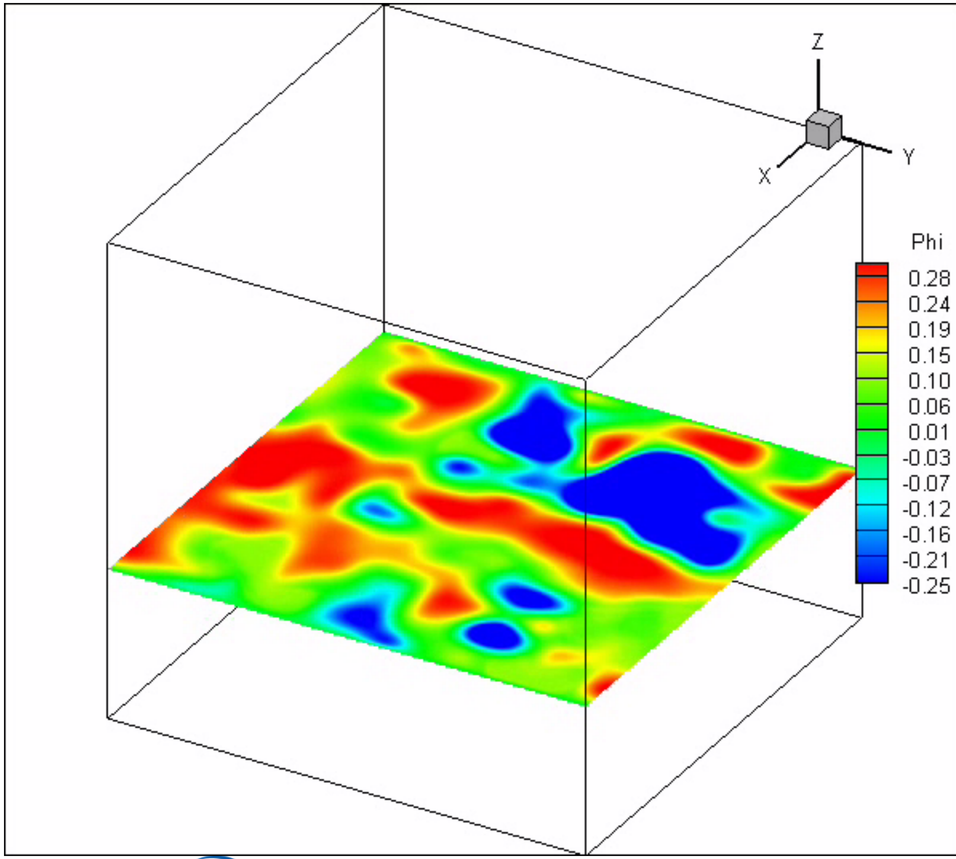
Nd-doped CeO_2 – Potential

- Use charge data to produce voltage using Poisson Equation

NDC10

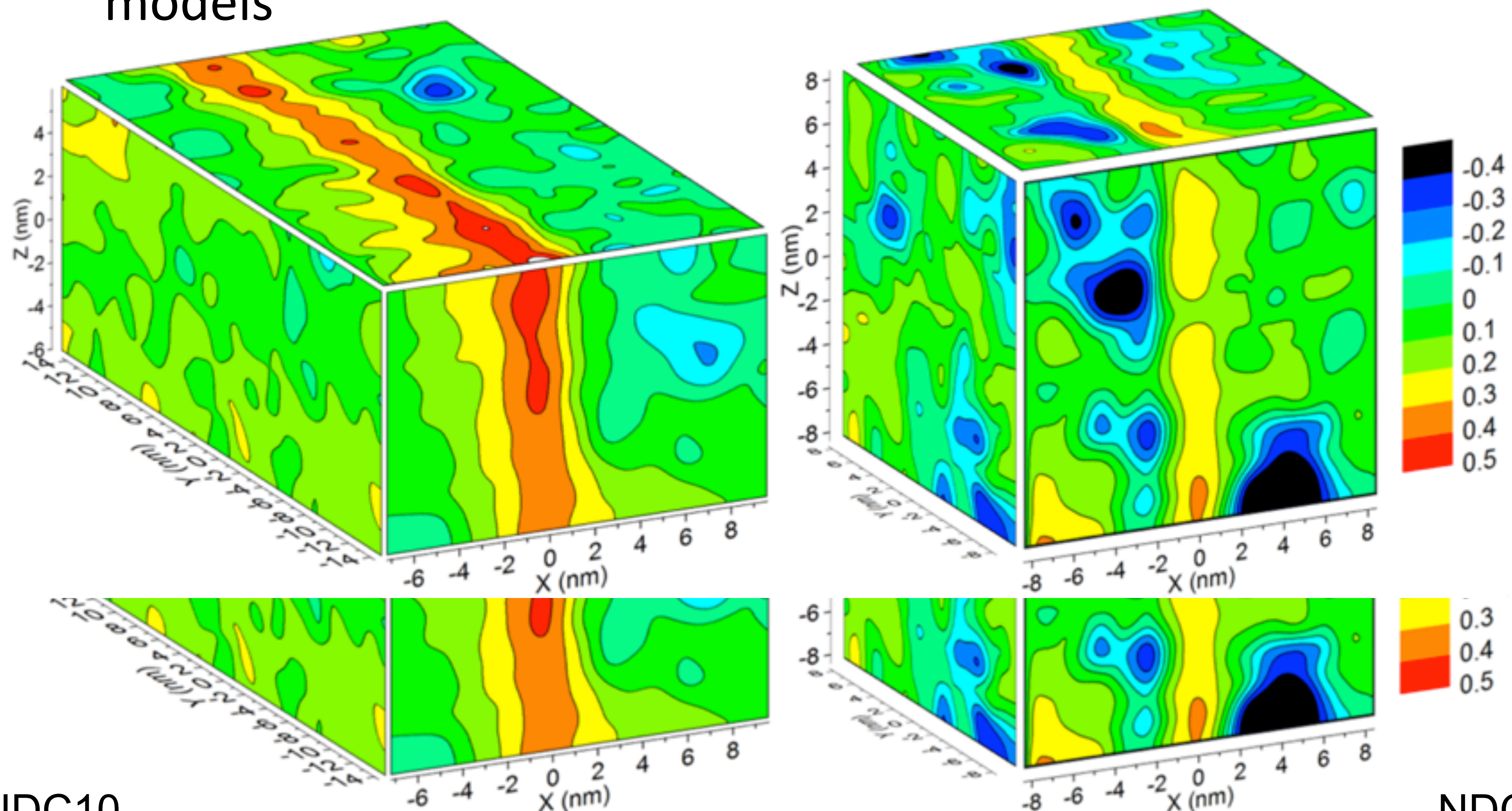


NDC30



Nd-doped CeO_2 – Potential

- APT space charge voltage matches that obtained from EIS models



NDC10

NDC30

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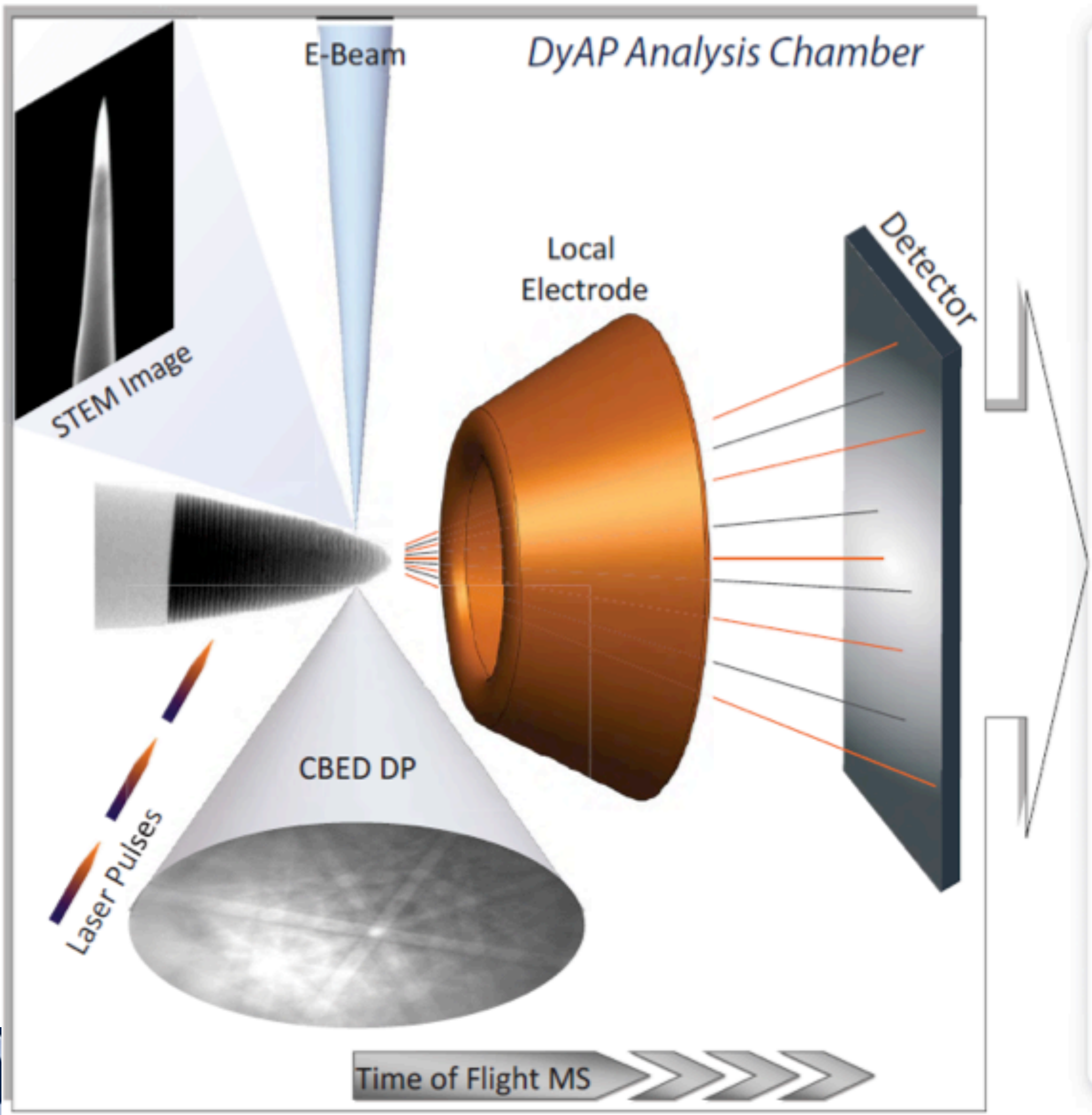
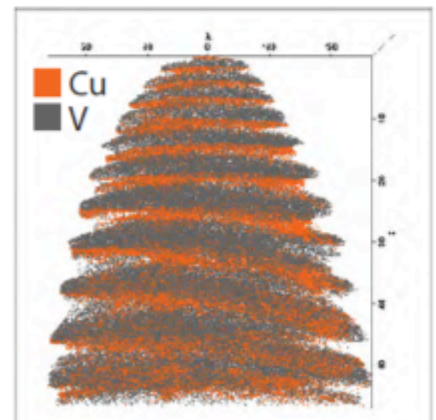
USING APT TO ACHIEVE AST?

Atom Probe Tomography (APT) Basics



3D Reconstruction

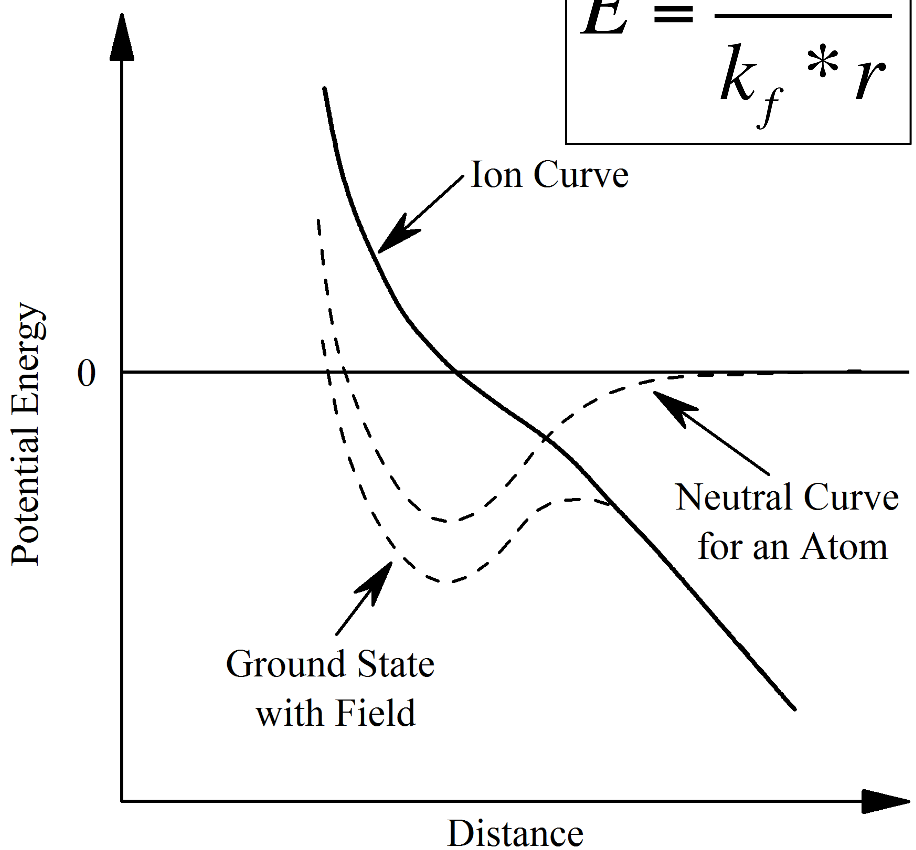
Specimen reconstruction from the ions collected



- Position (x,y) of atoms determined by detector.
- Timed evaporation events used to determine the z-position of the ions:
- Use Local Electrode fields in combination with laser pulses (ns time resolution).

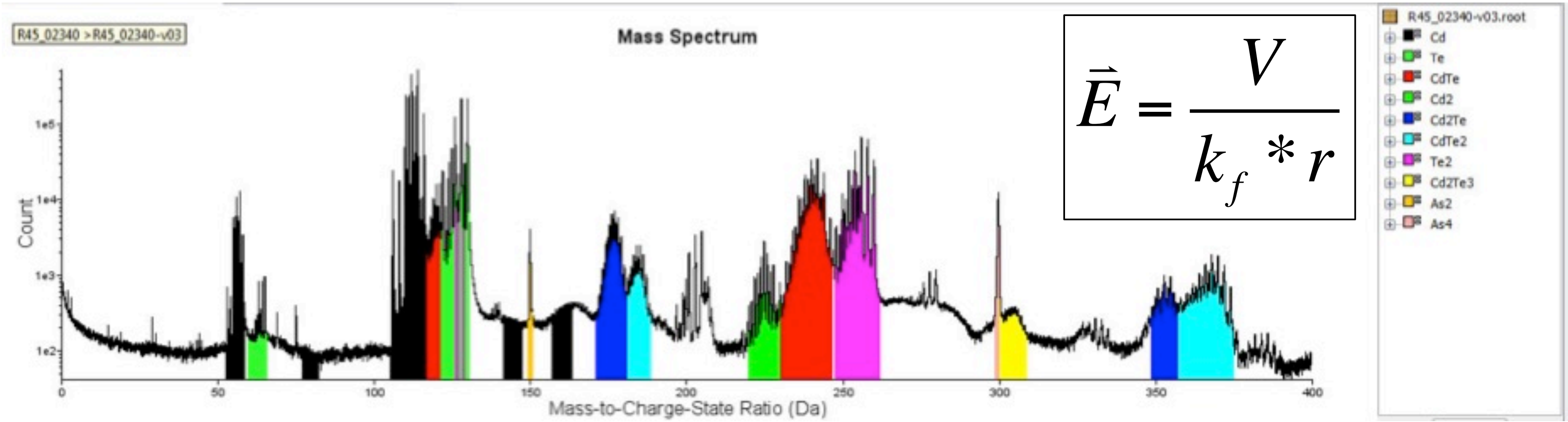
Field Evaporation Basics

$$\vec{E} = \frac{V}{k_f * r}$$

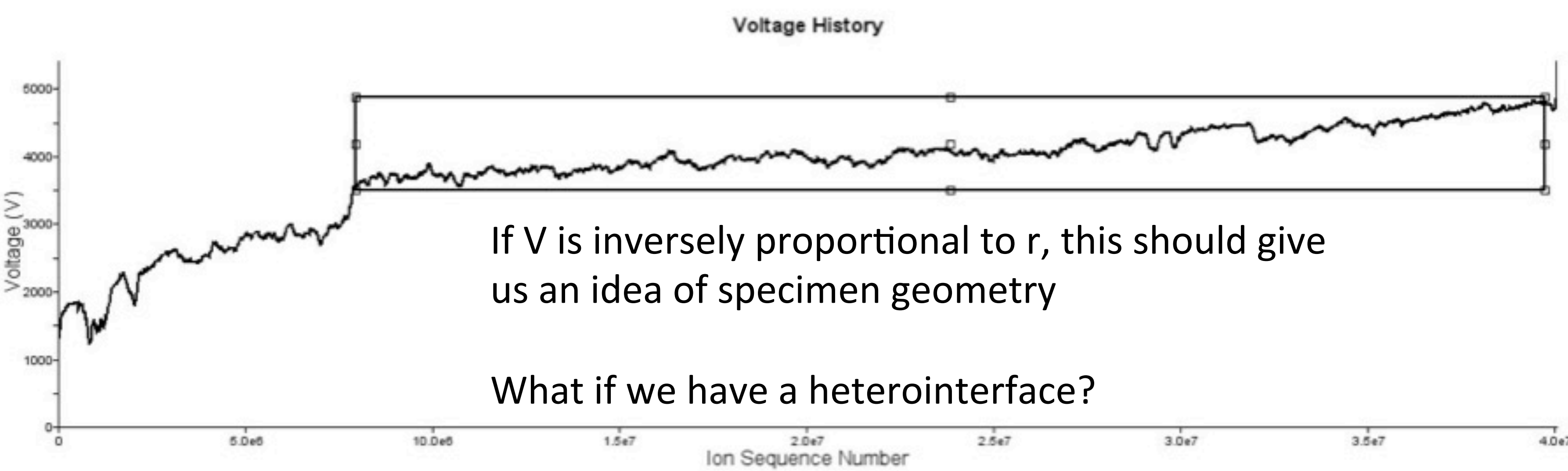


- Field evaporation similar to work function for electrons
- Evaporation field dependent upon material – bond strength, heat of formation
- Get above the evaporation threshold using voltage or thermal (Laser) pulse

Atom Probe Data Analysis



$$\vec{E} = \frac{V}{k_f * r}$$



If V is inversely proportional to r, this should give us an idea of specimen geometry

What if we have a heterointerface?

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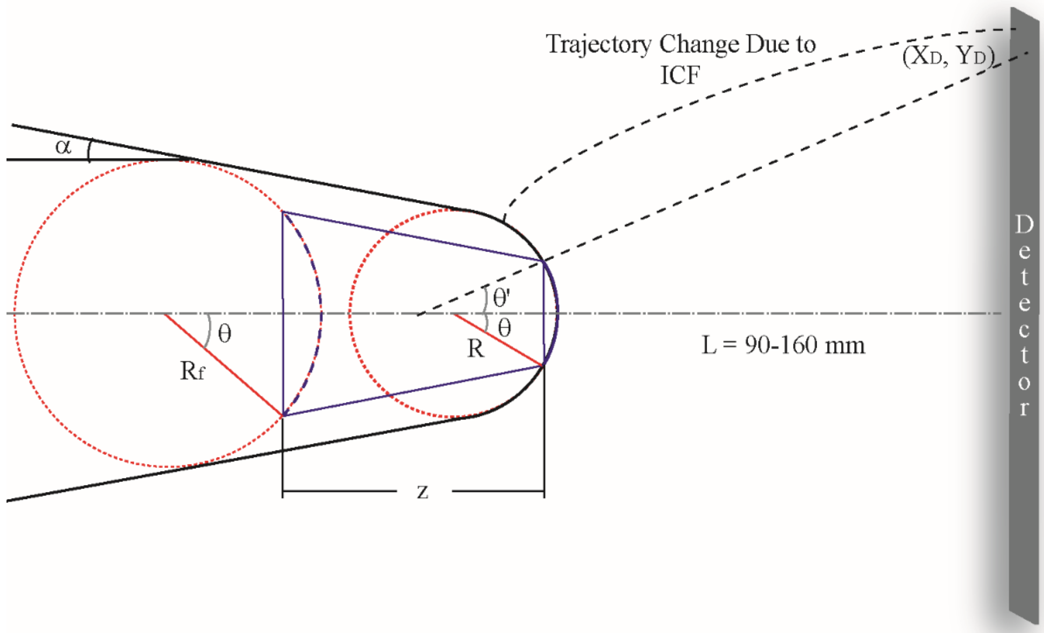
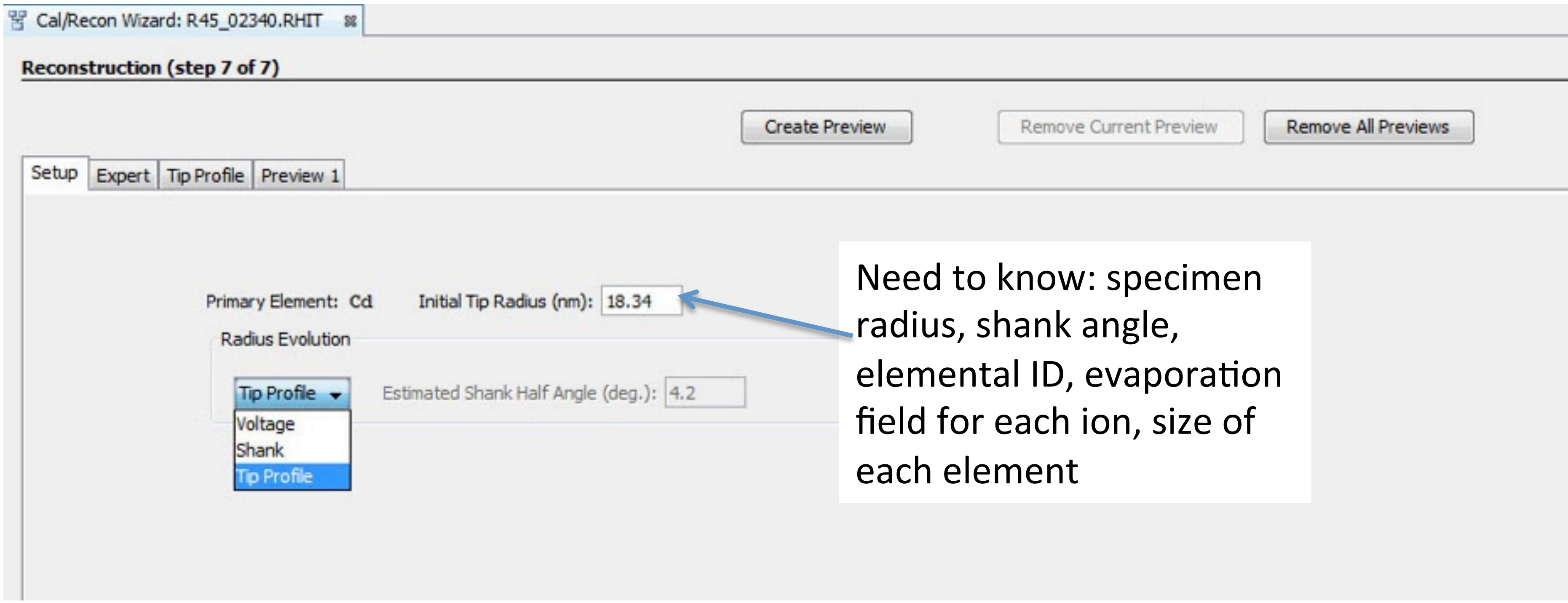
Specimen 3D Reconstruction



- Point projection scheme
  - Tip radius (r_s)
  - Shank Angle (α)
  - Image compression factor (1< ICF <8)
  - Detector efficiency < 100%
  - Assumed continuity of tip
    - $r_s/r_c = 1$
- Calculated FOV
- Best guesses used for
  - ICF, detector efficiency

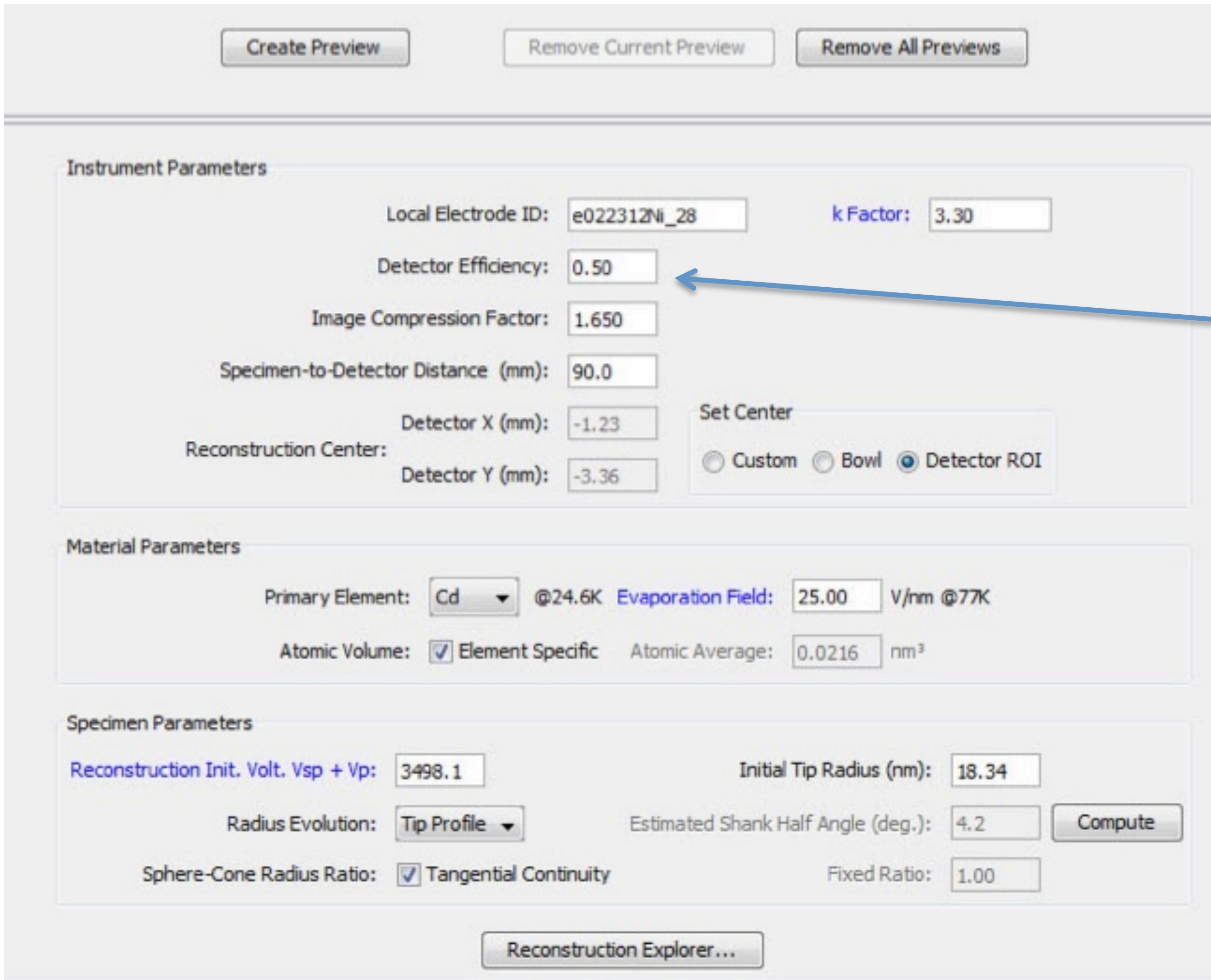
Gault, B. *et al. Ultramicroscopy* **111,** 448–57 (2011)

Let's Do a Reconstruction!



Need to know: specimen radius, shank angle, elemental ID, evaporation field for each ion, size of each element

Let’s Do a Reconstruction!

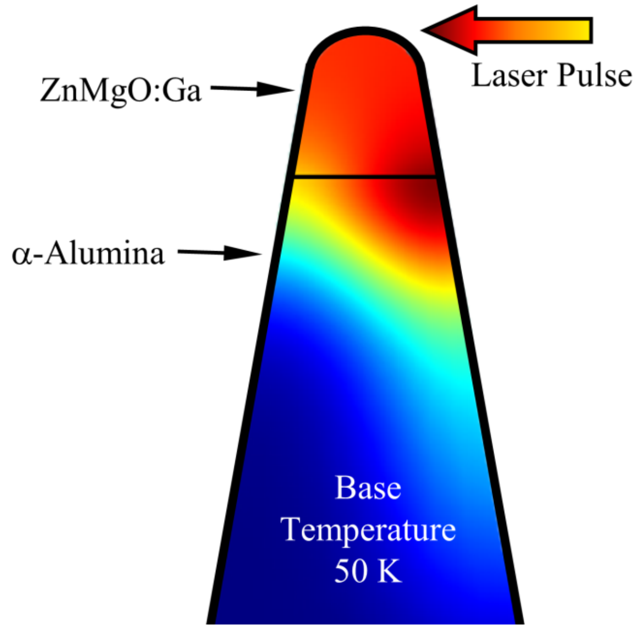


Also need to know: detection efficiency, image compression factor (dielectric permittivity of each phase), sphere-to-cone ratio during evaporation, magnification, field of view, atomic volume

Laser Assisted APT Reconstruction

- Also need to know:
  - Evaporation field for each atomic species as a function of T
  - Specimen T at peak laser pulse, thermal conductivity of specimen
  - Specimen geometry throughout the experiment

$$\vec{E} = \frac{V}{k_f * r}$$



Why Correlative (S)TEM / APT?

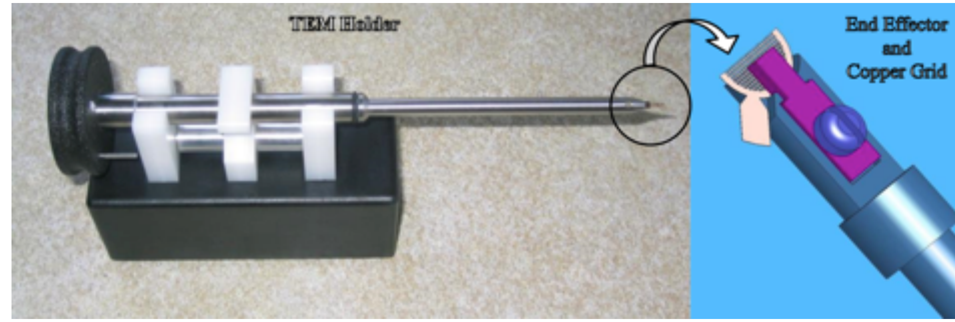
- Before / after high magnification images – specimen geometry!
  - Volume removed, scaled z-axis
  - Input to finite element models
- Evap field from geometry and voltage
  - 3-D shape if we do electron tomography or ptychography
- Electron diffraction = atomic volume and arrangements

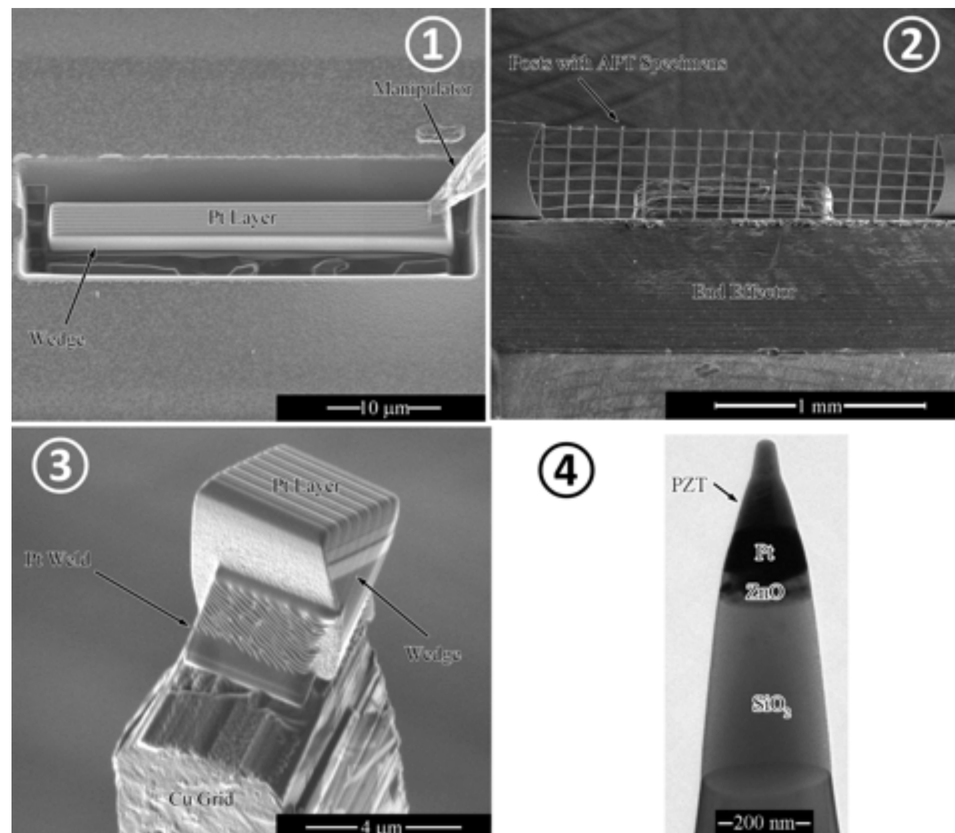
- Take all of these together, we know how many atoms we should have captured and (mostly) how to put them back together
  - Quantify ICF, detector efficiency, k-factor, sphere to cone ratio

- New reconstruction methods! (with U Sydney currently)

Correlative APT/TEM Ex-situ Hardware

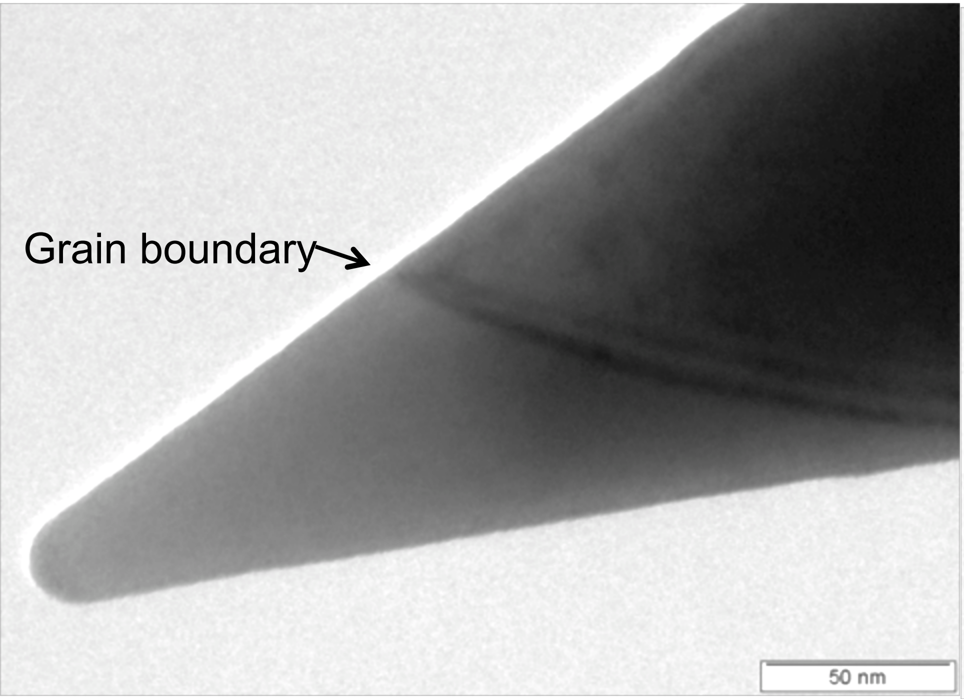
- Custom hardware for correlative technique
- Sample preparation
  - FIB prep in four “easy” steps
- Issues with ex-situ TEM
  - Specimen damage and loss
  - Time consuming

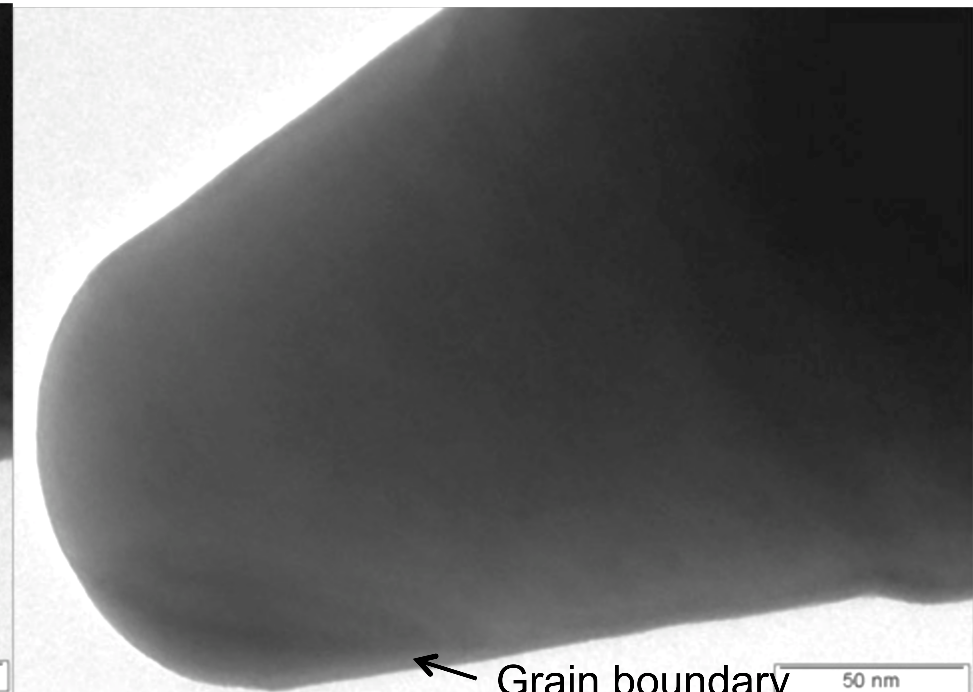




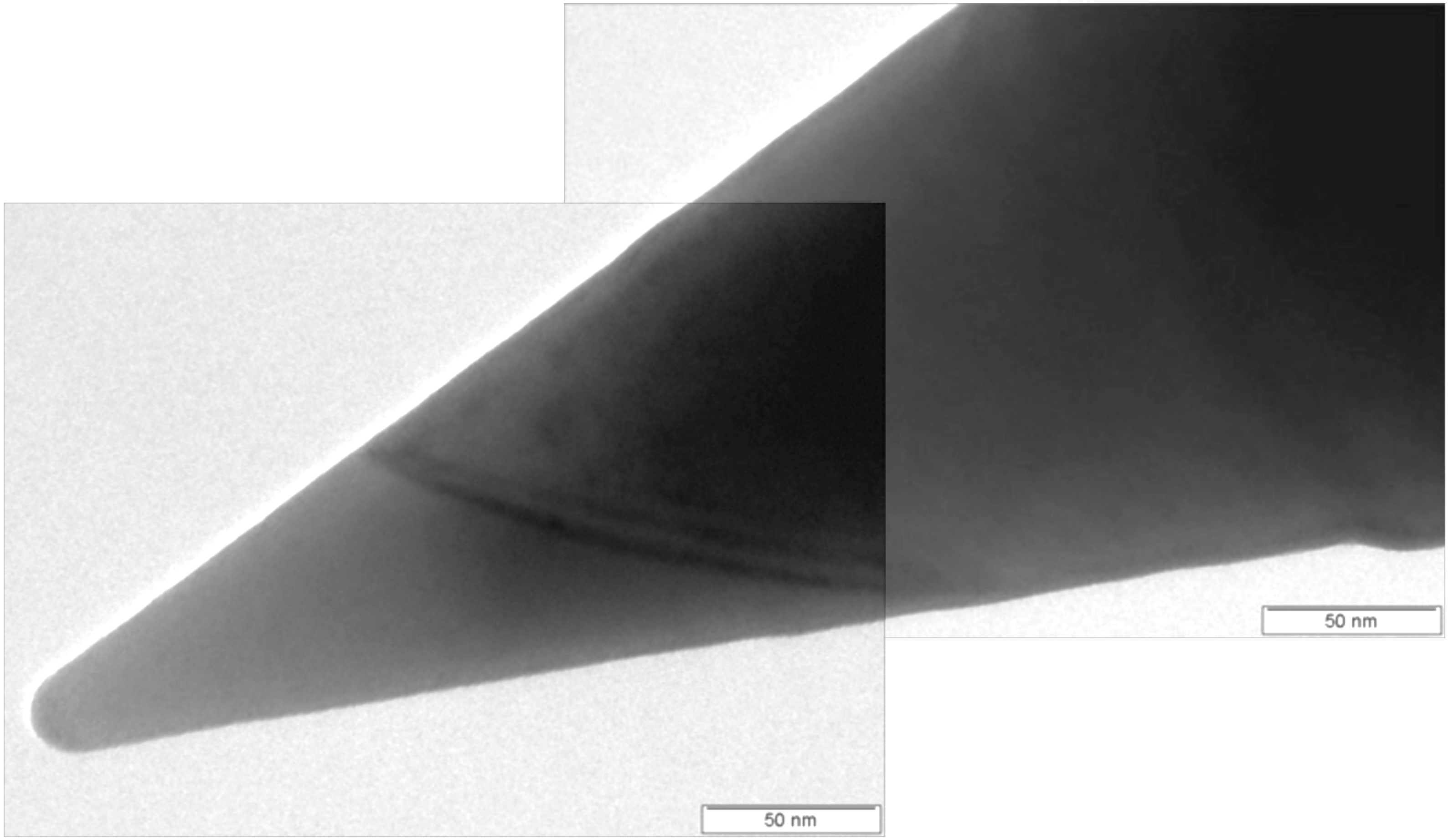
B. P. Gorman, etal, *Microscopy Today*, **4** (16), 2008.

$Ba(Ce,Zr,Y)O_3$





Ba(Ce,Zr,Y)O_3



Why In-situ STEM-APT?

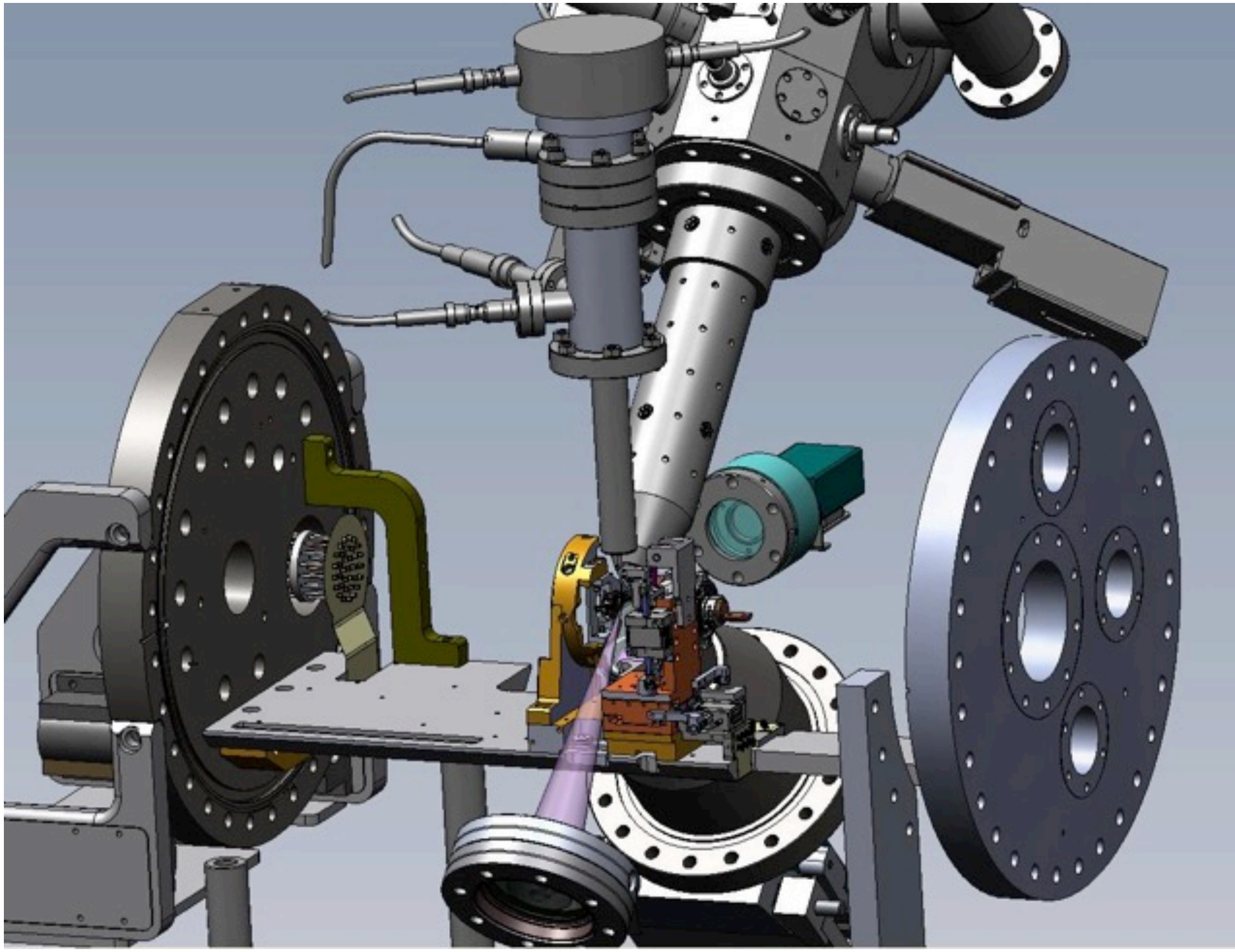
- I am tired of smashing carefully made specimens into the stage of the TEM

- I am tired of waiting for the LEAP to pump back down after doing a TEM analysis in the middle of a run

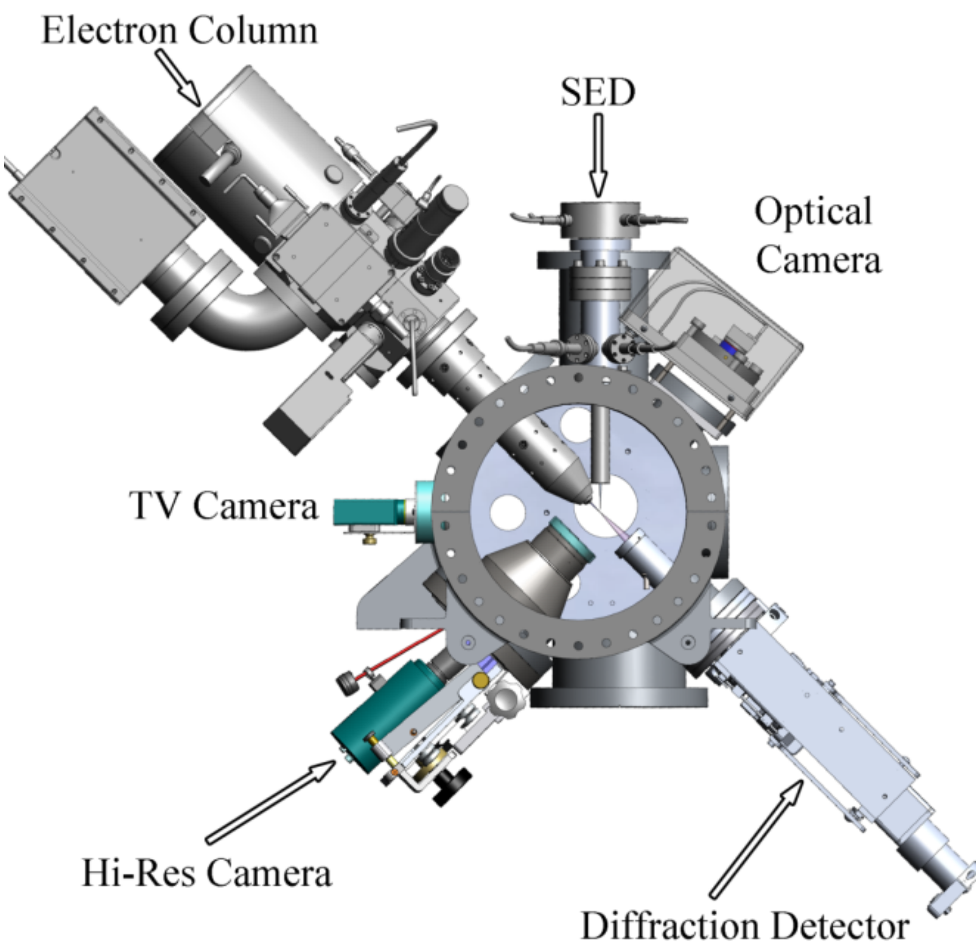
- I want to do dynamic experiments in-situ

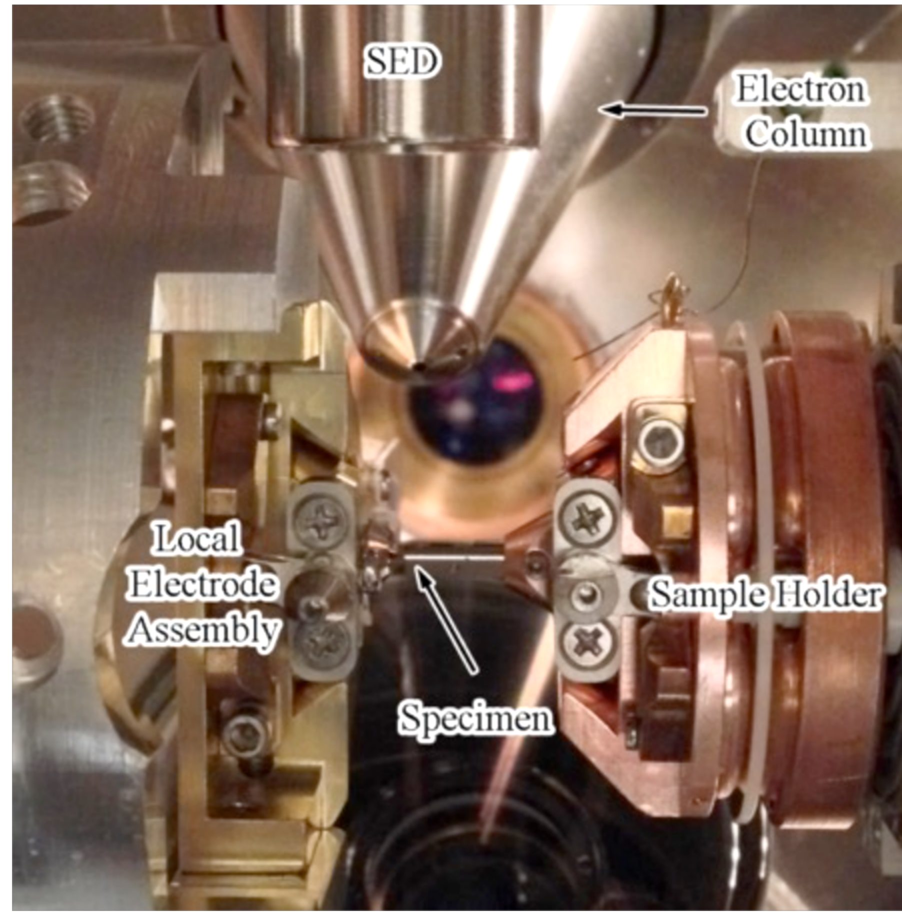
Instrumentation Design

- 25 keV, UHV compatible electron column with nm spatial resolution
- Very limited number of manufacturers
- Orsay Physics e-Clipse II highest resolution UHV SEM

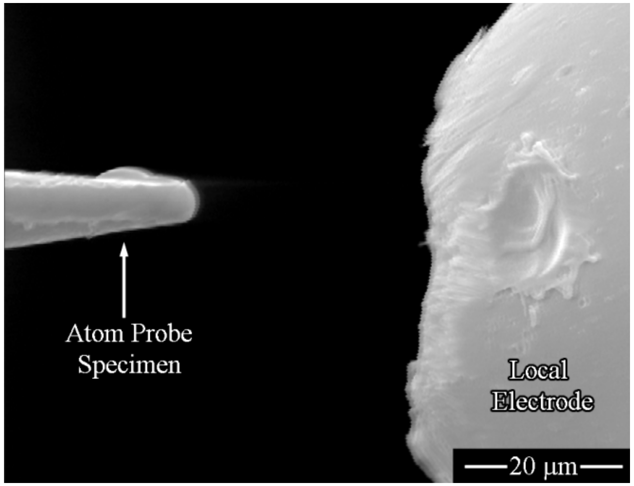


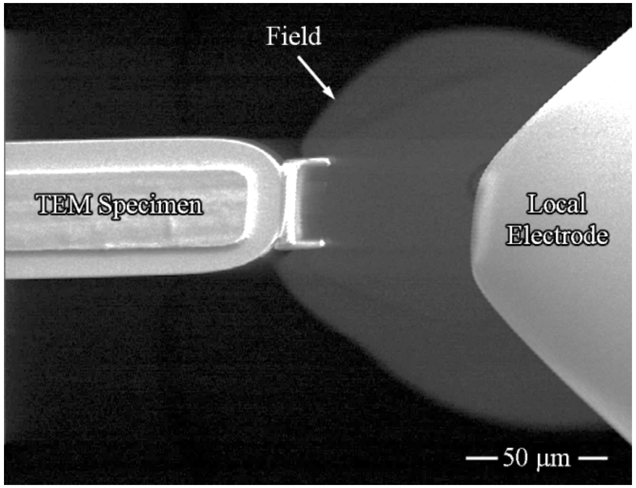
The "Ritatron"





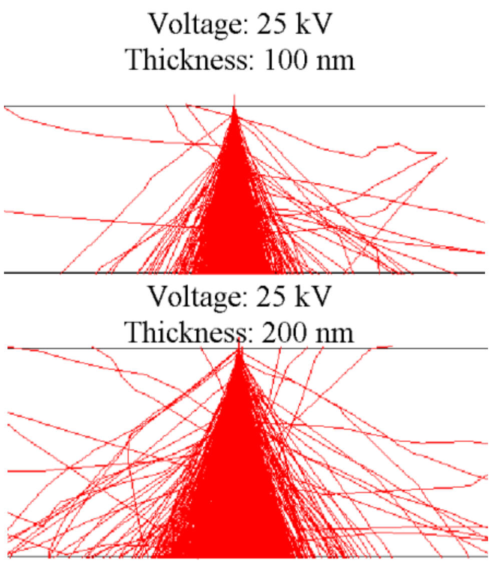
Secondary Electron Imaging

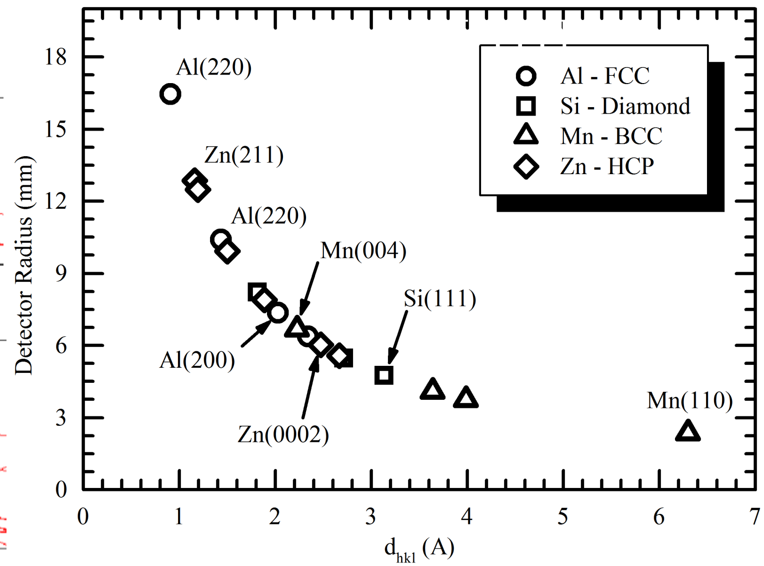


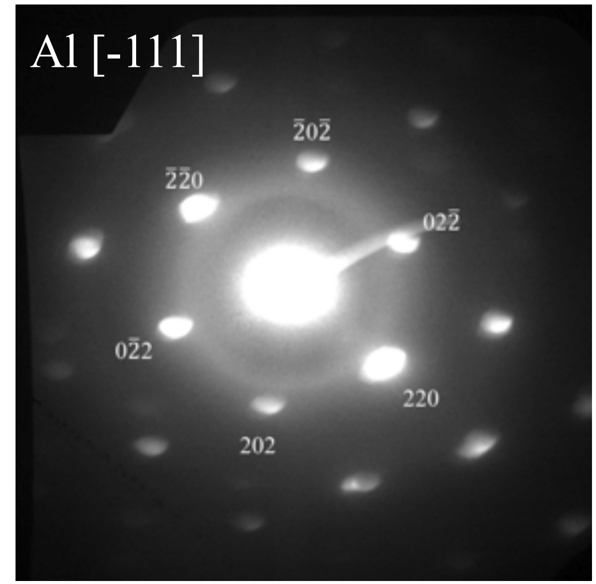


- STEM / APT
  - Tip alignment with local electrode (LE)
  - Tip shape monitoring
  - Active field cancellation necessary (DC to 1MHz)
- Field mapping
  - Around specimen shown (for TEM)
  - Field shape depends on specimen shape

Diffraction Detector



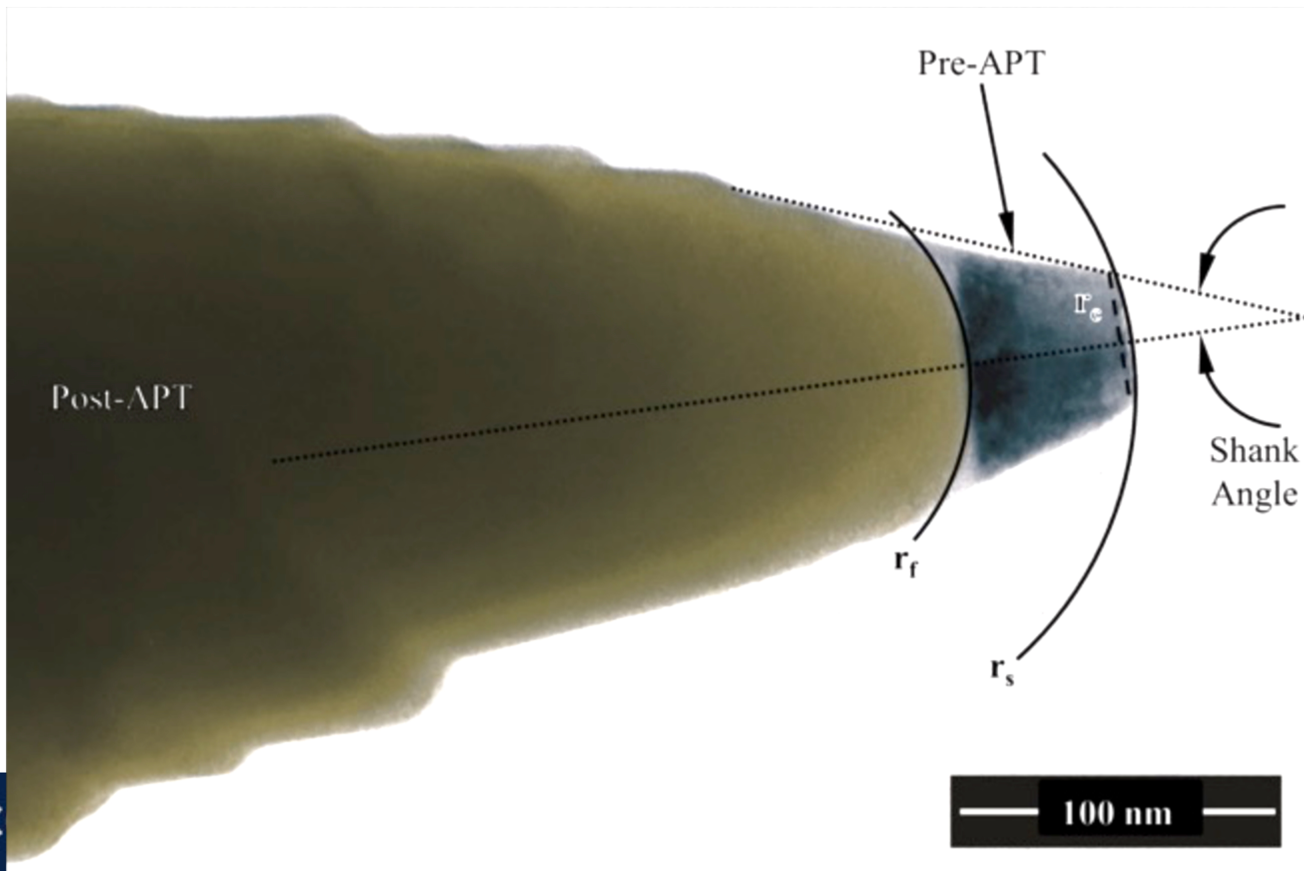




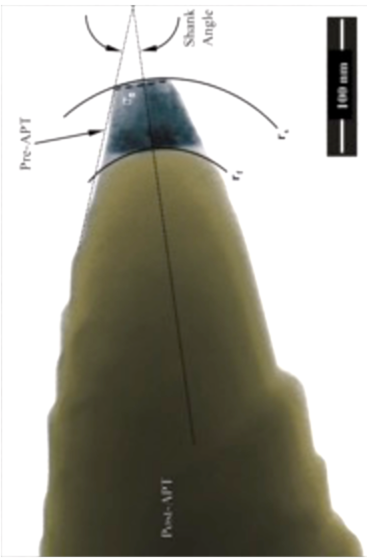
- 25 keV beam able to forward scatter on specimens 100-200 nm in thickness
  - Size of APT specimens
- Diffraction detector CL = 210 mm
  - Acquire DPs for multiple materials and d-spacings
- Able to capture diffraction patterns for several materials
  - Change DP magnification with digital camera

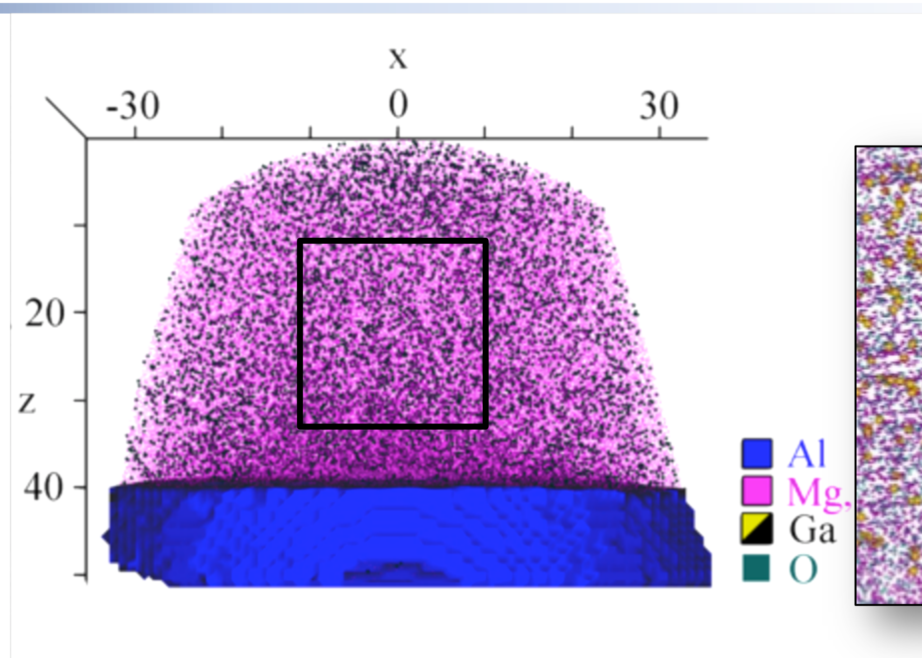
How to Fix Reconstructions

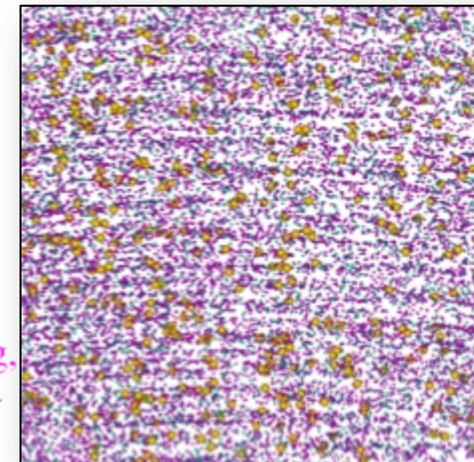
- Measure the specimen r_s, r_c, r_f, α
  - No continuity: $r_s/r_c > 1$
- Use known lattice spacing (from electron diffraction data)



Correlative APT/TEM



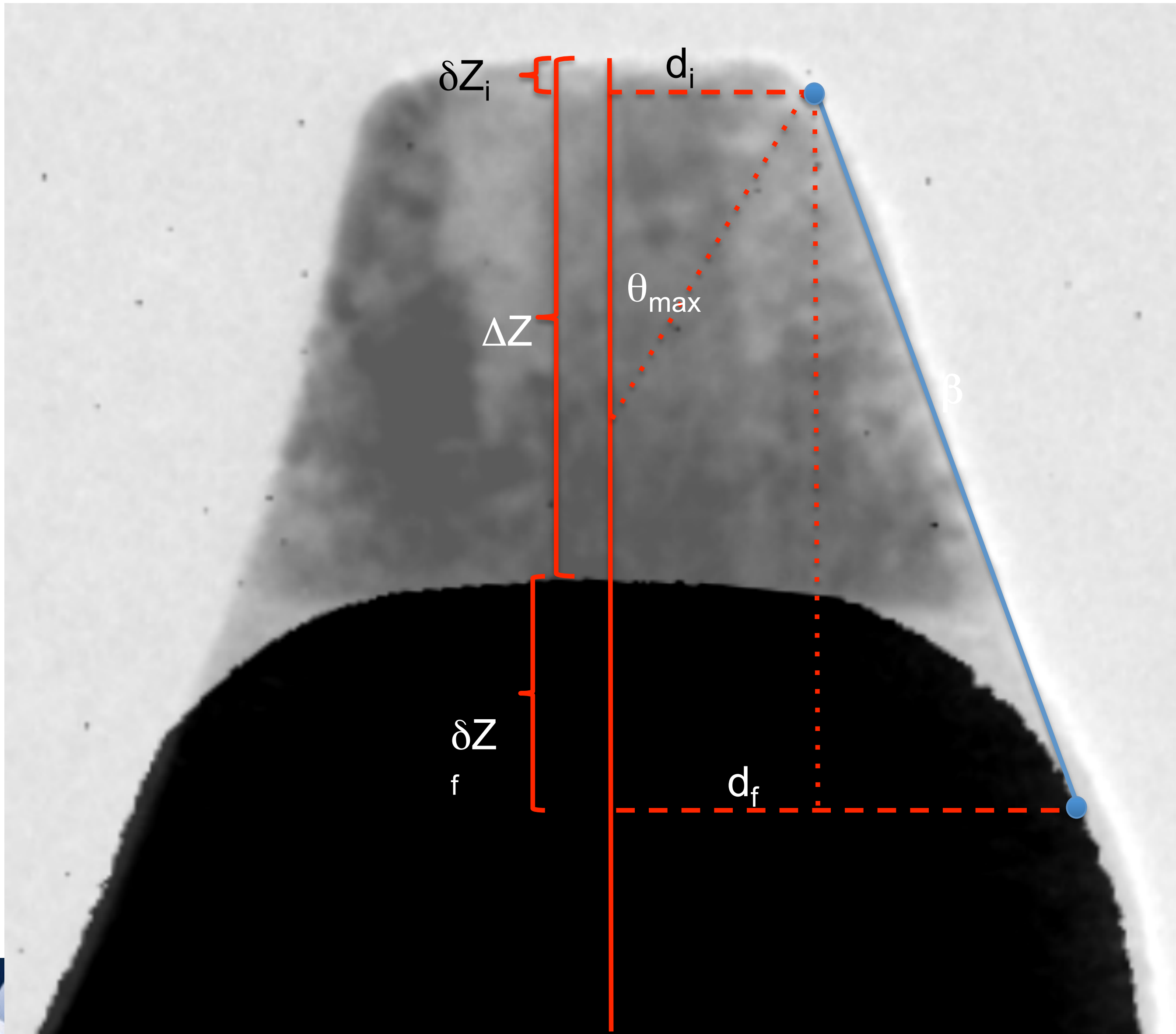




- Direct measurement of specimen geometry
  - Analyzed volume known
- Aid in adjusting reconstruction parameters

Kirchhofer, R.; Diercks, D. R.; Gorman, B. P.; "Near Atomic Scale Quantification of a Diffusive Phase Transformation in (Zn,Mg)O / Al_2O_3 using Dynamic Atom Probe Tomography", *Journal of Materials Research*, **30** (8), 1137-1147 (2015).

TEM Informed APT Reconstruction



- Use pre- and post-APT TEM / STEM imaging to quantify volume removed
- Electron diffraction allows for atomic positions to be quantified
- Place APT data points on lattice

Conclusions

- APT analyses can give atomic scale insight into material's properties
  - Not just metals anymore
  - Not always a straightforward reconstruction
- APT analyses allows for direct structure – property relationships in some materials
- Correlative STEM / APT can help inform traditional reconstructions
  - Future developments are aimed towards achieving true AST

THANK YOU!

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