Atom Probe Tomography and Secondary Ion Mass Spectrometry

Timothy P. Spila, Ph.D.
Sr. Research Scientist

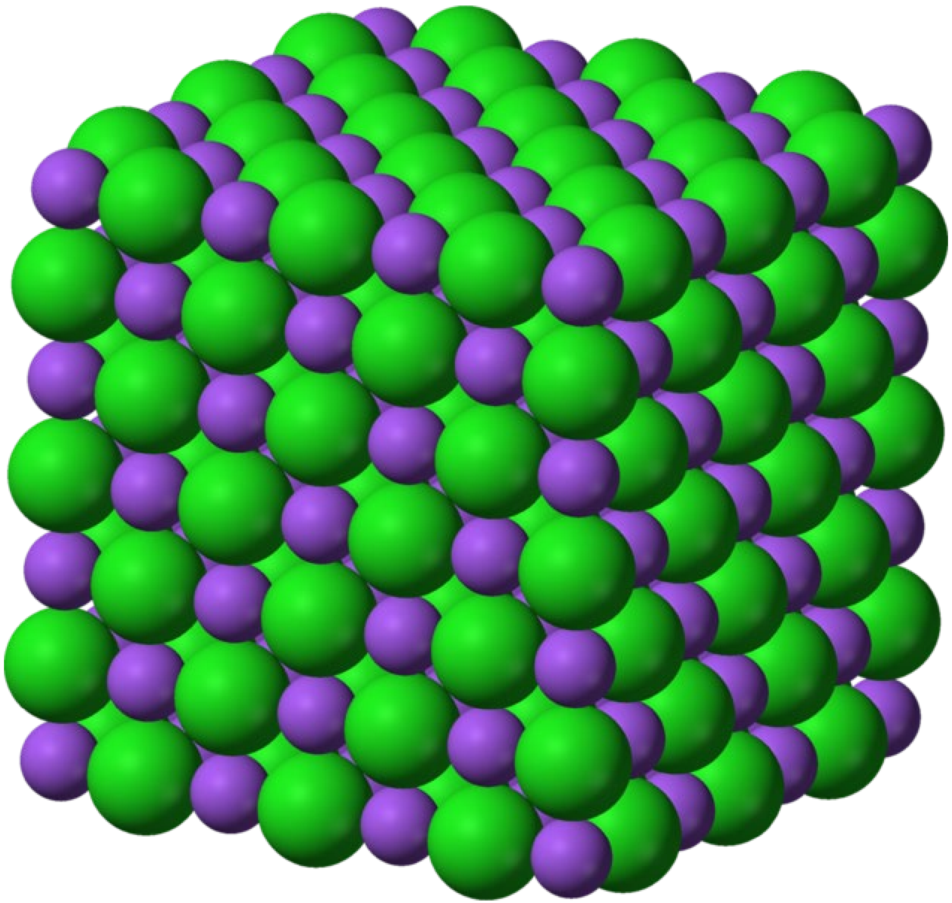
Materials Research Laboratory
MRL.Illinois.edu
University of Illinois at Urbana-Champaign

Atomistic Structure of Matter

Atom: derived from the ancient Greek word *atomos*, which means "uncuttable" (4th Century BC).

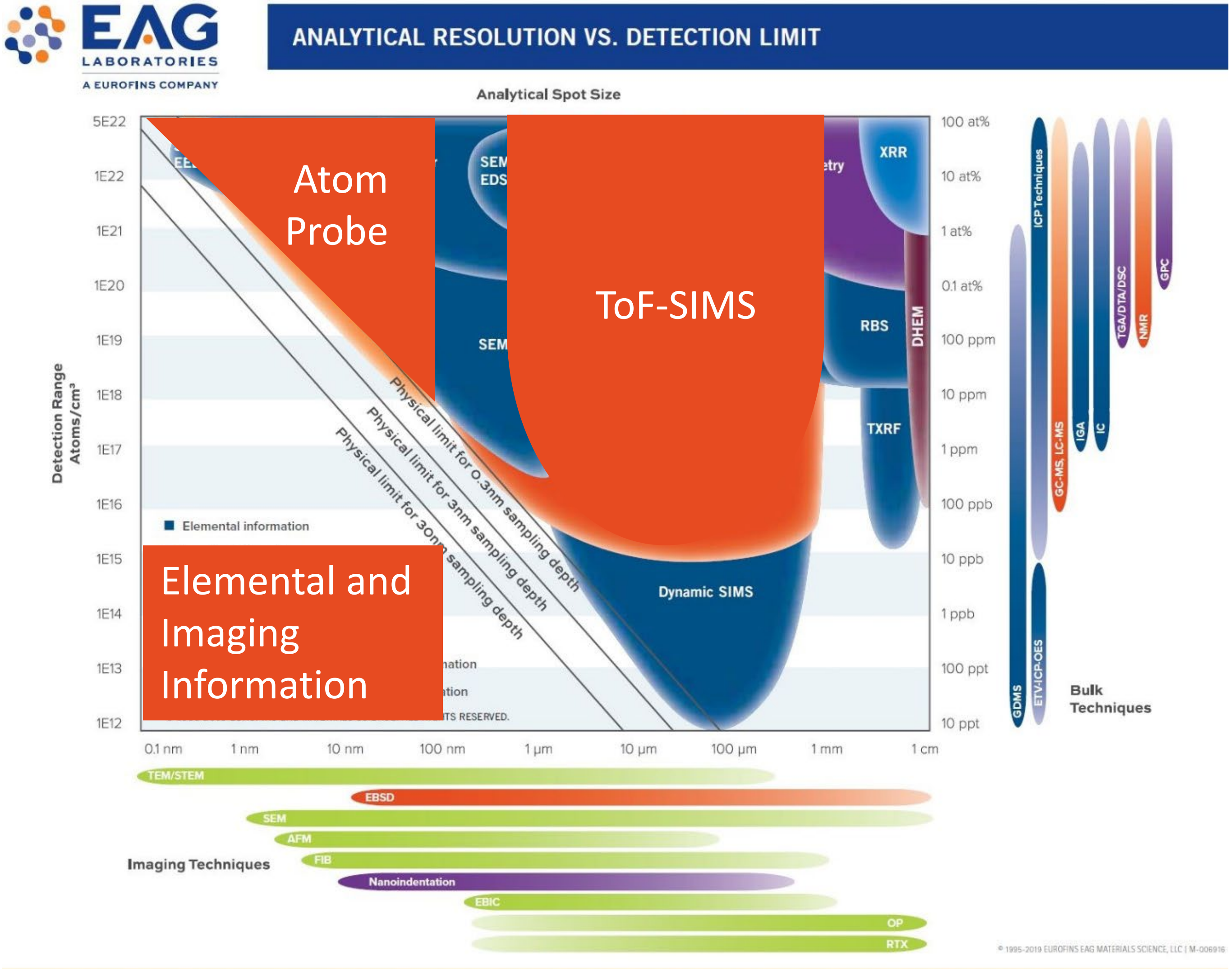
Modern view of the structure of an atom was derived by Rutherford (1913) and Bohr (1913).

Experiments on atomic nature of materials (packing of atoms in crystals) was deduced by Bragg and Bragg (1913).



https://commons.wikimedia.org/wiki/File:Sodium-chloride-3D-ionic.png

Adapted from D.J. Larson et al., Local Electrode APT, book 2013



EAG LABORATORIES
A EUROFINS COMPANY
ANALYTICAL RESOLUTION VS. DETECTION LIMIT
Analytical Spot Size
Detection Range Atoms/cm³
5E22
1E22
1E21
1E20
1E19
1E18
1E17
1E16
1E15
1E14
1E13
1E12
100 at%
10 at%
1 at%
0.1 at%
100 ppm
10 ppm
1 ppm
100 ppb
10 ppb
1 ppb
100 ppt
10 ppt
0.1 nm
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm
1 mm
1 cm
Atom Probe
ToF-SIMS
Elemental and Imaging Information
SEM EDS
SEM
XRR
RBS
DHEM
TXRF
Dynamic SIMS
Physical limit for 0.3nm sampling depth
Physical limit for 3nm sampling depth
Physical limit for 30nm sampling depth
Elemental information
ICP Techniques
GC-MS, LC-MS
IGA
IC
TGA/DTA/DSC
NMR
GPC
GDMS
ETV-ICP-OES
Bulk Techniques
TEM/STEM
EBSD
SEM
AFM
FIB
Nanoindentation
EBIC
OP
RTX
Imaging Techniques
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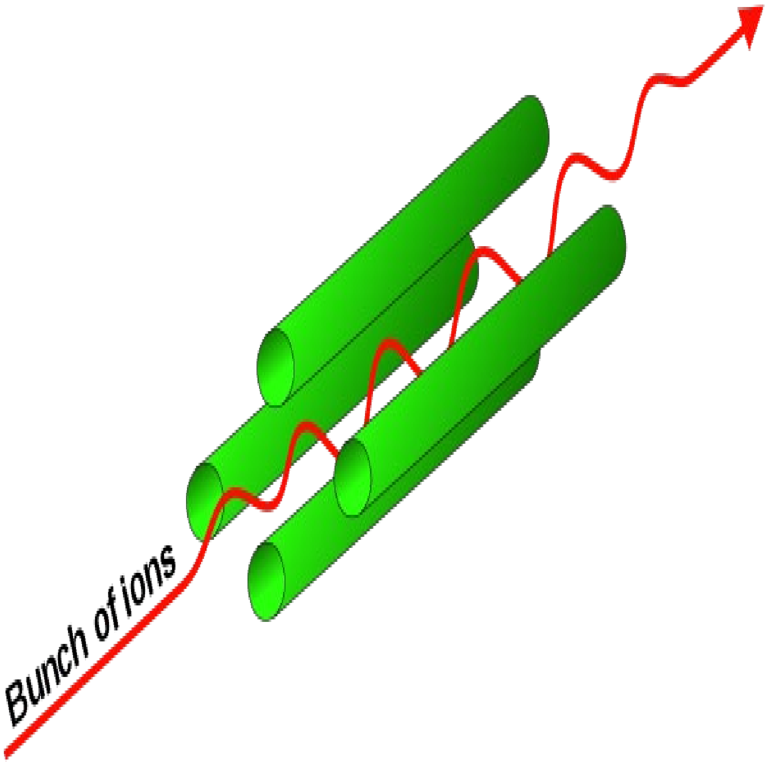
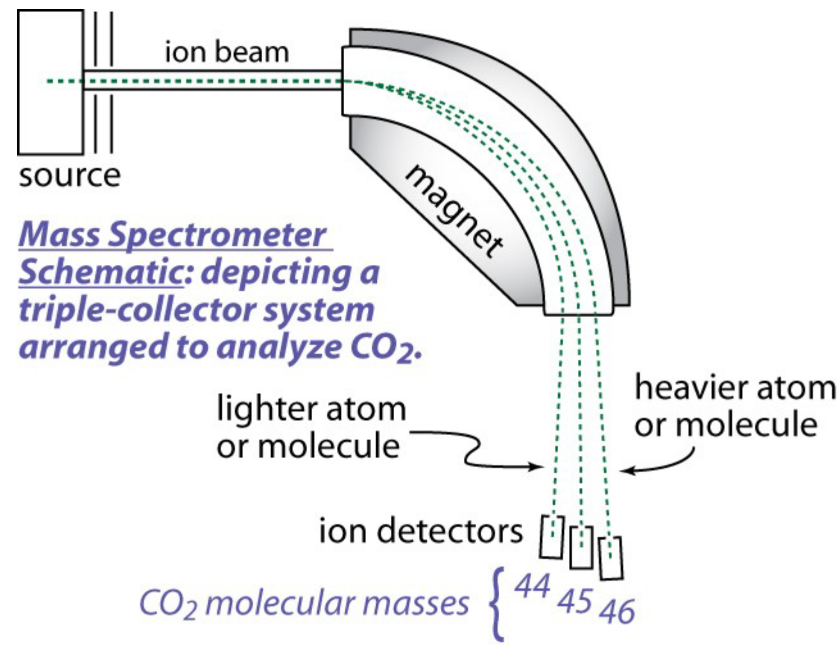
Quadrupole



Magnetic Sector



https://serc.carleton.edu/download/images/9094/massspecschematic.jpg

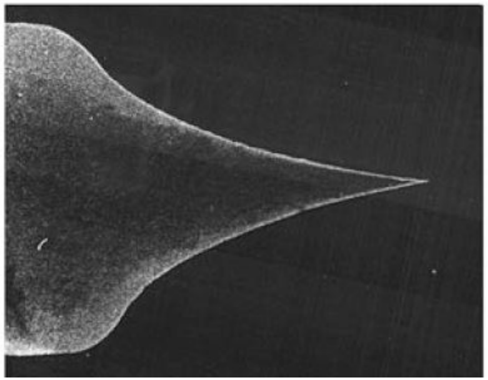
Time-of-Flight (ToF) Mass Spectrometry

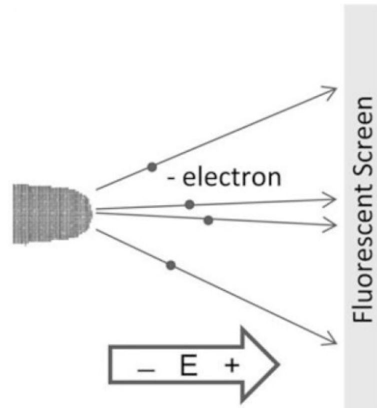
$$KE = eV_0 = \frac{1}{2}mv^2$$

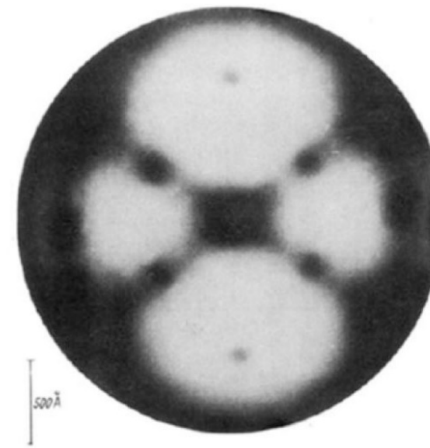
https://www.scienceskool.co.uk/tof-mass-spec.html

Field Electron Emission Microscope (FEEM)

Erwin Wilhelm Müller - 1935





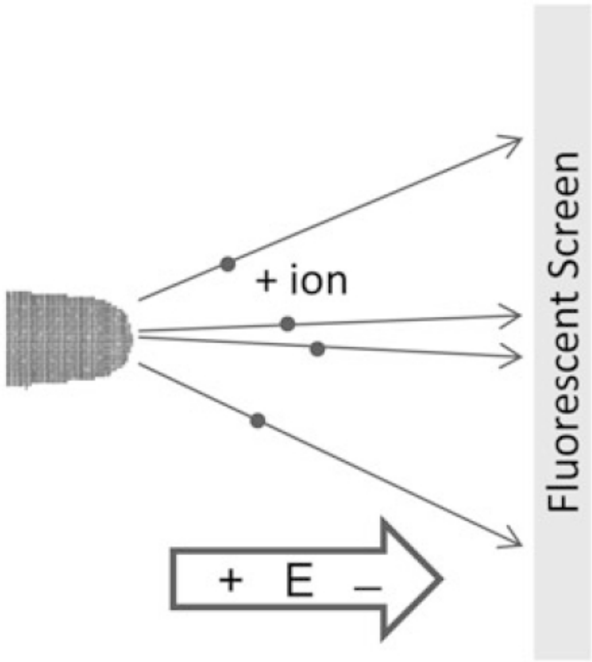


- 10^9 V/m needed to strip an electron from an atom
- Sharp point produces enhanced electric field
- 10,000 V with 1 um tip radius => 10^9 V/m

Adapted from D.J. Larson et al., Local Electrode APT, book 2013

Kanwar Bahadur and Erwin W. Müller - 1955

10^{-3} Pa He imaging gas, Tip cooled to 20-80K, Very sharp tip: 80 nm or less



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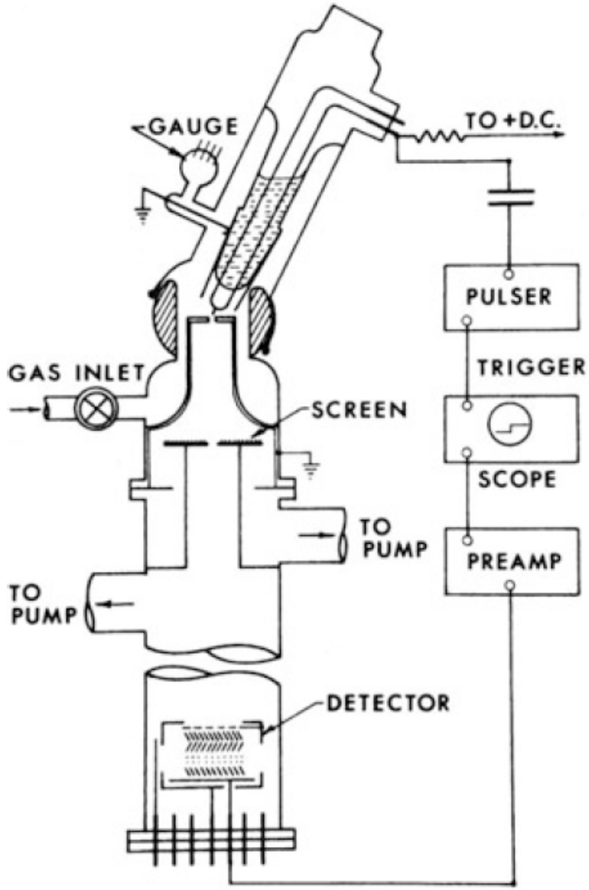
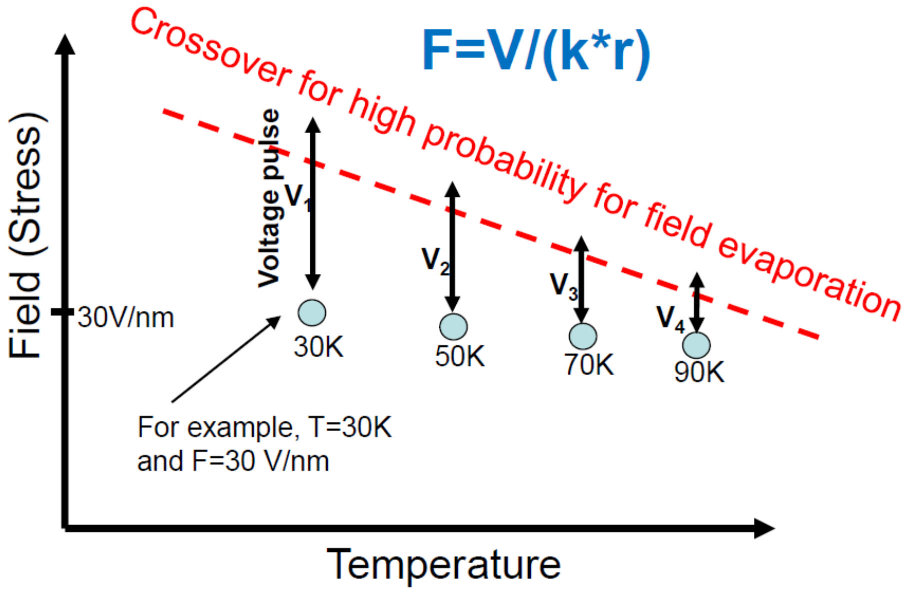
Adapted from D.J. Larson et al., Local Electrode APT, book 2013

Atom Probe Field Ion Microscope – Voltage Mode



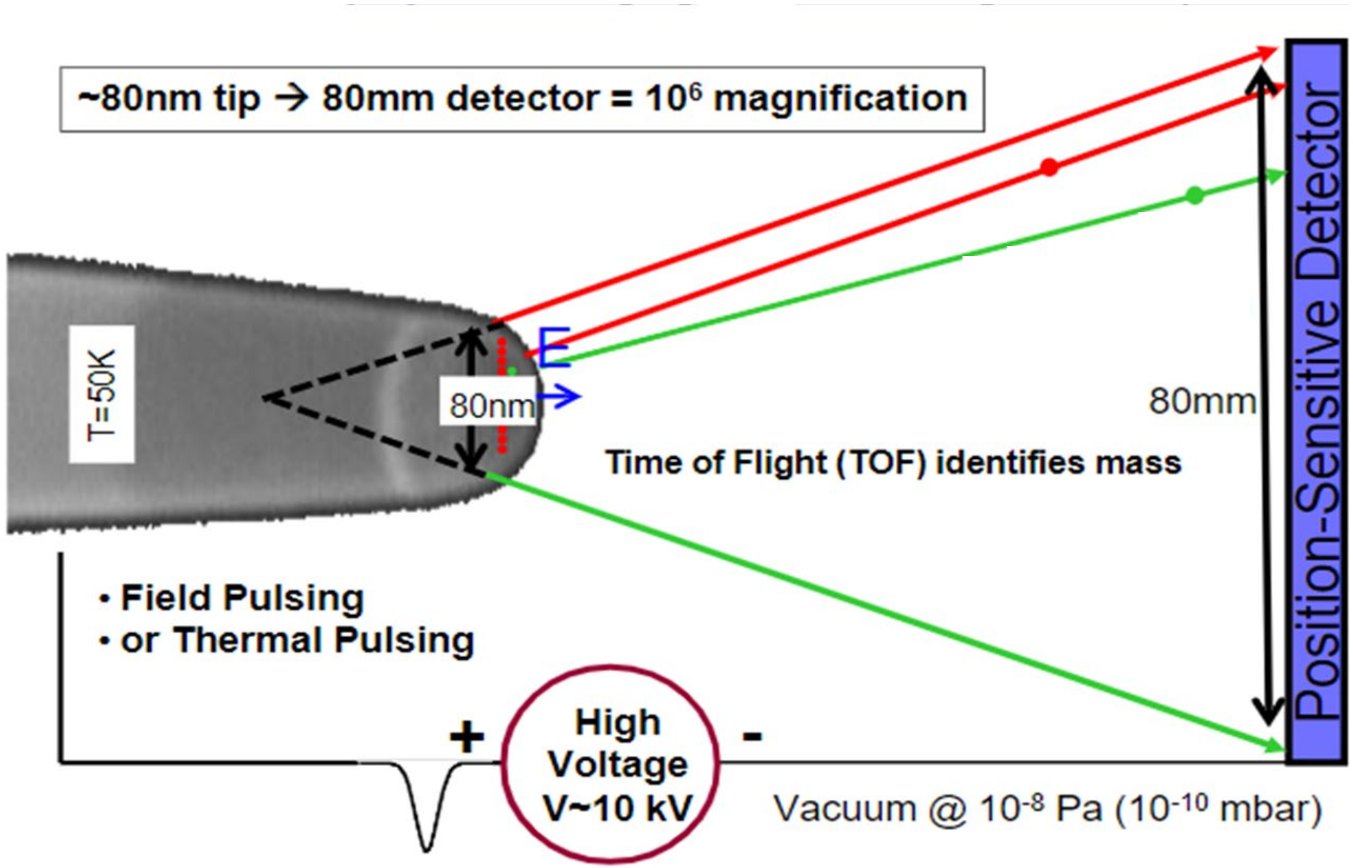
E. W. Müller, J. A. Panitz and S. B. McLane, *The atom-probe field ion microscope*. Rev. Sci. Instrum. **39** (1968) 83–86.

Field Evaporation



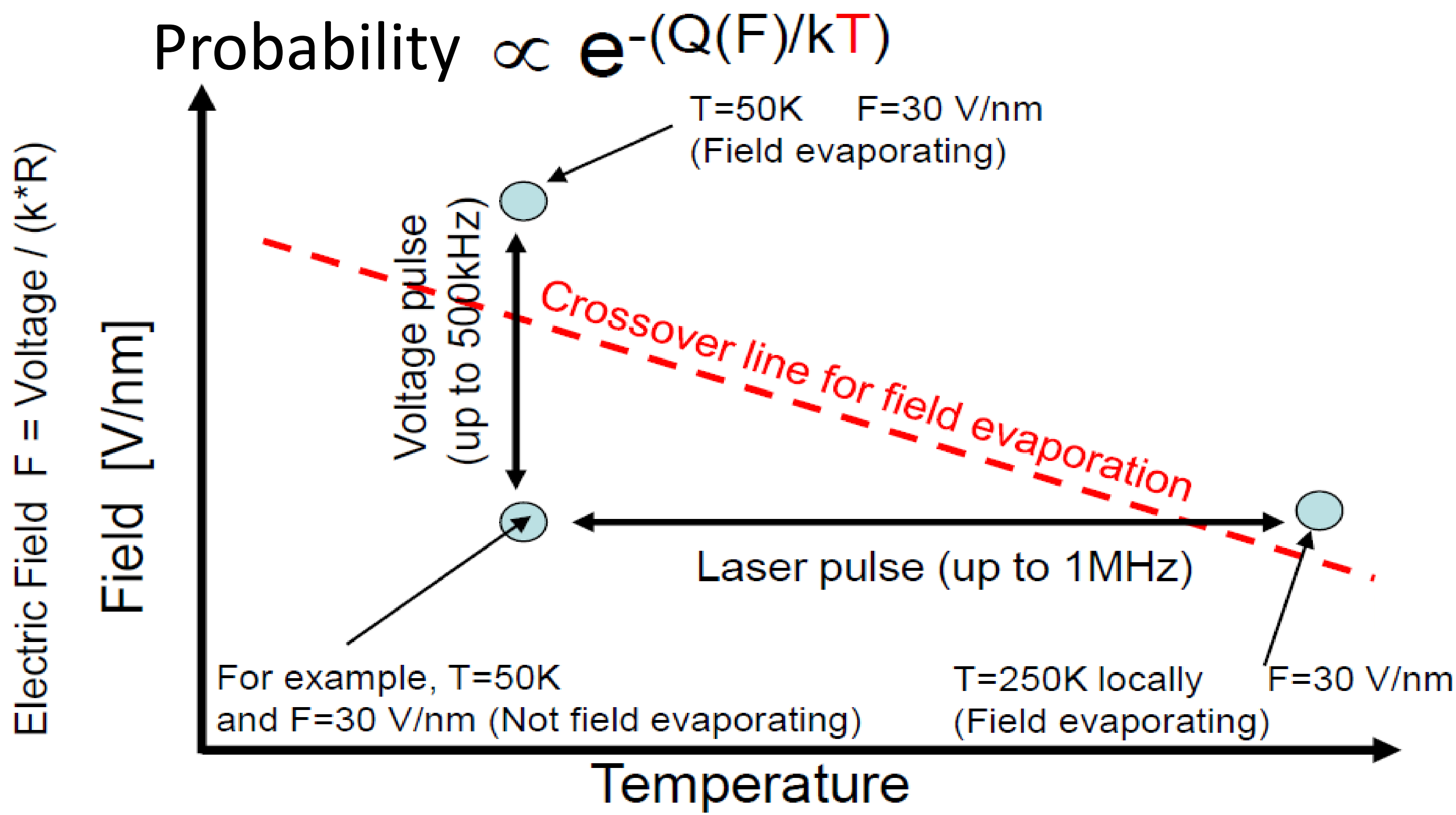
Adapted from: CAMECA, 2019

Atom Probe projection system



Adapted from: CAMECA, 2019

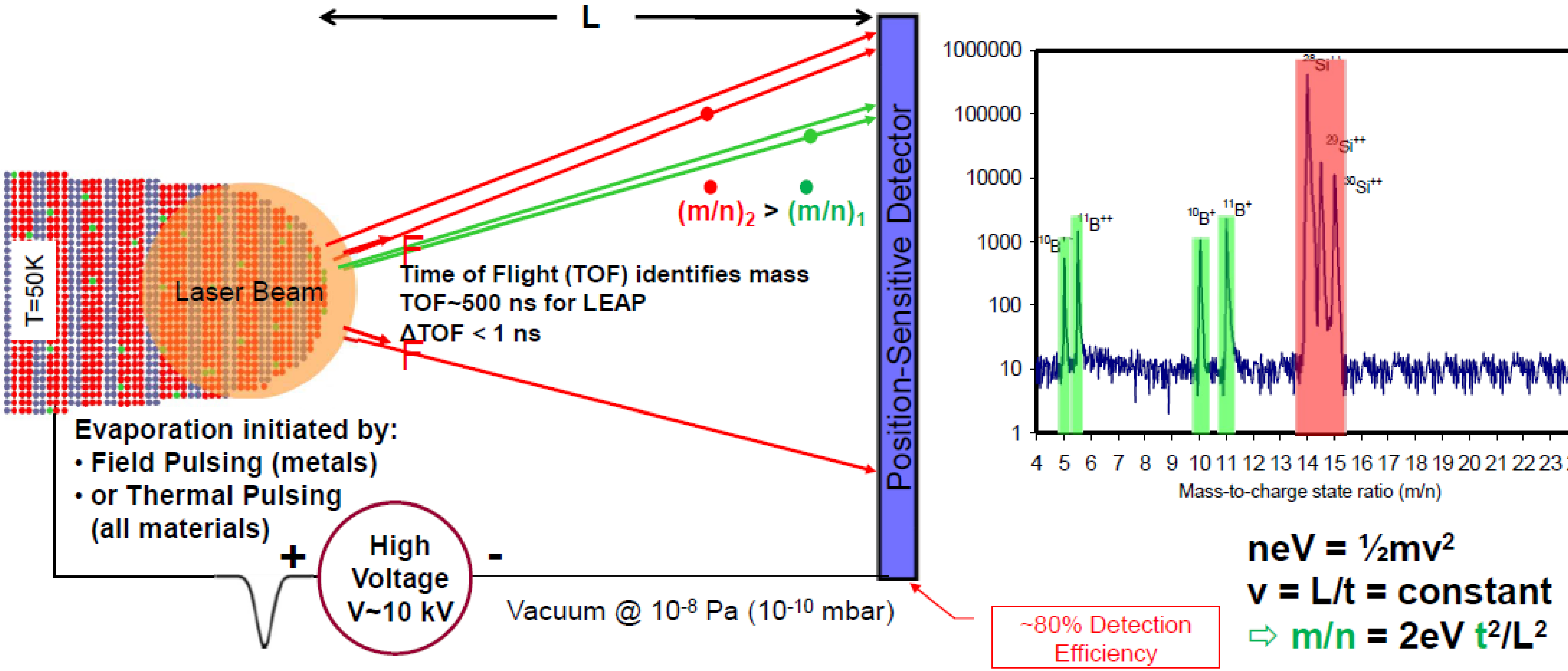
Atom Probe Ion Emission



Adapted from: CAMECA, 2019

Description of Atom-Probe Operation

Atom Probe = projection imaging with time-of-flight mass spectrometer



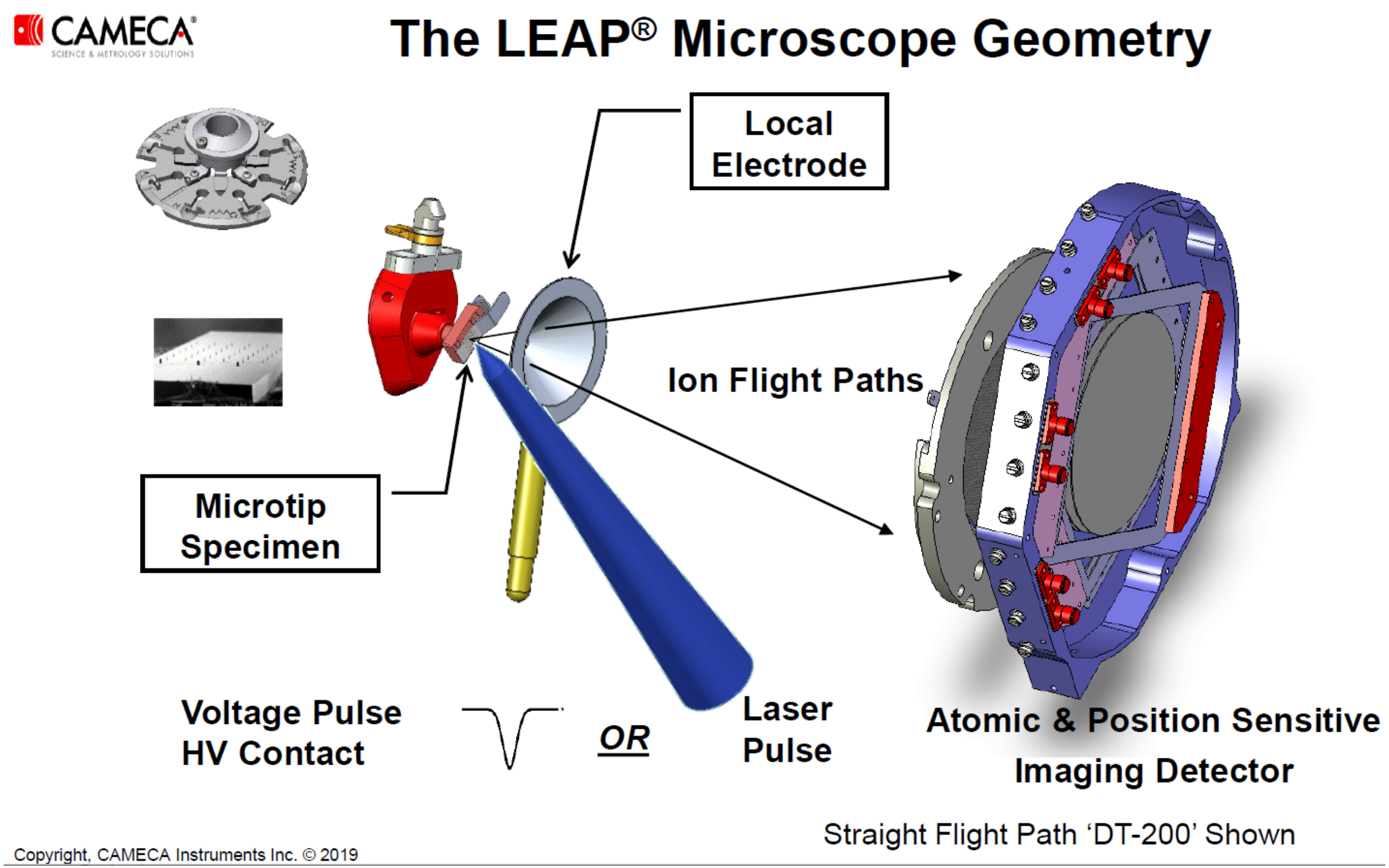
$neV = \frac{1}{2}mv^2$

$v = L/t = \text{constant}$

$\Rightarrow m/n = 2eV\, t^2/L^2$

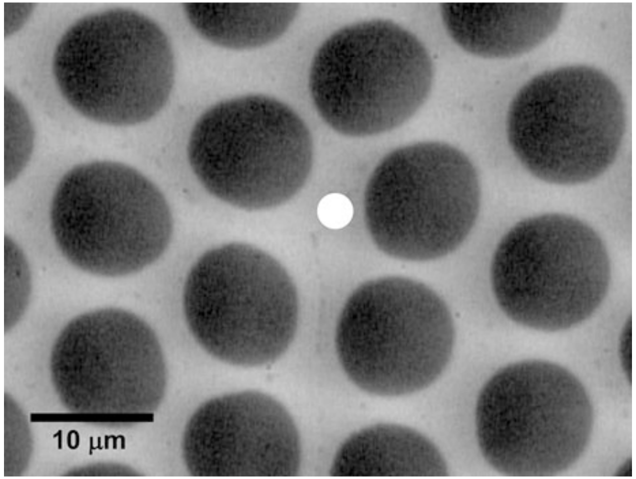
Adapted from: R.M. Ulfig (CAMECA, 2020)

Local Electrode Atom Probe

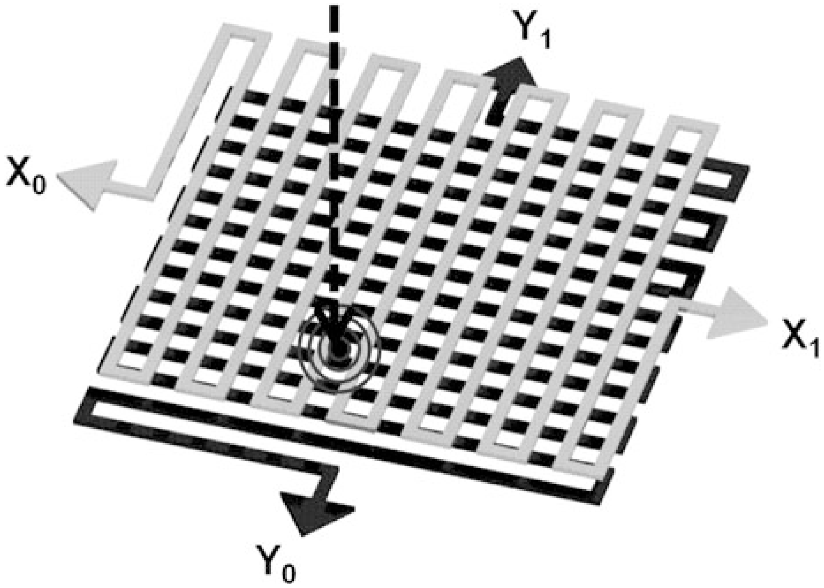


Position Sensitive Detector

Microchannel Plate (MCP)

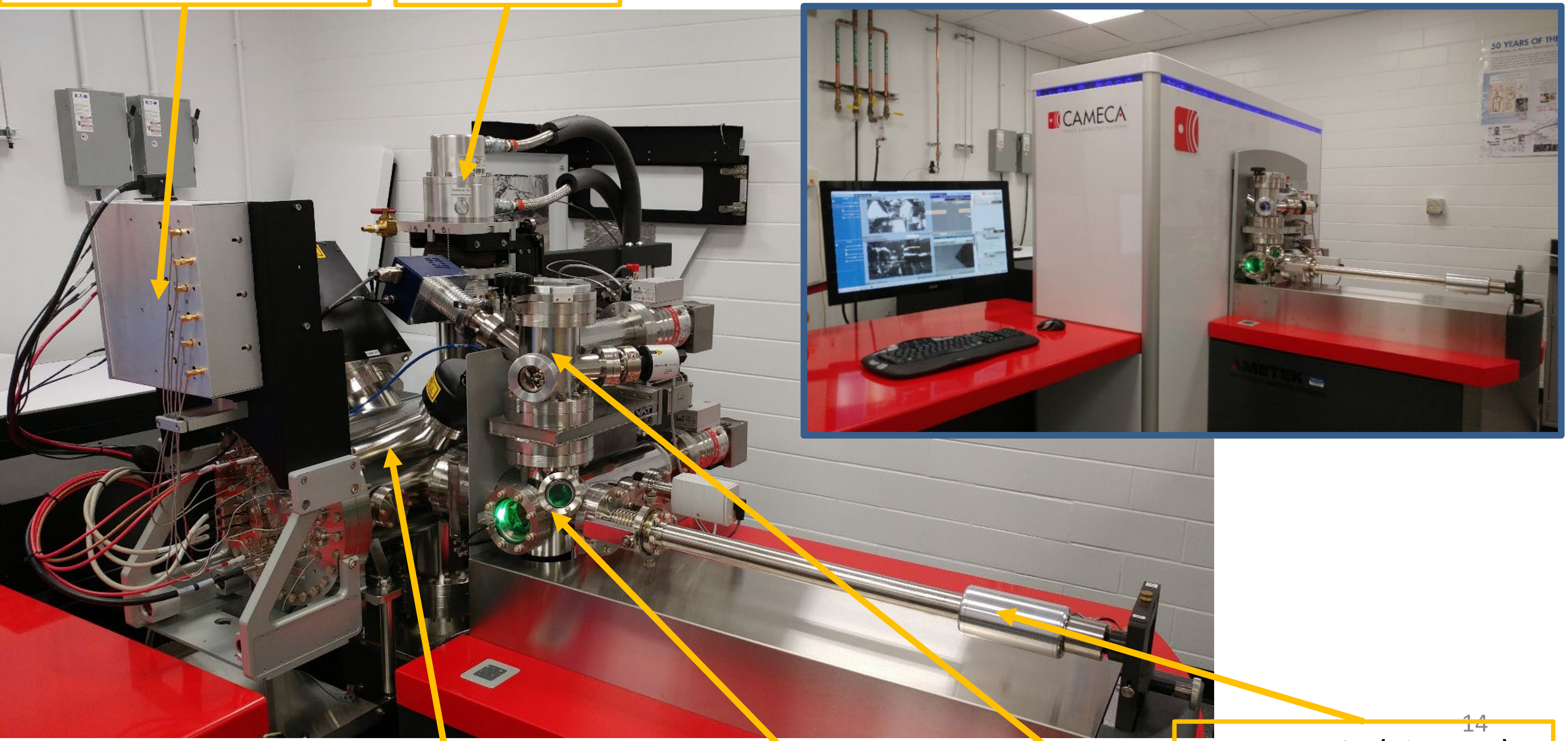


Delay Line Anode (DLA)



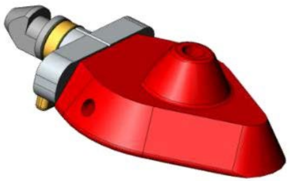
Adapted from D.J. Larson et al., Local Electrode APT, book 2013

LEAP 5000 XS / CAMECA (AMETEK)

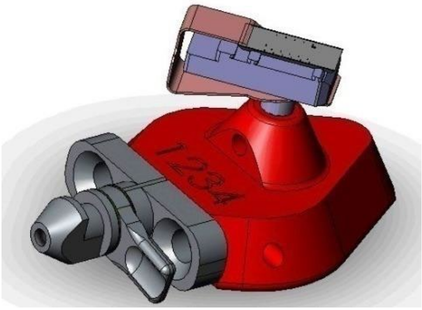


CAMECA LEAP Parts

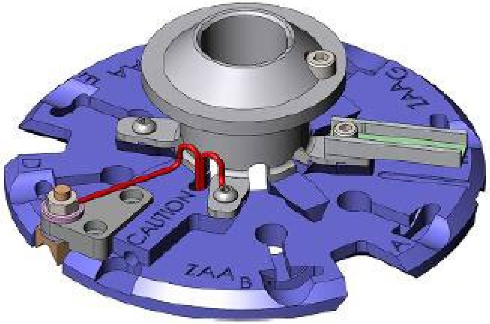
Sample Puck



Puck with Sample Coupon

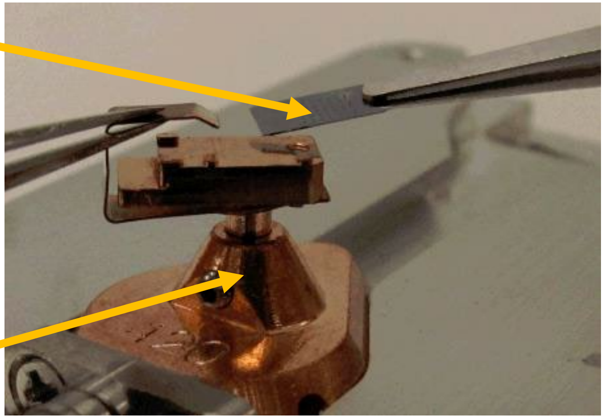


Sample or Local Electrode Storage Carousel

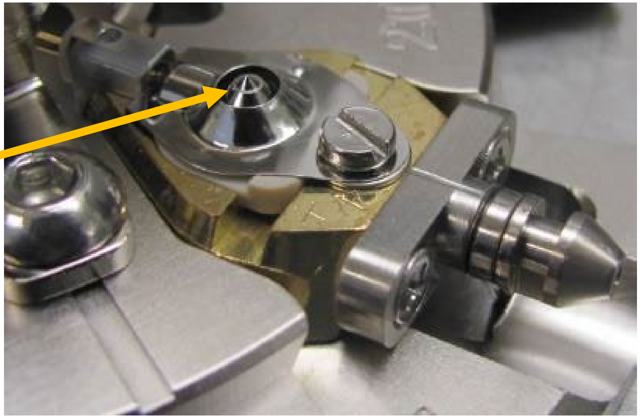


Coupon

Sample Puck

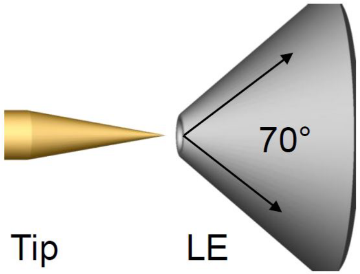


Local Electrode

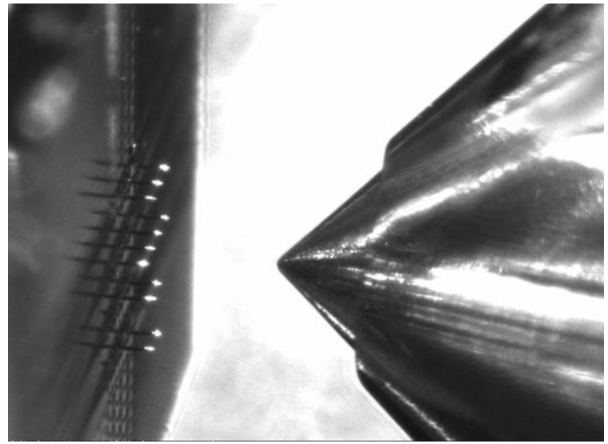


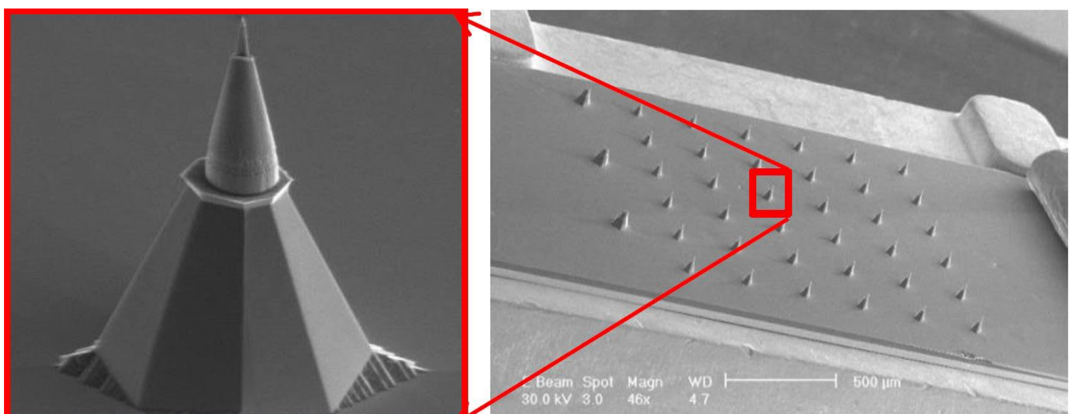
https://www.atomprobe.com/keyaptlinks/options-accessories-consumables

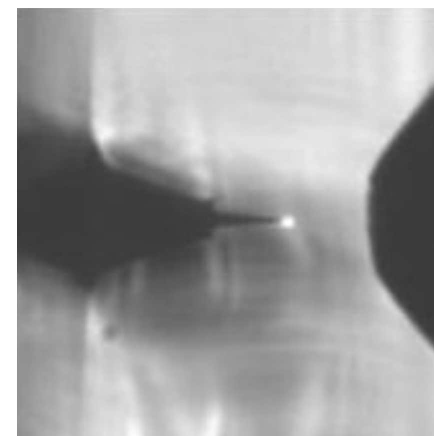
Local Electrode Atom Probe



Model Parameters
- 50 nm tip radius
- 10° shank angle
- 50 micron wire
- 1 mm long
- Specimen-to-local-electrode distance is that required to permit a 70° geometric FOV

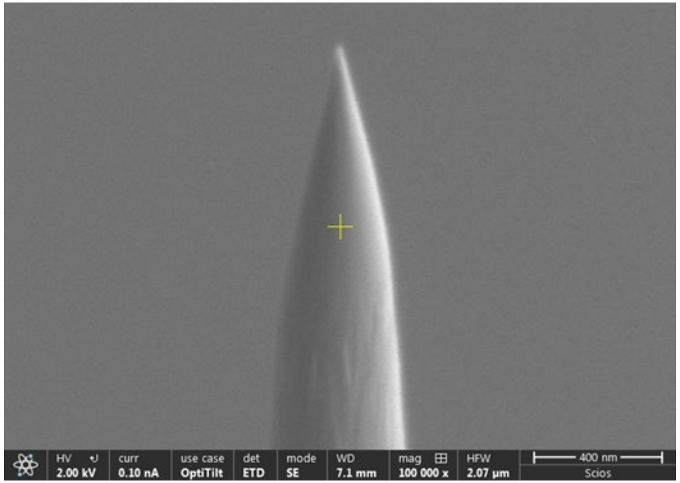






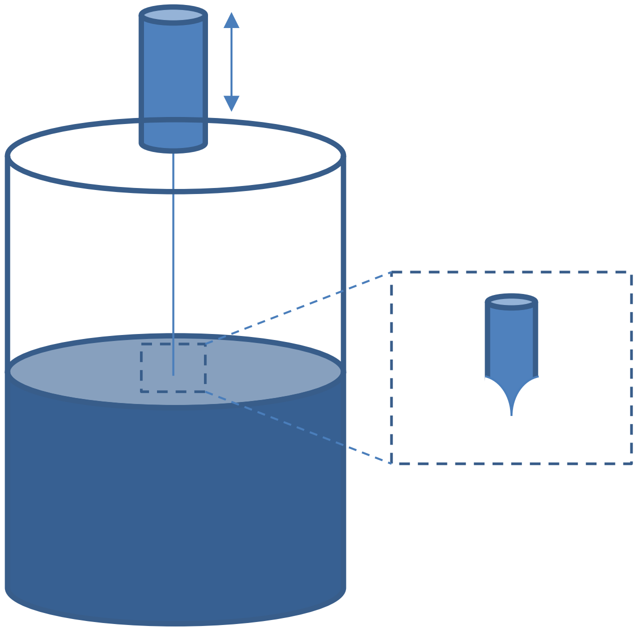
Sample Preparation

- Requirements for APT samples
  - Specimens must be sharp with a radius of curvature of ~100 nm or less
  - Feature of interest within 50 to 150 nm of specimen apex

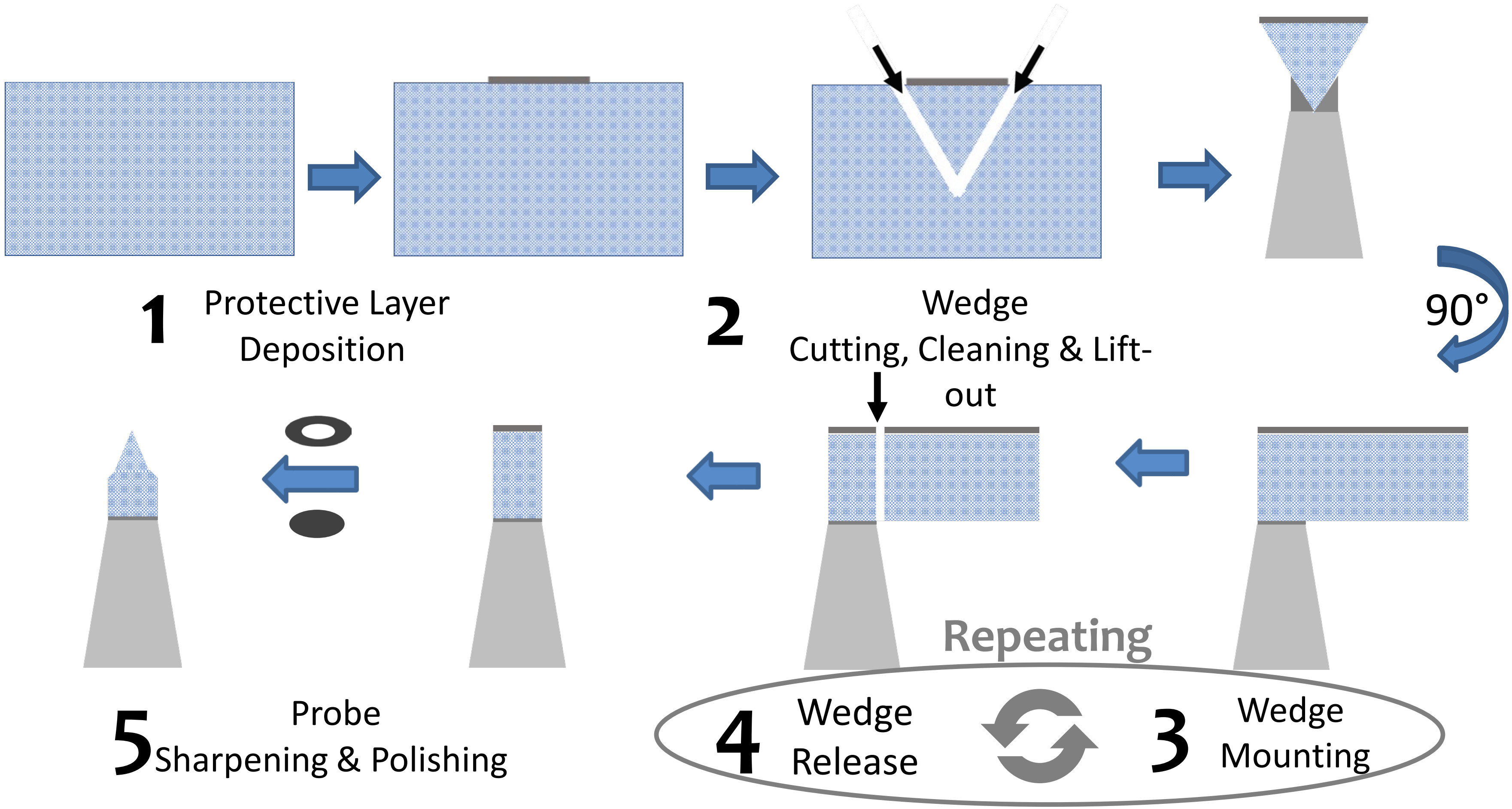


Electropolishing

- Electrochemical process where material is removed leaving a sharp tip
- Polishing done using meniscus of electrolyte
- Electrolyte chosen based upon material being polished



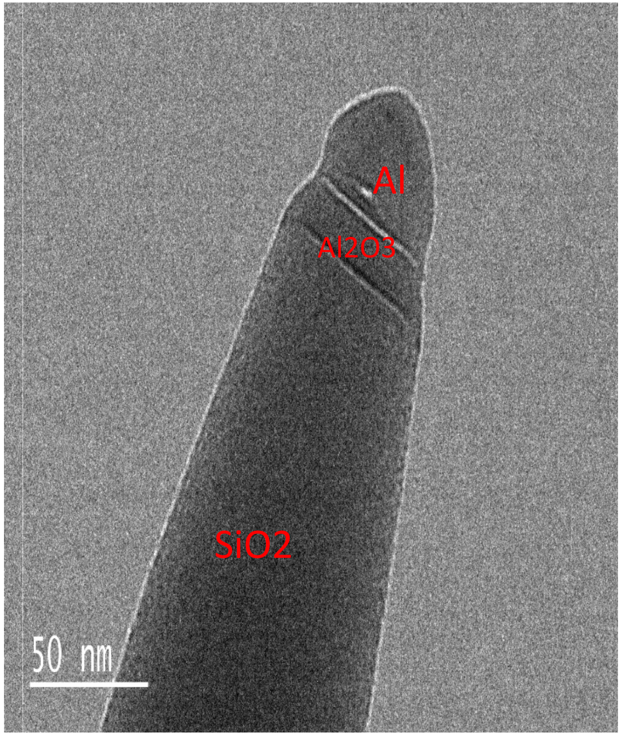
Schematic of APT-tip FIB Preparation



Analysis of Dielectric Layer of Quantum Dot Devices

APT analysis of semiconductor quantum dot devices to investigate the effects of impurities and roughness at the interfaces around the Al_2O_3 dielectric layer.

Goal: To determine the relationship between transport properties of the quantum dot and interface imperfections.



Sputtered Al (100 nm)

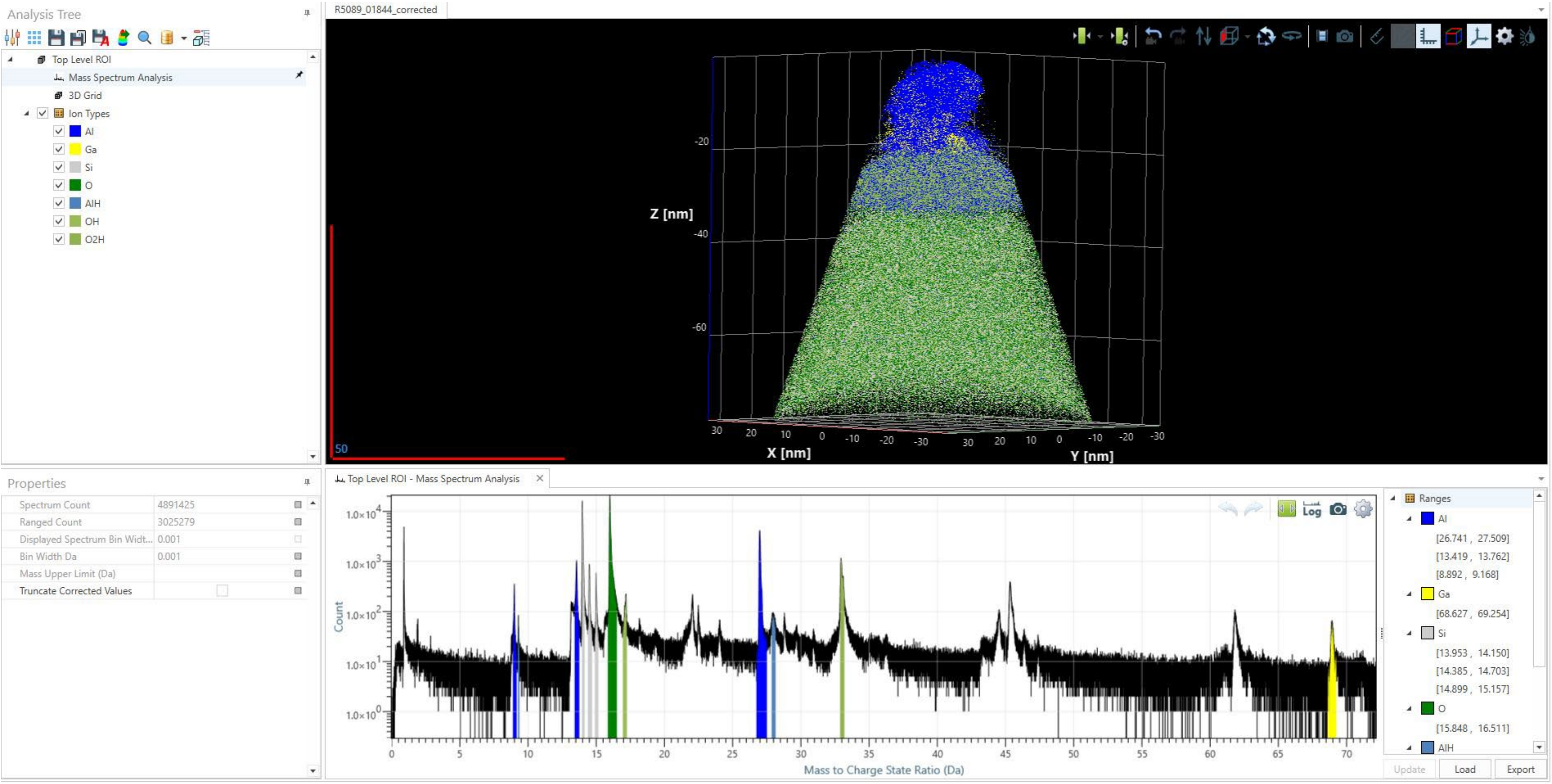
ALD Al_2O_3 (10-15 nm)

SiO_2 (1000 nm)

Si substrate

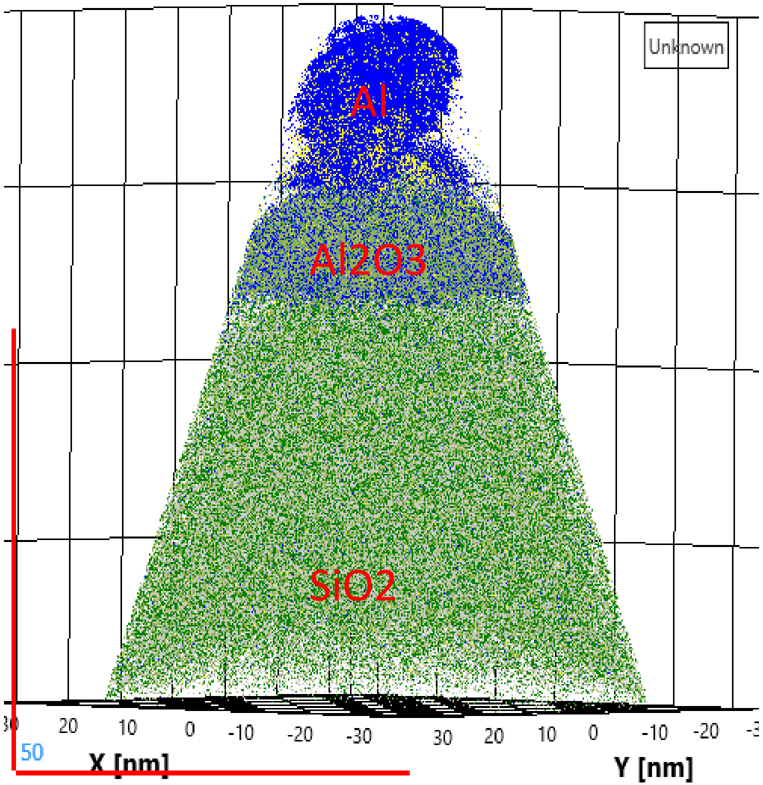
Courtesy: J. Huang and N. Mason, University of Illinois

Analysis of Dielectric Layer of Quantum Dot Devices

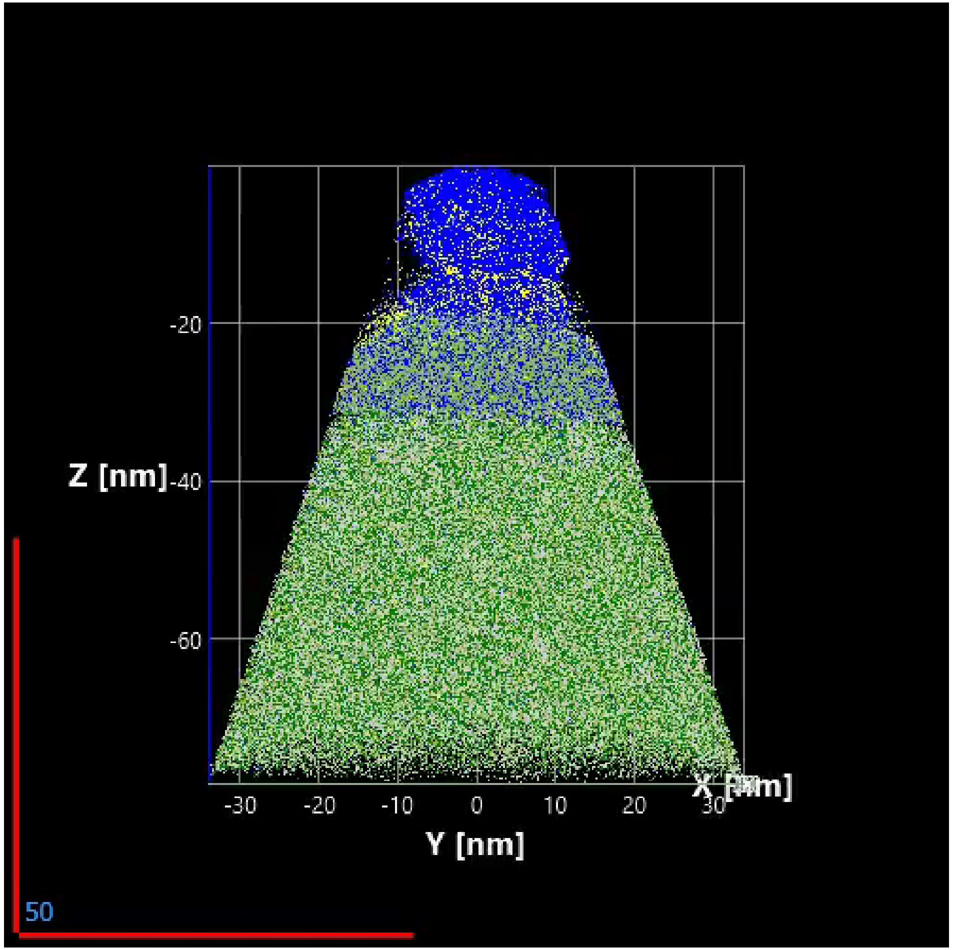


APT Reconstruction: Al in blue, O in green, Si in gray, Ga in yellow.

Analysis of Dielectric Layer of Quantum Dot Devices

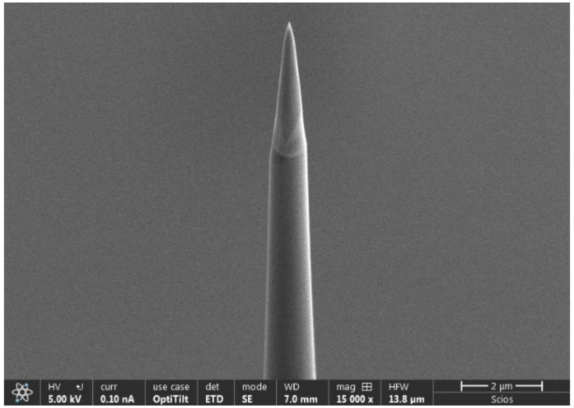


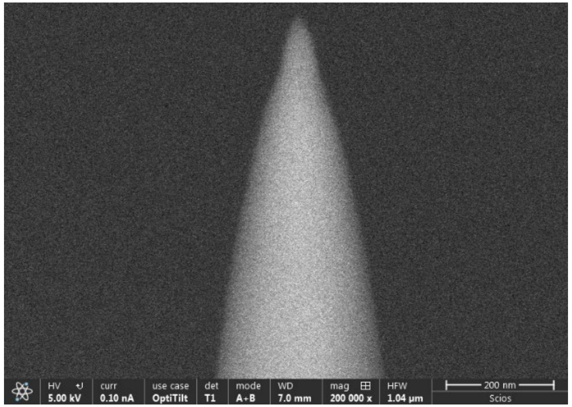
Al in blue, O in green, Si in gray



APT Analysis of Proton Irradiated Mixed Phase 308L Stainless Steel

- FIB of needle specimen
- Approximately 80M hits in laser pulse mode
- Standard analysis using IVAS:
  - 1-D concentration profile
  - Cluster Analysis
  - Nearest Neighbor Analysis
    - Local Concentration
    - Cluster composition analysis for two separate regions
  - Cluster Size Analysis
  - Cluster Composition Analysis
  - Iso-surfaces
    - Si/Ni
  - Frequency Distribution Analysis





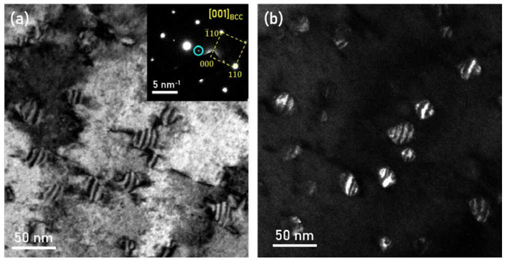
SEM Images

Samples courtesy: B. Heuser, University of Illinois
FIB preparation: H. Zhou, University of Illinois
APT measurement: W. Swiech, University of Illinois

APT Analysis of Proton Irradiated Mixed Phase 308L Stainless Steel

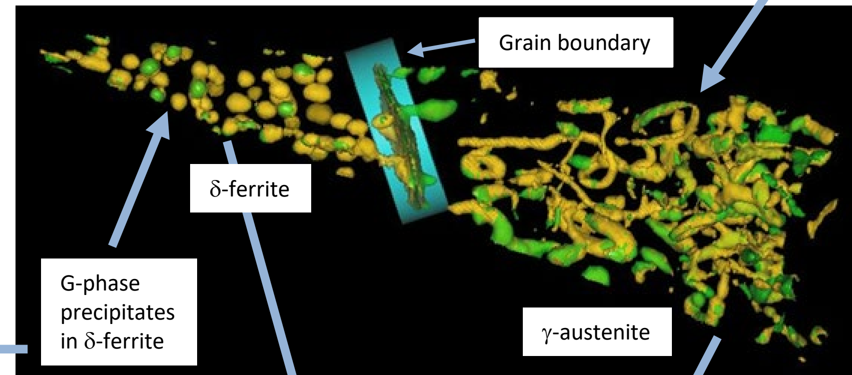
Mixed phase: δ-ferrite and γ-austenite

TEM dark field of G-phase particles



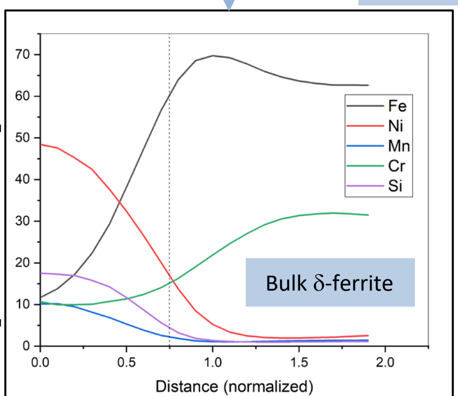
2:10% Si:Ni iso-surface

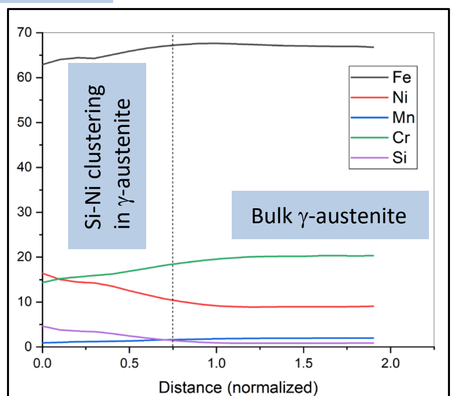
Si-Ni clustering in γ-austenite



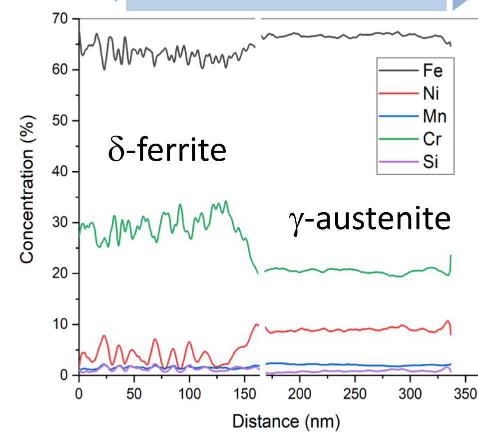
G-phase

Cluster Analysis





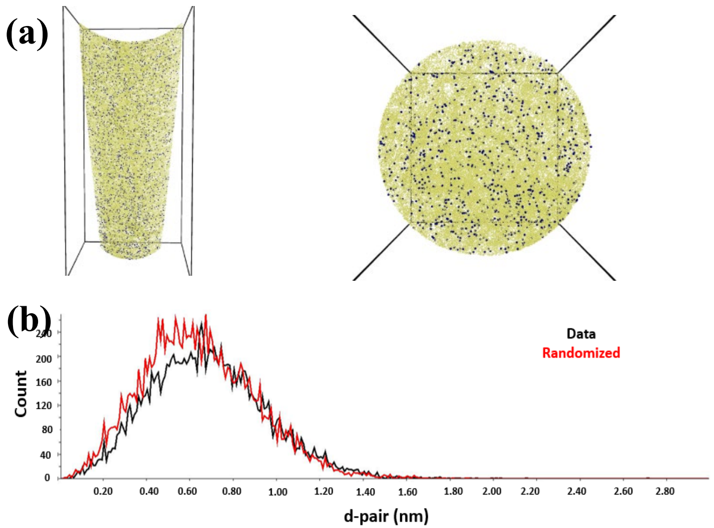
1-D composition profiles



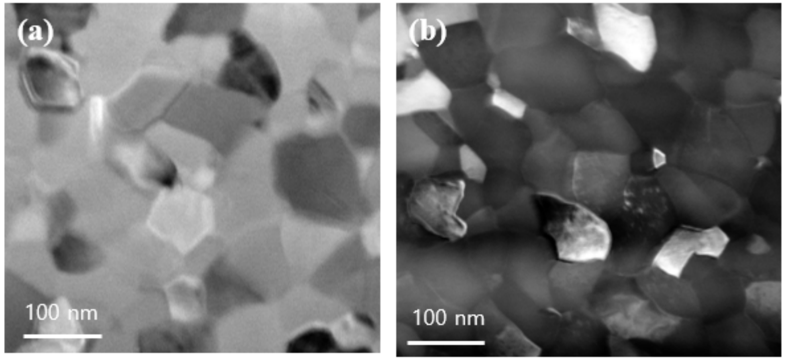
Courtesy: B. Heuser, University of Illinois

APT analysis

Atom	Al	Sc	Ga	O	C	Pt	H
Composition (at.%)	98.17	1.37	0.1	0.01	0.01	0.04	0.32



STEM analysis

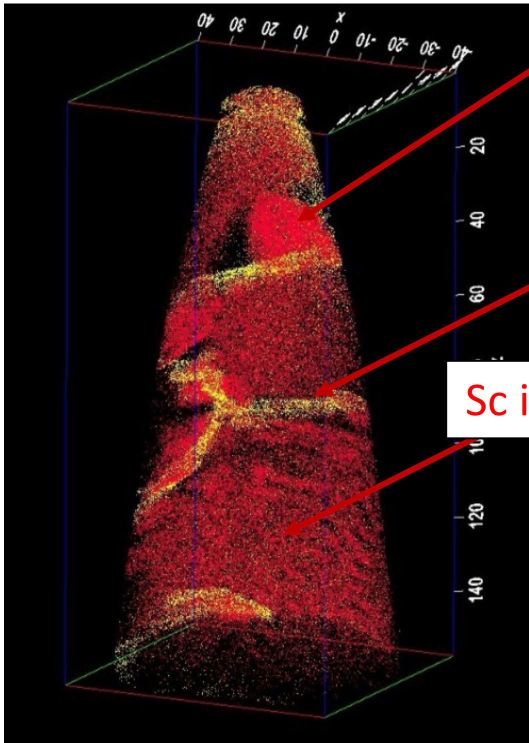


As-grown

Annealed for 1 hour at 150 °C

Courtesy: S. Jana, S. Kim, R.S. Averback, P. Bellon, University of Illinois

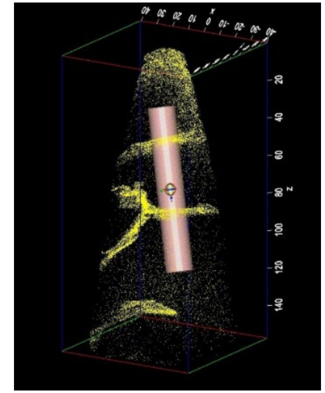
Grain Boundary Depletion: Annealing at 180 °C



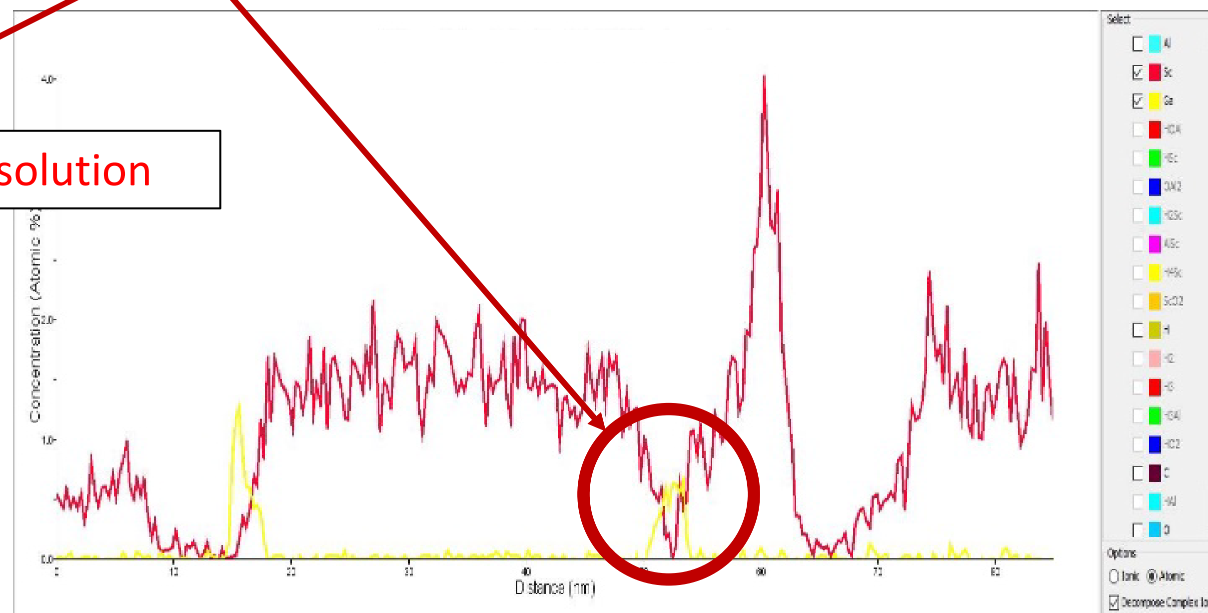
Sc-rich precipitate

Sc-depleted GB

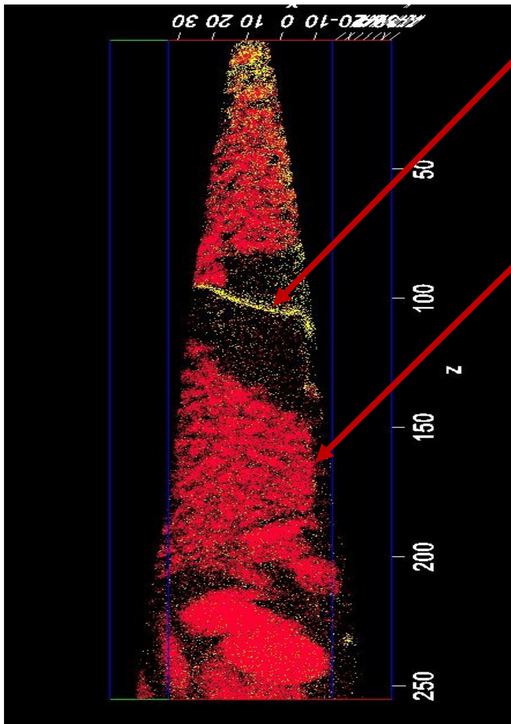
Sc in solution



1D concentration profile along cylinder

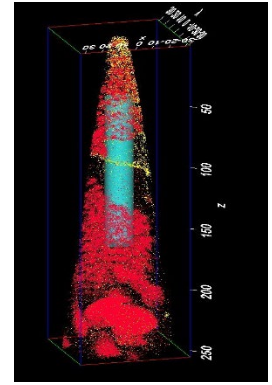


Grain Boundary Depletion: Annealing at 300 °C

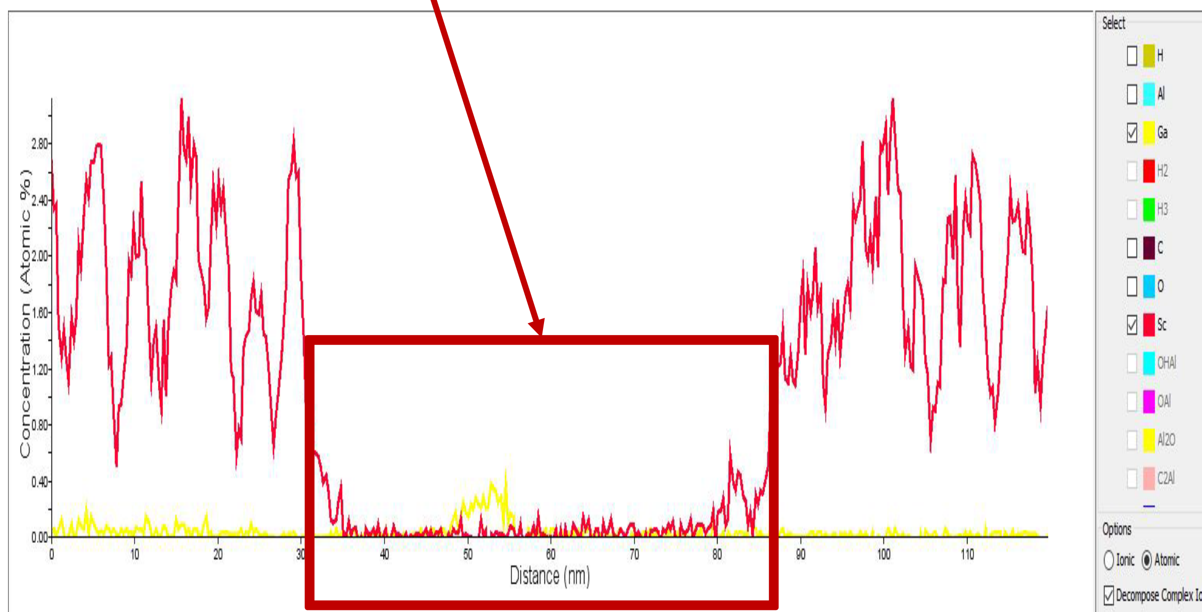


Sc-depleted GB

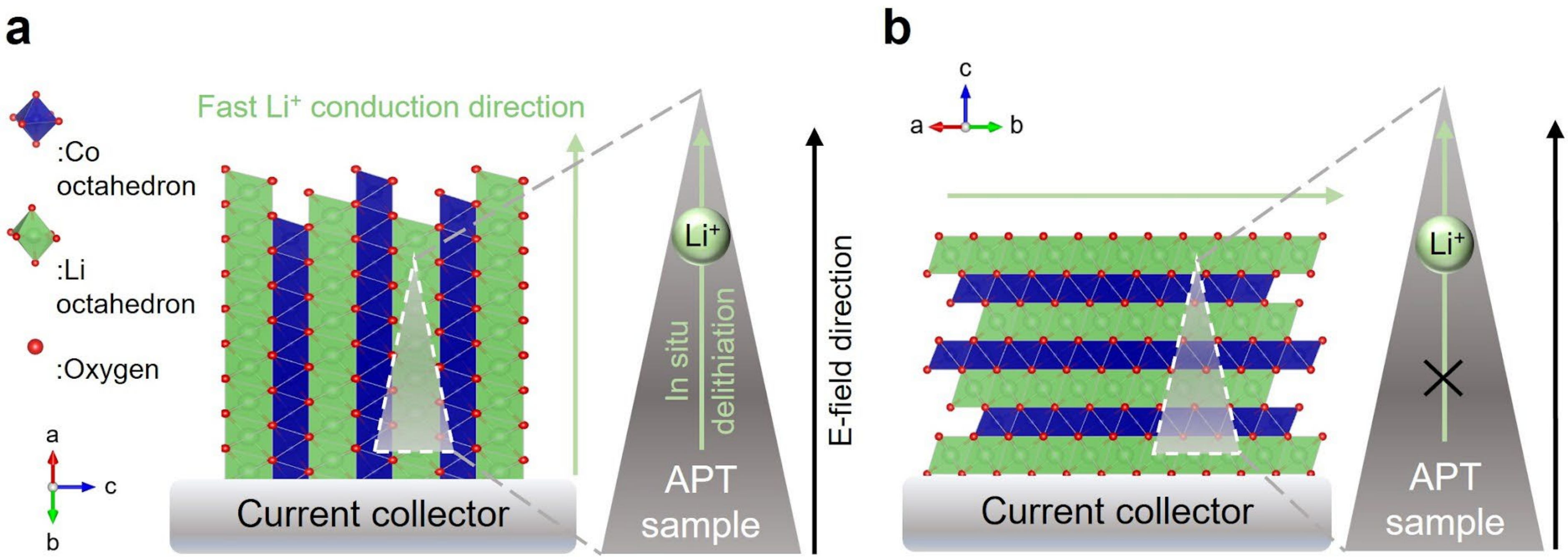
Sc-rich nanoclusters



1D concentration profile along cylinder

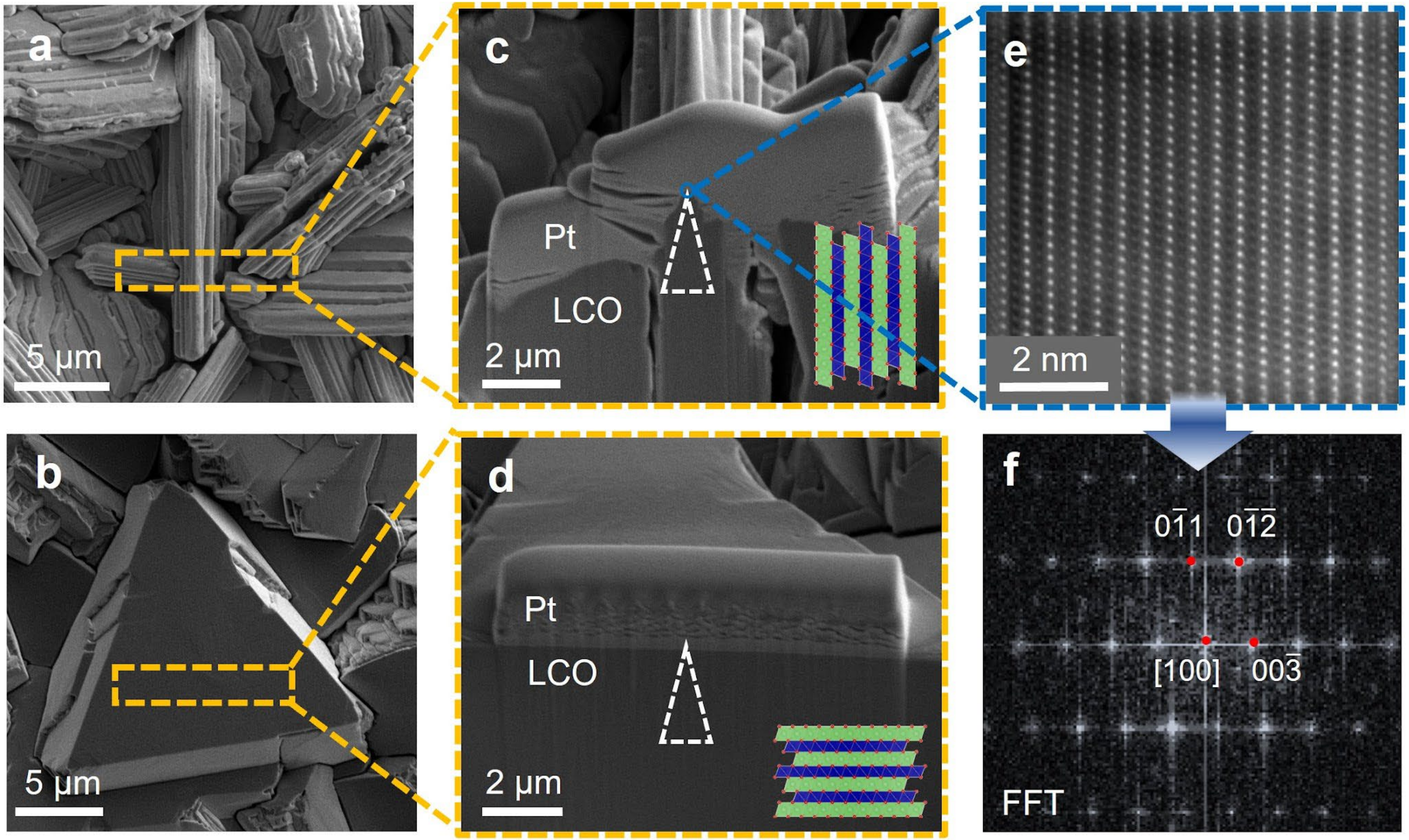


Li-ion battery cathode

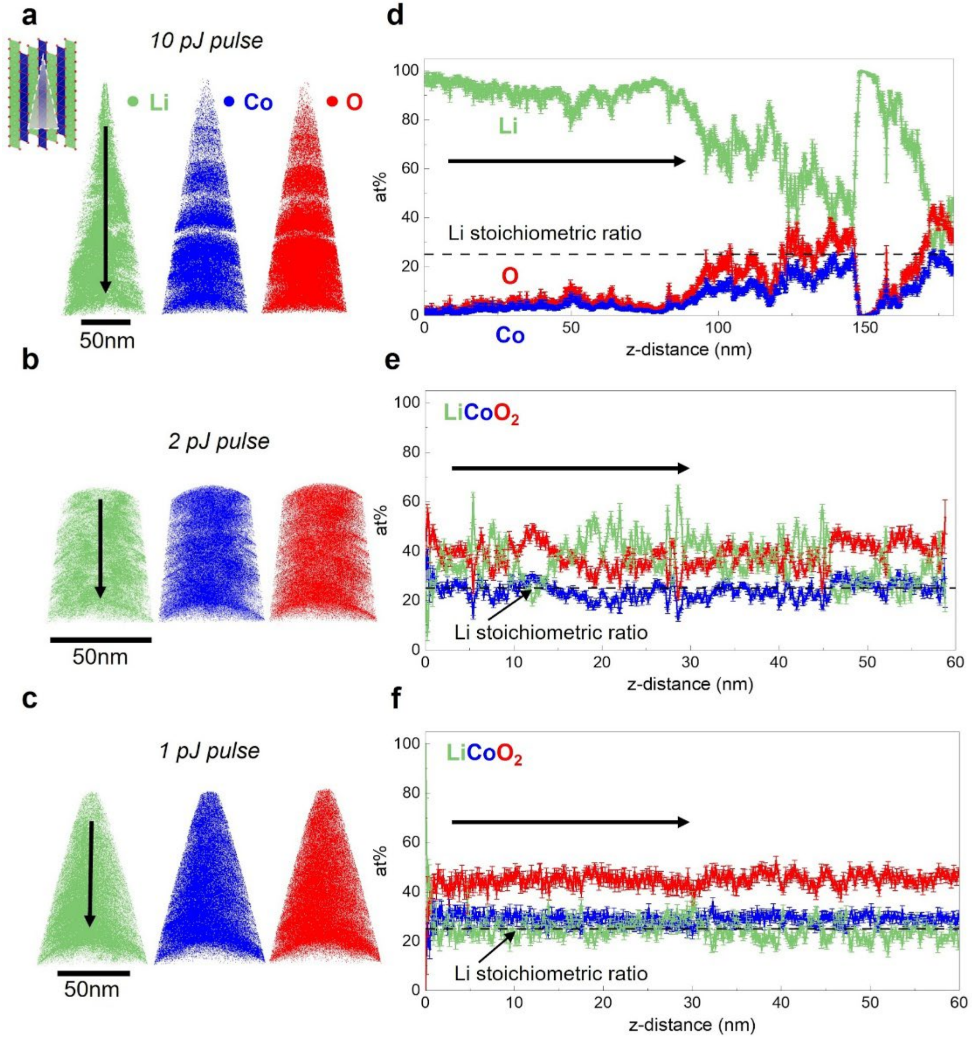


J.W. Lin, D. Xie, H. Jeong, A.J. Littlefield, T. Spila, B. Zahiri, and P.V. Braun. ***J. Mater. Chem. A***, 2025,**13**, 10910-10919.

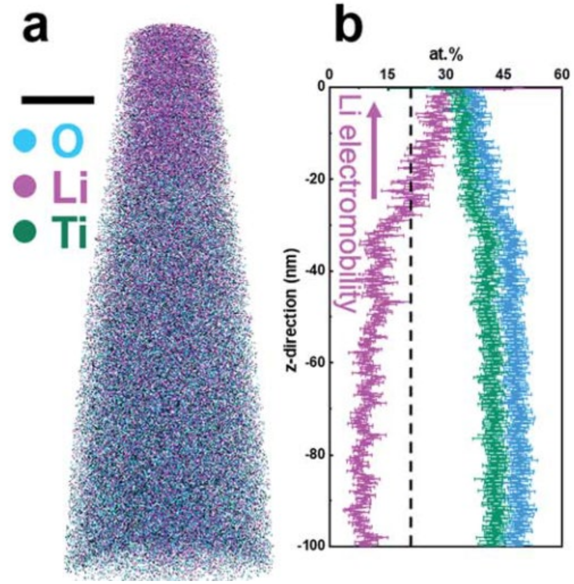
Li-ion battery cathode



Li-ion battery cathode



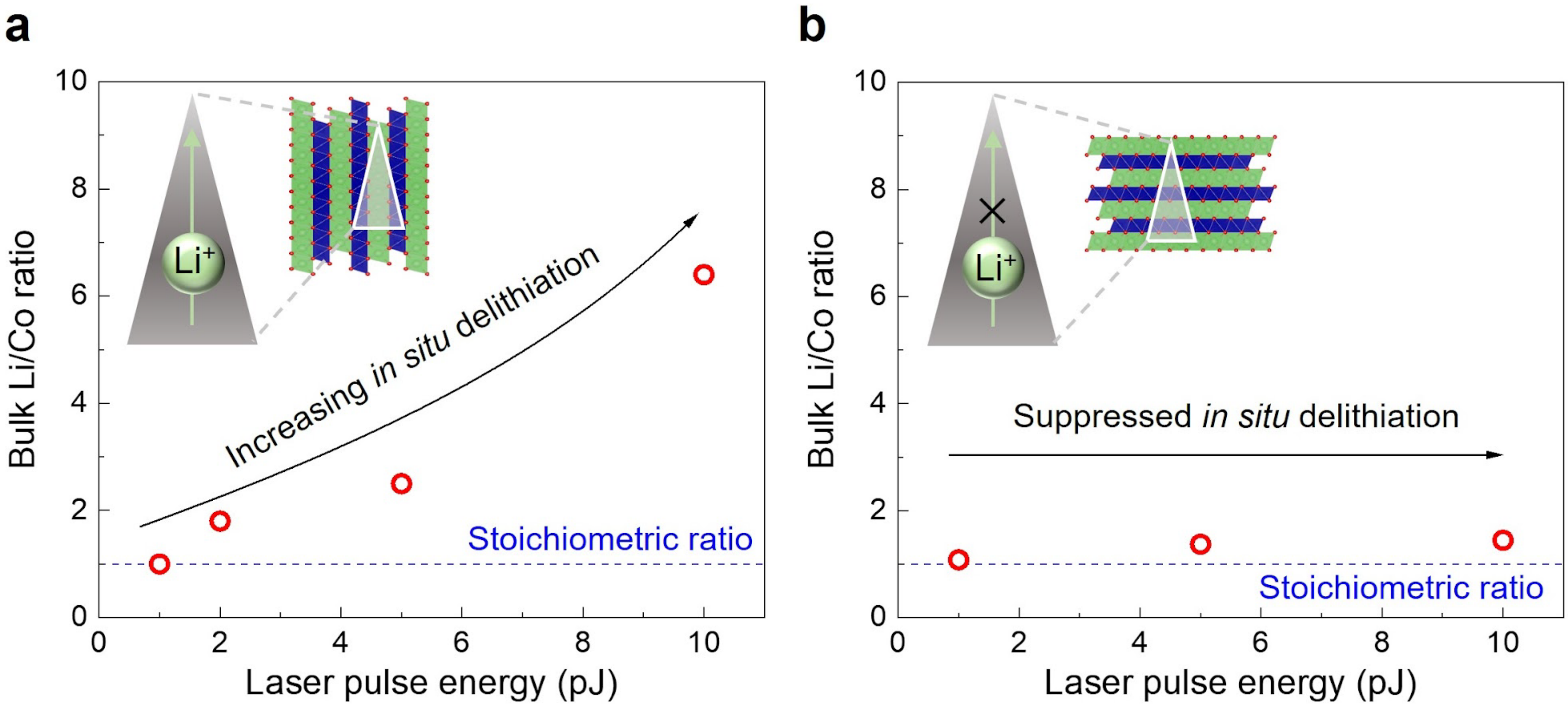
In situ delithiation for electrode materials



Highly mobile Li ions are susceptible to migration under intense applied field in APT analyses, leading to artifacts in results

Kim et al. *J. Mater. Chem. A*, **2022**, *10, 4926–4935*

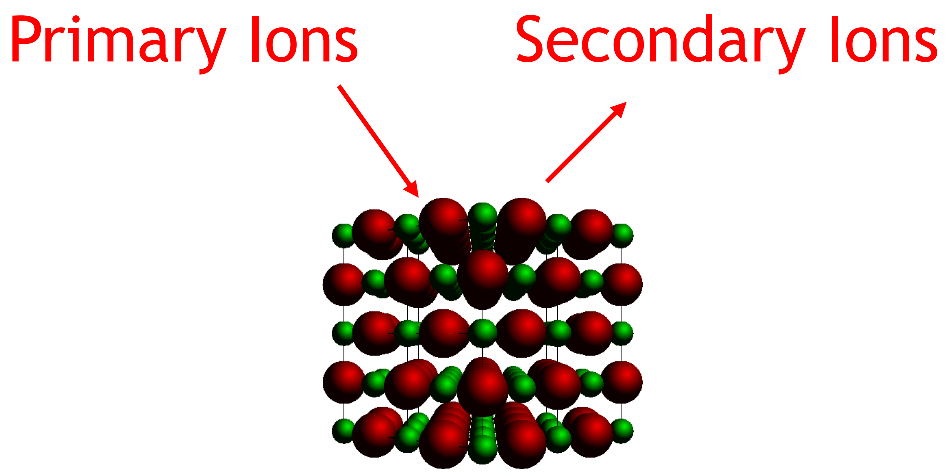
Li-ion battery cathode



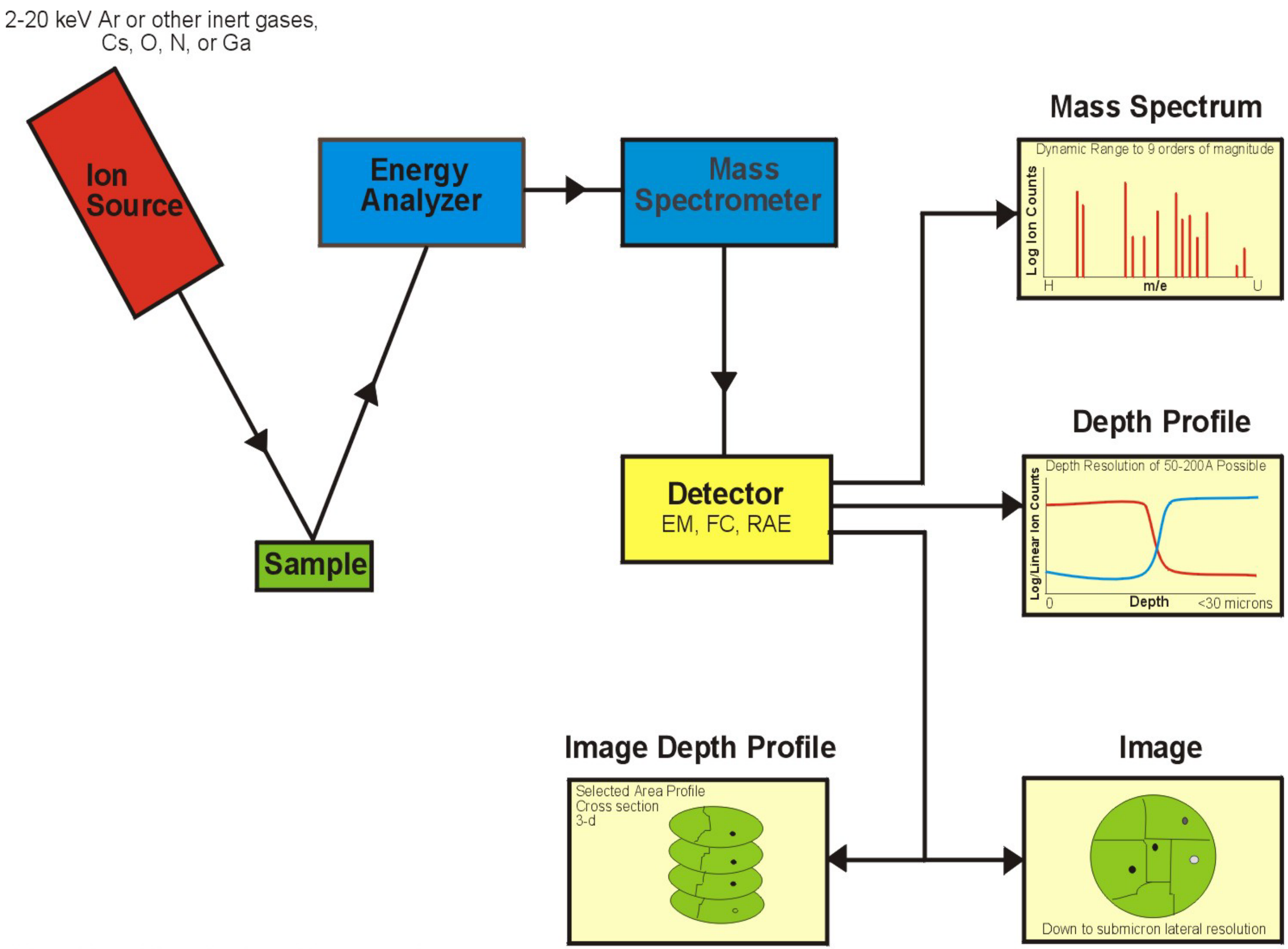
Drastic scaling relations between Li excess and laser heating energy were found for samples with Li conducting channels aligned with applied E-field

Suppressed correlation was discovered for samples with an alternate orientation, which validates the contributions of the anisotropic transport properties

SIMS is an analytical technique based on the measurement of the mass of ions ejected from a solid surface after the surface has been bombarded with high energy (1-25 keV) primary ions.



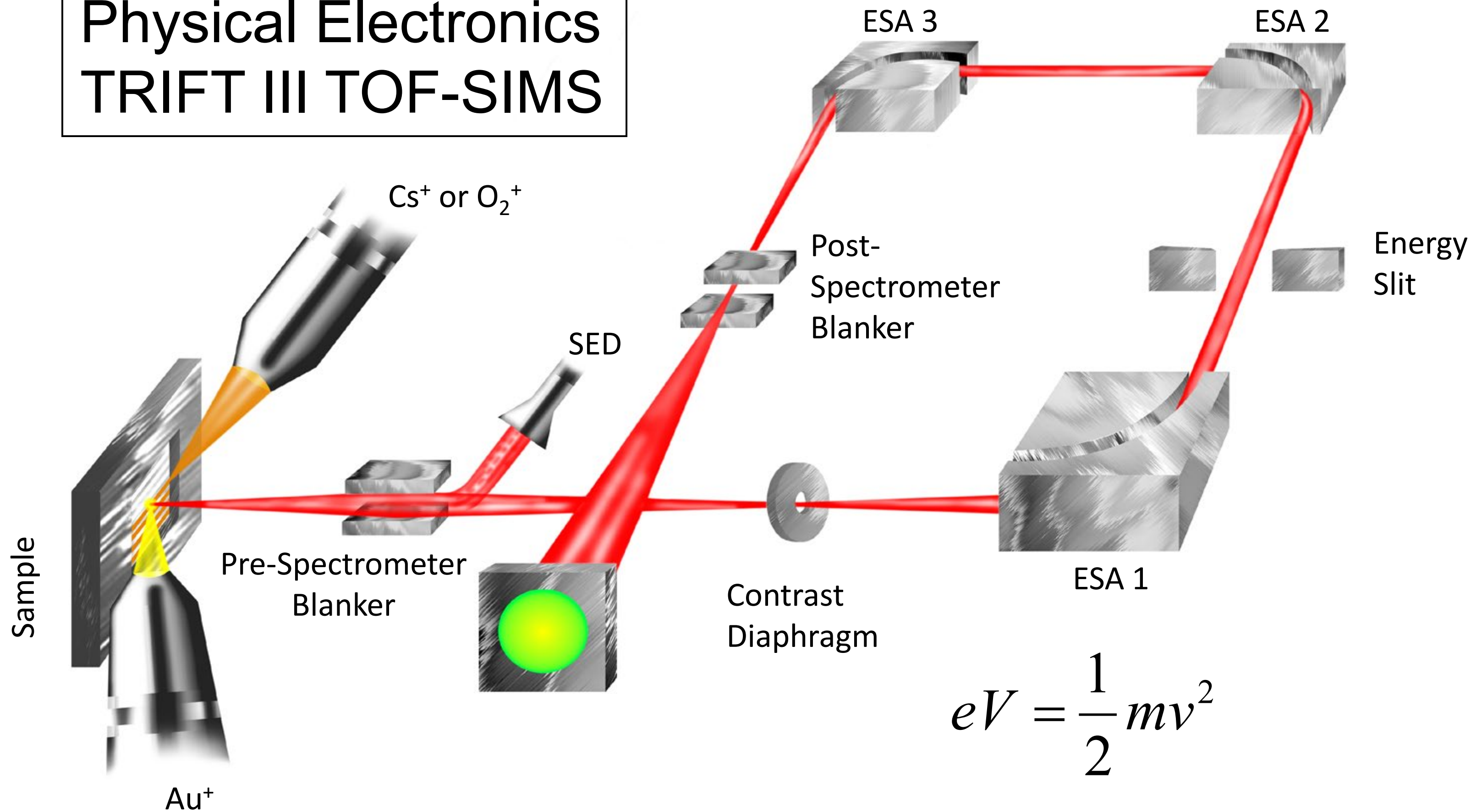
Block Diagram of SIMS Technique



Adapted from Wilson, Stevie, and Magee, p. I-8.

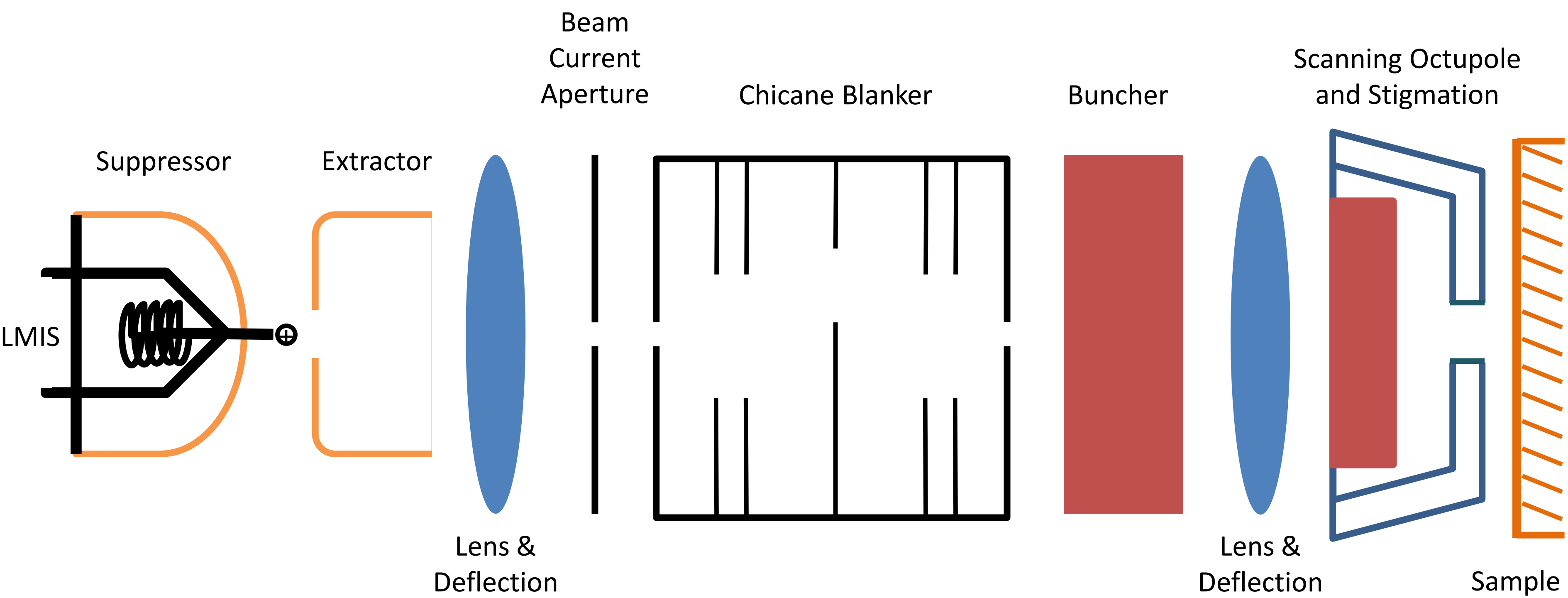
Time of Flight Mass Spectrometer

Physical Electronics
TRIFT III TOF-SIMS

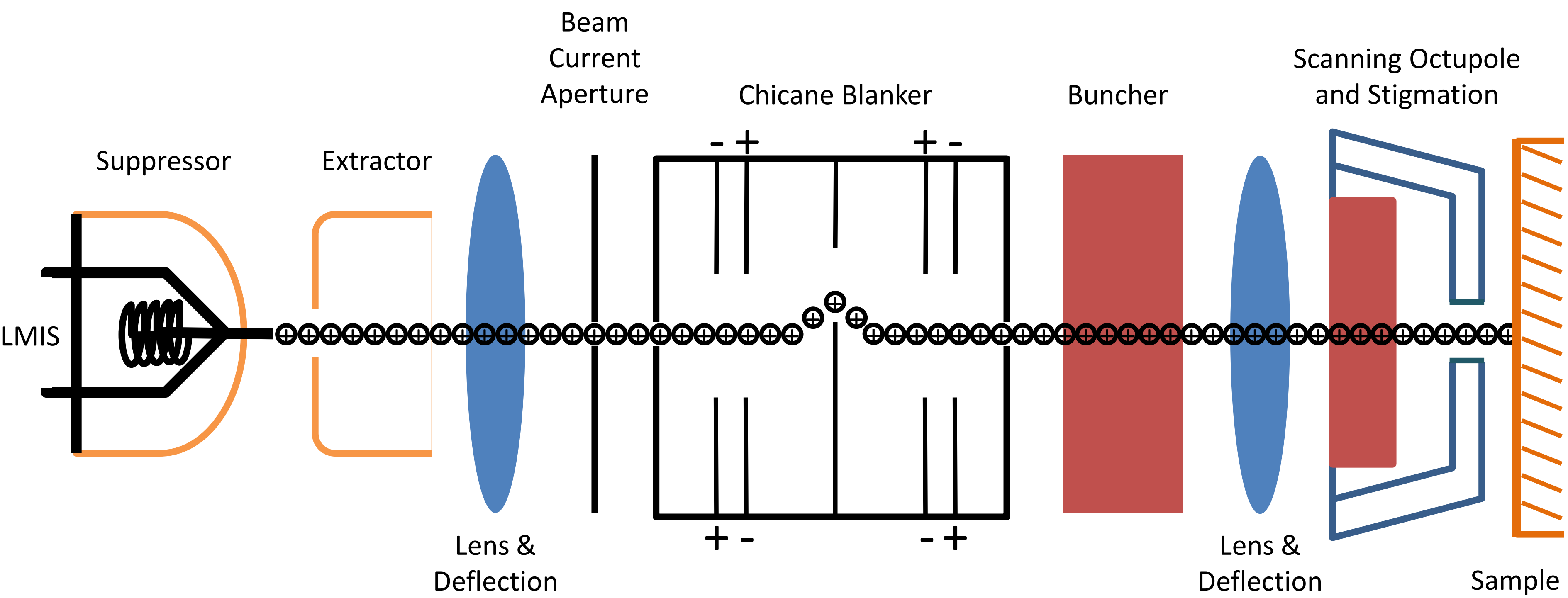


$$eV = \frac{1}{2}mv^2$$

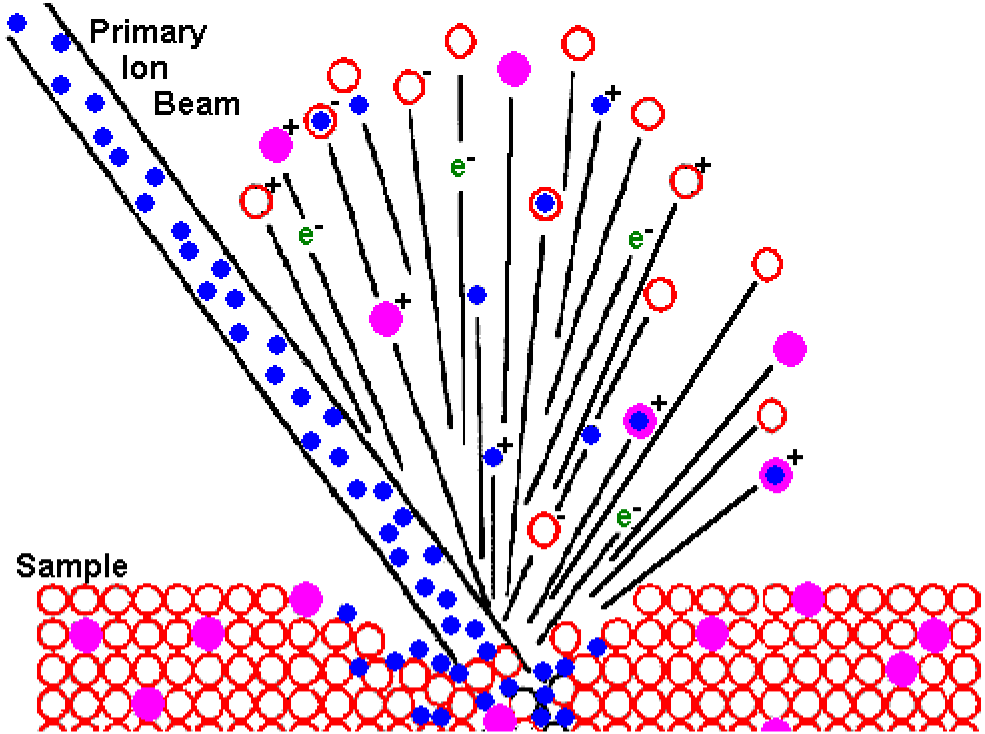
LMIG: Single Ion



LMIG: Un-bunched Beam



Ion Beam Sputtering



Graphic courtesy of
EAG Laboratories
http://www.eag.com

Sputtered species include:

- **Monoatomic and polyatomic particles of sample material (positive, negative or neutral)**
- **Resputtered primary species (positive, negative or neutral)**
- **Electrons**
- **Photons**

PHI *nanoTOF* II Parallel Imaging MS/MS

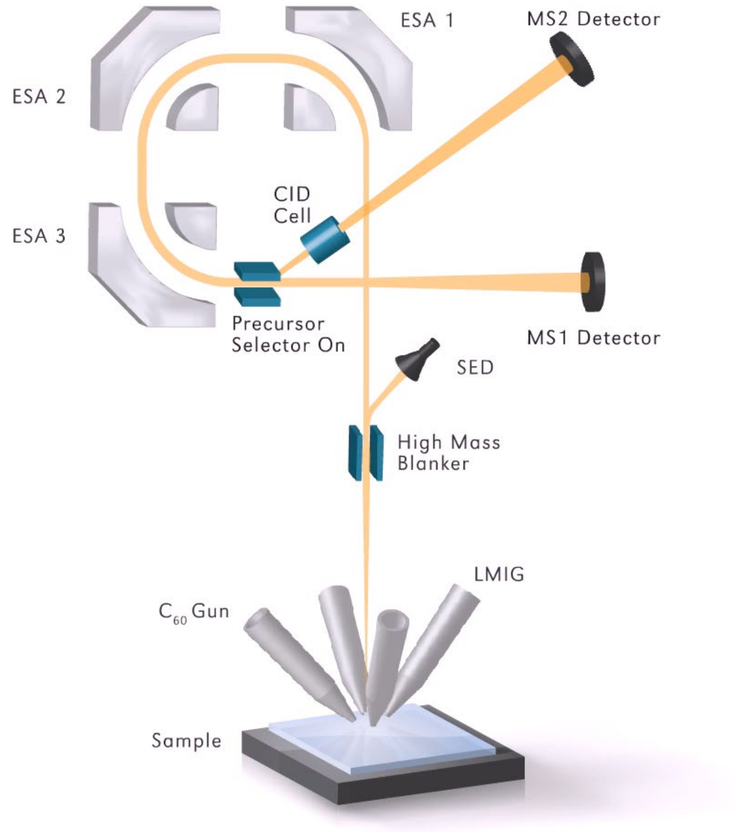
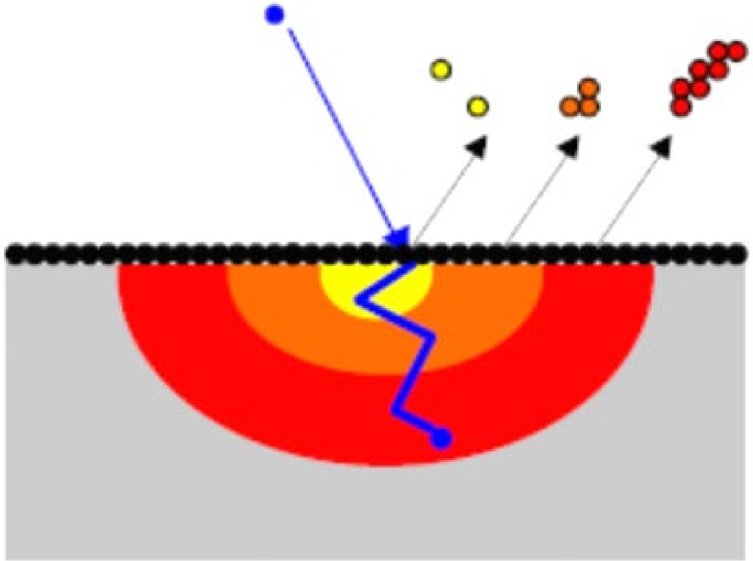


Diagram courtesy of:

PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

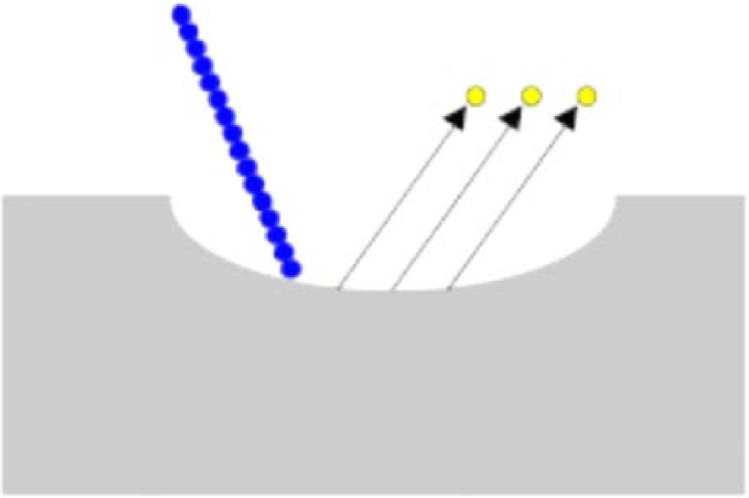
Static and Dynamic SIMS

Static SIMS



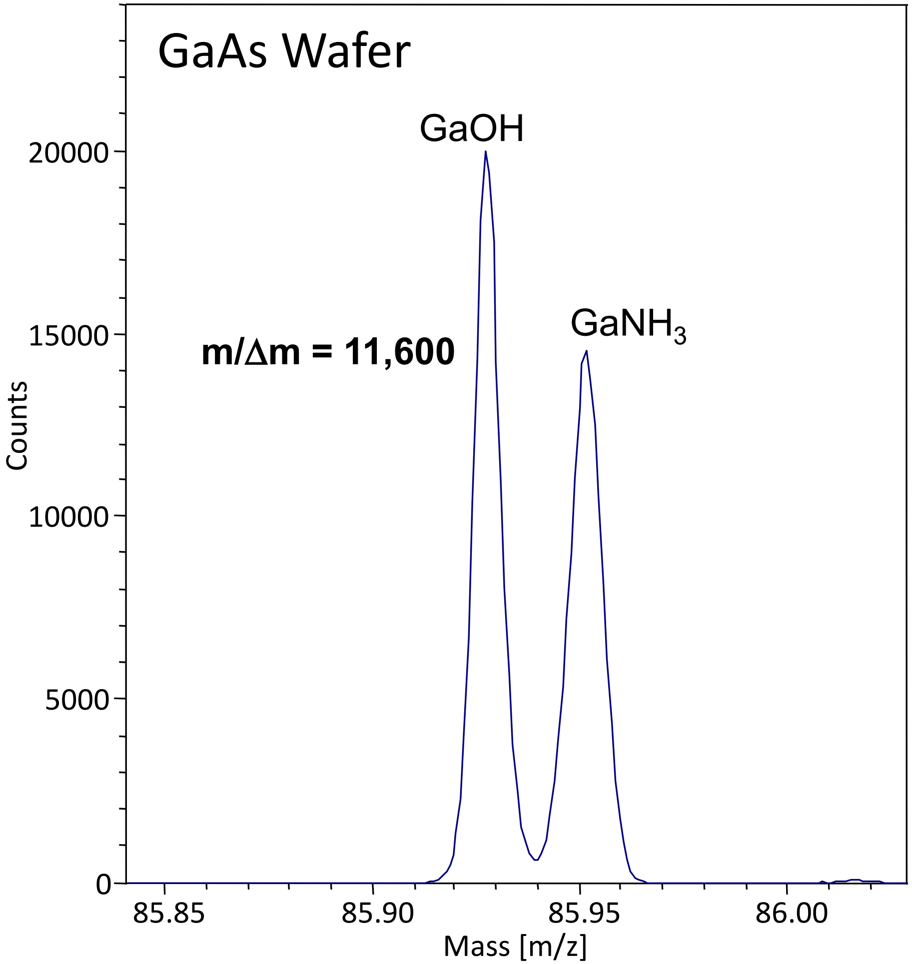
- Ultra surface analysis
- Elemental or molecular analysis
- Analysis complete before significant fraction of molecules destroyed

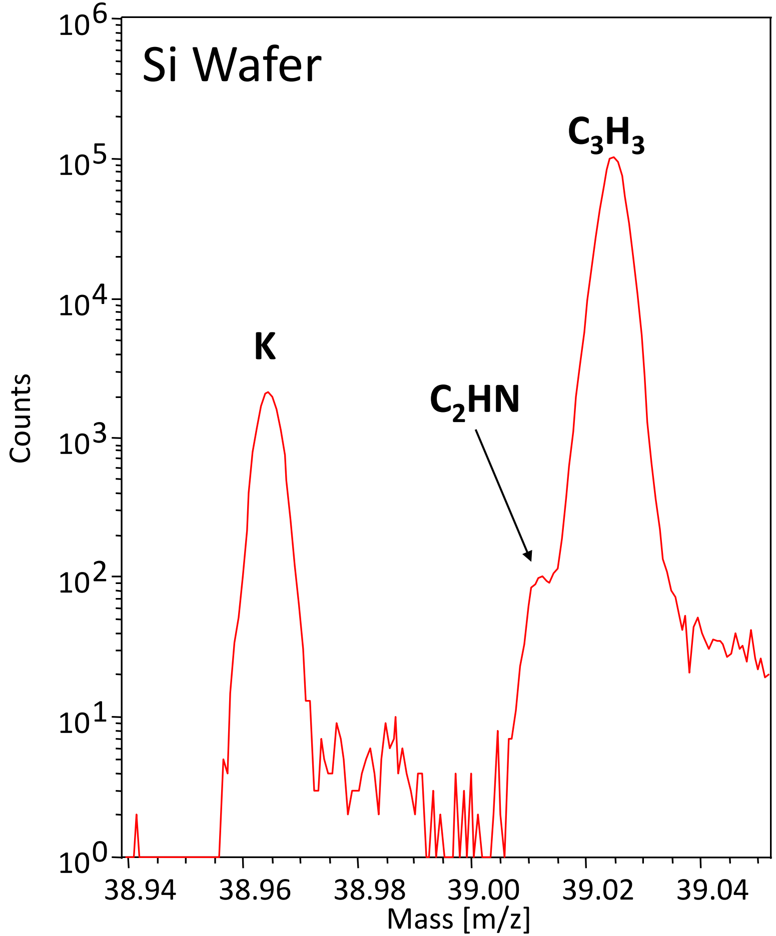
Dynamic SIMS



- Material removal
- Elemental analysis
- Depth profiling

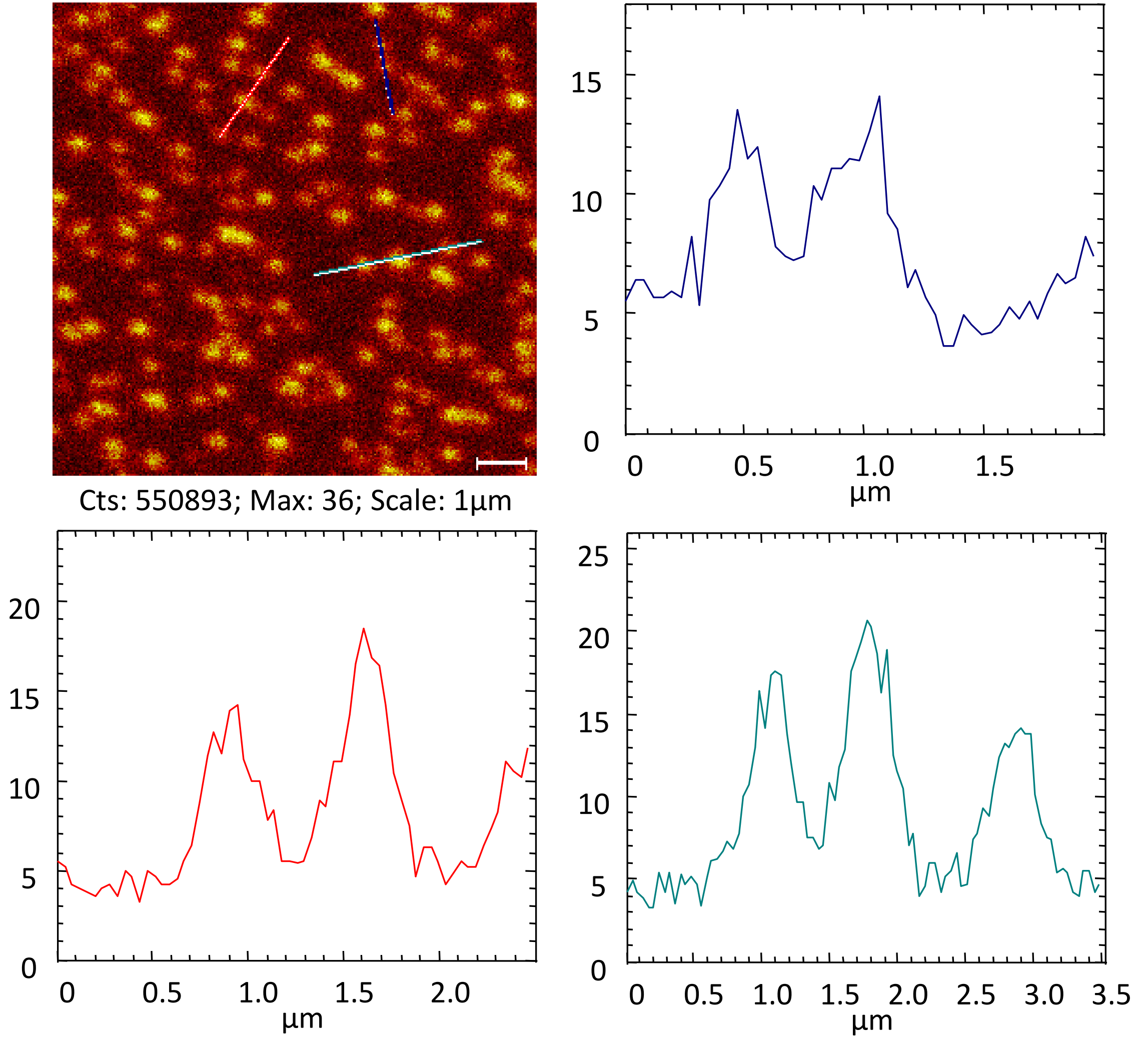
Courtesy Gregory L. Fisher, Physical Electronics





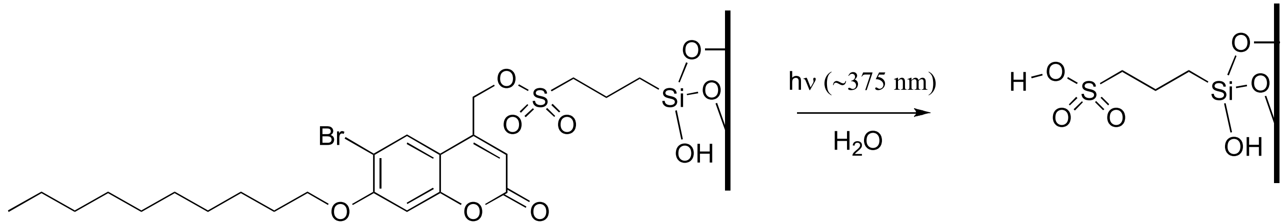
No sputtering to remove organics on surface. Large C_3H_3 peak does not have a tail to lower mass which would obscure C_2HN and K.

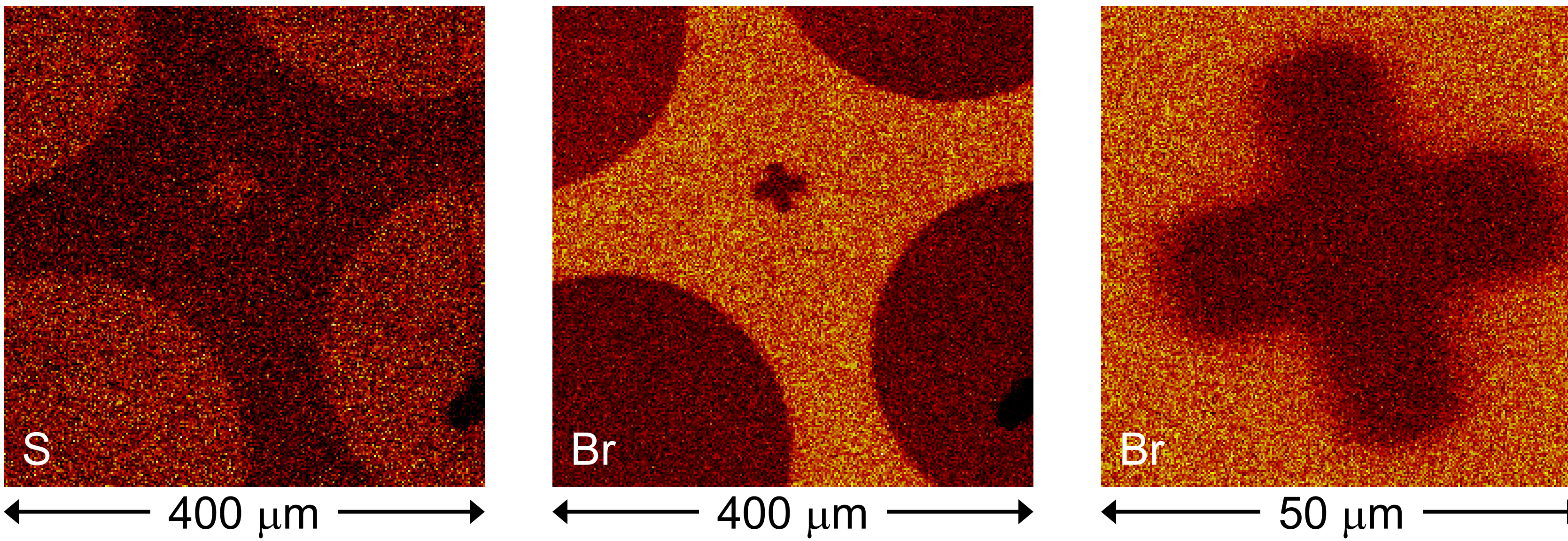
InAs/GaAs Quantum Dots



In^+ Linescans of Quantum Dots

TOF-SIMS Imaging of Patterned Sample



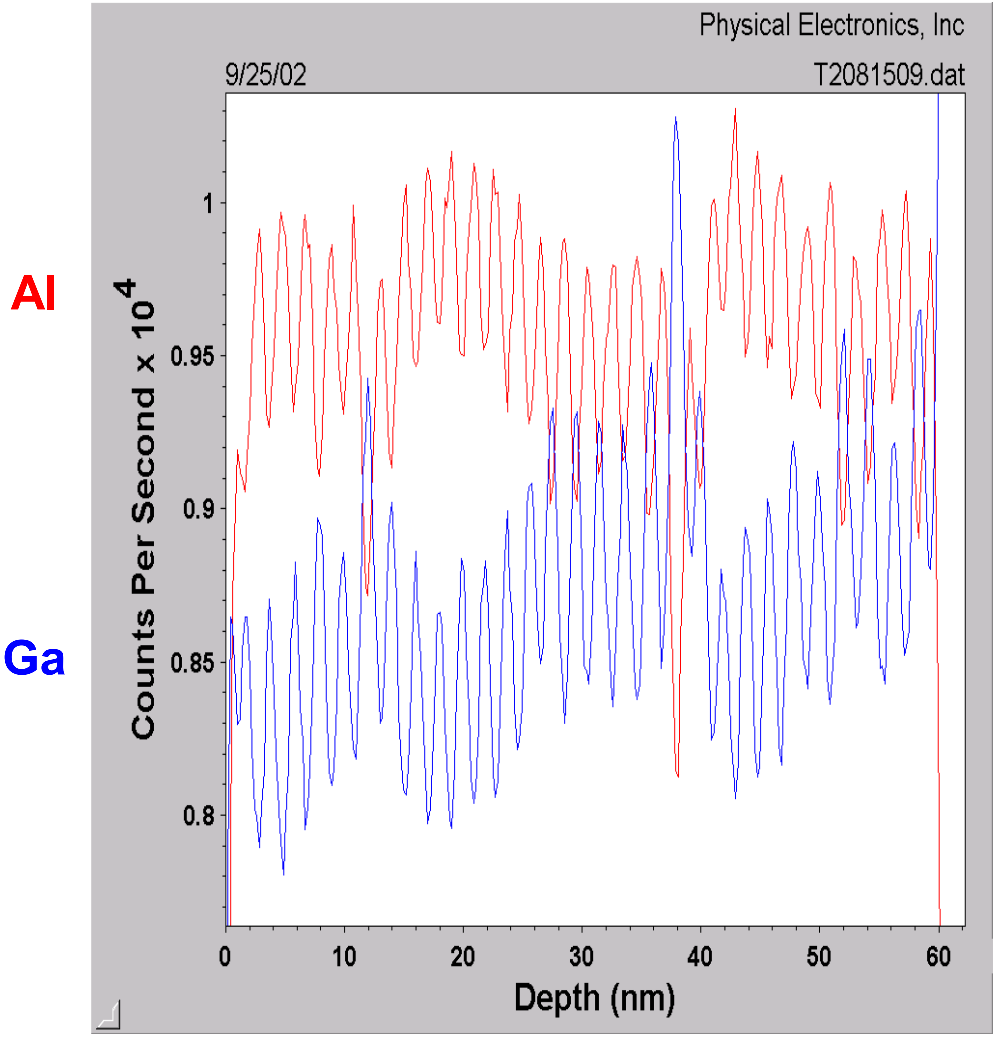


Courtesy Josh Ritchey, Audrey Bowen, Ralph Nuzzo and Jeffrey Moore, University of Illinois

Comparison of Static and Dynamic SIMS

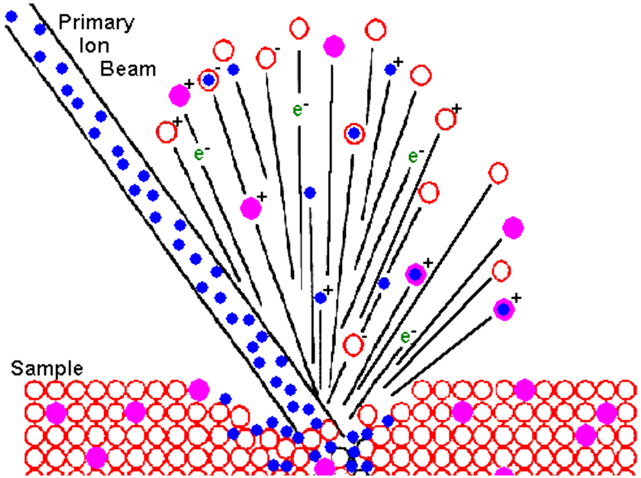
TECHNIQUE	STATIC	DYNAMIC
FLUX	< 10^{13} ions/cm^2 (per experiment)	~10^{17} ions/cm^2 (minimum dose density)
INFORMATION	Elemental + Molecular	Elemental
SENSITIVITY	1 ppm	< 1 ppm (ppb for some elements)
TYPE OF ANALYSIS	Surface Mass Spectrum 2D Surface Ion Image	Depth Profile Mass Spectrum 3D Image Depth Profile
SAMPLING DEPTH	2 monolayers	10 monolayers
SPATIAL RESOLUTION	0.1 – 1.0 μm	0.1 -1.0 μm
SAMPLE DAMAGE	Minimal	Destructive in analyzed area – up to 500 μm per area

GaAs/AlGaAs Depth Profile



Analysis beam: 15kV Ga^{+}
Sputter Beam: 300V O_2^{+}
with oxygen flood

Quantitative Analysis: SIMS



$$I_s^m = I_p y_m \alpha^+ \theta_m \eta$$

I_s^m = secondary ion current of species m
I_p = primary particle flux
y_m = sputter yield
α^+ = ionization probability to positive ions
θ_m = factional concentration of m in the layer
η = transmission of the analysis system

In SIMS, the yield of secondary ions is strongly influenced by the electronic state of the material being analyzed.

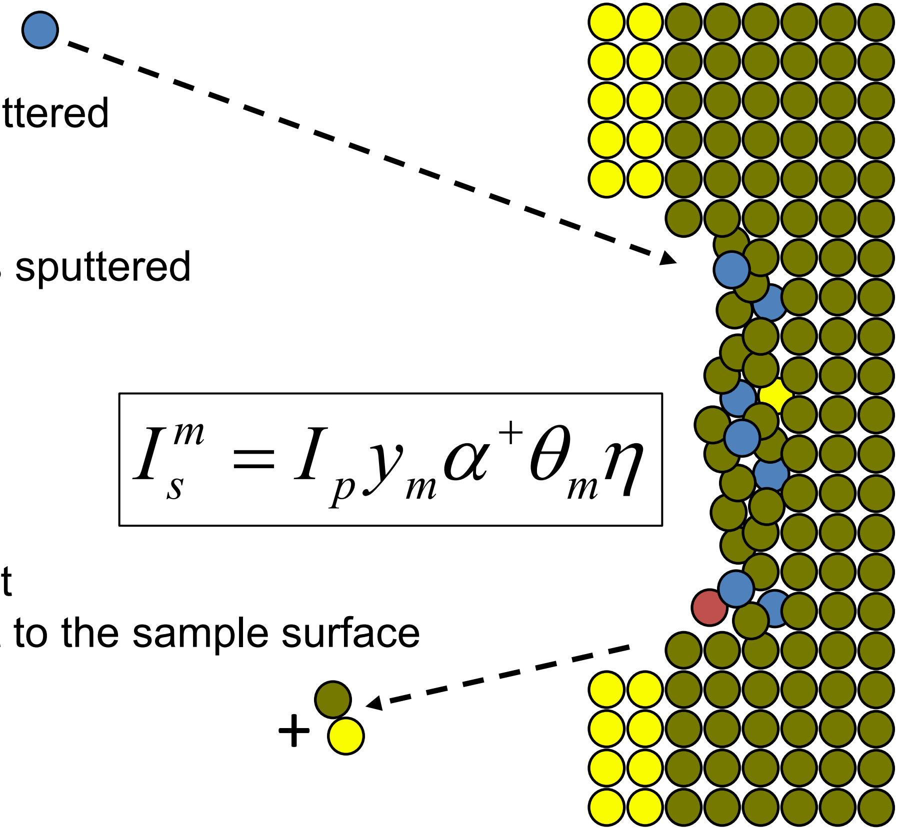
Total Ion Sputtering Yield

Sputter yield (y_m): ratio of number of atoms sputtered to number of impinging ions, typically 5-15

Ion sputter yield ($y_m \bullet \alpha^+$): ratio of ionized atoms sputtered to number of impinging ions, 10^{-6} to 10^{-2}

Ion sputter yield may be influenced by:
- Matrix effects
- Surface coverage of reactive elements
- Background pressure in the sample environment
- Orientation of crystallographic axes with respect to the sample surface
- Angle of emission of detected secondary ions

$$I_s^m = I_p y_m \alpha^+ \theta_m \eta$$



Courtesy of Prof. Rockett

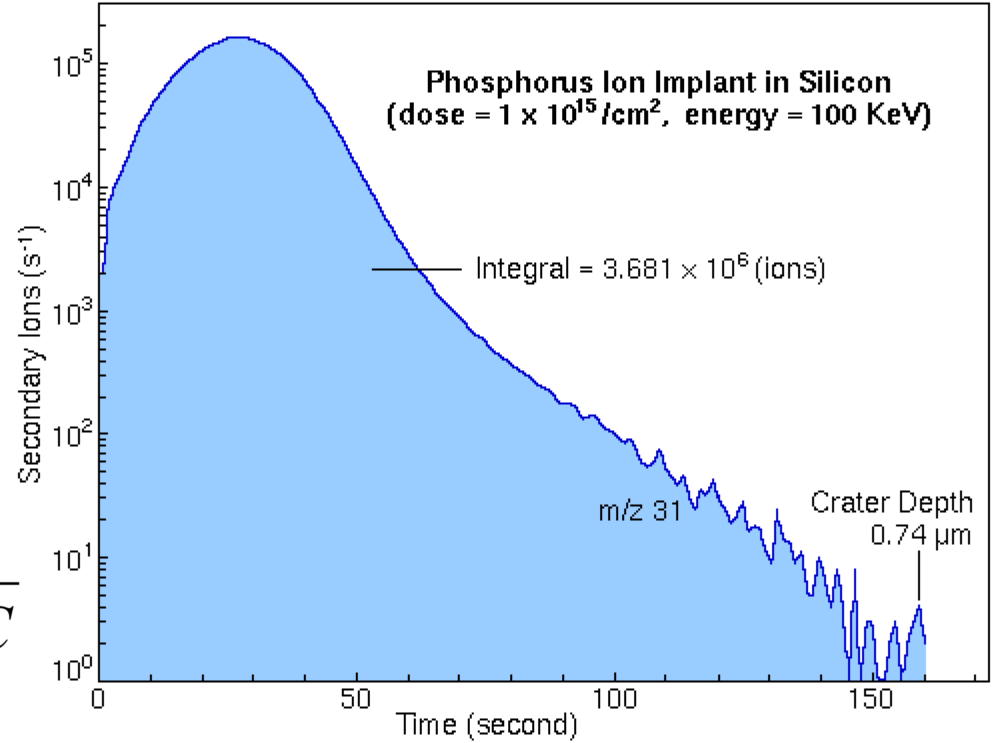
First principles prediction of ion sputter yields is not possible with this technique.

Determination of RSF Using Ion Implants

$$I_s^m = I_p y_m \alpha^+ \theta_m \eta$$

Level Profile: $$RSF = \frac{I_m}{I_i}\rho_i$$

Gaussian Profile: $$RSF = \frac{I_m \phi C t}{d\sum I_i - dI_b C}$$



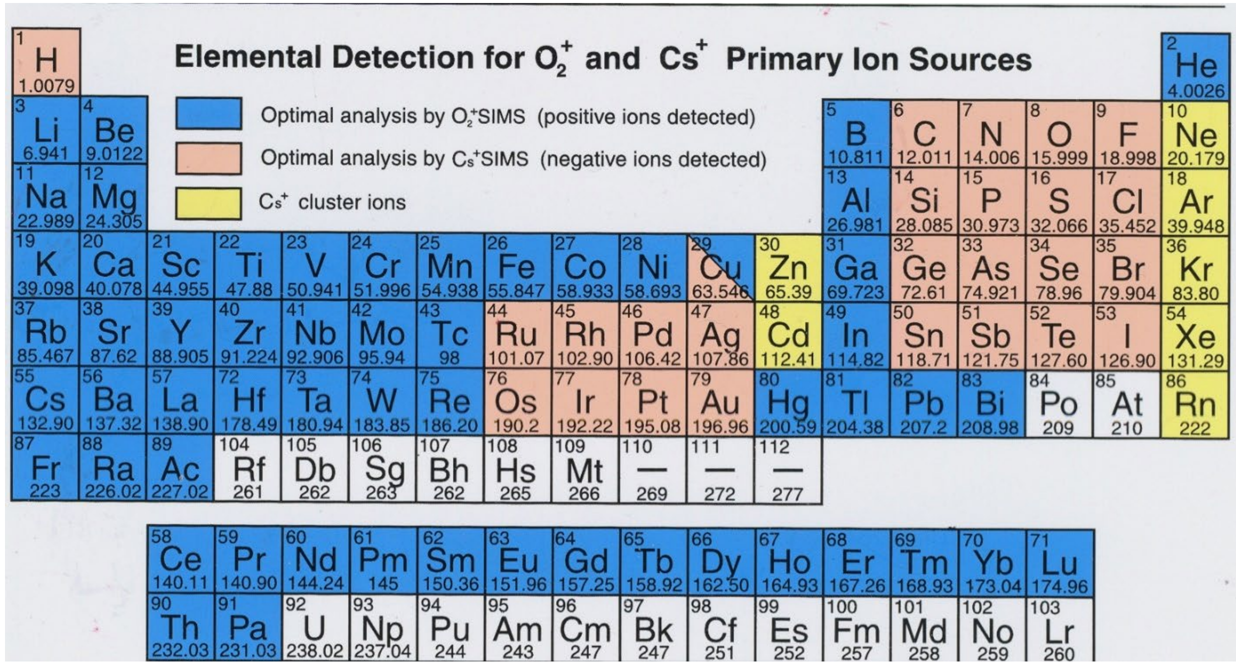
Graphic courtesy of
EAG Laboratories
http://www.eag.com

Where:

RSF = Relative Sensitivity Factor
I_m, I_i = ion intensity (counts/sec)
ρ = atom density (atoms/cm^3)
ϕ = implant fluence (atoms/cm^2)

C = # measurement cycles
t = analysis time (s/cycle)
d = crater depth (cm)
I_b = background ion counts

Effect of Primary Beam on Secondary Ion Yields

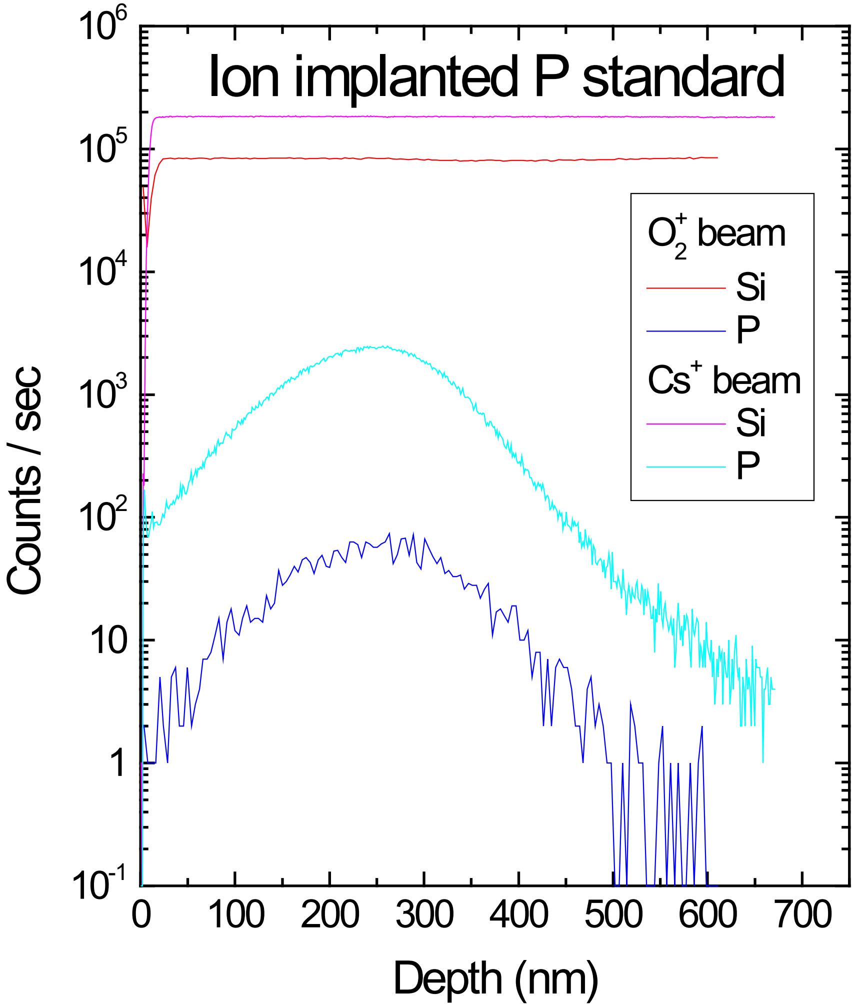


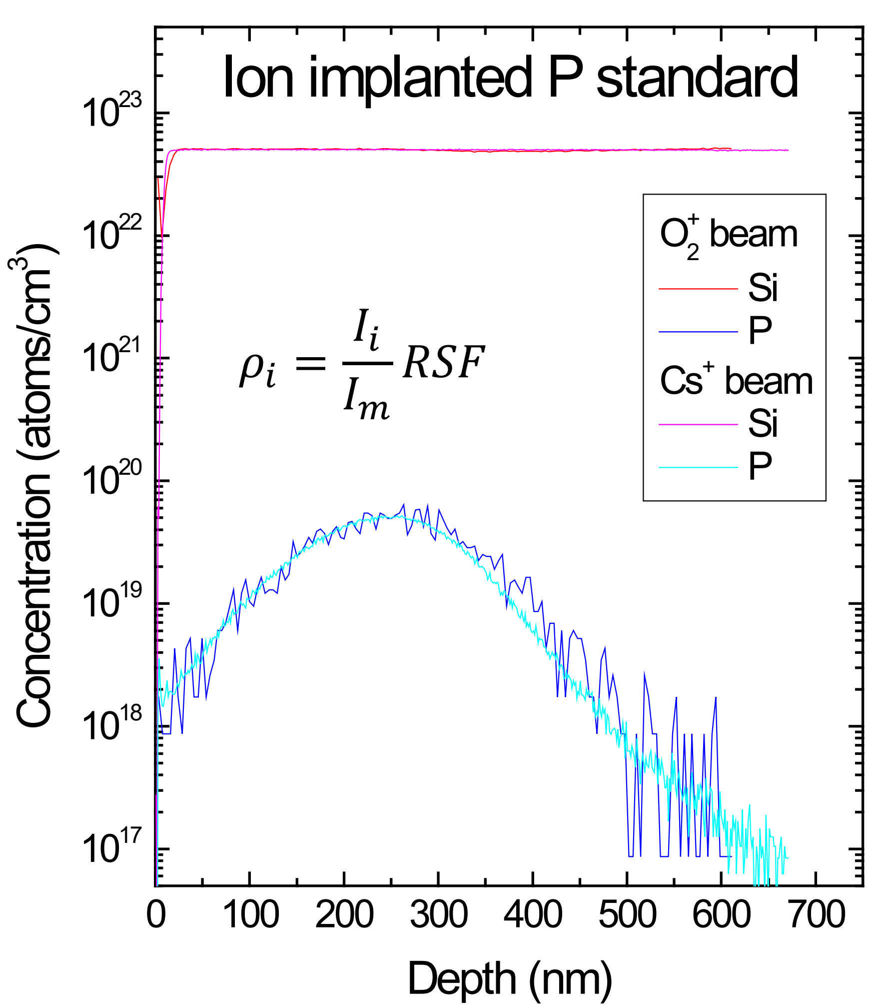
Graphic courtesy of
EAG Laboratories
http://www.eag.com

Oxygen bombardment
When sputtering with an oxygen beam, the concentration of oxygen increases in the surface layer and metal-oxygen bonds are present in an oxygen-rich zone. When the bonds break during the bombardment, secondary ion emission process, oxygen becomes negatively charged because of its high electron affinity and the metal is left with the positive charge. Elements in yellow analyzed with oxygen bombardment, positive secondary ions for best sensitivity.

Cesium bombardment
When sputtering with a cesium beam, cesium is implanted into the sample surface which reduces the work function allowing more secondary electrons to be excited over the surface potential barrier. With the increased availability of electrons, there is more negative ion formation. Elements in green analyzed with cesium, negative secondary ions for best sensitivity.

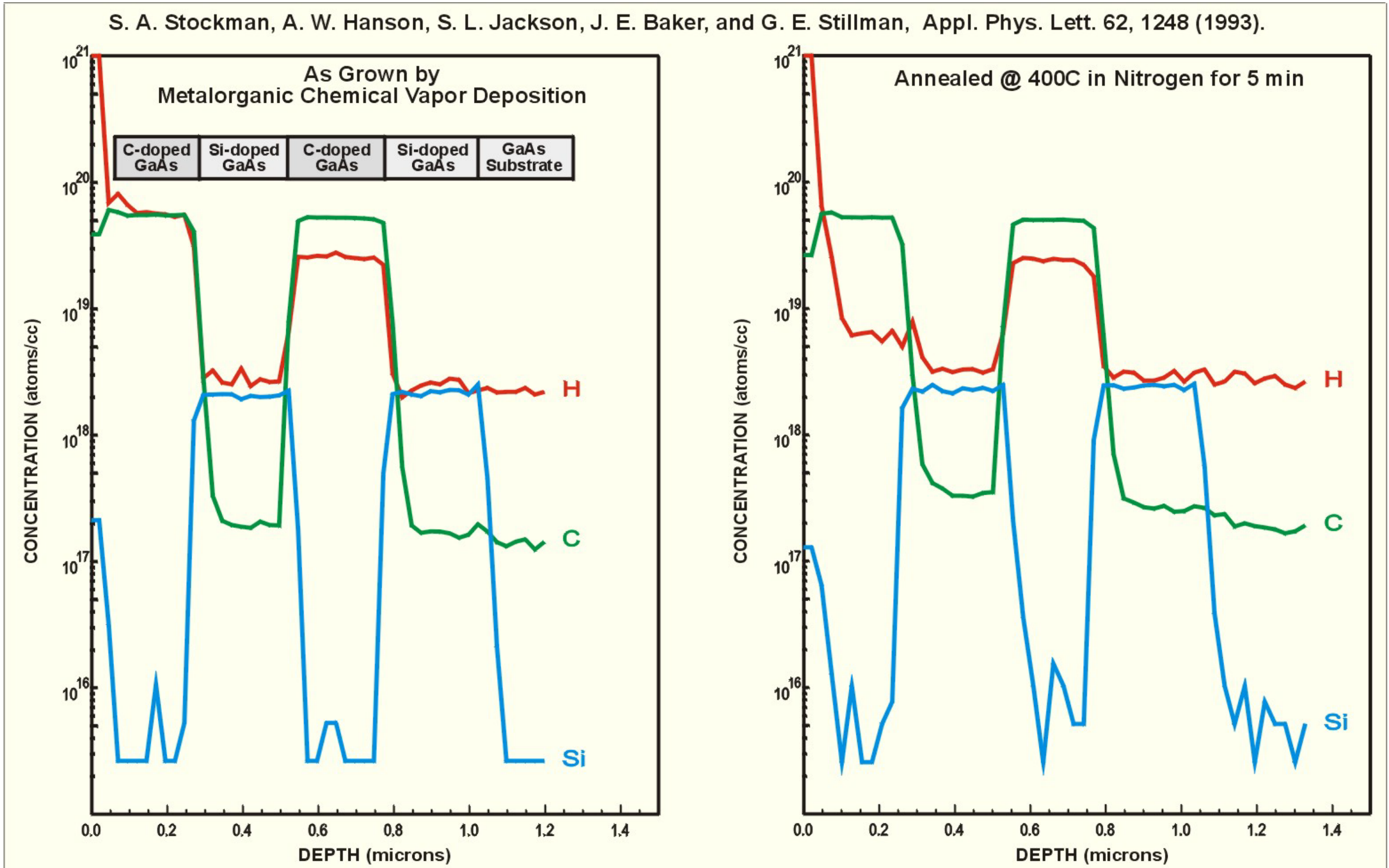
Positive and Negative Secondary Ions





$$\rho_i = \frac{I_i}{I_m} RSF$$

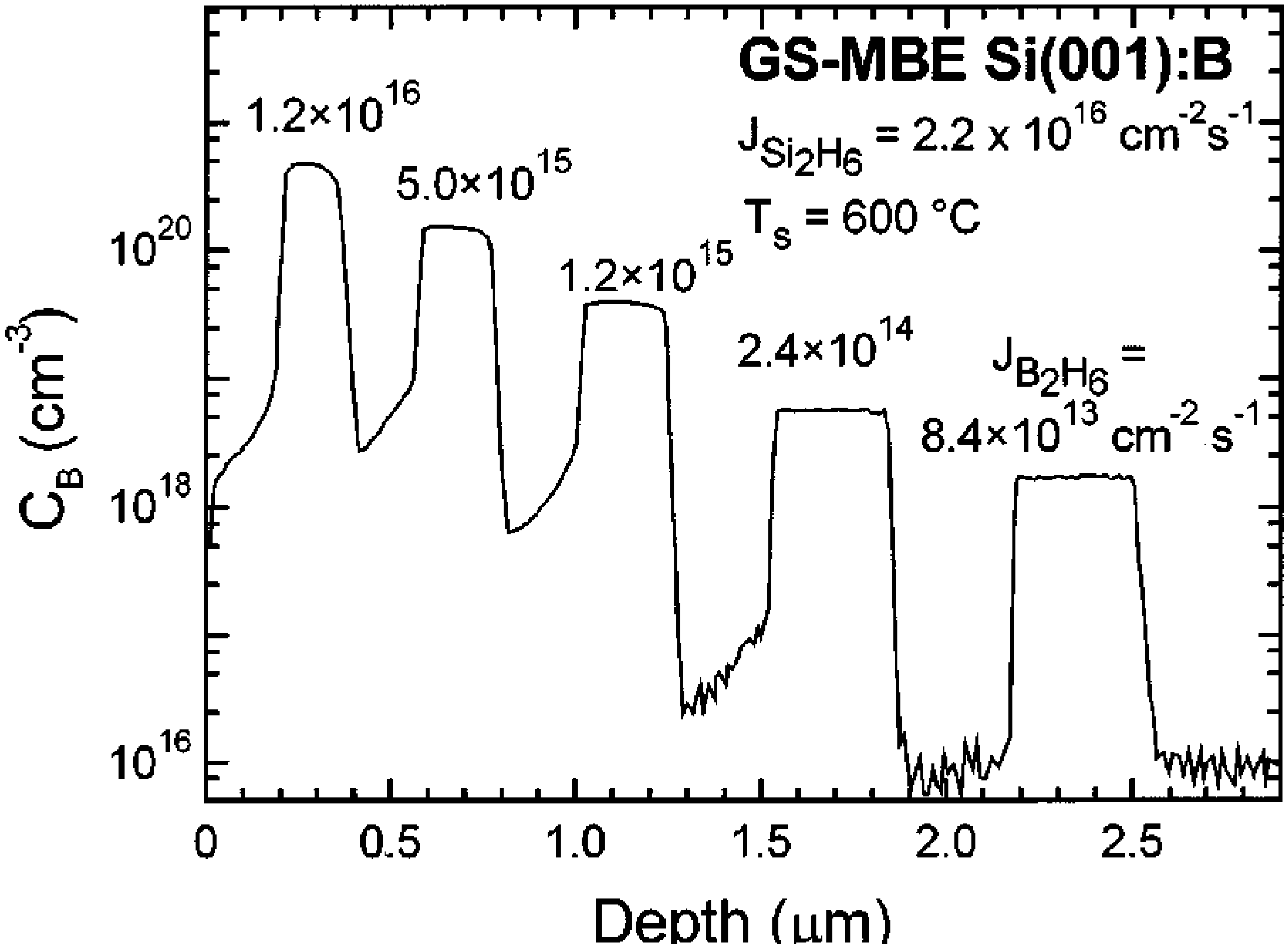
Depth Profile Application with Hydrogen



Detects hydrogen

Large dynamic range

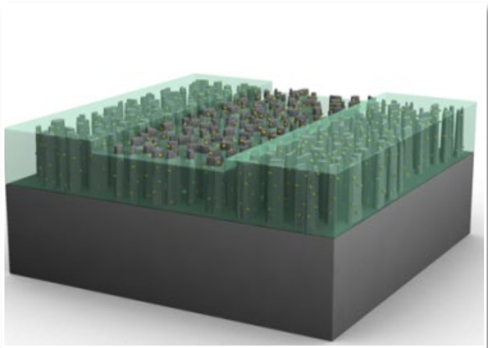
B Depth Profile in Si(001)



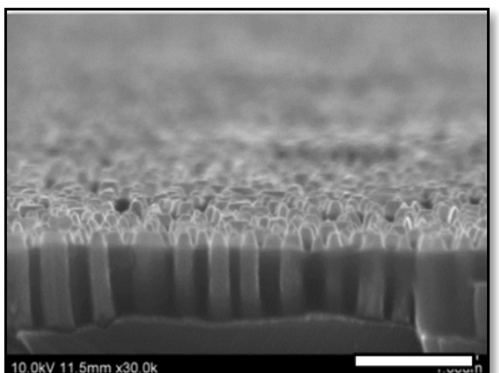
SIMS depth profiles through a B modulation-doped Si(001):B film grown by GS-MBE from Si_2H_6 and B_2H_6 at T_s=600 °C. The incident Si_2H_6 flux was J_{Si2H6} = 2.2x10^{16} cm^{-2} s^{-1} while the B flux J_{B2H6} was varied from 8.4x10^{13} to 1.2x10^{16} cm^{-2} s^{-1}. The deposition time for each layer was constant at 1 h.

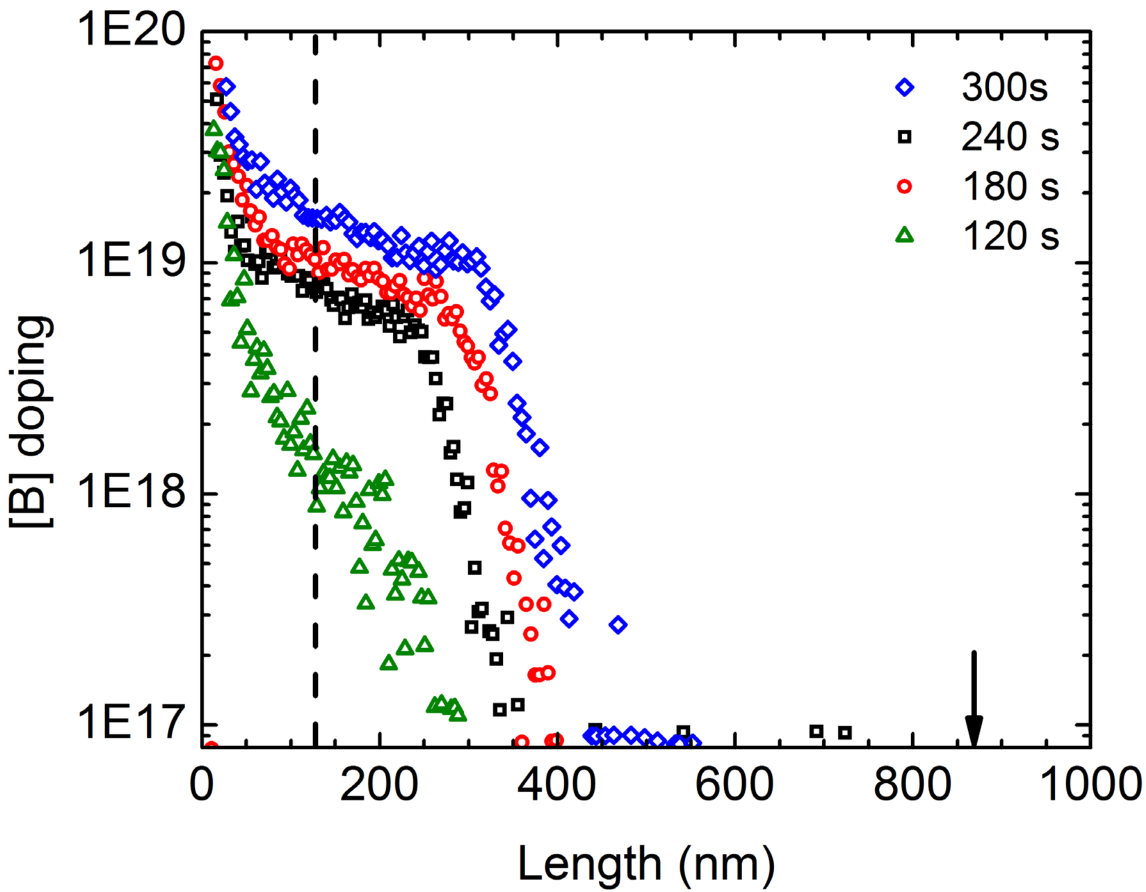
G. Glass, H. Kim, P. Desjardins, N. Taylor, T. Spila, Q. Lu, and J. E. Greene. Phys. Rev. B, **61**,7628 (2000).

Electrolessly etched silicon nanowire arrays



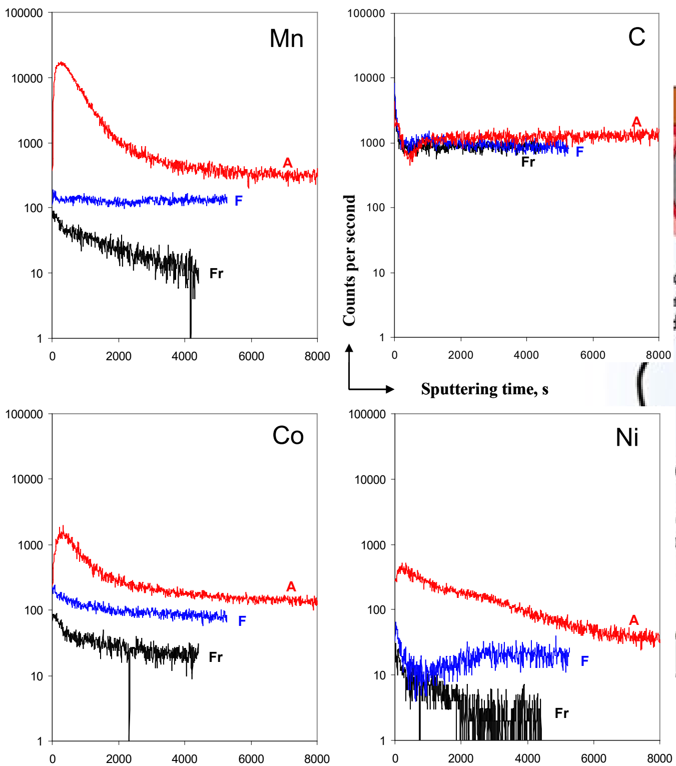
Dope NW tips by SODs

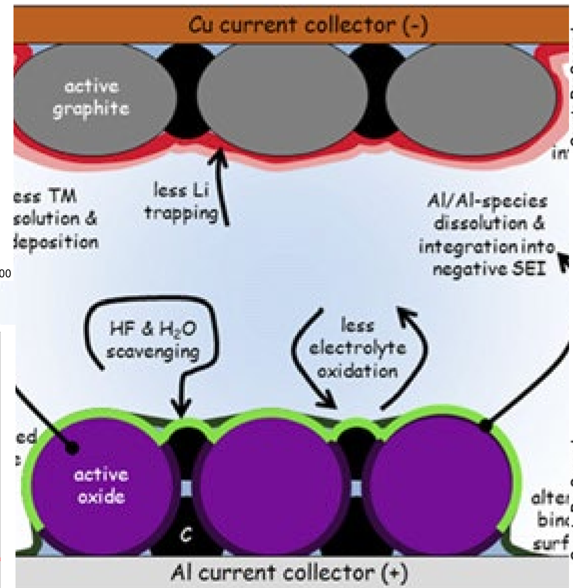


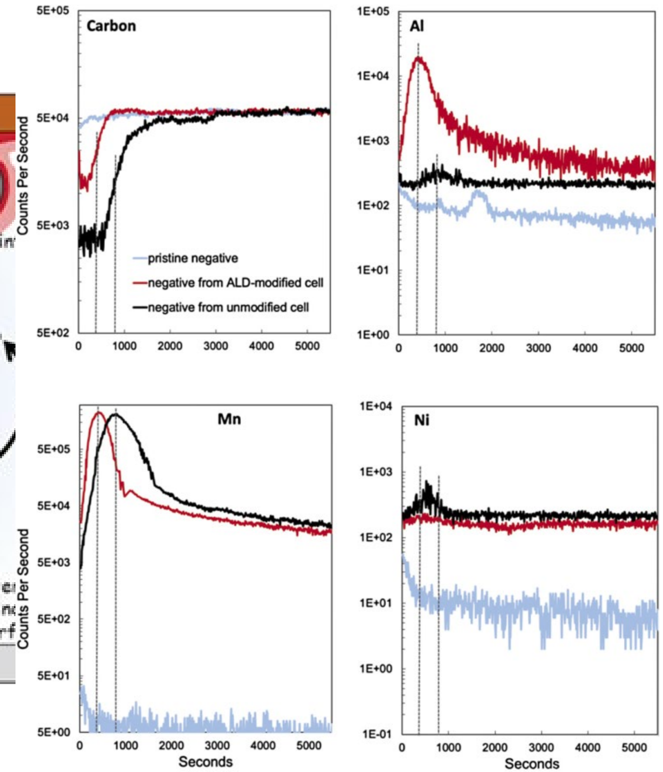


J.S Sadhu, H. Tian, T. Spila, J. Kim, B. Azeredo, P. Ferreira, and S. Sinha. *Nanotechnology* **25**, 375701 (2014).

Transition-Metal Accumulation on Anodes in Li-ion Batteries

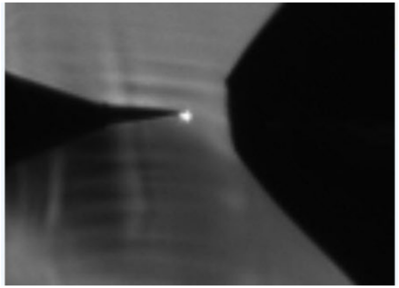






Summary

Atom Probe



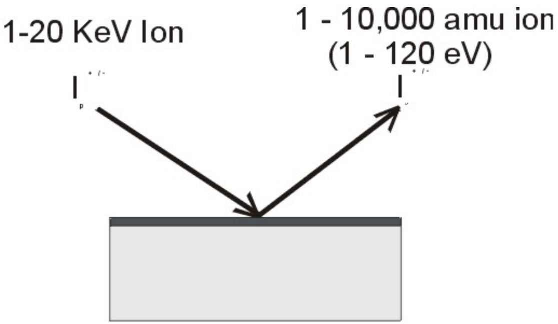
Spatial Resolution
0.1 – 0.3 nm in depth
0.3 – 0.5 nm laterally

Field of View
100 – 200 nm laterally

Time-of-flight mass analysis
Mass range from 1 – 600 amu

Compositional analysis
Near 100% ionization of emitted atoms
Up to 80% of all atoms analyzed
Sensitivity ~ ppm

SIMS



Information
Surface Mass Spectrum
2D Surface Ion Image
Elemental Depth Profiling
3D Image Depth Profiling

Elements Detectable
H and above

Sensitivity
ppb - atomic %

Analysis Diameter/Sampling Depth
~1 mm - several mm/0.5 - 1nm

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