Secondary Ion Mass Spectrometry

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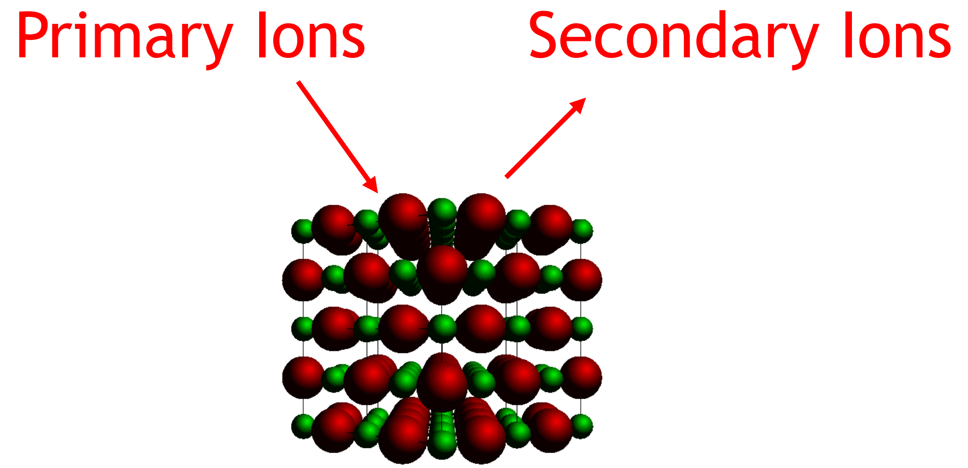
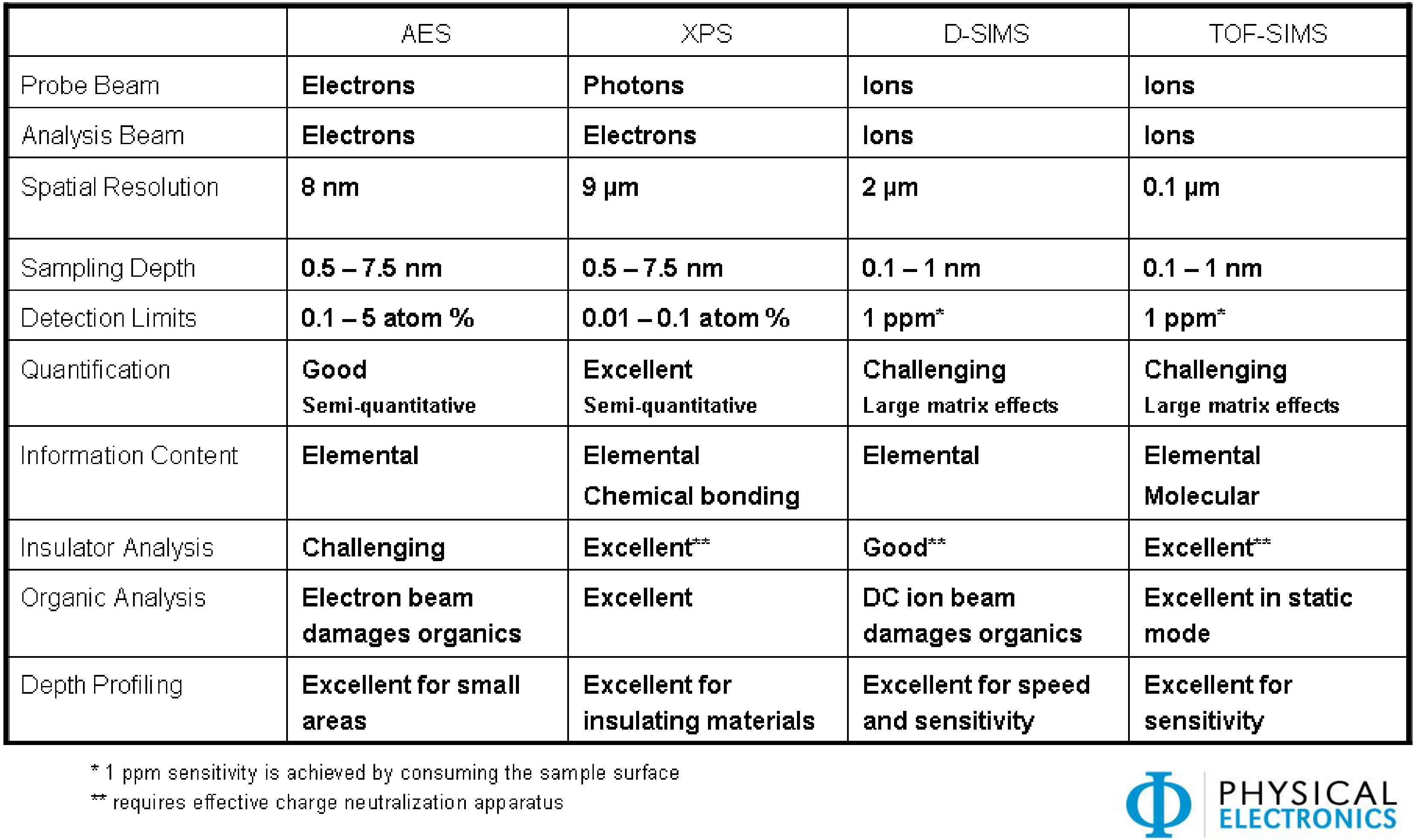
Secondary Ion Mass Spectrometry

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.



Technique Comparison



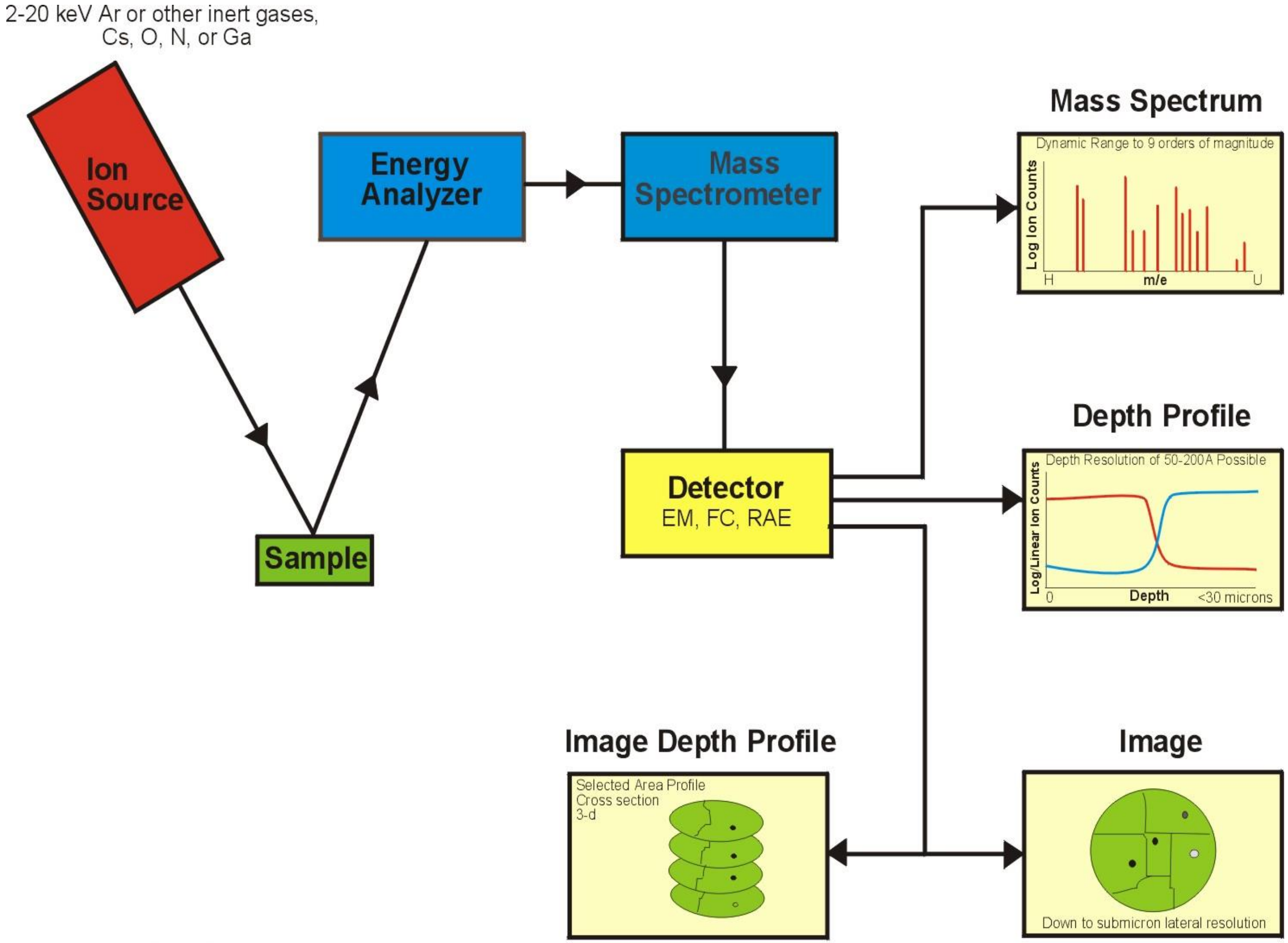
	AES	XPS	D-SIMS	TOF-SIMS
Probe Beam	**Electrons**	**Photons**	**Ions**	**Ions**
Analysis Beam	**Electrons**	**Electrons**	**Ions**	**Ions**
Spatial Resolution	**8 nm**	**9 µm**	**2 µm**	**0.1 µm**
Sampling Depth	**0.5 – 7.5 nm**	**0.5 – 7.5 nm**	**0.1 – 1 nm**	**0.1 – 1 nm**
Detection Limits	**0.1 – 5 atom %**	**0.01 – 0.1 atom %**	**1 ppm***	**1 ppm***
Quantification	**Good** **Semi-quantitative**	**Excellent** **Semi-quantitative**	**Challenging** **Large matrix effects**	**Challenging** **Large matrix effects**
Information Content	**Elemental**	**Elemental** **Chemical bonding**	**Elemental**	**Elemental** **Molecular**
Insulator Analysis	**Challenging**	**Excellent****	**Good****	**Excellent****
Organic Analysis	**Electron beam damages organics**	**Excellent**	**DC ion beam damages organics**	**Excellent in static mode**
Depth Profiling	**Excellent for small areas**	**Excellent for insulating materials**	**Excellent for speed and sensitivity**	**Excellent for sensitivity**

* 1 ppm sensitivity is achieved by consuming the sample surface

** requires effective charge neutralization apparatus

PHYSICAL ELECTRONICS

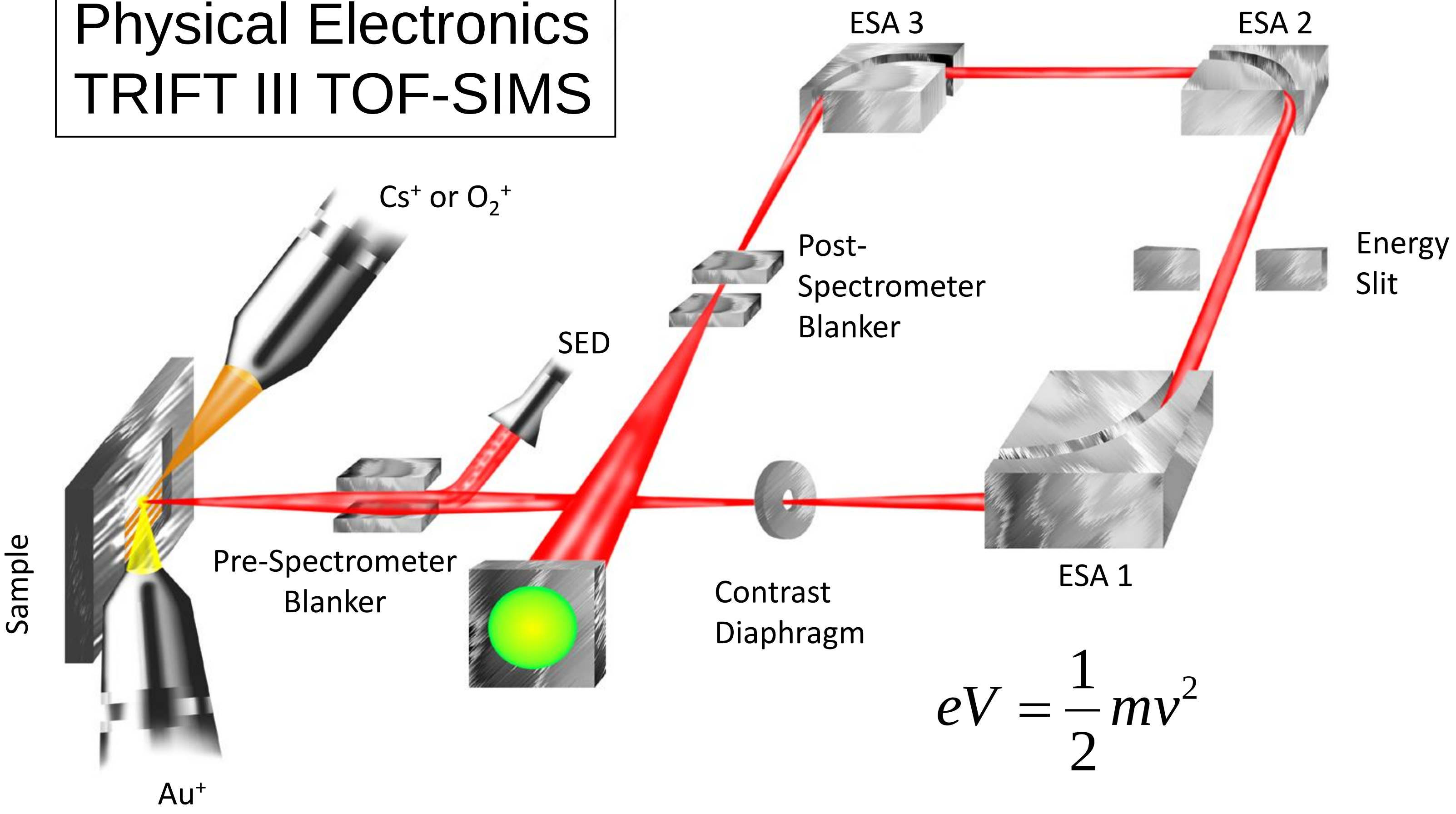
Block Diagram of SIMS Technique



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

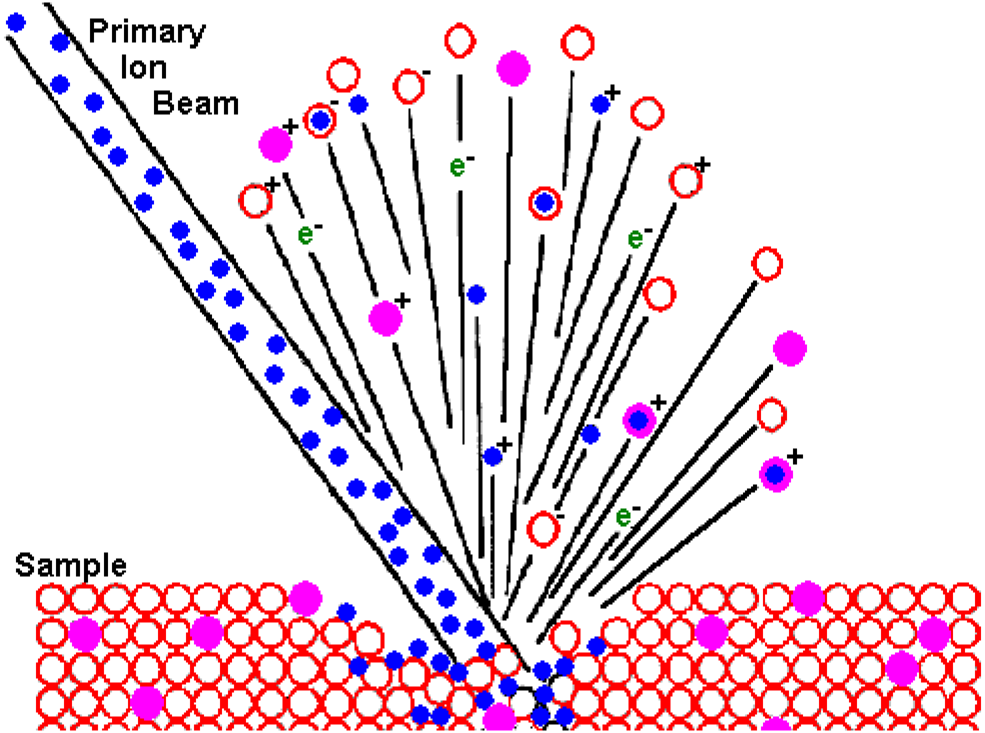
Time of Flight Mass Spectrometer

Physical Electronics
TRIFT III TOF-SIMS



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

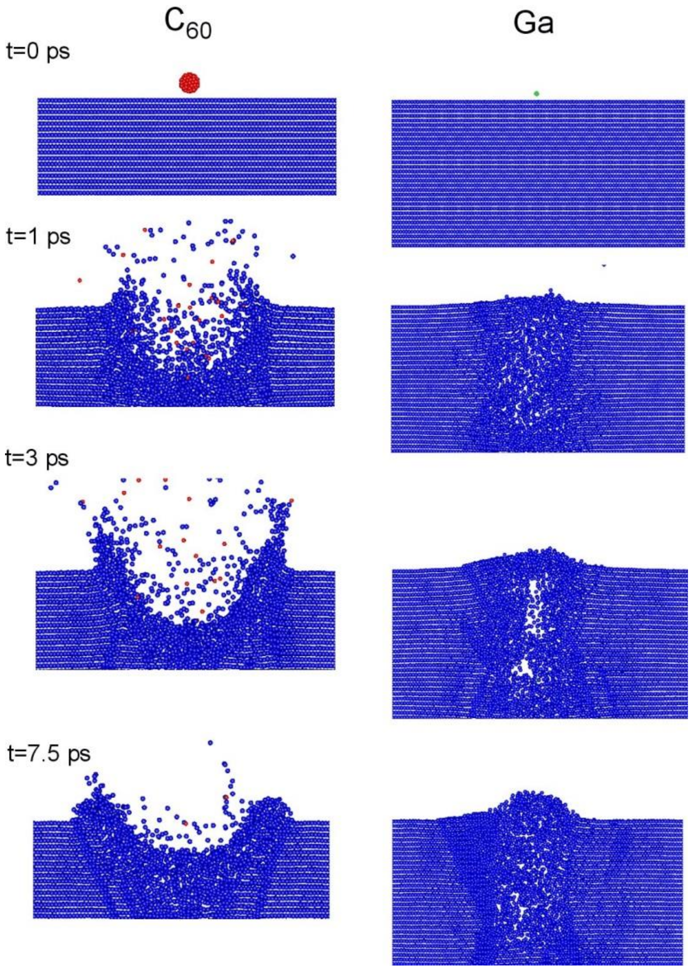
Ion Beam Sputtering



Sputtered species include:

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

MD Simulation of ion impact

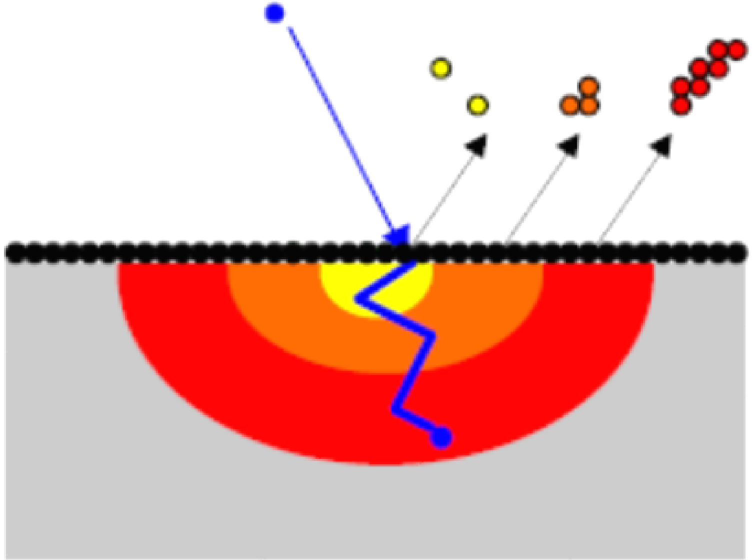


Enhancement of Sputtering Yields due to C_{60} vs. Ga Bombardment of Ag{111} as Explored by Molecular Dynamics Simulations, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, Anal. Chem., **75**, 4402-4407 (2003).

Animations downloaded from http://galilei.chem.psu.edu/sputtering-animations.html.

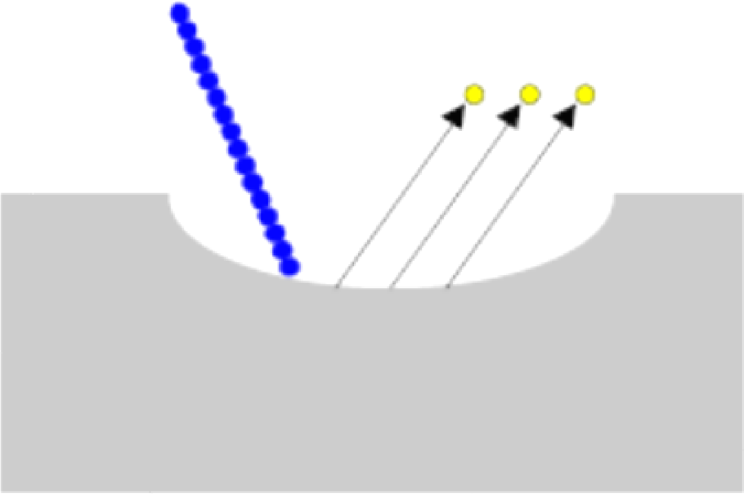
Static and Dynamic SIMS

Static SIMS



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

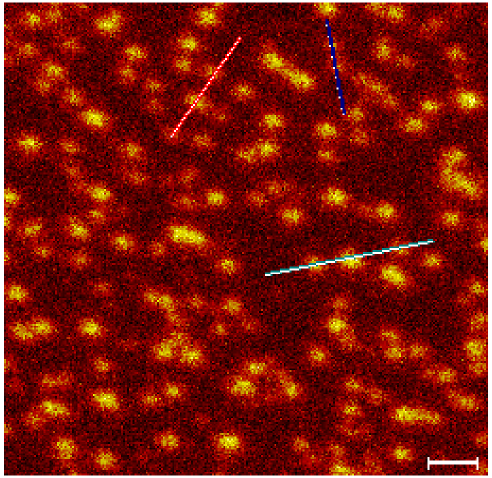
Dynamic SIMS



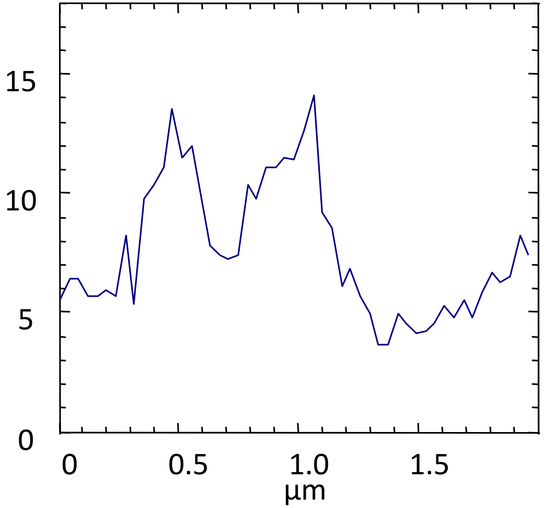
- Material removal
- Elemental analysis
- Depth profiling

Courtesy Gregory L. Fisher, Physical Electronics

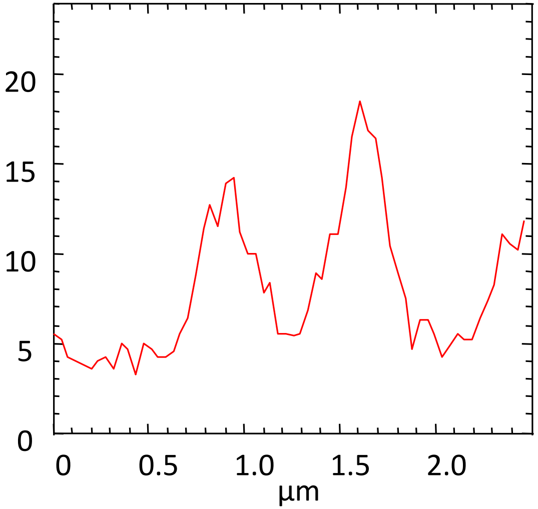
InAs/GaAs Quantum Dots

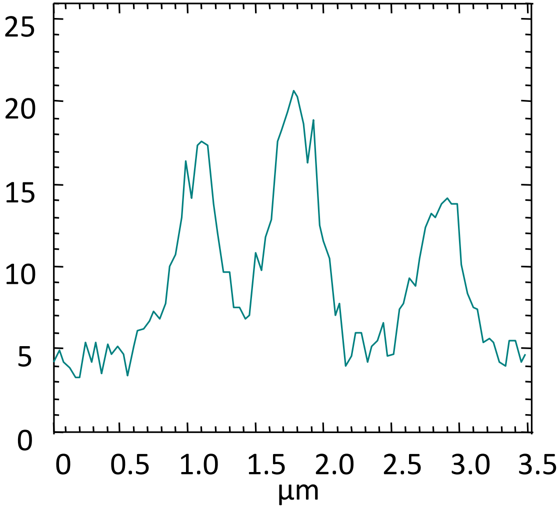


Cts: 550893; Max: 36; Scale: 1µm

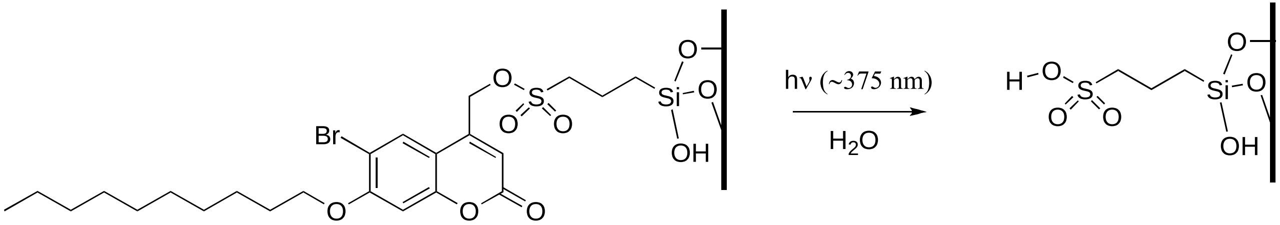


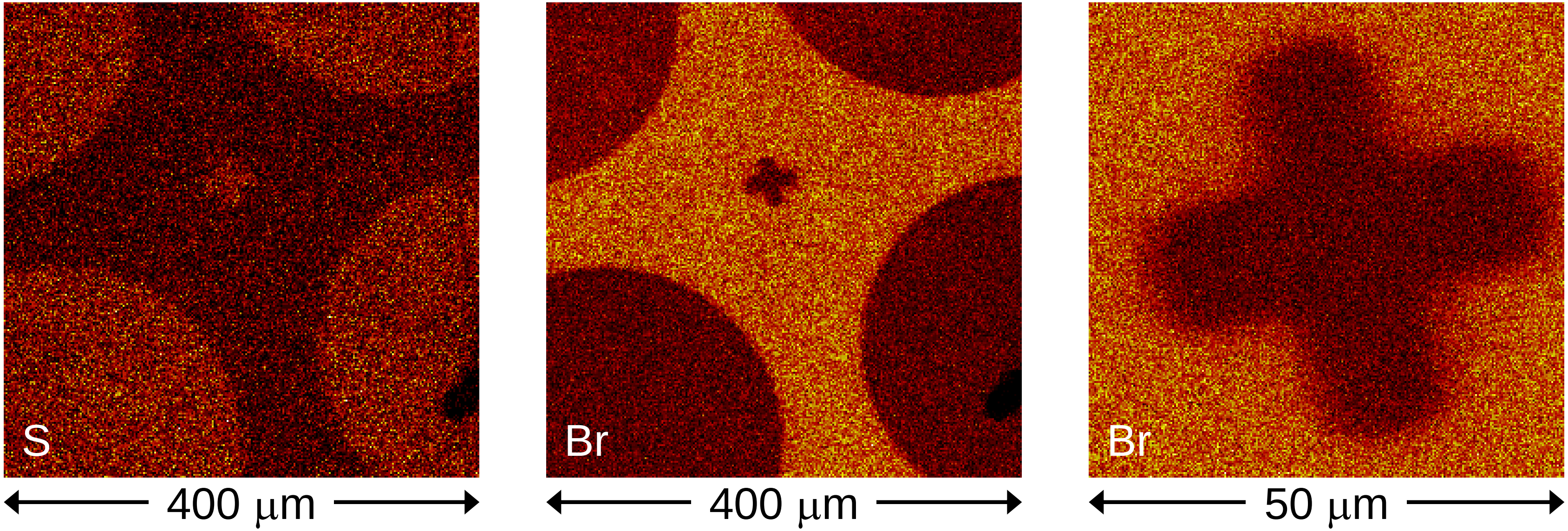
In$^+$ Linescans of Quantum Dots





TOF-SIMS Imaging of Patterned Sample

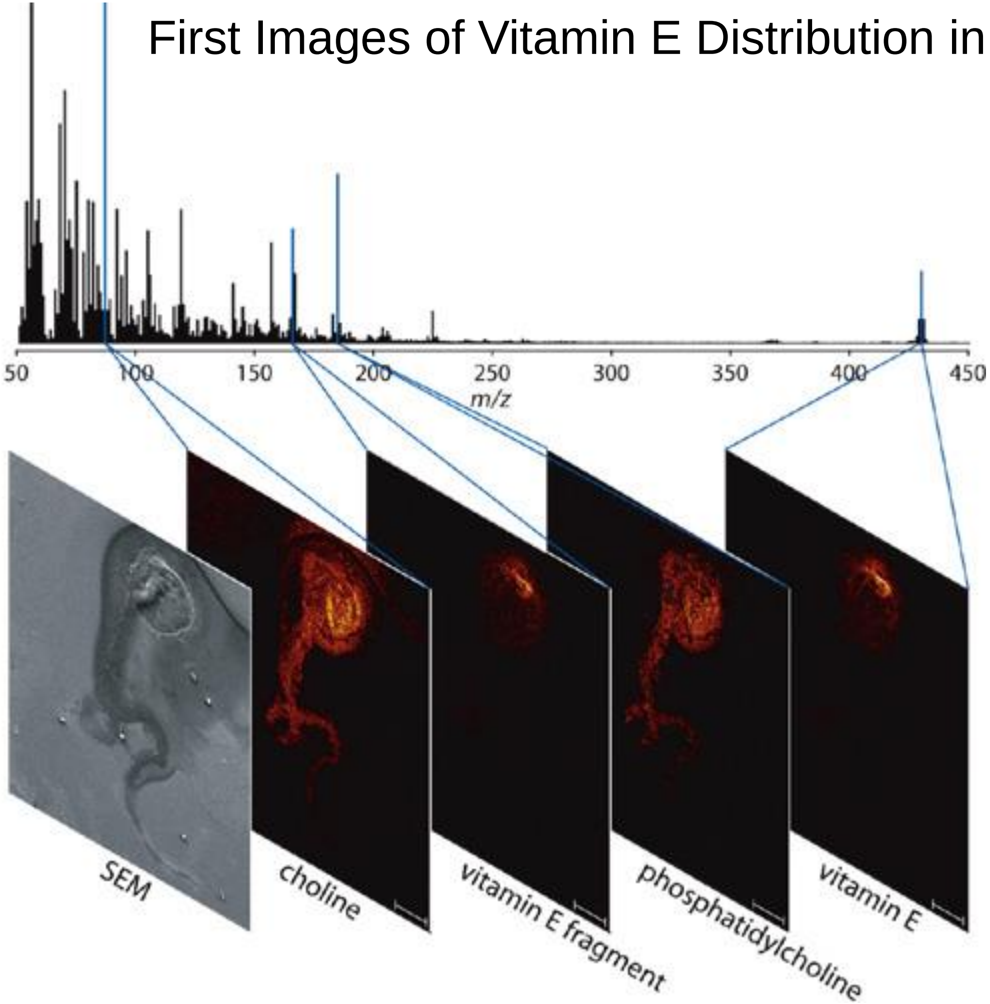




Courtesy Josh Ritchey, Audrey Bowen, Ralph Nuzzo and Jeffrey Moore, University of Illinois

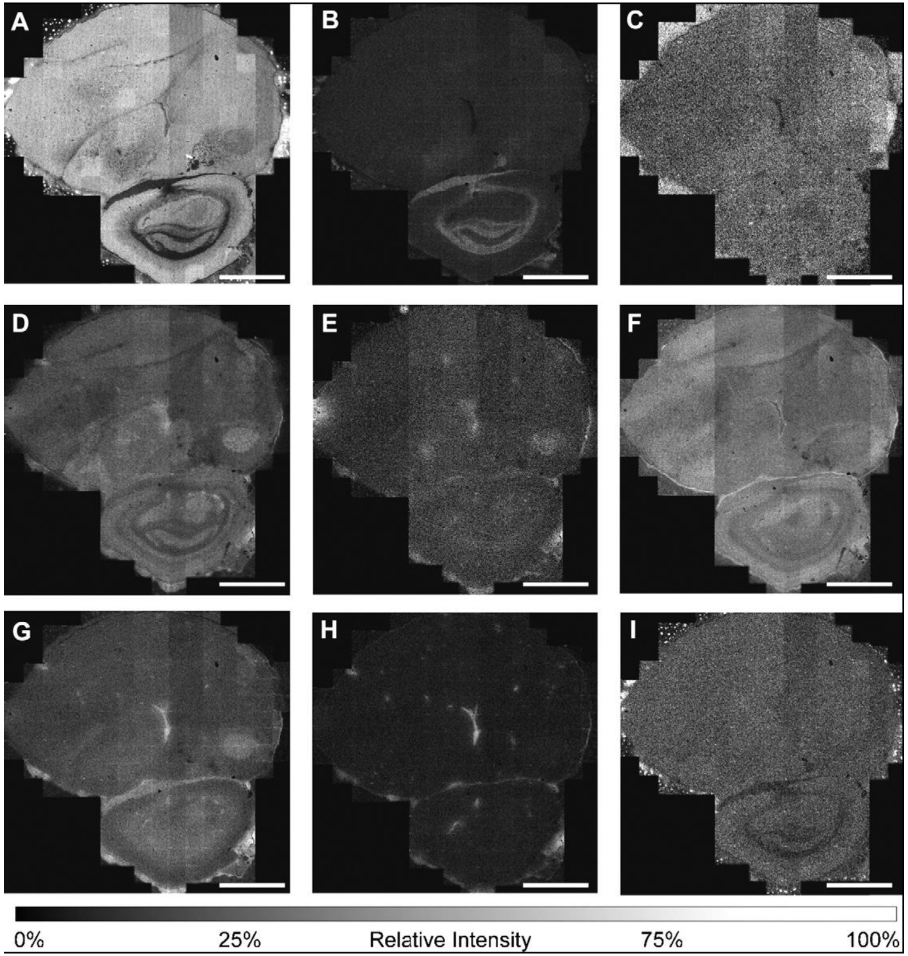
TOF-SIMS Ion Images of an Isolated Neuron

First Images of Vitamin E Distribution in a Cell



Courtesy E.B. Monroe,
J.C. Jurchen, S.S. Rubakhin,
J.V. Sweedler. University of
Illinois at Urbana-Champaign

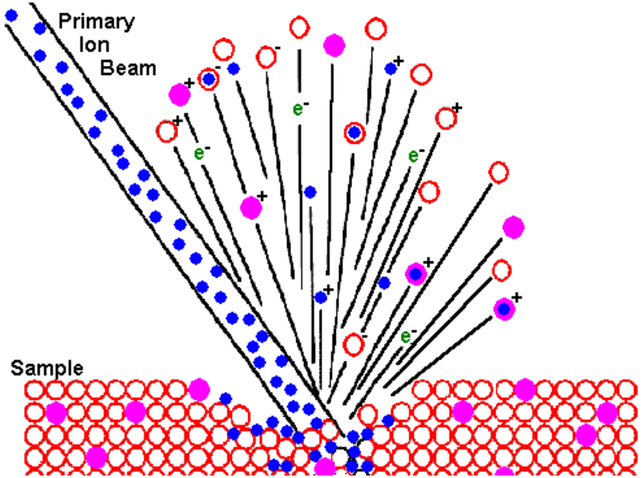
TOF-SIMS Ion Images of Songbird Brain



Selected ion images from the songbird brain. Each ion image consists of ~11.5 million pixels within the tissue section and is the combination of 194 individual 600m×600m ion images prepared on the same relative intensity scale. Ion images are (A) phosphate PO3− (*m/z* 79.0); (B) cholesterol (*m/z* 385.4); (C) arachidonic acid C20:4 (*m/z* 303.2); (D) palmitic acid C16:0 (*m/z* 255.2); (E) palmitoleic acid C16:1 (*m/z* 253.2); (F) stearic acid C18:0 (*m/z* 283.3); (G) oleic acid C18:1 (*m/z* 281.2); (H) linoleic acid C18:2 (*m/z* 279.23); and (I) -linolenic acid C18:3 (*m/z* 277.2). Scale bars = 2 mm.

Courtesy Kensey R. Amaya, Eric B. Monroe, Jonathan V. Sweedler, David F. Clayton.
International Journal of Mass Spectrometry **260**, 121 (2007).

Quantitative Surface 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

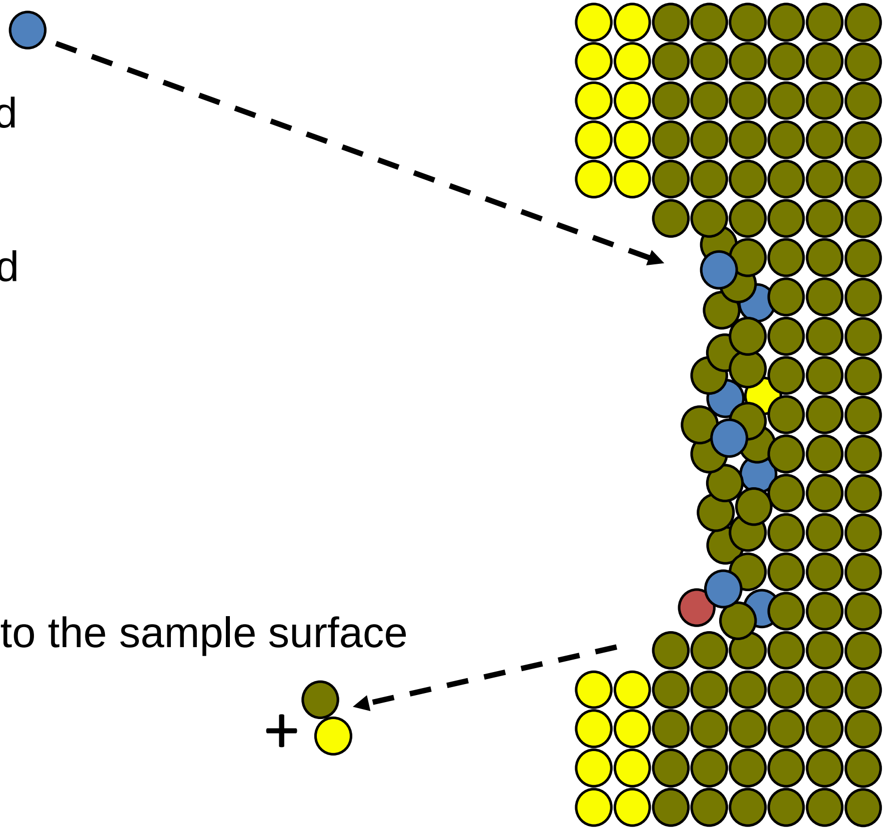
α^+ = ionization probability to positive ions

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



Courtesy of
Prof. Rockett

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

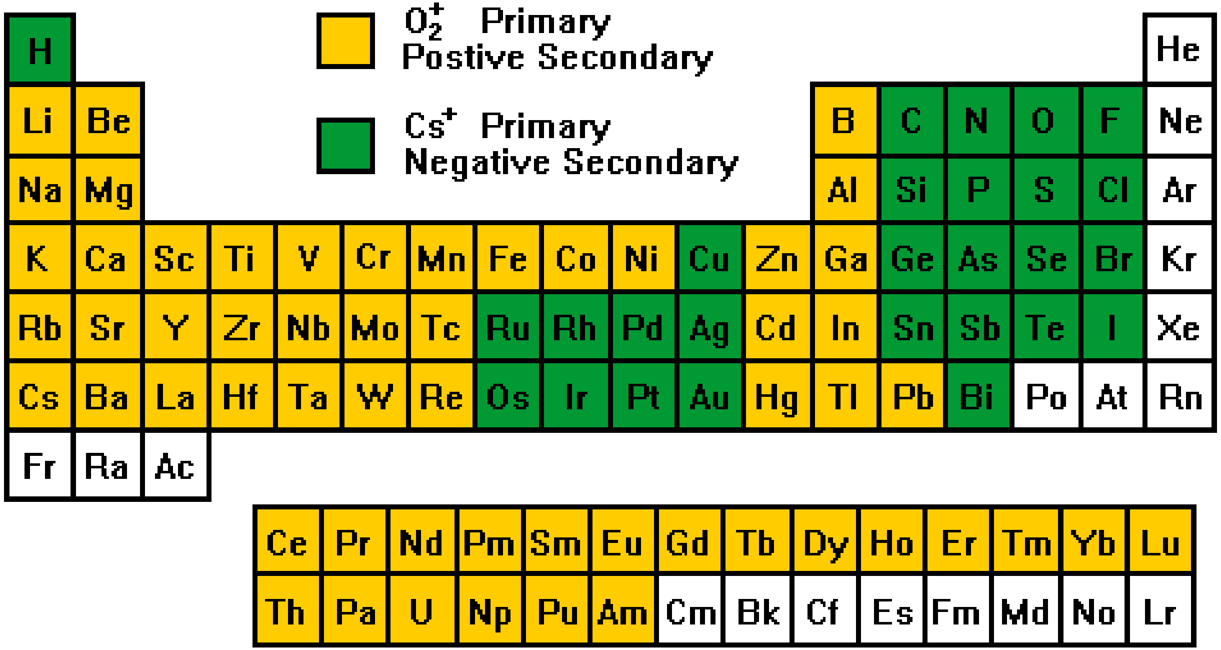
Ion sputter yield: ratio of ionized atoms sputtered to number of impinging ions, 10^{-6} to 10^{-2}

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

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

Effect of Primary Beam on Secondary Ion Yields



🟨 O_2^+ Primary
Postive Secondary

🟩 Cs^+ Primary
Negative Secondary

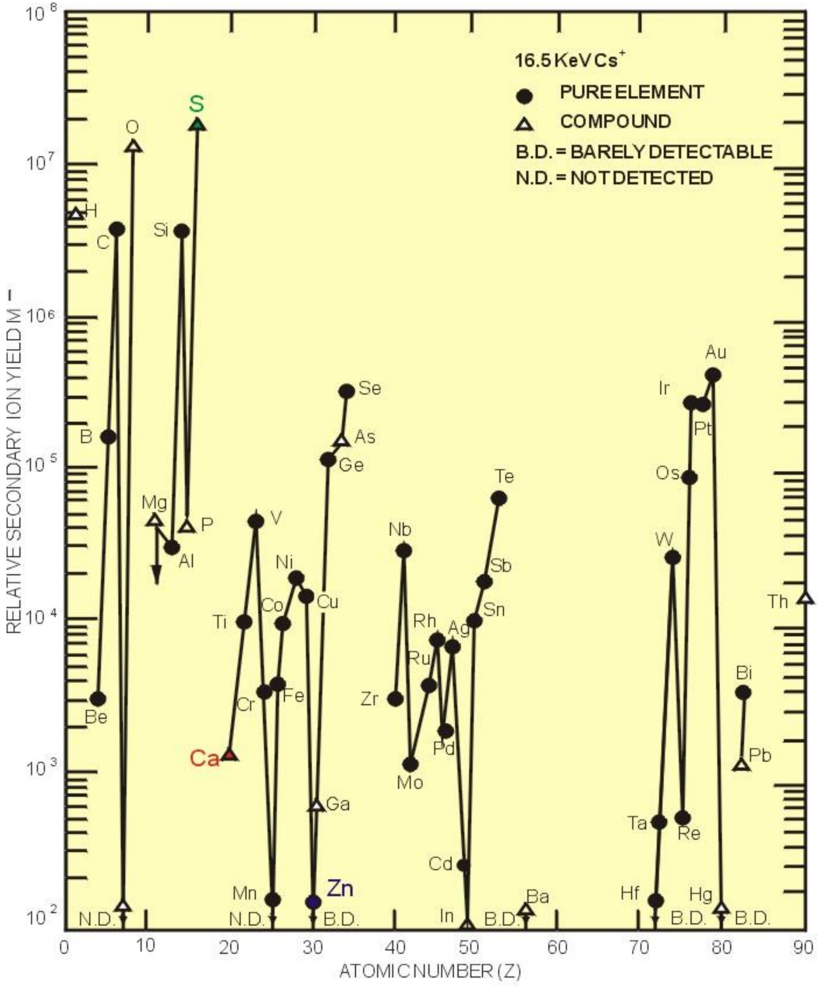
🟩 H																	He
🟨 Li	🟨 Be											🟨 B	🟩 C	🟩 N	🟩 O	🟩 F	Ne
🟨 Na	🟨 Mg											🟨 Al	🟩 Si	🟩 P	🟩 S	🟩 Cl	Ar
🟨 K	🟨 Ca	🟨 Sc	🟨 Ti	🟨 V	🟨 Cr	🟨 Mn	🟨 Fe	🟨 Co	🟨 Ni	🟩 Cu	🟨 Zn	🟨 Ga	🟩 Ge	🟩 As	🟩 Se	🟩 Br	Kr
🟨 Rb	🟨 Sr	🟨 Y	🟨 Zr	🟨 Nb	🟨 Mo	🟨 Tc	🟩 Ru	🟩 Rh	🟩 Pd	🟩 Ag	🟨 Cd	🟨 In	🟩 Sn	🟩 Sb	🟩 Te	🟩 I	Xe
🟨 Cs	🟨 Ba	🟨 La	🟨 Hf	🟨 Ta	🟨 W	🟨 Re	🟩 Os	🟩 Ir	🟩 Pt	🟩 Au	🟨 Hg	🟨 Tl	🟨 Pb	🟩 Bi	Po	At	Rn
Fr	Ra	Ac															
			🟨 Ce	🟨 Pr	🟨 Nd	🟨 Pm	🟨 Sm	🟨 Eu	🟨 Gd	🟨 Tb	🟨 Dy	🟨 Ho	🟨 Er	🟨 Tm	🟨 Yb	🟨 Lu	
			🟨 Th	🟨 Pa	🟨 U	🟨 Np	🟨 Pu	🟨 Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

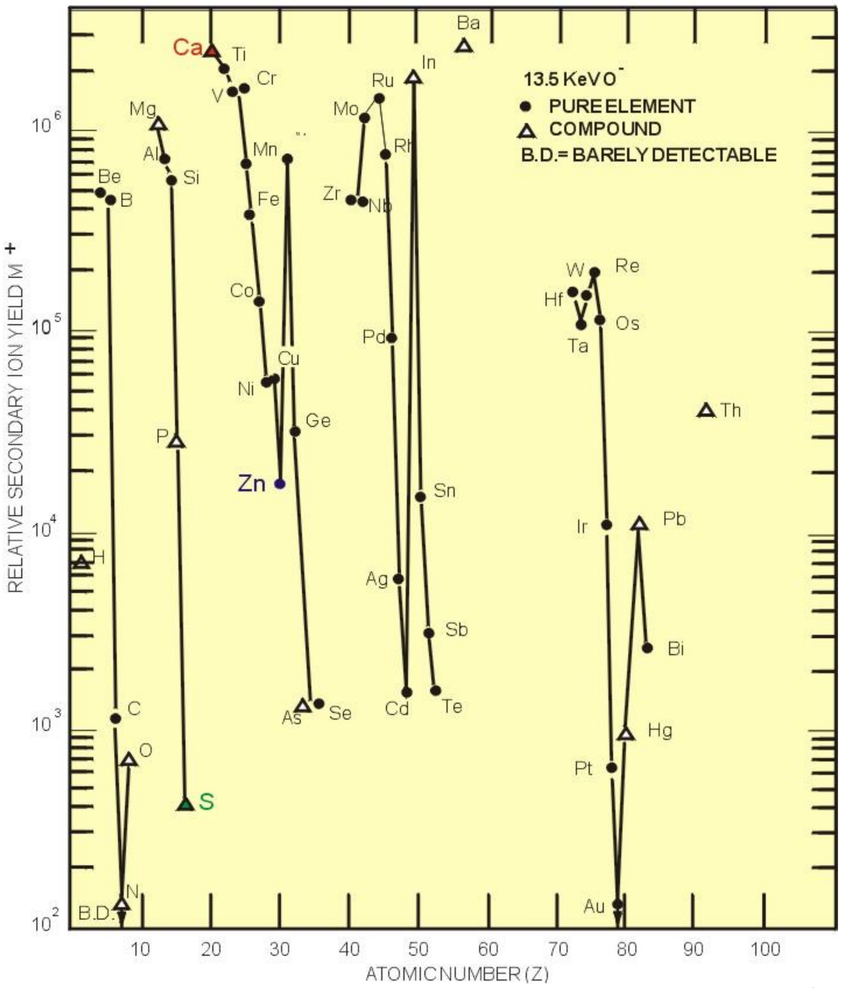
Graphics courtesy of
Charles Evans & Associates
web site
http://www.cea.com

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.

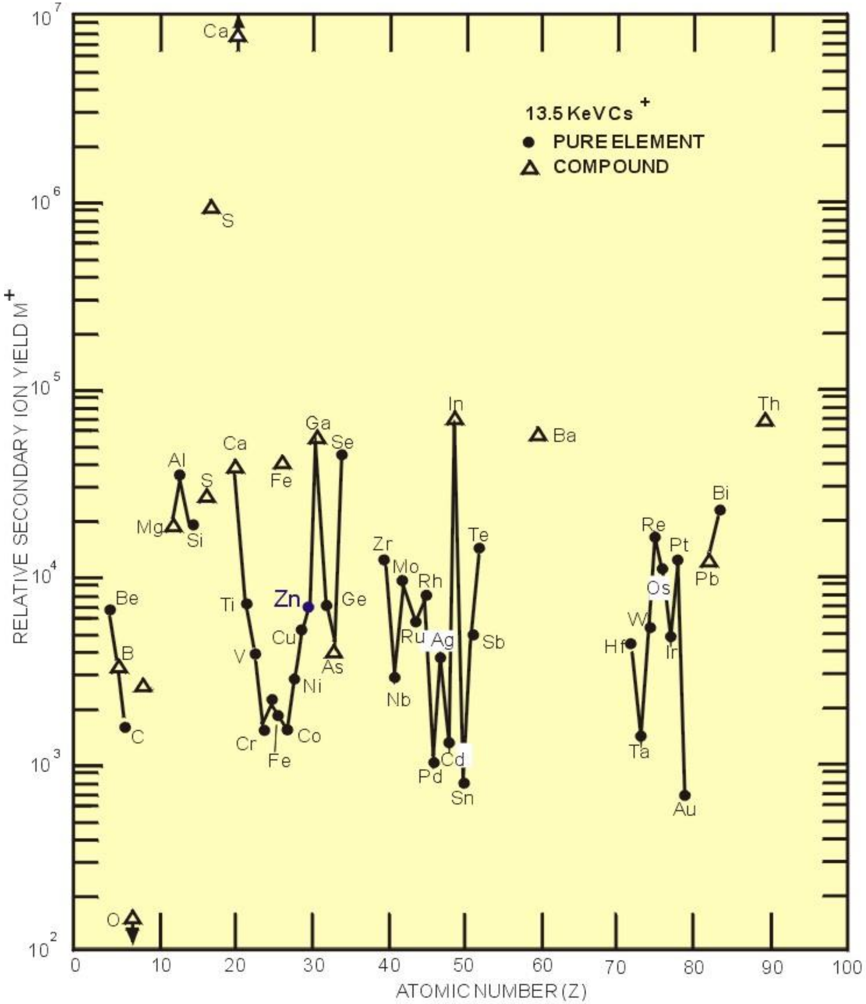
Relative Secondary Ion Yield Comparison

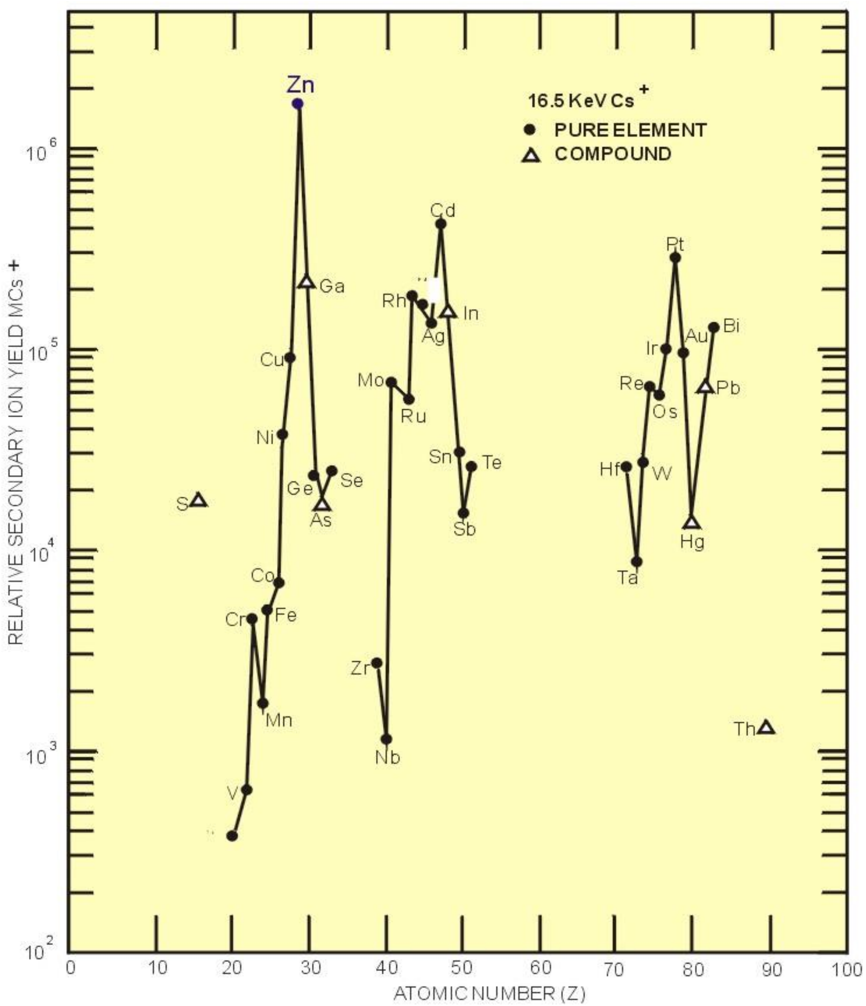




From Storms, et al., Anal. Chem. 49, 2023 (1977).

Relative Secondary Ion Yield Comparison



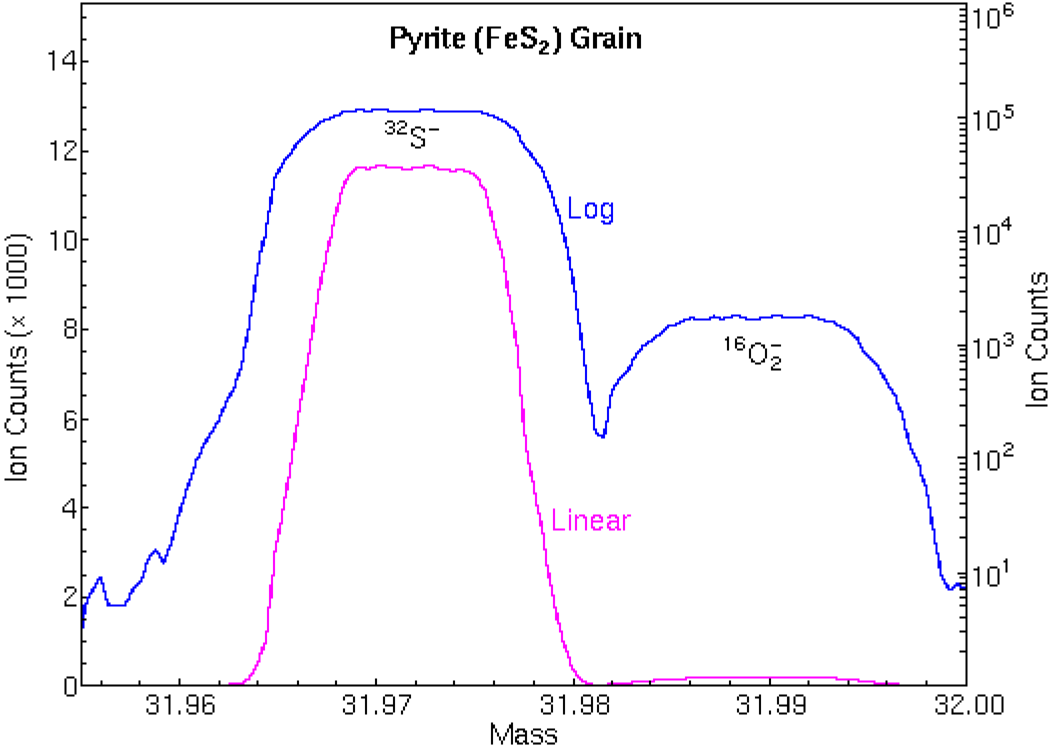


From Storms, et al., Anal. Chem. 49, 2023 (1977).

Definition of Mass Resolution

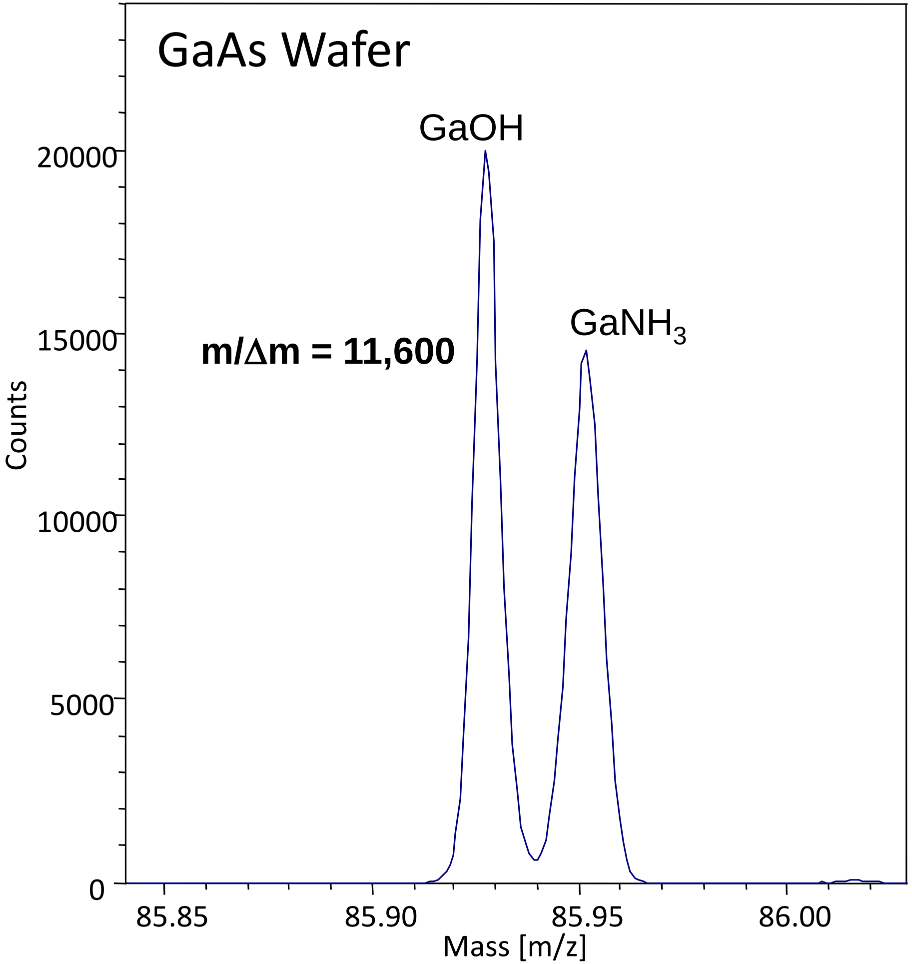
Mass resolution defined by m/Δm

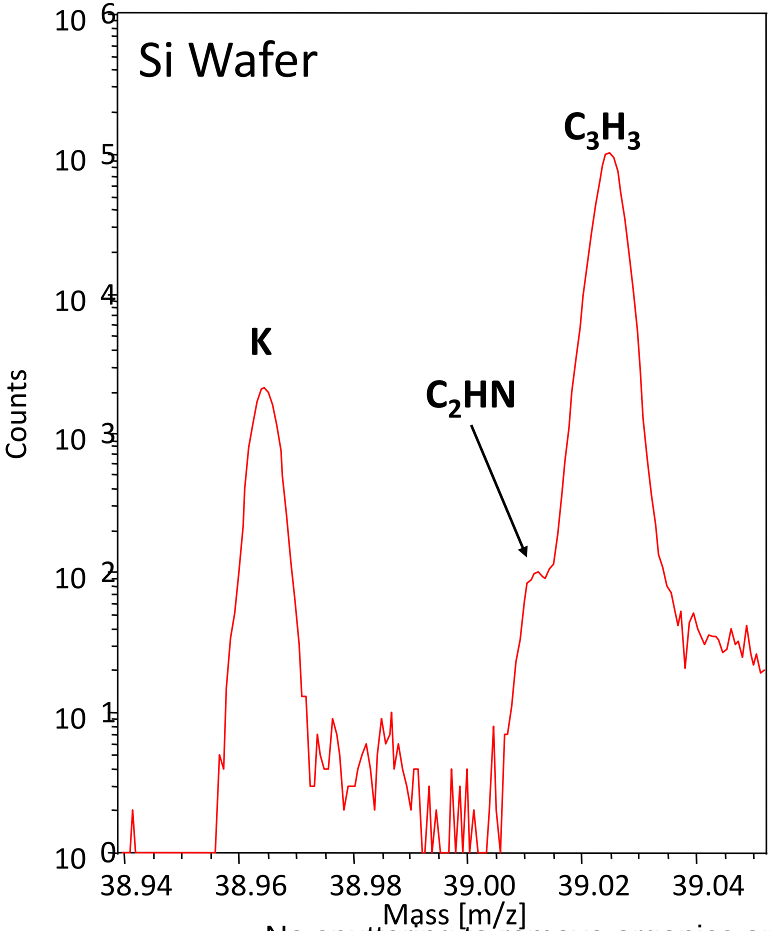
Mass resolution of ~1600 required to resolve ^{32}S from $^{16}O_2$



Graphic courtesy of Charles Evans & Associates web site
http://www.cea.com

Trace Analysis



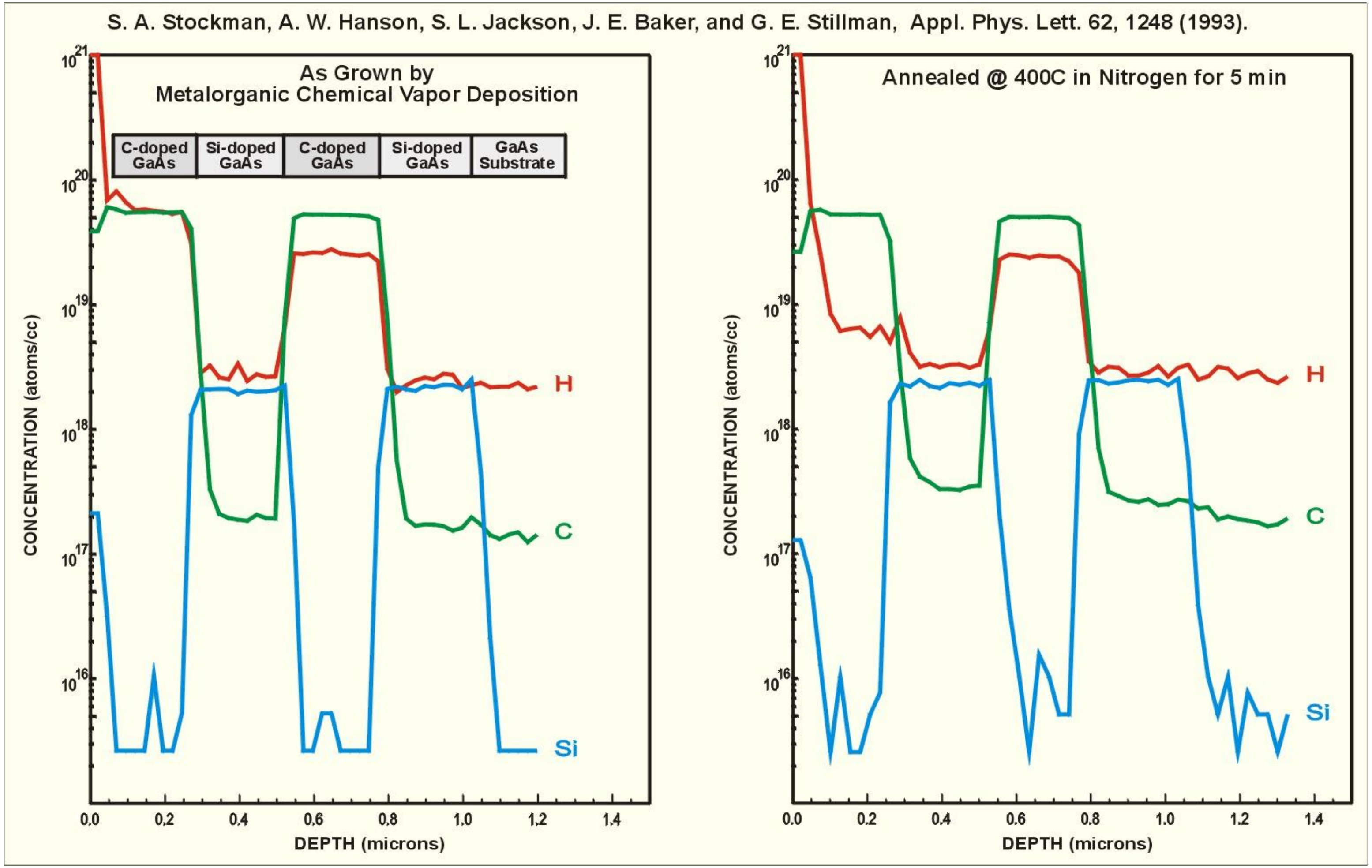


No sputtering to remove organics on surface. Large C_3H_3 peak does not have a tail to lower mass which would obscure C_2HN and K.

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

Depth Profile Application with Hydrogen



S. A. Stockman, A. W. Hanson, S. L. Jackson, J. E. Baker, and G. E. Stillman, Appl. Phys. Lett. 62, 1248 (1993).

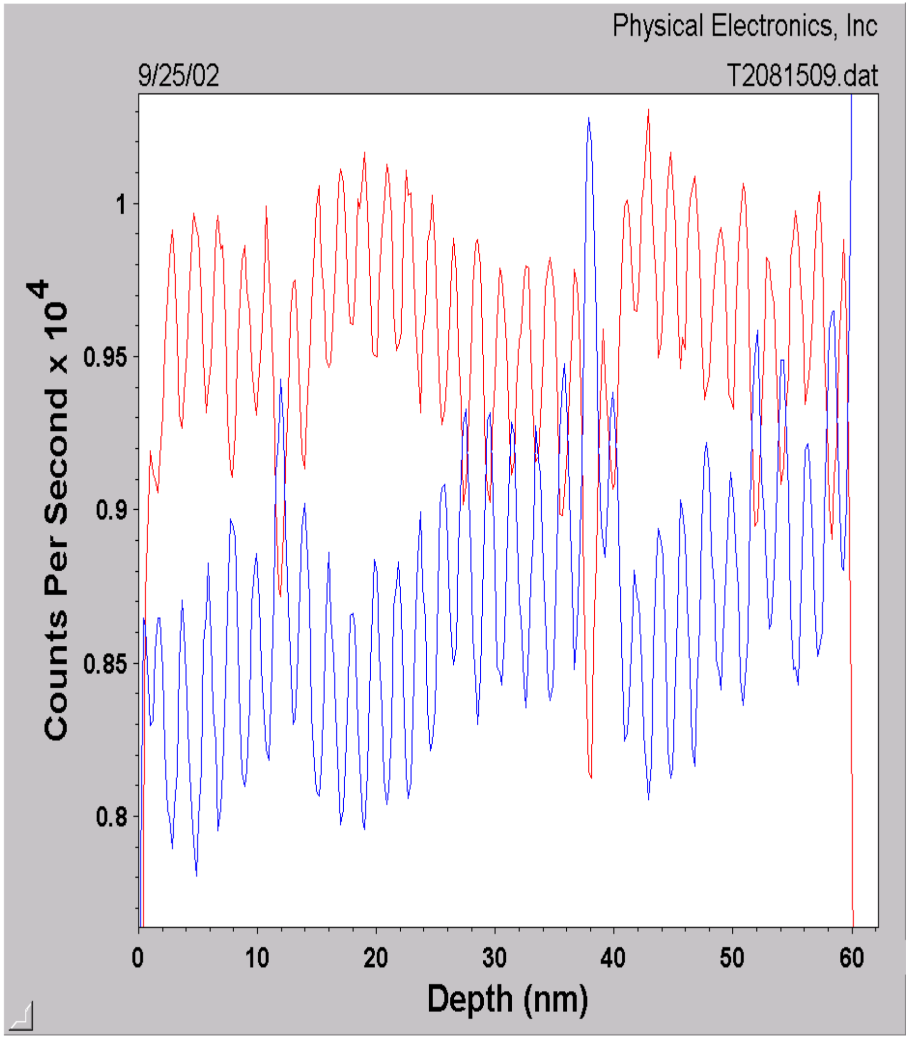
Detects hydrogen

Large dynamic range

GaAs/AlGaAs Depth Profile

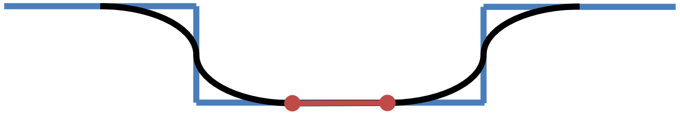
Al

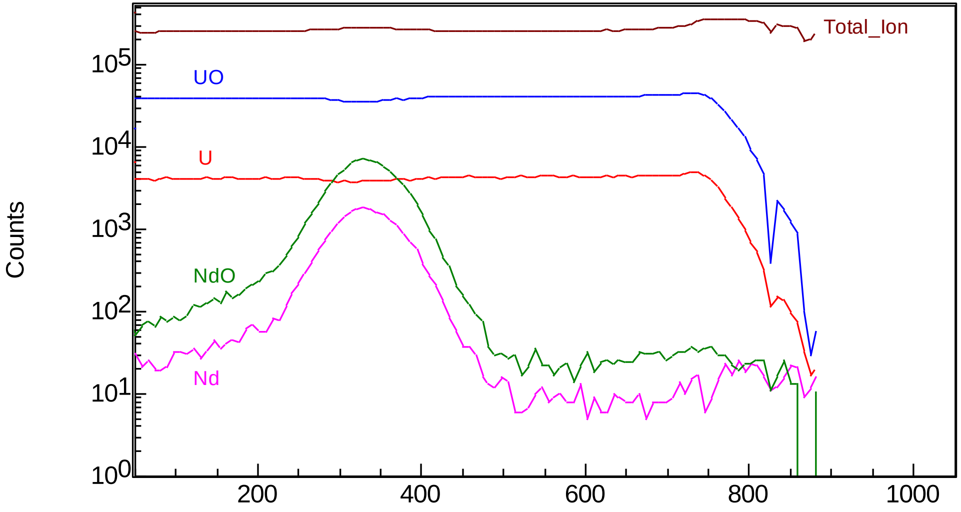
Ga

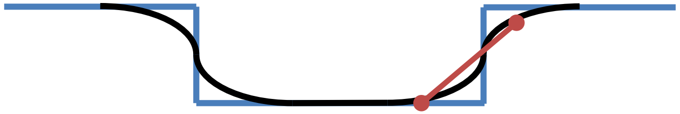


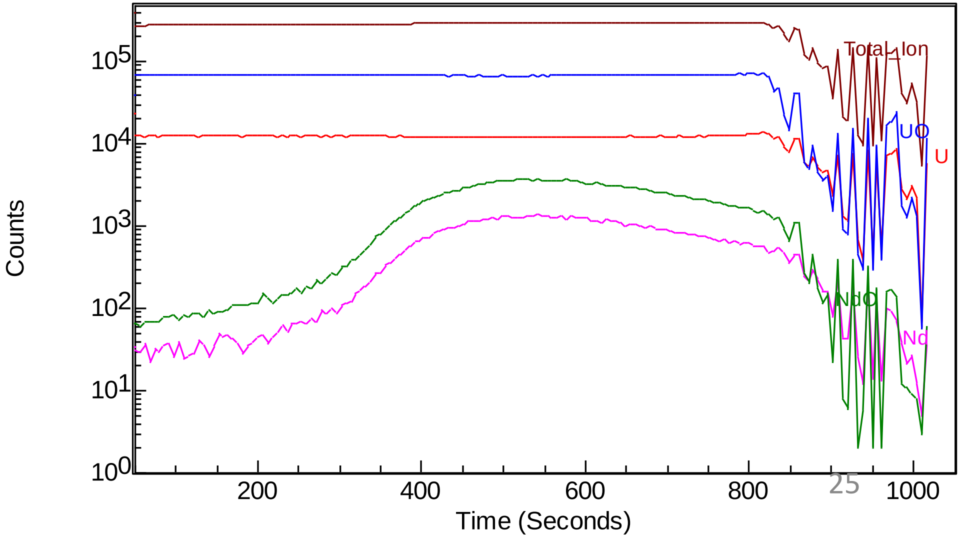
Analysis beam: 15kV Ga^+
Sputter Beam: 300V O_2^+
with oxygen flood

Depth Profile Beam Alignment







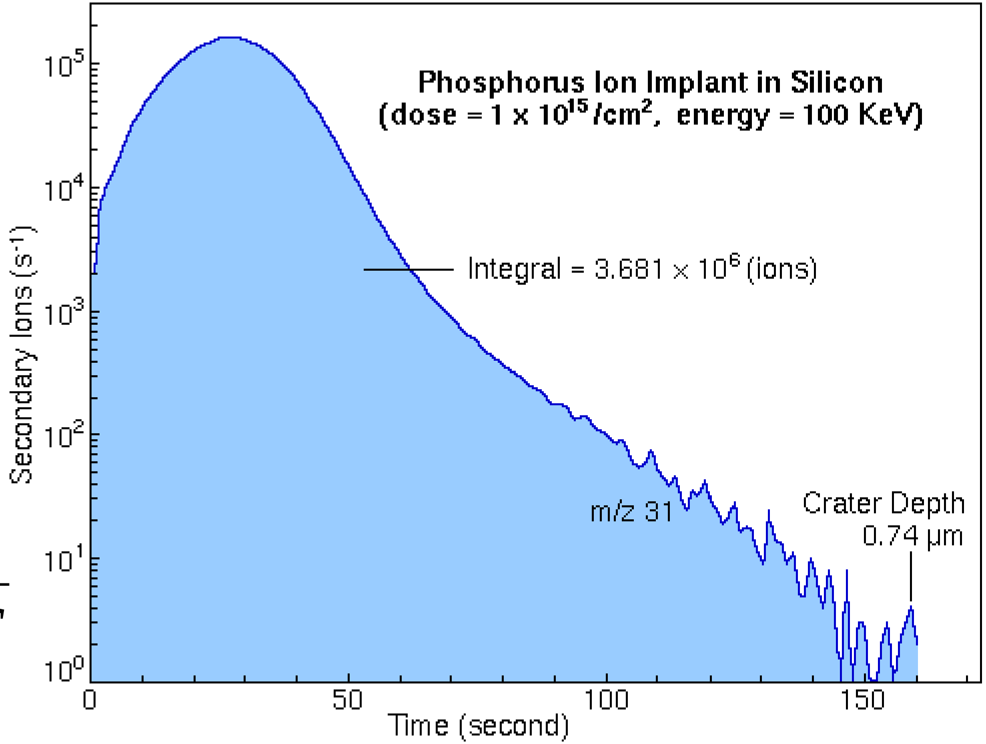


Determination of RSF Using Ion Implants

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

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

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



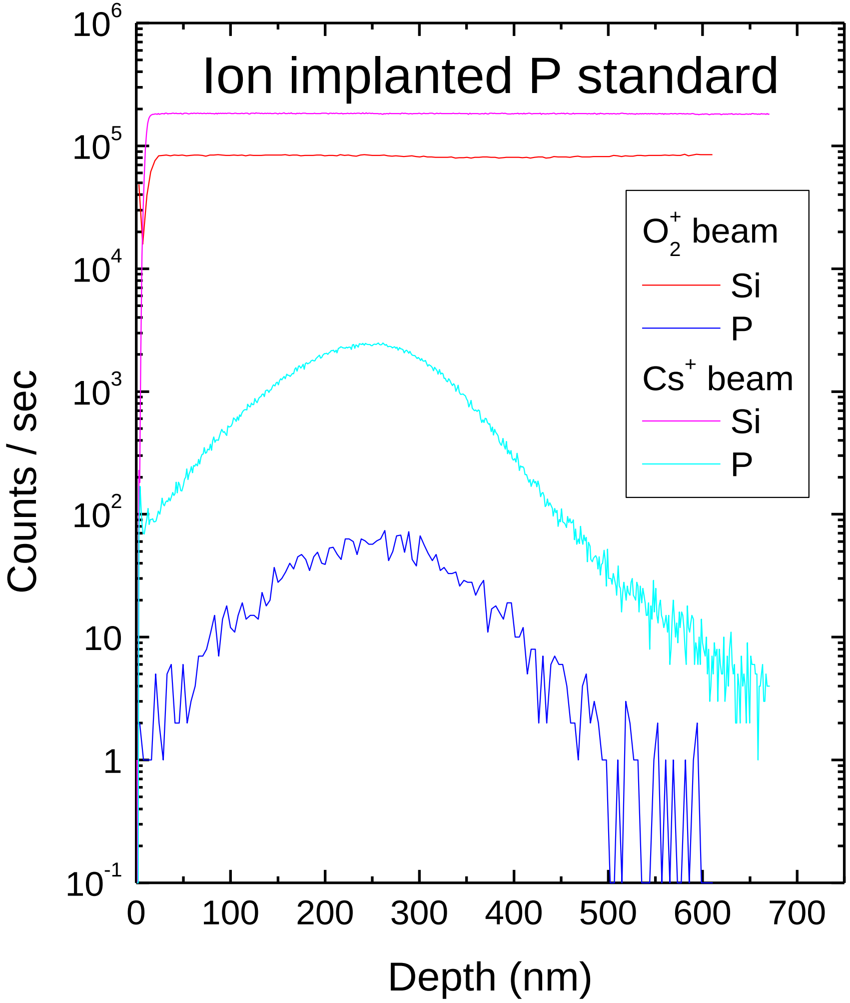
Where:

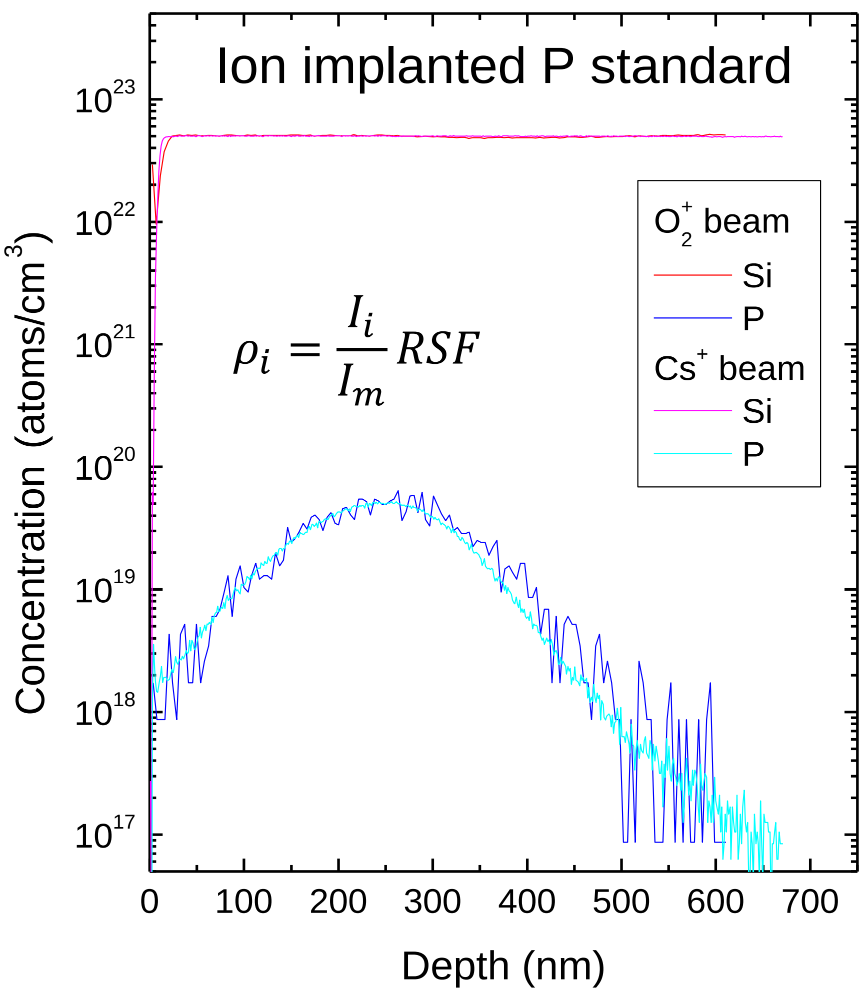
RSF = Relative Sensitivity Factor
I_m, I_i = ion intensity (counts/sec)
ρ = atom density (atoms/cm^3)
ϕ = implant fluence (atoms/cm^2)

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

Graphics courtesy of
Charles Evans & Associates web site
http://www.cea.com

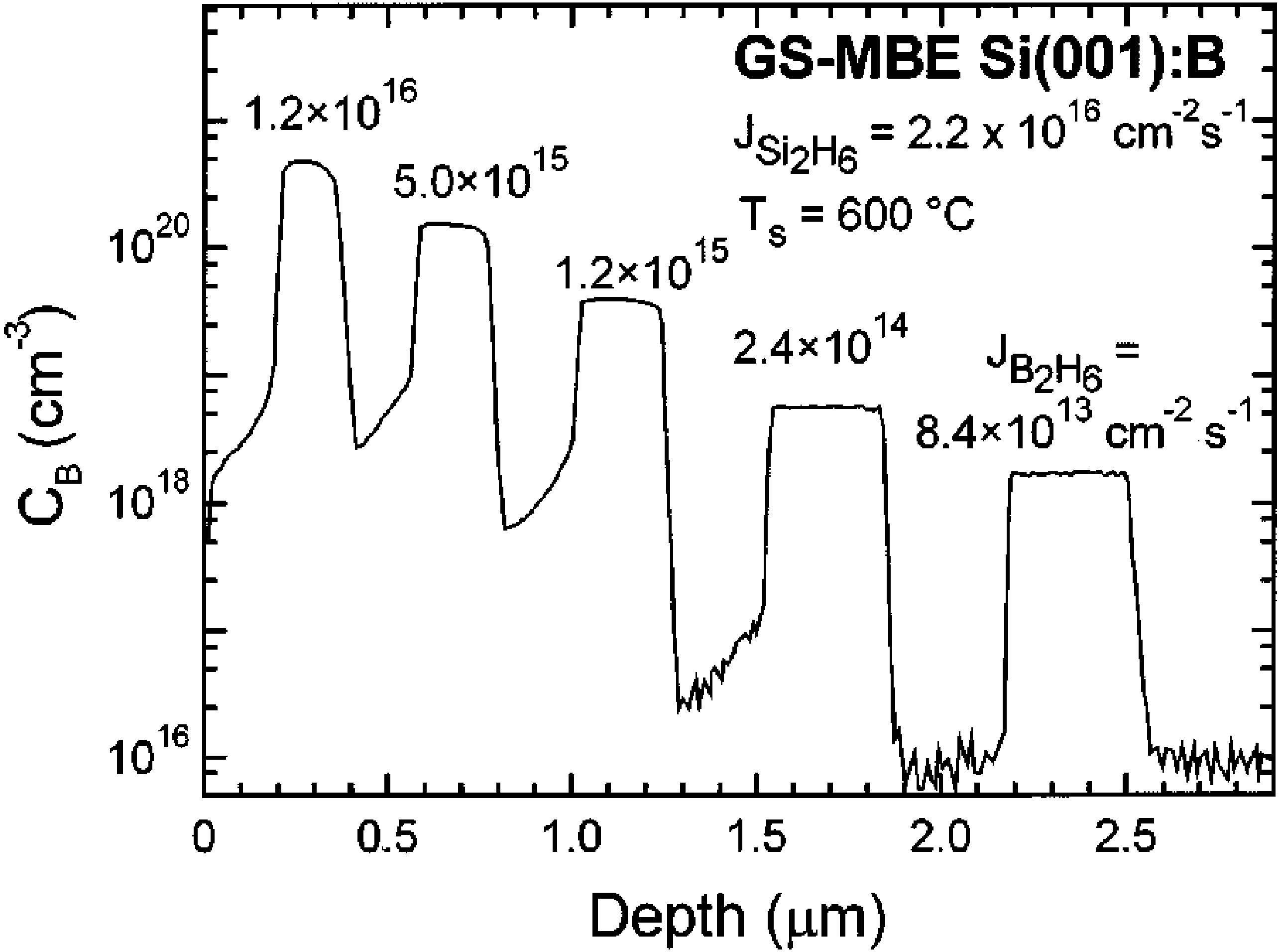
Positive and Negative Secondary Ions





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

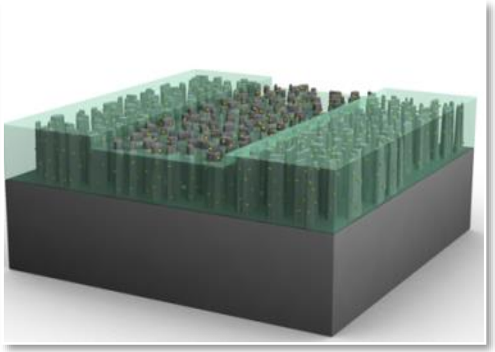
B Depth Profile in Si(001)



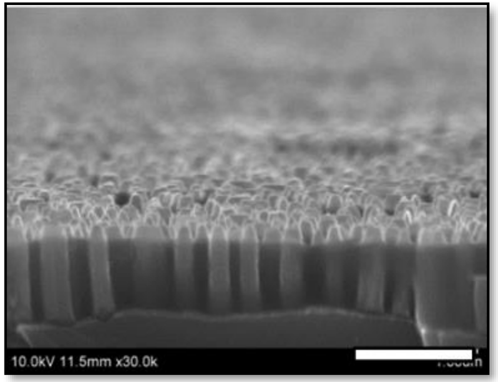
SIMS depth profiles through a B modulation-doped Si(001):B film grown by GS-MBE from Si_2H_6 and B_2H_6 at T_s=600 °C. The incident Si_2H_6 flux was J_{Si2H6} = 2.2×10^{16} cm^{-2} s^{-1} while the B flux J_{B2H6} was varied from 8.4×10^{13} to 1.2×10^{16} cm^{-2} s^{-1}. The deposition time for each layer was constant at 1 h.

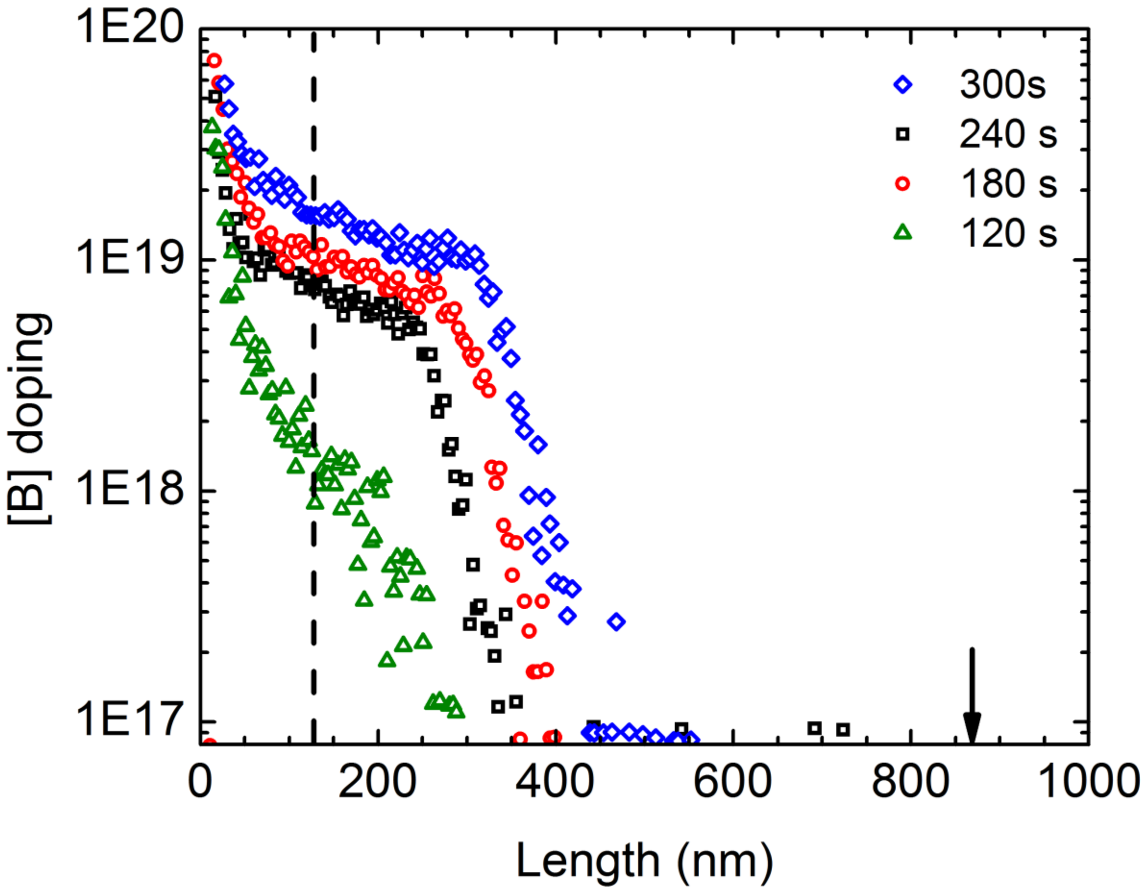
G. Glass, H. Kim, P. Desjardins,
N. Taylor, T. Spila, Q. Lu, and J. E. Greene.
Phys. Rev. B, **61**,7628 (2000).

Electrolessly etched silicon nanowire arrays



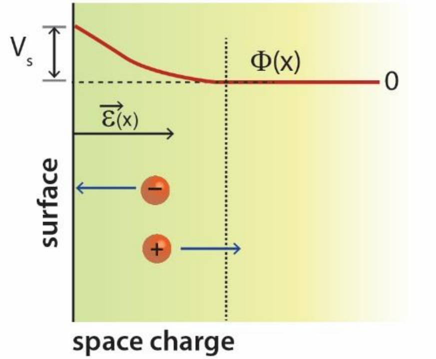
Dope NW tips by SODs





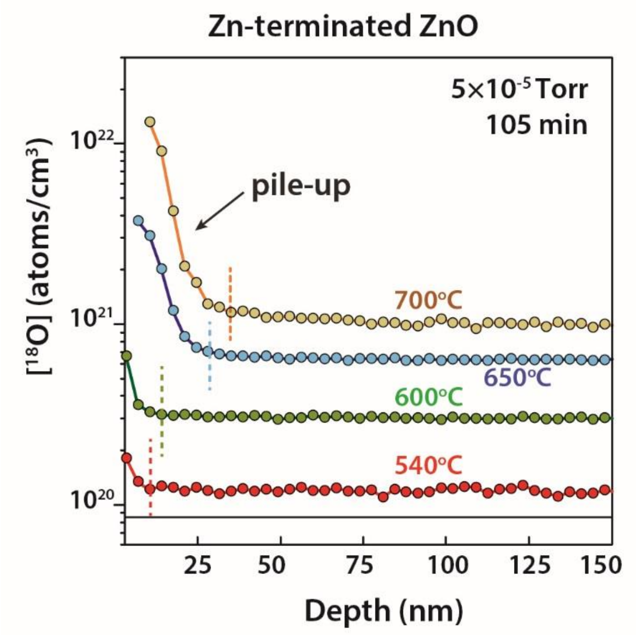
J.S Sadhu, H. Tian, T. Spila, J. Kim, B. Azeredo, P. Ferreira, and S. Sinha. *Nanotechnology* **25**, 375701 (2014).

Defect Engineering via Near-Surface Electrostatic Effects



Charged point defects interact with space charge in the near-surface region via 3 mechanisms

1. Field-induced drift (O in TiO_2)[1]
2. Change in charge state of defect with local potential (B in Si)[2]
3. Potential energy-dependent formation energy of V_O (O in $SrTiO_3$)[3]



^{18}O piles up in the first 10-30 nm in ZnO and TiO_2[1]

- Amount of pile-up (P) = integrated area between pile-up and bulk extrapolated profiles

Analytical model quantifies effects[4]

- Drift opposite to diffusion causes pile-up
- Drift in diffusion direction depletes near-surface of mobile defects
- P increases linearly with time & flux, quadratically with V_S
- V_s of only a few meV can cause the amount of pile-up observed

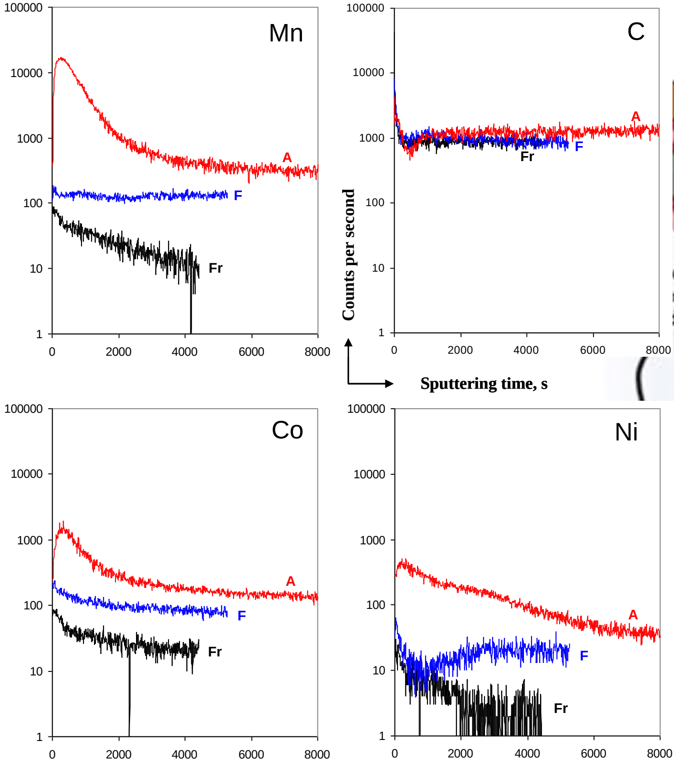
[1] P. Gorai et al., *Appl. Phys. Lett.* **103**, 141601 (2013).

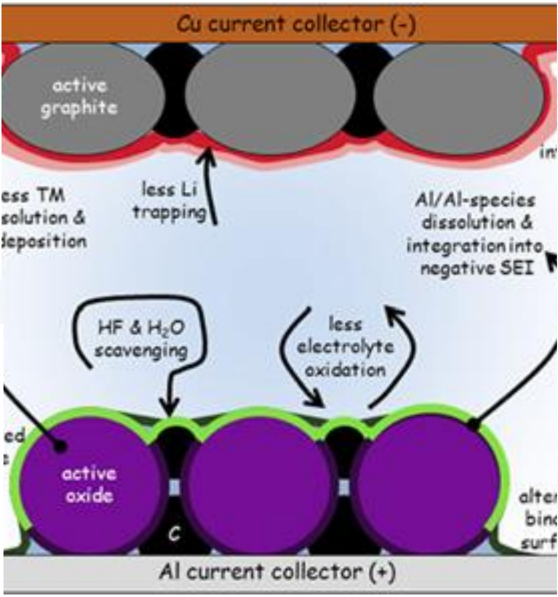
[2] P. Gorai et al., *J. Appl. Phys.* **111**, 094510 (2012).

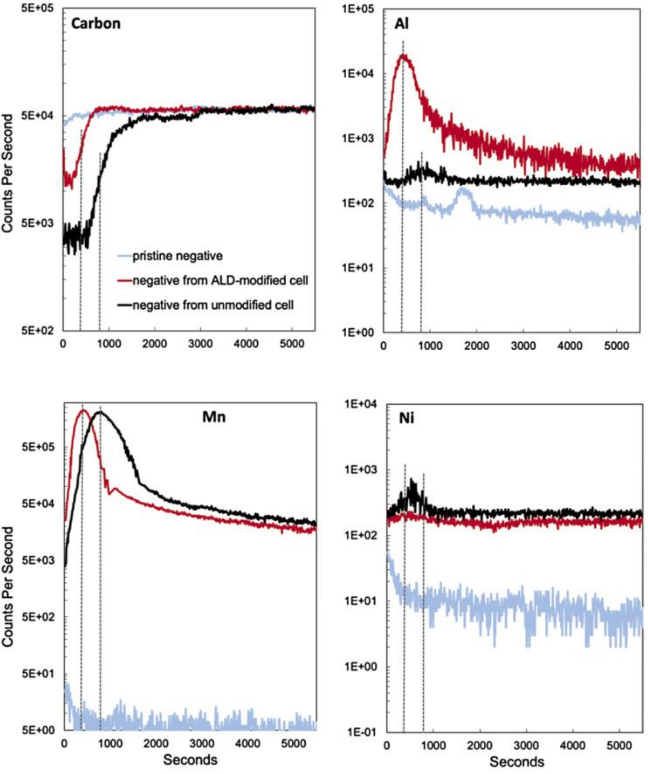
[3] R.A. De Souza and M. Martin, *PCCP* **10**, 2356 (2008).

[4] P. Gorai and E. G. Seebauer, *Appl. Phys. Lett.* 105, 021604 (2014).

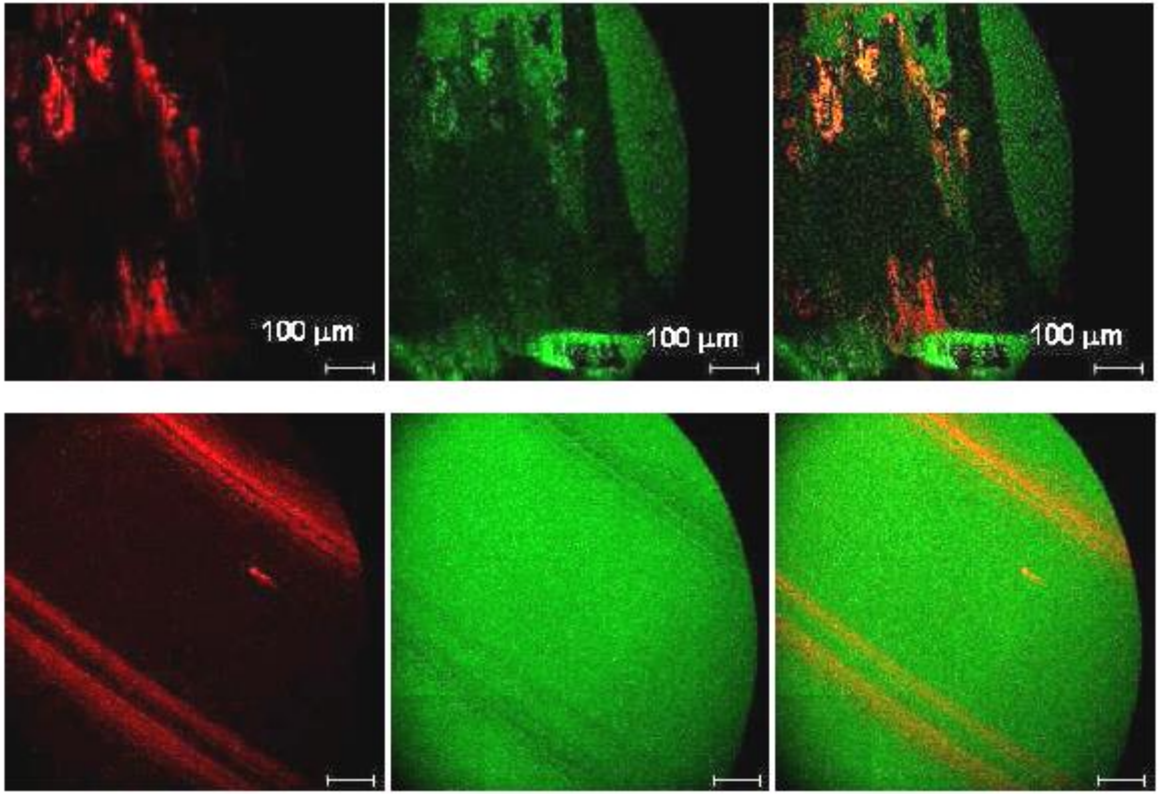
Transition-Metal Accumulation on Anodes in Li-ion Batteries







Diamond-Like-Carbon Friction Testing



DLC coated ball

DLC coated disk

Oxygen

Carbon

C + O
Overlay

wear tracks and scars formed on DLC-coated disk and ball sides during test in dry oxygen

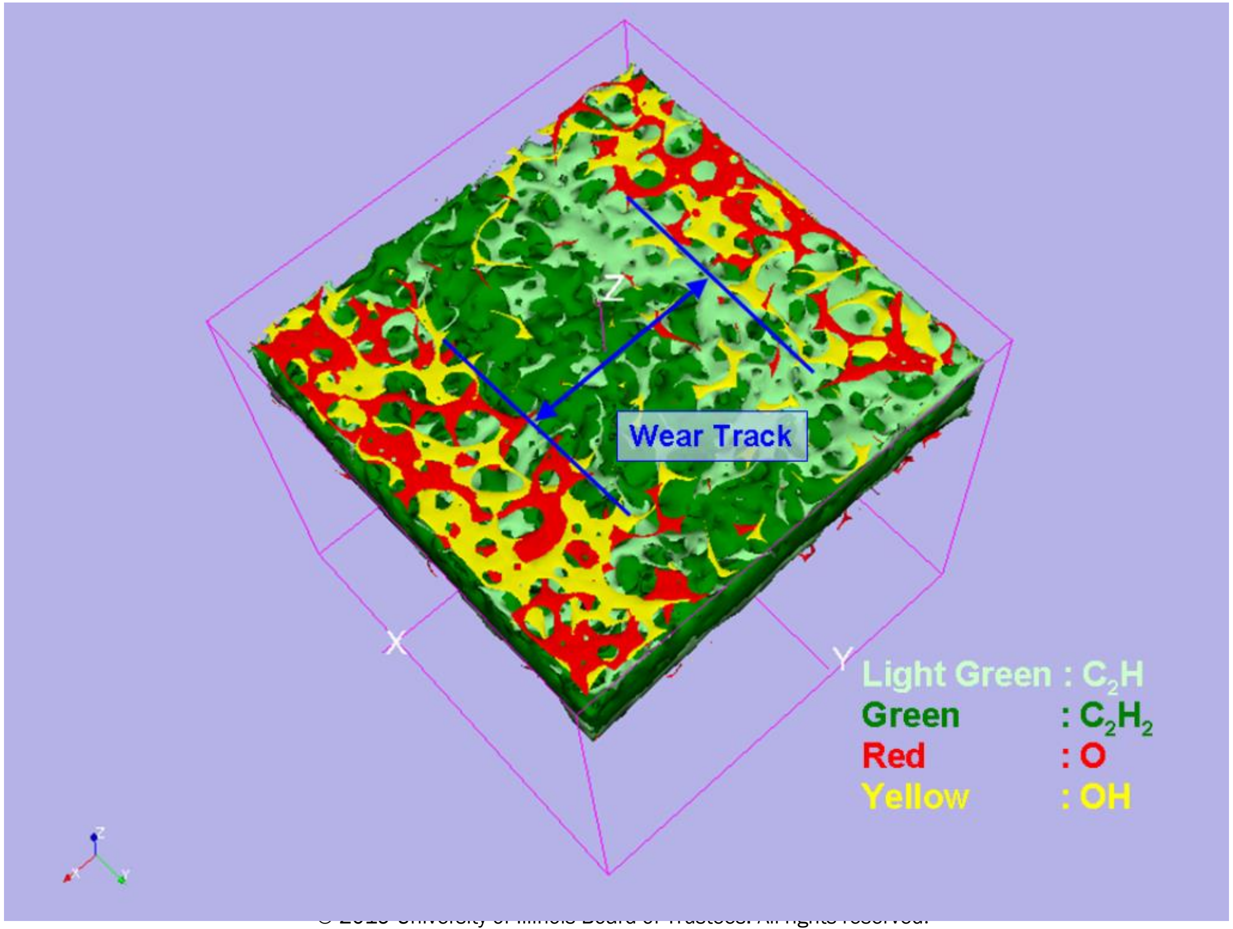
Courtesy O.L. Eryilmaz and A. Erdemir
Energy Systems Division,
Argonne National Laboratory
Argonne, IL 60439 USA

3-D TOF-SIMS imaging of DLC

Wear track from hydrogenated DLC tested in dry nitrogen

Courtesy O.L. Eryilmaz and A. Erdemir

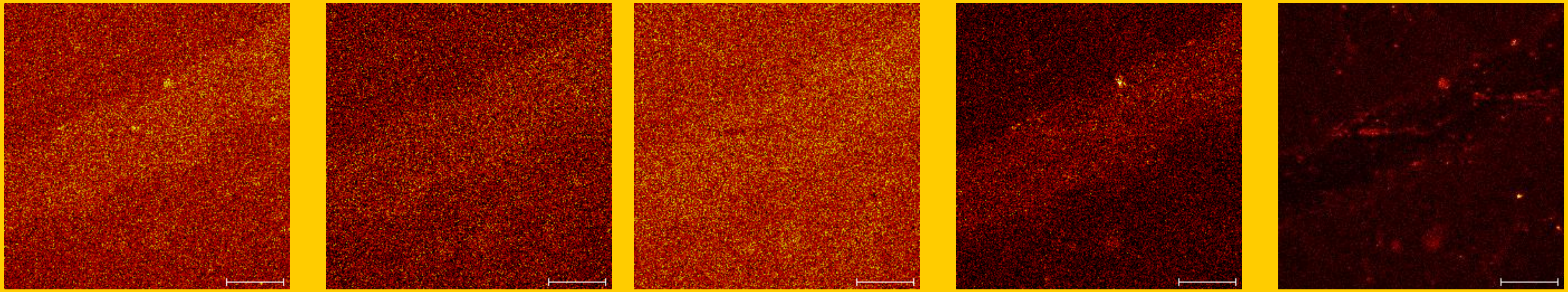
Energy Systems Division, Argonne National Laboratory Argonne, IL 60439 USA



3-D TOF-SIMS Movies of DLC

NFC6 H2 Environment TOF-SIMS Images

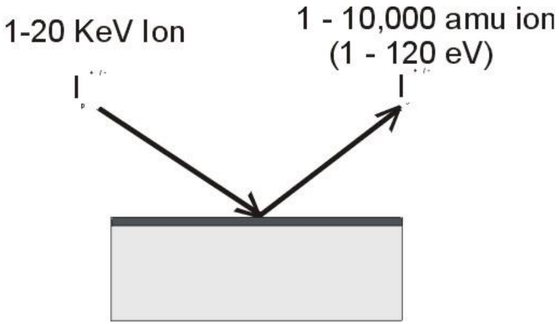
Courtesy O.L. Eryilmaz and A. Erdemir
Energy Systems Division, Argonne National Laboratory Argonne, IL 60439 USA



H **CH** **C_2H** **C_2H_2** **O**

SIMS Summary

Probe/Detected Species



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 µm - several mm/0.5 - 1nm

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A New Method to Probe the Composition of Cellular Organelles

Ashley Ellsworth[1], Corryn E. Chini[2], Ben Johnson[3],
Michael M. Tamkun[3], Gregory L. Fisher[1], and Mary L. Kraft[2]

[1] Physical Electronics, Chanhassen, MN, USA
[2] University of Illinois at Urbana-Champaign, School of Chemical Sciences, Urbana, IL, USA
[3] Colorado State University, Department of Biomedical Science, Fort Collins, CO, USA

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