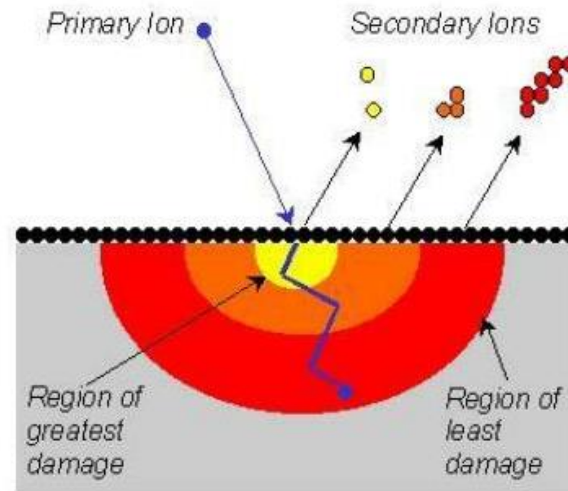
Principle and Applications of ToF-SIMS



Xinqi Chen

Keck-II

Introduction of Keck-II Instruments

XPS

ToF-SIMS

FT-IR

Mode:

- Transmission
- ATR
- DRIFT

Sample:

- Powder
- Film
- Solution
- Gel
- Micrometer spot

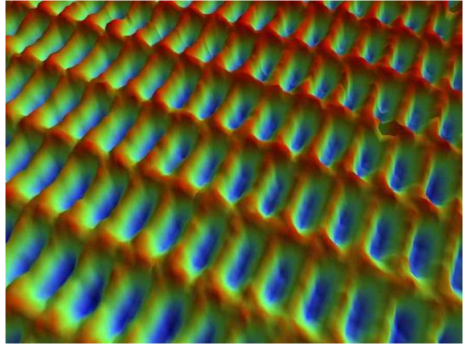
Bruker Lumos IR Microscope

Thermo Nicolet iS50 FT-IR spectrometer

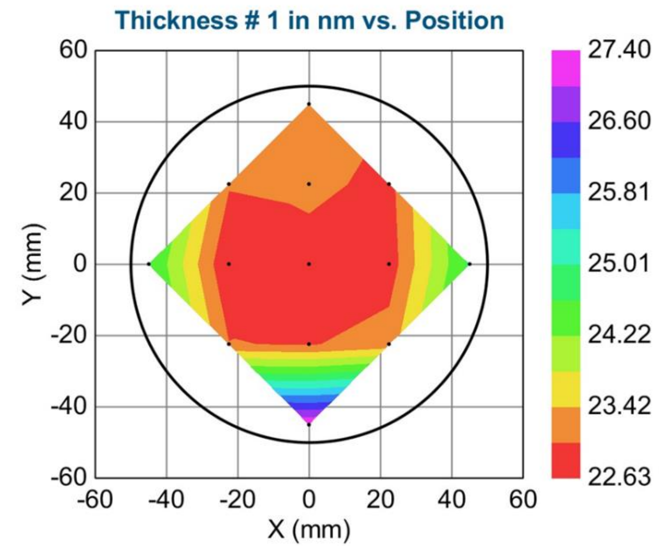
Surface Profiler

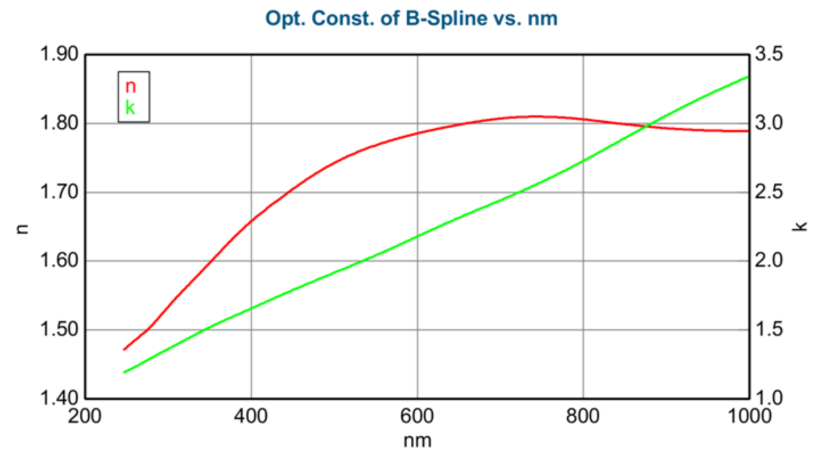
Optical profilometer
(3D optical microscope)

Stylus profilometer



Ellipsometer



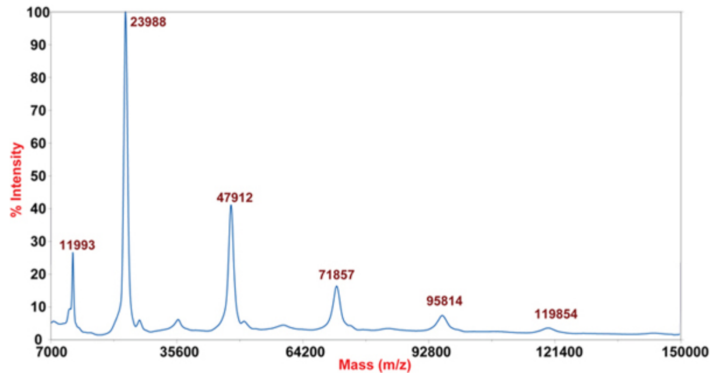


Zetasizer Nano ZS

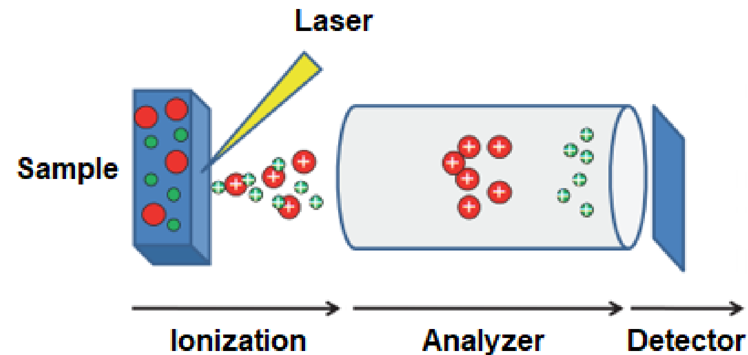
	Particle Size and Molecular Size	Zeta Potential (particle size diameter)	Molecular Weight
Measurement range:	0.3nm – 10.0 microns (diameter)	3.8nm – 100 microns	980Da – 20M Da
Measurement principle:	Dynamic Light Scattering	Electrophoretic Light Scattering	Static Light Scattering Using Debye Plot
Sample volume range:	12 – 20 µL	150µL	12 – 20 µL
Sample concentration:	Up to 40%w/v		
Temperature Range:	0 – 120 °C		

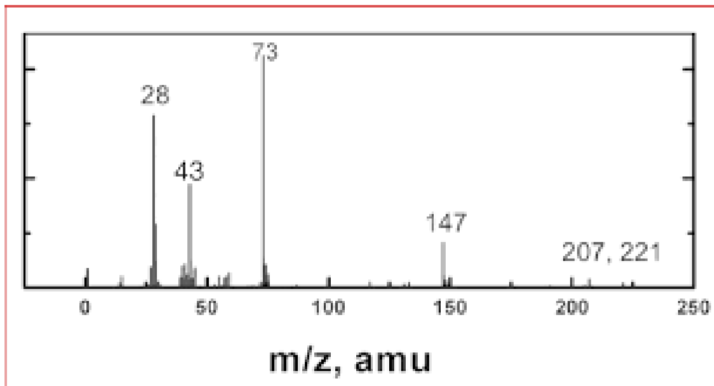
Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Not ToF MS (laser, solution)

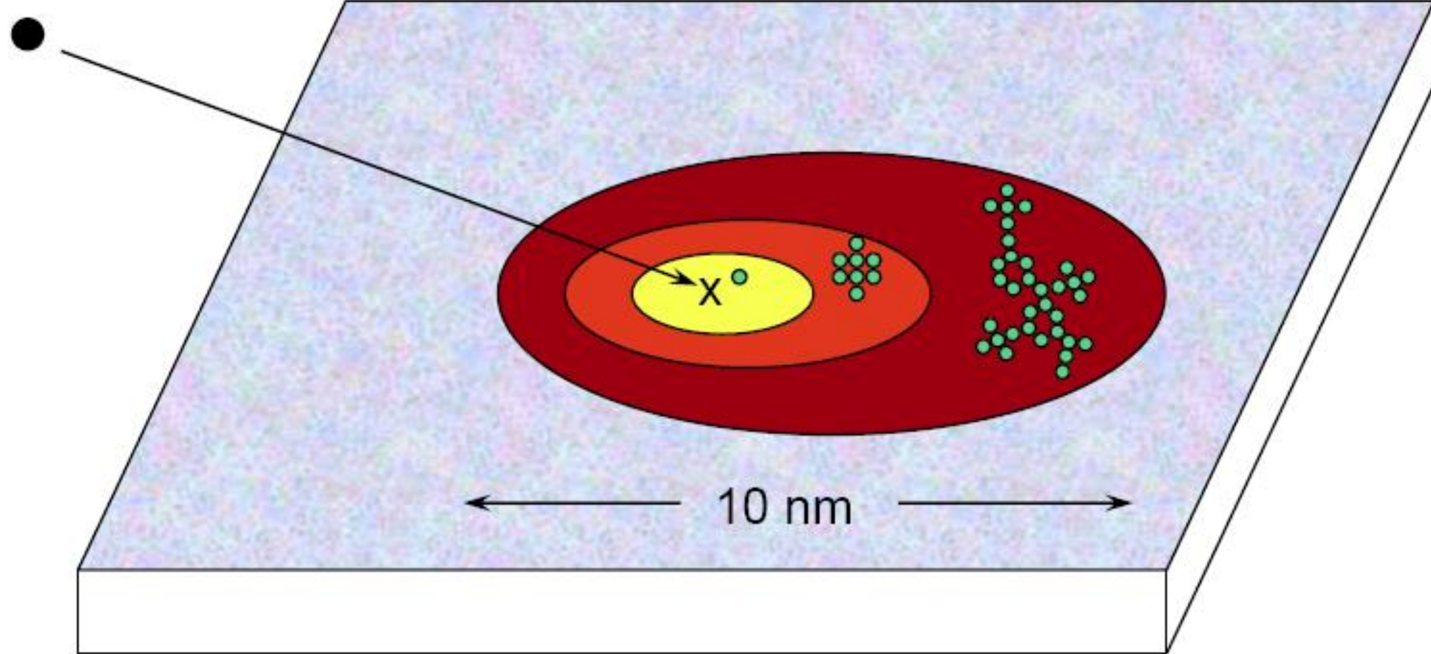


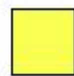
MALDI: Matrix Assisted Laser Desorption/Ionization





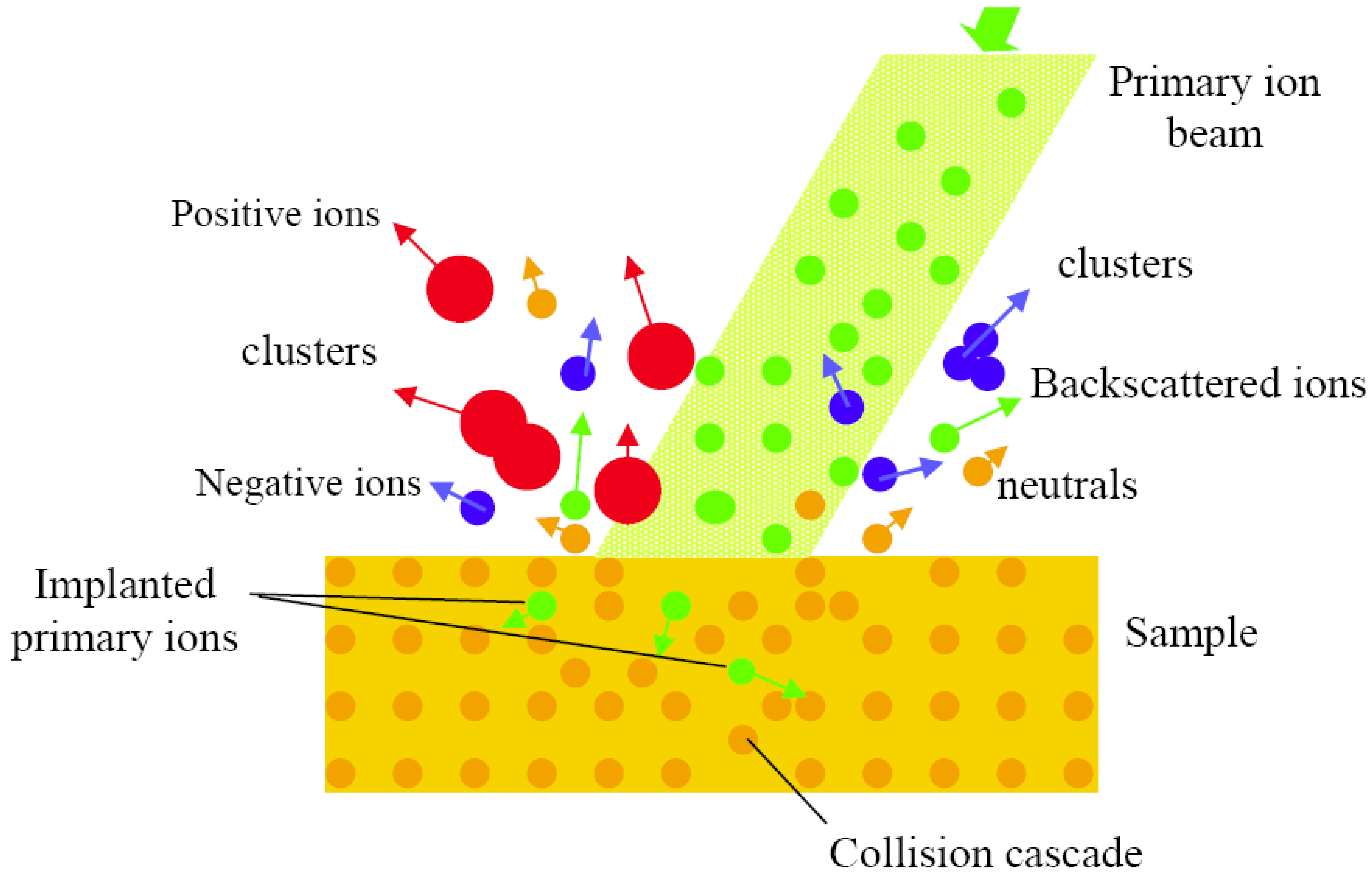
Secondary Ion Sputtering Process



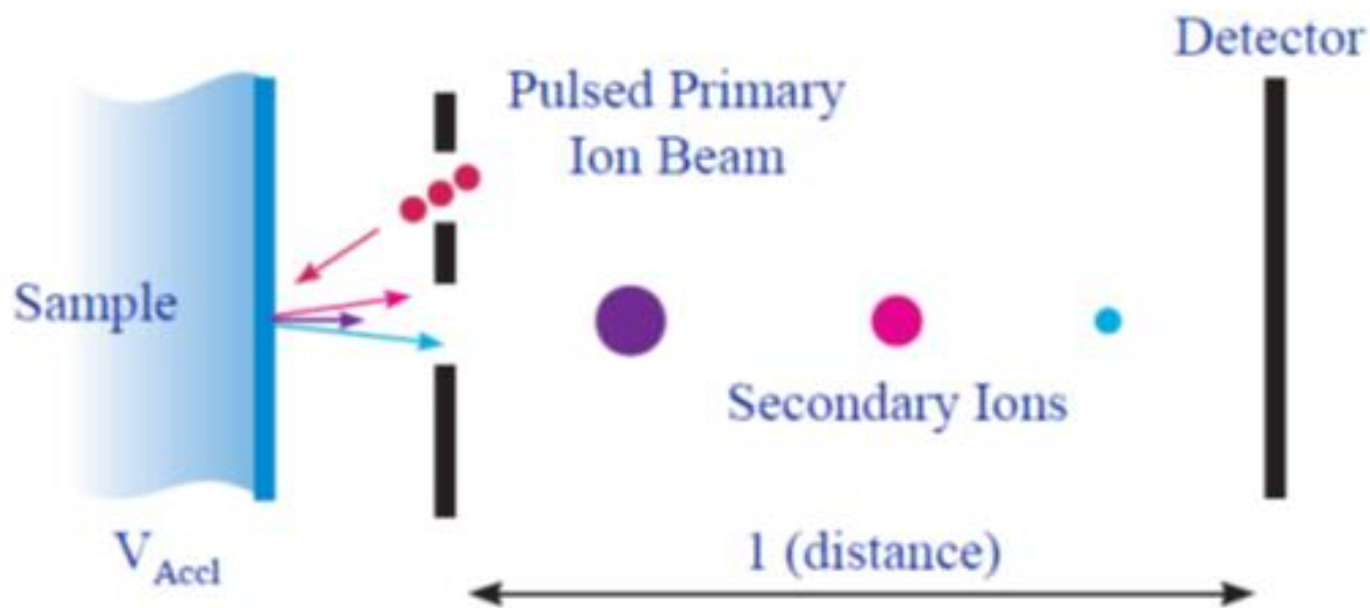
 Atomic Emission

Small Molecule Emission

Large Molecule Emission


Primary ion beam
Positive ions
clusters
clusters
Backscattered ions
Negative ions
neutrals
Implanted primary ions
Sample
Collision cascade

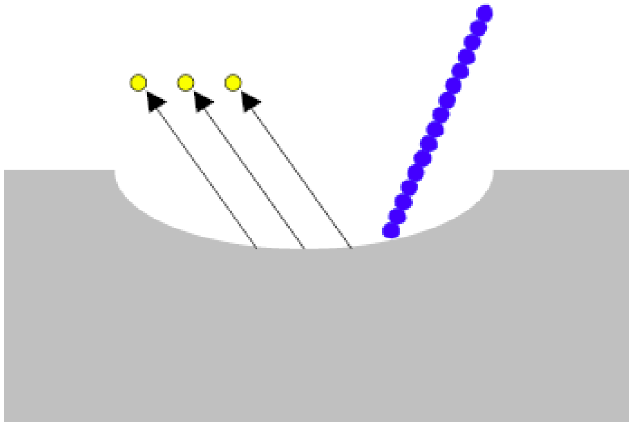
Time of Flight Mass Spectrometer



$$E_{kinetic} = {}^{1}/_{2}\, mv^2$$

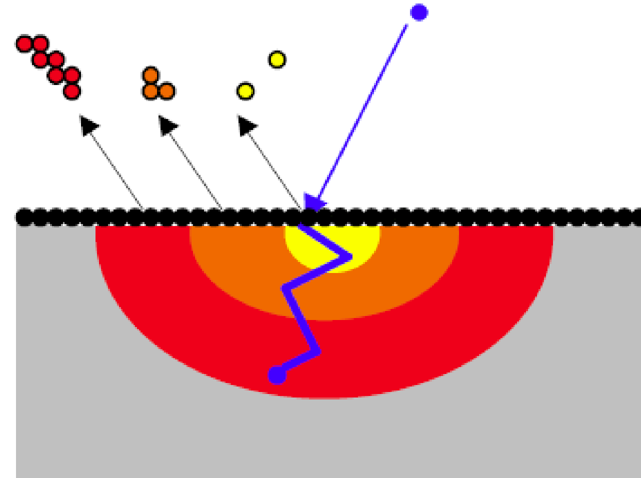
Modes of SIMS

Dynamic SIMS



- Material removal
- Elemental analysis
- Profiling

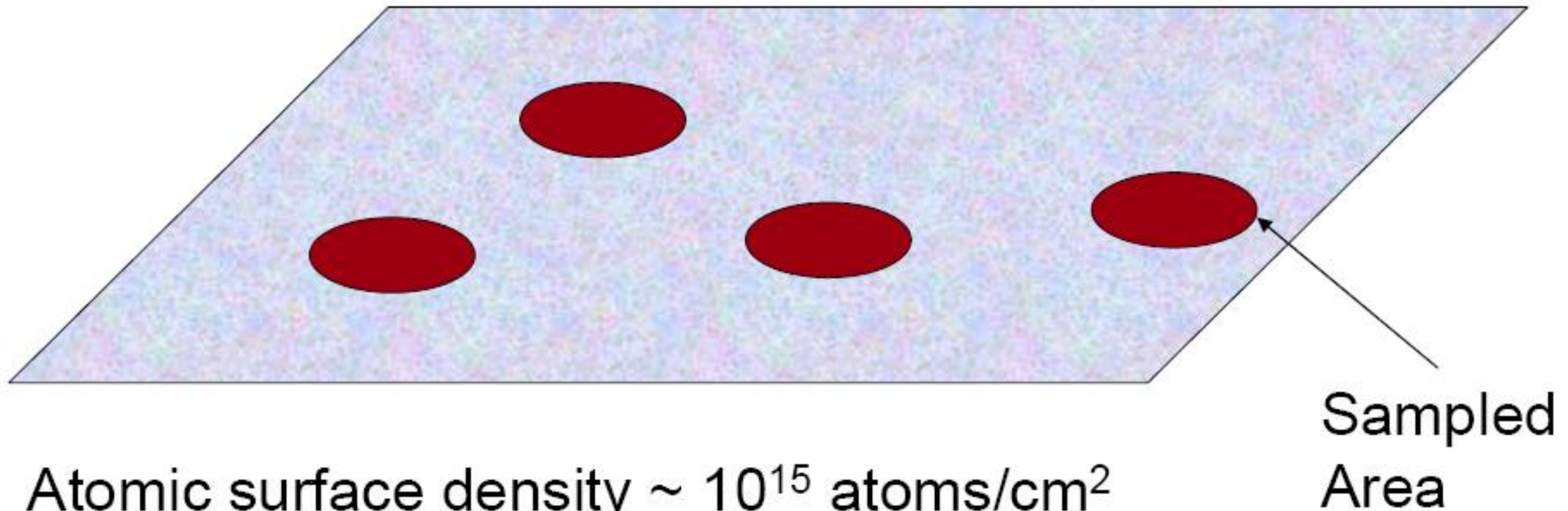
Static SIMS



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

Definition of Static SIMS

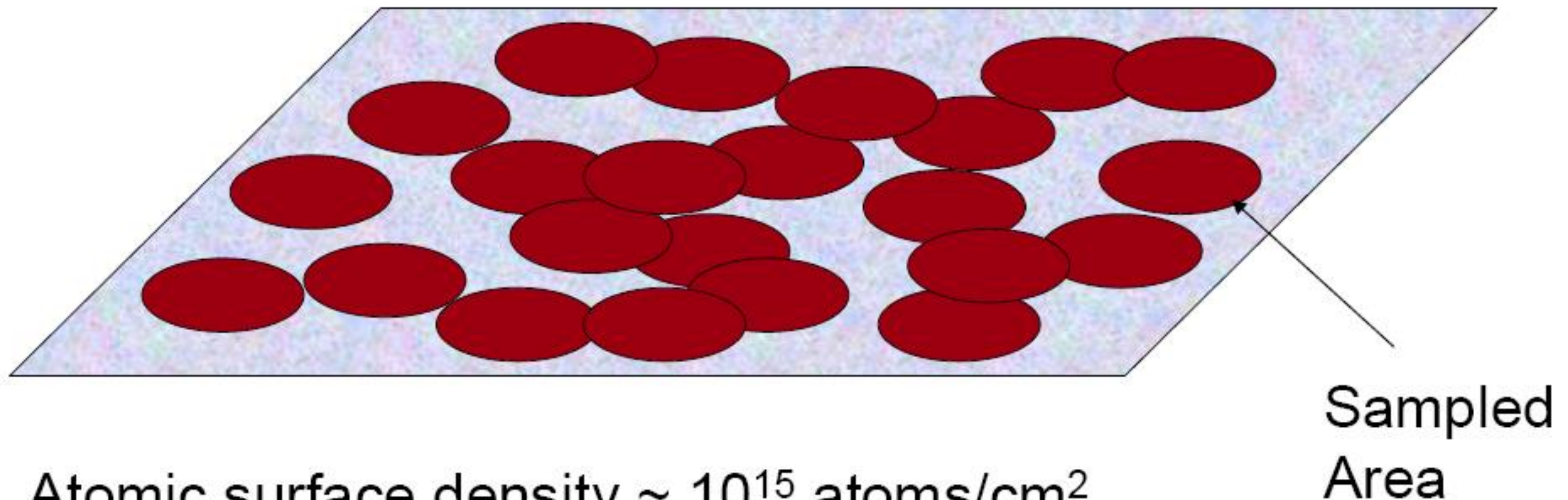
When 'dose' of primaries is <u>low</u>: each ion strikes a *new* area of the surface = Static SIMS



Atomic surface density ~ 10^{15} atoms/cm^2
Dose equivalent to ~ 10^{12} - 10^{13} atoms/cm^2
TOF-SIMS analysis optimized in this regime

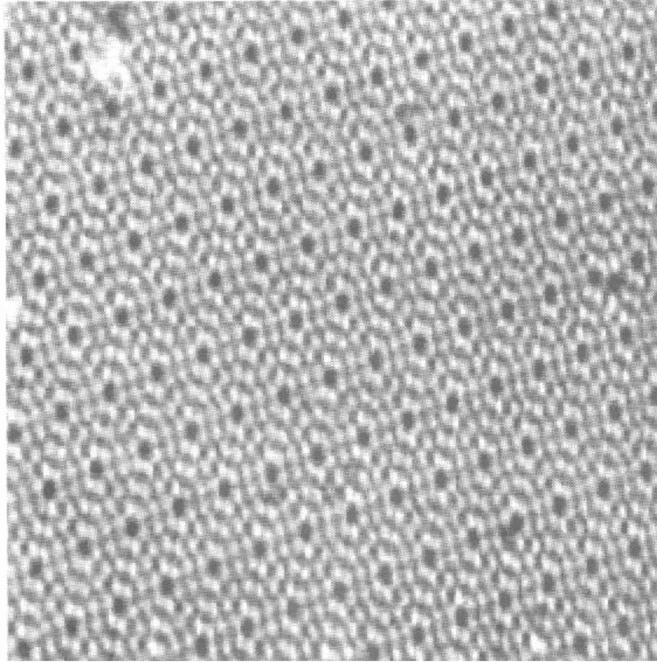
Exceeding Static SIMS

'Dose' of primaries is increased: significant chance of striking a previously sampled area, loss of high molecular weight information

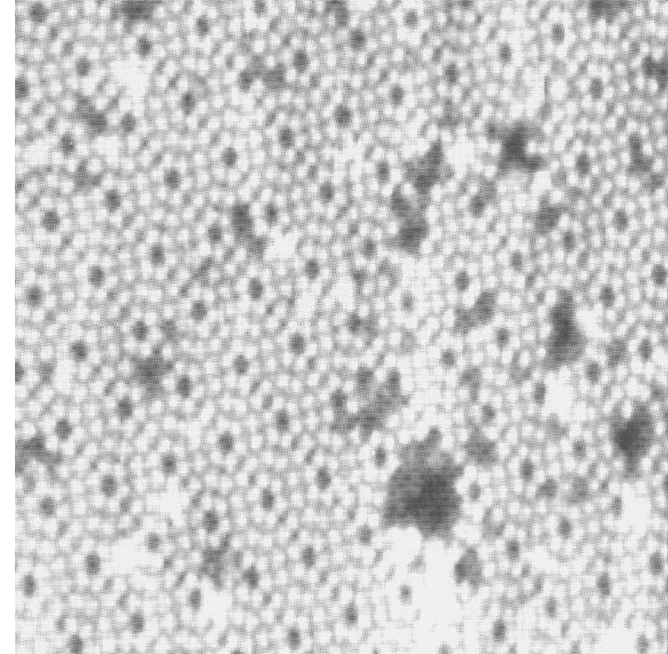


Atomic surface density ~ 10^{15} atoms/cm^2
Dose equivalent to ~ 10^{13}-10^{15} atoms/cm^2

STM Before & After Static SIMS



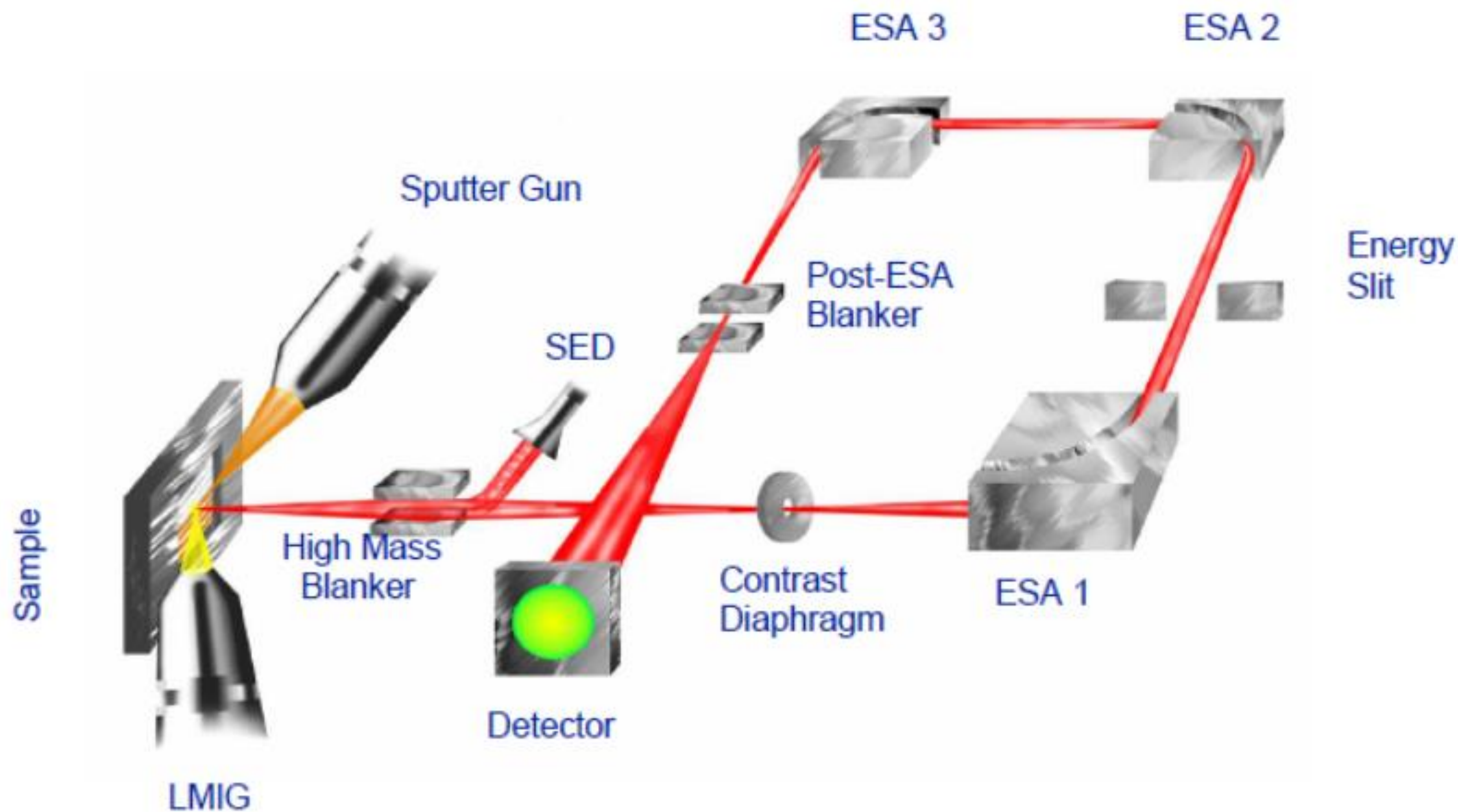
Si surface



Si surface exposed to 3 x 10^{12} ions/ cm^2

H.J.W. Zandvliet et al. in *SIMS VIII Proceedings*

TRIple Focused Time-of flight mass spectrometer (TRIFT)



Available LMIG Ion Sources

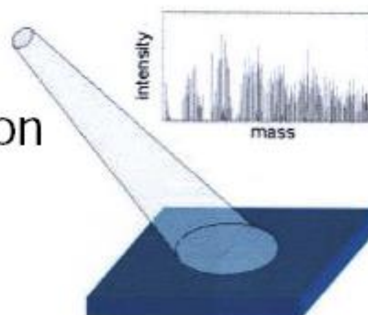
Species	Mass (Da)
Ga^+	69
In^+	115
Au^+	197
Au_2^+	394
Au_3^+	581
C_{60}^+	720

Bi^+ **209**

Modes of Operation

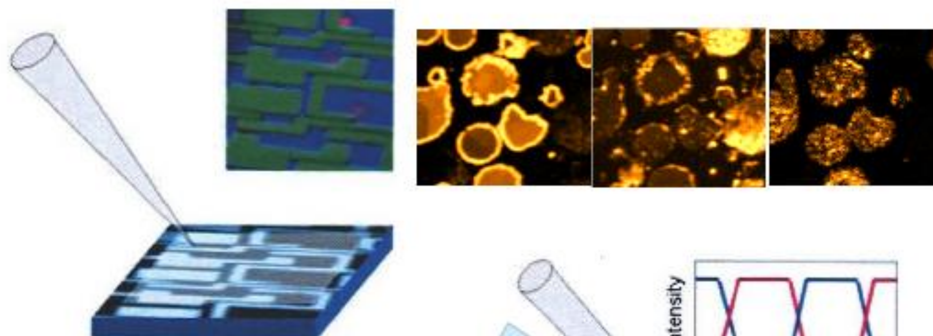
Surface Spectroscopy

- Elemental and molecular information
- Unlimited mass range
- ppm/ppb sensitivity
- Mass resolution > 10,000



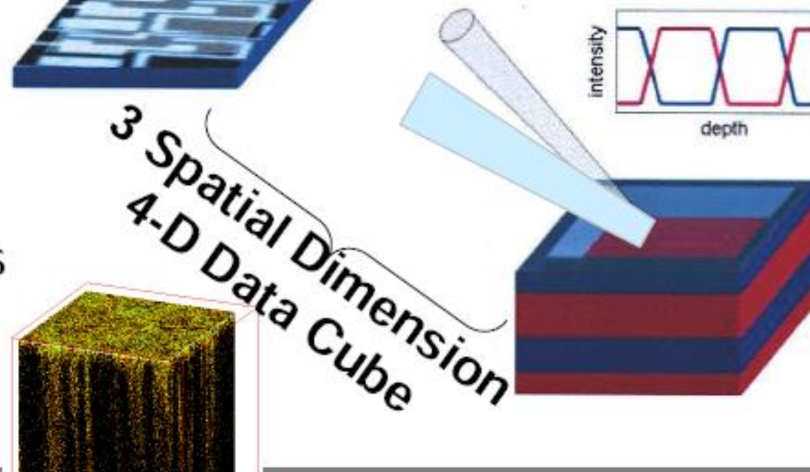
Surface Imaging

- *Parallel mass detection*
- *Lateral resolution < 100 nm*

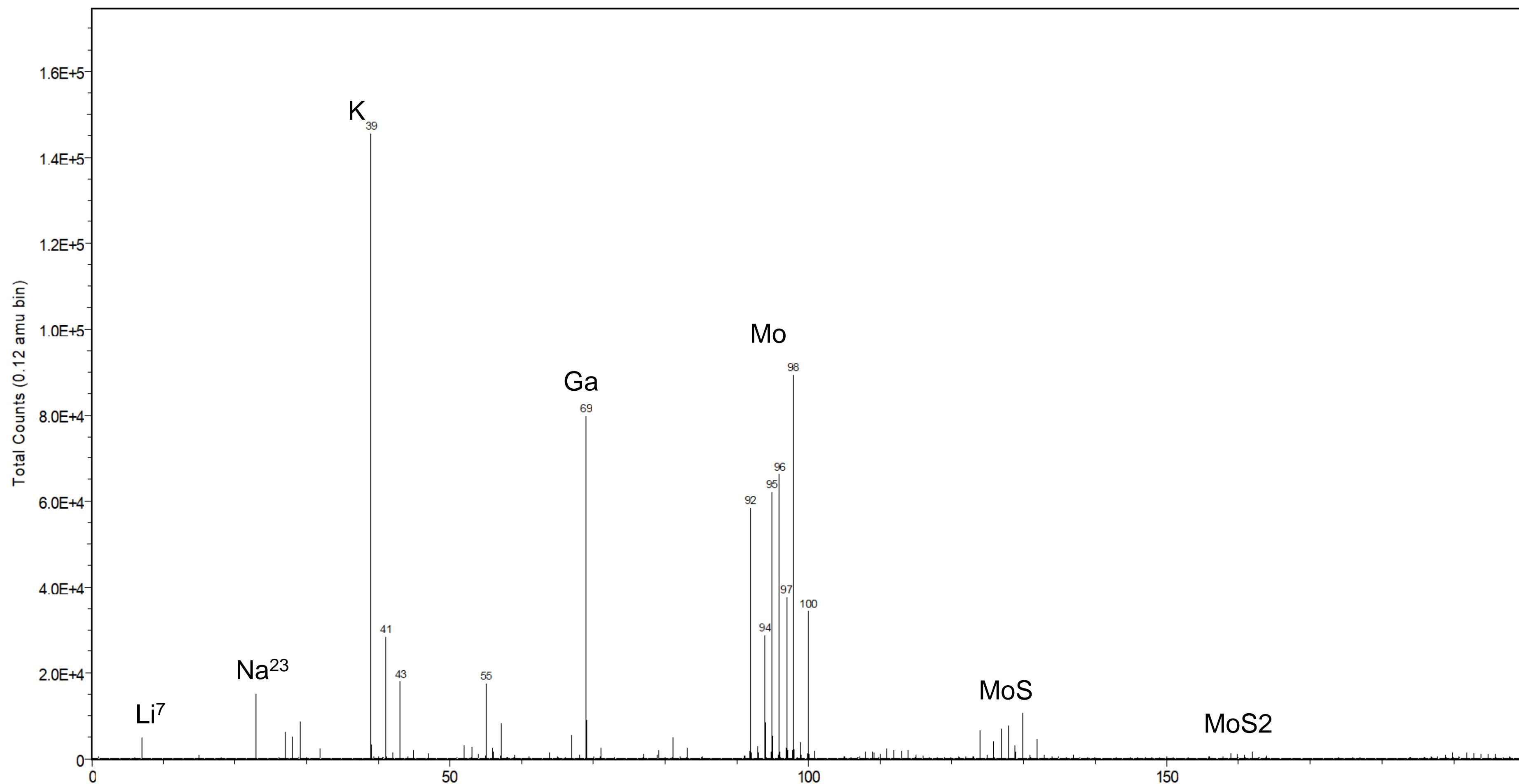


Depth Profiling

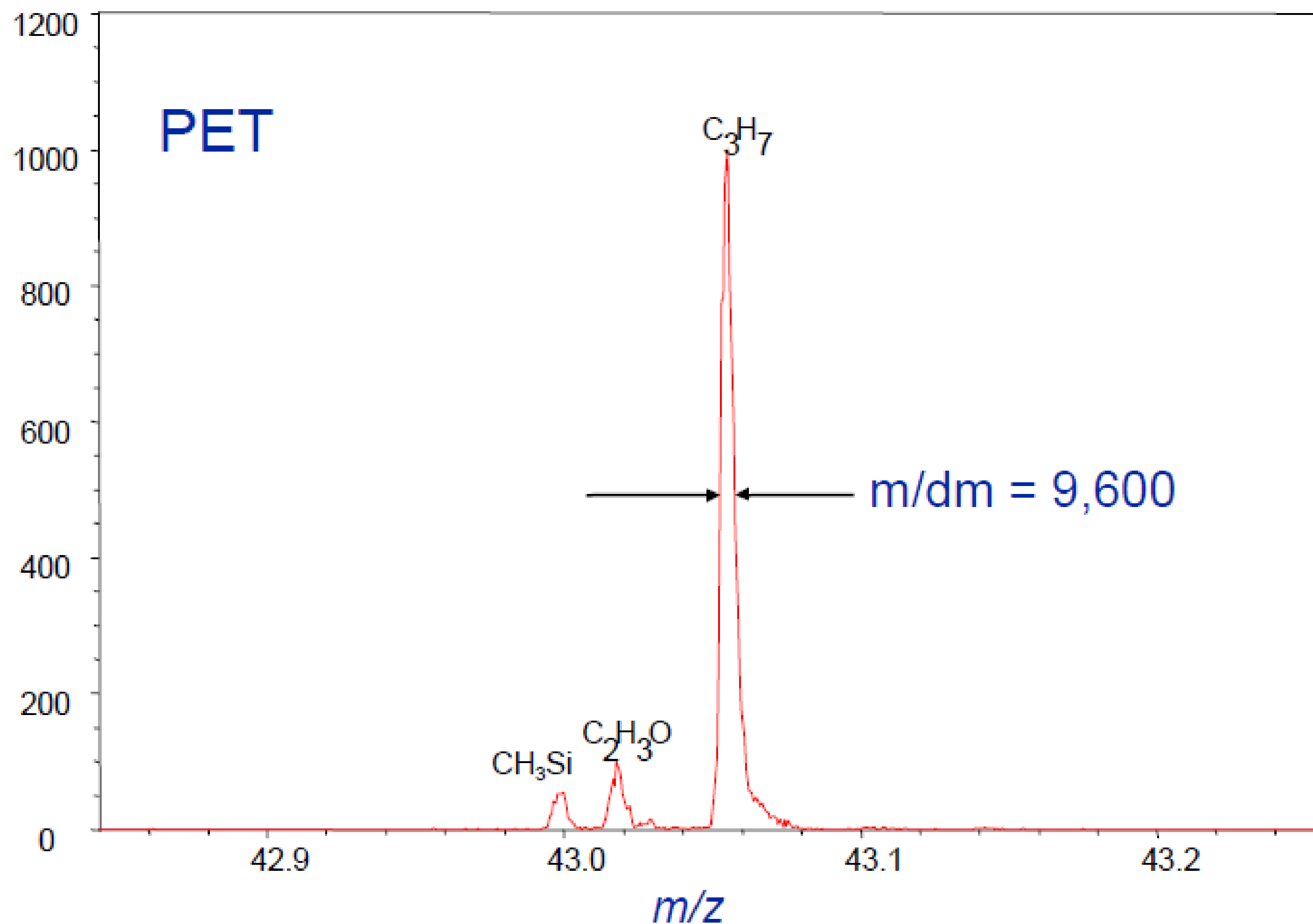
- Depth resolution < 1nm
- Thin layers from 1 nm to microns
- Parallel mass detection



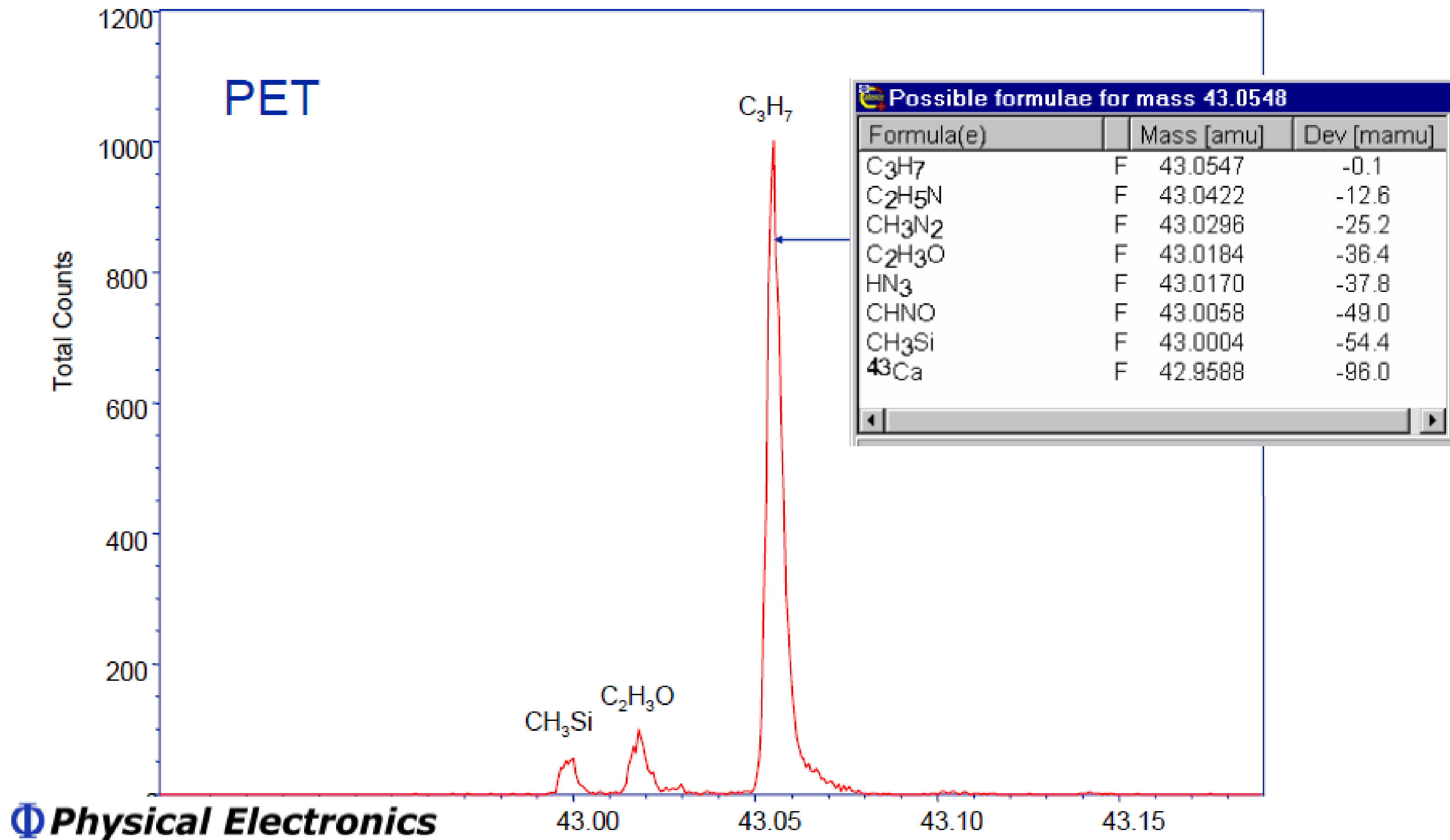
Positive spectrum of MoS_2 monolayer



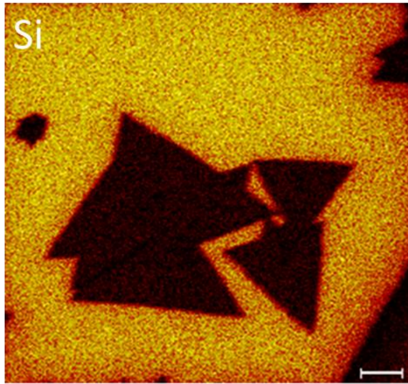
High Mass Resolution on PET Film

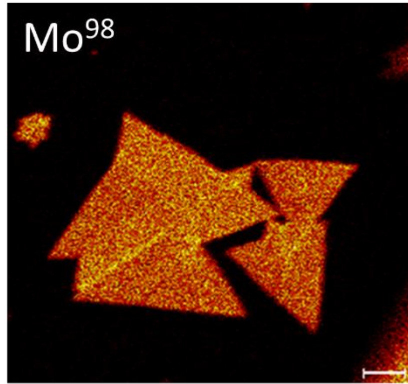


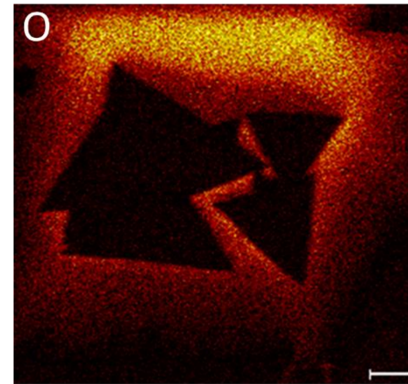
Mass Accuracy is Used for Peak ID

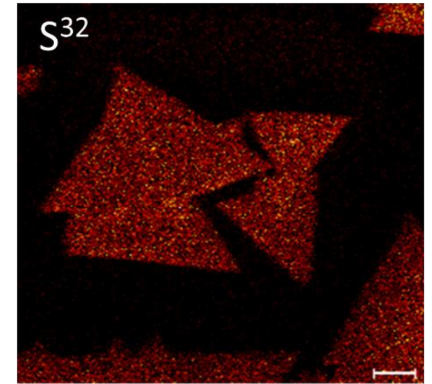


MoS_2 Flake Images

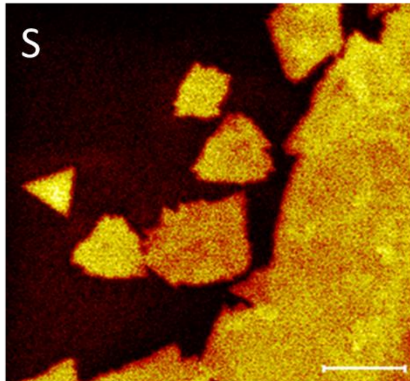


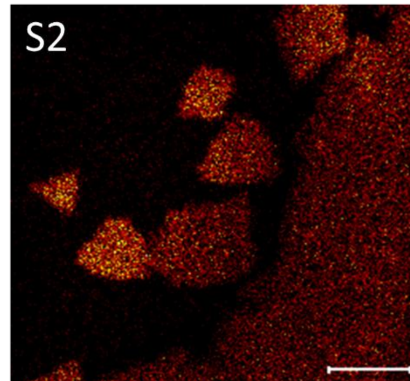


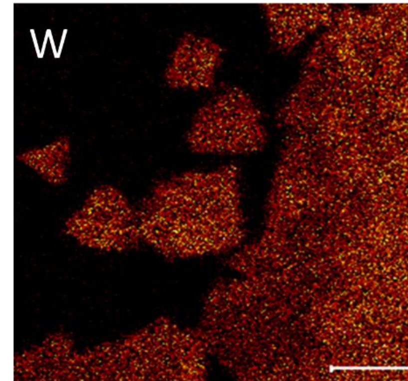


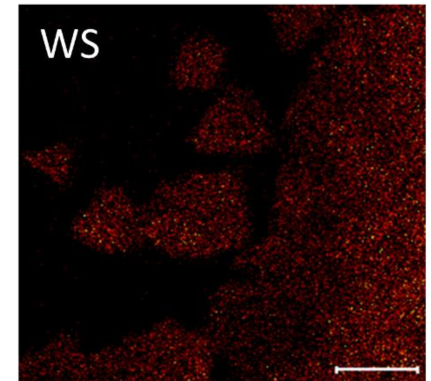


Scale bar 10um

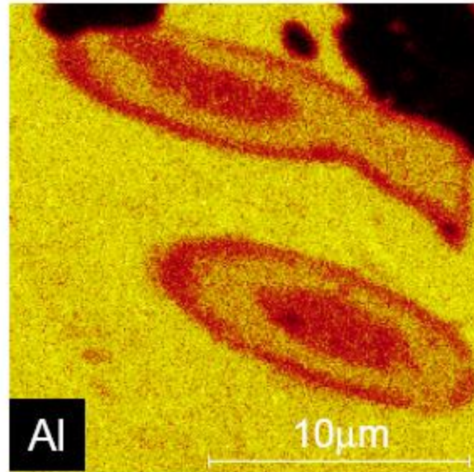


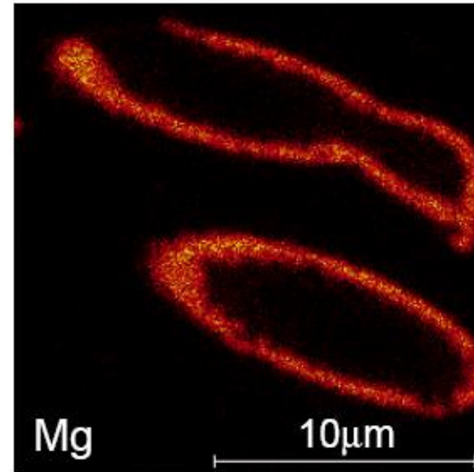


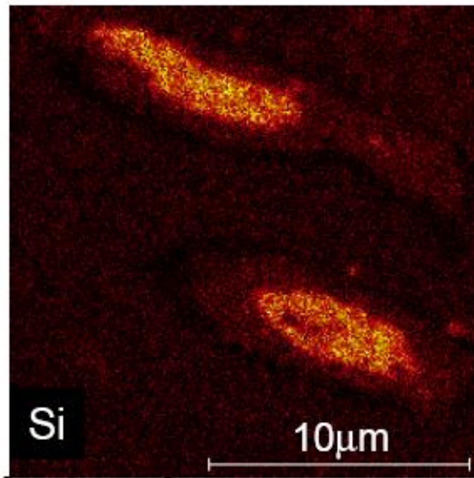


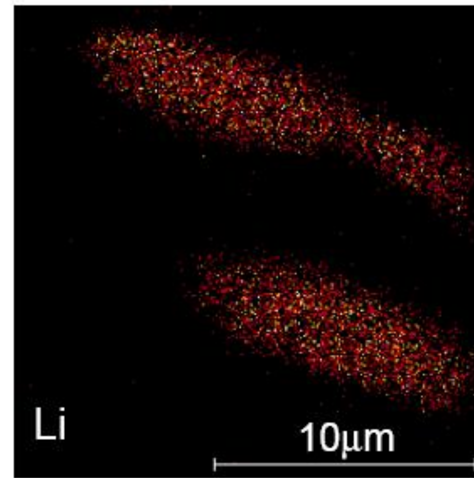


Images of Al Metal Matrix Composite Heat Treatment: 500°C, 6 hr.



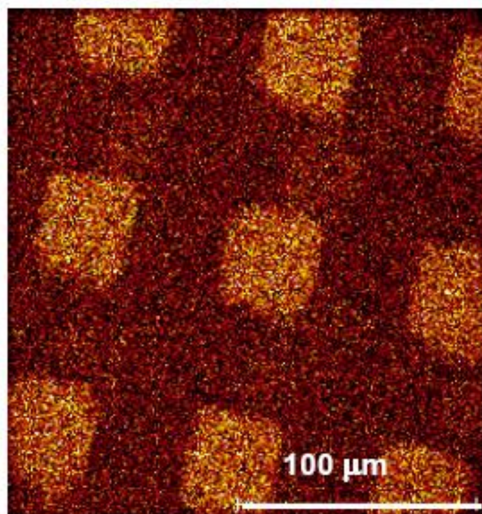


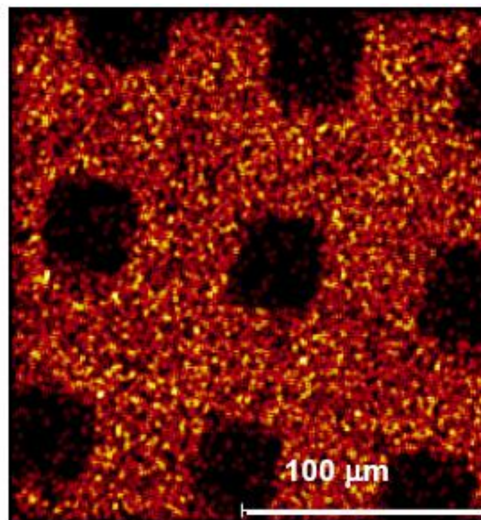




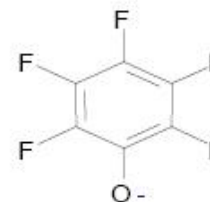
TOF-SIMS Imaging of Biotin Pattern on PFP and PET

Biotin
CN^-
m/z 26

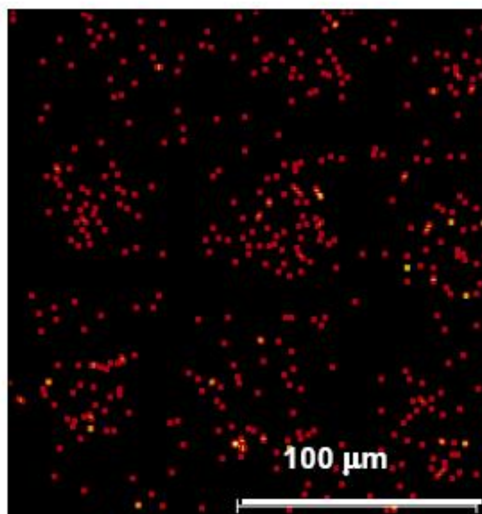


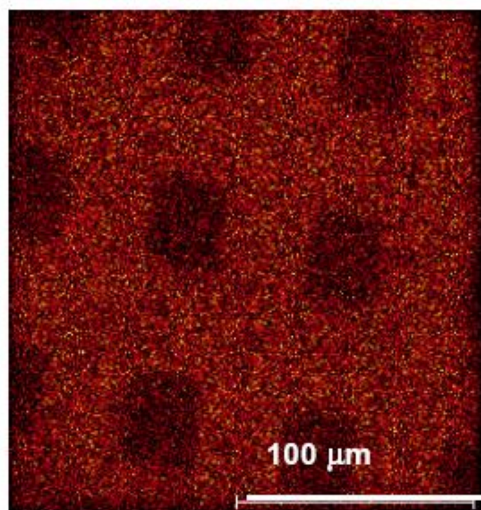


PFP
$C_6F_5O^-$
m/z 183



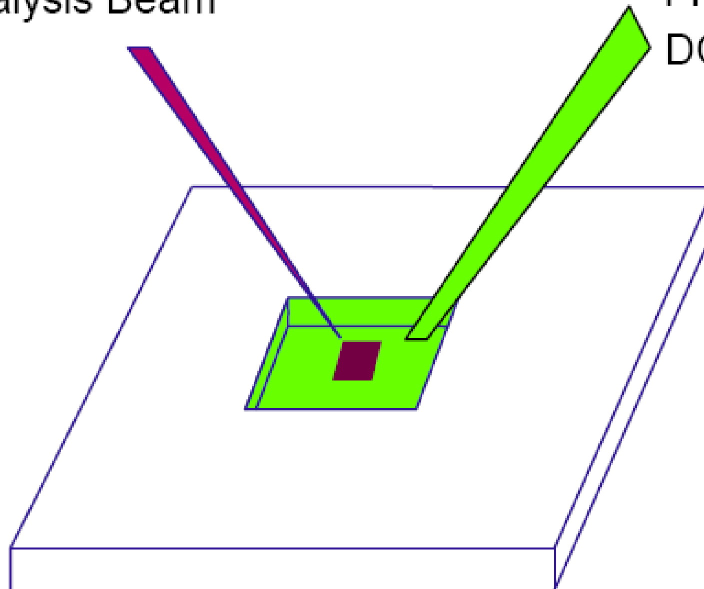
Biotin
$C_{10}H_{15}N_2SO_2^+$
m/z 227



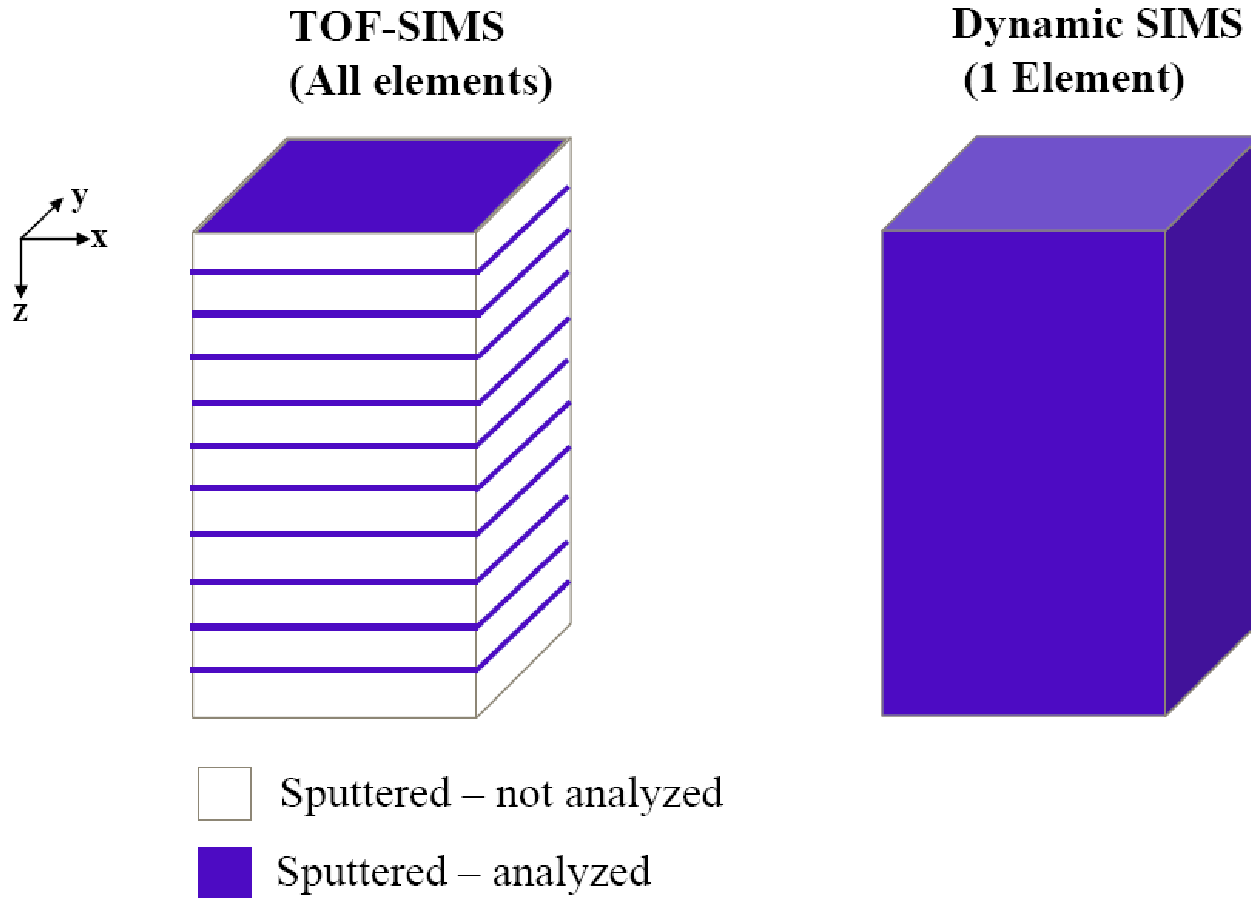


PET
$C_7H_4O^+$
m/z 104

Depth profiling

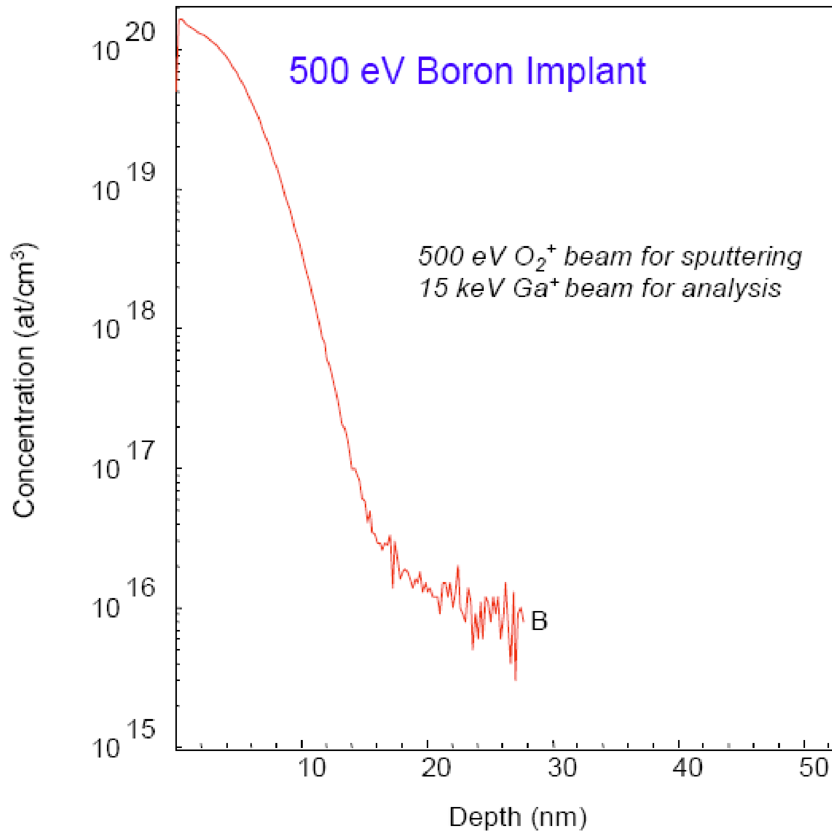


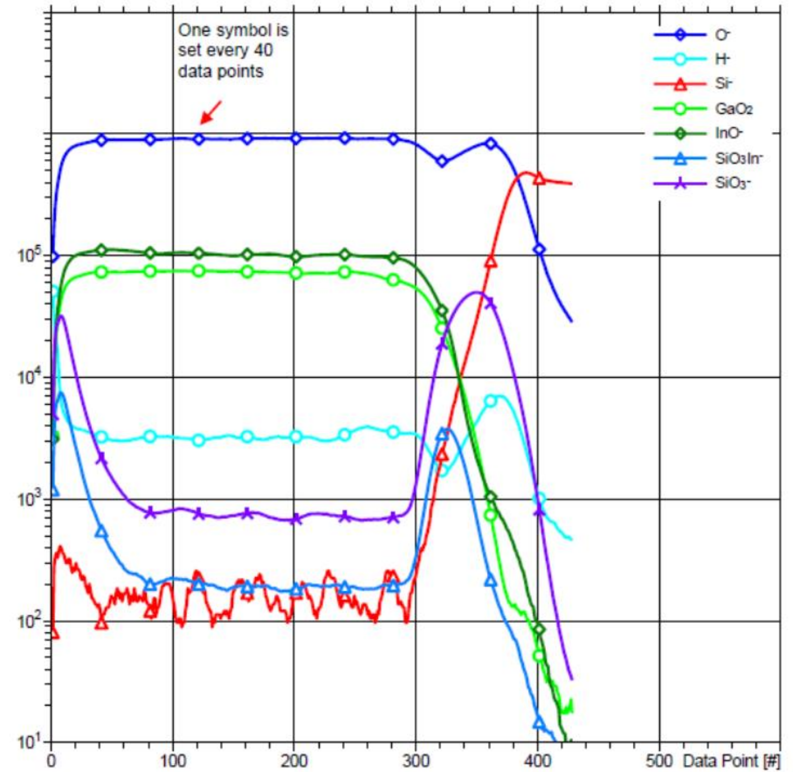
Comparison of Analyzed Volumes

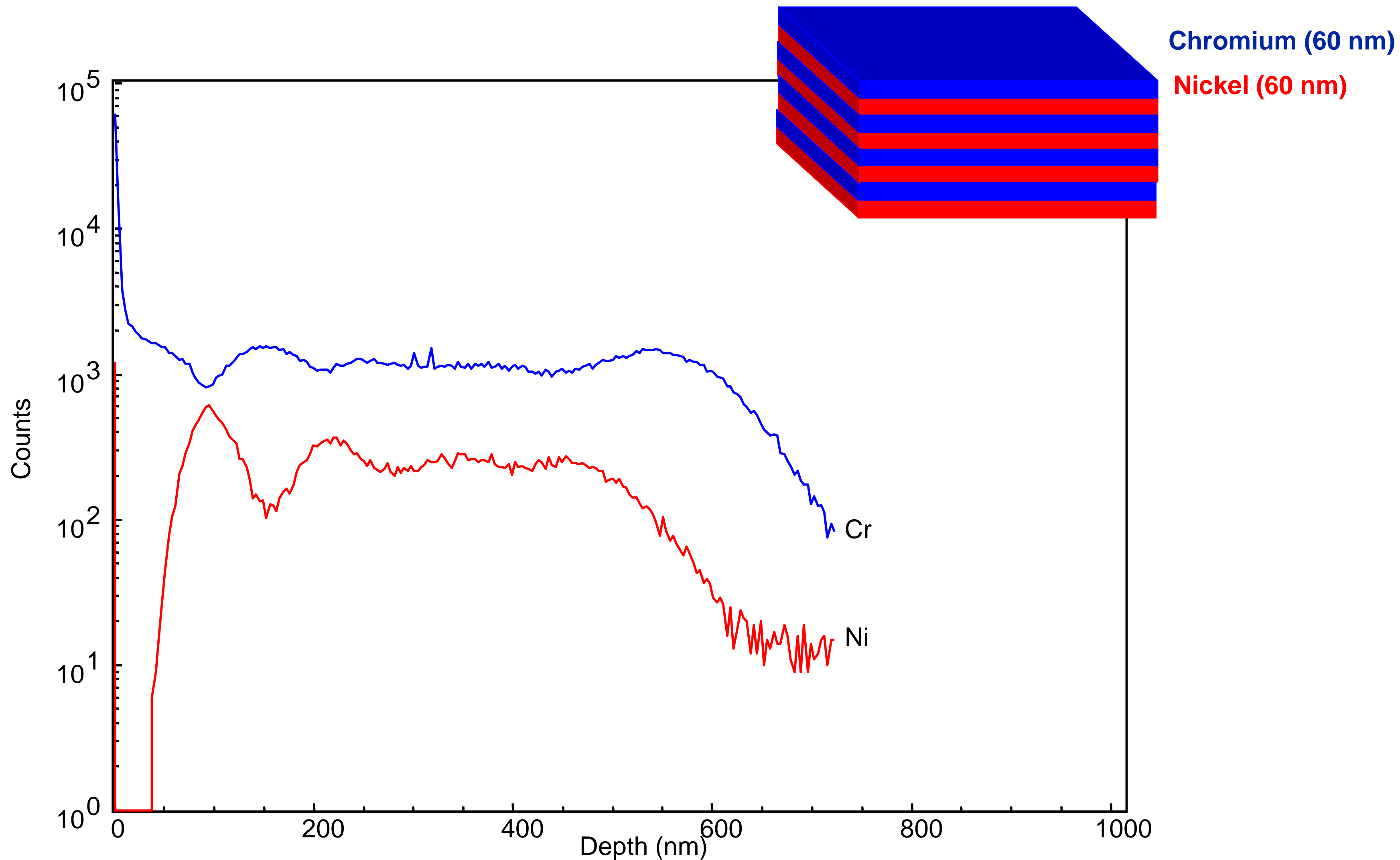


Boron Implant Depth Profile

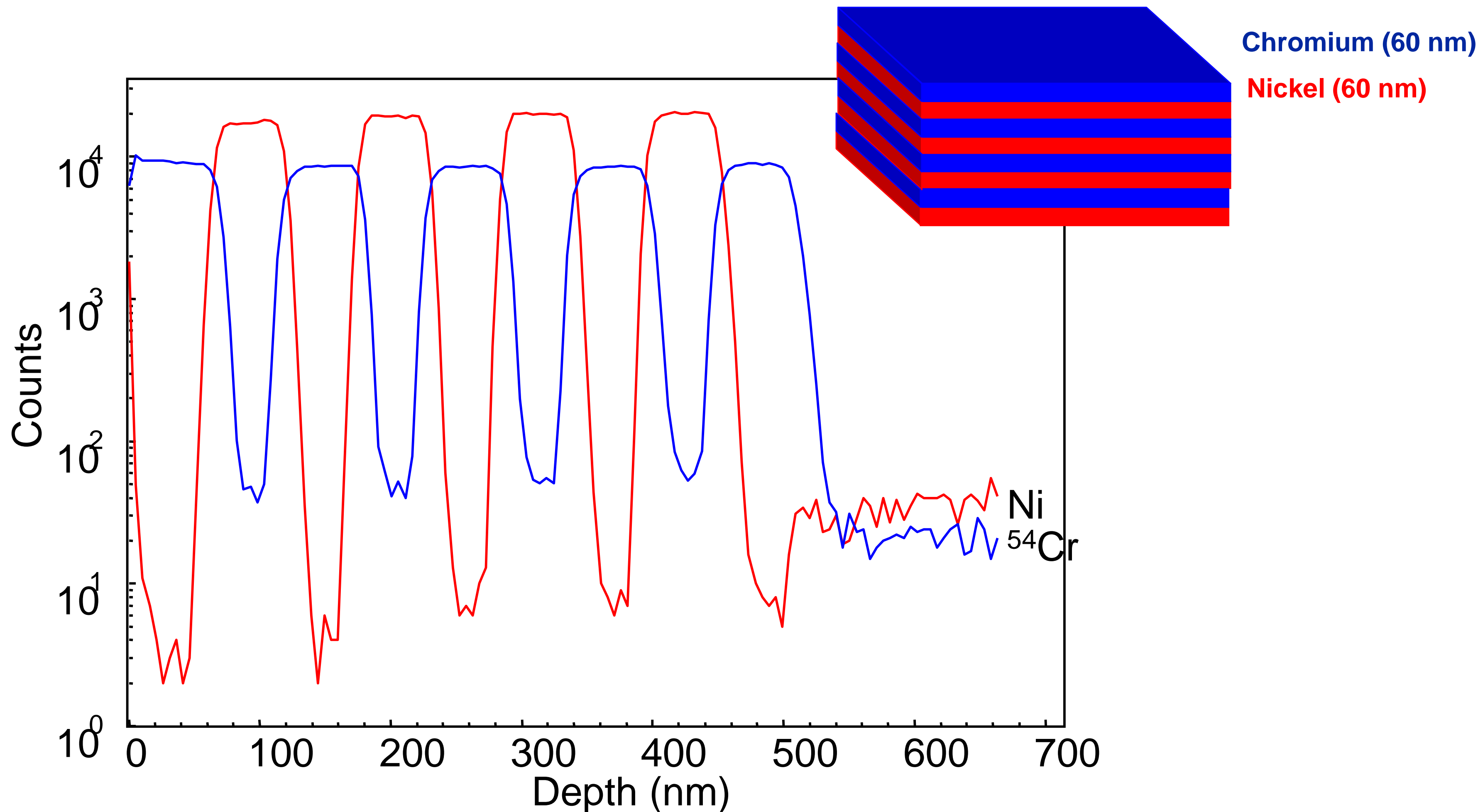
20 nm InGaO / Si





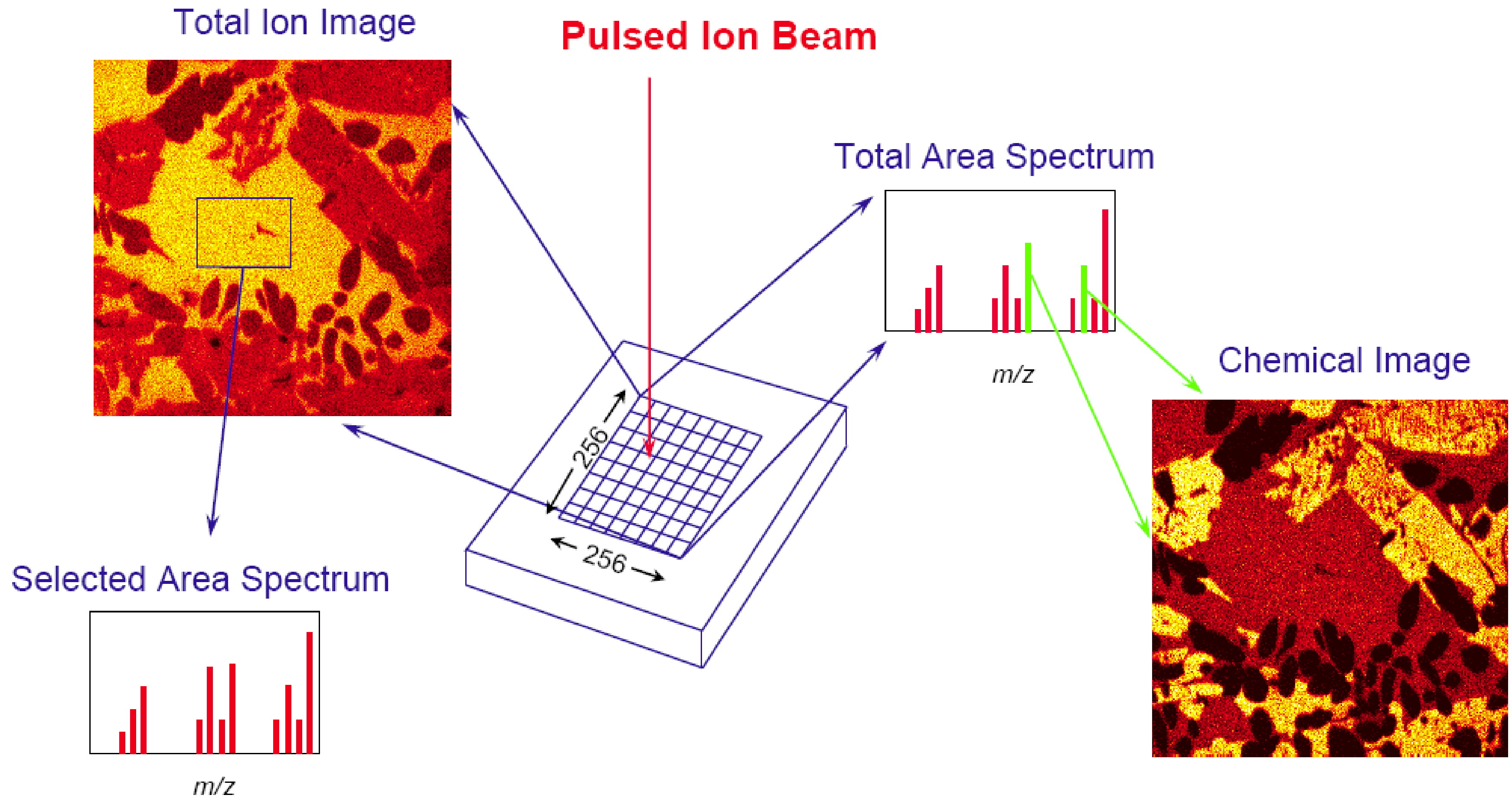


Depth profile of a Cr/Ni multi-layer standard using a 2 nA, 15 kV Ga^+ beam in the one-beam phase depth profiling mode. At this impact energy of 15 keV, the layers are not resolved beyond the second Ni layer.



Depth profile of a Cr/Ni multi-layer standard using a 2 nA, 5 kV Ga^{+} beam in the one-beam phase depth profiling mode. At this impact energy of 5 keV, the layers are well resolved throughout the entire structure.

Post Analysis with Raw Data



Advantage of ToF-SIMS

- Detection of All Elements – H, He, Li, etc.
- Isotopic Detection – 2H, 3H, 18O, 13C, etc.
- Trace Sensitivity – ppm to ppb range
- High Spatial Resolution
- –Typical Lateral Resolution < 100nm
- Parallel Detection of All Masses
- Detailed Molecular Information – organic or inorganic
- Molecular Imaging
- 3D profiling
- Analysis of All Materials – conductor, semiconductor, insulator

Disadvantages

- Secondary ion yields are often highly dependent on the matrix
- Secondary ion yields vary by more than six orders of magnitude across the elements
- Destructive
- Well-characterized reference standards that are as close as possible to the matrix of the samples of interest are needed for quantification
- Qualitative
- Data interpretation could be difficult.

Comparison Table

	XPS	ToF-SIMS	SEM-EDX
In	X-ray	Ion beam such as Ga, Au cluster, or Bi cluster	Electron beam
out	Photoelectron	Secondary ion	X-ray
Sampling depth	Up to 10 nm	Up to 5 nm	0.5 to 3um
Information	Elemental analysis except for H and He Chemical state	Elemental analysis for all elements	Elemental analysis above carbon
Quantitative or qualitative	Quantitative ±5%	Semi-quantitative	Quantitative ±15%
Detection limit	0.1 at%	ppm to ppb	0.5 weight%
Elemental mapping spatial resolution	>3 um	<1 um	0.3 um
Analysis spot size	20 um to 900 um	1 um to 800 um	10 nm
Depth profiling	Yes	Yes	No
Insulating sample	Yes	Yes	Need Au coating
Data interpretation	Easy	Difficult	Easy
Surface damage	Non-destructive	Destructive	Non-destructive

NEW TOF-SIMS: more powerful and user-friendly

Thank you!