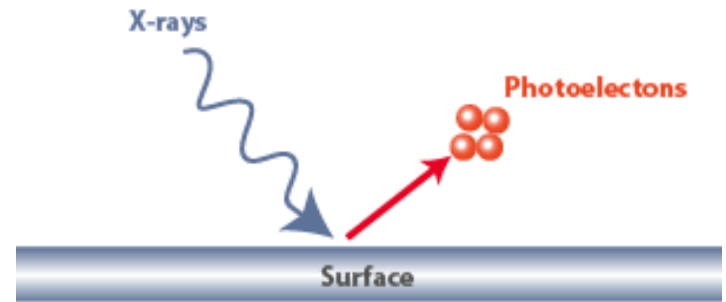
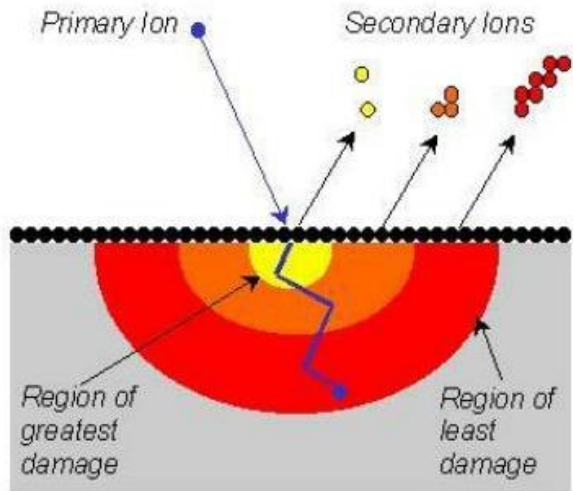


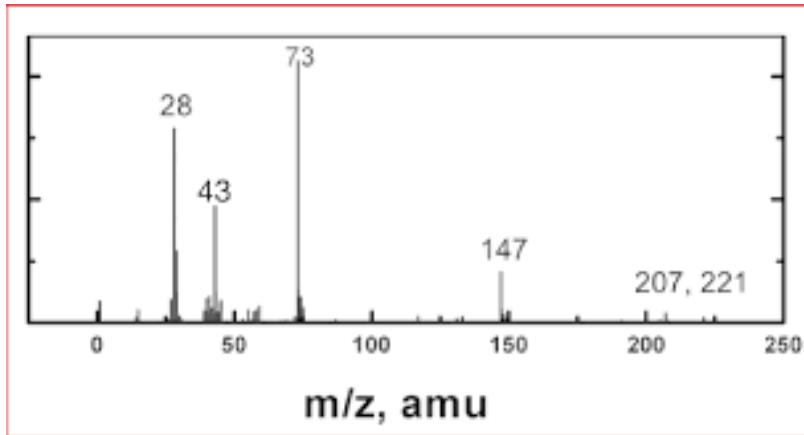
# ToF-SIMS or XPS ?



Xinqi Chen

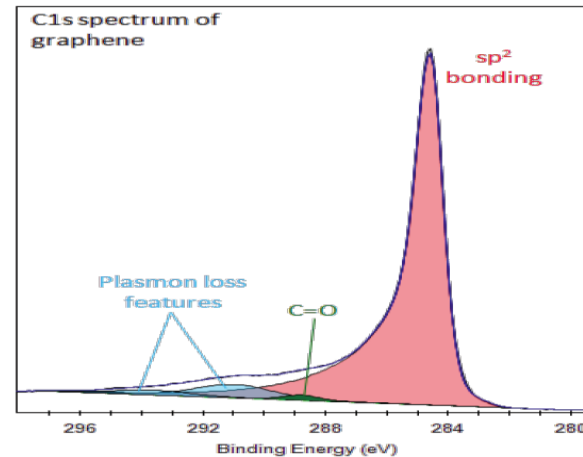
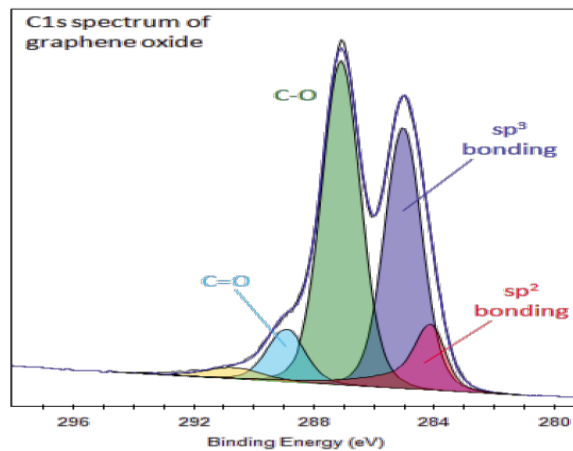
Keck-II

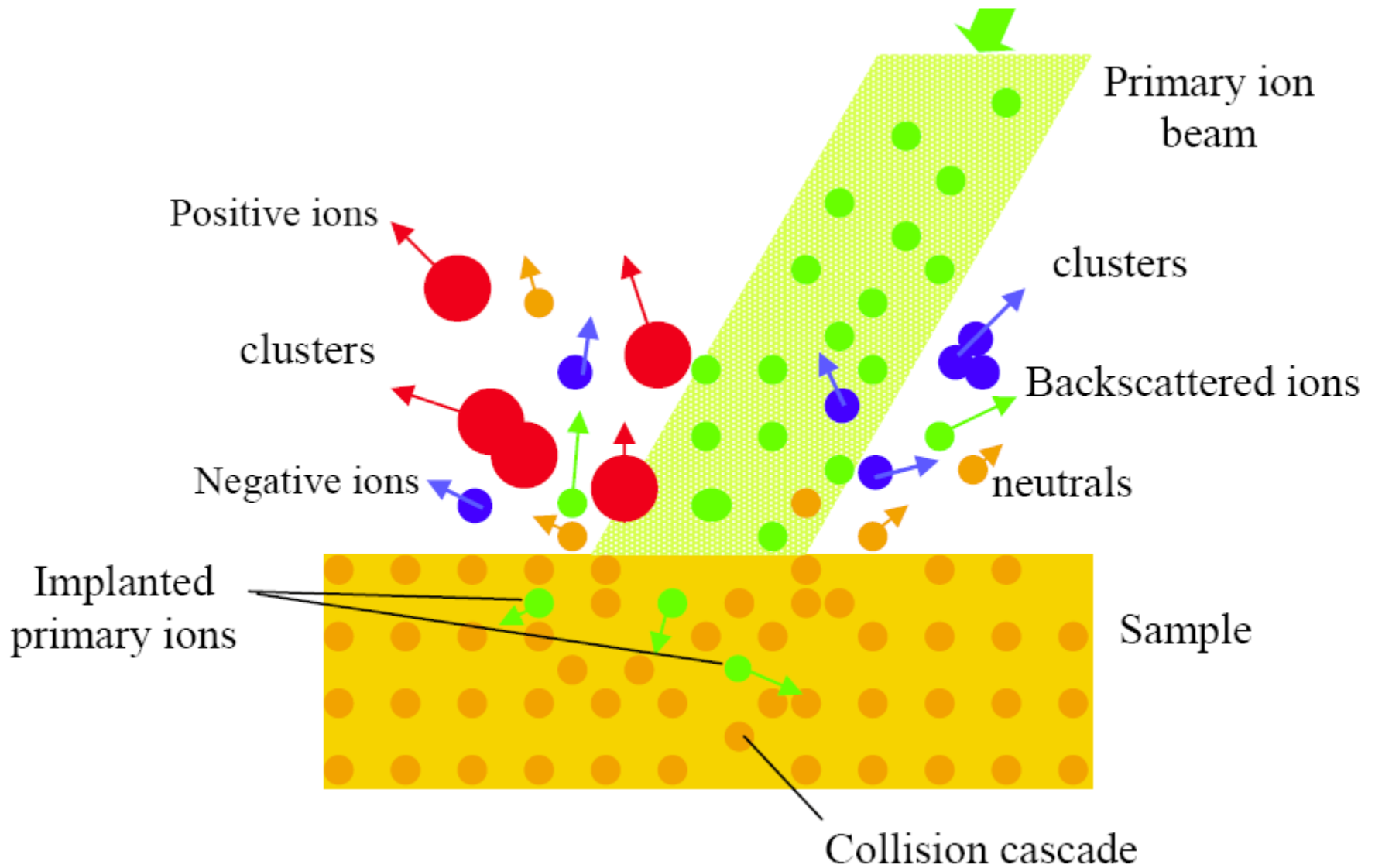
# Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)



Not ToF MS (laser, solution)

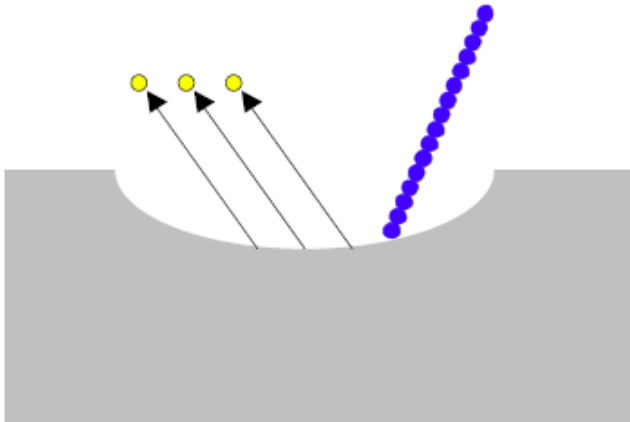
# X-ray Photoelectron Spectroscopy (XPS)





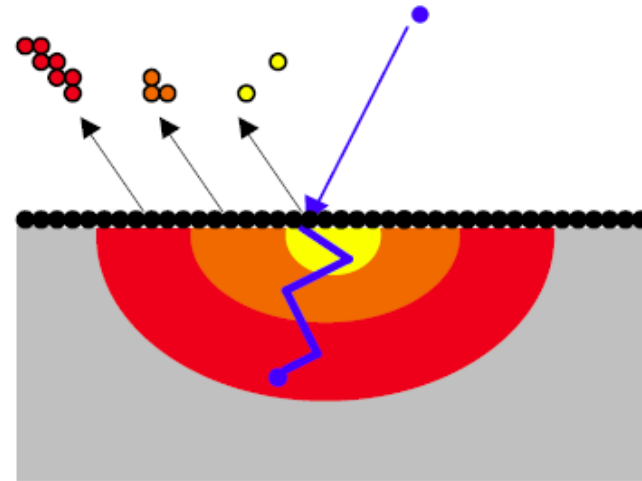
# Modes of SIMS

## Dynamic SIMS



- Material removal
- Elemental analysis
- Profiling

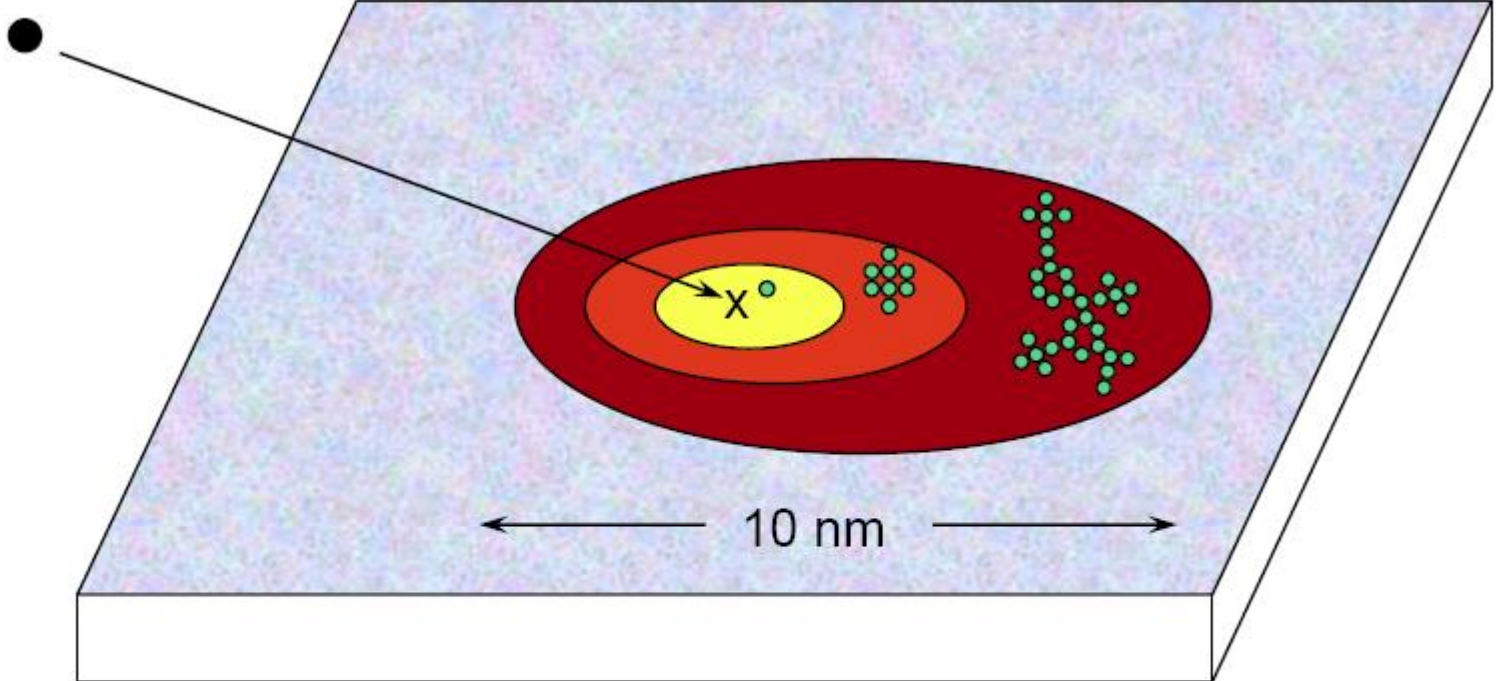
## Static SIMS



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

# Secondary Ion Sputtering Process

keV Primary Ion



Atomic Emission



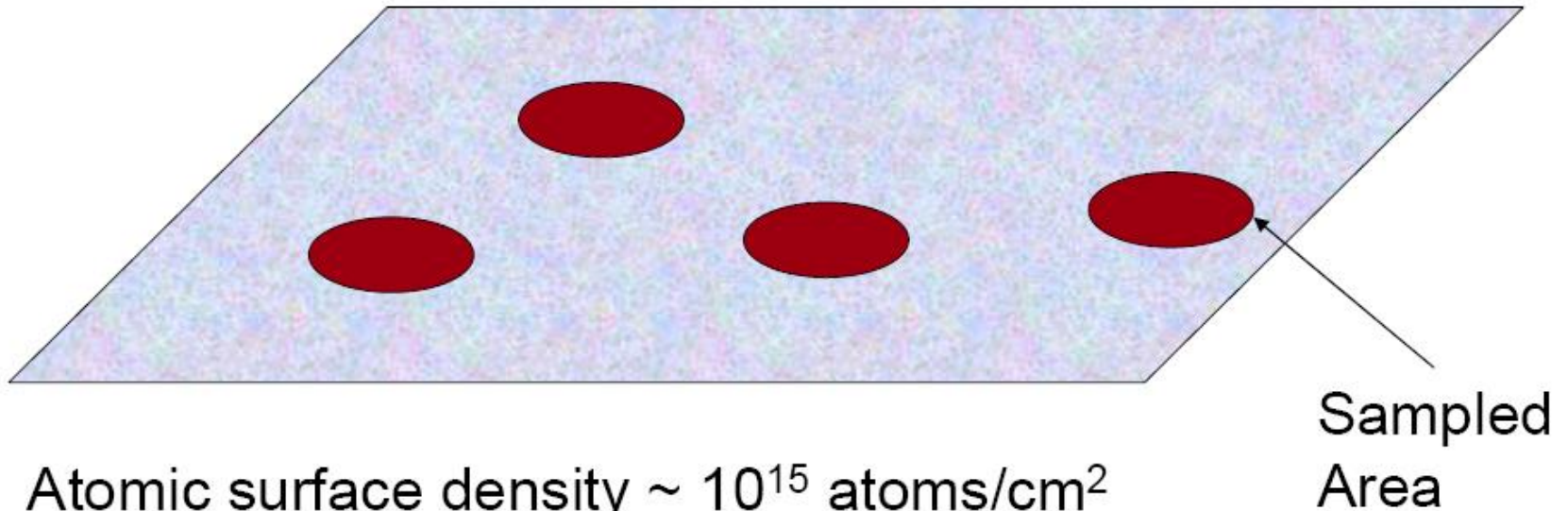
Small Molecule Emission



Large Molecule Emission

# Definition of Static SIMS

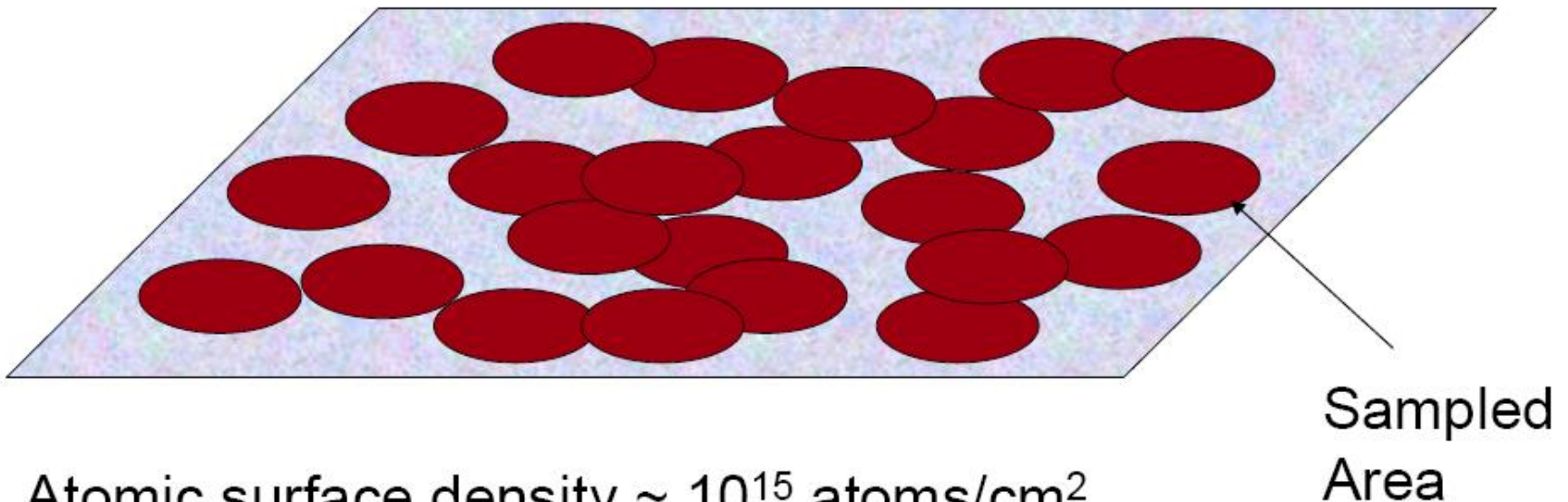
When 'dose' of primaries is low: each ion strikes a *new* area of the surface = Static SIMS



Atomic surface density  $\sim 10^{15}$  atoms/cm<sup>2</sup>  
Dose equivalent to  $\sim 10^{12} - 10^{13}$  atoms/cm<sup>2</sup>  
TOF-SIMS analysis optimized in this regime

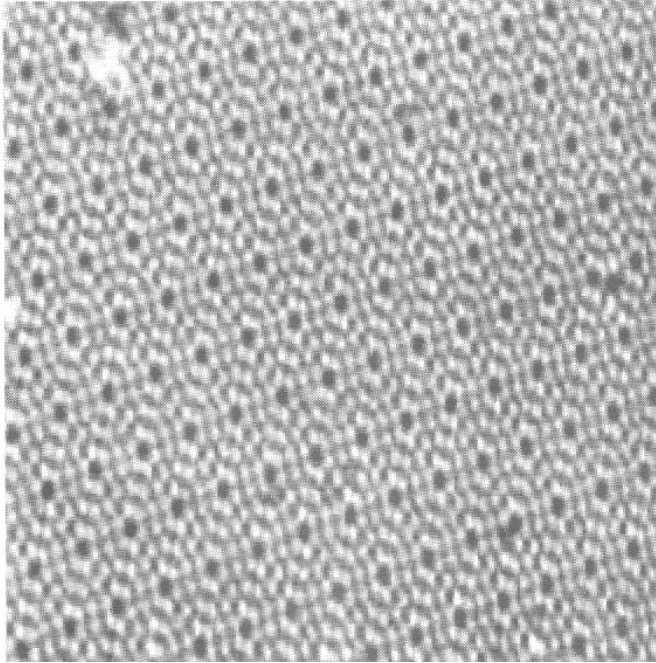
# Exceeding Static SIMS

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

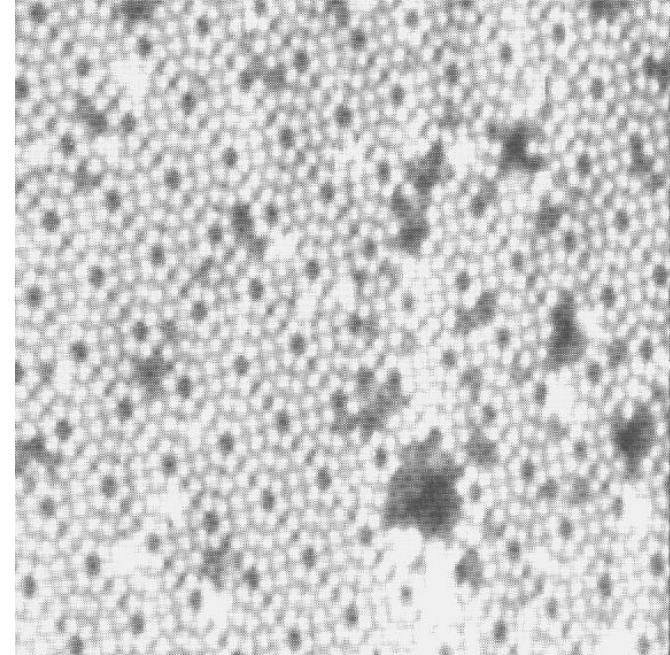


Atomic surface density  $\sim 10^{15}$  atoms/cm<sup>2</sup>  
Dose equivalent to  $\sim 10^{13}$ - $10^{15}$  atoms/cm<sup>2</sup>

# STM Before & After Static SIMS



Si surface

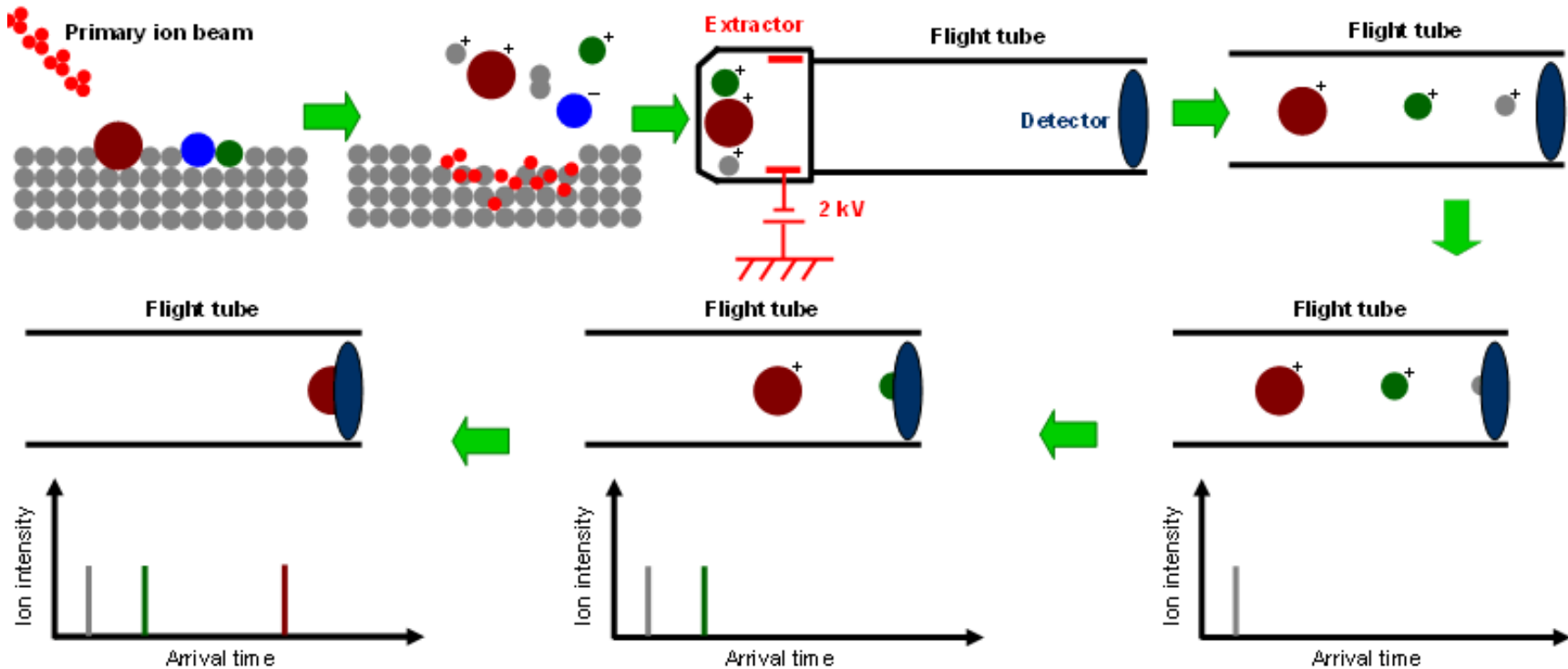


Si surface exposed  
to  $3 \times 10^{12}$  ions/  $\text{cm}^2$

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



# Basic Principles

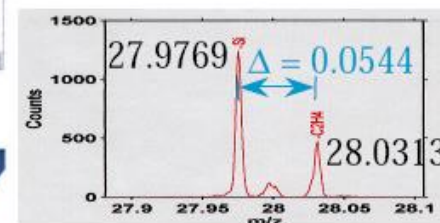
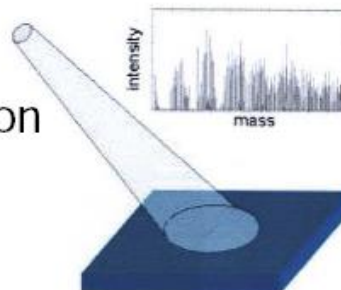


- Each pulse of primary ions creates a pulse of secondary ions
- Secondaries of different masses within a single 'cycle' arrive at the detector at different times according to the relation:  $K.E. = \frac{1}{2} mv^2$

# Modes of Operation

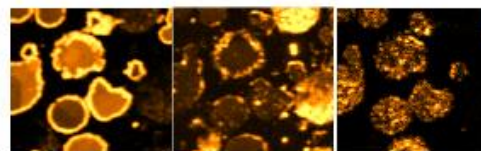
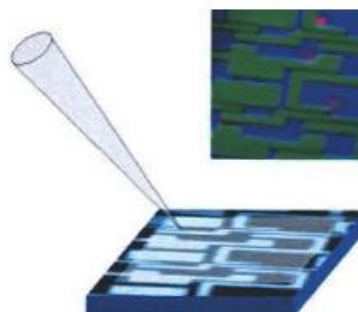
## Surface Spectroscopy

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



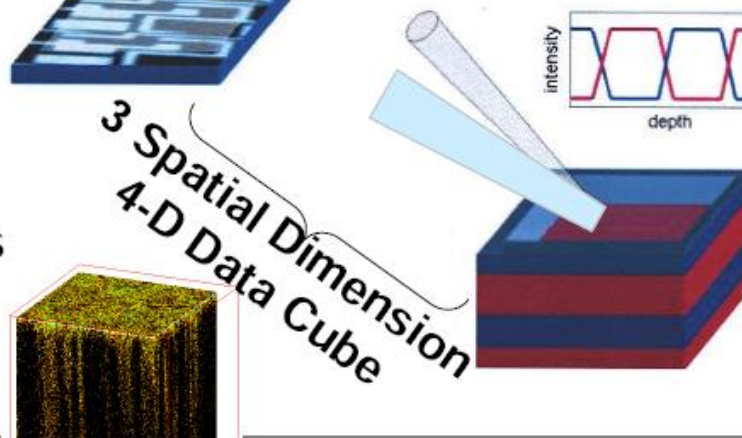
## Surface Imaging

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

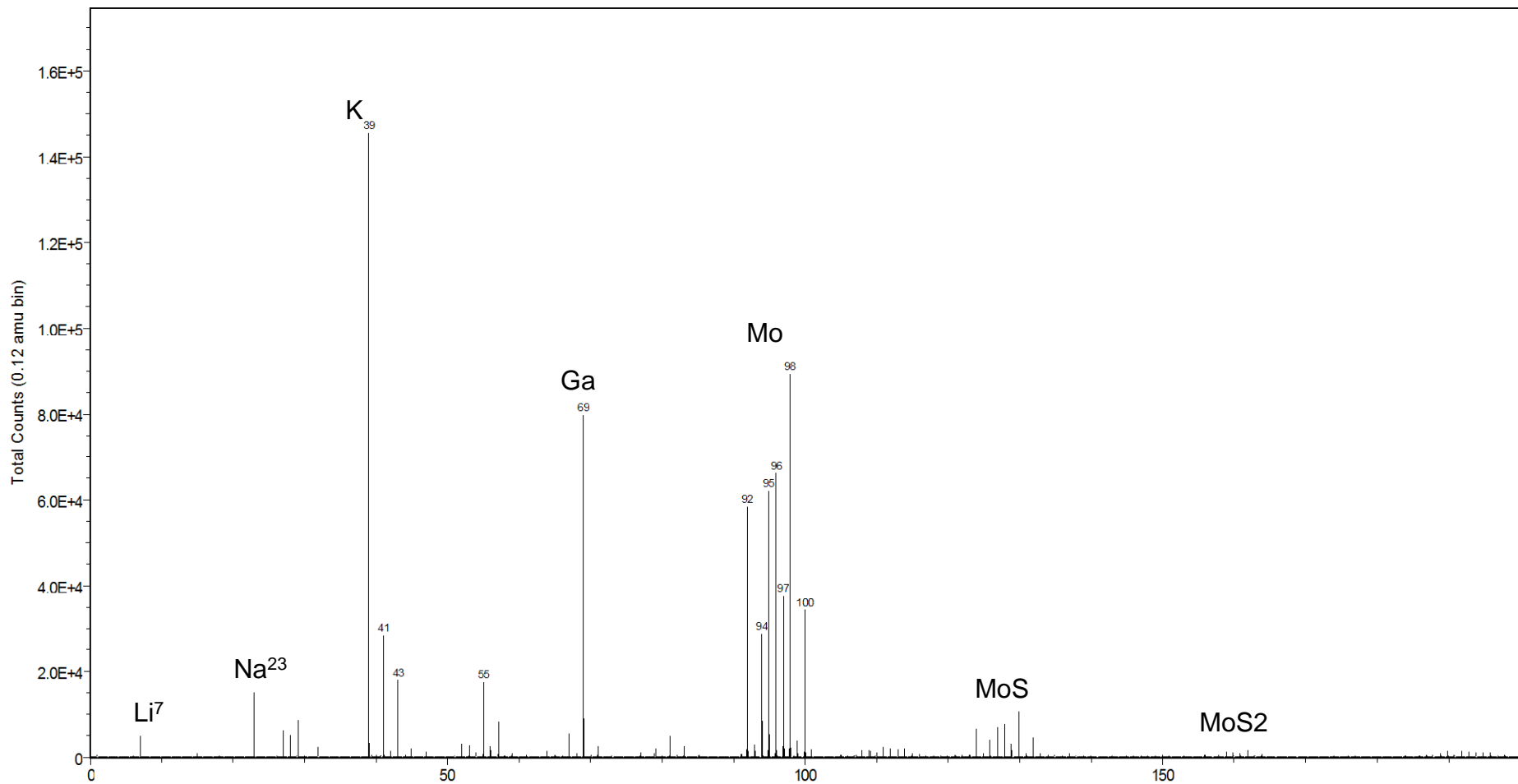


## Depth Profiling

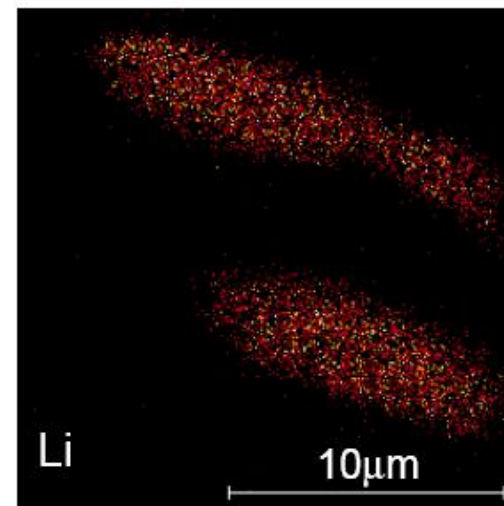
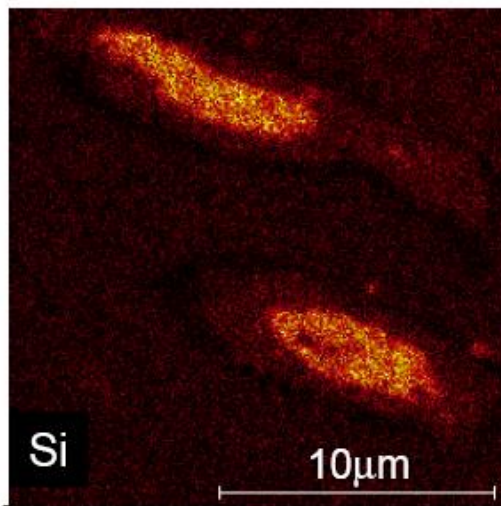
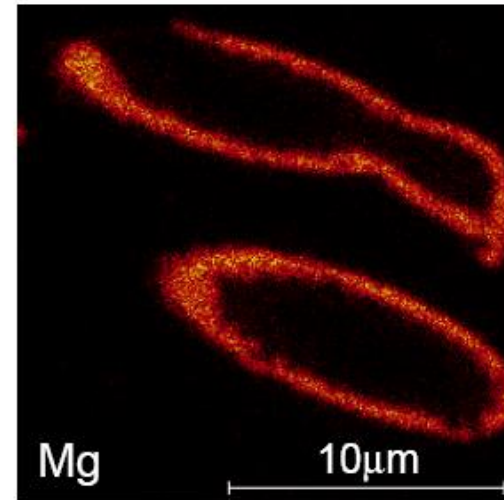
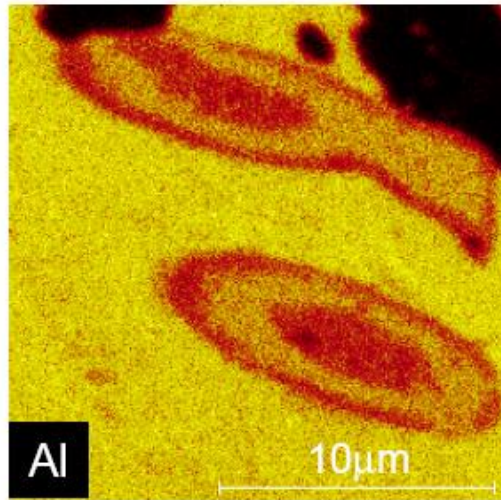
Depth resolution < 1 nm  
Thin layers from 1 nm to microns  
Parallel mass detection



# Positive spectrum of MoS<sub>2</sub> monolayer

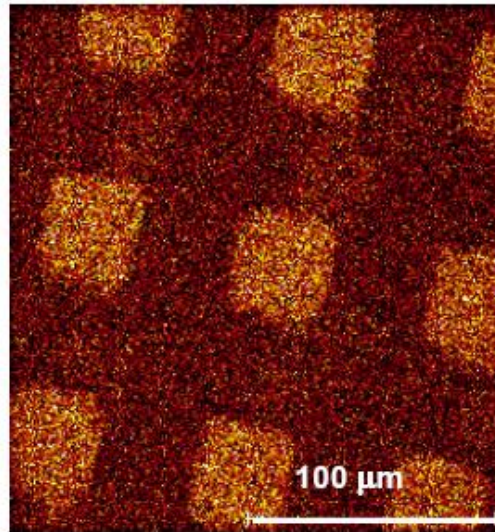


# Images of Al Metal Matrix Composite Heat Treatment: 500°C, 6 hr.

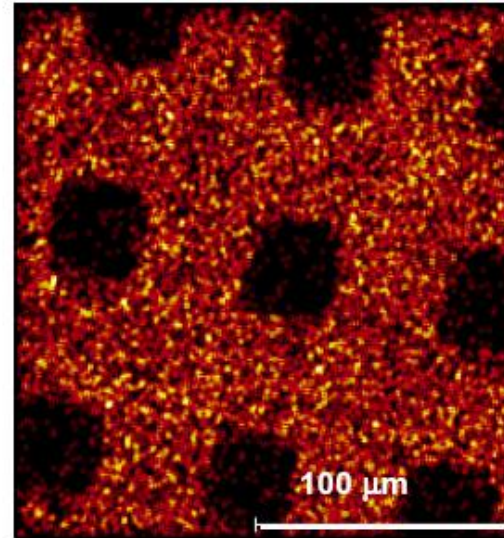


# TOF-SIMS Imaging of PET-Biotin

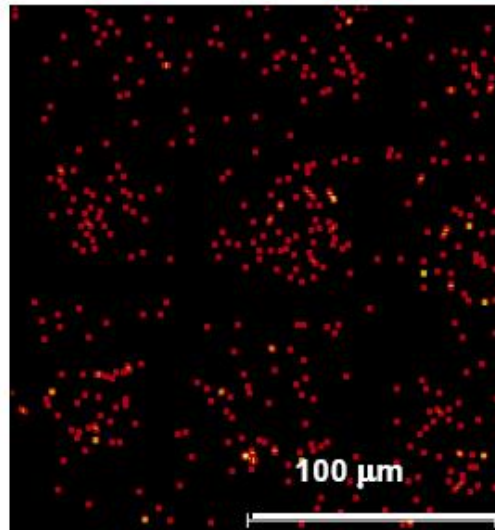
*Biotin*  
**CN<sup>-</sup>**  
m/z 26



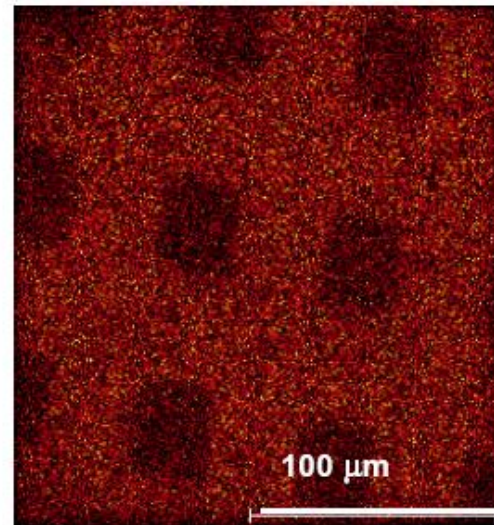
*PFP*  
**C<sub>6</sub>F<sub>5</sub>O<sup>-</sup>**  
m/z 183



*Biotin*  
**C<sub>10</sub>H<sub>15</sub>N<sub>2</sub>SO<sub>2</sub><sup>+</sup>**  
m/z 227



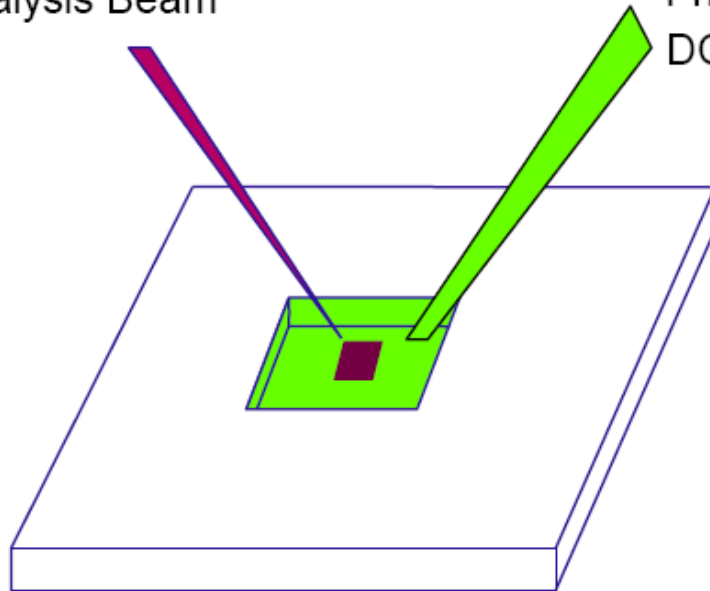
*PET*  
**C<sub>7</sub>H<sub>4</sub>O<sup>+</sup>**  
m/z 104



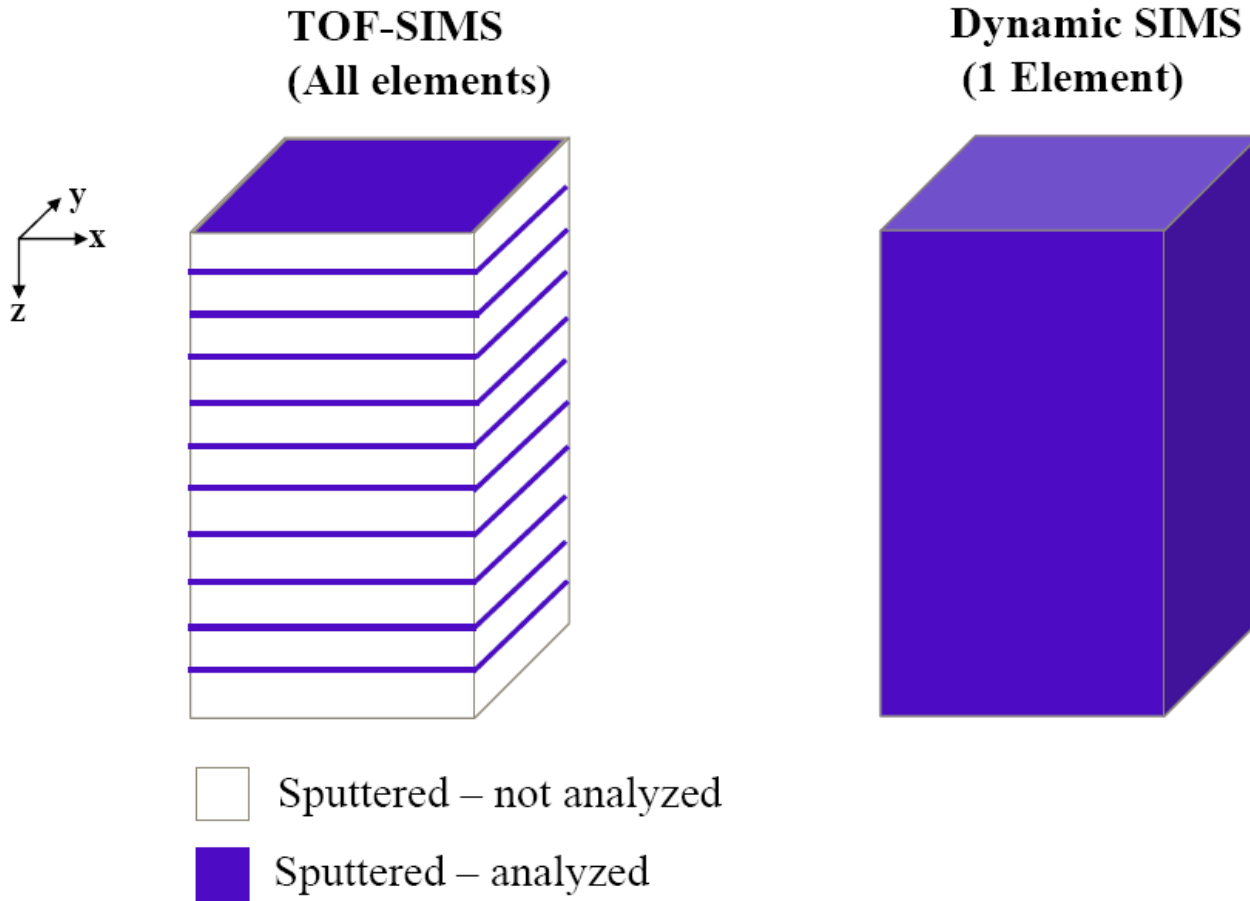
# Depth profiling

Ga<sup>+</sup> Ion Beam  
5-25 kV  
20 pA - 20 nA  
Pulsed Analysis Beam

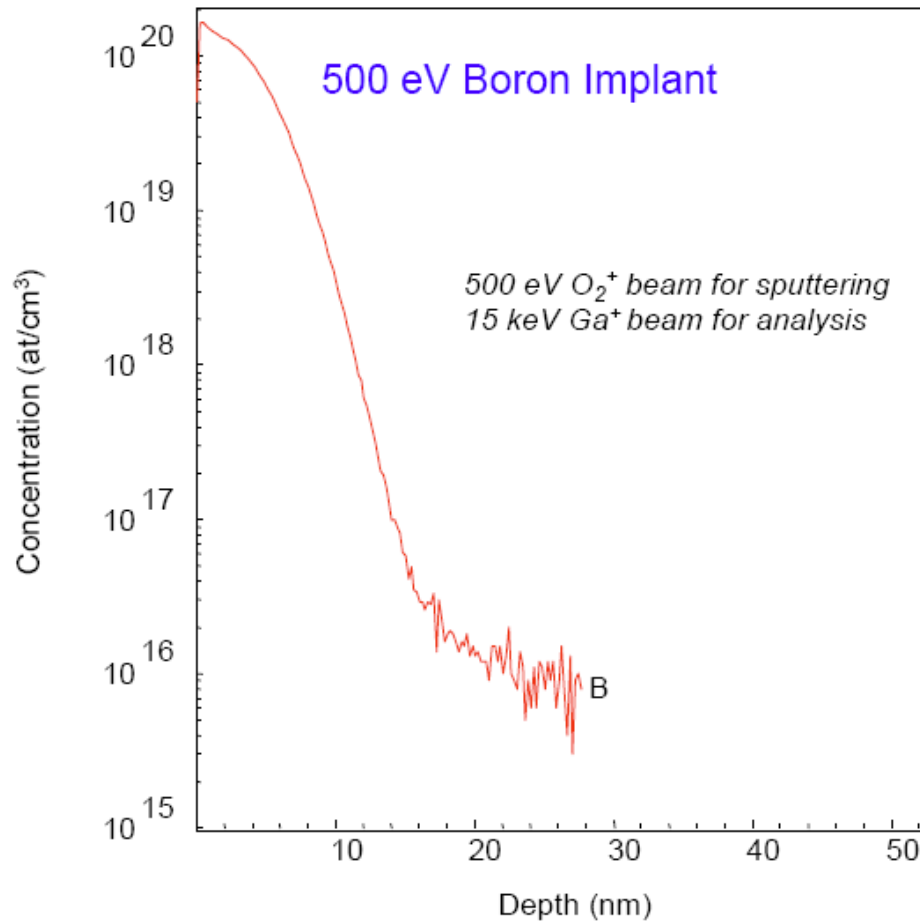
Cs<sup>+</sup> or O<sub>2</sub><sup>+</sup> Ion Beam  
250V-10kV  
1 nA - 200 nA  
DC Sputtering Beam



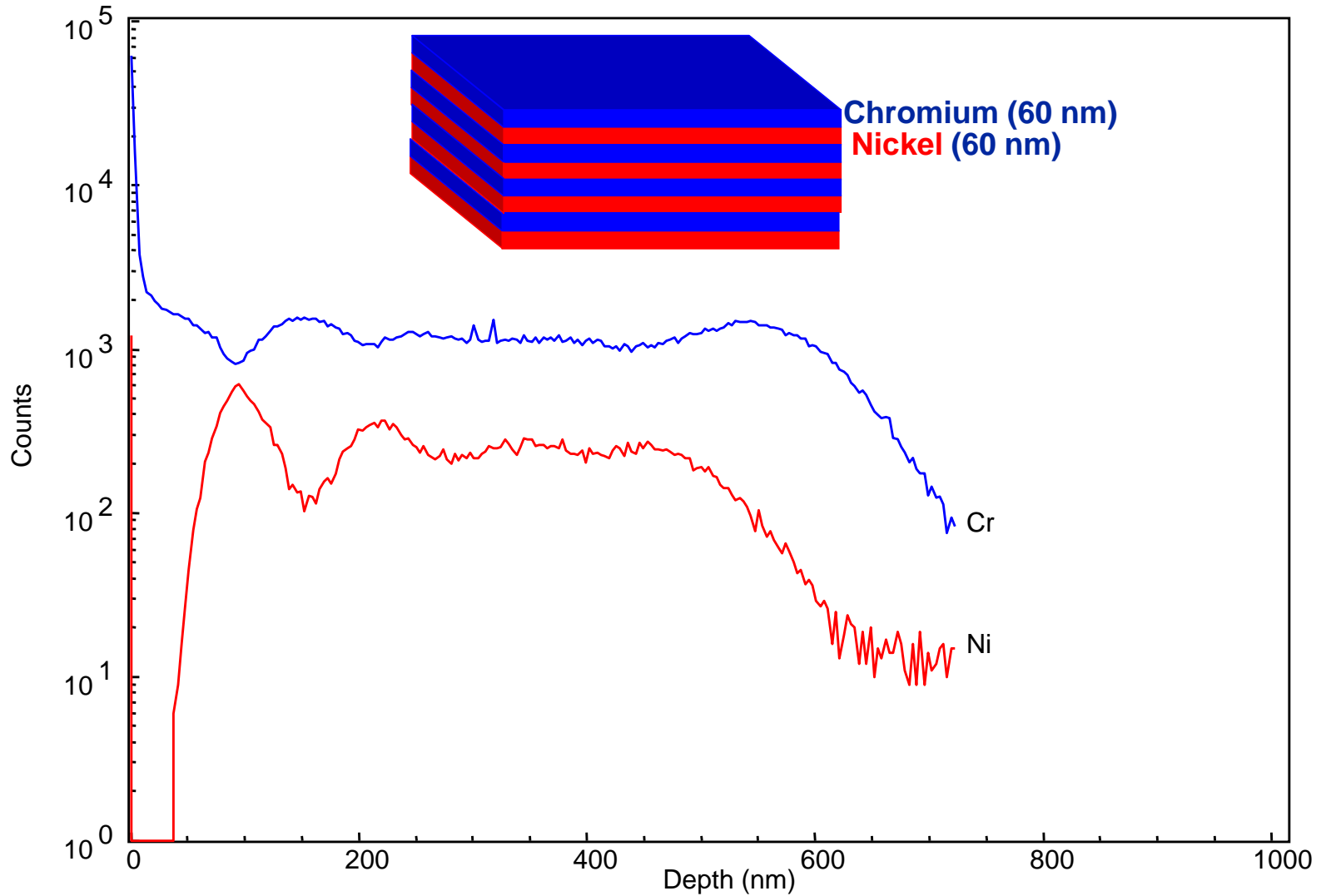
# Comparison of Analyzed Volumes



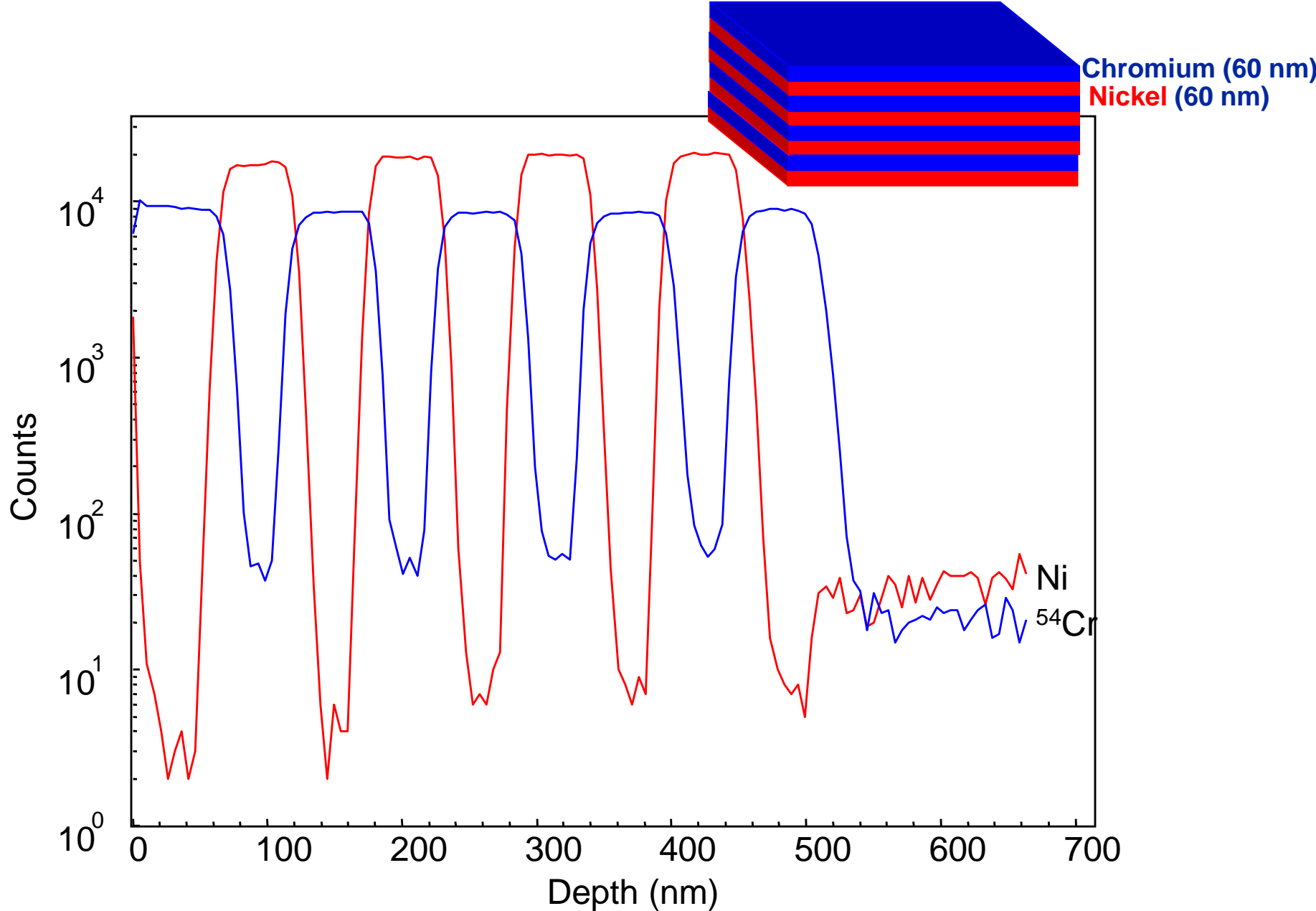
# Boron Implant Depth Profile





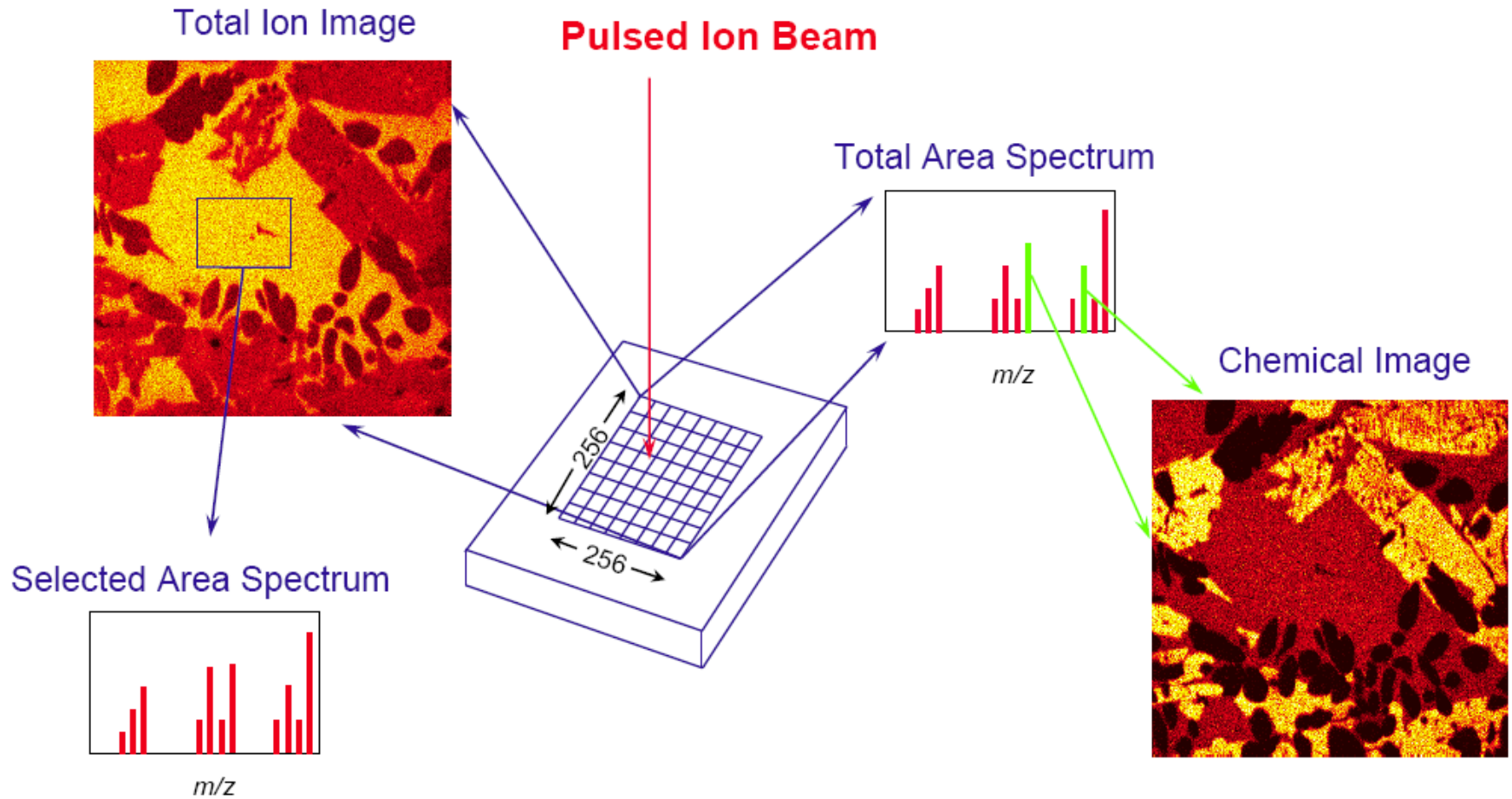


Depth profile of a Cr/Ni multi-layer standard using a 2 nA, 15 kV Ga<sup>+</sup> beam in the one-beam phase depth profiling mode. At this impact energy of 12 keV, the layers are not resolved beyond the second Ni layer.



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

# Post analysis with raw data



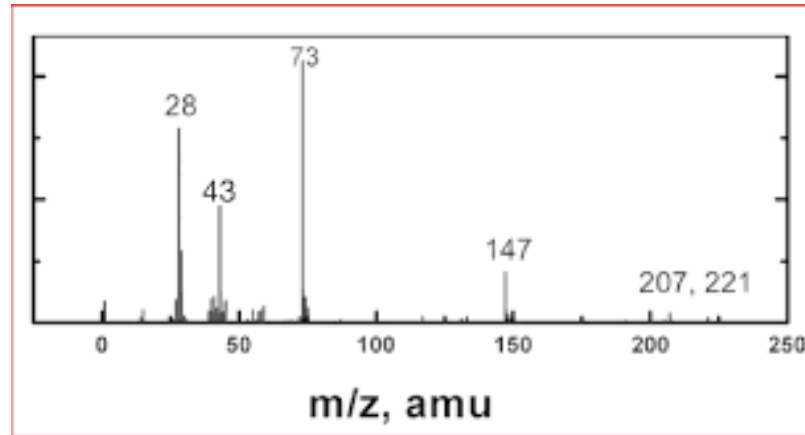
# Advantage of ToF-SIMS

- Detection of All Elements – H, He, Li, etc.
- Isotopic Detection –  $2\text{H}$ ,  $3\text{H}$ ,  $18\text{O}$ ,  $13\text{C}$ , 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

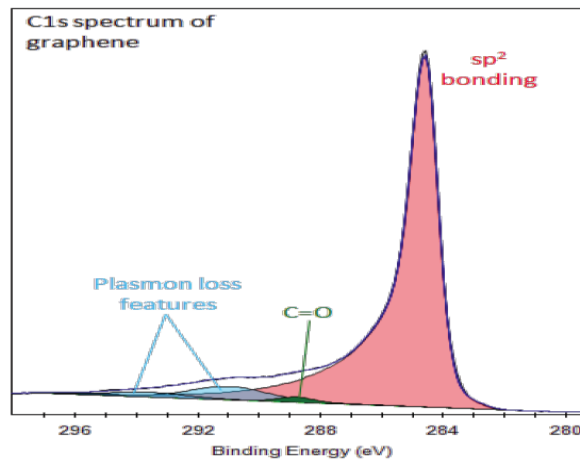
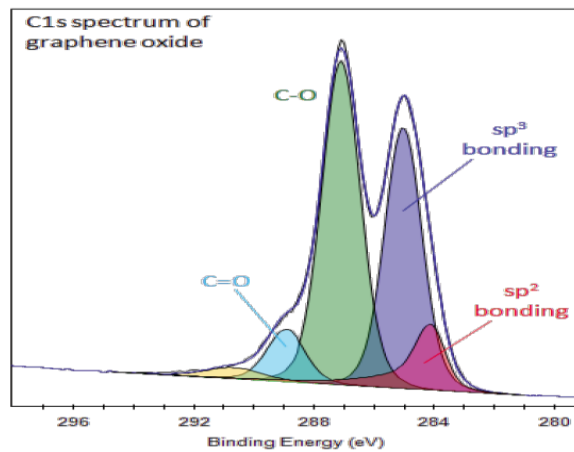
# Disadvantages

- 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.

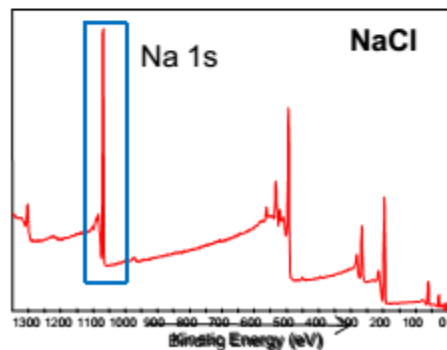
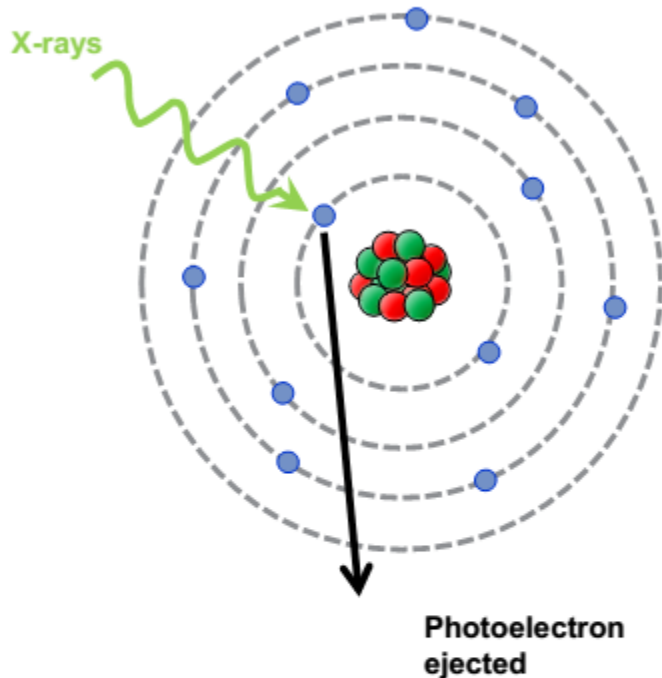
# Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)



## X-ray Photoelectron Spectroscopy (XPS)



# What is X-ray Photoelectron Spectroscopy (XPS)?

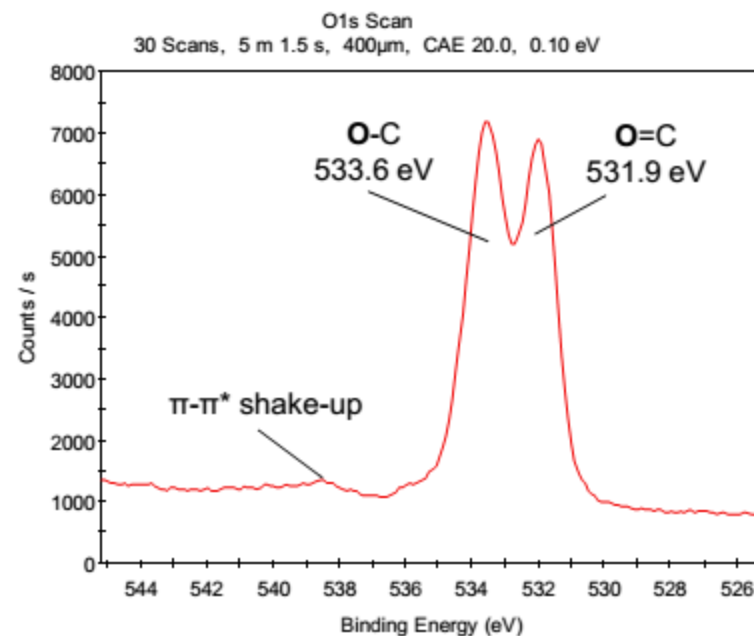
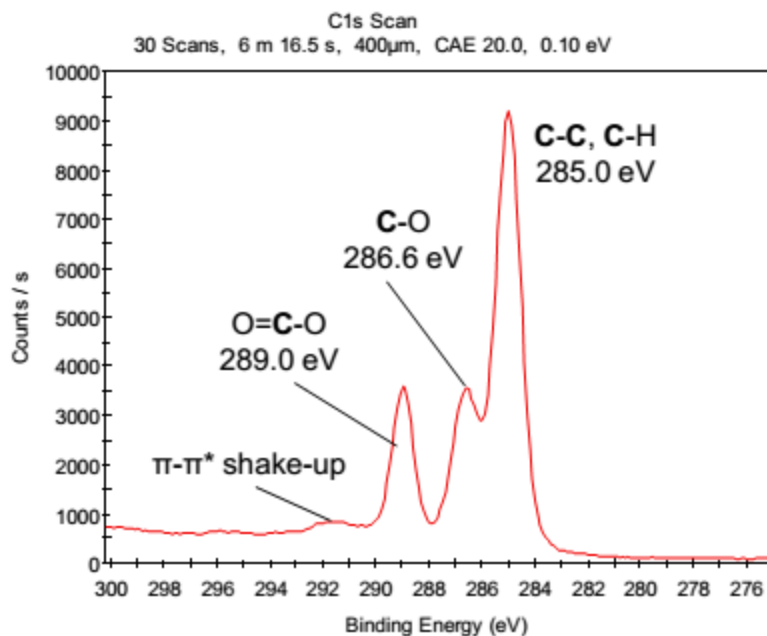
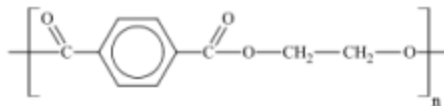


- Surfaces are composed of atoms of different elements.
- Electrons surround the nucleus of an atom, occupying orbitals at different energies (e.g., 1s, 2s, 2p, ... etc.).
- In XPS, the sample surface is irradiated with X-rays from a photon source (typically Al K $\alpha$ : 1486.6 eV).
- The X-rays cause electrons having lower binding energy to be ejected (photoelectrons) from the topmost surface ( $\leq 10$  nm) of the sample material.
- The kinetic energy (KE) of the photoelectrons is measured by an analyzer to create an energy/intensity spectrum.
- The original binding energy (BE) of the photoelectrons is deduced from the measured kinetic energy and the X-ray photon energy by the following equation:

$$BE = h\nu - KE$$

- The photoelectron binding energy depends upon:
  - Element of origin.
  - Orbital from which electron was ejected.
  - Chemical state of the element.

# High Resolution C 1s and O 1s XPS Spectra: PET

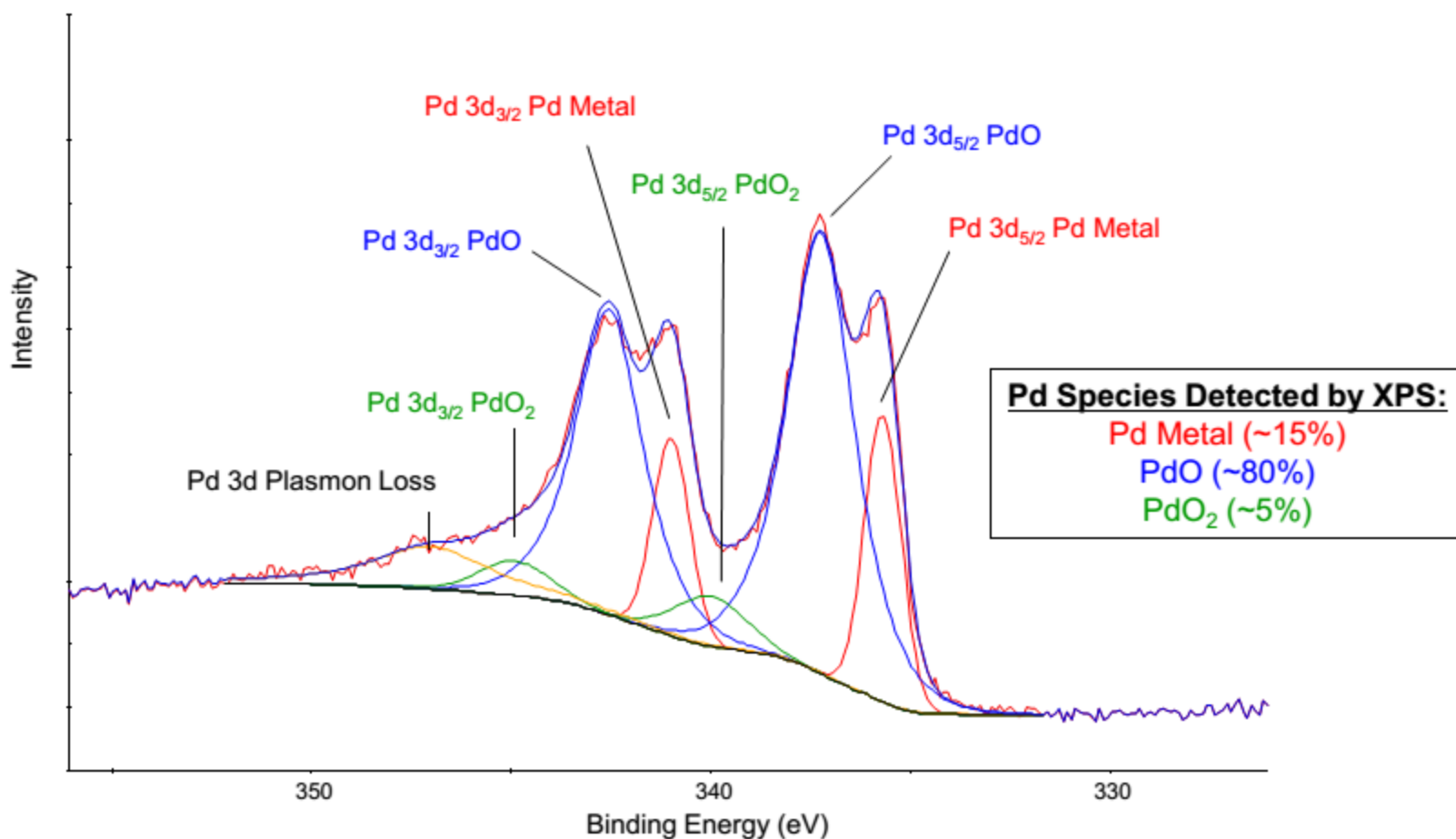


- High resolution chemical state results were consistent with the structure of PET.

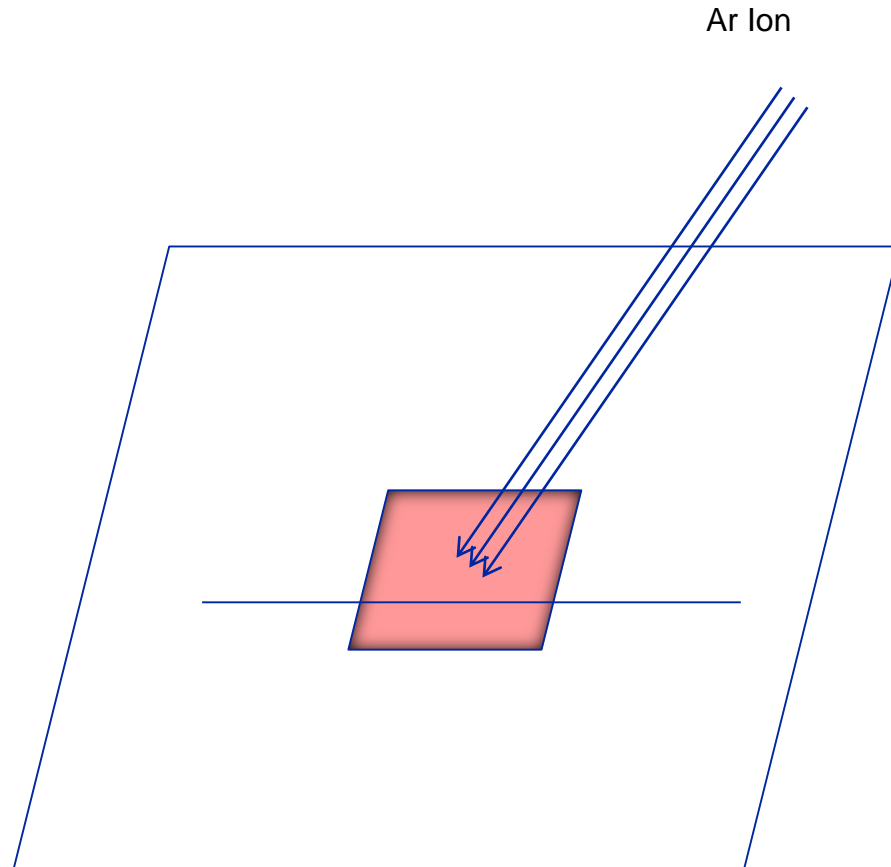
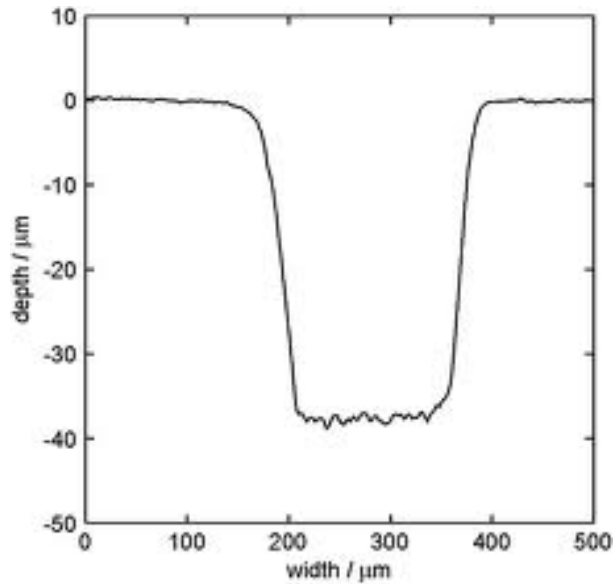


## Peak Fit for the Pd 3d XPS Spectrum: 10% Pd/Activated Carbon Catalyst

XPS provided surface chemical state information not obtainable by EDS.



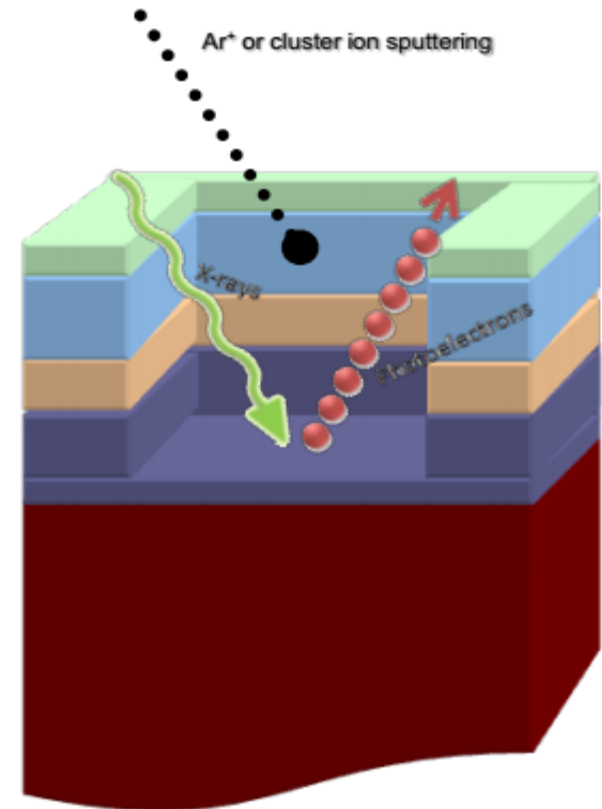
# Depth profiling by Ion Sputtering



# XPS Sputter-Cleaning and Depth Profiling

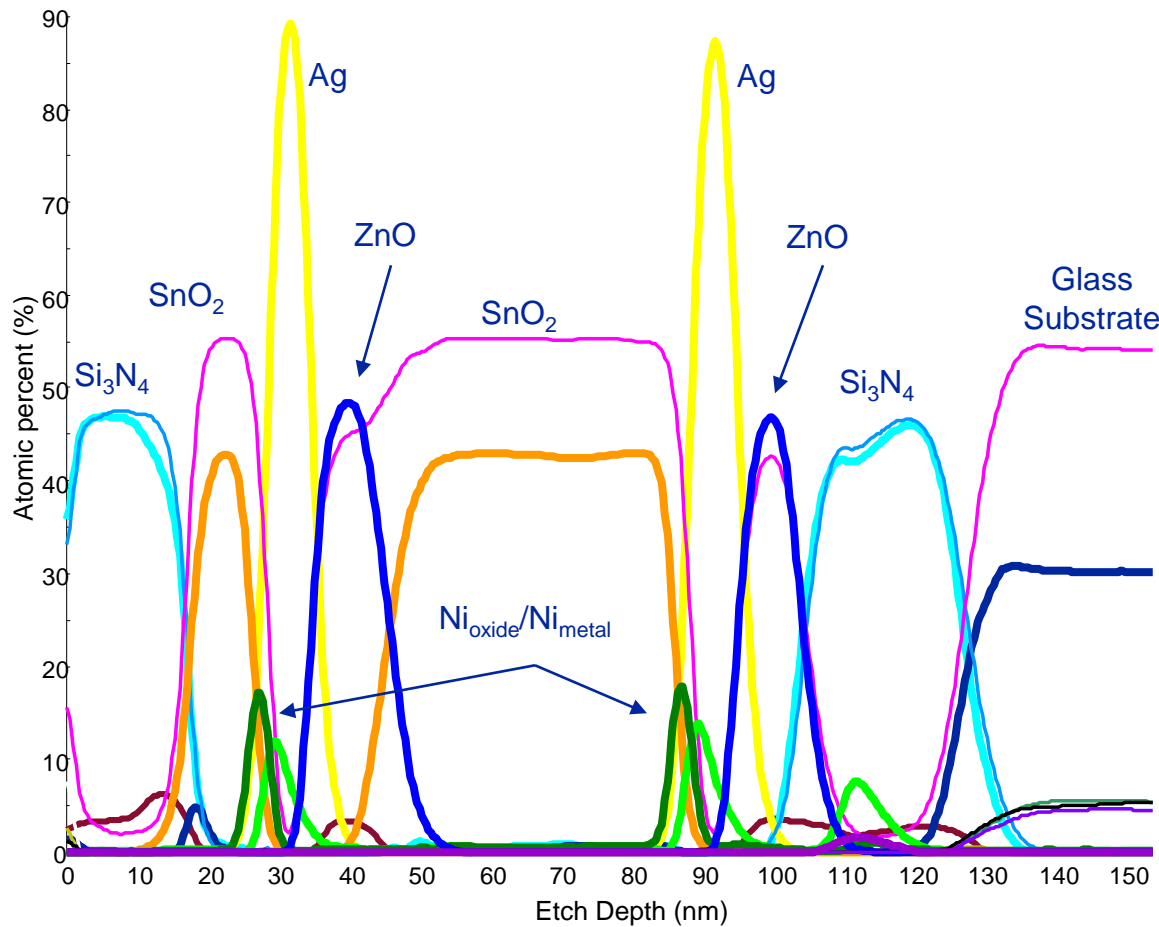
## ■ XPS sputter-cleaning and depth profiling

- How can we access deeper layers for analysis?
  - By progressively removing material from the surface and doing XPS analysis at each step.
  - Monatomic argon ion ( $\text{Ar}^+$ ) beam etching is the most common method.
  - XPS data is collected in the etch crater after each time period of ion sputtering.
  - $\text{Ar}^+$  ion etching damages some inorganic and most organic/polymeric materials.
  - Recently, argon cluster ion sources have been developed for “soft” depth profiling of beam sensitive materials, which maintains the chemical state information in XPS.



# XPS Depth Profile Analysis of a 10-Layer Low-E Glass Coating (Example-3)

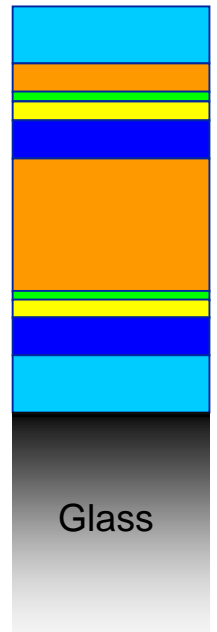
XPS Chemical State Depth Profile  
(All 10 layers are clearly resolved!)



- 500 eV  $Ar^+$  ions;  $> 1\mu A$  beam current
- 200  $\mu m$  X-ray spot size
- 2.5 mm x 5 mm raster area
- Azimuthal rotation of sample
- Charge compensation used

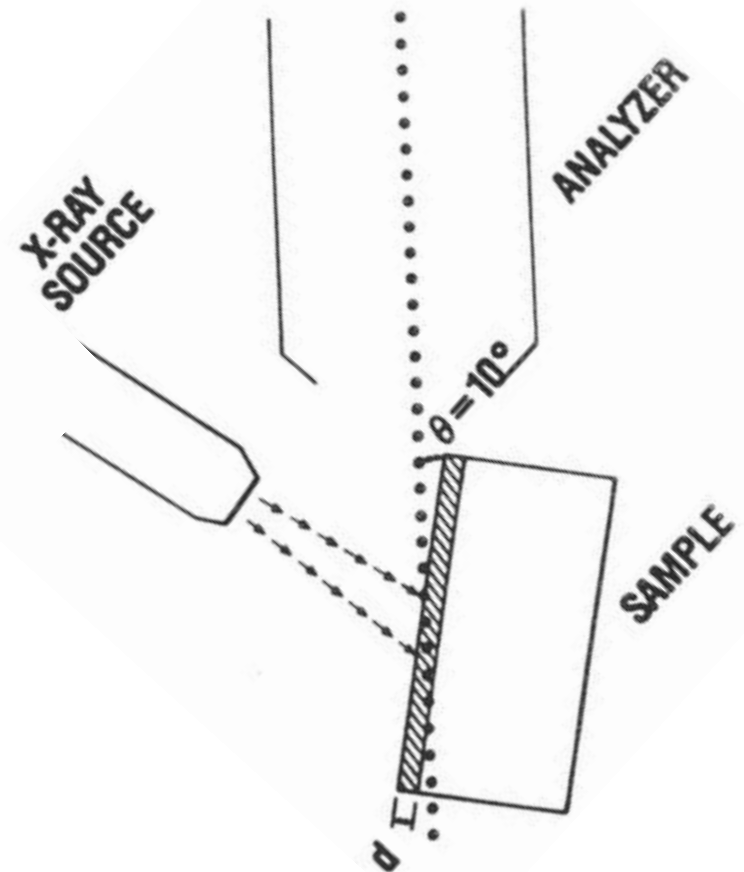
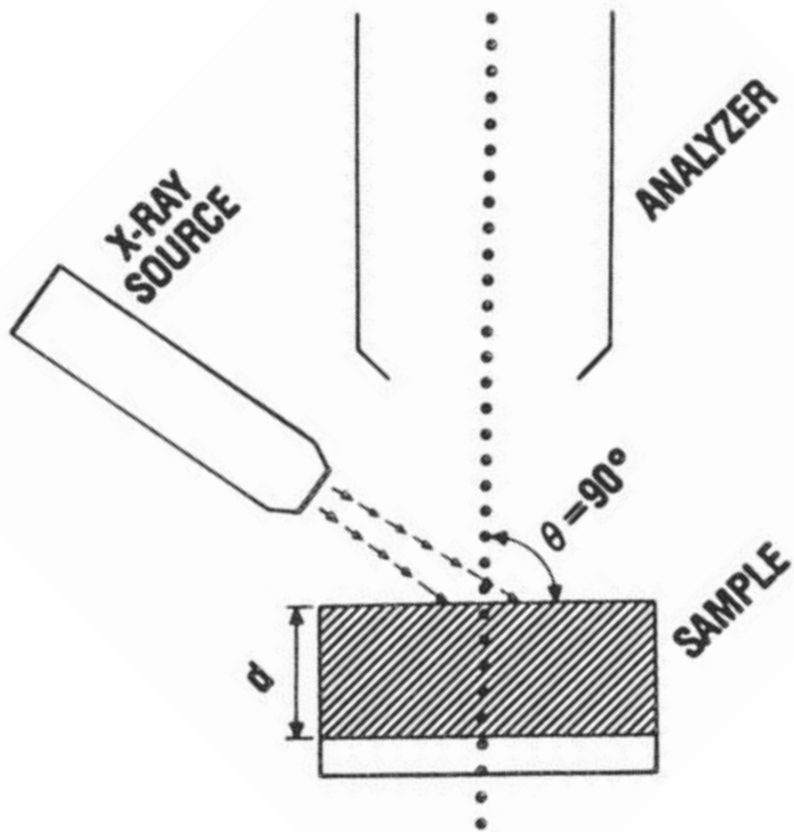
Model of 10-Layer Film Stack

- Al2p
- Si2p N
- Si2p Ox
- C1s C-C/C-H
- C1s carbonate
- Ca2p3
- Ag3d
- N1s
- Sn3d5
- O1s
- Cr2p3
- Ni2p3 metal
- Ni2p3 oxide
- Zn2p3
- Na1s
- Mg1s



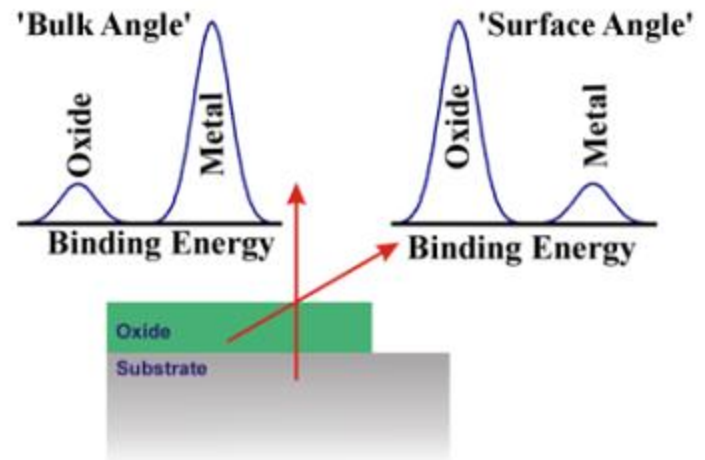
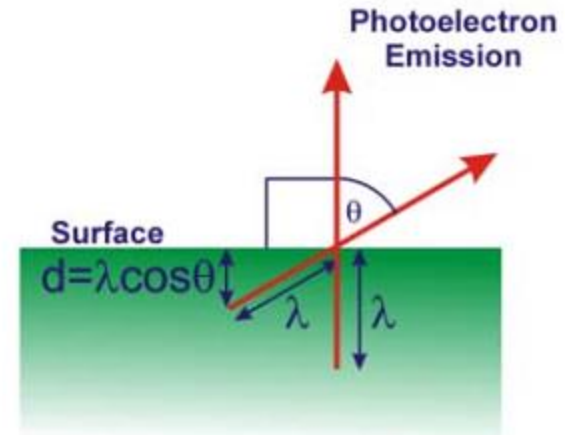
(Approximate relative thicknesses only.)

# Variation in Sampling Depth with Angle-Resolved XPS (ARXPS)

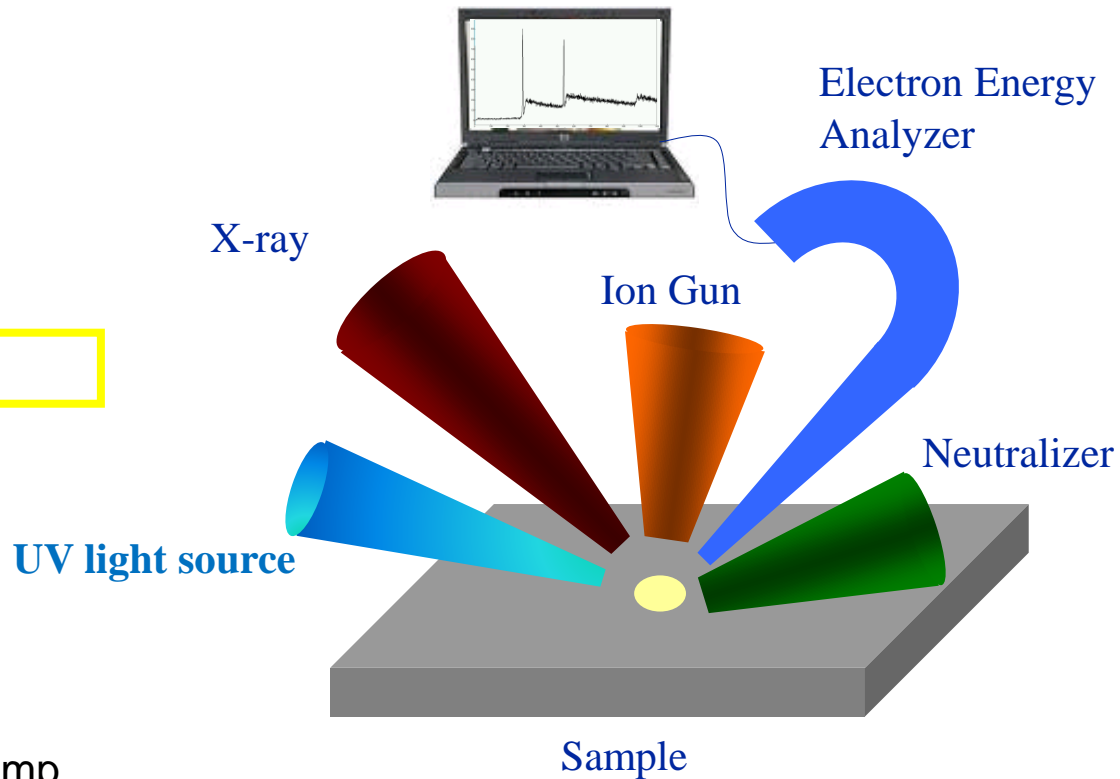


# Angle-Resolved XPS (ARXPS): Variation of Collection Angle

- By changing the electron collection angle, the XPS information depth varies.
- This variation gives a measured intensity:
$$I = I^{\infty} \exp(-d/\lambda \cos\theta)$$
- Electrons acquired at a grazing (“surface”) angle come exclusively from a shallow region of the sample.
- Electrons acquired at a near-normal (“bulk”) angle may come from deeper into the sample.
- Spectra acquired from thin films on substrates are affected by the collection angle.



# Ultraviolet Photoelectron Spectroscopy (UPS)



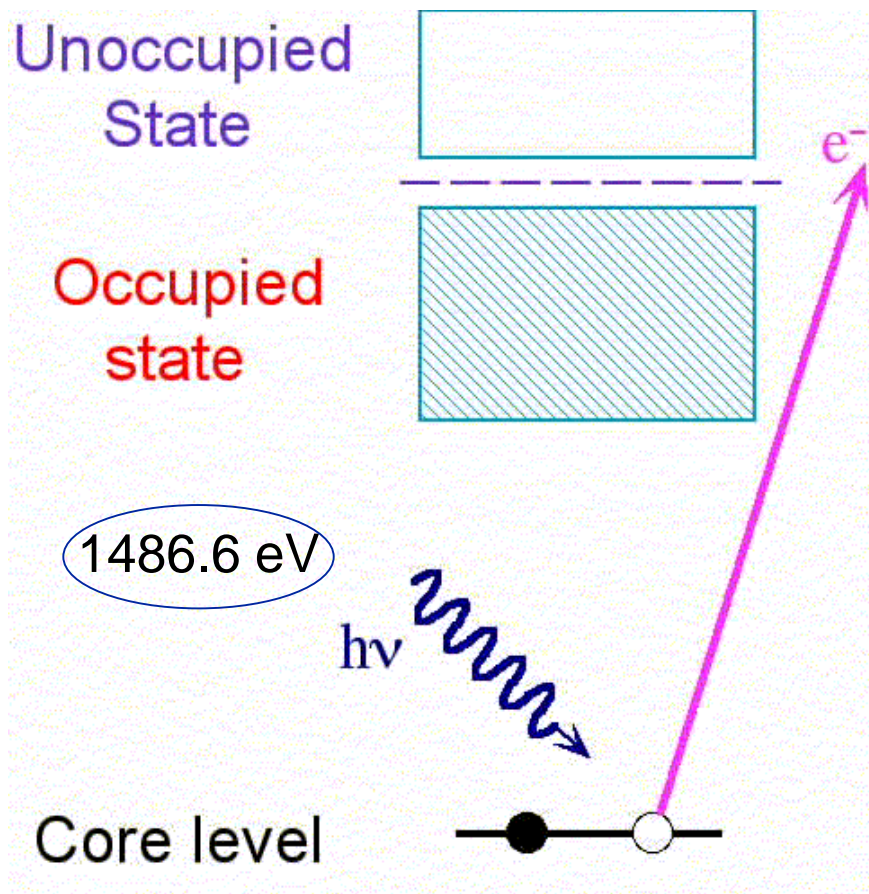
$$KE = h\nu - BE - \phi$$

Noble gas discharge lamp

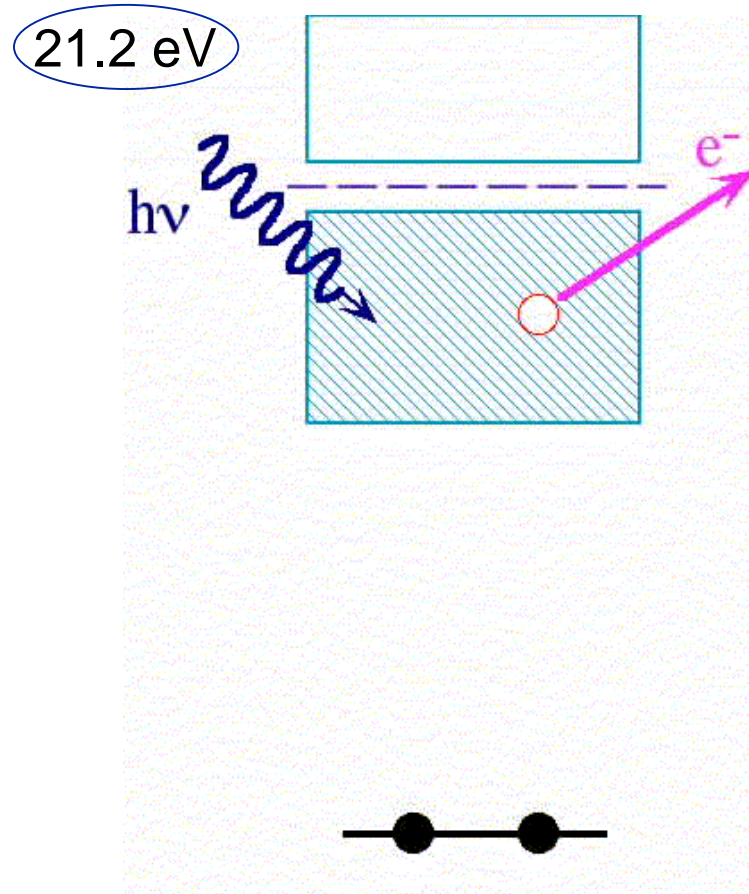
He I = 21.2 eV ± 0,01eV

He II = 40.8 eV ± 0,01 eV

# XPS

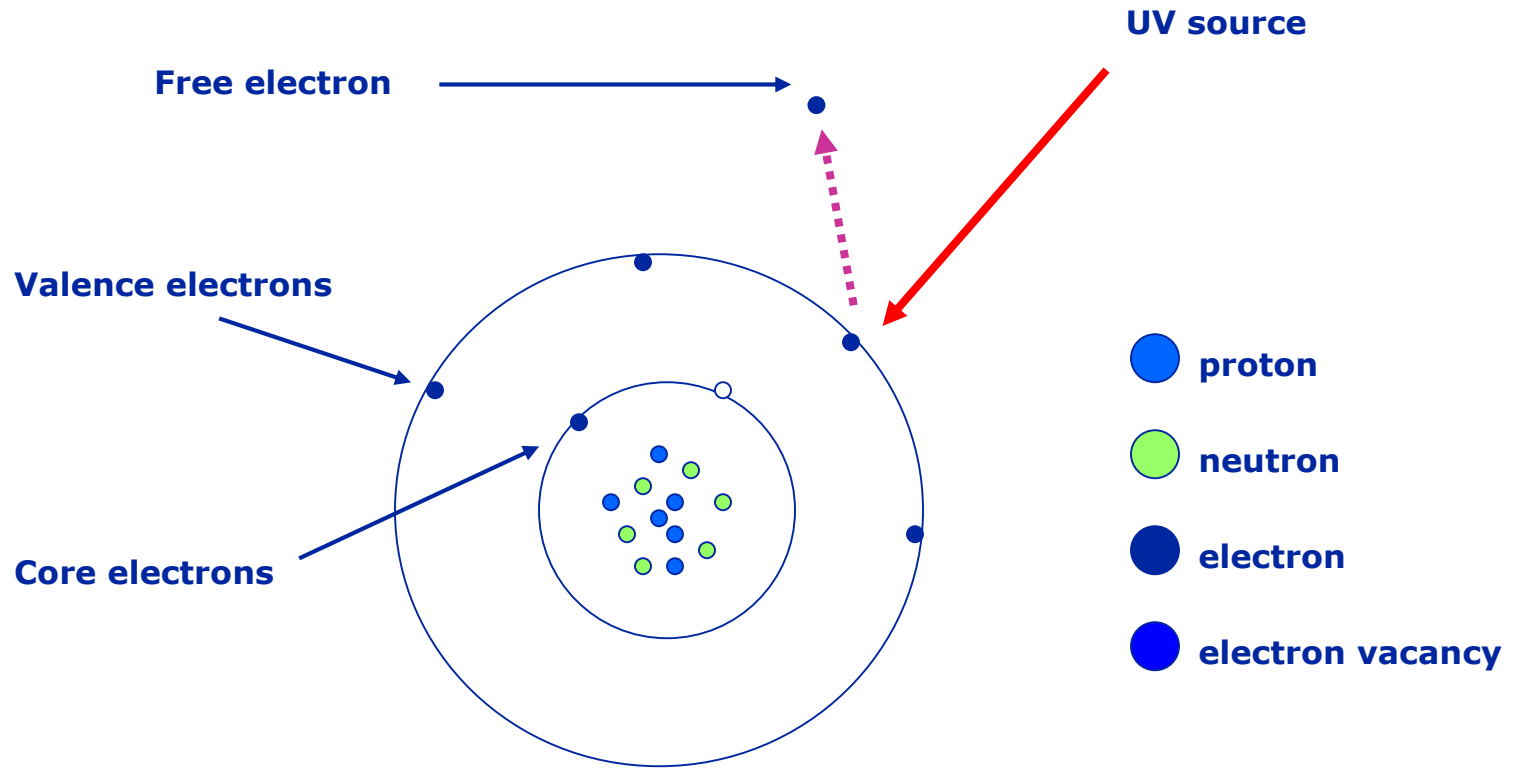


# UPS

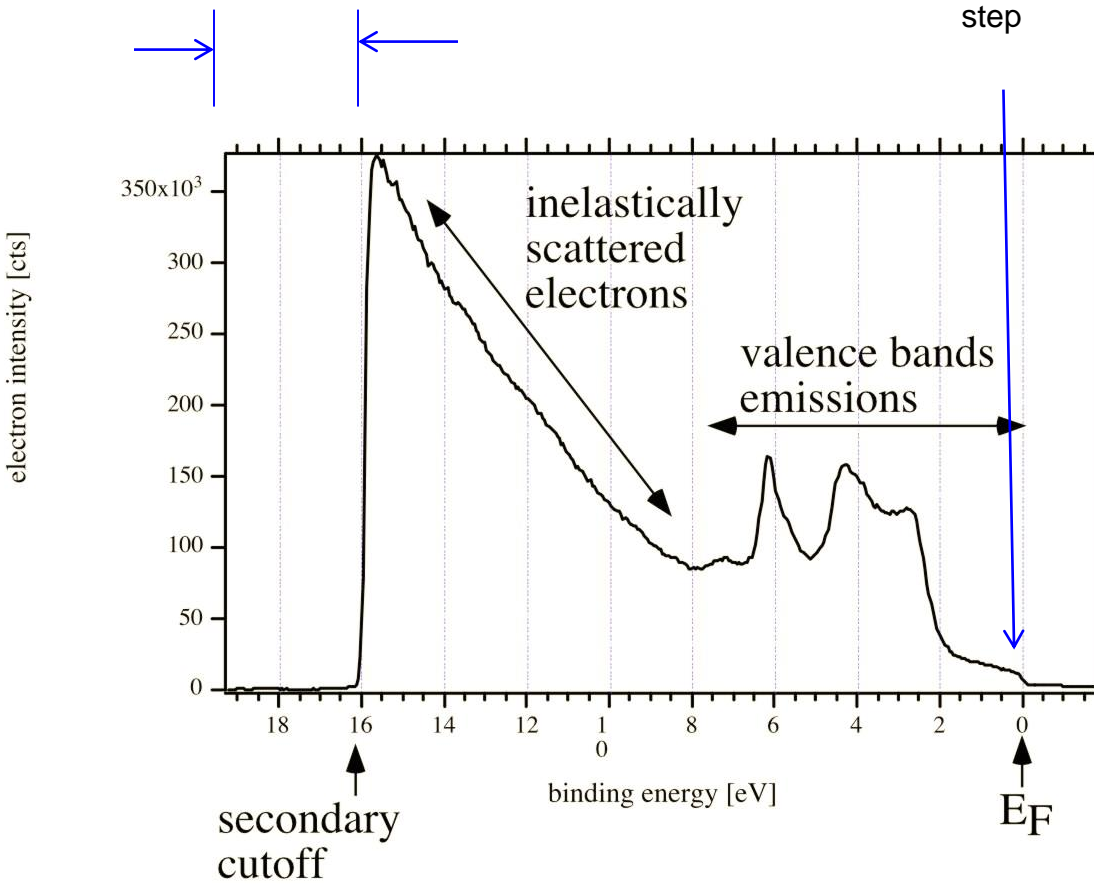




# Valence Electrons

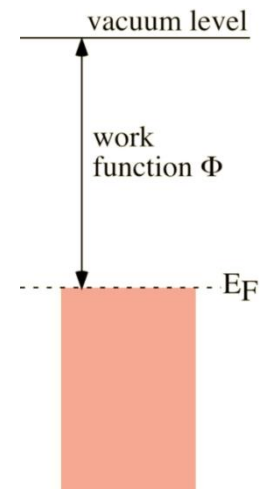


Work function =  $21.21 - 15.9 = 5.31$

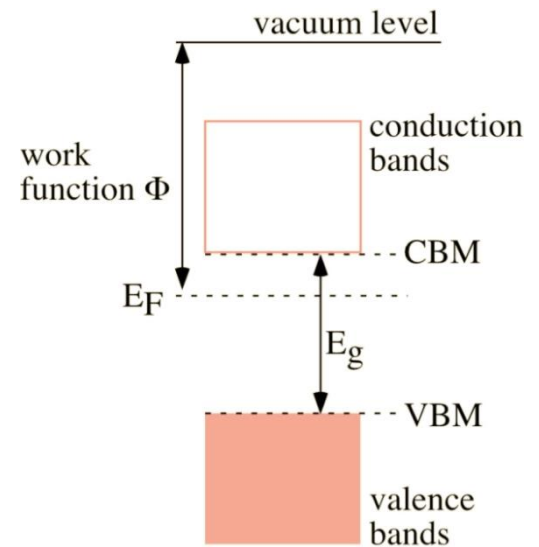


UPS spectrum of Au surface

Literature value 5.3 eV



Schematic energy diagram of a metal.



Schematic energy diagram of a semiconductor.

# 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 $\pm 5\%$	Semi-quantitative	Quantitative $\pm 15\%$
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

# Which instrument should be chosen for analysis?

1. Mapping MoS<sub>2</sub> flakes?
2. Check Fe<sup>2+</sup> and Fe<sup>3+</sup> ratio?
3. Concentration change along the depth?
4. Measure work function of a metal film?
5. Detect nitrogen or sulfur for monolayer molecular film?
6. Identify unknown spot?
7. Gel or solution sample?

Thank you!

