

Characterization, Testing of Nanotechnology Structures and Materials

E SC 216

Unit 5

Surface Analysis

Lecture 1

Particle Based Spectroscopies

Outline

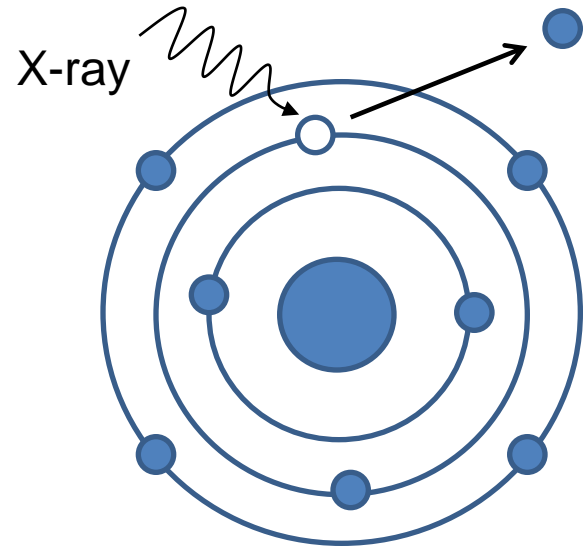
- X-Ray Photoelectron Spectroscopy
- Secondary Ion Mass Spectrometry

X-Ray Photoelectron Spectroscopy (XPS)

- X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is used to determine quantitative atomic composition and chemistry
- A sample is irradiated with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume.
- An XPS spectra is created by plotting the number of electrons verses their binding energy.

X-Ray Photoelectron Spectroscopy (XPS)

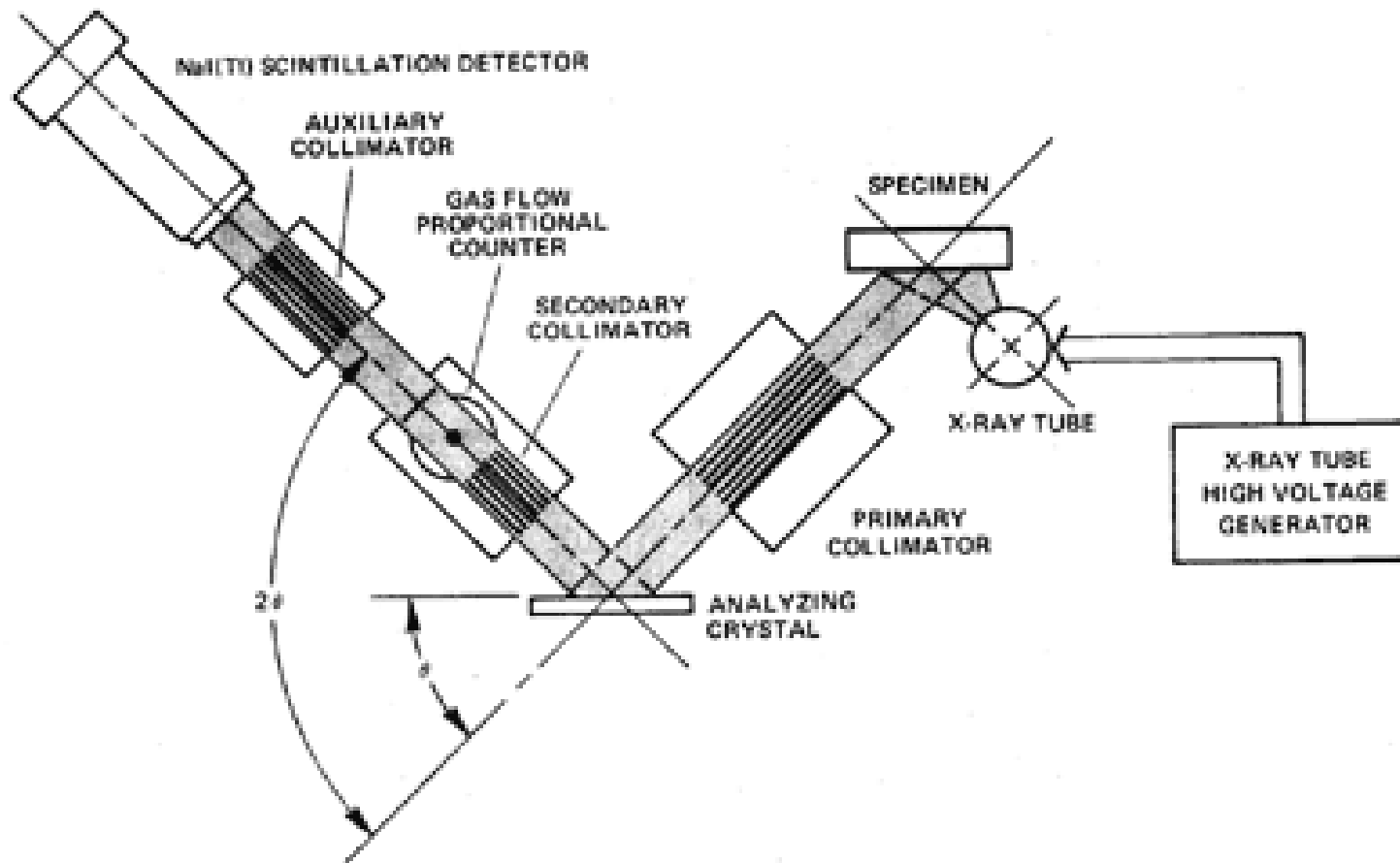
- An x-ray beam usually comprised of k-alpha x-rays is focused on the sample.
- The absorption of incident x-rays results in the ejection of electrons.
- The energy of the ejected electrons is measured by the detector.



X-Ray Photoelectron Spectroscopy (XPS)

- Each atom has a unique XPS spectra.
- XPS can determine elemental composition, stoichiometry, electrical/chemical states and examine surface contamination.
- XPS is an elemental analysis technique that is unique in providing chemical state information of the detected elements, such as distinguishing between sulfate and sulfide forms of the element sulfur

Block Diagram



archaeometry.missouri.edu/xrf_overview.html

Ranges & Material for XPS

- Vacuum Range
 - Requires ultra high vacuum
 - Sample compatibility with UHV environment may be an issue with biological samples
- Sensitivity
 - Measures the elemental composition of the top 10 nm
 - Can detect all elements except H and He
 - Detection limits typically ~ 0.1 atomic percent
 - Typically the smallest analytical area $\sim 10 \mu\text{m}$
- Material analysis
 - Can analyze metals, inorganic, polymers
 - Sample compatibility with UHV environment

Outline

- X-Ray Photoelectron Spectroscopy
- Secondary Ion Mass Spectrometry

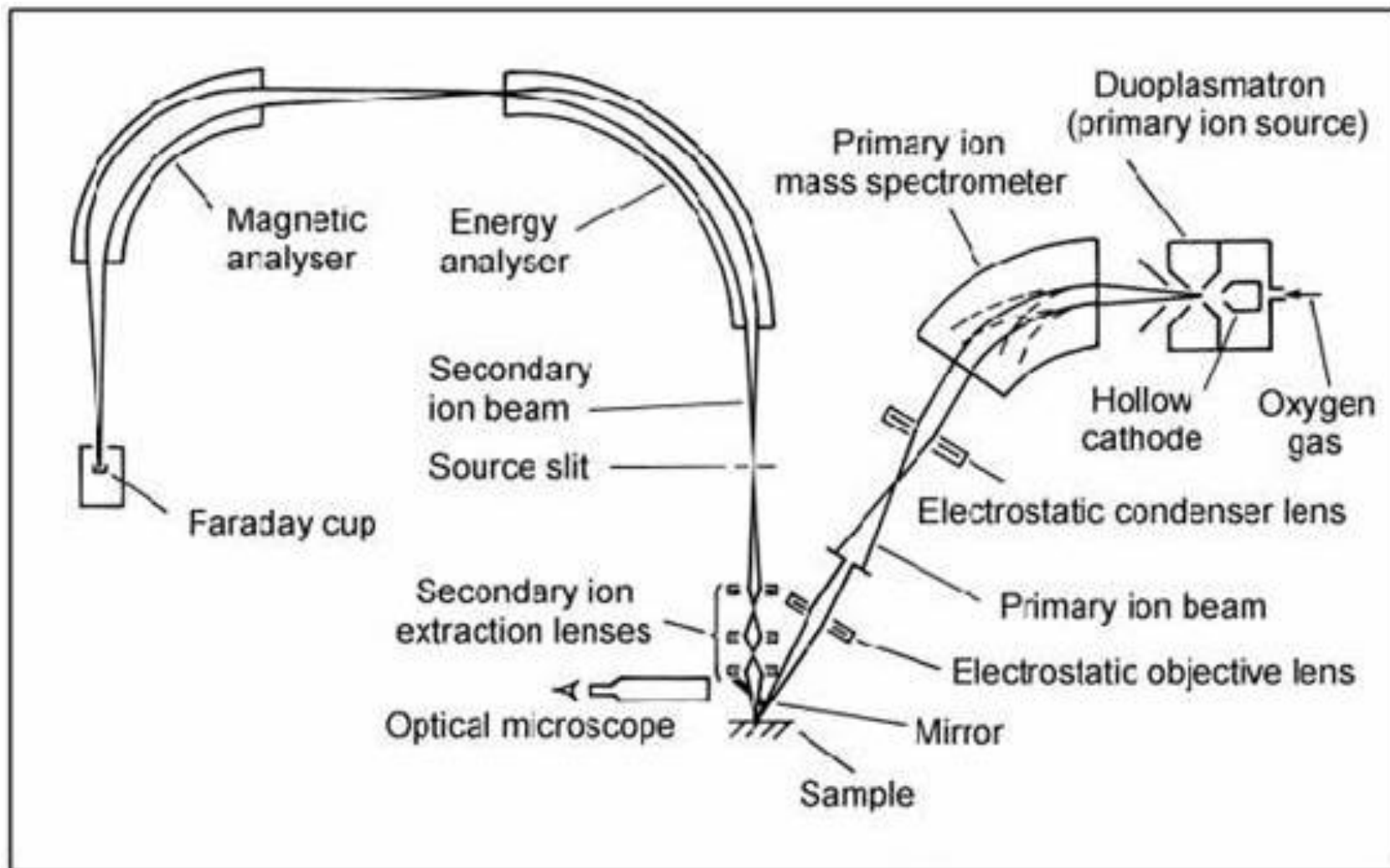
Secondary Ion Mass Spectrometry (SIMS)

- SIMS is destructive characterization method for determining the chemical composition of a material.
- The measurement can be done at the surface of a sample, or utilizing simultaneous ion milling, composition as a function of depth can be determined.
- The measurement tells what atoms are present, but it does not give information on chemical bonding
- SIMS is the most sensitive technique available for determining material composition. It can detect down to one part per billion

Principle of Operation

- Ions are accelerated into sample.
- When they strike the sample it emits secondary ions from the surface of the sample.
- The scattered ions are accelerated and positioned by a series of magnetic fields.
- The ions then go through a mass analyzer to separate ions for analysis.

Typical SIMs Block Diagram



SIMS

- The ion beam can be moved quickly across the surface for near surface chemical analysis, or the beam can be focused in one area to “dig” a profile into the sample.
- Typically the beam spot is approximately one micron in diameter. Of course this varies by tool.
- The ion source is typically Cs^+ , O_2^+ , O^+ , Ar^+ , and Ga^+ at energies between 1 and 30 keV.
- The ion species will contaminate and interact with the surface depth of approximately 1 – 10 nm.

Ion Emission

- Three types of ion emitters
 - Gaseous ionization by electron ionization
 - Surface ionization of Cs ions
 - Liquid metal ionization

Ion Source	Beam Current	Beam Focus
Gaseous Ionization	High	Rough
Surface Ionization	Small-High	Fine-Rough
Liquid Metal Ionization	Moderate	Very Fine

Gaseous Ionization

- Gaseous ionization uses an electron gun to ionize a gaseous source of elements or molecules. The ion beam created by this technique has a high current but is roughly focused.

Surface Ionization

- In surface ionization, cesium is evaporated through a tungsten plug. This creates cesium ions. This technique creates either a tightly focused ion beam or a high current beam.

Liquid Metal Ionization

- For liquid metal ionization, a tungsten tip is covered in a metal or metal alloy that is typically liquid at or near room temperature.
- When the tip is subjected to a high electric field the tip will emit ions from the covering metal. This process is capable of producing very tightly focused ion beams of less than 50 nm.
- The electric field used to create the ions can be turned on and off in order to create pulsed ion beam.

Some SIMS Issues

- The ion source is typically Cs^+ , O_2^+ , O^+ , Ar^+ , and Ga^+ at energies between 1 and 30 keV
- These ions can chemically interact with the substrate
- Beam chemistry is selected to minimize this reaction.
- Beam chemistry and energy selection are part of the art of this procedure.

Cs and O₂ Ion Selection

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					

O_2^+ Primary
Postive Secondary

Cs^+ Primary
Negative Secondary

O ₂ ⁺ Primary Ion Beam Positive Ions		Cs ⁺ Primary Ion Beam Negative Ions	
Element	DL (atoms/cm ³)	Element	DL (atoms/cm ³)
Li	1E+13	H	1E+18
B	5E+13	C	2E+17
N	2E+17	N	3E+16 – 2E+17 ¹
Na	2E+13	P	1E+15
Mg	2E+13	S	1E+16
Al	1E+14	Cl	1E+16
K	1E+13	Cr	2E+16
Ca	5E+13	Fe	3E+16
Ti	5E+13	Ni	3E+15
Cr	2E+13	Cu	2E+15
Mn	1E+14	As	2E+15
Co	2E+14	Ge	2E+15
Fe	2E+14 – 5E+14	Au	1E+15
Ni	1E+15	-	-
Cu	5E+14	-	-
Zn	3E+15	-	-
As	2E+16	-	-
Mo	5E+14	-	-
In	2E+14	-	-
Ta	5E+15	-	-
W	5E+15	-	-

Note: For dynamic sector O_2^+ Primary Ion Beam sputtering, the maximum oxide layer thickness should be less than 1.5 μm for proper charging compensation

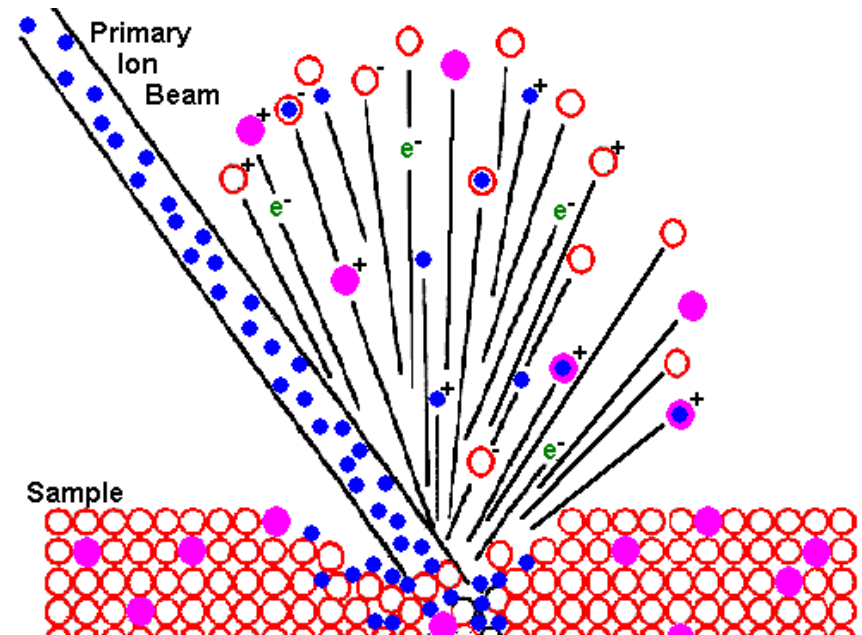
¹Higher detection limit for BPSG

SIMS

- The ion beam will sputter at a approximate rate of 0.5 to 5 nm/s. Naturally, sputter rates are a function of primary beam intensity, sample material, and crystal orientation.
- Sputtered substrate ions will be approximately 1% of the incident ion stream.

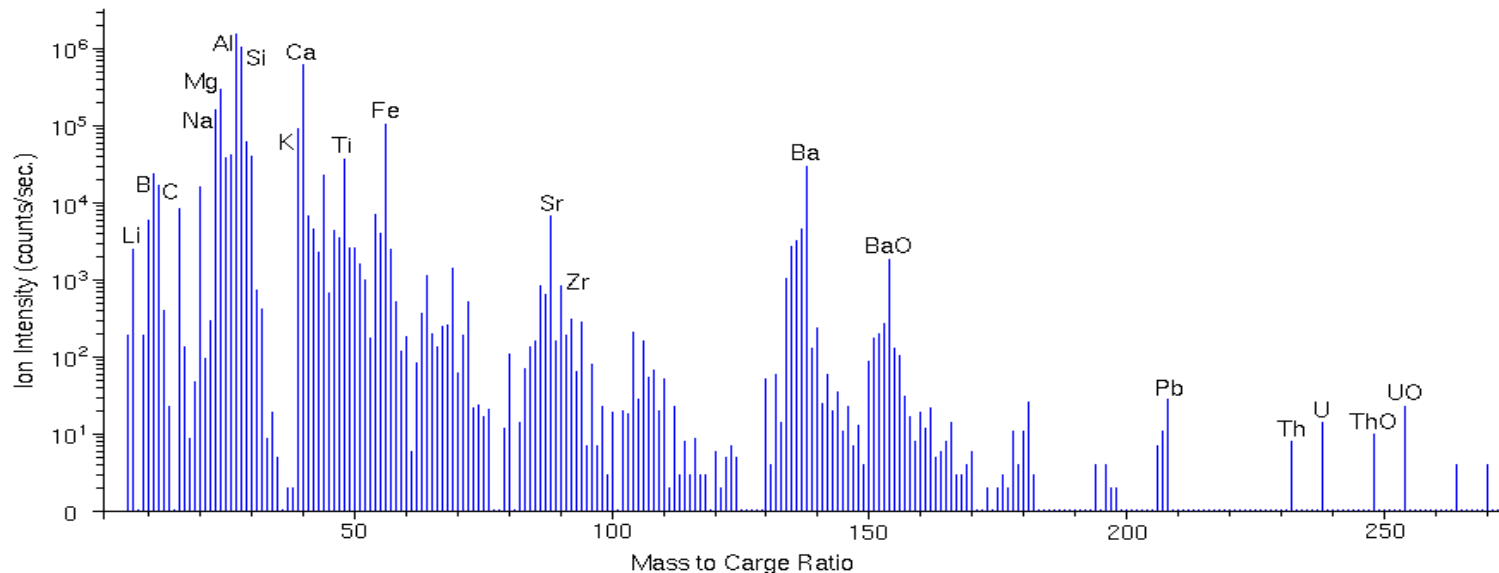
SIMS

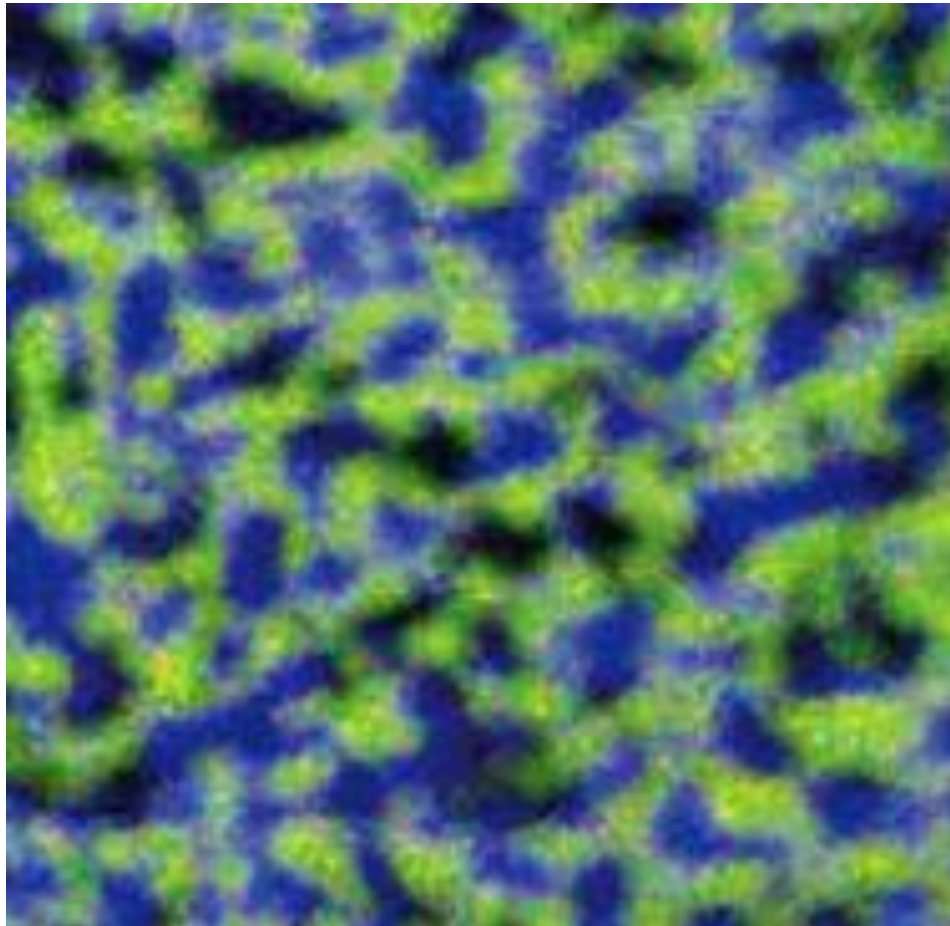
- Note the primary ion beam can contaminate the surface.
- The ejected species contain the incident ions, sample material, electrons, and photons.
- The secondary particles carry negative, positive, and neutral charges and they have kinetic energies that range from zero to several hundred eV.



SIMS Detection

The mass spectrum detects both atomic and molecular ions.
Mass to charge ratio can be misinterpreted.
Naturally the molecules can be dissociated into atomic fragments. This is especially true of organic media.





ToF-SIMS image of pharmaceutical ingredient distribution (Bentley).

Some SIMS Issues

- The secondary ion signal from the sample may be shielded from reaching the detector due to substrate charging.
- Dielectric samples may charge negatively and prevent positive ions from reaching the detector.

Some SIMS Issues

- There are a few ways of preventing this negative charge build up.
- High energy electron beams, are used to add negative charge to the sample. This e-beam may interfere with the quadrapole detector.
- Dielectric samples can be coated with a conductive layer. Naturally, this layer will be included in the analysis.
- Software can add an offset voltage to compensate for the negative charging. Not a total solution, but more of an aid.

Some SIMS Issues

Atoms from the sample's outer monolayer can be driven in about 10 nm.

This type of damage is commonly called “surface mixing” or “knock on”.

Sputtering also creates surface roughness lattice imperfections, roughness, etc.

It is a destructive test.

