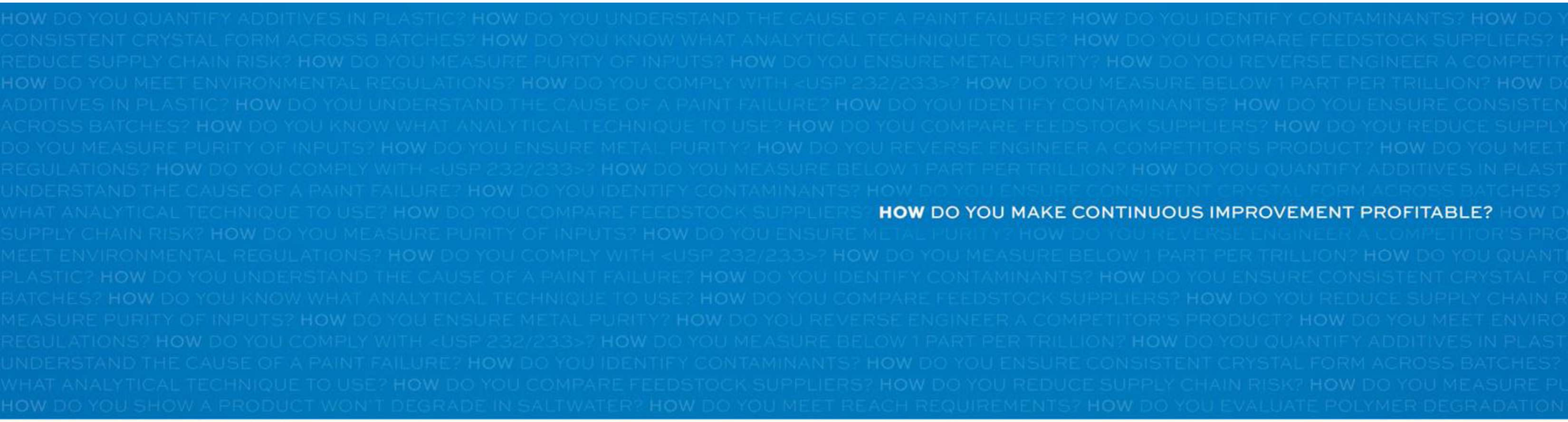


Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS -*Static SIMS*)

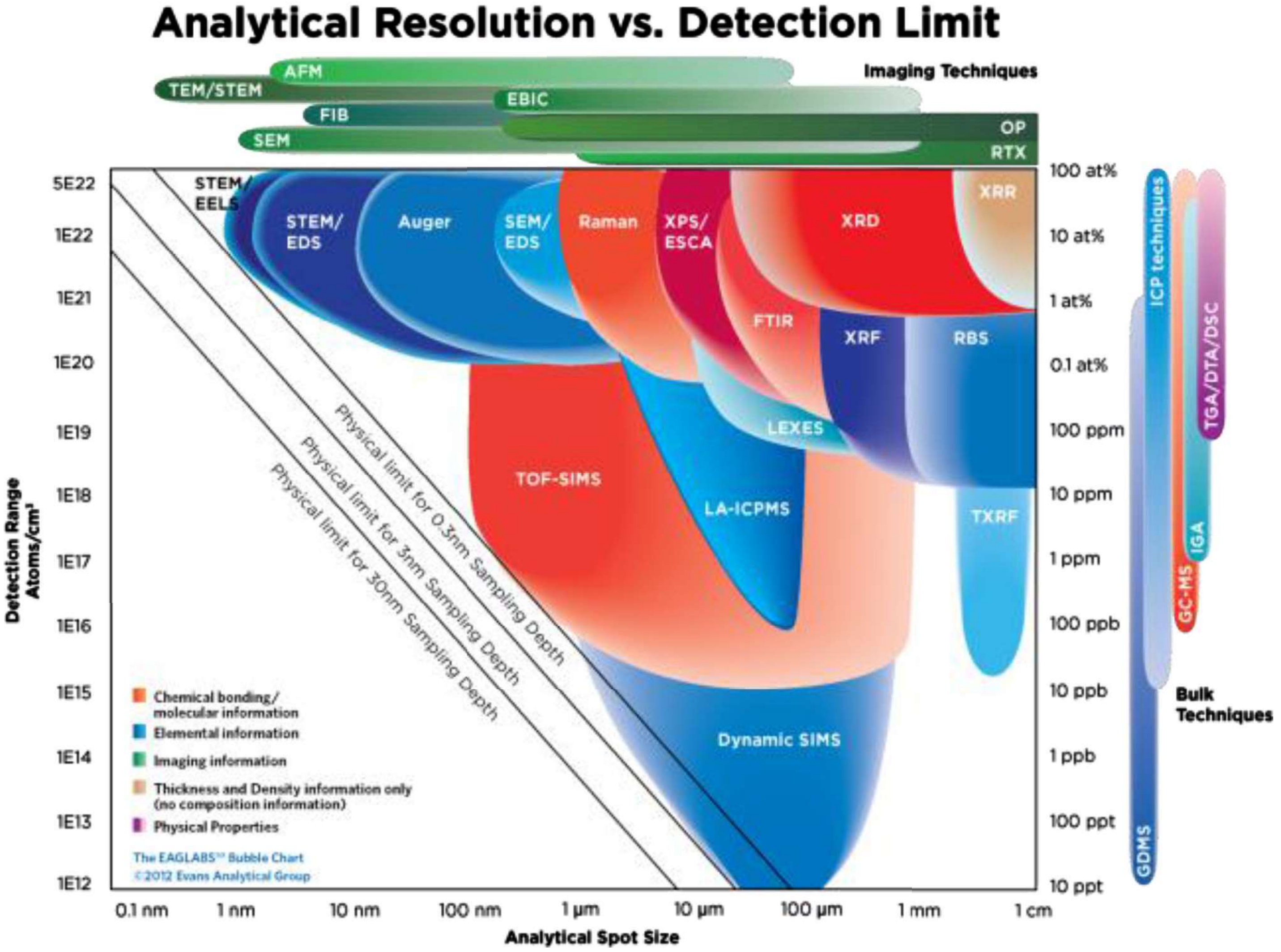
禹重科技® ÜZONGLAB

成分分析仪器|表面测试仪器|样品前处理仪器

EAG LABORATORIES

WE KNOW HOW™

TOF-SIMS



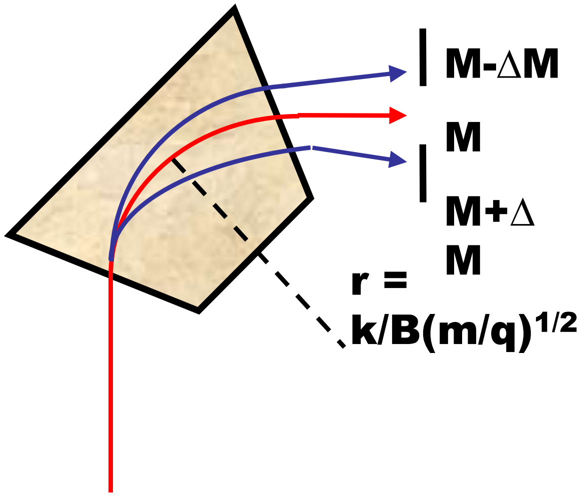
TOF-SIMS is a very surface sensitive technique providing full elemental and molecular analysis with very good detection limits.

Key Applications

- Surface characterization of organic and elemental materials
- Mapping distributions of surface species
- Contaminant identification (< ppm)
  - Elemental
  - Molecular
- Failure analysis
  - Adhesion
  - Bond Pads
  - Coatings
- Evaluation of cleaning processes (QA/QC)
- Identification of stains, discolorations, and hazes
- Molecular depth profiling of organic materials

SIMS Instrument Type

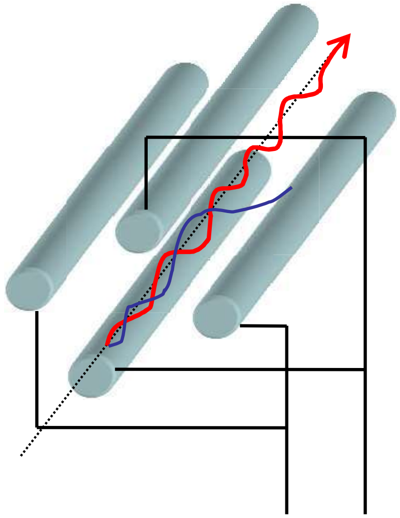
Magnetic sector



m/q ~ B

Cameca

Quadrupole

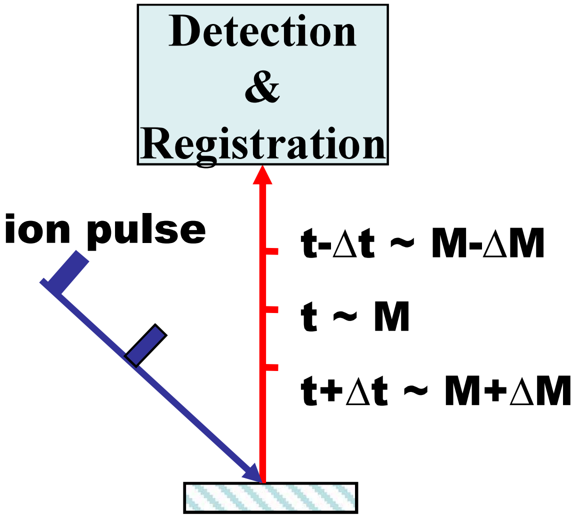


$Vo(t) = Vc+Vs \cos\omega t$

m/q ~ V(f)

PHI, Atomika

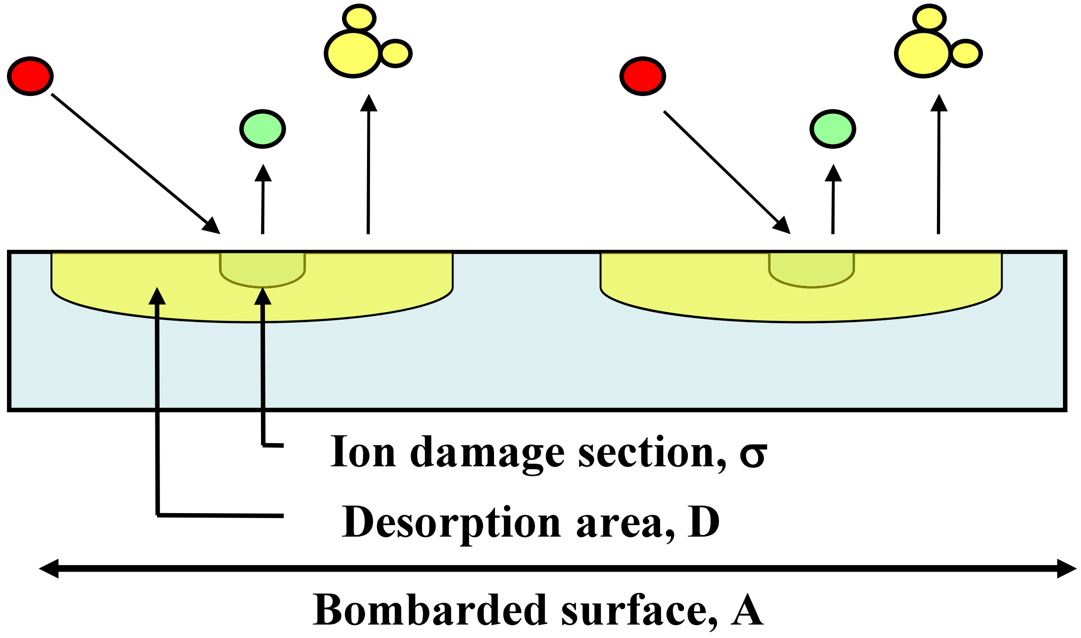
Time of Flight



m/q ~ t

PHI, IonTof

Dynamic vs. Static SIMS



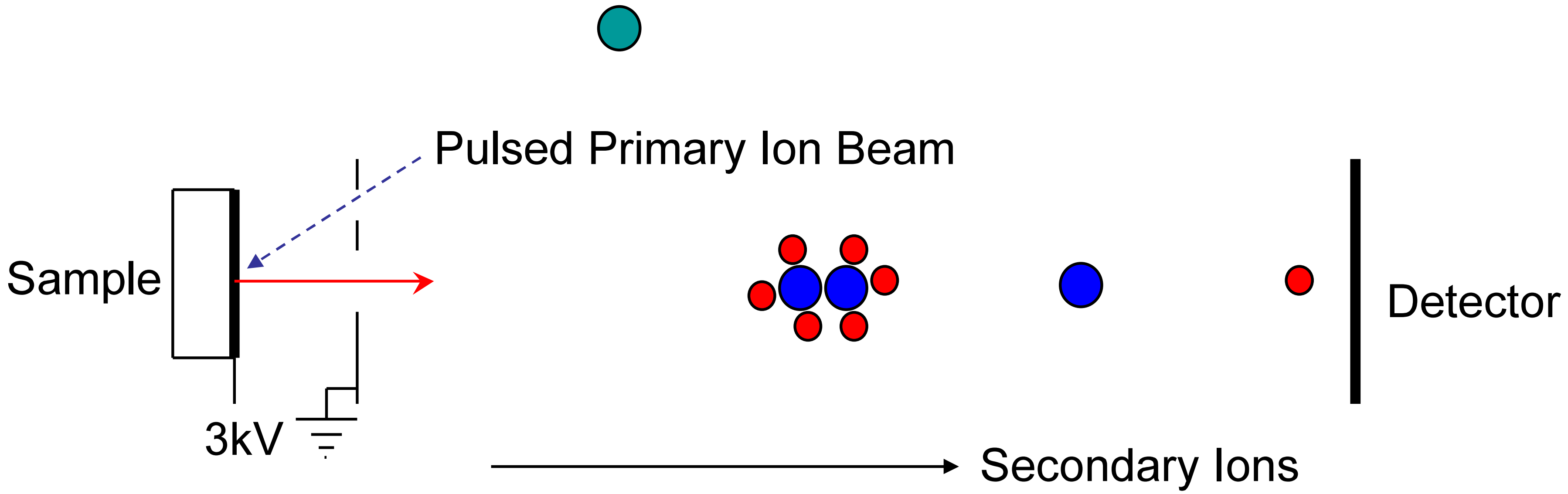
Ion damage section, σ

Desorption area, D

Bombarded surface, A

	$\Sigma\sigma \ll A$ **Static SIMS**	$\Sigma\sigma = A$ **Dynamic SIMS**
Primary ion dose	**<1E12 ions/cm2**	**>1E12 ions/cm2**
Information	**Chemical**	**Elemental**
Analysis	**Only surface**	**Depth profile**
Instrument	**TOF**	**Magnetic & Quad**

Time-of-Flight SIMS: Basic Principles



Pulsed Primary Ion Beam

Sample

3kV

Detector

Secondary Ions

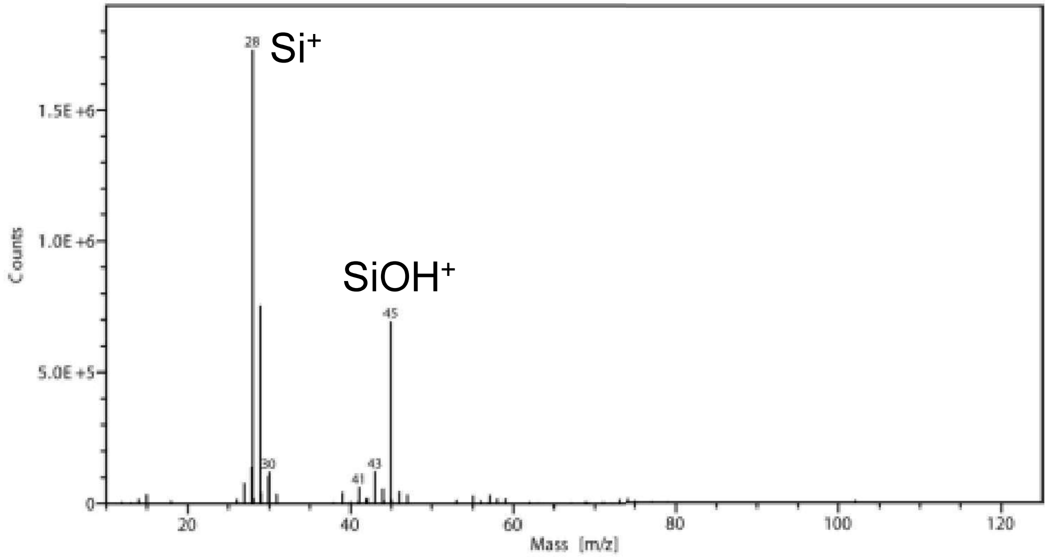
$$3\ \text{keV} = 1/2\ mv^2$$

Measure spectrum in flight time: $t = k(m)^{1/2}$

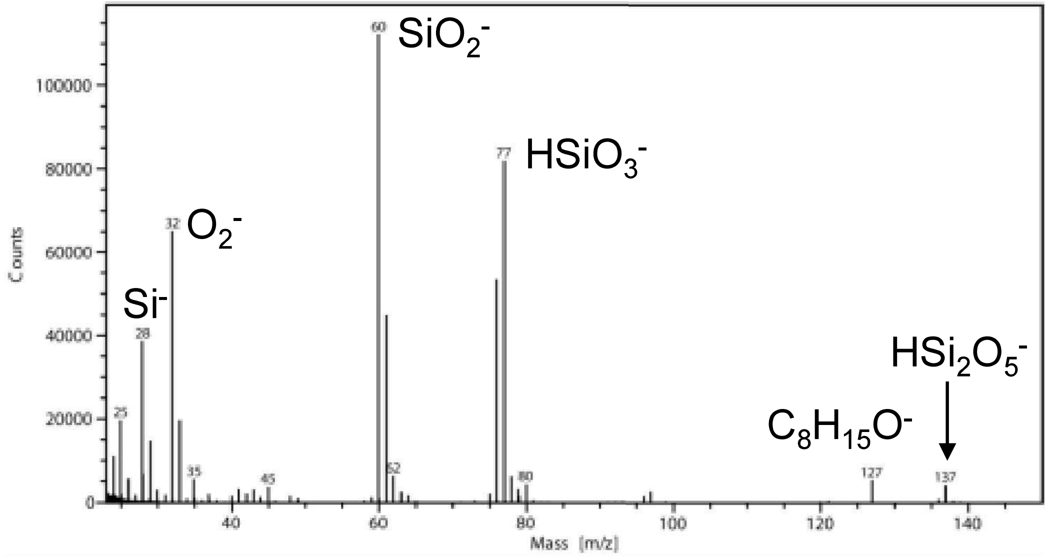
Convert time axis to mass: $m = at^2 + b$

Light Ions arrive at the detector first, with sequentially heavier Ions following later in time. Each pulse of primary ions produces a full mass spectrum of secondary ions

Typical Data (Silicon Wafer)



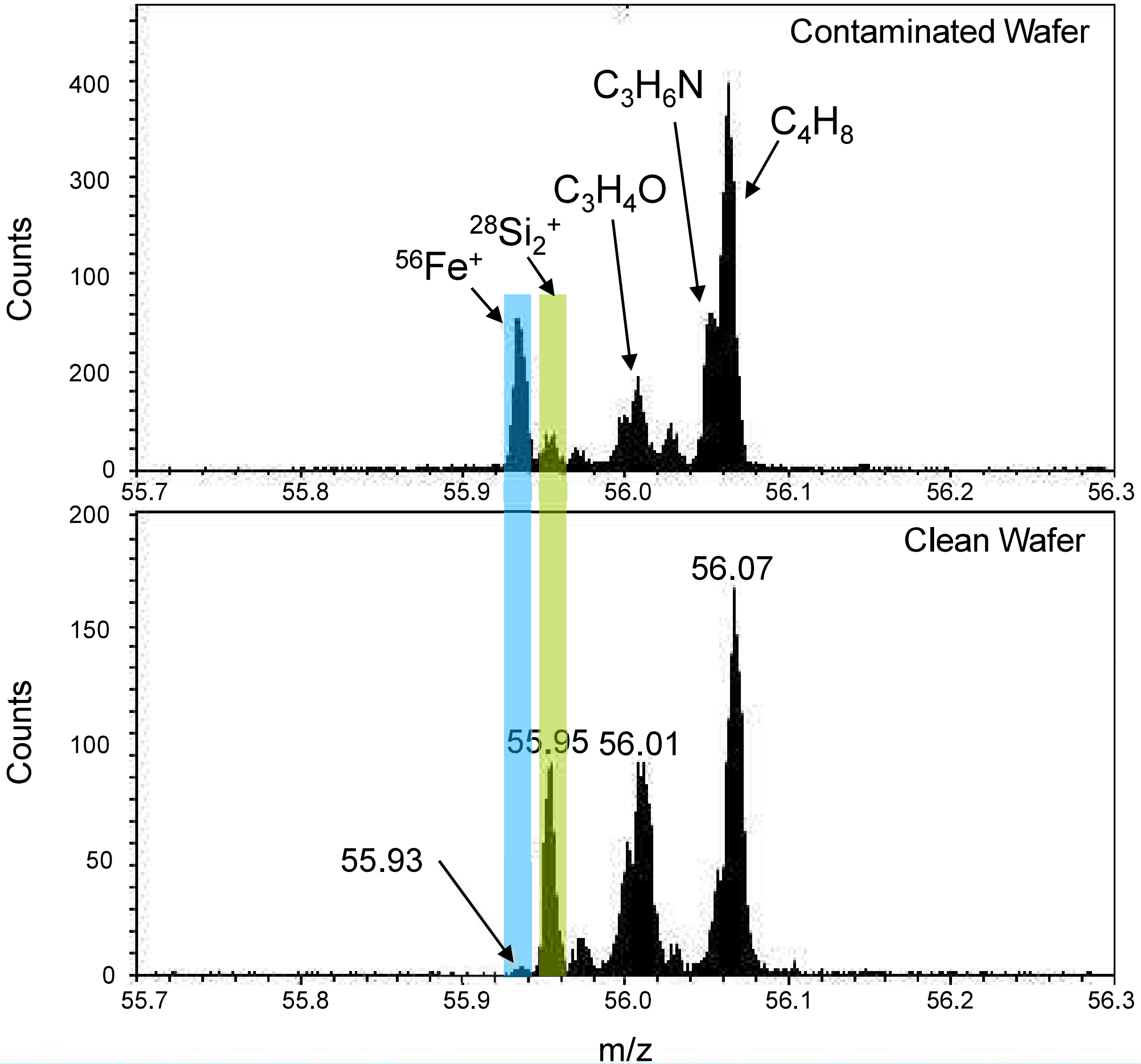
Positive ion spectrum



Negative ion spectrum

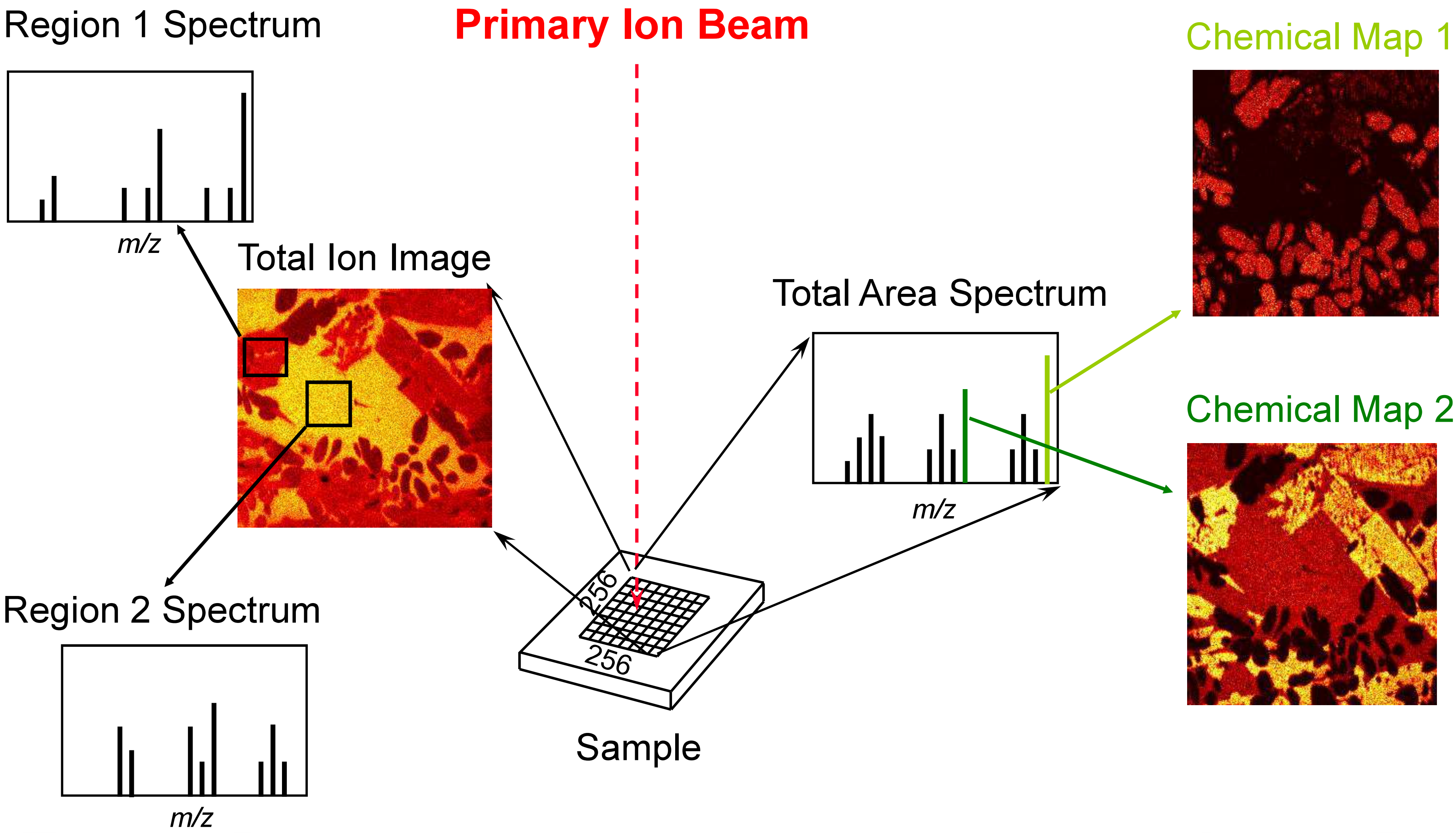
Typical Data

Silicon Wafer - High Mass Resolution



Typical Data

TOF-SIMS Imaging of Alumina-Zirconia-Silica Materials



Region 1 Spectrum

Primary Ion Beam

Chemical Map 1

Total Ion Image

Total Area Spectrum

Chemical Map 2

Region 2 Spectrum

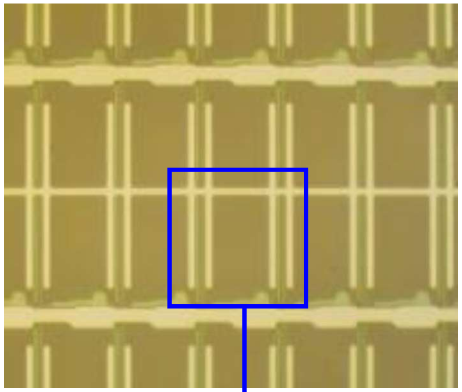
Sample

Example Applications

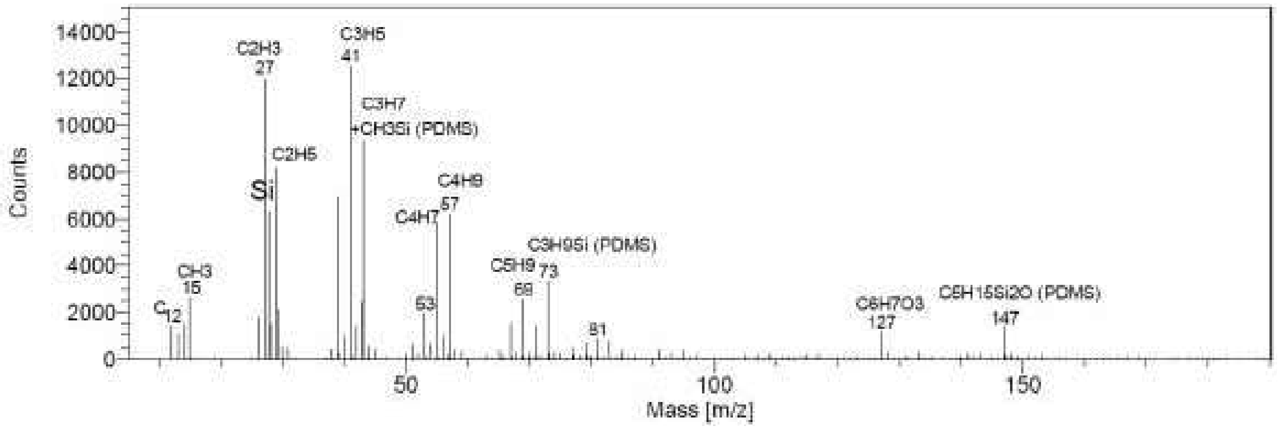
- Residue on flat panel display
- Organic contamination on Si surfaces

Residue on Flat Panel TFT

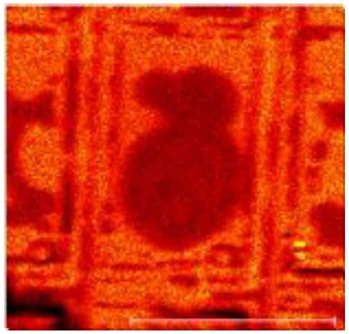
Photo of surface



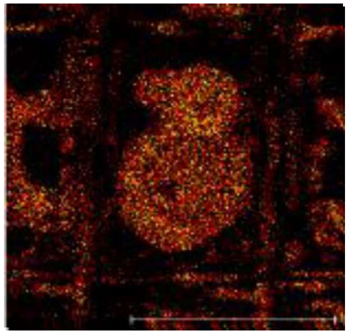
Mass spectrum



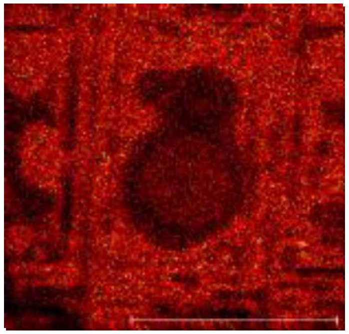
Total ion image



C_3H_9Si image
(silicone)



C_2H_3 image
(general hydrocarbon)

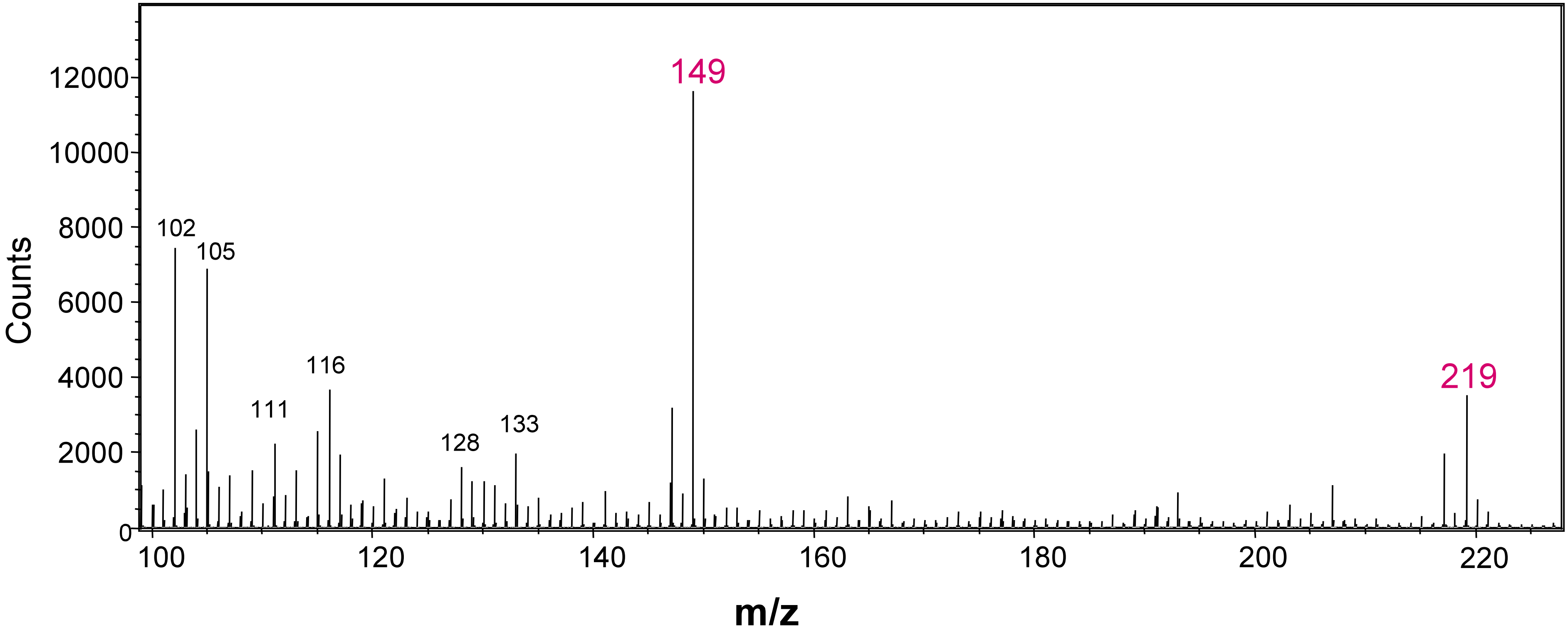


Organic Contamination on Surfaces

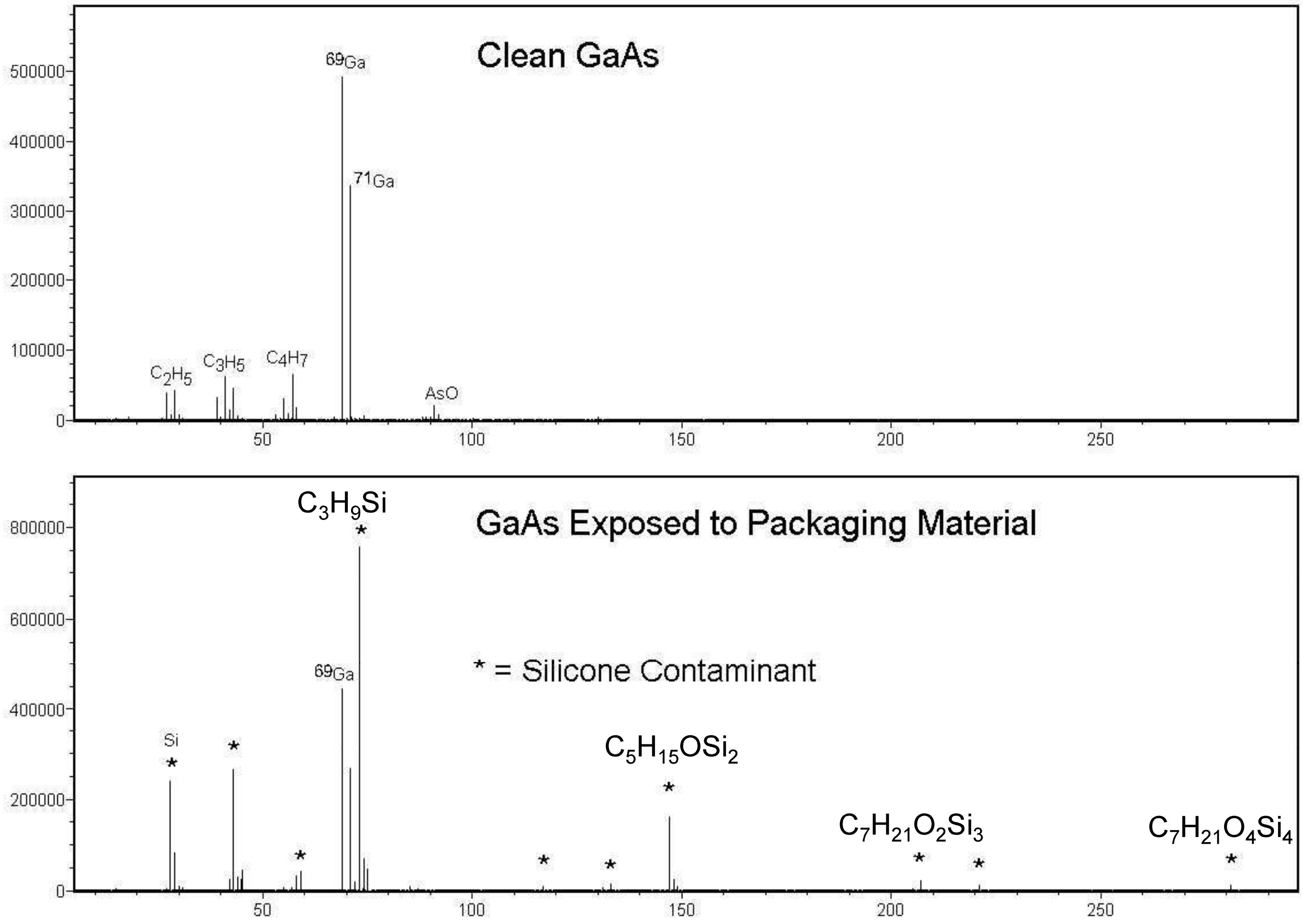
- Airborne Molecular Contamination (AMC) can deposit on product and processing equipment and cause yield loss, hazing of optics, etc.
- AMC can be produced by
  - cleanroom construction materials
  - process chemicals
  - outside environment
  - HVAC system
  - gloves, garments, wipers, people, etc.
- Reference spectra are available to identify a wide range of common organic materials that can contaminate surfaces

Organic Contamination on Si Wafer

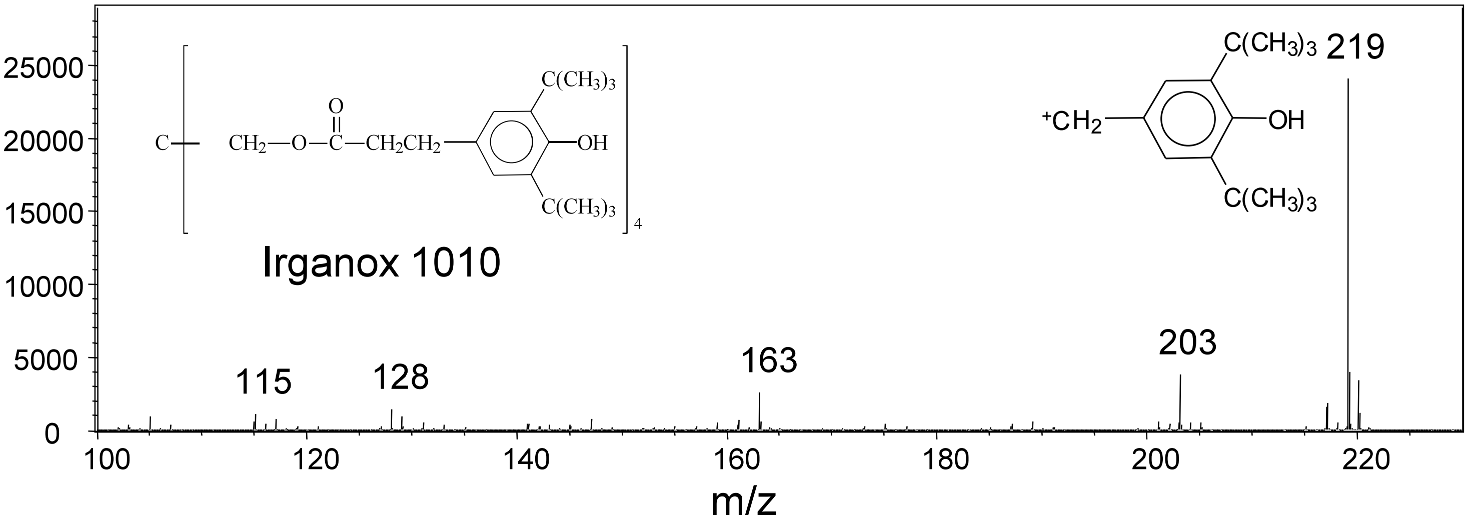
Positive ion spectrum

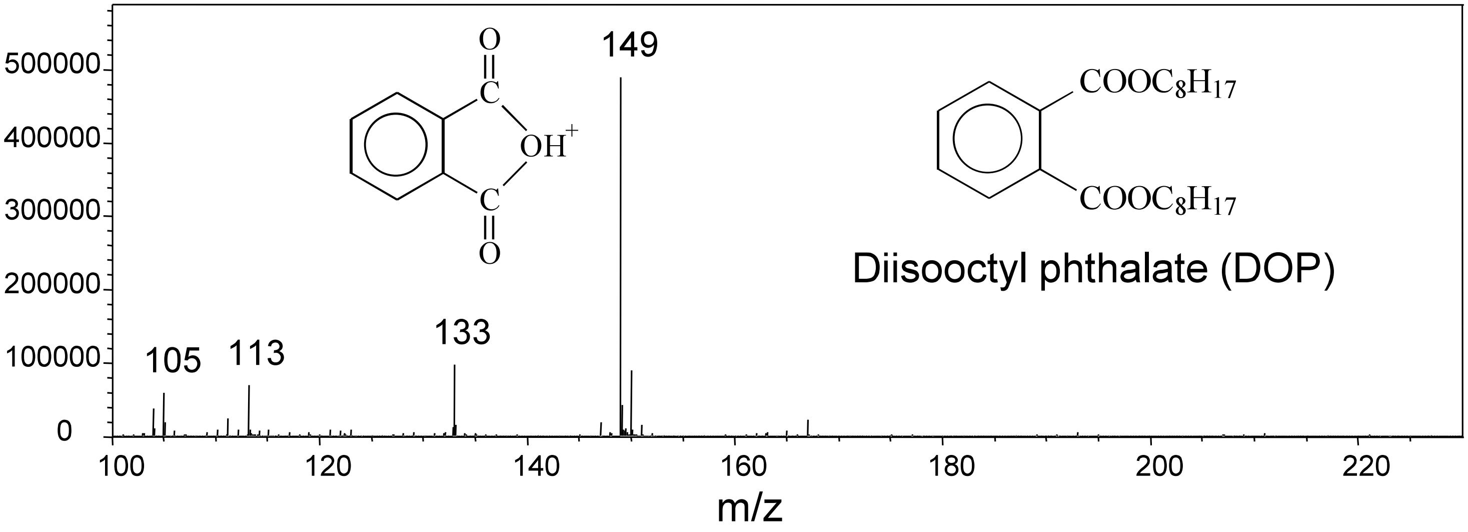


Contamination on GaAs Wafer from Packing Material



Reference Spectra from Compound Data Base





Common Organic Surface Contaminants Detected by TOF-SIMS

Species	**Possible Sources**
Siloxane, (Polydimethylsiloxane, PDMS)	Machine lubricant, release agent, tape
Polyethylene oxide or polyethylene glycol	Surfactants, plasticizer, printing inks
Fatty acids	Finger oils, lubricants, polymer additives
Glycerides	Soap, polymer additives, releasing agents
Phosphates, sulfates, etc.	Cleaning reagent, surfactants, additives
Phthalate, etc.	Polymer additives, plastic parts, containers

TOF SIMS profiling

By using an external sputtering gun, Intensity vs. Depth information can be obtained by two beam Sputtering/ Analysis process, just as Auger or XPS depth profiles

New generations of commercial TOF instrument often have options to add O2, Cs and Ar_n cluster sputtering beam

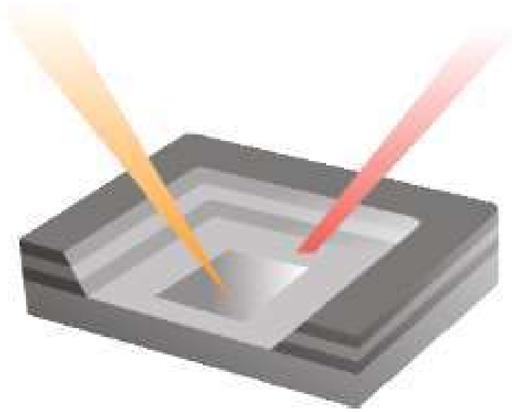
Gas Cluster Ion Beams (GCIB)

For ~40 years surface analysis of organics has been limited to the top surface or a surface accessible by cross sectioning. Traditional (monotonic) ion sputtering used on inorganics rapidly converts organics to amorphous carbon-like materials.

In the last 10 years it has been demonstrated that larger projectiles (SF_5, C_{60}, Ar clusters) sputter organics, but leave behind a pristine organic.

TOF Profiling Data Collection

Dual Beam Mode



Bi_3 : Analysis Beam

Ar_n /Cs/O2 Sputter Beam

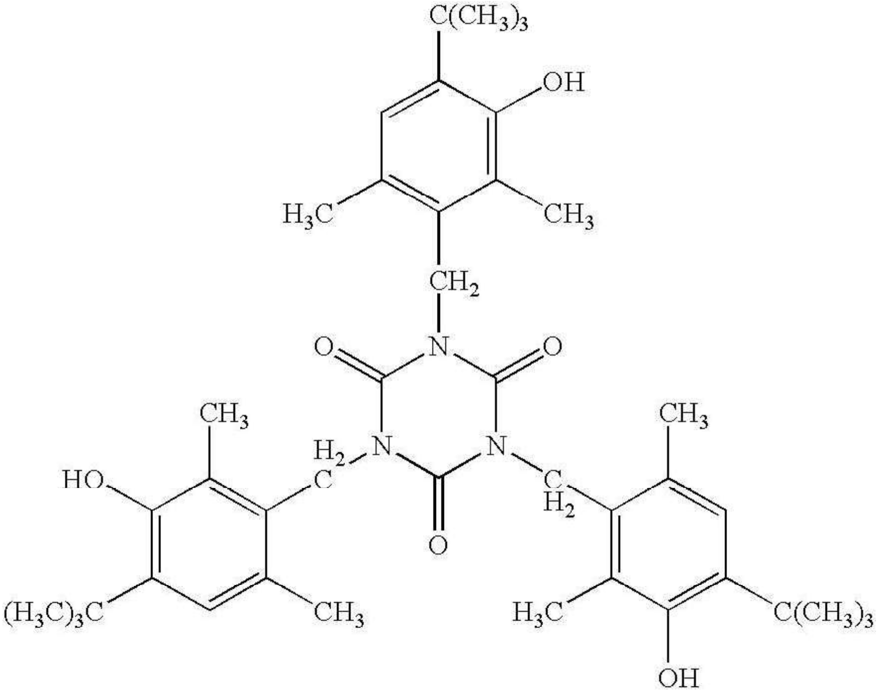
Ar+: 1-2 eV for organic materials

Profile formed by continuous sputtering by Ar_n interlaced with Bi_3 pulsed sputtering

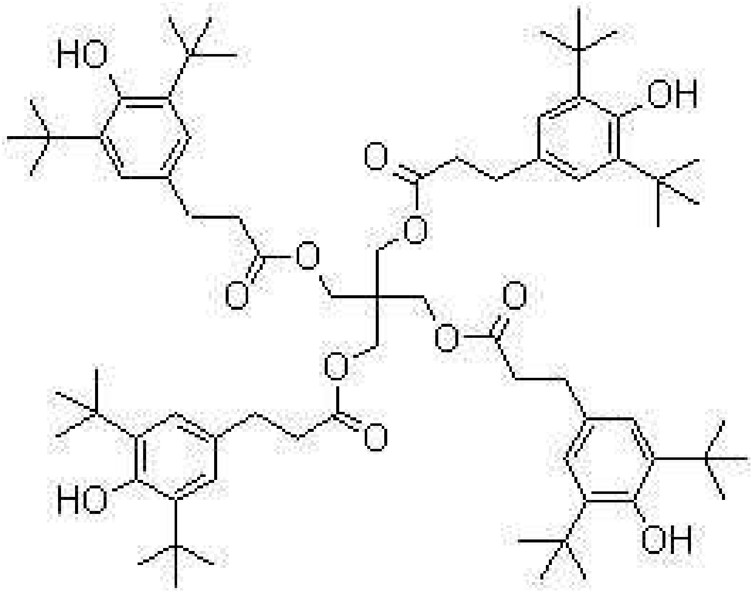
Molecular Depth Profiling

Reference film with organic delta layers

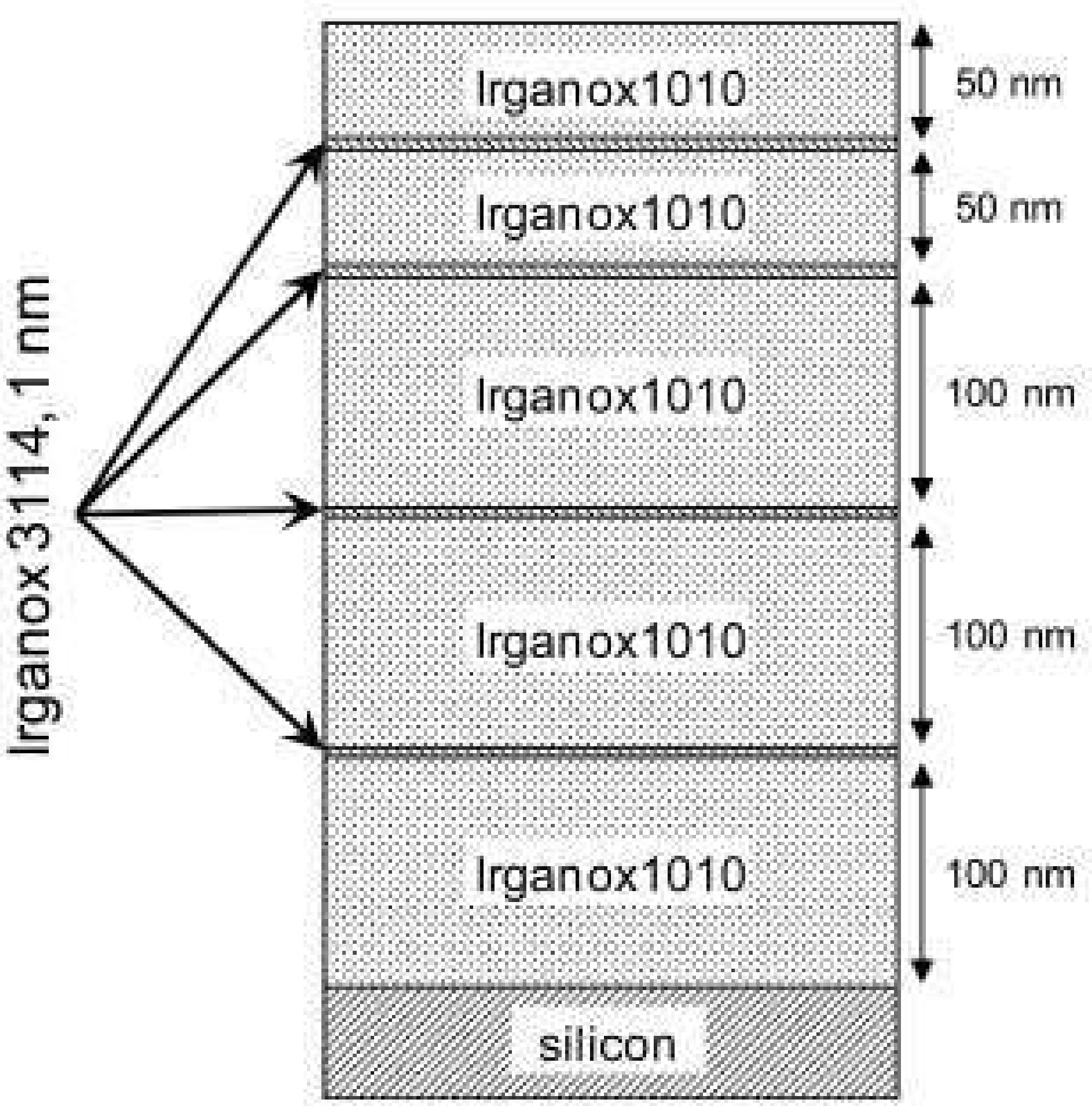
Irganox 3114, $C_{48}H_{69}N_3O_{12}$



Irganox 1010, $C_{73}H_{108}O_{12}$

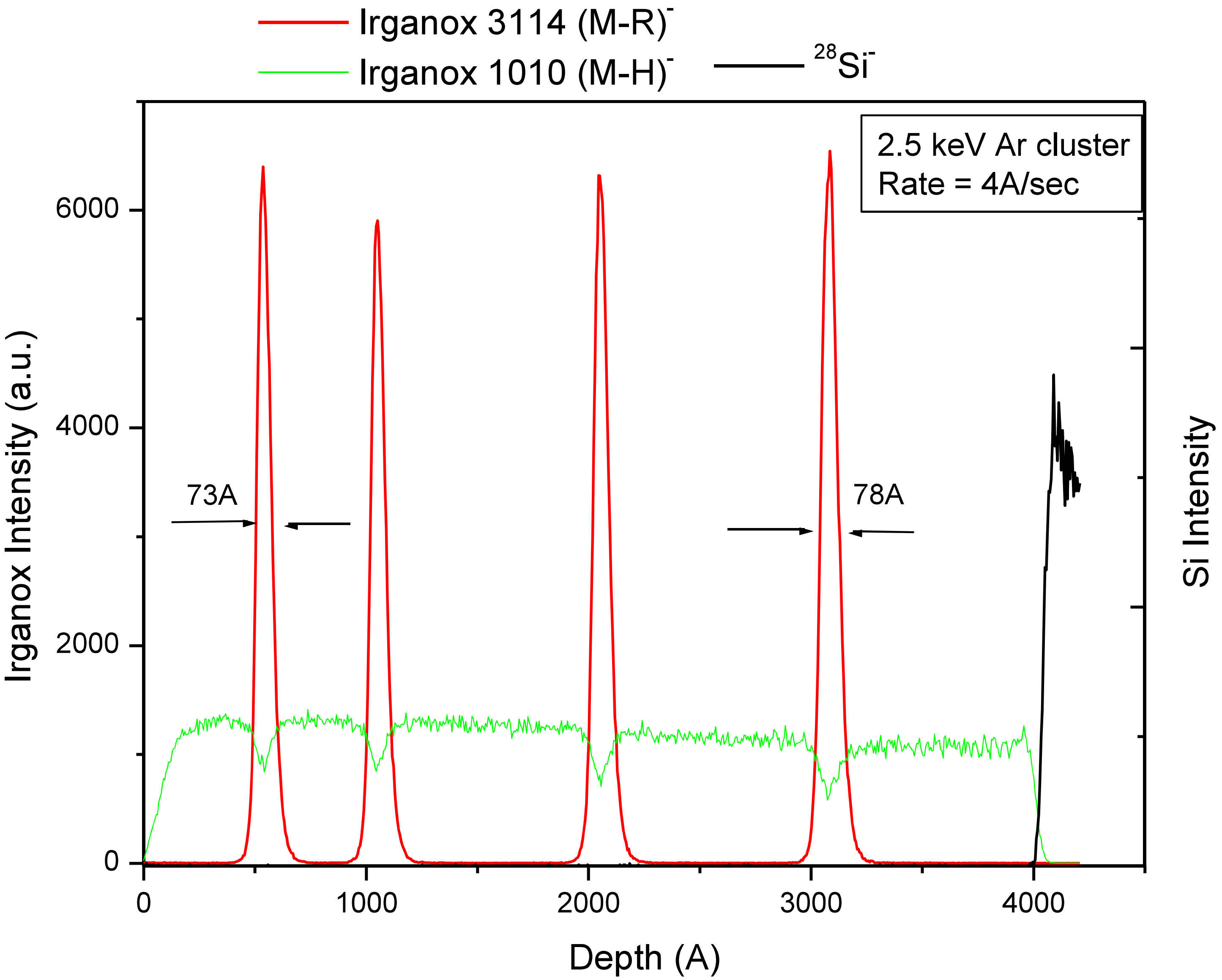


Molecular Depth Profiling



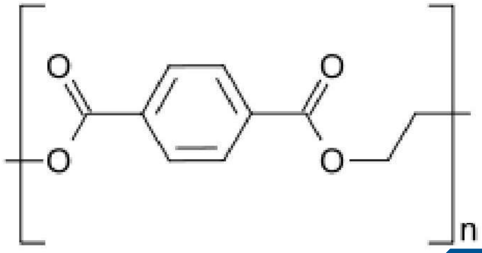
A. Shard et al, *Anal Chem* ***84*** *7865-7873 (2012)*

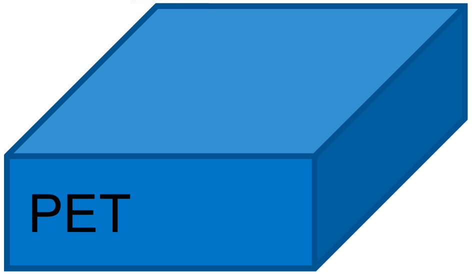
Molecular Depth Profiling

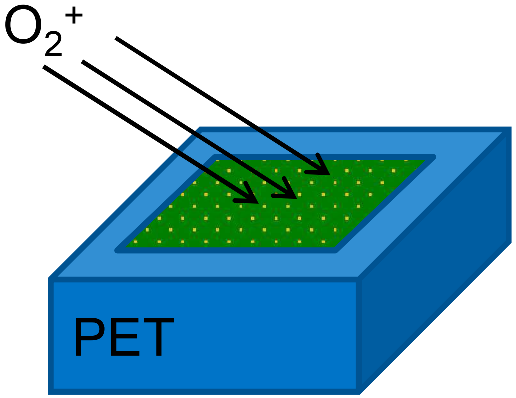


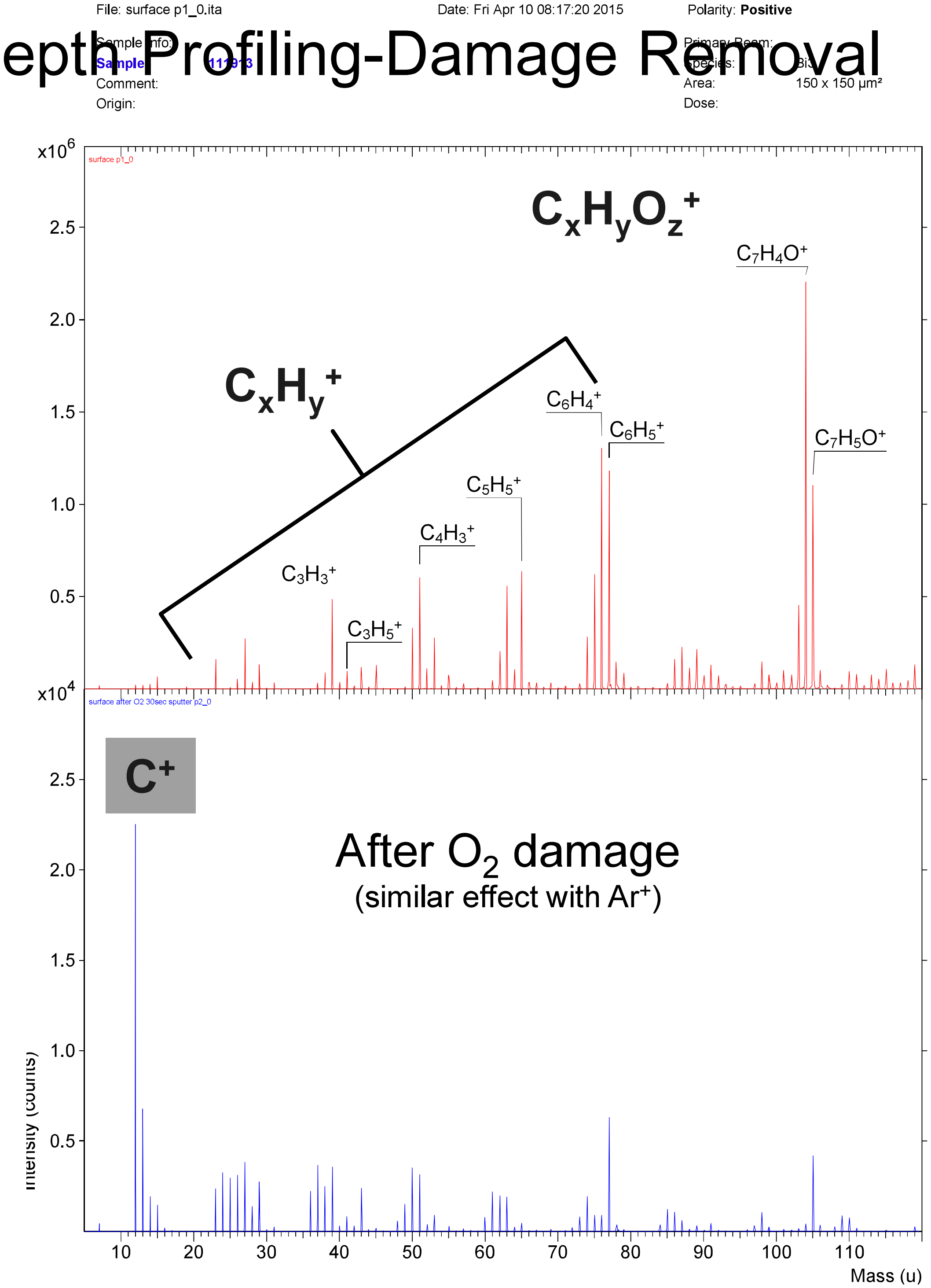
Molecular Depth Profiling-Damage Removal

Polyethylene terephthalate



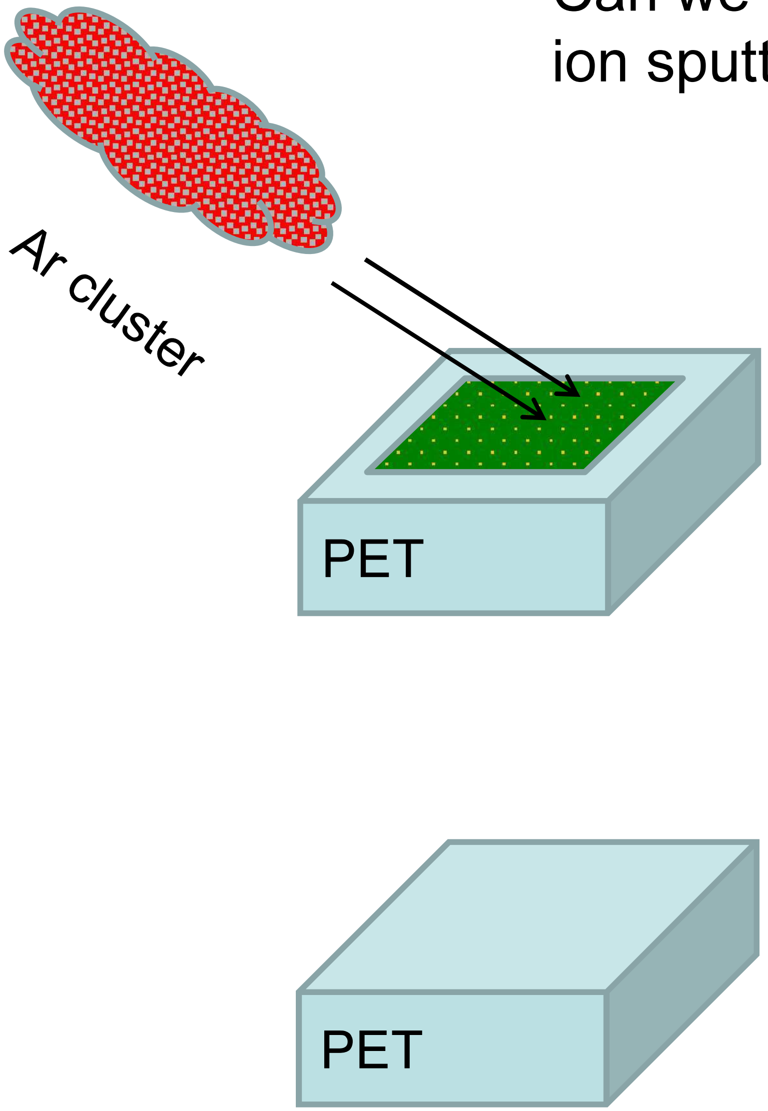


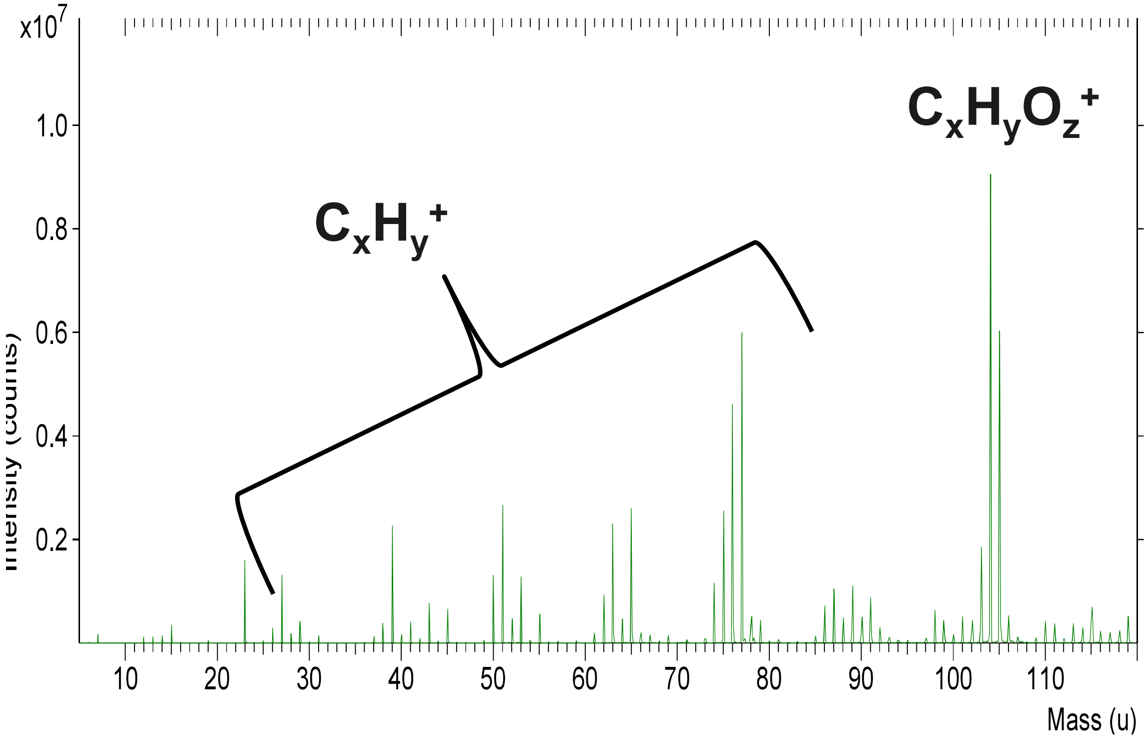




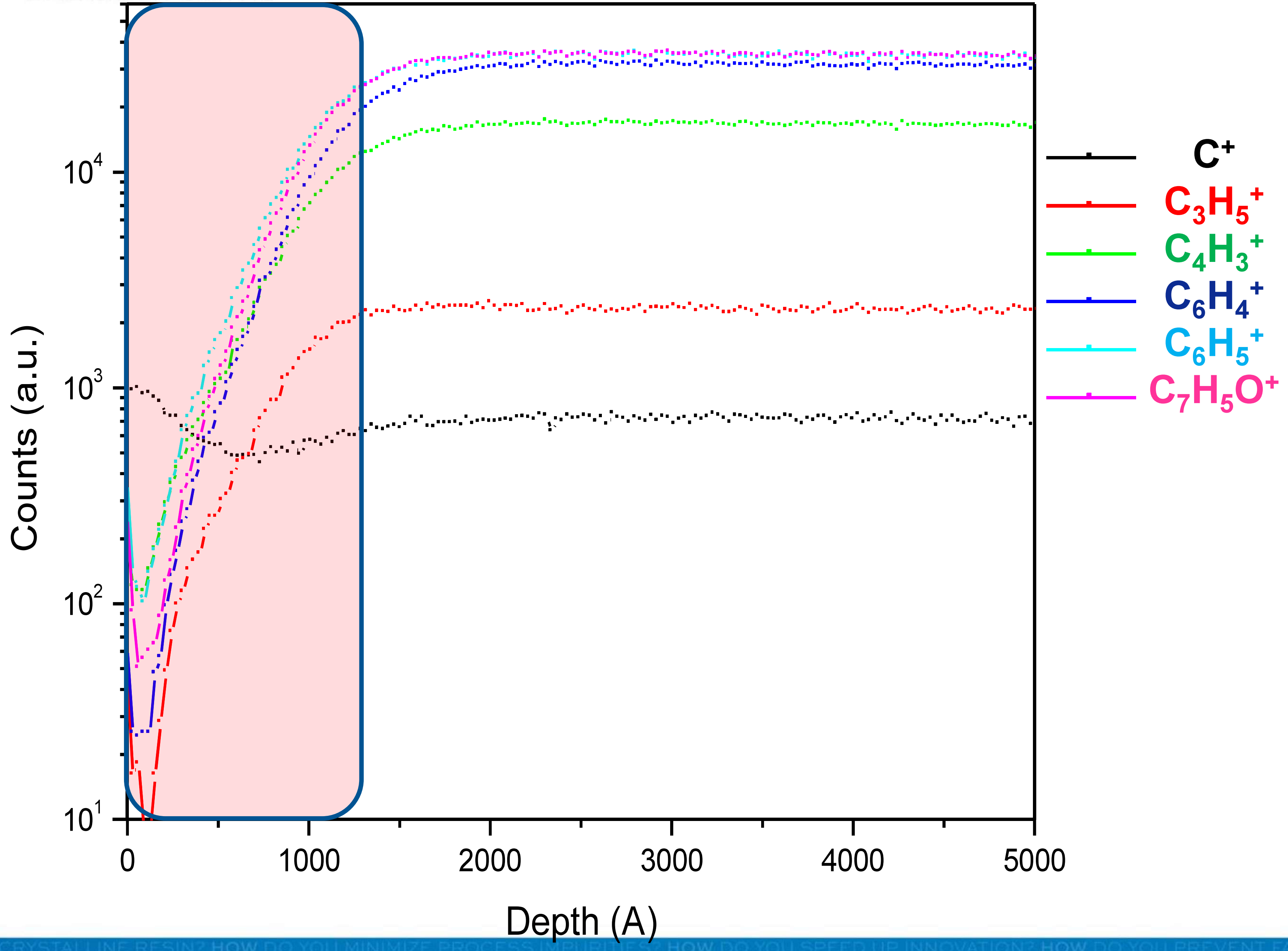
Molecular Depth Profiling-Damage Removal

- Can we recover a surface previously damaged by monato ion sputtering damage using Ar cluster bombardment?

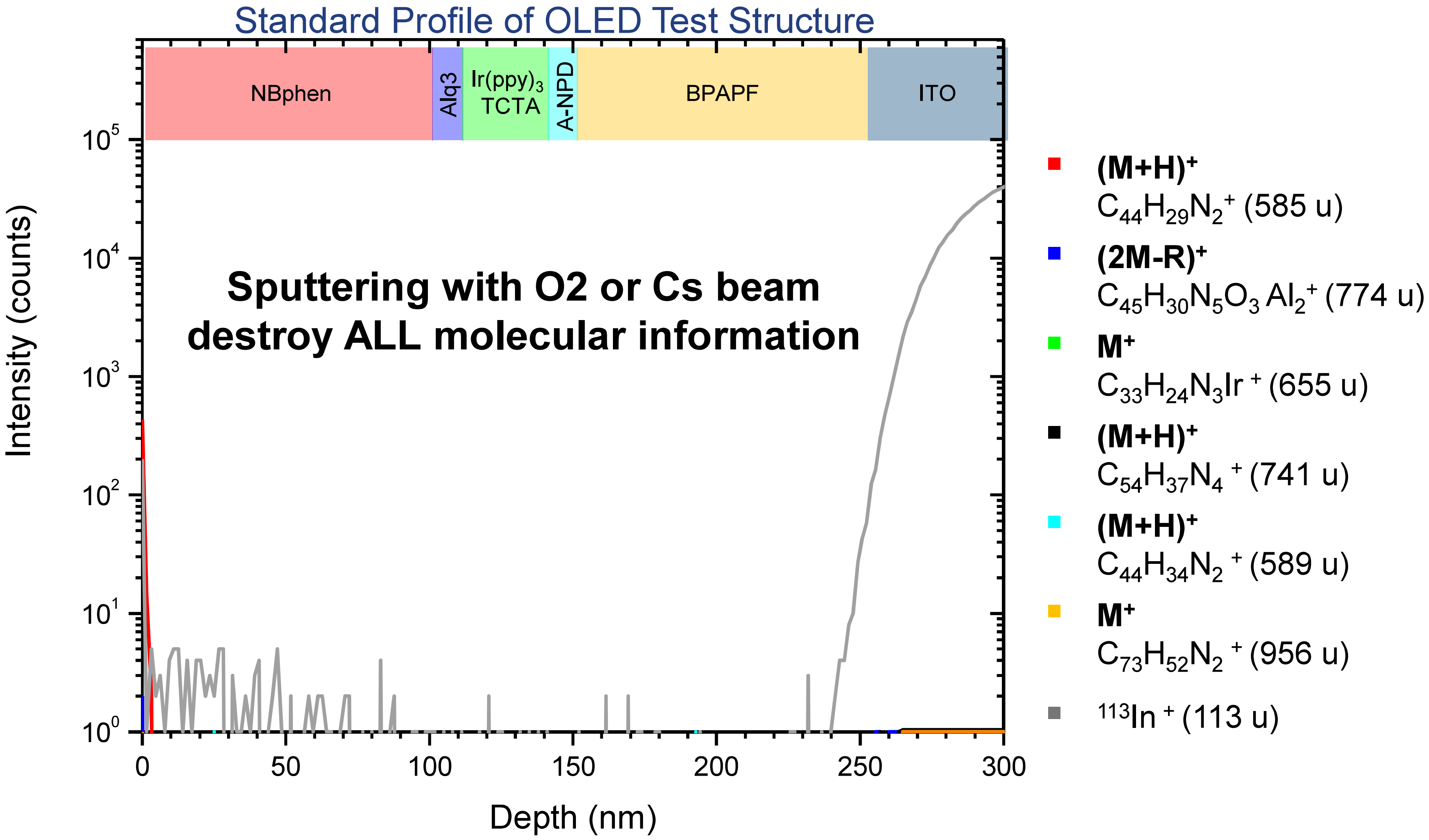




Molecular Depth Profiling-Damage Removal



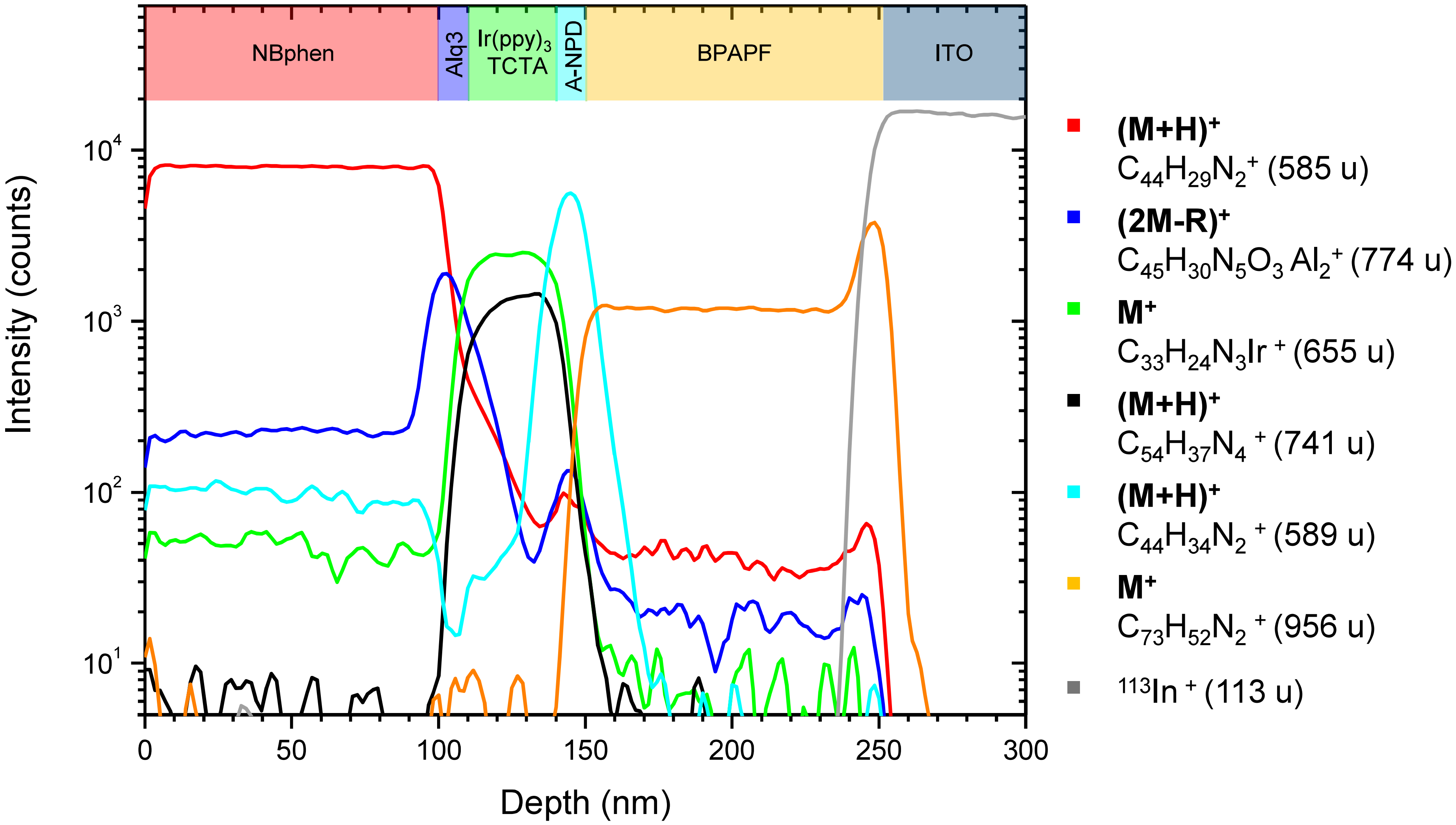
OLED Profiling with O2 beam sputtering



Sputtering with O2 or Cs beam destroy ALL molecular information

OLED Profiling using Ar cluster

→ all layers well resolved, intact molecules detected with high yield for all layers



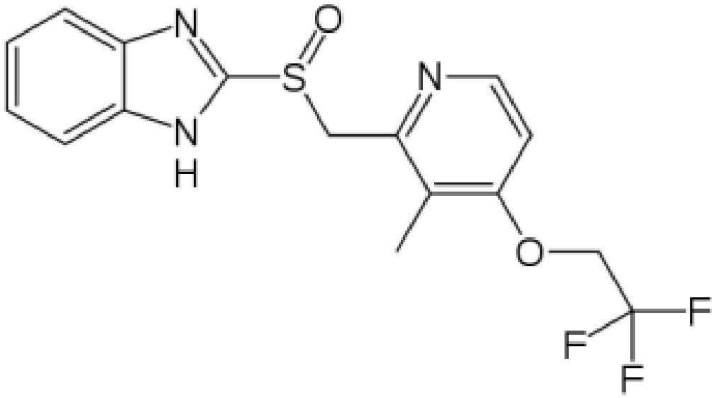
Drawback: Ar cluster will NOT sputter inorganic materials

Chemical Imaging of Finished Drug

Product: Delayed release proton pump inhibitor

API:

Lansoprazole, $C_{16}H_{14}F_3N_3O_2S$, 369.363 amu



Inorganic excipients:

SiO_2, $MgCO_3$, Talc, TiO_2

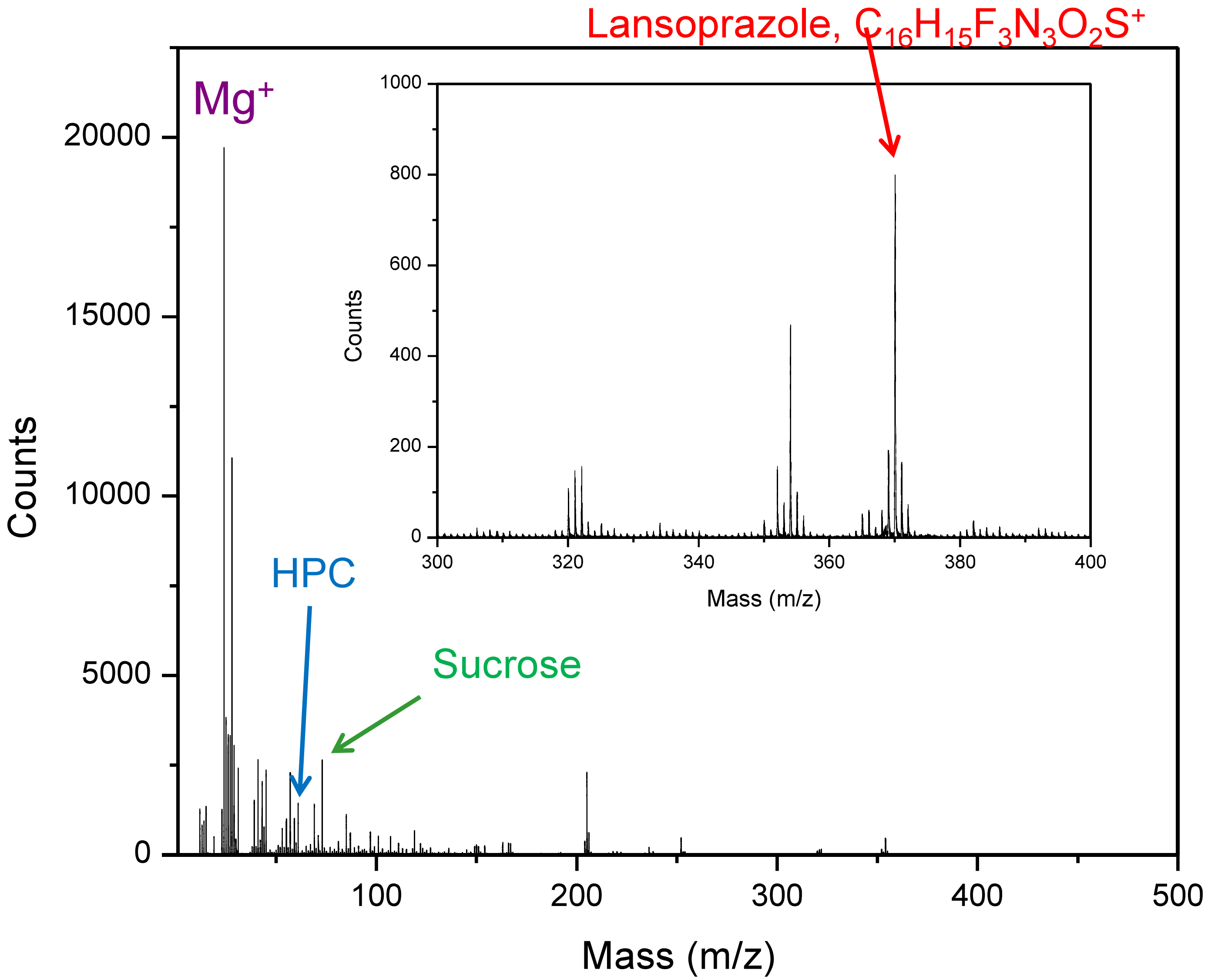
Organic excipients:

Hydroxypropyl cellulose
Methacrylic acid co-polymer
Polyethylene glycol (PEG)
Sucrose

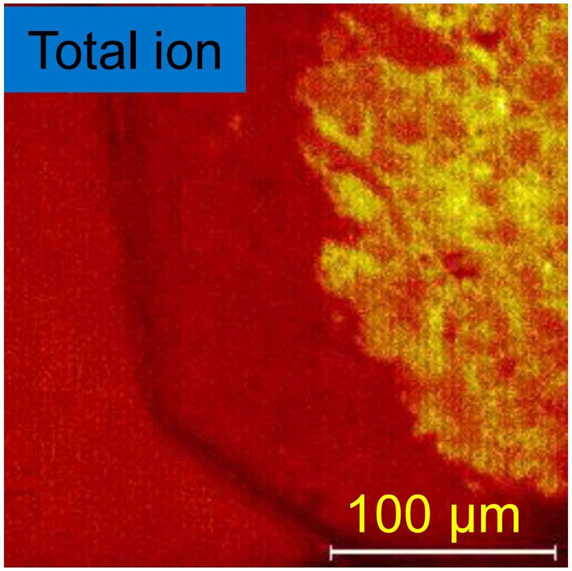
Objective: 2-dimensional imaging of API and excipients to determine location within product

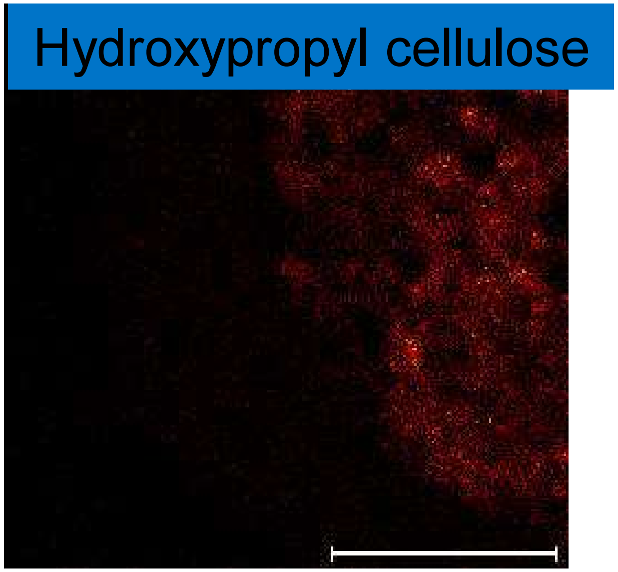
TOF Mass Spectrum (+ ions)

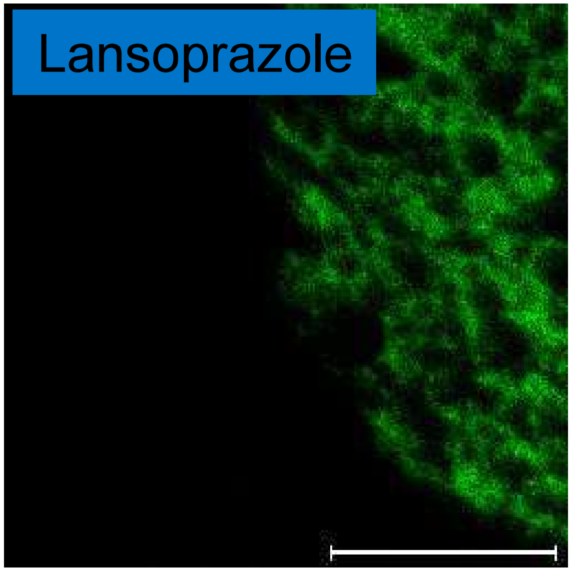
Identify unique ion(s) for each compound in sample in the mass spectrum.

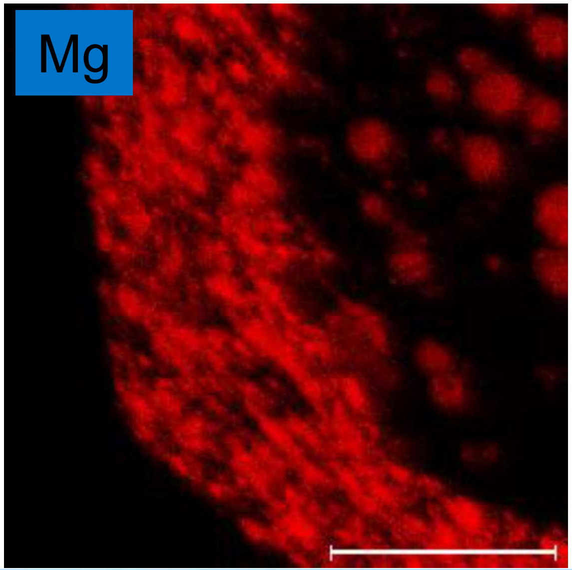


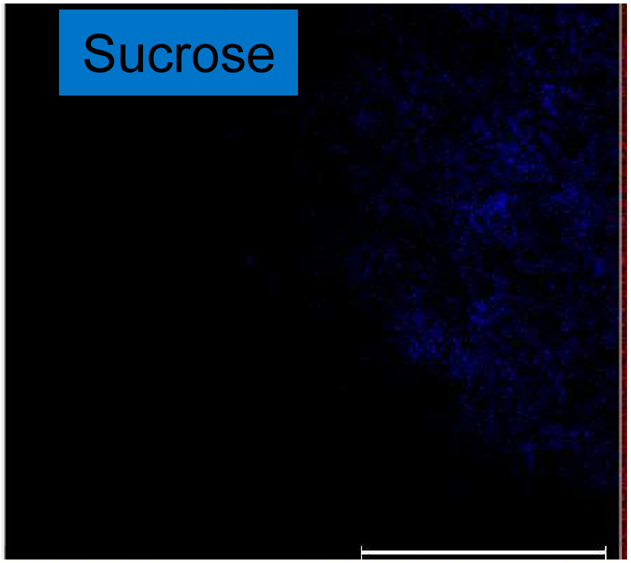
2-D TOF-SIMS Molecular Imaging

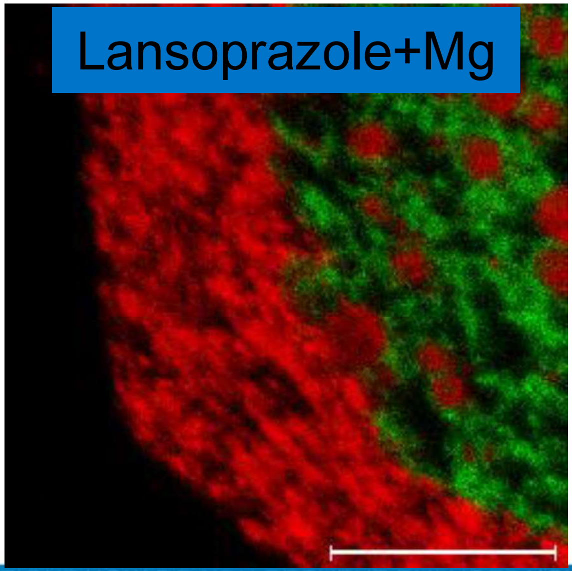

Total ion


Hydroxypropyl cellulose


Lansoprazole


Mg

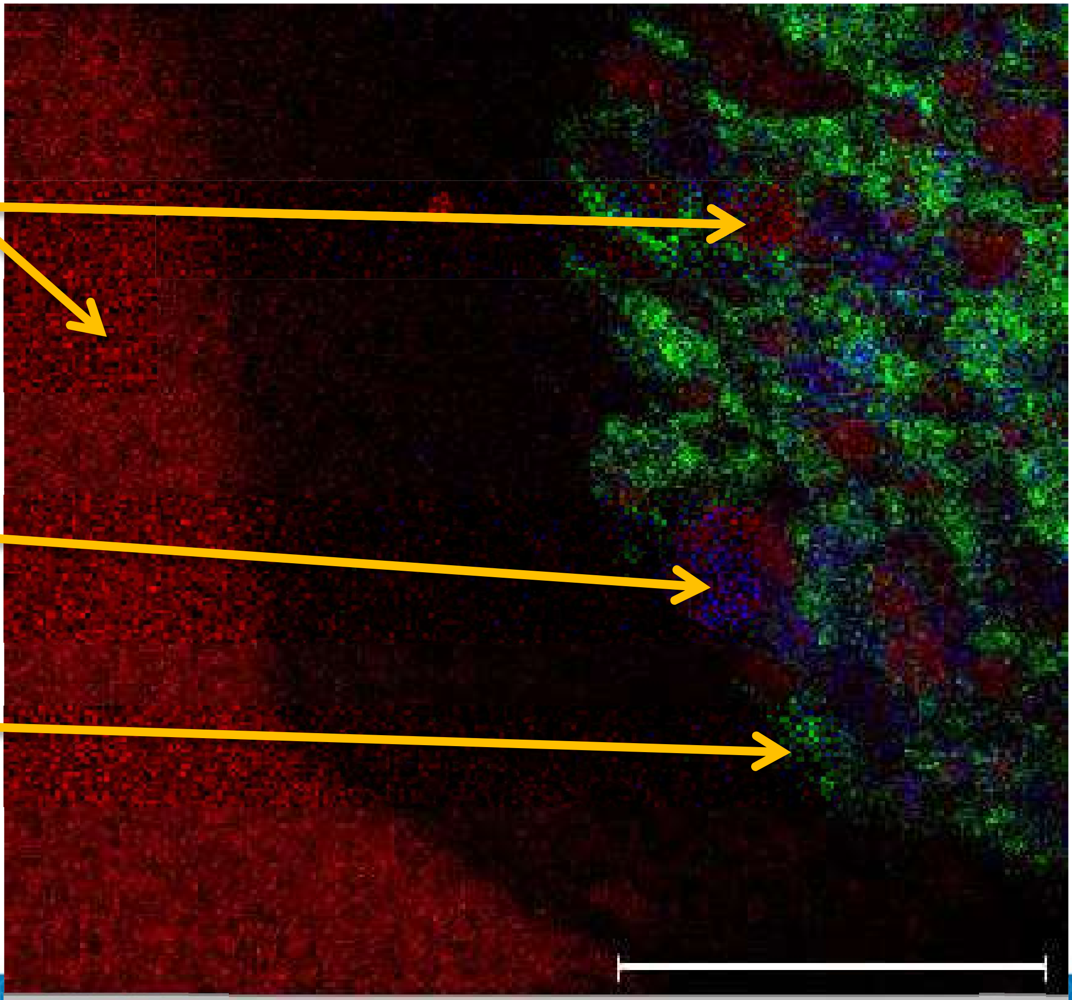

Sucrose


Lansoprazole+Mg

2-D Imaging of Finished Drug

SEM-EDS used to determine location/distribution of inorganic constituents

TOF-SIMS is able to map inorganic and organic constituents



Cl (from epoxy and minor contaminant in $MgCO_3$)

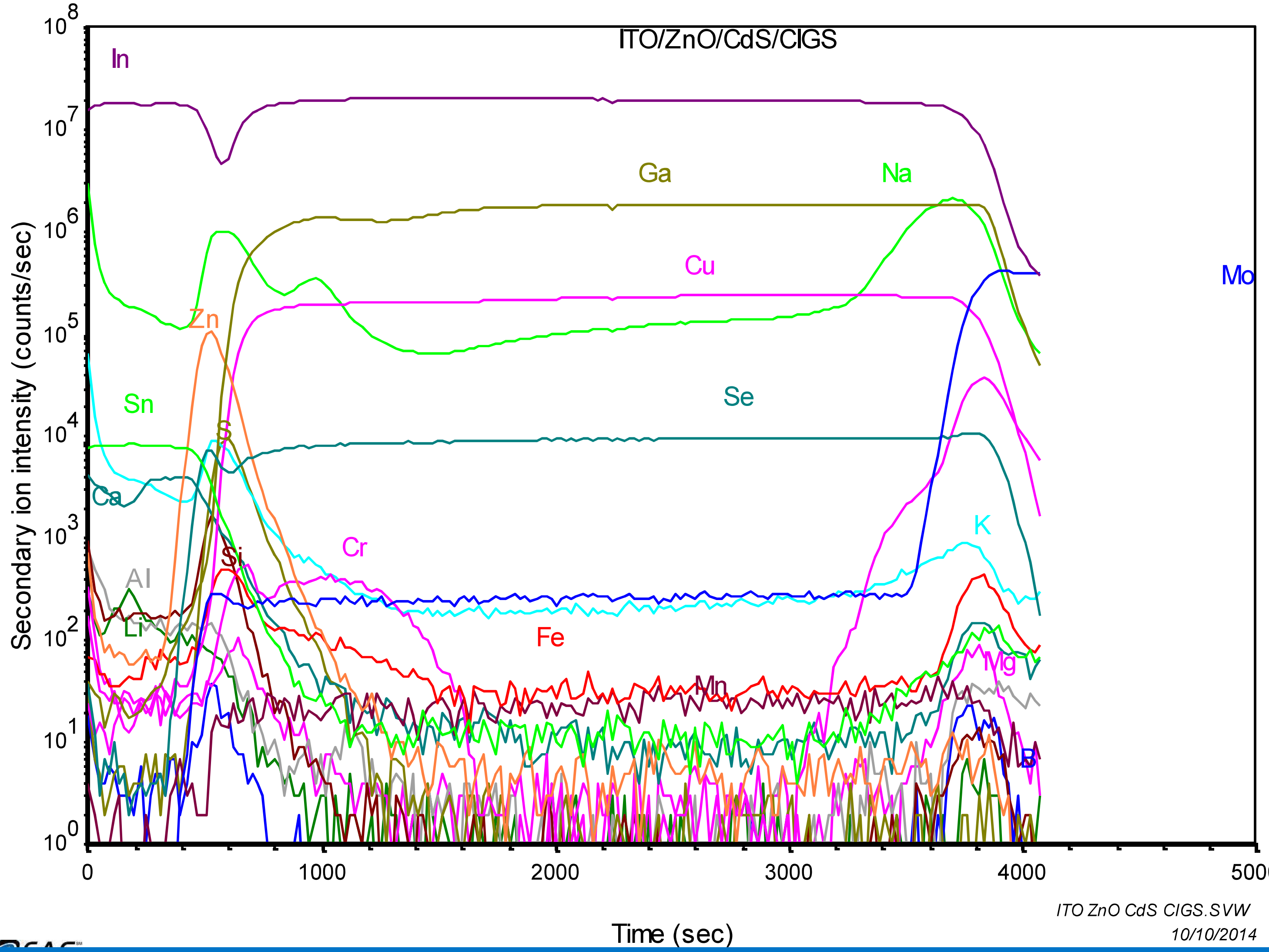
Sucrose

Lansoprazole

EAG LABORATORIES

Depth Profiles of inorganic materials -O2/Cs beam

Survey Depth Profile –ITO/ZnO/CIGS using O2 beam

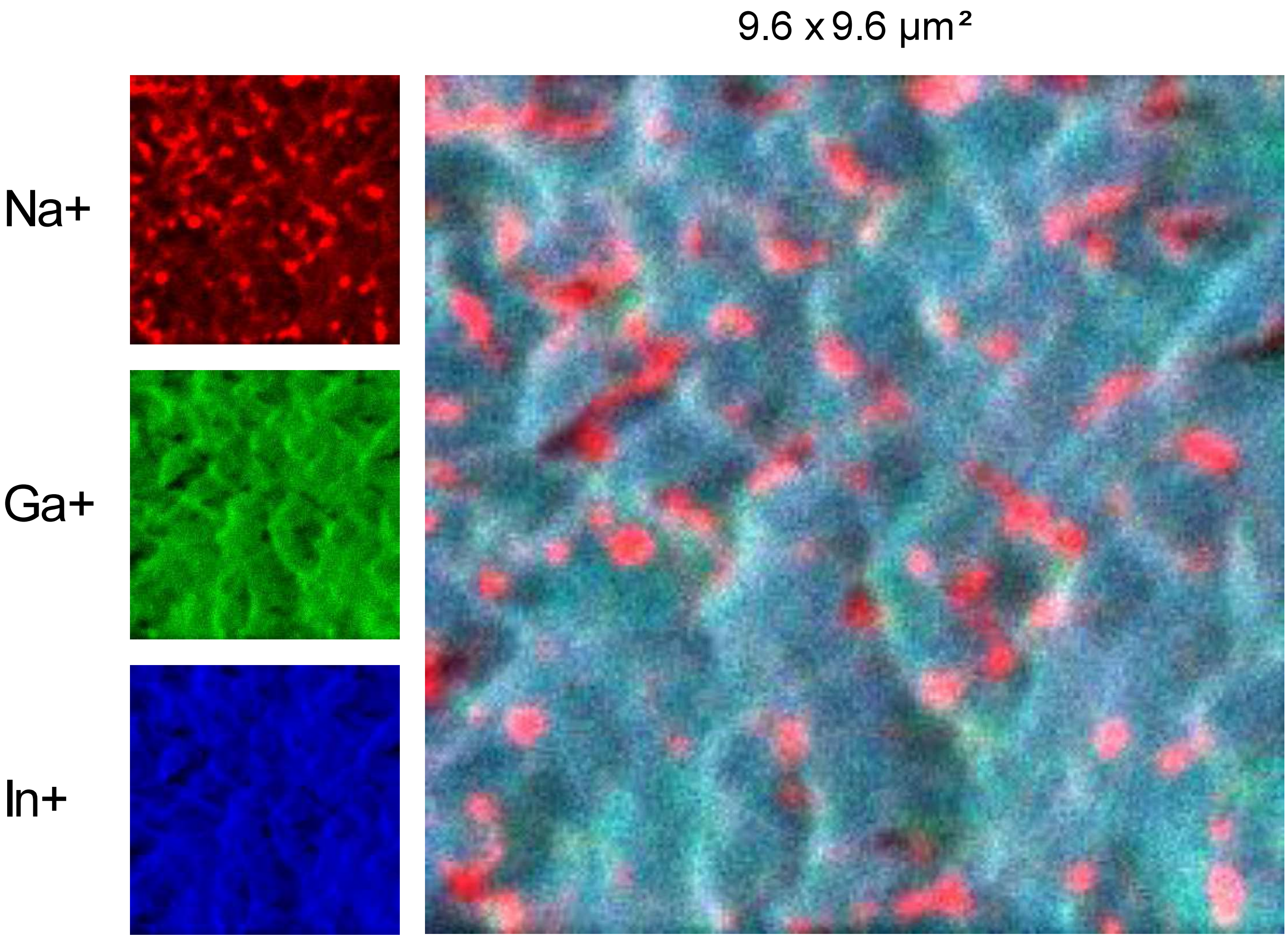


ITO ZnO CdS CIGS.SVW
10/10/2014

Detection sensitivities of inorganic profiling using TOF is 100-10,000 times poorer than using Dynamic SIMS

TOF- High Lateral Resolution Images

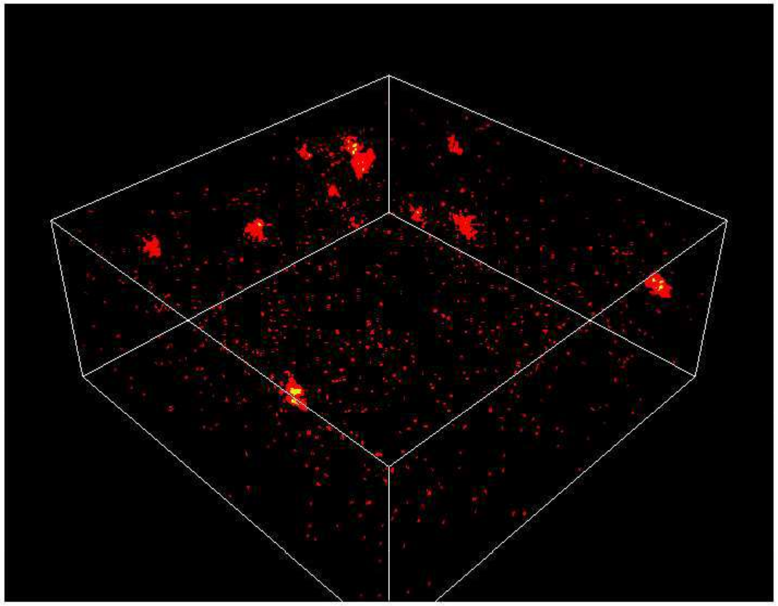
Na in CIGS



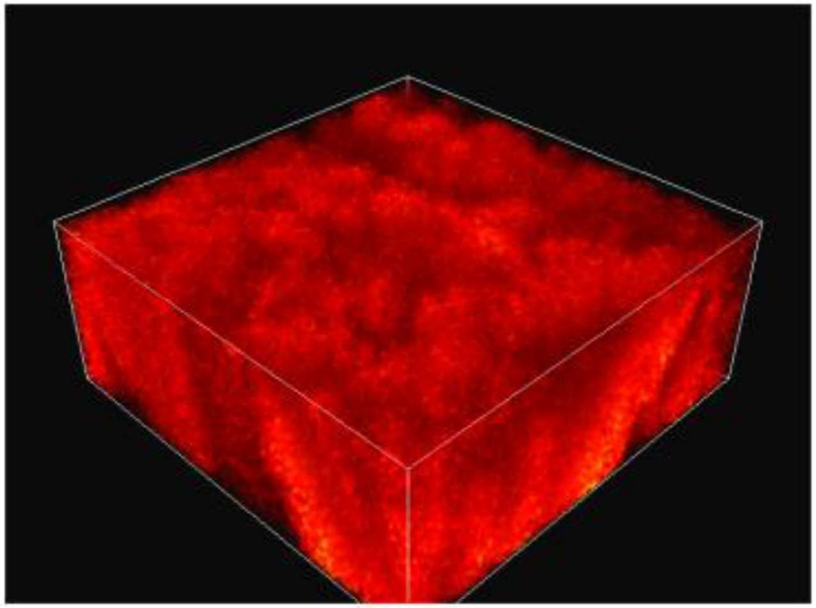
TOF 3-D Analysis

O2 beam sputtering of Al

75x75x3 um



Ti



Al

Summary

- Strengths
  - – elemental and molecular information on thin (submonolayer) organic films/contaminants
  - – survey analysis
  - – ppm detection limits
  - – small spot size (0.1 µm) and mapping
  - – analyzes insulators and conductors
  - – Molecular Profiling and 3D images
- Limitations
  - – organic information can be limited
  - – vacuum compatibility required
  - – Quantification very difficult
  - – at times, too surface sensitive