Welcome

to today's episode:

Unlock the Power of ToF-SIMS

Technique, Examples and Insights

Tatyana Kravchuk, PhD
Member of Technical Staff,
Covalent Metrology

Lyle Gordon, PhD
Director of Materials, Chemistry and Surfaces Group
Covalent Metrology

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11 AM Pacific Time

COVALENT METROLOGY

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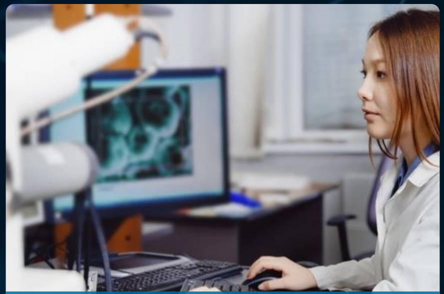
Modern, digitally-empowered analytical services platform delivering quality data and expert analysis to accelerate advanced materials and device innovation.

Comprehensive Solutions Stack

- *50+ Cutting-edge instruments in-house, 150+ Techniques*
- *Analytical Services*
- *Advanced Modeling*
- *Method Development*
- *Custom Consulting Solutions*

High-touch, High-Quality Services

- *Ionic Membership Program*
- *Enterprise Metrology Solutions*
- *Instant, Secure Access to Data and Reports*
- *Expanding Toolkit in Custom Digital Platform*



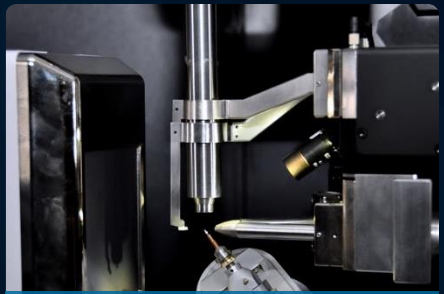
Flexible Business Models

- *LiveView™ (real-time collaboration)*
- *Co-op and Tool-share Opportunities*
- *Training and Certification on Instrumentation*
- *Laboratory Audits*

Rigaku, Anton Paar, ThermoFisher Scientific, Asylum Research, KEYENCE, J.A. Woollam, TA Instruments, PVA TePla, Teledyne CETAC Technologies, HORIBA Scientific, Digital Surf

Rich Network of Partnerships

- *Partner to World's Leading Instrument Manufacturers and Labs*
- *Expanding access to Advanced Instruments and Analysis Tools*
- *Lab Connections and Applications Learning*



Who We Are, Who We Serve

- *50+ People, 14 PhDs*
- *Comprehensive, Modern Analytical Capabilities*
- *Headquarter Lab in Sunnyvale, CA*
- *600+ Clients, 15-30 new clients / week*

Covalent's Analytical Services & Technical Groups

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Enterprise Metrology Solutions: Failure Analysis & EM

Electron Microscopy

- S/TEM
  with EDS; EELS; Electron Diffraction; SAED
- FIB-SEM & HR-SEM
  with EDS; EBSD; 3D Tomography
- Lamella Preparation
  incl. specialized lift-outs

Failure Analysis

- DPA / Mechanical X-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- NIR / IR Imaging
- Emission Microscopy
- Root-Cause Failure Analysis

Materials, Chemicals, and Surfaces

Microscopy & Profilometry

- Chromatic Aberration
- Digital Optical Microscopy
- Laser Scanning Confocal Microscopy
- White Light Interferometry
- Scanning Acoustic Microscopy (SAM)

Analytical Chemistry

- Mass Spectroscopy:
  ICP-MS and LA-ICP-MS; GCMS
- ICP-OES / GDOES
- Raman
- NMR (solid / liquid + 1,2,3 nuclei)
- XPS, UPS, ISS
- SIMS, TOF-SIMS

X-ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micro-computed X-ray Tomography (Micro-CT)
- 2D / 2.5D / 3D X-ray Inspection & X-ray Radiography
- ED-XRF / WD-XRF

Mechanical Testing

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM, PiFM)
- Nano-indent / Nano-scratch
- Rheometry / Viscosity
- DMA / TMA (bend/stretch/compression)
- Tensile testing

Misc. Material Properties

- Thermal Analysis: DSC, TGA
- Surface Zeta Potential
- Porometry / Pycnometry
- Gas Adsorption / Chemisorption
- Foam Density / Skeletal Density / Tap Density
- Particle Analysis: DLS / ELS / size distribution / zeta potential

Optical Characterization

- Fourier Transformed Infrared Spectroscopy (FTIR and ATR-FTIR)
- **Spectral Ellipsometry & Advanced Optical Modeling**
- UV-Vis-NIR Spectroscopy

Introducing today's speakers

Dr. Tatyana Kravchuk

Member of Technical Staff,
Covalent Metrology

Dr. Kravchuk has recently joined Covalent Metrology as a SIMS specialist. She has over 20 years of experience in Surface Science, with a background in both academia and industry. She also has an extensive track of record in material research and development with a particular focus on batteries and semiconductors. Dr. Kravchuk completed her Bachelor, Master and PhD degrees in Physical Chemistry at the Technion – Isreal Institute of Technology.

Dr. Lyle Gordon

Director of Materials, Chemistry & Surfaces Group,
Covalent Metrology

Dr. Gordon joined Covalent in 2023 where he manages the Materials, Chemistry and Surfaces group, overseeing X-ray metrology, analytical chemistry, and surface science. He has extensive expertise in time-of-flight mass spectrometry, particularly related to his work on atom probe tomography. Dr. Gordon completed his Bachelor of Applied Science at the University of Toronto, his PhD in Materials Science at Northwestern University, and was a postdoctoral fellow for the Department of Energy at Pacific Northwest National Lab.

Introduction - brief historical perspective and current use of ToF-SIMS

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1910s 1940s

- Early observations of secondary ion emission[1]
- Development of mass spectrometry foundations[2,3]

late 1940s

- First Time of Flight analyzer
- Herzog and Viehböck first describe SIMS[4]

1960s

- Fundamental SIMS studies on ionization and sputtering[5,6,7].
- First commercial SIMS instruments by GCA Corp. and ARL

1970s

- First TOF-SIMS was build by Benninghoven for molecular analysis[8].
- SIMS instruments from Cameca and Kratos Analytical

1980s

- Liquid metal ion guns introduced by Levi-Setti, improving resolution[9].
- PHI and IONTOF founded.
- Commercializing imaging SIMS

1990s

- Cluster ion sources expand applications to organics[10,11].
- TOF-SIMS introduced by PHI for organic and biological analysis

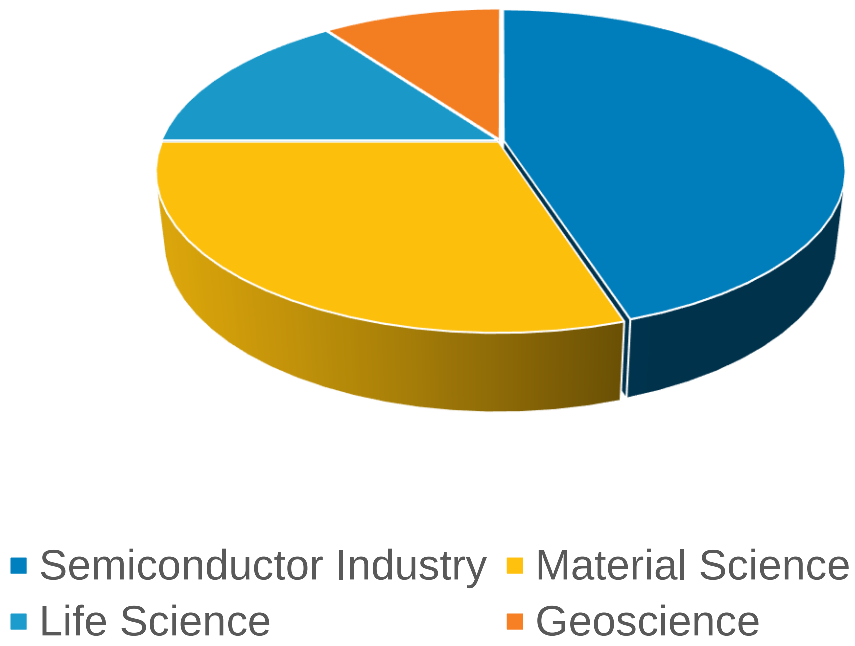
2000s

- 3D SIMS imaging pioneered by Vickerman[12].
- IONTOF introduces 5th gen TOF-SIMS with tandem MS.
- Expanded applications across diverse scientific fields[13]

Now

- 2023: IONTOF introduced the ToF-SIMS 6, enhancing lateral resolution and sensitivity. CAMECA implemented AI-driven data analysis
- 2024: Ulvac-Phi introduced automated sample handling. Kore Technology enhanced their SIMS systems' depth profiling capabilities, achieving a 20% improvement in depth resolution.

Introduction - current use of SIMS by industries



Examples:

- Contamination detection on semiconductor wafers
- Depth profiling in thin films
- Understanding the chemical composition of polymers
- Mapping the distribution of isotopes in a geological samples
- Analyzing drug distribution in tissue.
- Investigating element distributions in battery materials.

Basic principles of ToF-SIMS

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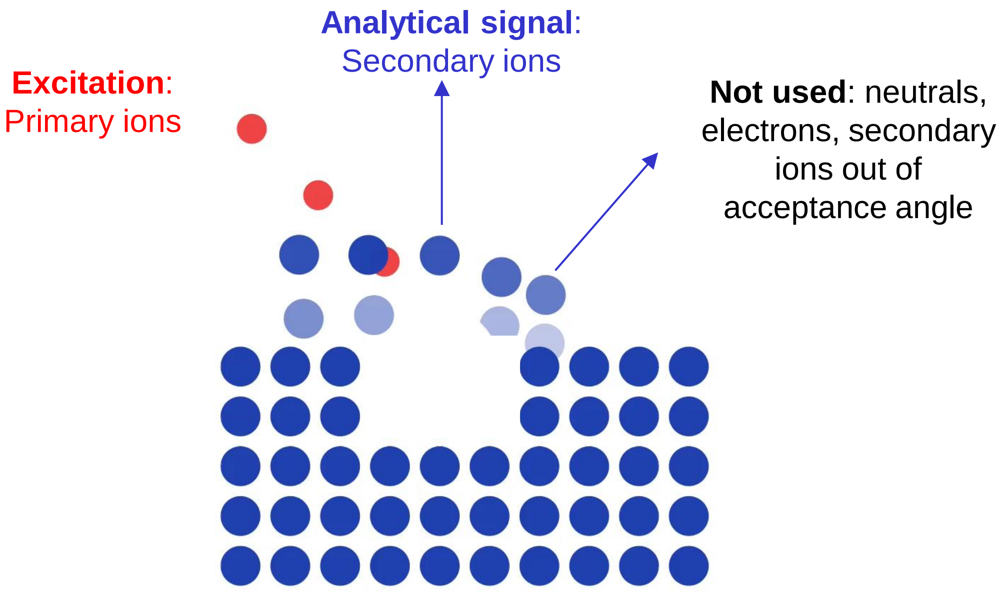
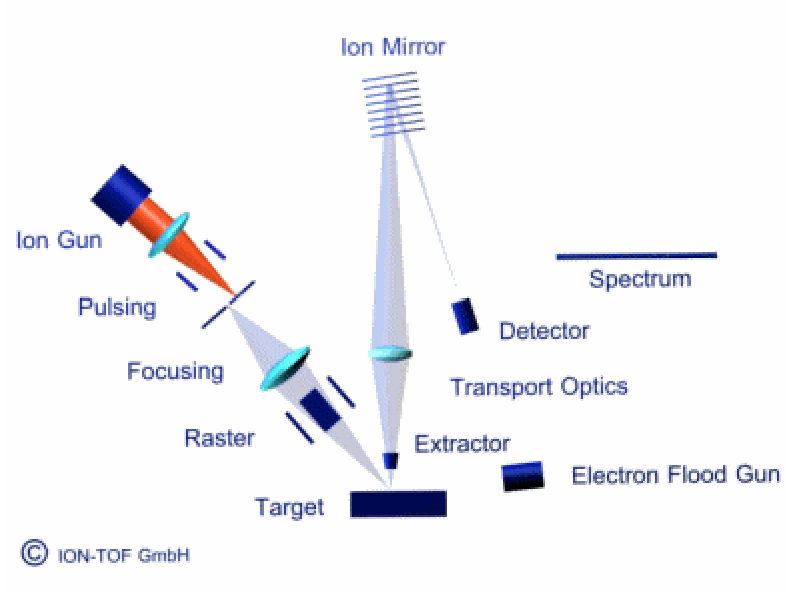
SIMS principles



- A solid surface is bombarded by primary ions of some keV energy.
- Part of the energy is transported to the surface allowing surface atoms and molecular compounds to overcome the surface binding energy.
- Most of the emitted particles are neutral in charge, but a small portion is also positively or negatively charged.

ToF principles



- TOF mass analysis is based on the fact that ions with the same energy, but different masses will travel with different velocities over a drift path to the detector.
- An electrostatic field accelerates the generated ions to a common energy, then the lighter ions arrive at the detector before the heavier ions.
- Measuring the flight time for each ion allows the determination of its mass.

Static SIMS vs Dynamic SIMS

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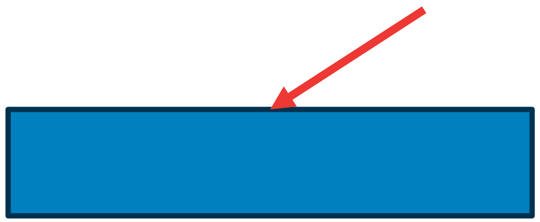
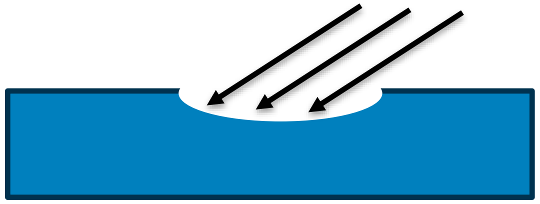
Static SIMS



- Low ion dose, $<10^{12}$ at/cm^2
- Ultra surface analysis
- Typically uses gold, bismuth or gallium primary ions
- Elemental and molecular analysis
- Mass analysis is typically performed with TOF spectrometer

Dynamic SIMS



- High ion dose, $> 10^{14}$ at/cm^2
- Material removal, depth profiling
- Typically uses oxygen or Cs primary ions
- Elemental analysis
- Usually, quadrupole or magnetic sector mass spectrometers are used

Instrumentation and key components

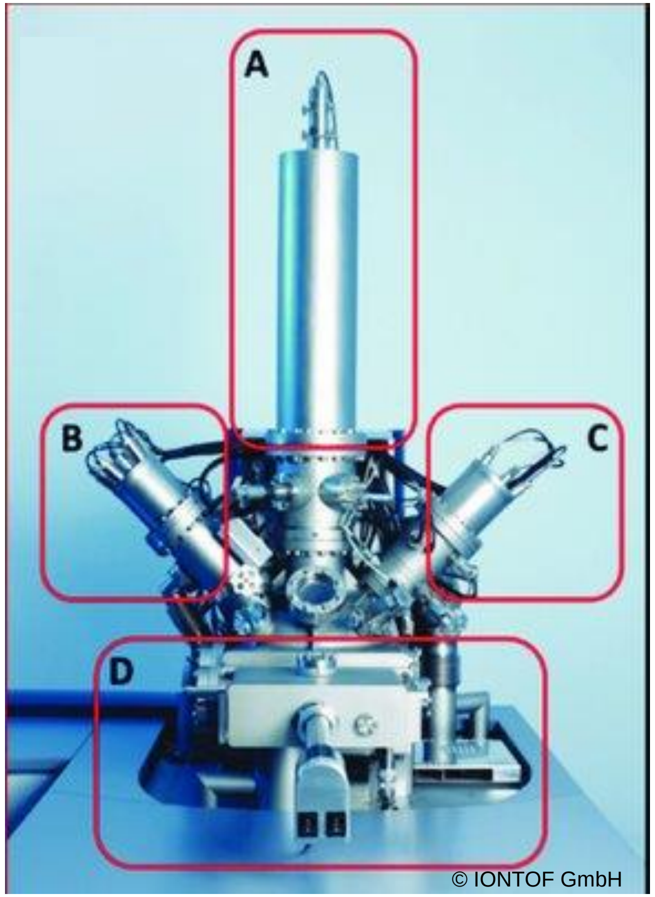
A. Time-of-flight mass analyser.

B. Bismuth cluster ion gun for analysis.

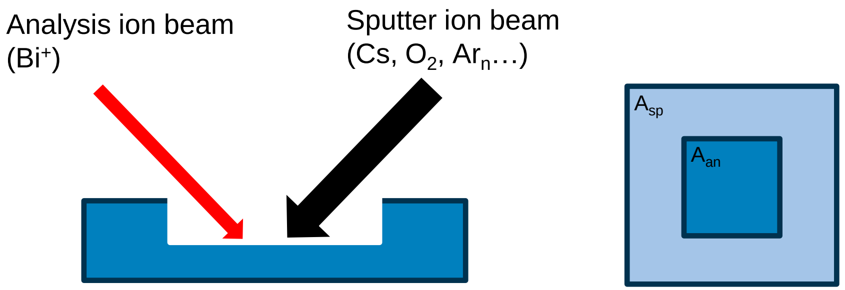
C. Ion gun, capable of generating Cs^+ and O_2^+ ions.

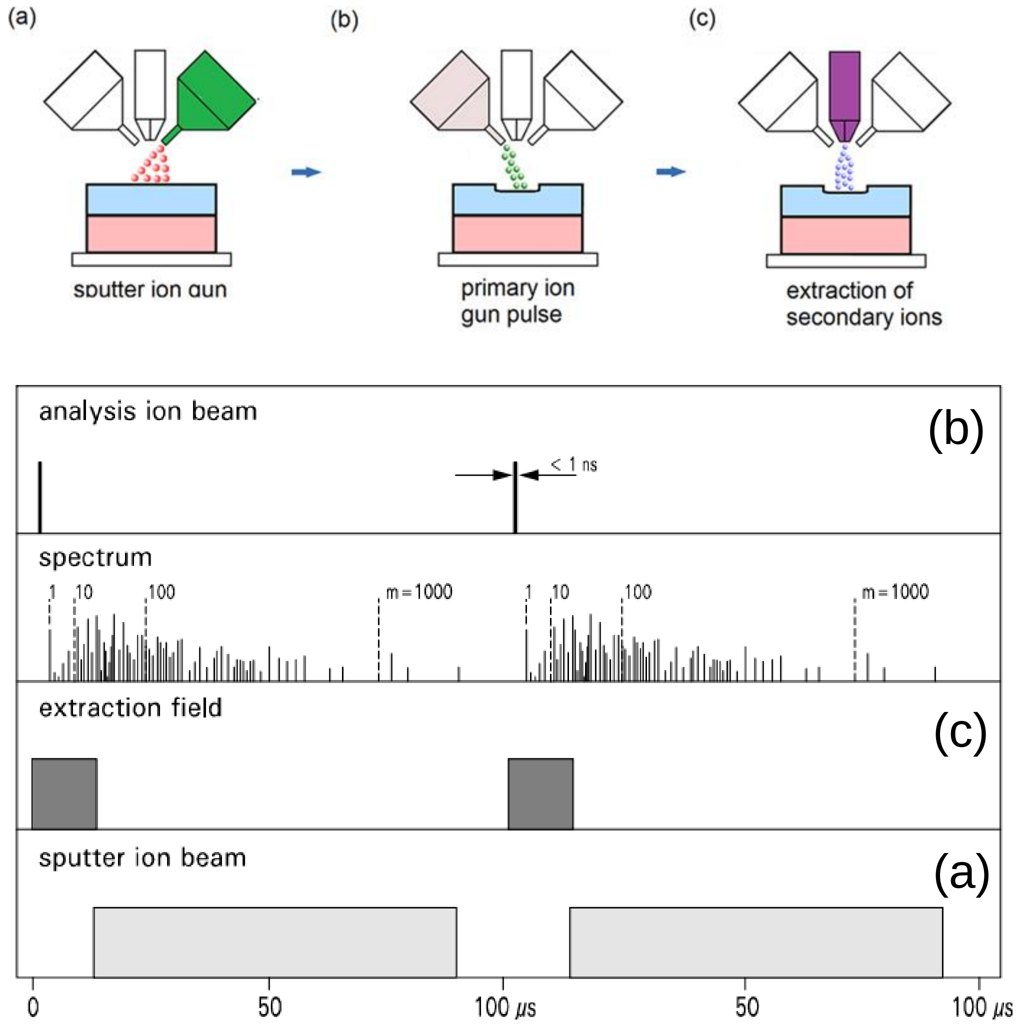
D. Load lock chamber and sample manipulator arm.

- Flood gun for charge compensation
- The 5 axes, X, Y, Z, rotation and tilt macro stage



Dual beam depth profiling advantage

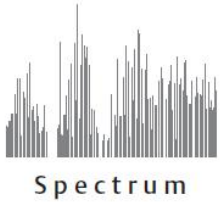


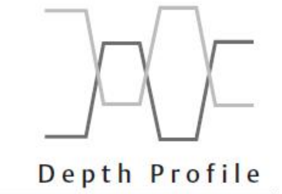


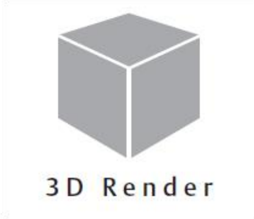
Sputter and analysis conditions can be independently optimized:

- Low energy, high current sputter ion beam provides high depth resolution and fast layers removing
- High energy, low current analysis ion beam provides high lateral resolution and minimal damage to the surface

What can be measured by ToF-SIMS







Surface spectrometry elemental and molecular information from the outer monolayers.	- High sensitivity in the ppm/ppb range - High mass resolution (0.005amu) and accuracy even on insulating samples - High mass range
Surface imaging mass resolved secondary ion image, “a chemical map”, can be obtained simultaneously for all masses.	- Lateral resolution: 0.3 mic - Field of view from μm^2 to cm^2
Depth Profiling Distribution of elements in depth can be measured for all masses over measured area	- High sputter speed (up to 10 µm/h) - Maximal depth: ~5mic - High mass resolution (0.005amu) - High sensitivity in the ppm/ppb range - Depth resolution: 1nm
3D reconstruction The visualization of 3D sample structures is possible by combining spectral, imaging and depth information.	- Parallel mass detection - High depth resolution - High image resolution (in image mode) - Retrospective analysis - 3D reconstruction

Comparing ToF-SIMS with other popular surface analysis techniques

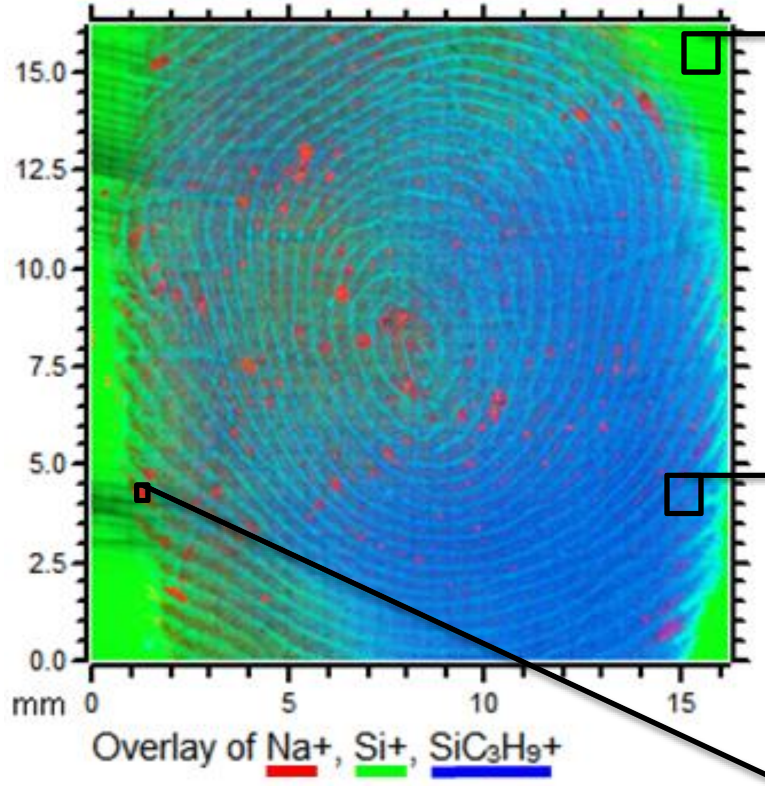
Property	Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)	X-ray Photoelectron Spectroscopy (XPS)	Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS)	Ion Scuttering Spectroscopy (ISS)
Surface Sensitivity	Extremely high (monolayer sensitivity)	High (5-10 nm sampling depth)	Low (Bulk material focus)	Extremely high (monolayer sensitivity)
Elemental Detection Range	All elements and isotopes	All elements except H and He	Elements from B to U	For elements heavier than N
Chemical State Information	Limited	Yes	Limited	No
Imaging Capability	Excellent (high spatial resolution)	Poor	Excellent (sub micromrter resolution)	No
Depth Profiling	Excellent depth resolution up to few microns profiling	Limited depth resolution up to a few microns profiling	No	Excellent depth resolution up to hundreds of nm profiling
Quantification	Qualitative with relevant reference	Quantitative in most cases	Limited	Qualitative with relevant reference
Typical Detection Limit	ppb	0.10%	0.10%	0.10%
Destructive Analysis	Yes if depth profiling	Yes if depth profiling	No	No

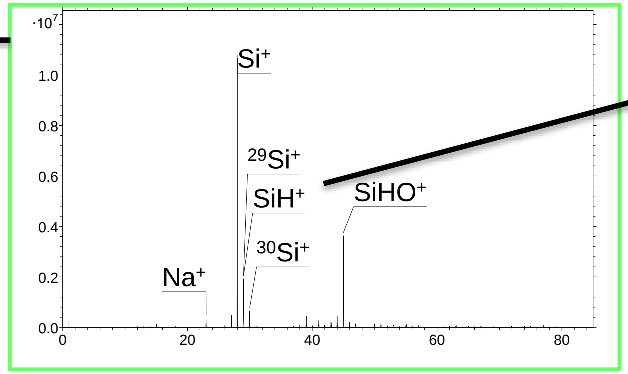
High

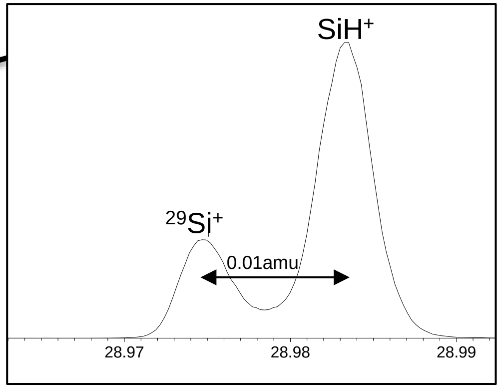
Limited

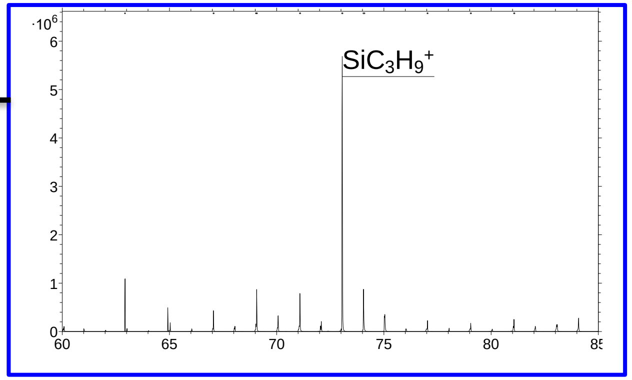
Low

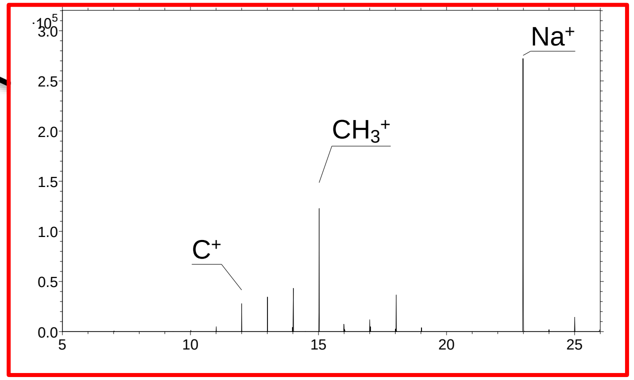
Example of study of surface contamination over large area, including a high-resolution spectra from 1amu up to thousands











- **Na^+**: originates in the salt from pores of the finger.
- **$SiC_3H_9^+$:** Identified as a PDMS contamination on finger.
- **Si^+**: Detected from the substrate which was a Si wafer.

Combination of large scale mapping with detailed chemical identification, allowing us to not just measure the spectra of contamination, but also create a chemical map.

3D rendering and data visualization of Ca and Na contamination on Al

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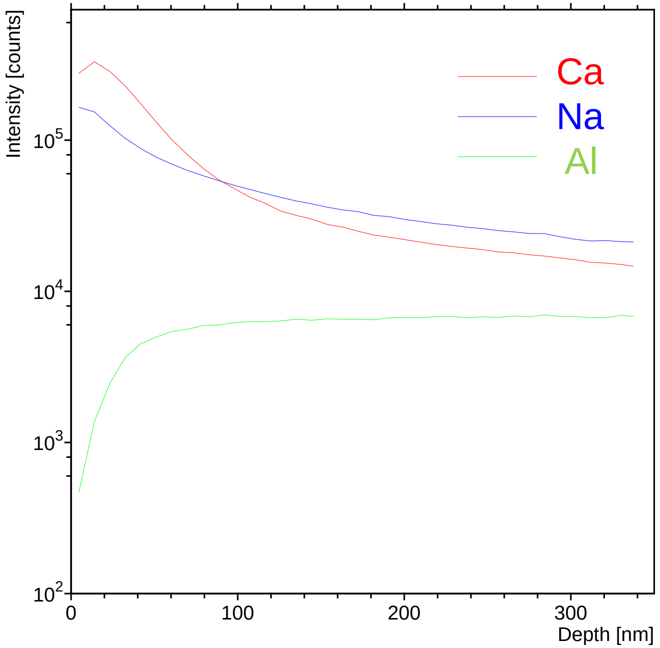
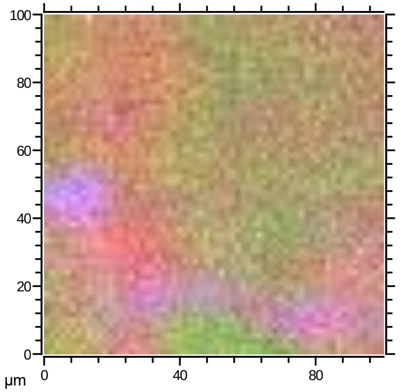
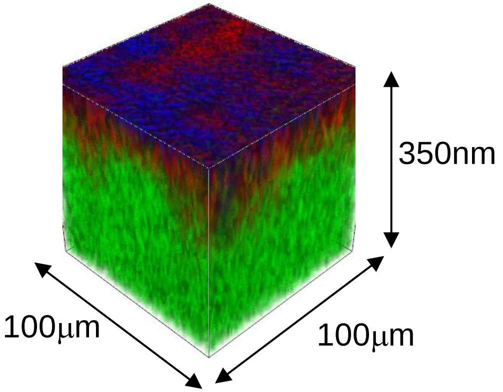
Depth profile



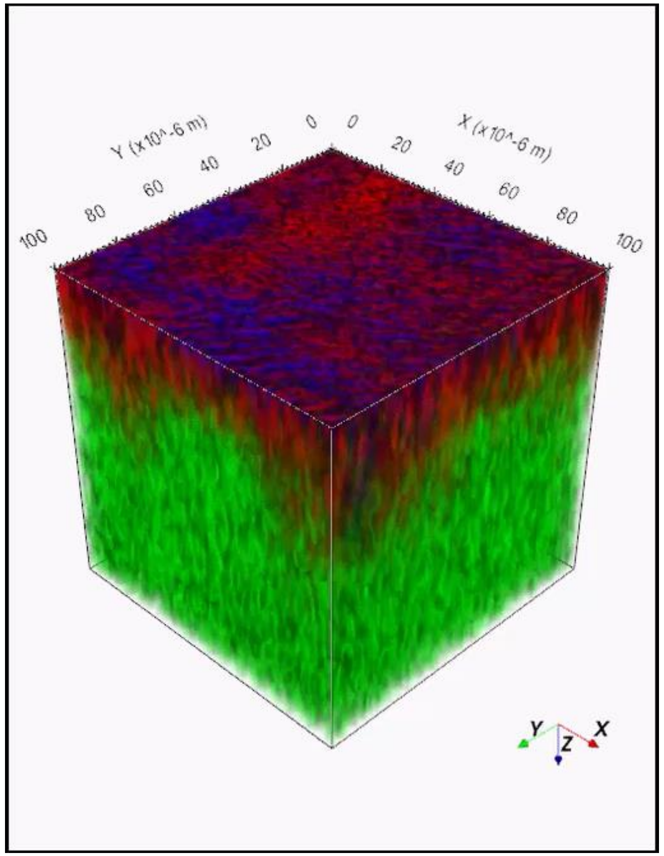
2D overlay of Ca, Al, Na



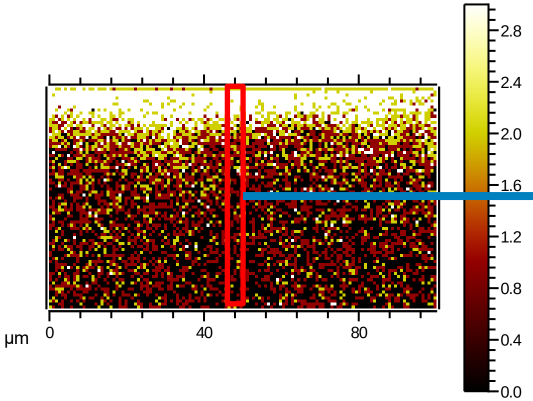
3D overlay of Ca, Al, Na



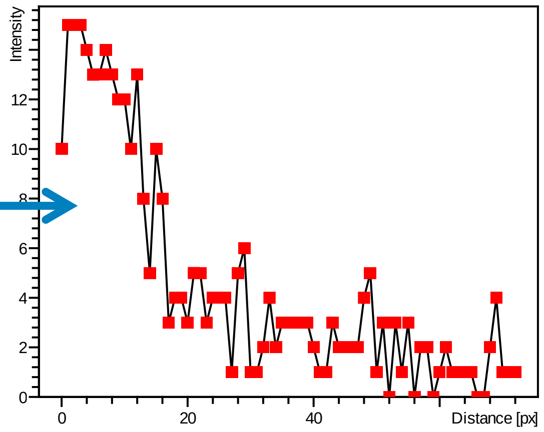
3D overlay of Ca, Al, Na movie



X-Z slice of Ca



Line scan of X-Z slice of Ca

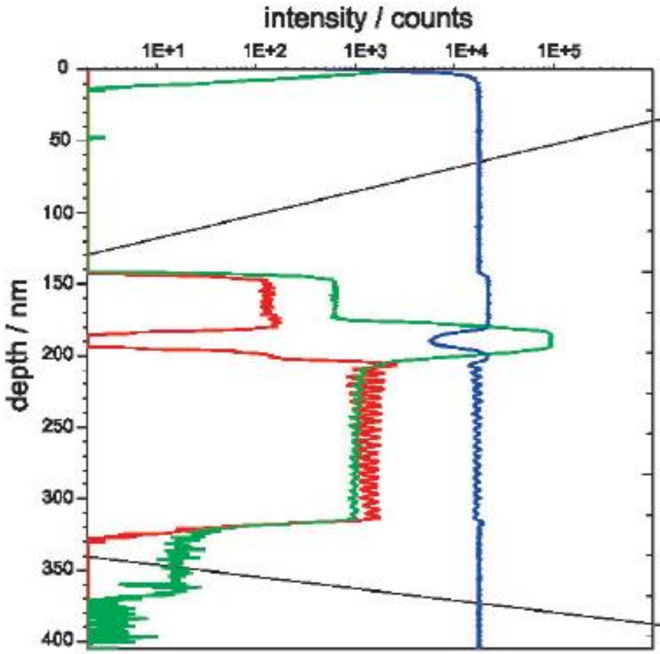


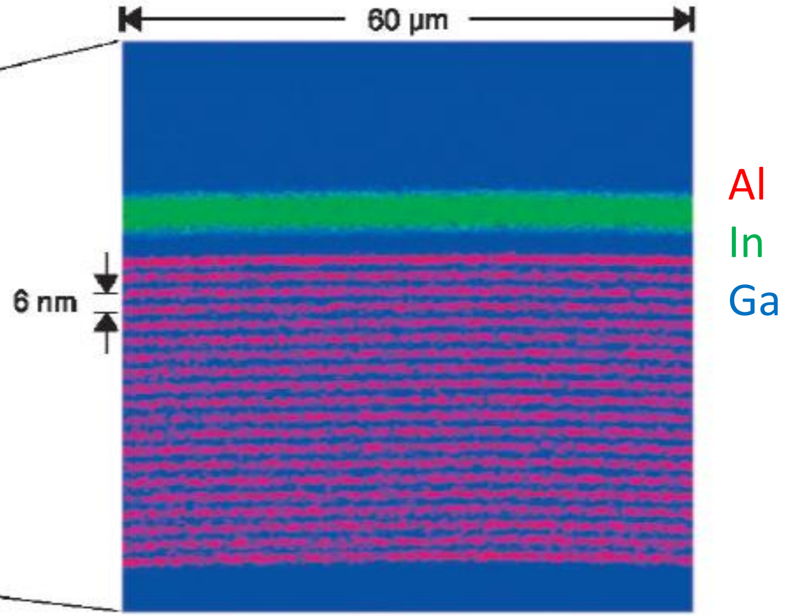
GaAs/AlGaAs superlattice depth profile

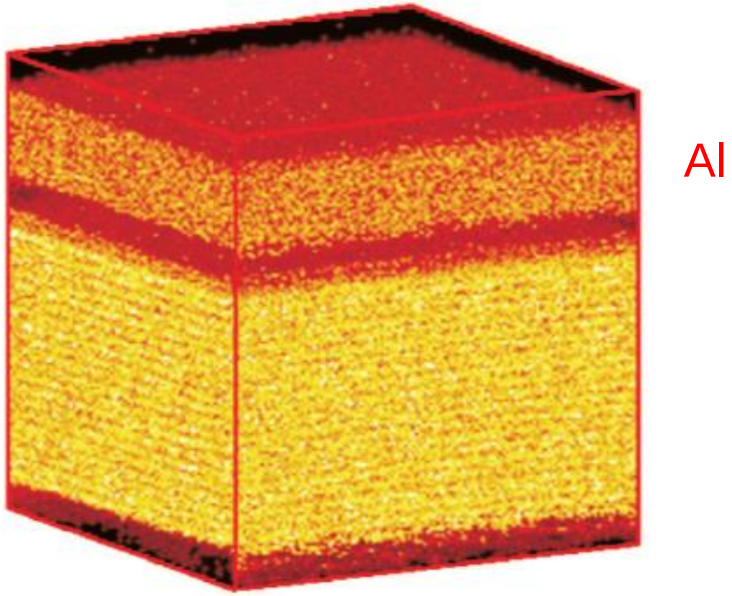
GaAs/AlGaAs superlattice depth profile

2D overlay of Al, In, Ga of part of the profile

3D rendering of Al from the part of the profile

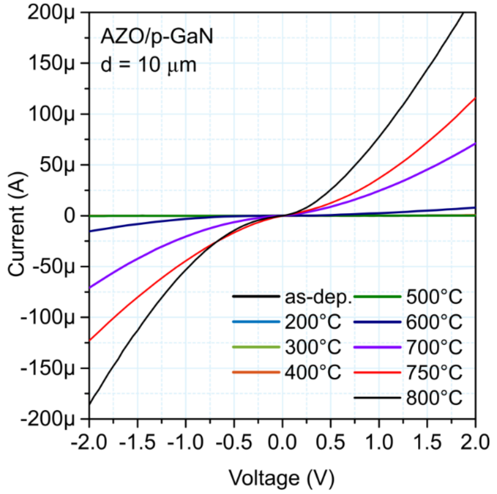






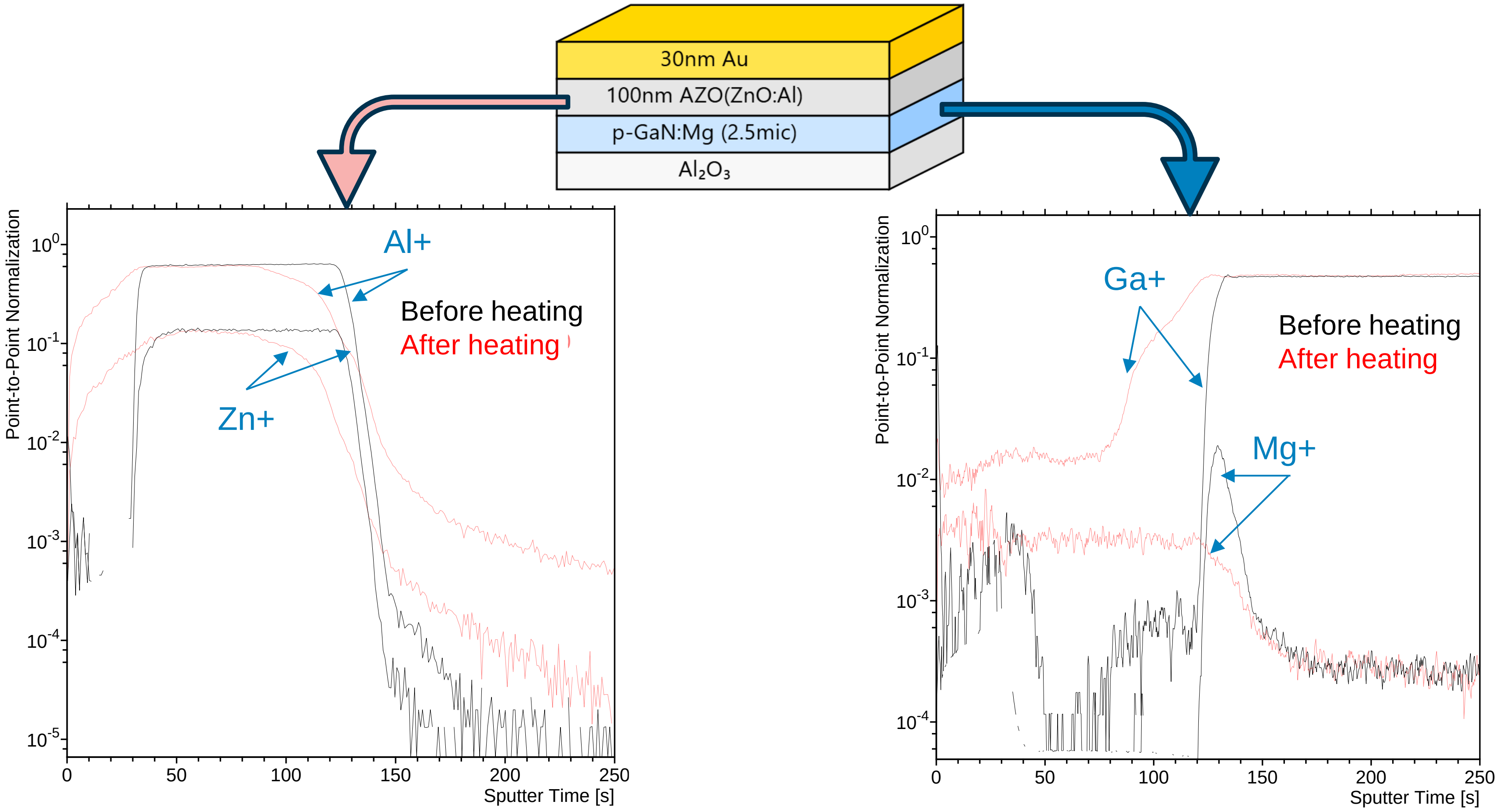
This TOF-SIMS depth profile of a GaAs/AlGaAs superlattice demonstrates high depth resolution, revealing precise elemental distribution at the nanometer scale. The profile (left) shows clear periodic layering of Al, Ga, and In, while the 2D overlay (center) highlights uniformity and interface sharpness down to 6 nm. The 3D rendering (right) further visualizes Al distribution, emphasizing TOF-SIMS' capability for detailed sub-surface analysis.

Developing ohmic contacts to GaN



Deposition of AZO (Aluminum-doped Zinc Oxide) on GaN followed by 800C annealing created the contact through mutual diffusion of GaN:Mg and AZO

Depth profiles **before** and **after** heating on



Delaminating metal pads investigation

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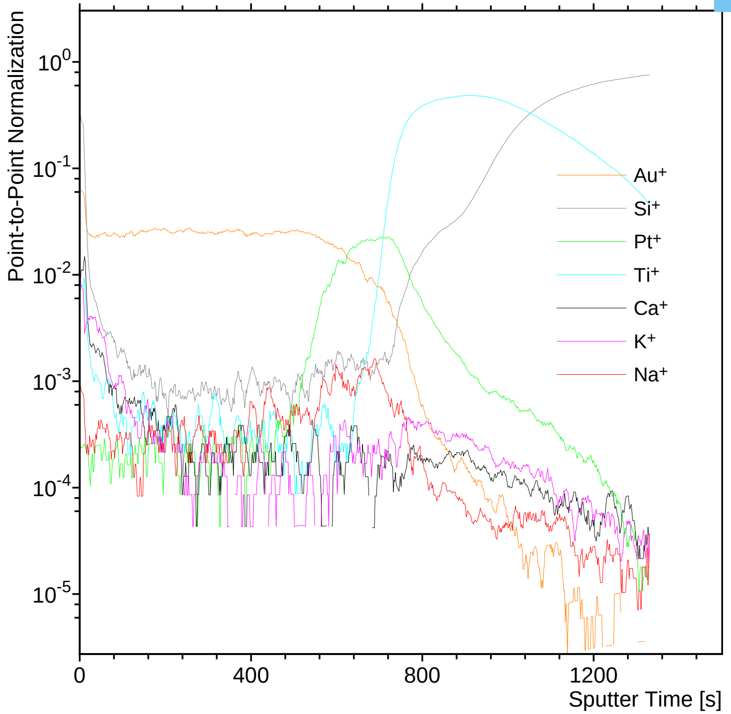
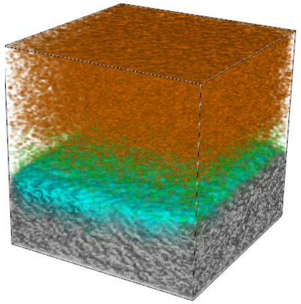
Good sample

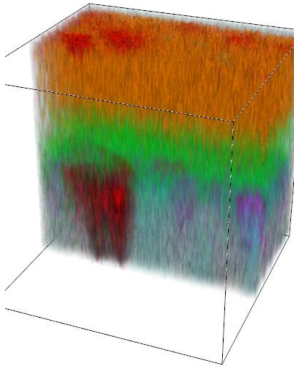
Metal pads deposited by e-beam evaporation.
500nmAu/100nmPt/30nmTi/Si

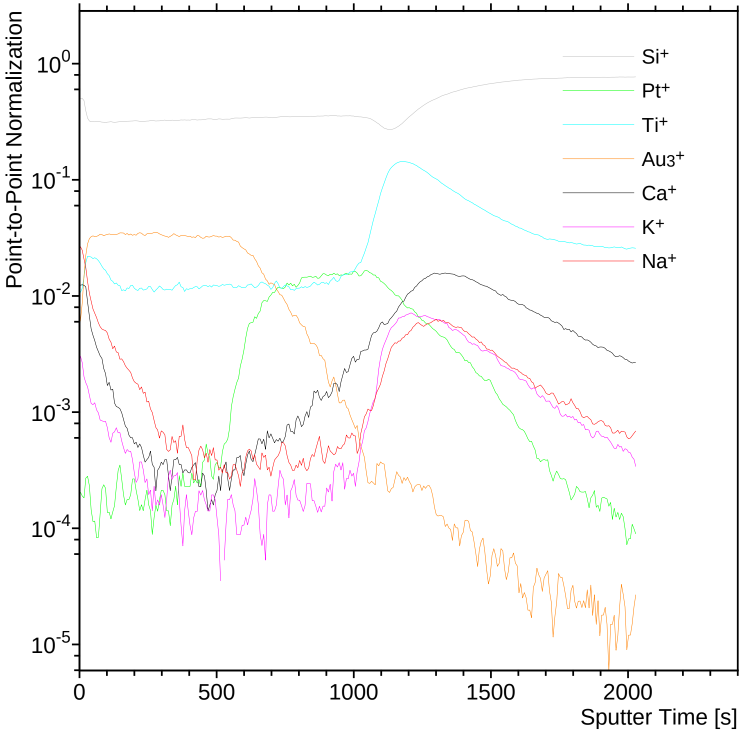
Bad sample



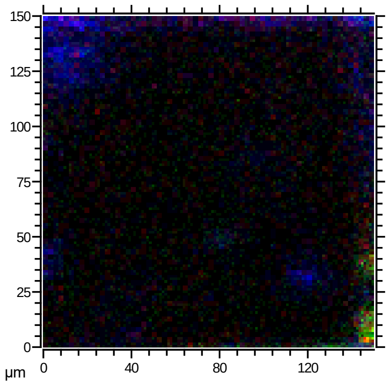
3D rendering overlay
Au^+, Si^+, Pt^+, Ti^+, Ca^+, K^+, Na^+

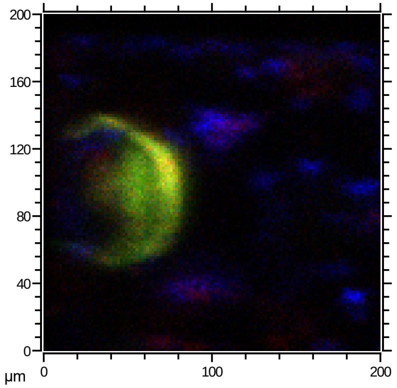






2D overlay of Na+, Ca+, K+

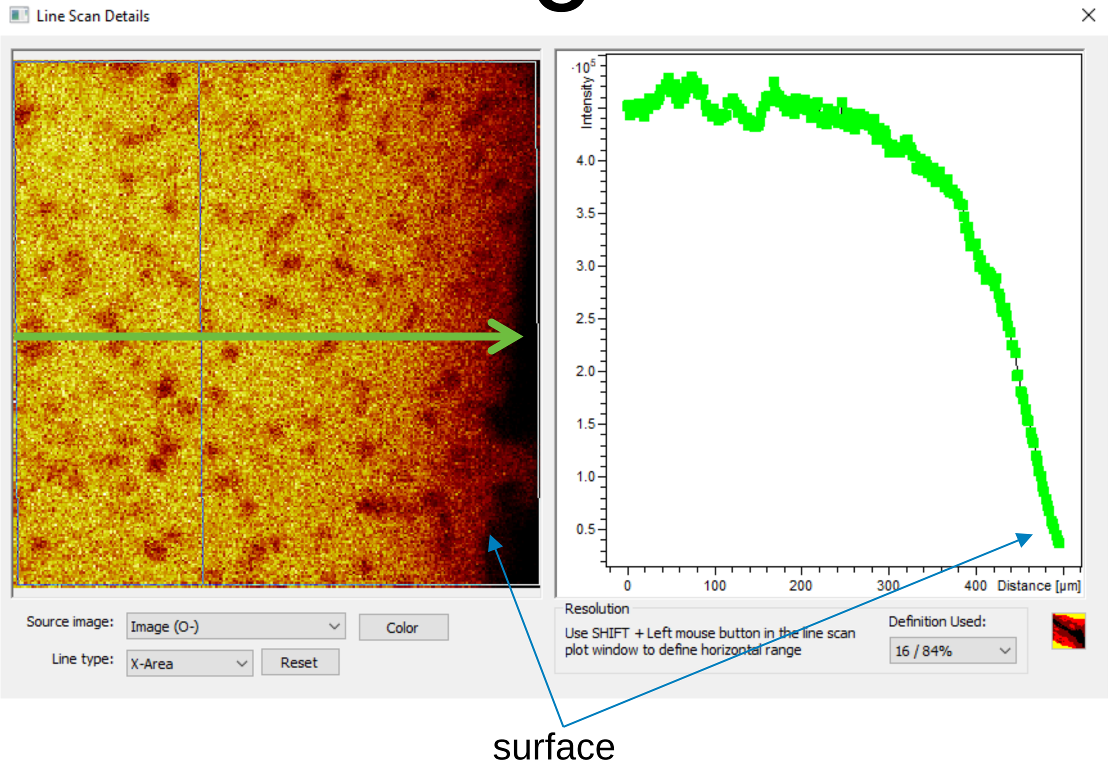




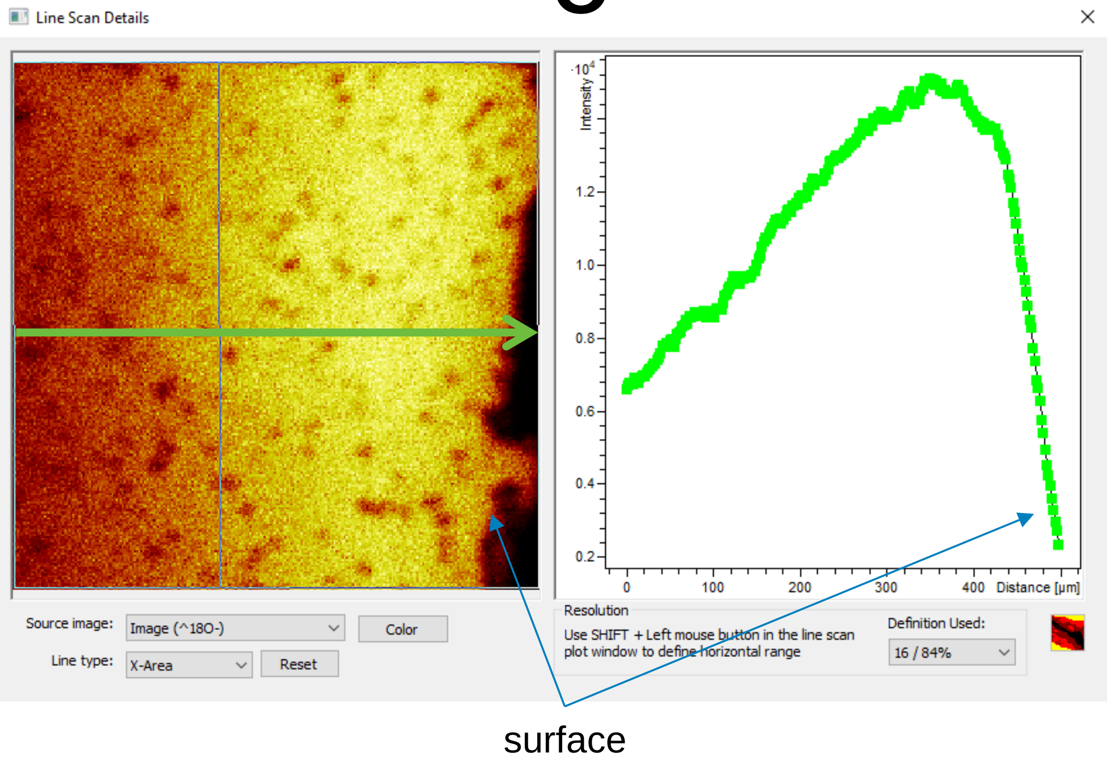
ToF-SIMS isotope sensitivity

TOF-SIMS reveals the distinct distribution of ^{18}O, infused through high-temperature and time-controlled process, versus native ^{16}O in a novel ceramic material, clearly tracking the isotope's 500 µm diffusion path from the surface into the bulk structure.

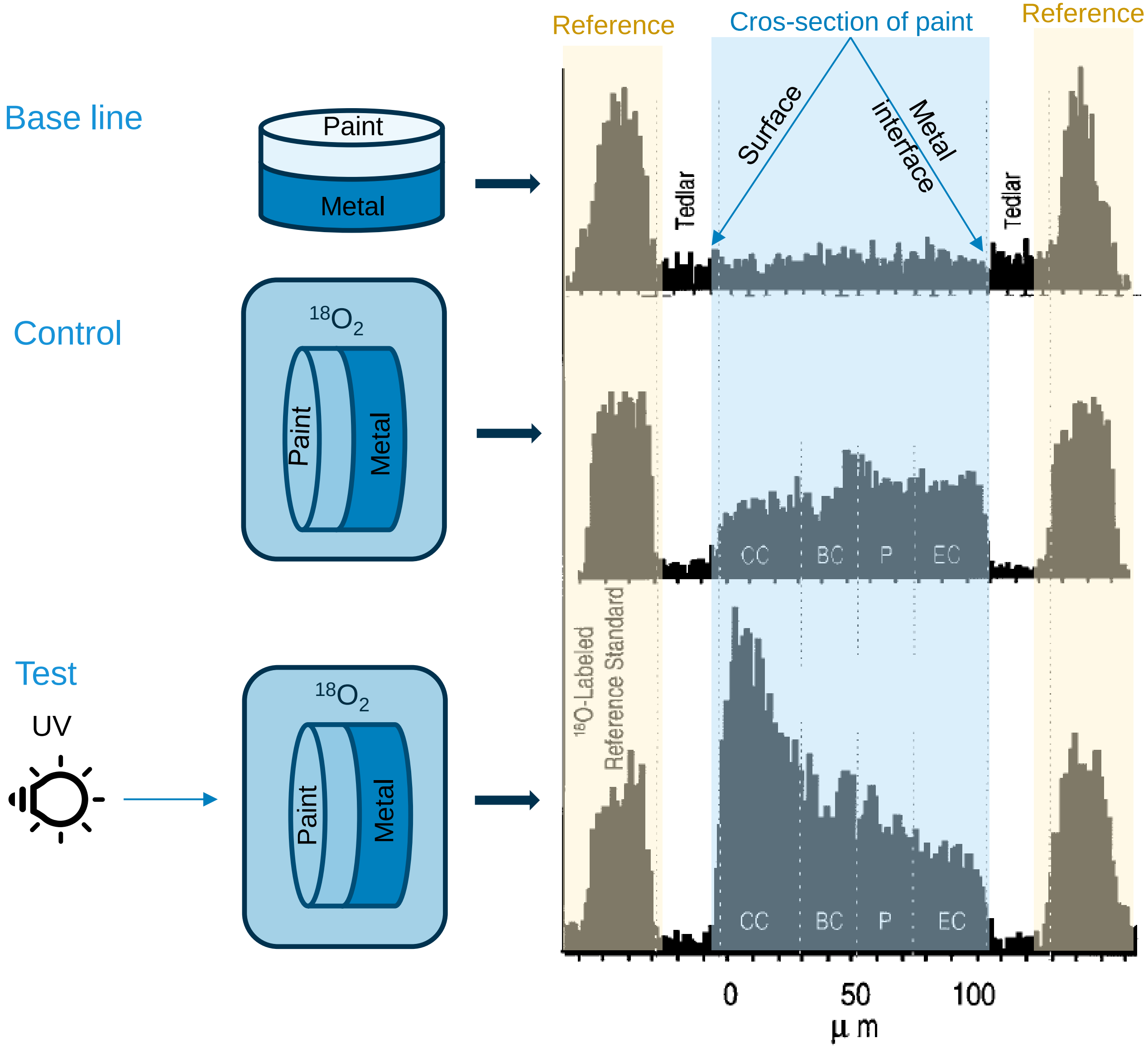
^{16}O



^{18}O



Investigating paint degradation mechanism using $^{18}O_2$ and TOF-SIMS image of paint cross-section



To investigate paint degradation mechanisms, researchers conducted an experiment using **^{18}O-labeled oxygen** as a tracer. Metal samples coated with paint were exposed to **UV light** in an atmosphere containing **$^{18}O_2$**, simulating environmental aging effects. After exposure, ToF-SIMS was used to measure the ^{18}O line-scan in paint cross-section which represents penetration depth of **^{18}O** within the paint layer.

The results demonstrated that UV exposure significantly enhanced oxygen diffusion, leading to deeper oxidation within the coating. By distinguishing induced oxidation from naturally occurring oxygen in the samples, this study provided valuable method to investigate **durability and failure mechanisms** for paints, polymers and coatings.

Sample preparation

- Which types of materials can be measured?
- What limitations are there for samples?
- How to handle samples?

✓ Semiconductors
✓ Polymers
✓ Paints and Coatings
✓ Biomaterials
✓ Pharmaceuticals
✓ Glass
✓ Paper
✓ Metals
✓ Powders
✓ Catalysts

✓ Solid phase
✓ Stable under ultra-high vacuum conditions
✓ Max dimensions: 10 mm (L) x 10 mm (W) x 6 mm (H)
✓ Flatter topographies improve signal detection
✓ For Powder Samples: 5-10 mg is sufficient (as long as it can cover 0.5 cm x 0.5 cm of In foil or Cu tape)

✓ Handle samples with gloves
✓ Pack in glass, hard plastic box or aluminum foil

Data acquisition

- Positive or negative? Check Slide 29
- Which sputter gun to choose? Check Slide 30
- Spectra or Image? Check Slide 31
- What is the max depth of profiling?
- And what if the sample is insulating?
- How do we know that the equipment is calibrated?

A few microns

There are a few technical adaptations to work with insulating samples like: flood gun and extraction bias. Also, an instrumental settings adjustments, like random raster mode and primary current adjustment

We are using Si wafer to check the mass resolution and perform mass calibration every measurement.

Data interpretation

- Can we have quantitative results?
- What is the detection limit?
- Can we say something about chemistry?
- How to ensure peak assignment?

Check Slide 32

DL is the lower signal detectable above the noise. It depends on many parameters both instrumental and sample-related. A few examples presented in the table show how big can be a deferens between DL

Detection Limits in Si			
O_2^+ Primary Ion Beam Positive Ions		Cs^+ Primary Ion Beam Negative Ions	
Element	DL (at/cm^3)	Element	DL (at/cm^3)
Al	2E+13	N	3E+14
B	2E+13	P	1E+14
Na	5E+12	C	1E+16

In some cases.
If the sample is an oxide, we will observe in the spectra mono ions as well as di- or tri-atom ions. However, their relative intensities will be proportional to ionization probability and not to stochiometric ratio.

For elements: check for relevant isotopes, double ions and oxides
For molecules: check for references

Strengths and Limitations of ToF-SIMS

Strengths

- Highly surface sensitive
- Exceptional sensitivity to trace elements (parts per million or parts per billion)
- Detects all elements, including hydrogen, and their isotopes simultaneously
- Non-destructive in static mode
- High-resolution depth profiling
- 3D visualization

Limitations

- Quantification requires specific standards
- Matrix effect
- Depth profiling is destructive
- Limited chemical information


Thank
You
Vinaka
köszönöm
Suksama
Maake
Asante
Shukria
Dhanyavadagalu
ارکش
Manana
Dankon
Kiitos
Suksama
Dankscheen
спасибо
Dank Je
Mauruuru
Biyan
Diolch i Chi
Gratias Tibi
Terima Kasih
Taiku
நன்றி
Dziekuje
Chokrane
Grazie
Juspaxar
Arigato
Paldies
Najis Tuke
Gracias
Matur Nuwun
감사합니다
Bedankt
Dakujem
धन्यवाद
cảm ơn bạn
Khap
Grazas
Ua Tsaug Rau Koj
Mèsi
Di Ou
Tack
Kop Khun
Obrigado
Nirringrazzjak
Děkuji
ありがとう
Rahmat
谢谢
хвала
Hvala
Eskerrik Asko
Danke
Merci
Go Raibh Maith Agat
Tingki
Salamat
ขอขอบคุณคุณ

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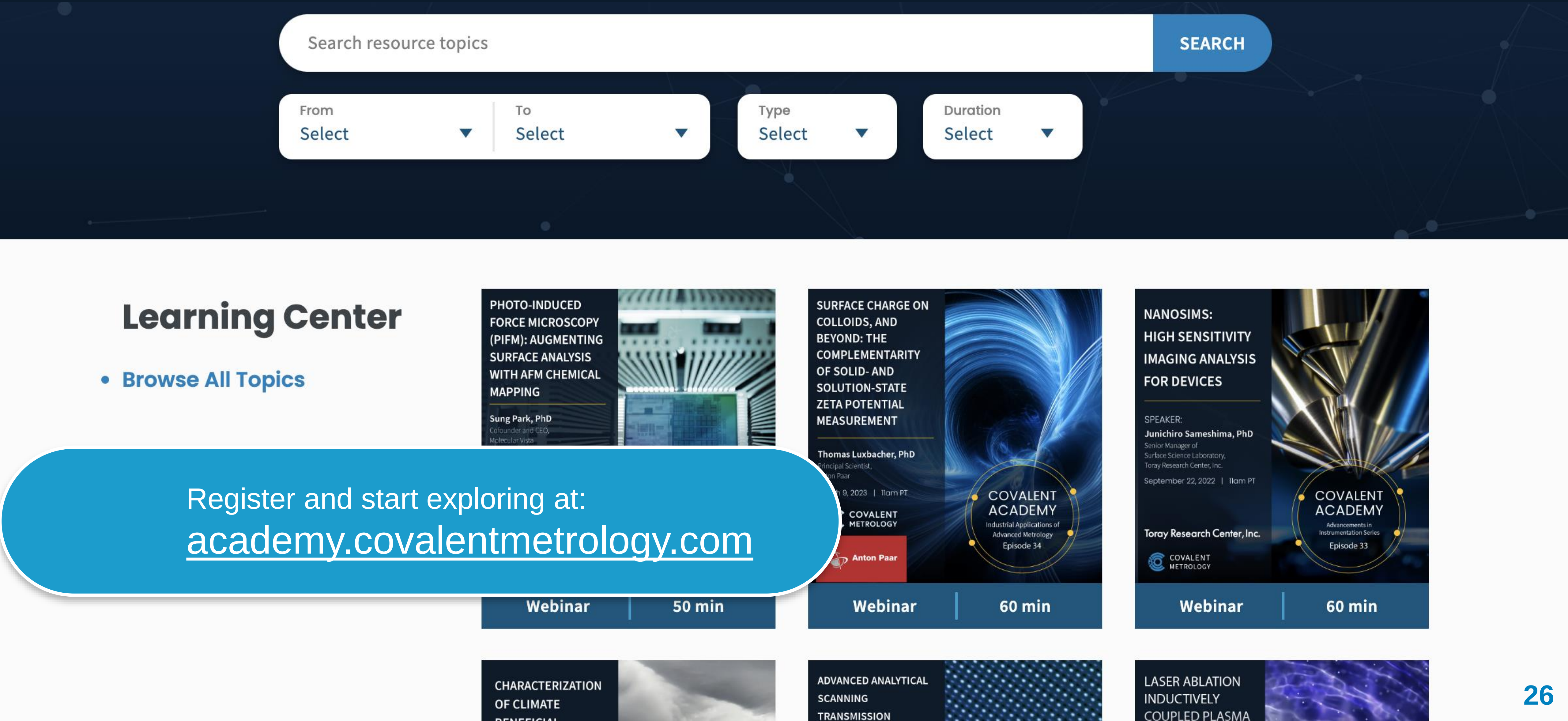

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Q & A Session

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Thank you.

Positive or negative?

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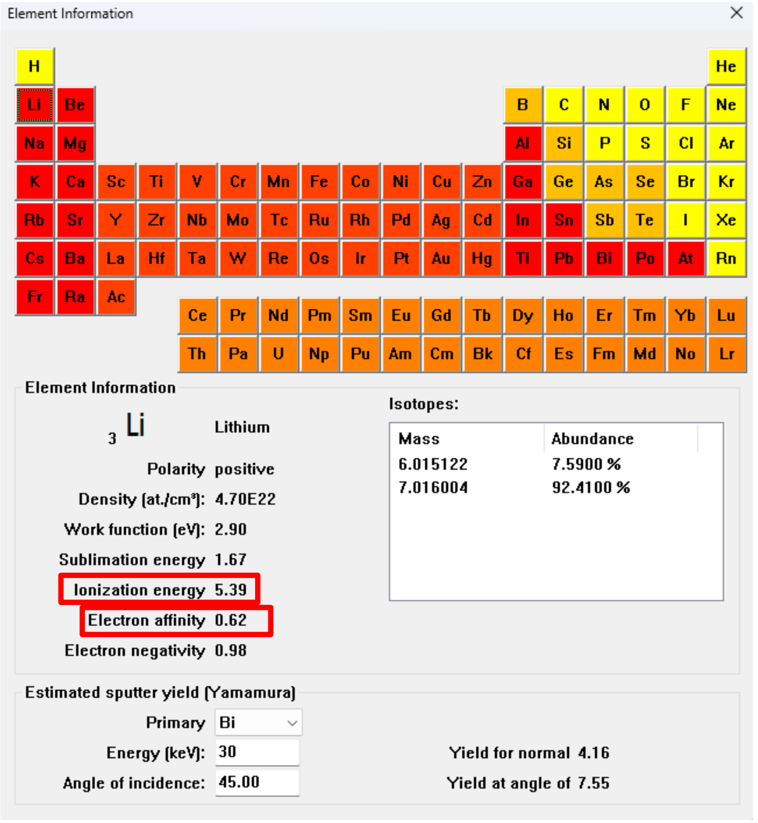

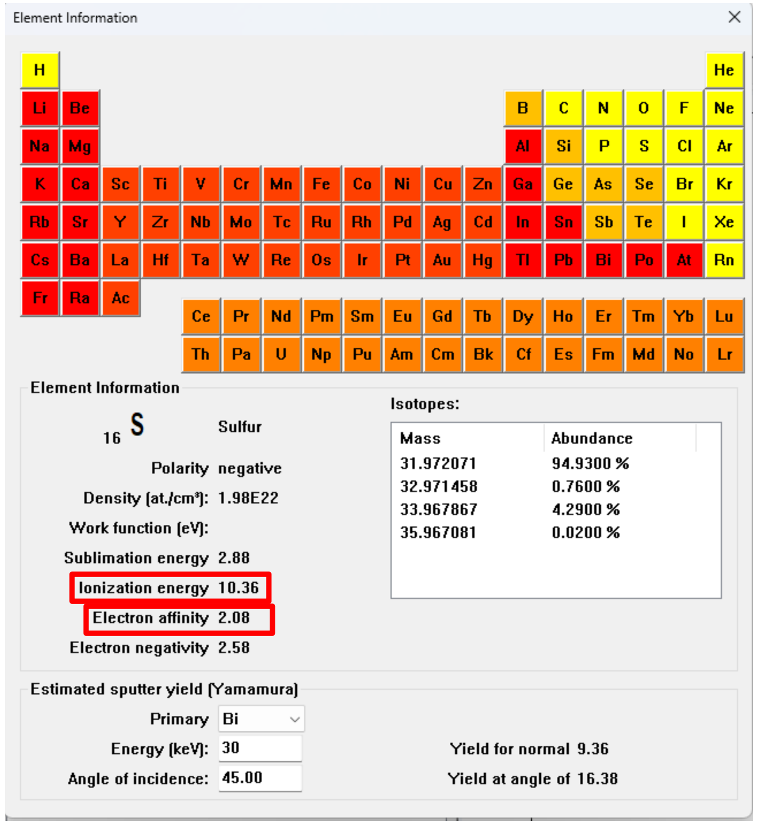

Lithium, with its low ionization energy of 5.39 eV and small electron affinity of 0.62 eV, strongly favors positive ion formation.

With a much higher ionization energy of 10.36 eV but a substantial electron affinity of 2.08 eV, Sulfur preferentially forms negative ions.

Which sputter gun to choose?

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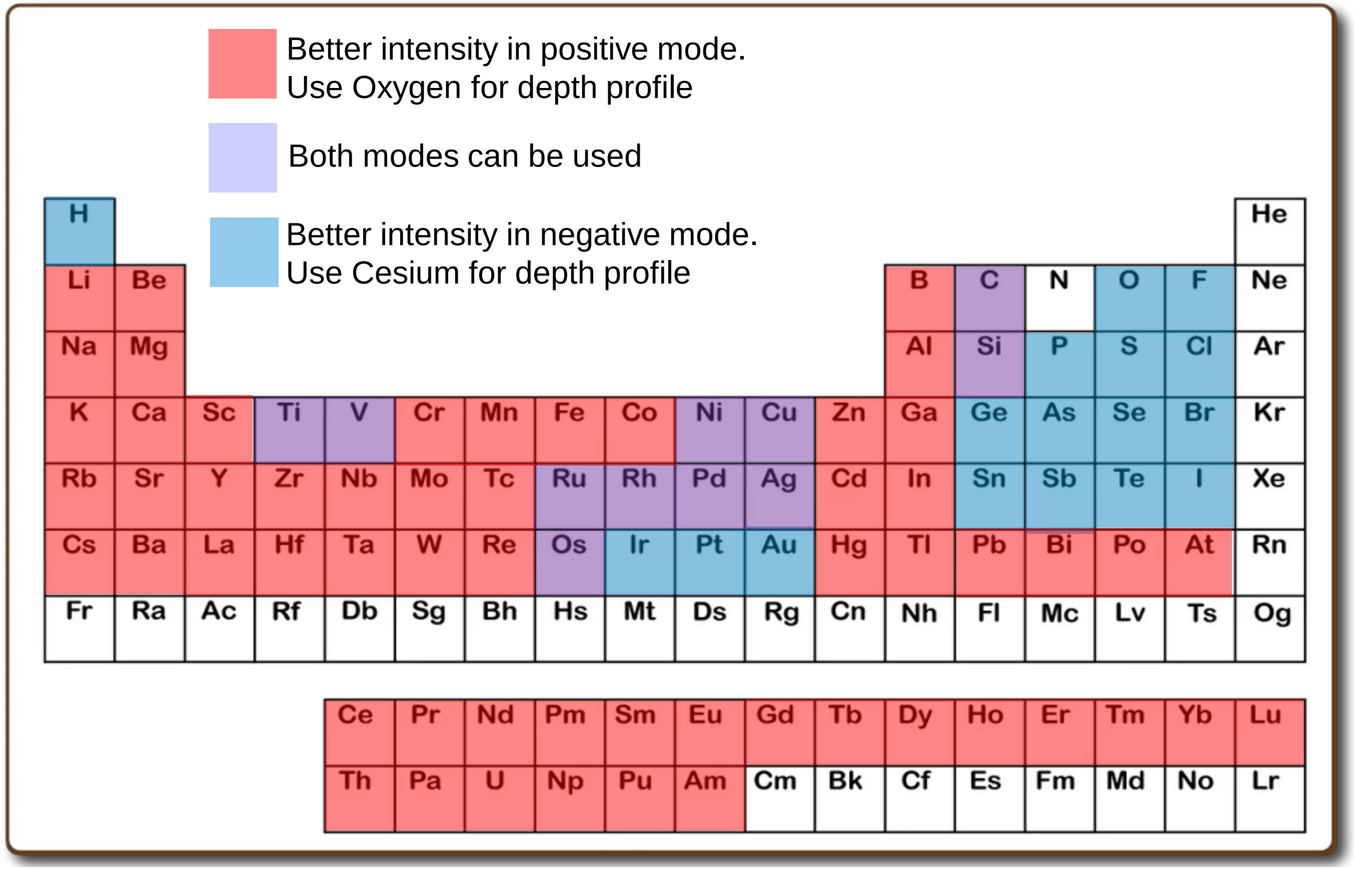
Oxygen boosts the signal of certain atoms by making them **positively charged**. It does this by forming bonds with metals and then taking electrons when those bonds break.

Cesium bombardment reduces the work function of the sample surface, making it easier for secondary electrons to escape. More available electrons lead to higher **negative ion** yields.

To measure **organic layers** use **Ar cluster ion beam**.



Spectra or Image?

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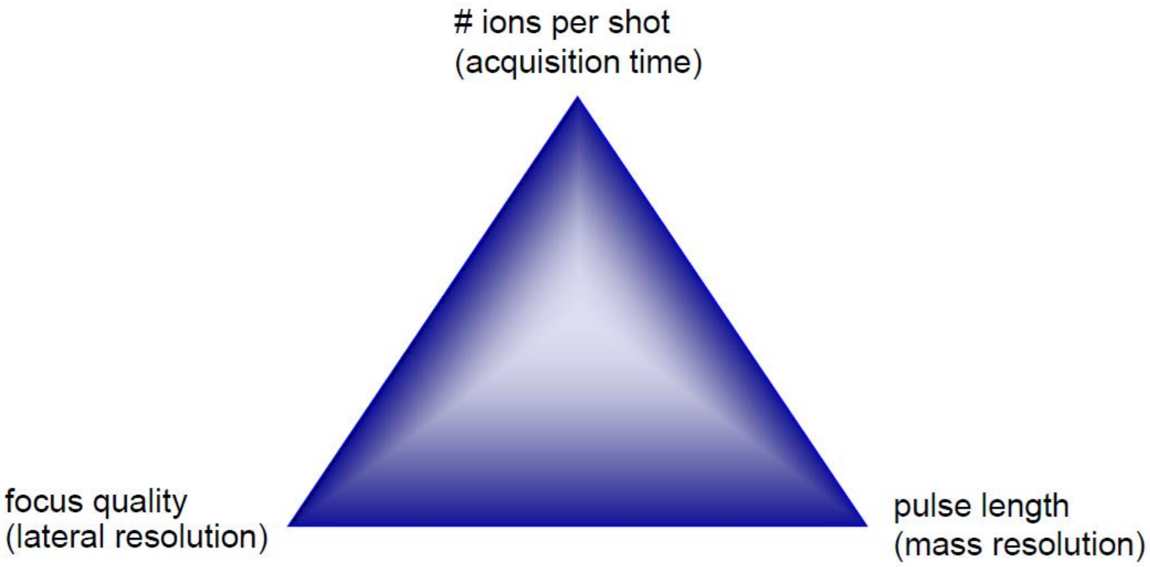
Given by laws of physics always a compromise has to be found within the following triangle:



Different positions within the triangle result in different operational modes.

- If you need to identify material -> spectra
- If you know your chemistry and need a good lateral resolution -> image
- If you don’t know the chemistry but need a good lateral resolution -> (1) spectra (2) image

Can we have quantitative results?

$$\frac{I_R}{C_R} = RSF_E \bullet \frac{I_E}{C_E}$$

RSF_E Relative Sensitivity Factor for Element E
I_E Secondary Ion Intensity for Element E
I_R Secondary Ion Intensity for Reference Element R
C_E Concentration of E
C_R Concentration of R

$$C_E = RSF \bullet \frac{I_E}{I_M}$$

I_M= intensity of ion related to matrix and not saturated

- **The standard is necessary for proper quantification. It must have the same species in the same matrix as the one we want to quantify.**

- The measurement conditions must be the same for standard and for sample.

<u>**Good news:**</u> Reference standards can typically be manufactured using ion implantation, where a precisely known quantity of the element you're studying is implanted into your material of interest.

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