Secondary Ion Mass Spectrometry

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Secondary Ion Mass Spectrometry

SIMS is an analytical technique based on the measurement of the mass of ions ejected from a solid surface after the surface has been bombarded with high energy (1-25 keV) primary ions.
## Technique Comparison

<table>
<thead>
<tr>
<th></th>
<th>AES</th>
<th>XPS</th>
<th>D-SIMS</th>
<th>TOF-SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Probe Beam</strong></td>
<td>Electrons</td>
<td>Photons</td>
<td>Ions</td>
<td>Ions</td>
</tr>
<tr>
<td><strong>Analysis Beam</strong></td>
<td>Electrons</td>
<td>Electrons</td>
<td>Ions</td>
<td>Ions</td>
</tr>
<tr>
<td><strong>Spatial Resolution</strong></td>
<td>8 nm</td>
<td>9 μm</td>
<td>2 μm</td>
<td>0.1 μm</td>
</tr>
<tr>
<td><strong>Sampling Depth</strong></td>
<td>0.5 – 7.5 nm</td>
<td>0.5 – 7.5 nm</td>
<td>0.1 – 1 nm</td>
<td>0.1 – 1 nm</td>
</tr>
<tr>
<td><strong>Detection Limits</strong></td>
<td>0.1 – 5 atom %</td>
<td>0.01 – 0.1 atom %</td>
<td>1 ppm*</td>
<td>1 ppm*</td>
</tr>
<tr>
<td><strong>Quantification</strong></td>
<td>Good Semi-quantitative</td>
<td>Excellent Semi-quantitative</td>
<td>Challenging Large matrix effects</td>
<td>Challenging Large matrix effects</td>
</tr>
<tr>
<td><strong>Information Content</strong></td>
<td>Elemental</td>
<td>Elemental Chemical bonding</td>
<td>Elemental</td>
<td>Elemental Molecular</td>
</tr>
<tr>
<td><strong>Insulator Analysis</strong></td>
<td>Challenging</td>
<td>Excellent**</td>
<td>Good**</td>
<td>Excellent**</td>
</tr>
<tr>
<td><strong>Organic Analysis</strong></td>
<td>Electron beam damages organics</td>
<td>Excellent</td>
<td>DC ion beam damages organics</td>
<td>Excellent in static mode</td>
</tr>
<tr>
<td><strong>Depth Profiling</strong></td>
<td>Excellent for small areas</td>
<td>Excellent for insulating materials</td>
<td>Excellent for speed and sensitivity</td>
<td>Excellent for sensitivity</td>
</tr>
</tbody>
</table>

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* 1 ppm sensitivity is achieved by consuming the sample surface
** requires effective charge neutralization apparatus
Block Diagram of SIMS Technique

2-20 keV Ar or other inert gases, Cs, O, N, or Ga

Mass Spectrum

Depth Profile

Image Depth Profile

Image

Adapted from Wilso, Stevie, and Magee, p. 1-8.

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Time of Flight Mass Spectrometer

Physical Electronics TRIFT III TOF-SIMS

\[ eV = \frac{1}{2} mv^2 \]
Sputtered species include:
- Monoatomic and polyatomic particles of sample material (positive, negative or neutral)
- Resputtered primary species (positive, negative or neutral)
- Electrons
- Photons
MD Simulation of ion impact


Static SIMS

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

Dynamic SIMS

- Material removal
- Elemental analysis
- Depth profiling

Courtesy Gregory L. Fisher, Physical Electronics
InAs/GaAs Quantum Dots

In$^+$ Linescans of Quantum Dots

Cts: 550893; Max: 36; Scale: 1µm
TOF-SIMS Imaging of Patterned Sample

Courtesy Josh Ritchey, Audrey Bowen, Ralph Nuzzo and Jeffrey Moore, University of Illinois
TOF-SIMS Ion Images of an Isolated Neuron

First Images of Vitamin E Distribution in a Cell

Courtesy E.B. Monroe, J.C. Jurchen, S.S. Rubakhin, J.V. Sweedler. University of Illinois at Urbana-Champaign
Selected ion images from the songbird brain. Each ion image consists of ~11.5 million pixels within the tissue section and is the combination of 194 individual 600m×600m ion images prepared on the same relative intensity scale. Ion images are (A) phosphate PO3− (m/z 79.0); (B) cholesterol (m/z 385.4); (C) arachidonic acid C20:4 (m/z 303.2); (D) palmitic acid C16:0 (m/z 255.2); (E) palmitoleic acid C16:1 (m/z 253.2); (F) stearic acid C18:0 (m/z 283.3); (G) oleic acid C18:1 (m/z 281.2); (H) linoleic acid C18:2 (m/z 279.23); and (I) -linolenic acid C18:3 (m/z 277.2). Scale bars = 2 mm.

In SIMS, the yield of secondary ions is strongly influenced by the electronic state of the material being analyzed. The yield of secondary ions, $I_s^m$, can be expressed as:

$$I_s^m = I_p y_m \alpha^+ \theta_m \eta$$

- $I_s^m =$ secondary ion current of species $m$
- $I_p =$ primary particle flux
- $y_m =$ sputter yield
- $\alpha^+ =$ ionization probability to positive ions
- $\theta_m =$ factional concentration of $m$ in the layer
- $\eta =$ transmission of the analysis system
**Total Ion Sputtering Yield**

_Sputter yield_: ratio of number of atoms sputtered to number of impinging ions, typically 5-15

_Ion sputter yield_: ratio of ionized atoms sputtered to number of impinging ions, $10^{-6}$ to $10^{-2}$

_Ion sputter yield may be influenced by:_
- Matrix effects
- Surface coverage of reactive elements
- Background pressure in the sample environment
- Orientation of crystallographic axes with respect to the sample surface
- Angle of emission of detected secondary ions

First principles prediction of ion sputter yields is not possible with this technique.
Effect of Primary Beam on Secondary Ion Yields

Oxygen bombardment
When sputtering with an oxygen beam, the concentration of oxygen increases in the surface layer and metal-oxygen bonds are present in an oxygen-rich zone. When the bonds break during the bombardment, secondary ion emission process, oxygen becomes negatively charged because of its high electron affinity and the metal is left with the positive charge. Elements in yellow analyzed with oxygen bombardment, positive secondary ions for best sensitivity.

Cesium bombardment
When sputtering with a cesium beam, cesium is implanted into the sample surface which reduces the work function allowing more secondary electrons to be excited over the surface potential barrier. With the increased availability of electrons, there is more negative ion formation. Elements in green analyzed with cesium, negative secondary ions for best sensitivity.

Graphics courtesy of Charles Evans & Associates
web site http://www.cea.com
Relative Secondary Ion Yield Comparison

Relative Secondary Ion Yield Comparison

Definition of Mass Resolution

Mass resolution defined by $\frac{m}{\Delta m}$
Mass resolution of ~1600 required to resolve $^{32}\text{S}$ from $^{16}\text{O}_2$
Trace Analysis

GaAs Wafer

- GaOH
- GaNH₃

\[ m/\Delta m = 11,600 \]

Counts

Mass [m/z]

Si Wafer

- C₃H₃
- C₂HN
- K

Counts

Mass [m/z]

No sputtering to remove organics on surface. Large C₃H₃ peak does not have a tail to lower mass which would obscure C₂HN and K⁺.
## Comparison of Static and Dynamic SIMS

<table>
<thead>
<tr>
<th>TECHNIQUE</th>
<th>STATIC</th>
<th>DYNAMIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLUX</td>
<td>&lt; $10^{13}$ ions/cm$^2$ (per experiment)</td>
<td>$\sim 10^{17}$ ions/cm$^2$ (minimum dose density)</td>
</tr>
<tr>
<td>INFORMATION</td>
<td>Elemental + Molecular</td>
<td>Elemental</td>
</tr>
<tr>
<td>SENSITIVITY</td>
<td>1 ppm</td>
<td>&lt; 1 ppm (ppb for some elements)</td>
</tr>
<tr>
<td>TYPE OF ANALYSIS</td>
<td>Surface Mass Spectrum</td>
<td>Depth Profile</td>
</tr>
<tr>
<td></td>
<td>2D Surface Ion Image</td>
<td>Mass Spectrum</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3D Image Depth Profile</td>
</tr>
<tr>
<td>SAMPLING DEPTH</td>
<td>2 monolayers</td>
<td>10 monolayers</td>
</tr>
<tr>
<td>SPATIAL RESOLUTION</td>
<td>0.1 – 1.0 µm</td>
<td>0.1 -1.0 µm</td>
</tr>
<tr>
<td>SAMPLE DAMAGE</td>
<td>Minimal</td>
<td>Destructive in analyzed area – up to 500 µm per area</td>
</tr>
</tbody>
</table>
Depth Profile Application with Hydrogen


As Grown by Metalorganic Chemical Vapor Deposition

- C-doped GaAs
- Si-doped GaAs
- C-doped GaAs
- Si-doped GaAs
- GaAs Substrate

Annealed @ 400C in Nitrogen for 5 min

- H
- C
- Si

Detected hydrogen

Large dynamic range
GaAs/AlGaAs Depth Profile

Analysis beam: 15kV Ga$^+$
Sputter Beam: 300V O$_2^+$ with oxygen flood
Depth Profile Beam Alignment
Determination of RSF Using Ion Implants

\[ I_s^m = I_p y_m \alpha^+ \theta_m \eta \]

Level Profile:

\[ RSF = \frac{I_m}{I_i} \rho_i \]

Gaussian Profile:

\[ RSF = \frac{I_m \phi Ct}{d \sum I_i - dI_b C} \]

Where:

- RSF = Relative Sensitivity Factor
- \( I_m, I_i \) = ion intensity (counts/sec)
- \( \rho \) = atom density (atoms/cm\(^3\))
- \( \phi \) = implant fluence (atoms/cm\(^2\))
- \( C \) = # measurement cycles
- \( t \) = analysis time (s/cycle)
- \( d \) = crater depth (cm)
- \( I_b \) = background ion counts

Phosphorus Ion Implant in Silicon (dose = \( 1 \times 10^{15} \) ions/cm\(^2\), energy = 100 KeV)

 Integral = \( 3.681 \times 10^6 \) ions

m/z 31

Crater Depth

0.74 \( \mu m \)

Positive and Negative Secondary Ions

Ion implanted P standard

Counts / sec

Depth (nm)

$\rho_i = \frac{I_i}{I_m} \text{RSF}$

Concentration (atoms/cm$^3$)
SIMS depth profiles through a B modulation-doped Si(001):B film grown by GS-MBE from Si$_2$H$_6$ and B$_2$H$_6$ at $T_s=600$ °C. The incident Si$_2$H$_6$ flux was $J_{\text{Si}_2\text{H}_6} = 2.2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$ while the B flux $J_{\text{B}_2\text{H}_6}$ was varied from $8.4 \times 10^{13}$ to $1.2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$. The deposition time for each layer was constant at 1 h.

Electrolessly etched silicon nanowire arrays

Dope NW tips by SODs

Defect Engineering via Near-Surface Electrostatic Effects

Charged point defects interact with space charge in the near-surface region via 3 mechanisms

1. Field-induced drift (O in TiO$_2$)$^1$
2. Change in charge state of defect with local potential (B in Si)$^2$
3. Potential energy-dependent formation energy of V$_{O}$ (O in SrTiO$_3$)$^3$

$^{18}$O piles up in the first 10-30 nm in ZnO and TiO$_2$$^1$

- Amount of pile-up (P) = integrated area between pile-up and bulk extrapolated profiles

Analytical model quantifies effects$^4$

- Drift opposite to diffusion causes pile-up
- Drift in diffusion direction depletes near-surface of mobile defects
- P increases linearly with time & flux, quadratically with V$_S$
- V$_S$ of only a few meV can cause the amount of pile-up observed

Transition-Metal Accumulation on Anodes in Li-ion Batteries

Graphs showing the sputtering time vs. counts per second for Mn, Co, and Ni. The graphs indicate the accumulation of transition metals on anodes over time.

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Diamond-Like-Carbon Friction Testing

wear tracks and scars formed on DLC-coated disk and ball sides during test in dry oxygen

DLC coated ball

DLC coated disk

Oxygen Carbon C + O Overlay

Courtesy O.L. Eryilmaz and A. Erdemir
Energy Systems Division,
Argonne National Laboratory
Argonne, IL 60439 USA

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Wear track from hydrogenated DLC tested in dry nitrogen

Courtesy O.L. Eryilmaz and A. Erdemir
Energy Systems Division, Argonne National Laboratory Argonne, IL 60439 USA
3-D TOF-SIMS Movies of DLC

NFC6 H2 Environment TOF-SIMS Images
Courtesy O.L. Eryilmaz and A. Erdemir
Energy Systems Division, Argonne National Laboratory Argonne, IL 60439 USA
**SIMS Summary**

**Probe/Detected Species**

- 1-20 KeV ion
- 1 - 10,000 amu ion (1 - 120 eV)

**Information**

- Surface Mass Spectrum
- 2D Surface Ion Image
- Elemental Depth Profiling
- 3D Image Depth Profiling

**Elements Detectable**

- H and above

**Sensitivity**

- ppb - atomic %

**Analysis Diameter/Sampling Depth**

- ~1 μm - several mm/0.5 - 1nm
Where do Drug Molecules go Inside of Cells?  
A New Method to Probe the Composition of Cellular Organelles

Ashley Ellsworth\textsuperscript{1}, Corryn E. Chini\textsuperscript{2}, Ben Johnson\textsuperscript{3}, Michael M. Tamkun\textsuperscript{3}, Gregory L. Fisher\textsuperscript{1}, and Mary L. Kraft\textsuperscript{2}

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\textsuperscript{2} University of Illinois at Urbana-Champaign, School of Chemical Sciences, Urbana, IL, USA  
\textsuperscript{3} Colorado State University, Department of Biomedical Science, Fort Collins, CO, USA
Atom Probe Tomography for Additive Manufacturing

Katherine P. Rice, Yimeng Chen Ty J. Prosa, Robert M. Ulfig

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