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 primary ions.
Sputtered species include:
- Monoatomic and polyatomic particles of sample material (positive, negative or neutral)
- Resputtered primary species (positive, negative or neutral)
- Electrons
- Photons
### Comparison of Static and Dynamic SIMS

<table>
<thead>
<tr>
<th>TECHNIQUE</th>
<th>DYNAMIC</th>
<th>STATIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLUX</td>
<td>~10^{17} ions/cm^2 (minimum dose density)</td>
<td>&lt; 10^{13} ions/cm^2 (per experiment)</td>
</tr>
<tr>
<td>INFORMATION</td>
<td>Elemental</td>
<td>Elemental + Molecular</td>
</tr>
<tr>
<td>SENSITIVITY</td>
<td>&lt; 1 ppm (ppb for some elements)</td>
<td>1 ppm</td>
</tr>
<tr>
<td>TYPE OF ANALYSIS</td>
<td>Depth Profile, Mass Spectrum, 2D Ion Image, 3D Image Depth Profile</td>
<td>Surface Mass Spectrum, 2D Surface Ion Image, Elemental Depth Profiling, 3D Image Depth Profiling</td>
</tr>
<tr>
<td>SAMPLING DEPTH</td>
<td>10 monolayers</td>
<td>2 monolayers</td>
</tr>
<tr>
<td>SPATIAL RESOLUTION</td>
<td>Cameca ims 5f, Probe mode: 200 nm, Microscope mode: 1 μm</td>
<td>PHI TRIFT III, 0.1 μm</td>
</tr>
<tr>
<td>SAMPLE DAMAGE</td>
<td>Destructive in analyzed area – up to 500 μm per area</td>
<td>Minimal</td>
</tr>
</tbody>
</table>

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### 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>Probe Beam</td>
<td>Electrons</td>
<td>Photons</td>
<td>Ions</td>
<td>Ions</td>
</tr>
<tr>
<td>Analysis Beam</td>
<td>Electrons</td>
<td>Electrons</td>
<td>Ions</td>
<td>Ions</td>
</tr>
<tr>
<td>Spatial Resolution</td>
<td>9 nm</td>
<td>9 μm</td>
<td>2 μm</td>
<td>0.1 μm</td>
</tr>
<tr>
<td>Sampling Depth</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>Detection Limits</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>Quantification</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>Information Content</td>
<td>Elemental</td>
<td>Elemental</td>
<td>Chemical bonding</td>
<td>Elemental, Molecular</td>
</tr>
<tr>
<td>Insulator Analysis</td>
<td>Challenging</td>
<td>Excellent**</td>
<td>Good**</td>
<td>Excellent**</td>
</tr>
<tr>
<td>Organic Analysis</td>
<td>Electron beam damages organics</td>
<td>Excellent</td>
<td>DD ion beam damages organics</td>
<td>Excellent in static mode</td>
</tr>
<tr>
<td>Depth Profiling</td>
<td>Excellent for small areas, Excellent for insulating materials</td>
<td>Excellent for speed and sensitivity</td>
<td>Excellent for sensitivity</td>
<td></td>
</tr>
</tbody>
</table>

* 1 ppm sensitivity is achieved by consuming the sample surface
** requires effective charge neutralization apparatus
Magnetic Sector Mass Spectrometer

CAMECA ims 5f

Time of Flight Mass Spectrometer

Physical Electronics TRIFT III TOF-SIMS
In SIMS, the yield of secondary ions is strongly influenced by the electronic state of the material being analyzed.

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

- \( I_s^m \): secondary ion current of species \( m \)
- \( I_p \): primary particle flux
- \( y_m \): sputter yield
- \( \alpha^+ \): ionization probability to positive ions
- \( \theta_m \): fractional concentration of \( m \) in the surface 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.
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.

Relative Secondary Ion Yield Comparison

Relative Secondary Ion Yield Comparison


Cs+, Positive Secondary Ions of M⁺

Cs⁺, Positive Secondary Ions of CsM⁺

Depth Profile Application with Hydrogen


Quantitative depth profiles to study correlation of unintentional hydrogen passivation of acceptors in heavily C-doped GaAs by ambient conditions during cool down following growth by MOCVD.

Detects hydrogen

Large dynamic range
Definition of Mass Resolution

Mass resolution defined by $m/\Delta m$

Mass resolution of ~1600 required to resolve $^{32}$S from $^{16}$O$_2$

Isotopic Analysis

**Ni$_3$Al 600 C: 4 h $^{18}$O$_2$, 16 h $^{16}$O$_2$$**$

(a) AES composition depth profile
(b) SIMS isotopic oxygen diffusion profile expressed as a percentage of the total oxygen
(c) Schematic of layered oxide structure

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 $J_{Si_2H_6} = 2.2 \times 10^{16}$ cm$^{-2}$ s$^{-1}$ while the B flux $J_{B_2H_6}$ 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.

SIMS depth profiles through a B $\delta$-doped layers in a Si(001) film grown by GS-MBE from Si$_2$H$_6$ at $T_s=700$ °C. The Si$_2$H$_6$ flux, $J_{Si_2H_6}$, was $5 \times 10^{16}$ cm$^{-2}$ s$^{-1}$ while the B$_2$H$_6$ flux, $J_{B_2H_6}$ varied from 0.16-7.8 $\times 10^{14}$ cm$^{-2}$ s$^{-1}$. The inset shows the two-dimensional B concentration $N_B$ as a function of $J_{B_2H_6}$.
Two Dimensional Imaging with Dynamic SIMS

CROSS-SECTIONAL ION IMAGES GENERATED FROM SEQUENTIAL IMAGES IN DEPTH PROFILE


Determination of RSF Using Ion Implants

\[ I_s = I_p v_m \alpha^+ \theta_m \eta \]

Level Profile: \[ RSF = \frac{I_m}{I_i} \rho_i \]

Gaussian Profile: \[ RSF = \frac{I_m \phi C t}{d \sum I_i - d I_i C} \]

RSF = Relative Sensitivity Factor
\[ I_{m, i} = \text{ion intensity (counts/sec)} \]
\[ \rho = \text{atom density (atoms/cm}^3\text{)} \]
\[ \phi = \text{implant fluence (atoms/cm}^2\text{)} \]
\[ C = \# \text{measurement cycles} \]
\[ t = \text{analysis time (s/cycle)} \]
\[ d = \text{crater depth (cm)} \]
\[ I_b = \text{background ion counts} \]
Positive and Negative Secondary Ions

Raw Data

Processed Data

Static and Dynamic SIMS

Dynamic SIMS

Static SIMS

- Material removal
- Elemental analysis
- Depth profiling

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

Courtesy Gregory L. Fisher, Physical Electronics
Extreme Mass Range

Total Counts (9.43 amu bin) 25601576 21661182 17731379

Trace Analysis

GaAs Wafer

Si Wafer

No sputtering to remove organics on surface. Large C₃H₃ peak does not have a tail to lower mass which would obscure C₂HN and K.
InAs/GaAs Quantum Dots

In+ Linescans of Quantum Dots

GaAs/AlGaAs Depth Profile

Analysis beam: 15kV Ga+
Sputter Beam: 300V O₂⁻ with oxygen flood
TOF-SIMS Imaging of Patterned Sample

TOF-SIMS Ion Images of an Isolated Neuron

First Images of Vitamin E Distribution in a Cell

Cellular lipids: fragment (m/z 69)

Vitamin E (m/z 430)
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 600µm x 600µm ion images prepared on the same relative intensity scale. Ion images are (A) phosphate PO$_3^-$ (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 279.2); and (I) α-linolenic acid C18:3 (m/z 277.2). Scale bars = 2 mm.

Diamond-Like-Carbon Friction Testing

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

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

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

H CH C₂H C₂H₂ O

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/irr
- (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

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Rutherford backscattering spectrometry

**2 MeV Van de Graaff accelerator**

**4.6 MeV Tandetron accelerator**

- magnet
- RBS chamber

- Beam lines

beam size φ1-3 mm
flat sample
can be rotated
Rutherford scattering cross section

Coulomb interaction between the nuclei: exact expression $\rightarrow$ quantitative method

$$\sigma_R(E, \theta) \propto \left(\frac{Z_1 Z_2}{4E}\right)^2 \left[\sin - \left(\frac{\theta}{2}\right) - 2\left(\frac{M_1}{M_2}\right)\right]$$

Elastic two-body collision

$$M_1 v_o^2 = M_1 v_1^2 + M_2 v_2^2$$
$$M_1 v_o = M_1 v_1 + M_2 v_2$$

$M_1 < M_2$, $0 \leq \theta \leq 180^\circ$
$0 \leq \Phi \leq 90^\circ$

RBS: He backscatters from $M_2 > 4$

$M_1 > M_2$, $0 \leq \theta \leq 90^\circ$
$0 \leq \Phi \leq 90^\circ$

ERD: He recoils H forward
Rutherford backscattering spectrometry

thin film projected on to a plane: \text{atoms/cm}^2

\[(N_t)[\text{at/cm}^2] = N[\text{at/cm}^3] \times t[\text{cm}]\]


RBS – simulated spectra
hypothetical alloy Au_{0.2}In_{0.2}Ti_{0.2}Al_{0.2}O_{0.2}/C

Element (Z,M): O(8,16), Al(13,27), Ti(22,48), In(49,115), Au(79,197)
Thickness effects

TiN/MgO

Incident angle effects

TiN/MgO

Surface peaks do not change position with incident angle;
Example: average composition $Ti_{0.27}Al_{0.20}Nb_{0.02}N_{0.51}$


RBS: Oxidation behavior

Experimental and simulated spectra by RUMP

As-deposited

Annealed

$T_a = 600 ^\circ C$ for 12 min in atmosphere.
SIMNRA simulation program for RBS and ERD

http://www.rzg.mpg.de/~mam/

Elastic Recoil Detection of Hydrogen

Polyethylene CH$_2$ vs. Nano-diamond film (ANL)

Dr. Yan Wu
Rutherford backscattering spectrometry

Summary

• Quantitative technique for elemental composition
• Requires flat samples; beam size $\Phi 1-3$ mm
• Non-destructive
• Detection limit varies from $0.1$ to $10^{-6}$, depending on Z
  * optimum for heavy elements in/on light matrix, e.g. Ta/Si, Au/C…
• Depth information from ML to 1 $\mu$m