Advanced Materials Characterization Workshop
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Rutherford Backscattering & Secondary Ion Mass Spectrometry

Timothy P. Spila, Ph.D.

Frederick Seitz Materials Research Laboratory
University of Illinois at Urbana-Champaign

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Rutherford Backscattering Spectrometry

RBS is an analytical technique where high energy ions (~2 MeV) are scattered from atomic nuclei in a sample. The energy of the back-scattered ions can be measured to give information on sample composition as a function of depth.
**Geiger-Marsden Experiment**

*Top:* Expected results: alpha particles passing through the plum pudding model of the atom undisturbed.

*Bottom:* Observed results: a small portion of the particles were deflected, indicating a small, concentrated positive charge.
Rutherford Backscattering Spectrometry

2 MeV Van de Graaff accelerator

beam size $\phi$1-3 mm
flat sample
can be rotated
Primary Beam Energy

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

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


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Elastic Two-Body Collision

Elastic Scattering
\[ M_1 v_0^2 = M_1 v_1^2 + M_2 v_2^2 \]
\[ M_1 \vec{v}_0 = M_1 \vec{v}_1 + M_2 \vec{v}_2 \]

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

RBS: He backscatters from M_2 > 4

\[ E_1 = KE_0 \]

\[ K = \left( \frac{\sqrt{M_i^2 - M_i^2 \sin^2 \theta + M_i \cos \theta}}{M_i + M_i} \right)^2 \]

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Rutherford Scattering Cross Section

Coulomb interaction between the nuclei: exact expression -> quantitative method

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

RBS – Simulated Spectra

hypothesis alloy $\text{Au}_{0.2}\text{In}_{0.2}\text{Ti}_{0.2}\text{Al}_{0.2}\text{O}_{0.2}/\text{C}$

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

$\sigma_R(E, \theta) \propto \left( \frac{Z^2}{E} \right)^2$

He$^4$

$\theta = 150^\circ$
Thickess Effects

300 nm

400 nm

600 nm

TiN/MgO
Incident Angle Effects

TiN/MgO

Surface peaks do not change position with incident angle;

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Example: Average Composition

TiN/\text{SiO}_2

As-deposited

Annealed in atmosphere for 12 min at $T_a = 600 \degree C$

Experimental spectra and simulated spectra by RUMP
RBS 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 monolayers to 1 $\mu$m
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>
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<th>AES</th>
<th>XPS</th>
<th>D-SIMS</th>
<th>TOF-SIMS</th>
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<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</td>
<td>Excellent</td>
<td>Challenging</td>
<td>Challenging</td>
</tr>
<tr>
<td></td>
<td>Semi-quantitative</td>
<td>Semi-quantitative</td>
<td>Large matrix effects</td>
<td>Large matrix effects</td>
</tr>
<tr>
<td><strong>Information Content</strong></td>
<td>Elemental</td>
<td>Elemental</td>
<td>Elemental</td>
<td>Elemental</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chemical bonding</td>
<td></td>
<td>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>

* 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

- Ion Source
- Energy Analyzer
- Mass Spectrometer
- Detector
  - EM, FC, RAE

Mass Spectrum
- Dynamic Range by 9 orders of magnitude

Depth Profile
- Depth Resolution of 0.02-0.04 mm

Image Depth Profile
- Selected Area Profile
- Cross section

Image
- Down to submicron lateral resolution

Adapted from Wilson, Stavie, and Magee, p. 1-8.
## Comparison of Static and Dynamic SIMS

<table>
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<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</td>
<td>Surface Mass Spectrum</td>
</tr>
<tr>
<td></td>
<td>Mass Spectrum</td>
<td>2D Surface Ion Image</td>
</tr>
<tr>
<td></td>
<td>3D Image Depth Profile</td>
<td></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</td>
<td>PHI TRIFT III</td>
</tr>
<tr>
<td></td>
<td>Probe mode: 200 nm</td>
<td>0.1 (\mu)m</td>
</tr>
<tr>
<td></td>
<td>Microscope mode: 1 (\mu)m</td>
<td></td>
</tr>
<tr>
<td>SAMPLE DAMAGE</td>
<td>Destructive in analyzed area – up to 500 (\mu)m per area</td>
<td>Minimal</td>
</tr>
</tbody>
</table>
Magnetic Sector Mass Spectrometer

CAMECA ims 5f

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Time of Flight Mass Spectrometer

Physical Electronics
TRIFT III TOF-SIMS

Sample

Cs⁺ or O₂⁺

Pre-Spectrometer Blanker

SED

Post-Spectrometer Blanker

Contrast Diaphragm

ESA 1

ESA 2

ESA 3

Energy Slit

$eV = \frac{1}{2}mv^2$
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


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
- \( \theta_m \): factional concentration of \( m \) in the layer
- \( \eta \): transmission of the analysis system
**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

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:

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

Where:

- \( RSF \) = Relative Sensitivity Factor
- \( I_m, I_i \) = ion intensity (counts/sec)
- \( \rho \) = atom density (atoms/cm\(^3\))
- \( \phi \) = implant fluence (atoms/cm\(^2\))
- \( \eta \) = measurement cycles
- \( C \) = # 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)

Concentration (atoms/cm$^3$)

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Definition of Mass Resolution

Mass resolution defined by $m/\Delta m$

Mass resolution of ~1600 required to resolve $^{32}\text{S}$ from $^{16}\text{O}_2$
Depth Profile Application with Hydrogen


As Grown by Metalorganic Chemical Vapor Deposition

Annealed @ 400C in Nitrogen for 5 min

Detects hydrogen

Large dynamic range

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Isotopic Analysis

Ni₃Al 600 C: 4 h $^{18}$O₂, 16 h $^{16}$O₂

(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 $J_{\text{Si}_2\text{H}_6} = 2.2 \times 10^{16}$ 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.

SIMS depth profiles through a B δ-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, $J_{Si2H6}$, was 5X10$^{16}$ cm$^{-2}$ s$^{-1}$ while the B$_2$H$_6$ flux, $J_{B2H6}$ varied from 0.16-7.8X10$^{14}$ cm$^{-2}$ s$^{-1}$. The inset shows the two-dimensional B concentration $N_B^{2D}$ as a function of $J_{B2H6}$.

Static and Dynamic SIMS

Dynamic SIMS

• Material removal
• Elemental analysis
• Depth profiling

Static SIMS

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

Courtesy Gregory L. Fisher, Physical Electronics

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Extreme Mass Range

Total Counts

Mass (amu)

Integral: 1922
TG_SCAN03_NEGSEC_AL2_22KV_BUNCHED_2NA_400UM_90MIN_CDOUT_CHGCOMP_0-10000AMU.TDC - ions 400µm 17452848 cts

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GaAs Wafer

- GaOH
- GaNH₃

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

Si Wafer

- C₃H₃
- K

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

Cts: 550893; Max: 36; Scale: 1µm
GaAs/AlGaAs Depth Profile

Analysis beam: 15kV Ga⁺
Sputter Beam: 300V O₂⁺
with oxygen flood

Counts Per Second x 10⁴

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Depth Profile Beam Alignment

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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.

Diamond-Like-Carbon Friction Testing

DLC coated ball

DLC coated disk

Oxygen

Carbon

C + O Overlay

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

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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

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
Acknowledgments

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