Secondary Ion Mass Spectrometry (SIMS)


Primary particles may be:

Secondary particles can be e⁻'s, neutral species (atoms or molecules), or atomic and cluster ions
Over 3 of the secondary particles originate from the top two layers of the solid – highly surface sensitive.

Primary information from ion signal can provide information on:

1. (cracking pattern as conditions varied)

Basic equation

\[ I_{m}^s = I_p y_m a^+ \theta_m \eta \]

- \( I_{m}^s \): secondary ion current of species \( m \)
- \( I_p \): primary particle flux
- \( y_m \): total sputter yield of species \( m \) (neutral or ionic) per primary particle impact
- \( a^+ \): ionization probability to positive ions
- \( \theta_m \): fractional concentration of \( m \) in surface layer
- \( \eta \): transmission of the analysis system
The two fundamental parameters are $y_m$ and $\alpha^+$. $y_m$ is influenced by:

- $y_m \uparrow$ linearly with
- primary particle
- $y_m \uparrow$ nonlinearly with these parameters
- crystallinity and topography of the bombarded material
- at a given bombardment energy, $y$ varies a factor of 3–5 through the periodic table.

$\alpha^+$ is influenced by:

- oxidation changes the elemental ion yields to differing extents (making quantitative analysis complicated)
- the yields of secondary ions vary by several orders of magnitude across the periodic table

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Experimental sputter yield data for aluminium as a function of primary ion energy for a number of different primary ions: $\Delta$, He; $\varnothing$, Xe; $\Box$, Ar; $+$, Xe (theoretical); $x$, Ar (theoretical)}
\end{figure}
Monolayer lifetime & Static limit

**Static conditions:** maintaining the integrity of the surface layer within the timescale of the analytical experiment

\[ t_m = \frac{10^{15}}{I_p} \times \frac{A}{y} \]

- \( t_m \): lifetime of the topmost atomic layer
- \( A \): \( \text{A cm}^2 \) of the surface is bombarded
- \( I_p \): primary beam flux density, usually measured in \( \text{Amps/cm}^2 \) (1 amp = charged particles/s)
- \( y \): sputter yield

### Table 5.1. Secondary ion yields from clean and oxidised metal surfaces

<table>
<thead>
<tr>
<th>Metal</th>
<th>Clean metals ( M^+ ) yield</th>
<th>Oxide ( M^+ ) yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.01</td>
<td>0.9</td>
</tr>
<tr>
<td>Al</td>
<td>0.007</td>
<td>0.7</td>
</tr>
<tr>
<td>Si</td>
<td>0.0084</td>
<td>0.58</td>
</tr>
<tr>
<td>Ti</td>
<td>0.0013</td>
<td>0.4</td>
</tr>
<tr>
<td>V</td>
<td>0.001</td>
<td>0.3</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0012</td>
<td>1.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0006</td>
<td>0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0015</td>
<td>0.35</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0006</td>
<td>0.045</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0003</td>
<td>0.007</td>
</tr>
<tr>
<td>Ge</td>
<td>0.0044</td>
<td>0.02</td>
</tr>
<tr>
<td>Sr</td>
<td>0.0002</td>
<td>0.16</td>
</tr>
<tr>
<td>Nb</td>
<td>0.0006</td>
<td>0.05</td>
</tr>
<tr>
<td>Mo</td>
<td>0.00065</td>
<td>0.4</td>
</tr>
<tr>
<td>Ba</td>
<td>0.0002</td>
<td>0.03</td>
</tr>
<tr>
<td>Ta</td>
<td>0.00007</td>
<td>0.02</td>
</tr>
<tr>
<td>W</td>
<td>0.00009</td>
<td>0.035</td>
</tr>
</tbody>
</table>
Each primary particle colliding with the surface disturbs an area of $10 \text{ nm}^2 \Rightarrow$ only require impacts cm$^{-2}$ to influence all atoms in the surface – static primary particle dose limit.

If an analysis requires 20 minutes (1200 s), then static condition can only be safely attained for primary beam current of $\leq \sim \ldots$.

For dynamic SIMS, high elemental sensitivity and rapid erosion rates are required, so high primary flux densities of $\geq 1 \mu\text{A cm}^{-2}$ are desirable.

### Table 5.2. The surface monolayer lifetime as a function of primary beam flux density

<table>
<thead>
<tr>
<th>$I_p \ (\text{A cm}^{-2})$</th>
<th>$t_m \ (\text{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-5}$</td>
<td>16</td>
</tr>
<tr>
<td>$10^{-7}$</td>
<td>1600</td>
</tr>
<tr>
<td>$10^{-9}$</td>
<td>$1.6 \times 10^5$</td>
</tr>
<tr>
<td>$10^{-11}$</td>
<td>$1.6 \times 10^7$</td>
</tr>
</tbody>
</table>

## Static vs. Dynamic SIMS

<table>
<thead>
<tr>
<th>Static SIMS</th>
<th>Dynamic SIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low sputter rates</td>
<td>High sputter rates</td>
</tr>
<tr>
<td>$\sim 1 \text{nA cm}^{-2}$</td>
<td>Up to $10 \text{mA cm}^{-2}$</td>
</tr>
<tr>
<td>$&lt;10 \text{Å hr}^{-1}$</td>
<td>Up to $100 \mu\text{Å hr}^{-1}$</td>
</tr>
<tr>
<td>Essentially &quot;non-destructive&quot;</td>
<td>Destructive</td>
</tr>
<tr>
<td>Surface analysis</td>
<td>Depth profiling</td>
</tr>
</tbody>
</table>

Static and dynamic SIMS are divided at the **static SIMS limit of damage**

- Incident ions can cause chemistry and interlayer mixing
- Generally limit incident ion to $\leq \sim \%$ of surface species sputtered ($\leq \sim \%$ ML)
Primary beam species used in SIMS include Cs+, O2+, Ar+, and Ga+ etc. at energies between 1 and 30 keV. Primary ions are implanted and mix with sample atoms to depths of 1 to 10 nm.

Sputter rates in typical SIMS experiments vary between 0.5 and 5 nm/s. Sputter rates depend on primary beam intensity, sample material, and crystal orientation.

The sputter yield is the ratio of the number of atoms sputtered to the number of impinging primary ions. Typical SIMS sputter yields fall in a range from 5 and 15.

Positive SIMS (cation) spectrum dominated by electropositive atom ions; negative SIMS (anion) spectrum dominated by electronegative atom ions

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**Instrumentation**

- UHV chamber
- primary particle source
- ion optical system
- mass spectrometer

*Figure 5.4. A schematic representation of a SIMS instrument. Reproduced by permission from J.C Vickerman, *Chem. Brit.* 969(1987)
Primary ion beam

- **Electron bombardment**
  - using a high current density of electrons to ionize the primary beam gas, usually or
  - ionization efficiency can ↑ using electrostatic or magnetic fields to increase the path length of the traveling electrons
  - versatile, easy to use, comparatively reliable
  - moderate brightness of ~ $10^5 \text{ A m}^{-2} \text{ Sr}^{-1}$
  - most commonly used de-focused over large areas (several mm²) for S-SIMS (not preferred for micro-focused studies)

- **Plasma**
  - reactive gases, such as O₂, can be ionized using the cold cathode discharge method
  - electric and magnetic fields are used to concentrate the discharge to increase output
  - high beam brightness of $10^4$~$10^7 \text{ A m}^{-2} \text{ Sr}^{-1}$
  - better suited for D-SIMS
- **Surface ionization**
  - sensitivity to electronegative species is enhanced when an electropositive primary beam is used
  - by surface ionization, alkali metal ion source is available
  - ion emission is thermally stimulated by warming an adsorbed layer of e.g. Cs on the surface of high work function metal (e.g. Ir) under vacuum
  - brightness depends on the size of the emitting area (> 10^6 A m^-2 Sr^-1 has been attained)
  - drawback: very careful handling & operation requirements

- **Field ionization sources**
  - the highest brightness sources (≈ 10^10 A m^-2 Sr^-1)
  - source of choice for work at the highest spatial resolution
  - spatial resolutions down to 200–20 nm have been realized
  - most commonly used liquid metal ion source is

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**Figure 5.7.** Principle of a liquid metal ion source: (a) source schematic; (b) energy diagram; (c) close up of extraction region. Reproduced by permission from [7], *Secondary Ion Mass Spectrometry – Principles and Applications*, Oxford Science Publications (1989)
Mass analyzer

- Magnetic sector
  - high transmission (10%–50%) and mass resolution
  - historically used for D-SIMS
  - drawbacks: large cumbersome device & difficult to incorporate in UHV (cannot easily be baked without seriously modifying the magnetic properties of the magnet)

\[ R = \frac{1}{B} \left( \frac{2mV}{z} \right)^{1/2} \]

- Quadrupole mass analyzer
  - widely used in early work in S-SIMS because it was easily incorporated in UHV due to its small size
  - low transmission (< 1%)
  - sequential transmission of ions – information loss is high
  - mass range is limited to ~1000 amu

- Time-of-flight mass spectrometer
  - very high transmission – quasi-parallel detectors
  - collect all ions generated
  - ~10^4 more sensitive than quadrupole instrument
  - mass resolution, m/Dm, can be 5000–10000
  - in theory, limitless mass range (usually in practice ~10000 amu)

\[ t = L \left( \frac{m}{2zV} \right)^{1/2} \]

<table>
<thead>
<tr>
<th>Type</th>
<th>Resolution</th>
<th>Mass range</th>
<th>Transmission</th>
<th>Mass detection</th>
<th>Relative sensitivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quadrupole</td>
<td>10^2–10^3</td>
<td>&lt;10^3</td>
<td>0.01–0.1</td>
<td>Sequential</td>
<td>1</td>
</tr>
<tr>
<td>Magnetic sector</td>
<td>10^4</td>
<td>&gt;10^4</td>
<td>0.1–0.5</td>
<td>Sequential</td>
<td>10</td>
</tr>
<tr>
<td>Time-of-flight</td>
<td>&gt;10^3</td>
<td>10^3–10^4</td>
<td>0.5–1.0</td>
<td>Parallel</td>
<td>10^4</td>
</tr>
</tbody>
</table>
Figure 5.11. (a) Positive (i) and negative (ii) ToFSIMS spectra of PMMA, 30 keV Ga⁺, primary dose = \(10^{10}\) ions cm⁻². (b) Positive (i) and negative (ii) quadrupole SIMS spectra of PMMA, 2 keV Ar⁺, primary dose = \(10^{15}\) atoms cm⁻². Reproduced by permission from A.J. Eccles and J.C. Vickerman, J. Vac. Sci. Technol., A7, 234, (1989)

Figure 5.10. A schematic diagram of a ToFSIMS instrument. Reproduced by permission from J.C. Vickerman, Analyst, 119, 513–523 (1994)
Time-of-Flight Secondary-ion mass spectrometry (TOF-SIMS)

二次離子質譜儀之操作模式

Mass Spectrometry

Ion Mapping

Depth Profiling
Sputtered Neutral Mass Spectrometry (SNMS)

Figure 5.37 Schematic diagram of an electron bombardment ioniser combined with a parallel plate energy analyser. Reproduced by permission from [7], Secondary Ion Mass Spectrometry – Principles and Applications, Oxford Science Publications (1995)

Figure 5.40 A schematic diagram of a ToF-SIMS system with laser photoinionisation. The potentials on the various electrodes are set so that only photoinionised ions are transmitted to the detector. Reproduced with permission from N. Lockyer, PhD Thesis UMIST, 1996
SIMS Summary

- Highly surface sensitive
- Excellent sensitivity ($<10^9$ atoms·cm$^{-2}$) $<10^{-4}$ ML for some elements
- Isotope sensitivity
- Adaptable to imaging (microprobe or microscope modes) with good resolution ($<100$ nm)
- Used in both depth profiling (dynamic SIMS) and "non-destructive" (static SIMS) modes
- Rich spectra for organics - biological samples, polymers - spectra are fingerprints for adsorbed species
- Semi-quantitative (if standardized)


<table>
<thead>
<tr>
<th>Source: Physical Electronics</th>
</tr>
</thead>
<tbody>
<tr>
<td>不同儀器比較表</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Probe beam</td>
</tr>
<tr>
<td>Analyzed beam</td>
</tr>
<tr>
<td>Sampling depth</td>
</tr>
<tr>
<td>Detection limit</td>
</tr>
<tr>
<td>Spatial resolution</td>
</tr>
<tr>
<td>Information</td>
</tr>
<tr>
<td>Materials</td>
</tr>
</tbody>
</table>
Vibrational Spectroscopy from Surfaces

Vibrational spectroscopy is one of the most powerful methods for surface chemical compositional analysis. The vibrational spectrum can:
- fingerprint adsorbed species
- use selection rules to deduce bonding orientation

Vibrations in molecules or in solid lattices are excited by:
- of photons (infrared spectroscopy)
- of photons (Raman spectroscopy)
- electrons (electron spectroscopy)
- neutrons (inelastic neutron scattering)
Advantages of FTIR (non-dispersive) instrument
- sample all channels simultaneously (advantage)
- high signal level at detector (advantage)
- high (use of accurate internal standard laser)

In transmission mode:

\[ \frac{l_1}{l_0} = \exp(k \cdot c \cdot l) \]
\[ \ln \frac{l_1}{l_0} = k \cdot c \cdot l \]
\[ A = \varepsilon \cdot c \cdot l \]

Transmittance
Absorbance

Experiments must be performed twice and difference calculated:
- reference spectrum with no absorbed material
- sample spectrum with adsorbed material

Surface transmission experiments are less common because:
- large bulk contribution unless sample very thin
- many interesting samples not sufficiently transparent to IR
Reflection, Refraction, and Absorption

The reflection and refraction angles are given by the Law:

\[ \Theta_1 = \Theta_2 \quad \text{and} \quad \frac{n_1}{n_2} = \frac{\sin \Theta_1}{\sin \Theta_T} \]

for \( \Theta_1 < \Theta_{\text{crit}} = \sin^{-1} \left( \frac{n_2}{n_1} \right) \)

Figure 7.10: The phase shift for light reflected from a metal surface as calculated for light polarised both parallel to (p) and perpendicular to (s) the plane of incidence, after Greenler [9]

Reflection-Absorption Infrared Spectroscopy (RAIRS)

also known as Infrared Absorption-Reflection Spectroscopy (IRAS)

The intensity of light reflected from a surface is related to phase shift \( \delta \) upon reflection

- Only \( p \)-polarized component light can be reflected from surface at high incidence angles
- Only vibrations with component dynamic dipole moment aligned \( \perp \) to surface plane can interact with \( p \)-polarized incident light - "surface selection rule"

resolution < 2 cm\(^{-1}\) can be achieved - useful for separating multiple peaks, phase transitions, lateral interactions, dynamics of coupling