Chapter 5
Secondary Ion Mass Spectrometry — the Surface Mass Spectrometry

講義下載:
http://www.che.ncku.edu.tw/FacultyWeb/LeeYL
**Secondary ion mass spectrometry (SIMS)** —
Mass spectrometry of **ionized particles** which are emitted when a surface is bombarded by energetic primary particles. (electrons, ions, neutrals or photons)

- “Secondary” particles can be **electrons, neutrals, cluster ions**.

  Vast majority of species emitted are neutral, but the secondary ions are detected in SIMS.

- The energy of ion beam is about 1~15 keV (primary beam).

  A cascade collision occurs between the atoms in the solid when the energetic particles transfer the energy to the solid surface.
Introduction

- The secondary particles emitted by the final collision are of low energy (ca. 20eV)
- Over 95% of the secondary particles originate from the top two layers.
2. Basic Concepts

2.1 The Basic equation

Ionization occurs at, or close to, emission of particles from the surface — as a consequence of the matrix participation in the electronic processes involved.

- The yield of secondary ions is strongly influenced by the electronic state of the material.
- The basic SIMS equation is

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

- \( I_{m}^s \): secondary ion current of species m.
- \( I_p \): primary particle flux.
- \( y_m \): sputter yield --- total yield of sputtered particles of species m (neutral and ionic)
- \( \alpha^+ \): ionization probability to positive ions.
- \( \theta_m \): fractional concentration of m in the surface layer.
- \( \eta \): transmission of the analysis system.
• $y_m$: increases with primary particle mass, charge and energy (shown in Fig5.2 for Al), $y_m$ tends to maximum with energy at around 10 keV. The crystallinity and topograph of material also affect the yield.

• At a given bombardment energy, the sputter yield varies by a factor of 3-5 through the periodic table.

• The yield of secondary ions vary by several orders of magnitude (Fig5.3), and are dependent on the chemical state of surface.
Figure 5.2. Experimental sputter yield data for aluminium as a function of primary ion energy for a number of different primary ions: Δ, He; ◊, Xe; □, Ar; +, Xe (theoretical); x, Ar (theoretical)
Yield of positive ions

Figure 5.3. The variation of positive ion yield as a function of atomic number for 1 nA 13.5 keV O bombardment: o from elements; [], from compounds. Reproduced with permission from H.A. Storms, K.F. Brown, and J.D. Stein, Anal. Chem., 49, 2023 (1977). (Copyright (1977) American Chemical Society)
The influence of oxidation state on the secondary ion yields.

The difference in the sputtering yields triggers complications in quantitative analysis.

<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>
It is difficult to measure the sputter rates for covalent organic materials.

Sputtering of organic materials resulting the removal of elements, structural fragments, and molecular species. The loss of any entities will destroy the molecular structure.

For a monolayer of organic material, some of the loss of signal will be due to:
- Removal of intact molecules.
- Bombardment induced chemical damage.
For a multilayer samples, the loss of structurally significant species from the SIMS spectrum is due to the increasing damage, which termed as damage cross-section.

The concept of disappearance cross-section, $\sigma$, is more useful instead of sputtering rate.

$$I_m = I_{mo} \exp(-\sigma \cdot I_p)$$

$I_m$: intensity of a secondary ion species

$\sigma$ is around $5 \times 10^{-14}$ cm$^2$ for amino acid
- **disappearance cross-section**: related to the **damage cross-section**, can be considered as the average area per incident particle from which the emission of the particular species being analyzed is excluded.

- $10^{-14} \text{ cm}^2 (10\text{A} \times 10\text{A})$ is about the size of the fragments detected.

![Thick layer of cholesterol under 15 keV Au$^+$ bombardment](image)

**Figure 4.4** Disappearance cross-section plot for a thick layer of cholesterol under 15 keV Au$^+$ bombardment ($\sigma = 6.8 \times 10^{-14} \text{ cm}^2$)
There has been increasing interest in the use of polyatomic cluster primary ions: $\text{SF}_5^+$, $\text{Au}_n^+$, $\text{Bi}_n^+$, $\text{C}_{60}^+$. These ions have significantly higher sputtering yields.

- The cluster breaks up as it hits the surface and the projectile energy is portioned between all the atoms.
- Each atom from 20 keV $\text{C}_{60}^+$ would have 666 eV—penetrate the material much less and generate much less chemical damage.

<table>
<thead>
<tr>
<th>Removed # of H$_2$O Equivalents</th>
<th>100</th>
<th>575</th>
<th>1190</th>
<th>2510</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Au}^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Au}_2^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Au}_3^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{C}_{60}^+$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Advantages of polyatomic cluster primary ions:

- High sputter rate.
- Penetrate the material much less and generate much less chemical damage.
- Most of the damage generated is removed by subsequent impacts. Therefore, the apparent damage cross-section is greatly reduced, removing the need for the static limit.
Thick cholesterol film on Si

Figure 4.5  Variation in relative intensity of the (M–H)$^+$ from a thick film of cholesterol as a function of ion fluence under 20 keV $\text{Au}^+$, $\text{Au}_3^+$ and $\text{C}_{60}^+$ bombardment ($m/z = 385$)
The kinetic energy distribution of sputtered ions (atoms, molecules, molecular fragments) is influenced by:

1. Binding of the species in the surface,
2. Number of bonds to be broken,
3. The degree to which internal energy can be stored by the emitted species.
• For atomic secondary ions: the kinetic energy distribution will generally be broad, typical of collisional sputtering.

The energy distribution of sputtered gold atoms due to the impact of 16 KeV Ar$^+$ on polycrystalline gold.
The kinetic energy distribution of cluster ions will be much narrower because they can lose energy by fragmentation or storing it in vibrations and rotations.

The distribution of large molecular species from organic materials are usually very narrow.
2.2 Monolayer lifetime and the static limit

- **Static conditions**: maintain the integrity of the surface layer within the time-scale of the analytical experiment. — very low primary beam dose is used.

- **Lifetime, \( t_m \), of the topmost atomic layer**:

  \[
  t_m = \left( \frac{10^{15}}{I_p} \right) \times \left( \frac{A}{y} \right) \quad \text{or} \quad t_m = \left( \frac{10^{15} e}{I_p y} \right)
  \]

  - \( A \): surface area (cm\(^2\)), (with atomic density of \( \approx 10^{15} \) atoms/cm\(^2\))
  - \( I_p \): flux density of primary beam (particle/cm\(^2\)) usually is measured in (Amp/cm\(^2\)), (1 Amp is equivalent to \( 6.2 \times 10^{18} \) charge particle/sec)
  - \( Y \): sputter yield

- \( t_m \) varies with \( I_p \) (table 5.2)

<table>
<thead>
<tr>
<th>( I_p ) (A cm(^{-2}))</th>
<th>( t_m ) (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>
• If an analysis required 20 min (1200sec), static conditions can be safely attained for $I_p \leq 1\text{nA/cm}^2$

• Static primary particle dose limit — primary particle colliding area.
  ◆ The surface area disturbed by the colliding of an primary particle is about $10 \text{ nm}^2$. To influence all the atoms in the surface of $1\text{cm}^2$, it requires $1\text{cm}^2 / (10 \text{ nm}^2/\text{particle}) = 10^{13} \text{ particles}$.

• For dynamic SIMS, $t_m$ should be small, $I_p$ should be large.
  $(1\mu\text{A/cm}^2 \leq I_p)$

• The magnitude of $y$ is significant in determining $t_m$. (for metallic targets, $y$ are well known, but the data for organic and molecular materials are not extensive)

Static limit using polyatomic cluster ion beams.

- For metal cluster beams: $\text{Au}_n^+$, $\text{Bi}_n^+$:
  - Have higher sputter yields by factor 100 to 1000 compared to their atomic ions. However, the damage cross-sections are comparable. Analysis using these ions is limited by the use of static conditions ($< 10^{13}$ ions/cm$^2$).
For ions such as SF$_5^+$ and C60$^+$:

- The zone of material damaged in close to the surface and is approximately contained within the volume of material sputtered away.
- The damage cross-sections are very much less than $10^{-14}$cm$^2$ from multilayer samples.
- The static limit can be ignored (the characteristic secondary ions continue to be emitted until all the material is removed).
- The depth profiling analysis can be carried out.
2.3 Surface Charging

- When an insulting sample is bombarded by a positive ion beam, the surface potential can rise rapidly by several hundred volts due to:
  1. input of positive charge,
  2. emission of secondary electrons.

- Resulting phenomenon: kinetic energy of the emitted positive ions rises well beyond the acceptance of the analyzer—loss of SSIMS spectrum.

- Solution to this problem
  1. For positive ions quadrupole SIMS

  Use neutral atom beam. (Fast Atom Bombardment, FAB). Surface potential also rises, due to the emission of the secondary electrons, but it quickly reaches a plateau of ≈ 20V.
2. For ToFSIMS (need pulse primary beam)

(a). Irradiating the sample surface with a beam of low energy electrons (widely used method) --- cause sample degradation.

• For negative ion collection (FAB), the surface potential should be negative. This required a higher flux of electrons (10 times than the ion flux) – give rise to sample degradation and electron stimulated ion emission.

(b). Deposit the material as a thin film on silver: Because the film is very thin, little charging occurs and the charge neutralization is not required. ---- the sample is considerably cationization by the silver support.
3. Experimental Requirements

- **Three main components:**
  - Primary particle source,
  - Ion optical system: selects ions with a defined energy band.
  - Mass spectrometer,

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

Wien filter for mass selected ion beam

$zV = \frac{mv^2}{2}$

$zE = zBv$

$m/z = 2V(B/E)^2$

*Figure 5.5.* A schematic diagram of (a) the main components of a scanning, focused ion gun: Source = ion source; Extr = extractor; Acc = accelerator; M.Filt = mass/energy filter; Stig = stimator; Defl = neutral elimination bend; Focus = focusing lens; scan = xy raster. (b) Operation of a Wien filter for mass selected ion beam. Balance condition is $m/z = 2V(B/E)^2$. Reproduced by permission from [7], *Secondary Ion Mass Spectrometry Principles and Applications*, Oxford Science Publications (1989).
3.1 Primary Beam

According to the mechanisms of the primary beam production, there are four types:

(1). electron bombardment
(2). Plasma
(3). surface ionization
(4). field ionization

Basic components of ion beam source:
- source regions / extraction zone, focusing and collimating regions,
- mass filter for beam purification,
- pulsing mechanism (for time-of-flight mass analyzer),
- stigmation/focus lenses and finally scan rods
• Scanning SIMS microprobe:
  Scan the primary ion beam across the surface region of interest mapping the distribution of secondary ions over area of interest.

• Ion microscopy — mapping of surface elements using an un-scanned primary ion beam. Positional sense of the ions is retained throughout mass analysis process.

• **Critical parameters of the primary beam:**
  brightness, energy spread, stability and reliability.
3.1.1 Electron Bombardment----without formation of plasma

- Maximum operating gas pressure is about $10^{-4}$ mbar, enabling operation without a mass filter.
- Electron of high current density are used to ionize the primary beam gas (Argon or Xenon). The electrons are accelerated towards the anode to obtain the required energy.
- Ion beam is extracted from the ion source, accelerated and focused with energy of 2keV-12 keV
Figure 2.6 Schematic representation of duoplasmatron (hot cathode) ion source
Generation of neutral beam: by charge exchanging of ion beam. (Wien filter is widely used)
Passing the ion beam through a chamber containing Ar (10^4 mbar).
About 10%~30% of ions lose their charge, but they retain the velocity and direction and thus, fast atom beam is formed.
(The residual ion beam can be deflected away)
Offer only moderate brightness (about 10^5 A/m^2-sr), commonly used de-focused over large area (~mm^2) for static SIMS.
Used for formation of cluster ion beams such as SF_5^+, C_60^+. 
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron emission current</td>
<td>$10 , \mu\text{A} - 10 , \text{mA}$</td>
</tr>
<tr>
<td>Source pressure</td>
<td>$10^{-7} - 5 \times 10^{-4} , \text{mbar}$</td>
</tr>
<tr>
<td>Ion energy spread</td>
<td>$10 , \text{eV}$</td>
</tr>
<tr>
<td>Ion energy</td>
<td>$0.1 - 5 , \text{keV}$</td>
</tr>
<tr>
<td>Beam size range at sample</td>
<td>$0.1 - 2 , \text{mm}$</td>
</tr>
<tr>
<td>Maximum ion current</td>
<td>$10^{-5} , \text{A}$</td>
</tr>
<tr>
<td>Corresponding spot size</td>
<td>$0.8 , \text{mm}$</td>
</tr>
<tr>
<td>Minimum beam diameter</td>
<td>$0.1 , \text{mm}$</td>
</tr>
<tr>
<td>Corresponding beam current</td>
<td>$800 , \text{nA}$</td>
</tr>
<tr>
<td>Current density at sample</td>
<td>$4 , \text{mA cm}^{-2}$</td>
</tr>
<tr>
<td>Beam brightness</td>
<td>$10^{-2} , \text{A cm}^{-2} , \text{sr}^{-1}$</td>
</tr>
<tr>
<td>Neutrals content (maximum)</td>
<td>$2 - 4%$</td>
</tr>
</tbody>
</table>
3.1.2 Plasma

- Ion beam is formed in a plasma (glow discharge)—
  Under higher gas pressure ($p > 10^{-2}$ torr), high density of electrons is sustained which generates a high ion beam current.
  - Ionizing efficiency is improved and a higher beam brightness of $10^4 \sim 10^7$ A/m$^2$-sr is attained.
  - Reliability is decreased.
  - Suited for dynamic SIMS（μA into ~ 50μm）and micro-focused scanning analysis（nA into ≤ μm）

<table>
<thead>
<tr>
<th>Table 2.2 Typical plasma and beam parameters of a duoplasmatron ion source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating pressure</td>
</tr>
<tr>
<td>Electron temperature</td>
</tr>
<tr>
<td>Ion density</td>
</tr>
<tr>
<td>Acceleration voltage</td>
</tr>
<tr>
<td>Extraction gap</td>
</tr>
<tr>
<td>Mass (argon)</td>
</tr>
<tr>
<td>Ion temperature</td>
</tr>
<tr>
<td>Current density of extracted beam</td>
</tr>
<tr>
<td>Beam brightness</td>
</tr>
<tr>
<td>Reduced beam brightness</td>
</tr>
</tbody>
</table>
3.1.3 Surface Ionization

- Ion source of **alkali metal** (in particular Cs\(^+\)) was commonly produced by the surface ionization.
  
  ◆ **Principle**: Ion emission is thermally stimulated by heating an adsorbed layer (ex. Cesium) on the surface of high work function metal (ex. iridium) under vacuum. **An ionization potential is applied** that the electrons can move freely from adlayer (Cs) to substrate (Ir) under thermal excitation.

  ◆ Ions of very low (0.2eV), uniform energy spread are emitted.

- **Special application**—
  
  ◆ Sensitivity to the **electronegative species**, that is, increases **negative secondary ion yield** (such as P, As, …)
  
  ◆ Play an important role in SIMS, especially for sputter depth profiling semiconductors.

  ◆ Source brightness > 10\(^6\) A/m\(^2\)-sec, depends on size of the emitting area.
Surface Ionization

extractor

Cs

+ 

Cs

+ + +

I_r

heating

Porous ionizer
### Table 2.3 Characteristics of a caesium surface ionization source

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>1200–1300 K</td>
</tr>
<tr>
<td>Initial energy spread</td>
<td>0.2 eV (2 kT)</td>
</tr>
<tr>
<td>Current density of extracted beam</td>
<td>100 mA cm(^{-2})</td>
</tr>
<tr>
<td>Beam brightness</td>
<td>50–500 A cm(^{-2}) sr(^{-1})</td>
</tr>
<tr>
<td>Reduced beam brightness</td>
<td>5–50 mA cm(^{-2}) sr(^{-1}) V(^{-1})</td>
</tr>
</tbody>
</table>

---

Cesium thermal surface ionization ion sources
3.1.4 Field Ionization sources

- Principal: A very fine tip (<1μm) is used, and an extremely high local electronic field (10 ~ 20 KV) is applied to strip electrons off source atoms.

- Liquid metal ion (LMI) source (with thin “skin” of liquid metal, typically Ga, In, Au, Bi) is widely used to produce beam currents.

- Most commonly used LMI source is based on liquid gallium which relies on field-ionization Ga⁺ from a W⁻ tip to generate a very bright (~10¹⁰ A/m²Sr) and highly focusable beam.

- Used for produce Au₃⁺, Bi₃⁺, Bi₅⁺, etc.

- Adapted for pulsing. Pulse width is approximately 20-50 ns.
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)
Figure 2.10  Schematic representation of a liquid metal ion gun for microbeam SIMS applications
3.2 Mass Analyzers

- **Demands for different modes of SIMS**
  1. **Static SIMS**: maximize the information achieved per unit surface damage.
  2. **Dynamic SIMS**: to have the highest sensitivity possible for specific elemental ions.
  3. **Scanning or imaging SIMS**: study the spatial distribution of surface chemical, the requirements are the same as for static SIMS.
The three most commonly used mass analyzer.

1. **Quadrupole RF mass filter**
   Used in early work in static SIMS (easily incorporated in a UHV due to its small size). Low transmission (<1%) A scanning instrument, only allows the sequential transmission. The information loss is high.

2. **Time-of-flight (TOF) analyzer:**
   Commonly used in SSIMS due to its high transmission. Collect all the ions generated. Highest sensitivity, quasi-parallel detectors (not for scanning).

3. **Magnetic sector analyzer:**
   Used for dynamic SIMS because of high transmission (10%~50%) and high mass resolution. A scanning device.
3.2.1 Magnetic Sector

- Principle
  - Ions are extracted from the sample and are accelerated to a fixed potential before entering the magnetic field:
    
    \[
    \text{energy} = ZV = \frac{m u^2}{2}
    \]
  - The ions are passed through a magnetic field (normal to the direction of ions). The magnitude of force exerted on the ions by the magnetic field is: \( ZuB \).
  - The radius of curvature, \( R \), of the ion path can be related to the mass to charge ratio, \( m/Z \)
    
    \[
    \frac{m u^2}{R} = ZuB
    \]
    
    \[
    R = \frac{m u}{ZB} = \left(\frac{1}{B}\right)(m/Z)(2ZV/m)^{1/2}
    \]
    
    \[
    R = \left(\frac{1}{B}\right) (2mV/Z)^{1/2}
    \]
  - The ions of different mass can be separated
Mass resolution: increase with radius of magnets decrease with increasing mass.
Secondary ions are emitted with a spread of kinetic energies.

- **Elemental ions (higher):** up to $= 100$ eV, peak around 10-20 eV
- **Multi-atomic (narrower):** width a few tens of ev, peak 1~5 ev

A wide energy spread can degrade the mass resolution

This problem can be solved by incorporating an electrostatic sector, which allows a small energy band of ions to be selected and focused.

$$EZ = \frac{mu^2}{R} = \frac{2KE}{R}, \quad R = \frac{2KE}{EZ}$$

- An attractive feature – positional sense of secondary ion (Can be operated as an ion microscope)
- Difficult in the generation of UHV
3.2.2 The Quadrupole Mass Analyzer

- Use a combination of a DC and a RF electric field applied to four parallel rods.
- for a specific dc and ac field, ions with certain mass to charge ratio (m/z) can be transmitted to detector. By increasing the ac and dc fields, all ions of various m/z ratio can be detected.
- A low transmission device (<1%).
  Scanning instrument, so only allows the sequential transmission of ions.
Figure 5.8. Operation of a quadrupole mass filter: (a) longtitudinal cross-section, showing stable and unstable trajectories; (b) radial cross-section, showing applied voltages; (c) ion trajectory stability diagram – ion trajectories are a function of two dimensionless parameters $a$ and $b$, (see text). Reproduced by permission from [7], Secondary Ion Mass Spectrometry-Principles and Applications, Oxford Science Publications (1989)
The simplest means of mass separation used in SIMS

- Pulses of secondary ions are accelerated by a given potential (3~8 kev) such that all ions possess the same kinetic energy. These ions are then allowed to drift through a field free space.

- Heavier masses travel more slowly, and the measured flight time ($t$) of an ion ($m/Z$) accelerated by a potential $V$ down a flight path $L$ provides a simple means of mass analysis.

  $$ t = L \left( \frac{m}{2ZV} \right)^{1/2} $$

- Basic experimental requirement → precisely pulsed primary ion source, accurate computer clock, drift tube.

- The pulse length of primary beam is typically very short (order of nanoseconds) — significantly affect the mass resolution.
Figure 2.26 Schematic of a TOF SIMS and its function
The energy distribution of secondary ions (ca 20~100ev) will affect the mass resolution. This is usually compensated by an energy analyzer in the flight tube. (The most commonly used device is ion mirror).

The transmission of TOFSIMS is 50~100%. Non-scanning device, non of the ions are discarded.

Sample charging is still a problem when analyzing insulators. —overcome by pulsing electrons on to the sample.
Ion-mirror for ToF mass analyzer

- Ion mirror: Consists of a series of precisely spaced rings to which is applied a gradually increasing retarding field.
- The more energetic ions (E2) penetrate deeply before they are reflected. While the less energetic ions (E1) take a shorter path.
- All ions of the same mass will arrive at the detector at the same time, despite their small energy differences.
ZV = \mu u^2/2, \quad u =(2ZV/m)^{1/2}, \quad t=L/u = L (m/2ZV)^{1/2}

Figure 5.10. A schematic diagram of a ToFSIMS instrument. Reproduced by permission from J.C. Vickerman, Analyst, 119, 513–523 (1994)
◆ Superiority of ToFSIMS for static SIMS — comparing with Quad-SIMS

**Example**: spectra of PMMA spin cast thin film (Fig. 5.11)

- Primary ions dose:
  - ToFSIMS: $10^{10}$ ions/cm$^2$
  - Quad-SIMS: $10^{12}$ ions/cm$^2$

- The yield of negative ion at $m/Z=85$ (methacrylate backbond) relative to the primary dose:
  - ToFSIMS: $4 \times 10^{-4}$
  - Quad-SIMS: $6 \times 10^{-8}$
Figure 5.11. (a) Positive (i) and negative (ii) ToF-SIMS 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 = \(10^{12}\) atoms cm\(^{-2}\). Reproduced by permission from A.J. Eccles and J.C. Vickerman, J. Vac. Sci. Technol., A7, 234, (1989)
Further **benefits of ToF analyzer** for the analysis of **organic materials** — **wide mass range**

- The more complex the organic materials being studied, the greater the mass range required.
  - for **quadrupole analyzer**: about 1000 amu, unit mass resolution
  - **TOF analyzer**: limitless mass range (~10000 amu), resolution $m/\Delta m = 5000\sim10000$

- Summaries of the performance of the mass analyzers .(Table 5.3)

<table>
<thead>
<tr>
<th><strong>Table 5.3. Comparison of mass analysers for SIMS</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type</strong></td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Quadrupole</td>
</tr>
<tr>
<td>Magnetic sector</td>
</tr>
<tr>
<td>Time-of-flight</td>
</tr>
</tbody>
</table>
• The ToF analyzers were not applied for the depth profileing, because the uses of pulsed analysis beam with duty cycle of about $10^{-4}$ (i.e. the time the beam is on, divided by the time it is off). ------ a time consuming process.

4. Mechanism of Secondary Ion Generation

• Ion formation in SIMS is a complex phenomenon. Simplistically the process can be divided into two components:
  (1) The dynamic process by which atoms and multi-atomic clusters are desorbed;
  (2) The ionization process in which a fraction of these sputtered particles becomes charged.
• Electronic factors are involved throughout the desorption event.
4.1 Model of sputtering

- The simplest approach: regards the atoms as hard spheres which obey Newtonian mechanics---- Sigmund’s linear cascade theory.

  The sputtering events were classified into: Knock-on sputtering, and electronic sputtering

- Other theoretical model had been proposed to simulate the sputtering process involving inorganic material, organic compounds.
4.2 Ionization

- The fraction of the sputtered particles which are in the ionized state is very small (only about less than 1 %). ----depends on the relative **probabilities of ionization** and **de-excitation** as it passes through the near surface region.

  ◆ Matrix effect--- dependence of ion yield on the electronic properties of the matrix.

  *Ex.: for metal* (with rapid electronic transitions, $10^{14}$-$10^{16}$ sec$^{-1}$), the probability of **de-excitation during** $10^{-13}$ sec (the time for a sputtered particles to traverse the near surface region) is high.
• Two models suggested to describe the process of secondary ion generation:

(A). *Nascent Ion Molecule Model*

◆ Assume that all ions are neutralized before they can escape due to rapid electronic transition.

◆ *Secondary ions* are thought to form as a consequence of *dissociation* of sputtered neutral molecular species some distance from the surface — where the electronic influence of the surface is smaller.
(B). The *Desorption Ionization Model*

- Considering the importance of **vibrational excitation**
  - Also emphasizes the separated processes of desorption and ionization.
  - At the initial excitation process, the energy is transformed into thermal/vibrational motion.
  - Some pre-formed ions may be directly emitted. Neutral molecules are desorbed in high yield.
  - To generate other ions, the model suggests that desorption is followed by two types of chemical reaction:
    1. In the selvedge or top surface layers----fast ion/molecules reactions can occur;
    2. In free vacuum----unimolecular dissociations may occur giving rise to fragment ions.
The relationship between spectra and surface structure

For the application of static SIMS as a method of surface chemical analysis, it should rely on a pragmatic experimental approach.

- Investigate surface chemistry which has been well characterized by other techniques and access the SSIMS data.

5.1 Surface Science Studies of the Adsorbate State

(A). CO Adsorption on Metal

- Distinguish molecules from dissociative adsorption of CO on metal surfaces.
  - On W (300 K): $M_xC^+$, $M_xO^+$ ions (dissociative adsorption)
  - On Cu, Pd, Ni, Ru (100-300 K): $M_xCO^+$ ions. (molecule adsorption)
  - On Fe (300 K): both types of ions were found. (Fig. 5.13)
There was no evidence from the data, when the low primary flux conditions were used, that the SSIMS process modified or destroyed the surface state.

Figure 5.13. Static SIMS spectrum following the exposure of a clean iron foil to $10^8$ torr of carbon monoxide. Reproduced by permission from [27], *J. Chem. Soc. Faraday I*, 71, 40 (1976)
The SSIMS investigations also demonstrated that the relative intensities of the $M_x CO^+$ ($X=1-3$) ions defined the adsorbate structure--- **linear**, **bridged**, or **triply bridges** of the adsorbate to the metal surfaces atoms. (Table 5.4).

**Table 5.4.** Secondary ion cluster emission and CO adsorbate structure

<table>
<thead>
<tr>
<th>Surface</th>
<th>SSIMS</th>
<th>CO structure IR/HREELS/LEED*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$MCO^+$</td>
<td>$M_2CO^+$</td>
</tr>
<tr>
<td>Cu(100)</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Ru(0001)</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni(100)</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>Pd(100)</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>0.65</td>
<td>0.35</td>
</tr>
</tbody>
</table>

*LEED = Low energy electron diffraction.
• The “fragmentation” patterns reflect the structure rather than the adsorption strength.--- various adsorption energies with the same ions detected. (Cu and Ru, Ru > Cu)

• The coordination of CO changes with coverage---Figure 5.14

◆ On Ni(111)---
Low coverage: predominantly bridge
At coverage of 0.5: about 70 % linear.

\[ \frac{\text{MCO}^+/\Sigma \text{MxCO}^+}{\Sigma \text{MxCO}^+} \]: represents the linear adsorption
- Distinguish between the effects of electronic charges and surface coverage on the increase of intensity
  - As an adsorbate (X) was adsorbed on the metal surface, electronic changes occurred which may cause changes in the ionization probability and thus, the intensity of both $M^+$ and $MX_{ads}^+$.  

- To eliminate the electronic effects --- the ion ratio $MX_{ads}^+/M^+$ was used. (Figure 5.15)
The ion ratio is directly proportional to CO coverage. That is, the increase of intensity is only a consequence of increasing amount of CO on the surface.

Figure 5.15. Variation of the sum of ion ratios, $\Sigma(M_x CO^+/M^+_x)$, as a function of CO coverage. reproduced by permission of Elsevier Science – NL from [30]
The investigation of more complex adsorbates by SSIMS, such as ethene, propene, and butene on Ru(0001)

**Example:** propene adsorption on Ru(0001)

Two mass spectra regions of particular interest:

\[ \text{CH}_x^+ \ (x = 0-3) \]

\[ \text{RuC}_y\text{H}_x^+ \] (weak signals in Ru_2C_yH_x^+)

- **Ru_xC_yH^+** region----formed by addition of the stoichiometric mass of the adsorbate to Ru

  - Ru has seven significant isotopes (m/z: 96-104)---makes the spectra more complex, the spectra from individual surface species interleave and overlap.----Figure 5.16

Isotopes: 96-104

Intensity

(a) Real spectrum

(b) Expected

135 140 145 135 140 145
Mass number

96+42 = 138
102+42 = 144
104+42 = 146

RuC₃H₆⁺
◆ Isolate signals at m/z values which are associated with each of surface species formed as alkene adsorbed at 150 K, and decomposed as the temperature is raised.

◆ m/z: 146----adsorption of propene, RuC$_3$H$_6^+$ (104+42)
  m/z: 145---decompose to propylidyne, RuC$_3$H$_5^+$
  m/z: 131---formation of ethylidyne, RuC$_2$H$_3^+$

● Normalizing the signals to Ru m/z 102 isotope ⇒ relative surface coverage of these species (Fig 5.17---variation with temperature)

● By SSIMS, it shows that alkenes adsorption at 150 K is accompanied by decomposition to alkylidyynes, further transitions to alkylidyynes and finally to CH$_X$
m/z=146, alkene adsorption, RuC$_3$H$_6^+$

m/z=145, propylidyne, RuC$_3$H$_5^+$

m/z=131, ethylidyne, RuC$_2$H$_3^+$

Figure 5.17. The variation in surface coverage as a function of surface temperature of (A) adsorbed propene from intensity of $m/z$ 146; (B) adsorbed propylidyne from intensity of $m/z$ 145 (C) adsorbed ethylidyne from intensity of $m/z$ 131 after exposure of Ru(0001) to propene at 150 K. Reproduced by permission from [35], Proc. Roy, Soc. London A, Math. Phys. Sci., 330, 147 (1990)
5.1.3 Surface Reaction

On small metal particles supported on oxide films which model supported catalysts.

**Example:** CO oxidation on 6 nm Pd particles supported on alumina.

Investigate the surface state of adsorbed CO, oxygen, and carbon, as the temperature rises.

- Temperature rises up to 350 K (no CO\(_2\) desorb)

  The surface coverage of CO decreases ---- from \(\Sigma Pd_x CO^+/\Sigma Pd_x^+\),
  but of carbon increases  ------ \(\Sigma Pd_x C^+/\Sigma Pd_x^+\)

  ◆ The coordination changes (measured from PdCO\(^+\)/ \(\Sigma Pd_x CO^+\))

  From: mix of linear and bridge CO \(\rightarrow\) predominantly bridge

  ◆ Some CO dissociation occur.
At about 400 K

- Production of gas phase CO$_2$ is rising.
- The surface coverage of C falls while surface coverage of oxygen (measured by Pd$_2$O$^+$/Pd$_2^+$) begin to rise.
- The coordination of the CO changes progressively toward linear.

Beyond 500 K:

- The surface coverage of CO and C is very small, while the coverage of O is high.
- The CO$_2$ production falls.

The data suggests that besides the well known surface reaction between adsorbed CO and adsorbed O (into CO$_2$), another route to formation of CO$_2$ is via adsorbed C presumably arising from CO dissociation. ---- more significant on small Pd particles.
$\text{CO}_{\text{ads}} + \text{O \ ads} \rightarrow \text{CO}_2$

Another

$\text{CO} \rightarrow \text{C} + \text{O}$

$\text{C} + 2\text{O} \rightarrow \text{CO}_2$
5.2 Surface Chemistry of Organic Materials

Organic materials are not easy for surface scientist to handle because: (1) they are chemically complex; (2) they are usually electrically insulating; (3) very sensitive to particle bombardment.

5.2.1 Static condition for organic analysis

- Static condition for inorganic materials:
  - $1 \text{nA/cm}^2$, total primary particle dose of about $10^{13} \text{/cm}^2$.
- For organic material, the experiment demonstrates that total dose of $10^{13}$ particles/cm$^2$ was the maximum permissible before new spectral features become evident due to bombardment induced effects.
- Total ion yield increased with particle mass ($\text{Xe} > \text{Ar} = \text{Ne} >> \text{He}$)
The studies of sputter degradation of polymers (PET, PTFE)---spectral time dependence under ion and atom bombardment. The variation of signal intensities of three ions was investigated as function of primary particle dose. (Fig. 5.18).

- Under ion bombardment: a dramatic fall in the intensities of all secondary ions signals.
- Under atom bombardment: little loss of intensity was observed by $10^{13}$ total dose.

- The influence of particle mass was also significant.
- Assuming a simple exponential decay:

$$S_t = S_o \exp (-kt)$$  
**half-life** for signal decay can be compared:

<table>
<thead>
<tr>
<th>Half-life/10^{12} particles cm^{-2}</th>
<th>Ar^0</th>
<th>Xe^0</th>
<th>Ar^+</th>
<th>Xe^+</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>26</td>
<td>9</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>

Atoms are least damaging whether they are argon or xenon. However, the higher mass of xenon does generate more damage than argon. Similar data was
Figure 5.18. Variation of signal for some PET cluster ions with: (a) primary ion dose; and (b) with primary atom dose. Reproduced with permission from [43]. Copyright (1991) American Chemical Society.
Atoms are least damaging. -----an explaining model:

- It is generally believed that incident ions are neutralized prior to impact with a solid. So the surface damage should be related to the particle-surface electronic interactions (PSEIs). These interactions involve the transfer of an electron from the solid to the approaching ion via resonant or Auger processes.

- This results in charging and in the creation of electronically excited states in the surface region. Bond dissociation may occur, possibly accompanied by desorption.

- The surface charging of insulator may cause disruption of the surface by Coulomb explosion mechanism.---localized charges in small region leads to Coulomb energy about 30 eV which greater than binding energy of atoms in a solid.

- To minimize surface damage during analysis, ToF analyzer is performed by using a pulsed ion beam. (below 10^{12} ions/cm^2)
Three spectral regions can be identified:

1. **Sub-monomer regions**: m/z below pseudo molecular ion M\(^{+/-}\) cationized sub-monomer: \((M_+ C)^{+/-}\).

   Provides the fragmentation patterns spectrum and the most precise information on the chemical structure. So, spectral assignment of the major peak should be accurate.

2. **n-mer region**: ions formed as a consequence of bonding of two or three monomer units plus fragment.

   It may contain valuable micro-structure information of the same type as from the fragmentation of the monomer unit. Also, they can provide more macromolecules information about the polymer structure.
**Example.**

◆ The extent of segregation in co-polymers

◆ The yield of n-mers of different lengths may point to folding or looping of a polymer chain at the interface. [50]

3. **Oligomer spectral region:** usually generated via metal ion cationization.

**Example:** A thin layer of an organic compound or polymer was deposit on a silver substrate.

◆ Oligomer distributions \((M_x-\text{Ag})^+\) to \(m/z > 8000\) can be generated. (Fig. 5.19)

◆ Permit an estimation of the **average molecular weight distribution** to be determined.
Figure 5.19. Positive secondary ion spectrum of polystyrene 7000 on silver. Reproduced with permission from [52]. Copyright (1991) American Chemical Society
5.3 Example of Surface Characterization

- Static SIMS to characterize complex chemical system had been reviewed [53]

5.3.1 Surface Analysis of an Adhesive System

The surface and interfacial chemistry of adhesive and organic coating can have major effect on their properties and performance.

- Four epoxides have been investigated using ToF-SIMS
  Epikotes 828, 1001, 1007, 1009
Figure 5.20. General structure of Epikote samples, listing their mean molecular masses and the central value of $n$. Reproduced with permission from J.C. Vickerman, *Analyst*, **119**, 513–523 (1994)
Two sets of studies are carried out:

1. **silver cationization** was used to obtain detailed information about the oligomer distribution.

   Thin layer of Epikote were deposited on silver.

2. **Thick films** were prepared on **aluminium foil**---to obtain data relevant to the real adhesive and coating system.

- **Experiment 1.** ----Figure 5.21 (Epikote 1007 deposited on Ag substrate)

  ◆ The intervals of peaks corresponding to the mass of single monomer unit. (284) That is, oligomer + two silver isotopes 107, 109 for n=2 to 11.

  ◆ The two isotopes of Ag can not be split due to wide mass range.
Each of Ag cation peaks is accompanied by signal at m/z
- 18 higher, ---- the presence of epoxide-glycol oligomer formed by hydrolysis of the epoxy group.
- 56 higher, --- the presence of propanol.

For Epikotes 1007 and 1009, additional m/z values occurs at
- 36 higher ---- presence of diglycol- terminated oligomers
- 56 lower ---- presence of phenol- (loss of epoxide) terminated
- 72 lower ---- presence of phenyl-(loss of epoxide+ O) ter--

detailed information of the chemical state of polymers can be obtained, and the composition of the resin mixture is qualitatively indicated. (not the actual surface state of the resins).
Figure 5.21. Spectrum of Epikote 1007 deposited on a silver substrate. Reproduced with permission from [54]. Copyright (1993) John Wiley & Sons Ltd
For the thick films, signals above \( n=2 \) oligomers did not appear. The most useful signals were fragments of the monomer: including terminal epoxide or bisphenol-A components

- **terminal epoxide group**: \( m/z = 191, 252, 269 \)

- **bisphenol-A component**: \( m/z = 135, 213 \)

![Scheme 5.1](image1.png)

![Scheme 5.2](image2.png)
Scheme 5.1

Scheme 5.2
◆ bisphenol-A m/z = 135, 213, epoxide: 191, 252, 269

MW: 880

MW: 2870

MW: 4000

Figure 5.22. Part of the positive ToFSIMS profiles (m/z 115-290) recorded for Epikote 1001 (a), 1007 (b), 1009 (c). BP = bisphenol-A component; E = epoxide
Changing of the **molecular weight** have a marked effect on the **relative intensities** of the signals specific to the terminal epoxide groups compared to those of the bisphenol-A groups.

- When the molecular weight of polymer increases, the ratio of epoxide end group to the bisphenol-A component would be expected to decrease.

- Ratio of characteristic ions to the reciprocal molecular mass——(Figure 5.23) — quantitatively relationship between the two groups.

- This observation should be useful in **probing the effect of cross-linking** in cured adhesive. The **bisphenol-A part** is relatively unaffected by cross-linking.
Figure 5.23. Plot of peak area ratios $\frac{191\text{ (epoxide)}}{191\text{ (epoxide)} + 135 \text{ (bisphenol-A)}}$ and $\frac{213\text{ (bisphenol-A)}}{269\text{ (epoxide)} + 213\text{ (bisphenol-A)}}$ the Epikote resins. A, epoxide ratio; B, bisphenol-A ratio. Reproduced with permission from J.C. Vickerman, Analyst, 119, 513–523 (1994)
5.3.2 Quantification of Surface Composition

- Surface segregation may be caused by:
  - Difference in surface free energy
  - Contamination
  - Surface treatment

- Ion ratios had been used to monitor the surface composition of methacrylate co-polymer:
  - **PMMA**: poly(methyl methacrylate) --- $M=100$
  - **PEMA**: poly(ethyl methacrylate) --- $M=114$
Two sets of negative ion were chosen to characterize:

- **PMMA**: m/z = 31, CH$_3$O-
  
  m/z = 141, M+41,

- **PEMA**: m/z = 45, C$_2$H$_5$O-,
  
  m/z = 155, M+41

**Common ions** of methacrylate polymer backbone:

m/z = 85, (Fig. 5.24)

- **PMMA** could be characterized by: $I_{31}/I_{85}^m = \alpha$
- **PEMA** could be characterized by: $I_{45}/I_{85}^e = \beta$
**Figure 5.24.** Negative ion spectra of PMMA (a), PEMA (b) and a copolymer of PMMA and PEMA (c). Reproduced with permission from [56], *J. Polym. Sci. B. Polym. Phys.*, 27, 2071. Copyright (1989) John Wiley & Sons Ltd.
\[ \frac{l_{45}}{l_{31}} = \gamma \left( \frac{n_{EMA}}{n_{MMA}} \right) \]

\[ \frac{l_{155}}{l_{141}} = \delta \left( \frac{n_{EMA}}{n_{MMA}} \right) \]

**Figure 5.25.** Plot of \( l_{45}/l_{31} \) and \( l_{155}/l_{141} \) against PMMA–PEMA copolymer composition. Reproduced with permission from [56], *J. Polym. Sci. B. Polym. Phys.*, 27, 2071. Copyright (1989) John Wiley & Sons Ltd.
• If $I_{45}/I_{31}$ or $(I_{155}/I_{141})$ was plotted against co-polymer composition, a linear relationship is obtained (Fig. 5.25)
  ◆ A small yield of $m/z = 45$ ions from PMMA, thus, $I_{45}/I_{31}$, is not zero when PEMA concentration is zero.

• The composition of the co-polymer is related to the SIMS ions:
  \[
  \frac{n_{EMA}}{n_{MMA}} = \frac{1}{\gamma} \left( \frac{I_{45}}{I_{31}} \right) = \frac{1}{\delta} \left( \frac{I_{155}}{I_{141}} \right)
  \]
  ($\gamma = 0.59$ ; $\delta = 0.88$)

• The formation of methacrylate $m/z = 85$ ion from PMMA and PEMA has different probability.
  \[
  I_{85}^e/I_{85}^m = 2.2 \text{ (estimated when } \frac{n_{EMA}}{n_{MMA}} = 1)\]
  ◆ The structure of alkyl group influences the efficiency of formation of the “side chain independent” methacrylate ion.
\[ I_{31}/I_{85}^m = \alpha \]
\[ I_{45}/I_{85}^e = \beta \]
\[ I_{85}^e/I_{85}^m = (\alpha/\beta)\gamma \]

From Figure 5.24, \( \alpha = 4.4 \), \( \beta = 1.1 \), and known \( \gamma = 0.59 \)

So,

\[ I_{85}^e/I_{85}^m = (\alpha/\beta)\gamma \rightarrow 2.2 \]
Using the n-mer ions to probe the statistical distribution of the component monomers:

- Dimer ions formed reflects the structures
  - MMA-MMA---- m/z = 185
  - MMA-EMA ----- m/z = 199
  - EMA-EMA ------m/z = 213

- If the distribution of the EMA and MMA monomers was statistical, the distribution of ions would be expected:
  \[ I_{\text{MMA-MMA}} : I_{\text{MMA-EMA}} : I_{\text{EMA-EMA}} = n_{\text{MMA}}^2 : 2n_{\text{MMA}}n_{\text{EMA}} : n_{\text{EMA}}^2 \]

- Comparison of the calculated and measured SIMS intensity (Table 5.1) --- the different values reflect a deviation from the random co-polymer structure.

- \[ I_{\text{AA}} : I_{\text{AB}} : I_{\text{BB}} = (n_A + n_B)^2 = n_A^2 + 2n_An_B + n_B^2 \]
Table 5.5. Comparison of calculated and measured SIMS intensity ratios for dimeric (2M-15) ions arising from MMA-MMA, MMA-EMA and EMA-EMA units from two samples of PMMA-PEMA co-polymers

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>Method of determination</th>
<th>$I_{\text{MMA-MMA}}$ m/z 185</th>
<th>$I_{\text{MMA-EMA}}$ m/z 199</th>
<th>$I_{\text{EMA-EMA}}$ m/z 213</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_{\text{MMA}} : n_{\text{EMA}}$ = 0.36 : 0.64</td>
<td>equation (9)</td>
<td>0.13</td>
<td>0.46</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>from spectrum</td>
<td>0.16</td>
<td>0.44</td>
<td>0.40</td>
</tr>
<tr>
<td>$n_{\text{MMA}} : n_{\text{EMA}}$ = 0.61 : 0.39</td>
<td>equation (9)</td>
<td>0.37</td>
<td>0.48</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>from spectrum</td>
<td>0.47</td>
<td>0.41</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Thank You!

化學工程系  李玉郎