Static SIMS: A Powerful Tool to Investigate Nanoparticles and Biology

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The ideas encompassed in this talk:

- Semiconductor processing
- Nanotechnology
- Biology
- Physics
- Surface Science
- Analytical Chemistry
- Multivariate Statistics
- Environmental Sciences
SIMS: The central focus of this talk
secondary ion mass spectrometry

1. Primary ions
2. Secondary ions
SIMS
secondary ion mass spectrometry

Mass Spectrometer

Secondary ions

Mass spectrum
Mass/charge
The pool table analogy for SIMS:

Can we reconstruct what was originally there by examining the events that occur and viewing what is left behind?
The Basic SIMS Experiment:

In a UHV chamber, a beam of accelerated ions (xenon in this case) is impacted into the sample of interest. Positive ions, negative ions, neutrals and free radicals are sputtered from the surface. The masses of the positive and negative ions are measured in a mass analyzer.

Additional neutral species can be ionized by a laser to yield a higher ion count.
SIMS Evolves

1960's
Prof. Alfred Benninghoven
(Static SIMS, 1969)

1980-2000
Quadrupole TOF-SIMS Imaging Cluster Ions

2000+
Information processing Image processing
SIMS Instrumentation

Time-of-flight (ToF) mass analyzer

Primary ion beam
3-12 KeV

ion pulses

pulsed ion source

heavier ions

lighter ions

High energy ion extraction field
3-20 KeV

$\mu = \text{velocity}$

$\mu = \left( \frac{2zV}{m} \right)^{0.5}$

time-of-flight $= \frac{l}{\mu} = \left( \frac{l^2}{2V} \right)^{0.5} \cdot \left( \frac{m}{z} \right)^{0.5}$

$V = \text{constant energy electric field}$
$m = \text{mass}$
$z = \text{charge}$
$l = \text{distance to the detector}$
Reflectron Time of Flight Analyzer

- Ion mirror (reflectron)
- Flight tube
- Electron flood gun (pulse)


Ion-ToF IV
http://www.ion-tof.com
Secondary Ion Mass Spectrometry (SIMS)
Time-of-flight (ToF) SIMS; Static SIMS

Probably the most information-rich of the modern surface analysis methods
What happens when a high energy projectile strikes a solid surface?
SIMS Surface Mechanisms

In the secondary ion mass spectrometry (SIMS) process, a surface is bombarded under vacuum with energetic ions (primary ions). Some of these ions transfer sufficient momentum to other atoms or molecules in the surface zone to permit their sputtering from the surface into the vacuum phase.

- We measure only ions
- It is surface sensitive because ions emitted from below the first layer or two are neutralized and lose their charge
- Two modes:
  - **Static SIMS** (10\(^{-9}\) ampere beam current of 1 cm\(^2\) for typically 10\(^2\)-10\(^3\) sec)
  - **Dynamic SIMS** (10\(^{-6}\) ampere beam current of 1 cm\(^2\) for typically 20 sec or more)
two SIMS modes

Static SIMS

10 min. to 1 hr.

Dynamic SIMS

3 min.

In an atomic solid, if there are $10^{15}$ atoms/cm$^2$< $10^{14}$ ions/cm$^2$  

Sputtering rates of 10nm/min are not uncommon.
Ion-Solid Interactions Modeled

Simulations at the femtosecond time scale

Images courtesy of Barbara Garrison and Nicholas Winograd, Penn State
Some of the events occurring:

- Ejection
- Molecular damage
- Scrambling
- Implantation

Figure 1 in:
Molecule Liftoff from Surfaces,
B. J. Garrison, A. Delcorde and K. D. Krantzman,
The Static SIMS Criterion

For semiconductors, there are approximately $10^{15}$ molecules/cm$^2$

You do not want to damage more than $10^{14}$ (10%).

The consequence of exceeding the static SIMS limit is increased atomic ions and decreased, information-rich molecules -- interpreted as evidence of extensive long-range damage to the polymer.

Factors important in fulfilling the static SIMS criterion:
- primary ion flux
- area analyzed
- time of bombardment
- rastered or diffuse beam
- sample density

Impact craters are well spaced apart.

In static SIMS we try to not sample already damaged areas.
Two Primary Ion Sources:

$\text{Bi}_3^+$:
Good mass resolution
Good spatial resolution
Sample damage

$\text{C}_{60}^+$:
Poor lateral resolution
Poor mass resolution
Minimal sample damage

Spectroscopy

Etching

Other primary ions: $\text{Cs}^+$, $\text{Au}^+$, $\text{Au}_3^+$
Special Advantages of SIMS

High mass resolution (easily >0.001 AMU)

High analytical sensitivity (very sensitive)

High information content

High spatial resolution (x,y, image) (15nm)

Shallow or deep sampling depth
Information from a static SIMS experiment

In the uppermost 10-15Å:

1. Atomics (what element is present?) (e.g., Na⁺ = 23)
2. Parent ions
3. Molecular fragments for structural determination
4. Molecular fragment/atomic fragment ratio
5. Molecular fragment ratios
   • mobility
   • conformation
   • molecular orientation
   • assembly orientation
   • molecular interactions
   • crystallinity
   • quantification
   • sample damage

“coded information“

6. Information on surface localization and depth
Organics spectral interpretation in SIMS

The principles of SIMS spectral interpretation are closely related to those used for mass spectrometry.

General books on mass spectrometry interpretation


Inorganics are easier for interpretation, but we need to look at isotopes

**HfO₂ Mesh Particles Positive Spectra**

(Hf Isotopes)

Red = Hf peak

Blue = Hf + H peaks

[Diagram showing Hf isotopes with peaks labeled]
## Commonly Observed SIMS Fragments

<table>
<thead>
<tr>
<th>Positive Ion</th>
<th>Negative Ion</th>
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<tbody>
<tr>
<td>m/z</td>
<td>m/z</td>
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<tr>
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<tr>
<td>12</td>
<td>13</td>
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<td>73</td>
<td>72</td>
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<tr>
<td>91</td>
<td>90</td>
</tr>
</tbody>
</table>

= hydrocarbon series
Characteristic Poly(dimethyl siloxane)(PDMS) SIMS Peaks

\[
\text{CH}_3 \quad (\text{Si} - \text{O})_n \quad \text{CH}_3
\]

<table>
<thead>
<tr>
<th>Molecular fragment</th>
<th>Nominal mass (Da)</th>
<th>Exact mass (Da)</th>
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<tbody>
<tr>
<td>Si(\text{CH}_3)^+</td>
<td>43</td>
<td>43.000403</td>
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<tr>
<td>Si((\text{CH}_3))_3^+</td>
<td>73</td>
<td>73.047353</td>
</tr>
<tr>
<td>((\text{CH}_3))_3\text{Si-O-Si(\text{CH}_3)_2}^+</td>
<td>147</td>
<td>147.06615</td>
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<tr>
<td>(\text{Si}_3\text{C}<em>5\text{H}</em>{15}\text{O}_3)^+</td>
<td>207</td>
<td>207.04460</td>
</tr>
</tbody>
</table>

Organosilicones are extremely common contaminants -- the characteristic positive ion peak signature of 43, 73, 147, 207 usually indicates silicones at the surface.
SIMS spectra are information-rich

High mass resolution

High S/N

Peaks up to >2000 AMU
Huge amounts of information from SIMS

We often use multivariate statistical methods to deal with this “data overload”
We can generate huge amounts of data!

How can we convert data into useful information?

Multivariate analysis methods, sometimes called “chemometrics”

Allows us to identify trends that might be hidden in the data

Makes use of large amounts of data

Uses all the data, not just that which we think is important

A hypothesis generator!
Addressing Large Data Sets

Data Table

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<th>3</th>
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<td>2</td>
<td>8</td>
<td>6</td>
<td>7</td>
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<tr>
<td>sample 2</td>
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<td>5</td>
<td>7</td>
<td>5</td>
<td>5</td>
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<td>0</td>
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<td>sample 3</td>
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<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>7</td>
<td>9</td>
</tr>
</tbody>
</table>

Classification Methods
- partitioning
- hierarchical

Multivariate Data Analysis

Factor Analysis Methods

A B C D E F

F1 F2
No clear relationship between points

A high correlation between points

We can visualize 2D and 3D, but we “lose it” at 4D – what about 1000D?
**PCA**

Principal Components Analysis

- **PC1**: direction of the greatest variance
- **PC2**: orthogonal axis defining the next greatest of variance
- **Scores**: projection of the samples onto the new PC axes
- **Loadings**: direction cosines of the matrix rotation
SIMS Imaging

A fluorinated area on our surface (blue)

Raster the focused ion beam and “map” the signal intensity for mass=19 (negative ion)

Also consider:
- 3D imaging (with depth profiling)
- Image processing

Storage Oscilloscope

Mass Analyzer (tuned to a specific m/e)
Negative ToF-SIMS images of patterned slides

\[ m/z \]

- Fresh
- Hydrolyzed
- Regenerated

<table>
<thead>
<tr>
<th>m/z</th>
<th>42</th>
<th>98</th>
<th>107</th>
<th>114</th>
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<tr>
<td>Regenerated</td>
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<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
</tbody>
</table>

500 µm x 500 µm images

Images by Prof. David Castner, University of Washington
Characteristics of Chemical State Imaging

Chemical State Imaging facilitates effective communication of information about spatial distributions of chemical information in a system.

but the image contains massive data content…

Data are not information!

Contemporary data manipulation routines are the route to extract the important information from the data.

There are critical problems that might be solved with SIMS imaging.
Challenges in SIMS Imaging

- Hard to distinguish topography and chemistry
- Compound identification requires several ions
- Low Signal-to-Noise Ratio
  - Poor image contrast
  - Poor resolution of regions
- Huge Data Sets
- 3D images using new cluster ions probes greatly magnify the amount of data.
Darwin’s Birth: Feb. 12, 1809

Biology Evolves

1700-1930
Cataloging birds & flowers

1930-1990
Molecular biology

1990+
Information science

Protein map, Rick Durrett
SIMS imaging of cells: The massive information challenge

PCA Studies from Castner, et al have shown that from the protein fragmentation pattern many proteins can be identified.

Other issues:

- cell fixation and dehydration
- sample damage
Toxicology/Safety Concerns About Nanoparticles

**Hypothesis:** It’s not the “nano-size” that leads to toxic properties. Rather, nanoparticles have high surface areas and high surface energies and thus will adsorb chemical from their manufacturing environments and take those chemicals into cells – *i.e.*, it’s the junk on the surface that’s toxic, not the particle.
SIMS OF NANOPARTICLES

SIMS looks at a 1nm surface zone; SIMS is hugely sensitive!
# Nanoparticle Impurities

## Negative Spectra Impurities

<table>
<thead>
<tr>
<th>Mass</th>
<th>ID</th>
<th>Ref Molecule</th>
<th>NP1 20 nm</th>
<th>NP2 1-2 nm</th>
</tr>
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<tbody>
<tr>
<td>13</td>
<td>CH</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>O</td>
<td>X</td>
<td>X</td>
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<tr>
<td>17</td>
<td>OH</td>
<td>X</td>
<td>X</td>
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<td>24</td>
<td>C2</td>
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<td>35</td>
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<td>37</td>
<td>C3H</td>
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<td>79</td>
<td>79Br</td>
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<tr>
<td>81</td>
<td>81Br</td>
<td>X</td>
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<tr>
<td>221</td>
<td>AuS</td>
<td>X</td>
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</table>

## Positive Spectra Impurities

<table>
<thead>
<tr>
<th>Mass</th>
<th>ID</th>
<th>Ref Molecule</th>
<th>NP1 20 nm</th>
<th>NP2 1-2 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>C2H3</td>
<td>X</td>
<td>X</td>
<td>X</td>
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<td>29</td>
<td>C2H5</td>
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<td>41</td>
<td>C3H5</td>
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<td>X</td>
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<td>43</td>
<td>C2H3O</td>
<td>X</td>
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<td>45</td>
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<td>55</td>
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<td>57</td>
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<td>91</td>
<td>C7H7</td>
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<td>118</td>
<td>C5H12NO2</td>
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<td>135</td>
<td>C7H6N3</td>
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<td>161</td>
<td>C11H13O</td>
<td>X</td>
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</table>

• “X” represents presence of molecule
• Molecules representative of influential loadings using PCA for negative spectra vs. tape
Surface Characterization Summary/
Preliminary Conclusions

SIMS Analysis

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Ref Micro</th>
<th>NP1 20 nm</th>
<th>NP2 1-2 nm</th>
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<tbody>
<tr>
<td>Light Organics (&lt;100 MW)</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Heavy Organics (&gt;100 MW)</td>
<td></td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Silicon</td>
<td>+</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>Chlorine</td>
<td>+</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Bromine</td>
<td></td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>Rare Earth Metals</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

- The nature of the impurities varied depending on the source of the NPs