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Molecular Depth Profiling

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http://simssociety.org/
Can the dynamic SIMS crowd finally find common ground with the organic SIMS community?

- **Inorganic agenda, semiconductor related**
  - Elemental dopant distributions very near the surface.
  - Study of epitaxial layers on Si.
  - Complex multilayer structures, quantum wells
  - Packaging issues (bonding)

- **Molecular depth profiling**
  - Buried interfaces -- OLED devices, pharmaceuticals.
  - Signal enhancement for molecular imaging
  - Key component of 3-dimensional imaging (biological cells)
Raison d'être for molecular depth profiling

• Sensitivity for imaging is limited with static SIMS.

\[
\text{Signal from } 1 \, \mu m^2 \text{ pixel} = 10^6 \text{ molecules} \\
\times 10^{-4} \text{ ionization efficiency}.
\times 10^{-2} \text{ damage threshold} \\
\times 10^{-1} \text{ instrument transmission}
\]

\[= 0.1 \text{ count per pixel} \]

\[
\text{Signal from } 1 \, \mu m^3 \text{ voxel is } 10^5 \times \text{ higher!}
\]

• Few methods exist for studying buried interfaces.

• Required for 3-dimensional imaging.
Molecular depth profiling – What makes it, what breaks it and what fixes it?
Molecular depth profiling requires larger clusters


But what projectiles to use?

<table>
<thead>
<tr>
<th>Projectile</th>
<th>m/z</th>
<th>Proponent(s)</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$_3^+$, Bi$_3^+$</td>
<td>591-627</td>
<td>Vickerman, ION-TOF,</td>
<td>2003</td>
</tr>
<tr>
<td>Au$_{400}^{4+}$</td>
<td>19,700</td>
<td>Schweikert</td>
<td>2008</td>
</tr>
<tr>
<td>C$<em>{60}^+$, C$</em>{60}^{++}$, C$_{60}^{+++}$</td>
<td>720</td>
<td>Vickerman</td>
<td>2005</td>
</tr>
<tr>
<td>Ar$_{2500}^+$</td>
<td>100,000</td>
<td>Yamada, Matsuo, ULVAC-PHI</td>
<td>1998, 2010</td>
</tr>
<tr>
<td>H$_2$O/Alcohol snowballs</td>
<td>massive</td>
<td>Hiraoka</td>
<td>2007</td>
</tr>
<tr>
<td>Cs$^+$ (&lt;300 eV)</td>
<td>133</td>
<td>Houssiau</td>
<td>2008</td>
</tr>
<tr>
<td>Liquid droplets</td>
<td>Massive</td>
<td>Cooks and DESI</td>
<td>2006</td>
</tr>
</tbody>
</table>
Trehalose/Peptide model system

**Trehalose** 2 nm rms surface roughness as determined by AFM

Mix peptide with trehalose

**Spin coat** solution on 5 × 5 mm Si wafer

Our first attempt at molecular depth profiling with $C_{60}$

- Si, m/z 28
- M-OH of trehalose, m/z 325
- M+H of GGYR, m/z 452

1 nm rms roughness

AFM crater shape

Integrated Peak Intensity (counts/nC)

Depth, nm

Trehalose + Gly-Gly-Tyr-Arg (100:1) film

Dynamically created preformed ions

• SIMS ion yield
• Yield of neutral molecule, via laser postionization

Ion yield increases to steady state after about 5 nm of erosion.


See also, Daniel Brenes, Monday, 16:20, Fundamentals, for more details
Why does it work? Molecular dynamics provides a clue.

Model Ag\{111\} crystal consisting of 800,000 target atoms. MD simulations performed at 20 keV using the MD/MC – CEM interaction potential

Courtesy of Zbigniew Postawa
And to compare at the end...

http://galilei.chem.psu.edu/  http://users.uj.edu.pl/~ufpostaw/
Why does it work?

**Erosion Dynamics**

\[ f_{\text{sputter}} = j_p \cdot Y_{\text{tot}} \cdot c_s \]

\[ f_{\text{damage}} = j_p \cdot \sigma_D (n \cdot d) \cdot c_s \]

Primary ion beam

altered layer \( d \)

\[ f_{\text{supply}} = j_p \cdot Y_{\text{tot}} \cdot c_{\text{bulk}} \]

*P.S. Ho et al., 1976; Gillen & Williams 1990*

Andreas Wucher
Erosion dynamics model

• assume: Signal \( (S) \propto c_S \)

\[
\frac{S_{\text{steady state}}}{S_0} = \frac{Y_{\text{tot}}}{Y_{\text{tot}} + nd\sigma_D}
\]

\[
S(f) = S_{ss} + (S_0 - S_{ss}) \exp\left[-\left(\frac{Y_{\text{tot}} + \sigma_D}{nd}\right) \cdot f\right]
\]

• disappearance cross section \( \sigma \)

• determine \( \sigma, S_0 \) and \( S_{ss} \) from fit to data

\[ \sigma_D = \sigma \left(1 - \frac{S_{ss}}{S_0}\right) \]

• determine \( Y_{\text{tot}} \) from erosion rate

\[ d = \frac{Y_{\text{tot}}}{n \cdot \sigma} \cdot \frac{S_0}{S_{ss}} \cdot \frac{1 - S_{ss}/S_0}{n \cdot \sigma} \]
Model parameters determined at different incident angles

300 nm cholesterol film on Si at 40 keV C\textsubscript{60}

\[ \varepsilon = \frac{Y_{\text{tot}}}{n d \sigma_D} \]

Δ-layer model systems

signal

ion fluence

fwhm

Lipid Bilayers

Dimyristoyl Phosphatidate (DMPA), 4 nm

Arachidic Acid (AA), 100 nm

Irganox 1010, 50 – 100 nm

Irganox 3114, 3 nm

20 laboratory VAMAS study, from National Physical Laboratory, U.K.
Construction of LB multilayer films

Temperature is a key variable for $C_{60}$ depth profiling

Combine low T with angle and KE to optimize.


<table>
<thead>
<tr>
<th>At 100 K</th>
<th>FWHM, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 keV at 40°</td>
<td>20.7</td>
</tr>
<tr>
<td>40 keV at 71°</td>
<td>15.5</td>
</tr>
<tr>
<td>20 keV at 40°</td>
<td>16.0</td>
</tr>
<tr>
<td>20 keV at 71°</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Stack images to begin 3-D protocols.
Molecular Depth Profiling and Sculptured Craters

Wedge beveling

- Topography and yield as a continuous function of depth
- Up to 10000X lateral magnifications via imaging

![Diagram of wedge beveling with dimensions and angles]
AFM Line Scans from Wedge

Room Temperature 300 K

90 K
Subtract 36-point Savitzky-Golay smoothed line from the original line to yield height fluctuation.

Quantitative Assessment:

\[ R_q(i) = \sqrt{\frac{1}{2N} \sum_{k=i-N}^{i+N} [\Delta h(k)]^2} \]

SIMS Images with Wedge-Beveling

Wedge Crater Side View

Wedge Crater Top View

Red: m/z 42 from Irganox 3114
Green: m/z 60 from Si Substrate

Improving Depth Resolution

This just in! Quality of depth profile depends upon ion dose

Irganox 3114/1010 Sample, with 40° 40 keV $C_{60}^+$ at 300 K

More at 17:40 today.
Difference between Irganox and lipid bilayer?

Projectile penetration of 15 keV C$_{60}$ Molecules

AA overlayer

Benzene crystal

Large penetration depth

Small penetration depth

Channeling of projectile fragments

Can molecular dynamics provide some insight into molecular depth profiling?


Barbara Garrison, Monday at 15:30

\[ RMS = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (z_i - \bar{z})} \]
RMS (at saturation) vs. kinetic energy and angle

We have a winner!

Next step: hybrid models

\[ \frac{d\theta_i}{dx} = -C_j \theta_i - \cdots - \]
\[ -D_{j \rightarrow j-1} \theta_i - D_{j \rightarrow j+1} \theta_i - \]
\[ -\cdots + D_{j-1 \rightarrow j} \theta_{i-1} + D_{j+1 \rightarrow j} \theta_{i+1} + \cdots \]

Wucher, Krantzman, Lu and Winograd, Monday Fundamentals, 10:30 am

Paruch, Garrison and Postawa, Thursday Poster
What does this all mean for 3-dimensional imaging?

- Deposit model organic film
  - ~ 300 nm Trehalose + Peptide | Si
- write pattern with Ga beam
- take topography data
  - before depth profiling
- take SIMS image stack
- take topography data
  - after sputtering
- calibrate depth scale
Differential sputtering highlights the need to independently provide depth information at each pixel.

Directly stacked images

Depth scale corrected

And, there can be large effects of lateral inhomogeneity

- Lateral variation of sample up to 40 nm
- "intrinsic resolution" of several nm
3-d imaging examples are emerging
And so....

• With the emergence of cluster projectiles, molecular depth profiling has become a major part of SIMS research.
• At least 6 factors are found to influence quality and our understanding is deepening quickly.
• 3-D imaging is the next big thing...
• Instrumentation poised for a change, I hope.
Copy of Leonardo’s lost painting.

The lost painting, The Battle of Anghiari (1505) believed to be still hidden beneath later frescoes in the Hall of Five Hundred (Salone dei Cinquecento) in the Palazzo Vecchio, Florence.