Surface mass spectrometry of organics and nano-objects
Part I - Watching chemistry in hi-definition with secondary ion mass spectrometry

www.npl.co.uk/nanoanalysis

Ian Gilmore, National Physical Laboratory (NPL), UK
Overview

1. Instrument optimisation and practical analysis
2. Interpretation, identification and informatics
3. Analysis of nano-objects
Organic and nano-analysis - What analysts need?

- Higher MSIY
- Higher spatial resolution
  - SIMS
  - AFM
- 3D analysis of nanolayers
- Nanoparticles

Accreditation, repeatability and constancy
Organic and nano-analysis - What analysts need?

Higher MSIY

 Higher spatial resolution

SIMS

AFM

3D analysis of nanolayers

Nanoparticles
(4) What can be done to increase the signal intensity?

\[ Y = Y_{\text{lin}} + B \left( \frac{U_0}{kT} \right) Y_{\text{lin}}^2 \]

\[ K_{n,1} = \frac{Y_n(E)}{nY_1(E/n)} \]

\[ \text{Total yield} \]

\[ \text{linear} \]

\[ \text{non-linear} \]

\[ n = 13 \]

\[ n = 2 \]

\[ n = 1 \]

\[ \text{M. P. Seah, SIA 39 (2007) 634} \]
(4) What can be done to increase the signal intensity?

For large molecules $\text{MSIY} \propto Y^2$

M. P. Seah, SIA 39 (2007) 890
(1) organic depth profiles - cholesterol

- Careful preparation of even films.
- Interface position measured using SiOH\(^{(1)}\) and molecular ion correlation method.

(2) Sputtering yield volumes, SY_v

- C₆₀ sputtering yield volumes (SY_v) approximately linear with energy.
- SY_v (25 keV Bi₃) approximately equivalent to SY_v (18 keV C₆₀)
(3) Useful lateral resolution (ULR)

We simply extend Kollmer’s\(^{(1)}\) useful lateral resolution (using a disappearance cross section) to the general case where a signal intensity is retained as material is consumed.  

\( L(d) = s \sqrt{ \frac{A}{\sum_{0}^{d} I} } \)

\( L(d) = \) ULR at dose, \( d \), giving a signal to noise, \( s \), in a pixel

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\( S=3 \)

\( C_{5H_{11}} \)

\( C_{21H_{37}O_{4}} \)

\( C_{27H_{45}} \)

\( C_{27H_{45}O} \)

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\( T \) Salter, in preparation

(3) ULR - cholesterol

To practically achieve 50 nm resolution in organics need:

- High brightness large cluster source OR increase ionisation efficiency

T Salter, in preparation
Cluster Primary Ion Signals

From published data using these concepts all primary ions may be related for signal output.
MALDI
G-SIMS & MS / MS
Cluster ions
G-tip
Increased ionisation efficiency
10 yrs
Large cluster sources
Bright Large cluster sources
Ultimate Spatial Resolution
Surface and Nanoanalysis
Full chemical structure
Analysis with some structure
Chemical state analysis
Elemental analysis
Material properties (modulus, density of states)
Simple material contrast
Bulk analysis
Electrospray MS
EI+MS
ICP-MS
TEM + PEELS
AES
XPS
SNO
AFM
STM
EPMA
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Conclusions

1. For many organic molecules ULR = 100 nm consuming material up to 30 nm.

2. Gas cluster sources limited brightness, spot size > 1 μm.

3. LMIS (e.g Bi₃) high brightness but ULR plateaus ~ 100 nm owing to damage.

4. High brightness large cluster sources are required < 100 nm resolution.

5. Increasing the ionisation efficiency is a future challenge.
Organic and nano-analysis - What analysts need?

Higher MSIY

Higher spatial resolution
- SIMS
- AFM

3D analysis of nanolayers

Nanoparticles
Strong growth in publications and understanding but limited take up in industry. Why?

Topic=(("depth profile" OR "depth profiling" OR "Three-dimensional") AND ("Organic" OR "Molecular" OR "polymer") AND ("SIMS" OR "secondary ion" OR "XPS" OR "x-ray photoelectron") NOT ("epitaxy" OR "molecular beam" OR "epitaxial" OR "molecular ion")
Organic depth profiling – a new chemical analytical capability

**Biological systems**

Top view


Side view


**Devices**


*A Shard et al, JPC B 112 (2008) 2596*

3D-SIM – subdiffraction optical techniques

[http://microscopy.lifesci.dundee.ac.uk/omx/](http://microscopy.lifesci.dundee.ac.uk/omx/)
Organic depth profiling – early days


- “Molecular depth profiling”
- Increase lateral resolution
- Model: “a competition between primary beam damage and its removal by sputtering”

G Gillen & S Roberson, RCM, 12 (1998) 1303
Erosion dynamics model – Cheng, Wucher & Winograd

Fluence-Dependent Erosion Rate

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


A Wucher, SIA, 40 (2008) 1545

Linear

Exp
Key analytical parameters and methods

<table>
<thead>
<tr>
<th>Parameter / method</th>
<th>Analytical performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Energy</td>
<td>• Profile quality</td>
</tr>
<tr>
<td>2. Projectile type</td>
<td>• Depth resolution</td>
</tr>
<tr>
<td>3. Angle of incidence</td>
<td>• Quantification</td>
</tr>
<tr>
<td>4. Sample rotation</td>
<td>• Speed</td>
</tr>
<tr>
<td>5. Sample cooling</td>
<td></td>
</tr>
<tr>
<td>6. Bevel methods</td>
<td></td>
</tr>
</tbody>
</table>

For nice reviews see:

C Mahoney, Mass Spectrom Reviews, 29 (2010) 247
PL developed delta layer to study fundamentals of cluster ion beam sputtering

- **Sputtering yields**
- **Novel ion beams** 
  \[ \text{Ar}_{500-1000} \text{ clusters} \]
  - J L S Lee et al., *Anal. Chem.* 2010, 82, 98

- **Depth resolution**

- **Quantification**

- **Rotation and cooling**

- **Repeatability and reproducibility**

- **Incidence angle**

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**Projectiles and energies**

- A Shard et al., *JPC B* 112 (2008) 2596

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**Volume fraction Irganox3114**

\[ X_{3114} \]

**Participant L:** 10 keV, 45°, -80° C

**Participant E:** 20 keV, 45°, rotation

**Participant S:** 20 keV, 76°

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**Incidence angle**


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**Repeatability and reproducibility**


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**Depth resolution**

- A Shard et al., *JPC B* 112 (2008) 2596
(1) Effect of ion beam energy – sputtering yield

\[ D = S_\infty F + \frac{(S_0 - S_\infty)}{\sigma_S} \left(1 - \exp\left(-\frac{\sigma_S F}{S_0 - S_\infty}\right)\right) \]

A Shard et al, JPC B 112 (2008) 2596

- Data from organic delta layers suggest that the sputtering yield in Irganox 1010 is not fully linear with dose.

SY approximately linear with energy
(1) Effect of ion beam energy – depth resolution

- 45° incidence, room temp
- Good signal for all 4 marker layers above 20 keV
- Sputtering yields reduce slowly with dose
- Higher energy degrades depth resolution

Depth resolution better with lower energy

A Shard et al, Submitted
(1) Effect of ion beam energy – depth resolution

- The depth resolution degrades with increasing energy and depth, consistent with AFM data.


Topography is an important issue
(2) Effect of primary ion type – $C_{60}^+$ and $Bi_n^+$

$C_{60}$ good, metal clusters not suitable for profiling (though fine for increased useful lateral resolution)

F M Green et al, submitted
(2) Effect of primary ion type – Ar\(^+\), Cs\(^+\), SF\(_5\)\(^+\)

- No molecular information!
- SF\(_5\)\(^+\) (8 keV) – detects first marker layer with sample cooling
- Ar\(^+\) (3 keV) – constant sputtering yield after large initial changes
- Cs\(^+\) (3 keV) – sudden catastrophic change after 2 layers
- Cs\(^+\) (150 eV) – successful profile but very low sputtering yields and extended tail

C\(_{60}\) good

A Shard et al, Submitted
(2) Effect of primary ion type – argon clusters

- Ar gas cluster ion gun mounted at 45° to sample surface
- Acceleration up to 20 keV
- Mean cluster size 500-1000 Ar atoms
- FWHM of cluster size distribution ~ mean cluster size
- For spectra, further mass filtering used
- DC beam current 8 nA
- Spot size < 0.5 mm
- New system in development

$C_{60}$ vs. Ar clusters – sputter induced roughness

AFM measurement of sputter-induced topography on Irganox 1010:

- Initial $R_q$ 0.3 nm
- $Ar_{500}$ (9.5 keV) sputtered depth 190 nm $R_q = 1.58$ nm
- $C_{60}$ (10 keV) sputtered depth 171 nm $R_q \sim 10$ nm!

- Ar clusters – $R_q < 5$ nm after sputtering to 420 nm for all cluster size and energy (up to 17 keV).
- $R_q$ increases with sputter depth and energy, and decreases with cluster size.
- $C_{60}$ standard condition – $R_q \sim 35$ nm after sputtering to 350 nm at 10 keV energy

Ar clusters offer potential for high depth resolution and significant benefits over $C_{60}$ under standard operating conditions

(2) Effect of primary ion type – argon clusters

PC and PS

Successful depth profile of OLED materials


$\text{C}_6\text{O}$ good but argon clusters better

5 keV $\text{Ar}_{2500}$ clusters – PI film

Miyayama et al, JVST A 28 (2010) L1
Sample: OML-05-G

Is the carboniferous period over?
(3) Effect of angle of incidence

20 keV C\textsubscript{60} sputtering of PC - PS (similar)


20 keV C\textsubscript{60} on Irganox 1010

A. Shard, 44\textsuperscript{th} IUVSTA Workshop, Edinburgh, 2007

<table>
<thead>
<tr>
<th>Angle</th>
<th>(S_{ss}/S_0)</th>
<th>(Y_{tot})</th>
<th>Interface width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.17</td>
<td>503</td>
<td>32</td>
</tr>
<tr>
<td>73</td>
<td>0.45</td>
<td>425</td>
<td>19</td>
</tr>
</tbody>
</table>

40 keV C\textsubscript{60} on cholesterol

(3) Effect of angle of incidence – depth resolution

- 76° incidence angle improves profiles dramatically
- Also allows $C_{60}$ depth profiling of PS and PC

(4) Effect of sample rotation – depth resolution & SY

- Rotation gives constant sputtering yields and maintains depth resolution throughout C$_{60}$ profile
- Initial sputtering yields and depth resolutions unaffected by rotation

(5) Effect of sample cooling – depth resolution & SY

- Cooling gives constant sputtering yields and maintains depth resolution throughout $C_{60}$ profile
- Initial sputtering yield reduces but uncorrelated to profile improvement

Conclusions (1)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Energy</td>
<td>Lower energy better depth resolution</td>
</tr>
<tr>
<td>2. Projectile type</td>
<td>C$_{60}$ good, argon cluster better</td>
</tr>
<tr>
<td>3. Angle of incidence</td>
<td>Grazing ($\sim$75°) major improvement depth resolution, constancy of SY, can profile PC, PS</td>
</tr>
<tr>
<td>4. Sample rotation</td>
<td>Major improvement of depth resolution, constancy of SY</td>
</tr>
<tr>
<td>5. Sample cooling</td>
<td></td>
</tr>
<tr>
<td>6. Bevel methods</td>
<td>Could be useful for some devices</td>
</tr>
</tbody>
</table>
From Antonino Licciardello’s talk at SIMS XVII, Toronto, 2009

standard

NO dosing


NB: m/z 105 (not reported in figure) has the same behaviour with initial decrease, plateau and fall at interface
The need for standards

Quantifiable, Repeatable, Reliable and Meaningful Results

£££ of Publicly funded research

• International Standards encapsulate the research knowledge.
• Uses best science to provide procedures and methods that give reliable, repeatable and meaningful analysis.
• In dynamic SIMS for the semiconductor industry 8 ISO standards have been published.
• ISO TC 201 is now looking at organic depth profiling. Recent VAMAS study has been an important start.
Conclusions (2) – The End

• **Many researchers** have contributed to the rapid knowledge base to understand organic depth profiling.

• Best conditions are **low energy** (but avoid C deposition), **grazing incidence, sample rotation, sample cooling**.

• Argon clusters are ultimately likely to be better than C$_{60}$ – but with above C$_{60}$ conditions is ~ as good.

• **NO and cooling** allows profiling of industrially relevant polymers.

• There is a need to develop standards for practical analysis.

   Exciting times …
Organic and nano-analysis - What analysts need?

Higher MSIY

3D analysis of nanolayers

Higher spatial resolution

Nanoparticles
Nanoparticles in industry

Drug Delivery

Catalysts

Standardisation, Regulatory requirements and (Eco)toxicology

Cosmetics & Sunscreens

Biodiagnostics
Sputtering of nanoparticles using SIMS

Fundamentals

• Collision cascade dimensions similar to size
• Increased surface area for emission
• Energy confinement

Potential applications

• Surface chemistry and functionalisation
• Composition depth profile of core-shell nanoparticles


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SEM images before sputtering

10 nm

20 nm

50 nm

100 nm
**Experimental**

- ION-TOF TOF-SIMS IV
- Bi\(^+\) and Bi\(_3^+\) depth profiles taken at 25 keV
- C\(_{60}^{2+}\) depth profiles taken using ‘dual beam’ mode, 20 keV:
  
  Higher energy used to avoid region of carbon deposition (< 6.5 keV from J L S Lee et al., *Appl. Surf. Sci.* (2008))

- Thin Au film as bulk sample for comparison
Sputtering of Au films

- Uniform Au films (29.4 nm) evaporated onto Si wafer
- Au\(^{-}\) ion yield is enhanced significantly in SiO\(_2\)
- C\(_{60}\)\(^{2+}\) shows the sharpest interface – ion beam of choice
**Negative ion profile of nanoparticles (20 nm)**

- APTES removed from exposed substrate
- Quasi steady state as NP sputters away
- SiO$_2$ removed from exposed substrate
- Au NPs and remaining APTES / SiO$_2$ removed

Dose (10$^{18}$ ions/m$^2$)

Normalised intensity (log)

- CN
- Si$_2$-
- SiO$_2$-
- Au-
- Au$_3$-
- C$_{60}^{++}$
- Bi$_3^+$
Negative ion profile of nanoparticles (100 nm)

- Consistent profiles were obtained for 10 nm, 20 nm, 50 nm and 100 nm NPs.
- All profiles show two clear interfaces, between SiO$_2$/Si and Au/Si.
- Sputtering and removal of NPs well behaved.

APTES and SiO$_2$ removed from exposed substrate.
Au NPs and remaining APTES / SiO$_2$ removed.

Quasi steady state as NP sputters away.
SEM images after sputtering (20 nm)

Nanoparticles stay intact during sputtering!
SEM images after sputtering (100 nm)

Gold topped ‘pillars’ consistent with interpretation

\[ C_{60}^{++} \]
Sputtering yields of nanoparticles

Sputtering yields expected to increase for NPs due to surface effect and energy confinement

\[ \text{Au (16 keV) } \rightarrow \text{Au NP (20 nm)} \]


Enhancement factor \( \sim 2.5 \)

First experimental data of nanoparticle sputtering yields – clear enhancement observed

\[ \text{C}_{60}^{2+} (20 \text{ keV}) \rightarrow \text{Au NP} \]
What about surface chemistry?

Citrate characteristic peaks $\text{CO}_2\text{H}^-$ and $\text{C}_2\text{O}_2\text{H}_3^-$ observed in all profiles

For 10 nm NPs, increased sputtering yields lead to a higher disappearance cross section!
Nanoparticles – melting effects (1)

Nanoparticles may melt during SIMS analysis from the large amount of energy deposited by primary ions.

For thermally isolated NPs

<table>
<thead>
<tr>
<th>NP size (nm)</th>
<th>No. impacts to melt at 20 keV</th>
<th>Melting dose (x 10^{16} ions/m^2)</th>
<th>% of depth profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1</td>
<td>0.5</td>
<td>1.3%</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>1.1</td>
<td>0.3%</td>
</tr>
<tr>
<td>50</td>
<td>53</td>
<td>2.7</td>
<td>0.2%</td>
</tr>
<tr>
<td>100</td>
<td>421</td>
<td>5.3</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

SEM of 100 nm NPs (after 5 x 10^{18} ions/m^2)

- Nanoparticles may have lower ‘static limit’ than bulk material.
- Low energy ion beams required for surface chemistry and depth profiling.
Nanoparticles – melting effects (2)

Sputtered using Ga$^+$ ions (30 keV) and simultaneously observed using SEM

Conclusion

- Significant enhancement in NP sputtering yields – first experimental data obtained

- Au nanoparticles model system gives consistent and interpretable depth profiles and allows detection of citrate coating

- ‘Static limit’ may be lower and nanoparticles may melt during analysis – low energy ion beams, very low doses and sample cooling recommended
Finis