XPS depth Profiling with the new MAGCIS cluster ion source, from polymers to inorganic samples

J.J. Pireaux, P. Louette
Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre Dame de la Paix

, R. G. White, P. Mack and T. S. Nunney
Thermo Fisher Scientific
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Thick tyrosine layer to check for compositional & chemical stability

Cluster profiling of phenylalanine and tyrosine multilayers
Intact and damaged multilayers of amino acids
Monatomic And Gas Cluster Ion Source - MAGCIS

- Monatomic And Gas Cluster Ion Source (MAGCIS)
  - Single source for monatomic and cluster beams
  - Available on K-Alpha, Theta Probe and E250Xi
  - Cluster mode
    - Variable cluster sizes (>2000 atoms)
    - Energy/atom: 1 eV upwards
- Monatomic mode
  - Based on existing EX06 ion source
  - 200 eV – 4 keV
  - Full control through Avantage software
MAGCIS

- Nozzle
- Cluster Gas inlet
- Ionization region
- Monatomic gas inlet
- Skimmers
- Electrical connections
- Focus & scanning electrodes
- Mass selection
Cluster ions v monatomic ions

Monatomic ion beam

Cluster ion beam
Introduction

Amino acid multilayer films

- Biosensor applications of amino acid multilayer films
  - Surface Plasmon Resonance (SPR) biosensors
    - Optical sensors exploiting electromagnetic interactions between\(^2\)
      - Analyte in solution
      - Biomolecule immobilized on SPR sensor surface
    - Offer benefit of real-time analysis
  - Role of amino acid multilayers in SPR biosensors
    - Creates a surface for bioactive ligands to bind to
    - Can control ligand packing density, which affects biosensor performance
    - Structure of the amino acid multilayer modifies resonance with detecting substrate, e.g. Au or Si

Schematic of SPR biosensor with amino acid multilayer\(^1\)

Introduction

- Biosensor applications of amino acid multilayer films
- **Amino acid multilayer studied in this work**
  - Multilayer of phenylalanine (Phe) and tyrosine (Tyr)
  - Films deposited by thermal evaporation
Introduction

X-ray Photoelectron Spectroscopy (XPS)

- Elemental identification & quantification
  - Which elements are present and how much?
  - Can detect all elements except H
  - Detection limit >0.05 At% for most elements

- Chemical identification & quantification
  - Chemical environment
  - Functional groups

- Surface sensitivity
  - Information sampling depth <10nm
  - Excellent depth resolution during profiling
Evaluation of XPS analysis

Elemental quantification table

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured At%</th>
<th>Expected At%</th>
<th>Measured At%</th>
<th>Expected At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tyr</td>
<td>69.67</td>
<td>69.23</td>
<td>74.05</td>
<td>75.00</td>
</tr>
<tr>
<td>Tyr</td>
<td>21.62</td>
<td>23.08</td>
<td>15.85</td>
<td>16.67</td>
</tr>
<tr>
<td>Phe</td>
<td>8.71</td>
<td>7.69</td>
<td>10.11</td>
<td>8.33</td>
</tr>
</tbody>
</table>

Measured *as received* surface composition is as expected for *Tyr* and *Phe*.
Evaluation of XPS analysis

- Chemical analysis of amino acid films
  - **XPS is chemically sensitive**
    - Spectrum of phenylalanine shows components due to aromatic ring, C-C-NH₂ and OH-C=O groups
    - Quantitative chemical & elemental analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Observed At%</th>
<th>Expected At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (aromatic)</td>
<td>53.34</td>
<td>50.00</td>
</tr>
<tr>
<td>C (C-C-NH₂)</td>
<td>13.18</td>
<td>16.67</td>
</tr>
<tr>
<td>C (CO₂H)</td>
<td>7.47</td>
<td>8.33</td>
</tr>
<tr>
<td>N</td>
<td>10.13</td>
<td>8.33</td>
</tr>
<tr>
<td>O</td>
<td>15.88</td>
<td>16.67</td>
</tr>
</tbody>
</table>

Elemental quantification table

Phenylalanine <sub>as received</sub>

![Graph showing XPS analysis of phenylalanine](image)
Evaluation of XPS analysis

- Chemical analysis of amino acid films
  - **XPS is chemically sensitive**
    - Addition of a single OH group to phenyl ring shows clearly in hi-resolution C1s spectrum
    - XPS can easily chemically resolve carbon bonding environments in Phe and Tyr

<table>
<thead>
<tr>
<th>Element</th>
<th>Observed At%</th>
<th>Expected At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_{\text{aromatic}} )</td>
<td>40.50</td>
<td>38.46</td>
</tr>
<tr>
<td>( \text{C}_{\text{CCNH}_2} )</td>
<td>22.47</td>
<td>23.08</td>
</tr>
<tr>
<td>( \text{C}_{\text{CO}_2\text{H}} )</td>
<td>6.70</td>
<td>7.69</td>
</tr>
<tr>
<td>N</td>
<td>8.71</td>
<td>7.69</td>
</tr>
<tr>
<td>O</td>
<td>21.62</td>
<td>23.08</td>
</tr>
</tbody>
</table>

Elemental quantification table
Evaluation of XPS analysis

- Chemical analysis of amino acid films
  - Oxygen chemical analysis
    - High energy resolution O1s spectra allow extra OH group in Tyr to be tracked and quantified
      - Ratio of “red:blue” components in Tyr is measured at ~2:1, as expected
    - Small amount of “contaminant” oxygen in Phe O1s spectrum
Evaluation of XPS argon cluster profiling

- **Monatomic And Gas Cluster Ion Source (MAGCIS)**
  - Single source for monatomic and cluster beams
    - Profiling solution for inorganic & organic samples
  - Cluster capability can be added to XPS tool without taking up valuable extra space
    - Available on K-Alpha, Theta Probe and E250Xi
  - Profiling in the analysis chamber, at the standard XPS analysis position

MAGCIS fitted to Thermo Scientific K-Alpha
Evaluation of XPS argon cluster profiling

- Profiling of amino acid films
  - Amino acid films cannot be sputtered with monatomic argon
    - Chemical information is destroyed & composition is strongly modified
    - Cannot observe expected layer structure
    - Elemental composition strongly modified

Schematic of expected structure of amino acid multilayer

Elemental profile of amino acid layers with 200eV monatomic Ar⁺ beam
Profiling of amino acid films

Amino acid films cannot be sputtered with monatomic argon

- Chemical information is destroyed & composition is strongly modified
- Cannot observe expected layer structure
- Elemental composition strongly modified
- Chemical information is destroyed

Evaluation of XPS argon cluster profiling

C1s spectra from monatomic Ar+ profile of amino acid layers

Elemental profile of amino acid layers with 200eV monatomic Ar+ beam
Profiling of amino acid films

- Previously demonstrated use of Ar cluster beam for amino acid profiling
  - Subtle compositional changes through multilayer structure can be observed
  - Only slight degradation of sample is observed throughout profile

Schematic of expected structure of amino acid multilayer

Argon cluster profile of amino acid layers
Profiling of amino acid films

- Previously demonstrated use of Ar cluster beam for amino acid profiling
  - Subtle compositional changes through multilayer structure can be observed
  - Only slight degradation of sample is observed throughout profile
  - Chemical information is preserved

C1s spectra from Ar\textsubscript{1000} cluster profile of amino acid layers

Argon (Ar\textsubscript{1000}) cluster profile of amino acid layers
Evaluation of XPS argon cluster profiling

- Profiling of Tyr films
  - Stability of Tyr during argon cluster profiling
    - 50nm Tyr on Si
    - Elemental composition stays constant throughout film
      - Cluster profiling is NOT modifying composition of Tyr film

MAGCIS cluster profile of Tyr on Si

Composition of Tyr layer not modified by cluster profiling
Evaluation of XPS argon cluster profiling

- Profiling of Tyr films
  - Chemical stability of Tyr during argon cluster profiling
    - Chemistry of Tyr film NOT destroyed by cluster profiling

\[ \text{MAGCIS cluster profile of Tyr on Si} \]

- C1s spectra during profile
- Depth:
  - 25nm
  - 15nm
  - 0 nm

\[ \pi-\pi^* \text{ peak retained} \]

- Atomic percent (%)
  - C
  - O
  - N
  - Si

\[ \text{Etch Depth (nm)} \]

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Tyrosine reference
Profiling of amino acid multilayer

- Expected structure of multilayer
  - Alternating Phe/Tyr layers, with layer of Phe on top surface and 3 Tyr layers

- All three Tyr layers observed
  - Quantification change between Phe and Tyr as expected
  - Slight increase in carbon signal over 300nm depth (~1.2 At%)
  - Chemical resolution of Phe and Tyr oxygen throughout profile
  - Reasonable stability on $O_{Tyr}$ quantification
  - Depth resolution on last Tyr layer slightly degraded
XPS argon cluster profiling of amino acids

- Profiling of amino acid multilayer
  - **Expected structure of multilayer**
    - Alternating Phe/Tyr layers, with layer of Phe on top surface and 3 Tyr layers
    - Top Phe layer not observed
      - Damaged **BEFORE** analysis
  - **All three Tyr layers observed**
    - Quantification change between Phe and Tyr as expected
    - Slight increase in carbon signal over 300nm depth (~1.2 At%)
    - Chemical resolution of Phe and Tyr oxygen throughout profile
    - Excellent stability on $O_{\text{Tyr}}$ quantification

MAGCIS cluster profile of damaged amino acid multilayer
Monatomic v cluster profiling

- Many polymers cannot be sputtered with monatomic argon
- Chemical information is destroyed & composition is modified
- C1s spectra shown for ion beam etched Kapton
Monatomic v cluster profiling

- Many polymers cannot be sputtered with monatomic argon
- Chemical information is destroyed & composition is modified
- C1s spectra shown for ion beam etched Kapton

![As received](image1)

![4 keV 2000 atom Clusters, 200s](image2)

- Counts / s
- Binding Energy (eV)
- Adventitious contamination
- Shake-up
- N-C=O
- C-N
- O
- C-C

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Monatomic And Gas Cluster Ion Source

- Profiling of Irganox δ-layers
  - Check for depth resolution capabilities
    - ~10nm layers Irganox 3114
    - FWHM of nitrogen-containing layers almost constant throughout 300nm sputter depth

- **Table**

<table>
<thead>
<tr>
<th>δ-layer</th>
<th>FWHM/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.9</td>
</tr>
<tr>
<td>2</td>
<td>10.1</td>
</tr>
<tr>
<td>3</td>
<td>9.8</td>
</tr>
<tr>
<td>4</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Nitrogen portion of MAGCIS cluster profile of Irganox δ-layers

MAGCIS cluster profile of Irganox δ-layers

Irganox sample sourced from NPL
Cleaning metal oxide surfaces

- Benefits of cluster-cleaning $\text{Ta}_2\text{O}_5$:  
  - Removal of attenuating carbon contamination.  
  - Increased overall photoelectron signal.

Comparison of XPS survey spectra before and after argon cluster ion cleaning

**Spectra offset for clarity**
Cleaning metal oxide surfaces

- **Tantalum oxide film:**
  - Even low energy monatomic Ar\(^+\) ion sputter-cleaning causes a significant amount of Ta\(_2\)O\(_5\) reduction.
  - Argon cluster-cleaning gives no visible sign of oxide reduction.

<table>
<thead>
<tr>
<th>Cleaning method</th>
<th>Ta 4f oxide</th>
<th>Ta 4f reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Cluster ions</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>200 eV monatomic</td>
<td>70.4</td>
<td>29.6</td>
</tr>
</tbody>
</table>

*Comparison of Ta 4f spectra for monatomic Ar\(^+\) and argon cluster ion sputter-cleaning of Ta\(_2\)O\(_5\)*

*Substantial Ta\(_2\)O\(_5\) reduction with monatomic Ar\(^+\) sputtering*

*Relative intensities of Ta 4f oxide and reduced components before & after sputter-cleaning*
Profiling of organic FET

- Copper phthalocyanine (CuPc) is an organic semiconductor component of field-effect transistors
- Electrical properties of FET modified by
  - Composition & chemistry of CuPc layer
  - Interfacial chemistry (CuPc / SiO₂ and SiO₂ / Si)
- Use XPS and MAGCIS to analyze a film of CuPc deposited on thick SiO₂ on Si
  - Cluster beam for film composition, chemistry & thickness of CuPc layer
  - Monomer beam for similar information from SiO₂ layer

Acknowledgements Prof. Dr. Dr. h.c. Dietrich R.T. Zahn, Dr Daniel Lehmann, Iulia Korodi
Profiling of organic FET

- Cluster profile of CuPc / SiO$_2$
  - Ratio of N : Cu is stable throughout the profile
    - cluster profiling is not adversely changing composition
Profiling of organic FET

- **Cluster profile of CuPc / SiO₂**
  - Profiling of copper chemistry
    - Satellite feature observed ~944eV, indicating Cu(II) chemical state
    - Ratio of “satellite/core-level” intensities is maintained throughout profile
      - Cu(II) chemistry is not being adversely modified by cluster beam
    - Some more reduced copper also observed prior to sputtering
      - Disappears after sputtering with cluster beam, indicating chemical state is localized to top surface
      - Successful profiling of Cu(II) versus more reduced copper
Profiling of organic FET

- CuPc film (0-2nm)
  - XPS analysis of *as received* CuPc surface
    - More carbon than expected (adventitious contamination)
  - C1s spectrum has some similarities and some differences compared to reference CuPc powder

<table>
<thead>
<tr>
<th></th>
<th>Expected At%</th>
<th>Observed At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>78.0</td>
<td>82.6</td>
</tr>
<tr>
<td>N</td>
<td>19.5</td>
<td>16.5</td>
</tr>
<tr>
<td>Cu</td>
<td>2.4</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Profiling of organic FET

- **CuPc film (4-8nm)**
  - Spectral data from MAGCIS cluster profile (after removing contamination layer)
  - XPS analysis of remaining organic layer
    - Quantification agrees well with expectation

<table>
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<th>Observed At%</th>
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<tr>
<td><strong>C</strong></td>
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<tr>
<td><strong>N</strong></td>
<td>19.5</td>
<td>19.4</td>
</tr>
<tr>
<td><strong>Cu</strong></td>
<td>2.4</td>
<td>1.9</td>
</tr>
</tbody>
</table>

- C1s spectrum similar to structure of CuPc reference powder
  - Core level peaks due to benzene and pyrrole rings
  - Complex band of satellite features observed
    - Due to shake-up transitions involving the conjugated \( \pi \)-system in Pc
- MAGCIS cluster beam has successfully cleaned contamination to reveal CuPc layer
  - No adverse chemical modification of CuPc carbon chemistry
MAGCIS profiling of organic FET

- Combined cluster/monomer profile of CuPc / SiO₂ / Si
  - MAGCIS has been used to profile mixed organic/inorganic field-effect transistor

- CLUSTER profiling of CuPc / SiO₂
  - Composition & chemistry of CuPc is not adversely affected by cluster profiling
    - Cu (II) successfully profiled
    - CuPc layer is 12.5nm thick

- MONOMER profiling of SiO₂ / Si
  - Composition of SiO₂ layer as expected
    - SiO₂ layer is 120nm thick
Summary

**MAGCIS** (/mæɡˈsɪs/)  
*noun*  
an ion source able to generate both monatomic and cluster beams of argon

- **Summary**
  - **XPS cluster profiling** is a strong characterization technique for amino acid multilayers
    - Excellent quantification
    - Chemical profiling with minimal damage
    - Good depth resolution throughout profile