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

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Amino acid multilayer films for biosensor applications

Evaluation of XPS for analysis of amino acids
Quantification & chemical bonding
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Organic Δ-layer standard to check depth resolution capabilities
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

Cluster Gas inlet

Skimmers

Ionization region

Nozzle

Monatomic gas inlet

Focus & scanning electrodes

Mass selection

Electrical connections
Cluster ions v monatomic ions

Monatomic ion beam

Cluster ion beam
Introduction

- **Biosensor applications of amino acid multilayer films**
  - **Surface Plasmon Resonance (SPR) biosensors**
    - Optical sensors exploiting electromagnetic interactions between
      - 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

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[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

**Schematic of expected structure of amino acid multilayer**

- **Phenylalanine (Phe)**
- **Tyrosine (Tyr)**
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**

**Phe and Tyr references**

<table>
<thead>
<tr>
<th>Element</th>
<th>Measured</th>
<th>Expected</th>
<th>Measured</th>
<th>Expected</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
<td>At%</td>
</tr>
<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*.

**Elemental quantification table**

![Tyr](image1.png)

![Phe](image2.png)
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></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_{CCNH₂}</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 as received

![Phenylalanine structure](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>C_{aromatic}</td>
<td>40.50</td>
<td>38.46</td>
</tr>
<tr>
<td>C_{CCNH2}</td>
<td>22.47</td>
<td>23.08</td>
</tr>
<tr>
<td>C_{CO2H}</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

![Graph showing binding energy vs. components for Phe and Tyr](image.png)
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
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

C1s spectra from monatomic Ar\(^+\) profile of amino acid layers

\(\pi-\pi^*\) shake-up disappears

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$_{1000}$ 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](image)

**Composition of Tyr layer not modified by cluster profiling**

- Atomic percent (%) vs. Etch Depth (nm)
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

MAGCIS cluster profile of Tyr on Si

- C1s spectra during profile
  - $\pi-\pi^*$ peak retained

- Atomic percent (%) vs Etch Depth (nm)
  - C
  - O
  - N
  - Si
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
  - 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

MAGCIS cluster profile of intact amino acid multilayer
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
Cleaning polyimide

- 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

![Graph showing binding energy and counts per second for As received and 4 keV, 2000 atom clusters, 200s profiles.](image)

Adventitious contamination

Counts / s

Shake-up

N-C=O, C-N, C-O, C-C
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

Nitrogen portion of MAGCIS cluster profile of Irganox Δ-layers

<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>

MAGCIS cluster profile of Irganox Δ-layers

Irganox sample sourced from NPL
Cleaning metal oxide surfaces

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

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

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

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
### 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

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**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 ∼944 eV, 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)

<table>
<thead>
<tr>
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<th>Expected At%</th>
<th>Observed At%</th>
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</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>

- C1s spectrum has some similarities and some differences compared to reference CuPc powder
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

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<td>19.5</td>
<td>19.4</td>
</tr>
<tr>
<td>Cu</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 / SiO$_2$ / Si
  - MAGCIS has been used to profile mixed organic/inorganic field-effect transistor

- CLUSTER profiling of CuPc / SiO$_2$
  - Composition & chemistry of CuPc is not adversely affected by cluster profiling
    - Cu (II) successfully profiled
    - CuPc layer is 12.5nm thick

- MONOMER profiling of SiO$_2$ / Si
  - Composition of SiO$_2$ layer as expected
  - SiO$_2$ layer is 120nm thick
Summary

**MAGCIS** (/mægˈsɪs/)  
*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