Depth Profiling of Organic Photovoltaic and OLED Materials by Cluster Ion Beams

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Challenges for Organic Electronics Research

- Efficiencies are based on optimum band matching and the physical dispersions of components
  - Work functions at discrete interfaces e.g. metal electrodes
  - Diffusion lengths of charge carriers

- Device lifetimes influence customer acceptance and profit margins
  - Atmospheric contamination (H₂O, O₂) degrade chemistry
  - Flexible designs challenge encapsulation technologies
  - Breakdown mechanisms are not well understood

- Chemical and molecular specific depth profiling is desired
  - Depth resolution of a few nm with high sensitivity
  - Cluster ion depth profiling interleaved with XPS and TOF-SIMS may be solution
Why use Depth Profiling for Organic Electronics?

- New “nanotechnology” products use extremely thin organic and polymer structures
  - OLEDs
  - Energy conversion materials and fuel cell membranes
- Fabrication process producing molecular gradients can result in significant differences in efficiency
- Product degradation can result from molecular oxidation and molecular diffusion
- Spectroscopy with a nano-scale depth of analysis (XPS and TOF-SIMS) needed for surface and depth profiling characterization of molecular composition and diffusion
## Comparison of XPS and TOF-SIMS

<table>
<thead>
<tr>
<th></th>
<th>XPS</th>
<th>TOF-SIMS</th>
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<tbody>
<tr>
<td>Probe Beam</td>
<td>Photons</td>
<td>Ions</td>
</tr>
<tr>
<td>Analysis Beam</td>
<td>Electrons</td>
<td>Ions</td>
</tr>
<tr>
<td>Spatial Resolution</td>
<td>10 µm</td>
<td>0.10 µm</td>
</tr>
<tr>
<td>Sampling Depth(Å)</td>
<td>5-75</td>
<td>1-10</td>
</tr>
<tr>
<td>Detection Limits</td>
<td>0.01atom %</td>
<td>1ppm</td>
</tr>
<tr>
<td>Information Content</td>
<td>Elemental</td>
<td>Elemental</td>
</tr>
<tr>
<td></td>
<td>Chemical</td>
<td>Chemical</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Molecular</td>
</tr>
<tr>
<td>Quantification</td>
<td>Excellent</td>
<td>Std. needed</td>
</tr>
</tbody>
</table>

www.phi.com
Scanning Micro Focused X-ray Source

- Electron Gun
- Aluminum Anode
- Raster Scanned Micro-Focused Electron Beam
- Monochromatic Raster Scanned Micro-Focused X-ray Beam
- Analyzer Input Lens
- Quartz Crystal Monochromator
- Sample
- Al X-rays
XPS survey spectra provide quantitative elemental information. High resolution XPS spectra provide quantitative chemical state information.
Unique Polymer "Fingerprint" Identification Using TOF-SIMS Spectra

XPS shows identical spectra for both polymers

\[ (\text{CH}_2\text{CHO})_n \quad \text{CH}_3 \]
Polypropylene glycol

\[ (\text{CH}_2\text{CH})_n \quad \text{O-CH}_3 \]
Polyvinylmethyl ether
Damage Accumulation Indicated by XPS

500 eV Ar⁺ Sputter

Damage is observed.
No Damage Observed by XPS

10keV C$_{60}^+$ Sputter

No damage observed.
Altered Volume & Sub-surface Damage

Residual $C_{60}$ sputter damage is mostly removed with the next $C_{60}$ impact event.

Non-$C_{60}$ sputter sources result in the accumulation of sub-surface damage.

Graphic courtesy B. Garrison & Z. Postawa.

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Molecular Dynamics: Ar$_{9000}^+$ GCIB on PS/Ag

The permission of the pictures is by courtesy of Professor Zbigniew Postawa, Jagiellonian University (Poland); L. Rzeznik, B. Czerwinski, B.J. Garrison, N. Winograd and Z. Postawa, "Microscopic Insights into the Sputtering of Thin Polystyrene Films on Ag(111) Induced by Large and Slow Ar Clusters", J. Phys. Chem C 112 (2008) 521.
Single Layer, Graded Composition OLED structure
Highly efficient, single-layer organic light-emitting devices based on a graded-composition emissive layer

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Graded Composition Structures Overview

- Graded Electron and Hole Transport Materials (ETM and HTM) with a green phosphorescent emitter
- 100% HTM at the Anode and 100% ETM at the Cathode
- Result
  - At 600 cd/m$^2$
    - Peak external quantum efficiency $\eta_{\text{E QE}} = (19.3 \pm 0.4)\%$
      - Corresponding to internal quantum efficiencies approaching 100%
    - Peak power efficiency $\eta_p = (66.5 \pm 1.3)$ lm/W
- These structures are simple to grow
- But need to confirm the chemistry of these structures is essential
Analytical Technique

- Thin film samples were characterized in a PHI VersaProbe II Scanning XPS system equipped with an Ar⁺ Gas Cluster Ion Beam source for depth profiling.
  - The GCIB source can be operated:
    * With Beam energies from 2.5 kV to 20 kV
    * Cluster size from <1000 to 5000

- The XPS system has excellent charge neutralization capability to compensate for differential charging at various interfaces.
Structure of the two molecules for OLED

- Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (Hole Transfer Material)

- Bathophenanthroline (BPhen) (Electron Transfer Material)
C 1s and N 1s Spectra for TCTA and BPhen

1.8 eV Separation
Sample Structure for OLED

**DEVICE**

- 150 nm ITO
- 100 nm BPhen/TCTA gradient
- 100 nm BPhen/TCTA gradient with Ir (ppy$_3$) dopant
- 1 nm LiF
- 75 nm Al

**XPS TEST STRUCTURES**

- 100 nm BPhen/TCTA gradient with and without dopant
- 100 nm TCTA
- 100 nm BPhen

**Silicon**
GCIB Depth Profile of TCTA:Bphen/SiO$_2$/Si

100 nm TCTA
100 nm BPhen
Silicon

$Ar_{2500}, 10$ kV, 2 nA, 3 mm x 3 mm
4 eV/atom GCIB
GCIIB Depth Profile of TCTA:Bphen/SiO$_2$/Si

100 nm TCTA
100 nm BPhen
Silicon

$\text{Ar}_{2500}$, 10 kV, 2 nA, 3 mm x 3 mm
4 eV/atom GCIIB

N 1s

Binding Energy (eV)

Atomic Concentration (%)
GCIB Depth Profile of Bphen:TCTA/SiO<sub>2</sub>/Si

Ar<sub>2500</sub>, 10 kV, 2 nA, 3 mm x 3 mm

4 eV/atom GCIB
**GCIB Depth Profile of Bphen:TCTA/SiO₂/Si**

- **BPhen Gradient**
- **TCTA Gradient**
- **Si**

Native Oxide

**Graphs:**
- **N 1s**
  - N1s (TCTA)
  - N1s (BPhen)

- **Atomic Concentration (%):**
  - C1s
  - O1s
  - Si2p

- **Binding Energy (eV):**
  - 410, 405, 400, 395, 390

- **Sputter Depth (nm):**
  - 0, 50, 100, 150

- **Ar₂₅₀₀, 10 kV, 2 nA, 3 mm x 3 mm**

- **4 eV/atom GCIB**

- **Peak Multiples:**
  - N1s (BPhen) 5x
  - N1s (TCTA) 5x

- **Other:**
  - GCIB Depth Profile of Bphen:TCTA/SiO₂/Si
N 1s Spectra from GCIB Depth Profile of Bphen:TCTA/SiO₂/Si

N1s (TCTA)
N1s (BPhen)

Binding Energy (eV)

Native Oxide
BPhen Gradient
TCTA Gradient

Si

100 nm

100%
Ir Emissive Compound from GCIB Depth Profile of Bphen:TCTA/SiO₂/Si

Ir 4f concentration 0.04 at %

Ar₂₅₀₀, 10 kV, 2 nA, 3 mm x 3 mm

4 eV/atom
Composite Multi-layer Inverted Organic Photovoltaic Device

Sample is comprised of various material types: Metal / Polymer / Oxide

PEDOT  PSS  P3HT

Ag Cap
PEDOT:PSS
P3HT:TiO₂ Nanorods
TiO₂
ITO
Glass

Hole Transport Layer
Bulk Heterojunction
Electron Transport Layer
Composite – Organic Photovoltaic Multi-layer

20 kV C\textsubscript{60} Cluster

- With Compucentric Zalar Rotation\textsuperscript{TM}
- Well defined layers
- Consistent sputter speed throughout the multilayer stack
Composite – Organic Photo Voltaic Multi-layer

20 kV Ar$_{1500}^+$ Gas Cluster, 13.3 eV/atom

- Poor layer definition
- Large variation in sputter rates
Fabrication Process versus OLED Efficiency

- Two fabrication processes of small molecular OLED’s
  - Spin coating (wet process): typically easier fabrication, lower efficiency
  - Evaporation has higher efficiency

- Emissive layers (ELs) studied for high efficiency green OLED’s
  - Guest
    - Bis[5-methyl-7-trifluoromethyl-5H-benzo©(1,5)naphthyridin-6-one]iridium (picolinate) (CF$_3$BNO)$_2$IrPLA
  - Host
    - 4,4’-bis(carbazol-9-y)biphenyl (CBP)
  - Wet efficiency 70 lm W$^{-1}$
  - Dry efficiency 21 lm W$^{-1}$

WHY?
Wet versus Dry Process: XPS Depth Profiles

- Same Ir composition similar when normalized by film thickness
- Wet process Ir guest has higher concentration at interface relative to dry process

Fig. 1. XPS elemental depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).
• TOF-SIMS with C\textsubscript{60} sputtering shows no change in molecular structure between outer surface spectra and 25 seconds sputtering

• XPS profile with C\textsubscript{60} is not a result of molecular decomposition
Wet versus Dry Process: TOF-SIMS Depth Profiles

**Fig. 3.** ToF-SIMS depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).

- Same Ir composition similar when normalized by film thickness
- Wet process Ir guest has higher concentration at interface relative to dry process
Wet versus Dry Process Model of Efficiencies

- Higher relative guest concentration at HT interface give lower turn-on voltage
- More hole trapping in dry process
- Wet process efficiency is ~ 3.5x higher than dry process

Fig. 4. Energy diagram and the route of charge carriers of OLED with EL prepared with (a) wet-process and (b) dry-process. The shade of CBP and (CF$_3$BNO)$_2$IrPLA indicates its relative concentration.
# Cluster Ion Source Summary

## The Choice of Ion Source for XPS Compositional Depth Profiling Is Application Dependent

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Ion Gun Type</th>
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<tbody>
<tr>
<td></td>
<td><strong>Ar Monoatomic</strong></td>
</tr>
<tr>
<td><strong>Metal</strong></td>
<td>• Preferred approach</td>
</tr>
<tr>
<td></td>
<td>• Differential sputtering and chemical change</td>
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<tr>
<td><strong>Ceramics</strong></td>
<td>• Differential sputtering and chemical change</td>
</tr>
<tr>
<td></td>
<td>• Not suitable for transition metal oxides TiO\textsubscript{2} / HfO\textsubscript{2} / WO\textsubscript{3}</td>
</tr>
<tr>
<td><strong>Organics</strong></td>
<td>• Significant Chemical Damage</td>
</tr>
<tr>
<td><strong>Polymers</strong></td>
<td>• Some Type-I crosslinking polymer to a depth of a few hundred nanometers</td>
</tr>
<tr>
<td><strong>Complex</strong></td>
<td>• Sample Dependent</td>
</tr>
<tr>
<td><strong>Materials</strong></td>
<td>• Preferred approach</td>
</tr>
<tr>
<td><strong>Semiconductors</strong></td>
<td>• Preferred approach</td>
</tr>
</tbody>
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*Note: The stars indicate the level of suitability for the given process.*
Summary and Conclusions

- Using Ar GCIB depth profiling and XPS we have been able to confirm the graded composition emissive layer structures.
- The chemistry of the materials remains unaltered by the Ar cluster ion beam.
- Sharp interfaces measured for layered structures.
- The depth profile of the Ir from Ir(ppy$_3$) dopant is clearly observable with a concentration of < 0.04 at. %.
- GCIB depth profiling is reliable reproducible and fast for these materials.
- C$_{60}$ provides excellent depth profiling of metal/organics/metal oxides/glass multi-layer structures.
- Similar use of C$_{60}$ and GCIB combined with TOF-SIMS can provide more molecular information.