Depth profiling of Organic Films using mixed C$_{60}^+$ and Ar$^+$ Ion-Sputtering

Jing-Jong Shyue, Ph.D.
Research Center for Applied Sciences, Academia Sinica
Department of Materials Science and Engineering, National Taiwan University

Principle of Depth Profile

• composition depth profiling with surface analysis techniques?
  erosion of specimen surface by energetic particle bombardment
• "sputtering"
• two possibilities for analysis:
  - freshly exposed surface (⇒ XPS, AES)
  - sputtered material (⇒ SIMS)
• depth profiling ⇒ remove controlled thickness

General Concepts of Sputtering
**XPS Depth Profiling**

- composition as a function of depth \( t \) in thin films
- XPS signal is generated near the surface (~3nm)
- sputtering provides layer sectioning
- depth profiles are usually shown as signal intensity versus sputter time (not depth)
- further calibrations required
  - convert sputter time to depth
  - signal intensity to atomic concentration
- however, ion sputtering can cause changes in the composition of the surface layers
  - surface segregation
  - preferential sputtering

**Sputtering with \( C_{60}^+ \) Ions**

- Traditional ion sources such as Ar and Ga can impart significant damage to a sample's surface
- \( C_{60} \) ions are more efficient in removing material and leave behind a relatively thin damage layer

**PHI 5000 VersaProbe SXM at Sinica (2007/6/18)**

- focused scanning XPS microprobe (<10μm spot size)
- dual beam charge neutralization
- xyzr five axis motorized sample manipulator
- floating column argon ion gun (0-5kV)
- 10kV \( C_{60} \) sputter ion gun
- Options:
  - UV light source for UPS
  - electron gun for AES (<μm resolution)
  - dual anode X-ray source (Mg, Zr)
Depth Profile of PEDOT:PSS on ITO Glass: Ar

<table>
<thead>
<tr>
<th>beam voltage</th>
<th>sputter time</th>
<th>atomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 kV</td>
<td>0.5 min</td>
<td>88% C, 3% O, 9% S</td>
</tr>
<tr>
<td>2 kV</td>
<td>1 min</td>
<td>88% C, 4% O, 8% S</td>
</tr>
<tr>
<td>1 kV</td>
<td>5 min</td>
<td>85% C, 6% O, 9% S</td>
</tr>
<tr>
<td>0.5 kV</td>
<td>15 min</td>
<td>85% C, 8% O, 7% S</td>
</tr>
<tr>
<td>expected</td>
<td>---</td>
<td>67% C, 24% O, 9% S</td>
</tr>
</tbody>
</table>

- sputter time extended with lowering the beam energy
- significant lost of O even at low beam energy
- Ar is not suitable for analyzing organic films

Depth Profile of PEDOT:PSS on ITO: C60

67% C, 24% O, 9% S
### Analysis of Organic Thin-Films with C60

- Chemical composition is preserved through the thickness.
- Chemical state of S is preserved and the PEDOT:PSS ratio does not change with sputtering.
- It is also possible to analyze organic/inorganic hybrid thin film (SiO$_2$/PEDOT:PSS).
  - Constant Si:PEDOT:PSS ratio through the thickness.
  - Uniform distribution of SiO$_2$ nano-dots.
- Preferential sputtering and sputtering-reduction did not be observed!!

### Sputter Depth Profile of Drug Distribution in a Biomedical Coating

#### 50-50 Rapamycin – PLGA Coating

- **Rapamycin**: Immunosuppressant Drug
- **Poly(lactic-co-glycolic acid)**: Biodegradable Host Polymer

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**Depth Profile of PEDOT:PSS on ITO: S Peak**

- 0.5kV Ar
- 10kV C60

**SiO$_2$/PEDOT:PSS on ITO Glass**

- 67% C, 24% O, 9% S
**Sputter Depth Profile of Drug Distribution in a Biomedical Coating**

50-50 Rapamycin – PLGA Coating

C$_{60}^+$ sputter depth profile reveals surface segregation of rapamycin

**Perfluoropolyester on CaF$_2$**

**OLED Device**

**OLED Device: EL/HTL/ITO**

- ETL
  - TPBi; 88%C, 11%N
- EL
  - CBP Host; 95%C, 5%N
  - Ir-containing Guest
- HTL
  - PEDOT:PSS; 67%C, 24%O, 9%S
- ITO
- Glass
**Full OLED Device**

- Atomic Concentration (%)
  - 88% C, 11% N
  - 95% C, 5% N

- Binding Energy (eV)
  - 410, 408, 406, 404, 402, 400, 398, 396, 394, 392

**Sputtering Rate of Cluster Ion Beam**

- Sputtering Rate of Cluster Ion Beam

**Electron Transporting Layer: TPBi**

- Electron Transporting Layer: TPBi

**10kV10nA C60 + 0.5kV220nA Ar**

- Slower sputtering rate, damage to chemical structure
**Depth Profile with Ar⁺/C₆₀⁺ Co-sputtering**

<table>
<thead>
<tr>
<th>beam voltage</th>
<th>sputter time</th>
<th>atomic concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.42 min</td>
<td>67% C, 24% O, 9% S</td>
</tr>
<tr>
<td>0.2 kV, 75 nA</td>
<td>4.24 min</td>
<td>67% C, 24% O, 9% S</td>
</tr>
<tr>
<td>0.1 kV, 300 nA</td>
<td>4.87 min</td>
<td>67% C, 24% O, 9% S</td>
</tr>
<tr>
<td>0.2 kV, 300 nA</td>
<td>3.76 min</td>
<td>67% C, 24% O, 9% S</td>
</tr>
<tr>
<td>0.1 kV, 600 nA</td>
<td>4.87 min</td>
<td>67% C, 24% O, 9% S</td>
</tr>
<tr>
<td>0.2 kV, 600 nA</td>
<td>4.29 min</td>
<td>67% C, 24% O, 9% S</td>
</tr>
<tr>
<td>0.25 kV, 600 nA</td>
<td>4.03 min</td>
<td>70% C, 21% O, 9% S</td>
</tr>
<tr>
<td>0.3 kV, 600 nA</td>
<td>4.49 min</td>
<td>72% C, 20% O, 8% S</td>
</tr>
<tr>
<td>0.5 kV, 600 nA</td>
<td>5.56 min</td>
<td>78% C, 14% O, 8% S</td>
</tr>
</tbody>
</table>

- Sputter time decreased with high dose and low dose Ar
- Lost of O at >0.25 kV Ar
- Dose of Ar is optimized with minimize damage and enhance sputtering rate

**Sputtering Rate of Mixed C₆₀⁺/Ar⁺ Ion Beam**

- Higher sputtering rate, no observable damage to chemical structure
- Extremely slow sputtering rate, still damage the chemical structure
Sputter Damage Thickness in Si (Angle-Resolved XPS)

- 0.2KV Ar⁺
- Top Layer (2.34 nm)
- Si₂p (96%)
- Ar₂p (4%)
- 0.2KV Ar⁺ + 10KV C₆₀⁺
- Top Layer (1.63 nm)
- Si₂p (83%)
- C₁s (17%)

Sputter Damage Thickness in Si (TEM)

- 0.2KV Ar⁺
- 5~7 nm thick
- 10KV C₆₀⁺
- 4~6 nm thick
- 0.2 KVAr⁺ + 10KV C₆₀⁺
- 2~4 nm thick

Sputter of Hard Materials (ZnSO₄·nH₂O)

- shallower sampling depth in hard materials
- overall damage thickness is comparable
- using cluster ion beams have no benefit
**Depth Profile of OLED**

**Polymer-based Inverted Solar Cell**

**Vertical Array of TiO$_2$ Nanotube**
**Conclusion**

- XPS is widely used to study the surface chemical composition of materials.
- To probe below the surface, Ar ion sputtering is typically used to remove material but it is generally not possible to apply to organic materials because of the high level of damage.
- C₆₀ ion sputtering has been demonstrated to remove organic materials while causing minimal damage to the surface.
- However, the sputtering rate decreased with sputtering time due to the C deposition.

**Conclusion**

- To avoid excessive damage to the surface while maintaining a steady sputtering rate, combination of high-energy C₆₀ and low-energy Ar beams are used concurrently.
- The surface is eroded by the C₆₀ beam and the residual carbon is removed by Ar.
- HREM and ARXPS revealed thinner and more localized damage layer with co-sputtering.
- However, the surface roughness is higher with C₆₀ beams and interface broadening was observed.
- Thick organo-electronic devices can be analyzed with this technique.
Acknowledgments

- Dr. John Hammond, Physical Electronics, USA
- Mr. Wensly Yip (温士輝), ULVAC-PHI, Japan
- Prof. Jwo-Huei Jou (周卓煇), DMSE, NTHU
- Prof. Chih-Wei Chu (朱治偉), RCAS, Academia Sinica
- Dr. Bang-Ying Yu (袁秉英), RCAS, Academia Sinica
- Miss. Ying-Yu Chen (陳映予), RCAS, Academia Sinica
- Mr. Wei-Ben Wang (王偉本), DMSE, NTHU
- Mr. Mao-Fen Hsu (徐茂峰), DMSE, NTHU
- Miss. Shu-Ping Tsao (蘇淑萍), RCAS, Academia Sinica
- Mr. Mark Cheng (張家榮), Veeco, Taiwan
- Sponsorship by Academia Sinica and NSC (through 96-2120-M-002-018 and 96-2113-M-001-012-MY2)