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 (H_20, O_2) 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

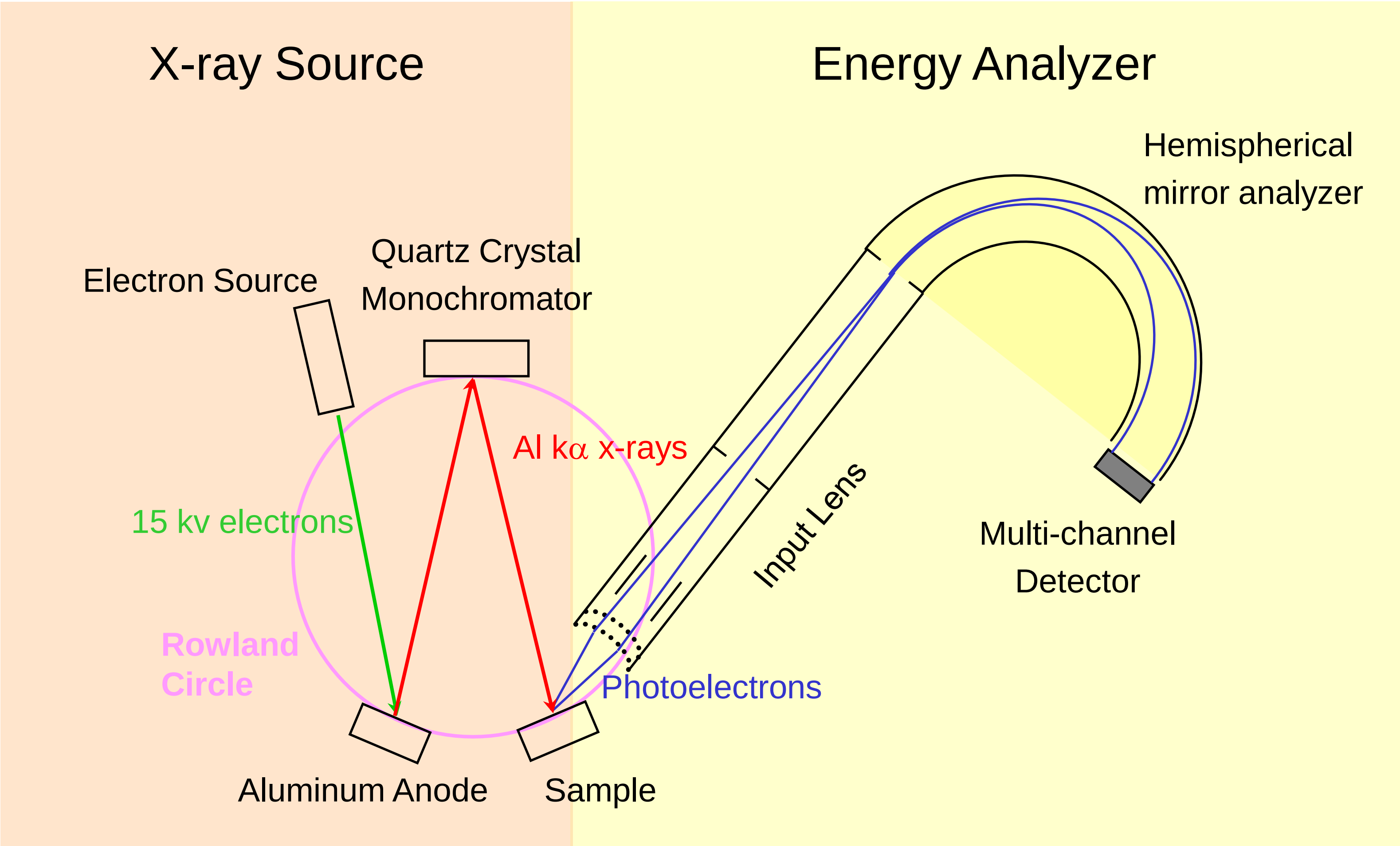
Why use Depth Profiling for Organic Electronics?

- **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**

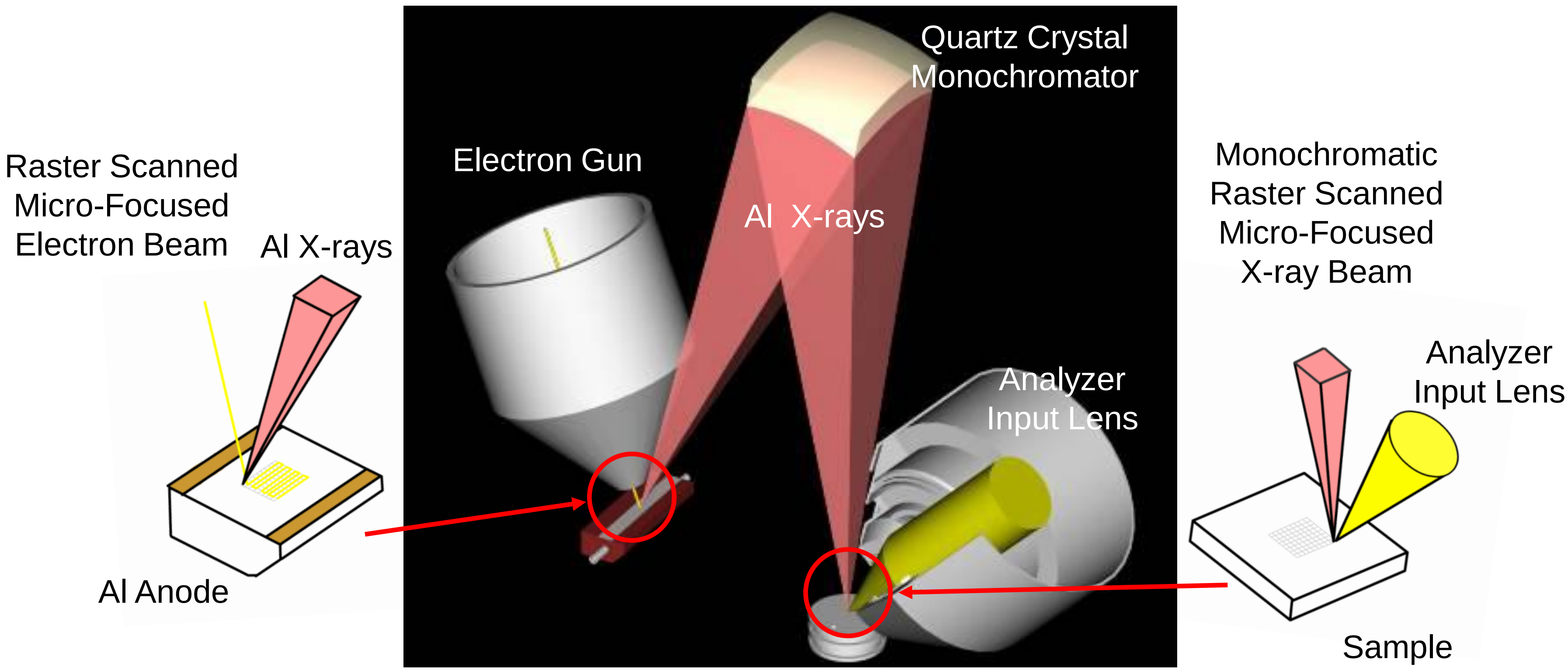
Comparison of XPS and TOF-SIMS

	XPS	TOF-SIMS
Probe Beam	**Photons**	Ions
Analysis Beam	Electrons	Ions
Spatial Resolution	10 µm	**0.10 µm**
Sampling Depth(Å)	5-75	**1-10**
Detection Limits	0.01atom %	1ppm
Information Content	Elemental Chemical	Elemental Chemical **Molecular**
Quantification	**Excellent**	Std. needed

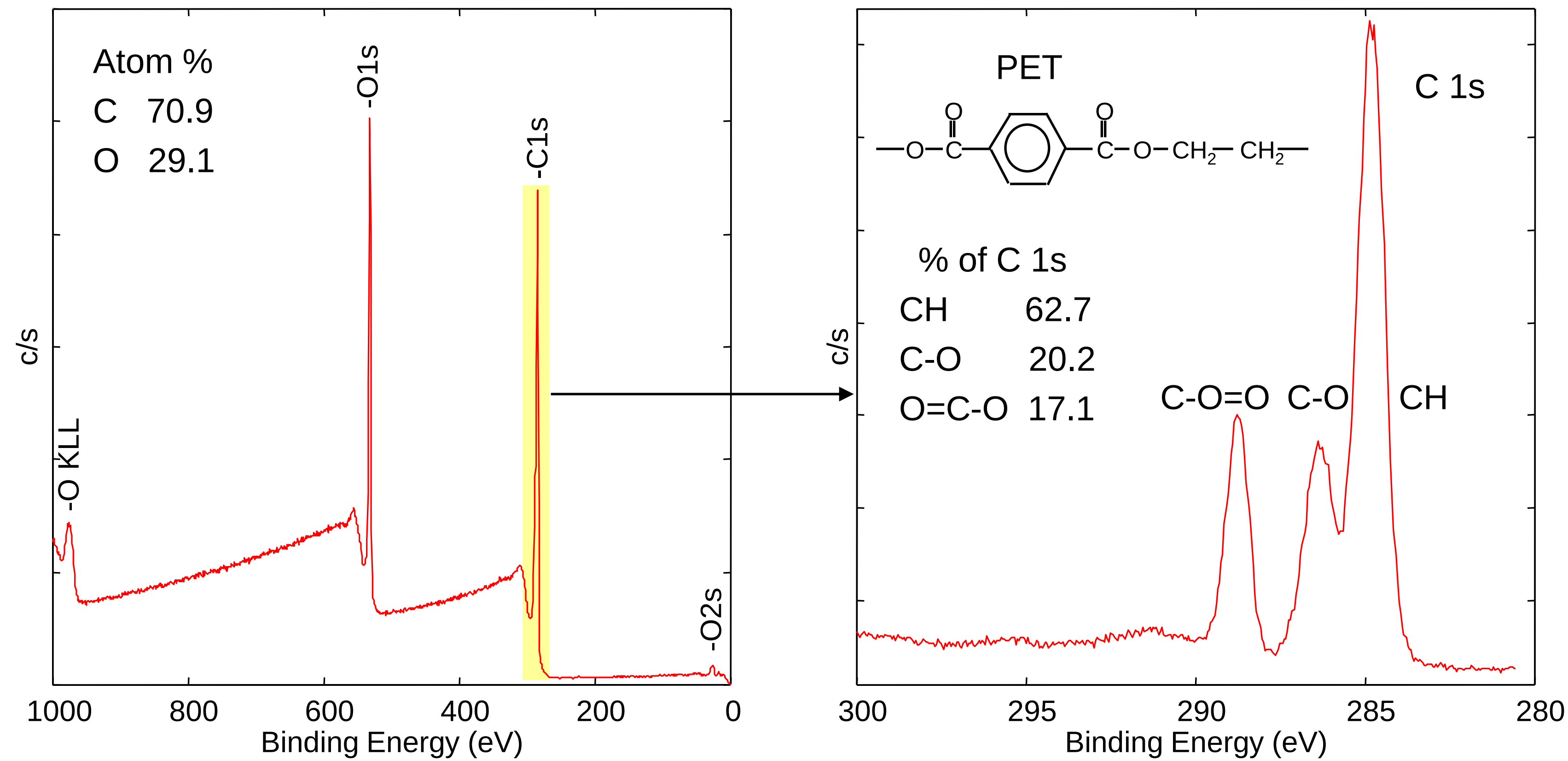
XPS System Schematic



Scanning Micro Focused X-ray Source



Typical XPS Spectra
Poly(ethylene terephthalate)



XPS survey spectra provide quantitative elemental information

High resolution XPS spectra provide quantitative chemical state information

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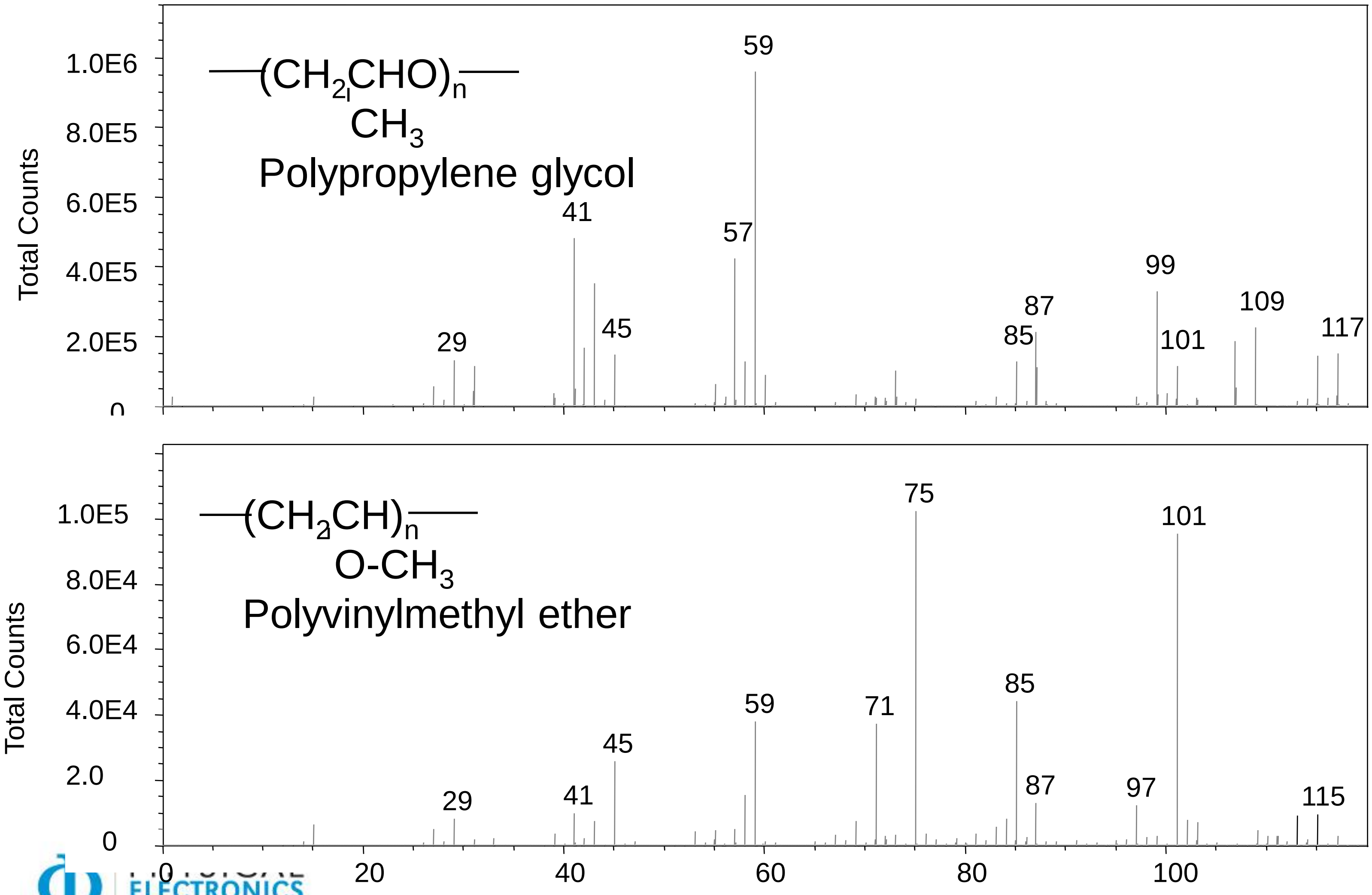
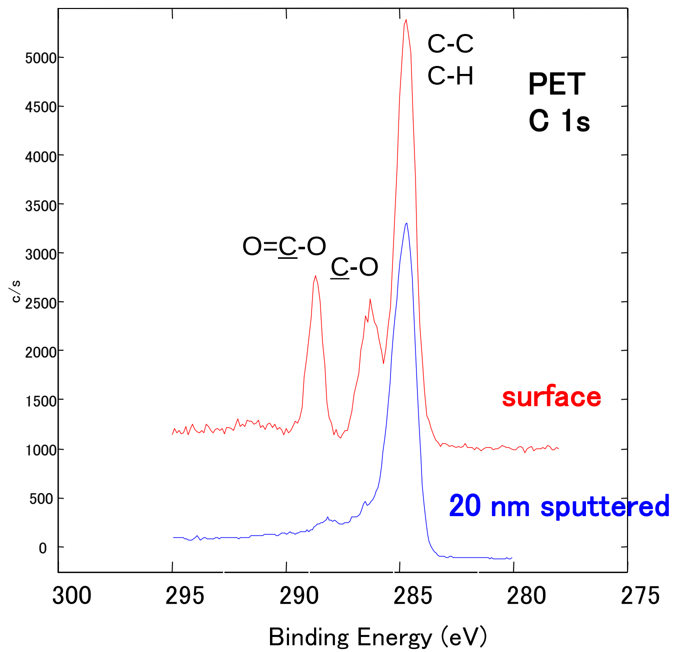
Unique Polymer "Fingerprint" Identification Using TOF-SIMS Spectra

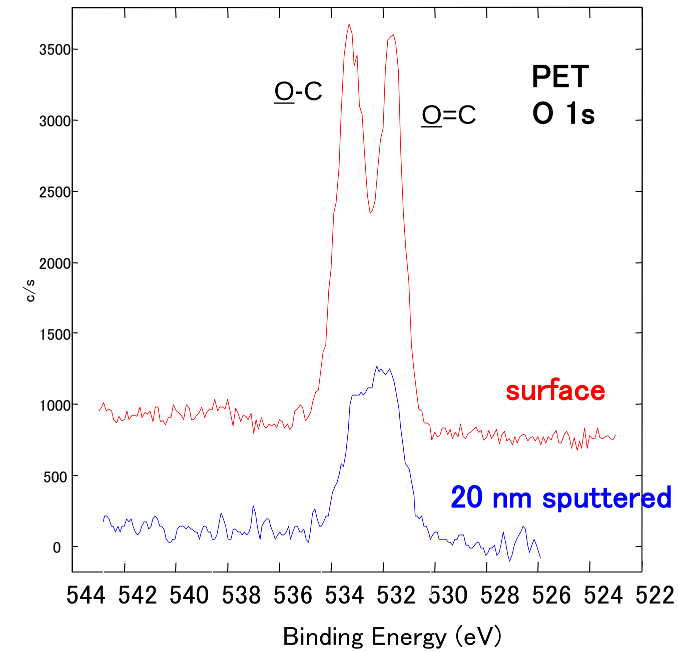
XPS shows identical spectra for both polymers



Damage Accumulation Indicated by XPS

500 eV Ar^+ Sputter

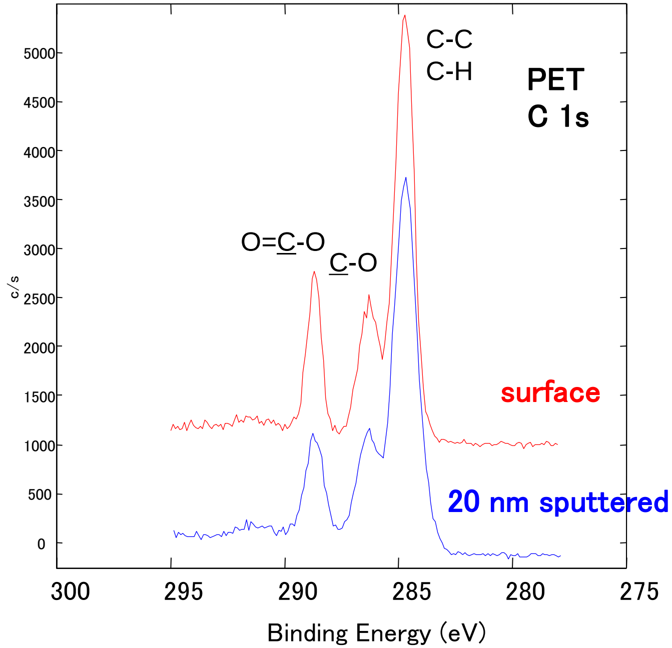


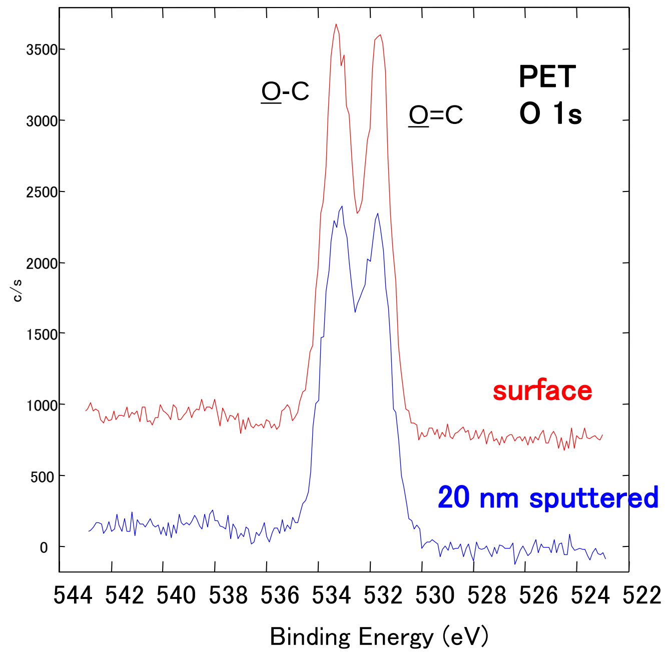


Damage is observed.

No Damage Observed by XPS

10keV C_{60}^{+} Sputter

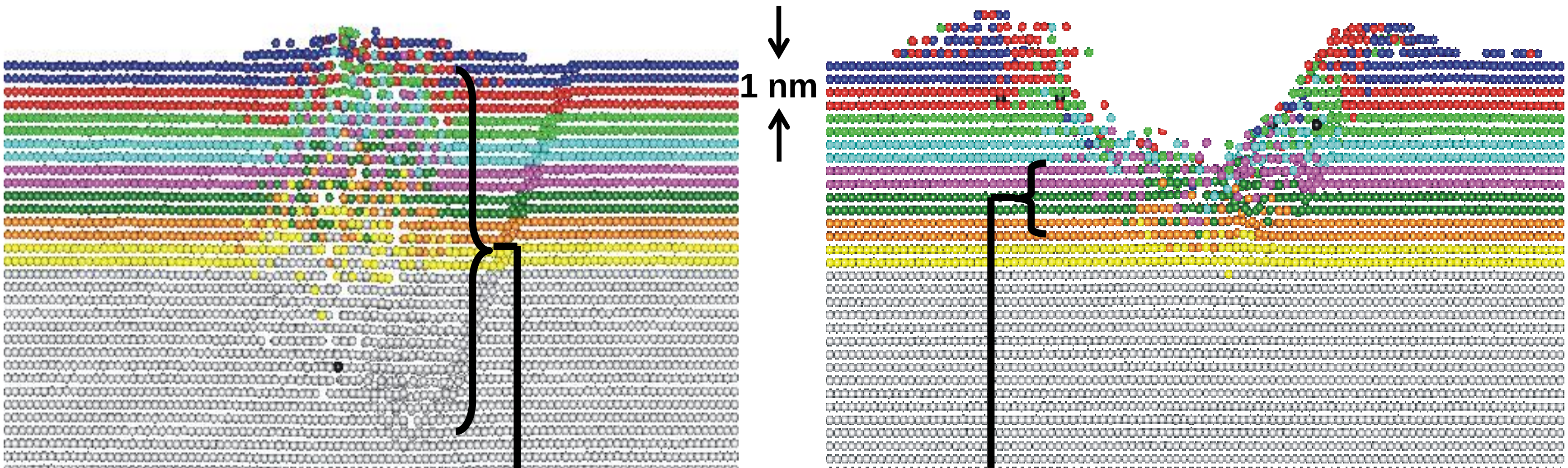




No damage observed.

Altered Volume & Sub-surface Damage

15 keV Ga | **15 keV C_{60}**



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**.

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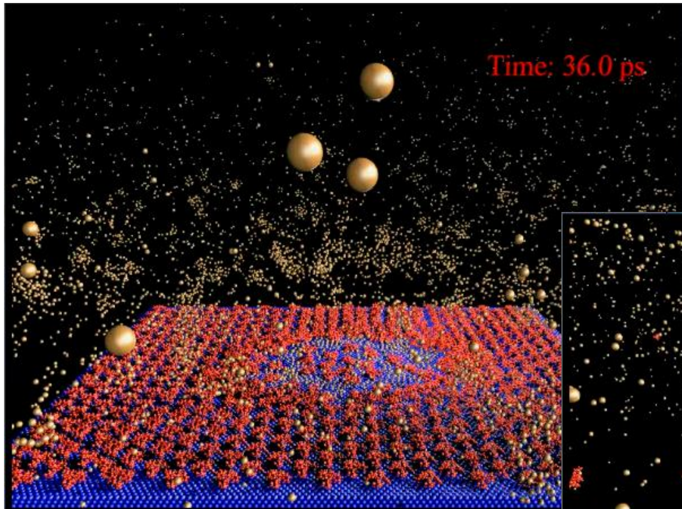
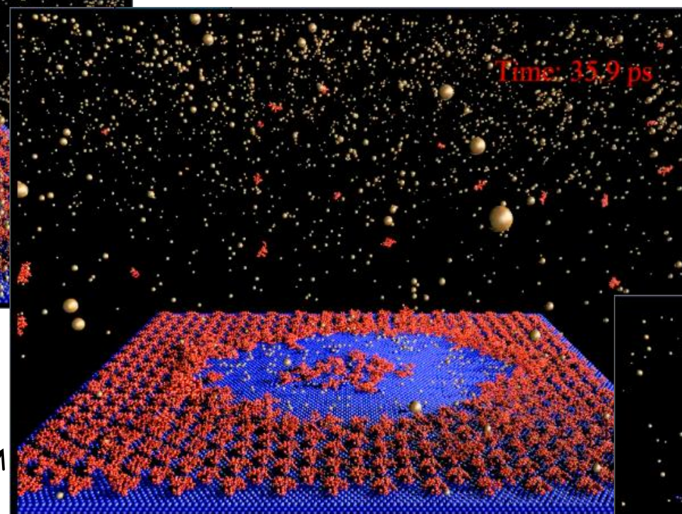
Graphic courtesy B. Garrison & Z. Postawa.

Molecular Dynamics: Ar_{9000}^{+} GCIB on PS/Ag

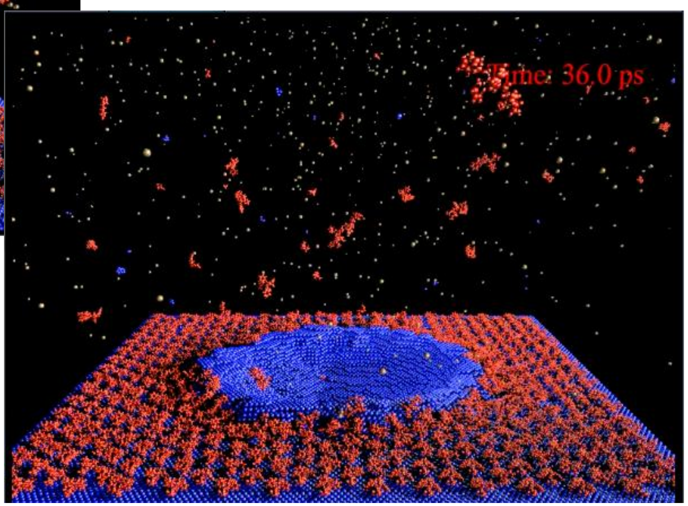
0.5eV/Ar atom



2.0eV/Ar atom



10eV/Ar atom



Lateral Jet Momentum Transfer Sputtering

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

Previous Graded Composition OLED Research

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Highly efficient, single-layer organic light-emitting devices based on a graded-composition emissive layer

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Graded Composition Structures Overview

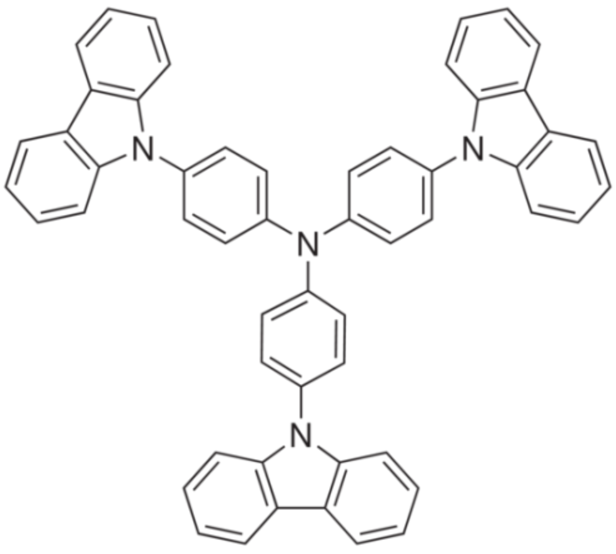
- **Graded Electron and Hole Transport Materials (ETM and HTM) with a green phosphorescent emitter**
- **100% HTM at the Anode and 100% ETM at the Cathode**
- **Result**
  - At 600 cd/m^2
    - Peak external quantum efficiency $\eta_{EQE} = (19.3 \pm 0.4)\%$
      - Corresponding to internal quantum 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

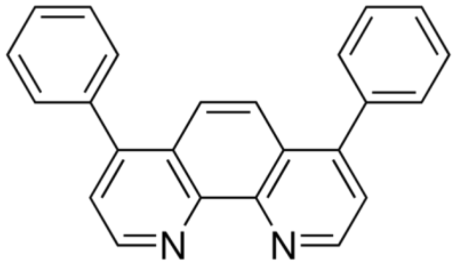
- **Thin film samples were characterized in a PHI *VersaProbe* II Scanning XPS system equipped with an Ar^{+} Gas Cluster Ion Beam source for depth profiling**
  - The GCIB source can be operated
    - With Beam energies from 2.5 kV to 20 kV
    - Cluster size from <1000 to 5000
- **The XPS system has excellent charge neutralization capability to compensate for differential charging at various interfaces**

Structure of the two molecules for OLED

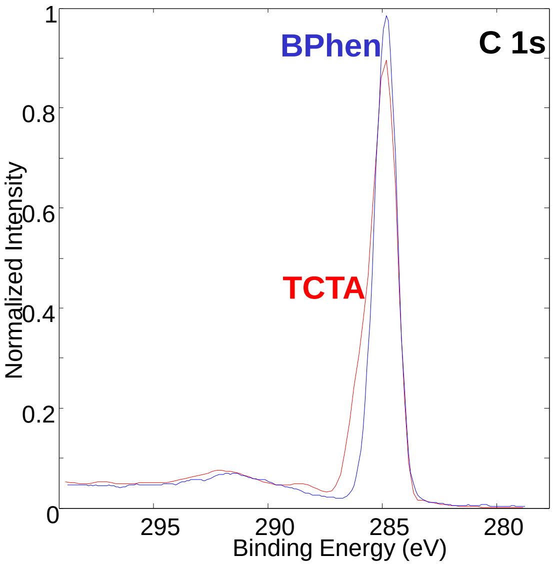
- **Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (Hole Transfer Material)**

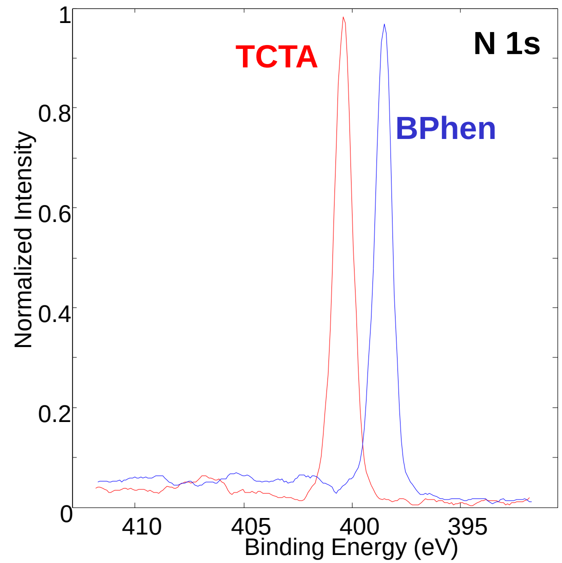


- **Bathophenanthroline (BPhen) (Electron Transfer Material)**

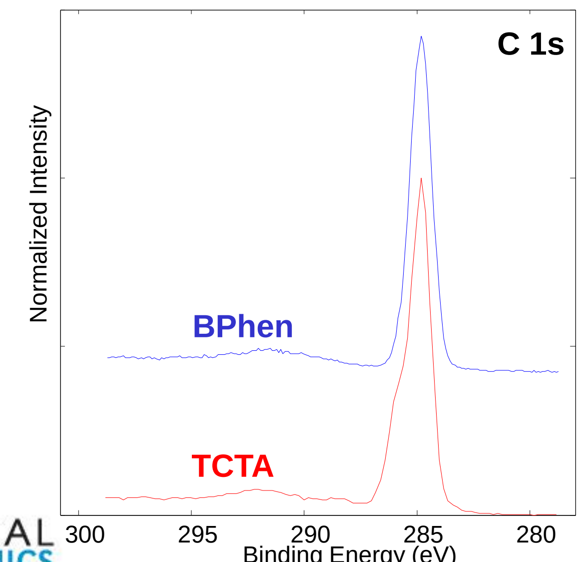


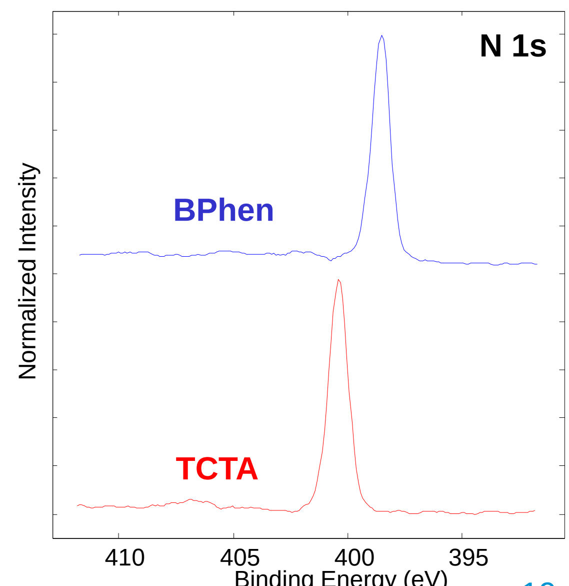
C 1s and N 1s Spectra for TCTA and BPhen





1.8 eV Separation





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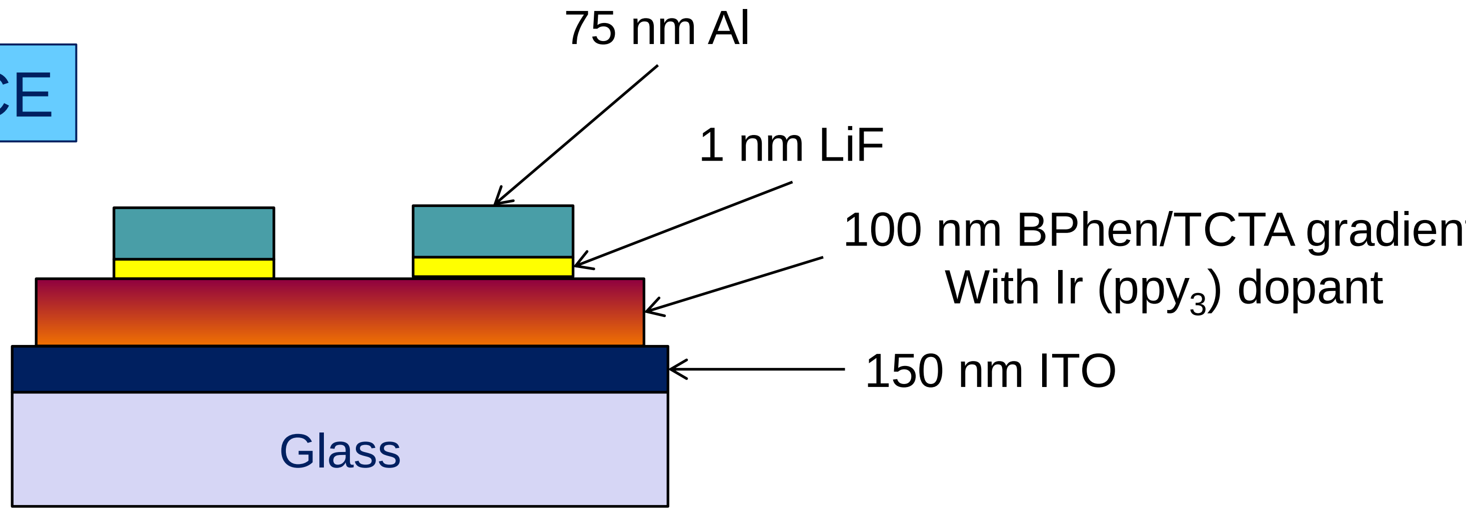
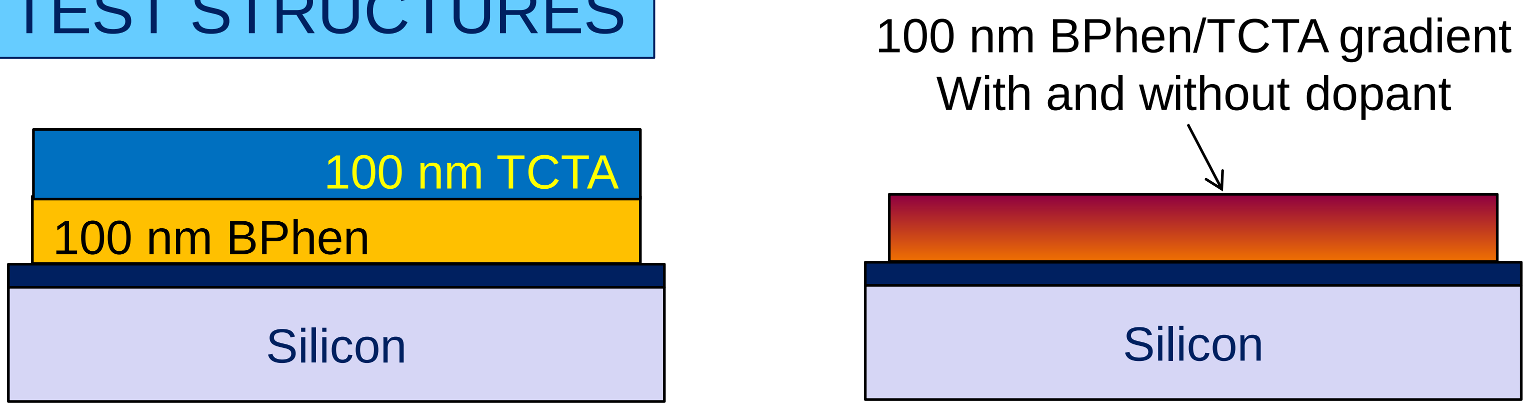
Sample Structure for OLED

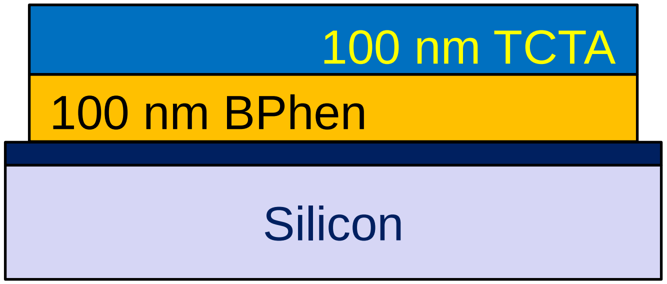
DEVICE



XPS TEST STRUCTURES

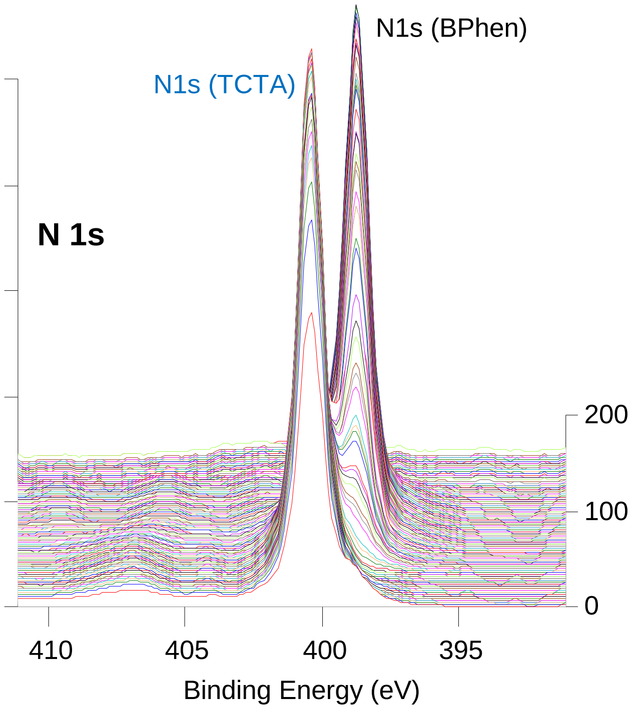


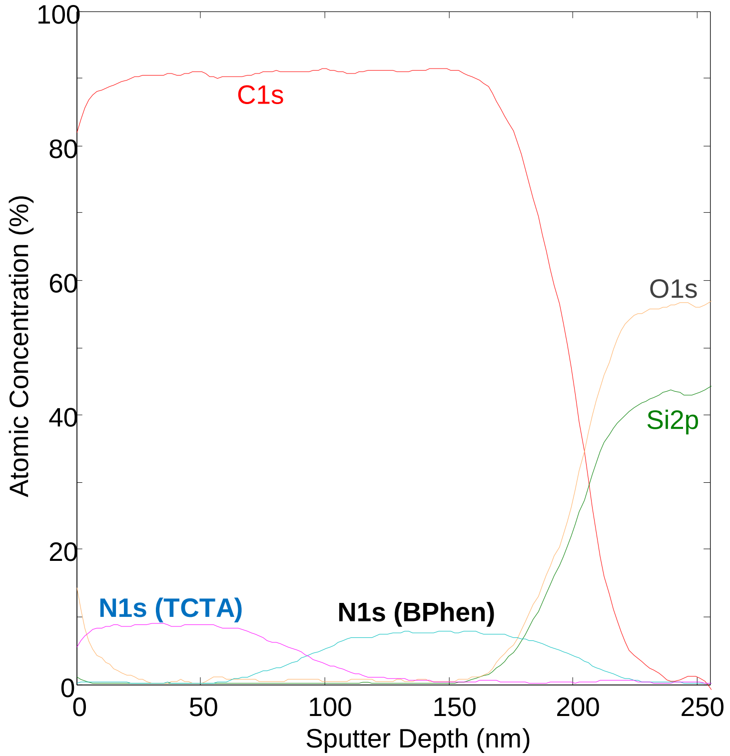
GCIB Depth Profile of TCTA:Bphen/SiO_2/Si



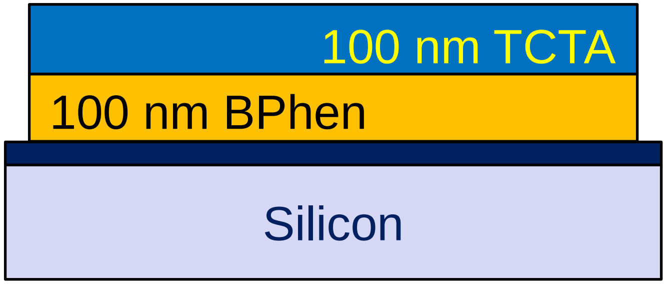
Ar_{2500},10 kV, 2 nA, 3 mm x 3 mm

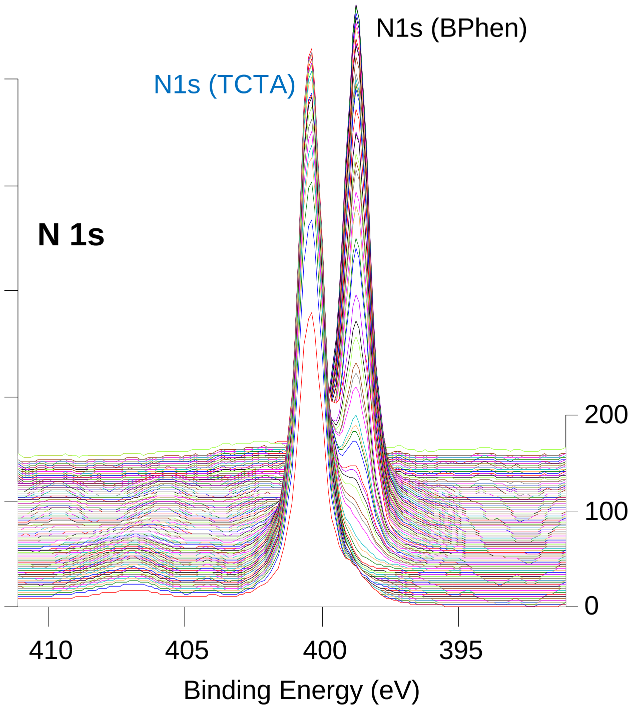
4 eV/atom GCIB





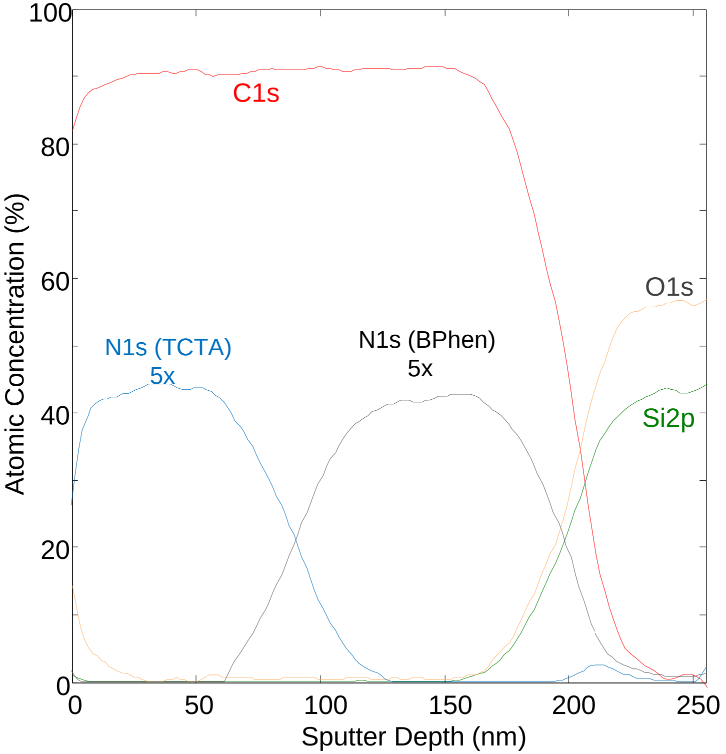
GCIB Depth Profile of TCTA:Bphen/SiO_2/Si



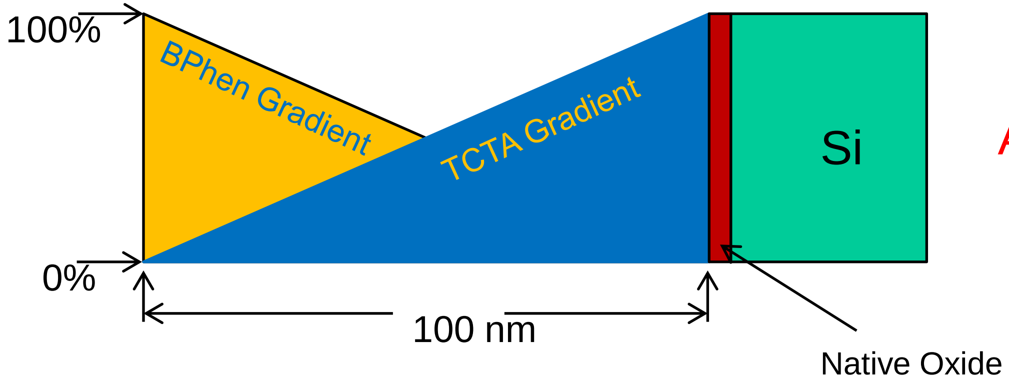


Ar_{2500},10 kV, 2 nA, 3 mm x 3 mm

4 eV/atom GCIB

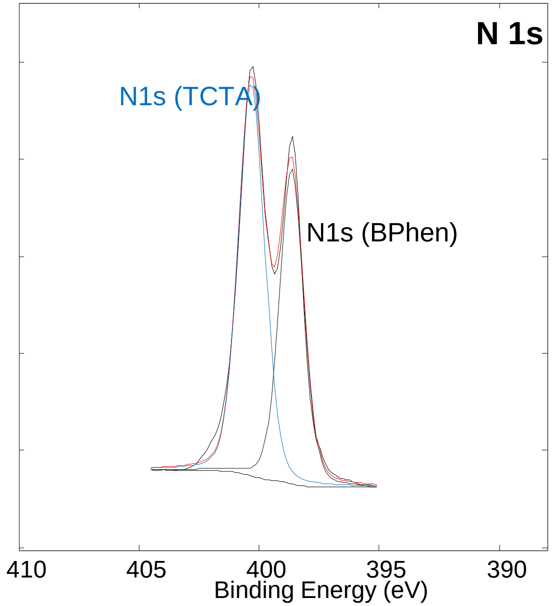


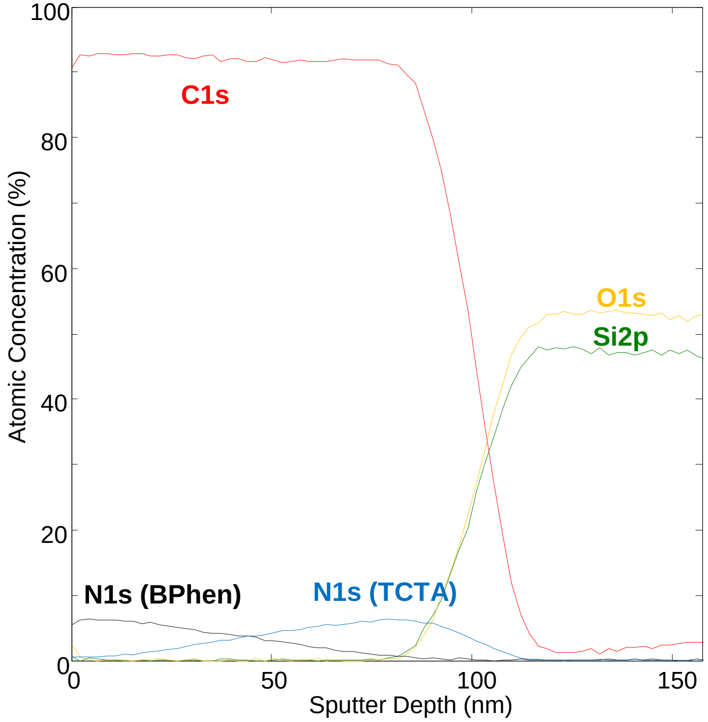
GCIB Depth Profile of Bphen:TCTA/SiO_2/Si



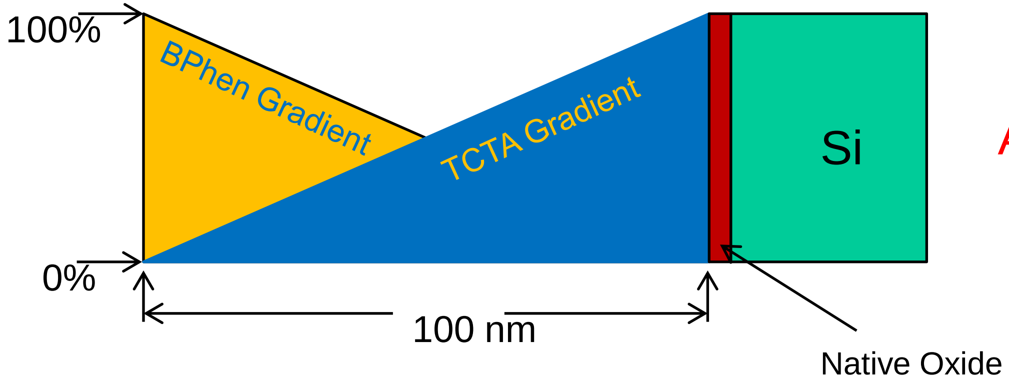
Ar_{2500},10 kV, 2 nA, 3 mm x 3 mm

4 eV/atom GCIB



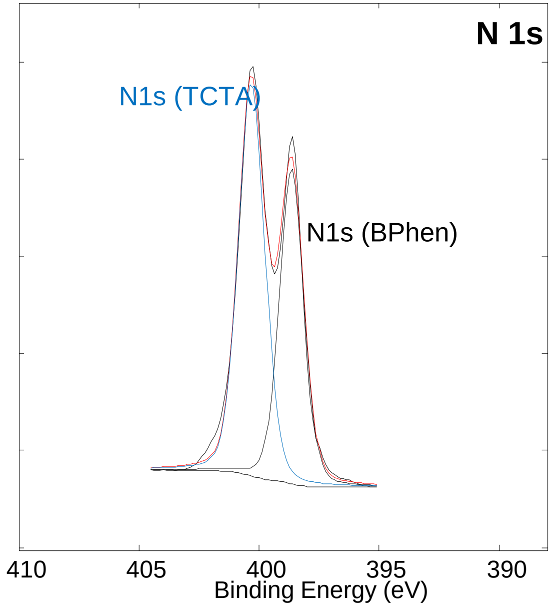


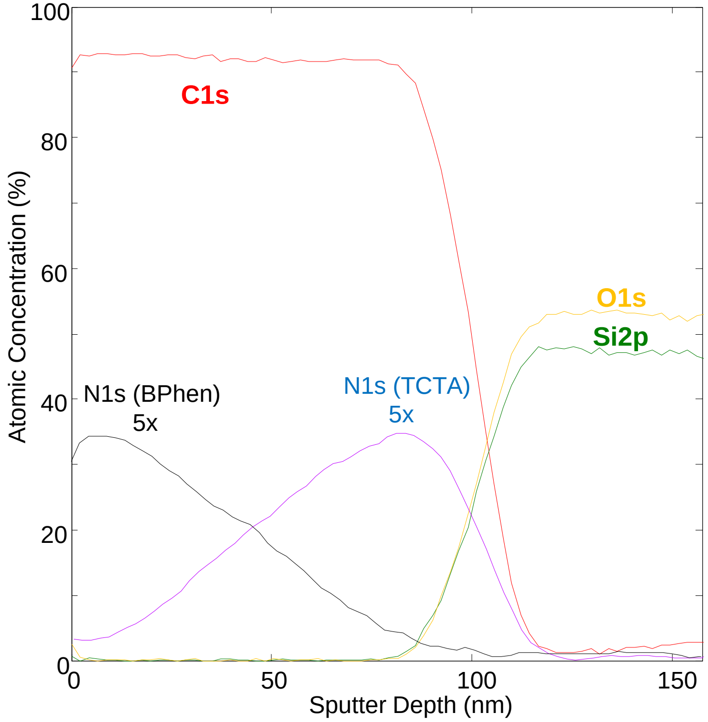
GCIB Depth Profile of Bphen:TCTA/SiO_2/Si



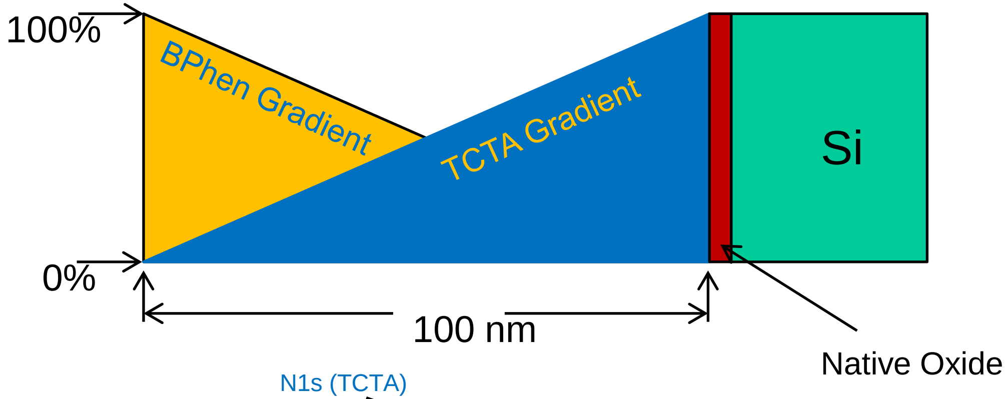
Ar_{2500},10 kV, 2 nA, 3 mm x 3 mm

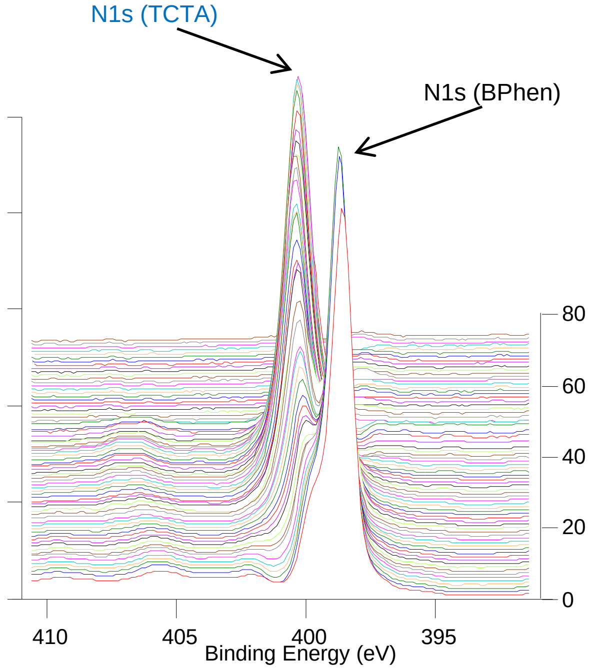
4 eV/atom GCIB

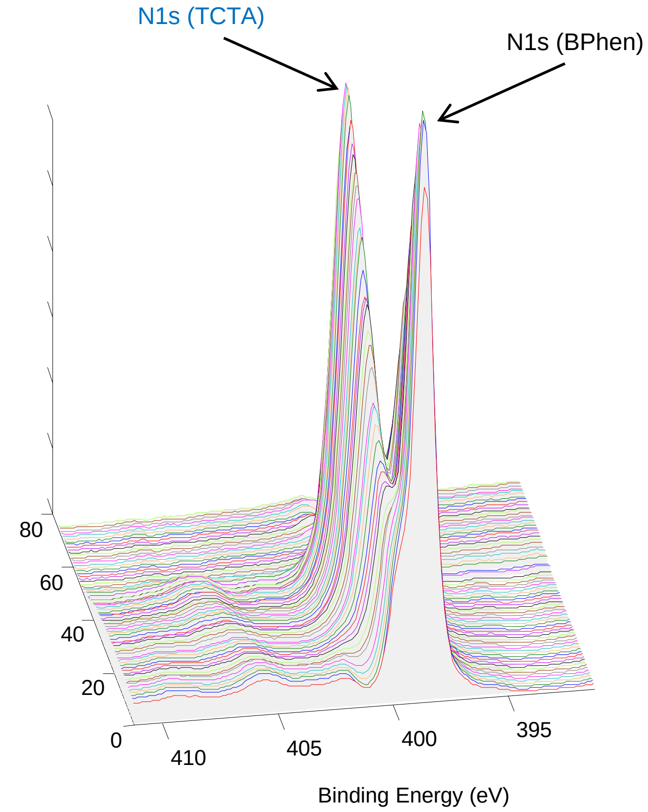




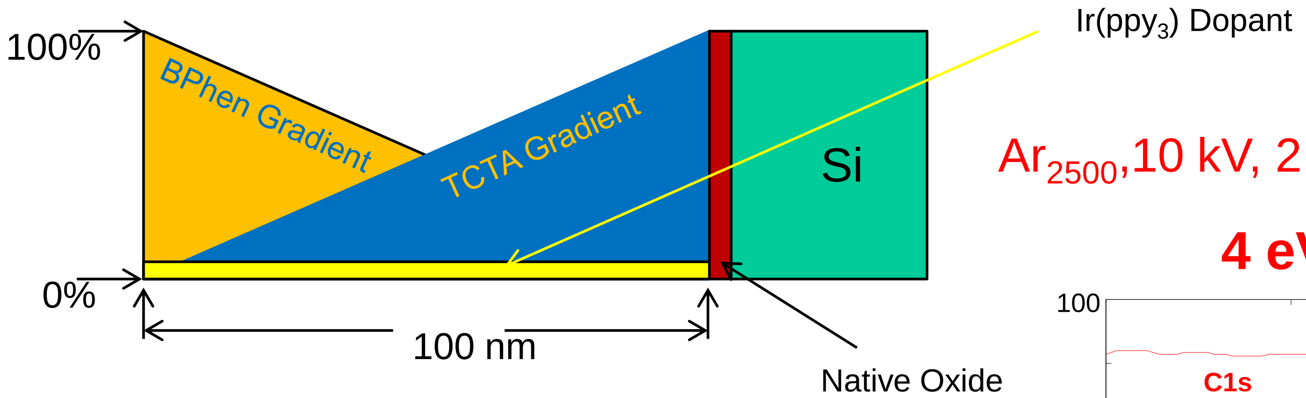
N 1s Spectra from GCIB Depth Profile of Bphen:TCTA/SiO_2/Si







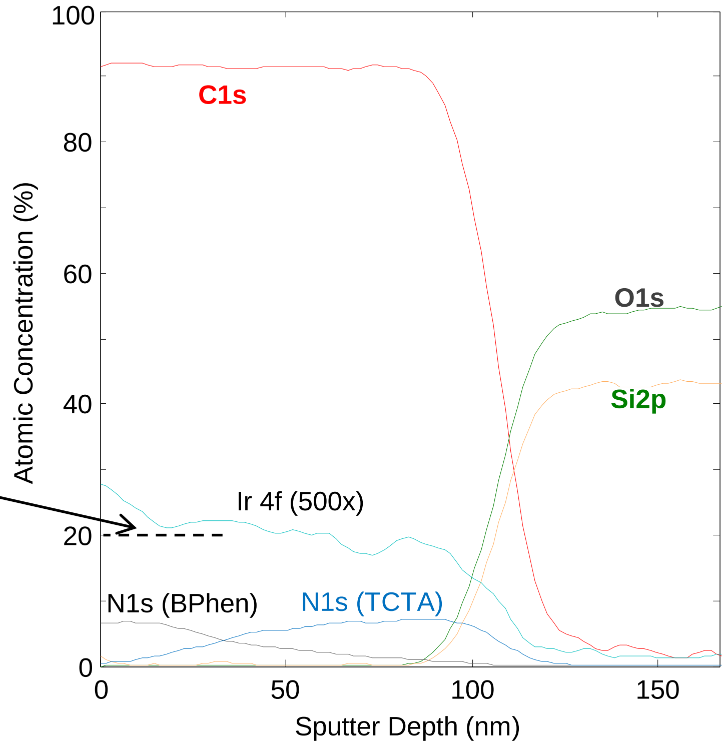
Ir Emissive Compound from GCIB Depth Profile of Bphen:TCTA/SiO_2/Si



Ar_{2500},10 kV, 2 nA, 3 mm x 3 mm

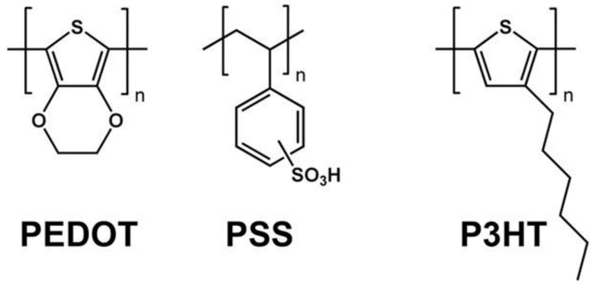
4 eV/atom

Ir 4f concentration 0.04 at %

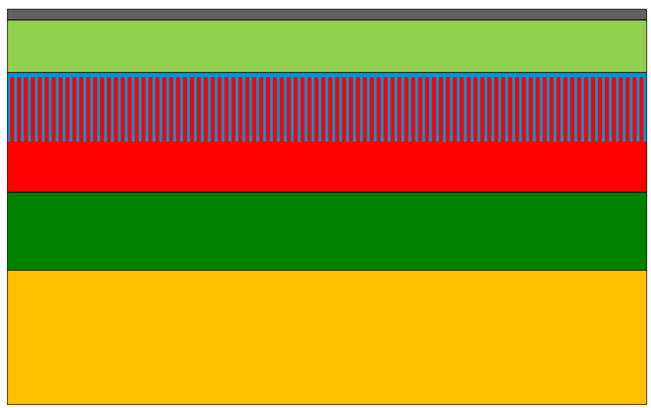


Composite Multi-layer
Inverted Organic Photovoltaic Device

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

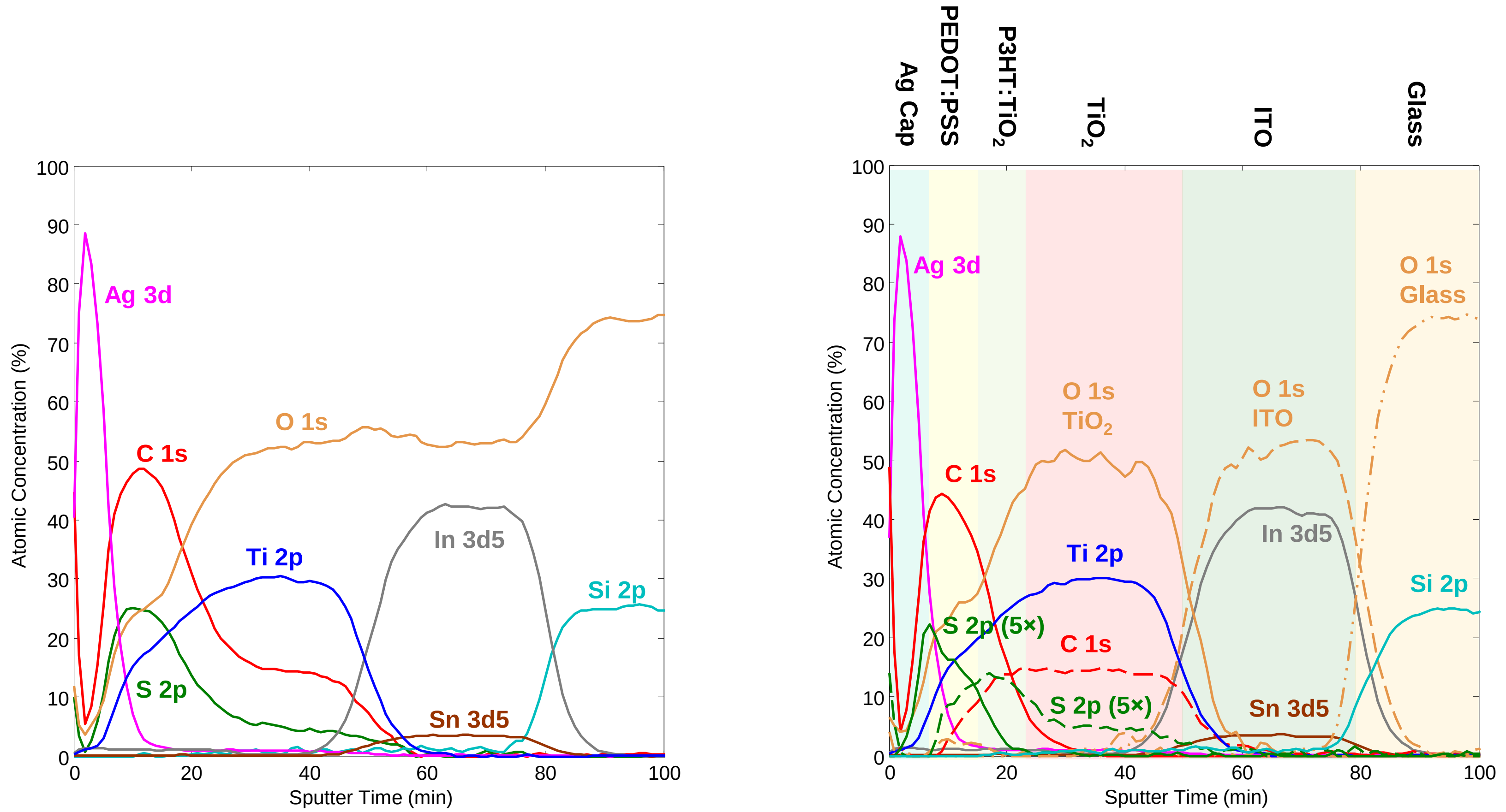


PEDOT PSS P3HT



Composite – Organic Photovoltaic Multi-layer

20 kV C_{60} Cluster



- **With Compucentric Zalar Rotation™**
- **Well defined layers**
- **Consistent sputter speed throughout the multilayer stack**

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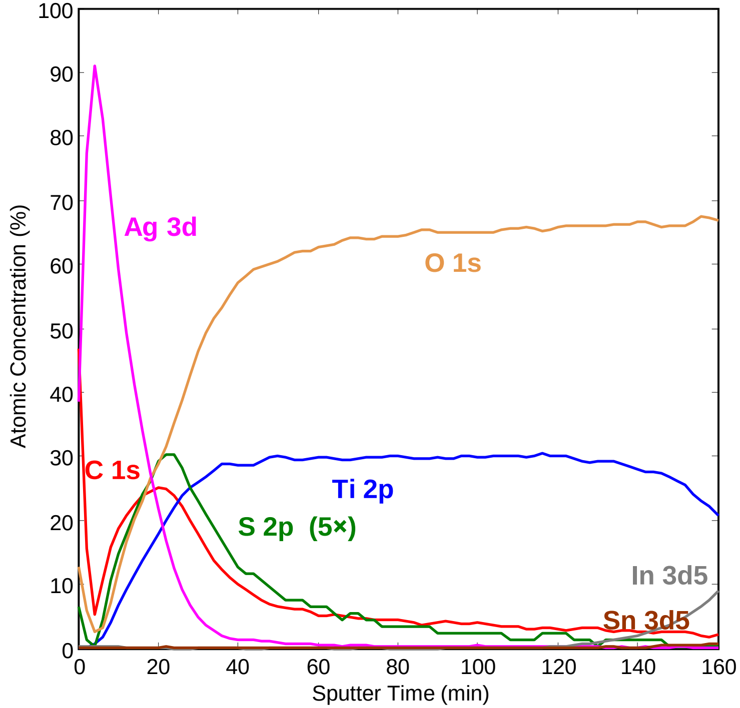
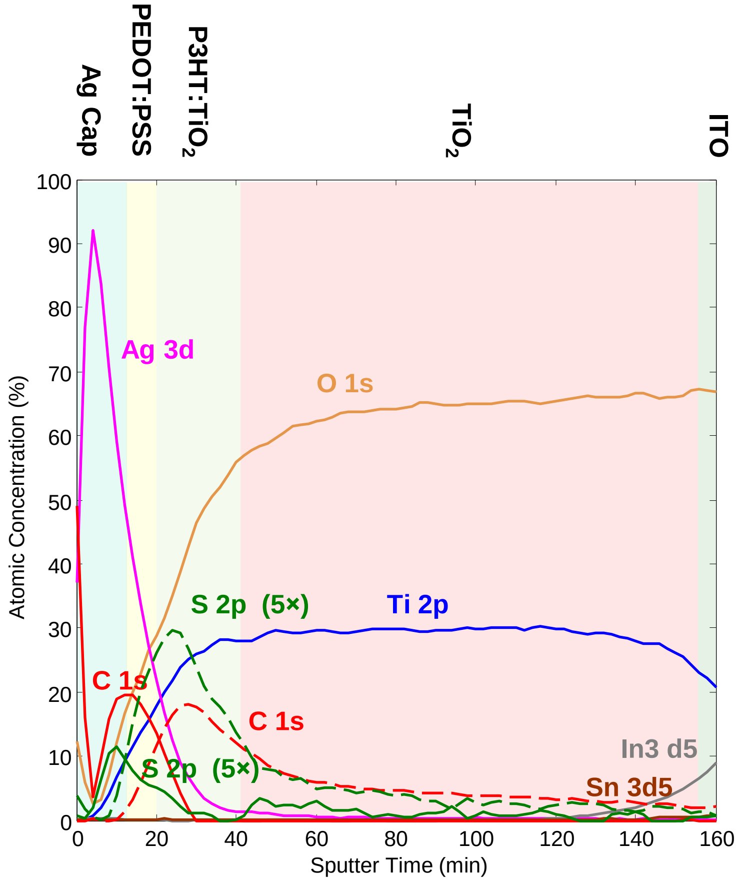
Composite – Organic Photo Voltaic Multi-layer

20 kV Ar_{1500}^{+} Gas Cluster, 13.3 eV/atom





(13 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) $(CF_3BNO)_2IrPLA$
  - 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

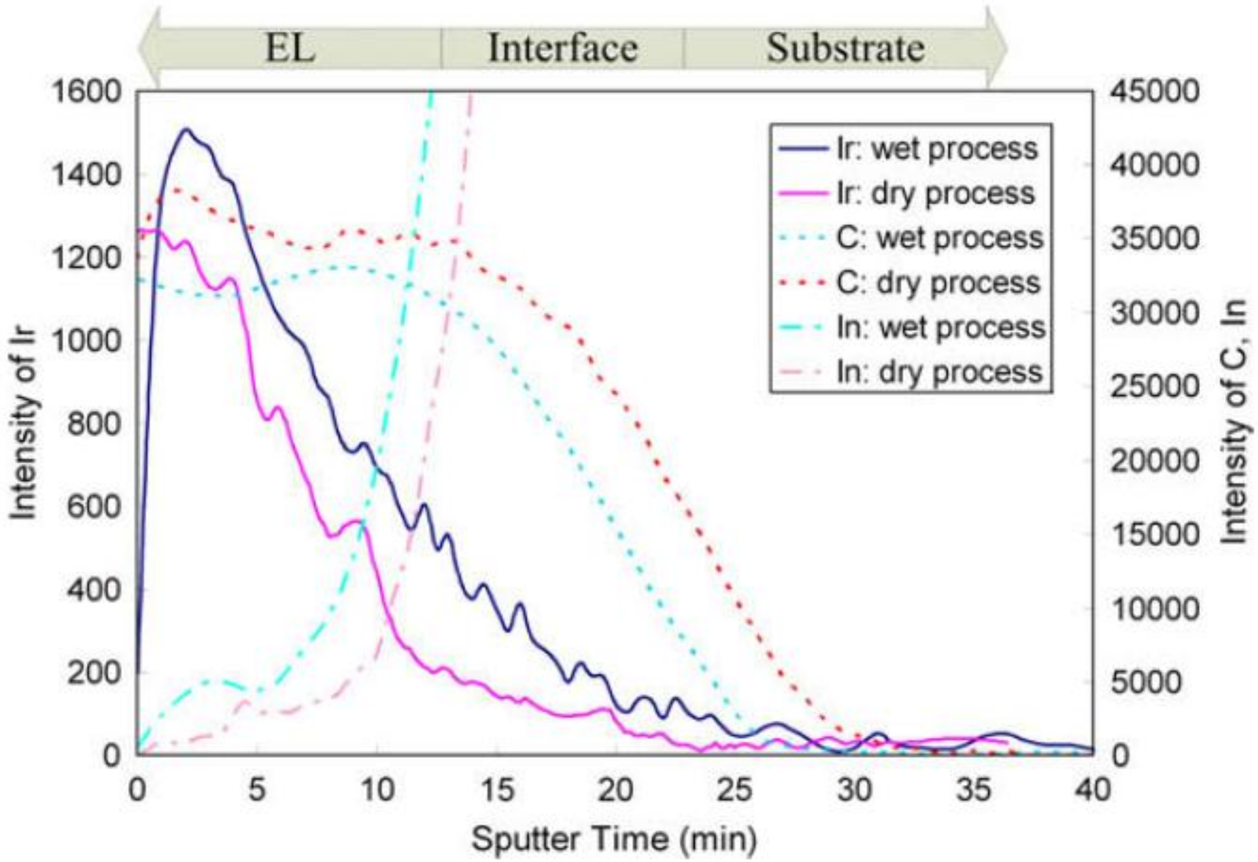
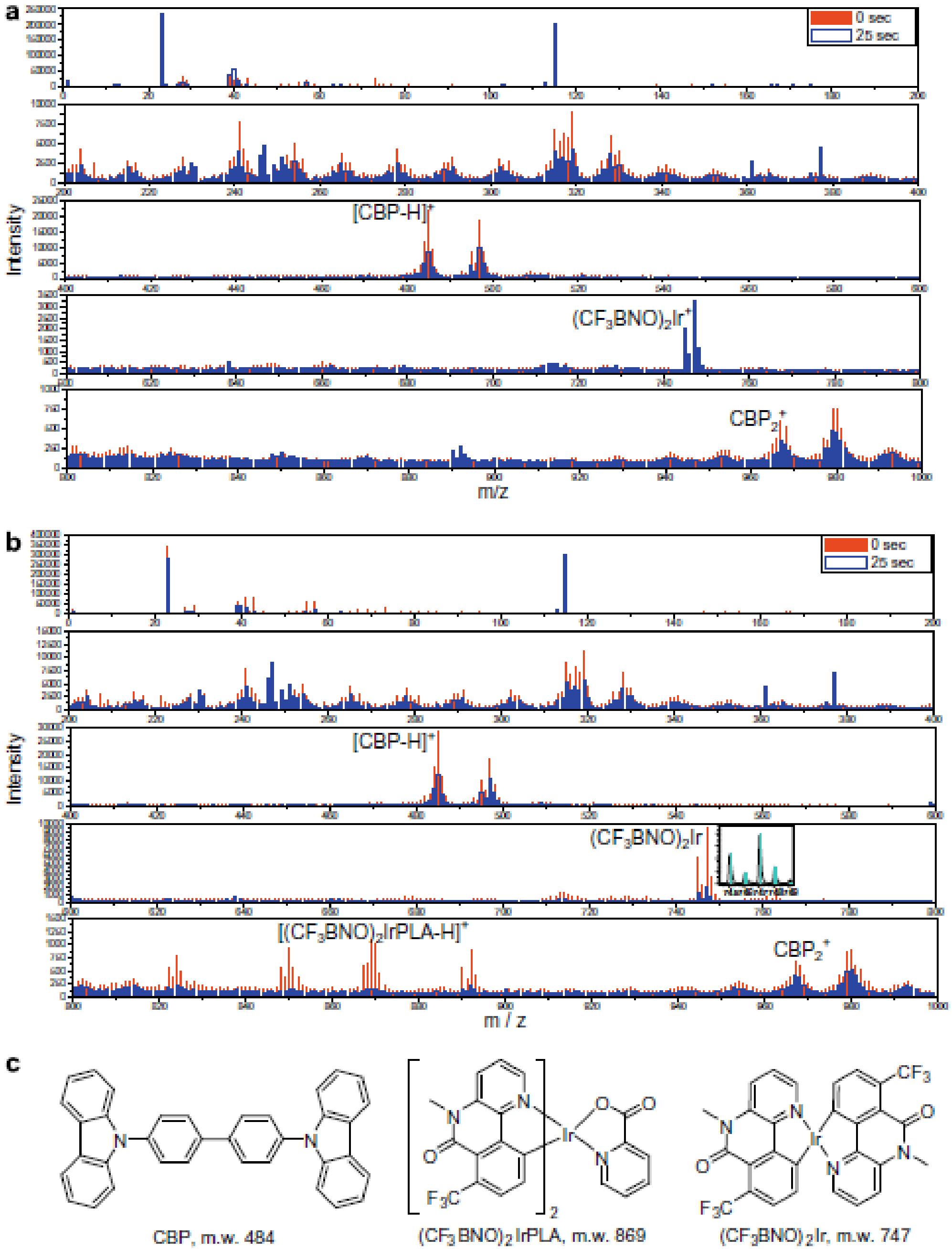


Fig. 1. XPS elemental depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).

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



- **TOF-SIMS with C_{60} sputtering shows no change in molecular structure between outer surface spectra and 25 seconds sputtering**

- **XPS profile with C_{60} is not a result of molecular decomposition**

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Wet versus Dry Process: TOF-SIMS Depth Profiles

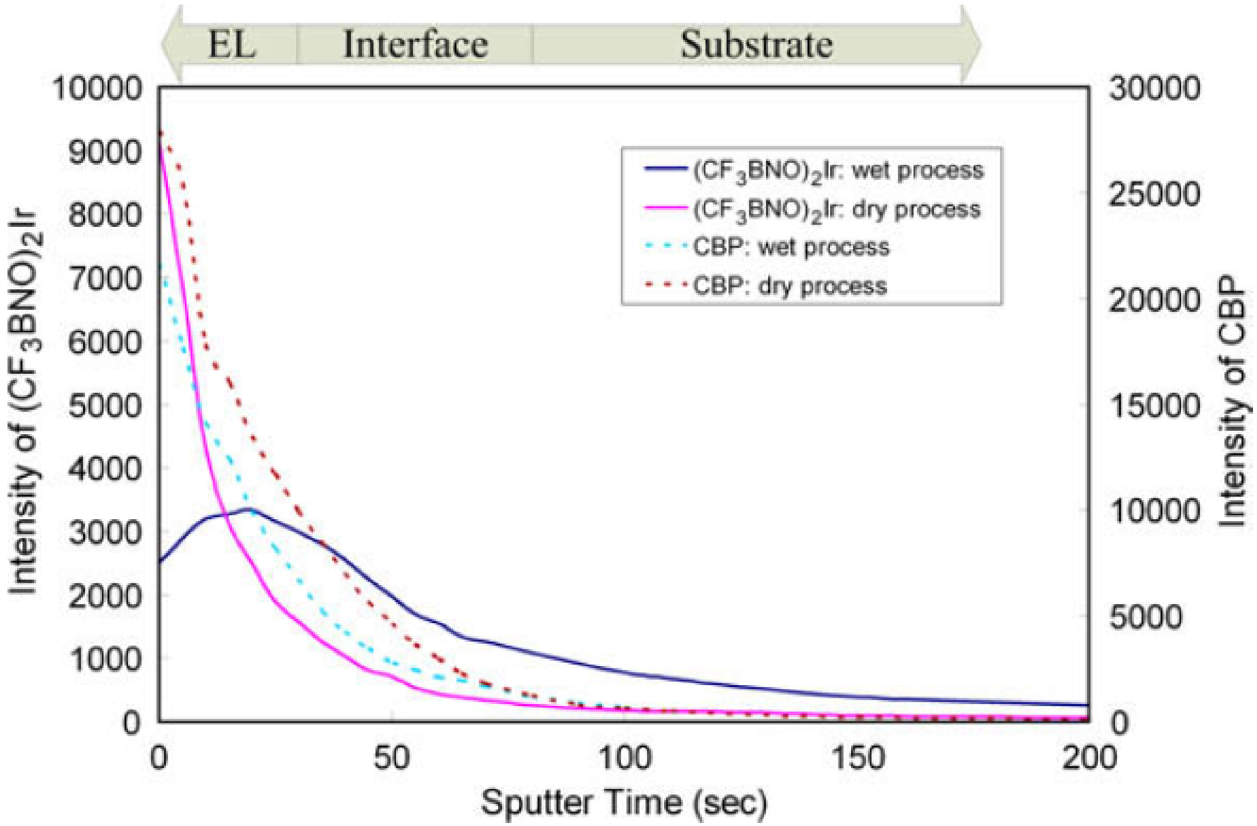

Fig. 3. ToF-SIMS depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).

- **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

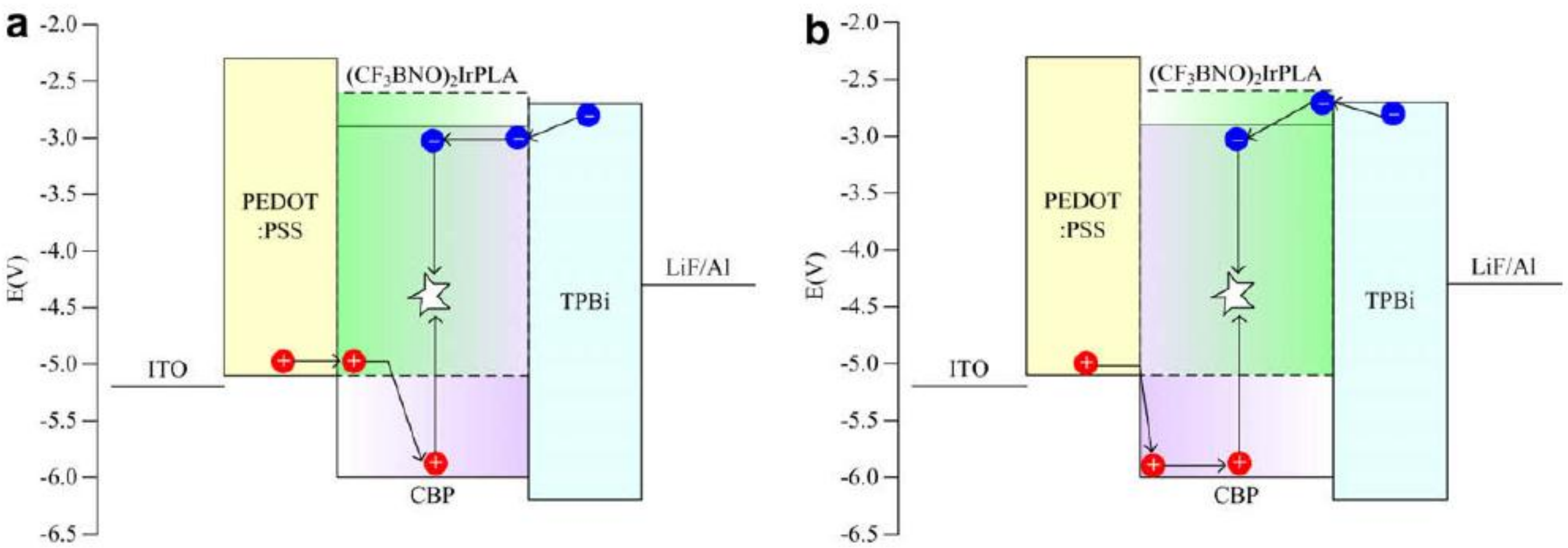

Fig. 4. Energy diagram and the route of charge carriers of OLED with EL prepared with (a) wet-process and (b) dry-process. The shade of CBP and $(CF_3BNO)_2IrPLA$ indicates its relative concentration.

- **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**

Cluster Ion Source Summary

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

Sample Type	Ion Gun Type		
	Ar Monoatomic	C_{60} Cluster	Ar Gas Cluster
Metal	• Preferred approach ★★★★	• Carbide formation 3 - 20 % on reactive metals ★★	• Slow etch rates • Small differential sputtering for some alloys ★
Ceramics	• Differential sputtering and chemical change ★	• Ideal Approach on Soda-lime glass • Works well on metalloid oxides and conducting oxides: ITO / InGaO ★★★★	• Slow etch rates • Small oxygen loss for some oxides at high acceleration voltages (ITO) ★★
		• Not suitable for transition metal oxides TiO_2 / HfO_2 / WO_3 ★★	• Not suitable for transition metal oxides TiO_2 / HfO_2 / WO_3 ★
Organics **Polymers**	• Significant Chemical Damage ★	• Suitable for Type-II degrading polymers (5 × to 10 × between Polymers and Metal oxides) ★★★	• Suitable for Type-II degrading polymers (50 × to 100 × between Polymers and Metal oxides) ★★★★
		• Some Type-I crosslinking polymer to a depth of a few hundred nanometers ★★	• Ideal Approach for Type-I crosslinking polymers, unless an inorganic filler is present ★★★★
Complex Materials	• Sample Dependent ★★	• Able to maintain sputter speed across layers, with low level damage on Carbon ★★★	• Large variation in sputter rate causes depth resolution problems ★
Semiconductors	• Preferred approach ★★★	• Carbide formation on reactive metals ★★	• Slow etch rates, variable sputter rates, surface roughening ★

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