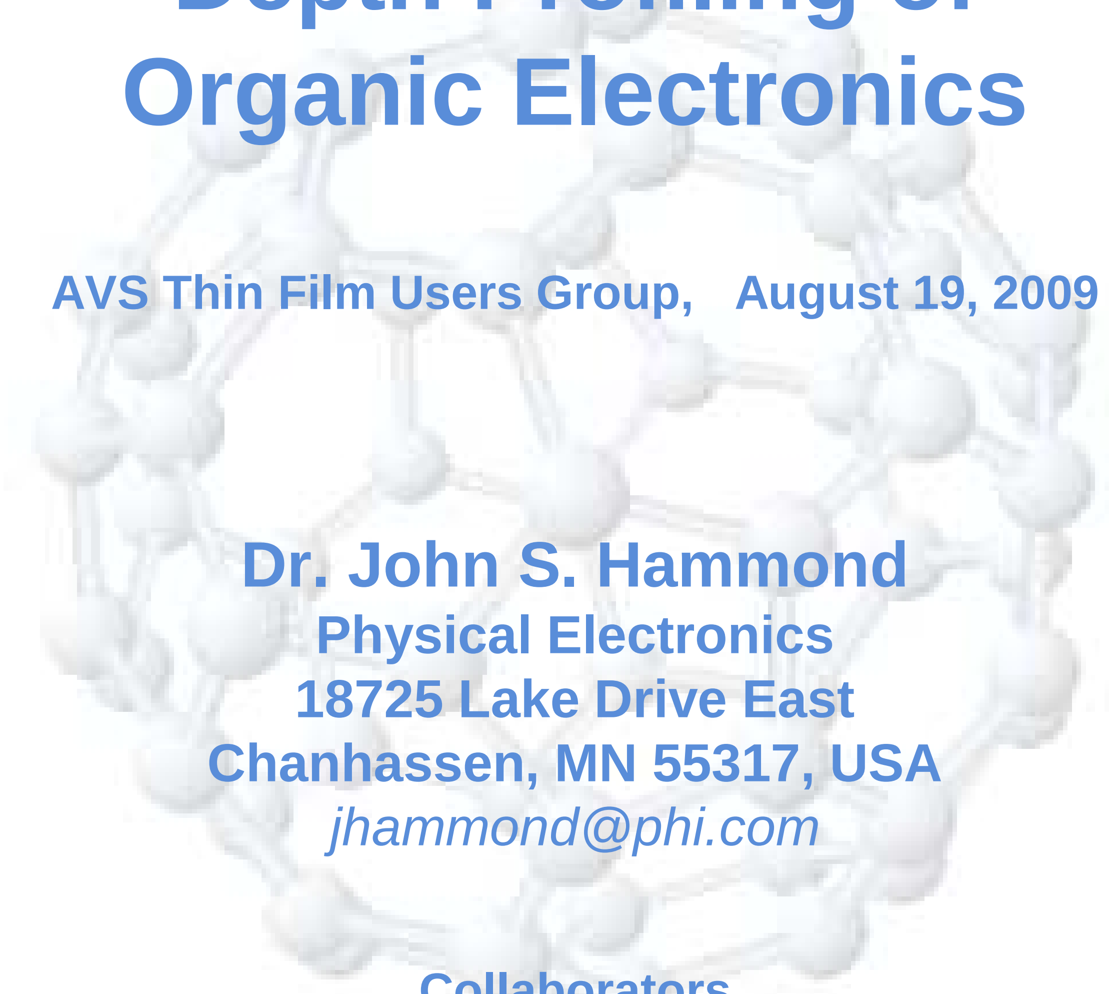

Depth Profiling of Organic Electronics

AVS Thin Film Users Group,   August 19, 2009

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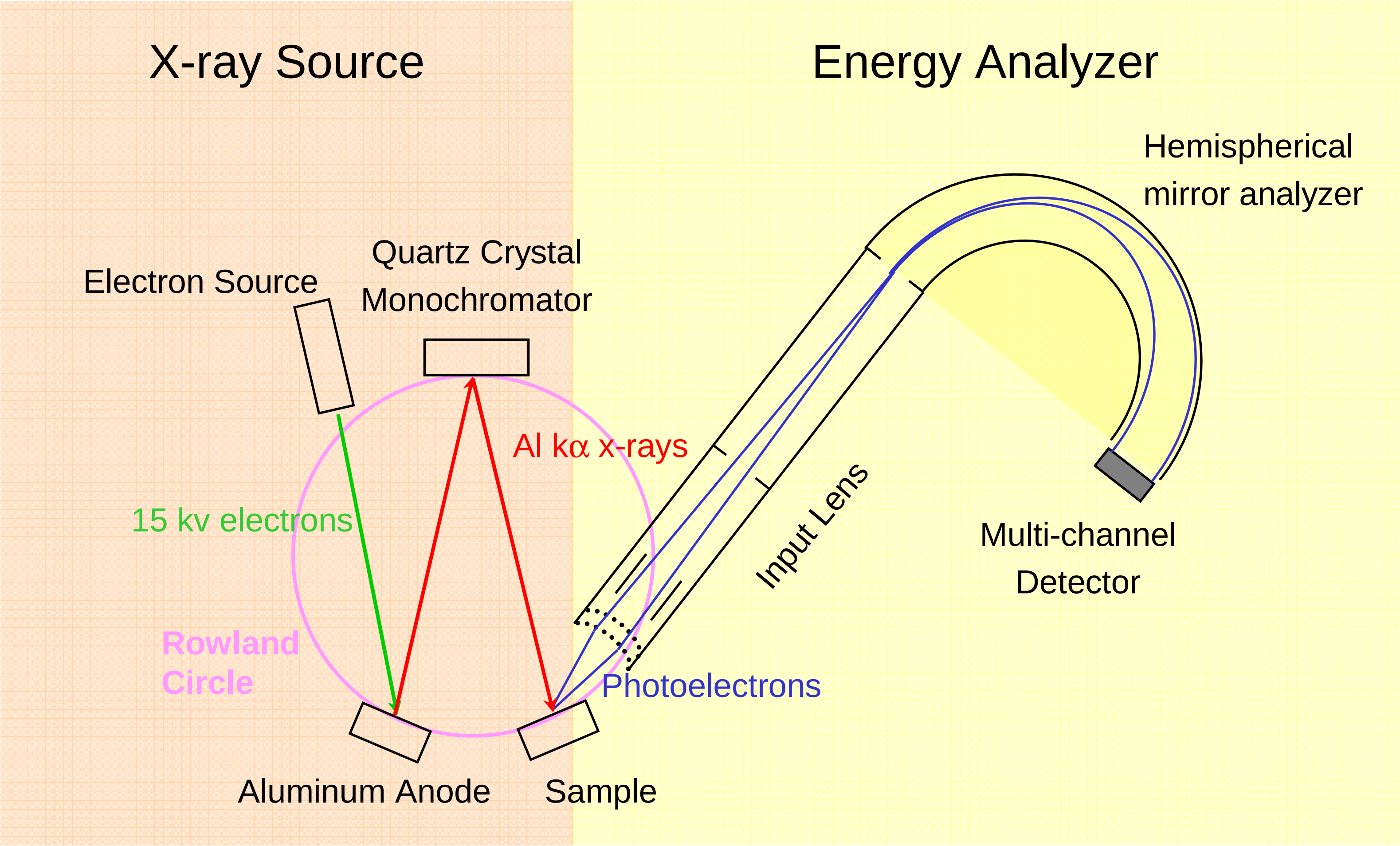
Why use Depth Profiling for Organic Electronics?

- **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**

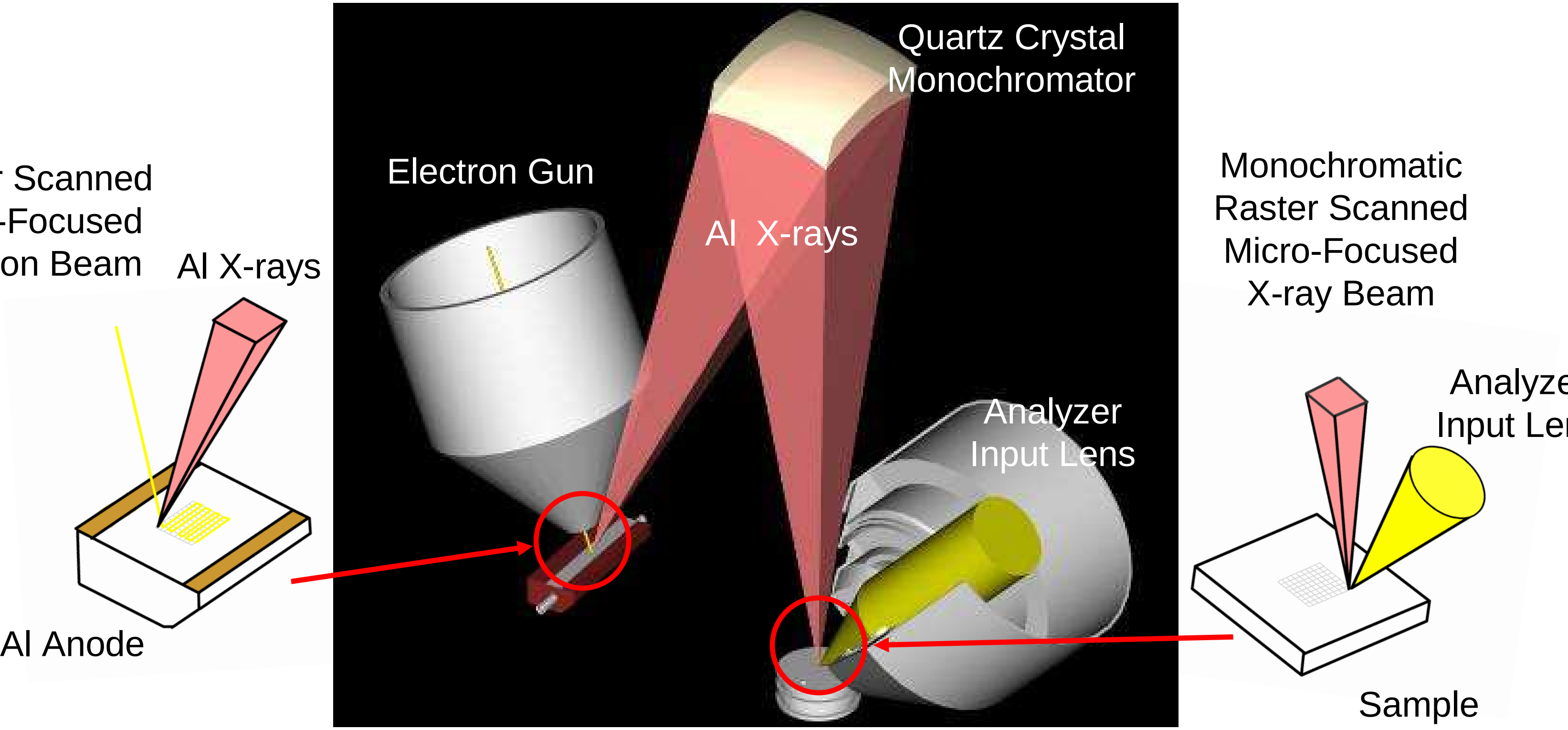
Comparison of XPS and TOF-SIMS

	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**
Depth Profile Speed	0.5 µm / hr	5 µm / hr
Quantification	**Excellent**	Std. needed

XPS System Schematic



Scanning Micro Focused X-ray Source



Raster Scanned
Micro-Focused
Electron Beam

Al X-rays

Al Anode

Electron Gun

Al X-rays

Quartz Crystal
Monochromator

Analyzer
Input Lens

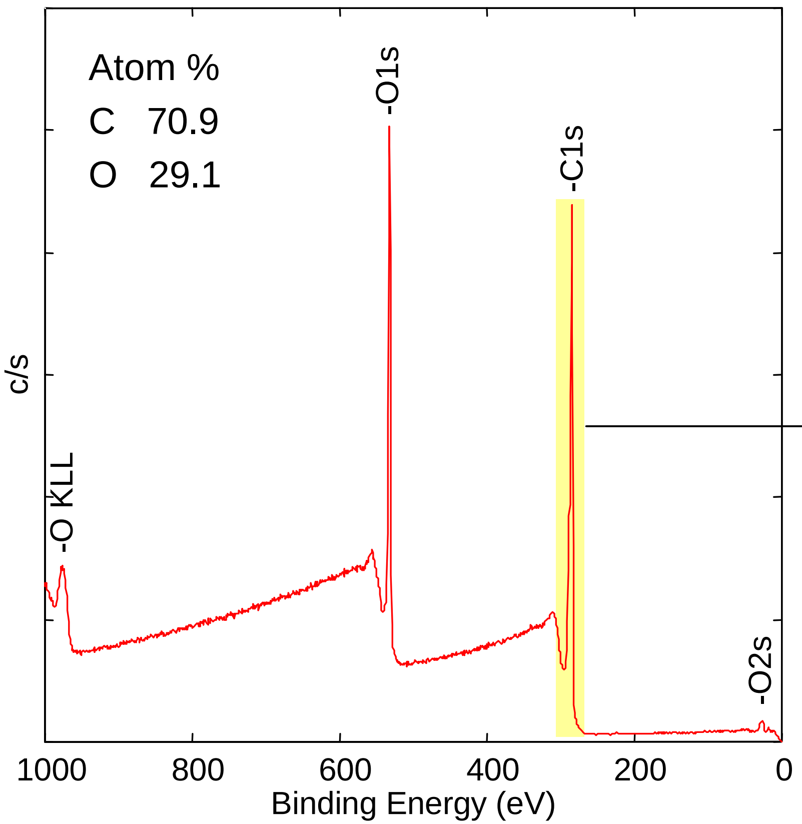
Monochromatic
Raster Scanned
Micro-Focused
X-ray Beam

Analyzer
Input Lens

Sample

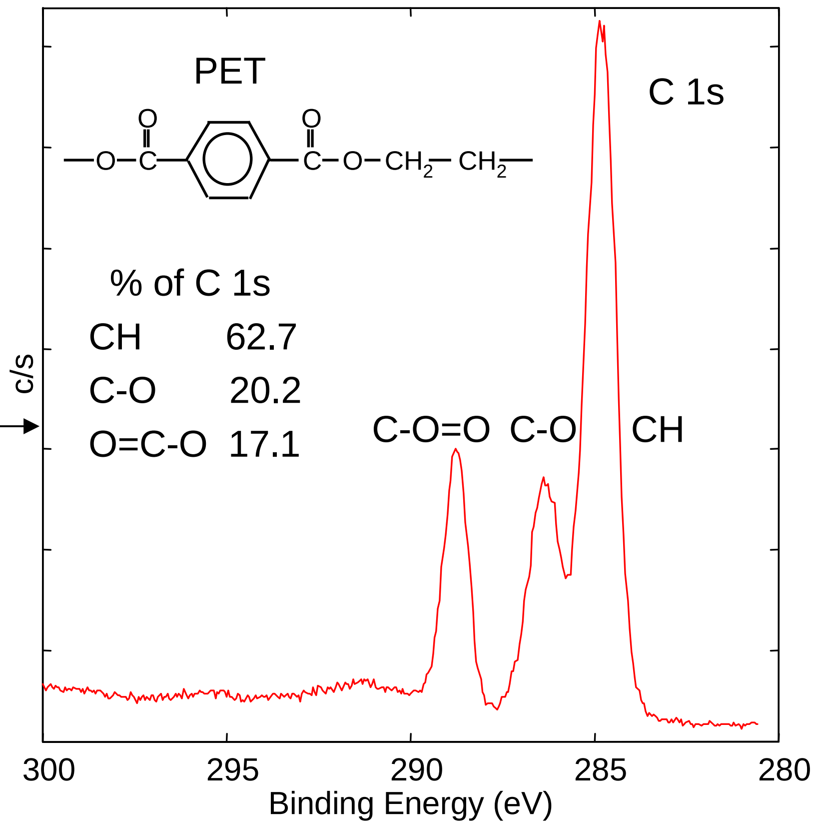
Typical XPS Spectra

Poly(ethylene terephthalate)



Atom %	
C	70.9
O	29.1

XPS survey spectra provide quantitative elemental information



% of C 1s	
CH	62.7
C-O	20.2
O=C-O	17.1

High resolution XPS spectra provide quantitative chemical state information

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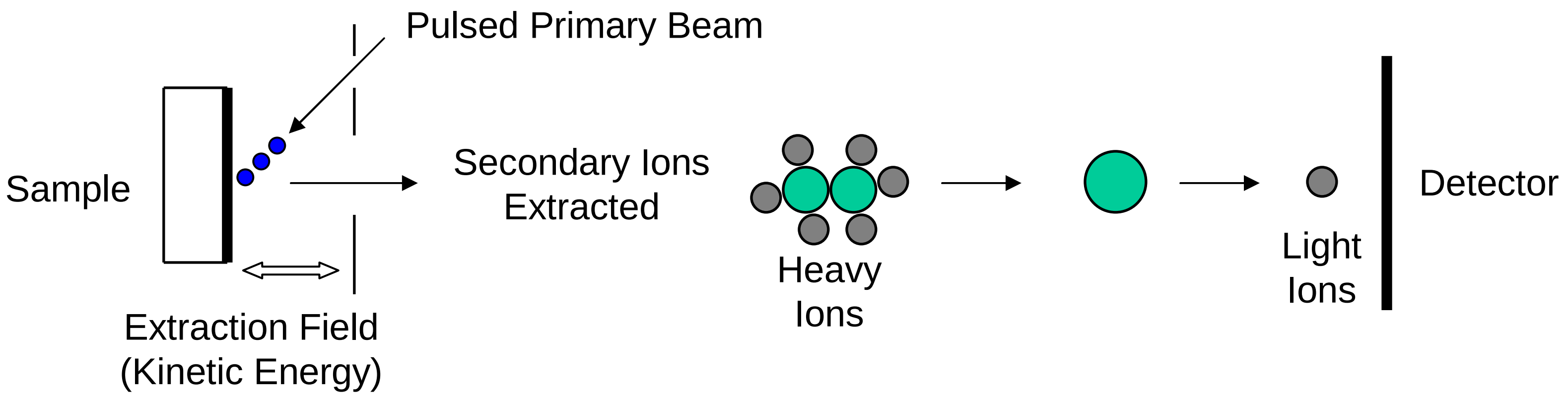
Basic Time-of-Flight Mass Spectrometry



(1) Each pulse of primary ions creates a pulse of secondary ions.

(2) Secondaries of different masses within a single ‘cycle’ arrive at the detector at different times according to the relation:

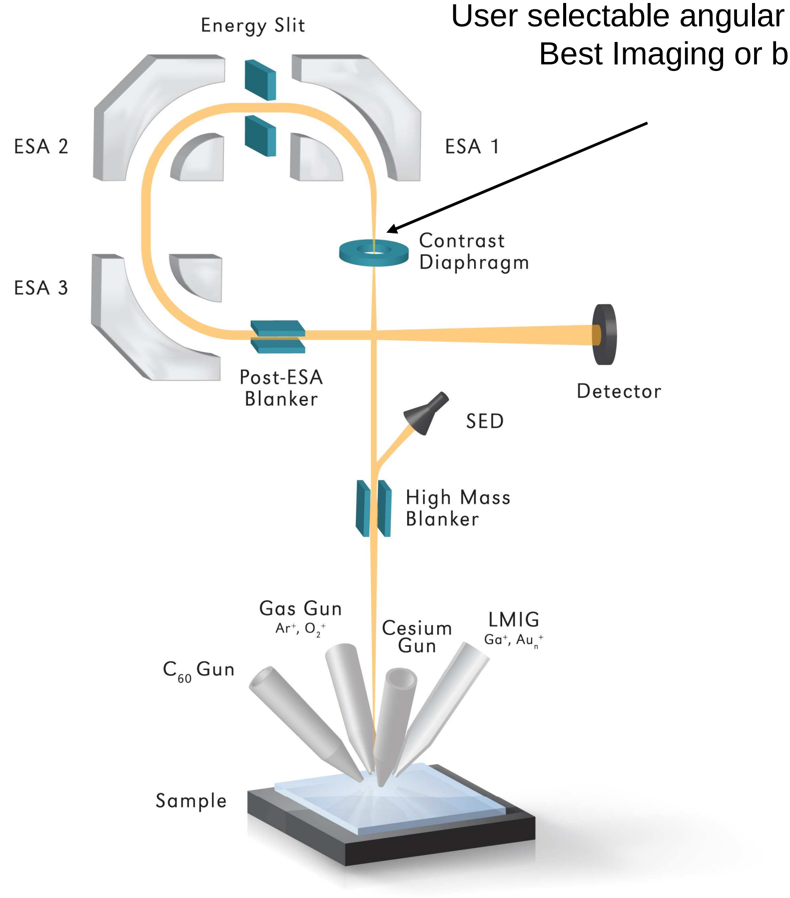
$$K.E. = mv^2/2.$$

(3) Secondary ion with $m/z = 1{,}000$ has flight time ~100µs, therefore ‘cycle time’ = 100µs, so typical pulsing frequency = 10kHz.

PHI TRIFT V *nanoTOF*

TRIFT: Third Generation Energy Compensating TOF Mass Analyzer

Triple Focusing Time-of-Flight Mass Analyzer

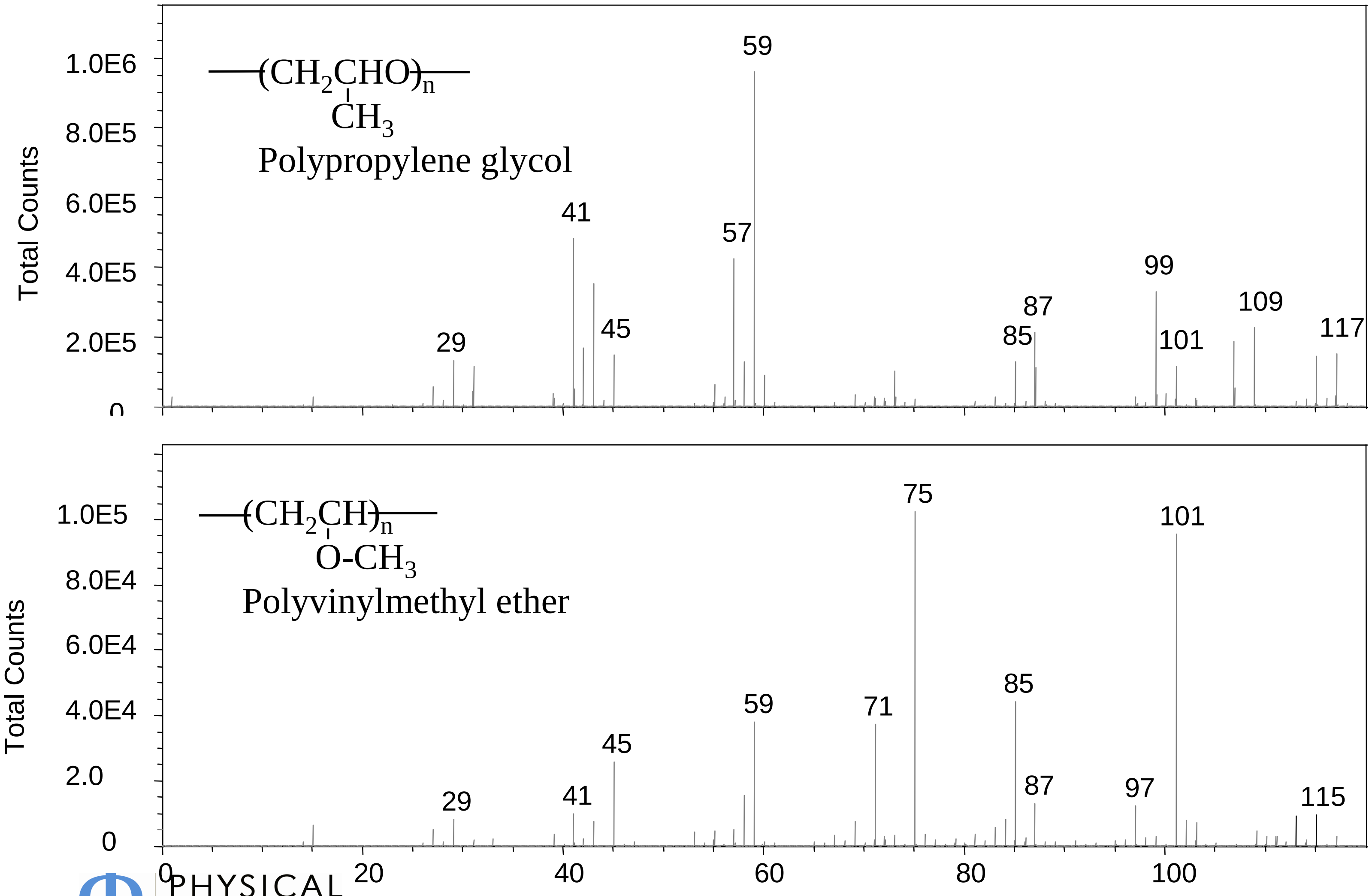


User selectable angular acceptance diaphragm
Best Imaging or best spectroscopy

- **Horizontal sample position**
- **High precision 5-axis stage**
- **100mm x 100mm sample holder**
- **Flexibility for up to 4 ion guns**
- **All new sample handling**

Unique Polymer“Fingerprint” Identification Using TOF-SIMS Spectra

XPS shows identical spectra for both polymers

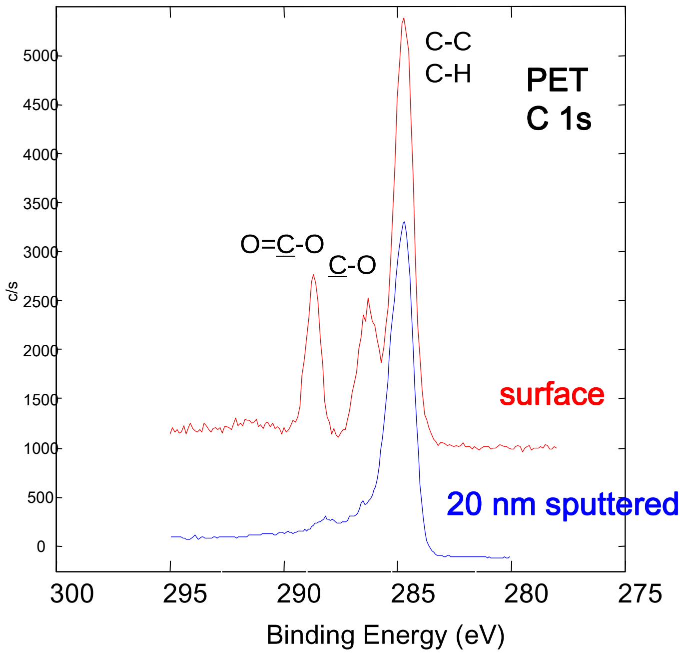


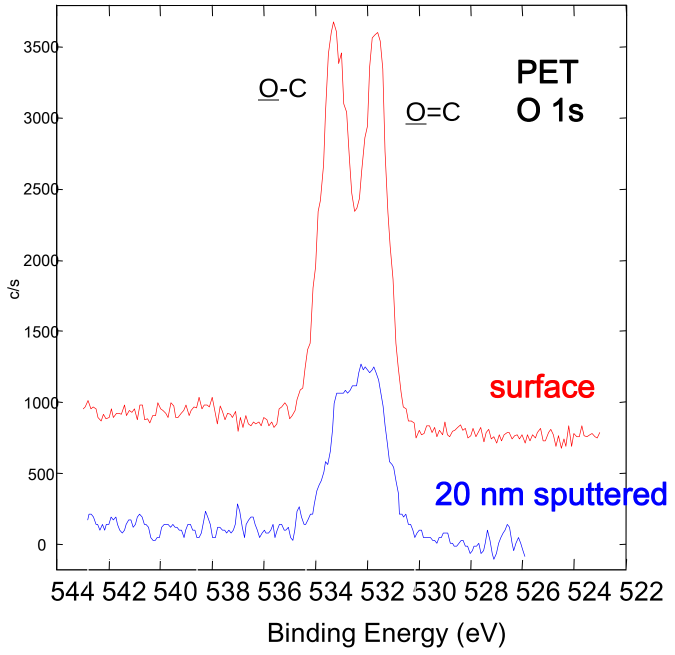
Why a C_{60} Ion Gun is Needed

- Polymer surface modifications deeper than 10 nm and multi-layer polymer structures need to be characterized
- Alternating surface spectroscopy and ion sputter ablation commonly used to obtain compositional depth profiles
- Ar ion sputtering has been the traditional approach to depth profile beyond 5 nm for inorganic and metals
- This approach is not useful for polymers or organic materials because of the high level of chemical damage produced just below the surface by the Ar ions
- C_{60} ion sputtering has been demonstrated to be effective for sputter etching many polymer and organic materials while causing minimal chemical damage to the remaining sample surface

Damage Accumulation Indicated by XPS

500 eV Ar^+ Sputter





Damage is observed.

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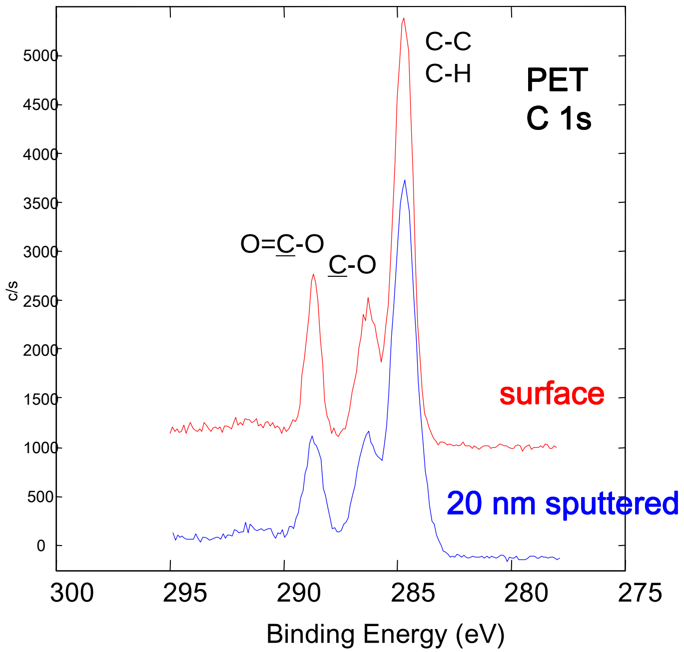
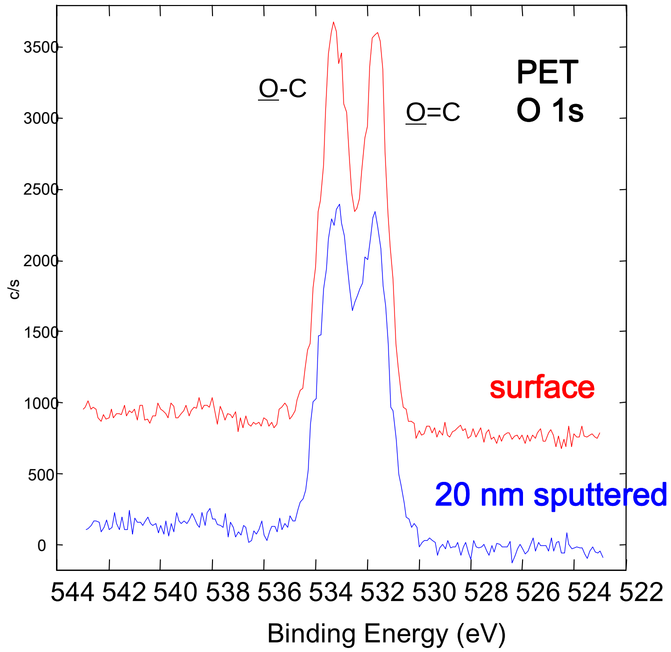
No Damage Observed by XPS

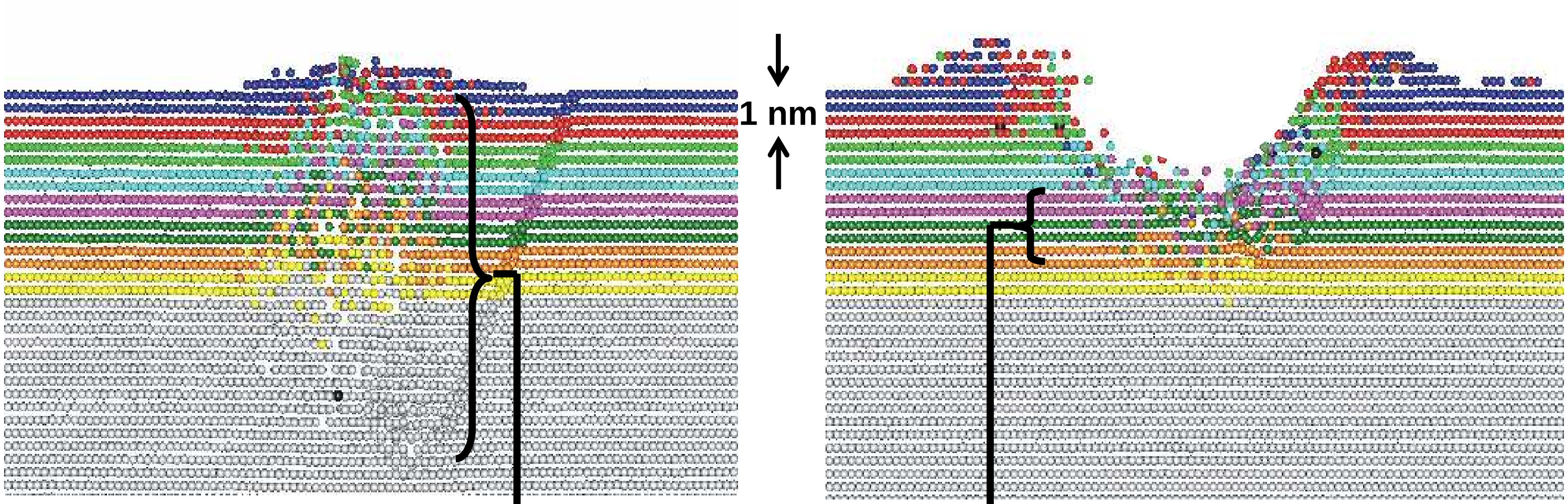
10keV C_{60}^{+} Sputter





No damage observed.

Altered Volume & Sub-surface Damage



15 keV Ga

15 keV C_{60}

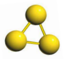
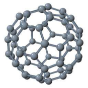
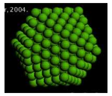
Residual C_{60} sputter damage is mostly removed with the next C_{60} impact event.

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

Graphic courtesy B. Garrison & Z. Postawa.

Requisites for Molecular Depth Profiling

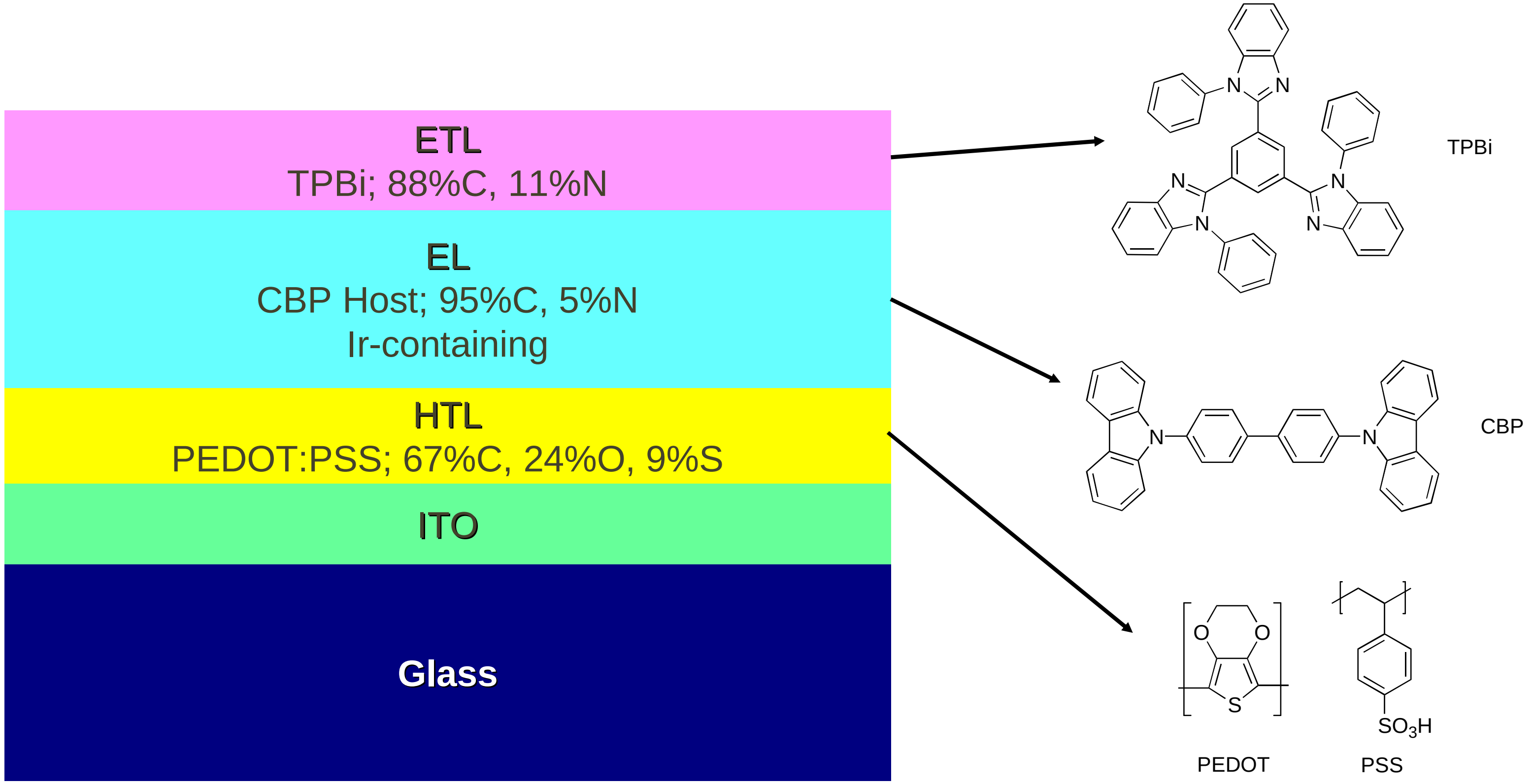
Condition for molecular depth profiling…
→ damage must be removed as fast as it is created.
∴ sputtered molecules >> penetration depth.

10 keV	rel. yield (Ga=1)[‡]	σ_d (cm^2)	range (nm)[*]	removed depth (nm)[**]
SF_5	100	5×10^{-13}	9.8	0.06
Au_3 	1,000	1×10^{-12}	19	0.3
C_{60} 	2,000	2×10^{-13}	2.6	3.3
Au_{400} 	20,000	[†]2×10^{-13}	6.6	3.4

[‡] Adapted from Kersting, et al. *Appl. Surf. Sci.* (2004) and Tempez, et al. *Rapid Comm. Mass Spectr.* (2004).
[†] Conservatively estimated lower limit. Values of σ_d are applicable to most organic systems. [*] Calculated using SRIM2003. [**] Calculated using relative yield and σ_d, in good agreement with Delcorte, et al. *NIMB* (2000) and Postawa, et al. *J. Phys. Chem. B* (2004).

Model of Multi-layer OLED Device

Y.-Y. Chen, et al., *Anal. Chem.* **80** (2008) 501.



ETL
TPBi; 88%C, 11%N

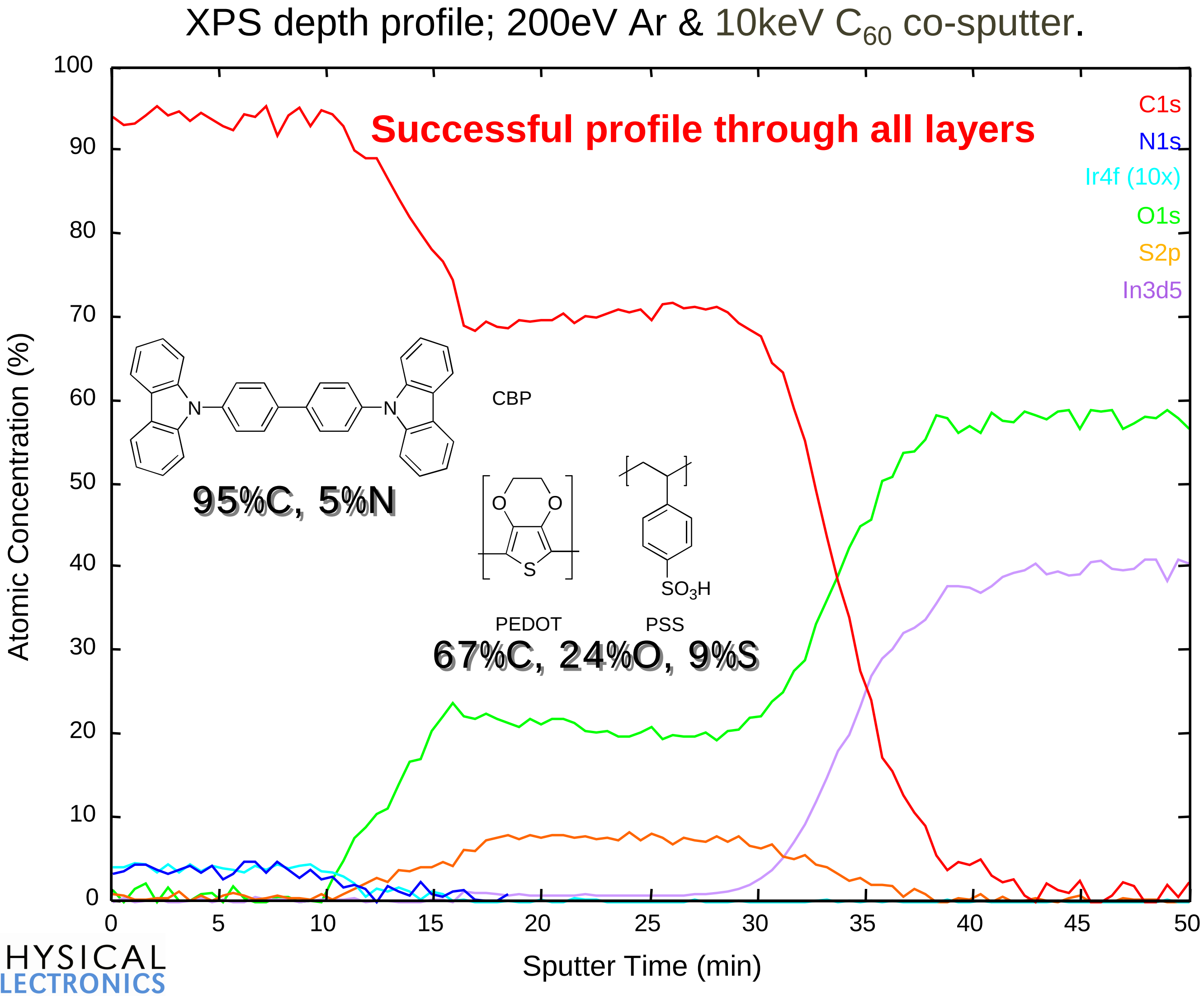
EL
CBP Host; 95%C, 5%N
Ir-containing

HTL
PEDOT:PSS; 67%C, 24%O, 9%S

ITO

Glass

Ar/C_{60} Co-Sputter Depth Profile of OLED Device



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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 Depth Profiles

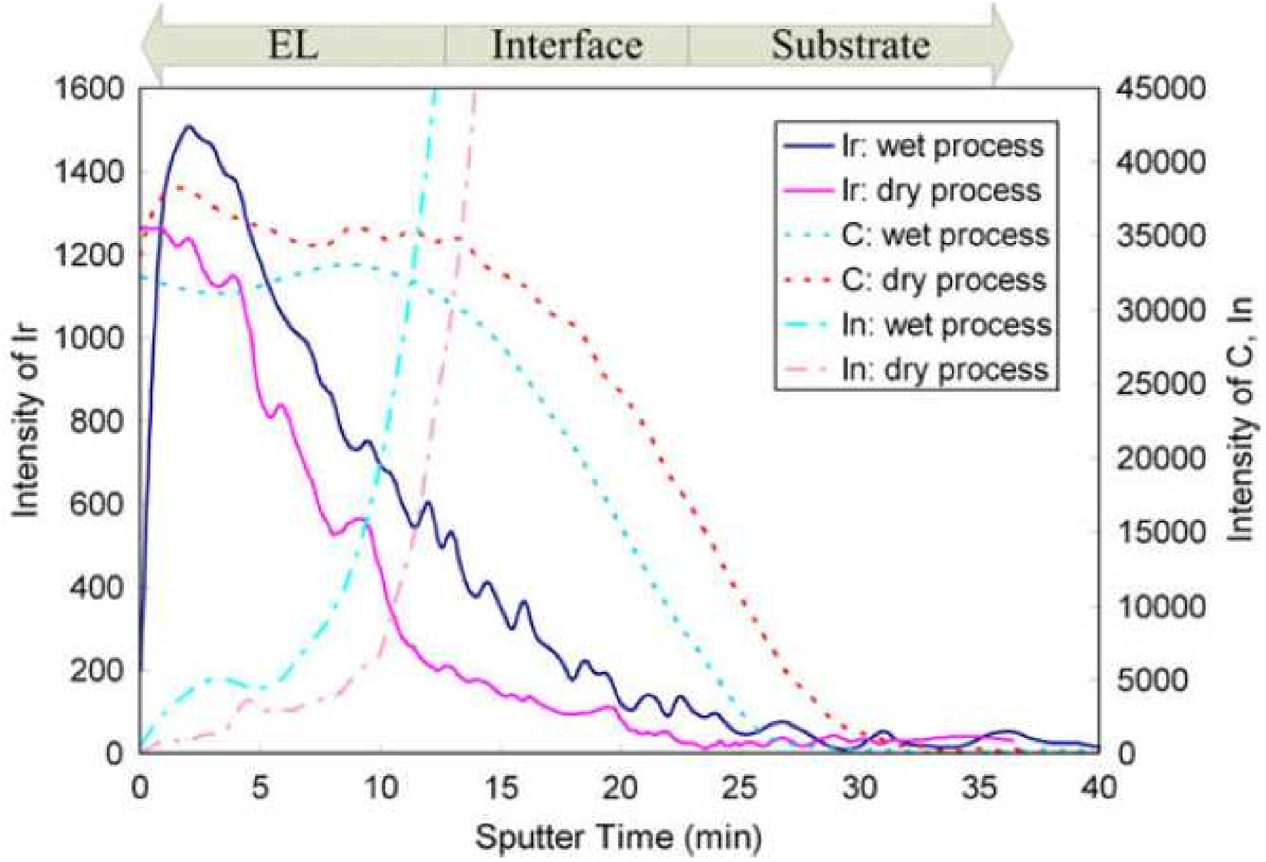
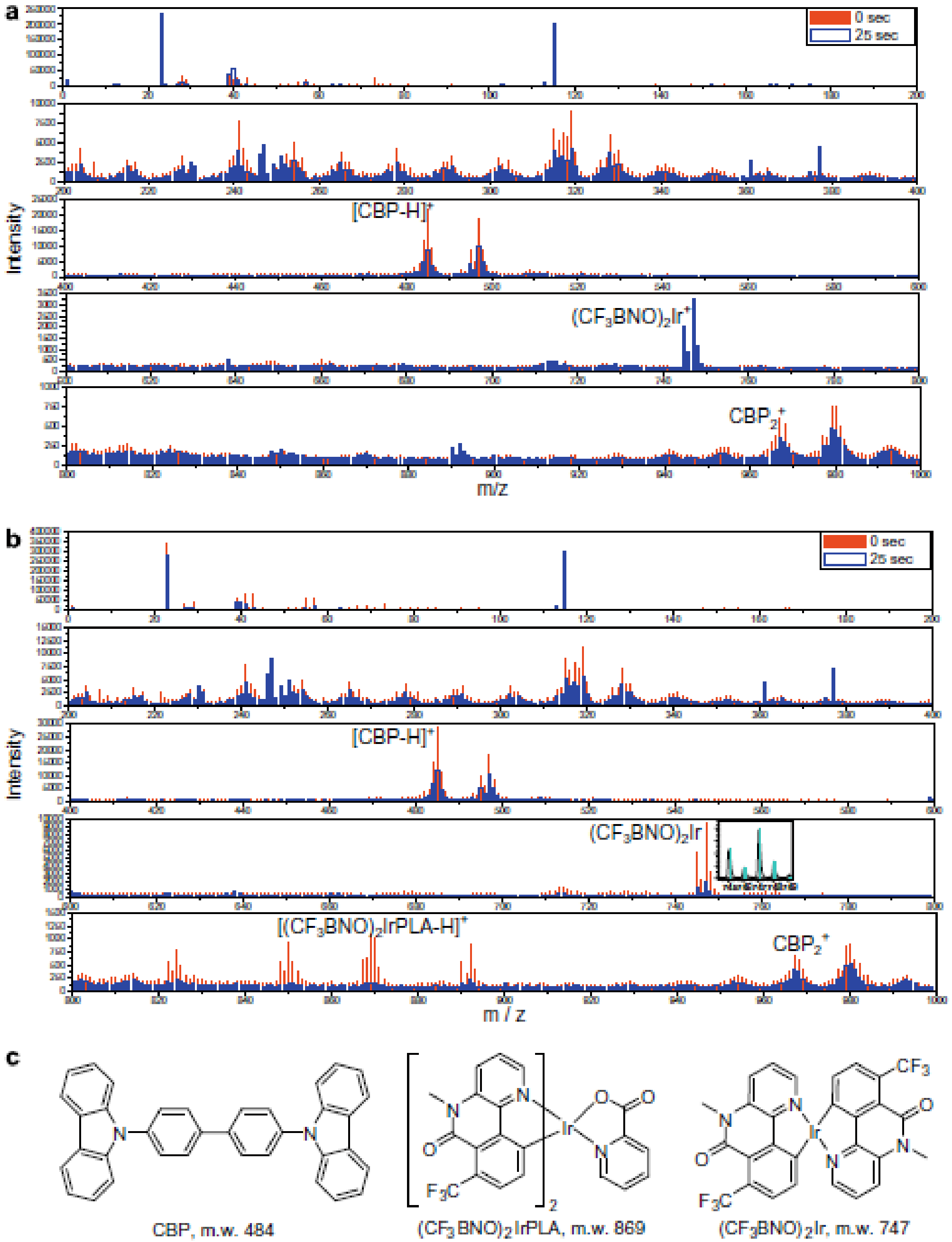


Fig. 1. XPS elemental depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).

- **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**

Wet versus Dry Process Depth Profiles

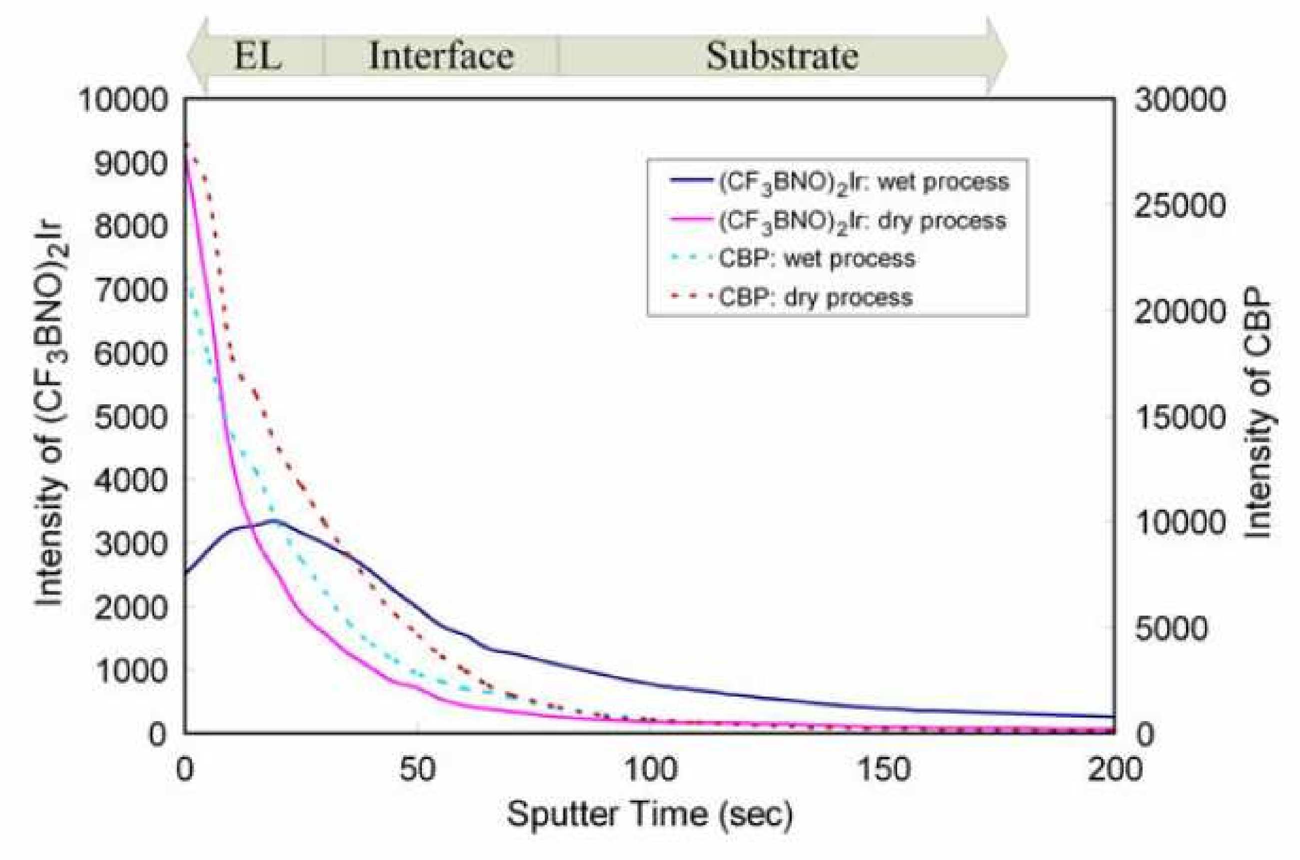


Fig. 3. ToF-SIMS depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).

- **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

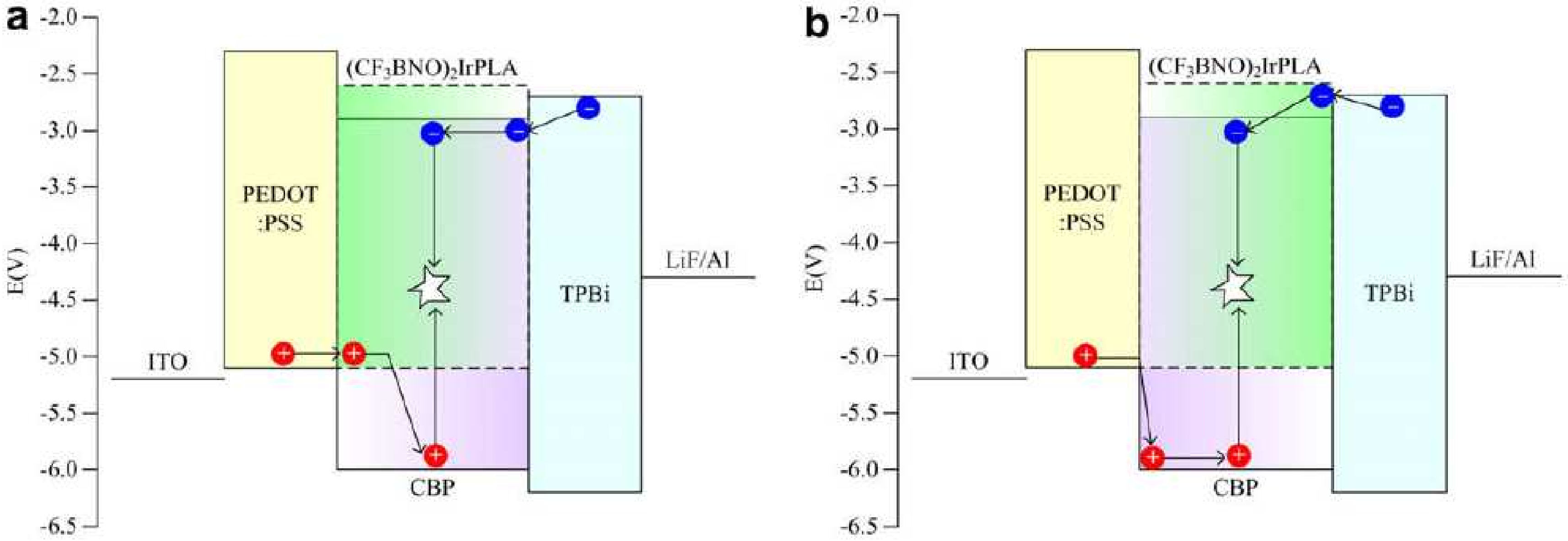


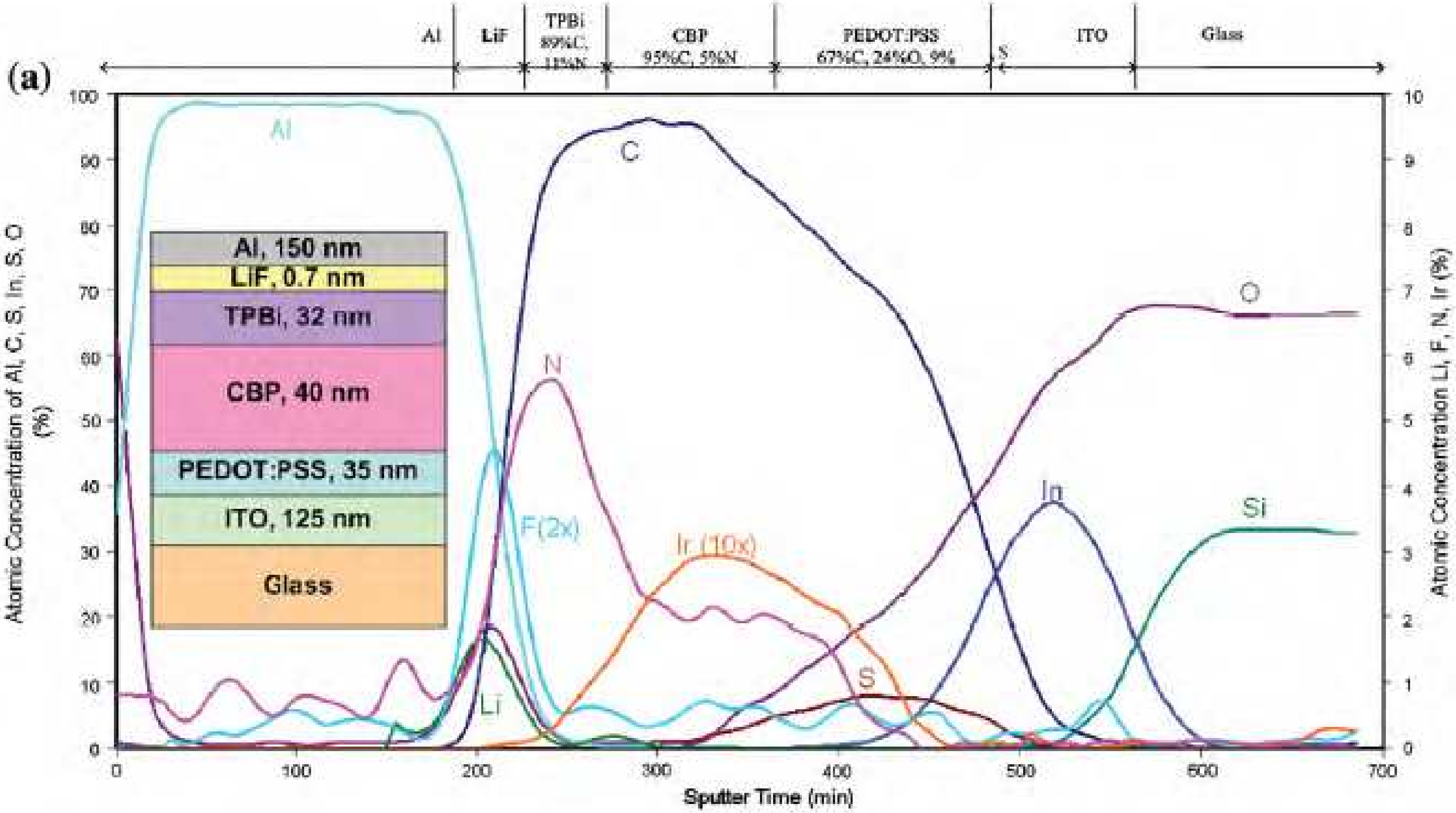
Fig. 4. Energy diagram and the route of charge carriers of OLED with EL prepared with (a) wet-process and (b) dry-process. The shade of CBP and $(CF_3BNO)_2IrPLA$ indicates its relative concentration.

- **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**

Degradation of OLED’s

- **Generally accepted intrinsic degradation mechanisms**
  - Morphological instabilities
  - Indium migration
  - Mobile ionic impurities
  - Immobile positive charge accumulation
- **Depth profiling of chemical and molecular compositions can evaluate these different degradation mechanisms**
- **XPS depth profiles after 0, 0.25, 1, 3, 6, and 12 hrs of constant 5 V forward bias**

Reference XPS Depth Profile of OLED with C_{60}



- Note diffusion of Al and Li and F into organic layer

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OLED Depth Profiles versus Bias Time

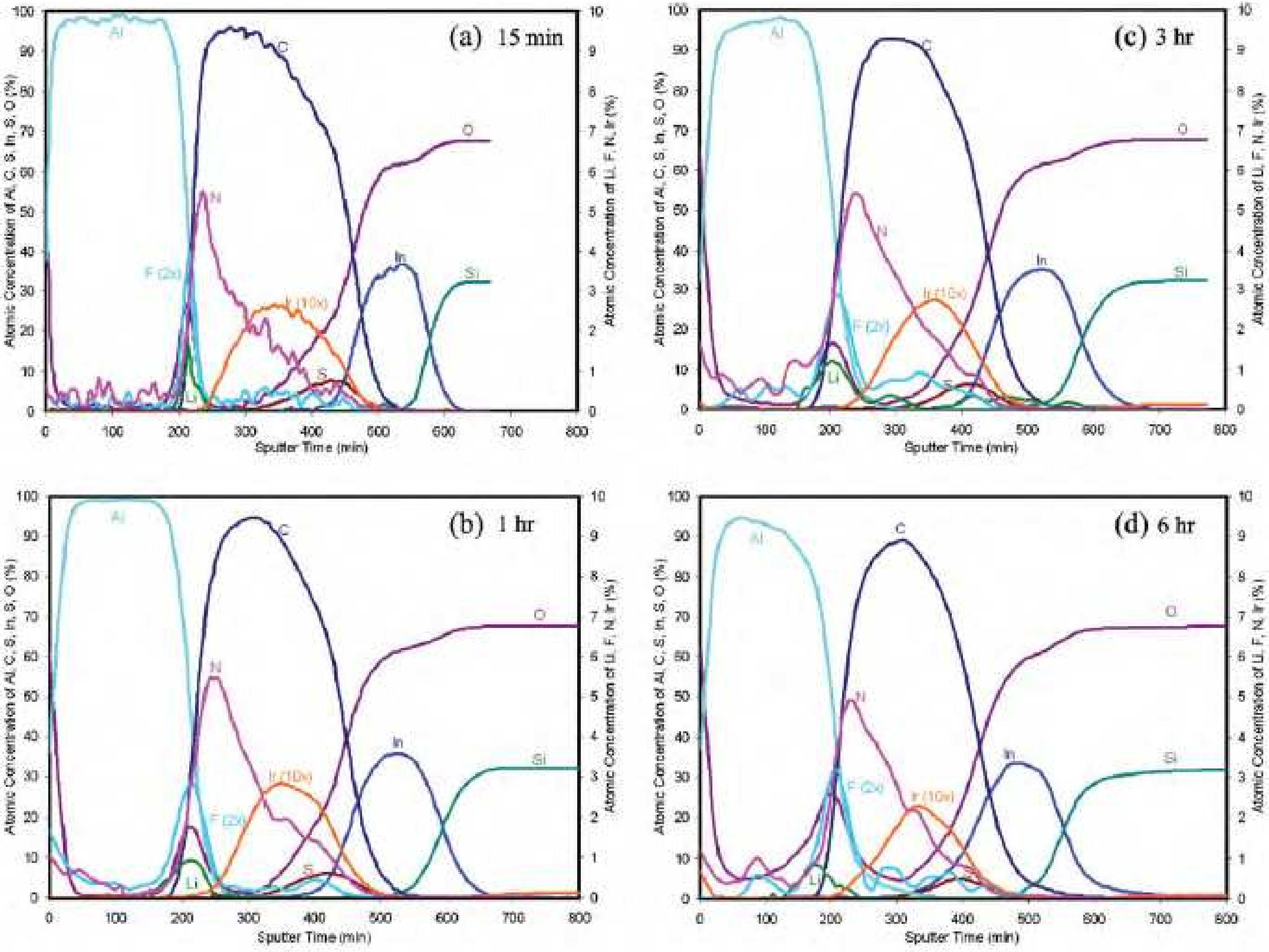
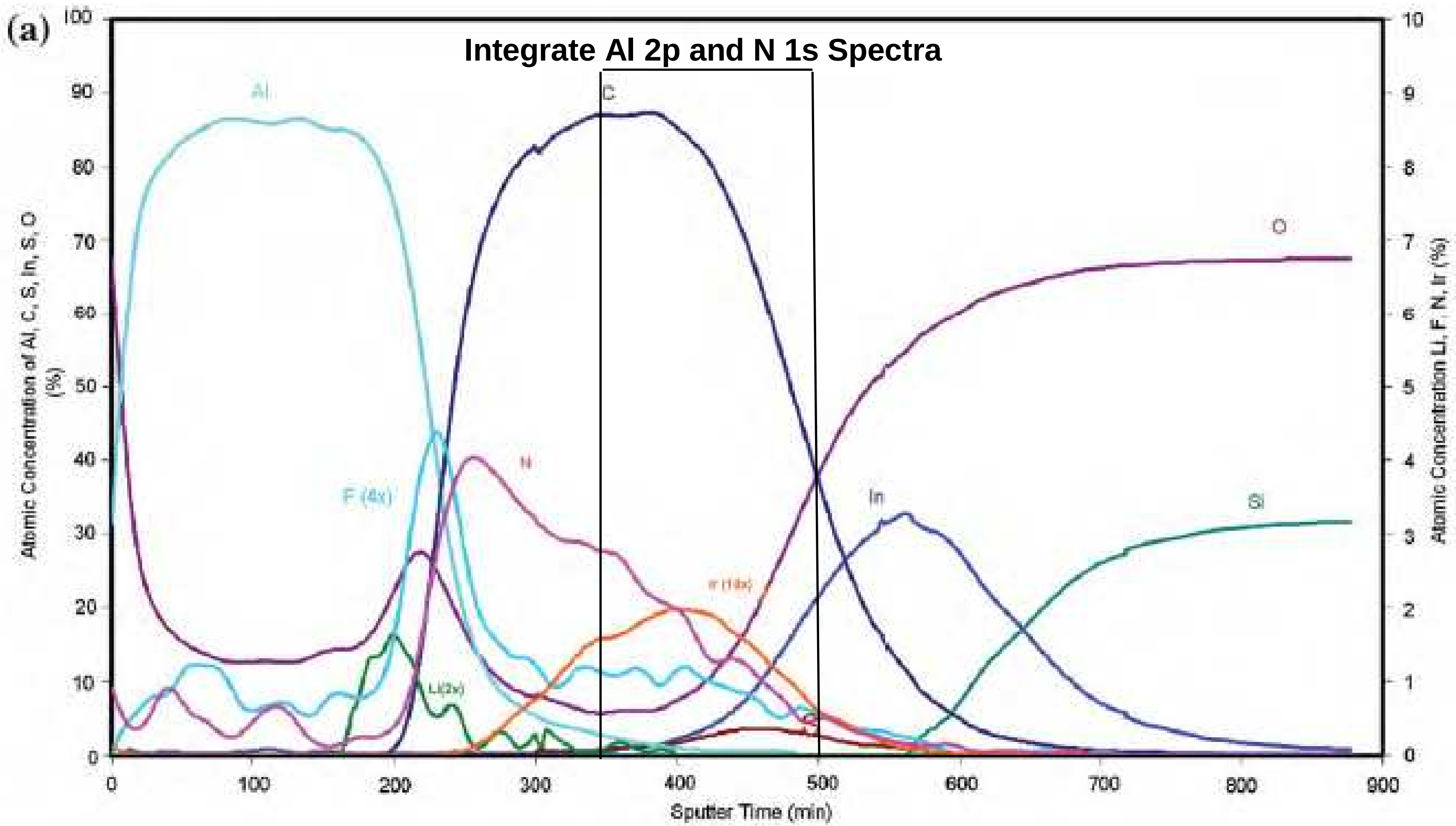


Fig. 3. XPS elemental depth profiles of OLED devices aged at 5 V forward bias for different times.

- Note broadening of interfaces, nitrogen migration and C into ITO

OLED Depth Profile versus 12 hrs. Bias Time



Integrate Al 2p and N 1s Spectra

- Note enhanced broadening of interfaces, nitrogen migration and more C into ITO

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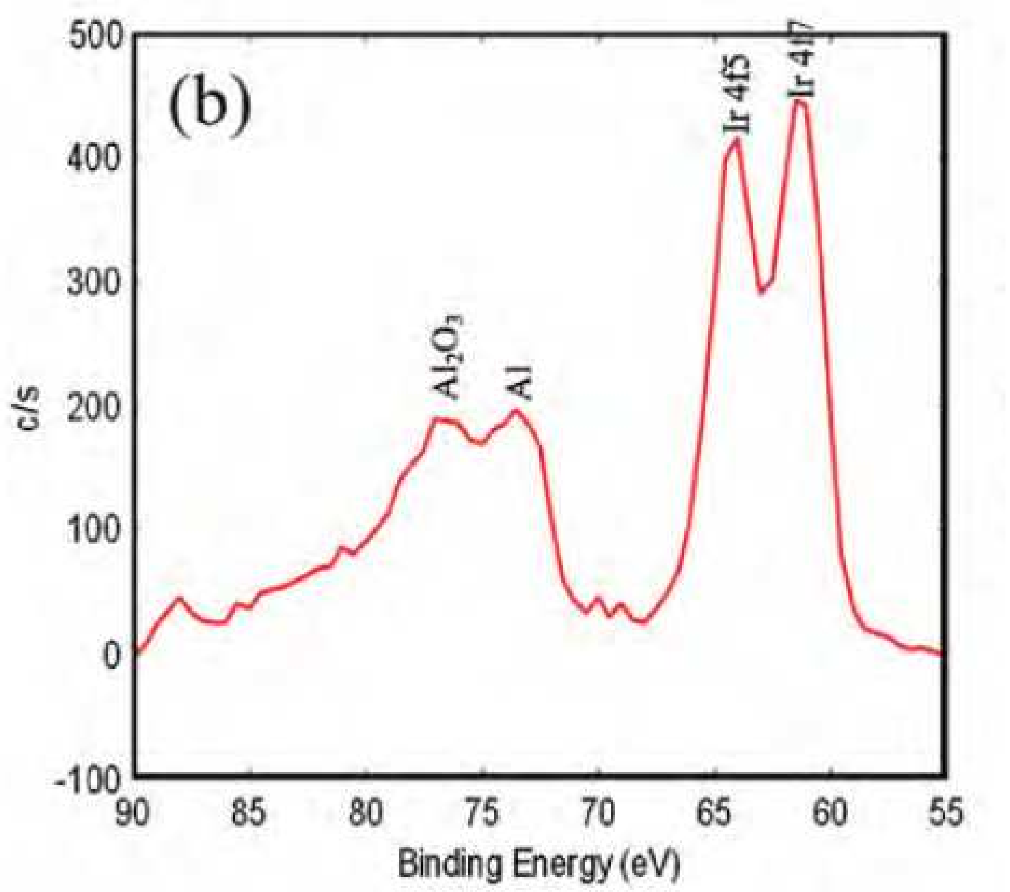
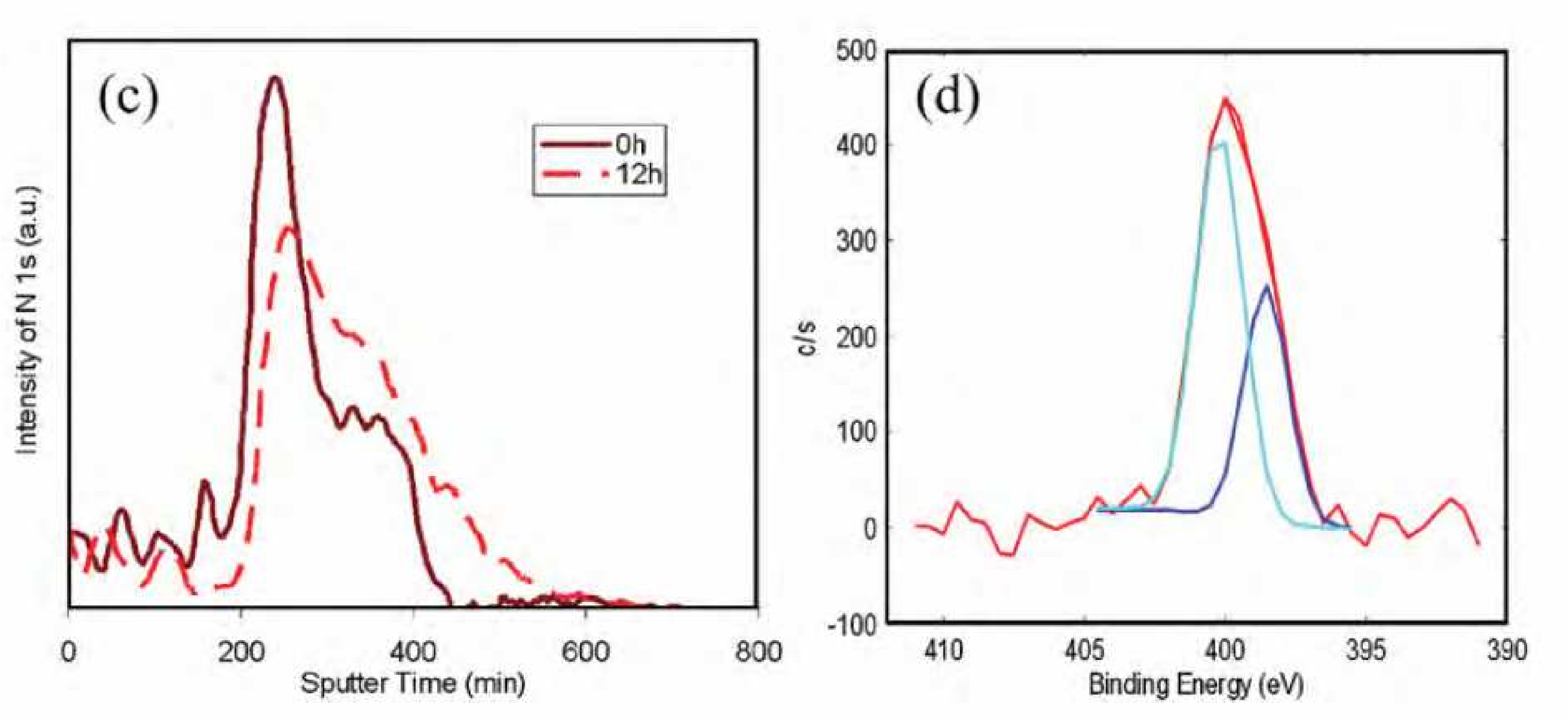
Intregrated Al 2p Spectra after 12 hrs. Bias



- Note migration of Al and formation of Al Oxide

Intregrated N Profile, Spectra after 12 hrs. Bias



- Note migration of N but N chemistry remains constant compared to reference N 1s spectrum

Depth Profiling for Organic Electronics

- **C_{60} depth profiling combined with XPS provides a powerful new tool for characterizing new “nanotechnology” products use extremely thin organic and polymer structures**
  - OLEDS
  - Energy conversion materials and fuel cell membranes
  - Differences in fabrication process producing molecular gradients can be characterized
- **Product degradation resulting from molecular oxidation and molecular diffusion can be characterized**

Thank You!