

# Depth Profiling of Organic Electronics

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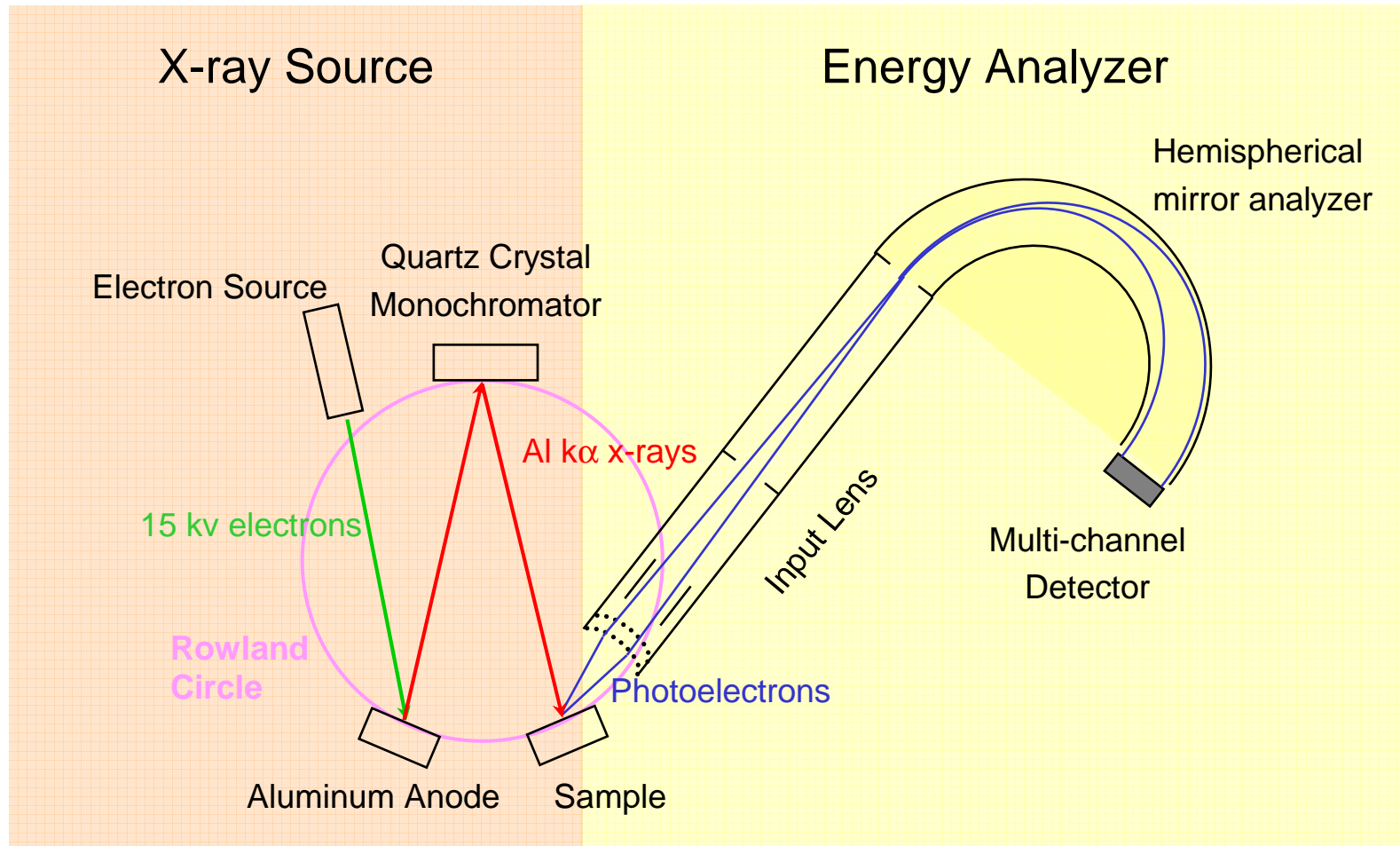
# Why use Depth Profiling for Organic Electronics?

- ❑ **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**

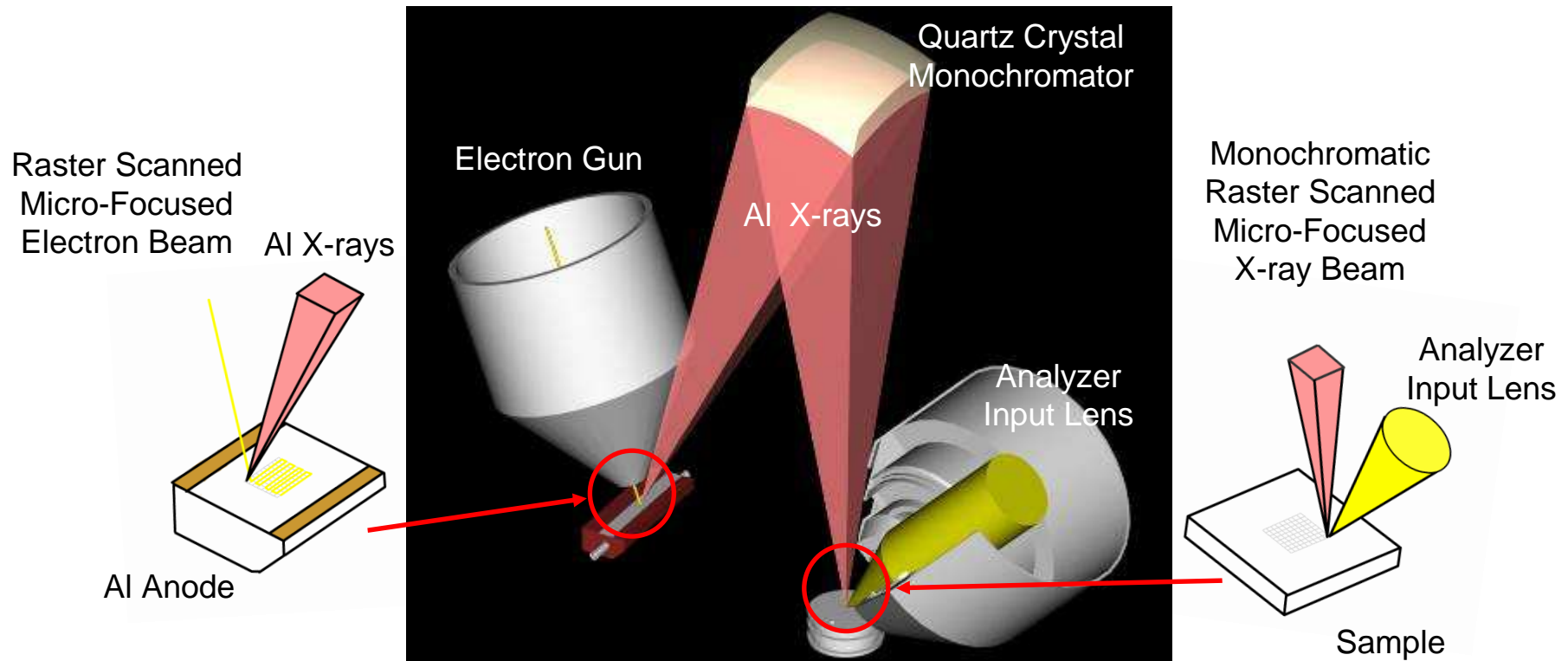
# Comparison of XPS and TOF-SIMS

	XPS	TOF-SIMS
Probe Beam	<b>Photons</b>	Ions
Analysis Beam	Electrons	Ions
Spatial Resolution	10 $\mu\text{m}$	<b>0.10 <math>\mu\text{m}</math></b>
Sampling Depth( $\text{\AA}$ )	5-75	<b>1-10</b>
Detection Limits	0.01atom %	1ppm
Information Content	Elemental Chemical	Elemental Chemical <b>Molecular</b>
Depth Profile Speed	0.5 $\mu\text{m}$ / hr	5 $\mu\text{m}$ / hr
Quantification	<b>Excellent</b>	Std. needed

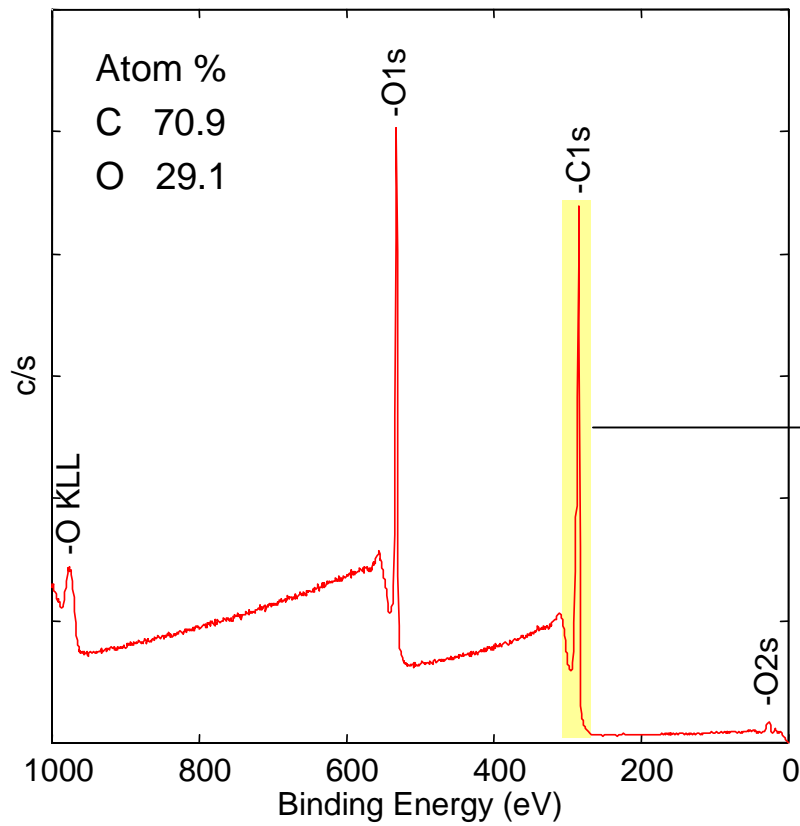
# XPS System Schematic



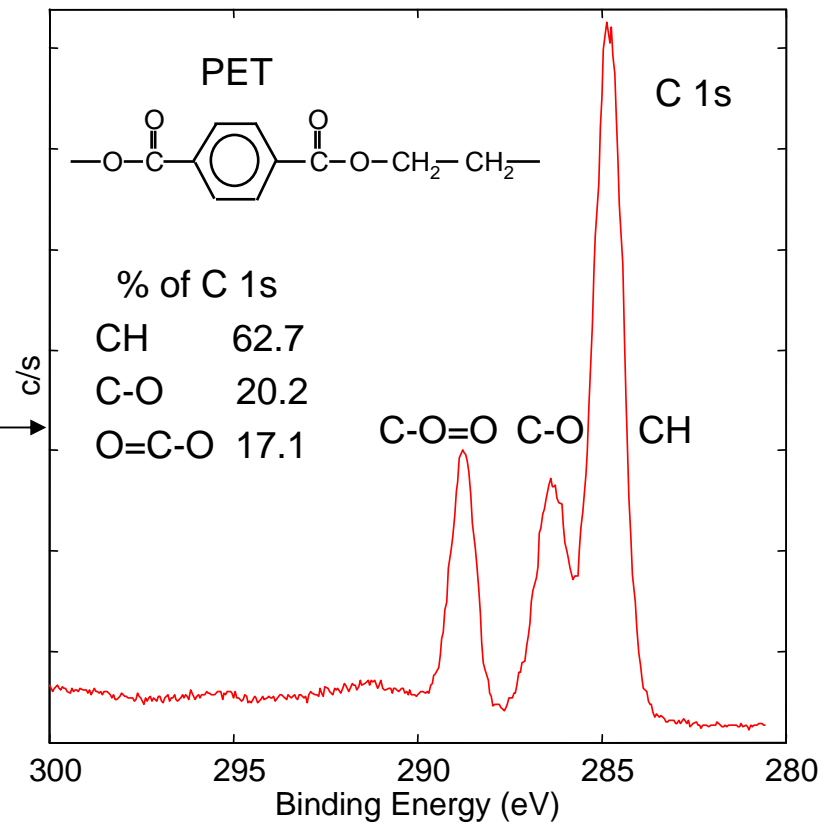
# Scanning Micro Focused X-ray Source



# Typical XPS Spectra Poly(ethylene terephthalate)

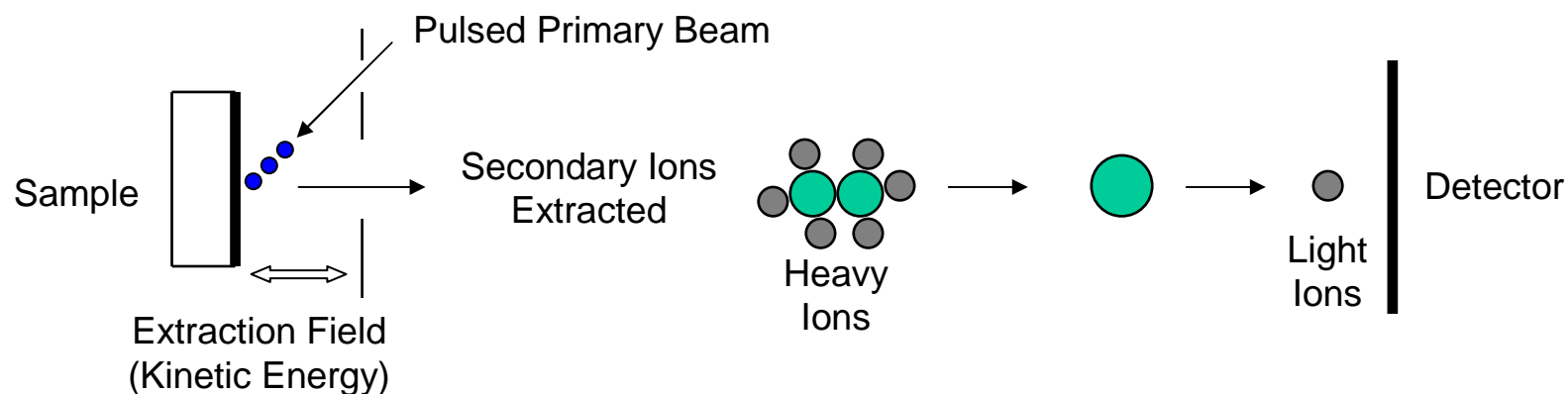


XPS survey spectra provide  
quantitative elemental information



High resolution XPS spectra provide  
quantitative chemical state information

# Basic Time-of-Flight Mass Spectrometry



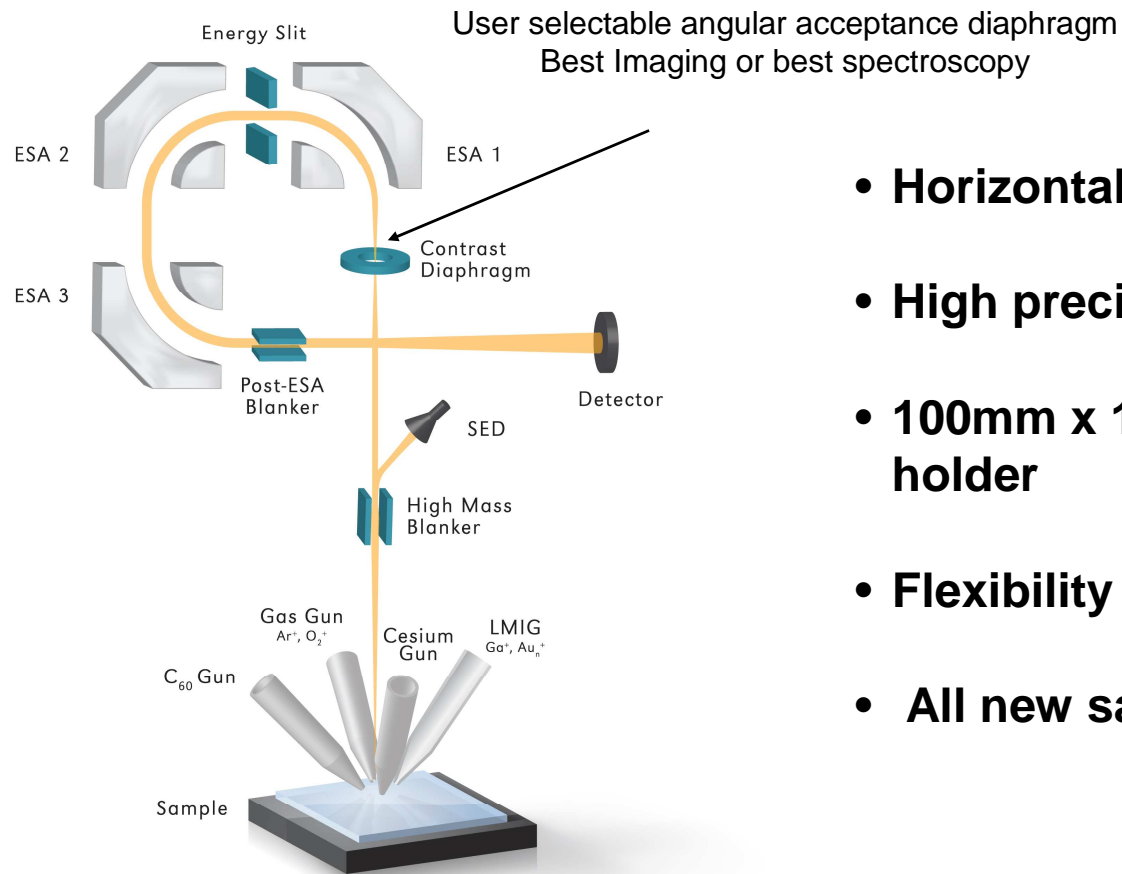
- (1) Each pulse of primary ions creates a pulse of secondary ions.
- (2) Secondaries of different masses within a single 'cycle' arrive at the detector at different times according to the relation:

$$\text{K.E.} = mv^2/2.$$

- (3) Secondary ion with  $m/z = 1,000$  has flight time  $\sim 100\mu\text{s}$ , therefore 'cycle time' =  $100\mu\text{s}$ , so typical pulsing frequency =  $10\text{kHz}$ .

# PHI TRIFT V *nanoTOF*

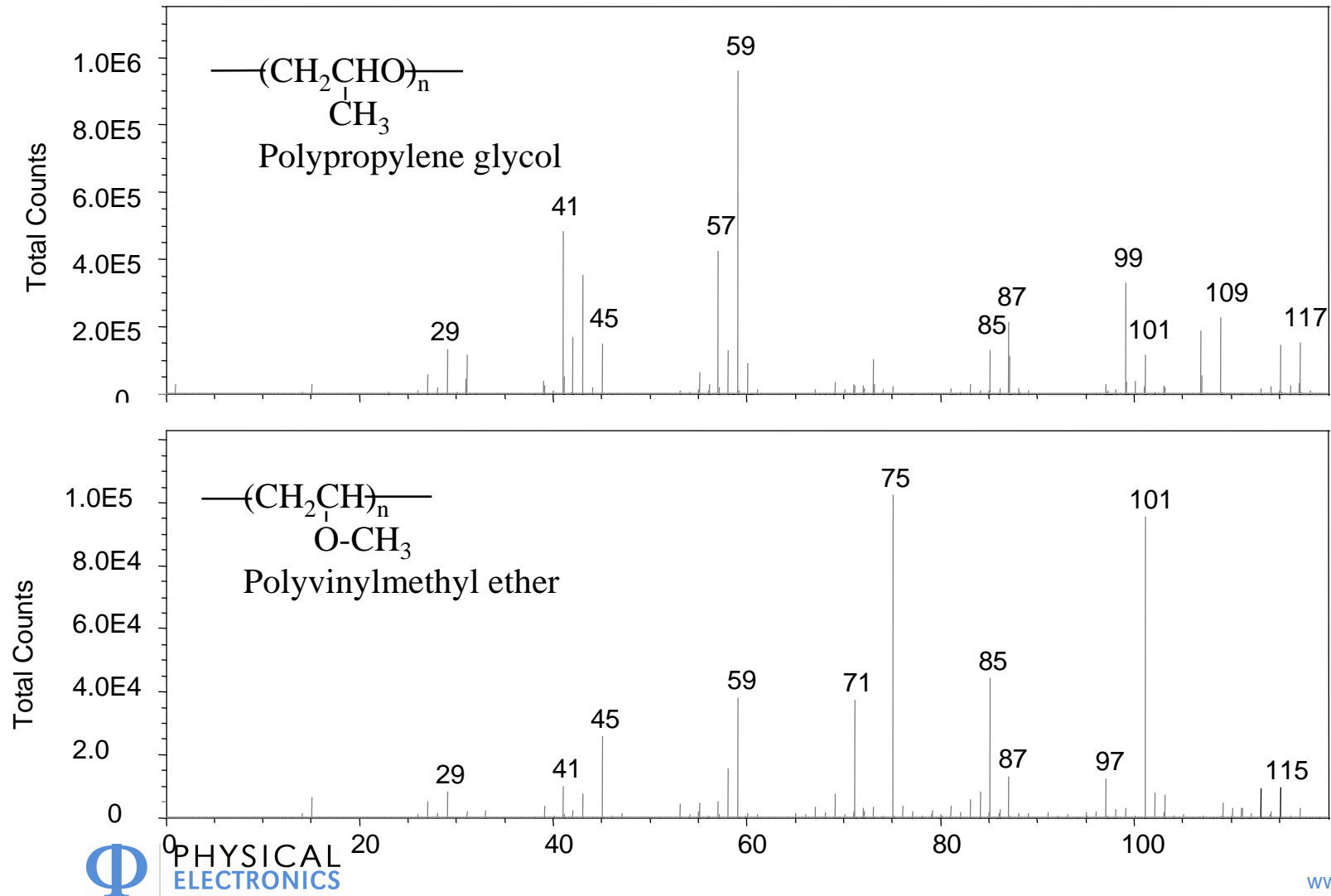
**TRIFT: Third Generation Energy Compensating TOF Mass Analyzer**  
Triple Focusing Time-of-Flight Mass Analyzer



- **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

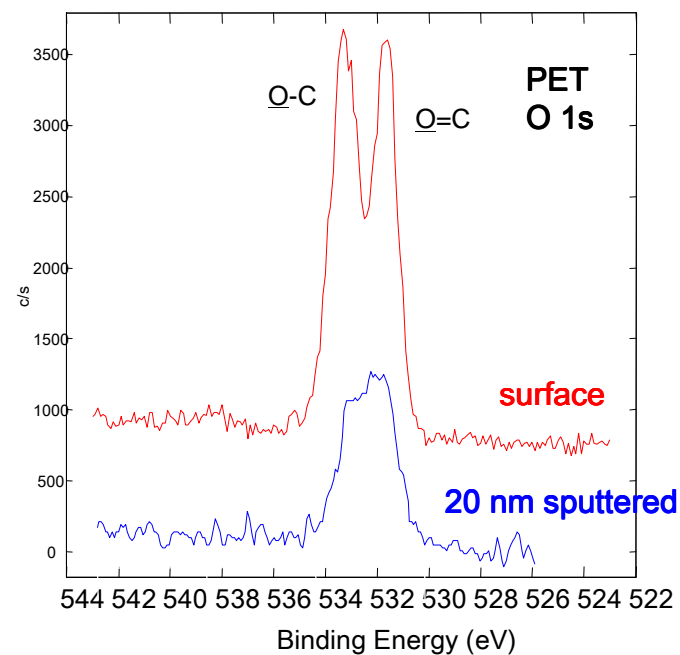
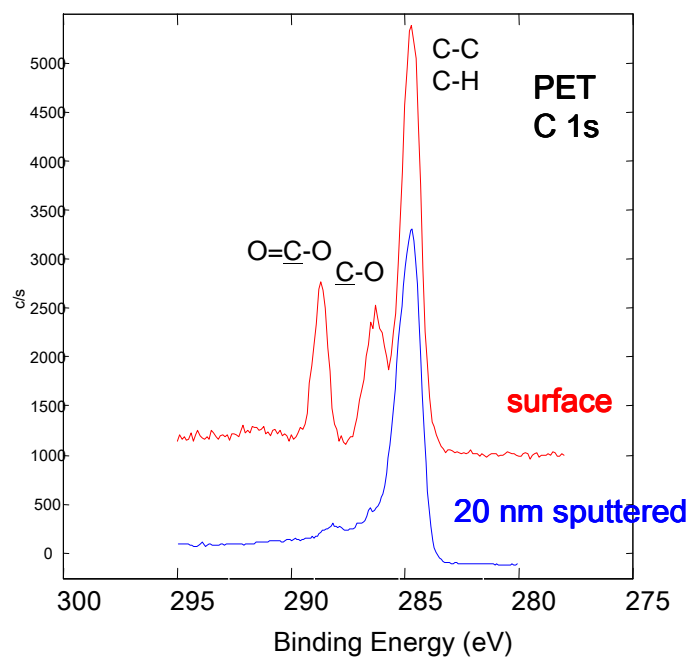


# Why a C<sub>60</sub> Ion Gun is Needed

- ❑ **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<sub>60</sub> 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

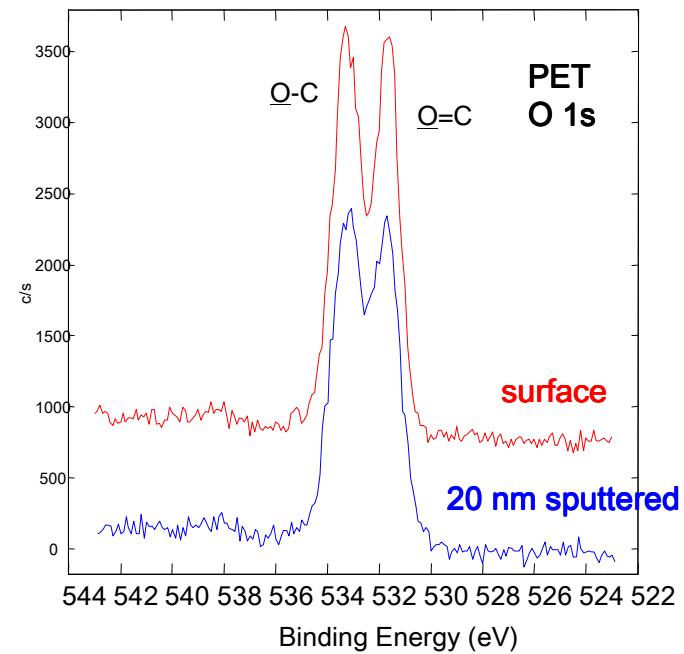
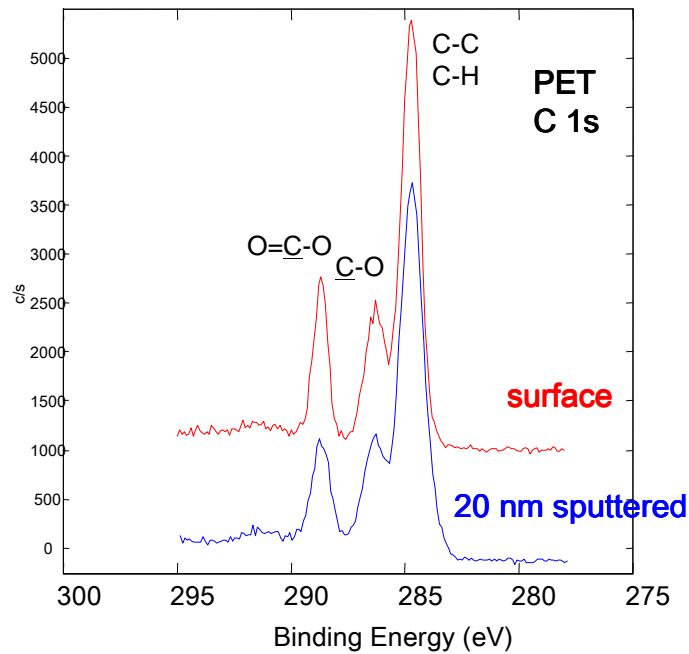
500 eV Ar<sup>+</sup> Sputter



Damage is observed.

# No Damage Observed by XPS

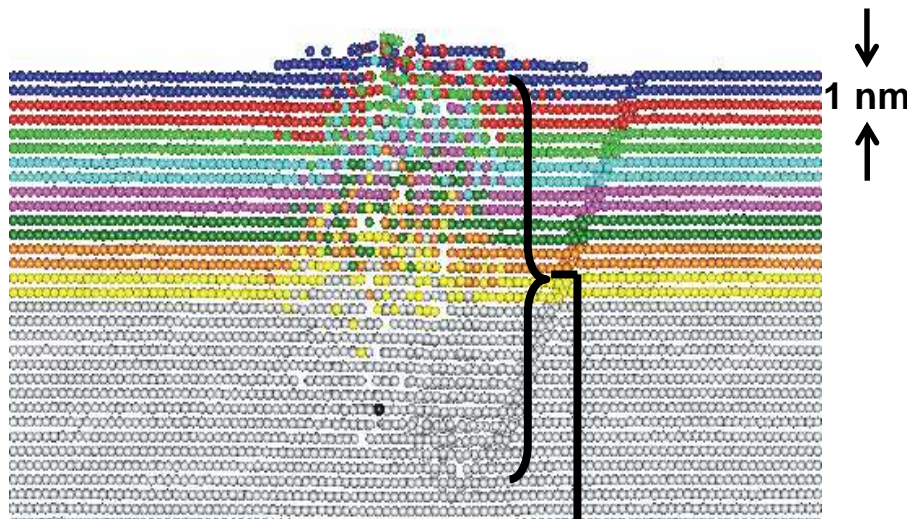
10keV  $C_{60}^+$  Sputter



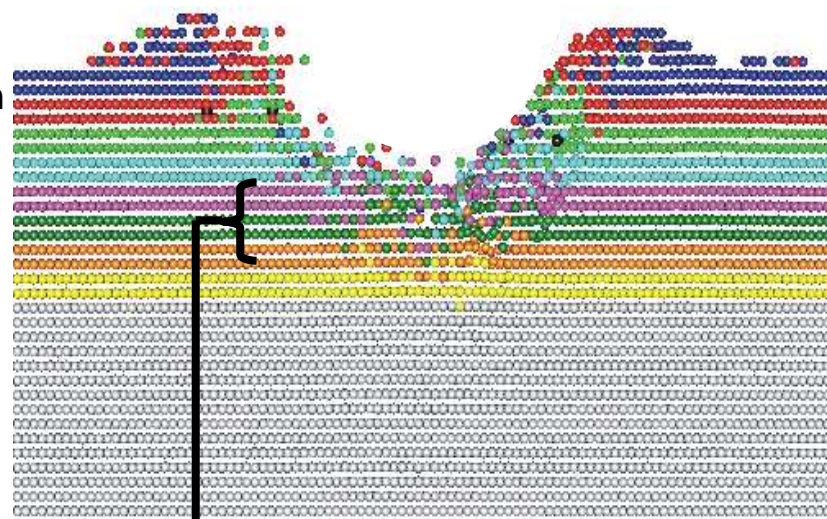
**No damage observed.**

# Altered Volume & Sub-surface Damage

15 keV Ga



15 keV C<sub>60</sub>



Residual C<sub>60</sub> sputter damage is mostly removed with the next C<sub>60</sub> impact event.



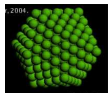
Non-C<sub>60</sub> sputter sources result in the **accumulation of sub-surface damage.**

# Requisites for Molecular Depth Profiling

Condition for molecular depth profiling...

→ damage must be removed as fast as it is created.

∴ sputtered molecules >> penetration depth.

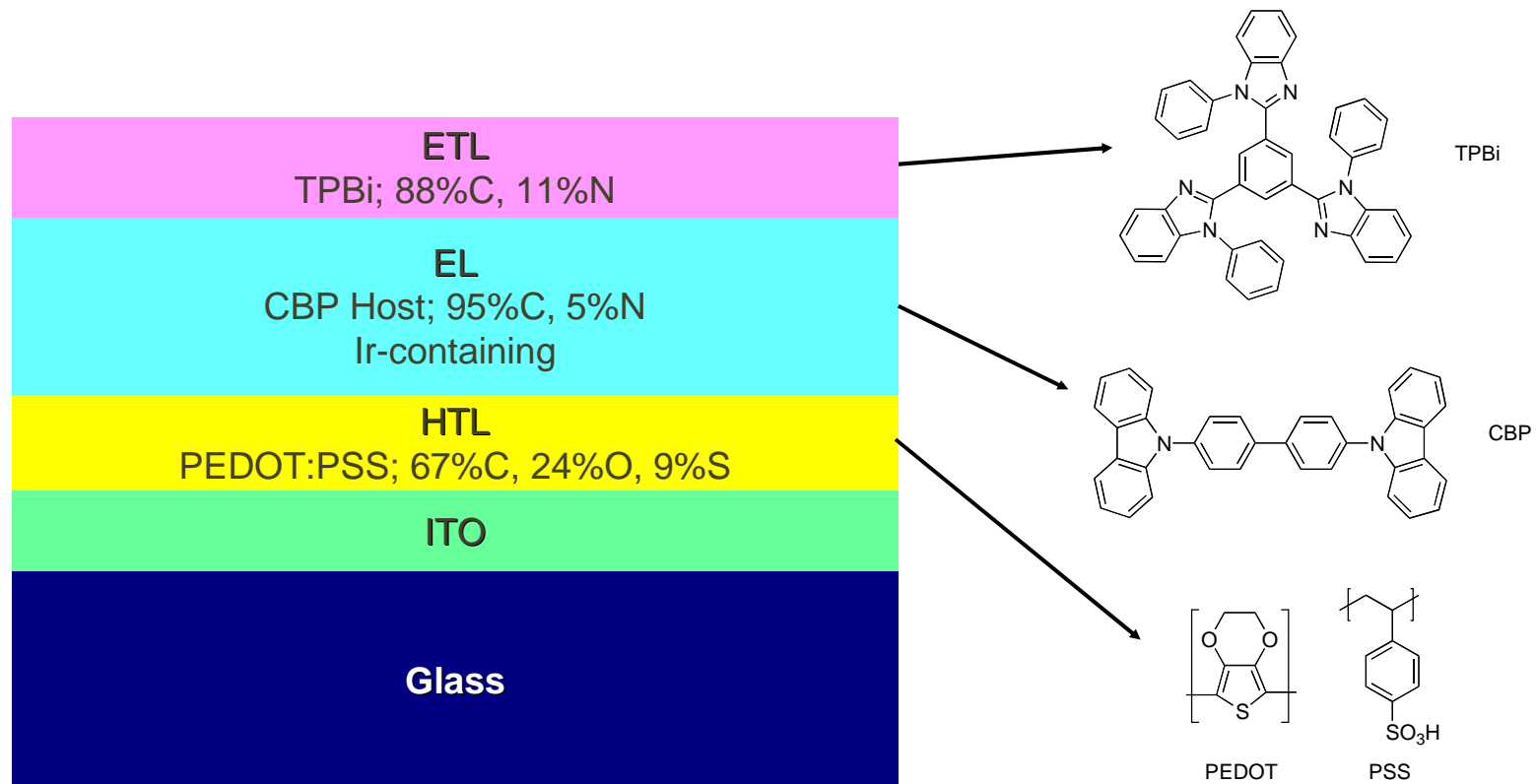
10 keV	rel. yield (Ga=1)‡	$\sigma_d$ (cm <sup>2</sup> )	range (nm)*	removed depth (nm)**
SF <sub>5</sub>	100	5×10 <sup>-13</sup>	9.8	0.06
Au <sub>3</sub> 	1,000	1×10 <sup>-12</sup>	19	0.3
C <sub>60</sub> 	2,000	2×10 <sup>-13</sup>	2.6	3.3
Au <sub>400</sub> 	20,000	†2×10 <sup>-13</sup>	6.6	3.4

‡Adapted from Kersting, et al. *Appl. Surf. Sci.* (2004) and Tempez, et al. *Rapid Comm. Mass Spectr.* (2004).

†Conservatively estimated lower limit. Values of  $\sigma_d$  are applicable to most organic systems. \*Calculated using SRIM2003. \*\*Calculated using relative yield and  $\sigma_d$ , in good agreement with Delcorte, et al. *NIMB* (2000) and Postawa, et al. *J. Phys. Chem. B* (2004).

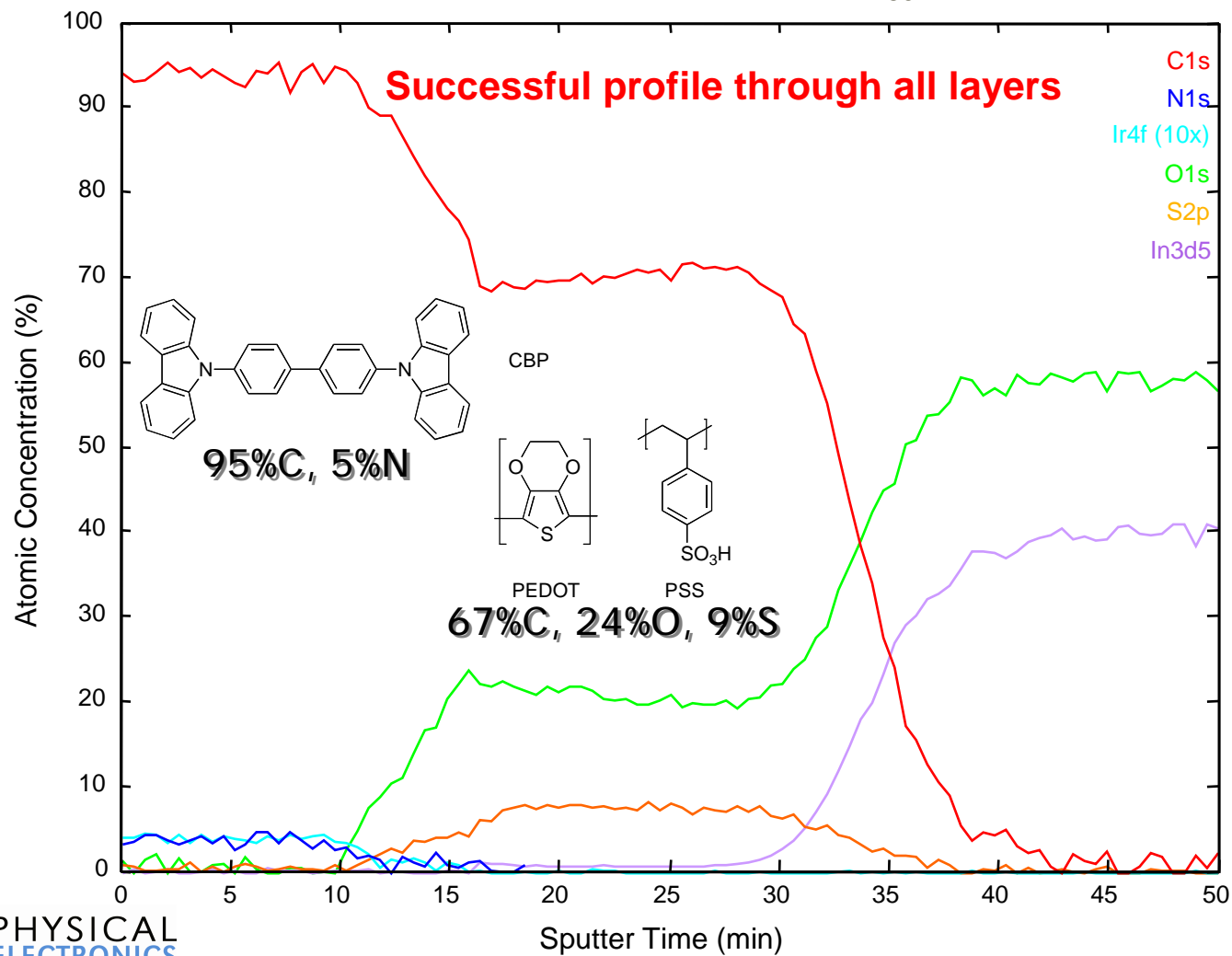
# Model of Multi-layer OLED Device

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



# Ar/C<sub>60</sub> Co-Sputter Depth Profile of OLED Device

XPS depth profile; 200eV Ar & 10keV C<sub>60</sub> co-sputter.



# Fabrication Process versus OLED Efficiency

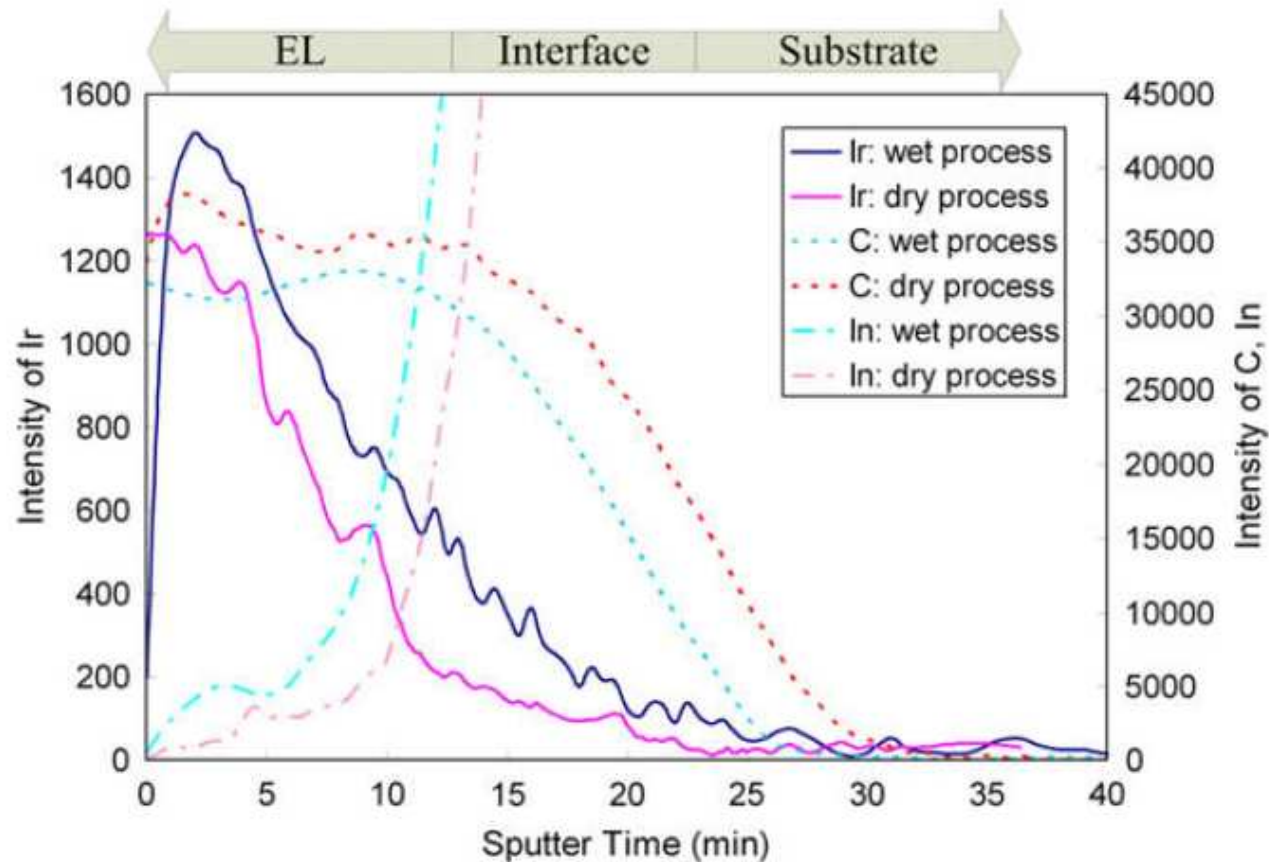
## □ Two fabrication processes of small molecular OLED's

- Spin coating (wet process): typically easier fabrication, lower efficiency
- Evaporation has higher efficiency

## □ Emissive layers (ELs) studied for high efficiency green OLED's

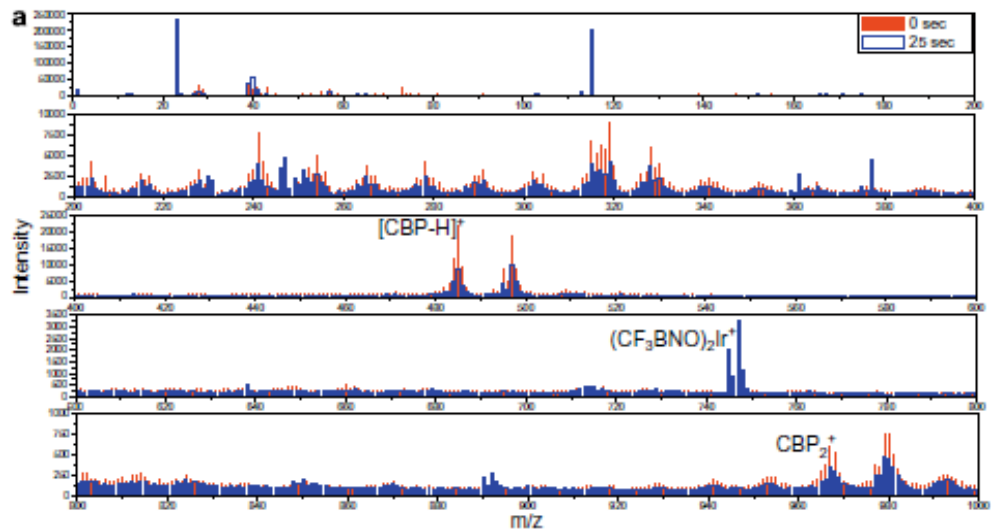
- Guest
  - Bis[5-methyl-7-trifluoromethyl-5H-benzo[*c*](1,5)naphthyridin-6-one]iridium (picolate) (CF<sub>3</sub>BNO)<sub>2</sub>IrPLA
  - Host
  - 4-4'-bis(carbazol-9-yl)biphenyl (CBP)
  - Wet efficiency 70 lm W<sup>-1</sup>
  - Dry efficiency 21 lm W<sup>-1</sup>
- WHY?

# Wet versus Dry Process Depth Profiles

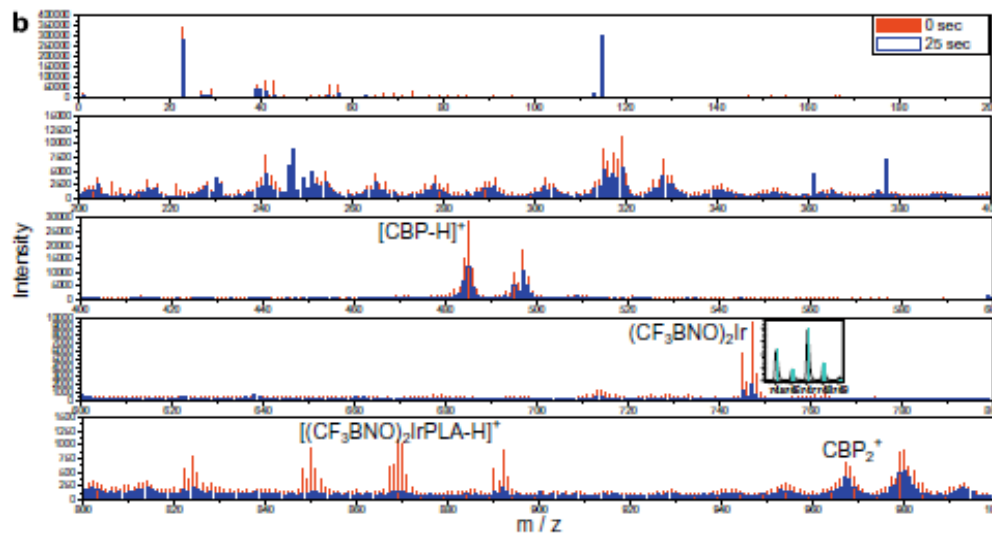


**Fig. 1.** XPS elemental depth profiles of emissive layers prepared with thermo-evaporation (dry-process) and spin-coating (wet-process).

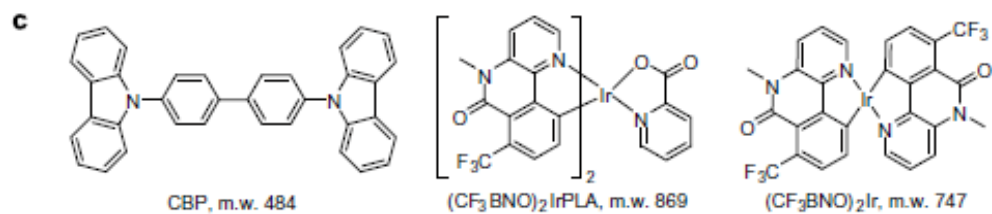
- **Same Ir composition similar when normalized by film thickness**
- **Wet process Ir guest has higher concentration at interface relative to dry process**



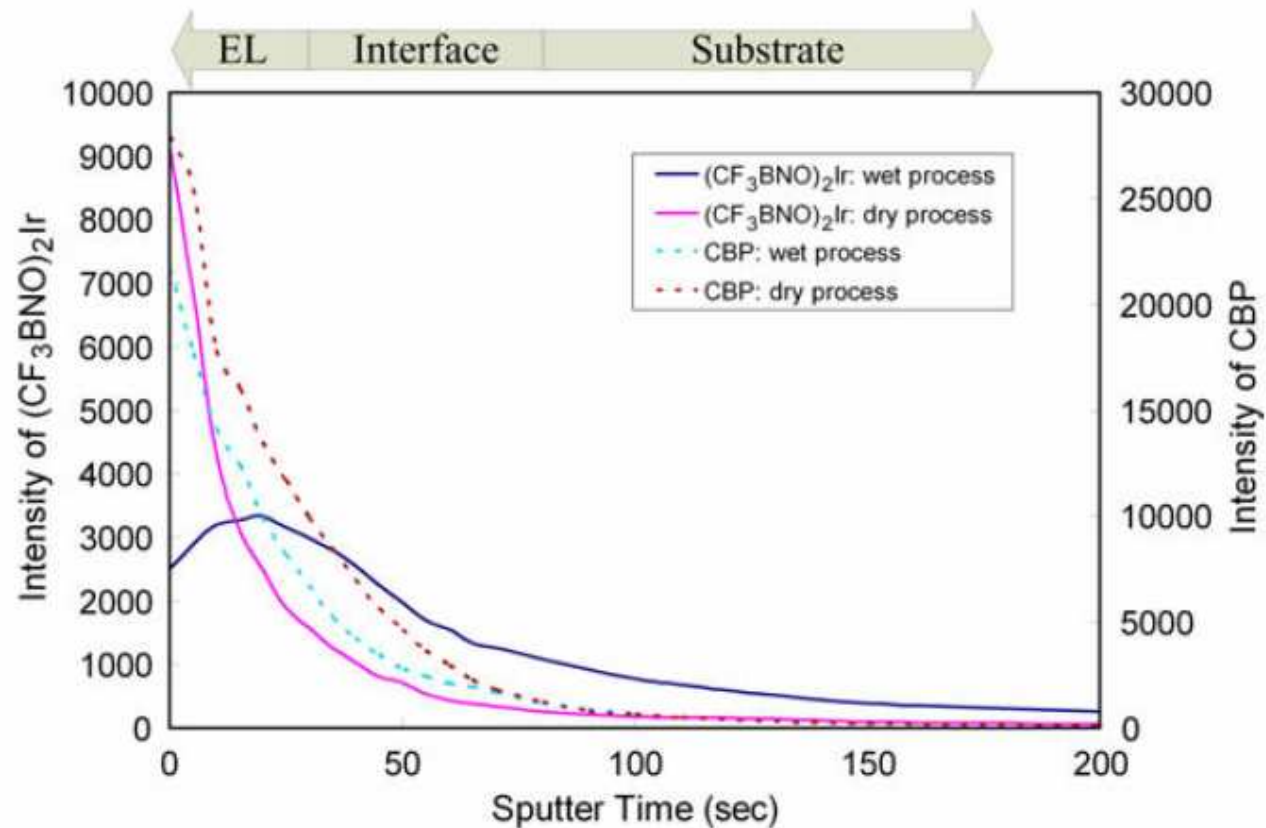
- TOF-SIMS with  $C_{60}$  sputtering shows no change in molecular structure between outer surface spectra and 25 seconds sputtering



- 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

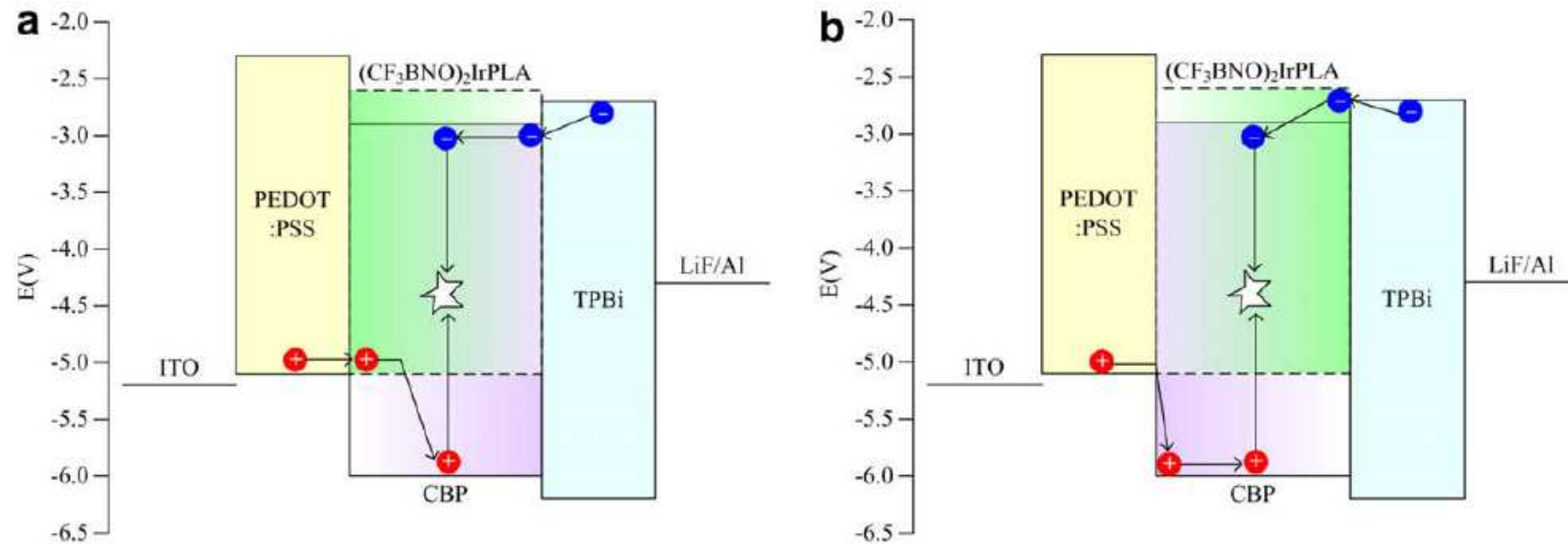


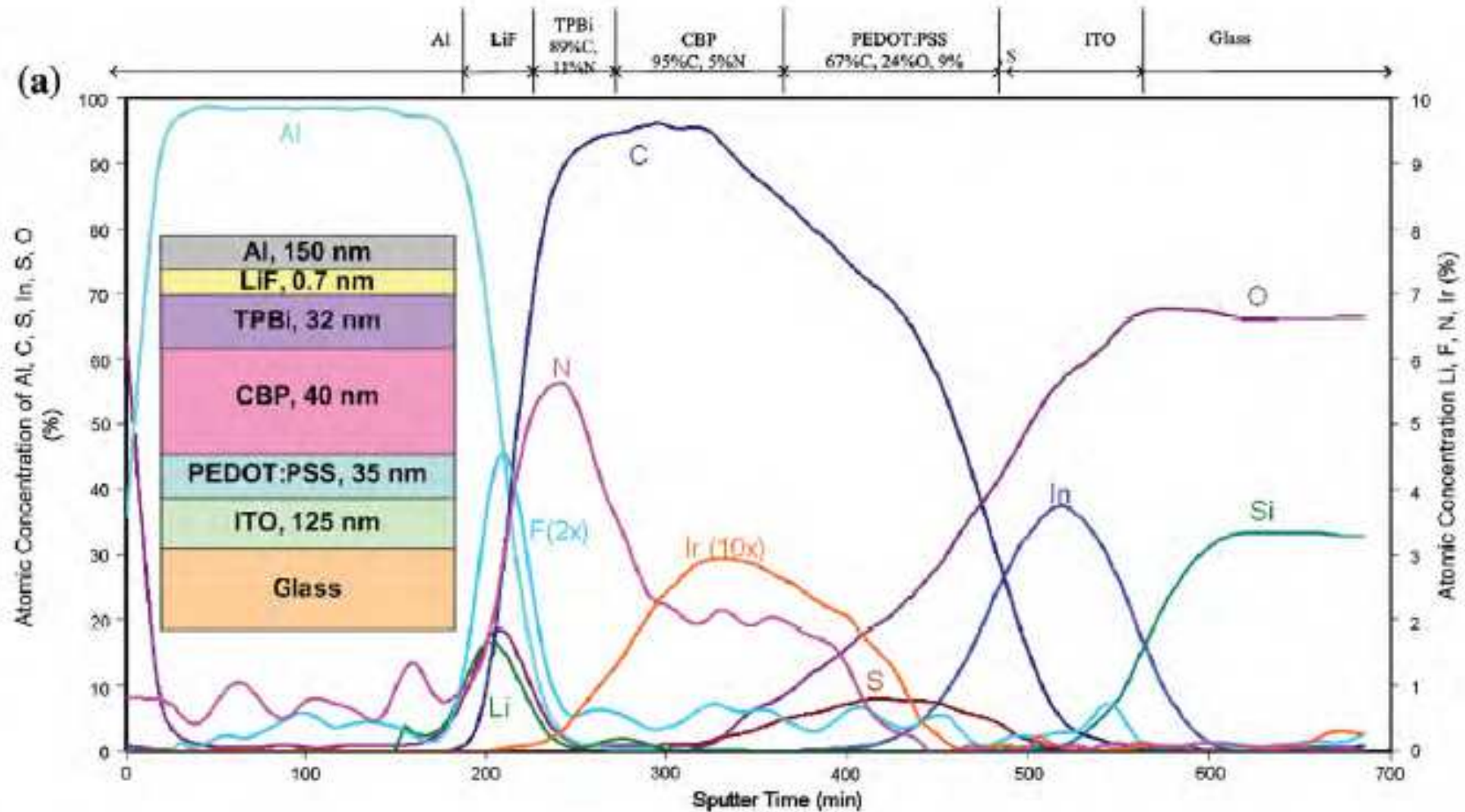
Fig. 4. Energy diagram and the route of charge carriers of OLED with EL prepared with (a) wet-process and (b) dry-process. The shade of CBP and (CF<sub>3</sub>BNO)<sub>2</sub>IrPLA indicates its relative concentration.

- 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**

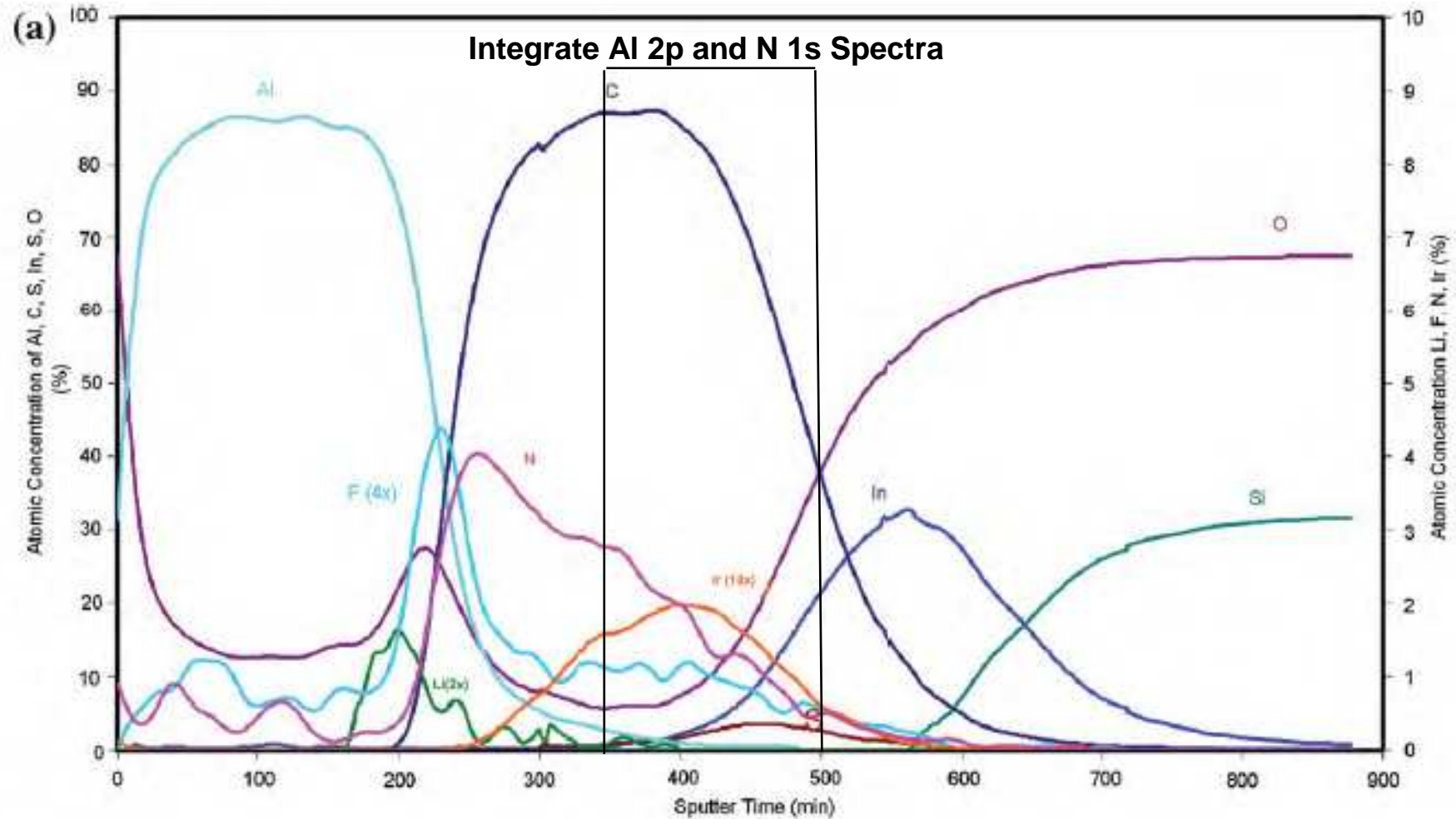
# Reference XPS Depth Profile of OLED with C<sub>60</sub>



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

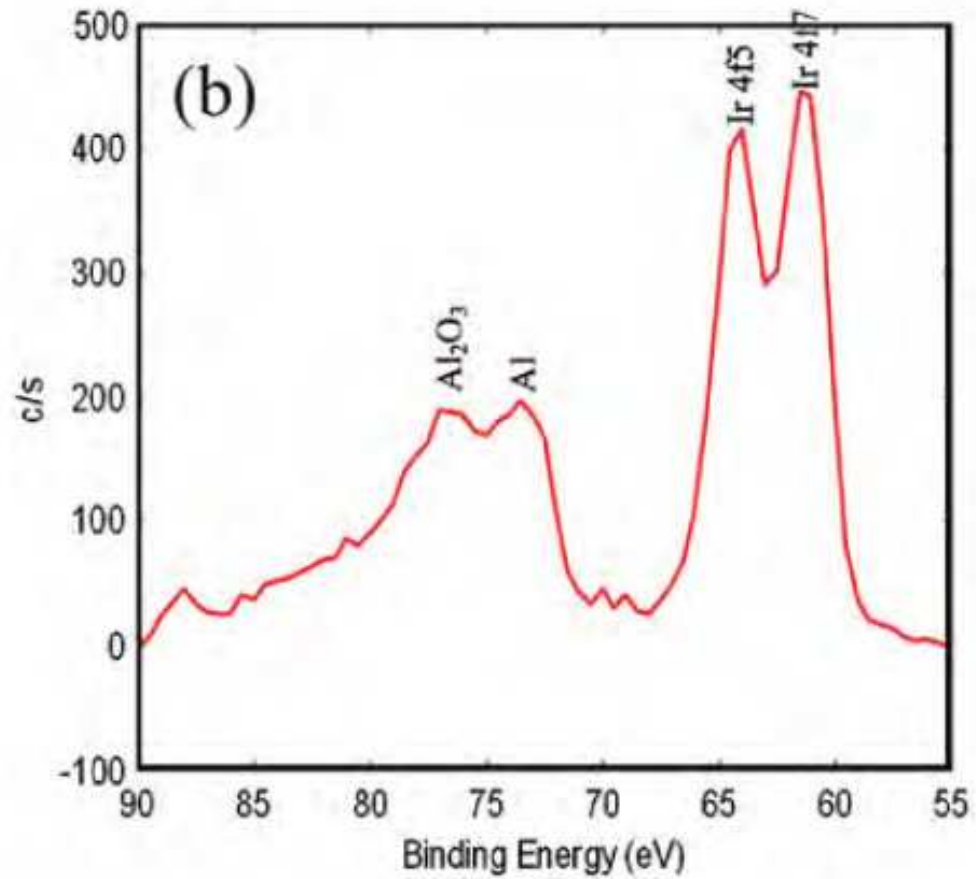


# OLED Depth Profile versus 12 hrs. Bias Time



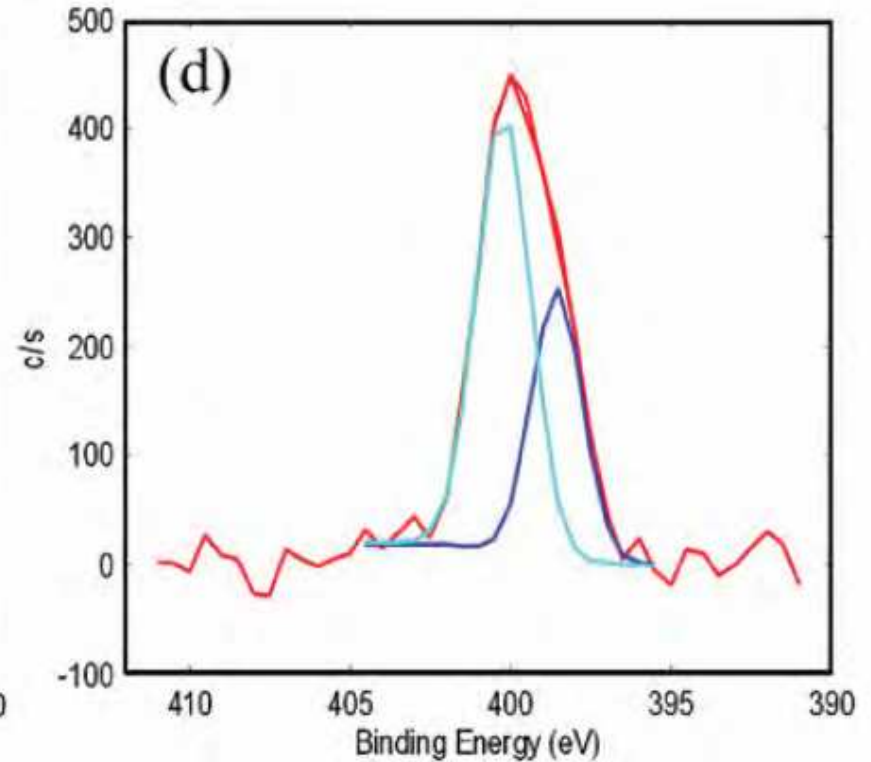
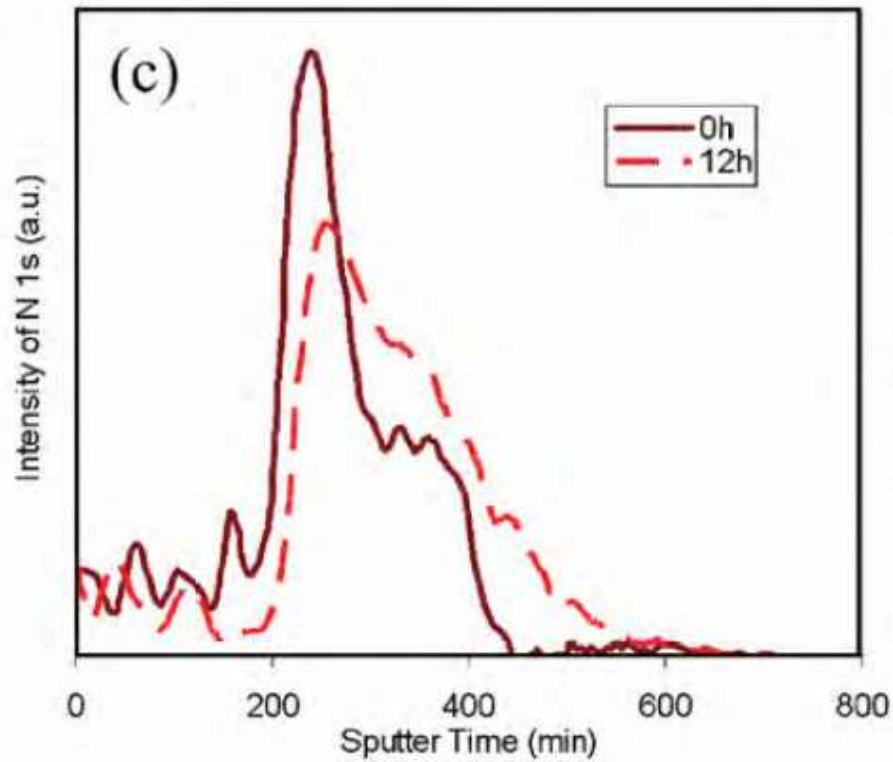
- Note enhanced broadening of interfaces, nitrogen migration and more C into ITO

# Intregrated Al 2p Spectra after 12 hrs. Bias



- Note migration of Al and formation of Al Oxide

# Intregated 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<sub>60</sub> 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!**