Characterizing the interfacial composition of organic bulk heterojunction solar cells

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Disclaimer

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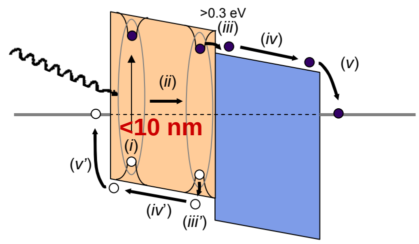
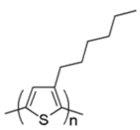
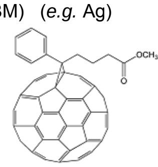
Organic Photovoltaics (OPV)

Planar Heterojunction (PHJ)

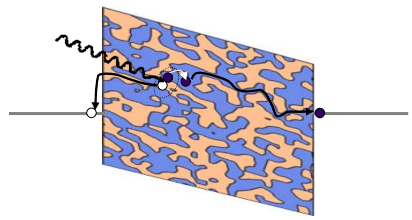


Cathode (*e.g.*, ITO) “Donor” (*e.g.*, P3HT) “Acceptor” (*e.g.*, PCBM) Anode (*e.g.* Ag)

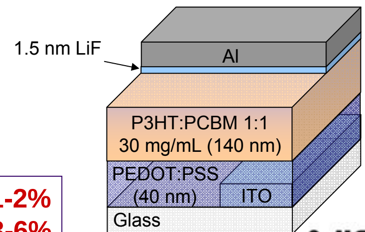




Bulk Heterojunction (BHJ)



Cathode (*e.g.*, ITO) Donor/Acceptor Blend (e.g., 1:1 P3HT:PCBM) Anode (*e.g.* Ag)



- Power conversion efficiencies are still relatively low, and vary widely depending on processing.
- Factors contributing to these limitations are not well understood.

PCE_{PHJ} ~ 1-2%
PCE_{BHJ} ~ 3-6%

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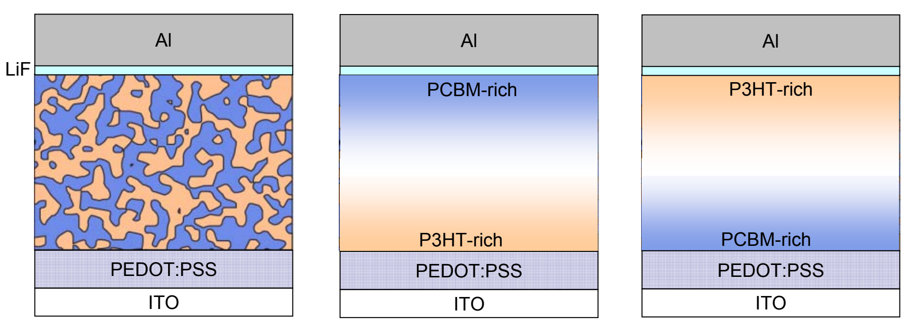
The Importance of Film Composition

- Film composition may have critical effects on OPV performance.
- Bulk composition is important for percolation pathways and may affect carrier mobility.
  - TEM: Moon *et al.*, *Nano Lett.* **9**, 230 (2009); Anderson *et al.*, *Nano Lett.* **9**, 853 (2009);
- Interface composition plays an important role in carrier extraction from an OPV.
  - XPS: Xu *et al.*, *Adv. Funct. Mater.* **19**, 1227 (2009)
  - NEXAFS/TFT: Germack and Chan *et al.*, *Appl. Phys. Lett.* **94**, 233303 (2009)



Good compositional arrangement | Good compositional arrangement | Bad compositional arrangement

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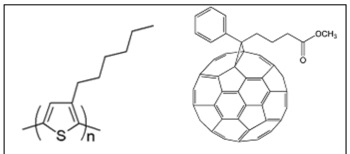
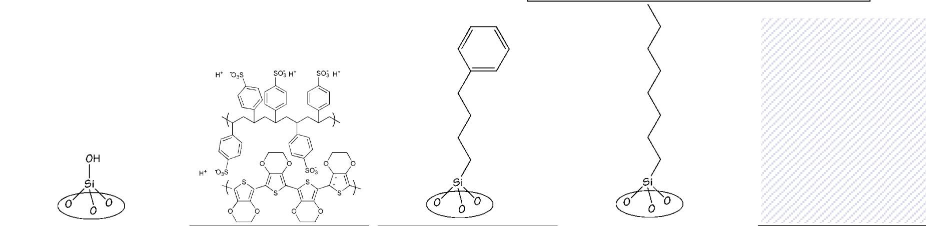
Control over the Interface Composition

- Interface composition driven by interface chemistry or surface/interface energy minimization.
  - Film/air interface
  - Film/substrate interface

➡ • Tailor by using different substrates.
• Self-assembled monolayers make model surfaces.





silicon oxide	PEDOT:PSS	PBTS	OTS	Nafion-based HIL
γ =77 mN/m^2	γ =45 mN/m^2	γ=26 mN/m^2	γ =20 mN/m^2	γ =18 mN/m^2
		(4-phenylbutyltrichlorosilane)	(Octyltrichlorosilane)	

[*Appl. Phys. Lett.* **90**, 133511 (2007)]
[*Appl. Phys. Lett.* 94, 203301 (2009)]

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Sample Preparation

- **Self-assembled monolayers**
  - OTS8:
    2 mM OTS8 in hexadecane overnight.
    Sonication in chloroform, isopropanol, and DI-water; 10 min at 150 °C.
  - PBTS:
    10 mM PBTS in toluene overnight.†
    Sonication in toluene, acetone, and isopropanol; 10 min at 150 °C.
- **Hole-injection layers**
  - PEDOT:PSS:
    Spin coat at 5000 rpm for 1 min; 60 min at 150 °C.
  - Nafion-based HIL:
    Spin coat at 2500 rpm for 1 min; 60 min at 150 °C.
- **Bulk heterojunction film**
  - 30 mg/mL 1:1 P3HT:PCBM by weight in o-dichlorobenzene at 60 °C.
  - Spin coat at 500 rpm for 1 min.
  - "As cast" (AC) = solvent annealed.‡
  - "Annealed" (AN) = 140 °C for 40 min.

† Kumaki, D. et. Al. Appl. Phys. Lett. **90**, 133511 (2007)
‡ Li, G. *et al. Adv. Funct. Mater.* **17**, 1636-1644 (2007)

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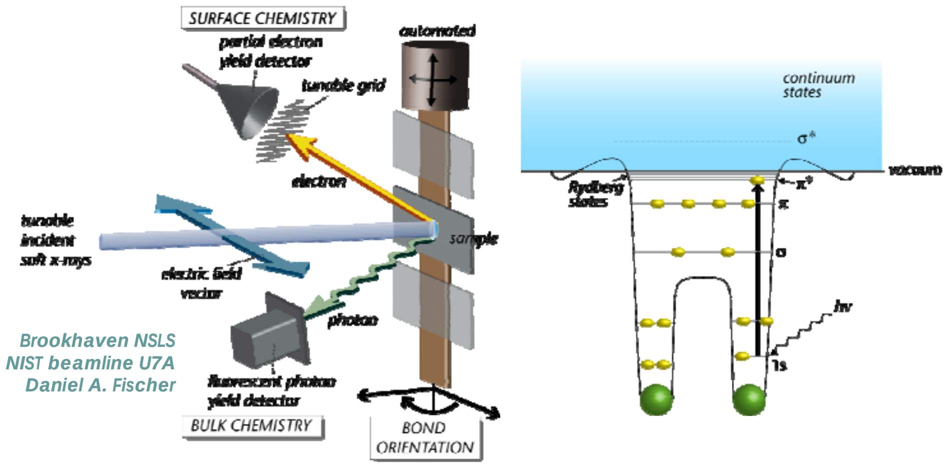
Characterizing the Interfacial Composition

- Near Edge X-ray Absorption Fine Structure (NEXAFS)



Strengths for Organic Electronics:
- Detects C, N, O, & F bonds.
- High sensitivity to π bonding.
- Measures orientation.
- Surface sensitive (<5 nm).

Does not Measure:
- Crystal packing style, prevalence, size, shape.
- HOMO, LUMO, orbandgaps.
- Vibrational or rotational structure.

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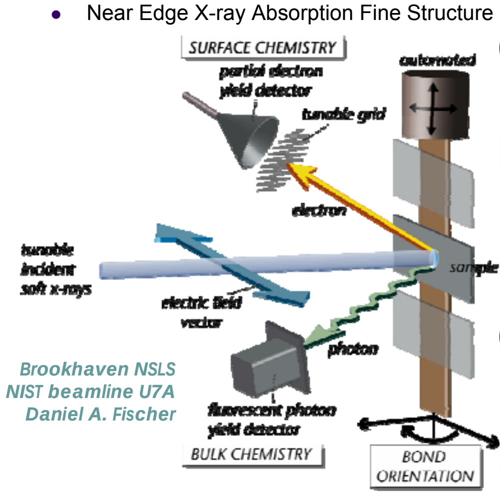
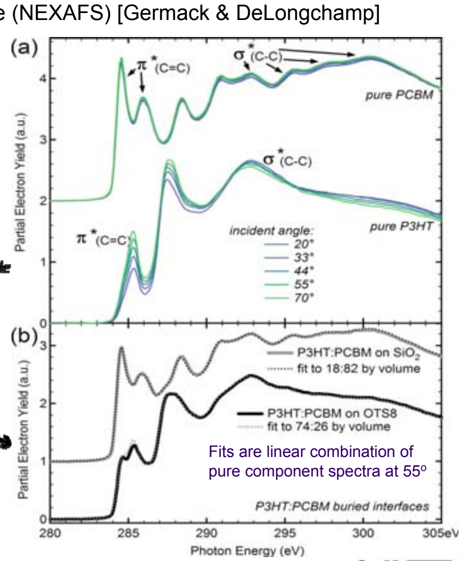
Characterizing the Interfacial Composition

- Near Edge X-ray Absorption Fine Structure (NEXAFS) [Germack & DeLongchamp]





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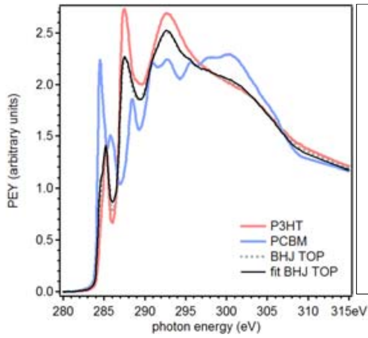
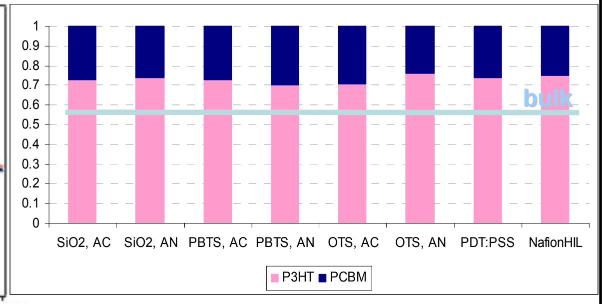
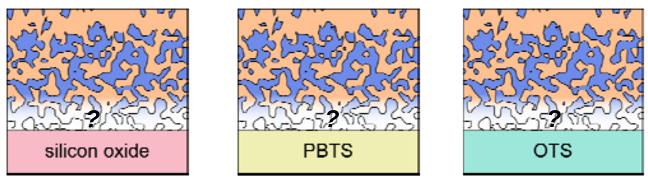
BHJ Film Composition at the Air Interface

- Corresponds to the top contact interface.







P3HT-rich at the top interface
Independent of substrate used and annealing process

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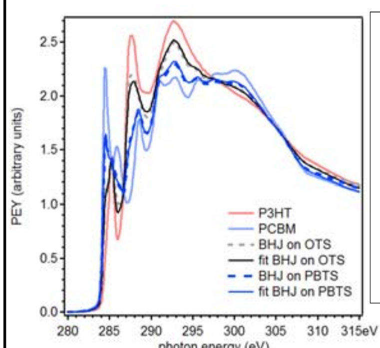
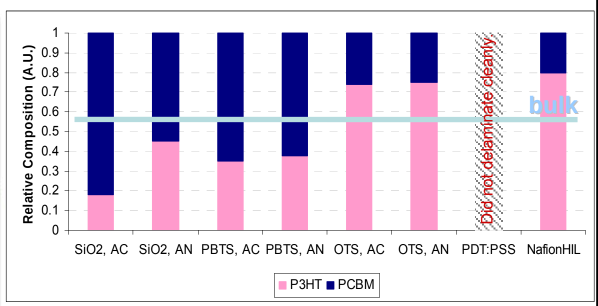
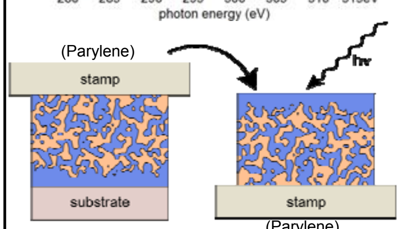
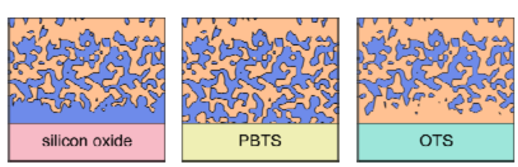
BHJ Film Composition at the Bottom Interface

- Surface energy controlled by SAMs









P3HT-rich on low γ
PCBM-rich on high γ

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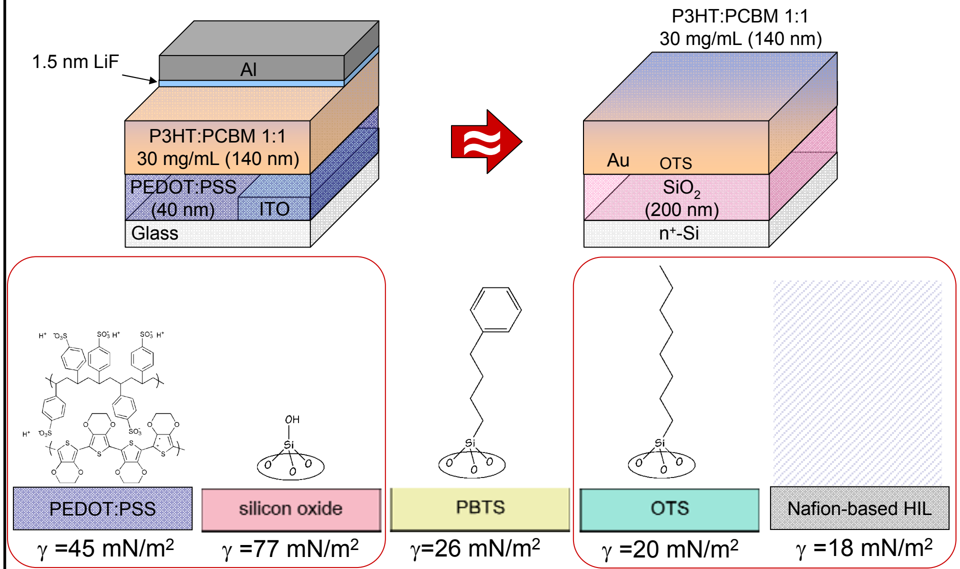
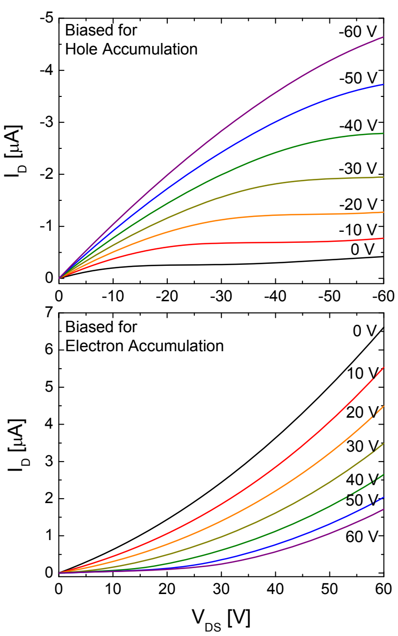
Characterizing the Interfacial Composition

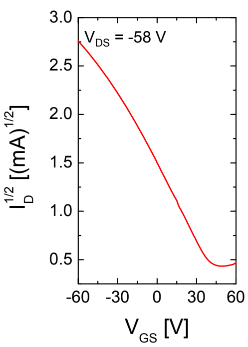
- Electrical Characterization of BHJ Thin Film Transistors

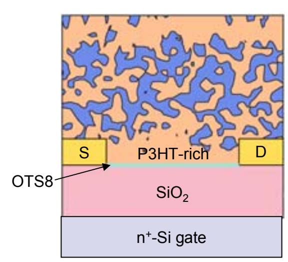


*Morana *et al.*, *Adv. Funct. Mater.* **17**, 3274 (2007); Germack and Chan *et al.*, *Appl. Phys. Lett.* **94**, 233303 (2009)

BHJ TFTs on Octyltrichlorosilane (OTS8)







$\mu_{h,sat}$ = 2 x 10^{-3} $cm^2V^{-1}sec^{-1}$
(μ_{P3HT} ~ 2 x 10^{-2} $cm^2V^{-1}sec^{-1}$)

Predominantly hole transporting
P3HT-rich bottom layer

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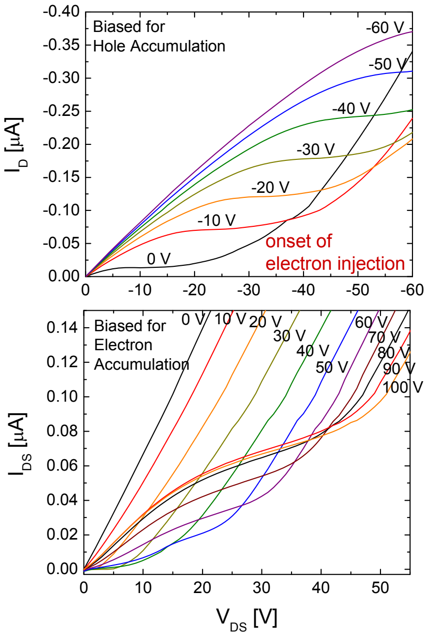
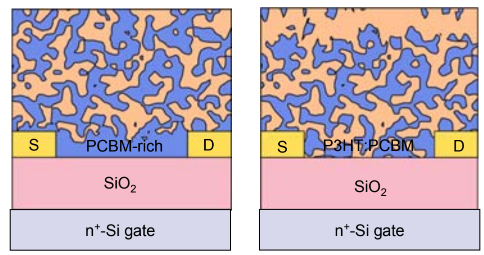
BHJ TFTs on SiO_2



Hole & Electron Transport
Two possibilities:

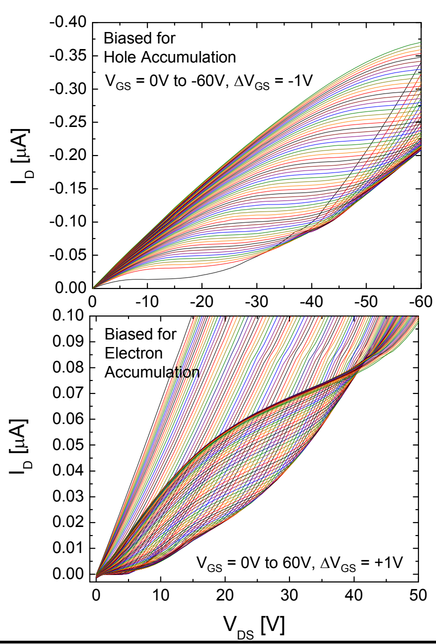
Ambipolar transport
PCBM-rich layer

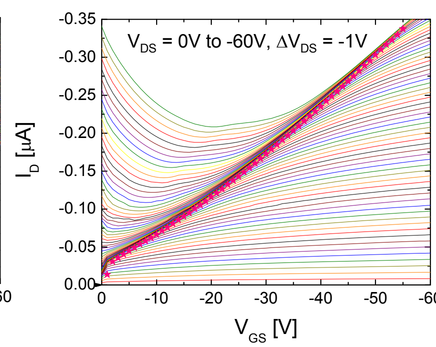
Tandem transport
P3HT:PCBM layer



Can we tell the difference?

BHJ TFT on SiO_2: Carrier mobility





Hole mobility observed
$\mu_{h,sat,ox}$ = 1 x 10^{-4} $cm^2V^{-1}sec^{-1}$
(Could not get hole transport in PCBM on SiO_2)

Tandem transport through P3HT and PCBM

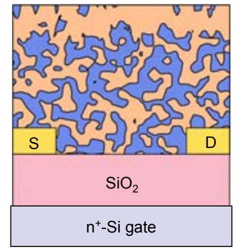
$\mu_{h,sat,ox} << \mu_{h,sat,OTS8}$
Less P3HT at the SiO_2 interface, PCBM-rich

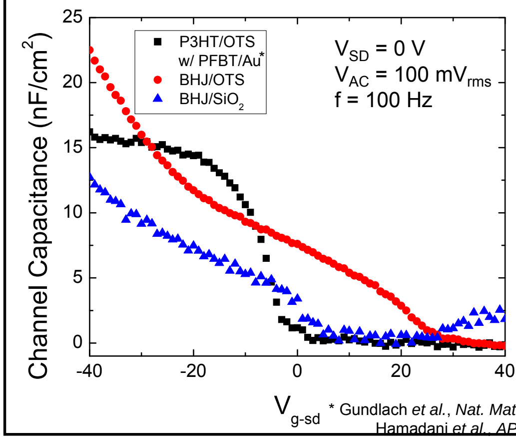
Capacitance Voltage on BHJ TFTs

- Induce charges in the channel at the dielectric/organic interface.
- $C = C_S + C_D + C_C$

$$\frac{\varepsilon_{Si}\varepsilon_o A_{P3HT}}{d}$$ Hole accumulation

$$\frac{\varepsilon_{Si}\varepsilon_o A_{PCBM}}{d}$$ Electron accumulation





More hole accumulation on OTS
Larger P3HT areas on OTS

Electron accumulation
evident on SiO_2
Presence of PCBM

Requires quantitative modeling

* Gundlach *et al.*, *Nat. Mater.* **7**, 216-221 (2008).
Hamadani *et al.*, *APL* **92**, 203303 (2008).

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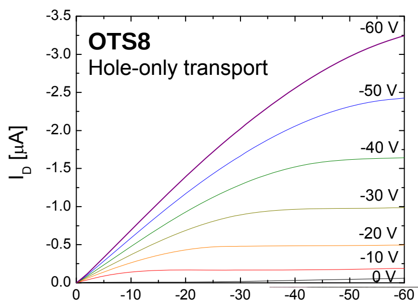
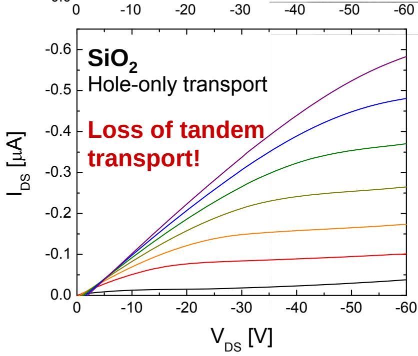
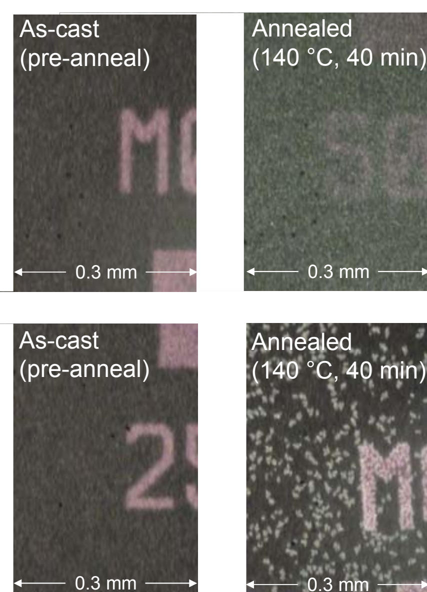
Annealed BHJ TFTs







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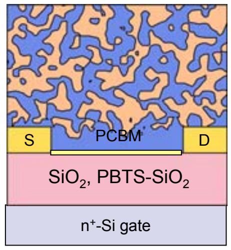
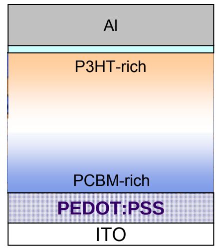
Implications for OPV performance



$\gamma_{SiO2}, \gamma_{PBTS} > \gamma_{P3HT}, \gamma_{PCBM}$

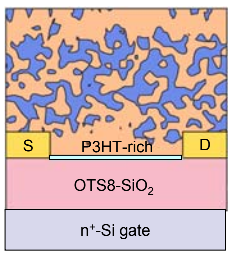
≈



$\gamma_{PEDOT:PSS} > \gamma_{P3HT}, \gamma_{PCBM}$

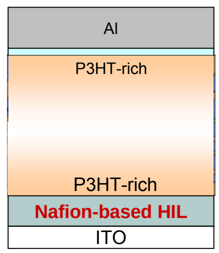
PCBM-rich at cathode
P3HT-rich at anode

Non-optimal composition



$\gamma_{OTS8} < \gamma_{P3HT}, \gamma_{PCBM}$

≈



$\gamma < \gamma_{P3HT}, \gamma_{PCBM}$

P3HT-rich at cathode,
But still PCBM-rich at anode

Better, but still
Non-optimal composition

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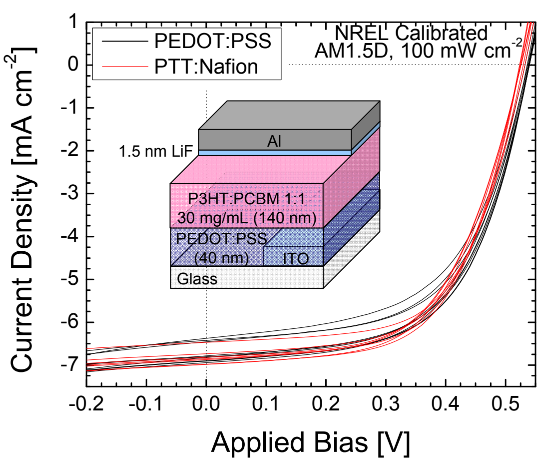
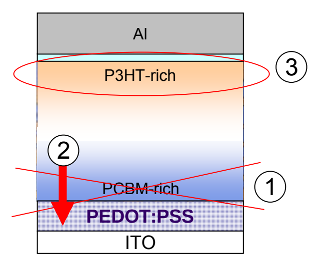
Correlation to BHJ OPV Performance?



Nafion HIL shows *marginally* better performance (but not statistically significant)



Device	V_{oc} [V]	J_{sc} [mA/cm²]	FF	η_{PCE} (%)
PEDOT:PSS (AC)	0.537 (0.003)	6.64 (0.26)	0.58 (0.01)	2.08 (0.13)
Nafion HIL (AC)	0.525 (0.001)	6.92 (0.07)	0.59 (0.01)	2.15 (0.05)

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Summary and Future Work

- TFTs are useful for quick qualitative determination of interface composition.
- Supplemented with NEXAFS, quantitative determination of interface composition is possible.
- Film composition at the BHJ/cathode interface varies depending on the substrate surface energy; vertical phase segregation is present.
  - BHJ films deposited on $\gamma_{subst} > \gamma_{P3HT},\gamma_{PCBM}$ result in PCBM-rich interfaces.
  - BHJ films deposited on $\gamma_{subst} < \gamma_{P3HT},\gamma_{PCBM}$ result in P3HT-rich interfaces.
  - The film/air interface is P3HT-rich.
- Film composition may have implications on OPV performance, *e.g.*, the P3HT-rich interface at the anode could limit electron extraction.

- Develop quantitative electrical characterization of interface composition (*i.e.*, capacitance-voltage measurements).
- Control vertical phase segregation by interface engineering.
- Explore inverted device architectures, keeping in mind that changing of the bottom interface could further affect film composition at the anode.

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Acknowledgements

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Surface and Microanalysis Division
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AIR PRODUCTS
Thanks to Air Products for providing the Nafion-based HIL