Soft X-ray Characterisation of Organic Semiconductor Films

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Overview

• Organic semiconductors
• Basic semiconductor physics
• Field-effect transistors
  – NEXAFS spectroscopy
  – Case study: P3AT transistors
• Solar cells
  – Scanning Transmission X-ray Microscopy
  – Case study: MDMO-PPV:PCBM
  – Soft X-ray reflectivity
• Conclusions
Organic semiconductors
Reel-to-reel processing

Substrate → ITO → PEDOT → Active layer → Cathode → Encapsulation → Completed modules
Basic semiconductor physics
Basic semiconductor physics
Influence of disorder

- Disorder (e.g., conformational, chemical, structural) further complicates transport.
Influence of disorder

- Transport is thermally activated, with a field dependent mobility

\[ \mu(T, E) = \mu_0 \exp \left[ -\frac{2}{3} \left( \frac{\sigma}{kT} \right)^2 \right] \exp \left\{ C \left[ \left( \frac{\sigma}{kT} \right)^2 - \Sigma^2 \right] E^{1/2} \right\} \]

Organic Field-Effect Transistors

- Au
- SiO₂
- Highly doped Si
Organic Field-Effect Transistors

(a) $V_d \ll V_g - V_{Th}$

(b) $V_{d,sat} = V_g - V_{Th}$

(c) $V_d > V_{d,sat}$

$V(x) = V_g - V_{Th}$ pinch-off point
Organic Field-Effect Transistors

\[ \mu_{sat} = \frac{\partial I_{d,sat}}{\partial V_g} \cdot \frac{L}{W C_i} \cdot \frac{1}{V_g - V_{Th}} \]

\[ \mu_{lin} = \frac{\partial I_d}{\partial V_g} \cdot \frac{L}{W C_i V_d} \]
Case Study: Poly(3-alkylthiophene)


Case Study: P3AT – influence of side chain

\[
\begin{align*}
* & \quad [ \ \ \ ] \quad * \\
\text{TTF} \quad & \quad \text{C}_n\text{AH}_{2A+1} \\
P3AT 
\end{align*}
\]

Key questions:

- What is the influence of the dielectric on interfacial order?
- What is the influence of the dielectric on interfacial charge transport?
- What is the origin of the alkyl side-chain length dependence of mobility?
NEXAFS Spectroscopy

Ionisation Threshold

LUMO

HOMO

Core state

Energy (eV)

X-ray Optical Density

σ*

π*
NEXAFS Spectroscopy
NEXAFS Spectroscopy
Further analysis

\[ I \sim 1 + (3 \cos^2 \theta - 1)(3 \cos^2 \langle \alpha \rangle - 1) \]

![Graph showing the relationship between incidence angle (\( \theta \)) and relative absorption intensity.](image)

- Incidence angle \( \theta \)
  - 90°
  - 55° (~Magic Angle)
  - 20°
  - 0°

*Average Thiophene tilt angle \( \langle \alpha \rangle \) in ° (vs substrate)*

DFT calculations: optimal tilt angle for \( \pi \)-stacked thiophenes is 67°

(Unpublished results removed)
Summary of Part I

• Have observed high field-effect mobilities in P3ATs using SiO$_2$ as the gate dielectric independent of alkyl chain length.

• Low mobilities previously observed with SiO$_2$ result not from the interfacial properties of the SiO$_2$ / P3AT junction, but rather from the disordered packing of P3AT when processed on SiO$_2$.

• Similarly, alkyl side-chain length only affects mobility in that it can affect the way P3AT orders at the substrate / film interface, and is not a general property of P3ATs.
Polymer solar cells
Basic photophysics

- Primary photoexcitations are strongly bound Frenkel-like excitons
- Localised by the strong electron-phonon interaction and low intermolecular coupling.
- Binding energies of 0.4 eV

Exciton dissociation and device types

Polymer:polymer

Polymer:fullerene

Polymer:nanocrystal

## Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m²) at 25°C

<table>
<thead>
<tr>
<th>Classification</th>
<th>Effic. (%)</th>
<th>Area (cm²)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Test centre (and date)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silicon</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Si (crystalline)</td>
<td>24.7 ± 0.5</td>
<td>4.00 (da)</td>
<td>0.706</td>
<td>42.2</td>
<td>82.8</td>
<td>UNSW PERL13</td>
<td></td>
</tr>
<tr>
<td>Si (multicrystalline)</td>
<td>20.3 ± 0.5</td>
<td>1.002 (ap)</td>
<td>0.664</td>
<td>37.7</td>
<td>80.9</td>
<td>fhG-ISE14</td>
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</tr>
<tr>
<td>Si (thin film transfer)</td>
<td>16.6 ± 0.4</td>
<td>4.017 (ap)</td>
<td>0.645</td>
<td>32.8</td>
<td>78.2</td>
<td>fhG-ISE (7/01)</td>
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</tr>
<tr>
<td>Si (thin film submodule)</td>
<td>10.4 ± 0.3</td>
<td>940 (ap)</td>
<td>0.492</td>
<td>29.5</td>
<td>72.1</td>
<td>fhG-ISE (8/07)</td>
<td>CSG Solar (1–2 μm on glass; 20 cells)9</td>
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<tr>
<td><strong>III–V Cells</strong></td>
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</tr>
<tr>
<td>GaAs (crystalline)</td>
<td>25.1 ± 0.8</td>
<td>3.91 (t)</td>
<td>1.022</td>
<td>28.2</td>
<td>87.1</td>
<td>NREL (3/90)</td>
<td>Kopin, AlGaAs window16</td>
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<td>GaAs (thin film)</td>
<td>24.5 ± 0.5</td>
<td>1.002 (t)</td>
<td>1.029</td>
<td>28.8</td>
<td>82.5</td>
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<td>GaAs (multicrystalline)</td>
<td>18.2 ± 0.5</td>
<td>4.011 (t)</td>
<td>0.994</td>
<td>23.0</td>
<td>79.7</td>
<td>NREL (11/95)</td>
<td>RTI, Ge substrate18</td>
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<tr>
<td>InP (crystalline)</td>
<td>21.9 ± 0.7</td>
<td>4.02 (t)</td>
<td>0.878</td>
<td>29.3</td>
<td>85.4</td>
<td>NREL (4/90)</td>
<td>Spire, epitaxial19</td>
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<td><strong>Thin Film Chalcogenide</strong></td>
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<td>CIGS (cell)</td>
<td>18.8 ± 0.6</td>
<td>1.00 (ap)</td>
<td>0.703</td>
<td>34.0</td>
<td>78.7</td>
<td>fhG-ISE (8/06)</td>
<td>NREL, CIGS on glass20</td>
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<td>CIGS (submodule)</td>
<td>16.6 ± 0.4</td>
<td>1.60 (ap)</td>
<td>0.661</td>
<td>33.4</td>
<td>75.1</td>
<td>fhG-ISE (3/00)</td>
<td>U. Uppsala, 4 serial cell21</td>
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<td>CdTe (cell)</td>
<td>16.5 ± 0.5</td>
<td>1.032 (ap)</td>
<td>0.845</td>
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<td>75.5</td>
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<td>NREL, mesa on glass22</td>
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<td>Amorphous/Nanocrystalline Si</td>
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<td>Si (amorphous)</td>
<td>9.5 ± 0.3</td>
<td>1.070 (ap)</td>
<td>0.859</td>
<td>17.5</td>
<td>63.0</td>
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<td>U. Neuchatel21</td>
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<td>Si (nanocrystalline)</td>
<td>10.1 ± 0.2</td>
<td>1.199 (ap)</td>
<td>0.539</td>
<td>24.4</td>
<td>76.6</td>
<td>JQA (12/97)</td>
<td>Kaneka (2 μm on glass)24</td>
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<td><strong>Photochemical</strong></td>
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<tr>
<td>Dye sensitised</td>
<td>10.4 ± 0.3</td>
<td>1.004 (ap)</td>
<td>0.729</td>
<td>21.8</td>
<td>65.2</td>
<td>AIST (8/05)</td>
<td>Sharp25</td>
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<tr>
<td>Dye sensitised (submodule)</td>
<td>7.9 ± 0.3</td>
<td>26.48 (ap)</td>
<td>6.27</td>
<td>2.01</td>
<td>62.4</td>
<td>AIST (6/07)</td>
<td>Sharp6</td>
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<td><strong>Organic</strong></td>
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<tr>
<td>Organic polymer</td>
<td>5.15 ± 0.3</td>
<td>1.021 (ap)</td>
<td>0.876</td>
<td>9.40</td>
<td>62.5</td>
<td>NREL (12/06)</td>
<td>Konarka7</td>
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<td><strong>Multijunction Devices</strong></td>
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<tr>
<td>GaInP/GaAs/Ge</td>
<td>32.0 ± 1.5</td>
<td>3.989 (t)</td>
<td>2.622</td>
<td>14.37</td>
<td>85.0</td>
<td>NREL (1/03)</td>
<td>Spectrolab (monolithic)</td>
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<tr>
<td>GaInP/GaAs</td>
<td>30.3</td>
<td>4.0 (t)</td>
<td>2.488</td>
<td>14.22</td>
<td>85.6</td>
<td>JQA (4/96)</td>
<td>Japan energy (monolithic)26</td>
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<tr>
<td>GaAs/CIS (thin film)</td>
<td>25.8 ± 1.3</td>
<td>4.00 (t)</td>
<td>—</td>
<td>—</td>
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<td>NREL (11/89)</td>
<td>Kopfmu/Boeing (4 terminal)27</td>
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<tr>
<td>a-Si/μc-Si (thin submodule)</td>
<td>11.7 ± 0.4</td>
<td>14.23 (ap)</td>
<td>5.462</td>
<td>2.99</td>
<td>71.3</td>
<td>AIST (9/04)</td>
<td>Kaneka (thin film)28</td>
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</table>
Device physics basics

$$k_{\text{diss}}(x, T, F) = \frac{3R}{4\pi a^3} e^{-E_B/k_BT} J_1(2\sqrt{-2b})/\sqrt{-2b}$$

$$= \frac{3R}{4\pi a^3} e^{-E_B/k_BT} (1 + b + b^2/3 + \cdots)$$

$$b = q^3 F / (8\pi\varepsilon k_BT^2)$$
Charge separation

Additional voltage dependence in photocurrent curves: Field dependent dissociation rate of interfacial electron-hole pairs

Charge separation

\[ J_{\text{ph}} \text{ [A/m}^2] \]

\[ V_0 - V \text{ [V]} \]

### Length scales in organic semiconductors

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exciton diffusion length</td>
<td>5 – 15 nm</td>
</tr>
<tr>
<td>Optical absorption length</td>
<td>200 nm</td>
</tr>
<tr>
<td>Thermal capture radius</td>
<td>20 – 30 nm</td>
</tr>
<tr>
<td>Transport length</td>
<td>3 – 50 μm</td>
</tr>
</tbody>
</table>
Bulk heterojunction architecture

NEXAFS for chemical differentiation

MDMO-PPV

PCBM
Scanning Transmission X-ray Microscopy

Order sorting aperture

Monochromatic X-rays

SEM of 15 nm spot size zone plate

Scintillator and PMT

Piezo stage scanned sample

Zone plate

STXM of 1:4 MDMO-PPV:PCBM blend from toluene

Comparison of STXM, TEM and AFM

Composition profiles

Composition profiles

- MDMO-PPV % composition
- PCBM % composition

Film thickness

Distance (μm)

Weight %

Film thickness (nm)

Photocurrent mapping

Photocurrent mapping

Photocurrent mapping

Photocurrent mapping

STXM – Pushing the limits of resolution


STXM – Pushing the limits of resolution

Soft X-ray Scattering

Complex index of refraction: \( n = 1 - \delta - i\beta \)
where \( \delta \) and \( \beta \) are the dispersion and absorption properties

\[ I(E) \propto F^2(E) \propto E^4|\delta(E) + i\beta(E)|^2, \text{ Material contrast } \propto \Delta\delta^2 + \Delta\beta^2 \]

Soft X-ray scattering

RSoXS measurements done at the ALS, Beamline 6.3.2 in transmission geometry.
Detector scan was taken at 284.7 eV

Soft X-ray scattering

Conclusions

• Scanning transmission X-ray microscopy is a powerful method for quantitatively mapping the chemical composition of conjugated polymer blends with sub-100 nm resolution.

• Composition of phase separated PPV:PCBM blends has been studied and compared with near-field photocurrent images.

• Resonant soft X-ray scattering is able to probe the sub 10-nm structural properties of thin polymer blend films in transmission geometry due to the resonant scattering of soft X-rays due to the optical properties of the materials.

• Soft X-ray scattering is a promising new method for providing new insight into the nanostructure of organic photovoltaic composites.
Acknowledgements

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