Photovoltaic Materials and Devices:
Organic Bulk Heterojunction Solar Cells

Chang-Yong Nam
Electronic Nanomaterials Group
Center for Functional Nanomaterials

NSLS-II Beamline Development Proposals Workshops, Soft X-ray Spectromicroscopy, May 20, 2011
Ultimate source of renewable energy: Sun

• Abundance of solar energy, in the form of light
• Conversion of light into electricity: High cost, low efficiency
• Better understanding and control over material/device parameters: Can soft x-ray techniques be useful?
Organic solar cells

- Inorganic solar cells: High materials and manufacturing costs
- Organic solar cells: Low material & fabrication costs
- Efficiency issue due to its distinctive PV conversion processes
Organic solar cells

- PV conversion process is “excitonic”: Low dielectric constant
- Exciton diffusion & dissociation at D-A interface
- Current output ~ absorber band-gap
- Voltage (potential energy) output ~ LUMO_{acceptor} – HOMO_{donor}
- Bilayer device: Low efficiency due to insufficient light absorption
Organic bulk heterojunction

- Bulk heterojunction: Blend of p- & n-type materials, using solution
- Active layer can be much thicker than exciton diffusion length ($L_D$)
- Best efficiency ~4-5% (P3HT-PCBM) & ~7% (PBDTTT-PCBM)
US DOE target efficiency

- Multi year plan for Solar Energy Technology Program
DOE target efficiency

- Multi year plan for Solar Energy Technology Program

<table>
<thead>
<tr>
<th>Table D-7 OPV Technology Performance Metrics</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameter</strong></td>
</tr>
<tr>
<td>Champion device efficiency</td>
</tr>
<tr>
<td>Cell degradation</td>
</tr>
<tr>
<td>Material figure-of-merit efficiency</td>
</tr>
</tbody>
</table>
- Large optical band gap: Not enough light absorption
- Low charge mobility (especially hole): Carrier recombination loss
- Why inefficient charge transport in these materials?
Charge transport in blend layer

- Complex blend morphology, low crystallinity, hopping, charge traps
- Very low charge mobility $\mu$ : $\sim 10^{-5}$-$10^{-3}$ cm$^2$/V-s
- Significant charge recombination loss
- How to measure charge mobility?

Carrier transit time, $\tau = \frac{L^2}{\mu_{\text{eff}} V_{bi}}$, e.g., $\tau \sim 10$ $\mu$s for $\mu = 10^{-5}$ cm$^2$/V-s

Glazing incidence x-ray scattering of P3HT

Limited crystallinity in polymer

“Dead ends”

Intermolecular hopping & charge traps
How to measure charge mobility?

- Field effect transistor: “Wrong” orientation, influence of interface
- Time of flight: Thick sample requires, dispersive transport
- Space charge limited current method
Space charge limited current

- Bulk limited transport: Built-up charge in organics due to low mobility
- Mott-Gurney law: $J \sim V^2$ with $\mu$ in the proportional constant
- Modification: Effects of traps, electric field
- Example: Mobility in air-processed P3HT:PCBM blend device
Air-processed P3HT:PCBM blend solar cells

1. Spin coating of active layer

   - P3HT:PCBM 1-2% Solution
   - Thickness ~100-140 nm

2. Top metal contact deposition

   - Al ~70-100 nm
   - Blend/PEDOT:PSS
   - ITO
   - Glass

- Spin-coating/contact deposition, ambient air processing
- Post-fabrication vacuum anneal for reduction of oxygen charge trap

Air-processed P3HT:PCBM blend solar cells

- Spin-coating/contact deposition, ambient air processing
- Post-fabrication vacuum anneal for reduction of oxygen charge trap
- Charge mobility through blend network?

Efficiency ~4%

$J_{sc} \sim 9-10 \text{ mA/cm}^2$

$V_{oc} \sim 0.65 \text{ V}$

P3HT hole mobility in the blend

- Hole mobility: Two conducting channels & selective contacts
- Mobility in $10^{-5}$ cm$^2$/V-s range, ~2 orders lower than reported
- Vacuum anneal improves mobility a bit (~20%)
- Poole transport at high bias: $N_T \sim 10^{20}$ cm$^{-3}$, oxygen trap at ~0.4 eV
- Nonetheless, decent PV performance

Open circuit voltage

Polymer solar cells with enhanced open-circuit voltage and efficiency

Hsiang-Yu Chen, Jianhui Hou, Shaoqing Zhang, Yongye Liang, Guanwen Yang, Yang Yang, Lunlin Yu, Yue Wu, and Gane Li

New polymer, PBDTTT: $E_g \approx 1.77$ eV ($\approx 700$ nm), $J_{sc} \approx 13$ mA/cm$^2$

Improved $V_{oc}$ ($\approx 0.76$ V) leads to PCE $\approx 6.77$

Chen et. al., Nat. Photon. 3 (2009), Solarmer & Yu’s group
What is open circuit voltage?

- Circuit model vs. energy band model: No driving electric field at $V_{oc}$
- $V_{oc,max}$ should be 1.4 V or 0.9 V (contact) for P3HT:PCBM
- In reality, $V_{oc} \sim 0.6$ V, why?
- Charge recombination should be considered
Quasi Fermi level, $V_{oc}$, and recombination

- Max potential energy $\sim$ quasi Fermi level difference: $qV_{oc} = E_{FN} - E_{FP}$
- Steady state charge density $n$ determines $V_{oc}$
  - At steady state: $G = R$, where $G$ and $R$ are generation and recombination rates

- When light is turned off, $V_{oc}$ decreases due to $R$: $\frac{dn}{dt} = -R = -n/\tau$
- $V_{oc}$ transient provides carrier lifetime $\tau$

$$V_{oc} = \frac{2kT}{q} \ln \left( \frac{n}{N_c} \right) - \frac{\Delta E}{q}$$

\[ n = N_c \exp \left( \frac{E_{FN} - E_C}{kT} \right) \]
\[ p = N_V \exp \left( \frac{E_V - E_{FP}}{kT} \right) \]
where $n = p$ and $N_c \sim N_V$ (effective density of states)
Preliminary transient $V_{oc}$ data

- Measure voltage required to force zero current under light
- Preliminary $\tau$ vs $V_{oc}$ data, valid only $V_{oc} < \sim 0.3$ V
- Linear in semi-log plot: Bimolecular recombination at low $n$
- If extrapolate, $\tau \sim 10 \mu$s at $V_{oc} = 0.575$ V (full illumination)

Bimolecular recombination

$V_{oc} = \frac{2kT}{q} \ln \left( \frac{n}{N_C} \right) - \frac{\Delta E}{q}$ and $R \equiv \frac{n}{\tau} = \gamma n^2$ (for bimolecular recombination)

$n = \frac{1}{\tau' \gamma} \Rightarrow \ln \tau = -\frac{q}{2kT} V_{oc} + \text{const.}$
Important material properties

Transmission electron microscopy (TEM) images of P3HT:PCBM blend before and after thermal anneal


- **Structural & energy characteristics**: Crystallinity, molecular orientation, interfaces, amorphous region, energy levels, electronic defects
- **How to spatially map these parameters and correlate them with device photovoltaic and electrical performance?**
Summary

• Organic bulk heterojunction solar cells
  – Blend of donor (p-type) and acceptor (n-type) organic semiconductor

• Charge transport and mobility measurement
  – Field effect transistor, time of flight, Space charge limited current
  – Oxygen effects on P3HT:PCBM blend

• Origin of open circuit voltage and transient measurement
  – Carrier lifetime
  – Bimolecular recombination

• Acknowledgement
  – Electronic Nanomaterials, CFN: Chuck Black, Jon Allen, Danvers Johnston
  – Electron Microscopy, CFN: Dong Su
  – Condensed Matter Physics: Ben Ocko, Htay Hliang