NCN Summer School: July 2011
Notes on the Fundamental of Solar Cell

Lecture 5
Physics of Organic Solar Cells

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Outline

1) Introduction: Rationale of organic solar cells
2) Planar Heterojunction OPV
3) Checkerbox Heterjunction OPV
4) Bulk Heterojunction devices
5) Percolation, fluctuation, and efficiency limits
6) Conclusions
Different types of solar cells

**p-n**
- n+ Si (300 nm)
- p Si (200 um)
- Metal

**p-i-n**
- FTO
- p a-Si:H (10 nm)
- i a-Si:H (250 nm)
- n a-Si:H (20 nm)
- AZO

**m-i-m**
- ITO
- NiO (10 nm)
- P3HT/PCBM (200 nm)
- LiF (~1 nm)
- Al

**Crystalline Silicon**

**Amorphous silicon**

**Flexible organic**

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*Google Images*
## Economics of solar cells

<table>
<thead>
<tr>
<th>Material/m²</th>
<th>C-Si</th>
<th>CdTe</th>
<th>a-Si</th>
<th>CIGS</th>
<th>OPV</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>207</td>
<td>50-60</td>
<td>64</td>
<td>100-125</td>
<td>37</td>
</tr>
<tr>
<td>Process/m²</td>
<td>123</td>
<td>86</td>
<td>73</td>
<td>130</td>
<td>23-37</td>
</tr>
<tr>
<td>Total/m²</td>
<td>350</td>
<td>130</td>
<td>138</td>
<td>230</td>
<td>50-80</td>
</tr>
<tr>
<td>Cost/W</td>
<td>1.75</td>
<td>0.94</td>
<td>-1.2</td>
<td>0.9-1.4</td>
<td>1.63</td>
</tr>
</tbody>
</table>

If efficiency exceeds 15% and lifetime 15 years, $/W \sim 0.36

- All costs are approximate
- Goodrich, PVSC Tutorial, 2011.
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Basics: Excitons, electrons, and holes

 Charge neutral excitons happily diffusing around ...

\[ m = 0.1 m_0, \kappa = 10 \]

\[ E_{1}^{Si} \sim 13.6 \text{ meV} \quad r_{B}^{Si} \sim 53 \text{ Å} \]

\[ E_{1} = \frac{m q^4}{32 \pi^2 \hbar^2 \varepsilon_0^2} \frac{1}{\kappa^2} \approx 13.6 \times \frac{1}{\kappa^2} \left(\frac{m}{m_0}\right) \text{ eV} \]

\[ r_{B} = \frac{4 \pi \varepsilon_0 \hbar^2}{mq^2} \kappa = 0.53 \times \kappa \left(\frac{m_0}{m}\right) \text{ Å} \]

\[ m = 0.1 m_0, \kappa = 3 \]

\[ E_{1}^{poly} \sim 151 \text{ meV} \quad r_{B}^{poly} \sim 15 \text{ Å} \]

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Basics: Excitons, electrons, and holes

$$E_1^{\text{poly}} \sim 151 \text{ meV} \quad r_B^{\text{poly}} \sim 15 \text{ Å}$$

Heterojunctions takes the exciton apart,
Build-in field sweeps electrons/holes away
Exciton recombination before dissociation at the junction makes it a poor cell …
Photocurrent in bilayer cells

\[ J_{ex} = \frac{\mu_n S}{\mu_n E + S} \]

\[ J_{ph} = \frac{\mu_n E(0)}{\mu_n E(0) + S} \]

\[ E(0) = \frac{V_{bi} - V}{W_n} \]

\[ J_{ex} = \frac{qG}{\ell_{ex}} = \ell_{ex} \left[ 1 - e^{-W/4\ell_{ex}} \right] \]

\[ J_{ex} = qG \ell_{ex} \quad W/2 \gg \ell_{ex} \]

\[ J_{ex} = qG W/4 \quad W/2 \ll \ell_{ex} \]
Photocurrent in bilayer cells

Defective interface

\[
\frac{J_{ph}}{J_{ex}} = \left[ \frac{\gamma_{L,n}}{\gamma_{L,n} + \gamma_{R,n} + \gamma_{rec}} - \frac{\gamma_{L,p}}{\gamma_{L,p} + \gamma_{R,p} + \gamma_{rec}} \right]
\]

\[
J_{ex} = \gamma n(0)^2 + \left[ S + \mu n E \right] n(0) \equiv \gamma n(0)^2 + \nu_T n(0)
\]

\[
J_{ph} = \left[ \frac{-\nu_T + \sqrt{\nu_T^2 + 4\gamma J_{ex}}}{2\gamma} \right] \nu_T
\]

Interface recombination a key challenge

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Dark current in bilayer organic PV

\[ J_d \approx \gamma n(0)p(0) \]

\[ \approx \gamma \left[ n_L e^{-qE_{n}/K_BT} \times p_R e^{-qE_{p}/K_BT} - n_{i,0}^2 \right] \]

\[ = \gamma \left[ n_L p_R e^{-q(V_{bi} - V)/K_BT} - n_{i,0}^2 \right] \]

Defective interface

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Anomally low fill factor!
Current collection and charge pileup

\[ \frac{J_{ph}}{J_{ex}} = \frac{\mu_n E(0)}{\mu_n E(0) + S} \quad E(0) < \frac{V_{bi} - V}{W_n} \]

The electrons stay too long close to a dangerous region …
Better mobility improves Fill factor

Higher mobility improves Fill factor
Nonlinear series resistance ....
The problem with planar heterojunction ...

Making such thin film is essentially difficult, the layers will short out ...
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Checkerboard organic solar cells
Decoupling exciton and electron-hole paths

\[ \frac{J_{ex}}{qG} = \frac{J_{L,ex}}{qG} = 2N \times \ell_{ex} \left[ 1 - e^{-W_s/2 \ell_{ex}} \right] \]

the balancing act ...

Finger density ...

\[ N_F \sim \frac{I}{2S^2} \quad V_F = WS^2 \]

Fraction of the charge collected/finger ...

\[ F(S) \sim 4S \times \sqrt{D_{ex} \tau_{ex}} / 2S^2 \]
\[ = 2\sqrt{D_{ex} \tau_{ex}} / S \]

Total charge collected ...

\[ J_{ex} = qG \times V_F \times F(S) \times N_F \]
\[ \sim qG \times W \sqrt{D_{ex} \tau_{ex}} / S \]

Two blocks

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Photo and dark currents (like a p-i-n diode)

Photocurrent with distributed recombination

\[
\frac{J_{ph}}{J_{ex} - R(V)} = \int_0^W dx \left[ \frac{\gamma_{L,n}}{\gamma_{L,n} + \gamma_{R,n}} - \frac{\gamma_{L,p}}{\gamma_{L,p} + \gamma_{R,p}} \right]
\]

\[
= W \times \frac{2L_D}{W} \log \cosh \frac{W}{2L_D} \approx W \left[ \frac{2L_D}{W} - \coth \frac{W}{2L_D} \right]
\]

Dark current with distributed recombination

\[
J_d = A \left[ \frac{\mu_n (V - V_{bi}) / d}{e^{q(V-V_{bi})/k_B T} + 1} \right] \left[ e^{qV/nk_B T} - 1 \right]
\]

Sokel and Hughes, JAP, 53(11), 1982.

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meso-structured organic solar cells

bilayer

checkerboard

Mixed Layers

\[
\frac{J_{ex}}{qG} = \frac{J_{L,ex}}{qG} = 2N \ell_{ex} \left[ 1 - e^{-W_s/2\ell_{ex}} \right]
\]

\[AW = NW_s 2W\]

\[2N = \frac{A}{W_s}\]
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Processing of a plastic bulk heterojunction cell

Polymer-A (Donor) → Solvent → Polymer-B (Acceptor)

Anneal for a certain duration at moderate temperature

Phase Separation occurs through Spinodal Decomposition

Cahn-Hilliard Eq:

\[
\frac{\partial \phi}{\partial t} = M_0 \left( \nabla^2 \frac{\partial f}{\partial \phi} - 2k \nabla^4 \phi \right)
\]

Nature Materials, 2009
Process model for phase segregation

Free energy:
\[ f_{\text{mix}} = U - TS \]

Cahn-Hilliard Eq:
\[ \frac{\partial \varphi}{\partial t} = M_0 \left( \nabla^2 \frac{\partial f}{\partial \varphi} - 2K \nabla^4 \varphi \right) \]

The free energy contains polymer details.
Demixing and self-organization in thin films

Anneal time

Grain-size $W(t)$

$W(t) \sim t^{1/3}$

Anneal time (sec)

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Response of BHJ cells to light pulses

Electron

Holes

Movie: How excitons are taken apart by the heterojunction

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Photocurrent in BHJ OPV

Anneal time

\[ W(t) \sim t_a^{1/3} \]

\[ L(t) \times W(t) = \frac{\text{Area}}{2} \]

\[ L(t) \sim \frac{\text{Area}}{2 	imes t_a^{1/3}} \]

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Photocurrent and exciton flux

Form defines function ....
Should we anneal at all?

\[ J_{ex} = \frac{Q}{\tau_{ex}} \cdot \sqrt{\frac{D_{ex}}{\tau_{ex}}} \cdot \frac{I}{t_a^{1/3}} \]

\[ L(t) \sim \frac{\text{Area}}{2 \times t_a^{1/3}} \]

\[ Q = q\sqrt{D_{ex}\tau_{ex}} \times L(t_a) \]
Photocurrent and annealing time

Ray et al., Solar Energy Mat and Solar Cells, 2011
How do they compare?

Bilayer

Typical BHJ

Ordered BHJ

Ray et al., PVSC, 2011

Low current
Poor fill factor

Bilayer

Typical BHJ

Ordered BHJ

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The challenge of a 15% cell ...

- New polymers with smaller bandgap
- Change solvent and mixing ratio
- Percolation dictates ~1:1 volume ratio
- Regularize morphology
- Random close to optimal

Solubility issues
Optimize anneal time
Very limited play

Conflicting system requires constraints the design,
Need to consider all improvement within this context
Mixing ratio and percolation

Moving away from 1:1 ratio is challenging ....
Ordered vs. Disordered Morphology

Reduced variability, optimal for a range of anneal conditions

Ray et al., PVSC, 2011
Fundamental constraint of reliability

Continued coarsening with anneal time

\[ W_C(t_a, T_a) \propto \left[D_{\text{eff}}(T_a)t_a\right]^n \]

\[ D_{\text{eff}}(T_a) = D_0 e^{-E_a/kT_a} \]

The difference between Arizona sun and an oven is negligible
Derivation of the reliability formula

\[ J_{SC} \propto \frac{L_{ex}}{W_C(t)} \]

\[ \frac{J_{SC}(t_0 + t_s)}{J_{SC}(t_0)} = \frac{W_C(t_0)}{W_C(t_0 + t_s)} \]

\[ = \left( \frac{D_{eff}(T_0)t_0 + D_{eff}(T_s)t_s}{t_s} \right)^n \]

\[ = \left[ 1 + e^{-E_a/kT_s} \left( \frac{t_s}{t_{eq}} \right) \right]^{-n} \]

\[ t_s = 10 \text{ hrs} \]

100 hrs

\[ J_{SC} (\text{deg}) = 10, 20, 30\% \]

\[ E_a = 1.2 \text{ eV} \]

\[ n = .25 \]

Ray et al., APL, 2011

Lifetime less than a year!
ordered vs. spinodal films

Bulk Heterojunction

Checkerboard

Double Gyroid

Good ...

better ...

Best ...

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Conclusions

Organic solar cells promises a low cost PV technology, lightweight, easy to install. Also, a beautiful physics problem with biomimetic transport.

Theory explains optimum of anneal time, the rationale of 1:1 mixing ratio, the fundamental constraints of reliability, limits of Voc and FF.

Reliability, variability, and efficiency are important concerns. Self assembled regularized structure, new class of optics, lower bandgap materials, may help us reach 15% efficiency targets.

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