Optimizing Transport through Organic-Inorganic Interfaces in Macroscale Thin Film Architectures

MURI-Thrust 3

Jeff Urban
Tie together organic and inorganic components over longer length scales.

Does transport through multiple organic-inorganic junctions obey similar rules as single molecule junctions?
Thrust 3: Goals and Objectives

- Discern role of organic-inorganic interfaces to develop design rules for composite devices.

Which theoretical model best describes thermoelectric transport at the nanoscale?

New theory and measurement techniques being developed to elucidate role of interfaces in controlling thermal and electrical transport in thin films.
Thrust 3: Goals and Objectives

- **Proof of Principle for real thermoelectric devices based on organic-inorganic composites.**

  What are the limits of multi-junction composite films/devices? Rational design of organic-inorganic composites promises optimization of thermal and electrical characteristics of thin films.
New Organic/Hybrid Materials Enable Flexible Thermoelectrics

Conventional Rigid TE Coolers

Tunable Flexible TE Modules

Fabric for wearable devices

Conformable thermal management
Unique Advantages of Organic/Hybrid Thermoelectrics

- Scalable manufacturing
- Potentially inexpensive components
- Durable/flexible devices
- Optimizing device interfaces

Forrest et al.
Thrust 3: Energetics of Organic Materials

Motivation

Thermopower and conductance can be increased by changing the energy landscape.

**Copper Selenide**

- **Energy level alignment achievable**
  - Match energy levels of organics with valence band of Cu$_{2-x}$Se

- **p-type semiconductor**

- **Copper chalcogenides**$^1$ nanocrystals have estimated carrier concentrations of $\sim 10^{21}$

- **Surface plasmon frequency**


Generally:
2.5 eV < LUMO < 4 eV
5 eV < HOMO < 6 eV
Synthesis of Cu$_{2-x}$Se Nanocrystals

• Compelling bulk thermoelectric properties; good chemistry for organic integration
• Ability to determine organic components effect through optical and electrical measurements.
• Comparative studies with single or polycrystalline thin films (Prof. Jeff Snyder).

Developing Controlled Assembly Methods

- Dip coating
- Layer-by-layer (LbL) assembly
- Simple ligand exchange with organic components
- Precisely controlled thickness

Number of dip coat cycles

Nanocrystal thin film
Layer by Layer Opportunities: Graded TE

Beating the maximum cooling limit with graded thermoelectrics

Traditional TE Cooling: $\Delta T = \frac{1}{2} ZT^2$

Graded TE: $\Delta T = \frac{1}{2} ZT^2 \sum_{n=1}^{N} \frac{1}{n^2}$

Enhanced cooling possible!

Bian and Shakouri, APL (2006)
Thermoelectric Properties of Cu\(_{2-x}\)Se Integrated with Small Molecules

<table>
<thead>
<tr>
<th>Ligand structure</th>
<th>replacing ligand</th>
<th>conductivity (S/cm)</th>
<th>seebeck ((\mu)V/K)</th>
<th>power factor ((\mu)W/m(\cdot)K(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDT</td>
<td>19.2 ± 0.3</td>
<td>44.1 ± 4</td>
<td>3.7 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>EDA</td>
<td>1817 ± 570</td>
<td>12.3 ± 3</td>
<td><strong>25.5 ± 3</strong></td>
<td></td>
</tr>
<tr>
<td>SuAcid</td>
<td>540 ± 46</td>
<td>17.2 ± 3</td>
<td>16.4 ± 5</td>
<td></td>
</tr>
<tr>
<td>Stripped</td>
<td>447 ± 82</td>
<td>14.9 ± 0.4</td>
<td>10.0 ± 2</td>
<td></td>
</tr>
<tr>
<td>BDT</td>
<td>5.5 ± 0.8</td>
<td>49.5(^{\dagger})</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>BDA</td>
<td>568 ± 240</td>
<td>17.3 ± 0.3</td>
<td>17.0 ± 5</td>
<td></td>
</tr>
</tbody>
</table>

= Cu\(_{2-x}\)Se nanocrystal

*All data are averages of 3 samples prepared and measured together.

\(^{\dagger}\)Only 2 samples were measured

Near highest power factor reported for colloidal NCs!

Characterization of Cu$_{2-x}$Se Nanocrystalline Hybrid Thin Films

- Reduction in C-H stretches, successful ligand exchange.
- Absorption spectra show red shifts and broadening.

Carboxylate coated (red), EDT (blue), EDA (pink), SuAcid (green), and Without Ligands (stripped using Meirwein salt solution, cyan).


<table>
<thead>
<tr>
<th>Molecules</th>
<th>Ionization Energy (eV)</th>
<th>Valence Band/HOMO edge (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag Standard</td>
<td>Raw</td>
<td>CubeRt</td>
</tr>
<tr>
<td>EDA</td>
<td>4.6</td>
<td>4.54</td>
</tr>
<tr>
<td>EDT</td>
<td>4.6</td>
<td>4.57</td>
</tr>
<tr>
<td>SUCC</td>
<td>4.6</td>
<td>4.57</td>
</tr>
<tr>
<td>Strip</td>
<td>4.7</td>
<td>4.64</td>
</tr>
</tbody>
</table>
What is the best way to translate single molecule, atomistic models to multi-junction, device based architectures?

1) Model disordered, nanocrystal assemblies with numerous interfaces and junctions.
   - Many variables
   - Several interfaces and junctions possible
2) Model ordered, thin film with single interface with multiple organic-inorganic junctions.
   - Defined interface, bulk properties of thin film
Novel Characterization Tool: Rastered Seebeck

- Insight into sample homogeneity
- Geometrical and packing effects
- Compositional variation effects on S
Macroscopic measurements do not reveal subtleties of junctional effects, local order, and chemistry.
Novel Characterization Tool 2: Gated Seebeck

- New technique to elucidate carrier transport in networks of hybrid interfacial junctions
- Spectroscopic measurement of Seebeck coefficient

Can scan through DOS by varying $E_f$ without changing lattice or morphology

What do we learn from gated Seebeck?

- $S$ vs. $E_f$ data: develop models for carrier transport and DOS in these new hybrid inorganic-organic materials systems
- Transport landscape: optimizing thermoelectric transport by understanding role of organic-inorganic interfaces on carrier distribution

Chen, C.E., Coates, N.E., Chabinyc, M.C., Snyder, G.J., Urban, J.J.
Seebeck vs. Gated Seebeck

Seebeck coefficient is related to asymmetry in e- and h+ distributions

slope = - Seebeck coefficient

S = \frac{k_B}{e} \int \frac{E - E_F}{k_B T} \sigma(E) dE

Seebeck coefficient is related to asymmetry in e- and h+ distributions

Analogous to concepts in Thrust 2 (Ef scan)
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