Optical Spectroscopy and Microscopy of PV Materials and Devices: Carrier Lifetimes, Mobilities, Interface Recombination Velocities, and Other Electro-Optical Characteristics

SUN UP Webinar

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We can collaborate in electro-optical characterization of PV materials and devices

Example: (New PV absorber)

Martinez et al, Solar energy conversion properties and defect physics of ZnSiP₂, Energy and Environmental Science 9, 1031 (2016)
PI: A. Tamboli

Optical spectroscopy and microscopy to study:

1. Minority carrier lifetimes;
2. Dopants;
3. Defects and recombination;
4. Band tails /compensation;
5. Charge carrier transport;
6. Optical device analysis;
7. Metastability (cell level reliability)

Logistics – plan at least 3 months at NREL, at least 6 months for EO microscopy
1. “EO approach” and minority carrier lifetimes

Optical spectroscopy/microscopy uses photons similar to solar photons; results are relevant for solar cells:

- Increase in charge carrier lifetime leads to higher open circuit voltage:

Approach:
(a) precisely target excitation/generation;
(b) time-resolve properties at interfaces, space charge region, bulk, etc.

With time-resolved PL, we measure lifetimes in the 0.01 ns to 1000 ns range
2. Dopant activation energies in CdTe

AsTe with $E_a = 90$ meV - double heterostructures (MBE)

P$_{Te}$ with $E_a = 80$ meV
Burst et al, APL Materials (2016) - single crystals

Cu$_{Cd}$ with $E_a = 150$ meV (px)
Kuciauskas et al, APL (2015) - polycrystalline devices

Undoped (px)
Albin et al, APL (2014) - polycrystalline films
3. Defects and Recombination

Recombination model in high-voltage CdTe solar cells

\[ E_A = 0.11 - 0.15 \text{ eV} \]
\[ N_{Cu} \approx 1 \times 10^{16} \text{ cm}^{-3} \]
\[ \sigma_{Cu} \approx 1.3 \times 10^{-16} \text{ cm}^{-2} \]

\( E_g = 1.57 \text{ eV} \)

\( E_g = 1.61 \text{ eV} \)

\( E_A \approx 0.11 - 0.15 \text{ eV} \)

\( N_{Cu} \approx 1 \times 10^{16} \text{ cm}^{-3} \)

\( \sigma_{Cu} \approx 1.3 \times 10^{-16} \text{ cm}^{-2} \)

\( E_A \approx 0.11 - 0.15 \text{ eV} \)


Excitation 632.8 nm
1 microW
4K
Film side

Solar cell - no Cu

Solar cell with Cu

single crystal
4. Band tails and compensation

Polycrystalline CIGS films

Amplitude of potential fluctuations $\gamma$ reduced 2× by KF post deposition treatment.

Jensen et al., J. Appl. Phys. 120, 063106 (2016)

Low energy PL tail at 4 K:

Lifetimes:
5. Optical Charge Carrier Transport Microscopy

Time-resolved microscopy is used to visualize and analyze charge carrier transport and recombination. Movie frames in 0.2 ns steps show real-time carrier dynamics:

Detector 1
TRPL 840nm

Detector 2
SHG-515nm

Laser excitation

Dichroic beam splitters

Microscope Objective

Cap: CdTe 10 nm
CdMgTe 30 nm
CdTe 5 um
CdMgTe 30 nm
Buffer: CdTe 1.5um
Substrate: (100) InSb

Generation

Collection

X-Y-Z scanning

(MBE: Texas State University)
5. Optical Charge Carrier Transport Microscopy

- Circles (in 4ns image) indicate threading dislocations;
- Graph (right) shows time-dependent diffusion for red and brown areas.

Map of diffusion lengths in CdTe epitaxial heterostructure (range of 5-12 microns)

Kuciauskas et al, IEEE JPV (2016)
5. Perovskites—lifetime and transport microscopy

“Dark” grain boundaries indicate barriers for carrier transport

2PE time-resolved photoluminescence microscopy (excitation 1030 nm)

<table>
<thead>
<tr>
<th>Spot</th>
<th>$D$, cm$^2$/s</th>
<th>mobility, cm$^2$/V·s</th>
<th>$\tau_B$, ns</th>
<th>$L_B = \sqrt{D\tau_B}$, um</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot A</td>
<td>1.79 ± 0.03</td>
<td>68.8</td>
<td>50.2 ± 0.4</td>
<td>3.00</td>
</tr>
<tr>
<td>Spot B (bright grain)</td>
<td>0.48 ± 0.01</td>
<td>18.5</td>
<td>74.9 ± 0.9</td>
<td>1.90</td>
</tr>
<tr>
<td>Spot C</td>
<td>0.83 ± 0.01</td>
<td>31.9</td>
<td>46.6 ± 0.4</td>
<td>1.97</td>
</tr>
<tr>
<td>Spot D (bright grain)</td>
<td>0.56 ± 0.01</td>
<td>21.5</td>
<td>84.6 ± 1.0</td>
<td>2.18</td>
</tr>
<tr>
<td>Spot E</td>
<td>2.56 ± 0.08</td>
<td>98.5</td>
<td>39.3 ± 0.3</td>
<td>3.17</td>
</tr>
</tbody>
</table>

HOIP Synthesis: Kai Zhu, NREL
6. Optical spectroscopy of CIGS solar cells

From device analysis we determine carrier lifetimes, mobilities, interface recombination velocities, thermionic emission properties, etc.

\[ \frac{1}{\tau_{th}} = \frac{1}{l_w} \sqrt{\frac{k_B T}{2 \pi m}} \exp\left(\frac{-\Delta E}{k_B T}\right) \]

\[ \frac{1}{\tau_S} = \alpha S \]

\[ \frac{1}{\tau_D} = \pi^2 D \]

\[ \frac{1}{\tau_R} = \frac{1}{\tau_{th}} + \frac{1}{\tau_{b,n}} + \frac{1}{\tau_S} + \frac{1}{\tau_D} \]

\[ \tau_R^{-1} < 10^{-6} \text{ s}^{-1} \]

\[ \tau_{b,n} = 11.6 \pm 2.9 \text{ ns} \]

\[ \mu_n = 22 \pm 2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \]
7. Metastability

Material and device metastability is based on physics and defects. We use spectroscopy and theory to understand metastability. Example: $V_{Se}/V_{Cu}$ divacancy model in CIGS, where irradiation is predicted to convert between the “−” and “+” states. To apply this model with EO spectroscopy we measure doping, lifetime, defect activation energies, and defect spectra.

Orange – 20.6% efficient CIGS device;
Yellow – device after exposure to sub-band gap light
Electrooptical PV characterization at NREL

TRPL spectrometer. Detectors:
Si APD: 40 ps <1050 nm
R5509 PMT: 300 ps <1350 nm
InGaAs APD: 100 ps <1750 nm

Yb:KGW laser
1.1 MHz 11 W 1030 nm, 300fs

Two-photon excitation (2PE)

Time-resolved PL microscope

Optical parametric amplifier
~200 fs, 1.1 MHz tunable from 320-2550 nm

Cryostation
4-350 K
Closed loop He cryostat
Vibrational stability <20 nm

Two-photon excitation variable-temperature microscope
For PL emission spectroscopy

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