Thin Film Photovoltaics

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The University of Toledo

Principles and Varieties of Solar Energy (PHYS 4400)
Requirements/conditions for constructing a valuable solar cell

A partial list…

- Efficiently absorb a large fraction of irradiance to optimize photogeneration of carriers
- Achieve charge separation, directing electrons and holes to different contacts (e.g., use doped materials for p-n junction)
- Demonstrate strongly-rectifying (diode) behavior
- Avoid excessive electron-hole recombination within the solar cell (maximize photocurrent)
- Maintain as much of the electric potential as possible (avoid resistive losses, and optimize energy band offsets)
- Resist/avoid degradation by air and water (seal the modules) – i.e. achieve stability
- Do all of these things (a) with high yield, (b) inexpensively, and (c) produce at mass scale
- What else?
Getting everything right...

\[ \eta \approx 33\% \]

Graph showing Max Efficiency (%) vs. Bandgap (eV): The graph illustrates a peak at a bandgap of approximately 1 eV, with a maximum efficiency of around 33%.
Semiconductor bandgaps relative to the solar spectrum

Dr. Jianbo Gao
Fig. 3. Performance gaps between best device efficiencies in the laboratory and attainable efficiencies for several solar cell technologies.
A look at the TF PV market

**Figure 1. Market shares PV thin-film technologies 2011** (Source: EuPD Research)

**Figure 2. Photovoltaic market shares 2015** (Source: EuPD Research)
Commercial Thin Film Photovoltaics (2011)


...energizing Ohio for the 21st Century
What is Thin Film PV?

A straight-up comparison of light absorption in three different semiconductor absorbers used for PV -- c-Si, CIGS, and CdTe:

<table>
<thead>
<tr>
<th>Material (t = 1 μm)</th>
<th>Band Gap Energy</th>
<th>Absorption coefficient, α(600 nm) in cm⁻¹</th>
<th>% of 600 nm light absorbed in 1 μm film</th>
</tr>
</thead>
<tbody>
<tr>
<td>c-Si</td>
<td>1.12</td>
<td>2.5 x 10³</td>
<td>22</td>
</tr>
<tr>
<td>CIGS</td>
<td>1.2</td>
<td>6 x 10⁴</td>
<td>99.7</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.5</td>
<td>6 x 10⁴</td>
<td>99.7</td>
</tr>
<tr>
<td>a-Si</td>
<td>1.7</td>
<td>3 x 10⁴</td>
<td>95</td>
</tr>
</tbody>
</table>

*Short answer* – thin film PV utilizes direct-bandgap materials with strong absorption coefficient throughout the visible spectrum, which absorb a large fraction of sunlight for thicknesses on the order of 1 μm.
Absorbing sunlight efficiently

What matters for absorption of sunlight to make a good solar cell?

High extinction coefficient, short absorption length, large **absorption coefficient**.

\[ I = I_0 e^{-\alpha x} \]

\[ I(\lambda) = I_0(\lambda) e^{-\alpha(\lambda)x} \]

**Bandgap**

Low **reflection** loss (can’t convert reflected photons).

How do we measure the parameters in **bold**?
CIGS = CuInGaSe$_2$

Quaternary material;
Substrate configuration;

http://upload.wikimedia.org/wikipedia/commons/d/d7/CIGSdevice.JPG
Attained vs. attainable open circuit photovoltage

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>$E_g$ at RT (eV)</th>
<th>$V_{OC}^{MAX}$ (V)</th>
<th>$V_{OC}$ (V)</th>
<th>$V_{OC}$ loss (V)</th>
<th>$V_{OC}/V_{OC}^{MAX}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-Si</td>
<td>1.12</td>
<td>0.84</td>
<td>0.71</td>
<td>0.13</td>
<td>85</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>1.14</td>
<td>1.02</td>
<td>0.12</td>
<td>90</td>
</tr>
<tr>
<td>InP</td>
<td>1.28</td>
<td>1.00</td>
<td>0.88</td>
<td>0.12</td>
<td>88</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.45</td>
<td>1.17</td>
<td>0.84</td>
<td>0.33</td>
<td>72</td>
</tr>
<tr>
<td>CIGS</td>
<td>1.14</td>
<td>0.86</td>
<td>0.72</td>
<td>0.14</td>
<td>84</td>
</tr>
<tr>
<td>a-Si</td>
<td>1.7</td>
<td>1.42</td>
<td>0.86</td>
<td>0.56</td>
<td>61</td>
</tr>
<tr>
<td>DSSC (black dye)</td>
<td>1.4</td>
<td>1.12</td>
<td>0.72</td>
<td>0.40</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>1.6</td>
<td>1.32</td>
<td>0.85</td>
<td>0.47</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.72</td>
<td>0.80</td>
<td>0.92</td>
<td>47</td>
</tr>
<tr>
<td>OPV</td>
<td>1.55</td>
<td>1.27</td>
<td>0.75</td>
<td>0.52</td>
<td>59</td>
</tr>
</tbody>
</table>
### Attained vs. attainable short-circuit photocurrent

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>$E_g$ at RT (eV)</th>
<th>$J_{SC}^{MAX}$ (mA/cm²)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$J_{SC}/J_{SC}^{MAX}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC-Si</td>
<td>1.12</td>
<td>43.8</td>
<td>42.7</td>
<td>98</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.42</td>
<td>32.0</td>
<td>28.5</td>
<td>89</td>
</tr>
<tr>
<td>InP</td>
<td>1.28</td>
<td>36.3</td>
<td>29.5</td>
<td>81</td>
</tr>
<tr>
<td>CdTe</td>
<td>1.45</td>
<td>30.8</td>
<td>25.9</td>
<td>84</td>
</tr>
<tr>
<td>CIGS</td>
<td>1.15</td>
<td>42</td>
<td>33.5</td>
<td>80</td>
</tr>
<tr>
<td>a-Si</td>
<td>1.7</td>
<td>22.4</td>
<td>17.5</td>
<td>78</td>
</tr>
<tr>
<td>DSSC (black dye)</td>
<td>1.4</td>
<td>33.3</td>
<td>20.5</td>
<td>62</td>
</tr>
<tr>
<td>(Red N719)</td>
<td>1.6</td>
<td>25.5</td>
<td>17.7</td>
<td>70</td>
</tr>
<tr>
<td>(Red N3)</td>
<td>2.0</td>
<td>14.4</td>
<td>9.2</td>
<td>64</td>
</tr>
<tr>
<td>OPV</td>
<td>1.55</td>
<td>26.9</td>
<td>14.7</td>
<td>55</td>
</tr>
</tbody>
</table>
Basic CdTe PV Device Architecture(s)

Light

Glass substrate
ITO (low resistivity TCO)
SnO₂ (high resistivity TCO)
n-doped CdS (window layer)
p-doped CdTe (absorber)
Au or Ni-Al metal contact

“superstrate”

http://www.nrel.gov/pv/thinfilm.html

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EQE for typical CdTe solar cell

Naba R. Paudel, University of Toledo Dissertation: “Stability issues in sputtered CdS/CdTe solar cells”
TCO materials for used w/ CdTe solar cells

<table>
<thead>
<tr>
<th>Materials</th>
<th>Resistivity</th>
<th>Transmission</th>
<th>Stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$:F</td>
<td>$5 \times 10^{-4}$ Ω-cm</td>
<td>~80%</td>
<td>excellent</td>
</tr>
<tr>
<td>SnO$_2$:In$_2$O$_3$</td>
<td>$2.5 \times 10^{-4}$ Ω-cm</td>
<td>~85%</td>
<td>good</td>
</tr>
<tr>
<td>In$_2$O$_3$:F</td>
<td>$2.5 \times 10^{-4}$ Ω-cm</td>
<td>~85%</td>
<td>good</td>
</tr>
<tr>
<td>In$_2$O$_3$:GeO$_2$</td>
<td>$2 \times 10^{-4}$ Ω-cm</td>
<td>~85%</td>
<td>good</td>
</tr>
<tr>
<td>Cd$_2$SnO$_4$</td>
<td>$2 \times 10^{-4}$ Ω-cm</td>
<td>&gt;85%</td>
<td>fair</td>
</tr>
<tr>
<td>ZnO:Al$_2$O$_3$</td>
<td>$(4-6) \times 10^{-4}$ Ω-cm</td>
<td>&gt;85%</td>
<td>fair</td>
</tr>
<tr>
<td>ZnO:In</td>
<td>$8 \times 10^{-4}$ Ω-cm</td>
<td>~85%</td>
<td>good</td>
</tr>
</tbody>
</table>

Naba R. Paudel, University of Toledo Dissertation: “Stability issues in sputtered CdS/CdTe solar cells”
Figure 2-2. CdS/CdTe sputtering system designed by AJA International located at MH3023 in University of Toledo. [Inset shows CdTe plasma through the viewport of chamber B during sputter deposition. The CdTe deposition is going on the glass substrate which is face down and rotating continuously for uniform coating.]

Naba R. Paudel, University of Toledo Dissertation: “Stability issues in sputtered CdS/CdTe solar cells”
Figure 1-14. Secondary electron micrograph of as grown CdS film sputtered on SnO$_2$:F coated glass substrate.
Sputter deposition

- Sputtered atoms have a wide range of energies;
- Ballistic atoms or ions can result in resputtering from thin film;
- Control of the atom energetic distribution can be accomplished through variation of chamber inert gas pressure (e.g., Ar);
- Note that CdTe sputters (and evaporates) congruently, i.e., as a CdTe molecule. This maintains very close 1:1 stoichiometry of the resulting film.


http://en.wikipedia.org/wiki/Sputter_deposition
CdCl$_2$ treatment (recrystallization of CdTe)

PVD CdTe films: (a) untreated, (b) and (c) after CdCl$_2$ heat treatment at 350$^\circ$ and 400$^\circ$C, respectively.

Effects of CdCl$_2$ treatment on as-deposited CdTe films
- Results in CdTe grain growth (especially w/ sputtered films and PVD-grown films, less so w/ CSS)
- Reduces lattice strain (also promotes grain growth)
- Increases minority carrier lifetime (~ x10), perhaps due to reduction in deep level defect densities within the bandgap.

Studies of Recrystallization of CdTe Thin Films After CdCl Treatment
Presented at the 26th IEEE Photovoltaic Specialists Conference, September 29–October 3, 1997, Anaheim, California
CdTe module production and scribing steps

| TCO | Glass |

- Start with **TCO Coated Glass**
- Start with **TCO** Coated Glass
- Deposition 1 – **CdS**
- Deposition 2 – **CdTe**
Start with **TCO Coated Glass**

- Deposition 1 – **CdS**
- Deposition 2 – **CdTe**
- Process 1 – P1 – 1064 nm **Scribe** through TCO/CdS/CdTe

Note: All scribes from sunny side
• Start with TCO Coated Glass
• Deposition 1 – CdS
• Deposition 2 – CdTe
• Process 1 – P1 – 1064 nm Scribe through TCO/CdS/CdTe
• Process 2 – Shunt resistance layer
- Start with TCO Coated Glass
- Deposition 1 – CdS
- Deposition 2 – CdTe
- Process 1 – P1 – 1064 nm Scribe through TCO/CdS/CdTe
- Process 2 – Shunt resistance layer
- Process 3 – P2 – 532 nm Scribe through CdS/CdTe
• Start with **TCO** Coated Glass
• Deposition 1 – **CdS**
• Deposition 2 – **CdTe**
• Process 1 – P1 – 1064 nm **Scribe** through TCO/CdS/CdTe
• Process 2 - **Shunt resistance layer**
• Process 3 – P2 – 532 nm **Scribe** through CdS/CdTe
• Process 4 – Cu treatment
• Process 5 – **Metallization**
Start with **TCO Coated Glass**

- **Deposition 1** – *CdS*
- **Deposition 2** – *CdTe*

**Process 1** – P1 – 1064 nm **Scribe** through CdTe/CdS/TCO

**Process 2** – **Shunt resistance layer**

- **Process 3** – P2 – 532 nm **Scribe** through CdTe/CdS
- **Process 4** – Cu treatment
- **Process 5** – **Metallization**
- **Process 6** – P3 – 532 nm Scribe through Metal/CdTe/CdS
- **Process 7** – Post Metal Heat Treatment
9:36AM First Solar sets CdTe module efficiency world record, launches Series 3 Black module: Co announced it set a new world record for cadmium-telluride (CdTe) photovoltaic (PV) module conversion efficiency, achieving a record 16.1% total area module efficiency in tests confirmed by the U.S. Department of Energy's National Renewable Energy Laboratory. The new record is a substantial increase over the prior record of 14.4% efficiency, which the co set in Jan 2012. Separately, First Solar also set a record for CdTe open circuit voltage (VOC), reaching 903.2 millivolts (mV) in NREL-certified testing. Co also launched a new evolution of its proven Series 3 thin-film PV module platform, the Series 3 Black.