Polycrystalline CdS/CdTe solar cells

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(Lecture for Heben/Ellingson solar cells class)
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Absorption spectra of various semiconductors
actual and attainable single junction cell efficiencies (inorganic materials)

Attainable cell efficiencies for AM0 (solid line) and AM1.5 spectra (dashed line) and best efficiencies achieved for several materials as single junctions. (Kazmerski 2006)
the traditional silicon solar cell

- sunlight
- metal grid
- transparent conductor
- n-type silicon
- p-type silicon
- metal electrode

~200 µm
band diagram for a homojunction (n on p)

- Si (indirect band gap) will have typically a thick neutral region--carrier collection by diffusion
- most thin-film (direct band gap materials) will have mostly field-assisted collection

Solar cell structure and energy band diagram showing valence (VB) and conduction bands (CB), Fermi level (EF), photoabsorption, electron-hole pair generation, thermalization, and drift.
(from Compaan, APS News April, 2005)
CdTe is difficult to dope p-type extrinsically.

Depletion width in a single-sided step junction:
\[ W = \left(\frac{2\varepsilon_0 V_{bi}}{qN_a}\right)^{1/2} \]

(for Si with \( N_a = 1 \times 10^{16} \text{ cm}^{-3} \), \( W \approx 0.35 \mu\text{m} \))
Construct a band diagram of the CdS/CdTe solar cell….
What information do we need?

Electron affinity of CdTe
$E_a = 4.4 \text{ eV}$

Work functions of common metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Work Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (silver)</td>
<td>4.26</td>
</tr>
<tr>
<td>Al (aluminum)</td>
<td>4.28 see notes</td>
</tr>
<tr>
<td>Au (gold)</td>
<td>5.1</td>
</tr>
<tr>
<td>Cs (cesium)</td>
<td>2.14</td>
</tr>
<tr>
<td>Cu (copper)</td>
<td>4.65</td>
</tr>
<tr>
<td>Li (lithium)</td>
<td>2.9</td>
</tr>
<tr>
<td>Pb (lead)</td>
<td>4.25</td>
</tr>
<tr>
<td>Sn (tin)</td>
<td>4.42</td>
</tr>
<tr>
<td>Chromium</td>
<td>4.6</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>4.37</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>4.4</td>
</tr>
<tr>
<td>Gold</td>
<td>4.8</td>
</tr>
<tr>
<td>Tungsten</td>
<td>4.5</td>
</tr>
<tr>
<td>Copper</td>
<td>4.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>4.6</td>
</tr>
</tbody>
</table>

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S-H Wei, S.B. Zhang, A. Zunger (T = 0 K band gaps)
Band structure?
(Construct on board with class discussion)

• Cliff or spike at the CdS/CdTe interface?

• Doping densities in CdTe, in CdS?

• Back barrier for hole transport?
UT CdTe sputtered cell on aluminosilicate glass

14.0% efficiency at one-sun illumination

sunlight

aluminosilicate glass
zinc oxide
cadmium sulfide
 cadmium telluride
metal

V_{oc} = 0.8140 \text{ V} \\
I_{sc} = 3.5429 \text{ mA} \\
J_{sc} = 23.563 \text{ mA/cm}^2 \\
Fill ~ Factor = 73.25 \% \\
Kelvin probe, series resistance 19.8 ohms.

V_{oc} = 3.1571 \text{ mA} \\
I_{sc} = 0.6691 \text{ V} \\
P_{max} = 2.1123 \text{ mW} \\
Efficiency = 14.0 \% 

Voltage Bias: 0.0 \text{ V} \\
Light bias for 1.23 \text{ mA} \\
Light Bias region area: 0.1504 \text{ cm}^2 \\
Light Bias Density: 8.206 \text{ mA/cm}^2 \\

Device ID: SSC011-2.36 \\
Device Temperature: 25.0 \pm 1.0 \text{ °C} \\
Device Area: 0.150 \text{ cm}^2 \\
Irradiance: 1000.0 \text{ W/m}^2 \\
Jun 24, 2002 10:56 \\
Reporting Spectrum: AM1.5 Global 

Device ID: SSC011-2.36 \\
Device Temperature: 25.0 \pm 1 \text{ °C} \\
Device Area: 0.1504 \text{ cm}^2 \\
Jun 24, 2002 1:27 PM 

Filter QE System 
PV Performance Characterization Team

NREL
New record CdTe cell: First Solar, 2011 efficiency = 17.3%
(done “on production equipment”)
Typically the back contact is a metal or carbon paste rather than the transparent ZnTe shown here.

Note particularly the following:
- Loss due to CdS absorption edge at 2.4 eV or 517 nm
- Loss due to intermixing
- Increased red response due to intermixing (1.5 eV ~ 830 nm; 1.4 eV ~880 nm)

Figure 2. Photon accounting for a) Record cell and b) Production cell.
PL in CdS/CdTe junctions (from D-H Kwon)

- Film side and junction side PL at 10 K from as-deposited cells
- Intermixing of S at the junction changes the bandgap of the material and ratio of S can be indirectly estimated

Fig. 10 from: DoHyoung Kwon, X. Liu, N. R. Paudel, K. A. Wieland, and A. D. Compaan, “INFRARED PL STUDIES OF SPUTTERED CdTe FILMS AND CELLS”, 35th IEEE PVSC conference proceedings, June 2010

Fig. 11 from: Antonio Luque and Steven Hegedus, “Handbook of Photovoltaic Science and Engineering”, p638, Wiley, West Sussex England, 2003
Figure 14.14 CdTe–CdS pseudobinary phase diagram. (Data listed in order from References [72, 139, 144, 147])

Figure 14.6 Schematic representations of eight CdTe thin-film deposition techniques. The substrate in each view is the cross-lined rectangle. Film thickness, $d$, and growth rate are shown at the bottom of each panel.
Calculated impurity levels in CdTe

<table>
<thead>
<tr>
<th>Primary complex</th>
<th>Native</th>
<th>Impurity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBM</td>
<td>Cd$_{Te}$ 0.1 (+2)</td>
<td>Cu$_i^a$ -0.01 (+1)</td>
</tr>
<tr>
<td></td>
<td>Cl$_{Te}$ 0.35 (+1)</td>
<td>Na$_i$ 0.01 (+1)</td>
</tr>
<tr>
<td></td>
<td>Cd$_i^a$ 0.33 (+2)</td>
<td>Cu$_i^c$ 0.01 (+1)</td>
</tr>
<tr>
<td></td>
<td>Cd$_i^c$ 0.56 (+2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>V$_{Te}$ 0.71 (+2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te$_i$ 0.74 (-2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.67 (-1)</td>
<td></td>
</tr>
<tr>
<td>VBM</td>
<td>V$_{Cd}$ 0.21 (-2)</td>
<td>Sb$_{Te}$ 0.23 (-1)</td>
</tr>
<tr>
<td></td>
<td>0.13 (-1)</td>
<td>Cu$_{Cd}$ 0.22 (-1)</td>
</tr>
<tr>
<td></td>
<td>0.10 (-2) complex</td>
<td>As$_{Te}$ 0.1 (-1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na$_{Cd}$ 0.02 (-2)</td>
</tr>
</tbody>
</table>

Figure 14.5  CdTe band structure with doping and defect levels. Charge states are in parentheses; energy is in electron volts measured from the conduction band for donor (positive) states and valence band for acceptor (negative) states. The superscripts a and c represent alternative interstitial sites. (Adapted from Wei S, Mtg. Record, National CdTe R&D Team Meeting (2001) Appendix 9 [59])
Discuss Cu distributions

- Secondary Ion Mass Spectroscopy (usually done in conjunction with ion beam etching for depth profiling)
- Cu is used in the back contact
- CdCl$_2$ “activation” anneal is used just prior to the back contact deposition
- CdCl$_2$ activation is done in the presence of O$_2$ at 387 C
• small spot XRF data from Umich’s EMAL

EDS mapping and High Angle Annular Dark Field (HAADF)

1. A high concentration of Cu at back contact
2. Au layer has high Cu content, Cu-Au alloy phases
3. Relatively high concentration in the CdS layer and some in SnO$_2$:F accounts for most of the ~10% Cu diffused from the back contact.
Little evidence for Cu concentrated at grain boundaries:
XTEM with small spot EDS

- evidence of some voids near the CdS/CdTe interface
- high Cu concentration at interface and in the Au layer
- little evidence of Cu along grain boundaries

Data obtained in collaboration with Kai Sun UMich EMAL.
SIMS profiles of Cu and S in CdTe/CdS
(data from Matt Young and Sally Asher (NREL)

- S not present in CdTe before CdCl$_2$ activation
- Activation produces S-gradient decreasing from ~1% at the junction
- Because of band bowing in the CdSTe system, S gradient will yield band bending that should aid electron collection
Plasma dependence on magnetic field

Unbalanced field magnetron

Balanced field magnetron
Grain morphology vs magnetron B-field

Strongly **unbalanced** gun (39,1), CdTe: 25 W RF, 300 C, 18 mT

Nearly **balanced** gun (13,12), CdTe: 25 W RF, 300 C, 18 mT

UT SEM data from magnetron-sputtered samples grown at UT
Grain boundaries: the challenge of polycrystalline thin-film cells

Fig. 4.2  Structure of the polycrystalline CIGS and CdTe cells. From Noufi 2006.
EBSD data of grain size and low-angle grain boundaries
(Data taken on UT cell SSC548 by Matt Nowell of EDAX-TSL / U. Utah)
(sputtered CdTe-center region CdCl₂ treated)

secondary electron Image  
EBSD orientation map
Grain size increases with CdCl$_2$ activation: EBSD

Data from Matt Nowell of EDAX-TSL / U. Utah obtained on UT films

**SSC548 Center As-Grown**

- Grain map and size distribution **including** twins (ave. grain size = 115 nm)
- Grain map and size distribution **excluding** twins ($\Delta \theta < 5^\circ$) (ave. grain size = 176nm)

**SSC548 Center CdCl$_2$ treated**

- Grain map and size distribution **including** twins (ave. grain size = 400 nm)
- Grain map and size distribution **excluding** twins (ave. grain size = 710 nm)
from cell to module--
series integration

assembly from smaller cells

monolithic integration

nonconducting substrate
Diodes in parallel with variable performance
(model and analysis by Victor Karpov, Diana Shvydka of U. Toledo)

Schematic band diagram of the CdS/CdTe cell emphasizing the presence of a hole barrier, \( V_2 \), at the back contact typically \( \sim 300 \) meV.

Elements of a random diode model which can result from variations in the back barrier leading to weak diodes which can shunt large amounts of current if the diodes are strongly linked with low resistance paths.