ME 432 Fundamentals of Modern Photovoltaics

Class 34:
Thin Film Photovoltaics
11 November 2020
Summary of the Most Common Commercial (or close) PV Technologies Today

PV Market

Wafer-Based

Monocrystalline Silicon
- 35% of market
- Typically use CZ grown wafers
- Key players: SunPower, REC, Sanyo
- Commercial Cell Efficiencies: 18-22%

Polycrystalline Silicon
- 50% of market
- Typically use Bridgman wafers
- Key players: Q-Cells, Suntech, REC
- Commercial Cell Efficiencies: 16-18%

Thin Film

- 15% of market
- Key players: First Solar (CdTe)
- CdTe now “established”
- a-Si ... what happened?
- CIGS: “emerging” (start-ups: Nanosolar, Heliovolt)
- Commercial Cell Efficiencies: 10-15%

Readings on Thin Film Solar

• Luque and Hegedus, *Handbook of Photovoltaic Science & Engineering*:
  – Chapter 11: Crystalline Silicon Thin Films
  – Chapter 12: Amorphous Silicon Thin Films
  – Chapter 13: Cu(InGa)Se₂ Thin Films
  – Chapter 14: CdTe Thin Films

• Poortmans and Arkhipov, *Thin Film Solar Cells: Fabrication, Characterization, and Applications*. 
Lots of Options for Thin Film PV

- Multijunction System, Spectrolab
- Amorphous Silicon, Inverter-China
- Poly-Crystalline Silicon Helmholtz Institute, Germany
- CIGS, Greentech Media
- Dye-Sensitized Solar Cells, Src: celcias.com
- Organic, Src: ScienceDaily.com
- CdTe, UTEP
Materials properties to make thin films

Absorption: High
Charge separation: Efficient
Charge transport: Can be slow(er)

Direct band gap, or use light-trapping
Thin-Film Photovoltaics

- Use less material
- Lighter
- Flexible

Traditional

- Can use more expensive materials!
- Can put places we wouldn’t otherwise
- Easier to install
General Considerations

**Advantages**

- Thin layers (few µm) ... less material used ... potential for cost savings
- Potential for low-temperature processing ... potential cost savings
- Potential for roll-to-roll deposition ... good for BIPV, ease of installation

**Disadvantages**

- Lower cell and module efficiencies ... potentially larger costs
- Elements used: some are scarce
- Low temperature processing ... film stoichiometry, uniformity issues
Market Share in 2016

*Source: Fraunhofer ISE*
CIGS : Cu(In$_{1-x}$Ga$_x$)Se$_2$

Nanosolar CIGS module, printed on metal foil substrate
Heterojunction Solar Cells

• CIGS (and many thin film technologies) are examples of heterojunction solar cells
• This means that the p-type side and the n-type side of the cell are made from different materials
• We’re lucky that it is possible to dope silicon both p-type and n-type; most materials seem to be dopable only in one way
• e.g. CIGS solar cells are actually composed of CdS/CIGS where CdS is n-type and CIGS is p-type
• Note that CdS is often called the “window layer” – it has too large a band gap (2.2 eV) to contribute to substantial light absorption – but is included to obtain the desired band alignment for charge separation
• The CIGS layer is often called the “absorber layer” since it is where most of the light absorption takes place.
Heterojunction Solar Cells

Very generally, if we integrate two different semiconductors together by joining them at an interface, there are three possible band alignments that can occur:

- **Type I: Offset**
- **Type II: Staggered**
- **Type III: Broken**

**Question:** Which band offset is most desirable for a photovoltaic heterojunction??
CIGS – Chalcopyrite Crystal Structure

CuInSe$_2$  
**direct gap**: 1.04 eV

CuGaSe$_2$  
**direct gap**: 1.68 eV

Alloy Cu(InGa)Se$_2$  
**tunable direct gap!**
Why CIGS?

• Direct gap, can be tuned to near-optimal value, high absorption coefficient
• Intrinsically a good p-type conductor
  – Likely due to copper deficiency (vacancies)
• Highest demonstrated thin-film efficiency of any material (19.5%, NREL)
CIGS - Typical Device Structure example

Al:ZnO as transparent conducting oxide

ZnO as highly resistive oxide

CdS window layer (chemical bath decomposition)

CIGS absorber layer, p-type (evaporated)

Molybdenum for back contact, also used for reflection (sputtered)

Soda-lime glass substrate
Why CIGS cells can be efficient

Short answer: we don’t really know all the details, but we have some ideas ...

- Demonstrate a remarkable insensitivity to the quality of the interface between CIGS/CdS
  - possibly due to the formation of an ordered defect compound (ODC) at the interface \((\text{Cu(InGa)}_3\text{Se}_5)\), which can be promoted by growing Cu-deficient films
  - ODC suspected to reduce interface recombination
- Also, CIGS cells are quite forgiving of defects, off-stoichiometry
  - Cu-deficient growth: Energetically favorable defect complexes \((2\text{V}_{\text{Cu}}+\text{In}_{\text{Cu}})\) are electrically inactive
- Sodium (Na) deliberately incorporated into CIGS increases p-type conductivity and may passivate grain boundaries
  - Fortuitously discovered via use of soda-lime glass substrates, which introduces Na into CIGS films
- Other reasons too ... we will talk about these later.
Commercialization


Early stages, but a number of new efforts underway: Nanosolar, Heliovolt, Miasole

Nanosolar

- 640 MW per year fully-automated manufacturing facility for CIGS
- Now fully operational in Germany
- And producing about 10 MW per year
- Cell efficiencies around 16.4%, module efficiencies 11%
Summary - CIGS

• Advantages
  – High efficiencies (~20% in laboratory)
  – Inexpensive manufacturing

• Challenges
  – Uniform deposition (stoichiometry & thickness) over large areas
  – Defects, interface structure are complex
  – Some analyses suggest that there may not be enough Indium in the world for widescale deployment
  – Replacing the n-type window layer with Cd-free material (e.g. doped ZnO)
Cadmium Telluride

GE Solar, CdTe Modules
Cadmium Telluride

- Back Contact: Metal, Buffer Layer, p⁺-Te-rich Layer
- Front Contact: Glass, substrate
- Irradiation: TCO (FTO), 0.3 μm, 0.5-1 μm, 3-5 μm, ~50 nm, ~10 nm

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Cadmium Telluride

ADVANTAGES:
• Optimal band gap for our sun
• Technology developed for application on glass (BIPV), deposition seems cheap and simple
• Radiation hard

CHALLENGES:
• Tellurium: not much of it
• Cadmium:
  • Suspected carcinogen
  • Marketability
  • e.g., banned in Japan, Greenpeace opposed
• Improving $V_{OC}$
  • Higher crystallinity films?
  • Better interface quality?
  • Better doping of CdTe?
Cadmium: Environmental Concerns

• Arguments in Against:
  – Known toxin, suspected carcinogen
  – Industrial emissions tightly regulated, especially in the E.U. (Cradle-to-Grave requirements)

• Arguments in Favor:
  – By-product of Zn, Cu mining [1]
    • “Better to tie it up in CdTe than dump it in the ground.”
  – “Negligible” Cd released during processing [2]
  – Public fear is a “perception issue” [3]
  – CdTe is a stable compound. Much less Cd released per kWh than a battery [4]
  – Full recycling guaranteed by law in Europe.

Cadmium Telluride Commercialization

First Solar ... a proven technology!

- First Solar module uses vapor deposition of CdTe on moving substrates (goal: high throughput, reported at 2.9m² per minute)
- Modules grown on soda-lime glass coated with tin oxide TCO
- Offer the lowest cost modules presently on the market
- Manufacturing costs have dropped from $1.47 per watt in 2005 to $0.75 per watt in 2010 to $0.55 per watt in 2015 (primarily due to economies of scale)
- Production capacity: 46 production lines, 2.7 GW capacity, fully operating in 2016
- Average module efficiencies: 14.7% in Jan 2015, 15.8% in Jan 2016
Grain Boundary Magic in CdTe

• A puzzle: Single crystal silicon solar cells outperform their multi-crystalline counterparts, whose grain boundaries trap carriers, promoting recombination. In contrast, record efficiencies are:
  – 15.2% in single crystal CdTe, 21.5% in polycrystalline CdTe
• Several investigations have attempted to answer the puzzling question. Some of these conclude that the electronic structure of the grain boundaries is the key to understanding the superior performance.
• CdCl$_2$ annealing: most important post-deposition processing step, exposing the CdS/CdTe structure to CdCl$_2$ at elevated temperature.
  – Improves $V_{OC}$, $J_{sc}$, FF
  – Time-resolved photoluminescence measurements: CdCl$_2$ annealing induces recrystallization of the CdTe films and promotes grain growth, which lead to enhanced minority carrier lifetimes.
  – CdCl$_2$ annealing introduces Cl into the CdTe film
Grain Boundary Magic in CdTe

One proposed mechanism.
Approach

• Scanning Microwave Impedance Spectroscopy (SMIM)

• Scan tip over sample, including over exposed grain boundaries and bulk regions
• Map the conductivity and carrier concentrations locally

Courtesy: Mohit Toteja, Angus Rockett
Measured Results

Courtesy: Mohit Toteja, Angus Rockett

Higher hole concentration

Higher electron concentration

as-deposited

CdCl₂ annealed
Which microstructure is better?

Courtesy: Mohit Toteja, Angus Rockett
Searching for Earth-Abundant Thin Films

Searching for Earth-Abundant Thin Films

Materials Genome Initiative (MGI)

“...To help businesses discover, develop, and deploy new materials twice as fast, we’re launching what we call the Materials Genome Initiative. The invention of silicon circuits and lithium ion batteries made computers and iPods and iPads possible, but it took years to get those technologies from the drawing board to the market place. We can do it faster.” — Barack Obama (6/11)

Goal:
- Double the pace of advanced materials discovery, innovation, manufacture, and commercialization
- Improve global competitiveness
- Revitalize US manufacturing

To date: NSF, DOE, NIST, DOD

Courtesy: Cyrus Wadia, White House OSTP — adapted from Gerd Ceder (UC Berkeley)

Discovery to Application in the 20th Century


- Teflon
- Velcro
- Titanium production
- Polycarbonate
- Diamond-like thin films
- GaAs
- Amorphous soft magnets
- Lithium-ion batteries
- Core-shell electro-catalysts for fuel cells
- Catalysts for olefin metathesis

We need to do better!

**Cu$_2$ZnSnS$_4$ (CZTS): CIGS w/o the Indium**

- Kesterite structure (like chalcopyrite)
- $E_G = 1.5$ eV, direct
- First PV investigations in late 1990’s (Katagiri, Friedlmeier)

$\eta = 11\%$ for evaporated cells*

*(IBM)*

*Wang APL 97 143508 (2010)
Searching for Earth-Abundant Thin Films

Example: CuInGaSe$_2$
Which components are rare?

Try instead: Cu$_2$ZnSnSe$_4$


*Figure 4.* $J$−$V$ characteristics under standard ASTM G173 global spectrum (certified by NREL PV Cell Performance Laboratory) of devices with low (A) and intermediate (B) sulfur content, showing higher $V_{oc}$ and efficiency in the second case. The efficiencies are calculated using total area of the device (including Ni/Al grid-covered area).
Observations: Earth-Abundant PV Materials

What about some other candidate earth-abundant materials?

**Cu₂(ZnSn)S₄ (kesterite)**
- Conversion efficiency: ~11%

**FeS₂ (iron pyrite)**
- Conversion efficiency: 1.1%

Fundamentally, why the difference in performance?