Thin Films: Materials Choices & Manufacturing

Lectures 12 & 13

MIT Fundamentals of Photovoltaics
2.626/2.627 – Fall 2011

Prof. Tonio Buonassisi

Further Reading

- Suggested chapters in the "Handbook of Photovoltaic Science and Engineering."
    - 12: Amorphous Silicon Thin Films
    - 13: CIGS Thin Films
    - 14: CdTe Thin Films
    - 15: Dye-Sensitized Solar Cells
- Additional resource:
    – J. Poortmans and V. Arkhipov, *Thin Film Solar Cells: Fabrication, Characterization and Applications*. Wiley: West Sussex, 2006. ISBN 0470091266

Diversity in the PV Market

Multijunction Cells

Copper Indium Gallium Diselenide (CIGS)

Amorphous Silicon

High-Efficiency Silicon

Please see lecture video for visuals of each technology.

Dye-sensitized Cells

Thin Silicon

Cadmium Telluride

Hybrid O/I

Organics

Future technologies must consider:

- **Cost ($/kWh)**
- **Resource availability**
- **Environmental impact**

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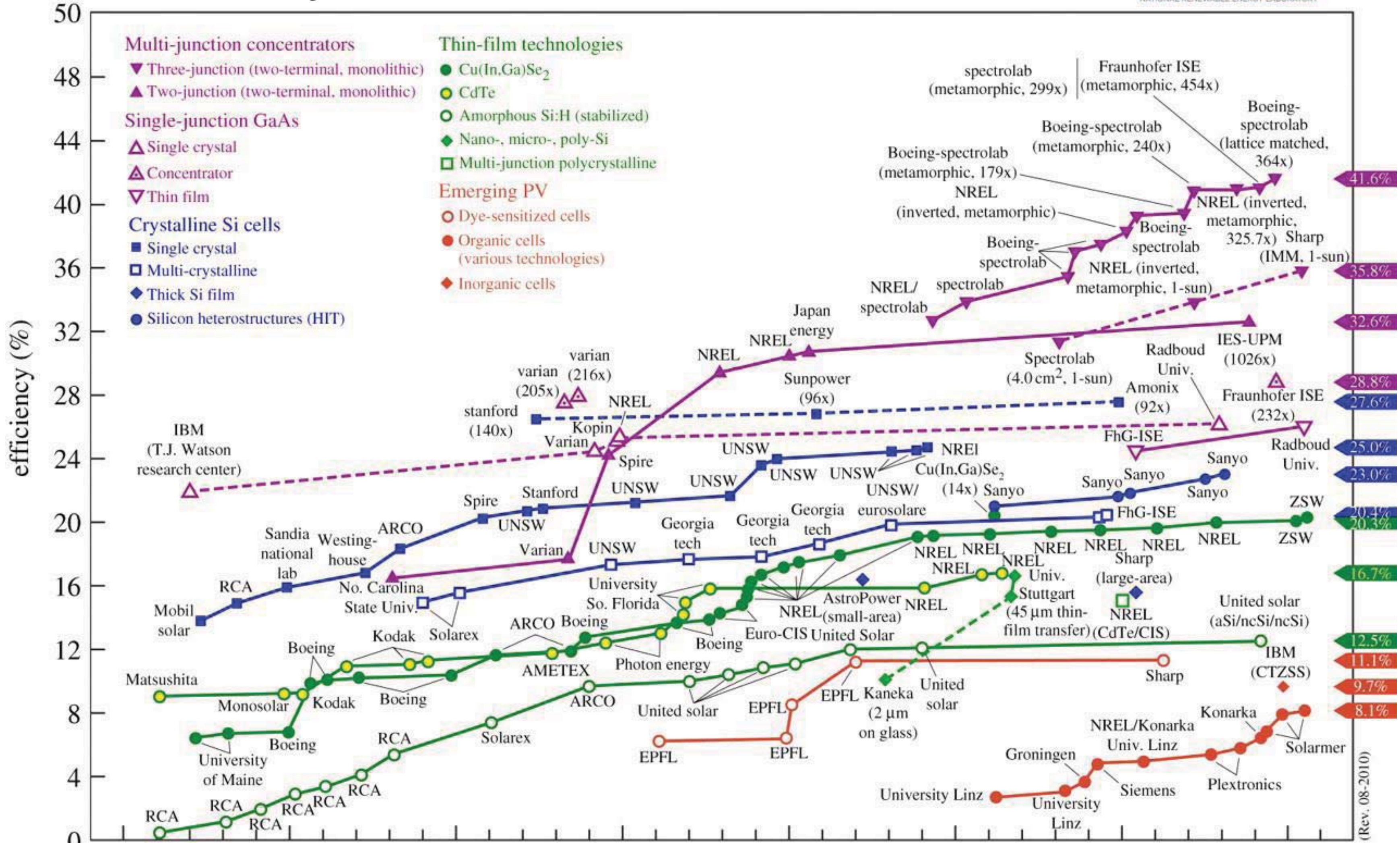
Record laboratory efficiencies of various materials



Latest version online: http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

Old version referenced at: L.L. Kazmerski, Journal of Electron Spectroscopy and Related Phenomena 150 (2006) 105–135

NOTE: These are record cell efficiencies under ideal conditions (25°C, ~1000 W/m^2)! Actual commercially-available silicon solar cells are typically 14-17% efficient. Modules are typically around 11-13%.

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Thin Films: General Issues

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Thin Films

Advantages

- 1 μm layers ➔ less material used ➔ potential cost decrease
- Potential for lower thermal budget ➔ potential cost decrease
- Potential for roll-to-roll deposition on flexible substrate
    - Technology transfer with TFT, flat panel display industry
    - Good for BIPV applications
- Radiation hardness
    - Good for space applications

Disadvantages

- Lower efficiencies than c-Si ➔ potentially larger module costs
- Potential for capital-intensive production equipment
- Potentially scarce elements sometimes used
- Spatial uniformity a challenge during deposition

Thin Films

<u>Advantages:</u>

Roll-to-roll deposition of µm-sized layers ➔ potentially high throughput, large-area deposition, and <u>cheap</u>.

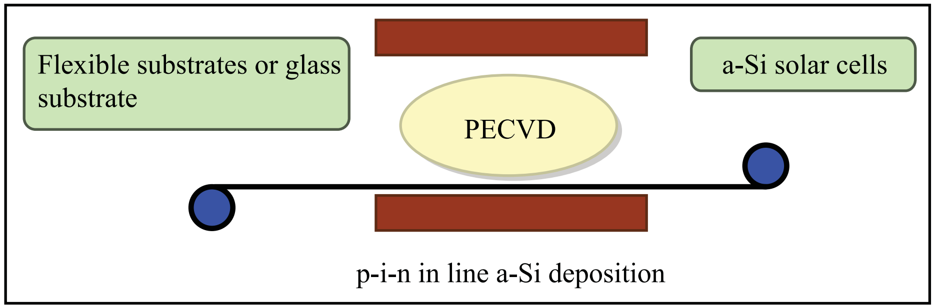

Image by MIT OpenCourseWare.

Building-integrated solutions

Please see lecture video for visuals of each technology.

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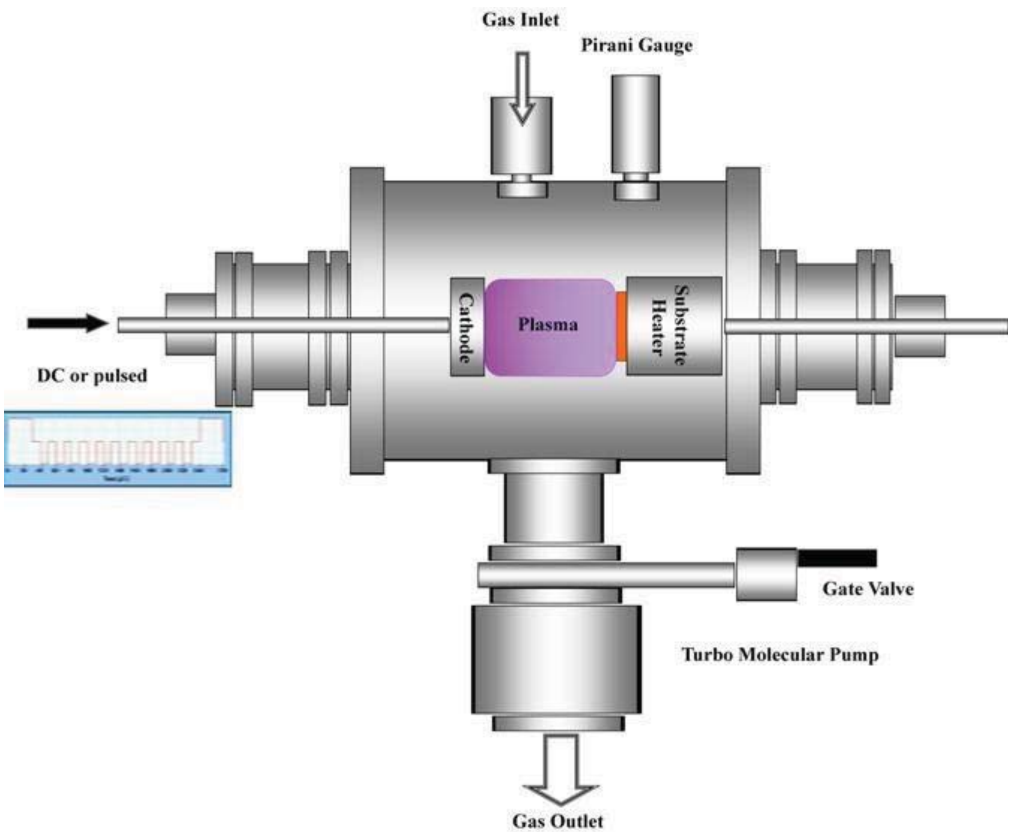
Common Growth Methods

1. Vacuum-Based Thin-Film Deposition Technologies

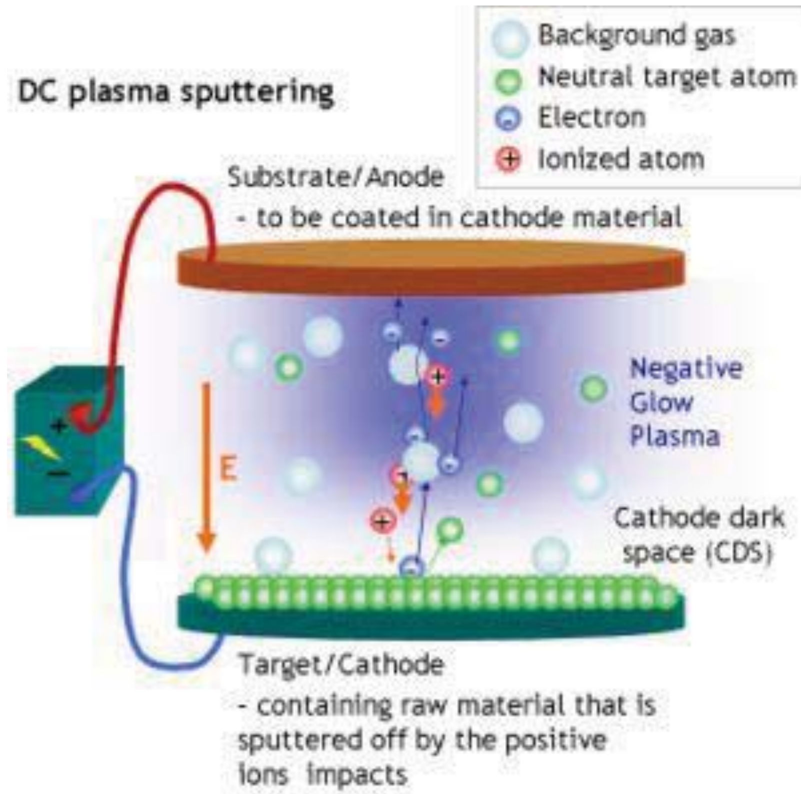


Courtesy of Prof. Satyendra Kumar, Dr. Sanjay K. Ram, et al. Used with permission.

Characteristics: Large capex, high performance

- Chemical Vapor Deposition (CVD)
  - Plasma-enhanced CVD (PECVD)
  - Low-pressure CVD (LPCVD)
  - Metalorganic CVD (MOCVD)
- Physical Vapor Deposition (PVD)
  - Sputtering
  - Thermal evaporation
  - Electron-beam evaporation
  - Vapor transfer deposition (VTD)
  - Closed-space sublimation (CSS)
  - Pulsed-laser deposition (PLD)
  - Atomic layer deposition (ALD)
  - Molecular-beam epitaxy (MBE)

Sputtering



http://www.etafilm.com.tw/PVD_Sputtering_Deposition.html

Radio-frequency modulation of bias voltage (RF sputtering) also employed

Industrial application usually involves large, rotating targets (to increase homogeneity)

Films generally less homogeneous, less conformal surface coverage

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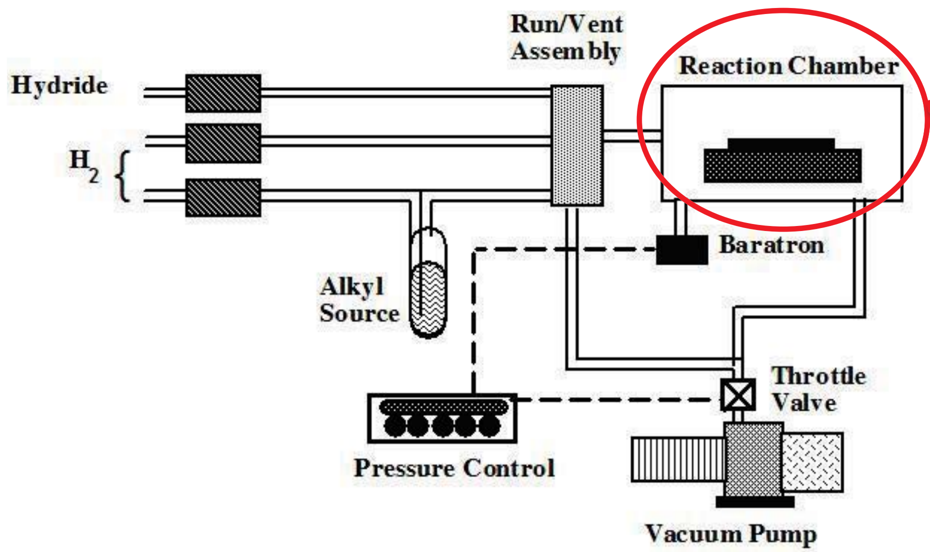
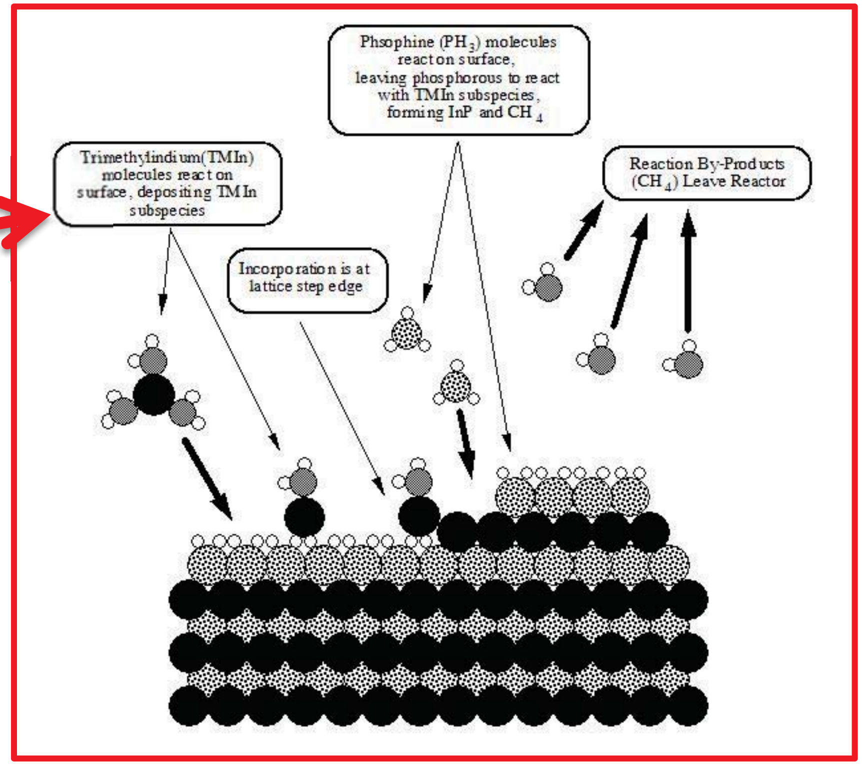
Metalorganic Chemical Vapor Deposition (MOCVD)



Public domain image.



Figures: http://en.wikipedia.org/wiki/Metalorganic_vapour_phase_epitaxy

Generally good conformal surface coverage
Proper design of metalorganic precursors essential
Deposition sensitive to temperature, pressure, surfaces, carrier gasses (chemistry)
Byproducts need to be managed

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Plasma Enhnaced Chemical Vapor Deposition (PECVD)

Please see lecture video for related PECVD images.

Fig: http://www.plasmetrex.com/plasmaschool_pv.html,courses

Excellent conformal surface coverage
Deposition sensitive to temperature, pressure, power, carrier gasses (chemistry)
Byproducts need to be managed

2. Solution-Based Deposition Technologies

- Printing
- Electrodeposition
- Spin casting
- Colloidal synthesis
- Layer-by-layer deposition

Non-Vacuum Based: Small(?) capex, (traditionally) lower performance

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General Issues

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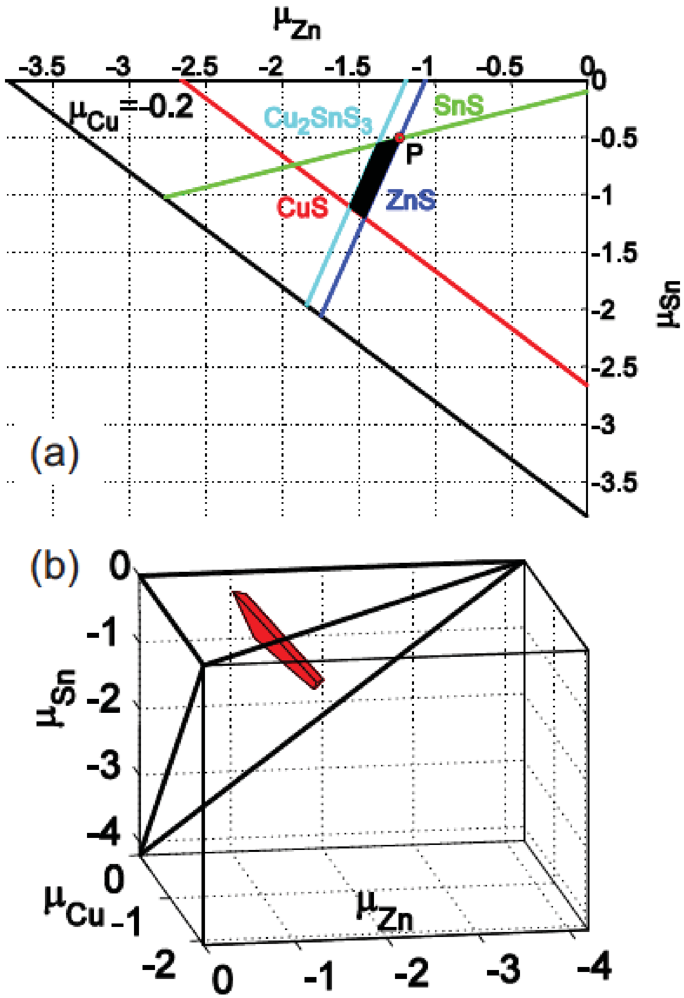
Stoichiometry and Self-Doping

Phase Stability



Chen *et al*., *Appl. Phys. Lett*. **96**, 021902 (2010)

- Stoichiometry refers to the ratio of different constituent atoms in a multinary (multi-element) compound.
- Small stoichiometric excursions can result in "self-doping." *I.e.*, small deviations from perfect stoichiometry result in increase of free hole or electron concentrations. Excess elements can also segregate to surfaces (incl. internal surfaces, *e.g.*, GBs).
- Large stoichiometric excursions can result in phase decomposition.

Grain Size and Efficiency

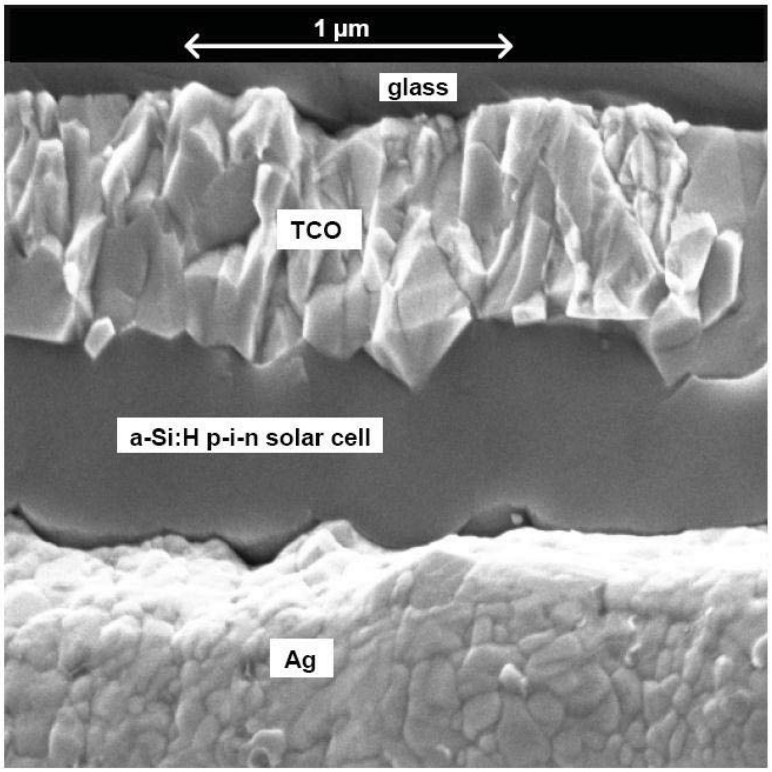
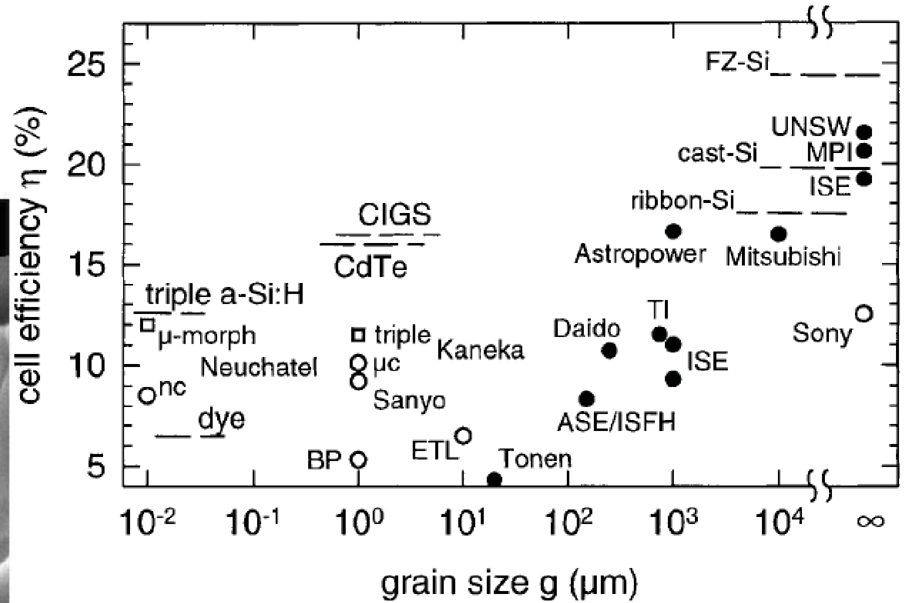
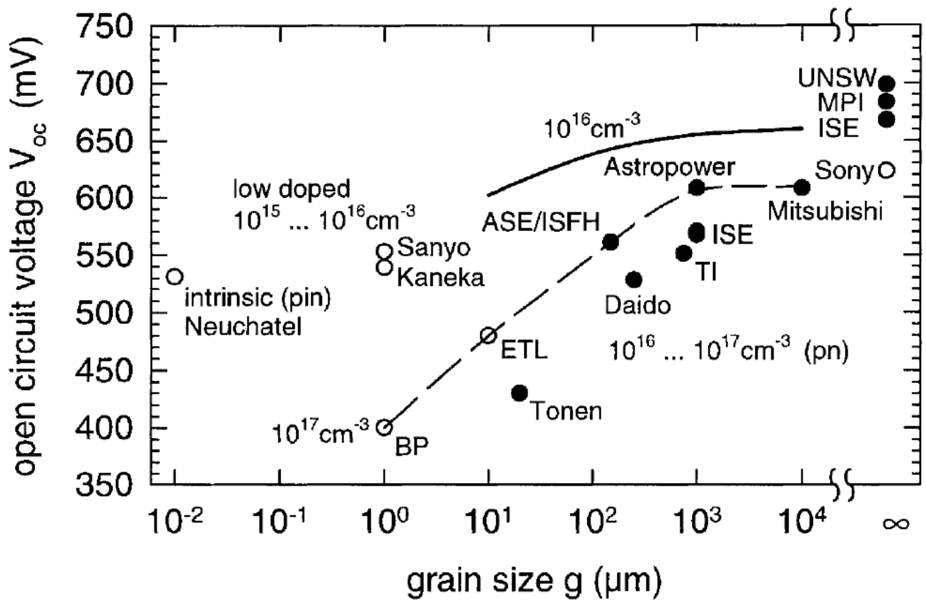


Fig. 1. High-resolution scanning electron (HRSEM) cross section of an a-Si:H p-i-n solar cell

Source: Fig. 1 in Rech, B., and H. Wagner. "Potential of amorphous silicon for solar cells."*Applied Physics A* 69 (1999): 155-67.



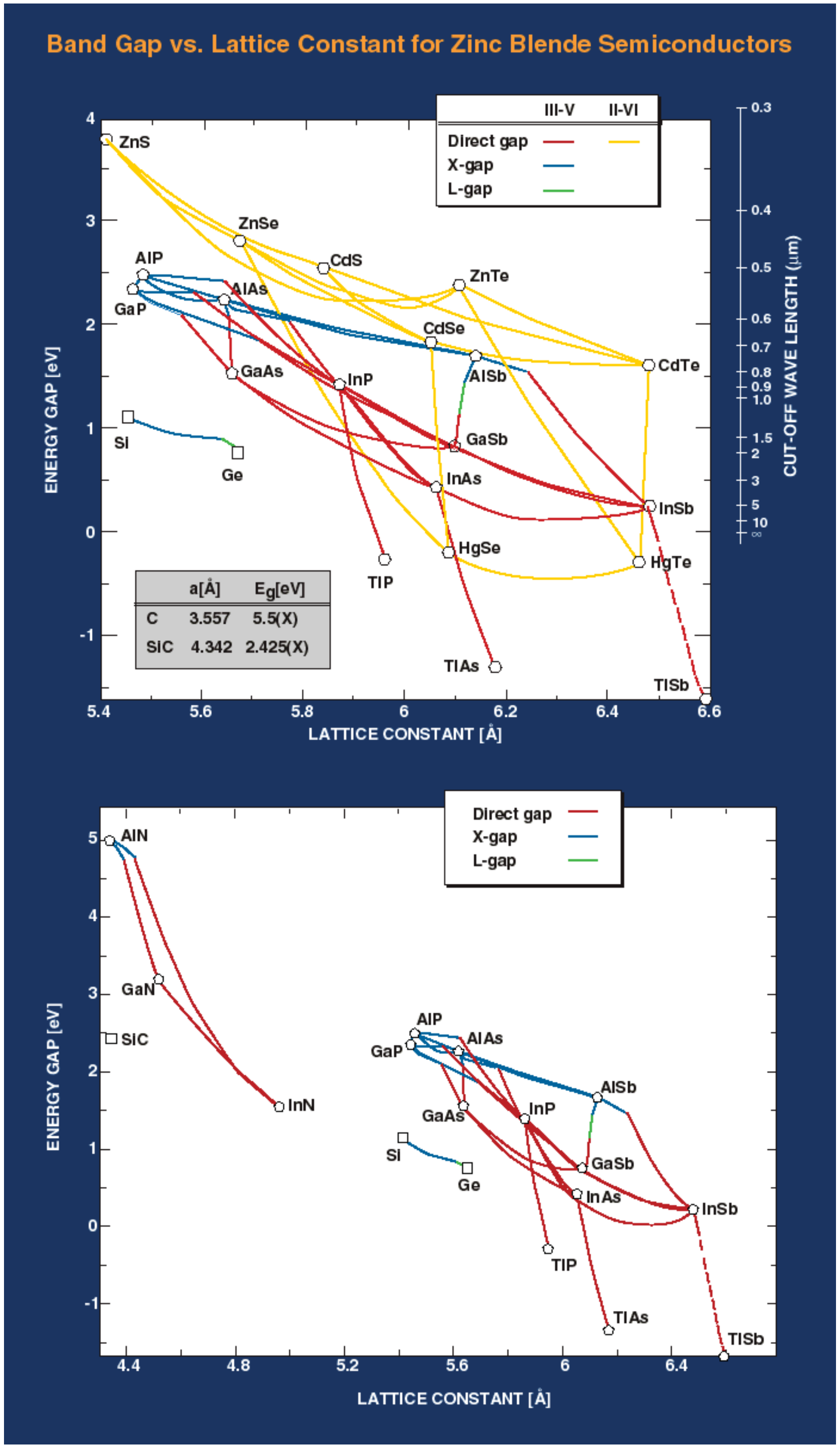


Source: Fig. 1 and 2 in Bergmann, R. B. "Crystalline Si thin-film solar cells: a review."*Applied Physics A 69 (1999): 187-194.*

Epitaxial Growth: Heterostructures and Lattice Matching

To prevent interface recombination and achieve high carrier mobilities, atoms in the different layers must line up (adjacent hetero-epitaxial layers must be lattice matched). Otherwise, defects form at these interfaces.

An good example of a heteroepitaxial system is Ge / GaAs / InGaP / AlAs, in order of increasing bandgap.



http://www.sri.com/psd/apsl/images/zincbg.gif

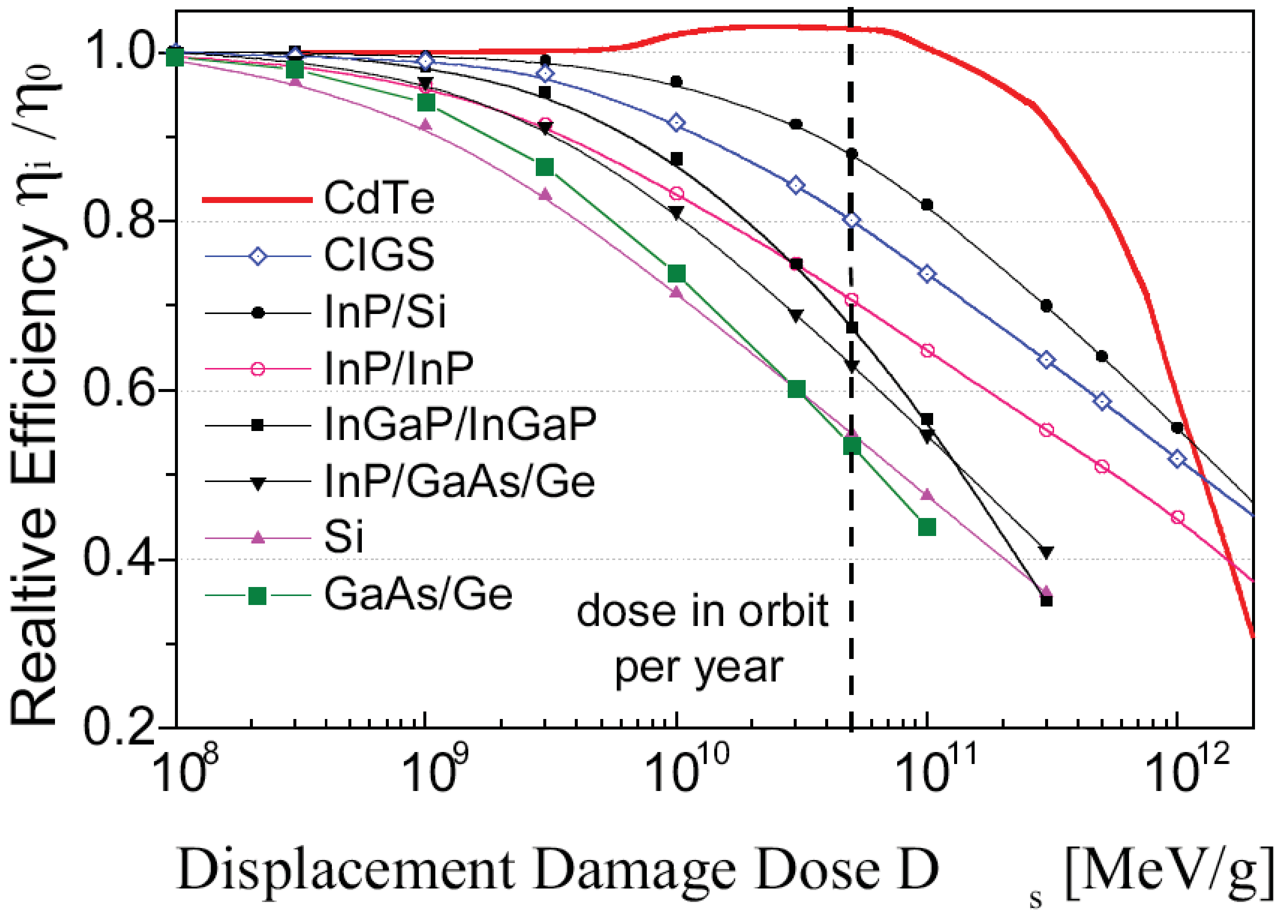
Material Abundances

Table 1. Materials requirements and indicators for the solar cells in four solar energy systems, each based on a specific thin-film technology supplying 100,000 TWh/yr.

	Materials requirements (g/m^2)	Total material requirements[b] (Gg)	Total material requirements /reserves[c]	Total material requirements /max. resources[d]	Annual material requirements[e] /refined materials[f]	Potential losses[g]/ weathered amounts[h]	Material cost share[i] (%)
a-SiGe[a]							
Sn	3.3	1700	0.20	0.004	0.079	2	0.04
Ge	0.22	110	51	0.0003	21	0.1	0.5
Si	0.54	270	Negligible	Negligible	0.0031	0.000002	0.002
Al	2.7	1400	0.00032	Negligible	0.00075	0.00005	0.008
CdTe							
Sn	0.66	330	0.056	0.0009	0.016	0.4	0.008
Cd	4.9	2400	4.6	0.03–0.1	1.2	10–50	0.02
Te	4.7	2400	110	1–20	120	500–10 000	0.5
Mo	10	5100	0.93	0.01	0.47	6	0.1
CIGS							
Zn	9.1	4600	0.030	0.0003	0.0062	0.1	0.02
Cu	1.8	880	0.0017	0.00009	0.00098	0.04	0.008
In	2.9	1400	650	0.03–0.4	110	10–200	0.8
Ga	0.53	270	25	0.00007	48	0.03	0.4
Se	4.8	2400	30	0.3	12	100	0.1
Cd	0.19	95	0.18	0.001–0.005	0.048	0.4–2	0.0008
Mo	10	5100	0.93	0.01	0.47	6	0.1
Grätzel							
Ru	0.1	50	7.5	0.3–3	88	100–1000	0.09
Pt	0.05	25	0.83	0.01–0.1	2.4	6–60	1
Ti	1.2	600	0.0021	Negligible	0.0024	0.0002	0.03
Sn	5.5	2800	0.47	0.007	0.13	3	0.07

B.A. Andersson et al., *Energy* **23** (1998) 407
C. Wadia et al., *Env. Sci. Tech.* **43** (2009) 2072
APS Energy Critical Elements: http://www.aps.org/about/pressreleases/elementsreport.cfm
DOE Critical Materials Strategy: http://energy.gov/epsa/initiatives/department-energy-s-critical-materials-strategy

Radiation hardness of different compounds



Courtesy Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

‚Master data' by courtesy of S.Messenger, G. Summers

Space payloads cost ~\$1400–\$6000/pound (~\$2866–\$13228/kg) ➔ Key parameter not \$/W. Instead, it's W/kg and reliability!

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Reliability and degradation

Crystalline silicon module being loaded into an environmental chamber for reliability testing. Courtesy Fraunhofer CSE.

- Thinner absorber layers + non-inert absorber compounds = module performance more sensitive to encapsulation quality.
- Some unique failure modes for thin-film modules (*e.g.*, electromigration)
- New protocol for thin-film reliability testing: IEC 61853.

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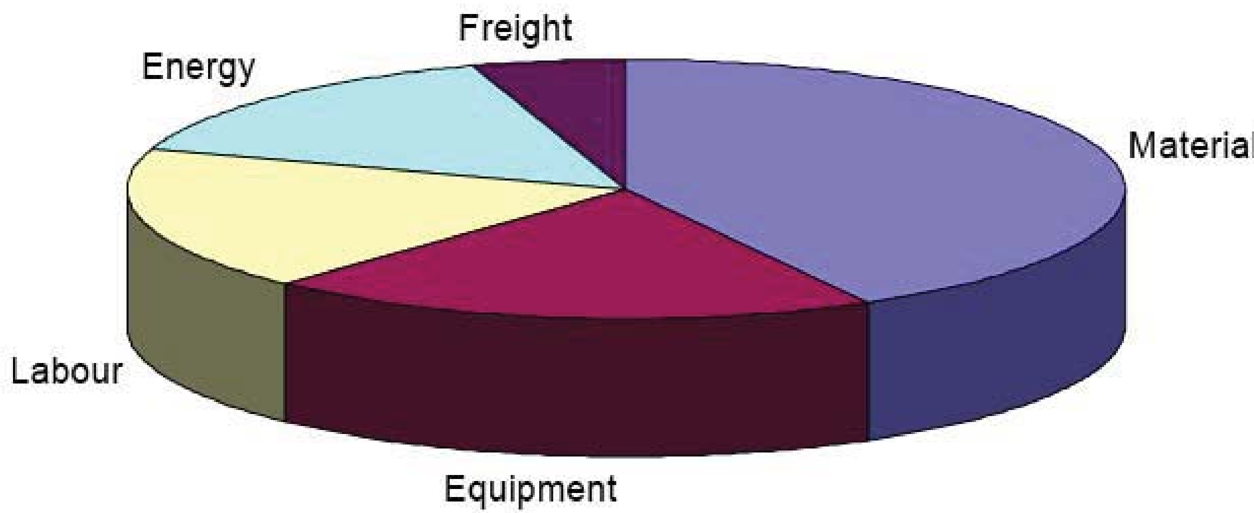
Average Thin Film Cost Structure



Technology dependent Drivers

Deposition Process: Dominates Energy
Deposition Materials: Dominates Depreciation
Package/Assembly: Dominates Materials

Common Drivers

Material Cost: Volume, Efficiency
Depreciation: Throughput, Efficiency
Labour: Throughput, Automation, Efficiency
Energy: Throughput, Efficiency

Renewable Energies

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22nd EU PVSEC 12

Courtesy of Arnulf Jäger-Waldau. Used with permission.

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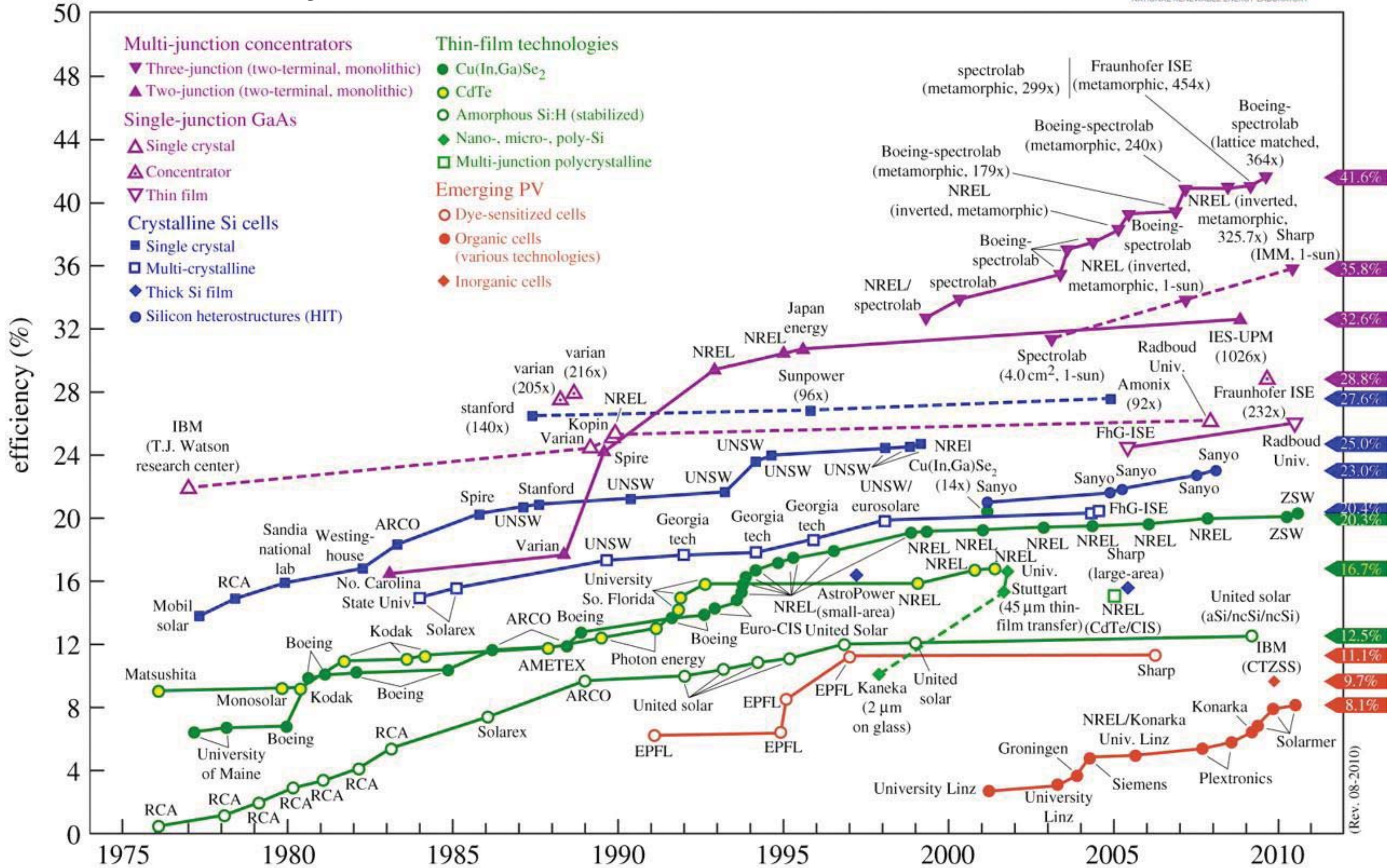
Record laboratory efficiencies of various materials



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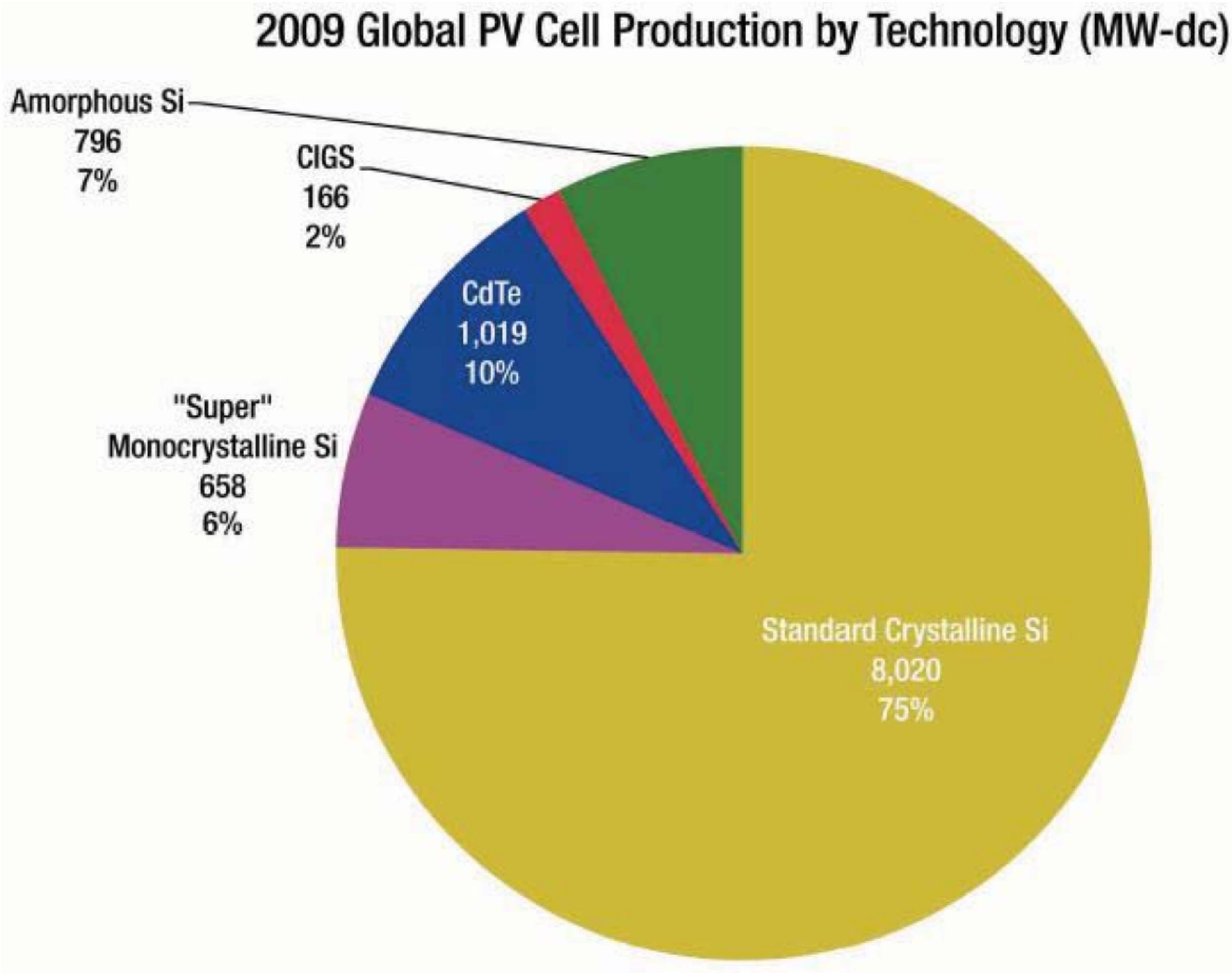
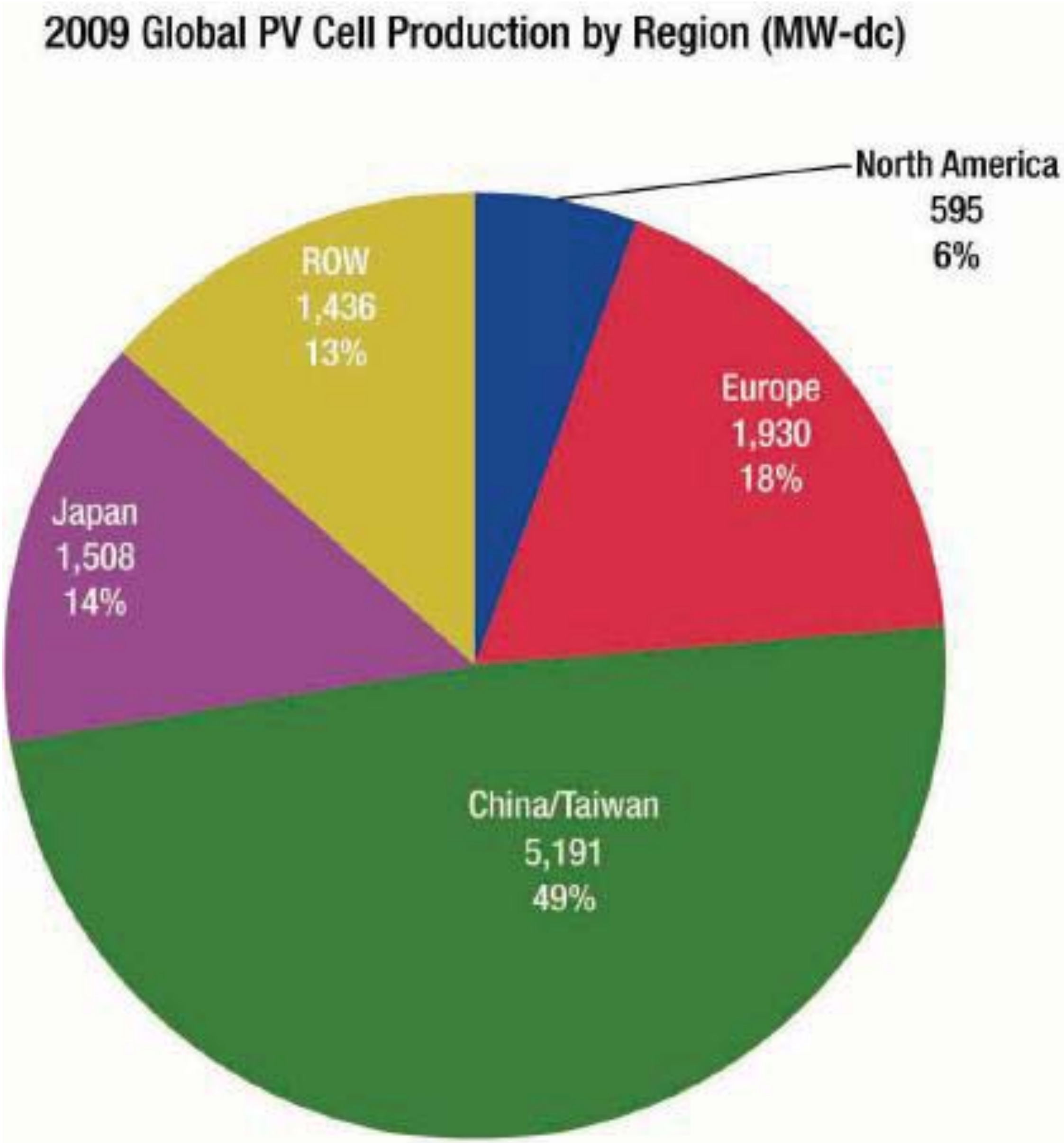
Production Volumes of Various PV Materials



Source: PVNews, v.**29**, No.5 (2010)

PV Cell Production by Region



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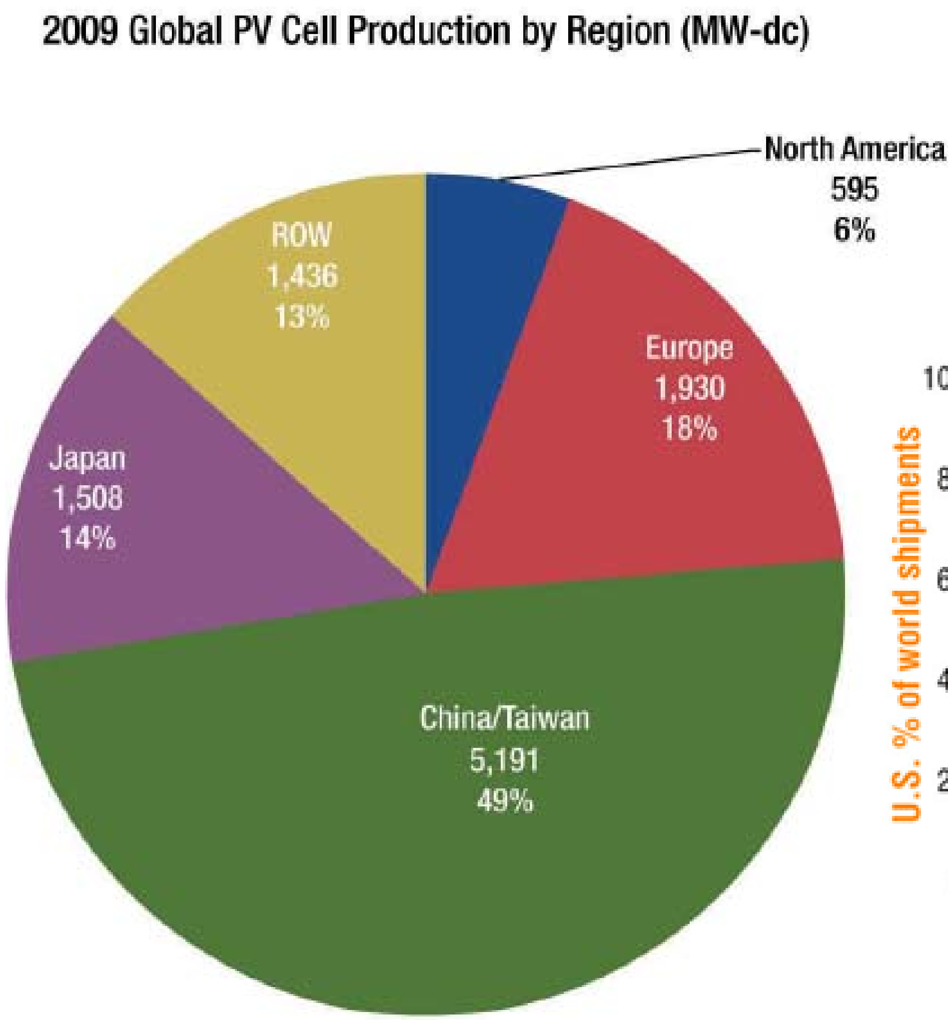

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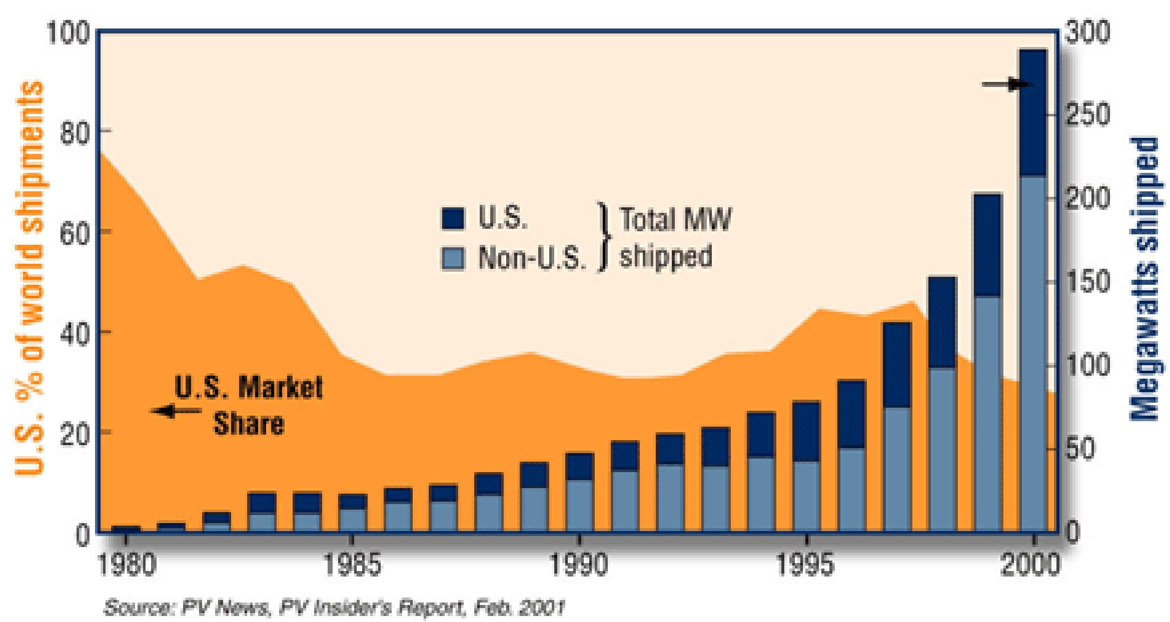

Cadmium Telluride (CdTe)

Cadmium Telluride (CdTe)

Please see the lecture video for the images or see Fig. 1 in Klein, A., et al. “Interfaces in Thin Film Solar Cells.”*Record of the 31st IEEE Photovoltaic Specialists Conference* (2005): 205-210*.*

Light

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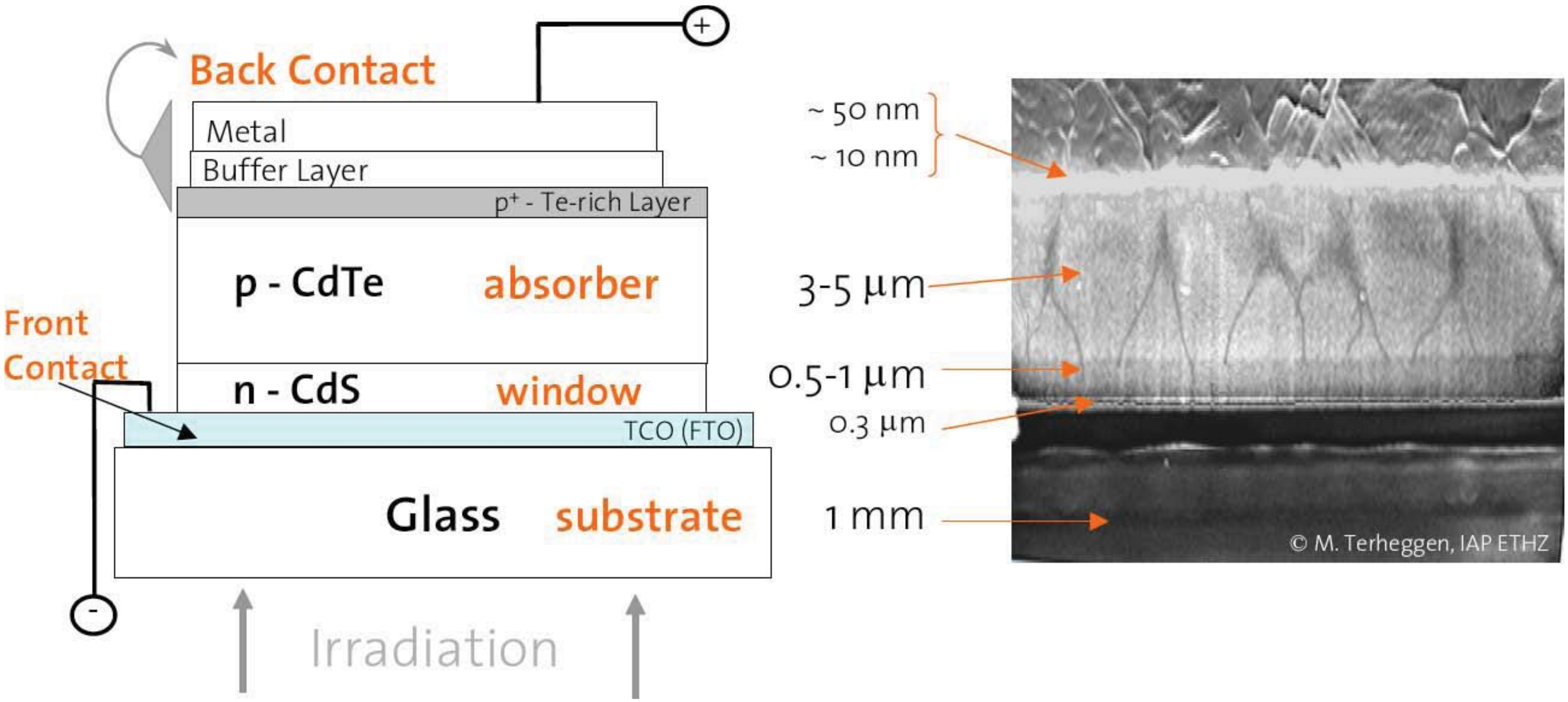
Cadmium Telluride (CdTe)



Courtesy of M. Terheggen. Used with permission.

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CdTe

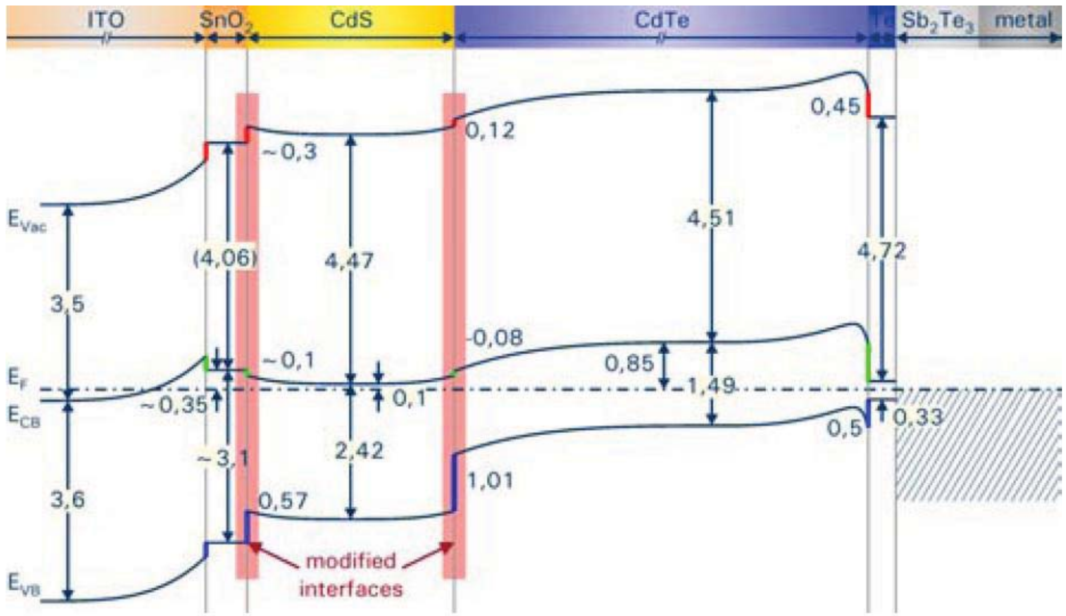

Fig. 6. Energy band diagram of a CdTe thin film solar cell as determined from photoemission experiments [12,43].

Source: Fig. 6 in Klein, A., et al. "Interfaces in Thin Film Solar Cells." *Record of the 31st IEEE Photovoltaic Specialists Conference* (2005): 205-210.

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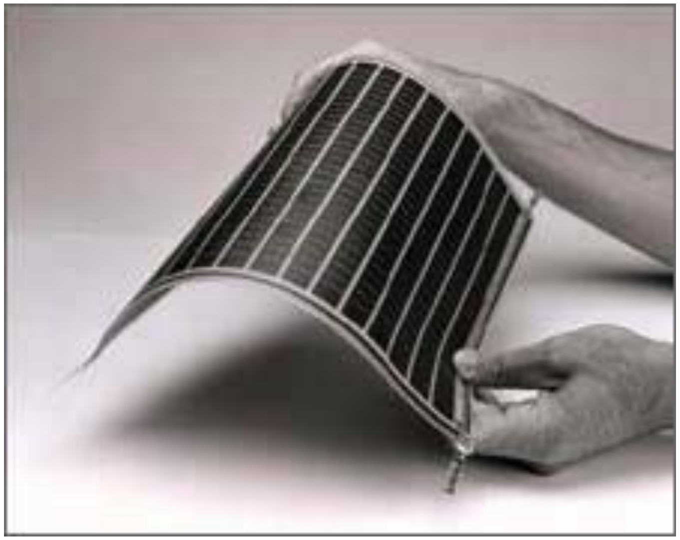
Amorphous Silicon (a-Si)



Courtesy of EERE.

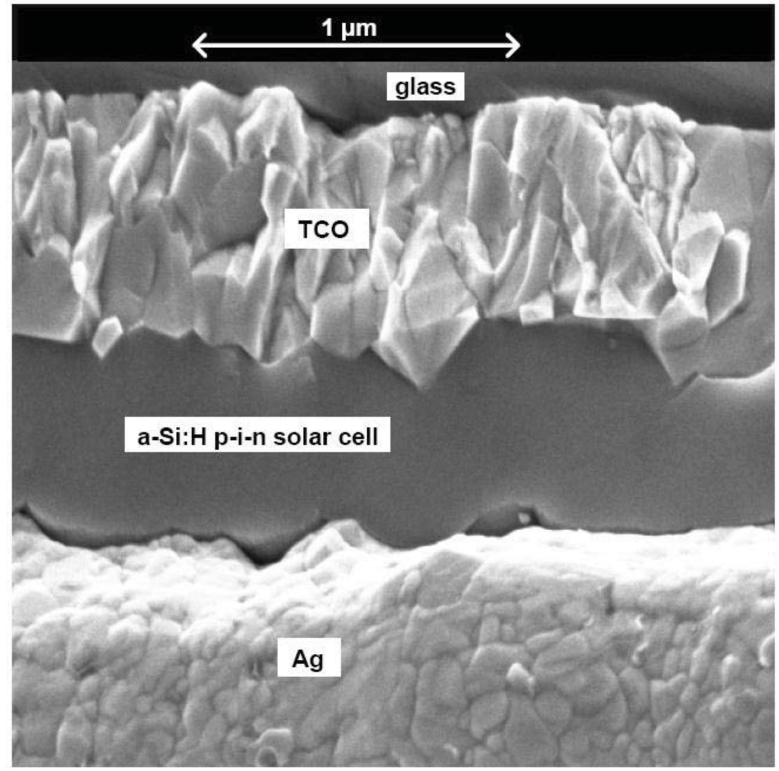


Fig. 1. High-resolution scanning electron (HRSEM) cross section of an a-Si:H p-i-n solar cell

Source: Fig. 1 in Rech, B., and H. Wagner. "Potential of amorphous silicon for solar cells." *Applied Physics A* 69 (1999): 155-67.

Advantages:

- Potentially very cheap, low-temperature.

Challenges:

- Overcoming the Staebler–Wronski effect (SWE)
- Low hole mobility
- Uniform (thickness, quality) film deposition.

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Environmental Concerns: Cadmium

<u>Arguments Against:</u>

- Suspected carcinogen.
- Industrial emissions tightly regulated, esp. in E.U.
    - Cradle-to-grave requirement.

<u>Arguments in Favor:</u>

- By-product of Zn, Cu mining [1].
    - "Better to tie it up in CdTe than dump it in the ground."
- "Negligible" Cd released during fires [2].
- "Public fear a perception issue" [3].
- CdTe is a stable compound.
    - Much less Cd released per kWh than a battery [4].
- Safe production.
- Full recycling guaranteed (by <u>law</u> in Europe).

[1] http://www.firstsolar.com
[2] V.M. Fthenakis et al., *Proc. 19th EU-PVSEC* (Paris, France, 2004); Paper 5BV.1.32
[3] NREL. "Cadminum Use in Photovoltaics." October 2008.
[4] V.M. Fthenakis, *Renewable and Sustainable Energy Reviews* **8** (2004) 303.

Amorphous Silicon

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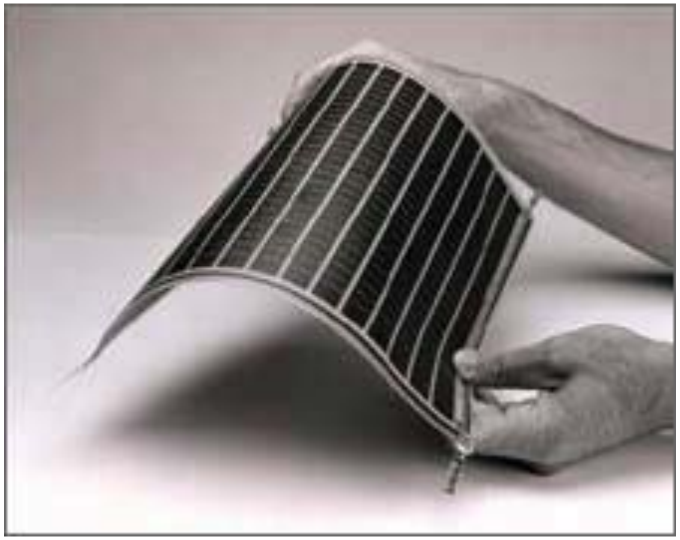
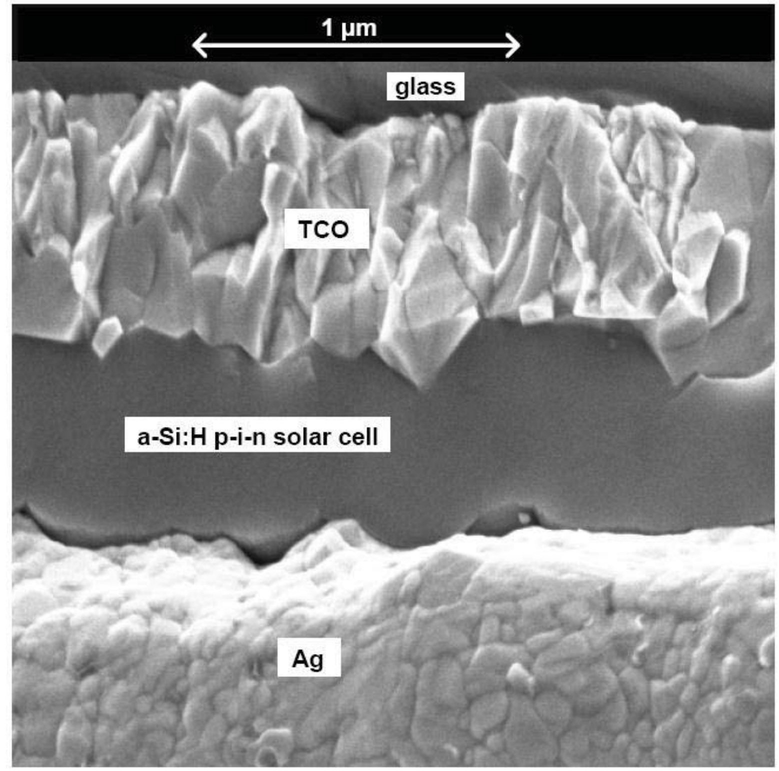
Amorphous Silicon (a-Si)



Courtesy of EERE.



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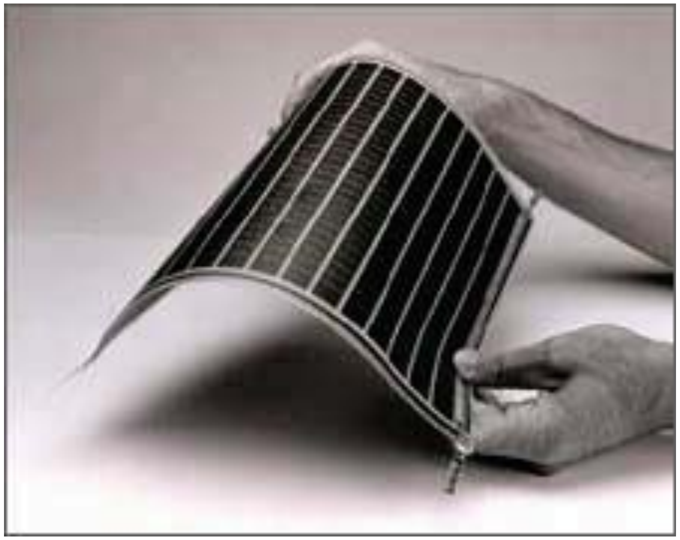
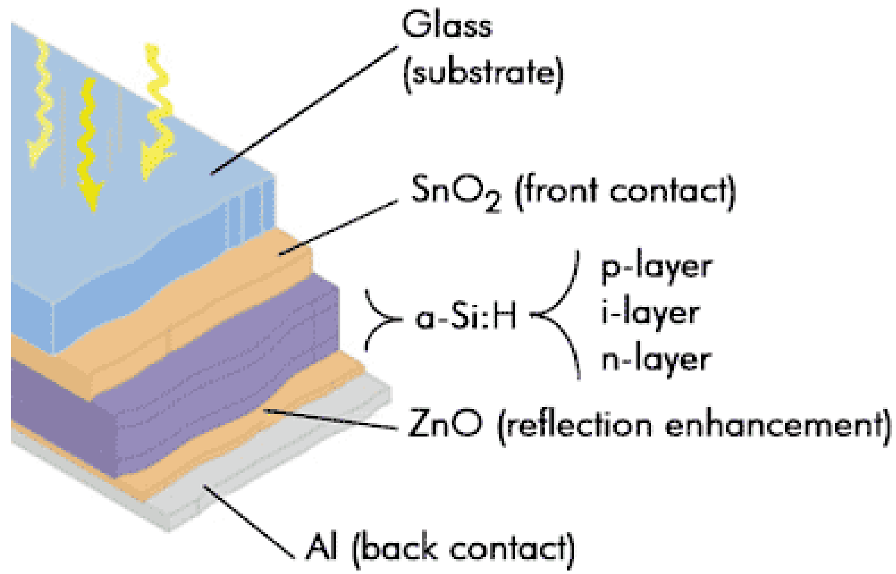


Courtesy of EERE.



Courtesy of Azonano.com. Used with permission.

http://www.azonano.com/details.asp?ArticleId=2164

Advantages:

- Potentially very cheap, low-temperature.

Challenges:

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- Uniform (thickness, quality) film deposition.

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Energy Band Diagram of a-Si

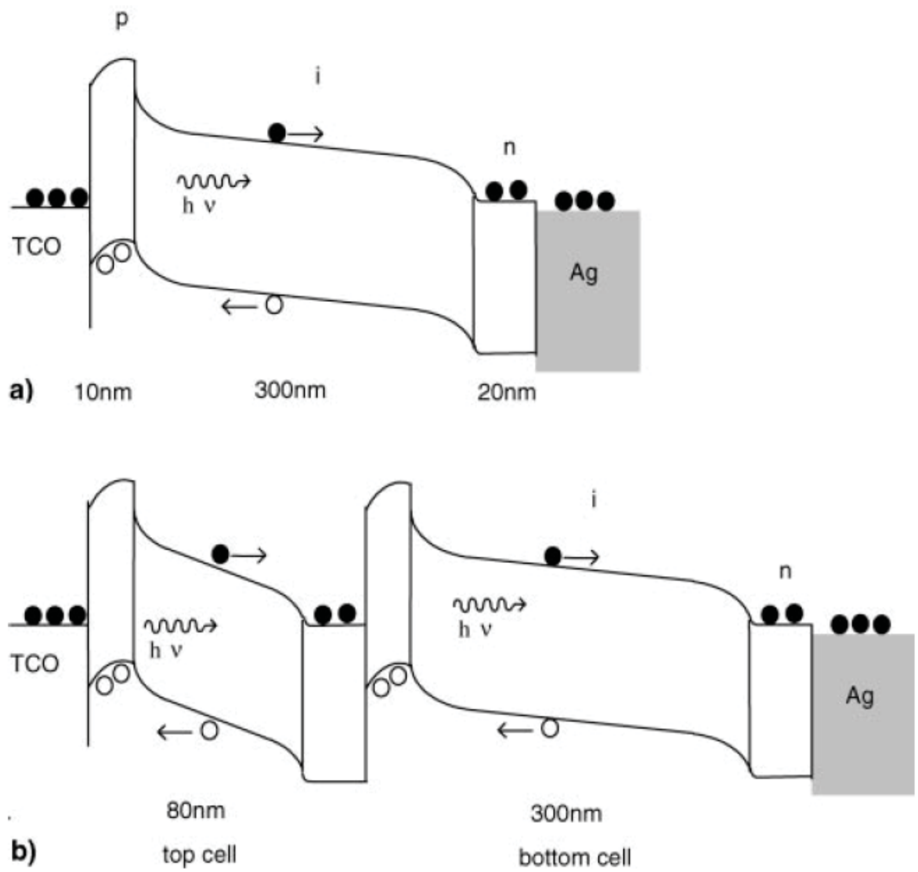

Fig. 2a,b. Schematic sketch of the band diagramm of an a-Si:H p-i-n single junction (**a**), and an a-Si:H/a-Si:H p-i-n/p-i-n stacked junction solar cell (**b**)

Source: Fig. 2 in Rech, B., and H. Wagner. "Potential of amorphous silicon for solar cells. "*Applied Physics A* 69 (1999): 155-67.

a-Si heterostructures

Image removed due to copyright restrictions. Please see http://photovoltaics.sandia.gov/images/PVFSC36.jpg

Please see lecture video for graph or Fig. 4 in Rech, B., and H. Wagner. "Potential of amorphous silicon for solar cells."*Applied Physics A* 69 (1999): 155-167.

Staebler–Wronski effect (SWE)

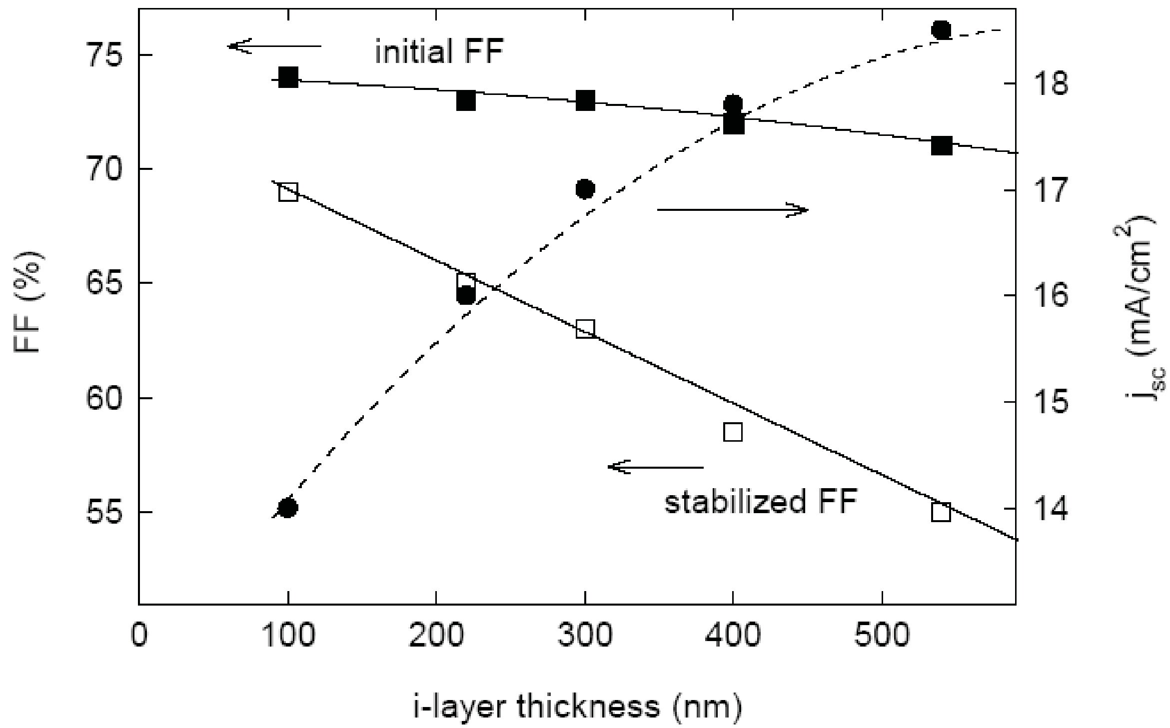

Fig. 3. Initial and stabilized fill factor *FF* and initial short-circuit current density j_{sc} of a-Si:H p-i-n solar cells as a function of i-layer thickness (light-soaking conditions: AM1.5, 100 mW/cm^2, 50 °C, open circuit)

Source: Fig. 2 in Rech, B., and H. Wagner. "Potential of amorphous silicon for solar cells." *Applied Physics A* 69 (1999): 155-67.

The a-Si → μ-Si transition…

…is determined by deposition temperature…

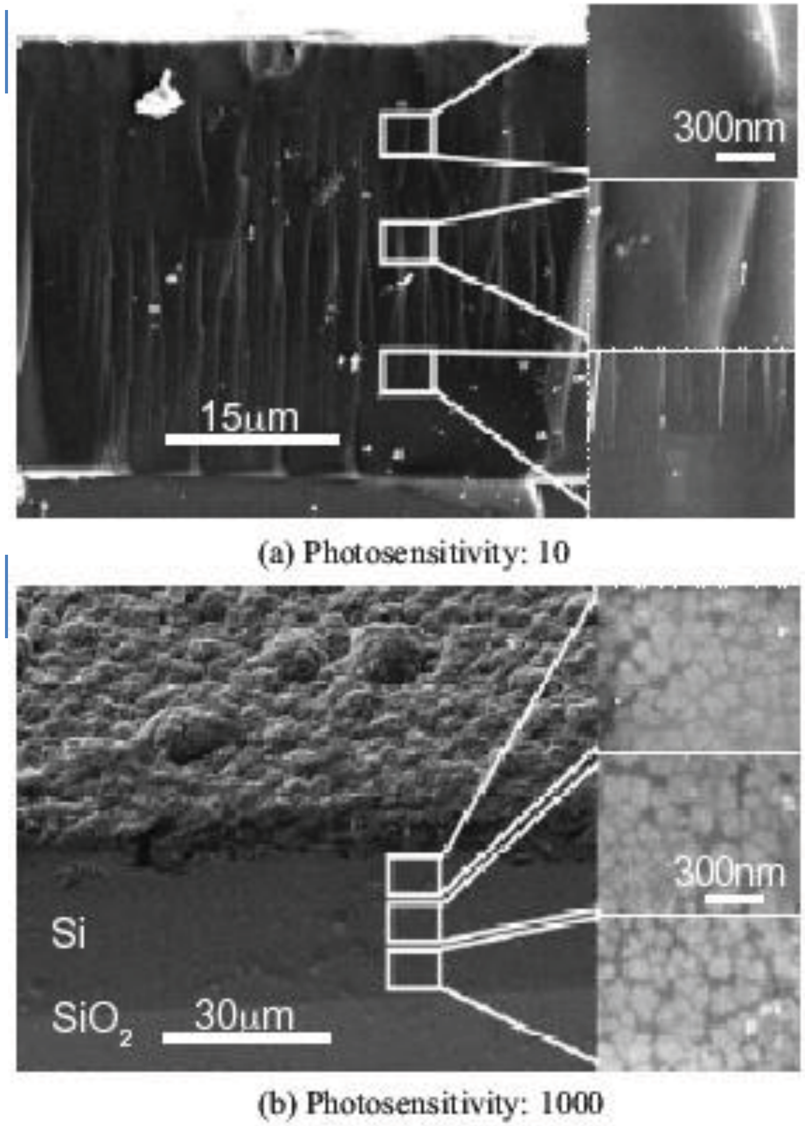

Fig.5 SEM images of the film deposited at different substrate temperature; (a) 150 and (b) 133°C.

http://www.plasma.t.u-tokyo.ac.jp/pict/silicon/Fig5.gif

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…ambient gas content, and other factors.

Please see the lecture 13 video for related images or follow the links below.

http://www.nrel.gov/docs/fy99osti/29586.pdf
http://www.nrel.gov/docs/fy05osti/38355.pdf

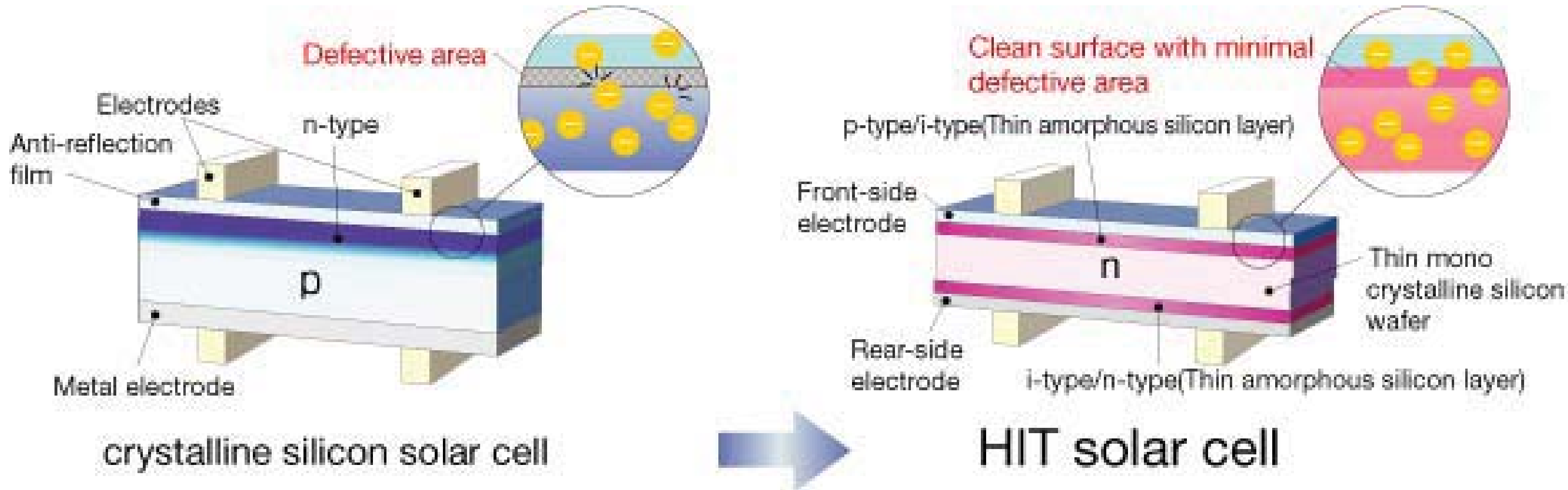
Record a-Si:H Efficiencies

Please see the lecture 13 video or Table 1 in Rech, B., and H. Wagner. "Potential of amorphous silicon for solar cells."*Applied Physics A 69 (1999): 155-167.*

Commercialization attempts of a-Si / µ-Si

http://www.betasights.net/wordpress/?p=1059
http://www.pv-tech.org/editors_blog/_a/applied_materials_sunfab_failure_more_questions_than_answers

Heterojunction with Thin Intrinsic layer (HIT) Cells



Courtesy of Panasonic Corporation. Used with permission.

Advantages:
- Less surface recombination.
- Higher maximum voltages (V_{oc} > 710 mV).
- Efficiency less temperature sensitive.
- High efficiencies (21.5% on 100 cm^2 cell)

Challenges:
- Deposition: doping, nano-to-micro-crystalline phase transition
- Optimizing the c-Si and a-Si interface, low-damage plasma.

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Copper Indium Gallium Diselenide (CIGS)

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CIS and its variants

Basic Facts:

- CIS = Copper Indium Diselenide = $CuInSe_2$ = Chalcopyrite
- Zincblende-like structure
- Record efficiencies: 20% lab; >13% large area

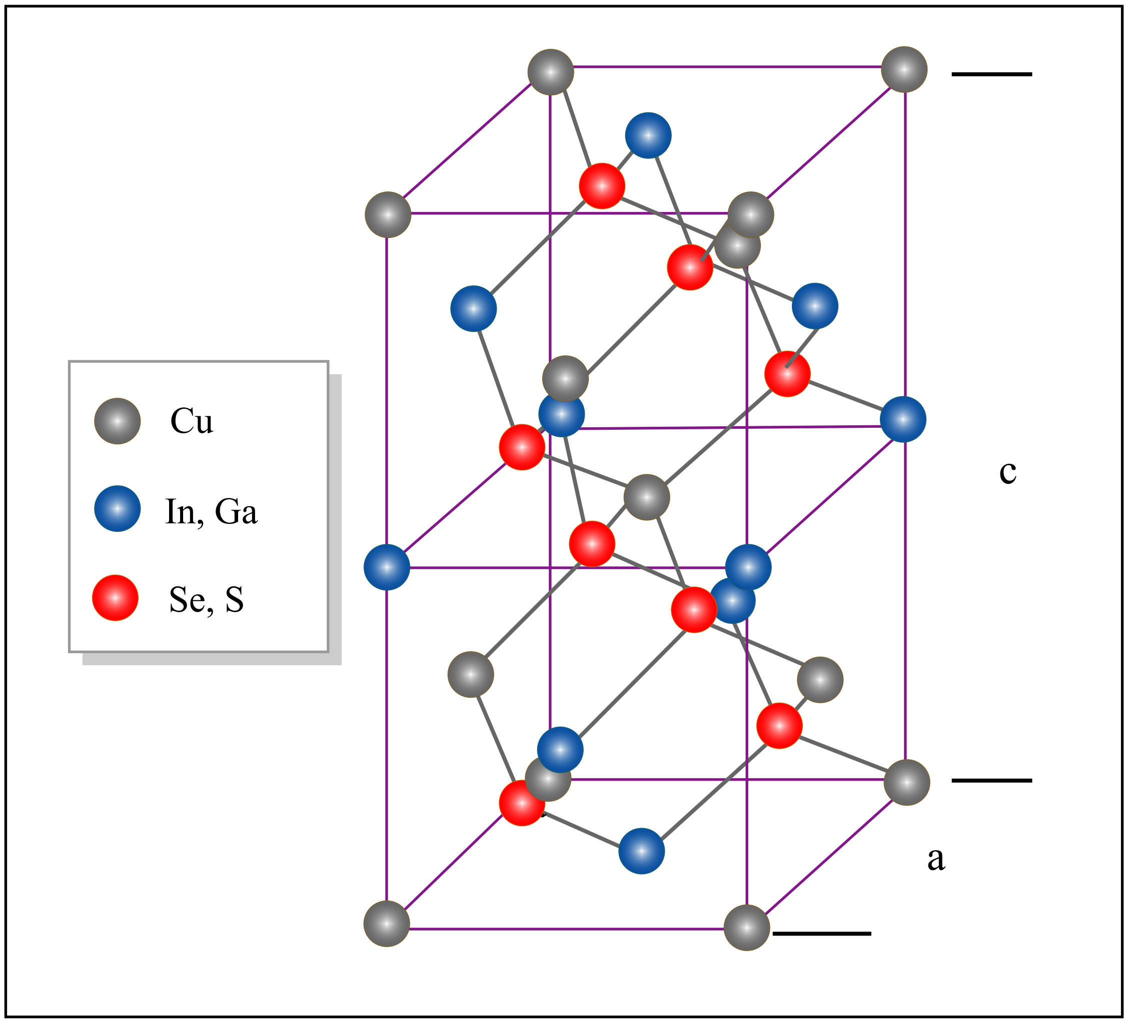
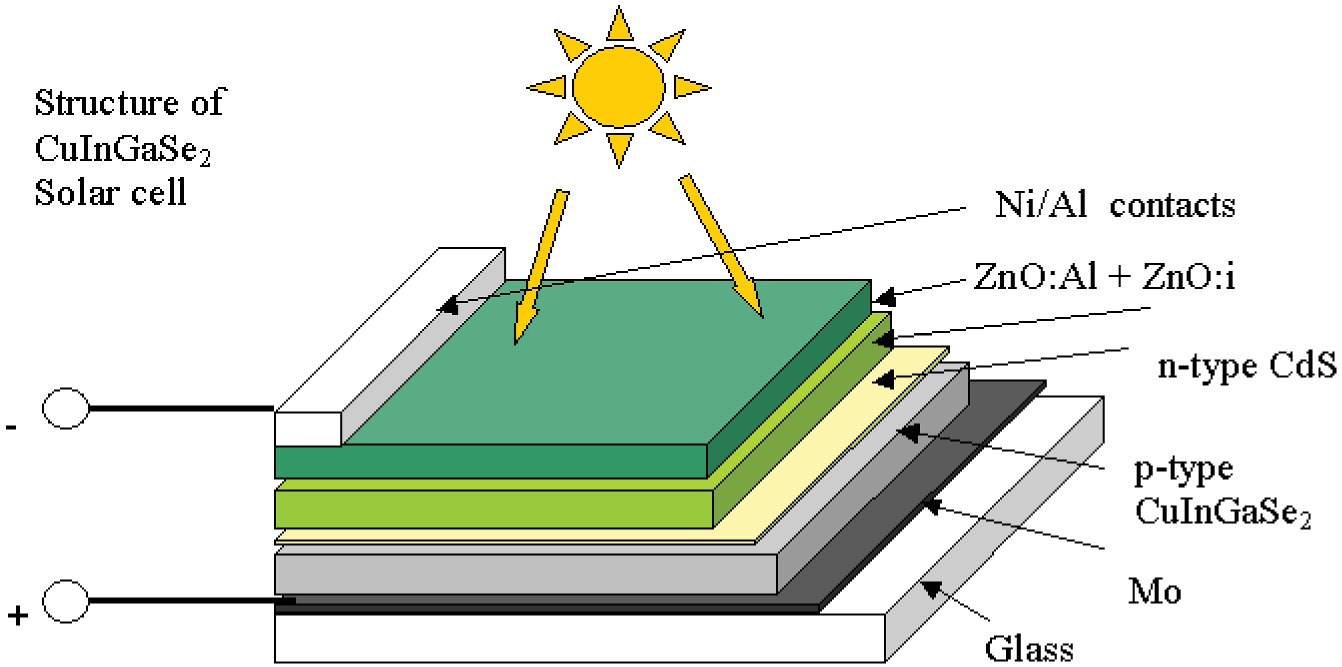


Image by MIT OpenCourseWare. Buonassisi (MIT) 2011

Thin-film polycrystalline CIGS



http://level2.phys.strath.ac.uk

Please see the lecture 13 video for additional structure visual, or see Fig. 1 in Klein, A., et al. "Interfaces in Thin Film Solar Cells." *Record of the 31st IEEE Photovoltaic Specialists Conference* (2005): 205-210.

CIS Band Structure Debated

Please see the lecture 13 video for visuals and explanations of two example attempts at describing band structure.

Fig. 1 in Klein, A., et al. "Interfaces in Thin Film Solar Cells."*Record of the 31st IEEE Photovoltaic Specialists Conference* (2005): 205-210.

Fig. 3 in Weinhardt, L., et al. "Band alignment at the i-ZnO/CdS interface in Cu(In,Ga)(S,Se)2 thin-film solar cells."*Applied Physics Letters* 84 (2004): 3175-3177.

CIGS Characteristics

Advantages:
- High efficiencies (20% record lab cells).

Challenges:
- Uniform deposition (stoichiometry & thickness) over large areas, quickly.
- Defects, Interface States are complex, poorly understood.
- Replacing n-type emitter with Cd-free material (e.g., doped ZnO).

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Promising News for CIGS

http://www.pv-tech.org/news/tsmc_to_sell_own_branded_cigs_thin-film_modules_as_first_200mw_fab_starts_c

http://www.renewableenergyworld.com/rea/news/article/2010/07/the-rise-of-cigs-finally

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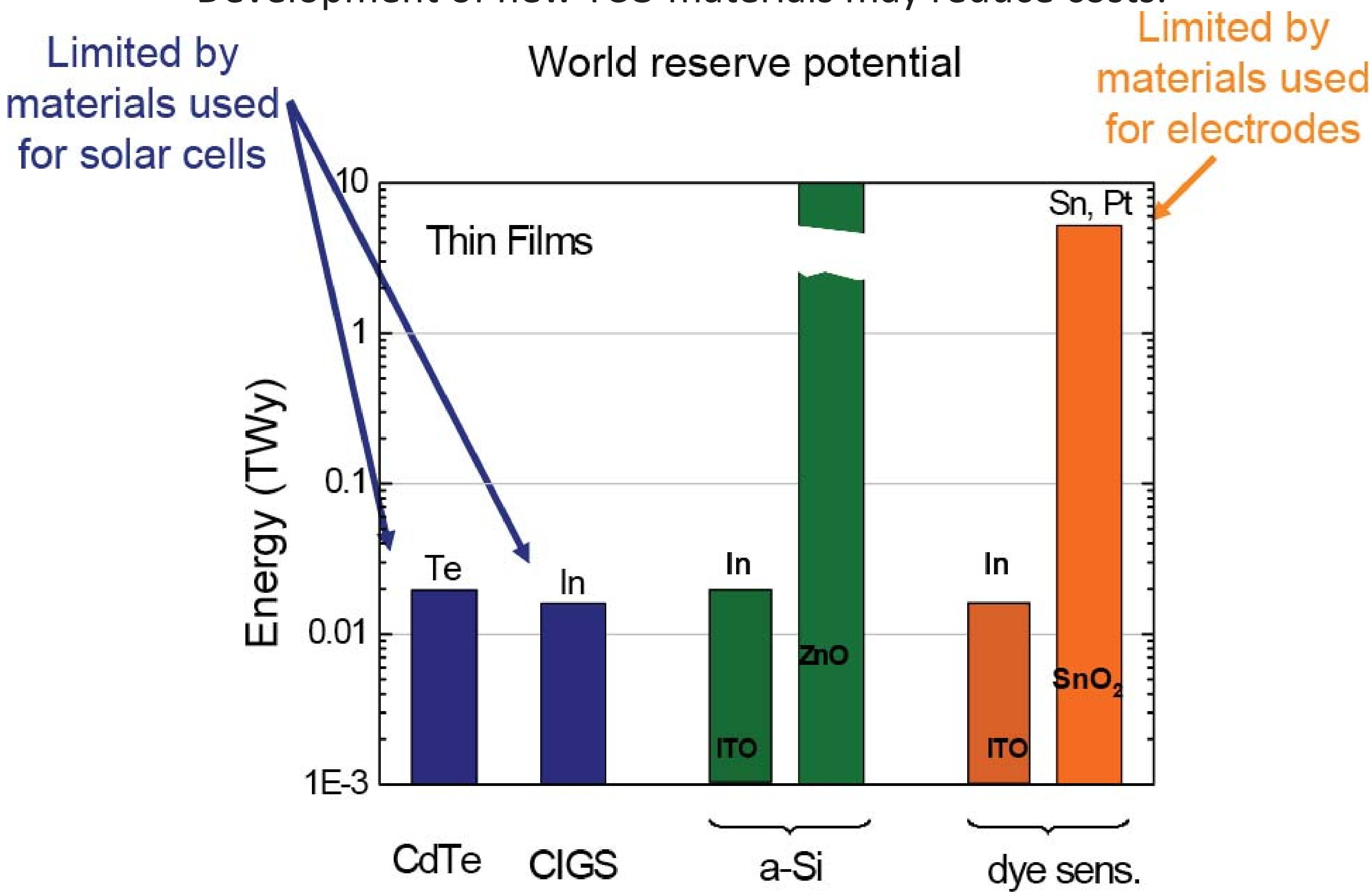
Materials Availability

Most experts agree: not enough In, Te to produce TW of PV.

Development of new TCO materials may reduce costs.



Source: Feltrin, A., and A. Freundlich. "Material Considerations for Terawatt. Level Deployment of Photovoltaics." *Renewable Energy* 33 (2008): 180-5. Courtesy of Alex Freundlich. Used with permission.

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