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International Centre for Theoretical Physics**



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Winter College on Optics and Energy

8 - 19 February 2010

Thin Film Technologies

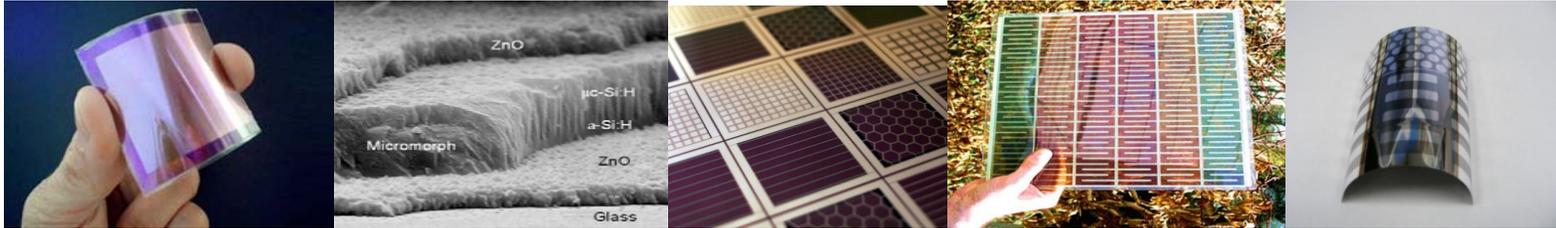
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Thin Film Technologies

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Introduction

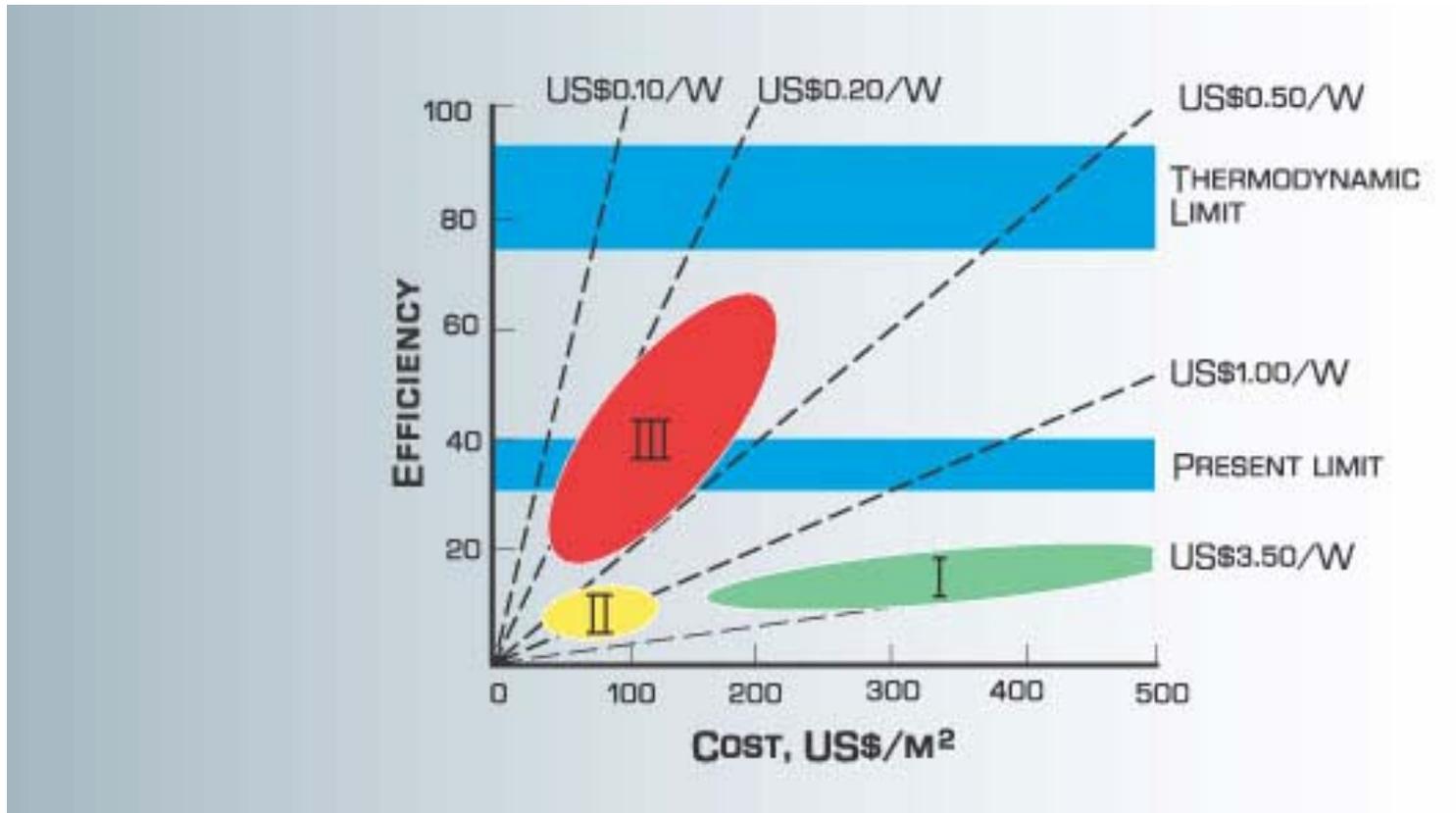
Ought to:

- fabricated on cheap substrates (glass, plastic, metal)
- use less energy to fabricate
- use roll-to-roll processing
- have a much **lower \$/W** than wafer Silicon

Probably won't:

- have good semiconductor properties
 - more structural defects
 - more impurities
- be as efficient as wafer silicon
 - less absorption (for thin devices/low coefficients)
 - less carrier collection (for thick devices)

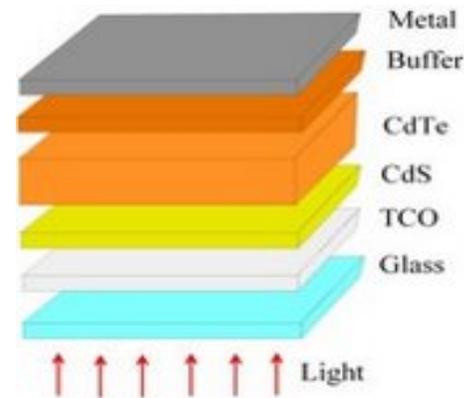
3 “Generations” of PV



(M.A. Green, Prog. Photovolt: Res. Appl. 2001; 9:123-135)

Thin Film Technologies

Cadmium Telluride/Cadmium Sulphide

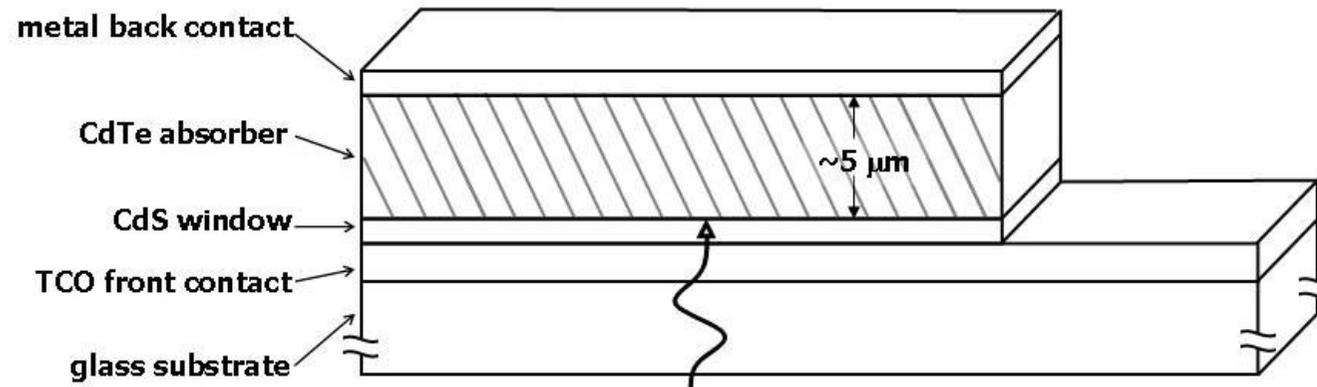


- Cadmium telluride (CdTe) has a direct bandgap of 1.45eV and typically forms with p-type conductivity.
- It forms a good heterojunction with Cadmium Sulphide (CdS) that has a wide bandgap of 2.4eV and typically forms with n-type conductivity.
- Laboratory CdTe/CdS devices have reached efficiencies of 16.5% and modules have reached 10.9%. Typically modules are 7% - 10% efficient.
- In 2009 First Solar indicated that its manufacturing cost has fallen 93 cents per watt, by 2014, it expects to drive down cost per watt to make solar modules to fall to between 52 and 63 cents. The biggest driver of the lower costs is better efficiency

[X Wu X, *et al.* "16.5% Efficient CdS/CdTe Polycrystalline Thin-film Solar Cell" Procs of 17th European pvsec 2001; Munich. p. 995]

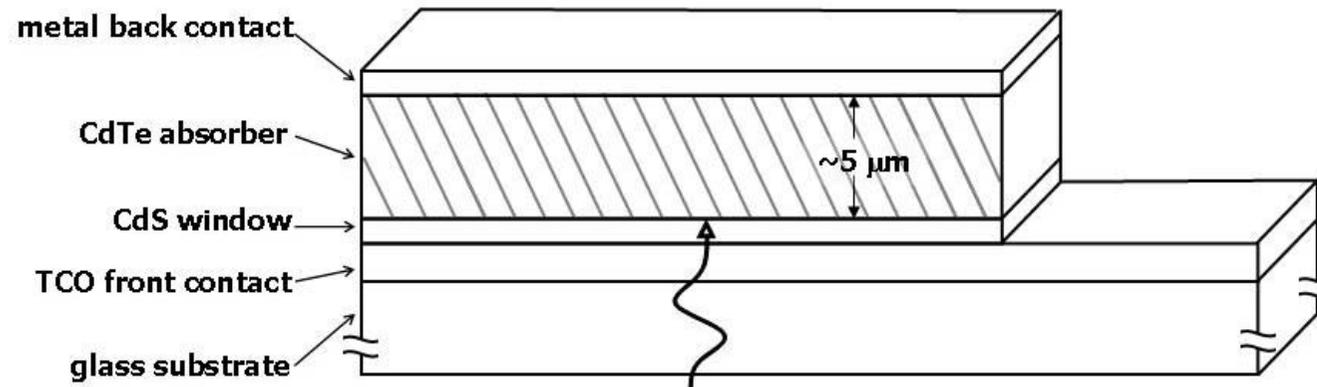
[D. Cunningham *et al.* Large Area Apollo Module Performance and Reliability. In: Proceedings of the 28th IEEE PVSC; 2000; Alaska. p. 13]

CdTe/CdS



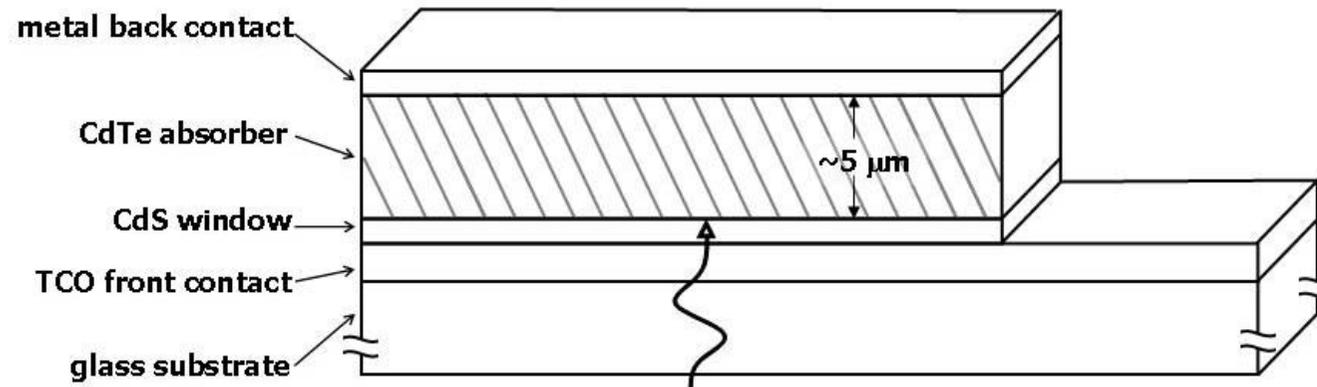
- A typical device process begins with the deposition of a transparent conducting oxide (TCO), typically indium oxide, tin oxide or indium tin oxide (ITO), onto a glass substrate.
- A 100 nm layer of n-type CdS is deposited on the TCO by any number of techniques, but typically by an inexpensive chemical bath deposition.
- After the CdS, a thick ($>5 \mu\text{m}$) layer of n-type CdTe is deposited, typically by vacuum deposition with a substrate temperature of around $400 \text{ }^\circ\text{C}$.
- The final back contact is formed by the deposition of a suitable metal, typically copper.

CdTe/CdS



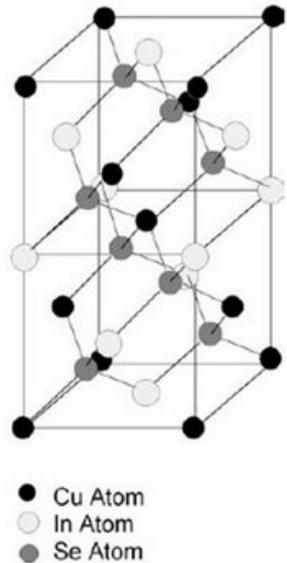
- both CdTe and CdS have strong tendencies to form suitable stoichiometric layers of p and n-type material as required,
- one of the key strengths of this technology is the ability to form suitable layers across large substrate areas in commercial module production.
- devices are efficient, stable and can be produced cheaply.
- with First Solar's <math><1\\$/W</math> PV module production announcement, it is now possible to argue that CdTe is now the leading PV technology, it is certainly expected to make significant inroads into the world PV market over the next few years, displacing C-Si and mC-Si technologies.
- these devices are finally realizing the true cost-reduction potential long expected of 2nd generation (thin film) technologies.

CdTe/CdS



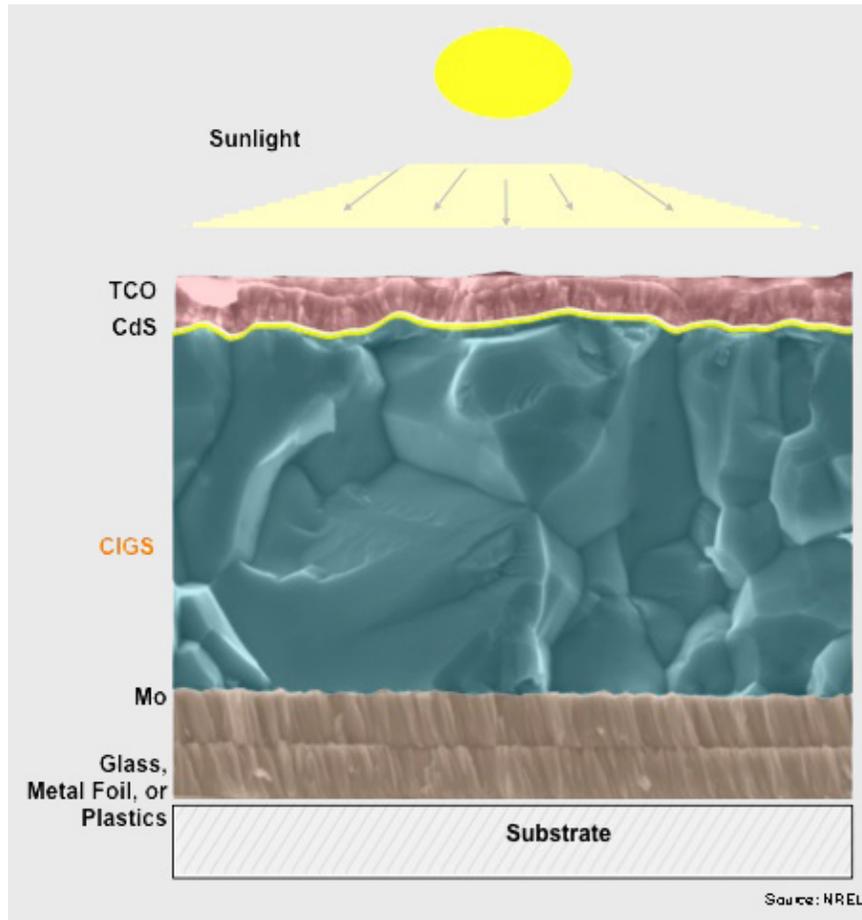
- In spite of recent commercial successes there still remains some potential for increased efficiency and reduced cost of CdTe based modules.
- In particular:
 - reducing losses associated with absorption in the TCO, CdS or in deep within the CdTe by reducing layer thicknesses.
 - Improving the quality and, to some extent, the stability of the back contact are complex challenges that could also improve efficiency.
 - further cost reductions could be realized by reducing thickness, using less of expensive (rare) materials such as indium and developing a roll-to-roll processes for use with flexible substrates.

Copper Indium Gallium Diselenide



- The chalcopyrite semiconductor, CuInSe₂ (CIS), has the highest absorption coefficients across the broadest spectral range
- It has a slightly less than optimum energy bandgap of 1.04eV that can be increased by the addition of Gallium to form CuIn_{1-x}Ga_xSe₂ (CIGS)
- Solar cells based on CIS and CIGS have been under continuous development for a number of years, and are now mature device technologies
- Of all the thin film technologies it is the CIGS laboratory cells that have the highest efficiency record of 19.4%
- Unfortunately scalability of this technology into large area modules is a challenge sub-module efficiencies have been reported up to 16.7%, the best full module efficiency is 13.5%

Copper Indium Gallium Diselenide



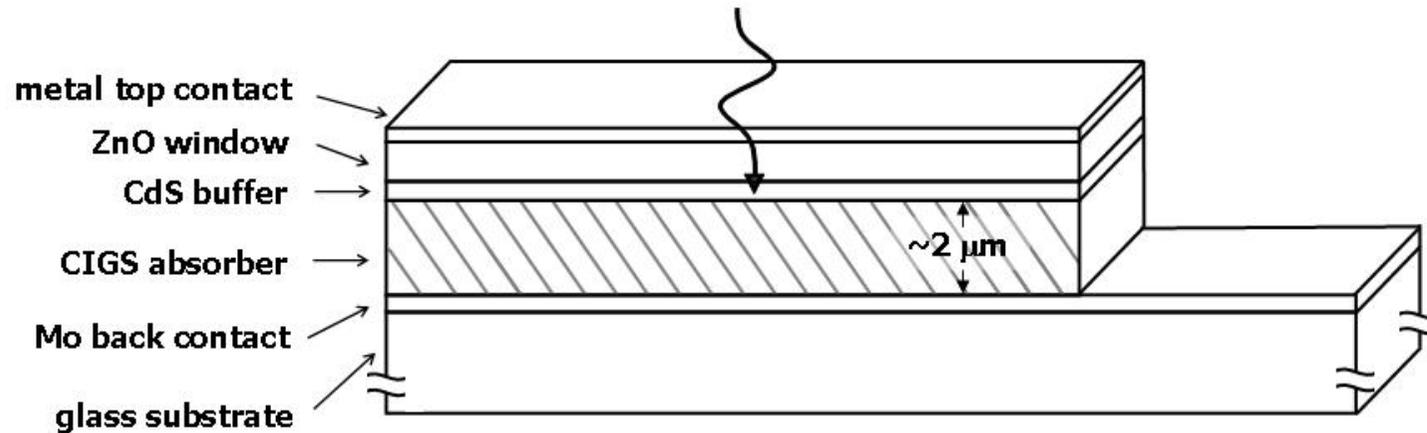
- Typically, a $\sim 1 \mu\text{m}$ layer of molybdenum is deposited on a soda-lime glass substrate to form the back contact.
- 1 - 2 μm of a p-type CIGS absorber layer is formed on the Mo by either co-evaporation or by the controlled selenisation (using H_2Se) of metal layers.
- a heterojunction is formed by a 50 nm n-type CdS layer that is usually deposited by chemical bath deposition and a sputter-deposited $\sim 70 \text{ nm}$ layer of undoped but intrinsically n-type ZnO, which provides the top contact TCO.



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<http://www.nrel.gov/>

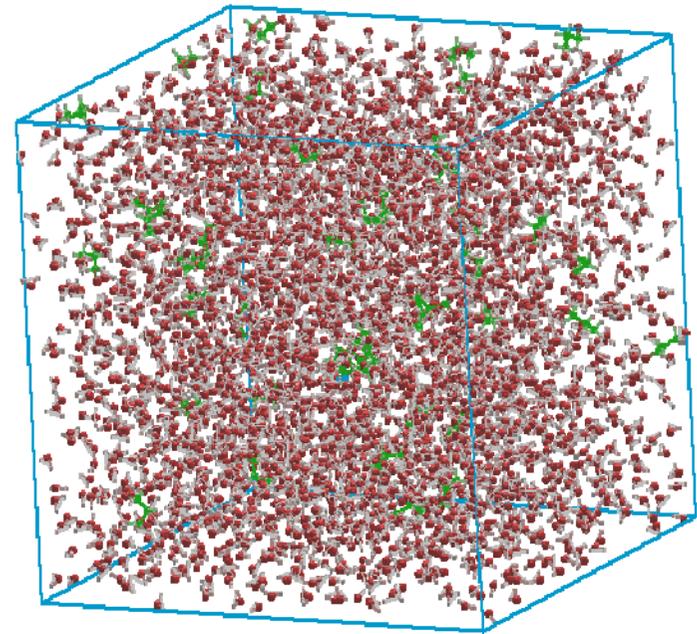
Copper Indium Gallium Diselenide



- Light is incident on the ZnO *window* layer, so called because almost no light is absorbed as the light passes through the top of the device.
- Some of the short-wavelength photons are then absorbed within the thin layer of CdS and will generate electron-hole pairs. Here holes will be swept across the junction to form part of the external current.
- most of the available light is absorbed in the CIGS very close to the junction. This ingenious configuration ensures that there is a minimum requirement on long carrier diffusion lengths (as these can be short in the regions close to the substrate).
- this configuration also exploits the relatively high mobility of electrons when compared to holes. In any case n-type window materials are not commonly found.

Copper Indium Gallium Diselenide

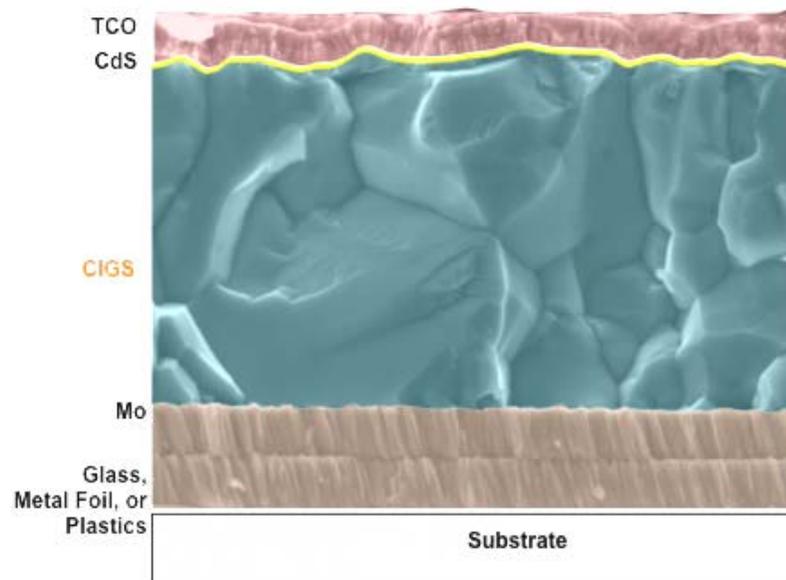
- Commercialization has been hampered by **low yields and high cost production**
- These difficulties can, at least in part be attributed to the **complex nature of CIGS** which has multiples phases and complex defect chemistries with strong dependence on temperature and film composition.
- For example, relatively small variations in In(+Ga)/Cu ratio have significant effects on resistivity for example



<http://chemistry.usf.edu/>

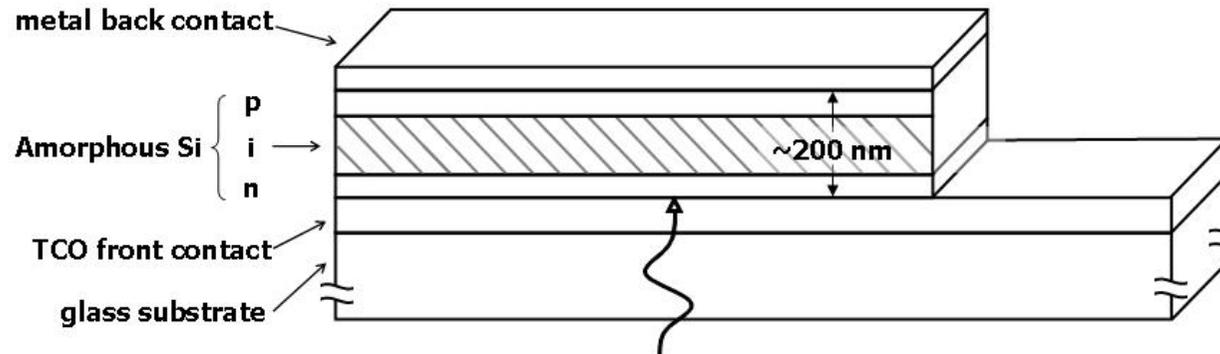
Copper Indium Gallium Diselenide

- CIGS devices have been extensively researched and it seems unlikely that laboratory cells will increase significantly beyond the 20% already demonstrated.
- Successful large-area fabrication, higher module efficiencies, and a reduction in the volumes of indium required to make devices are three important research objectives.



Source: NREL

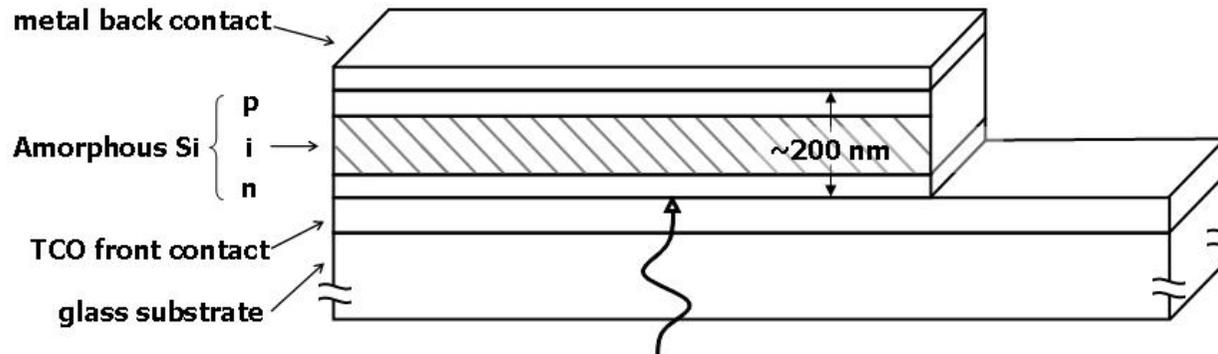
Amorphous Silicon



- Amorphous hydrogenated silicon (a-Si:H) is a disordered network of silicon and hydrogen atoms that is usually deposited from a silane precursor onto a heated substrate.
- The effective bandgap of a-Si:H is near 1.7 eV so it cannot usefully absorb photons with wavelengths much longer than 700nm.
- However, the absorption of short-wavelength light in a-Si:H is strong so solar cells built around the a-Si system are good for indoor use

[Fritzsche H, editor. Amorphous Silicon and Related Materials. Singapore: World Scientific Publishing Co.; 1989]

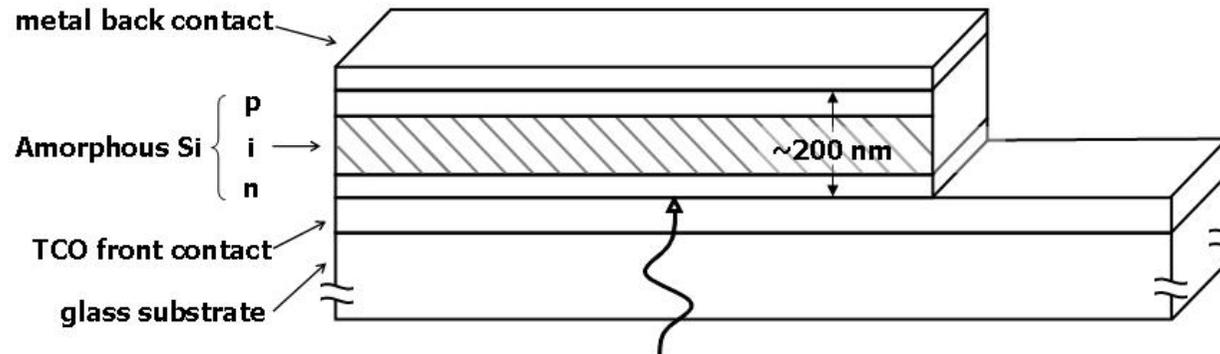
Amorphous Silicon



- Staebler and Wronski *discovered that the photocurrent of an a-Si:H cell would slowly decrease with exposure to light.
- The original photocurrent of a cell was found to be restorable with an anneal at 150 °C or sometimes a large reverse bias.
- Termed the Staebler-Wronski (SW) effect, this degradation was attributed to the breaking of Si-Si or Si-H bonds within the random amorphous network.
- This increases the midgap defect density and hence recombination current.
- The S-W effect is a serious limitation of basic a-Si:H technology as cells can lose as much as 10% of their initial efficiency after a few months of use, before reaching a *stabilized* efficiency.

[* Staebler DL, Wronski CR. Reversible Conductivity Changes in Discharge-produced Amorphous Si. Applied Physics Letters. 1977;31:292-294]

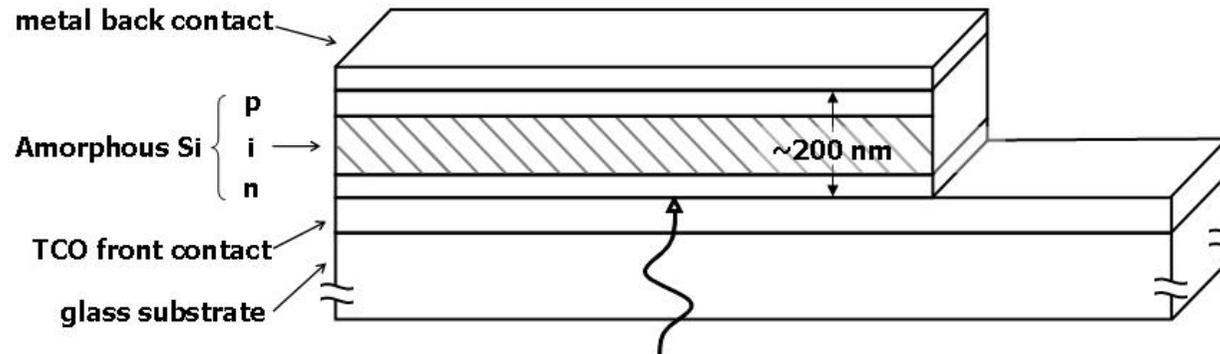
Amorphous Silicon



- the deposition process is very flexible - by varying process conditions, the grain size of the material can be altered from amorphous to nano, micro, or polycrystalline.
- a-Si:H is often deposited at temperatures of 200-300 °C or lower which allows deposition onto flexible polymer substrates that can not readily support CIGS or CdTe deposition.
- The record efficiency for a-Si:H laboratory scale devices is 9.5% (stable)*; the best modules are usually 8%-10% efficient (initial).
- The devices typically used in pocket calculators are generally around 5% efficient.

[*Meier J et al. "Potential of Amorphous and Microcrystalline Silicon Solar Cells". Thin Solid Films.2004;451]

Amorphous Silicon



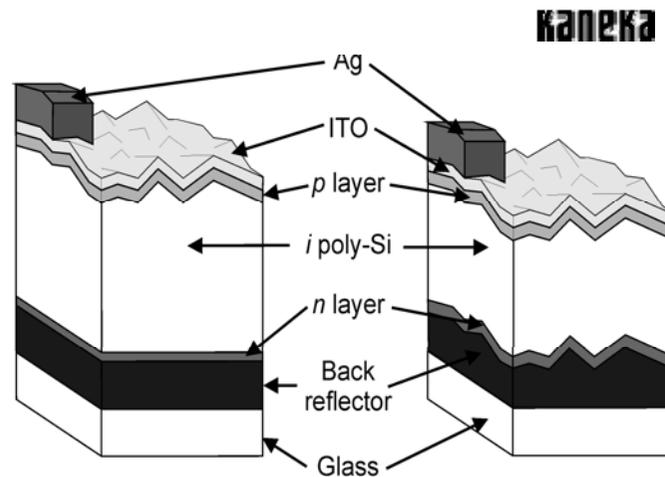
- devices incorporate p-type/intrinsic/n-type (*pin*) designs.
- a region of low-impurity concentration placed between heavily doped p and n regions sits within an electric field so carriers will form drift rather than diffusion currents between the n and p-type regions.
- this design combats poor diffusion mobility and ensures effective minority carrier collection that is much less upon the carrier diffusion lengths.
- the use of texturing schemes to provide light-trapping that increase effective absorption lengths by as much as twenty times the actual silicon thickness

[*Meier J et al. "Potential of Amorphous and Microcrystalline Silicon Solar Cells". Thin Solid Films.2004;451]

Amorphous Silicon

- It is unlikely that a-Si:H will ever be able to challenge
 - CIGS on the basis of lab-scale device efficiency
 - or CdTe in module efficiency
- but considering cost-per-Watt, a-Si:H remains an important technology and although
- it will be displaced by micromorph modules in large scale production it will maintain a niche in low-power indoor applications.

Polycrystalline-Silicon



- Polycrystalline silicon (polysilicon) on glass offers an enticing system
- near optimum band gap at 1.12eV and full utilization of the spectral bandwidth
- It is immune from the SW-effect
- Unfortunately, it has very low absorption levels across a broad spectral range: 50 μm of crystalline silicon struggles to absorb enough light
- the grain boundaries act as recombination centres
- but now 10.5% [1] cell efficiencies and 8.2% module efficiencies are reported [2]

[1] M.J. Keevers *et al.*, "10% Efficient CSG Minimodules" Procs of the 22nd PVSEC, 2007; Milan.

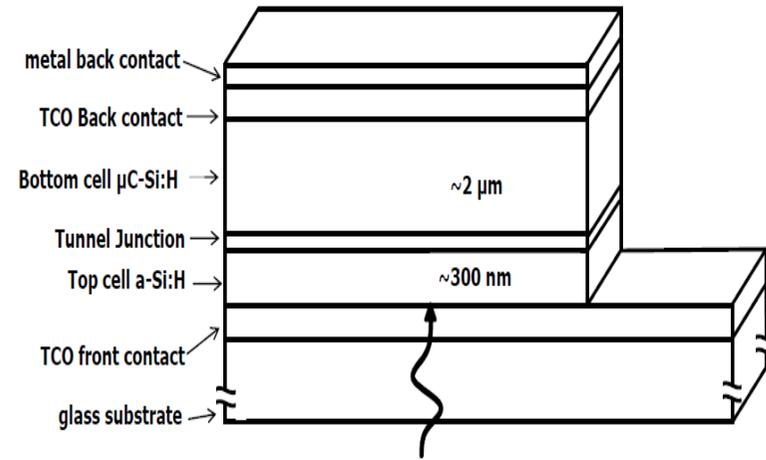
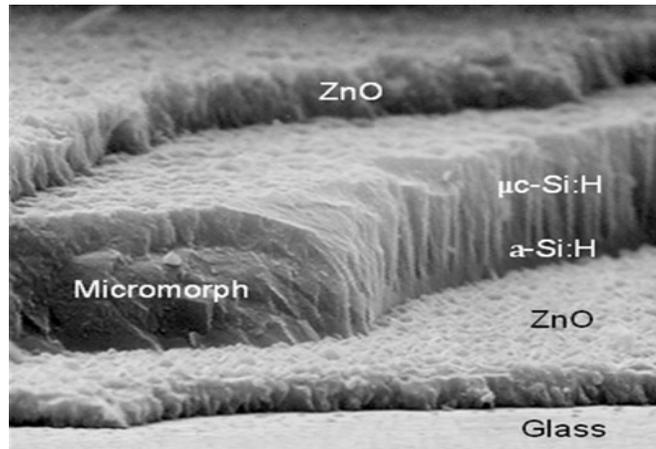
[2] Basore PA. "Pilot Production of Thin-film Crystalline Silicon on Glass Modules" Procs of the 29th IEEE PVSC; 2002; New Orleans. p. 49

Polycrystalline-Silicon

- devices also incorporate p-type/intrinsic/n-type (*pin*) designs.
- the use of texturing schemes is even more important
- the best layers consist of relatively small crystalline grains surrounded by hydrogenated a-Si grain boundaries that provide adequate passivation.
- the distinction between a-Si and p-Si devices becomes a continuum, now the best devices are constructed from nano- or proto-silicon layers that share p-Si and a-Si properties

[*Meier J et al. "Potential of Amorphous and Microcrystalline Silicon Solar Cells". Thin Solid Films.2004;451]

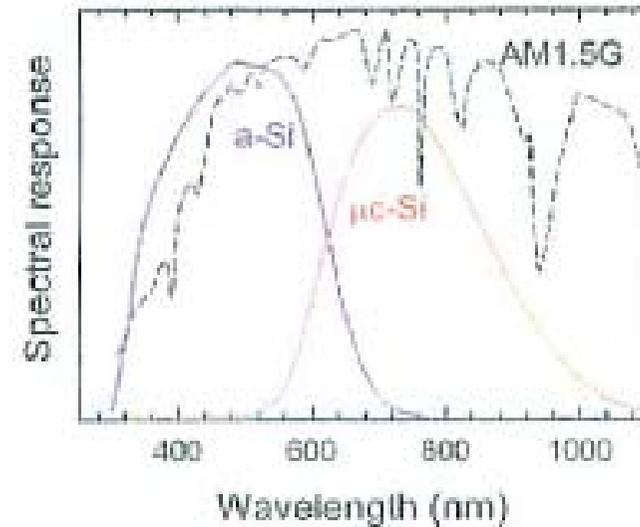
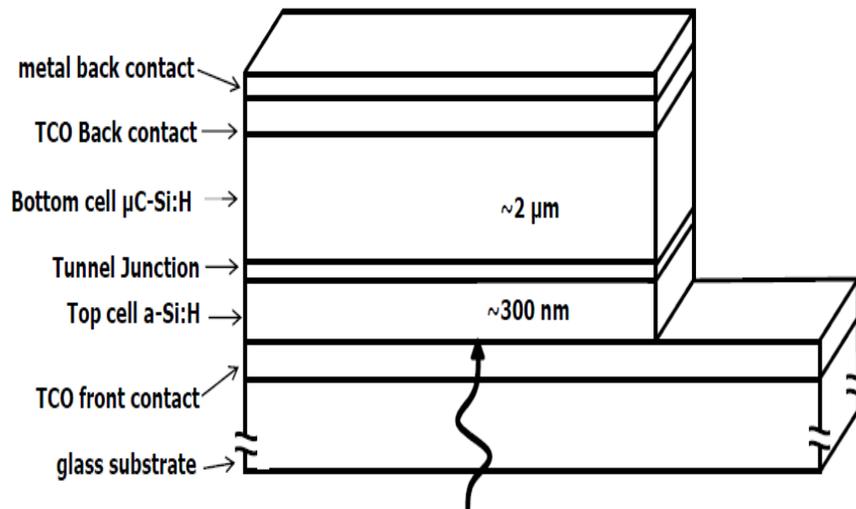
Micromorph



- Using a combination of a-Si and p-Si in a tandem “micromorph” (microcrystalline-amorphous) arrangement, d
- Devices with higher efficiencies ($\sim 12\%$) that are less susceptible to the SW effect can be produced [1]

Keppner H, Meier J, Torres P, Fischer D, Shah A. Microcrystalline Silicon and Micromorph Tandem Solar Cells. *Applied Physics A*. 1999;69:169-177.]

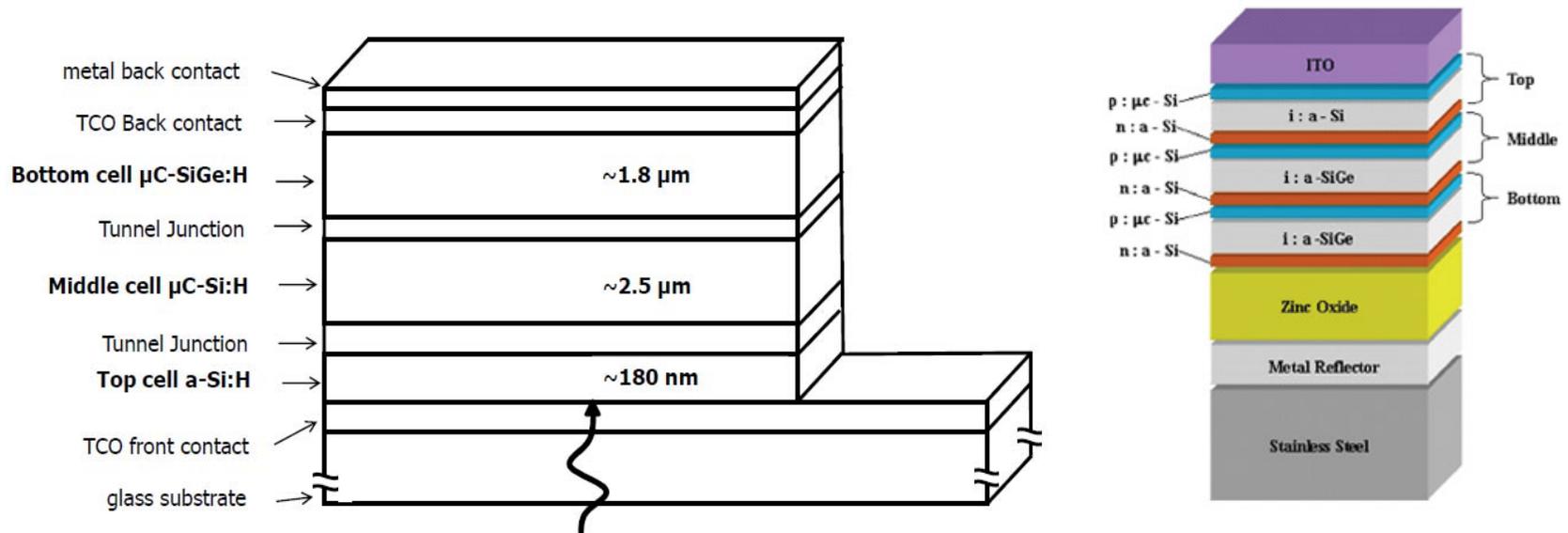
Micromorph



- top cell is a thin a-Si solar cell that absorbs most of the high-energy photons to produce
- the bottom cell is a p-Si device that absorbs the red and infrared light, producing the same current
- current (and therefore efficiency through the whole device is limited by the device that produces the least current,
- lab efficiencies of 12% and module efficiencies of 9% under standard conditions [*].
- "micromorph" devices are replacing conventional a-Si devices

[* S. Dubail et al. Microcrystalline Silicon and the Impact on Micromorph Tandem Solar Cells. Solar Energy Materials and Solar Cells. 2002;74(1-4):457]

Triple-junction silicon



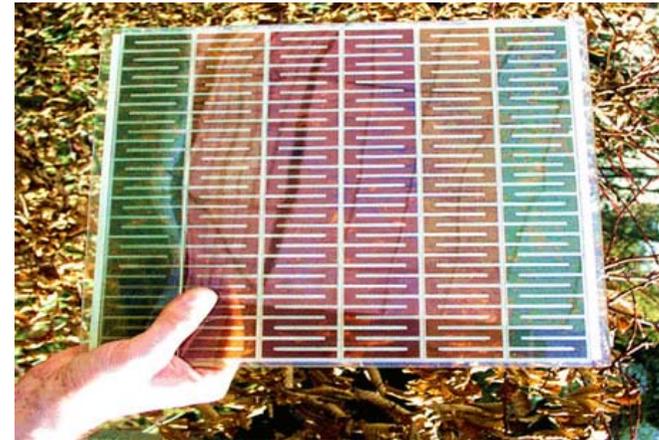
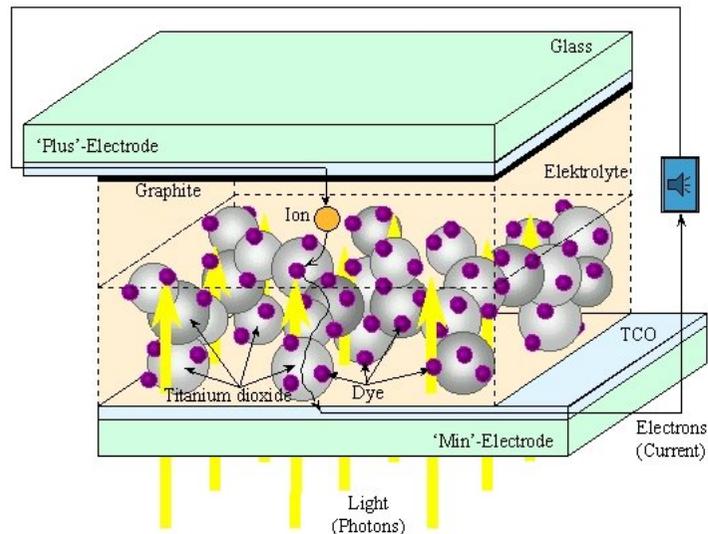
- Triple-junction silicon devices have also been produced, generally by adding a-SiGe or p-SiGe bottom cell to the tandem structure
- each sub-device must be current matched.
- Lab cells with initial efficiencies as high as 15.4% have been reported [1]
- modules produced with an a-Si, a-SiGe, a-SiGe combination have reached 10.4% [2]
- current matching is a key challenge

[1] B. Yan et al "Correlation of Current Mismatch and Fill Factors in Amorphous and Nanocrystalline Silicon Based High Efficiency Multijunction Solar Cells". Procs of 33rd IEEE PVSC 2008. p. 1-6.

[2] Yang et al, "Progress in Triple-junction Amorphous Silicon-based Alloy Solar Cells and Modules Using Hydrogen Dilution. In: Proceedings of the 1st World Conference on Photovoltaic Energy Conversion; 1994; Hawaii. p. 380

Emergent Technologies

Dye-Sensitised Solar Cells



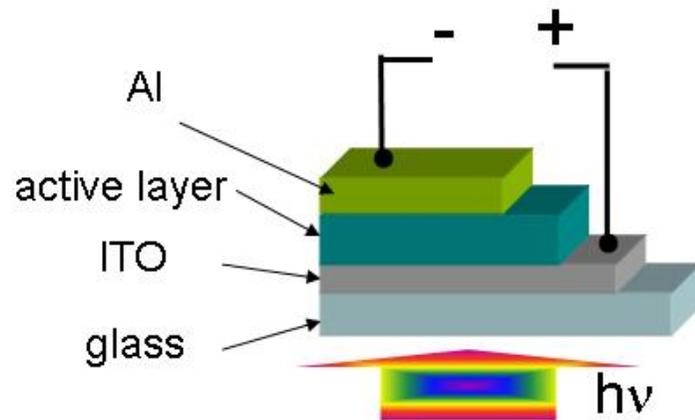
- The first dye sensitized solar cells (DSSCs), or Grätzel Cells, were produced by O'Regan and Grätzel in 1991 [1]
- Impressive progress has been made over the last 20 years and now DSSCs have demonstrated laboratory cell efficiencies of 10.4% [2] and small sub-module efficiencies of 8.4% [3].
- DSSCs are *bulk-heterojunction* devices: instead of having planar junctions formed by n-type material being deposited on p-type material (typical of all devices discussed so far)

[1] O'Regan B, Gratzel M, *Nature*. 1991;353(6346):737-740.

[2] Y. Chiba et al, *Technical digest of 15th International PVSEC 2005*; Shanghai. p. 665-666.

[3] M. Morooka M, and K. Noda K, *88th Spring Meeting of the Chemical Society of Japan*; 2008; Tokyo.

Organic

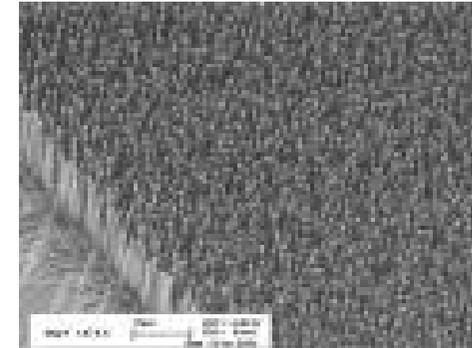
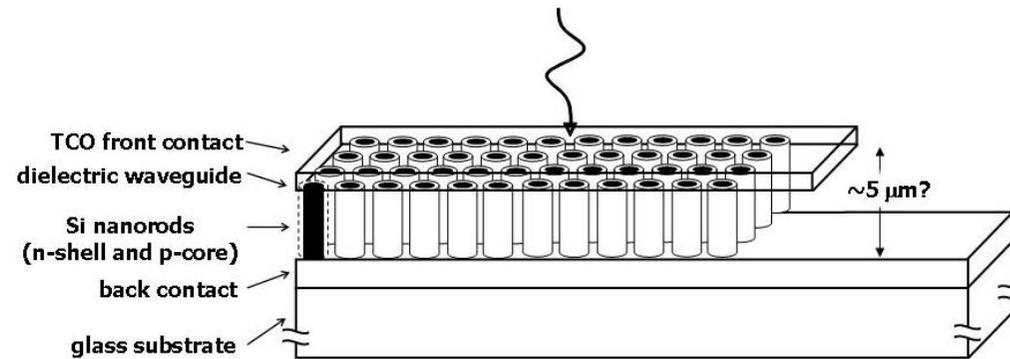


- bulk-heterojunction devices in which n and p-type materials are mixed
- separation of electrons and holes (in excitonic form) is a challenge
- best lab and module efficiencies, 5.15% and 2.05%, respectively [1,2]. Significant volume of red and IR photons are not utilized
- serious stability issues as light-soaking significantly degrades efficiency over relatively short timescales.
- organic polymer solar cells are not yet commercially viable but have many promising properties that offer considerable hope for the future

[1] [Internet]. Available from: www.konarka.com.

[2] D. Laird et al. "Advances in Plexcore Active Layer Technology Systems for Organic Photovoltaics: Rooftop and Accelerated Lifetime Analysis of High Performance Organic Photovoltaic Cells" Proceedings of the SPIE. 2007;6656

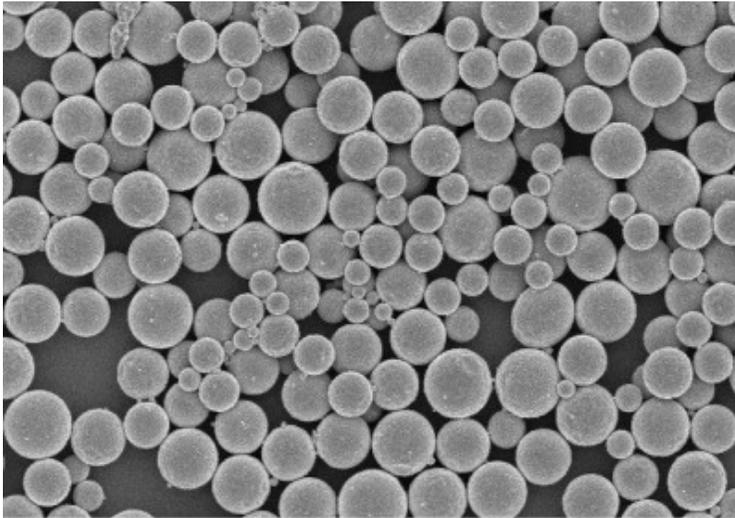
Nanorod Devices



- inorganic bulk-heterojunction system
- In this device, self-organised p-type nanowires are grown by a physical deposition processes using a patterned silicon template.
- A second deposition regime deposits an n-type layer around the p-type wires creating an array of *core-shell* nanodevices that each form classic single crystal solar cells
- These nanodevices can act as standalone energy harvesting units – possibly to individually power single CMOS gates for example

[1] Kayes BM, Atwater HA, Lewis NS. Comparison of the Device Physics Principles of Planar and Radial p-n Junction Nanorod Solar Cells. *Journal of Applied Physics*. 2005;97:114302.

Nanosolar (?)



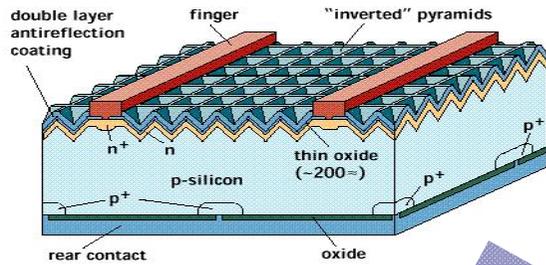
- A CIS nanosphere based system
- “painted” onto plastic substrates
- commercial venture, modules have been manufactured but relatively little is known.
- another “bulk-heterojunction system!”

[1] www.nanosolar.com

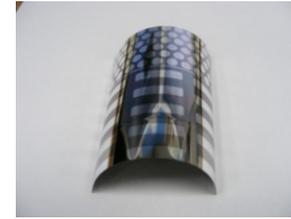
Conclusions

- many different thin-film technologies
- CdTe (First Solar) and Micromorph (many) are substantial commercial entities
- First Solar's CdTe devices at <1 \$/W perhaps marks the start of the 2nd Generation
- 2nd and 3rd generation combinations (starting with tandem and triple junctions) are becoming more popular
- Future developments have great promise.....
 - bulk-hetero-junctions
 - self-organized nanotechnologies
 - roll-to-roll processing

Emerging Trends



Flexible Substrates →

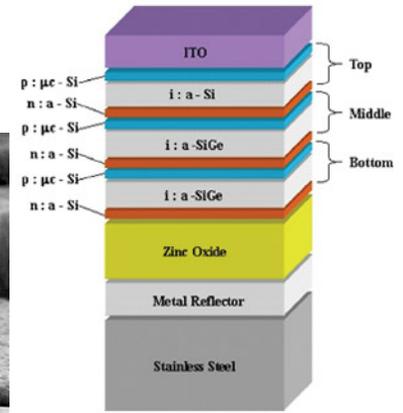
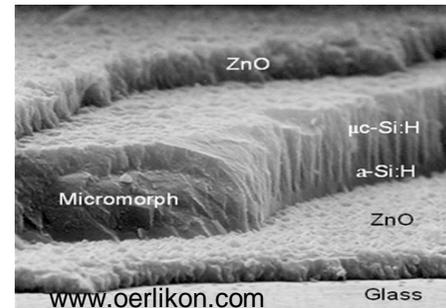
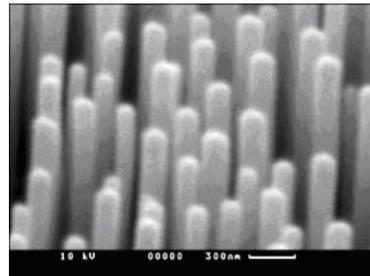
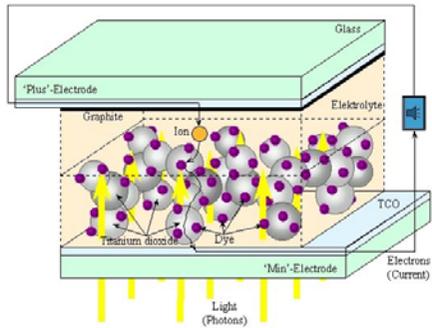
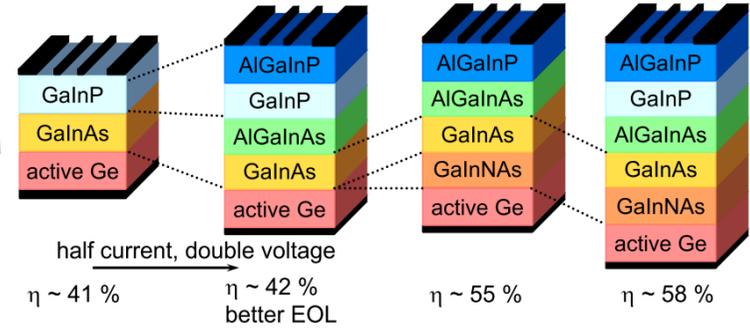


Bulk hetero-junctions



Thin film multi-junctions

Multi-junction (3G)



Conclusions

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- CdTe (First Solar) and Micromorph (many) are substantial commercial entities
- First Solar's CdTe devices at <1 \$/W perhaps marks the start of the 2nd Generation
- 2nd and 3rd generation combinations (starting with tandem and triple junctions) are becoming more popular
- Future developments
 - bulk-hetero-junctions
 - self-organized nanotechnologies
 - roll-to-roll processing
 - **photon management**