Solar Cell Technology

Current State of the Art

Where are we headed?

Gerald Gourdin

Introduction to Green Chemistry
Fall 2007

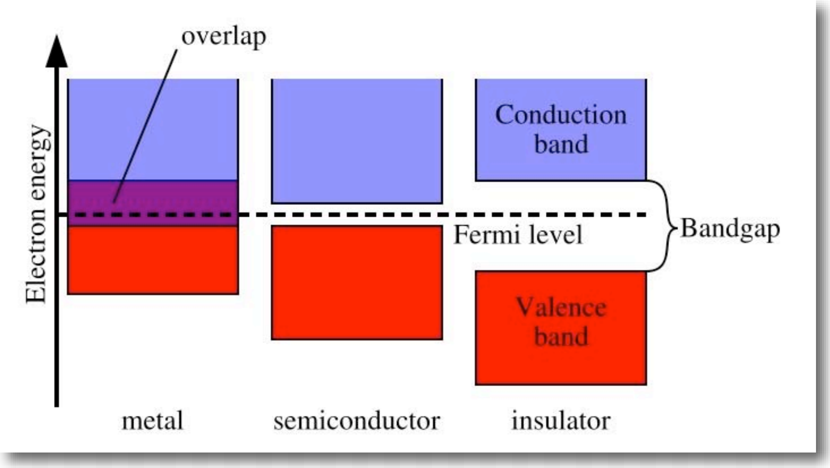
Introduction

- 1839: Photovoltaic effect was first recognized by French physicist Alexandre-Edmond Becquerel.
- 1883: First solar cell was built by Charles Fritts, who coated the semiconductor selenium with an extremely thin layer of gold to form the junctions (1% efficient).
- 1946: Russell Ohl patented the modern solar cell
- 1954: Modern age of solar power technology arrives - Bell Laboratories, experimenting with semiconductors, accidentally found that silicon doped with certain impurities was very sensitive to light.
- The solar cell or photovoltaic cell fulfills two fundamental functions:
  - Photogeneration of charge carriers (electrons and holes) in a light-absorbing material
  - Separation of the charge carriers to a conductive contact to transmit electricity

Photon Absorption

Photons absorption creates mobile electron-hole pairs

- Photon is absorbed and energy is given to an electron in the crystal lattice
    - Usually this electron is in valence band, tightly bound in covalent bonds.
    - Energy given by the photon “excites” it into the conduction band
- Covalent bond now has one fewer electron (hole).
- Bonded electrons of neighboring atoms can move into the ‘hole’, leaving another hole behind – hole can propagate through lattice.
- Free electrons flow through the material to produce electricity.
- Positive charges (holes) flow in opposite direction.
- Different PV materials have different band gap energies.
- Photons with energy equal to the band gap energy are absorbed to create free electrons.
- Photons with less energy than the band gap energy pass through the material

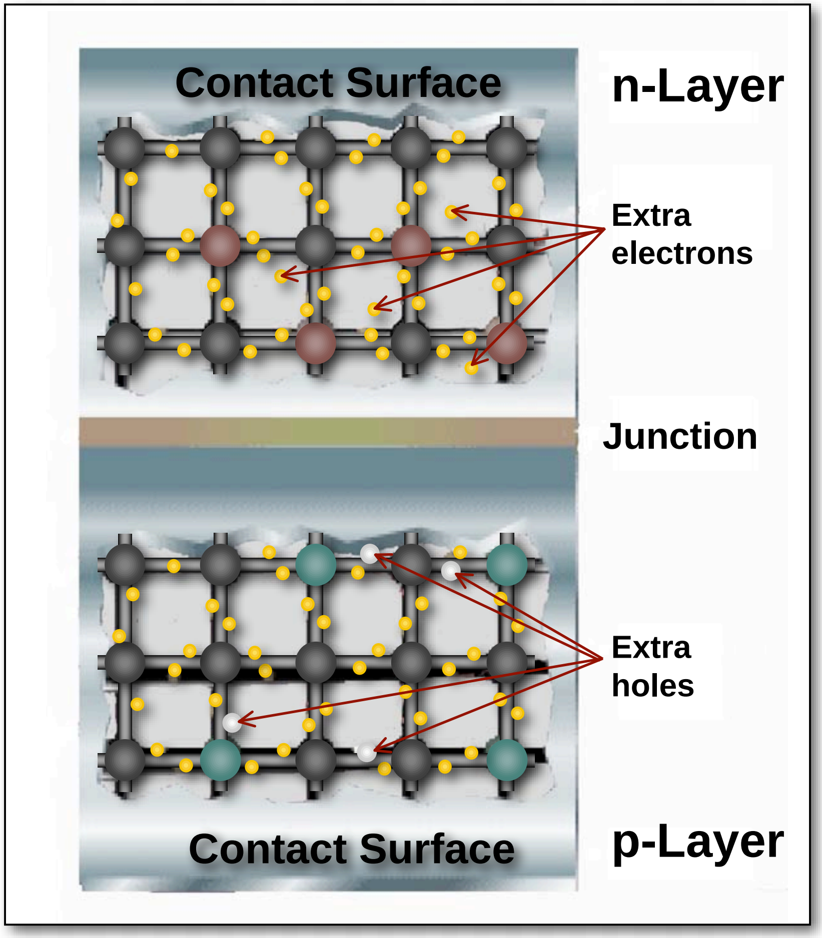


Doped Semiconductor

p-n Junction Diode

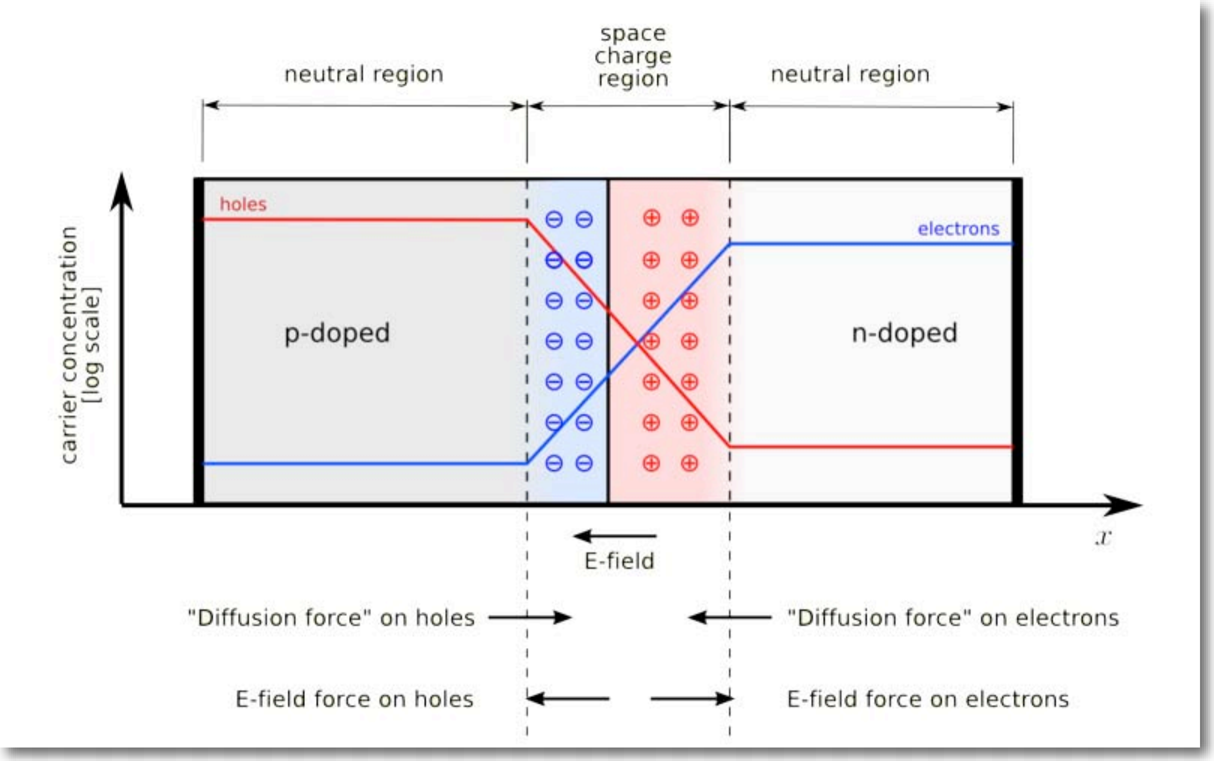
- Semiconductor doped to change electronic properties
- n-type semiconductor
  - increase number free electrons
- p-type semiconductor
  - increase number free 'holes'

1. Absorption of a photon
2. Formation of electron-hole pair (exciton)
3. Exciton diffusion to Junction
4. Charge separation
5. Charge transport to the anode (holes) and cathode (electrons)
6. Supply a direct current for the load.



Nov-21-07

Electricity Generation



- p-n junction in thermal equilibrium w/ zero bias voltage applied.
- Electrons and holes concentration are reported respectively with blue and red lines.
- Gray regions are charge neutral.
- Light red zone is positively charged; light blue zone is negatively charged.
- Electric field shown on the bottom, the electrostatic force on electrons and holes and the direction in which the diffusion tends to move electrons and holes.

Cell Structures

- Homojunction Device
    - Single material altered so that one side is p-type and the other side is n-type.
    - p-n junction is located so that the maximum amount of light is absorbed near it.
- Heterojunction Device
    - Junction is formed by contacting two different semiconductor.
    - Top layer - high bandgap selected for its transparency to light.
    - Bottom layer - low bandgap that readily absorbs light.
- p-i-n and n-i-p Devices
    - A three-layer sandwich is created,
    - Contains a middle intrinsic layer between n-type layer and p-type layer.
    - Light generates free electrons and holes in the intrinsic region.

Overview

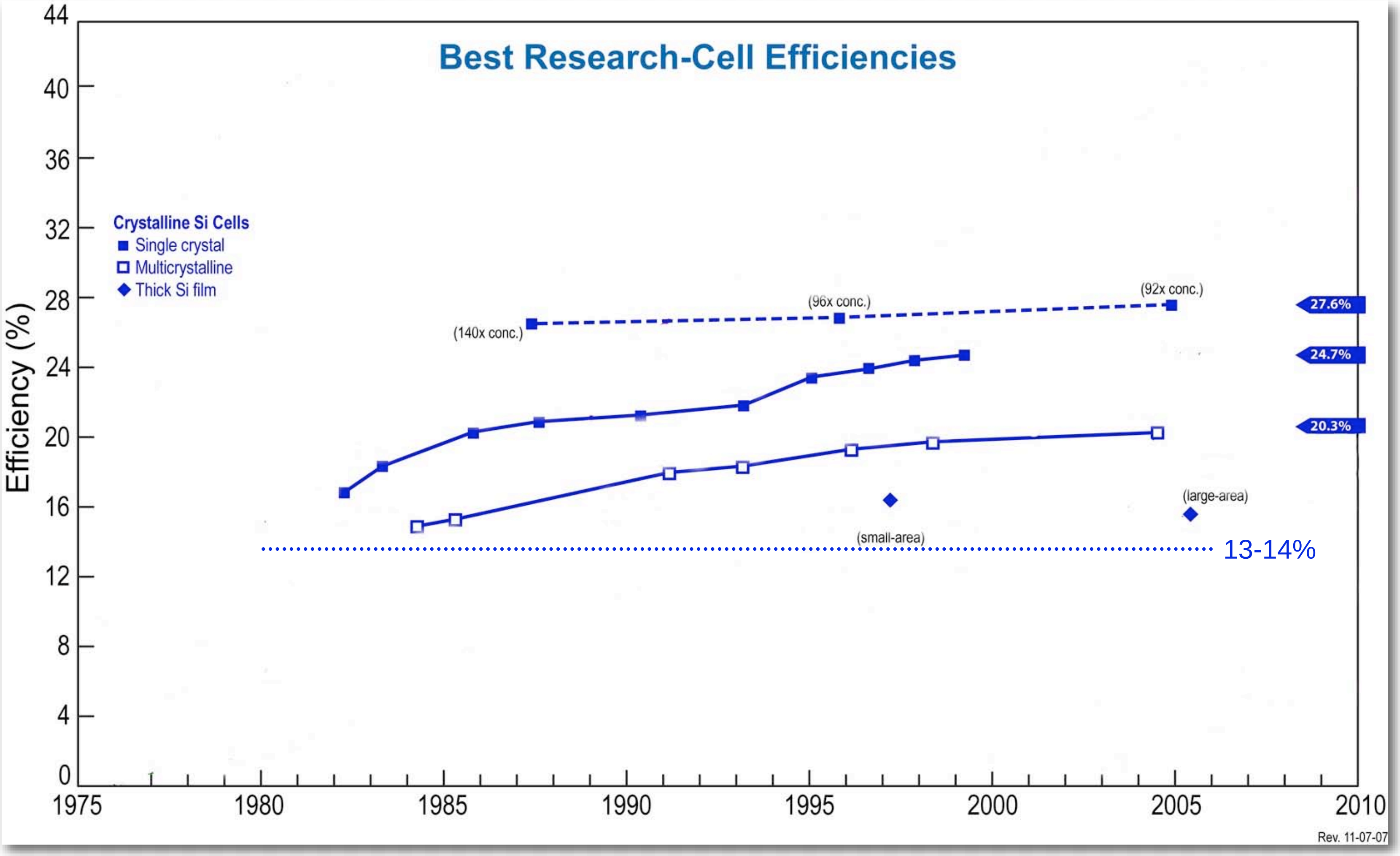
- First Generation
  - Single crystal silicon wafers (c-Si)
- Second Generation
  - Amorphous silicon (a-Si)
  - Polycrystalline silicon (poly-Si)
  - Cadmium telluride (CdTe)
  - Copper indium gallium diselenide (CIGS) alloy
- Third Generation
  - Nanocrystal solar cells
  - Photoelectrochemical (PEC) cells
    - Gräetzel cells
  - Polymer solar cells
  - Dye sensitized solar cell (DSSC)
- Fourth Generation
  - Hybrid - inorganic crystals within a polymer matrix

First Generation (Silicon)

First generation photovoltaic cells are the dominant technology in the commercial production of solar cells, accounting for more than 86% of the solar cell market.

- Cells are typically made using a crystalline silicon wafer.
- Consists of a large-area, single layer p-n junction diode.
- Approaches
  - Ingots can be either monocrystalline or multicrystalline
  - Most common approach is to process discrete cells on wafers sawed from silicon ingots.
  - More recent approach which saves energy is to process discrete cells on silicon wafers cut from multicrystalline ribbons
- Band gap ~1.11 eV

First Generation: Research Cells



Source: National Renewable Laboratory

First Generation: Evaluation

- Advantages
  - Broad spectral absorption range
  - High carrier mobilities
- Disadvantages
  - Requires expensive manufacturing technologies
  - Growing and sawing of ingots is a highly energy intensive process
  - Fairly easy for an electron generated in another molecule to hit a hole left behind in a previous photoexcitation.
  - Much of the energy of higher energy photons, at the blue and violet end of the spectrum, is wasted as heat

Second Generation: Overview

Thin-film Technology

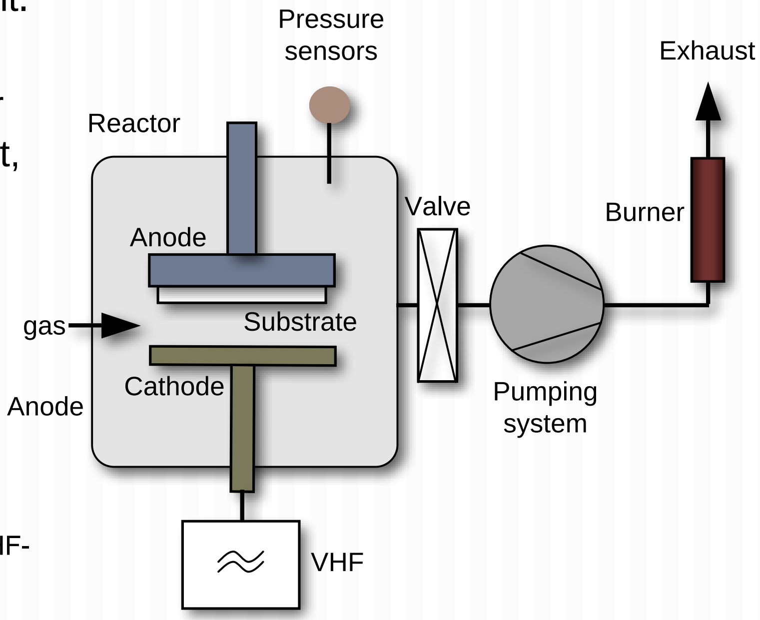
- Based on the use of thin-film deposits of semiconductors.
- Using of thin-films reduces mass of material required for cell design.
- Contributes greatly to reduced costs for thin film solar cells.
- Several technologies/semiconductor materials currently under investigation or in mass production
- Deposition of thin layers of non-crystalline-silicon materials on inexpensive substrates using PECVD.
- Devices initially designed to be high-efficiency, multiple junction photovoltaic cells.

Second Generation: PECVD

Plasma **E**nhanced **C**hemical **V**apor **D**eposition

- Thin-film deposition
  - Technique for depositing a thin film of material onto a substrate.
  - Layer thickness can be controlled to within a few tens of nanometers
  - Single layers of atoms can be deposited

- Chemical vapor deposition (CVD)
  - Chemical process using a gas-phase precursor.
  - Often a halide or hydride of the deposited element.
- PECVD - Plasma Enhanced CVD
  - Uses an ionized vapor, or plasma, as a precursor
  - Relies on electromagnetic means (electric current, microwave excitation) to produce plasma.

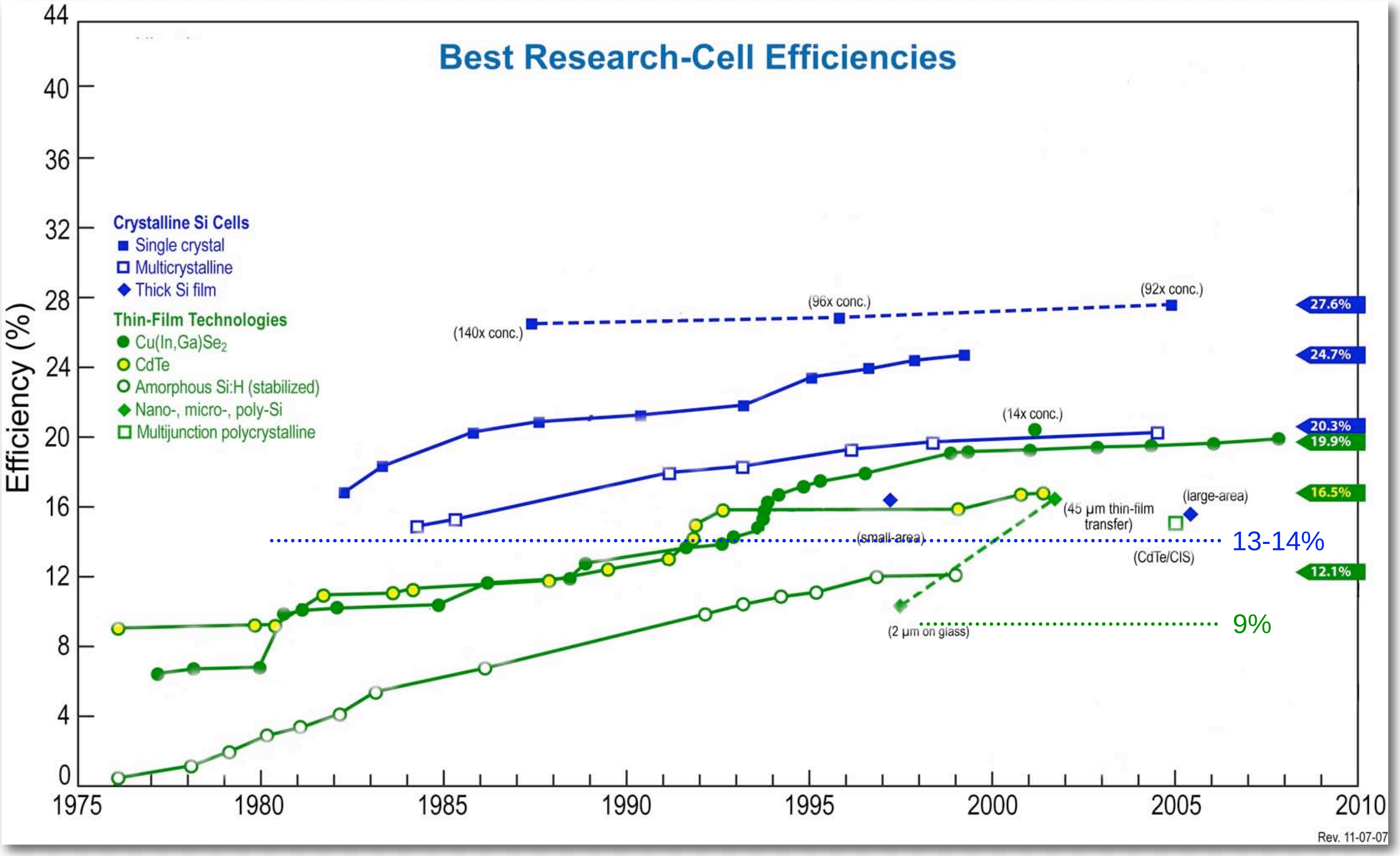


Schematic of a single-chamber VHF-GD deposition system

Second Generation: Types

- Amorphous silicon cells deposited on stainless-steel ribbon
  - Can be deposited over large areas by plasma-enhanced chemical vapor deposition
  - Can be doped in a fashion similar to c-Si, to form p- or n-type layers
  - Used to produce large-area photovoltaic solar cells
  - Band gap ~ 1.7 eV
- Polycrystalline silicon
  - Consists solely of crystalline silicon grains (1mm), separated by grain boundaries
  - Main advantage over amorphous Si: mobility of the charge carriers can be orders of magnitude larger
  - Material shows greater stability under electric field and light-induced stress.
  - Band gap ~ 1.1 eV
- Cadmium telluride (CdTe) cells deposited on glass
  - Crystalline compound formed from cadmium and tellurium with a zinc blende (cubic) crystal structure (space group F43m)
  - Usually sandwiched with cadmium sulfide (CdS) to form a p-n junction photovoltaic solar cell.
  - Cheaper than silicon, especially in thin-film solar cell technology - not as efficient
  - Band gap ~ 1.58 eV
- Copper indium gallium diselenide (CIGS) alloy cells
  - Deposited on either glass or stainless steel substrates
  - More complex heterojunction model
  - Band gap ~ 1.38 eV

Second Generation: Research Cells



Source: National Renewable Laboratory

Second Generation: Evaluation

- Advantages
  - Lower manufacturing costs
  - Lower cost per watt can be achieved
  - Reduced mass
  - Less support is needed when placing panels on rooftops
  - Allows fitting panels on light or flexible materials, even textiles.
- Disadvantages
  - Typically, the efficiencies of thin-film solar cells are lower compared with silicon (wafer-based) solar cells
  - Amorphous silicon is not stable
  - Increased toxicity

Third Generation: Overview

Different Semiconductor Technology

- Very different from the previous semiconductor devices
- Do not rely on a traditional p-n junction to separate photogenerated charge carriers.
- Devices include:
  - Nanocrystal solar cells
  - Photoelectrochemical cells
    - Gräetzel Cell
  - Dye-sensitized hybrid solar cells
  - Polymer solar cells

Third Generation: Types

Nanocrystal solar cells

- Solar cells based on a silicon substrate with a coating of nanocrystals
- Silicon substrate has small grains of nanocrystals, or quantum dots
  - Lead selenide (PbSe) semiconductor
  - Cadmium telluride (CdTe) semiconductor
- Quantum dot is a semiconductor nanostructure
  - Confines the motion of conduction band electrons, valence band holes, or excitons in all three spatial directions.
- Thin film of nanocrystals is obtained by a process known as “spin-coating”
- Excess amount of solution placed onto a substrate then rotated very quickly
- Higher current potential for solar cells

Third Generation: Types

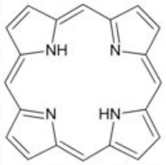
Photoelectrochemical (PEC) cells

- Separate the two functions provided by silicon in a traditional cell design
- Consists of a semiconducting photoanode and a metal cathode immersed in an electrolyte.
  - $K_3\ Fe(CN)_6/K_4\ Fe(CN)_6$
  - Iodide/Triiodide
  - $Fe(CN)_6^{4-}/Fe(CN)_6^{3-}$
  - Sulphide salt/sulphur
- Charge separation not solely provided by the semiconductor, but works in concert with the electrolyte.
- Gräetzel cells
  - Dye-sensitized PEC cells
  - Semiconductor solely used for charge separation,
  - Photoelectrons provided from separate photosensitive dye
  - Overall peak power production represents a conversion efficiency of about 11%

Third Generation: Gräetzel Cells

Dyes

- ruthenium metal organic complex
- carboxylic acid functionalized porphyrin arrays

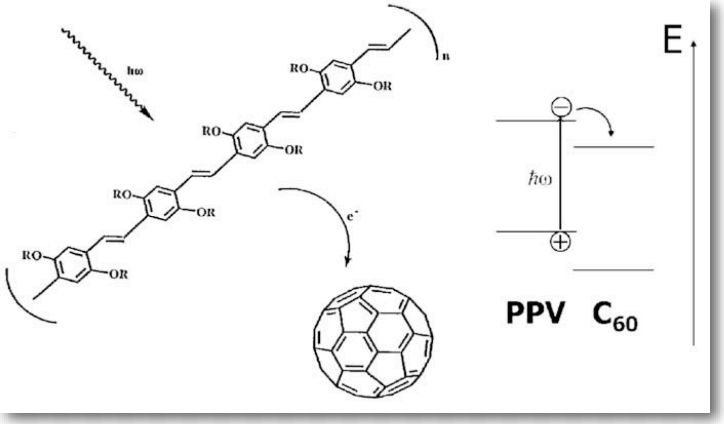


- Dye molecules are hit by light
- Electrons in the dye are transmitted to TiO_2.
- The electrons are collected by front electrode and supplied to external load.
- Dye molecules are electrically reduced to their initial states by electrons transferred from redox couple in the electrolyte.
- The oxidized ions in the electrolyte, diffuse to the back electrode to receive electrons

Third Generation: Types

Polymer solar cells

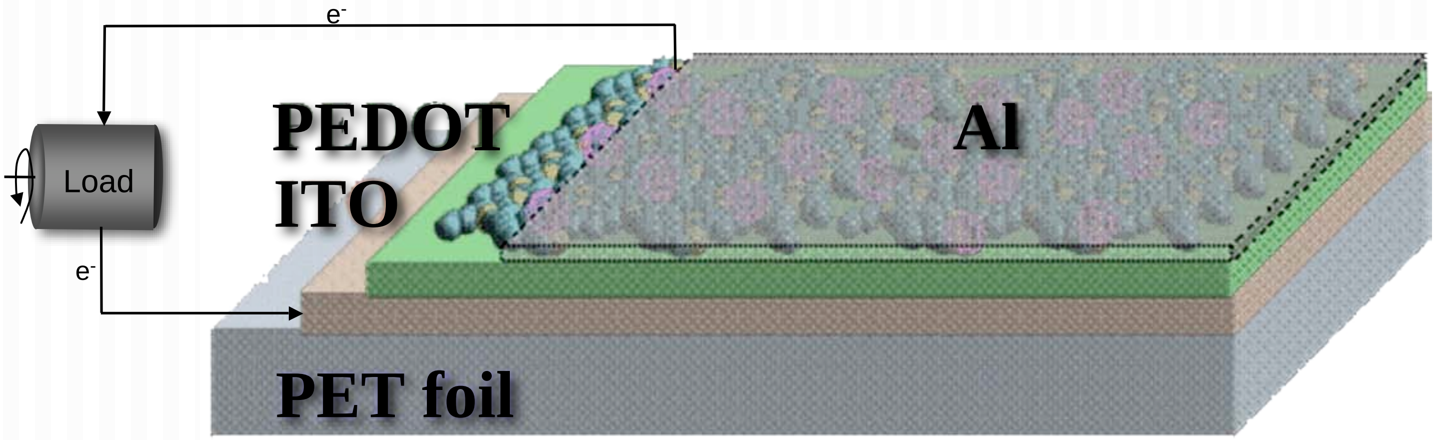
- ‘Bulk heterojunctions’ between an organic polymer and organic molecule as electron acceptor.
- Fullerene embedded into conjugated polymer conductor
- Lightweight, disposable, inexpensive to fabricate, flexible, designable on the molecular level, and have little potential for negative environmental impact.
- Present best efficiency of polymer solar cells lies near 5 percent
- Cost is roughly one-third of that of traditional silicon solar cell technology
- Band gaps ≥ 2eV



Nov-21-07

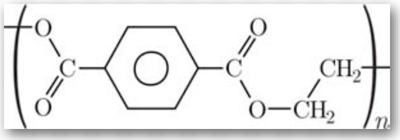
Third Generation: Polymer Cell

- After excitation in photoactive polymer, the electron is transferred to the C_{60} due to its higher electron affinity
- Photoinduced quasiparticle (polaron P^+) formed on the polymer chain and fullerene ion-radical C_{60}^-

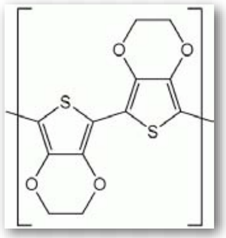


The scheme of plastic solar cells.

- PET - Polyethylene Terepthalate
- ITO - Indium Tin Oxide (In_2O_3/SnO_2)
- PEDOT - Poly(3,4-ethylenedioxythiophene)
- Al - Aluminium



PET



PEDOT

Third Generation: Types

Dye sensitized solar cell (DSSC)

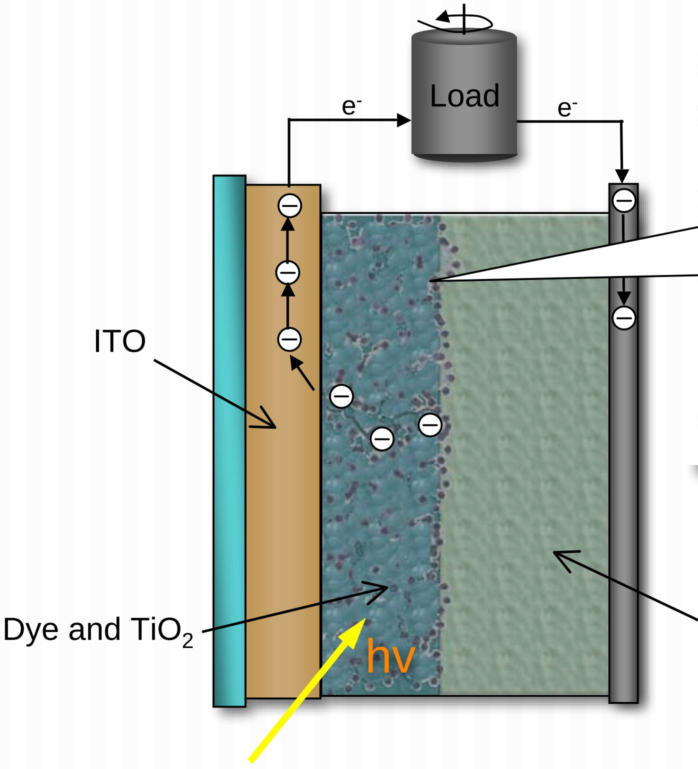
- Separate the two functions provided by silicon in a traditional cell design
- Semiconductor used solely for charge separation
- Photoelectrons provided from separate photosensitive dye
  - Typically a ruthenium metal organic dye

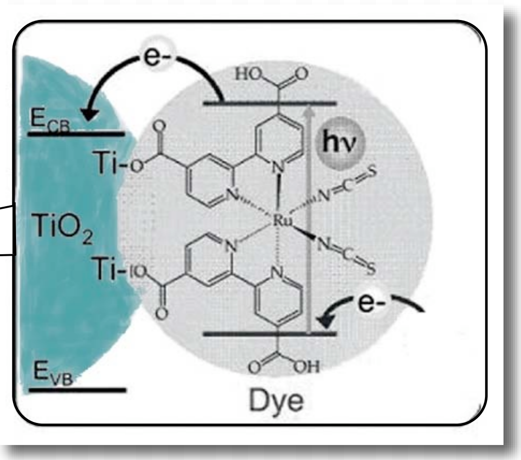
- Cell Design:
  - Dye-sensitized titanium dioxide
  - Coated and sintered on a transparent semi-conducting oxide (ITO)
  - p-type, polymeric conductor, such as PEDOT or PEDOT:TMA, which carries electrons from the counter electrode to the oxidized dye.

- Similar to Gräetzel cell except the electrolyte is replaced with a conductive polymer.

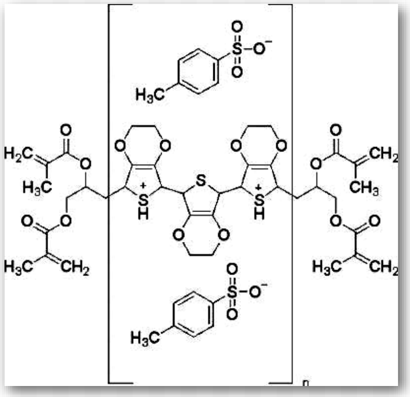
Third Generation: DSSC

Dye-sensitized, hole-conducting polymer cell





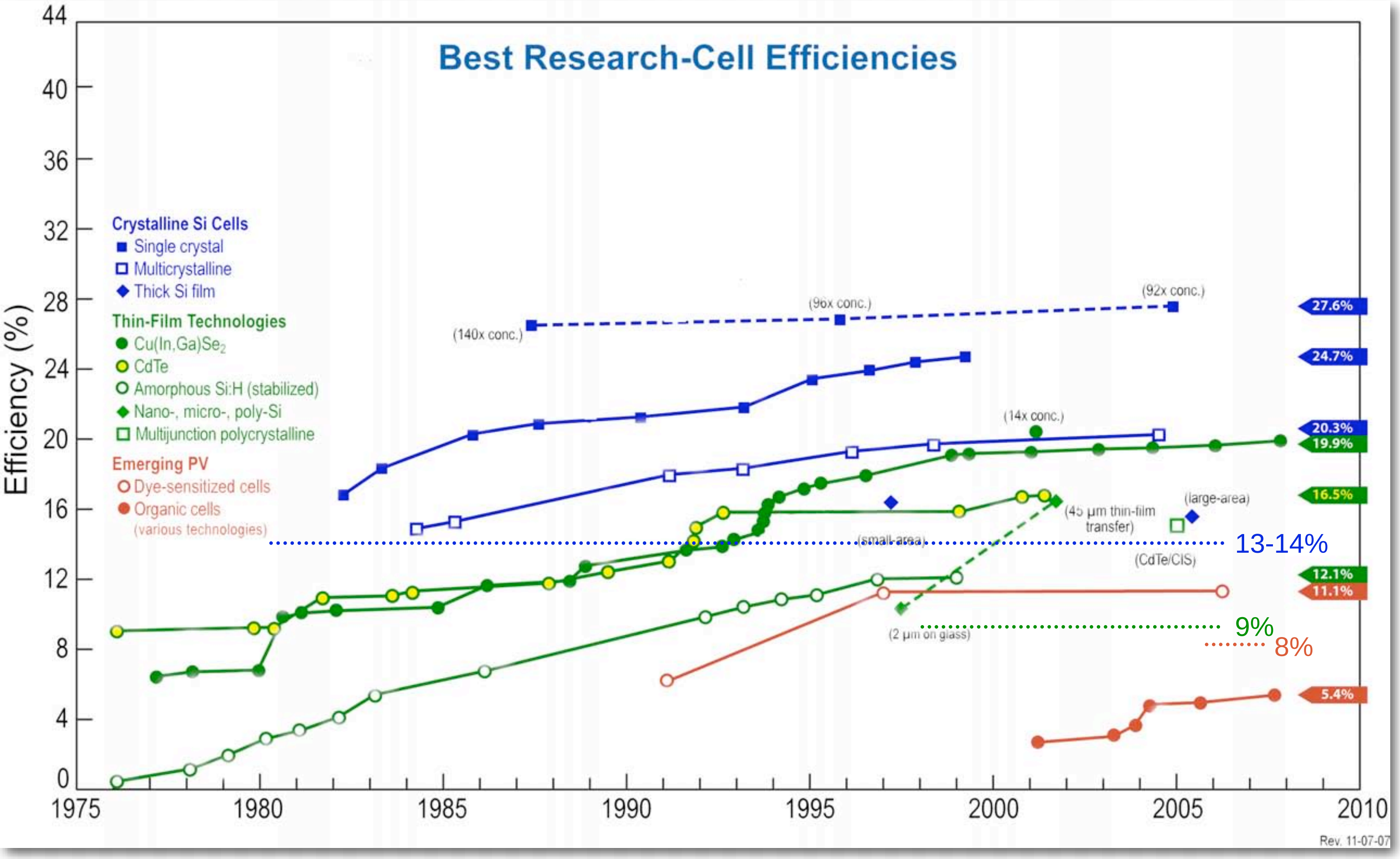
PEDOT:TMA



The scheme of DSSC.

- PET - Polyethylene Terephtalate
- ITO - Indium Tin Oxide
- PEDOT:TMA - Poly(3,4-ethylenedioxythiophene)-tetramethacrylate

Third Generation: Research Cells



Source: National Renewable Laboratory

Third Generation: Evaluation

- Advantages
  - Low-energy, high-throughput processing technologies
  - Polymer cells - solution processable, chemically synthesized
  - Polymer cells - low materials cost
  - Gräetzel cells - attractive replacement for existing technologies in “low density” applications like rooftop solar collectors
  - Gräetzel cells - Work even in low-light conditions
  - DSSC - potentially rechargeable => upgradeable?

- Disadvantages
  - Efficiencies are lower compared with silicon (wafer-based) solar cells
  - Polymer solar cells:
    - Degradation effects: efficiency is decreased over time due to environmental effects.
    - High band gap
  - PEC cells suffer from degradation of the electrodes from the electrolyte

Fourth Generation

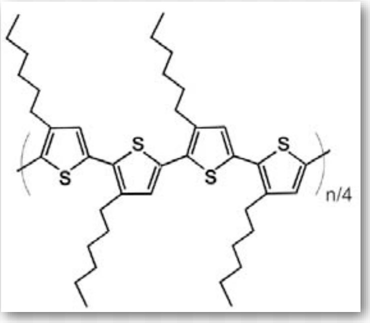
Hybrid - nanocrystal/polymer cell

Composite photovoltaic technology
combining elements of the solid
state and organic PV cells

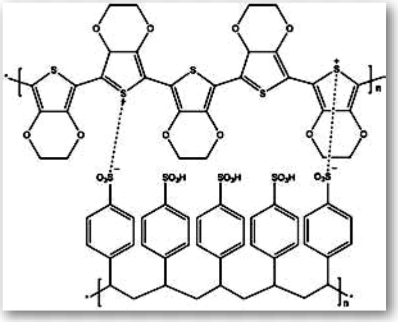
Fourth Generation: Overview

- Use of polymers with nanoparticles mixed together to make a single multispectrum layer.
- Significant advances in hybrid solar cells have followed the development of elongated nanocrystal rods and branched nanocrystals
- More effective charge transport.
- Incorporation of larger nanostructures into polymers required optimization of blend morphology using solvent mixtures.

- Cell Design:
    - Solid state nanocrystals (Si, In, $CuInS_2$, CdSe)
    - Imbedded in light absorbing polymer (P3HT)
    - p-type, polymeric conductor, such as PEDOT:PS, carries ‘holes’ to the counter electrode.
    - Coated on a transparent semi-conducting oxide (ITO)

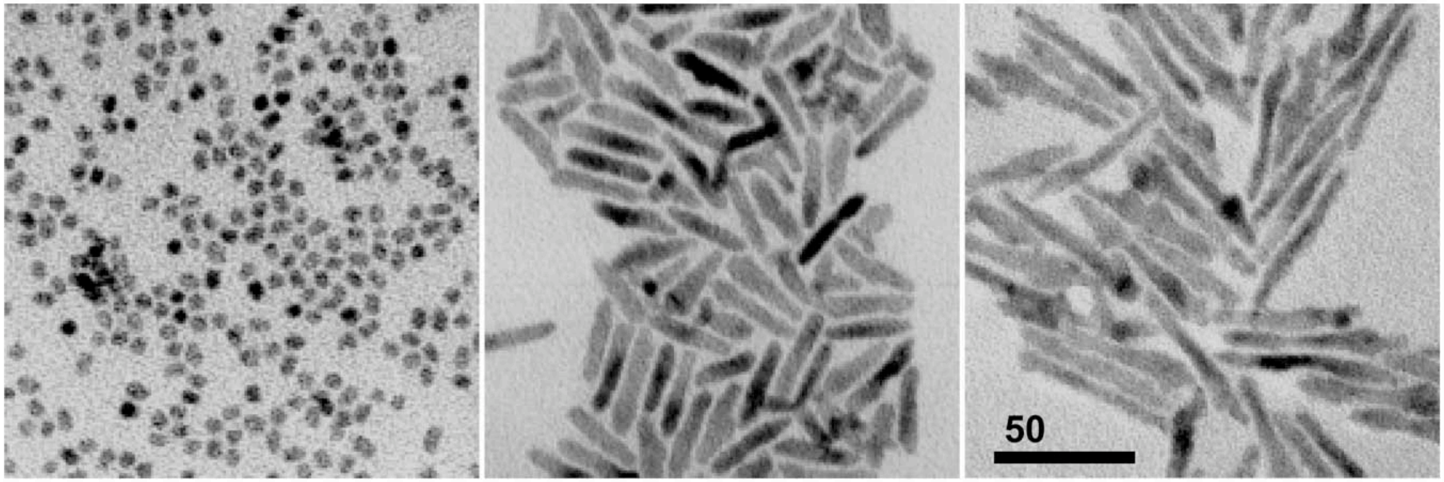


P3HT



PEDOT:PS

Fourth Generation: Nanocrystals

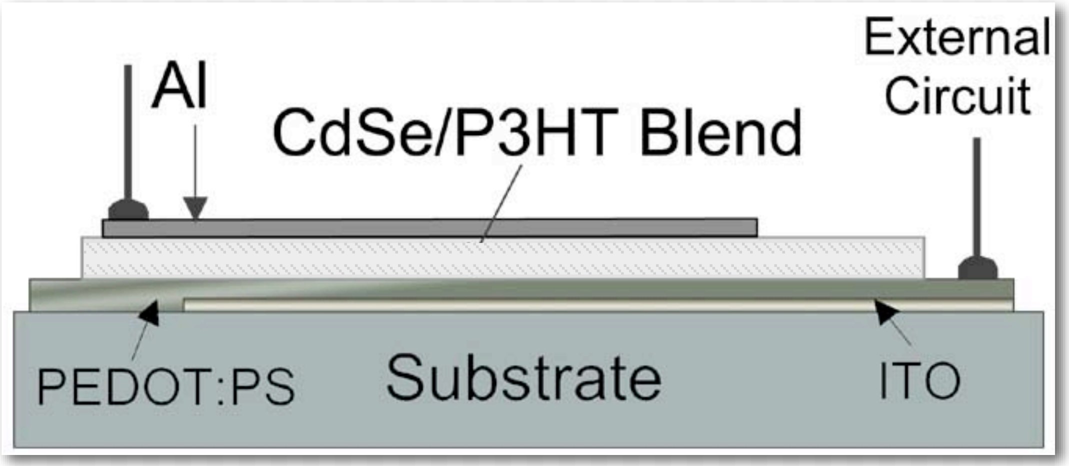


CdSe nanocrystals shown by transmission electron micrographs (TEMs) at the same scale, have dimensions:
(A) 7 nm by 7 nm, (B) 7 nm by 30 nm and (C) 7 nm by 60 nm.

Fourth Generation: Hybrid

- Hybrid - nanocrystalline oxide polymer composite cell

1. Photon absorbed by polymer (P3HT)
2. Photon excites electron in nanocrystal
3. Excited electron is conducted to electrode
4. Polymer (PEDOT:PS) conducts ‘hole’ to counter electrode
5. Current used to drive load
6. Electron recombines with hole



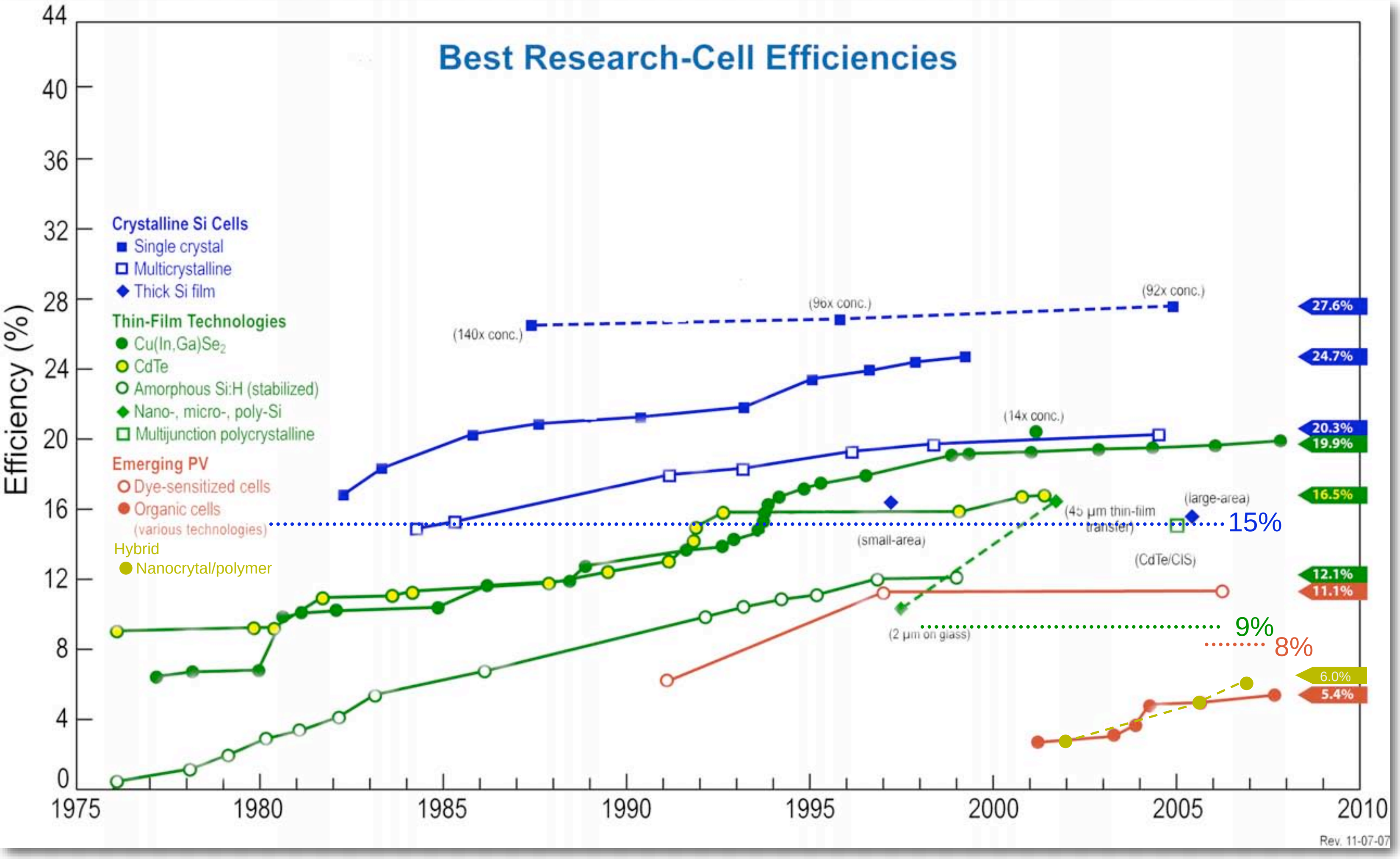
Scheme of hybrid solar cells.

- CdSe - cadmium (II) selenide
- P3HT - Poly-3-hexylthiophene
- ITO - Indium Tin Oxide (In_2O_3/SnO_2)
- PEDOT:PS - Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)
- Al - Aluminium

Fourth Generation: Future

- Thin multi spectrum layers can be stacked to make multispectrum solar cells.
  - Layer that converts different types of light is first
  - Another layer for the light that passes
  - Lastly is an infra-red spectrum layer for the cell
  - Converting some of the heat for an overall solar cell composite
  - More efficient and cheaper
  - Based on polymer solar cell and multi junction technology
- Future advances will rely on new nanocrystals, such as cadmium telluride tetrapods.
  - potential to enhance light absorption and further improve charge transport.
- Gains can be made by incorporating application-specific organic components, including electroactive surfactants which control the physical and electronic interactions between nanocrystals and polymer.

Fourth Generation: Research Cells



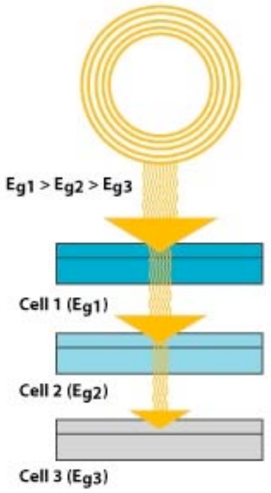
Source: National Renewable Laboratory

Fourth Generation: Evaluation

- Advantages
  - Solution processable
  - Lower materials cost (polymer)
  - Self-assembly
  - Printable nanocrystals on a polymer film
  - Improved conversion efficiency (potentially)
- Disadvantages
  - Efficiencies are lower compared to silicon (wafer-based) solar cells
  - Potential degradation problems similar to polymer cells
  - Optimize matching conductive polymers and nanocrystal

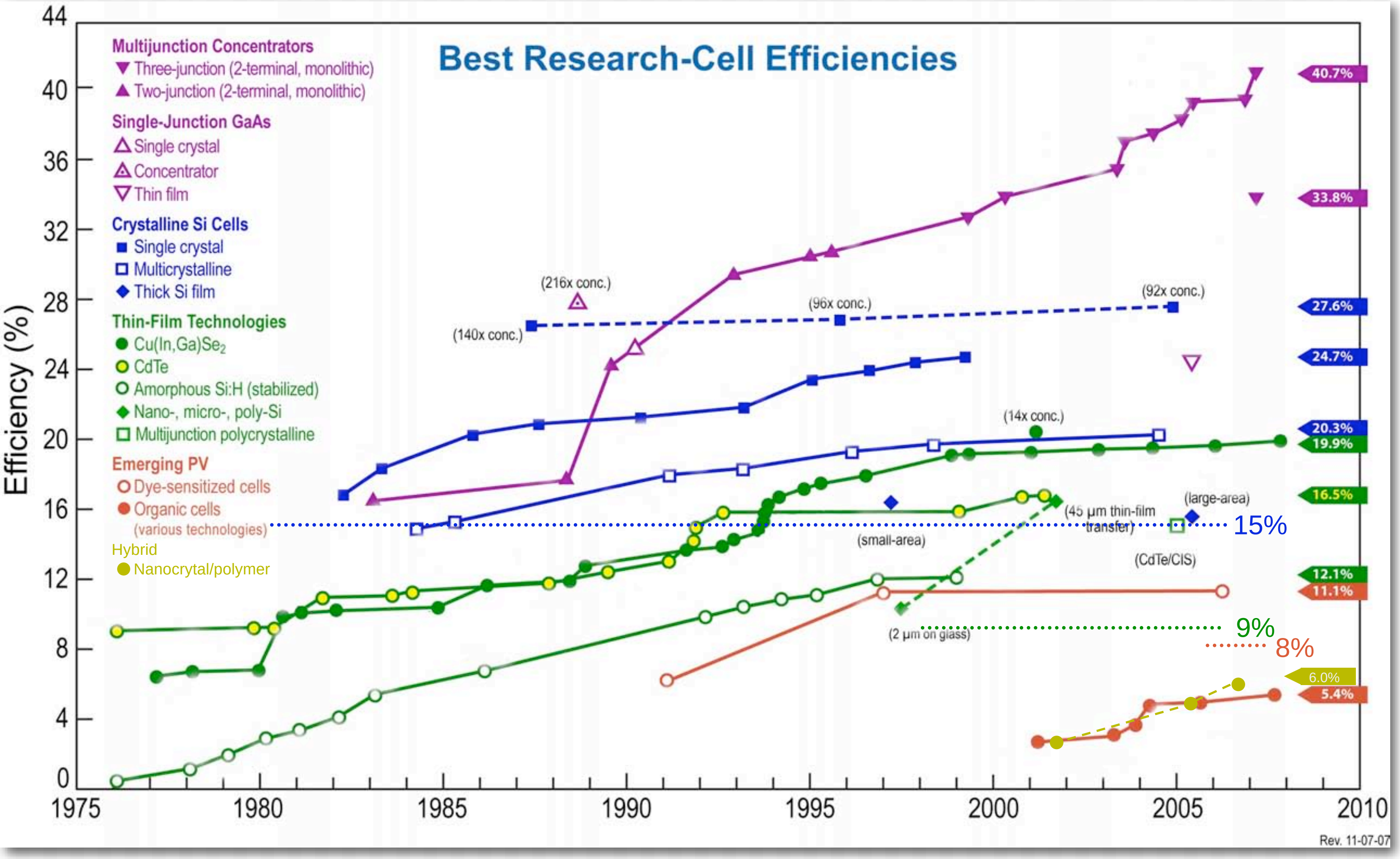
Technological Improvements

- Multijunction Devices
  - Stack of individual single-junction cells in descending order of bandgap.
  - Top cell captures high-energy photons and passes rest on to lower-bandgap cells.
  - Mechanical stack:
    - Two individual solar cells are made independently
    - Then are mechanically stacked, one on top of the other.
  - Monolithic stack:
    - One complete solar cell is made first
    - Layers for subsequent cells are grown or deposited.
  - Example: GaAs multijunction
    - Triple-junction cell of semiconductors: GaAs, Ge, and $GaInP_2$



- Concentrator Photovoltaic (CPV)
  - Use large area of lenses or mirrors to focus sunlight on a small area of photovoltaic cells
  - Increase efficiency ~35%

Research Cells



Nov-21-07

Summary

Technology	Com Eff (%)	Champ Eff (%)	Module ($/W)	Installed ($/W)	LCOE (cents/kWh)
Wafer Si	15	25	2	8	17
a-Si	6.5	13	1.2	4.5	21.7
c-Si	5	10	1.3	4.8	18.3
CdTe	9	16.5	1.21	4.5	19.9
CIGS	9.5	19.5	1.8	6.3	22.2
Organic PV	-	5.2	*0.70*	-	-
DSSC	8	11	1.9	-	-
Hybrid	-	6	-	-	-
Coal					5 to 8

- Polymer Cells
  - Not commercially available yet
  - Much lower cost
  - Shorter payback period (<1 yr)
- DSSC
  - 1st commercial plant Oct 07 - *G24 Innovations*
  - Build your own lab kits - 5 cells/$66 (www.solideas.com)
- Hybrid
  - Not commercially available yet
  - Similar costs to polymer cell
  - Potentially much greater efficiency

Efficiency (η) is calculated:

$$\eta = \frac{P_m}{E \times A_c}$$

- AM 1.5
- $P_m = 1000\ W/m^2$
- $A_c = 1\ m^2$
- E = energy output (W)

References

1. Efficient Titanium Oxide/Conjugated Polymer Photovoltaics for Solar Energy Conversion. Advanced Materials, 2000. 12(22): p. 4.
2. Alivisatos, A.P., Hybrid Nanorod-Polymer Solar Cell, in Subcontractor Report, NREL, Editor. 2002, National Renewable Energy Laboratory: Golden, CO. p. 13.
3. Arici, E., N.S. Sariciftci, and D. Meissner, Advanced Functional Materials, 2003. 13(2): p. 7.
4. Baumann, A., et al., Photovoltaic Technology Review. 2004, University of California at Berkeley: Berkeley, CA. p. 40.
5. C. J. Brabec, N.S.S.J.C.H., Plastic Solar Cells. Advanced Functional Materials, 2001. 11(1): p. 15-26.
6. Campbell, W., Harvesting the Sun with Synthetic Porphyrin Dyes Massey University: Auckland, New Zealand.
7. Capper, P. and Inspec, Properties of narrow gap cadmium-based compounds. EMIS datareviews series, no. 10. 1994, London: INSPEC, the Institution of Electrical Engineers.
8. Cravino, A. and N.S. Sariciftci, Double-cable polymers for fullerene based organic optoelectronic applications. Journal of Materials Chemistry, 2002. 12: p. 12.
9. Energy, U.S.D.o. Photovoltaics. Solar Energy Technologies Program 2006 04/13/2006 [cited 2007 November 8]; Available from: http://www1.eere.energy.gov/solar/photovoltaics.html.
10. Feitknecht, L.A., Microcrystalline Silicon Solar Cells In The N-I-P Configuration: Optimisations On Light Scattering Back-Reflectors, in Institut de Microtechnique. 2003, Universit´e de Neuchˆatel.
11. Gasman, L. Thin-film and Organic PV on the Rise. 2006 2006 [cited 2007 11/9/07]; Available from: http://www.renewableenergyaccess.com/rea/news/story?id=44634.
12. Gebeyehua, D., et al., Synthetic Metals 2001. 125(3): p. 8.
13. Ginley, D., National Solar Technology Roadmap: Organic PV in National Solar Technology Roadmap. 2007, National Renewable Energy Laboratory: Golden, CO. p. 5.
14. Gratzel, M., J. of Sol-Gel Sci. and Tech., 2001. 22: p. 7.
15. Halme, J., Dye-sensitized nanostructured and organic photovoltaic cells: technical review and preliminary tests, in Department of Engineering Physics and Mathematics. 2002, Helsinki University of Technology. p. 115.
16. Hoppe, H. and N.S. Sariciftci, Organic solar cells: An overview. Journal of Materials Research, 2004. 19(7): p. 22.
17. Hoppe, H. and N. Serdar Sariciftci, Organic solar cells: An overview J. Mater. Res, 2004. 19(7): p. 1924-1945.
18. Keyes, B., National Solar Technology Roadmap: Film-Silicon PV in National Solar Technology Roadmap. 2007, National Renewable Energy Laboratory: Golden, CO. p. 7.

References (cont)

19. Laboratory, N.R.E. [cited; Available from: www.nrel.gov.
20. Licht, S., A Description of Energy Conversion in Photoelectrochemical Solar Cells. Nature, 1987. 300(12): p. 148-151.
21. Licht, S. and D. Peramunage, Efficient Photoelectrochemical Solar Cells from Electrolyte Modification. Nature, 1990. 345(24): p. 330-33.
22. Lorenzo, E., Solar electricity engineering of photovoltaic systems. 1994, Sevilla, Spain: PROGENSA.
23. Luque, A. and S. Hegedus, Handbook of photovoltaic science and engineering. 2003, Hoboken, NJ: Wiley.
24. Matson, R., National Solar Technology Roadmap: Sensitized Solar Cells, in National Solar Technology Roadmap. 2007, National Renewable Energy Laboratory: Golden, CO. p. 6.
25. Mozer, A.J. and N.S. Sariciftci, Conjugated polymer photovoltaic devices and materials. Comptes Rendus Chimie 2006. 9(5-6): p. 568-577.
26. Noufi, R. and K. Zweibel, High Efficiency CdTe and CIGS Thin Film Solar Cells: Highlights of the Technologies Challenges, in 006 IEEE 4th World Conference on Photovoltaic Energy Conversion (WCPEC-4). 2006: Waikoloa, Hawaii.
27. Sopori, B., National Solar Technology Roadmap: Wafer-Silicon PV in National Solar Technology Roadmap. 2007, National Renewable Energy Laboratory: Golden, CO. p. 6.
28. Tennakone, K., et al., An efficient dye-sensitized photoelectrochemical solar cell made from oxides of tin and zinc. Chemical Communications, 1998: p. 2.
29. Tongpoola, R., et al., Dye-SensitizedSolarCell (DSSC), National Metal and Materials Technology Center (MTEC): Klongluang, Pathumthani, 12120, Thailand. p. 1.
30. Ullal, H., National Solar Technology Roadmap: CdTe PV in National Solar Technology Roadmap. 2007, National Renewable Energy Laboratory: Golden, CO. p. 6.
31. von Roedern, B., National Solar Technology Roadmap: CIGS PV in National Solar Technology Roadmap. 2007, National Renewable Energy Laboratory: Golden, CO. p. 6.
32. Watt, A.R., et al., Lead sulfide nanocrystal: conducting polymer solar cells. J. Phys. D: Appl. Phys, 2005. 38: p. 2006-2012.
33. Wikipedia. Solar Cell. 2007 6 November 2007 [cited 2007 November 8]; Available from: http://en.wikipedia.org/wiki/Solar_cell.
34. Wormser, P. and R. Gaudiana, Polymer Photovoltaics –Challenges and Opportunities, in NCPV and Solar Program Review Meeting 2003. 2003, NREL/CD.

The End

Thank you!