Solar Cells: Alternatives to Crystalline Silicon

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The Energy Crisis

- The world uses about 13 TW of power today. (TW = 10^{12} W)
- We probably need to generate ~ 30 TW of power in 2050.
- •Current supply of petroleum and natural gas will eventually run out.
- •If we do not dramatically reduce our emissions of carbon dioxide, the average temperature of the planet will probably rise by several degrees.

A Renewable Energy Economy



M.H. Hoffert et al. *Science* **298** (2002) p. 981.

Potential of Carbon-Free Energy

- Biomass: 7-10 TW available from the entire agricultural land mass of the planet
- *Wind*: 2.1 TW from covering all suitable (class 3) global land with wind mills
- *Nuclear*: 8 TW if we build one new nuclear power plant every 2 days until 2050
- *Hydroelectric*: 1.5 TW left to tap by damming all available rivers.

Inorg. Chem. 2005, 44, 6799-6801.

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Why Solar?

- We need ~ 30 TW of power, the sun gives us 120,000 TW.
- Solar cells are safe and have few non-desirable environmental impacts.
- Solar cells can be easily incorporated into distributive systems.
- Solar cells provide electricity exactly when we need it the most (hot sunny days when people run their air conditioners).

Where is Solar Industry Now

600 55 50 45 Megawatts 35 30 200 150 100 50 2000 2001 1969 1992 1994 1995 1996 1997 1998 1999 2002 1993 1988 1990 1991 Rest of World э 4.6 4.4 6.35 9.75 9.4 18.7 20.5 23.42 32.62 47 5 5.6 53.55 13.4 21.7 33.5 Europe 6.7 7.9 10.2 16.4 16.55 20.1 18.8 30.4 40 60.66 135.05 86.38 12.0 14.2 19.9 16.7 16.5 21.2 35 🖬 Japan 16.8 18.8 16.4 48 80 128.6 171.22 251.07 14.1 25.64 34.75 74.97 100.32 120.60 11.1 14.8 17.1 18.1 22.44 38.85 51 53.7 60.8 United States 55.4 33.6 40.2 46.5 57.9 60.09 69.44 77.6 88.6 125.8 154.9 201.3 Total 287.65 390.54

It isn't a major energy provider yet, but it is growing at over 30% per year.

MRS Bulletin, Jan. 2005

Crystalline Silicon Solar Cell (c-Si)

- World Record: $\eta = 24\%$
- Typical Module: η=12%-18%
- Advantage:
 - Well-developed and reliable (typical life time > 25 yr)
 - Economics of scale
- Disadvantage:
 - Still too expensive for large-scale "solar power plant"
 - Incompatible with flexible substrates





Band Diagram of c-Si Solar Cell

p-n junction: diffusion transport & drift transport



Shockley-Queisser Limit: $\eta_{max} = 32\%$

Why is c-Si Solar Cell so Pricey?

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- Price of raw material: high-purity silicon
 - Competition from semiconductor industry
 - Silicon is indirect band-gap material -> need 300µm
- Rigidity of the cell and module
 - Transportation
 - Installation



The Generations of Solar Cell Technology

1st Generation: Single crystals solar cells (Si, GaAs)

2nd Generation: Thin Film (uses less material)

3rd Generation: Uses advanced concepts to break the 32 % efficiency limit for single semiconductor cells.



M. Green, University of New South Wales

Requirement for thin-film materials

- Low-cost
- Non-toxic
- Strong light absorber
- Mechanically Robust
- Stable
- Good charge transport
- Can be easily doped

Types of Gen-II Solar Cells

Thin-Film solar cells

- Amorphous silicon (a-Si:H)
- Copper-Indium-Gallium-Selenide (CIGS)
- Cadmium Telluride (CdTe)
- Solar cells with donor-acceptor pair
 - Dye-sensitized solar cells (DSC)

Amorphous Silicon (a-Si:H)

- Second most produced type of solar cell (mostly for calculators)
 - first made in 1974
 - efficiencies in the lab for multijunction cells are up to ~13%, but modules are only 5-9%





a-Si:H Properties

- Tetrahedral bonding with no long range order
- Variation in bond lengths and strain
- Direct band gap at ~1.7eV
- Dangling bonds are passivated with hydrogen, films are typically ~10 atomic % hydrogen







Deposition of a-Si:H – PECVD

- PECVD =plasma enhanced chemical vapor deposition
- Can be deposited over large areas in ~1 hour
- CVD technique is well developed by the display industry. Gen 7 uses 2.16 m x 2.46 m sheets



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Light Degradation: Staebler-Wronski Effect

 Strained Si-Si & Si-H bonds -> bond-breaking under light and creating defects



- This usually decreases the efficiency 10-30%, and efficiencies are usually reported as "stabilized efficiencies"
- People are performin g research on alternative deposition techniques

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Properties of CIS/CIGS solar cells

- CIGS = Copper Indium Gallium Diselenide, CuGa_xIn_{1-x}Se
- Due to high absorptivity, only 2 µm of CIS/CIGS is needed
- CIS has direct band gap of 1.05 eV
- Record Efficiency: 19.2%.
- Tolerant of defects/impurities



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CIS/CIGS Solar Cell Structure





A. Bosio et al.: CulnGaSe2 and CdTe polycrystalline thin film solar cells

CIGS Physical Vapor Codeposition

- ^{1.} Form the $(In,Ga)_2Se_3$ precursor then heat to 560C in an Se vapor.
- 2. Cu and Se are evaporated to bring the overall composition to be Cu-rich (0.97< [Cu]/[In]+[Ga]<1.08).
- 3. Deposit In+Ga+Se to make it Cu-poor.
- 4. Slow cool in Se vapor



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NREL, 1994

Scarcity / Toxicity of Materials

Indium is scarce

- Price fluctuates around \$900/kg
- Supply is mostly driven by LCD manufacturing
- No enough indium in earth's crust to generate 30 TW

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Cd is toxic

- Cd intake is cumulative
- Cd is highly deadly toxin



Non-toxic / abundant alternatives

- Absorbing layer: CIGS -> CZTS
 - Indium -> Zinc (Zn)
 - Gallium -> Tin (Sn)
 - Selenium -> Sulfur (S)
- Windows layer:
 CdS -> ZnO
- World record of CZTS: 5.4%



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Properties of CdTe solar cells

- Direct bandgap, Eg=1.5eV
- High absorption coefficient (5x10⁴ cm⁻¹) -> 3~8 micron
- High efficiency (Record:16.5%; Industry: 10.5%)
- Cheap substrate (commercial glass)
- Long term stability (20 years)

CdTe Solar Cell Structure



Deposition: Close-Spaced Sublimation (CSS)

- Sublimation of CdTe onto substrate that is ~mm away
- High deposition rate
- Larger grains (compare to other methods)
- Low vacuum (~1 torr)
 and temperature (<700 ° C)
- Easy to scale up



 Alternatives: Gas phase evaporation, spray pyrolysis, screen printing...

Health and Environmental Risks

- Cd has detrimental effects on lung, kidney and bone.
- CdTe is an inert compound. The release of Cd only happens at temperature above 1000 °C.
- CdTe PV modules is classified by federal government as non-hazardous waste.
- Most concerns lies within the Cd release in residential fires



"CdTe PV: Real and Perceived EHS Risks", Brookhaven National Laboratory.

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Dye-Sensitized Solar Cells (DSCs)

- Main distinction from semiconductor p-n junction:
 - Light absorption and charge transport by different materials.
 - Charge separation because of energy level difference.
- Conducting Record: 11% alass Module: 7% Electrolyte Cathode TiO₂ Dve Injection --hν Maximum voltage p-type hv n-type Red Mediator Interception Diffusion S°/S+

Materials used in DSCs

- Semiconductor: mesoporous metal oxide (TiO2) film
- Monolayer of Ruthenium-based dye molecules adsorbed onto mesoporous semiconductor.

Mesoporous TiO₂







Advantages of DSCs

- Cheap and not energy intensive to manufacture.
- Flexible substrate compatibility.
- Aesthetic potential market entry.
 - The color and transparency can be varied by dye loading
- Electron injection reduced recombination
 - Works better than other types of solar cell in low-light intensity





Main challenges facing DSCs

Improving Stability

- Detachment of dye from TiO2 surface
- Decomposition of dye
 - (20 year lifetime = 100 million turnovers)
 - -> Molecular engineering of dye molecules
- Evaporation of liquid electrolyte
 - -> Change to solid-state molecules or ionic liquids
- Improving Efficiency
 - Increase spectral overlap of dye ("black dye")
 - Use light-scattering techniques

Summary: Performance / R&D needs

Type of cell	Efficier Cell	ncy (%)* Module	Research and technology needs
Crystalline silicon	24	10–15	Higher production yields, lowering of cost and energy content
Multicrystalline silicon	18	9–12	Lower manufacturing cost and complexity
Amorphous silicon	13	7	Lower production costs, increase production volume and stability
CulnSe ₂	19	12	Replace indium (too expensive and limited supply), replace CdS window layer, scale up production
Dye-sensitized nanostructured materials	10–11	7	Improve efficiency and high- temperature stability, scale up production

Photoelectrochemical cells; Gratzel, M; Nature; Nov 15 2001; v.414, no.6861, p.338-344

Solar Cell Companies (partial list)





- Solar power is a viable renewable energy source.
- Solar cell market is still emerging, and it expects 20%+ annual growth in the next two decades.
- Various approaches are being pursued by multiple companies as alternatives to crystalline silicon solar cells.

A good (and short) review article of thin-film solar cells: "Photovoltaic Technology: The Case for Thin-Film Solar Cells." Shah et. al. *Science*, **285**, pp. 692-698 (1999).



