

CHEM 140a

Principles and Applications of Semiconductor Photoelectrochemistry



With
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Lecture Notes # 1a

Welcome to Semiconductor Photoelectrochemistry!

Semiconductors are very important. They are used in just about every electronic device, and they are the basis for solar energy. Although APh 183 and other APh classes are electronic device oriented, this class is focused more on solar energy devices. There will be some overlap between these classes at first as we cover fundamentals, but then we will apply them to solar energy.



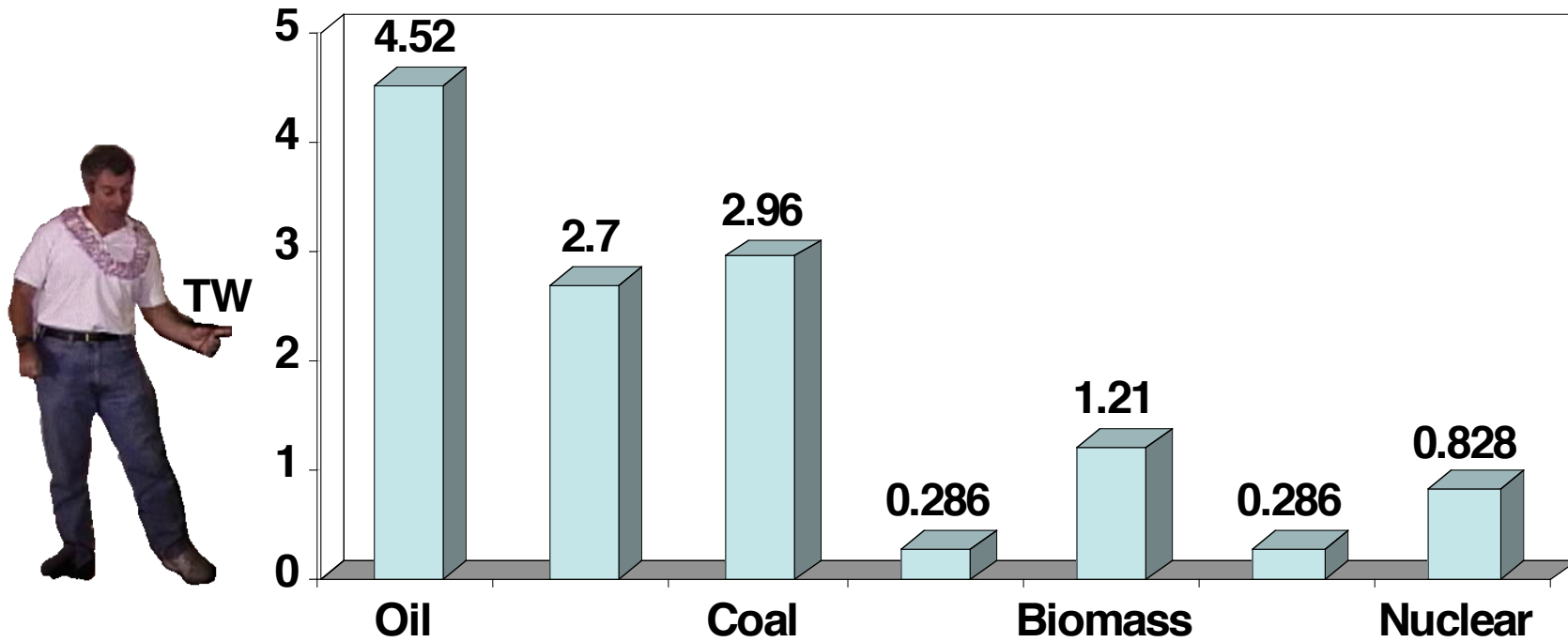
Course Syllabus

- Introduction
- Electronic Properties of Semiconductors
- Equilibrium at a Semiconductor/Liquid Junction
- Charge Transfer at Semiconductor/Liquid Junctions
- Recombination and Other Theories
- Techniques
- Strategies for the Design of Semiconductor/Liquid Junctions for Energy Conversion
- Recent Advances in Applications of Large Band Gap Semiconductor/Liquid Junctions

Why Study Solar Energy?

- Because anyone can tell you that:
 - Eventually the oil reserves will run out
 - Solar energy is quite clean
- Let's take a look at the numbers

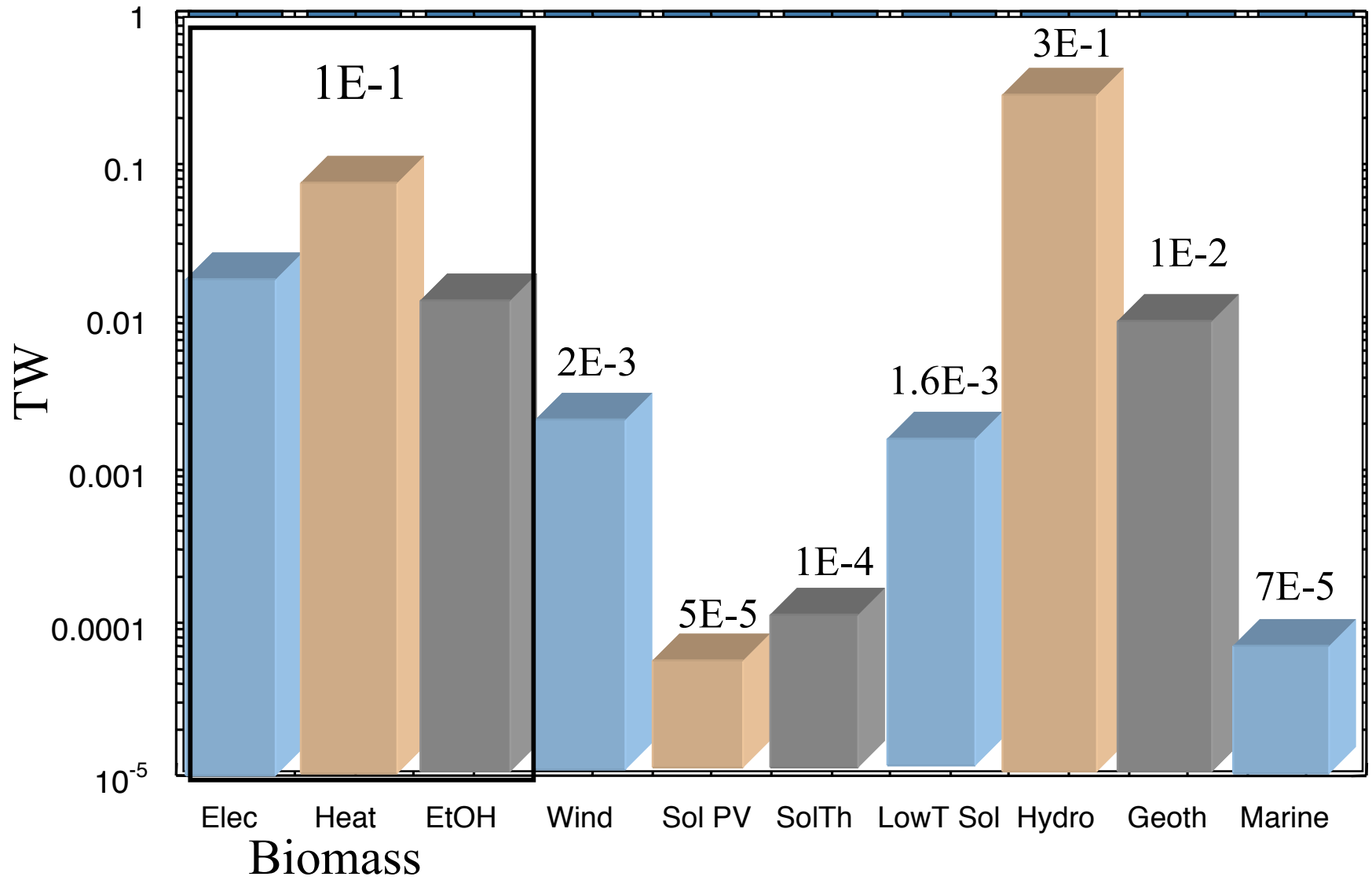
Mean Global Energy Consumption, 1998



Total: 12.8 TW

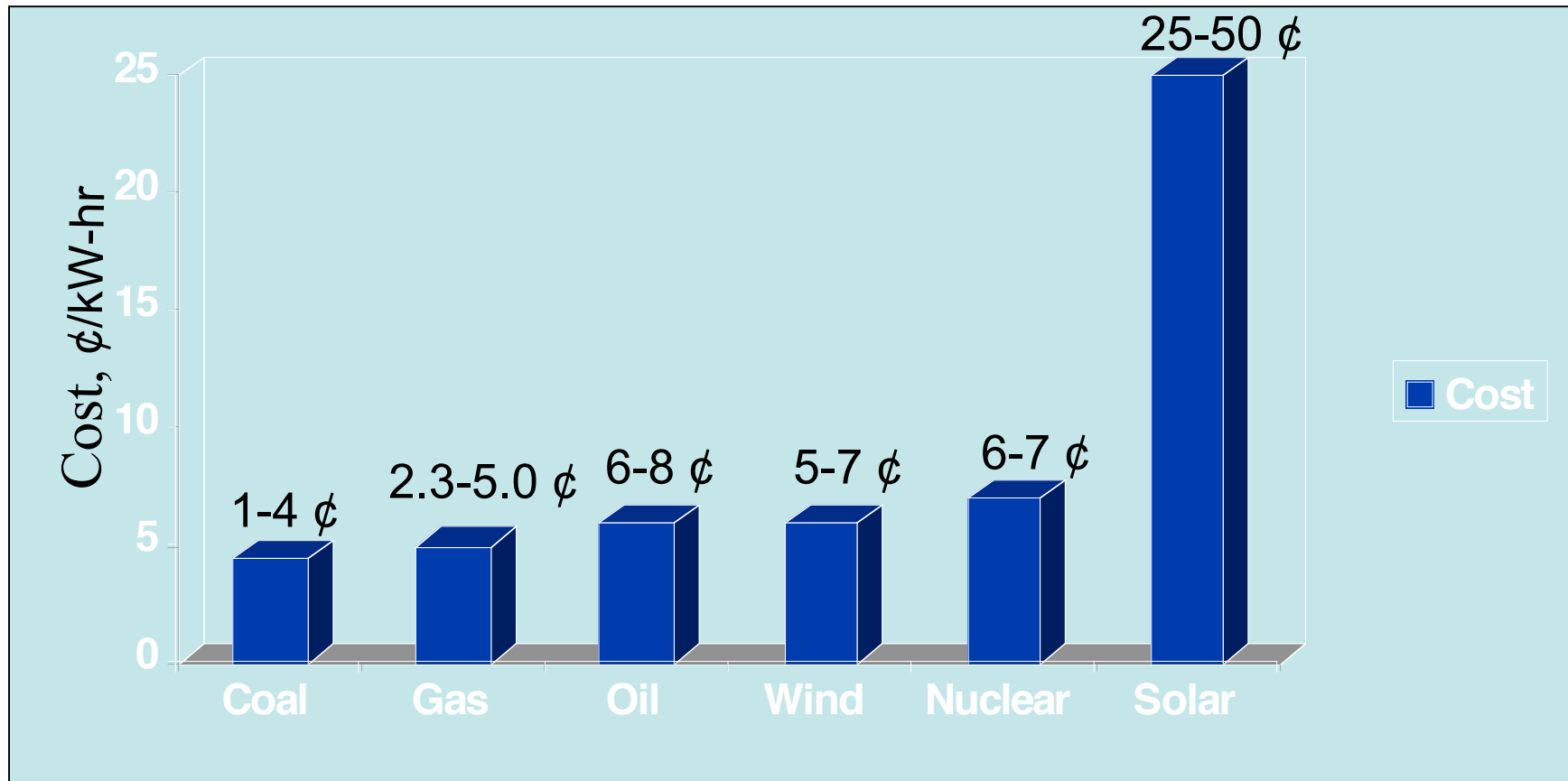
U.S.: 3.3 TW (99 Quads)

Energy From Renewables, 1998

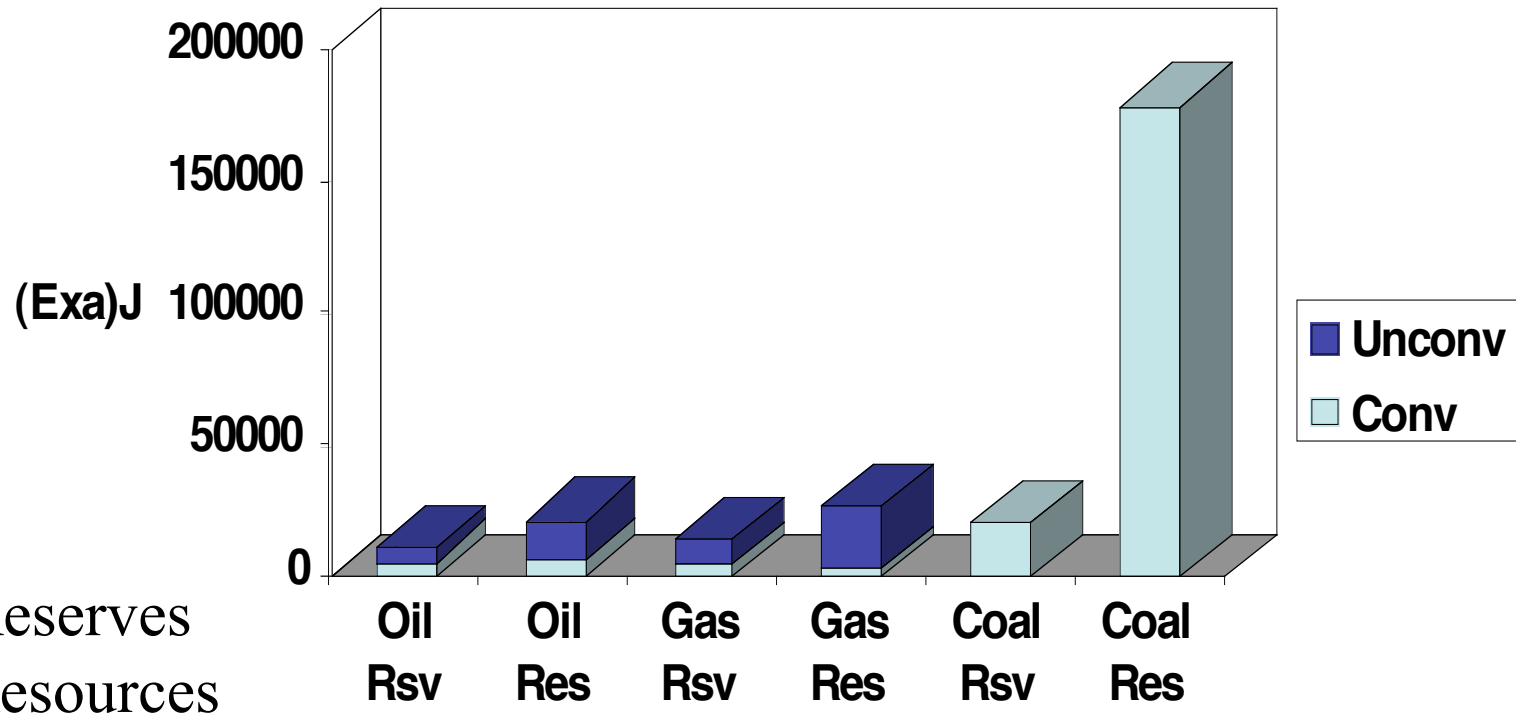


Today: Production Cost of Electricity

(in the U.S. in 2002)



Energy Reserves and Resources



Reserves/(1998 Consumption/yr)

Resource Base/(1998 Consumption/yr)

Oil	40-78
Gas	68-176
Coal	224

51-151
207-590
2160

Conclusions

- Abundant, Inexpensive Resource Base of Fossil Fuels
- Renewables will not play a large role in primary power generation unless/until:
 - technological/cost breakthroughs are achieved, or
 - unpriced externalities are introduced (e.g., environmentally -driven carbon taxes)

What is the Problem?

- Abundance of fossil fuels
- These fuels emit C (as CO₂) in units of Gt C/(TW*yr) at the following:

Gas ~ 0.5

Oil ~ 0.6

Coal ~ 0.8

Wood ~ 0.9

For a 1990
total of 0.56

- How does this translate into an effect in terms of global warming?

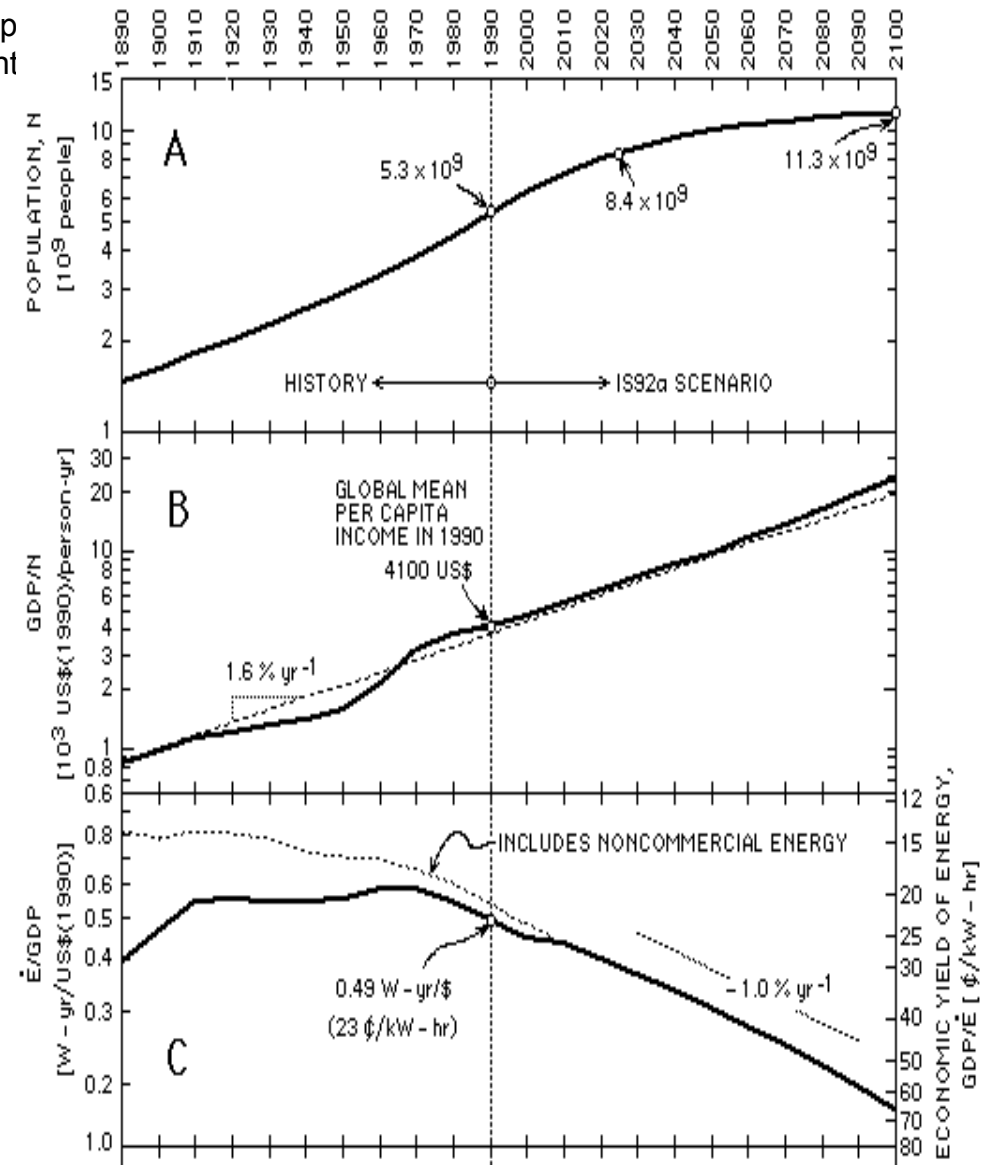
Energy Demands of the Future

- M. I. Hoffert et. al., *Nature*, 1998, 395, 881, "Energy Imp of Future Atmospheric Stabilization of CO2 Content"

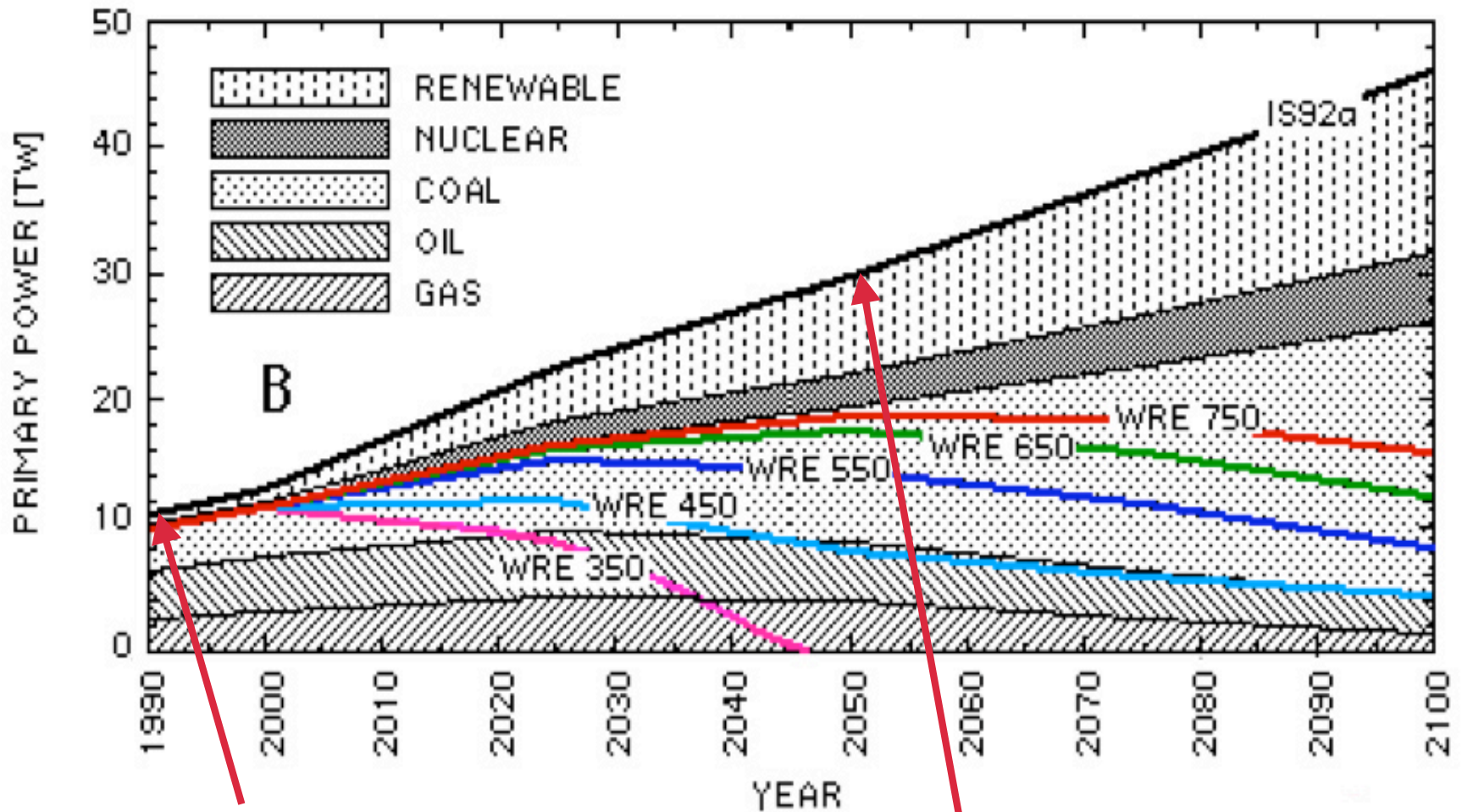
Population Growth to 10 - 11 Billion People in 2050

Per Capita GDP Growth at 1.6% yr⁻¹

Energy consumption per Unit of GDP declines at 1.0% yr⁻¹

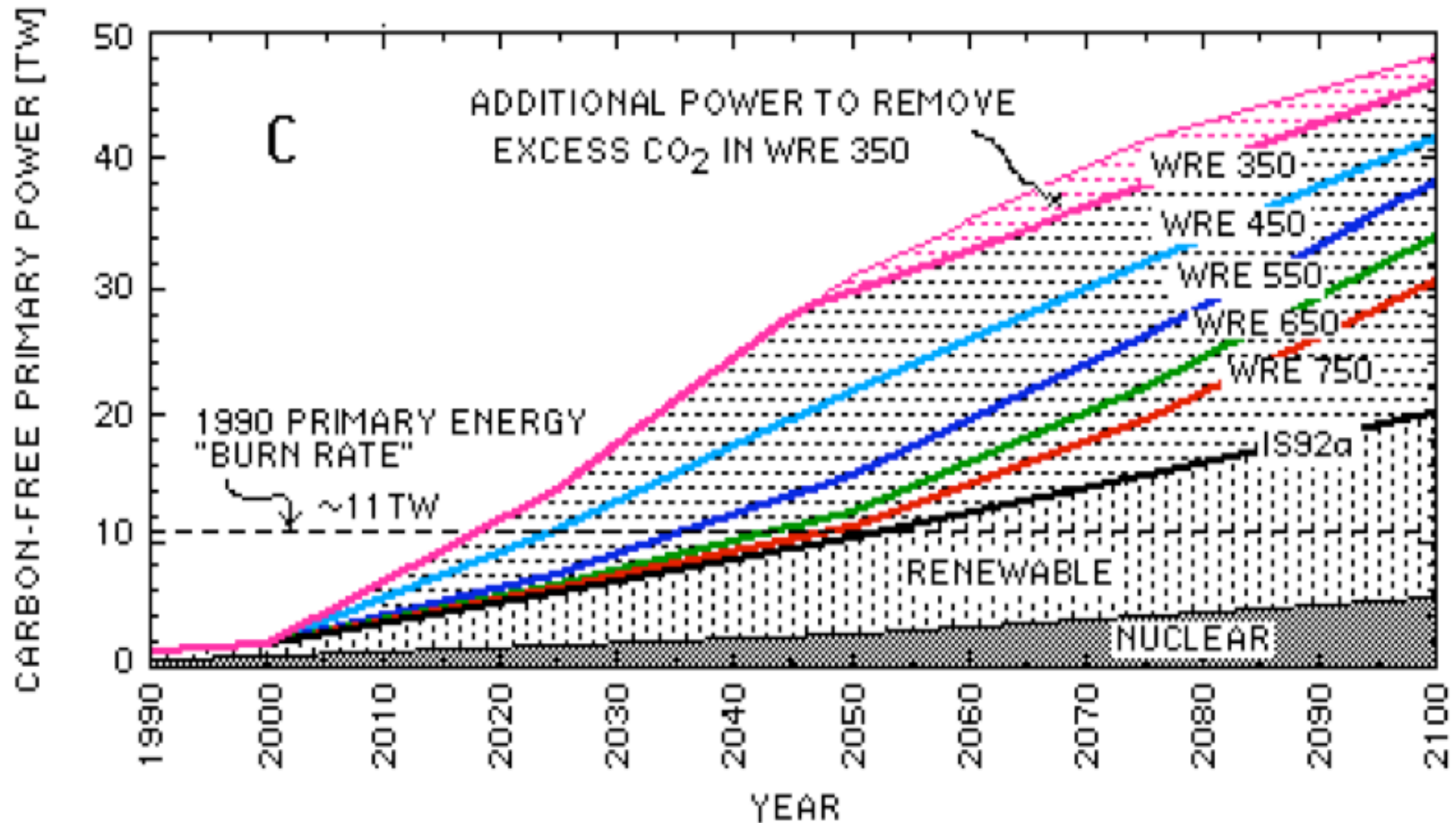


Total Primary Power vs Year



1990: 12 TW 2050: 28 TW

Projected Carbon-Free Primary Power



To fix atmospheric CO₂ at 350 ppm – need all 28 TW in 2050 to come from renewable carbon-free sources

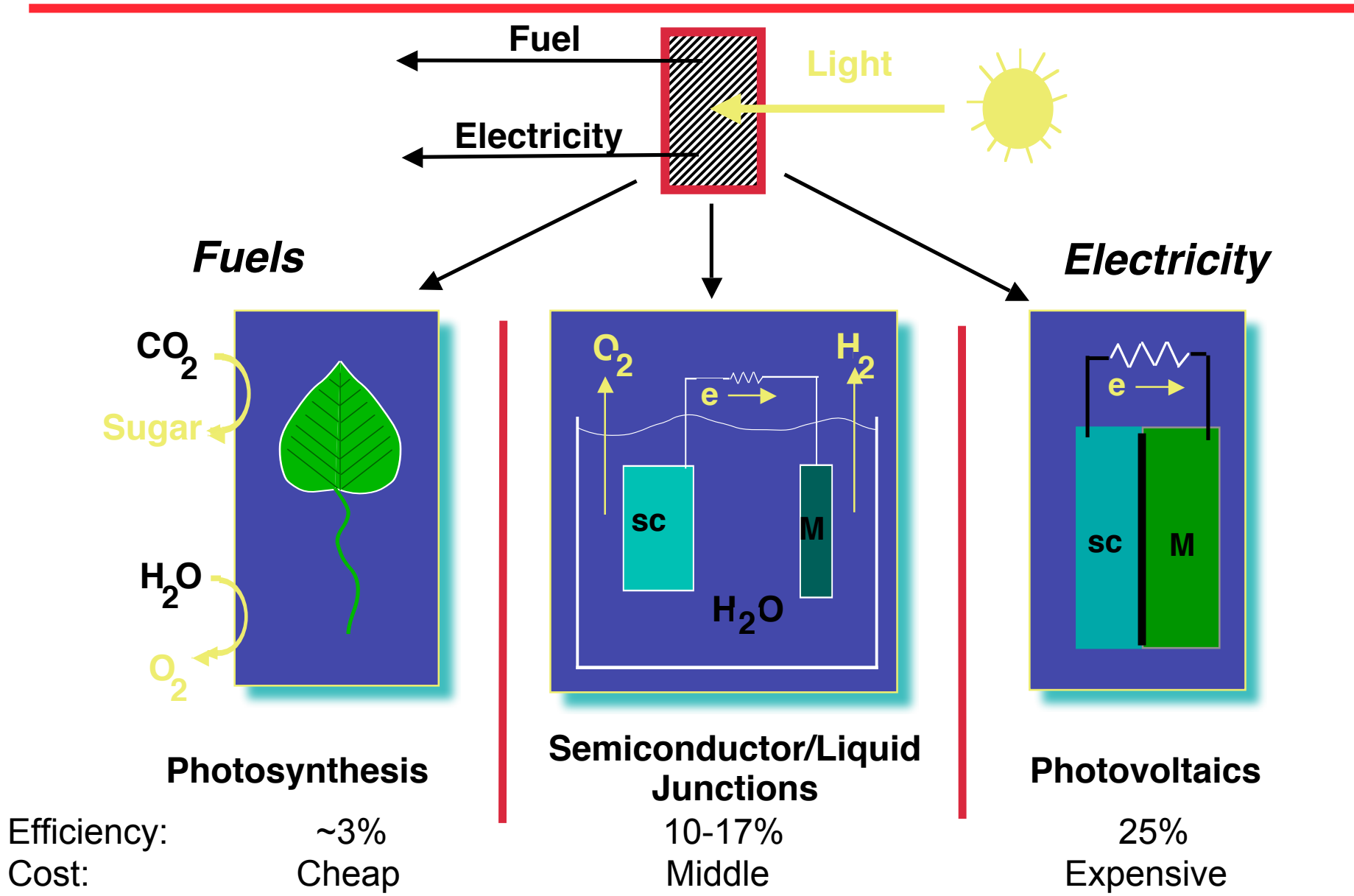
Lewis' Conclusions

- If we need such large amounts of carbon-free power, then:
 - current pricing is not the driver for year 2050 primary energy supply
- Hence,
 - Examine energy potential of various forms of renewable energy
 - Examine technologies and costs of various renewables
 - Examine impact on secondary power infrastructure and energy utilization

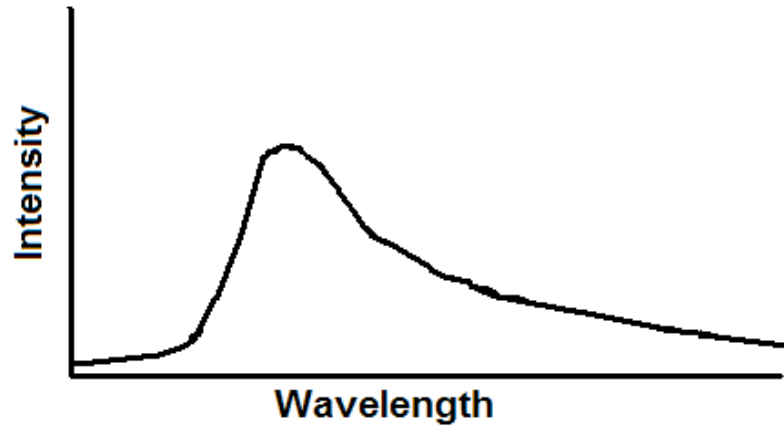
Feasibility of Renewables

- Hydroelectric
 - Economically feasible: 0.9 TW
- Wind
 - 2 TW possible
 - 4% land utilization of Class 3 wind or higher
- Biomass (to EtOH)
 - 20 TW would take 31% of Earth's land area
 - 5-7 TW possible by 2050 but likely water resource limited
- Solar
 - 1×10^5 TW global yearly average power hitting Earth
 - 60 TW of practical onshore generation potential
 - 90 TW goes to photosynthesis

Energy Conversion Strategies

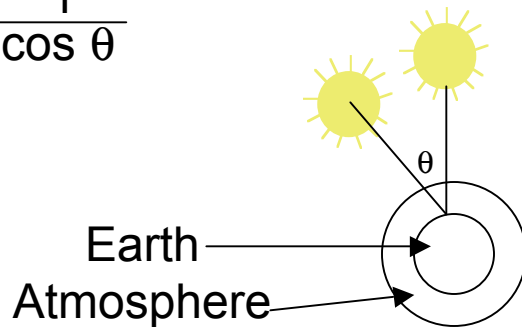


Sunlight



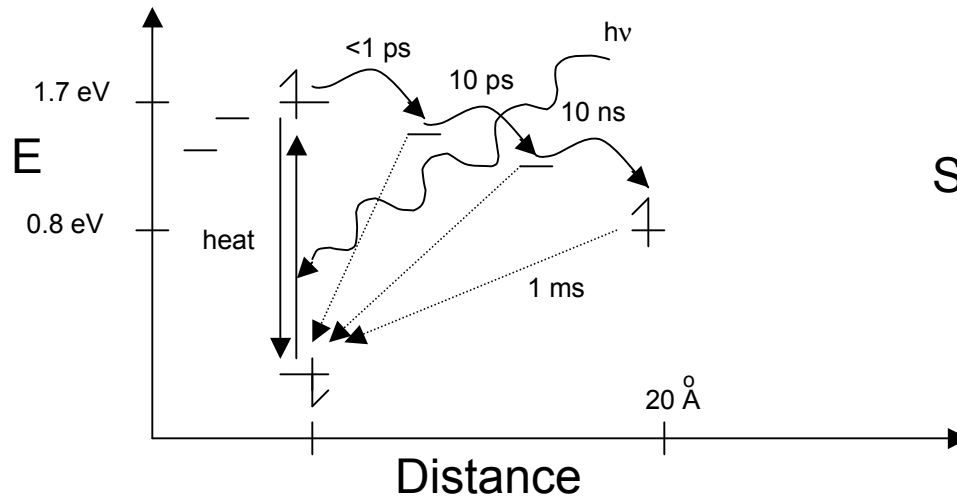
6400° blackbody

$$AM = \frac{1}{\cos \theta}$$



- High noon = 100 mW/cm²
- There is NO standard sun
 - Air mass 1.5 (~48°)
- To convert solar energy a device must
 - Absorb light
 - Separate charge
 - Collect/use it

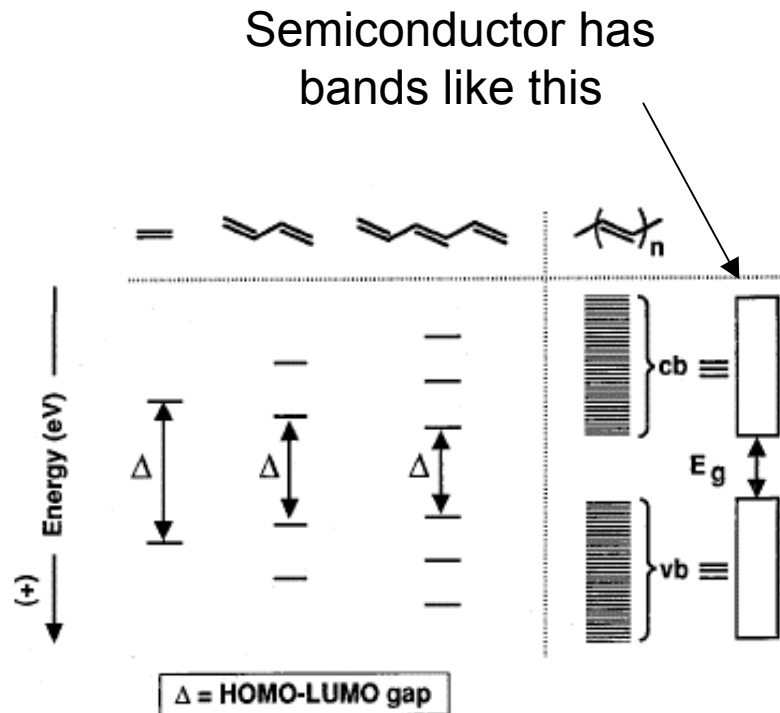
Plants



Charge is physically separated otherwise
Sugar + O₂ → CO₂ + H₂O
No net gain

- Have special pair in chlorophy dimer
- Plant lost 1 eV in separating the charge for use – part of 3% efficiency penalty in using organic materials with low e⁻ mobility
- NOT so for solids
 - Because $\mu_{\text{solid}} \gg \mu_{\text{plant}}$ (10^6 times greater) waste less energy to separate charge
 - Plant takes 1 eV to move 20 angstroms, semiconductor takes 0.3 eV to move 2 μm

Semiconductor as Solar Absorber

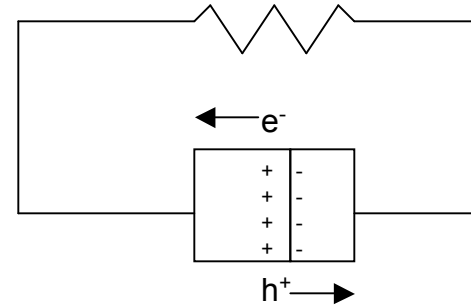


The development of a polyene band structure from the MOs of ethylene. From left to right, the MOs progressively develop into a band structure as the length of the conjugated chain is increased. For shorter polyene chains, Δ represents the HOMO-LUMO gap. For the infinite polyene chain, vb and cb denote the valence band and the conduction band, respectively, and E_g is the band gap energy.

- Tune semiconductor band gap to solar spectrum
 - Too blue vs. too red (1100 – 700 nm, 1.1 – 1.7 eV)
 - Peak at 1.4 eV
- Max efficiency at 34% of total incident power
 - Some photons not absorbed
 - Higher energy photons thermalize
 - Have to collect e^- and h^+ directionally

Semiconductor as Solar Absorber

- Directionality achieved by adding asymmetry of an electric field



- By stacking 2 devices, can increase max to 42%
 - Series connection adds the voltages
 - Current limited by bluest device
- Why not increase area of single device? It is total power we're most interest in.