

**INTERNATIONAL  
SYMPOSIUM  
ON  
CONTEMPORARY  
PHYSICS**

**2<sup>nd</sup> day(26-30 mar 2007)**

**QAU, ISLAMABAD, PAKISTAN**

# Pakistan Energy

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- Cow Manure, Bagasse (the woody residue left over from crushed sugarcane), and firewood furnished about 32 percent of all energy in FY 1988



# Pakistan Energy

- Bagasse (the woody residue left over from crushed sugarcane), dung, and firewood furnished about 32 percent of all energy in FY 1988
- Some localities had been denuded of firewood.

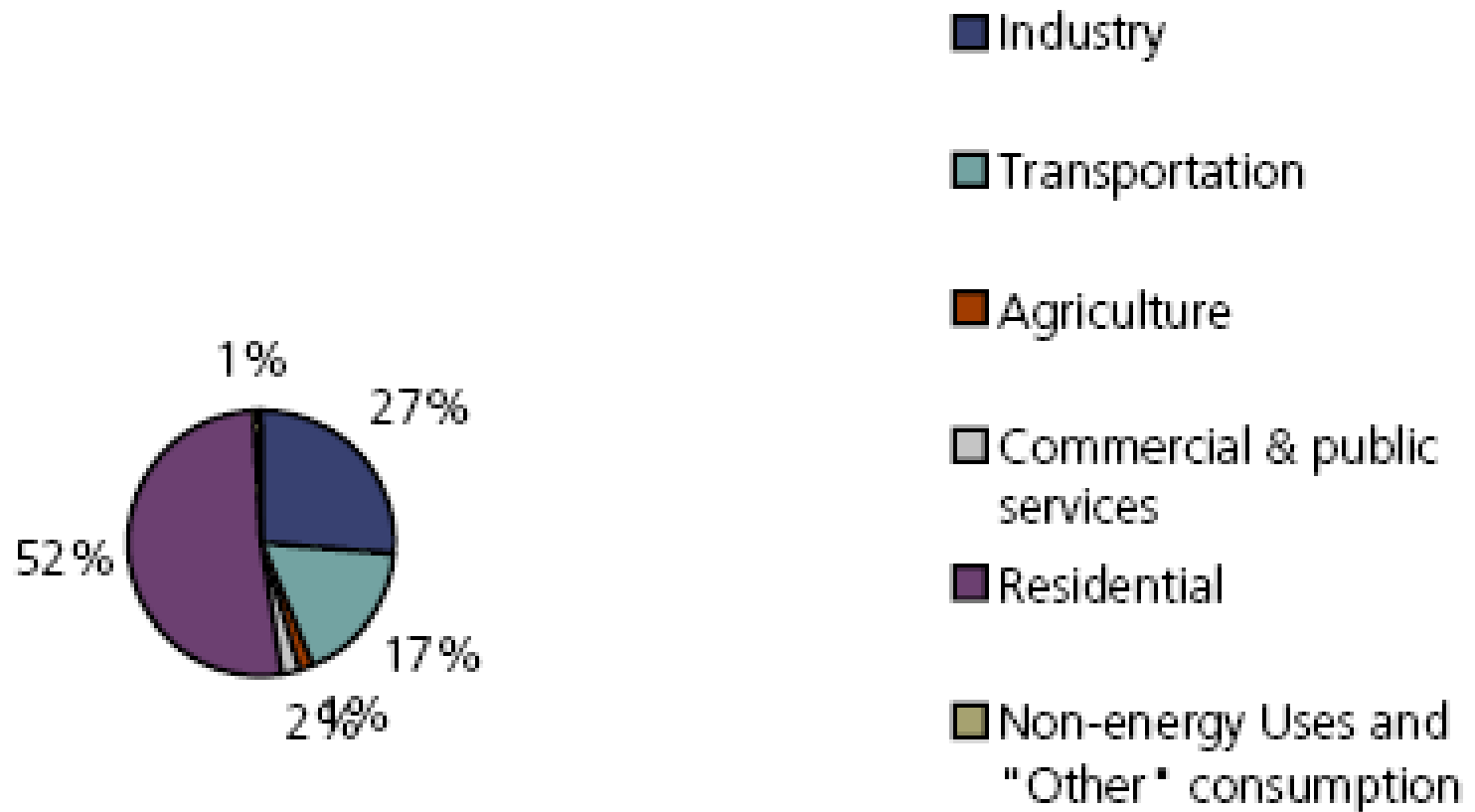
# Pakistan Energy

- Bagasse (the woody residue left over from crushed sugarcane), dung, and firewood furnished about 32 percent of all energy in FY 1988
- Some localities had been denuded of firewood.
- Domestic sources of commercial energy accounted for 77 percent of all commercial energy in FY 1990.

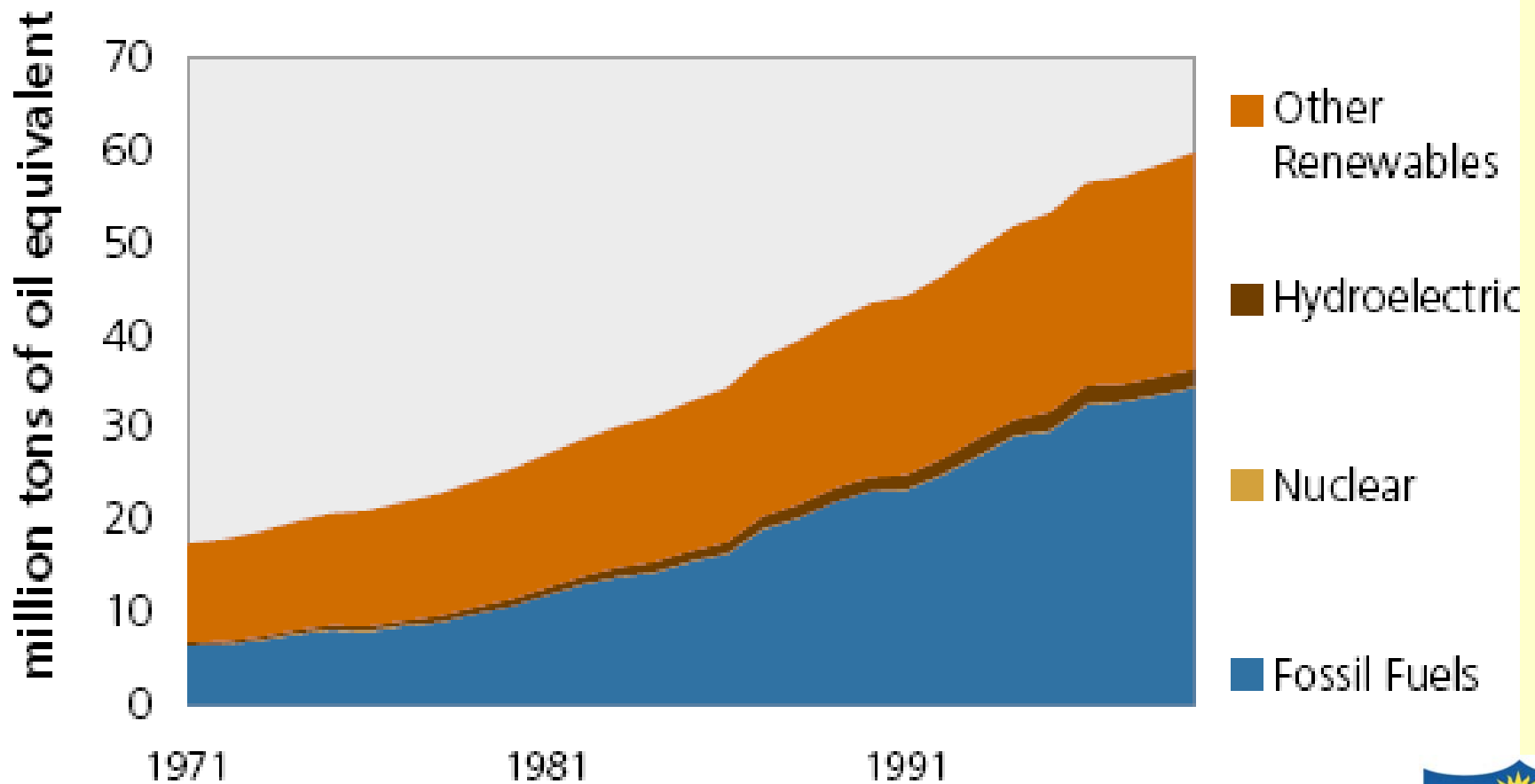
# Pakistan Energy

- Bagasse (the woody residue left over from crushed sugarcane), dung, and firewood furnished about 32 percent of all energy in FY 1988
- Some localities had been denuded of firewood, forcing the local population to use commercial energy sources, such as kerosene or charcoal.
- Domestic sources of commercial energy accounted for 77 percent of all commercial energy in FY 1990.
- The major domestic energy resources are natural gas, oil, and hydroelectric power. The remainder of energy requirements are met by imports of oil and oil products.

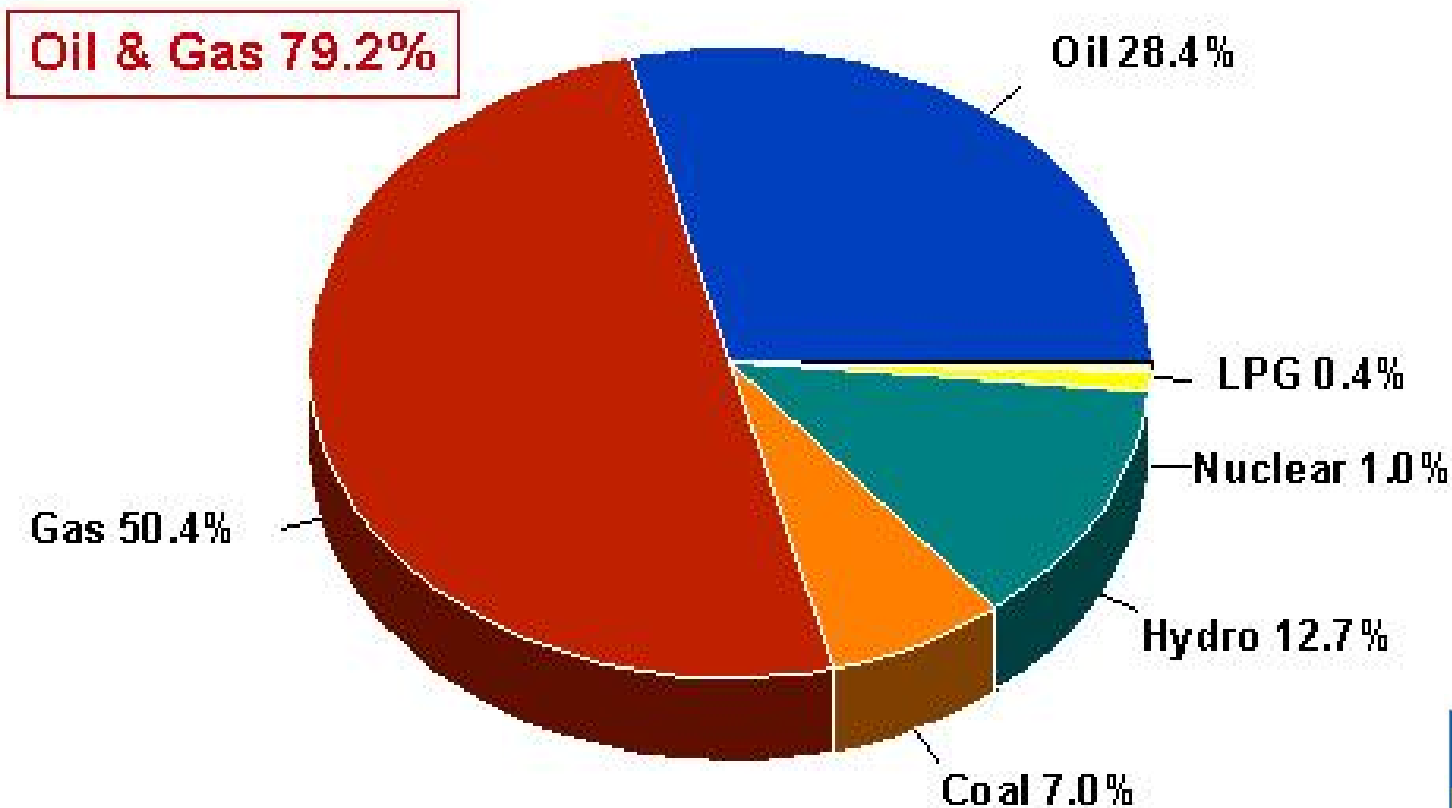
# Energy Consumption by Sectors



# Energy Consumption by Source



# PAKISTAN'S PRIMARY ENERGY SUPPLIES 2005-06





# Oil Production

Year	Oil - production	Rank	Percent Change	Date of Information
2003	62,870	53		2001 est.
2004	62,870	53	0.00 %	2001 est.
2005	61,000	54	-2.97 %	2004 est.
2006	63,000	58	3.28 %	2005 est.

bbl/day



# OIL

- **Oil - production: 63,000 bbl/day (2005)**
- **Oil - consumption: 324,000 bbl/day (2005)**



The



/



issue !!

- Oil Bill 6.7 Billion Dollars (2005)



**The**



**/**



**issue !!**

- **Oil Bill** **6.7 Billion Dollars**
- **Total Expenditure** **13.8 Billion Dollars**



# The



/



# issue !!

- Oil Bill 6.7 Billion Dollars
- Total Expenditure 13.8 Billion Dollars
- Some encouraging numbers:
- Allocation to education including HEC has been increased to \$0.4 billion (up by 52.7 percent).
- Allocation to the Science & Technology up \$1.6 Billion (up by 95.3 percent )



# The



/



# issue !!

**In addition, there is a direct environment cost that is associated with the fossil fuel consumption.**

- Number of automobiles rose from 680,000 in 1980 to 5 million in 2003
- Average Pakistani vehicle emits 25 times as much carbon dioxide, 20 times HC, 3.5 times more NO<sub>x</sub> than an average U.S. vehicle
- 0.5 B dollars/year medical tab due to emissions related illnesses.
- Some incentives given for conversion to lesser polluting LPG/CNG and seems to be having some positive effect.
- This is just the tip of the iceberg.

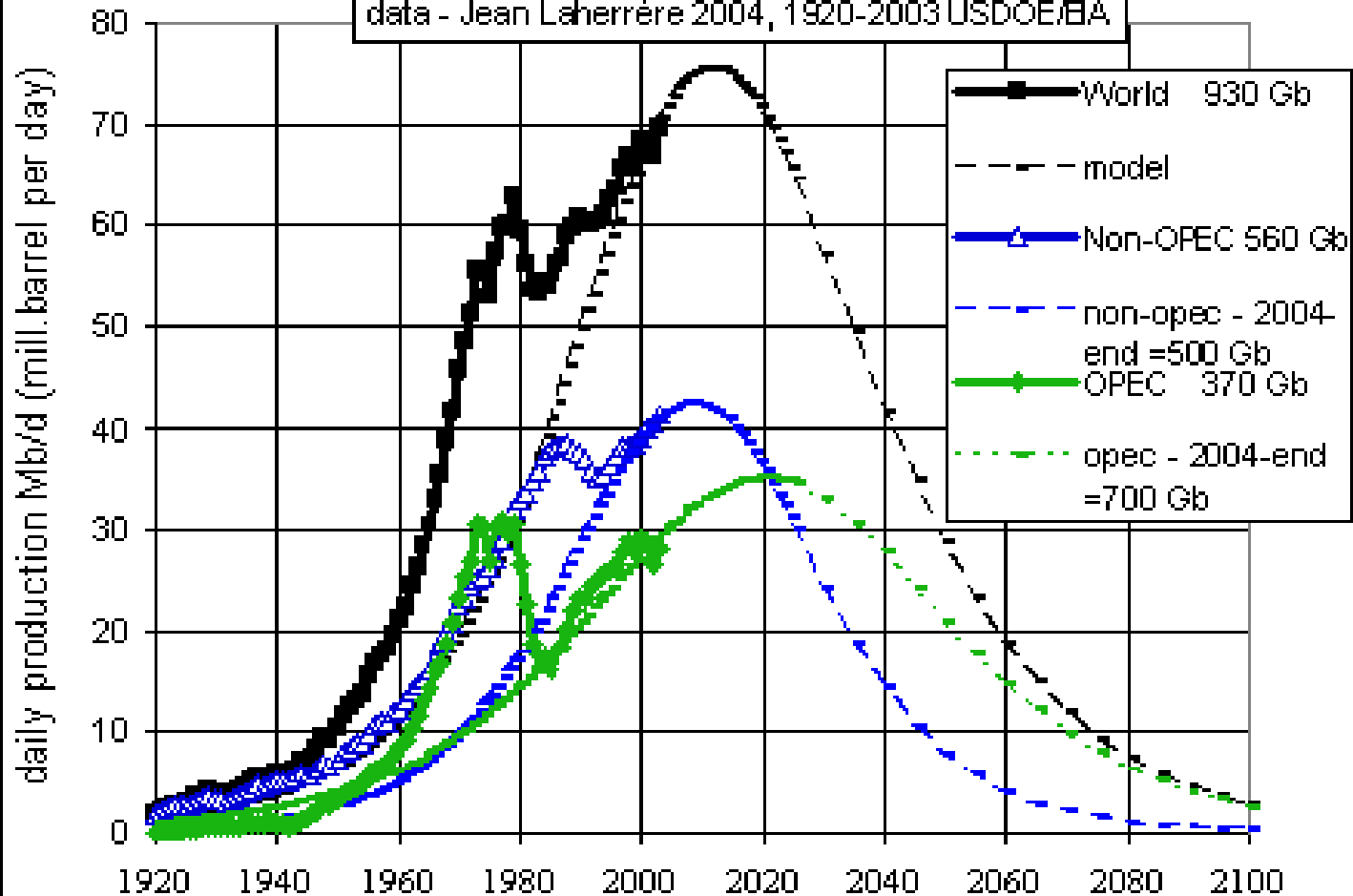


# Global Picture



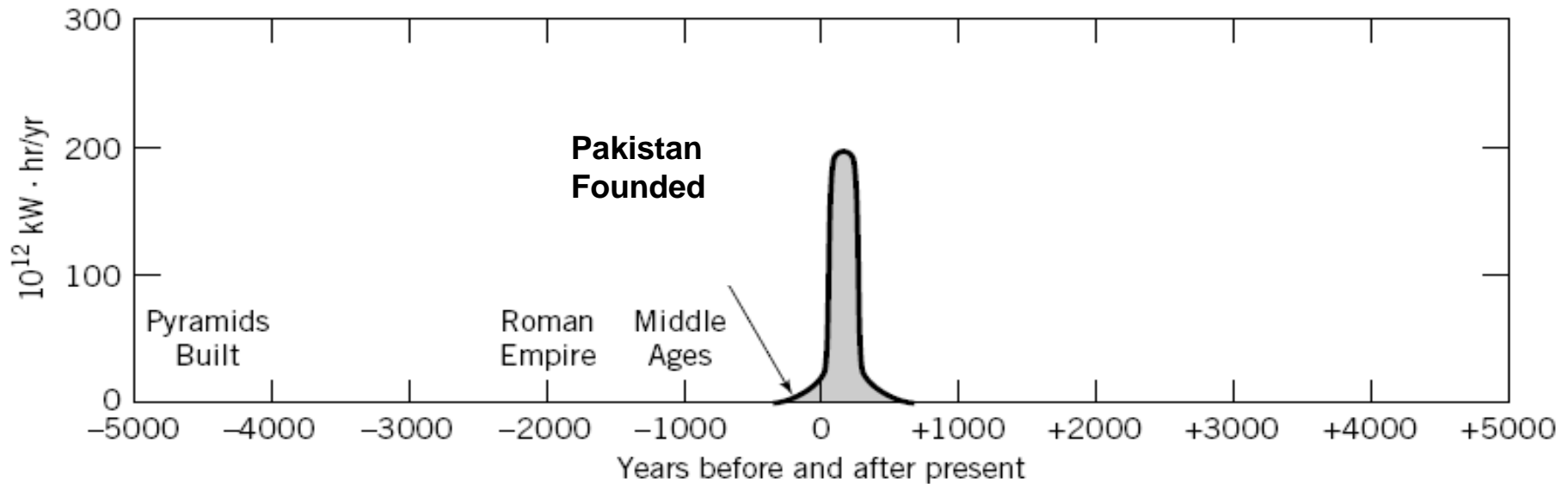
## World conventional crude oil production and forecast for an ultimate of 2.1 Tb (no demand constraint)

Grandfather Economic Report -  
<http://mwhodges.home.att.net/>  
 data - Jean Laherrère 2004, 1920-2003 USDOE/BA





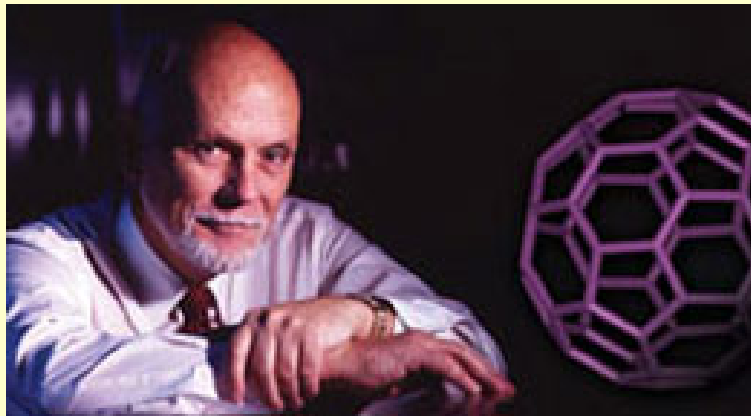
# The Global Picture



**Fossil Fuel Derived Energy**

# Future Global Energy Prosperity: The Terawatt Challenge

Richard E. Smalley



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*"There has been a lot of talk about the hydrogen economy, which I believe is, despite its virtues, likely to remain a distraction from the real, practical solutions to our energy needs."*

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## Top Ten Global Concerns

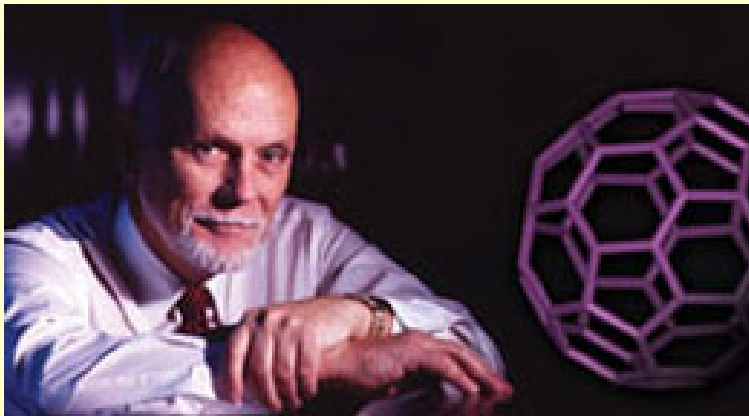
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*"At some point, almost certainly within this decade, we will peak in the amount of oil that is produced worldwide."*

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- 9.
10. **Population**

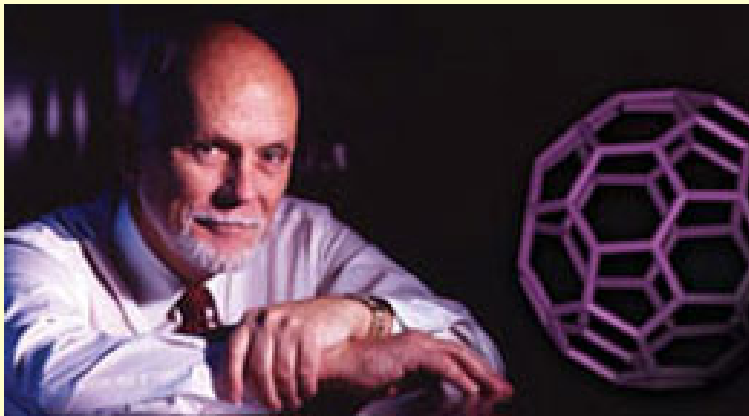
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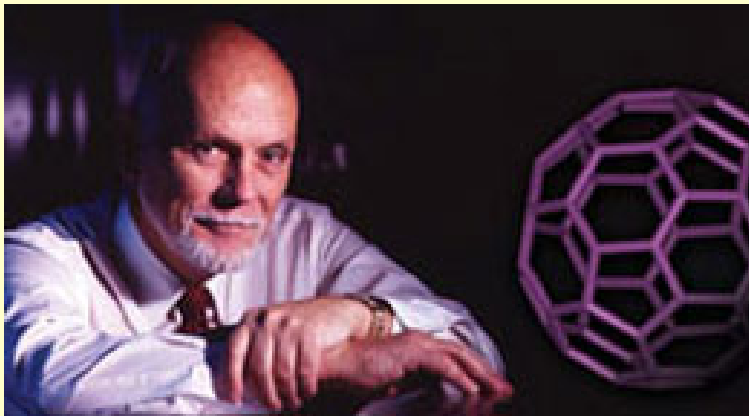
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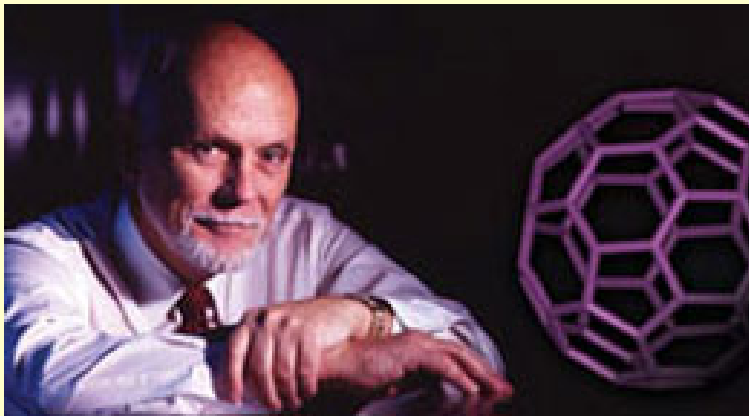
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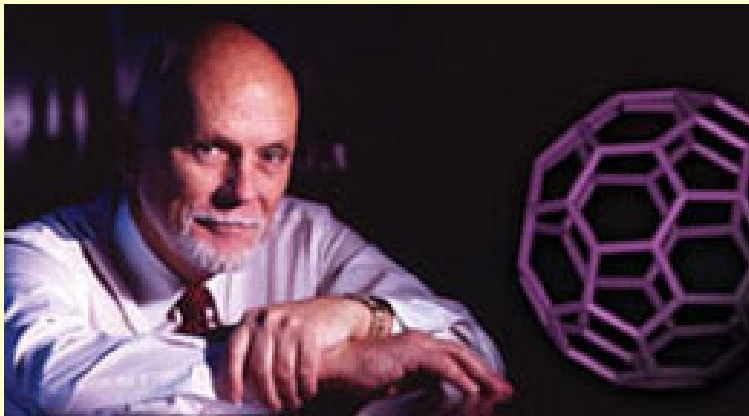
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7. **Disease**
8. **Education**
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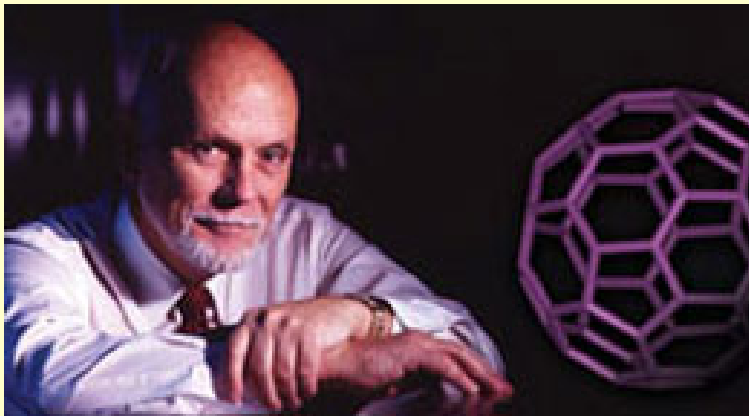
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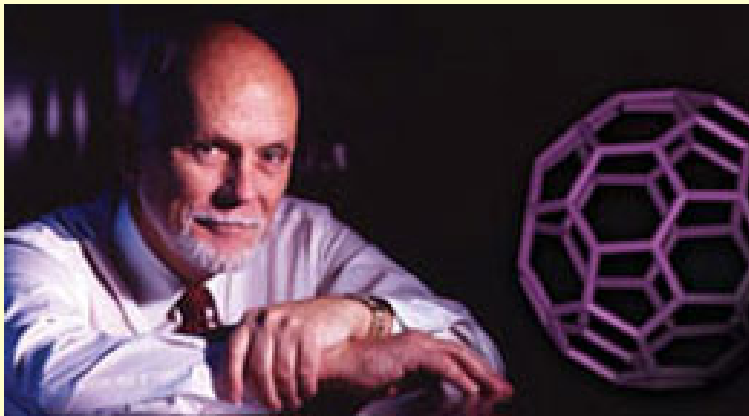
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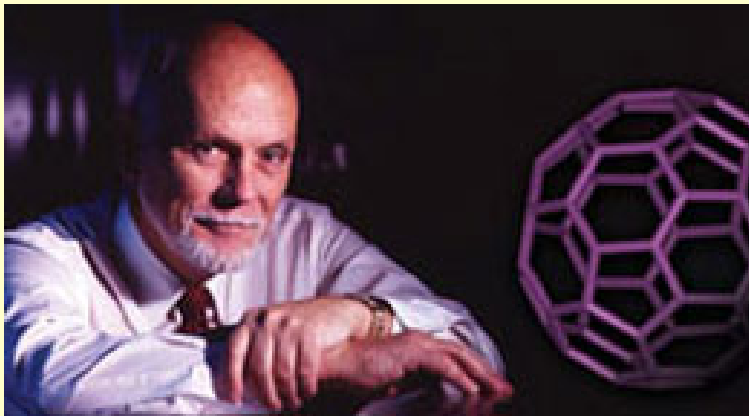
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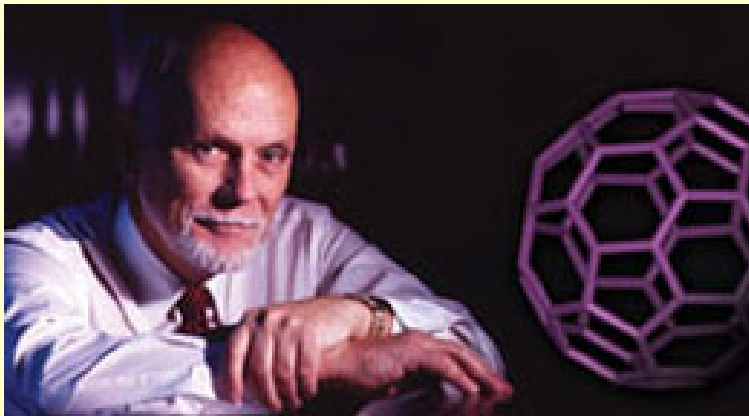
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## Top Ten Global Concerns

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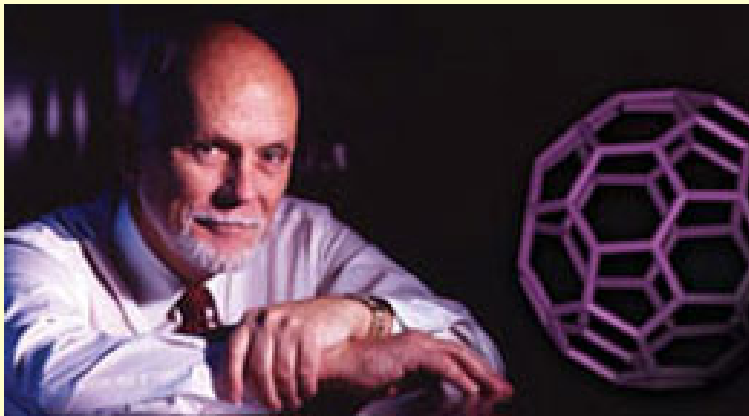
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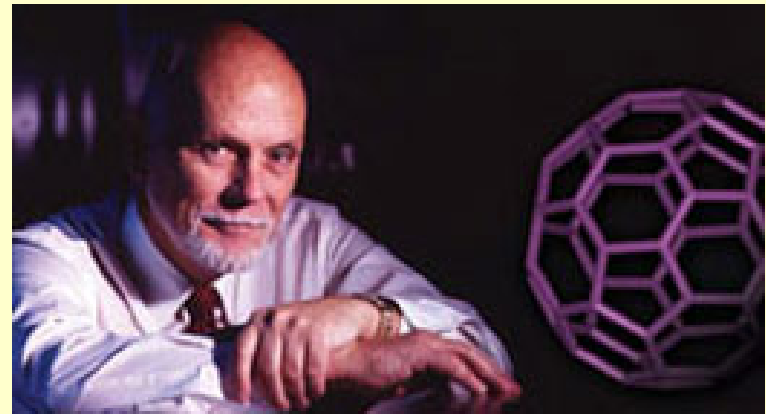
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*“To give all 10 billion people on the planet the level of energy prosperity we in the developed world are used to, a couple of kilowatt-hours per person, we would need to generate 60 terawatts around the planet—the equivalent of 900 million barrels of oil per day.”*

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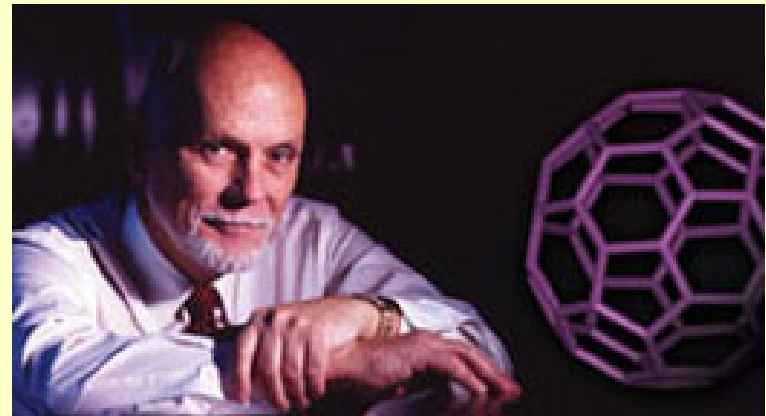
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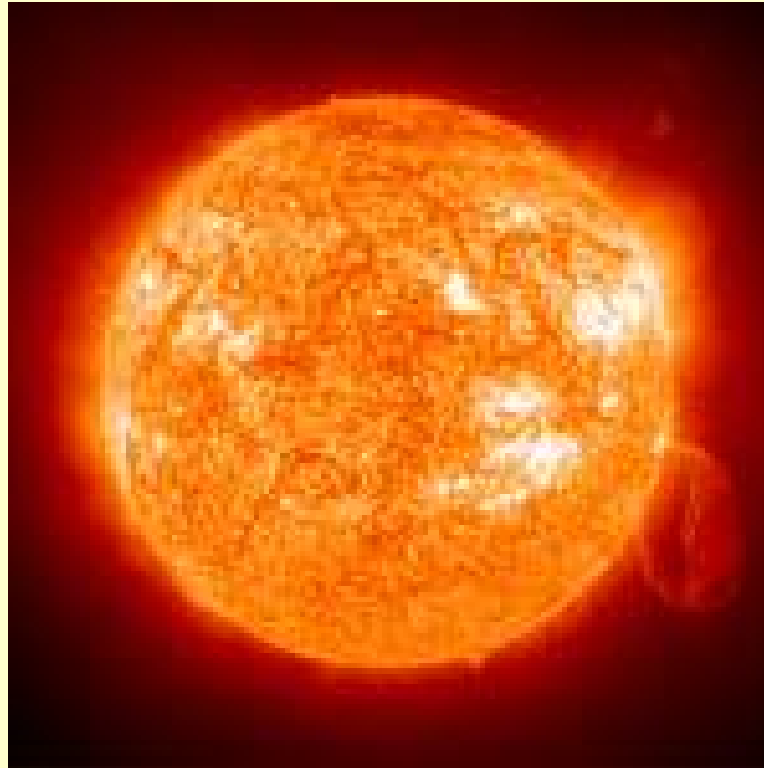
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---



**And we produce 90 million barrels of oil per day right now.....**

# Radiant Facts



**Diameter: About 100 times that of earth**

**Mass: 99.8% of the Solar System (Jupiter has most of the rest)**

**Core Temperature:  $15.6 \times 10^6$  K    Surface Temperature: 5800K**

**Energy Production: 386 billion billion megawatts**

**Insolation: 1000 - 250 Watts per square meter**

**Age: 4.5 billion Years (5 billion years more to go)**



# PV Land Area Requirements

- $1.2 \times 10^5$  TW of solar energy potential globally
- Generating  $2 \times 10^1$  TW with 10% efficient solar farms requires  $2 \times 10^2 / 1.2 \times 10^5 = 0.16\%$  of Globe =  $8 \times 10^{11}$  m<sup>2</sup> (i.e., 8.8 % of U.S.A)
- Generating  $1.2 \times 10^1$  TW (1998 Global Primary Power) requires  $1.2 \times 10^2 / 1.2 \times 10^5 = 0.10\%$  of Globe =  $5 \times 10^{11}$  m<sup>2</sup> (i.e., 5.5% of U.S.A.)



# PV Land Area Requirements



# PV Land Area Requirements

Nate Lewis (CIT) calculations



6 Boxes at 3.3 TW Each



# Means of Harvesting Solar Energy

**SUN**

Photovoltaic

Photothermal

Photochemical

Active

Passive

Photo-  
thermoelectric

Photo-  
electrolysis

Photocatalysis

# **Alternate Energy Paths**

# **The Magic Wand of Nanotechnology**

**S. Ismat Shah**

**Physics and Astronomy**

**Materials Science and Engineering**

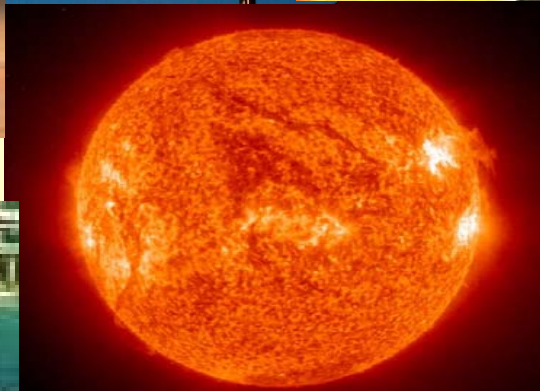
**University of Delaware**







# Applications



The vehicle was launched in 2005.  
JPL/NASA IMAGE



Georgia Tech's Aquatic Center is powered by one of the world's largest grid-connected rooftop solar arrays



Figure 2. Flexible solar cell technology incorporated into a military tent



# Unique uses of Solar Cells



Solar Purse



Solar Charger

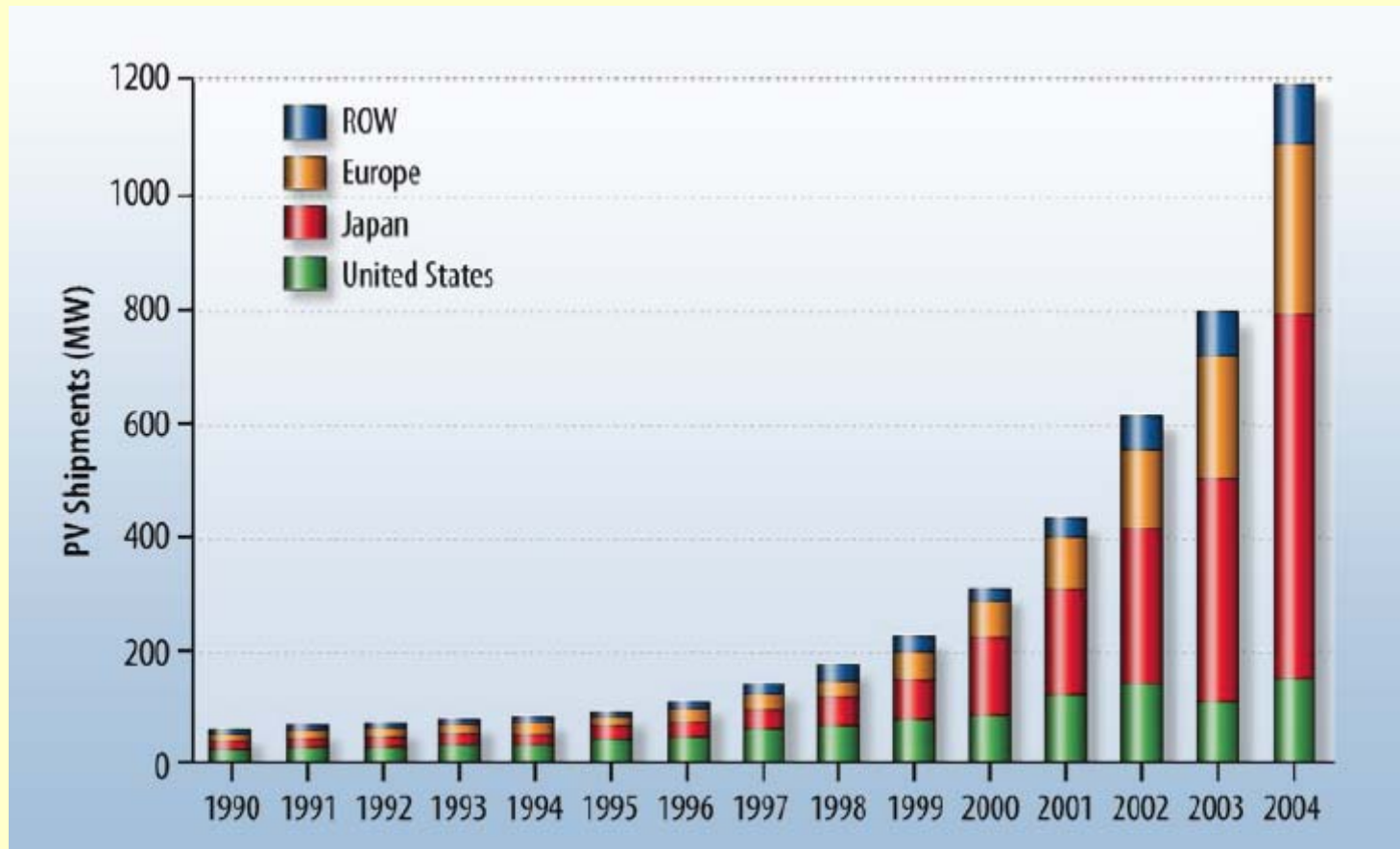


Flexible Solar Cells



Rural Electrification (Brazil)

# World PV Shipment



# Solar cell materials

- Single crystal silicon
- Polycrystal silicon
- Single crystal III-V semiconductors
- Amorphous silicon
- CdTe
- $\text{CuInGaSe}_2$

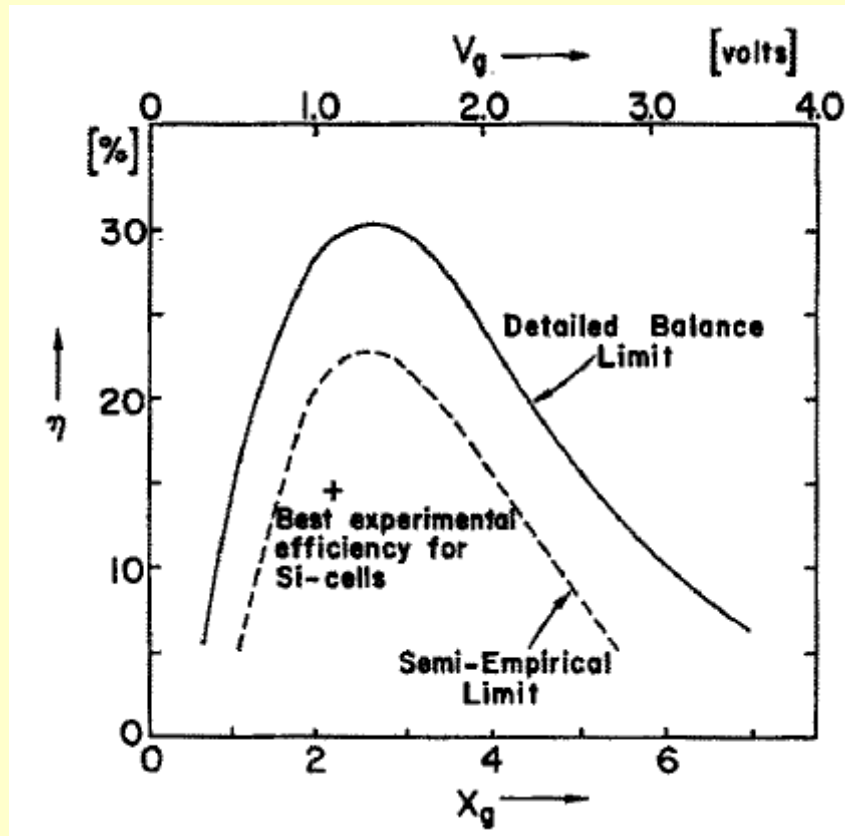
Mostly as single junction devices

Cell Type		Area ( $\text{cm}^2$ )	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	FF	Efficiency (%)
c-Si	UNSW PERL	4.0	0.696	42.0	83.6	24.9
c-GaAs	Kopin	3.91	1.022	28.2	87.1	25.1
poly-Si	UNSW/Eurosolare	1.0	0.628	36.2	78.5	19.8
a-Si	Sanyo	1.0	0.887	19.4	74.1	12.7
$\text{CuInGaSe}_2$	NREL	1.04	0.669	35.7	77.0	18.4
Cd Te	NREL	1.131	0.848	25.9	74.5	16.4





# Shockley–Queisser (S–Q) limit



JOURNAL OF APPLIED PHYSICS

VOLUME 32, NUMBER 3

MARCH, 1961

## Detailed Balance Limit of Efficiency of $p$ - $n$ Junction Solar Cells\*

WILLIAM SHOCKLEY AND HANS J. QUEISSER

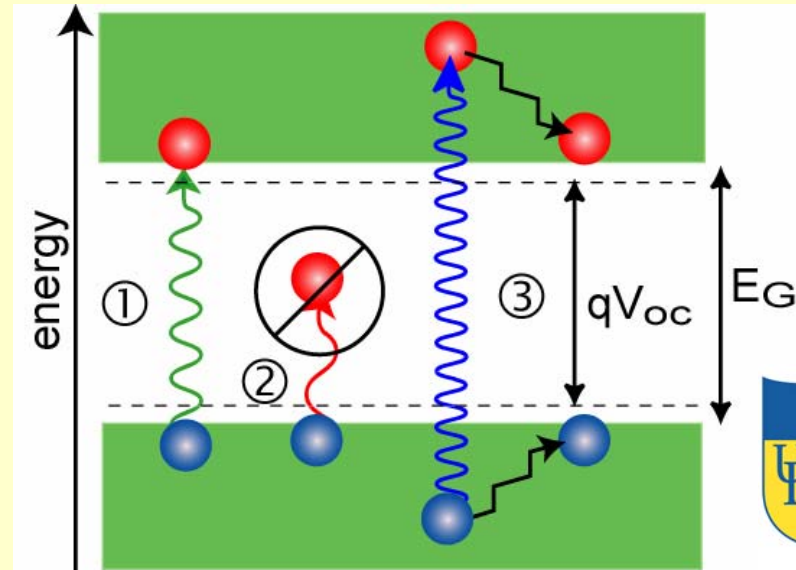
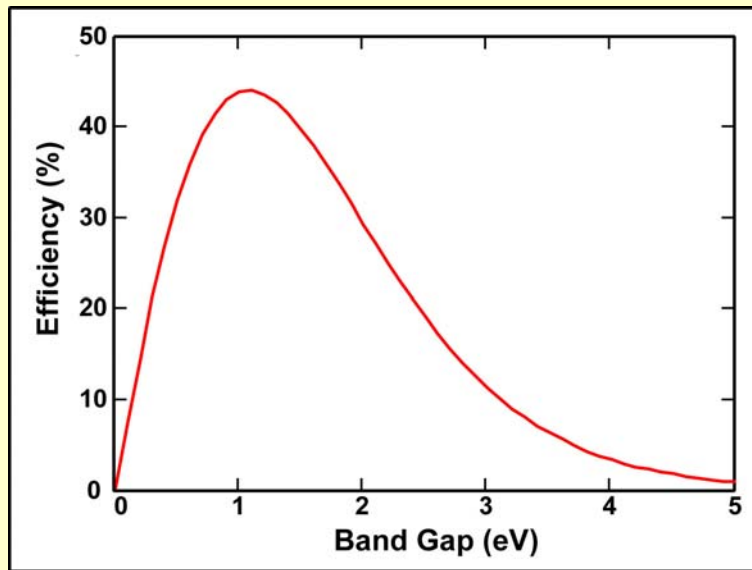
*Shockley Transistor, Unit of Cleveite Transistor, Palo Alto, California*

(Received May 3, 1960; in final form October 31, 1960)



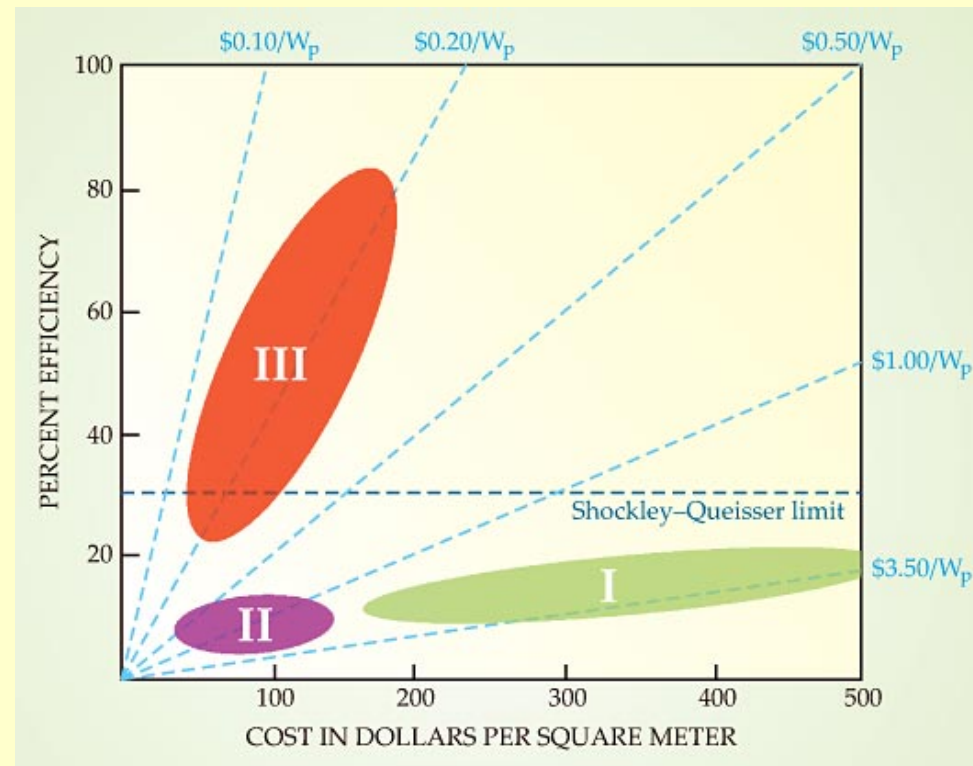
# Solar Cell Efficiencies: Shockley-Queisser Limit

- Efficiency depends on optical concentration, details of input spectrum (i.e. if spectrum is black body, measured spectrum, etc)
- Trade-off between voltage and current: high band gap gives large voltage, but absorbs small fraction of solar spectrum and so gives a small current.
- Maximum efficiency for band gap  $\sim 1.3$  eV for space radiation, 1.1 eV and 1.34 eV for terrestrial radiation.
- Maximum single junction efficiency = 30.8% under one sun and 40.8% under max concentration (called Shockley-Queisser limit).



# Efficiency Enhancement

- **First-generation cells:**  
Based on expensive silicon wafers.
- **Second-generation cells:**  
Based on thin films of less expensive materials.
- **Third-generation cells:**  
Research goals: may use carrier multiplication, hot electron extraction, multiple junctions, sunlight concentration, or new materials.



George W. Crabtree and Nathan S. Lewis  
Physics Today, March 2007, page 37



# Exceeding Shockley–Queisser limit

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1. Tandem cells (University of Delaware DARPA \$57M (\$147M) Project).
2. Hot carrier solar cells
4. Multiband and impurity solar cells
5. Thermophotovoltaic/thermophotonic cells
3. Solar cells producing multiple electron-hole pairs per photon through impact ionization
6. Nanocomposite solar cells



# Approaches to High Efficiency

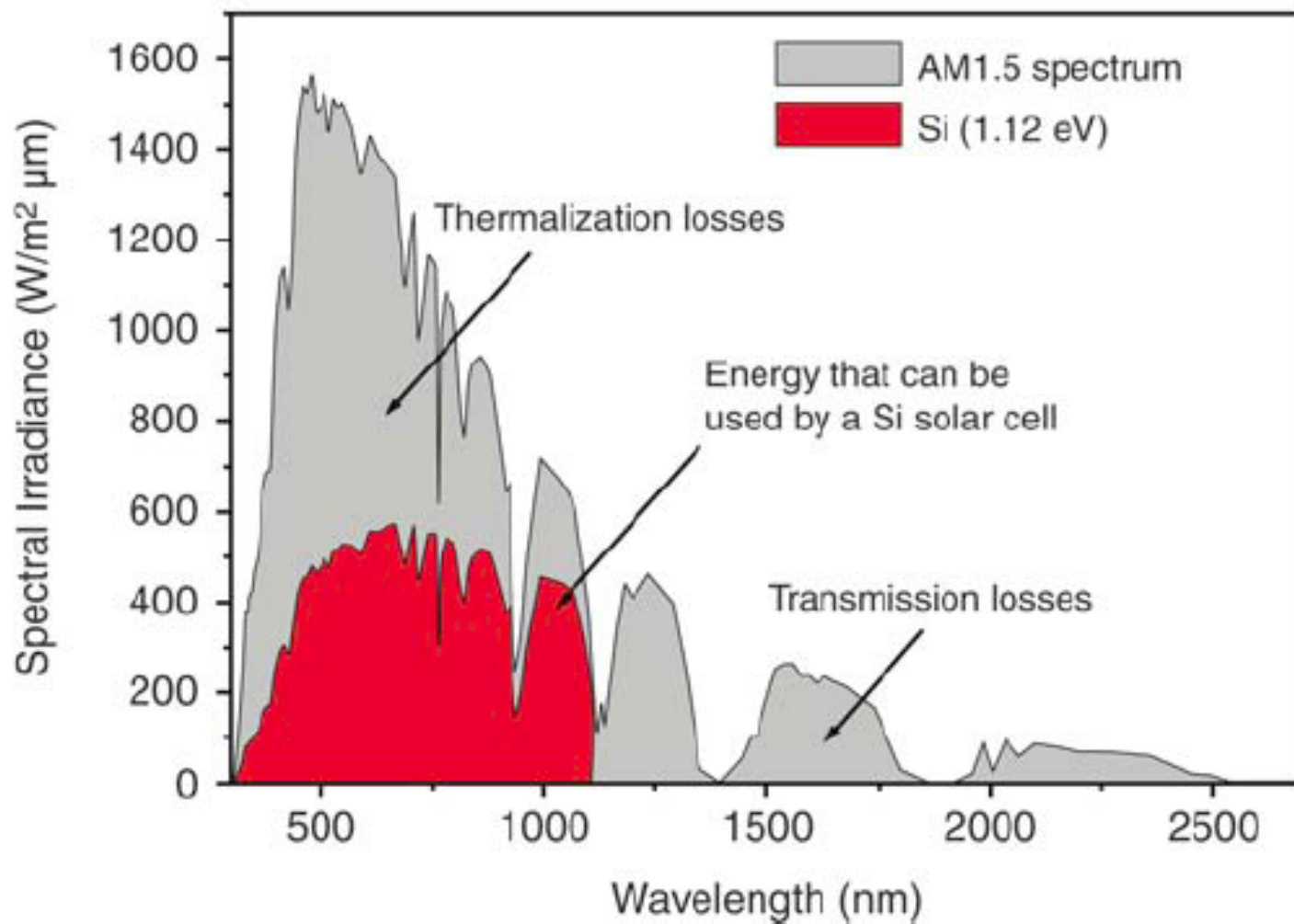
Assumption in Shockley-Queisser	Approach which circumvents assumption	Examples
Input is solar spectrum	<u>Multiple spectrum solar cells</u> : transform the input spectrum to one with same energy but narrower wavelength range	Up/down conversion Thermophotonics
One photon = one electron-hole pair	<u>Multiple absorption path solar cells</u> : any absorption path in which one photon $\neq$ one-electron hole pair	Impact ionization Two-photon absorption
One quasi-Fermi level separation	<u>Multiple energy level solar cells</u> : Existence of multiple meta-stable light-generated carrier populations within a single device	Intermediate band Quantum well solar cells
Constant temperature = cell temperature = carrier temperature	<u>Multiple temperature solar cells</u> . Any device in which energy is extracted from a difference in carrier or lattice temperatures	Hot carrier solar cells
Steady state ( $\approx$ equilibrium)	<u>AC solar cells</u> : Rectification of electromagnetic wave.	Rectenna solar cells



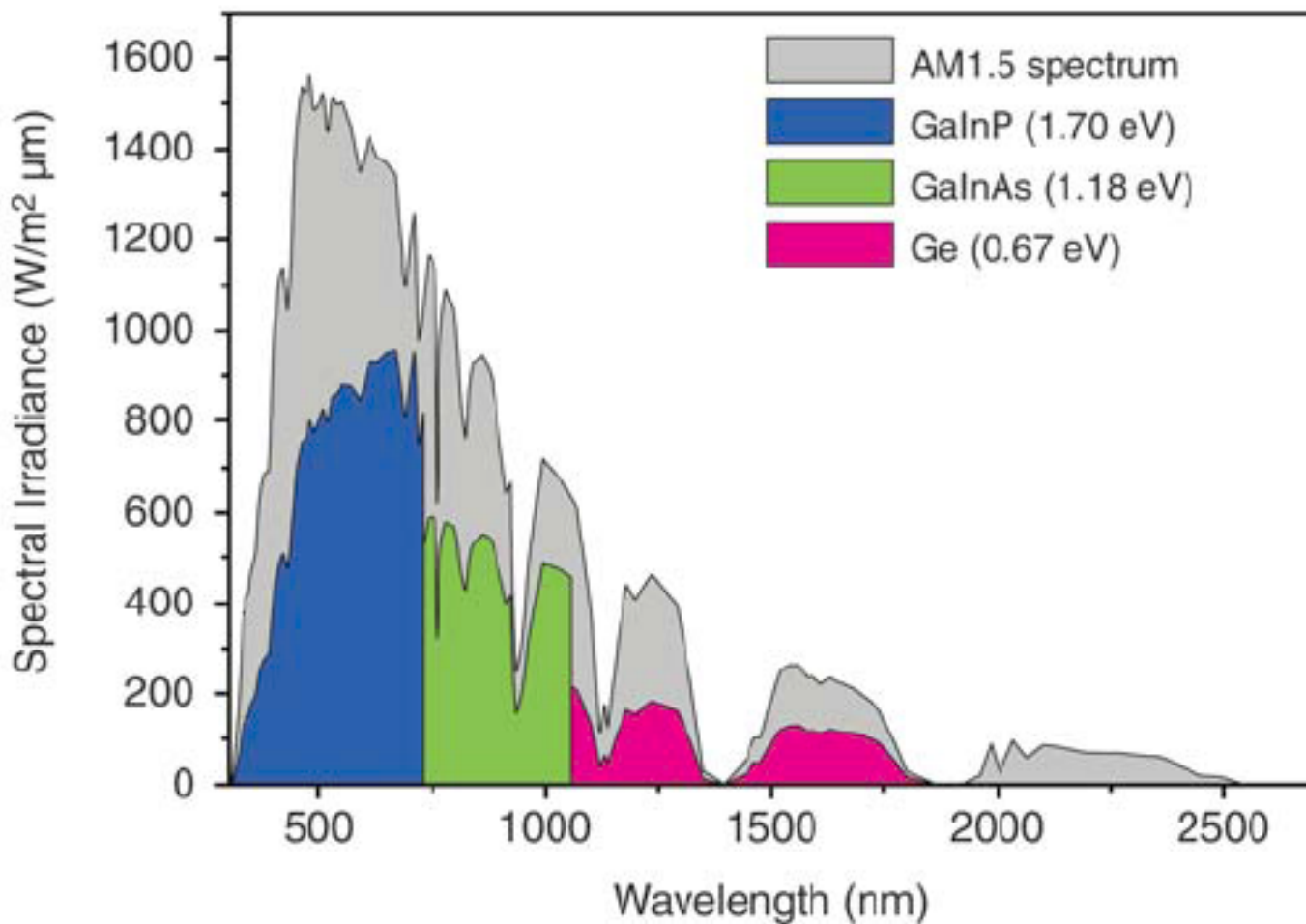
# Multiple Junction (Tandem) Solar Cells



# Tandem Solar Cells



# Tandem Solar Cells





# Multiple Junction (Tandem) Solar Cells

- Multiple junction (tandems) are first class of approaches to exceed single junction efficiency.
- To reach >50% efficiency, need ideal  $E_g$  6-stack tandem or equivalent, assuming can reach ~75% of detailed balance limit.
- Key issue in tandem is to identify materials which can be used to implement ideal tandem stack.

# junctions in solar cell	1 sun $\eta$	Max con. $\eta$
1 junction	30.8%	40.8%
2 junction	42.9%	55.7%
3 junction	49.3%	63.8%
$\infty$ junction	68.2%	86.8%

$n$	Values of Band Gap (eV)	$\eta$ %
4	0.60, 1.11, 1.69, 2.48	62.0
5	0.53, 0.95, 1.40, 1.93, 2.68	65.0
6	0.47, 0.84, 1.24, 1.66, 2.18, 2.93	67.3
7	0.47, 0.82, 1.19, 1.56, 2.0, 2.5, 3.21	68.9
8	0.44, 0.78, 1.09, 1.4, 1.74, 2.14, 2.65, 3.35	70.2

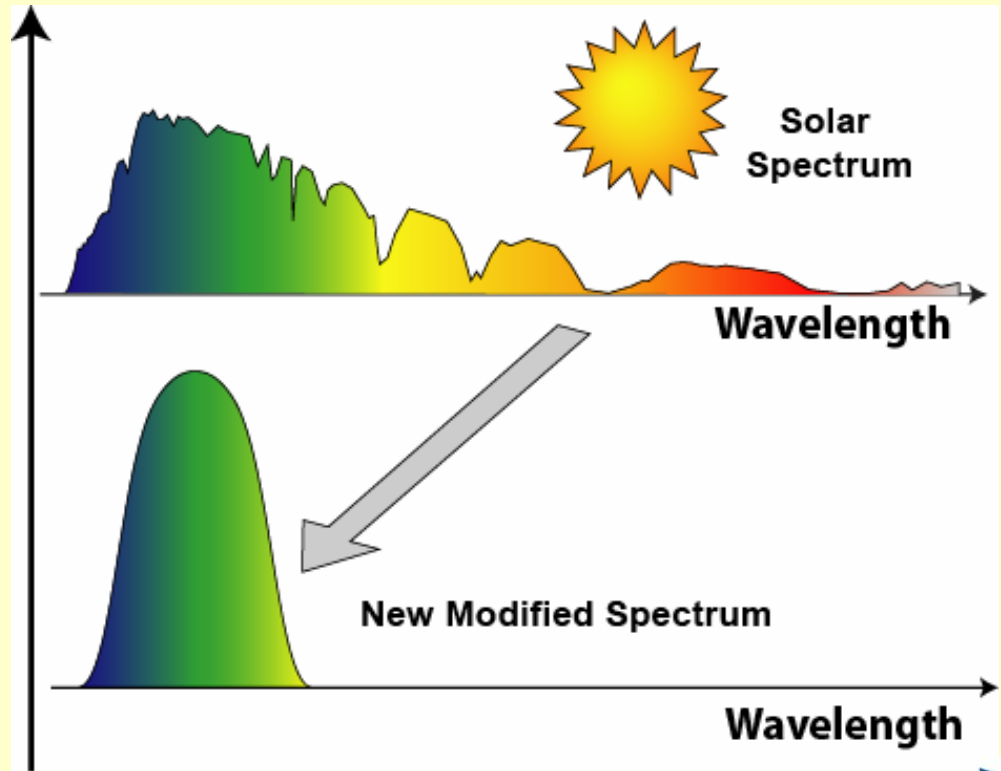


# Multiple Spectrum Solar Cells



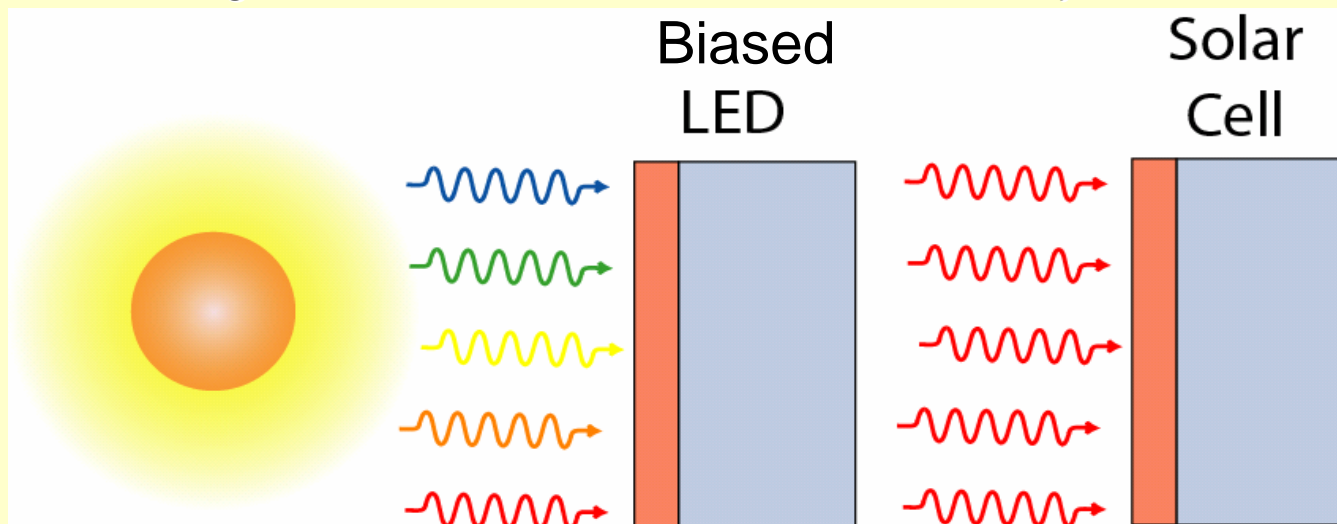
# Multiple Spectrum Solar Cells

- Multiple spectrum devices: take the input solar spectrum, and change it to a new spectrum with the same power density
  - Does not need to be incorporated into solar cell – can use existing solar cells, and add additional optical coatings
  - Does not require electrical transport of generated carriers – no contacts, collection, resistivity, mobility issues.
  - Efficient optical processes desired for applications other than solar – development effort is shared.
  - Requires efficient optical conversion over broad spectrum.



# Multiple Spectrum Solar Cells

- Approaches for multiple spectrum solar cells.
  - Thermophotonics: Use thermally-excited LED to generate a narrow solar spectrum.
    - Assuming efficient spectrum conversion and max concentration, efficiency can be  $>80\%$
    - Requires demonstration of efficient thermally-excited LED and cooling from light emission
    - Using known materials and biases, efficiency is 50%.

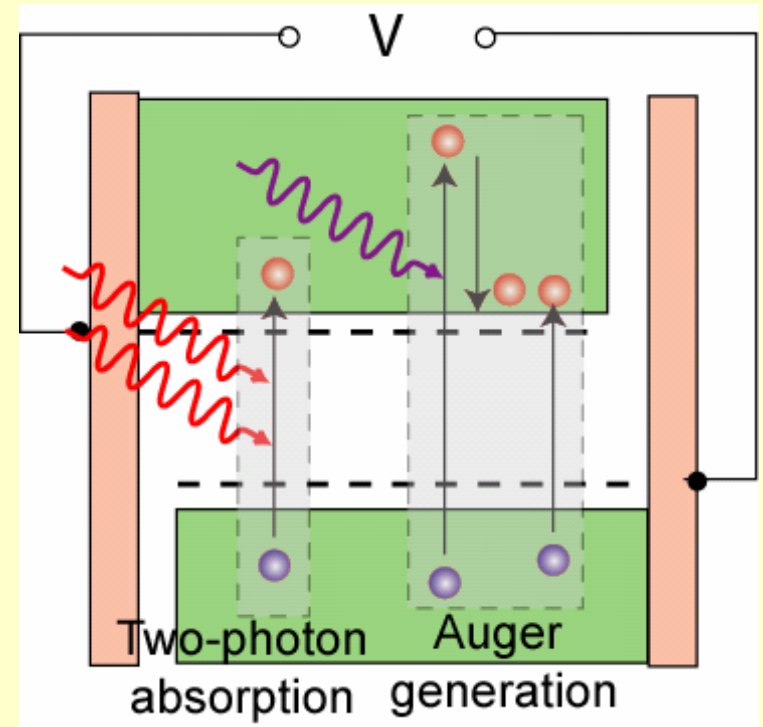


# Multiple Absorption Path (Impact Ionization) Solar Cells



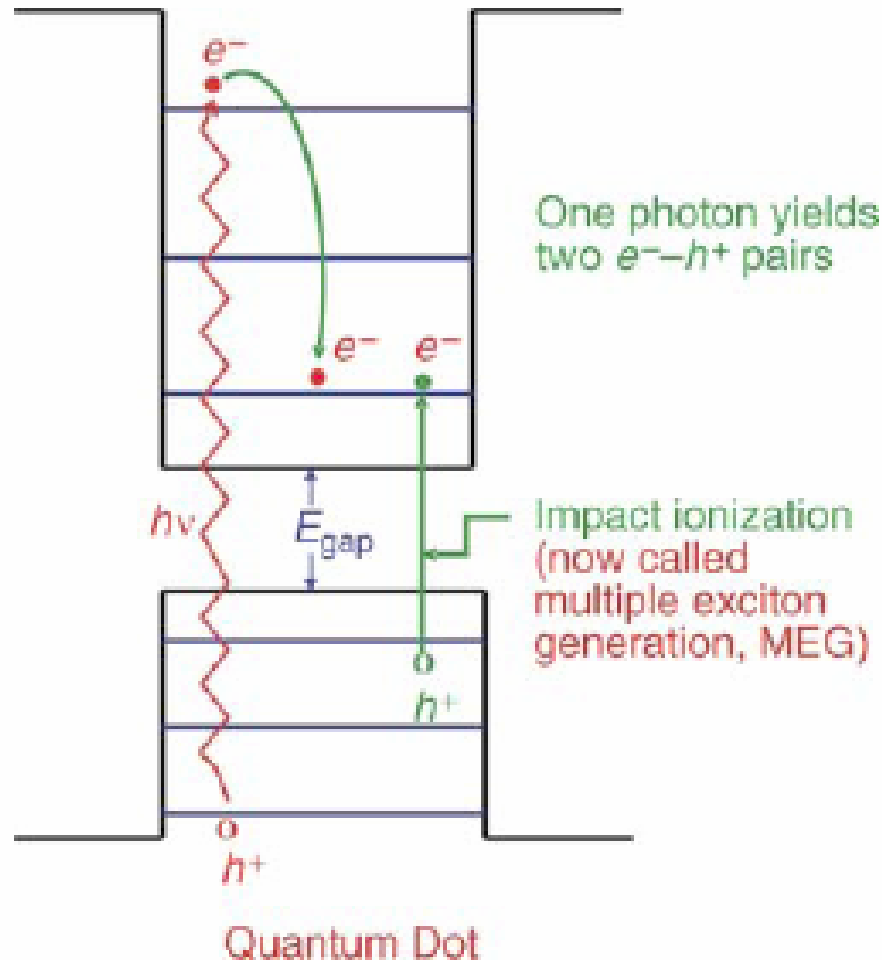
# Multiple Absorption Path Solar Cells

- Change absorption mechanisms such that one photon  $\neq$  one electron-hole pair
- Mechanisms include:
  - Two-photon absorption
  - Impact ionization/Auger generation
- Absorption processes have been observed in bulk materials, but absorption coefficient is very small – e.g., quantum efficiency  $> 80\%$  in silicon solar cells.
- Materials with quantum confinement allow increases in alternate absorption processes.



# Multiple Exciton Generation

Hot electron cooling generates multiple excitations via **Reverse Auger Process**.



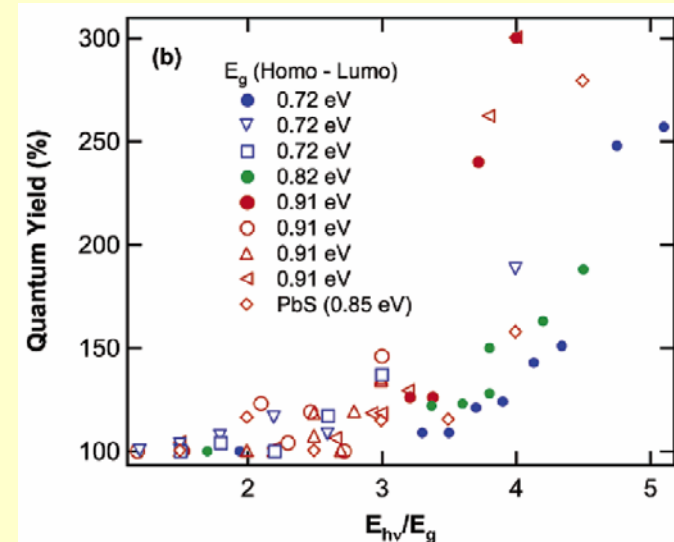
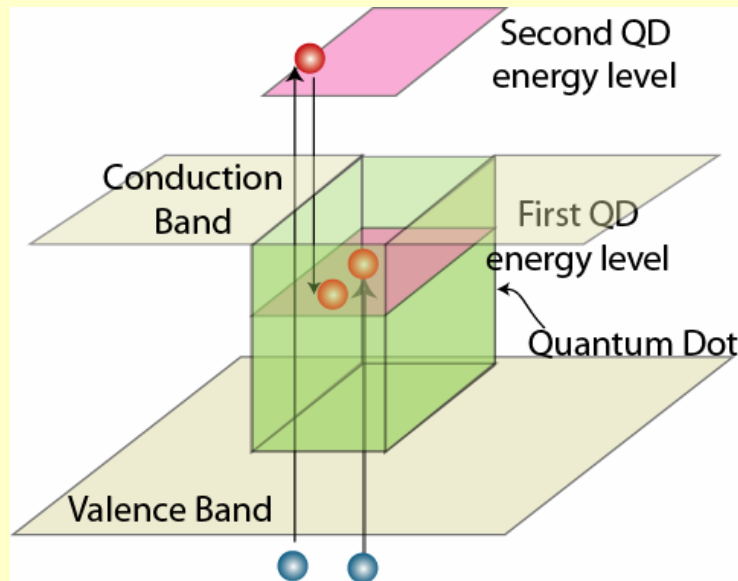
**Higher voltage:** Extracting hot-electrons before they cool down.

**Higher Current:** Reverse Auger process is faster than the hot electron cooling.



# Multiple Absorption Path Solar Cells

- Impact ionization or multiple exciton generation demonstrated efficient absorption processes in PbS and PbSe colloidal **quantum dots**.
- Efficiency depends on number of excitons generated (measured by quantum efficiency) and threshold energy ( $E_{th}$ ). For a photon with energy  $m \times E_g$ , should generate  $m$  electron-hole pairs.
- Efficiency for demonstrated processes is similar to three junction tandem.



R.J. Ellingson, M.C. Beard, J.C. Johnson, P.Yu, O.I. Micic, A.J. Nozik, A. Shabaev, and A.L. Efros "Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots" Nano Letters Vol. 5, No. 5 p. 865-871 (2005)

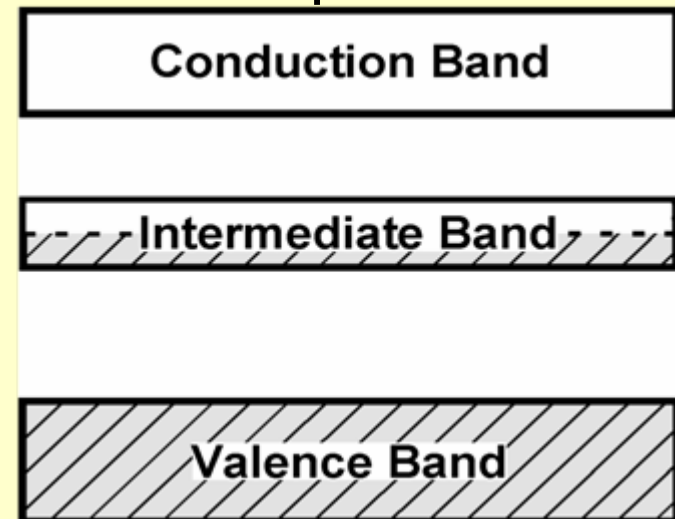
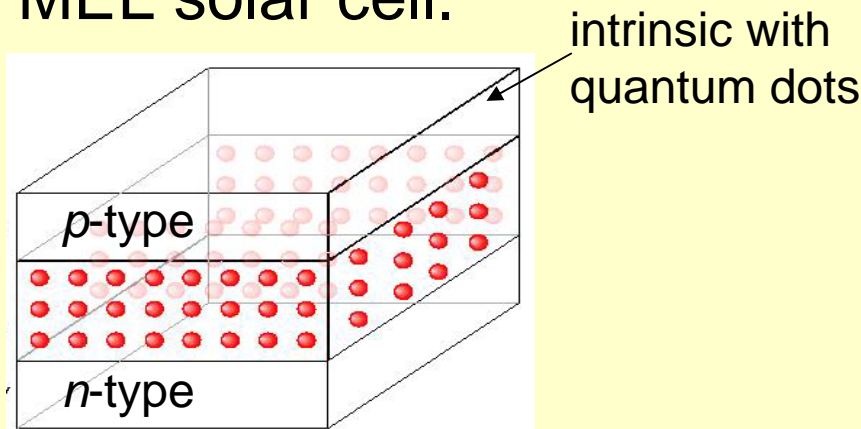


# Multiple Energy Level / Quantum Dot Solar Cells



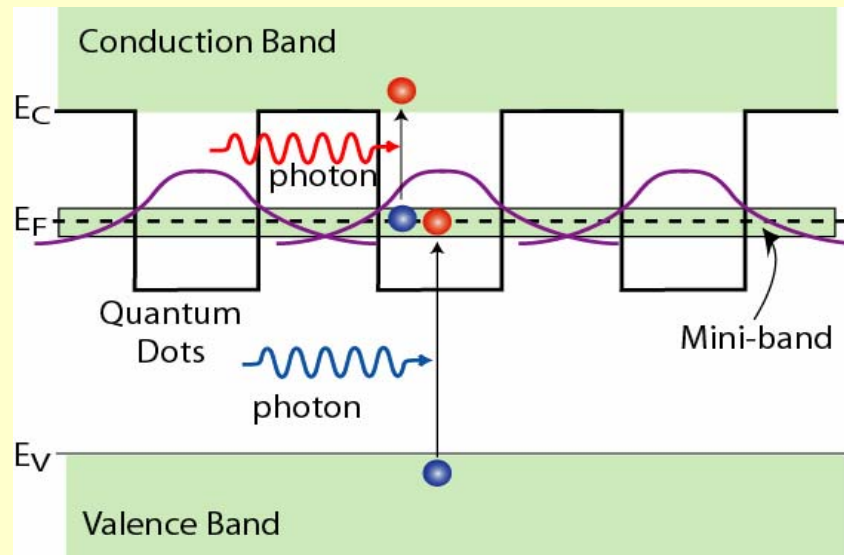
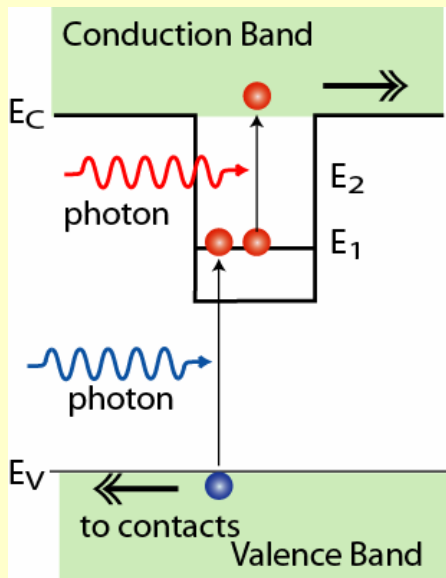
# Quantum Dot Solar Cells

- An ordered array of QD allows a multiple energy level solar cell via formation of mini-bands (also called intermediate band or hot carrier solar cells).
- Bands formed by overlap of energy levels in QD array.
- Band structure of an intermediate band solar cell requires: (1) Three-level band structure; (2) Fermi-level at intermediate band.
- Need to determine material system to implement QD MEL solar cell.



# Multiple Energy Level Solar Cells

- Introduce more than a single quasi-Fermi level separation by introducing additional energy levels or bands, such that extracted energy of photon  $\neq$  energy of band gap and
- The energy levels must all simultaneously be radiatively coupled.
- Energy levels can be spatially localized (energy levels) or interacting to form mini-bands.
- Lower  $V_{oc}$ .
- Can use quantum dots, quantum wires, quantum wells.



# Ultra-High Efficiency Approaches

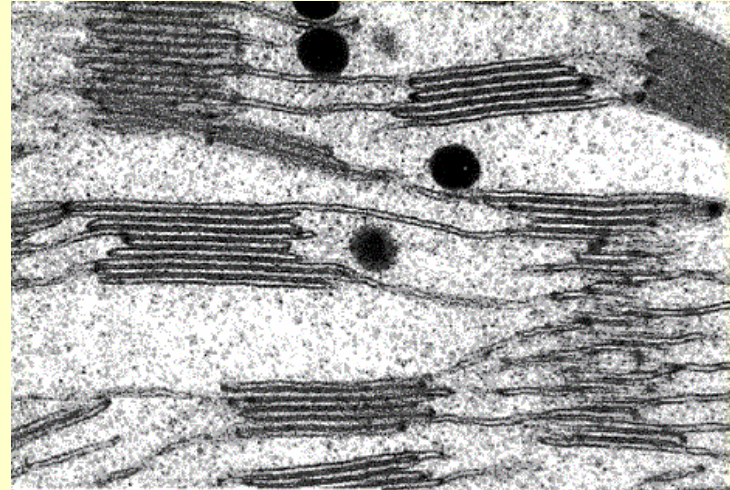
- Similarities in new high efficiency approaches:
  - Most of the approaches require control over band structure, and use of band structure which promotes interaction among different energy levels.
    - Implemented by either new materials to photovoltaics (ie phosphors, materials with multiple energy levels) or, more generally by **nanostuctures**.
- Types of nanostructures – key issues are how they are fabricated, materials, periodicity, and spacing of nanostructures.
  - Most approaches use QDs, because of zero density of states.
  - QD fabrication can be colloidal (low cost but difficult to achieve periodicity) or **epitaxially grown (high cost, periodic, widely spaced)**.
  - Localized MEL solar cells can use well or wires, as long as transport is NOT in plane with nanostructure.
    - Since carriers cross interface, susceptible to recombination at interface.



# Nanocomposite Solar Cells



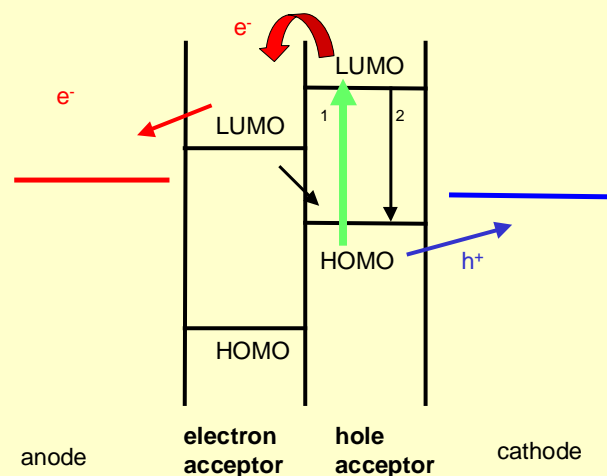
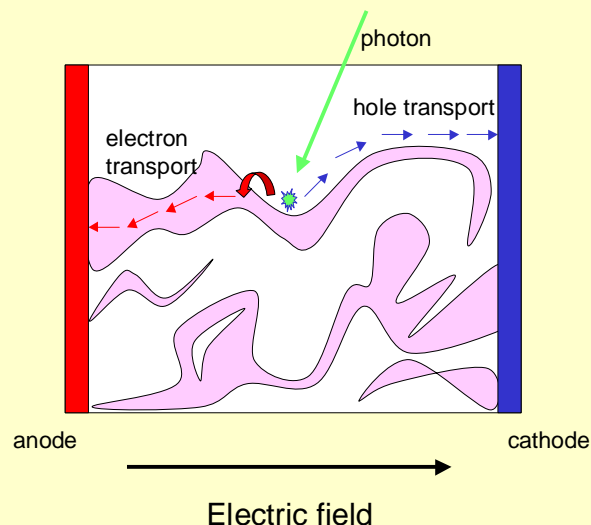
# Nature's way



- Photosynthesis: Light harvesting complex embedded in folded membrane (Chloroplast)
- Multiple interfaces  $\Rightarrow$  high optical depth

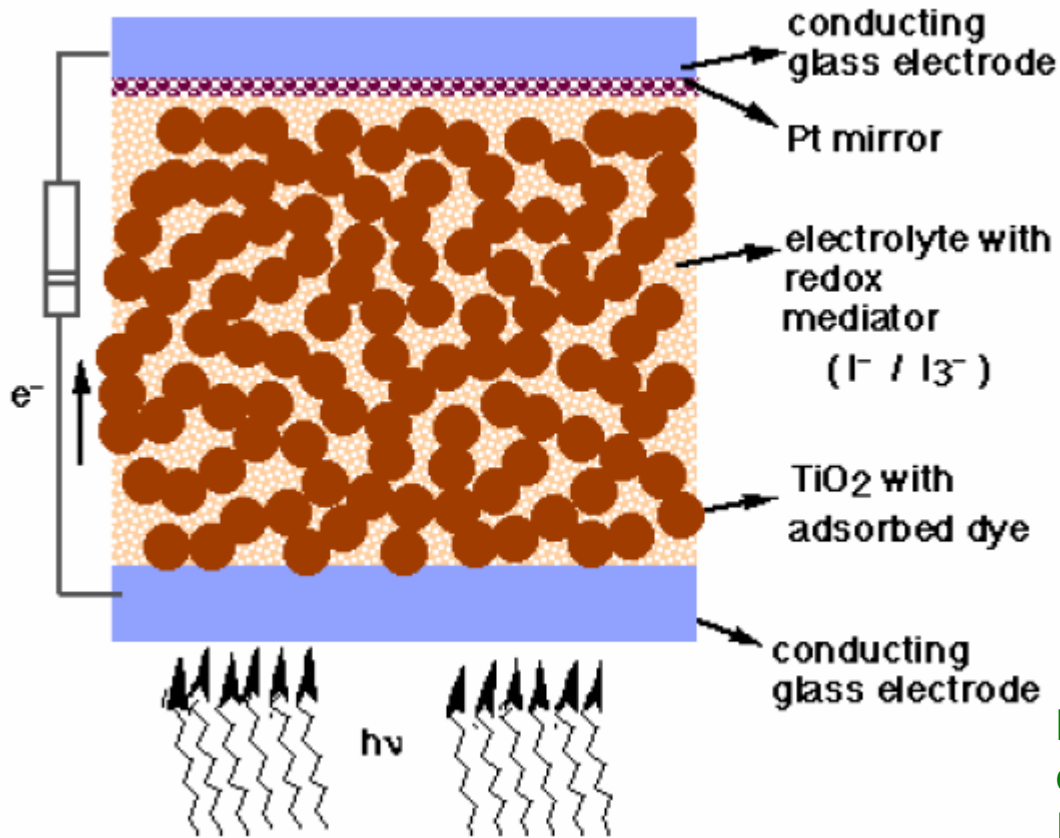
# Blended Molecular Materials

- Blend hole accepting with electron accepting material
- Length scale of blend  $\sim$  exciton diffusion length
- Charge separation at D-A interface
- Continuous paths for electron and hole percolation





# Dye Sensitized Solar Cell



**Electrolytes:**  
**Room Temperature Ionic liquids (RTILs) (Redox Couple in a solvent).**

Ionic Liquids	Viscosity (mPa s)	$J_{sc}$ (mA cm <sup>2</sup> )	$V_{oc}$ (mV)	FF	$\eta$ (%)
EMImTFSI	39	9.4	550	0.45	2.4
EMImBF <sub>4</sub>	43	9.9	602	0.55	3.3
BMImPF <sub>6</sub>	352	4.3	576	0.62	1.6
BPTFSI	72	6.3	577	0.56	2.0
EMImDCA	21	7.8	703	0.66	3.8

**Dyes:**  
**N3: cis-(NCS)<sub>2</sub>bis(4,4'-dicarboxy-2,2'-bipyridine)-ruthenium(II).**  
**Black Dye:**



# Quantum Confinement Effect

- Efros and Efros (1982 *Sov. Phys. Semicond.*) first proposed the quantum confinement effect based on the experimental findings by Ekimov and Onushchenko (1981 *JETP Lett.*) of the size effect on the blue shift in the main exciton absorption of CuCl (30 Å) nanocrystallite.
- The confinement effect on the band gap,  $E_G$ , of a nanosolid of radius  $R$  was expressed as:

$$E_G(R) = E_G(\infty) + \frac{\hbar^2 \pi^2}{2\mu R^2}$$



# Band Gap Variation with Particle Size

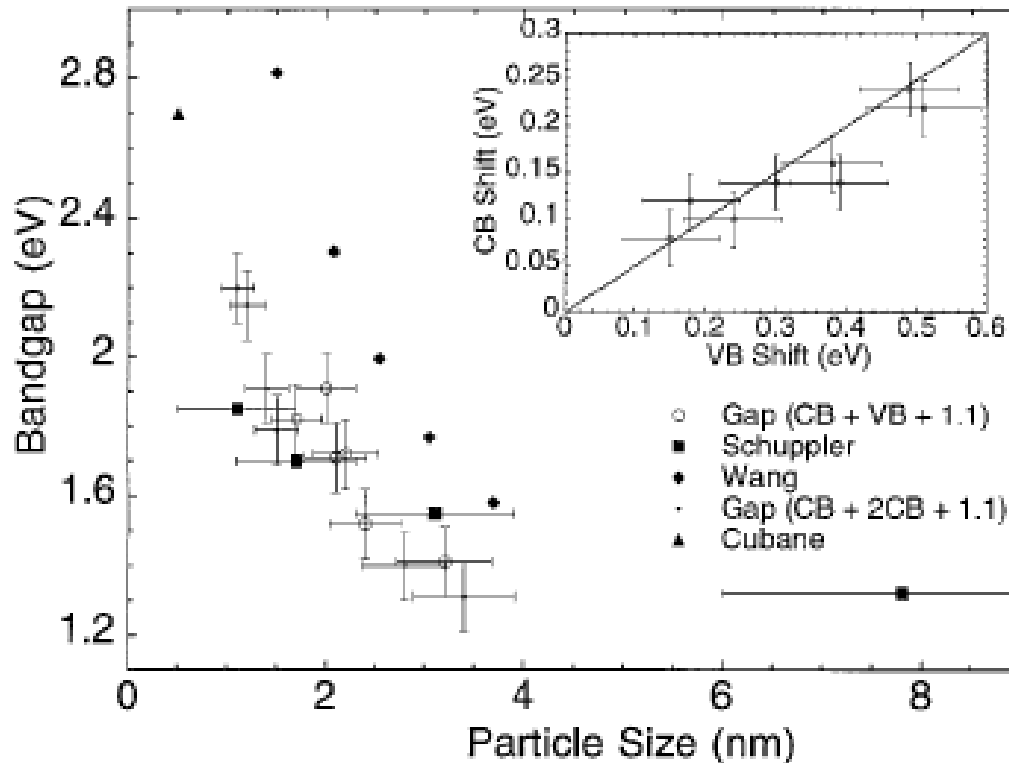


FIG. 4. Band gap of the nc-Si as a function of particle size.

**Bohr Radius of Si = 4.6 nm at 300K, Band Gap of Bulk Si = 1.1. eV**

**Bohr radius of Ge = 24 nm at 300K, Band Gap of bulk Ge = 0.66 eV**

## Changes in the Electronic Properties of Si Nanocrystals as a Function of Particle Size

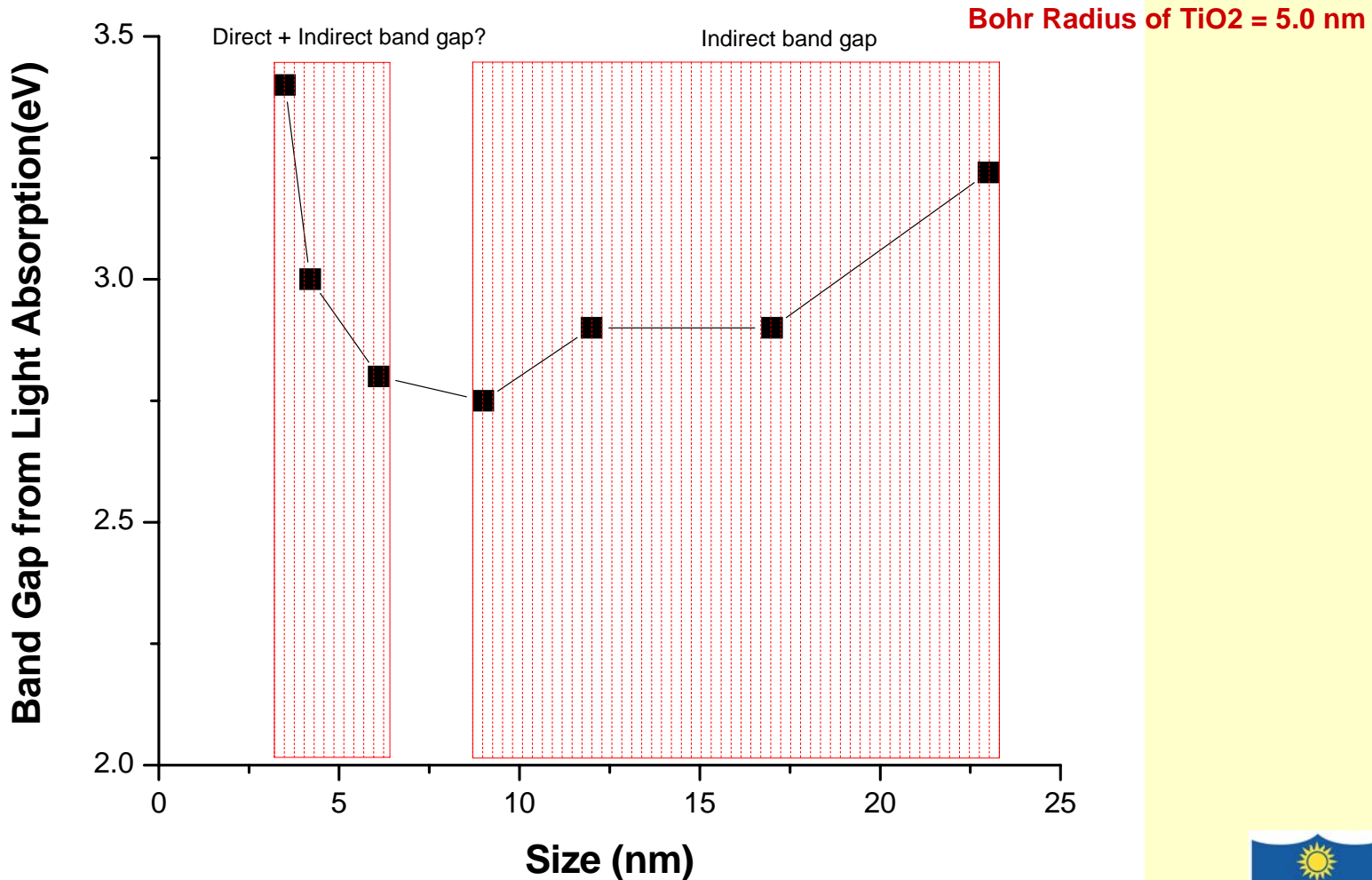
T. van Buuren, L. N. Dinh, L. L. Chase, W. J. Siekhaus, and L. J. Terminello

Chemistry and Materials Science Department, Lawrence Livermore National Laboratory, Livermore, California 94550

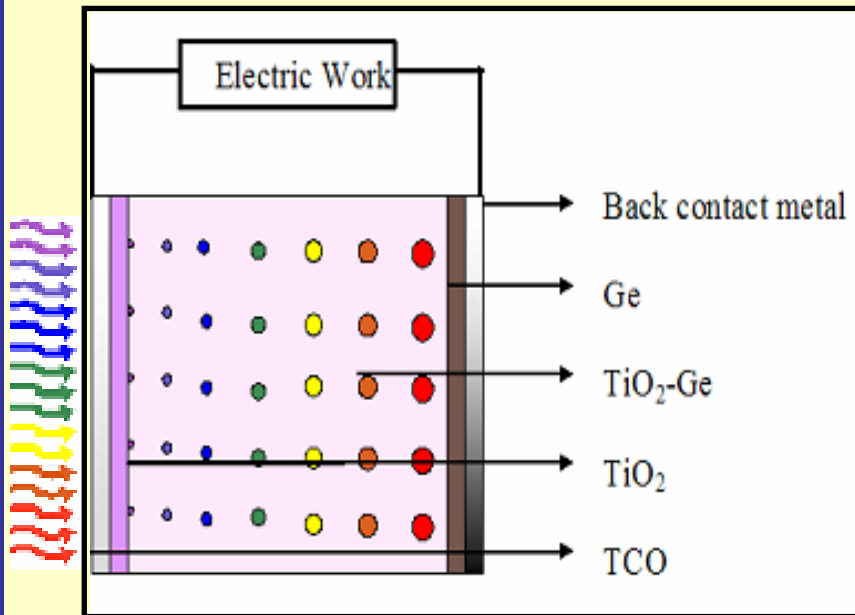
(Received 31 October 1997)



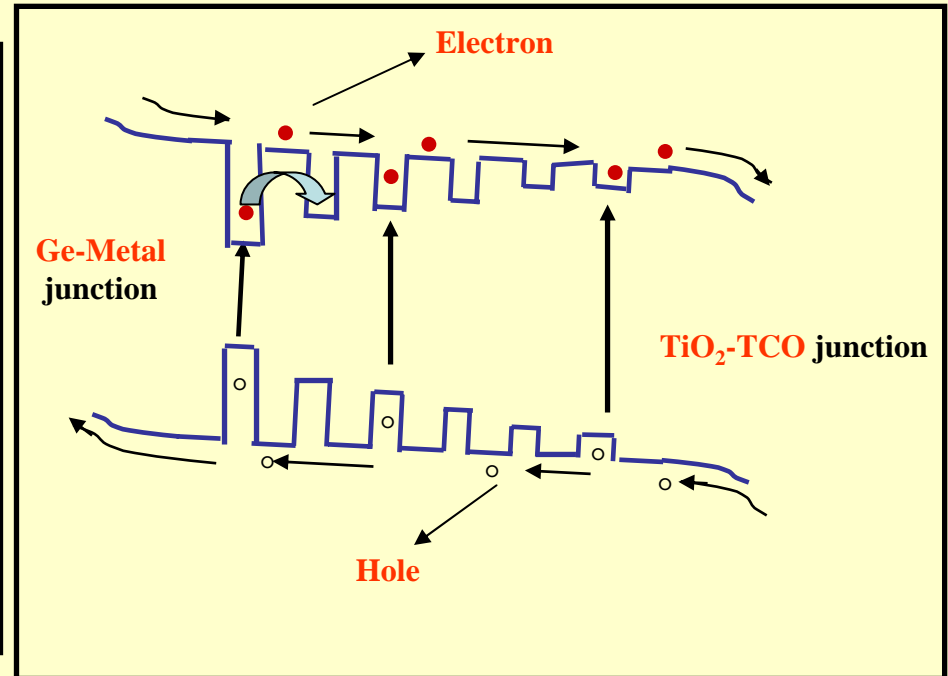
# Size Dependence of Band Gap ( $\text{TiO}_2$ )



# Composite Cell Schematics



*Schematic of Desired Solar cell*



*Energy Band Diagram of TiO<sub>2</sub>-Ge Nanocomposite*

**Bohr radius of Ge = 24 nm at 300K, Band Gap of bulk Ge = 0.66 eV**

# Why TiO<sub>2</sub>-Ge?

- A very simple fabrication process can be used.
- An initial amorphous composite of TiO<sub>2</sub>-Ge can be deposited as a thin films.
- The electronegativity of Ti (1.54 Pauling) is lower than that of Ge (2.01 Pauling)
- The enthalpies of formation ( $\Delta H_f^\circ$ ) for TiO<sub>2</sub> and GeO<sub>2</sub> are -944.0 and -580 kJ/mol, respectively.
- The thermodynamics and relative stabilities of the GeO<sub>2</sub> and TiO<sub>2</sub> can be exploited by a controlled deposition and annealing procedures to obtain the right size and size distribution of the Ge nanodots.

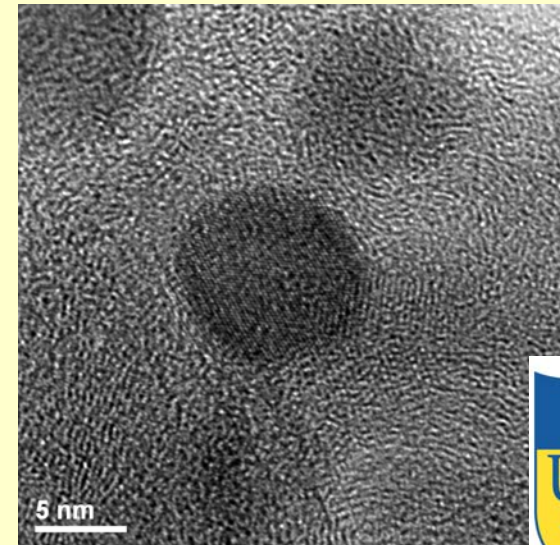
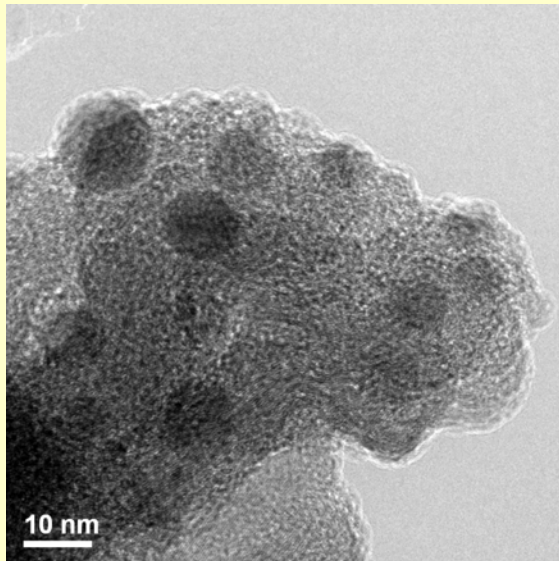
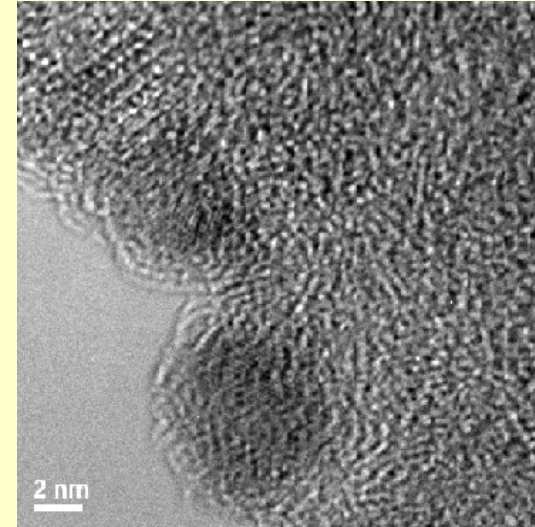
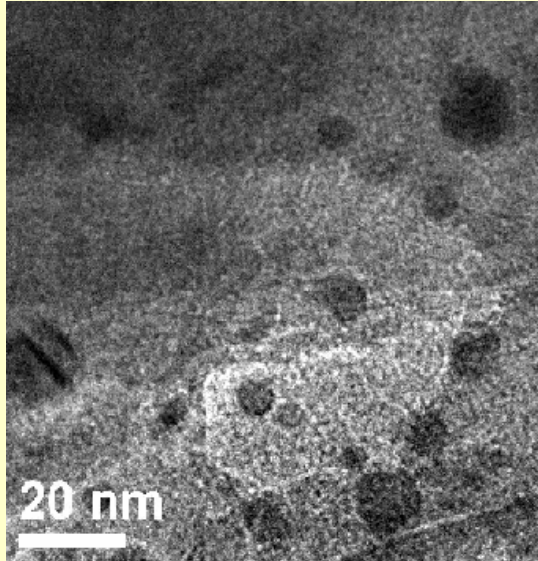


# Why TiO<sub>2</sub>-Ge?

- All layers (including active and non-active) can be fabricated in a single multi-target sputtering system.
- Without any multi-junction configuration, and only by the introduction of different sizes Ge nanodots in TiO<sub>2</sub> matrix, it is possible to absorb a wide range of solar radiation with energies in UV to VIS to IR.
- All this is accomplished in a single active layer.
- Bohr radius of Ge is relatively large, 24 nm, therefore, it is easy to make size gradient of Ge nanodots in the TiO<sub>2</sub> matrix.
- TiO<sub>2</sub>-Ge is cost effective and environmentally stable and the processes involved have very small, if any, environmental footprints.

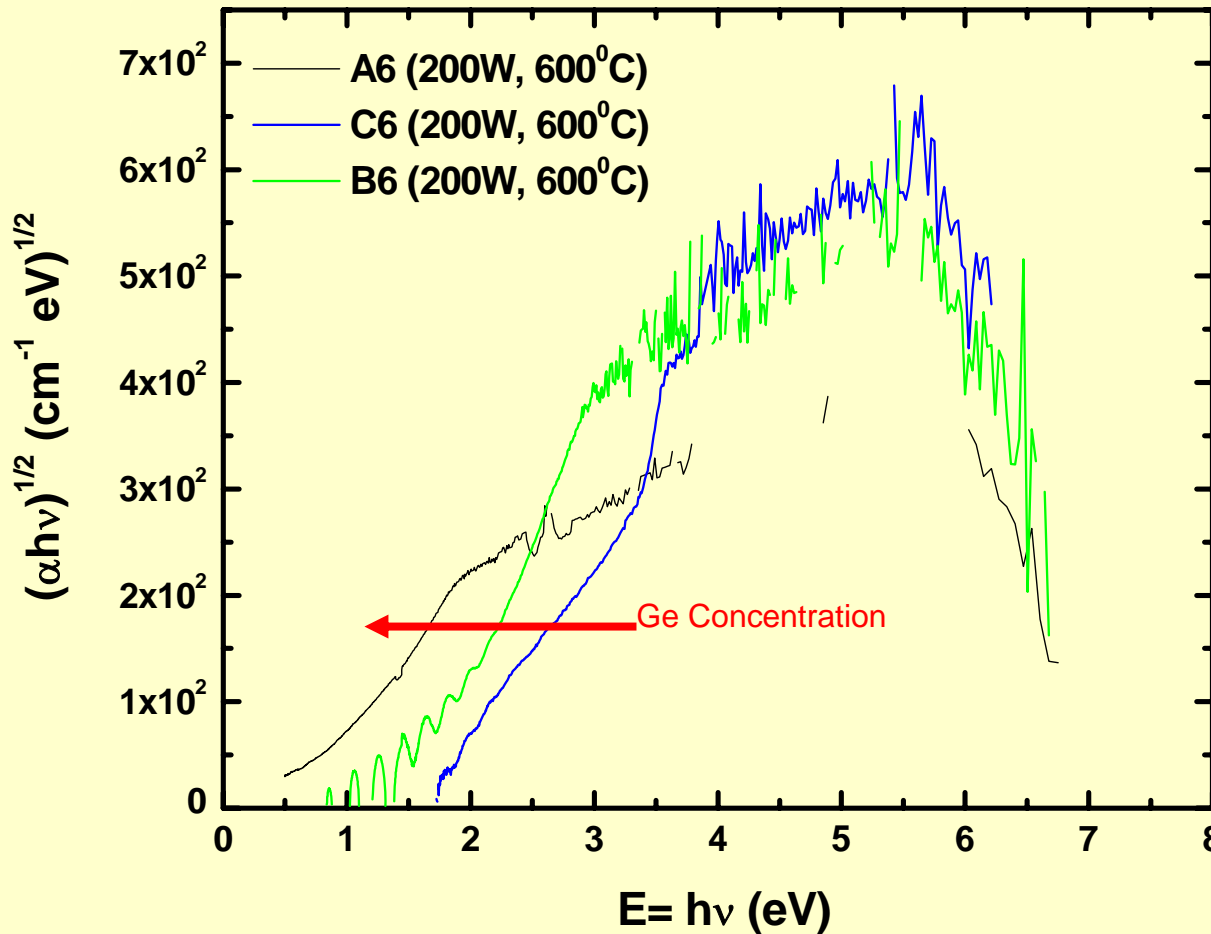


# HRTEM (Planar)





# Transition in optical band gap due to change in Ge concentration in target



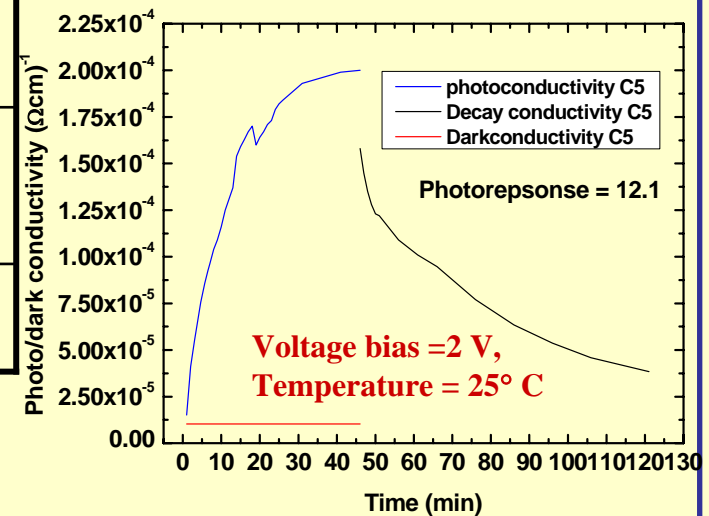
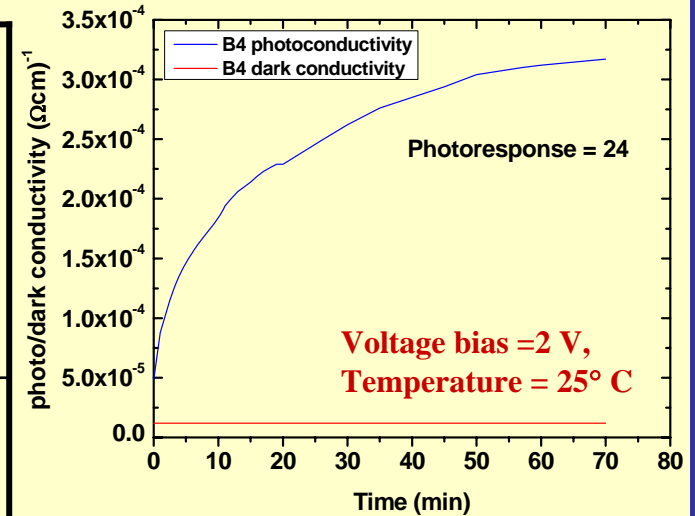
Ge concentration and particle size are related





# Photoconductivity

Sample	Dark conductivity $(\Omega\text{cm})^{-1}$ $\sigma_{\text{dark}} = \frac{I_{\text{dark}} L}{V w t}$	Photoconductivity $(\Omega\text{cm})^{-1}$ $\sigma_{\text{light}} - \sigma_{\text{dark}}$	Photoresponse $\frac{\sigma_{\text{light}} - \sigma_{\text{dark}}}{\sigma_{\text{dark}}}$
A5 (150W, 600°C)	$1.72 \times 10^{-2}$	0	0
A6 (200W, 600°C)	$3.84 \times 10^{-3}$	0	0
C5 (150W, 600°C)	$1.5 \times 10^{-5}$	$1.85 \times 10^{-4}$	12
B4 (100W, 600°C)	$1.2 \times 10^{-5}$	$3.17 \times 10^{-4}$	24

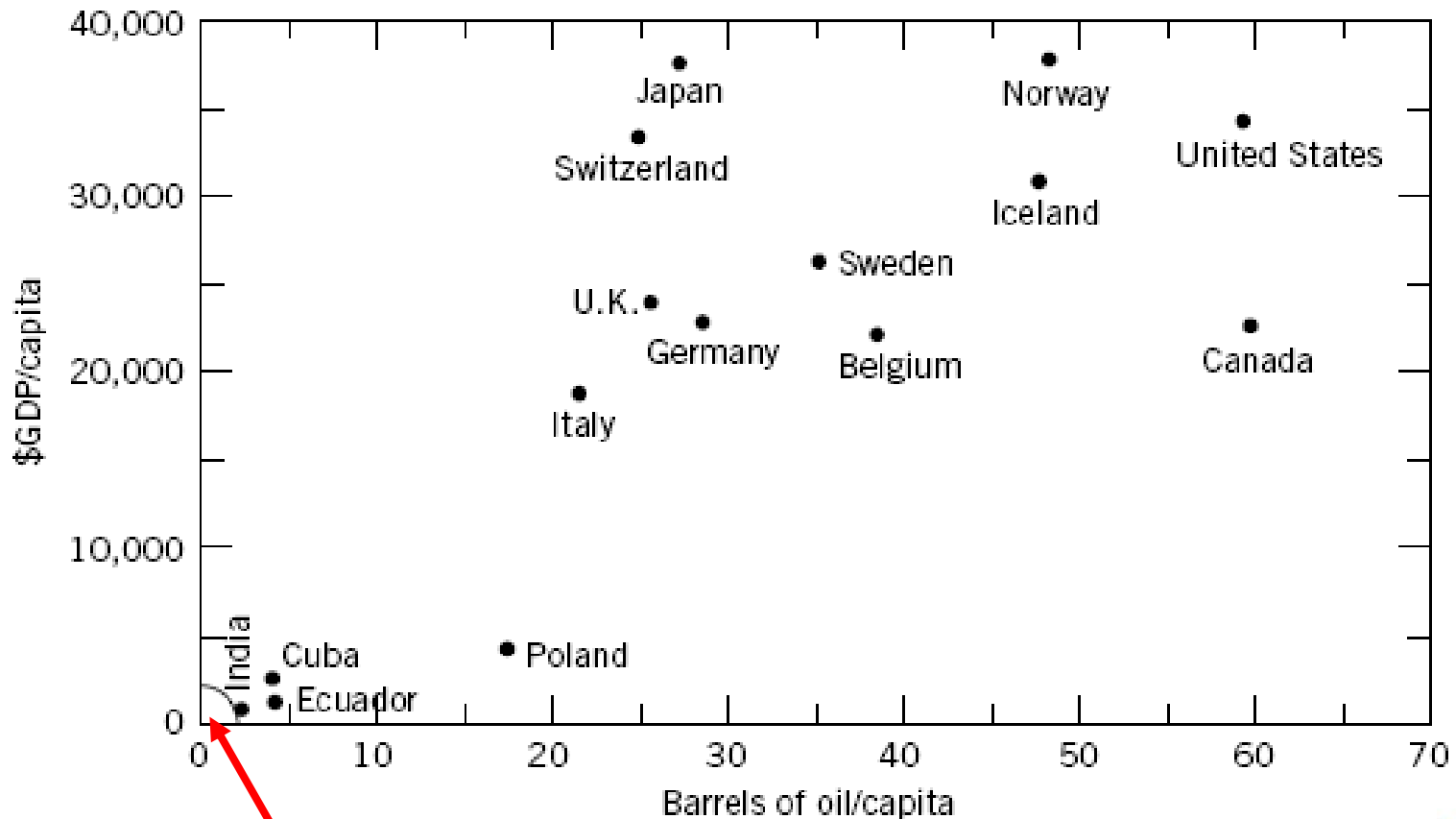


# QUO VADIMOS...

- Tremendous amount of activity in recent years on all approaches to enhance efficiency.
- The current technology will benefit from more Si production units that are coming on line to offset demand related price increase.
- More public awareness and pressure on policy makers that **alternative energy sources** have to immediately become a part of the solution. Photovoltaics is just one of the approaches.
- Invert the Paradigm.



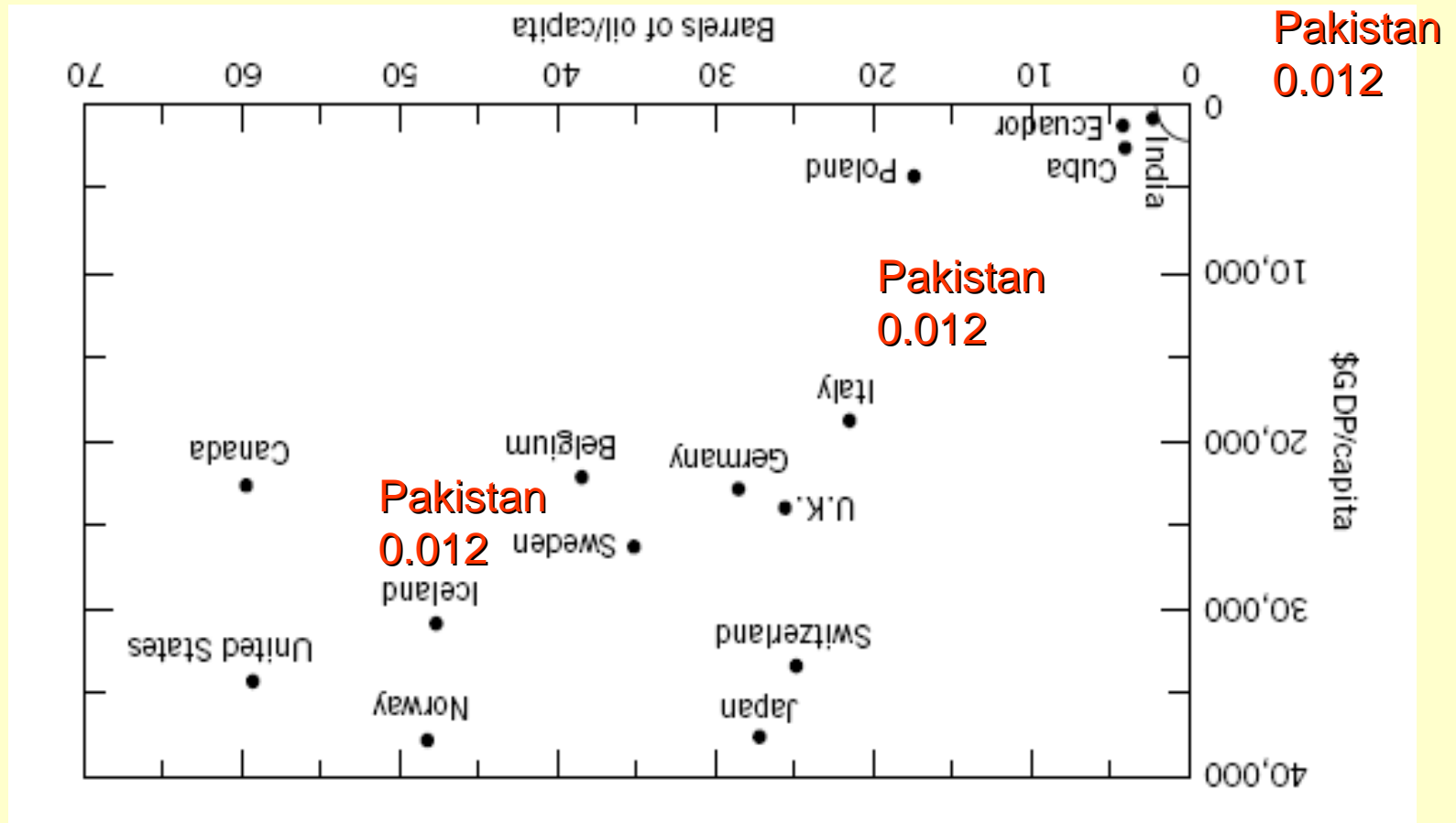
# Current Paradigm



Pakistan  
0.012



# Inverted Paradigm



**Fin !**