Nanostructures in Green Photonics

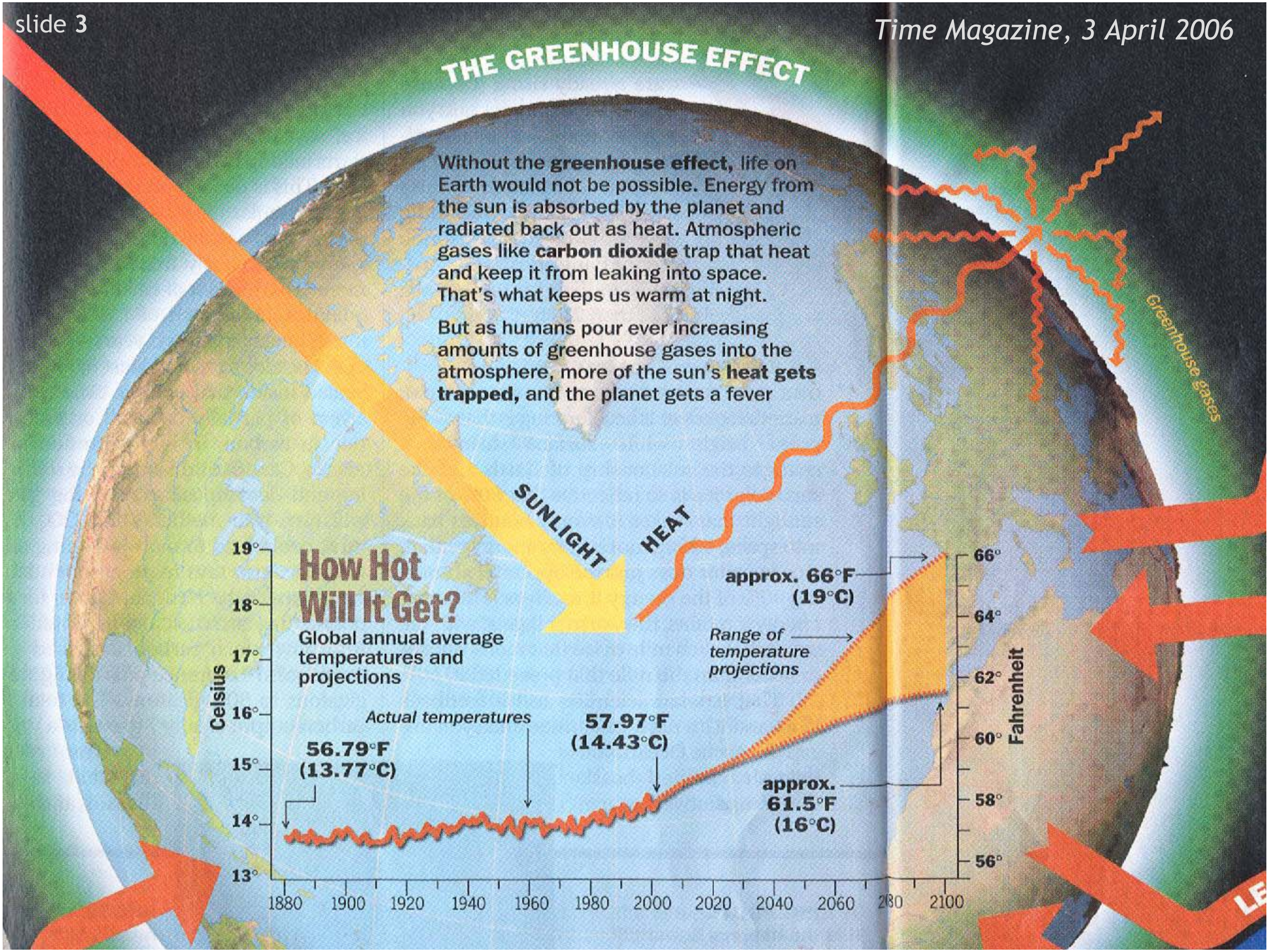
Vladimir Bulović, EECS

Artificial Lighting consumes 8% of US energy and 22% of US electricity
The energy cost is estimated at $50B annually or $200 per capita

	EFFICIENCY	PENETRATION
Incandescent	5%	12%
Fluorescent	20%	62%
HID lamps	25%	26%
White LEDs	35%	----

Note: Electric Motor Efficiency 85~90%

Time Magazine, 3 April 2006



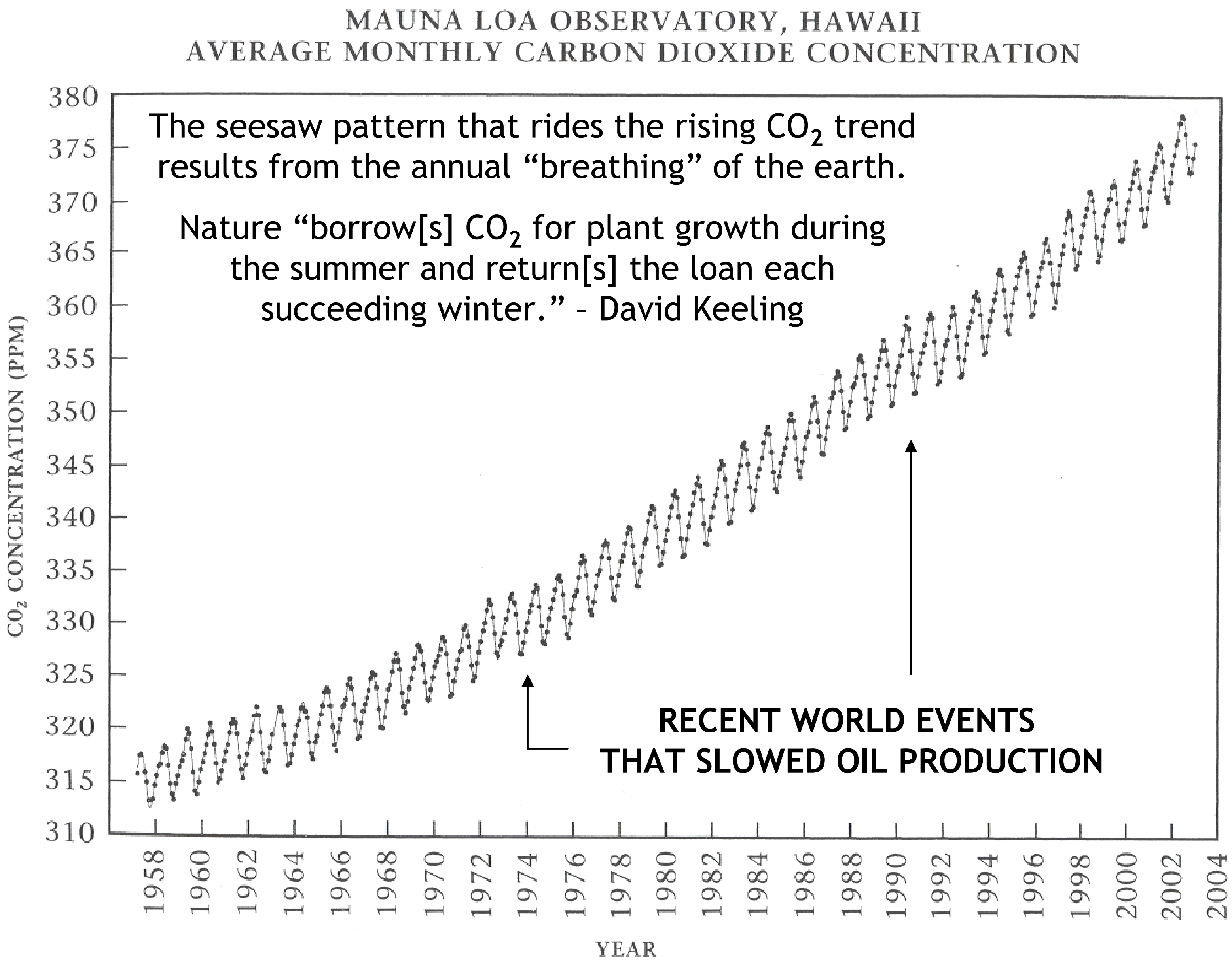
THE GREENHOUSE EFFECT

Without the **greenhouse effect,** life on Earth would not be possible. Energy from the sun is absorbed by the planet and radiated back out as heat. Atmospheric gases like **carbon dioxide** trap that heat and keep it from leaking into space. That's what keeps us warm at night.

But as humans pour ever increasing amounts of greenhouse gases into the atmosphere, more of the sun's **heat gets trapped,** and the planet gets a fever

How Hot Will It Get?

Global annual average temperatures and projections



MAUNA LOA OBSERVATORY, HAWAII
AVERAGE MONTHLY CARBON DIOXIDE CONCENTRATION

The seesaw pattern that rides the rising CO_2 trend results from the annual “breathing” of the earth.

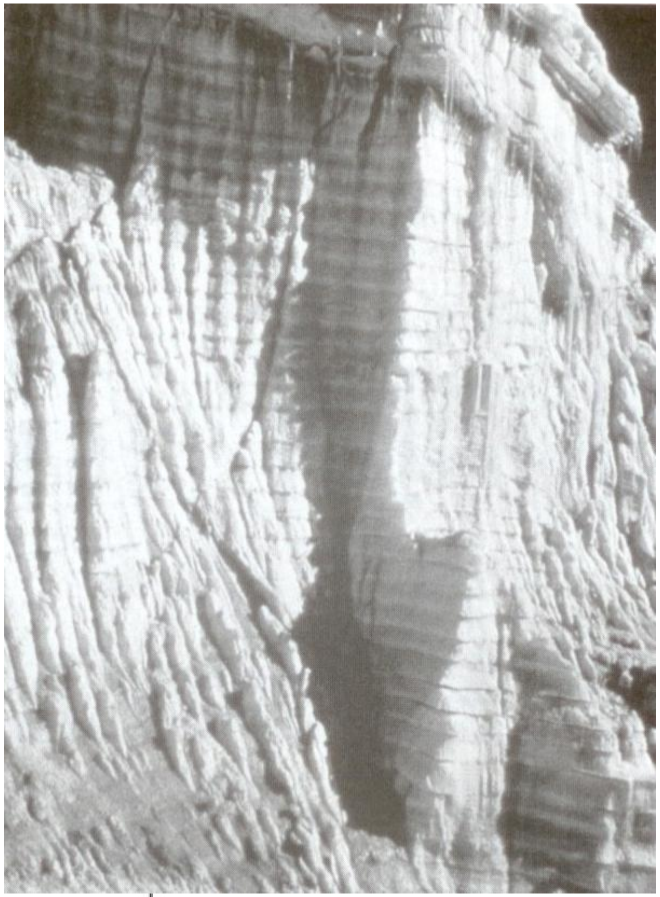
Nature “borrow[s] CO_2 for plant growth during the summer and return[s] the loan each succeeding winter.” – David Keeling

**RECENT WORLD EVENTS
THAT SLOWED OIL PRODUCTION**

Science <u>*310*</u>*, 1313 (2005)*

**IS THERE ANY HUMAN EFFECT
ON THE ENVIRONMENT ?**

TEMPERATURE TRACKS CARBON DIOXIDE at Vostok, Antarctica

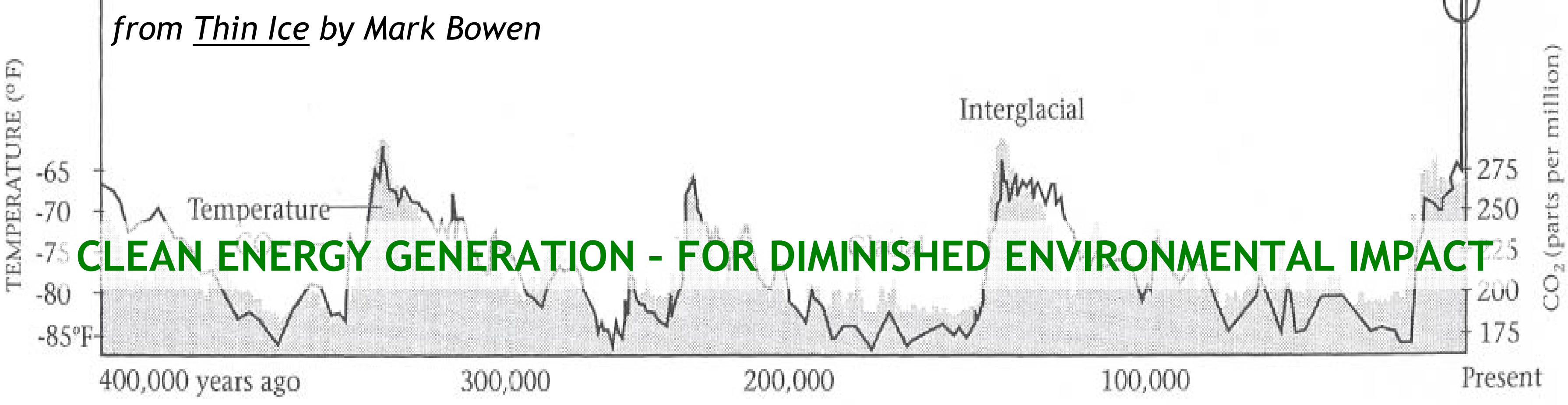


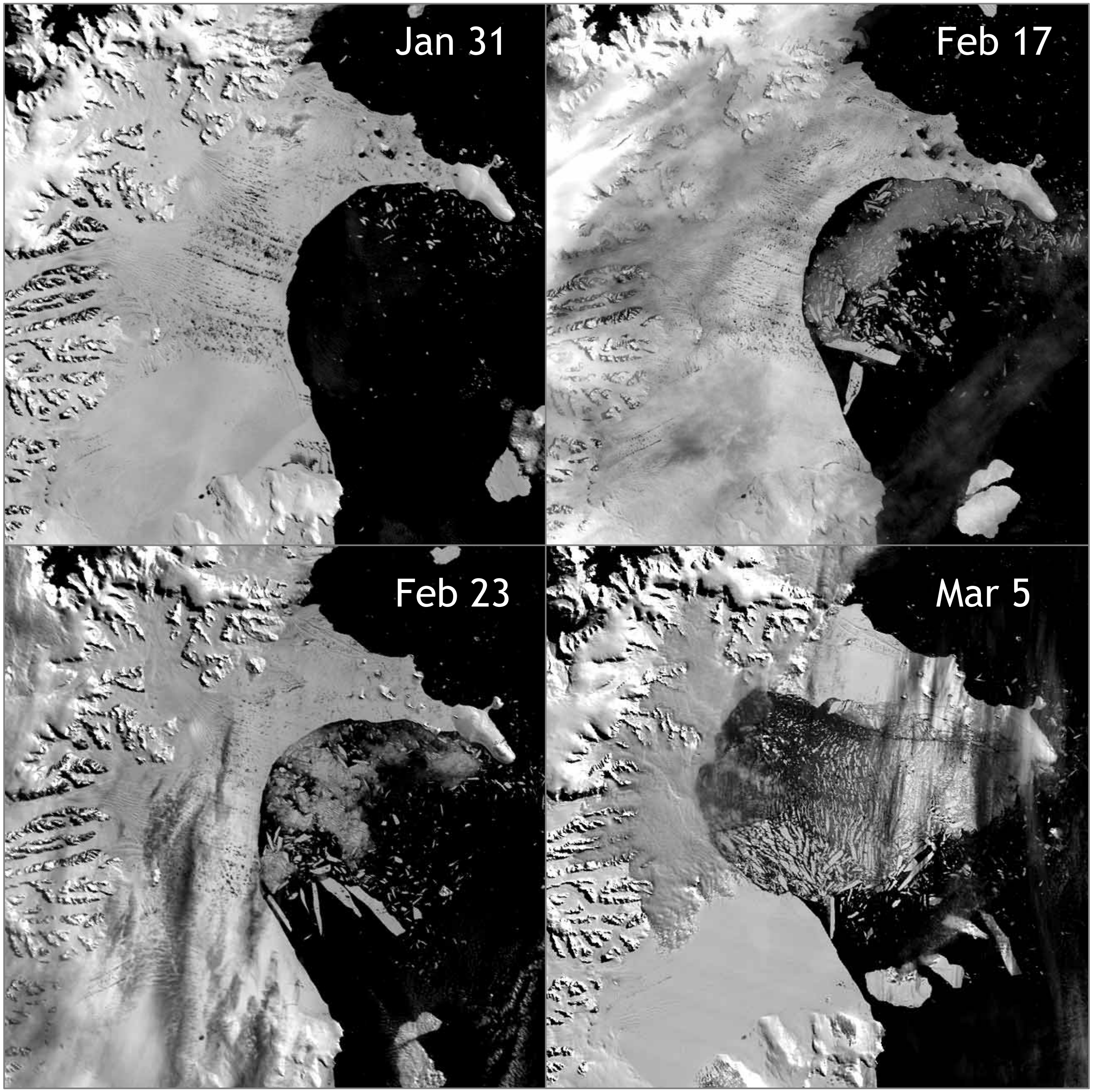
from Thin Ice by Mark Bowen

Temperature inferred from isotope ratios in the Vostok ice core

Carbon dioxide levels measured in the trapped air bubbles in the same core

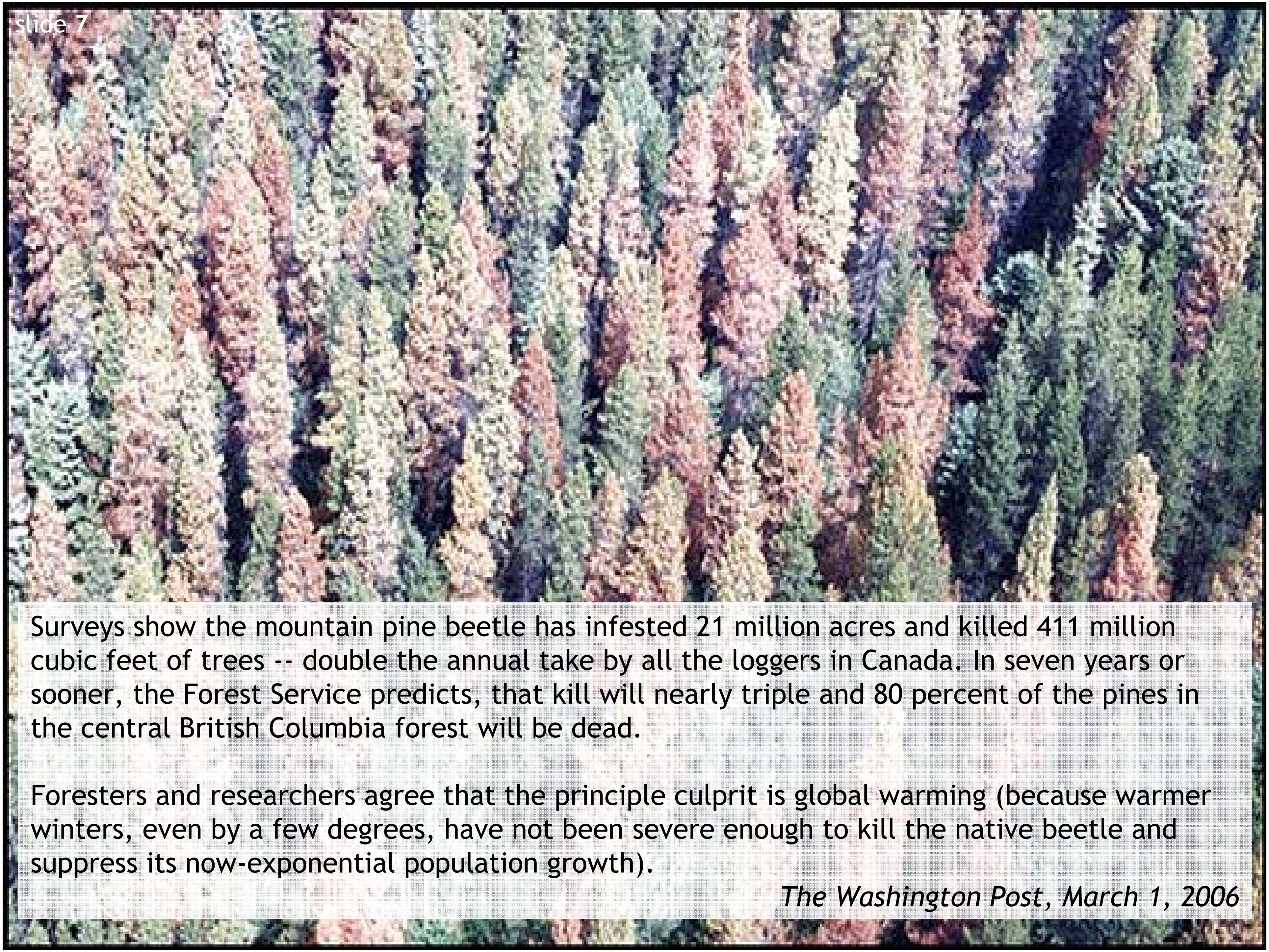
CO_2 TWICE AS HIGH
AS IT HAS EVER BEEN
IN THE LAST 400,000 YEARS





Between
Jan 31, 2002 and
March 5, 2002
a chunk of the
Larsen B ice shelf
the size of
Rhode Island
disintegrated.

Images from NASA's
Terra satellite,
National Snow and Ice
Data Center,
University of
Colorado, Boulder.

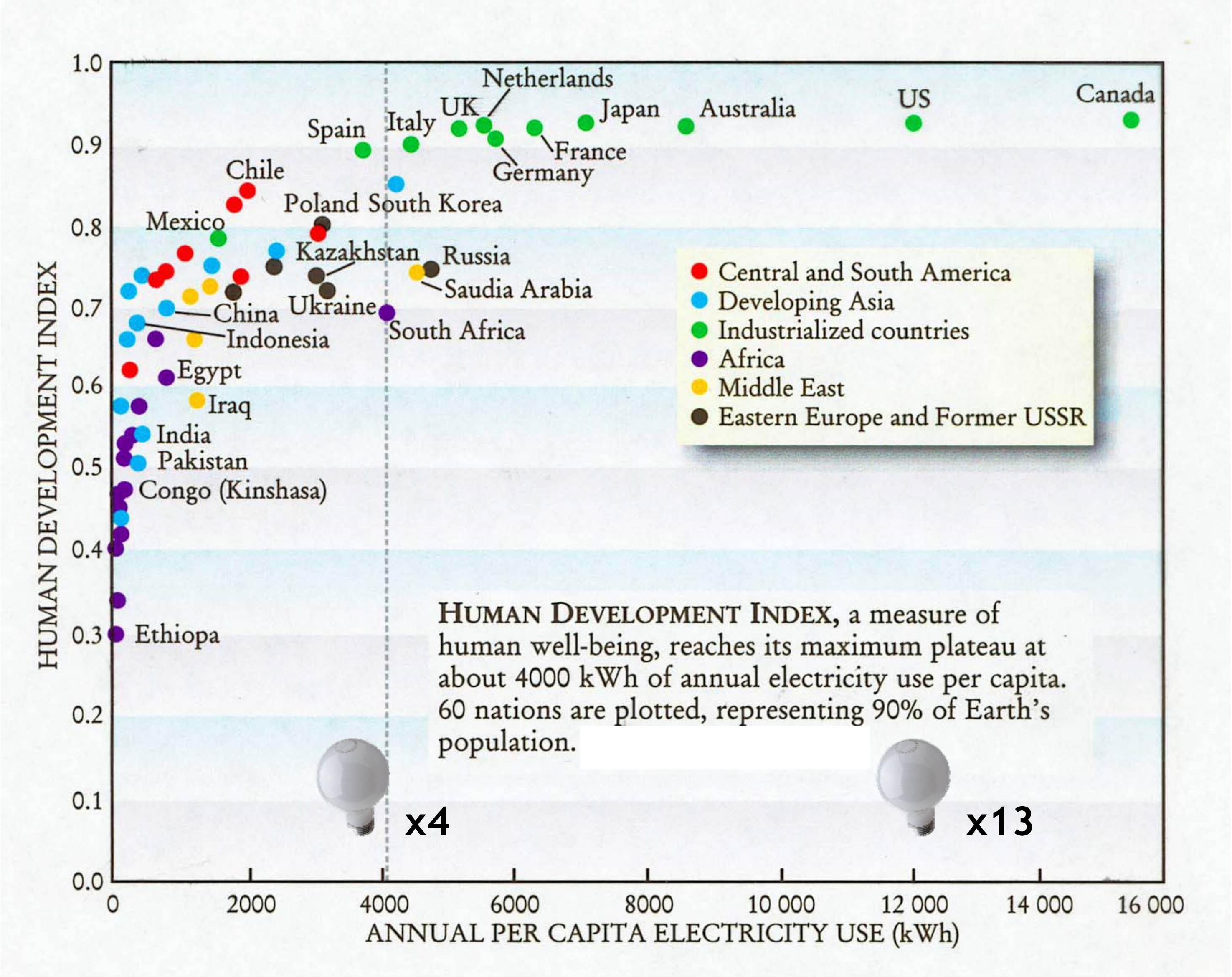


Surveys show the mountain pine beetle has infested 21 million acres and killed 411 million cubic feet of trees -- double the annual take by all the loggers in Canada. In seven years or sooner, the Forest Service predicts, that kill will nearly triple and 80 percent of the pines in the central British Columbia forest will be dead.

Foresters and researchers agree that the principle culprit is global warming (because warmer winters, even by a few degrees, have not been severe enough to kill the native beetle and suppress its now-exponential population growth).

The Washington Post, March 1, 2006

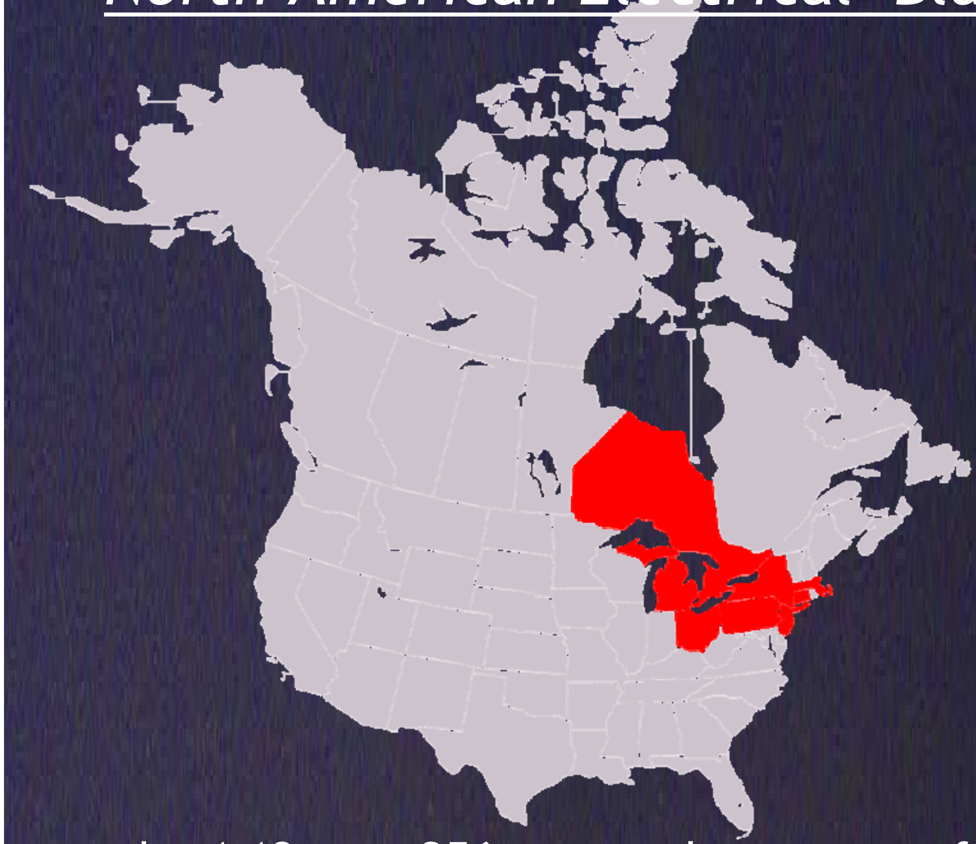
ABUNDANCE OF AFFORDABLE ENERGY RESOURCES CAN UPLIFT THE WORLD



Human Development Index, a measure of human well-being, reaches its maximum plateau at about 4000 kWh of annual electricity use per capita. 60 nations are plotted, representing 90% of Earth's population.

HUMAN WELL-BEING INCREASES WITH INCREASED PER-CAPITA ENERGY USE

August 14, 2003
North American Electrical Blackout



by 4:13 pm 256 power plants were off-line

… August 15 …
just 24 hours into blackout
Air Pollution was Reduced

SO_2 >90%

O_3 ~50%

Light Scattering
Particles ~70%

“This clean air benefit was realized over much of eastern U.S.”

Marufu et al., Geophysical Research Letters 2004

New York City Skyline

CLEANER AIR - BENEFIT OF HEALTHIER ENVIRONMENT

CLEAN and AFFORDABLE ENERGY CAN

UPLIFT THE WORLD

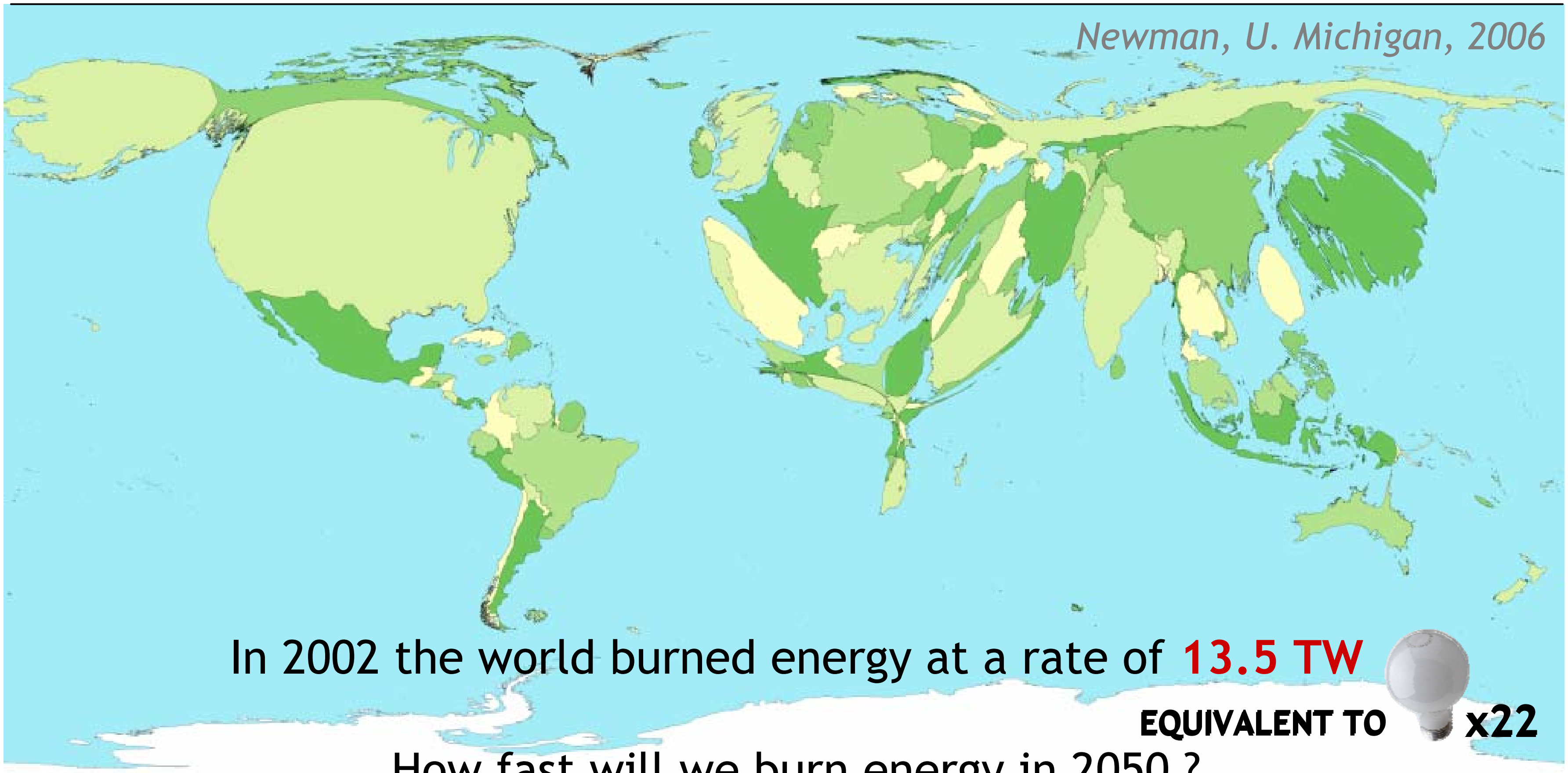
DIMINISH ENVIRONMENTAL IMPACT

GIVE US HEALTHIER ENVIRONMENT

WHERE DOES THE RESPONSIBILITY FOR TECHNOLOGY DEVELOPMENT LIE ?

~ LET’S HIGHLIGHT THE USERS ~

Map of the World Scaled to Energy Consumption by Country



Newman, U. Michigan, 2006

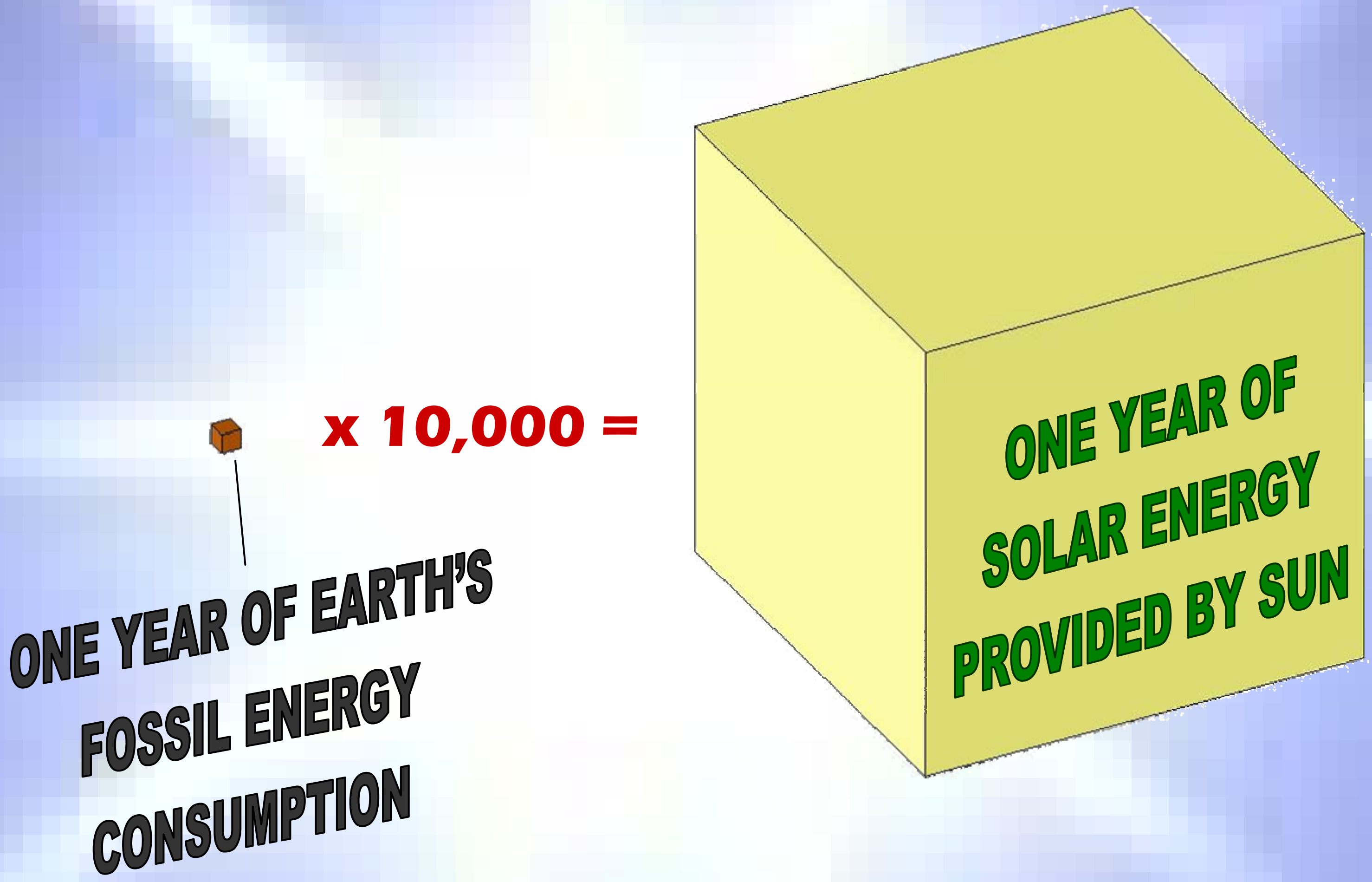
In 2002 the world burned energy at a rate of **13.5 TW**

EQUIVALENT TO **x22**

How fast will we burn energy in 2050 ?
(assume 9 billion people)

If we use energy like in U.S. we will need 102TW
Conservative estimate **28~35TW**

Energy use estimates from Nocera, Daedalus 2006 & Lewis and Nocera, PNAS 2006



ONE YEAR OF EARTH'S FOSSIL ENERGY CONSUMPTION

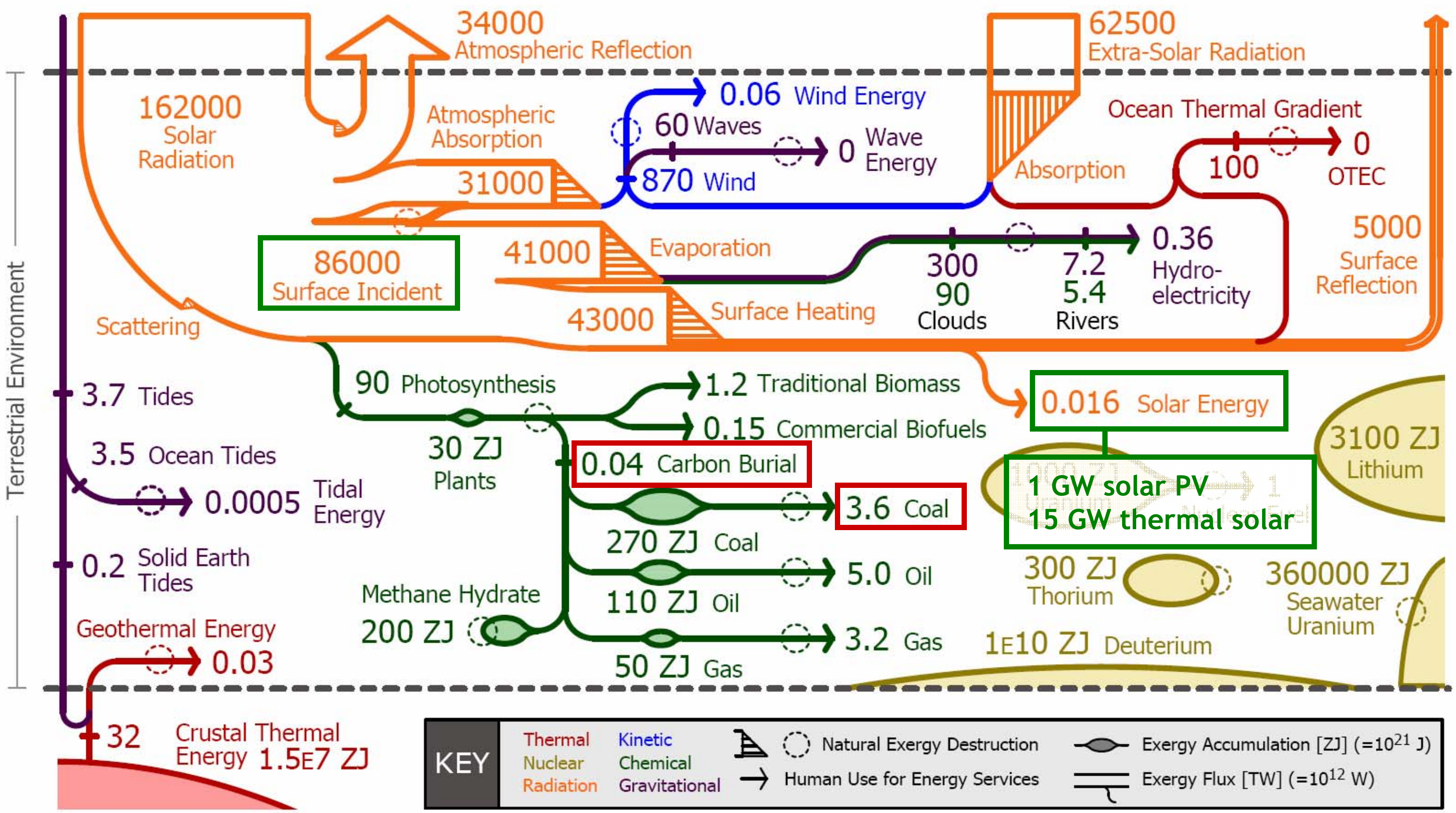
x 10,000 =

ONE YEAR OF SOLAR ENERGY PROVIDED BY SUN

SOLAR ENERGY = RENEWABLE RESOURCE

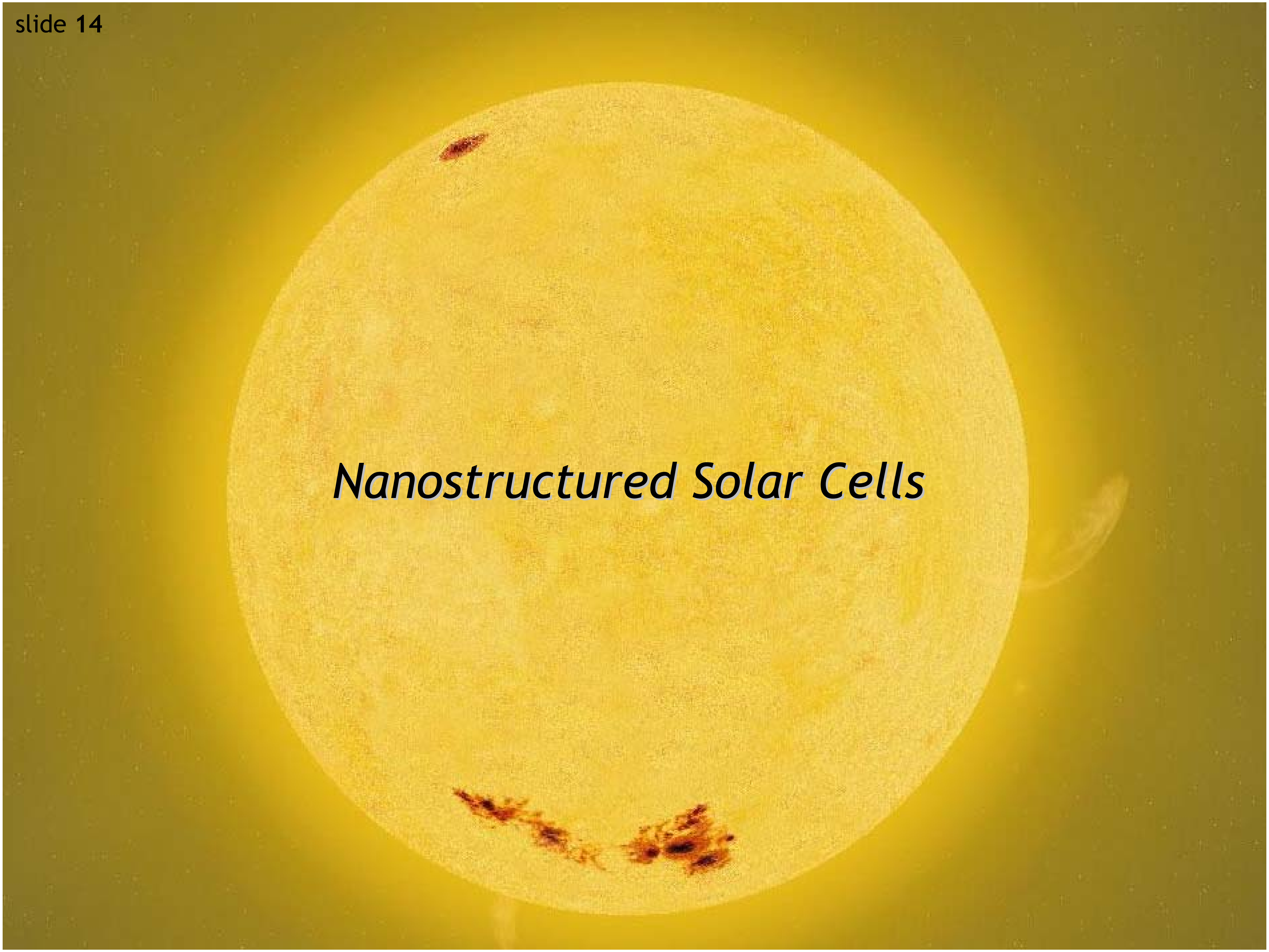
GCEP

Global Exergy Flux, Reservoirs, and Destruction



Exergy is the useful portion of energy that allows us to do work and perform energy services. We gather exergy from energy-carrying substances in the natural world we call energy resources. While energy is conserved, the exergetic portion can be destroyed when it undergoes an energy conversion. This diagram summarizes the exergy reservoirs and flows in our sphere of influence including their interconnections, conversions, and eventual natural or anthropogenic destruction. Because the choice of energy resource and the method of resource utilization have environmental consequences, knowing the full range of energy options available to our growing world population and economy may assist in efforts to decouple energy use from environmental damage.

Prepared by Wes Hermann and A.J. Simon
Global Climate and Energy Project at Stanford University (http://gcep.stanford.edu)



Nanostructured Solar Cells

PV PERFORMANCE BENCHMARKS (independently confirmed)

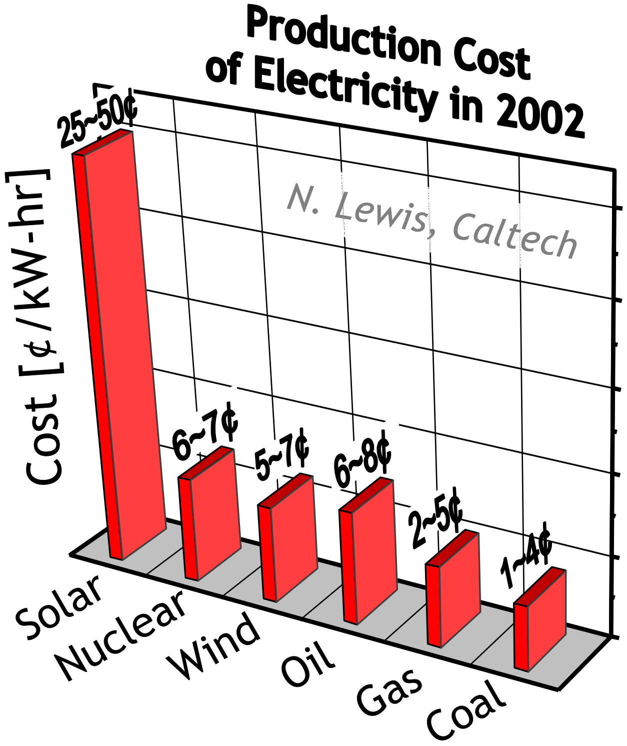
from Progress in Photovoltaics:
Research and Applications, 11, 347 (2003)

at AM0: satellites / space vehicles

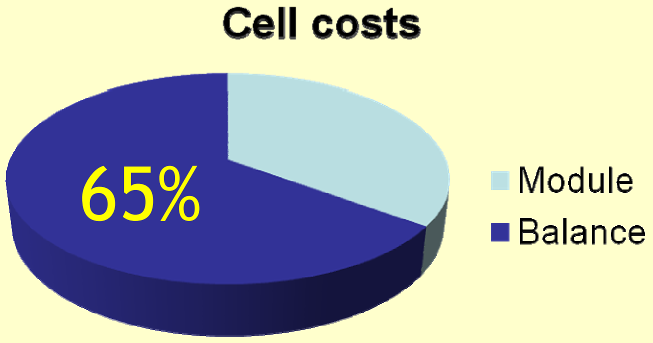
Best performance:
GaInP/GaAs/Ge multijunction
η_P = (35.2±1.6)%, under 66 suns

at AM1.5: Terrestrial

Best crystalline Si:	η_P = (24.7±0.5)%
Best polycrystalline Si:	η_P = (19.8±0.5)%
Best amorphous Si:	η_P = (10.1±0.2)%
Best organic (Gratzel):	η_P = (8.2±0.3)%



Inverter, charge controller,
Circuit breaker, cables, mounting frames
Real estate
Labor
System integrator margins
Permitting, design, shipping
Warranty
Maintenance



from M. Baldo

INSTALLATION COSTS

At present, installation costs for small scale domestic solar systems are ~ \$500/m^2

This is equivalent to about \$50/sq ft

FOR COMPARISON:
house construction including materials is ~\$100/sq ft
warehouse construction including materials is ~\$50/sq ft

Installation costs give a large advantage to high efficiency PV systems, e.g.

Case 1: Crystalline Si PV	Case 2: Thin Film PV
Module cost \$3/W	Module cost \$1/W
Efficiency = 20% (200W/m^2)	Efficiency = 10% (100W/m^2)
For 10kW system	For 10kW system
Solar cells = \$30,000	Solar cells = \$10,000
Installation = \$25,000	Installation = \$50,000
Total = \$55,000	**Total = \$60,000**

from M. Baldo

HOW CAN WE RADICALLY LOWER THE COST OF SOLAR CELLS?

Use metric $\$/W_p$:

(cost of PV cell divided by power generated at peak solar illumination)

$$\$/W_p = \frac{\text{PV cost}}{\eta_p L}$$

η_p: power efficiency
L: solar power

Example:

The CdTe process at First Solar

(100 MW/year of 8-10% modules, throughput = 4μm thick films every 40s)

Capital cost of CdTe evaporation = **$\$0.04/W_p$***

Semiconductor cost = **$\$0.04/W_p$***

Total manufacturing cost = **$\$1.25/W_p$**†

* *See Zweibel, Solar Energy Materials & Solar Cells, 59, 1-18 (1999)*

† *Recent production data from First Solar*

CdTe associated costs < 10% of manufacturing cost.

Remainder dominated by substrate (glass) and module costs (labor, wiring etc..).

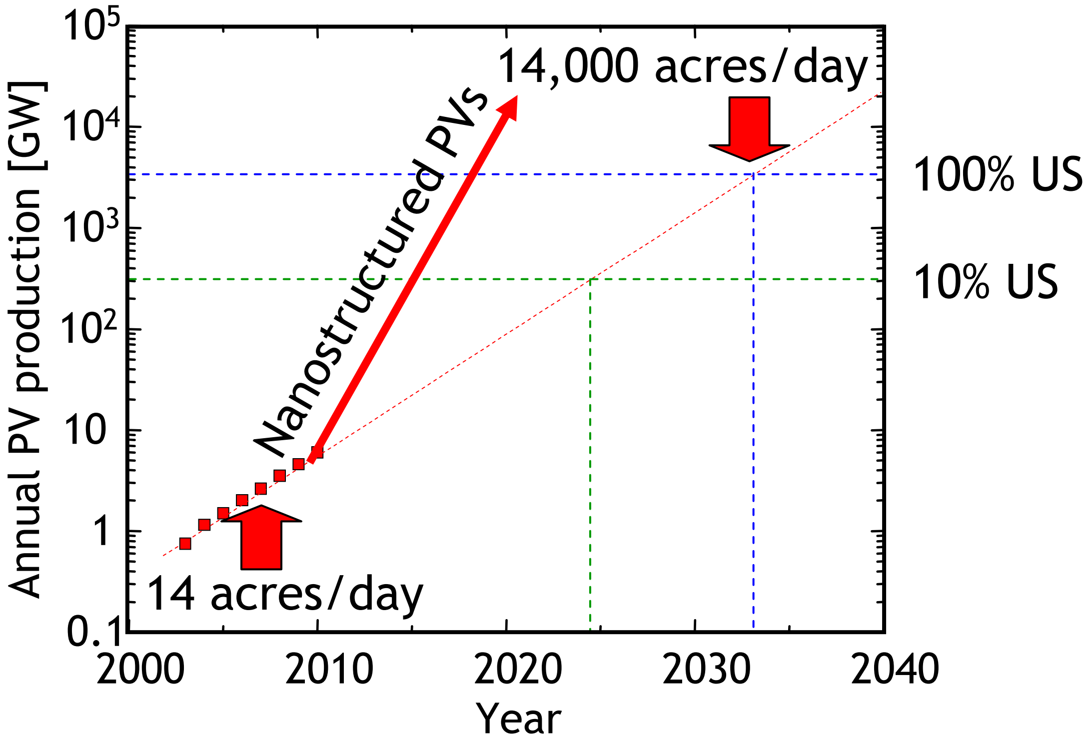
New semiconductors/fabrication techniques alone will not achieve large cost savings.

Best option? Improve efficiency. 1% increase in efficiency = $\$0.12 / W_p$

Including installation costs: 1% increase in efficiency > $\$0.40 / W_p$

Production is the real issue …

Expected Global Solar Cell Production (Mike Rogol)



2006: Solar Cell Production Rate: 14 acres / day

2035: Required Solar Cell Production Rate: 14,000 acres / day

To survive as a technology NANOSTRUCTURED PVs need to:

- ACCELEREATE OVER THE Si-PRODUCTION
- REACH HIGHER EFFICIENCIES and/or LOWER INSTALLATION COSTS

Advantages of Nanostructured PVs

Absorption constant for organic and nanostructured materials is 10-fold larger than for inorganic thin films (due to large dipole moments in organics and quantum size effects in quantum dots and rods)

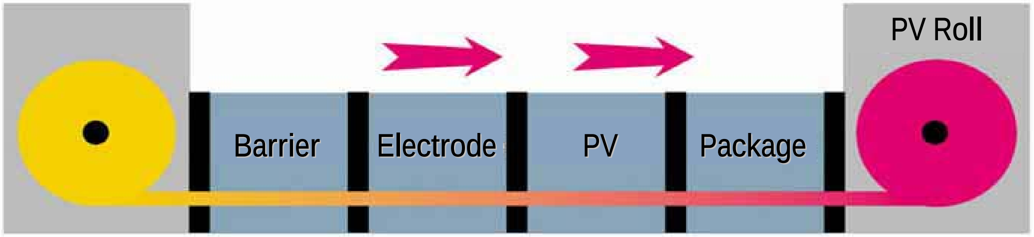
- TUNABLE SPECTRAL ABSORPTION -

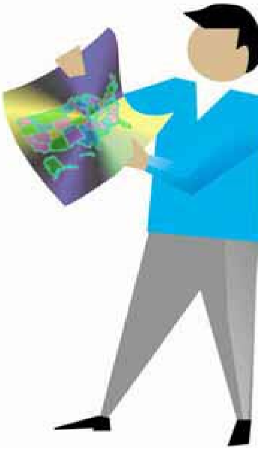
- EFFICIENT MATERIALS USE -

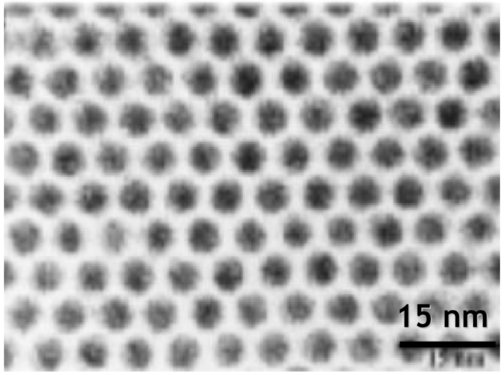
- ROOM TEMPERATURE DEPOSITION -
(on an arbitrary form factor)

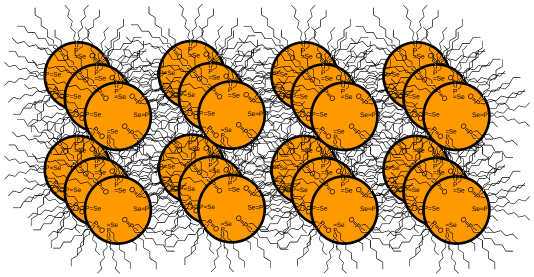
Thin Film Nanostructured PV efficiency ~6 %
Nanocrystalline dye electrochemical PV ~8 %

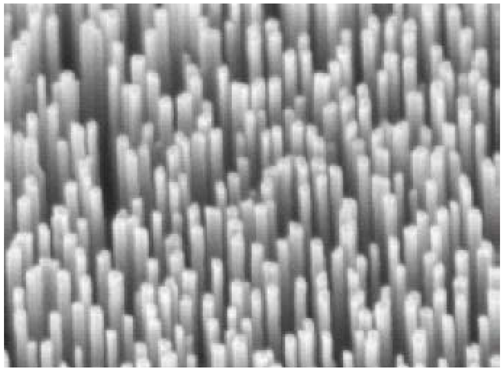
MANUFACTURING PARADIGM SHIFT





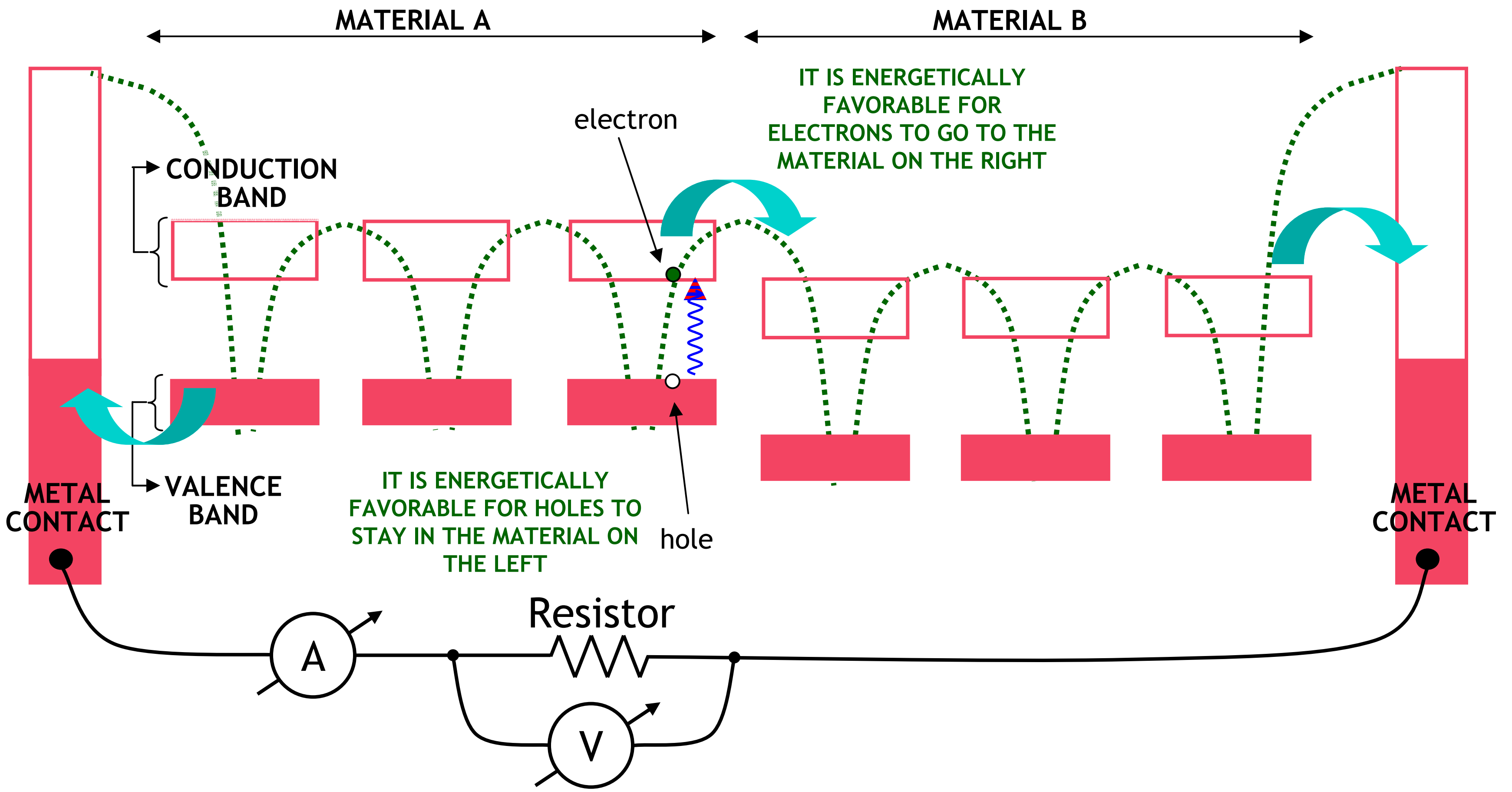






(junction of two different semiconductors)

Semiconductor Heterojunction Solar Cell

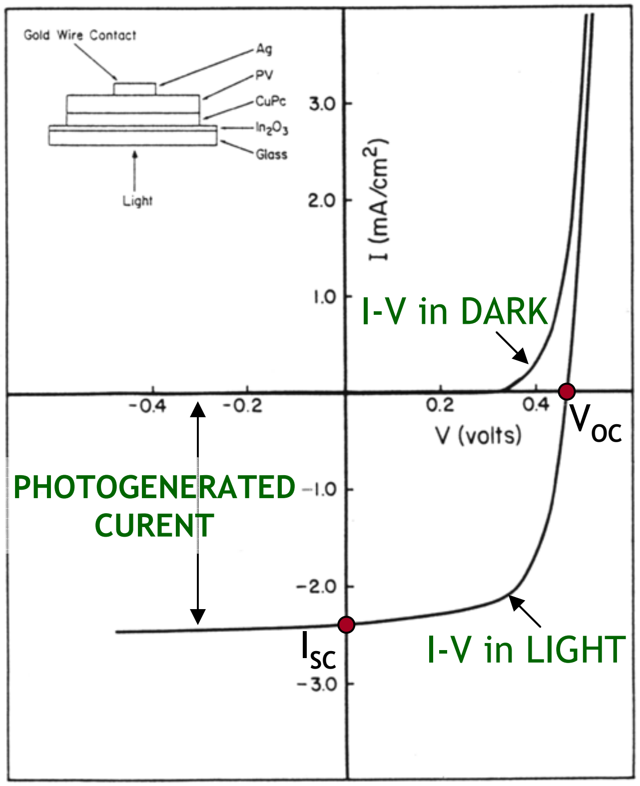


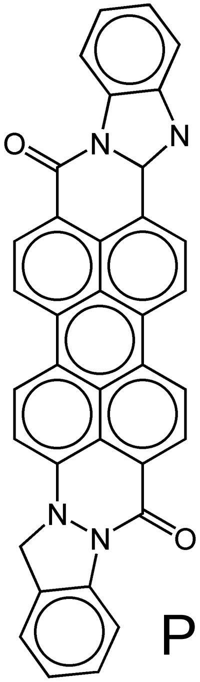
IT IS ENERGETICALLY FAVORABLE FOR ELECTRONS TO GO TO THE MATERIAL ON THE RIGHT

IT IS ENERGETICALLY FAVORABLE FOR HOLES TO STAY IN THE MATERIAL ON THE LEFT

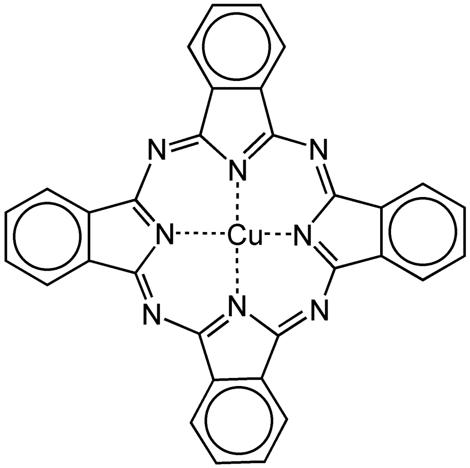
Example: First Organic Heterojunction Solar Cell

Power conversion efficiency ~ 1%

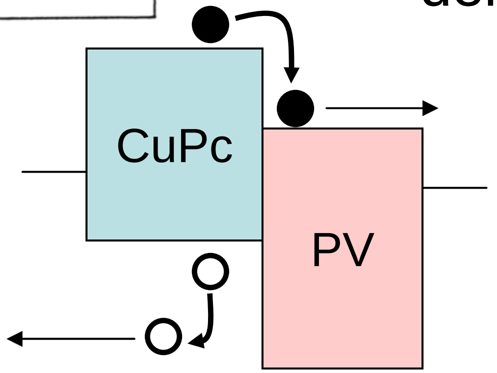




Perylene tetracarboxylic derivative (PV)



CuPc



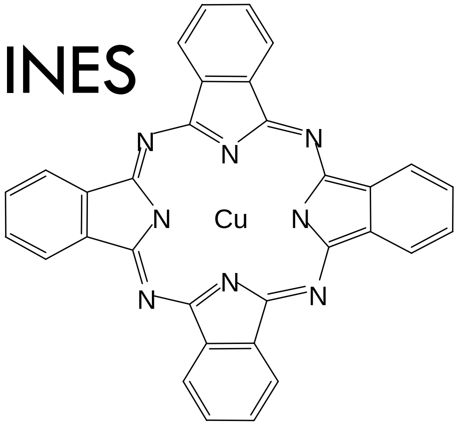
Need interface to maximize exciton dissociation

V_{OC} = open-circuit voltage

I_{SC} = short-circuit current

from Tang, Applied Physics Letters, 48 183 (1985)

Organic Material Example: PHTHALOCYANINES



Abundant: BASF makes 75,000,000 kg/yr

Non Toxic

Low cost: ~$1/g ➡ $0.17/m^2

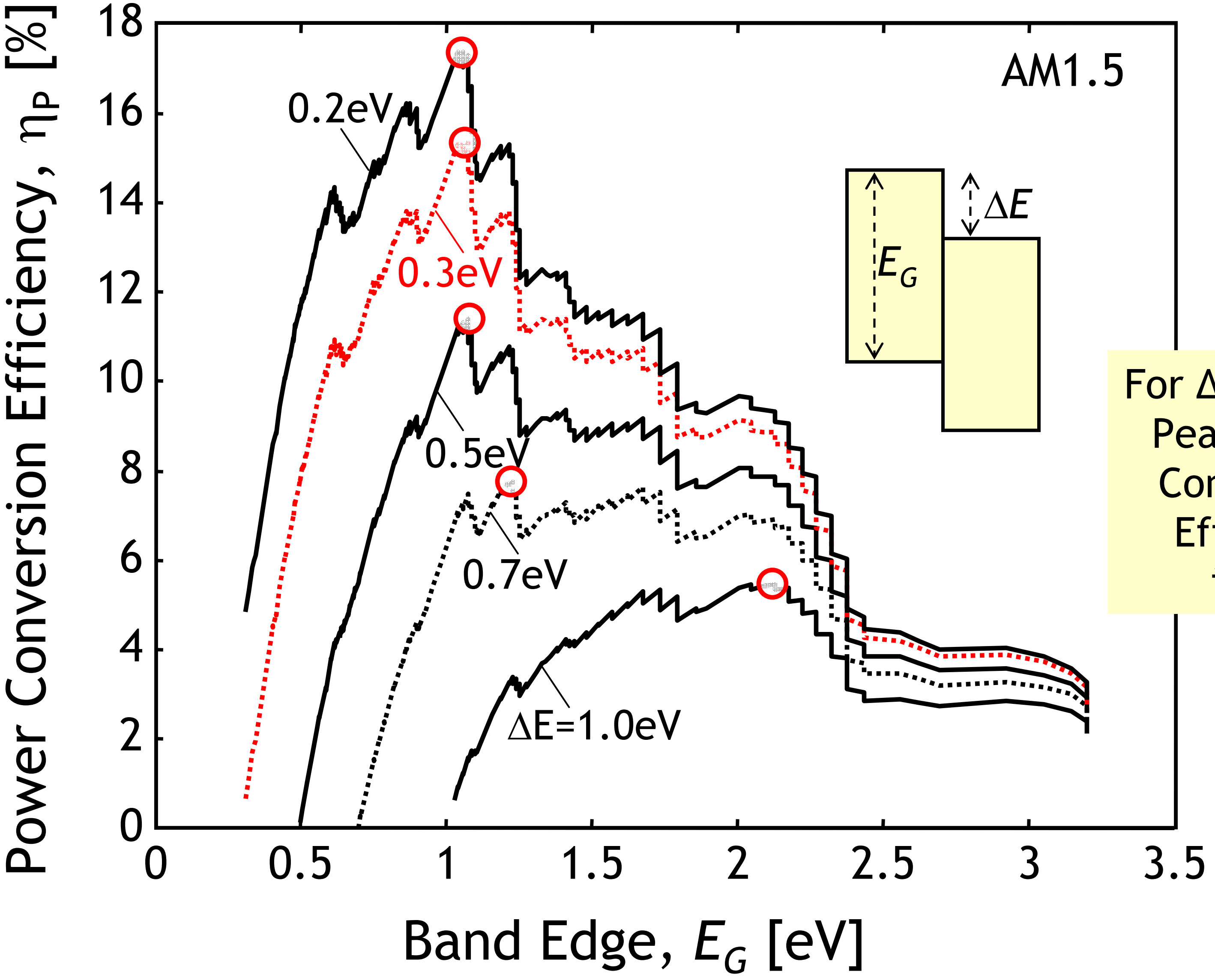
Stable

after Peumans

silicon production: ~35,000,000 kg/yr (2005) *slide courtesy P. Peumans*

Power Conversion Efficiency

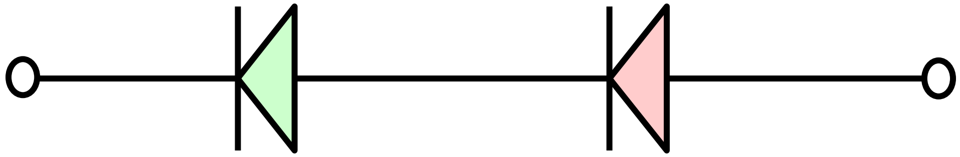
~ Effect of Band Offset, ΔE ~

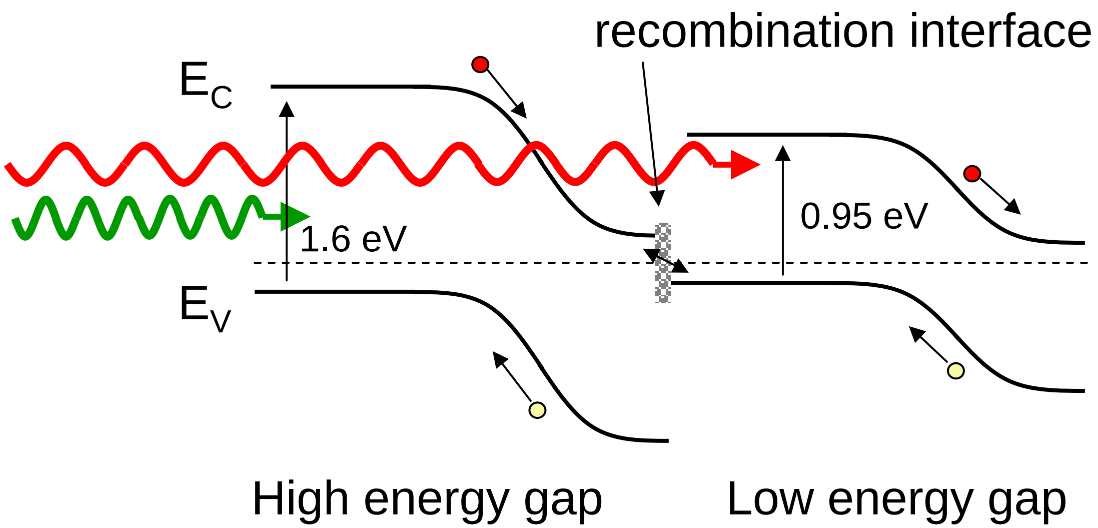


For ΔE = 0.3 eV
Peak Power
Conversion
Efficiency
is 15%

Multiple Junction Cells

Connect solar cells in series.
Usually wide gap cells in series with narrow gap cells.





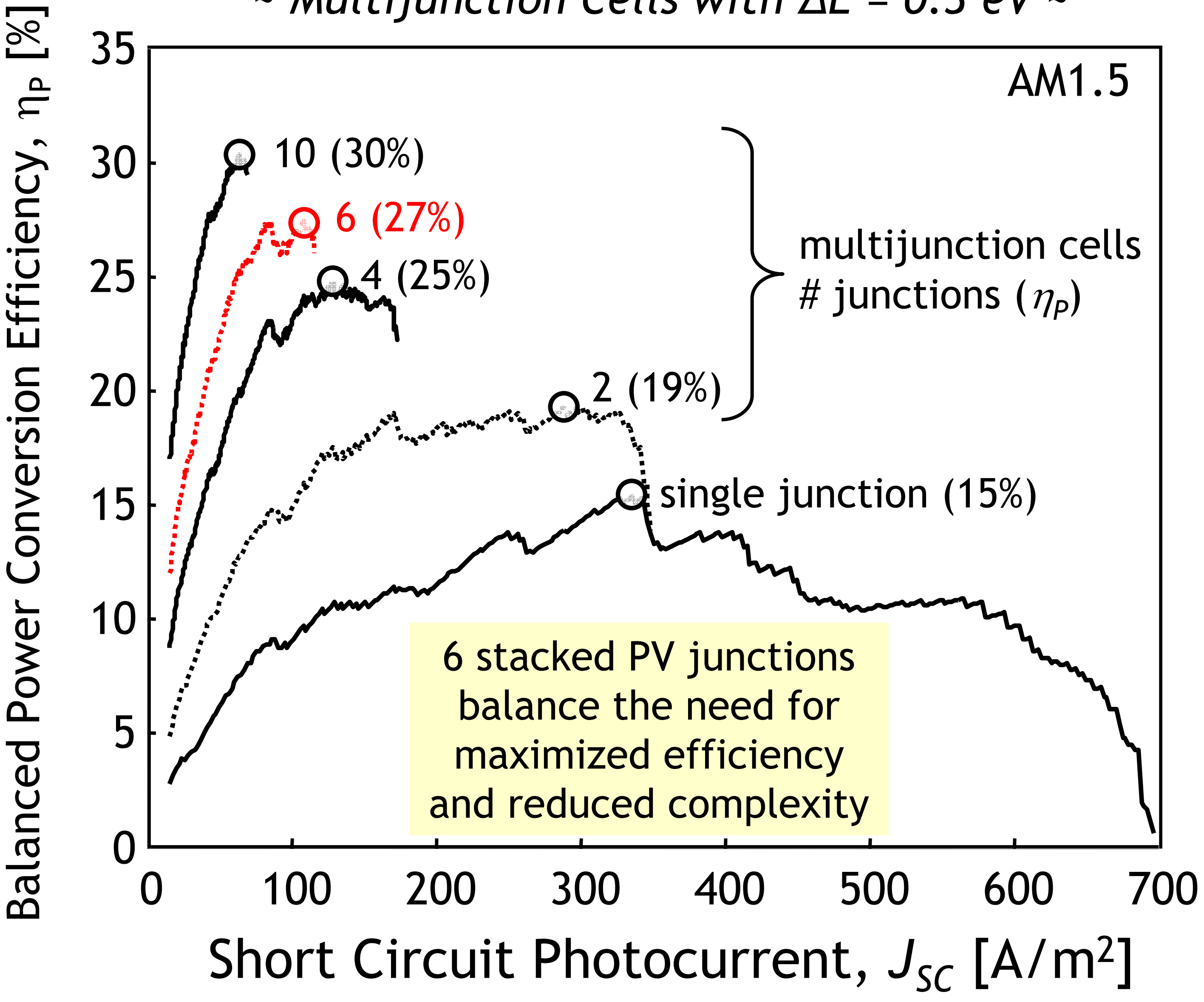
Voltage of cells adds.
But need same current through each cell. Must carefully tune absorption.

Advantage: highest performance cells made this way.

slide courtesy P. Peumans

Power Conversion Efficiency

~ Multijunction Cells with ΔE = 0.3 eV ~



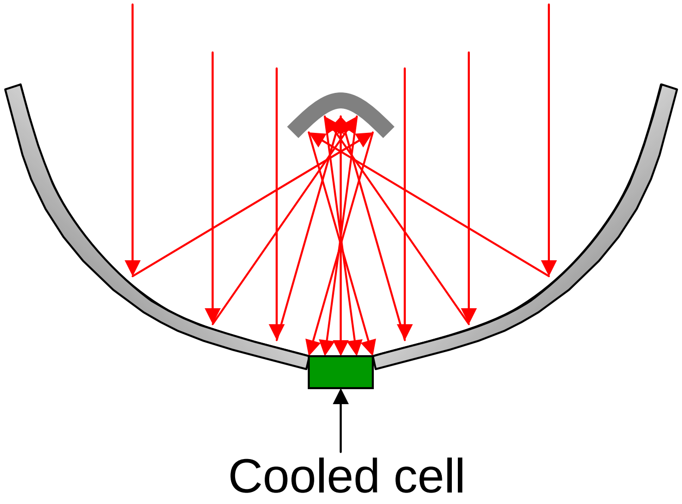
6 stacked PV junctions balance the need for maximized efficiency and reduced complexity

from M. Baldo

A SHORT TERM GOAL: SOLAR CONCENTRATORS

Efficiency of devices increases with light intensity:

- Short circuit current increases linearly with incident power
- Open circuit voltage increases



FIXED LENS OR MIRROR COLLECTOR

- Concentration factor limited to n^2. (G ~ 2) (n: refractive index)

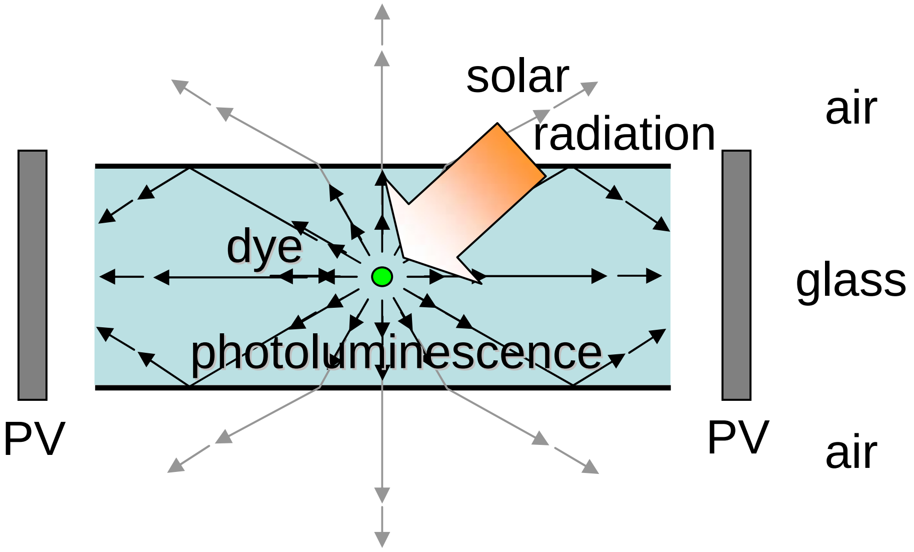
TRACKING COLLECTORS

- Mechanical – adds cost and maintenance
- PV needs cooling
- Must be widely spaced to avoid shadowing

from M. Baldo

A different approach:
use Organics only for Optical Function of solar cells …

Simple construction: dye in or on waveguide



Structure collects and <u>concentrates</u> light onto PV cells.

This is not a new idea…

‘LUMINESCENT SOLAR CONCENTRATOR’

W. H. Weber and J. Lambe, Applied Optics 15, 2299 (1976)

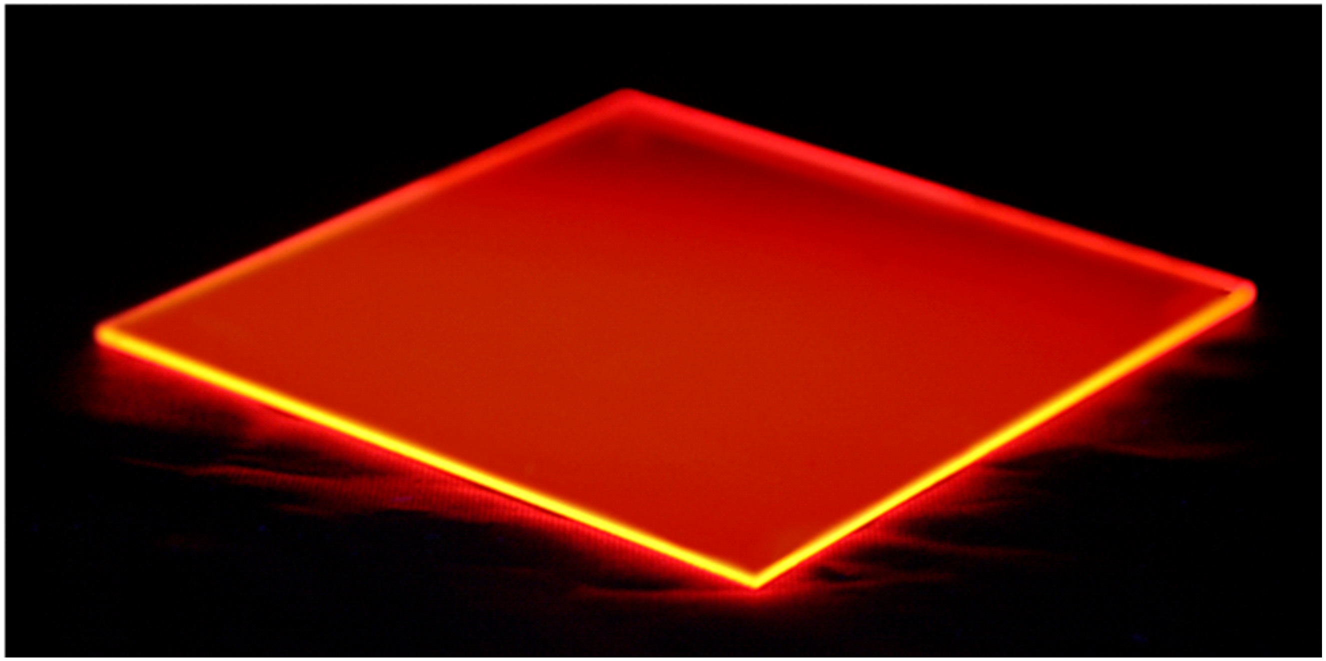
from M. Baldo

The ideal solar concentrator

1. Static (does not need to track sun)
2. Theoretically unlimited concentration factor
3. No excess heat incident on PVs (pumped at bandgap)

Example of luminescent solar concentration

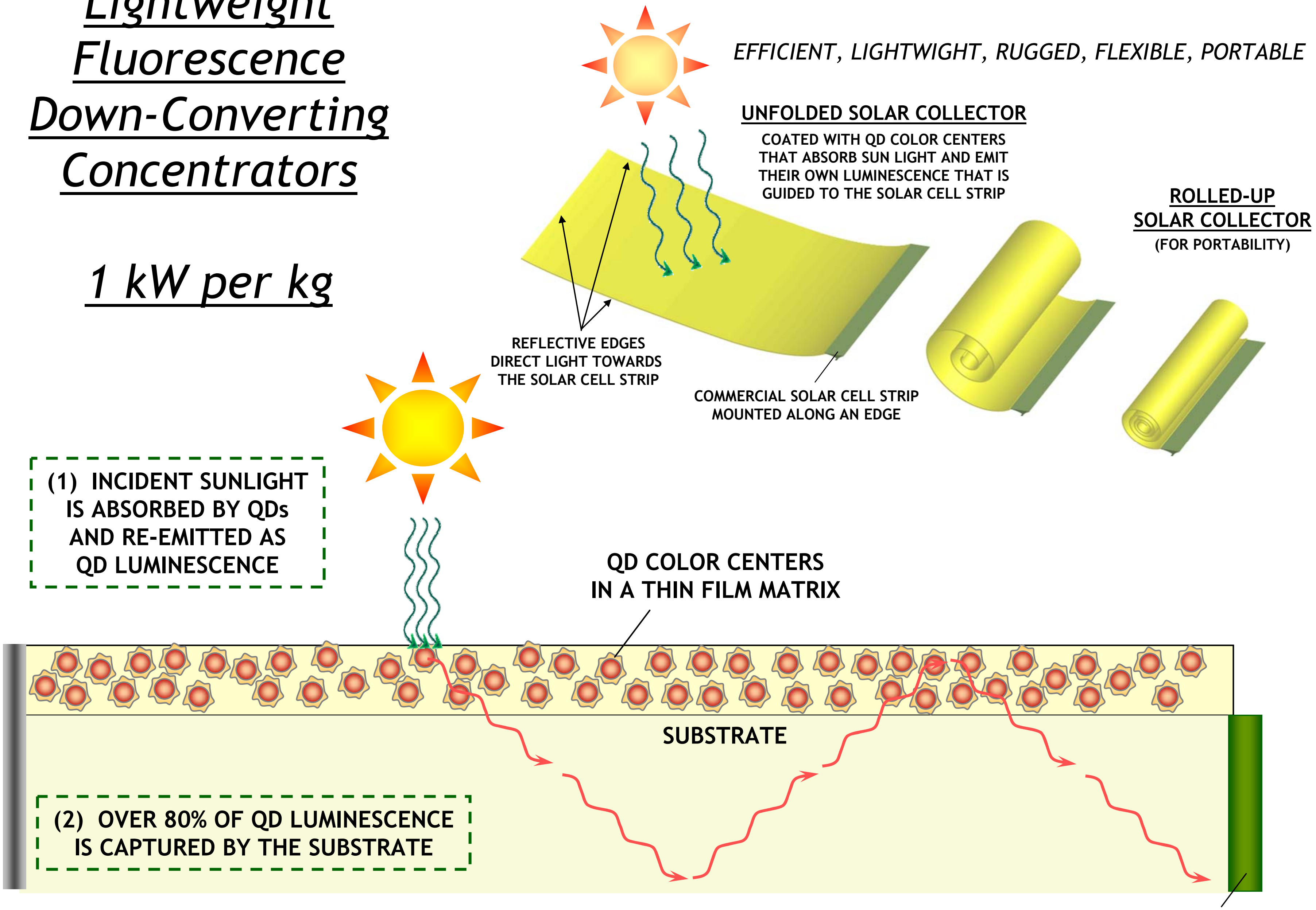
Baldo lab proto-types are 10x10x0.1cm. Characterized with Sunpower Si PV cell at one edge



Bulović, Baldo, and Bawendi

Lightweight Fluorescence Down-Converting Concentrators

1 kW per kg



EFFICIENT, LIGHTWIGHT, RUGGED, FLEXIBLE, PORTABLE

UNFOLDED SOLAR COLLECTOR

COATED WITH QD COLOR CENTERS
THAT ABSORB SUN LIGHT AND EMIT
THEIR OWN LUMINESCENCE THAT IS
GUIDED TO THE SOLAR CELL STRIP

ROLLED-UP SOLAR COLLECTOR
(FOR PORTABILITY)

REFLECTIVE EDGES
DIRECT LIGHT TOWARDS
THE SOLAR CELL STRIP

COMMERCIAL SOLAR CELL STRIP
MOUNTED ALONG AN EDGE

(1) INCIDENT SUNLIGHT
IS ABSORBED BY QDs
AND RE-EMITTED AS
QD LUMINESCENCE

QD COLOR CENTERS
IN A THIN FILM MATRIX

SUBSTRATE

(2) OVER 80% OF QD LUMINESCENCE
IS CAPTURED BY THE SUBSTRATE

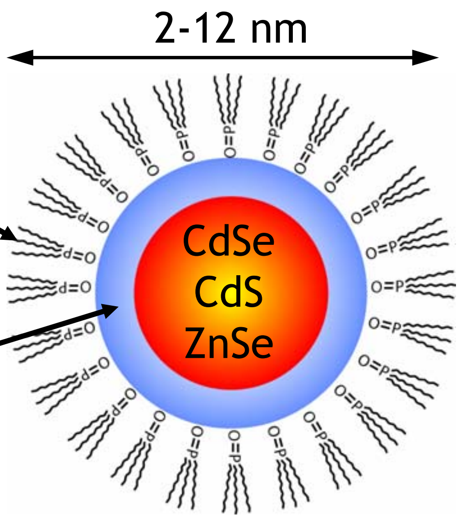
COMMERCIAL SOLAR CELL STRIP
MOUNTED ON THE SUBSTRATE EDGE

Quantum Dots in LEDs

Demonstrated:

- Spectrally Tunable – single material set can access most of visible range.
- Saturated Color – linewidths of < 30nm FWHM.
- Can separately engineer "external" chemistry, emitting core, stabilizing shell.
- Can generate large area infrared sources.
- Inorganic – more stable than organic dyes

THE IDEAL DYE MOLECULES



Caps
usually alkane organics
- TOPO, Oleic Acid, etc

Shell
wider bandgap
semiconductor - ZnS,
CdS, CdZnS

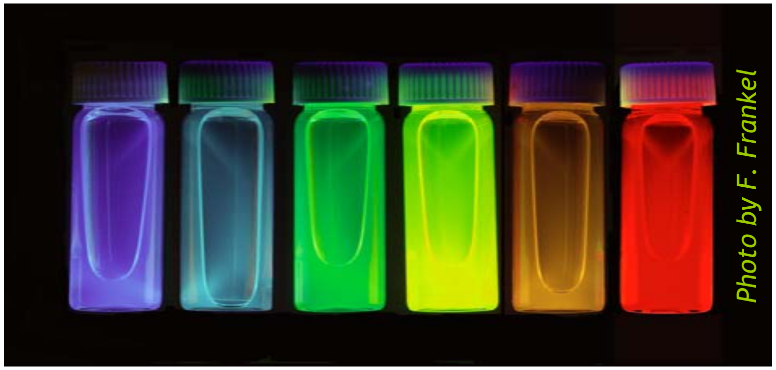
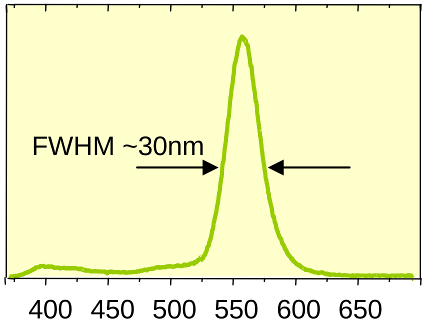
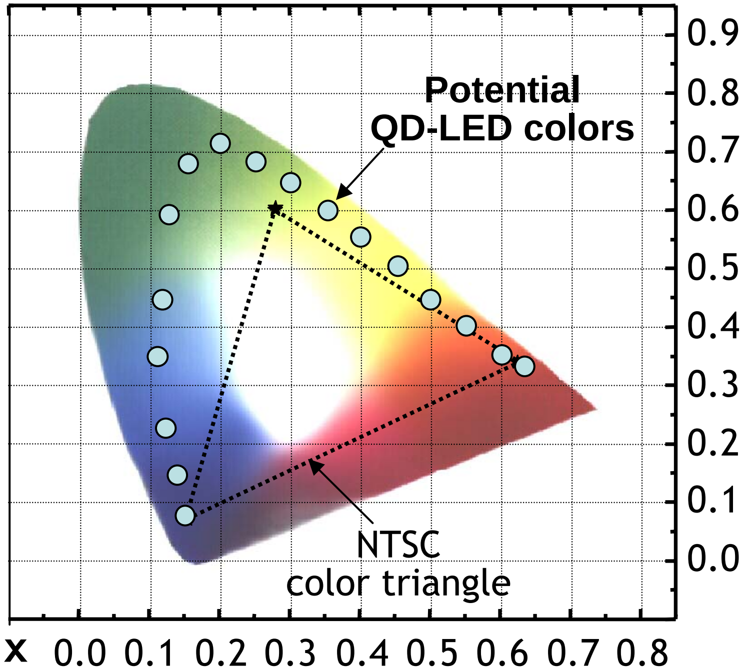


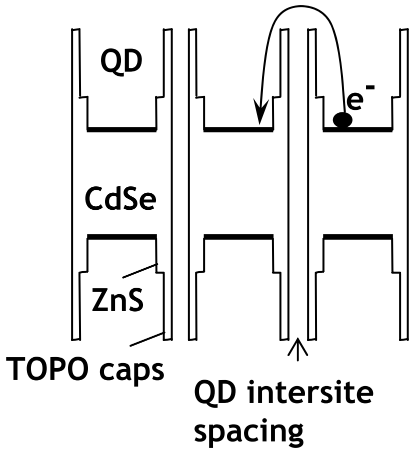
Photo by F. Frankel



Coe *et al*, Nature 420, 800 (2002).



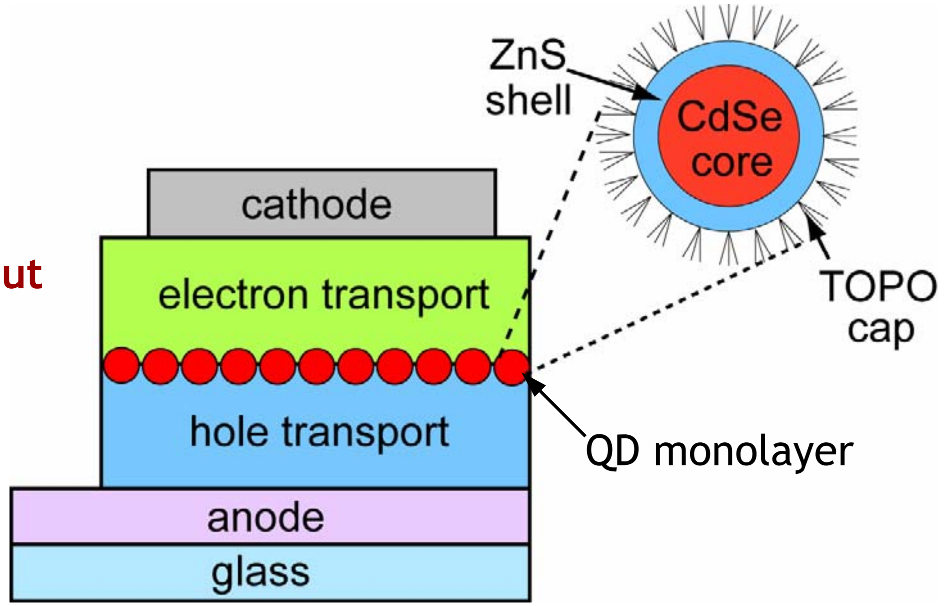
Design of QD-LEDs

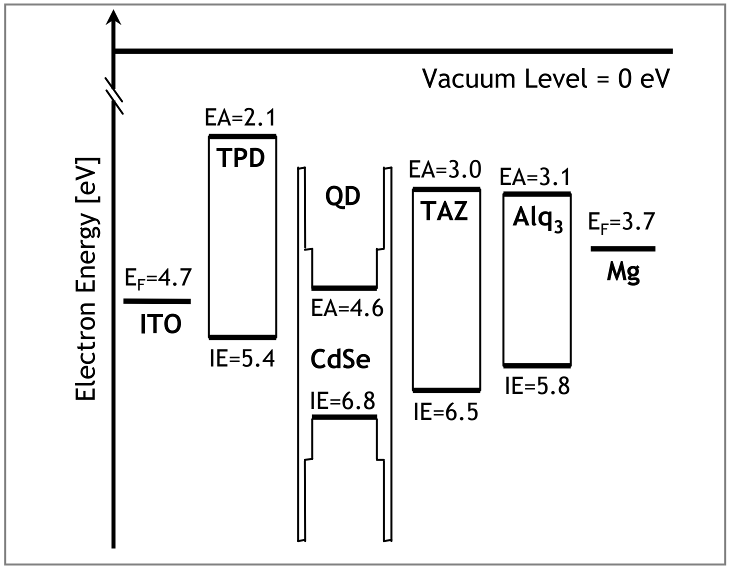


QDs are POOR CHARGE TRANSPORT MATERIALS but EFFICIENT EMITTERS …

↓

use ORGANICS for CHARGE TRANSPORT





Isolate layer functions of maximize device performance:

1. Generate excitons on organic sites.
2. Transfer excitons to QDs via Förster or Dexter energy transfer.
3. QD electroluminescence.

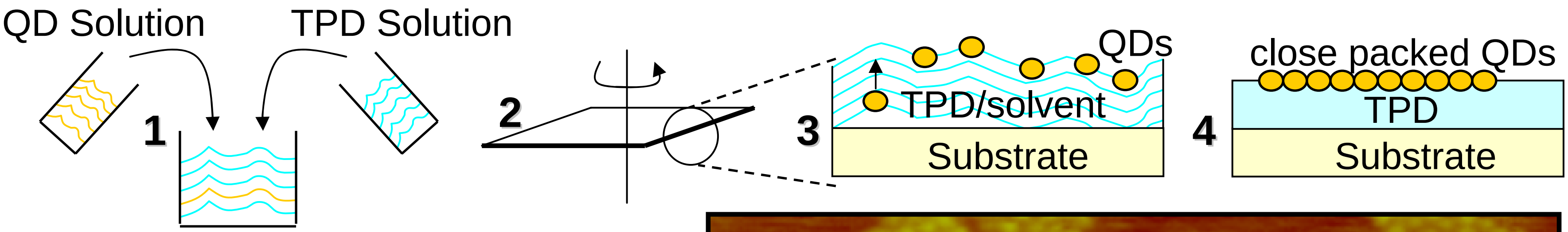
Need a *new fabrication method* in order to make QD layers:

⇩

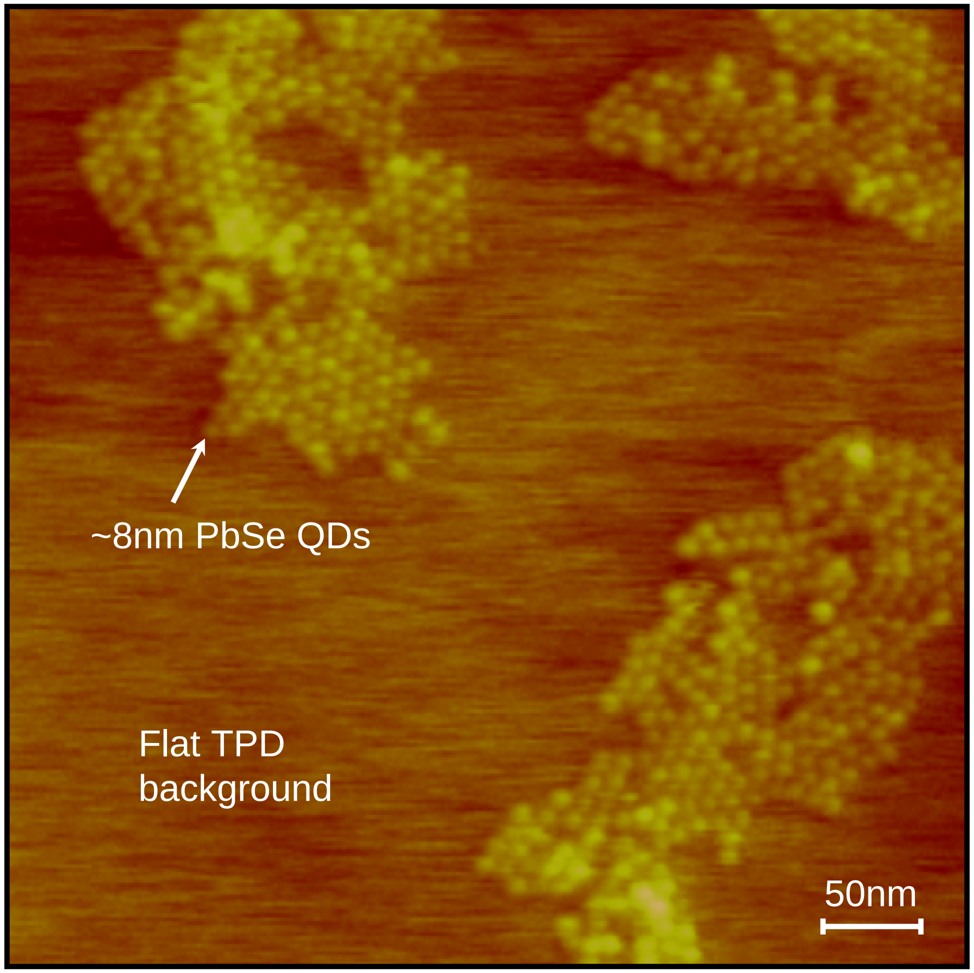
Phase Separation

Coe et al., Nature 420, 800 (2002).

QD Monolayers ~ Phase Separation and Self-Assembly of QDs ~

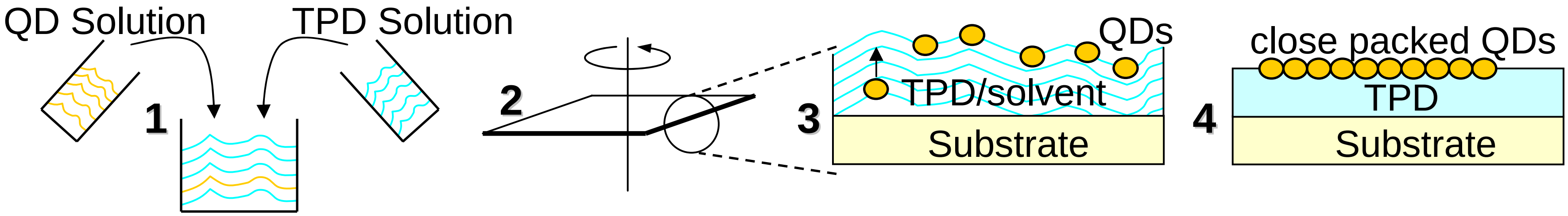


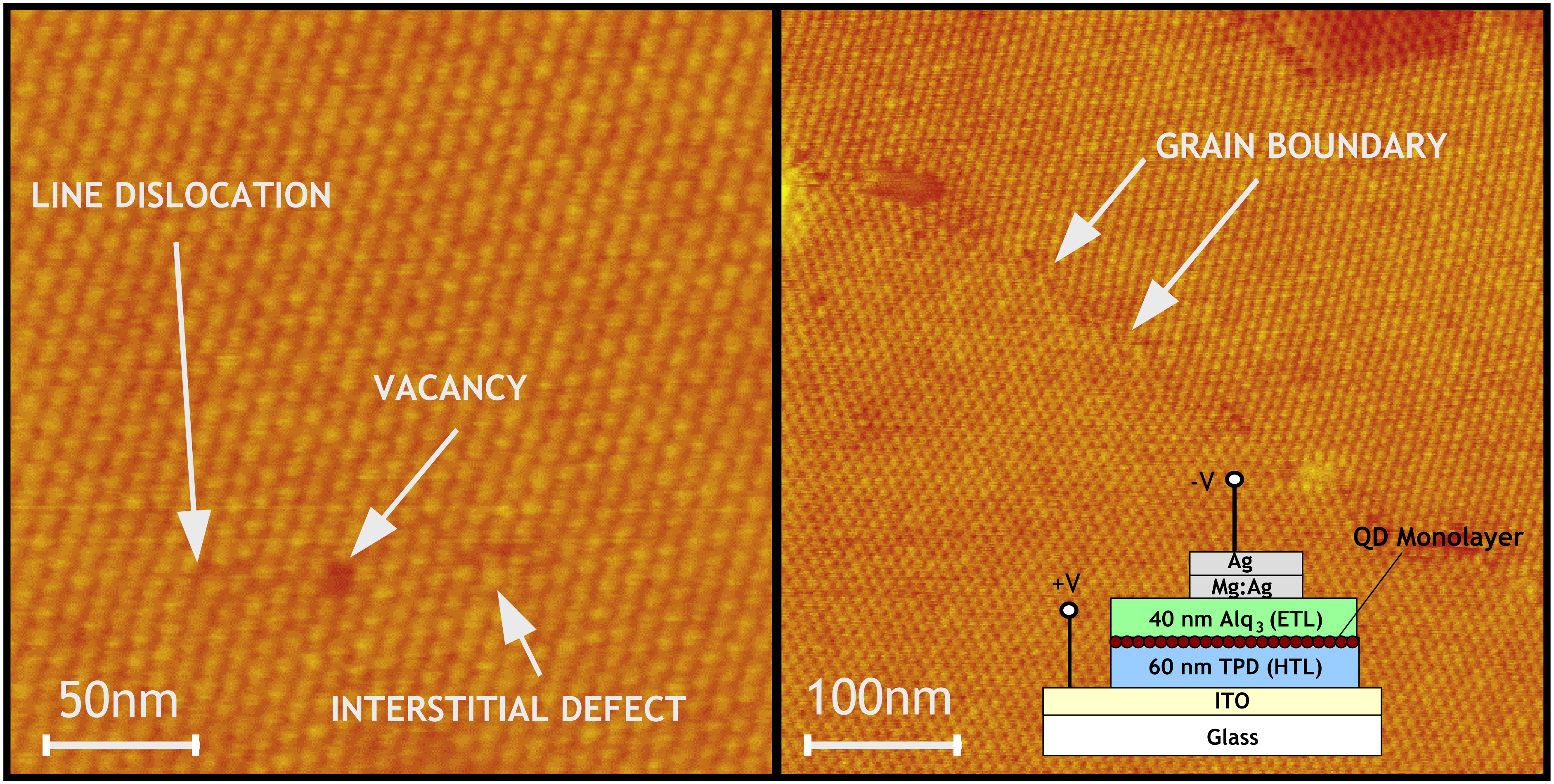
1. A solution of an organic material, QDs, and solvent…
2. is spin-coated onto a clean substrate.
3. During the solvent drying time, the QDs rise to the surface…
4. and self-assemble into grains of hexagonally close packed spheres.



Coe-Sullivan et al., Adv. Funct. Mater. (2005)

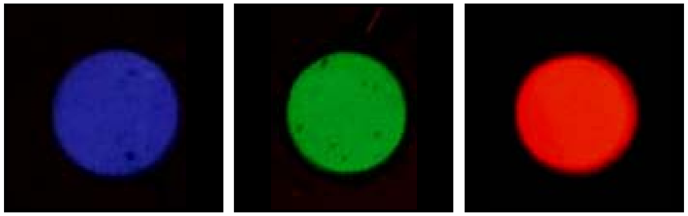
Phase Separation and Self-Assembly of QDs

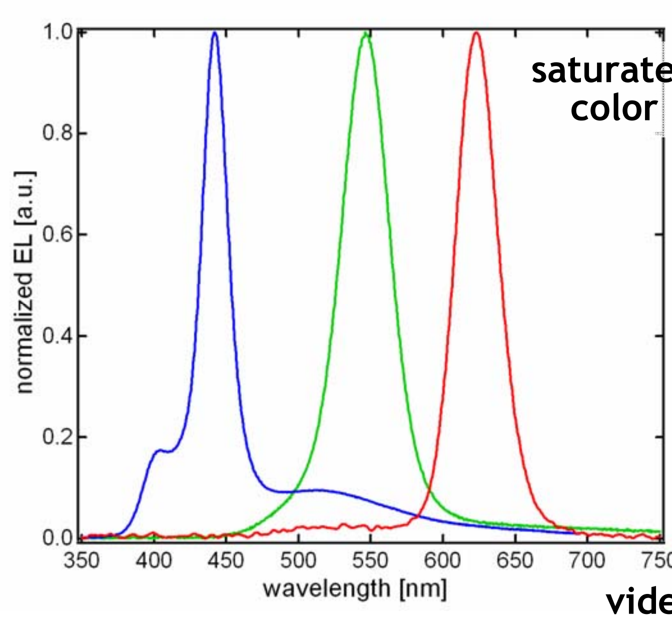




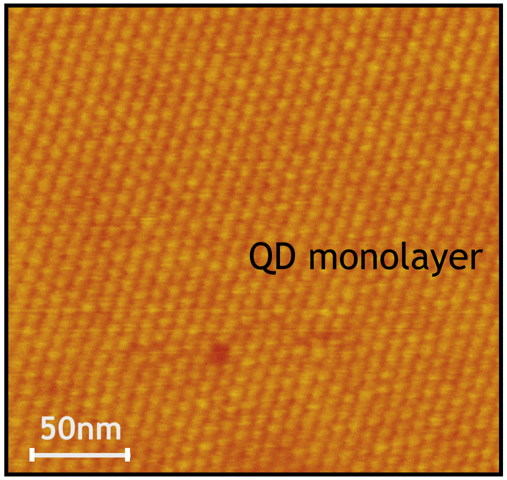
Coe-Sullivan et al., Adv. Funct. Mater. (2005)

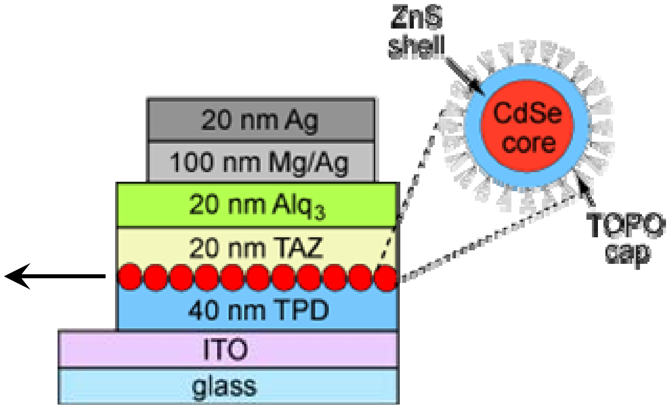
QD-LEDs



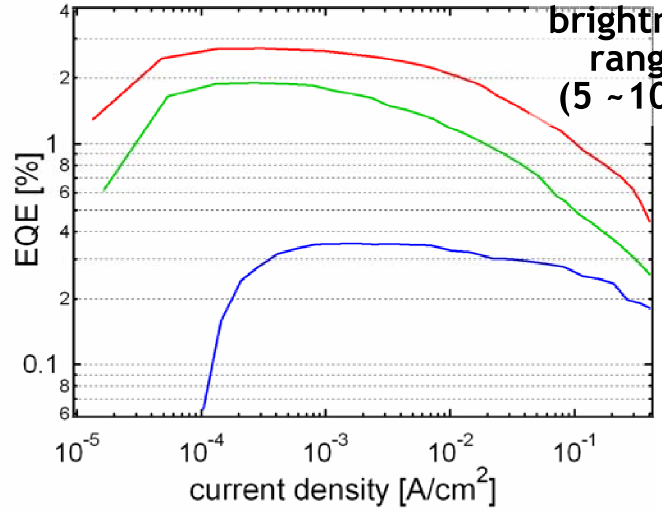


saturated color





same ETL,HTL,HBL
in all QD-LEDs
⇩
simplified
manufacturing

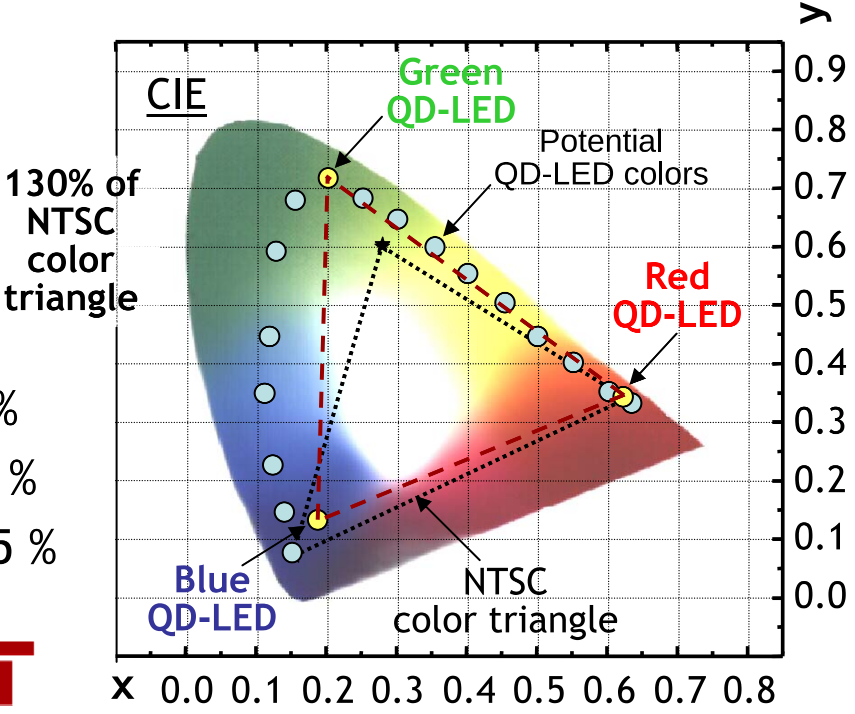


video brightness range (5 ~10 V)

R EQE_{max} = 2.8%

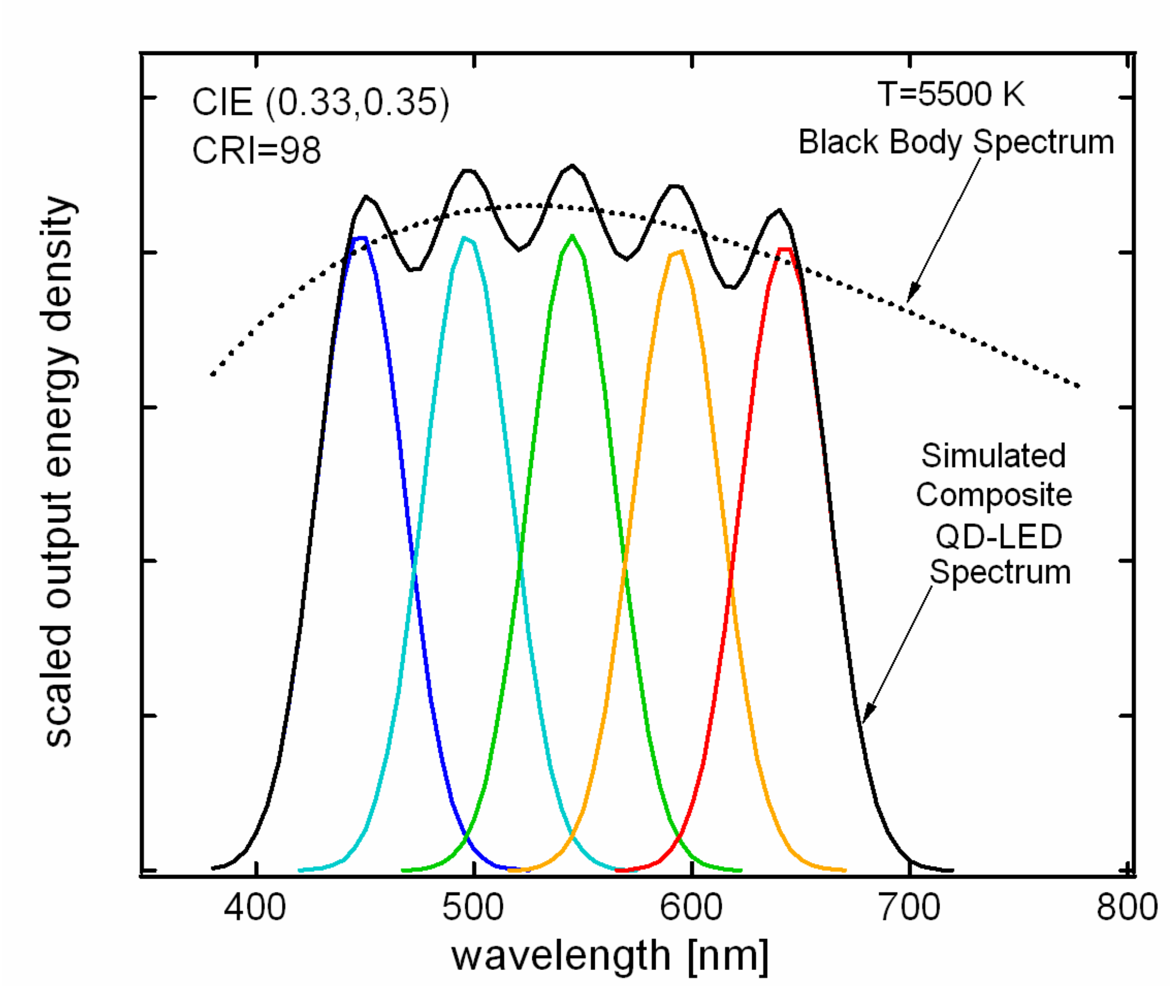
G EQE_{max} = 1.9 %

B EQE_{max} = 0.35 %



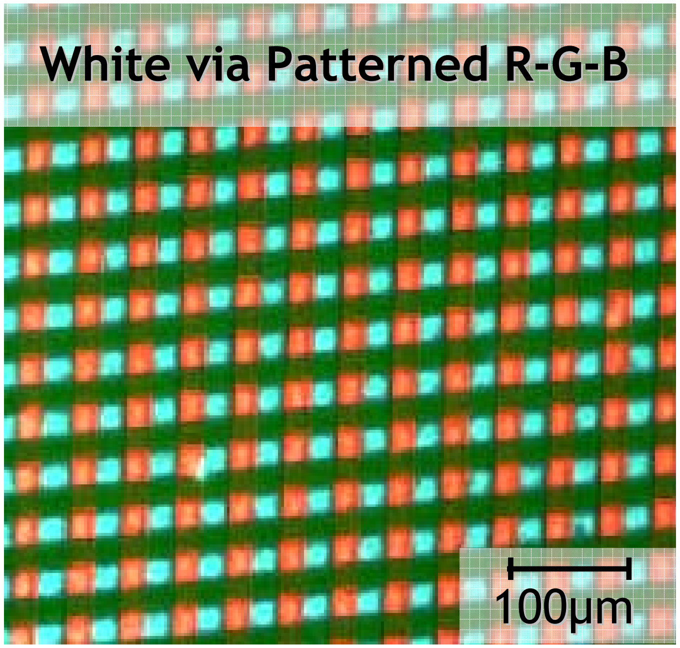
White QD-LEDs

~ Calculated Spectra, Using 40 nm PL FWHM QDs ~



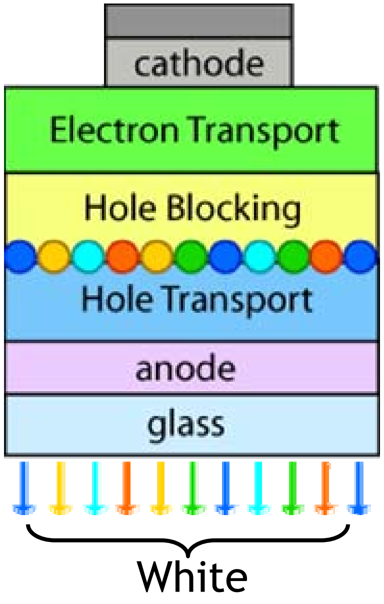
~ Precise Color Temperature Tuning ~
~ No "Wasted" Photons in IR or UV ~

White via Patterned R-G-B



White via Mixed R-G-B

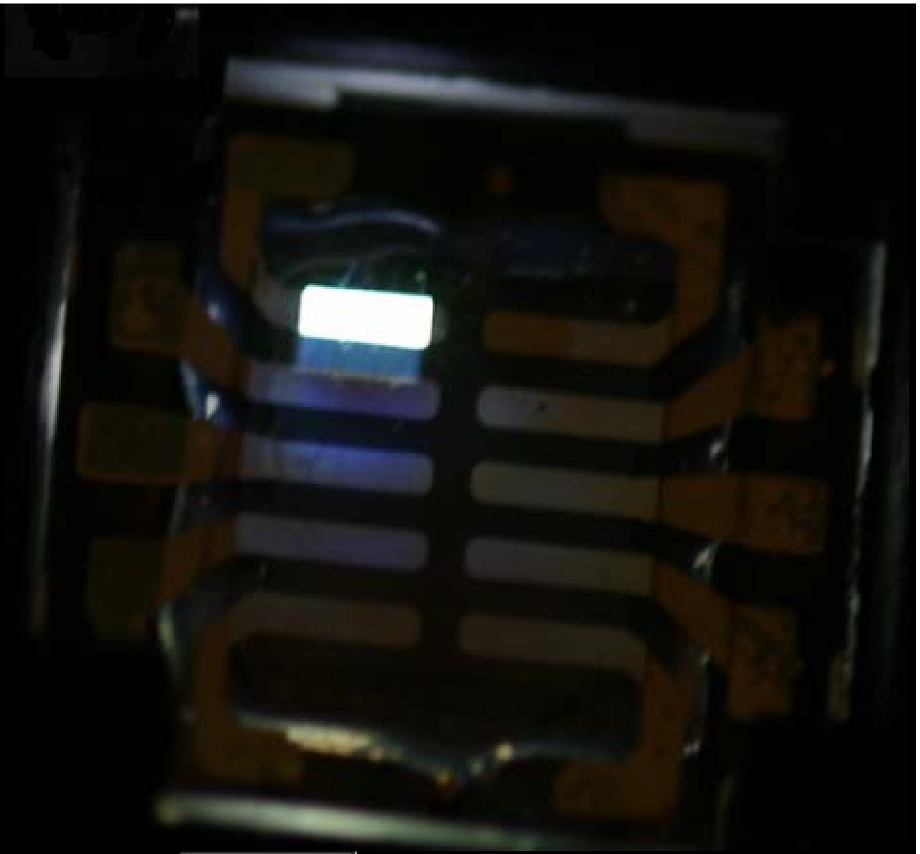
Enabled by the identical
ETL, HTL, HBL for all QD-LEDs

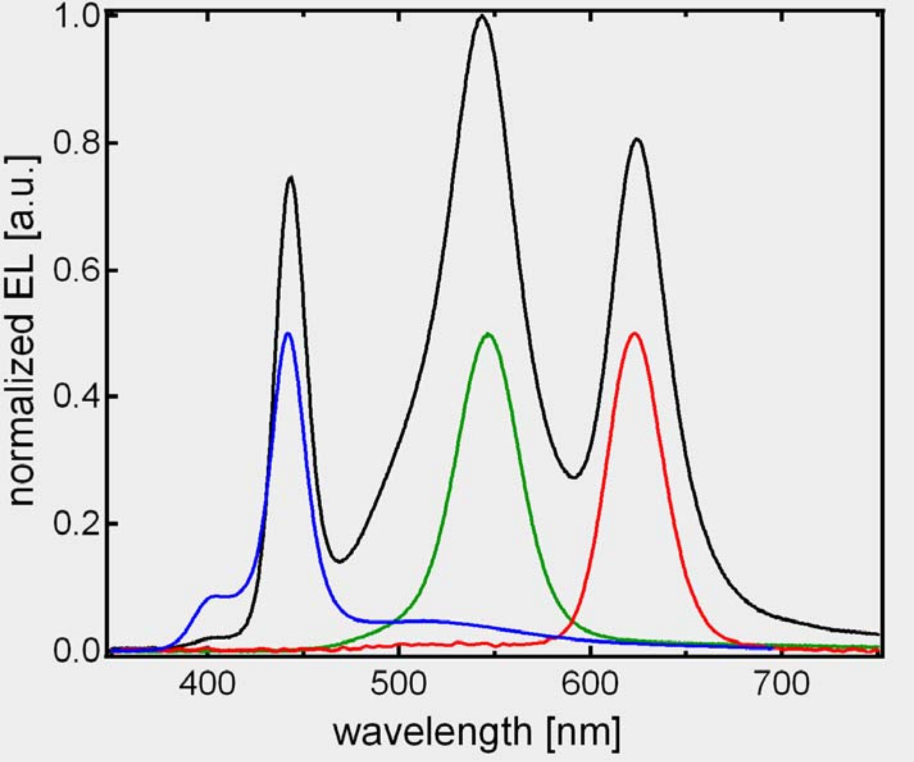


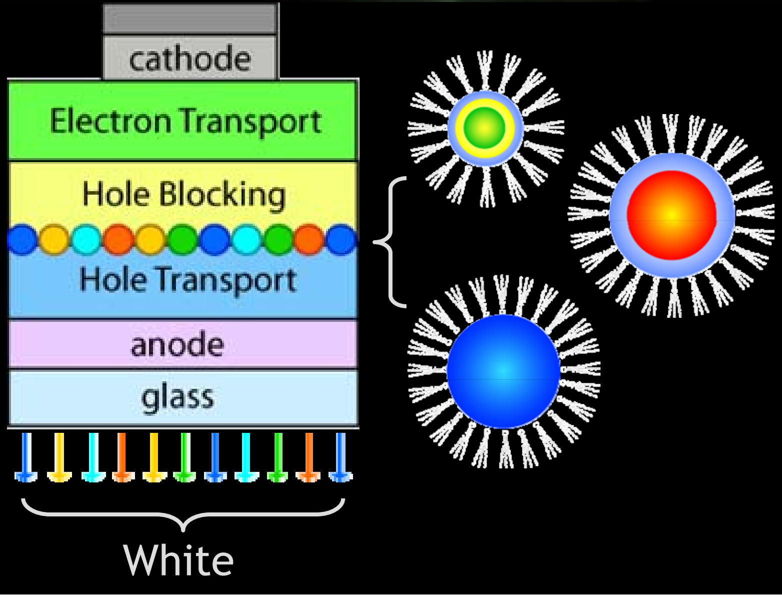
Mixed Layer White QD-LEDs

(Anikeeva, et al., Nano Letters (2007))

5 V: (0.35,0.47) and CRI = 76
9 V: (0.35,0.41) and CRI = 86

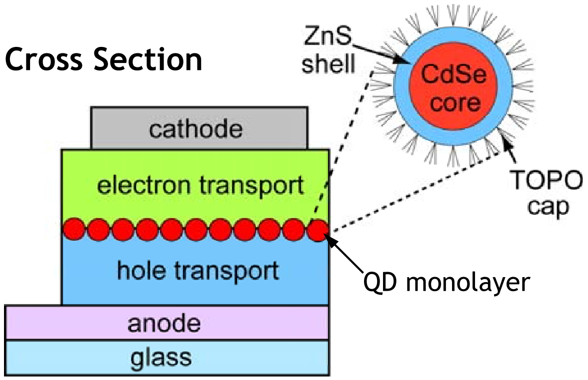




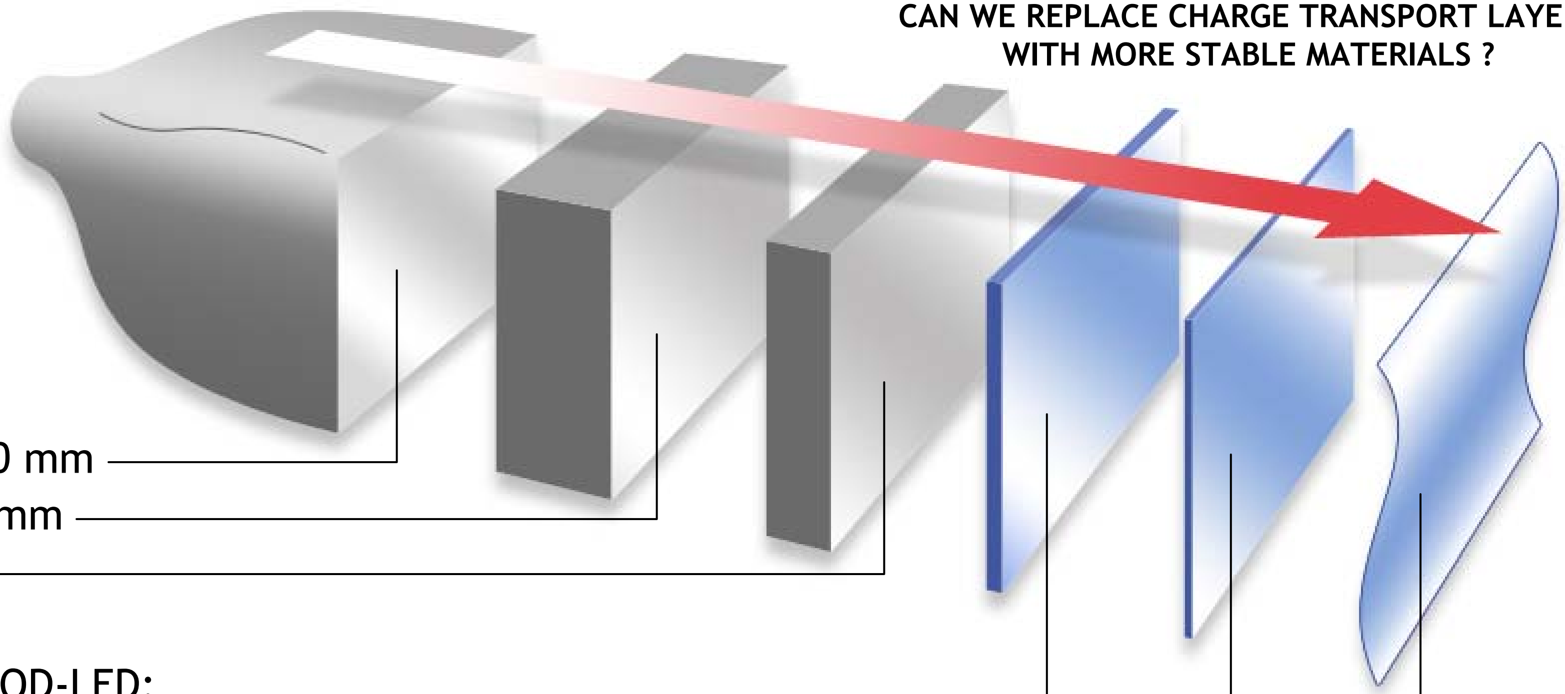


Evolution of Display Technologies

QD-LED Cross Section



CAN WE REPLACE CHARGE TRANSPORT LAYERS WITH MORE STABLE MATERIALS ?



CRT 300-500 mm

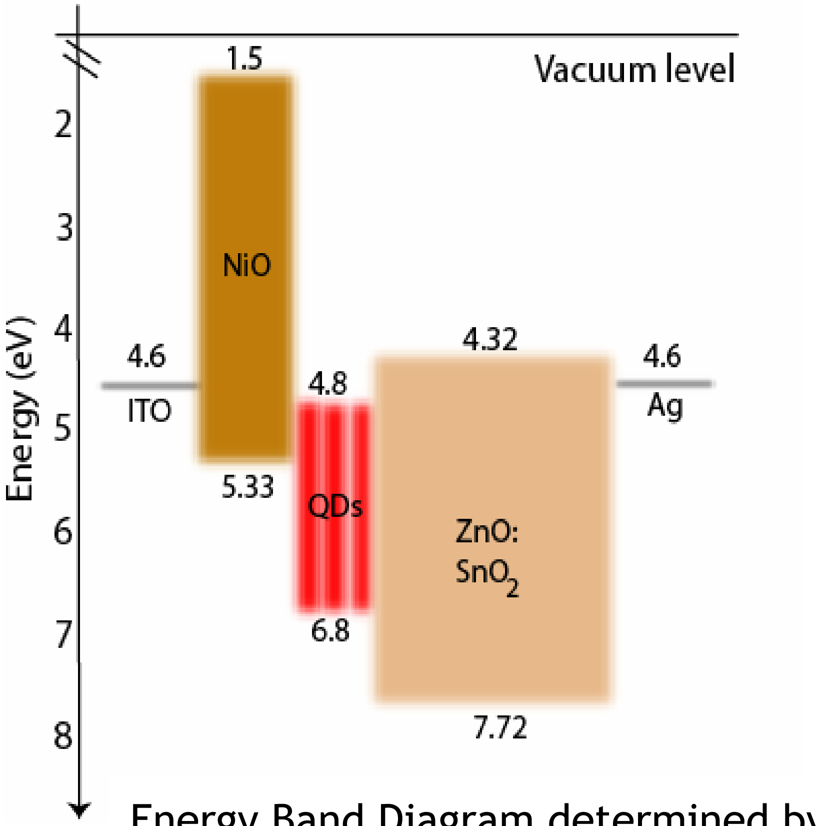
Plasma - 25 mm

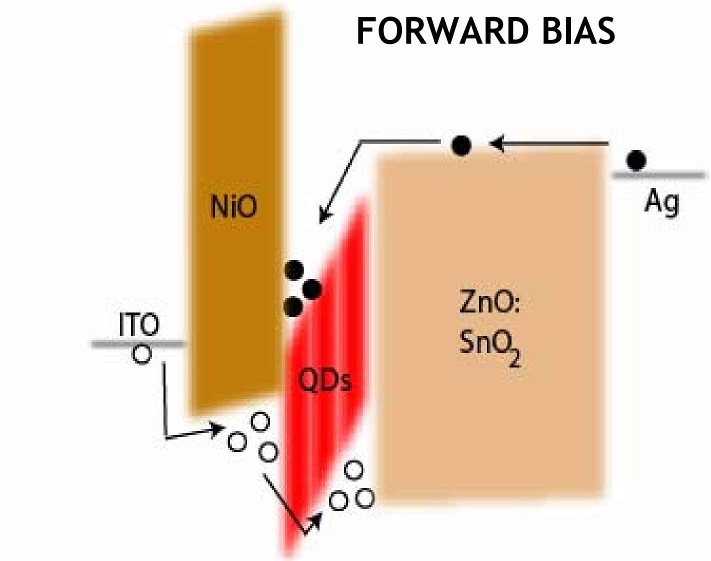
LCD - 8 mm

PLED/OLED/QD-LED:
- 1st Generation - 2 mm (Glass + metal can encapsulation)
- 2nd Generation - 1 mm (Thin film encapsulation)
- 3rd Generation - 0.1 mm (**Self-encapsulating QD-LED Flexible substrates**)

graphic adapted from Adams Harkness - Bright Ideas 2004

QD LEDs with ZnO:SnO_2 Electron Transport Layer

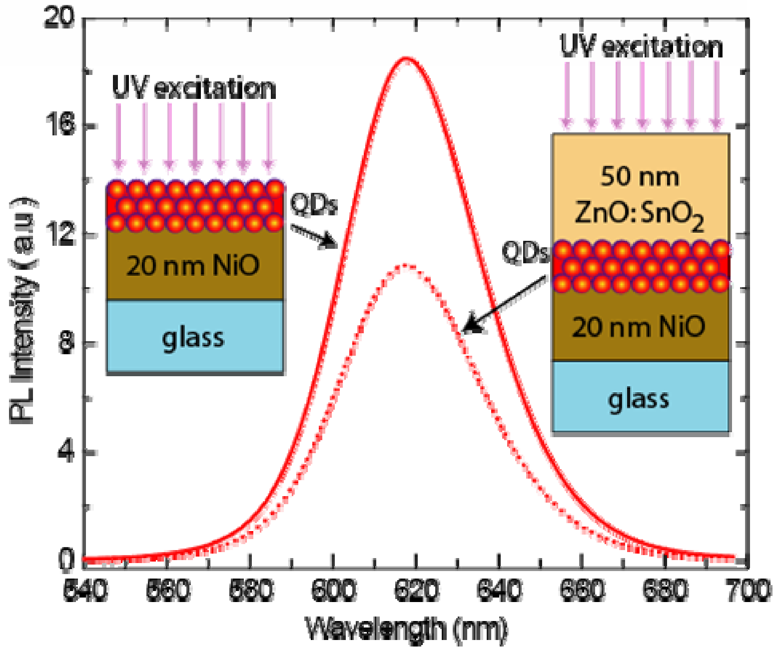




Energy Band Diagram determined by:

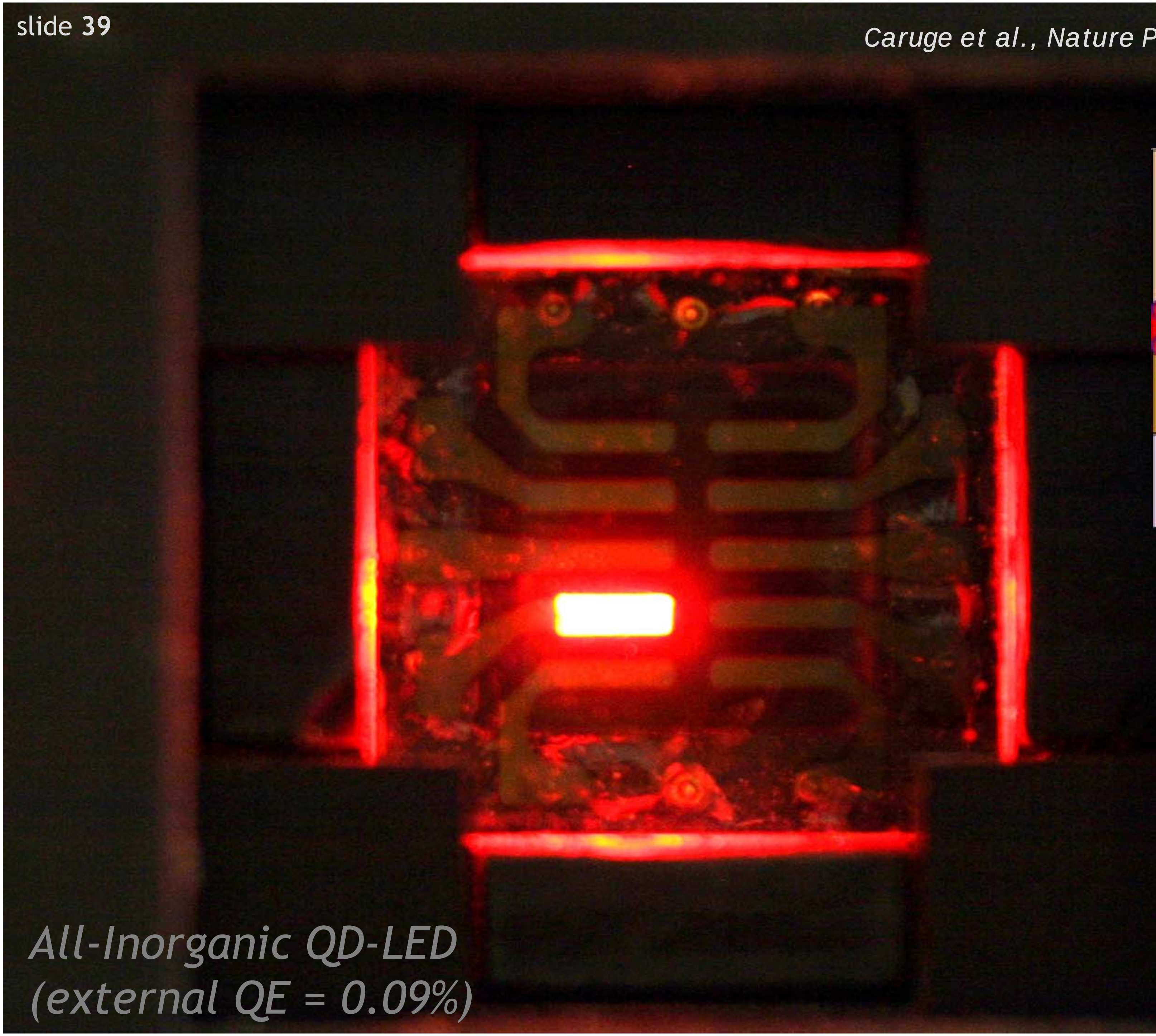
- Ultraviolet Photoelectron Spectroscopy
- Optical absorption measurements

Non-Catastrophic Damage to QD film during ZnO:SnO_2 RF sputter deposition



Caruge et al., Nature Photonics (2008).

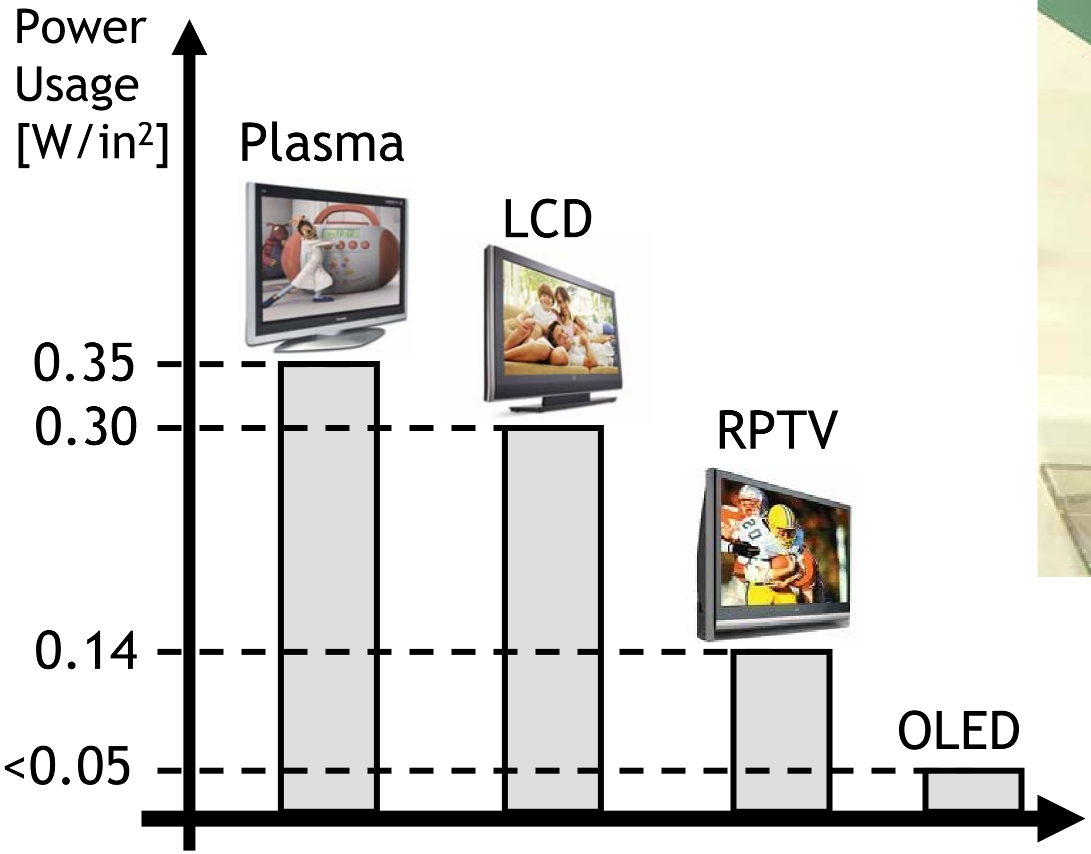
Caruge et al., Nature Photonics (2008).



All-Inorganic QD-LED
(external QE = 0.09%)

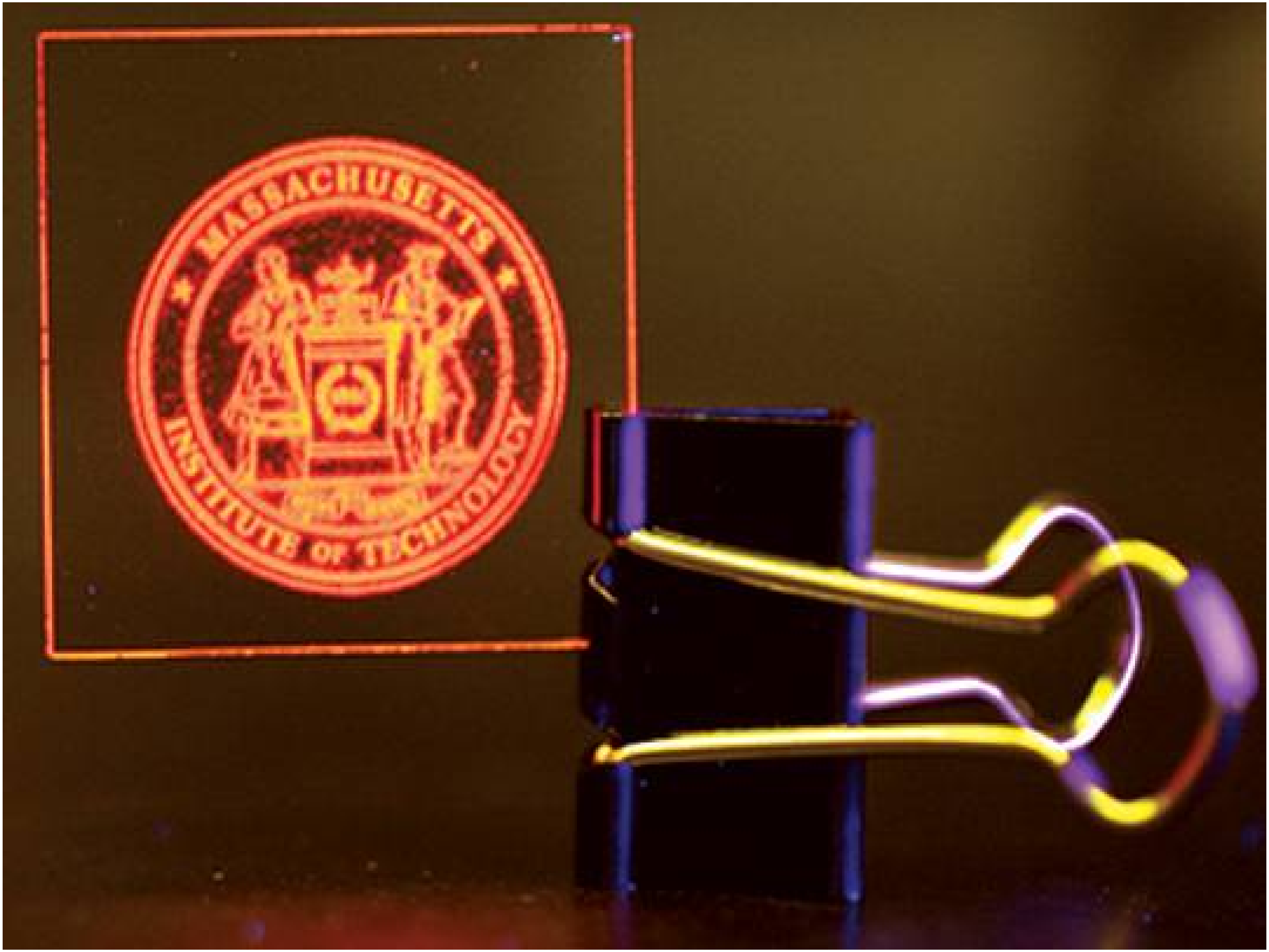
OLED: The Green Display

TV and PC Account for 1% each of US Electricity Usage



First OLED TV: Sony XEL-1
(Est. 40% less power than LCD)

Plasma, LCD, RPTV power usage values from 2007 CNet report on commercial TV power consumption. OLED value projected from SID 2007 demo. US household power usage data from 2004 report by the Natural Resources Defense Council.


MASSACHUSETTS
INSTITUTE OF TECHNOLOGY