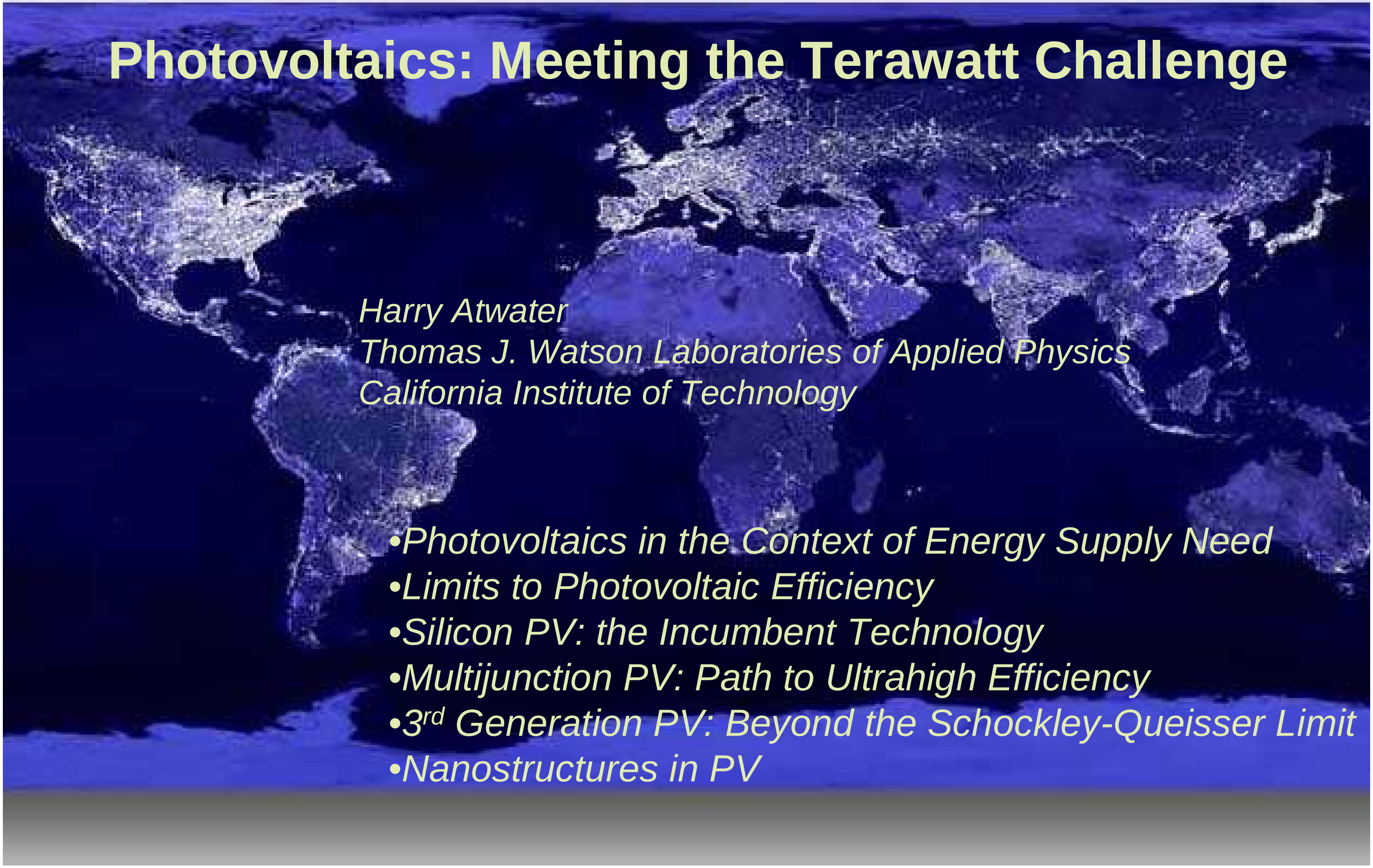

Photovoltaics: Meeting the Terawatt Challenge

Harry Atwater
Thomas J. Watson Laboratories of Applied Physics
California Institute of Technology

- *Photovoltaics in the Context of Energy Supply Need*
- *Limits to Photovoltaic Efficiency*
- *Silicon PV: the Incumbent Technology*
- *Multijunction PV: Path to Ultrahigh Efficiency*
- *3rd Generation PV: Beyond the Schockley-Queisser Limit*
- *Nanostructures in PV*

Acknowledgments

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Martin Green - UNSW
Nate Lewis - Caltech

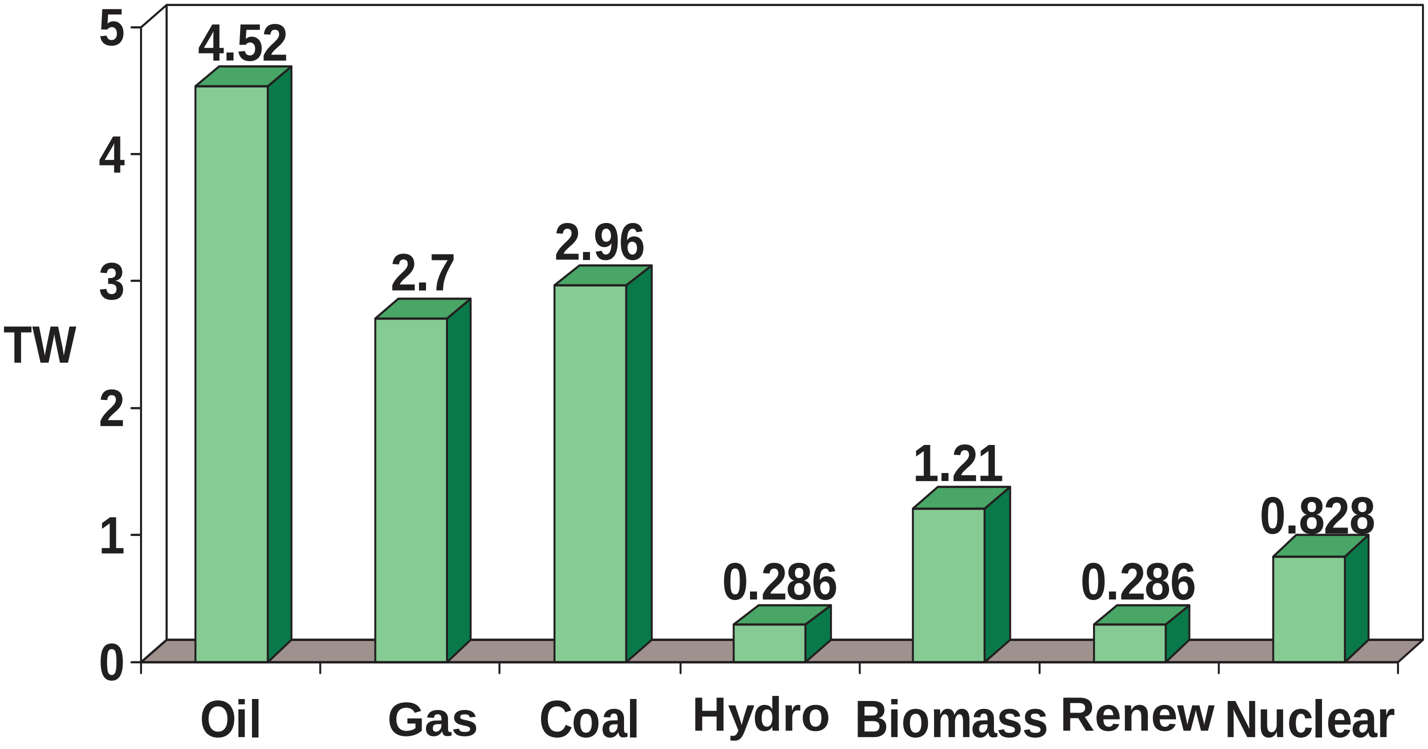
Provided ideas, slides, inspiration...

Caltech Group:

Brendan Kayes
Christine Richardson
James Zahler
Melissa Griggs
Katsu Tanabe

Thank You!

Mean Global Energy Consumption, 1998



Total: 12.8 TW U.S.: 3.3 TW (99 Quads)

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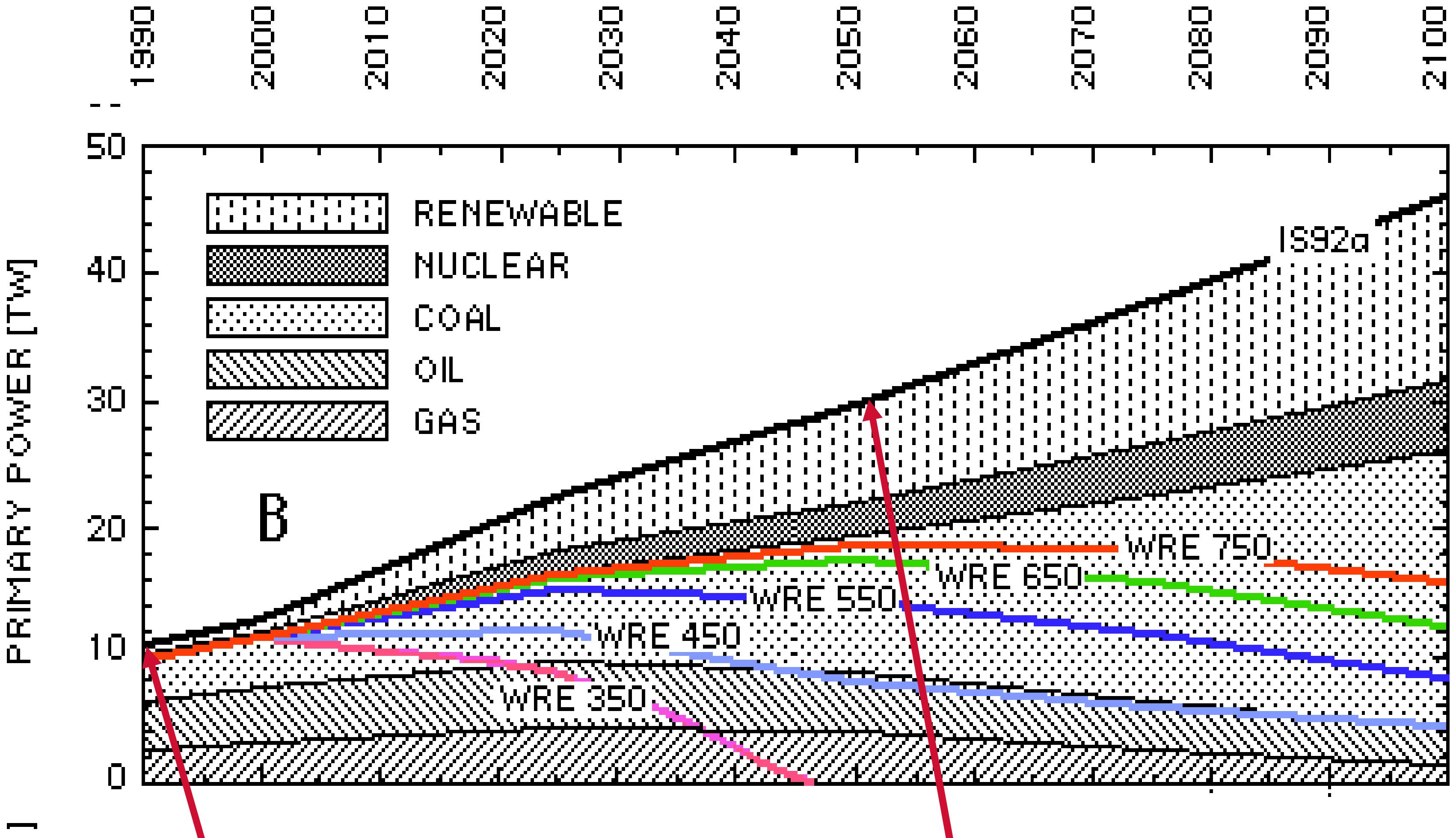
H. Atwater Caltech

Nate Lewis

Total Primary Power vs Year



1990: 12 TW 2050: 28 TW

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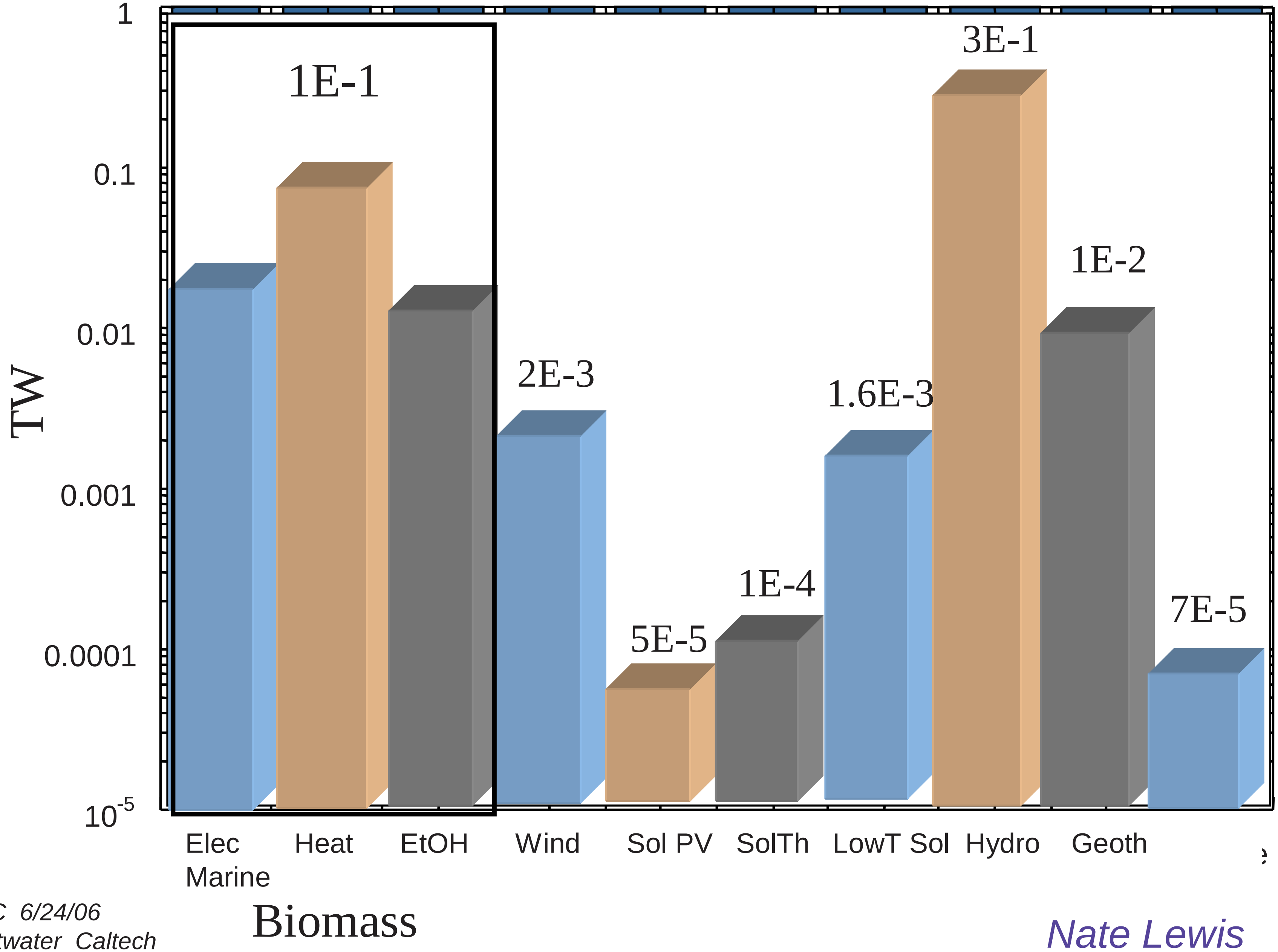
Marty Hoffert, NYU

Energy From Renewables, 1998



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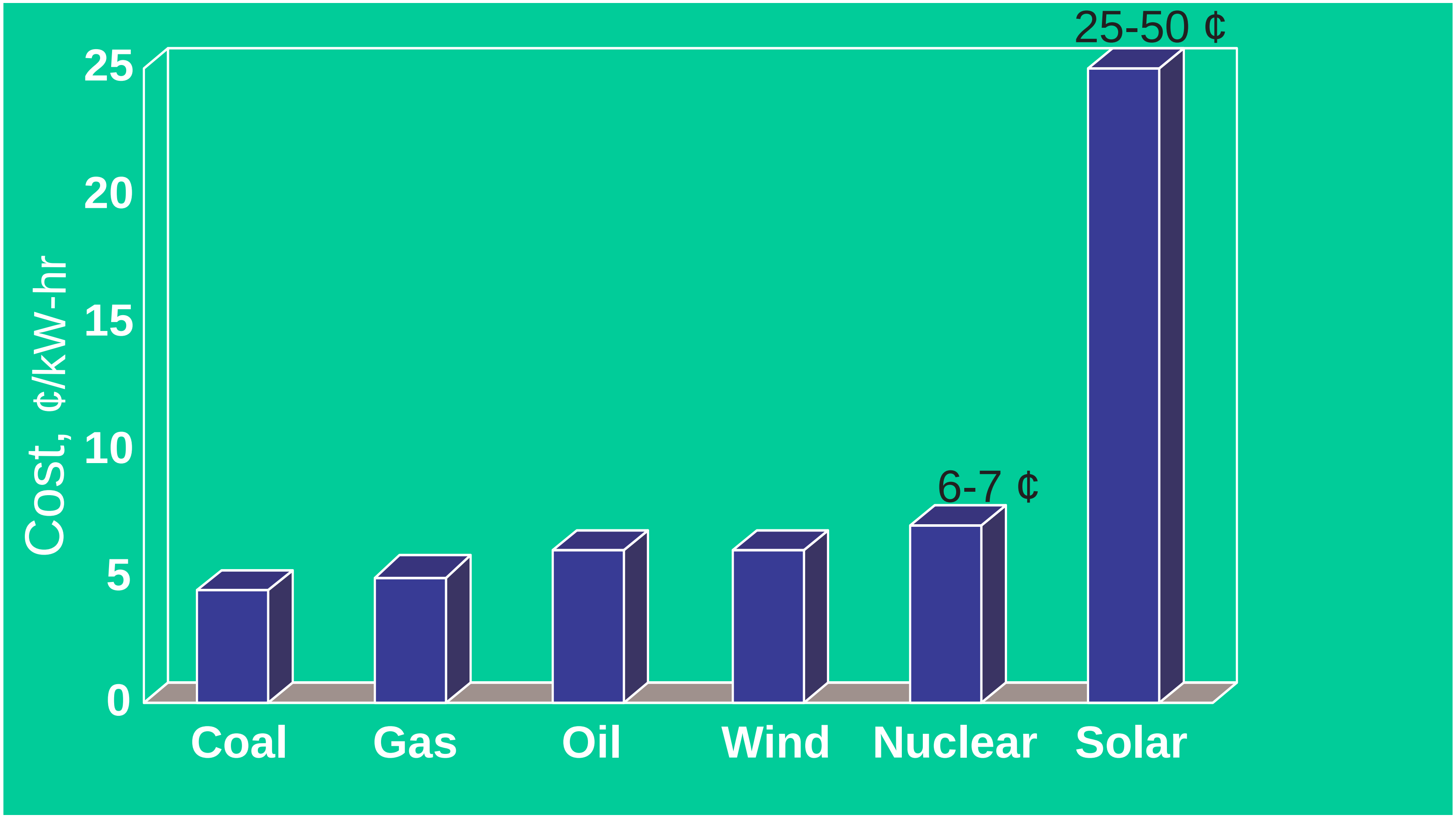
Production Cost of Electricity

(in the U.S. in 2002)



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US DOE

Potential of Renewable Energy

- Hydroelectric 0.9 TW
- Geothermal (limited by drilling technology)
- Wind 2 TW
- Biomass 5-7 TW (using > 20% of earth land mass)
- Solar 50 – 1500 TW (resource: 1.2×10^5 W)

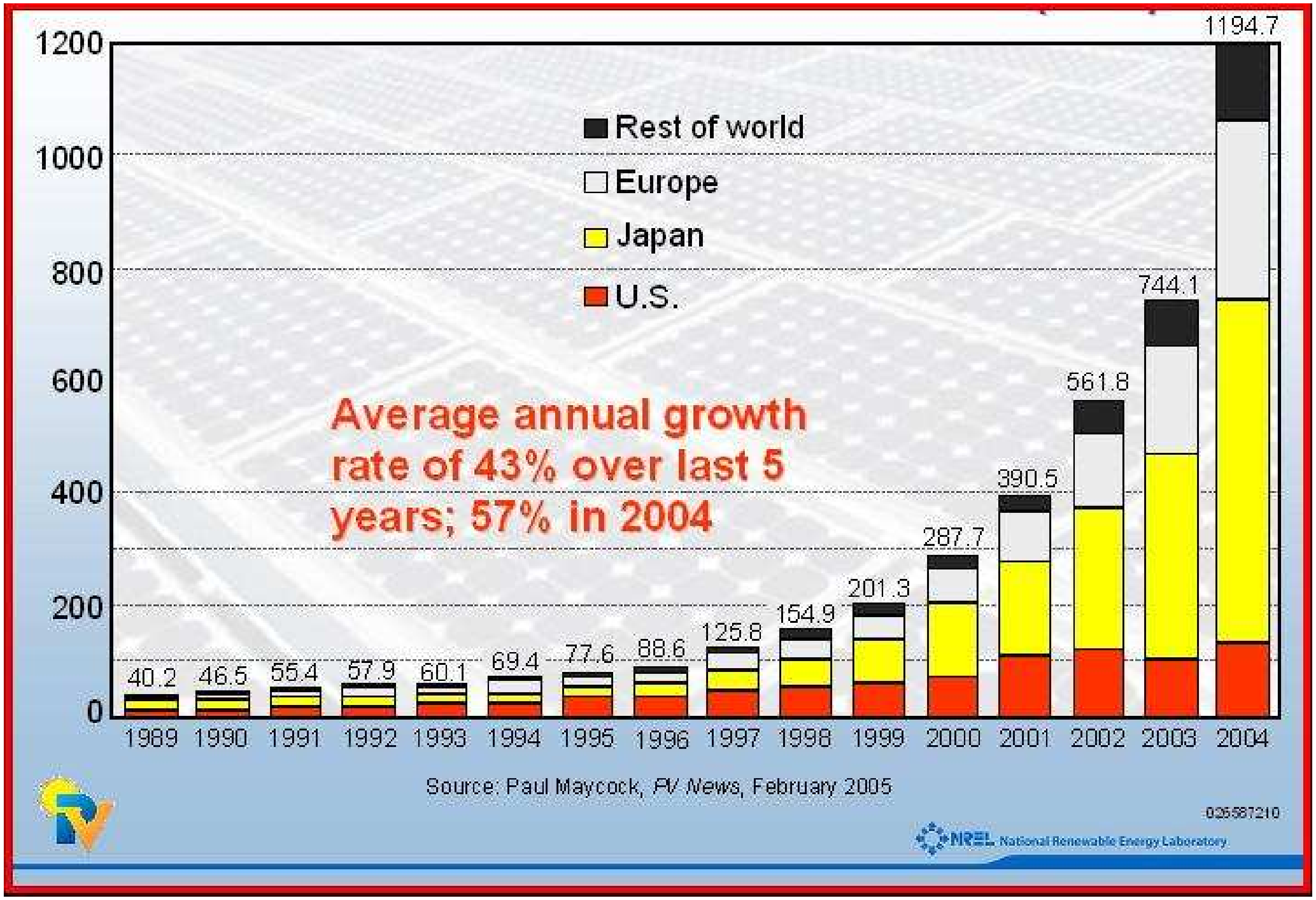
Nate Lewis

PV Land Area Requirements for US Power

Global PV Land Area Requirements

6 Boxes at 3.3 TW Each

Explosive Growth in PV Manufacturing

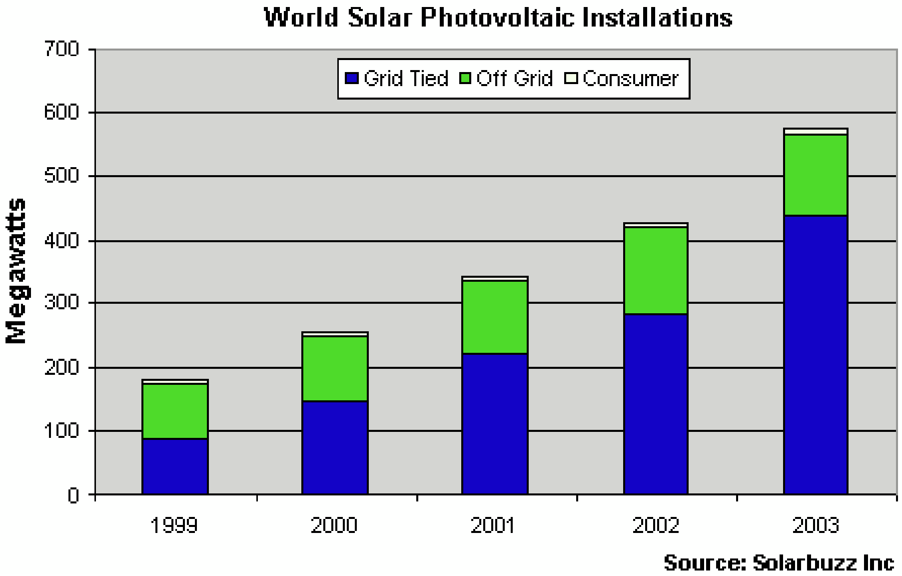


Average annual growth rate of 43% over last 5 years; 57% in 2004

Source: Paul Maycock, *PV News*, February 2005

Photovoltaics Growth

Solar energy:



- Greater than 40% growth per year for the last 5 years
- Si dominant technology
- Si supply currently limited and expensive

Cost : \$5.42 / W_p*

Goal : \$1.00 / W_p

1. Increase Efficiency

2. Lower Cost

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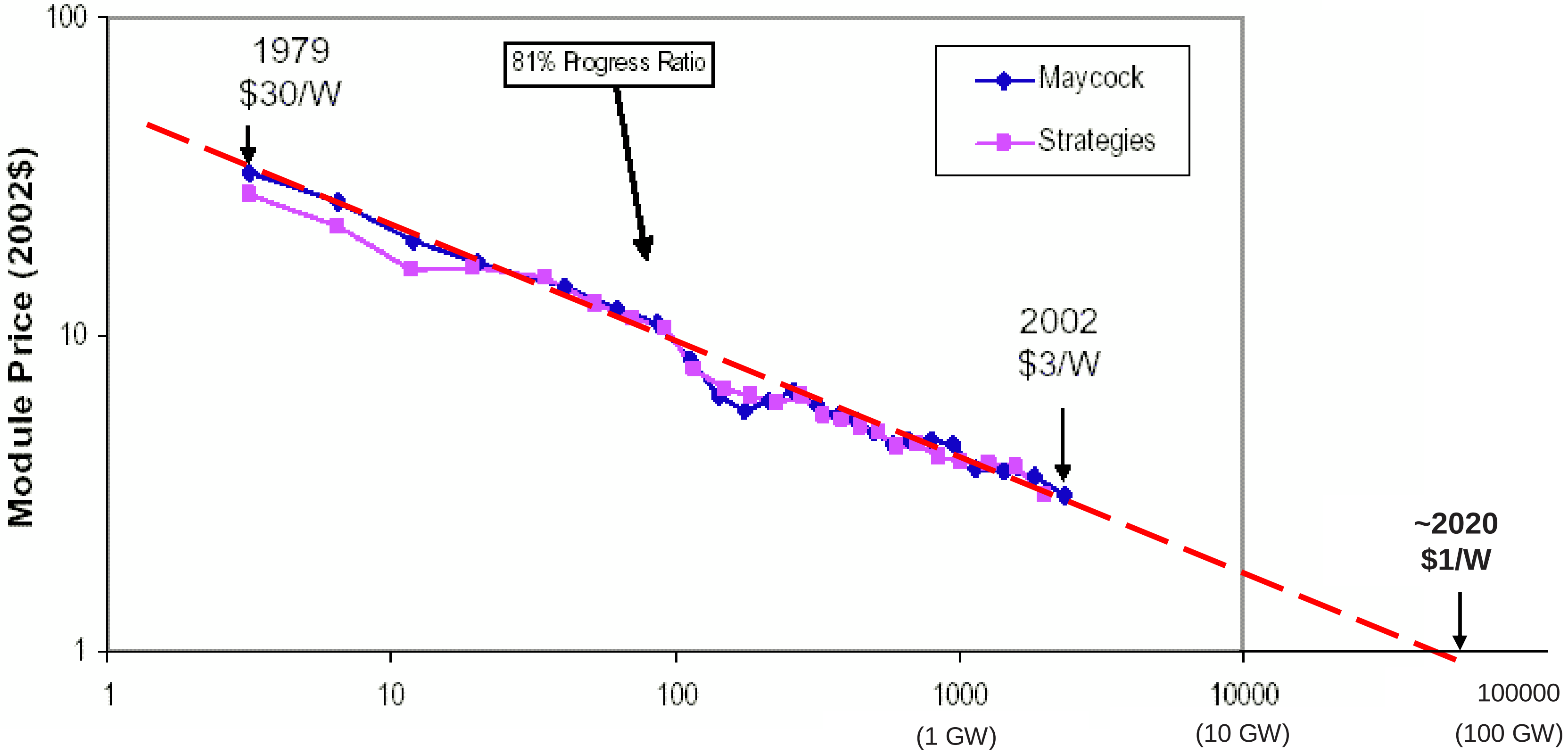
*USA module price index from solarbuzz.com 6/06

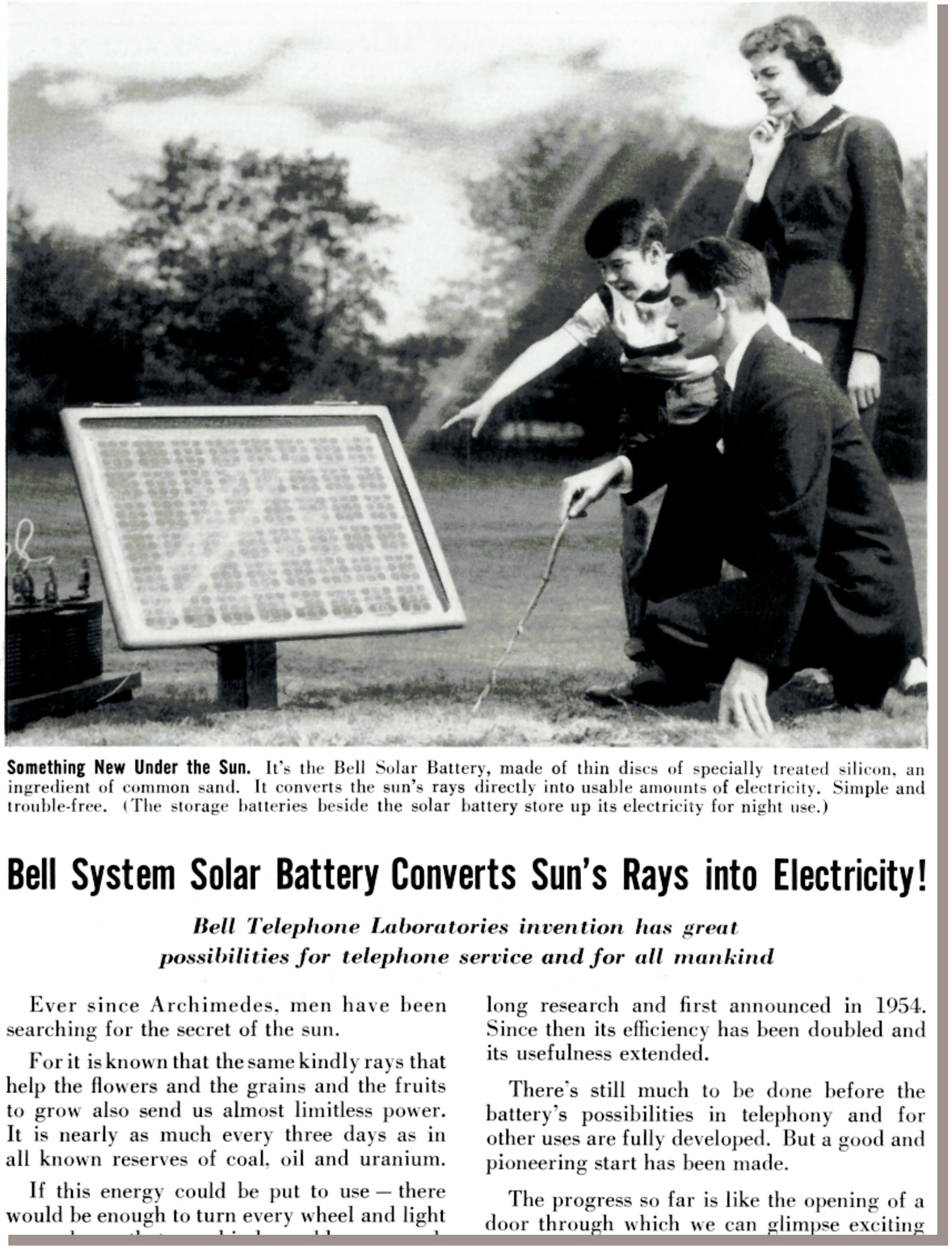
Silicon vs. “Nano-solar”

Philosophical and Technical Approach

- ***Disruptive Solar – seek to alter present PV landscape***
- ***Opportunity for TW Energy Supply (otherwise, why do it?)***
- ***10 Year Time Scale (not longer, because c-Si progress forbids it)***
- ***Ideally, solar technology suitable for electricity and fuel generation***



The First Practical Solar Cell-1954



Something New Under the Sun. It's the Bell Solar Battery, made of thin discs of specially treated silicon, an ingredient of common sand. It converts the sun's rays directly into usable amounts of electricity. Simple and trouble-free. (The storage batteries beside the solar battery store up its electricity for night use.)

Bell System Solar Battery Converts Sun's Rays into Electricity!

Bell Telephone Laboratories invention has great possibilities for telephone service and for all mankind

Ever since Archimedes, men have been searching for the secret of the sun.

For it is known that the same kindly rays that help the flowers and the grains and the fruits to grow also send us almost limitless power. It is nearly as much every three days as in all known reserves of coal, oil and uranium.

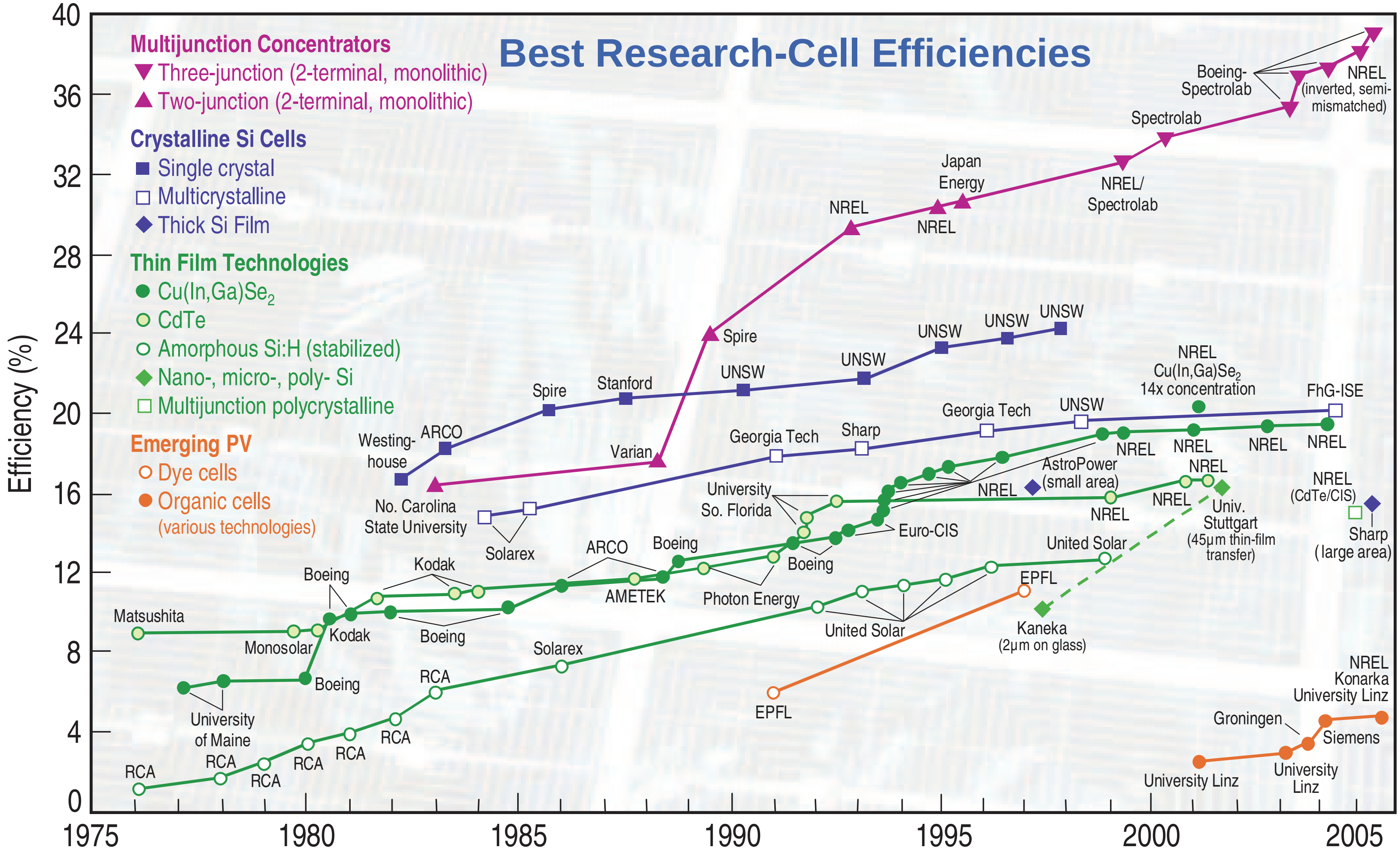
If this energy could be put to use – there would be enough to turn every wheel and light

long research and first announced in 1954. Since then its efficiency has been doubled and its usefulness extended.

There's still much to be done before the battery's possibilities in telephony and for other uses are fully developed. But a good and pioneering start has been made.

The progress so far is like the opening of a door through which we can glimpse exciting

Improvements in Solar Cell Efficiencies



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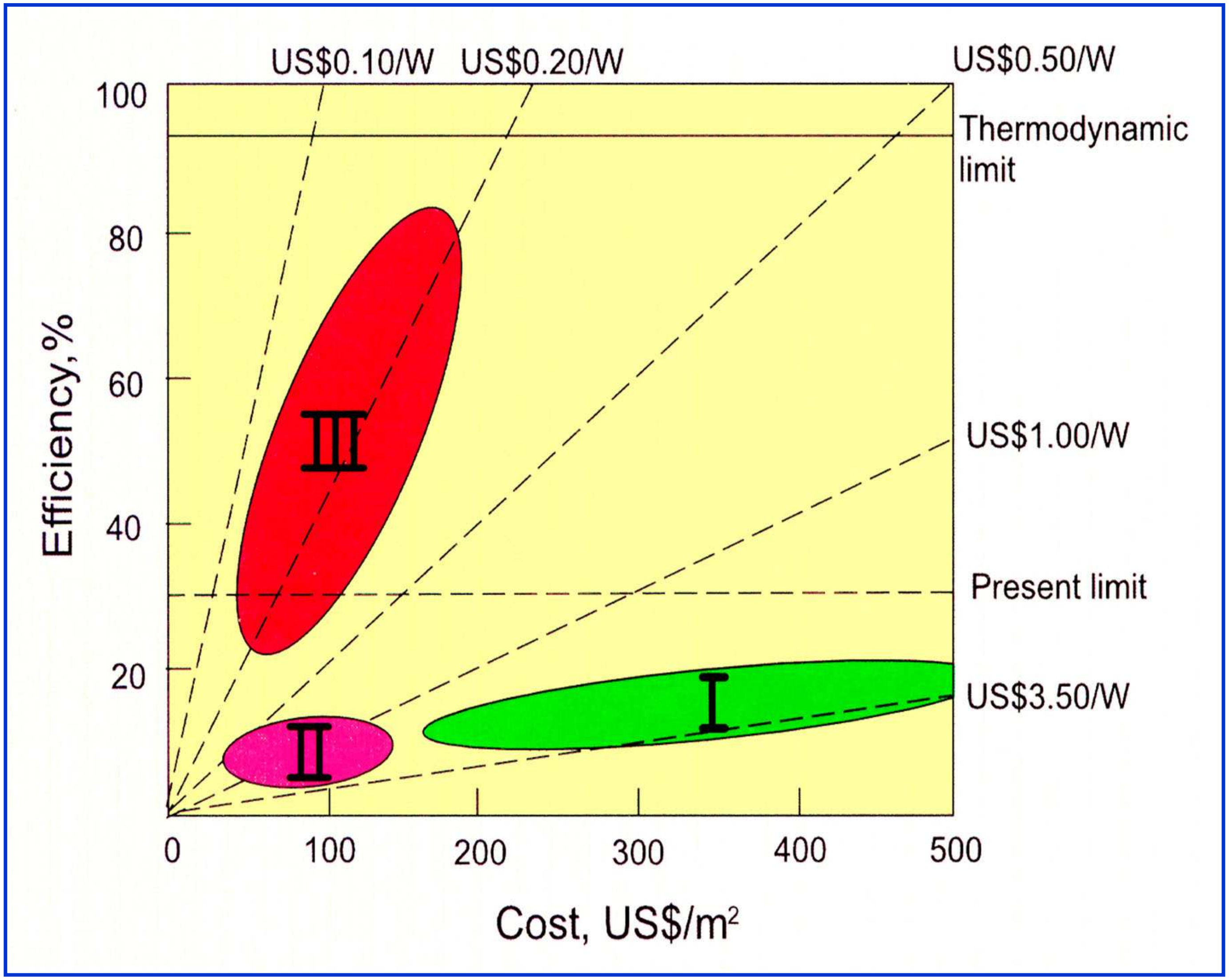
US DOE

Cost/Efficiency of Photovoltaic Technology



Martin Green

Photovoltaic Solar Cell

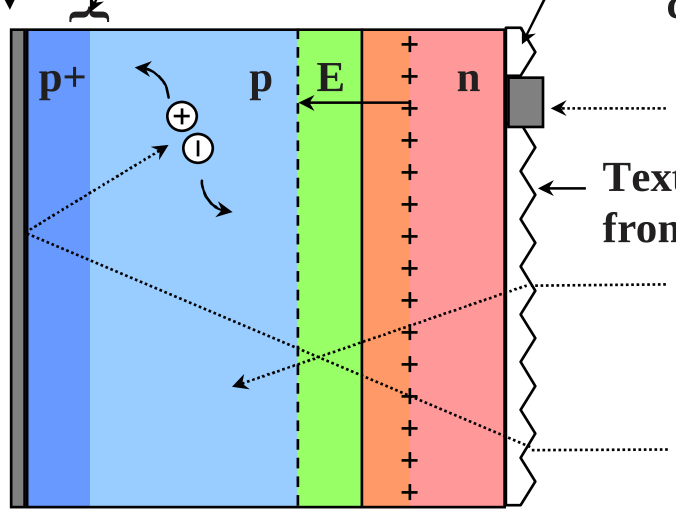
Rear Contact

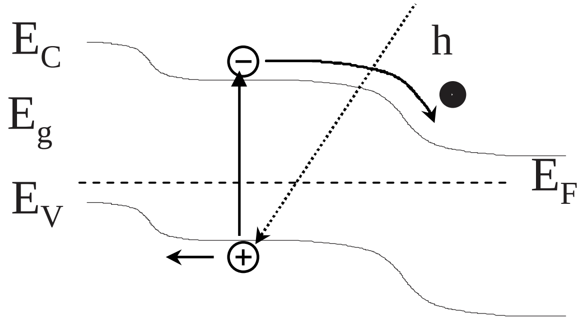
Back surface field

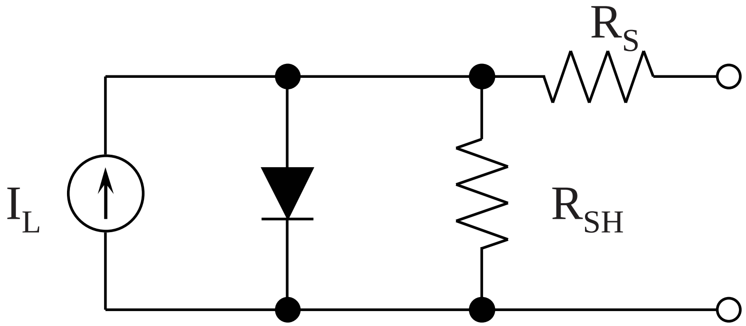
Anti-reflection coating

Front Contact

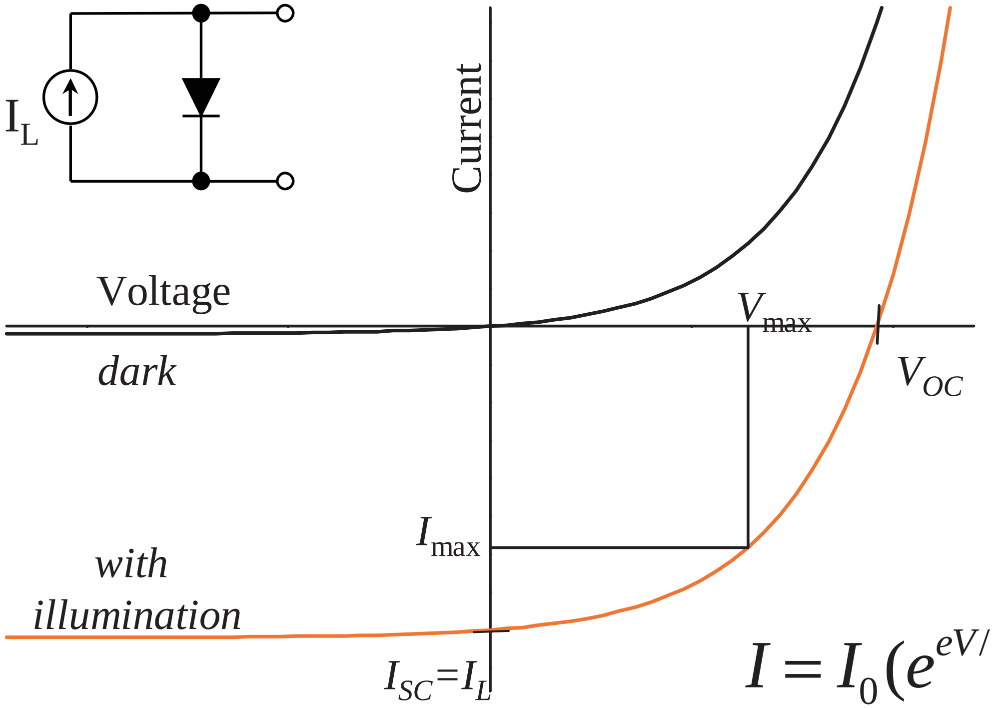
Texturing of front surface







Solar Cell Performance



$$I = I_0(e^{eV/k_BT} - 1) - I_L, \quad I_0 = \text{saturation current}$$

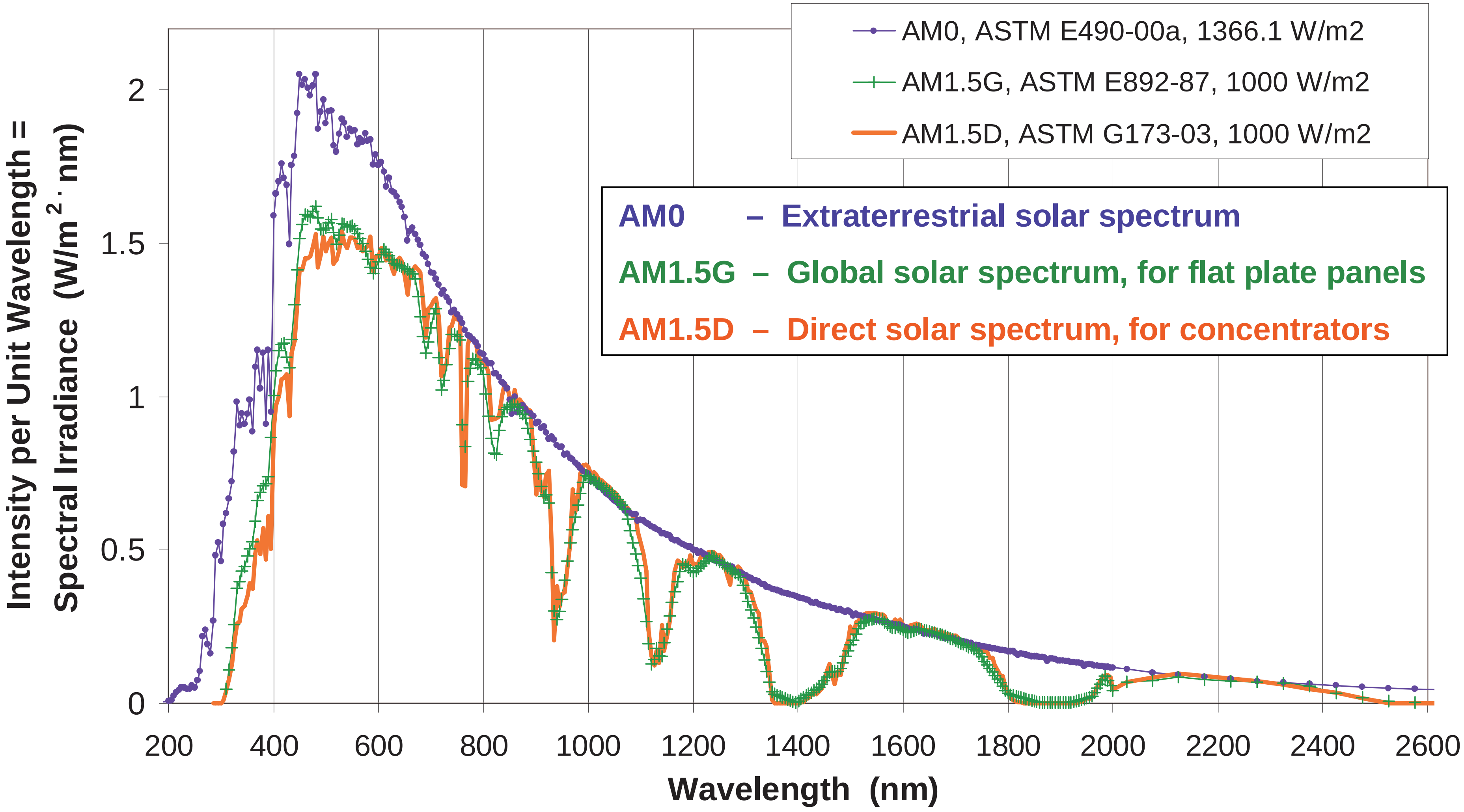
$$P_{\max} = V_{\max} I_{\max} = FF \cdot V_{OC} I_L$$

Conversion efficiency: $\eta = P_{out} / P_{in}$

where incident power: $P_{in} = A\int_0^\infty F(\lambda)\frac{hc}{\lambda}d\lambda$

power out: $P_{out} = FF \cdot V_{OC} I_L$

Standard Solar Spectra



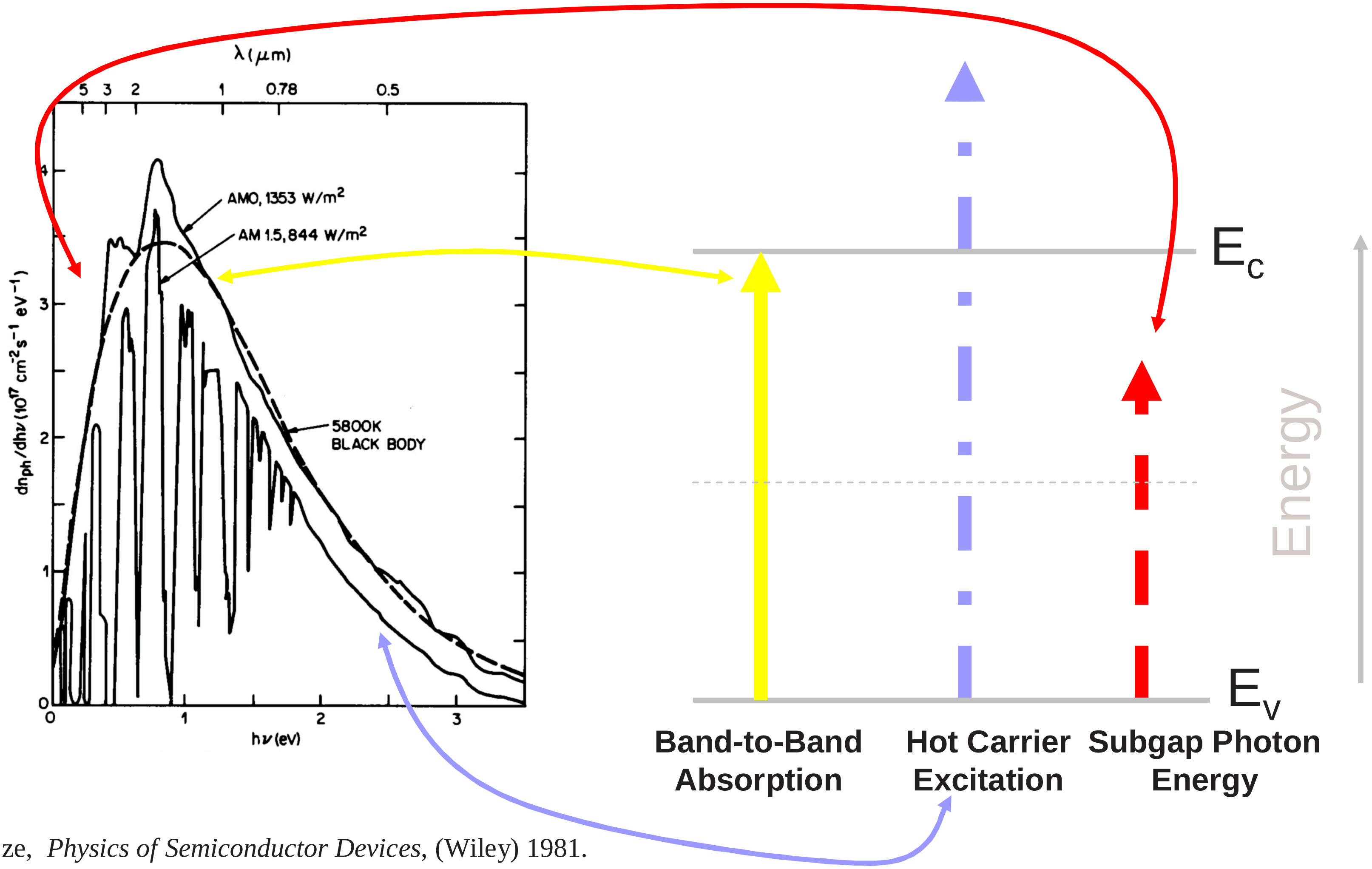
AM0 – Extraterrestrial solar spectrum

AM1.5G – Global solar spectrum, for flat plate panels

AM1.5D – Direct solar spectrum, for concentrators

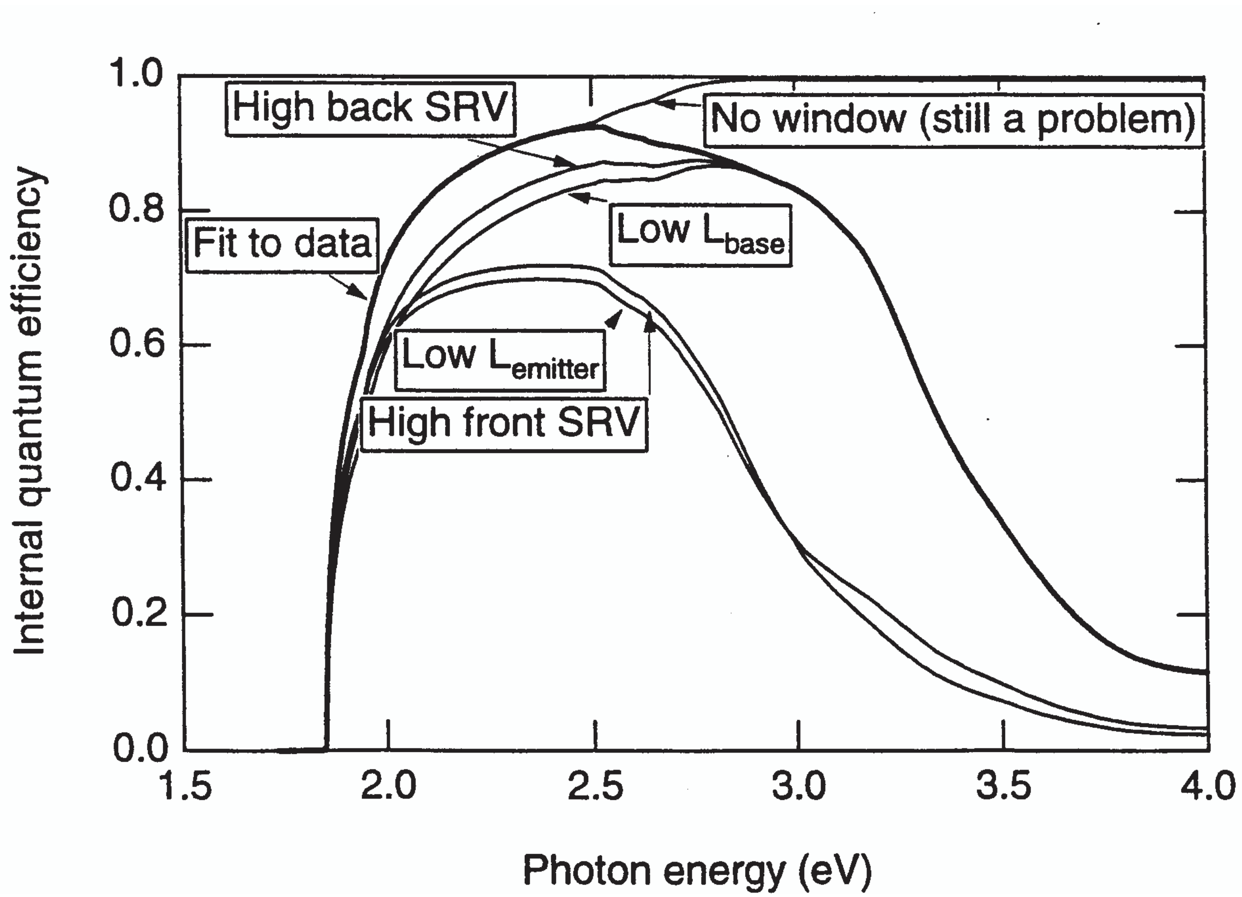
Richard King

Limits to Efficiency: Spectral Absorption



S. M. Sze, *Physics of Semiconductor Devices*, (Wiley) 1981.

Quantum Efficiency Losses



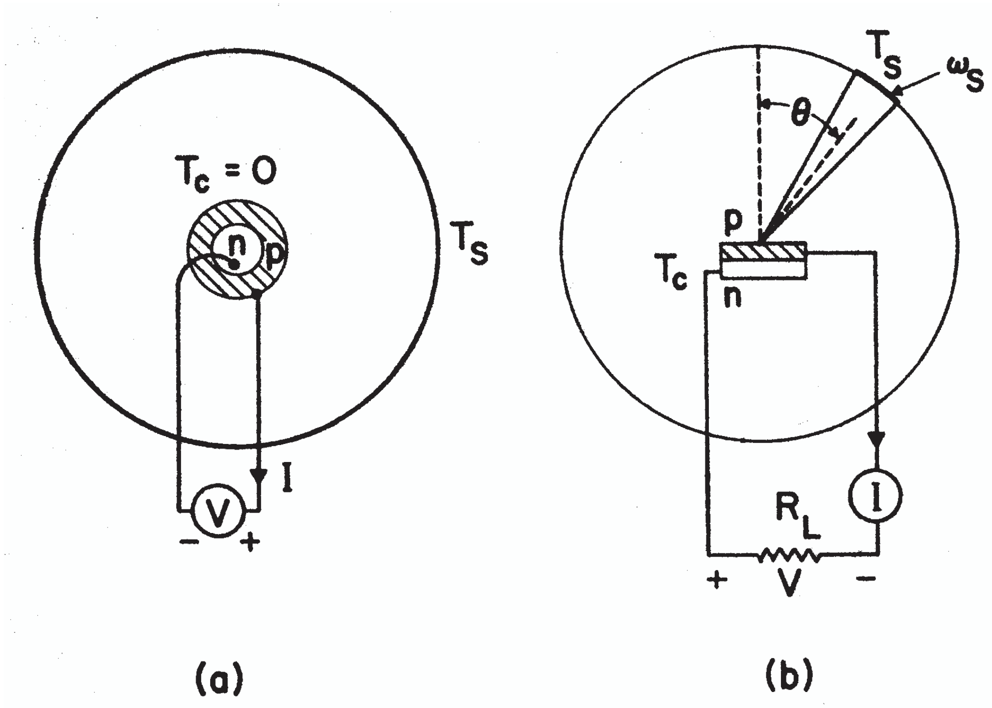
Three types of losses are distinguished:

Base Emitter Window

Courtesy S. Kurtz and D. Friedman

Richard King

Detailed Balance Limit for Solar Cell Efficiency



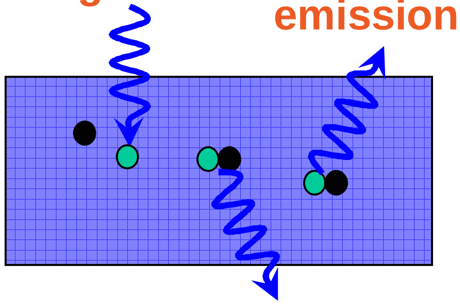
(a) (b)

Shockley and Queisser (1961)

absorption of sunlight

radiative emission

Cell



$$\frac{J_1}{q} = {}^{AM1.5}N - {}^{rad}N_1$$

charge carrier flux

generation rate by sunlight absorption

radiative recombination rate

Detailed Balance Principle And Assumptions

P. Wurfel, Journal of Physics C: Solid State Physics **15,** 3967-3985 (1982)

- Detailed Balance → "What goes in must come out"
- Balance of energy carriers (not energy):
  - Absorbed incident photons from the solar spectrum
  - Loss of carriers due to radiative recombination
  - Extraction of carriers as photocurrent

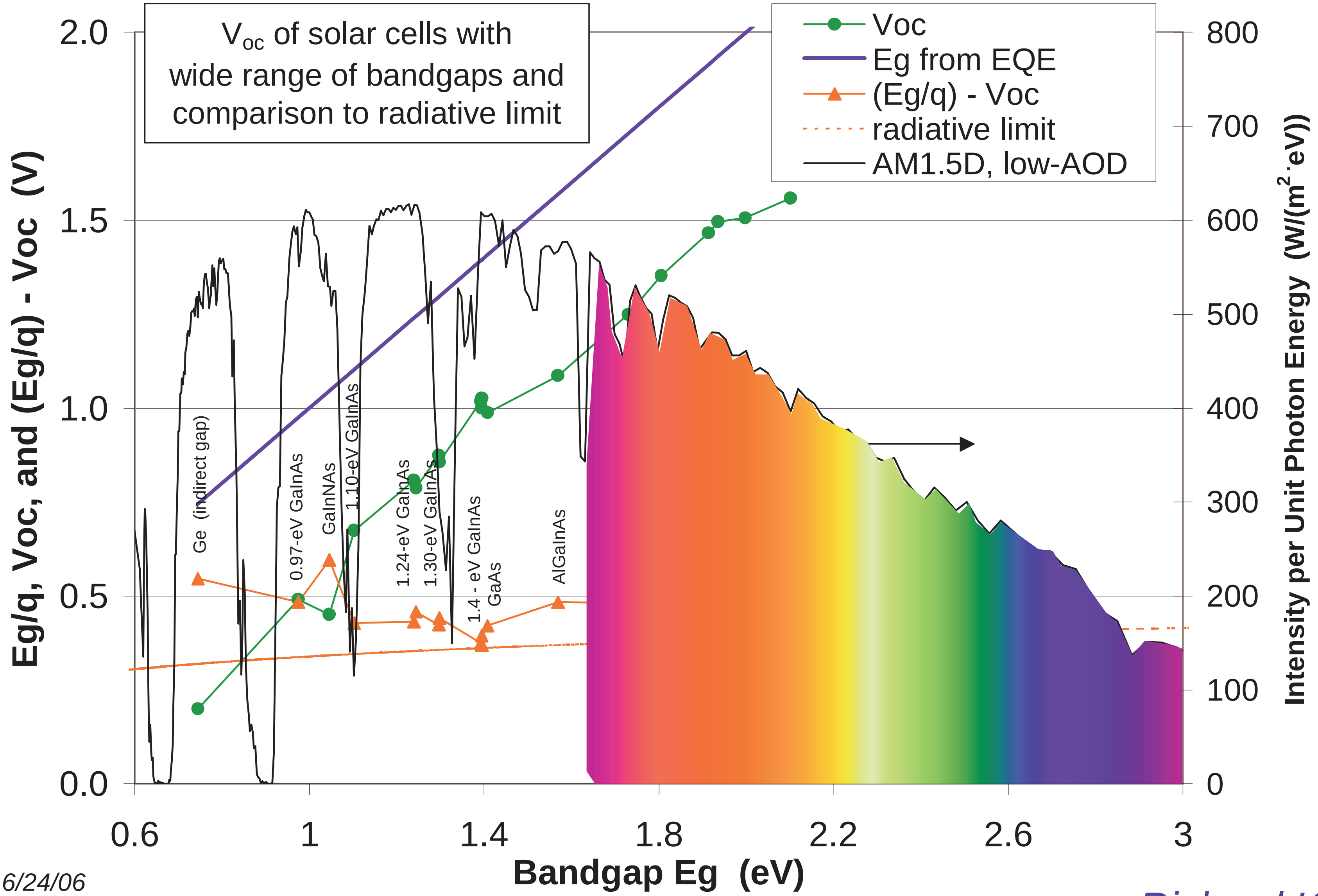
$$\eta = \frac{J(V)\cdot V}{P_{incident}}$$

- Assumptions:
  - Perfect absorption of incident photons
  - Photo-current loss through radiative reemission:

$$^{rad}N(E_G, E, T, V, \varepsilon) = \frac{\pi n^2 \sin^2\theta_c}{4\pi^3\hbar^3 c^2} \int_{E_G}^{E} \left\{ (\hbar\omega)^2 \left[\exp\left(\frac{\hbar\omega - qV}{kT} \right) - 1 \right]^{-1} \right\} d\hbar\omega$$

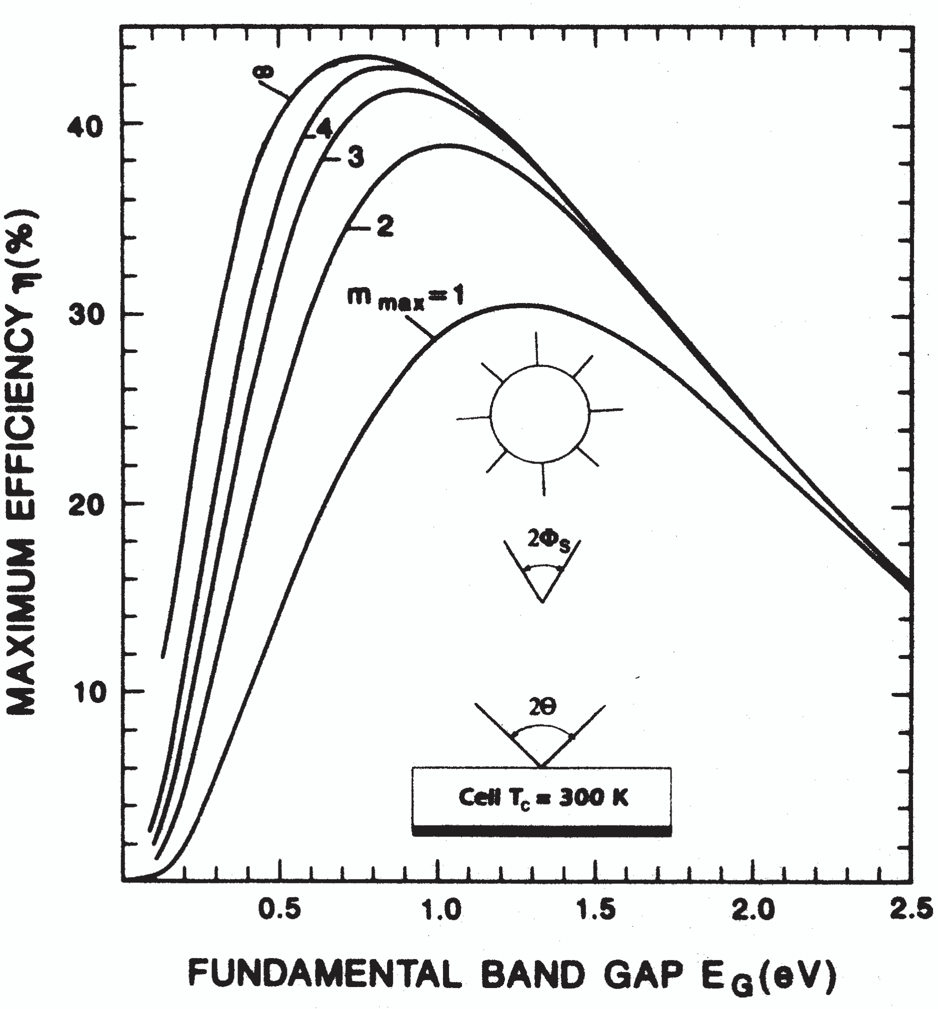
Radiative recombination limits cell operating potential to < bandgap potential

Bandgap - Voltage Offset $(E_g/q) - V_{oc}$ for Single-Junction Solar Cells


V_{oc} of solar cells with wide range of bandgaps and comparison to radiative limit

Richard King

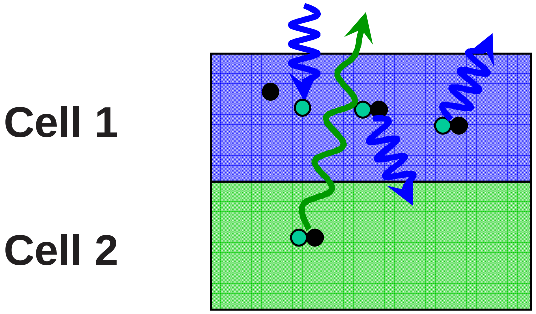
Detailed Balance:
Maximum Cell Efficiency Including Carrier Multiplication



Werner, Kolodinski, and Queisser (1994)

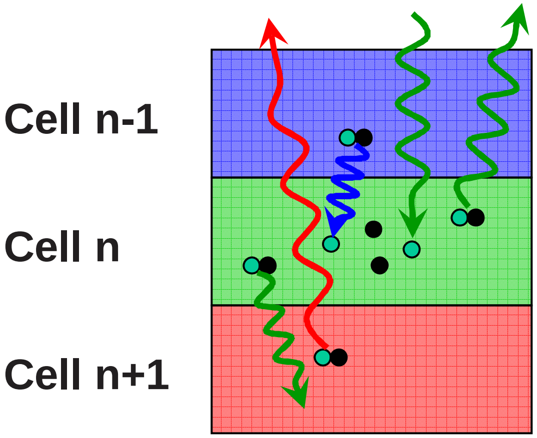
Detailed Balance in Multijunction Solar Cells

Detailed Balance of First Subcell



$$\frac{J_1}{q} = {}^{AM1.5}N - {}^{rad}N_1$$

Detailed Balance of n^th^ Subcell



$$\frac{J_n}{q} = {}^{AM1.5}N + {}^{rad}N_{n-1} - {}^{rad}N_n$$

Maximum Solar Cell Efficiencies

References
C. H. Henry, “Limiting efficiencies of ideal single and multiple energy gap terrestrial solar cells,” *J. Appl. Phys.*, **51**, 4494 (1980).
W. Shockley and H. J. Queisser, “Detailed Balance Limit of Efficiency of *p-n* Junction Solar Cells,” *J. Appl. Phys.*, **32**, 510 (1961).
J. H. Werner, S. Kolodinski, and H. J. Queisser, “Novel Optimization Principles and Efficiency Limits for Semiconductor Solar Cells,” *Phys. Rev. Lett.*, **72**, 3851 (1994).
M. Green, K. Emery, D. L. King, Y. Hisikawa, W. Warta, "Solar Cell Efficiency Tables (Version 27)", *Progress in Photovoltaics*, **14**, 45 (2006)
R. R. King *et al.*, "Pathways to 40%-Efficient Concentrator Photovoltaics," *Proc. 20th European Photovoltaic Solar Energy Conf.*, Barcelona, Spain, 6-10 June 2005.
R. R. King *et al.*, "Lattice-Matched and Metamorphic GaInP/ GaInAs/ Ge Concentrator Solar Cells," *Proc. 3rd World Conf. on Photovoltaic Energy Conversion*, May 11-18, 2003, Osaka, Japan, p 622.
A. Slade, V. Garboushian, "27.6%-Efficient Silicon Concentrator Cell for Mass Production," *Proc. 15th Int'l. Photovoltaic Science and Engineering Conf.*, Beijing, China, Oct. 2005.
R. P. Gale *et al.*, "High-Efficiency GaAs/CuInSe$_2$ and AlGaAs/CuInSe$_2$ Thin-Film Tandem Solar Cells," *Proc. 21st IEEE Photovoltaic Specialists Conf.*, Kissimmee, Florida, May 1990.
J. Zhao, A. Wang, M. A. Green, F. Ferrazza, "Novel 19.8%-efficient 'honeycomb' textured multicrystalline and 24.4% monocrystalline silicon solar cells," *Appl. Phys. Lett.*, **73**, 1991 (1998).

Measured

3-gap GaInP/GaAs/Ge cell @236 suns (Spectrolab)
39.0%

3-gap GaInP/GaAs/Ge cell @ 1 sun (Spectrolab)
32.0%

1-gap solar cell (Si, 1.12 eV) @92 suns (Amonix)
27.6%

1-gap solar cell (GaAs, 1.424 eV) @1 sun (Kopin)
25.1%

1-gap solar cell (silicon, 1.12 eV) @1 sun (UNSW)
24.7%

Theoretical

95% **Carnot eff. = $1 - T/T_{sun}$ $T = 300$ K, $T_{sun} \approx$ 5800 K**

93% **Max. eff. of solar energy conversion $= 1 - TS/E = 1 - (4/3)T/T_{sun}$ (Henry)**

72% **Ideal 36-gap solar cell at 1000 suns (Henry)**

56% **Ideal 3-gap solar cell at 1000 suns (Henry)**

50% **Ideal 2-gap solar cell at 1000 suns (Henry)**

44% **Ultimate eff. of device with cutoff E_g: (Shockley, Queisser)**

43% **1-gap cell at 1 sun with carrier multiplication (>1 e-h pair per photon) (Werner, Kolodinski, Queisser)**

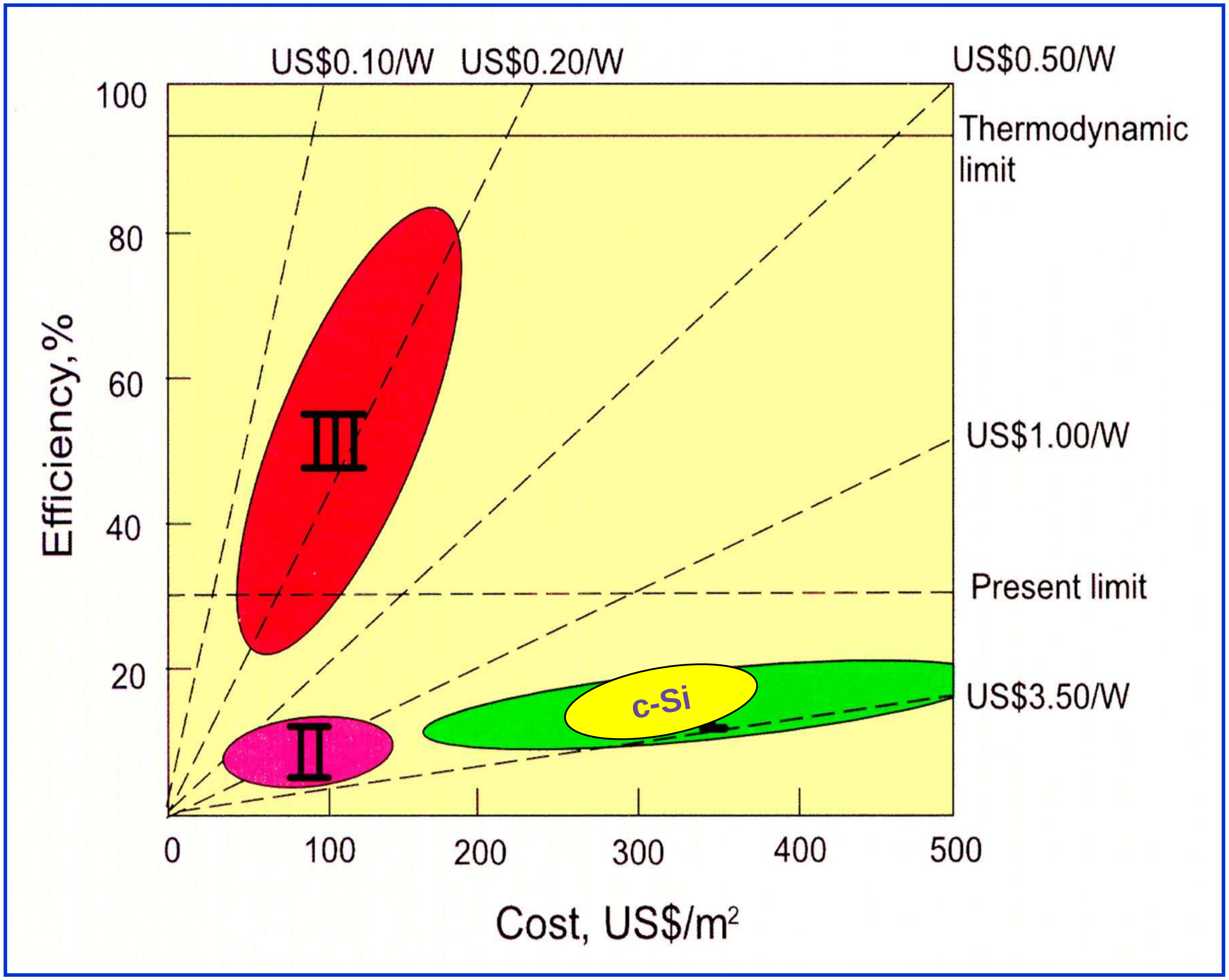
37% **Ideal 1-gap solar cell at 1000 suns (Henry)**

31% **Ideal 1-gap solar cell at 1 sun (Henry)**

30% **Detailed balance limit of 1 gap solar cell at 1 sun (Shockley, Queisser)**

Richard King

Cost/Efficiency of Photovoltaic Technology



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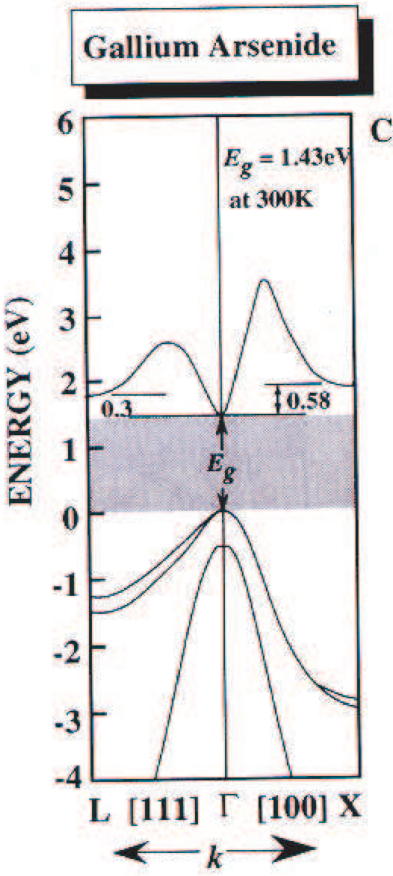
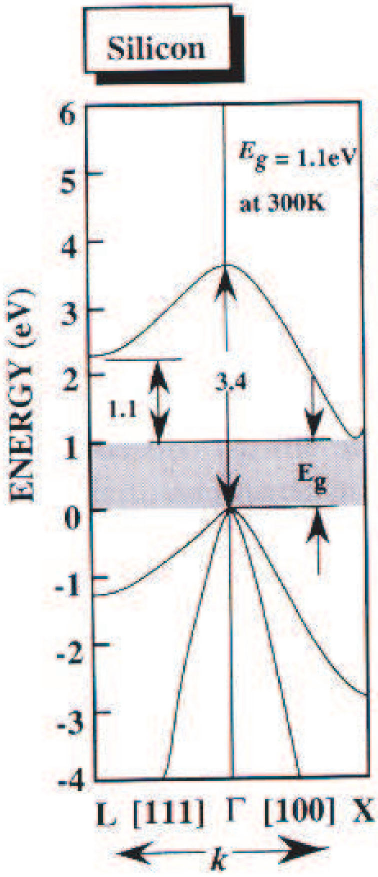
Absorption via Direct and Indirect Interband Transitions



Conduction Band:

Lowest Valley: Γ- vall

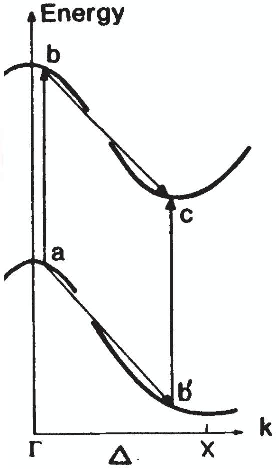
Upper Valley: L-valle

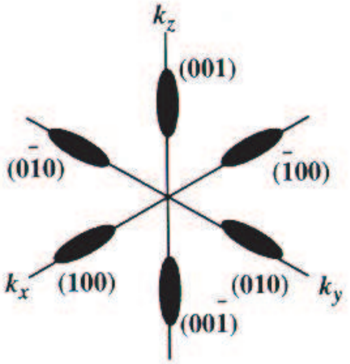


Γ point : $k = (0,0,0)$

X point : $k = \frac{2\pi}{a}(1,0,0)$

L point : $k = \frac{\pi}{a}(1,1,1)$





Six equivalent valleys at conduction bandedge

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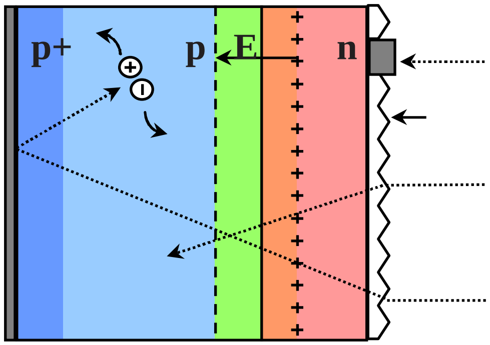
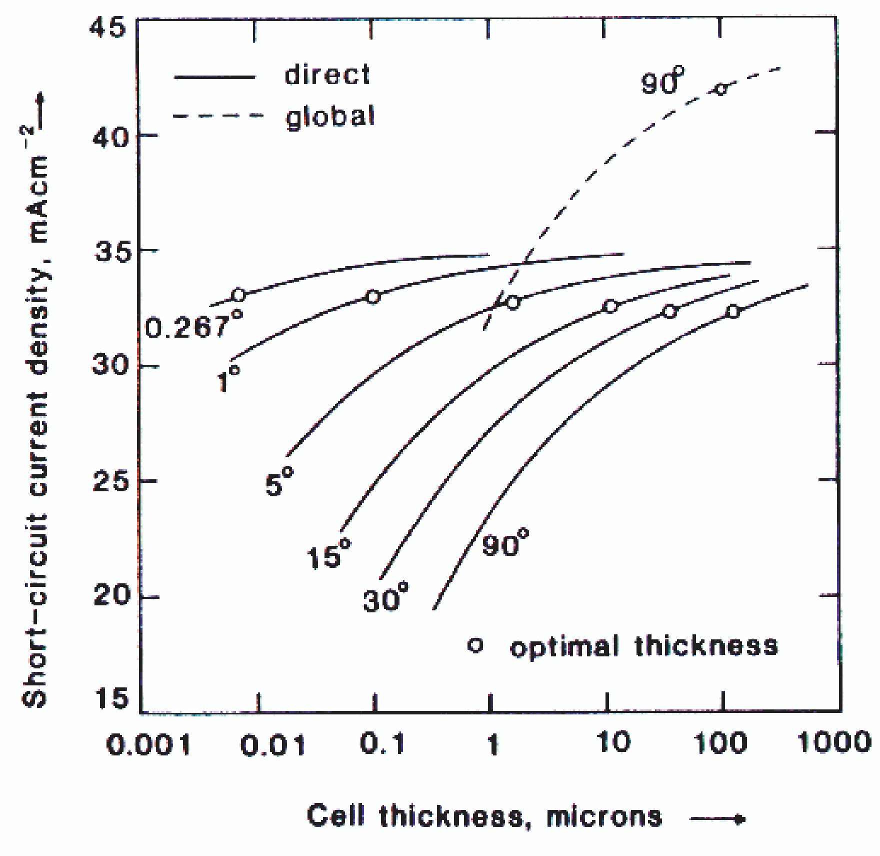
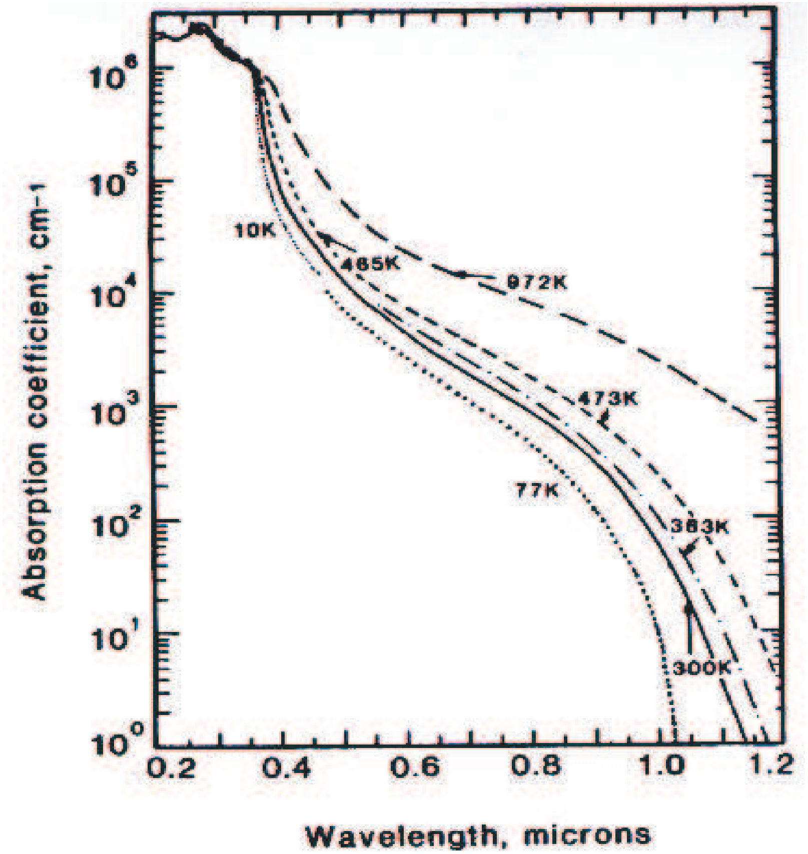
Light Absorption and Current Collection

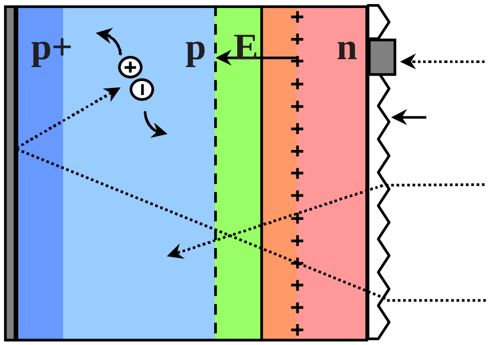


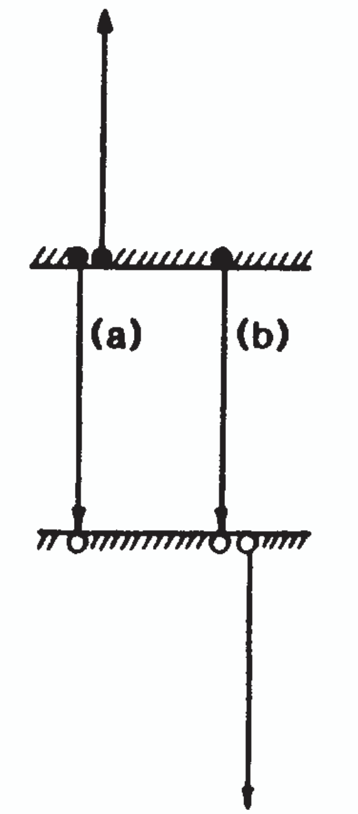


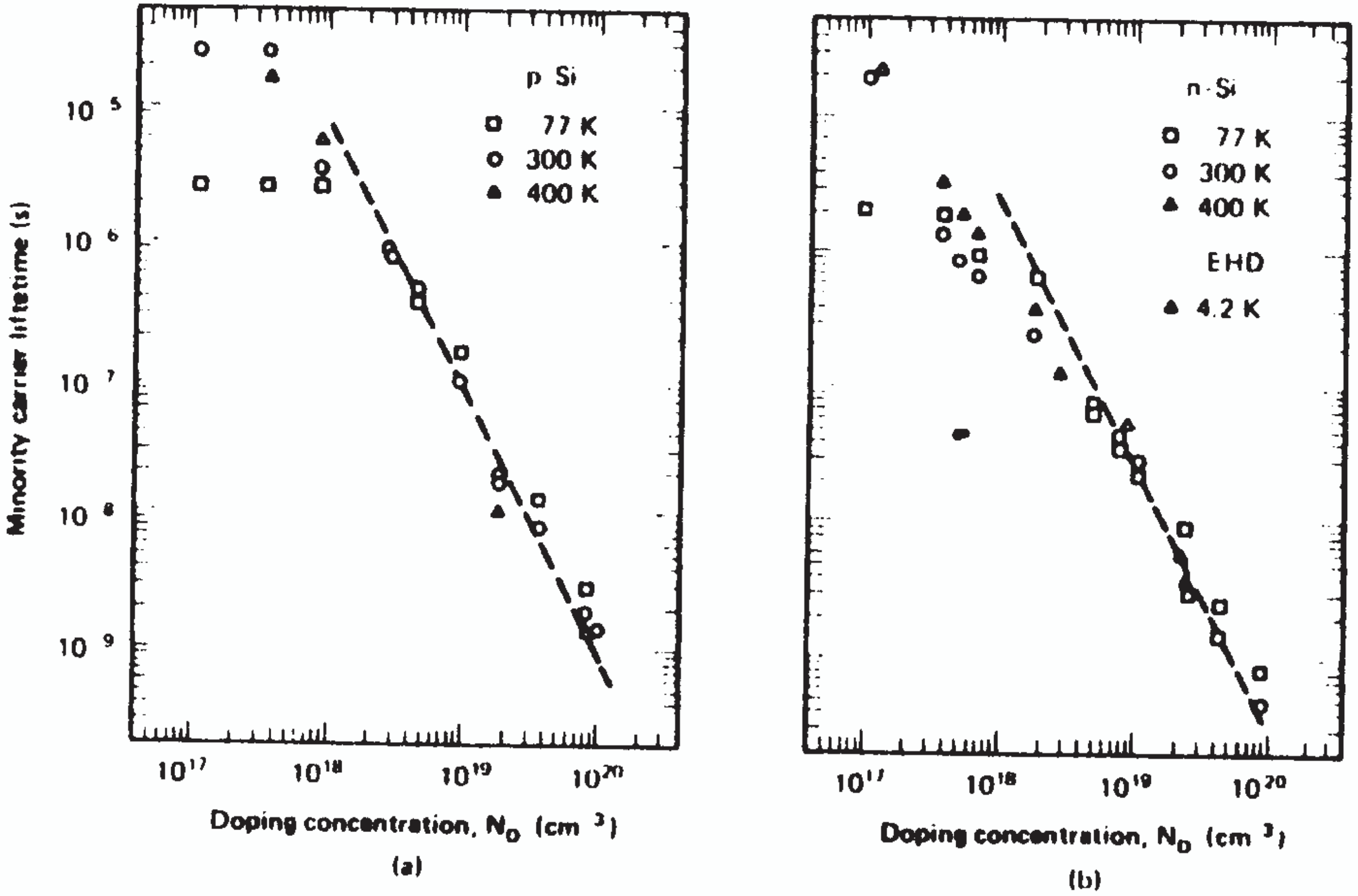


Auger Recombination

Limits to Minority Carrier Lifetime

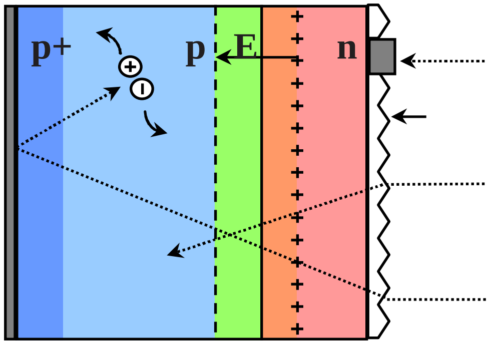


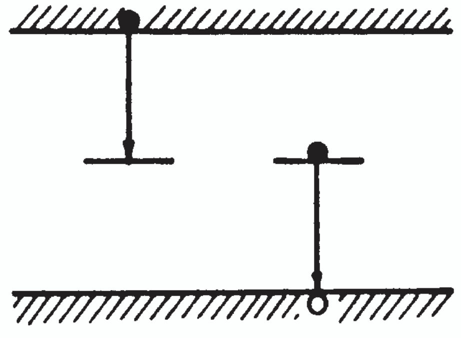


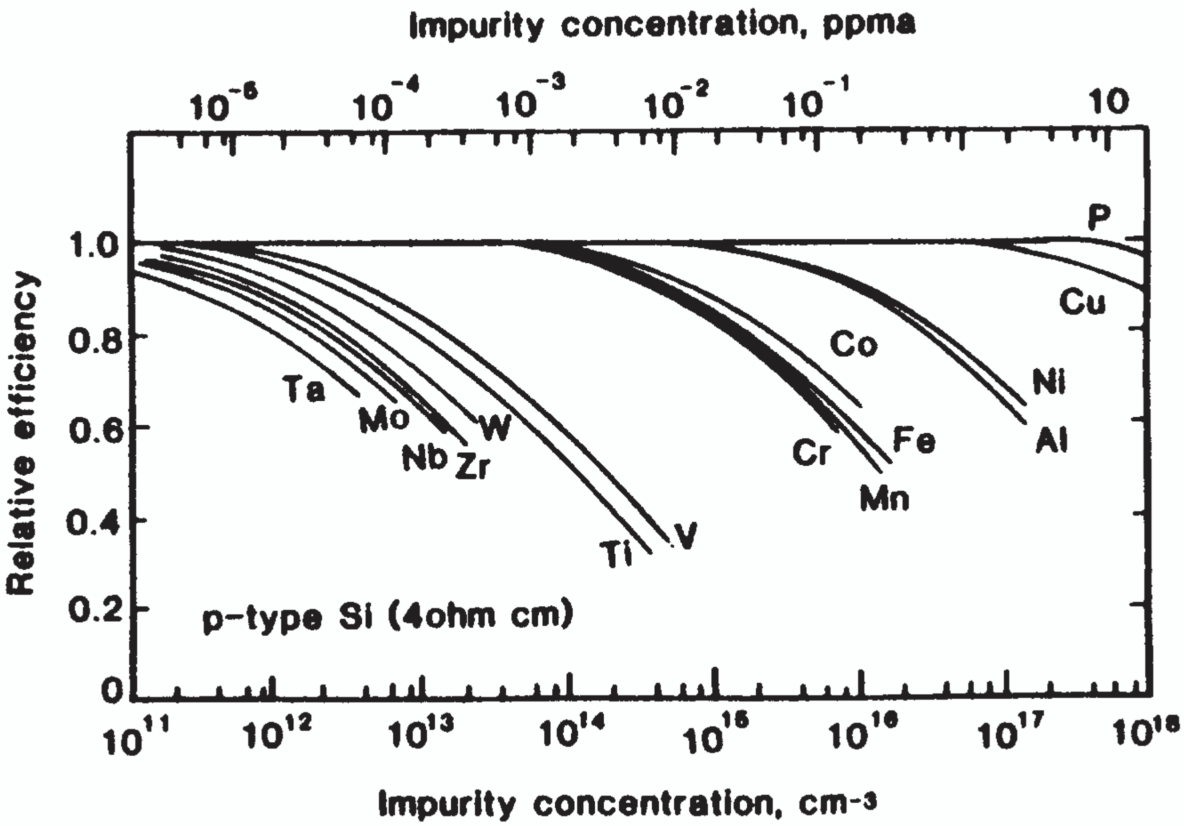


Deep Level Impurity Recombination

Limits to Minority Carrier Lifetime in p-type Si

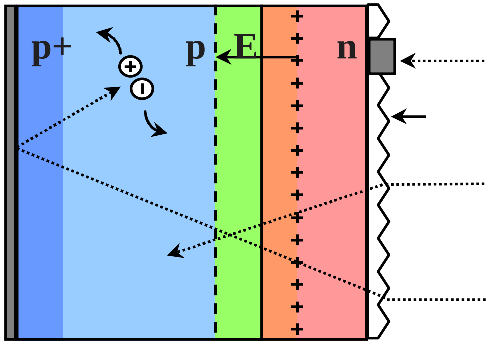


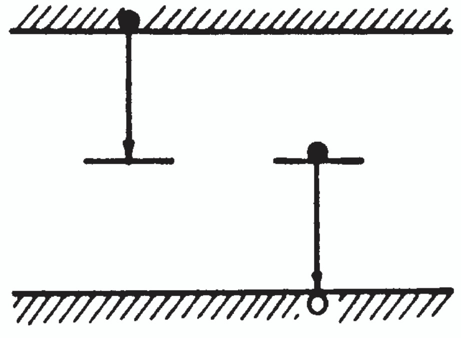


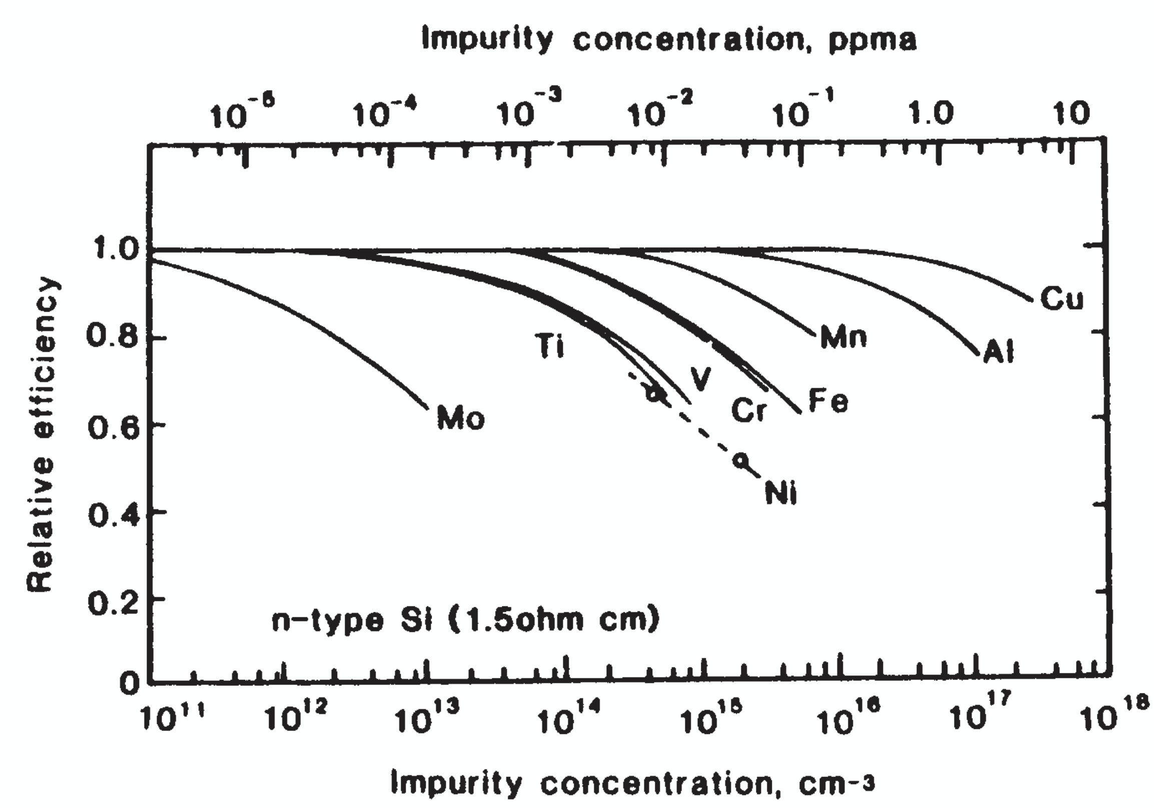


Deep Level Impurity Recombination

Limits to Minority Carrier Lifetime in n-type Si

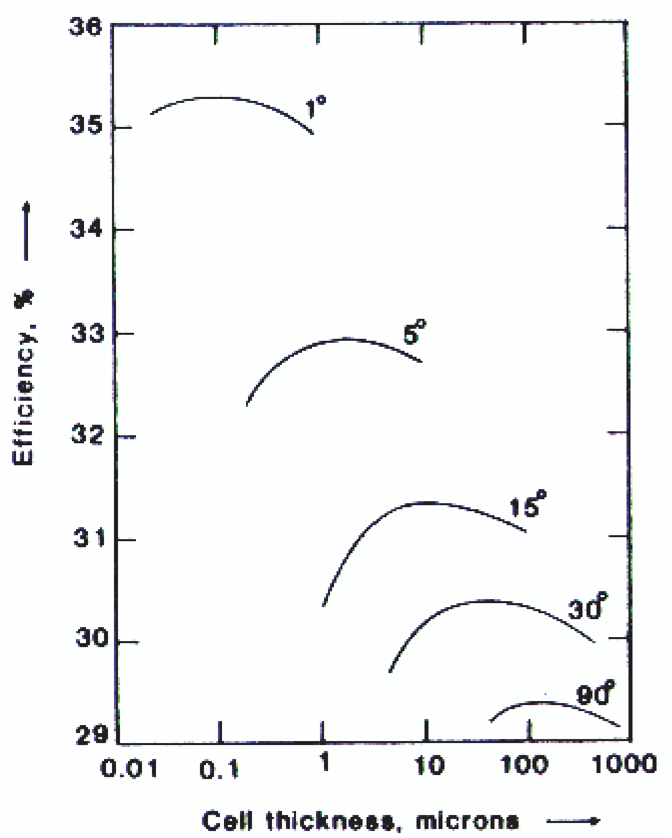




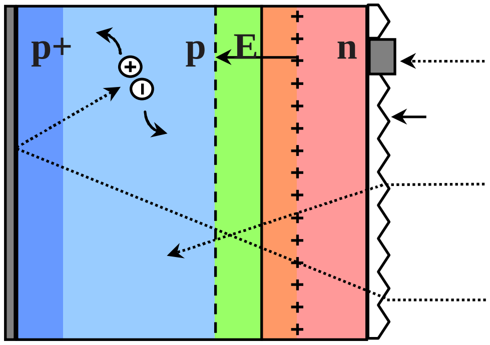


Open Circuit Voltage

limited by Recombination via a Single Deep Level



M.A. Green, *High Efficiency Si Solar Cells*, Trans Tech, 1987



$$R=\frac{np}{[\tau_{no}(p+p')+\tau_{po}(n+n')]}$$

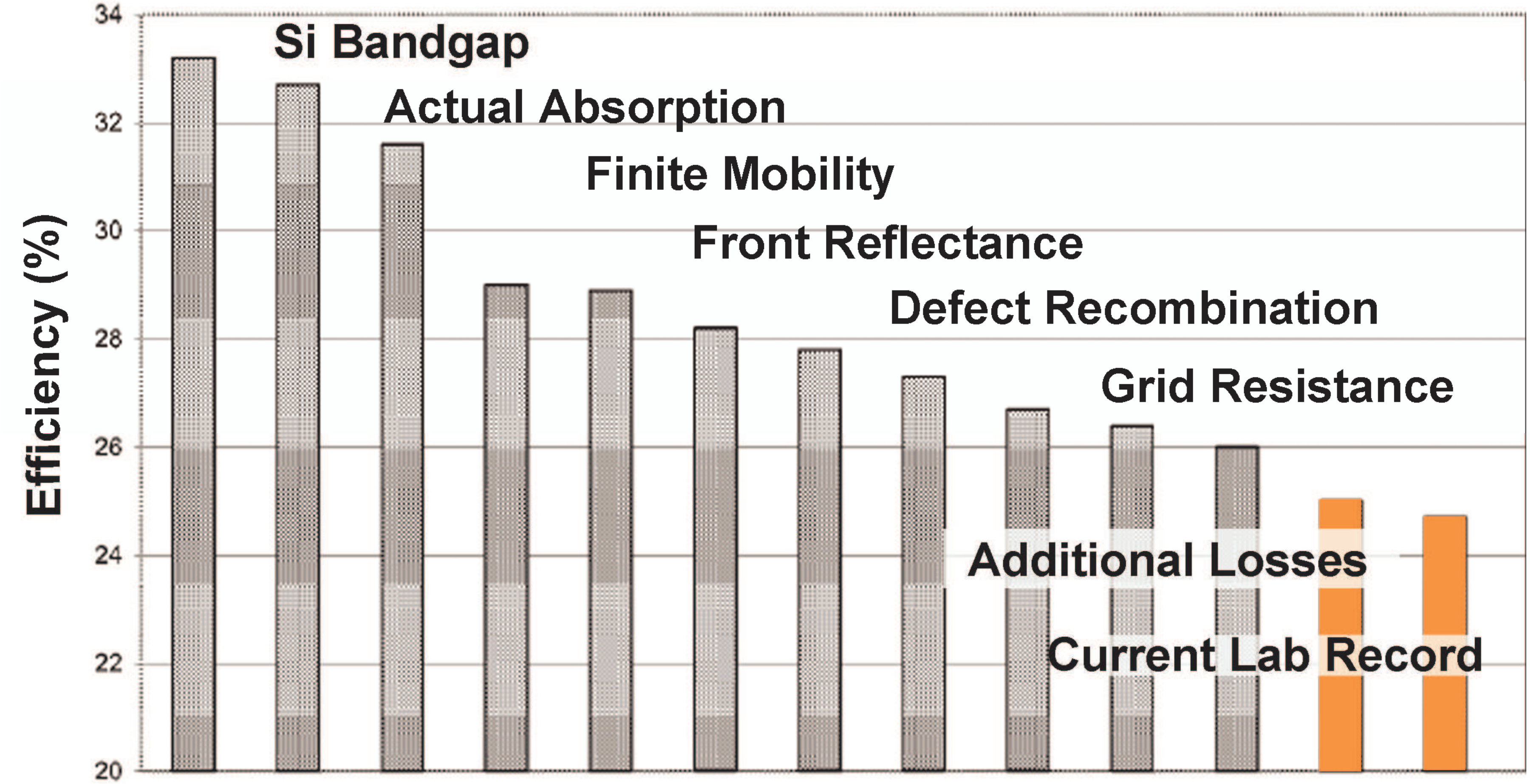
Under low level injection, p-type Si:

$$\text{Recombination rate}: \; R=\frac{n}{\tau_{no}}$$

$$\frac{j_L}{qW_b}=\frac{n_o p_o}{N_b \tau_{no}}\exp[\frac{qV_{oc}}{kT}]$$

$$V_{oc}=(\frac{kT}{q})\ln[\frac{j_L N_b \tau_{no}}{q n_o p_o W_b}]$$

Factors Limiting Silicon Solar Cell Efficiency



Must work towards lower cost!

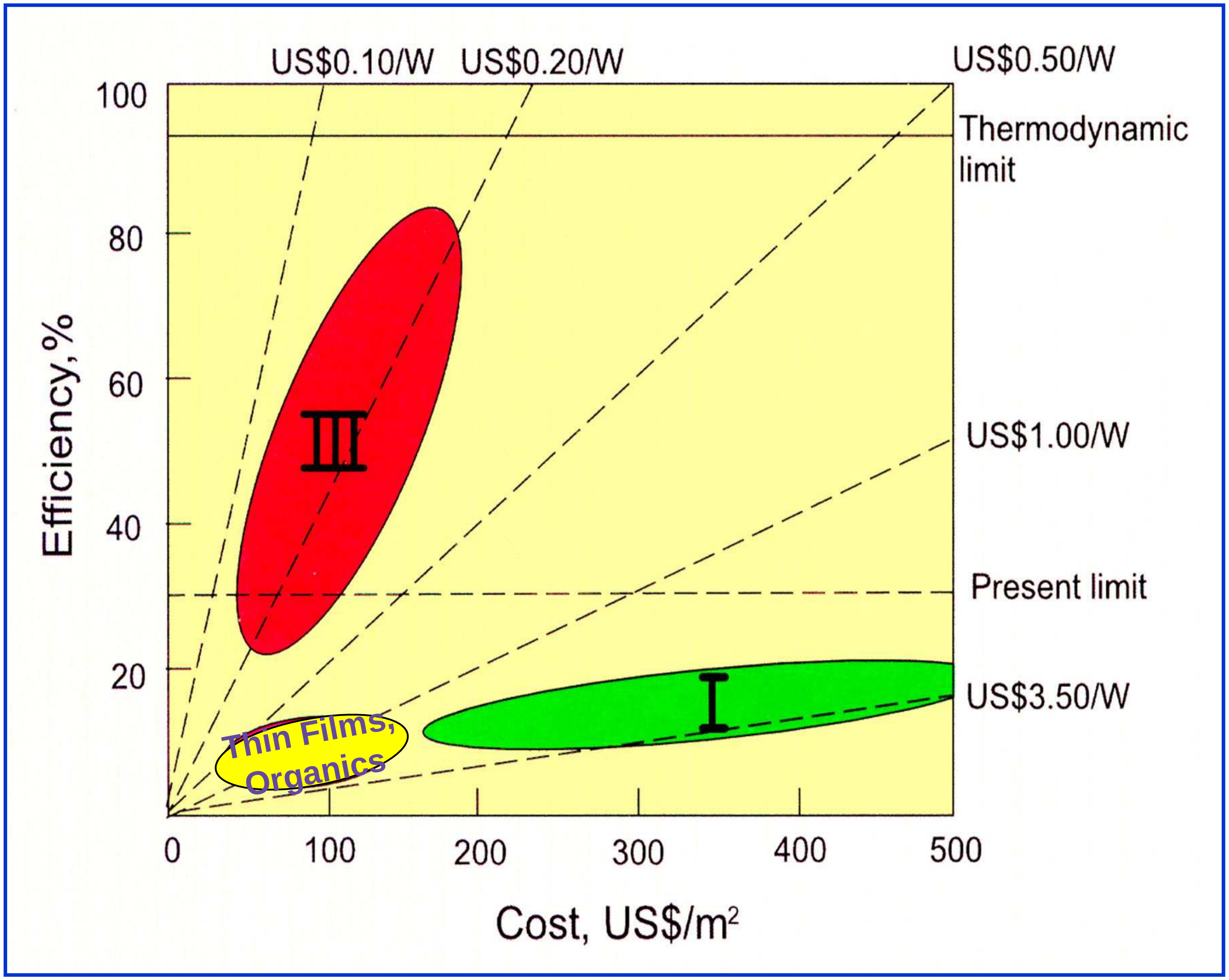
Adapted from R.M. Swanson, *Proceedings of the 31st IEEE Meeting* (2005) p. 889.

Taxonomy of Si Photovoltaics

Si Classification	Si Thickness	Efficiency (%)	Source
Crystalline	260 µm	24.7±0.5	UNSW PERL
Multicrystalline	99 µm	20.3±0.5	FhG-ISE
Thin-film Transfer	45 µm	16.6±0.4	University of Stuttgart
Polycrystalline	2-10 µm	9.5±0.5	Sanyo
Nanocrystalline	2 µm	10.1±0.2	Kaneka
Amorphous	i-layer ~250 nm	9.5±0.3	U. Neuchatel

M.A. Green, K. Emery, D. L. King, Y. Hisikawa, W. Warta. *Prog. Photovolt: Res. Appl.* **14**,45 (2006).

Cost/Efficiency of Photovoltaic Technology



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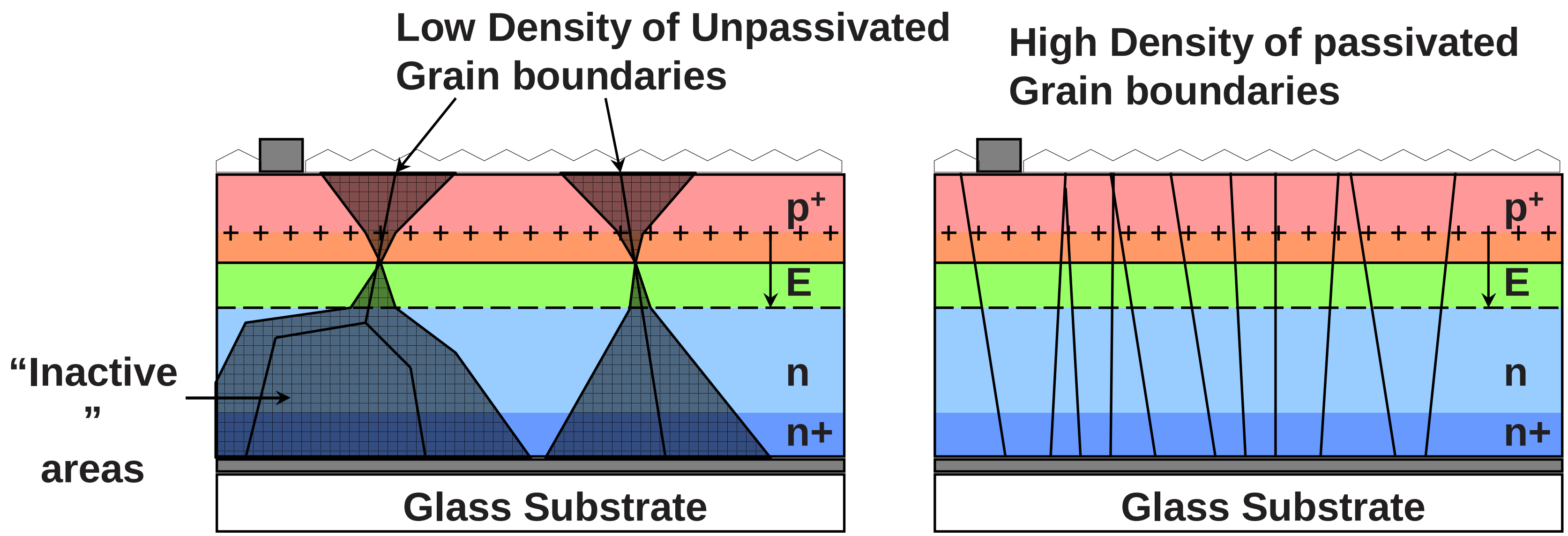
H. Atwater Caltech

Thin Film Solar Cells

Materials: CdTe, $CuIn_xGa_{1-x}Se_2$, poly-Si, amorphous Si

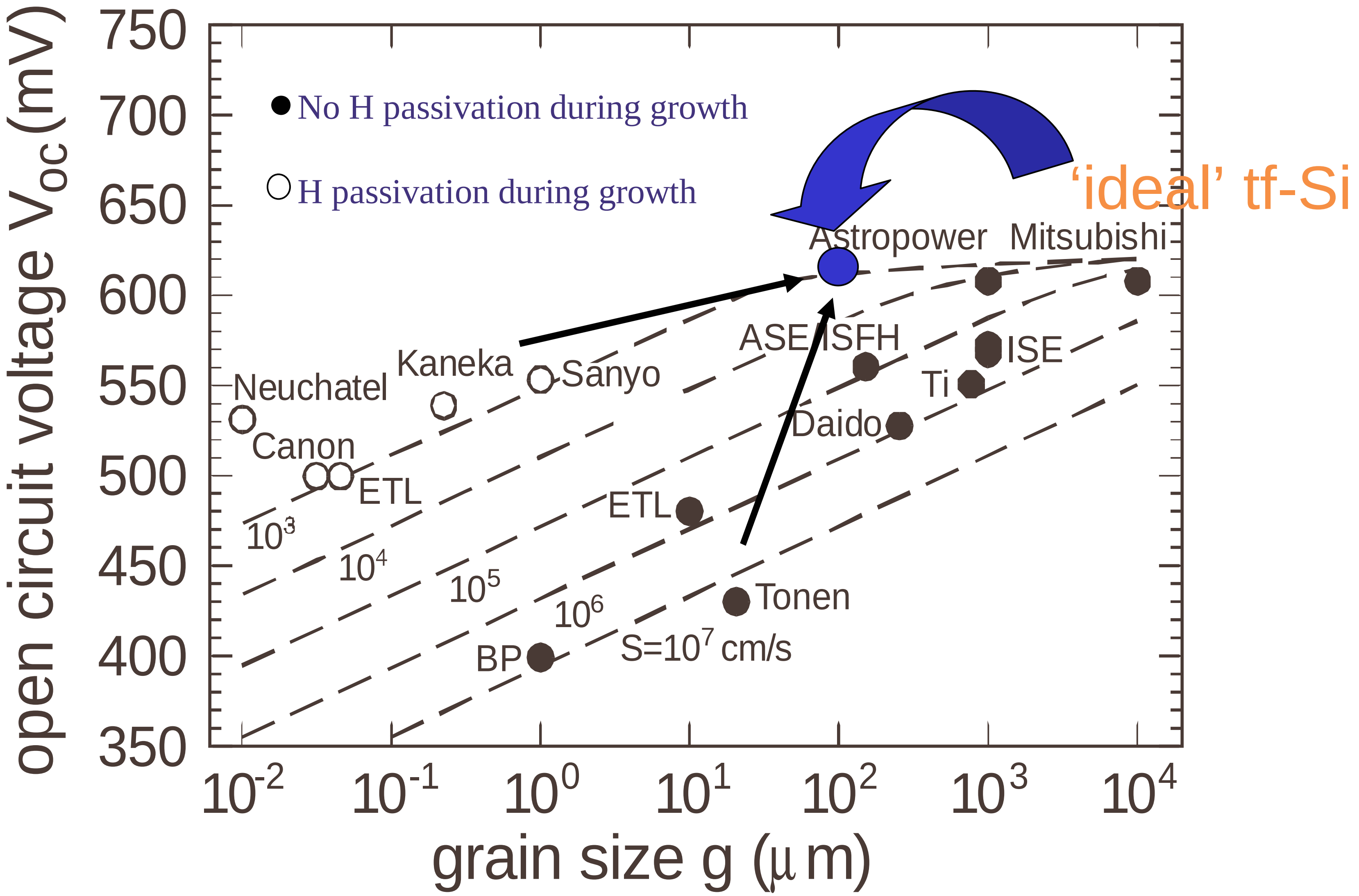


Low Density of Unpassivated Grain boundaries

High Density of passivated Grain boundaries

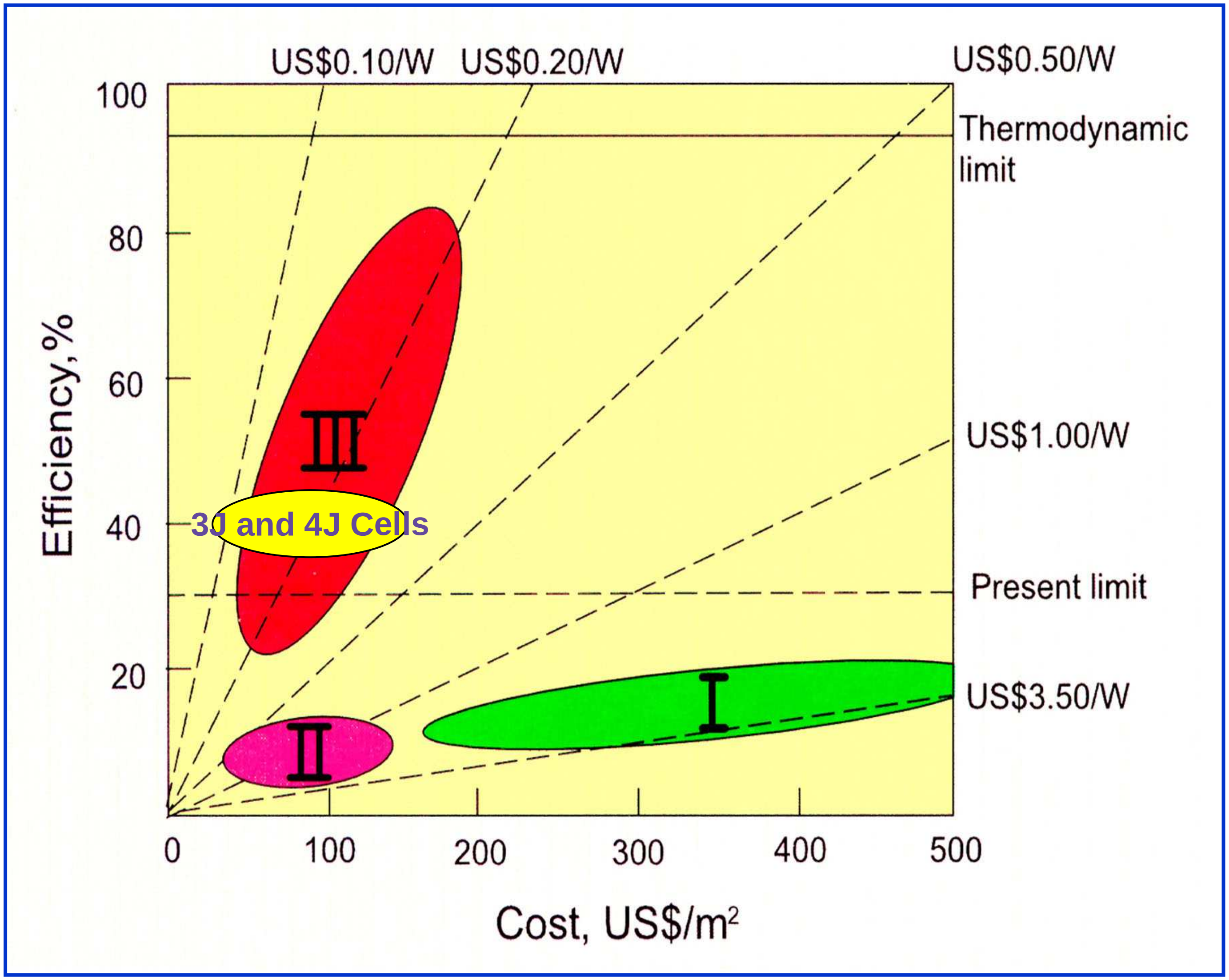
“Inactive” areas

Poly-Si: Open Circuit Voltage vs. Grain Size



Jurgen Werner

Cost/Efficiency of Photovoltaic Technology



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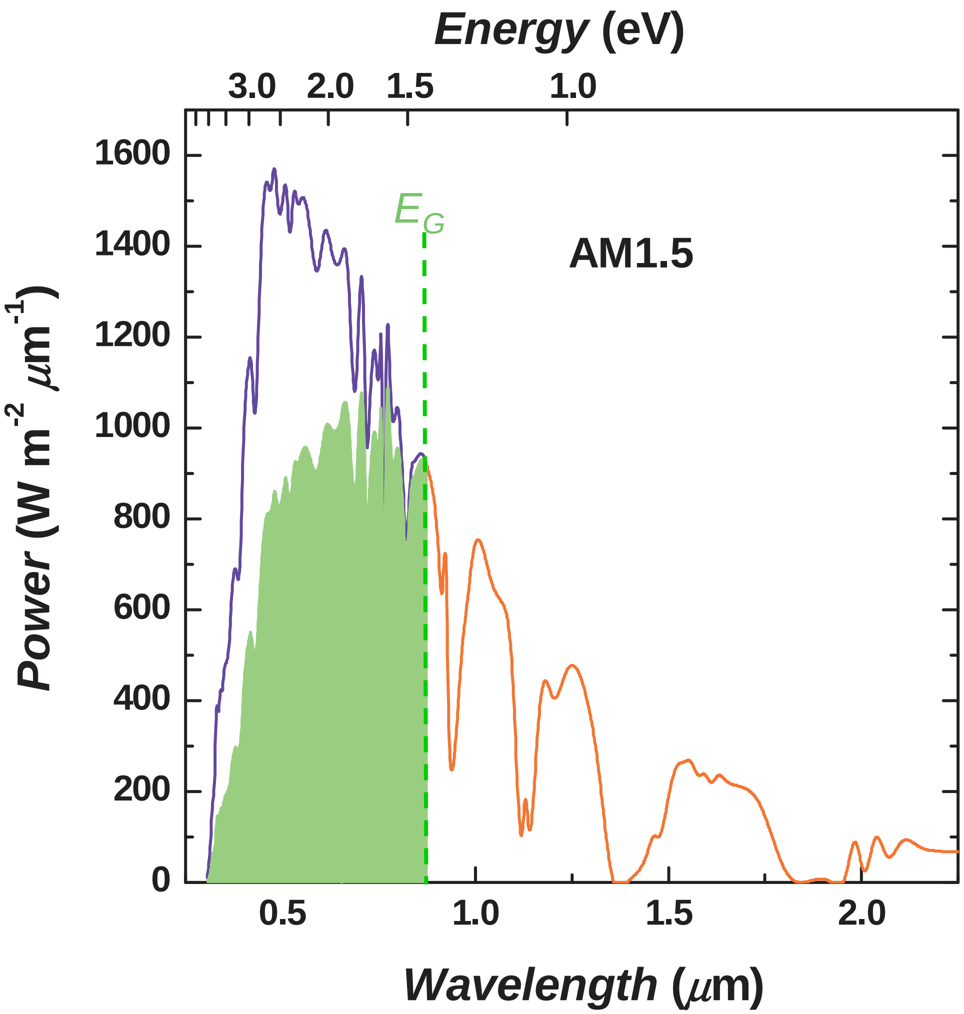
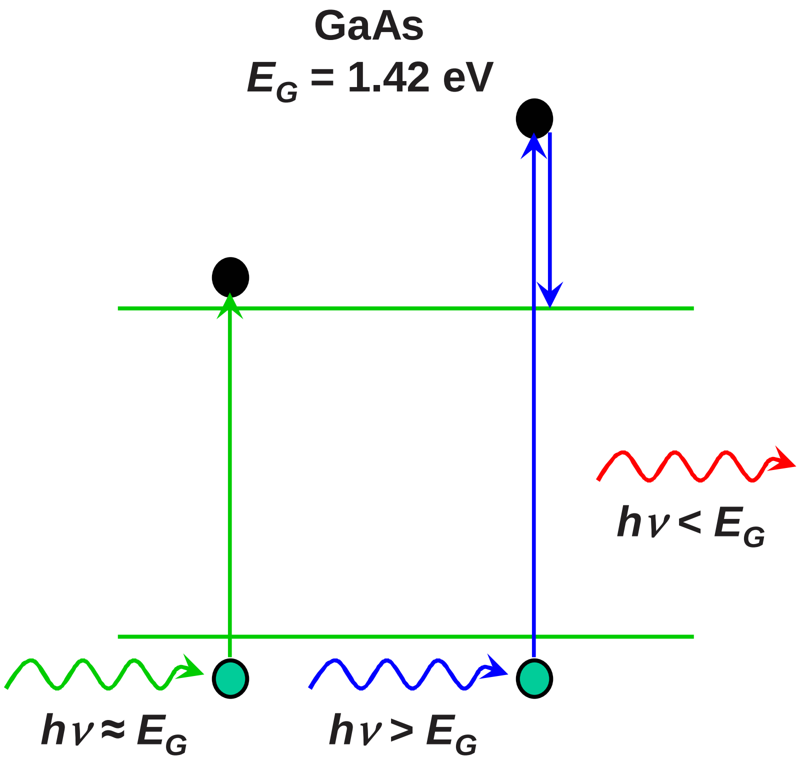
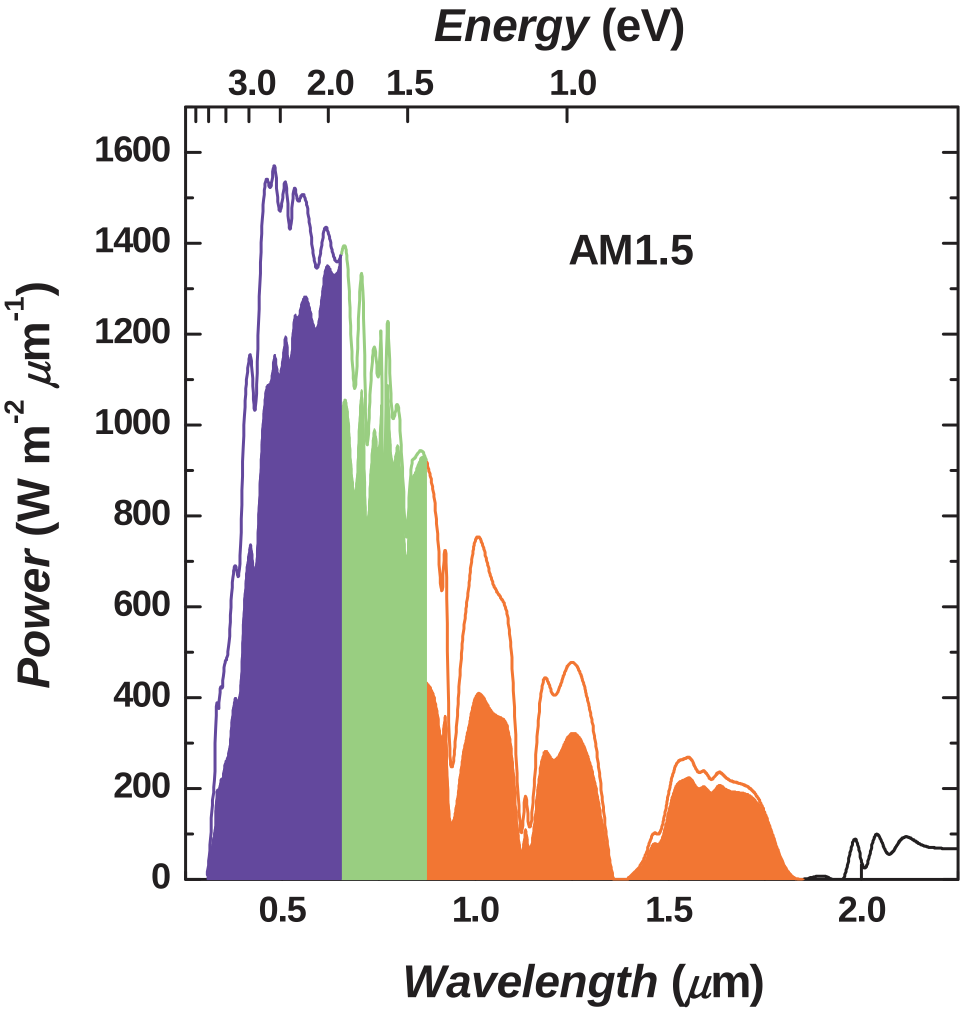
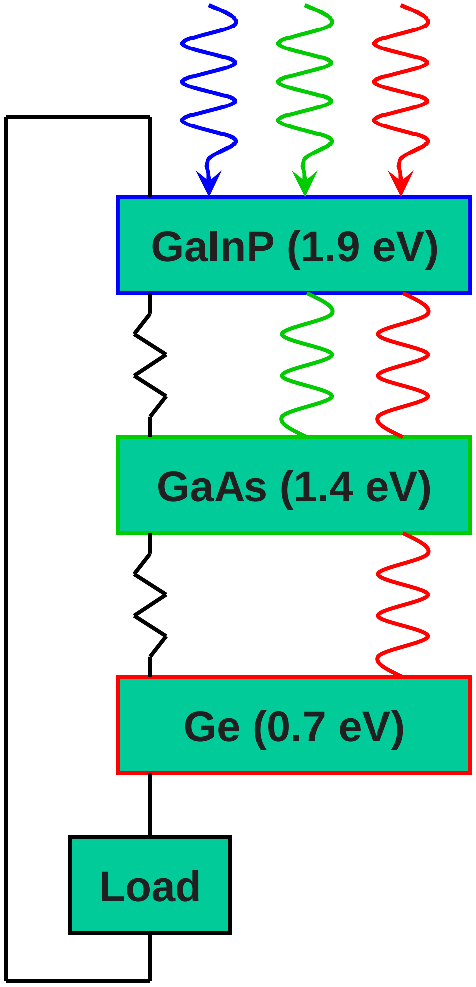
Power Generation Limit in a (GaAs) Single Junction Cell





Power Generation Limit in a GaInP/GaAs/Ge Triple Junction Cell





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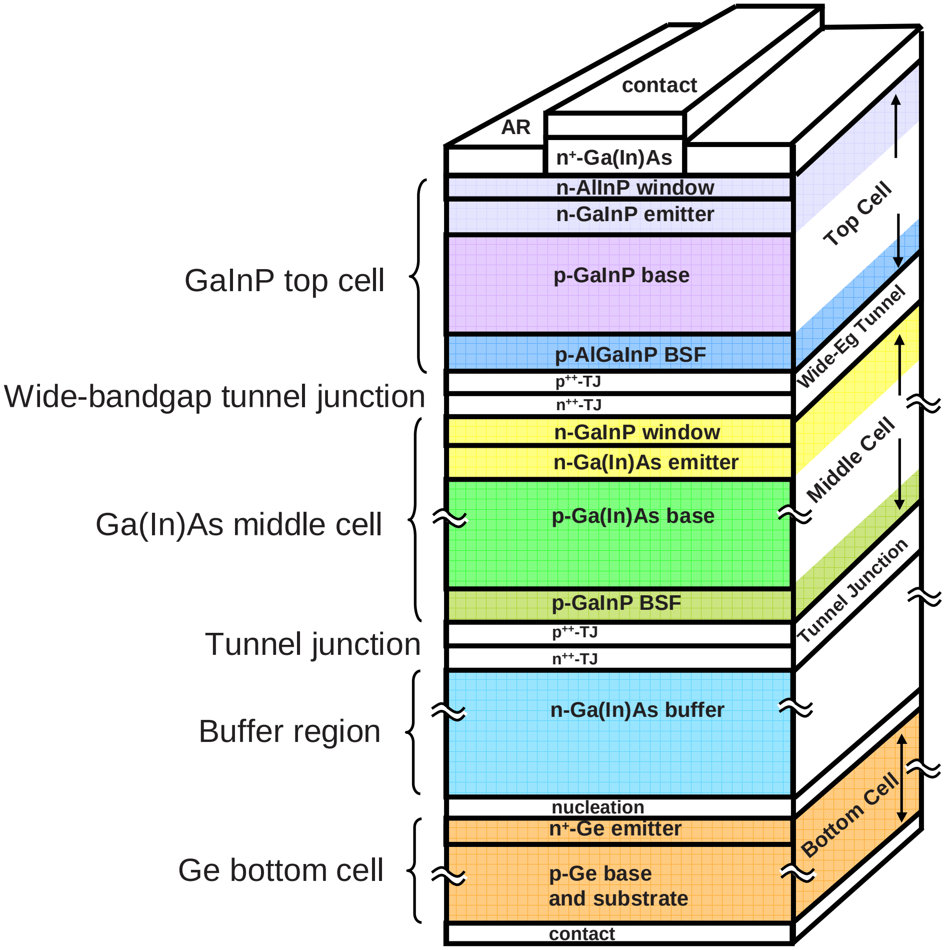
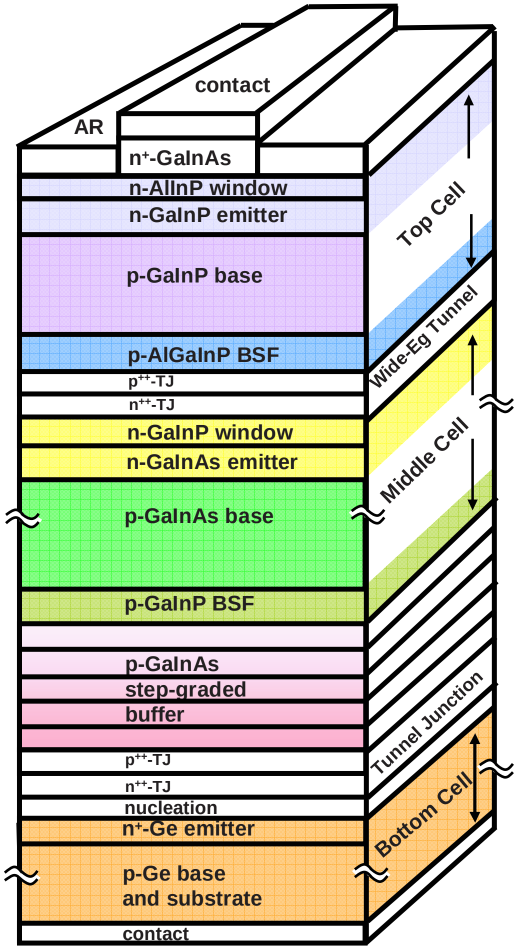
Lattice Matched and Metamorphic 3-Junction Cell Cross-Sections



Lattice-Matched (LM)



Lattice-Mismatched or Metamorphic (MM)

Richard King

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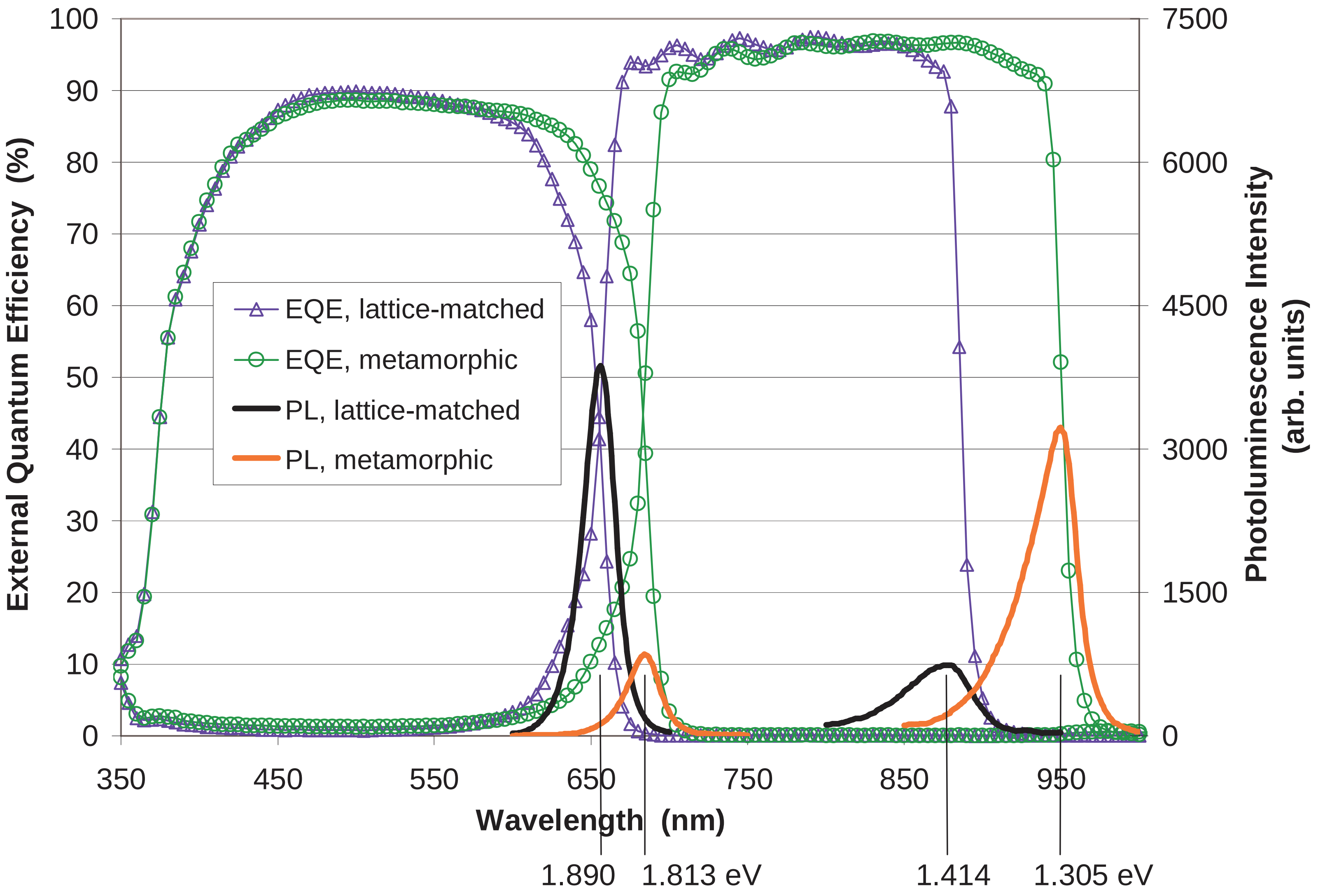
EQE and PL of Subcells Matched to 1%-In and 8%-In GaInAs



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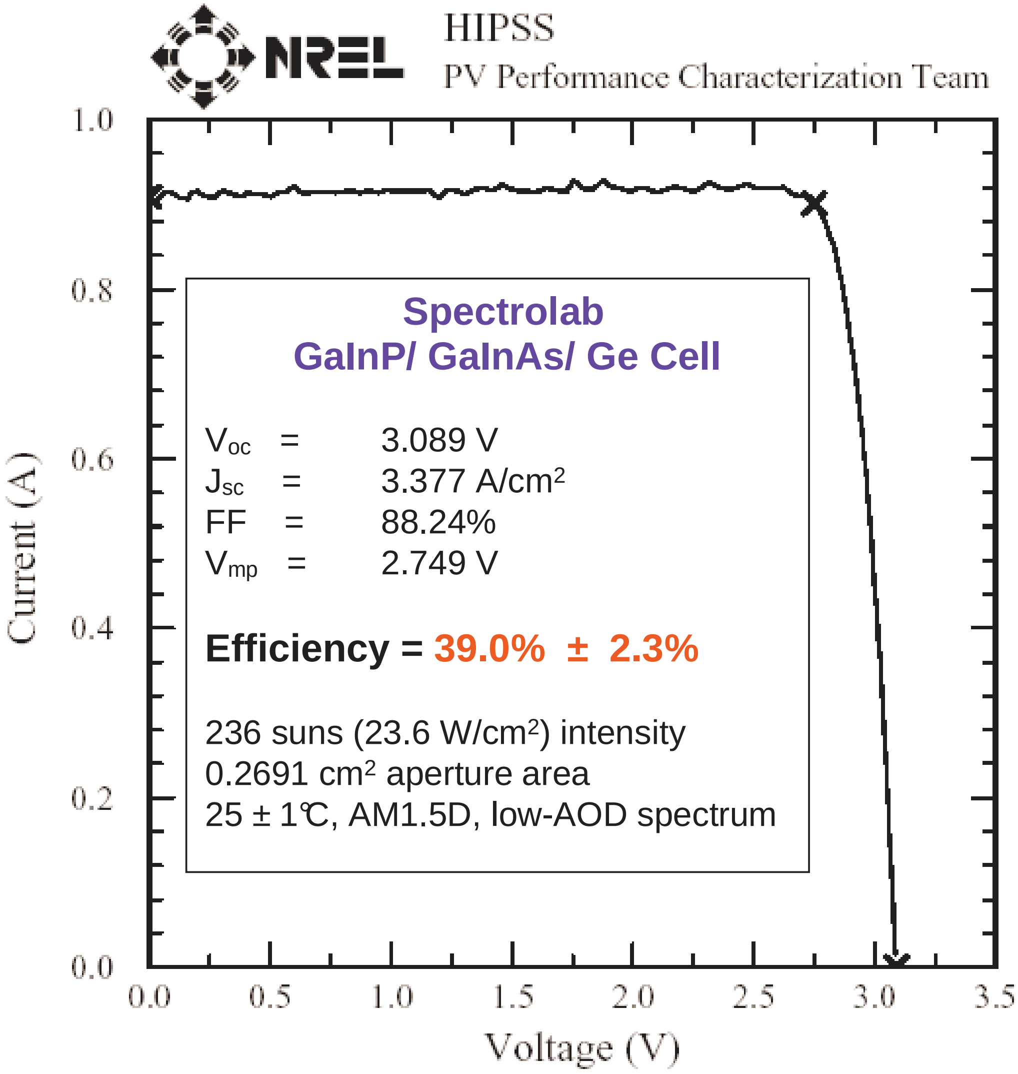
Record Efficiency Solar Cell

- AM1.5 Direct, Low-AOD standard spectrum
- 0.269 cm^2 aperture area
- **39.0% record efficiency,** 236 suns, 25℃



Spectrolab
GaInP/ GaInAs/ Ge Cell

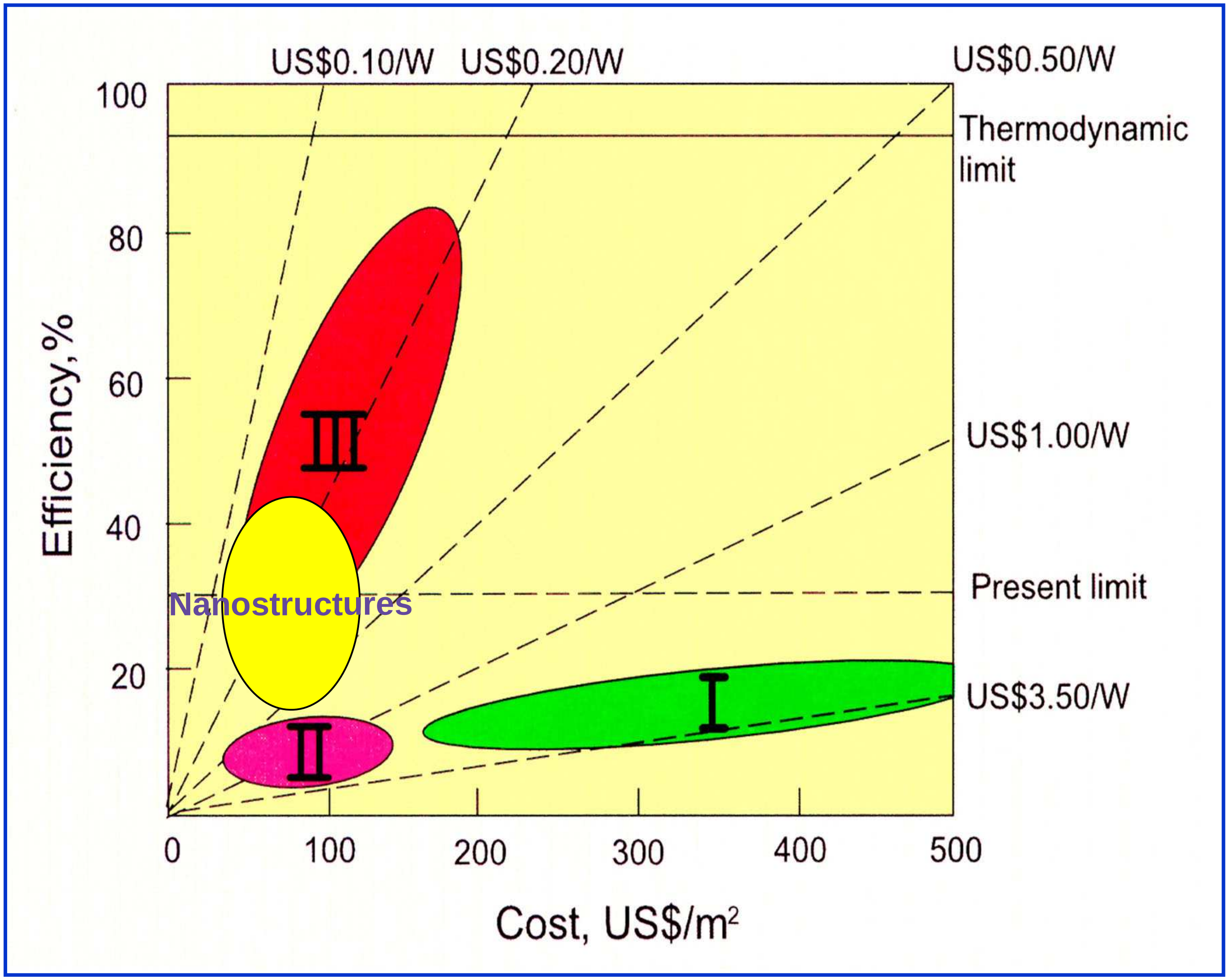
V_{oc} = 3.089 V
J_{sc} = 3.377 A/cm^2
FF = 88.24%
V_{mp} = 2.749 V

Efficiency = 39.0% ± 2.3%

236 suns (23.6 W/cm^2) intensity
0.2691 cm^2 aperture area
25 ± 1℃, AM1.5D, low-AOD spectrum

Richard King

Cost/Efficiency of Photovoltaic Technology



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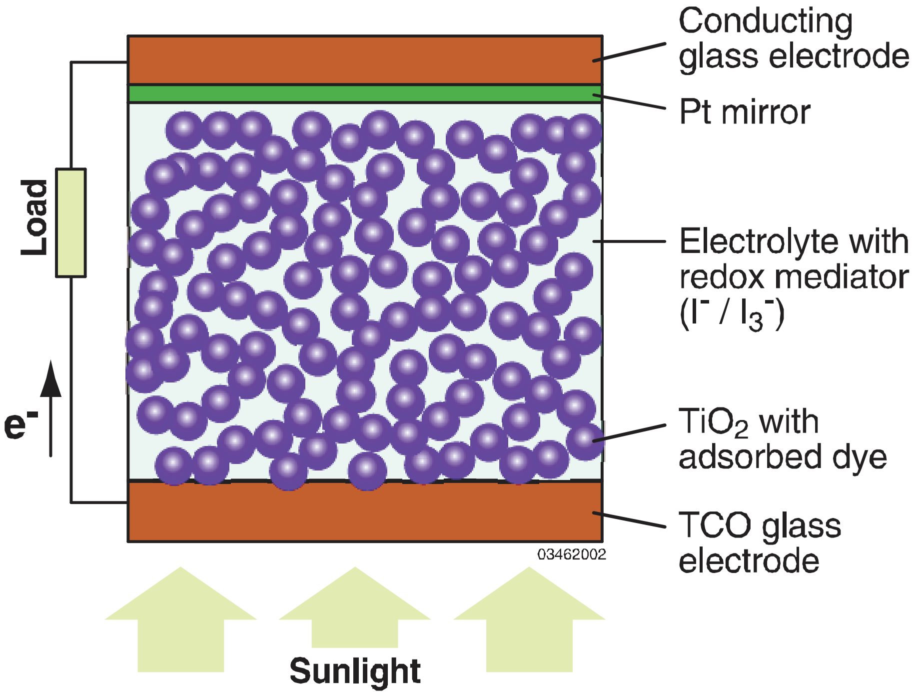
Mesocopic Injection Dye-Senstized Solar Cells

- Electron-hole pairs generated as excitons in a dye absorber (Ru-bpy)
- Excitons diffuse to TiO_2 interface
- Excitons dissociated into electrons and holes
- Electrons injected in TiO_2
- Holes injected into liquid electrolyte
- Potentially low costs for materials and processing

Dye Sensitized Solar Cell



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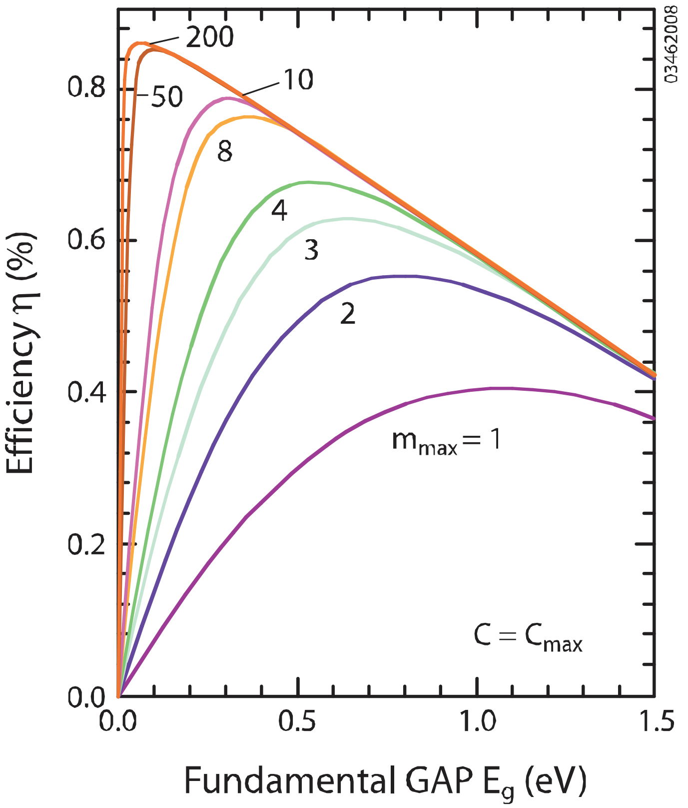
Christiana Honsberg

Multiple Exciton Generation Solar Cells

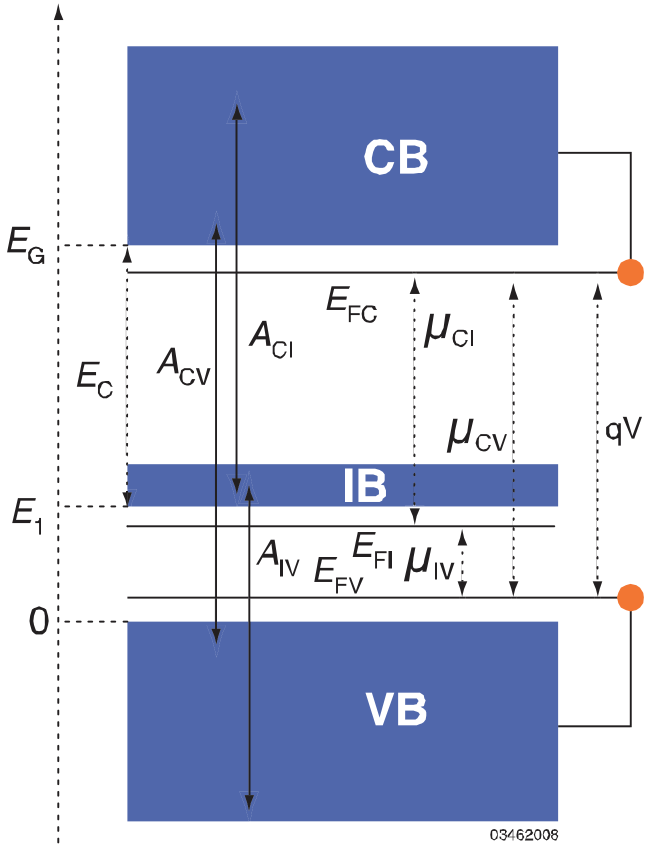
- **Electron and hole created simultaneously**
- **Hot electron and hole create multiple (m) electron-hole pairs through Auger emission and absorption instead of thermalizing**
- **Need materials (e.g., quantum dots) susceptible to creation of multiple Auger electron-hole pairs**
- **Recently report by NREL and Los Alamos …3 carriers for 1 photon in PbSe**



H. Queisser et al., Max Planck Inst.,
Solar Energy Materials and Solar Cells, 41/42, 1996

Intermediate-Band Solar Cells

- Multiple transition paths via intermediate band
- Theoretical efficiency advantages over equivalent multijunction cells
- Can simplify and augment multijunction solar cell efficiencies



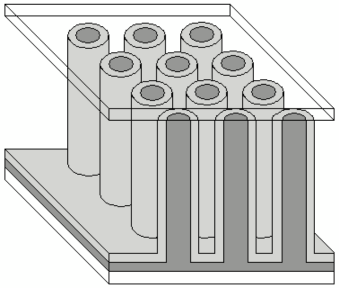
Band diagram of a solar cell with an intermediate band.

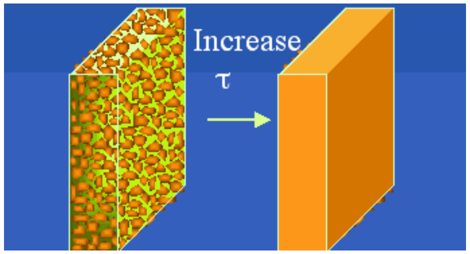
A. Luque et al., U. Politecnica de Madrid
Phys. Rev. Lett., 78, No. 26, 1997

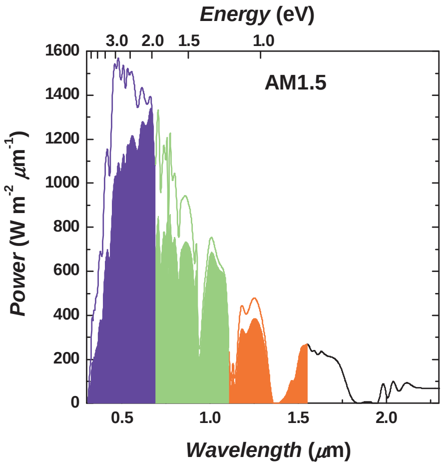
Nanowire Photovoltaic Cells

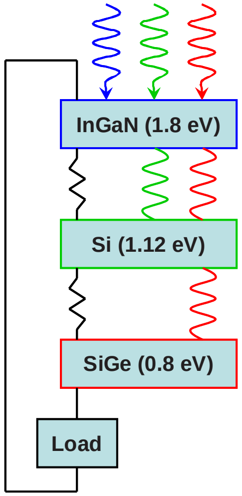
Emergent Concepts for Photovoltaic Nanostructures:

1. Nanowires are a significant opportunity: carrier collection at low diffusion length – ‘improve’ poor quality materials
2. Passivation is essential in nanostructures
3. Multijunction architecture highly desirable for efficiency
4. Sheet Processing: Large-area low-cost reliable processing



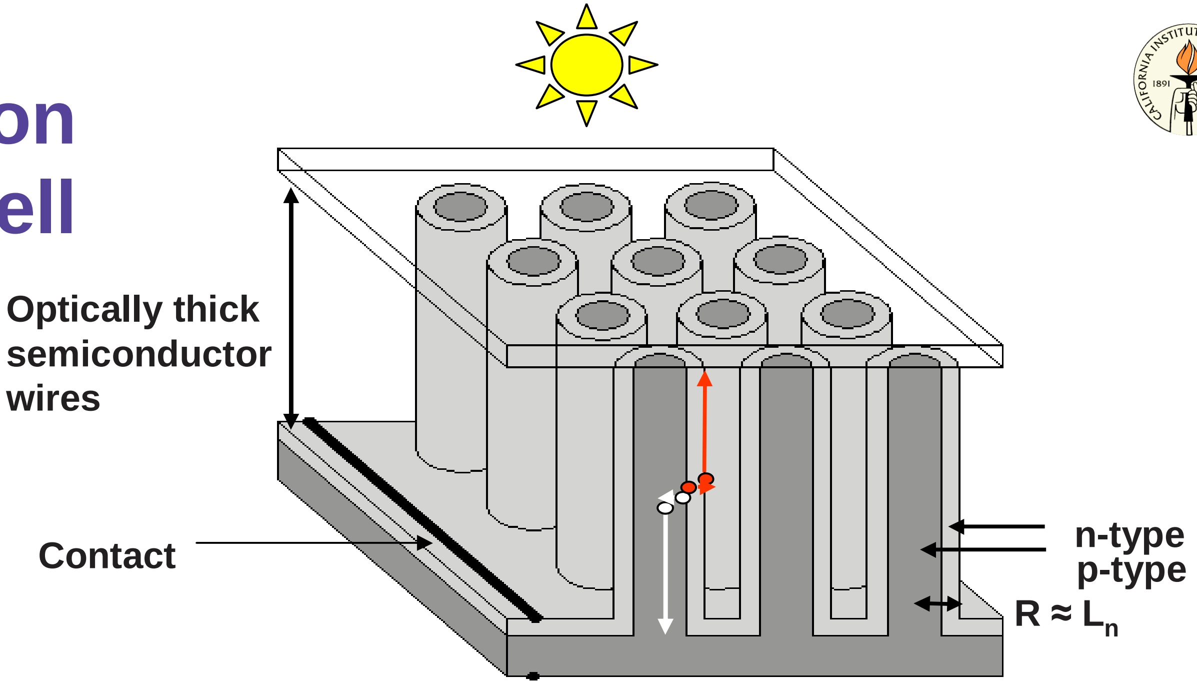






Radial p-n junction nanowire solar cell

B.M. Kayes, et.al.,
J. Appl. Phys. 2005



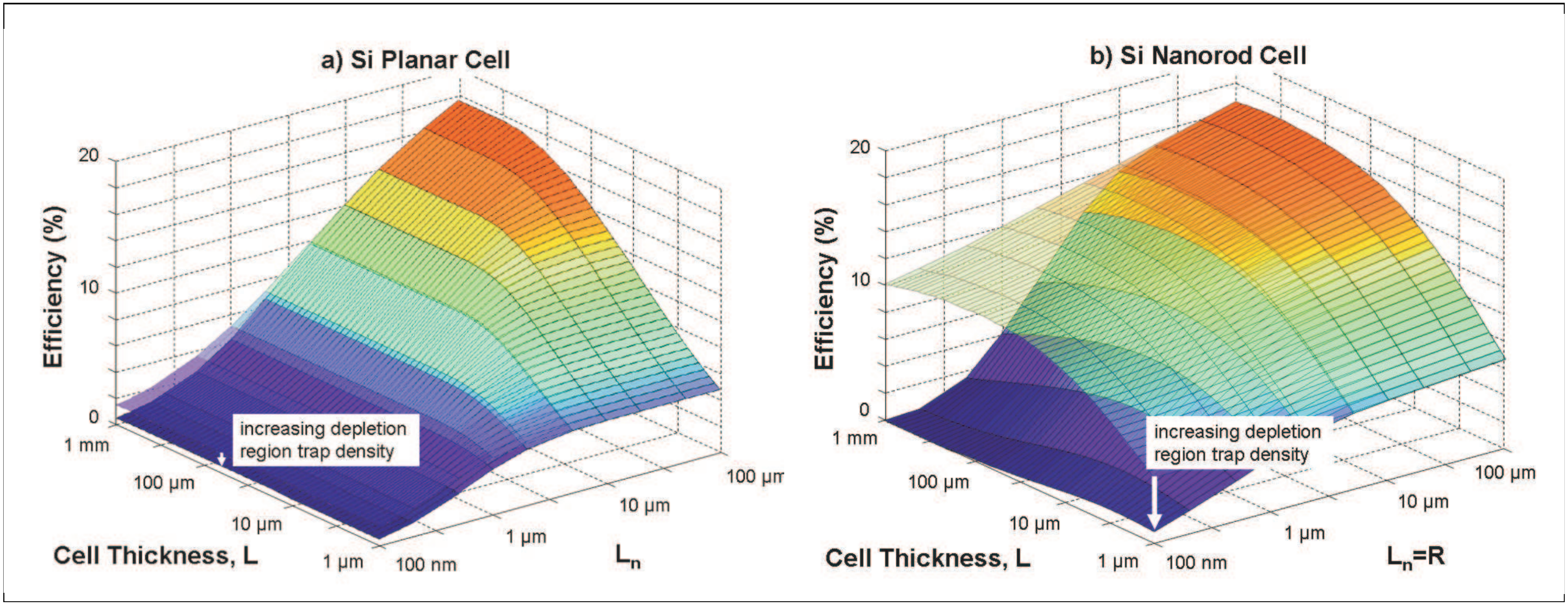
Optically thick semiconductor wires

Contact

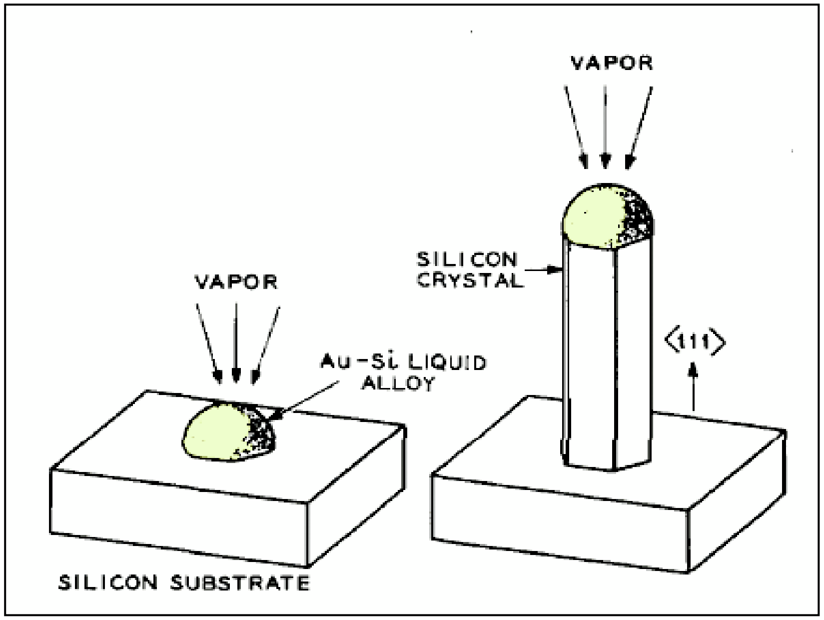
n-type

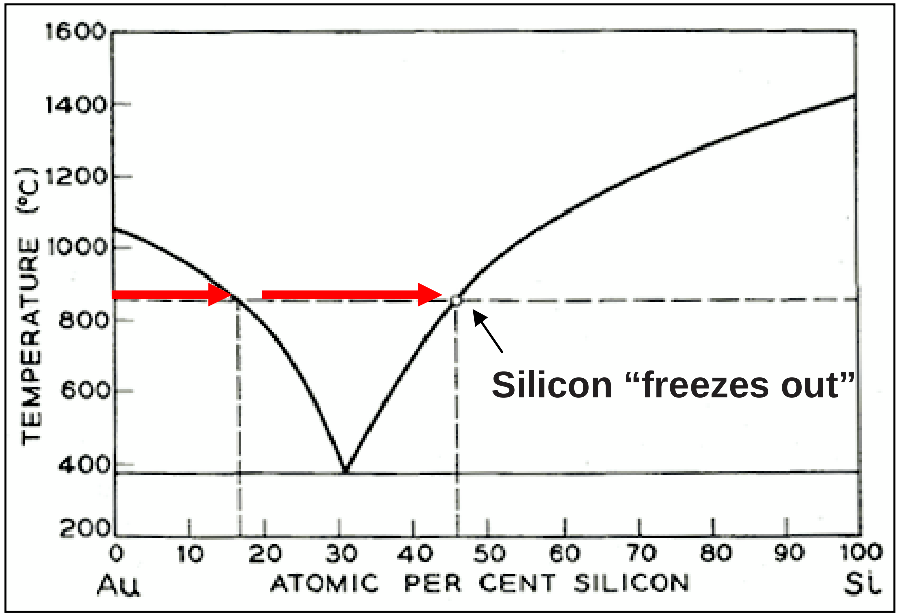
p-type

$R \approx L_n$

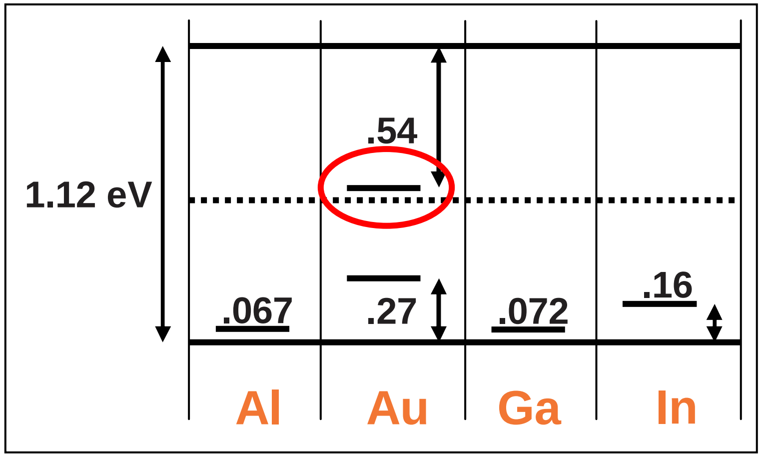


Vapor-Liquid-Solid (VLS) Growth



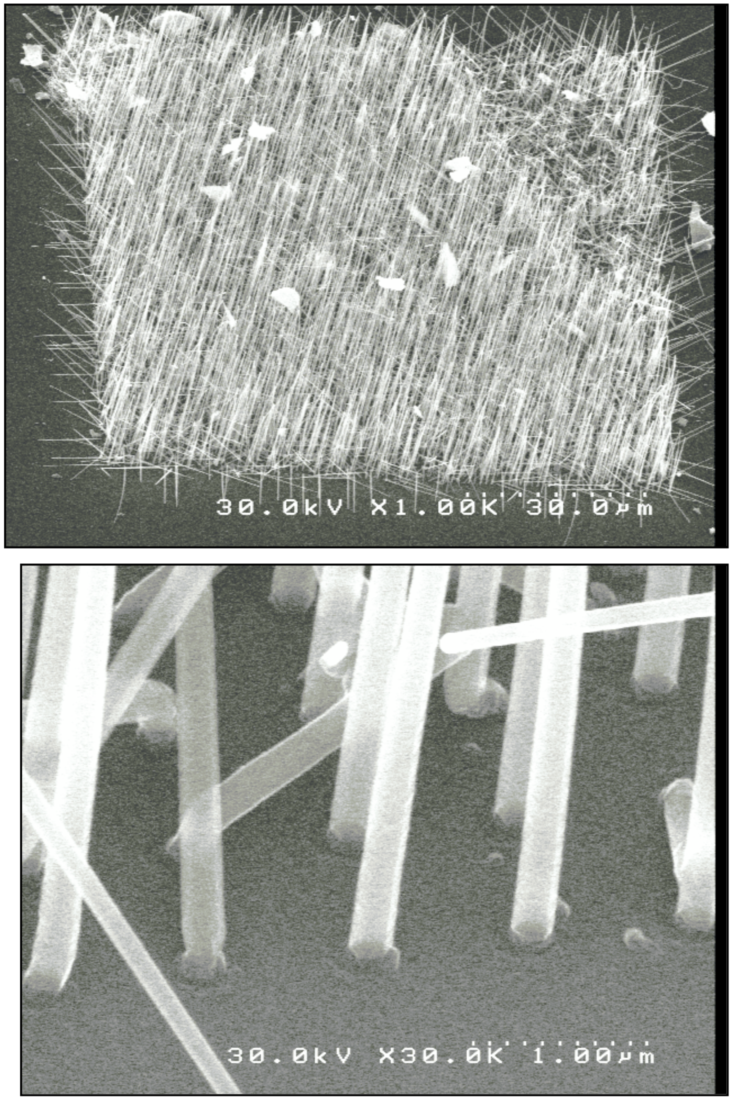


Photovoltaics may require use of alternative VLS catalysts

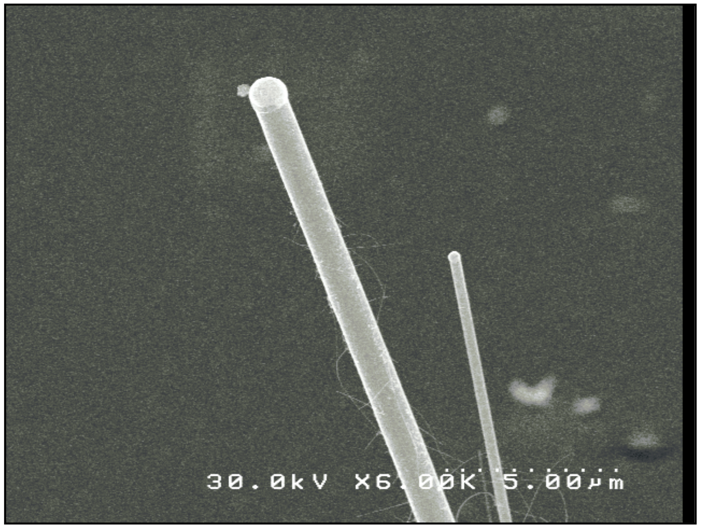


R.S. Wagner and W.C. Ellis, Appl. Phys. Lett. 4, 89-90 (1964)
R.S. Wagner and W.C. Ellis, Trans. Metall. Soc. AIME 233, 1053-1064 (1965)
S.M. Sze *Physics of semiconductor devices* (New York, Wiley-Interscience, 1969)

Vapor-Liquid Solid Synthesis of Si nanowire arrays

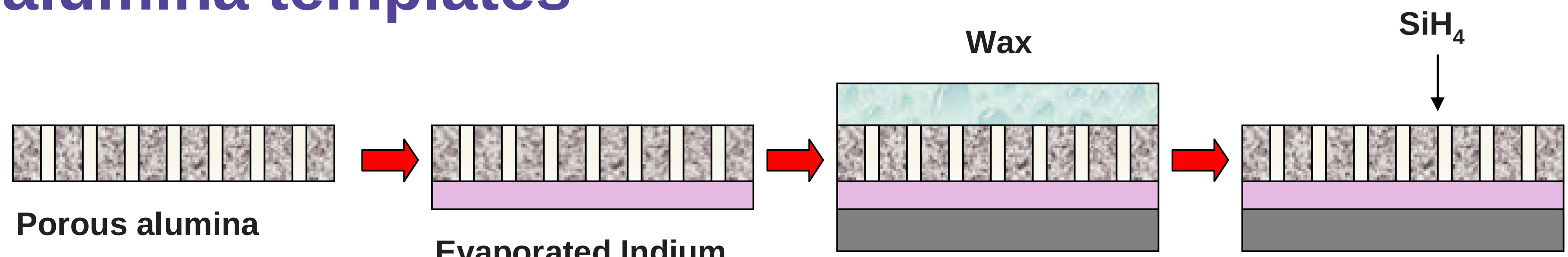


Au catalyst



In catalyst

VLS nanowire growth in porous alumina templates



Wax

SiH_4

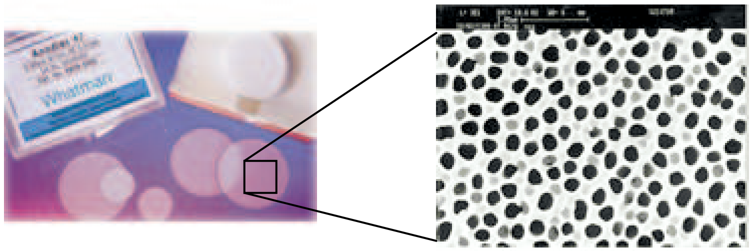
Porous alumina

Evaporated Indium

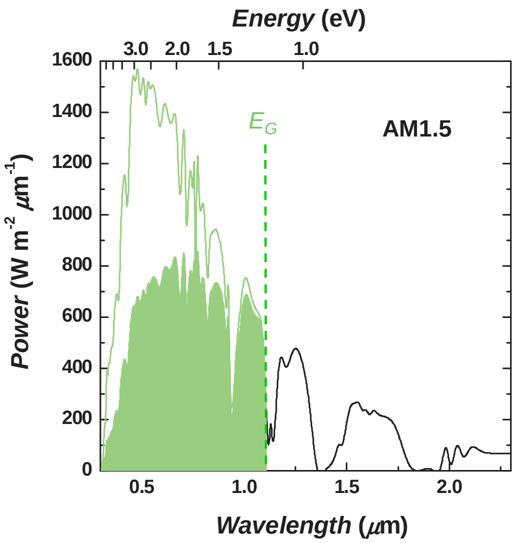
Electrodeposited Nickel

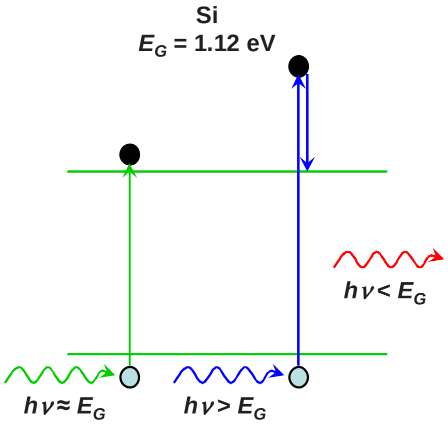
After dissolution of the alumina membrane:

In catalyst:



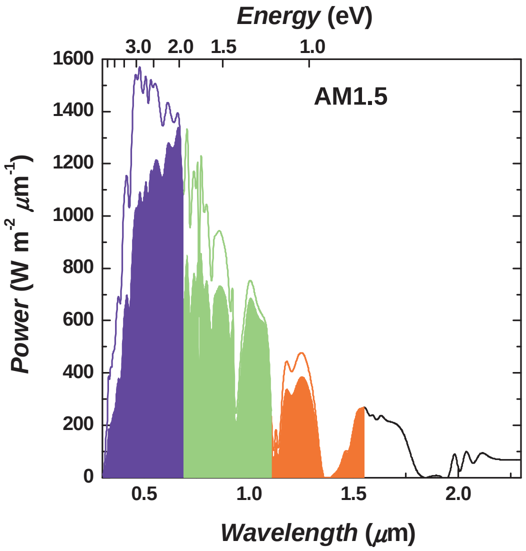
Multijunction Nanowires

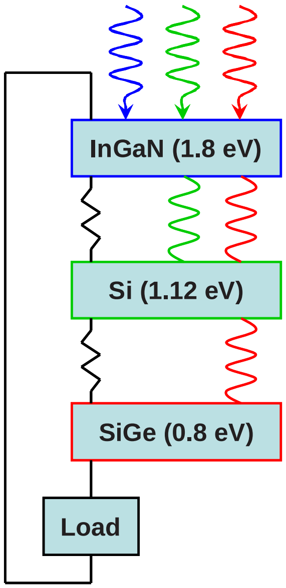




Si Homojunction

$\mathbf{In_xGa_{1-x}N/Si}/\mathrm{Si_xGe_{1-x}}$
Heterojunction





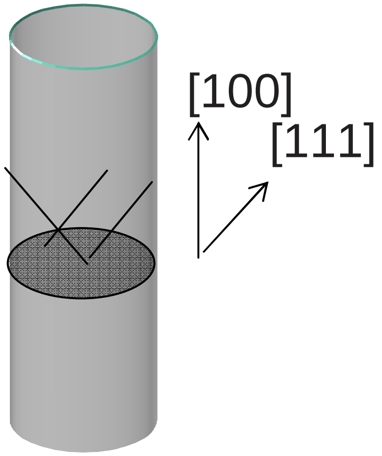
Multijunction Nanowires

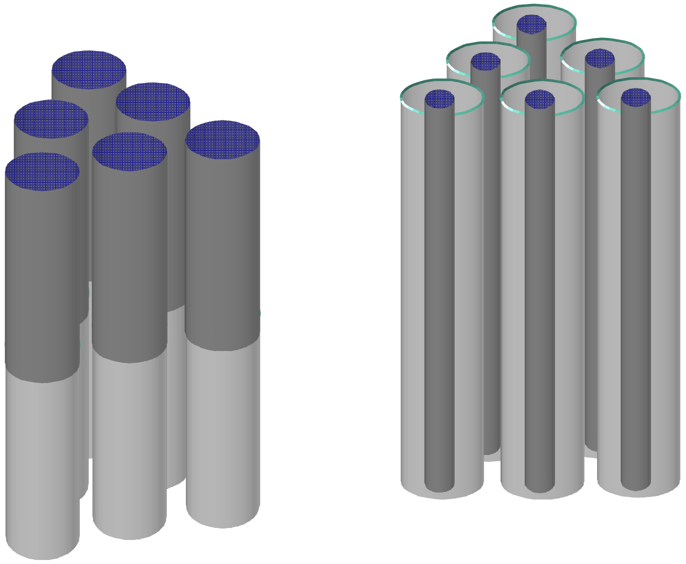
Nanorods are attractive for multijunction PV because:

•Facilitate accommodation of the lattice mismatch between pseudomorphically strained semiconductor materials comprising the heterojunctions structure.

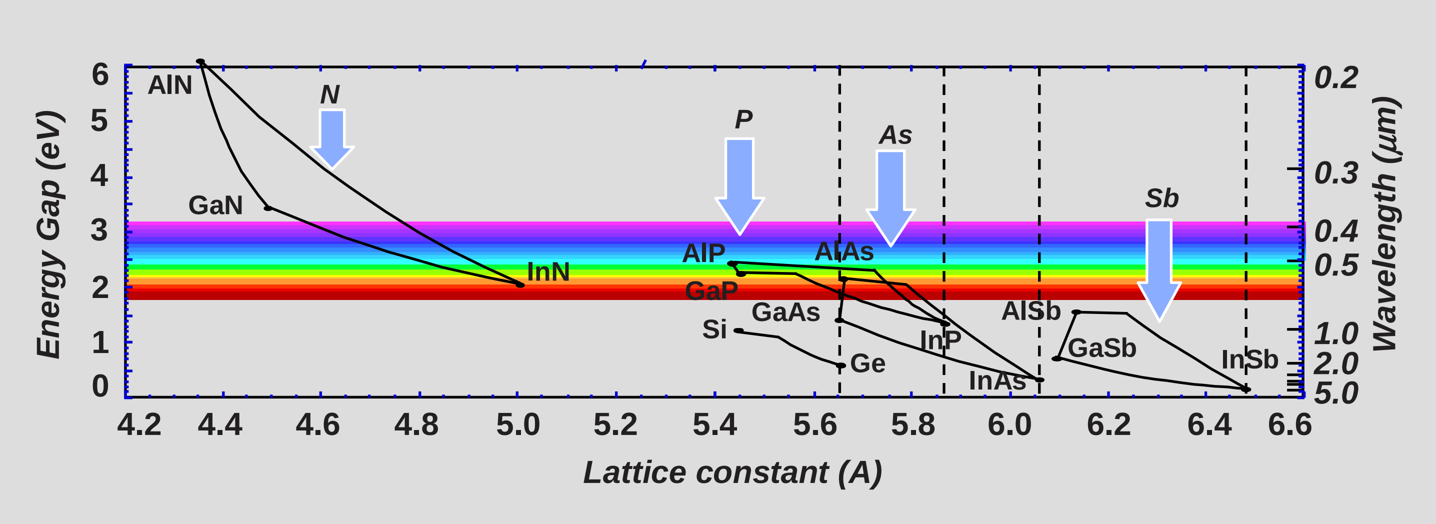
•Force crystallographic defects in strain-relieved dislocated structures to emerge from the rod during growth→ single crystal and defect-free rods except near heterojunction interfaces

•Facilitate carrier collection in either axially-oriented or radially-oriented pn junctions.

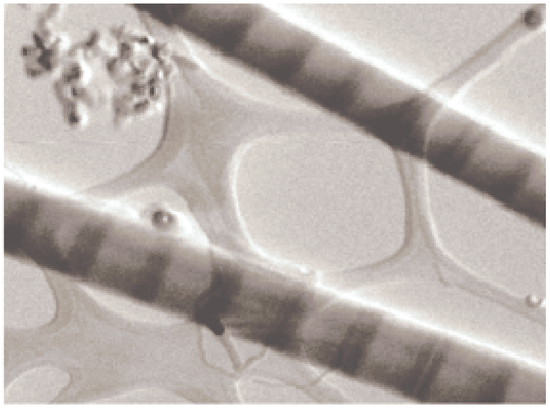




Multijunction Nanowires

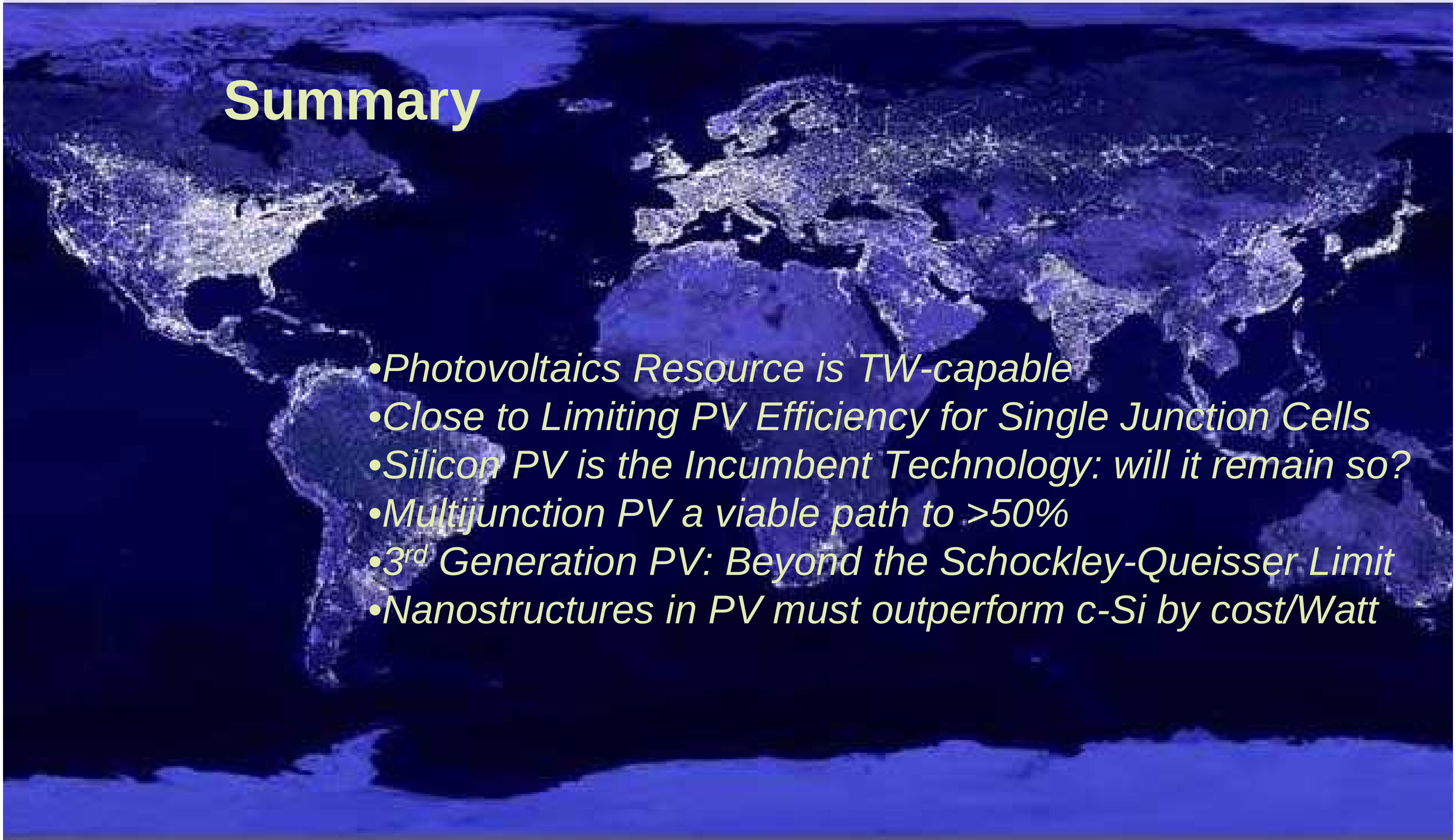


3 junction heterostructure with 1.85 eV bandgap $In_xGa_{1-x}N$ top cell and 0.75 eV Ge_xSi_{1-x} bottom cell; the middle cell is a 1.1 eV Si structure.



Single-Crystalline Si/SiGe Superlattice Nanowires
Yiying Wu, Rong Fan, and Peidong Yang, Nano Lett.; **2002;** *2*(2) pp 83 - 86;

Summary



- Photovoltaics Resource is TW-capable
- Close to Limiting PV Efficiency for Single Junction Cells
- Silicon PV is the Incumbent Technology: will it remain so?
- Multijunction PV a viable path to >50%
- 3rd Generation PV: Beyond the Schockley-Queisser Limit
- Nanostructures in PV must outperform c-Si by cost/Watt