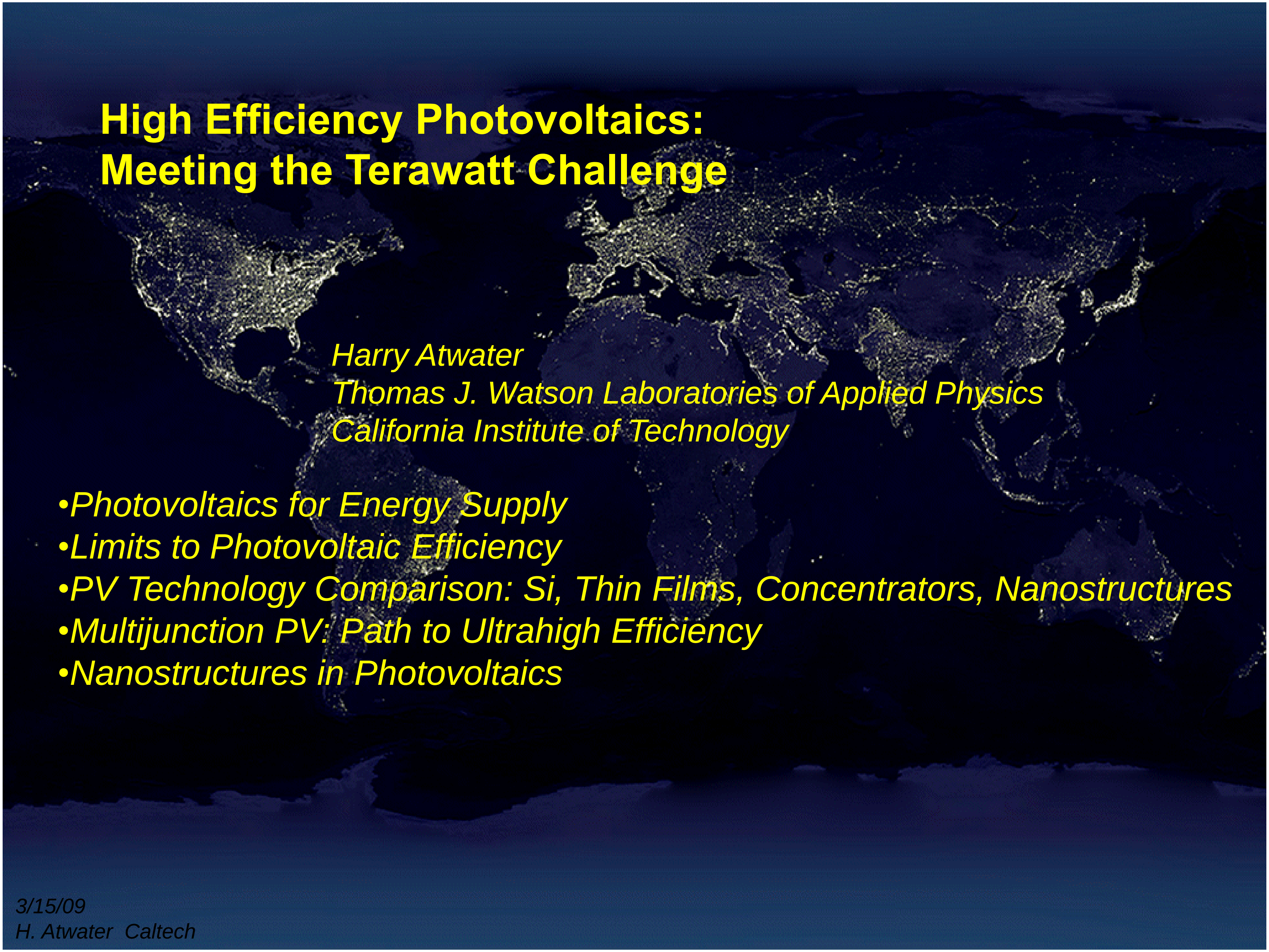


High Efficiency Photovoltaics: Meeting the Terawatt Challenge

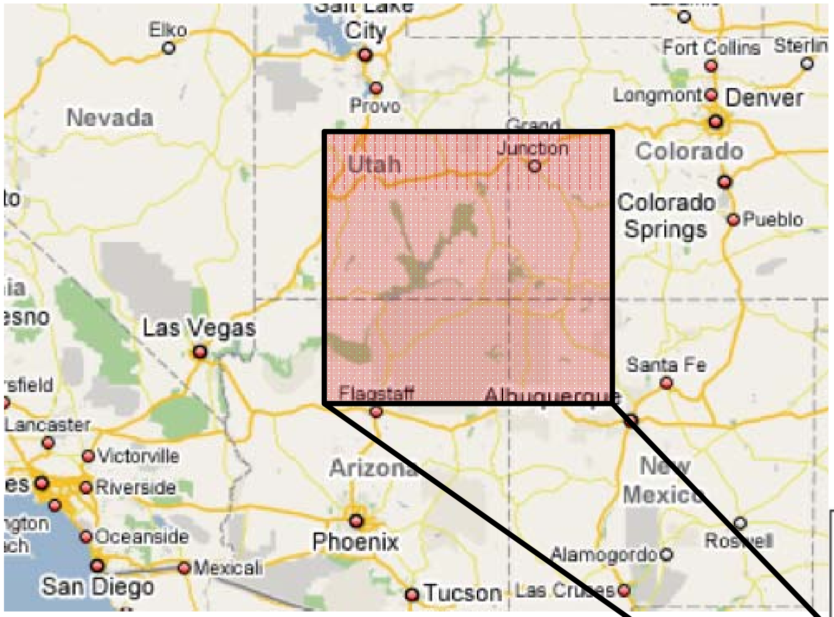
Harry Atwater
Thomas J. Watson Laboratories of Applied Physics
California Institute of Technology

- *Photovoltaics for Energy Supply*
- *Limits to Photovoltaic Efficiency*
- *PV Technology Comparison: Si, Thin Films, Concentrators, Nanostructures*
- *Multijunction PV: Path to Ultrahigh Efficiency*
- *Nanostructures in Photovoltaics*

PV Land Area Requirements

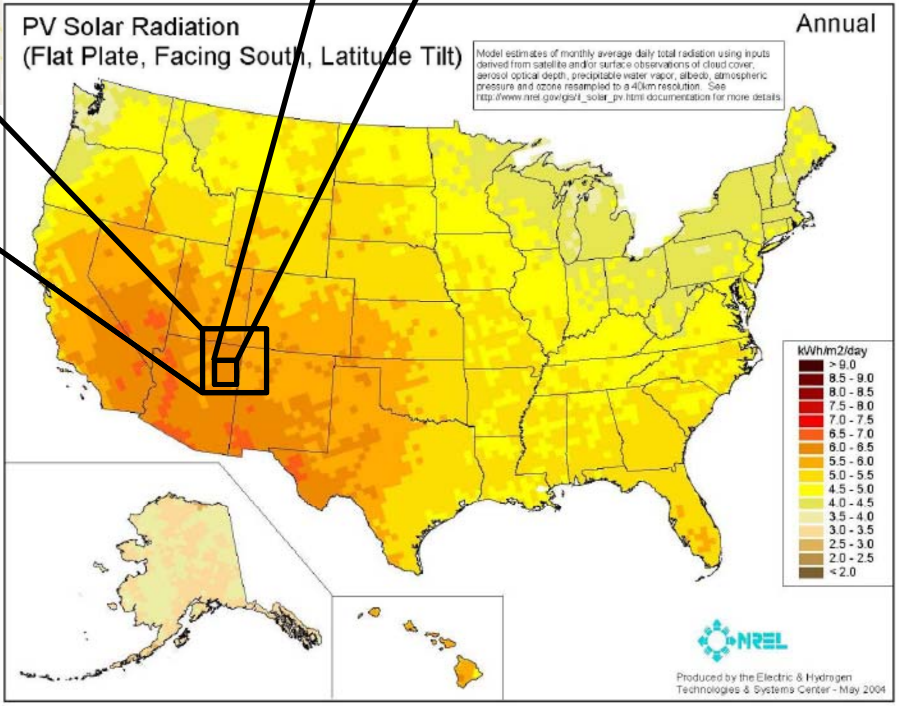
All US Primary Energy

4.1 Terawatts w/ 10% modules



All US Electricity

800 Gigawatts w/ 10% modules



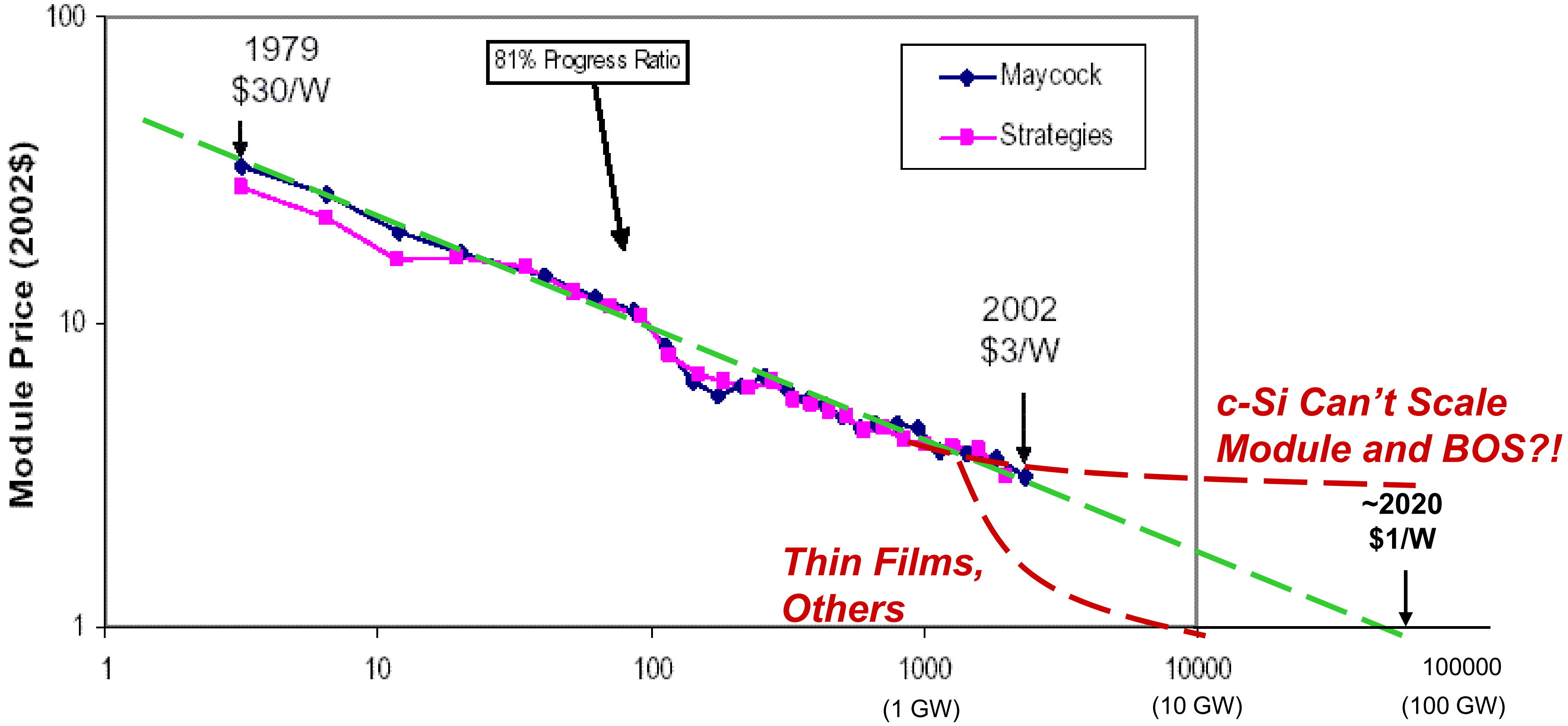
Model estimates of monthly average daily total radiation using inputs derived from satellite and/or surface observations of cloud cover, aerosol optical depth, precipitable water vapor, albedo, atmospheric pressure and ozone resampled to a 40km resolution. See http://www.nrel.gov/gis/il_solar_pv.html documentation for more details.

Produced by the Electric & Hydrogen Technologies & Systems Center - May 2004

3/15/09
H. Atwater Caltech

Crystalline Silicon vs. other Solar Technology

- *Now appears that c-Si can eventually reach DOE cost goals*
- *Thin film modules can get there first, but efficiency limits, materials issues*
- *Innovative and disruptive technologies must have “film-like” cost/area and >20% efficiency*



1979
$30/W

81% Progress Ratio

2002
$3/W

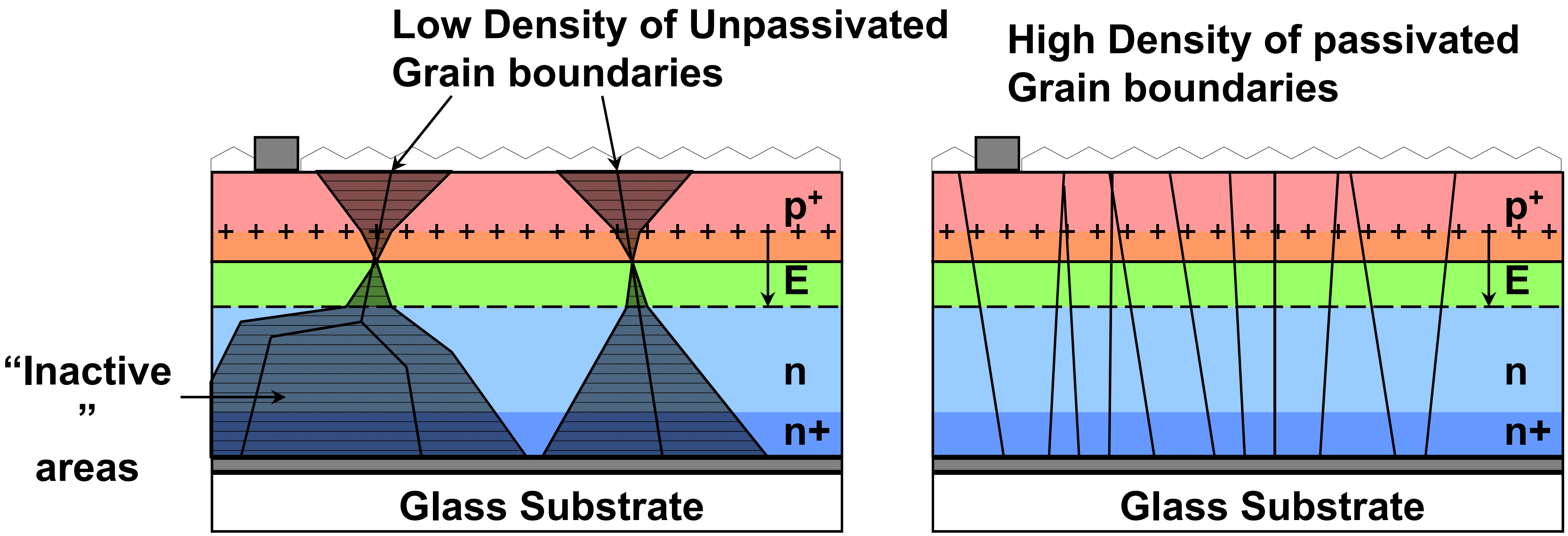
c-Si Can’t Scale Module and BOS?!

~2020 $1/W

Thin Films, Others

Thin Film Solar Cells

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

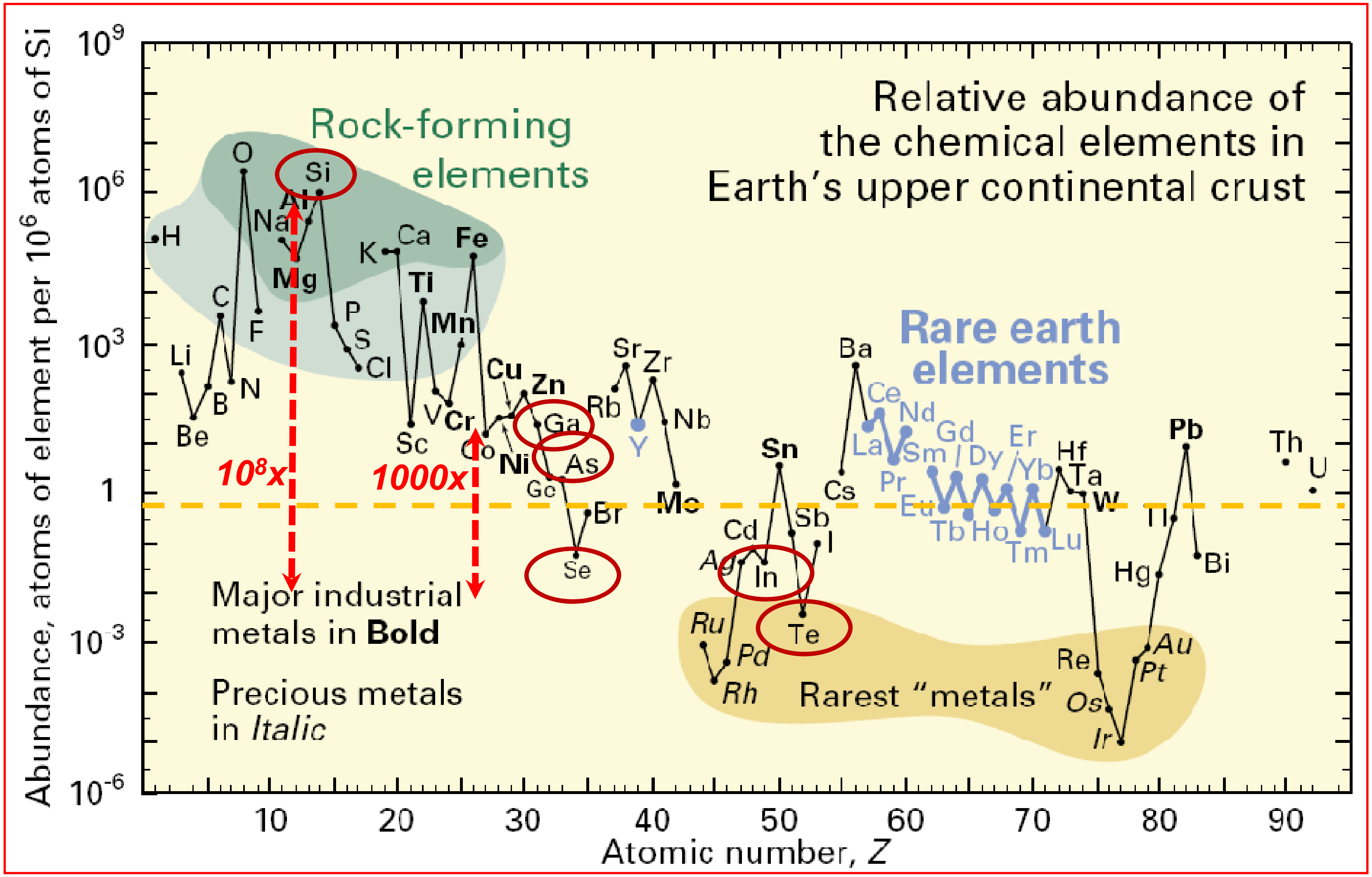


CdTe Thin Film

- Q4 2008 $1.08/Watt
- 56% gross margin
- 750 MW production capacity

PV Resources: Materials

Relative abundance of elements vs. atomic number*



**from P.H. Stauffer et al, Rare Earth Elements - Critical Resources for High Technology, USGS (2002)*

PV Materials by Production and Reserve

PV Feedstock Production and Reserve Base			**Annual PV Production** (GigaWatts/year)		
			0.3 (2000)	**1.5** (2005)	**50** (2020)
			PV Feedstock Consumption (1000s of ton/year)		
Feedstock Material	**World Production** (1000s of ton/year)	**Reserve Base*** (1000s of ton/year)	(2000)	(2005)	(2020)
Si (c-Si)	**1 000**	**abundant**	**4** $^{(1)}$	**15** $^{(2)}$	**150** $^{(3)}$
Te $^{(4)}$ **(CdTe)**	**0.3 (Cu)**	**47**	**0.030**	**0.15**	**5**
In $^{(4)}$ **(CIGS)**	**0.5 (Zn)**	**6**	**0.030**	**0.15**	**5**
Ga$^{(5)}$ **(GaAs)**	**184 (Al)**	**>1100**	**0.008**	**0.041**	**1.4**
As$^{(5)}$**) (GaAs)**	**59**	**1100**	**0.008**	**0.041**	**1.4**

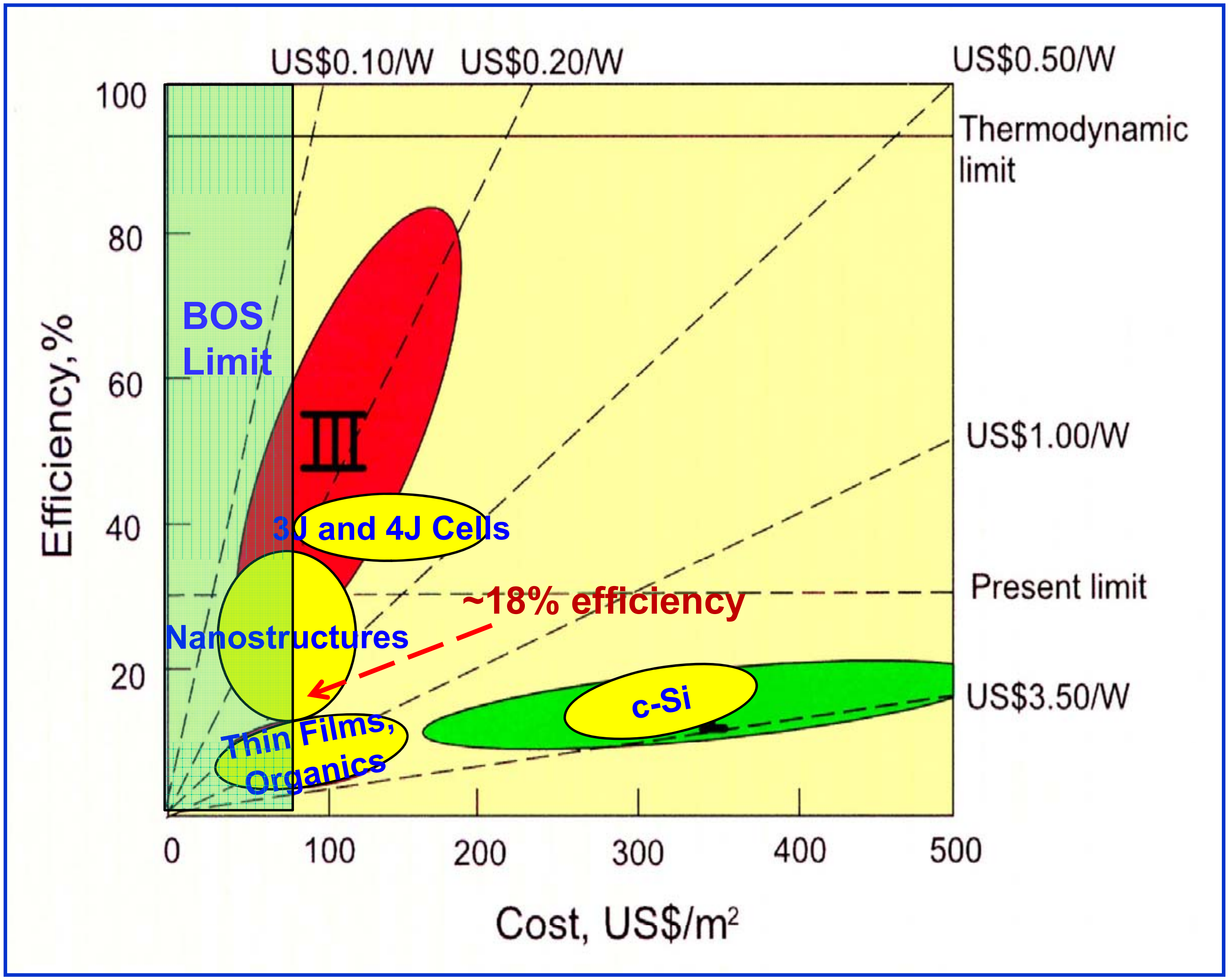
Material use in module production (grams / Watt): $^{(1)}$ 13, $^{(2)}$ 10, $^{(3)}$ 3, $^{(4)}$ 0.1, $^{(5)}$0.025

***: Resources that are currently economic, marginally economic and some of those that are currently subeconomic**

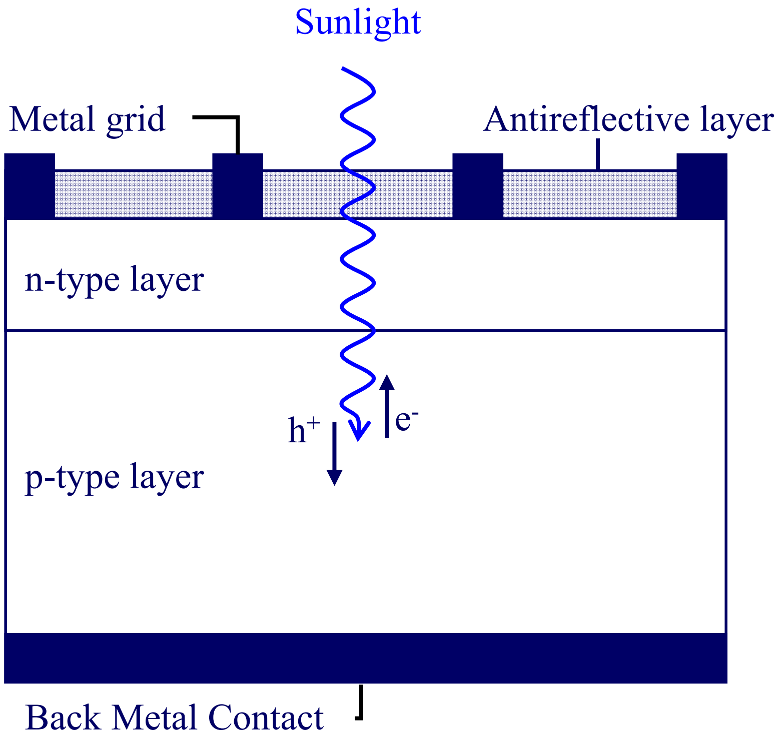
Sources: US Geological Survey 2004 (http://minerals.usgs.gov/minerals/pubs/mcs/),
M.A. Green, Prog. Phot. 14 (2006) 743-751; G. Willeke, Fraunhofer Institut

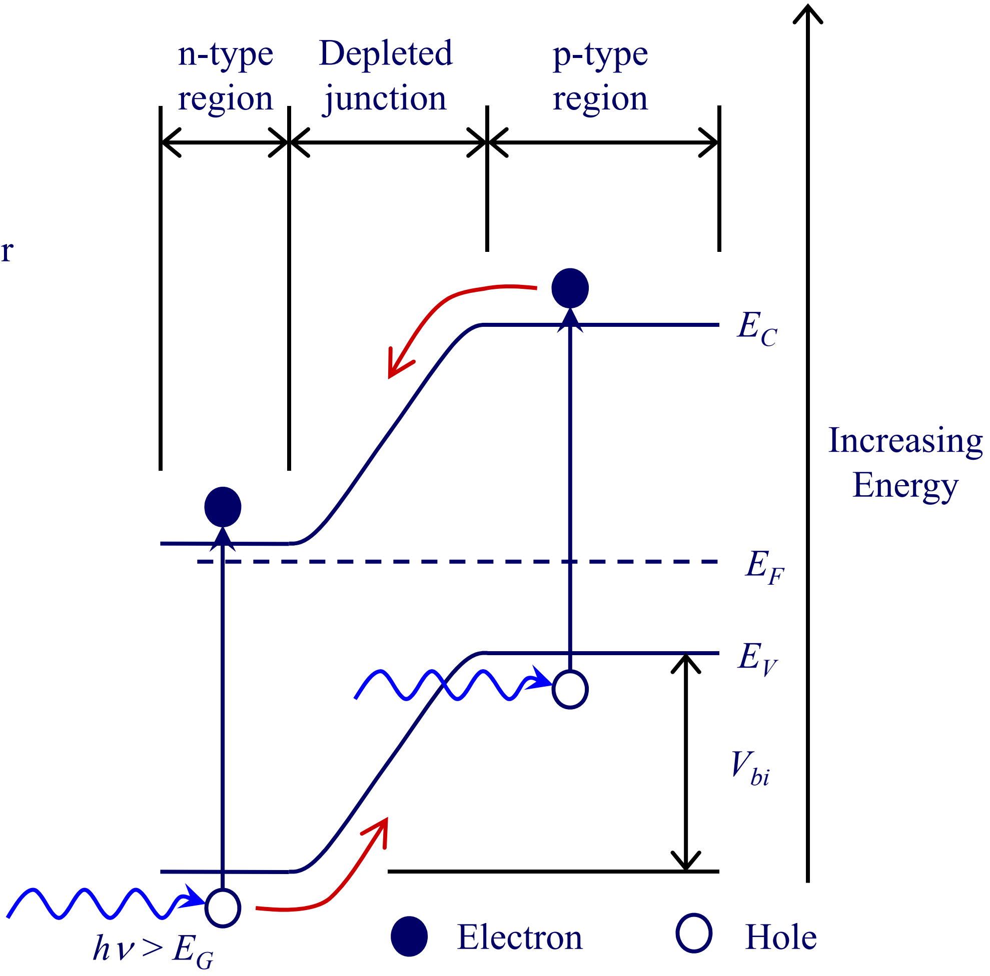
Si and Te Data From G. Willeke, Fraunhofer ISE

Cost/Efficiency of PV Technology Argues for High Efficiency



Single Junction Solar Cells





PV Figures of Merit

Maximum Power Output:

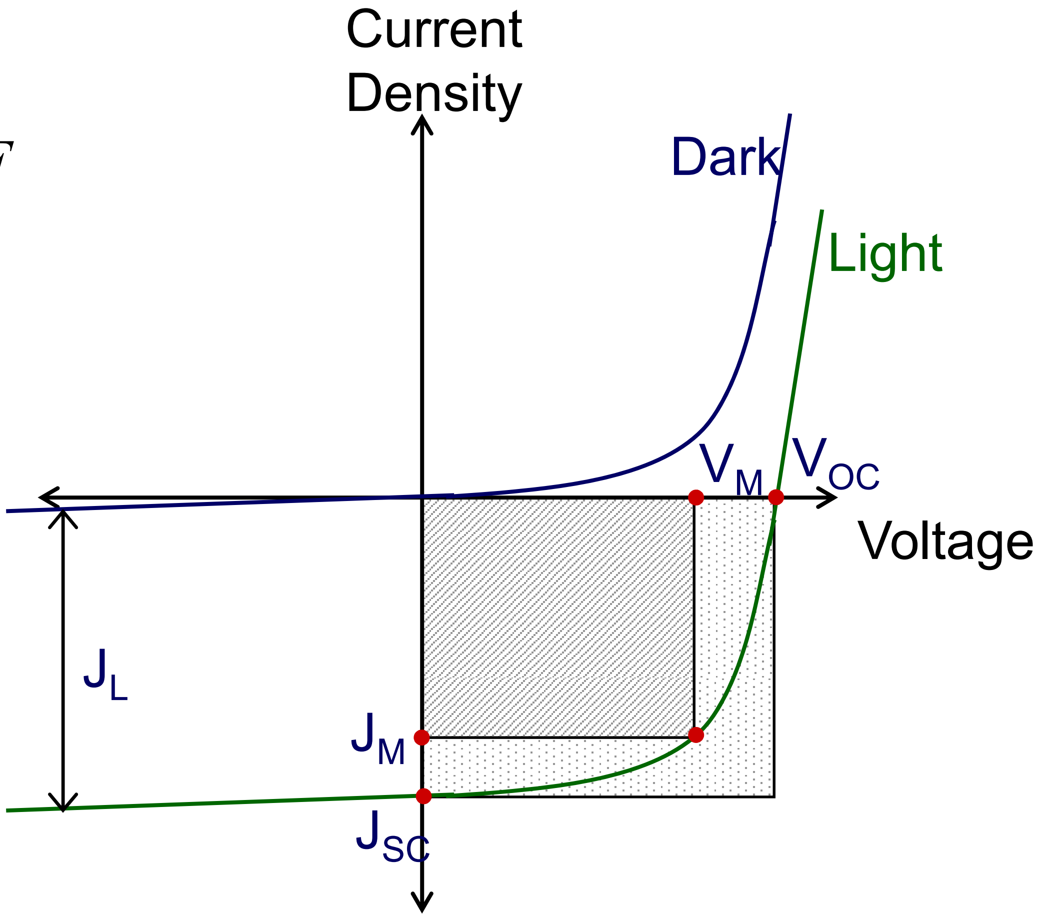
$$P_M = J_M V_M = J_{SC} V_{OC} FF$$

Fill Factor:

$$FF = \frac{J_M V_M}{J_{SC} V_{OC}}$$

Efficiency:

$$\eta = \frac{P_M}{P_{incident}}$$



Maximum Solar Cell Efficiencies

Measured

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).

3-gap GaInP/GaAs/Ge cell @240suns (Fraunhofer)
41.1 %

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)
25.0%

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)**

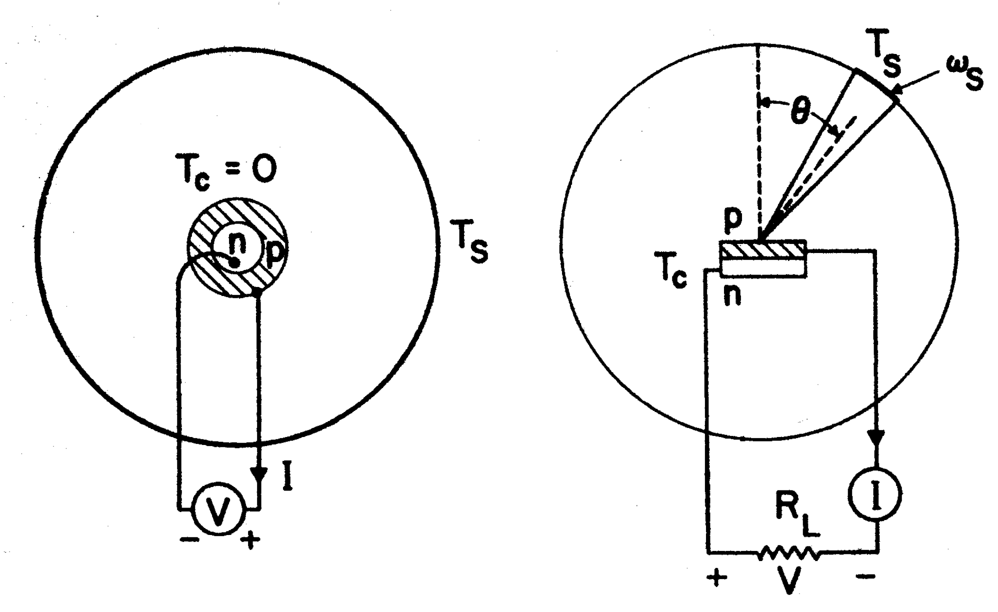
37% **Ideal 1-gap solar cell at 1000 suns (Henry)**

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

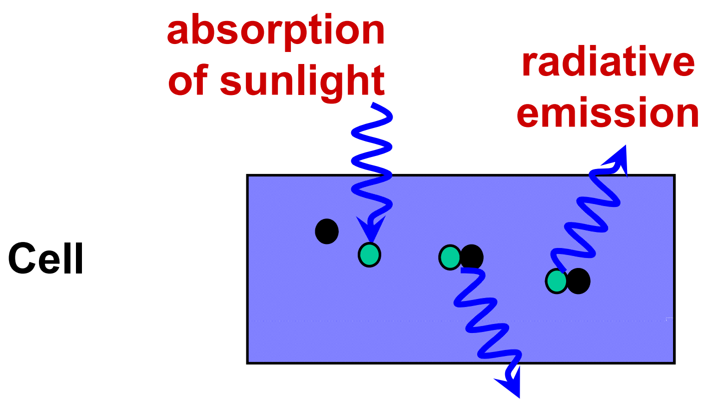
Detailed Balance Limit for Solar Cell Efficiency



(a)

(b)

Shockley and Queisser (1961)



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

charge carrier flux

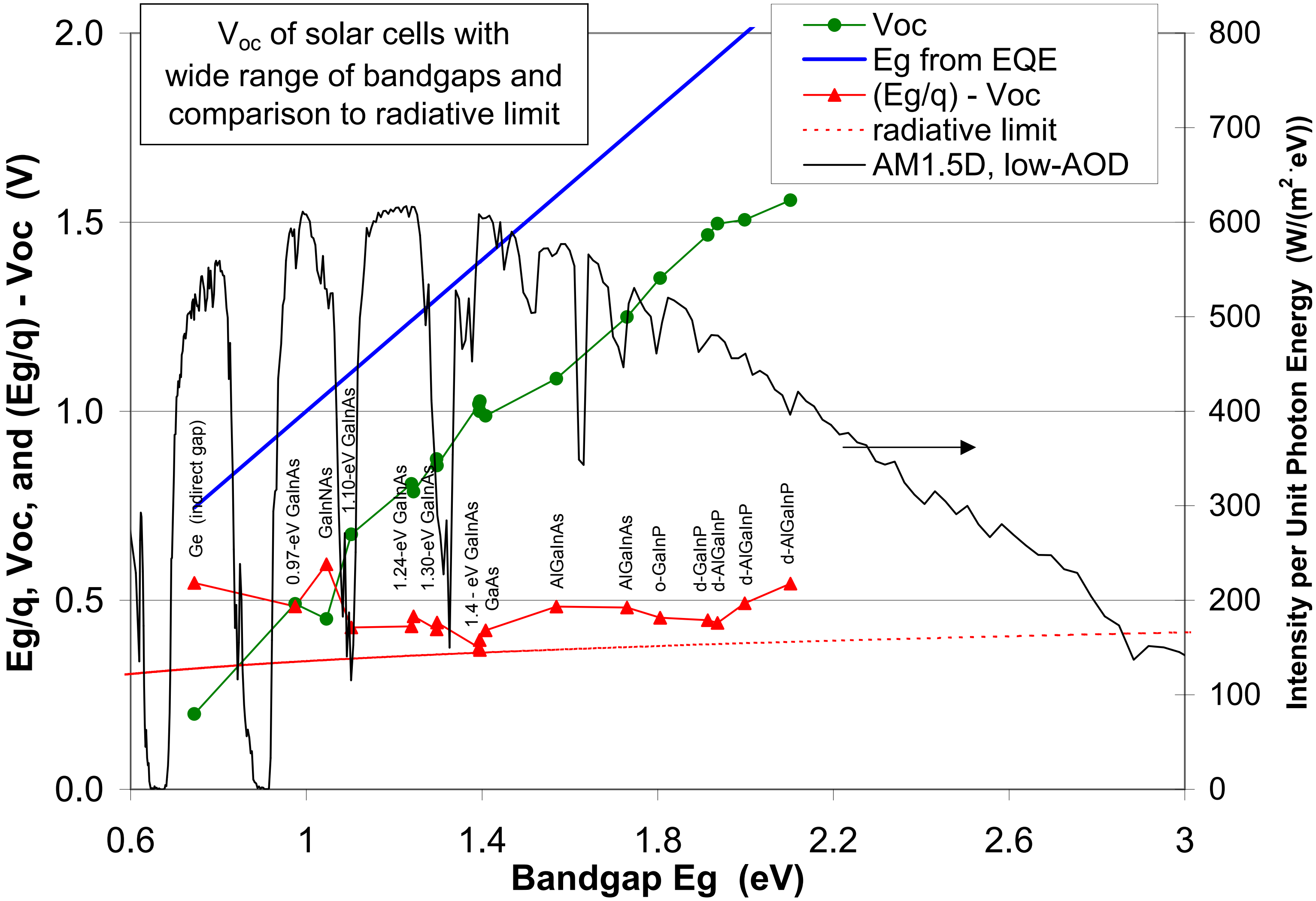
generation rate by sunlight absorption

radiative recombination rate

Open Circuit Voltage Offset from Bandgap: Photon Entropy

$$\Delta F = \Delta H - T\Delta S$$

$$qV_{oc} = E_g - T\,k\ln\Omega = E_g - kT\ln 46{,}200 = E_g - 10.7\,kT$$



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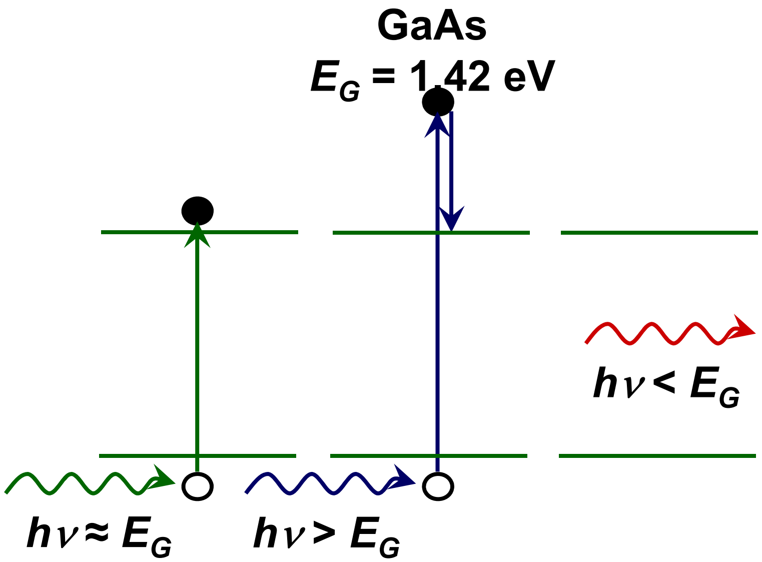
Single-junction Cells vs. Multijunctions



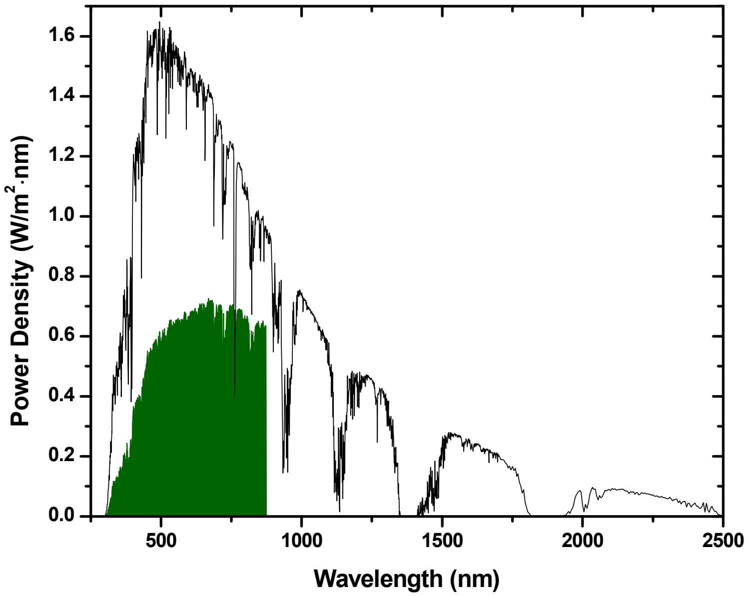
GaAs

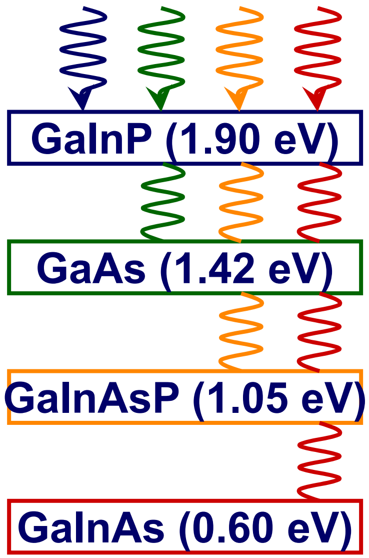
E_G = 1.42 eV

$h\nu \approx E_G$

$h\nu > E_G$

$h\nu < E_G$



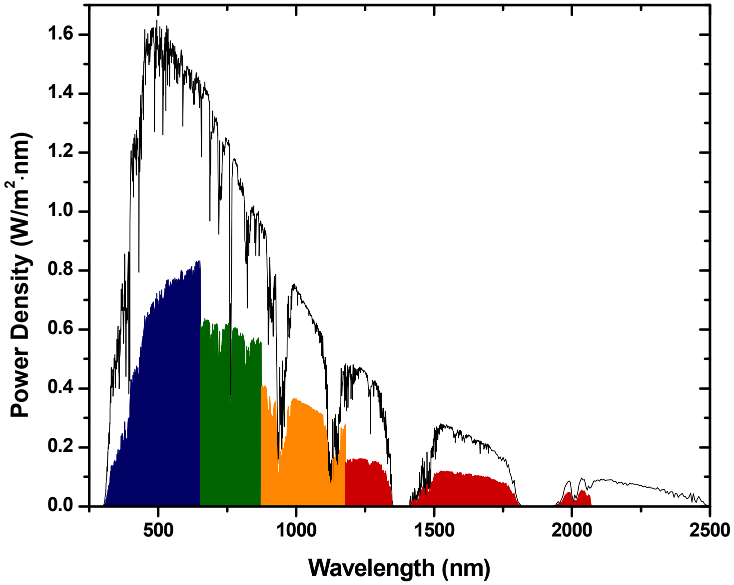


GaInP (1.90 eV)

GaAs (1.42 eV)

GaInAsP (1.05 eV)

GaInAs (0.60 eV)

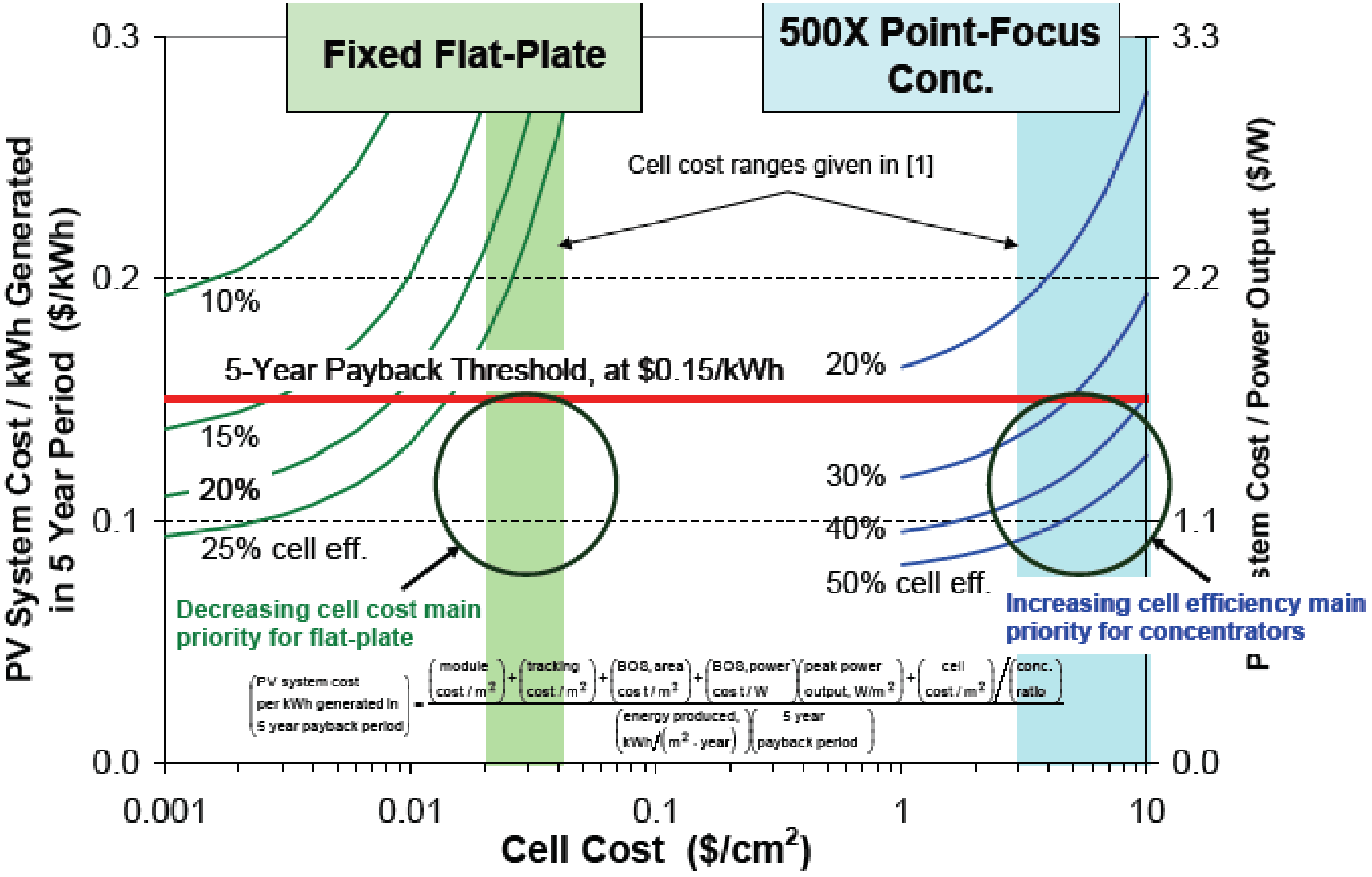


Concentrator Photovoltaics: An Approach to Reap Benefit from Expensive Ultrahigh Efficiency Cells

UMUWA SOLAR POWER STATION

Solar Systems

Cost per Watt and Levelized Cost of Electricity in Flat Plate vs. Concentrator System



Module and BOS cost assumptions from: [1] Swanson, Prog. Photovolt. Res. Appl. ***8****, 93-111 (2000).*

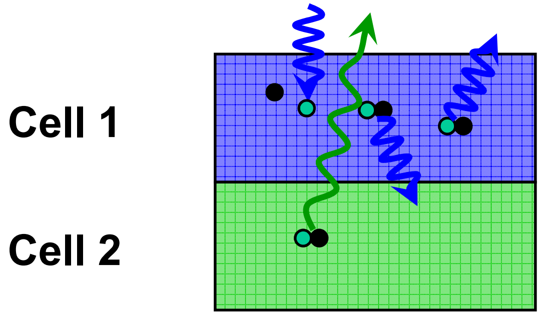
Detailed Balance Models

Assumptions:

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

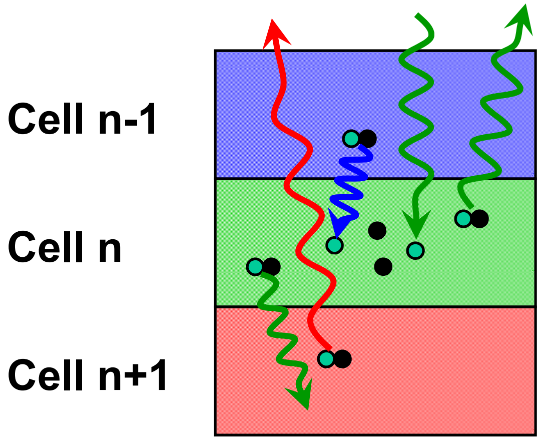
- Perfect absorption of incident photons
- Photo-current loss through radiative reemission:

Detailed Balance of First Subcell



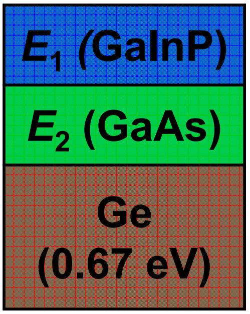
$$\frac{J_1}{q} = {}^{AM1.5}N - {}^{rad}N_1$$

Detailed Balance of nth Subcell



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

Detailed Balance: Ge-based Triple-junction Isoefficiency Plot



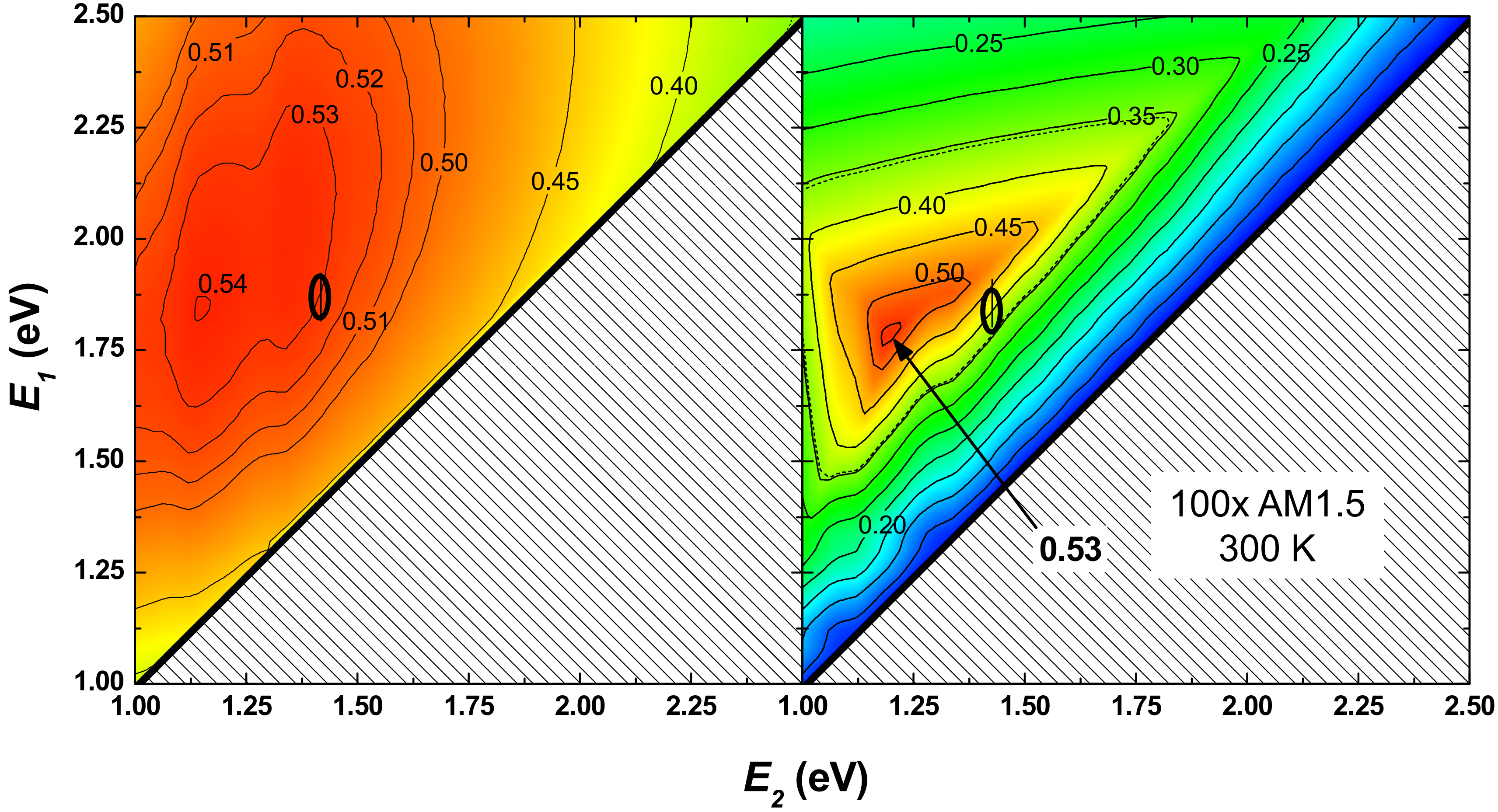
E_1 (GaInP)

E_2 (GaAs)

Ge (0.67 eV)

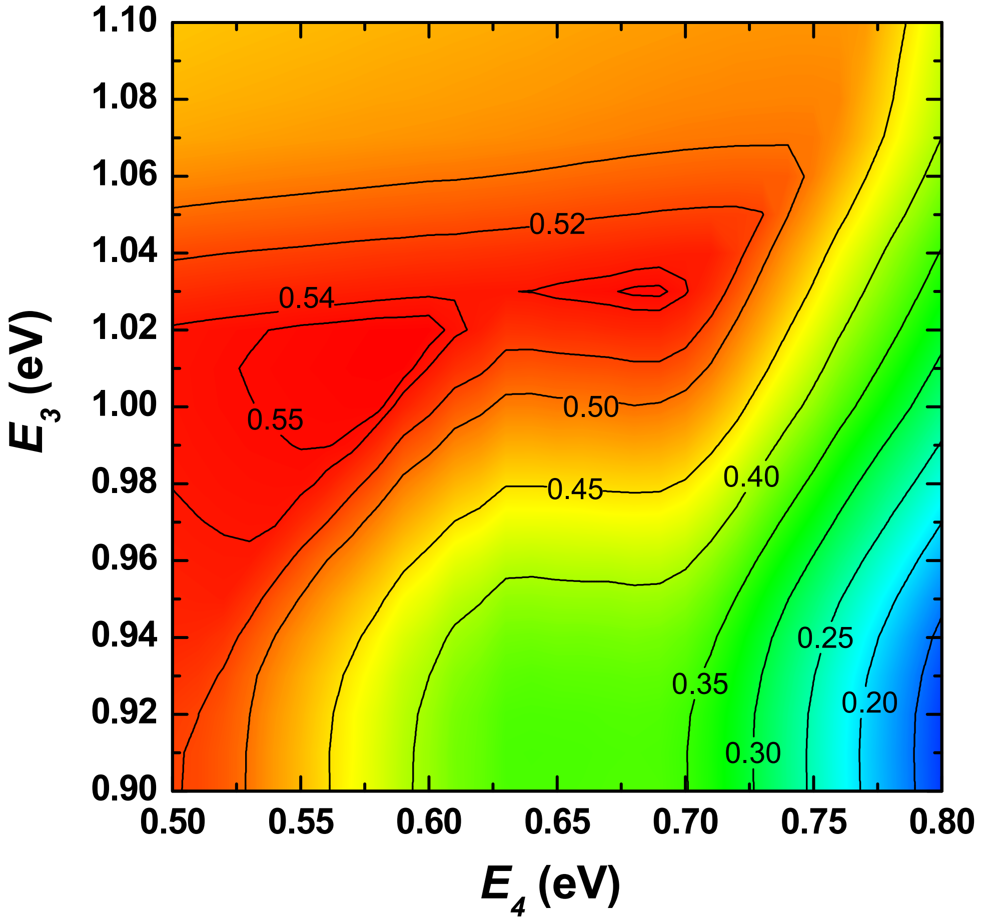
Independently Connected

Series Connected

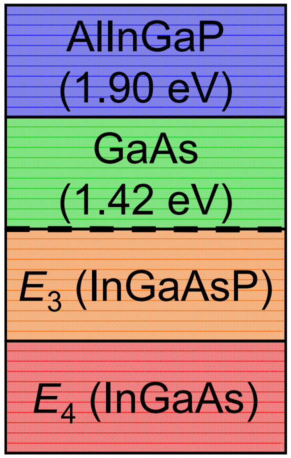


100x AM1.5
300 K

Detailed Balance: GaInP/GaAs-Based Four-Junction Isoefficiency Plot



100x AM1.5
300 K



AlInGaP
(1.90 eV)

GaAs
(1.42 eV)

E_3 (InGaAsP)

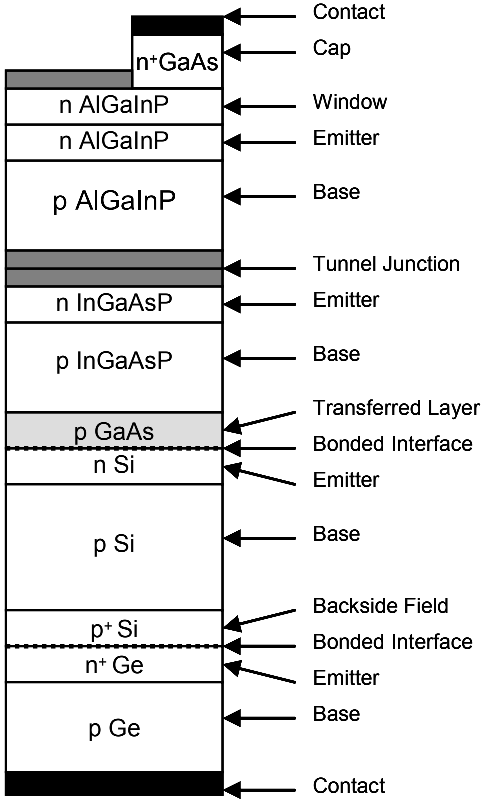
E_4 (InGaAs)

- **Narrow-gap bottom subcell eases current-matching requirements for E_3**
- **Iso-efficiency contours → atmospheric absorption**

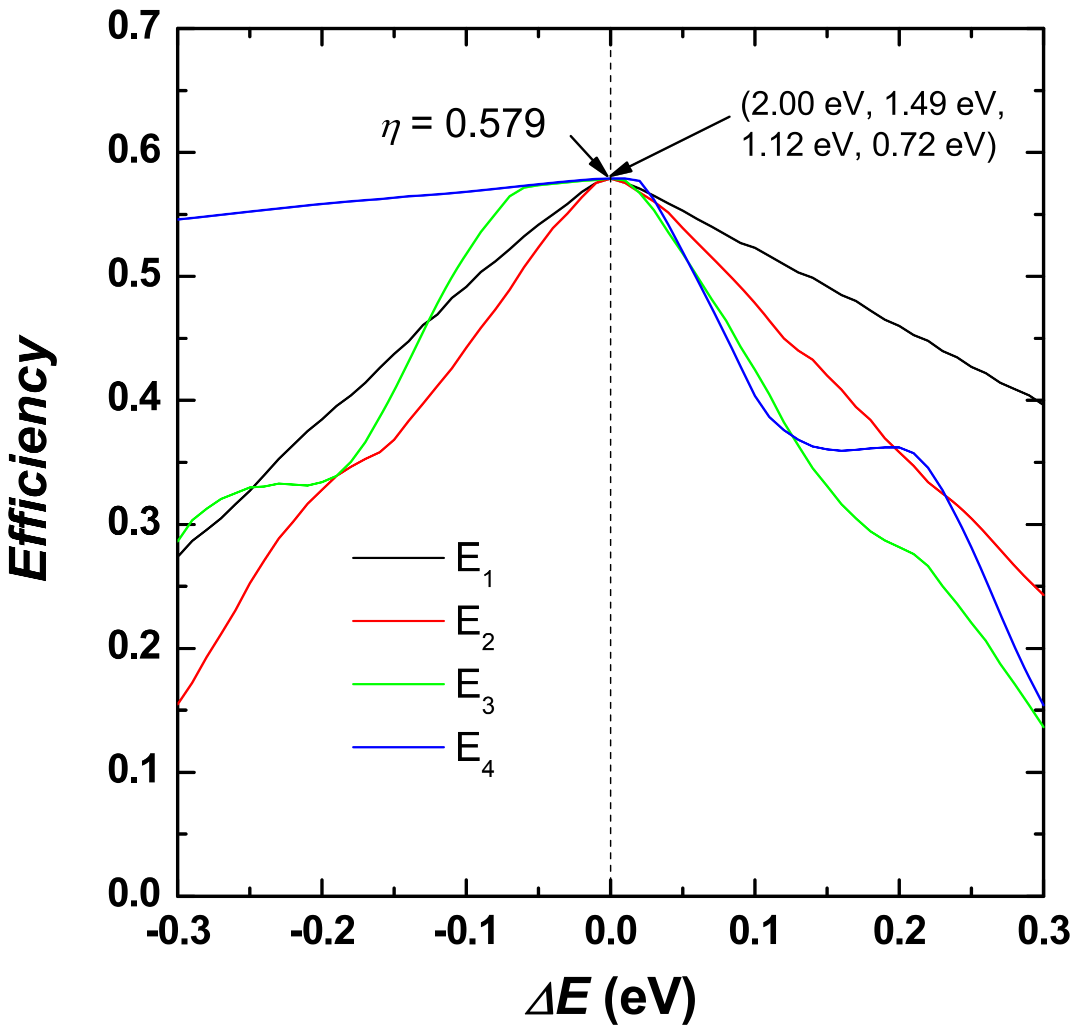
Detailed Balance: Summary

Configuration	Optimal Subcell Bandgaps (eV)	Maximum Efficiency
Ge-Based Triple-Junction (Series connected)	1.90, 1.42, 0.67	46.3%
Si-Based Triple-Junction (Series connected)	2.00, 1.49, 1.12	51.2%
Optimal Four-Junction (Series connected)	2.00, 1.49, 1.12, 0.72	57.9%
GaInP/GaAs-Based Four-Junction (Series connected)	1.90, 1.42, 1.02, 0.60	54.9%

Efficiency vs. Bandgap Variation in 4 Junction Cell

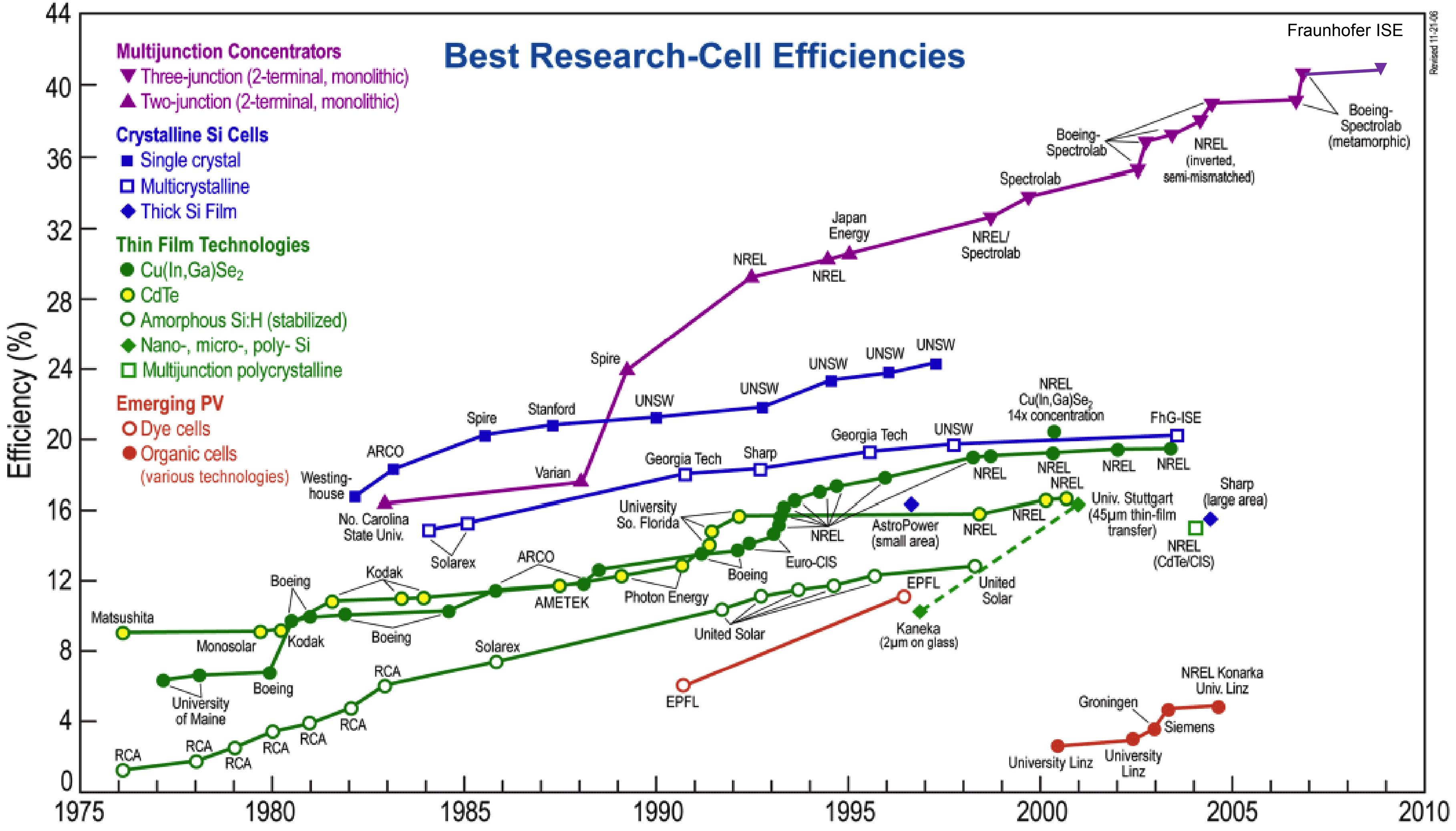


	Contact
n^+GaAs	Cap
n AlGaInP	Window
n AlGaInP	Emitter
p AlGaInP	Base
	Tunnel Junction
n InGaAsP	Emitter
p InGaAsP	Base
p GaAs	Transferred Layer
	Bonded Interface
n Si	Emitter
p Si	Base
p^+ Si	Backside Field
	Bonded Interface
n^+ Ge	Emitter
p Ge	Base
	Contact



Variation of efficiency of optimal 100 sun AM1.5 series-connected four-junction solar cell with changes of each subcell bandgap. Each subcell is varied independently, maintaining the other subcells at their optimum bandgap of 2.00, 1.49, 1.12, and 0.72 eV respectively.

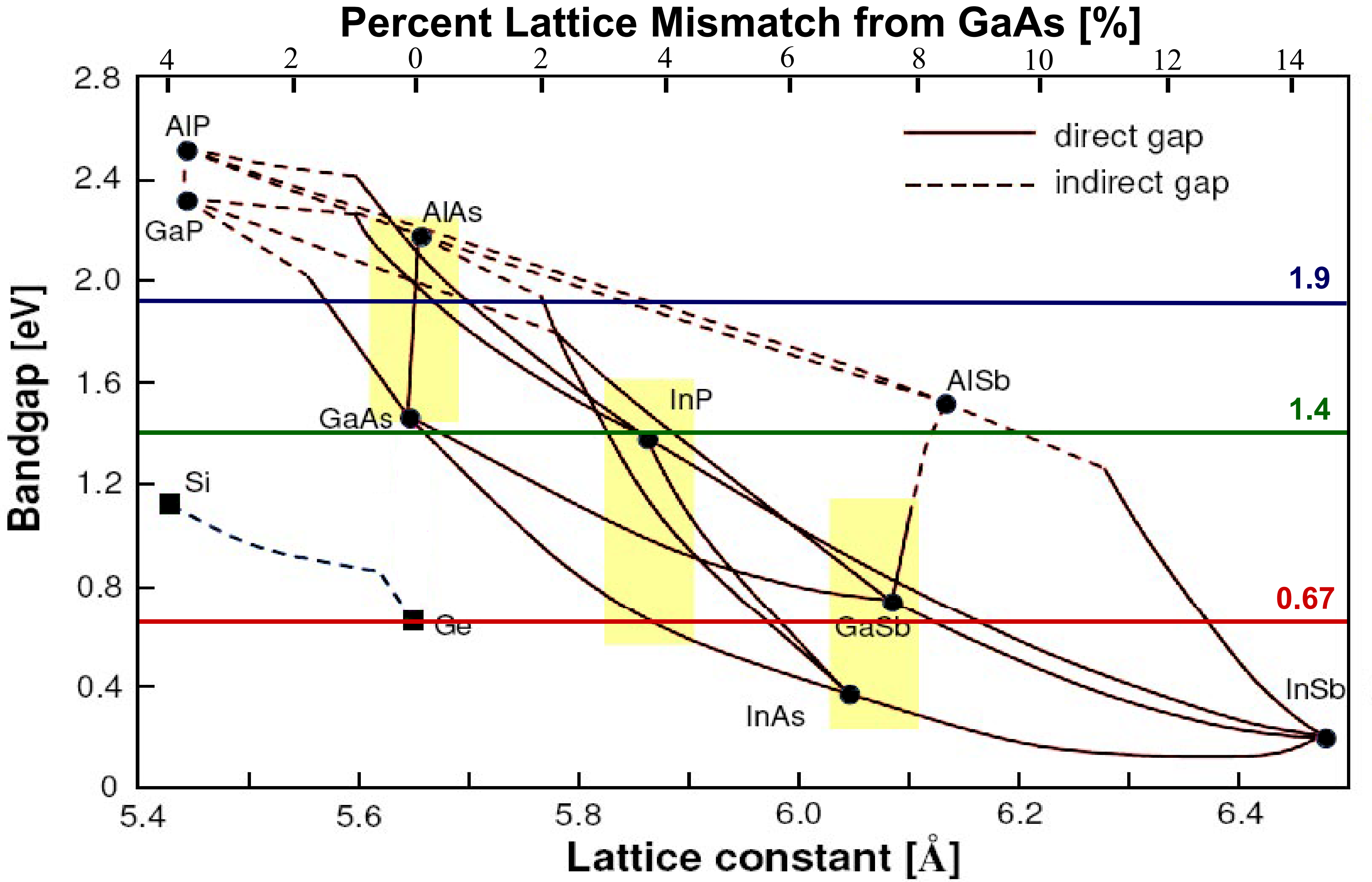
Improvements in Solar Cell Efficiencies



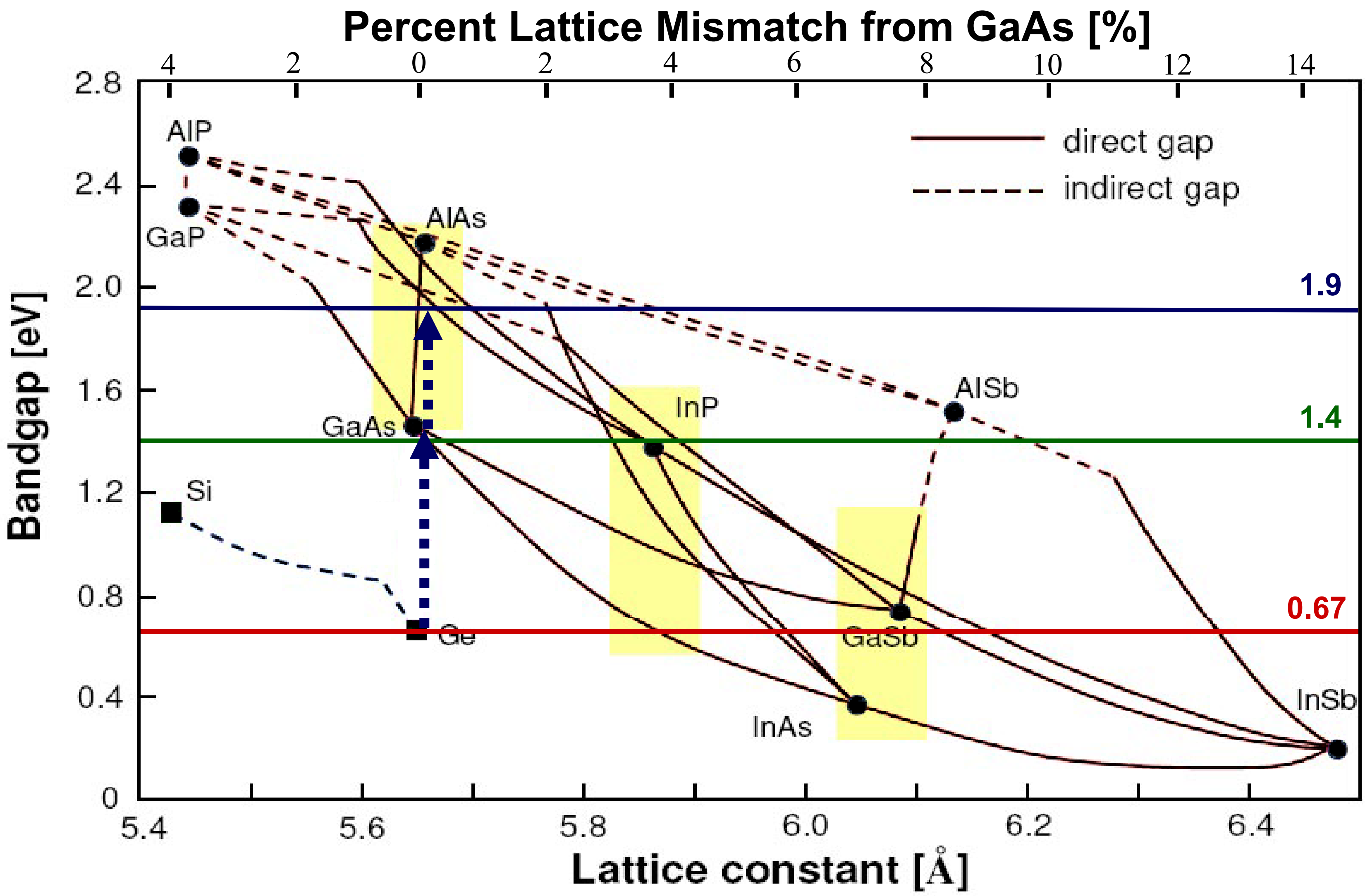
3/15/09
H. Atwater Caltech

US DOE

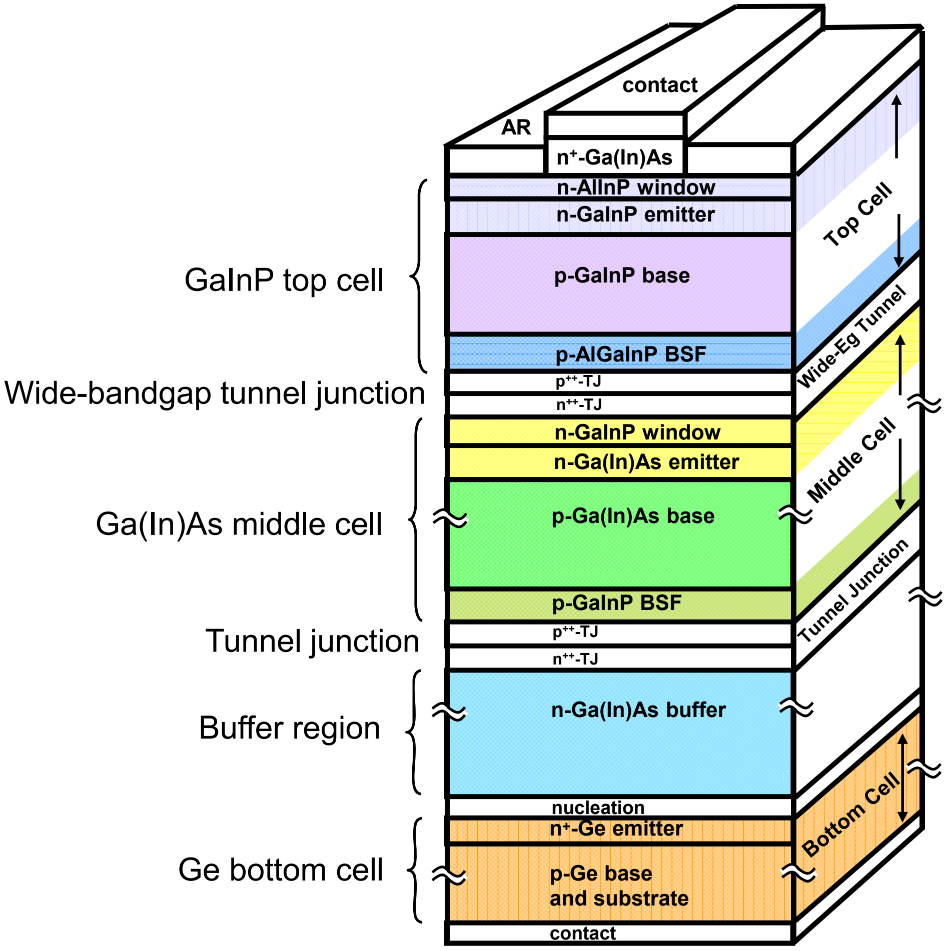
Band Gap versus Lattice Constant



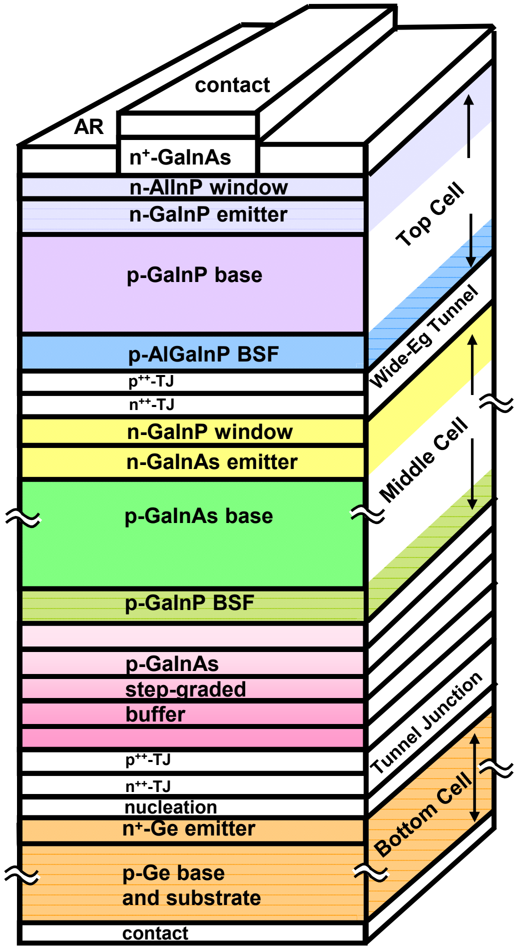
Band Gap versus Lattice Constant



Lattice Matched and Metamorphic 3-Junction Cell Cross-Sections



Lattice-Matched (LM)



Lattice-Mismatched or Metamorphic (MM)

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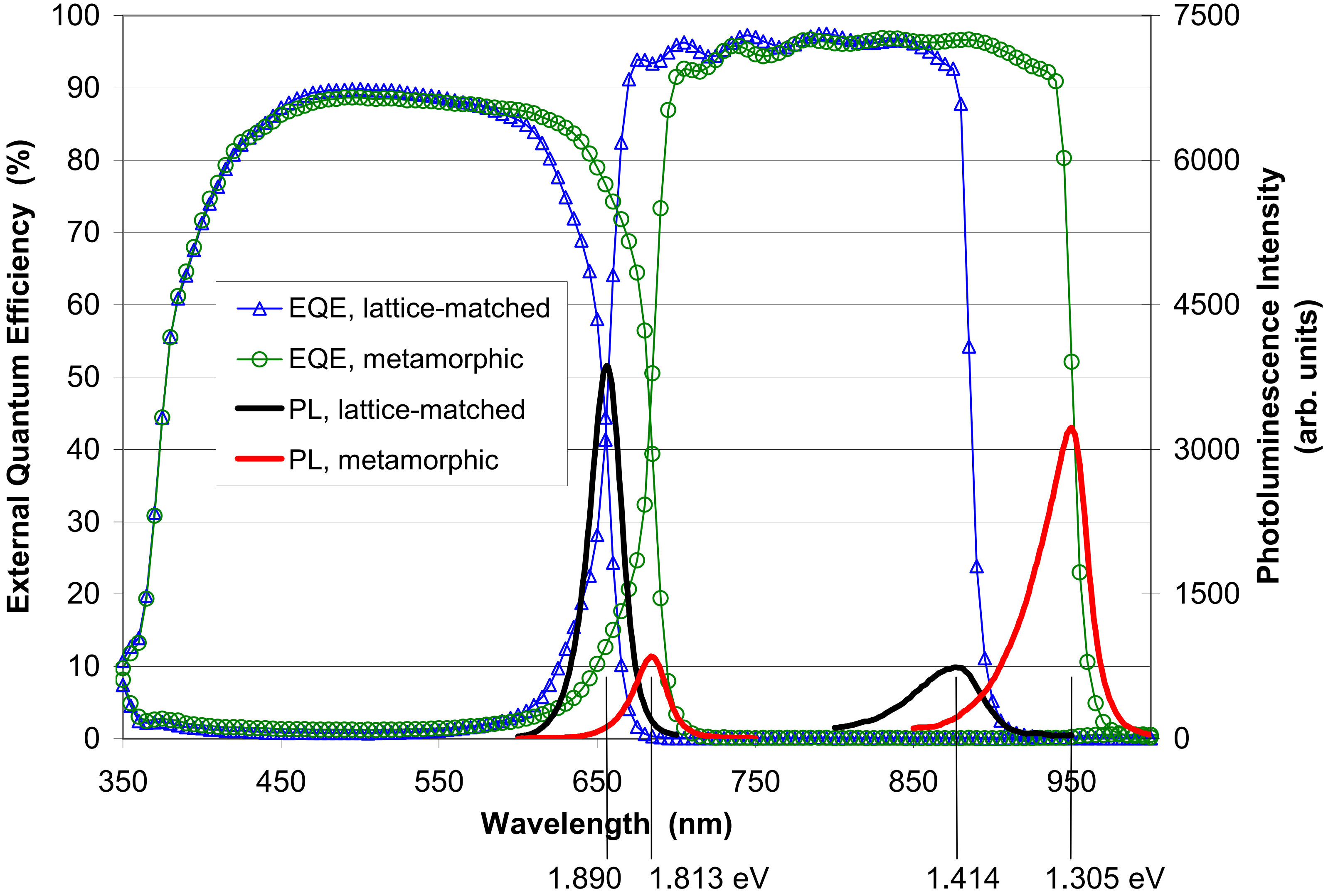
EQE and PL of Subcells Matched to 1%-In and 8%-In GaInAs

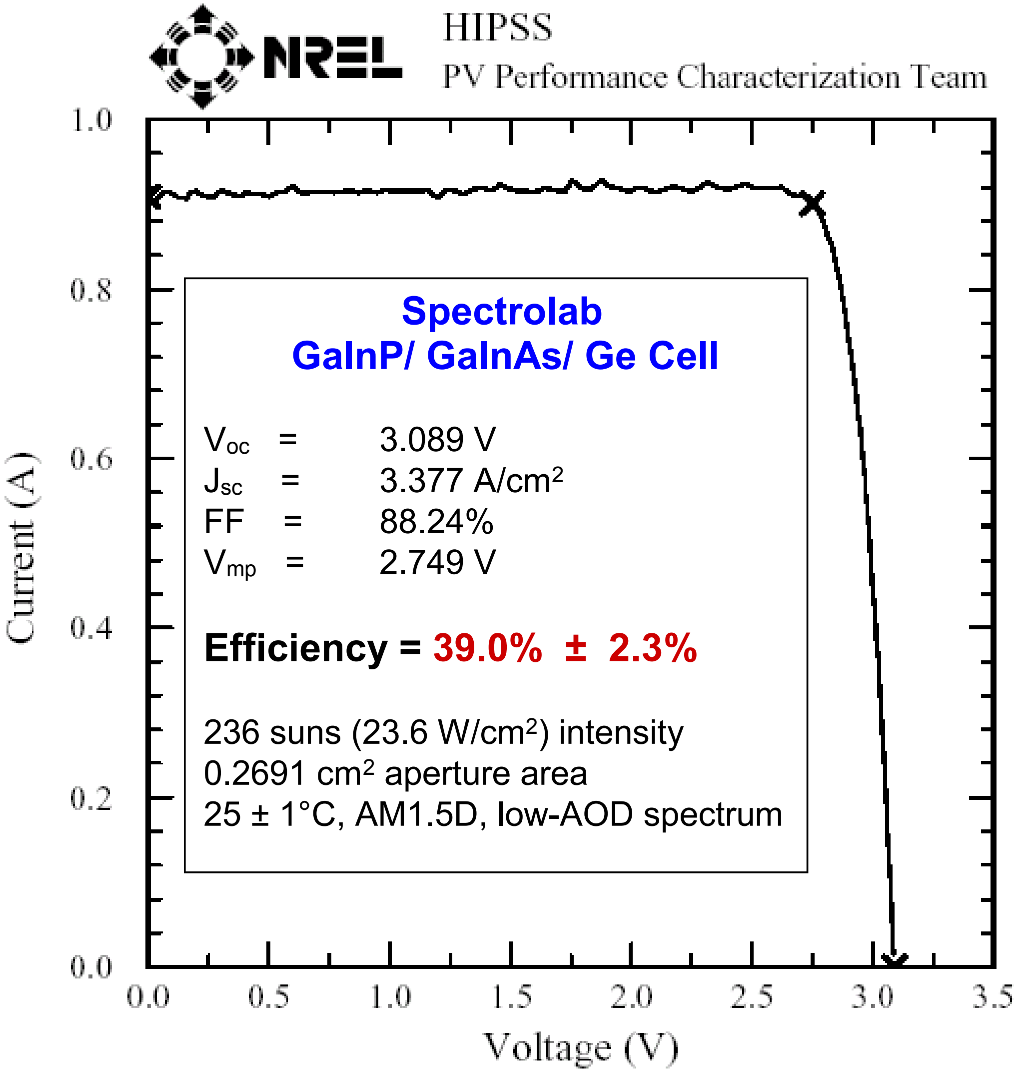


3/15/09
H. Atwater Caltech

Richard King

High Efficiency GaInP/GaInAs/Ge Triple Junction

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



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°C, AM1.5D, low-AOD spectrum

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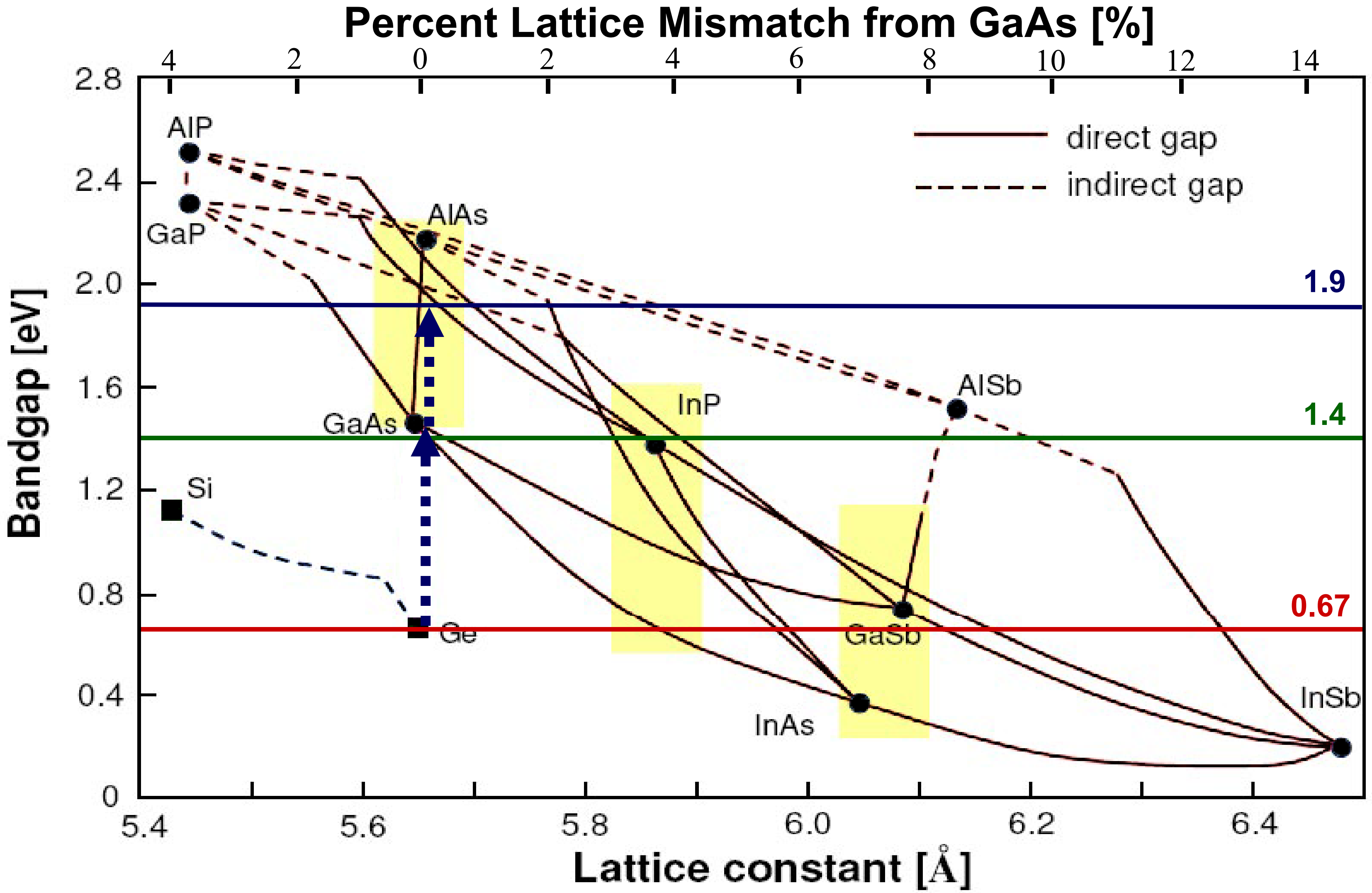
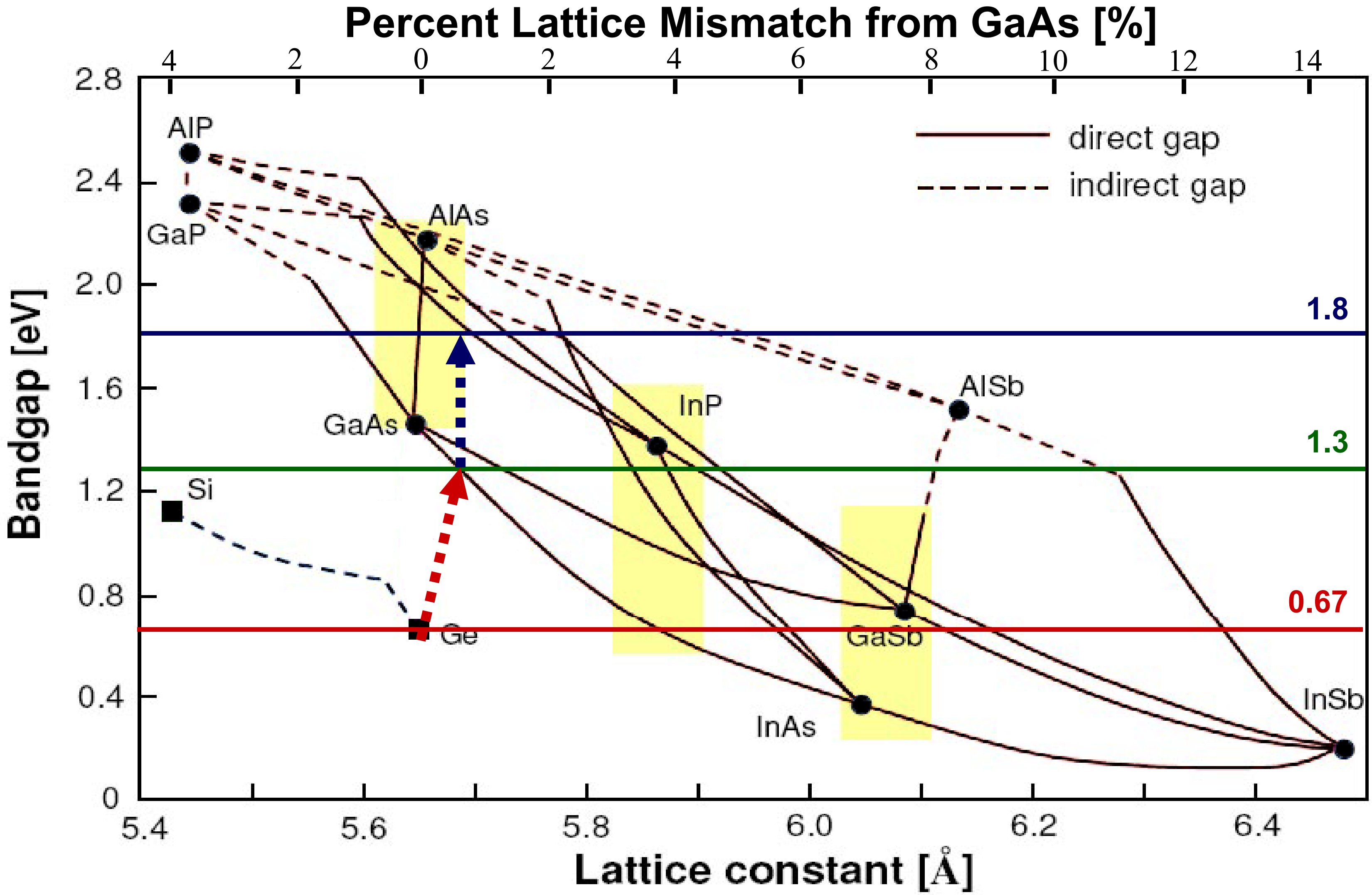
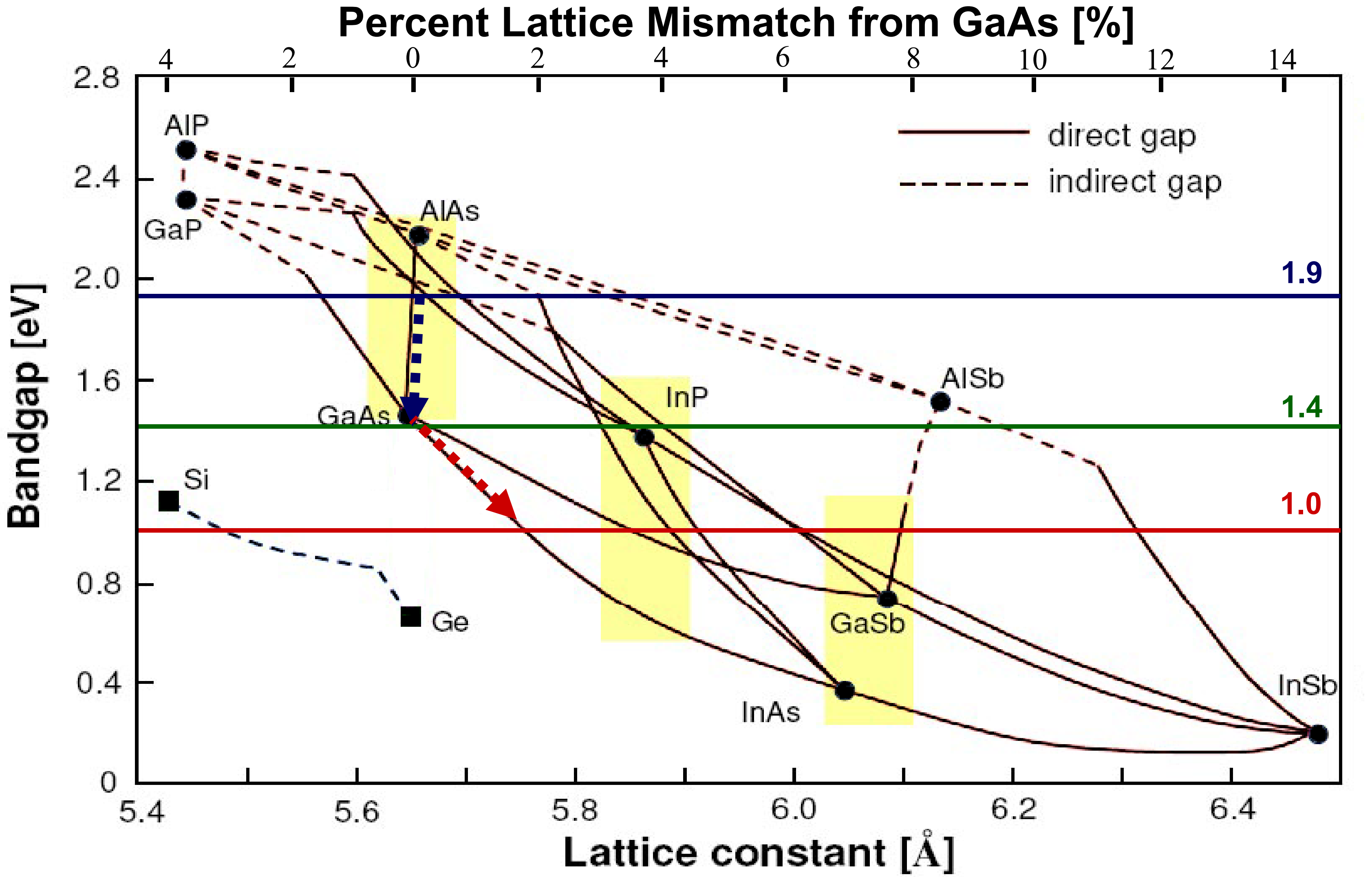
Band Gap versus Lattice Constant



Band Gap versus Lattice Constant

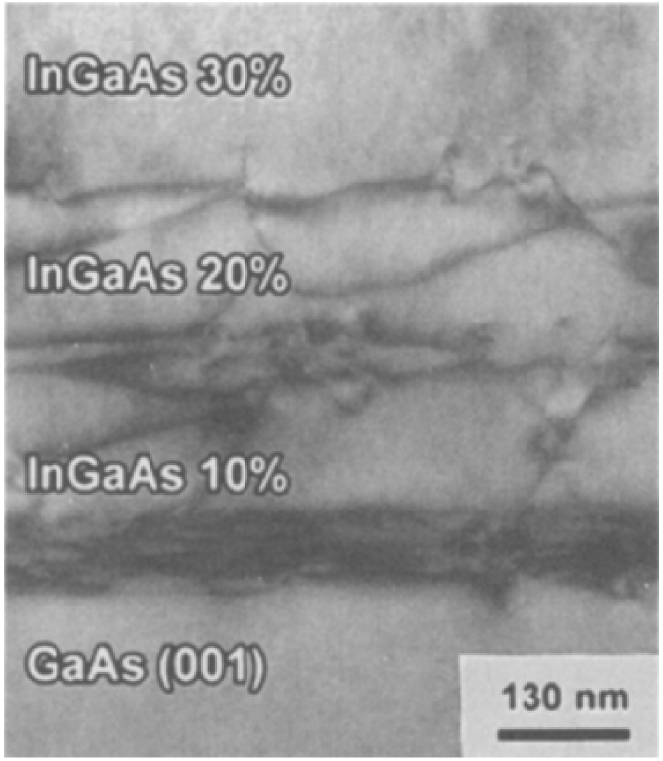


Band Gap versus Lattice Constant

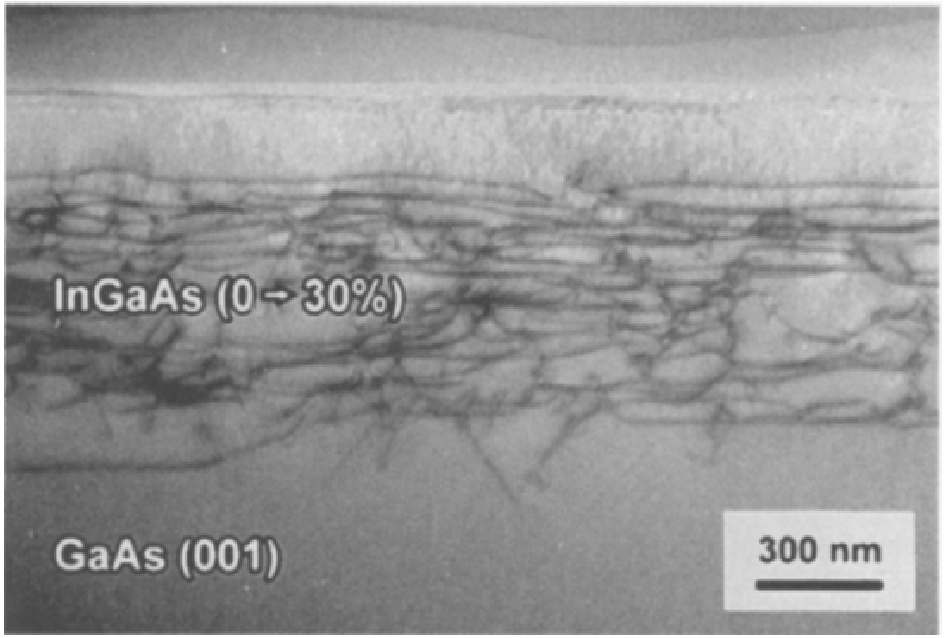


Metamorphic InGaAs Buffer Layers

Step Graded Buffer

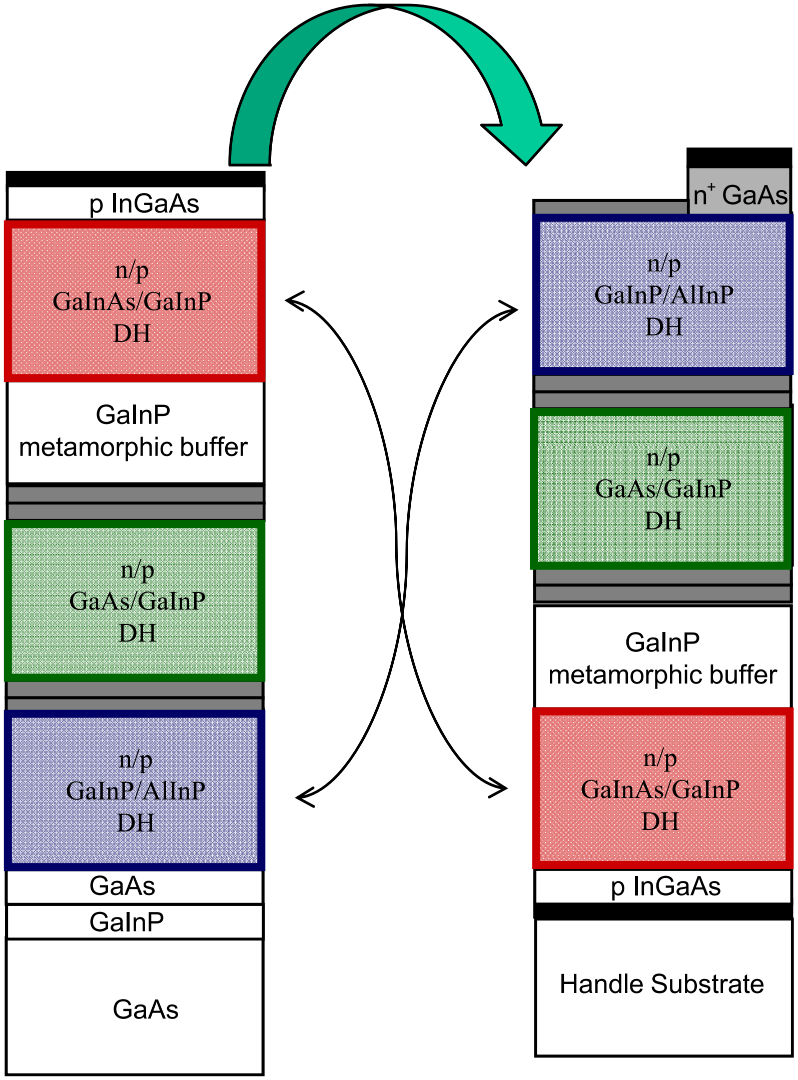


Linearly Graded Buffer



P. Kidd et al. Journal of Crystal Growth (1996)

Metamorphic 3J Solar Cells



p InGaAs

n/p
GaInAs/GaInP
DH

GaInP
metamorphic buffer

n/p
GaAs/GaInP
DH

n/p
GaInP/AlInP
DH

GaAs

GaInP

GaAs

n^+ GaAs

n/p
GaInP/AlInP
DH

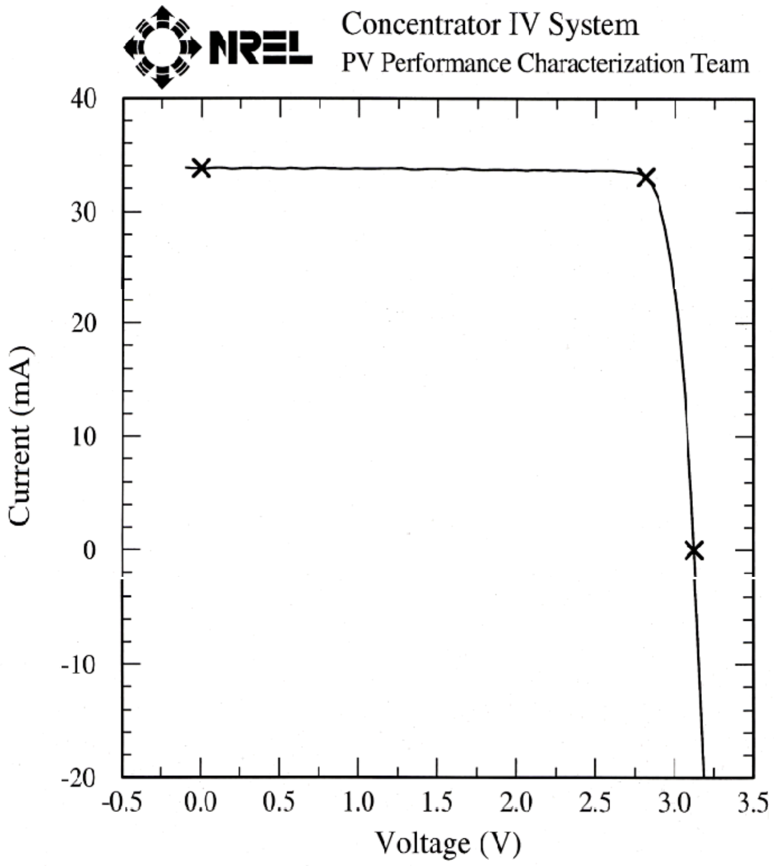
n/p
GaAs/GaInP
DH

GaInP
metamorphic buffer

n/p
GaInAs/GaInP
DH

p InGaAs

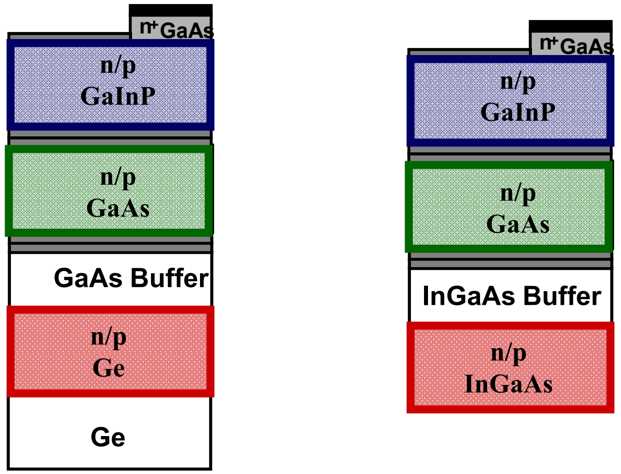
Handle Substrate



Efficiency = 37.9%

M.W. Wanlass et al, Proceedings of the 4th WCPEC (2006)

Record Efficiency 3J Solar Cells

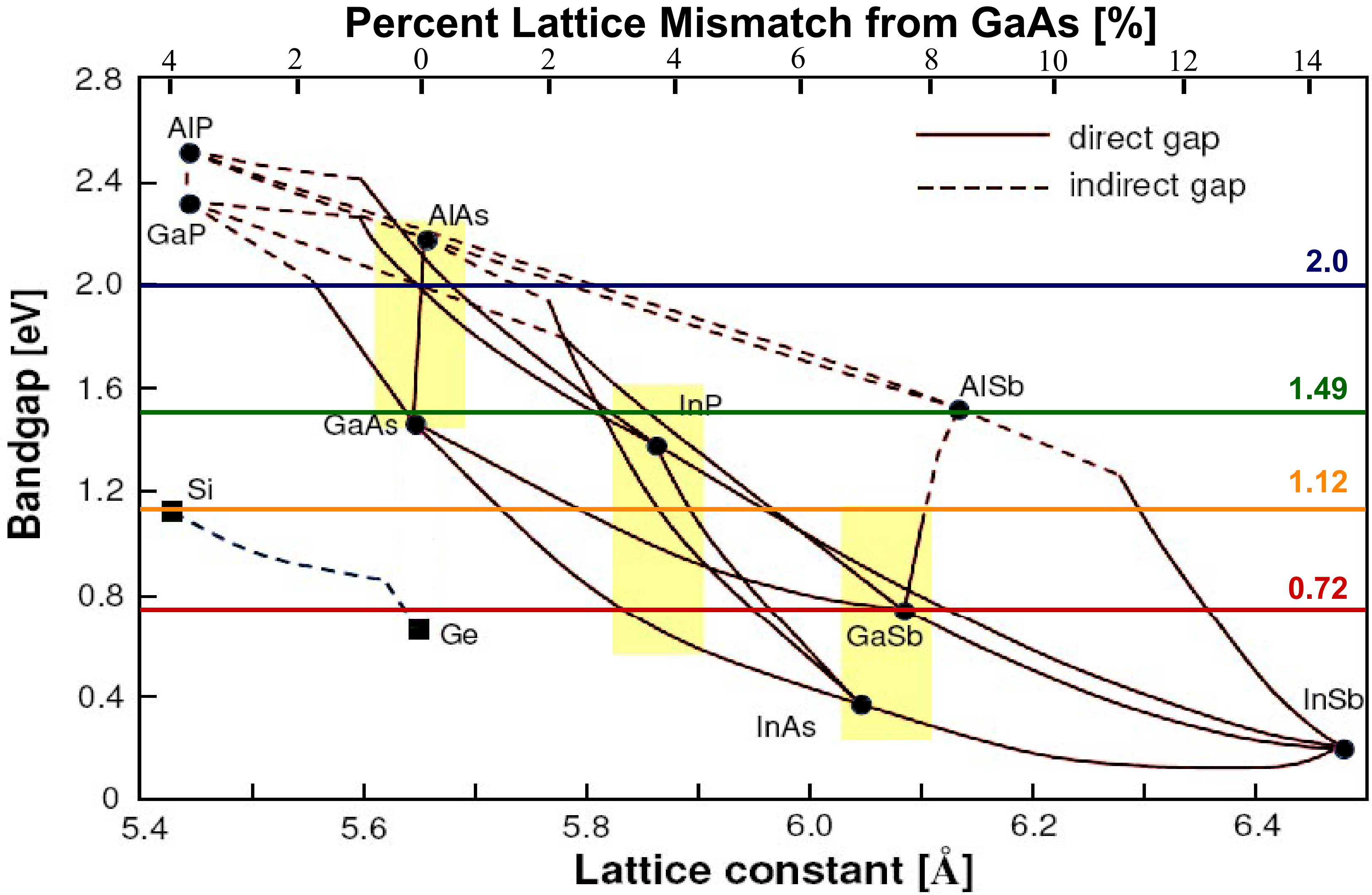


	Lattice Matched	Lattice Mismatched
V_{OC}	3.054 V	2.911 V
J_{SC}	0.1492 A/W	0.1596 A/W
FF	0.881	0.875
Concentration	454 suns	326 suns
Efficiency	41.1%	40.8%
	Fraunhofer	NREL

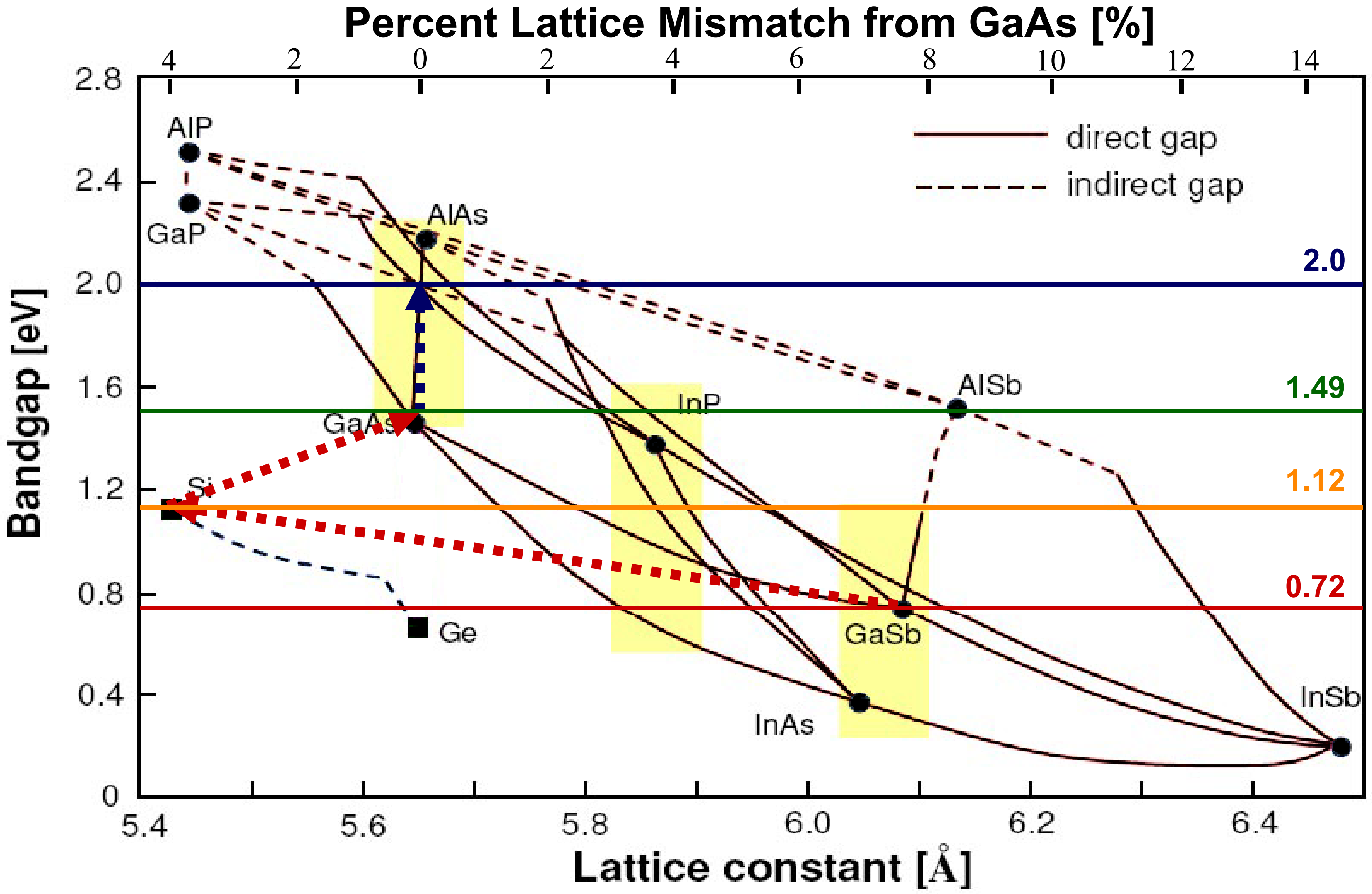
40.1%	40.7%
Spectrolab	Spectrolab

R.R. King et al. APL 90 183516 (2006)

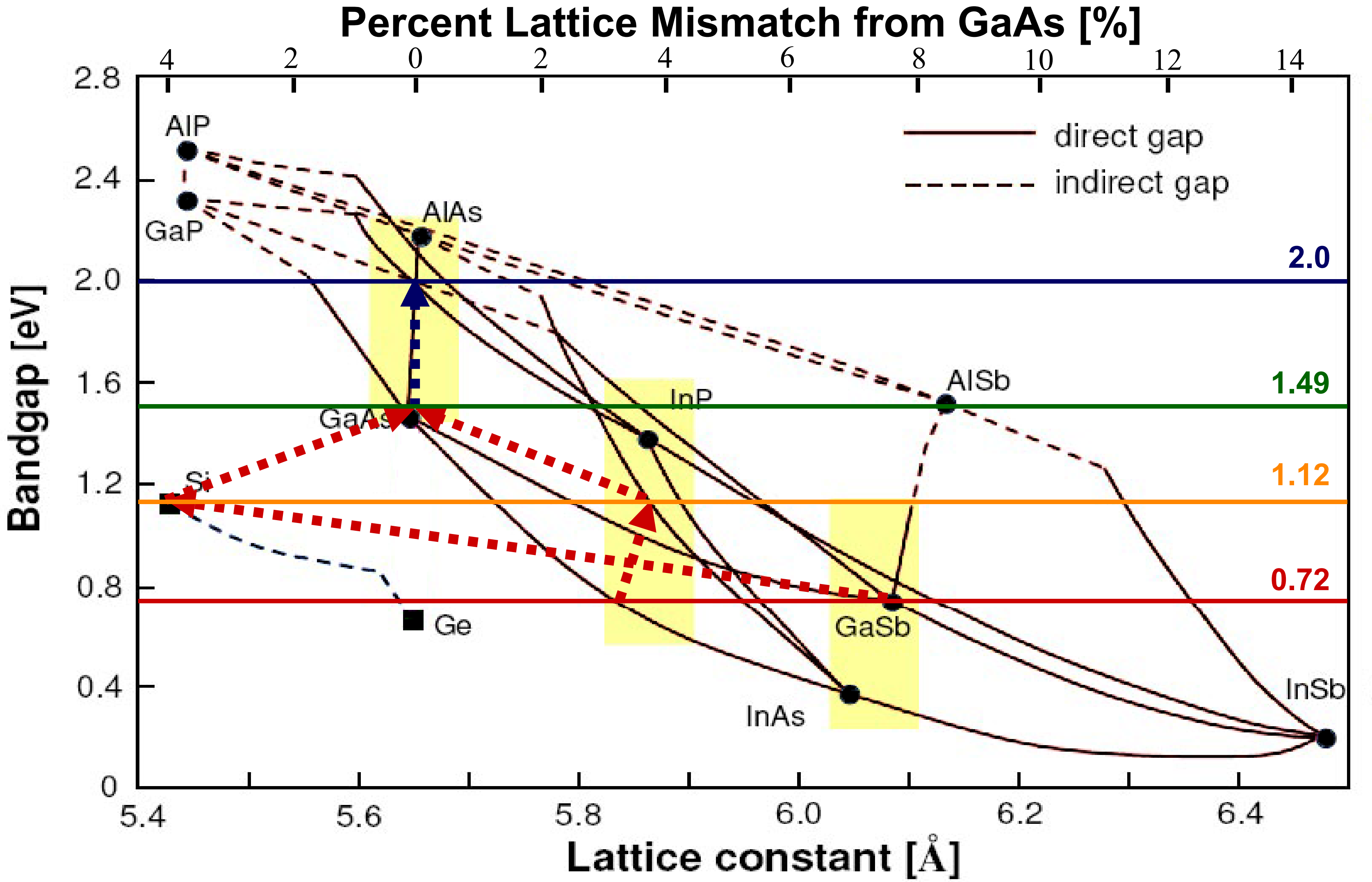
Band Gap versus Lattice Constant



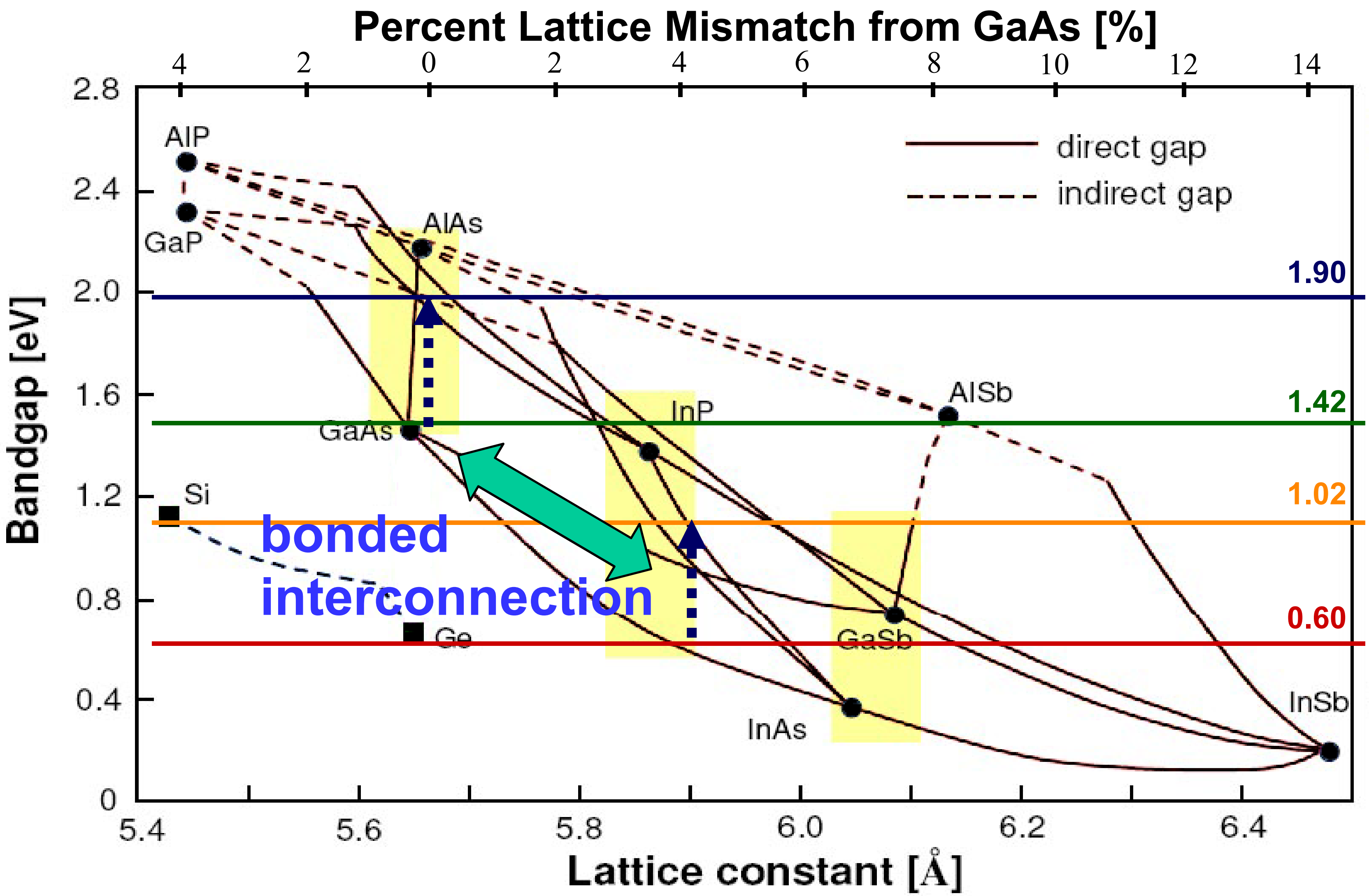
Band Gap versus Lattice Constant



Band Gap versus Lattice Constant

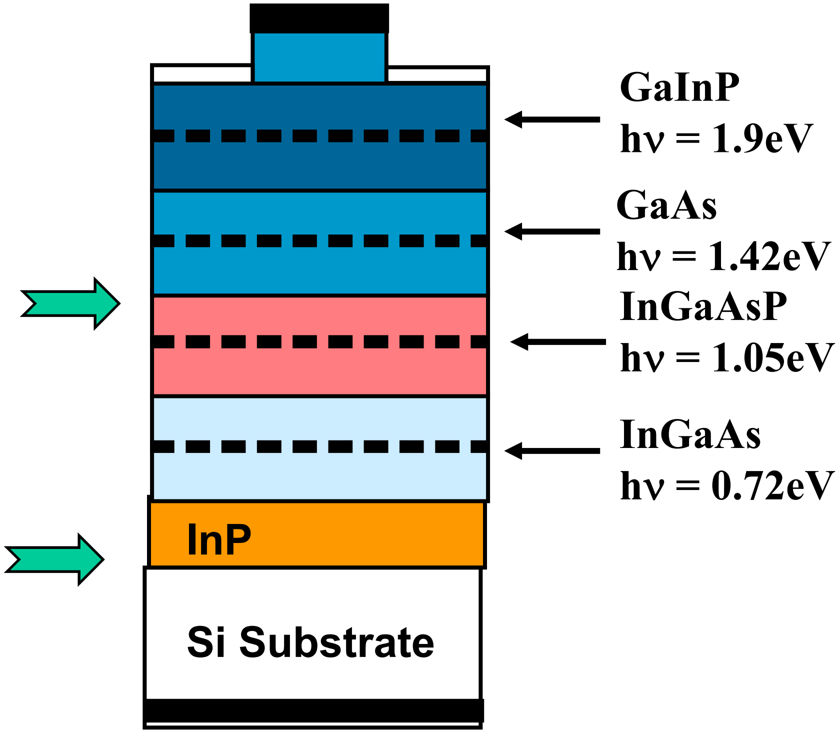


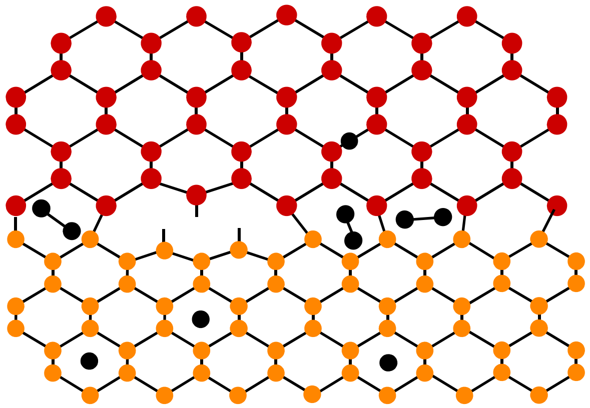
Band Gap versus Lattice Constant



bonded interconnection

Subcell Integration by Bonding





High-performance solar cells:

- Multi-junction, current-matched tandem monolithic solar cell
- Optimal bandgap sequence achievable

Wafer bonding:

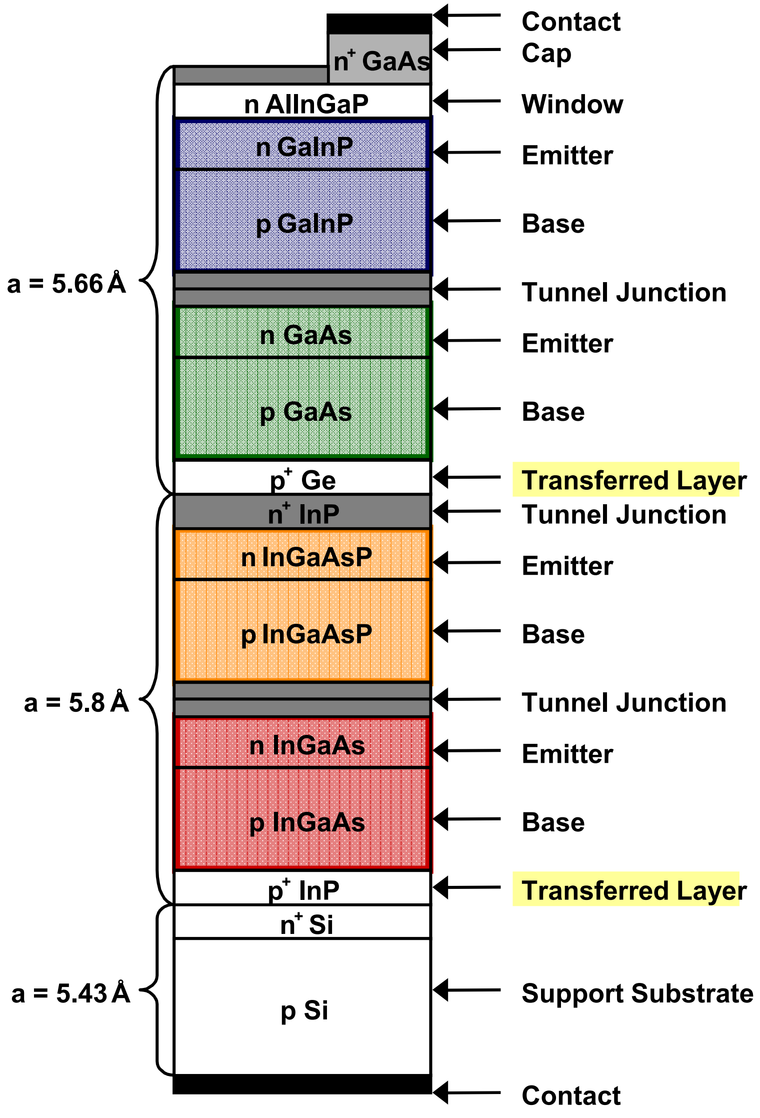
- Non-lattice-matched materials integration
- Misfit defect isolation at only bonded interface

4 Junction Solar Cell Device via Bonding/Layer Transfer

Series-connected GaInP/GaAs/ InGaAsP/InGaAs	Band Gap (eV)	GaInP	1.90
		GaAs	1.42
		InGaAsP	1.02
		InGaAs	0.60

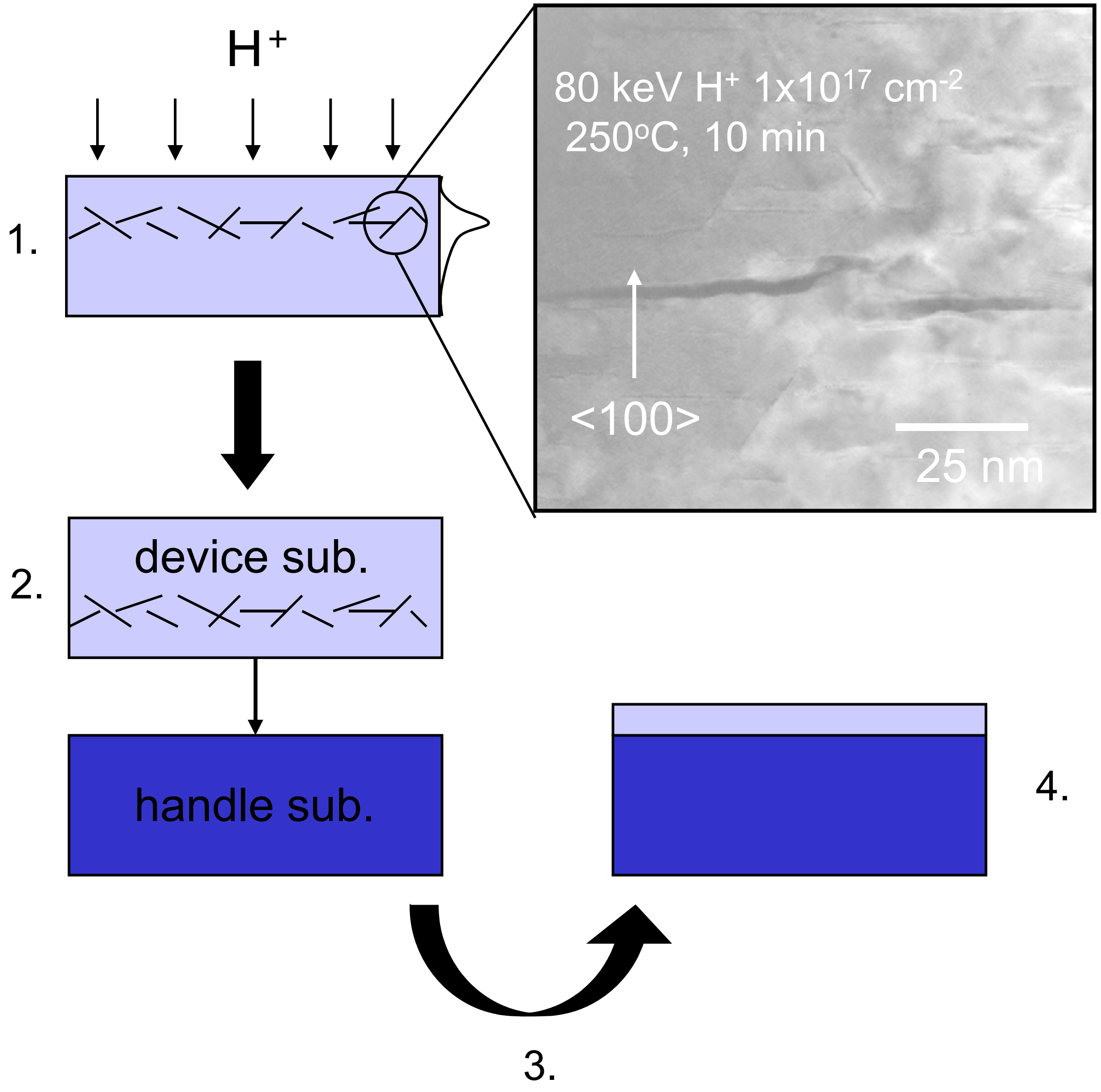
Detailed Balance Efficiency = 54.9%

J.M. Zahler Ph.D. Thesis, California Institute of Technology (2005)

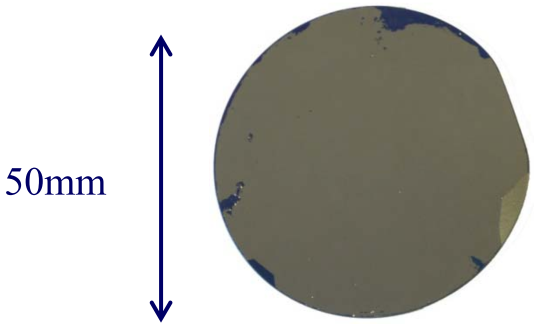


Wafer Bonding/Layer Transfer Process

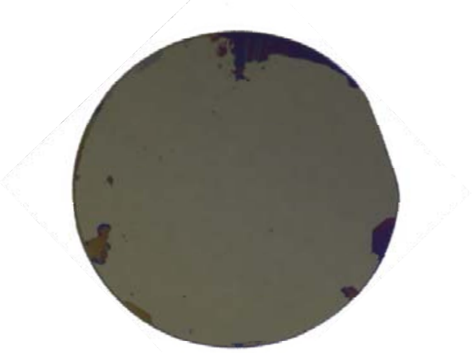
1. Ion implantation:
    - Defects / Internal Surfaces
    - Pressure
2. Bond formation:
    - Smooth, particle-free surfaces
    - Surface activation
3. Thermal processing:
    - Bond strengthening
    - Exfoliation
4. Result:
    - Thin, uniform transferred film



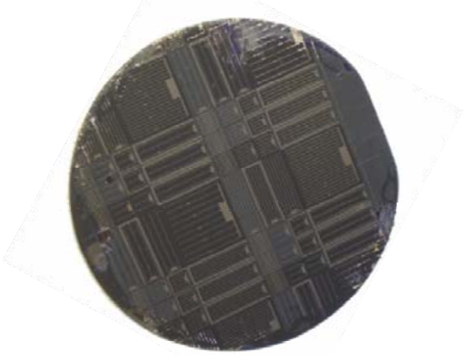
InGaP/GaAs/Ge/SiO$_2$/Si Two Junction Cells Fabricated by Wafer Bonding/Layer Transfer



As-Transferred Ge/Si

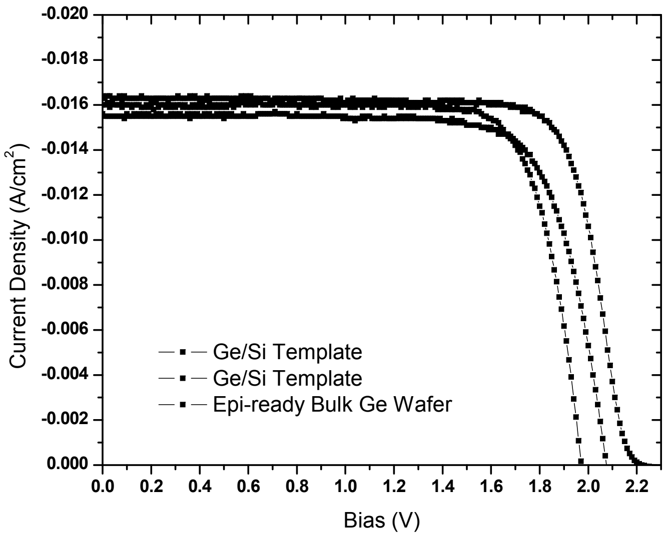


After Ge wet etch & CMP

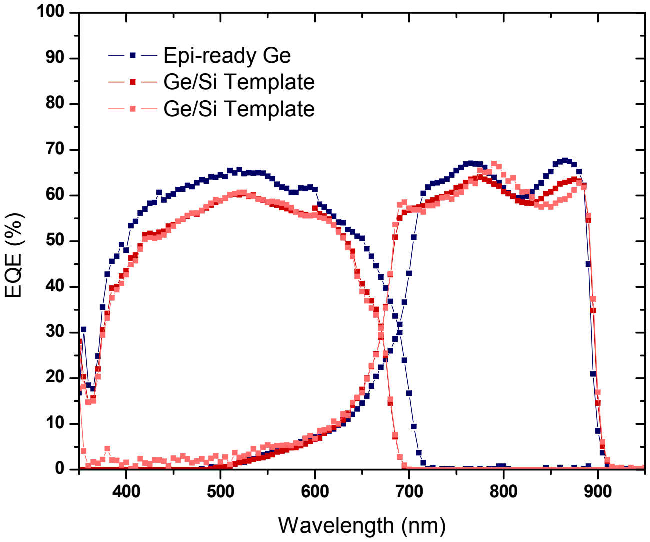


After InGaP/GaAs Growth and Cell Processing

AM 1.5D Light I-V



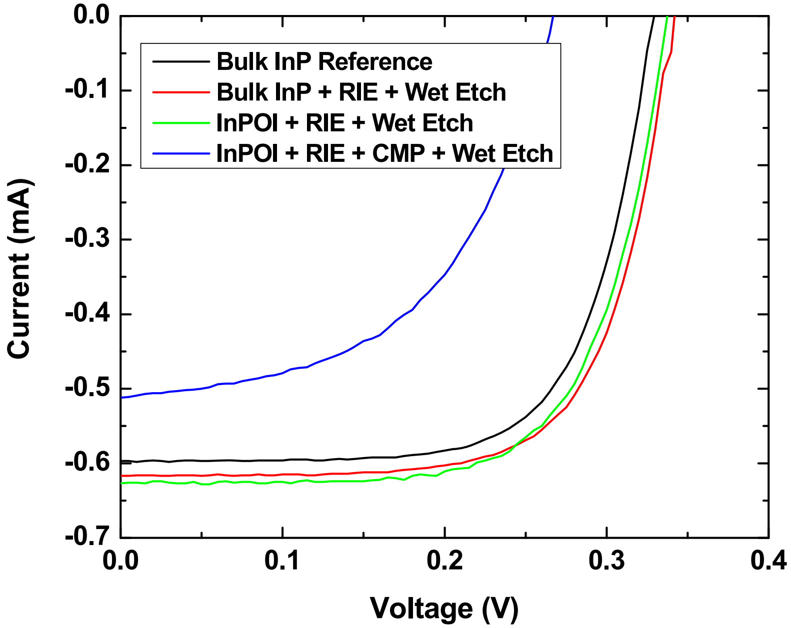
AM 1.5D Spectral Response

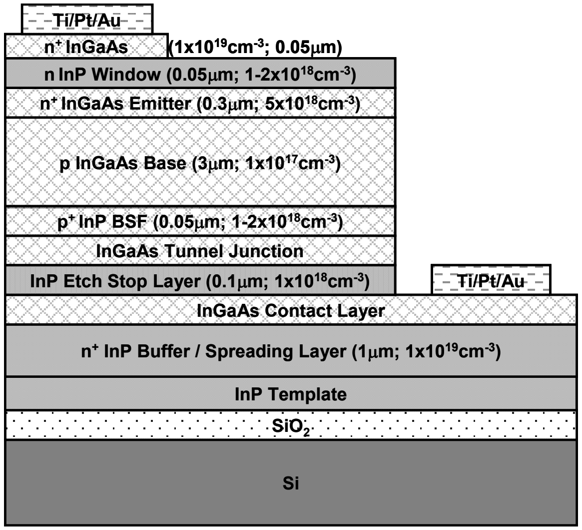


Cell Data

	Bulk Ge Control	Ge/Si Template
J_{sc}	0.016	0.016
V_{oc}	2.22	1.97
FF	0.77	0.79
Eff	~28%	~25%

InGaAs/InP/Si Low Bandgap Cell with Performance Equivalent to State-of-the-Art InGaAs/InP




Ti/Pt/Au

n$^+$ InGaAs (1x10^{19}cm^{-3}; 0.05μm)

n InP Window (0.05μm; 1-2x10^{18}cm^{-3})

n$^+$ InGaAs Emitter (0.3μm; 5x10^{18}cm^{-3})

p InGaAs Base (3μm; 1x10^{17}cm^{-3})

p$^+$ InP BSF (0.05μm; 1-2x10^{18}cm^{-3})

InGaAs Tunnel Junction

InP Etch Stop Layer (0.1μm; 1x10^{18}cm^{-3})

Ti/Pt/Au

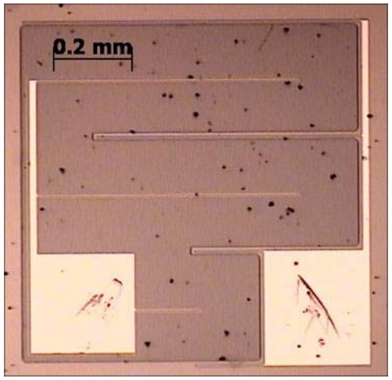
InGaAs Contact Layer

n$^+$ InP Buffer / Spreading Layer (1μm; 1x10^{19}cm^{-3})

InP Template

SiO_2

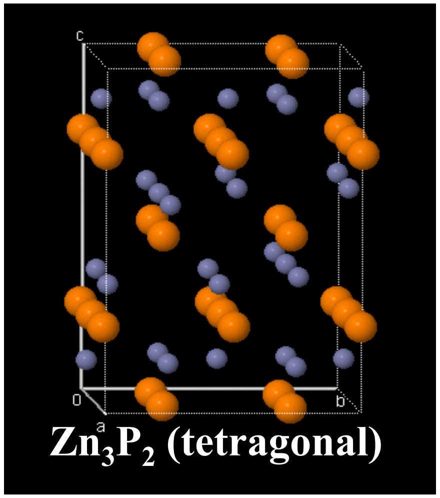
Si



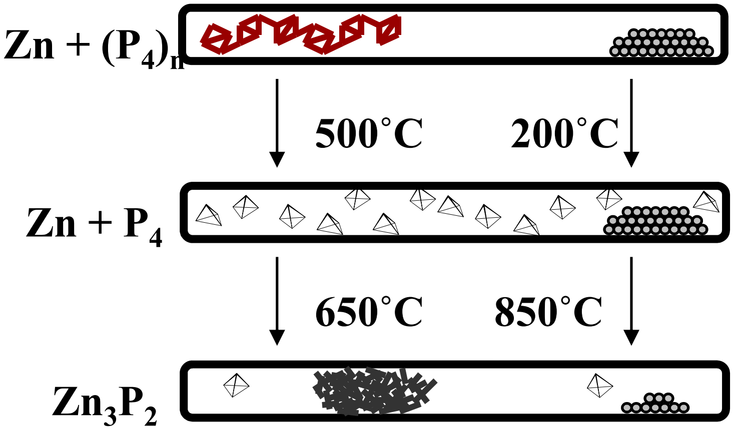
Cell Description	***Jsc*(mA/cm²)**	***Voc*(mV)**	**Fill Factor**
Bulk InP Reference Cell	-59.7	329	0.686
Bulk InP + RIE + wet etch	-61.7	342	0.685
InPOI #1			
(InPOI + RIE + wet etch)	-62.7	338	0.675

- ***Process Eliminates InP Substrate Cost***
  - ***Template Fabrication Cost ~ Epi Cost***

Zn_3P_2 - An Earth Abundant Semiconductor



Zn_3P_2 (tetragonal)



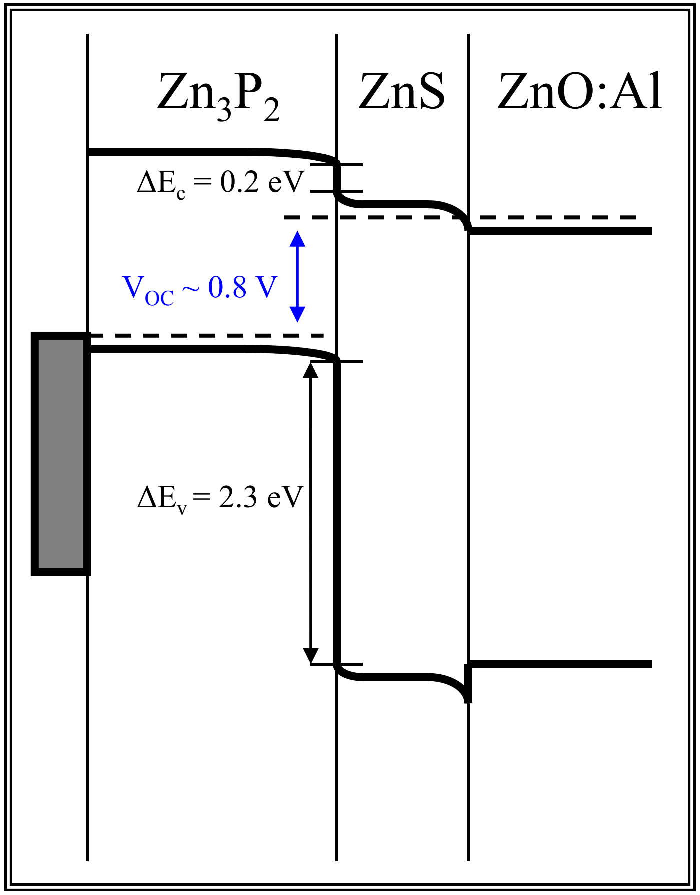
- Energy Gaps – Direct and Indirect nearly aligned @ ~1.3 eV

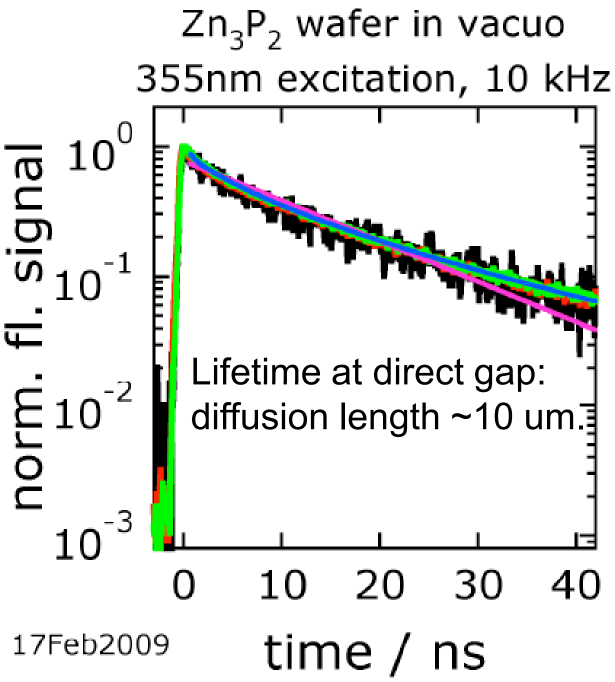
- Zinc Phosphide not commercially available – have to grow crystals

Zn_3P_2 Energy Bands and Heterojunction Cell

Zn_3P_2:ZnS:ZnO Band Alignment

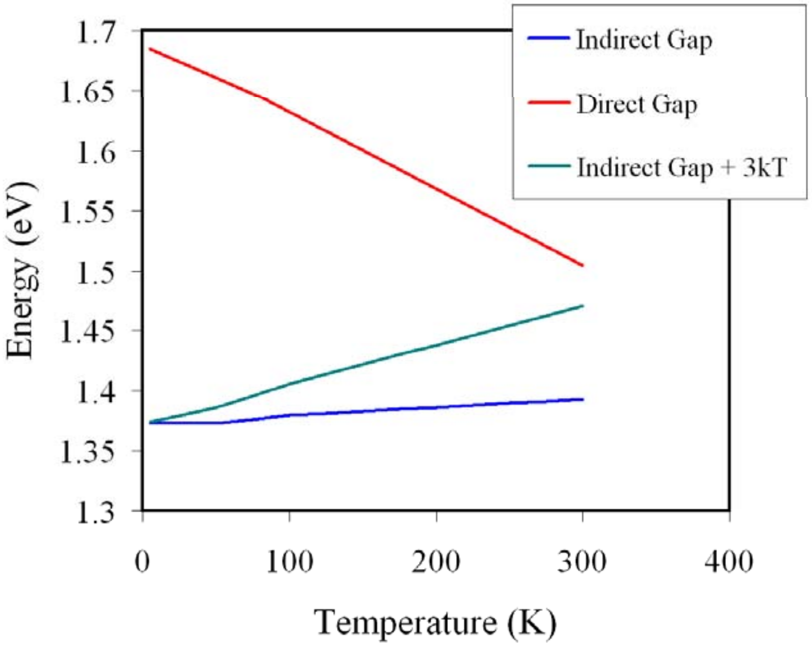
AM 1.5 G Illumination



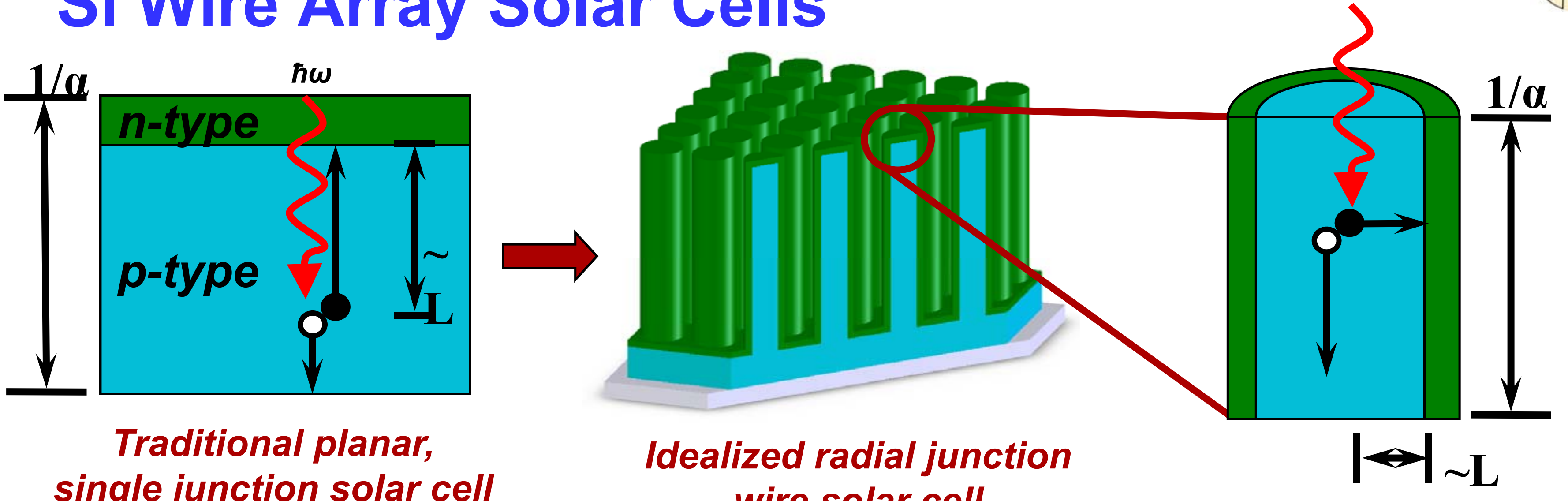


Lifetime at direct gap:
diffusion length ~10 um.

17Feb2009



Si Wire Array Solar Cells



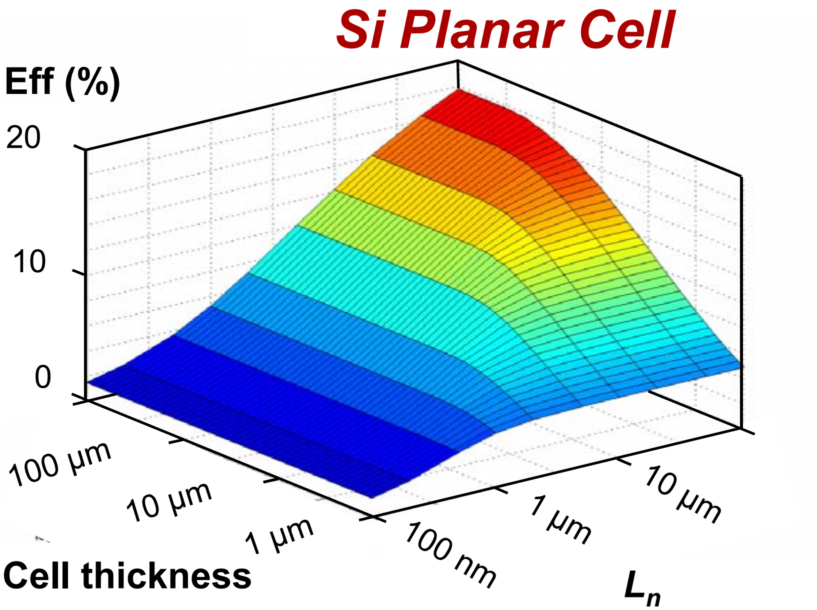
Traditional planar, single junction solar cell

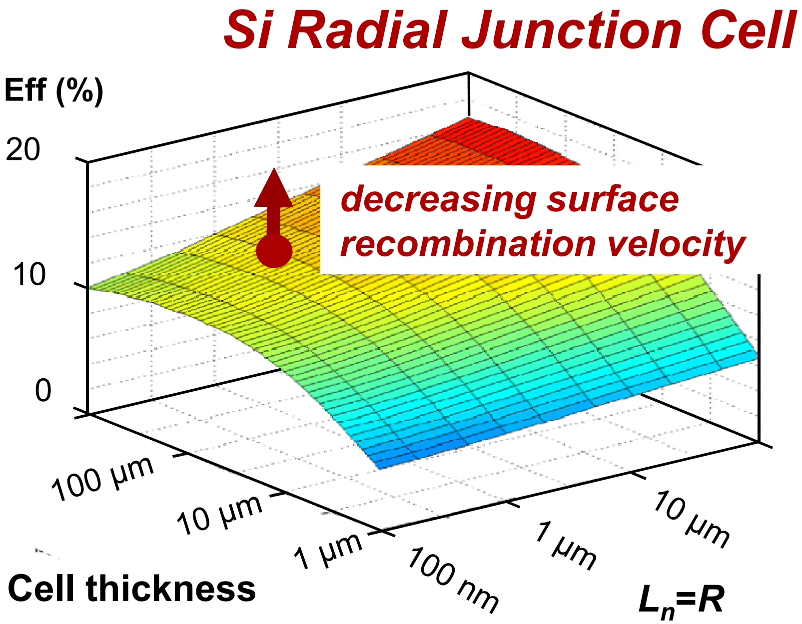
Idealized radial junction wire solar cell

solar cell based on arrays of Si wires features:

- Orthogonalize light absorption and photocarrier collection
- Retain efficiencies competitive with planar, crystalline Si solar cells
- Compatible with low minority carrier diffusion length
- Si wire arrays formed by $SiCl_4$ chemical vapor deposition
- Can be formed into flexible that are peeled off template Si

Device Modeling



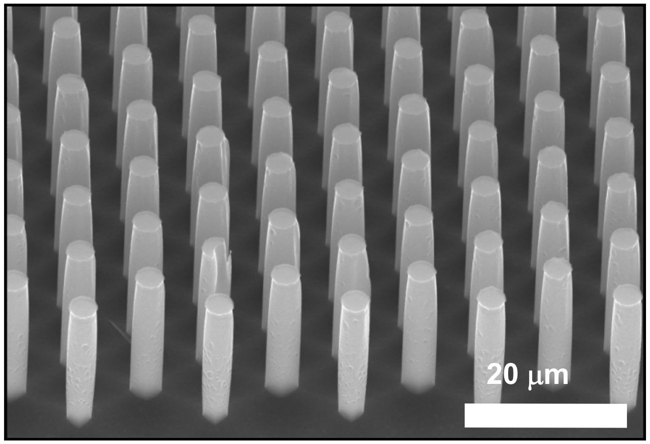


1-D carrier transport modeling indicates that high efficiencies can be maintained for low diffusion length materials

Modeling indicates η > 15%, V_{oc} > 500 mV achievable with
L_n = 1 µm in Si, provided junction recombination is not limiting

B. M. Kayes et al., J. Appl. Phys. 97, 114302 (2005)

Prototype Si Wire Array Devices



Reactive Ion Etching used to define wires, to deconvolute

- Device geometry effects

from

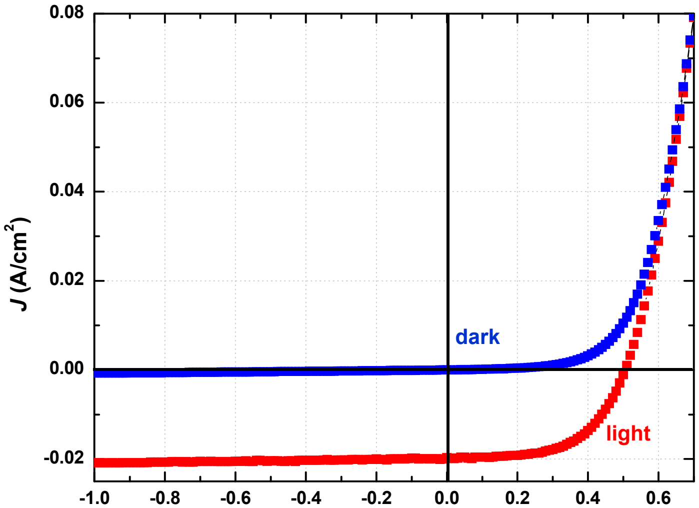
- material quality issues, and
- device fabrication difficulties

With 5 μm diameter, 50 μm long wires we see:

device size ~0.1 cm^2, V$_{oc}$ = 505 mV,
J$_{sc}$ ≈ 20 mA/cm^2, FF = 58 %, η≈ 5.7 %

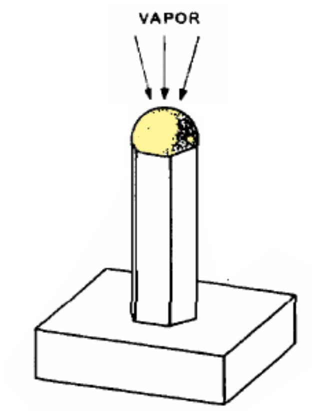
(diffused B emitter, 5 Ω cm n-Si(100) base)

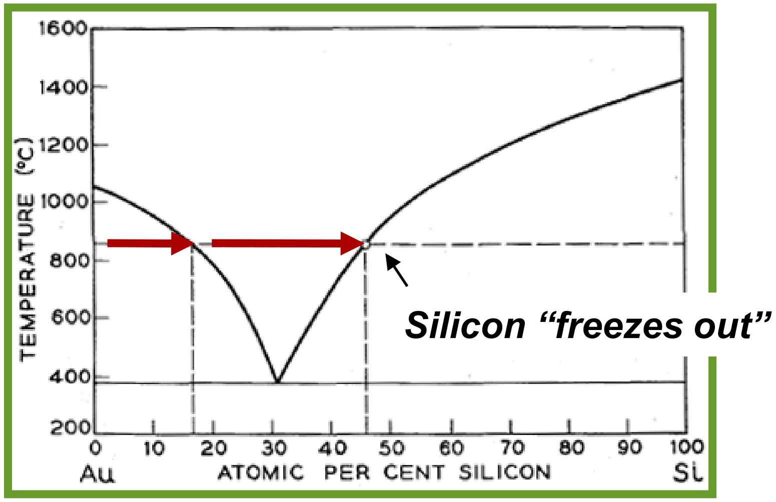
High V$_{oc}$ achievable in Si wire array cells



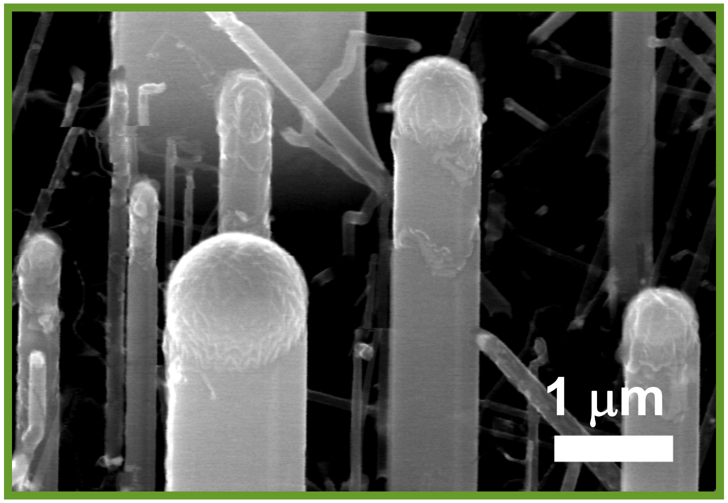
B. M. Kayes et al., Proc. of 33rd IEEE PVSC (2008)

Vapor-Liquid-Solid (VLS) Growth





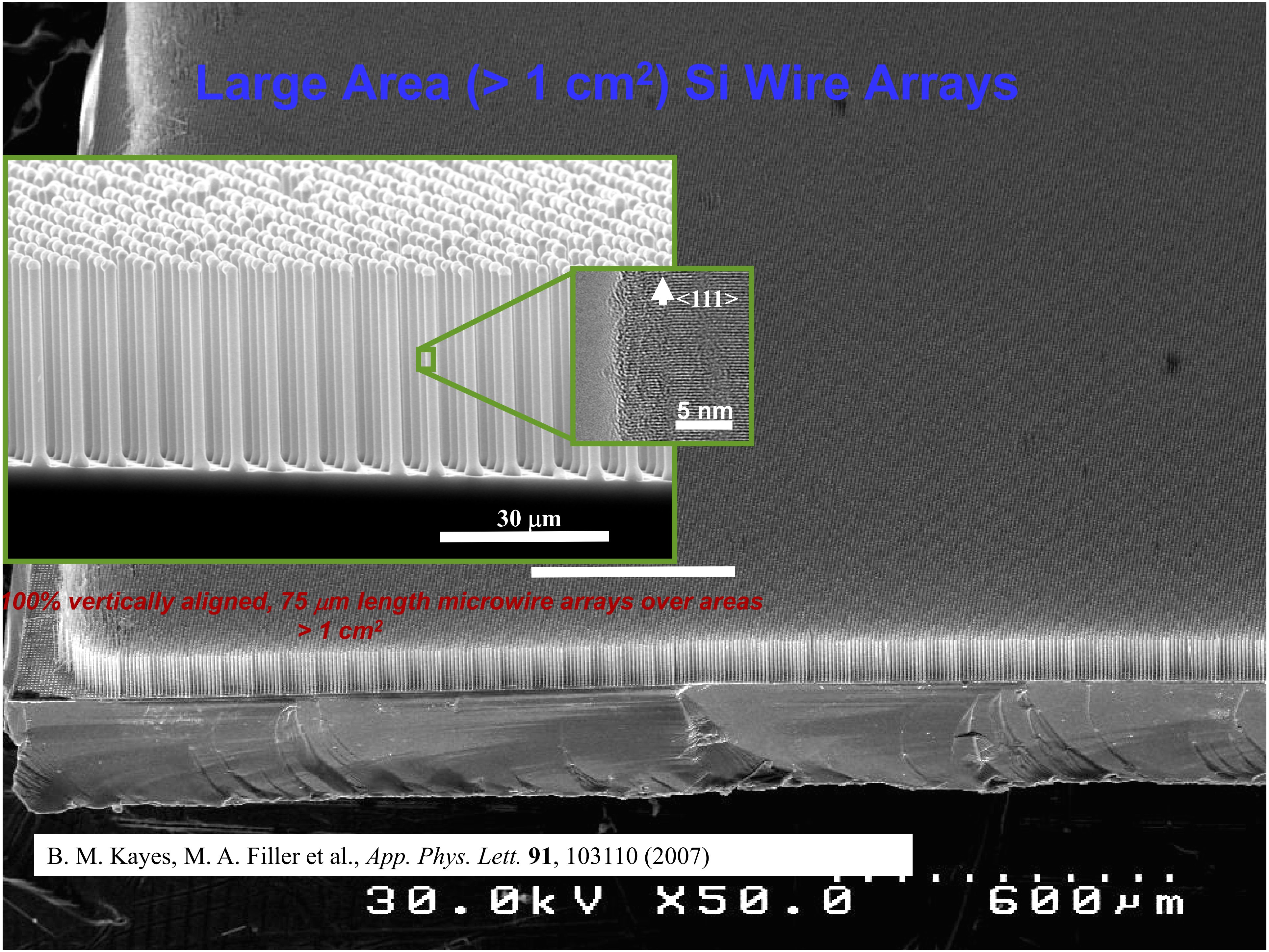
Silicon "freezes out"



- Single crystal wires
- Growth direction controlled by substrate orientation
- High growth rates (up to ~ μm/s)
- Inexpensive gas phase precursors
- Atmospheric pressure growth possible
- Wide range of diameters possible

R. S. Wagner and W. C. Ellis, *App. Phys. Lett.* **4**, 89 (1964)

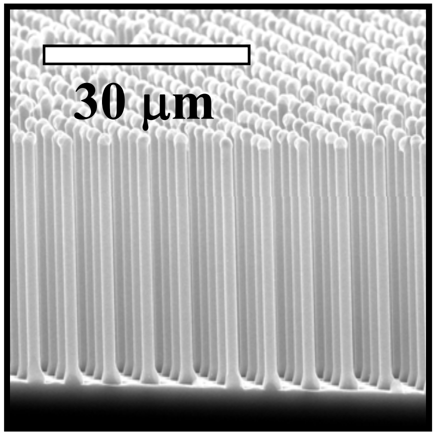
Large Area (> 1 cm^2) Si Wire Arrays



100% vertically aligned, 75 µm length microwire arrays over areas > 1 cm^2

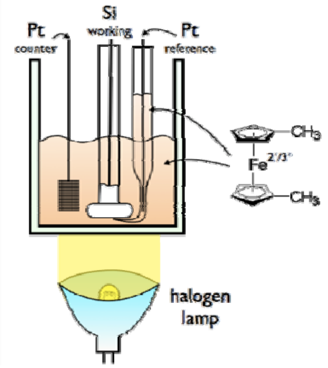
B. M. Kayes, M. A. Filler et al., *App. Phys. Lett.* **91**, 103110 (2007)

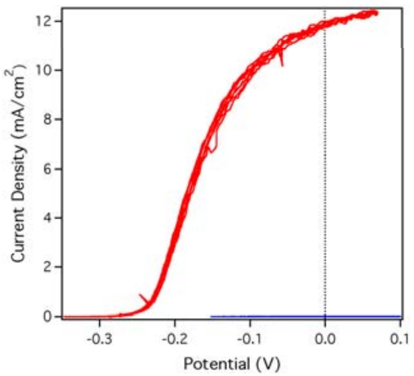
Si Wire Array Cell Milestones



Growth of vertically-aligned, patterned Si wire arrays over large (>1 cm^2) areas, using Au, Cu, and Ni catalyst metals.

Kayes, B. M.; Filler, M. A.; Putnam, M. C.; Kelzenberg, M. D.; Lewis, N. S.; Atwater, H. A. *Applied Physics Letters* **2007,** 91, (10), 103110-3.



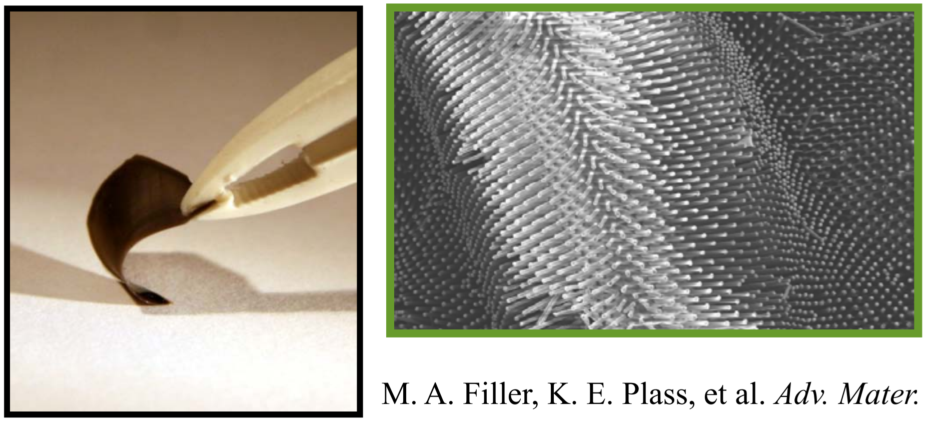


Demonstration of Si wire array photoelectrochemical cell

Maiolo, J. R. I.; Kayes, B. M.; Filler, M. A.; Putnam, M. C.; Kelzenberg, M. D.; Atwater, H. A.; Lewis, N. S. *Journal of the American Chemical Society* **2007,** 129, (41), 12346-12347.

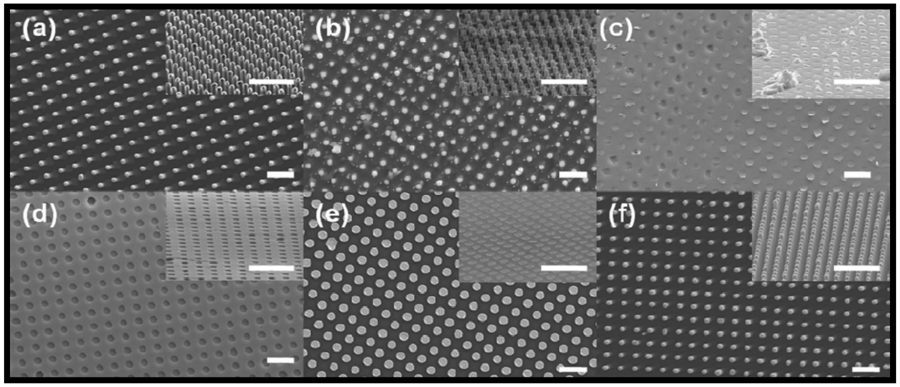
Goodey, A. P.; et. al. *J. Am. Chem. Soc.* **2007,** 129, 12344-12345.

Si Wire Array Cell Milestones



M. A. Filler, K. E. Plass, et al. *Adv. Mater.* (2008)

Removal of wires from growth substrate as a flexible, polymer-embedded, ordered wire array

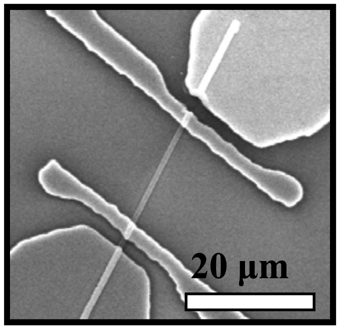


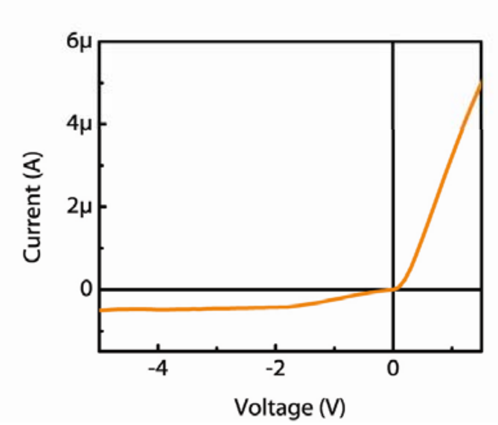
Recycling of patterned growth substrate and repeated re-growth of wire arrays

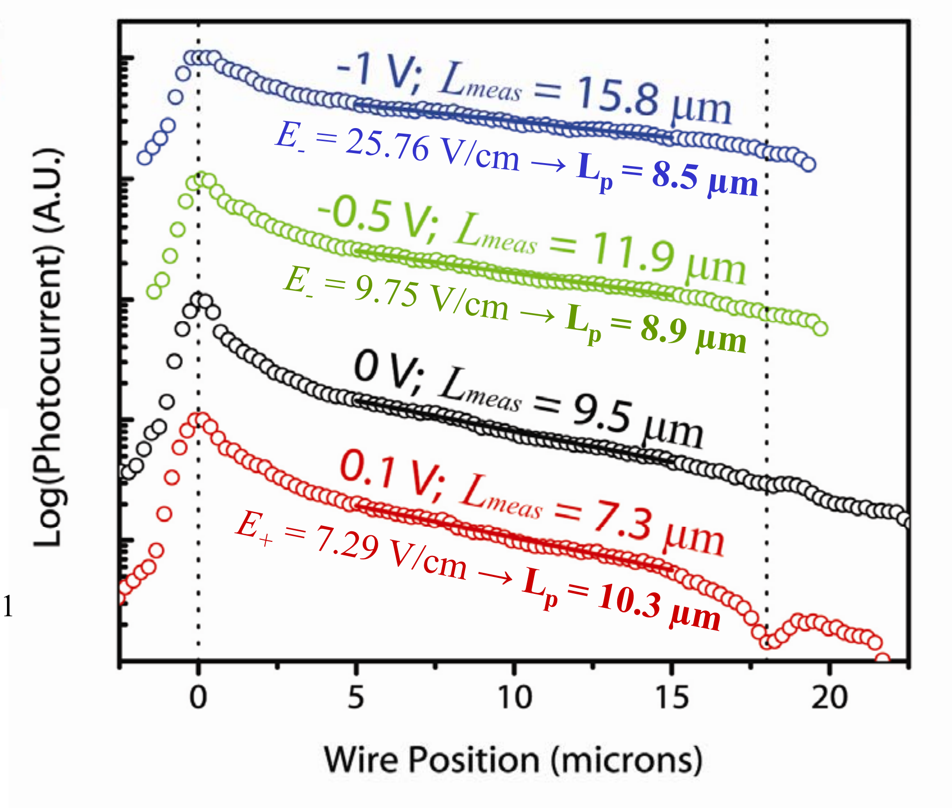
Spurgeon, J. M.; Plass, K. E.; Kayes, B. M.; Brunschwig, B. S.; Atwater, H. A.; Lewis, N. S. *Applied Physics Letters* **2008,** 93, (3), 032112-3.

Diffusion Length from Scanning Photocurrent of Single Wires

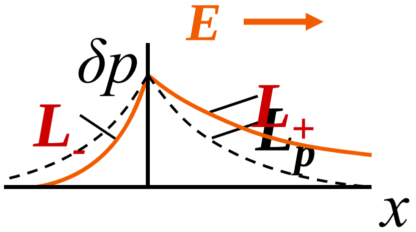
Ni-catalyzed NW







R_{wire} = 230 kΩ → N = 10^{16} cm^{-3}

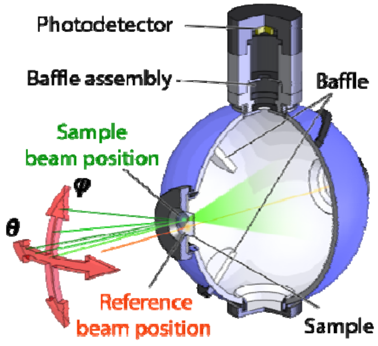


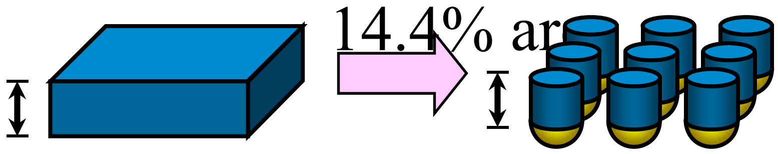
$$L_\pm = L_p\left(\frac{qL_p}{kT}E + 1\right)^{\mp 1}$$

A. L. Fahrenbuch and R. H. Bube.
“Fundamentals of Solar Cells”, pp. 83

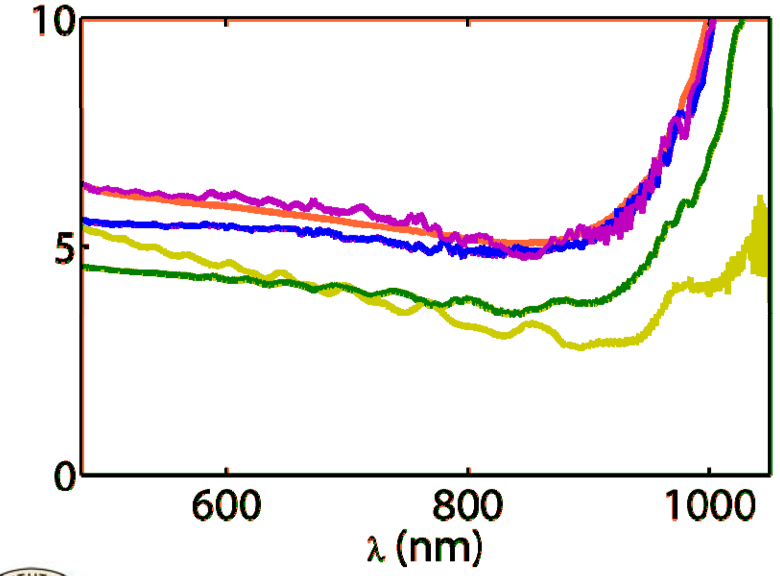
$L_{p,eff} \sim 10\ \mu m$

Absorption concentration: Si wires act as waveguide array

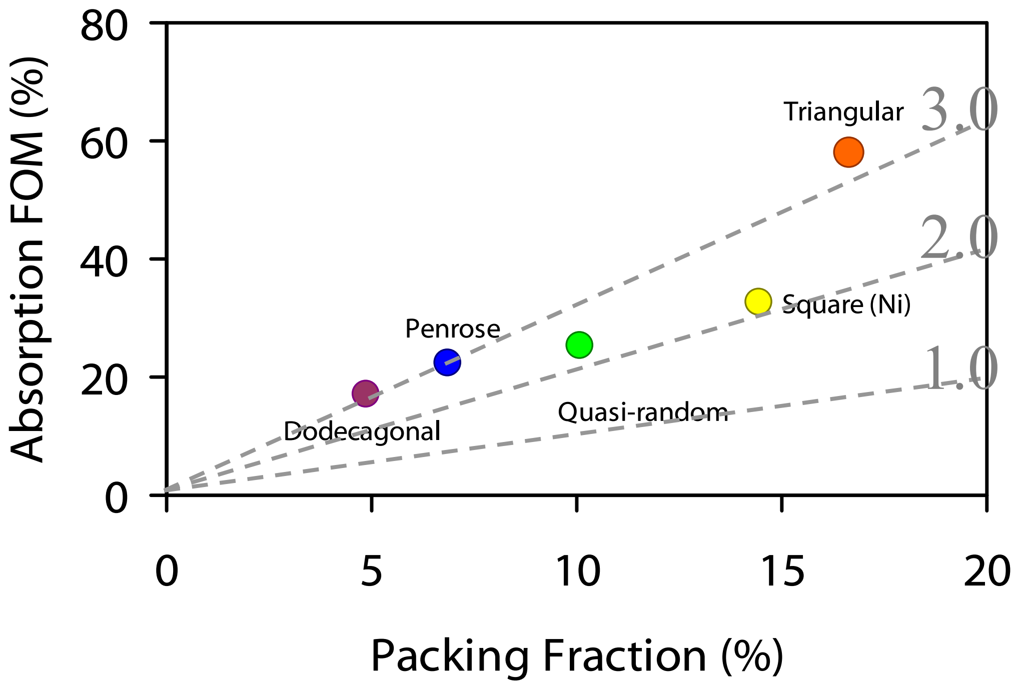




Volumetric absorption concentration

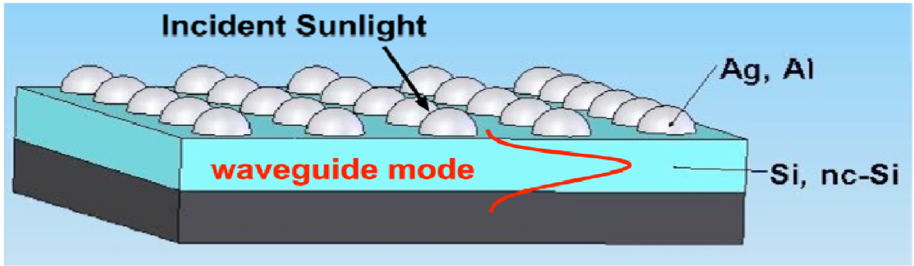


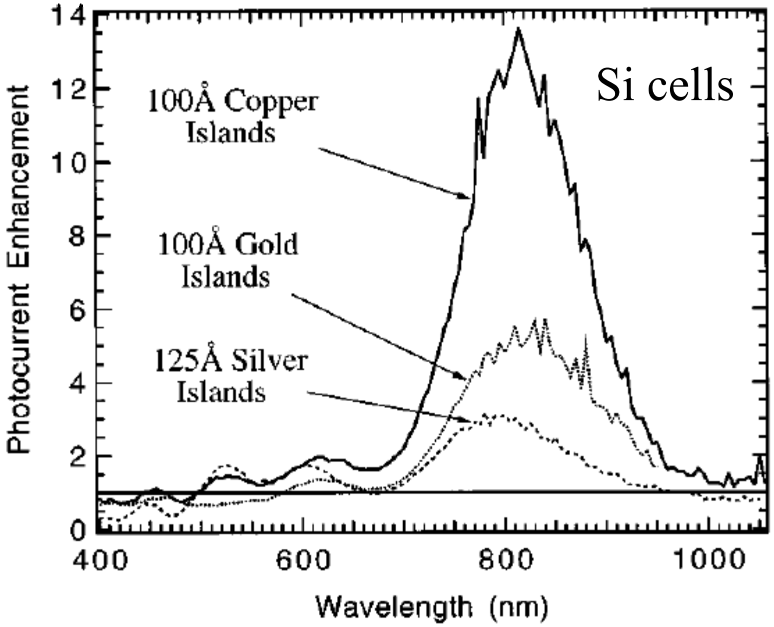
Percent solar absorption vs. area fraction



Two Plasmonic PV concepts

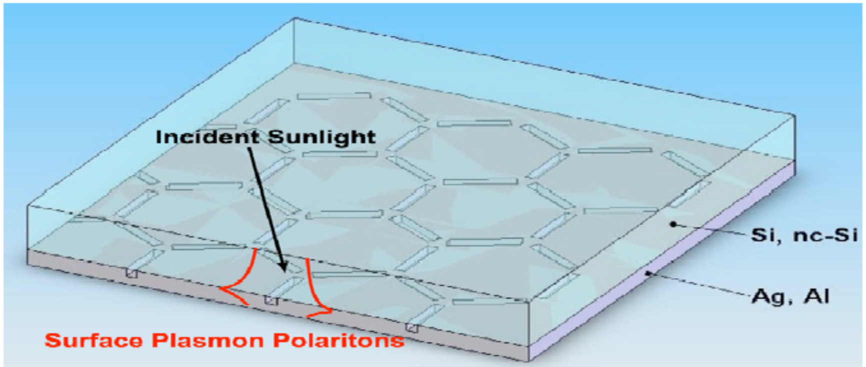
Nanoparticle Scatterer/ Dielectric Waveguide

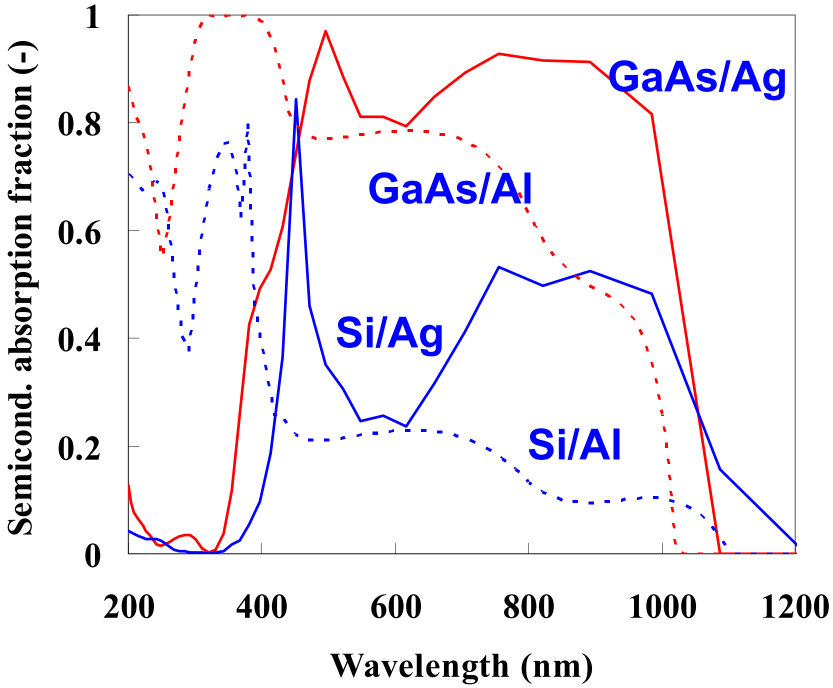




H. R. Stuart and D. G. Hall, APL 69, 2327, 1996
S. Pillai et al, APL 88, 161102, 2006

Backside SPP Waveguide

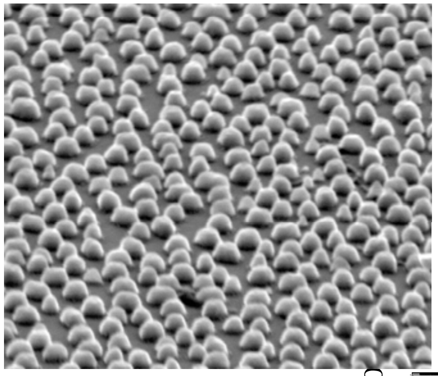




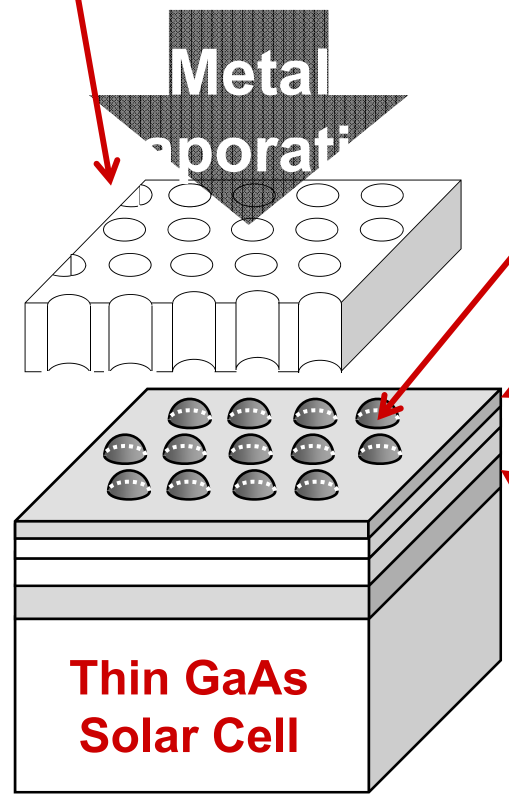
V.E. Ferry, et.al. Nano Letters, 8, 4391-4397 (2008)

Optically thin plasmonic GaAs solar cell

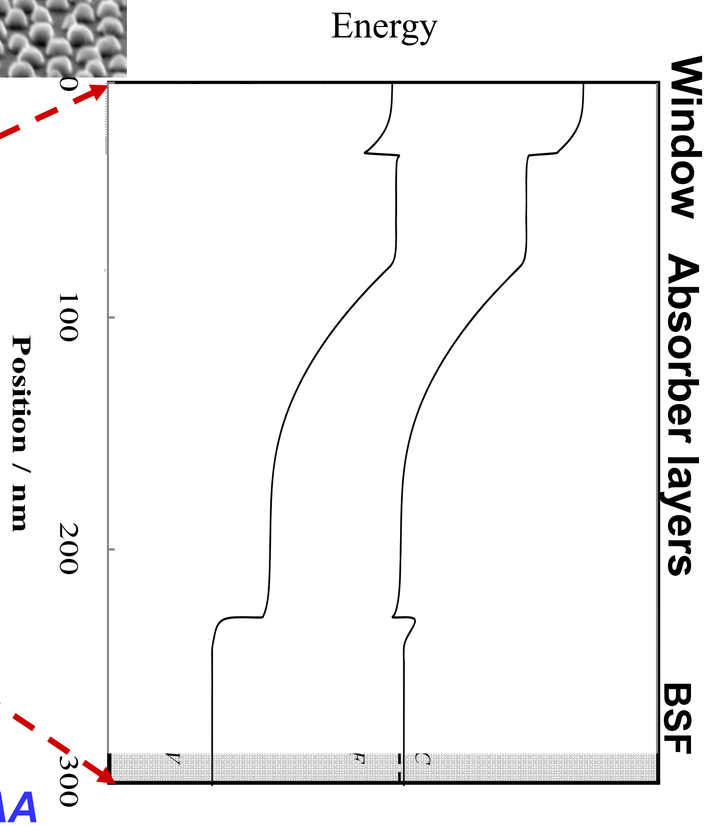
Ag, Al Nanoparticles



Porous Al_2O_3 Template

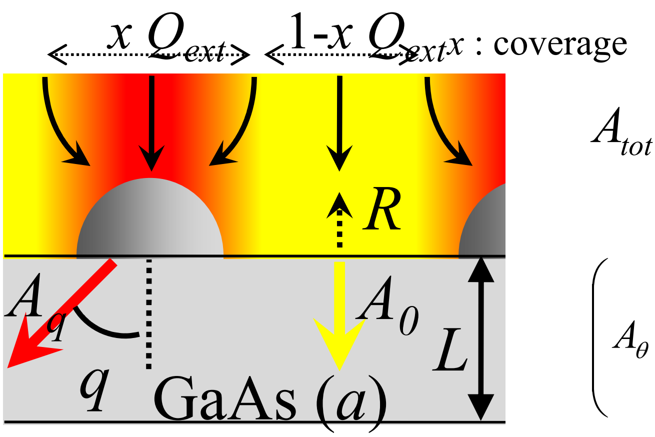


Thin GaAs Solar Cell



K.Nakayama, K.Tanabe, and HAA
Appl. Phys. Lett. 93, 121904 (2008)

Particle scattering and absorption effects on spectral response

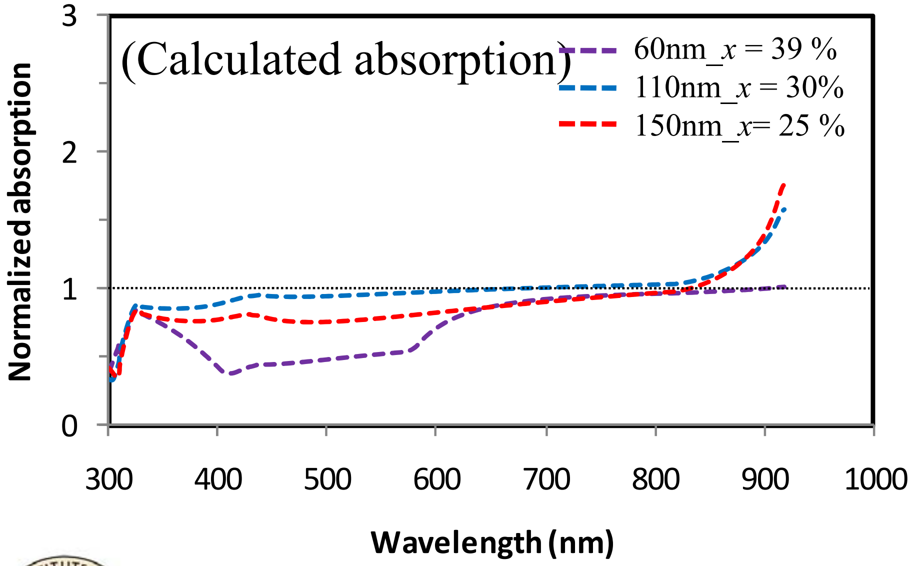


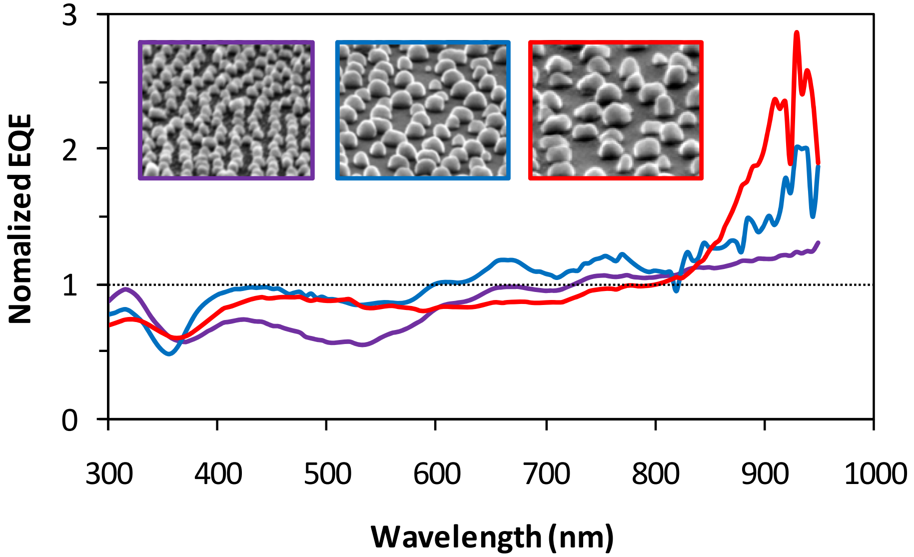
Total absorption

$$A_{tot}(\lambda) = \xi Q_{ext}(\lambda)\eta_{rad}(\lambda)A_\theta(\lambda) \quad \text{(scattered)}$$

$$+\left(1-\xi Q_{ext}(\lambda)\right)\left(1-R(\lambda)\right)A_0(\lambda) \quad \text{(direct)}$$

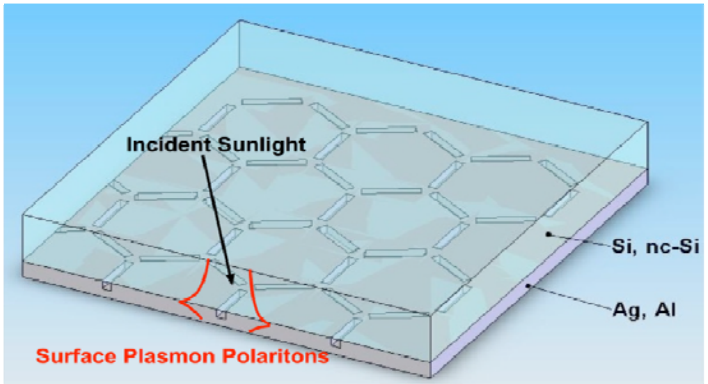
$$\left(A_\theta(\lambda) = \int_0^{\pi/2} \frac{1+\cos^2\theta}{\int_0^{\pi}\left(1+\cos^2\theta\right)d\theta} \left\{1-\exp\left(-\alpha(\lambda)\frac{L}{\cos\theta}\right)\right\} d\theta \right)$$

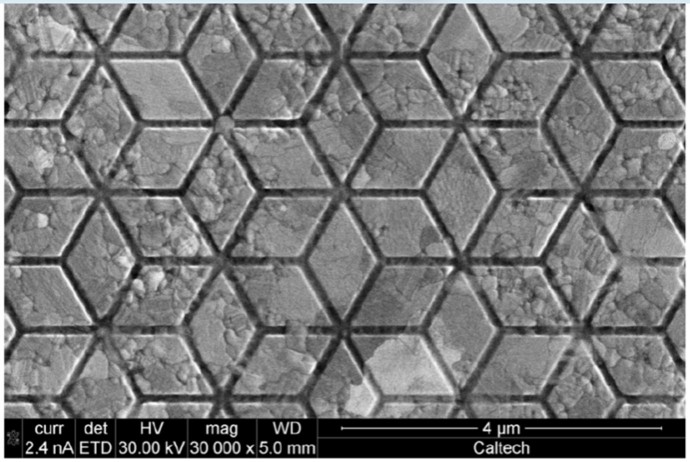


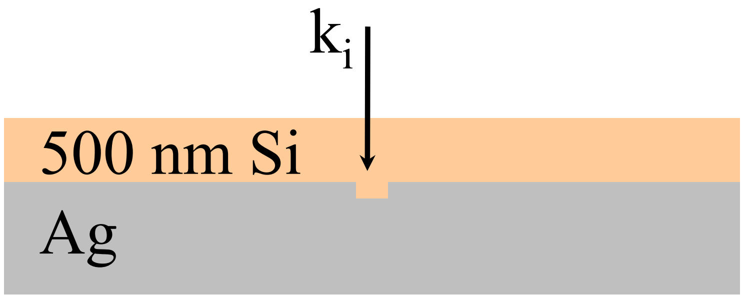


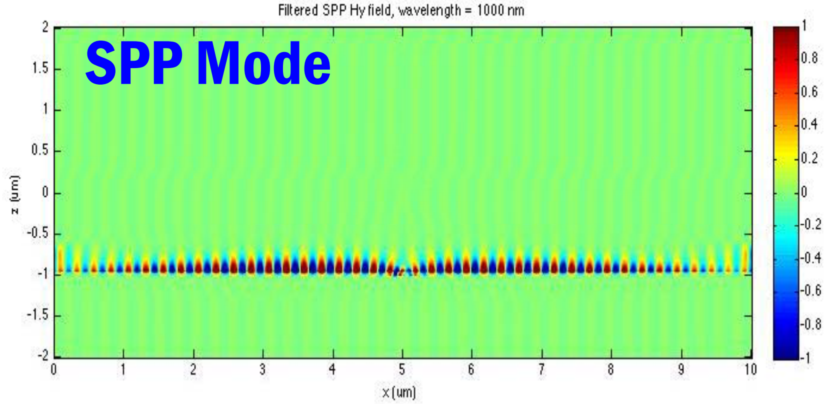
K.Nakayama, K.Tanabe, and HAA Appl. Phys. Lett. 93, 121904 (2008)

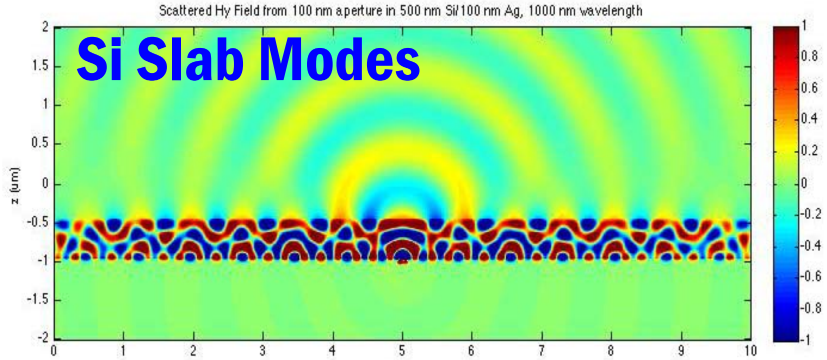
Surface Plasmon Incoupling at Sub-λ (100 nm)Grooves





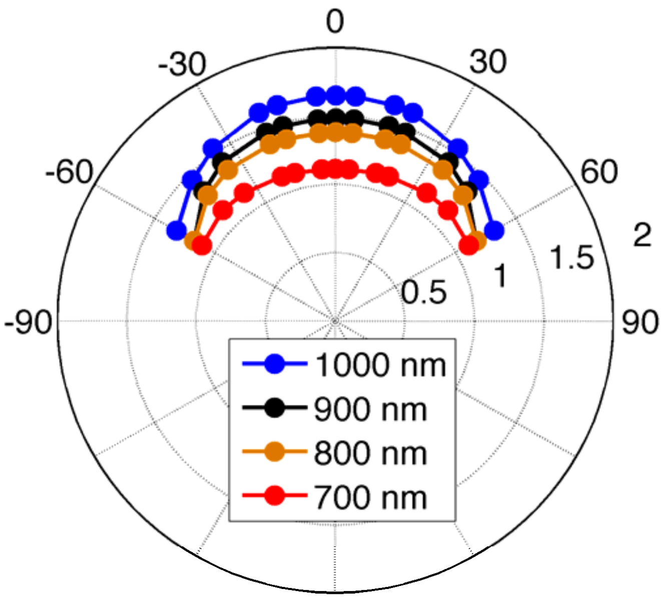




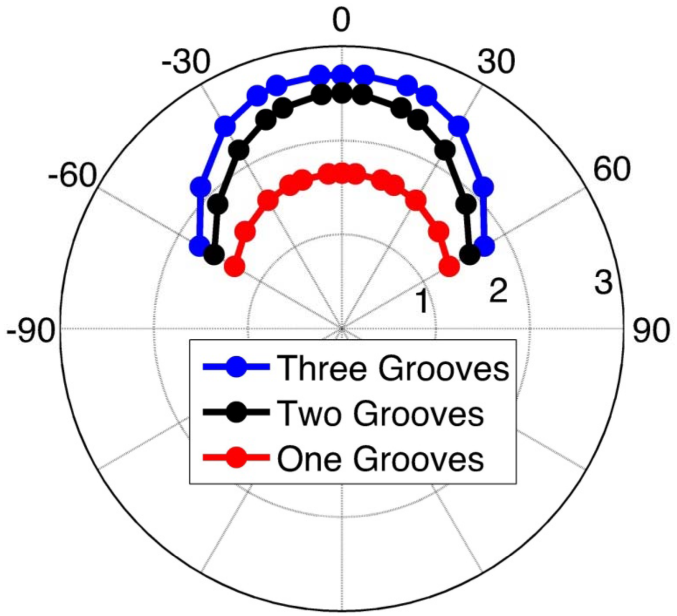


Angular Dependence of Absorption Enhancement

$$AbsorptionEnhancement = \frac{u_a}{u_{nogrooves}} \qquad u_a = \nabla \cdot \mathbf{S} = \frac{1}{2}\int \omega\epsilon''|\mathbf{E}|^2 dxdz$$



Wavelength Dependence

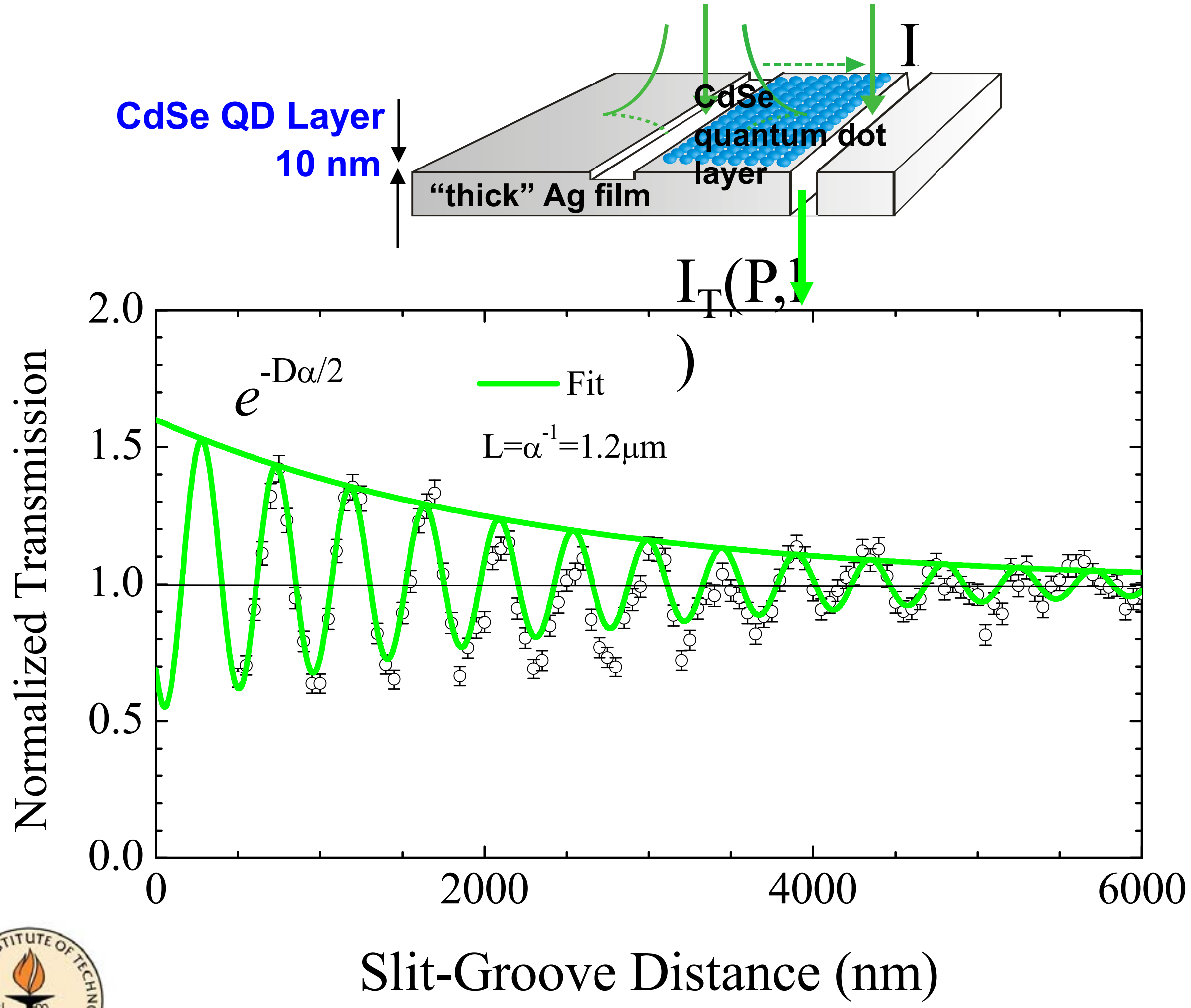


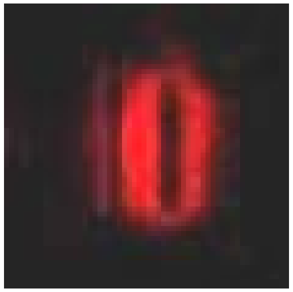
Single vs. Multiple Grooves

V.E. Ferry, et.al. Nano Letters, 8, 4391-4397 (2008)

SPP-Induced Quantum Dot Excitonic Absorption

$$\sigma = 3.5\times10^{-15}\,\mathrm{cm}^2$$
$$\rho \approx 3\times10^{18}\,\mathrm{cm}^{-3}$$
$$\Rightarrow \quad \alpha = \sigma\times\rho \approx 10^4\,\mathrm{cm}^{-1} \quad \Rightarrow \quad L = \alpha^{-1} \approx 10^{-4}\,\mathrm{cm} = 1\,\mu\mathrm{m}$$



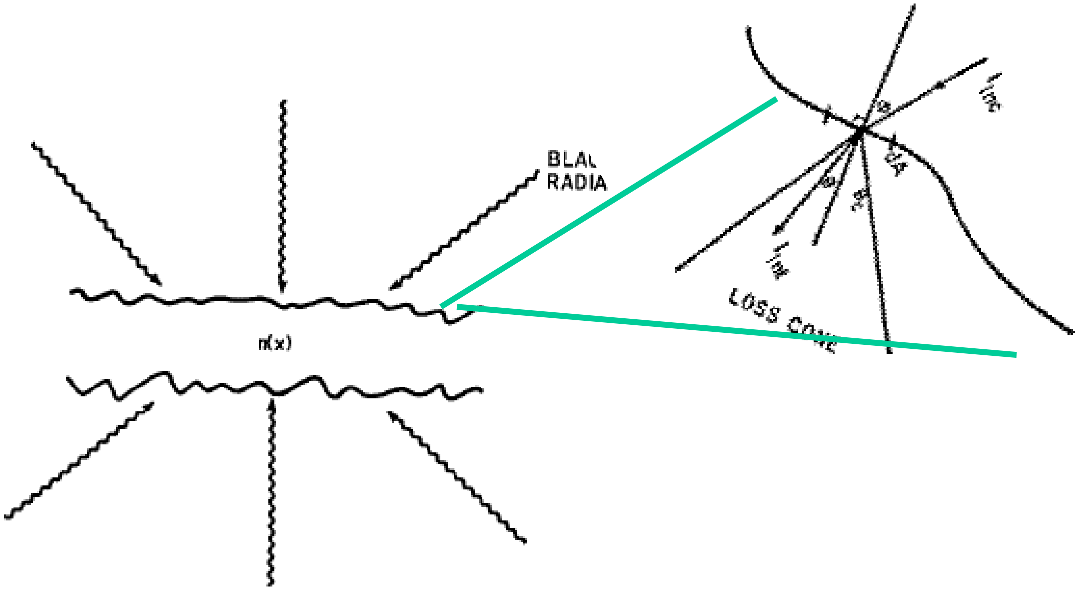


50-100x reduction in optical thickness

Pacifici, et.al., Nature Photonics July 2007

‘Ergodic’ Light Trapping in Thin Sheets

E. Yablonovitch, JOSA 72, 899, (1982)



Assumptions:

geometrical ray optics

optically thin sheet

random texture

Detailed balance between absorption and emission cones

Results:

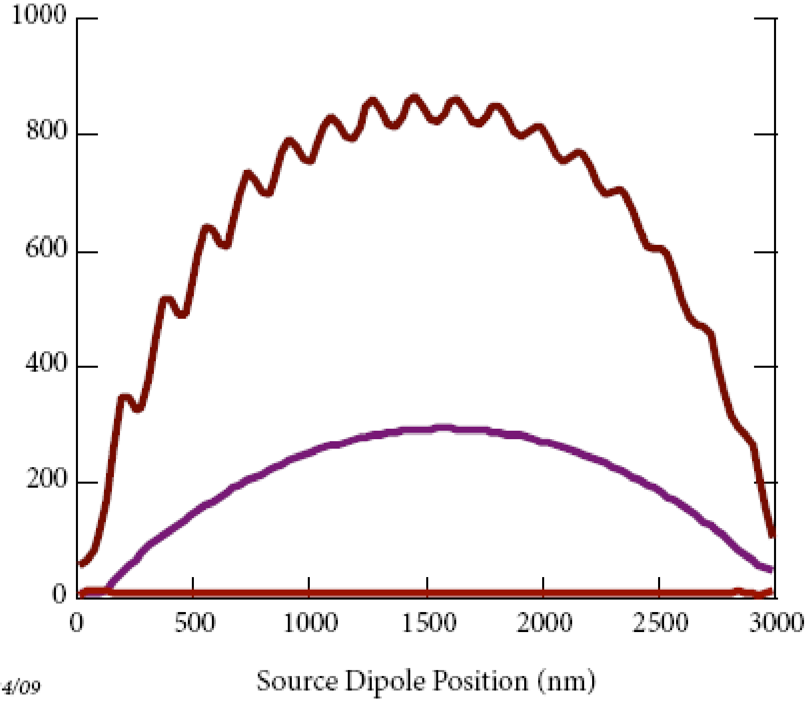
light in medium will be randomized in direction

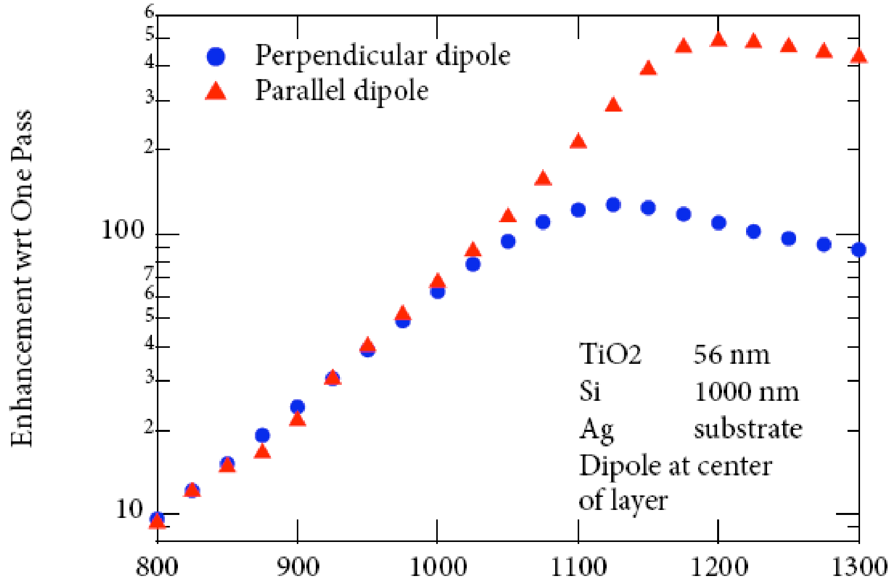
In medium, $2n^2(x)$ times greater intensity than incident light (for Si, ~50x)

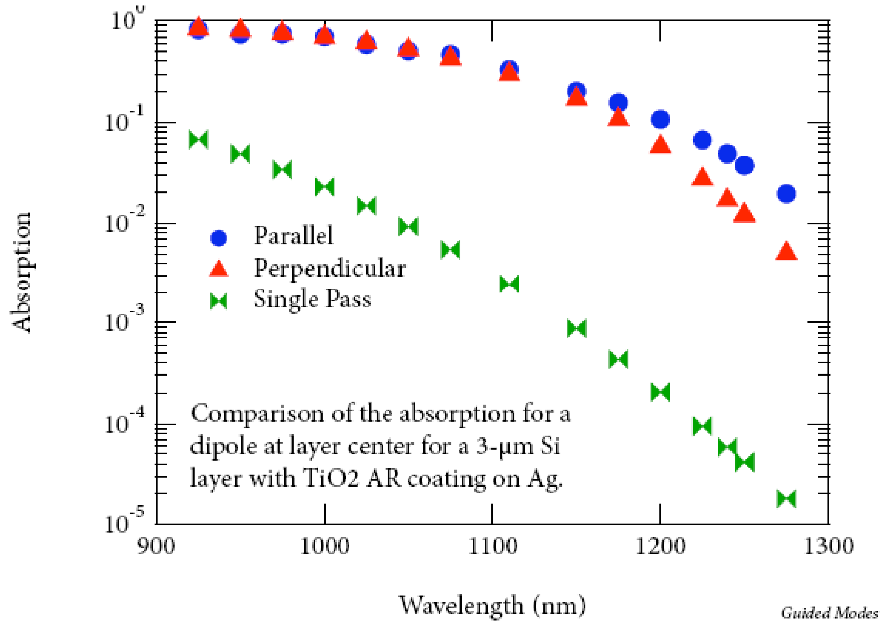
Coupling to Slab Guided Modes Beats the Ergodic Limit

Assumptions:

- Dipole excites modes of a Si slab
- Ag back-side metal
- AR Coating







Comparison of the absorption for a dipole at layer center for a 3-μm Si layer with TiO2 AR coating on Ag.

Summary

- Photovoltaics Resource is TW-capable
- Close to Limiting PV Efficiency for Single Junction Cells
- Silicon PV being overtaken by thin films as leading technology
- Multijunction PV a viable path to >50%
- Wire Array PV – scaleable large area technology

For Terawatt PV:

- Reduce Material Thickness – plasmonics
- Earth-Abundant Materials!

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