Nanotechnology Pathways to Next-Generation Photovoltaics

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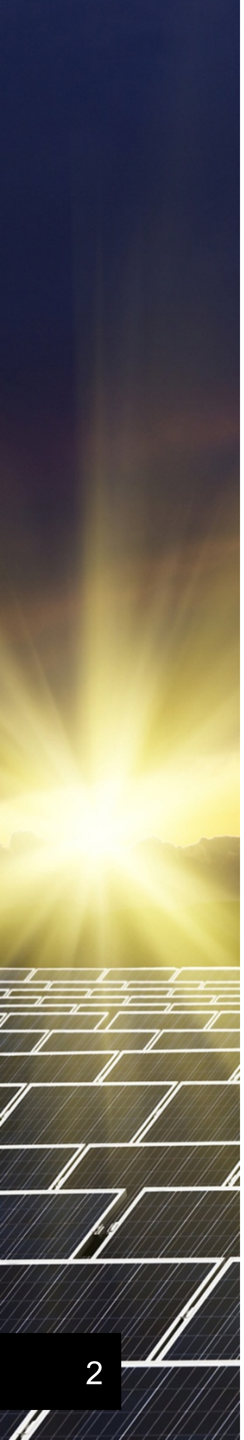
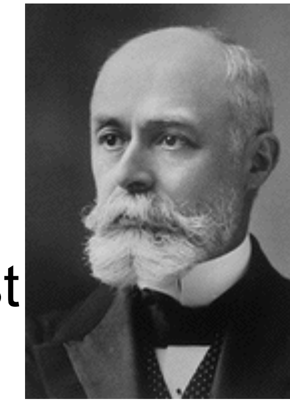


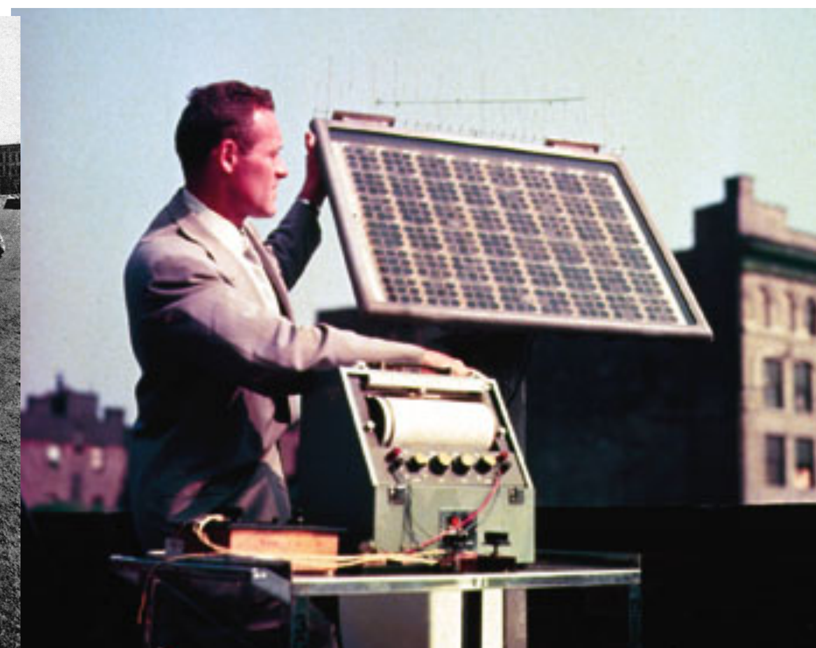
Outline

- **Overview of photovoltaics**
- **Advanced concept approaches for high efficiency**
- **Nanotechnology enabled approaches**
- **Hybrid photovoltaics/solar thermal approaches**

Overview of Photovoltaics

- Direct conversion of sunlight into electricity via the photovoltaic effect
- Photovoltaic effect first discovered by Bequerel (1839); Se/Au solar cell (C. Fritts, 1883)
- Modern junction solar cell (R. Ohl, 1946)
- Silicon junction formation allowed formation of first practical devices, at Bell Labs (1954)

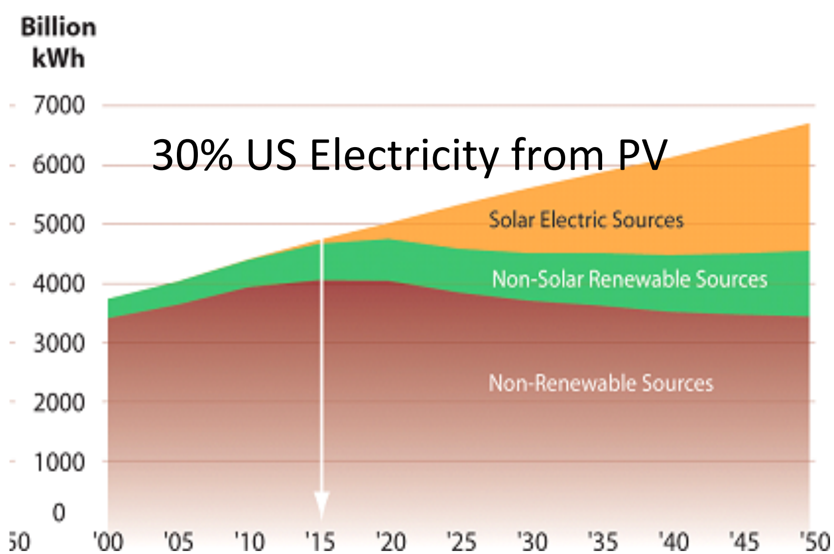


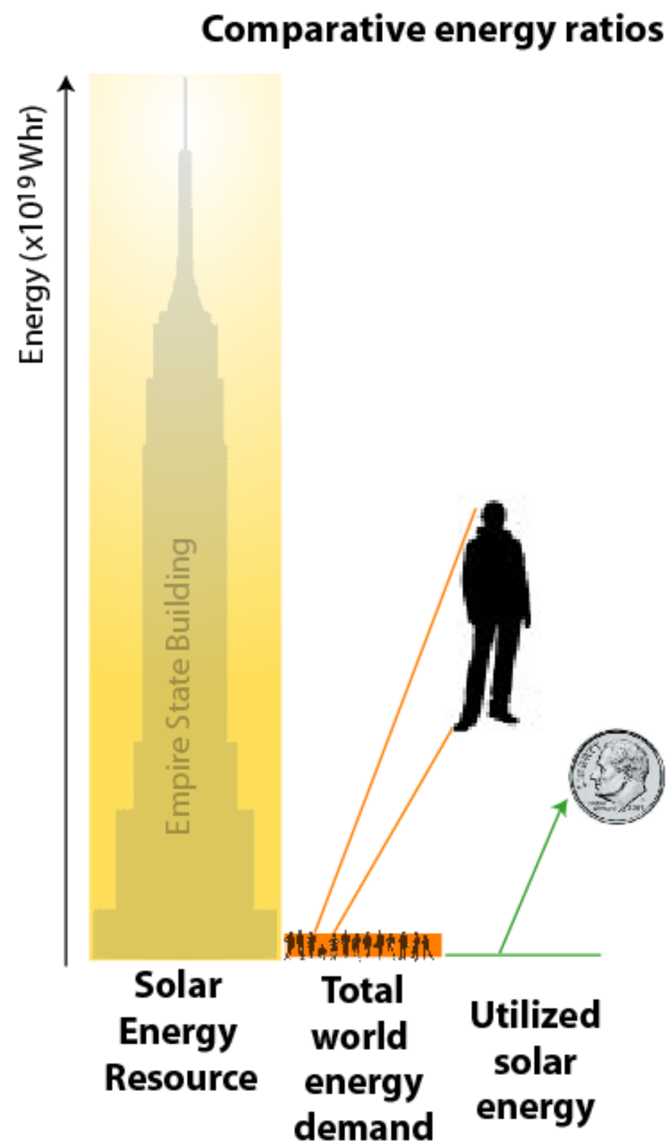


Solar Electricity Opportunity

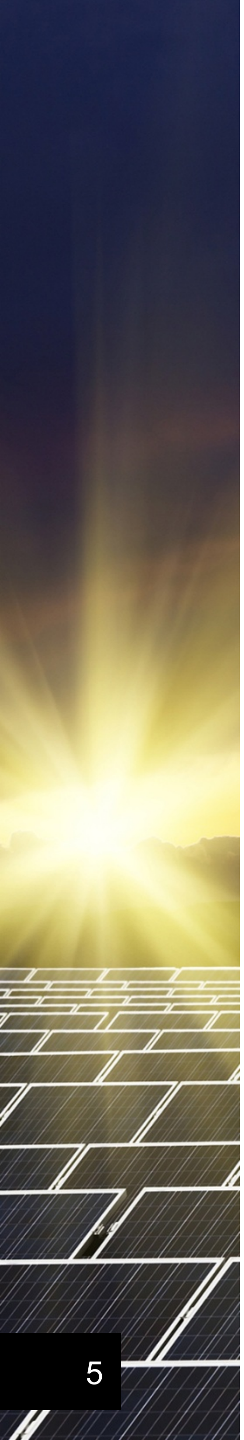
Solar energy is a unique source of energy:

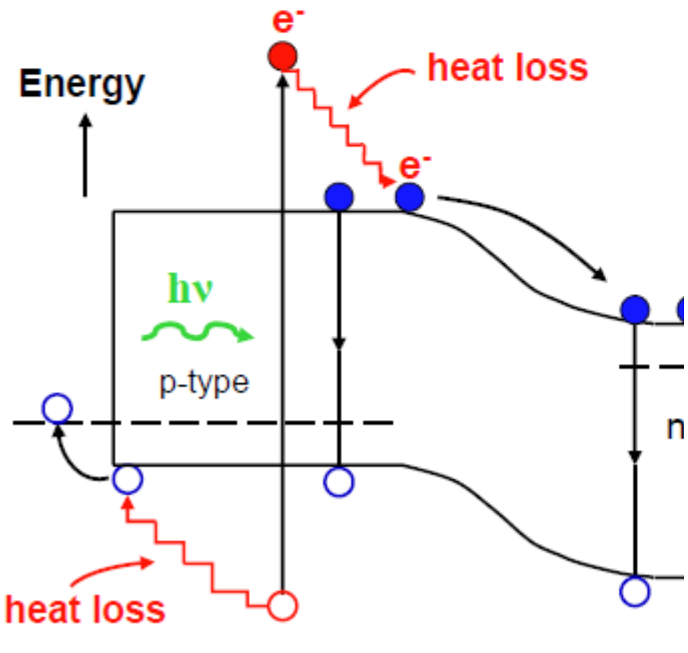
- Large resource & renewable
- Distributed generation



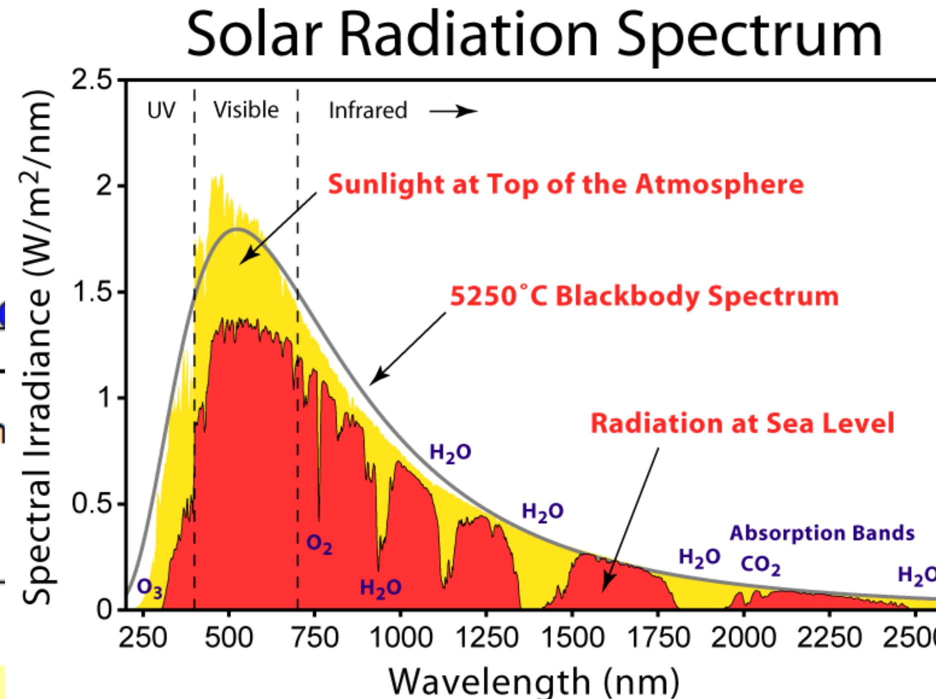


Photovoltaics (PV)

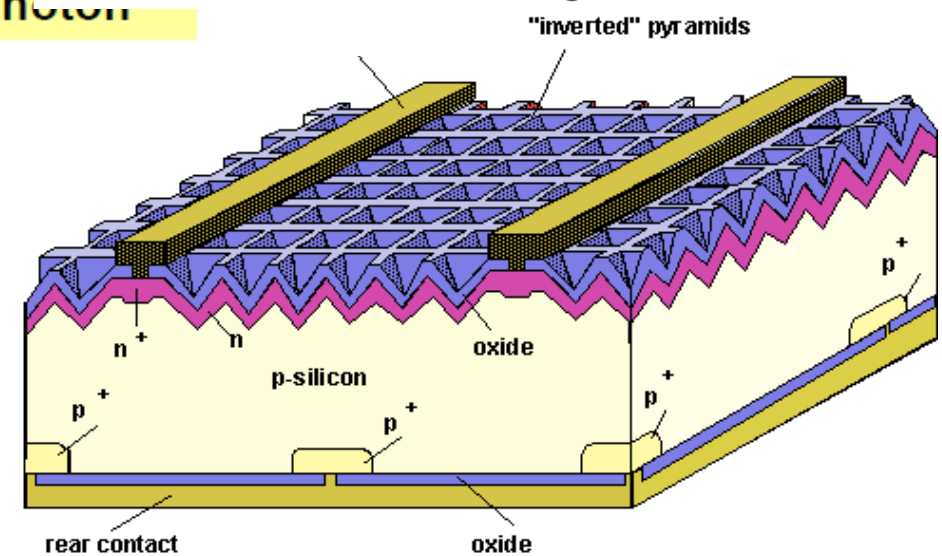




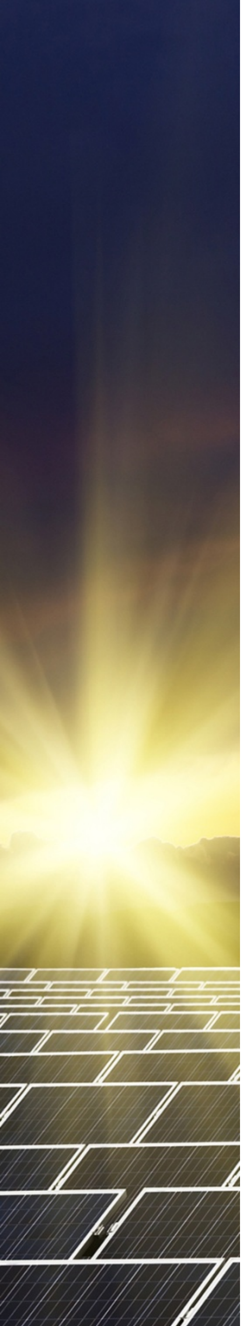
1 e⁻ - h⁺ pair/photon



First Generation single crystal Si PV technology



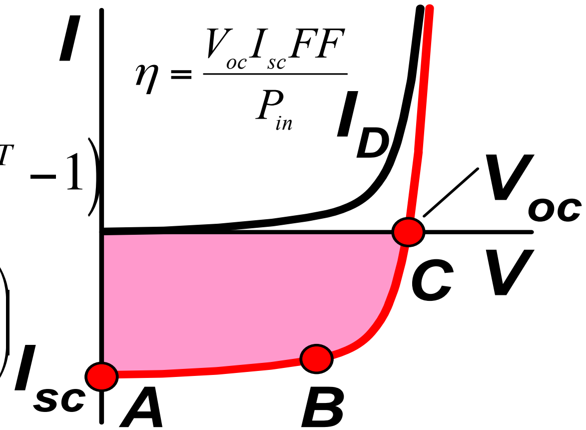
Photovoltaics



$$I_D = I_0\left(e^{qV_D/nkT} - 1\right)$$

$$V_{oc} = \frac{nkT}{q}\ln\left(\frac{I_{sc}}{I_o} + 1\right)$$

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{in}}$$



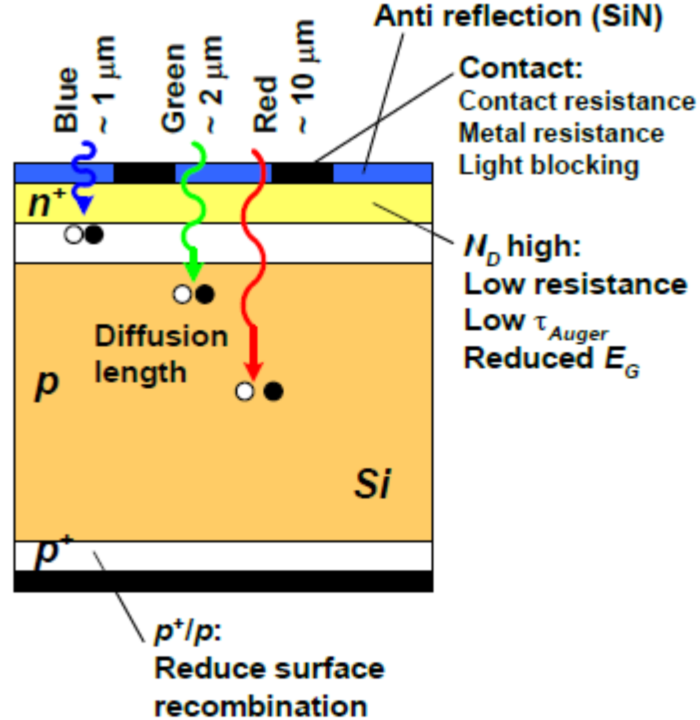
Figures of merit:

Open Circuit Voltage, V_{oc}

Short Circuit Current, I_{SC}

Efficiency, η

Top View



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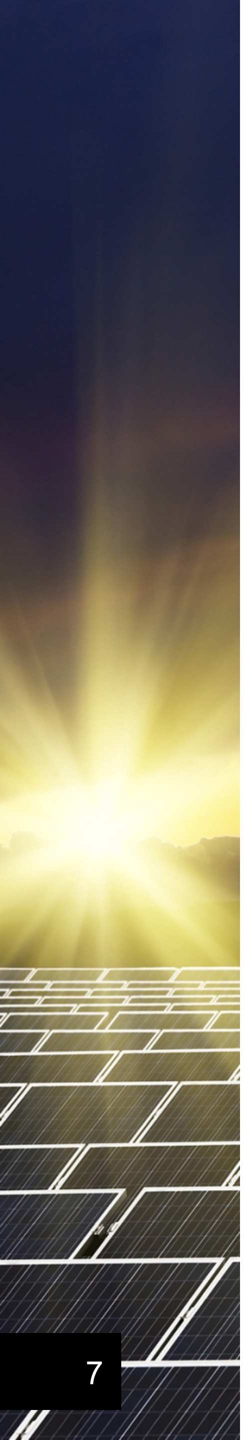
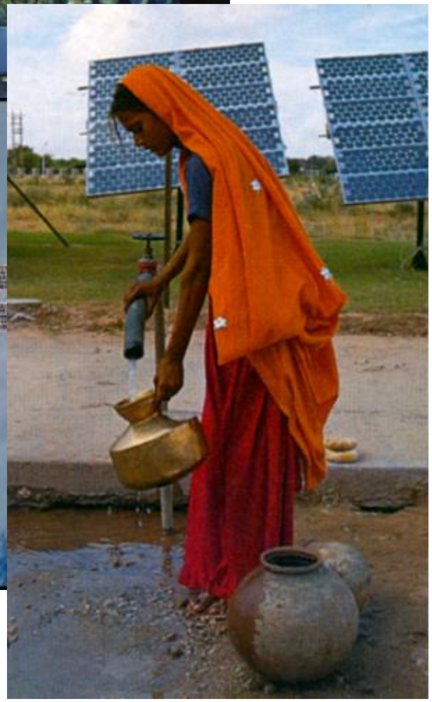
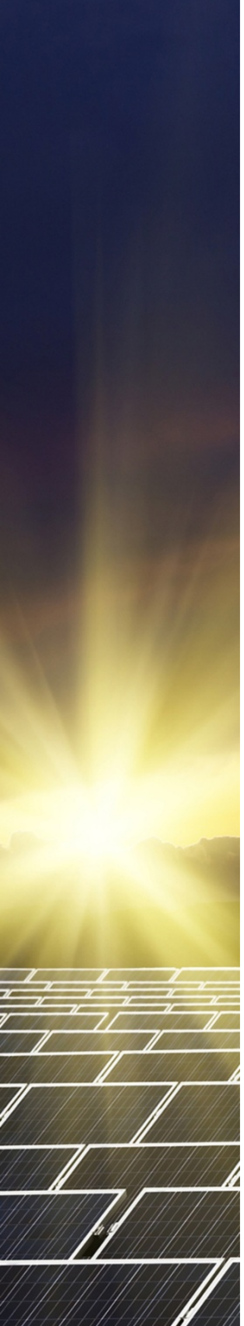


Why and Where to Use Photovoltaics

- Features of Photovoltaics
  - High efficiency
  - Distributed energy source
  - Low energy payback time
  - Clean energy source
  - Low water usage
  - Modular
- Markets
  - Remote area power
  - Grid-connected: residential and utility
  - Niche markets





Solar Cell Technologies

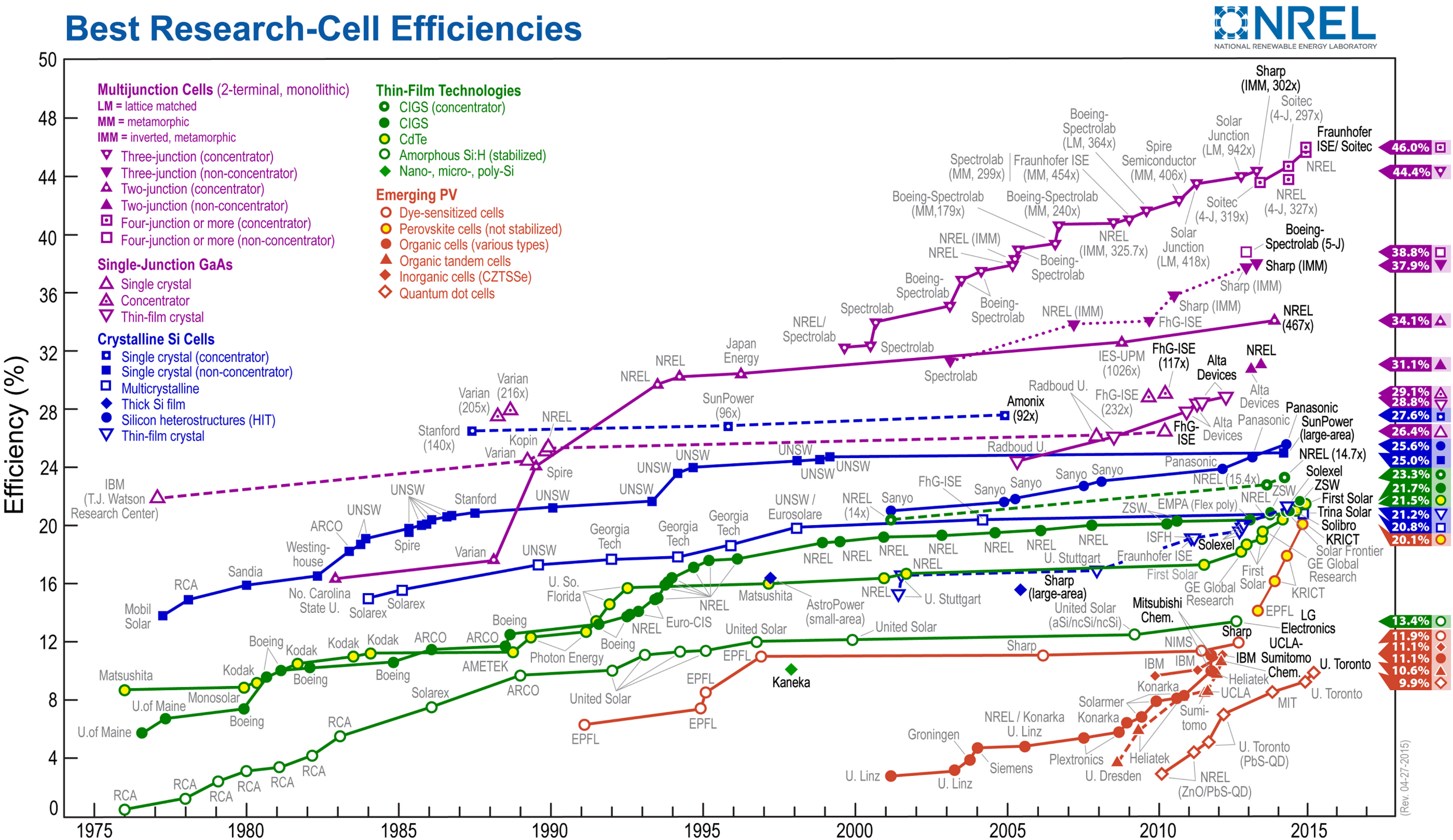
Established technologies

- *First Generation*: Silicon (single and polycrystalline) and III-V solar cells
  - GaAs/AlGaAs
  - GaAs/InGaAsP
  - InP
- *Second Generation*: Thin Film
  - $CuInSe_2$ (CIS)
  - $CuInGaSe_2$ (CIGS)
  - CdTe
  - Amorphous Si (a-Si)
  - Organic

IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
							2 He 4.003
		5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
		13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.909	36 Kr 83.80
47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)

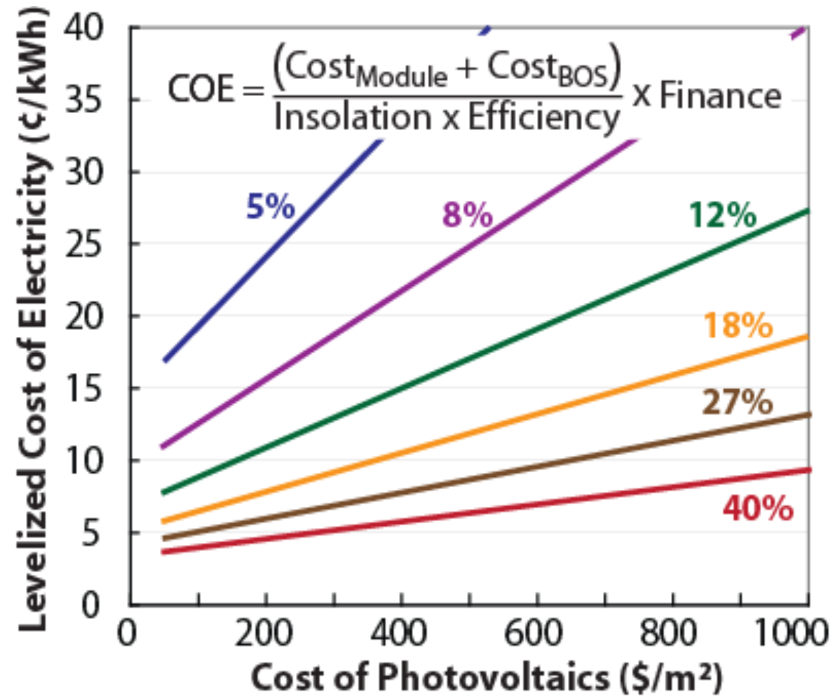
- *Third Generation*
  - Multijunction
  - Advanced concepts
  - Organic/Perovskite
  - Dye sensitized solar cells

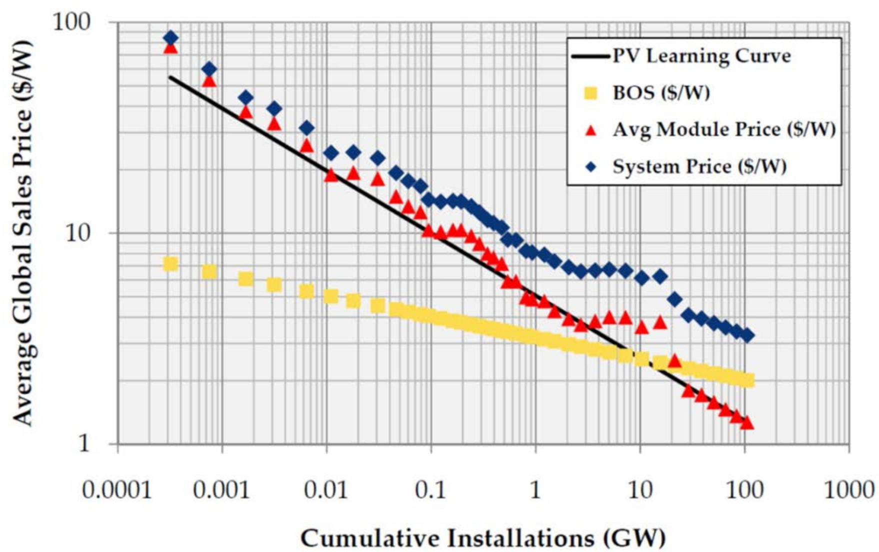
Solar Cell Efficiencies

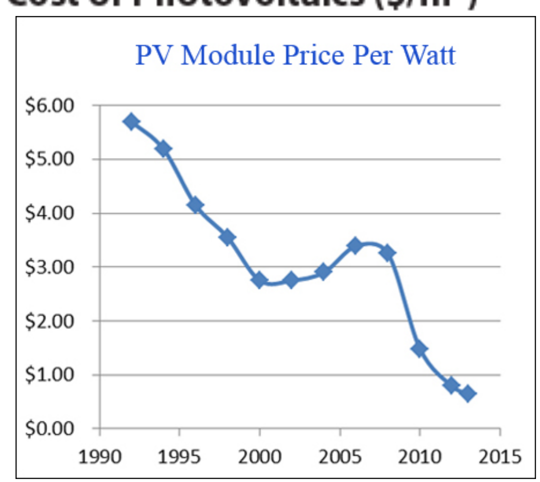


Efficiency as Critical Metric

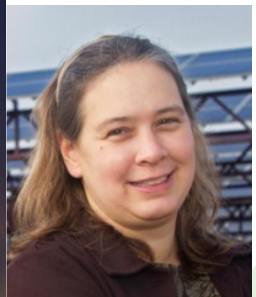
- Why is efficiency important?
- Cost of electricity
- Reducing PV costs ineffective if PV costs go below BOS costs

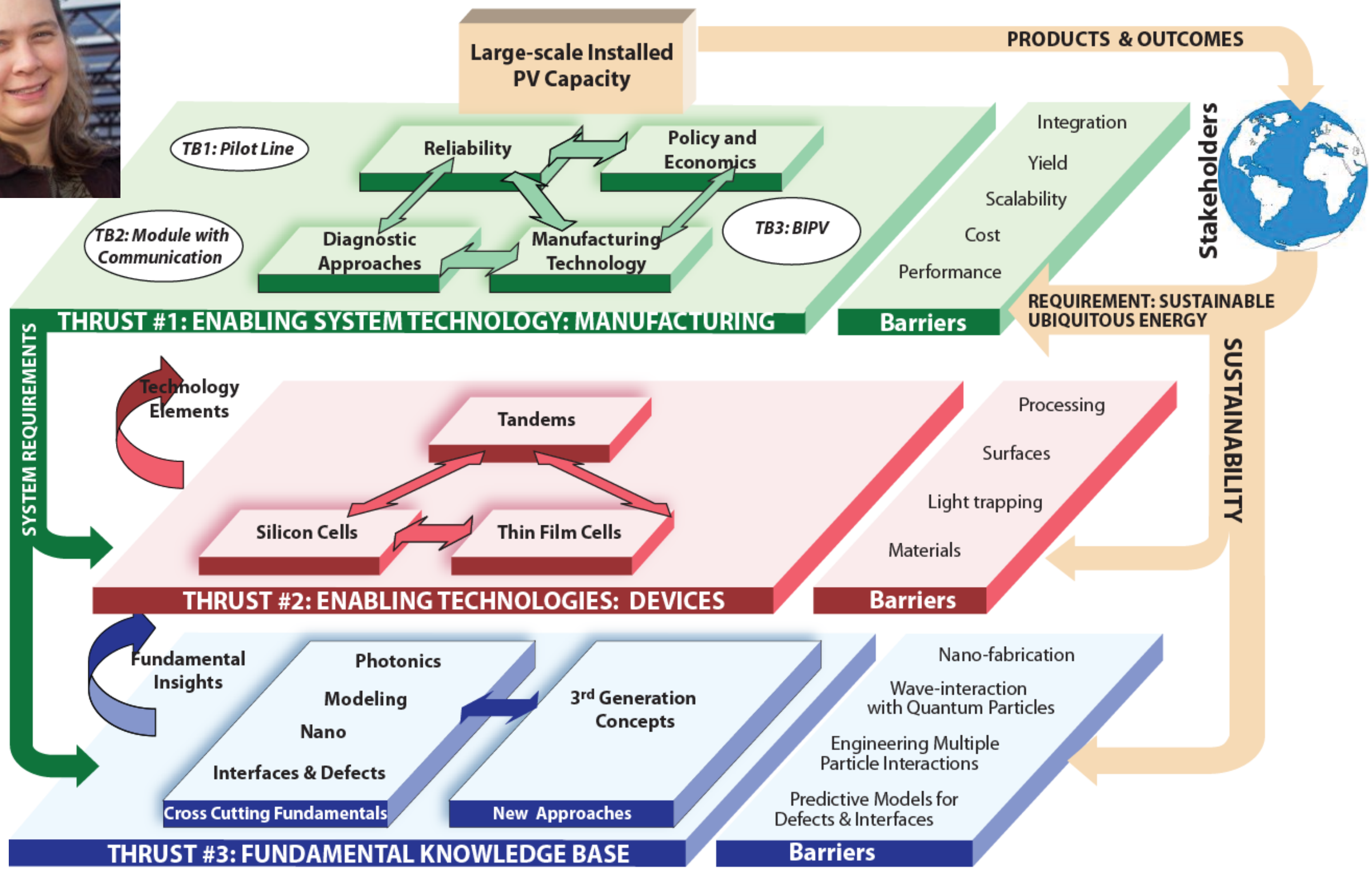




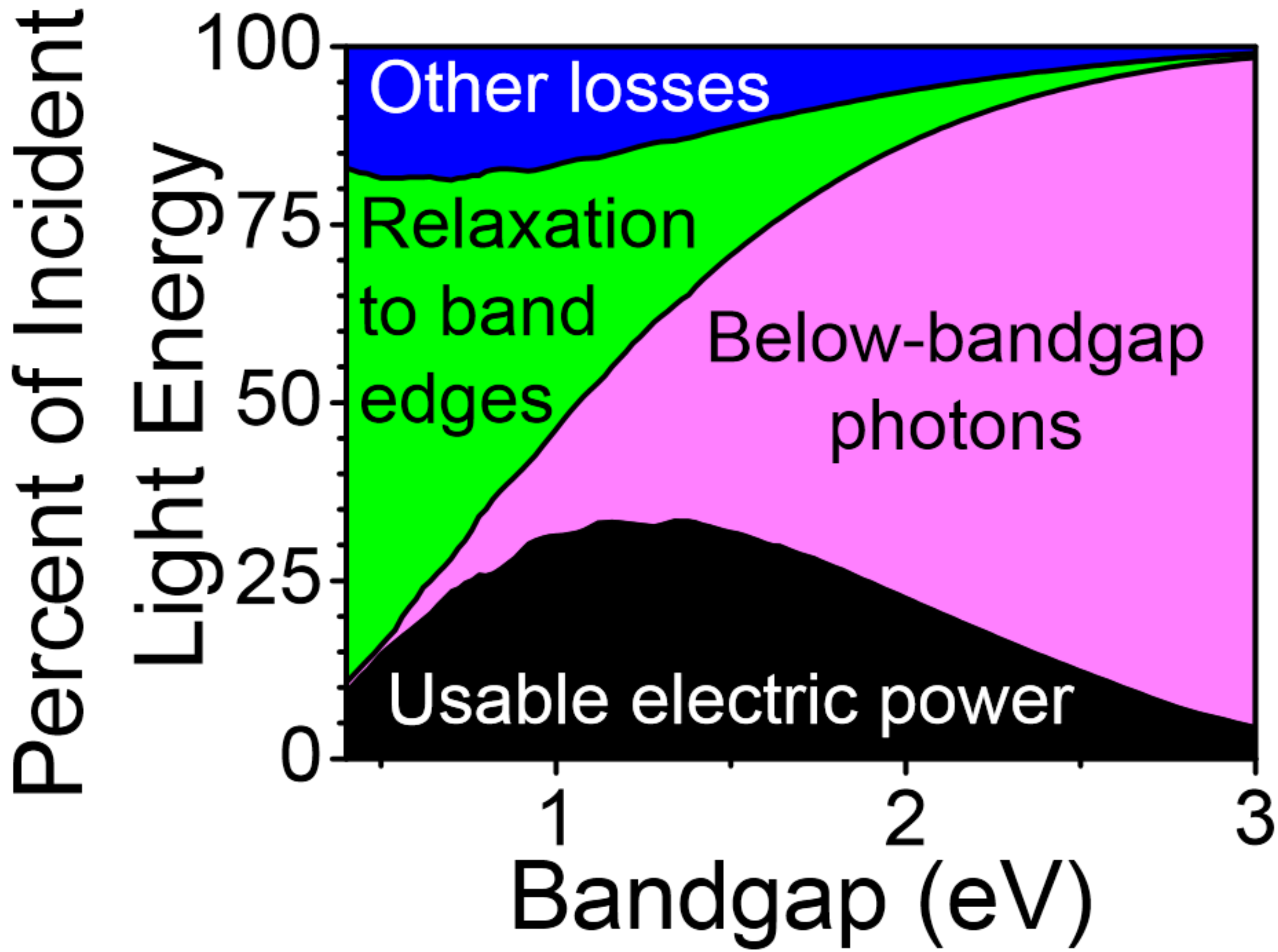


NSF/DoE Quantum Energy for Sustainable Solar Technologies (QESST) Engineering Research Center





Single Gap Solar Cell Efficiencies



W. Shockley and H. Queisser, JAP32, 510 (1961)

Overcoming the Shockley-Queisser Limit

Assumption in Shockley-Queisser	Approach which circumvents assumption	Examples
Input is solar spectrum	<u>Multiple spectrum solar cells</u>: transform the input spectrum to one with same energy but narrower wavelength range	Up/down conversion Thermophotonics
One photon = one electron-hole pair	<u>Multiple absorption path solar cells</u>: any absorption path in which one photon ≠ one-electron hole pair	Impact ionization Two-photon absorption
Excitation across a single bandgap	<u>Multiple bandgap solar cells</u>: Existence of multiple meta-stable light-generated carrier populations within a single device	Multijunction, Intermediate band, Quantum well solar cells
Cell temperature = carrier temperature	<u>Multiple temperature solar cells</u>. Any device in which energy is extracted from a difference in carrier or lattice temperatures	Hot carrier solar cells
Energy lost by cell does no work	<u>Hybrid solar energy systems</u>: PV used together with thermal, electrochemical	Thermophotonics, hybrid PV/hot water

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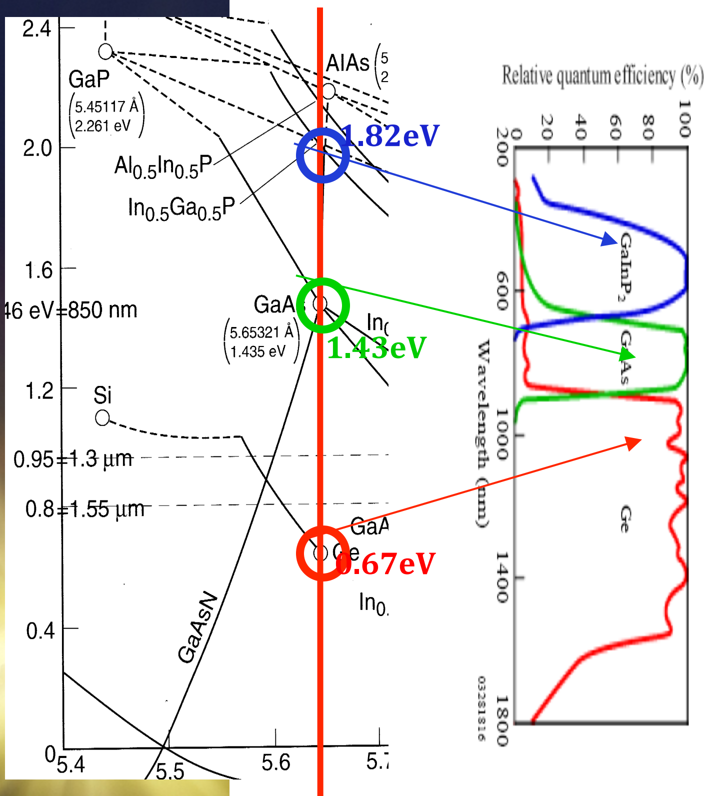
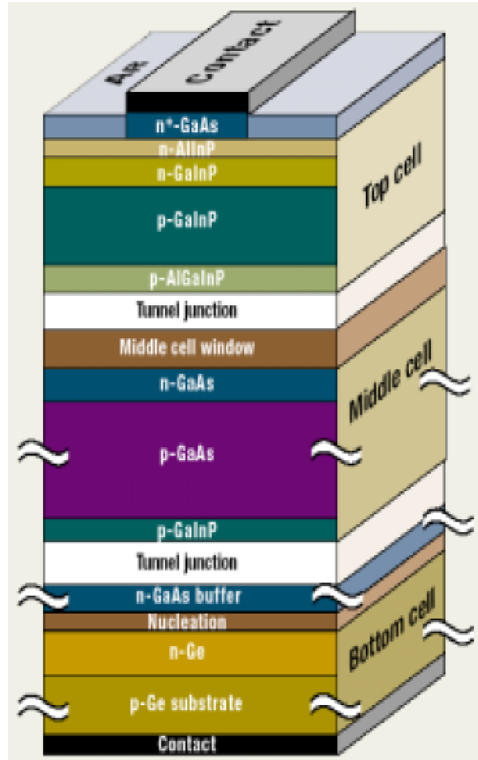
Multijunction (Tandem) Solar Cells



GaInP lattice matched to Ge and GaAs



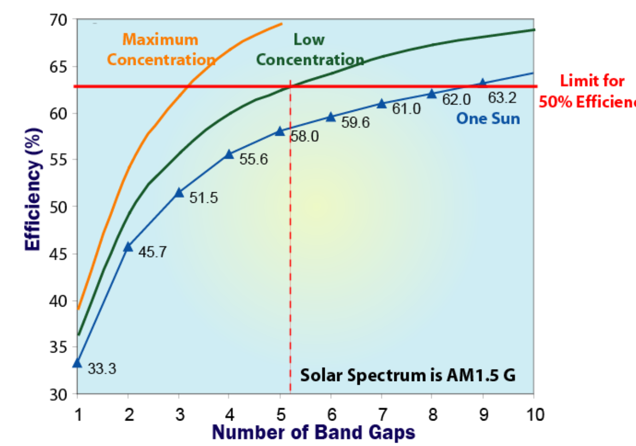
Triple Junction Technology

Challenges :

- Lattice matched materials with ideal bandgaps (series connected)
- Material quality
- Poor V_{oc} in small bandgap materials ($V_{oc}=E_g-0.4$)

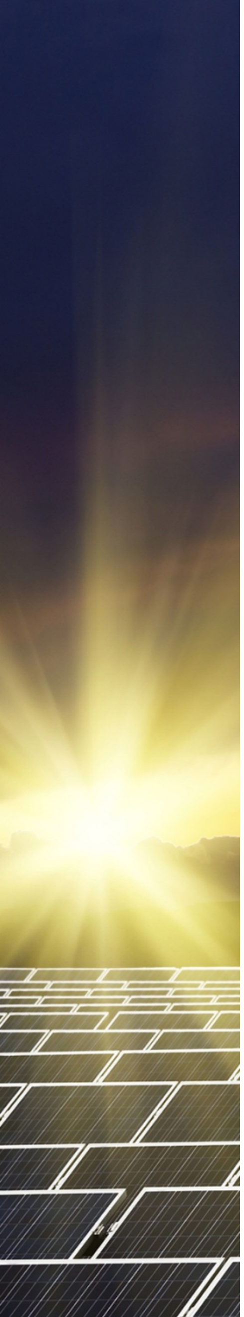
Approaches:

- Dilute nitrides
- Multi-quantum well systems

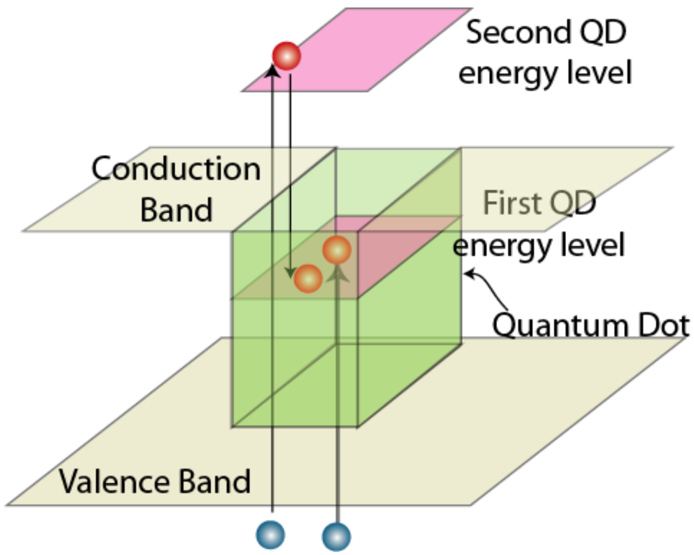


Issues: GaInP: (4-1.82)=2.18 eV heat/waste
GaAs: (1.82-1.42)=0.4eV heat/waste
Ge: (1.42-0.67=0.75 eV heat/waste

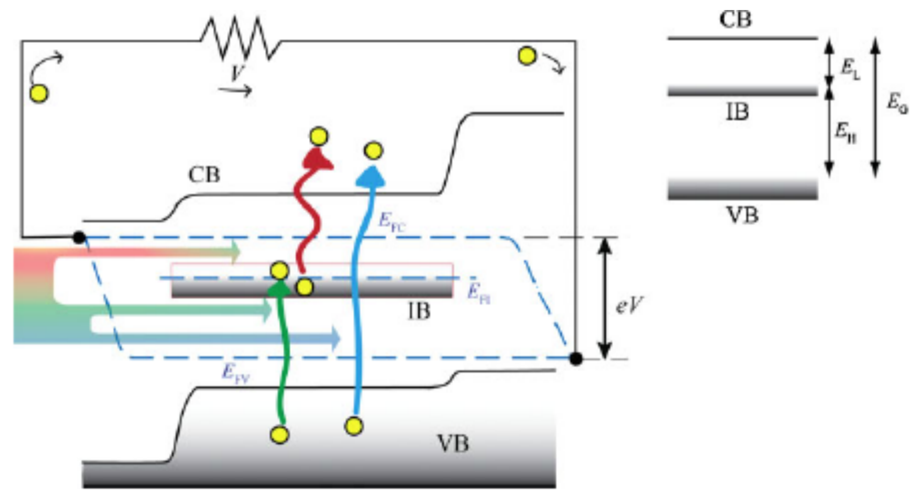
Current record: 46% 4J
(SOITEC, ISE, Helmholtz, LETI)



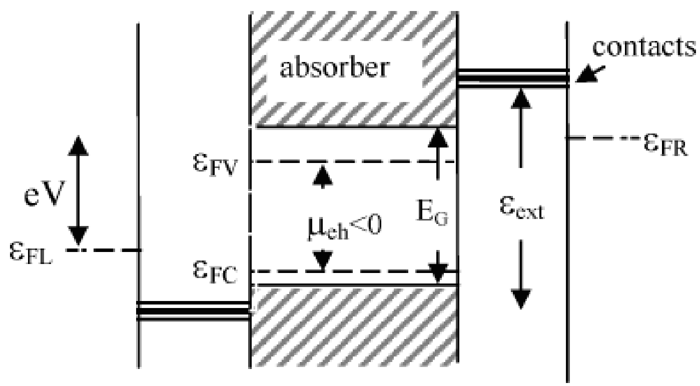
Advanced Concepts



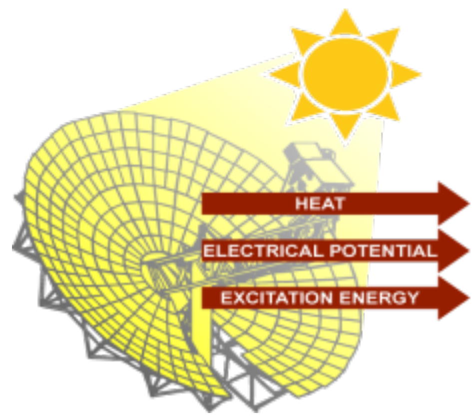
Multi-Exciton Generation (MEG)

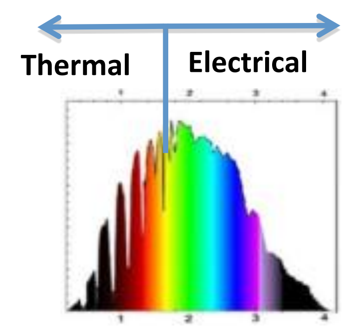


Intermediate Band (IB)



Hot Carrier Solar Cell



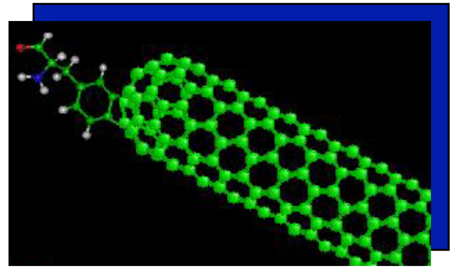


Spectral splitting for electrical and thermal energy

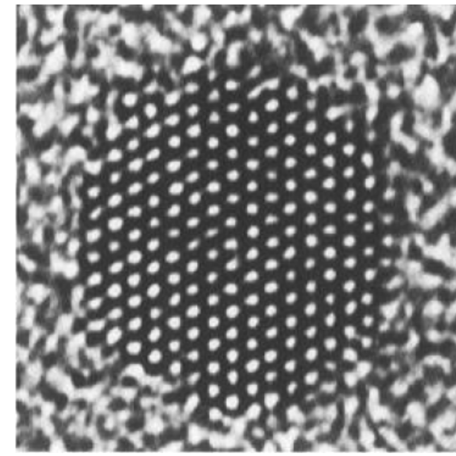
Hybrid PV

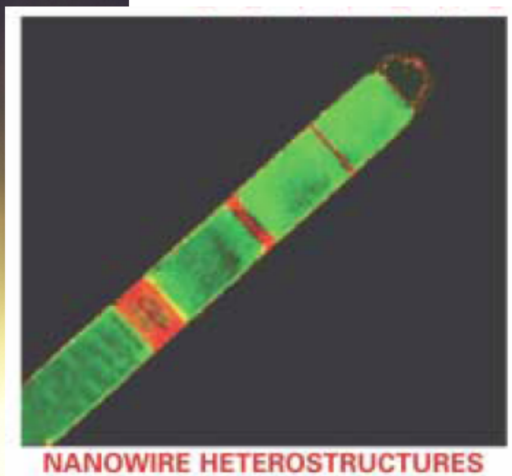
Nanotechnology Components

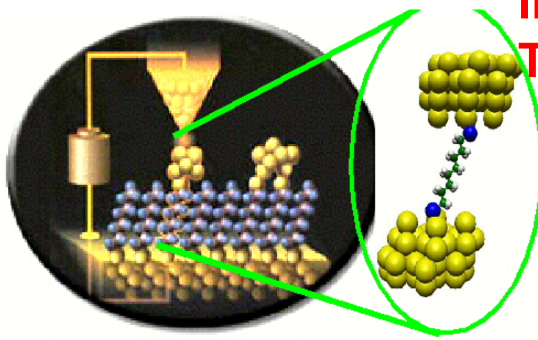
Nanowires, Nanotubes, Molecular wires



Nanoparticles, Quantum dots

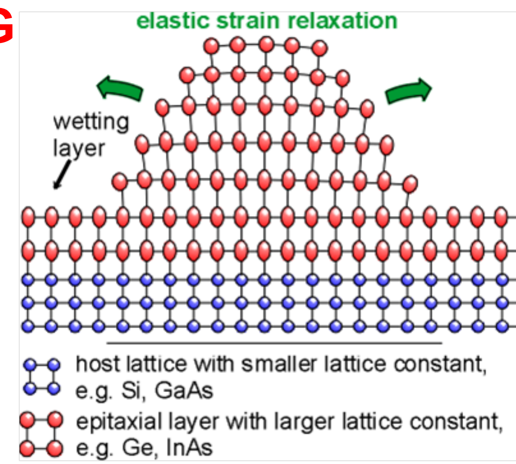




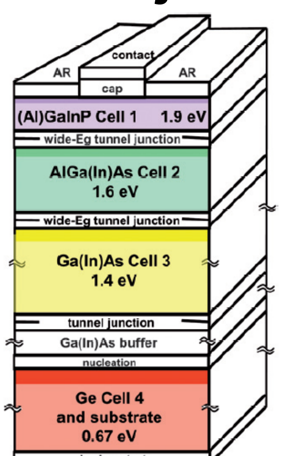


Tandems, IB, MEG, TEs

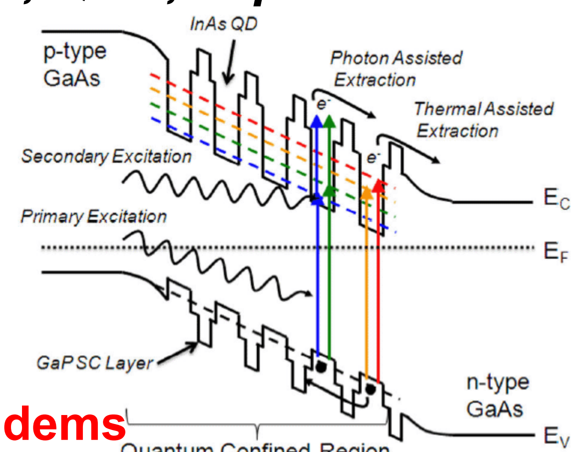
IB, MEG

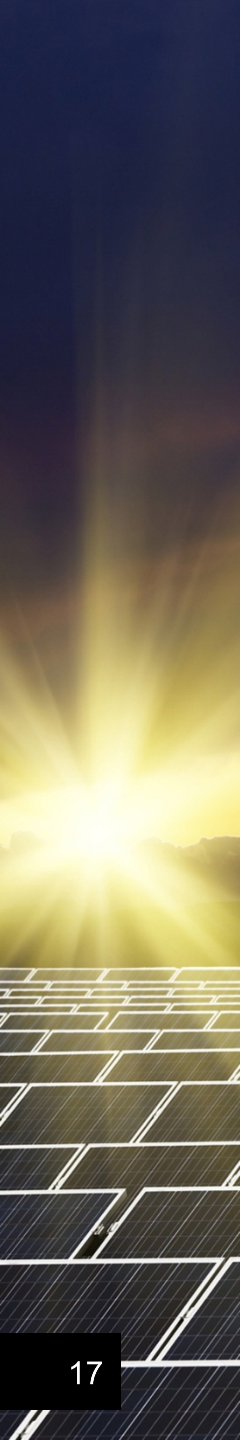


Heterojunctions, QWs, superlattices



Tandems





Nanotechnology and Energy

Energy sources → Energy change → Energy distribution → Energy storage → Energy usage

Energy sources

Regenerative

Photovoltaics: Nano-optimized cells (polymeric, dye, quantum dot, thin film, multiple junction), antireflective coatings

Wind Energy: Nano-composites for lighter and stronger rotor blades, wear and corrosion protection nano-coatings for bearings and power trains etc.

Geothermal: Nano-coatings and -composites for wear resistant drilling equipment

Hydro-/Tidal Power: Nano-coatings for corrosion protection

Biomass Energy: Yield optimization by nano-based precision farming (nanosensors, controlled release and storage of pesticides and nutrients)

Fossil Fuels

Wear and corrosion protection of oil and gas drilling equipment, nanoparticles for improved oil yields

Nuclear

Nano-composites for radiation shielding and protection (personal equipment, container etc.), long term option for nuclear fusion reactors

Energy change

Gas Turbines

Heat and corrosion protection of turbine blades (e.g. ceramic or intermetallic nano-coatings) for more efficient turbine power plants

Thermoelectrics

Nanostructured compounds (interface design, nanorods) for efficient thermoelectrical power generation (e.g. usage of waste heat in automobiles or body heat for personal electronics (long term))

Fuel Cells

Nano-optimized membranes and electrodes for efficient fuel cells (PEM) for applications in automobiles/mobile electronics

Hydrogen Generation

Nano-catalysts and new processes for more efficient hydrogen generation (e.g. photoelectrical, elektrolysis, biophotonic)

Combustion Engines

Wear and corrosion protection of engine components (nano-composites/-coatings, nano-particles as fuel additive etc.)

Electrical Motors

Nano-composites for superconducting components in electro motors (e.g. in ship engines)

Energy distribution

Power Transmission

High-Voltage Transmission: Nanofillers for electrical isolation systems, soft magnetic nano-materials for efficient current transformation

Super Conductors: Optimized high temperature SC's based on nanoscale interface design for loss-less power transmission

CNT Power Lines: Super conducting cables based on carbon nanotubes (long term)

Wireless Power Transmission: Power transmission by laser, microwaves or electromagnetic resonance based on nano-optimized components (long term)

Smart Grids

Nanosensors (e.g. magneto-resistive) for intelligent and flexible grid management capable of managing highly decentralised power feeds

Heat Transfer

Efficient heat in- and outflow based on nano-optimized heat exchangers and conductors (e.g. based on CNT-composites) in industries and buildings

Energy storage

Electrical Energy

Batterries: Optimized Li-ion-batteries by nanostructured electrodes and flexible, ceramic separator-foils, application in mobile electronics, automobile, flexible load management in power grids (mid term)

Supercapacitors: Nanomaterials for electrodes (carbon-aerogels, CNT, metall(-oxides) and elektrolytes for higher energy densities)

Chemical Energy

Hydrogen: Nanoporous materials (organometals, metal hydrides) for application in micro fuel cells for mobile electronics or in automobiles (long term)

Fuel Reforming/Refining: Nano-catalysts for optimized fuel production (oil refining, desulphurization, coal liquefaction

Fuel Tanks: Gas tight fuel tanks based on nano-composites for reduction of hydrocarbon emissions

Thermal Energy

Phase Change Materials: Encapsulated PCM for air conditioning of buildings

Adsorptive Storage: Nano-porous materials (e.g. zeolites) for reversible heat storage in buildings and heating nets

Energy usage

Thermal Insulation

Nanoporous foams and gels (aerogels, polymer foams) for thermal insulation of buildings or in industrial processes

Air Conditioning

Intelligent management of light and heat flux in buildings by electrochromic windows, micro mirror arrays or IR-reflectors

Lightweight Construction

Lightweight construction materials using nano-composites (carbon nanotubes, metal-matrix-composites, nano-coated light metals, ultra performance concrete, polymer-composites)

Industrial Processes

Substitution of energy intensive processes based on nanotech process innovations (e.g. nano-catalysts, self-assembling processes etc.)

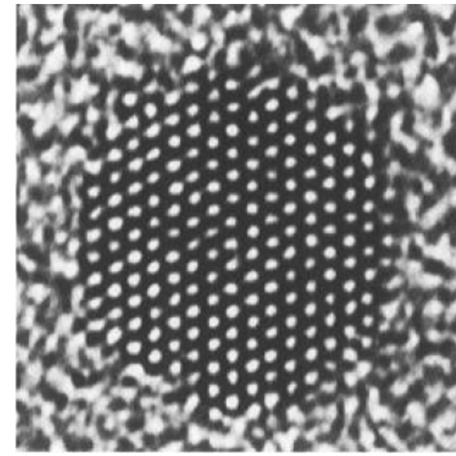
Lighting

Energy efficient lighting systems (e.g. LED, OLED)

Examples for potential applications of nanotechnology along the value-added chain in the energy sector (source: VDI TZ GmbH)

Nanotechnology Advantages

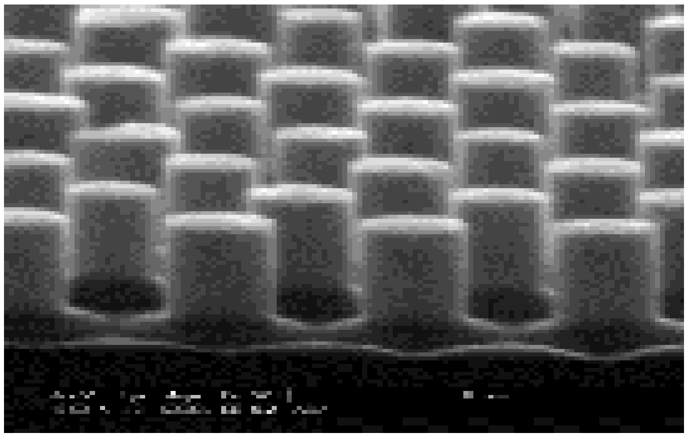
- New materials with bandgaps and electronic structure different than bulk materials: multigap devices
- Surface effects lead to new material and chemical properties
- Light management using nanophotonics to increase absorption

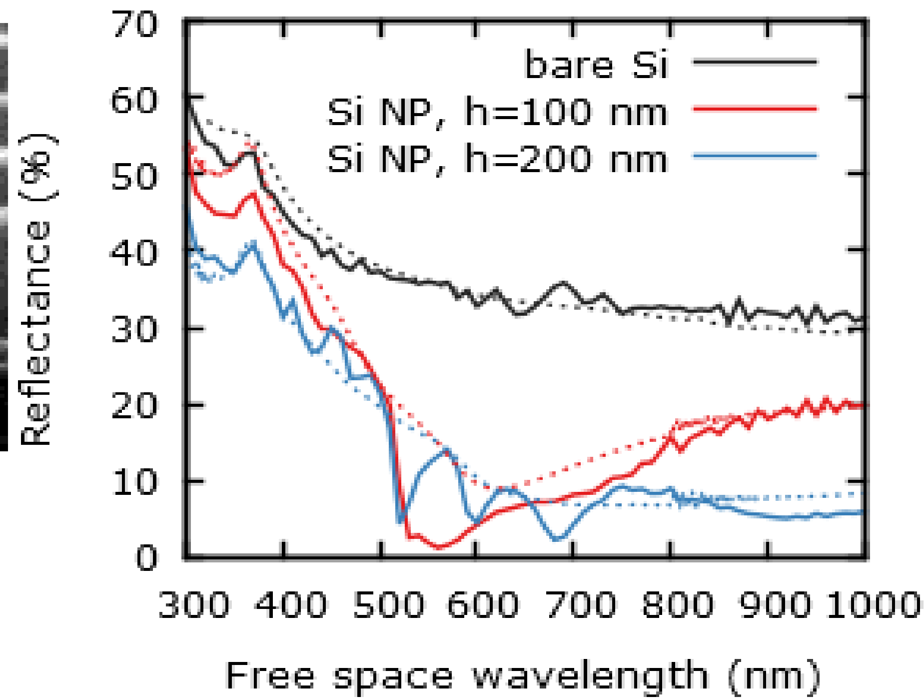


Disadvantages

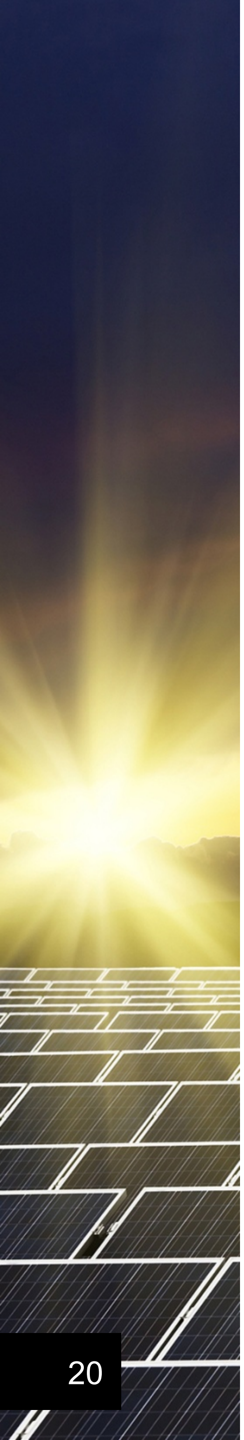
- High surface to volume ratio of nanostructured materials means surface defects may dominate
- Recombination generally degrades performance of solar cells reducing both photocurrent and voltage: Passivation

Nanostructures for Light Trapping





Left: Micrograph of nanosphere lithographically defined nanopillars. Right: FDTD Simulated (solid) and measured (dashed) reflectance spectra from a regular hexagonal array of Si NPs with period, p=600 nm, for cylinder heights of a) 100 (red) and 200 nm (blue) (C. Jeayeong and N. Vulic, ASU)



nature energy
ARTICLES
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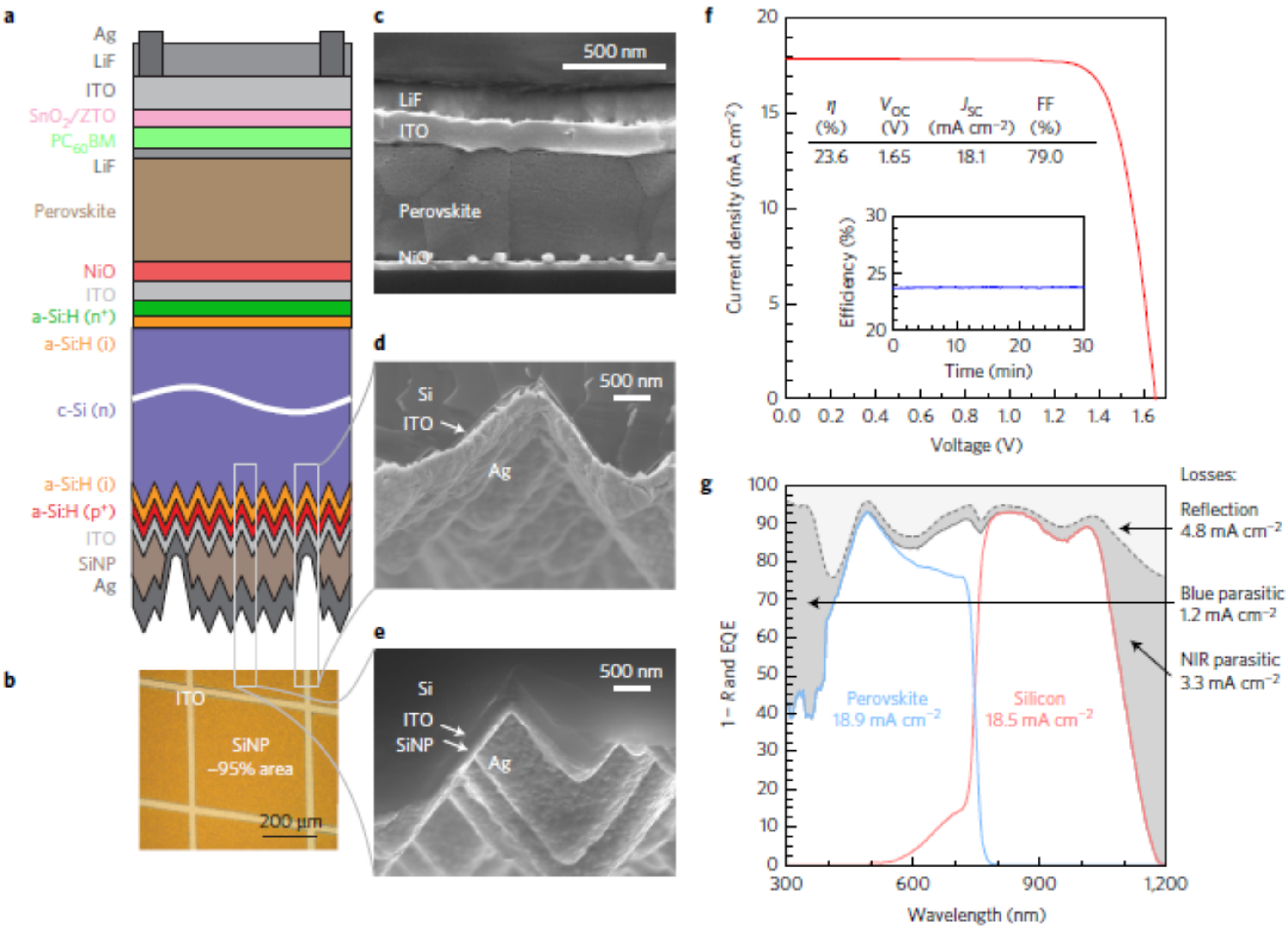
23.6%-efficient monolithic perovskite/silicon tandem solar cells with improved stability



Si HIT bottom cell with Si nanoparticle layer; Perovskite top cell

Stanford (Michael McGehee), ASU (Zachary Holman)

nature energy

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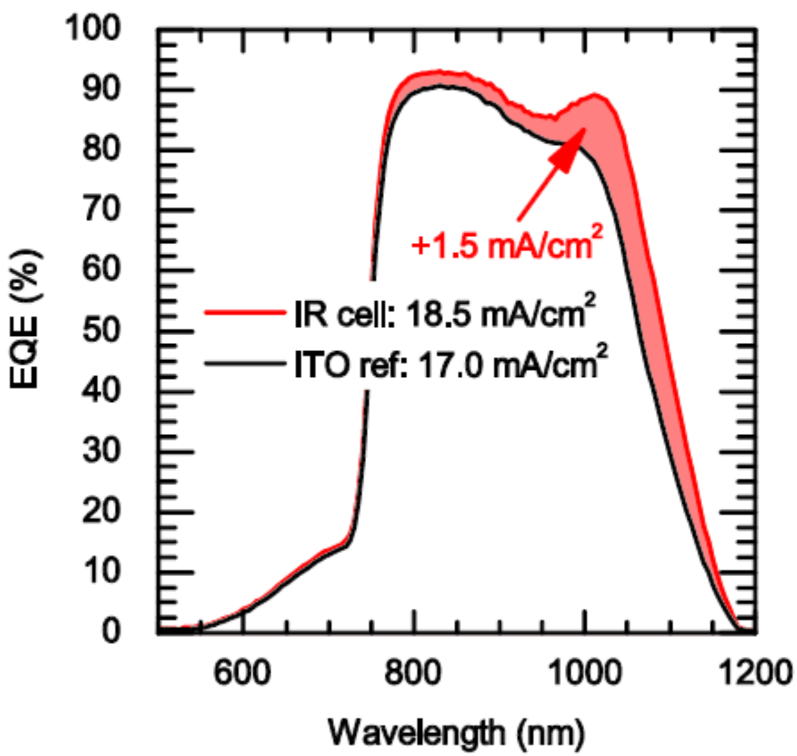
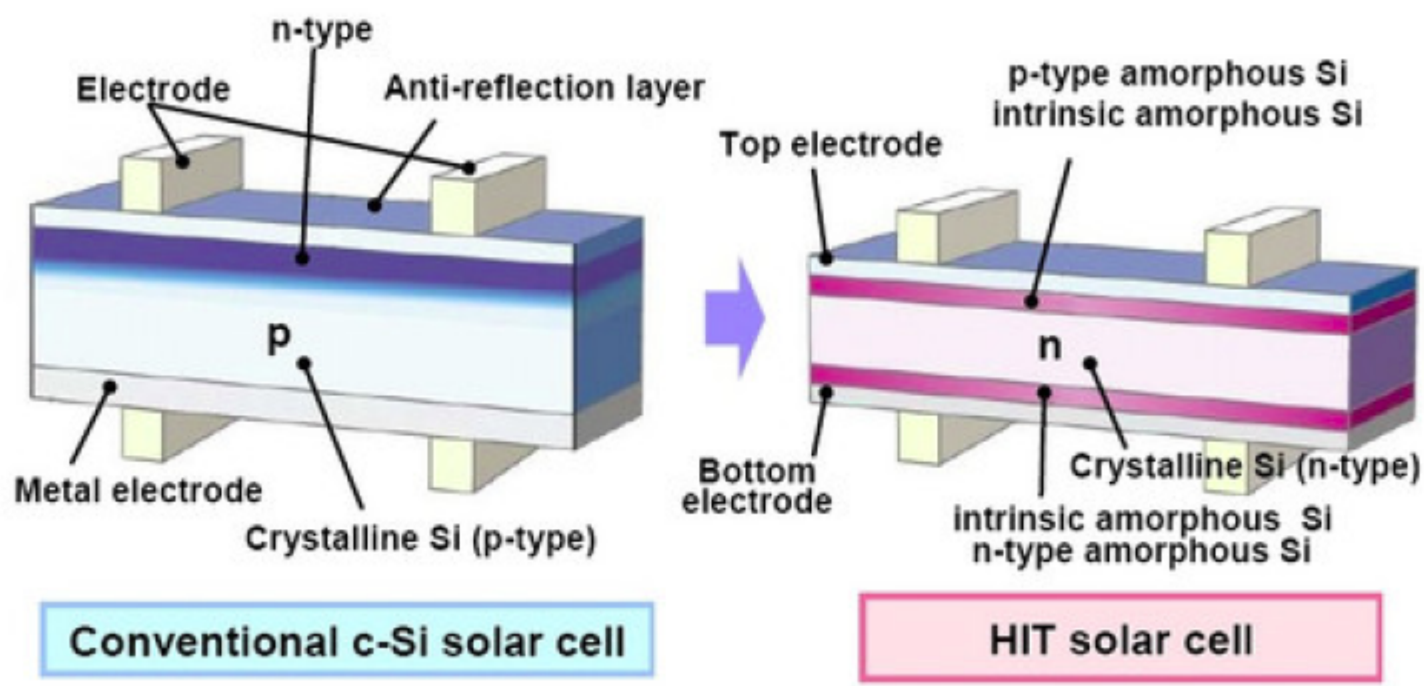


Quantum efficiency of Si bottom cells with and without Si *nanoparticle* rear reflector

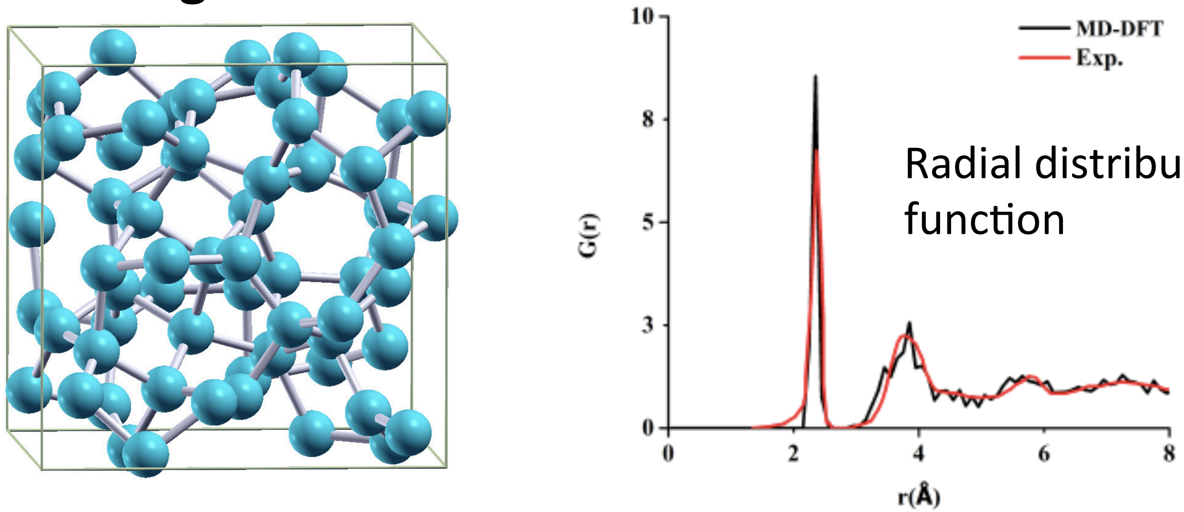
Heterojunction with Intrinsic Thin Layer (HIT) Solar Cells



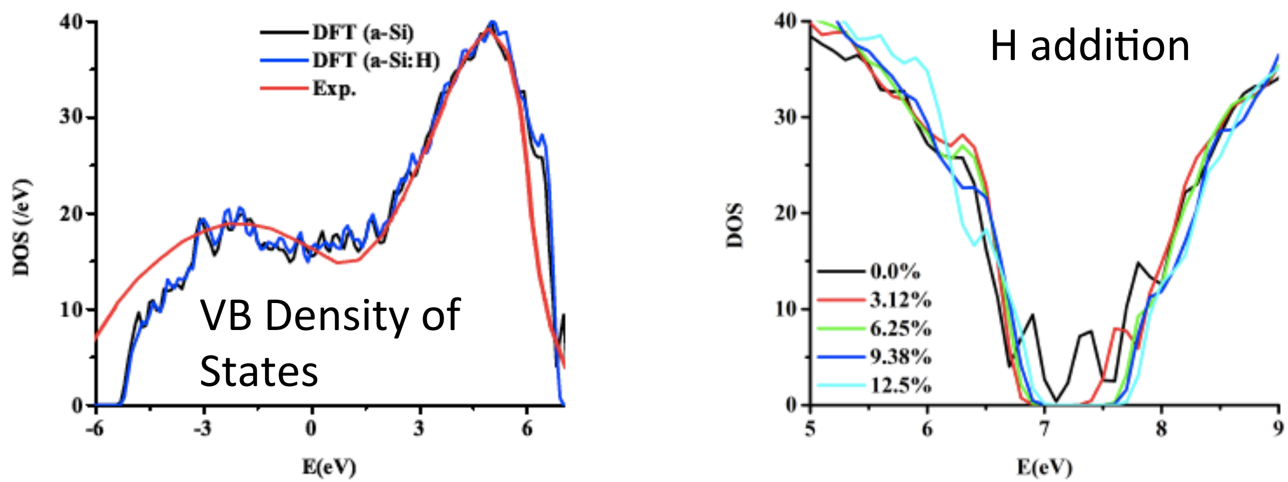
- **HIT cell is presently highest efficiency Si device at 26.3% (Kaneka 2016)**
- **Record open circuit voltage of 0.76 V (ASU 2015)**

Electronic Structure of a-Si/c-Si

- **Electronic structure of a-Si from DFT and molecular dynamics quenching**



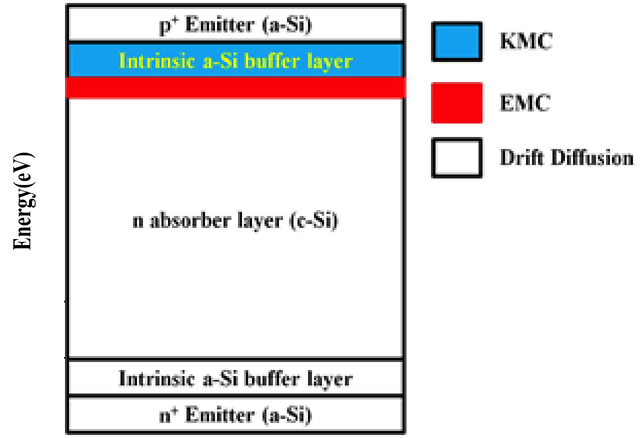
(a) (b)

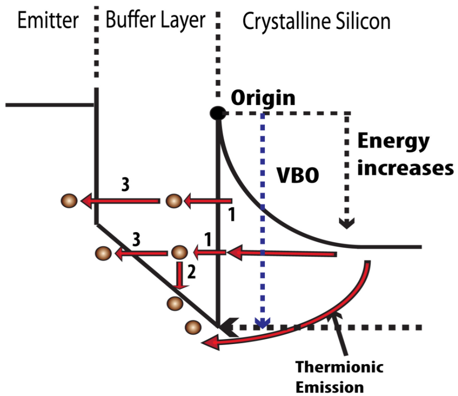


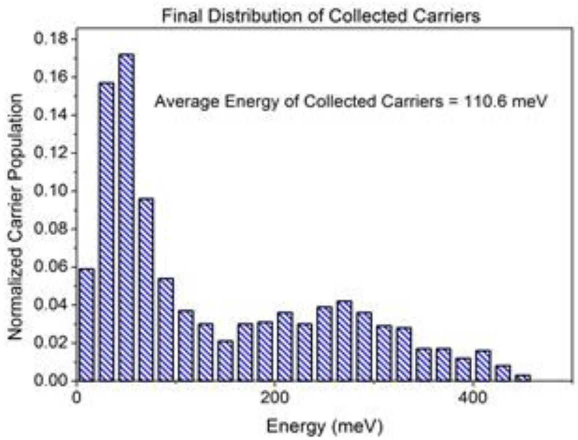
R. Vatan, S. Bowden, S. M. Goodnick, MRS 2015, Submitted to PRB

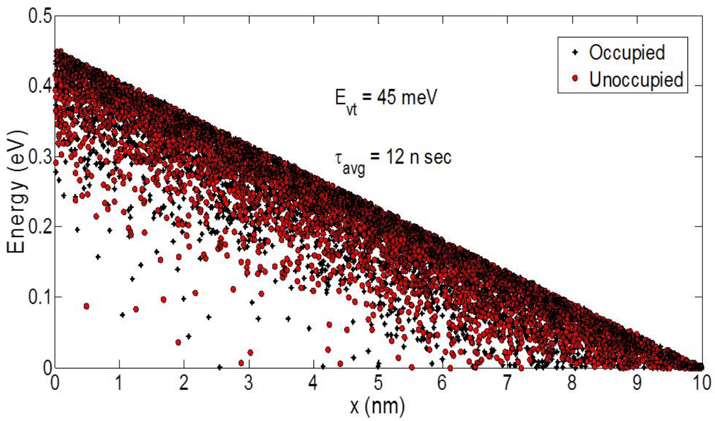
Transport at the a-Si/c-Si Interface

- **Continuum transport coupled with particle based simulation at interface (EMC+KMC)**



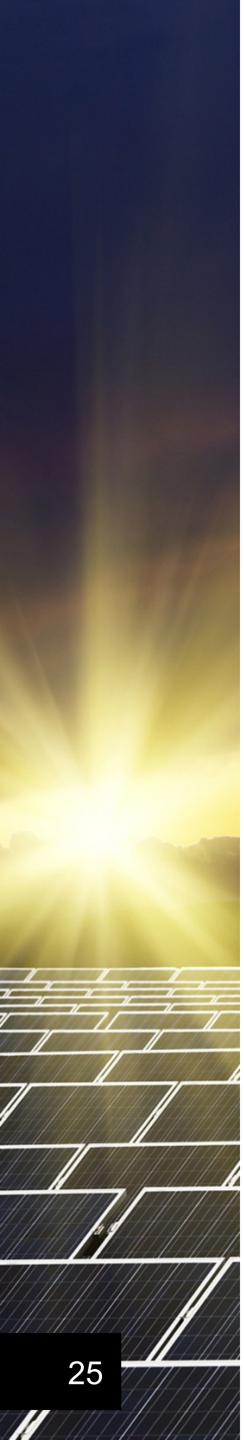




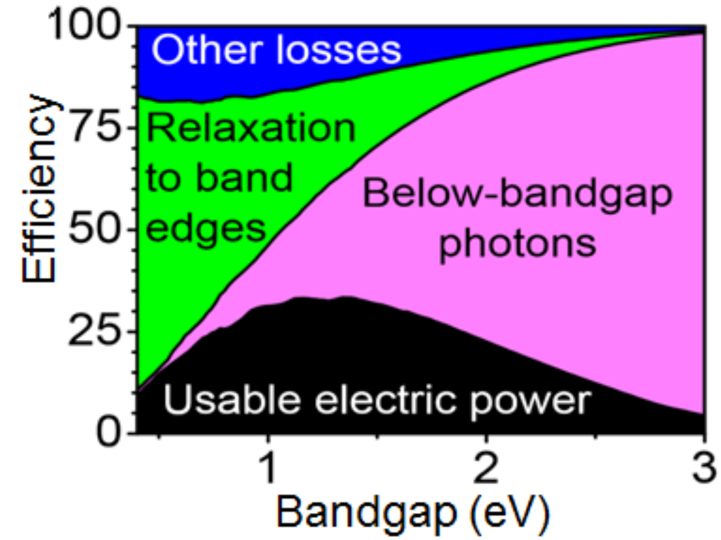


P. Muralidharan, D. Vasileska, S. M. Goodnick and S. Bowden, PVSC 2015

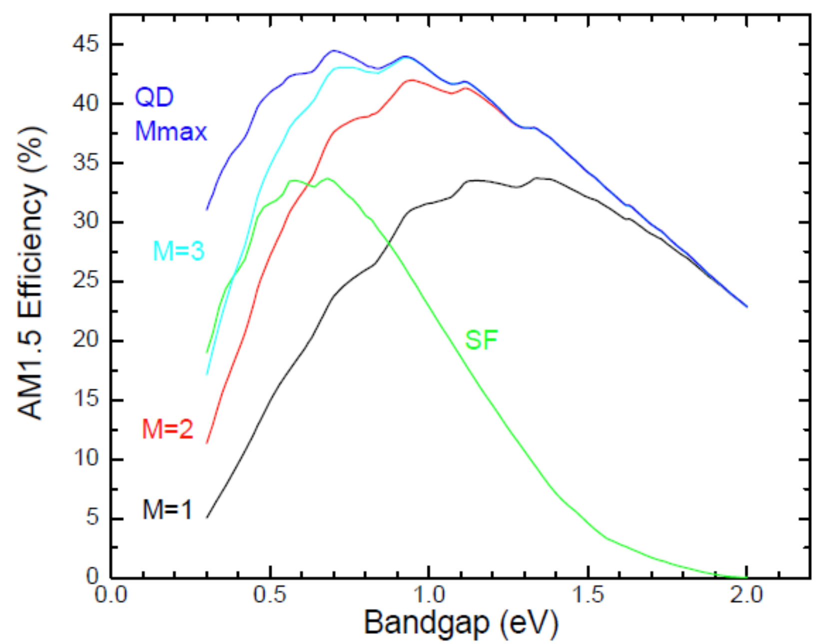
Multi-Exciton Generation Solar Cells



- **Ultrafast energy relaxation processes a major loss mechanism in photovoltaic devices**

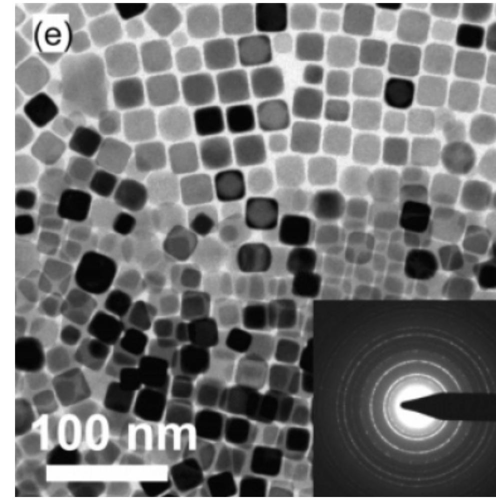


- **Impact ionization or multi-exciton generation uses the excess photon energy to increase the quantum yield above 100%**

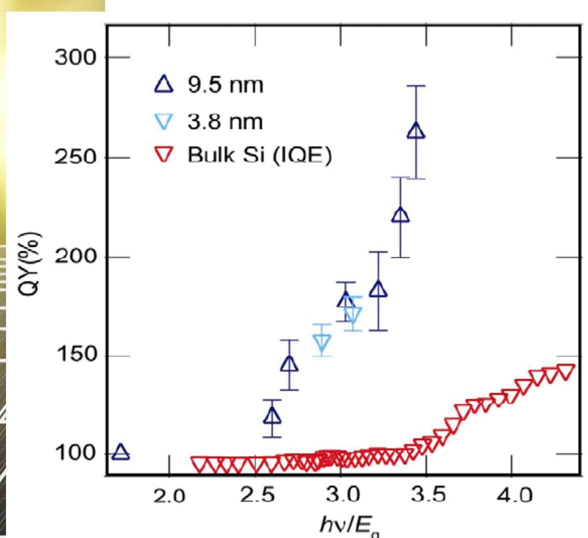


Multiple Exciton Generation (MEG) in QDs

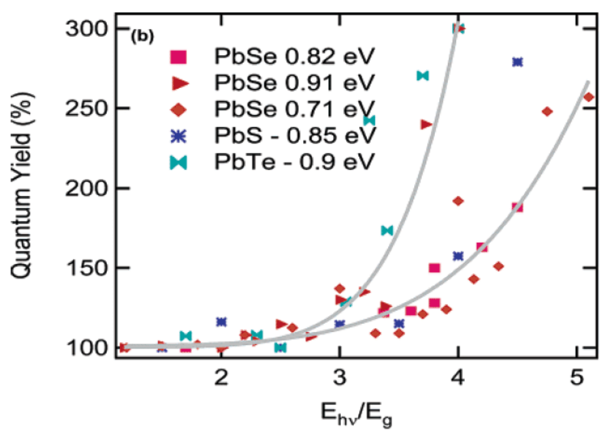
- **Multiple other QD and nanowire materials show substantial quantum yields**
- **Due to lack of crystal momentum, threshold for impact excitation =nE_g**
- **Si QDs, CdSe; > 600 % QY with PdSe; PdS; PdTe; InAs systems**

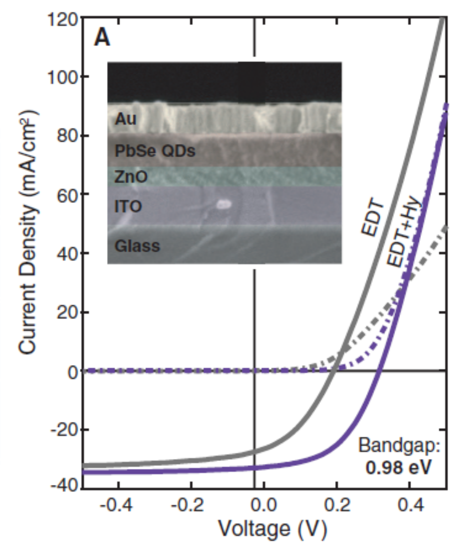


J. E. Murphy, et al, *Journal of the American Chemical Society*, 128, 10, 3241-3247, (2006).



M.C. Beard, et al, “Multiple Exciton Generat Colloidal Silicon Nanocrystals,” *Nano Letters*, vol. 7, no. 8, p. 2506-2512, (2007).





Science 334, 1530 (2012)

MEG in Nanowires

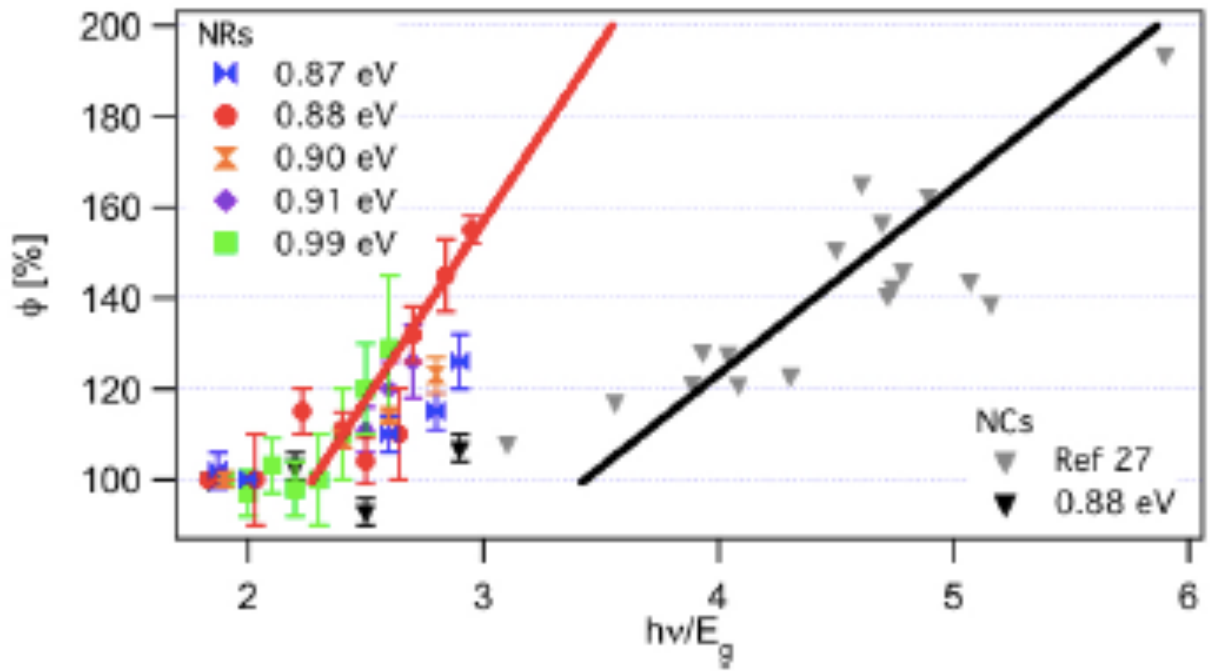
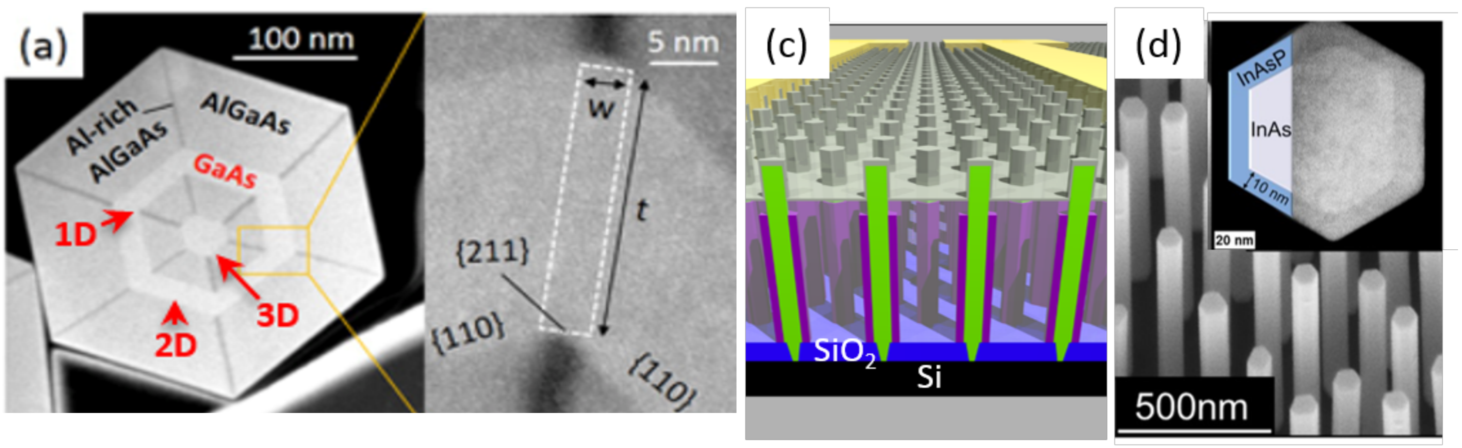


Figure 4. The exciton quantum yield as a function of relative photon energy ($h\nu/E_g$) for PbSe nanorods and nanocrystals. The energies of the first excitonic absorption are listed for each batch of nanostructures. Lines are best fits to equation 2. The MEG efficiency is 0.78 for nanorods and 0.41 for nanocrystals. Literature values taken from Beard, et al. [27].

P. D. Cunningham et al., Proc. SPIE
Vol. 8256, 2012,

Nanowires Solar Cells

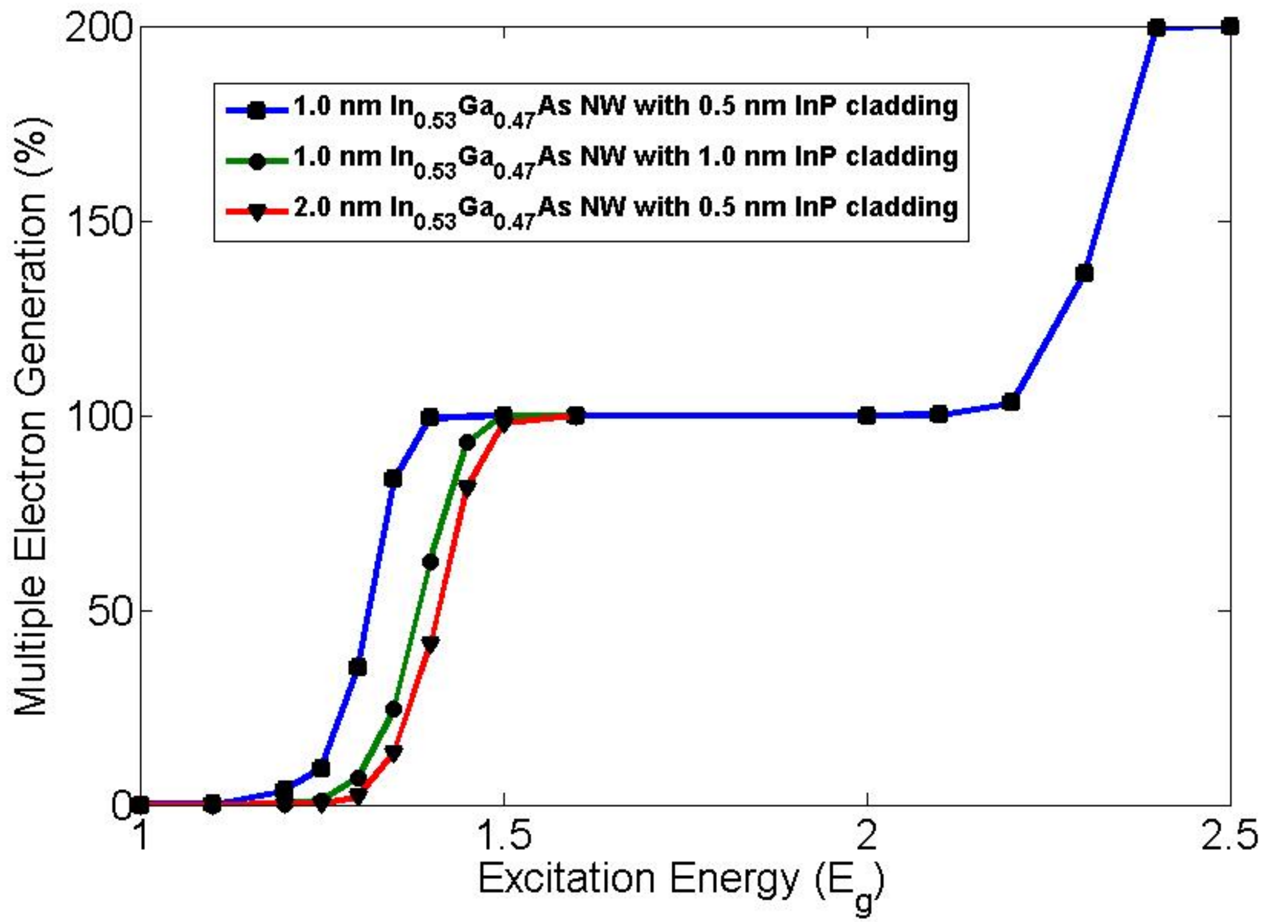
- Enhancement of light trapping
- Multiple bandgap materials with relaxed lattice matching issues
- Realization of advanced concepts such as multi-exciton generation (MEG)



- **Lund University (2015): η=15.3%**
- **TU Eindhoven (2016): η=17.8%**

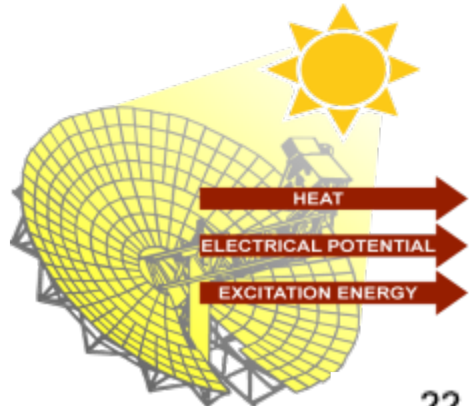
(G. Kobelmüller, G. Abstreiter, et al., 2015)

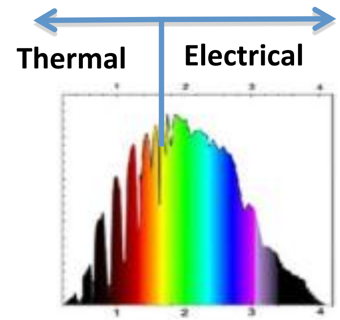
Simulation of Impact Ionization Event in III-V Nanowires



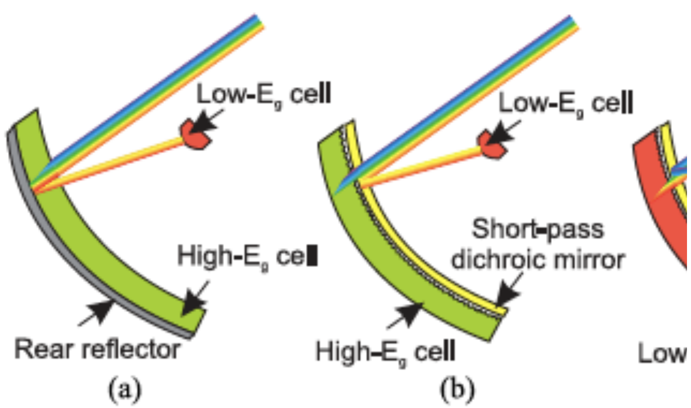
Full band NW Monte Carlo simulation (MRS 2016, R. Hathwar et al)

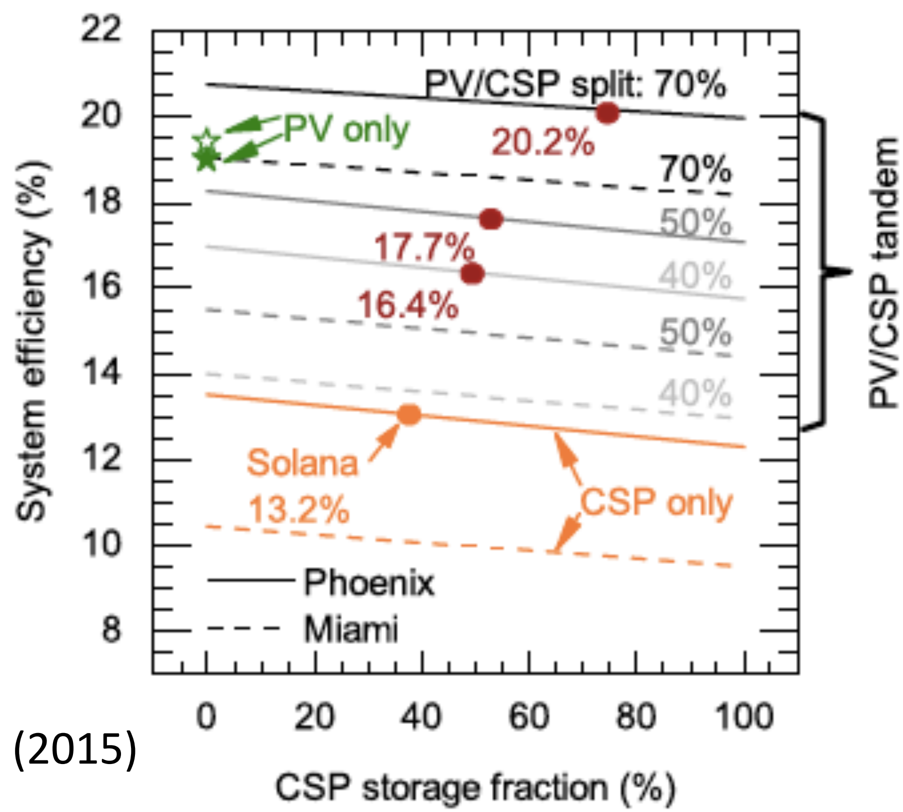
Hybrid Solar Systems





Spectral splitting for electrical



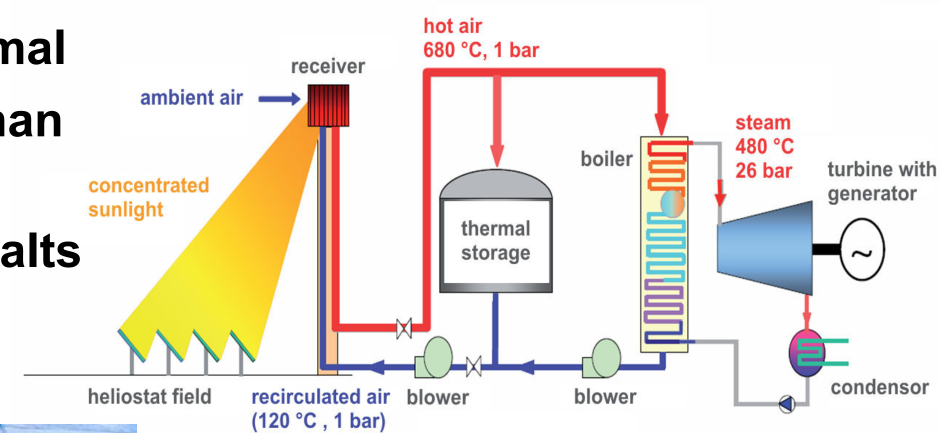


Z. Holman group, IEEE JPV 5, 1791 (2015)

PV and CSP

CSP-Concentrating solar thermal

- Currently more expensive than PV in $/watt
- Thermal storage in molten salts



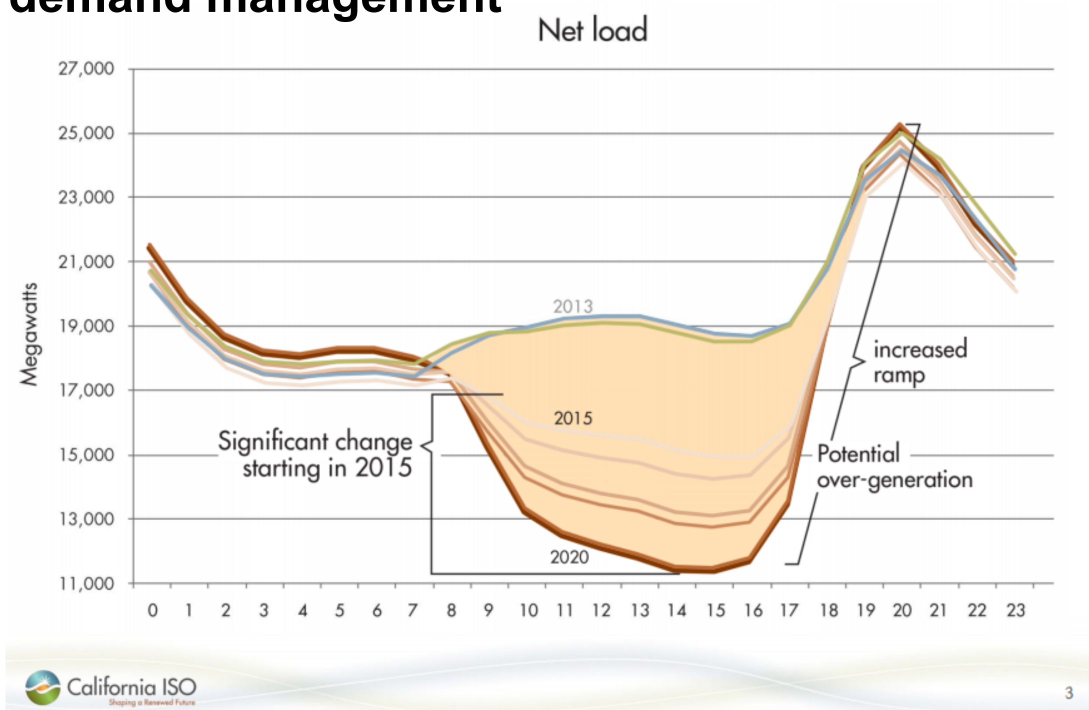
Agua Caliente (NRG/First Solar) 250-397 MW PV

APS Solana 280 MW CSP

Challenges for PV: Intermittency

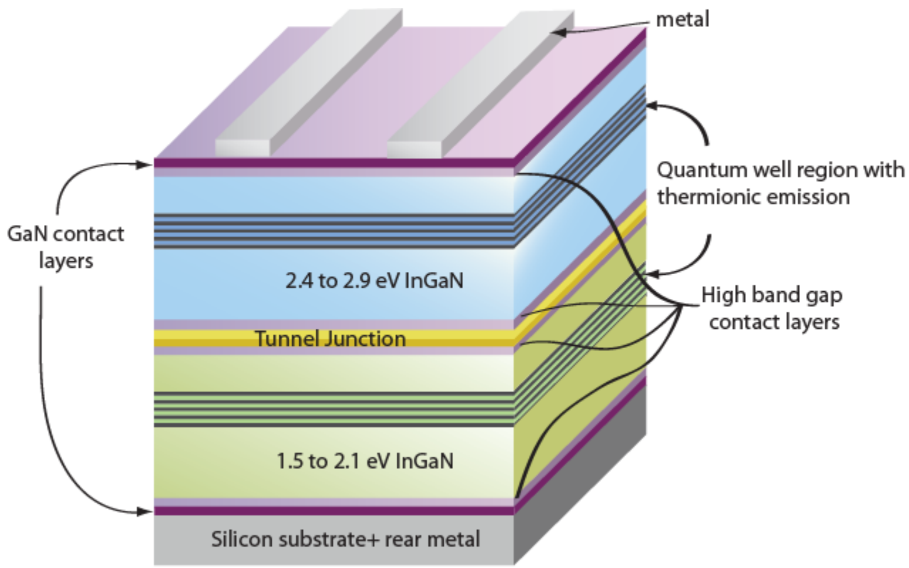
Intermittency (rapid fluctuations, diurnal) limit penetration solar onto current grid without:

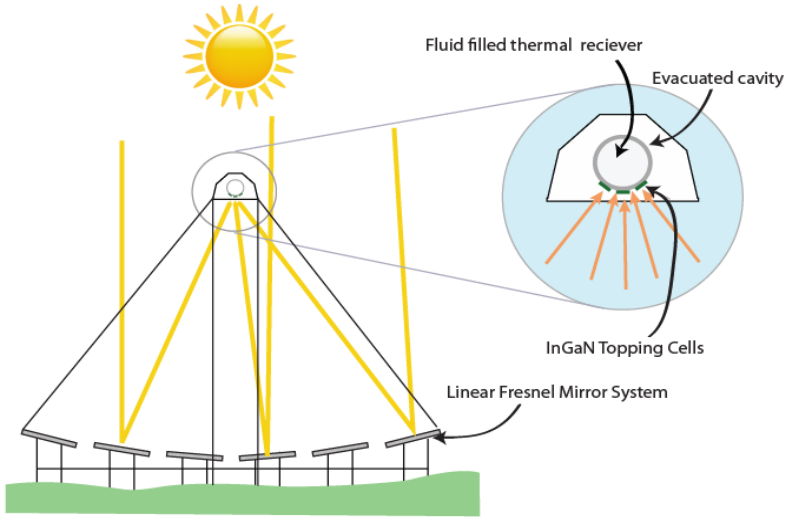
- **Storage**
- **Geographic averaging, mixed renewables**
- **Load demand management**



"Duck curve", showing hourly system load for a typical March day for the California ISO, less projected yearly rise in renewable (including PV) generation. Problems of increased renewables include potential over-generation in late afternoon and high ramp rates (14000 MW in ~1 hour).

High Temperature InGaN Thermionic Topping Cells





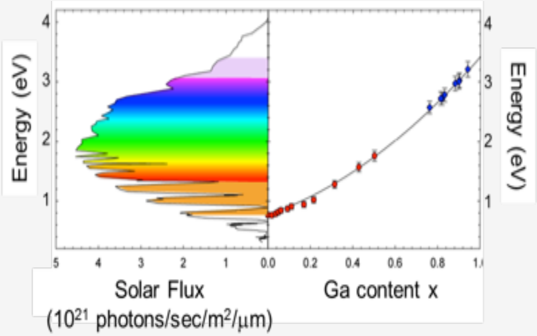
TECHNOLOGY SUMMARY

- A two junction InGaN based tandem solar cell operating up to 450 C
- Advanced device structures and fabrication methods such as refractory metal contact metallurgy with low specific contact resistance and all nitride based semiconductor components
- Novel heterostructure carrier selective contact structures in the absorber layer to increase V_{oc} and relax doping requirements
- Thermionic escape from “shallow” quantum wells (QWs).

Why InGaN?

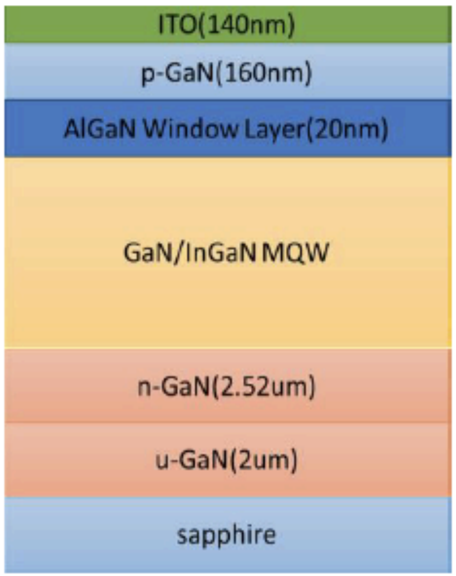
Opportunities for III-Nitride Solar

- *Tunable bandgap*
- *High absorption coefficients*
- *High thermal stability*
- *Existing $6 Billion+ dollar industry with existing Infrastructure*
  - *Blue and UV LEDS, Lasers*
  - *White Lighting*
  - *Power Switching, RF Electronics*
- *Falling Price Structure*
- *III-Nitrides are substantially cheaper and safer to produce than traditional III-V's*

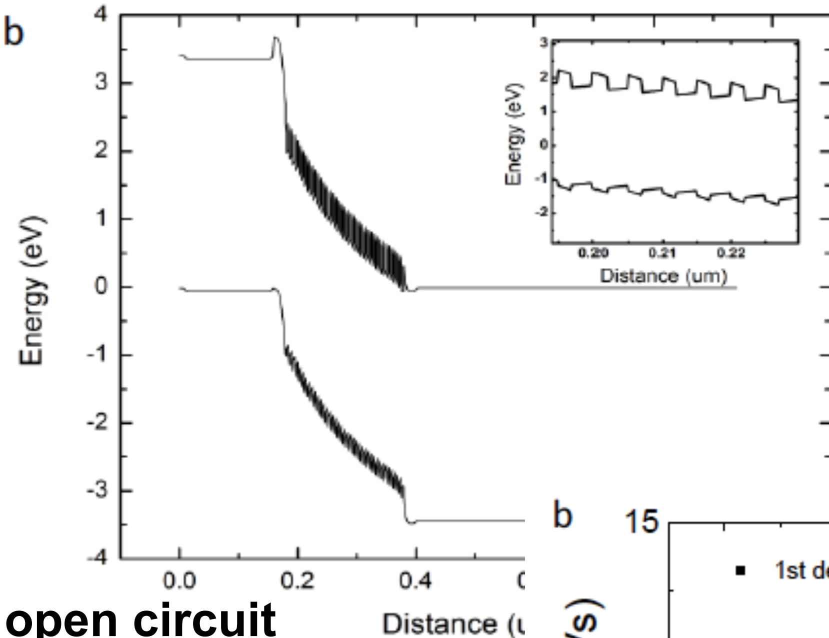


Multi-Quantum Well (MQW) Cells

a



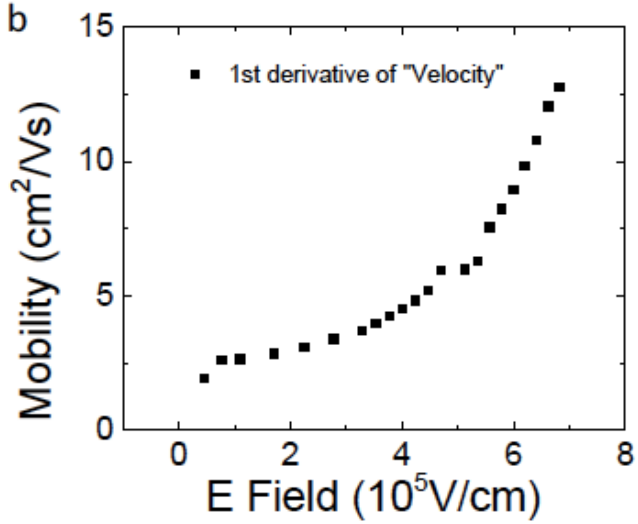
b



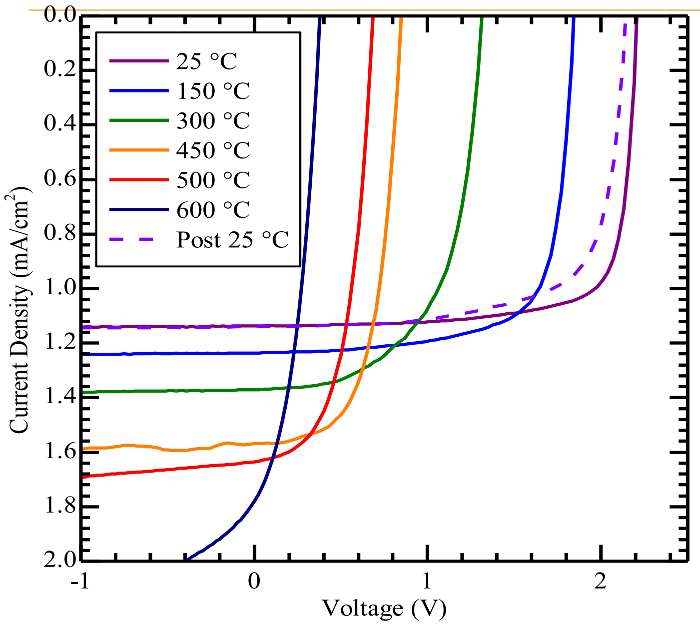
MQW Advantages: Large open circuit voltage of high bandgap materials, current collection of smaller bandgap material

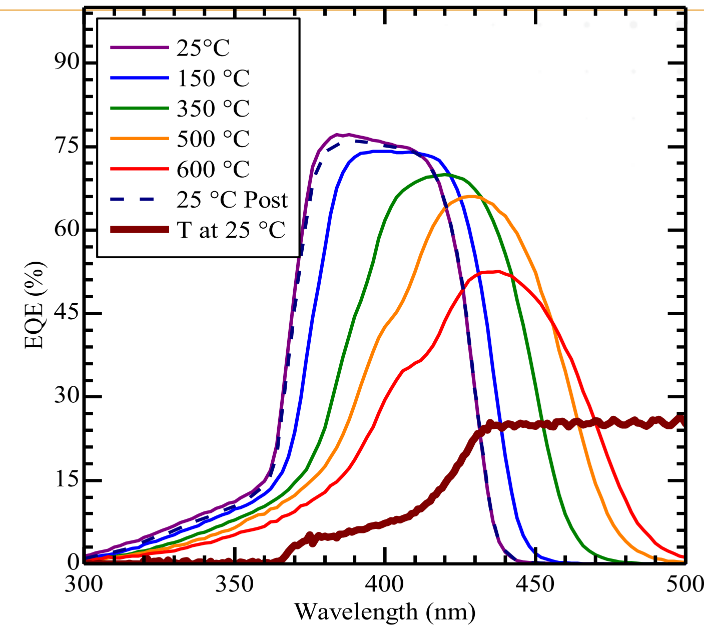
MQW problems: transport across MQW is difficult, reduced mobility and diffusion length, enhanced carrier recombination

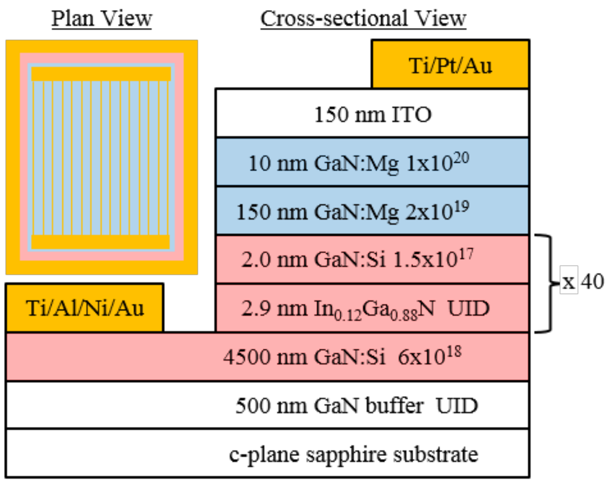
b



High Temperature InGaN MQW Devices

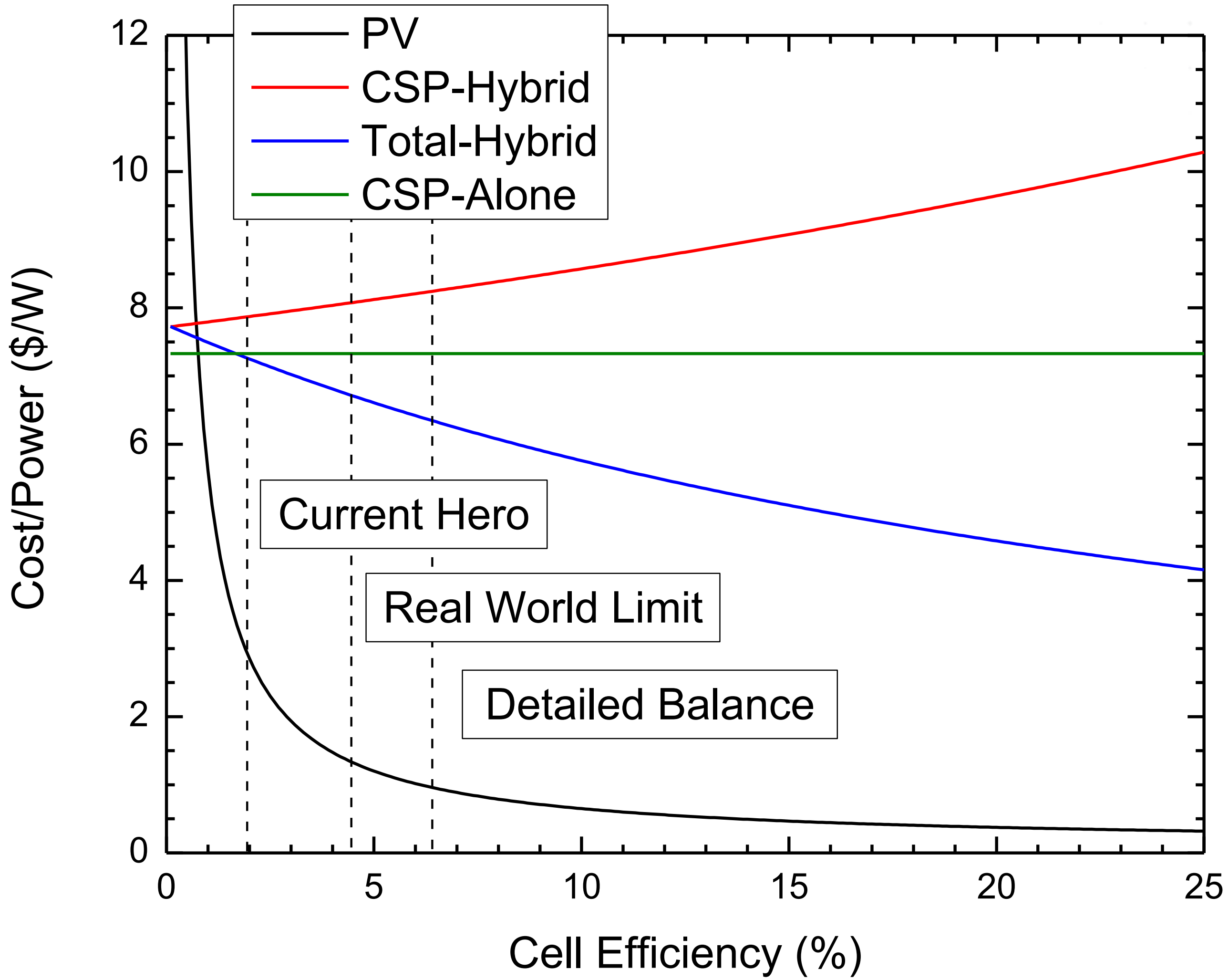






- Multi-quantum well InGaN (13%)/ GaN single junction
- Little degradation with testing now up to 700 C
- Suitable for power tower application

$/W Curves of Components vs. Cell Efficiency



Summary

- Achieving high efficiency solar cells requires overcoming limitations of traditional single bandgap junction solar cells
- Nanostructured materials provide multiple opportunities for both high efficiency and low cost energy converters circumventing S-Q limits.
- Requires materials advances, fundamental advances in physical understanding, technological improvements.
- Central challenges are improved physical understanding, materials, transport and surfaces

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Collaborators/Students

Christiana Honsberg, ASU
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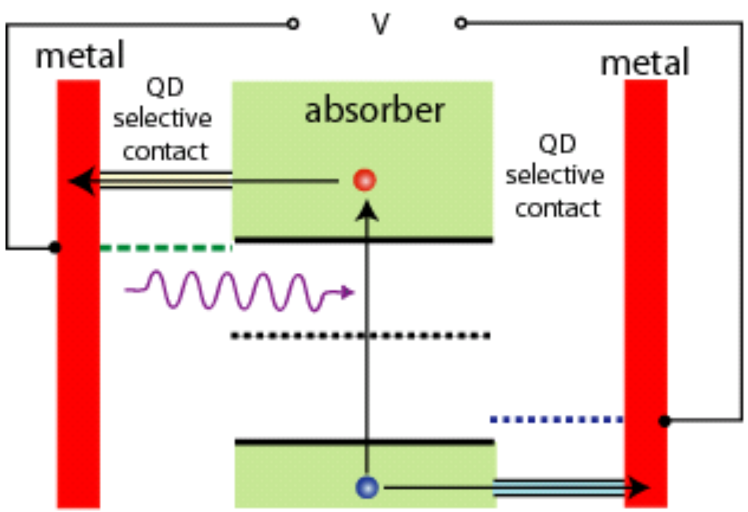
Gavin Conibeer, UNSW
Prad Muralidharan, ASU
Raghu Hathwar, ASU
Yi Fang, ASU

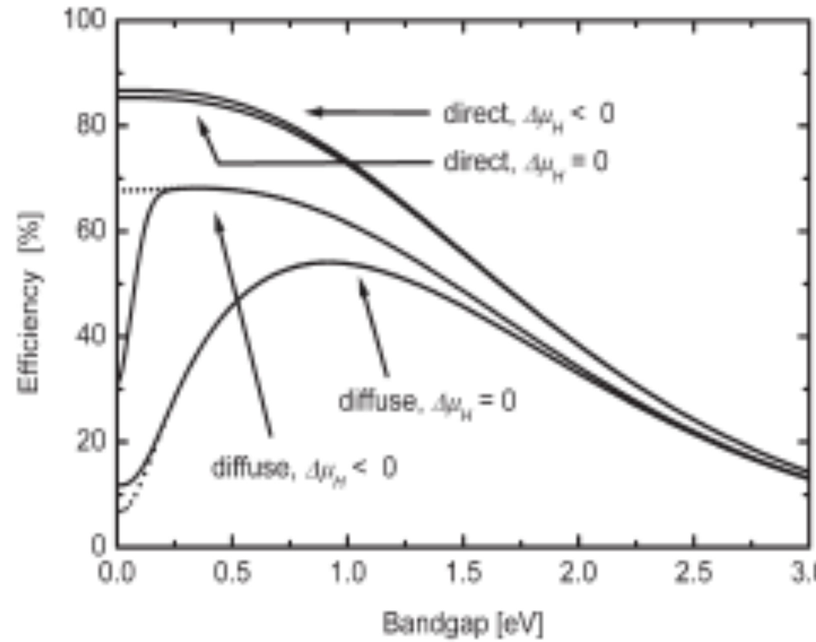
Hot Carrier Solar Cells

- Energy of electron (hole) extracted before thermal relaxation occurs; optimal $T_{e,h}$ is on order of 3000K
- Energy selective contacts (wide bandgap, resonant tunneling QW, QDOTs)
- Efficiency improves with concentration, absorber electron temperature
- Suppression of energy loss critical: reduced dimensionality, nonequilibrium phonons

$$P_{out} = \left(I_{ph}/q\right)\Delta\mu_H T_a/T_H + \left(I_{ph}/q\right)\varepsilon_{ext}(1 - T_a/T_H)$$

Schematic of a hot-carrier solar cell (Würfel 2005)

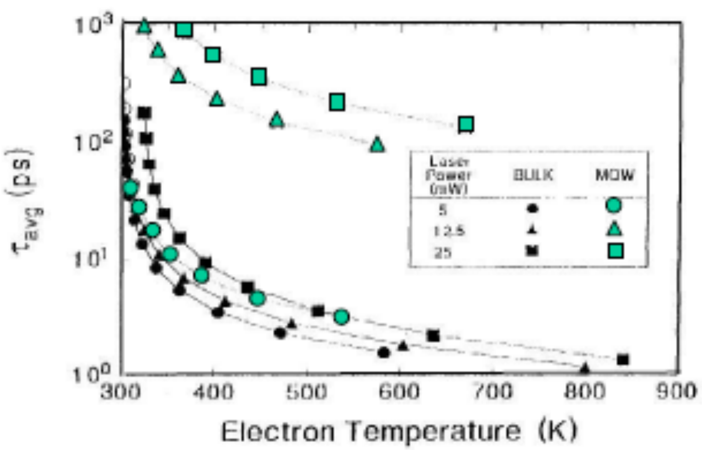




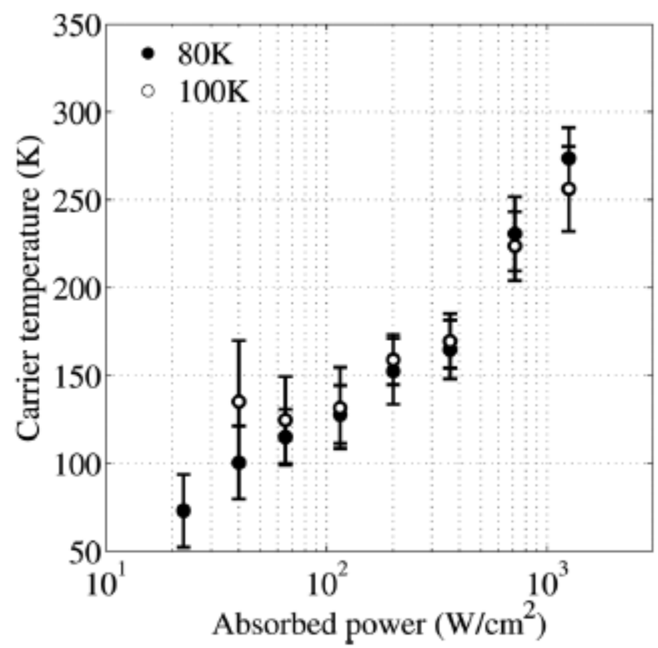
Ross and Nozik, JAP **53**, 3813 (1982)

Hot Carrier Solar Cell Realization in Nanostructures

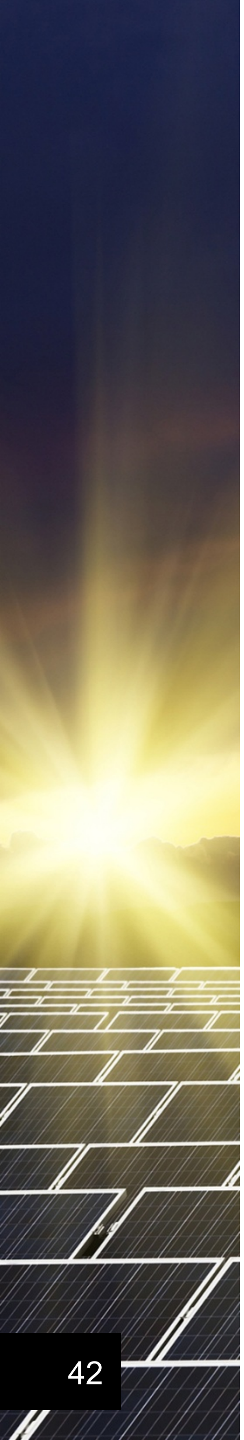
- In order to realize sufficiently high T_H, must have greatly reduced electron-phonon relaxation time
- Quantum dot systems show strong reduction in cooling
- Reduced energy loss rates have been observed in QW systems:
  - Pelouch et al., PRB 45, 1450 (1992)
  - Hirst et al., PVSC 2011
  - Le Bris et al., Energy and Einv. Sci. 5, 6225-6232 (2012)



Y. Rosenwaks et al, Phys. Rev.B 48, 14675 (1993)

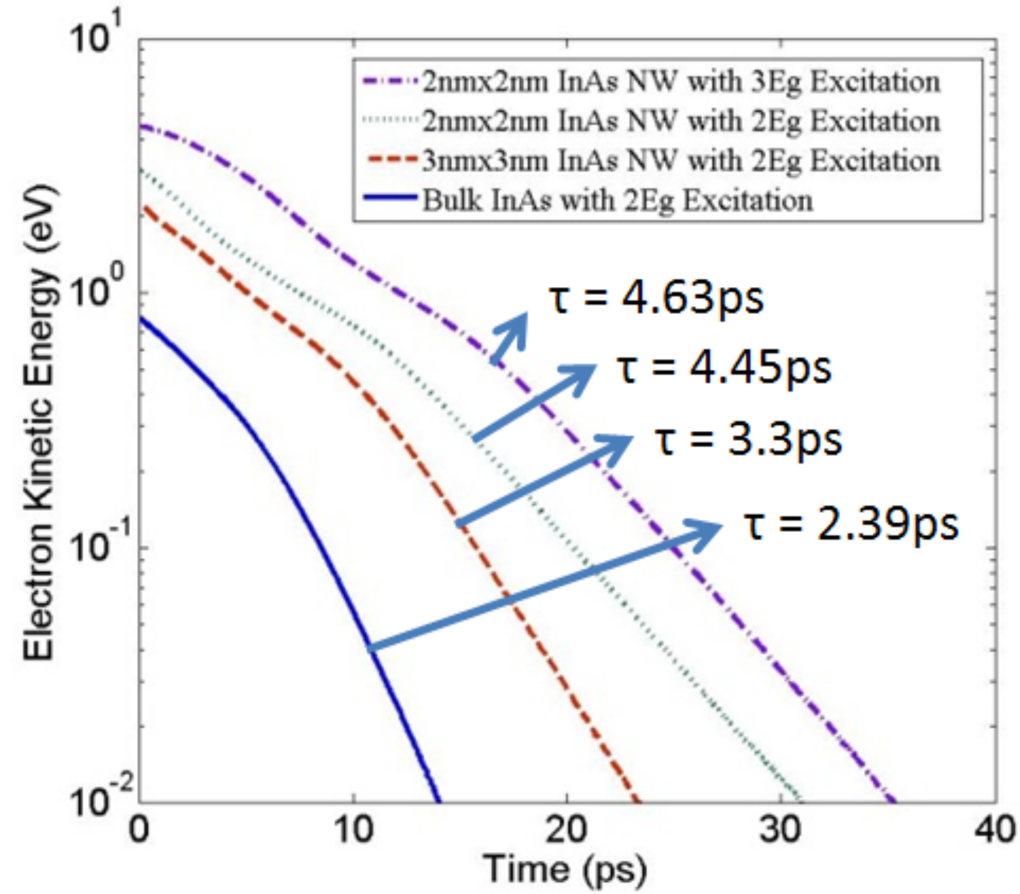


Le Bris et al.



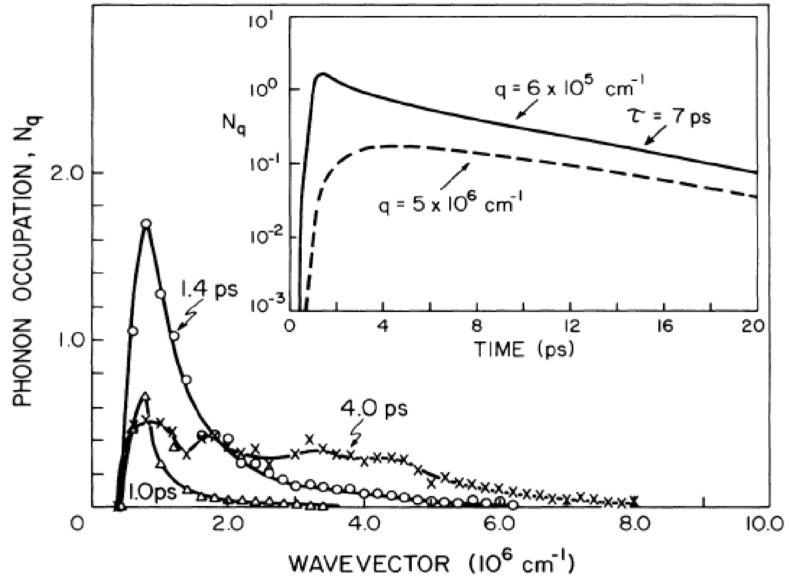
Monte Carlo Simulation of Energy Decay Times

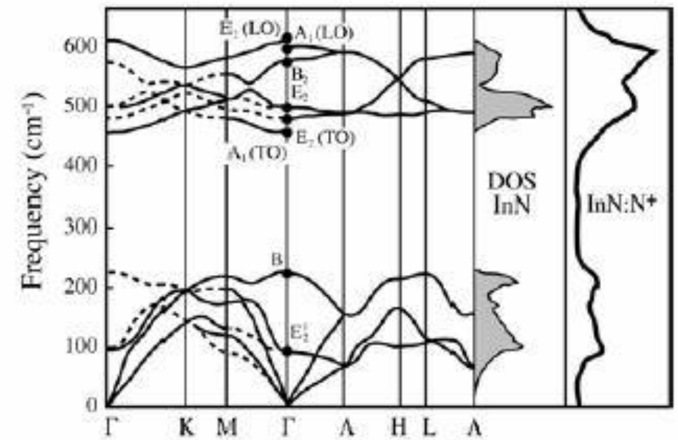
- Relaxation times extracted from the exponential tail of the energy time curve.
- Higher relaxation times for NW compared to Bulk.
- Relaxation times for different excitation energies of the same NW are similar.



(R. Hathwar et al., EDISON 2015)

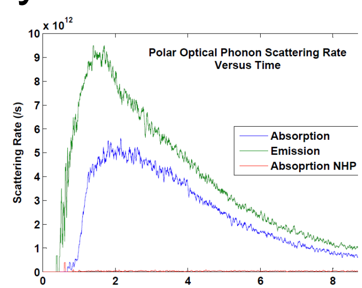
Nonequilibrium Phonons

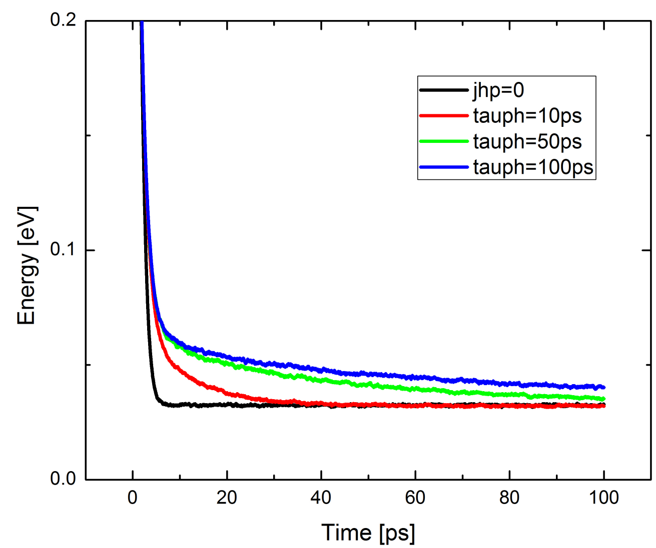




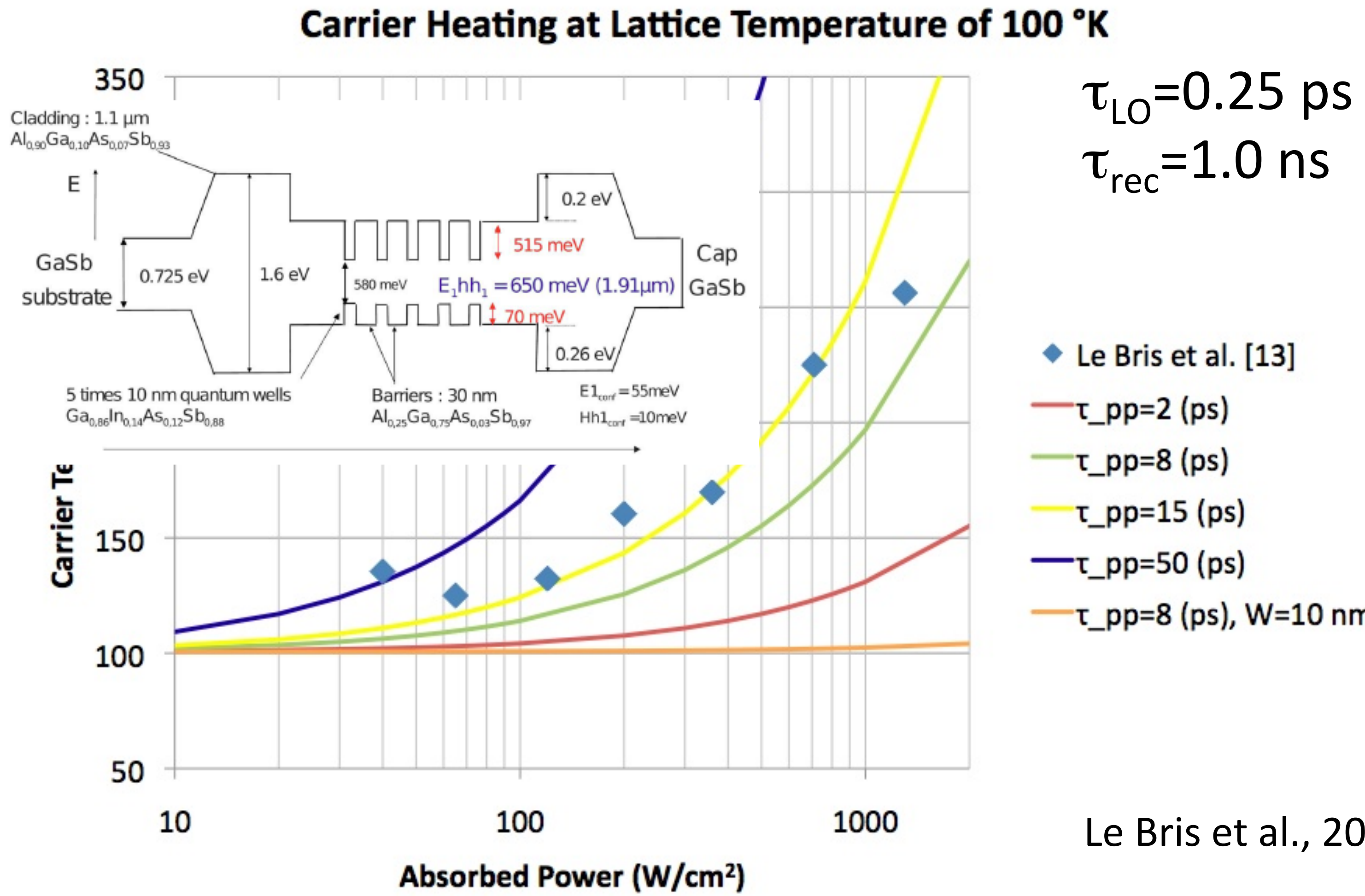
G. Conibeer et al, PVSEC 19, 2004
V. Davydov Appl.Phys.Lett. 75, 3297 (1999)

Another way to keep energy in the system is to trap phonons and keep the energy in the coupled electron-phonon system





Carrier Relaxation in GaSb QWs



τ_{LO}=0.25 ps

τ_{rec}=1.0 ns

Le Bris et al., 2012

Solid lines correspond to calculated carrier temperatures for different phonon lifetimes for a GaSb quantum well system. Data points correspond to carrier temperature measurements made of a GaSb quantum well system.