Multi-Exciton Generation in Nanostructured Solar Cells

The energy challenge is one of the greatest moral and intellectual imperatives of our age

The science of energy is challenging, philosophically satisfying and fun

G.T. Zimanyi
UC Davis

Multi-Exciton Generation in Nanostructured Solar Cells

I. Why study Solar Energy Conversion?

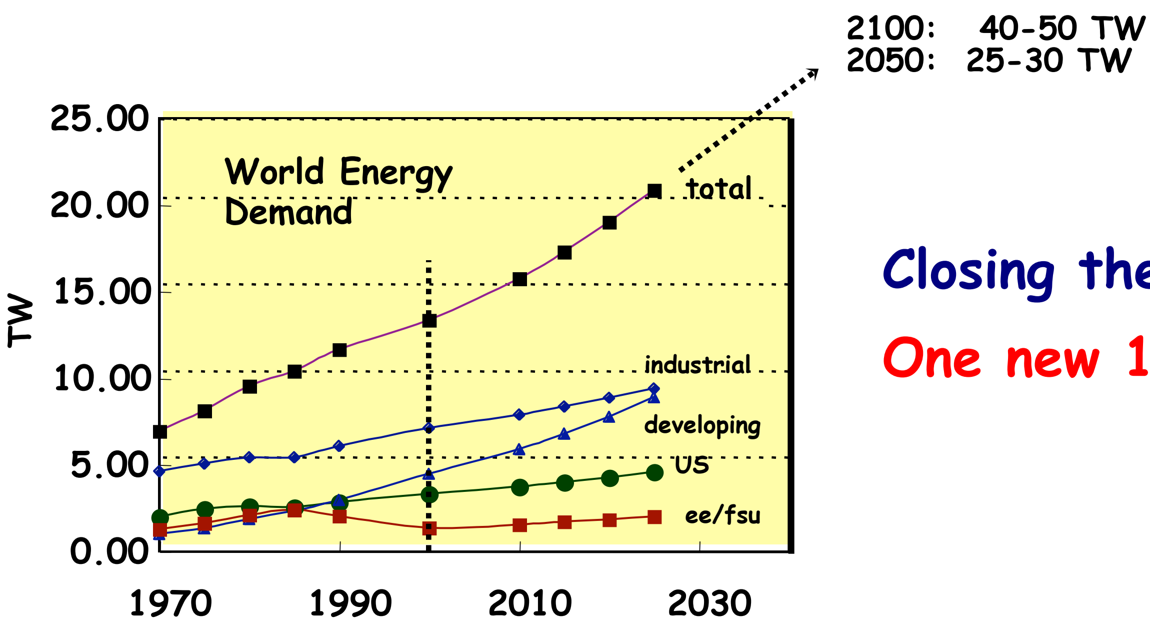
II. Entry points for physicists into Energy Science

III. Multi-Exciton Generation: the UC Davis Solar Collaborative

Grand Energy Challenge

Demand gap

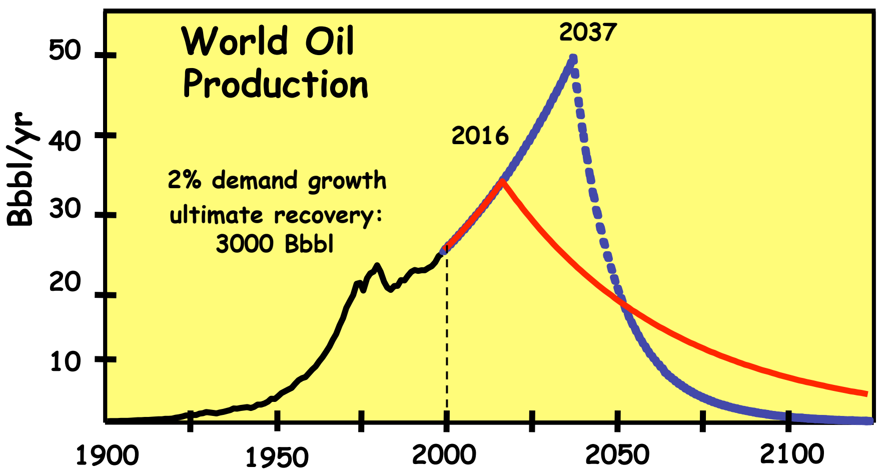
- double demand by 2050, triple demand by 2100
- gap between production and demand:
  14TW(2050)-33TW(2100)

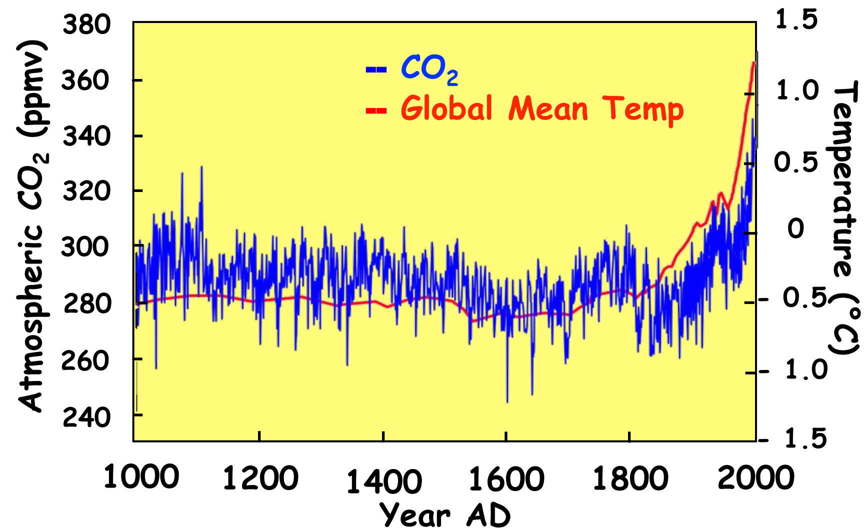


Closing the demand gap requires:

One new 1GW power plant/day!

Oil: Works today, Hurts tomorrow





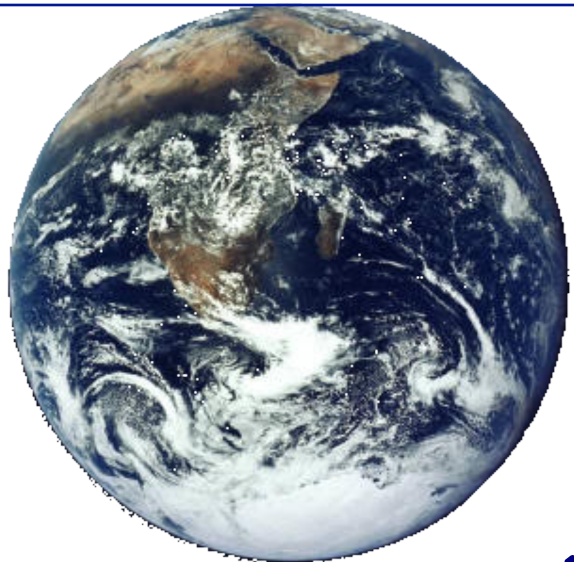
1. Oil and coal will run out
2. Produced by regions of conflict
3. Uneven distribution of production, wealth
4. Primary cause of climate change

Sources of Renewable Energy

Solar
1.2 x 10^5 TW on Earth's surface
36,000 TW on land (world)
2,200 TW on land (US)

Wind
2-4 TW extractable

Biomass
5-7 TW gross (world)
0.29% efficiency for all cultivatable land not used for food



Tide/Ocean Currents
2 TW gross

Hydroelectric
4.6 TW gross (world)
1.6 TW technically feasible
0.6 TW installed capacity
0.33 gross (US)

Geothermal
9.7 TW gross (world)
0.6 TW gross (US)
(small fraction technically feasible)

Solar is the Most Promising Energy Resource

Sunlight is a singularly suitable energy resource

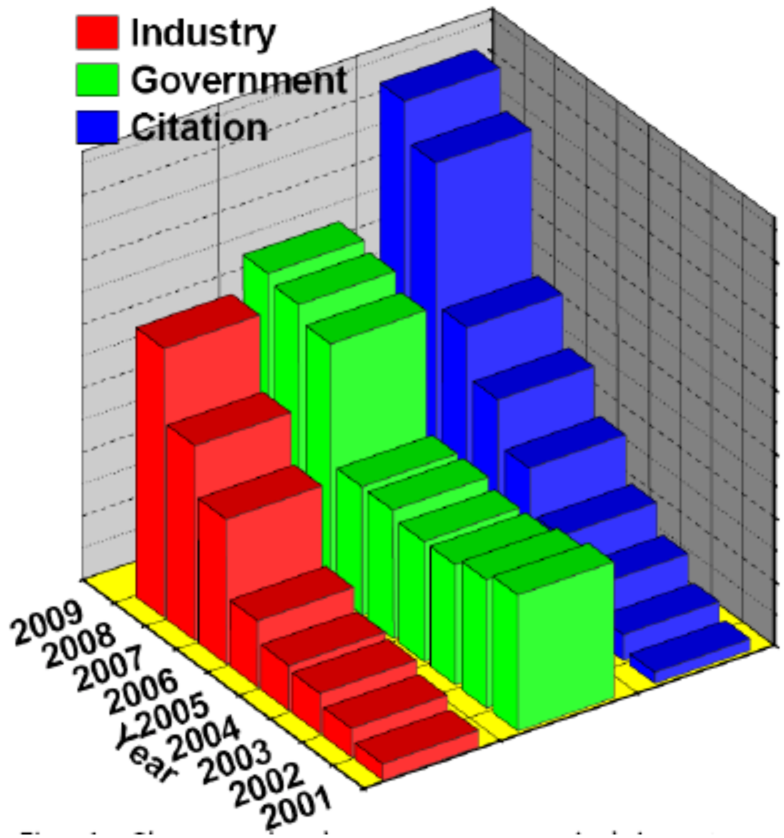
1. the only resource in sufficient quantity
2. environmental impact is minimal and benign
3. no catastrophic breakdown mode
4. politically safest, conflict-free
5. non-man-made price volatility is minimal

The Solar Opportunity: Recent Expansion

Venture capital investments

DOE solar technologies budget

Photovoltaics citations in ISI database

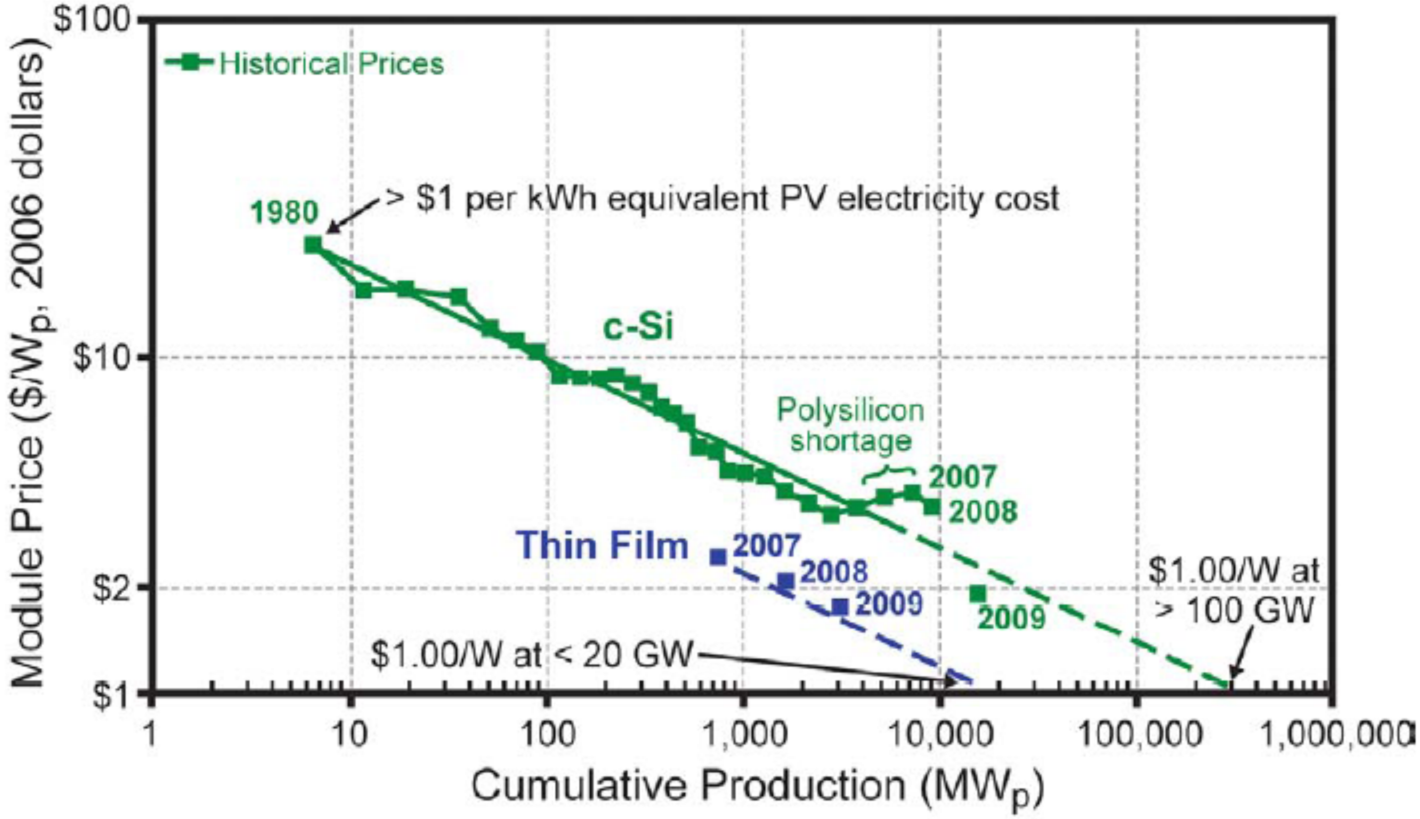


Opportunity, Lost

1. A 100x100 mile area covered with PV can provide all of the energy needs of the US, completely eliminating the need for burning oil

2. On today's prices installing this would be ~ $500bn, 25-50% of the bank bailout of 2009!

The Solar Moore's Law



Price drops by 20% for every doubling of production
No doubling per 18 months as area is not scaled down as in chips

Market Situation up to 2010

1.	Base grid energy price, cent/kWh	Solar price,* cent/kWh
US, residential	10-20	20-30

* without incentives

Solar/fossil energy price ratio in US ~ 2-3

2. Solar/fossil energy price ratio in EU ~ 1.5

3. Solar/fossil energy price ratio in JP ~ 1

SunShot initiative by DOE: 1$/W for wafers will provide "grid parity"

Generations of Solar Technologies

Figure of merit: Power/Price

1st generation: Increase power by increasing quality crystalline silicon: *SunPower*: 20-22%

2nd generation: Decrease price (decrease production temperature) amorphous Si, CIGS, CdTe: *First Solar*: 13-15%

3rd generation: Increase power, decrease price

2011/2012 Developments

1. Market:

- Ampulse Energy: 0.92 \$/W (Mar. 2012),
- Since then 0.72 \$/W: Price of imported Si wafers plummeted because of Chinese over-production and market collapse: SunShot goal achieved!

- But: fracking of natural gas moved grid parity to 0.3\$W

2. Science:

- GaAs: Alta Devices: 28% lab, 23.5% NREL verified

- Organic solar cells: Sumitomo 10.6% efficiency

DOE Scientific Priorities - 2010

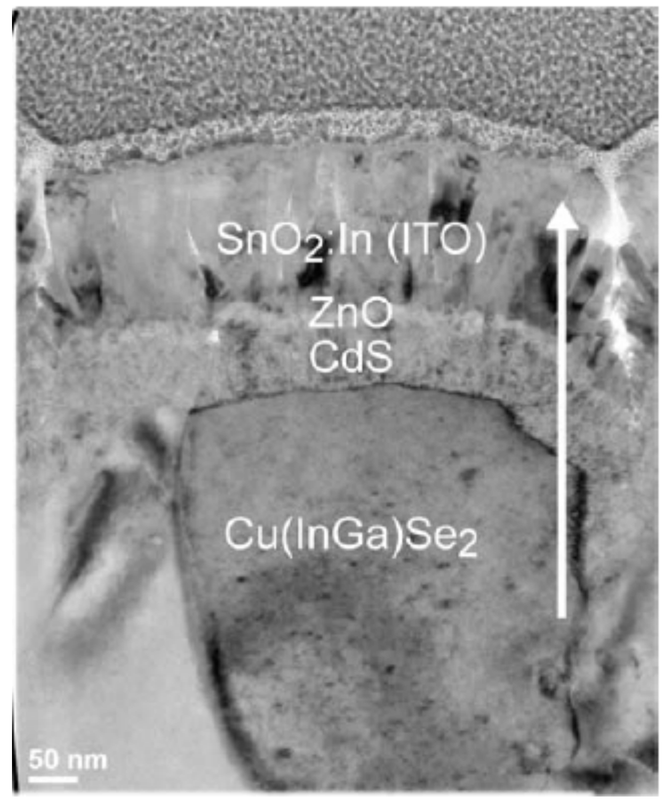
"Progress largely driven empirically, understanding of even existing cells is lacking" – The opportunity for physics

1. Characterization and modeling of interface processes:
   - dopant diffusion,
   - gap states caused by metal defects,
   - real effect of laser litography,
   - band alignment

2. Defects, grain boundaries

3. Interface inhomogeneities

4. Processes at contact



II. Entry Points for Physicists: Energy Science is Kool

"Progress largely driven empirically,
understanding of even existing cells is lacking"

1. Correlated impurities + Coulomb interaction

2. Multiple scattering theory

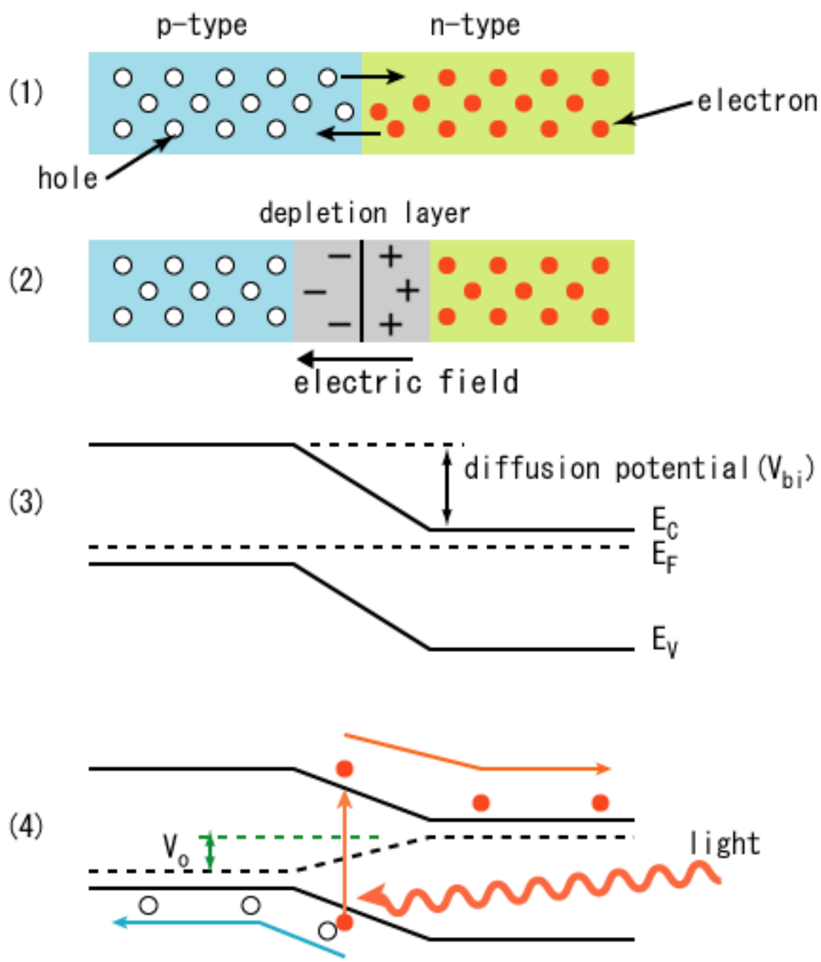
3. Plasmon-enhanced solar cells

4. Avalanches on driven Bethe-lattices

5. Path-breaking PV designs

6. Strong Coulomb interaction in nanoparticles

0. Solar Energy Conversion: Basics



Challenges include:

1. Capture much of the solar energy in electronic sector

2. Drive photo-electrons to electrodes with little loss to recombination

3. Cell needs to be cheap

4. Cell needs to be durable (20 yrs!)

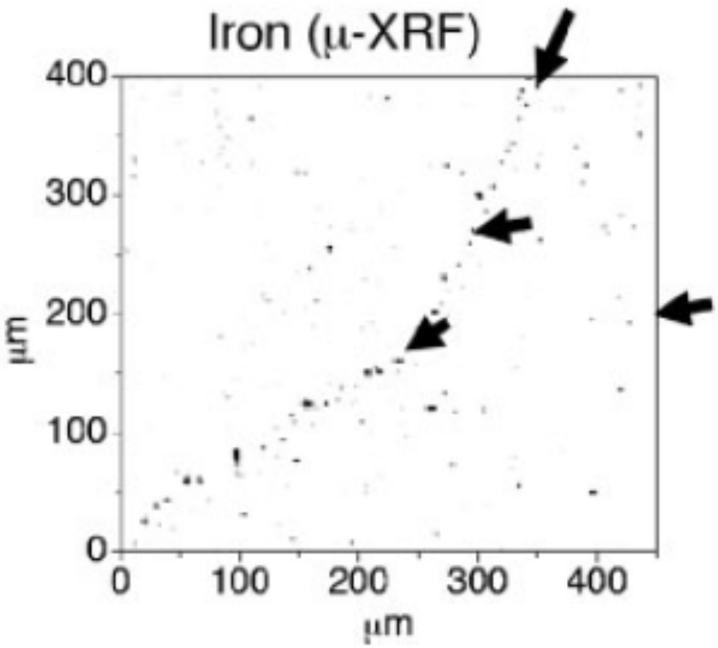
1. Correlated Impurities + Coulomb Interaction

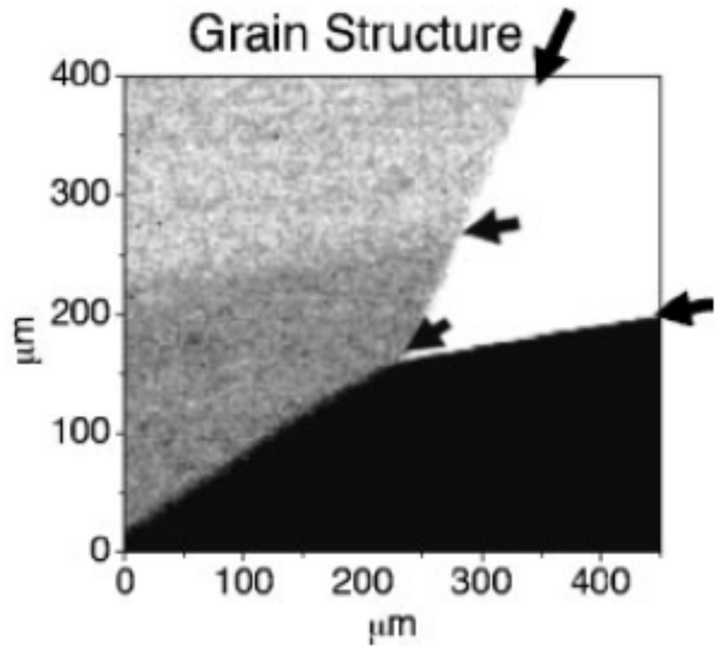
- Recombination is primary enemy of photo-electron extraction

- Driven by Coulomb interaction, enhanced by metallic impurities

- Metal impurities are lethal recombination centers even at $n=10^{16}cm^{-3}$

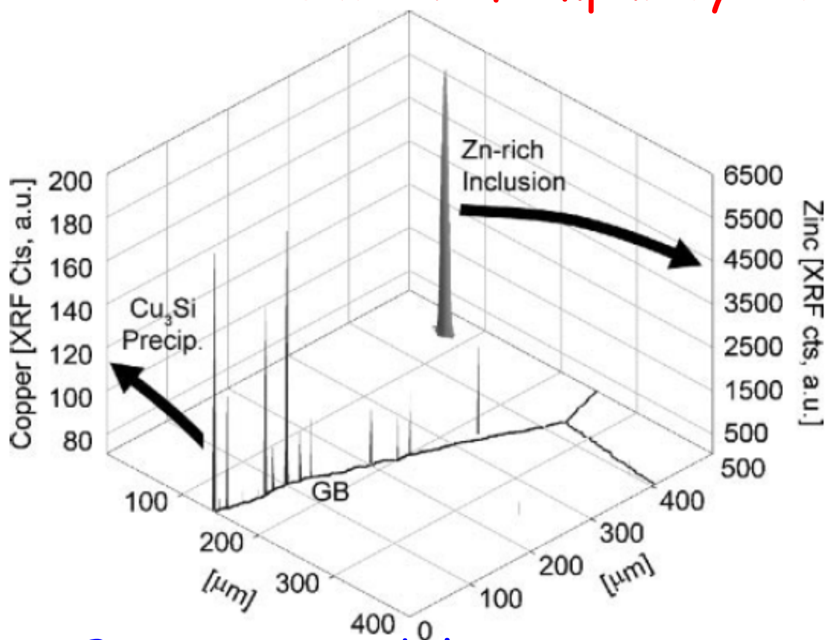
Weber: if you can't eliminate them, precipitate them to grain boundaries

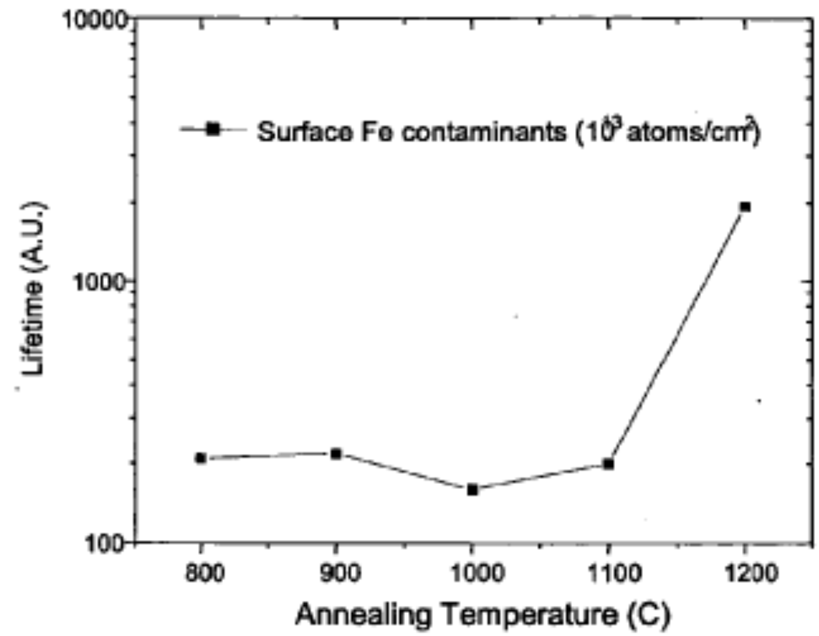




Exciton Lifetime Extended

Physics: - electron-hole recombination driven by Coulomb attraction
- enhanced by metallic impurity sites
- location of impurity sites is correlated



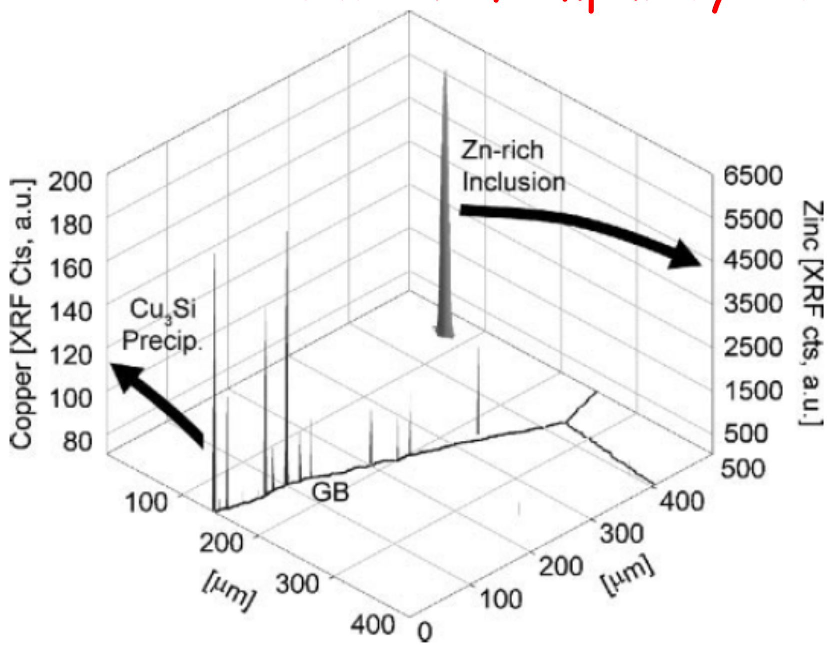


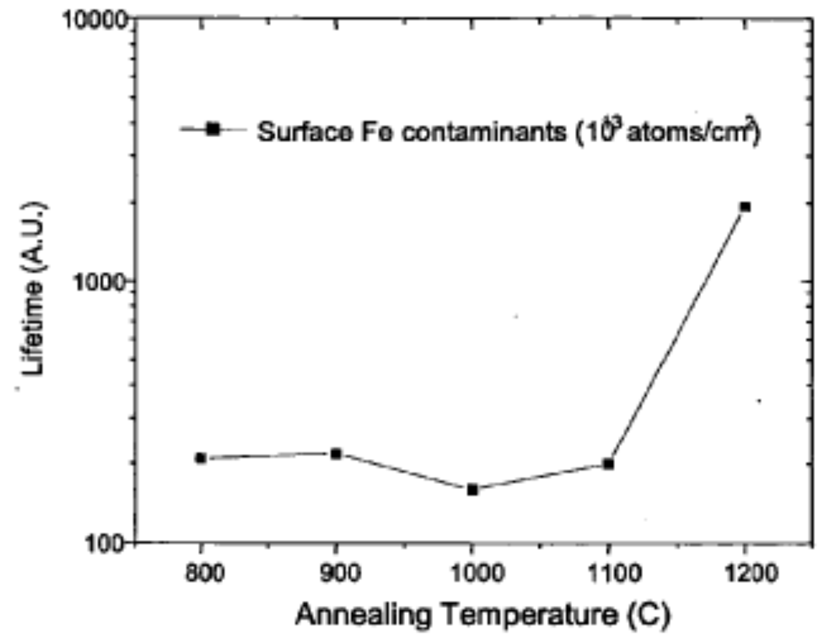
Business model:

- reduce costs by buying low grade ingots instead of expensive wafers
- precipitate impurities by gettering
- reach 16% conversion efficiency

Exciton Lifetime Extended

Physics: - electron-hole recombination driven by Coulomb attraction
- enhanced by metallic impurity sites
- location of impurity sites is correlated



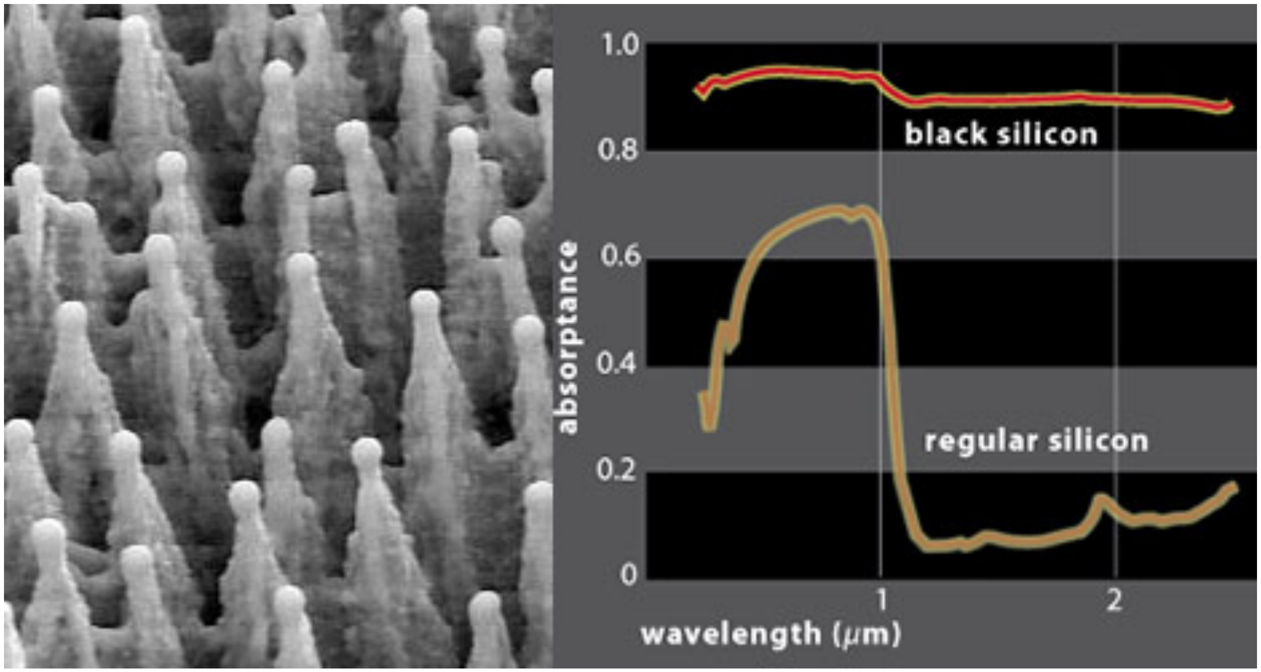


Founded Calisolar Inc.

Shook hands with Schwarzenegger

CALISOLAR

2a. Multiple Scattering Theory: Black Silicon



E. Mazur (Harvard)

- blast crystalline Si with femtosecond laser pulses in a dense pattern
- in SF6 atmosphere

Absorption increases close to unity!

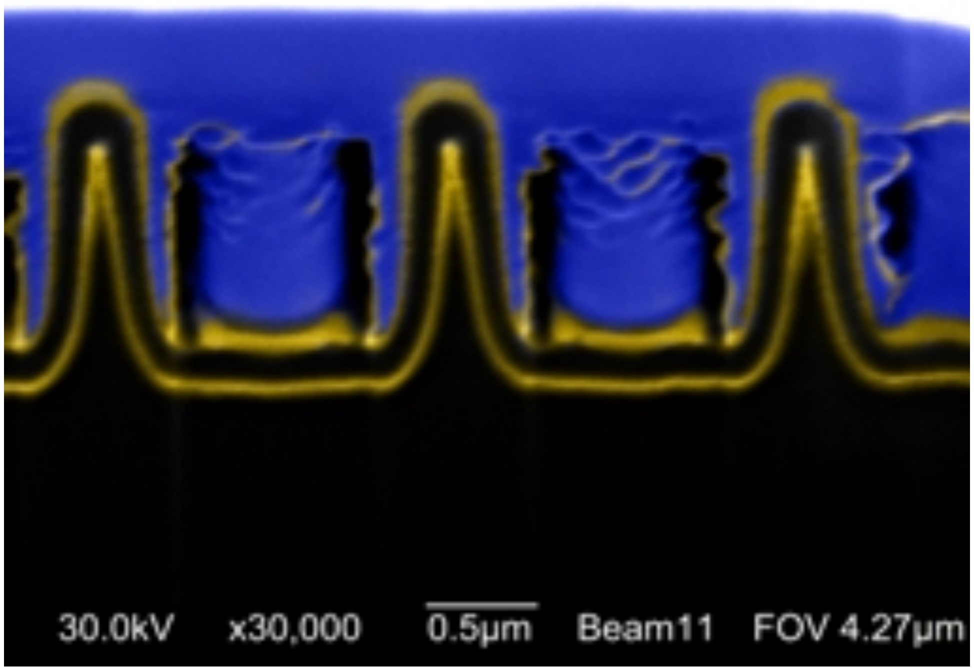
Absorption high in bandgap!

Physics:

1. Nanostructure forms on surface, multiple reflections enhance absorption
2. High density of defect states in gap
3. "Hyper-doping" of top junction layer: sulfur

Founded **SiOnix Inc.**

2b. Nano-Coaxial Cable



M. Naughton (BC)
Thick and thin problem

PV needs to be
thin to minimize material cost, and
thick to still absorb light

Nano-sized "coaxial cable" formed in amorphous Si can optimize these constraints

Achieved 8% efficiency
Founded **Solasta Inc.**

3a. Plasmon-enhanced Solar PV Cells

"Thick and thin" redux:

Silicon is expensive

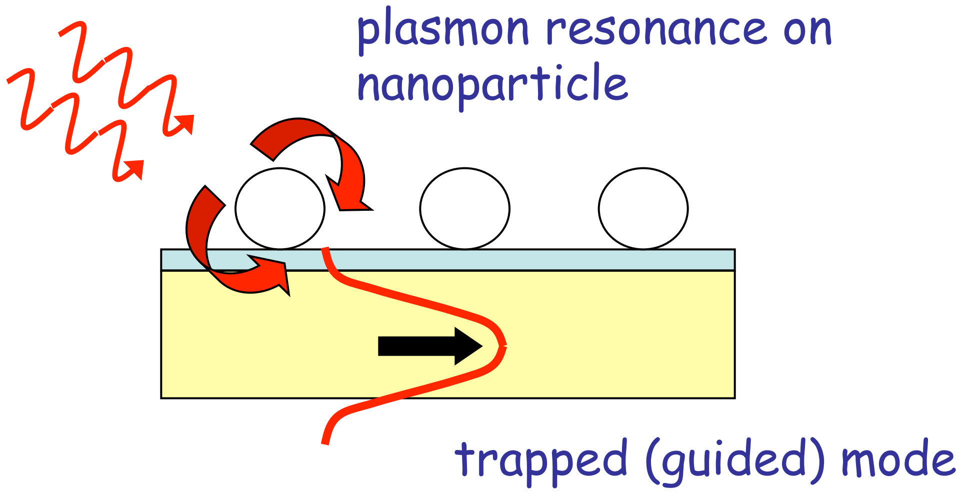
Today's solar cells: 300 micron thick

Make them 30 micron thick: cheaper

But: light will go through

Physics:

Redirect and capture light with plasmon resonance of nanoparticles

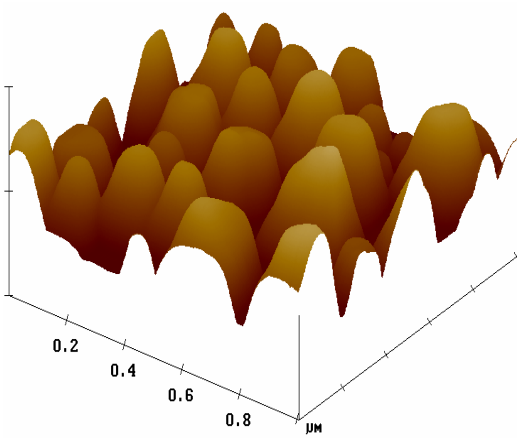


AFM/SEM Imaging

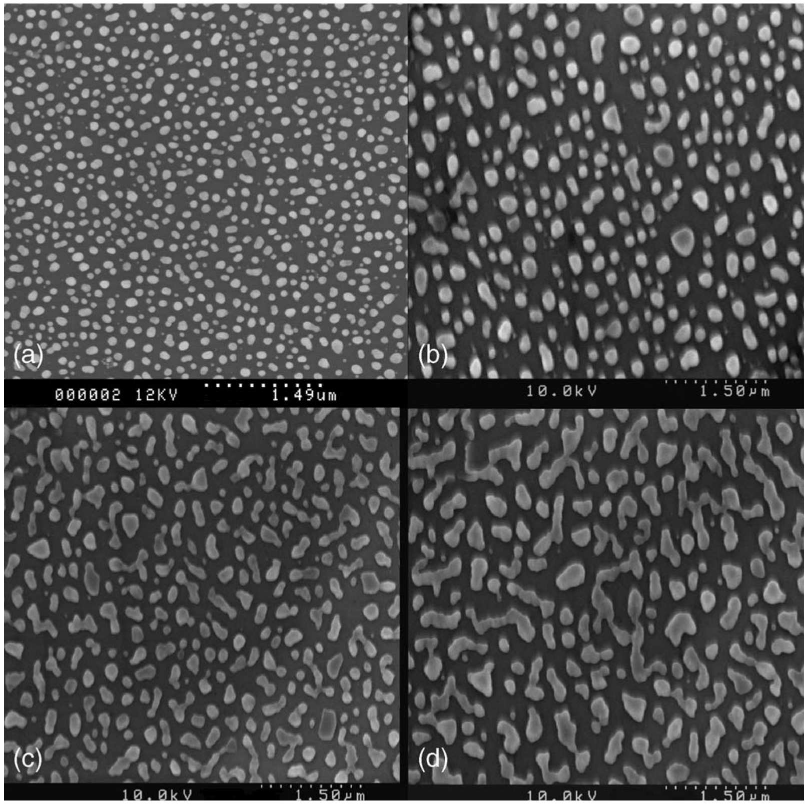
Islands on SOI formed by evaporation of silver followed by annealing for 1 hour at 200°C

film thickness z=14 nm

grain d=120nm



z=16 nm

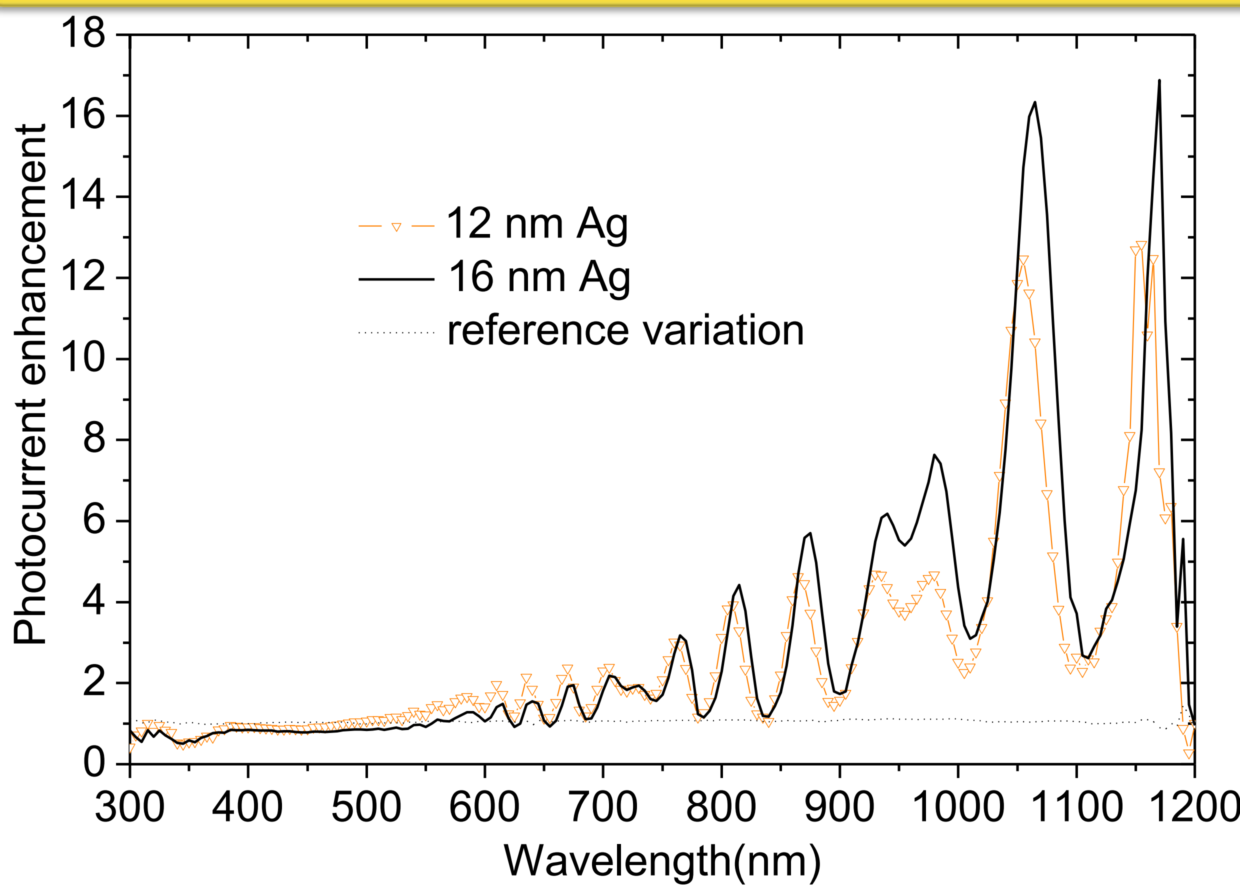


z=18 nm

d=350nm

z=27 nm

Plasmon-enhanced absorption in thin film cells



16X enhancement at 1050nm

30% enhancement over AM1.5G spectrum

Featured in the news section of Science, 2007: "New Solar Cells See the Light"

S. Pillai, K.R. Catchpole et al., J. Appl. Phys. 101, 093105 (2007)

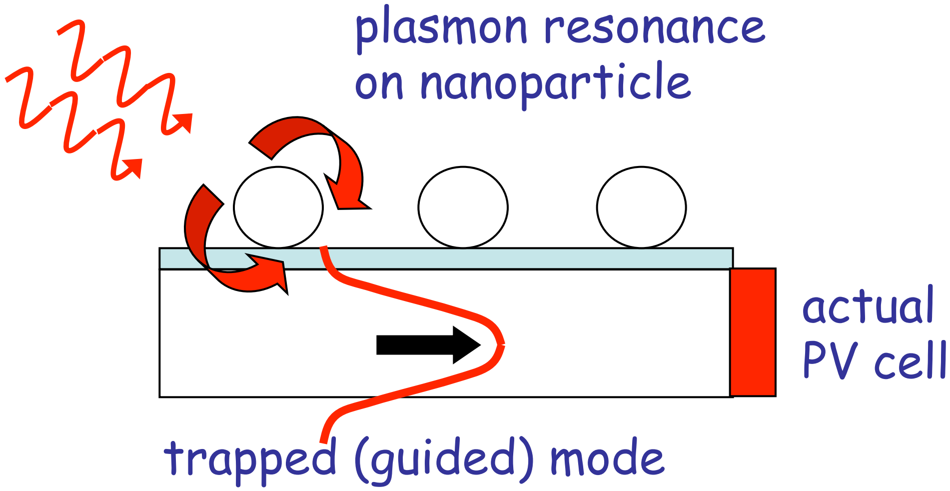
3b. Plasmon-enhanced Solar Concentrator Cells

"Thick and thin" max:

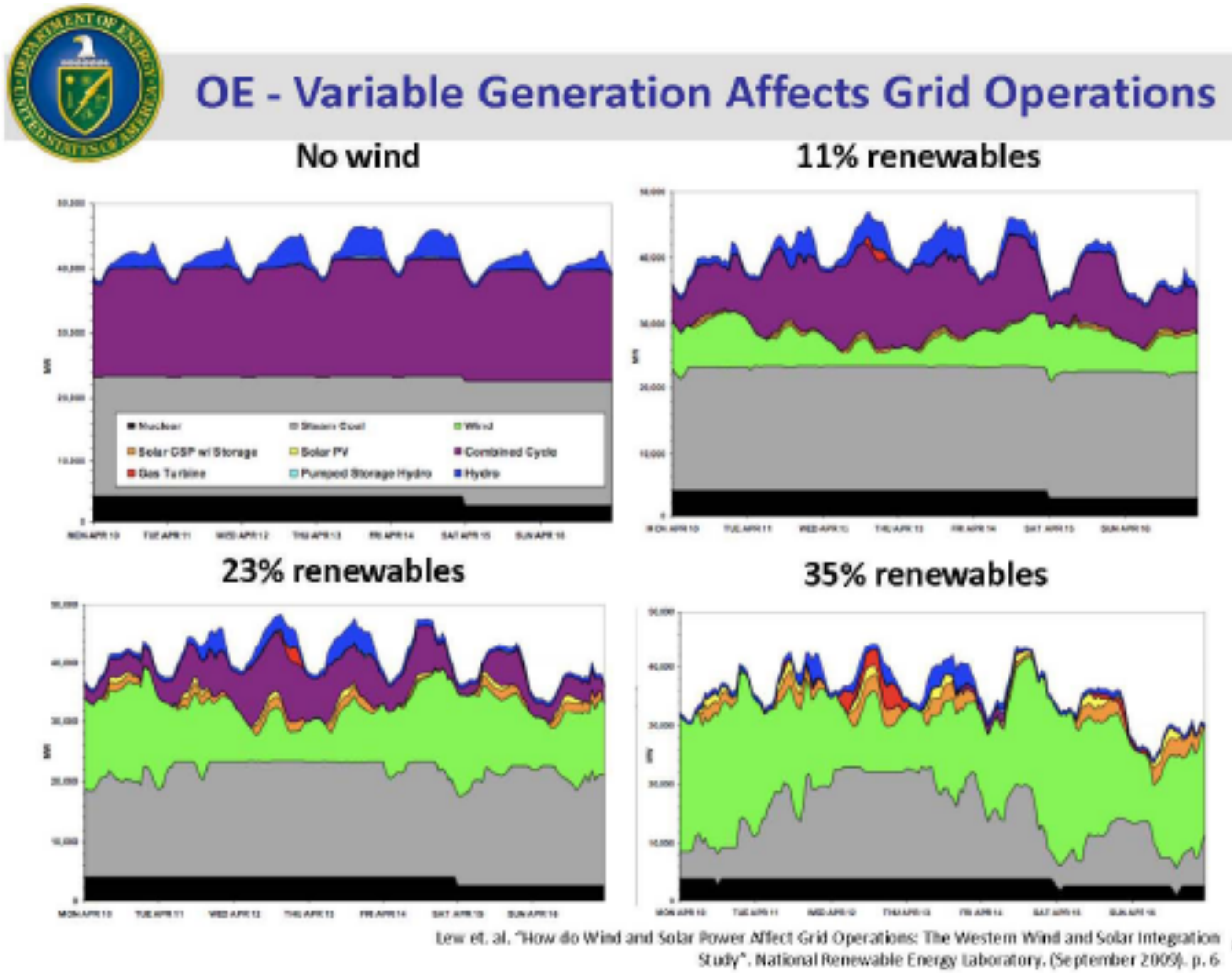
Silicon is expensive

Put small PV cell to

the edge of the glass!



4. Renewables Can Induce Grid Instabilities



Up-Driven Bethe-trees

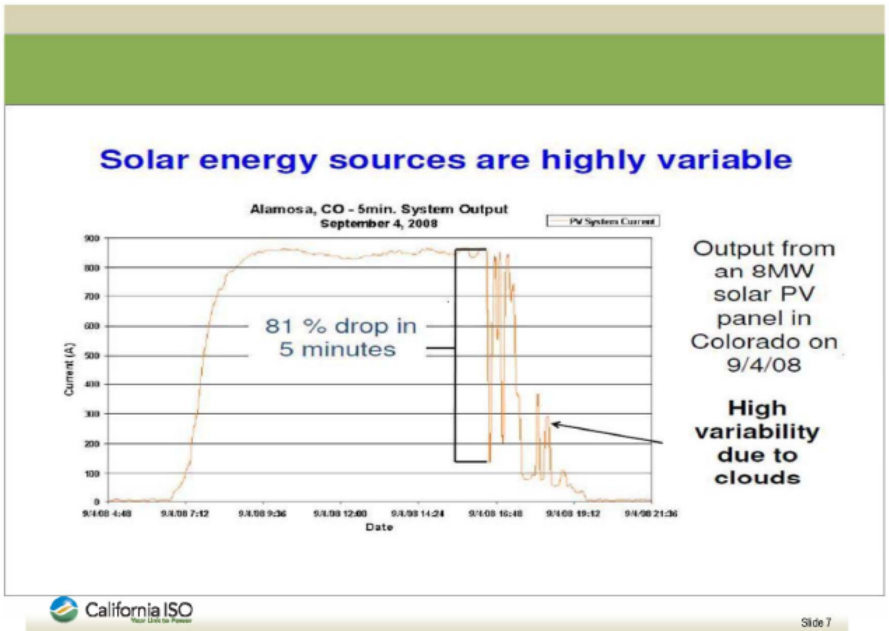
1. Power transmission systems are Bethe-lattices, formed for downstream energy transfer

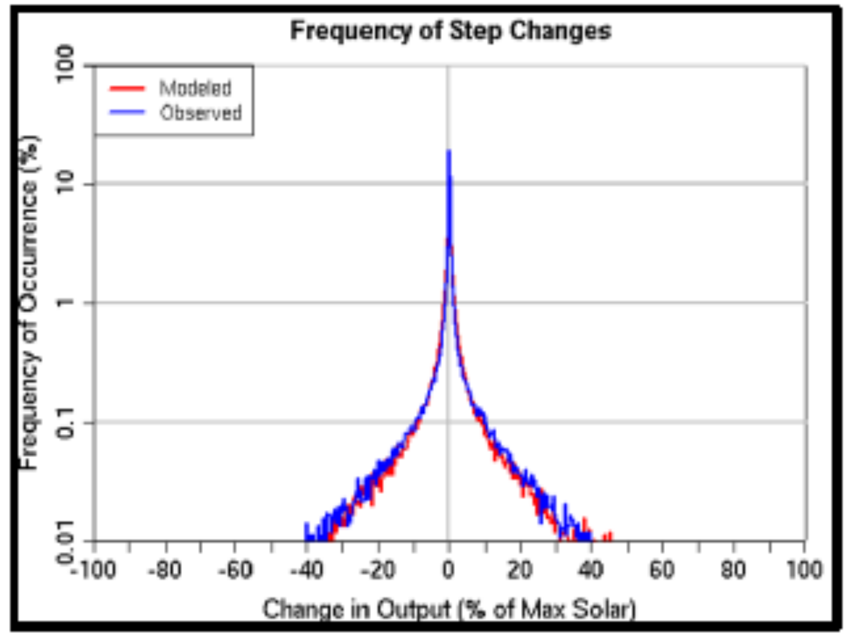
2. PV cells feed energy

- upstream

- intermittently

Avalanches on Up-Driven Bethe-trees





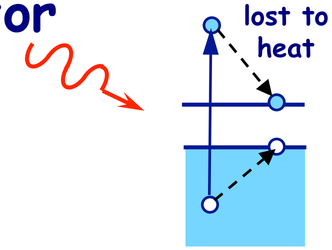
Large fluctuations

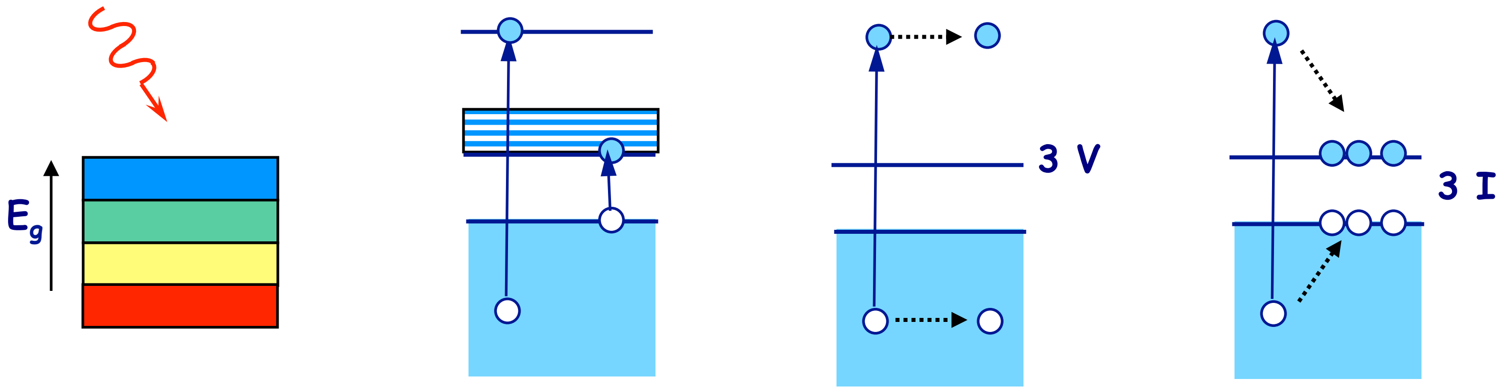
Broad distribution
of avalanches

5. Other Path-breaking PV Designs

Present technology: 31% limit for

- single junction
- one exciton per photon
- relaxation to band edge





multiple junctions | multiple gaps | hot carriers | multiple excitons per photon

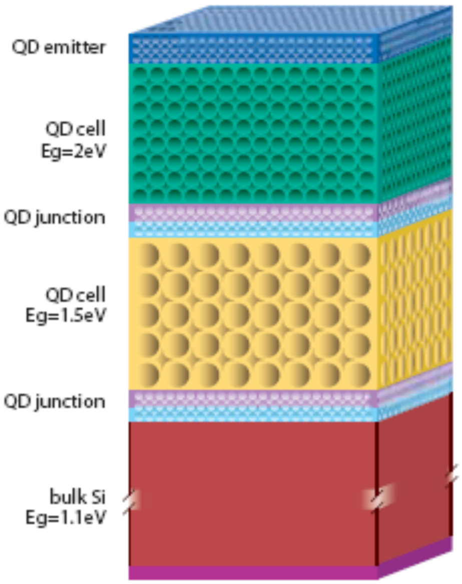
All Si Multi-junction Tandem Cell

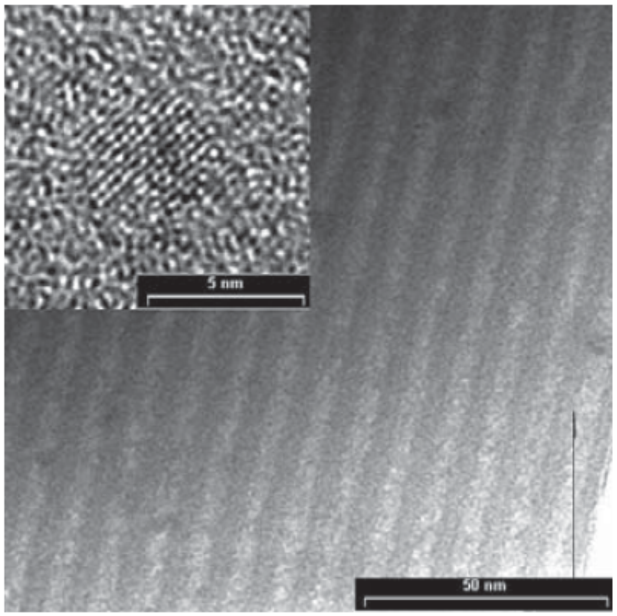
Layers of embedded quantum dots modify the Si bandgap:

-higher energy photons absorbed in top cell,

-medium energy photon in middle cell

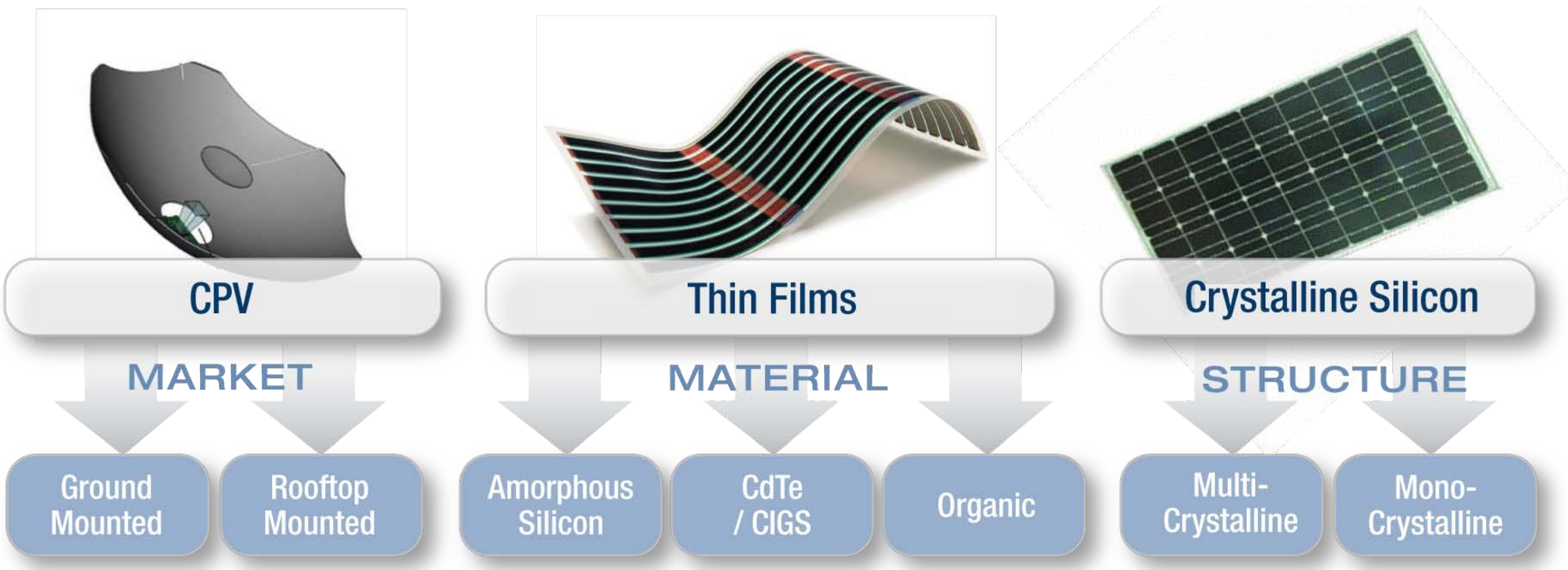
-low energy photons in lowest cell





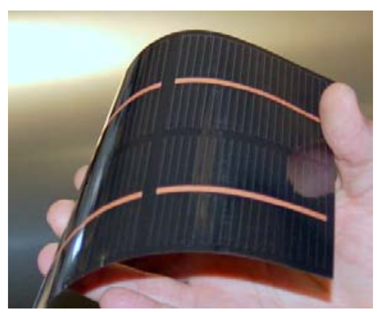
much less energy is wasted to phonons

Multiple Promising PV Technologies
Dan Arvidzu NREL Director, Sep. 2012

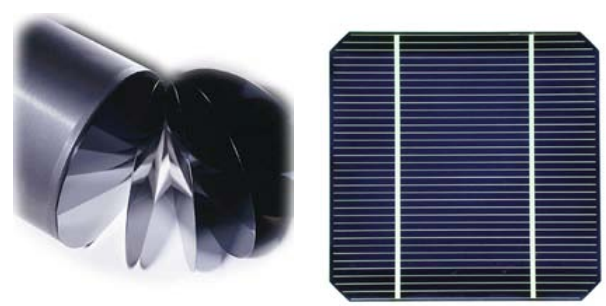


20x-100x

500x



$Cu(In,Ga)Se_2$ ~ 1-2 um



c-Si ~ 180 um


NREL
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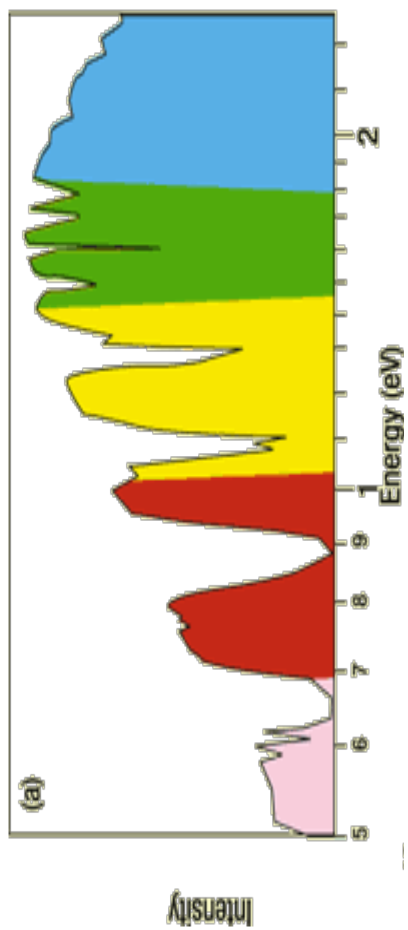
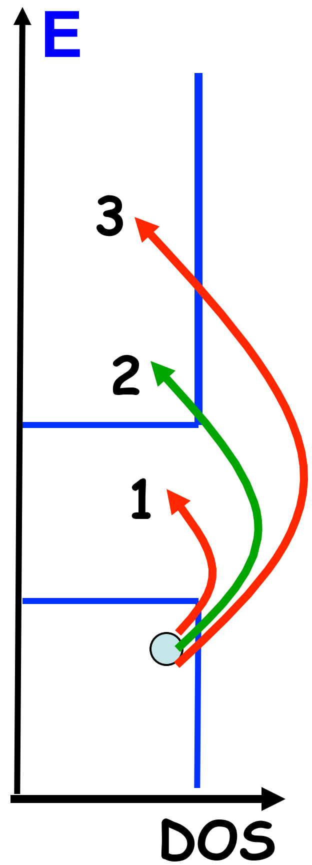
IIIA. Multiple Exciton Generation: Basics





1. No absorption below gap:
   photon wasted

2. Absorption to bottom of
   conduction band: optimal

3. Absorption high into band:
   excess energy to phonons: heats cell

Optimization of gap:
   max efficiency: **31%**
   (Shockley Queisser 1961)

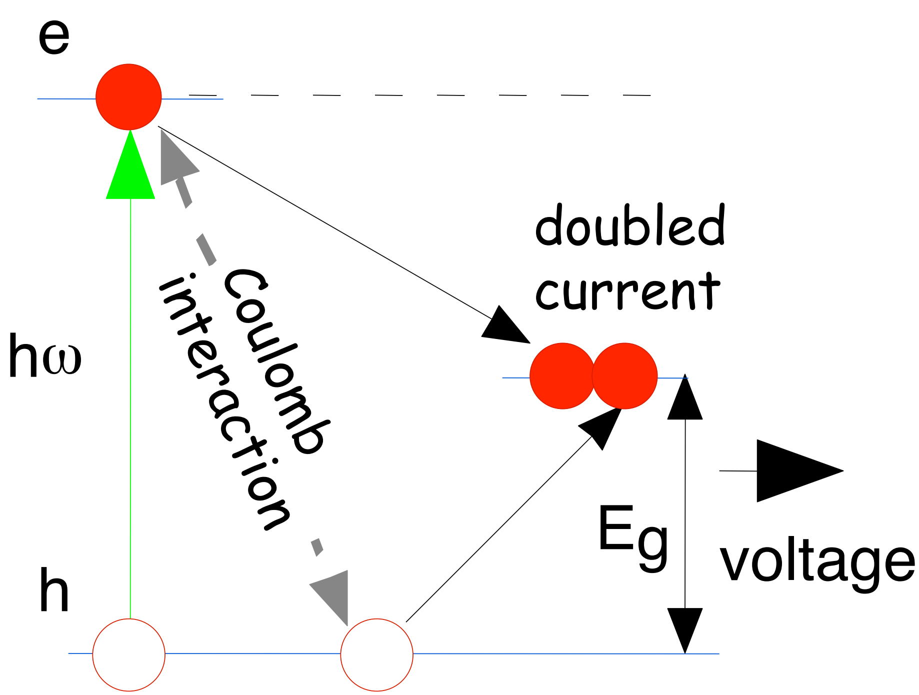
In real PV cells 80-85% of incident solar energy is lost!!

Problem: 1 photon in-1 electron out

Multiple Exciton Generation

How to keep energy in electronic sector?

Photo-electron can relax by exciting second electron across gap



Need: stronger Coulomb interaction

1. In nanoparticles electrons cannot avoid each other ~ screening is reduced

(Nozik 2001-2005)

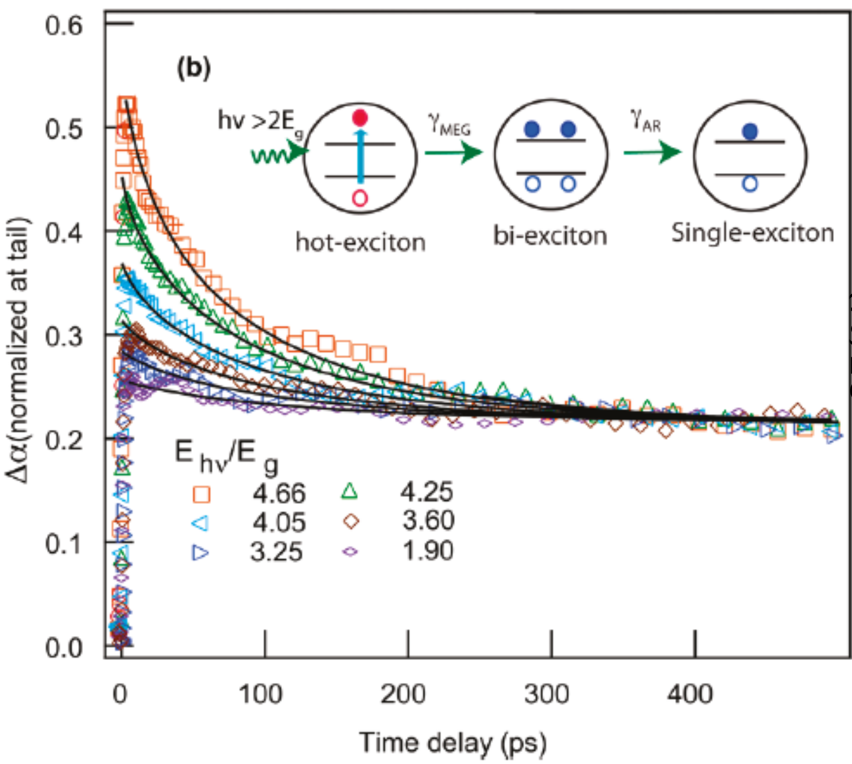
2. Alternative: Use Mott insulators - Manousakis

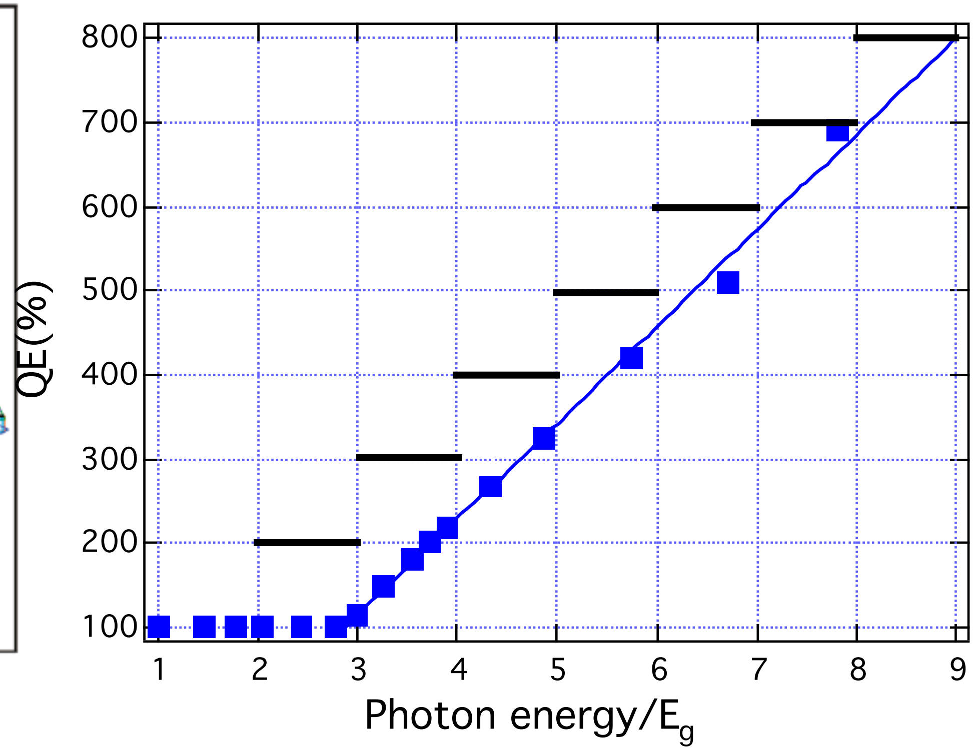
Max efficiency: 44-70%

MEG in Nanoparticles: The Discovery

Klimov, Schaller (2004) pump & probe:

Quantum Yield (QY=#(electrons)/photon) up to 700%

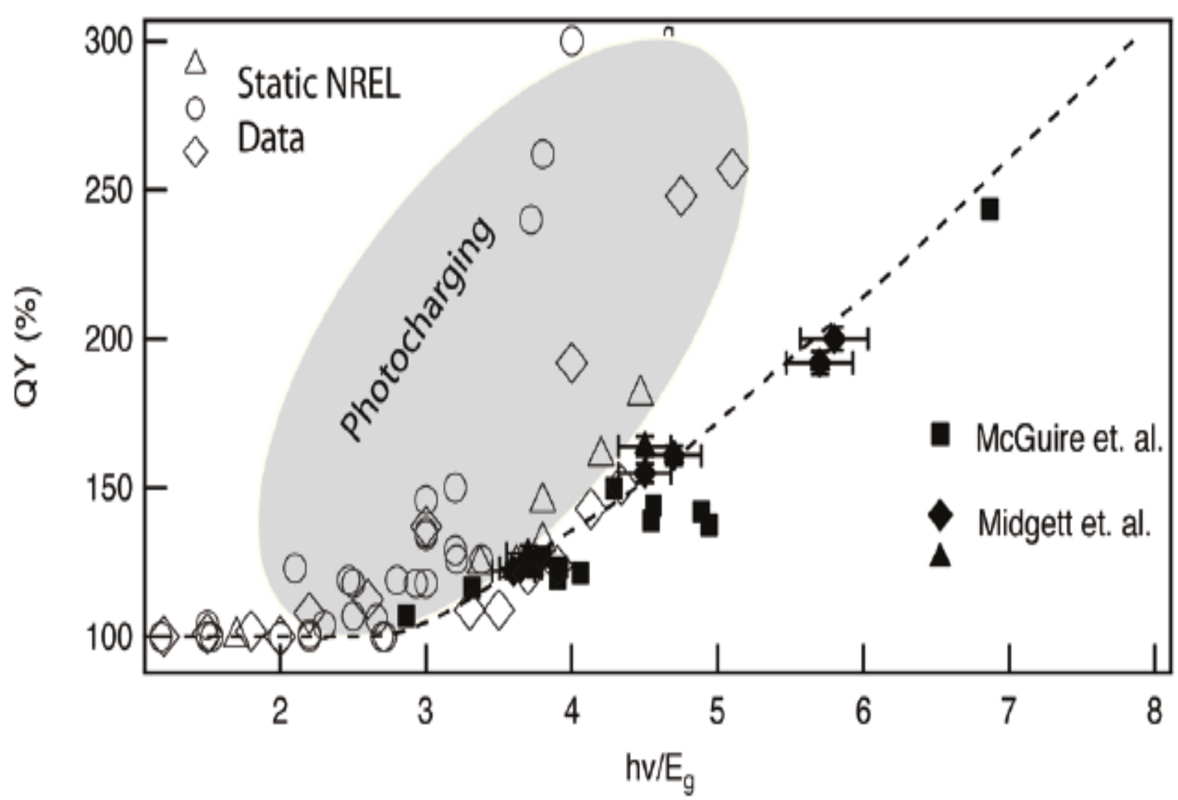




MEG: Consensus Status

Beard(2011):

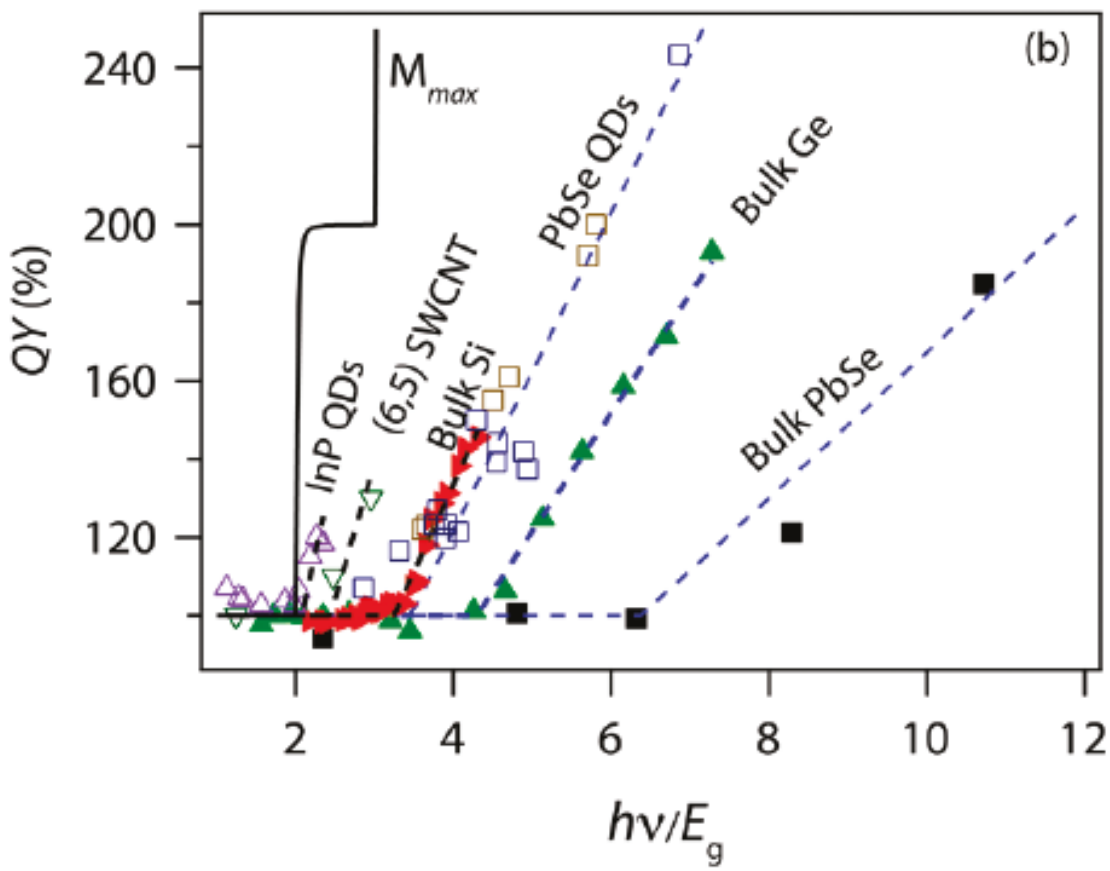
MEG is certainly present in NPs, albeit with lower efficiency



MEG: Efficient on Relative Scales, but Gap Big

* Conversion efficiency good: MEG more efficient in NPs than in bulk, as slope on relative energy scale hν/Eg is closer to theoretical max.

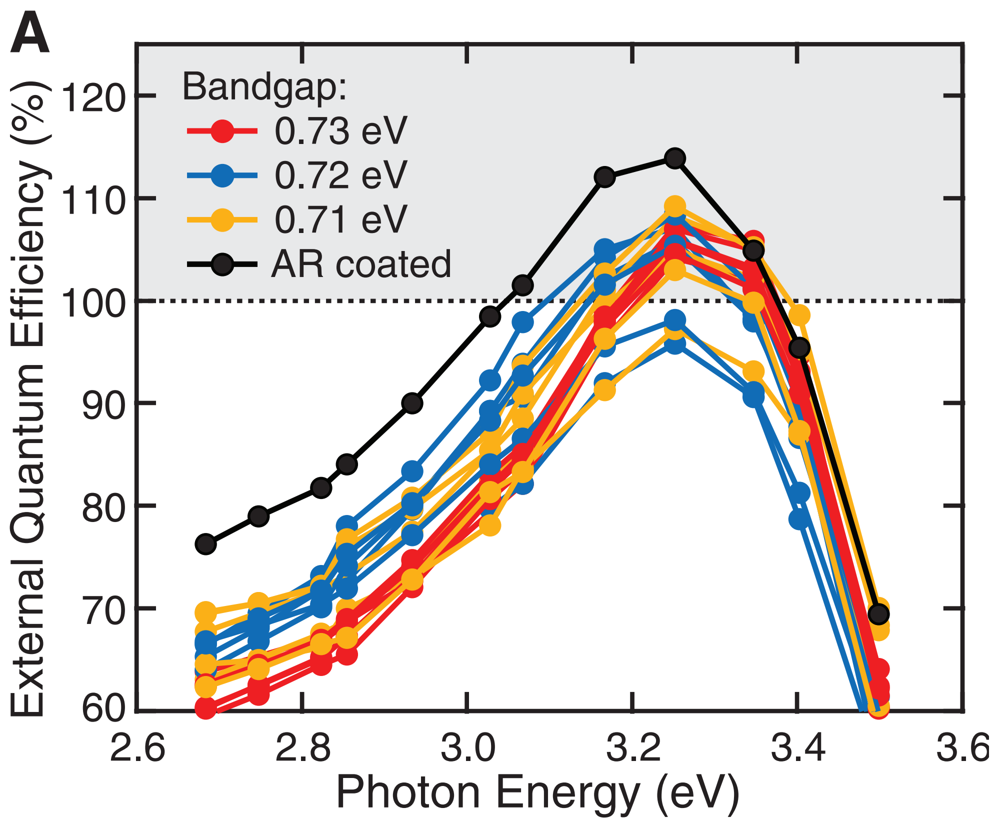
* Threshold energy bad: But Eg is larger in NPs, so on absolute energy scale NP solar cells absorb smaller fraction of solar spectrum



First working MEG solar cell: Dec. 2011

Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell

Octavi E. Semonin,[1,2] Joseph M. Luther,[1] Sukgeun Choi,[1] Hsiang-Yu Chen,[1] Jianbo Gao,[1,3] Arthur J. Nozik,[1,4]* Matthew C. Beard[1]*



EQE > 100%:

Good

Fabrication needed flammable hydrazine:

Not so much

IIIB. The Solar Collaborative at UC Davis

1. Optimize/resolve competing demands/processes:

Quantum Confinement enhances Coulomb and thus MEG

Quantum Confinement increases gap out of solar spectrum

Quantum Confinement reduces mobility & charge extraction

2. MEG primarily demonstrated with toxic materials:

Environmental regulations discourage their use

The Solar Collaborative at UC Davis/UCSC

Experiment:

S.Kauzlarich – synthesize NPs

D.Larsen – photoluminescence (PL/TA) characterization of NPs

S.Carter – assemble NPs into working solar cells

Theory:

G.Galli,G.Zimanyi – gap reduction by manipulating NP shape,
A. Gali, M. Voros reconstruction, embedding
S. Wippermann

Z.Bai,D.Rocca – code development for Bethe-Salpeter

D.Paul – multivariate analysis of PL/TA data

Experiment: Synthesize Si, Ge Nanoparticles

- synthesize Si, Ge, core-shell NPs with good yield
- narrow size distribution
- stable over long term

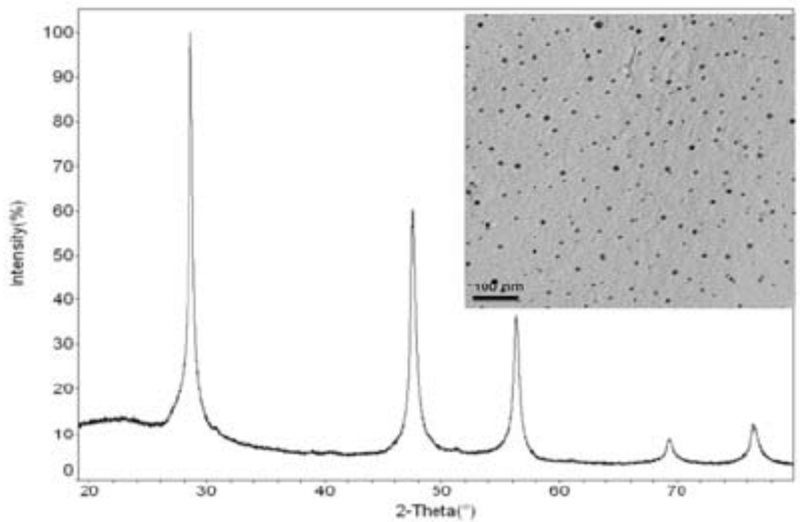
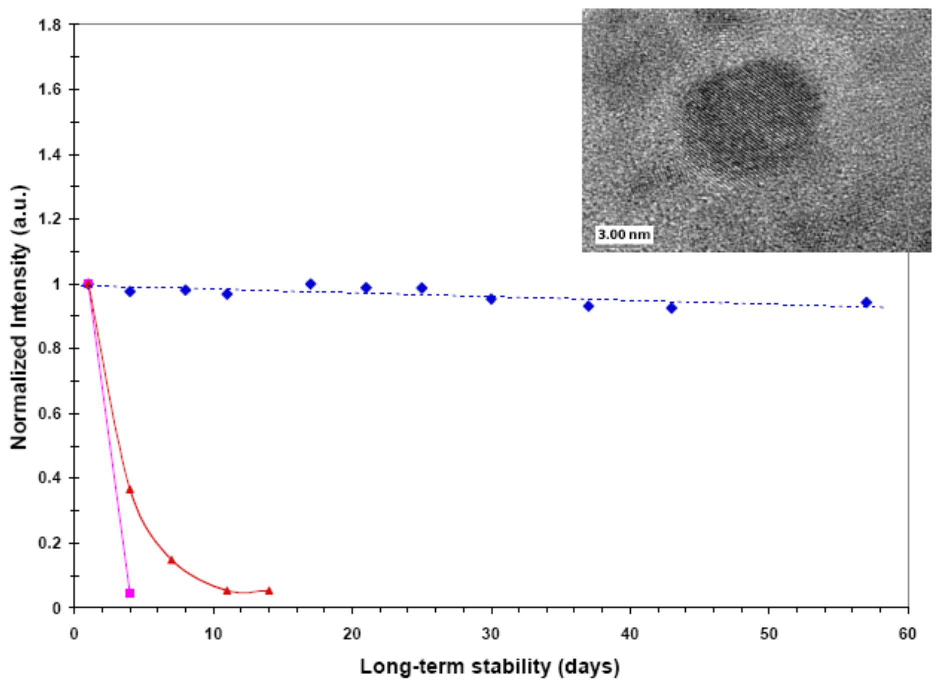
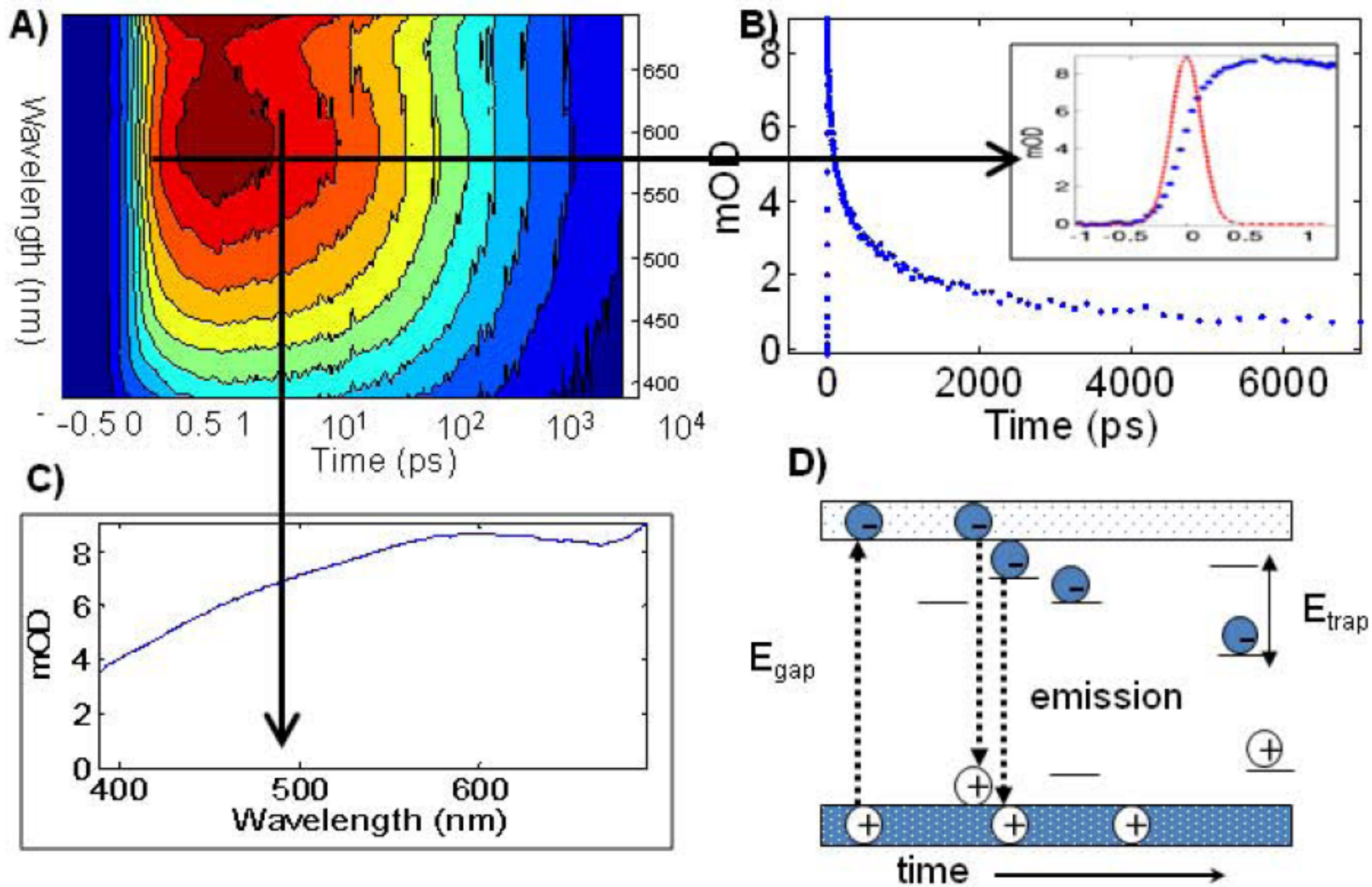


Fig. 5. Powder XRD pattern and corresponding TEM of Si NPs capped with APS prepared by a colloidal solution route.

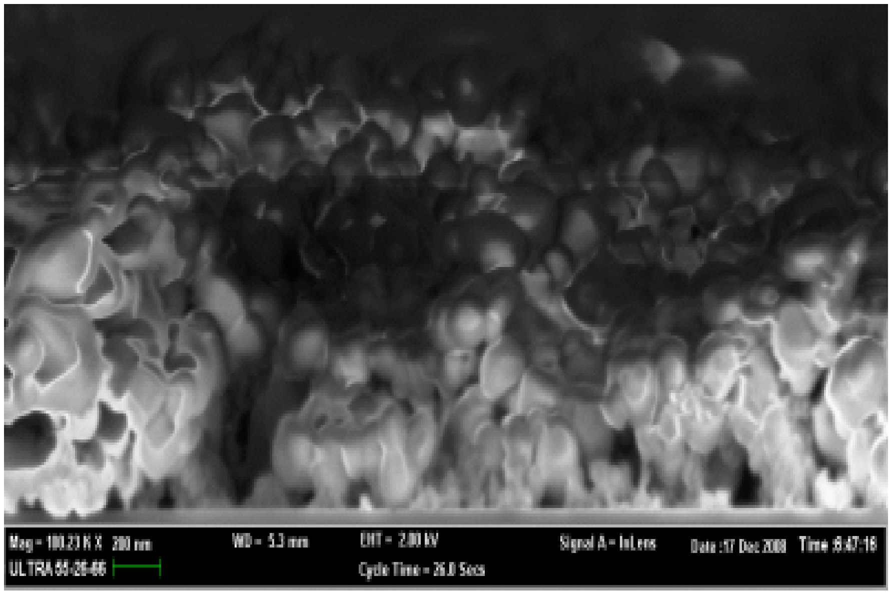


Multivariate Time Domain Analysis with Pump & Probe Lasers

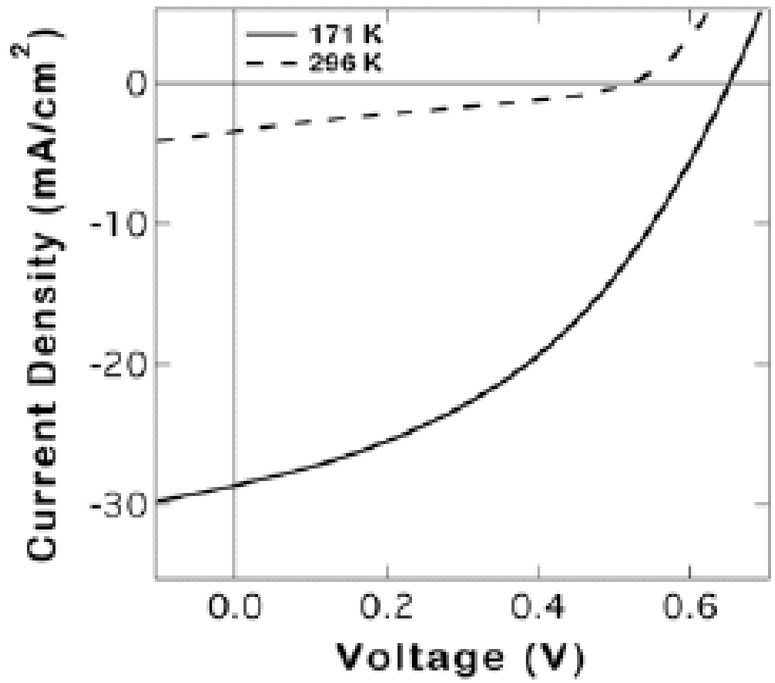
- separate different decay channels reliably
- 100 GB datasets, use advanced factor analysis



Fabricating Nanoparticle Solar Cells

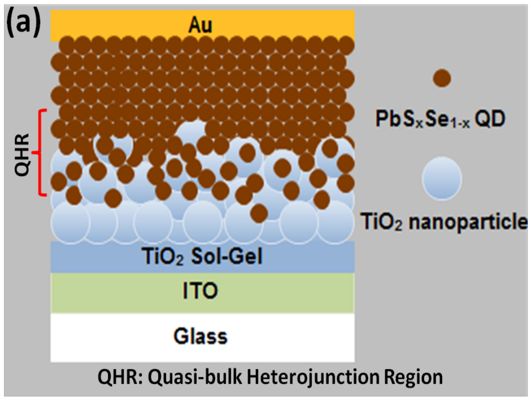


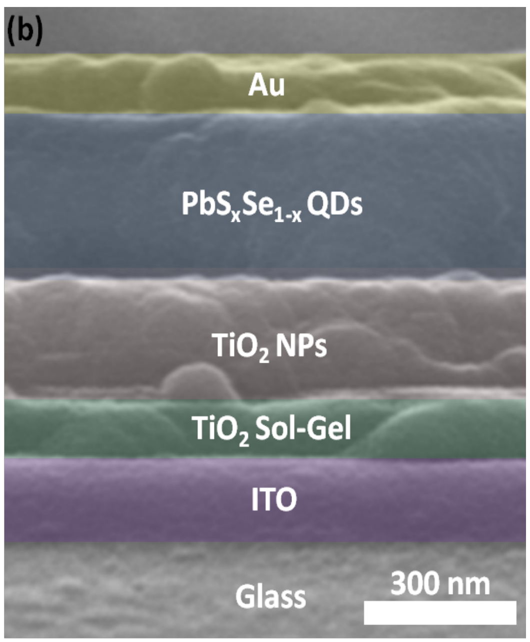
TEM image of ALD of Cu_2S onto TiO_x nanoparticle film with pore size of<1nm

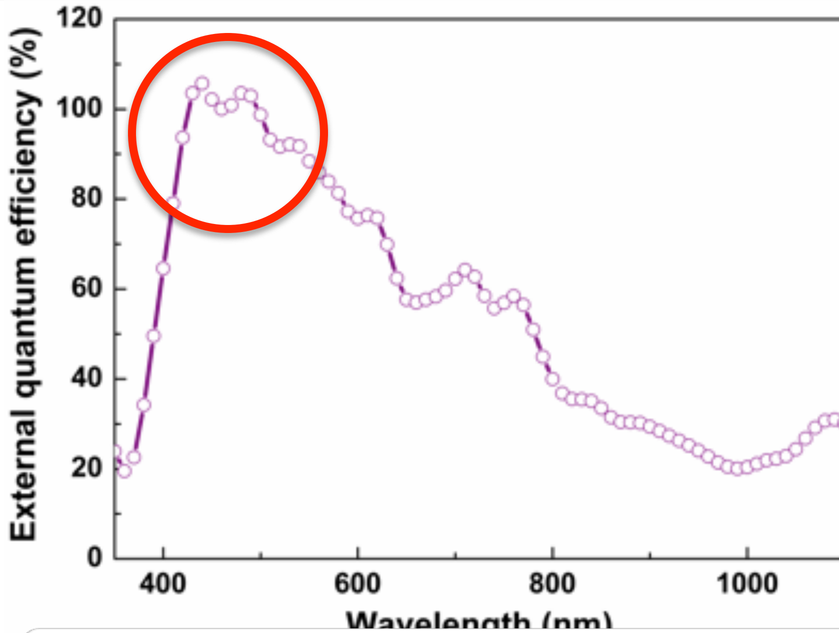


I-V of PbS NP solar cell

Observation of Multiple Exciton Generation in a Functioning Solar Cell







Beard & Nozik (Dec. 2011): MEG in working solar cell. Used hydrazine: combustible

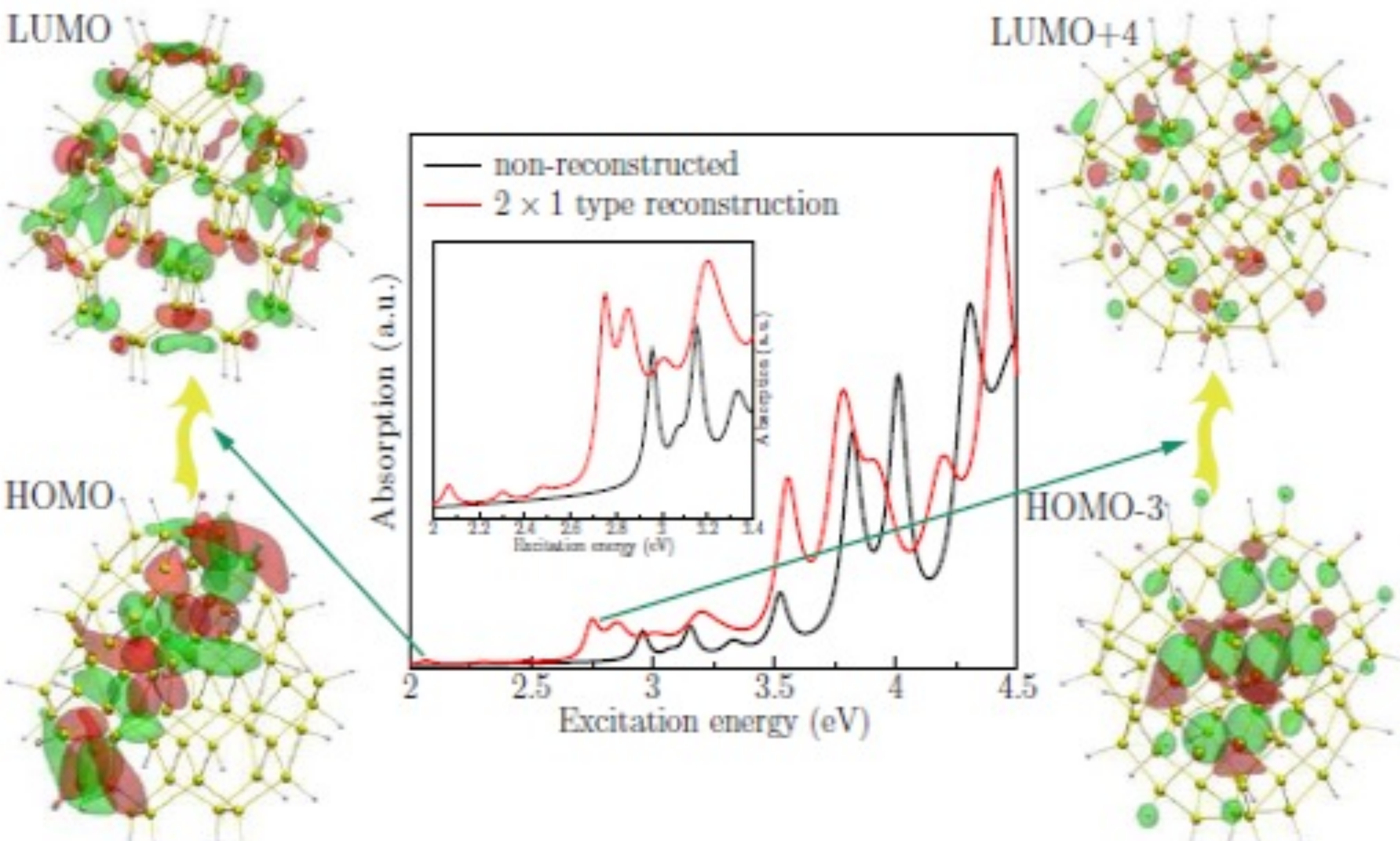
Carter lab: EQE>100% in a functioning solar cell Optimized cell performance not by the use of hydrazine, but by varying the composition PbS$_x$Se$_{1-x}$.

The paper has been accepted in Nanotechnology

Theory: Turbo-charged Time-Dependent Density Functional Analysis

1. Managing Quantum Confinement
    1.1. Surface reconstruction reduces the gap
    1.2. Asymmetry reduces the gap
    1.3. Charge extraction
2. Multi-Exciton Generation
    2.1. Reconstruction can compensate confinement
    2.2. Particle and hole localization
3. Si NPs with different phases
    3.1. Another pathway to reduce the gap
    3.2. The Harvard-MIT experiment
4. Si NPs with different embeddings
    4.1. Precipitation- Delocalization – gap reduction

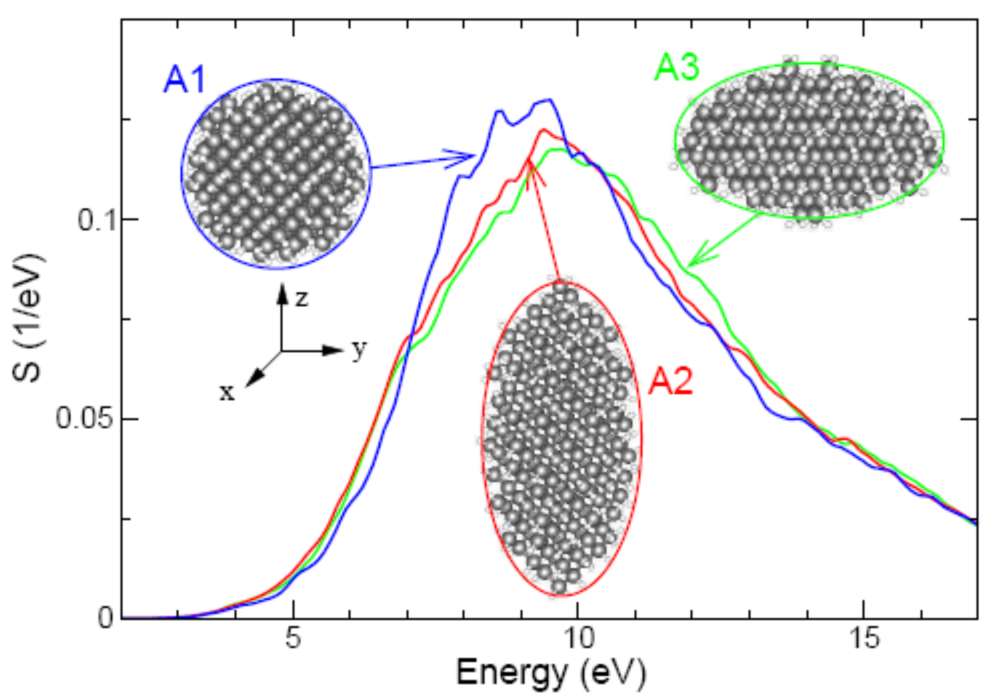
1. Managing Quantum Confinement:
1.1. Surface Reconstruction Reduces the Gap

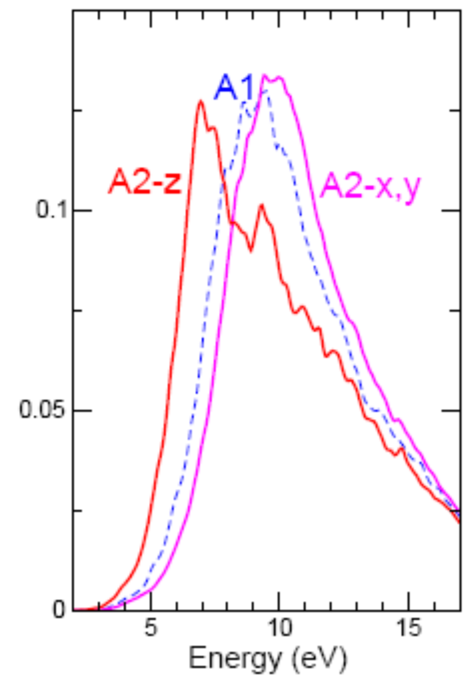


Surface reconstruction reduces gap by ~10% or more

Gali, Zimanyi et al, NanoLetters 2009

1. Managing Quantum Confinement:
1.2. Asymmetry Reduces the Gap

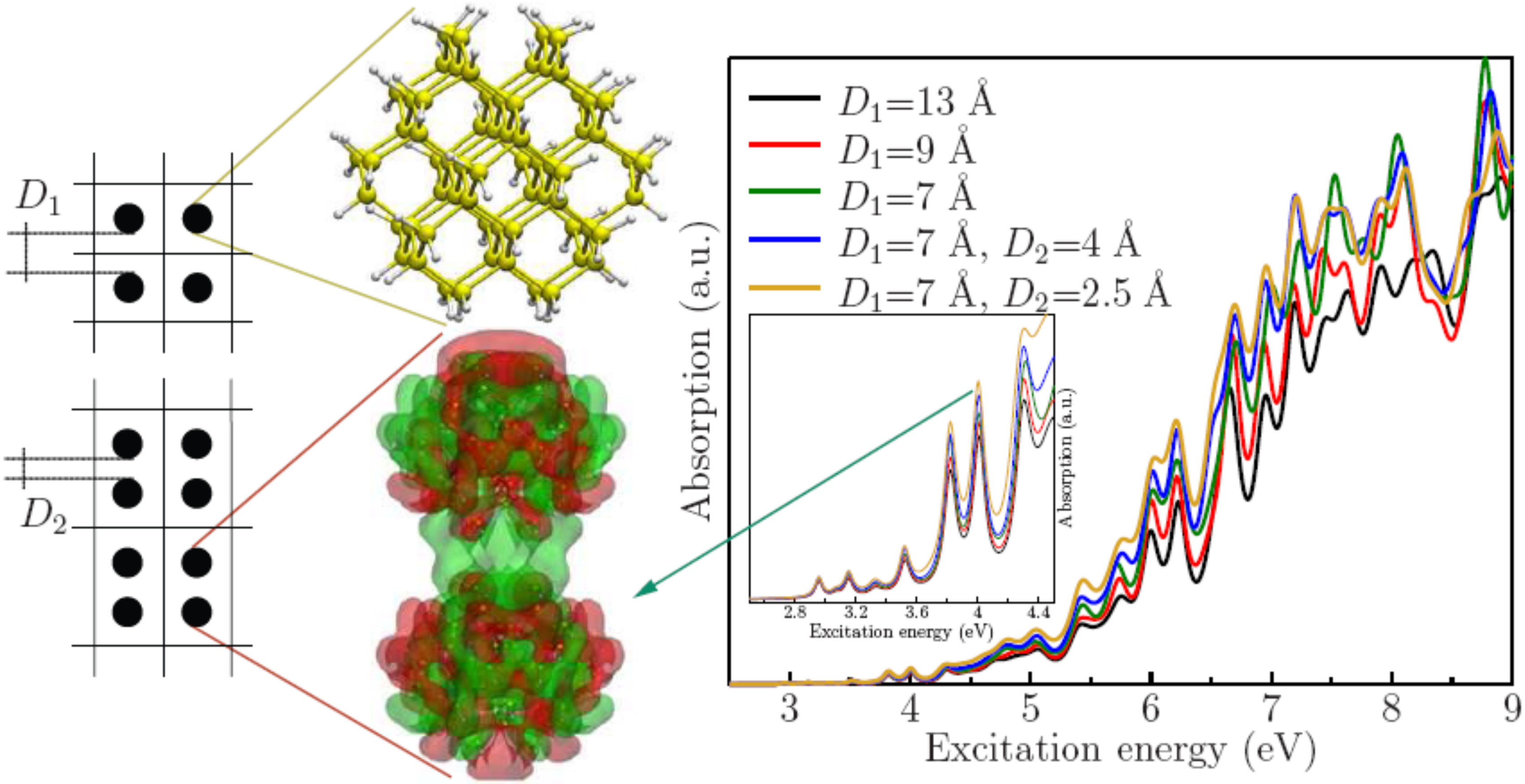




Reducing symmetry of shape reduces gap because a lot of transitions which were forbidden by selection rules become allowed: nanorods show strong MEG

Gali, Kaxiras, Zimanyi et al, PRB 2010

1. Managing Quantum Confinement:
1.3. Charge Extraction less of a Problem



Wavefunction overlap at surprisingly large NP-NP separations -> can explain good charge extraction

2. Multi-Exciton Generation
2.1. Calculational details

Fermi's golden rule for exciton->biexciton process with static RPA screened Coulomb interaction:

$$\boxed{\Gamma_i = 2\pi \sum_f |\langle X_i|W|XX_f\rangle|^2 \delta(E_i - E_f)}$$

$$\begin{cases} \Gamma_j^+ = 2\pi \sum_{klc} (2|V_{lckj} - V_{kclj}|^2 + |V_{lckj}|^2 + |V_{kclj}|^2)\delta[\epsilon_j - (\epsilon_l - \epsilon_c + \epsilon_k)] \\ \Gamma_a^- = 2\pi \sum_{lbc} (2|V_{aclb} - V_{ablc}|^2 + |V_{aclb}|^2 + |V_{ablc}|^2)\delta[\epsilon_a - (\epsilon_b - \epsilon_l + \epsilon_c)] \end{cases}$$

Huge triple summation!

$$\Gamma_{ja} = \Gamma_a^- + \Gamma_j^+$$

$$V_{rsut} = \int\int d^3r d^3r' \psi_r^*(\mathbf{r})\psi_s(\mathbf{r})W(\mathbf{r},\mathbf{r}')\psi_u^*(\mathbf{r}')\psi_t(\mathbf{r}')$$

$$W(\mathbf{r},\mathbf{r}') = \int d^3r'' \epsilon_{\mathrm{RPA}}^{-1}(\mathbf{r},\mathbf{r}'')\frac{2}{|\mathbf{r}' - \mathbf{r}''|}$$

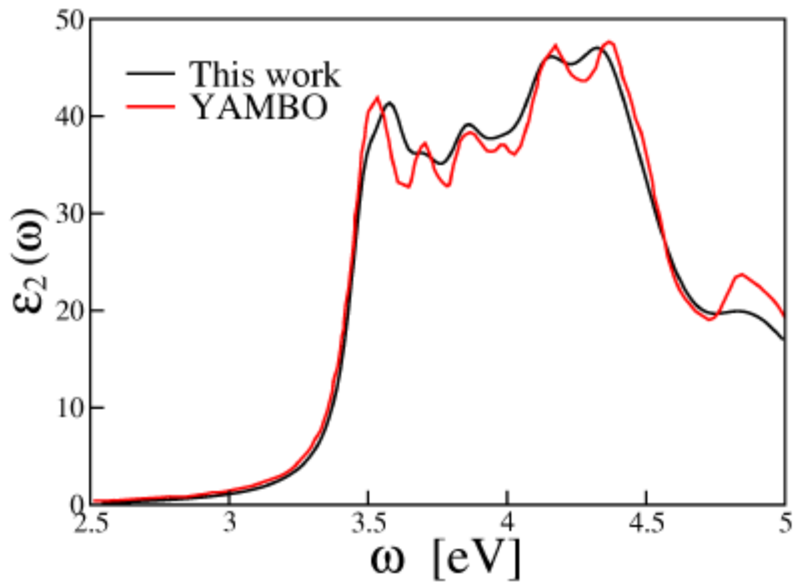
2. Multi-Exciton Generation
2.1. Calculational details

a. Liouvillian super-operator matrix formalism

b. Projecting out unoccupied states – summation only over occupied states

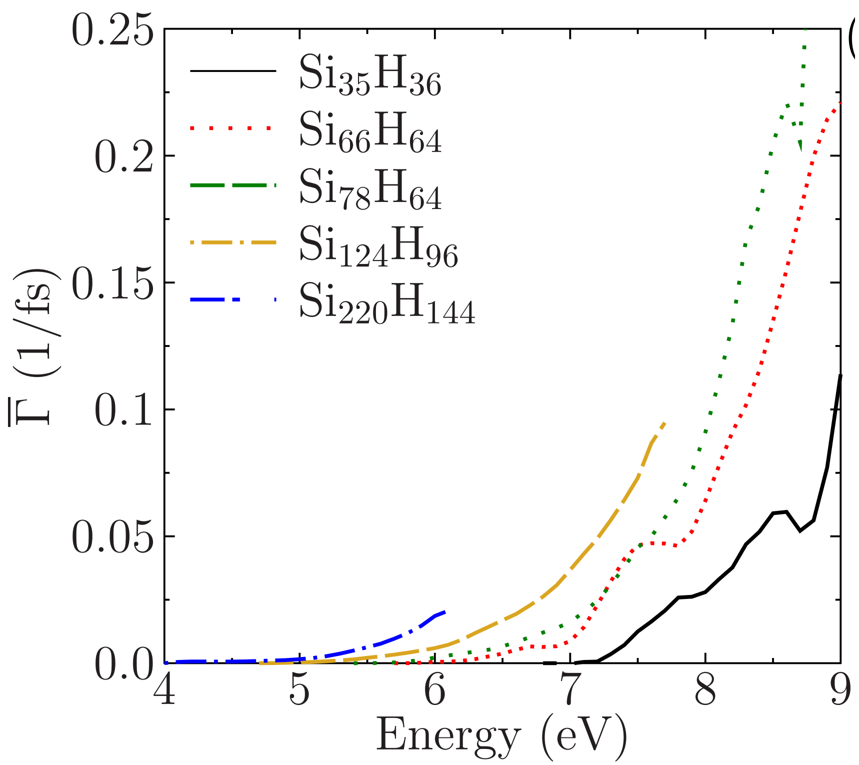
c. Lanczos continued fraction solution of Bethe-Salpeter eq.

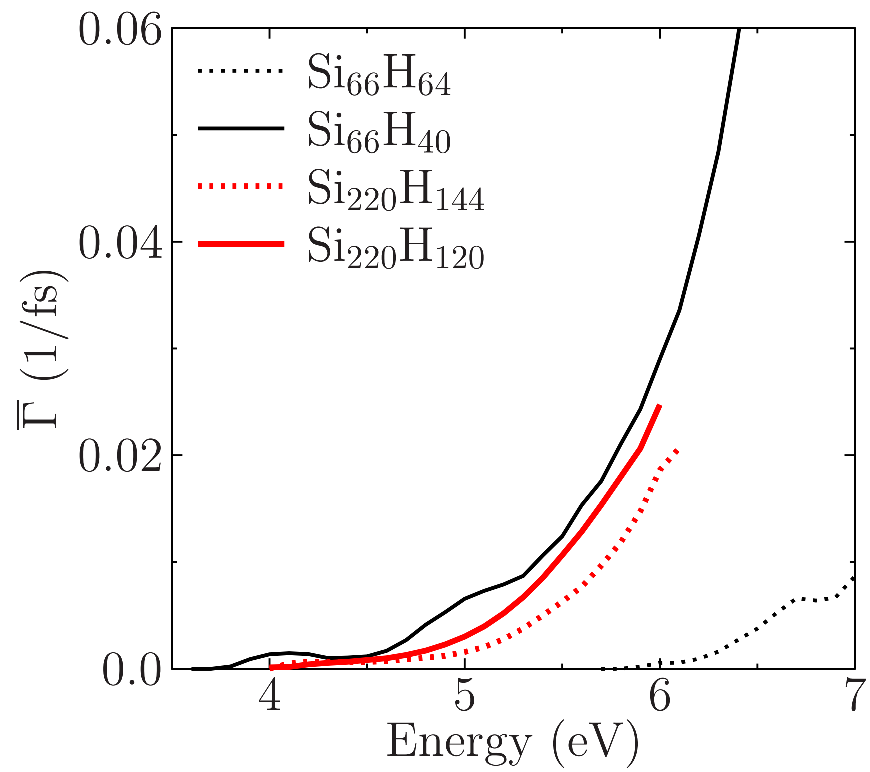
d. Comparison with YAMBO code - benzene: same results, considerably faster



Yambo results from CPC 180, 1392 (2009)

2. Multi-Exciton Generation
2.2. Reconstruction Can Compensate Confinement

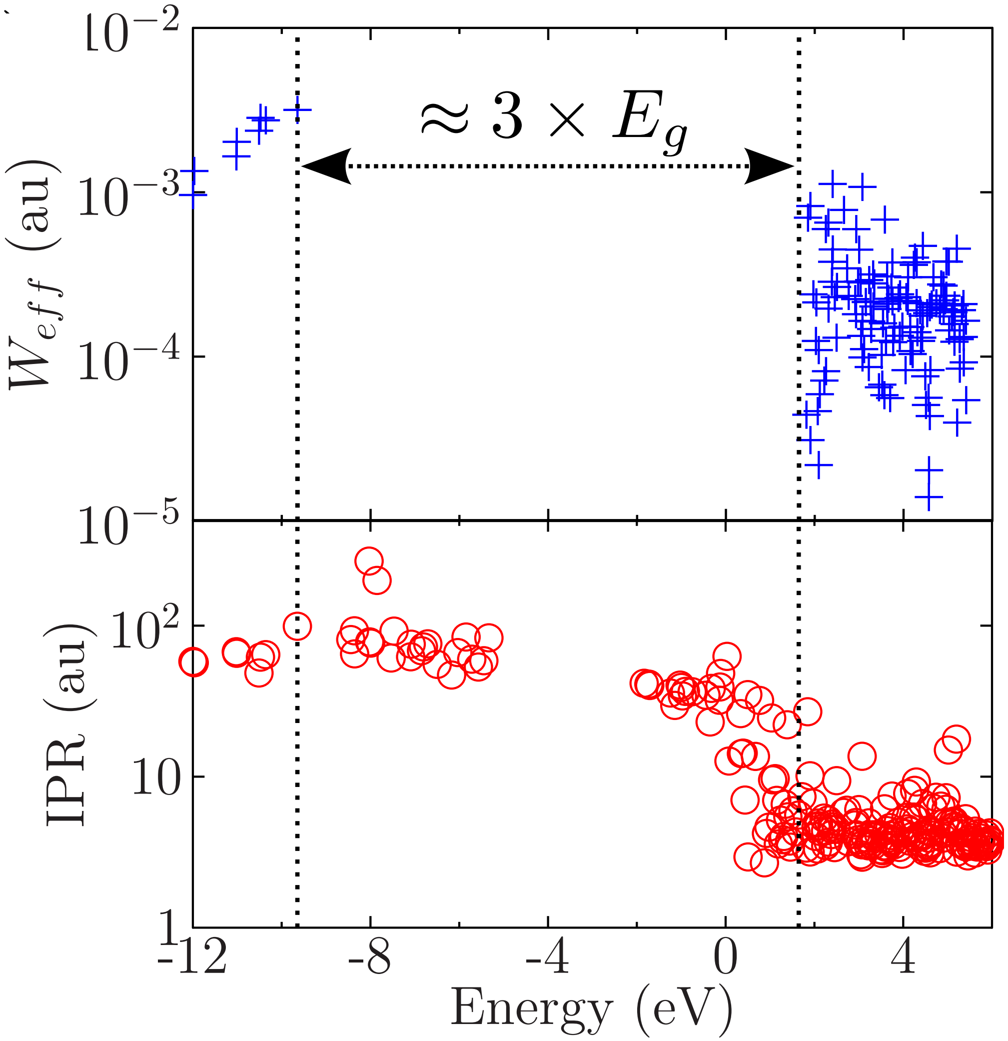




Quantum confinement enhances the gap in unreconstructed NPs

Reconstruction can completely compensate the gap enhancement

2. Multi-Exciton Generation
2.3. Of Particles and Holes



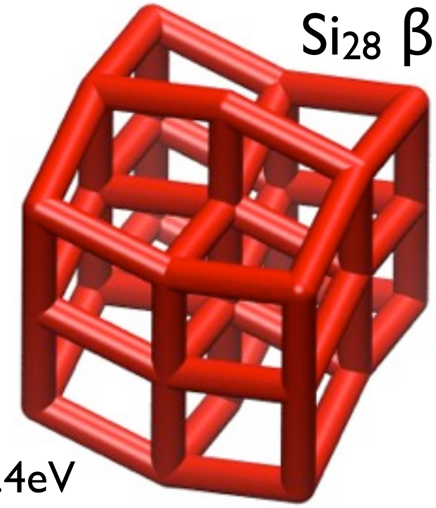
Effective Coulomb interaction is very different for electrons and holes

Inverse Participation Ratio (IPR) explains:

Holes are much more localized than electrons

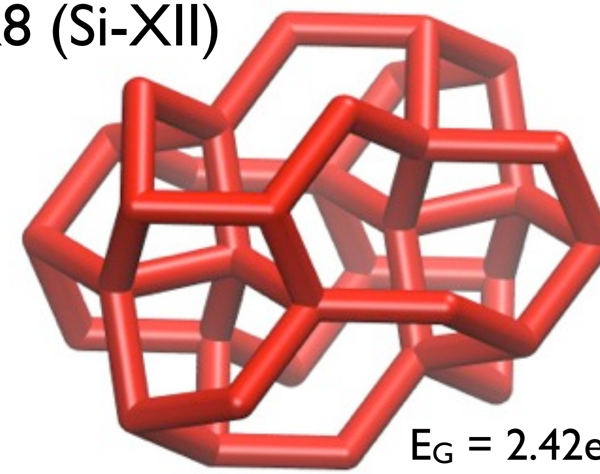
3. High Pressure Phases of Si NPs:
3.1. Reduce Gap by using Bulk-Gapless Si Phases

Si_{28} β-tin (Si-II)



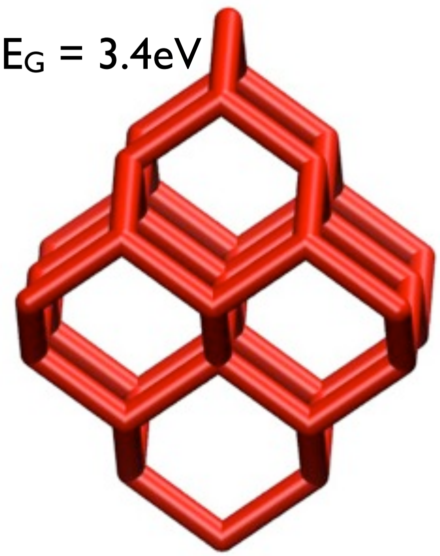
E_G = 0.4eV
(passivation issue)

Si_{34} R8 (Si-XII)

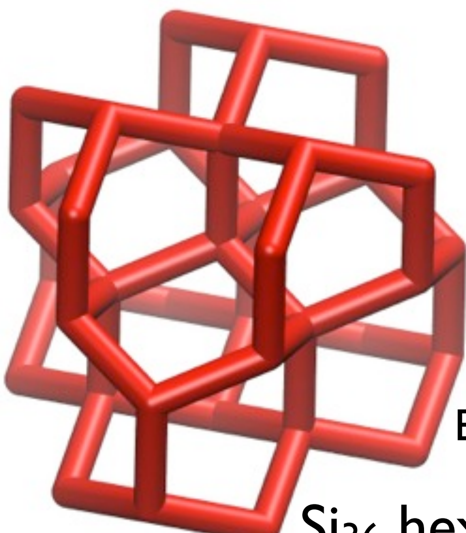


E_G = 2.42eV

E_G = 3.4eV

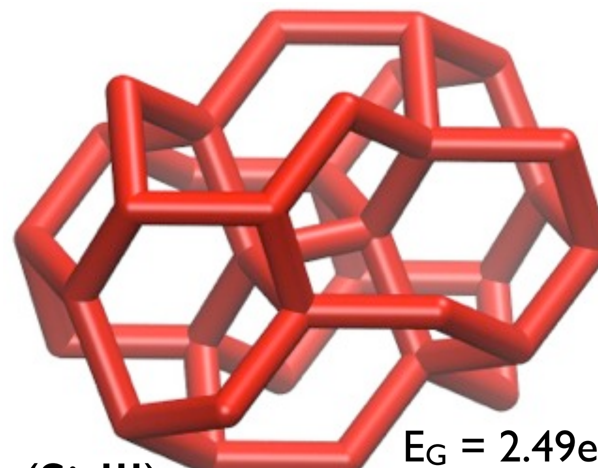


Si_{35} (Si-I)



E_G = 3.01eV

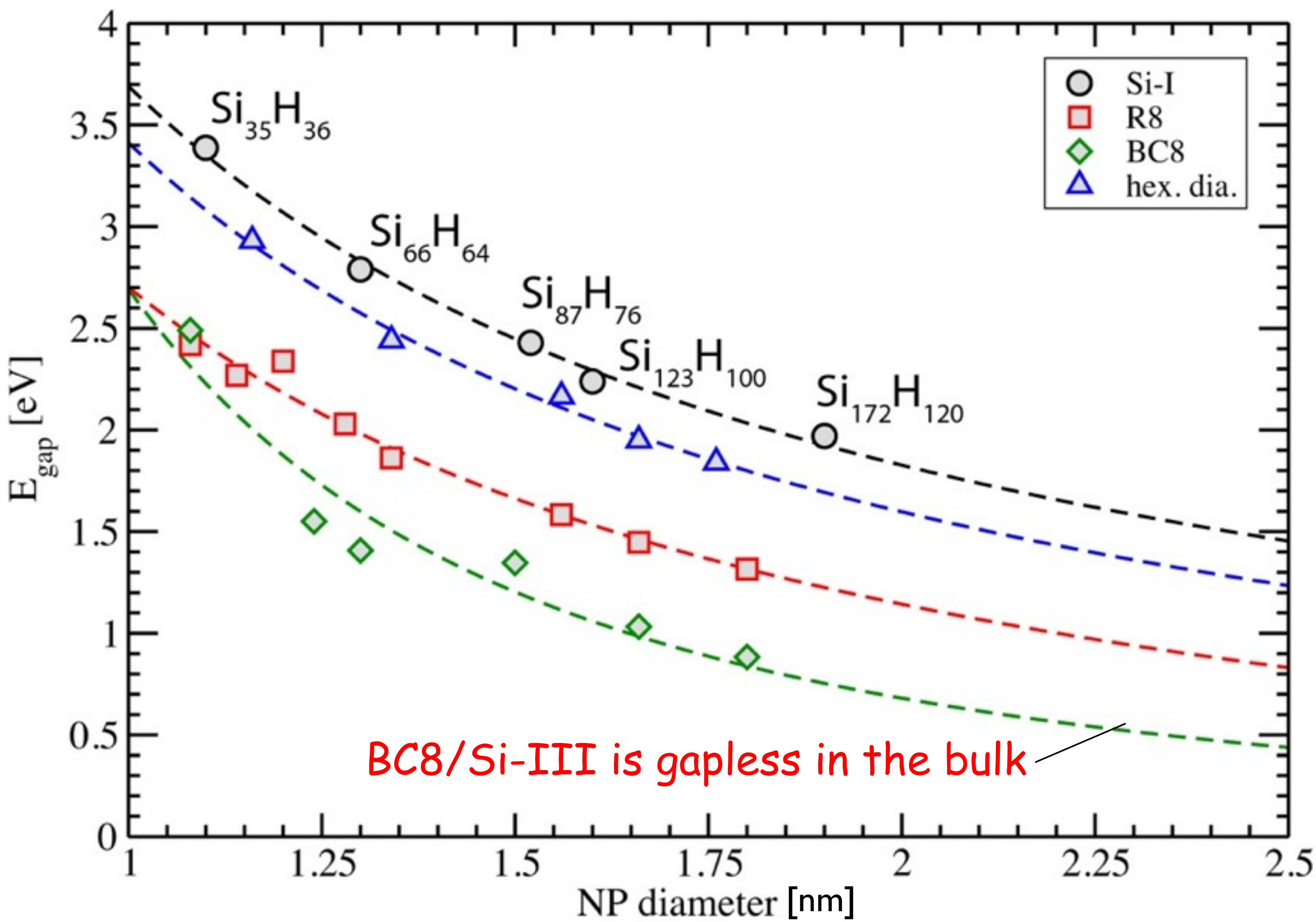
Si_{36} hex. dia. (Si-IV)



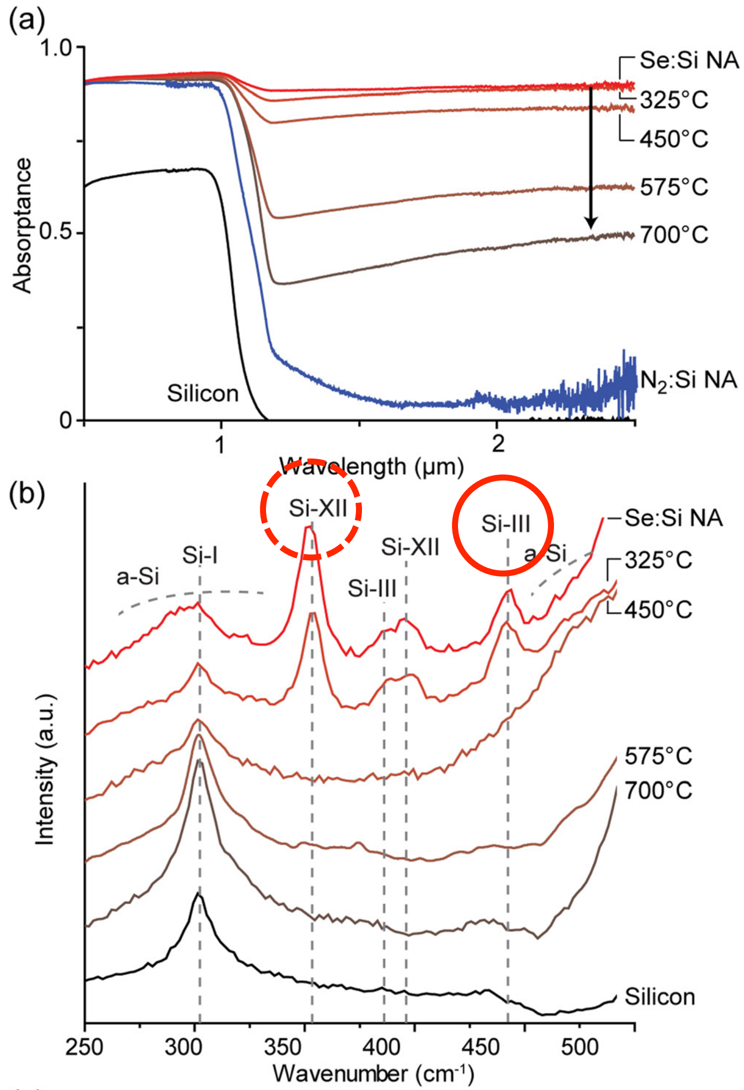
E_G = 2.49eV

Si_{34} BC8 (Si-III)

3. High Pressure Phases of Si NPs:
3.1. Gap reduction in BC8/Si-III



3. High Pressure Phases of Si NPs:
3.2. Mazur/Gradecak group results



JOURNAL OF APPLIED PHYSICS **110**, 053524 (2011)

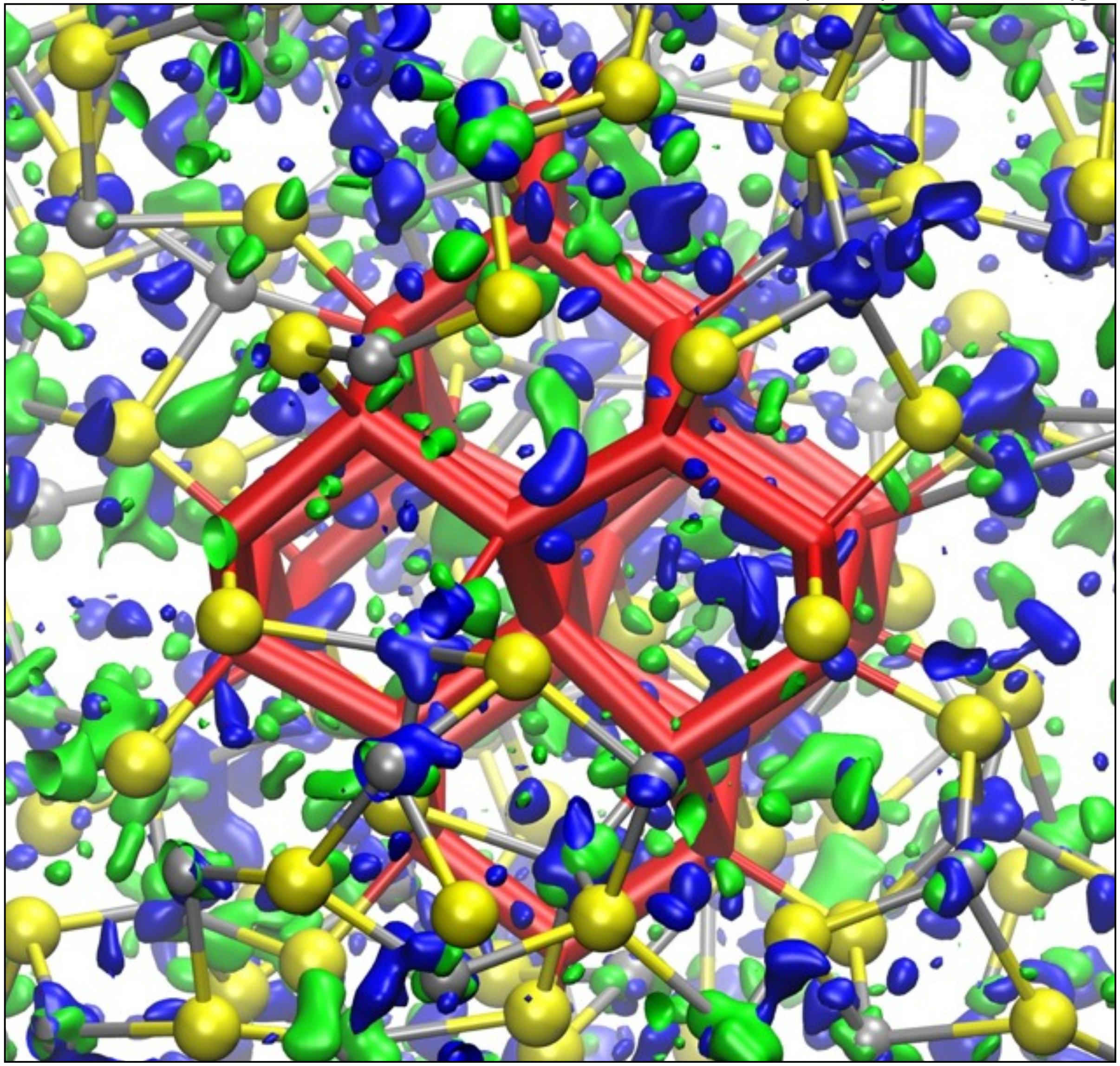
Pressure-induced phase transformations during femtosecond-laser doping of silicon

Matthew J. Smith,[1] Yu-Ting Lin,[2] Meng-Ju Sher,[3] Mark T. Winkler,[3] Eric Mazur,[2,3] and Silvija Gradečak[1,a)]

1. The presence of BC8/Si-III phase confirmed by Raman scattering

2. When BC8/Si-III phase is annealed away, subgap absorptance is greatly reduced

4.1. Embedding: Si NPs in ZnS



HOMO: blue
LUMO: green
Courtesy of Jelly Beans Co.

1. HOMO and LUMO orbits delocalized: good for charge extraction

2. S precipitates on NP boundary, Zn forms a metallic outer host

3. Host gap reduced allowing NP wave fc. to delocalize

SUMMARY

1. Solar energy problem is intellectually complex & morally honorable

2. There are many entry points for physicists

3. Multiple Exciton Generation is a most promising paradigm

4. Quantum Confinement enhances the Coulomb interaction and MEG

5. Its two negative effects, the gap enhancement and the charge localization can be reduced or eliminated by:

   (a) surface reconstruction

   (b) symmetry reduction: nanorods

   (c) NPs with bulk-gapless phases

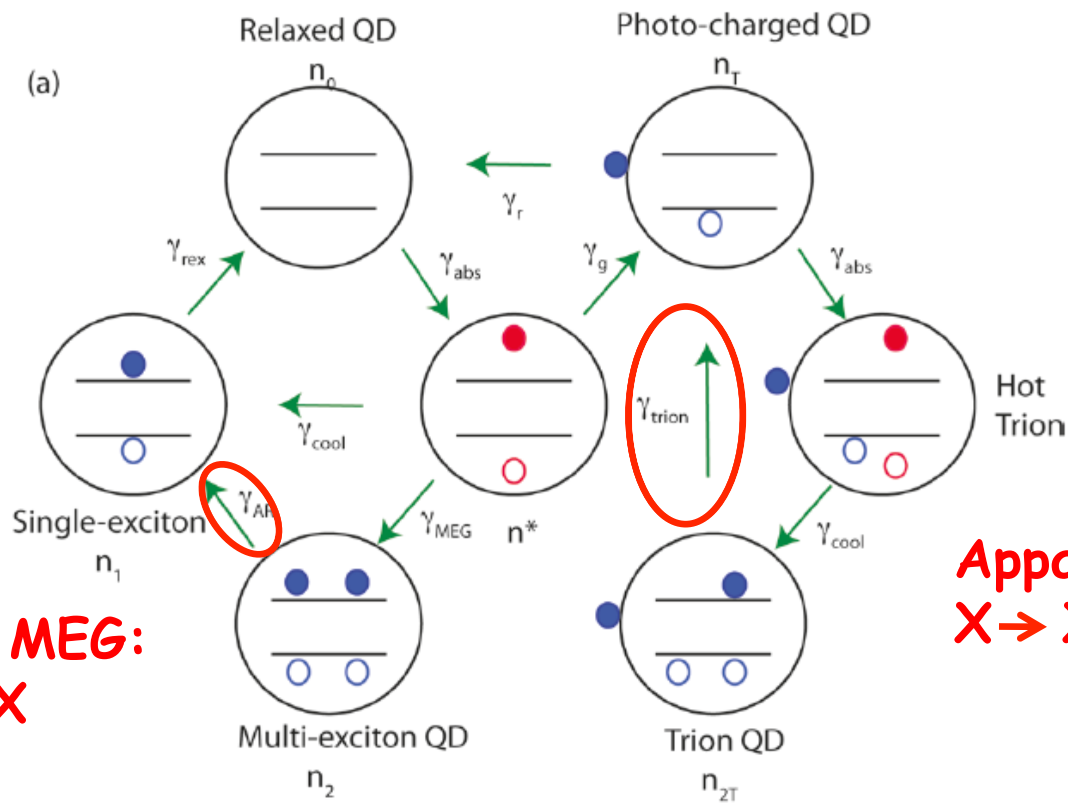
   (d) judicious NP embedding

6. Theory uses advanced many-body methods: Liouville operators, Bethe-Salpeter eq., Self-consistent self-energy ImΣ, Projection methods for summations, Lanczos continued fractions

MEG: A Charged Debate

Bawendi(2008):

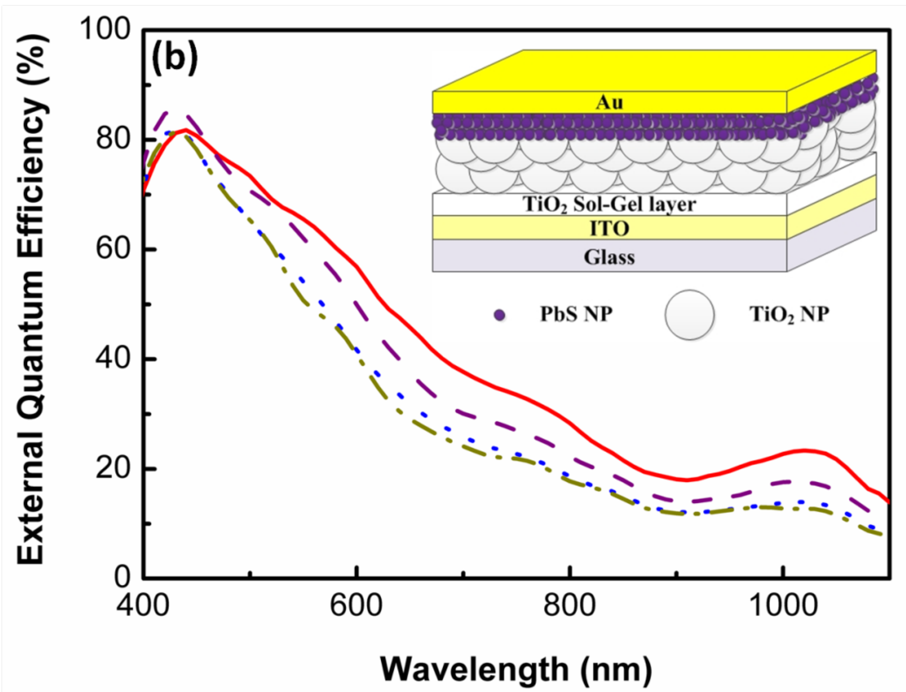
- could not reproduce MEG
- QY depended on stirring, flow, surface chemical treatment
- suggested that surface charging can appear as MEG
- charge state can live ~10sec, pulse separation ~1msec

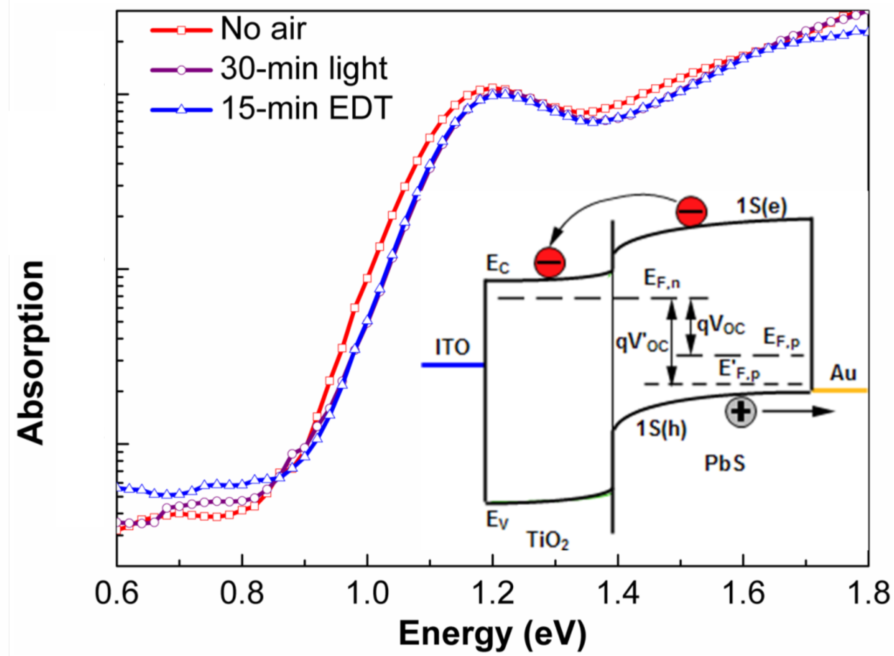


True MEG:
XX→X

Apparent MEG:
X→ X

Assembling Nanoparticle Solar Cells

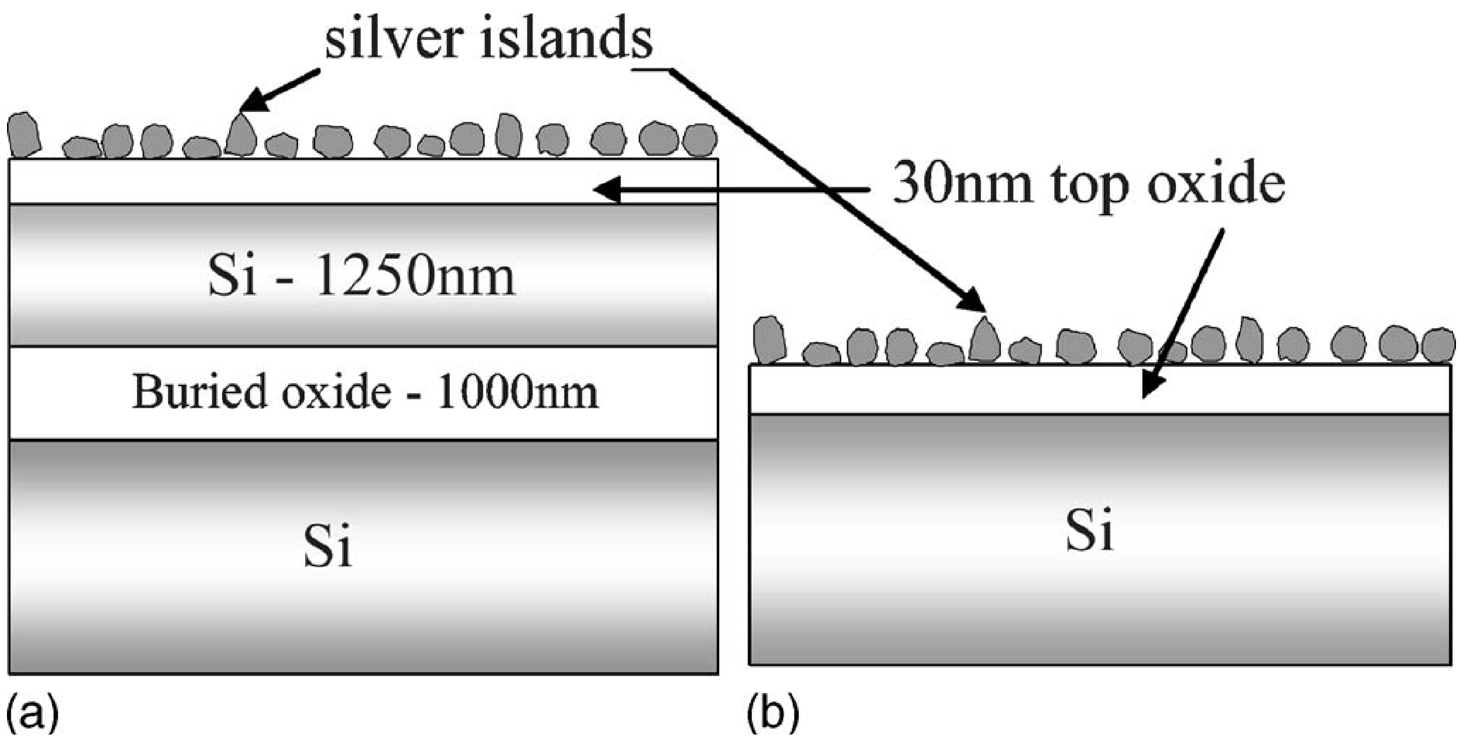




External Quantum Efficiency = QY
#(electrons)/photon

Stability analysis

Plasmon-PV Cell Architecture



SOI thin film cells

Wafer cells

Installed Solar Capacity vs. Other Non-Oil/Coal

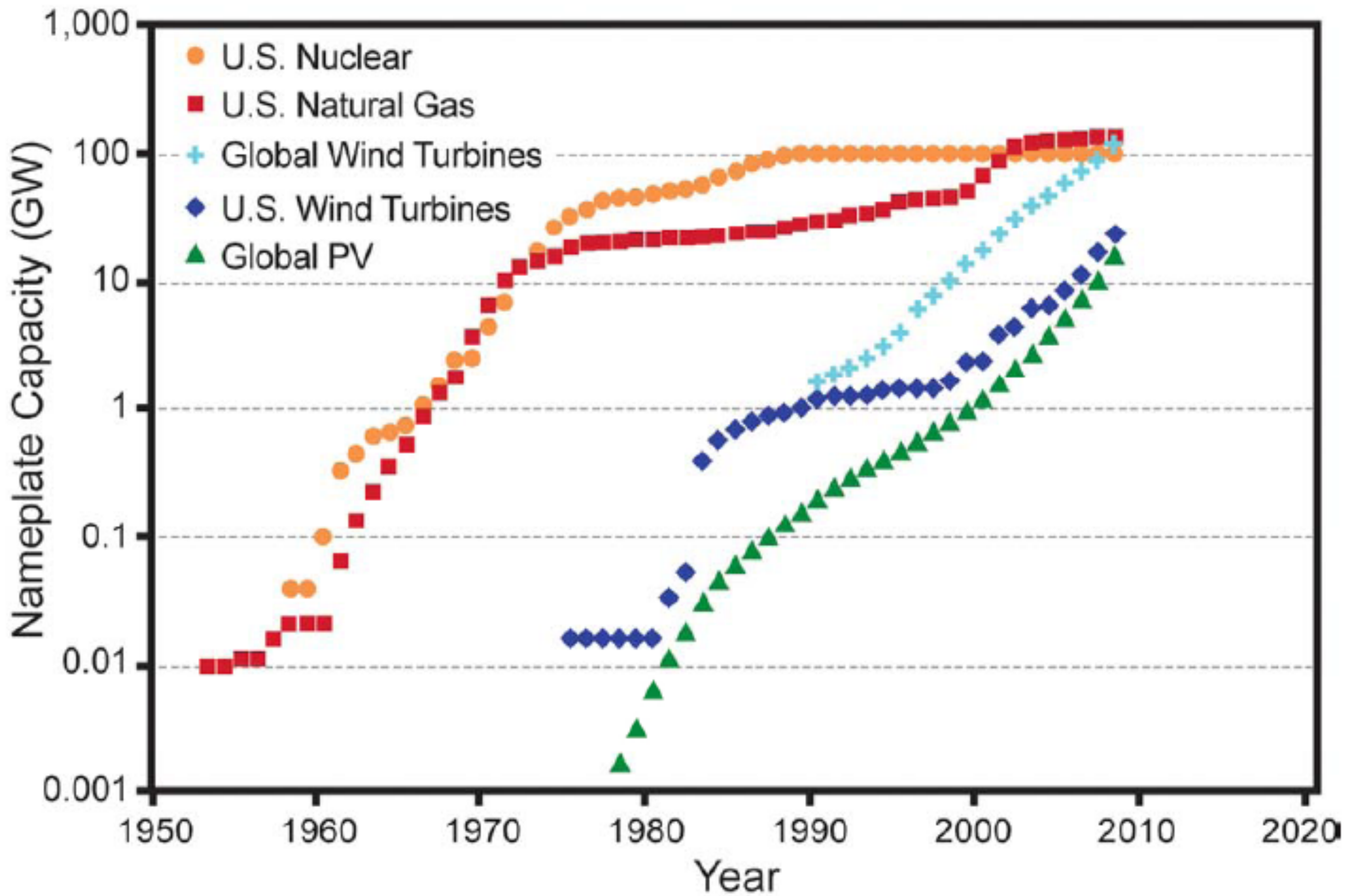


Figure 3-2 Nuclear, natural gas turbines, and wind turbines have been rapidly adopted by the energy industry and, to date, photovoltaics are on a parallel path. Source: International Energy Agency.

3. Code Development for Bethe-Salpeter Equation
3.1. Liouvillian super-operator formalism

For a small external perturbation we have

$$i\frac{d\hat{\rho}'(t)}{dt} = \left[\hat{H}_{COHSEX}, \hat{\rho}'(t)\right] + \left[\hat{\Sigma}'_{COHSEX}[\hat{\rho}'](t), \hat{\rho}_0\right] + \left[\hat{v}'_{ext}(t), \hat{\rho}_0\right]$$

that can be formally written as

$$i\frac{d\hat{\rho}'(t)}{dt} = \mathcal{L}\cdot\hat{\rho}'(t) + \left[\hat{v}'_{ext}(t), \hat{\rho}_0\right]$$

By Fourier analyzing we obtain

$$\boxed{(\omega - \mathcal{L})\cdot\hat{\rho}'(\omega) = \left[\hat{v}'_{ext}(\omega), \hat{\rho}_0\right]}$$

The eigenvalues of $\mathcal{L}$ are the EXCITATION ENERGIES of the system.

3. Code Development for Bethe-Salpeter Equation

In order to solve the BSE we need to compute the screened Coulomb potential:

$$W(\mathbf{r},\mathbf{r}') = \int \epsilon^{-1}(\mathbf{r},\mathbf{r}'')v_c(\mathbf{r}'',\mathbf{r}')d\mathbf{r}''$$

The standard approach to compute ϵ^{-1} requires a SUMMATION OVER EMPTY STATES.
We efficiently compute ϵ^{-1} using an iterative method based on DFPT which DOES NOT require calculations of empty states and

Instead of using explicitly the conduction states we use the PROJECTOR onto the conduction state subspace

$$\hat{Q} = 1 - \sum_v |\phi_v\rangle\langle\phi_v|.$$

Density Functional Perturbation Theory representation:

3. Code Development for Bethe-Salpeter Equation
3.3. Polarizability–Lanczos Continued Fractions

The polarizability α is the tensor that connects the induced dipole d_i' to the external electric field $\mathbf{E}$:

$$d_i'(\omega) = \sum_j \alpha_{ij}(\omega) E_j(\omega)$$

In the density matrix formulation the induced dipole is given by

$$\mathbf{d}'(\omega) = \mathrm{Tr}\left(\hat{\mathbf{r}}\hat{\rho}'(\omega)\right)$$

The external perturbation is

$$v_{ext}'(\mathbf{r}, \omega) = -\mathbf{E}(\omega) \cdot \mathbf{r}$$

Within our formalism we finally obtain

$$\boxed{\begin{aligned} \alpha_{ij}(\omega) &= -\mathrm{Tr}\left(\hat{r}_i(\omega - \mathcal{L})^{-1} \cdot [\hat{r}_j, \hat{\rho}_0]\right) \\ &= -\left\langle \hat{r}_i | (\omega - \mathcal{L})^{-1} \cdot \hat{s}_j \right\rangle \end{aligned}}$$

3. Code Development for Bethe-Salpeter Equation
3.3. Polarizability–Lanczos Continued Fractions

$$g(\omega) = \langle v|(\omega - \mathcal{H})^{-1}|v\rangle$$

Performing the iterative procedure

$$\begin{aligned} q_0 &= 0 \\ q_1 &= v \\ \beta_{j+1}q_{j+1} &= \mathcal{H} \;\; q_j - \alpha_j q_j - \beta_j q_{j-1} \\ \langle q_{j+1}|q_{j+1}\rangle &= 1 \qquad \alpha_j = \langle q_j|\mathcal{H}|q_j\rangle \end{aligned}$$

we obtain

$$\mathcal{H} \approx T^j = \begin{pmatrix} \alpha_1 & \beta_2 & 0 & \cdots & 0 \\ \beta_2 & \alpha_2 & \beta_3 & 0 & \vdots \\ 0 & \beta_3 & \alpha_3 & \ddots & 0 \\ \vdots & 0 & \ddots & \ddots & \beta_j \\ 0 & \cdots & 0 & \beta_j & \alpha_j \end{pmatrix}$$

3. Code Development for Bethe-Salpeter Equation
3.3. Polarizability–Lanczos Continued Fractions

$$g(\omega) = \langle v|(\omega - \mathcal{H})^{-1}|v\rangle$$

Performing the iterative procedure

$$\begin{aligned}
q_0 &= 0 \\
q_1 &= v \\
\beta_{j+1} q_{j+1} &= \mathcal{H}\ \ q_j - \alpha_j q_j - \beta_j q_{j-1} \\
\langle q_{j+1}|q_{j+1}\rangle &= 1 \qquad \alpha_j = \langle q_j|\mathcal{H}|q_j\rangle
\end{aligned}$$

we obtain

$$g(\omega) \approx \cfrac{1}{\omega - \alpha_1 - \cfrac{\beta_2^2}{\omega - \alpha_2 - \cfrac{\beta_3^2}{\omega - \cdots}}}$$

Implementation

Plane-wave code, PWscf

RPA static screening: without explicitly considering empty states, eigenvector decomposition based on DFPT (Huy-Viet Nguyen and Stefano de Gironcoli, PRB 79, 205114 (2009)):

- **cutoff** on the screening is $\mathbf{4\times E_{kin}}$ (100 Ry)
- **no matrix inversion** needed
- number of eigenpotentials needs to be converged (tipically hundreds)
- the screening is evaluated at a small and finite q

Other calculational details:

- 25Ry wfc cutoff, 100Ry charge density cutoff
- >=10Å vacuum, PBE functional
- Integrals calculated in G-space (summation over G-vectors can be reduced)

QUANTUMESPRESSO

Conclusion & Outlook

Impact ionization rates using Fermi's golden rule from DFT energies, wavefunctions & RPA statically screened coulomb interaction:

- **The effect of screening might be approximated by division by a constant**
- **Reconstruction strongly enhances the transition rate**
- **Size effect: no real difference at relative energies without screening**

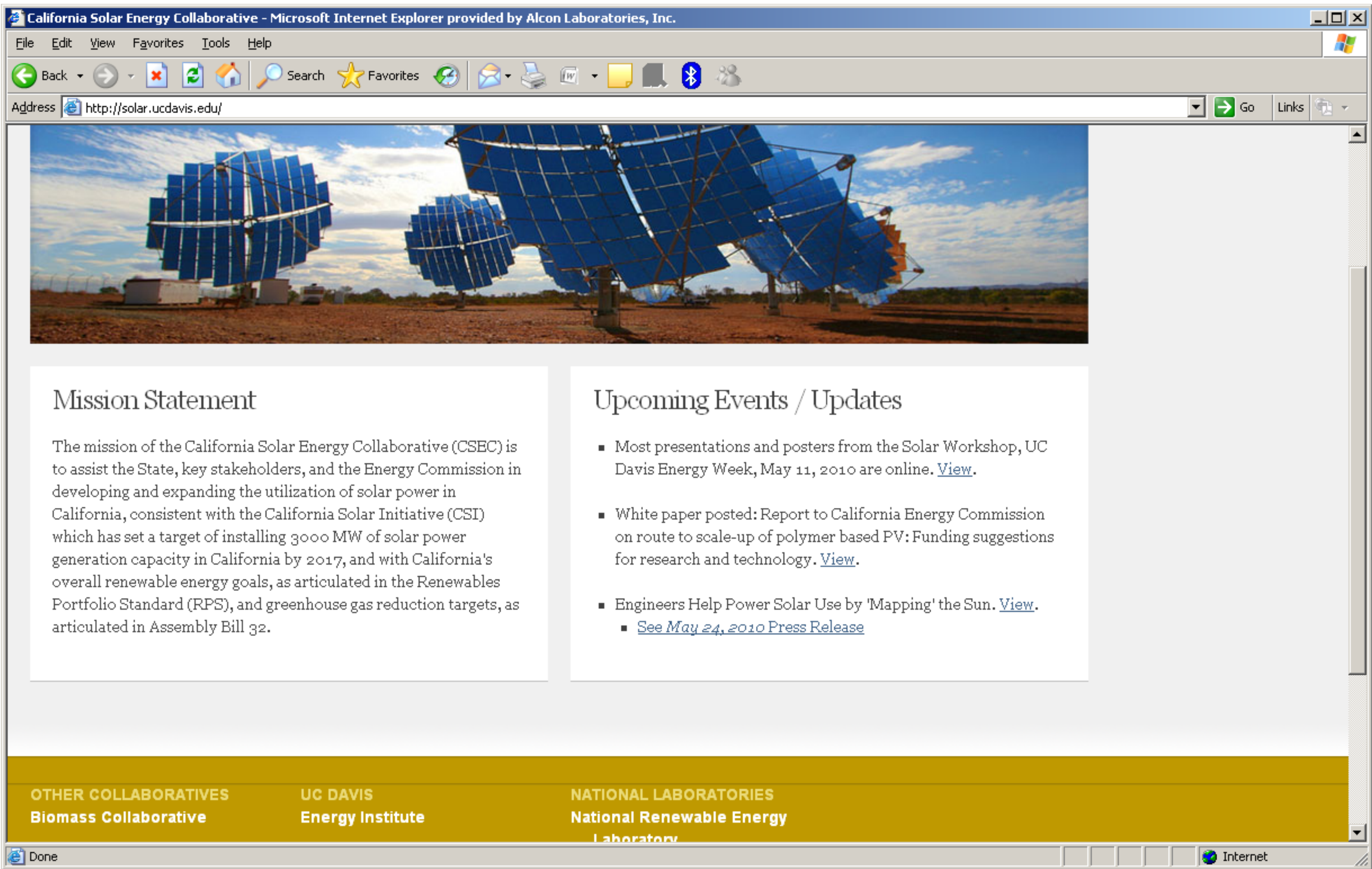
Work in progress:

- **Auger rate**

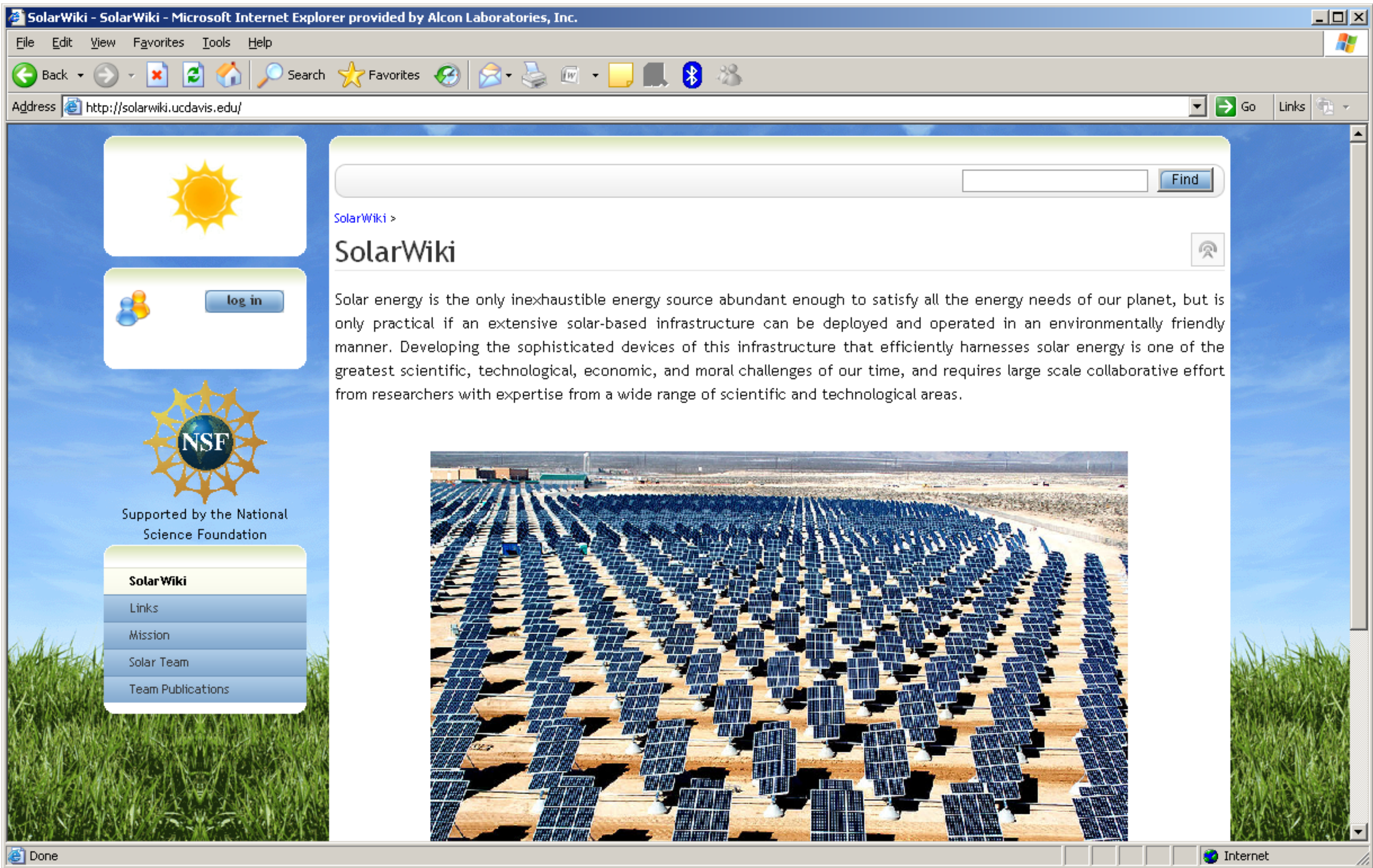
  easy, same matrix element, summation is different, possibility to recycle current results

Future work:

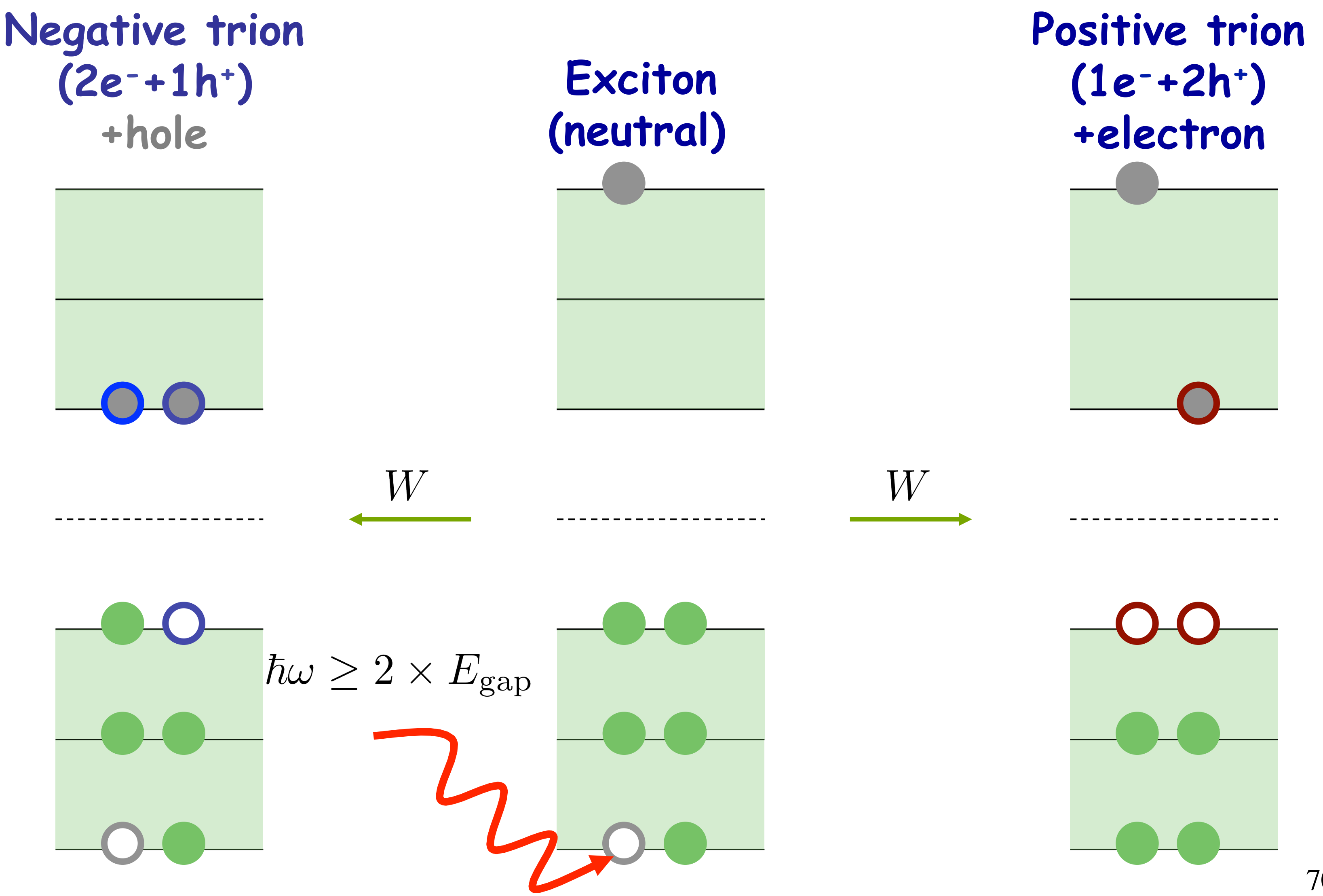
Outreach: California Solar Collaborative



Outreach: Solarwiki



2. Multi-Exciton Generation



Summary

1. Energy research and in particular PhotoVoltaics is a preeminent intellectual and moral challenge of our times

2. There are terrific challenges where the physicist community is uniquely poised to contribute and lead

3. ICAM can play a crucial leadership role in this adventure

Solar Thermal Technology

Kramers Junction, CA

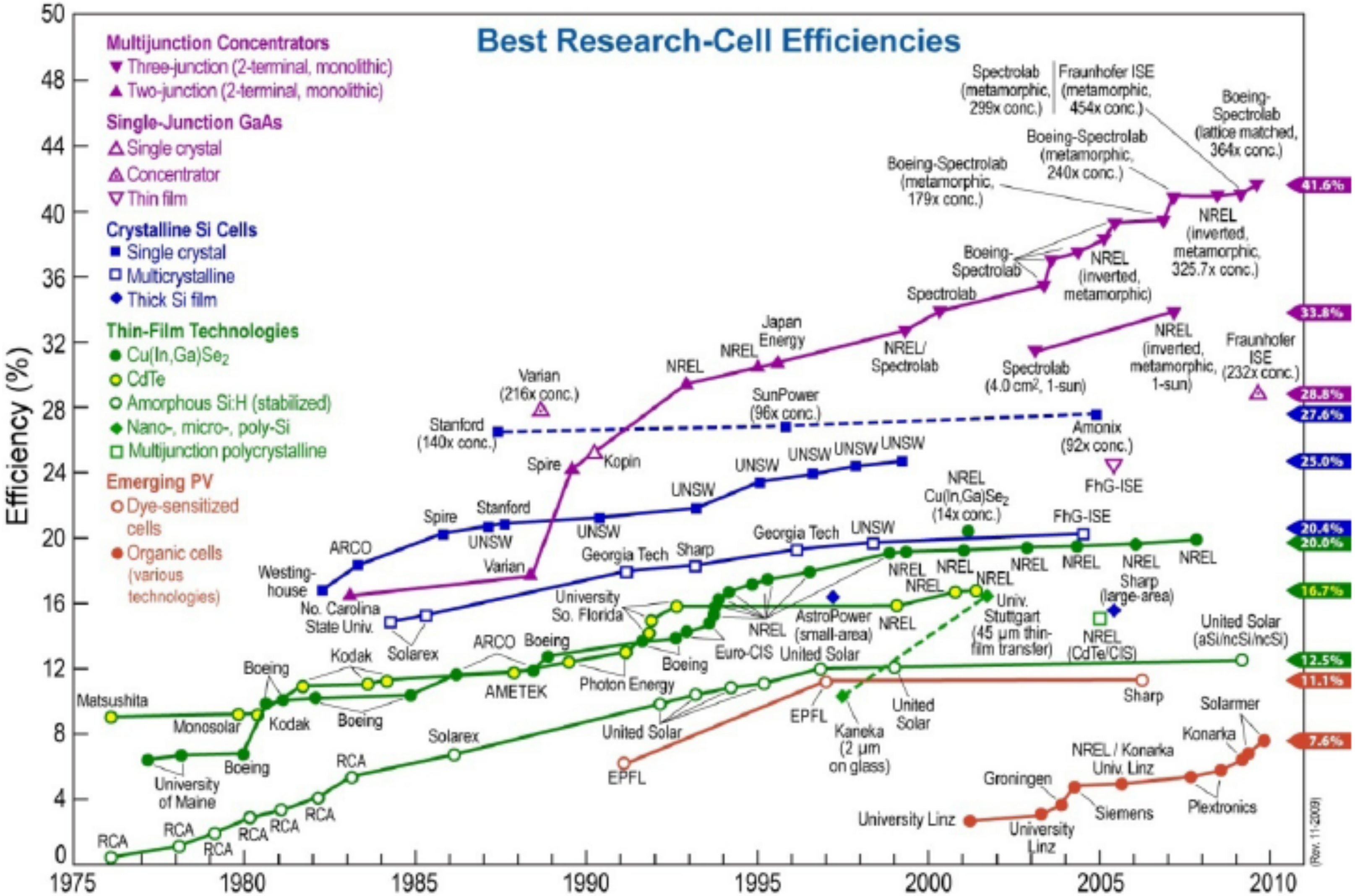
Mojave Desert, CA

Solar US Corporate Leaders

Table 3-1 Photovoltaic Technologies and U. S. Corporate Leaders

Technology	Company (U.S. Leadership)	Comment
Mono-crystalline silicon	SunPower	Ultra-high efficiency modules and low-cost trackers
Polycrystalline silicon		Dominated by China
Cadmium telluride	First Solar	World's largest photovoltaic module manufacturer; lowest cost photovoltaic technology (<$1/W)
Copper indium selenide alloys	Several contenders	Emerging technology with no clear leader
Thin film amorphous and microcrystalline silicon alloys	UniSolar (ECD) and Applied Materials	Lead shared with Japan and Europe
III-V multijunctions for concentrators	Spectrolab and Emcore	Direct descendant of U.S. space program
Concentrator photovoltaic	Amonix and SolFocus	Emerging technology with no clear leader
Organic photovoltaic	Konarka, Plextronics, Solarmer	Emerging technology

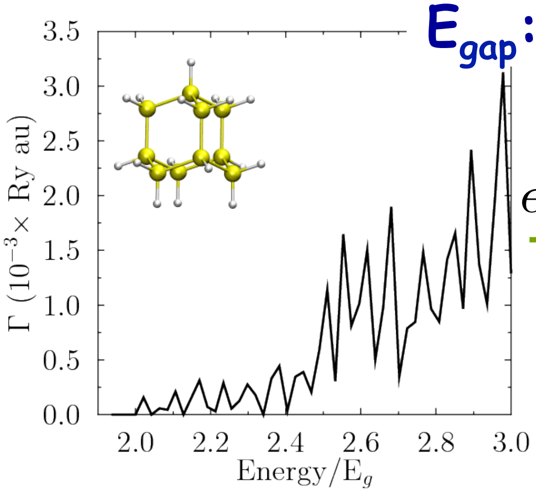
Records for Various Technologies



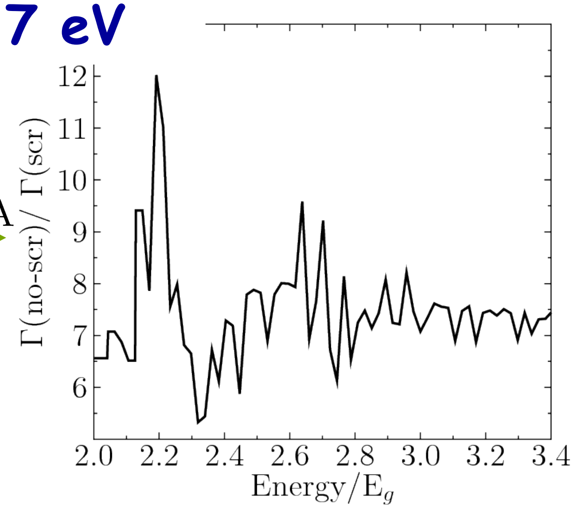
2. Multi-Exciton Generation:
2.1. Effect of Screening

- static screening approximation
- hydrogenated surface

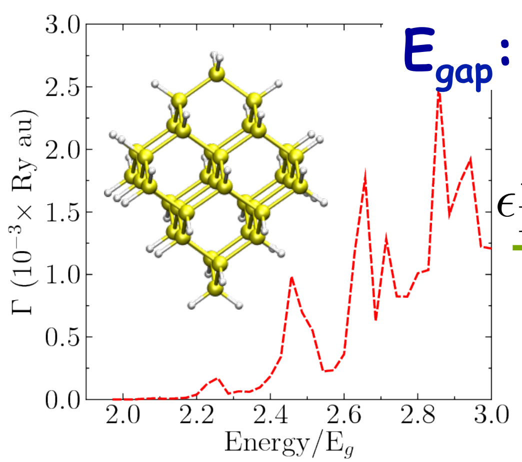
E_{gap}: 4.7 eV



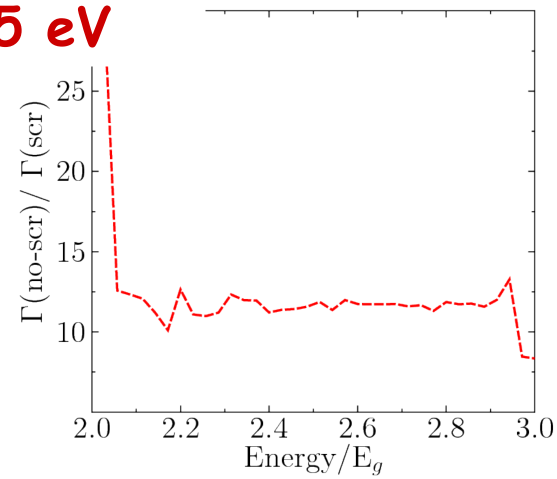
ϵ_{RPA}^{-1} →



E_{gap}: 3.5 eV



ϵ_{RPA}^{-1} →



Screening is surprisingly strong even for smallest NPs

- screening is smaller for the smaller NP (ε~7.5 vs. 12)

- energy dependence of screening is minimal: static approximation is self-consistent

static dielectric const. of bulk Si ε~12

2. Multi-Exciton Generation:
2.2. Self-consistent treatment of self-energy ImΣ

- line broadening Δ is needed to evaluate Γ: Δ~ImΣ
- what Δ to use?

$$\boxed{\Gamma_i = 2\pi \sum_f |\langle X_i|W|XX_f\rangle|^2 \delta(E_i - E_f)}$$

$$\Gamma_j^+ = 2\pi \sum_{klc} (2|V_{lckj} - V_{kclj}|^2 + |V_{lckj}|^2 + |V_{kclj}|^2)\delta[\epsilon_j - (\epsilon_l - \epsilon_c + \epsilon_k)]$$

$$\Gamma_a^- = 2\pi \sum_{lbc} (2|V_{aclb} - V_{ablc}|^2 + |V_{aclb}|^2 + |V_{ablc}|^2)\delta[\epsilon_a - (\epsilon_b - \epsilon_l + \epsilon_c)]$$

$$\Gamma(E) = \frac{\sum_{ja} \Gamma_{ja}\delta[(\epsilon_a - \epsilon_j) - E]}{\sum_{ja} \delta[(\epsilon_a - \epsilon_j) - E]}$$

$$|\epsilon_j - (\epsilon_l - \epsilon_c + \epsilon_k)| \le \Delta_2$$

$$|\epsilon_a - (\epsilon_b - \epsilon_l + \epsilon_c)| \le \Delta_2$$

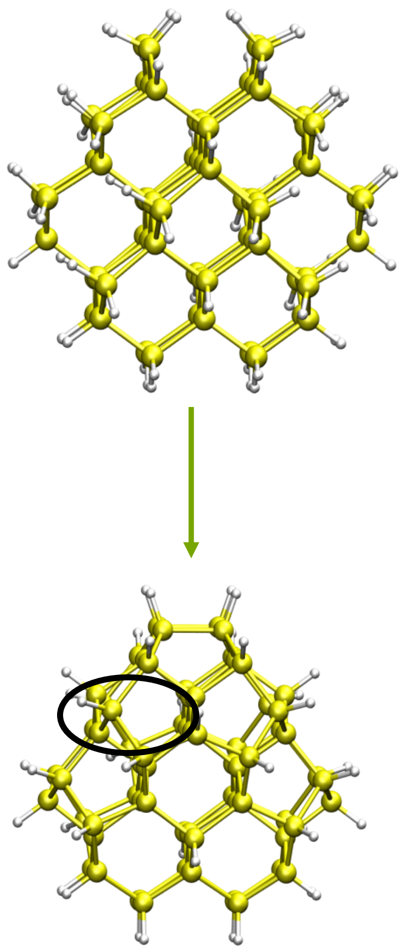
$$|\epsilon_a - \epsilon_j - E| \le \Delta_1$$

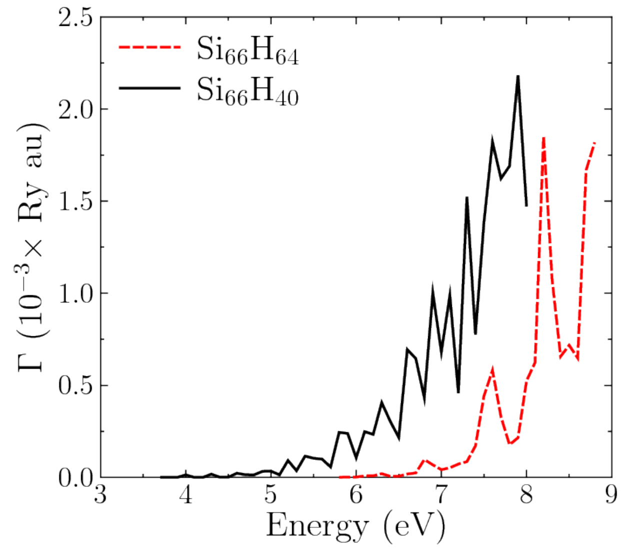
1. $\Delta_1 = \Delta_2 =$ **50 meV?**

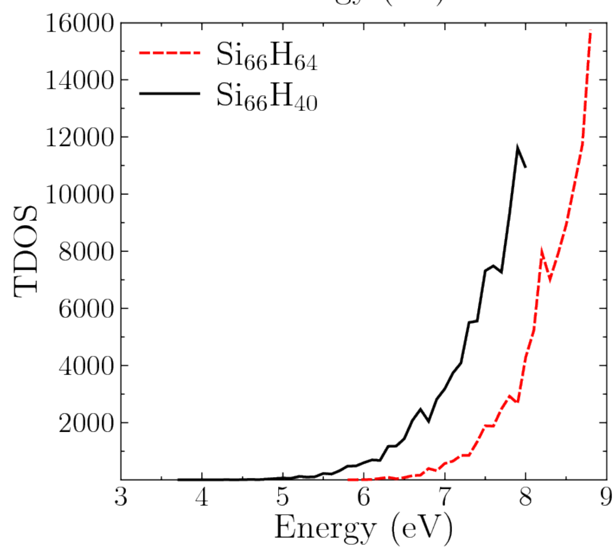
2. $\Delta = \Gamma$: Self-consistent treatment of ImΣ

calculationally demanding

2. Multi-Exciton Generation:
2.3. Effect of Surface Reconstruction







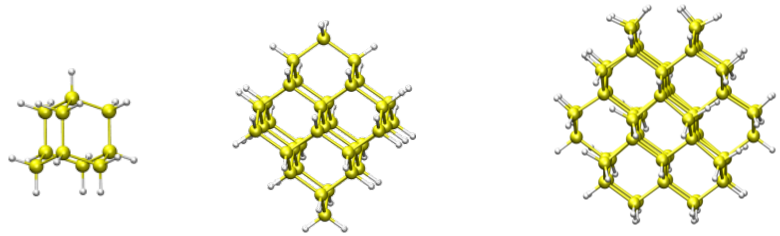
1. **Reconstruction (H64 -> H40):**

   MEG creation starts at 30% lower energies: gap reduced

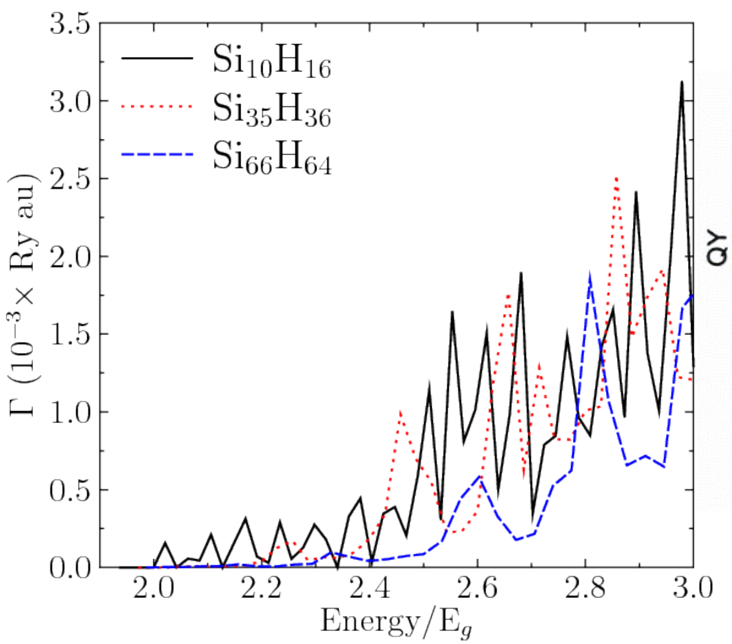
2. **Gap reduction:**

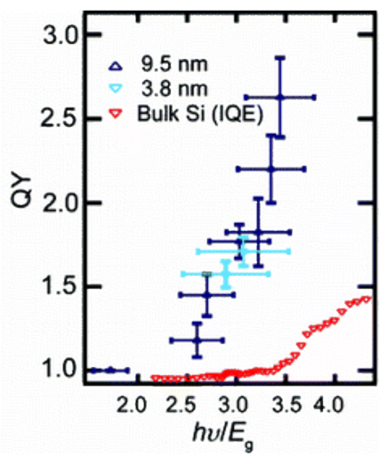
   Driven by increased trion density of continuum states, not isolated defect states

2. Multi-Exciton Generation: 2.4. Size Dependence



d: 0.5 nm < 1.1 nm < 1.2 nm
E_{gap}: 4.7 eV > 3.5 eV > 2.9 eV





Beard et al., *Nano Lett.* 7, 2506 (2007)

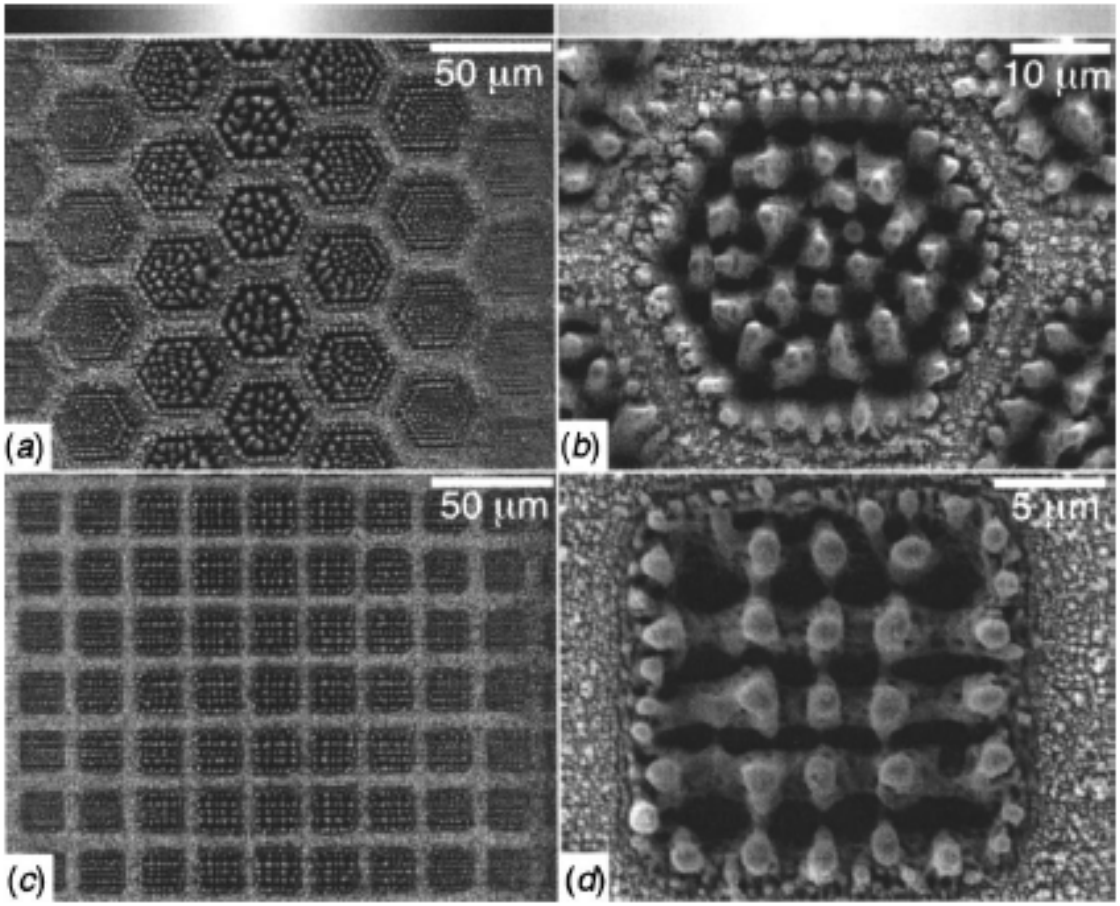
1st level:

MEG shows little size dependence when scaled for relative energies ~ Experiments

2nd level:

MEG seems to be somewhat more efficient for smaller sizes ~ Experiments

Black Silicon – Great control



Appl. Phys. Lett., Vol. 82, No. 11, 17 March 2003

Business model:
- develop great control
- found **SiOnix Inc.**

4.1. Embedding: Si NPs in ZnS

- hydrogenated Si-NP slightly expands as compared to Si-bulk bond length
- Si-NP in ideal crystalline ZnS slightly compressed due to smaller ZnS lattice constant
- up to 4% bond length deviation for Si-NP in amorphous ZnS, significant variance
- How about electronic structure?