Marek Lipiński

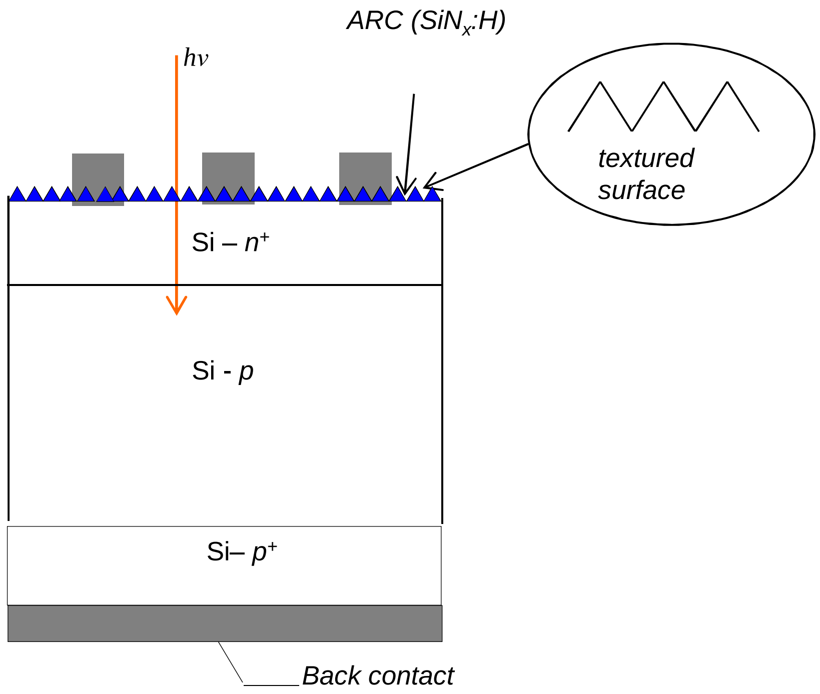
New Concepts of Photovoltaics

Institute of Metallurgy and Materials Science
Polish Academy of Sciences

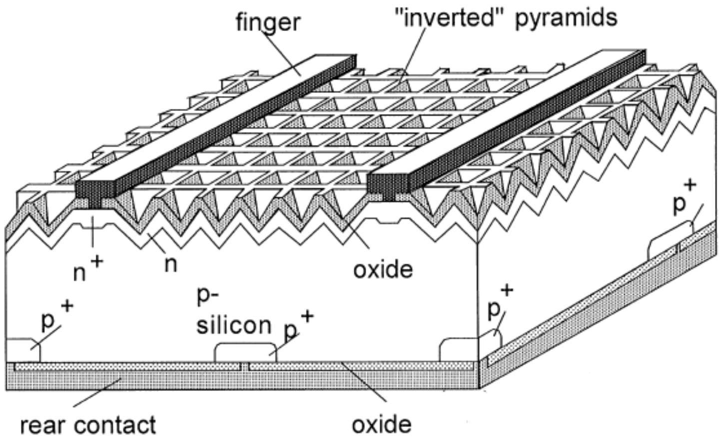
Kraków, 2013

Introduction

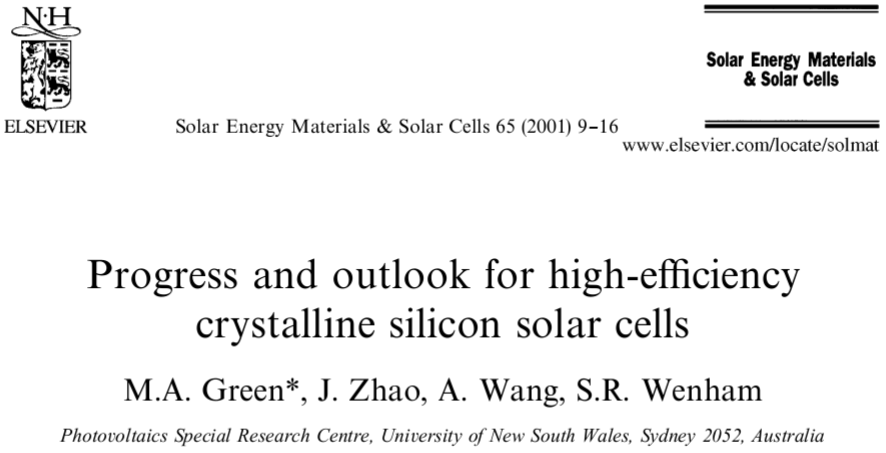
Silicon solar cells – I generation



Schematic structure of a typical industrial silicon solar cell



Schematic structure of a PERL silicon solar cell (UNSW, E_{ff} = 25%)



N·H
ELSEVIER

Solar Energy Materials & Solar Cells 65 (2001) 9–16

Solar Energy Materials & Solar Cells

www.elsevier.com/locate/solmat

Progress and outlook for high-efficiency crystalline silicon solar cells

M.A. Green*, J. Zhao, A. Wang, S.R. Wenham

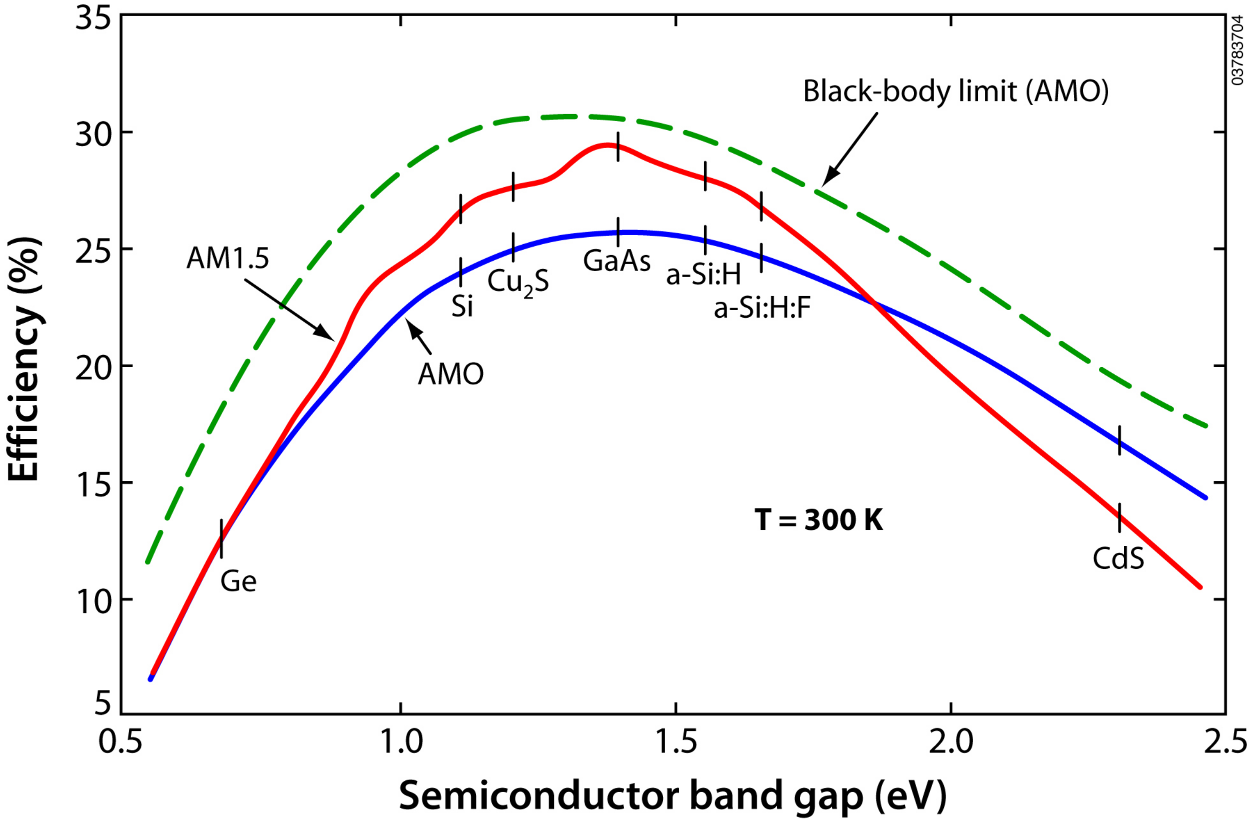
Photovoltaics Special Research Centre, University of New South Wales, Sydney 2052, Australia

Commercial solar cells

	Thin – films cells					**Si crystalline**		**CPV**
	a-Si	CdTe	CI(G)S	a-Si/μc-Si	DSC	Mono	Multi	**III-V** multi-junction
η (cell)	4-8%	10-11%	7-12%	7-9%	2-4%	**16-22%**	**14-18%**	**30-38%**
η (PV module)						13-19%	11-15%	~25%
Area of PV solar cells 1kW	15 m^2	10 m^2	10 m^2	12 m^2		7 m^2	8 m^2	

Source: EPIA 2010. Photon International, March 2010, EPIA analysis.

Limits of solar cells – I and II generations

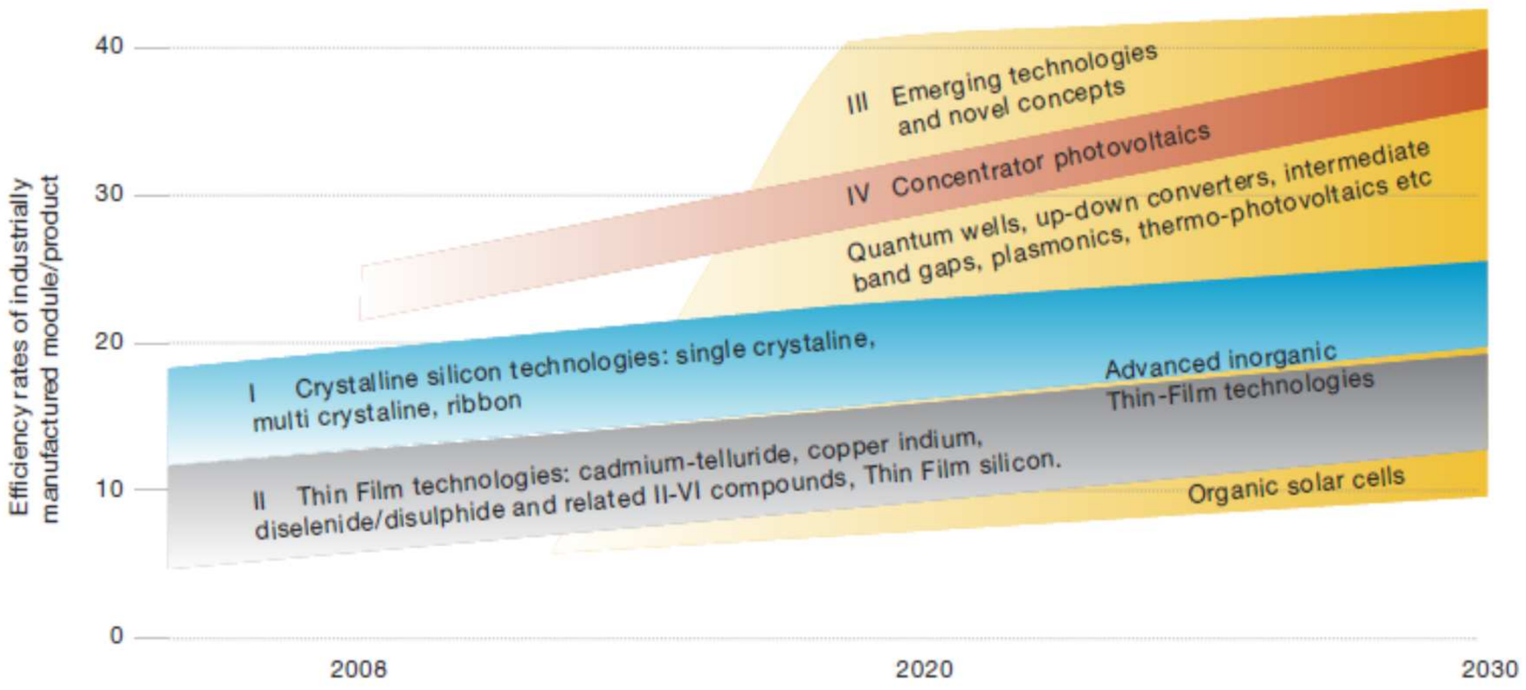


Maximum achievable efficiency of single junction solar cell as a function of the band gap for AM 0 and AM 1.5. The dashed curve is a limit efficiency for a black body solar cell

Green, *Solar Cells*, Prentice Hall, Englewood Cliffs, N.J. (1982).

Photovoltaic technology status and prospects

FIGURE 20
PHOTOVOLTAIC TECHNOLOGY STATUS AND PROSPECTS
%



source: IEA PVPS.

Source: IEA PVPSInternational Energy Agency Photovoltaic Power System Programme, http://www.iea-pvps.org/

Photovoltaic energy conversion

The basic four steps needed for photovoltaic energy conversion:

1. a light absorption process which causes a transition in a material (the absorber) from a ground state to an excited state

2. the conversion of the excited state into (at least) a free negative and a free positive-charge carrier pair

3. a discriminating transport mechanism, which causes the resulting free negative-charge carriers to move in one direction (to a contact that we will call the cathode) and the resulting free positive-charge carriers to move in another direction (to a contact that we will call the anode).

4. combining with an arriving positive-charge carrier, thereby returning the absorber to the ground state.

S.J. Fonash, *Solar Cell Device Physics*, Elsevier Inc.(2010)

Materials for solar cells

Materials used in solar cells:
- **inorganic**
- **organic**

- **Solid :** crystalline, polycrystalline, or amorphous:
  metals, semiconductors, insulators, solide electrolytes.
  type of cells: homojunction, heterojunction, metal-semiconductor, some dye-sensitized solar cells

- **Liquid materials** : electrolytes
  type of solar cells: liquid- semiconductor, dye-sensitized cells

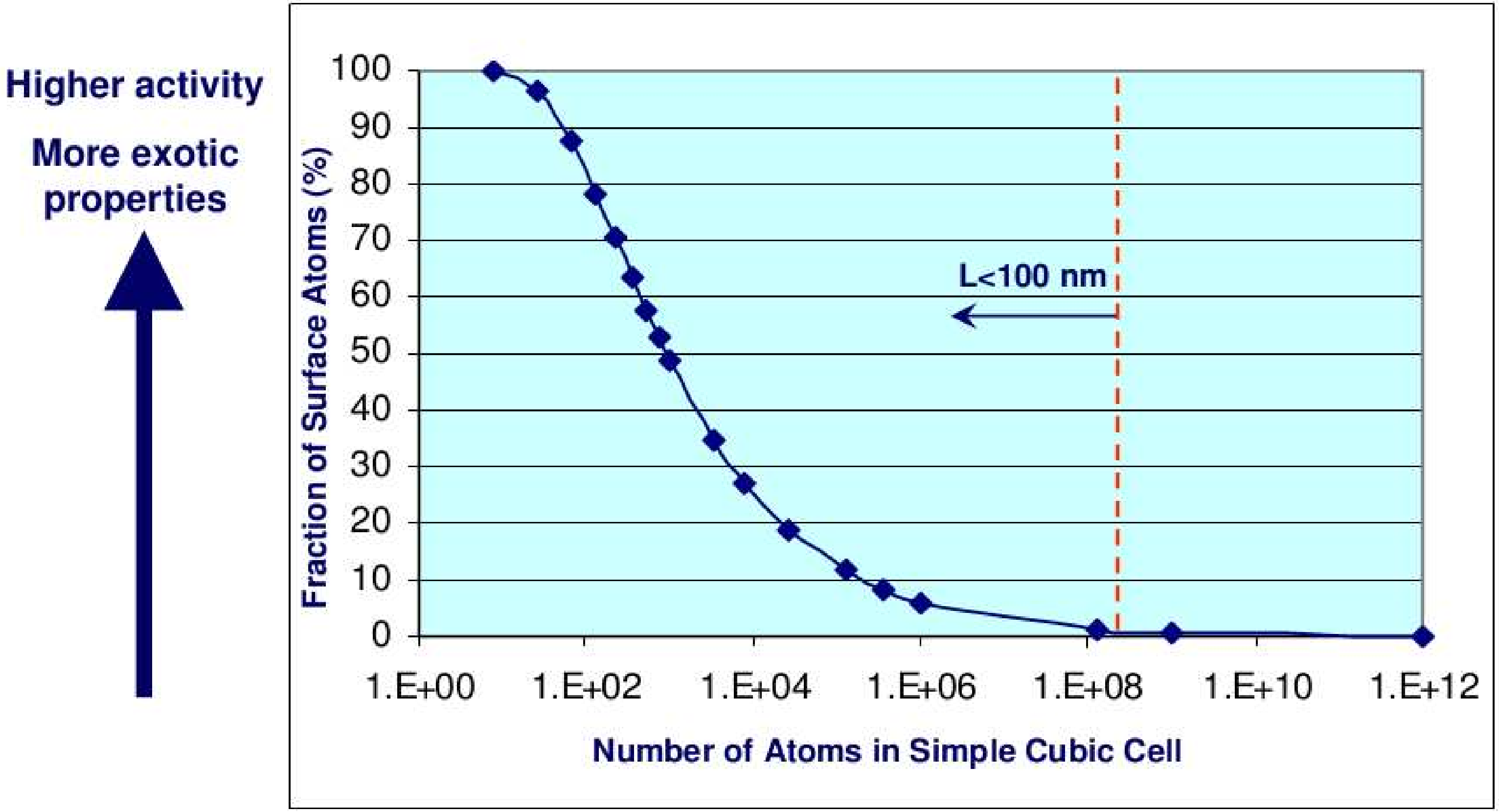
Crystalline and polycrystalline solids

Some Material Structure Types

Material type	Size of single-crystal grain	Comments
Nanoparticle	Particle size <100 nm. single crystal, polycrystalline, or amorphous.	Spherical and columnar-like. Quantum size effects possible for particles <10 nm. Semiconductor nanoparticle when size effects are present - quantum dots
Nanocrystalline (nc) material	Single-crystal grains each < 100 nm	Polycrystalline. The nc-Si has small grains of crystalline silicon within an amorphous Si phase. Quantum size effects possible for grains <10 nm.
Microcrystalline (μc) material	Single-crystal grains <1000 μm to 100 nm.	Polycrystalline. Often simply called polycrystalline material
Multicrystalline (mc)	Single-crystal grains >1 mm.	Polycrystalline. Grains can be many cm or larger in size.
Single-crystal material	No grains nor grain boundaries.	Whole material is one crystal.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc.(2010).

Nanoparticles and nanocrystalline solids



Typically, the particles smaller than 100 nm are classified as nanoparticles. When the cluster size becomes larger than 700^3 atoms (L=~100 nm), most atoms are in the bulk. Particles larger than 100 nm but smaller than optical wavelength is still of interest for optical and catalysis applications

Eal Lee, KAERI Lecture Serie, 2011

Amorphous solids

Disordered materials, contain large number of structural and bonding defects.

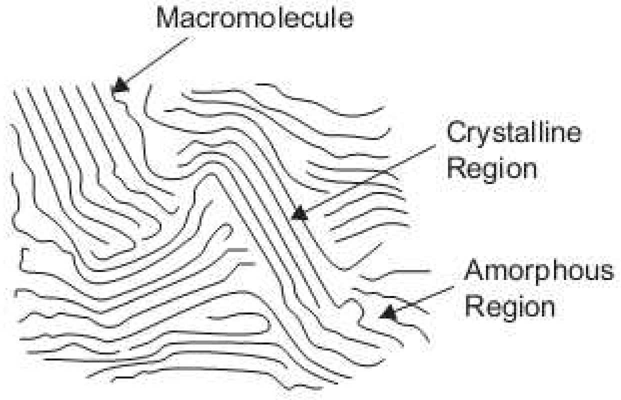
No long-range structural order

- there is no a unit cell and lattice

Amorphous solids are composed of atoms or molecules that display only short-range order.

Exemple: a-S:H materials

Mixed-phase solids crystalline and amorphous phases



Organic solid containing crystalline and amorphous regions. Some of the polymer molecules constituting this solid are found in both regions.

S.J. Fonash, *Solar Cell Device Physics*, Elsevier Inc.(2010)

Phonon spectra of solids

Because of the interactions among its atoms, a solid has vibrational modes. The quantum of vibrational energy is termed the phonon.

In thermodynamic equilibrium, the distribution of phonons among allowed modes of vibration (phonon energy levels, E_{pn}) is dictatedby Bose-Einstein statistics.

Dispersion relationship - phonon spectrum or phonon energy bands in a solid:
$E_{pn} = E_{pn}(\mathbf{k})$, where **k** wave vector, $|\mathbf{k}|=2\pi/\lambda$

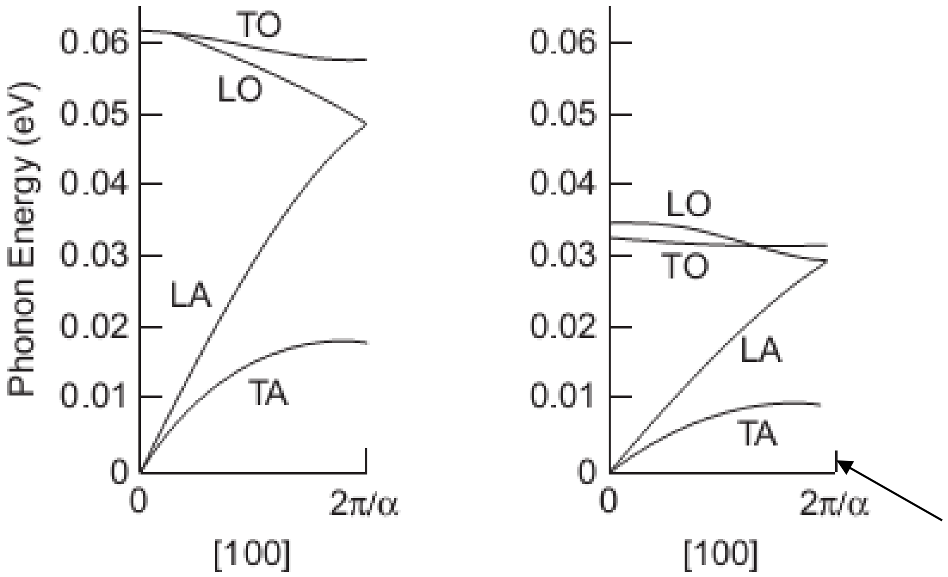
$h\mathbf{k}$ has the interpretation of particle momentum where *h* is Planck’s constant *h* divided by 2π.
For photon:
$E_{ph} = hc|(k)|$

In single-crystal, multicrystalline, and microcrystalline materials, both total energy and total momentum are conserved in phonon – electron interactions.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc. (2010).

Phonon spectra of solids

Single-crystal, multicrystalline, and microcrystalline solids



~10^8 cm^{-1}

Phonon bands in two crystalline solids: (a) silicon, and (b) gallium arsenide.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc. (2010).

Phonon confinement

Heisenberg’ s rule:

$\Delta x . \Delta p \geq h$ → $\Delta x \, \Delta k \geq (2\pi)$

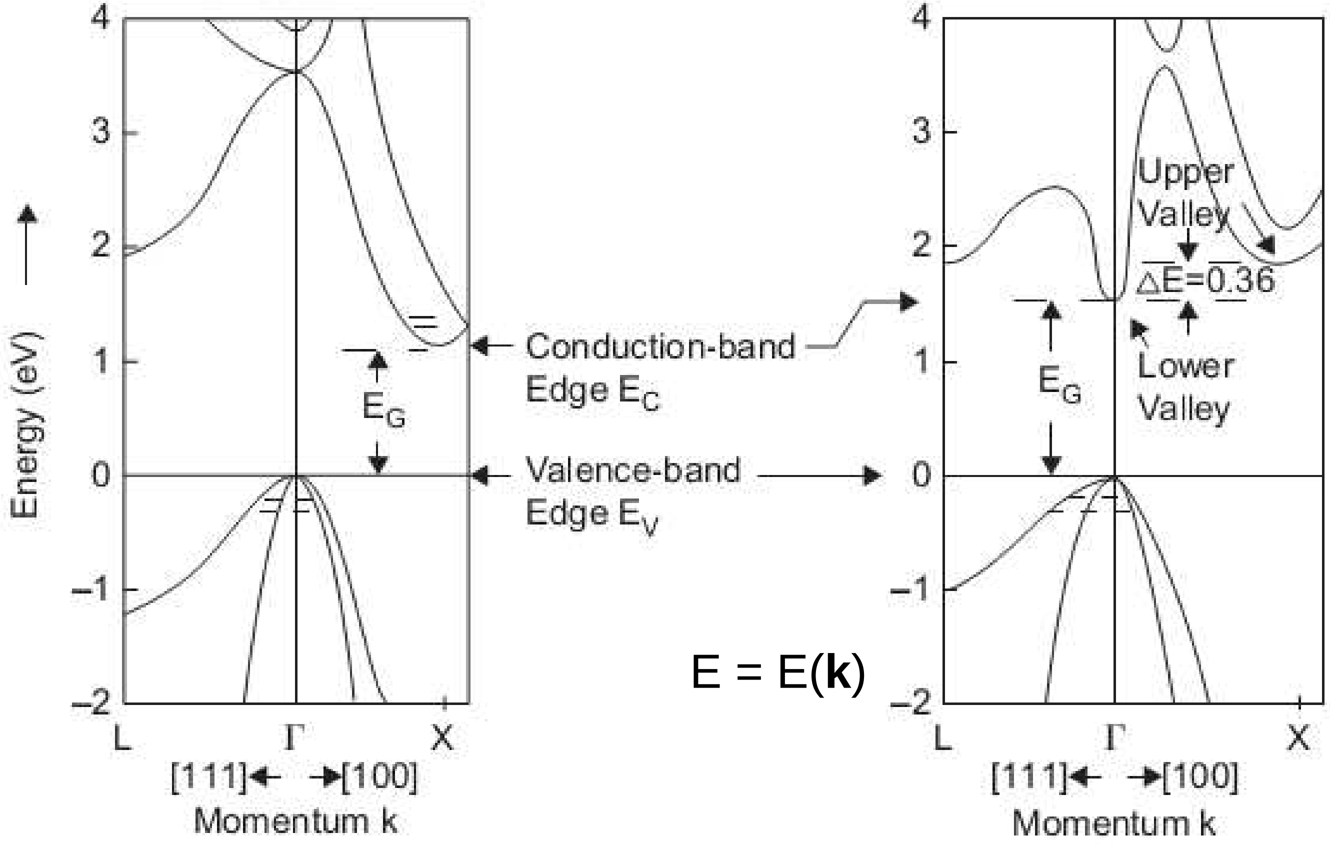
In nanoparticles : Δx becomes smaller due to confinement and Δk becomes very large .

The phonon momentum in nanoparticels is ill-defined. This is called phonon confinement.

As a particle becomes even smaller, the vibrational modes can become discrete in energy.

Electron energy levels in solids

Single-crystal, Multicrystalline, and Microcrystalline Solids

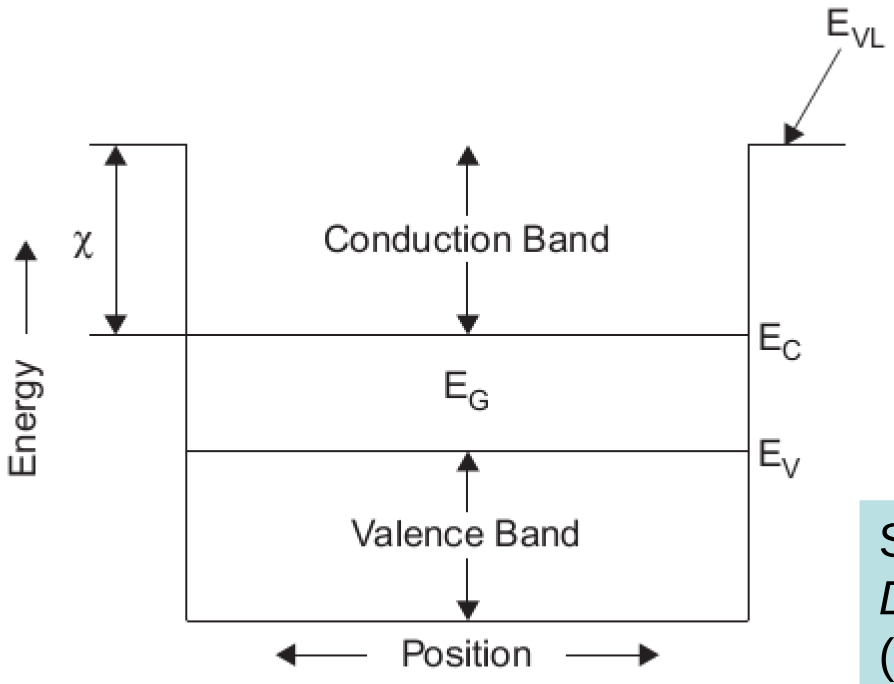


E = E(**k**)

Allowed electron energies versus k-vectors (wave vectors) for two crystalline, inorganic semiconductors: (a) silicon (the gap is indirect); (b) gallium arsenide (the gap is direct).

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc. (2010).

Electron energy levels in solids

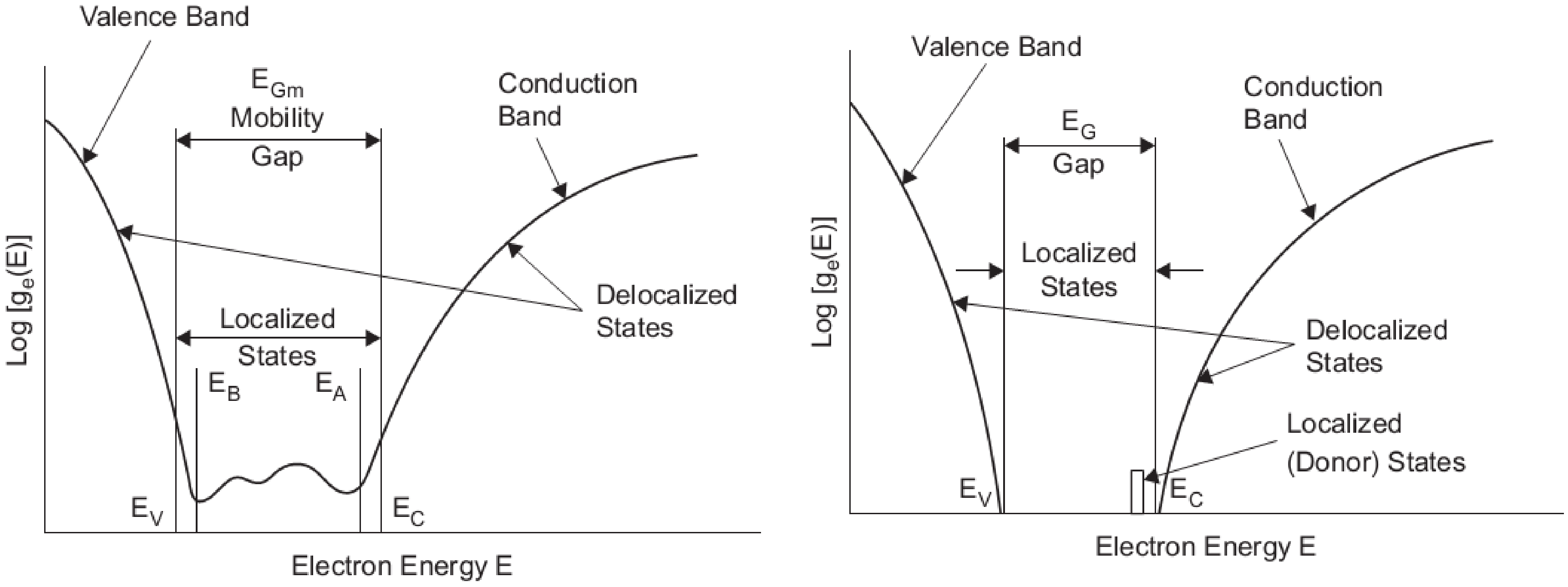


S.J. Fonash, *Solar Cell Device Physics*, Elsevier Inc (2010).

Schematic showing the energy bands available in a semiconductor as a function of position for ideal crystal. Reference energy here is the vacuum energy E_{VL}

- semiconductor $0 < E_G < 2.5$ eV
- ideal insulator $E_G \geq 2.5$ eV. The real point isthat, if a material isan insulator at room temperature, then its E_G is too wide to give any significant intrinsic carrier
- metal when the gap $E_G = 0$ or when the valence electrons only partially fill the lowest band at T = 0.

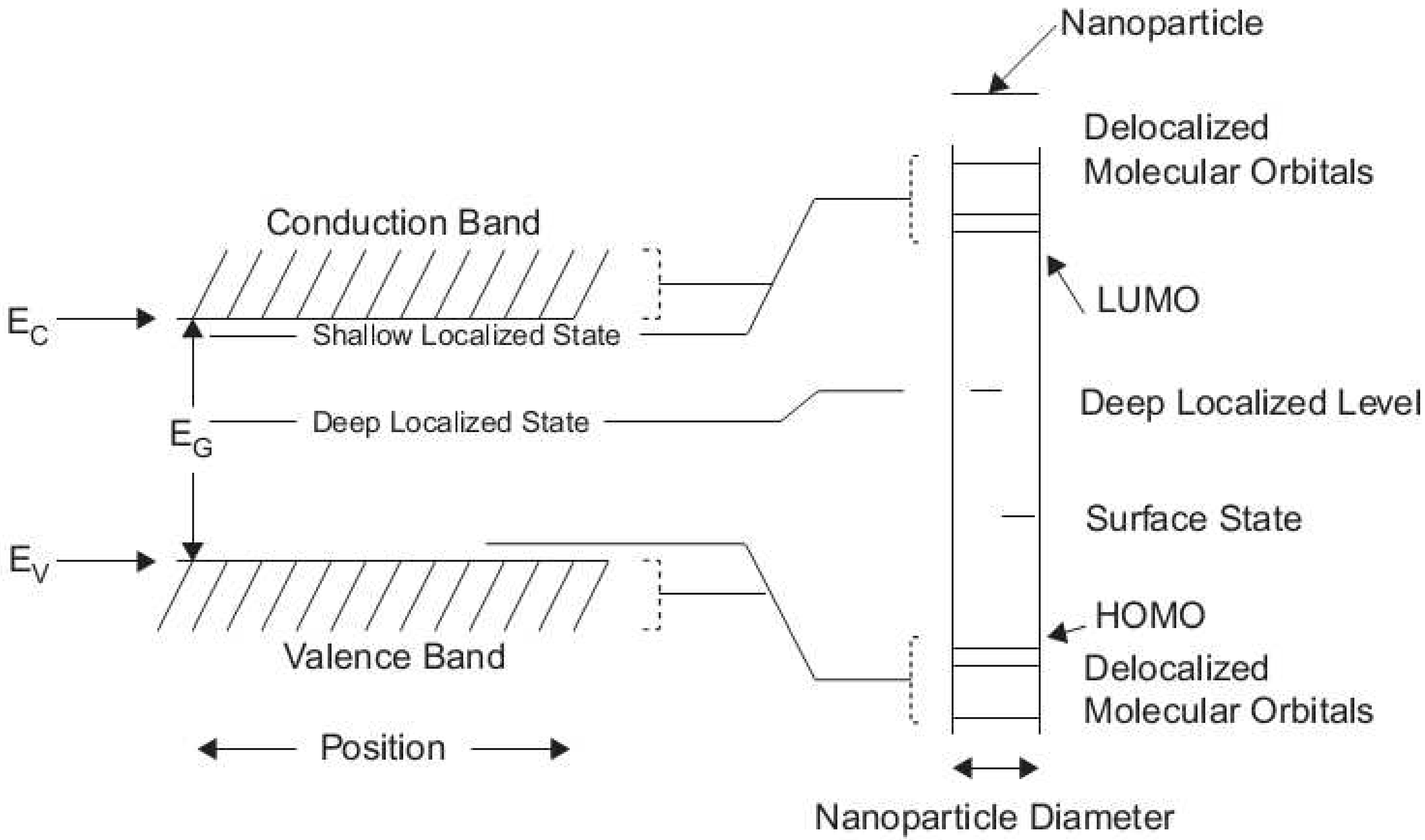
Amorphous solids



Schematic showing the density of states function $g_e(E)$ for (a) an amorphous solid and (b) a crystalline solid.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc. (2010).

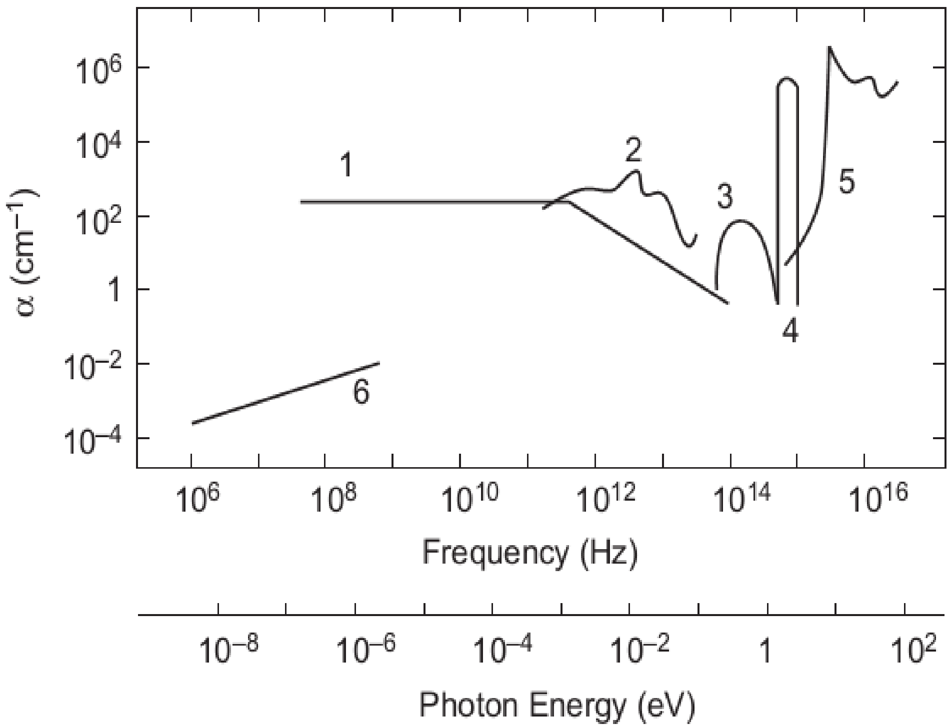
Nanoparticles and nanocrystalline Solids



Schematic single-electron energy level diagram showing, with increasing confinement, the evolution from bands to molecular orbitals.

A.D. Yoffe, *Low-dimensional systems: quantum size effects and electronic properties of semiconductor microcrystallites (zero-dimensional systems) and some quasi-two-dimensional systems*, Adv. Phys. 51 (2002) 799.

Optical phenomena in solids



1.free-carrier absorption
2. phonon absorption
3. all the photon-induced transitions between states in the gap as well as between gap states and a band
4. exciton-producing absorption
5. band-to-band transitions
6. a loss observed in some amorphous material) due to electrons that are hopping from localized site to localized site?).

A schematic portrayal of the range of optical absorption processes in solids. The Process 3, 4, and 5 contributions to α are the mechanisms we will be interested in because they can lead to free electrons and free holes. The process 3 may or may not be present at all.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc. (2010).

The absorption of light in crystalline and amorphous materials

In **single-crystal, multicrystalline, and microcrystalline** semiconductors the band-to-band absorption increases for h v $\geq E_G$.

In direct-gap material (for example GaAs), an electron can be excited from the top of the valence band to the bottom of the conduction band with essentially no change in **k** -vector required.

In indirect-gap material (for example Si) the electron excited must change its **k** -vector.The photon simply cannot supply the momentum. The phonons can supply the necessary momentum. The necessity of a three-body interaction in indirect-gap materials results the smaller value of the light absorption in indirect than in direct gap material.

This rule of conserving the total **k**-vector during band-to-band transitions can disappear for small-enough crystalline nanoparticles and nanocrystalline materials for two reasons: the constraint of a well-defined **k**-vector can disappear for phonons and electrons with confinement.

Because of this, nanocrystalline silicon, for example, exhibits stronger absorption than its single-crystal, multicrystalline, and microcrystalline silicon.

In amorphous solids, a vibrational mode may extend over only a few nanometers. The wave vector **k** is not good defined and there is no phonon **k**-selection rule.

Overall, due to the relaxation of the **k**-vector conservation rules, absorption can be stronger for amorphous materials than for corresponding crystalline material.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc.(2010).

Origins of photovoltaic action

When a materials system is driven out of TE, then J_n J_n are given by

$$J_n = e\mu_n n \frac{dE_{Fn}}{dx} - en\mu_n S_n \frac{dT_n}{dx} \qquad J_p = e\mu_p p \frac{dE_{FP}}{dx} - ep\mu_p S_p \frac{dT_p}{dx}$$

$$J_n = e\mu_n n\xi + e\mu_n n\xi'_n + eD_n \frac{dn}{dx} + eD_n^T \frac{dT_n}{dx}$$

ξ'_n electron effective force field,
ξ_n the electrostatic field

$$\xi'_n = -\left(\frac{d\chi}{dx} + kT_n \frac{d\ln N_C}{dx}\right)$$

$$D_n^T = \left[\frac{\mu_n n(V_n + S_n T_n)}{T_n}\right]$$

D^T_n electron thermal diffusion coefficient
(or Soret coefficient)

Here μ_n is the electron mobility and S_n is the Seebeck coefficient for electrons, a negative quantity. The Seebeck coefficient is also called the thermo-electric power.

Equations are very general and are valid for current transport by electrons in the conduction band in the presence of electrostatic fields, variable material properties, and a gradient in the effective electron temperature

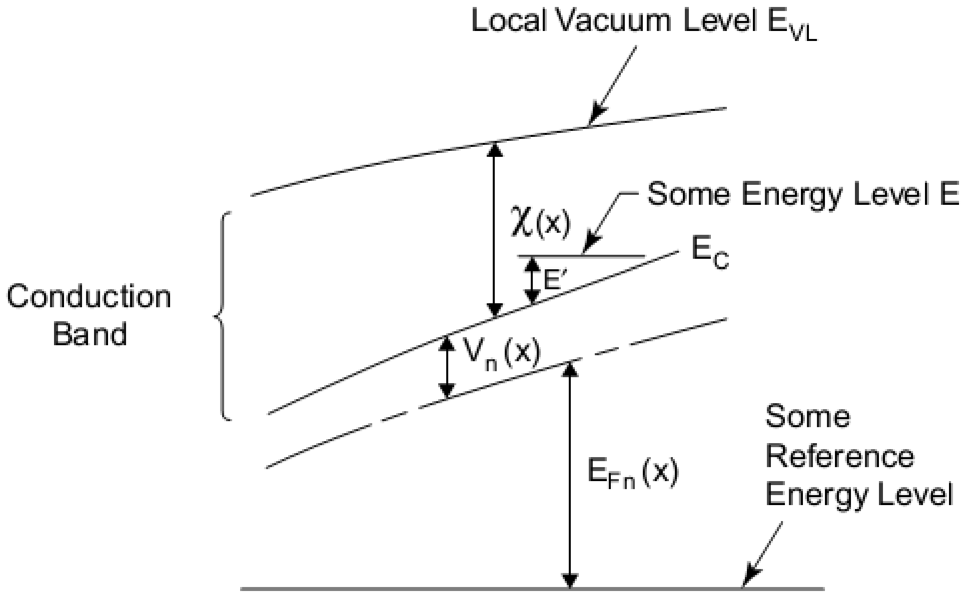
S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc.(2010).

Origins of photovoltaic action

These equations show that the origins of the photovoltaic action are:
(1) the presence of an electric field,
(2) the presence of effective force fields (changes with position in affinities and band effective densities of states),
(3) diffusion,
(4) if there is temperature gradient, thermal diffusion.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc.(2010).

Origins of photovoltaic action

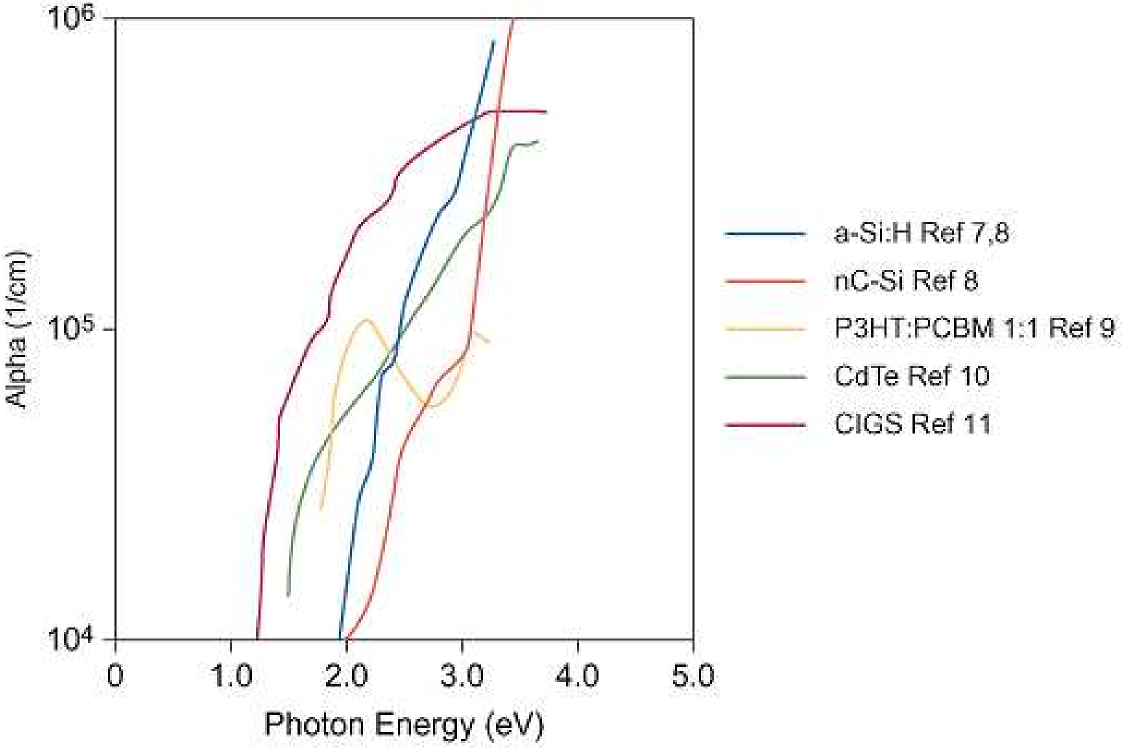


A very general semiconductor conduction band with an electron affinity that is a function of position.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc.(2010).

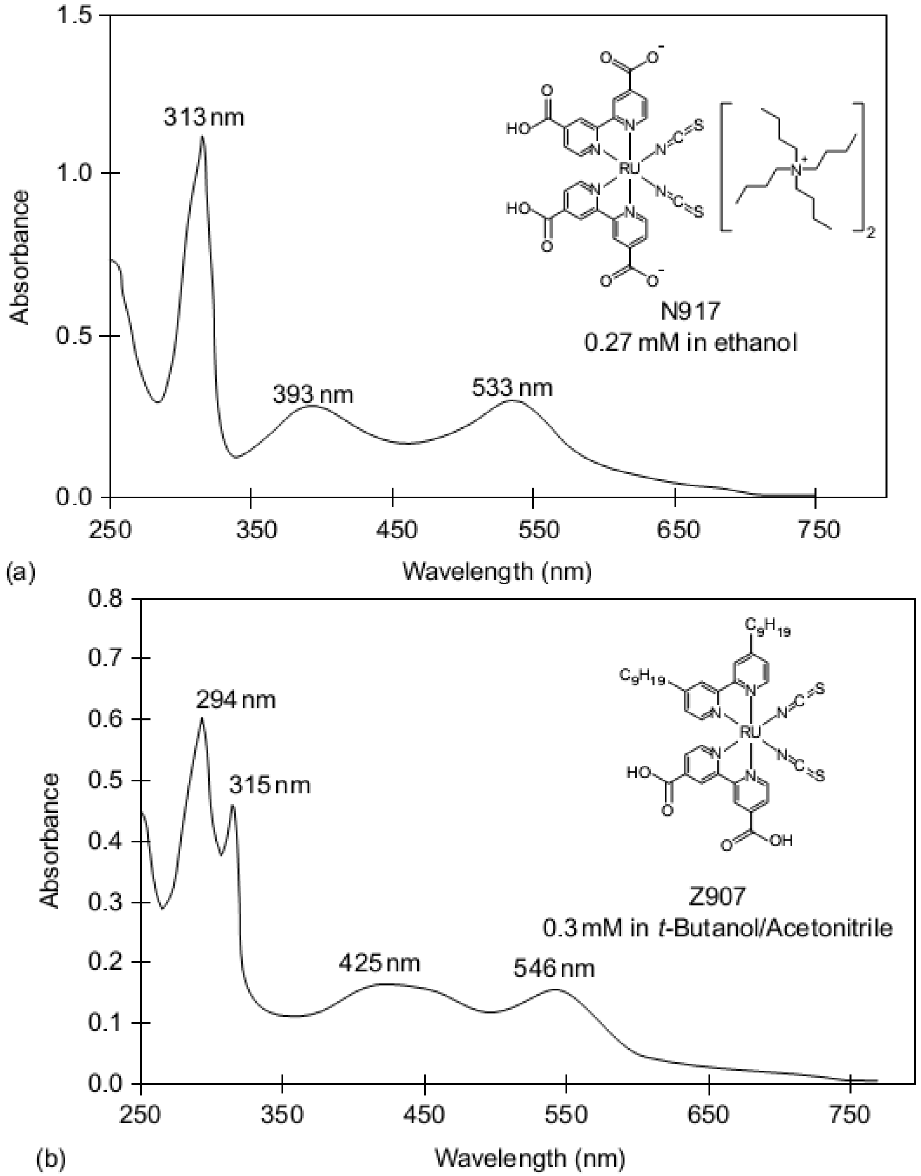
Absorber materials

Absorber materials may be classified as semiconductors or dyes. There are inorganic and organic absorbers.



Absorption coefficients for an amorphous silicon-hydrogen (a-Si:H), a nanocrystalline silicon (nC-Si), a poly (3-hexylthiophene): phenyl buckyball butyric acid methyl ester mixture(P3HT:PCBM), CdTe, and copper indium-gallium-selinide (CIGS) thin films.

S.J. Fonash, *Solar Cell Device Physics,* Elsevier Inc.(2010).



$$I(\lambda) = T(\lambda) + R(\lambda) + A(\lambda)$$

$$T(\lambda) = [I(\lambda) - R(\lambda)][\exp(-\alpha(\lambda)d)]$$

$$\frac{T(\lambda)}{I(\lambda) - R(\lambda)} = [\exp(-\alpha(\lambda)d)]$$

$$A_{abs}(\lambda) = -\ln\left[\frac{T(\lambda)}{I(\lambda) - R(\lambda)}\right]$$

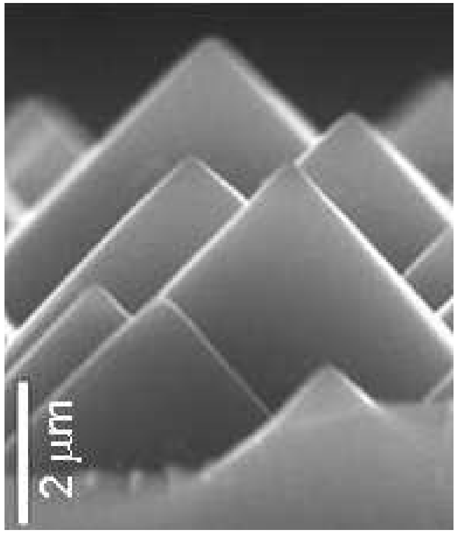
$$\alpha(\lambda) = \frac{A_{abs}(\lambda)}{d}$$

The absorbance for the ruthenium-based dyes (a) $C_{58}H_{86}N_8O_8RuS_2$ (N917) and (b) $C_{42}H_{52}N_6O_4RuS_2$ (Z907) for a 1-cm path length in solution.

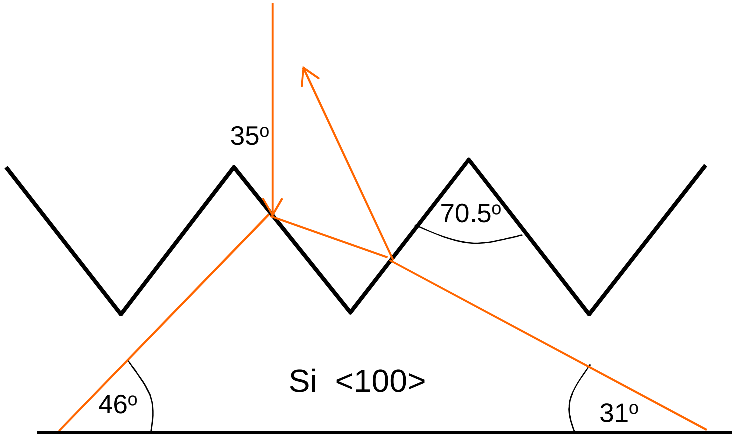
(http://www.sigmaaldrich.com

Application of metal nanoparticles to photovoltaic

Texturization of the surfaces in Si solar cells – the old technology used in industry



SEM micrograph of mono-Si (sc-Si) wafer textured a KOH solution.



Normal incident light path from air into Si with pyramidal (111) surfaces, indicated a second chance to enter the cell after the first partial reflection

1. **Reduction of reflectance**
2. **Light trapping**

Application of surface plasmons for solar cells – the new concept which can replace the texturization of the surface

What are the surface plasmons?

In a classical electromagnetic model:

Surface plasmons are the collective oscillation of free electrons in a metal. They occur at the interfaces between metals and dielectrics.

In a quantum mechanics model:

Surface plasmons are the quantized excitations at the interface between a metals and dielectrics.They behaves like a particles with a discrete energy and in the case of propagating SPs, momentum.

Localized surface plasmons - surface plasmons generated in the metal particles

Localized surface plasmons

For small particles in the $R << \lambda$ quasi-static limit, the scattering and absorption cross-sections are given by

$$C_{sct} = \frac{1}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4 |\alpha|^2 \propto R^6$$

$$C_{abs} = \frac{2\pi}{\lambda} \mathrm{Im}[\alpha] \propto R^3$$

$$\alpha = 4\pi R^3 \left[\frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}\right] \longrightarrow$$

resonance for:
$\varepsilon = -2\varepsilon_m$

R – diameter of particle, α is the polarizability of the particle, ε the permittivity of the metal and ε_m the permittivity of the surrounding medium

The scattering efficiency Q_{sca}, absorption efficiency Q_{abs} and extinsion efficiency Q_{ext} are given by:

$$Q_{sca} = C_{sca} / (C_{sca} + C_{abs})$$

$$Q_{ext} = Q_{sca} + Q_{abs}$$

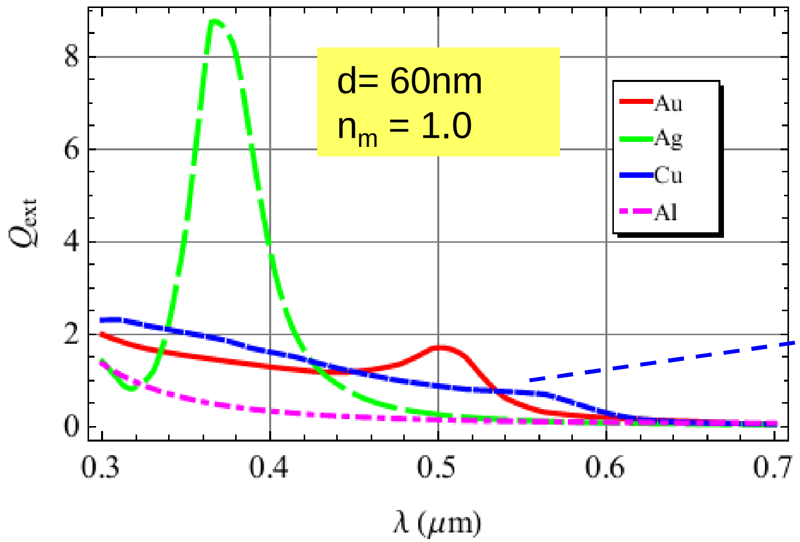
$$Q_{abs} = C_{abs} / (C_{sca} + C_{abs})$$

For R≤40 nm: $C_{sct} << C_{abs}$ → fotothermic conversion

For R≥100 nm: $C_{sct} >> C_{abs}$ → suitable for solar cells

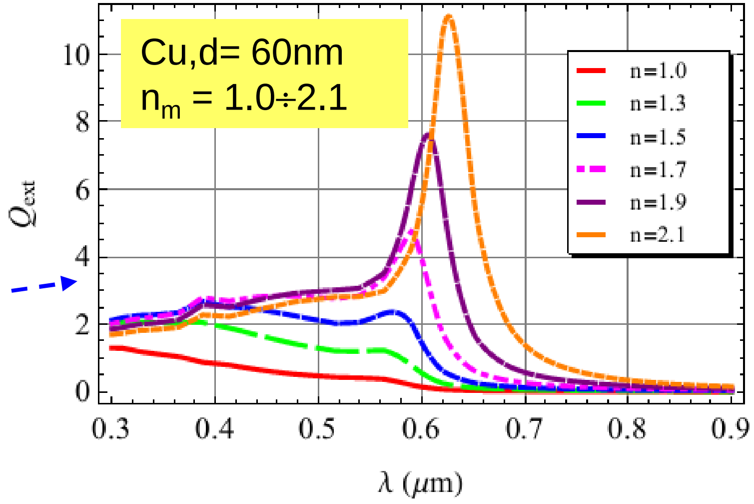
Localized surface plasmons

(a) Influence the kind of metal



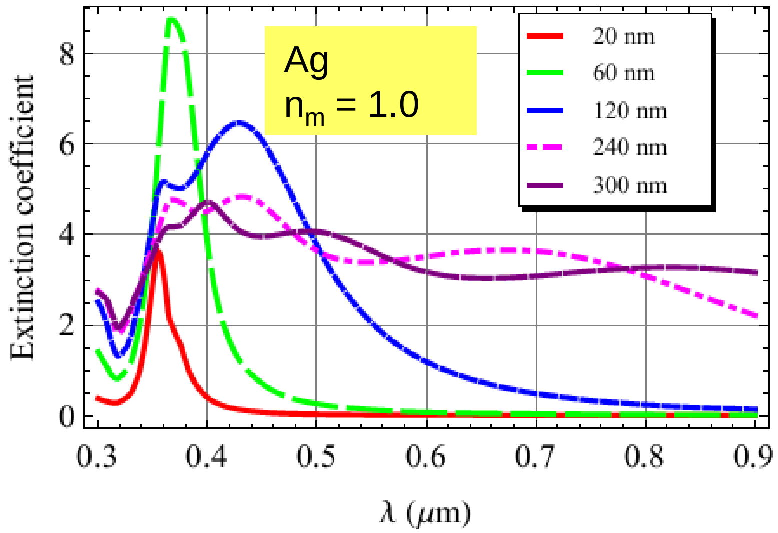
d= 60nm
n_m = 1.0

(b) Influence the environment



Cu,d= 60nm
n_m = 1.0÷2.1

(c) Influence the diameter



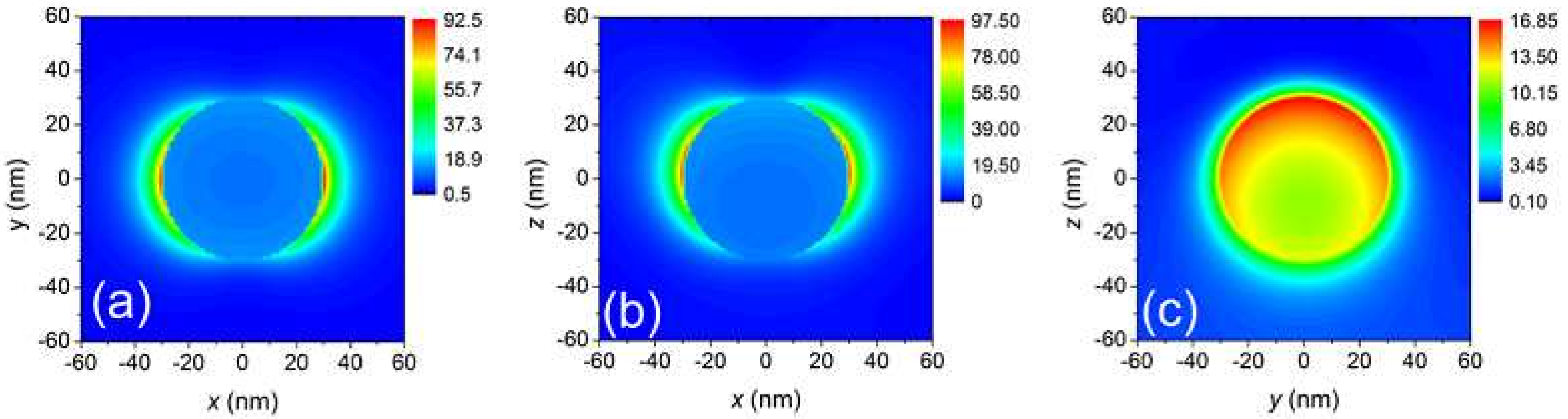
Ag
n_m = 1.0

Extinction coefficient as a function of wavelength, for a sphere particles.

Sarid D. and. Challenger W, *Modern Introduction to Surface Plasmons*, Cambridge Univ.Press (2010)

Localized surface plasmons

Near –field. Simulation – Mie theory [Sarid,2010]

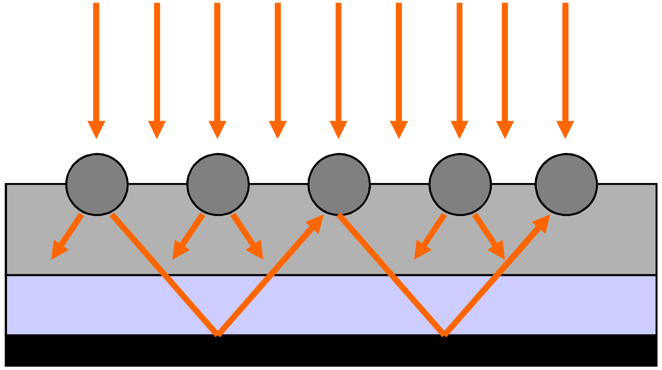


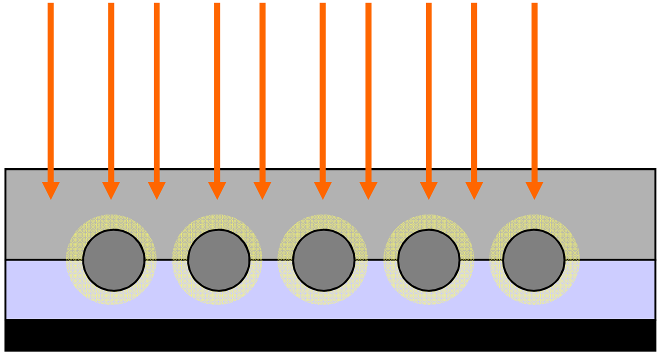
The field intensity, in the vicinity of a 60 nm silver sphere in air at the resonance wavelength of 367nm when excited by a plane wave of unit amplitude traveling in the -z-direction and polarized along the x-direction.

The peak field intensity at the sphere is about two orders of magnitude larger than that of the incident field at the resonant wavelenght !

D. Sarid and W. Challenger, *Modern Introduction to Surface Plasmons*, Cambridge Univ..Press (2010)

Application of localized surface plasmons for solar cells





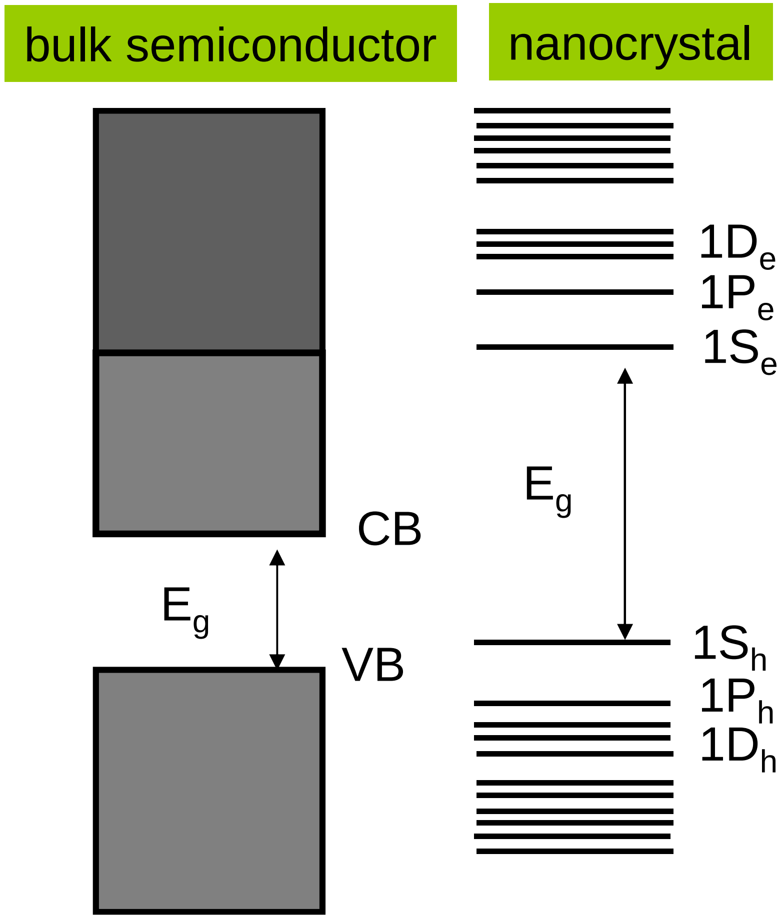
The scattering from the metal particles. Light is scattered and trapped into the semiconductor thin film causing an increase in the effective optical path length in the cell.

Light trapping by the excitation of localized surface plasmons in metal nanoparticles embedded in the semiconductor. The near field enhancement and direct generation of charge in the semiconductor substrate

H. A. Atwater and A. Polman, *Plasmonics for improved photovoltaic devices*, Nature materials, 9(2010)205

Application of semiconductor nanoparticles to photovoltaic

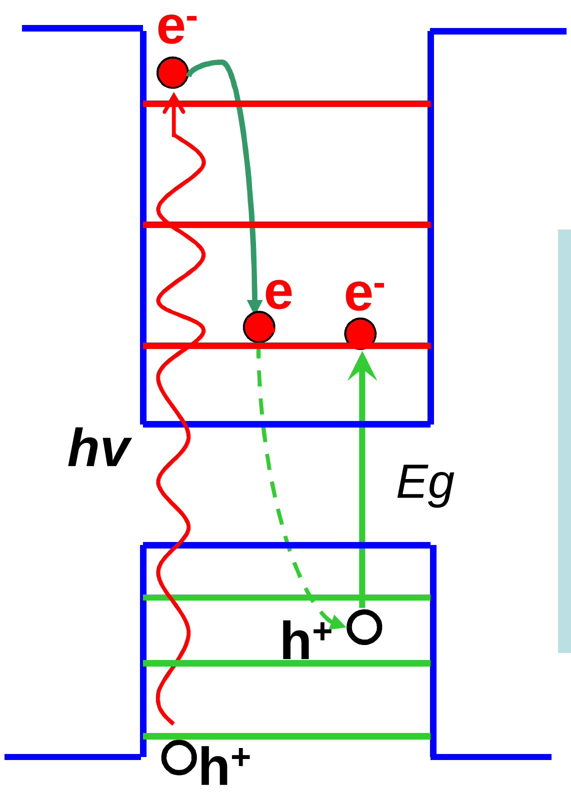
Application of semiconductor nanoparticles to photovoltaic



Fluorescence induced by exposure to UV light in vials containing various sized CdSe Q-dots

Eal Lee, *Quantum Dot Solar Cell*, KAERI Lecture Series, 2011.

Application of semiconductor nanoparticles to photovoltaic



- **Greatly slowed relaxation and cooling of photogenerated hot electrons and holes due to phonon bottleneck**

- **Enhanced impact ionization (inverse Auger recombination). Multi exitons generation.**
- **Increasing the energy gap**

- A.J. Nozik, Physica E 14 (2002) 115
- A. Luque, A. Marti, and A.J. Nozik, MRS Bulletin Vol. 32 (2007) 236

Enhanced electron–hole pair (exiton) multiplication in quantum dots that could lead to enhanced solar photon conversion efficiency in QD solar cells.

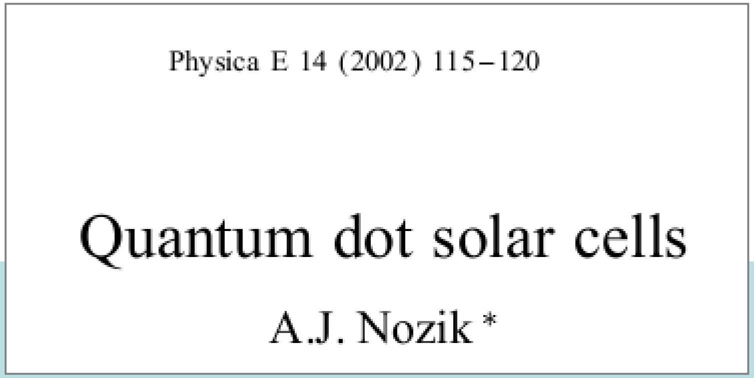
Aplication of semiconductor nanoparticles to photovoltaic

Semiconductor	Size (nm)	E_g (eV)
PbSe	bulk	0.27 i
PbSe	5.4	0.73
PbSe	4.7	0.82
PbSe	3.9	0.91
PbS	bulk	0.41 i
PbS	5.5	0.85
PbTe	bulk	0.31 i
PbTe	5.5	0.91
Si	bulk	1.12
Si	2	1.7

Application of semiconductor nanoparticles to photovoltaic

Three configurations of Quantum Dot Solar Cells (Nozik, 2002):

1. QDs array used as a photoelectrode for a photoelectrochemical or as the i-region of a p–i–n photovoltaic cell
2. QDs used to sensitize a nanocrystalline of a wide band gap oxide semiconductor (viz., TiO_2) to visible light.
3. QDs dispersed in a blend of electron- and hole-conducting polymers.



Physica E 14 (2002) 115–120

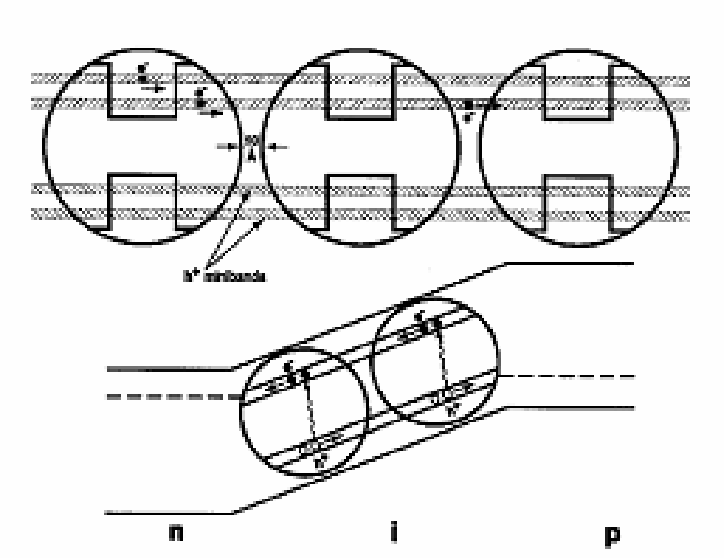
Quantum dot solar cells

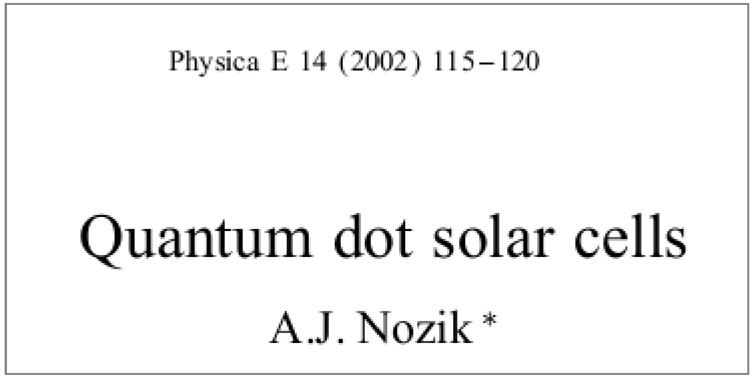
A.J. Nozik *

A.J. Nozik, Physica E 14 (2002) 115

Application of semiconductor nanoparticles to photovoltaic

1. QDs array, p-i-n structure




Physica E 14 (2002) 115–120

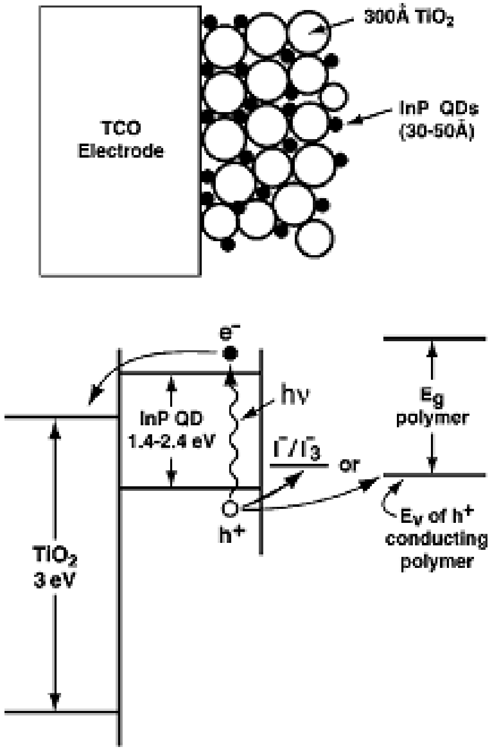
Quantum dot solar cells

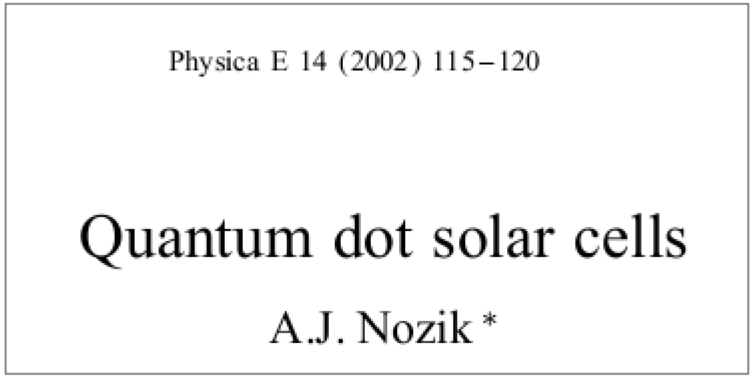
A.J. Nozik *

A.J. Nozik, Physica E 14 (2002) 115

Application of semiconductor nanoparticles to photovoltaic

2.QDs used to sensitize a nanocrystalline of a TiO_2





Physica E 14 (2002) 115–120

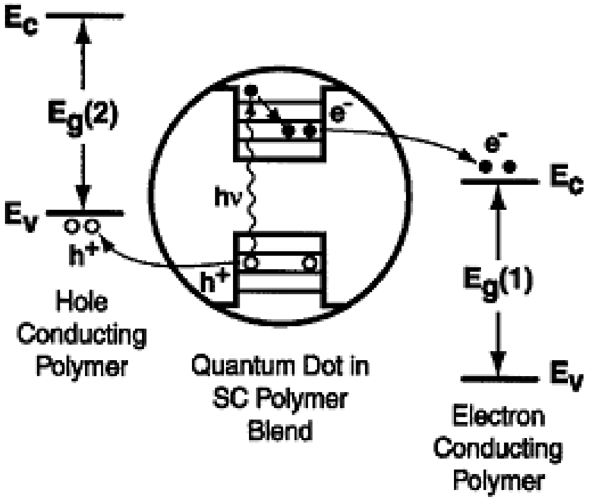
Quantum dot solar cells

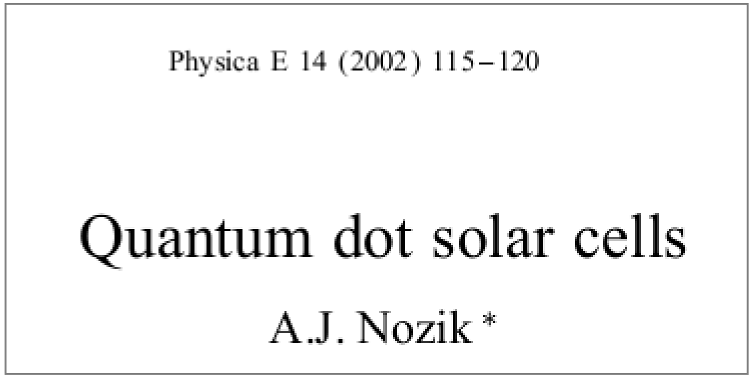
A.J. Nozik *

A.J. Nozik, Physica E 14 (2002) 115

Application of semiconductor nanoparticles to photovoltaic

3. QDs dispersed in a blend of electron- and hole-conducting polymers




Physica E 14 (2002) 115–120

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Thank you for your attention