“Solar Energy” WS 2014/2015

Lecture 3: Semiconductors for Photovoltaics

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Semiconductors

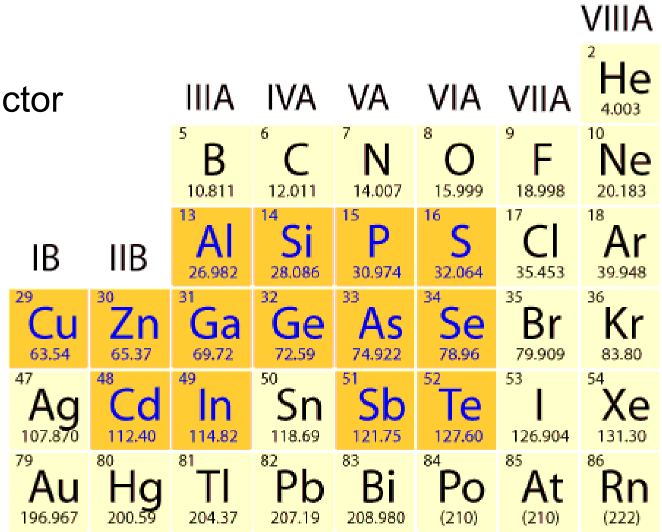
Semiconductor materials typically from either group IV of the periodic table, or combination of III-V or II-VI

As semiconductors made from different elements the properties vary

Silicon (group IV)

- most commonly used semiconductor material as it forms the basis for integrated circuit (IC) industry
- most mature technology
- most solar cells are Si based

∴ Si will be used as a model material over next few lectures



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)

Source: http://www.pveducation.org/pvcdrom/pn-junction/semiconductor-materials

Silicon

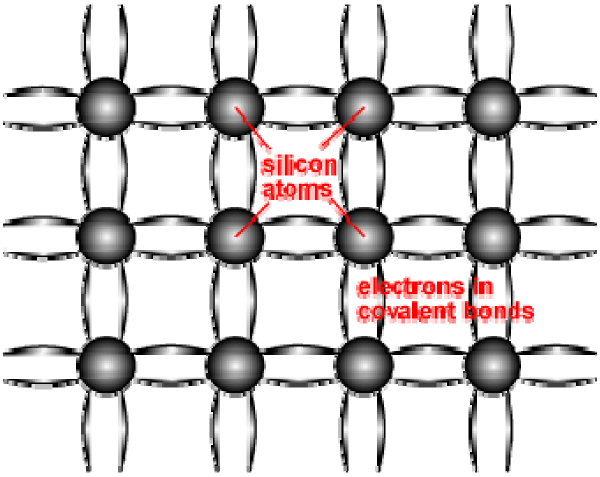
Silicon – individual atoms bonded together in a periodic structure so that each atom is surrounded by 8 electrons.

Si atom – nucleus contains a core of protons (positively charged particles) and neutrons (particles having no charge)
surrounded by electrons.

Number of electrons (e^-) = protons so as atom is overall electrically neutral

Electrons form a covalent bond – two atoms sharing a single e^- (eight overall between four covalent bonds)

Bond structure determines the material properties of a semiconductor

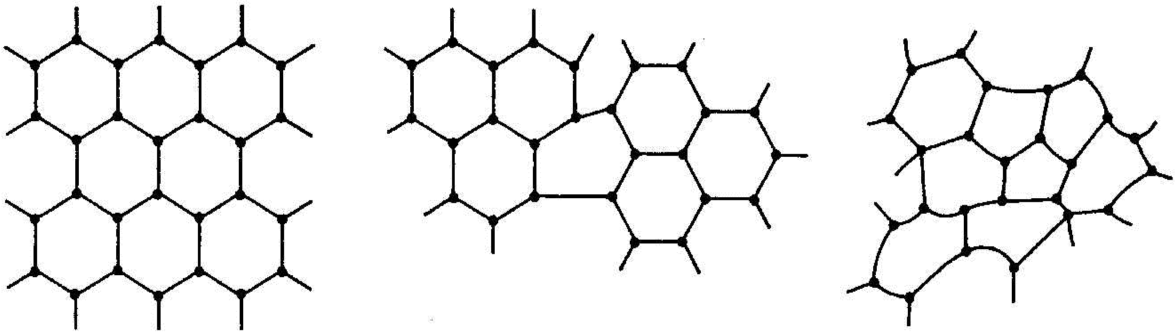


Source: http://www.pveducation.org/pvcdrom/pn-junction/semiconductor-structure

Silicon

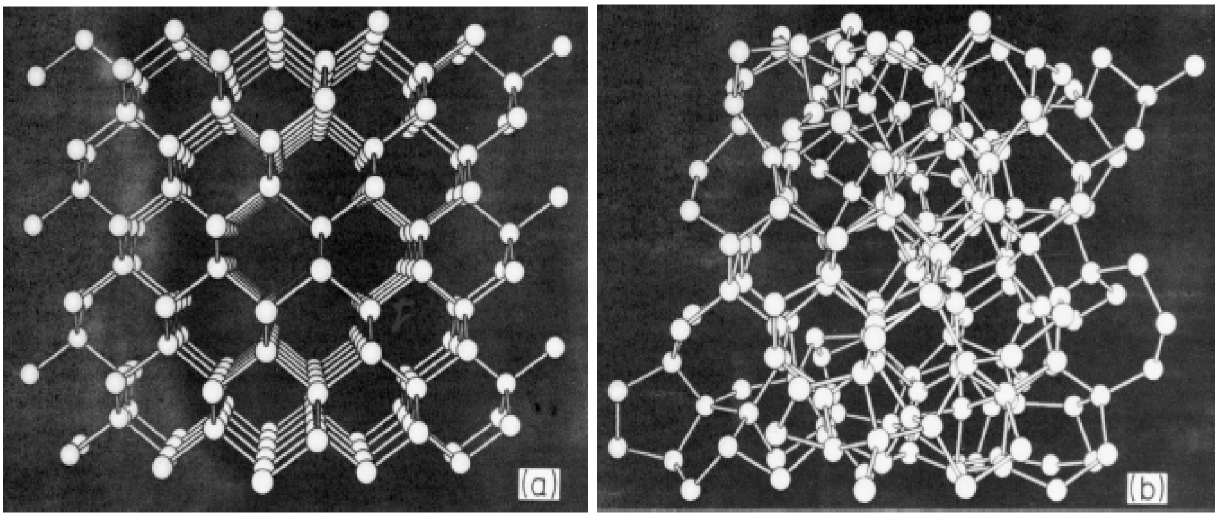
Silicon – depending on fabrication technique can get different material structure that affect properties greatly:

- Single crystal (c-Si): atoms are periodically arranged in a lattice
- Poly- or multi-crystalline (mc-Si): there are regions of crystallinity but no long range order
- Amorphous silicon (a-Si): only short range order exists and no periodicity

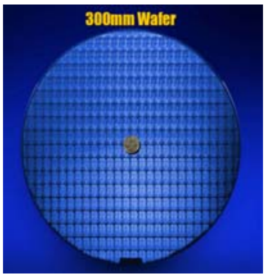


Source: Wolfe, Holonyak, Stillman

Silicon

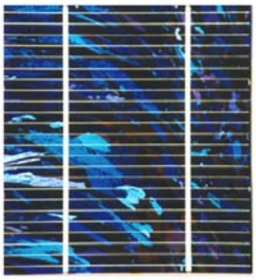


Silicon

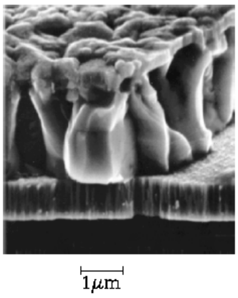


300 mm wafer
for Si microelectronics

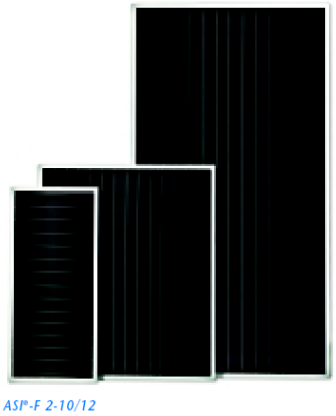
Monocrystalline
Si solar cell



Multicrystalline
Si solar cell



Electron microscope image
of thin film solar cell



PV modules made
from amorphous
silicon

Conduction in Semiconductors

Effect: which *E* levels e^- can occupy and how they move within crystal

Bonded e^- typically regarded as being bound, i.e. are not considered "free" to participate in current flow, absorption, or other physical processes of interest in solar cells.

Only strictly true at absolute zero – at elevated *T* (at which solar cells operate) e^- can gain enough energy to escape the bond. Thus, is no longer in its low energy state but is now "free" in a high energy state

Two distinct energy states for e^- (no intermediate level possible)
$\Rightarrow$ minimum energy called the semiconductor "bandgap"

Empty space left behind by e^- allows covalent bond to move, appearing to be positive charge moving through the crystal lattice – commonly called a "hole", h^+ (similar to e^- but with positive charge)

Source: http://www.pveducation.org/pvcdrom/pn-junction/semiconductor-structure

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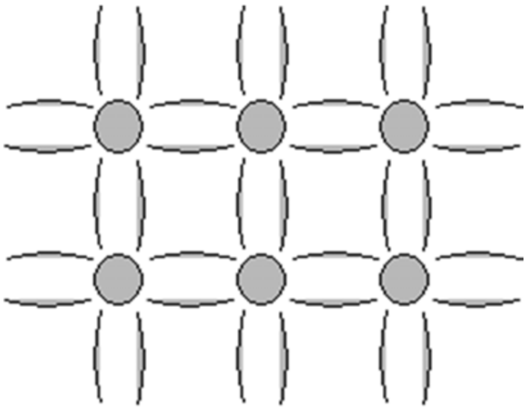
Conduction in Semiconductors

Most important parameters of a semiconductor for solar cell operation are:

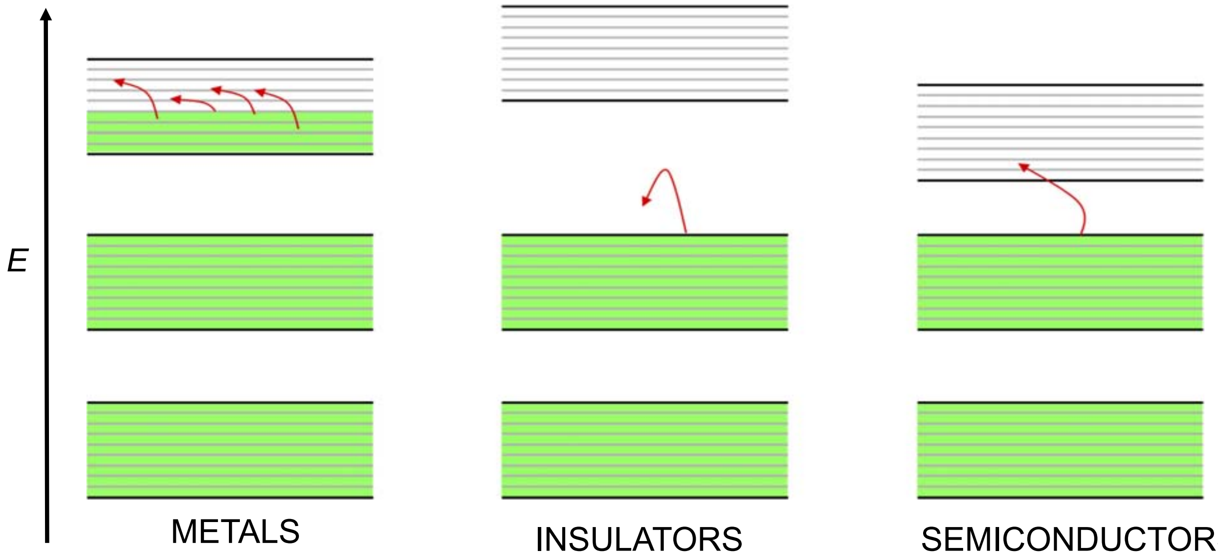
- the band gap;
- the number of free carriers (electrons or holes) available for conduction;
- the "generation" and recombination of free carriers (electrons or holes) in response to light shining on the material.



Source: http://www.pveducation.org/pvcdrom/pn-junction/conduction-in-semiconductors

Semiconductors

- Bands of allowed energy states for electrons form when atoms join to make solids
- Empty energy states are needed for free electrons to move



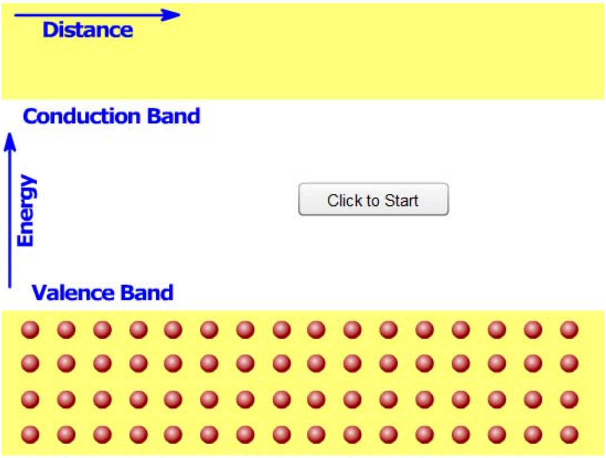
METALS
½ full top band
Easy conduction

INSULATORS
Empty top band
No conduction

SEMICONDUCTORS
Empty top band
BUT small gap

Conduction in Semiconductors

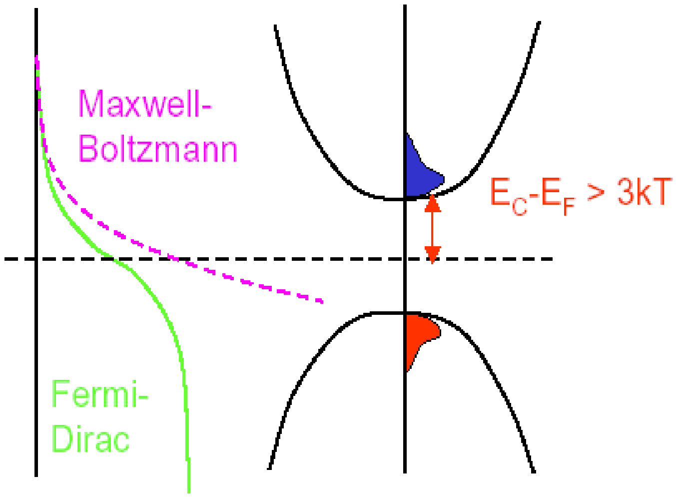
- Lower energy level called the "valence band" (E_v)
- “Conduction band" (E_c) – energy level at e^- is considered free
- Band gap (E_g) – energy between these bound and free states



Source: http://www.pveducation.org/pvcdrom/pn-junction/band-gap

Conduction in Semiconductors

- We also define the Fermi level as $E_g/2$
- Occupation of E_c and E_v follows Fermi-Dirac distribution and the Maxwell-Boltzmann approximation:



$$f_{\mathrm{FD}}(E,T) = \frac{1}{1+\mathrm{e}^{\frac{E-E_F}{kT}}}$$

$$f_{\mathrm{MB}}(E,T) = \mathrm{e}^{-\frac{E-E_F}{kT}}$$

Conduction in Semiconductors

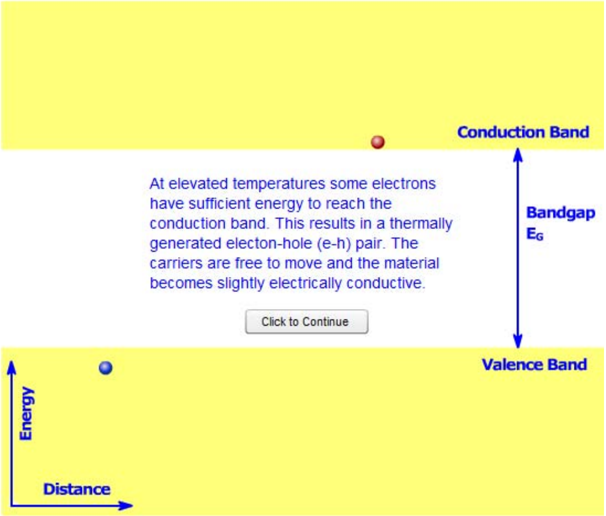
Semiconductor material with no added impurities to change the carrier concentrations is called <u>intrinsic</u> material. Concentration of the carriers (e^- and h^+) is called the intrinsic carrier concentration, n_i

$n_i \propto E_g$ and T

Intuitively:

- large E_g makes it harder and $\therefore$ n_i is lower in wide E_g materials
- Increasing T makes it more likely that e^- will be excited into E_c, which increases n_i

Impacts directly on solar cell efficiency



At elevated temperatures some electrons have sufficient energy to reach the conduction band. This results in a thermally generated electon-hole (e-h) pair. The carriers are free to move and the material becomes slightly electrically conductive.

Source: *http://www.pveducation.org/pvcdrom/pn-junction/intrinsic-carrier-concentration*

Conduction in Semiconductors

At 300 K, the exact value of n_i in silicon is generally accepted to be 9.65×10^{9} cm^{-3} (Altermatt *et al.*) and a general formula for n_i in Si as function of T is given by (Misiakos and Tsamakis):

$$n_i(T) = 5.29\times10^{19}(T / 300)^{2.54}\exp(-6726/T)$$

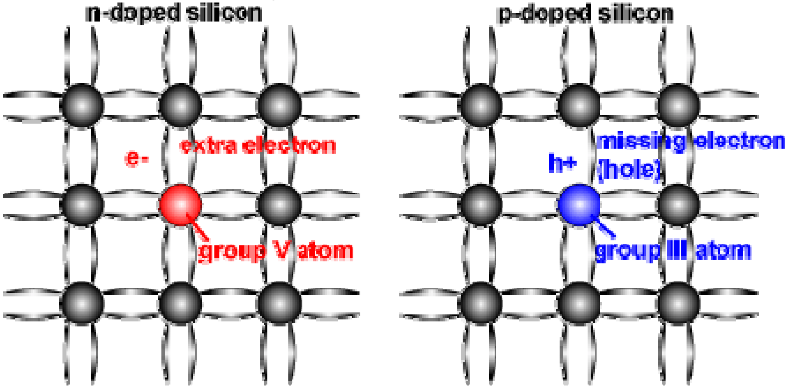
Source: *Altermatt et al. Journal of Applied Physics. 2003 ;93(3):1598.*
Misiakos and Tsamakis. Journal of Applied Physics. 1993 ;74(5):3293.

Conduction in Semiconductors

Change balance of e^- and h^+ in Si crystal lattice by doping with other atoms

- group V elements have one more valence e^- than Si and produce "*n*-type" semiconductor material
- group III elements have one less valence e^- than Si and produce “p-type" semiconductor material

In doped material, there is always more of one type of carrier than the other. Carrier with the higher concentration is called a "majority carrier", while the lower concentration carrier is called a "minority carrier."

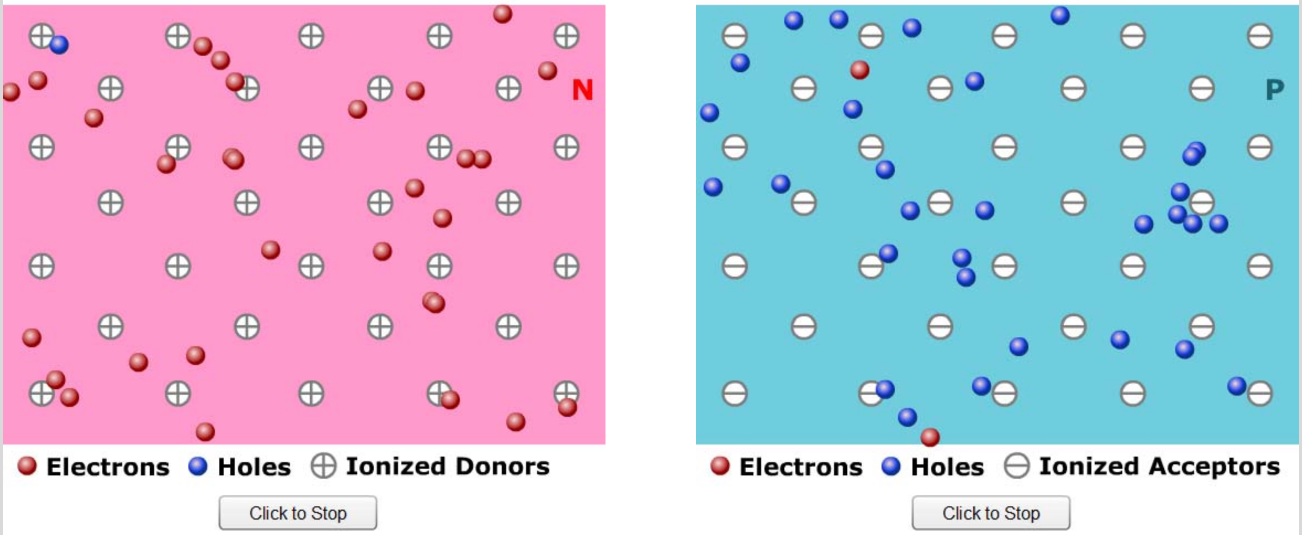


Source: http://www.pveducation.org/pvcdrom/pn-junction/doping

Conduction in Semiconductors

n-type Si (majority carriers are Negatively charged electrons)
p-type Si (majority carriers are Positively charged holes)

e.g. 10^{17} cm^{-3} majority carriers and 10^{6} cm^{-3} minority carriers



Source: http://www.pveducation.org/pvcdrom/pn-junction/doping

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Conduction in Semiconductors

No. carriers in E_c and E_v with no external bias ≡ equilibrium carrier concentration

For majority carriers, this is equal to the n_i plus the number of free carriers added by doping. Usually semiconductor doping is >> n_i such that the number of majority carriers is approximately equal to the doping.

At equilibrium, the product of majority and minority carrier concentration is a constant - Law of Mass Action:

$$n_0 p_0 = {n_i}^2$$

where n_0 and p_0 are the electron and hole equilibrium carrier concentrations

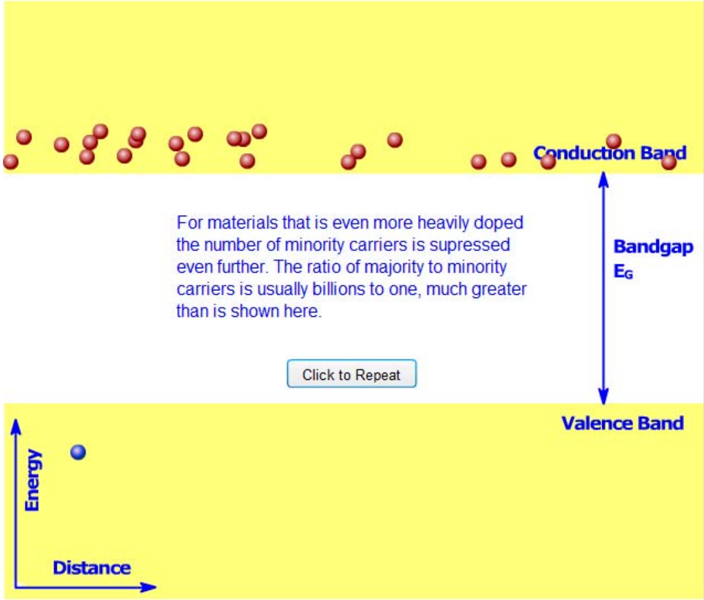
Conduction in Semiconductors

Thus, the majority and minority carrier concentrations are:

n-type: $n_0 = N_D, \;\; p_0 = \frac{{n_i}^2}{N_D}$

p-type: $p_0 = N_A, \;\; n_0 = \frac{{n_i}^2}{N_A}$

where N_D and N_A are the concentration of donor and acceptor atoms, respectively.



For materials that is even more heavily doped the number of minority carriers is supressed even further. The ratio of majority to minority carriers is usually billions to one, much greater than is shown here.

Source: http://www.pveducation.org/pvcdrom/pn-junction/equilibrium-carrier-concentration

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Absorption of Light

Photons incident on semiconductor will be either:

i. reflected from the top surface,
ii. absorbed in the material or,
iii. transmitted through the material.

For PV devices, i) and iii) reflection and transmission are losses
⇒ photons which are not absorbed do not generate power

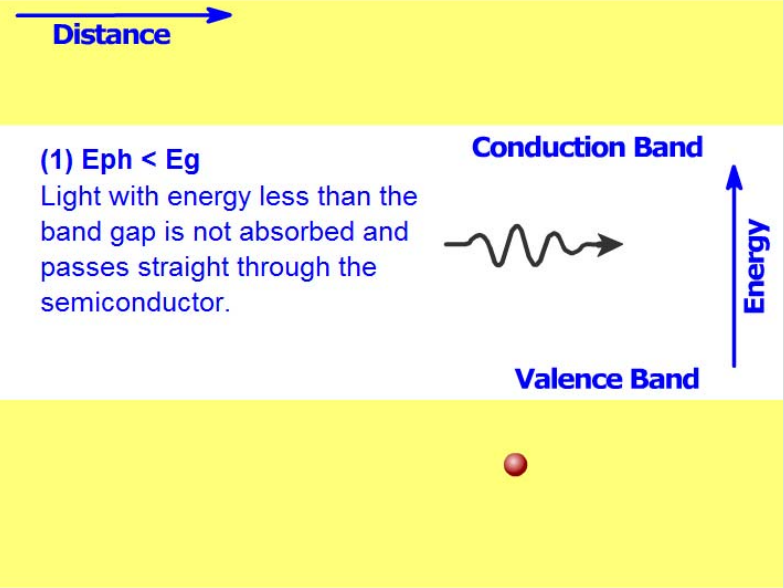
If photon is absorbed, possibility of exciting an e^- from E_v to E_c but depends on energy of photon, E_{ph}:

$E_{ph} < E_g$: pass through semiconductor as if it were transparent

$E_{ph} = E_g$: enough energy to create an e^--h^+ pair and are efficiently absorbed

$E_{ph} > E_g$: strongly absorbed, but the excess photon energy is wasted as carriers quickly thermalize back down to the band edges

Absorption of Light



(1) Eph < Eg

Light with energy less than the band gap is not absorbed and passes straight through the semiconductor.

Source: http://www.pveducation.org/pvcdrom/pn-junction/absorption-of-light

Absorption of Light

Absorption of photons creates both a majority and a minority carrier

Typically, the number of light-generated carriers are << number of majority carriers already present in the solar cell due to doping

Thus, number of majority carriers in an illuminated semiconductor does not alter significantly, but number of photo-generated minority carriers >> number of minority carriers existing in the doped solar cell in the dark

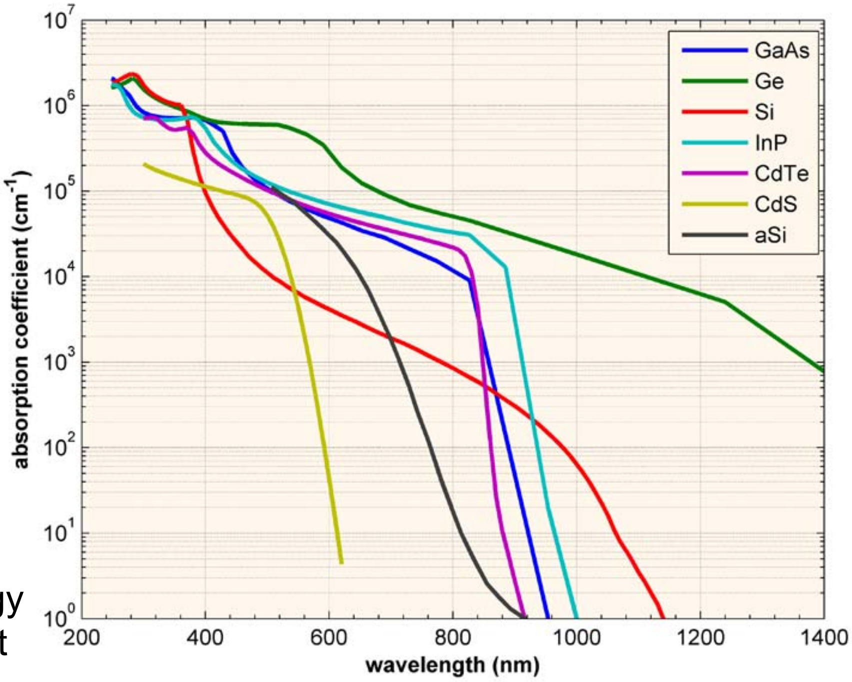
Absorption of Light

Absorption coefficient (α) determines how far into a material light of a particular wavelength can penetrate before it is absorbed.

For photons with energy close to E_g, α is quite low since only those e^- directly at band edge can interact with photon to cause absorption.

At higher energies, more e^- can interact with photon $\Rightarrow$ increased absorption

N.B. even high energy photons α is not constant and still $\propto \lambda$



Source: http://www.pveducation.org/pvcdrom/pn-junction/absorption-coefficient

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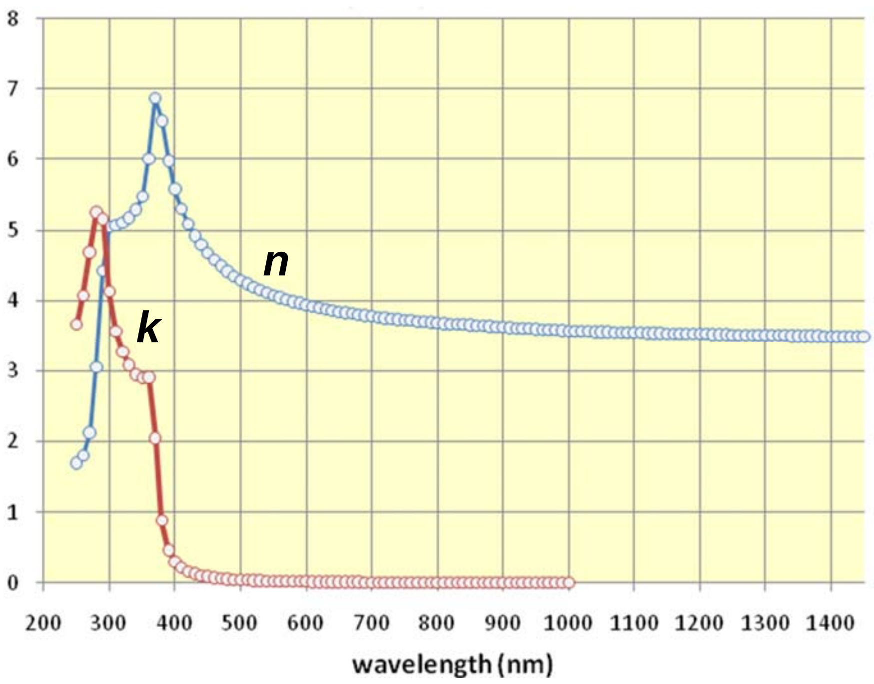
Absorption of Light

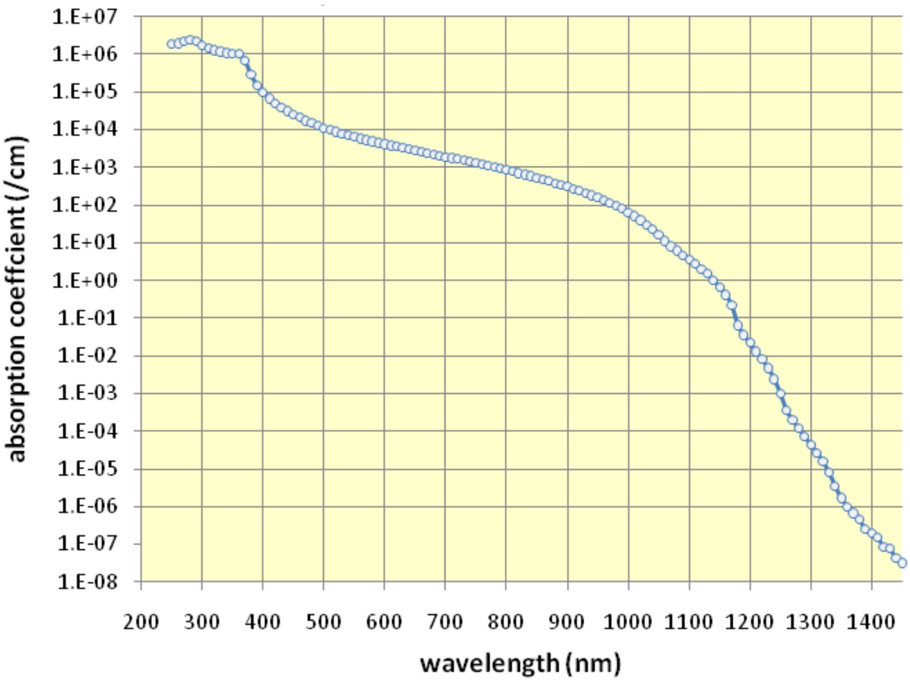
Refractive index (*n*) and extinction coefficient (*k*) of silicon



Source: http://www.pveducation.org/pvcdrom/materials/optical-properties-of-silicon

Absorption of Light

Revisiting the absorption coefficient plot….



Source: http://www.pveducation.org/pvcdrom/materials/optical-properties-of-silicon

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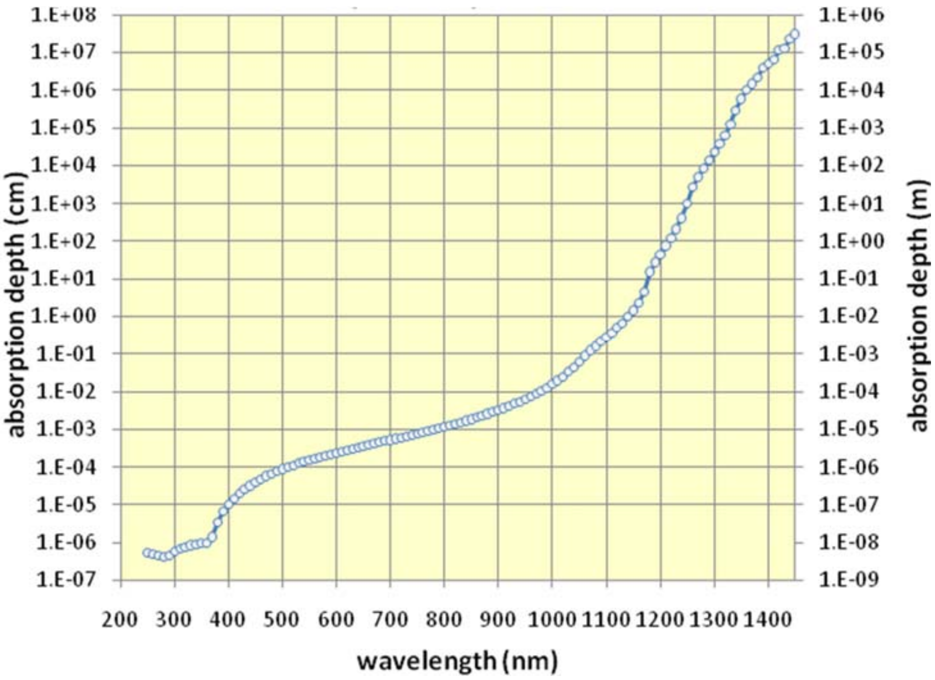
Absorption of Light

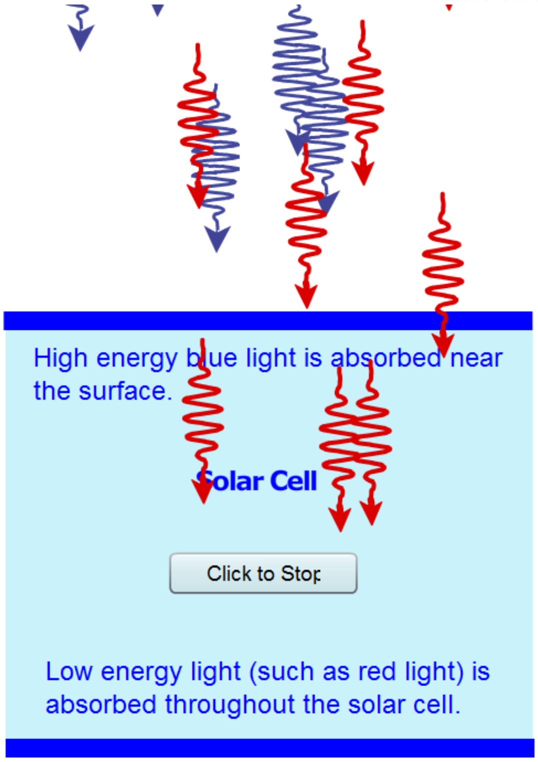
…. and we now look at absorption depth

Absorption depth of 1 μm ⇒ light intensity fallen to 36% (1/e) of its original value



Source: http://www.pveducation.org/pvcdrom/materials/optical-properties-of-silicon

Absorption of Light

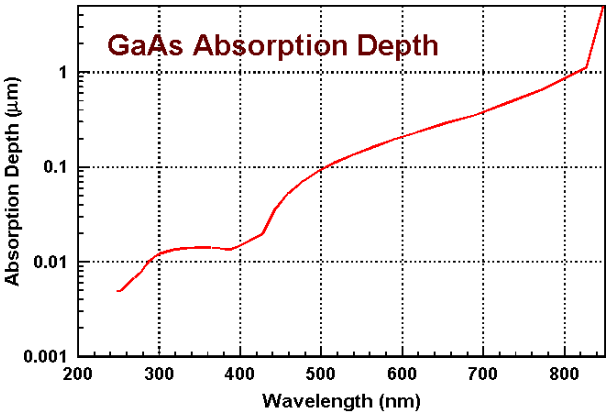

High energy blue light is absorbed near the surface.

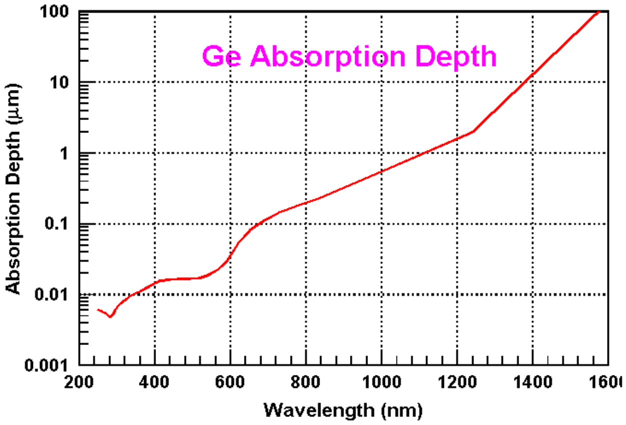
Low energy light (such as red light) is absorbed throughout the solar cell.

Source: *http://www.pveducation.org/pvcdrom/pn-junction/absorption-depth*

Absorption of Light

For two other common semiconductors:
gallium arsenide (GaAs) and germanium (Ge)





Source: *http://www.pveducation.org/pvcdrom/pn-junction/absorption-depth*

Absorption of Light

The generation rate = no. e^{-} generated at each point in the device due to the absorption of photons

Neglecting reflection, amount of light absorbed α and the thickness of the absorber. Intensity of light can be calculated according to:

$$I = I_0\, e^{-\alpha x}$$

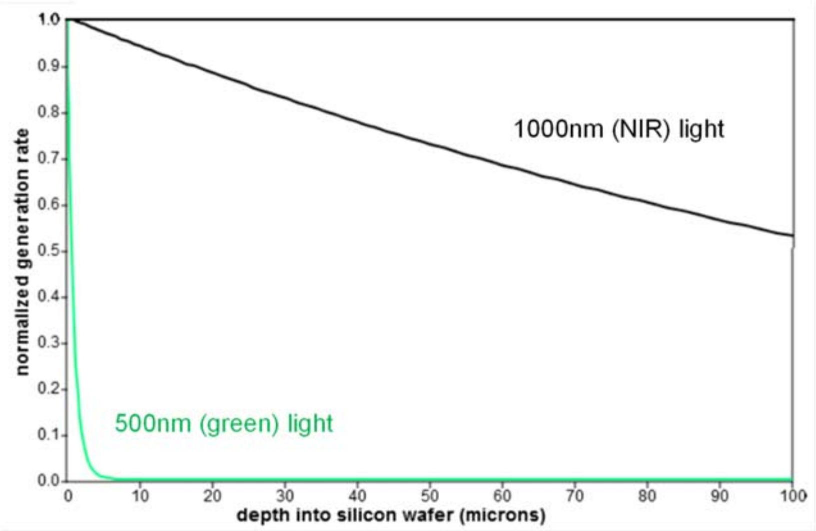
where:
α is absorption coefficient (cm^{-1});
x is the distance into the material; and
I_0 is the light intensity at the top surface.

Absorption of Light

Same equation can be used to calculate the number of e^{-}-h^{+} pairs being generated in a solar cell. Assuming that the loss in light intensity is due to the absorption of photons and the generation of an e^{-}-h^{+} pair, generation G is determined by finding the change in light intensity across this slice. Thus, differentiating gives the generation at any point in the device:

$$G = \alpha N_0 e^{-\alpha x}$$

where
N_0 = photon flux at surface



Source: Adapted from http://www.pveducation.org/pvcdrom/pn-junction/generation-rate

Recombination

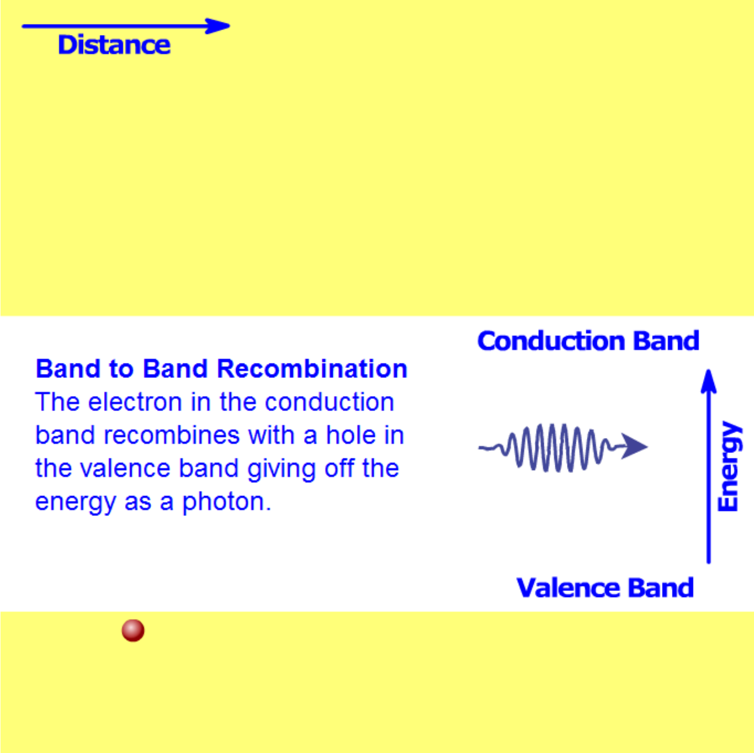
Any e^- in E_c is in meta-stable state and will eventually stabilize to a lower energy position in E_v

For this to happen, it must move into an empty valence band state. Thus, when e^- stabilizes back down into E_v it effectively removes a h^+ $\Rightarrow$ process called recombination.

There are three basic types of recombination in the bulk of a single-crystal semiconductor. These are:

- Radiative recombination
- Auger recombination
- Shockley-Read-Hall recombination

Recombination



Band to Band Recombination
The electron in the conduction band recombines with a hole in the valence band giving off the energy as a photon.

Source: *http://www.pveducation.org/pvcdrom/pn-junction/types-of-recombination*

Recombination

Radiative (Band-to-Band) Recombination dominates in direct bandgap semiconductors. The light produced from a LED is most obvious example of radiative recombination in a semiconductor device.

While some concentrator and space solar cells are made from direct bandgap materials (e.g. GaAs) and radiative recombination dominates. However, most terrestrial solar cells are made from Si, which is an indirect bandgap semiconductor and radiative recombination is extremely low

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Recombination

Recombination Through Defect Levels, also called Shockley-Read-Hall (SRH) recombination only occurs in material with defects.

SRH recombination is a two-step process.

i) e^- (or h^+) is trapped by an energy state in the forbidden region, introduced through defects in the crystal lattice. Defects can be either unintentionally introduced or deliberately added to material, e.g. doping

ii) if h^+ (or e^-) moves up to the same energy state before the e^- is thermally re-emitted into E_c, then it recombines

Rate at which a carrier moves into the energy level in the forbidden gap depends on the distance of the introduced energy level from either of the band edges. If an energy level is introduced close to either band edge, recombination is less likely as the e^- is likely to be re-emitted to E_c edge rather than recombine with a h^+ which moves into the same energy state from E_v. For this reason, energy levels near mid-gap are very effective for recombination.

Recombination

Auger Recombination involves three carriers. An e^- and h^+ recombine, but rather than emitting the energy as heat or as a photon, the energy is given to a third carrier, an e^- electron in E_c. This e^- then thermalizes back down to edge of E_c. edge.

Auger recombination is most important at high carrier concentrations caused by heavy doping or high level injection under concentrated sunlight. In Si solar cells, Auger recombination limits the lifetime and ultimate efficiency.

Recombination

If the no. of minority carriers is increased above the equilibrium value by some transient external excitation (e.g. sunlight), excess minority carriers will decay back to that equilibrium carrier concentration due via a process of recombination.

⇒ critical solar cell parameter is the "recombination rate“, which links to minority carrier lifetime and the minority carrier diffusion length

Recombination

Minority carrier lifetime, denoted by τ_n or τ_p, is average time which a carrier can spend in an excited state after e^-- h^+ generation before recombining

Often just called "lifetime" but has nothing to do with material stability

The low level injected material (where the number of minority carriers is less than the doping) the lifetime is related to the recombination rate by:

$$\tau = \frac{\Delta n}{R}$$

where Δn is the excess minority carriers concentration and R is the recombination rate

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Recombination

And

$$\frac{1}{\tau_{bulk}} = \frac{1}{\tau_{band}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}}$$

And the Auger lifetime is a function of the carrier concentration, given by:

$$\tau_{Auger} = \frac{1}{C{N_A}^2}$$

where the auger coefficient, C, for Si is typically 1.66×10^{-30}cm^6/s

Recombination

Second parameter related to recombination rate, is "minority carrier diffusion length" = average distance a carrier can move from point of generation until it recombines

In Si, τ can be $\geq$ 1 ms. $\Rightarrow$ for single crystal silicon solar cell, the diffusion length is typically 100 – 300 µm (gives indication of material quality).

The diffusion length *L* is related to τ by the diffusivity according to:

$$L = \sqrt{D\tau}$$

where *L* is the diffusion length in meters and *D* is the diffusivity in m²/s

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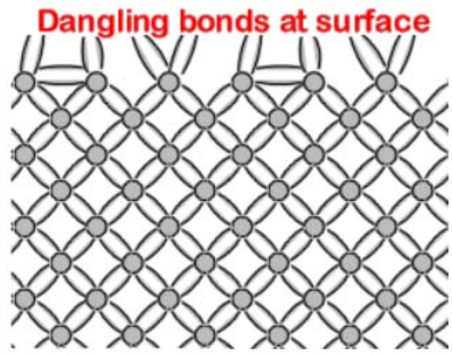
Recombination

Surface recombination is high as large amounts of defects exist where the crystal lattice is disrupted. Understanding the impacts and the ways to limit surface recombination leads to better and more robust solar cell designs.

The high recombination rate in the vicinity of a surface depletes this region of minority carriers. A localized region of low carrier concentration causes carriers to flow into this region from the surrounding, higher concentration regions. Therefore, the surface recombination rate is limited by the rate at which minority carriers move towards the surface. A parameter called the "surface recombination velocity“ (units of cm/s) is used to specify the recombination at a surface. In a surface with infinitely fast recombination, the movement of carriers towards this surface is limited by the maximum velocity they can attain, and for most semiconductors is on the order of 1 x 10^7 cm/sec



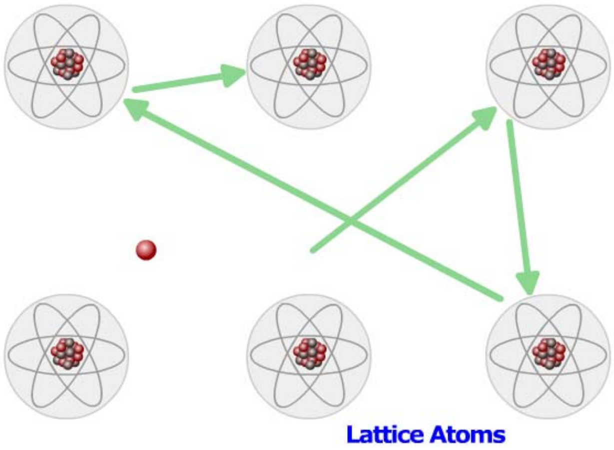
Source: *http://www.pveducation.org/pvcdrom/pn-junction/surface-recombination*

Movement of Carriers in Semicond.

e^- in E_c *and* h^+ in E_v are "free" carriers – can move throughout the semiconductor lattice

Simple but adequate description of carrier movement views each carrier as moving in a random direction at a certain velocity.

Carrier moves in random direction for a distance called scattering length before colliding with a lattice atom. After collision, carrier then moves away in a different random direction.



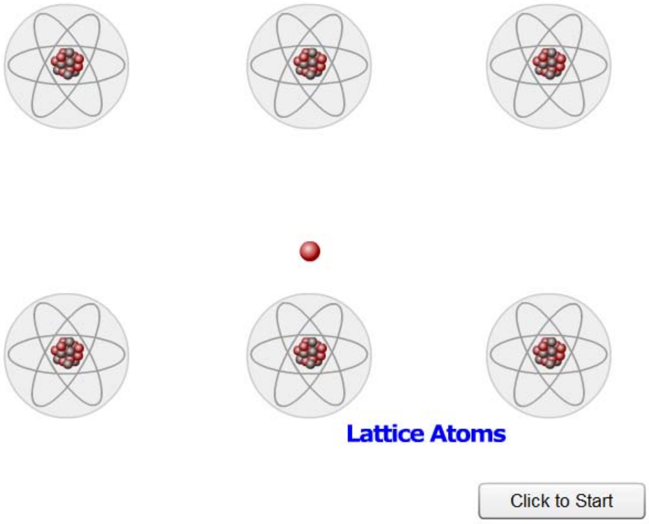
Source: *http://www.pveducation.org/pvcdrom/pn-junction/movement-of-carriers-in-semiconductors*

Movement of Carriers in Semicond.

e^- in E_c and h^+ in E_v are "free" carriers – move through Si crystal.

Carrier moves in random direction for a distance called scattering length before colliding with a lattice atom. After collision, carrier then moves away in a different random direction.

The velocity of the carriers is determined by the temperature of the lattice



Source: *http://www.pveducation.org/pvcdrom/pn-junction/movement-of-carriers-in-semiconductors*

Movement of Carriers in Semicond.

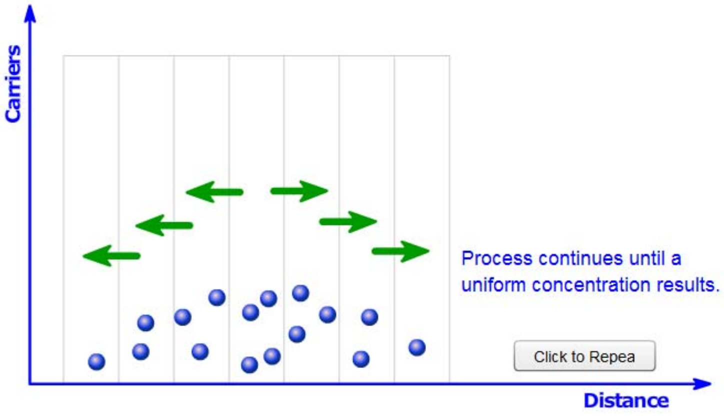
Although carriers in a semiconductor are in constant random motion, there is **<u>no net motion of carriers</u>** – unless there is a concentration gradient or an electric field

Source: *http://www.pveducation.org/pvcdrom/pn-junction/movement-of-carriers-in-semiconductors*

Movement of Carriers in Semicond.

Diffusion - random motion of carriers can lead to a net movement of carriers if one particular region has a higher concentration than another (i.e. concentration gradient) $\Rightarrow$ net movement of carriers from areas of high concentration to low.

Rate of diffusion depends on velocity at which carriers move and on the distance between scattering events – termed diffusivity and measured in cm^2s^{-1}



Process continues until a uniform concentration results.

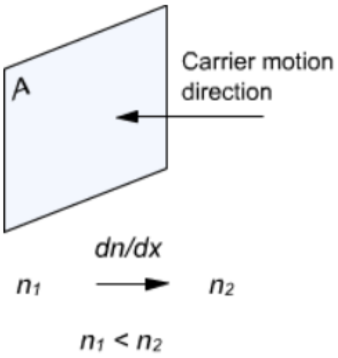
Source: *http://www.pveducation.org/pvcdrom/pn-junction/diffusion*

Movement of Carriers in Semicond.

Flux of diffusing particles is $\propto$ to concentration gradient

For ELECTRONS:

$$\boldsymbol{\Phi_n(x) = -D_n \frac{dn(x)}{dx}}$$



For HOLES:

$$\boldsymbol{\Phi_p(x) = -D_p \frac{dp(x)}{dx}}$$

where Φ_n is the electron flux, D_n is the electron diffusion coefficient (units cm^2/s), and n_1 and n_2 are the electron concentrations. Minus sign arises from the fact that the vector of the concentration gradient is directed toward the increase of the concentration (particles diffuse from n_1 to n_2)

Movement of Carriers in Semicond.

Diffusion current density = carrier flux density × carrier charge
(denoted by q)

$$J_{n\_diff} = qD_n \frac{dn}{dx} \qquad J_{p\_diff} = -qD_p \frac{dp}{dx}$$

where the elementary charge, $q = 1.602 \times 10^{-19}$ coulombs

Diffusion and drift (next slide) properties are fundamentally related via the Einstein relations:

$$D_n = \frac{kT}{q}\mu_n \quad \text{and} \quad D_p = \frac{kT}{q}\mu_p$$

where μ_n and μ_p are carrier mobilities for electrons and holes, respectively (units: cm^{2}V^{-1}s^{-1})

Movement of Carriers in Semicond.

Earlier, we noted that in the absence of an electric field, carriers move a certain distance at a constant velocity in a random direction.

Now, with an electric field superimposed on this random direction, carriers move in a net direction. There is an acceleration in direction of the electric field if the carrier is h^+ , or opposite to the electric field if the carrier is e^-

Net carrier movement in the presence of an electric field is characterized by mobility (varies between different semiconductor materials)

Transport due to the movement of carriers due to the presence of an electric field is called "drift transport“, e.g. same type of transport that also occurs in metals

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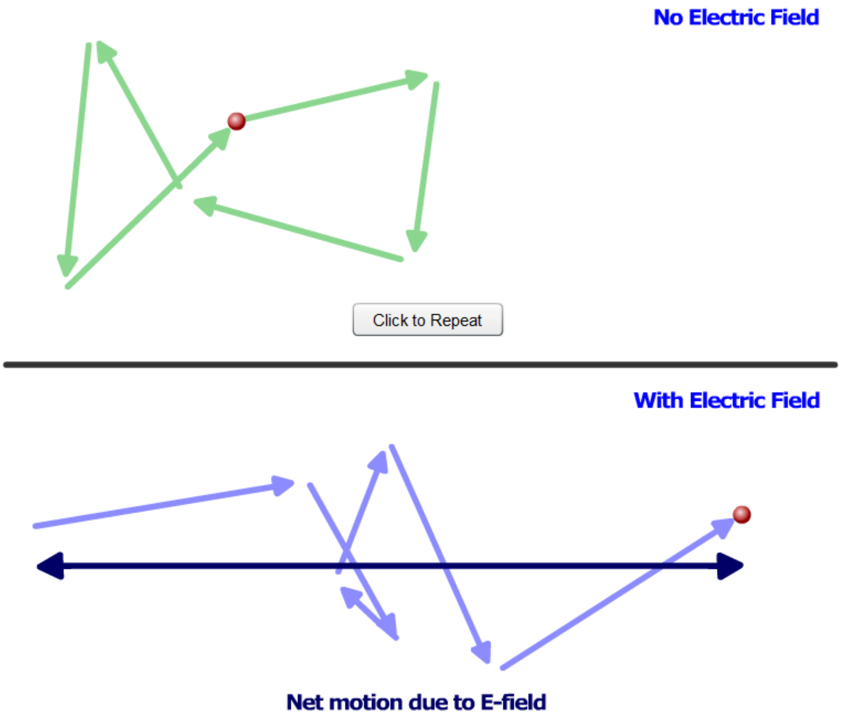
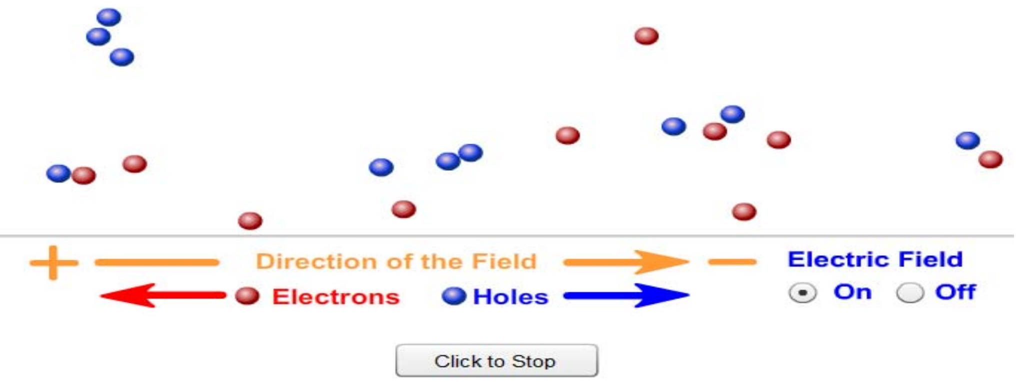
Movement of Carriers in Semicond.



Source: http://www.pveducation.org/pvcdrom/pn-junction/drift

Movement of Carriers in Semicond.



Source: <u>*http://www.pveducation.org/pvcdrom/pn-junction/drift*</u>

Movement of Carriers in Semicond.

One-dimensional current density flow due to drift is given by:

$$J_{n\_drift} = q\, n\, \mu_n\, E_x \qquad\qquad J_{p\_drift} = q\, p\, \mu_p\, E_x$$

where:

J_x is the current density in the *x*-direction,
E_x (or ξ) - electric field applied in the x-direction,
q - electron charge,
n and *p* - electron and hole concentrations,
μ_n and μ_p - electron and hole mobilities

Total current flow is the sum, hence conductivity σ can be defined as:

$$\sigma = \frac{1}{\rho} = \frac{J}{\xi_n} = q\, n\, \mu_n + \; q\, p\, \mu_p$$

where ρ is the resistivity (typical unit: Ω.cm)

Movement of Carriers in Semicond.

Poisson's equation relates the divergence of electric field to the space charge density, ρ :

$$\frac{d\xi}{dx} = \frac{\rho}{\epsilon} \qquad \text{where } \epsilon = \text{permittivity}$$

Contributions to charge density in semiconductor:

- e^- in E_c contribute negative charge, whereas h^+ give positive charge
- donor impurity that is ionised, i.e. had extra electron removed, has a net positive charge due to unneutralised positive charge at nucleus ($N_D{}^+$) and vice versa for an ionised acceptor ($N_A{}^-$)

Hence

$$\rho = q\left(p - n + N_D{}^+ - N_A{}^-\right)$$

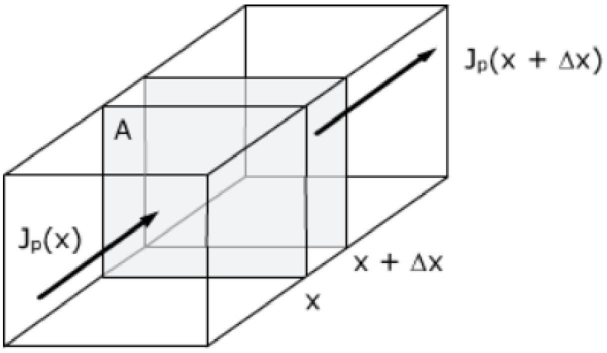
N.B. most donors and acceptors are ionised under normal conditions so that $N_D{}^+ \approx N_D \quad and\ N_A{}^- \approx N_A$

Movement of Carriers in Semicond.

Overall total current densities for e^- and h^+ are the sum of the drift and diffusion processes:

$$J_n = q\,n\,\mu_n\,E_x + qD_n\frac{dn}{dx} \qquad\qquad J_p = q\,p\,\mu_p\,E_x - qD_p\frac{dp}{dx}$$

Final "book-keeping" equations to keep track of no. of e^- and h^+ in system, e.g. consider a volume of cross-sectional area *A* and of length Δx



Movement of Carriers in Semicond.

Net rate of increase of e^- = rate at which e^- enter – rate at which e^- exit + rate at which they are generated – rate at which they recombine

Rates of entering and exiting $\propto$ current densities, hence:

$$\text{Rate of entering – rate exiting} = \frac{A}{q}\{-J_n(x) - [-J_n(x+\Delta x)]\}$$

$$= \frac{A}{q}\,\frac{dJ_n}{dx}\Delta x$$

$$\text{Rate of generation – rate of recombination} = \frac{A}{q}\,\Delta x\,(G-U)$$

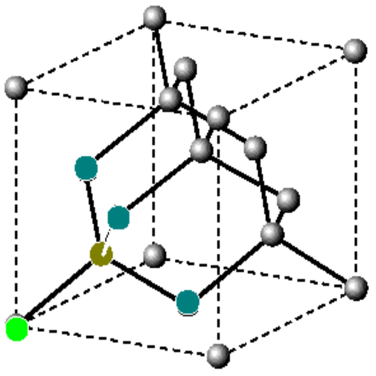
where *G* is net generation rate by external processes (e.g. light) and *U* is the recombination rate. Under steady-state conditions the net rate of increase must be zero such that:

$$\frac{1}{q}\,\frac{dJ_n}{dx}\Delta x = U - G \qquad \text{and} \qquad \frac{1}{q}\,\frac{dJ_p}{dx}\Delta x = -(U-G)$$

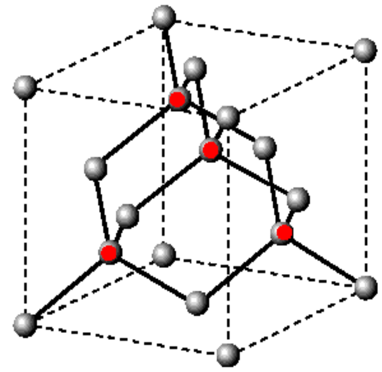
Choice of Semiconductor

- Maximise absorption of sunlight – ideal solar cell is black!
- Efficiency of converting absorbed energy into electrical energy
- Avoid to many energy conversion processes (e.g. thermal losses)
- Cost
- Environmentally-friendly?
- Stability (under UV, water vapour, etc)

Choice of Semiconductor



Diamantstruktur



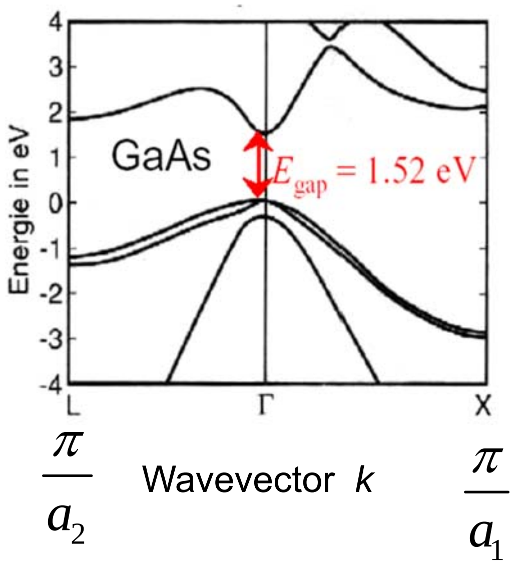
Zinkblendestruktur (ZnS)

e.g. Si

e.g. GaAs

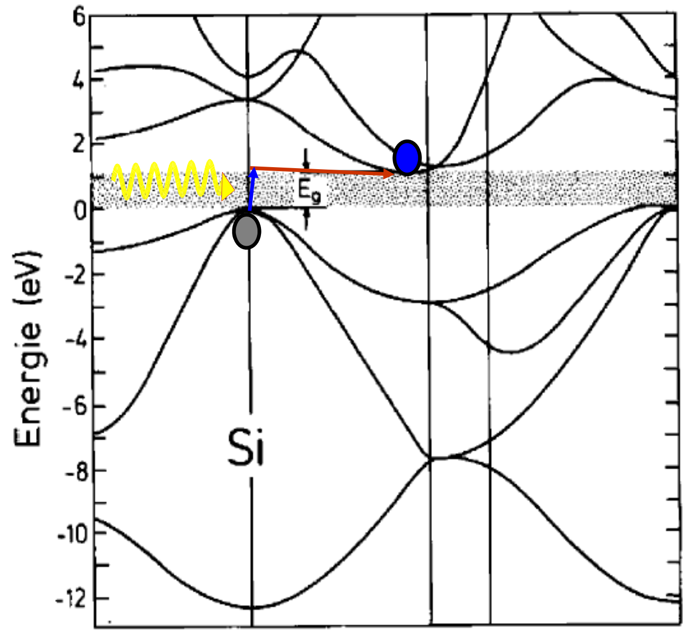
Choice of Semiconductor

- GaAs is a direct bandgap semiconductor



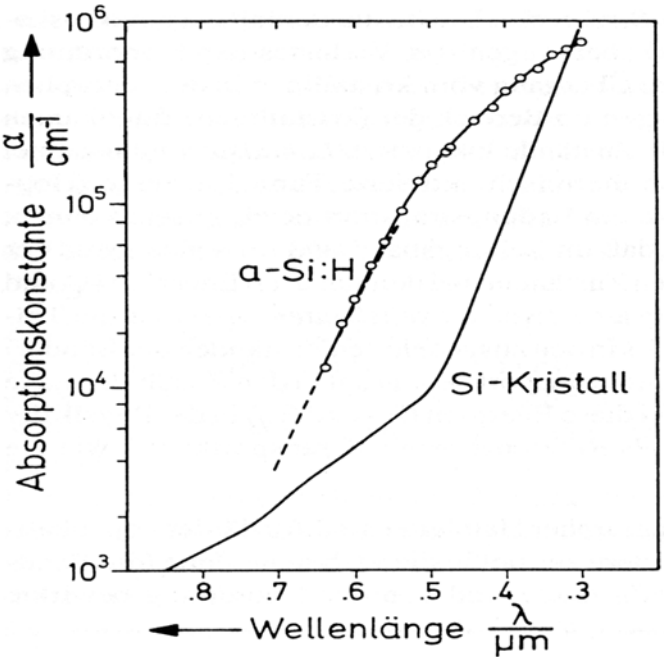
Choice of Semiconductor

- Whereas c-Si is an indirect semiconductor
- Optical absorption is a 2-step process with greatly reduced probability



Choice of Semiconductor

- But a-Si is direct!
- Optical absorption greatly enhanced



Choice of Semiconductor

Overall, there is a compromise between:

- Absorption of widest possible spectral range (narrow bandgap)
- And the losses due to relaxation at the band edges (wide bandgap)

⇒ trade-off!