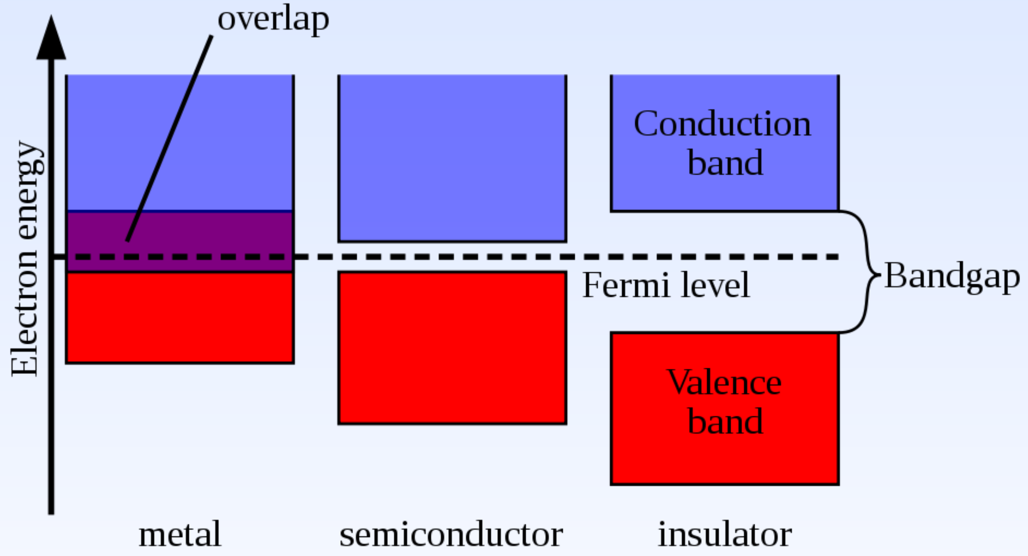
Semiconductor Physics for Photovoltaics



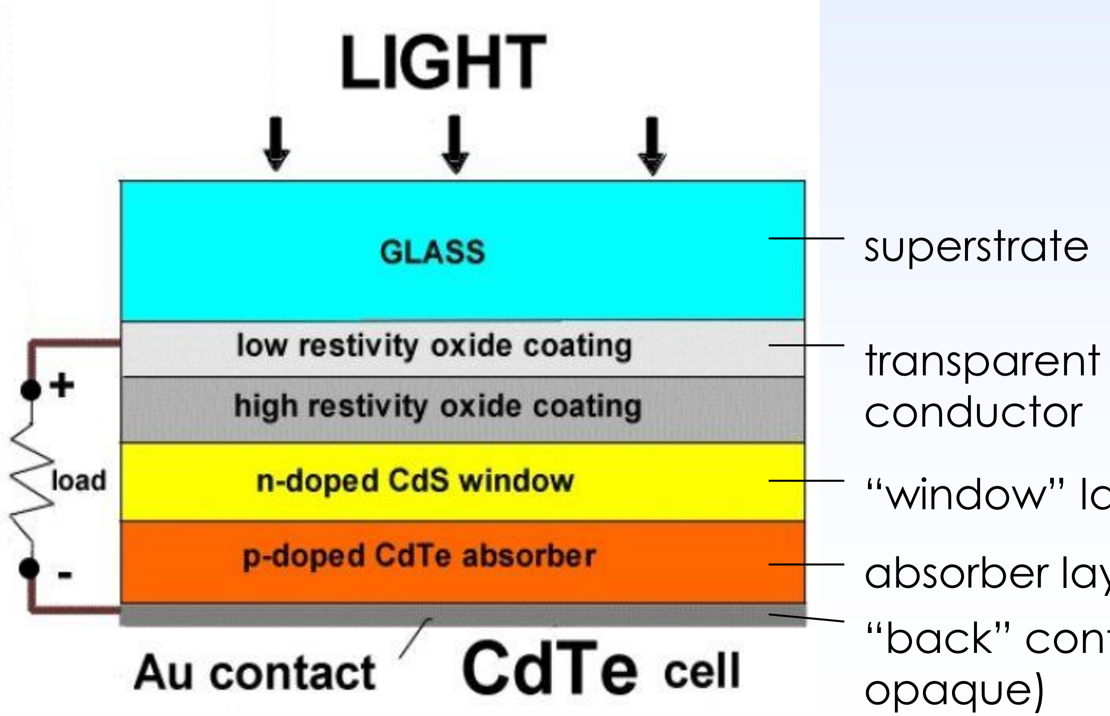
PHYS 4400, Principles and Varieties of Solar Energy

Instructor: Randy J. Ellingson
The University of Toledo

March 3, 2015

Anatomy of a Photovoltaic Device

Construction of a PV cell: components/features include substrate (or superstrate), transparent conducting layer, light-absorbing layer, charge-separating interface, back electrical contact.



External and internal quantum efficiency

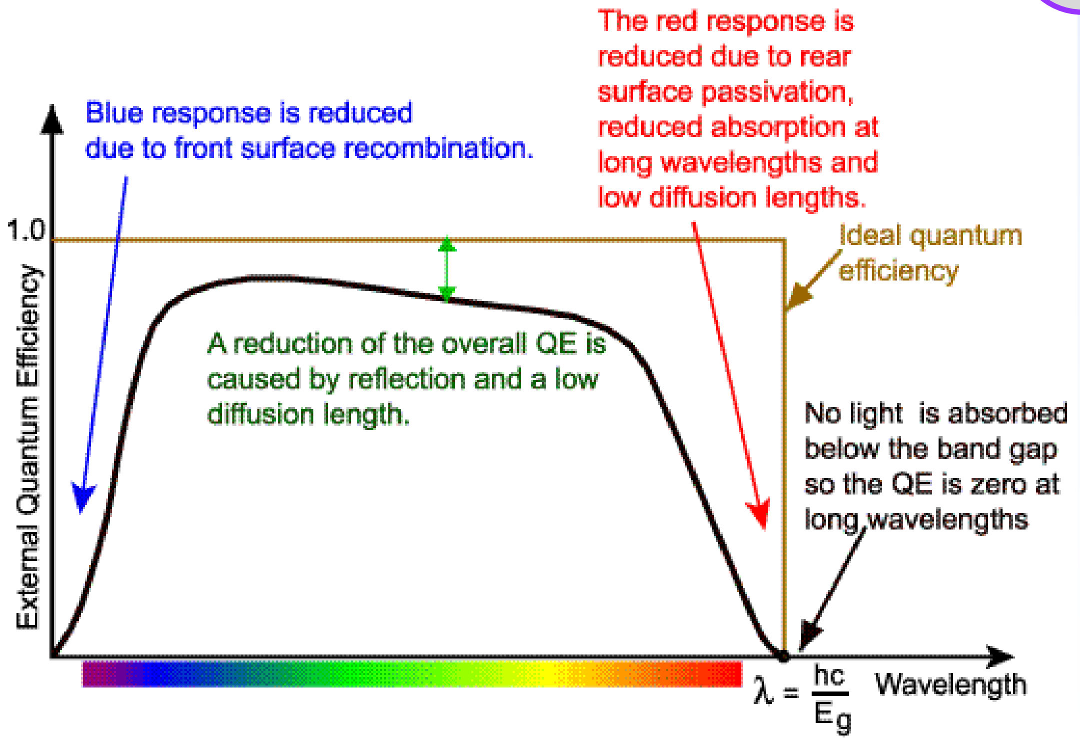
Internal and external quantum efficiency are functions of wavelength, i.e., EQE(λ) and IQE(λ):

External quantum efficiency (EQE):

$$EQE(\lambda) = \frac{\text{Electrons collected as photocurrent, per second}}{\text{Photons } \textit{incident} \text{, per second}}$$

Internal quantum efficiency (IQE):

$$IQE(\lambda) = \frac{\text{Electrons collected as photocurrent, per second}}{\text{Photons } \textit{absorbed} \text{, per second}}$$



Introduction to semiconductor physics concepts

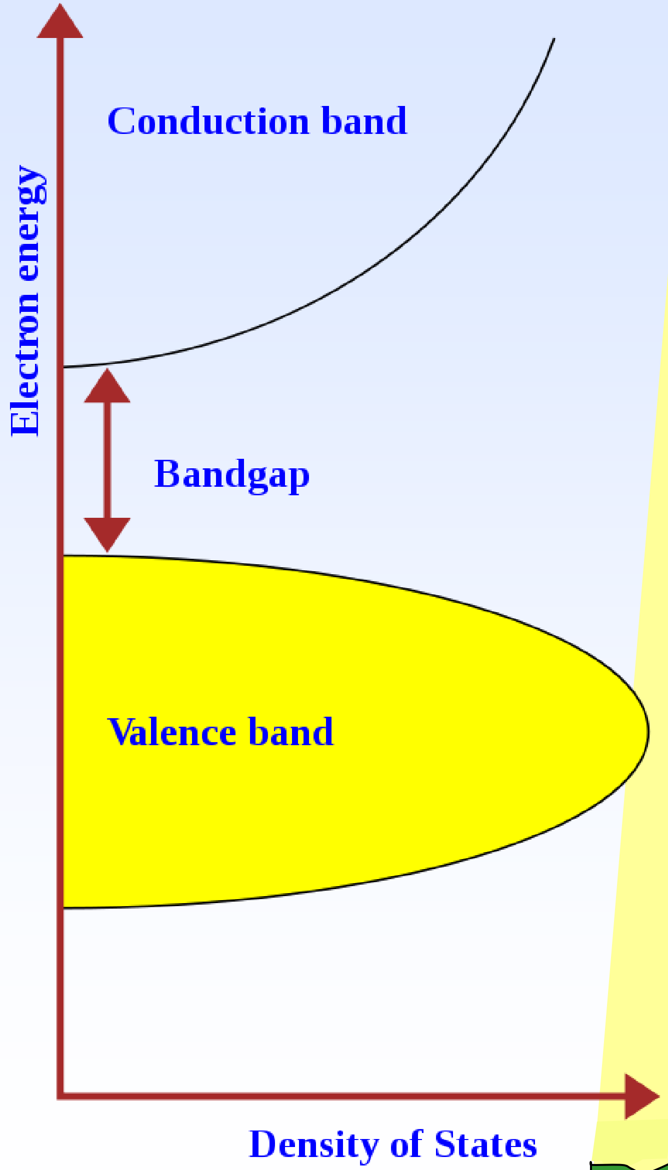
- semiconductors
- band structure
- valence and conduction bands (HOMO-LUMO levels)
- bandgap energy
- direct vs. indirect gap
- electrons and holes ("charge carriers")
- light absorption
- n-type and p-type doping
- p-n junction
- charge carrier transport: drift and diffusion
- charge carrier processes: carrier cooling, charge separation, recombination mechanisms (radiative and non-radiative)

Semiconductors - overview

Electrical conductivity due to electron flow (as opposed to ionic conductivity) – conductivity between that of a conductor and an insulator.

Foundation of modern electronics: transistors, solar cells, light-emitting diode (LED), and digital and analog integrated circuits.

Note: In metals, current is carried by the flow of electrons. In semiconductors, current is often schematized as being carried either by the flow of electrons or by the flow of positively charged "holes" in the electron structure of the material (in both cases only electron movements are actually involved).



http://en.wikipedia.org/wiki/Semiconductor

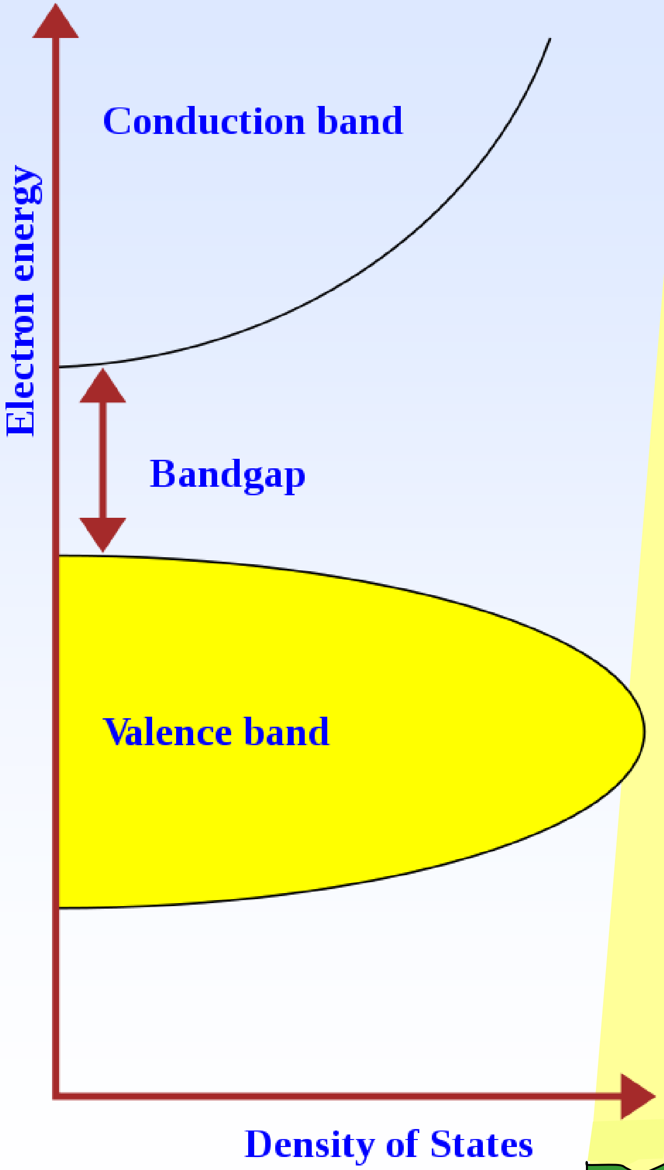
Semiconductor band structure

The **valence band** for solid is the highest-energy region of the electronic structure (see diagram) where electrons are found at a temperature of absolute zero (and, by definition, in the dark).

In a semiconductor, each *valence electron* is <u>bound</u> to an atom. I contrast, so-called conduction electrons reside in the **conduction band**, and contribute to the electrical (and thermal) conduction of the material.

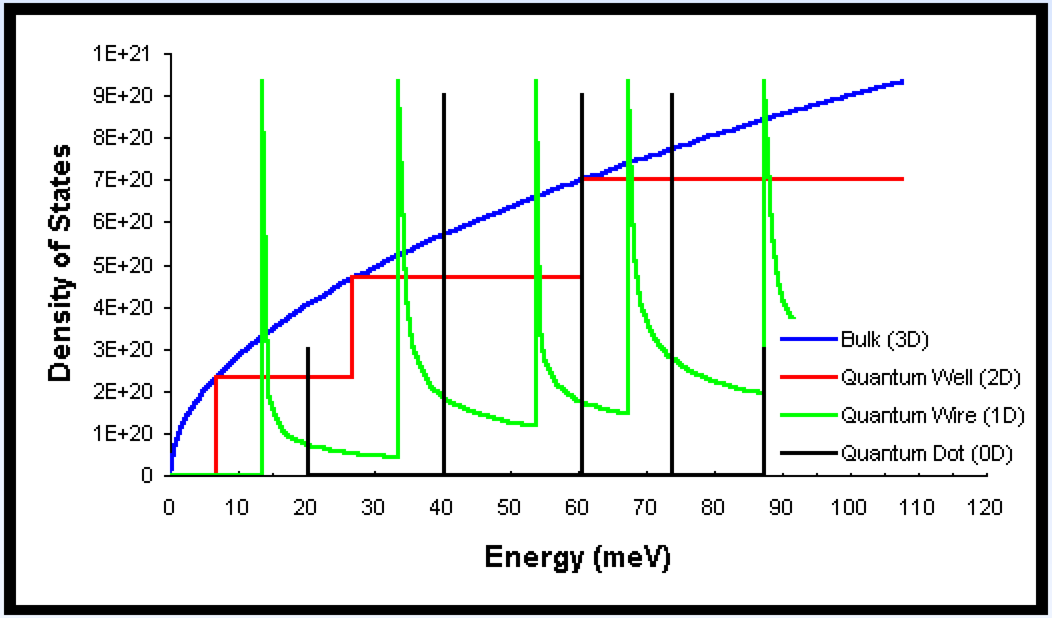
Conduction electrons are <u>mobile</u>.

Note that there are no state available within the band gap.



http://en.wikipedia.org/wiki/Semiconductor

Semiconductor density of states



From quantum mechanics, the density of states (or the number of electron states per unit energy and per unit volume of material) in a 3D material is given as:

$$g_C(E) = \frac{m_e^* \sqrt{2m_e^*(E - E_C)}}{\pi^2 \hbar^3} \qquad \text{for } E \geq E_C$$

$$g_V(E) = \frac{m_h^* \sqrt{2m_h^*(E_V - E)}}{\pi^2 \hbar^3} \qquad \text{for } E \leq E_V$$

http://britneyspears.ac/physics/dos/dos.htm

Transition probability and Fermi's Golden Rule

From hyperphysics.phy-astr.gsu.edu : "In general conceptual terms, a transition rate depends upon the strength of the coupling between the initial and final state of a system and upon the number of ways the transition can happen (i.e., the density of the final states). In many physical situations the transition probability is of the form:"

$$\lambda_{if} = \frac{2\pi}{\hbar} \left| M_{if} \right| \rho_{if}$$

In this formulation of **Fermi's Golden Rule**, *I* and *f* represent the *initial* and *final* states, and M_{if} is the matrix element for the interaction. ρ_{if} is the density of final states available to the transition.

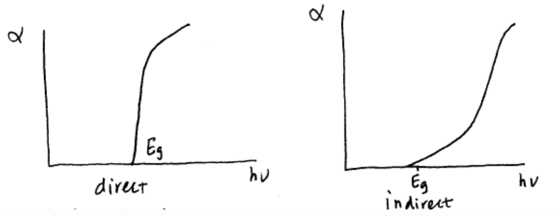
So the density of available states plays a key role in the probability (λ_{if}) that a photon will be absorbed and promote and electron from an initial state (e.g., in the valence band) to a final state (in the conduction band).

http://hyperphysics.phy-astr.gsu.edu/%E2%80%8Chbase/quantum/fermi.html

Absorption and recombination

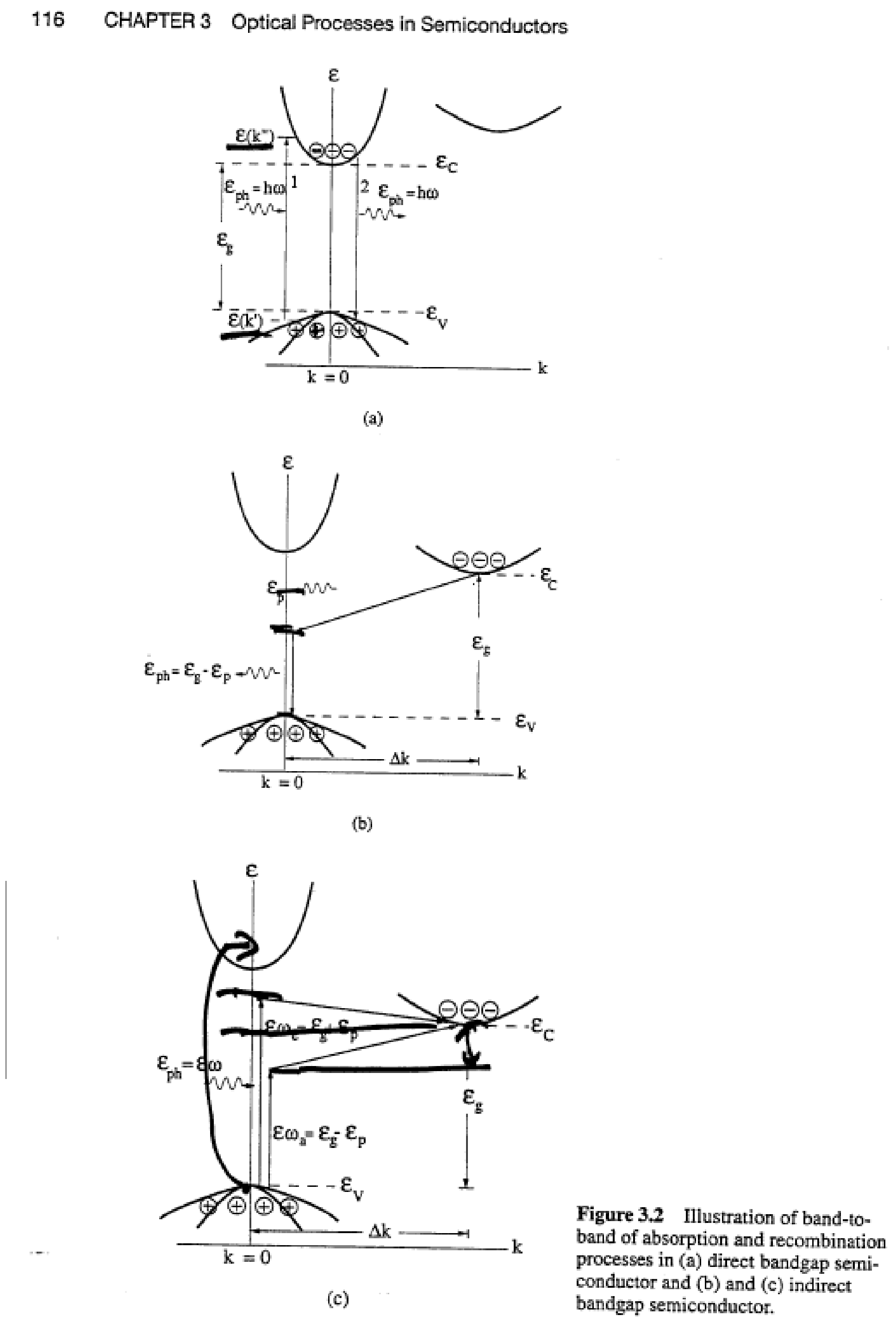
Schematic diagrams of light absorption showing changes in electron energy and momentum for direct and indirect transitions. Note that for direct gap semiconductors, the absorption coefficient α increases more rapidly with energy above the band gap.

- Absorption edge:



e- +hv → direct transition
e- +hv +phonon – indirect gap transition

http://www-ee.uta.edu/Online/Tao/Lect7.PDF



116 CHAPTER 3 Optical Processes in Semiconductors

Figure 3.2 Illustration of band-to-band of absorption and recombination processes in (a) direct bandgap semiconductor and (b) and (c) indirect bandgap semiconductor.

What about “thermal” populations?

The distribution of electrons (in terms of their energy) in a solid depends on the temperature.

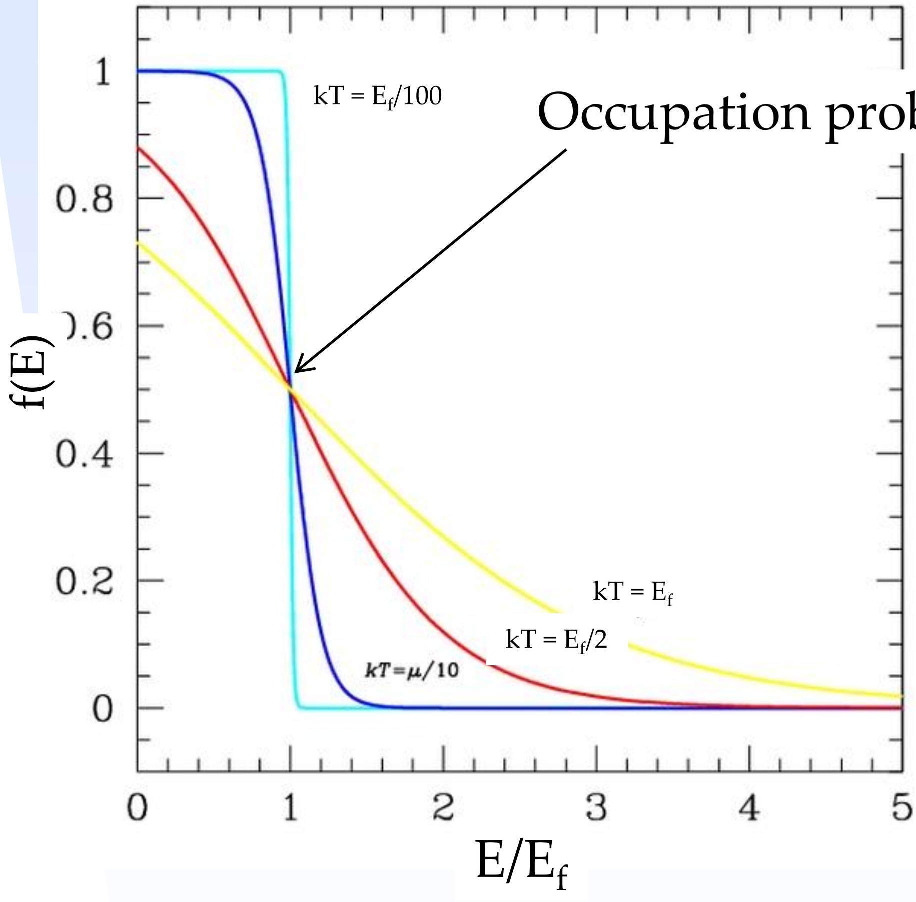
Electrons and holes in a semiconductor behave as **fermions**.

Fermions are particles having spin quantized in half-integers, and follow the Pauli exclusion principle (no two electrons can have the same set of quantum numbers).

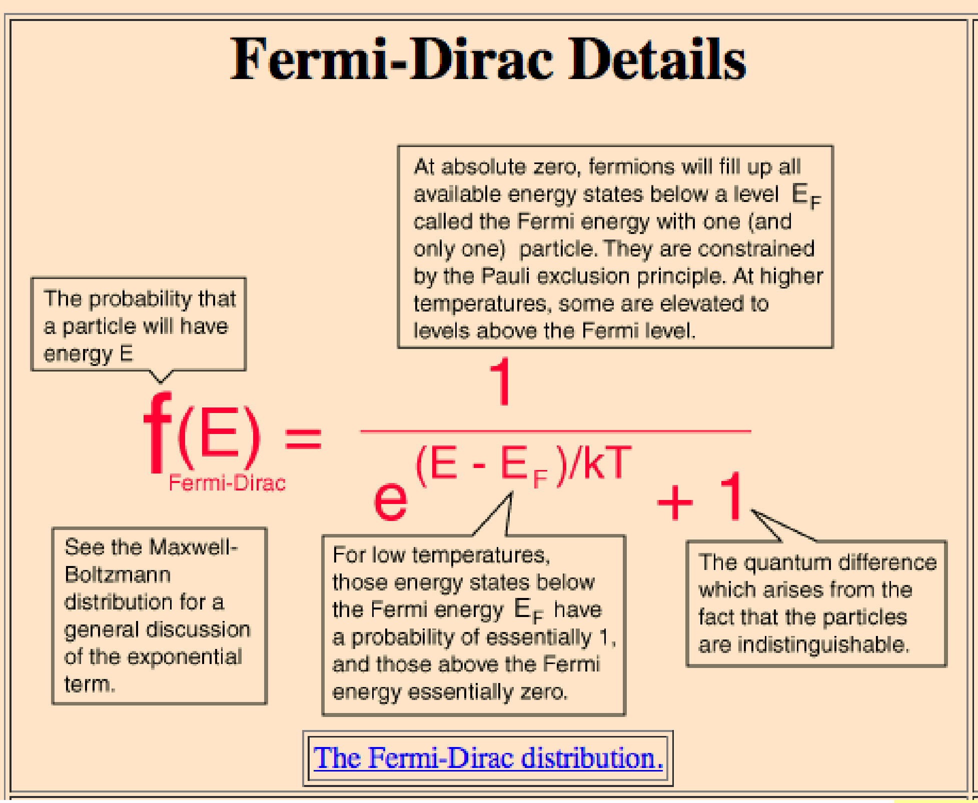
The fermion nature of electrons determines the behavior of electrons in a metal or semiconductor: at T = 0, the electron states are filled up until the Fermi energy, and the distribution of electrons at a temperature T is determined by Fermi-Dirac statistics (next slide).

http://www-ee.uta.edu/Online/Tao/Lect7.PDF

Fermi-Dirac statistics



Occupation probability at E_F is 1/2



Fermi-Dirac Details

The probability that a particle will have energy E

At absolute zero, fermions will fill up all available energy states below a level E_F called the Fermi energy with one (and only one) particle. They are constrained by the Pauli exclusion principle. At higher temperatures, some are elevated to levels above the Fermi level.

$$f(E)_{\text{Fermi-Dirac}} = \frac{1}{e^{(E-E_F)/kT} + 1}$$

See the Maxwell-Boltzmann distribution for a general discussion of the exponential term.

For low temperatures, those energy states below the Fermi energy E_F have a probability of essentially 1, and those above the Fermi energy essentially zero.

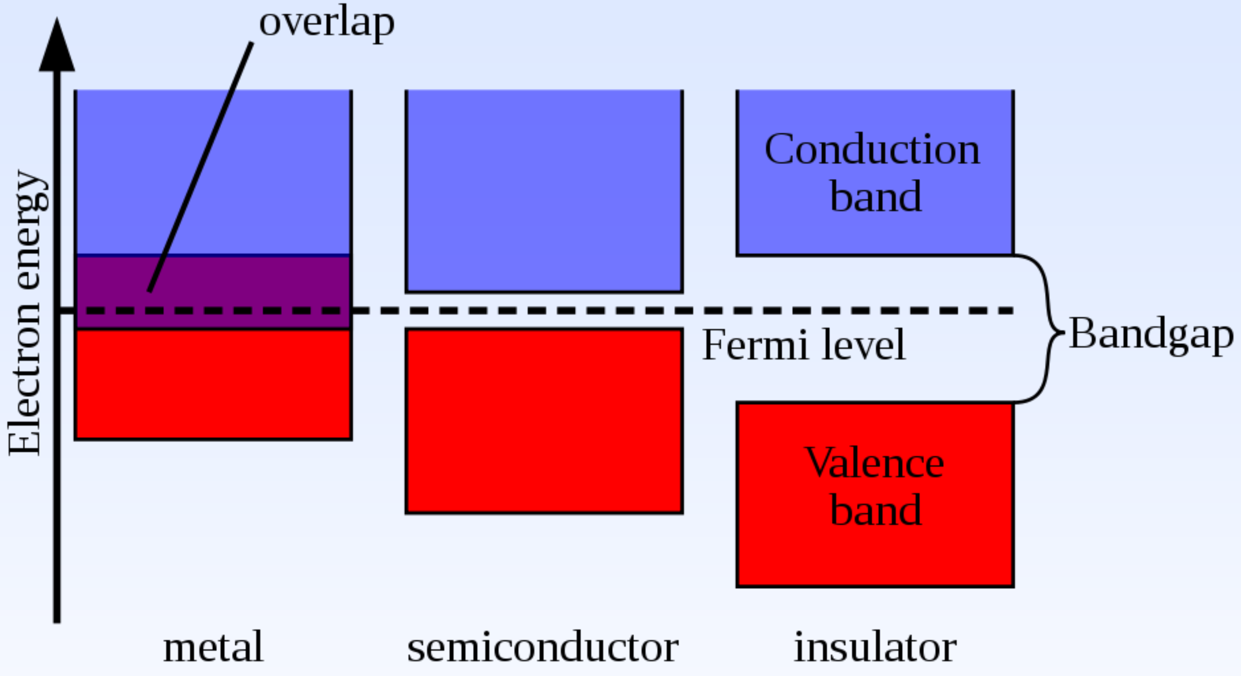
The quantum difference which arises from the fact that the particles are indistinguishable.

The Fermi-Dirac distribution.

kT ~ 26 meV at 300 K

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/disfd.html

Insulators, semiconductors, and conductors

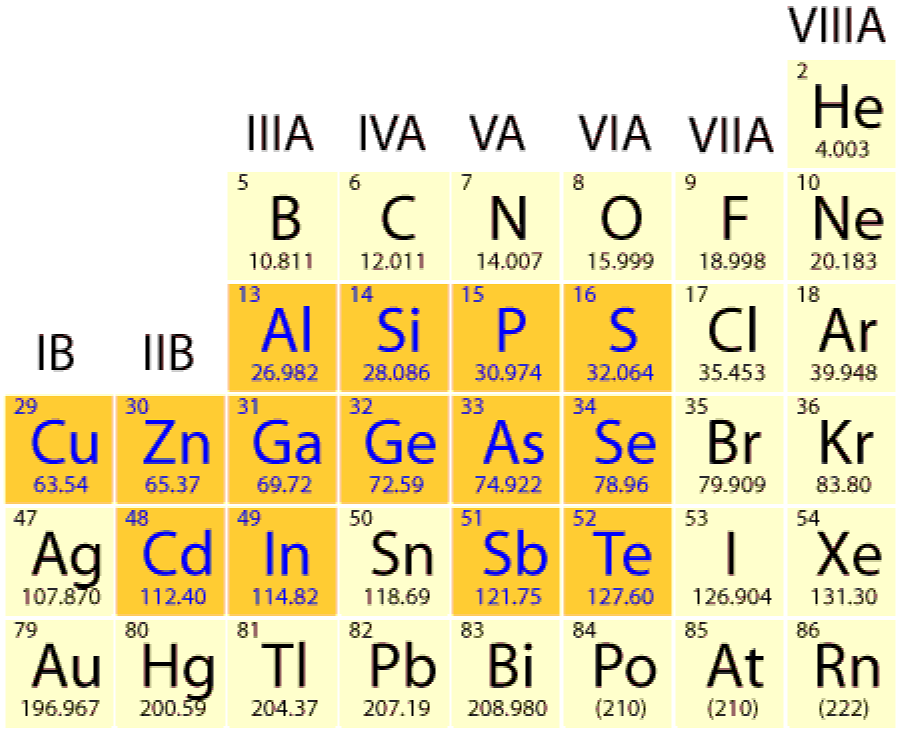


The **Fermi level** is the energy, also called the chemical potential (μ) that appears in the electrons' Fermi-Dirac distribution function. A state at the Fermi level has a 50% chance of being occupied by an electron.

$$\overline{n}_i = \frac{1}{e^{(\varepsilon_i - \mu)/kT} + 1}$$

http://en.wikipedia.org/wiki/Fermi_level

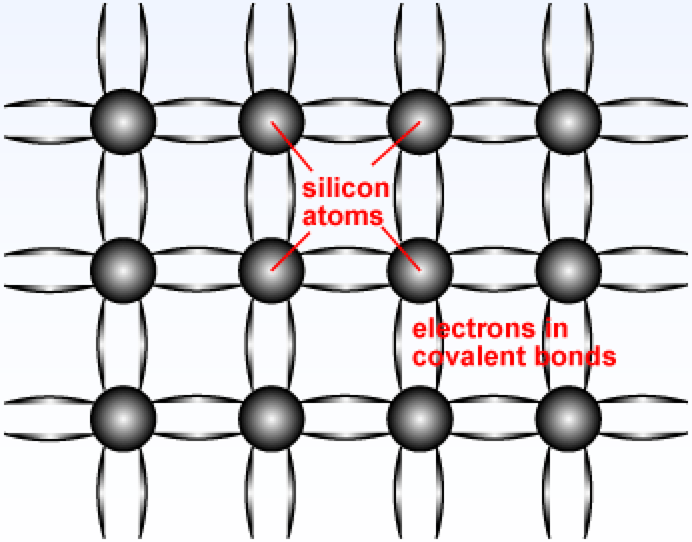
Common elemental components of semiconductors



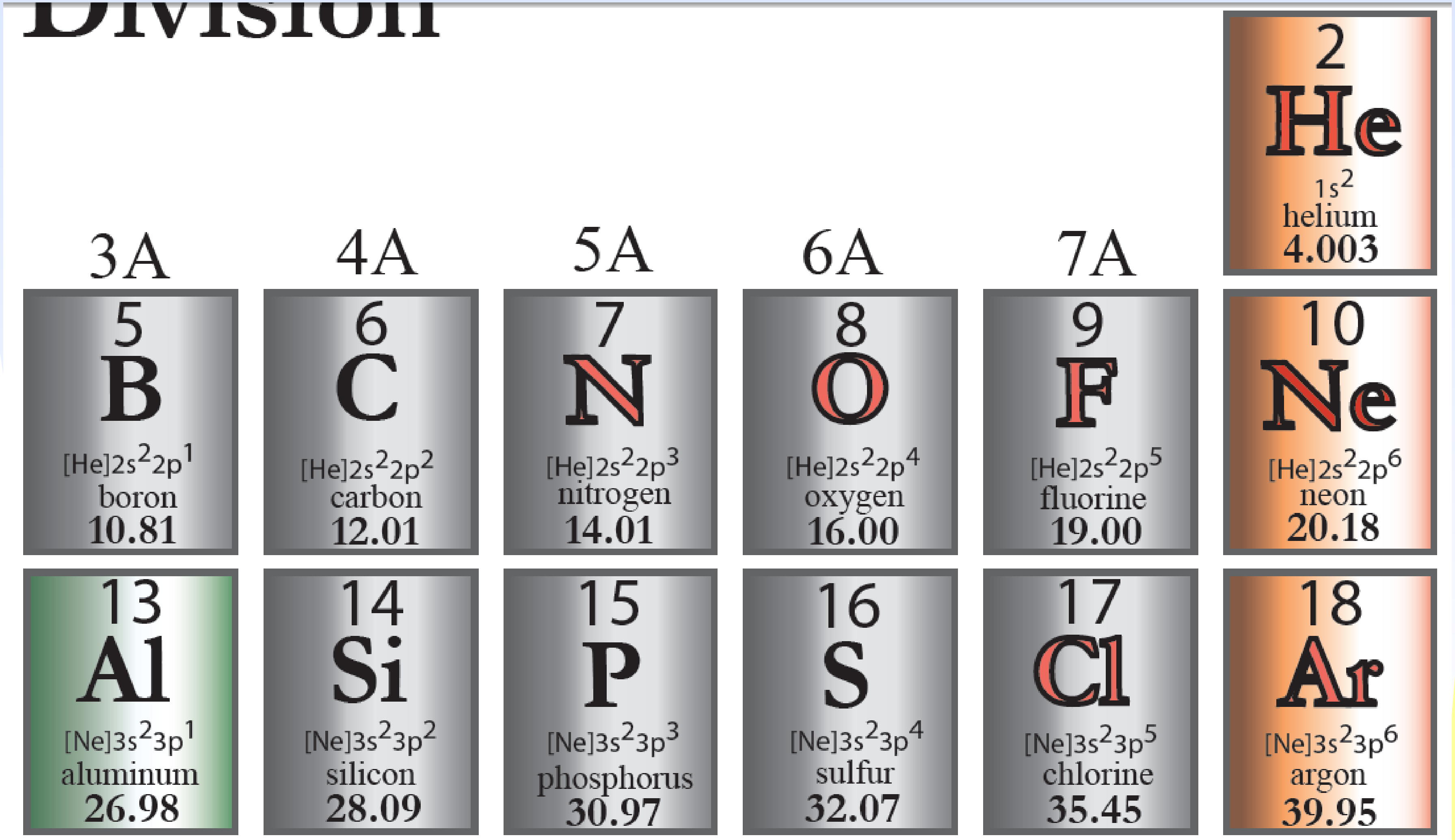
IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
							2 He 4.003
		5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.183
		13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.909	36 Kr 83.80
47 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)

Silicon (a semiconductor)

Silicon is a semiconductor with individual atoms bonded together in a regular, periodic structure to form an arrangement whereby each atom is surrounded by 8 electrons. Each atom consists of a nucleus made up of a core of protons (positively charged particles) and neutrons (particles having no charge) surrounded by electrons. The number of electrons and protons is equal, such that the atom is overall electrically neutral. The electrons occupy certain energy levels, based on the number of electrons in the atom, which is different for each element in the periodic table. The structure of a semiconductor is shown in the figure below.



Electron configuration of the elements



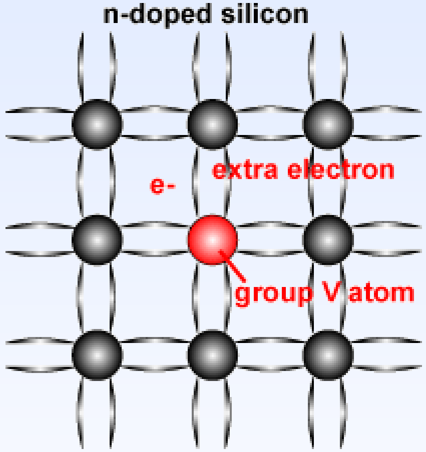
Division

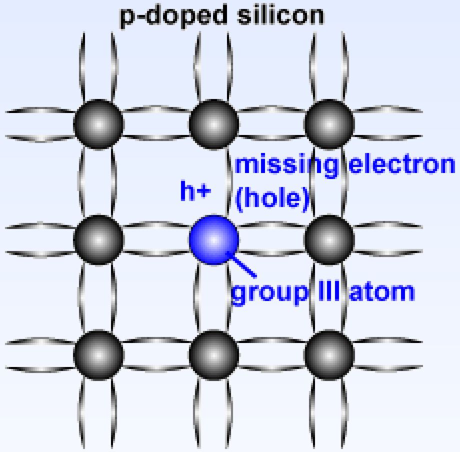
3A	4A	5A	6A	7A	
					2 He $1s^2$ helium 4.003
5 B $[\mathrm{He}]2s^22p^1$ boron 10.81	6 C $[\mathrm{He}]2s^22p^2$ carbon 12.01	7 N $[\mathrm{He}]2s^22p^3$ nitrogen 14.01	8 O $[\mathrm{He}]2s^22p^4$ oxygen 16.00	9 F $[\mathrm{He}]2s^22p^5$ fluorine 19.00	10 Ne $[\mathrm{He}]2s^22p^6$ neon 20.18
13 Al $[\mathrm{Ne}]3s^23p^1$ aluminum 26.98	14 Si $[\mathrm{Ne}]3s^23p^2$ silicon 28.09	15 P $[\mathrm{Ne}]3s^23p^3$ phosphorus 30.97	16 S $[\mathrm{Ne}]3s^23p^4$ sulfur 32.07	17 Cl $[\mathrm{Ne}]3s^23p^5$ chlorine 35.45	18 Ar $[\mathrm{Ne}]3s^23p^6$ argon 39.95

http://www.sciencegeek.net/tables/LosAlamosperiodictableColor.pdf

Intrinsic, p-type, and n-type semiconductors

“Doping” in a silicon crystal lattice with other atoms enables one to shift the balance of free electrons and holes. Choose an atom with an extra valence electron to produce "*n*-type" semiconductor material (this adds a free electron to the conduction band. Choose an atom with one too few valence electrons to produce “*p*-type" semiconductor material (this results in acceptance of an electron from the valence band, adding a free hole to the valence band. In *p*-type material, the number of electrons trapped in bonds is higher, increasing the number of holes. In an n- or p-type doped material, there is always more of one type of carrier than the other and the type of carrier with the higher concentration is called a "majority carrier", while the lower concentration carrier is called a "minority carrier."

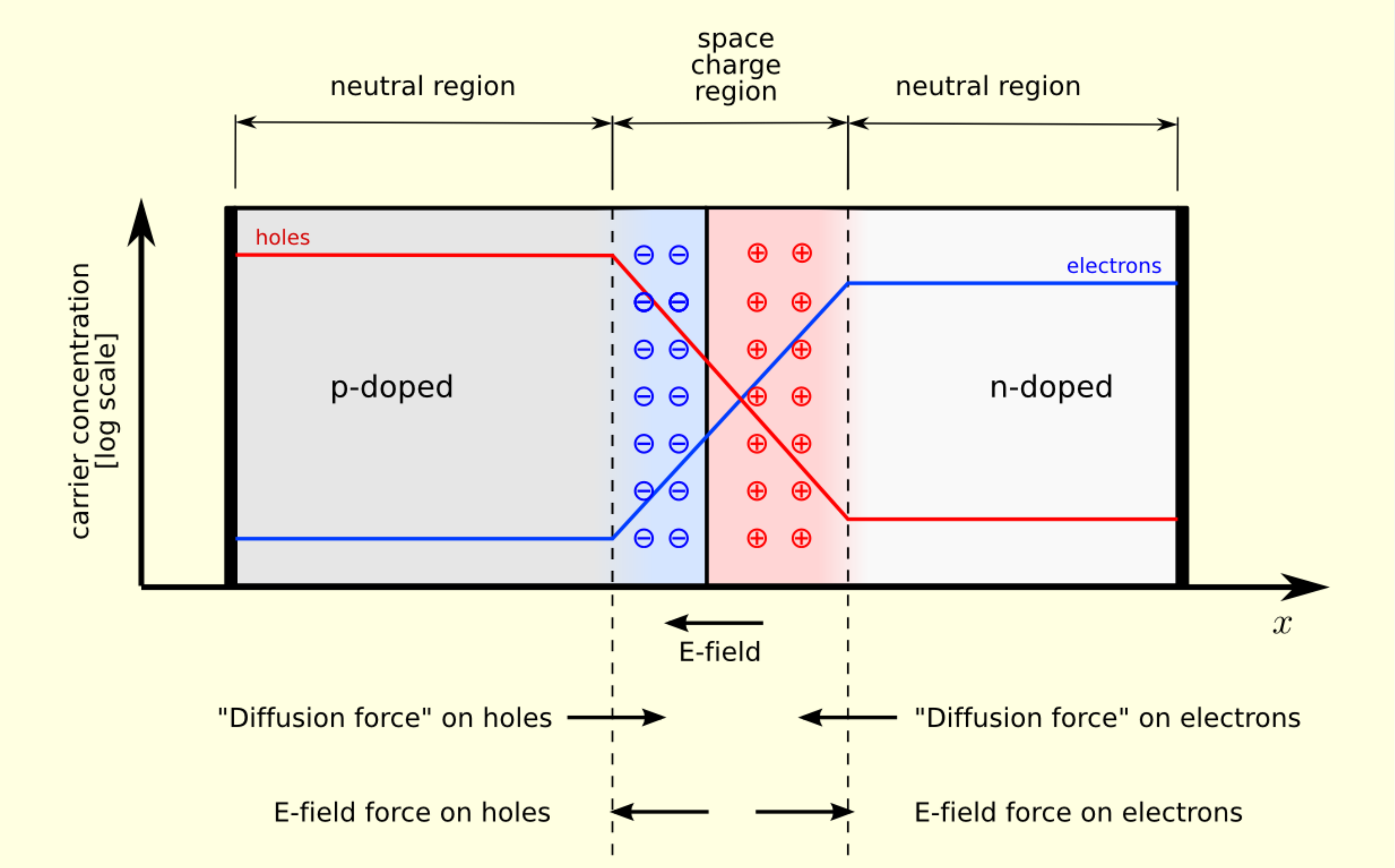




	P-type (positive)	**N-type (negative)**
Dopant	Group III (e.g. Boron)	Group V (e.g. Phosphorous)
Bonds	Missing Electrons (Holes)	Excess Electrons
Majority Carriers	Holes	Electrons
Minority Carriers	Electrons	Holes

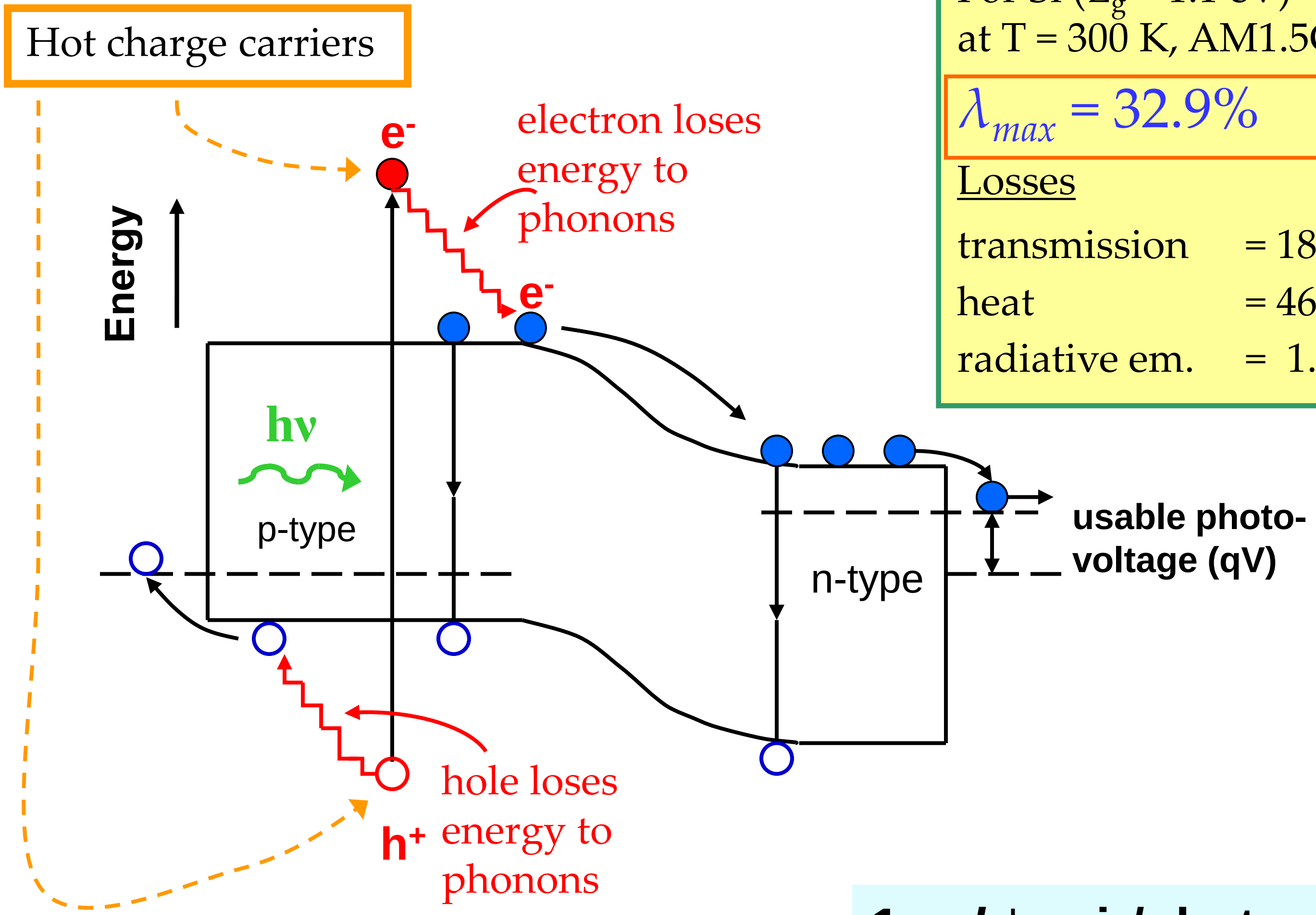
Photovoltaic effect

The photovoltaic effect is the creation of a voltage (or a corresponding electric current) in a material upon exposure to light.



http://en.wikipedia.org/wiki/P-n_junction

Conventional p-n junction photovoltaic cell



For Si (E_g = 1.1 eV)
at T = 300 K, AM1.5G

λ_{max} = 32.9%

Losses

transmission	= 18.7%
heat	= 46.8%
radiative em.	= 1.6%

1 e^--h^+ pair/photon

Principle of detailed balance

Detailed balance

From Wikipedia, the free encyclopedia

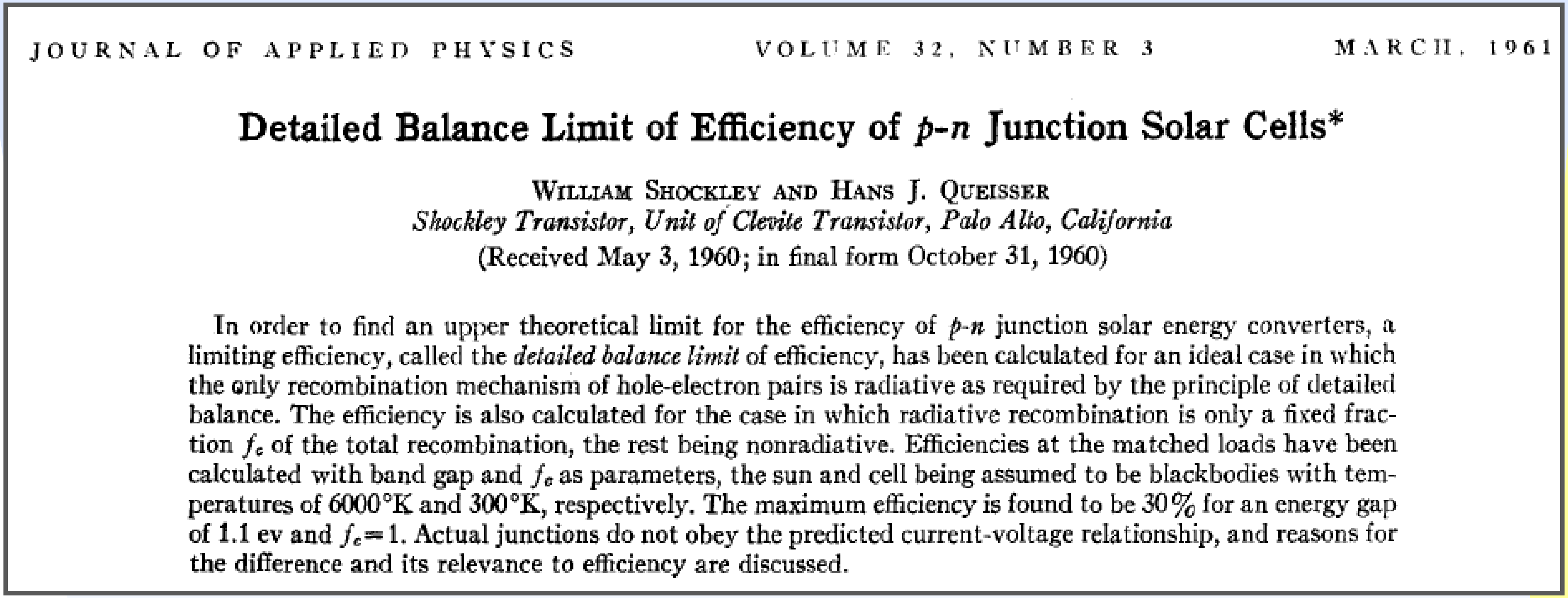
In mathematics and statistical mechanics, a Markov process is said to show **detailed balance** if the transition probability, *P*, between each pair of states *i* and *j* in the state space obey

$$\pi_i P_{ij} = \pi_j P_{ji}$$

where *P* is the Markov transition matrix (transition probability), *i.e.*, $P_{ij} = P(X_t = j \mid X_{t-1} = i)$; and π_i and π_j are the equilibrium probabilities of being in states *i* and *j*, respectively.

For solar cells, detailed balance refers to the idea that in equilibrium, any process taking place also occurs in the reverse direction with an equal probability.

Principle of detailed balance (cont.)



JOURNAL OF APPLIED PHYSICS VOLUME 32, NUMBER 3 MARCH, 1961

Detailed Balance Limit of Efficiency of *p-n* Junction Solar Cells*

WILLIAM SHOCKLEY AND HANS J. QUEISSER
Shockley Transistor, Unit of Clevite Transistor, Palo Alto, California

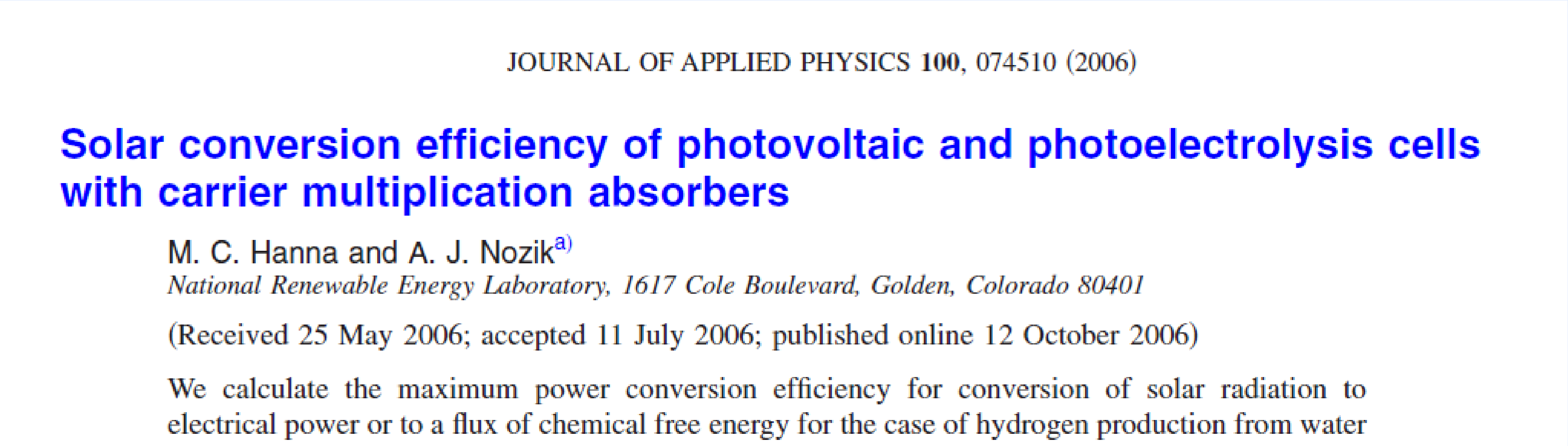
(Received May 3, 1960; in final form October 31, 1960)

In order to find an upper theoretical limit for the efficiency of *p-n* junction solar energy converters, a limiting efficiency, called the *detailed balance limit* of efficiency, has been calculated for an ideal case in which the only recombination mechanism of hole-electron pairs is radiative as required by the principle of detailed balance. The efficiency is also calculated for the case in which radiative recombination is only a fixed fraction f_c of the total recombination, the rest being nonradiative. Efficiencies at the matched loads have been calculated with band gap and f_c as parameters, the sun and cell being assumed to be blackbodies with temperatures of 6000°K and 300°K, respectively. The maximum efficiency is found to be 30% for an energy gap of 1.1 ev and $f_c=1$. Actual junctions do not obey the predicted current-voltage relationship, and reasons for the difference and its relevance to efficiency are discussed.

Detailed balance as applied to solar cells assumes that:

- charge carrier mobility: infinite (every photogenerated carrier is collected)
- every incident photon with $h\nu > E_g$ is absorbed
- every absorbed photon creates exactly one electron-hole pair
- (thermal) radiative emission = (thermal) photon absorption in the dark

Principle of detailed balance (cont.)



JOURNAL OF APPLIED PHYSICS **100**, 074510 (2006)

Solar conversion efficiency of photovoltaic and photoelectrolysis cells with carrier multiplication absorbers

M. C. Hanna and A. J. Nozik[a)]
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

(Received 25 May 2006; accepted 11 July 2006; published online 12 October 2006)

We calculate the maximum power conversion efficiency for conversion of solar radiation to electrical power or to a flux of chemical free energy for the case of hydrogen production from water

"There are four unavoidable losses that limit the solar conversion efficiency of a device with a single absorption threshold or band gap E_g:

1. ***incomplete absorption***— photons with energy below E_g *are not absorbed;*
2. ***thermalization*** (carrier cooling) — the excess energy of carriers generated by absorption of photons with energy greater than E_g *is usually lost as heat;*
3. ***thermodynamic loss*** — the available energy, Gibbs free energy, or chemical potential of the thermalized excited states is always less than the internal energy, with the consequence that the photovoltage or output chemical potential must be less than E_g; *and*
4. ***radiative recombination*** — a small fraction of the excited states radiatively recombine with the ground states at maximum power output."

Principle of detailed balance (equilibrium, no illumination)

Consider a solar cell in the dark, which is in thermal equilibrium with its surrounding environment. Radiative losses (the cell’s blackbody emission) will equal radiative gains (i.e., due to absorption of blackbody photons from the surrounding).

Since the cell’s outgoing (emitted) photon flux must equal the incoming (absorbed) photon flux at equilibrium, one can deduce that the energy-dependent emissivity equals the energy-dependent absorptivity.

Detailed balance – under illumination

An illuminated solar cell absorbs photons at a rate G of:

$$G = \left(1 - R(E)\right)\left(a(E)\right)b_s(E)$$

where b_s is the incident solar photon flux normal to the surface of the solar cell.

The emitted photon flux depends on the chemical potential $\Delta\mu$, the refractive index of the surrounding medium n_s, and the ambient temperature, T_a:

$$b_e(E, \Delta\mu) = F_e \frac{2n_s^2}{h^3c^2} \frac{E^2}{e^{(E-\Delta\mu)/k_BT} - 1}$$

where $F_e = \pi \sin^2 \theta_c = \pi(n_0/n_s)^2$ and $\theta_c = \sin^{-1}(n_0/n_s)$; n_0 is the index of the surrounding medium. It follows that the net photon absorption depends on:

$$j_{abs(net)} = q\left(1 - R(E)\right)a(E)\left(\underline{b_e(E, \Delta\mu)} - \underline{b_e(E,0)}\right)$$

Light (non-equilibrium), and dark (equilibrium) contributions

Detailed balance – under illumination (cont.)

In the case of the limiting (highest possible) photocurrent, where all incident photons with $h\nu > E_g$ are absorbed and generate an electron which is ultimately collected, the short-circuit current is given by:

$$J_{SC} = q\int_{E_g}^{\infty} b_s(E)\,dE$$

where b_s is the spectrum of incident sunlight.

The limiting (lowest) dark current can be written as:

$$J(V) = J_{SC} - J_{dark} = J_{SC} - J_0\left(e^{\frac{qV}{kT}} - 1\right)$$

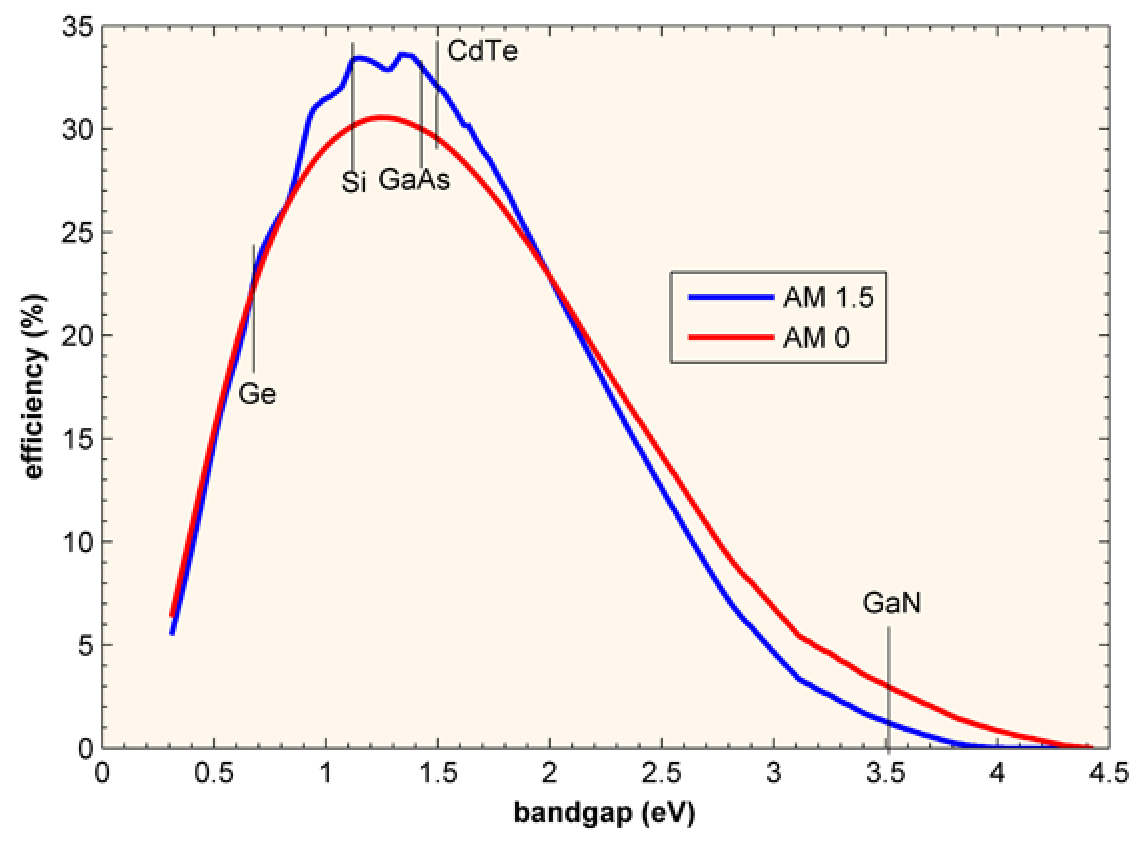
The limiting efficiency follows:

$$P_S = \int_{E_g}^{\infty} E b_s(E_S)\,dE \qquad P = VJ(V) \qquad \eta = \frac{VJ(V)}{P_S}$$

(Incident power)

One must optimize load resistance to operate at maximum power conversion efficiency.

Bandgap influence on efficiency



- Too large a bandgap, and you get insufficient absorption (GaN)
- Too narrow a bandgap, and you get insufficient photovoltage (Ge, PbS, PbSe)

GENERATION AND RECOMBINATION OF CHARGE CARRIERS IN SOLAR CELLS;

TRANSPORT MECHANISMS: DRIFT AND DIFFUSION

- generation of free carriers
- recombination of electrons and holes
- Transport:
  - Drift
  - Diffusion

Charge carriers (electrons and holes)

Masses:

$m_e = 9.11 \times 10^{-31}$ kg
$m_n = 1.67 \times 10^{-27}$ kg
$m_p = 1.67 \times 10^{-27}$ kg

Electron charge = -1.602×10^{-19} C
Hole charge = $+1.602 \times 10^{-19}$ C

Effective Mass of electrons and holes:

A particle's **effective mass** is the mass it appears to carry in transport in a crystal. Electrons and holes in a crystal respond to electric and magnetic fields almost as if they were particles with a mass dependent on their direction of travel (an effective mass tensor). **Simplified picture**: ignoring crystal anisotropies, electrons and holes behave as free particles in a vacuum, but with a different mass.

http://en.wikipedia.org/wiki/Effective_mass_(solid-state_physics)

Material	Electron effective mass	Hole effective mass
	Group IV	
Si (4.2K)	1.08 m_e	0.56 m_e
Ge	0.55 m_e	0.37 m_e
	III-V	
GaAs	0.067 m_e	0.45 m_e
InSb	0.013 m_e	0.6 m_e
	II-VI	
ZnO	0.19 m_e	1.21 m_e
ZnSe	0.17 m_e	1.44 m_e

Important charge carrier processes in semiconductors

The free electron and hole concentrations in bulk semiconductors can be modified by the processes of generation and recombination, and also by the transport of electrons and holes through drift and diffusion.

Generation: e.g., absorption of a photon generates a free electron and a free hole (an electron-hole pair).

Recombination: can be **radiative**, in which case a photon is emitted as the electron returns to the valence band, or **non-radiative**, in which case the energy associated with the e-h pair is converted to heat, or transferred to another charge carrier (Auger recombination) – non-radiative corresponds to no photon.

Transport is the movement of charge carriers under forces based either on an electric field, or on a concentration gradient:

Drift refers to the motion of charge carriers under the force of an electric field. Motion is typically not “ballistic”, and instead includes the resistive action of scattering.

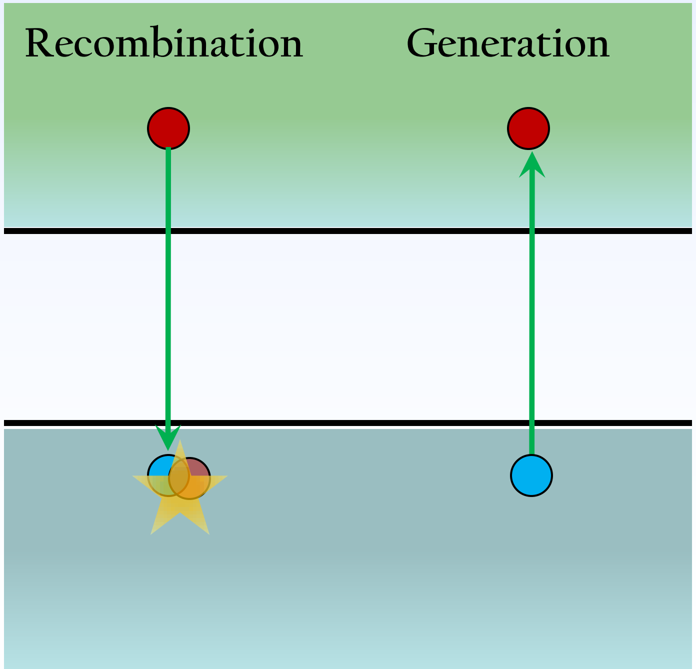
Diffusion refers to motion of electron and holes due to the presence of a concentration gradient.

Generation and recombination

Charge carriers move between valence and conduction bands under thermal influence (thermal excitation within the Boltzmann tail of the Fermi-Dirac distribution). In the dark and at equilibrium, the concentration of electrons and holes are unaffected by these processes.

Generation, under influence of light absorption for example, promotes electrons from the valence band to the conduction band, resulting in a new free electron in the CB, and a new hole in the VB.

Recombination is essentially the reverse process, in which an electron returns to the valence band, giving up it electronic potential energy to a photon, or a third carrier, or to phonons.



Absorption of light

Light incident on a semiconductor consist of photons with energy $E = h\nu = hc/\lambda$. Photons interact with the semiconductor depending on their energy:

$E_{photon} < E_g$: Photons with energy below the band gap energy are transmitted through the material;

$E_{photon} = E_g$: These photons have sufficient energy to be absorbed in a band-to-band transition, and generate an electron-hole pair. Absorption of these photons will be relatively weak.

$E_{photon} > E_g$: Photons with significantly greater energy than the semiconductor’ s bandgap are relatively strongly absorbed, and generate electron-hole pairs with initial excess kinetic energy. This excess kinetic energy is, in general, quickly lost to the lattice as phonons).

Absorption of light – the generation rate

The generation rate quantifies the number of electron-hole pairs created per unit time. As the light enters and travels through the semiconductor, the intensity of the light drops exponentially as the photons are converted to electron-hole paires by the process of "photogeneration":

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

where a is the absorption coefficient typically in cm^{-1}, and x is the distance into the material. I_0 is the light intensity just inside the surface of the semiconductor.

Since each photon absorbed generates an e-h pair, this exponential decay also mimics the generation of carriers as a function of depth.

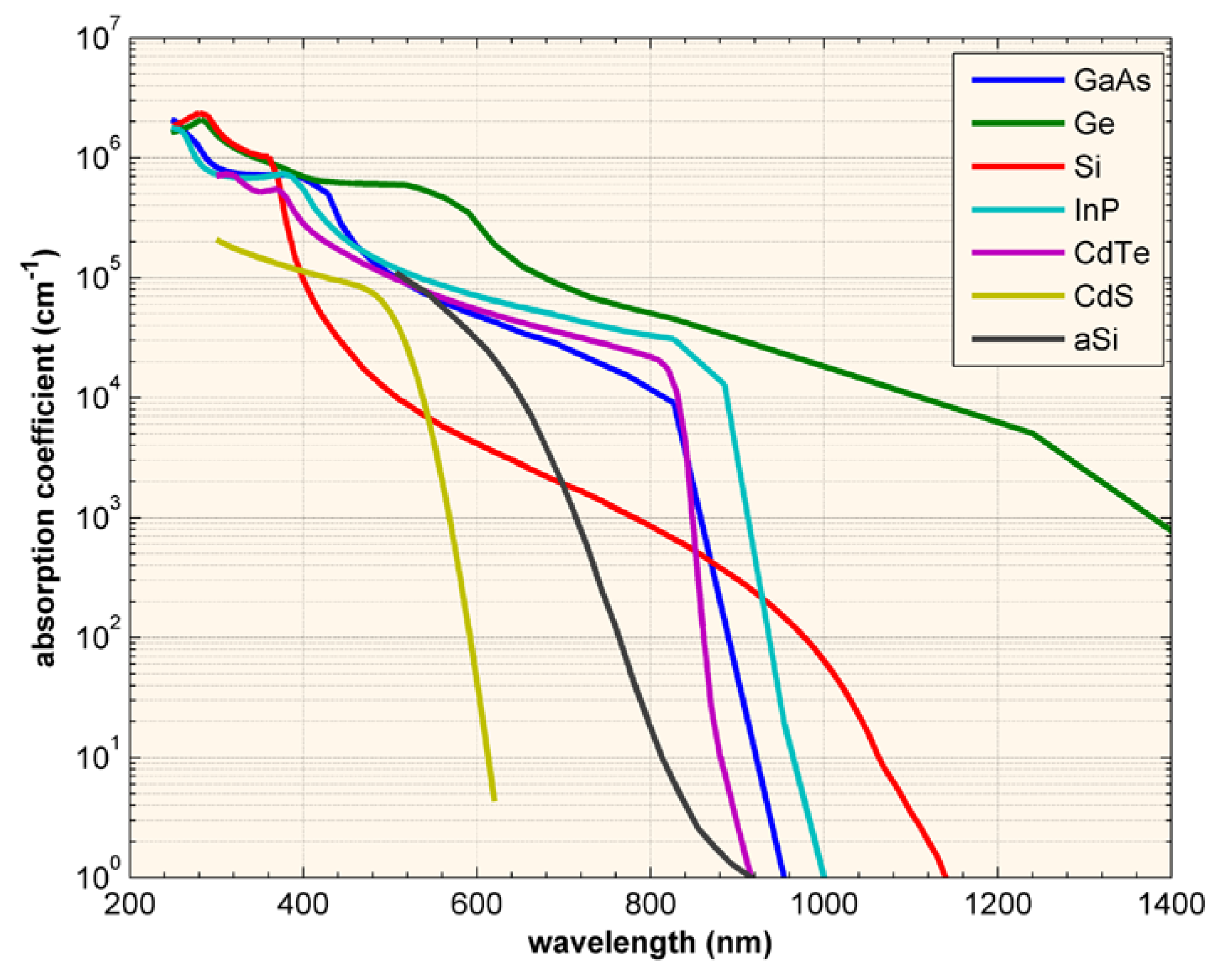
The generation rate, G, is given by:

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

where N_0 is the photon flux at the surface (photons/unit-area/sec), α is absorption coefficient, and x is the distance into the material.

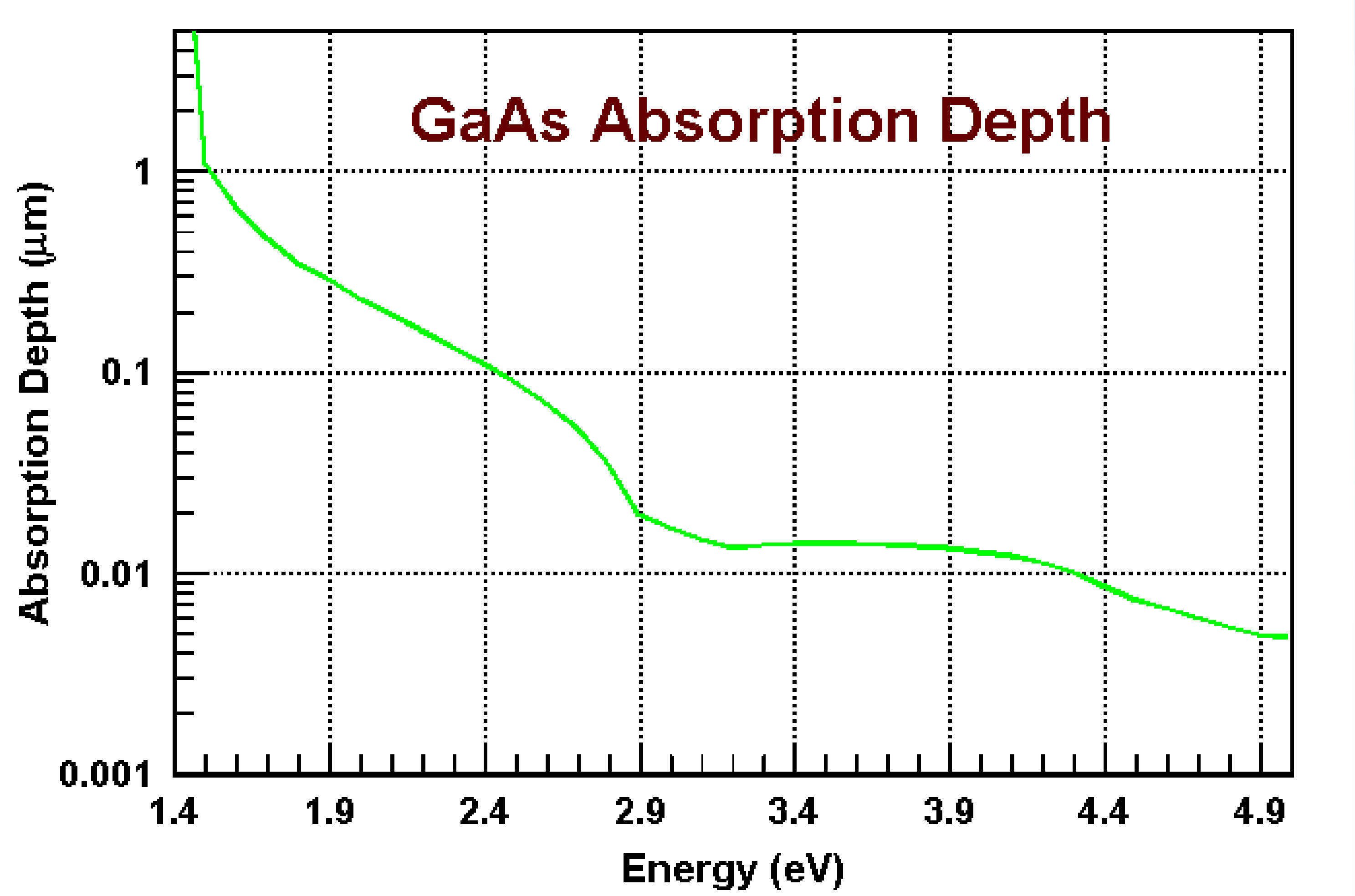
Absorption *coefficient*

Generation occurs in PV cells by absorption of light, and the formation of electron-hole pairs. The absorption coefficient, α, in units of cm^{-1}, provides a measure of the strength of the light absorption at a given photon energy.

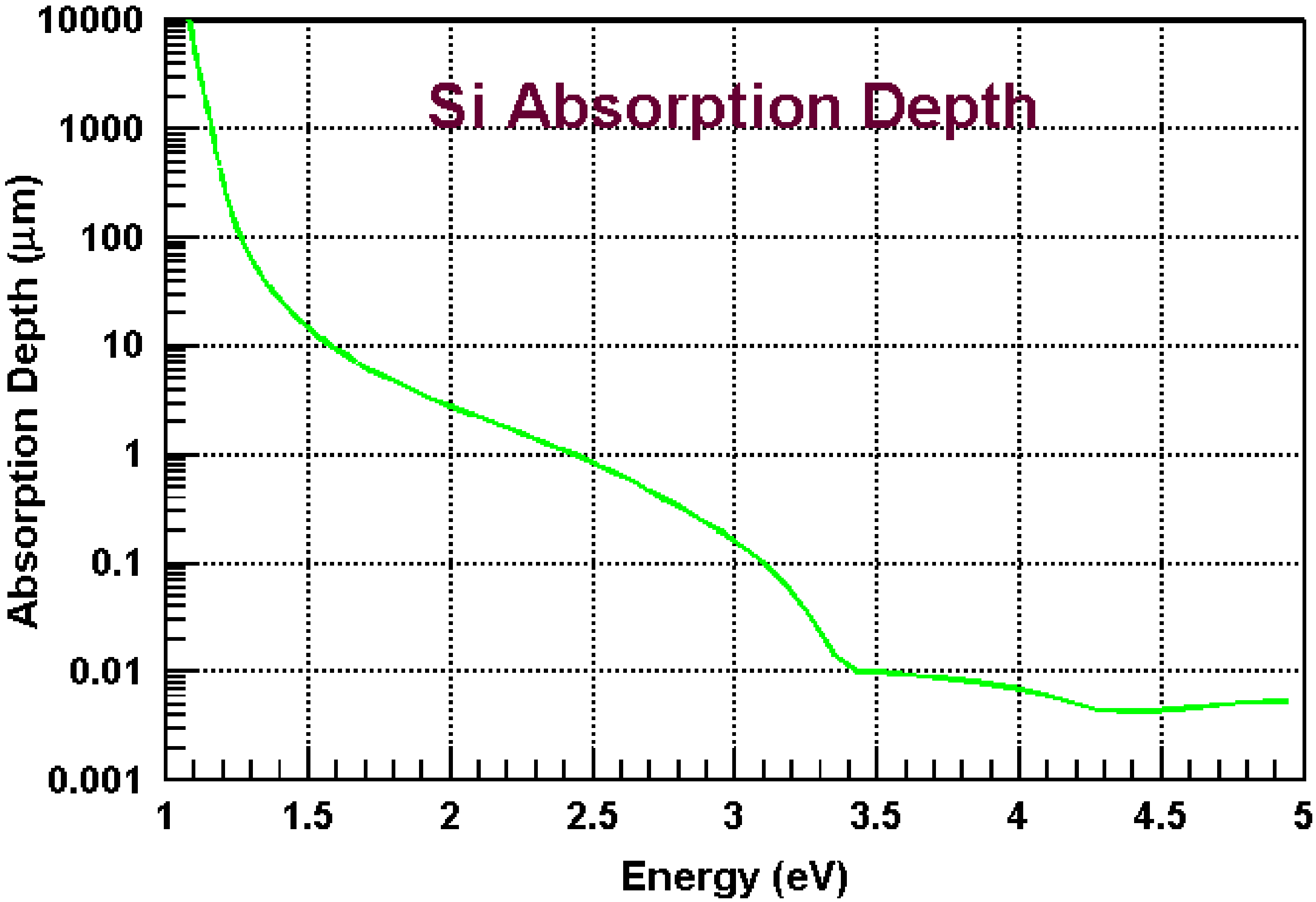


Absorption *depth*

The absorption depth for a materials is photon-energy-dependent, and is simply the inverse of the absorption coefficient. I.e., it is the depth at which the intensity of the light has dropped to a value of $(1/e)*I_0(\lambda)$.



Absorption *depth*



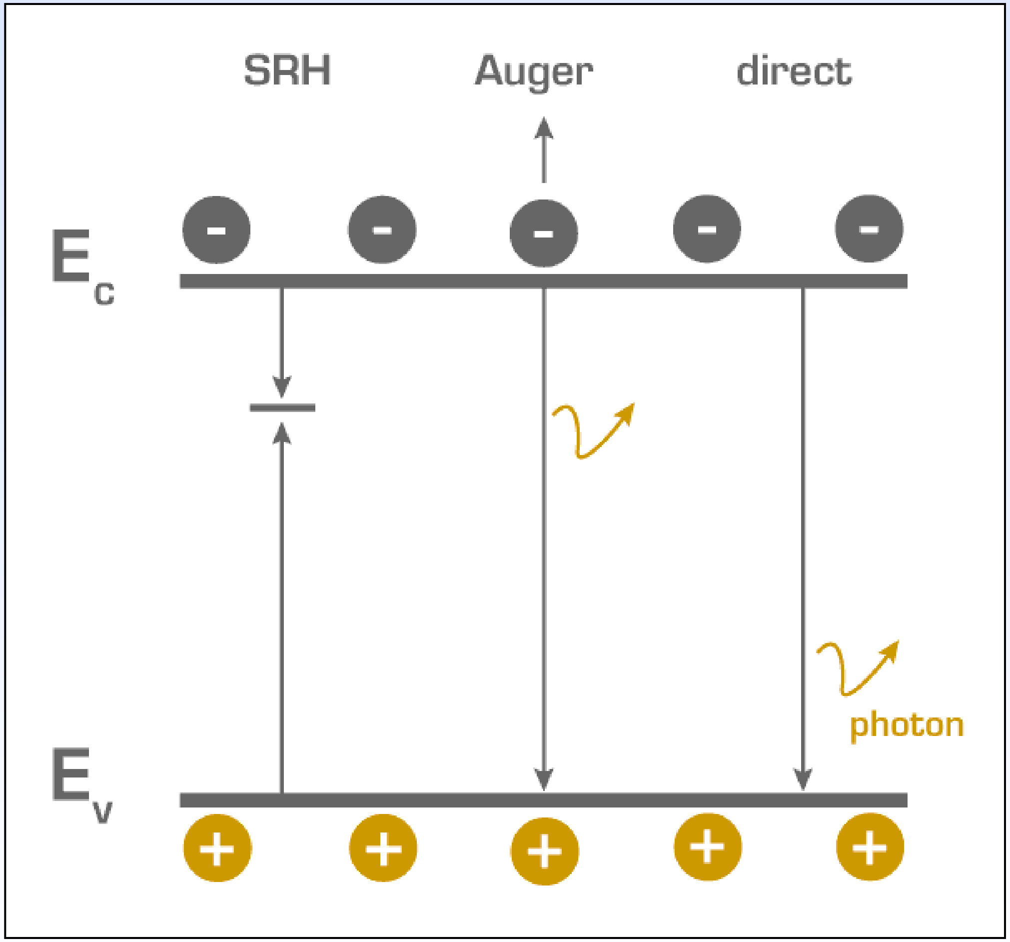
Recombination of electrons and holes in a semiconductor

Photons incident on the surface of a semiconductor will be either reflected from the top surface, absorbed, or transmitted. For PV, reflection and transmission are typically considered loss mechanisms (photons which are not absorbed do not generate power). An absorbed photon will raise an electron from the valence band to the conduction band (this process is called ***generation***). A key factor in determining if a photon is absorbed or transmitted is the energy of the photon.

An electron which exists in the conduction band is in a meta-stable state and will eventually fall back to a lower energy position in the valence band. It must move back into an empty valence band state and consequently, when the electron falls back down into the valence band, it effectively removes a hole. This process is called ***recombination***. There are three basic types of recombination in the bulk of a single-crystal semiconductor. These are:

(1)Radiative (band-to-band) recombination
(2)Auger recombination
(3)Shockley-Read-Hall (SRH) recombination

Types of recombination (revisited)



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

Free carriers (free electrons and holes)

Free carriers -- consisting of electrons, holes, or both – are able to carry current in a semiconductor material or solar cell.

In contrast, trapped carriers are bound to a specific impurity atom, defect (such as a vacancy) in the crystal, or bound to a specific surface state. Trapped carriers are typically not in the valence band, and cannot carry current.

Free carriers are subject to move under the mechanisms of drift (as in an electric field, with force of qE where q is the electron charge and E is the electric field strength), and of diffusion.

Drift of free carriers in solar cells

Drift refers to the motion of a charged particle within an electric field (typically DC and in a steady direction);

The **drift velocity** is the average velocity that a particle, such as an electron, attains due to an electric field. In general, an electron will 'rattle around' in a conductor at the Fermi velocity randomly. An applied electric field will give this random motion a small net velocity in one direction.

http://en.wikipedia.org/wiki/Drift_velocity

Diffusion of free carriers in solar cells

Diffusion describes the spread of particles through random motion from regions of higher concentration to regions of lower concentration. The time dependence of the statistical distribution in space is given by the diffusion equation. The concept of diffusion is tied to that of mass transfer driven by a concentration gradient, but diffusion can still occur when there is no concentration gradient (but there will be no net flux).

http://en.wikipedia.org/wiki/Diffusion

Diffusion current is a current in a semiconductor caused by the diffusion of charge carriers (holes and/or electrons). Diffusion current can be in the same or opposite direction of a drift current.

At equilibrium (i.e., in the dark) in a p-n junction, the forward diffusion current in the depletion region is balanced with a reverse drift current, so that the net current is zero.

Semiconductor physics review

Density of States in Conduction and Valence Band (parabolic band approximation)

$$N_C(E) = \frac{m_n^{3/2}\sqrt{2}}{\pi^2\hbar^3}\sqrt{E - E_C}$$

$$N_V(E) = \frac{m_p^{3/2}\sqrt{2}}{\pi^2\hbar^3}\sqrt{E_V - E}$$

Look at units:
(note that 1 J = 1 kg-m^2-s^{-2},
and [*h*] = m^{2}kg s^{-1})

$$\frac{kg^{3/2}J^{1/2}s^3}{m^6kg^3} = \frac{kg^{3/2}kg^{1/2}s^3m}{m^6kg^3s} = kg^{-1}s^2m^{-5} = J^{-1}m^{-3}$$

Fermi function (state occupation probability)

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Boltzmann approximation

Fermi function (state occupation probability)

$$f(E) = \frac{1}{1+\exp\left(\frac{E-E_F}{k_B T}\right)}$$

If E_F is sufficiently far from either band edge, then *f*(*E*) can be approximated by:

$$f(E) \approx \exp\left(\frac{E_F - E}{k_B T}\right)$$

From the textbook’s (3.27), then, we can integrate to arrive at *n*:

$$n = \int_{E_C}^{\infty} N_C(E) f(E, E_F, T)\, dE$$

Integrating/solving for *n* yields (3.31):

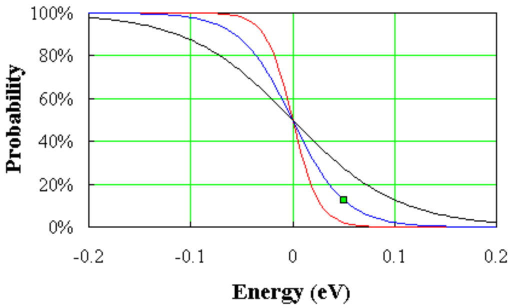
$$\boxed{n = N_0 \exp((E_F - E_C)/k_B T)}$$

Where N_0 is called the effective conduction band density of states and is given by

$$N_0 = 2\left(\frac{m_c^* k_B T}{2\pi\hbar^2}\right)^{3/2}$$

….The Fermi function tells us about the occupation of these states

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

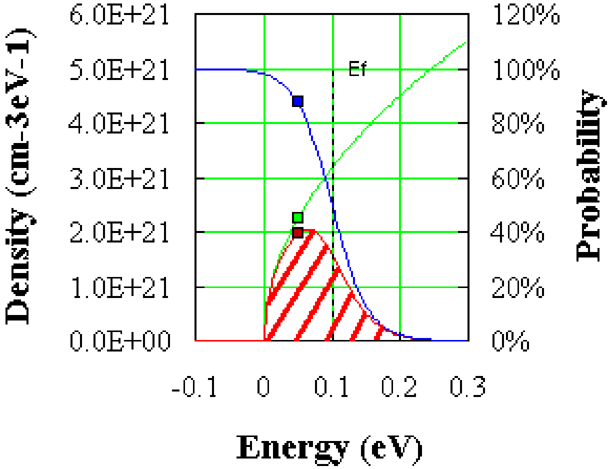


Density of carriers in the band can be obtained (for, e.g., electron in the conduction band):

$$n = \int_{E_C}^{\text{top of the conduction band}} n(E)\,dE = \int_{E_C}^{\text{top of the conduction band}} g_c(E) f(E)\,dE$$

$$n = \int_{E_C}^{\infty} \frac{8\pi\sqrt{2}}{h^3} m_e^{*3/2} \sqrt{E - E_C}\, \frac{1}{1 + e^{\frac{E-E_F}{kT}}}\, dE$$

(with units of #/cm^{-3})



http://ecee.colorado.edu/~bart/book/carriers.htm

Optical absorption: direct vs. indirect gap

$$\alpha(E) \propto \int g_c\left(\boldsymbol{k}\left(E_i + E\right)\right) g_v\left(\boldsymbol{k}\left(E_i\right)\right) dE_i$$

Quantity in integral known as the joint density of states (JDOS). For the parabolic band approximation and a direct-gap semiconductor, it follows that:

$$\alpha(E) = \alpha_0 \left(E - E_g\right)^{\frac{1}{2}}$$

where α_0 is a material-specific constant.

For an indirect gap semiconductor, one needs to account for the probability of finding a suitable phonon for the 3-particle (indirect) transition process.

$$\alpha(E) \propto \left(E - E_g\right)^2$$

Radiative (direct) and Auger recombination

$$U = Bnp$$

where U is the rate of recombination of e-h pairs due to radiative band-to-band recombination, *n,p* are the electron and hole concentrations, and *B* is a constant dependent on the material and the specific process.

Auger recombination is a 3-carrier (or 3-particle) process involving either two electrons and a hole, *or* one electron and two holes:

$$U_{Auger} = A_p\left(n^2 p - n_0^2 p_0\right)$$ for two-electron collisions

$$U_{Auger} = A_n\left(np^2 - n_0 p_0^2\right)$$ for two-hole collisions

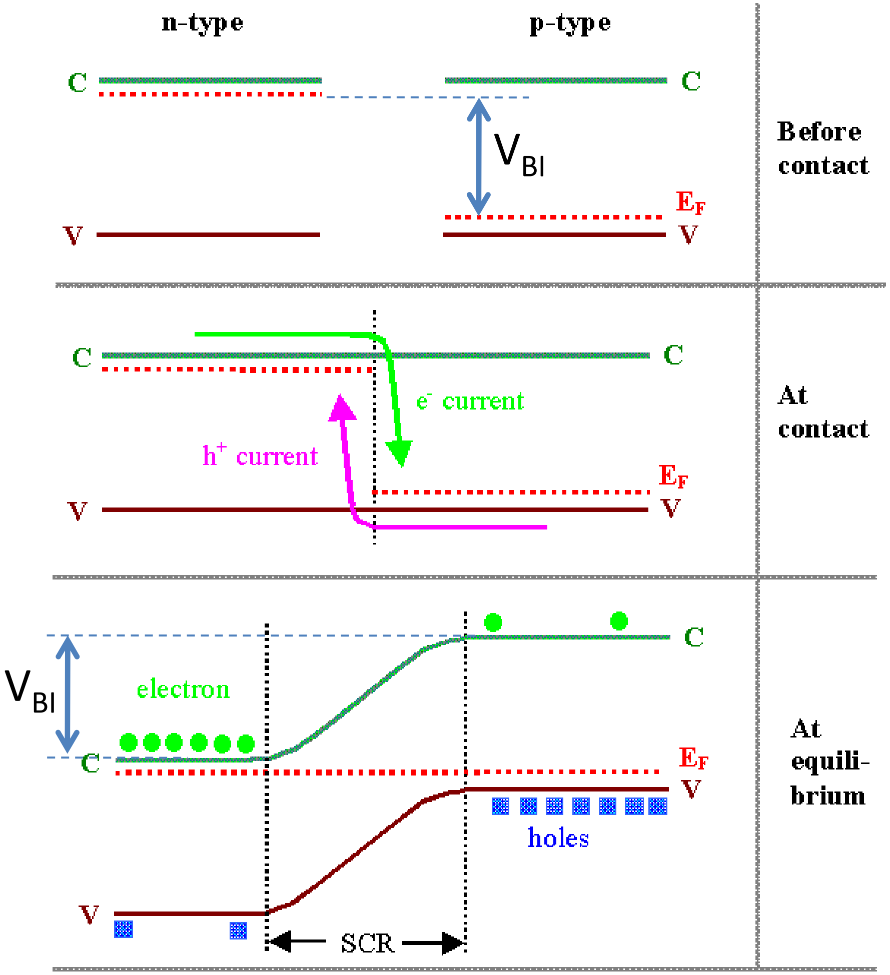
The p-n Homojunction

Consider the the band diagram for a *homojunction*, formed when two bits of the same type of semiconductor (e.g. Si) are doped p and n type and then brought into contact.

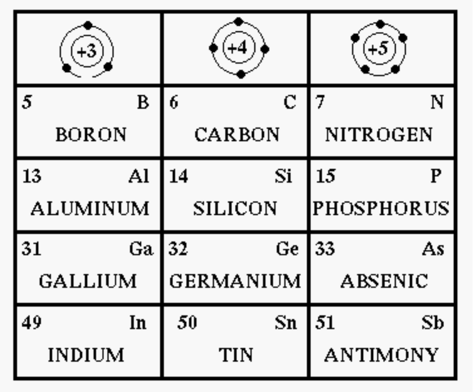
Electrons in the two bits have different electrochemical potentials (i.e. different E_f's)

Charge transfer occurs at contact (electron go down from the vacuum level, holes go "up")

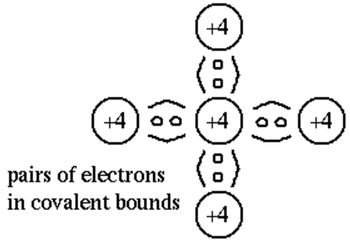
At equilibrium, there is no net transport (E_f is constant throughout the device)

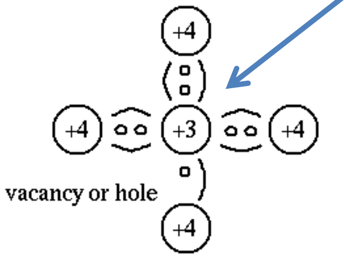


H. Föll: http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_2_4.html



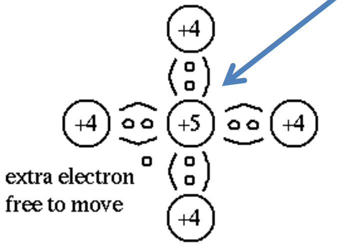
+3	+4	+5
5 B BORON	6 C CARBON	7 N NITROGEN
13 Al ALUMINUM	14 Si SILICON	15 P PHOSPHORUS
31 Ga GALLIUM	32 Ge GERMANIUM	33 As ABSENIC
49 In INDIUM	50 Sn TIN	51 Sb ANTIMONY





p-type

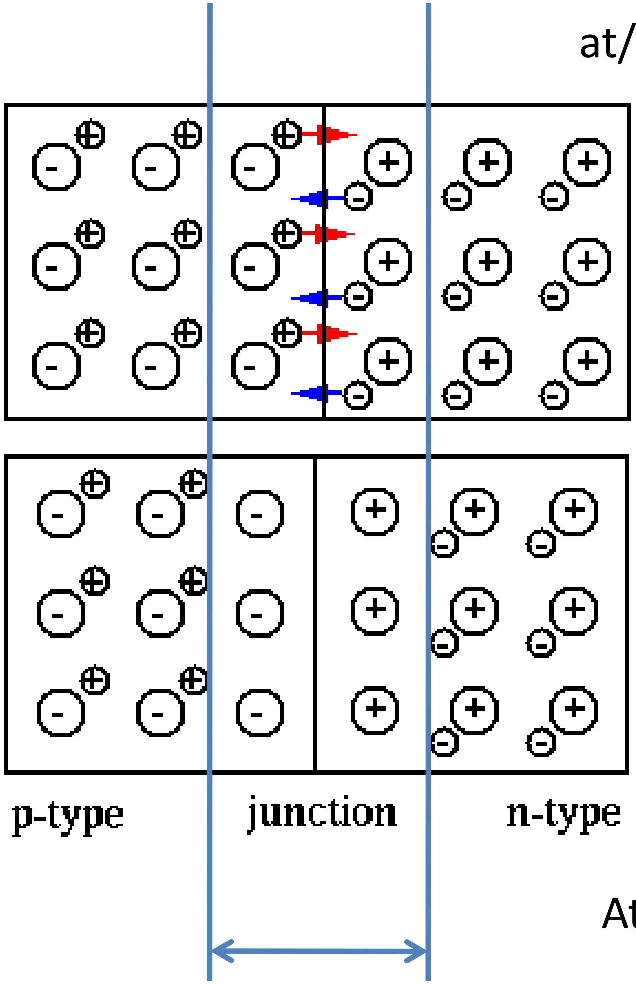
Charge of -1 relative to the other atoms (N_A^-)



n-type

Charge of +1 relative to the other atoms (N_D^+)

at/during contact



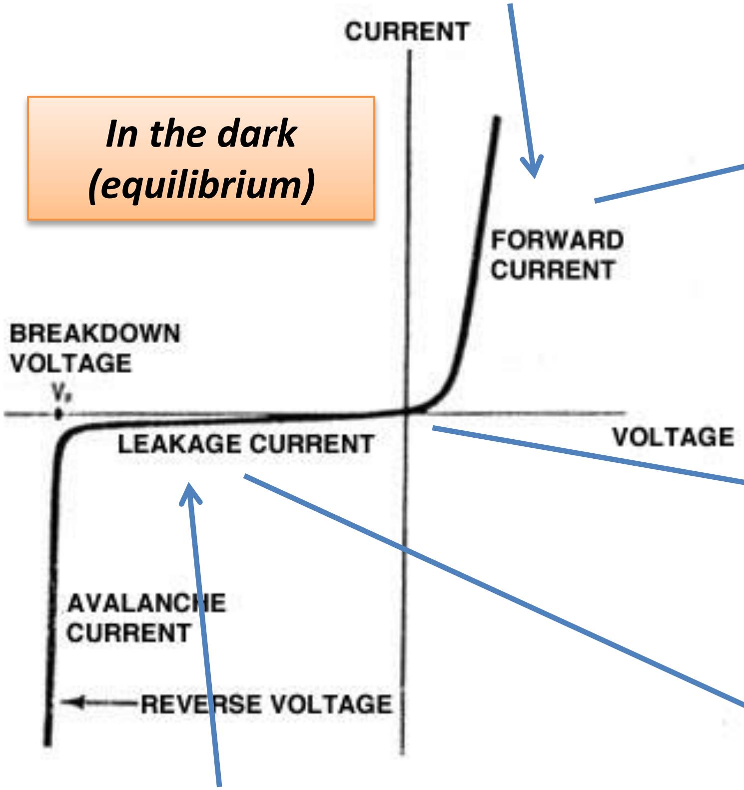
At equilibrium

Space charge region (SCR) or Depletion region

R. Wang: http://fourier.eng.hmc.edu/e84/lectures/ch4/node1.html

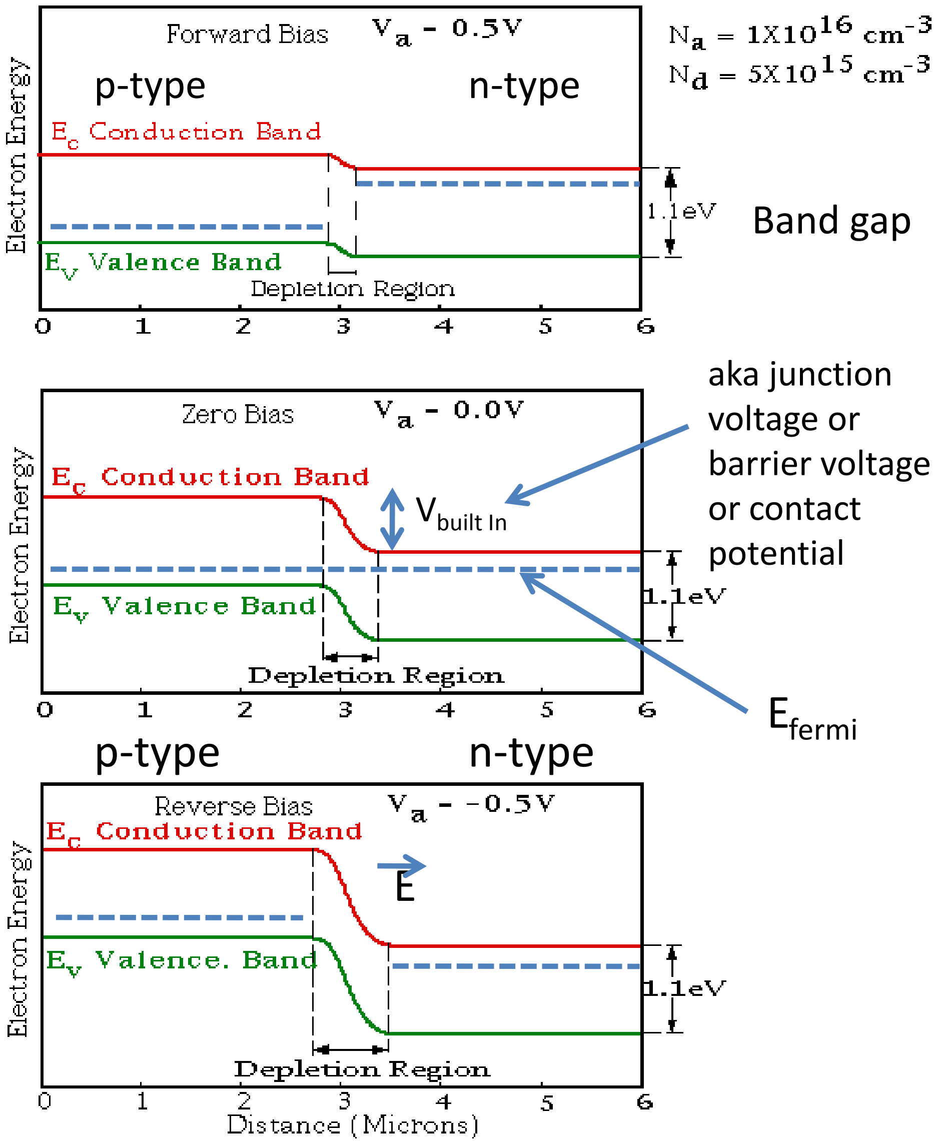
Majority carriers diffuse across the Depletion Region (because the electric field is reduced), where they become minority carriers and recombine (a.k.a. minority carrier injection)

In the dark (equilibrium)



a.k.a. Reverse Saturation Current: **minority carriers drift** across the Depletion Region with the assistance of the larger electric field, where they become minority carriers and recombine

Energy Band Diagram for p-n diode



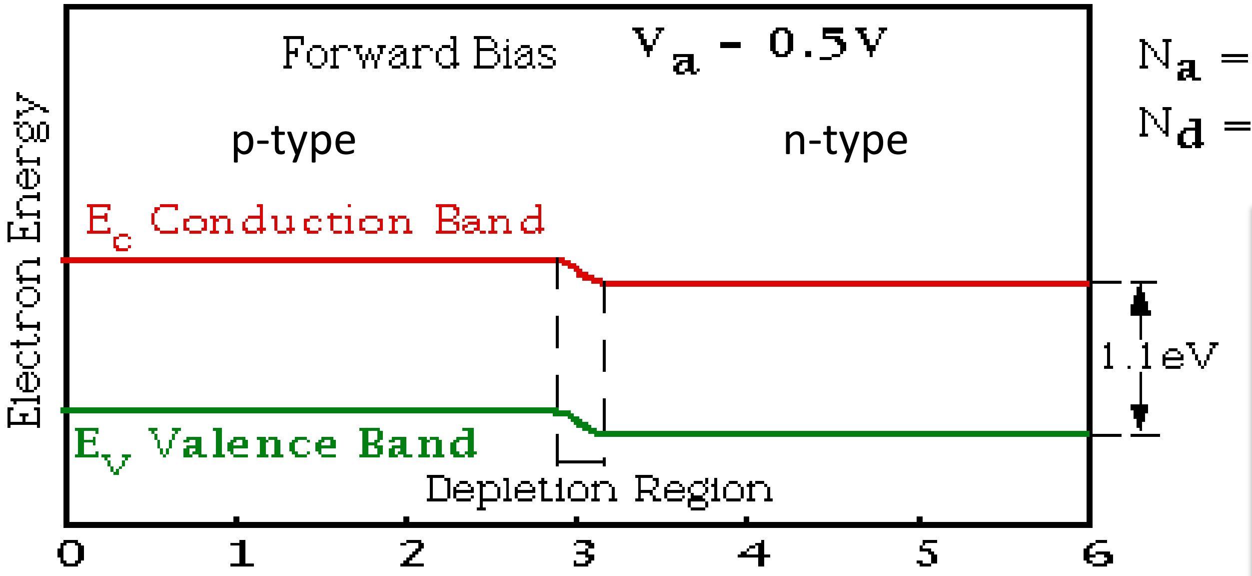
Band gap

aka junction voltage or barrier voltage or contact potential

E_{fermi}

http://www-tcad.stanford.edu/tcad/education/anim.html

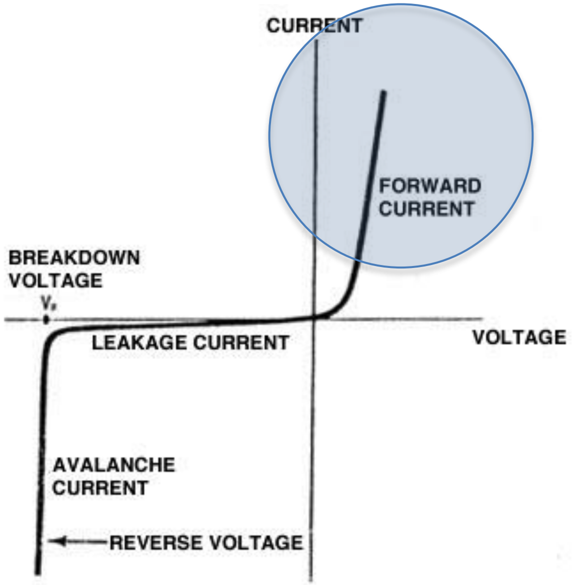
Forward Biased p-n junction



$N_a = 1X10^{16}\ cm^{-3}$

$N_d = 5X10^{15}\ cm^{-3}$

Majority carriers cross the junction, and become minority carriers (e.g., electrons from n-side to p-side), and recombine w/ a majority carrier supplied by external circuit (net current flow).

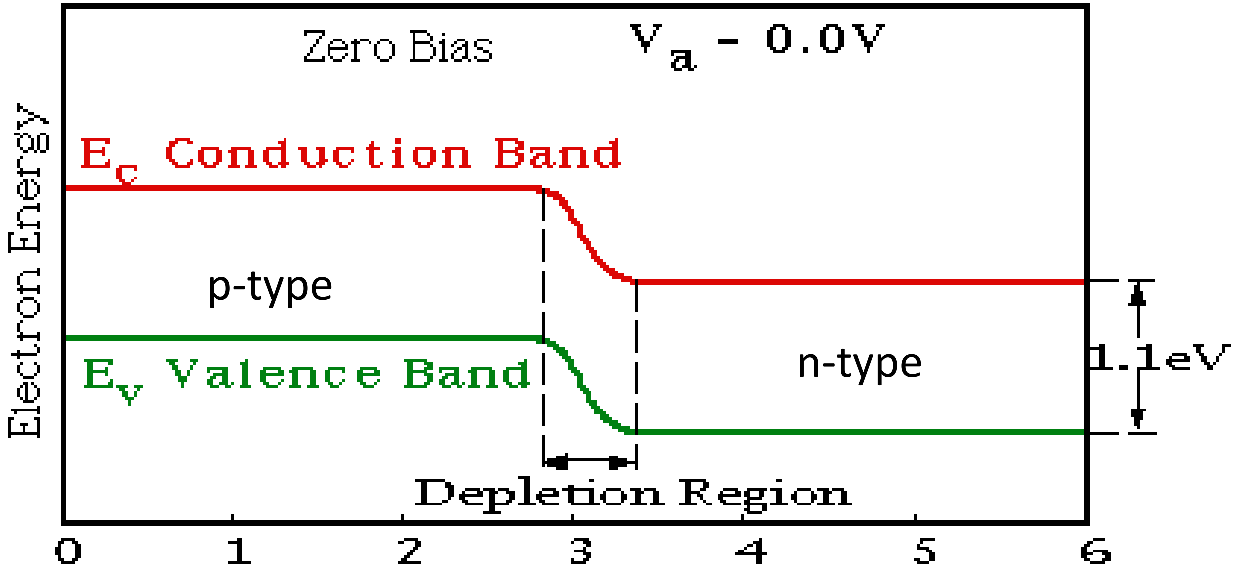


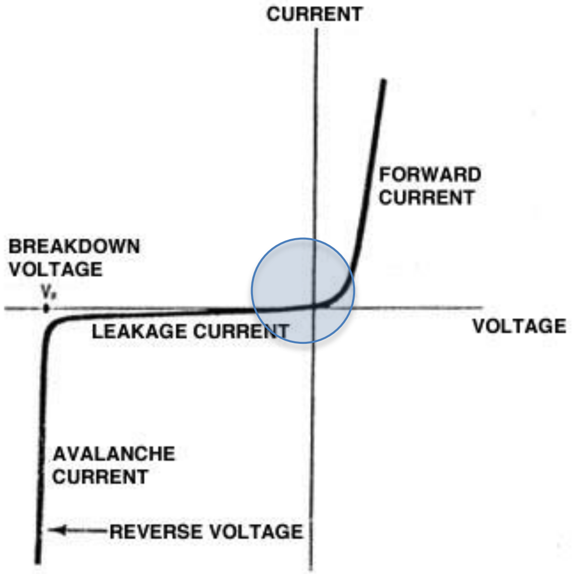
- Applied voltage reduces E- field across the depletion region
- Positive voltage to the *p*-type and negative voltage to the *n*-type
- Resistivity in depletion region high (few free carriers)
- Resulting E-field consists of the built-in field minus the applied field (built-in field > applied field)
- Barrier to diffusion is reduced, and diffusion current increases
- Drift current changes little -- depends on carriers generated near or within depletion region
- Depletion region width decreases very slightly → minority carriers changes little.

http://pveducation.org

Unbiased p-n junction

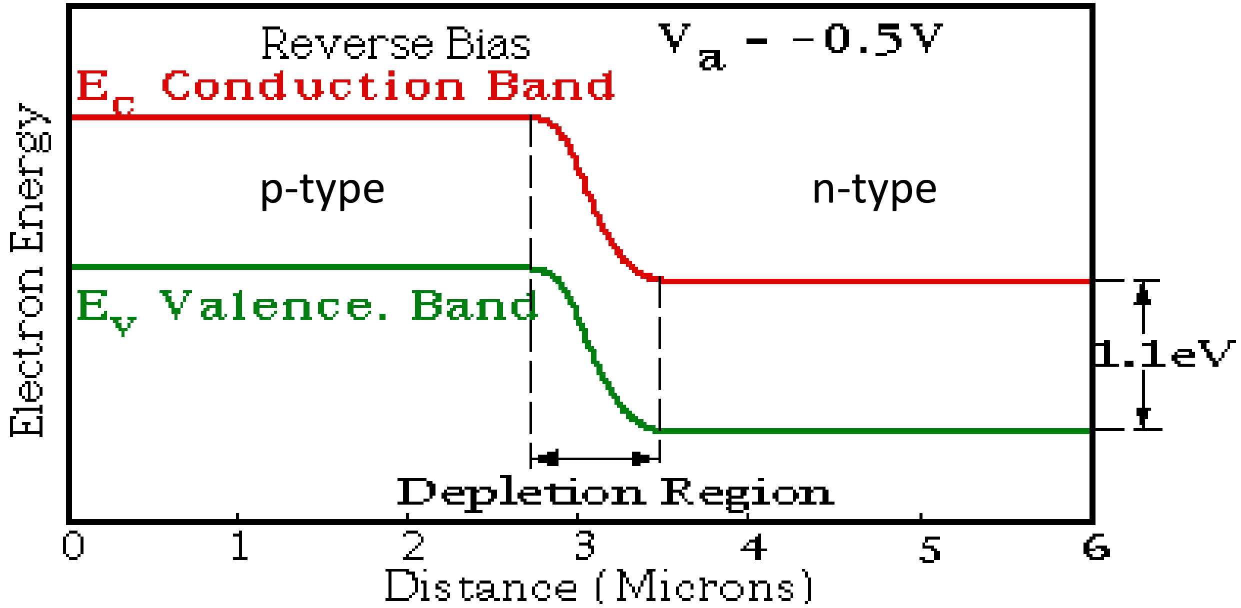
http://www-tcad.stanford.edu/tcad/education/anim.html

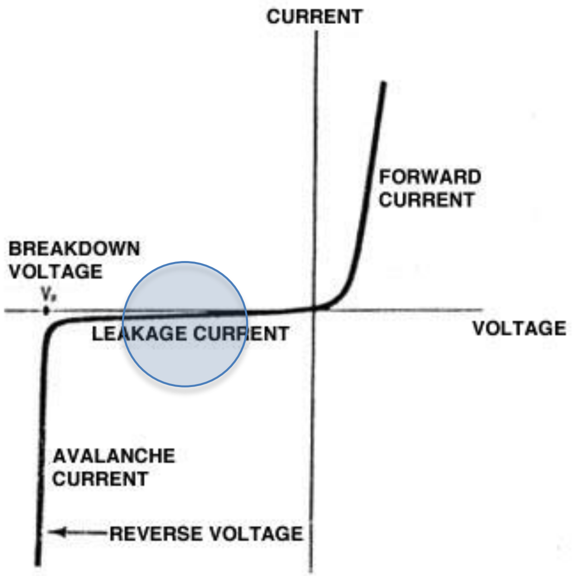




- Diffusion of majority carriers balances the drift of minority carriers across the junction, resulting in no net current (only the case in the dark)
- Diffusion current is “uphill”
- Drift current is “downhill”
- Which carriers in n-type (or p-type) contribute to diffusion current? And which to drift current?
- In n-type (p-type), which carrier type predominates?

Reverse Biased p-n junction

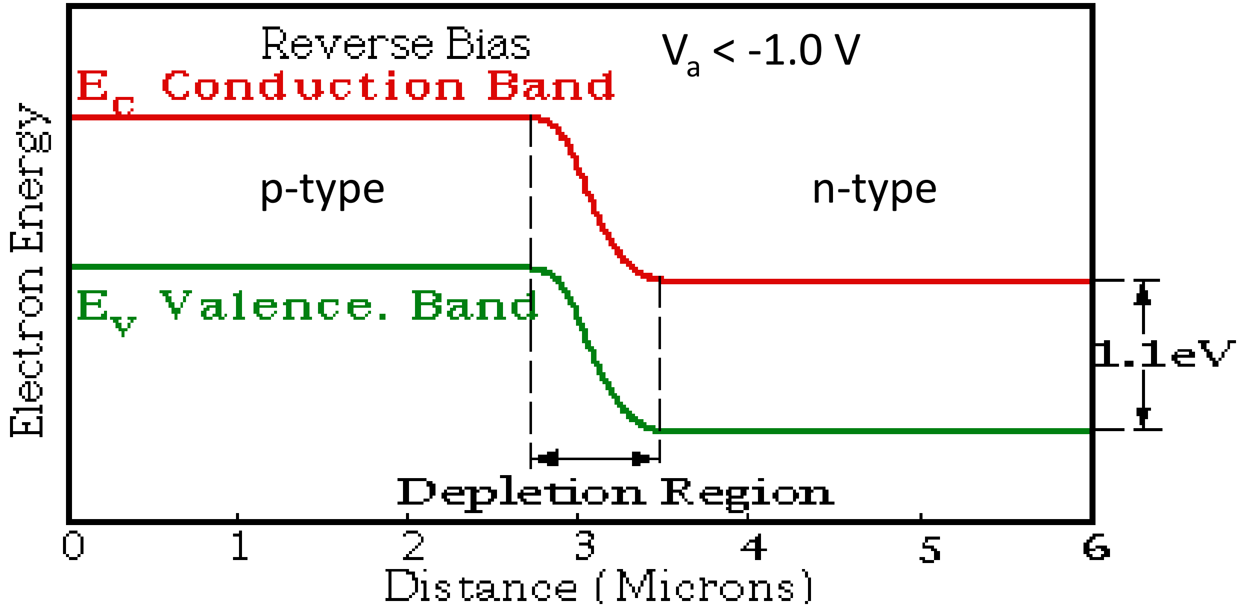




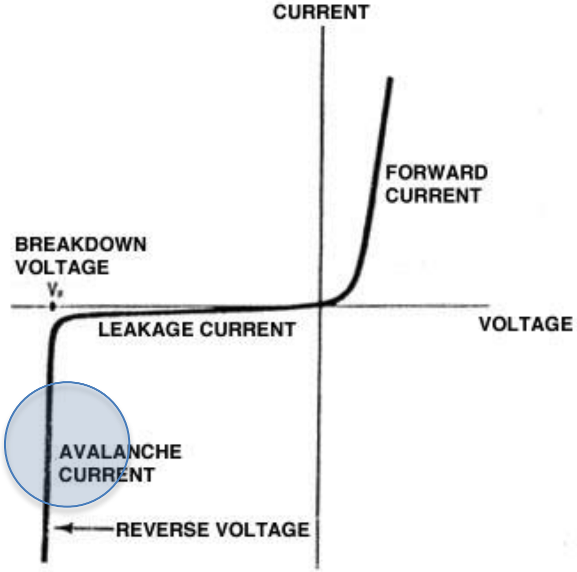
- Voltage applied such that the E-field at the junction increases
- Negative voltage to p-type, and positive voltage to n-type
- Higher E-field in depletion region decreases diffusion across the junction → diffusion current decreases
- Drift current limited by the number of minority carriers, and changes little
- Drift current increases slightly (depletion region width increases slightly) – minor effect in Si solar cells, which are much thicker than the depletion region width
- Why is the reverse saturation current so small?

http://pveducation.org

Reverse Biased p-n junction (breakdown, avalanche current)



In breakdown, electrons can tunnel from the p-type material valence band through the depletion region material to contribute to large negative current flow (electrons to the right through n-type material)



http://pveducation.org

Basic Equations for Solving for the Electric Field, Transport, and Carrier Concentrations: see http://www.pveducation.org/pvcdrom/pn-junction/basic-equations, up through "Solving for Region With Electric Field"

1. **Poisson's equation:**

$$\frac{\partial \vec{E}}{dx} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon}\left(p(x) - n(x) - N_A^- + N_D^+\right)$$

$$\nabla^2 \phi(x, y, z) = -\frac{\rho(x, y, z)}{\varepsilon}$$

$$\frac{d\phi(x)}{dx} = -\mathcal{E}(x)$$

2. **Transport equations:**

$$J_n = q\mu_n n(x)\vec{E} + qD_n \frac{dn(x)}{dx}$$

(first term is drift, second is diffusion)

$$J_p = q\mu_p p(x)\vec{E} - qD_p \frac{dp(x)}{dx}$$

3. **Continuity equations:**

General conditions

$$\frac{dn}{dt} = \frac{1}{q}\frac{\partial J_n}{\partial x} - (U - G)$$

$$\frac{dp}{dt} = \frac{1}{q}\frac{\partial J_p}{\partial x} + (U - G)$$

Under thermal equilibrium and steady state conditions

$$\frac{1}{q}\frac{\partial J_n}{\partial x} = (U - G)$$

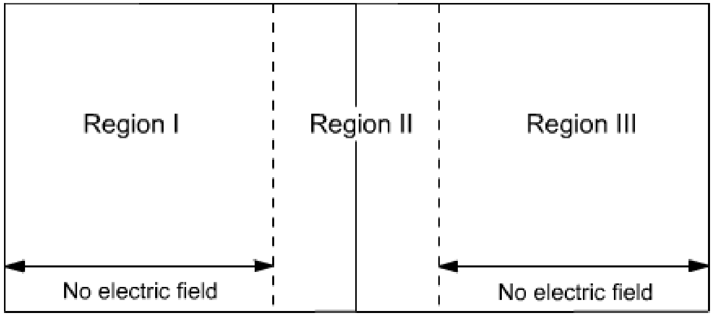
$$\frac{1}{q}\frac{\partial J_p}{\partial x} = -(U - G)$$

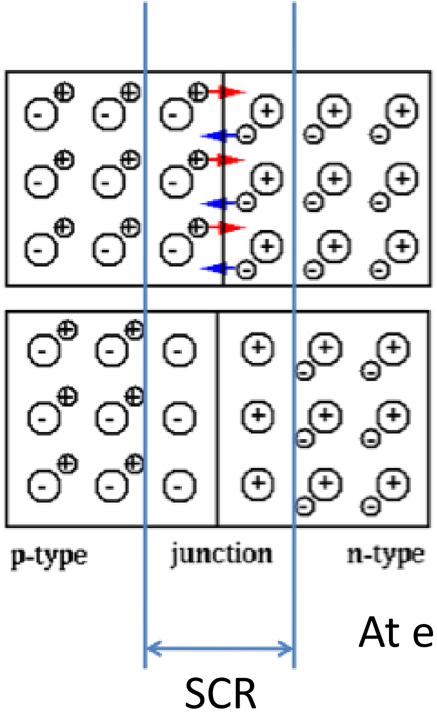
where U and G are the recombination and generation rates in the particular material and depend on the details of the device and may also depend on distance.

General Approach to Solving for the Electric Field, Transport, and Carrier Concentrations

For arbitrary charge distributions, band diagrams, junction types, the equations ***may*** be solved using numerical approaches, and many device simulators are available. Simplifying assumptions include one-dimensionality of the device, and that the **depletion approximation**.

The **depletion approximation** assumes that the electric field in the device is confined to some region of the device, creating a region that has an electric field and regions that do not. This is shown at right for a pn junction, where Regions I and III do not have an electric field (so-called quasi-neutral regions, or QNR) and Region II has an electric field (which is called the space-charge region or the depletion region).





At equilibrium

http://ecee.colorado.edu/~bart/book/carriers.htm

General Procedure using the depletion approximation:

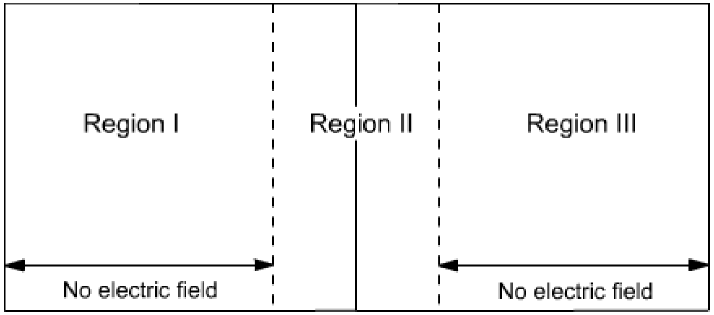
1. Divide the device into regions with an electric field and without an electric field.

2. Solve for electrostatic properties in the depletion region (Region II on the diagram). This solution depends on the doping profile assumed. Here we will restrict the calculations to constant doping profiles.

3. Solve for the carrier concentration and current in the quasi-neutral regions (Regions I and III on the diagram) under steady-state conditions.

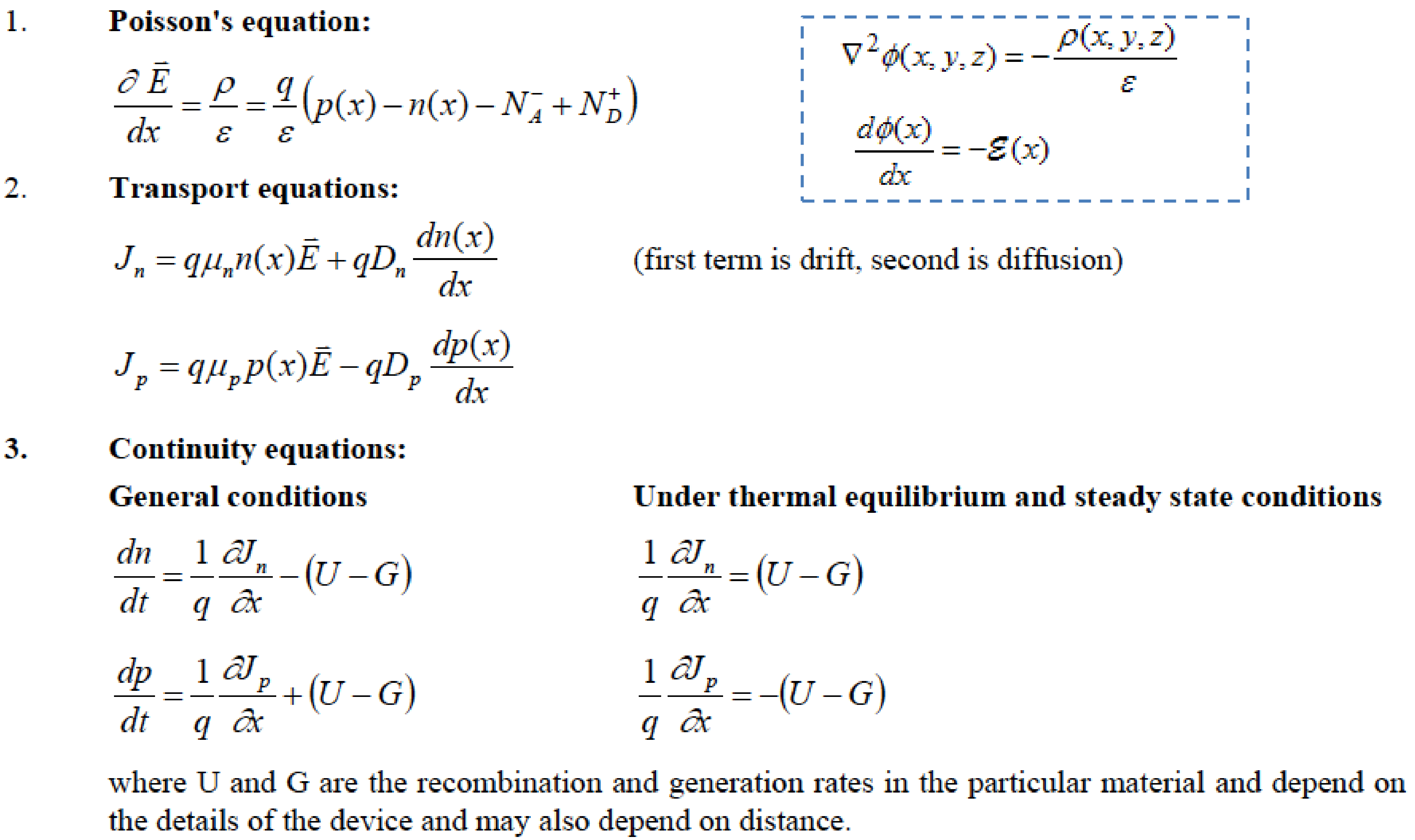
   The steps in this are:
   (a) Determine the general solution for the particular device. The general solution will depend only on the types of recombination and generation in the device.
   (b) Find the particular solution, which depends on the surfaces and the conditions at the edges of the depletion region.

4. Find the relationship between the currents on one side of the depletion region and the currents on the other side. This depends on the recombination/generation mechanisms in the depletion region.



http://www.pveducation.org/pvcdrom/pn-junction/basic-equations

Basic Equations for Solving for the Electric Field, Transport, and Carrier Concentrations



1. **Poisson's equation:**

$$\frac{\partial \vec{E}}{dx} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon}\left(p(x) - n(x) - N_A^- + N_D^+\right)$$

$$\nabla^2 \phi(x, y, z) = -\frac{\rho(x, y, z)}{\varepsilon}$$

$$\frac{d\phi(x)}{dx} = -\mathcal{E}(x)$$

2. **Transport equations:**

$$J_n = q\mu_n n(x)\vec{E} + qD_n \frac{dn(x)}{dx}$$

(first term is drift, second is diffusion)

$$J_p = q\mu_p p(x)\vec{E} - qD_p \frac{dp(x)}{dx}$$

3. **Continuity equations:**

General conditions

$$\frac{dn}{dt} = \frac{1}{q}\frac{\partial J_n}{\partial x} - (U - G)$$

$$\frac{dp}{dt} = \frac{1}{q}\frac{\partial J_p}{\partial x} + (U - G)$$

Under thermal equilibrium and steady state conditions

$$\frac{1}{q}\frac{\partial J_n}{\partial x} = (U - G)$$

$$\frac{1}{q}\frac{\partial J_p}{\partial x} = -(U - G)$$

where U and G are the recombination and generation rates in the particular material and depend on the details of the device and may also depend on distance.

http://www.pveducation.org/pvcdrom/pn-junction/basic-equations

Solving for Region With Electric Field

1. Depletion approximation: the electric field is confined to a particular region.
2. No free carriers (*$n(x)$, $p(x) = 0$) in depletion region.*
3. *We can assume no free carriers since the electric field sweeps them out of the depletion region quickly. No free carriers means (1) transport equations drop out and (2) no recombination or generation, so the continuity equation becomes:*

   $$\frac{1}{q}\frac{\partial J_n}{\partial x} = (U - G) = 0$$

   This means that J_n is constant across the depletion region. Similarly, J_p is also constant across the depletion region.
4. *Abrupt or step doping profile (N_A-, N_D^+ are constant).*
5. *All dopants are ionized $N_A^- = N_A$, $N_D^+ = N_D$).*
6. *One-dimensional device.*

Solution

The only equation left to solve is Poisson’s Equation, with *n(x) and p(x) =0, abrupt doping profile and ionized dopant atoms. Poisson’s equation then becomes:*

$$\frac{\partial \hat{E}}{\partial x} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon}(-N_A + N_D)$$

$$\rho = \begin{cases} -qN_A, & when -x_p \le x \le 0 \\ qN_D, & when\, 0 \le x \le x_n \end{cases}$$

Where $\varepsilon = \varepsilon_0 \varepsilon_s$, ε_0 is the permittivity in free space, and ε_s is the permittivity in the semiconductor and x_p and x_n are the edges of the depletion region in the p- and n-type side respectively, measured from the physical junction between the two materials. The electric field then becomes

$$E = \begin{cases} \int -\frac{qN_A}{\varepsilon} dx = -\frac{qN_A}{\varepsilon} x + C_1, & for -x_p \le x < 0 \\ \int \frac{qN_D}{\varepsilon} dx = \frac{qN_D}{\varepsilon} x + C_2, & for\, 0 \le x < x_n \end{cases}$$

http://www.pveducation.org

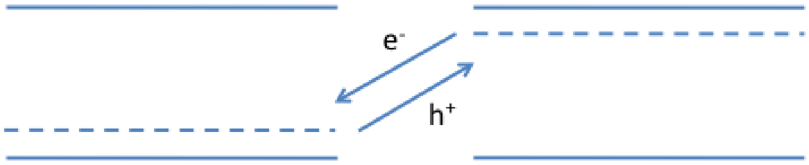
Solution (continued…)

The integration constants C_1 *and* C_2 *can be determined by using the depletion approximation, which states that the electric field must go to zero at the boundary of the depletion regions. This gives:*

$$E(x=-x_p)=0 \quad \Longrightarrow \quad C_1=\frac{-qN_A}{\varepsilon}x_p$$

$$E(x=x_n)=0 \Longrightarrow C_2=-\frac{qN_D}{\varepsilon}x_n$$

Before/during contact

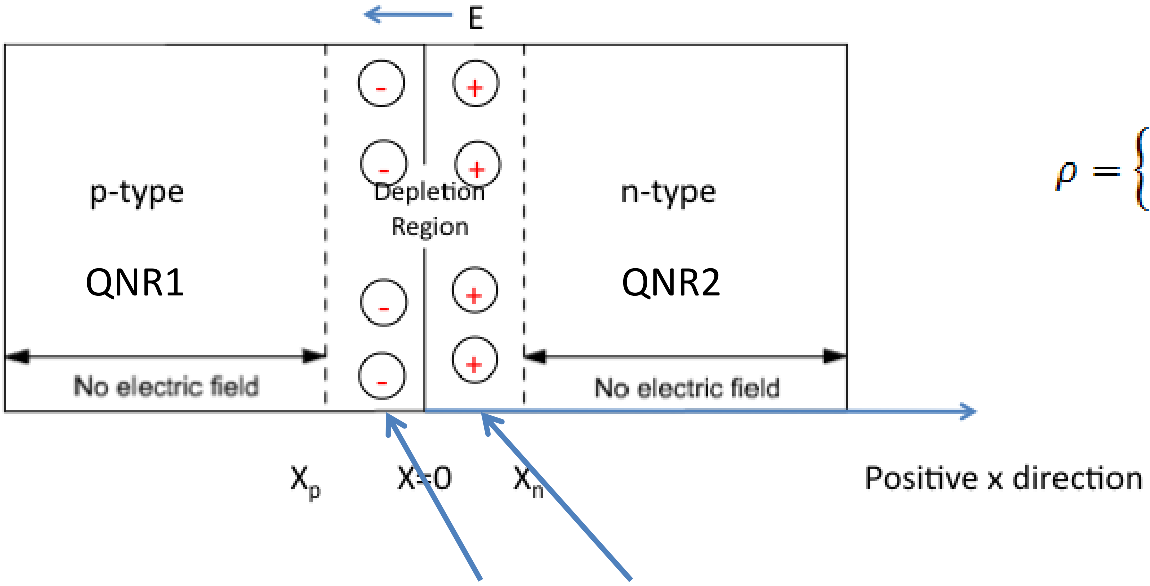


What is the electric field?

$$\frac{\partial \hat{E}}{\partial x} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon}(-N_A + N_D)$$

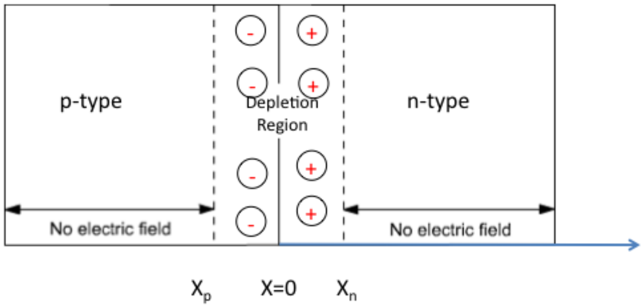
$$\rho = \begin{cases} -qN_A, & when -x_p \le x \le 0 \\ qN_D, & when\ 0 \le x \le x_n \end{cases}$$

At equilibrium, Electric field develops to oppose further charge



- net charge density is zero outside SCR
- p(x) and n(x) = 0 within SCR
- all dopants are ionized, so $N_A^- = N_A$ and $N_D^+ = N_D$

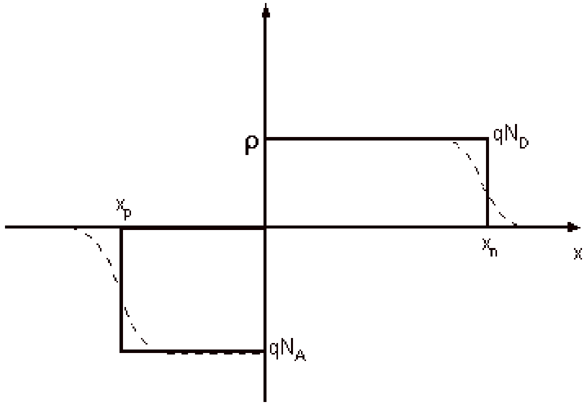
Charge neutrality: $X_pN_A^- = X_nN_D^+$



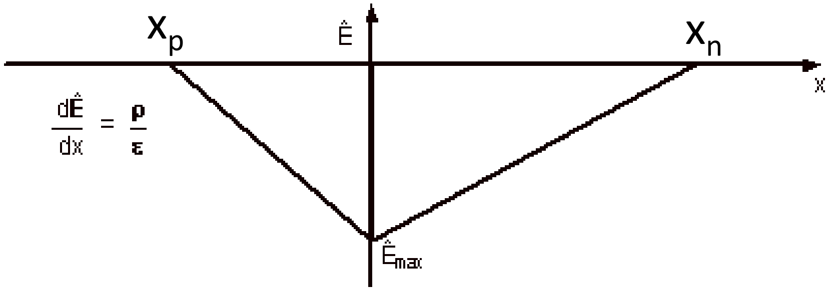
$$E = \begin{cases} \int -\dfrac{qN_A}{\varepsilon}\,dx = -\dfrac{qN_A}{\varepsilon}x + \dfrac{-qN_A}{\varepsilon}x_p & for -x_p \le x < 0 \\ \int \dfrac{qN_D}{\varepsilon}\,dx = \dfrac{qN_D}{\varepsilon}x - \dfrac{qN_D}{\varepsilon}x_n & for\ 0 \le x < x_n \end{cases}$$

The two parts of the solution must give the same value for E when x = 0

so $-N_A x_p = -N_D x_n$, which is the charge neutrality relation written earlier



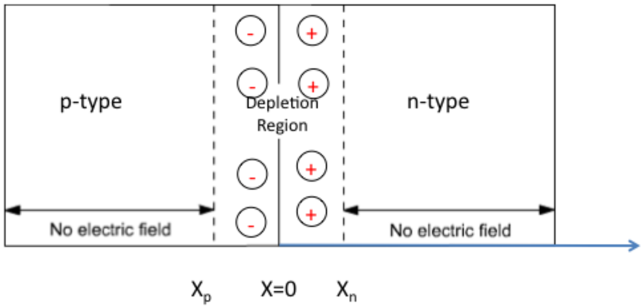
Plots shown for $N_A \neq N_D$



$|E|_{max}$ at x = 0

What is the potential distribution?

- Integrate the electric field over distance.



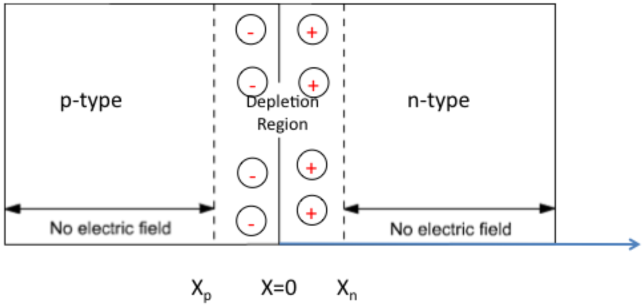
$$E = \begin{cases} \int -\frac{qN_A}{\varepsilon}dx = -\frac{qN_A}{\varepsilon}x + \frac{-qN_A}{\varepsilon}x_p & for - x_p \le x < 0 \\ \int \frac{qN_D}{\varepsilon}dx = \frac{qN_D}{\varepsilon}x - \frac{qN_D}{\varepsilon}x_n & for\ 0 \le x < x_n \end{cases}$$

$$V(x) = \begin{cases} \int -E(x)dx = \int \frac{qN_A}{\varepsilon}(x + x_p)dx = \frac{qN_A}{\varepsilon}\left(\frac{x}{2} + x_p\right)x + C_3, & for - x_p \le x < 0 \\ \int -E(x)dx = \int \frac{qN_D}{\varepsilon}(x_n - x)dx = \frac{qN_D}{\varepsilon}\left(x_n - \frac{x}{2}\right)x + C_4, & for\ \ 0 \le x < x_n \end{cases}$$

Since we are interested in the potential difference, we can set the voltage on the p-type side to be zero, such that at *x= −*x_p*, V=0.*

Thus: $C_3 = \frac{qN_A}{2\varepsilon}{x_p}^2$ and $V(x) = \frac{qN_A}{2\varepsilon}(x + x_p)^2, \quad for\ - x_p \le x < 0$

C_4 may be determined by using the fact that the potential on the n-type side and p-type side are identical at the interface.



$$V(x) = \begin{cases} = \dfrac{qN_A}{\varepsilon}\left(\dfrac{x}{2} + x_p\right)x + \dfrac{qN_A}{2\varepsilon}{x_p}^2 & for - x_p \le x < 0 \\ = \dfrac{qN_D}{\varepsilon}\left(x_n - \dfrac{x}{2}\right)x + C_4 & for \;\; 0 \le x < x_n \end{cases}$$

Thus, at x = 0:

$$V_p(x=0) = \frac{qN_A}{2\varepsilon}{x_p}^2 = V_n(x=0) = \frac{qN_D}{2\varepsilon}\left(x_n - \frac{x}{2}\right)x + C_4$$

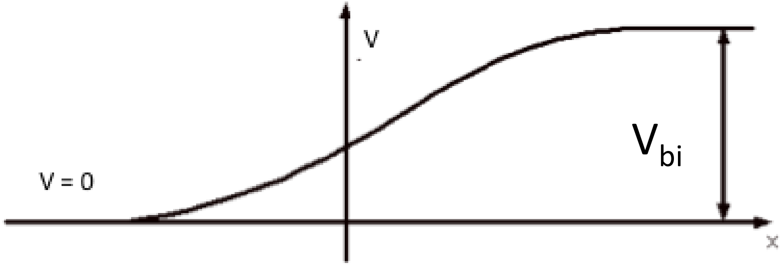
So: $C_4 = \dfrac{qN_A}{2\varepsilon}{x_p}^2$

Overall:

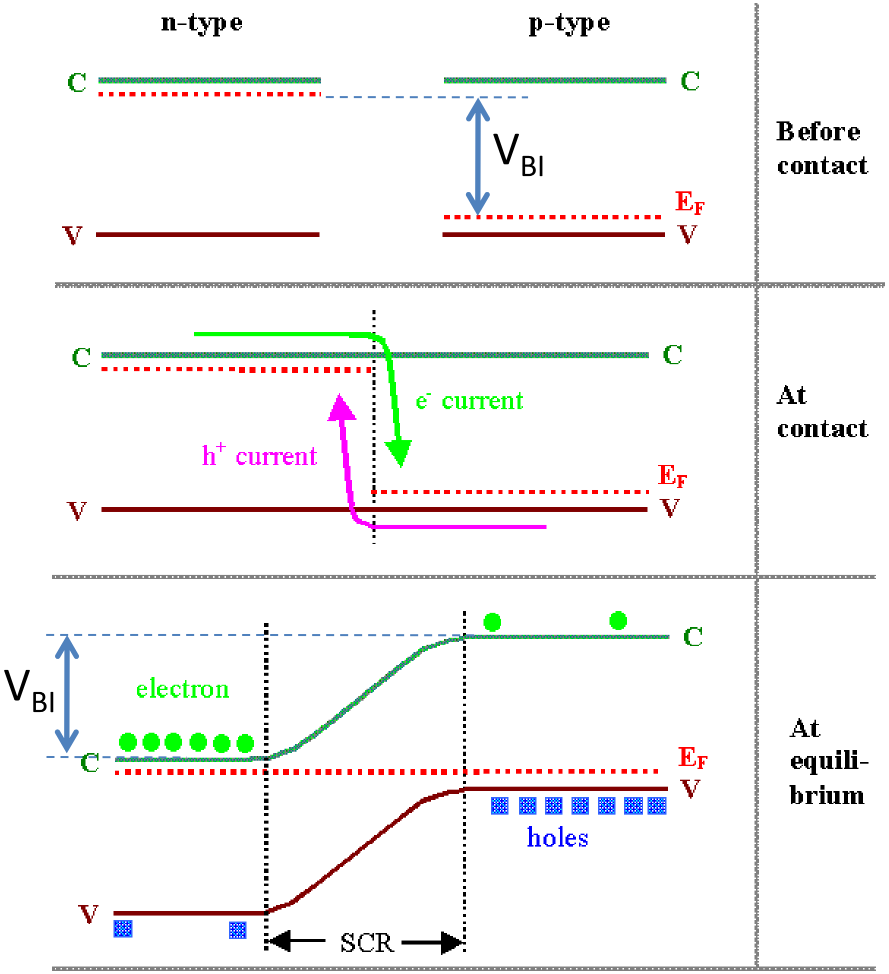
$$V(x) = \begin{cases} \dfrac{qN_A}{2\varepsilon}(x + x_p)^2, & for \; -x_p \le x < 0 \\ \dfrac{qN_D}{\varepsilon}\left(x_n - \dfrac{x}{2}\right)x + \dfrac{qN_A}{2\varepsilon}{x_p}^2, & for \;\; 0 \le x < x_n \end{cases}$$

Voltage is a max at x = x_n:

$$V(x = x_n) = \frac{q}{2\varepsilon}\left(N_D {x_n}^2 + N_A {x_p}^2\right) = V_{bi} \text{ (aka } V_o\text{)}$$



V_o (aka V_{BI}) is the difference between the Fermi Levels in the two contacting “bits”



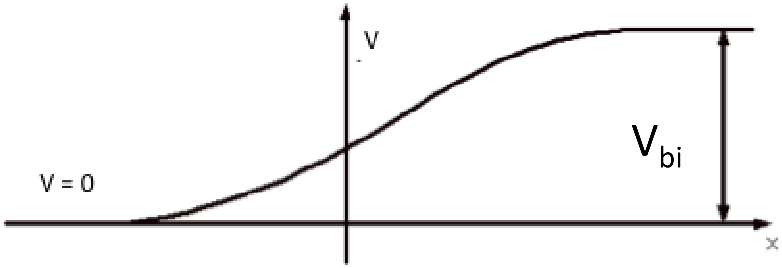
Electrons in the two bits have different electrochemical potentials (i.e. different E_f’s)

Charge transfer occurs at contact (electron go down from the vacuum level, holes go “up”)

At equilibrium, there is no net transport (E_f is constant throughout the device)

H. Föll: http://www.tf.uni-kiel.de/matwis/amat/semi_en/kap_2/backbone/r2_2_4.html

$$V_{bi} = \frac{q}{2\varepsilon}\left(N_D {x_n}^2 + N_A {x_p}^2\right)$$



Using the condition for charge neutrality:

$$N_A x_p = N_D x_n$$

We can determine the edges of the DR in terms of V_o:

$$x_n = \left[\frac{2\varepsilon V_0}{q}\frac{N_A}{N_D(N_A + N_D)}\right]^{\frac{1}{2}} \quad \text{and} \quad x_p = \left[\frac{2\varepsilon V_0}{q}\frac{N_D}{N_A(N_A + N_D)}\right]^{\frac{1}{2}}$$

Which gives the Depletion Width, W:

$$W = x_n + x_p = \sqrt{\frac{2q}{\varepsilon}\frac{V_0}{\left(\frac{1}{N_A} + \frac{1}{N_D}\right)}}$$

Or, x_p and x_n in terms of W:

$$W = \left[\frac{2K_s\epsilon_0}{q}\left(\frac{N_A + N_D}{N_A N_D}\right)(V_{bi} - V)\right]^{\frac{1}{2}}$$

From wiki

$$x_p = W\frac{N_D}{N_A + N_D} \qquad x_n = W\frac{N_A}{N_A + N_D}$$