Кинетика процессов в конденсированных фазах и на межфазных границах.

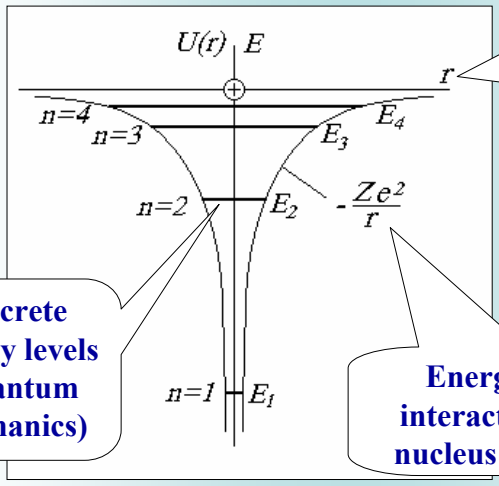
Границы раздела и кинетика реакций на полупроводниковых электродах.

Lecture 1. What are Semiconductors? Metal/Semiconductor and Semiconductor/Solution Interface. Space Charge.

Dr. O.A. Semenikhin

МГУ-2017

Energy Levels of An Isolated Atom



Distance between the nucleus and the electron

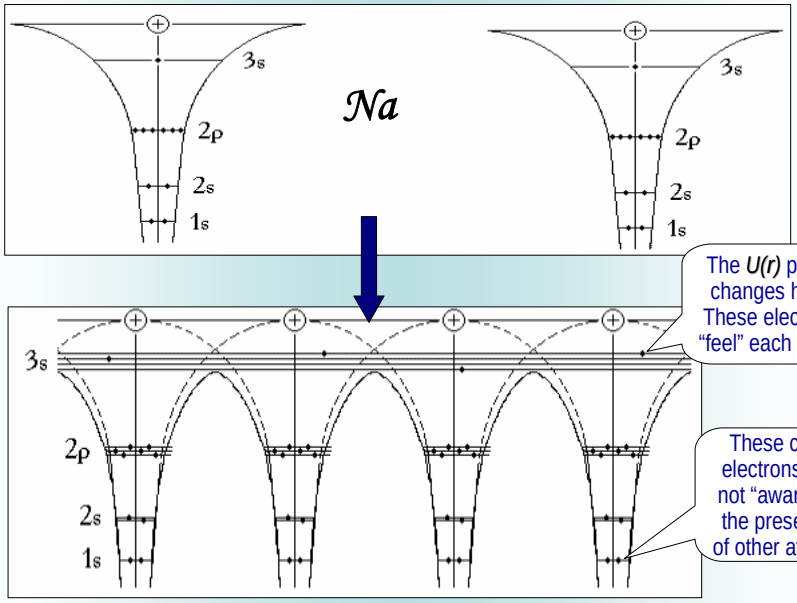
Discrete energy levels (quantum mechanics)

Energy of Coulomb interaction between the nucleus and the electron

2

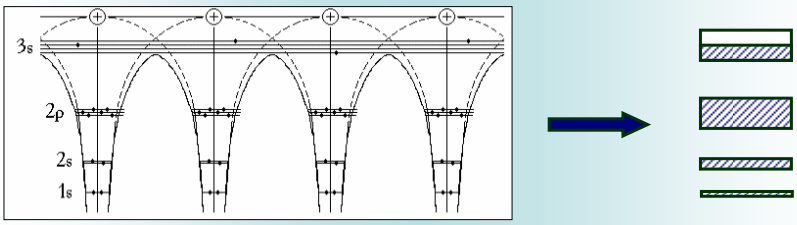
http://ktf.krk.ru/courses/foet/

Energy Levels of Interacting Atoms



3

Energy Levels of Interacting Atoms: Orbitals turn into Bands



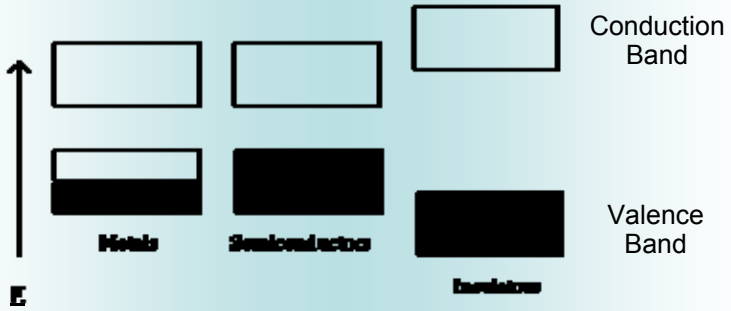
Closed shells -> filled bands. Non-closed shells -> half-filled bands!

Note that the closer we bring the atoms, the stronger the interaction between them, and the greater the splitting of electron levels.

If we bring the atoms too close, the increase in the electron energy becomes too high. This is one of the origins of the repulsive forces between atoms.

4

Band Structure of Solids: Metals, Semiconductors, Insulators

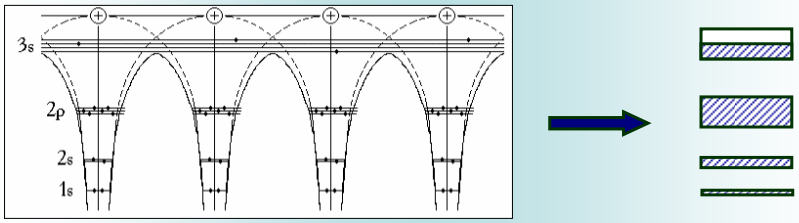


- As dependent on the band arrangement, we can have one of the situations above: a semi-filled band; a filled and an empty band separated with a narrow gap; a filled and an empty band separated with a wide gap.
- These cases are known as metals, semiconductors and insulators, respectively.

5

http://matse1.mse.uiuc.edu/~tw/sc/prin.html

Energy Levels of Interacting Atoms: Metals



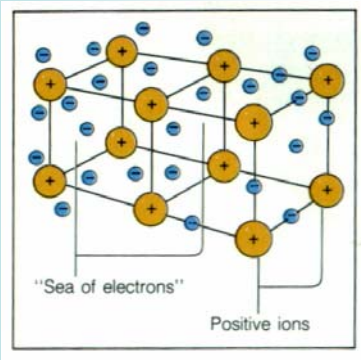
➢When the outmost electron shell forms a semi-filled band, as is the case with metals, electrons can travel freely within this band. There is no energy barrier to overcome to move an electron within a band, and the bands extend throughout the whole lattice.

➢It is said that the electrons form an "electron gas" in the metal. Sometimes this situation is associated with formation of a "metallic bond", whereby all positively charged lattice ions are held together by mutual attraction with negatively charged electrons of the electron gas.

6

Band Structure of Solids: Metals

- Electrons in metals: the sea of electrons or electron gas. These exotic substances are just free electrons moving in the periodic field set up by the positive lattice ions.



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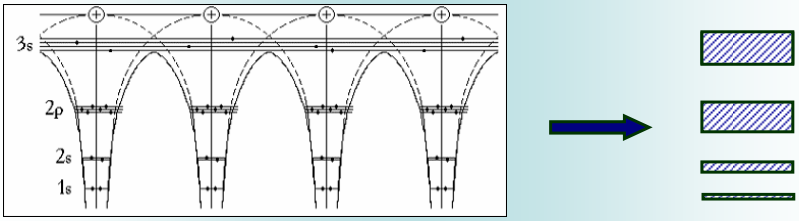
http://mws.mcallen.isd.tenet.edu/mchi/ipc/ch07htm/ch07sec4.htm

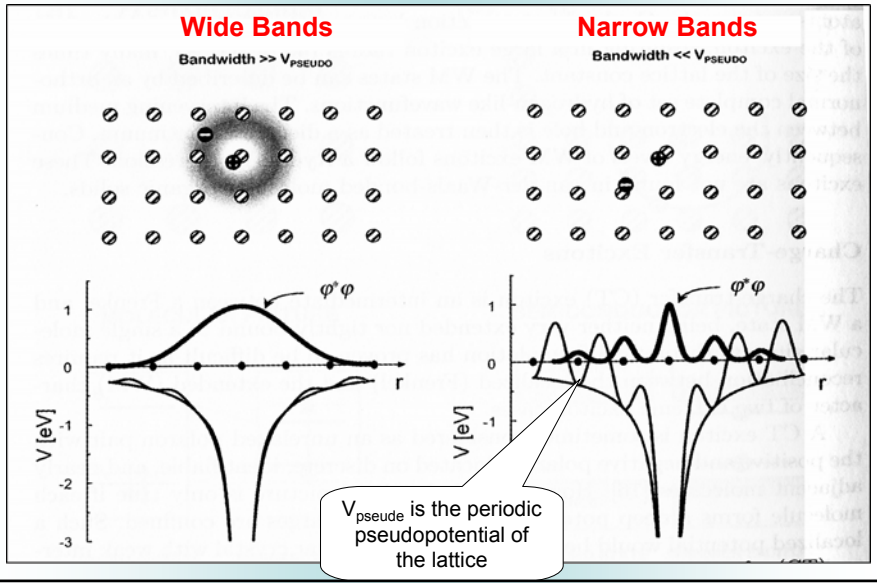
Energy Levels of Interacting Atoms: Covalent Solids, Mott Insulators



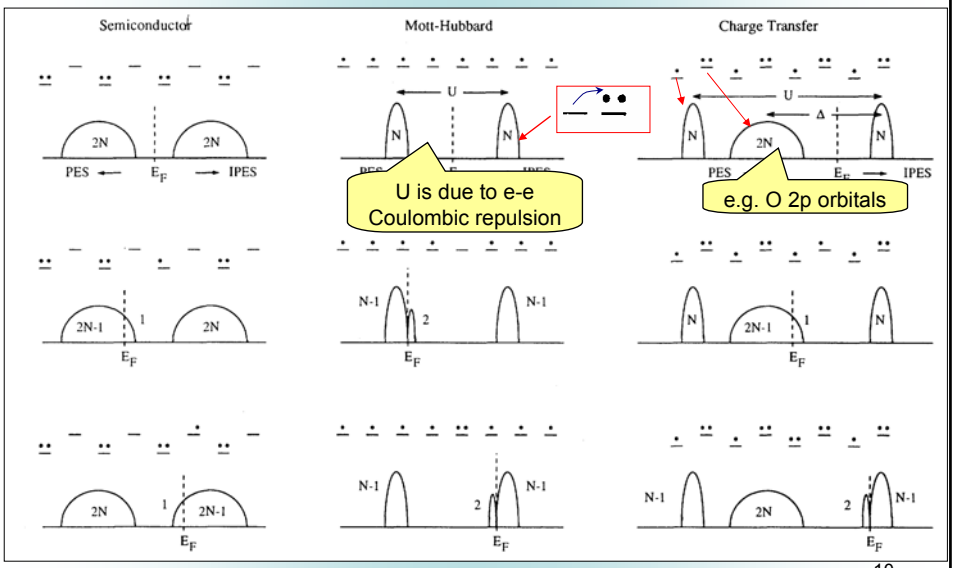
- However, if the interaction is not strong enough to form extended bands (as is the case with 2p electrons above), the electrons remain localized on the specific atoms. This means that to move an electron, one needs to promote it to an upper empty band first. There is an energy barrier.
- The valence electrons in this case can still form covalent bonds between adjacent atoms, as was the case in single molecules. This means that the electron clouds are distorted by the interaction so that the electrons are "shared" between neighboring atoms, but not among all atoms of the lattice. The resulting materials are called covalent solids or Mott insulators.

8

The Effect of Electron-Lattice Interaction (Localized/Strongly Correlated Electrons)



Doped/Undoped Mott-Hubbard Insulators



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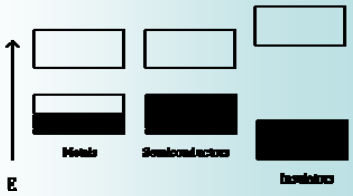
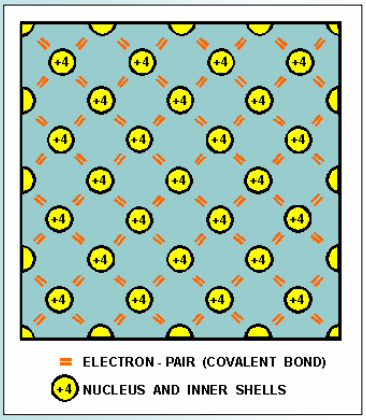
M. B. J. MEINDERS, H. ESKES, AND G. A. SAWATZKY, PHYSICAL REVIEW B, VOL. 48, p. 3916

Band Structure of Solids: Semiconductors and Insulators



- In semiconductors and especially insulators, all valence electrons form covalent bonds.
- Making an electron mobile would require breaking the bond. This is the origin of the energy gap.
- This also demonstrates the fundamental difference between metallic and covalent bonds.

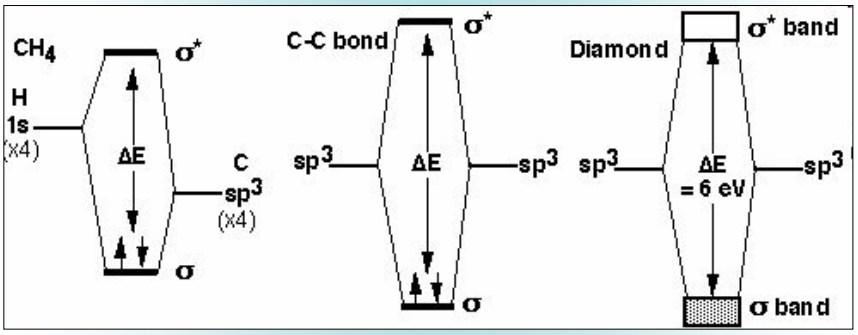


Si lattice

11

http://modernworldview.net/covalent/

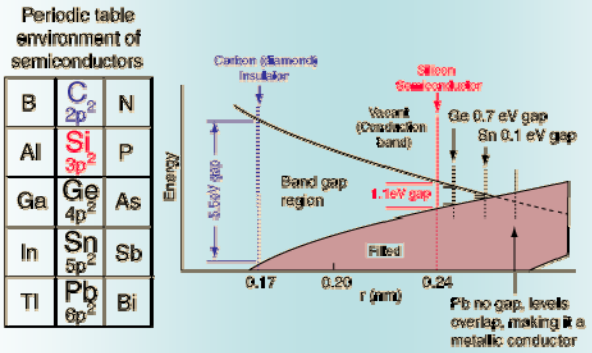
Energy Levels of Interacting Atoms: Diamond



➢For 2 C atoms, mixing of two σ sp^3 orbitals produces σ bonding and σ* antibonding levels with a large energy separation. In diamond, which is a crystal built from C sp^3 atoms, the σ and σ* levels undergo some degree of broadening to form bands; however, the energy gap remains very wide. Diamond is an insulator.

12

Band Structure and Interatomic Distances

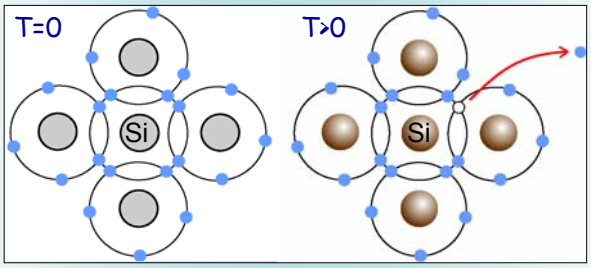


- The structure of the outermost (valence) electrons is qualitatively similar for carbon, silicon, germanium and tin. However, C (diamond) is an insulator, Si and Ge are semiconductors, and Pb is a metal.
- The stronger the atoms interact, the shorter the interatomic distance and the greater the splitting of the energies of electrons (and the bandgap).

13

Images: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/bandper.html#c1;

Intrinsic Semiconductors

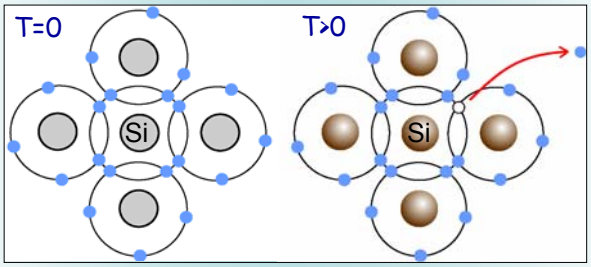


- Let us consider undoped Si. At T=0, all valence electrons form covalent bonds between Si atoms. There are no free electrons.
- However, if we increase the temperature, an electron could gain enough energy to leave its bonding orbital and become a free charge carrier. In doing so, the electron leaves behind a vacant energy level.
- This level can be filled by a nearby valence electron. In doing so, it again leaves behind a vacant energy level, but now at a neighbouring Si atom.
- This process is absolutely equivalent to the movement of a free positive charge carrier. The latter is called a hole (=an absence of an electron).

14

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html#c5

Intrinsic Semiconductors



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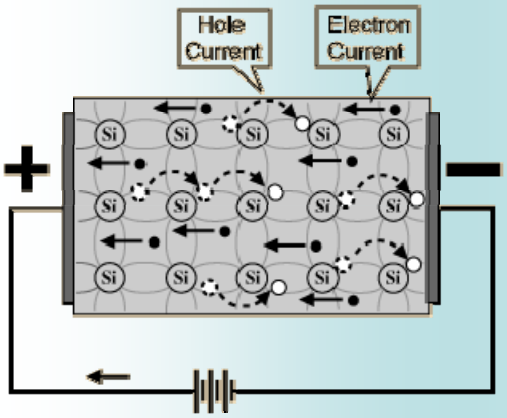
15

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html#c5

Charge Carriers in Intrinsic Semiconductors: Electrons and Holes

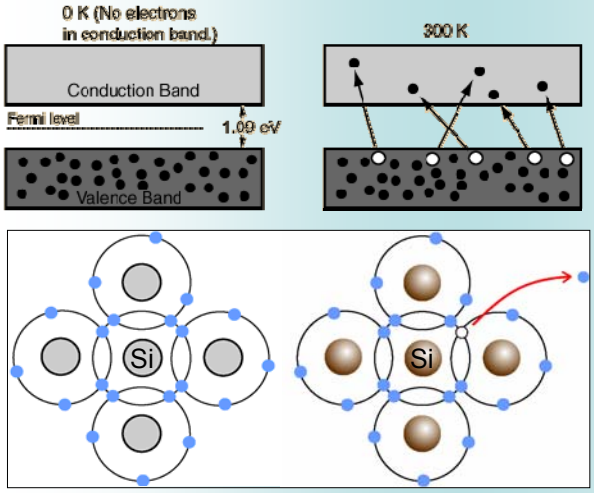


- If we apply voltage to an intrinsic semiconductor, we observe two types of currents: the hole current and the electron current.
- Semiconductors, unlike metals, have two different types of mobile charge carriers: electrons and holes.

16

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/intrin.html#c1

Intrinsic Semiconductors

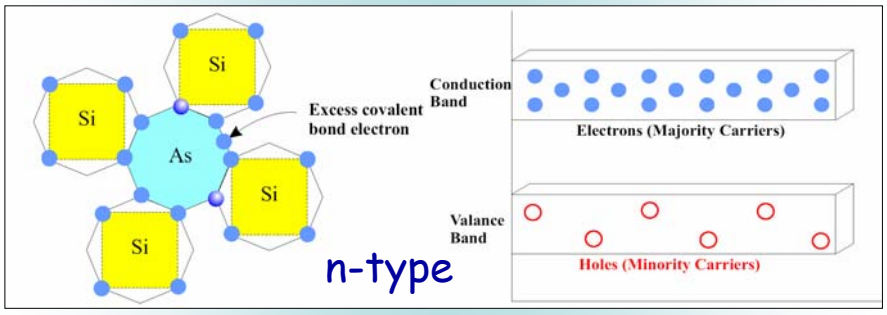


- Free electrons are generated in the conduction band, free holes are found in the valence band.
- On the contrary, bound electrons are in the valence band and bound holes are in the conduction band. The energy for holes goes from top to bottom.
- Intrinsic semi-conductors always have equal # of electrons and holes.

17

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/band.html#c5

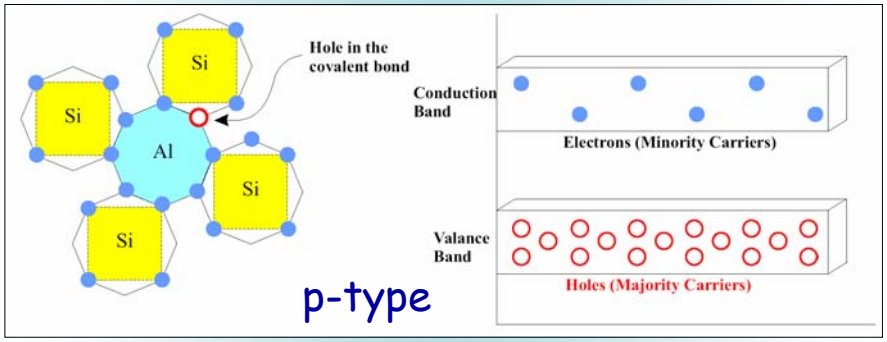
Doped Semiconductors



- To form a doped semiconductor, we add to intrinsic semiconductors special additives called dopants. Dopants substitute native atoms in the Si lattice. However, because the electronic structure of dopants differs from that of Si, the properties of the whole phase are changed.
- In this example, we add arsenic. As has 5 valence electrons rather than 4. Therefore, we have one excess electron per As atom that has nowhere to go except the conduction band (the valence band is full).
- Therefore, we now have more electrons than holes. Electrons are called here majority carriers. We have an n-type semiconductor.

18

Doped Semiconductors



- In this example, we add aluminum. Al has 3 valence electrons rather than 4. Therefore, we have one less electron per Al atom. We have made a mobile hole in the valence band.
- We have here a p-type semiconductor with holes as majority carriers.
- Note that in both cases we also have small number of minority carriers. They are generated in the same way as in intrinsic semiconductors. However, because the majority and minority carriers should be in equilibrium, an increase in the doping level (the # of majority carriers) decreases the concentration of minority carriers, and vice versa.

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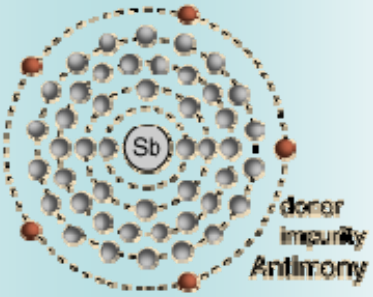
Other Dopant Impurities

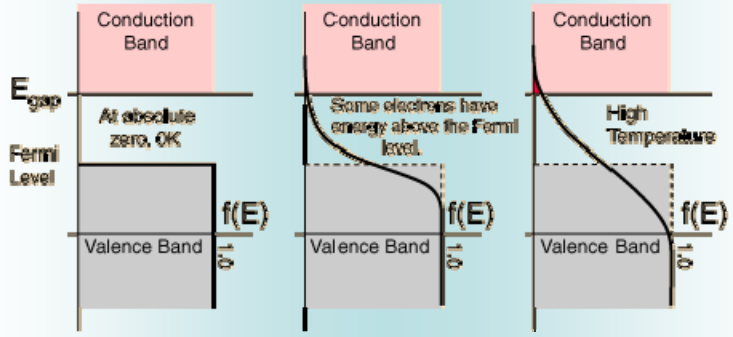
Antimony
Arsenic
Phosphorous



Boron
Aluminum
Gallium

20

Fermi Energy in Intrinsic Semiconductors

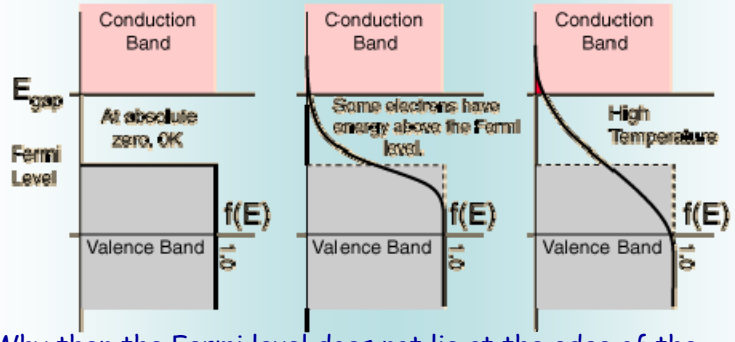


- The Fermi level in an intrinsic semiconductor lies not at the edge of the valence band (the topmost filled energy level) but halfway between the valence and conduction bands in the band gap.
- There are no allowed energy levels below the Fermi level down to the VB edge so at T=0K the highest energy of real electrons will be the top of the valence band.

21

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/fermi.html#c2

Fermi Energy in Intrinsic Semiconductors



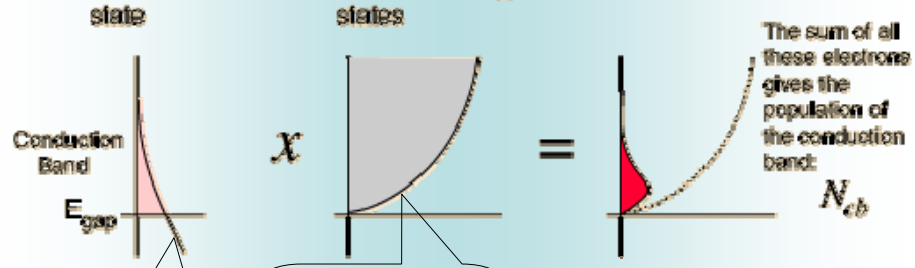
- Why then the Fermi level does not lie at the edge of the valence band?
- If we increase the temperature, we will excite some electrons into the conduction band leaving holes in the valence band.
- The probability of finding an electron in the conduction band and finding a hole in the valence band should be described by the same Fermi-Dirac distribution.
- In intrinsic semiconductors the # of electrons and holes are equal; therefore, the Fermi energy lies in the mid-gap.

22

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/fermi.html#c2

Population of Conduction Band for a Semiconductor

Probability of occupation of state x Number of available energy states $=$ Actual population of conduction band.



The "tail" of the Fermi-Dirac distribution

Density of states inside the band vs. energy

$$n^e = \int_{Ec}^{E} D(E) \cdot f(E,T) \cdot dE$$

23

Image: http://hyperphysics.phy-astr.gsu.edu/hbase/solids/fermi.html#c4

Concentrations of Majority and Minority Carriers In Respective Zones

$$n^e = \int_{Ec}^{E} D(E) \cdot f(E,T) \cdot dE$$

$$n^h = \int_{E}^{Ev} D(E) \cdot [1 - f(E,T)] \cdot dE$$

The probability of having a hole on a certain level is 1 minus probability of having there an electron.

The probability of having either electron or hole is 1 ☺

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

24

Concentrations of Majority and Minority Carriers In Respective Zones

- For relatively wide band gap semiconductors we can replace the Fermi-Dirac distribution with a simpler Boltzmann distribution.
- We can also simplify our equations by replacing true energy-dependent density of states with an effective energy-independent value $\mathcal{N}_{eff}$ and integrating from the band edge to infinity.
- We obtain:

$$n^e = N^e_{eff} \cdot \exp(-\frac{E_C - E_F}{k_B T}) \qquad n^h = N^h_{eff} \cdot \exp(-\frac{E_F - E_V}{k_B T})$$

- The carrier concentration (and hence, conductivity) exponentially decreases with an increase in the separation between the Fermi level and the band edges, that is, with an increase in the band gap width.
- As a result, wide band gap semiconductors have extremely low conductivity, while small band gap ones can be even considered half-metals.

25

Concentrations of Majority and Minority Carriers and the Position of Fermi Level

For an intrinsic semiconductor, $n^e = n^h = n_0$

If we also assume that $N^e_{eff} = N^h_{eff} = N_{eff}$,

we obtain:

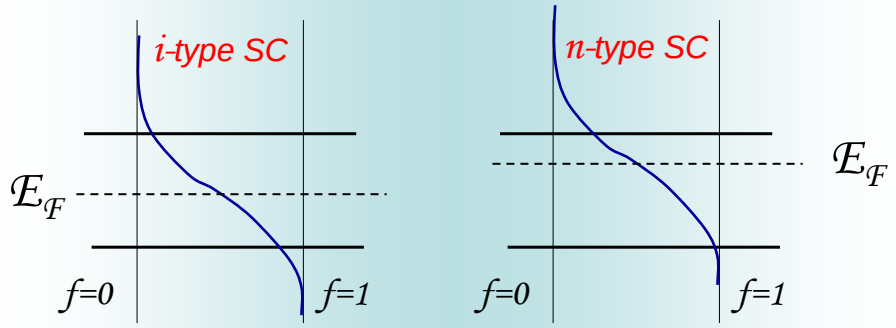
$$N_{eff} \cdot \exp(-\frac{E_C - E_F}{k_B T}) = N_{eff} \cdot \exp(-\frac{E_F - E_V}{k_B T})$$

$$-E_C + E_F = -E_F + E_V \qquad E_F = \frac{E_C + E_V}{2}$$

For an intrinsic semiconductor the Fermi level indeed lies in the middle of the bandgap ☺

26

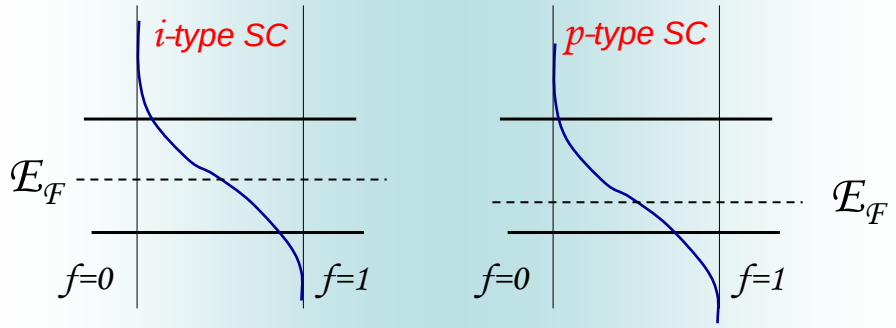
Fermi Energy in Doped Semiconductors



- In doped semiconductors the # of electrons and holes are not equal.
- To preserve the Fermi-Dirac distribution, the Fermi energy moves closer to the band of the majority carriers.
- It is also highly logical: to make a semiconductor material n-type, we add a dopant with an excess of electrons. Therefore, the Fermi energy should go up as compared to the undoped semiconductor (the level of the Fermi sea should increase to accommodate the extra electrons).

27

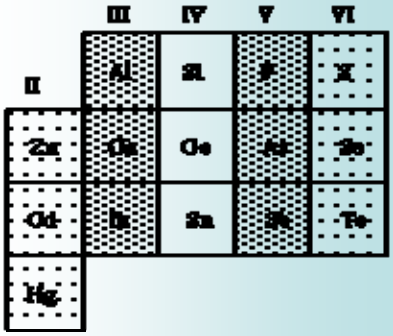
Fermi Energy in Doped Semiconductors



- Obviously, the same applies to a p-type semiconductor as well.
- To make a semiconductor material p-type, we add a dopant with a deficit of electrons. We have removed some electrons but left the number of available levels unchanged. The Fermi energy should go down as compared to the undoped semiconductor (the level of the Fermi sea decreases).

28

Other Types of Semiconductors

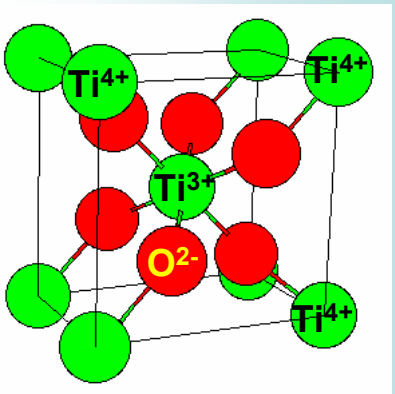


- So far we have talked only about Si. However, there are other types of semiconductors.
- For instance, GaAs will be isoelectric to Si-Si (3e+5e=4e+4e). Therefore, GaAs should be a semiconductor as Si.
- Actually, it is a better semiconductor (although much more expensive ☺). It feature very high carrier mobilities and is used in ultra-high frequency electronics.
- Si and Ge are called elemental semiconductors. GaAs, CdTe and similar materials are called compound semiconductors.
- Materials like GaAs are also called III-V semiconductors.
- How would we call ZnSe?

29

Image:http://matse1.mse.uiuc.edu/~tw/sc/prin.html

Oxide Semiconductors



- Yet another very important class of semiconductors are metal oxides.
- For example, TiO_2 is a wide-band-gap n-type semiconductor
- The reason for its n-type conductivity is the presence of a small number of Ti^{3+} rather than Ti^{4+} ions. A Ti^{3+} ion has an extra electron ☺
- Similarly, iron (III) oxide is an n-type semiconductor due to the presence of Fe^{2+} ions.
- On the contrary, uranium dioxide UO_2 is a p-type semiconductor due to the presence of U^{6+}. So is Cu_2O because of…yes, Cu^{2+} ☺

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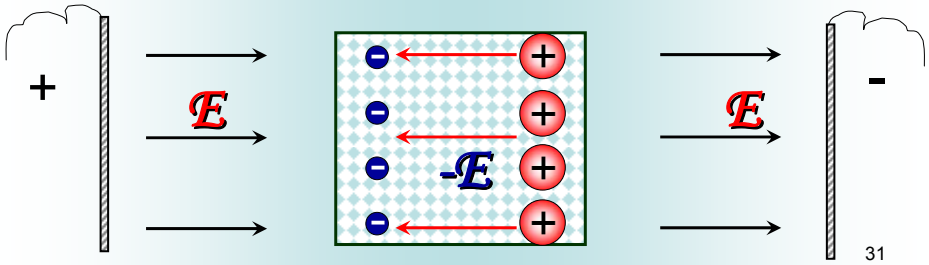
Image: http://cst-www.nrl.navy.mil/lattice/struk/c4.html

Materials In External Electric Field

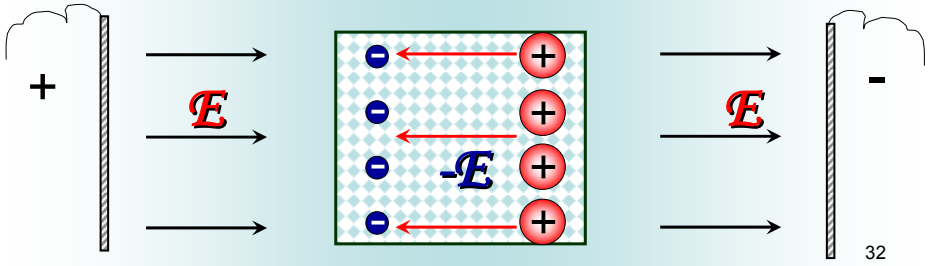
- An interesting and important question is what would happen if we put a metal, a semiconductor, or an insulator in an external electric field, or the field from the charged surface of another phase being in contact with the one in question.
- If we do this with a material that has mobile charge carriers, like a metal or a semiconductor, these carriers will move in the field.
- This will modify the charge distribution inside the material.



31

Materials In External Electric Field

- If a material has plenty of mobile charge carriers, they will be able to move to the interfaces until they set up their own electric field that will cancel the external field. This is the case for metals.
- It is said that electric field cannot penetrate metals. Metals are good shields against electric and magnetic fields.



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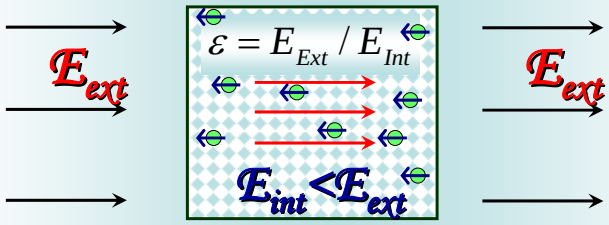
Non-metals In Electric Field

- If we put into an external electric field a material that has no mobile charges, like an insulator, there will be no charge redistribution to set up the counter-field.
- The material cannot shield the external electric field.
- The only thing that can happen with insulators is the occurrence of induced dipoles (polarization) and re-orientation of existing dipoles in the external field.
- These processes reduce (but not cancel out) the field inside the phase. This change is characterized by the dielectric constant ε.



33

Semiconductors. Debye Length.

- So we have seen that everything depends on whether or not there are mobile charge carriers in the material.
- We have seen that the electric field cannot penetrate into metals and easily penetrate into insulators.
- However, how about semiconductors? There are mobile charge carriers in semiconductors; just their concentration is smaller than in metals. Can electric field penetrate into semiconductors?
- Intuitively, we can say that in these cases the field can penetrate into these materials…to a certain length.
- And that is right, and this length is called the Debye length.

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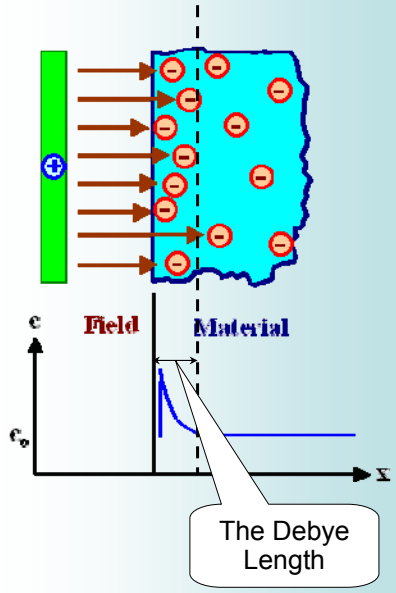
Debye Length



- When we put a material with a bulk concentration c_0 of mobile charge carriers into external electric field, charge redistribution occurs.
- In the example shown on the left, mobile negative charges (probably, electrons, but maybe also anions ☺) move towards the interface.
- If we have several types of mobile charge carriers, they all redistribute according to their charge, but the outcome will be the same: an excess net negative charge at the interface.
- This negative charge will screen the external field so it will be completely cancelled in the bulk beyond the Debye length, which is sometimes also called Debye screening length.

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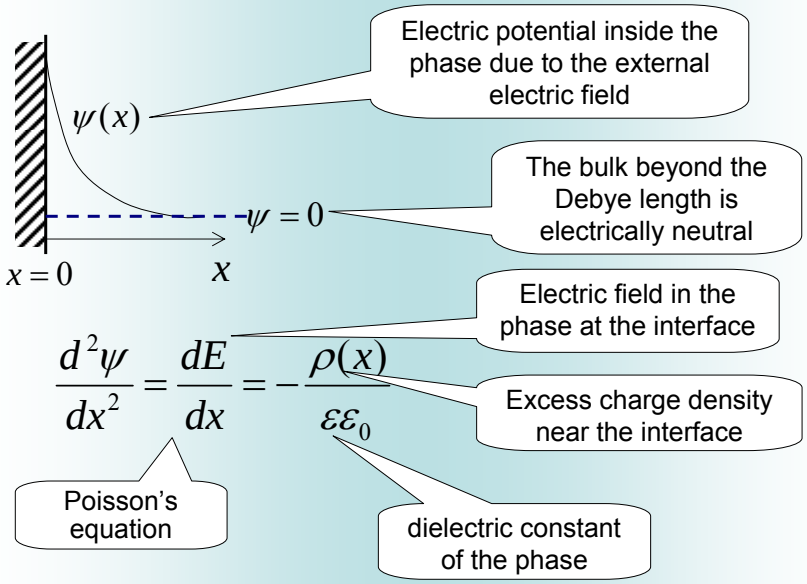
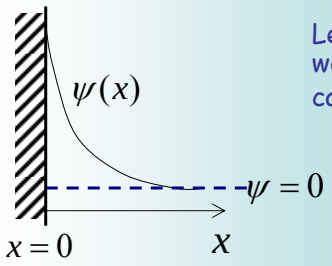
Calculating the Debye Length



36

Calculating the Debye Length - Insulators



Let's check how the Poisson's equation works for insulators (no mobile charge carriers), charge density $\rho(x)$ is zero.

$$\frac{d^2\psi}{dx^2} = \frac{dE}{dx} = -\frac{\rho(x)}{\varepsilon\varepsilon_0} = 0$$

Therefore,

$$\frac{dE}{dx} = 0; E = const; \Delta\psi = E \cdot \Delta x; E = \frac{\Delta\psi}{\Delta x}$$

The electric field in an insulator is constant and proportional to the applied voltage.

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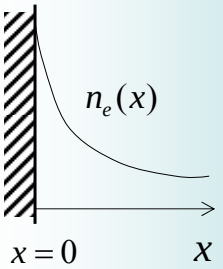
Calculating the Debye Length - Semiconductors



Let's suppose for simplicity that the only mobile charge carriers are electrons. They obey Boltzmann's distribution in the electric field $\Psi(x)$ and their bulk concentration is n_0.

$$\rho(x) = -e_0 \cdot n_e(x)$$

Electrons are negatively charged

Elementary charge

Concentration of electrons

Field-dependent concentration. Follows Boltzmann's distribution

$$n_e(x) = n_0 \exp\left(\frac{e_0\psi(x)}{k_B T}\right)$$

Bulk electron concentration

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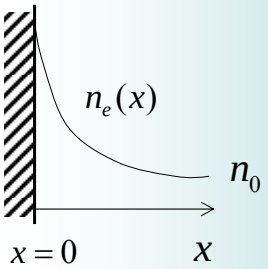
Calculating the Debye Length



If $\frac{e_0\psi(x)}{k_BT} << 1$

Surface excess is small compared to the bulk electron concentration. The external field is not very strong, or there are too many electrons ☺

$$\exp\left(\frac{e_0\psi(x)}{k_BT}\right) \approx 1 + \frac{e_0\psi(x)}{k_BT}$$

Taylor expansion

$$n_e(x) = n_0 \exp\left(\frac{e_0\psi(x)}{k_BT}\right) \approx n_0 + \frac{n_0 e_0\psi(x)}{k_BT}$$

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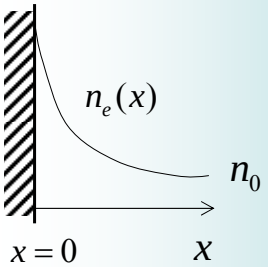
Calculating the Debye Length



$$n_e(x) \approx n_0 + \frac{n_0 e_0\psi(x)}{k_BT}$$

Constant

Potential-dependent term

$$\frac{d^2\psi(x)}{dx^2} = \frac{dE}{dx} = +\frac{e_0 n_0}{\varepsilon\varepsilon_0} \cdot \frac{e_0\psi(x)}{k_BT}$$

Electrons are "-"vely charged. Therefore, we have "+" rather than "-"

This is the Modified Poisson-Boltzmann equation.
Note that the electric field is no longer constant!!!

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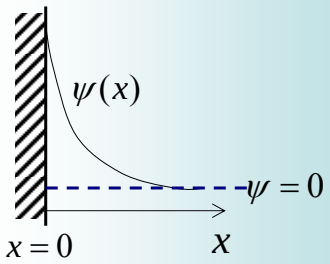
Calculating the Debye Length



$$\frac{d^2\psi(x)}{dx^2} = \frac{e_0^2 n_0 \psi(x)}{\varepsilon\varepsilon_0 k_B T}$$

$$\frac{d^2\psi(x)}{dx^2} = k^2 \cdot \psi(x)$$

$$k = \left[\frac{e_0^2 n_0}{\varepsilon\varepsilon_0 k_B T}\right]^{\frac{1}{2}}$$

$$\psi(x) = const \cdot \exp(-kx) = const \cdot \exp(-\frac{x}{L_D})$$

Debye length, L_D, is the length at which the electric potential induced by the external field decreases by a factor of e=2.71828.

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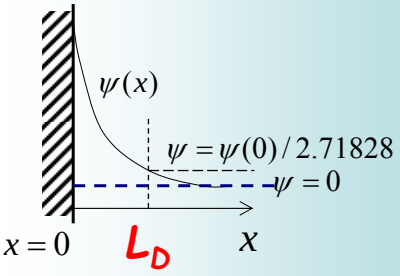
Calculating the Debye Length



$$\psi(x) = const \cdot \exp(-\frac{x}{L_{D_1}})$$

$$L_D = 1/k = \left[\frac{\varepsilon\varepsilon_0 k_B T}{e_0^2 n_0}\right]^{\frac{1}{2}}$$

- The electric potential induced by the external field exponentially decays from the surface into the bulk.
- The Debye screening length determines the characteristic distance of the potential decay. Virtually no electric field exists in the phase beyond L_D.
- L_D depends on the concentration of free charge carriers inside the phase. The higher the carrier concentration, the smaller the Debye length.

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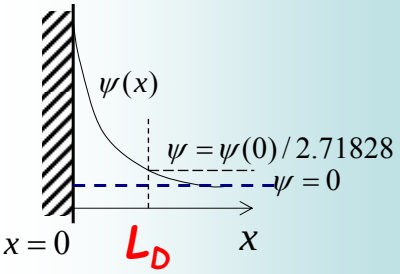
Estimating the Debye Length



$$\psi(x) = const \cdot \exp(-\frac{x}{L_D})$$

$$L_D = 1/k = \left[\frac{\varepsilon\varepsilon_0 k_B T}{e_0^2 n_0}\right]^{\frac{1}{2}}$$

In heavily doped semiconductors, n_0 is of the order of 10^{18} cm^{-3} (10^{24} m^{-3} ☺). For doped Si (ε=12) at T=300K, the Debye length can be estimated as:

$$L_D \cong \left[\frac{12 \times 8.85 \cdot 10^{-12} \times 1.38 \cdot 10^{-23} \times 300}{(1.6 \cdot 10^{-19})^2 \times 10^{24}}\right]^{\frac{1}{2}} \approx 4 \cdot 10^{-9} m$$

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Space-Charge Region

- The region within the semiconductor where there is an electric field is also called a space-charge region. Normally materials are electrically neutral, that is, there is no net charge. However, for semiconductors in the external electric field this is no longer true and space charge is formed at the contacts.
- Outside the space-charge region the semiconductor remains electrically neutral. This region is called quasi-neutral region (quasi because electroneutrality can be slightly disturbed by the current flowing through the semiconductor).
- The width of such a space-charge region L_{sc} is determined by the properties of a semiconductor and the applied voltage $\Delta\psi$. It can be found by solving the modified Poisson-Boltzmann equation with appropriate boundary conditions. We will go through the derivation later but first let us look into how the space charge is formed and what kinds of space charge are found at semiconductor interfaces.

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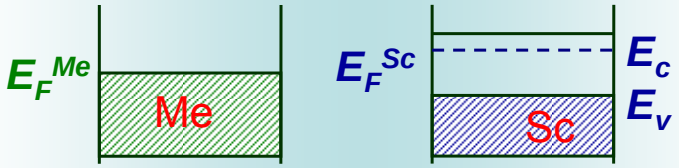
Schottky Junction

$\bar{\mu}_e^{Me} \neq \bar{\mu}_e^{Sc}$



➢Let us consider several practical cases of space charge formation. We may start with a very simple case of bringing an n-type semiconductor in contact with a metal so that an electronic equilibrium will be established.

➢Let's assume that the Fermi level of metal before contact is lower than that of semiconductor.

➢Upon contact, electrons will flow from metal to semiconductor. The interface will be charged.

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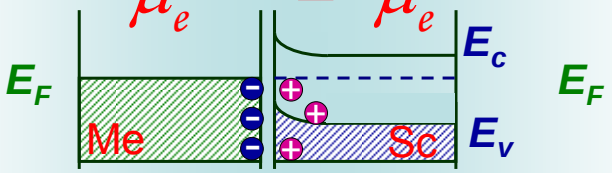
Schottky Junction

$\bar{\mu}_e^{Me} = \bar{\mu}_e^{Sc}$



- The surface of metal is charged negatively. It repulses the electrons in semiconductor from the interface. Since electrons are majority carriers, the resulting space-charge layer is called a depletion layer.
- Another results in a change in the electrostatic energy of electrons near the interface, in particular, in the energies of the edges of the valence and conduction bands. This is called band bending.
- Where the bands are bent, there exists an electric field in the semiconductor. Therefore, the region with band bending is the space charge region. Outside the space charge region the bands are flat. There is no electric field. This is the quasi-neutral region.

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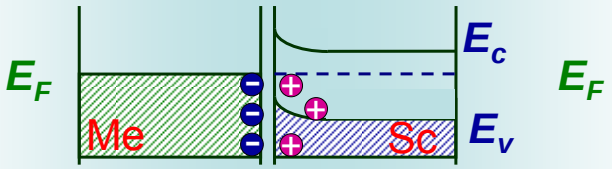
Schottky Junction



- Note that while the electrostatic energy of electrons varies with distance from the interface, the electrochemical potential (E_F) is the same across the semiconductor. The variation in the electrostatic energy is compensated by the variation in the electron concentration.
- Another important note is that the positive charges in the SCR are not holes; there are too few holes in an n-type semiconductor; rather, the positive charges are ionized donors introduced into semiconductor to make it n-doped.
- Since the donors are also ions of the lattice, they cannot move. There are no mobile carriers in the SCR. However, there are mobile carriers in the quasi-neutral region.

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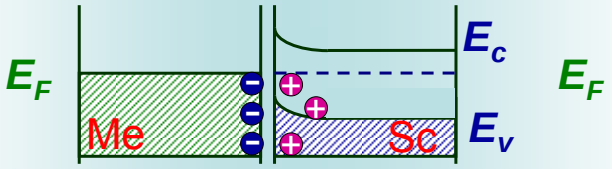
Schottky Junction



- What will happen if we try to pass current across this interface with the depletion layer?
- There are no electrons in the depletion layer, they have been swept away from the interface by the interfacial charge. There are too few holes to speak of. And the ionized donors cannot move and therefore they cannot carry current.
- There will be no current across the interface. Such an interface is called a Schottky junction. It features rectifying properties. it behaves like a diode.
- Similar structures are very widely used in various Metal-Oxide-Semiconductor devices (MOS), e.g., all memory chips .

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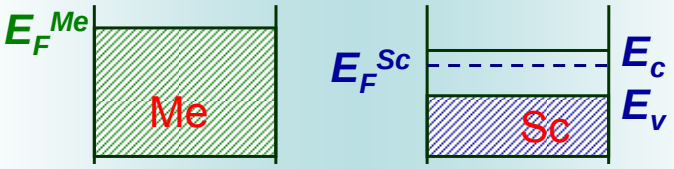
Metal/Semiconductor Interface. Accumulation Layer.

$$\overline{\mu}_e^{Me} \neq \overline{\mu}_e^{Sc}$$



- Let us now consider a metal and an *n*-type semiconductor when the Fermi level of metal before contact is higher than that of semiconductor. We again bring them in contact so that an electronic equilibrium will be established.
- Upon contact, electrons will flow from metal to semiconductor. The interface will be charged.

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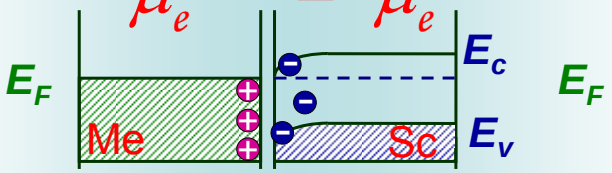
Metal/Semiconductor Interface. Ohmic Contact

$$\overline{\mu}_e^{Me} = \overline{\mu}_e^{Sc}$$



- The surface of metal is charged positively. It attracts the electrons (majority carriers) in semiconductor to the interface!
- This results in formation of a so-called accumulation layer. Unlike the previous case, when the space-charge region had no mobile carriers with sufficiently high concentration, the accumulation layer is able to sustain electric current through the interface.
- The surface concentration of electrons could be made even higher by additional surface doping. Then the resulting situation is known as Ohmic contact.
- In many practical cases it is very essential to have Ohmic contacts. All semiconductor chips must have metal leads…

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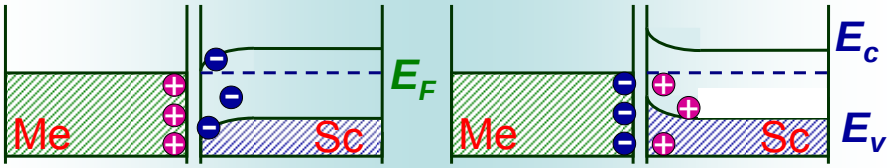
Ohmic Contacts, Schottky Junctions and Work Functions



- Let us look a bit back and see what is the difference between our two cases that resulted in so different interfacial properties.
- The ultimate reason is the different relative positions of the Fermi energies of the metal and the semiconductor before contact.
- When the Fermi energy of the metal was higher than that of semiconductor, we had accumulation layer and Ohmic contact.
- When the Fermi energy of the metal was lower than that of semiconductor, we had depletion layer and Schottky junction.
- Fermi levels are related to work functions of the materials.
- Metals with low work functions form Ohmic contacts; metals with high work functions form Schottky diodes (with n-type Sc).

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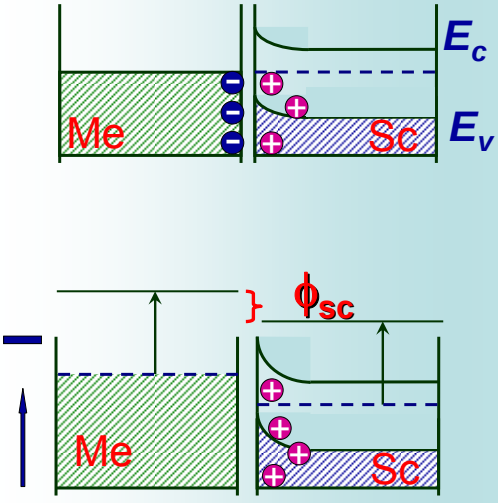
Polarized Metal-Semiconductor Interface



- We can bias the interface to increase or decrease the width of the space charge layer.
- In the above case of a Schottky junction with an n-type semiconductor, applying negative potential to the metal will increase the band bending and extend the space charge layer in the semiconductor.

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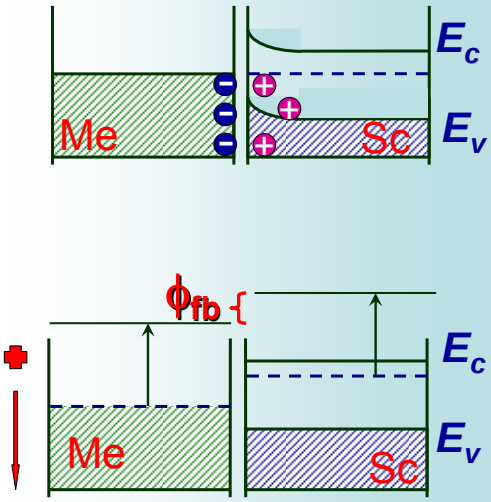
Flat-Band Potential



- We can also bias the interface so that we compensate the build-in contact potential difference.
- There will be no interface charging and no band bending in the semiconductor phase.
- The electrode potential at which such a situation happens is called **flat-band potential**.
- Flat-band potential is a special case of the potential of zero charge (pzc).

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Appendix. Contact Potential Differences, Work Functions and Fermi Levels. Electrochemical and Vacuum Scale of Electrode Potentials.

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Interface at Equilibrium: Equality of Electrochemical Potentials

- When we bring two phases in contact, they come to equilibrium with respect to a given species which exists in both phases and can pass from one phase to the other.
- Prior to establishing of the equilibrium, there is a transfer of charge between the phases until the difference in chemical potentials of the charged species is balanced by the electrical energy of the species.
- The equilibrium condition is the equality of electrochemical potentials of the species in the two phases:

$$\overline{\mu}_e^A = \overline{\mu}_e^B$$

- Since we have movement of charged species across the interface, the phases become charged versus one another.

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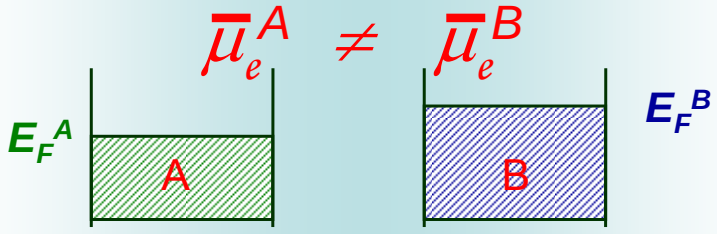
Interface at Equilibrium: Bringing Two Phases In Contact



- Let us consider two phases that have different compositions and hence different Fermi levels, electrochemical potentials, etc.
- Assume for simplicity that these phases are two pieces of different metals or of a metal and a semiconductor and the only species that exists in both phases are electrons.
- The phases are not in contact. There is no electron flow between the phases. The electrochemical potentials of electrons in phases A and B are different.

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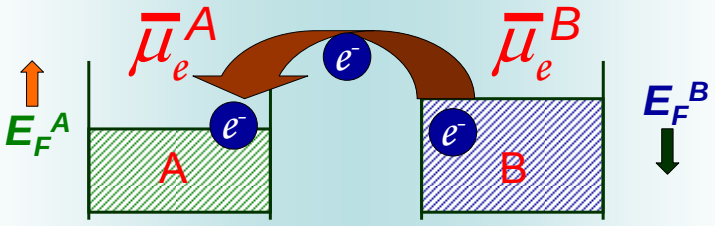
Interface at Equilibrium: Bringing Two Phases In Contact



- If we bring the phases into contact, the electrochemical potentials of electrons will be equalizing.
- The electrons will flow from the phase with a higher Fermi level to the phase with the lower one (or from the phase with the higher electrochemical potential to the phase with the lower one).
- This electron flow is transient and occurs only until the electrochemical potentials of electrons in the two phases become equal. In the process, the Fermi level of phase A goes up, and that of phase B goes down.

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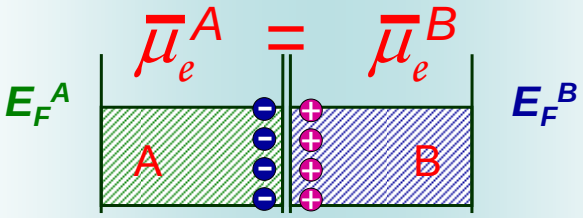
Interface at Equilibrium: Bringing Two Phases In Contact



- When the electrons flowed from phase B to phase A, they left behind the ions of the lattice whose charge is no longer balanced.
- Similarly, electrons that came to phase A have their charge uncompensated by lattice ions of phase A.
- The result is that the interface between phases A and B becomes polarized.
- This shows itself as a change in the inner potentials of the phases A and B (naturally, since electrochemical potentials change upon contact and chemical potentials do not, why should they???)

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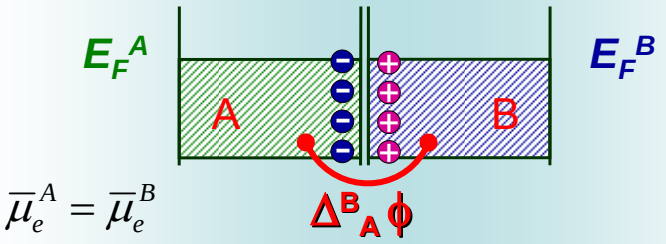
Interface at Equilibrium: Bringing Two Phases In Contact



$$\bar{\mu}_e^A = \bar{\mu}_e^B$$

$$\mu_e^A - F\phi^A = \mu_e^B - F\phi^B$$

electron has a negative charge!!!

$$\Delta_A^B\phi = \phi^B - \phi^A = \frac{\mu_e^B - \mu_e^A}{F}$$

- The inner potential difference $\Delta^B_A\phi$ between two phases brought in contact is equal to the difference in chemical potentials of electrons in these phases
- The work of transfer of electrons from one phase to the other in equilibrium is **zero**.

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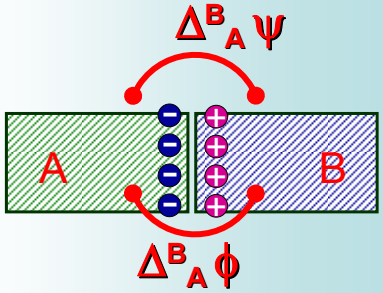
Contact Potential Difference



$$\Delta^B_A\phi = \Delta^B_A\chi^A + \Delta^B_A\psi^A$$

- However, we cannot measure inner potentials (and chemical potentials of electrons, by the way).
- So does anything happens that we can measure???
- Yes. There is a change in the outer potentials of the phases.
- The value $\Delta^B_A\psi$ is called **contact potential difference**.
- It can be measured because it occurs between two points in the same phase (vacuum).

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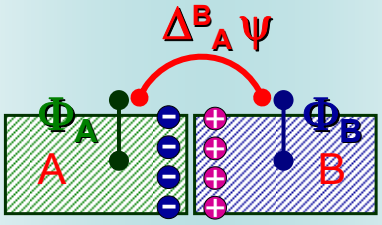
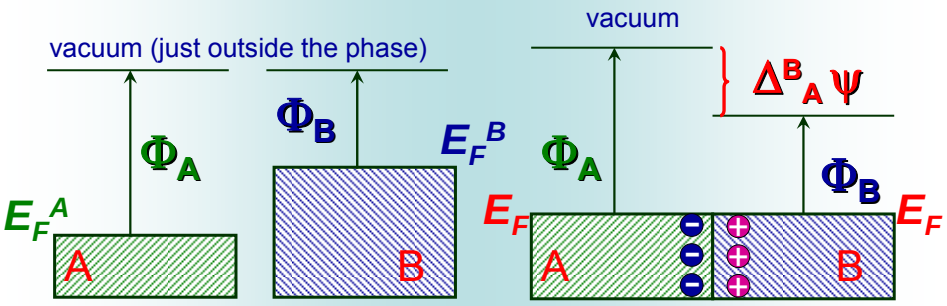
Contact Potential Difference



- Let's take an electron from the Fermi level of phase A to the point just outside it. The work required for this is the work function Φ_A of the phase A.
- We then take the electron in the vacuum from the point just outside phase A to a point just outside phase B; this requires the work $-e_0 \Delta^B_A \psi$
- We then take the electron to the Fermi level of phase B and gain the energy Φ_B
- Since we are at equilibrium the sum of these three works must be zero and

$$\Delta^B_A \psi = \frac{-(\Phi_B - \Phi_A)}{e_0}$$

Contact Potential Difference



- The contact potential difference between two phases is equal to the difference in work functions of these phases.
- Similarly, the contact potential difference is equal to the difference in Fermi levels of these phases **before contact**.

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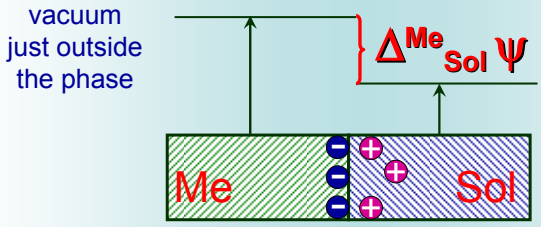
Hydrogen Scales of Electrode Potentials



- We can take the potential of an electrode containing a certain redox couple as zero and reckon all other potentials by comparing them to the electrode potential of this electrode.
- If this standard redox reaction is ½ $H_2 \Leftrightarrow H^+ + e^-$, the resulting potential scale is called the hydrogen scale of electrode potentials.
- Electrochemical standard potentials in the reference literature are tabulated vs. this standard hydrogen electrode (SHE).
- There are a few other widely used reference electrodes, such as the saturated calomel electrode (SCE). Of course, the conversion factors from one scale to another are known very precisely.

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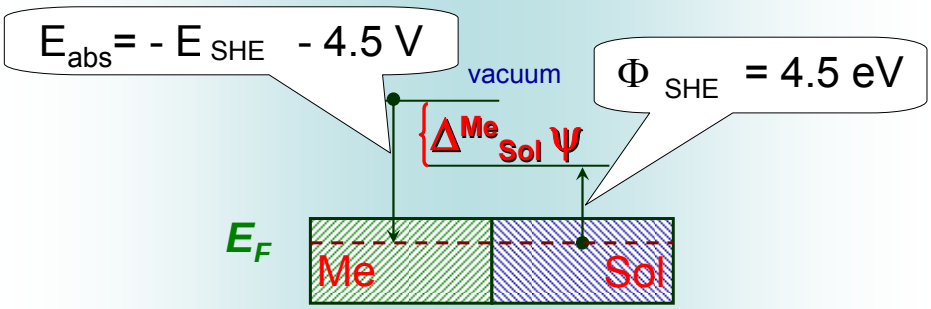
Absolute Scale of Electrode Potentials



- If electrode potentials are reckoned vs. the vacuum level, the resulting potentials are said to be measured on the absolute scale.
- The difference between the hydrogen and absolute scales is the work function of solution containing the hydrogen/hydrogen ion redox couple under standard conditions.
- The work function of the standard hydrogen electrode (SHE) is estimated as 4.5 ±0.2 eV.
- Note that the absolute electrode potentials are reckoned from the level of free electrons in vacuum… they are always negative!

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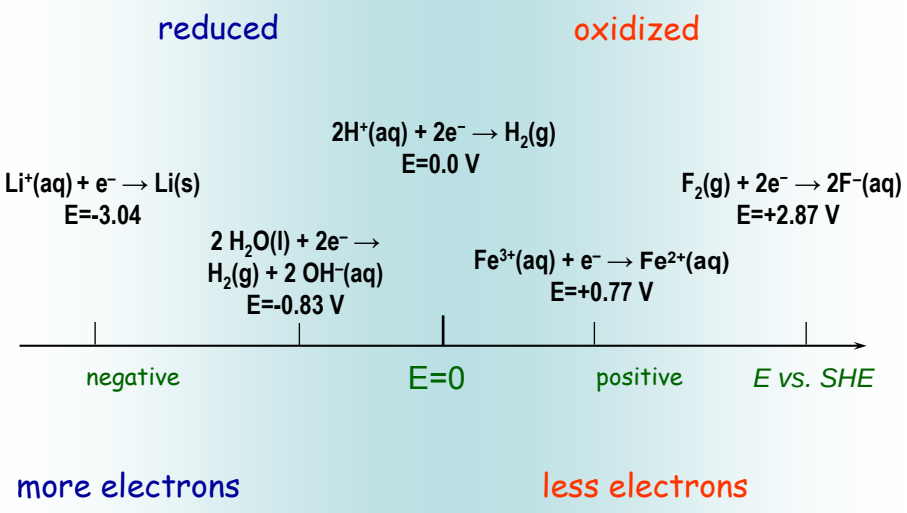
Standard and Absolute Electrode Potentials



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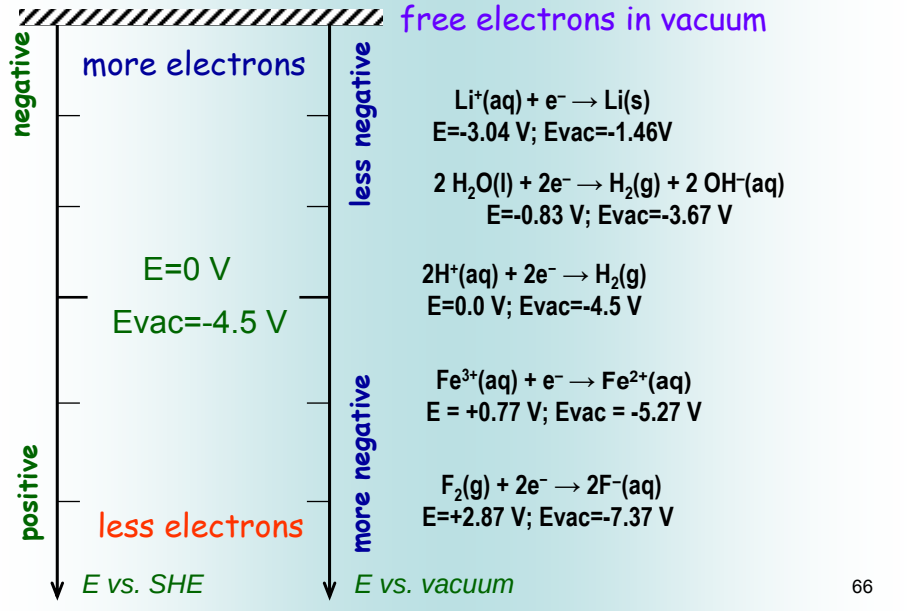
Standard and Absolute Electrode Potentials



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Positions of Semiconductor Bands

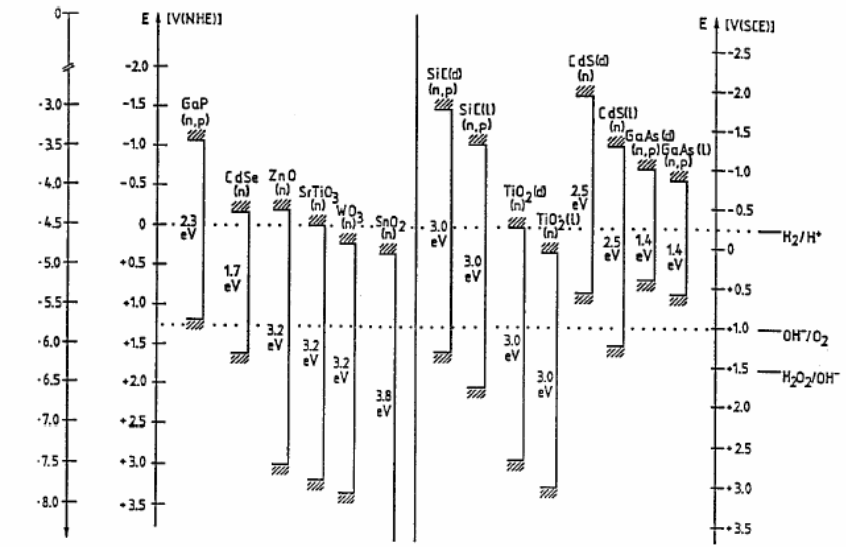

Image Source: Arthur J. Nozik; *J. Phys. Chem.* **1996,** 100, 13061-13078.

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