



DIPARTIMENTO di ELETTRONICA, INFORMAZIONE e
BIOINGEGNERIA

POLITECNICO DI MILANO



Lecture 3

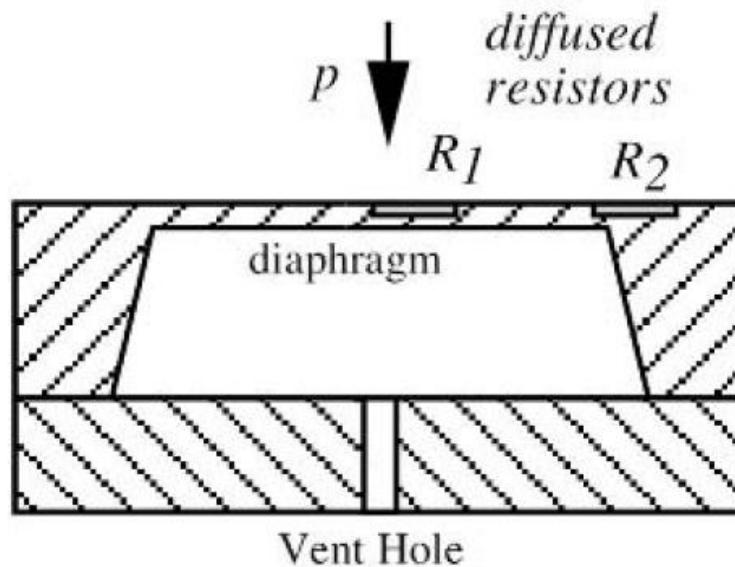
Electrical properties of materials

Semiconductors

⇒ Semiconductors;

- ceramics;
- thin/thick film;
- polymeric film deposition;
- optical fibers

Example: piezoresistive pressure sensor



Example: gas microflow sensor with capacitive pressure sensor

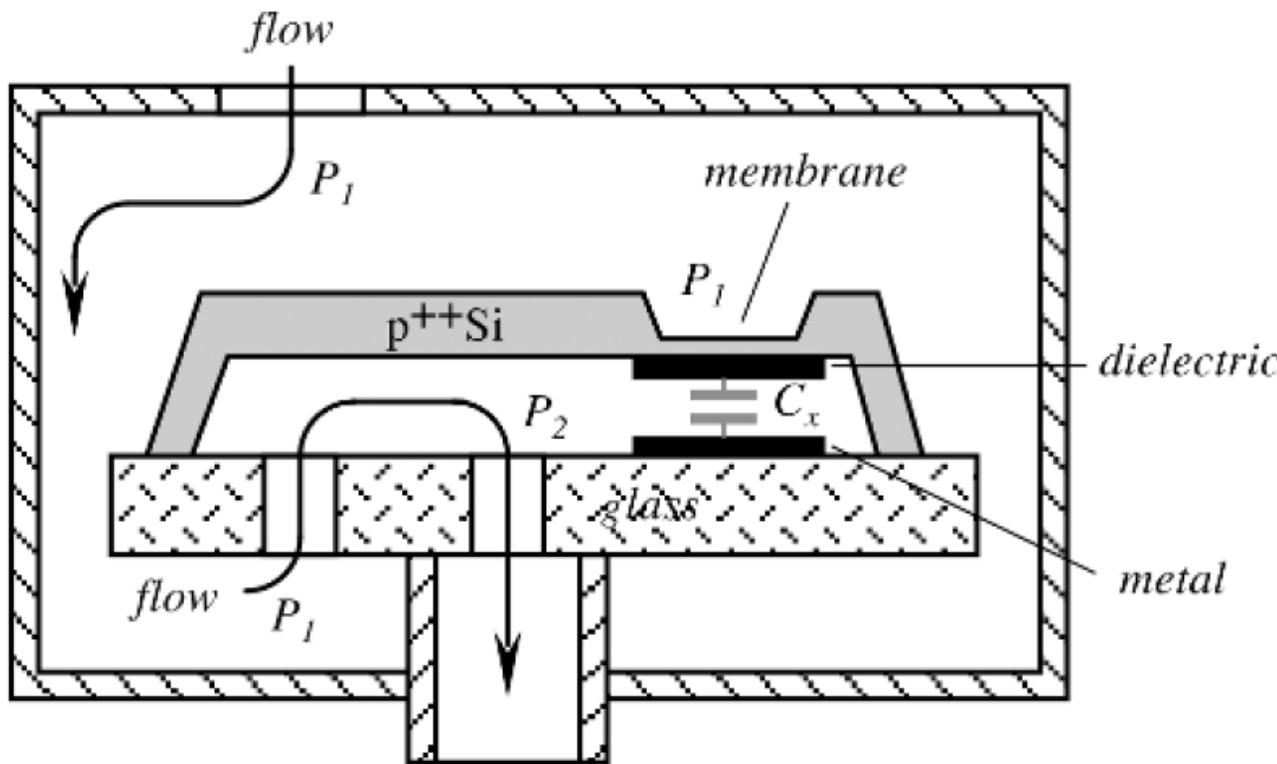


Fig. 11.14. Structure of a gas microflow sensor utilizing capacitive pressure sensor. (Adapted from Ref. [9].)

Each atom is characterized by a given number of electrons, each having a given energy;

Energy levels of electrons are quantized (i.e., it exists a finite number of energy levels). An electron submitted to the Coulomb potential of atomic nucleus, can occupy an energy level with energy equal to:

$$E_n = \frac{-Z^2 m_0 q^4}{8 \varepsilon_0^2 h^2 n^2}$$

(below a reference value equal to 0),

where: q = electron charge; Z = number of protons in the nucleus; m_0 = free electron mass; ε_0 = dielectric constant in vacuum; h = Planck constant; $n = 1, 2, 3, \dots$ = identifier of energy level identifier (*main quantum number*)

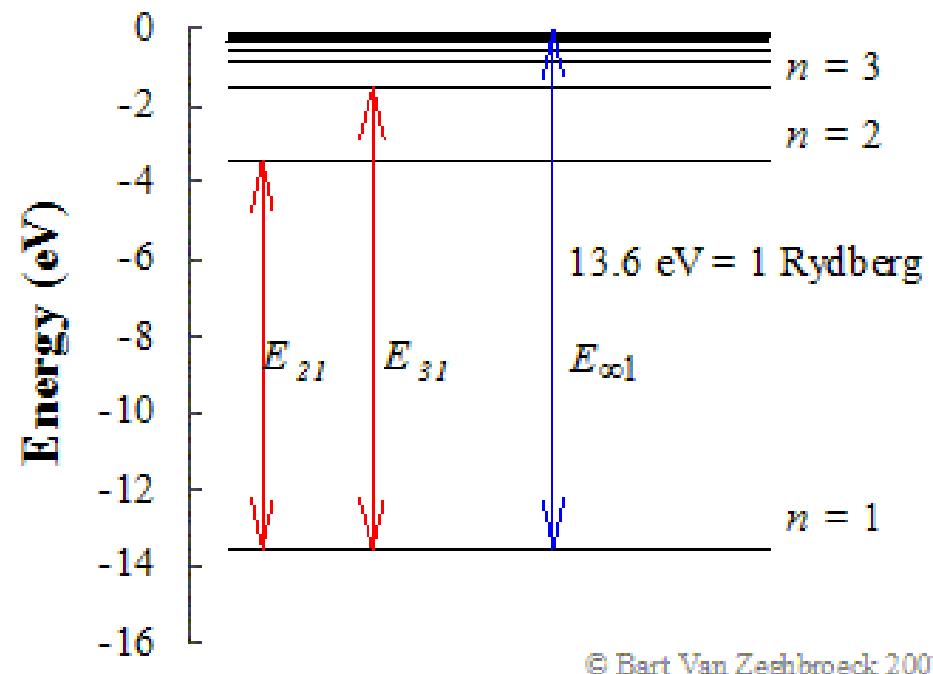
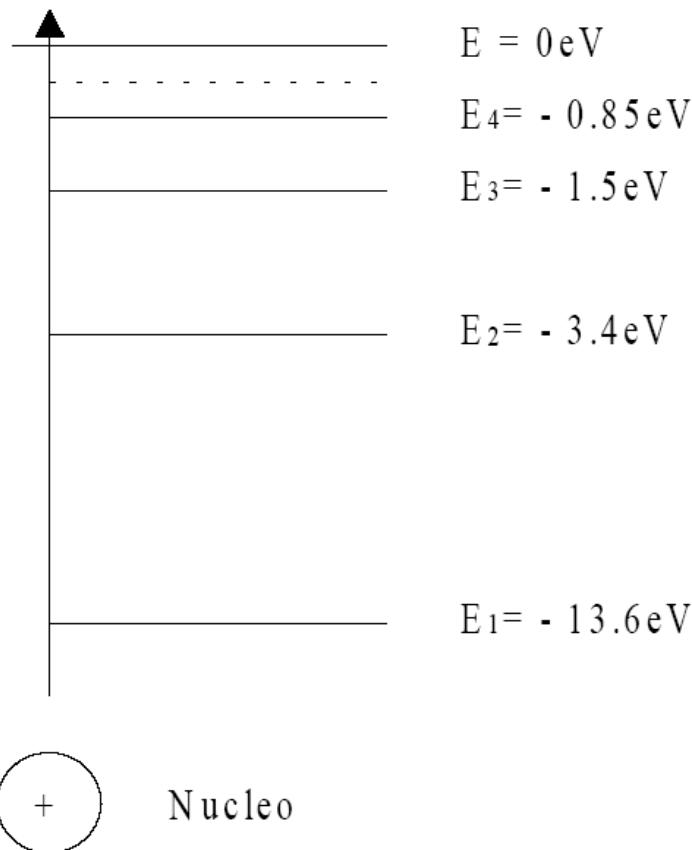
For hydrogen atom ($Z=1$), energy levels are equal to
 $-2.19 \times 10^{-18}/n^2$ J

$$E_n = \frac{-13.6}{n^2} [eV]$$

(with $1\text{eV} = 1.6 \times 10^{-19}$ J);

Example: hydrogen atom

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By supplying energy, an electron can be brought to a higher energy level; on the contrary, an excited electron can relax to a lower energy level by emitting a photon

At each level correspond different spatial configurations of the electrons, represented by quantum numbers

n ($=1, 2, 3, \dots$) (*principal quantum number*)

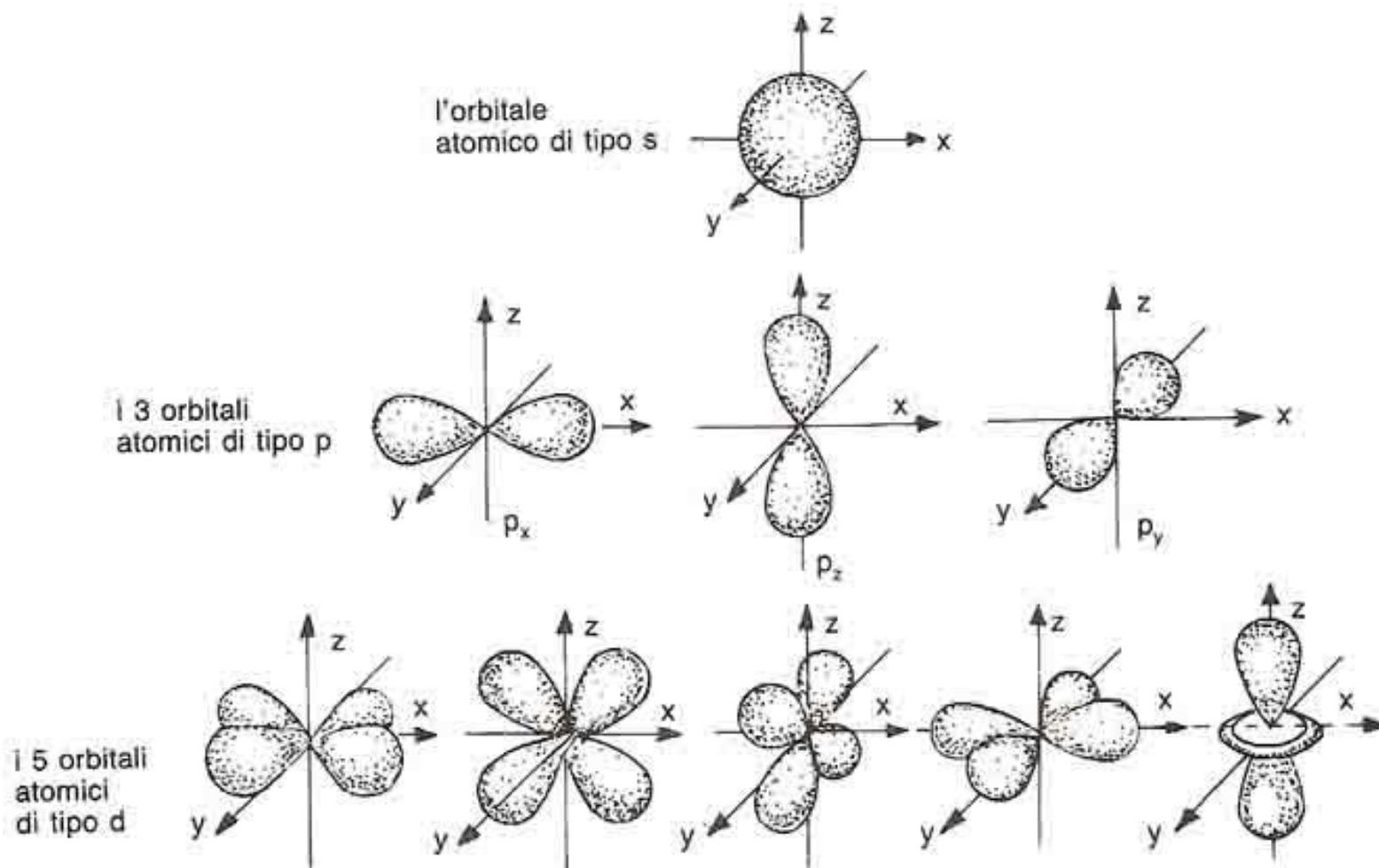
l ($=0, 1, 2, 3, \dots (n-1)$) (*angular quantum number*)

m ($=0, \pm 1, \pm 2, \pm 3, \dots, \pm l$) (*magnetic quantum number*)

s ($=+1/2, -1/2$) (*spin quantum number*)

| <i>n</i> | <i>l</i> | <i>m</i> | <i>s</i> | <i>N_{max}</i> |
|----------|----------|----------|-----------|------------------------|
| 1 | 0 | 0 | $\pm 1/2$ | 2 |
| | 0 | 0 | $\pm 1/2$ | |
| 2 | | -1 | $\pm 1/2$ | |
| | 1 | 0 | $\pm 1/2$ | 8 |
| | | +1 | $\pm 1/2$ | |
| 3 | 0 | 0 | $\pm 1/2$ | |
| | | -1 | $\pm 1/2$ | |
| | 1 | 0 | $\pm 1/2$ | |
| | | +1 | $\pm 1/2$ | 18 |
| | | -2 | $\pm 1/2$ | |
| | | -1 | $\pm 1/2$ | |
| | 2 | 0 | $\pm 1/2$ | |
| | | +1 | $\pm 1/2$ | |
| | | +2 | $\pm 1/2$ | |

| <i>n</i> | <i>l</i> | <i>m</i> | <i>s</i> | | <i>N_{max}</i> |
|----------|----------|----------|-----------|---------------|------------------------|
| 1 | 0 | 0 | $\pm 1/2$ | 1 orbital 1s | 2 |
| | 0 | 0 | $\pm 1/2$ | 1 orbital 2s | |
| 2 | | -1 | $\pm 1/2$ | | |
| | 1 | 0 | $\pm 1/2$ | 3 orbitals 2p | 8 |
| | | +1 | $\pm 1/2$ | | |
| 3 | 0 | 0 | $\pm 1/2$ | 1 orbital 3s | |
| | | -1 | $\pm 1/2$ | | |
| 3 | 1 | 0 | $\pm 1/2$ | 3 orbitals 3p | |
| | | +1 | $\pm 1/2$ | | |
| | | -2 | $\pm 1/2$ | | |
| | | -1 | $\pm 1/2$ | | |
| | 2 | 0 | $\pm 1/2$ | 5 orbitals 3d | 18 |
| | | +1 | $\pm 1/2$ | | |
| | | +2 | $\pm 1/2$ | | |



Lowest energy state: **1s**: $(n,l,m)=(1,0,0)$ (2 electrons)

State **2s**: $(n,l,m)=(2,0,0)$ (2 electrons)

State **2p**: $(n,l,m)=(2,1,-1), (2,1,0), (2,1,1)$ (6 electrons)

...

Once the energy levels of an atom are known, one can find the electron configurations of the atom, provided the number of electrons occupying each energy level is known. Electrons are Fermions since they have a half integer spin. They must therefore obey the Pauli exclusion principle. This exclusion principle states that no two Fermions can occupy the same energy level corresponding to a unique set of quantum numbers n, l, m or s. The ground state of an atom is therefore obtained by filling each energy level, starting with the lowest energy, up to the maximum number as allowed by the Pauli exclusion principle.

According to Pauli exclusion principle, on a given energy level can not exist more than $2n^2$ electrons.

Each electron is characterized by an unique 'state' (set of 4 quantum numbers n, l, m, spin).

In a given atom with more electrons not more than two electrons (with opposite spin) with the same spatial configuration can occupy the same level (Pauli exclusion principle).

In other words, two or more electrons with the same 4 quantum numbers can NOT exist

| 1A | | Abridged Periodic Table of the Elements 4/17/96 ghw | | | | | | | | | | noble |
|---------------------------------------|---|---|---|---|---|---|---|---|--|--|--|-----------------------|
| H 1s ¹ | | | | | | | | | | | | He 1s ² |
| Li 1s ² 2s ¹ | Be 1s ² 2s ² | B 1s ² 2s ² 2p ¹ | C 1s ² 2s ² 2p ² | N 1s ² 2s ² 2p ³ | O 1s ² 2s ² 2p ⁴ | F 1s ² 2s ² 2p ⁵ | Ne 1s ² 2s ² 2p ⁶ | | | | | |
| Na [Ne]3s ¹ | Mg [Ne]3s ² | Al [Ne]3s ² 3p ¹ | Si [Ne]3s ² 3p ² | P [Ne]3s ² 3p ³ | S [Ne]3s ² 3p ⁴ | Cl [Ne]3s ² 3p ⁵ | Ar [Ne]3s ² 3p ⁶ | | | | | |
| K [Ar]4s ¹ | Cu [Ar]3d ¹⁰ 4s ¹ | Zn [Ar]3d ¹⁰ 4s ² | Ga [Ar]3d ¹⁰ 4s ² 4p ¹ | Ge [Ar]3d ¹⁰ 4s ² 4p ² | As [Ar]3d ¹⁰ 4s ² 4p ³ | Se [Ar]3d ¹⁰ 4s ² 4p ⁴ | Br [Ar]3d ¹⁰ 4s ² 4p ⁵ | Kr [Ar]3d ¹⁰ 4s ² 4p ⁶ | | | | |
| Rb [Kr]5s ¹ | Ag [Kr]4d ¹⁰ 5s ¹ | Cd [Kr]4d ¹⁰ 5s ² | In [Kr]4d ¹⁰ 5s ² 5p ¹ | Sn [Kr]4d ¹⁰ 5s ² 5p ² | Sb [Kr]4d ¹⁰ 5s ² 5p ³ | Te [Kr]4d ¹⁰ 5s ² 5p ⁴ | I [Kr]4d ¹⁰ 5s ² 5p ⁵ | Xe [Kr]4d ¹⁰ 5s ² 5p ⁶ | | | | |
| Cs [Xe]6s ¹ | Au [Xe]4f ¹⁴ 5d ¹⁰ 6s ¹ | Hg [Xe]4f ¹⁴ 5d ¹⁰ 6s ² | Tl [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹ | Pb [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ² | Bi [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³ | Po [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁴ | At [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁵ | Rn [Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶ | | | | |

Elements (2)

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| New Original | | Alkali metals | | Actinide series | | Solid | | 18 VIIIA | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 1 IA | 2 | 2 | Alkaline earth metals | 3 | Poor metals | 4 | Liquid | 13 IIIA | 14 IVA | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 H Hydrogen 1.00794 | 2 IIA | 2 | Transition metals | 3 | Nonmetals | 4 | Gas | 15 VA | 16 VIA | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1 Li Lithium 6.941 | 2 Be Beryllium 9.012182 | 2 | Lanthanide series | 3 | Noble gases | 4 | Synthetic | 17 VIIIA | 18 VIIIA | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 11 Na Sodium 22.989770 | 12 Mg Magnesium 24.3060 | 3 | 13 Mg Magnesium 24.3060 | 4 | 14 Al Aluminum 26.981539 | 5 | 15 Si Silicon 28.0856 | 6 C Carbon 12.0107 | 7 N Nitrogen 14.00674 | 8 O Oxygen 16.9994 | 9 F Fluorine 18.9984032 | 10 Ne Neon 20.1797 | 11 Ar Argon 39.948 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3 Na Sodium 22.989770 | 4 Mg Magnesium 24.3060 | 3 IIIB | 4 IVB | 5 VB | 6 VIIB | 7 VIIIB | 8 VIIIB | 9 IB | 10 IIB | 11 IIB | 12 IIB | 13 IIB | 14 IIB | 15 IIB | 16 IIB | 17 IIB | 18 IIB | 19 IIB | 20 IIB | 21 Sc Scandium 44.955910 | 22 Ti Titanium 47.867 | 23 V Vanadium 50.9415 | 24 Cr Chromium 51.9961 | 25 Mn Manganese 54.938049 | 26 Fe Iron 55.8457 | 27 Co Cobalt 58.933200 | 28 Ni Nickel 58.6934 | 29 Cu Copper 63.546 | 30 Zn Zinc 65.409 | 31 Ga Gallium 69.723 | 32 Ge Germanium 72.64 | 33 As Arsenic 74.92160 | 34 Se Selenium 78.96 | 35 Br Bromine 79.904 | 36 Kr Krypton 83.798 | 37 Rb Rubidium 85.4678 | 38 Sr Strontium 87.62 | 39 Y Yttrium 88.90585 | 40 Zr Zirconium 91.224 | 41 Nb Niobium 92.90638 | 42 Mo Molybdenum 95.94 | 43 Tc Technetium (98) | 44 Ru Ruthenium 101.07 | 45 Rh Rhodium 102.90550 | 46 Pd Palladium 106.42 | 47 Ag Silver 107.8682 | 48 Cd Cadmium 112.411 | 49 In Indium 114.818 | 50 Sn Tin 116.710 | 51 Sb Antimony 121.760 | 52 Te Tellurium 127.60 | 53 I Iodine 126.90447 | 54 Xe Xenon 131.293 | 55 Cs Cesium 132.90545 | 56 Ba Barium 137.327 | 57 57 to 71 | 58 Hf Hafnium 178.49 | 59 Ta Tantalum 180.9479 | 60 W Tungsten 183.84 | 61 Re Rhenium 186.207 | 62 Os Osmium 190.23 | 63 Ir Iridium 192.217 | 64 Pt Platinum 195.078 | 65 Au Gold 196.96655 | 66 Hg Mercury 200.59 | 67 81 Tl Thallium 204.3833 | 68 82 Pb Lead 207.2 | 69 83 Bi Bismuth 208.96038 | 70 84 Po Polonium (209) | 71 85 At Astatine (210) | 72 86 Rn Radon (222) | 73 87 Fr Francium (223) | 74 88 Ra Radium (226) | 75 89 to 103 | 76 104 Rf Rutherfordium (261) | 77 105 Db Dubnium (262) | 78 106 Sg Seaborgium (266) | 79 107 Bh Bohrium (264) | 80 108 Hs Hassium (269) | 81 109 Mt Meitnerium (265) | 82 110 Ds Darmstadtium (271) | 83 111 Rg Roentgenium (272) | 84 112 Uub Ununbium (285) | 85 113 Uut Ununtrium (284) | 86 114 Uuo Ununquadium (289) | 87 115 Uup Ununpentium (288) | 88 116 Uuh Unurhexium (292) | 89 117 Uus Ununseptium (293) | 90 118 Uuo Ununoctium (294) |

Atomic masses in parentheses are those of the most stable or common isotope.

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|--|------------------------------------|---|------------------------------------|--|------------------------------------|--|------------------------------------|--|------------------------------------|---------------------------------------|------------------------------------|--|------------------------------------|---|------------------------------------|---|------------------------------------|--|------------------------------------|---|------------------------------------|--------------------------------------|------------------------------------|--|------------------------------------|--|------------------------------------|---|------------------------------------|
| 57 La Lanthanum 138.9055 | 2 8 18 18 9 2 | 58 Ce Cerium 140.116 | 2 8 18 19 9 2 | 59 Pr Praseodymium 140.90765 | 2 8 18 21 8 2 | 60 Nd Neodymium 144.24 | 2 8 18 22 8 2 | 61 Pm Promethium (145) | 2 8 18 23 8 2 | 62 Sm Samarium 150.36 | 2 8 18 24 8 2 | 63 Eu Europium 151.964 | 2 8 18 25 8 2 | 64 Gd Gadolinium 157.25 | 2 8 18 25 9 2 | 65 Tb Terbium 158.92534 | 2 8 18 27 8 2 | 66 Dy Dysprosium 162.500 | 2 8 18 28 8 2 | 67 Ho Holmium 164.93032 | 2 8 18 29 8 2 | 68 Er Erbium 167.259 | 2 8 18 30 8 2 | 69 Tm Thulium 168.93421 | 2 8 18 31 8 2 | 70 Yb Ytterbium 173.04 | 2 8 18 32 8 2 | 71 Lu Lutetium 174.967 | 2 8 18 32 9 2 |
| 89 Ac Actinium (227) | 2 8 18 32 18 9 2 | 90 Th Thorium 232.03681 | 2 8 18 32 18 9 2 | 91 Pa Protactinium 231.03588 | 2 8 18 32 20 9 2 | 92 U Uranium 238.02891 | 2 8 18 32 21 9 2 | 93 Np Neptunium (237) | 2 8 18 32 22 9 2 | 94 Pu Plutonium (244) | 2 8 18 32 24 8 2 | 95 Am Americium (243) | 2 8 18 32 25 8 2 | 96 Cm Curium (247) | 2 8 18 32 25 8 2 | 97 Bk Berkelium (247) | 2 8 18 32 27 8 2 | 98 Cf Californium (251) | 2 8 18 32 28 8 2 | 99 Es Einsteinium (252) | 2 8 18 32 29 8 2 | 100 Fm Fermium (257) | 2 8 18 32 30 8 2 | 101 Md Mendelevium (258) | 2 8 18 32 31 8 2 | 102 No Nobelium (259) | 2 8 18 32 32 8 2 | 103 Lr Lawrencium (262) | 2 8 18 32 32 9 2 |

Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

In the case of **silicon** ($Z=14$), 10 out of 14 electrons occupy all available energy levels closest to the nucleus, characterized by quantum numbers $n=1$ (2 levels) and $n=2$ (8 levels). For these electrons the bond with the nucleus is so strong that they are not perturbed by the chemical reactions that normally occur or by the forces of contiguous atoms (in multiple atom structures).

The remaining 4 electron of the Silicon atom, instead, occupy only 4 levels among those with quantum number $n=3$. They are weakly attracted by the nucleus, because they are more distant and because the positive charge of the nucleus is in part shielded by the other 10 electrons. These 4 electrons are called ‘valence electrons’ and actively participate at the bonding with other atoms.

8 levels occupied
by 4 e-



$$n = 3$$

8 levels occupied
by 8 e-



$$n = 2$$

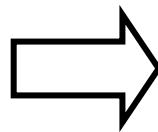
2 levels occupied
by 2 e-



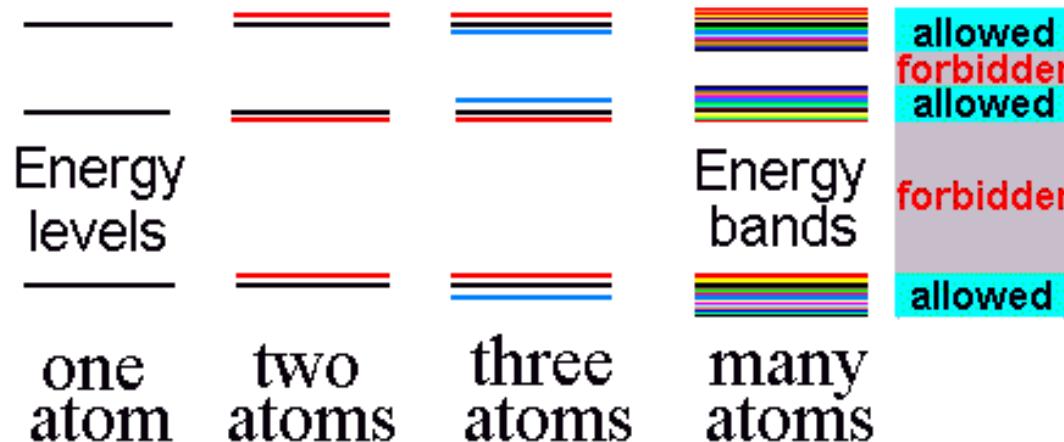
$$n = 1$$

14 +

- When in a given material atoms are insulated (e.g. in a gas), each atom has electrons with identical energy.
- With diminishing distance between atoms, the nucleus applies a force on the electrons of the other atoms, and the potential that determines the energy levels varies. The allowed energy levels, therefore, vary.
- If we consider a system composed by only two atoms, only two electrons (with opposite spin) can be associated to a given energy level E_n . Therefore, the energy level E_n (relative to isolated atoms) must split into two slightly different levels to allow 4 electrons to occupy that level.
- When more atoms (N) form a crystal, the forces are altered even more, and each original energy level E_n must split into N different energy levels



Spreading of atomic energy levels into **energy bands**



- Each energy band can contain until a maximum of $2N$ electrons
 - number of atoms in a crystal: generally high (order of 10^{22} cm^{-3});
 - the wideness of each band is few eV
- ⇒ Separation between energy levels in each band < thermal energy of the electron at ambient temperature
- ⇒ The electron is free to move between the energy levels in each energy band

The number of electrons within each band determines the electrical properties of a given material.

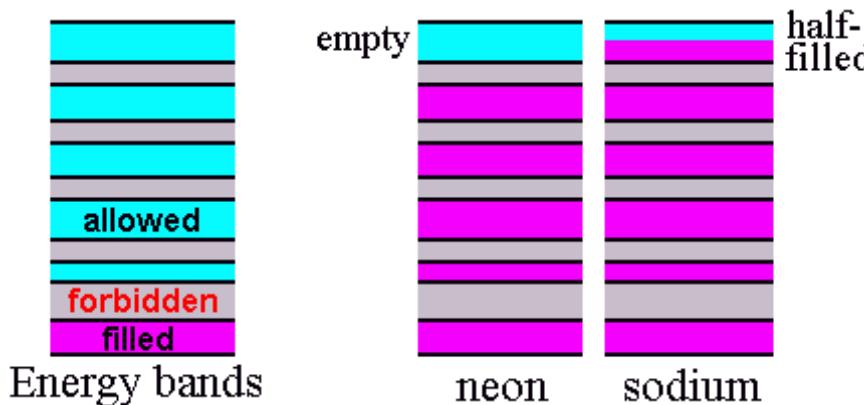
E.g.:

| atom | #electron | Configuration |
|------|-----------|-------------------------------------|
| Ne | 10 | $1s2, 2s2, 2p6$ |
| Na | 11 | $1s2, 2s2, 2p6 3s1$ [neon] $3s1$ |

Because the number of electron in neon atom is even, the higher band is totally filled, while in sodium the lower band is filled only by half

Occupation of energy bands and electrical properties of the materials

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- In **neon**, the separation between the first available energy band and the closest band filled by electrons is about 20 eV. In order to have electrical conduction, it is necessary that electrons do such a “quantum jump”, which is practically impossible at ambient temperature
- In **sodium**, the energy band with maximum energy is only partially filled by electrons, therefore it is not necessary that electrons do a ‘quantum jump’ to move into the empty, available energy levels. Electrons 3s1 can easily absorb small quantities of energy from an applied electrical field and move to available energy levels. They act, in practice, as “free electrons”.

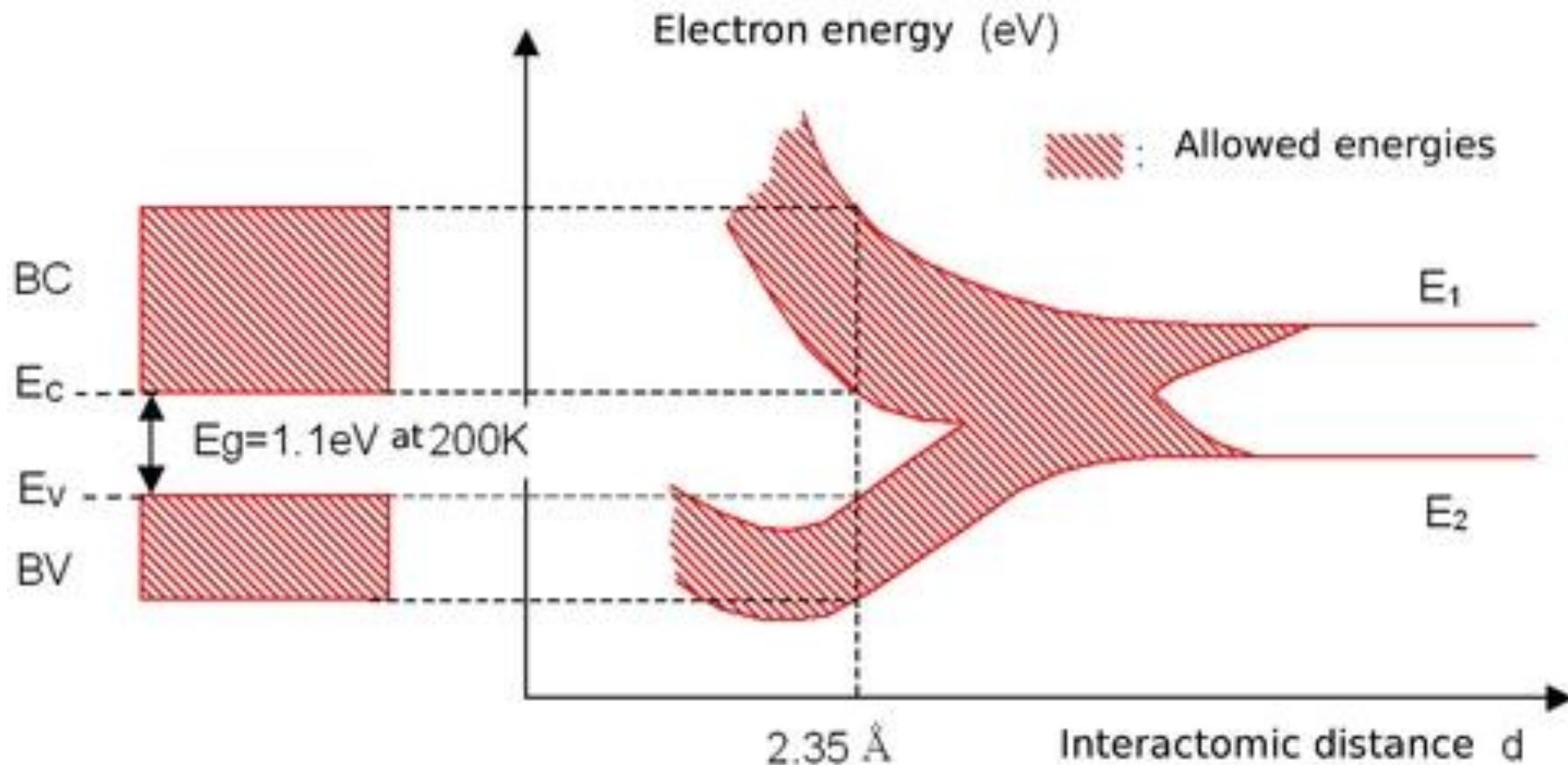
In a **silicon** crystal, the inner energy levels (the two states with quantum numbers with $n=1$ and the 8 with quantum numbers with $n=2$) consider orbits so small that in practice they do not interact with the corresponding atoms nearby. The outer energy levels (i.e., those characterized by the quantum number $n=3$, partially occupied by 4 valence electrons), instead, interact strongly: 4 of them generates 4 energy bands that overlap to form a large band called "**valence band**" (VB) that can host $4N$ electrons. The other levels generate bands that overlap to form a single large band called "**conduction band**" (CB). The two bands are separated by an interval called "**energy gap**" (E_g), in which there are no possible states for electrons.

Valence band, conduction band and energy gap are fundamental to determine the physical properties of the material.

In a silicon crystal ($d_0=2.5$ angstrom), two continuous energy bands exist (CB and VB), separated by a forbidden band, which is not accessible for electrons. This forbidden region is called the ‘gap’ and its width Eg is a characteristic of the material.

The lowest energy level of the conduction band is denoted EC and the highest energy level of the valence band is called EV so that we have the relationship $Eg=EC-EV$.

The conduction and valence bands CB and VB represent the energies accessible to electrons, or the energies of the states *potentially* occupied by electrons: they do not provide any information about the *effective* occupation of the energy states by electrons.



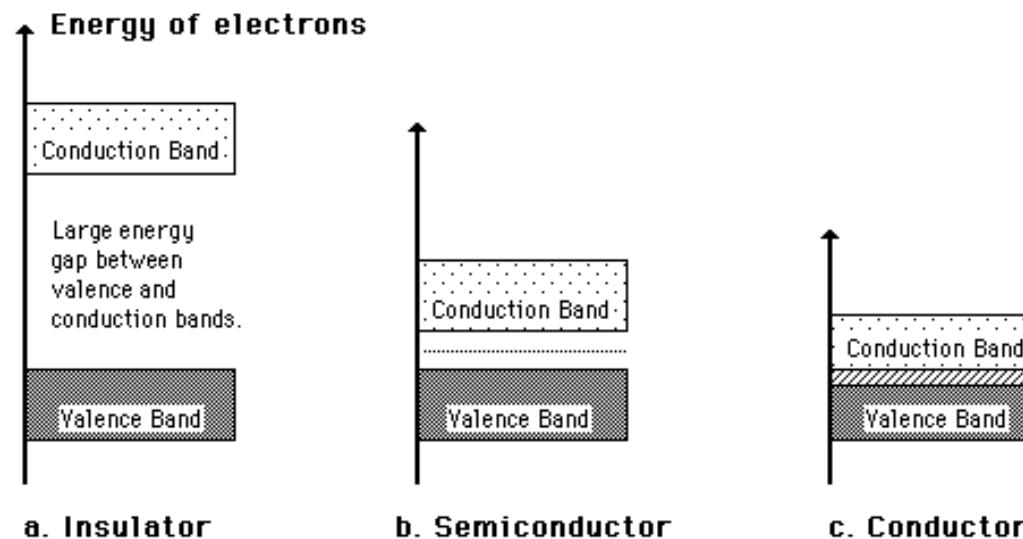
Solid-state materials can be classified into three groups:

Insulators: materials having an electrical conductivity $\sigma < 10^{-8}$ S/cm (like diamond: $\sigma = 10^{-14}$ S/cm);

Semiconductors: have a conductivity 10^{-8} S/cm $< \sigma < 10^3$ S/cm (for silicon it can range from 10^{-3} S/cm to 10^3 S/cm);

Conductors: materials with high conductivities, $\sigma > 10^3$ S/cm (like silver: 10^6 S/cm.)

The electrical properties of a given material depend on the electronic populations of the different allowed bands. Electrical conduction is the result of electron motion within each band. When an electric field is applied to the material, electrons start to move in the direction opposed to the direction of the electric field. An empty energy band (in which there is no free electron) does not of course participate in the formation of an electric current. It is also the case for a *fully occupied* band. Indeed, an electron can move provided that, whenever it leaves its site, it can find some free space elsewhere (another available site within its energy band, called a “hole”), where it can go.



A material with fully occupied or empty energy bands is an **insulator**. This is the case when the gap energy exceeds ~ 9 eV, because for such gaps, the thermal energy at 300K (~ 25 meV) is clearly insufficient to allow electrons from the valence band to be promoted to the conduction band. In this case the valence band (and all bands of lower energy) is fully occupied, and the conduction band is empty.

In terms of bonds, atoms have such strong bonds that it is difficult to break them to free an electron to become a charge carrier. In the VB, which is full, it is not possible the electrical conduction because electrons can only exchange position each other without generating a net current flow.

A very good insulator, widely used in electronic devices, is **Silicon Dioxide**, **SiO₂**, in which $E_g \approx 8$ eV.

A **semiconductor** is primarily an insulator at 0K. However, since the energy gap is lower compared to insulators ($\sim 1\text{eV}$), the valence band is slightly thermally populated at room temperature, whereas the conduction band is slightly depopulated. Since electrical conduction is directly connected to the number of electrons in the “almost empty” conduction band and to the number of holes in the “almost fully occupied” valence band, it can be expected that the electrical conductivity of such an intrinsic semiconductor will be very small.

In other words, VB and CB are quite close each other ($0.2 < E_g < 2\text{eV}$), therefore, it is not impossible to provide for a valence electron a quantity of energy that allows conduction. In terms of bonding, this means that a covalent bond can be broken quite easily and its electron can become free and therefore able to bring current.

For a **conductor**, conduction bands and valence bands are not separated and there is therefore no energy gap. The conduction band is then partially occupied (even at low temperatures), resulting in a “high” electrical conductivity.

VB overlaps with CB. Electrons can easily occupy any level and therefore be associated at any atom.

The abundance of free carriers free to move makes metals optimal conductors of electrical current.

| | # electrons | Configuration |
|----------------|-------------|-----------------------|
| Aluminium (Al) | 13 | [Ne], 3s2, 3p1 |
| Copper (Cu) | 29 | [Ar], 3d10, 4s1 |
| Silver (Ag) | 47 | [Kr], 4d10, 5s1 |
| Gold (Au) | 70 | [Xe], 4f14, 5d10, 6s1 |

| element | Eg (eV) | Configuration (at ambient temperature) |
|----------------|---------|---|
| Carbonium (C) | 5.5 | [He], 2s2, 2p2 |
| Silicon (Si) | 1.1 | [Ne], 3s2, 3p2 |
| Germanium (Ge) | 0.7 | [Ar], 4s2, 4p2 |

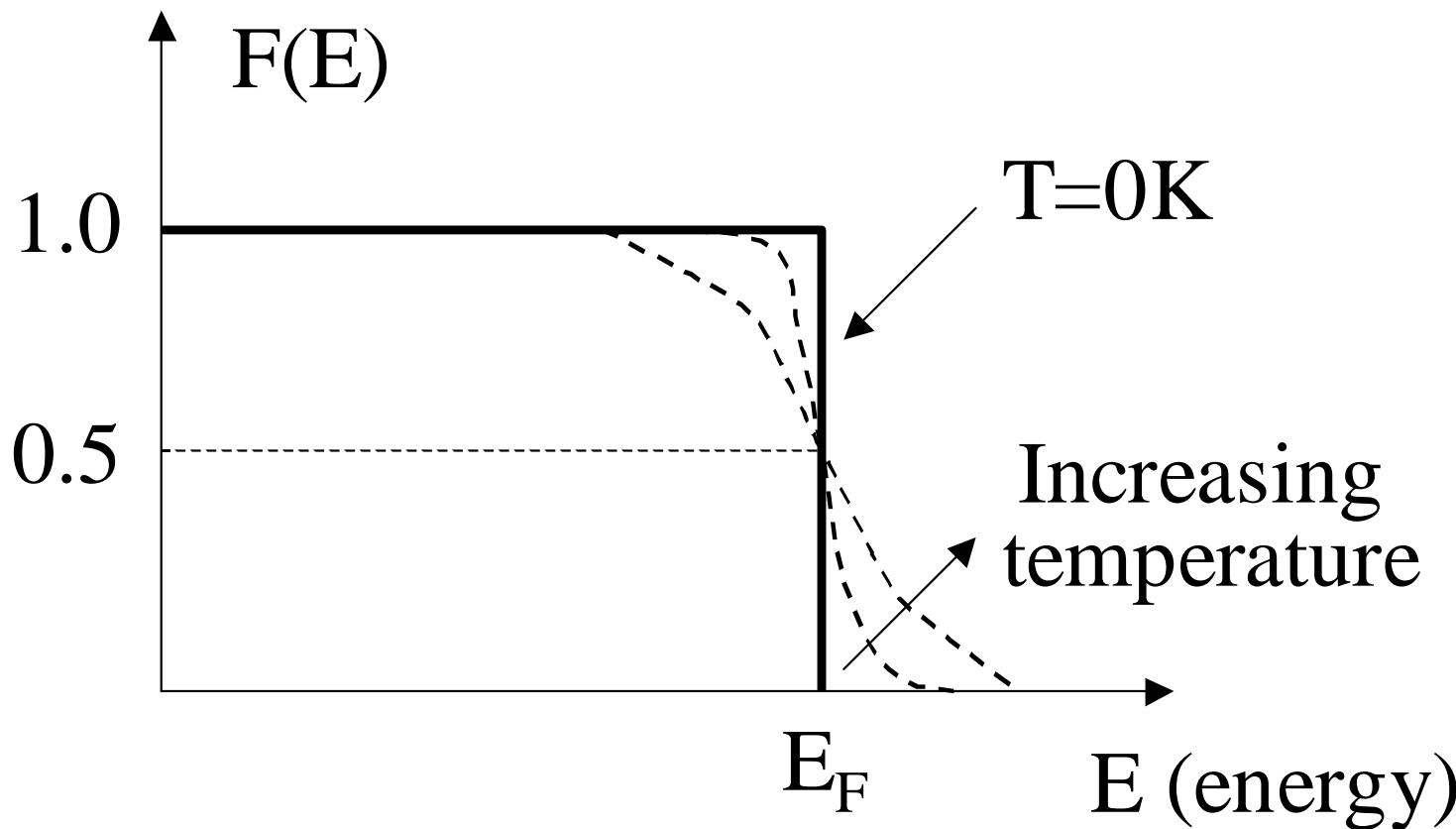
Fermi level = the highest energy level where an electron at T=0K (therefore without thermal energy kT) can be found

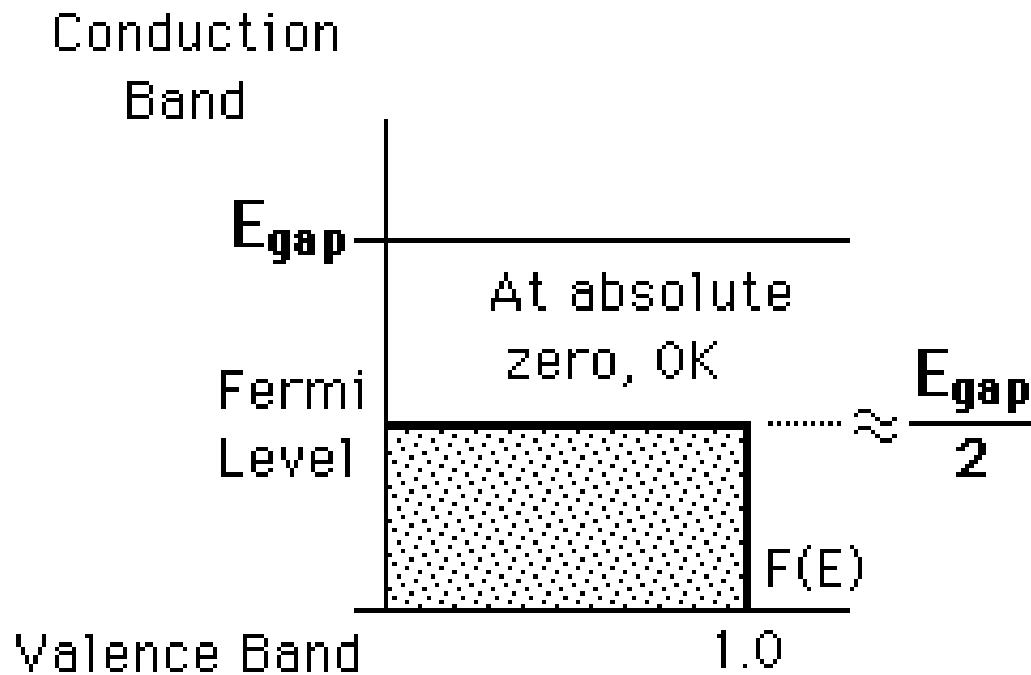
Fermi-Dirac distribution

gives the probability that, at a given temperature T, an electron will occupy a state having energy E.

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

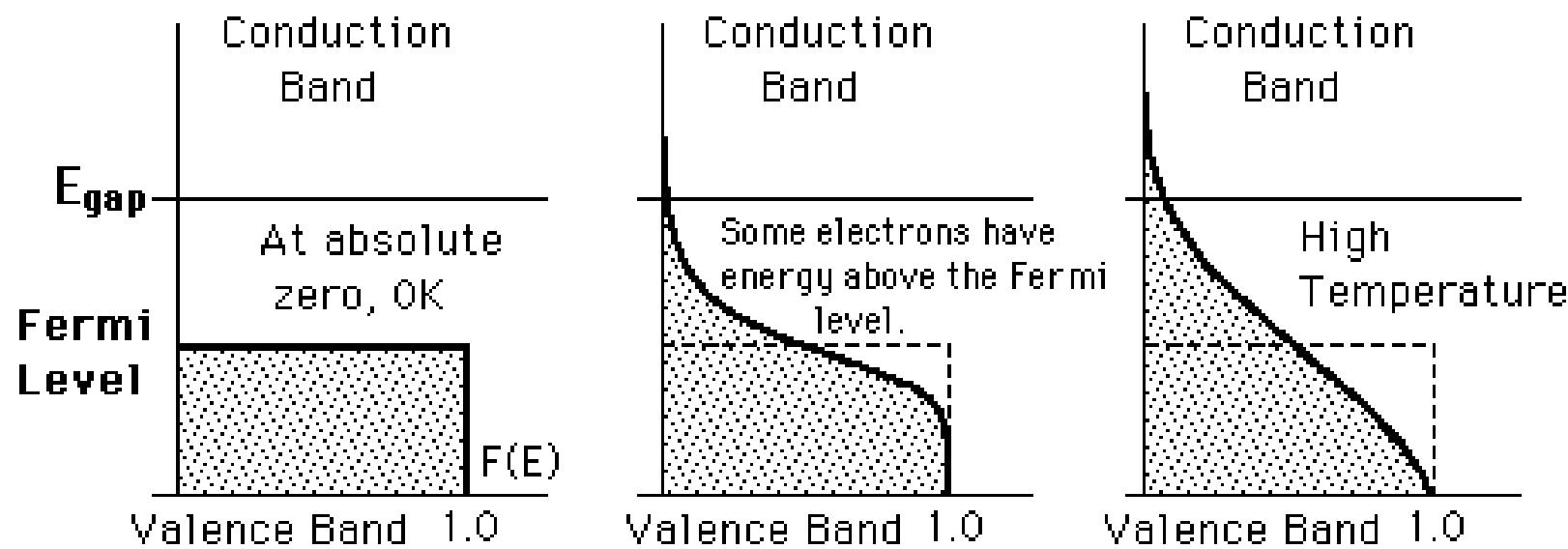
(E_F = Fermi level)



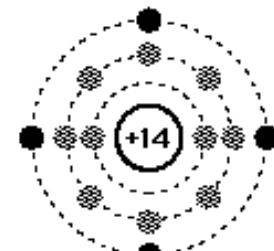


The probability that an electron will occupy a state above the Fermi level increases with increasing temperature.

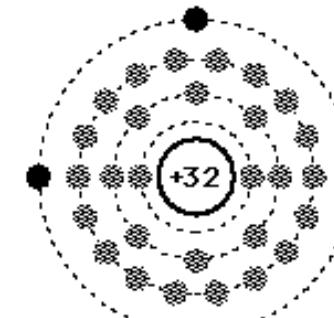
The probability that an electron will be in the conduction band increases with increasing temperature and it is higher with lower gap between Fermi level (and therefore valence band) and conduction band



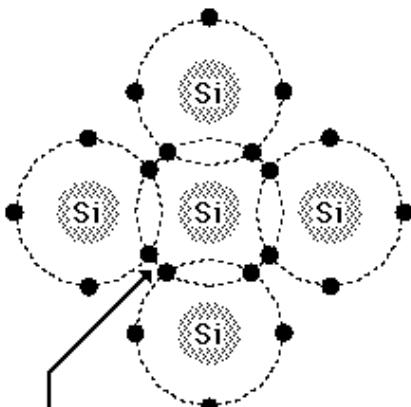
In a Silicon (or Germanium) crystal, the 4 valence electrons are shared between contiguous atoms in the crystal



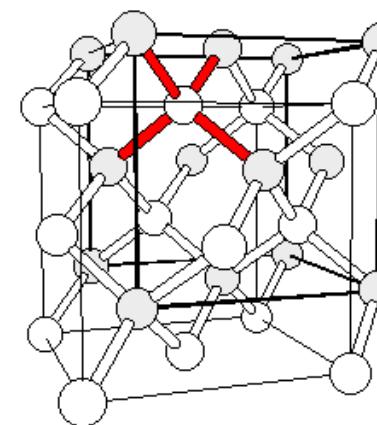
Silicon



Germanium



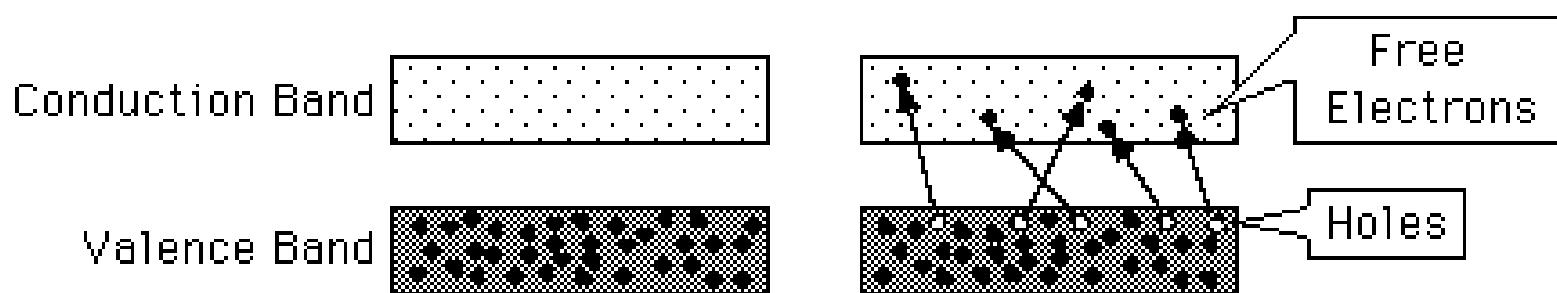
Shared electrons
of a covalent
bond.





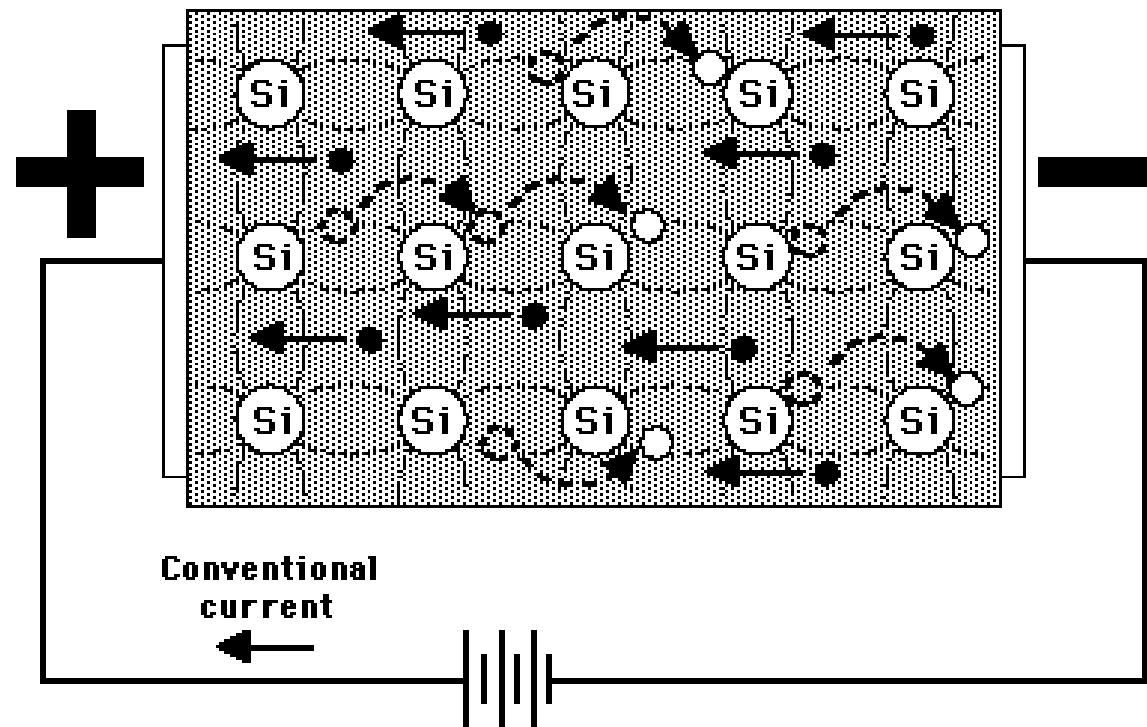
In a Si (or Ge) crystal, at any temperature above 0K, there is a not null probability that an electron stays in the conduction band.

The electron leaves the relative atom (which becomes a ion with positive charge), leaving behind it a hole.



Silicon and Germanium

In presence of an applied voltage, both electrons and holes contribute to a small current.



Conductors

- electronic (metallic)
- ionic or electrolytic (acid, base and saline)

A potential difference applied between two points at a distance L generates an electric field $E = V / L$

Which accelerates electrons by

$$a = \frac{qE}{m} = \frac{qV}{mL}$$

(m= electron mass, q=electron charge)

In addition to their motion due to thermal agitation, therefore, electrons move with a velocity whose direction is the same of the applied electric field.

Such mean ‘**drift**’ velocity is

$$v_d = a\tau = \frac{qE}{m}\tau = \frac{q\tau}{m}E = \mu_e E$$

where

τ = average time between collisions

μ_e = electronic mobility

Density current per surface area, therefore, is

$$J = N_e q v_d = \frac{N_e q^2 \tau}{m} E$$

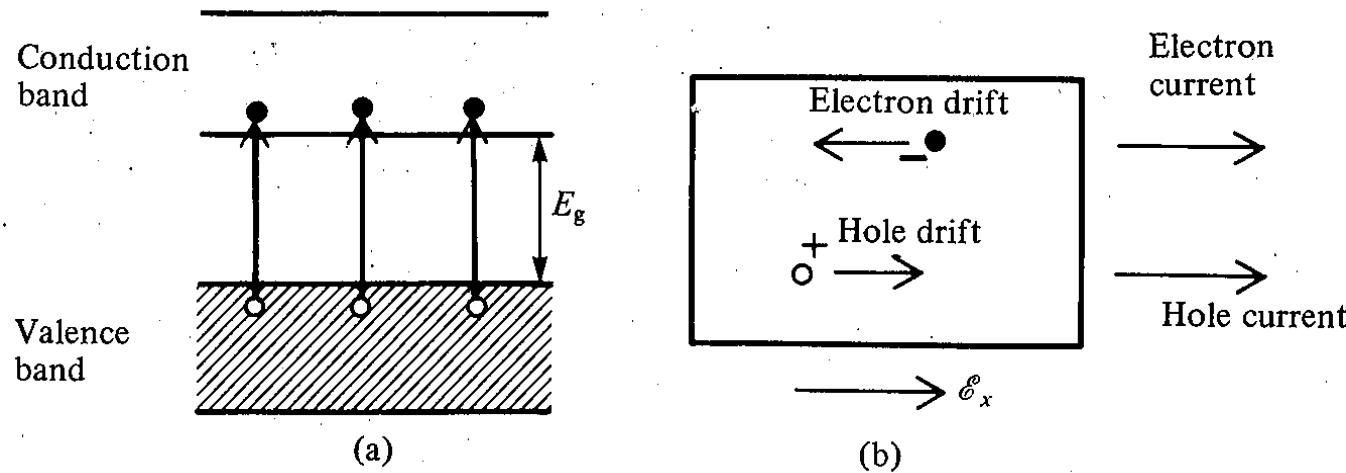
(N_e =electronic density)

Electrical conductivity:

$$\sigma = \frac{N_e q^2 \tau}{m} = \mu_e (N_e q)$$

In a semiconductor charge conduction is obtained simultaneously and independently by:

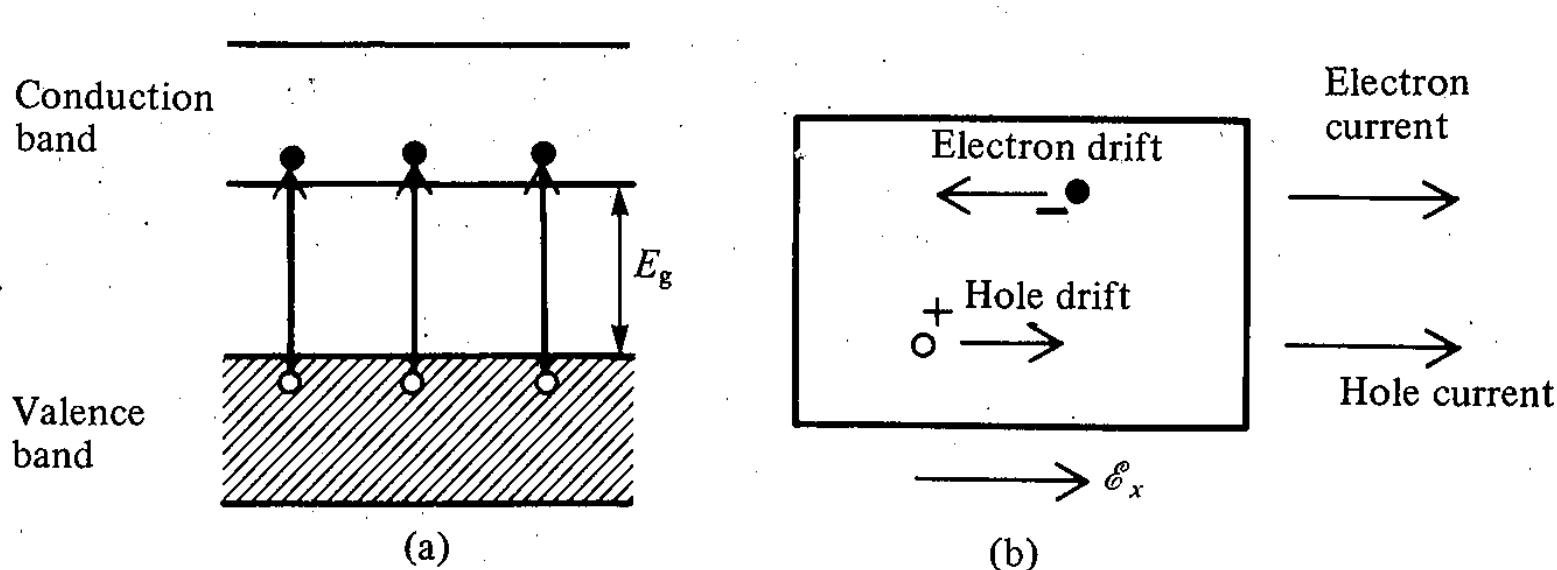
- **free electrons** (or conduction electrons) that move 'between' atoms and therefore 'between' covalent bonds in the Si crystal. This is represented as current of electrons in the conduction band.
- **valence electrons** that move 'along' the covalent bonds of the Si crystal. This transport mechanism is usually visualized as the movement of the respective holes in opposite direction. It is therefore represented as current of holes in the valence band.



Current density:

$$J = (n \cdot q \cdot \mu_e + p \cdot q \cdot \mu_l) E_x$$

(μ_e, μ_l = mobility of electrons and holes)



In an intrinsic semiconductor (i.e., extremely pure, with a negligible percentage of impurities, so that the physical characteristics of the crystal depend uniquely on the considered semiconductor) at thermal equilibrium charge carriers are only due to electron-hole generation from thermal excitation.

Electron density, n [electrons/cm³], is therefore equal to hole density, p [holes/cm³]:

$$n = p = n_i$$

where n_i is the intrinsic carrier density. It depends on temperature T , i.e. on the energy available to ionize the atom of the semiconductor, and on E_g .

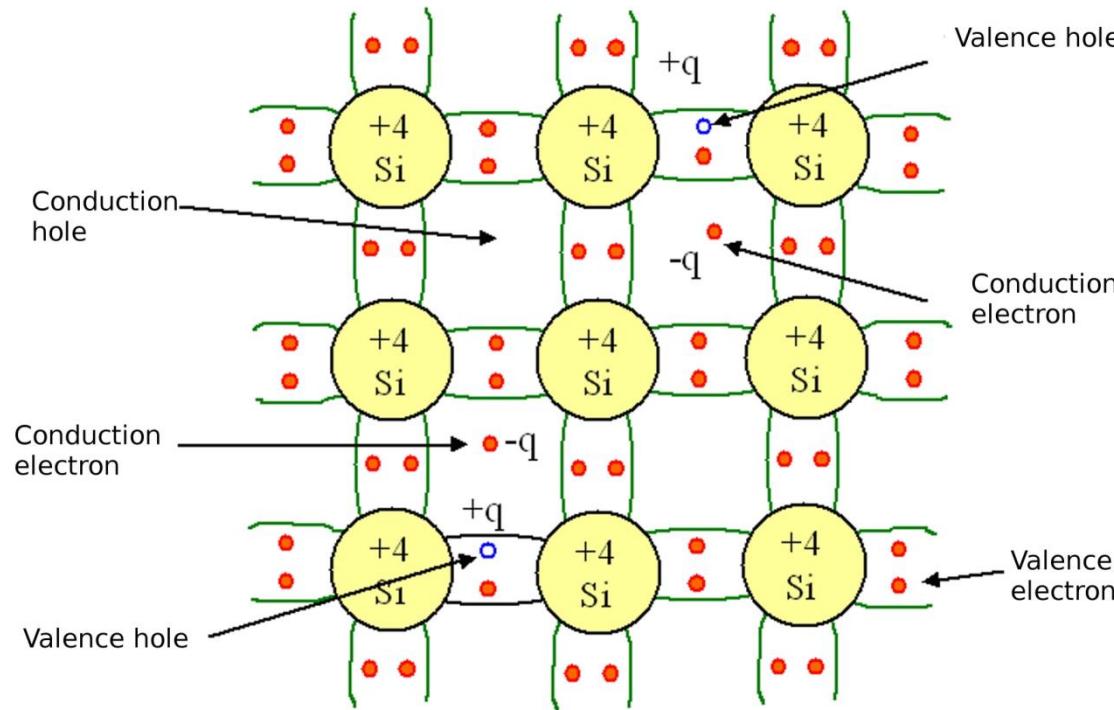
In silicon:

$$n_i = 1.45 \times 10^{10} \text{ [carriers/cm}^3\text{]} \text{ at } T = 300K$$

The value of n_i , although large in absolute terms, is small relatively to the number of links that could be broken ($\approx 5 \times 10^{22} \text{ cm}^{-3}$).

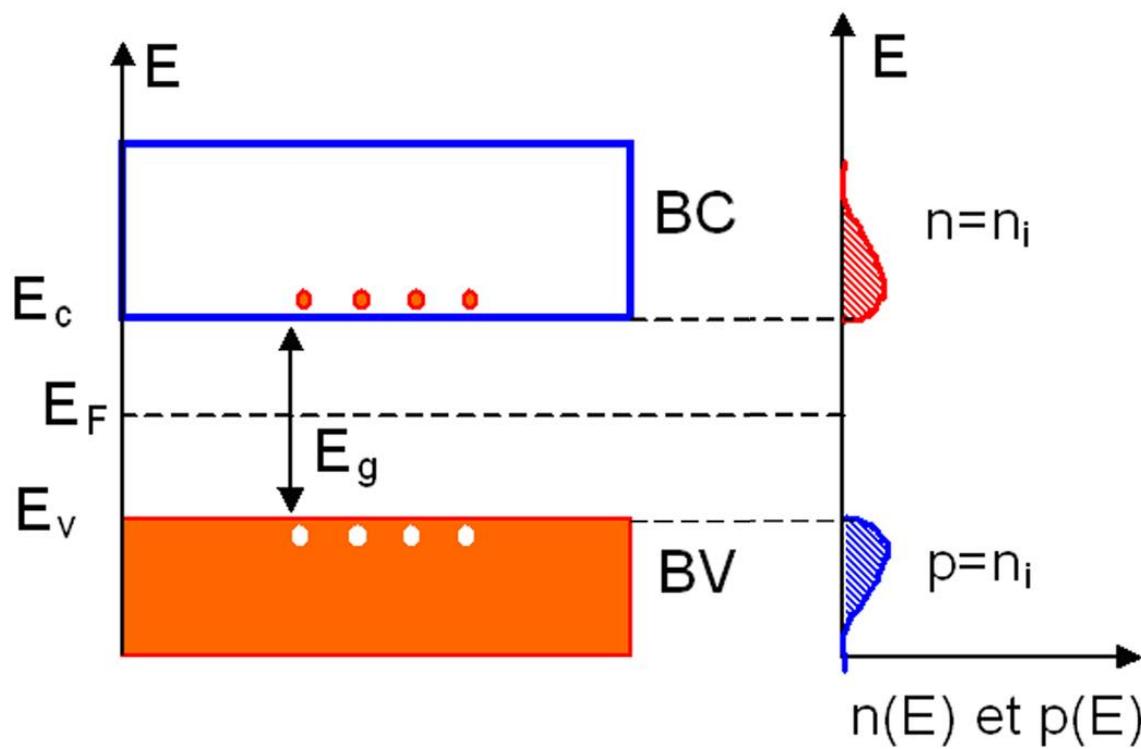
That means that about one atom every 10^{12} loses a valence electron.

⇒ Conductivity in the order of $(\mu_e + \mu_l) 10^{10}$



For an intrinsic semiconductor (without impurities), each electron in the conduction band is associated with a hole in the valence band. We conclude that the electron and hole densities are equal :

$$n = p = n_i$$

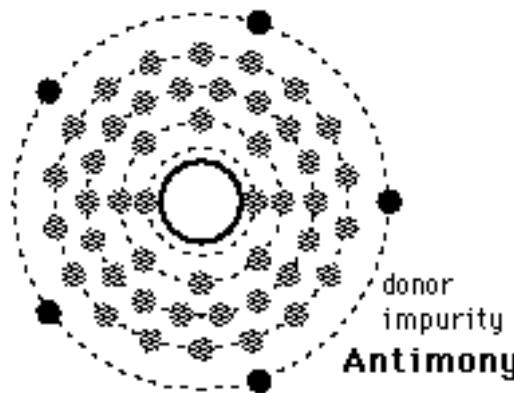


$$E_{F,i} = \frac{E_c + E_v}{2} + \frac{kT}{2} \ln \frac{N_v}{N_c} \cong \frac{E_c + E_v}{2}$$

Silicon and germanium form crystal lattices in which the electrical properties can be substantially modified by a limited substitution of atoms ('*doping*')

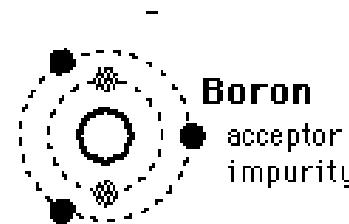
Adding a small percentage of atoms of other elements in the crystal determines important changes in the electrical properties of the crystal, that is called 'doped'.

Antimony
Arsenic
Phosphorous

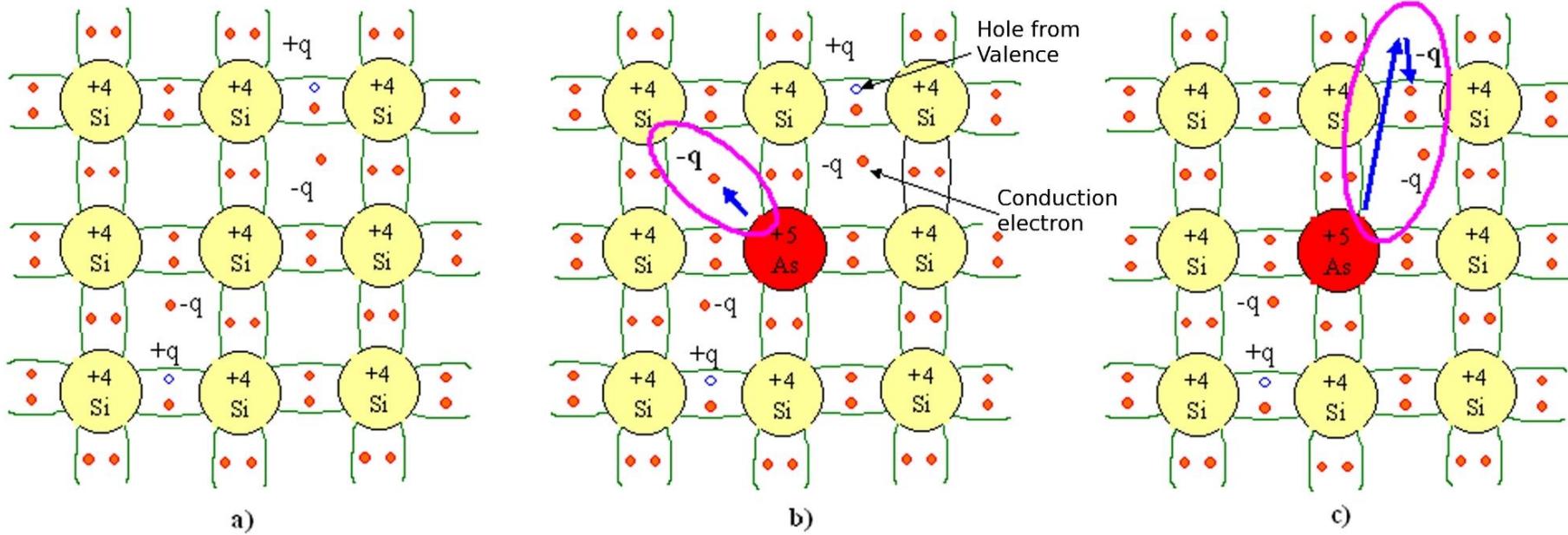


(5 valence electrons)
provide 1 electron in addition
(‘donors’)
n-type doping

Boron
Aluminum
Gallium

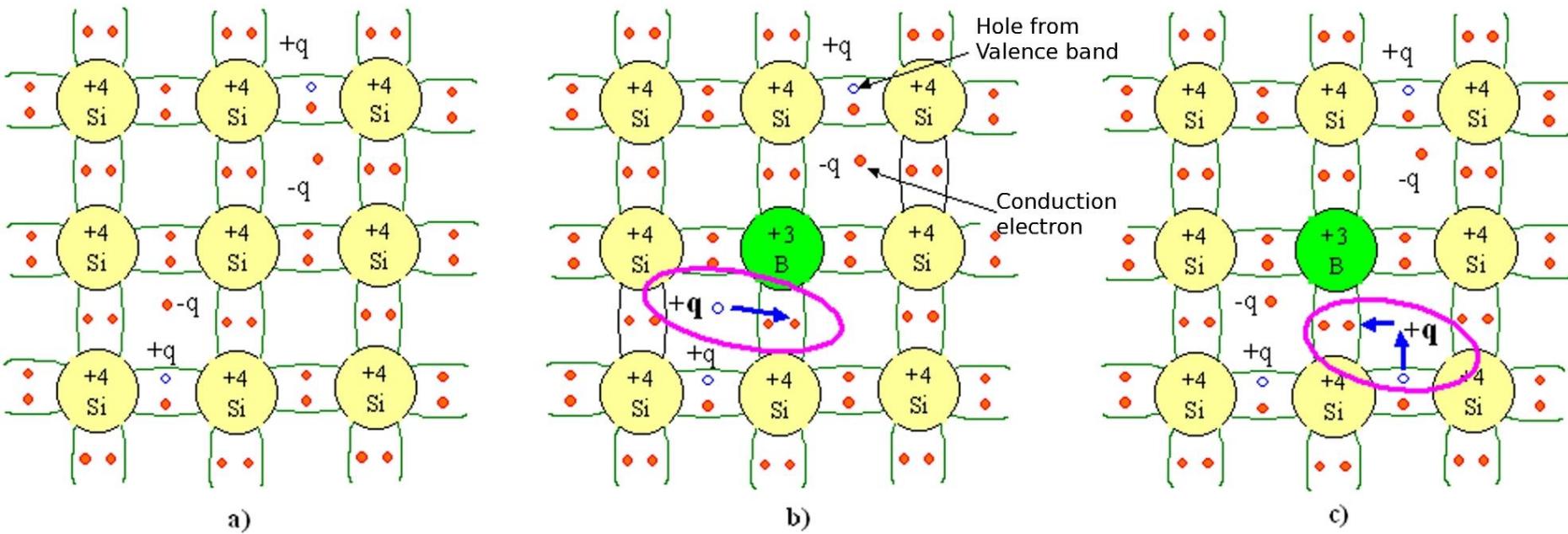


(3 valence electrons)
provide 1 hole in addition
(‘acceptors’)
p-type doping



A **N-type semiconductor** is an intrinsic semiconductor (e.g. silicon Si) in which a donor impurity (e.g. arsenic As in Si, or Si in GaAs) has been intentionally introduced. The impurities are called donor impurities since they have to give an extra electron to the conduction band in order to make all the bonds with neighboring atoms (As is pentavalent while Si is tetravalent).

A n-type semiconductor has a higher electron density n and a lower hole density p than the same intrinsic semiconductor. Holes are said to be the **minority carriers** whereas electrons are the **majority carriers**.



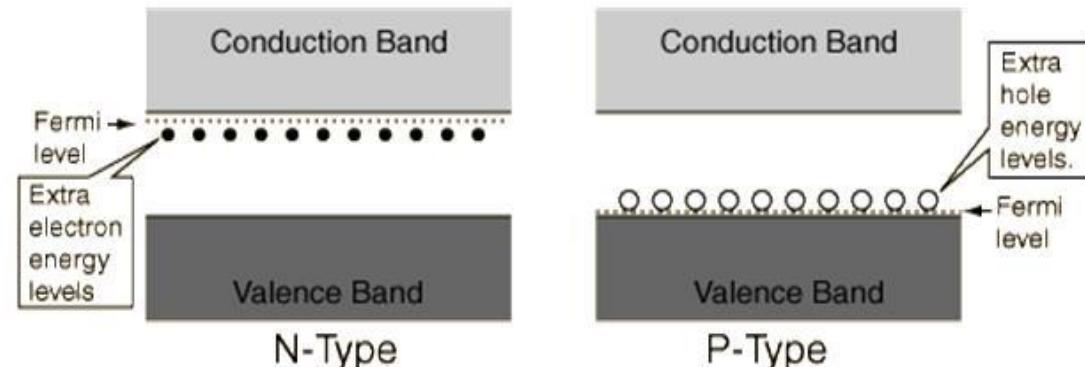
A **P-type semiconductor** is an intrinsic semiconductor (like Si) in which an impurity acting as an **acceptor** (like e.g. boron B in Si) has been intentionally added. These impurities are called acceptors since once they are inserted in the crystalline lattice, they lack one or several electrons to realize a full bonding with the rest of the crystal.

A p-type semiconductor has a lower electron density n and a higher hole density p than the same intrinsic semiconductor. Electrons are said to be the **minority carriers** whereas holes are the **majority carriers**.

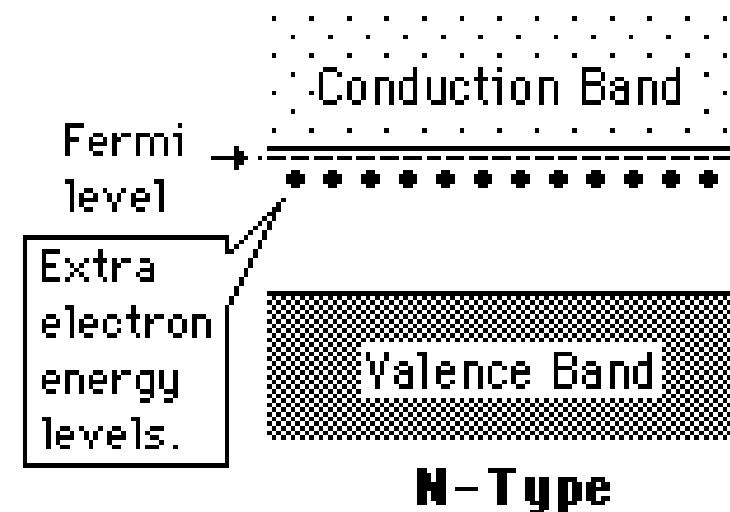
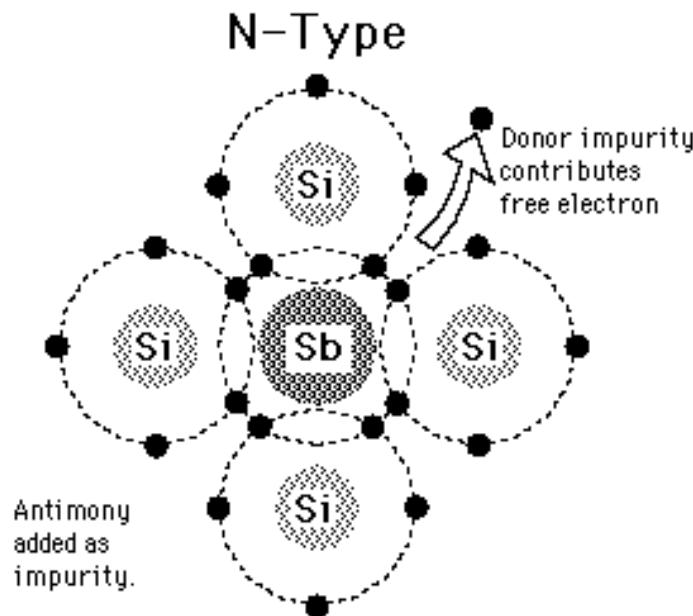
The application of band theory to n-type and p-type semiconductors shows that extra levels have been added by the impurities.

In n-type material there are electron energy levels near the top of the band gap so that they can be easily excited into the conduction band.

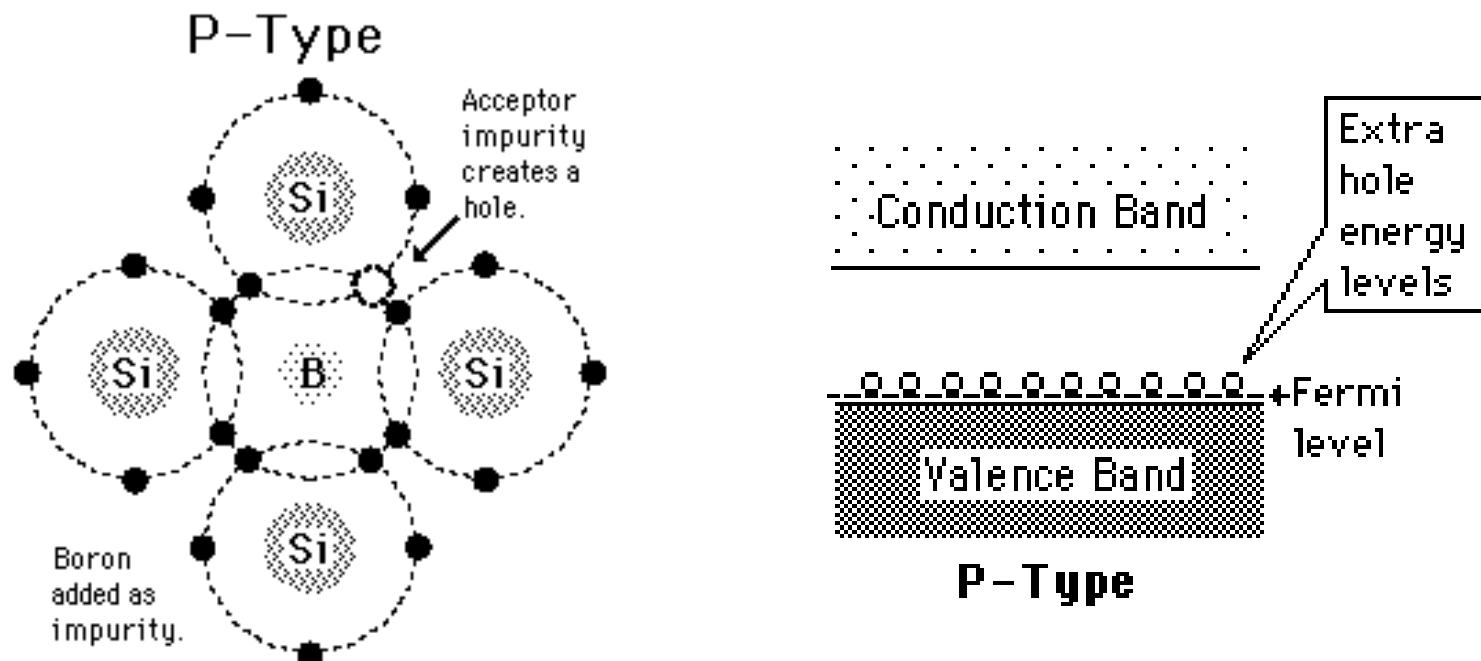
In p-type material, extra holes in the band gap allow excitation of valence band electrons, leaving mobile holes in the valence band.



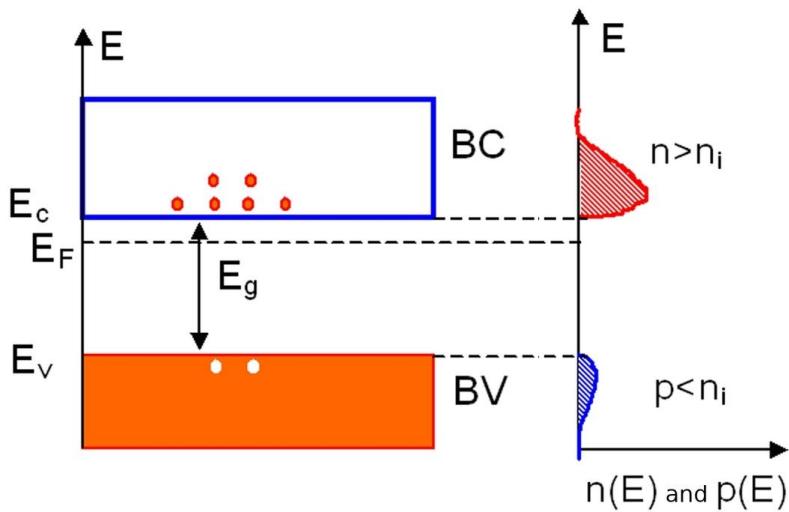
Adding pentavalent impurities (Sb, As, P) introduces free electrons in the crystal lattice, and increases the conductivity of the semiconductor



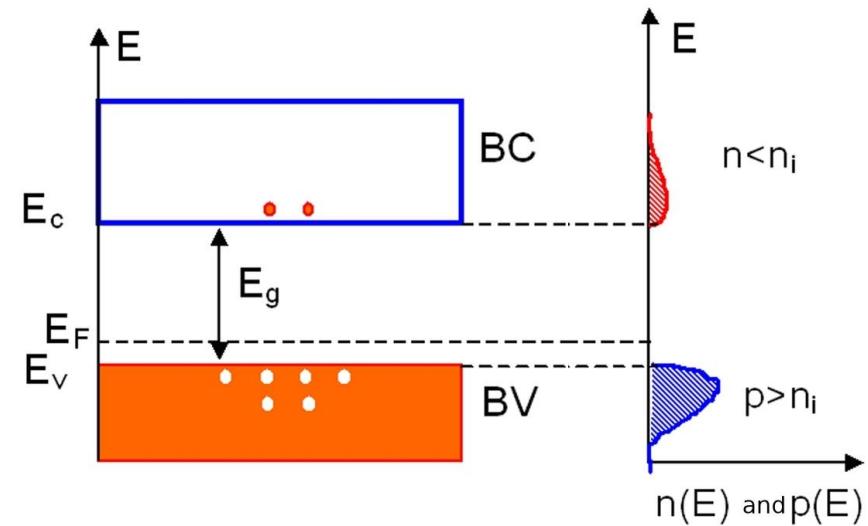
Adding trivalent impurities (B, Al, Ga) determines a deficiency of valence electrons, creating holes, and so increasing the conductivity of the semiconductor



N-type semiconductor



P-type semiconductor



For extrinsic semiconductors, the dopant density is always far higher than the intrinsic carrier density : $NA \gg ni$. In the case of a p-type material, the hole density is then close to the dopant density NA .

Typically in the order of 10^{15} atoms/cm³ (one doped atom out of 10^7).

Number n_n of electrons in a n-doped crystal (or p_p holes in p-doped crystal) in the order of 10^{15} electrons/cm³, therefore due, in practice, only to doping.

Decrease of holes in n-doped crystal (or electrons in p-doped crystal) for recombination.

Therefore

$$\begin{aligned}n_n &>> n_i = p_i >> p_n \\p_p &>> p_i = n_i >> n_p\end{aligned}$$

In general, it can be demonstrated that the product of electrons and holes concentrations is independent on doping:

$$n_n \cdot p_n = n_i \cdot p_i = n_p \cdot p_p$$

This is in the order of 10^{20} .

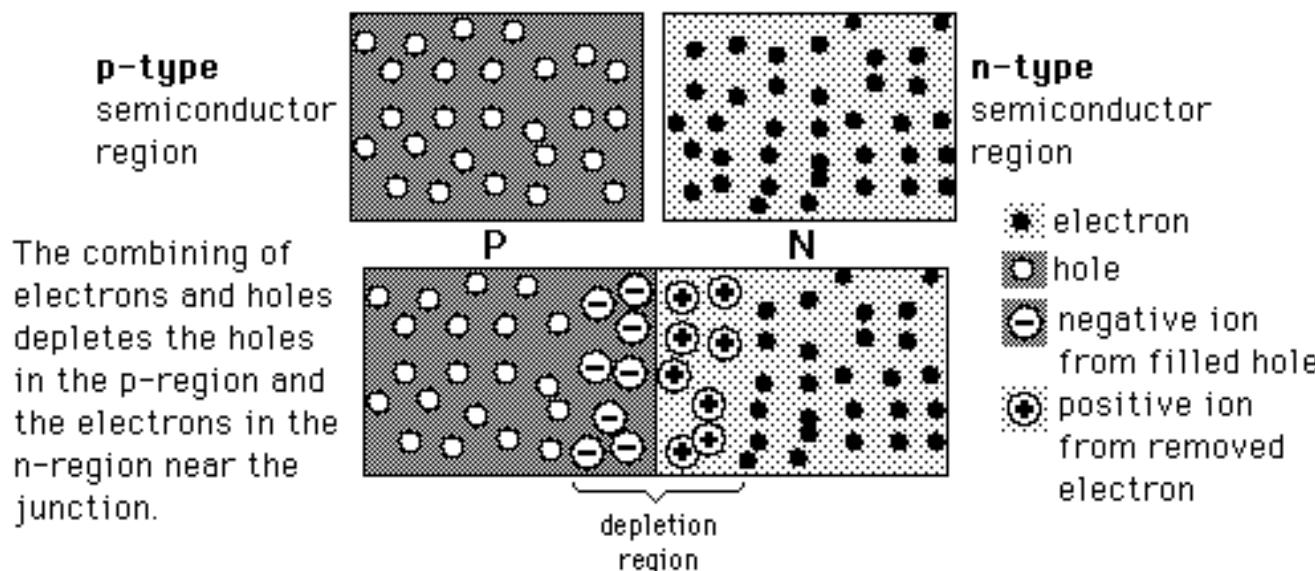
Therefore, n_p and p_n are *in the order of 10^5 parts/cm³*.

Because conductivity in semiconductors is $q(n\mu_e + p\mu_l)$ it derives that conductivity in n-doped semiconductors is in the order of $q\mu_e 10^{15}$ (or $q\mu_l 10^{15}$ in p-doped semiconductors)

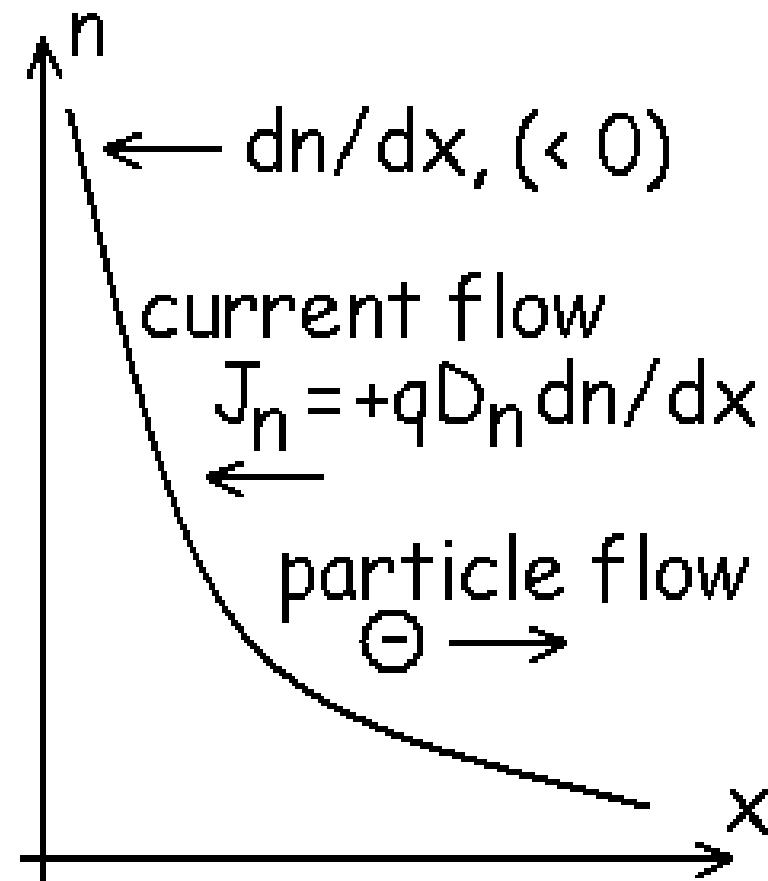
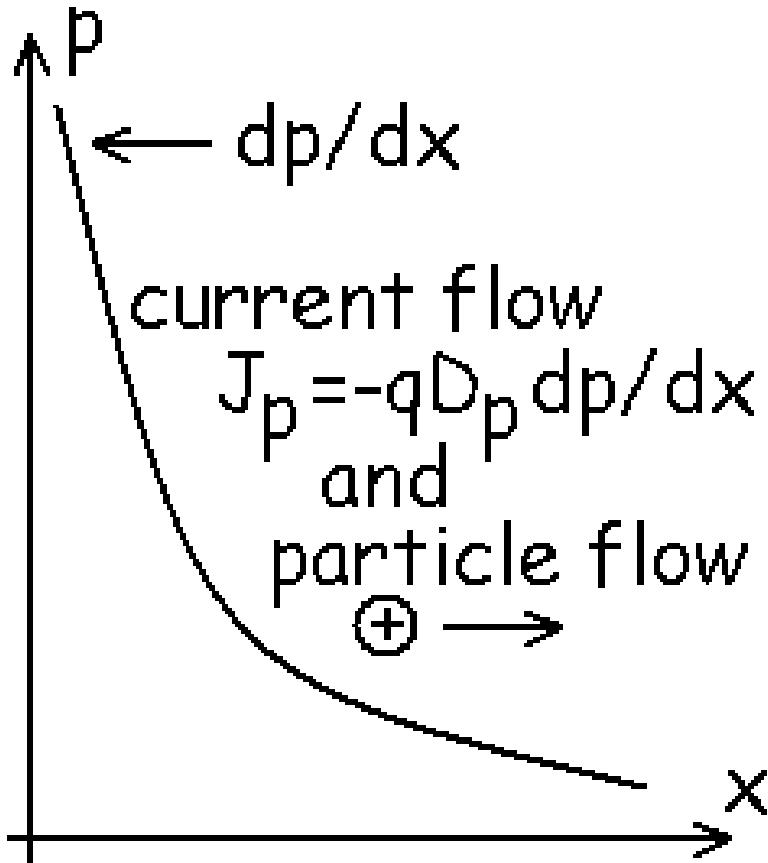
→ A doped semiconductor is able to bring current 100.000 (10^5) times more than an intrinsic semiconductor (not doped).

By putting in contact semiconductors doped in opposite way, so creating a **junction**, allows to obtain very interesting electrical properties.

When n- and p-type materials are in contact, the junction behaves in a very different way compared to the way in which the materials behave when they are single.



- a) diffusion of holes from zone p to zone n (who leave behind a negative-charged zone) and electrons from zone n to zone p (who leave behind a positive-charged zone)
⇒ creation of an electric field E (directed from n- to p-zone);
- b) the electric field induces a drift of electrons from zone p to zone n (and holes from zone n to zone p);
- c) When diffusion and drift currents are equal, the junction is in equilibrium; across the junction there is a null net current flow, Fermi level is constant, contact potential is equal to V_0 .



In presence of electrons and holes gradient, ∇p e ∇n are not null.

Diffusion current therefore is:

$$\mathbf{J} = \bar{\mathbf{J}}_p + \bar{\mathbf{J}}_n$$

(where D_p e D_n are diffusion coefficients)

$$\vec{J}_p = -qD_p \nabla p = -qD_p \left(\frac{\partial p}{\partial x} \mathbf{i} + \frac{\partial p}{\partial y} \mathbf{j} + \frac{\partial p}{\partial z} \mathbf{k} \right)$$

$$\vec{J}_n = +qD_n \nabla n = +qD_n \left(\frac{\partial n}{\partial x} \mathbf{i} + \frac{\partial n}{\partial y} \mathbf{j} + \frac{\partial n}{\partial z} \mathbf{k} \right)$$

because $\vec{E} = -\nabla V$

$$\vec{J}_{p,drift} = \sigma_p \vec{E} = pq\mu_p \vec{E} = -pq\mu_p \nabla V$$

$$\vec{J}_{n,drift} = \sigma_n \vec{E} = nq\mu_n \vec{E} = -nq\mu_n \nabla V$$

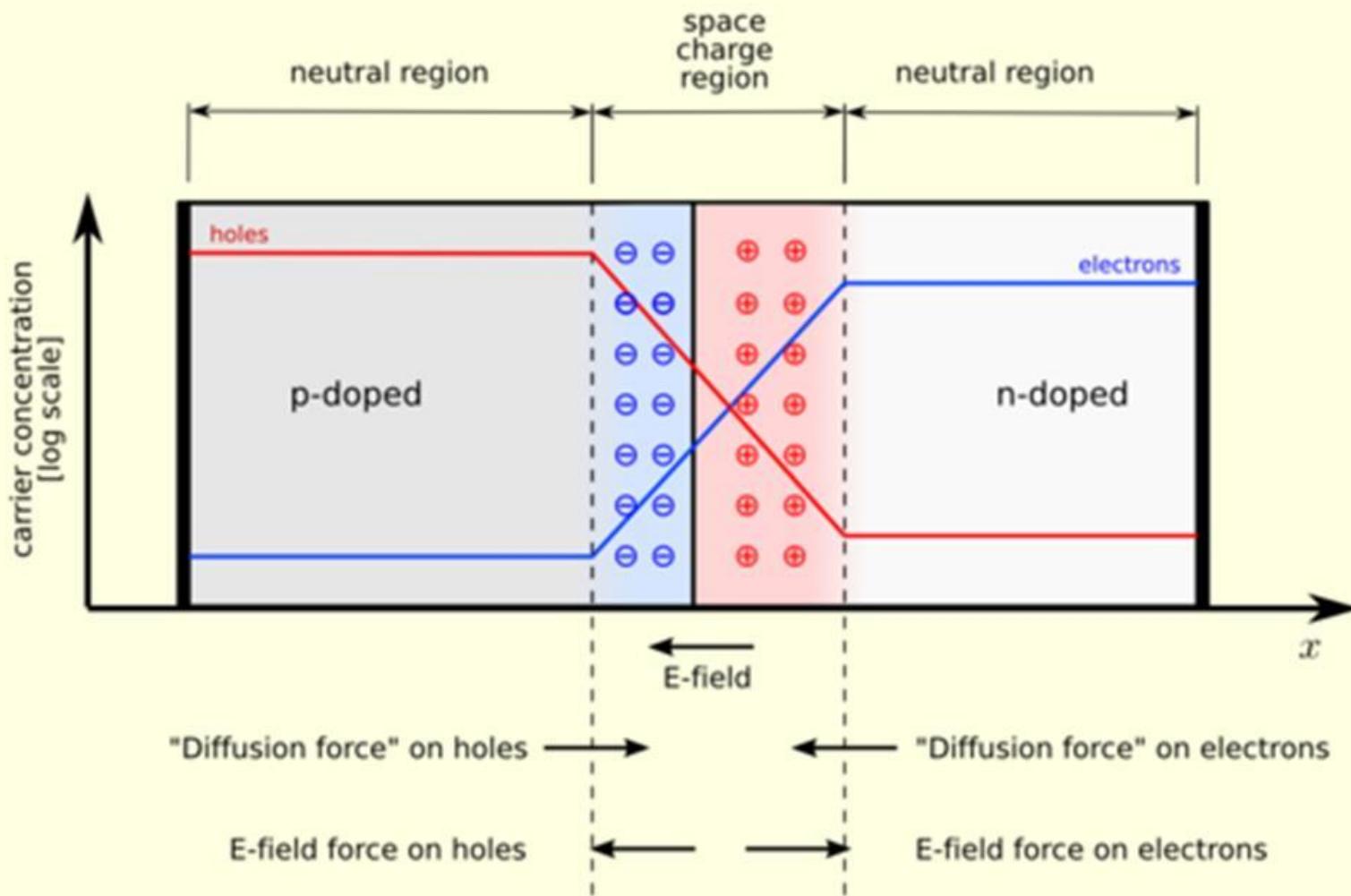
$$\vec{J}_{p,diffusion} = -qD_p \nabla p$$

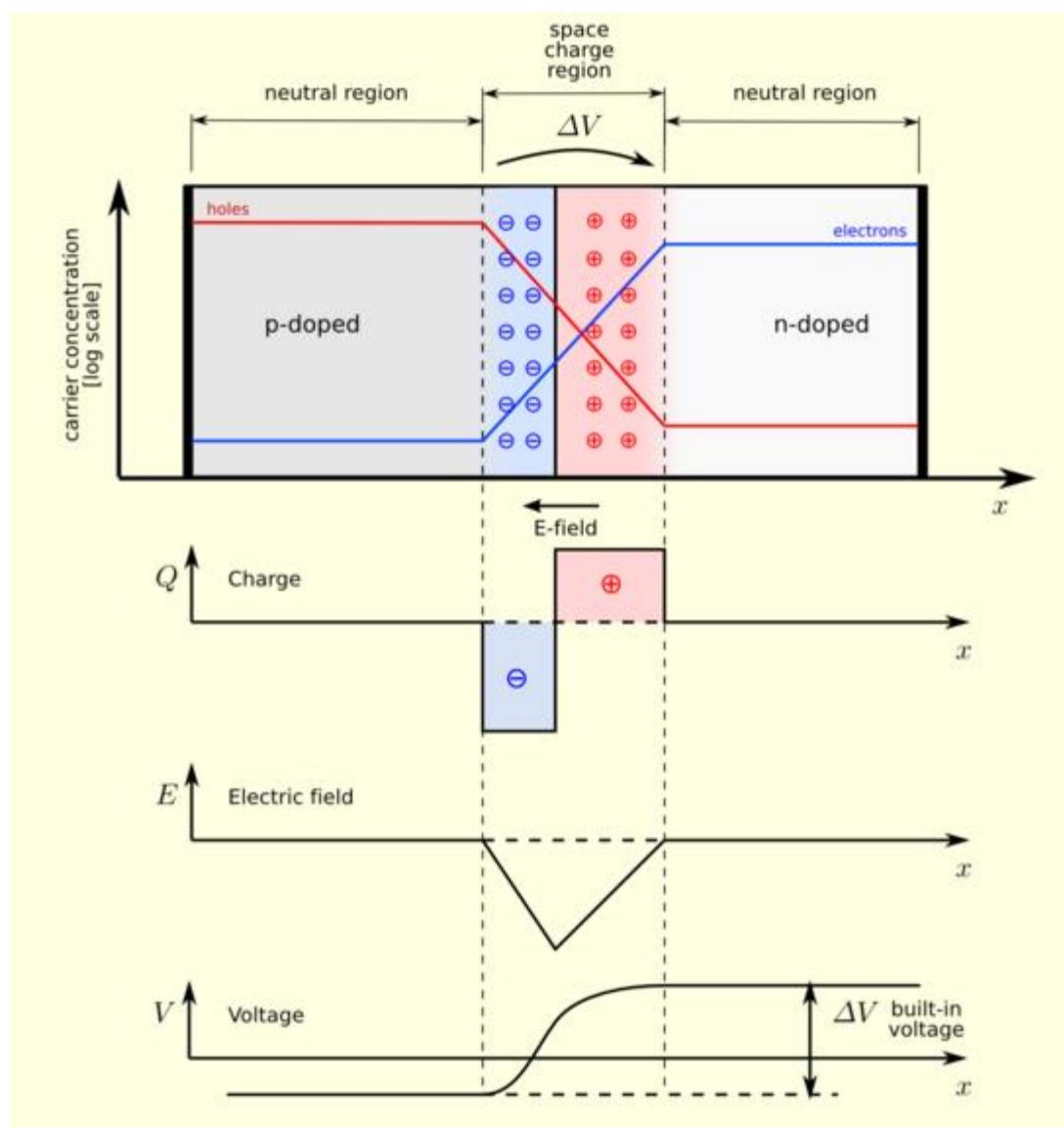
$$\vec{J}_{n,diffusion} = +qD_n \nabla n$$

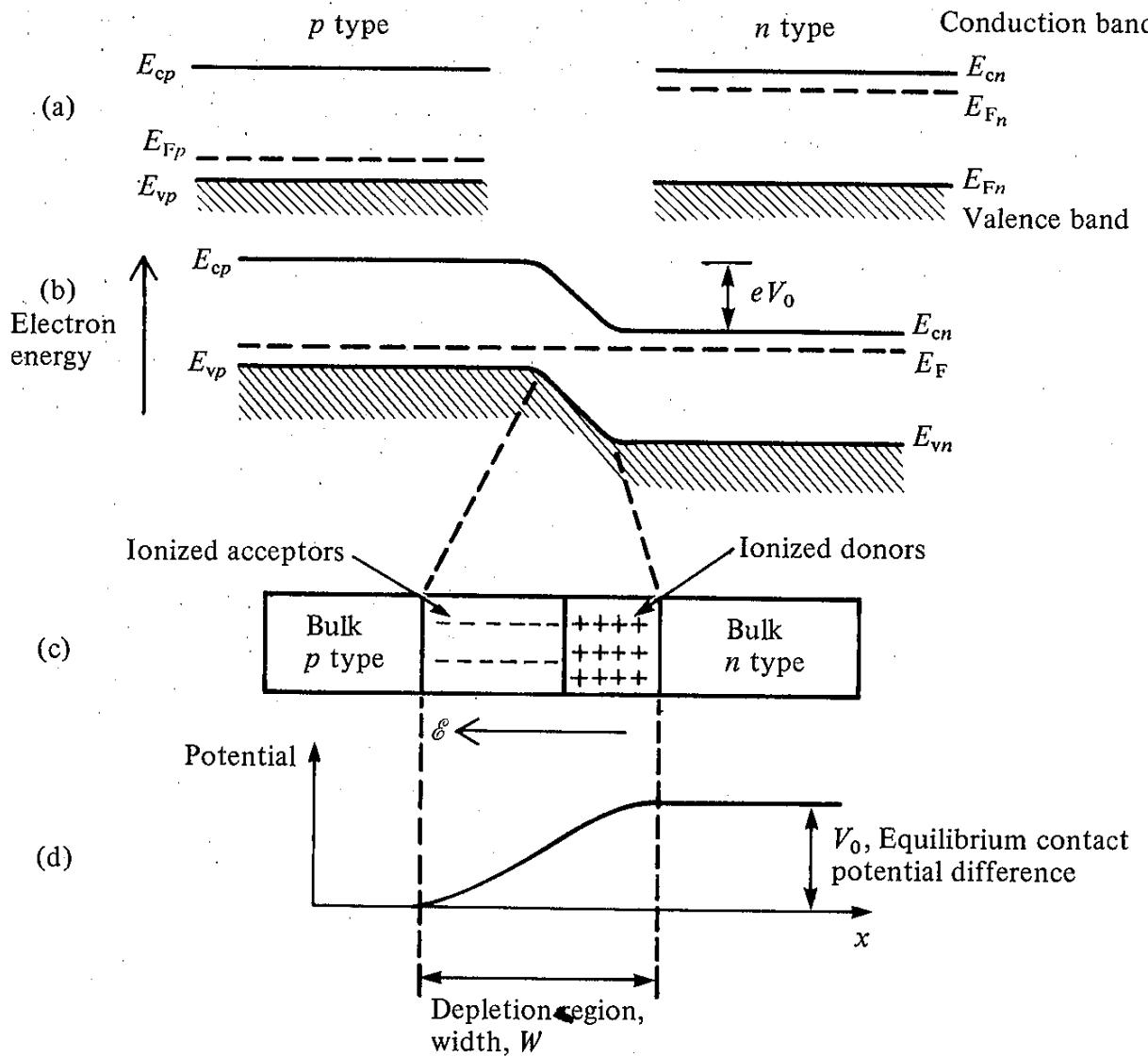
Total current density is determined by charge carriers gradient and by electrical potential gradient :

$$\vec{J}_{total} = \vec{J}_{p,drift} + \vec{J}_{n,drift} + \vec{J}_{p,diff.} + \vec{J}_{n,diff.}$$

$$\vec{J}_{total} = -(\sigma_p + \sigma_n) \nabla V - qD_p \nabla p + qD_n \nabla n$$



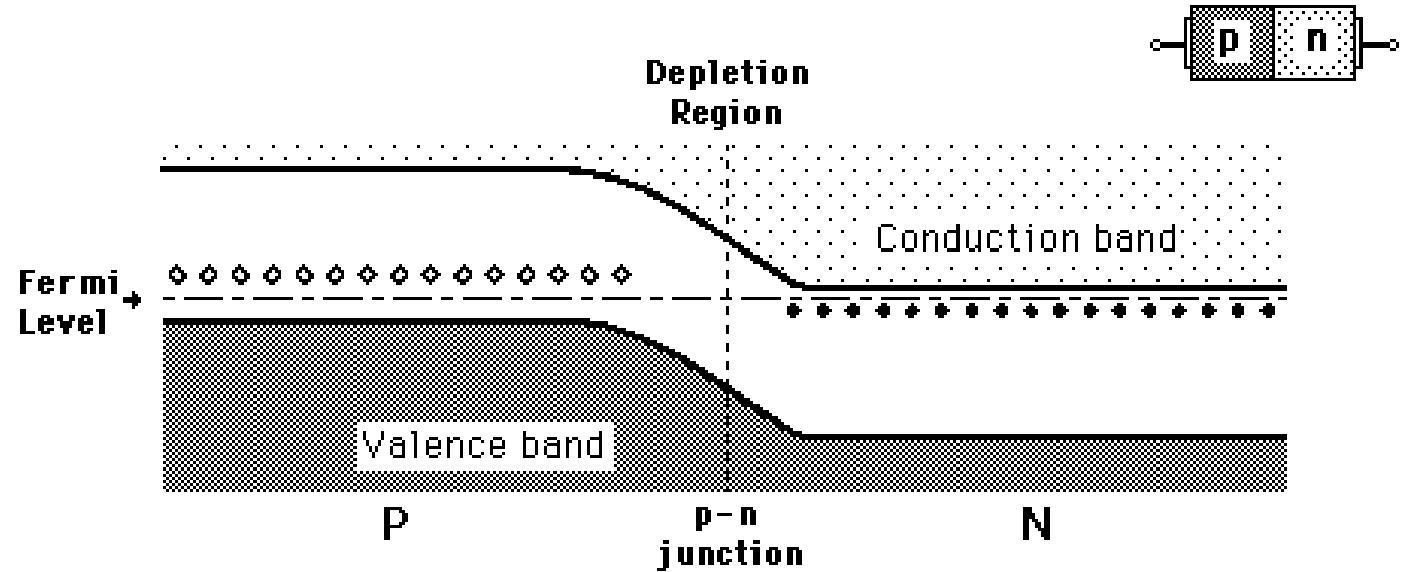
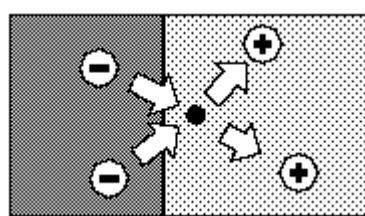




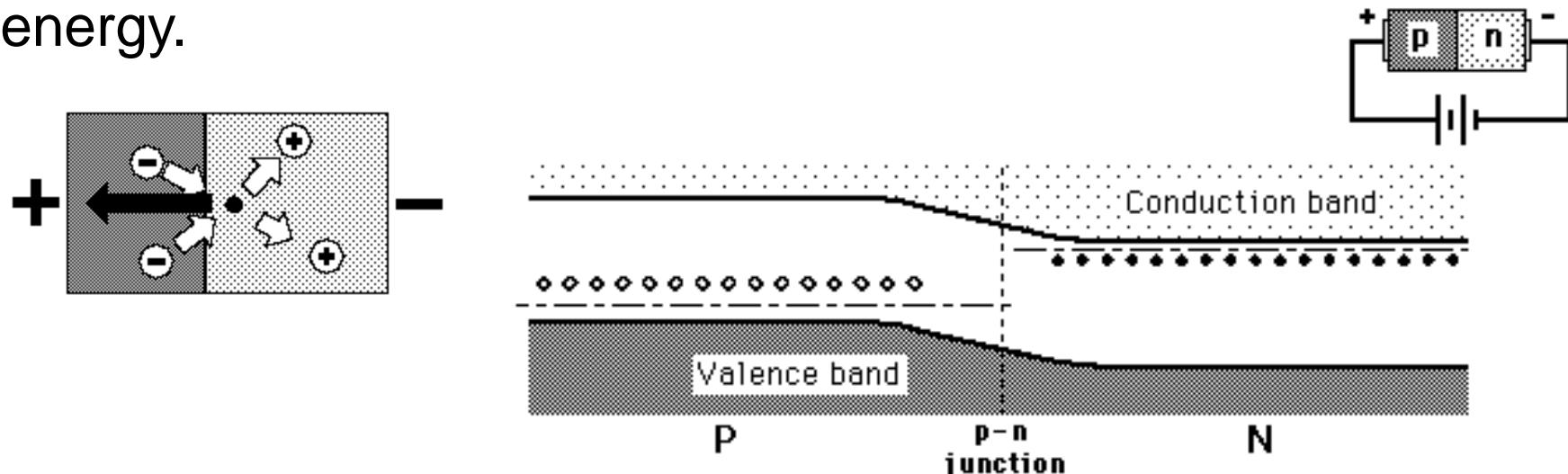
$$V_0 = \frac{kT}{e} \ln \left(\frac{N_a N_d}{n_i^2} \right)$$

for $100 \text{ K} \leq T \leq 400 \text{ K}$,
 $n_n = N_d$, $p_p = N_a$ (the concentrations
of 'majority' carriers are equal to
doping level)

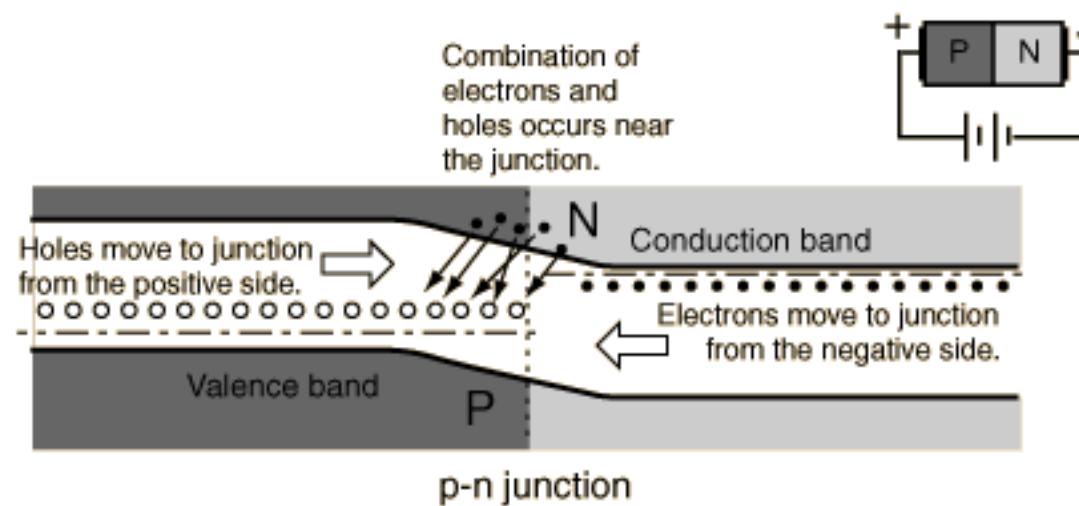
$$np = n_i^2$$



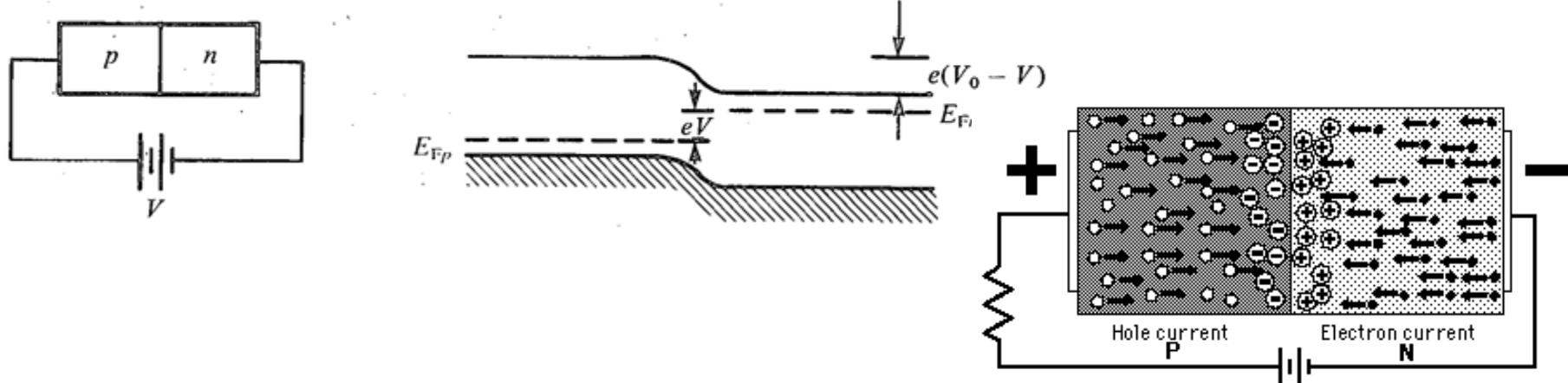
To forward bias the p-n junction, the p side is made more positive, so that it is "downhill" for electron motion across the junction. An electron can move across the junction and fill a vacancy or "hole" near the junction. It can then move from vacancy to vacancy leftward toward the positive terminal, which could be described as the hole moving right. The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.



When the p-n junction is forward biased, the electrons in the n-type material which have been elevated to the conduction band and which have diffused across the junction find themselves at a higher energy than the holes in the p-type material. They readily combine with those holes, making possible a continuous forward current through the junction.

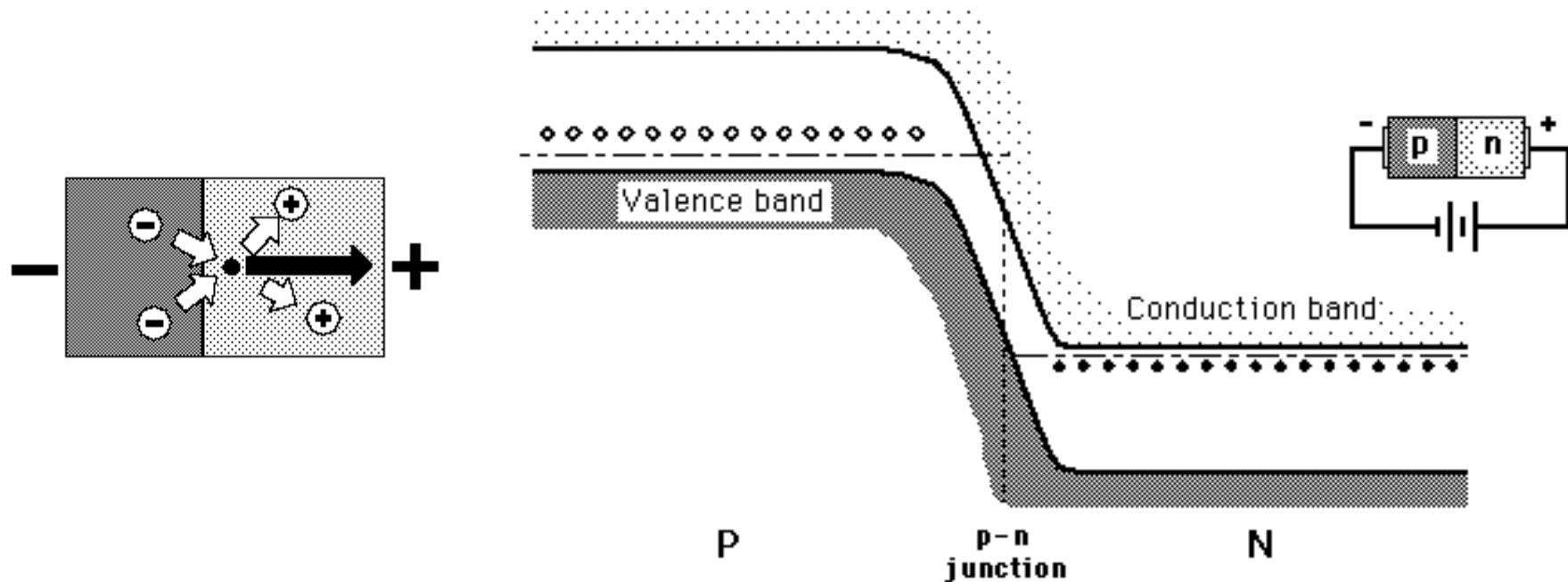


The forward current in a p-n junction when it is forward-biased (illustrated below on the right) involves electrons from the n-type material moving leftward across the junction and combining with holes in the p-type material. Electrons can then proceed further leftward by jumping from hole to hole, so the holes can be said to be moving to the right in this process.



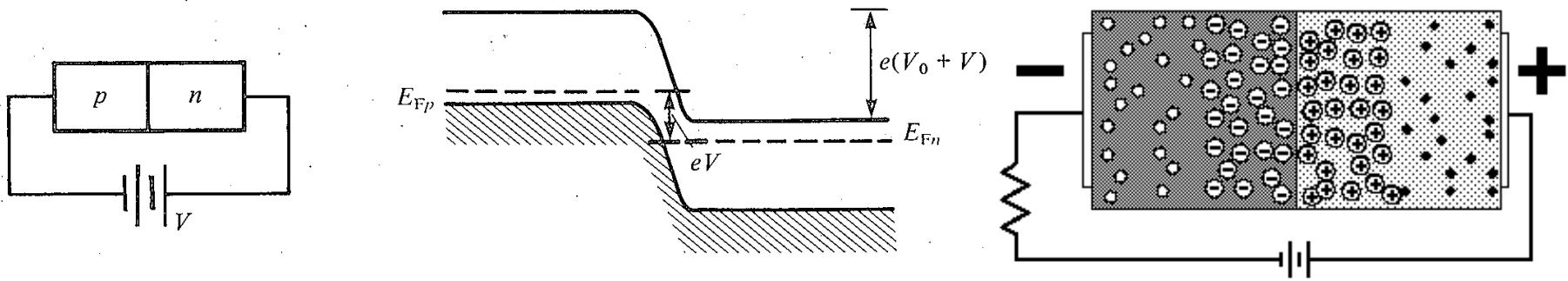
An applied voltage with the indicated polarity further impedes the flow of electrons across the junction.

For conduction in the device, electrons from the N region must move to the junction and combine with holes in the P region. A reverse voltage drives the electrons away from the junction, preventing conduction.

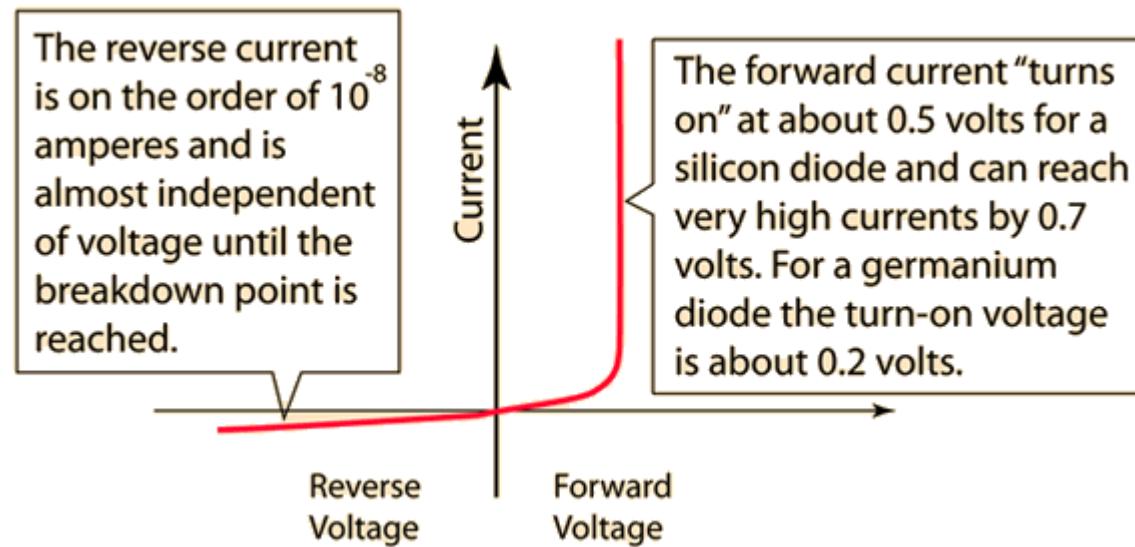
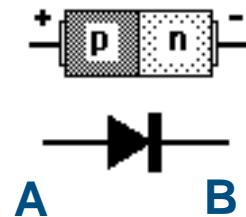


Because the p side is made more negative, it is made "uphill" for electrons moving across the junction.

The conduction direction for electrons in the diagram is right to left, and the upward direction represents increasing electron energy.



The nature of the p-n junction is that it will conduct current in the forward direction but not in the reverse direction. It is therefore a basic tool for rectification in the building of DC power supplies. It is a **diode**.



If $V_A > V_B$ (forward biased junction), in the diode a current flows from A to B.
If $V_A < V_B$ (reverse biased junction), the diode offers a very high resistance and a very low current flows (intrinsic conduction) from B to A.