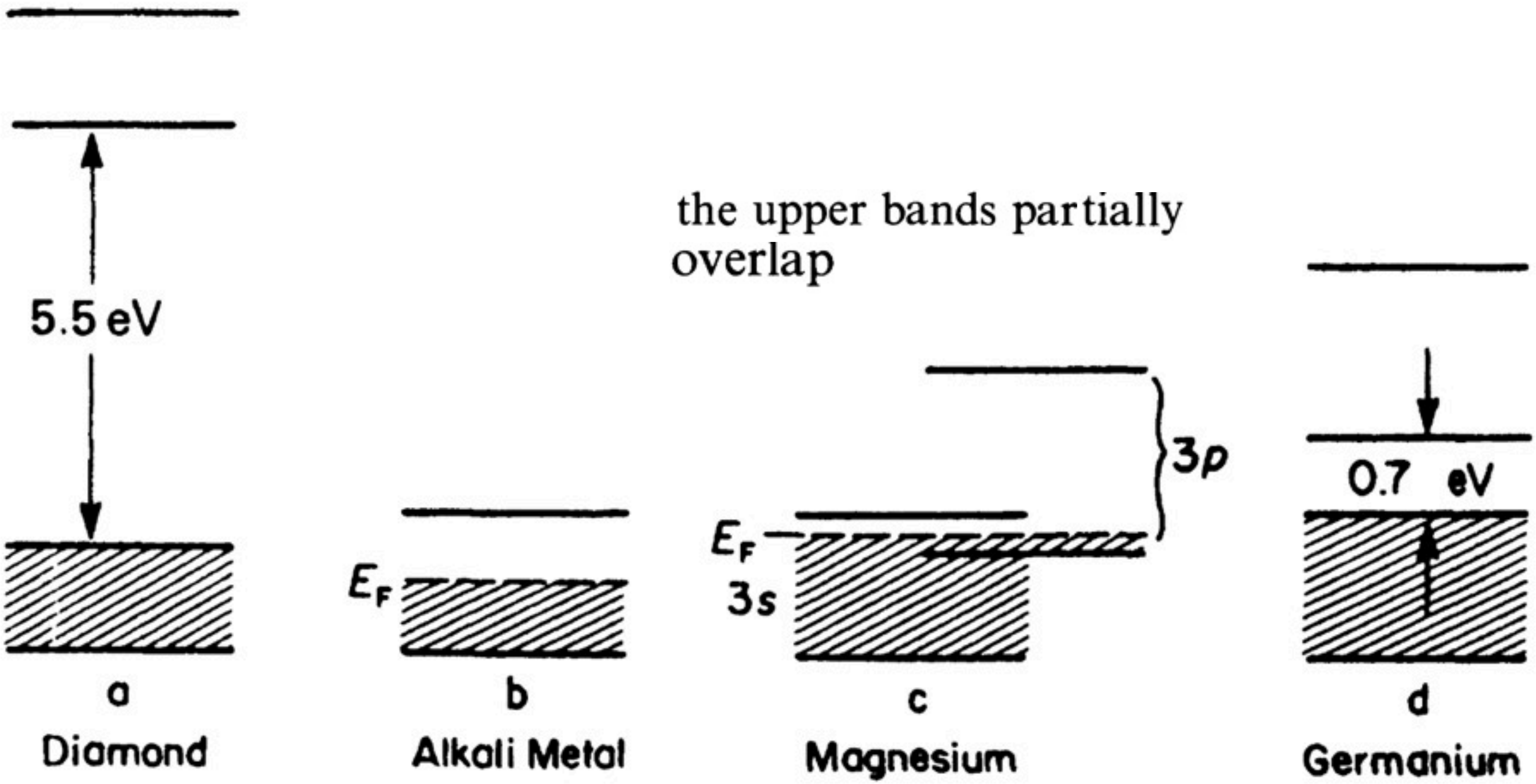
CHAPTER 8

Semiconductors

8.1. Band Structure



the upper bands partially overlap

the highest filled band is completely occupied

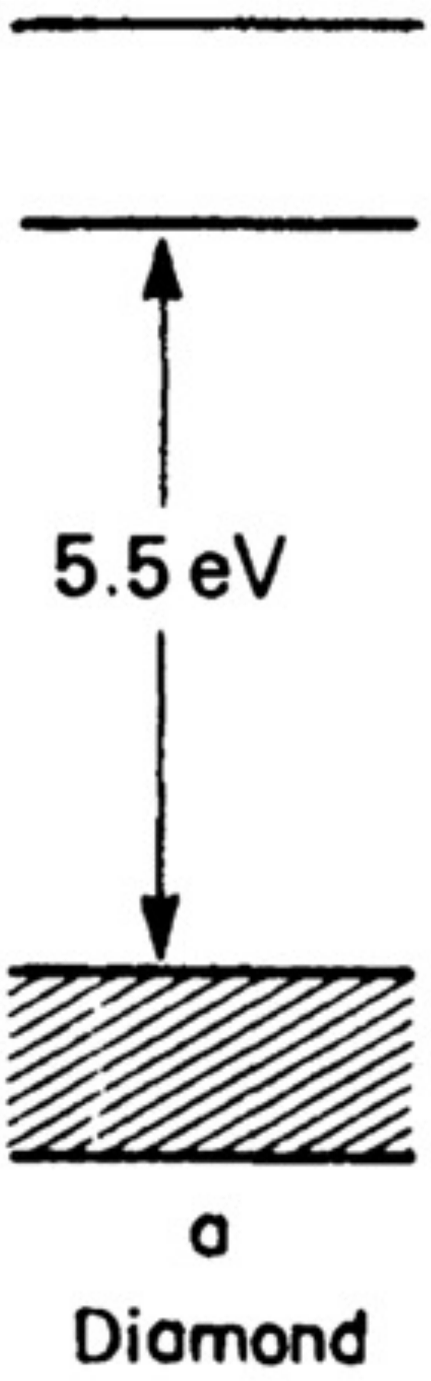
the valence band is essentially half-filled

bivalent metals should be insulators

intrinsic semiconductors

small band gap

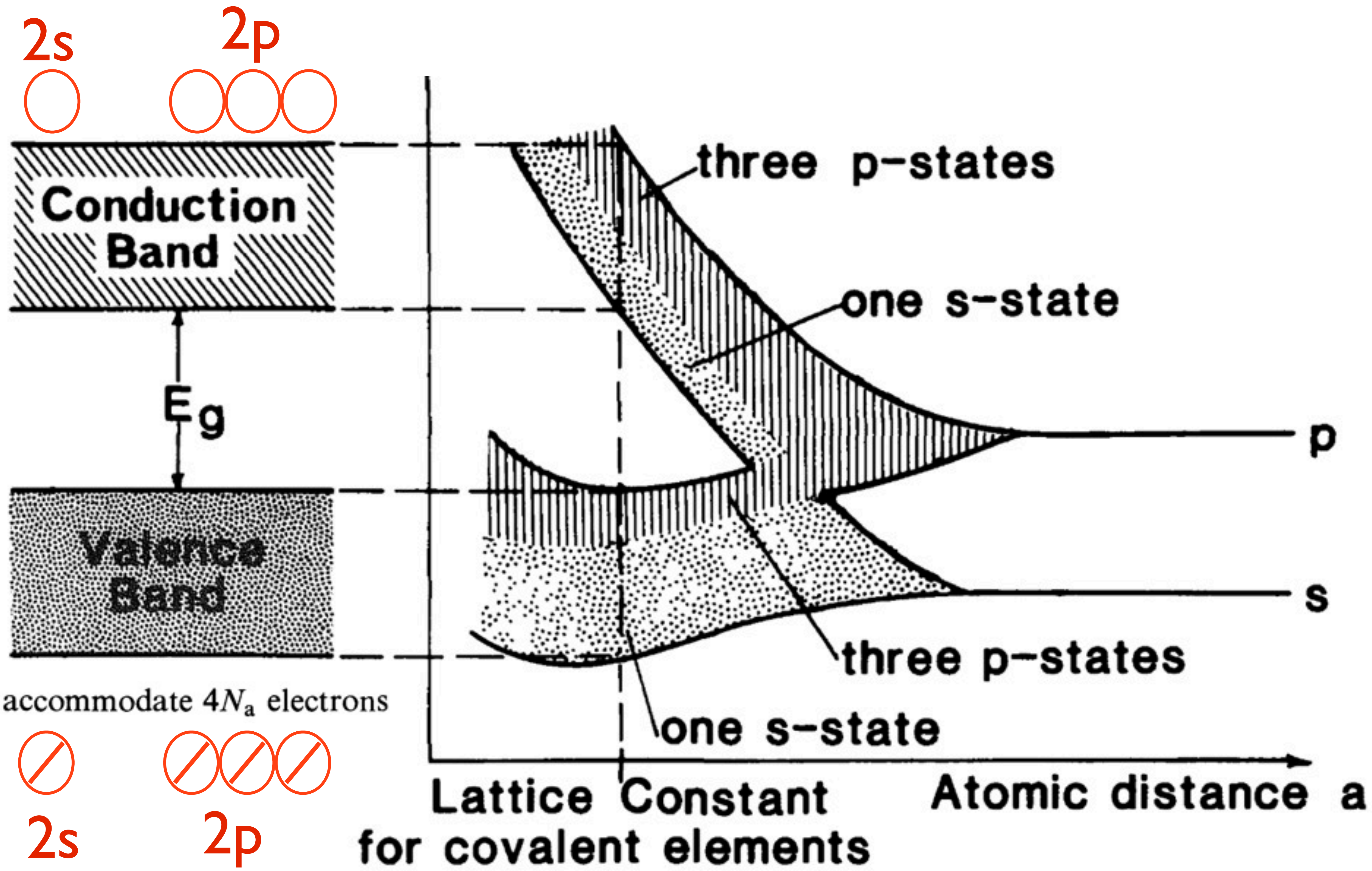
conduction band



upper (conduction) band
empty

small gap

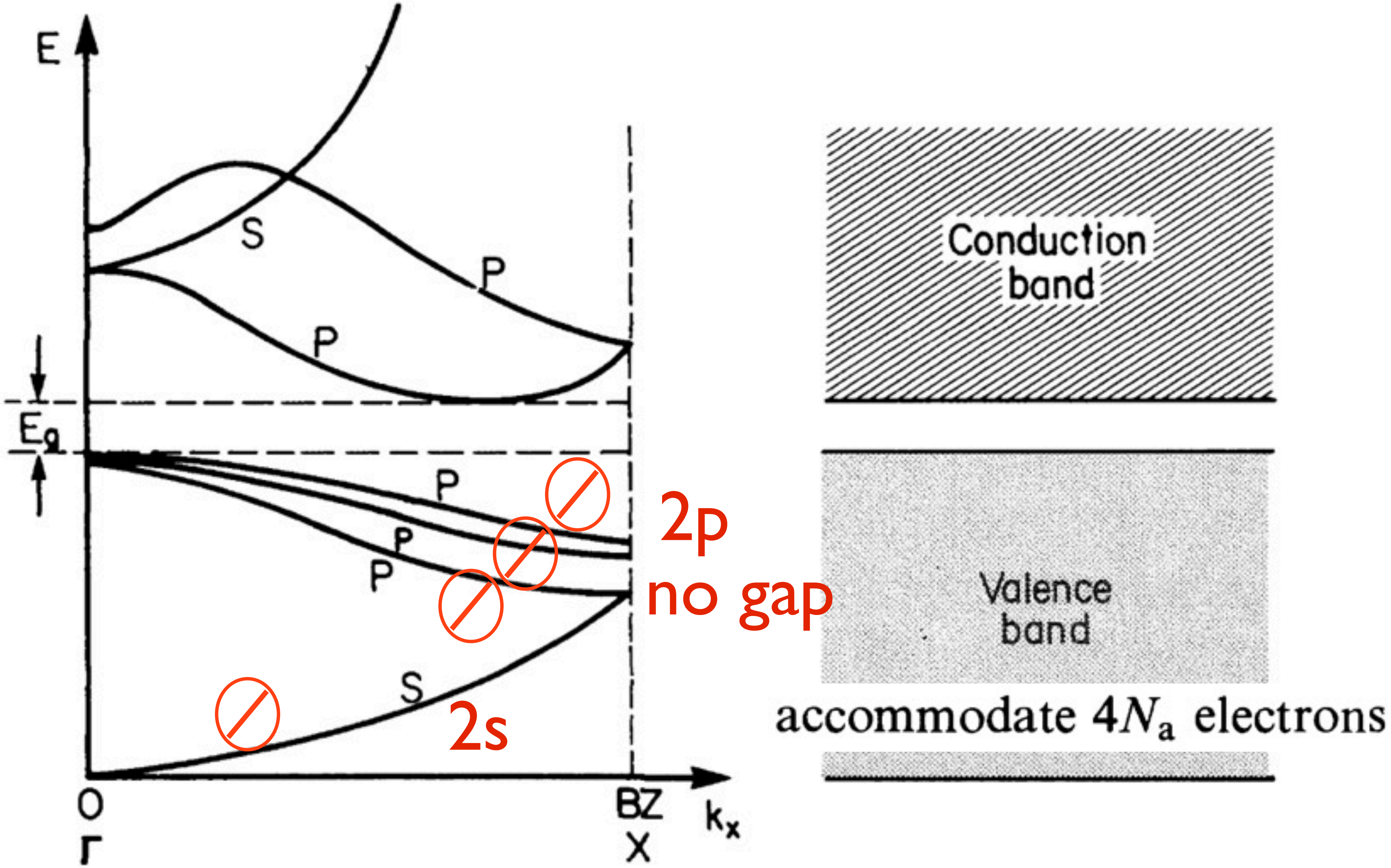
valence band
filled



accommodate $4N_a$ electrons

hybrid (s+p)band

bands in different directions in **k**-space usually have different shapes so that a complete assessment can only be made by inspecting the entire band

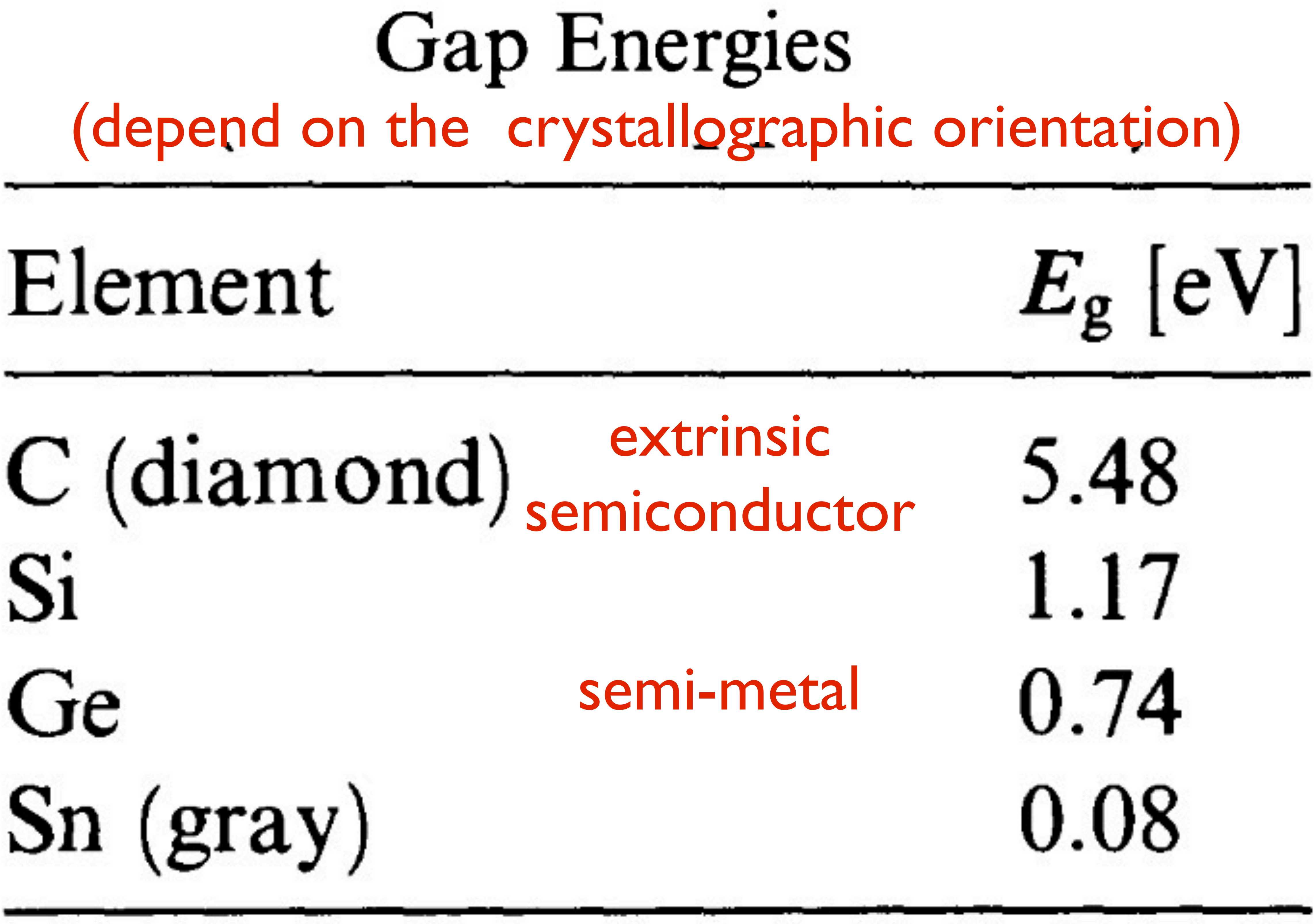


accommodate $4N_a$ electrons

Schematic band structure of silicon in the k_x (or X) direction

Gap Energies

(depend on the crystallographic orientation)



Element	E_g [eV]
C (diamond)	5.48
Si	1.17
Ge	0.74
Sn (gray)	0.08

extrinsic semiconductor

semi-metal

gap energy is slightly temperature dependent

$$E_{\mathrm{gT}} = E_{\mathrm{g0}} - \frac{\xi T^2}{T + \theta_{\mathrm{D}}}$$

E_{g0} is the band gap energy at $T = 0$ K

$\xi \approx 5 \times 10^{-4}$ eV/K

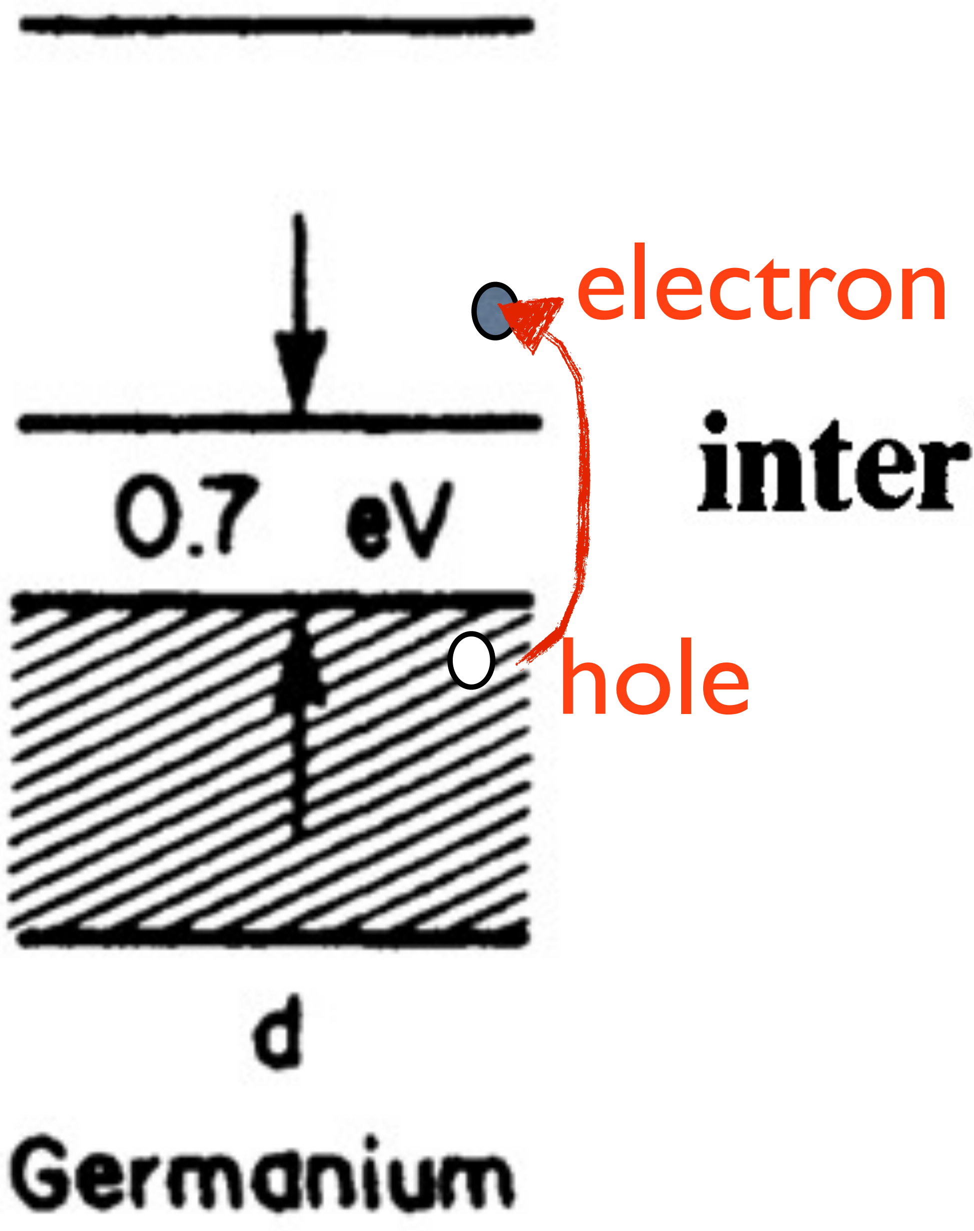
θ_{D} is the Debye temperature

E_{g} becomes smaller with increasing temperature

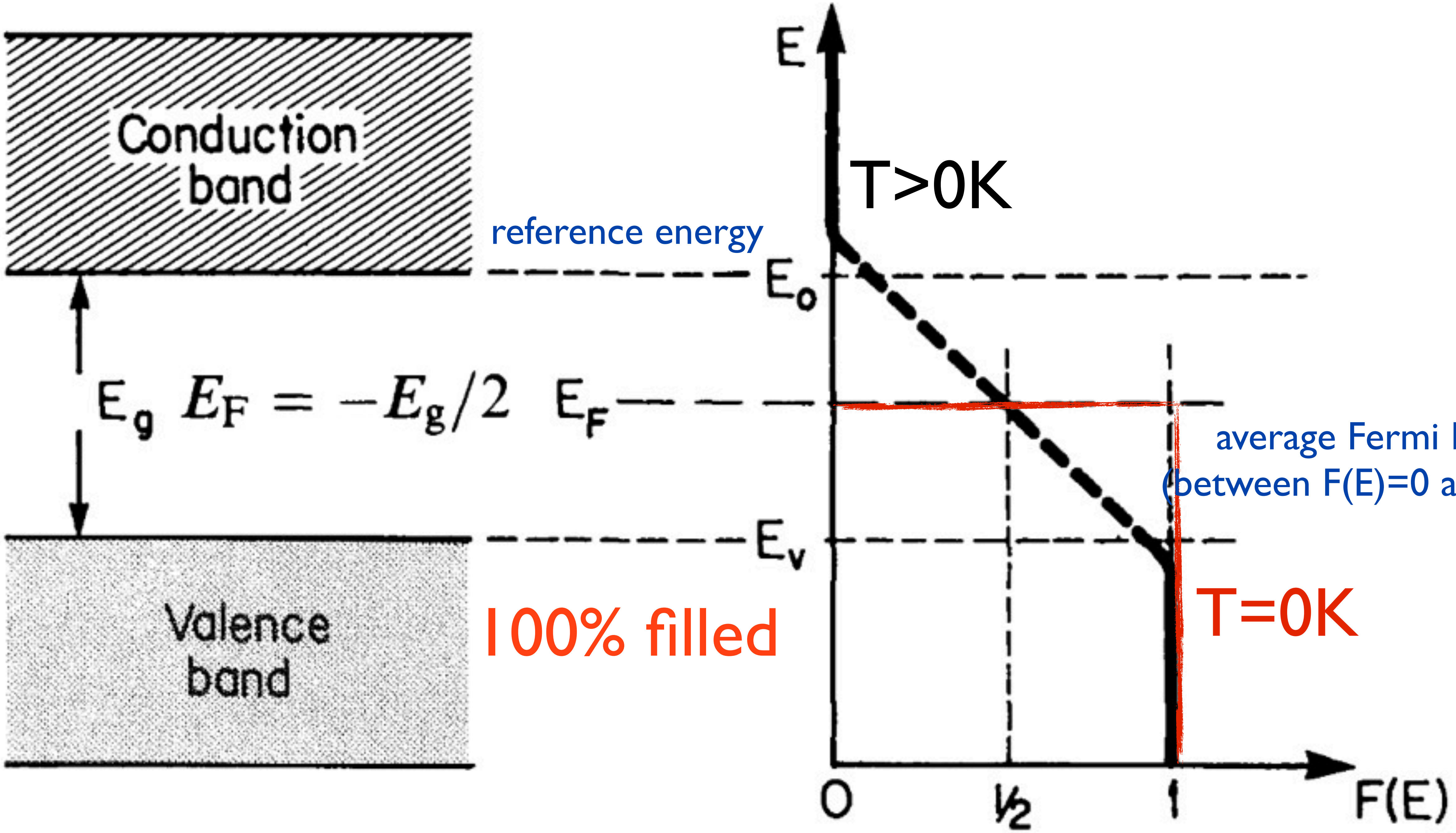
8.2. Intrinsic Semiconductors

Semiconductors become conducting at elevated temperatures.

In order for a semiconductor to become conducting,
electrons have to be excited from the valence band into the conduction band
where they can be accelerated by an external electric field
electron holes which are left behind in the valence band contribute to the conduction. They migrate in the opposite direction to the electrons.



interband transitions



Fermi distribution function and Fermi energy for an intrinsic semiconductor for $T > 0$ K

Recall,

$$N(E) = 2 \cdot Z(E) \cdot \mathrm{F}(E)$$

$$Z(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Population density

$$\mathrm{F}(E) = \frac{1}{\exp\left(\frac{E - E_\mathrm{F}}{k_\mathrm{B} T}\right) + 1} \simeq \exp\left[-\left(\frac{E - E_\mathrm{F}}{k_\mathrm{B} T}\right)\right]$$

(for energy above E_F)

$E - E_\mathrm{F}$ is about 0.5 eV

$k_\mathrm{B} T = 10^{-2}$ eV at room temperature

$$dN^* = N(E)\,dE$$

(number of conduction electrons between E and E+dE above E_F or E_c)

$$N^* = \frac{V}{2\pi^2}\cdot\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty E^{1/2}\cdot\exp\left[-\left(\frac{E-E_F}{k_B T}\right)\right]dE$$

(bottom of conduction band)

$$N^* = \frac{V}{2\pi^2}\cdot\left(\frac{2m}{\hbar^2}\right)^{3/2}\exp\left(\frac{E_F}{k_B T}\right)\int_0^\infty E^{1/2}\cdot\exp\left[-\left(\frac{E}{k_B T}\right)\right]dE$$

$$\int_0^\infty x^{1/2}e^{-nx}\,dx = (1/2n)\sqrt{\pi/n}.$$

$$N^* = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\exp\left(\frac{E_F}{k_B T}\right)\frac{k_B T}{2}(\pi k_B T)^{1/2}$$

$$= \frac{V}{4}\left(\frac{2mk_B T}{\pi\hbar^2}\right)^{3/2}\exp\left(\frac{E_F}{k_B T}\right).$$

$$E_F = -E_g/2$$

$$N_e = N^*/V$$

$$N_e = \frac{1}{4}\left(\frac{2mk_B}{\pi\hbar^2}\right)^{3/2}\left(\frac{m_e^*}{m_0}\right)^{3/2} T^{3/2} \exp\left[-\left(\frac{E_g}{2k_BT}\right)\right]$$

The constant factor $\frac{1}{4}\left(\frac{2mk_B}{\pi\hbar^2}\right)^{3/2}$ has the value 4.84×10^{15} ($\mathrm{cm}^{-3}\ \mathrm{K}^{-3/2}$)

$$\boxed{N_e = 4.84 \times 10^{15}\left(\frac{m_e^*}{m_0}\right)^{3/2} T^{3/2} \exp\left[-\left(\frac{E_g}{2k_BT}\right)\right].}$$

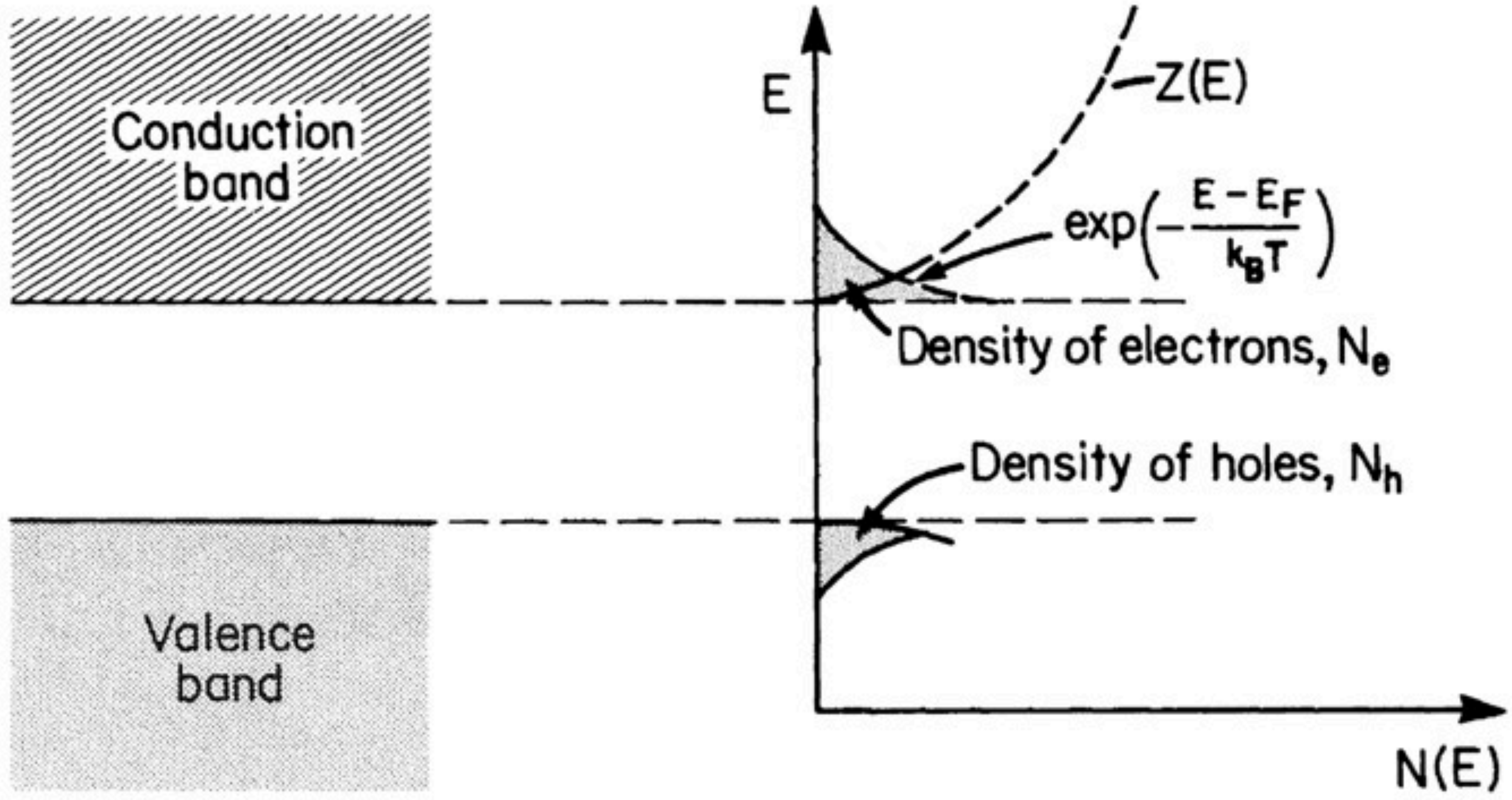
number of electrons in the conduction band per cm^3

At room temperature, $N_e \sim 10^9/\ \mathrm{cm}^3$

$1\,\mathrm{cm}^3 \sim 10^{22}$ Si atoms

only one in every 10^{13} atoms contributes an electron to conduction band

~poor conductivity



Density of electrons (N_e) and holes (N_h) for an intrinsic semiconductor.

Mobility, μ

$$\mu = \frac{v}{\mathscr{E}}$$

(drift) velocity per unit electric field

$$j = \sigma \mathscr{E} \qquad j = Nve$$

$$\sigma = N \frac{v}{\mathscr{E}} e = N \mu e$$

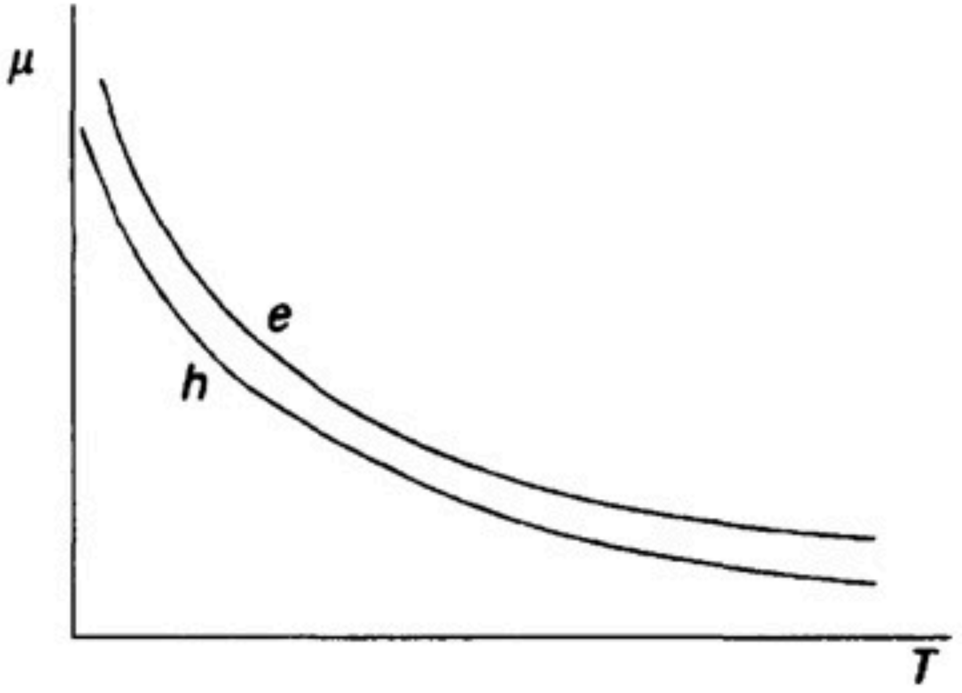
Taking both electrons and holes into consideration we can write

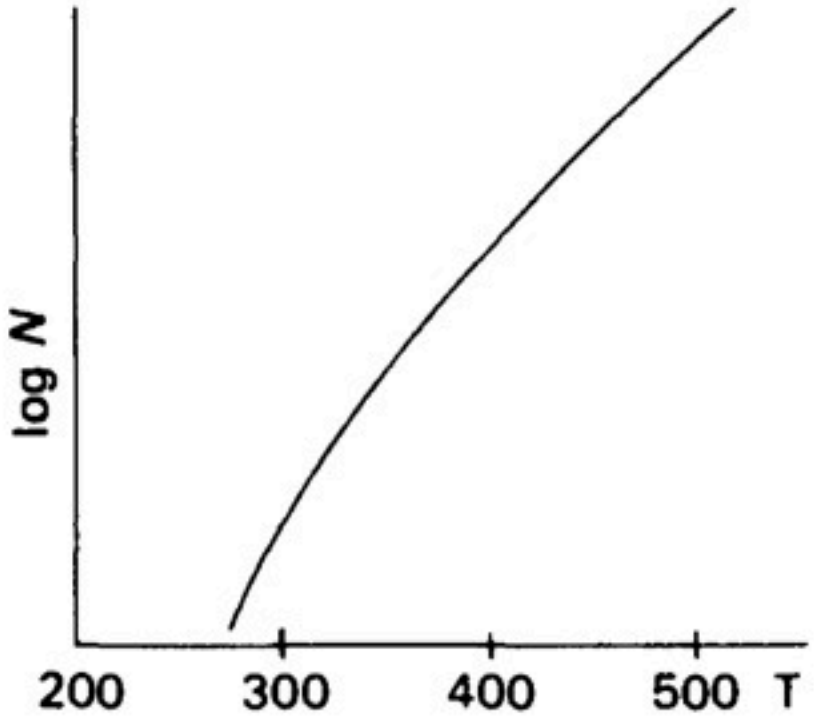
$$\sigma = N_{\mathrm{e}} e \mu_{\mathrm{e}} + N_{\mathrm{h}} e \mu_{\mathrm{h}},$$

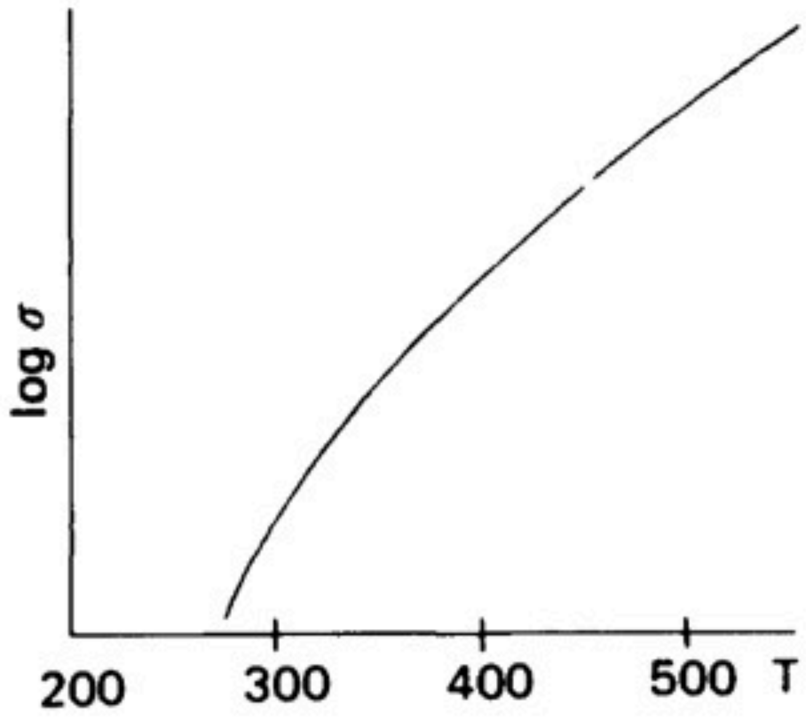
$$\sigma = 4.84 \times 10^{15} \left(\frac{m^*}{m_0}\right)^{3/2} T^{3/2} e(\mu_{\mathrm{e}} + \mu_{\mathrm{h}}) \exp\left[-\left(\frac{E_{\mathrm{g}}}{2k_{\mathrm{B}}T}\right)\right],$$

lattice vibrations

more electrons to conduction band







$$\sigma = N_e e \mu_e + N_h e \mu_h,$$

$$\sigma = 4.84 \times 10^{15} \left(\frac{m^*}{m_0} \right)^{3/2} T^{3/2} e(\mu_e + \mu_h) \exp\left[- \left(\frac{E_g}{2k_B T} \right) \right]$$

8.3. Extrinsic Semiconductors

8.3.1. Donors and Acceptors

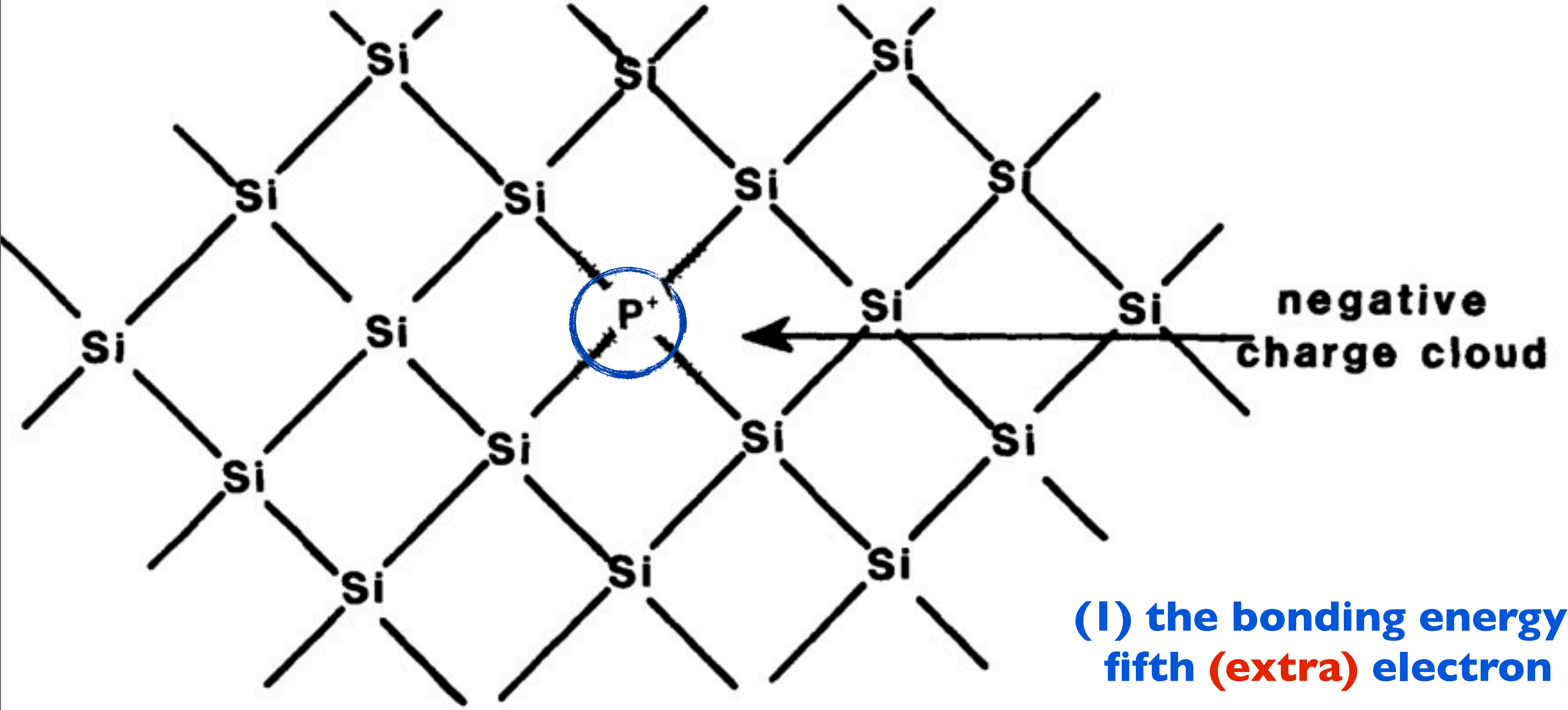
intrinsic semi-conductor, very small amount of electrons in conduction band $10^9/\mathrm{cm}^3$

extrinsic semi-conductor, by doping elements form III and V groups

n type semi-conductor, donor impurities (P, As, Sb)
major carrier: electrons

p type semi-conductor, acceptor impurities (B, Al, Ga, In)
major carrier: holes

donor electrons

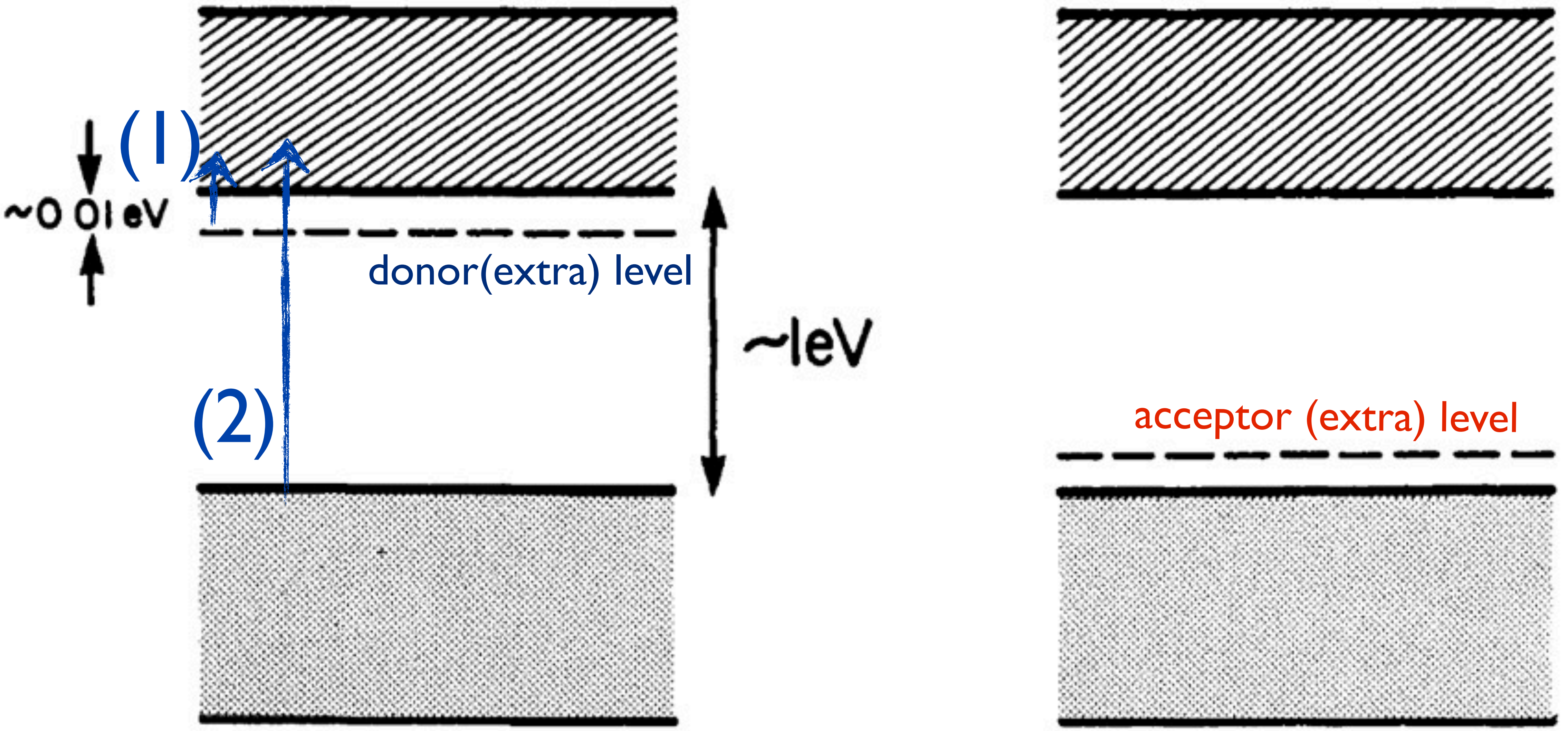


(1) the bonding energy of Si to the fifth (extra) electron is 0.045eV.

(2) more electrons in valence bands are excited to conduction band
~the number of conduction electron increases

8.3.2. Band Structure

of extrinsic semiconductor

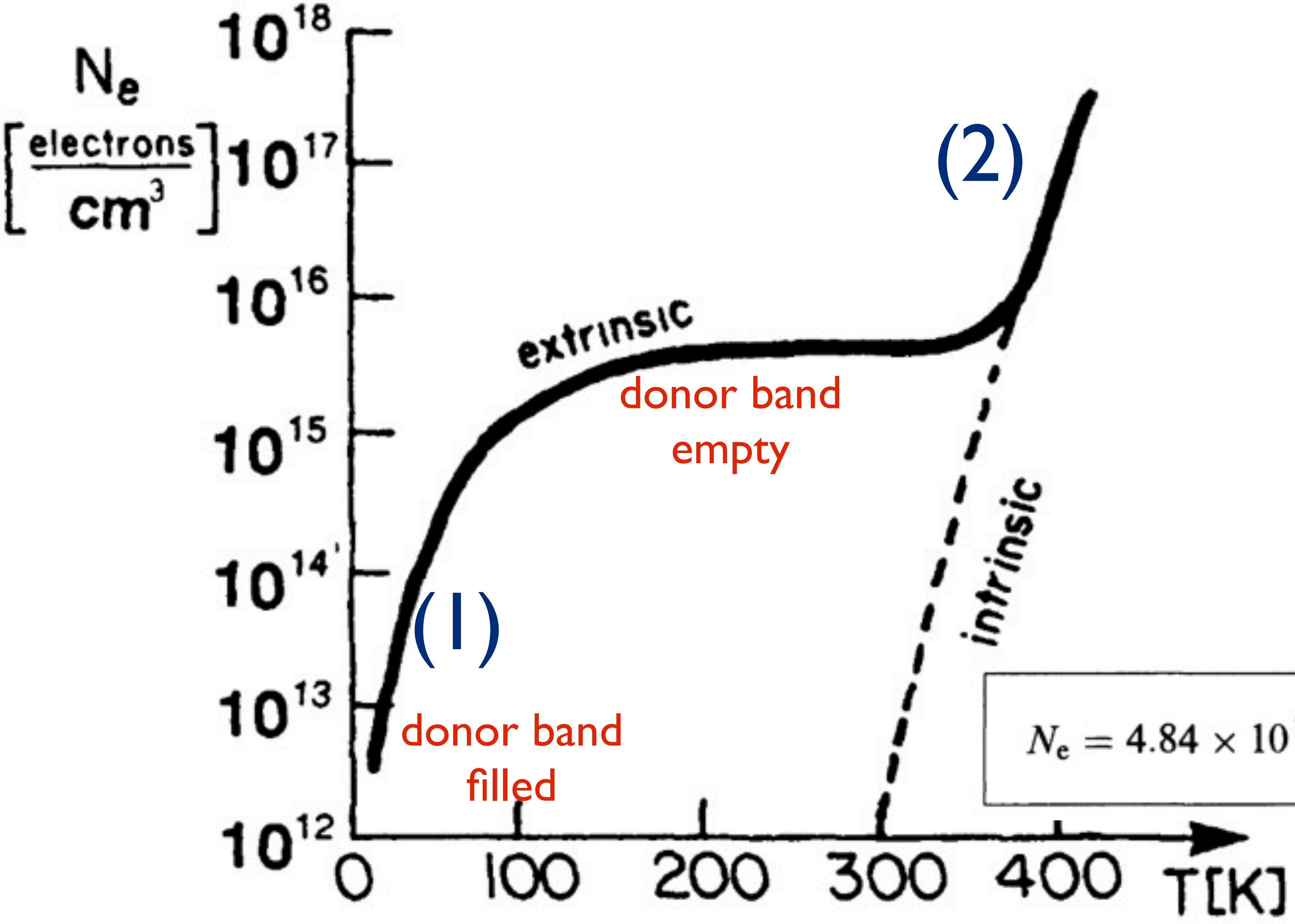


(a)

(b)

8.3.3. Temperature Dependence of the Number of Carriers

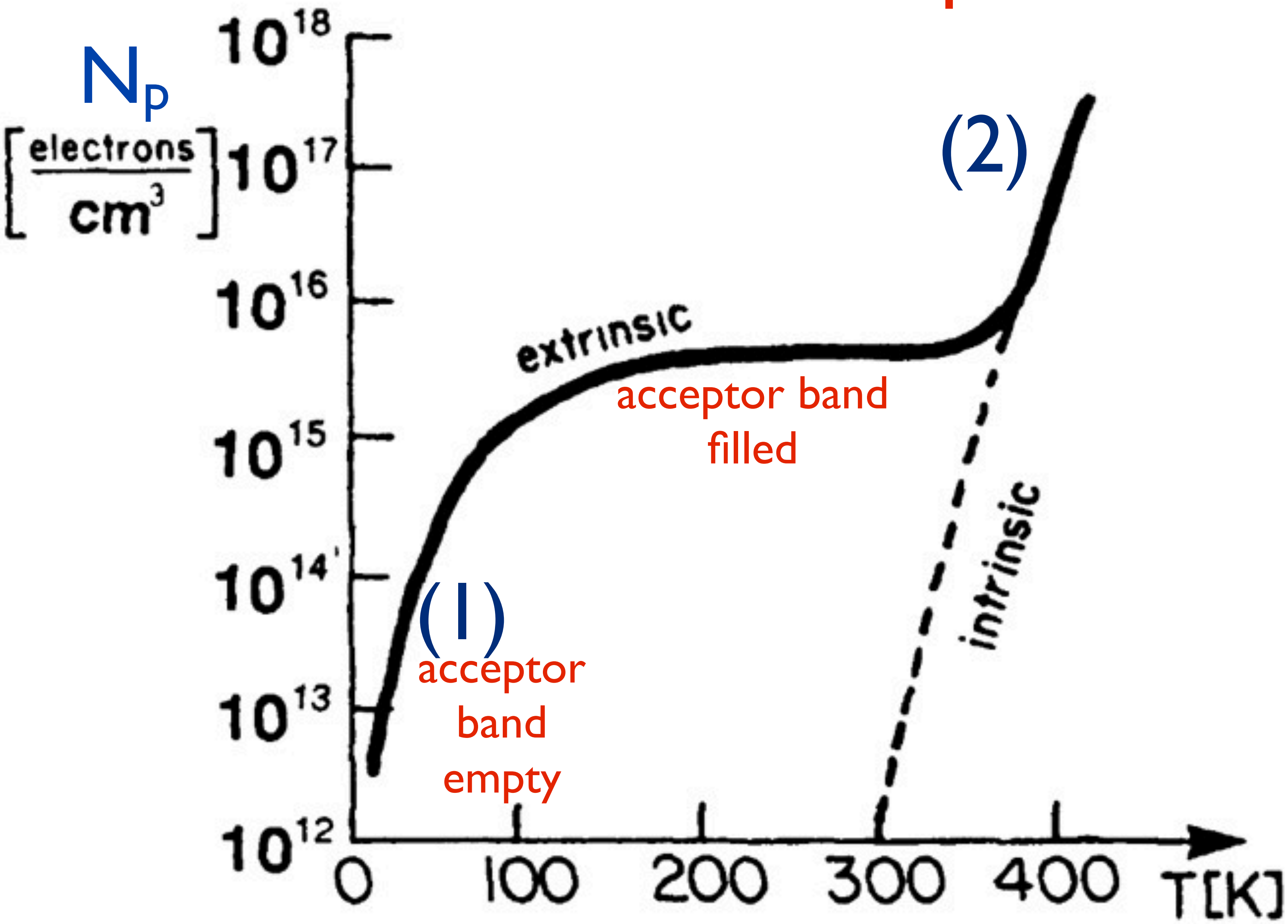
At 0 K the excess electrons of the donor impurities remain in close proximity to the impurity atom and do not contribute to the electric conduction. We express this fact by stating that all donor levels are filled. With increasing temperature, the donor electrons overcome the small potential barrier and are excited into the conduction band



$$N_e = 4.84 \times 10^{15} \left(\frac{m_e^*}{m_0}\right)^{3/2} T^{3/2} \exp\left[-\left(\frac{E_g}{2k_B T}\right)\right].$$

p-type semiconductor

with increasing temperature, the electrons are excited to acceptor band



8.3.4. Conductivity

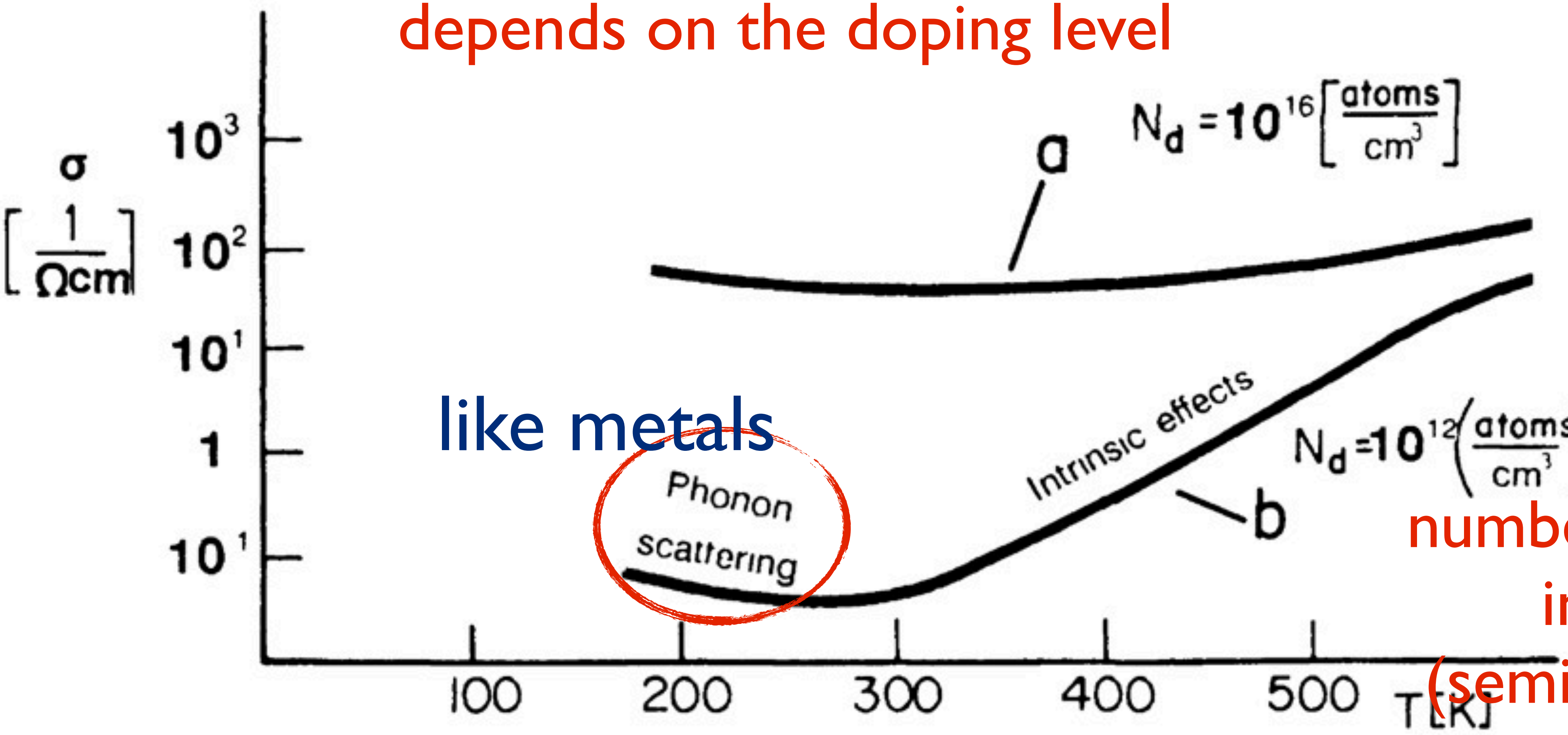
of extrinsic semiconductor

$$\sigma = N_{\mathrm{de}} e \mu_{\mathrm{e}}$$

At room temperature, $N_{e(\mathrm{intrinsic})}$ is very small,

$N_{de} >> N_{e(\mathrm{intrinsic})}$ $N_{de} \sim N_d$ (number of doping atoms)

depends on the doping level

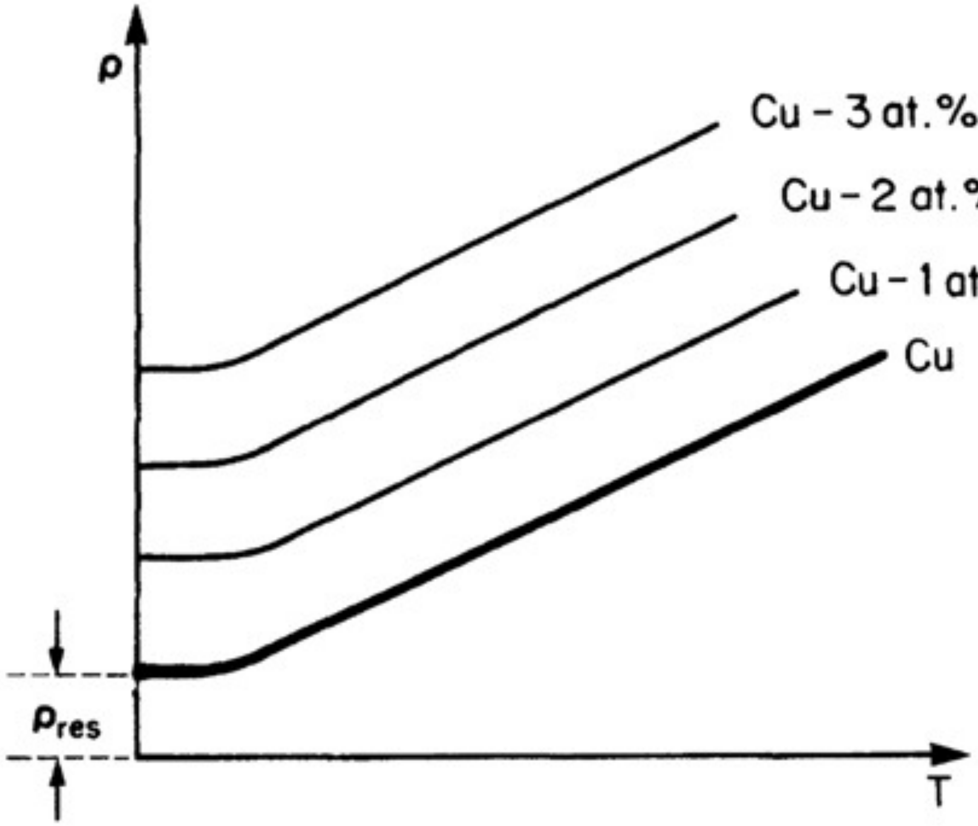


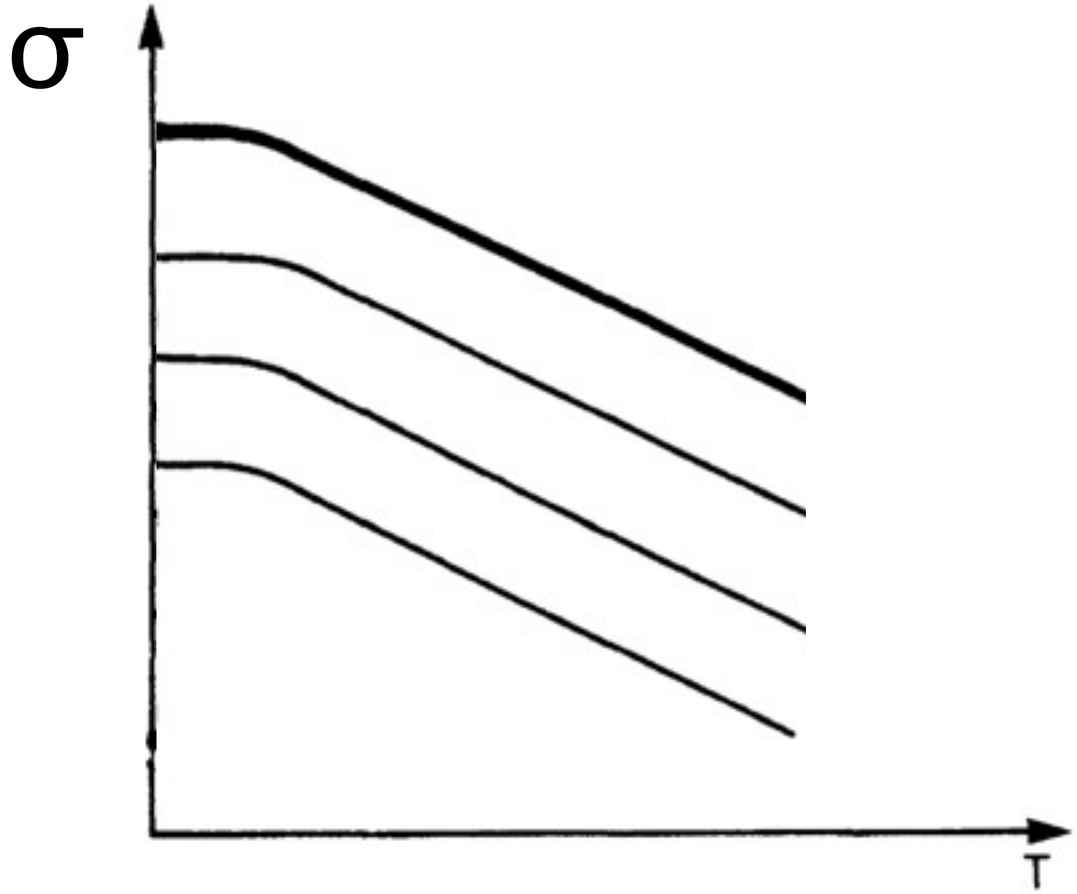
like metals

number of carrier increase (semiconductor)

Conductivity of Metals

at high temperature, the phonon scattering dominates





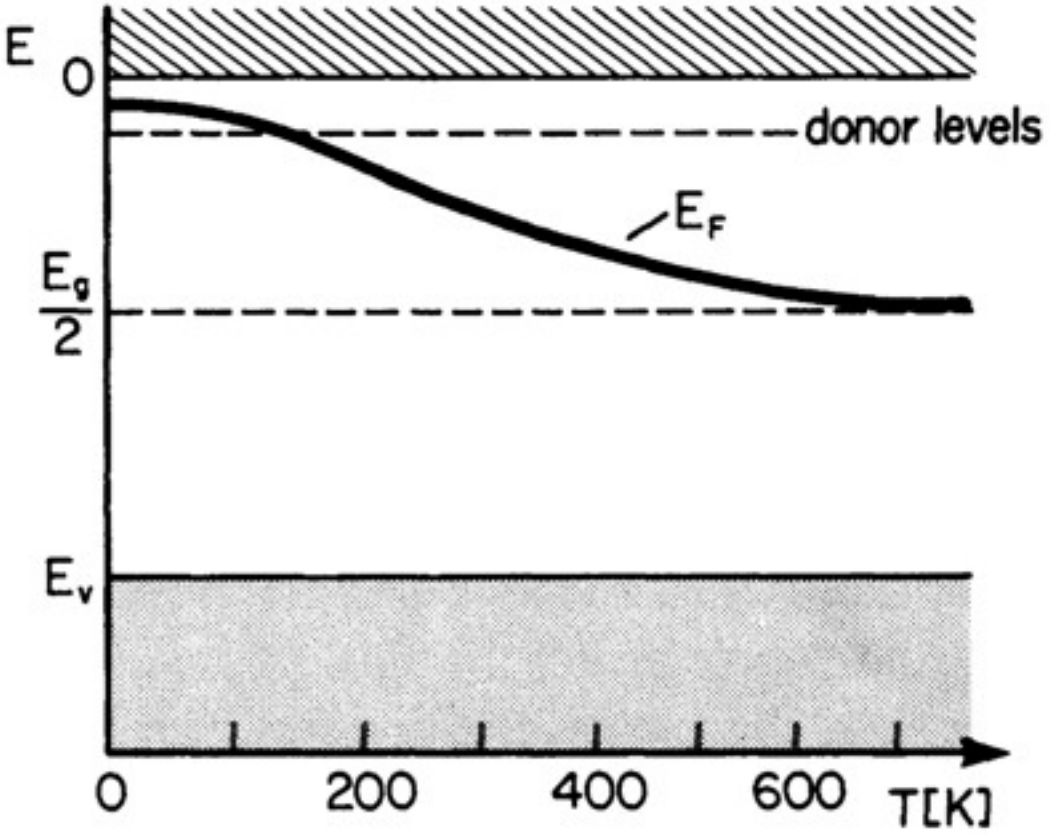
measure the conductivity of material at very low temperature, we know the behavior of metal or semiconductor

8.3.5. Fermi Energy

temperature dependent

In an *n*-type semiconductor, more electrons can be found in the conduction band than holes in the valence band. This is particularly true at low temperatures. The Fermi energy must therefore be between the donor level and the conduction band

With increasing temperatures, an extrinsic semiconductor becomes progressively intrinsic and the Fermi energy approaches the value for an intrinsic semiconductor, i.e., $-(E_g/2)$.

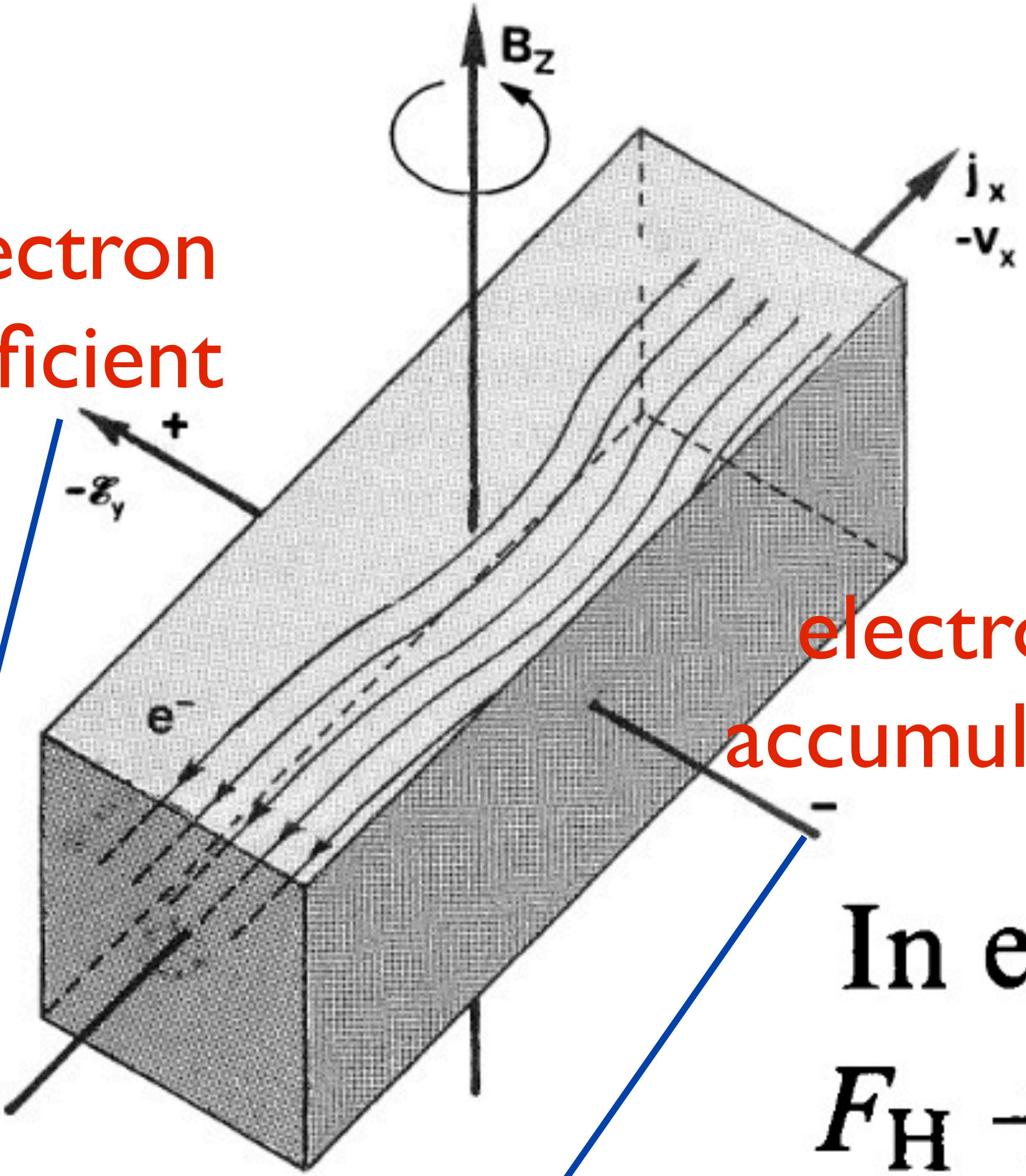


the Fermi energy for a *p*-type semiconductor rises with increasing temperature from below the acceptor level to $-(E_g/2)$.]

8.5. Hall Effect

(measure types and number of charge carriers)

n-type dopant



electron deficient

electron accumulates

Hall field builds up

Lorentz force

$$F_L = v_x B_z e$$

Hall force

$$F_H = -e\mathcal{E}_y$$

In equilibrium

$$F_H + F_L = 0$$

$$\mathcal{E}_y = v_x B_z$$

$$j_x = -N v_x e$$

the number of conduction electrons (per unit volume)

$$N = \frac{j_x B_z}{e \mathscr{E}_y}$$

Hall constant,

$$R_{\mathrm{H}} = -\frac{1}{Ne}$$

Hall constant is negative for electron carrier

The electron holes are deflected in the same direction as the electrons but travel in the opposite direction

8.6. Compound Semiconductors

III-V	II-VI
GaAs	ZnO
GaP	ZnS
GaN	ZnSe
InP	CdS
InAs	CdTe
InSb	HgS

GaAs

~ direct band gap

~ high speed device

large electron mobility
smaller effective mass

~ Laser/ LED
(Optical Application)

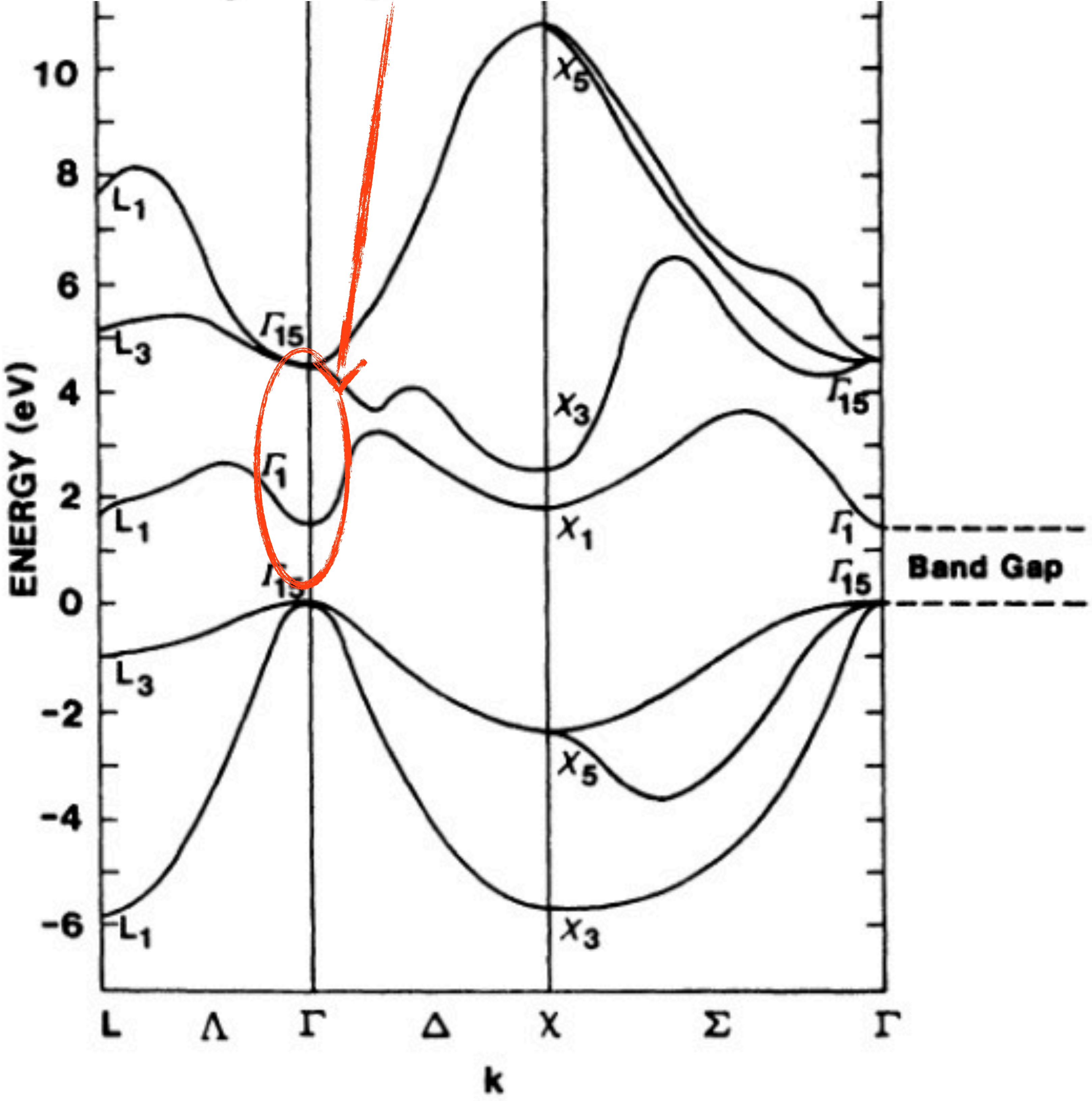
~ high frequency device

Tele-communication
military applications,
Satellite Pre-amplifier

Doping of GaAs is accomplished, for example, by an excess of Ga atoms (*p*-type) or an excess of As (*n*-type). Si acts as a donor if it replaces Ga atoms

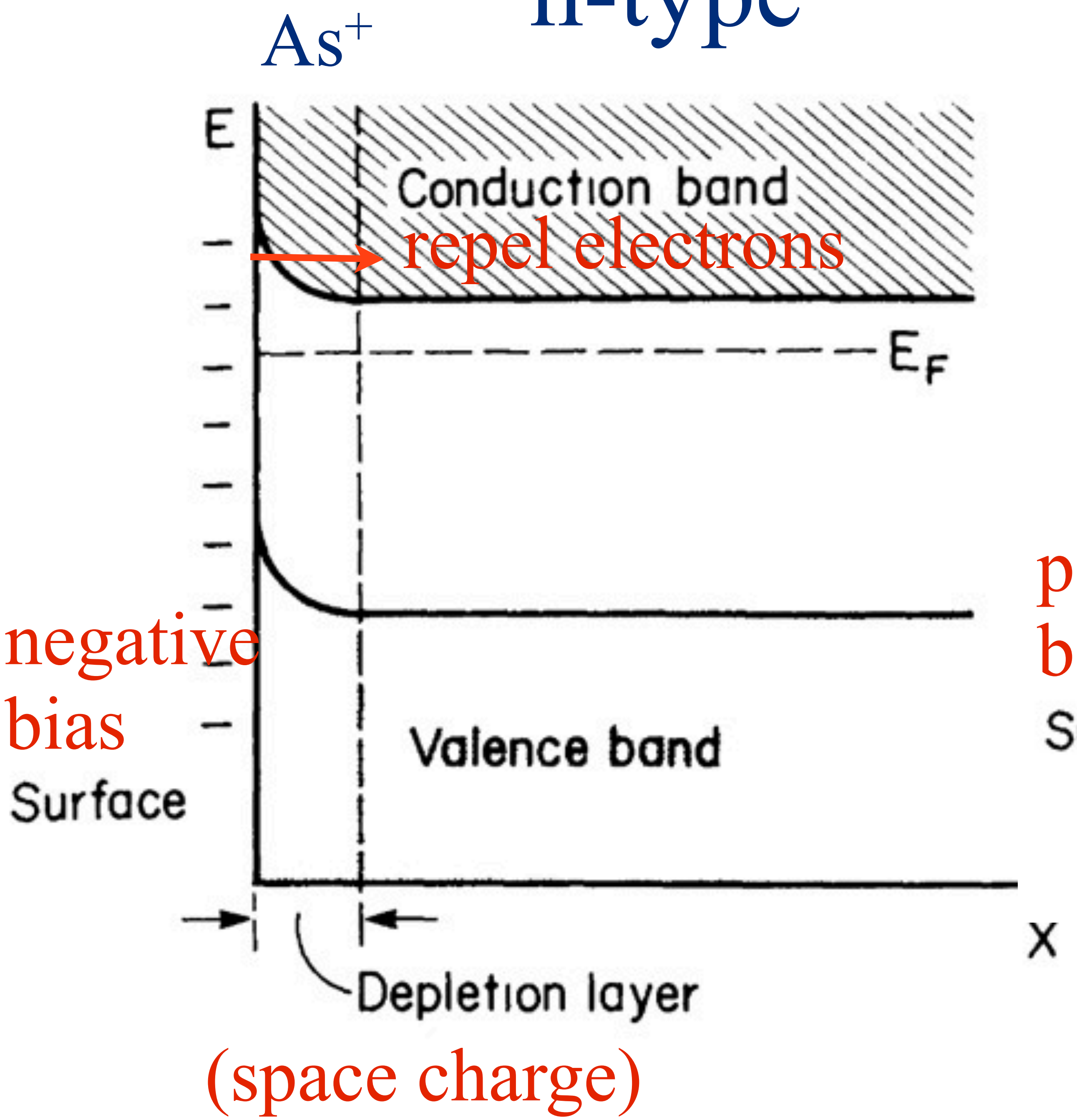
Calculated energy band structure of GaAs.

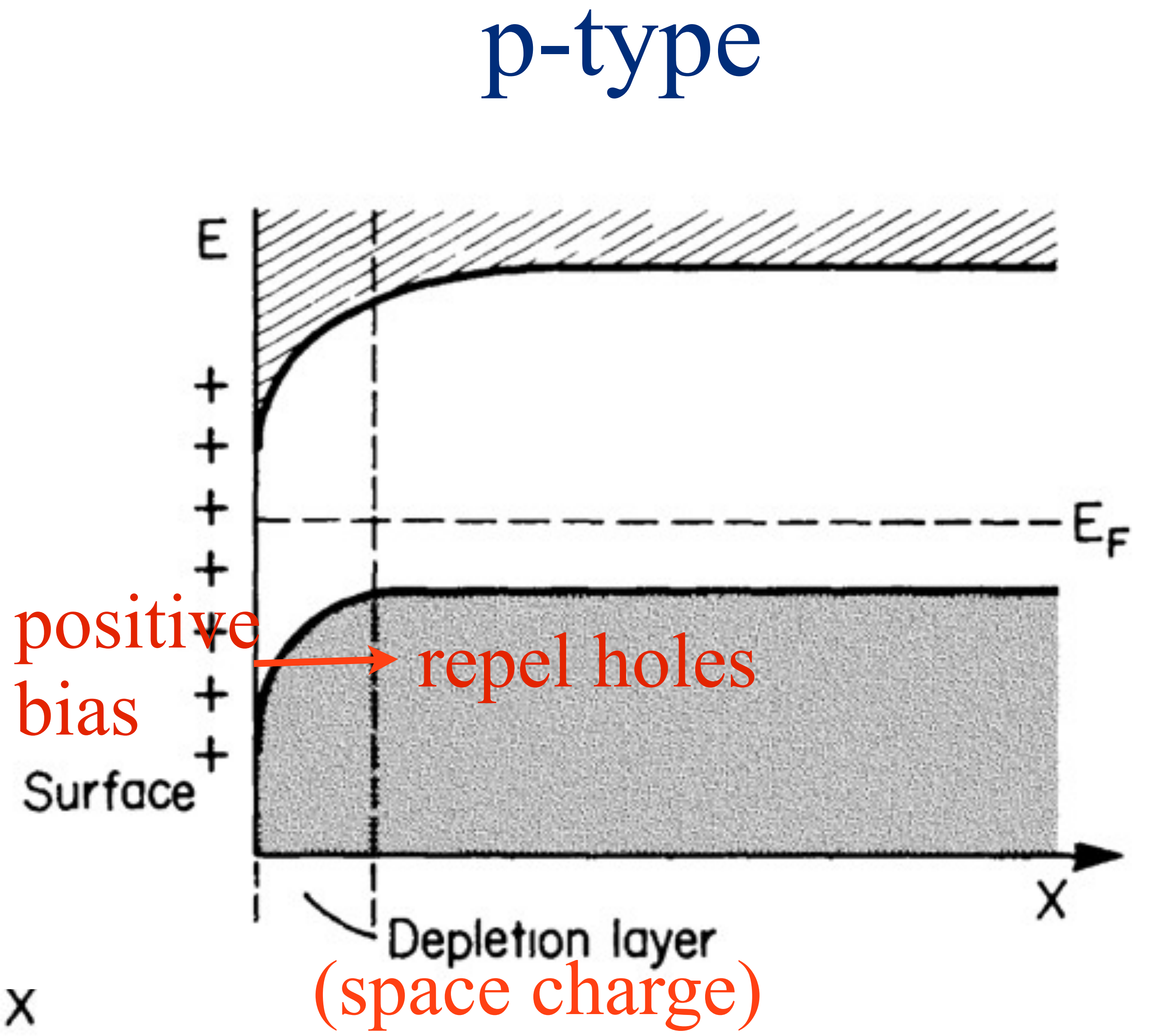
comparatively large convex upward curvature



8.7. Semiconductor Devices

8.7.1. Metal–Semiconductor Contacts





holes “want to drift upward”

8.7.2. Rectifying Contacts (Schottky Barrier Contacts)

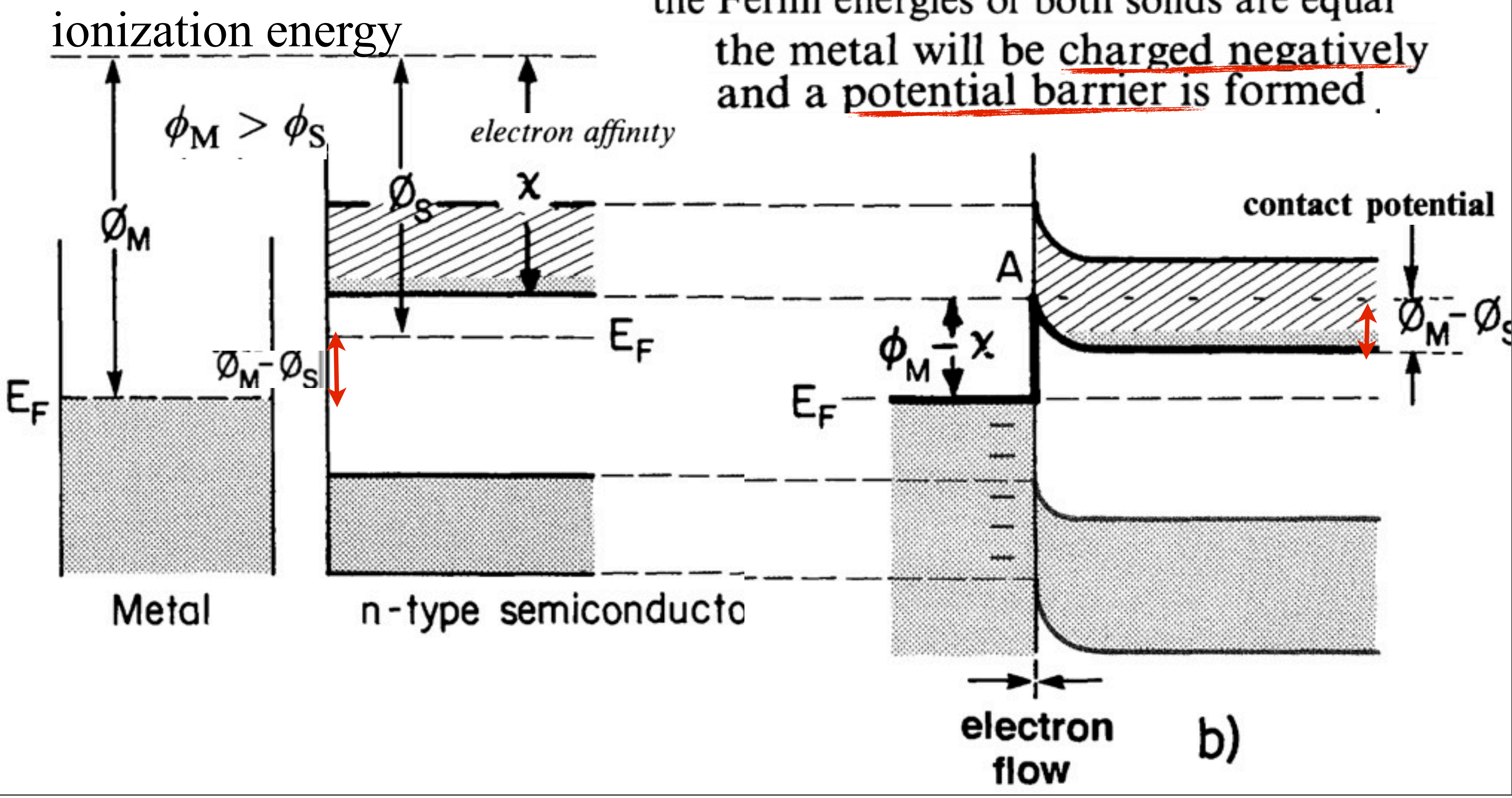
to convert alternating current into direct current.

work function, ϕ,

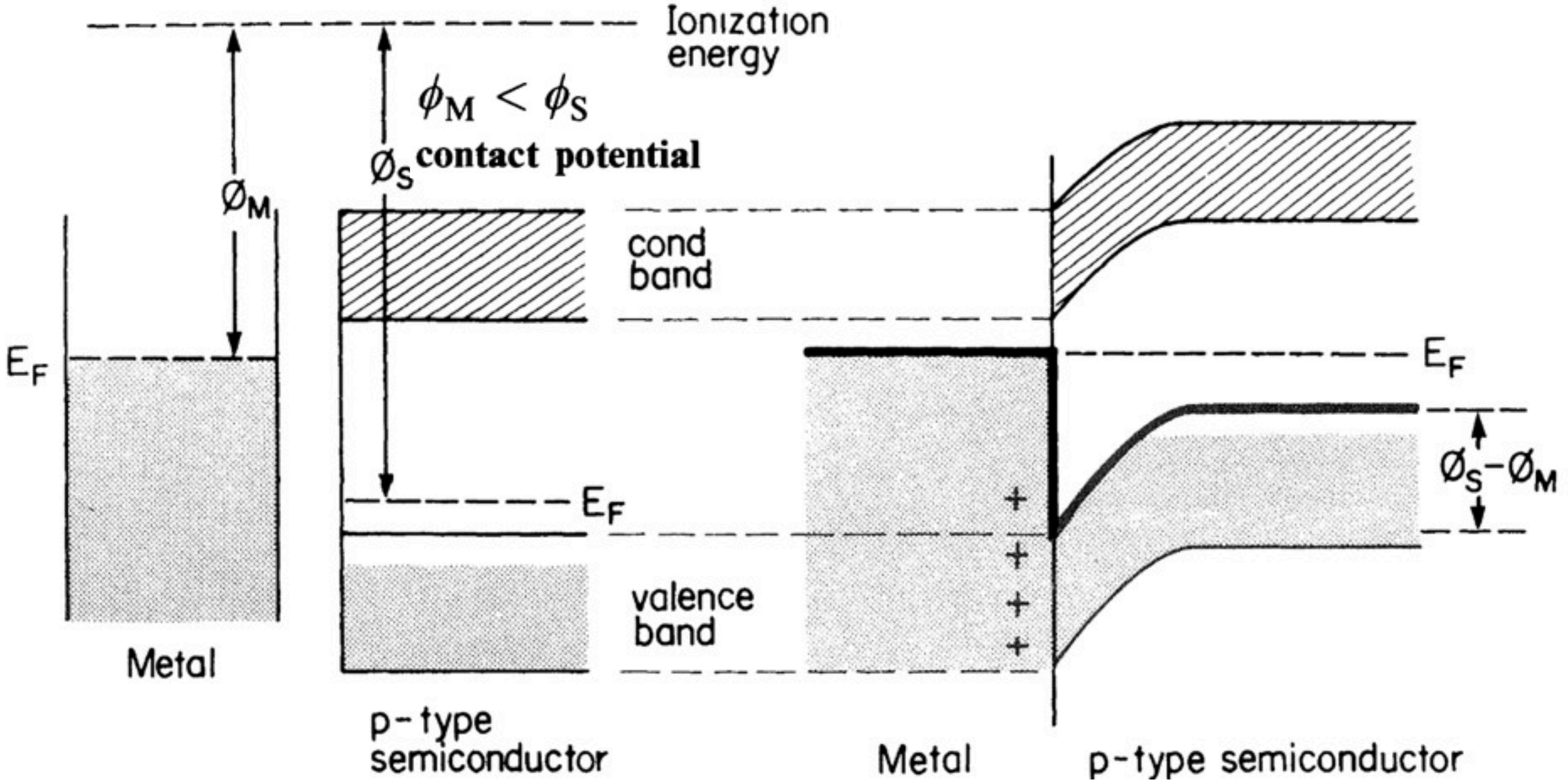
the energy difference between the Fermi energy and the ionization energy

electrons start to flow from the semiconductor "down" into the metal until the Fermi energies of both solids are equal

the metal will be charged negatively and a potential barrier is formed.



a *p*-type semiconductor is brought into contact with a metal
electrons diffuse from the metal into the semiconductor
“downward” potential barrier (for the holes)

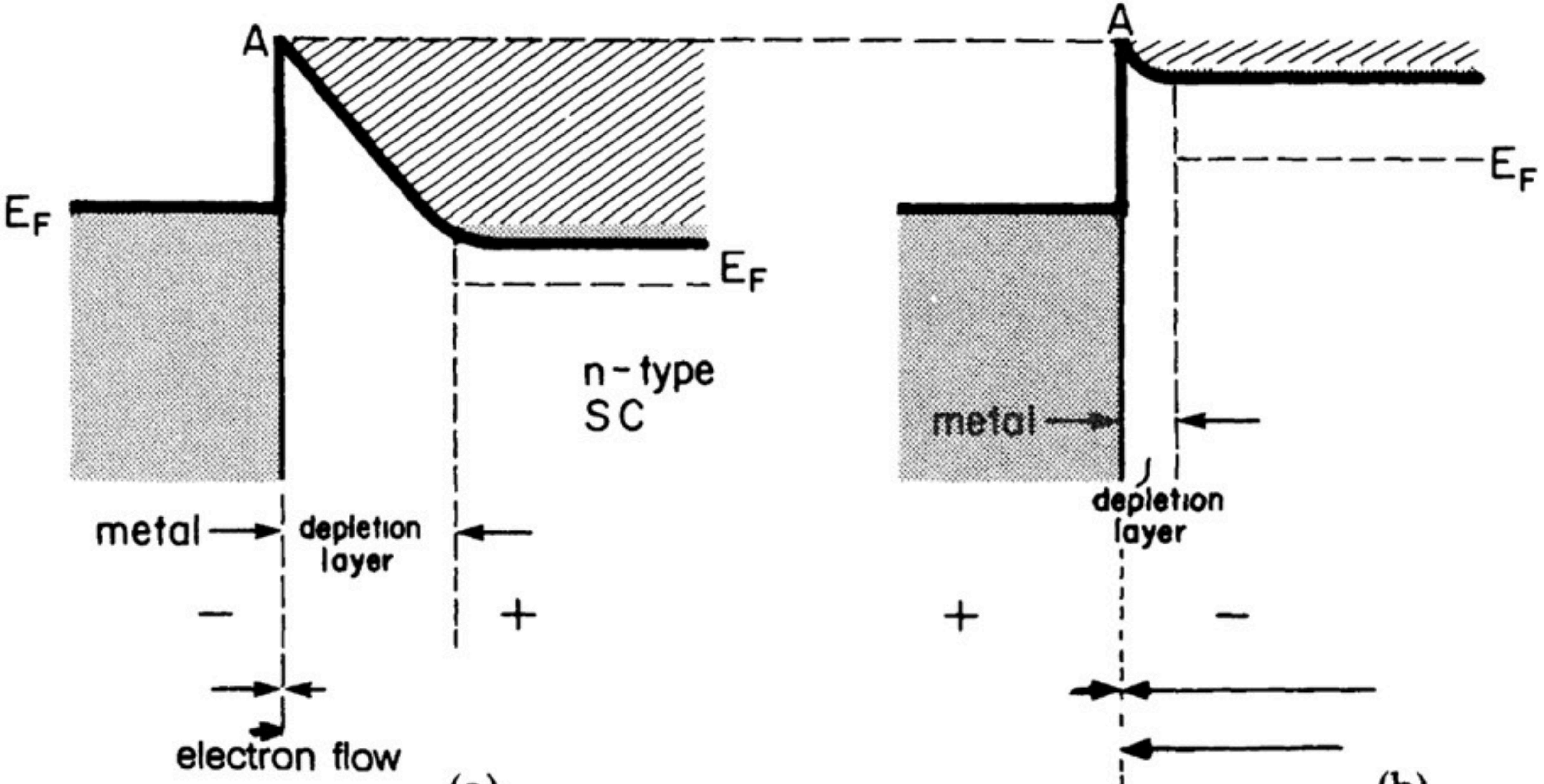


In the equilibrium state, electrons from both sides cross the potential barrier. This electron flow constitutes the so-called **diffusion current**. The number of electrons diffusing in both directions must be identical for the following reason: the metal contains more free electrons, but these electrons have to climb a higher potential barrier than the electrons in the semiconductor, whose conduction band contains fewer free electrons.

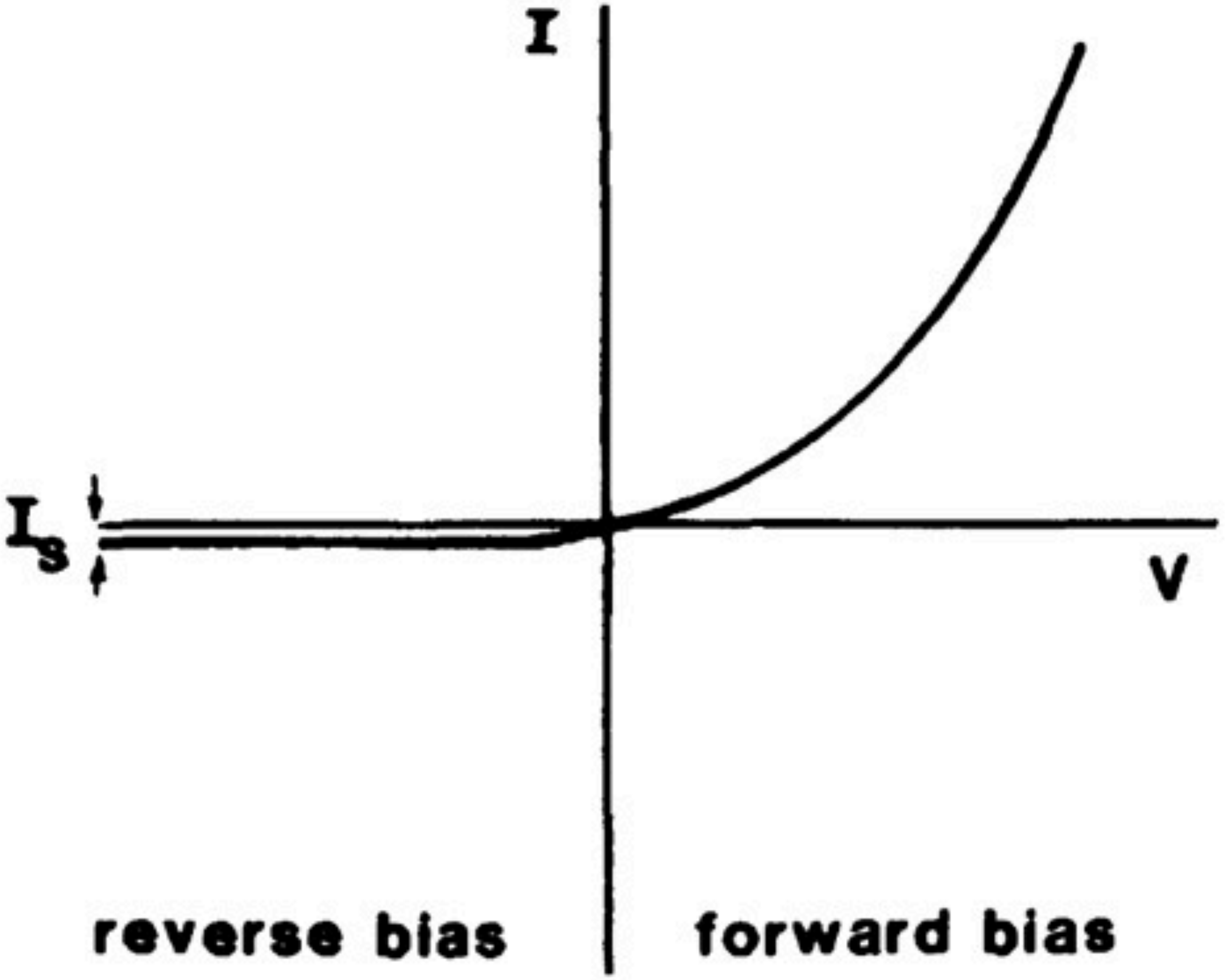
In addition to the diffusion current just mentioned, a "**drift current**" needs to be taken into consideration. Let us assume that an electron–hole pair was thermally created in or near the depletion layer. Then, the thermally created electron in the conduction band is immediately swept down the barrier, and the hole in the valence band is swept up the barrier. This drift current is usually very small (particularly if the band gap is large, such as in GaAs) and is relatively insensitive to the height of the potential barrier. The total current across a junction is the sum of drift and diffusion components.

reverse bias forward bias

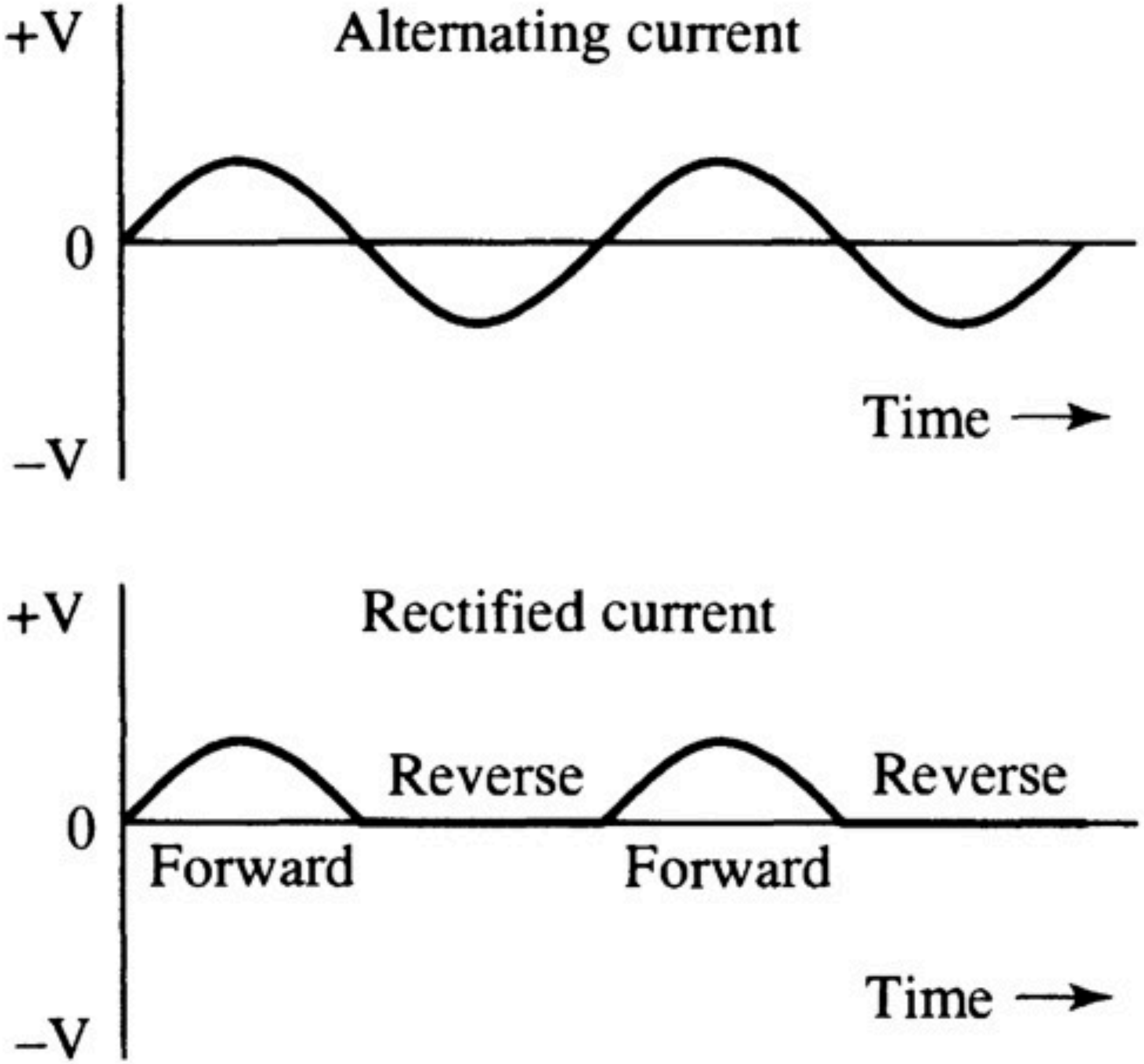
At first, the metal is assumed to be connected to the negative



(a) (b)

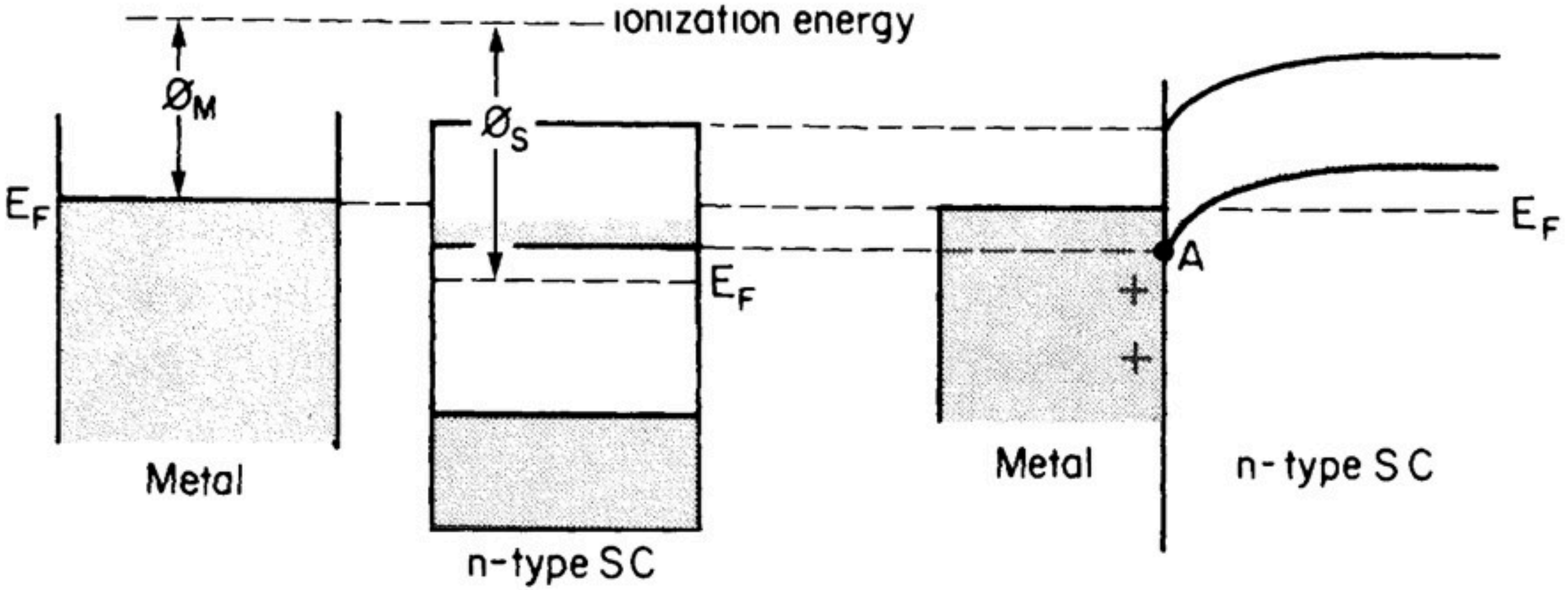

I
I_s
V
reverse bias
forward bias

(a)

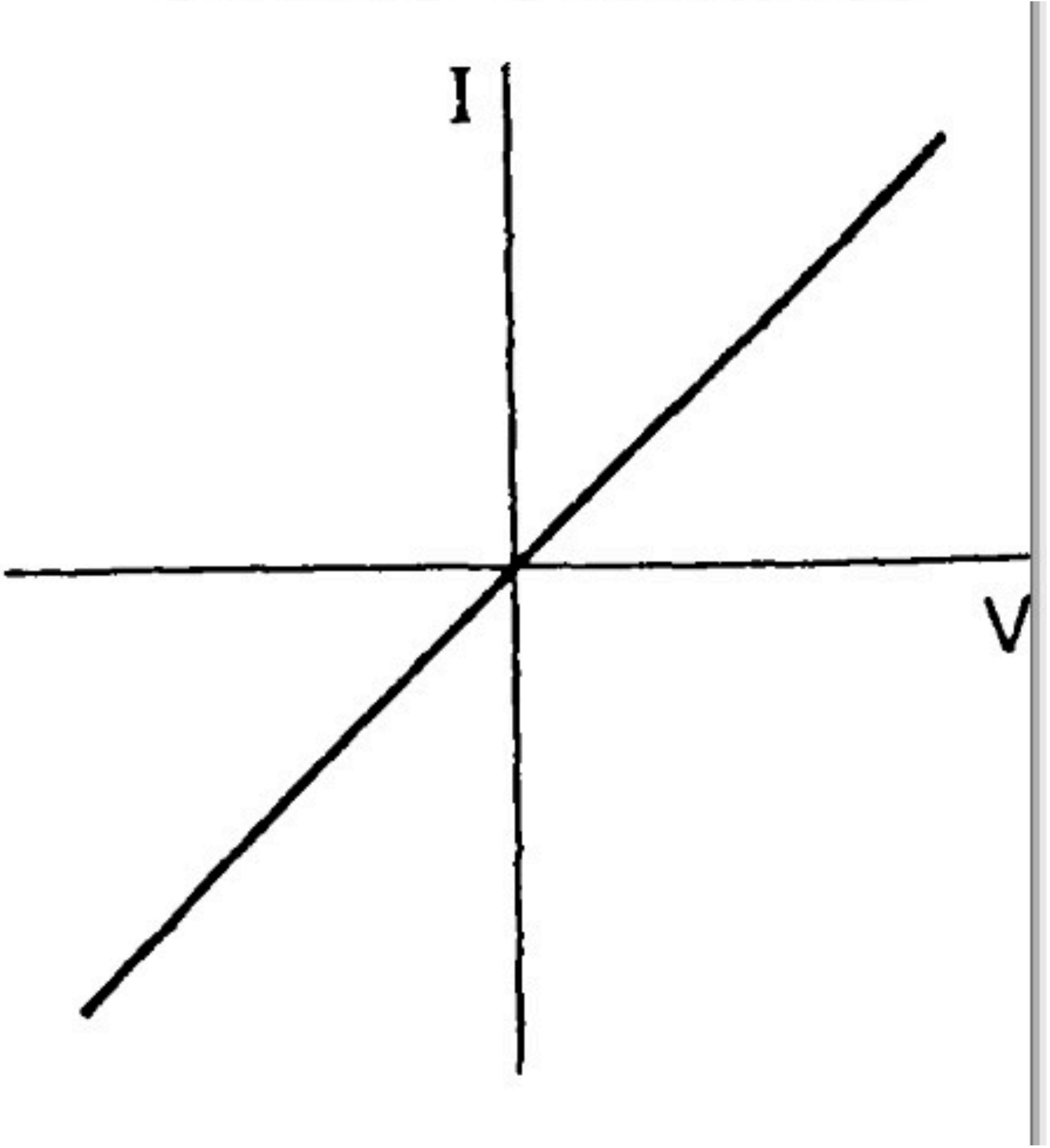

+V
Alternating current
0
Time →
–V
+V
Rectified current
Reverse
Reverse
0
Forward
Forward
Time →
–V

ohmic contacts

band diagrams are shown for the case where a metal is brought into contact with an *n*-type semiconductor. It is assumed that $\phi_M < \phi_S$. Thus, electrons flow from the metal into the semiconductor, charging the metal positively. The bands of the semiconductor bend “downward” and no barrier exists for the flow of electrons in either direction. In other words, this configuration allows the injection of a current into and out of the semiconductor without suffering a sizable power loss.



ohmic contacts



Photoelectric effect and Solar cell

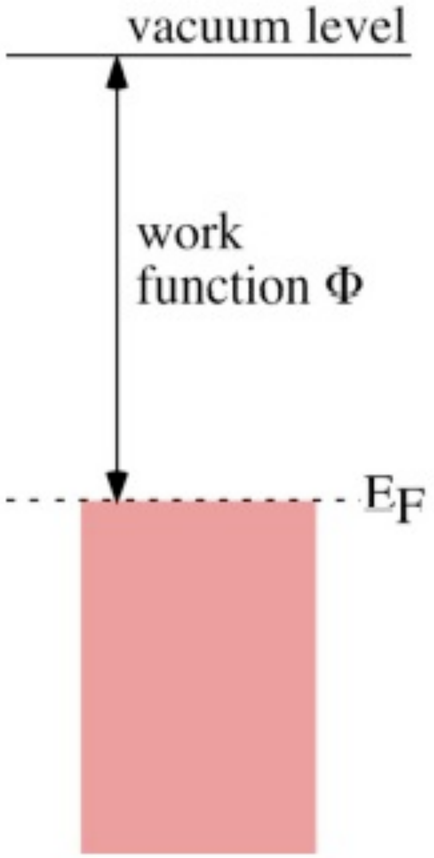
of Metal

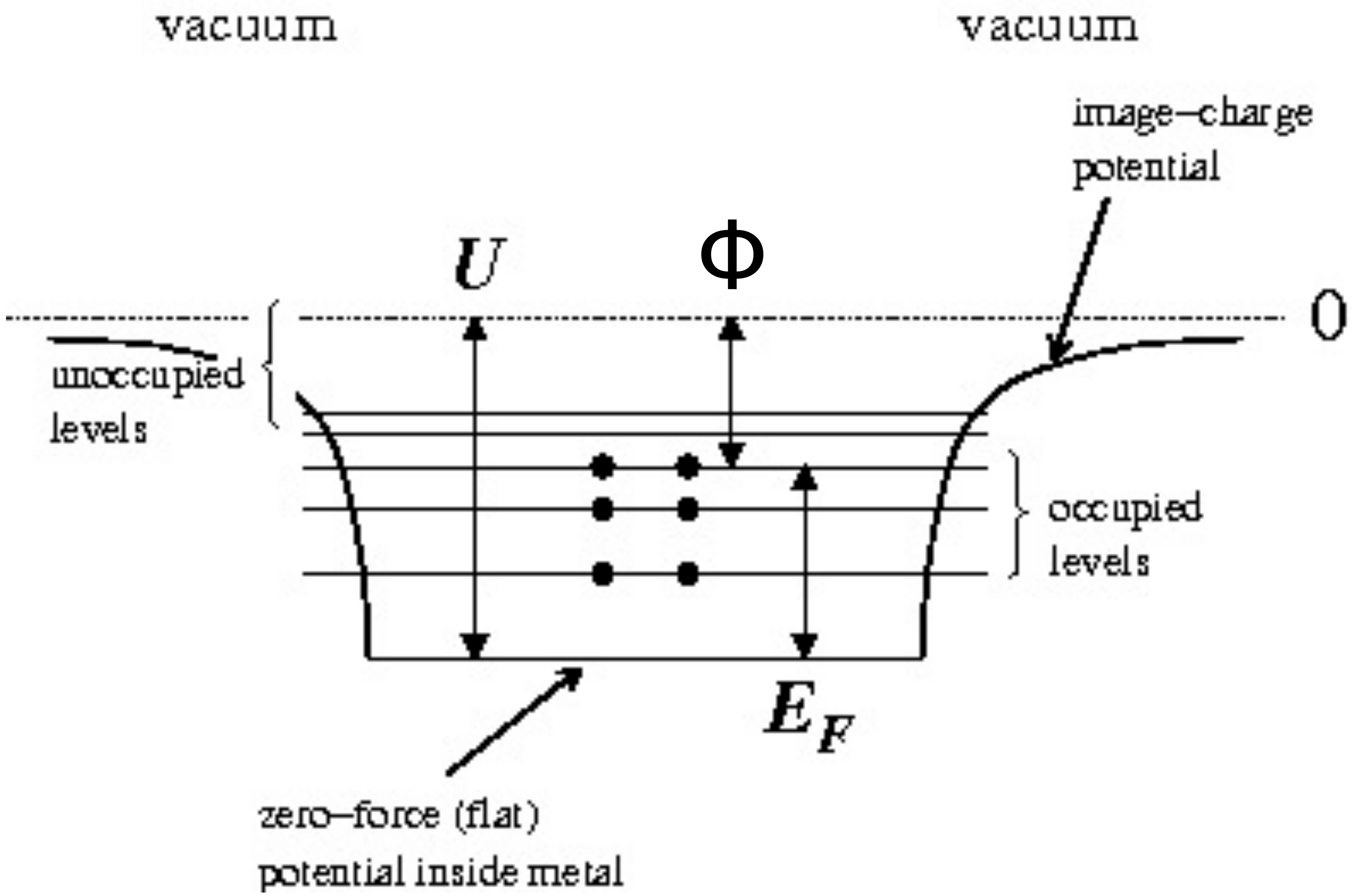
Photon in -------> Electron out

在金屬的光電效應中，光子的能量被吸收，讓電子從費米能附近躍升至真空能階。

Work function and Fermi energy

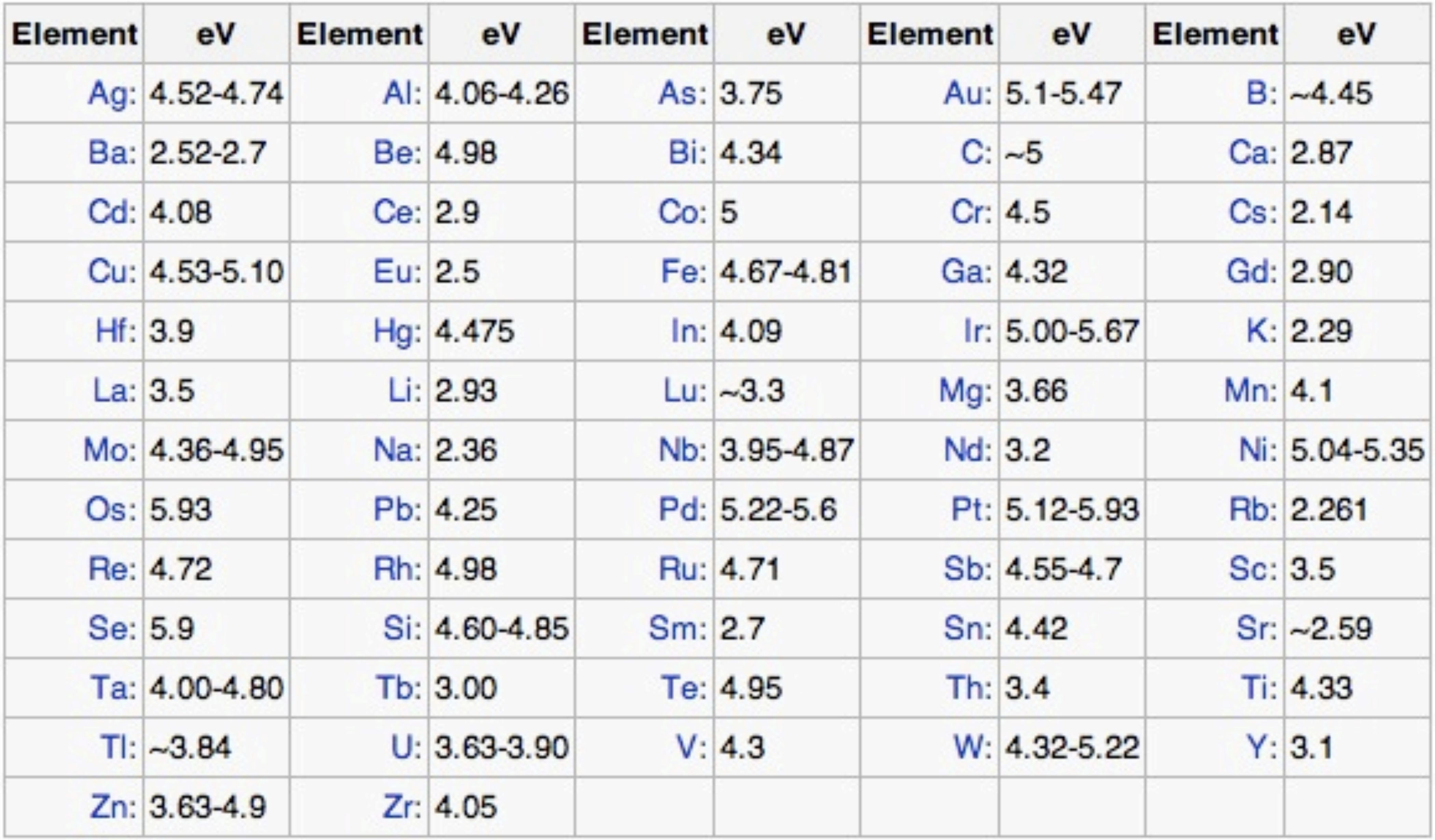
(Metal)





E_f: the highest energy of the occupied levels at 0K

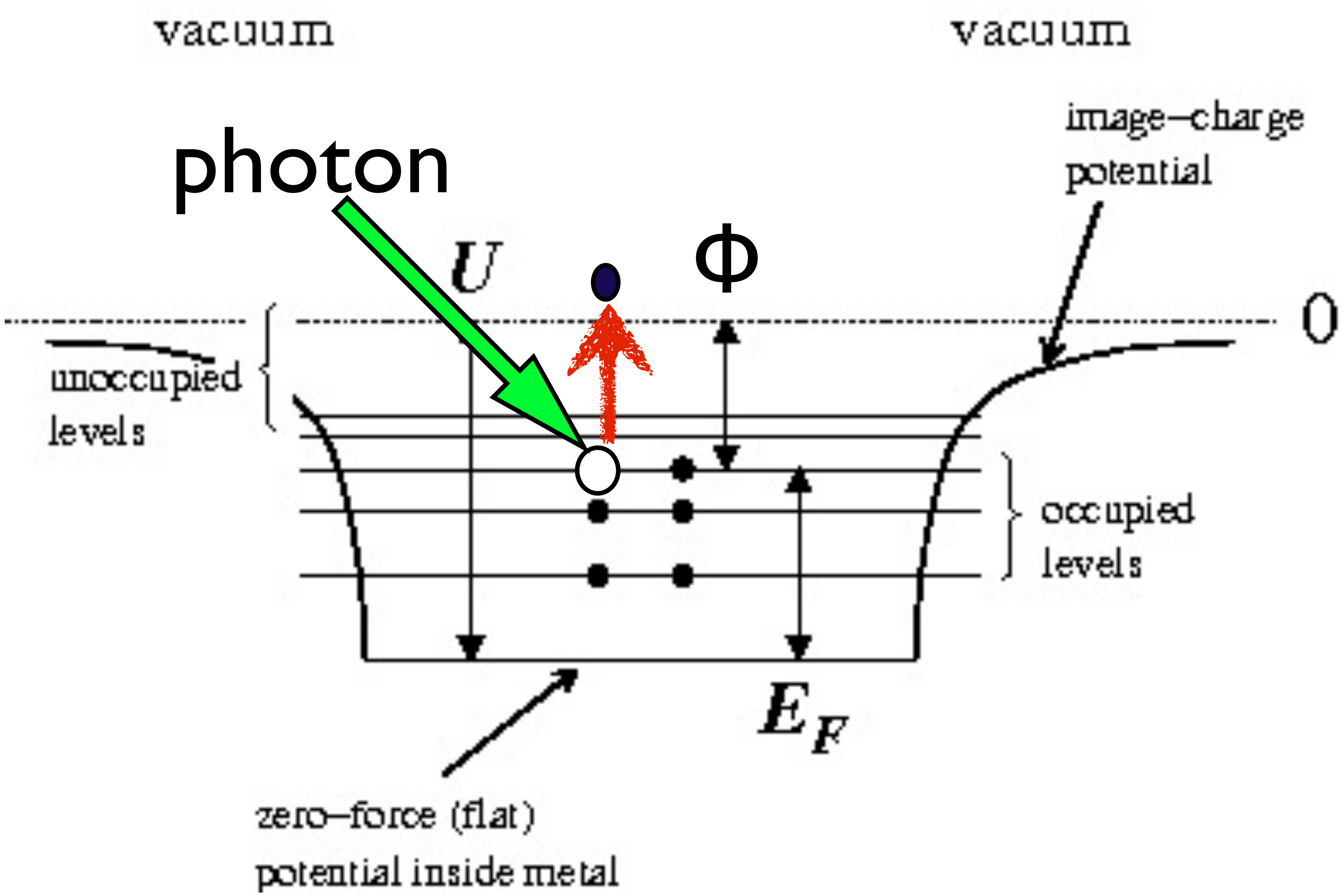
Work function of Metals

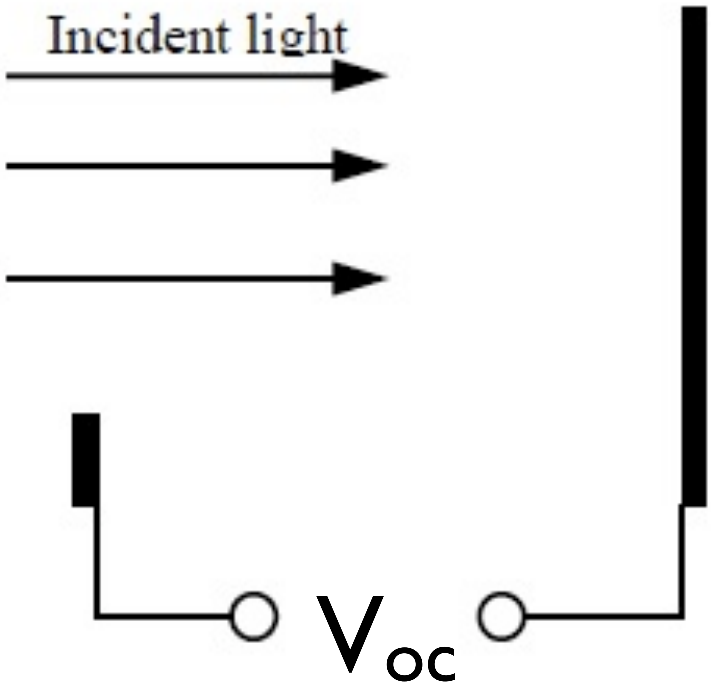


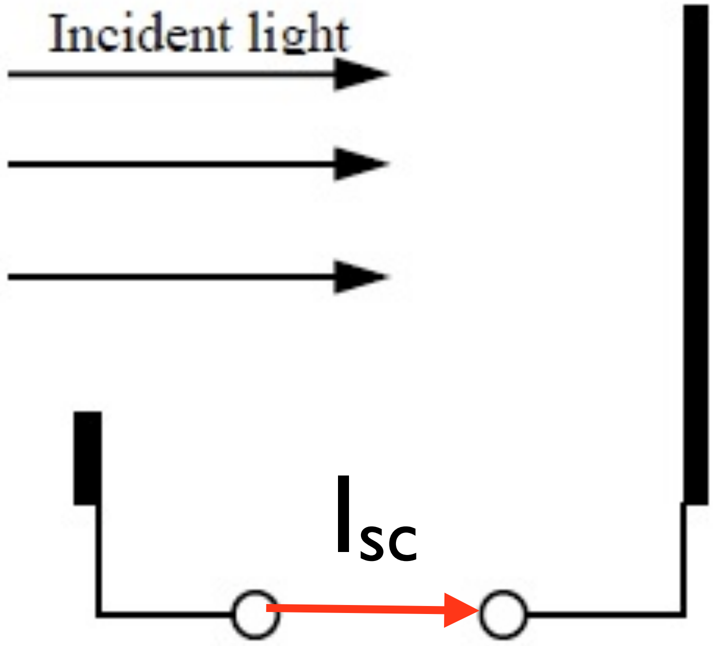
Element	eV	Element	eV	Element	eV	Element	eV	Element	eV
Ag:	4.52-4.74	Al:	4.06-4.26	As:	3.75	Au:	5.1-5.47	B:	~4.45
Ba:	2.52-2.7	Be:	4.98	Bi:	4.34	C:	~5	Ca:	2.87
Cd:	4.08	Ce:	2.9	Co:	5	Cr:	4.5	Cs:	2.14
Cu:	4.53-5.10	Eu:	2.5	Fe:	4.67-4.81	Ga:	4.32	Gd:	2.90
Hf:	3.9	Hg:	4.475	In:	4.09	Ir:	5.00-5.67	K:	2.29
La:	3.5	Li:	2.93	Lu:	~3.3	Mg:	3.66	Mn:	4.1
Mo:	4.36-4.95	Na:	2.36	Nb:	3.95-4.87	Nd:	3.2	Ni:	5.04-5.35
Os:	5.93	Pb:	4.25	Pd:	5.22-5.6	Pt:	5.12-5.93	Rb:	2.261
Re:	4.72	Rh:	4.98	Ru:	4.71	Sb:	4.55-4.7	Sc:	3.5
Se:	5.9	Si:	4.60-4.85	Sm:	2.7	Sn:	4.42	Sr:	~2.59
Ta:	4.00-4.80	Tb:	3.00	Te:	4.95	Th:	3.4	Ti:	4.33
Tl:	~3.84	U:	3.63-3.90	V:	4.3	W:	4.32-5.22	Y:	3.1
Zn:	3.63-4.9	Zr:	4.05						

In general, the work function of metals is between 3~5 eV

Photoelectric Effect and Solar Cell of Metal







有光照的金屬其化學勢會稍微大於
沒有光照的金屬的化學勢。因此，有光照的和無光照的二金屬之間存在一個電壓差，也就是太陽電池開路電壓。

Photoelectric Effect and Solar Cell of Metal

利用金屬的光電效應來做太陽電池的最大物理限制，乃在於一般金屬的功函數大部分在3 至 5eV 之間，因此只有能量是紫外線以上的光子才能被 吸收來產生光電流，而太陽光紫外線以上的輻射只占 整體的很小部分。也就是說，金屬光電效應的太陽電池其最大光-電轉換效率可能不超過1% ，而實際實 驗的結果，更只有約0.001%。我們可以結論地說， 利用金屬的光電效應來做太陽電池，其輸出電流甚微小，而輸出電壓也不很大，因此輸出的電功率是沒辦法作實際應用的。

就像是金屬真空管二極體被半導體固態二極體取代一樣，至今絕大部分的太陽電池使用半導體材料，而非今屬材料。

太陽電池是應用半導體的光伏特效應，而不是金屬的光電效應，雖然二者在原理上是類似的

(photovoltaic)

Photovoltaic effect of Semiconductor

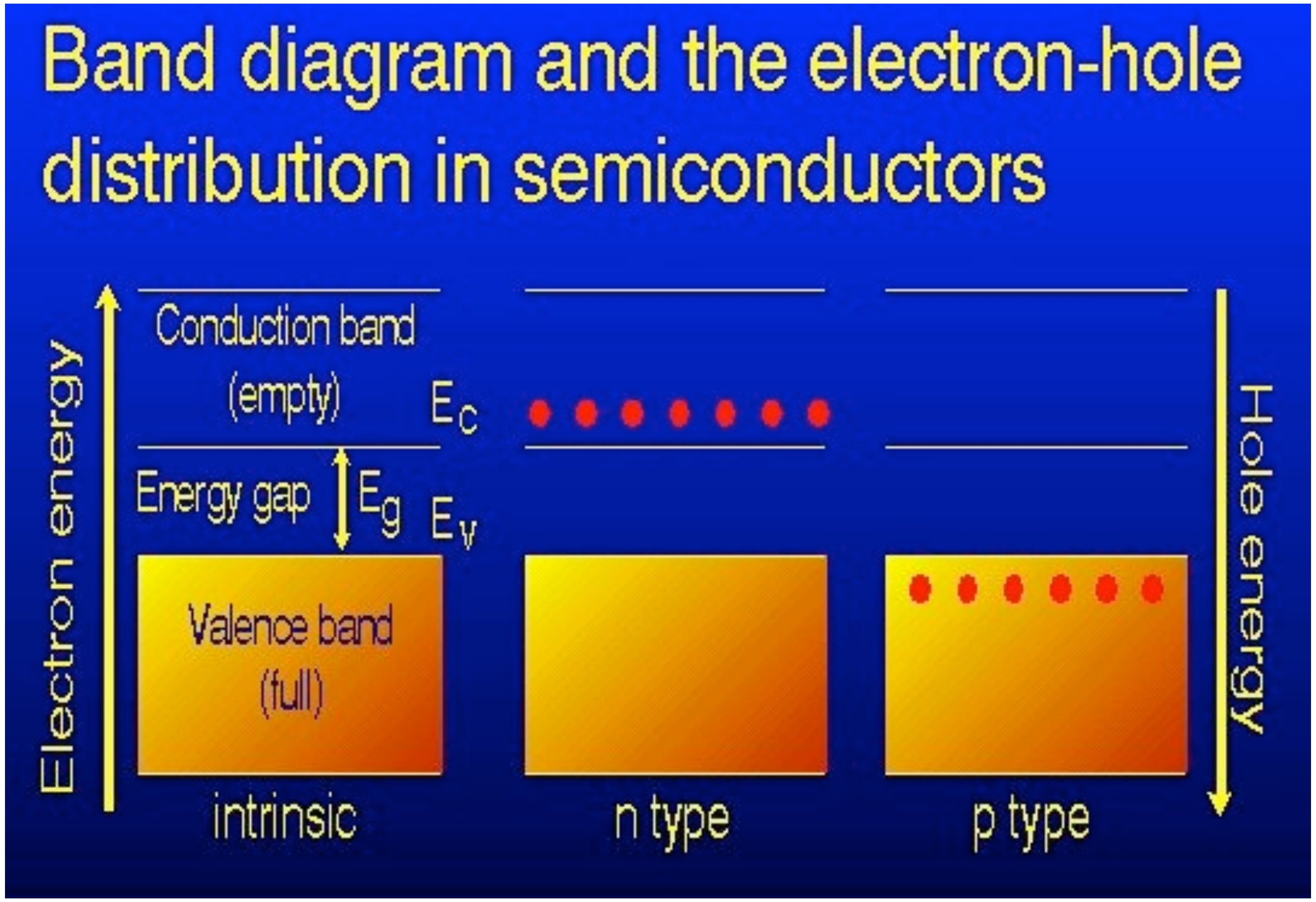
Photon in -------> Electron out

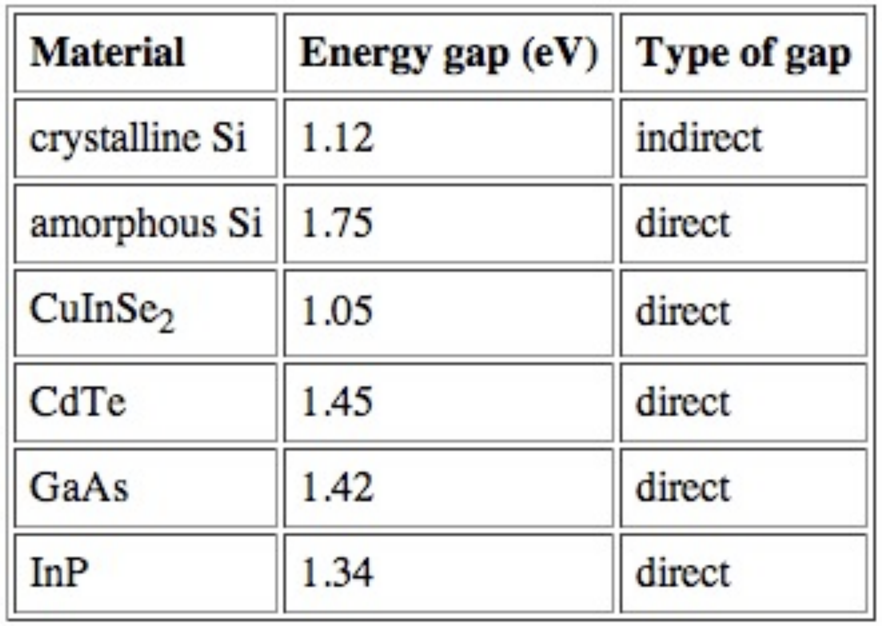
在金屬的光電效應中，光子的能量被吸收，讓電子從費米能附近躍升至真空能階。而在半導體的光 伏特效應中，光子的能量被吸收，讓電子從價帶躍過能隙至導帶

一般的半導體能隙約為1~2eV，其可吸引的光是紅外線或可見光，其最大光-電轉換效率自然遠超過於金屬的。另外半導體可以傳導電的，除了帶負電荷的導帶的電子，還有帶正電荷的價帶的電洞(也就是價帶中能態空缺)，這種雙極性的導電，也是金屬不具有的特性

Some semiconductor physics

a) Band structure and Doping





Material	Energy gap (eV)	Type of gap
crystalline Si	1.12	indirect
amorphous Si	1.75	direct
$CuInSe_2$	1.05	direct
CdTe	1.45	direct
GaAs	1.42	direct
InP	1.34	direct

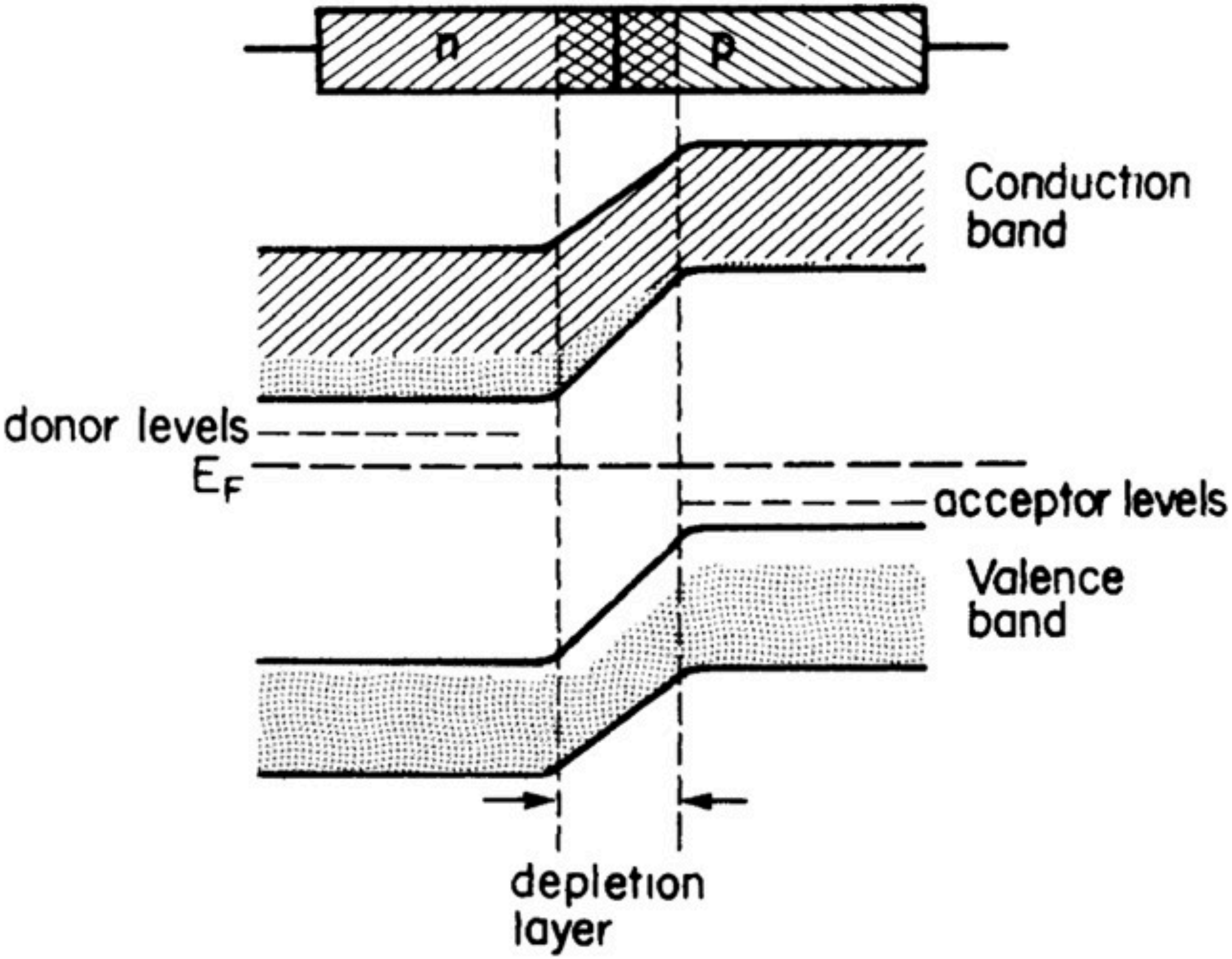
when silicon is doped with group 5 impurity atoms (for example, phosphorus) which are called *donnors*.
this doping creates extra electron in this band. The extra electrons - called *electrons*

A semiconductor where the electric current is carried predominantly by electrons is called *n-type*

when silicon is doped with group 3 impurity atoms (for example, boron) which are called *acceptors*.
this doping creates electron deficiency in this band. The missing electrons - called *holes*
A semiconductor where the electric current is carried predominantly by holes is called *p-type*

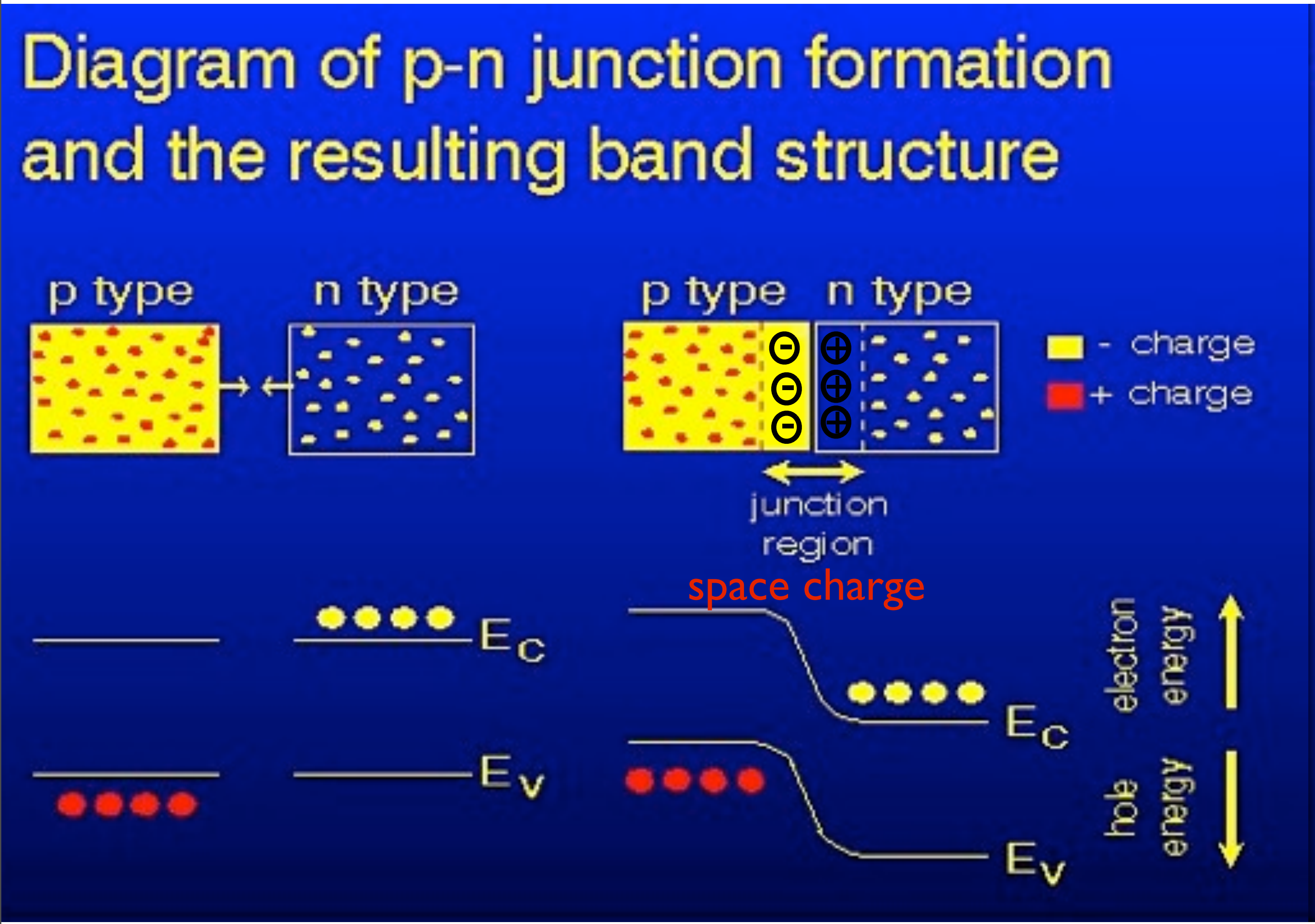
8.7.4. *p–n* Rectifier (Diode)

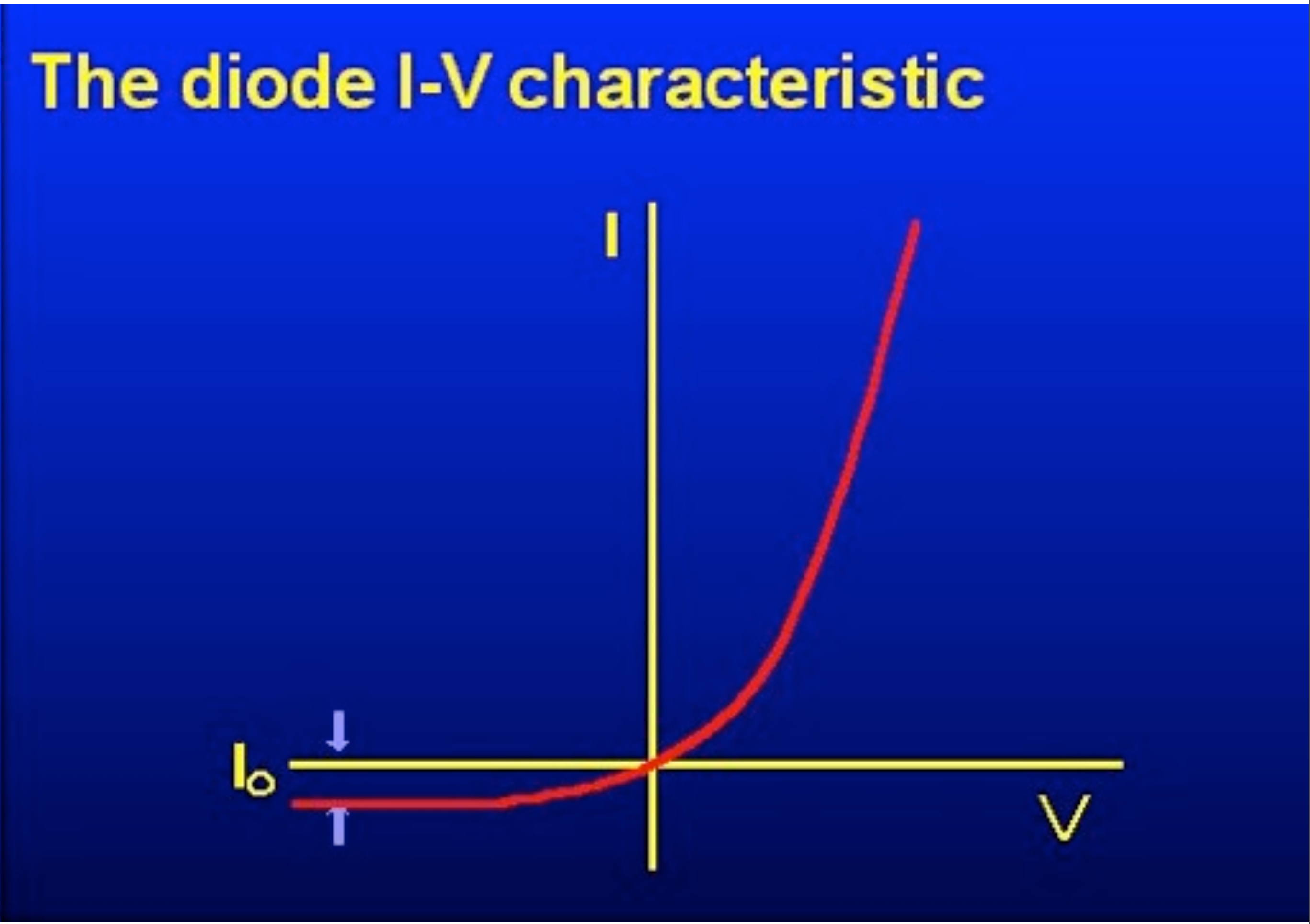
As before, electrons flow from the higher level (*n*-type) "down" into the *p*-type semiconductor so that the *p*-side is negatively charged. This proceeds until equilibrium is reached and both Fermi energies are at the same level.



8.7.4. *p–n* Rectifier (Diode)

b) Semiconductor Junction

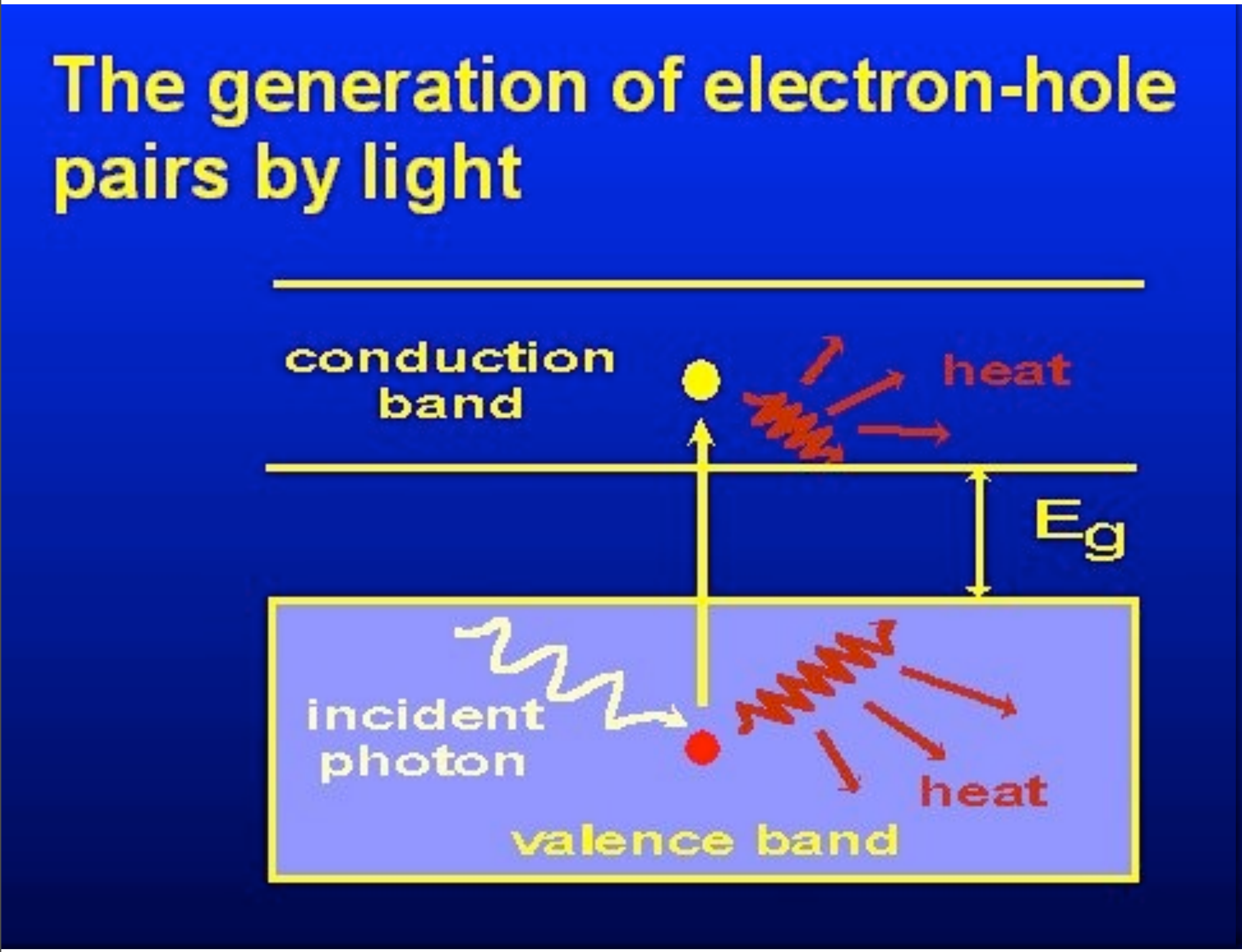




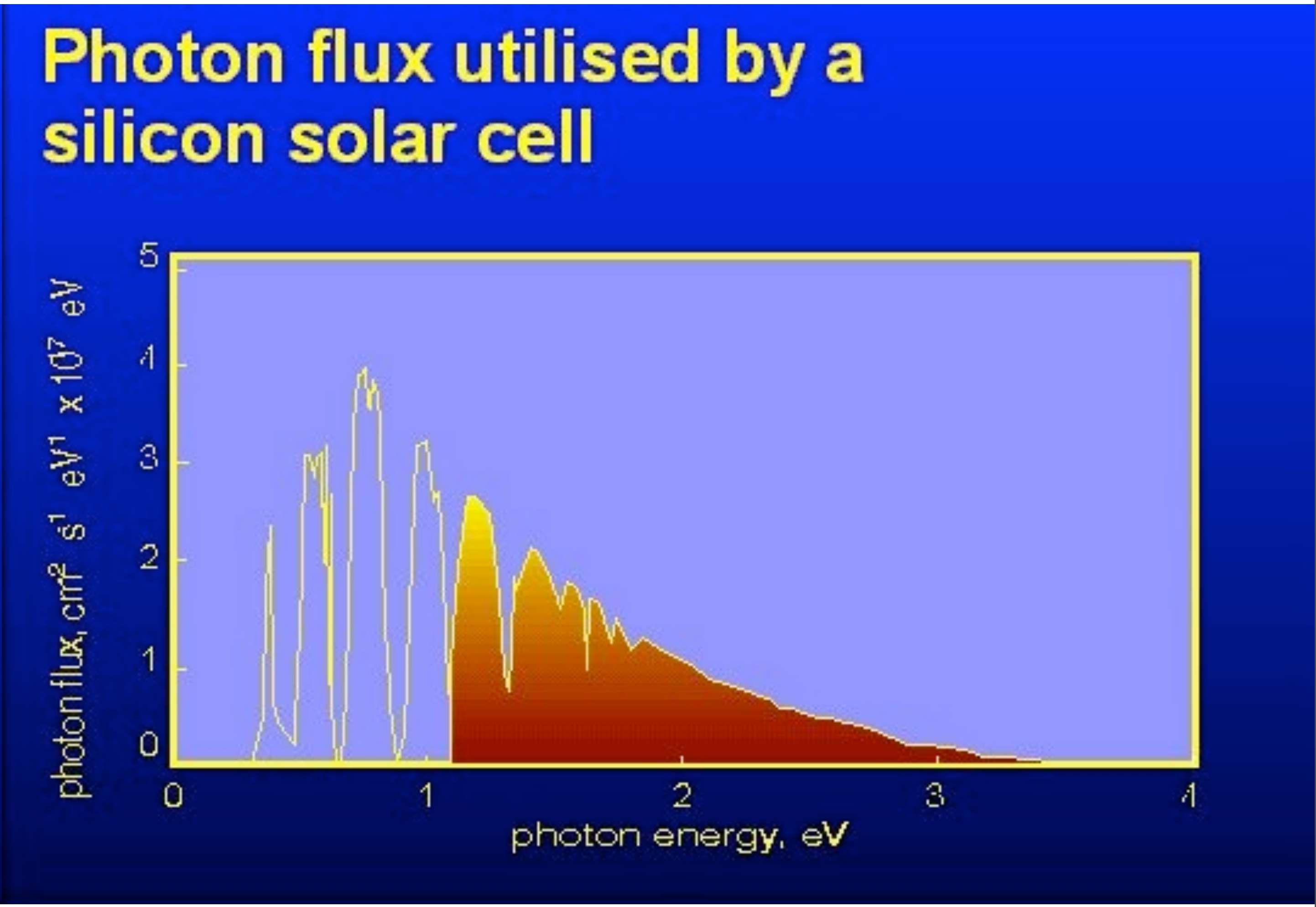
The potential barrier of a junction permits the flow of electric current in only one direction - the junction acts as a rectifier, or diode. This can be seen in our example where electrons can only flow from the p region to the n region, and holes can only flow in the opposite direction. Electric current, which is the sum of the two, can therefore flow only from the p-side to the n-side of the junction (remember that it is defined as the direction of flow of the positive carriers!)

Some semiconductor physics

c) Light absorption by a semiconductor = generation



The generation of electron-hole pairs by light

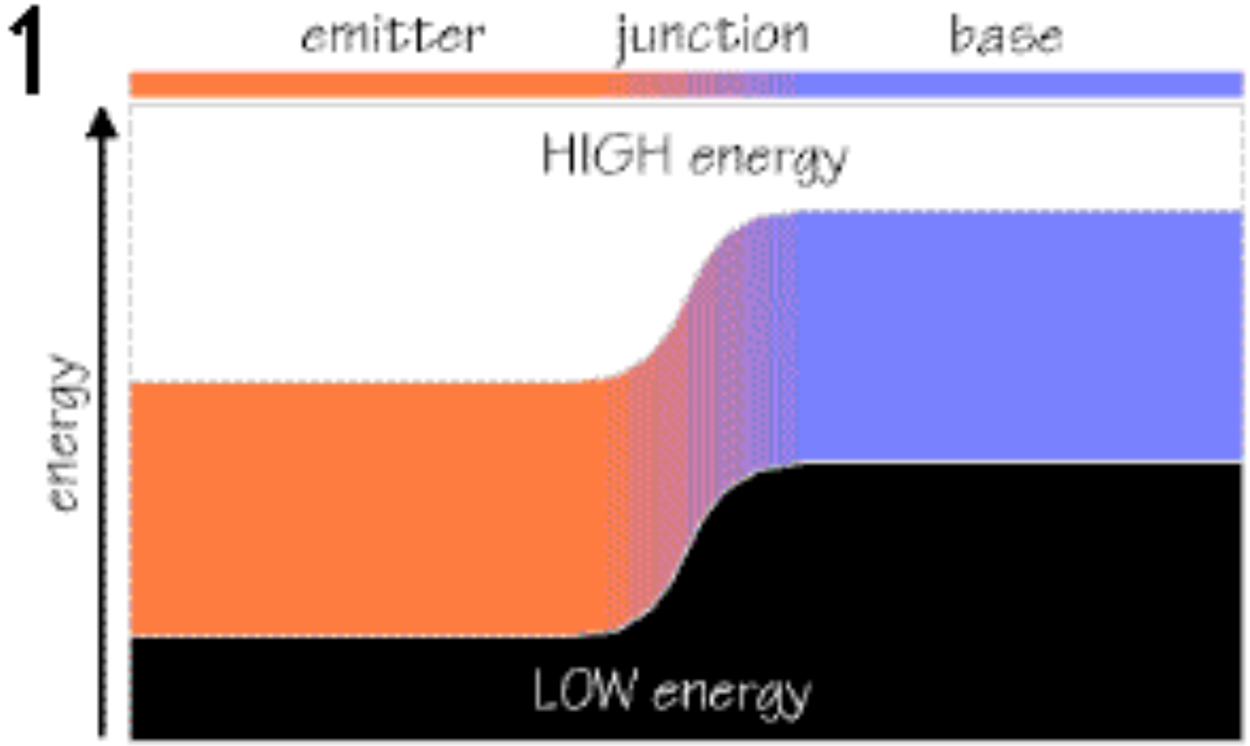


Photon flux utilised by a silicon solar cell

Only some of these photons - those with energy in excess of the bandgap - can be converted into electricity by the solar cell.

Each semiconductor is restricted to converting only a part of the solar spectrum.

How a p-n junction solar cells work ?



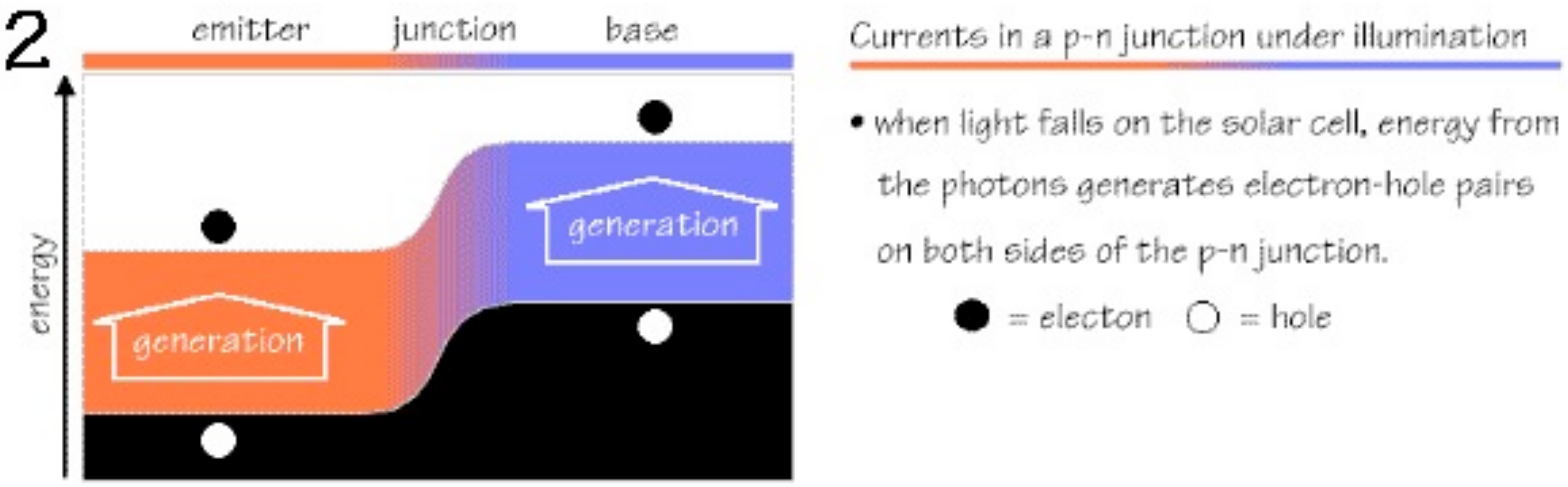
Currents in a p-n junction under illumination

- this diagram shows a typical silicon solar cell
- note the two possible electron energy bands:

  LOW (black) - known as the valence band

  HIGH (white) - known as the conduction band

How a p-n junction solar cells work ?

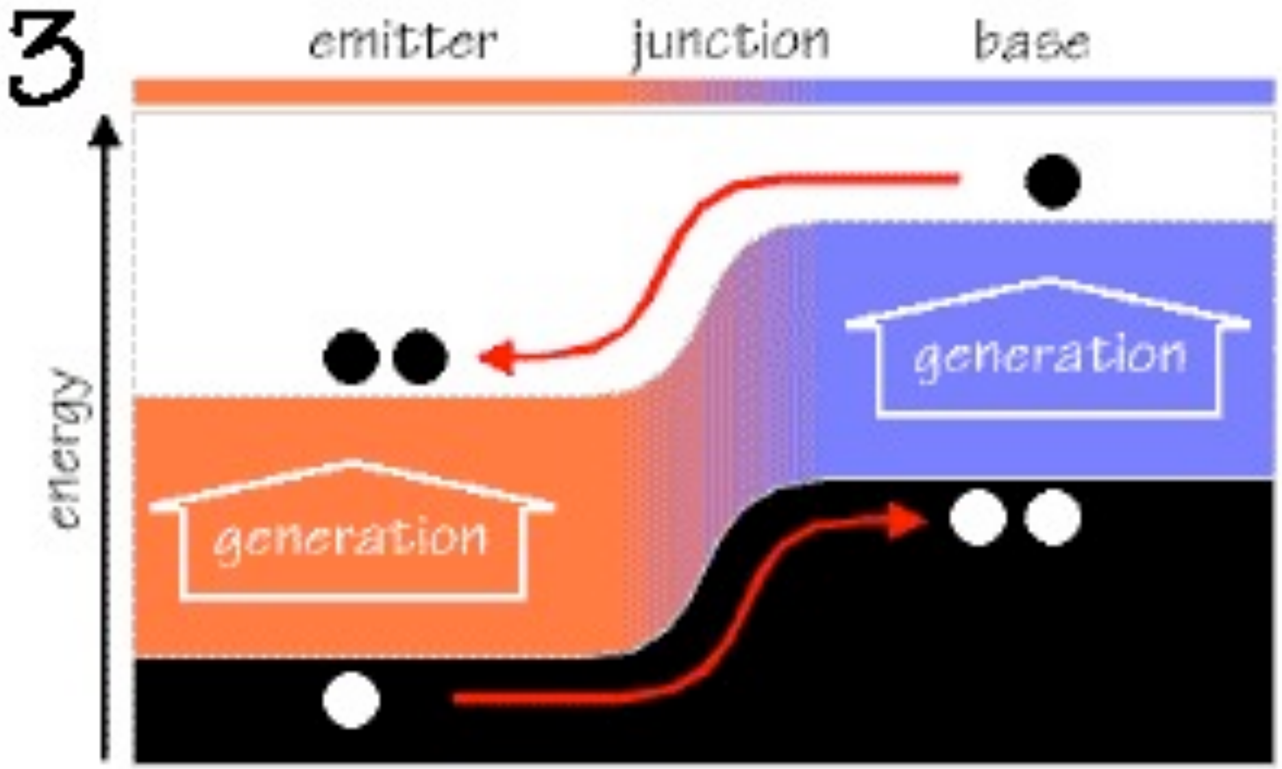


Currents in a p-n junction under illumination

- when light falls on the solar cell, energy from the photons generates electron-hole pairs on both sides of the p-n junction.

● = electon ○ = hole

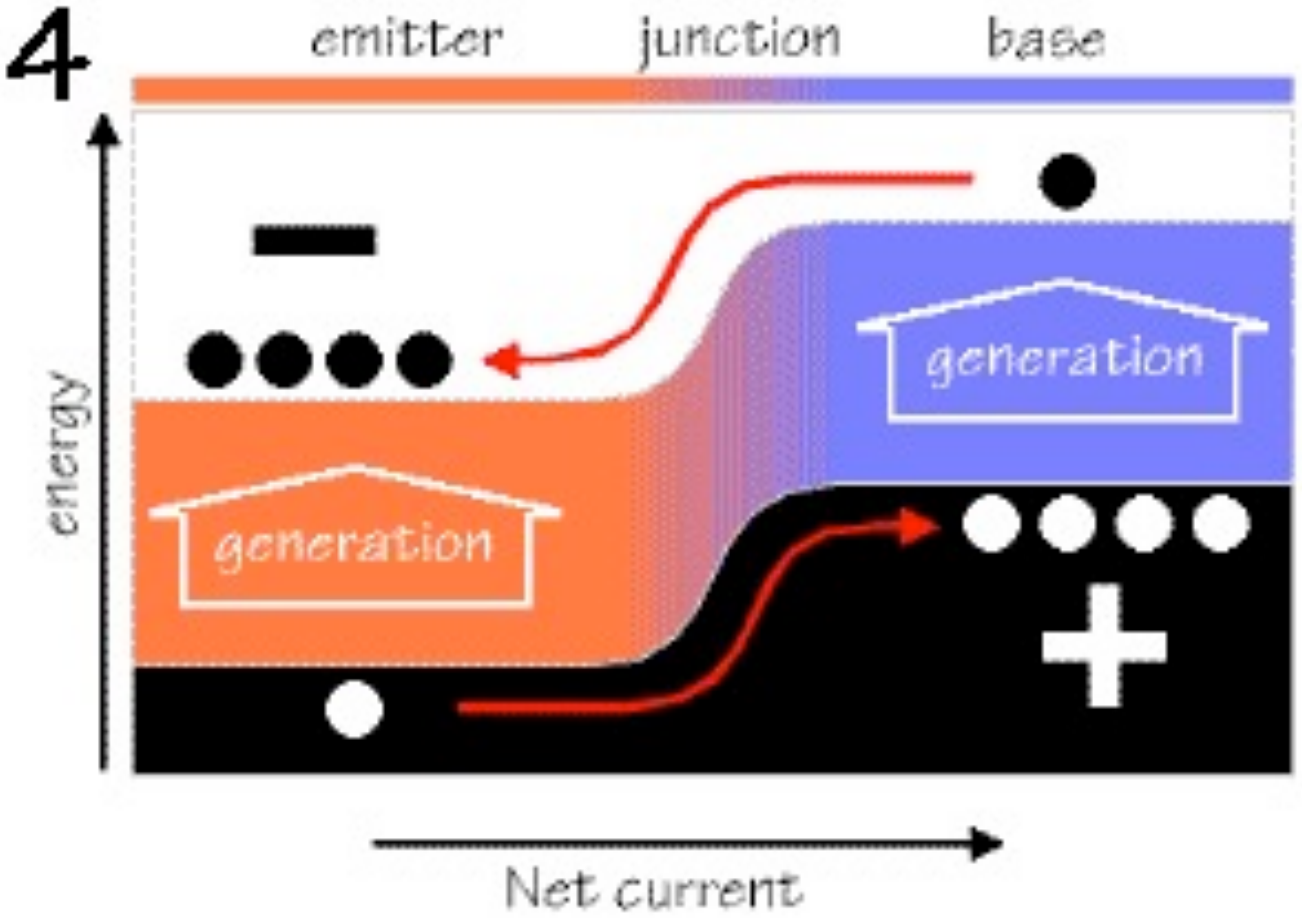
How a p-n junction solar cells work ?



Currents in a p-n junction under illumination

- electrons diffuse across the p-n junction to a lower energy level.
- holes diffuse in the opposite direction.
- new electron-hole pairs continue to be formed while light falls on the solar cell.

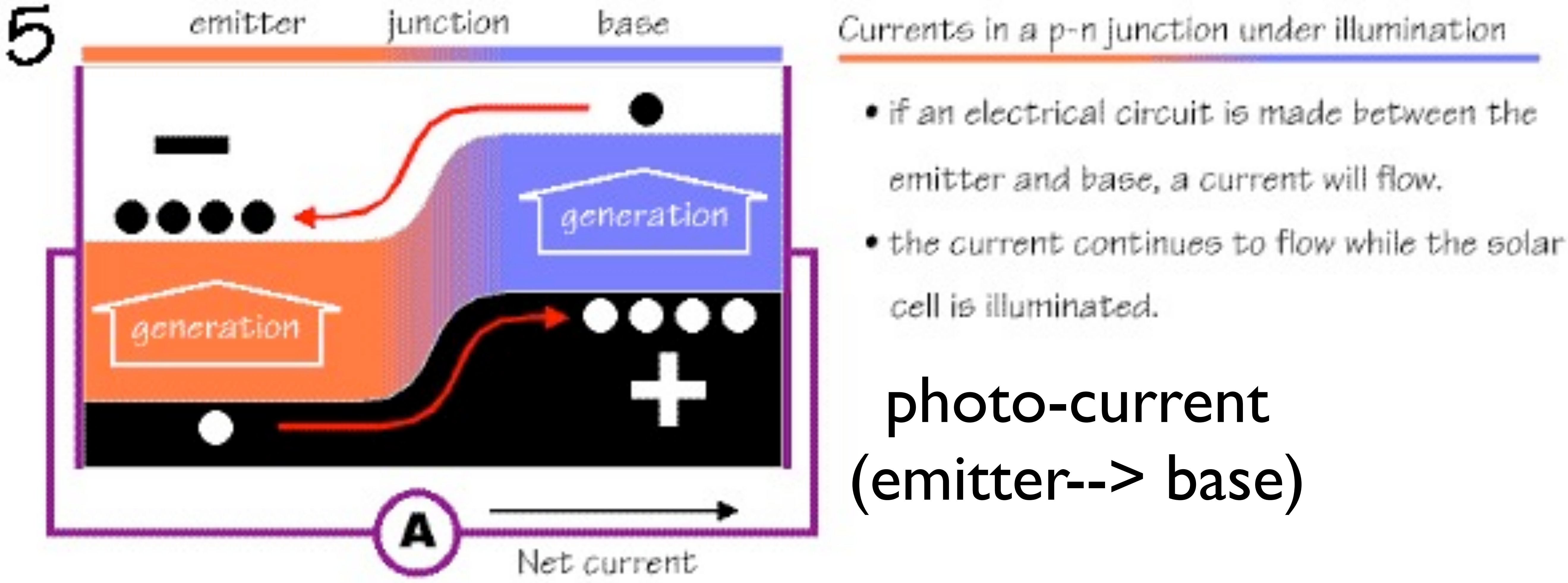
How a p-n junction solar cells work ?



Currents in a p-n junction under illumination

- as electrons continue to diffuse, a negative charge builds up in the emitter.
- a corresponding positive charge builds up in the base.
- the p-n junction has separated the electrons from the holes and transformed the generation current between the bands into an electric current across the p-n junction.

How a p-n junction solar cells work ?



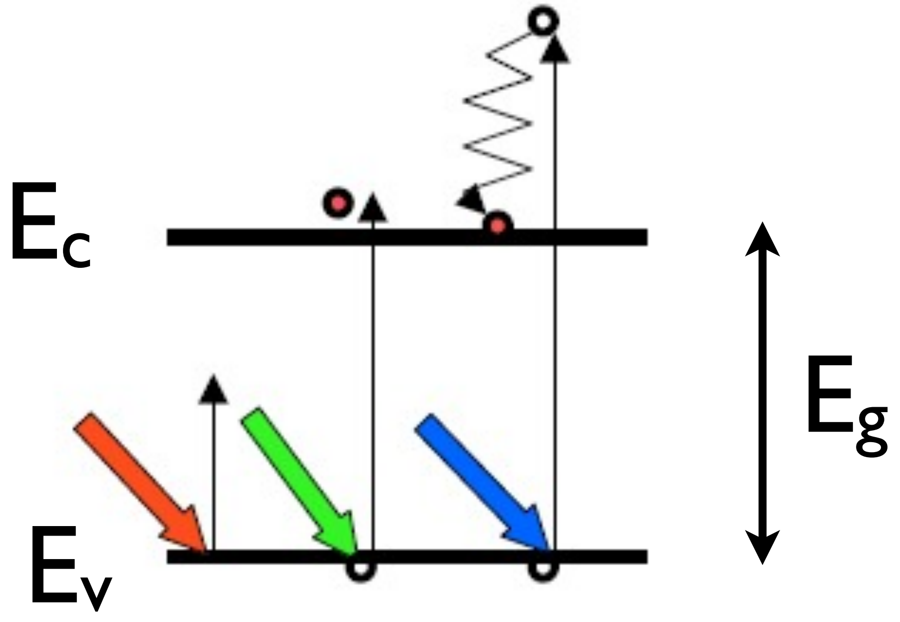
Currents in a p-n junction under illumination

- if an electrical circuit is made between the emitter and base, a current will flow.
- the current continues to flow while the solar cell is illuminated.

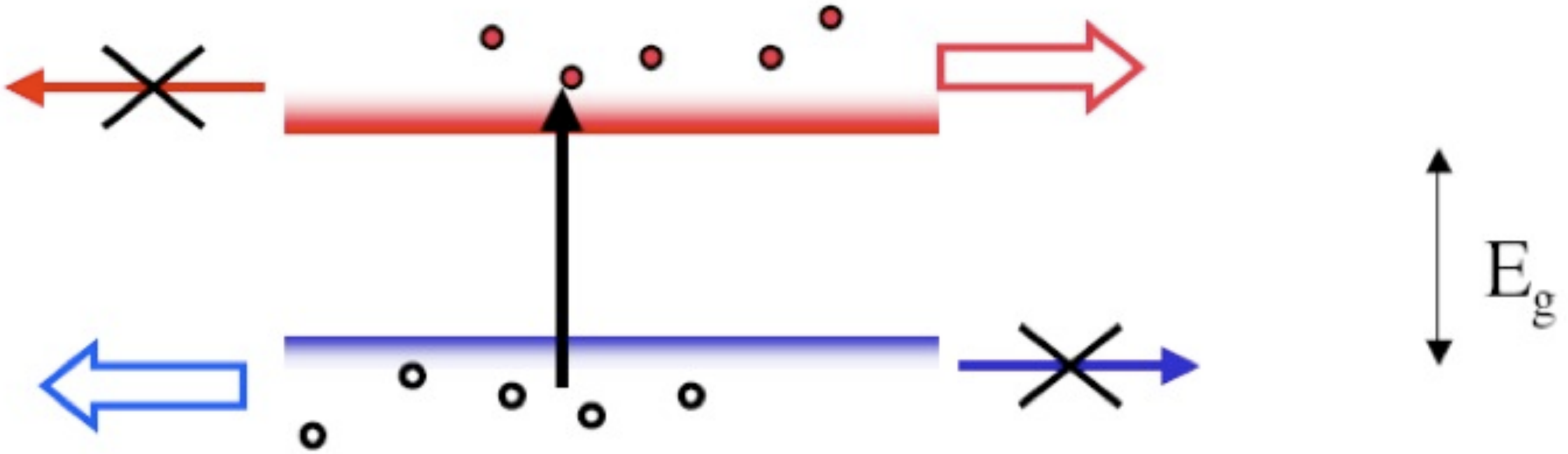
photo-current
(emitter--> base)

How solar cells work ?

- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - charge separation (space charge)
  - charge transport Metal-semiconductor contact)

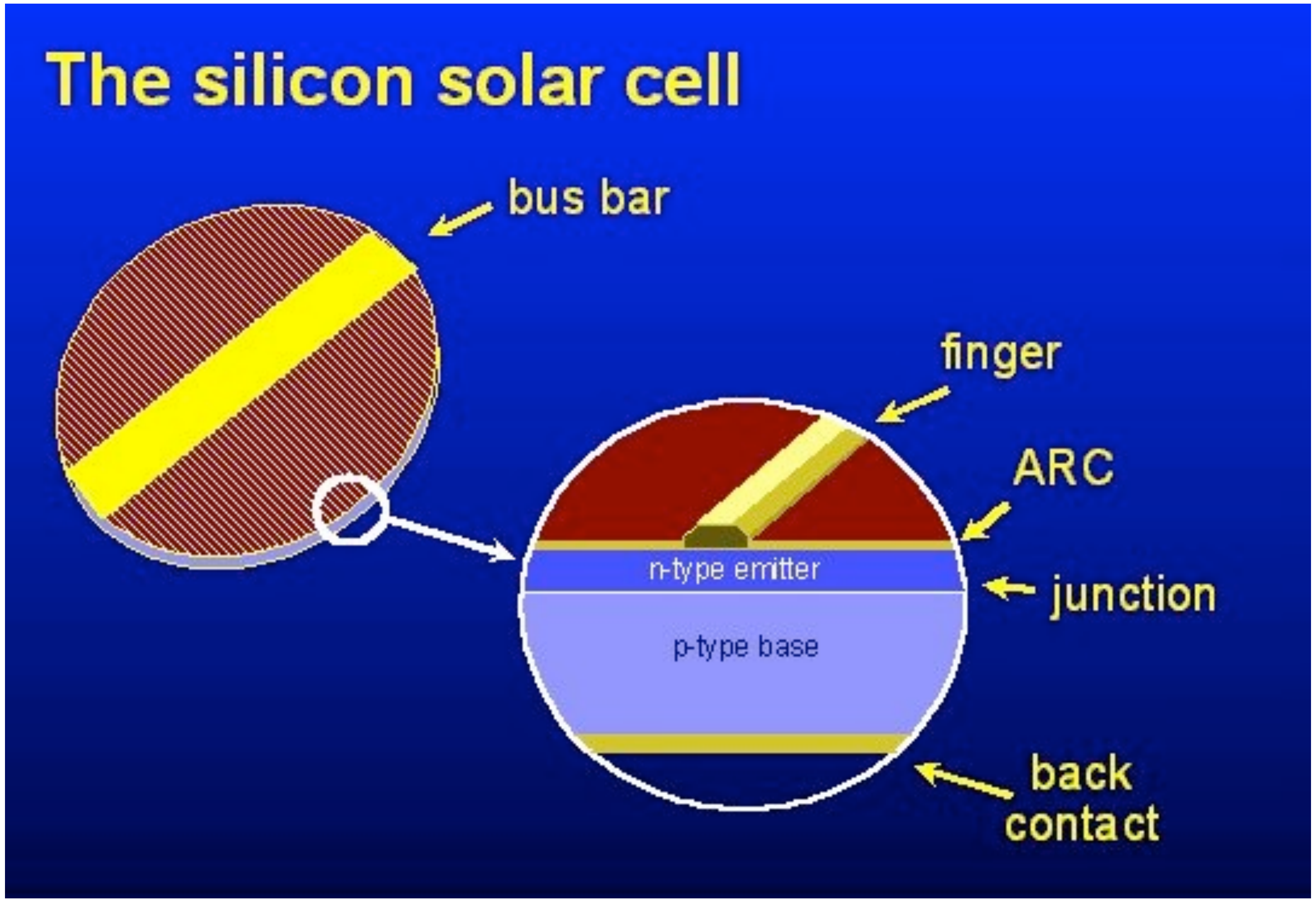


Single band gap



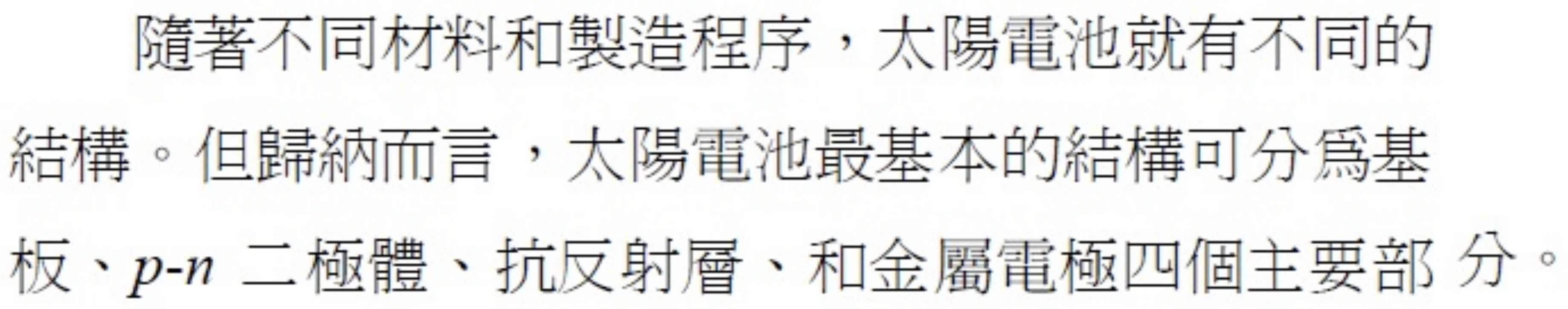
Immediately after their creation, the electron and hole decay to states near the edges of their respective bands. The excess energy is lost as heat and cannot be converted into useful power. This represents one of the fundamental loss mechanisms in a solar cell.

How solar cells work ?

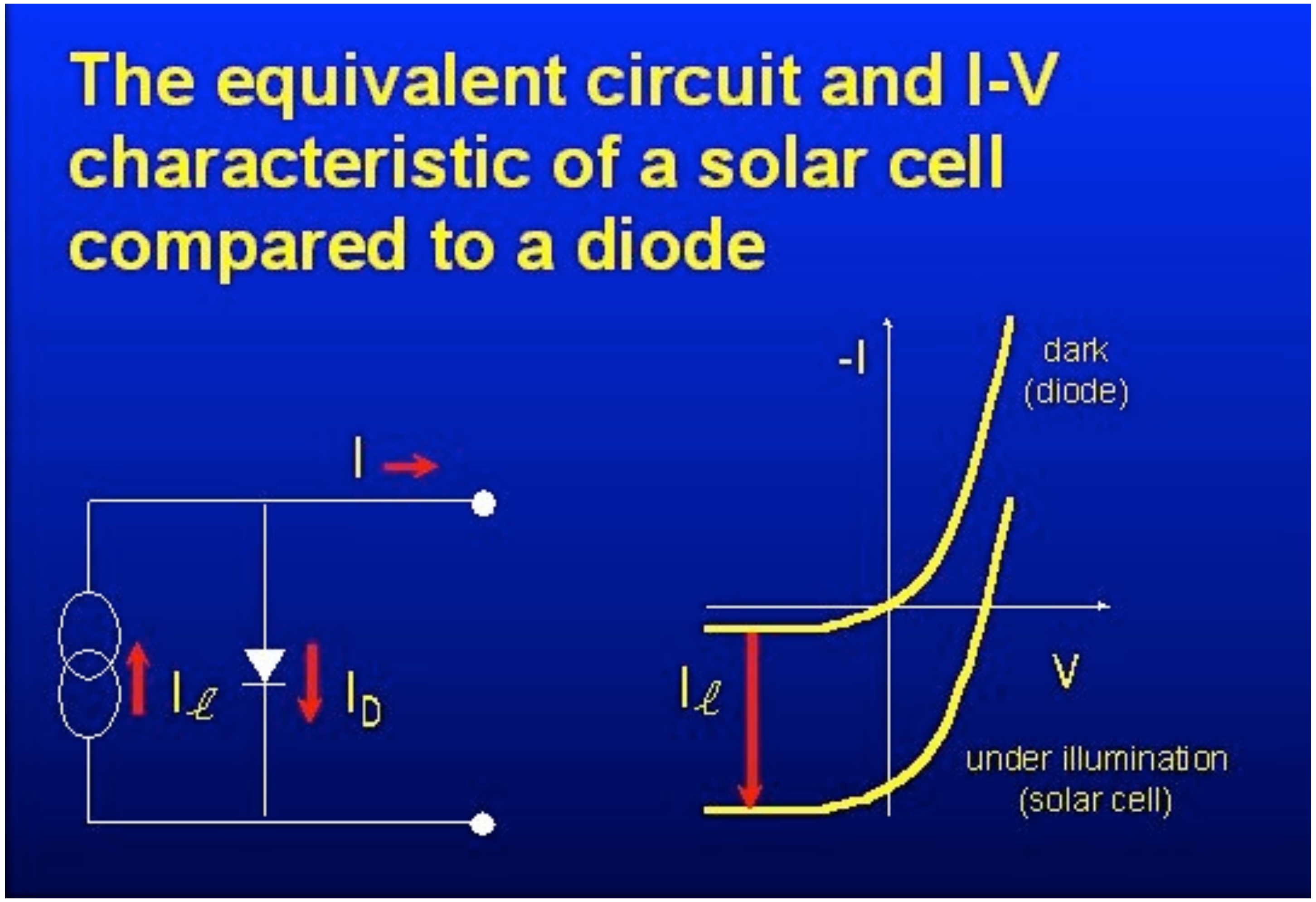


This diagram shows a typical crystalline silicon solar cell. The electrical current generated in the semiconductor is extracted by contacts to the front and rear of the cell.

The top contact structure which must allow light to pass through is made in the form of widely-spaced thin metal strips (usually called *fingers*) that supply current to a larger bus bar. The cell is covered with a thin layer of dielectric material - the *anti-reflection coating*, ARC (Si_3N_4)- to minimize light reflection from the top surface.



隨著不同材料和製造程序，太陽電池就有不同的
結構。但歸納而言，太陽電池最基本的結構可分爲基
板、*p-n* 二極體、抗反射層、和金屬電極四個主要部 分。



The equivalent circuit and I-V characteristic of a solar cell compared to a diode

$$I = I_s(e^{V/V_T} - 1)$$ diode

其中 I 代表電流，V 代表電壓，I_s 是飽和電流 (saturation current)，和 $V_T \equiv k_B T/q_0$，其中 k_B 代表 Boltzmann 常數，q_0 是單位電量，T 是溫度。在室溫下，$V_T \approx 0.026\text{V}$

$$I = I_s(e^{V/V_T} - 1) - I_L$$ solar cell

當太陽電池短路，短路電流 就是入射光產生的光電流

則爲 $I_{sc} = -I_L$ photo-current

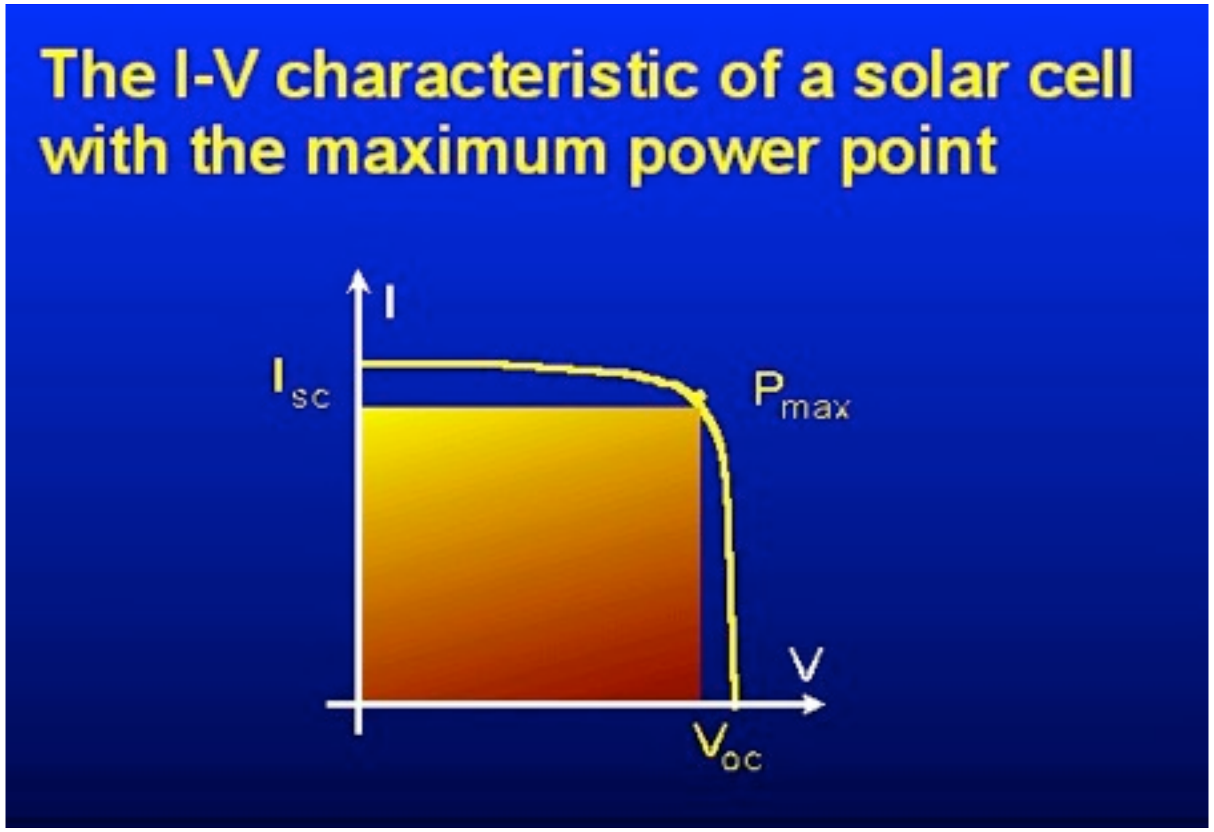
- Photovoltaic energy conversion requires:
  - photon absorption across an energy gap
  - charge separation (space charge)
  - charge transport Metal-semiconductor contact)

這三要件也往往是決定設計光伏特電池效率高低的重要因素。

太陽電池的效率(efficiency)就是指太陽電池將入射光的功率 P_{in} 轉換成最大輸出之電功率的比例，也就是

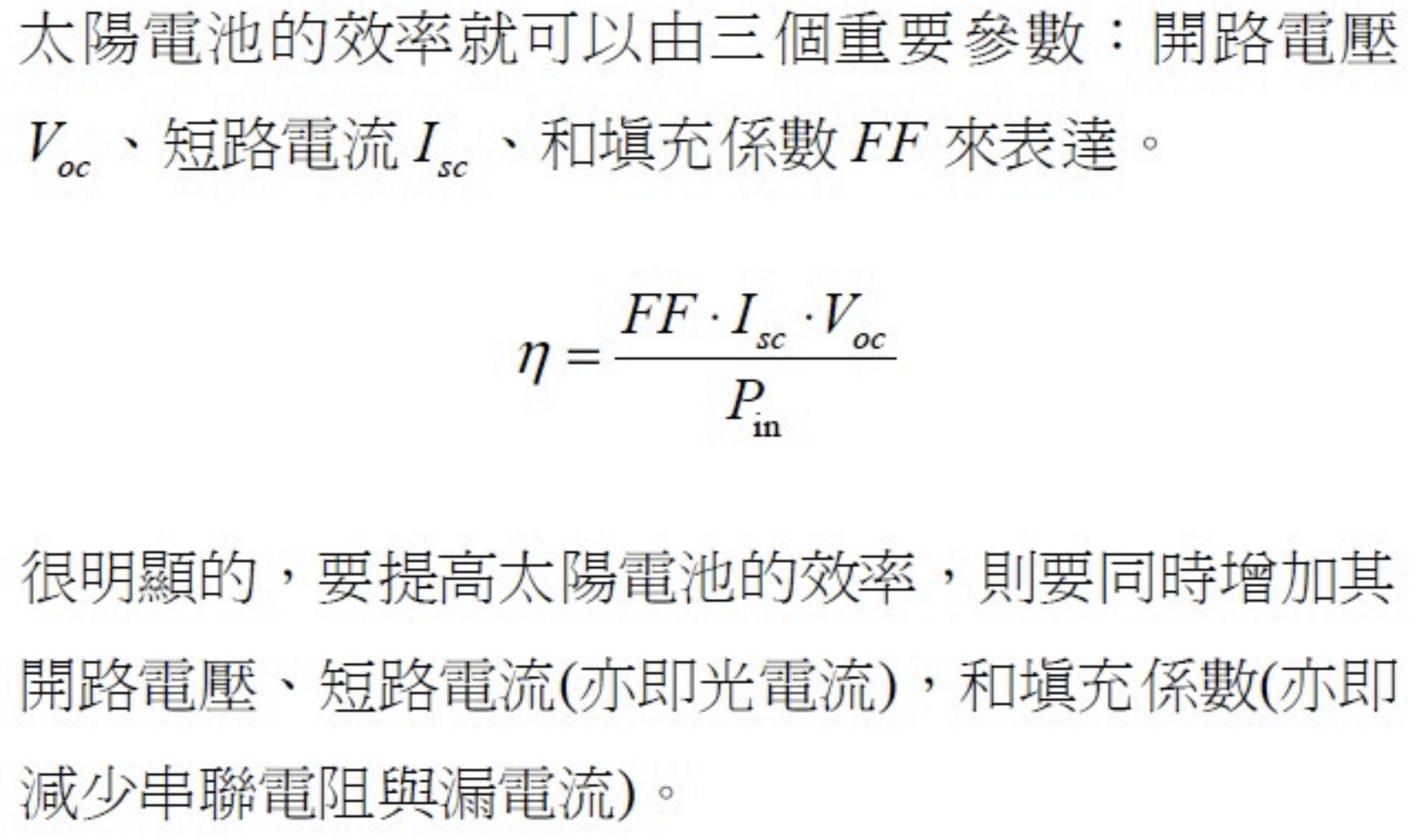
$$\eta \equiv \frac{P_{\max}}{P_{\mathrm{in}}}$$

一般的太陽電池的效率量測，都是使用 $P_{\mathrm{in}} = 1000\ \mathrm{W/m^2}$ 的類似太陽光的燈光光源。



The I-V characteristic of a solar cell with the maximum power point

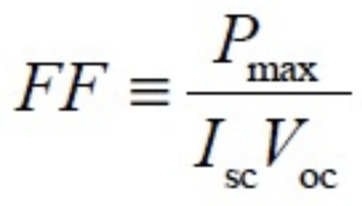
Efficiency of Solar Cell



太陽電池的效率就可以由三個重要參數：開路電壓 V_{oc} 、短路電流 I_{sc} 、和塡充係數 FF 來表達。

$$\eta = \frac{FF \cdot I_{sc} \cdot V_{oc}}{P_{\mathrm{in}}}$$

很明顯的，要提高太陽電池的效率，則要同時增加其開路電壓、短路電流(亦即光電流)，和塡充係數(亦即減少串聯電阻與漏電流)。



$$FF \equiv \frac{P_{\mathrm{max}}}{I_{\mathrm{sc}} V_{\mathrm{oc}}}$$