

“Complementi di Fisica”

Lecture 35

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Università di Trieste

Trieste, 18/19-12-2012

Course Outline - Reminder

- **Introduction to Quantum Mechanics**
 - Waves as particles and particles as waves (the crisis of classical physics); atoms and the Bohr model
 - The Schrödinger equation and its interpretation
 - (1-d) Wave packets, uncertainty relations; barriers and wells
 - ((3-d) Hydrogen atom, angular momentum, spin; many particles)
- **Introduction to Solids and Semiconductors**
 - Periodic potentials in crystals; Bloch waves and packets
 - Energy bands, density of states, Fermi-Dirac pdf
 - Electrons and holes, effective mass
- **Introduction to the physics of semiconductor devices**
 - Equilibrium carrier concentration (“intrinsic”, “extrinsic”)
 - Charge carriers, transport phenomena:
 - Ingredients: external fields and scattering (defects, phonons)
 - drift and diffusion, generation and recombination
 - Boltzmann transport and carrier continuity equations

In this lecture

- **Ingredients of the photovoltaic action and junctions**
 - charge generation, charge separation and charge transport
 - Junctions: metal-semiconductor, semiconductor-semiconductor, semiconductor-electrolyte, ...
- **p-n junction**
 - approximations: “depletion”, “linear minority carrier recombination”
 - behaviour in the dark
 - behaviour under illumination
- **Monocrystalline solar cells**
- **Other cell types**
- **Reference textbooks**
 - P.Wurfel, Physics of Solar Cells, Wiley-VCH, 2005
 - J.Nelson, The Physics of Solar Cells, Imperial College Press, 2003

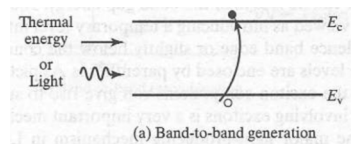
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Photovoltaic action: 3 ingredients

- **Charge generation**
 - Photogeneration, already discussed
- **Charge separation: asymmetry for conduction (and removal) of electrons and holes**
 - Light-induced gradient in quasi-Fermi levels for electrons and holes, that can also be described as a sort of “selective filter”:
 - Two paths of very different resistance for electrons and holes
 - (Can be realized in different ways... pn junction is an example)
- **Charge transport**
 - Drift, diffusion
 - Recombination (radiative, Auger, trap-mediated)
 - Transport continuity equations + Gauss (Poisson) law



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Currents and quasi-Fermi levels

- Remember: in equilibrium ($n = n_0$, $p = p_0$)
quasi-Fermi levels are equal and constant
 $\Rightarrow$ the net current density is zero everywhere

$$J_x = J_{x,n} + J_{x,p} = \mu_n n \frac{\partial F_N}{\partial x} + \mu_p p \frac{\partial F_P}{\partial x} = 0$$

"electron affinity" χ

$F_N = F_P = E_F = \text{const.}$

$F_N = E_C - kT \ln(N_C/n) = (E_{vac} - \chi) - kT \ln(N_C/n)$

$F_P = E_V + kT \ln(N_V/p) = (E_{vac} - \chi - E_g) + kT \ln(N_V/p)$

E_{vac}

ϕ "work function"

E_C

E_V

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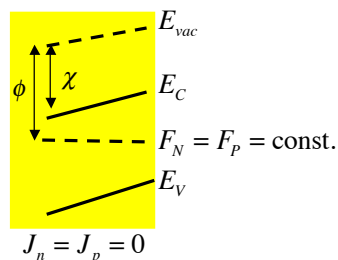
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charge separation, in general

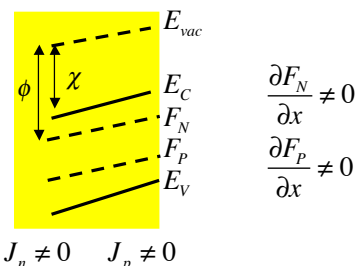
$$J_{x,n} = \mu_n n \frac{\partial F_N}{\partial x} = +|q| D_n \frac{\partial n}{\partial x} + \mu_n n \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_C}{\partial x} \right)$$

$$J_{x,p} = \mu_p p \frac{\partial F_P}{\partial x} = -|q| D_p \frac{\partial p}{\partial x} + \mu_p p \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_g}{\partial x} + kT \frac{\partial \ln N_V}{\partial x} \right)$$



diffusion and drift add up to zero
for both electrons and holes

Non-uniform material in the dark



gradients in quasi-Fermi levels
drive non-zero net currents

Non-uniform material under illumination

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charge separation, in general

$$J_{x,n} = \mu_n n \frac{\partial F_n}{\partial x} = \underbrace{+|q| D_n \frac{\partial n}{\partial x}}_{\text{diffusion}} + \underbrace{\mu_n n \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_c}{\partial x} \right)}_{\text{drift}}$$

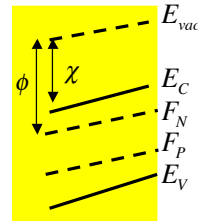
$$J_{x,p} = \mu_p p \frac{\partial F_p}{\partial x} = \underbrace{-|q| D_p \frac{\partial p}{\partial x}}_{\text{diffusion}} + \underbrace{\mu_p p \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_g}{\partial x} + kT \frac{\partial \ln N_v}{\partial x} \right)}_{\text{drift}}$$

Excess charges (electron and holes),
generated by illumination, are separated by:

non-zero “**electric field**” (*)
⇒ **net drift currents**

carrier density gradients
⇒ **net diffusion currents**

(*) Electric field origin:
(1) “**built-in**” field at equilibrium,
due to a varying work function ϕ
(2) “**effective**” fields, due to
gradients in χ, E_g, N_c, N_v



$$\frac{\partial F_n}{\partial x} \neq 0$$

$$\frac{\partial F_p}{\partial x} \neq 0$$

$$J_n \neq 0 \quad J_p \neq 0$$

gradients in quasi-Fermi levels
drive non-zero net currents (diffusion+drift)

Non-uniform material under illumination

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charge separation

$$J_{x,n} = \mu_n n \frac{\partial F_n}{\partial x} = \underbrace{+|q| D_n \frac{\partial n}{\partial x}}_{\text{diffusion}} + \underbrace{\mu_n n \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_c}{\partial x} \right)}_{\text{drift}}$$

$$J_{x,p} = \mu_p p \frac{\partial F_p}{\partial x} = \underbrace{-|q| D_p \frac{\partial p}{\partial x}}_{\text{diffusion}} + \underbrace{\mu_p p \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_g}{\partial x} + kT \frac{\partial \ln N_v}{\partial x} \right)}_{\text{drift}}$$

Excess charges (electron and holes),
generated by illumination, are separated by:

non-zero “**electric field**” (*)
⇒ **net drift currents**

carrier density gradients
⇒ **net diffusion currents**

(*) Electric field origin:
(1) “**built-in**” field at equilibrium,
due to a varying work function ϕ
(2) “**effective**” fields, due to
gradients in χ, E_g, N_c, N_v

$$E_x = \frac{1}{|q|} \frac{\partial E_c}{\partial x} = \frac{1}{|q|} \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} \right) \quad \text{electric field for electrons}$$

$$E_x = \frac{1}{|q|} \frac{\partial E_v}{\partial x} = \frac{1}{|q|} \left(\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_g}{\partial x} \right) \quad \text{el. field for holes}$$

neglecting gradients
in N_c, N_v

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Work function and junctions

- Work function of a material**

“energy required to remove the least tightly bound electrons”

$$\phi = E_{vac} - E_F$$

- Electrostatic energy difference across a junction at equilibrium**

Junction between regions with different work functions: ϕ_+ , ϕ_-
built-in electric field $\Rightarrow$ electrostatic potential energy difference

$$\Delta\phi = \phi_+ - \phi_- = |q| \int_{x_-}^{x_+} E_x dx$$

- Gauss' equation: electric field and local charge**

The difference in work functions

implies a redistribution of charges

and non-neutrality in the junction region

$$\frac{\partial E_x}{\partial x} = \frac{|q|}{\epsilon_s} (p - n + N_d^+ - N_A^-)$$

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Different junction types

- The built-in potential difference (and electrical field) can be established in several ways:**

- Metal-Semiconductor Junction (Schottky barrier)
- Semiconductor-Semiconductor Junctions
 - p-n junction
 - p-i-n junction
 - p-n heterojunction
- Electrochemical Semiconductor-Electrolyte Junction
- Junctions in Molecular Organic Materials

- We will restrict the analysis to p-n junctions and cells:**

- p-n junction: electrostatics at equilibrium and under bias
- p-n junction: volt-ampere characteristic (ideal diode)
- p-n junction under illumination
- Monocrystalline solar cells

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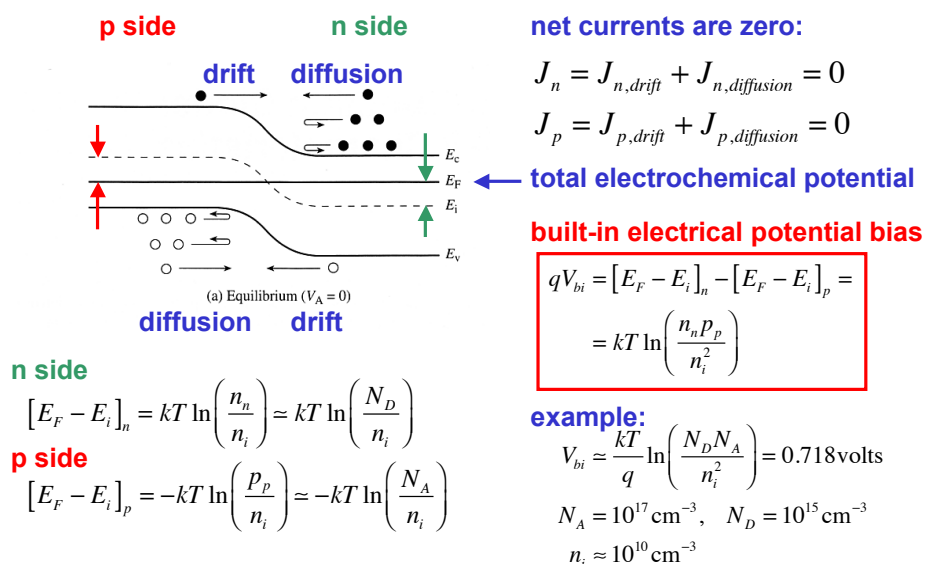
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pn junction at equilibrium in the dark

Electrostatics

pn junction at equilibrium

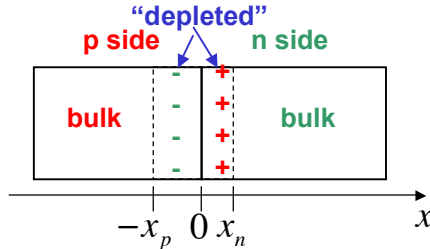


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Electrostatics: approximations



$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\epsilon_s} \quad \text{Gauss-Poisson}$$

$$\frac{\partial E_x}{\partial x} = \frac{q}{\epsilon_s} (p - n + N_D^+ - N_A^-)$$

$$\frac{\partial^2 V}{\partial x^2} = -\frac{q}{\epsilon_s} (p - n + N_D^+ - N_A^-)$$

Depletion approximation

Abrupt junction, constant N_D (n-side) and N_A (p-side)

Mobile charges recombine at the junction: only fixed ions are left

$$-x_p \leq x \leq 0: \quad N_A \gg n_p, p_p \Rightarrow \rho = -qN_A^- \Rightarrow \frac{\partial E_x}{\partial x} = \frac{-qN_A}{\epsilon_s}$$

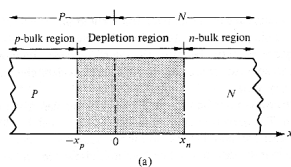
$$0 \leq x \leq x_n: \quad N_D \gg n_n, p_n \Rightarrow \rho = qN_D^+ \Rightarrow \frac{\partial E_x}{\partial x} = \frac{qN_D}{\epsilon_s}$$

$$x < -x_p, \quad x > x_n: \quad \rho \approx 0, \quad E_x \approx 0$$

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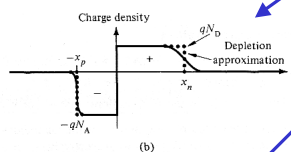
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Depletion approximation - 1

Charge density and global neutrality

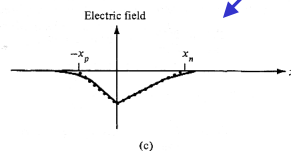
$$N_A x_p = N_D x_n$$



Electrostatic field

$$-x_p \leq x \leq 0 \quad E_x(x) = \frac{-qN_A}{\epsilon_s} (x_p + x)$$

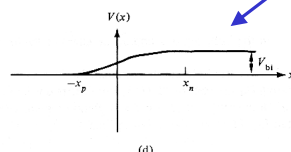
$$0 \leq x \leq x_n \quad E_x(x) = \frac{-qN_D}{\epsilon_s} (x_n - x)$$



Electrostatic potential

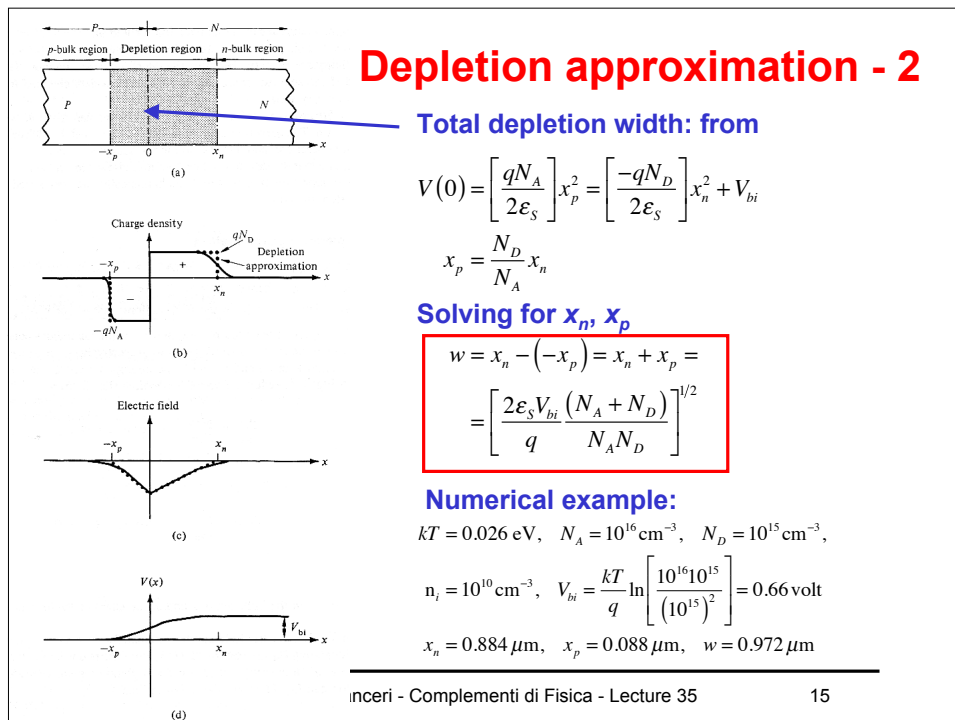
$$-x_p \leq x \leq 0 \quad V(x) = \frac{qN_A}{2\epsilon_s} (x_p + x)^2$$

$$0 \leq x \leq x_n \quad V(x) = \frac{-qN_D}{2\epsilon_s} (x_n - x)^2 + V_{bi}$$



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pn junction biased in the dark

Electrostatics

Forward bias

External bias, **positive** on the p side
($0 < V_A < V_{bi}$): potential difference **decreases!**

(a) Depletion region narrowing as $V_A > 0$.

(b) Charge density: $-qN_A$ on the p-side, $+qN_D$ on the n-side.

(c) Electric field: $E_x(x) = \frac{-qN_A}{\epsilon_s}(x_p + x)$ for $-x_p \leq x \leq 0$ and $E_x(x) = \frac{-qN_D}{\epsilon_s}(x_n - x)$ for $0 \leq x \leq x_n$.

(d) Potential: $V(x) = (V_{bi} - V_A) - \frac{qN_D}{2\epsilon_s}(x_n - x)^2$ for $0 \leq x \leq x_n$ and $V(x) = \frac{qN_A}{2\epsilon_s}(x_p + x)^2$ for $-x_p \leq x \leq 0$.

The p-depletion region shrinks

The n-depletion region shrinks

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Reverse bias

External bias, **negative** on the p side
($V_A < 0$); the potential difference **increases**

(a) Depletion region widening as $V_A < 0$.

(b) Charge density: $-qN_A$ on the p-side, $+qN_D$ on the n-side.

(c) Electric field: $E_x(x) = \frac{-qN_A}{\epsilon_s}(x_p + x)$ for $-x_p \leq x \leq 0$ and $E_x(x) = \frac{-qN_D}{\epsilon_s}(x_n - x)$ for $0 \leq x \leq x_n$.

(d) Potential: $V(x) = (V_{bi} - V_A) - \frac{qN_D}{2\epsilon_s}(x_n - x)^2$ for $0 \leq x \leq x_n$ and $V(x) = \frac{qN_A}{2\epsilon_s}(x_p + x)^2$ for $-x_p \leq x \leq 0$.

The p-depletion region becomes wider

The n-depletion region becomes wider

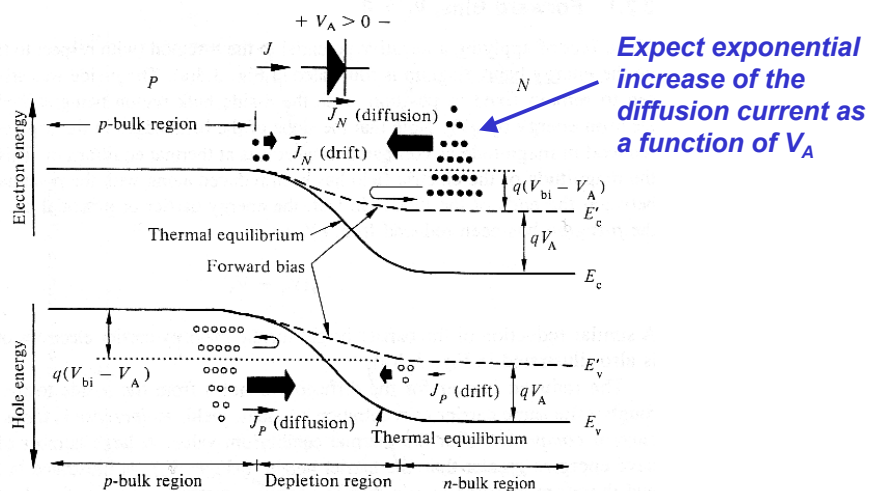
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Current-voltage (I-V) qualitative

Forward bias ($V_A > 0$)

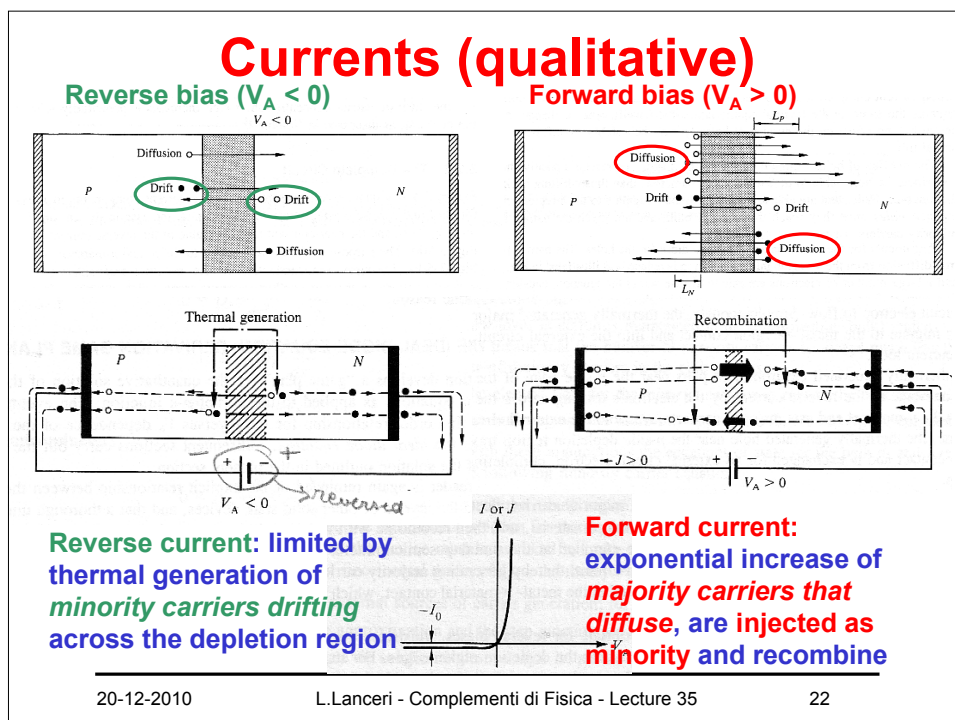
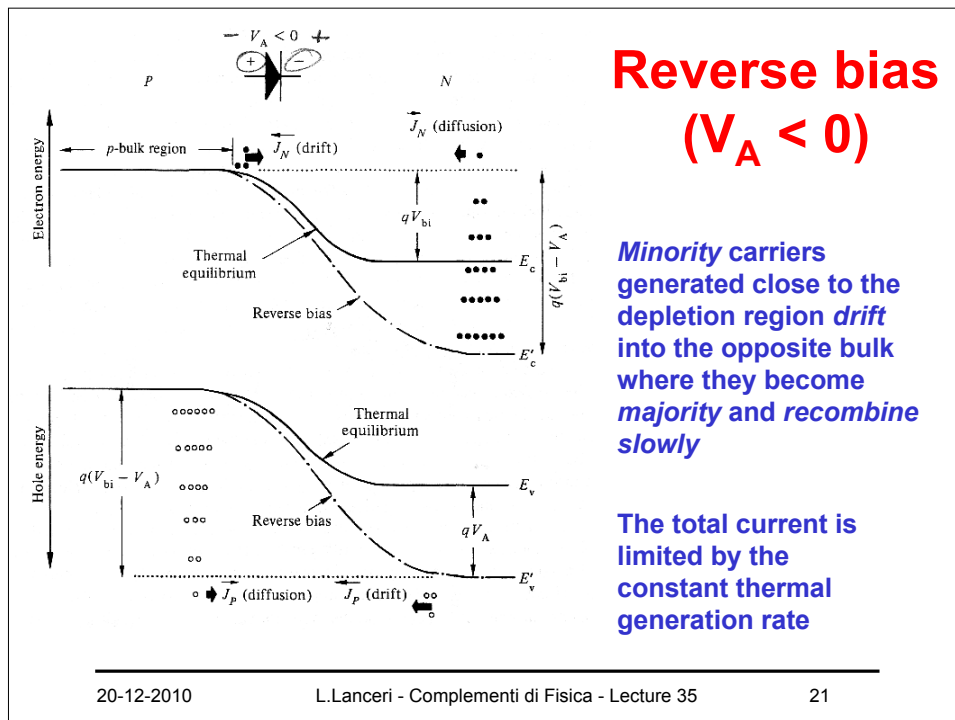
majority carriers diffuse across the depletion region and are injected as minority carriers in the opposite bulk, where they recombine quickly



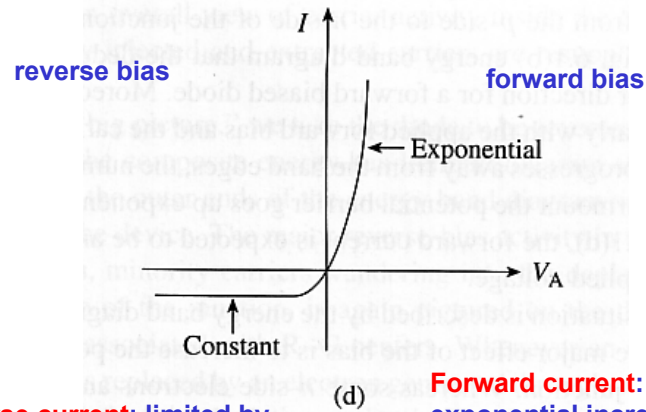
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I - V characteristics



Reverse current: limited by thermal generation of minority carriers drifting across the depletion region

Forward current: exponential increase of majority carriers that diffuse, are injected as minority and recombine

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Current-voltage (I-V)
quantitative

$$0 = D_p \frac{d^2 \Delta p_n}{dx^2} - \frac{\Delta p_n}{\tau_p}$$

$$J_p \cong -qD_p \frac{d\Delta p_n}{dx}$$

$$p_n = p_{n0} + \Delta p_n(x)$$

Excess electrons
Diffusion, recombination

$$0 = D_p \frac{d^2 \Delta p_n}{dx^2} - \frac{\Delta p_n}{\tau_p}$$

$$J_p \cong -qD_p \frac{d\Delta p_n}{dx}$$

$$p_n = p_{n0} + \Delta p_n(x)$$

Excess holes
Diffusion, recombination

• **Approximations:**

- abrupt pn junction, constant N_A and N_D , depletion approx.
- no external generation processes (dark, no light)
- **Steady state**
- Negligible generation or recombination in the depletion region
- Low-level injection in the quasi-neutral bulk regions
- Negligible electric field for the *injected minority carriers* in the bulk regions $\Rightarrow$ predominantly *diffusion and recombination*

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$$0 = D_n \frac{d^2 \Delta n_p}{dx^2} - \frac{\Delta n_p}{\tau_n}$$

$$J_n \cong -qD_n \frac{d\Delta n_p}{dx}$$

$$n_p = n_{p0} + \Delta n_p(x)$$

Excess electrons
Diffusion, recombination

$$0 = D_p \frac{d^2 \Delta p_n}{dx^2} - \frac{\Delta p_n}{\tau_p}$$

$$J_p \cong -qD_p \frac{d\Delta p_n}{dx}$$

$$p_n = p_{n0} + \Delta p_n(x)$$

Excess holes
Diffusion, recombination

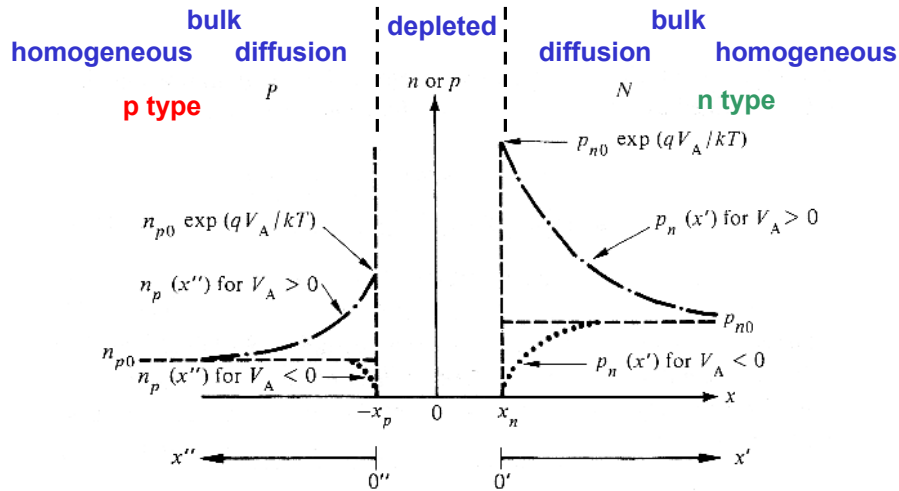
• **Method:**

- Solve the minority carrier continuity equations in the bulk regions for Δn_p and Δp_n (see example, previous lecture)
- Apply boundary conditions to determine Δn_p and Δp_n in terms of the applied voltage V_A
- Determine the current densities $J_p(x_n)$ and $J_n(-x_p)$ from the slopes of Δp_n at x_n and of Δn_p at $-x_p$ respectively
- The total current can be estimated as the sum of the currents at the edges of the depletion region

$$J = J_p(x_n) + J_n(-x_p)$$

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Results: concentrations



$$n_p(x'') = n_{p0} + n_{p0} \left(e^{qV_A/kT} - 1 \right) e^{-x''/L_n}$$

$$p_n(x') = p_{n0} + p_{n0} \left(e^{qV_A/kT} - 1 \right) e^{-x'/L_p}$$

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Results: current

$$L_n = \sqrt{D_n \tau_n} \quad L_p = \sqrt{D_p \tau_p}$$

$$J = J_n(-x_p) + J_p(x_n) = q \left[\frac{D_n}{L_n} n_{p0} + \frac{D_p}{L_p} p_{n0} \right] \left(e^{qV_A/kT} - 1 \right)$$

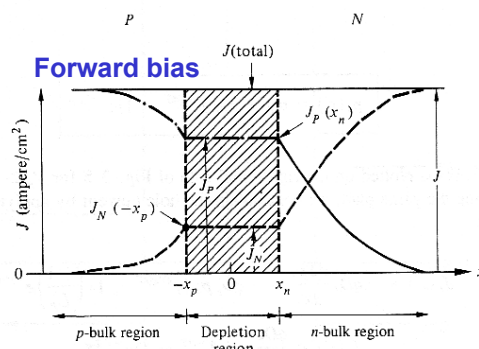


Fig. 3.9 Current density in the forward-biased case. $N_A > N_D$.

$$I = JA = I_0 \left(e^{qV_A/kT} - 1 \right)$$

Junction area A

Exponential

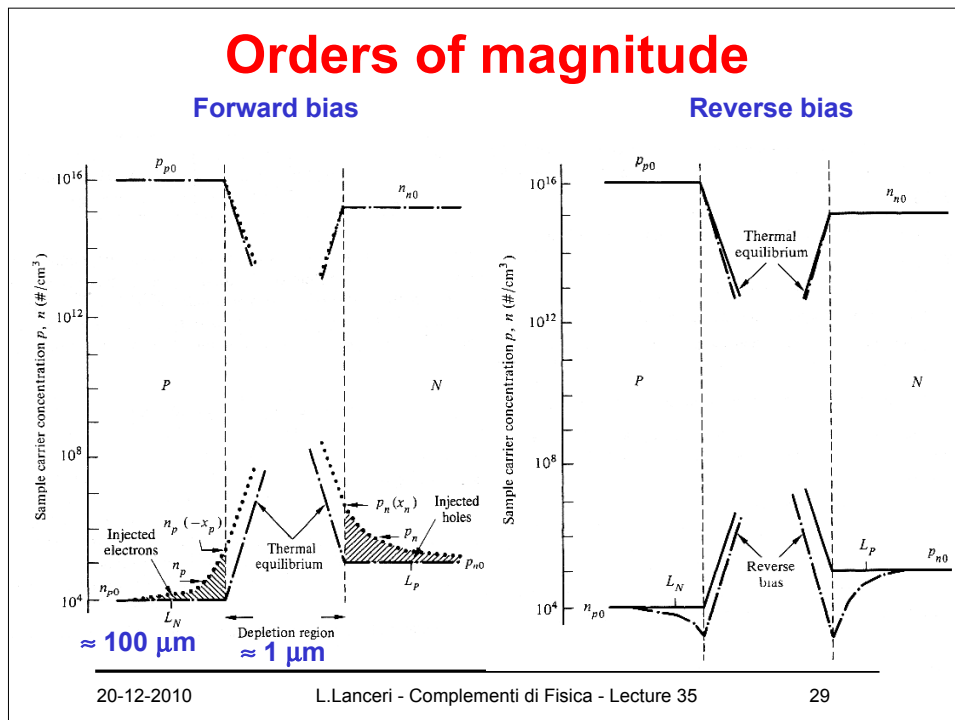
Constant
 $-I_0$

(d)

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Orders of magnitude

Depleted region width (depends on doping and bias) $\approx 1 \mu\text{m}$

Diffusion of minority carriers in the bulk (several L_p, L_n) $\approx 100 \mu\text{m}$

Built-in electric field $\approx 10^6 \text{ V/m}$

Taking into account mobility and diffusivity for electrons:

Corresponding drift velocity for electrons $\approx 10^5 \text{ m/s}$

Depleted region crossing time (drift) $\approx 10^{-11} \text{ s}$

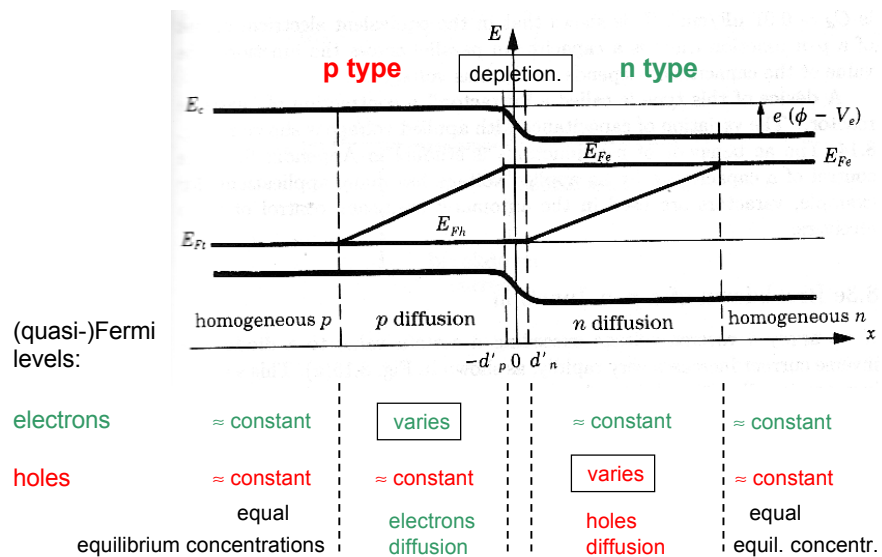
Depleted region crossing time (diffusion) $\approx 10^{-9} \text{ s}$

Typical carrier lifetime $\approx 10^{-6} \text{ s}$

pn junction biased in the dark

Quasi-Fermi levels

Quasi-Fermi levels (forw. biased, dark)

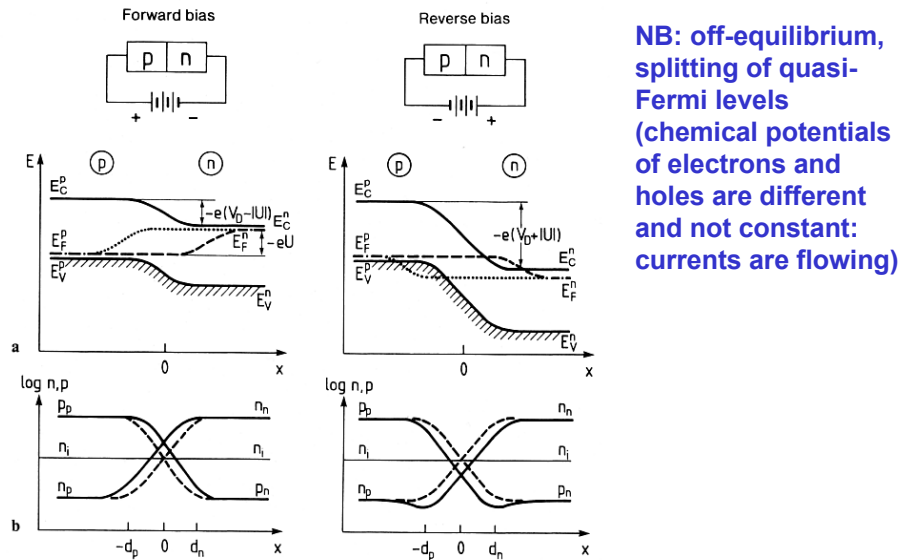


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pn junction, biased (in the dark)



NB: off-equilibrium, splitting of quasi-Fermi levels (chemical potentials of electrons and holes are different and not constant: currents are flowing)

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pn junction illuminated

Illuminated pn junction (open circuit)

Energy conversion:
 from electromagnetic energy:
 Light (sun, $T \approx 6000$ K) absorption
 (e, h) generation ($T \approx 6000$ K)
 (e, h) thermalization ($T \approx 300$ K)
 $\Rightarrow$ "chemical energy"
 Selective filtering of e (h)
 $\Rightarrow$ "electric energy"
 delivered to an external circuit

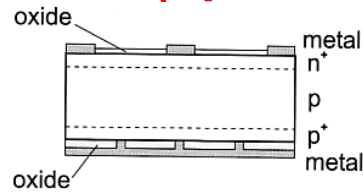
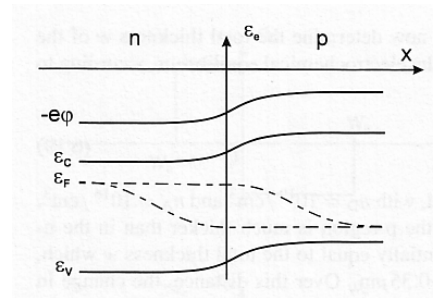
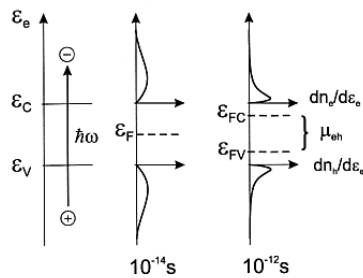


Figure 7.4: Cross-section of a silicon pn solar cell.



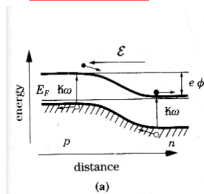
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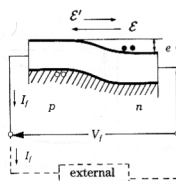
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photocells

in the dark
 $I = 0$
 $V = 0$

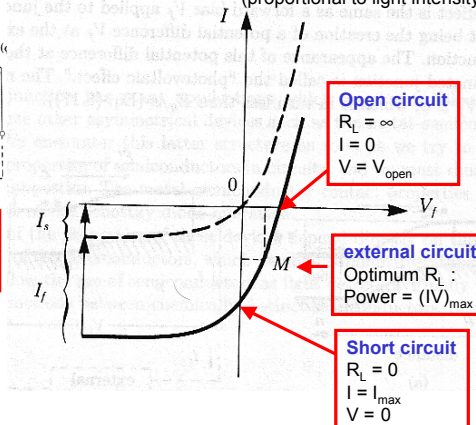


Illuminated:
 "forward" V
 "reverse" I



external circuit
 Optimum R_L :
 Power = $(IV)_{\max}$

--- Ideal diode I-V in the dark
 — Illuminated diode I-V:
 The "reverse" (generation)
 negative current I_L is added
 (proportional to light intensity)



Open circuit
 $R_L = \infty$
 $I = 0$
 $V = V_{\text{open}}$

external circuit
 Optimum R_L :
 Power = $(IV)_{\max}$

Short circuit
 $R_L = 0$
 $I = I_{\max}$
 $V = 0$

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monocrystalline silicon solar cells

Silicon pn solar cell

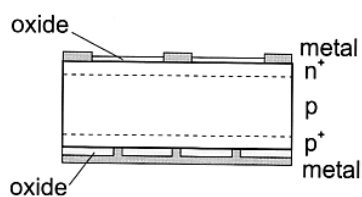
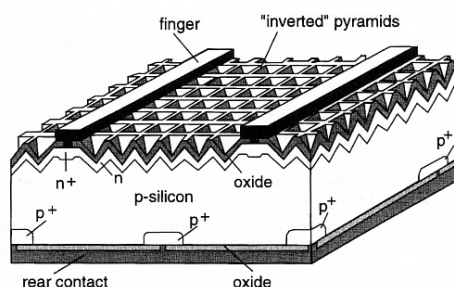


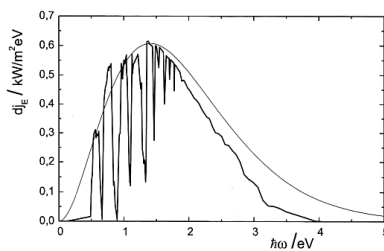
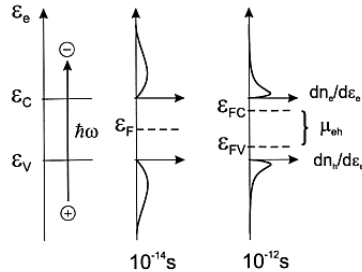
Figure 7.4: Cross-section of a silicon pn

e⁻ filter
absorber: photons → e⁻h⁺
h⁺ filter

**an experimental optimized
 version, to trap light and
 increase efficiency up to
 about 26%
 (commercially available:
 about 15% typical now)**



solar cell efficiency factors



Light trapping
Light absorption
Thermalization of e,h pairs
Chemical energy at open circuit
Electrical energy delivered at the maximum power point (...)

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solar cell efficiency factors

A challenging engineering problem: design a device that maximizes the overall efficiency for power output, minimizing the production costs

The product of all these efficiencies gives the overall efficiency

$$\eta = \underbrace{\frac{j_{E,abs}}{j_{E,in}}}_{\eta_{abs}} \underbrace{\frac{\langle \epsilon_c + \epsilon_h \rangle}{\langle \hbar\omega_{abs} \rangle}}_{\eta_{thermalization}} \underbrace{\frac{eV_{oc}}{\langle \epsilon_c + \epsilon_h \rangle}}_{\eta_{thermodynamic}} \underbrace{\frac{j_{mp}V_{mp}}{j_{sc}V_{oc}}}_{FF} = \frac{-j_{mp}V_{mp}}{j_{E,in}} \quad (7.26)$$

For silicon, and in particular, for the 20 μm thick cell with light trapping, whose absorptivity is shown in Figure 7.7, exposure to the AM1.5 spectrum gives the following values

$$\langle \hbar\omega_{abs} \rangle = 1.80 \text{ eV}$$

$$\langle \epsilon_c + \epsilon_h \rangle = \epsilon_G + 3kT = 1.2 \text{ eV}$$

$$j_{sc} = 413 \text{ A/m}^2 \quad j_{mp} = 401 \text{ A/m}^2$$

$$V_{oc} = 0.770 \text{ V} \quad V_{mp} = 0.702 \text{ V}$$

The efficiencies are therefore

$$\eta_{abs} = 0.74$$

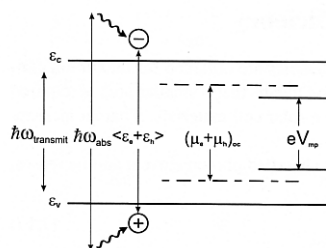
$$\eta_{thermalization} = 0.67$$

$$\eta_{thermodynamic} = 0.64$$

$$FF = 0.89$$

The overall efficiency is then $\eta = 0.74 \times 0.67 \times 0.64 \times 0.89 = 0.28$.

The efficiencies for thermalization and for the conversion of the energy of the electron-hole pairs into chemical energy are particularly small and thus in need of improvement.



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Lecture 35 - exercises

- **Exercise 1:** In (SZE 2.5.1), nonpenetrating illumination of a semiconductor bar was found to cause a steady state, excess-hole concentration of $\Delta p_n(x) = \Delta p_{n0} \exp(-x/L_p)$. Given low-level injection conditions, and noting that $p = p_0 + \Delta p_n$, we can say that $n \approx n_0$ and $p \approx p_0 + \Delta p_{n0} \exp(-x/L_p)$.
 - (a) Find the quasi-Fermi levels $F_N(x)$ and $F_P(x)$ as functions of x .
 - (b) Show that $F_P(x)$ is a linear function of x when $\Delta p_n(x) \gg p_0$.
 - (c) Sketch the energy band diagram under equilibrium (no illumination) and in illuminated steady-state conditions, assuming negligible electric field.
 - (d) Is there a hole current in the illuminated bar, under steady state conditions? Explain.
 - (e) Is there an electron current in the illuminated bar, under steady state conditions? Explain.