"*Complementi di Fisica*" *Lecture 27*

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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 Schrȍdinger 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**

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**

Currents and quasi-Fermi levels

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

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

\n"electron
\naffinity" χ \downarrow $\frac{1}{\text{effinity}^n} \chi$ $\frac{1}{\text{effensity}^n} \chi$ $\frac{1}{\text{effensity}^n} \chi$ $\frac{1}{\text{free}} \chi$

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

 $\neq 0$ $J_p \neq 0$

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

Non-uniform material under illumination

charge separation, in general

 $J_{x,n} = \mu_n n$ ∂ F_N $\frac{\partial^2 N}{\partial x}$ = + |q|D_n ∂*n* ∂*x* $+$ $\mu_n n$ $\frac{\partial E_{\text{vac}}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_C}{\partial x}$ $\sqrt{2}$ $\left(\frac{\partial E_{\text{vac}}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_C}{\partial x}\right)$ $J_{x,p} = \mu_p p$ ∂ F_p $\frac{\partial^2 P}{\partial x^2}$ = $-q \frac{q}{D_p}$ ∂*p* ∂*x* $+$ $\mu_p p$ $\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_{g}}{\partial x}$ $+ kT \frac{\partial \ln N_v}{\partial x}$ ∂*x* \int $\overline{\mathcal{K}}$ ' ()

diffusion 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** $\chi, E_{\varrho}, N_C, N_V$

Evac ^χ *EC FN EV* φ *FP* ∂*FN* ∂*x* ≠ 0 ∂*FP* ∂*x* ≠ 0

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

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

Non-uniform material under illumination

charge separation

 $J_{x,n} = \mu_n n$ ∂ F_N $\frac{\partial^2 N}{\partial x}$ = + |q|D_n ∂*n* ∂*x* $+$ $\mu_n n$ $\frac{\partial E_{\text{vac}}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_C}{\partial x}$ $\sqrt{2}$ $\left(\frac{\partial E_{\text{vac}}}{\partial x} - \frac{\partial \chi}{\partial x} - kT \frac{\partial \ln N_C}{\partial x}\right)$ $J_{x,p} = \mu_p p$ ∂ F_p $\frac{\partial^2 P}{\partial x^2}$ = $-q \frac{q}{D_p}$ ∂*p* ∂*x* $+$ $\mu_p p$ $\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_{g}}{\partial x}$ $+ kT \frac{\partial \ln N_v}{\partial x}$ ∂*x* \int $\overline{\mathcal{K}}$ ' () **diffusion 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** $\chi, E_{\varrho}, N_C, N_V$ $E_x = \frac{1}{10}$ *q* $rac{\partial E_C}{\partial x} = \frac{1}{|q|}$ $\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x}$ $\sqrt{}$ \backslash $\left(\frac{\partial E_{\text{vac}}}{\partial x} - \frac{\partial \chi}{\partial x}\right)$ (a) electric field for electrons $E_x = \frac{1}{1}$ *q* $rac{\partial E_V}{\partial x} = \frac{1}{|q|}$ $\frac{\partial E_{vac}}{\partial x} - \frac{\partial \chi}{\partial x} - \frac{\partial E_{g}}{\partial x}$ $\sqrt{}$ $\overline{\mathcal{K}}$ ' (\int el. field for holes **neglecting gradients** in N_c , N_V

Work function and junctions

• **Work function of a material**

"**energy required to remove the least tightly bound electrons**"

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

• **Electrostatic energy difference across a junction at equilibrium**

Junction between regions with different work functions: $\phi_{\scriptscriptstyle +}^{}, \phi_{\scriptscriptstyle -}^{}$ **built-in electric field** ⇒ **electrostatic potential energy difference** $\Delta \phi = \phi_{+} - \phi_{-} = |q| \int_{r}^{r} E_{x}$ *x*− *x*+ $\int_{x_+}^{\infty} E_x dx$

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

The difference in work functions implies a redistribution of charges and non-neutrality in the junction region

$$
\frac{\partial E_x}{\partial x} = \frac{|q|}{\varepsilon_s} \Big(p - n + N_{\scriptscriptstyle D}^+ - N_{\scriptscriptstyle A}^- \Big)
$$

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**

pn junction at equilibrium in the dark

Electrostatics

pn junction at equilibrium

 net currents are zero:

$$
J_n = J_{n, drift} + J_{n, diffusion} = 0
$$

$$
J_p = J_{p, drift} + J_{p, diffusion} = 0
$$

 total electrochemical potential

built-in electrical potential bias

$$
qV_{bi} = \left[E_F - E_i\right]_n - \left[E_F - E_i\right]_p =
$$

$$
= kT \ln\left(\frac{n_n p_p}{n_i^2}\right)
$$

example:
\n
$$
V_{bi} \approx \frac{kT}{q} \ln \left(\frac{N_D N_A}{n_i^2} \right) = 0.718 \text{ volts}
$$
\n
$$
N_A = 10^{17} \text{ cm}^{-3}, \quad N_D = 10^{15} \text{ cm}^{-3}
$$
\n
$$
n_i \approx 10^{10} \text{ cm}^{-3}
$$

Electrostatics: approximations

$$
\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_S} \qquad \text{Gauss-Poisson}
$$
\n
$$
\frac{\partial E_x}{\partial x} = \frac{q}{\varepsilon_S} \left(p - n + N_D^+ - N_A^- \right)
$$
\n
$$
\frac{\partial^2 V}{\partial x^2} = -\frac{q}{\varepsilon_S} \left(p - n + N_D^+ - N_A^- \right)
$$

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 $-x_p \le x \le 0$: $N_A \gg n_p, p_p \implies \rho = -qN_A^- \implies$ $rac{\partial E_x}{\partial x} = \frac{-qN_A}{\varepsilon_S}$ $0 \le x \le x_n$: $N_D \gg n_n, p_n \Rightarrow \rho = qN_D^+ \Rightarrow$ $rac{\partial E_x}{\partial x} = \frac{qN_D}{\varepsilon_S}$ $x < -x_p$, $x > x_n$: $\rho \approx 0$, $E_x \approx 0$

Depletion approximation - 2

Total depletion width: from

$$
V(0) = \left[\frac{qN_A}{2\varepsilon_S}\right] x_p^2 = \left[\frac{-qN_D}{2\varepsilon_S}\right] x_n^2 + V_{bi}
$$

$$
x_p = \frac{N_D}{N_A} x_n
$$

Solving for *x_n*, *x*_p $w = x_n - (-x_p) = x_n + x_p = 0$ $=\left(\frac{2\varepsilon_{\rm S}V_{bi}}{2\varepsilon_{\rm S}V_{bi}}\right)$ *q* $(N_A + N_D)$ $N_A N_D$ \lceil L $\left[\frac{2 \varepsilon_s V_{bi}}{g} \frac{(N_A + N_D)}{N_N} \right]$ & **|** $1/2$

Numerical example: $kT = 0.026$ eV, $N_A = 10^{16}$ cm⁻³, $N_D = 10^{15}$ cm⁻³, $n_i = 10^{10} \text{ cm}^{-3}, \quad V_{bi} = \frac{kT}{a}$ *q* ln $10^{16}10^{15}$ $\left(10^{15}\right)^{\!2}$ \lceil # $\overline{}$ I $\mathcal I$ & ' ' $= 0.66$ volt

 $x_n = 0.884 \mu \text{m}$, $x_p = 0.088 \mu \text{m}$, $w = 0.972 \mu \text{m}$

$$
C \text{large density}
$$
\n
$$
-x_p
$$
\n
$$
x_n
$$
\n
$$
x_n
$$
\n
$$
x_p
$$
\n
$$
x_n
$$
\n
$$
x_n
$$

 (b)

pn junction biased in the dark

Electrostatics

External bias, positive on the p side

 $(0 < V_A < V_{\text{bi}})$: potential difference decreases!

 $V(x) = \frac{qN_A}{2}$ $2\varepsilon_{\text{\tiny S}}$ $\left(x_{p}+x\right) ^{2}$ The p-depletion region $E_x(x) = \frac{-qN_A}{2}$ $\frac{{\mathcal E}_S}{\delta}$ $(x_p + x)$ $0 \le x \le x_n$ $x_n = \left(\frac{2\varepsilon_s}{q} (V_{bi} - V_A) \frac{N_A}{N_D (N_A + N_D)} \right)$ \lceil $\mathsf L$ $\left[\frac{2\varepsilon_{\rm s}}{a}(V_{bi}-V_{A})\frac{N_{A}}{N_{A}N_{A}+N_{A}}\right]$ \perp $\overline{}$ $V(x) = (V_{bi} - V_{A}) - \frac{qN_{D}}{2g}$ $2\varepsilon_{\text{\tiny S}}$ $(x_n - x)^2$ **shrinks**

 $E_x(x) = \frac{-qN_D}{2}$ $\bm{\mathcal{E}}_{\mathcal{S}}$ $(x_n - x)$ **The n-depletion region shrinks**

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pn junction biased in the dark

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*

Reverse bias $(V_A < 0)$

Minority **carriers generated close to the depletion region** *drift* **into the opposite bulk where they become** *majority* **and** *recombine slowly*

The total current is limited by the constant thermal generation rate

pn junction biased in the dark

Current-voltage (I-V) quantitative

• **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** ⇒ **predominantly** *diffusion and recombination*

- **Method:**
	- **Solve the minority carrier continuity equations in the bulk regions for** Δ*np* **and** Δ*pn* **(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 $-\dot{x}_p$ respectively
	- **The total current can be estimated as the sum of the currents at the edges of the depletion region** $J = J_p(x_n) + J_p(-x_p)$

Results: concentrations

Orders of magnitude

Forward bias Access Reverse bias

Orders of magnitude

Diffusion of minority carriers in the bulk (several L_p, L_n) ≈ 100 µm Built-in electric field ≈ **106 V/m Depleted region width (depends on doping and bias)** $≈ 1 \mu m$

Taking into account mobility and diffusivity for electrons:

Corresponding drift velocity for electrons ≈ **105 m/s**

Depleted region crossing time (drift) ≈ **10-11 s Depleted region crossing time (diffusion)** ≈ **10-9 s Typical carrier lifetime** ≈ **10-6 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)

Forward bias

0

d_n

0

(n)

 $\frac{1}{2}$ –e(V_D–IUI)_{En}

لاء-

x

 n_{n}

n,

Pn

x

EĄ

a

b

log n,p

Po

n,

 $n_{\rm o}$

 E_C^p

(P)

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

-d.

0

 d_{n}

X

X

pn junction illuminated

Illuminated pn junction (open circuit)

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

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

photocells

monocrystalline silicon solar cells

Silicon pn solar cell

Figure 7.4: Cross-section of a silicon pn

absorber: photons → **e-h+ h+ filter e- 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 (…)

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

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

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

 $\langle \hbar \omega_{\rm abs} \rangle = 1.80 \,\rm eV$ $\langle \varepsilon_{\rm e} + \varepsilon_{\rm h} \rangle = \varepsilon_{\rm G} + 3kT = 1.2 \,\text{eV}$ $j_{\rm sc} = 413 \,\mathrm{A/m^2}$ $j_{\rm mp} = 401 \,\mathrm{A/m^2}$ $V_{\text{oc}} = 0.770 \text{ V}$ $V_{\text{mp}} = 0.702 \text{ V}$.

The efficiencies are therefore

 $\eta_{\rm abs} = 0.74$

 η thermalization = 0.67

 $\eta_{\text{thermodynamic}} = 0.64$

 $FF = 0.89$.

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 electronhole pairs into chemical energy are particularly small and thus in need of improvement.

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.**