Series - Electronic and optical semiconductor devices

Series 5 Density of states, ionization and activation energies, statistics of donor levels

Exercise 1- Two-dimensional and one-dimensional density of states (DOS)

1- We consider an isotropic band structure so that $E(k) = E_1 + \frac{\hbar^2 k^2}{2m^*}$ (1.1)

The surface occupied by each k value is $\frac{4\pi^2}{S}$ where $S = N^2 a^2$ is the surface associated with the two-dimensional layer.

The DOS being a constant in k-space, the number of states which are in a disk of radius k is given by:

$$N_{2D} = \underbrace{\pi k^2}_{S_{disk}} \times \underbrace{\frac{S}{4\pi^2}}_{\text{surface density}} \times \underbrace{2}_{\text{spin degeneracy}} \quad (1.2)$$

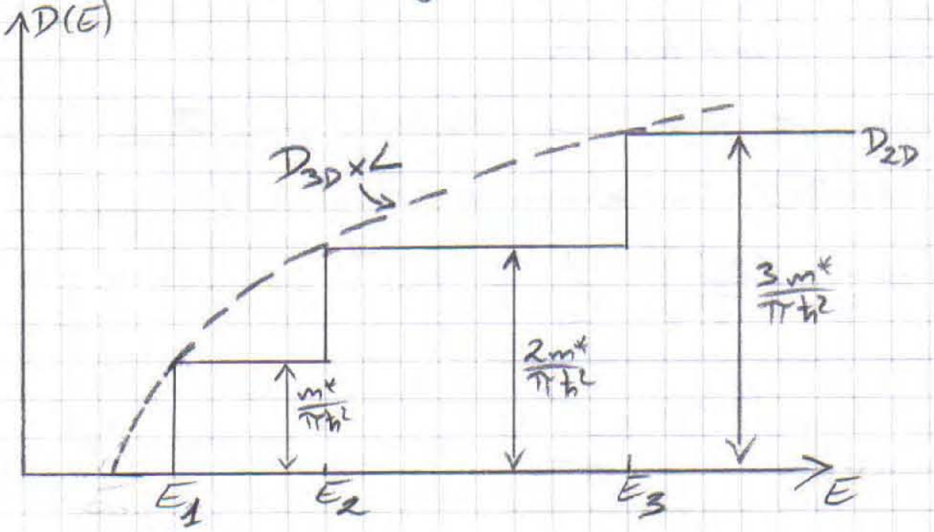
From (1.2) we get: $k^2 = \frac{2m^*}{\hbar^2}(E - E_1)$ (1.3)

As a result $N_{2D} = \frac{m^*}{\pi\hbar^2} S (E - E_1)$ and the DOS per energy and surface unit will express as:

$$\boxed{D_{2D}(E) = \frac{1}{S}\frac{dN_{2D}}{dE} = \frac{m^*}{\pi\hbar^2} H(E - E_1)} \quad (1.4)$$

where H is the Heaviside function.

2-



2D case: staircase density of states

3D case: DOS $\propto E^{1/2}$

Comparison between the 2D-DOS of an infinitely deep potential well and the 3D-DOS of a bulk layer whose thickness is identical to that of the well (thickness L).

Note here that the energy spacing between the quantized levels increases when moving toward excited states as expected from the infinitely deep square potential well problem. Indeed, in this latter case

$V(x) = 0$ for $0 \leqslant x \leqslant a$

$V(x) = +\infty$ for $x \in]-\infty, 0[\cup]a, +\infty[$

The dispersion relation is such that $k = \left(\frac{2m^* E}{\hbar^2}\right)^{1/2}$ and the wave function is equal to $\varphi(x) = 0$ for x values $\notin [0,a]$ and $\varphi(x) = A e^{ikx} + A' e^{-ikx}$ for $x \in [0,a]$. In addition, $\varphi(0) = 0$ (as $\varphi(x)$ is a continuous function in $x = 0$) so that $A' = -A$, hence $\varphi(x) = 2iA \sin kx$.

For continuity reasons in $x = a$, $\varphi(a) = 0$ which implies that $k = \frac{n\pi}{a}$ with $n \in \mathbb{N}^*$. Moreover, $\varphi(x)$ is a normalized function so that

$$\boxed{\varphi_n(x) = \left(\frac{2}{a}\right)^{1/2} \sin\left(\frac{n\pi x}{a}\right)} \quad \text{and} \quad \boxed{E_n = \frac{n^2\pi^2\hbar^2}{2m^* a^2}}$$

The energetic dependence is proportional to n^2.

3- By analogy with the 2D case, the "length" occupied by each value of k is equal to $\frac{2\pi}{L}$ where $L = Na$. The number of states which are lying on a $2k$ length portion will express as:

$$N_{1D} = 2k \times \underbrace{\frac{L}{2\pi}}_{\text{linear density}} \times \underbrace{2}_{\text{spin degeneracy}} = \frac{2kL}{\pi}$$

As we still consider an isotropic band structure $k^2 = \frac{2m^*}{\hbar^2}(E - E_0)$ which lead to the 1D-DOS per energy and length unit:

$$D_{1D}(E) = \frac{1}{L}\frac{dN_{1D}}{dE} = \frac{2}{\pi} \times \left(\frac{2m^*}{\hbar^2}\right)^{1/2} \times \frac{1}{2}(E - E_0)^{-1/2}$$

i.e. $$\boxed{D_{1D}(E) = \left(\frac{8m^*}{h^2}\right)^{1/2} (E - E_0)^{-1/2}}$$

Contrary to the 2D case, $D_{1D}(E)$ is not a constant.

Exercise 2 - Ionization energies

1- The situation is identical to that of the hydrogen atom except the fact that acceptors (or donors) lie in a layer characterized by a large dielectric constant. The ionization energy will express as $\boxed{E_i = \frac{\hbar^2}{2ma_0^2}\,\frac{m_r^*}{\varepsilon_r^2}\,\frac{1}{n^2}}$ (2.1)

which resumes to $E_i = 13.6\,\frac{m_r^*}{\varepsilon_r^2}\,\frac{1}{n^2}$ if we want to get energies in eV.
$m_r^* = \frac{m}{m_0}$ is the reduced mass of the carrier under consideration and $\varepsilon_r = \varepsilon/\varepsilon_0$ is the relative dielectric constant of the semiconductor and n is the principal quantum number of the orbital of interest (a_0 is the hydrogen Bohr radius, $a_0 = \frac{\hbar}{me^2} = 0.53\,\text{Å}$).
The ionization energy is the energy difference between the $n=1$ energy state ($n=1$, energetic level of the acceptor) and the top of the valence band ($n=+\infty$). We will thus have $E_{ionization} = 13600 \times \frac{0.53}{(11.9)^2} \times \frac{1}{(1)^2} \sim 50.9\,\text{meV}$

The various peaks seen in figure 1 correspond to transitions between the level $n=1$ and levels $n=2$ to 4.

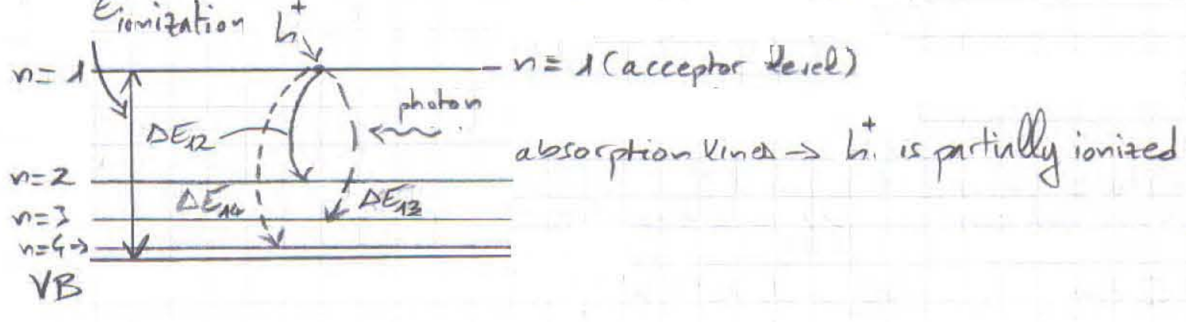
$$\Delta E_{12} = E_{ionization} \times \left(1 - \frac{1}{(2)^2}\right) = \frac{3}{4} E_{ionization} = 38.2\,\text{meV}$$

$$\Delta E_{13} = E_{ionization} \times \left(1 - \frac{1}{(3)^2}\right) = \frac{8}{9} E_{ionization} = 45.2\,\text{meV}$$

$$\Delta E_{14} = E_{ionization} \times \left(1 - \frac{1}{(4)^2}\right) = \frac{15}{16} E_{ionization} = 47.7\,\text{meV}$$

Graphically, we deduce the following energies:
33.8 meV, 39 meV, 42.9 meV and 51.9 meV

We see here the limits of the hydrogen-like model as the effective masses change considerably in the vicinity of impurities



Such a measurement can only be carried out at low temperature, i.e. when donors and acceptors are neutral. It will also limit the impact of phonons. The decrease of the absorption coefficient for energies superior to the broad peak at ~ 51 meV results from the strong decrease of the transition probability away from the top of the valence band. The limited extent of the acceptor in momentum space is then responsible for the declining absorption at photon energies greater than the binding energy of the acceptor state.

Exercise 3 - Activation energies

Data are plotted on a semilogarithmic scale.

↳ ① linear slopes ⇒ exponential dependence

② $\rho(\Omega\,cm)$ vs. $1/T$

③ when T increases, ρ decreases

$$①+②+③ \Rightarrow \rho \propto \exp\left(\frac{E}{k_B T}\right)$$

Low temperature range (curve A)

$\rho_1 = 0.05\,\Omega\,cm \qquad 1/T_1 = 3\times10^{-3}\,K^{-1}$

$\rho_2 = 8\,\Omega\,cm \qquad 1/T_2 = 1.2\times10^{-2}\,K^{-1}$

$$E_{LT} = k_B\left(\frac{1}{T_1}-\frac{1}{T_2}\right)^{-1}\ln\left(\frac{\rho_1}{\rho_2}\right) \sim 7.78\times10^{-21}\,J \text{ i.e. } \sim 48.6\,meV$$

This value has to be compared to the ionization energy of phosphorus atoms in silicon (donor state) ~ 45 meV given in the lecture (idem in the article by G.L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949)).

High temperature range (curve A)

$\rho_3 = 2.1\times10^{-3}\,\Omega\,cm \qquad 1/T_3 = 5\times10^{-4}\,K^{-1}$

$\rho_4 = 0.07\,\Omega\,cm \qquad 1/T_4 = 1\times10^{-3}\,K^{-1}$

$E_{HT} \sim 0.604\,eV$, this value has to be compared to the band gap of Si ($E_g(Si) \sim 1.12$ eV at 300K). It is thus seen that at "high" temperature the transport properties (electrical properties to be more precised) are governed by the intrinsic density of free carriers as $\rho \propto \exp\left(\frac{E_g}{2k_BT}\right)$ and $n_c = p_v = n_i = (N_c(T)N_v(T))^{1/2}\exp\left(-\frac{E_g}{2k_BT}\right)$

Exercise 4 - Generalization of the statistics of donor levels

1- First, we can establish the relationship giving the number density of electrons n_d bound to donor sites: $n_d = N_d \langle n \rangle$ where $\langle n \rangle$ corresponds to the mean number of electrons in the levels at thermal equilibrium.

The donor level can be occupied in the following way:

(a) empty level, $N_j = 0$, $E_j = 0$, $g_j^{-1} = 1$ ↳ 1 configuration is associated with this level!

(b) singly occupied level, $N_j = 1$, $E_j = \varepsilon_d$, $g_j^{-1} = 2$ because the donor level can be occupied by an e^- of spin ↑ or ↓

(c) doubly occupied level, $N_j = 2$, $E_j = 2\varepsilon_d + \Delta$, $g_j^{-1} = 1$

As a result we get: $\langle n \rangle = \dfrac{2e^{-\beta(\varepsilon_d-\mu)} + 2e^{-\beta(2\varepsilon_d+\Delta-2\mu)}}{1+2e^{-\beta(\varepsilon_d-\mu)} + e^{-\beta(2\varepsilon_d+\Delta-2\mu)}}$

i.e. $\langle n \rangle = \dfrac{\cancel{2e^{-\beta(\varepsilon_d-\mu)}}}{\cancel{2e^{-\beta(\varepsilon_d-\mu)}}} \; \dfrac{1+e^{-\beta(\varepsilon_d+\Delta-\mu)}}{\frac{1}{2}e^{\beta(\varepsilon_d-\mu)} + 1 + \frac{1}{2}e^{-\beta(\varepsilon_d+\Delta-\mu)}}$

and finally

$$\boxed{n_d = \frac{N_d\left(1+e^{-\beta(\varepsilon_d+\Delta-\mu)}\right)}{\frac{1}{2}e^{\beta(\varepsilon_d-\mu)} + 1 + \frac{1}{2}e^{-\beta(\varepsilon_d+\Delta-\mu)}}} \qquad (4.2)$$

2- As $\Delta \to +\infty$, $e^{-\beta(\varepsilon_d+\Delta-\mu)} \to 0$ so that eq. (4.2) is reduced to

$$\boxed{n_d = \frac{N_d}{\frac{1}{2}e^{\beta(\varepsilon_d-\mu)}+1}} \qquad (4.3)$$

3- As $\Delta \to 0$, (4.2) can be simplified in the following way:

$$\boxed{n_d = \frac{1+e^{-\beta(\varepsilon_d-\mu)}}{\frac{1}{2}e^{\beta(\varepsilon_d-\mu)} + 1 + \frac{1}{2}e^{-\beta(\varepsilon_d-\mu)}}\, N_d}$$

By putting $x = \beta(\varepsilon_d - \mu)$, we get $n_d = 2N_d \dfrac{1+e^{-x}}{2+e^{x}+e^{-x}}$

As $e^{x}+e^{-x}+2 = (e^{x}+1)(e^{-x}+1)$, we then obtain

$$n_d = 2\,\frac{\cancel{(1+e^{-x})}}{\cancel{(1+e^{-x})}} \times \frac{1}{1+e^{x}}\, N_d$$

i.e. $n_d = 2N_d \underbrace{[1+e^{\beta(\varepsilon_d-\mu)}]^{-1}}$ Fermi-Dirac distribution

and finally $\boxed{n_d = \underset{\smile}{2} N_d f_{FD}(\varepsilon_d)}$

factor indicating that the donor levels can be occupied by 2 e^- of opposite spin.

4- We still have the relationship $n_d = N_d \langle n \rangle$. However, each donor level will introduce many bound electronic orbitals of energy ε_i. As a consequence in (4.3) ε_d must be replaced with the ε_i. If we consider a system where donor levels possess two orbitals, we get from (4.3) (in fact from (4.1)) $n_d = N_d \left[\dfrac{2e^{-\beta(\varepsilon_1-\mu)} + 2e^{-\beta(\varepsilon_2-\mu)}}{1+2e^{-\beta(\varepsilon_1-\mu)}+2e^{-\beta(\varepsilon_2-\mu)}} \right]$

$$\text{i.e. } n_d = 2N_d \frac{\sum_{i=1}^{2} e^{-\beta(\varepsilon_i-\mu)}}{2\sum_{i=1}^{2} e^{-\beta(\varepsilon_i-\mu)}} \times \frac{1}{\frac{1}{2}\left(\sum_{i=1}^{2} e^{-\beta(\varepsilon_i-\mu)}\right)^{-1}+1}$$

and finally $$n_d = N_d \frac{1}{\frac{1}{2}\left(\sum_{i=1}^{2} e^{-\beta(\varepsilon_i-\mu)}\right)^{-1}+1}$$

Such an equation can be extended to a larger number of orbitals which finally leads to (4.4).