07.02.12

Surfaces and interfaces [Heinzel ch. 3]

Infinite crystal $\Rightarrow \psi_k = u_k e^{i\vec{k}\cdot\vec{r}}$ (Bloch functions)

All allowed states have <u>real</u> $\vec{k}$

$\Rightarrow |\psi_k|^2 = |u_k|^2$ is periodic in Bravais lattice

$\Rightarrow$ <u>extended</u> (delocalized) state

Surface(s) / interface(s) $\Rightarrow$ translational invariance broken

$\Rightarrow$ <u>localized</u> states possible

To be verified with simple model:

1D, N atoms, $x_j = j \cdot a$ $(j = 1, 2, \cdots, N)$, 1 s-state pr atom, energy E_0, nearest neighbour tight binding approx.

$$H_j |j\rangle = E_0 |j\rangle$$

$$H_j = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V_a(x - x_j) = T + V_j$$

$|j\rangle$ = s-state on atom j $\quad (\langle l | j\rangle = \delta_{lj})$

$$H|\psi\rangle = E|\psi\rangle, \quad \text{LCAO: } |\psi\rangle = \sum_l c_l |l\rangle \qquad \left(\sum_l = \sum_{l=1}^{N}\right)$$

$$H = T + \sum_j V_j = H_j + \sum_{m\neq j} V_m = H_j + (H - H_j)$$

Multiply with $\langle j|$:

$$\langle j|E|\psi\rangle = E c_j$$

$$\langle j|H|\psi\rangle = \underbrace{\langle j|H_j}_{\langle j|E_0}|\psi\rangle + \langle j| \sum_{m\neq j} V_m \sum_l c_l |l\rangle$$

$$= E_0 c_j + \sum_l \sum_{m\neq j} c_l \langle j|V_m|l\rangle$$

3 possibilities for $\sum_{m\neq j} \langle j|V_m|l\rangle$:

1) $l = j$, $j \neq 1, N$ (<u>not</u> at surface):

$$\sum_{m\neq j} \langle j|V_m|j\rangle = -\alpha < 0 \qquad (\underline{2}\ m\text{-values are n.n. to } j)$$

2) $\ell = j$, $j = 1$ or N (at surface):

$$\sum_{m \neq j} \langle j | V_m | j \rangle = -\alpha' < 0 \qquad (1 \text{ m-value is n.n. to } j \Rightarrow \alpha > \alpha')$$

3) $\ell = j \pm 1$:

$$\sum_{m \neq j} \langle j | V_m | j \pm 1 \rangle = -\gamma < 0$$

Signs: $V_m < 0$ and s-states $\Rightarrow$ positive α, α', γ

Notation: $\varepsilon = E - E_0 + \alpha$, $\varepsilon_0 = \alpha - \alpha' = \varepsilon - (E - E_0 + \alpha') > 0$

$\Rightarrow$ N linear eqns. for $\{c_j\}$:

① $(\varepsilon - \varepsilon_0) c_1 + \gamma c_2 = 0$

② $\gamma c_{n-1} + \varepsilon c_n + \gamma c_{n+1} = 0 \qquad (2 \leq n \leq N-1)$

③ $\gamma c_{N-1} + (\varepsilon - \varepsilon_0) c_N = 0$

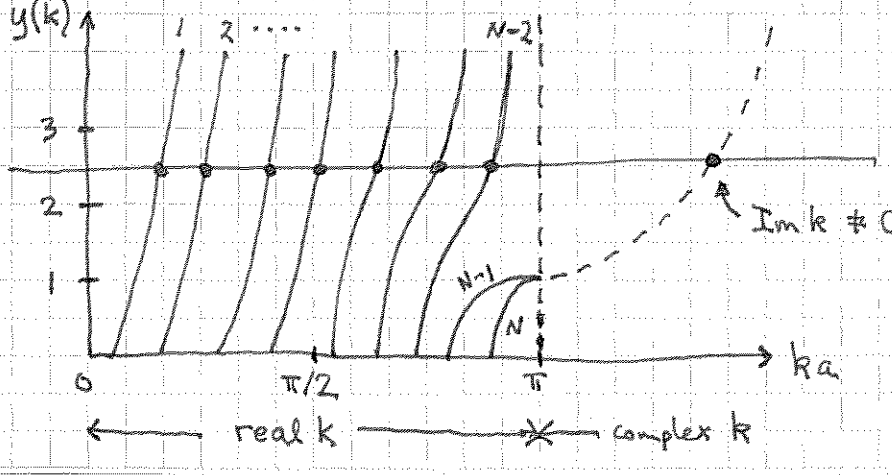
Try $c_n = A e^{ikna} + B e^{-ikna}$ in ② $\Rightarrow \varepsilon(k) = -2\gamma \cos ka$

① and ③ $\Rightarrow$

$$\begin{bmatrix} (\varepsilon-\varepsilon_0)e^{ika} + \gamma e^{2ika}, & (\varepsilon-\varepsilon_0)e^{-ika} + \gamma e^{-2ika} \\ (\varepsilon-\varepsilon_0)e^{ikNa} + \gamma e^{ik(N-1)a}, & (\varepsilon-\varepsilon_0)e^{-ikNa} + \gamma e^{-ik(N-1)a} \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = 0$$

$\det[\ldots,\ldots] = 0 \Rightarrow$ possible k-values given by $y(k) = \varepsilon_0/\gamma > 0$,

with $y(k) = \dfrac{-\sin Nka \pm \sin ka}{\sin (N-1)ka}$; N atomic states $\Rightarrow$ N allowed k-values



If $\varepsilon_0/\gamma > 1 + \frac{2}{N-1} \overset{N\gg 1}{\approx} 1$, we have only $N-2$ states with <u>real</u> k (delocalized states)

$\Rightarrow$ 2 states with <u>complex</u> k: $ka = \pi + i\varkappa a$

$\Rightarrow \sin Nka = (-1)^N \left(-\frac{1}{i}\right) \sinh N\varkappa a \overset{N\gg 1}{\approx} (-1)^N \left(-\frac{1}{i}\right) \frac{1}{2} e^{N\varkappa a}$

$\sin(N-1)ka \approx (-1)^{N-1} \left(-\frac{1}{i}\right) \frac{1}{2} e^{(N-1)\varkappa a}$

$\sin ka = \frac{1}{i} \sinh \varkappa a = \frac{1}{2i}\left(e^{\varkappa a} - e^{-\varkappa a}\right)$

$\cos ka = -\cosh \varkappa a = -\frac{1}{2}\left(e^{\varkappa a} + e^{-\varkappa a}\right) = -\frac{\varepsilon}{2\gamma}$

$\Rightarrow y \approx \frac{e^{N\varkappa a}}{e^{(N-1)\varkappa a}} = e^{\varkappa a} = \varepsilon_0/\gamma$

① $\Rightarrow c_2 = -\frac{\varepsilon-\varepsilon_0}{\gamma} c_1 = -e^{-\varkappa a} c_1$

② $\Rightarrow c_3 = -\frac{\varepsilon}{\gamma} c_2 - c_1 = e^{-2\varkappa a} c_1$

$\vdots$

③ $\Rightarrow c_{N-1} = -\frac{\varepsilon-\varepsilon_0}{\gamma} c_N = -e^{-\varkappa a} c_N$

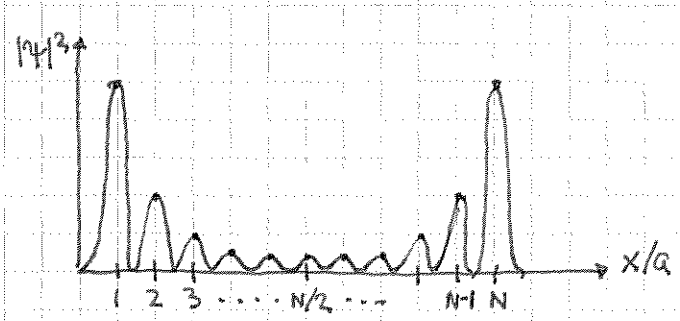
② $\Rightarrow c_{N-2} = \ldots = e^{-2\varkappa a} c_N$

$\vdots$

By symmetry: $|c_N| = |c_1|$

$\Rightarrow |c_1| > |c_2| > \ldots > |c_{N/2}| < \ldots < |c_{N-1}| < |c_N|$

$\Rightarrow |\psi(1)|^2 > |\psi(2)|^2 > \ldots > |\psi(\tfrac{N}{2})|^2 < \ldots < |\psi(N-1)|^2 < |\psi(N)|^2$

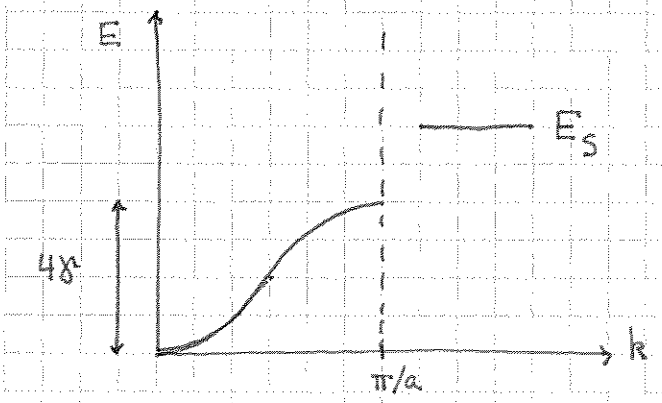


State $\psi(x)$ with complex k is <u>localized</u> at the surface; ψ is a <u>surface state</u>

Energies:

real k : $E(k) = E_0 - \alpha - 2\beta \cos ka$

complex $k = \pi/a + i\varkappa$: $E(\varkappa) = E_0 - \alpha + 2\beta \cosh \varkappa a = E_s$



$\cosh \varkappa a > 1 \Rightarrow E_s > E(k)$

$\Rightarrow$ energy of surface state is outside the band of delocalized states

Surfaces in 3D crystals

Bulk (3D) $\xrightarrow{\text{cut bonds}}$ Surface (2D)

$\Rightarrow$ modified geometry and electronic structure

- "Dangling bonds" $\Rightarrow$ Surface reconstruction

  Example: 7×7 reconstr. on Si (111) surface

  G. Binnig et al, PRL 50, 120 (1983)

  Scanning Tunneling Microscopy (STM) (Nobel prize 1986)

- model 1D crystal $\Rightarrow$ 0D surface states

  real 3D crystal $\Rightarrow$ 2D surface bands

Typical numbers?

Density of atoms on surface:

$n_s = 1/A_{atom} \sim 1/a^2 \sim 1/(3\text{-}5\,\text{Å})^2 \sim 5 \cdot 10^{18}\ m^{-2}$

Surface DOS pr unit area:

$$\frac{D_2}{A} \overset{(Ex.1)}{=} \frac{g \cdot m^*}{2\pi\hbar^2} \sim \frac{2 \cdot 10^{-31}}{2\pi \cdot 10^{-68}}\ J^{-1} m^{-2} \sim 5 \cdot 10^{17}\ eV^{-1} m^{-2}$$

$\Rightarrow$ Nr. of surface states pr unit area:

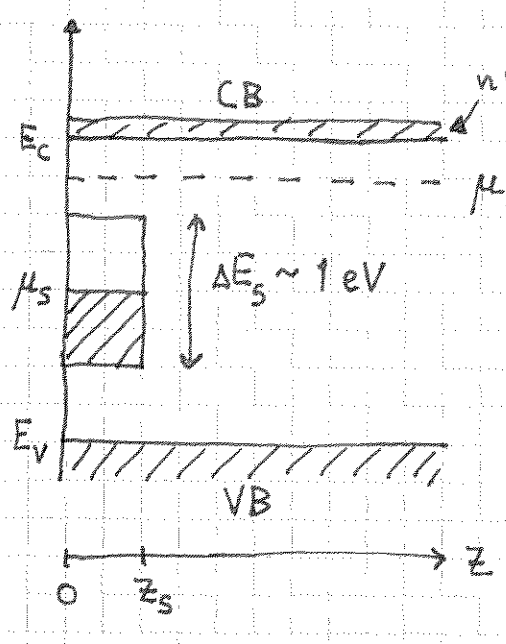
$$\frac{N_s}{A} = \frac{D_2 \cdot \Delta E_s}{A} \sim \left[5 \cdot 10^{17}\ eV^{-1} m^{-2}\right] \cdot \Delta E_s$$

Width of surface band: $\Delta E_s \sim 1$ eV

Semi-quantitative example:

n-doped SC, N_D donors pr unit volume, donor level E_D

Before equilibration between bulk (B) and surface (S):



- $\mu_B \approx E_D \neq \mu_S$ ("fairly low T")
- surface in $z = 0$
- surface states localized within $(0, z_S)$, i.e., $\psi \sim e^{-\beta z z}$ with $\beta z \sim \frac{1}{z_S}$

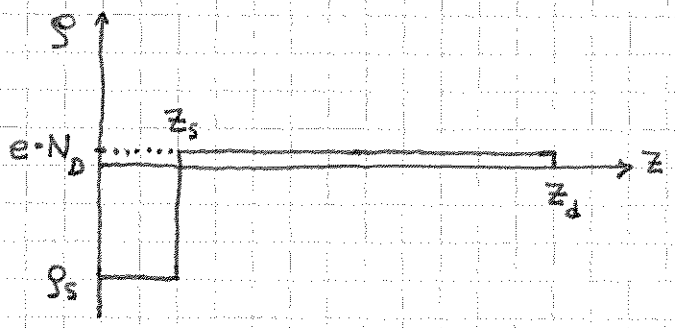
Equilibration: electrons in CB lower their energy by entering surface states at energy μ_S

$\Rightarrow$ negative surface layer $(0 < z < z_S)$ and positive depletion layer $(z_S < z < z_d)$ ("surface dipole")

$\Rightarrow$ electric field $\vec{E}(z)$ and built-in potential $V(z)$

$\Rightarrow$ energy band bending until $\mu_S = \mu_B$ (= equilibrium condition)

Simple model: (ρ = net charge pr unit volume)



Overall charge neutrality

$$\Rightarrow \int_0^\infty \rho(z)\,dz = 0$$

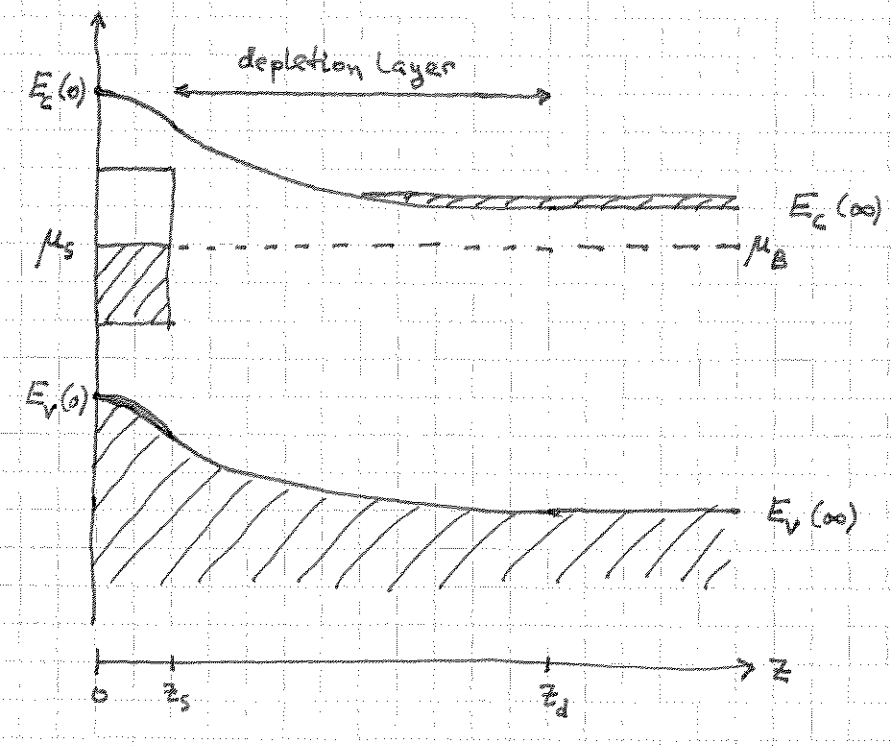
$$\Rightarrow \rho_s = -eN_D\,\frac{z_d - z_s}{z_s}$$

Use Gauss' law, $\nabla\cdot\vec{E} = \rho/\varepsilon$, and Poisson's eqn., $\nabla^2 V = -\rho/\varepsilon$

$$\Rightarrow V(z) = \begin{cases} -\dfrac{eN_D}{2\varepsilon}(z - z_d)^2 & ;\quad z_s < z < z_d \\ -\dfrac{eN_D}{2\varepsilon}\dfrac{z_d - z_s}{z_s}(z_d z_s - z^2) & ;\quad 0 < z < z_s \end{cases}$$

(choosing $V(z_d) = 0$, i.e., $V = 0$ in the bulk region)

$\Rightarrow$ Equilibrium band diagram:



Typical numbers:

$\varepsilon \sim 12\varepsilon_0$, $N_D \sim 10^{24}\ m^{-3}$, $V(0) \sim -E_g/2e \sim -0.7$ V

$\Rightarrow z_d \approx \frac{1}{e}\sqrt{\frac{\varepsilon E_g}{N_D}} \sim 30$ nm $\gg z_s \sim$ 2 or 3 atomic layers ~ 1 nm

Surface charge density: (charge pr unit area)

$\sigma_s \approx \rho_s \cdot z_s = -eN_D(z_d - z_s) \approx -eN_D z_d$

which corresponds to extra carrier density at surface: (carriers pr unit area)

$N_D \cdot z_d \sim 10^{24} \cdot 30 \cdot 10^{-9}\ m^{-3} \cdot m = 3 \cdot 10^{16}\ m^{-2}$

(upper limit, since $n < N_D$)

Big or small number? Compare with nr of surface states pr unit area: (p.31)

$\frac{N_s}{A} = \frac{D_2 \cdot \Delta E_s}{A} \sim 5 \cdot 10^{17}\ m^{-2} \gg N_D \cdot z_d$

$\Rightarrow \mu_s$ is <u>not</u> much affected by charge transfer, band bending

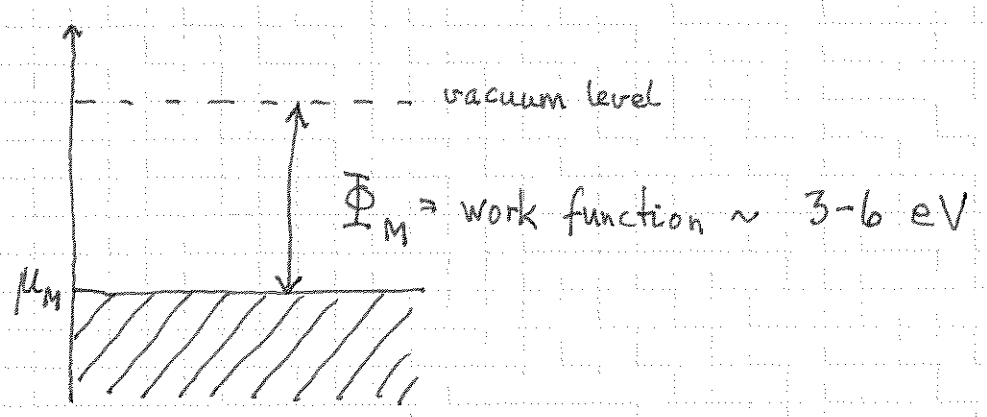
$\Rightarrow$ <u>pinning</u> of Fermi level μ to value in intrinsic SC, μ_s

Semiconductor - Metal interfaces (Qualitatively only)

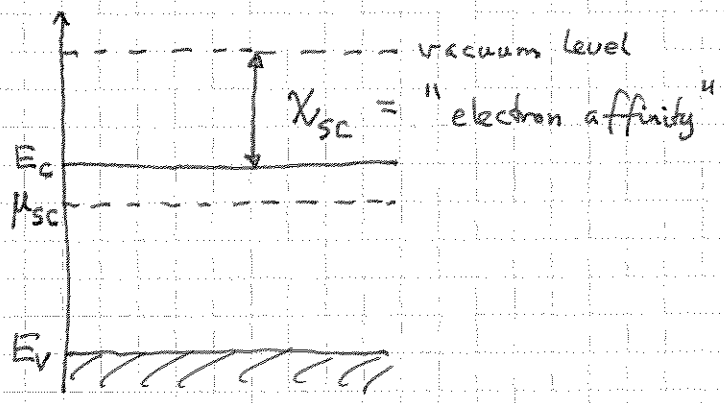
Device is SC, connecting wires are M (= metal)

$\Rightarrow$ cannot avoid SC - M interfaces

Metal:



Semiconductor (n-doped):



Make M - nSC interface

⇒ electron transfer from CB in nSC to M
(⇒ reduction in total energy)

⇒ dipole layer at interface

⇒ band bending until $\mu_M = \mu_{SC} = \mu$ (equilibrium)

End 07.02.12