Class 08
Surface and Interfaces

25.03.2025

Gott schuf das Volumen, der Teufel die Oberfläche.
God created the bulk; surfaces were made by the devil.

attributed to W. Pauli

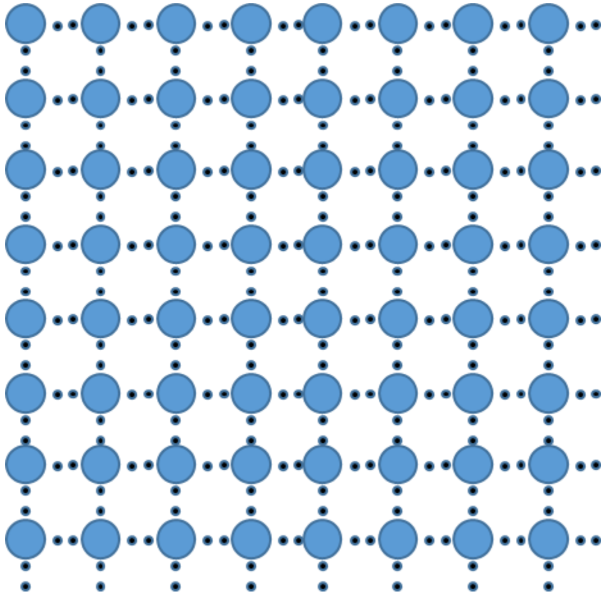
- ☐ Atomic description of surface
    - Reconstruction, oxidation, adatoms

- ☐ Electronic description of surface
    - Ohmic and Schottky contact
    - Fermi Energy pinning

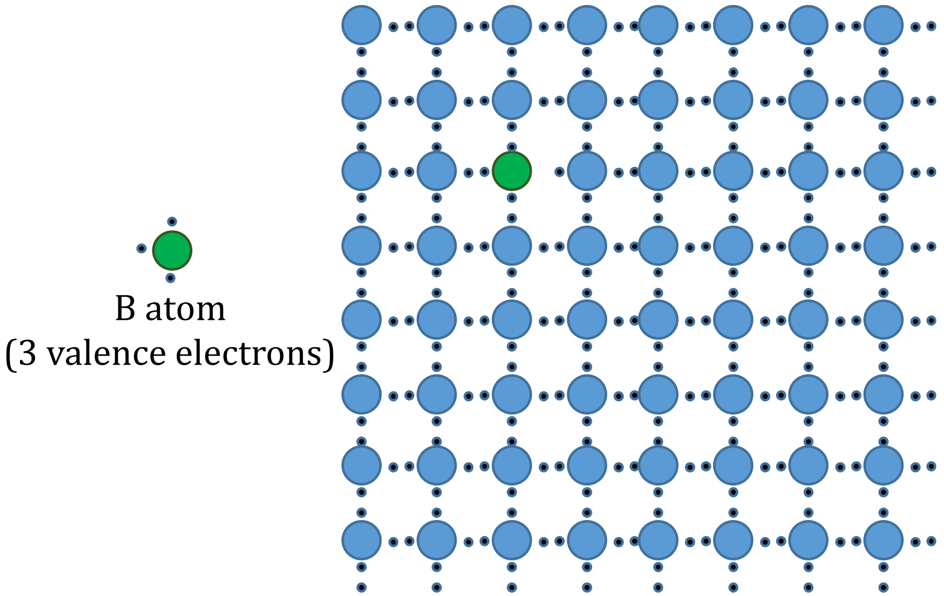
- ☐ Surface and Nanomaterials
    - S/V ratio
    - Passivation

Intrinsic and p-doped semiconductors

From Class 05



Pure Silicon (100% Si)



Almost pure silicon (99.99999% Si + 0.00001% B)

Lattice constant: 0.54 nm
10^{22} atoms/cm^3

ni = 10^{10} cm^{-3} at room temperature

One atom every 10^{12} contributes to the electrons in the conduction band

0.00001% B = 1 B atom every 10^7 Si atoms.
10^{15} B atoms/cm^3

As the B has one valence electron less, the valence band can gain 1 h+ per B atom (acceptor).

p = 10^{15} cm^{-3} at room temperature
(100’000 times higher than intrinsic)

Degenerate semiconductors

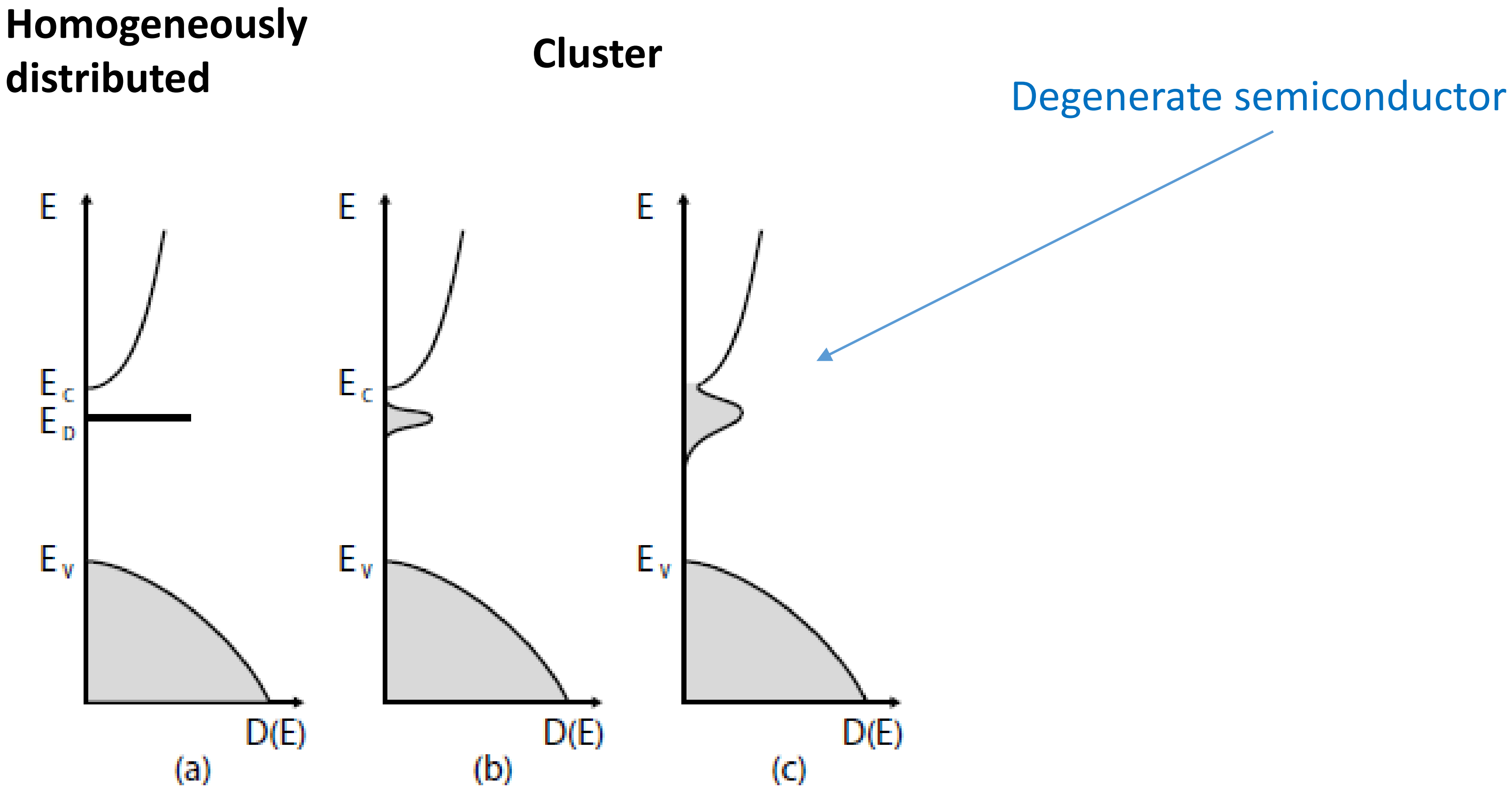
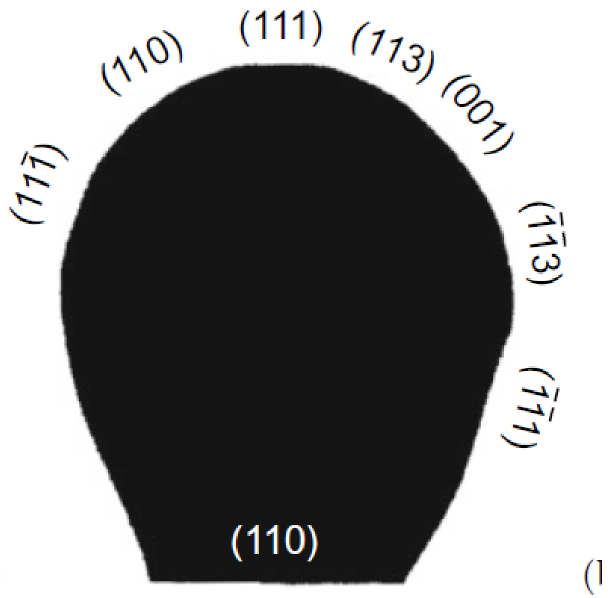


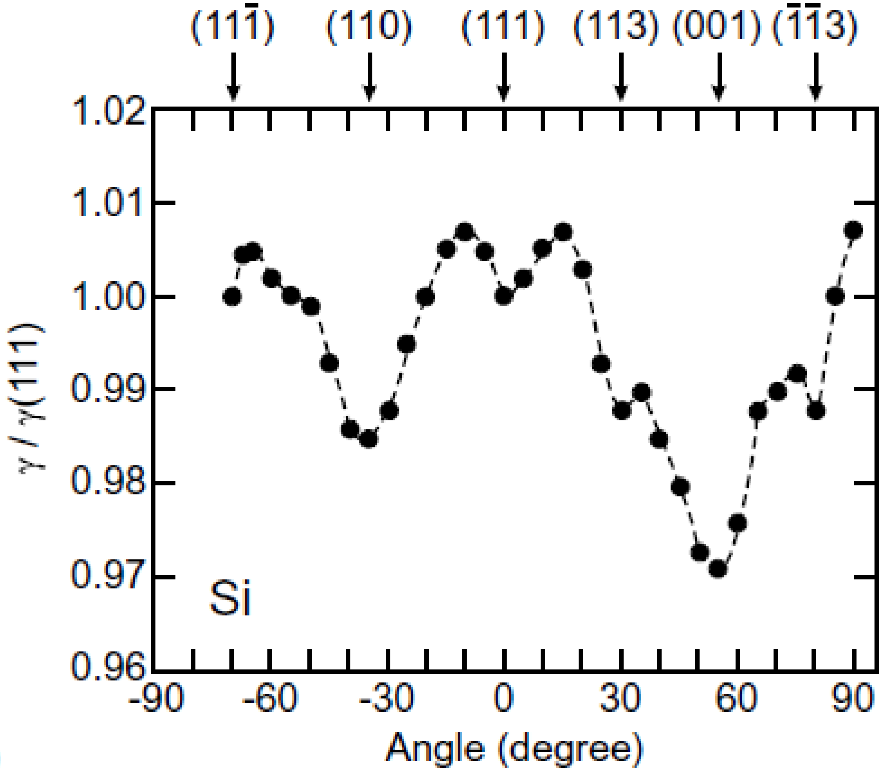
Fig. 7.25 Principle of the formation of a (donor) impurity band. **a** Small doping concentration and sharply defined impurity state at E_D, **b** increasing doping and development of an impurity band that **c** widens further and eventually overlaps with the conduction band for high impurity concentration. The *shaded areas* indicate populated states at $T = 0\,K$

Crystal surface

Bulk: saturated bond

Surface: unsaturated bonds

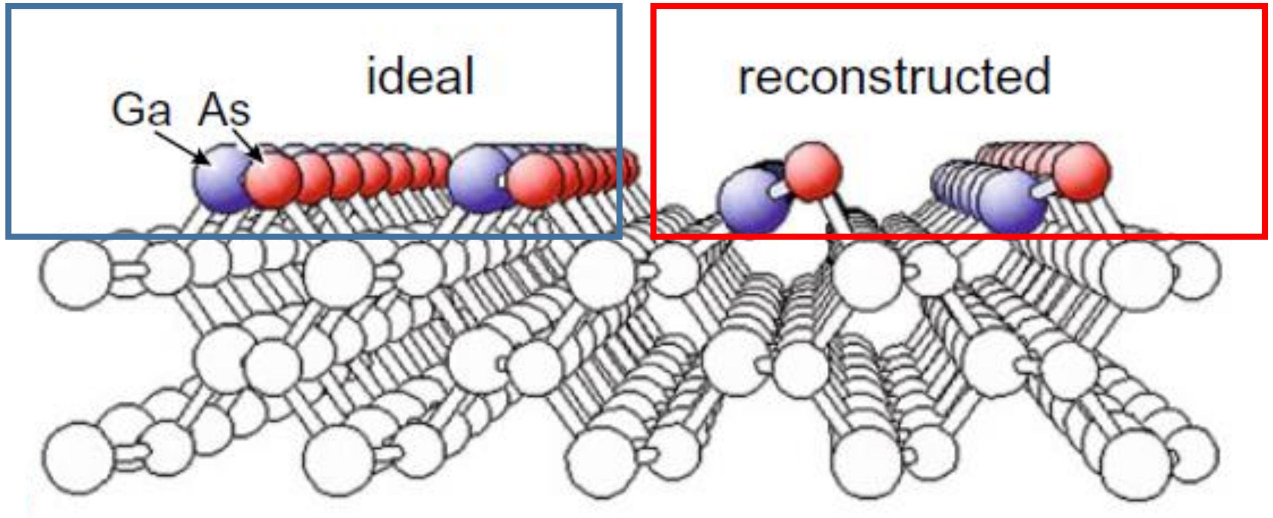


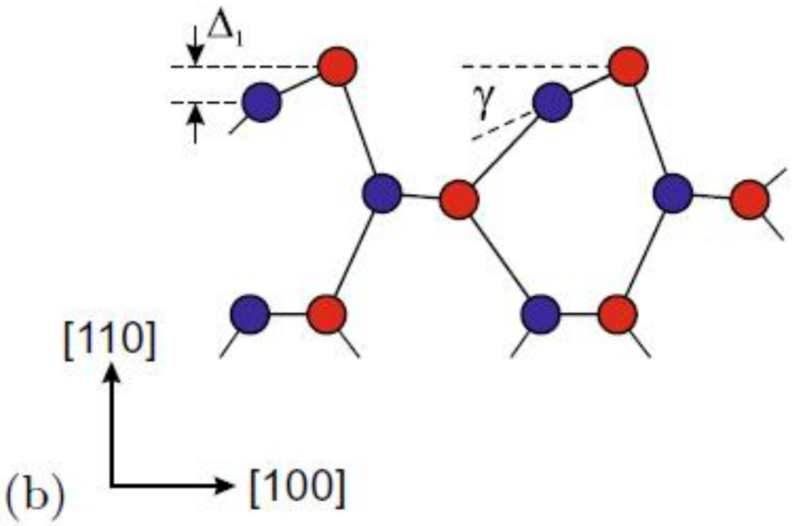


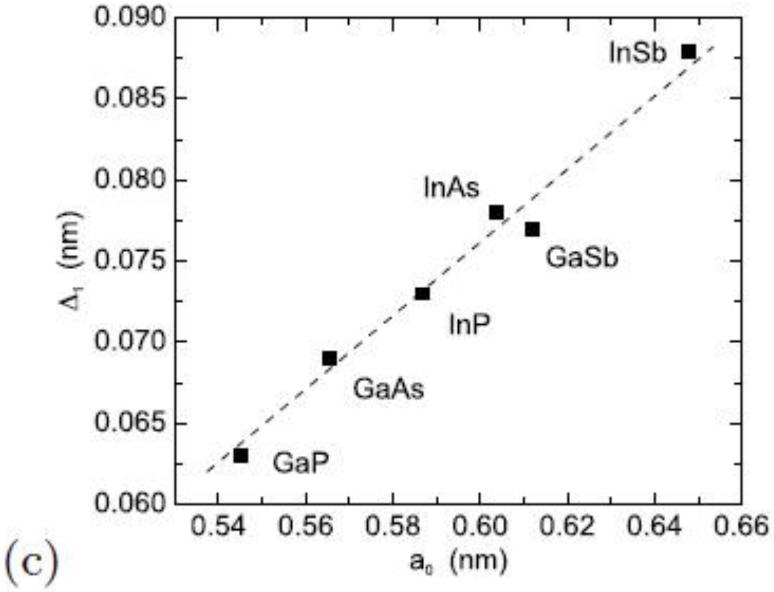
Surface energy depends on the crystal planes

Surface energy affects the crystal planes

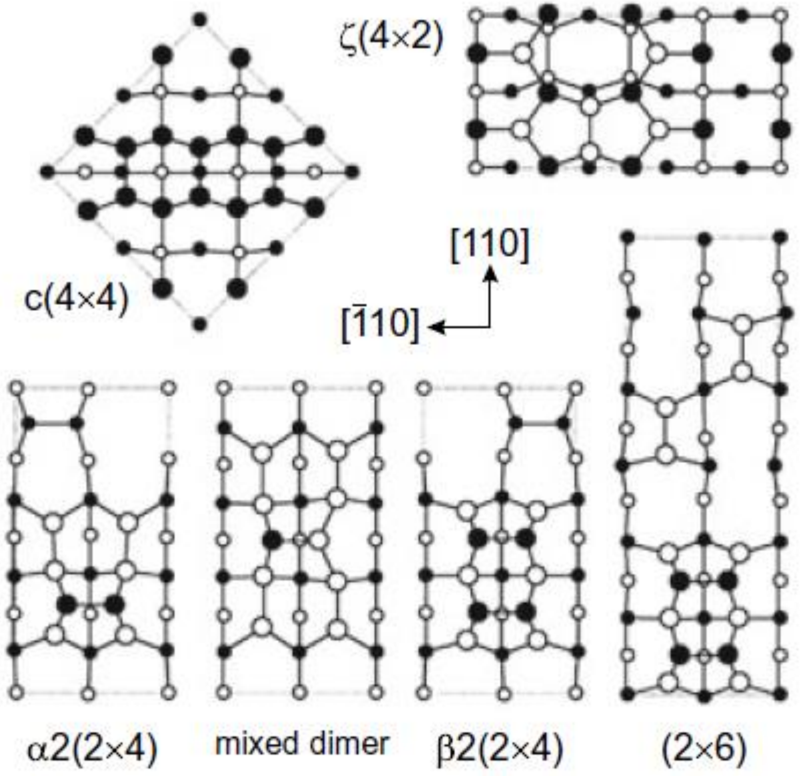
Surface reconstruction







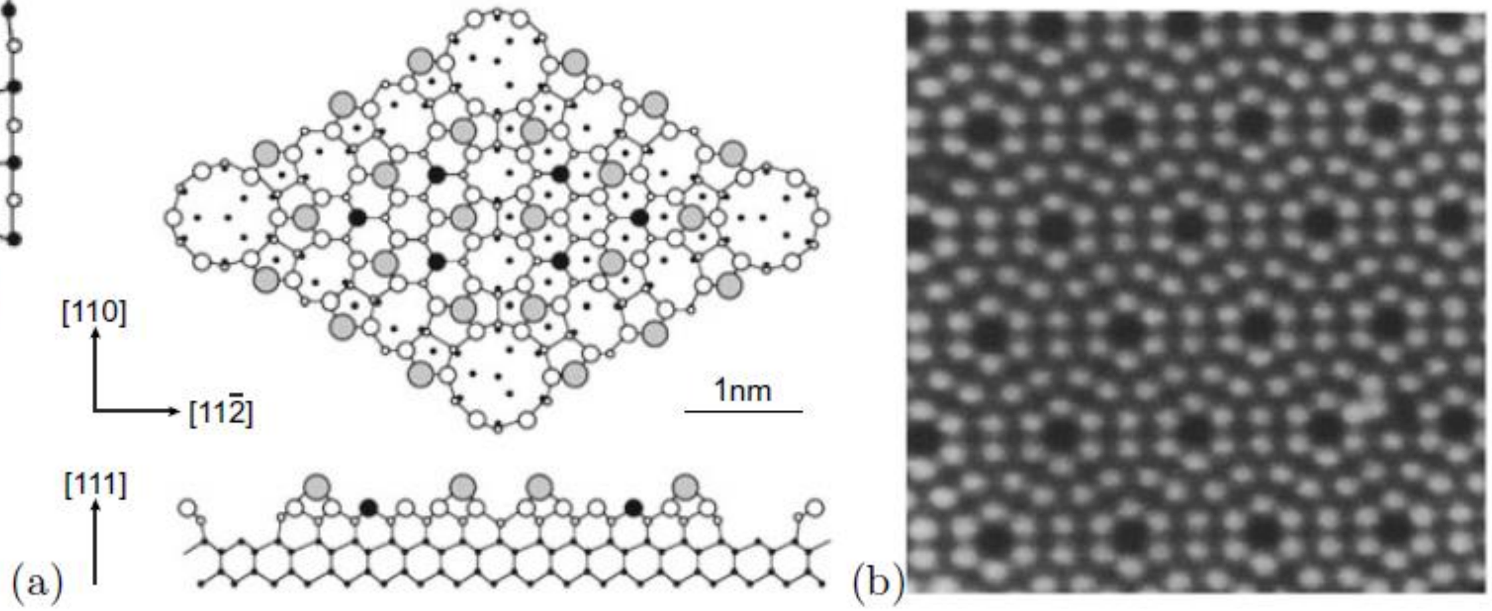
Impact of external conditions



Possible GaAs (100) surface reconstructions depending on thermodynamic conditions

Question:

Do you know other phenomena which minimize the total surface energy ?



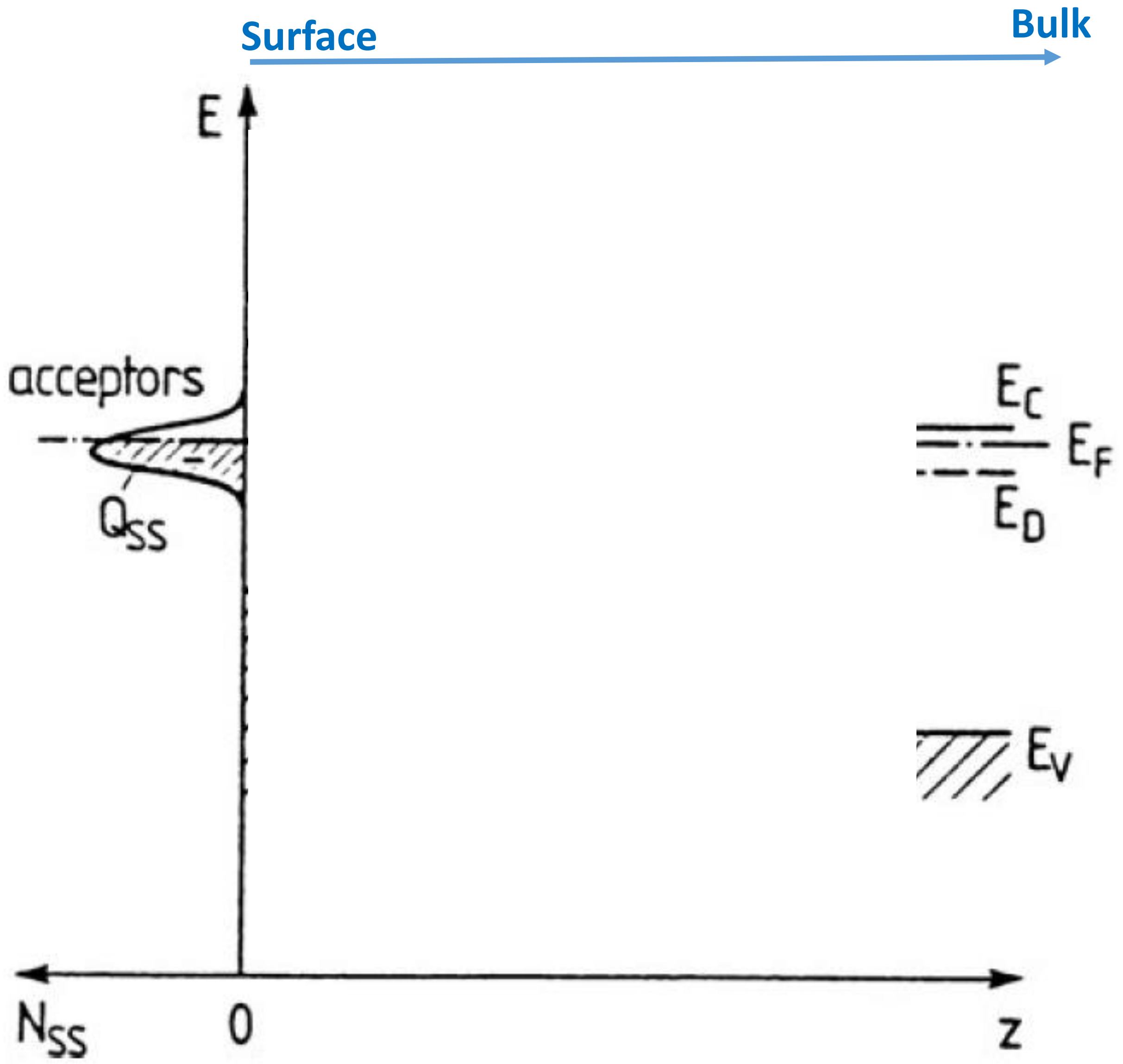
Si(111)surface reconstructions in presence of adatoms
(Schematic and STM micrograph)

Surface States

We can summarize the variety of modifications at the surface as the presence of surface states

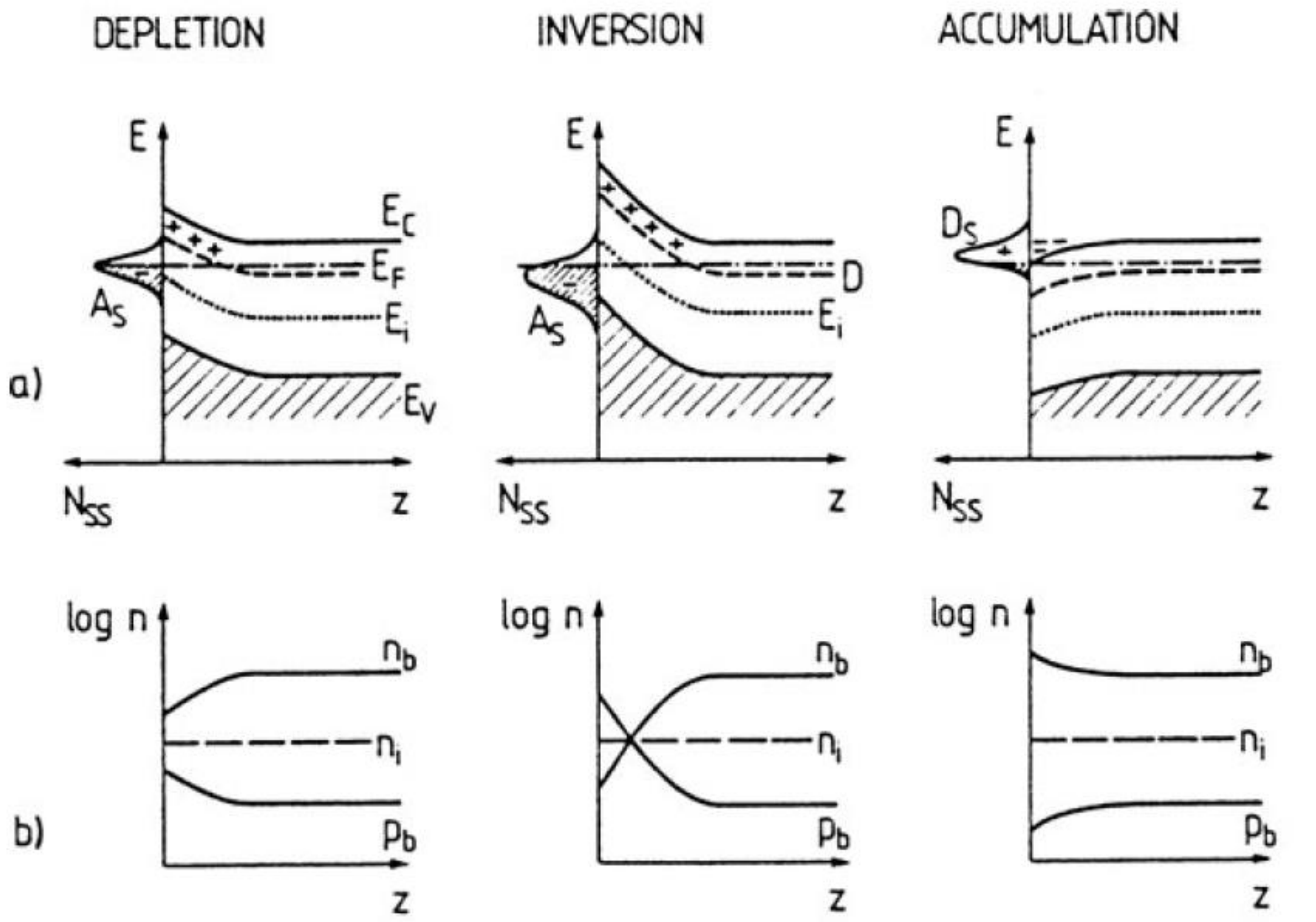
The surface states can be conductive depending on their density, energetic position and distribution.

The presence of surface states modify the behaviour of the semiconductor close to the surface



Density of surface states

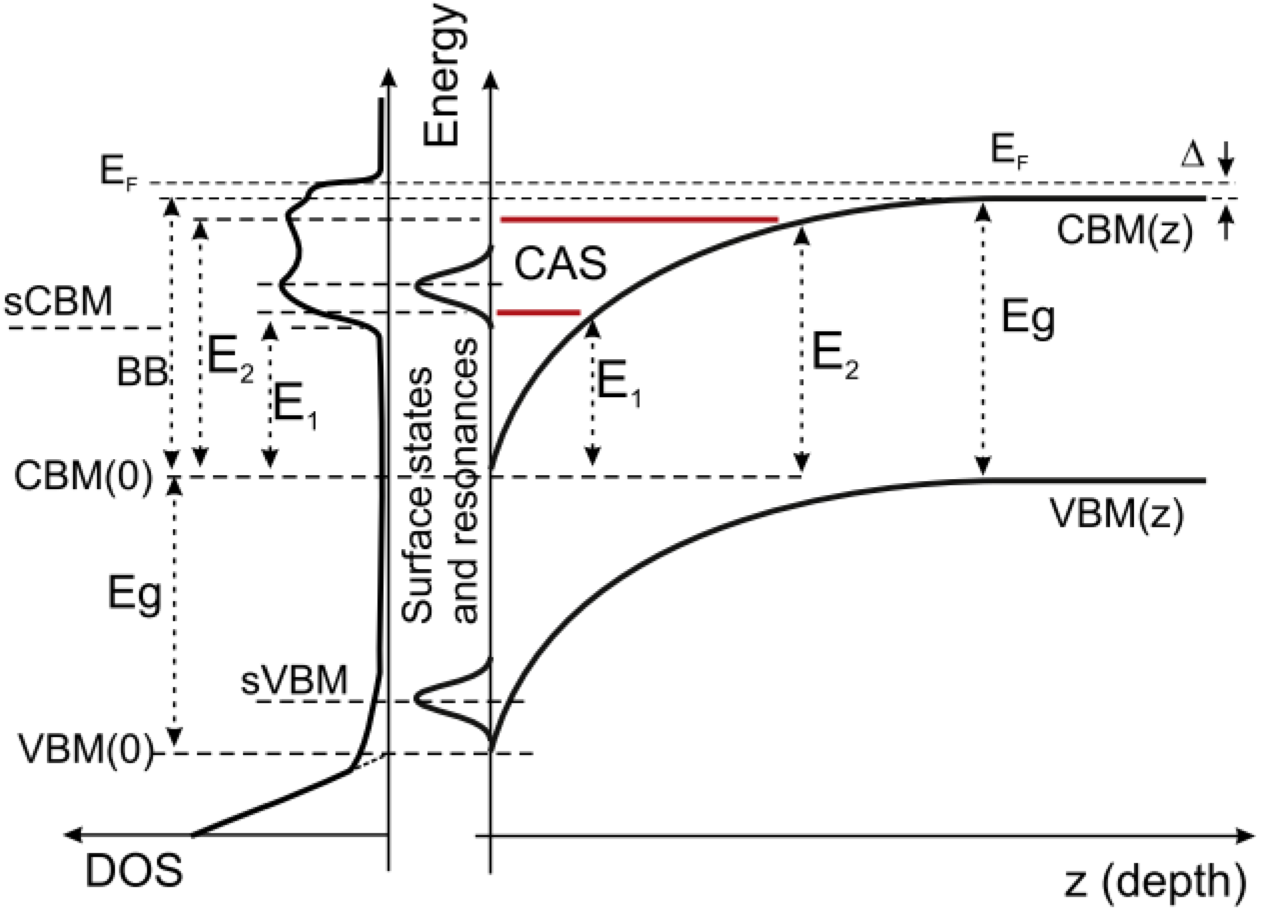
Surface band bending



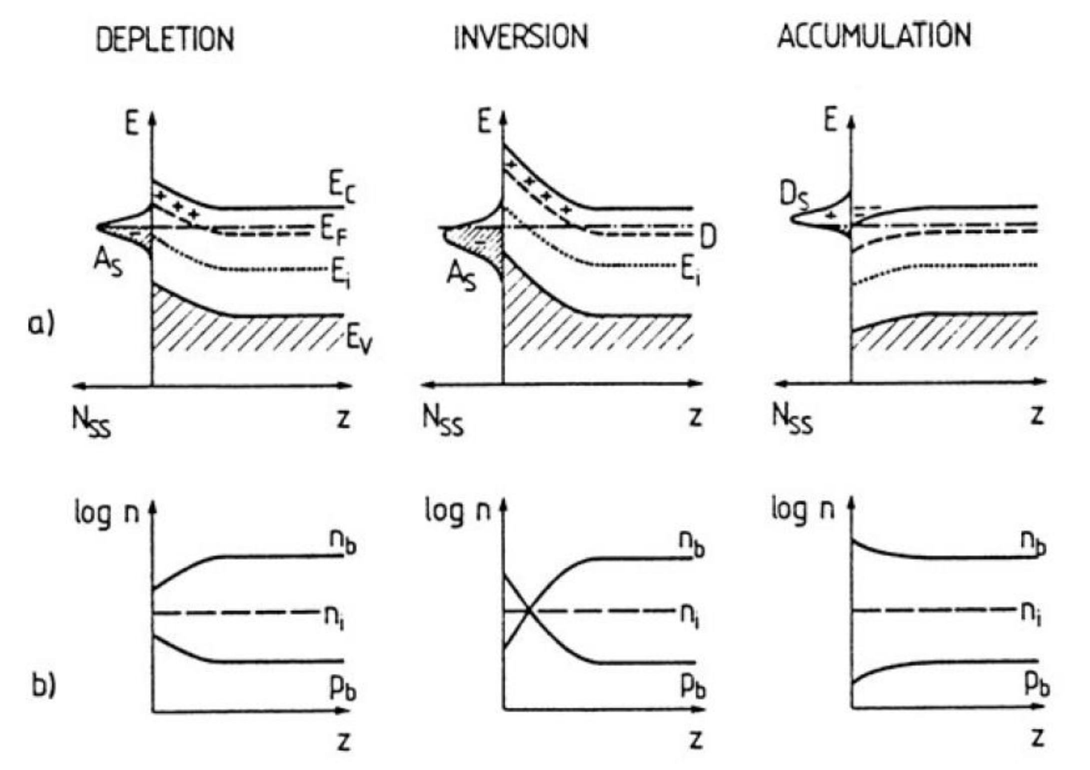
The energetic position of surface states with respect to conduction and valence band induces:

- Charge accumulation at the surface
- Conduction and valence band bending
- Modifications to the carrier concentration close to the surface

The InAs case



DOI:10.1016/j.susc.2014.09.019 0039-6028



QUESTION

Which type of band diagram applies to InAs?
What does it mean?

Fermi Energy pinning

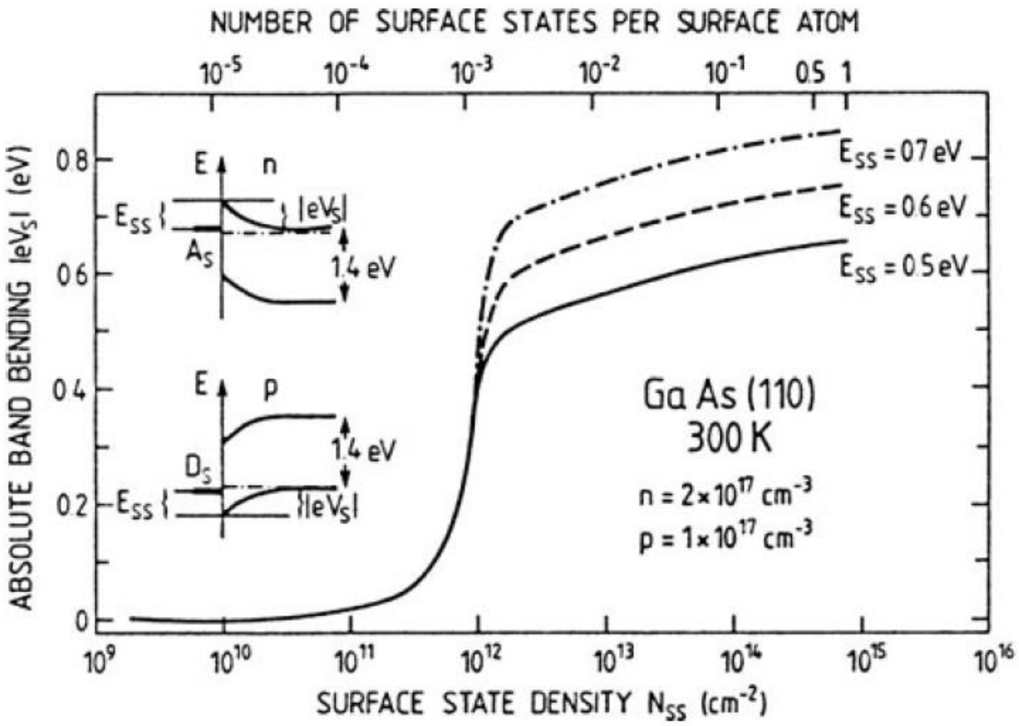


Fig. 7.7 Calculated absolute band bending $|V_s|$ due to an acceptor surface-state level A_s and a donor level D_s for n- and p-type GaAs. $|V_s|$ is plotted versus the surface state density N_{ss} (lower scale) and related to the number of surface states per surface atom (upper scale). With the different definition of the energetic position E_{ss} for n- and p-type crystals (insets) the calculated curves for n- and p-type material are not distinguishable on the scale used [7.3]

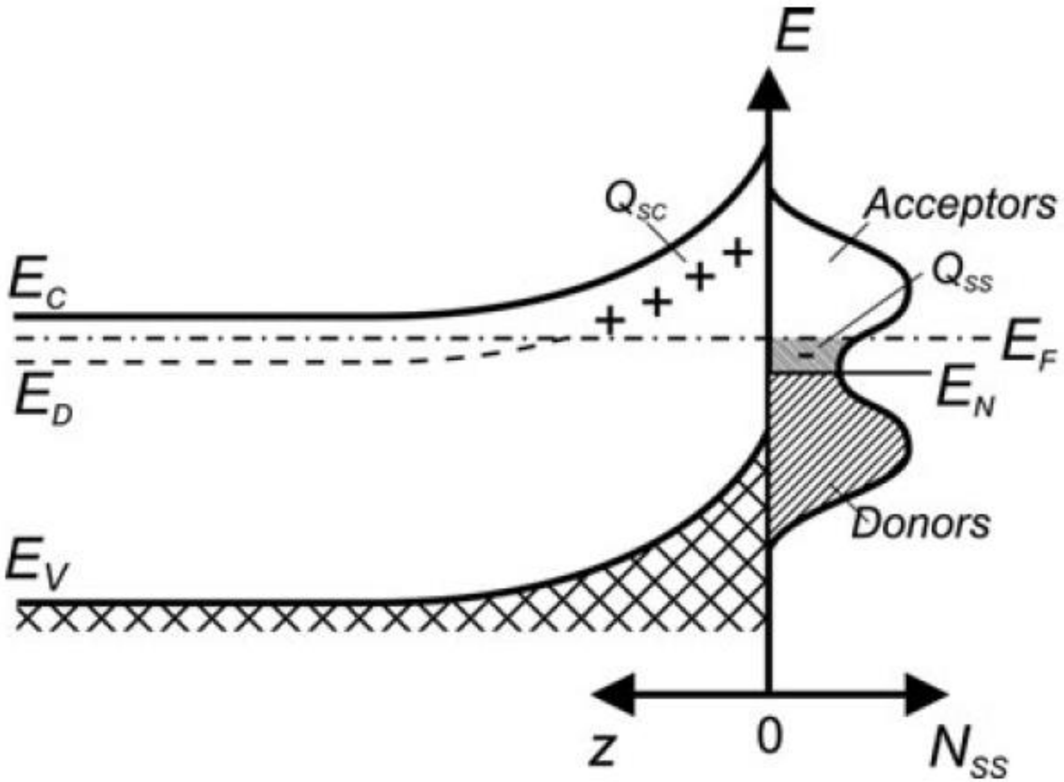
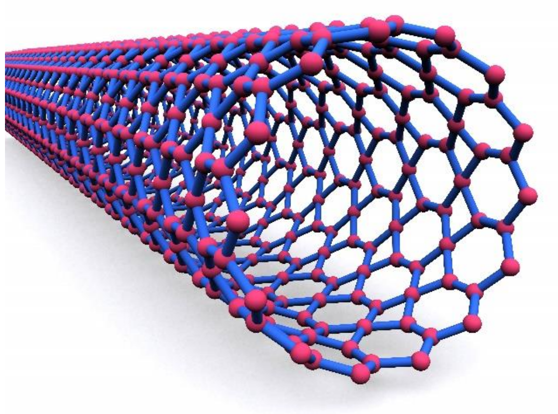
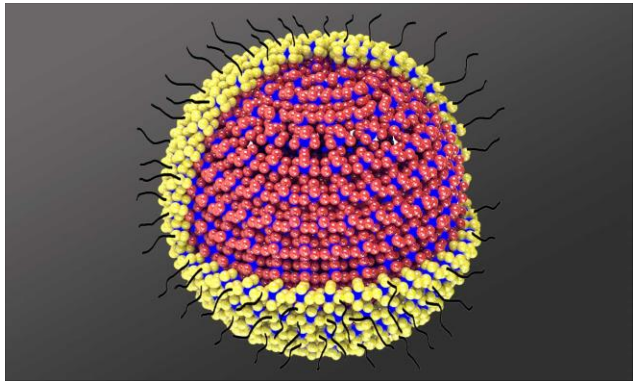
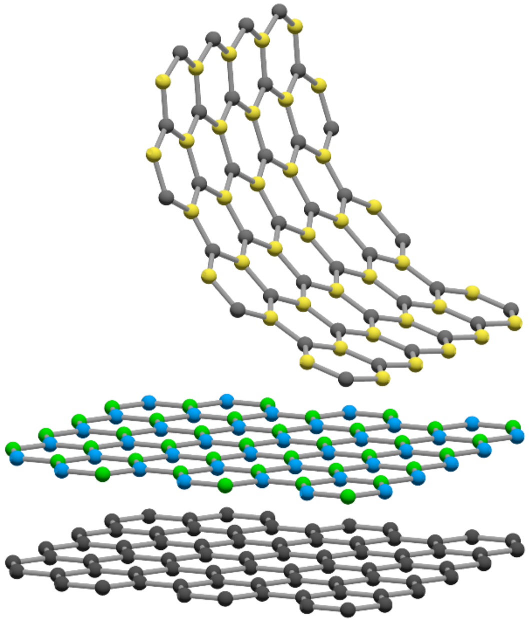


Fig. 7.8 Qualitative explanation of Fermi-level (E_F) pinning on an n-type semiconductor surface at $z = 0$; bulk donors at energy E_D, E_C, and E_V conduction and valence band edges. A broad band of surface states (density N_{SS}), donor-like in the lower and acceptor-like in the upper energy range, has a neutrality level E_N. The Fermi energy at the surface is fixed somewhat above E_N such that negatively charged surface acceptors (surface state charge Q_{SS}) compensate the positive space charge Q_{SC} arising from ionized bulk donors. The energetic distance $E_F - E_N$ is exaggerated for clarity. On the plotted E scale this value is negligibly small

Nanomaterials and surfaces



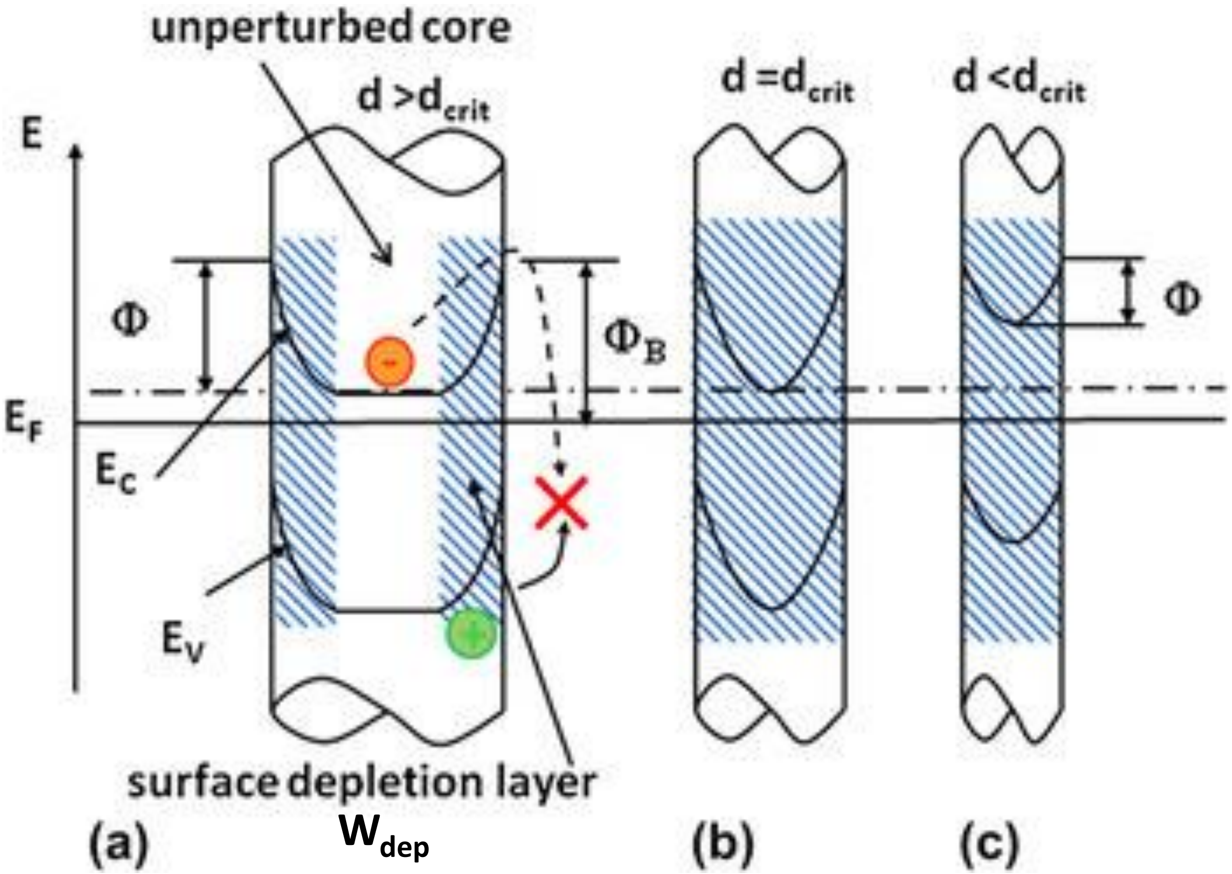




$$\frac{Surface}{Volume} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} \propto \frac{1}{r}$$

As the characteristic dimension shrinks, the surface becomes predominant.

Charge transport in NWs



Φ_B = Energy difference between E_C at the surface and E_F

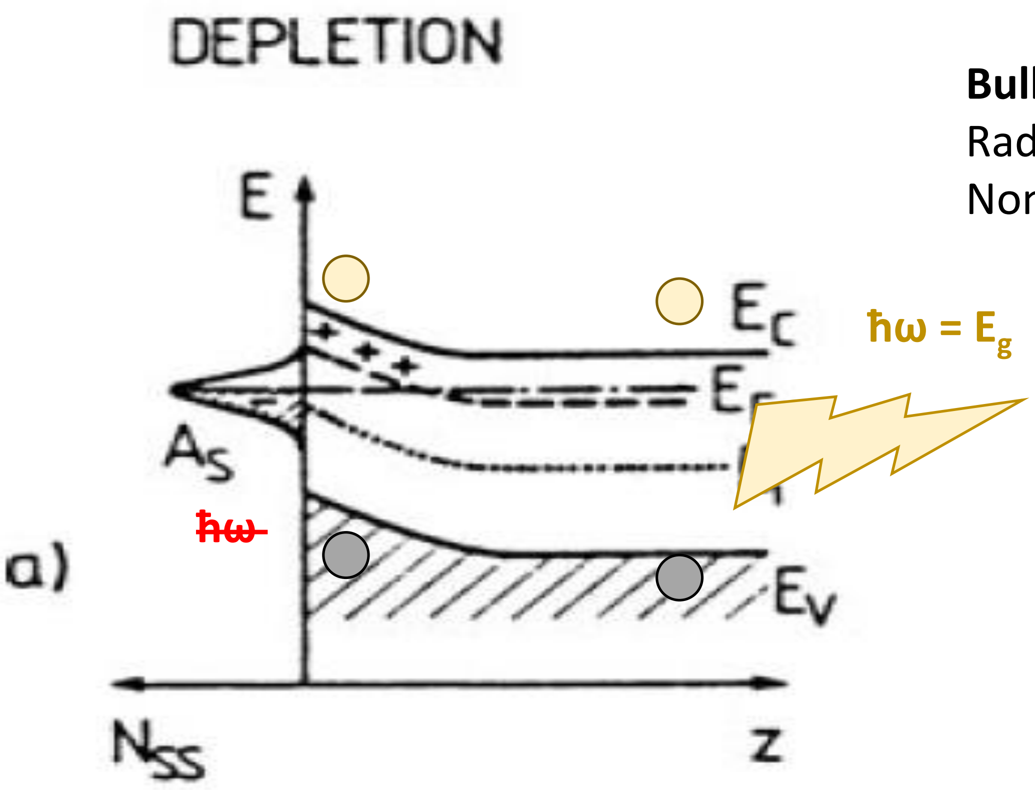
Φ = Energy difference between E_C at the surface and in bulk

$d_{crit} \sim 2 \times W_{dep}$

For $d < d_{crit}$:
- n ↓
- σ ↓

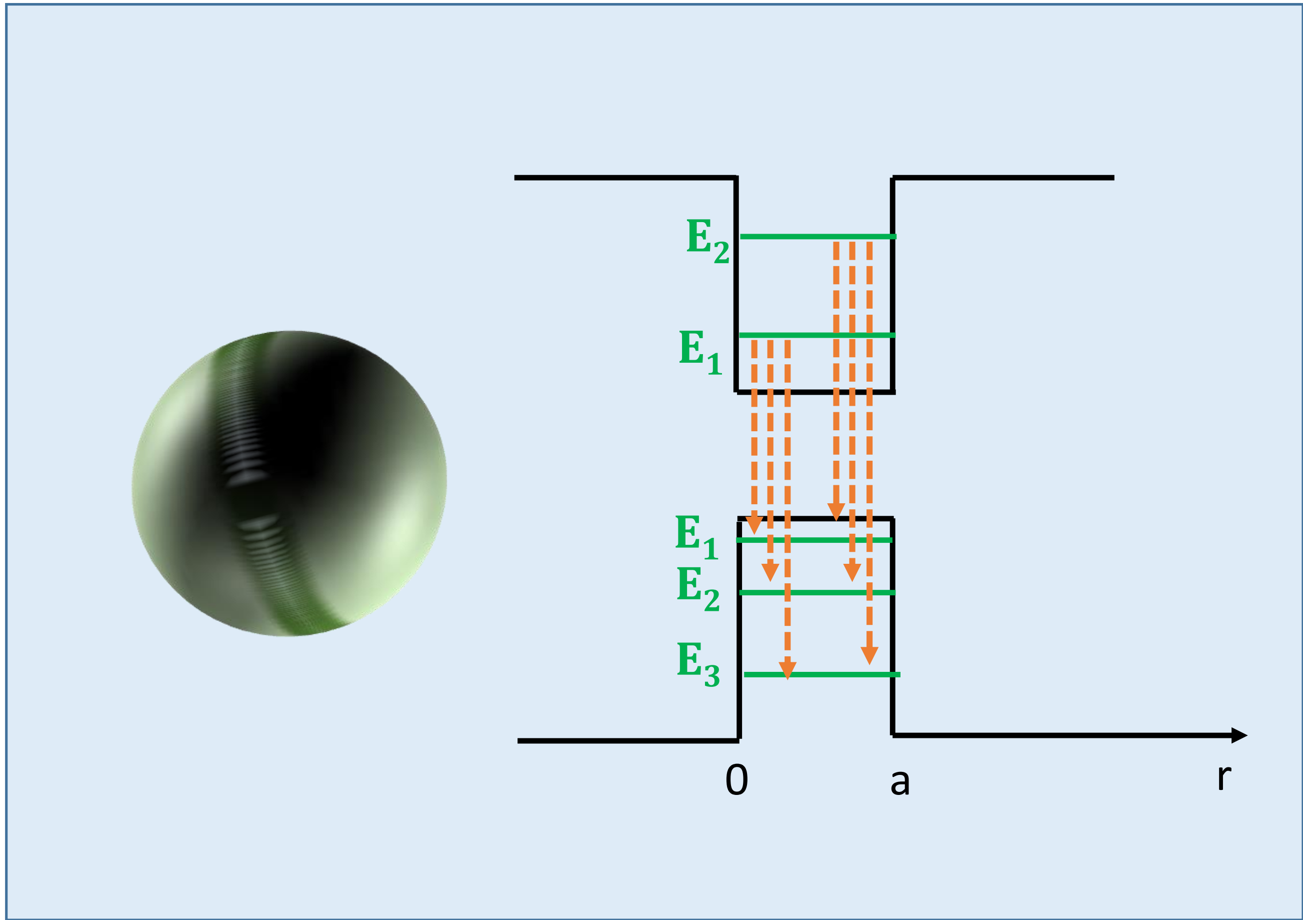
Size-dependent Photoconductivity in MBE-Grown GaN–Nanowires, R. Calarco, 2005

Photon emission in quantum dots

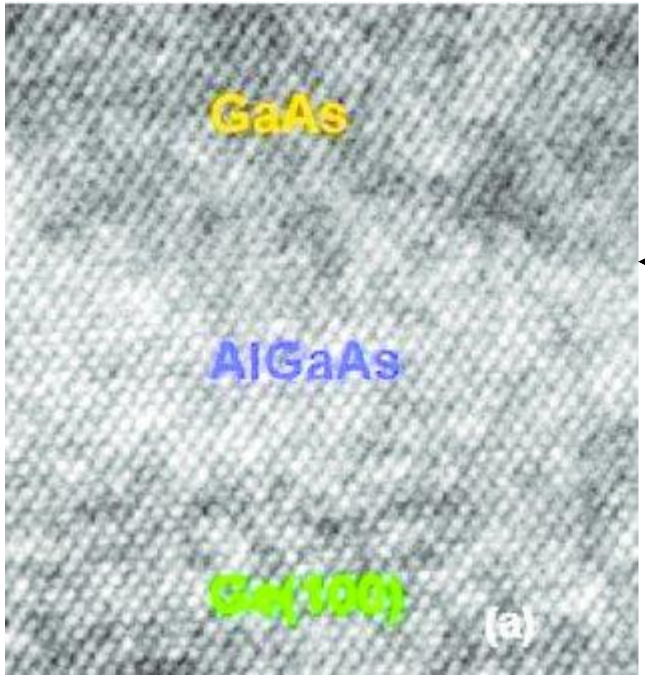


Surface:
Radiative recombination (low)
Non-radiative recombination (high)

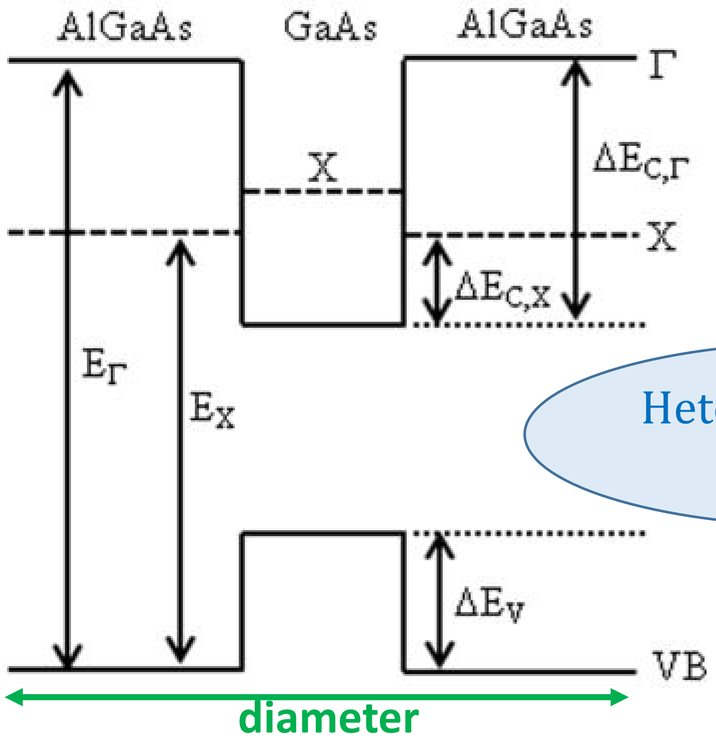
Bulk (ideal crystal):
Radiative recombination (high)
Non-radiative recombination (low)



Surface passivation

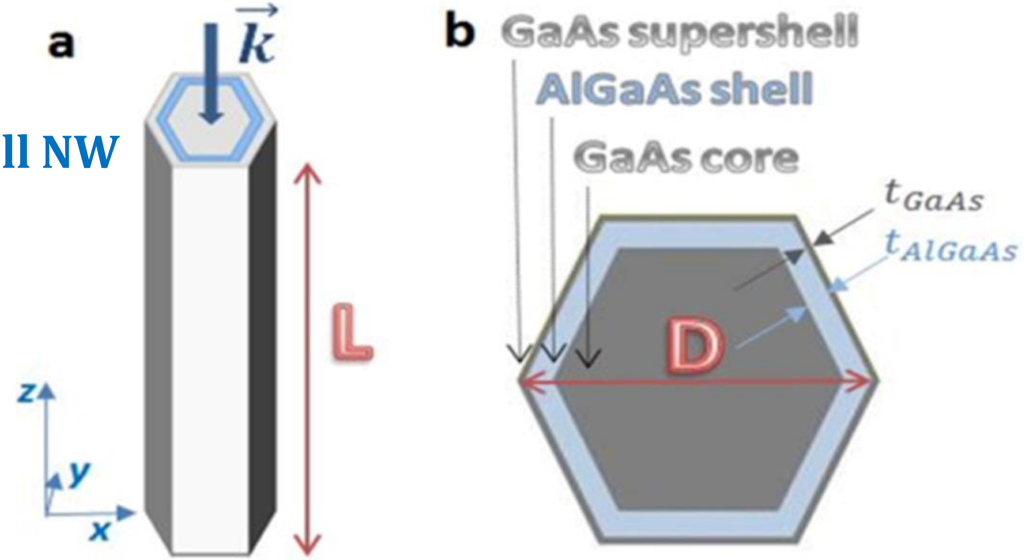


GaAs dangling bonds are saturated

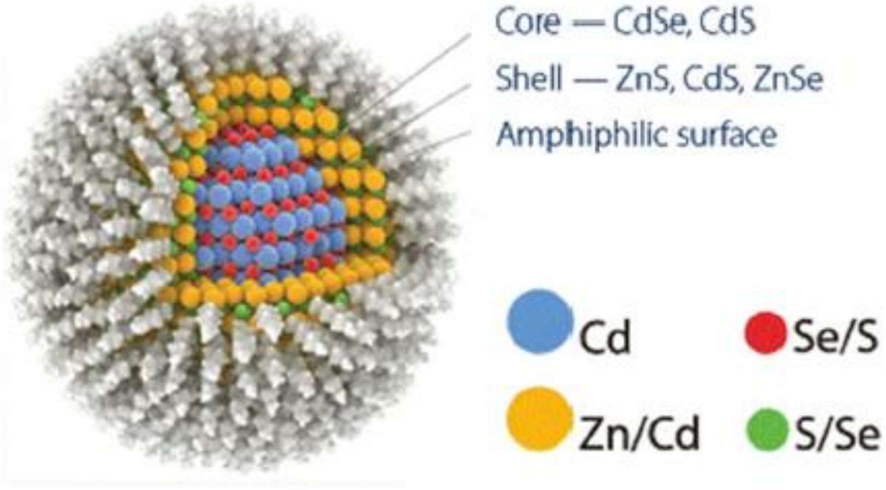


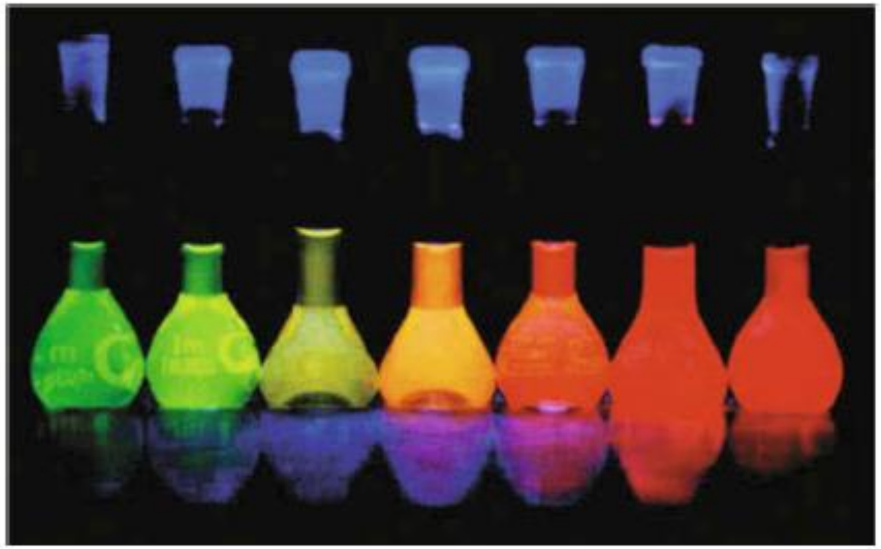
Heterostructures – next class

Core/shell NW



Surface passivation





https://www.wesrch.com/gp/how-cdse-zns-quantum-dots-work-6466

Absorbance of CdSe QDs

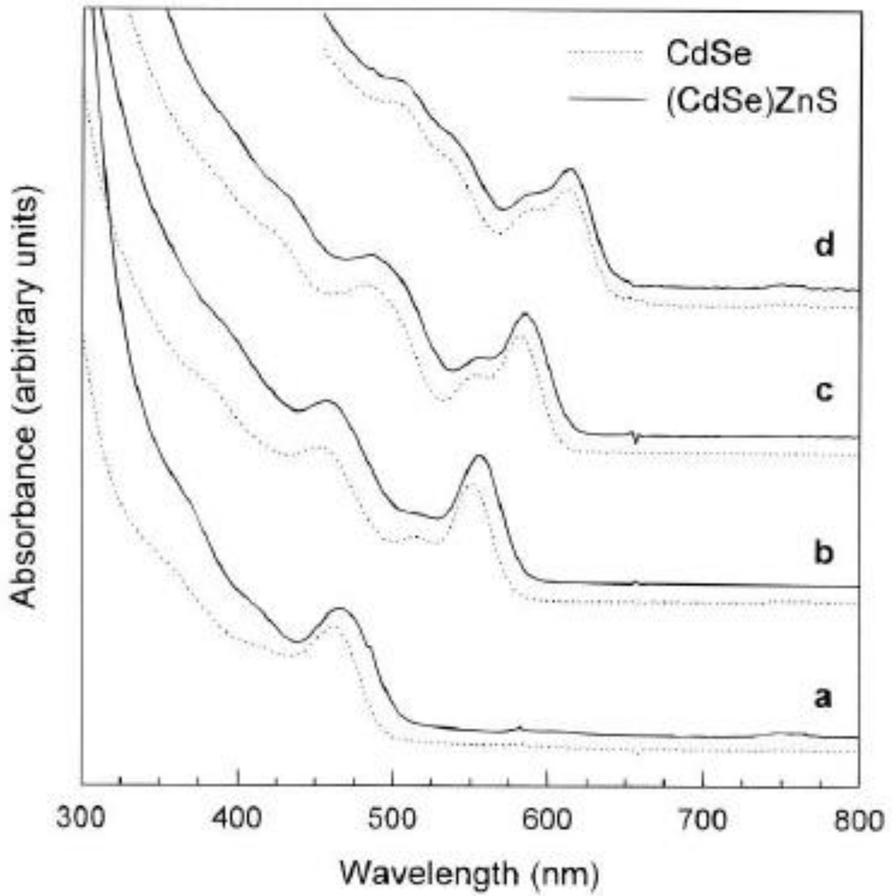
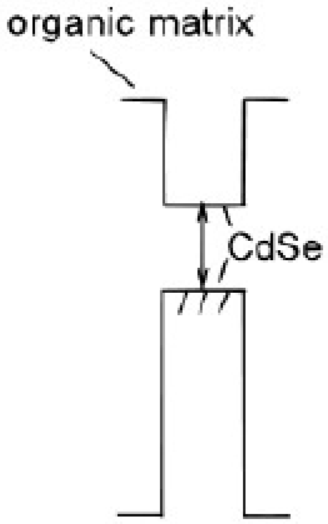
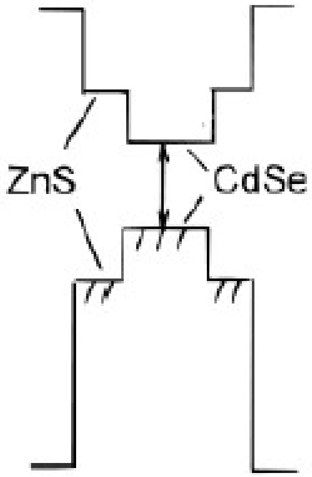


Figure 1. Absorption spectra for bare (dashed lines) and 1−2 monolayer ZnS overcoated (solid lines) CdSe dots with diameters measuring (a) 23, (b) 42, (c) 48, and (d) 55 Å. The absorption spectra for the (CdSe)ZnS dots are broader and slightly red-shifted from their respective bare dot spectra.





Absorbance of CdSe QDs

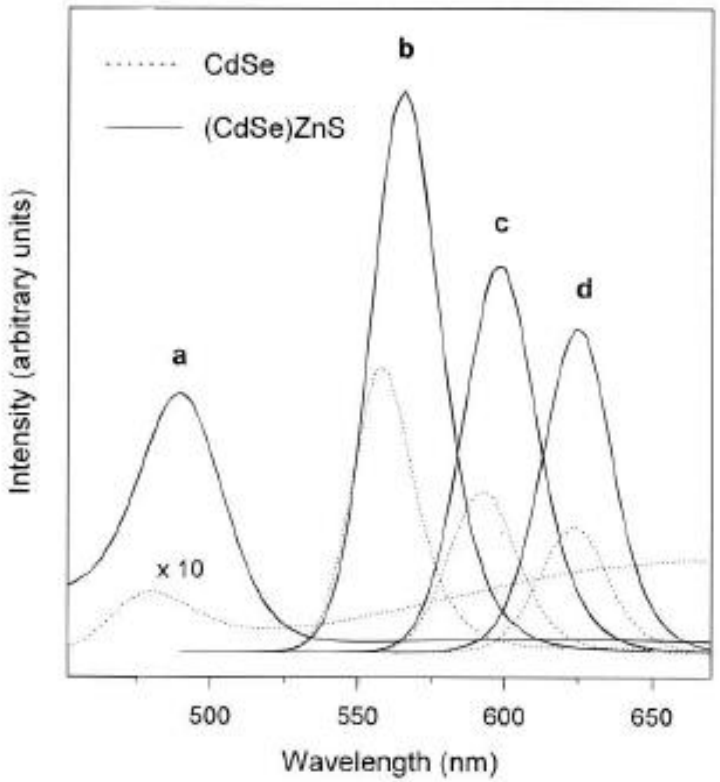
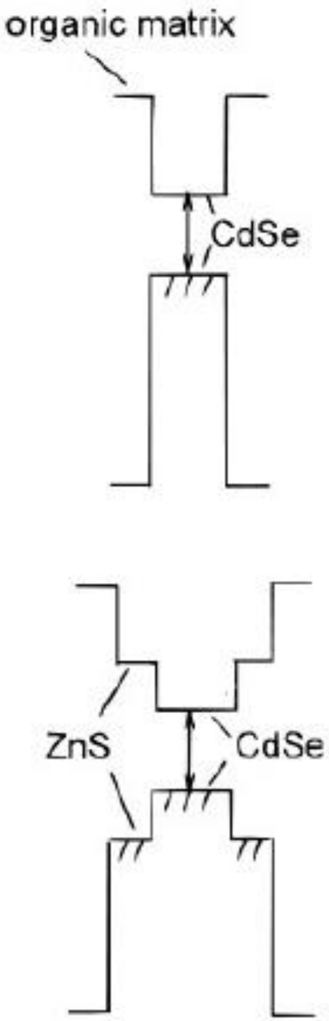


Figure 2. Photoluminescence (PL) spectra for bare (dashed lines) and ZnS overcoated (solid lines) dots with the following core sizes: (a) 23, (b) 42, (c) 48, and (d) 55 Å in diameter. The PL spectra for the overcoated dots are much more intense owing to their higher quantum yields: (a) 40, (b) 50, (c) 35, and (d) 30.



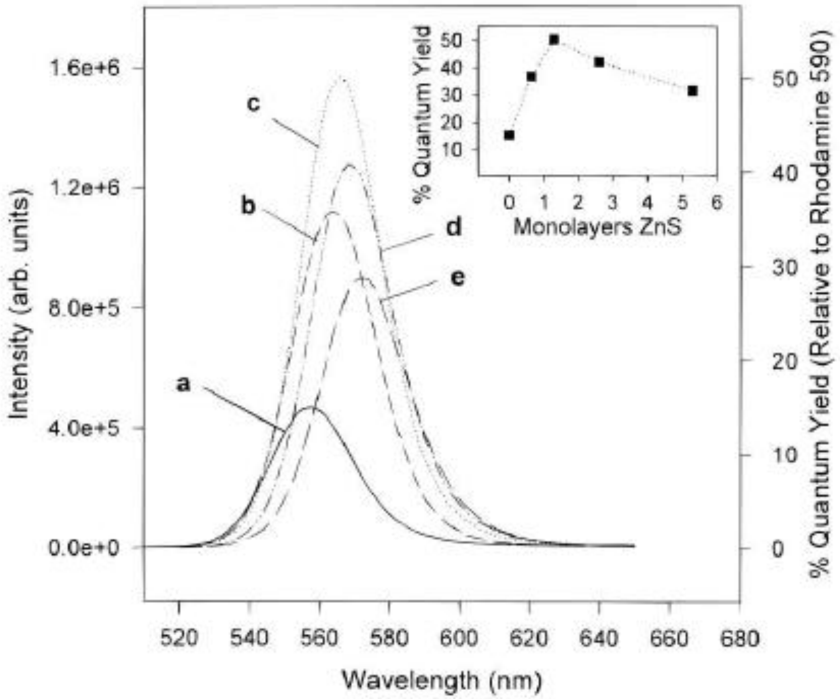
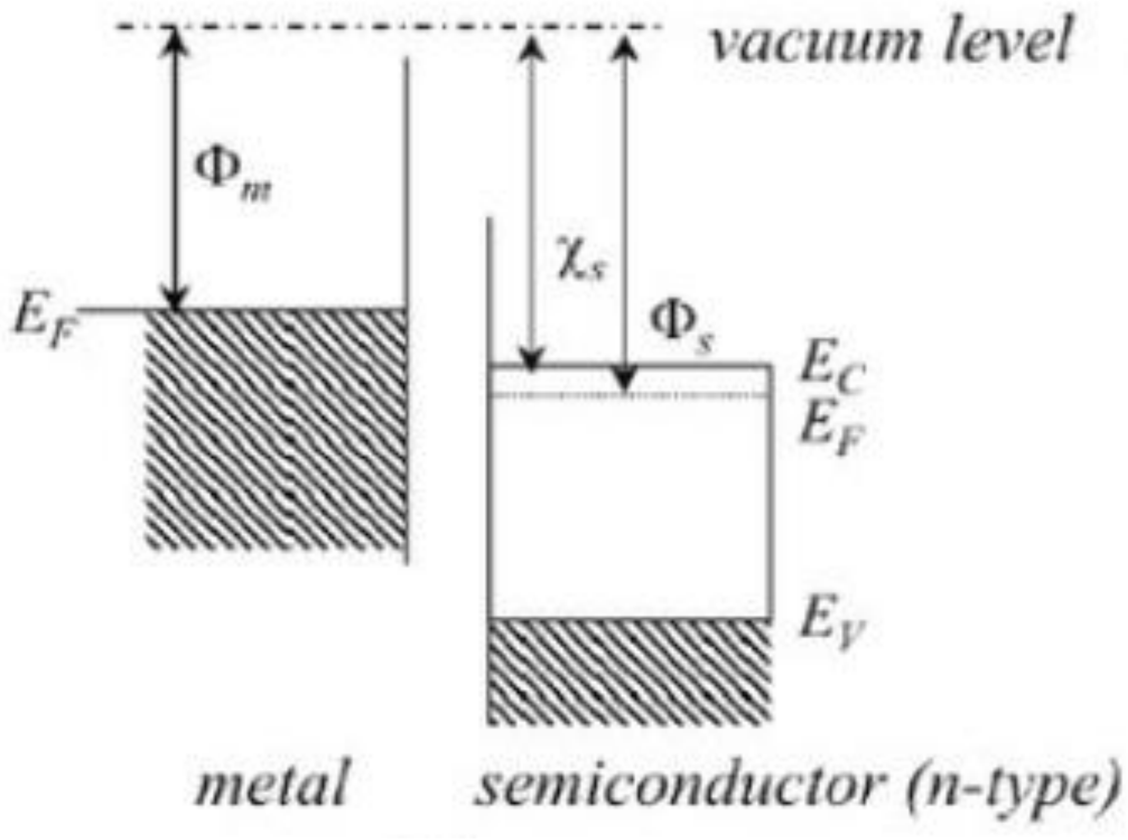
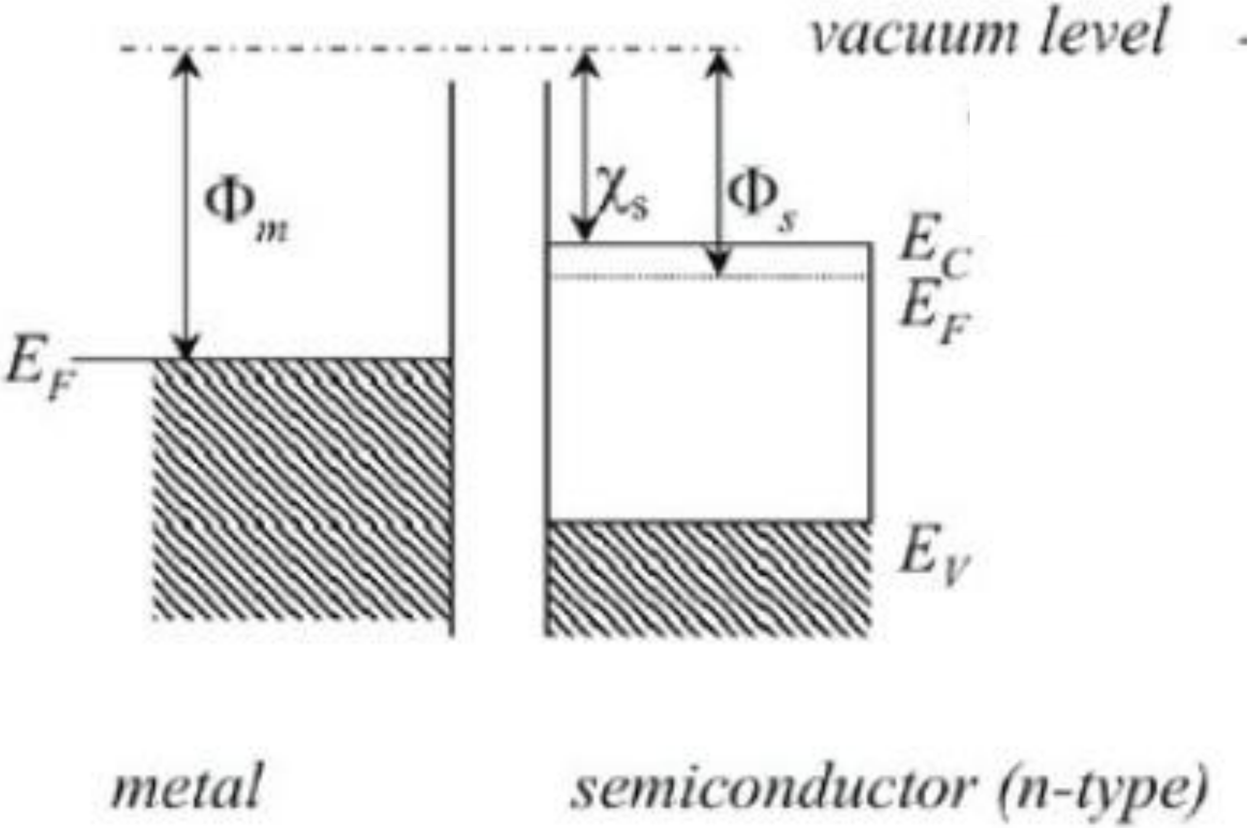


Figure 5. PL spectra for a series of ZnS overcoated dots with 42 ± 10% Å diameter CdSe cores. The spectra are for (a) 0, (b) 0.65, (c) 1.3, (d) 2.6, and (e) 5.3 monolayers ZnS coverage. The position of the maximum in the PL spectrum shifts to the red, and the spectrum broadens with increasing ZnS coverage. (inset) The PL quantum yield is charted as a function of ZnS coverage. The PL intensity increases with the addition of ZnS reaching, 50% at ~1.3 monolayers, and then declines steadily at higher coverage. The line is simply a guide to the eye.

Exercise (5 minutes):

Sketch the band profile of these material once they are placed in contact.
What is the difference between the two cases? Which parameters define the band bending?





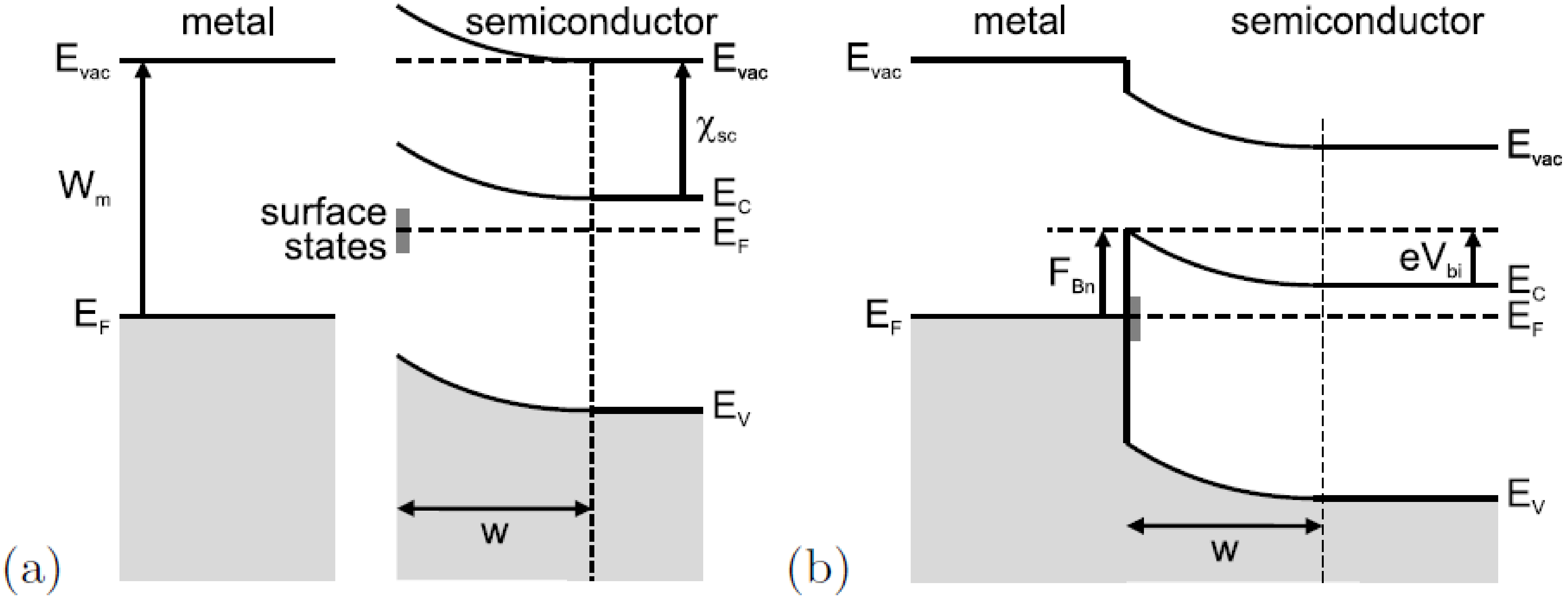
Ohmic contact

To be discussed in class

Schottky contact

To be discussed in class

Metal-Semiconductor contact with surface states



Bardeen model

Due to Fermi energy pinning, a band bending is present in the semiconductor even before the contact with the metal. Thus, this barrier at the interface does not depend on the workfunction.