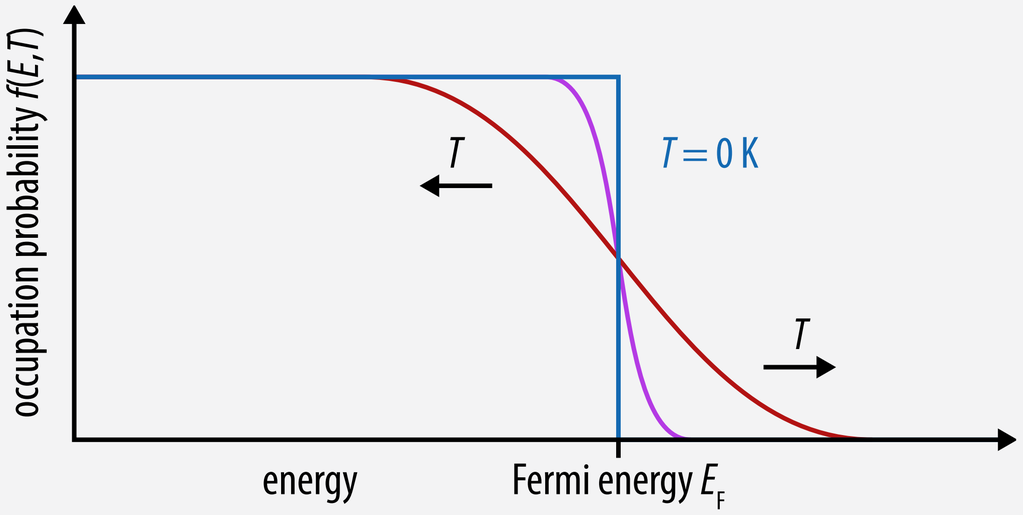
5.4 Charges at Interfaces

Fermi Distribution and Fermi Level

- Fermi-Dirac distribution for thermal distribution of electron energies

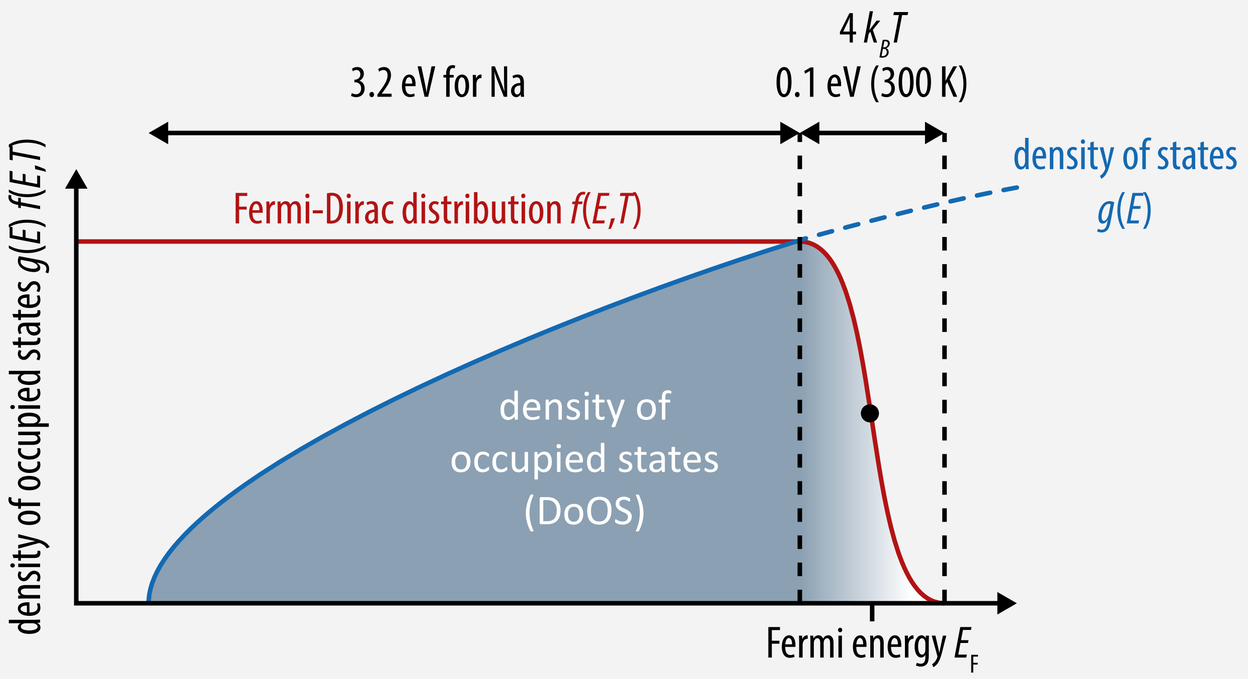
$$f(E) = \frac{1}{e^{\frac{(E - E_F)}{k_B T}} + 1}$$



- **for $E–E_F \gg k_B T$, the Fermi-Dirac distribution becomes the Boltzmann distribution**
- **Fermi energy E_F is defined as the energy with the probability to find an electron $f(E_F) = 0.5$**

Density of Occupied States (DOS)

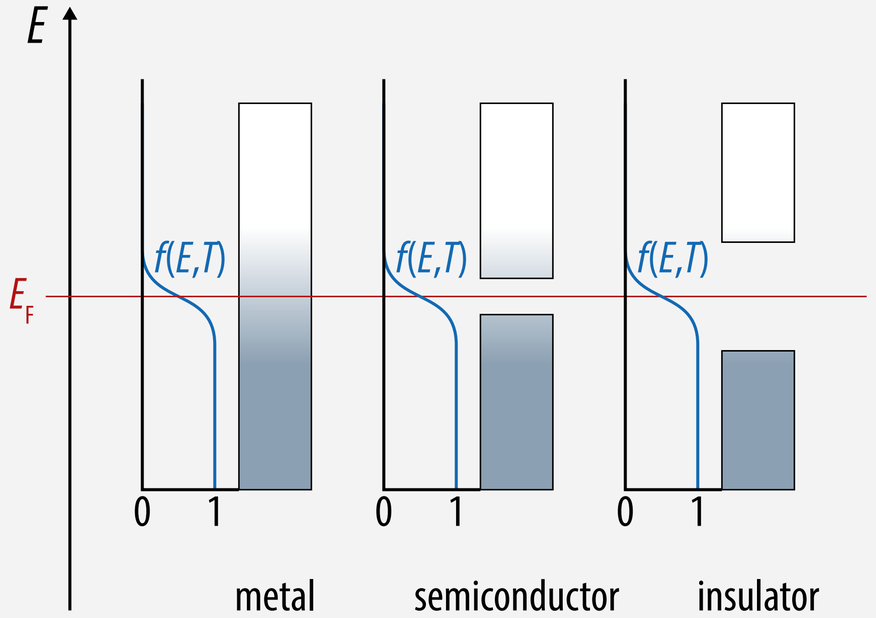
- electronic structure of a material is described by the density of occupied states (DoOS)



- **density of states $g(E)$ represents all allowed states of a material (e.g., the 3*s* band in Na)**
- **these available states filled according to Fermi-Dirac distribution $f(E,T)$**
- **density of occupied states $g(E) \cdot f(E,T)$ represents states of all electrons at given temperature**

Density of Occupied States in Metals, Semiconductors, Insulators

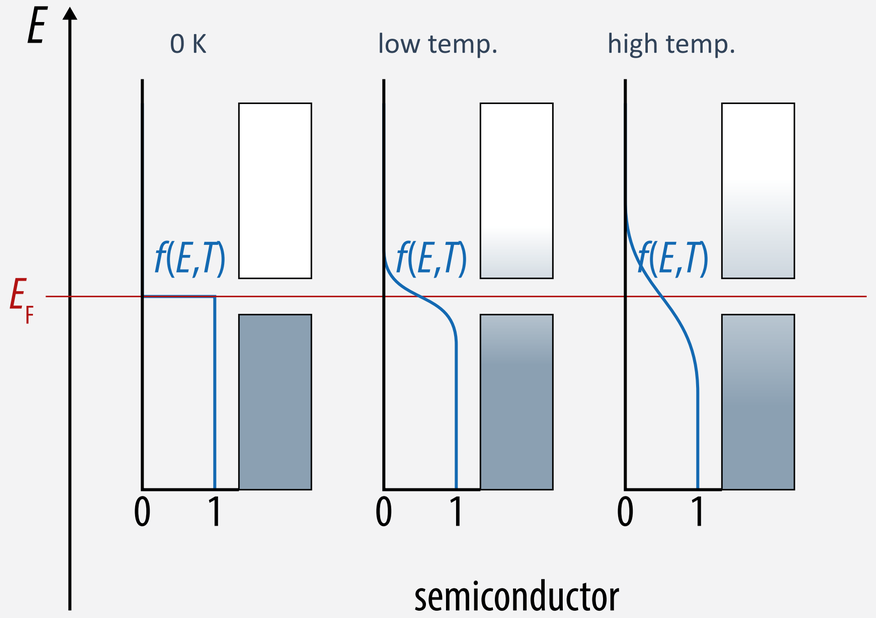
- in metallic conductors, Fermi level is equal to the “work function” (ionization energy) !
- in semiconductors / insulators, the Fermi level is, by definition, in the middle of the bandgap !



- **for semiconductors and insulators, density of states within the bandgap $g(E) = 0$**
- **hence, also density of occupied states is $g(E) \cdot f(E,T) = 0$ within the bandgap**
- **Fermi level not equal to work function (ionization energy, HOMO level)**

Temperature-Dependent Density of Occupied States in Semiconductors

- Fermi distribution of electron energies is temperature-dependent
- a good approximation for “thermal spread” of electron energies is 4 $k_B T$

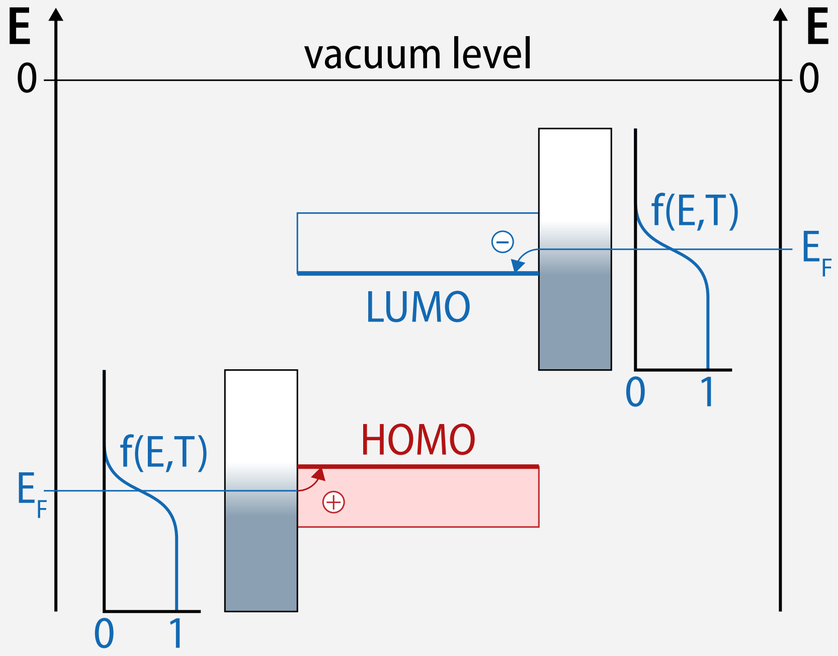


- **only a tiny fraction of “intrinsic” charge carriers in organic semiconductors** (large $E_g \gg 4\ k_B T$)
- **for silicon (bandgap 1.1 eV): 10^{10} cm^{-3} (10^{-12} *at*%) at 300 K,10^{14} cm^{-3} (10^{-9} *at*%) at 500 K**

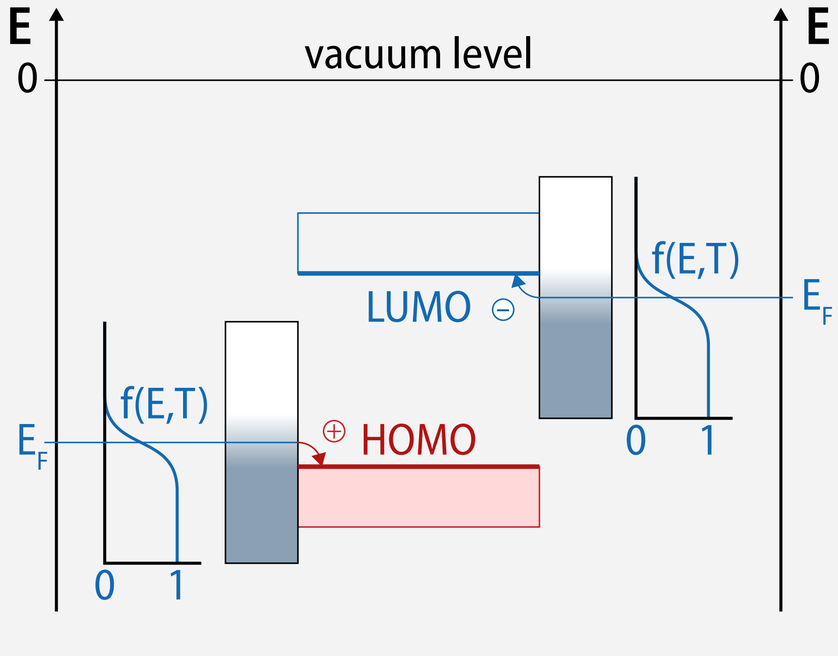
Ideal Metallic Electrodes in Organic Semiconductor Device

- organic semiconductors have low intrinsic charge carrier density and low charge mobility
- like for a metal-insulator contact, all energy levels pinned at the interface without variation

spontaneous charge injection

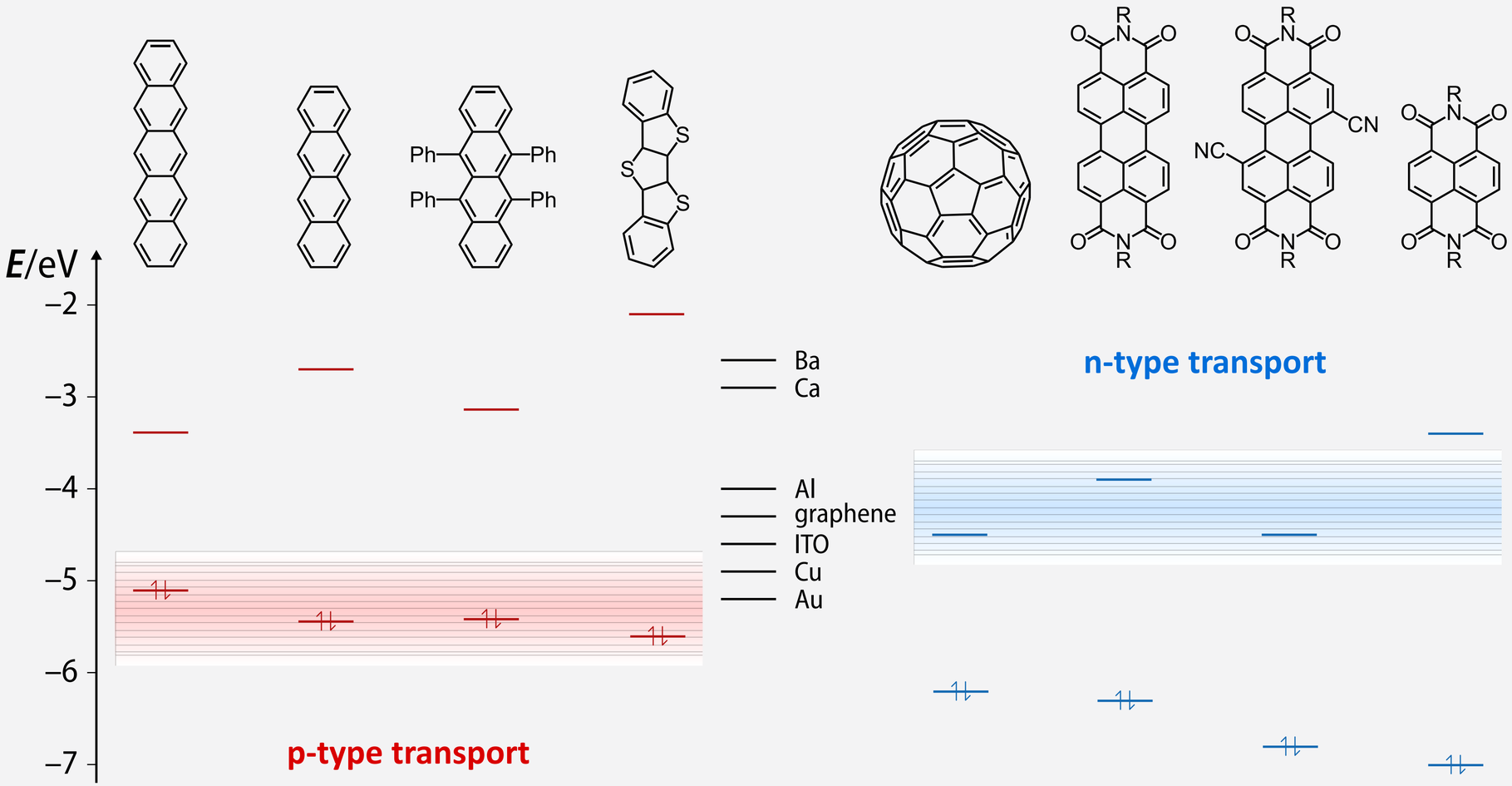


charge injection with energy barrier



- **spontaneous electron (hole) injection if HOMO (LUMO) above (below) electrode Fermi level**
- **otherwise, charge injection with an energy barrier, can be forced in an electric field**

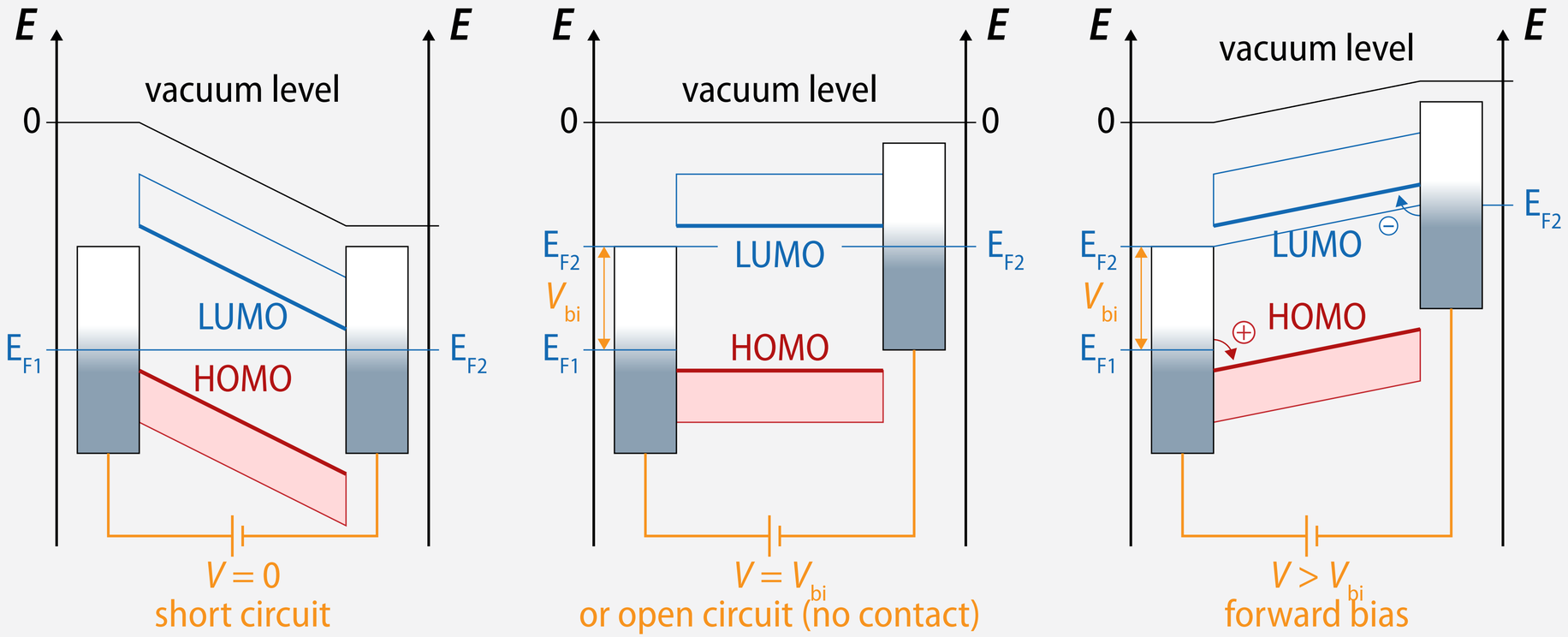
Typical Electrode Materials and Organic Semiconductors



- difficult to find materials with good work functions that are chemically stable & processable
- particularly spontaneous electron injection requires non-noble metals (not air stable)

Materials Interfaces in Electric Contact

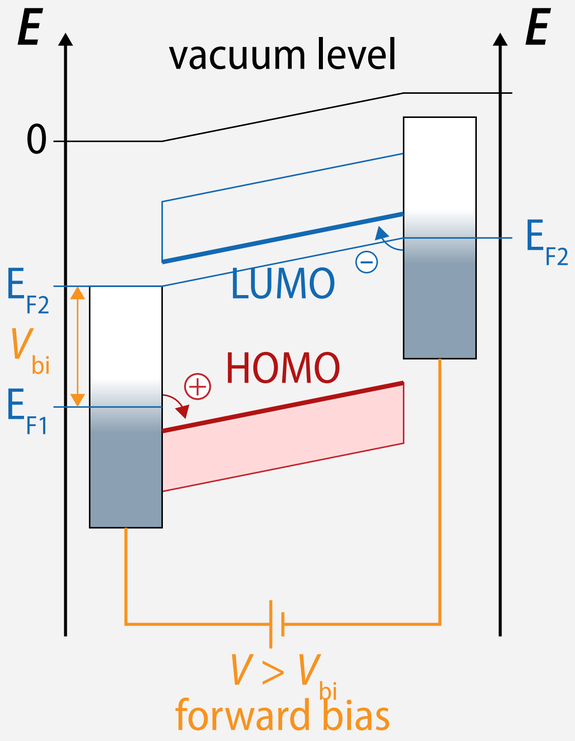
- flat & unaltered HOMO/LUMO levels as long as two (different) electrodes not connected
- built-in potential V_{bi} corresponds to difference in the Fermi levels of the electrodes

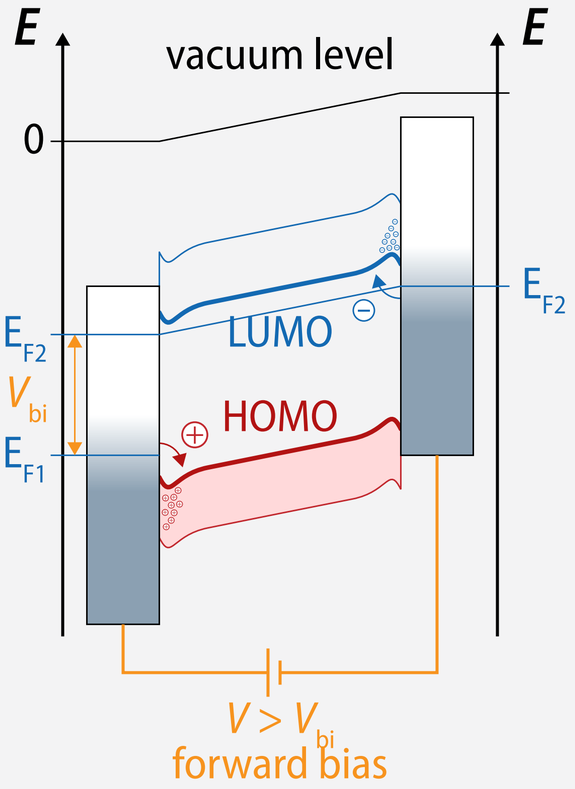


- **upon external connection, charges flow to equilibrate the Fermi levels of the electrodes**
- **potential drop across the organic semiconductor layer according to $dU = -e\,(V_{bi}/x_0)\,dx$**
- **charge injection from the electrodes only possible for forward bias $V > V_{bi}$**

Band Bending

- metal electrodes form “Ohmic contact” with organic semiconductor
- anode (cathode) has an unlimited capacity to inject holes (electrons)

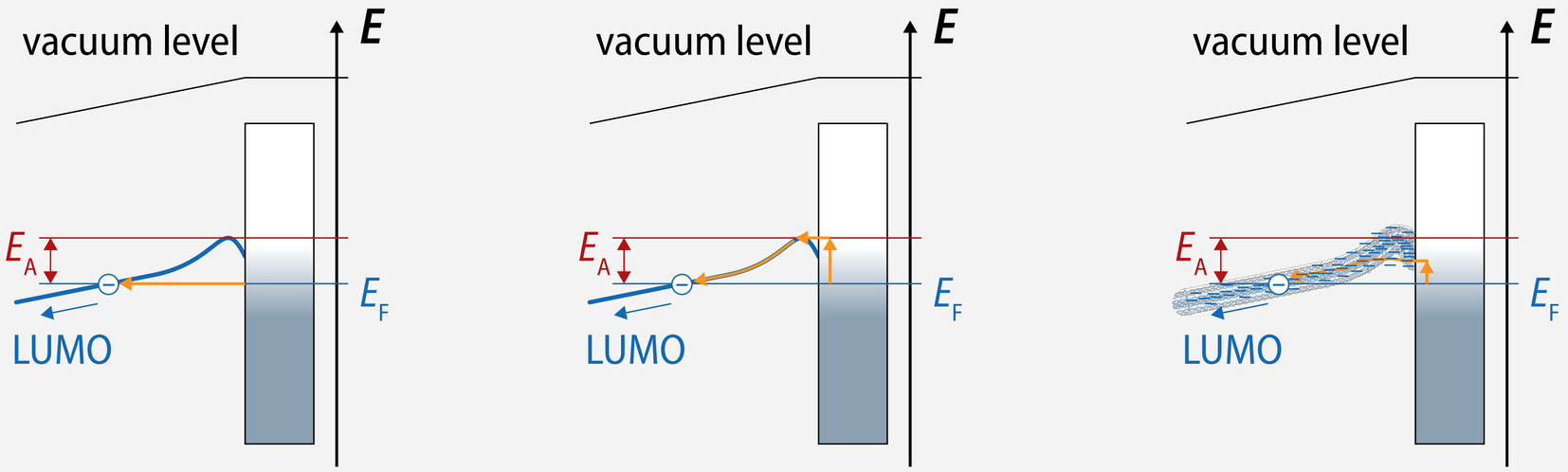




- **formation of a “space charge layer” results in additional potential, “band bending”**
- **layer width $W \propto \varepsilon_r^{1/2}$, therefore smaller for organic materials, about 10–30 nm**

Band Bending

- activation energy barrier E_A for injection due to work function mismatch and band bending



Fowler-Nordheim tunneling

Richardson-Schottky thermionic injection

hopping injection into disordered semiconductor

- **tunneling: at high applied electric field electrons can quantum-mechanically tunnel through the narrow (5–10 nm) triangular barrier**
- **thermionic emission: electrons are thermally excited above the activation barrier and diffuse out of the interface**
- **hopping: in a disordered material, the energy distribution of localized states offers pathways with lower thermal activation via “trap states”**

Learning Outcome

- **metal electrodes in contact with organic semiconductor**
  - work function of the metal should be close to active transport region
  - high work function (noble metals) for hole injection/extraction
  - low work function metals for electron injection/extraction
  - Ohmic “metal-insulator”-type contact results in space charge layer and band bending
- **energy barrier for charge injection due to work function mismatch and band bending**
  - energy barrier can be overcome in case of a “forward bias” electric field
  - injection possible via tunneling, thermionic injection, or hopping
  - injection most commonly occurs by hopping, making use of “trap states”