Modern Methods in Heterogeneous Catalysis Research

Charge transport in catalysis

*10th January 2014*

Maik Eichelbaum / FHI

Outline

1. Introduction: Some practical examples

2. Semiconductors

3. Surface states and space charge

4. Bulk-surface charge transfer

5. Literature

1. Introduction

Experimental hints for the participation of "lattice" oxygen (oxygen covalently bound to the active transition metal ion) and "lattice" charge carriers in the reaction:

1) Reaction runs (awhile) without gas phase oxygen present (riser reactor concept)

2) Different oxidation states of the transition metal are monitored in dependence on the partial pressures of reaction gases or on contact time

3) By using $^{18}O_2$ in isotope exchange experiments, first ^{16}O (from the catalyst) is found in the reaction product, and only after some time ^{18}O

4) After long $^{18}O/^{16}O$ exchange, ^{18}O is found in the catalyst lattice (e.g. in ToF-SIMS or Raman experiments)

5) Conductivity changes upon reaction conditions, correlation between conductivity and activity/selectivity for differently doped semiconductors
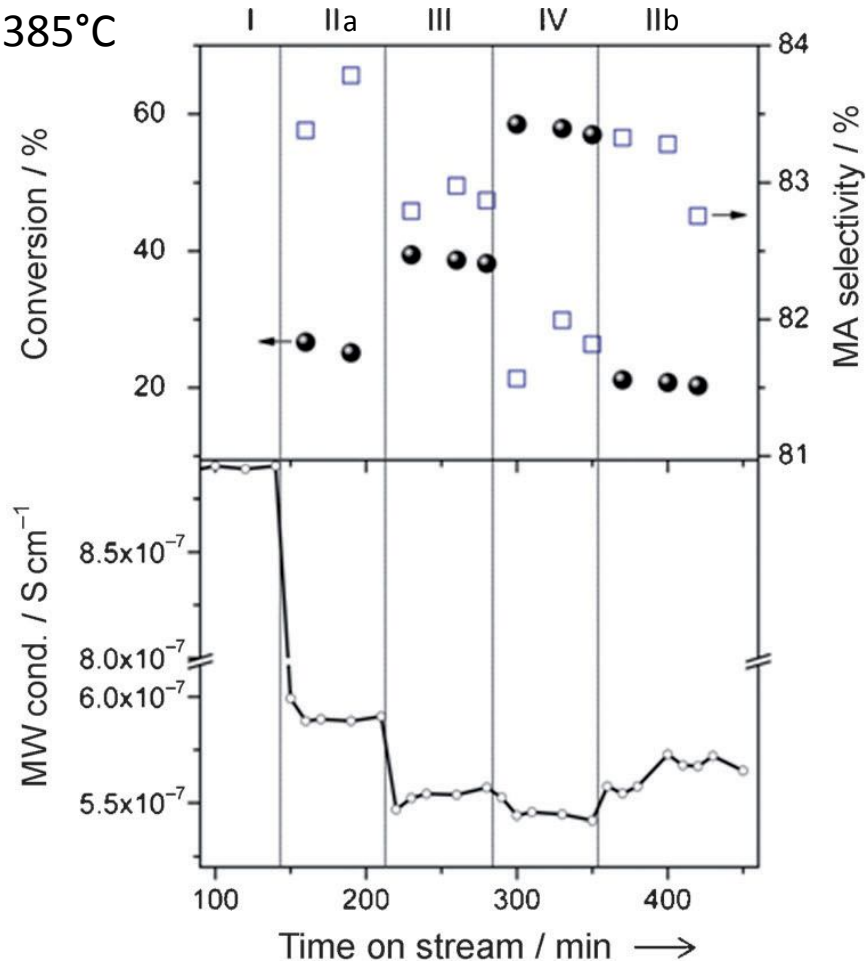
1. Introduction

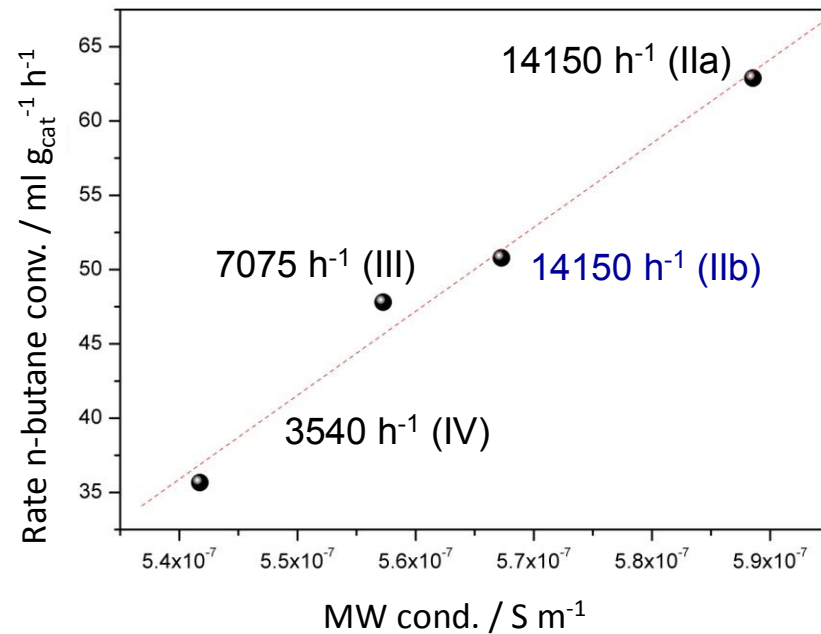**n-butane**   **maleic anhydride**

$$C_4H_{10} + 7/2\ O_2 \xrightarrow{VPP} C_4H_2O_3 + 4\ H_2O$$
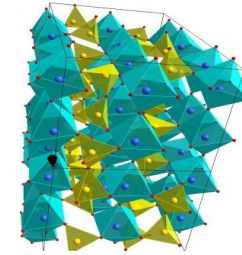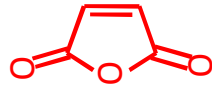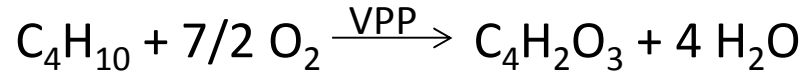
385°C

I: 100% N_2, GHSV: 14150 h^{-1}

II: 2% n-C_4H_{10}, 20% O_2 in N_2, GHSV: 14150 h^{-1} (a,b)

III: 2% n-C_4H_{10}, 20% O_2 in N_2, GHSV: 7075 h^{-1}

IV: 2% n-C_4H_{10}, 20% O_2 in N_2, GHSV: 3540 h^{-1}

→ **Relationship between conductivity and activity**

1. Introduction

MoVTeNbO$_x$ M1

T/°C

GHSV: 16980 12730 8490 4240 16980   *in h^{-1}*

395°C

N$_2$ **1.5% n-butane; 18% O$_2$**   N$_2$

S$_{MA}$ ≈ 30%

MW cond. $(\varepsilon_0 \omega)^{-1}$

n-butane conversion / %

Time on stream / min

Rate n-butane conv. / ml g$_{cat}^{-1}$ h^{-1}

16980 h^{-1} (a)
16980 h^{-1} (b)
12730 h^{-1}
8490 h^{-1}
4240 h^{-1}

MW cond. / S cm^{-1}

→ **Relationship between conductivity and activity**

C. Heine et al.

Neuere Gedanken zur Natur der heterogenen Katalyse

Von Prof. Dr. GEORG-MARIA SCHWAB[1])

Physikalisch-Chemisches Institut der Universität München

In letzter Zeit sind nähere Aufschlüsse über die Natur der Grenzflächenkatalyse durch die Anwendung der Festkörperphysik erreicht worden. Versuche an Legierungen haben gezeigt, daß die Aktivierung in einem Übergang von Elektronen entweder zum oder vom Katalysator besteht. Inzwischen haben diese Gesichtspunkte sich auch auf halbleitende Oxydkatalysatoren übertragen lassen. Die Chemisorption ist somit als Elektronenübergang deutbar. Verschiedene neuere Einzelfälle werden beschrieben.

1. Introduction

Dehydrogenation of formic acid with different bronze alloys: **activation energy** and **resistivity**
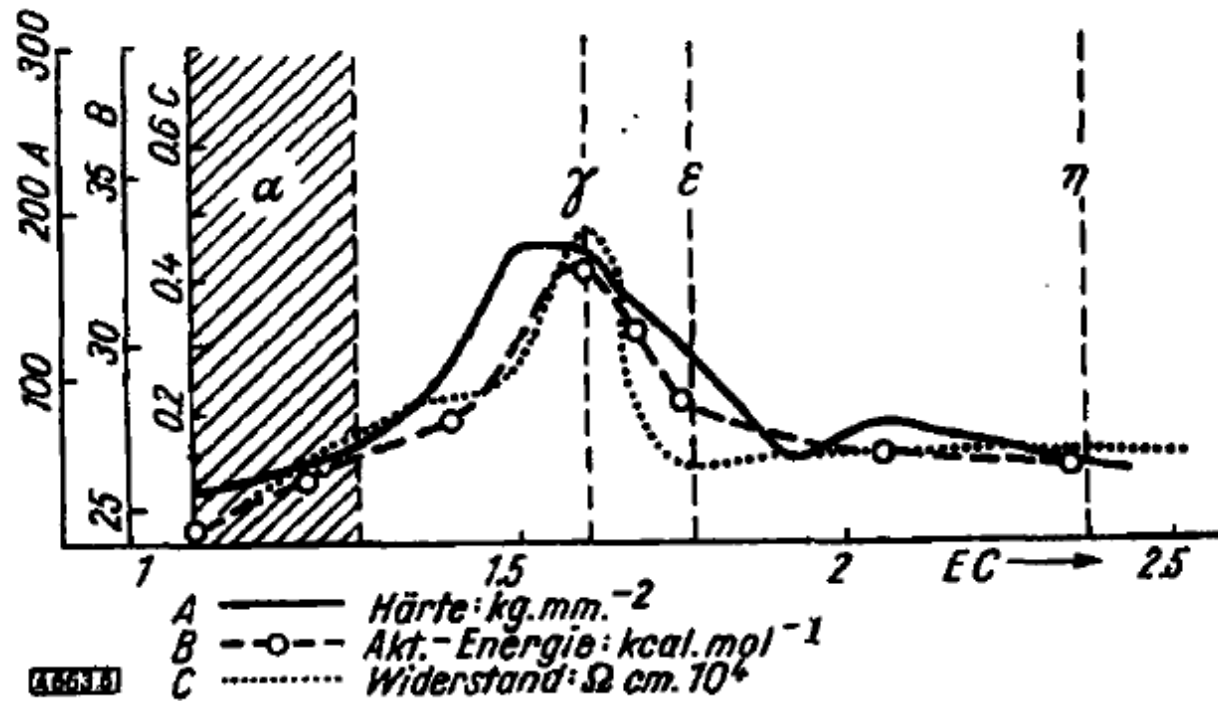
$$HCOOH \rightarrow CO_2 + H_2$$

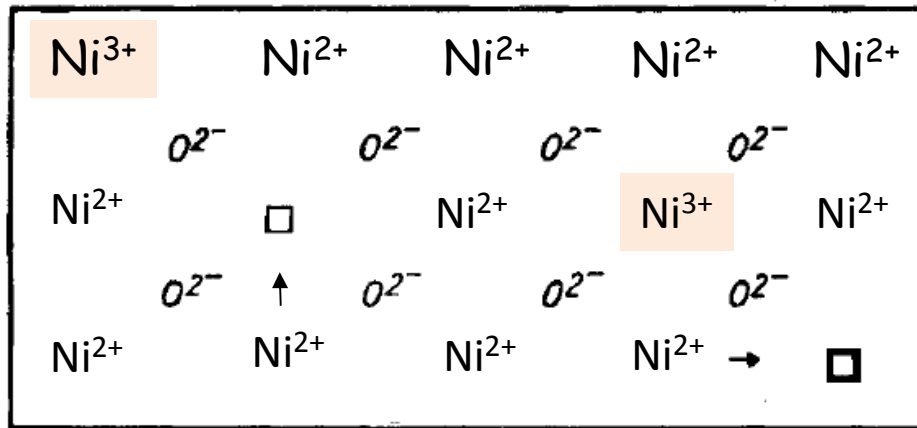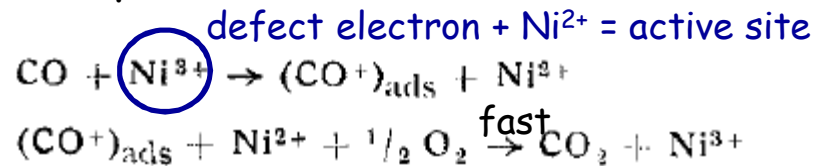| A | ——————— | Härte: $kg.mm.^{-2}$ |
| B | --o-- | Akt.-Energie: $kcal.mol^{-1}$ |
| C | ·········· | Widerstand: $\Omega\ cm.\ 10^4$ |

Bild 6

Aktivierungsenergie, Widerstand und Härte bei Bronzen
verschiedener Elektronenkonzentration EC

1. Introduction

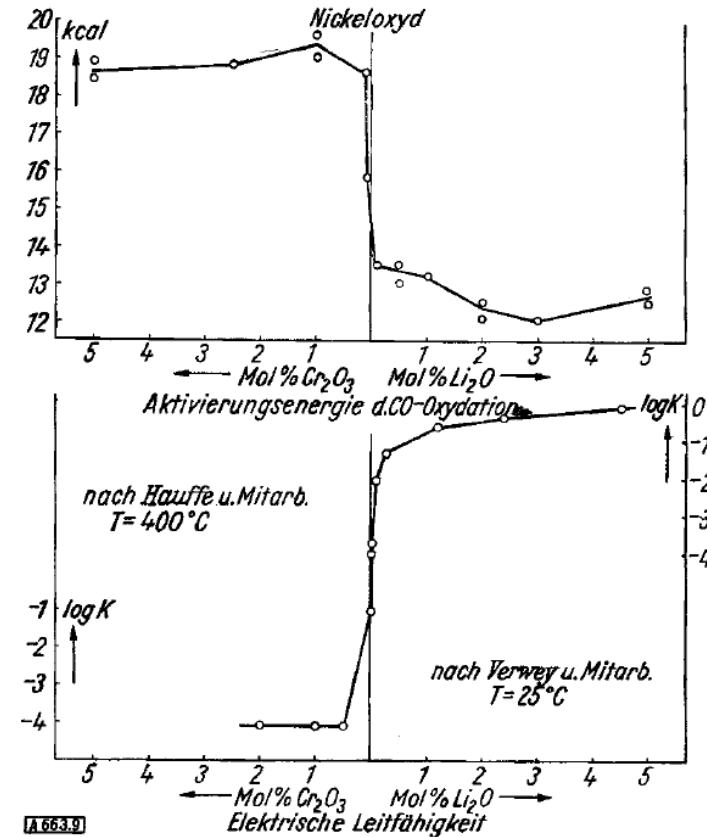Defect electrons (holes) in NiO (with O excess): **p-type semiconductor**

Increase of defect electrons by Li_2O, decrease by Cr_2O_3 addition:
$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

Ni^{3+}	Ni^{2+}	Ni^{2+}	Ni^{2+}	Ni^{2+}
O^{2-}	O^{2-}	O^{2-}	O^{2-}	
Ni^{2+}	□	Ni^{2+}	Ni^{3+}	Ni^{2+}
O^{2-} ↑	O^{2-}	O^{2-}	O^{2-}	
Ni^{2+}	Ni^{2+}	Ni^{2+}	Ni^{2+} →	■

Explanation: donor reaction

defect electron + Ni^{2+} = active site

$$CO + Ni^{3+} \rightarrow (CO^+)_{ads} + Ni^{2+}$$
$$(CO^+)_{ads} + Ni^{2+} + {}^1/_2 O_2 \xrightarrow{fast} CO_2 + Ni^{3+}$$

→ *CO chemisorption rate-determining*

Nickeloxyd

Mol% Cr_2O_3 Mol% Li_2O
Aktivierungsenergie d.CO-Oxydation

nach Hauffe u.Mitarb.
T= 400°C

nach Verwey u.Mitarb.
T= 25°C

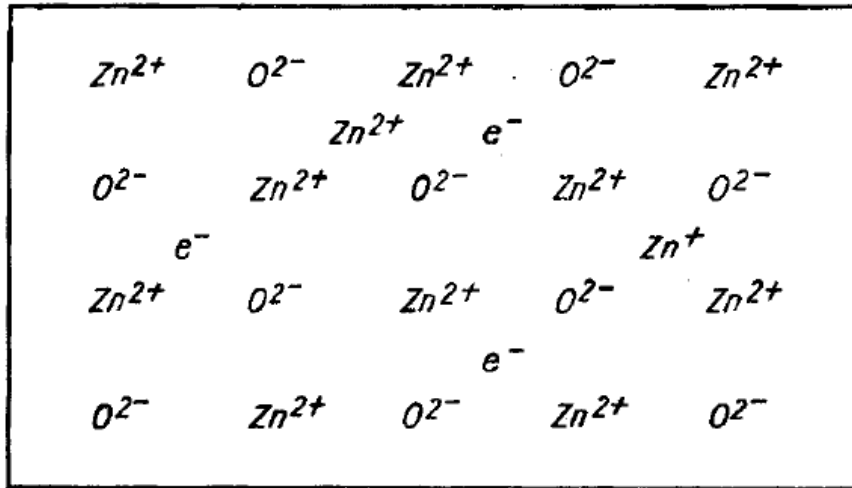Mol% Cr_2O_3 Mol% Li_2O
Elektrische Leitfähigkeit

A 663.9

Bild 9
Leitfähigkeit und Aktivierungsenergie an dotiertem NiO

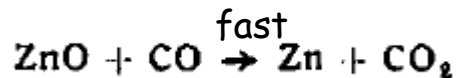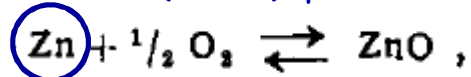# 1. Introduction

Excess electrons in ZnO (with Zn excess): **n-type semiconductor**

Explanation: acceptor reaction

Zn^{2+} + (1 or 2) quasi-free electrons = active site

$$Zn + \tfrac{1}{2} O_2 \rightleftarrows ZnO \, ,$$

fast
$$ZnO + CO \rightarrow Zn + CO_2$$

→Oxidation of active site rate-determing (strong influence of oxygen on rate)

Increase of quasi-free electrons by Ga_2O_3, decrease by Li_2O addition:
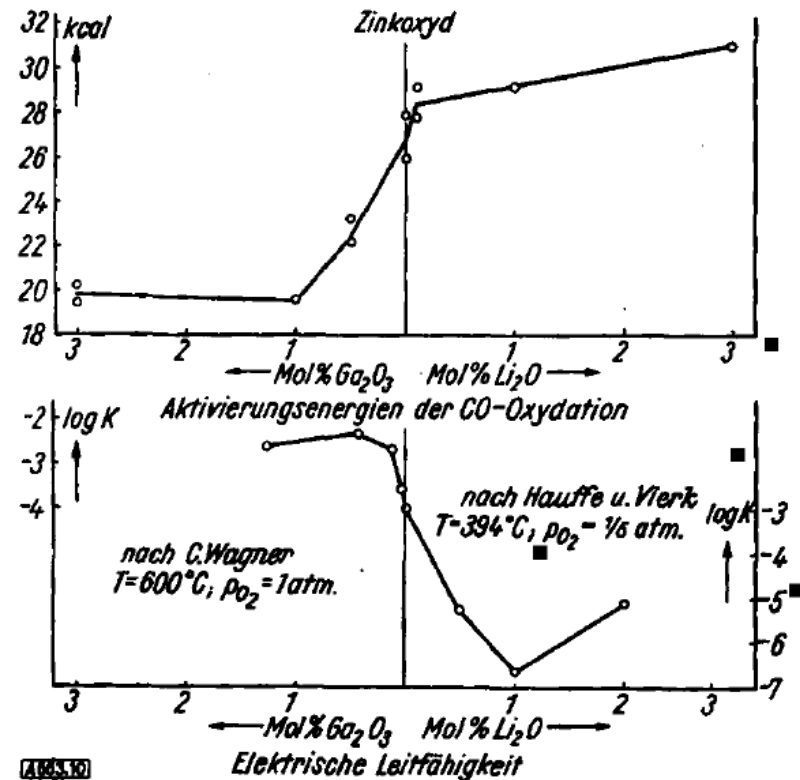$$CO + \tfrac{1}{2} O_2 \rightarrow CO_2$$

Bild 10

Leitfähigkeit und Aktivierungsenergie an dotiertem ZnO

1. Introduction

✖ Oxidation catalysts are most often metal oxides, and most oxides are semiconductors!

- n-type semiconductor oxides contain anionic vacancies (V_O^{2-}) associated with deficit anionic oxygen
- p-type semiconductor oxides contain positive holes (h^+) as charge carriers associated with excess anionic oxygen

✖ Semiconductors: electrical conductivity varies exponentially with increasing temperature:
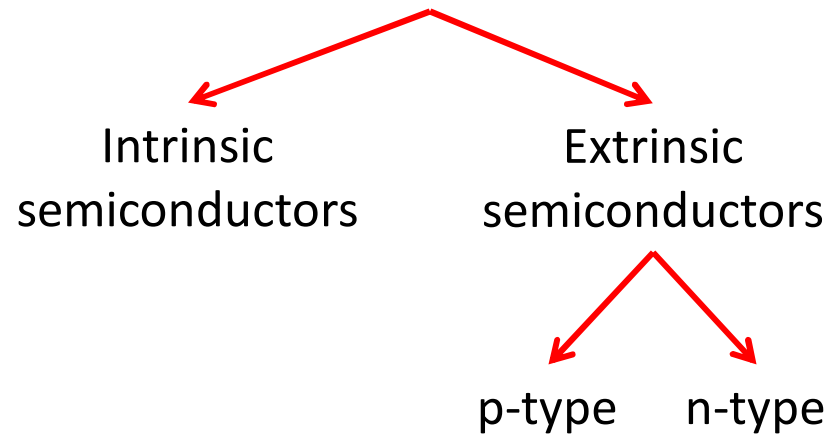
$\sigma = \sigma_0 \exp(-E_c/RT)$
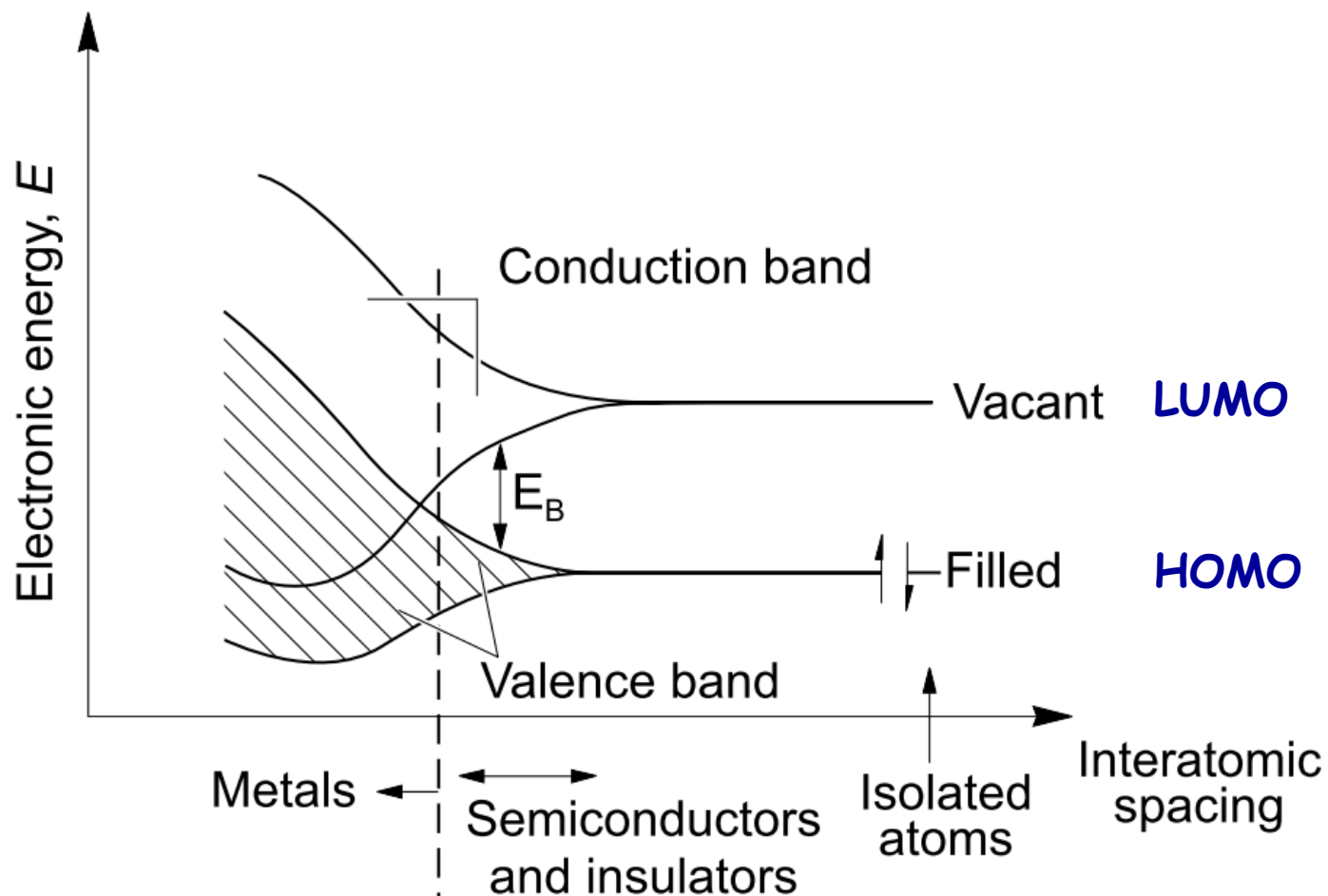
1. Introduction

Electric conductivity

10^{-14} 10^{-12} 10^{-4} 10^{-2} 1 10^{6} 10^{35}

$\sigma/\Omega^{-1}cm^{-1}$

insulators   Semiconductors   pseudometallic   metals and alloys   superconductors

Metal oxide catalysts

Intrinsic semiconductors   Extrinsic semiconductors

p-type   n-type

Some semiconductor theory

2. Semiconductors

A. W. Bott, *Current Separations* **1998**, *17*, 87

2. Semiconductors

Occupancy of electrons in a band is determined by **Fermi-Dirac statistics**

Fermi-Dirac distribution (for an electron gas):

$$f(E) = \cfrac{1}{\exp\left(\cfrac{E - \mu}{k_B T}\right) + 1}$$

$\mu\,(T = 0) = E_{\text{Fermi}}$

$f(E = \mu) = 1/2$

= Fermi level

E...Energy

k_B...Boltzmann constant

T...Temperature

μ...(Electro-)Chemical
potential

Vacuum level

Population density
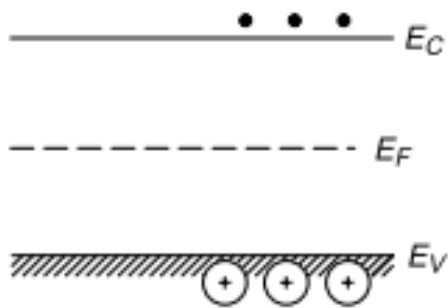
W_A
(work function)

Conduction band
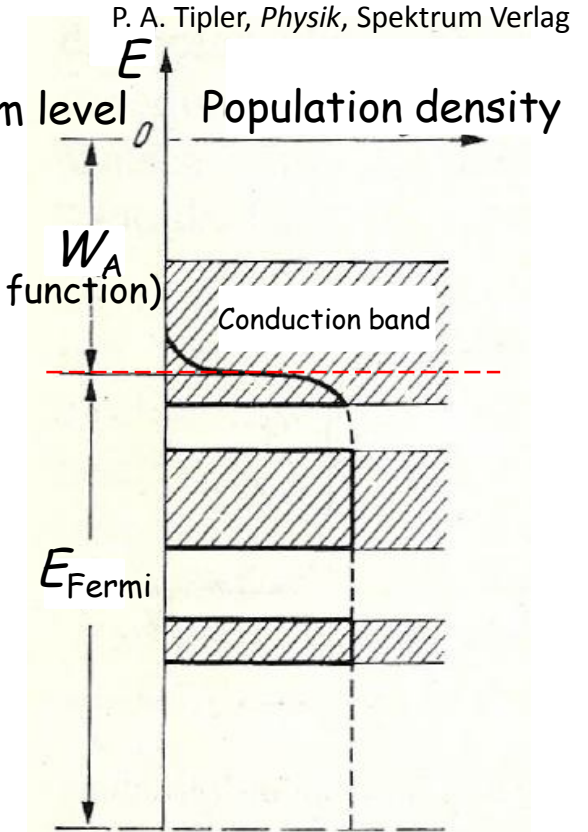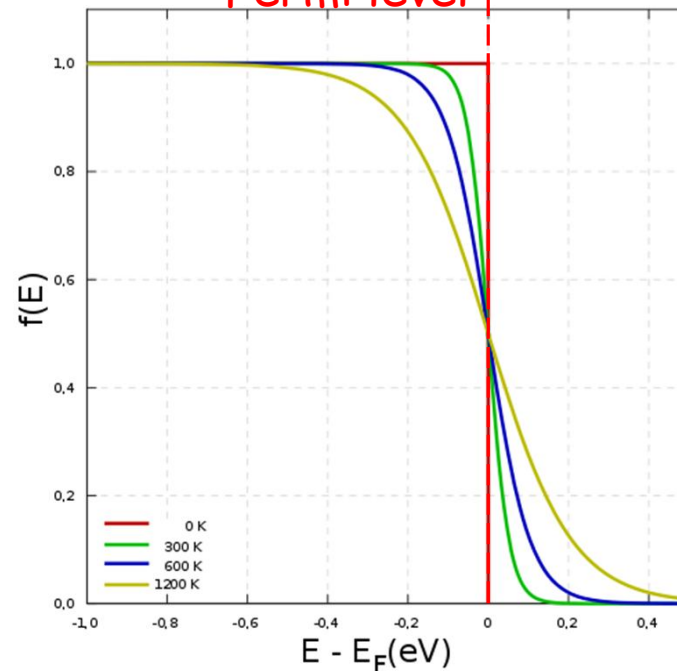
E_{Fermi}

The Fermi curve determines the population of occupied states, independent of the existence of states in the regarded E region

2. Semiconductors
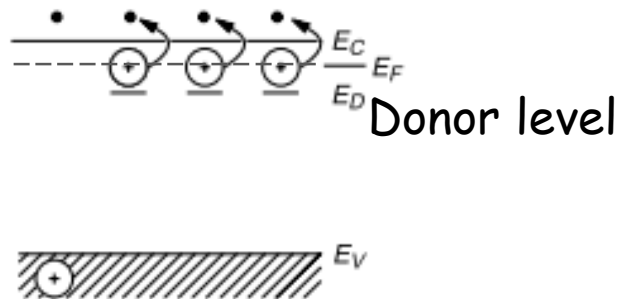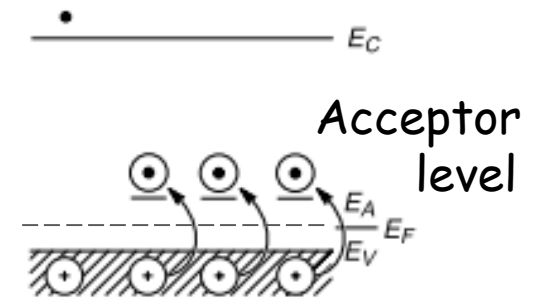
Intrinsic semiconductor

E_C

E_F

E_V

e.g. Si (band gap at 300 K = 1.12 eV)
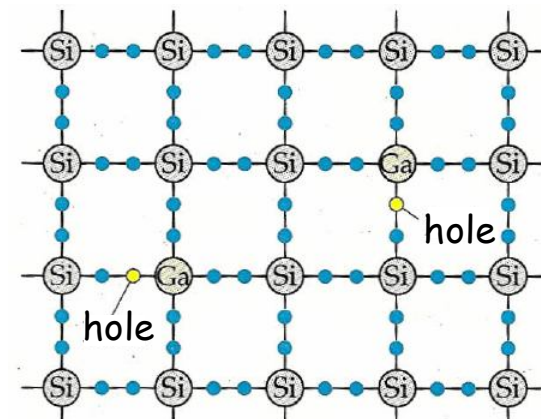
(Extrinsic) n-type semiconductor

E_C

E_F

E_D Donor level

E_V

e.g. As-doped Si

additional electrons

(Extrinsic) p-type semiconductor

E_C

Acceptor level

E_A

E_F

E_V
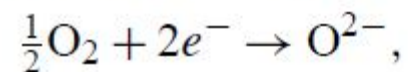
e.g. Ga-doped Si

hole

hole
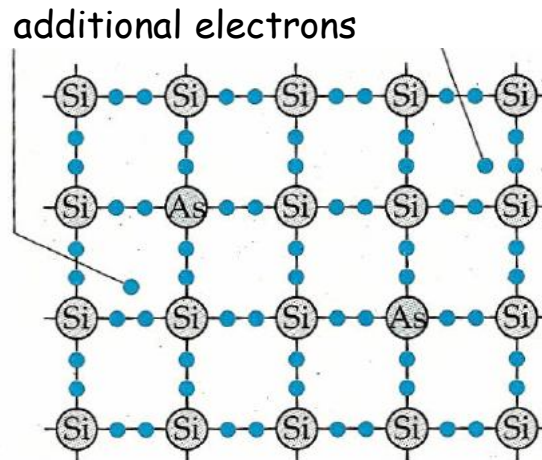
2. Semiconductors

Selective oxidation of hydrocarbons, consideration of bands and frontier orbitals:

$$RH + O^{2-} \rightarrow R{-}O^{-} + H^{+} + 2e^{-},$$
$$\tfrac{1}{2}O_2 + 2e^{-} \rightarrow O^{2-},$$
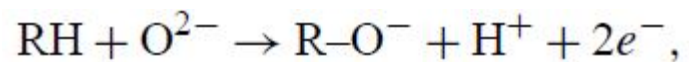
Rigid band assumption (no local surface states)
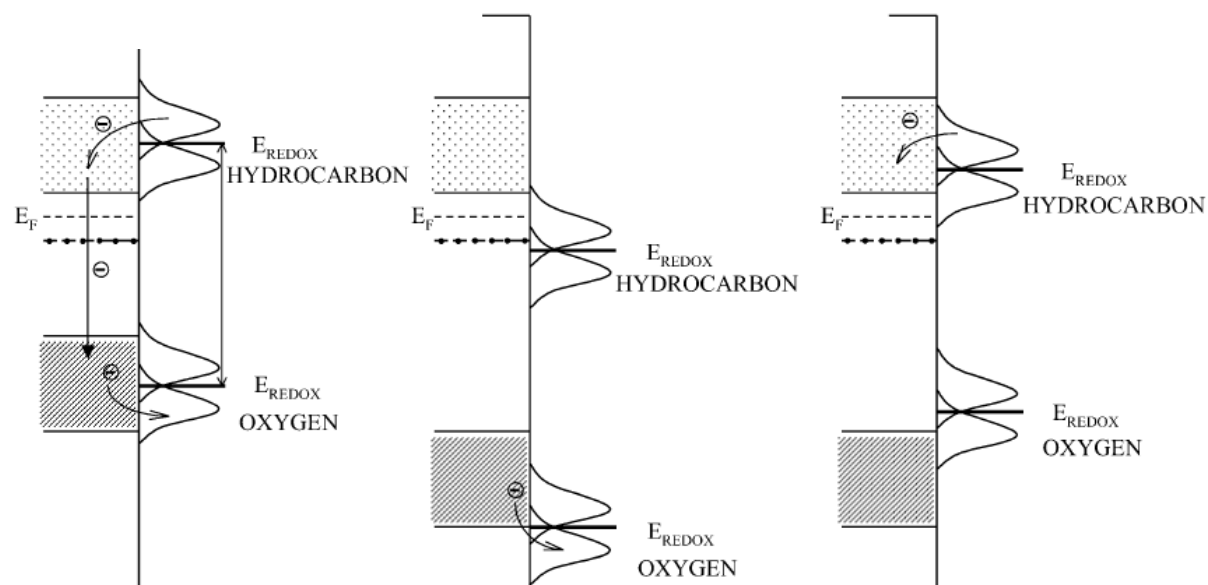
CATALYTIC OXIDATION OF HYDROCARBON MOLECULE CAN PROCEED

CATALYTIC OXIDATION OF HYDROCARBON MOLECULE CANNOT PROCEED, BECAUSE THE MOLECULE IS NOT ACTIVATED

CATALYTIC OXIDATION OF HYDROCARBON MOLECULE CANNOT PROCEED, BECAUSE THE CATALYST IS NOT REOXIDIZED

J. Haber, M. Witko, *J. Catal.* **2003**, *216*, 416-424

2. Semiconductors

V$_2$O$_5$/P$_2$O$_5$ 1-butene→maleic anhydride

Nakamura et al., *J. Catal.* **1974**, *34*, 345
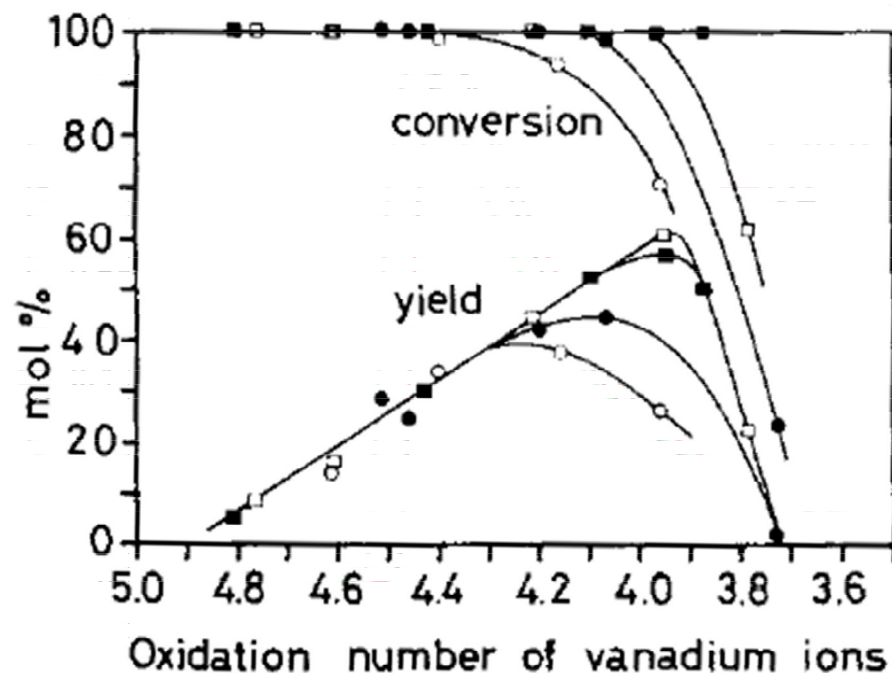
XP spectrum of VPP:
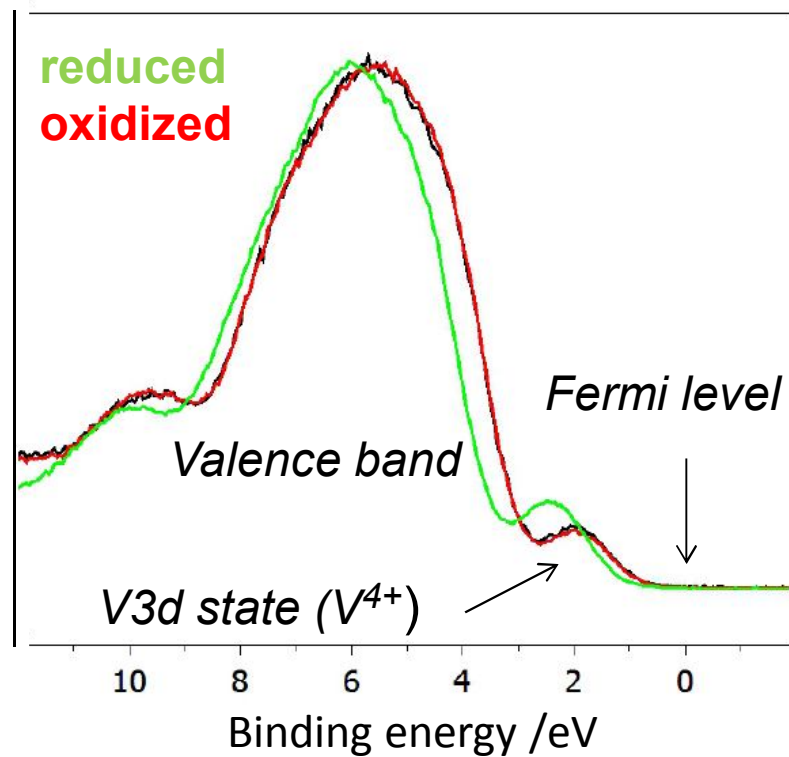
- Rate limiting: reduction of O$_2$
- High V^{4+}/V^{5+} ratio → V^{4+}/V^{5+} band almost completely occupied → highest Fermi energy → most rapid O$_2$ reduction
- Empty levels needed for electron injection from olefin

Catalysis occurs at interfaces: the formation of surface states and space charge regions

Atomistic model:

(a)

O_2^-	O_2^-	O_2^-	O_2^-
M^+	M^+	M^+	M^+
M	M	M	M
M	M	M	M
M	M	M	M

O_2^-		O_2^-	O_2^-
Ge	Ge	P^+	Ge
Ge	Ge	Ge	Ge
Ge	P^+	Ge	Ge
Ge	Ge	Ge	P^+

surface charge Q

(space) charge density ρ

Double layers: parallel plate   space charge model
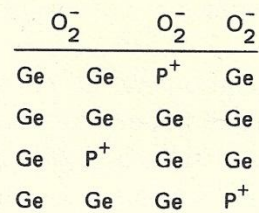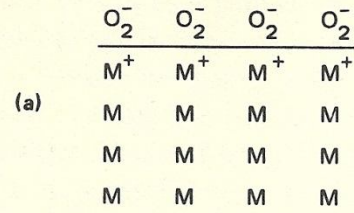
Band model:

(b)

O_2^- — E_F

O_2^- —

$|eV_s|$ surface barrier
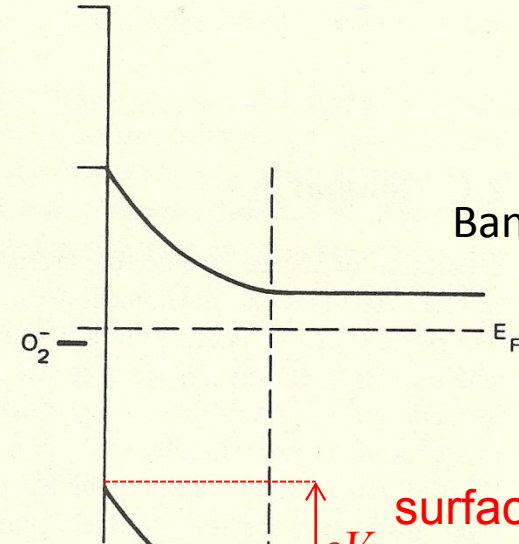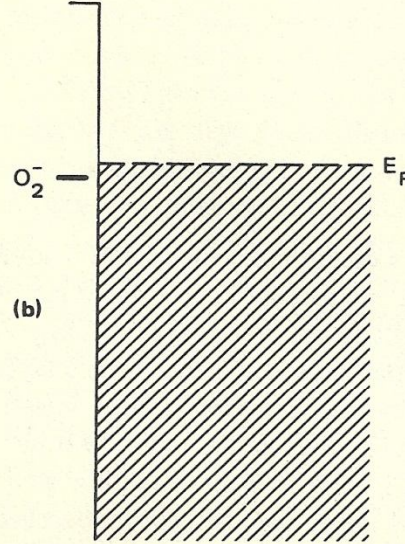
$x_0 = \sqrt{\dfrac{\varepsilon\varepsilon_0 k_B T}{2\pi q^2 n_i}}$

Band bending function:

$$V = \phi_{bulk} - \phi$$

$x = 0; V = V_s:$

$$\frac{dV}{dx} = \frac{Q}{\varepsilon\varepsilon_0}$$

Potential:

(c)

ϕ

ϕ — ϕ_{bulk}

x_o

$$\frac{d^2\phi}{dx^2} = -\frac{\rho}{\varepsilon\varepsilon_0}$$

$x = 0:$

$$\frac{d\phi}{dx} = -\frac{Q}{\varepsilon\varepsilon_0}$$

Morrison, *The chemical physics of surfaces*
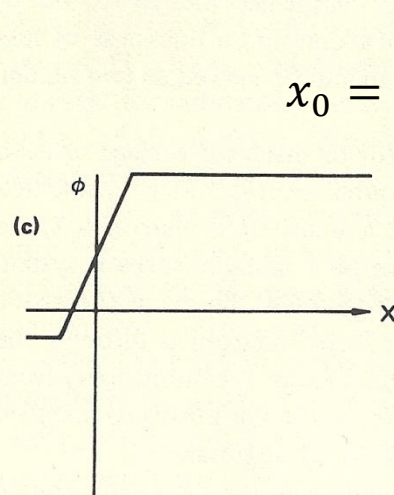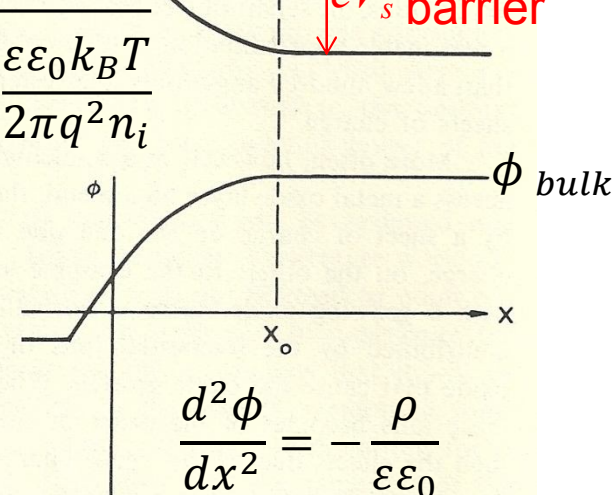
3. Surface states and space charge

Models for the adsorbate/solid bond

Weak   *Intermediate*   *Strong*

Interaction

Rigid band model   Atomistic model

antibonding orbital

bonding orbital

E

DOS

Electronic state of an adsorbate atom

Local density of states (LDS) of a surface atom on solid

3. Surface states and space charge

Broadening of molecular orbitals of adsorbing species into (apparent) bands can occur through several mechanisms:

1) Heterogeniety of surface sites
2) Overlap of the orbitals of the adsorbate
3) Temporal fluctuations due to the presence of polar species
4) Interaction of the molecular orbitals of the adsorbate with the bands of the solid

3. Surface states and space charge

Surface states of a 3D crystal
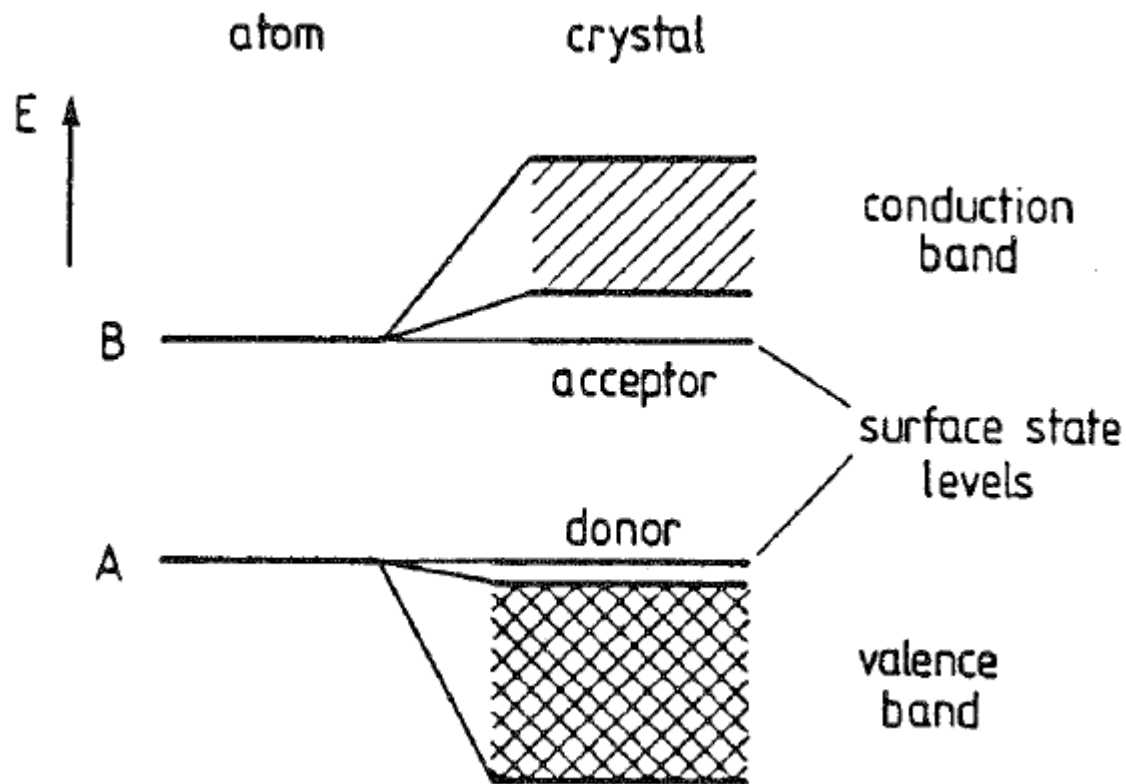
Intrinsic surface states: On ideal surfaces (perfect termination with 2D translational symmetry)

Extrinsic surface states: On surfaces with imperfections (e.g. missing atom)

3. Surface states and space charge

Sources of surface states:

Figure 1.4. Some sources of heterogeneity in adsorption sites.

Morrison, *The chemical physics of surfaces*
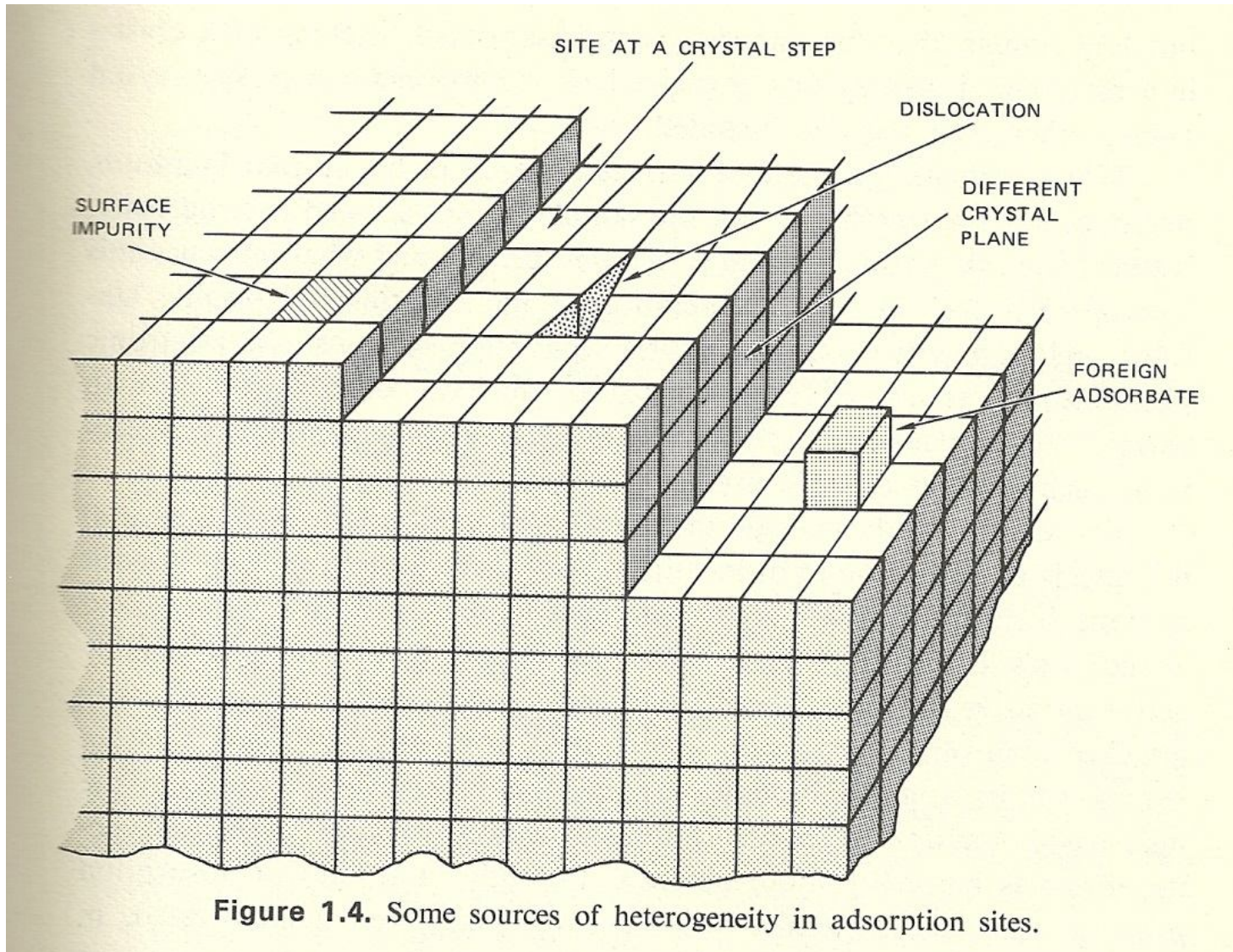
3. Surface states and space charge

Surface states in the rigid band model

Intrinsic states
(e.g. Shockley states, Tamm states)
- Broken periodicity on the surface
- Undercoordinated surface atoms
- Surface termination with translational symmetry
- Relaxed, reconstructed or relocated surface

Extrinsic states
(e.g. adsorbates, defects, dislocations, surface enrichment of bulk impurities)
- Heterogeneous surface without translational symmetry

3. Surface states and space charge

Blocking grain boundary → formation of space charge region
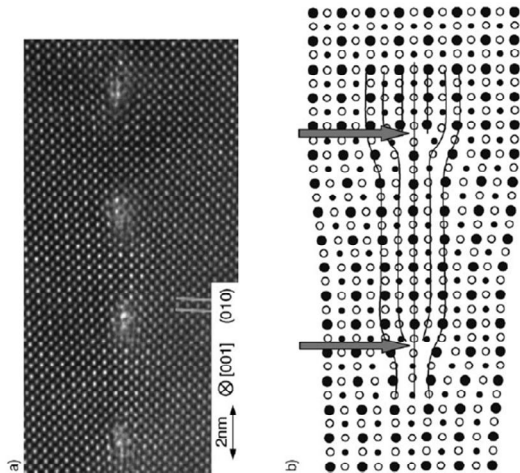
Localized Impedance Spectroscopy

SrTiO$_3$

R. Merkle, J. Maier, *Angew. Chem. Int. Ed.* 2008, 47, 3874−3894
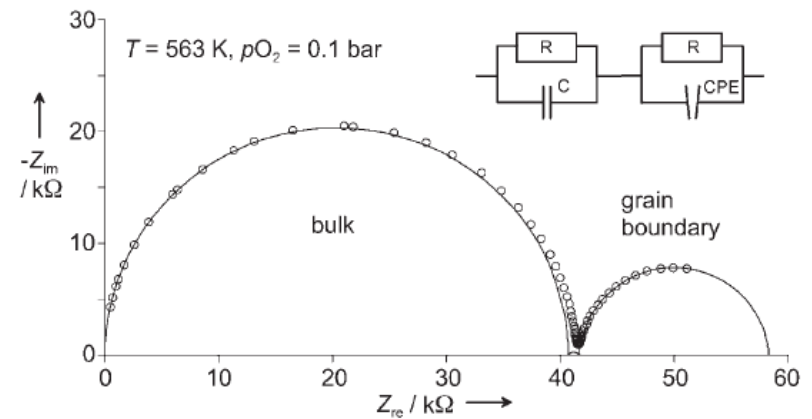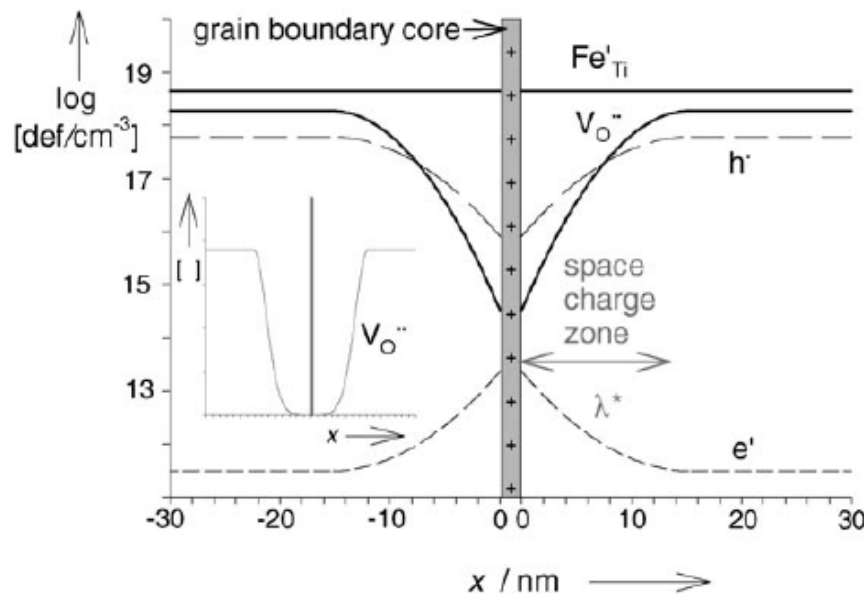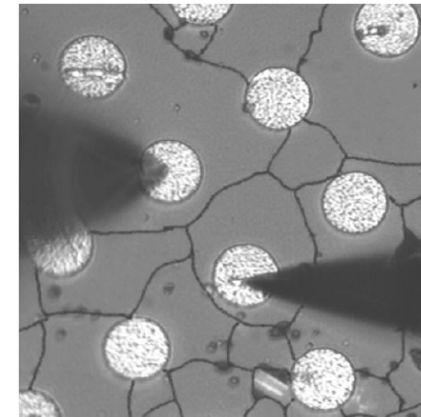
3. Surface states and space charge

Redox couples on surfaces forming surface states:
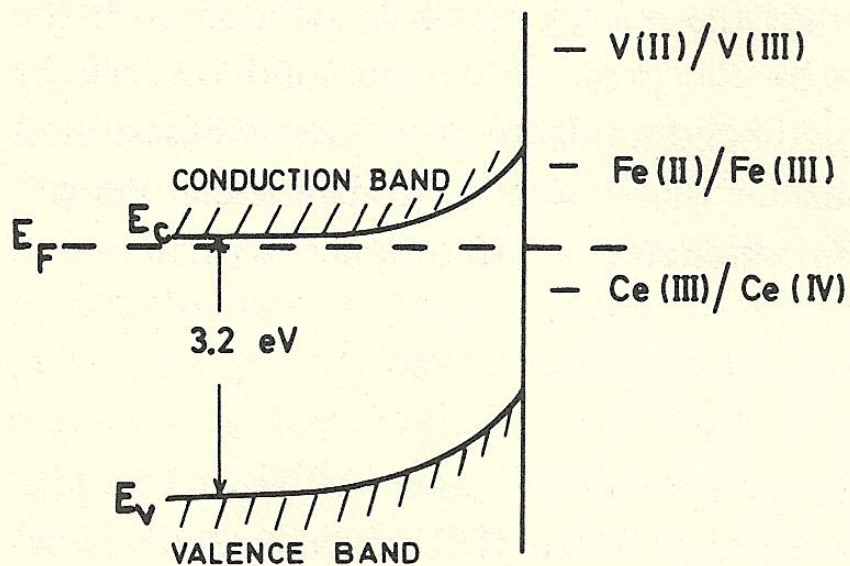
Figure 1.1. Surface states of chemical couples, to illustrate the expected energy level as the chemical properties of the species is varied. ZnO is used as the example semiconductor; the indicated position of the surface states relative to the bands is discussed further in the text.

Morrison, *The chemical physics of surfaces*

3. Surface states and space charge

Flatband situation (not equilibrated):
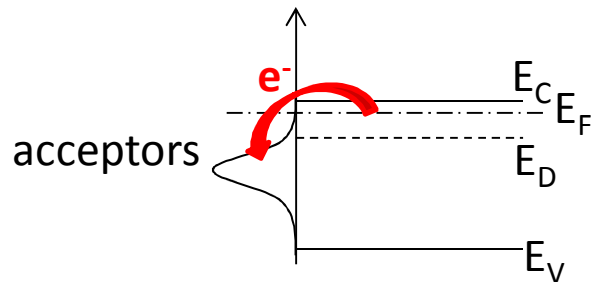
Build-up of negative charge in surface acceptor state is compensated by oppositely charged space charge region

Formation of (depletion) space charge layer:

Space charge (to compensate surface charge)

Surface state charge
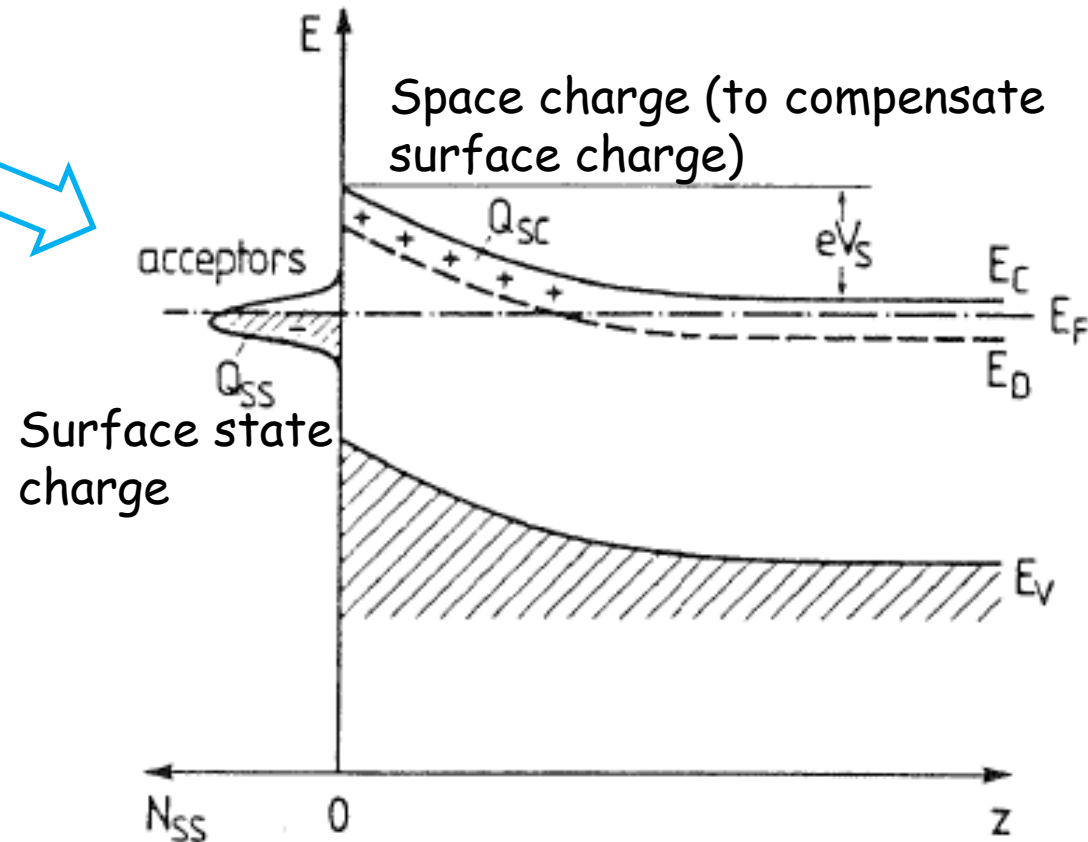
Neutrality condition $\boxed{Q_{ss} = -Q_{sc}}$ determines the Fermi level

H. Lüth, *Solid Surfaces, Interfaces and Thin Films*, Springer **2001**

3. Surface states and space charge

n-SC:

Band schemes:
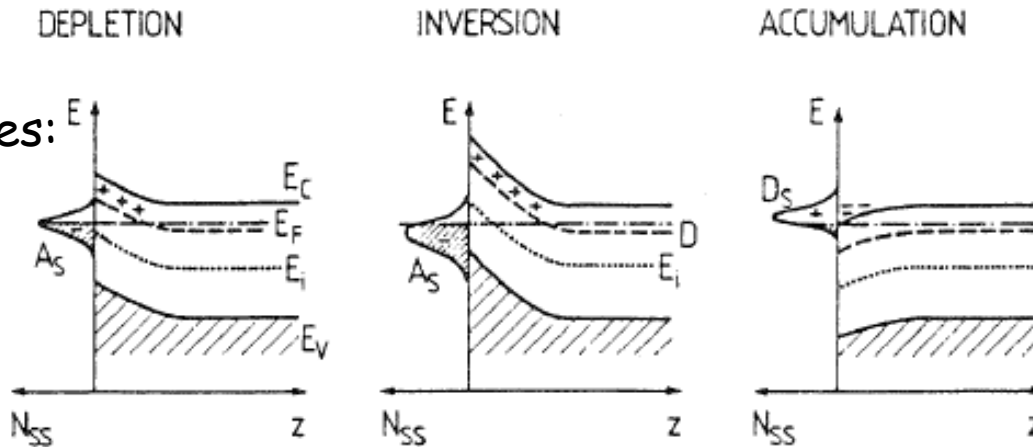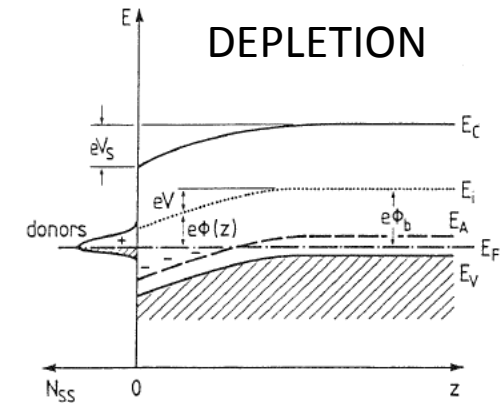
Free charge carrier densities:

Local conductivity:

p-SC:

DEPLETION   INVERSION   ACCUMULATION   DEPLETION

H. Lüth, *Solid Surfaces, Interfaces and Thin Films*, Springer **2001**
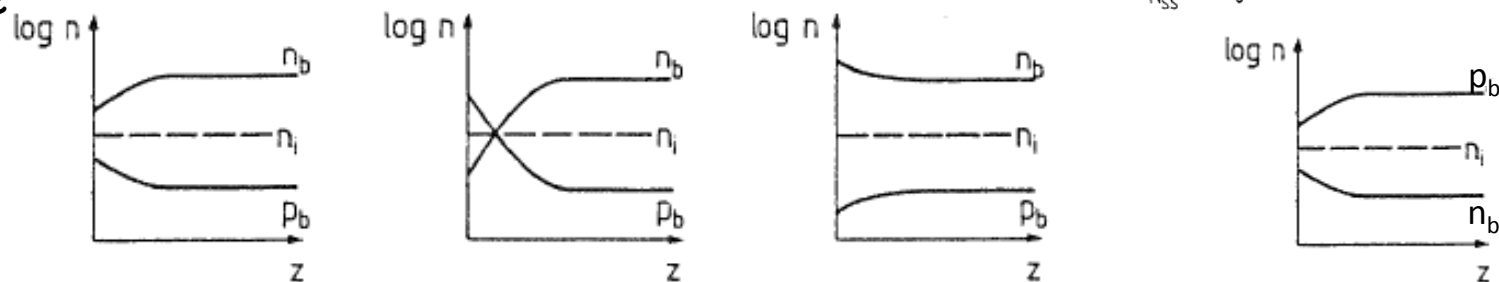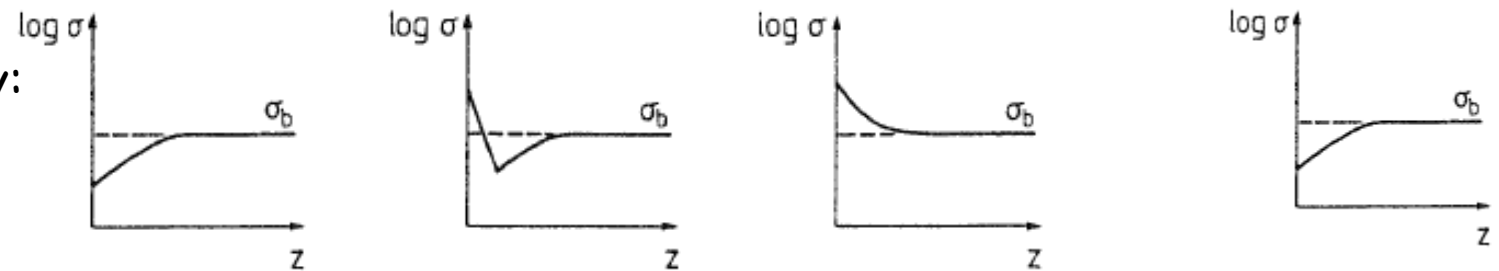
3. Surface states and space charge

Surface Fermi energy can be pinned by

1) **Surface states**

2) **Partially filled narrow band (e.g. d-band)**

3) **Reactant**

high density of surface states

partially filled d-band or impurity band

reactant surface state
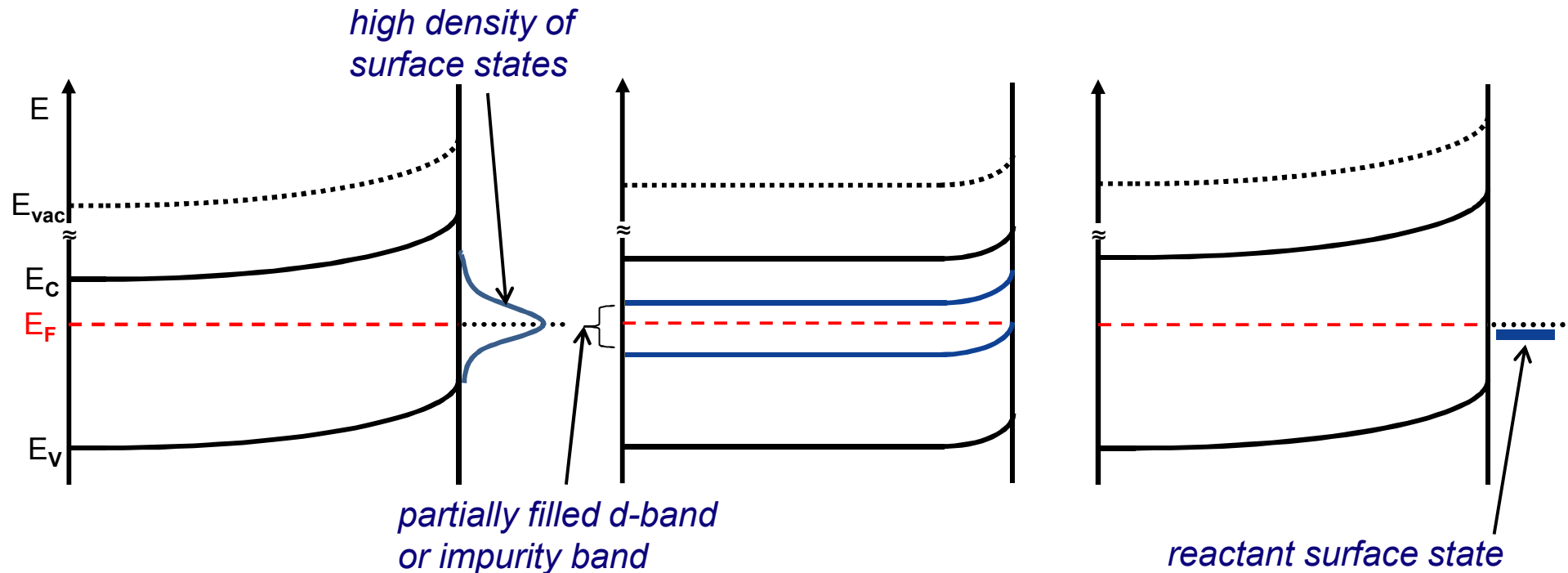
localized surface levels, e.g. Cr^{3+} on Cr_2O_3, Mn^{2+}/Mn^{3+} on MnO, O^-, foreign surface impurities

in many transition metal oxides, e.g. Co_2O_3, VO_2, impurity band associated with vacancies (bonding→surface molecule model)

little local interaction, direct electron exchange with conduction band, e.g. ZnO

Morrison, *The chemical physics of surfaces*

3. Surface states and space charge

Spectroscopic evidence? Semiconductor characterized by:

-the work function Φ
-the electron affinity χ
-the surface barrier eV_s (binding energy shift of valence band edge)
-the Debye length x_0 (width of depletion or accumulation layer)

-the conductivity: $\sigma(x) \approx en_e(x)\mu_e, \quad n_e = N_{eff}^C \, exp\left[-\dfrac{E_C(x) - E_F}{k\,T}\right]$

$$x_0 = \sqrt{\frac{\varepsilon\varepsilon_0 k_B T}{2\pi q^2 n_i}}$$
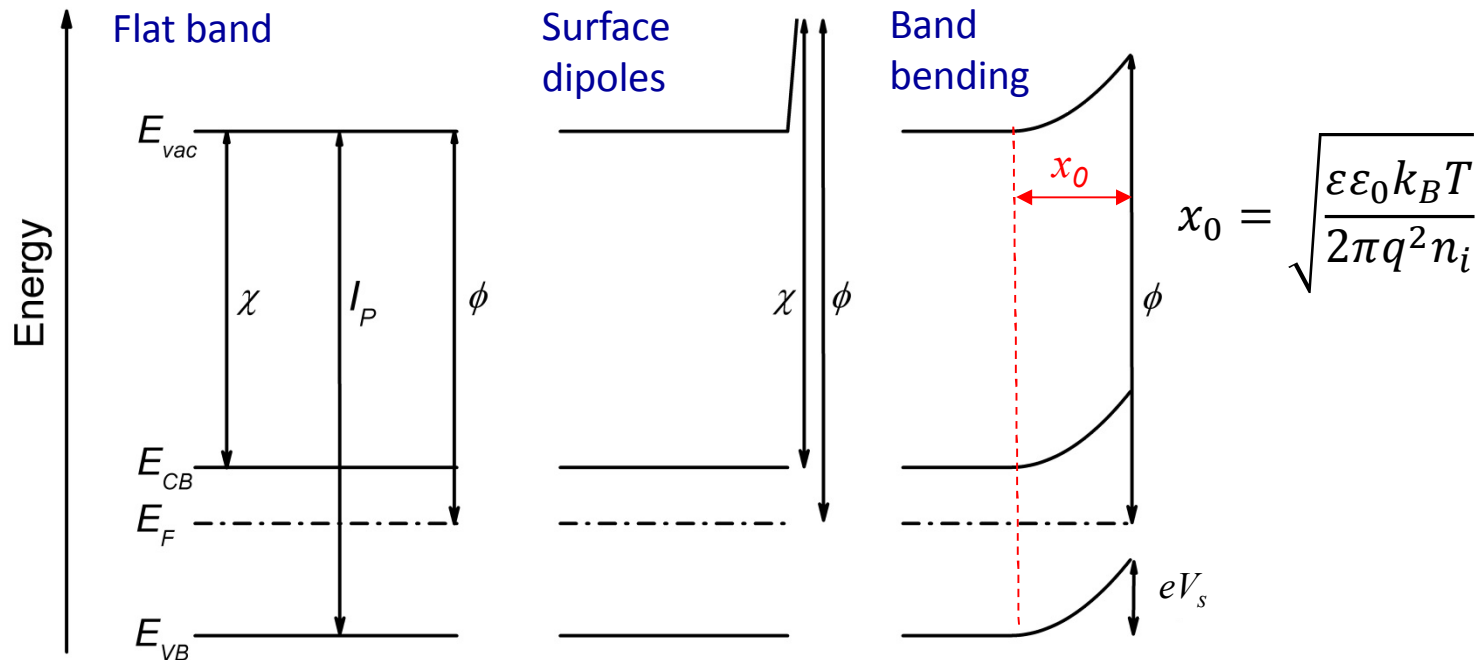
3. Surface states and space charge

Spectroscopic evidence? → Photoemission spectroscopy

Work function $\Phi = h\nu - E_{cutoff}$

Chapter: Surface Studies of Layered Materials in Relation to Energy Converting Interfaces. In: JÄGERMANN, W.:
Photoelectrochemistry and Photovoltaics of Layered Semiconductors. Dordrecht, Boston, London : Kluwer Academic Press, 1992

3. Surface states and space charge

n-butane   **maleic anhydride**

$$C_4H_{10} + 7/2\ O_2 \xrightarrow{VPP} C_4H_2O_3 + 4\ H_2O$$
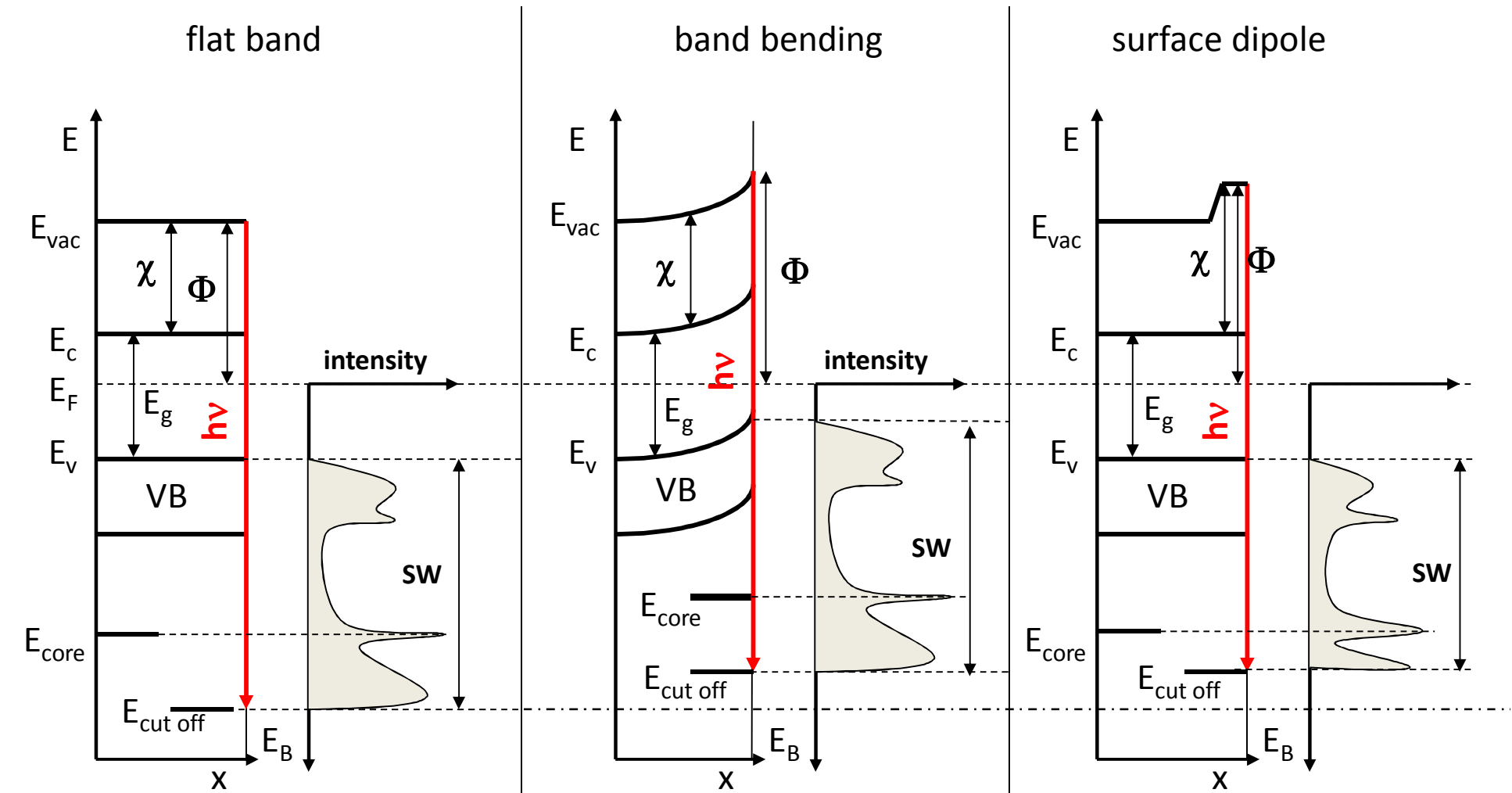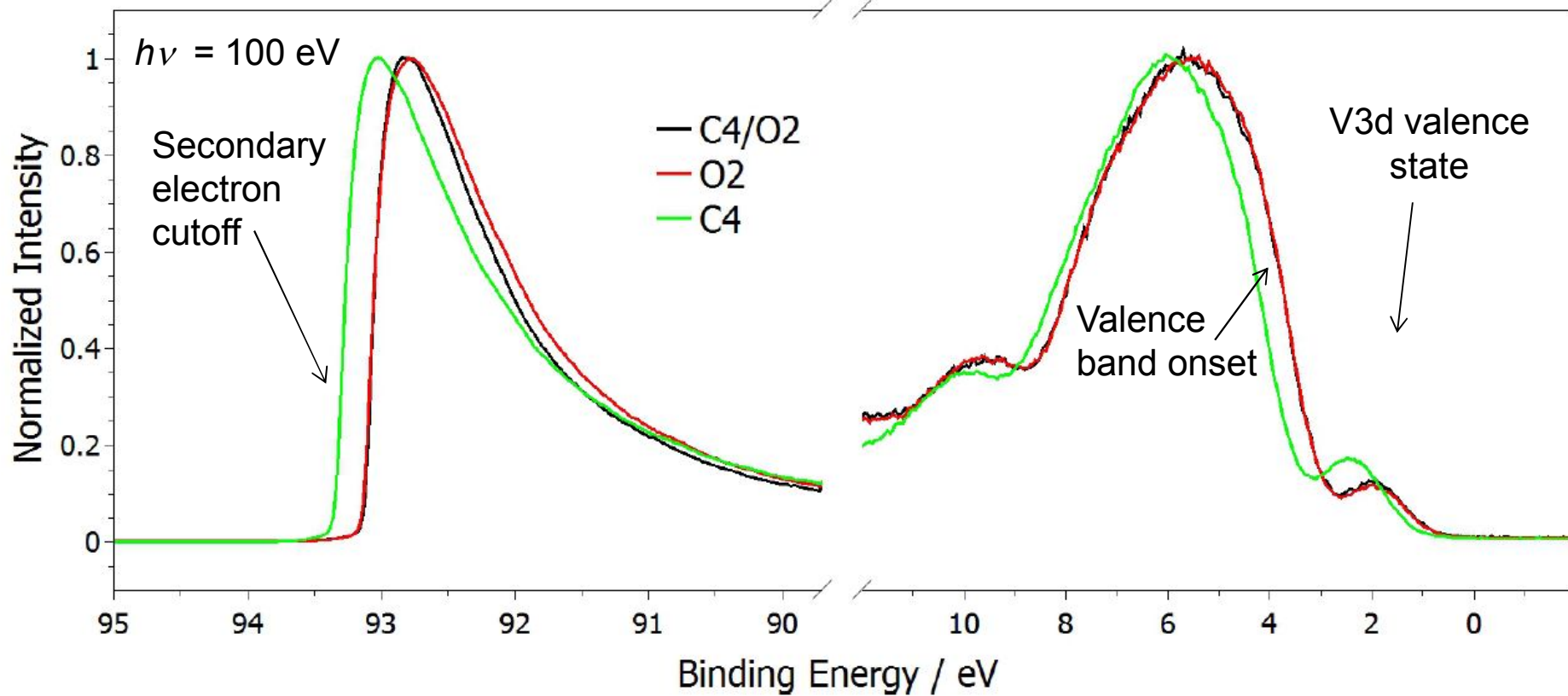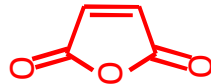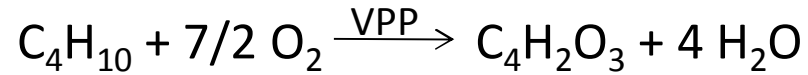
Work function $\Phi = h\nu - E_{cutoff}$

3. Surface states and space charge
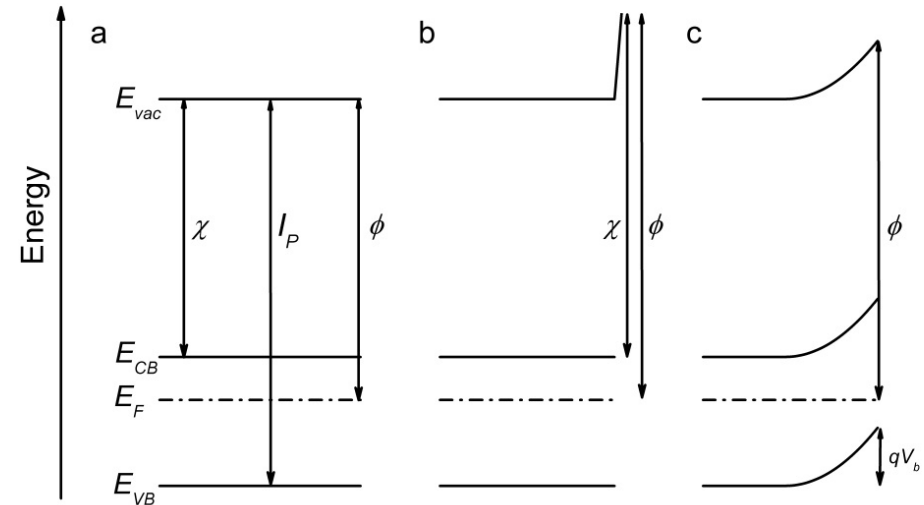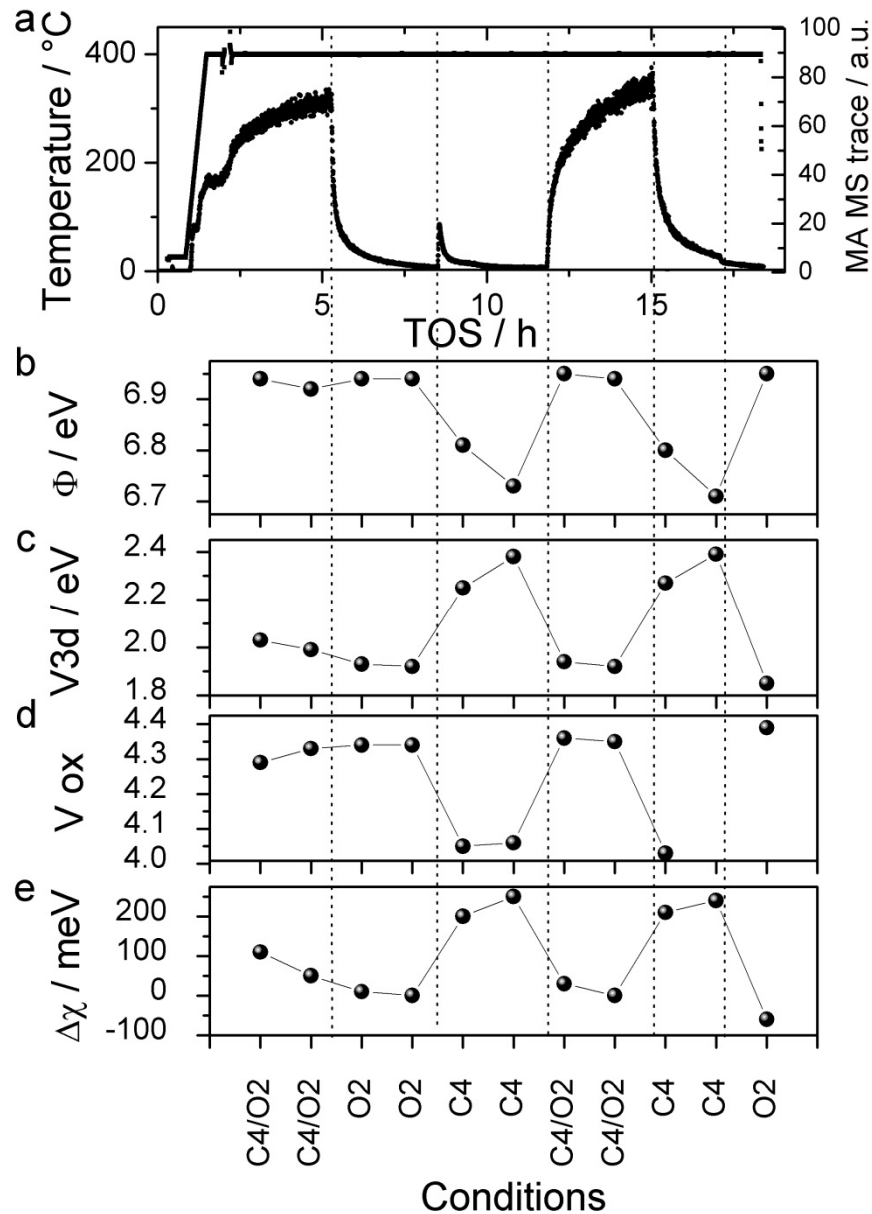
Work function $\Phi = h\nu - E_{cutoff}$

O2→C4: $\Delta\Phi$ = -240 meV

$\Delta BE(V3d)$ = 540 meV

Electron affinity change $\Delta\chi = \Delta\Phi + \Delta BE(V3d)$

= +300 meV

3. Surface states and space charge
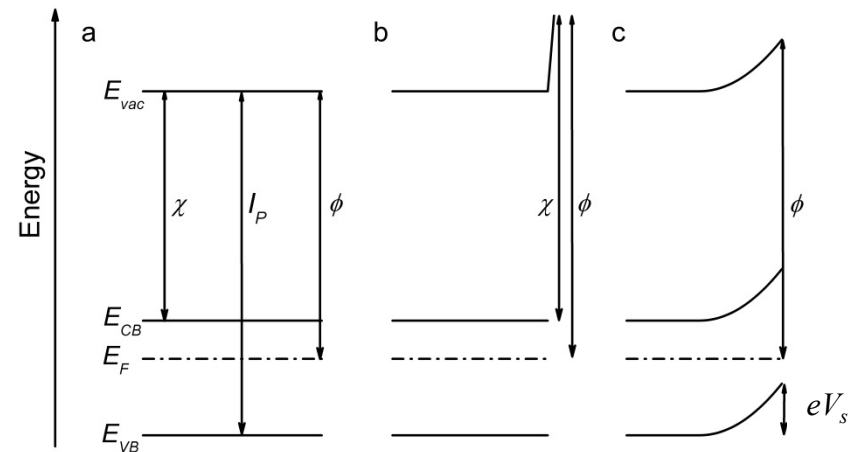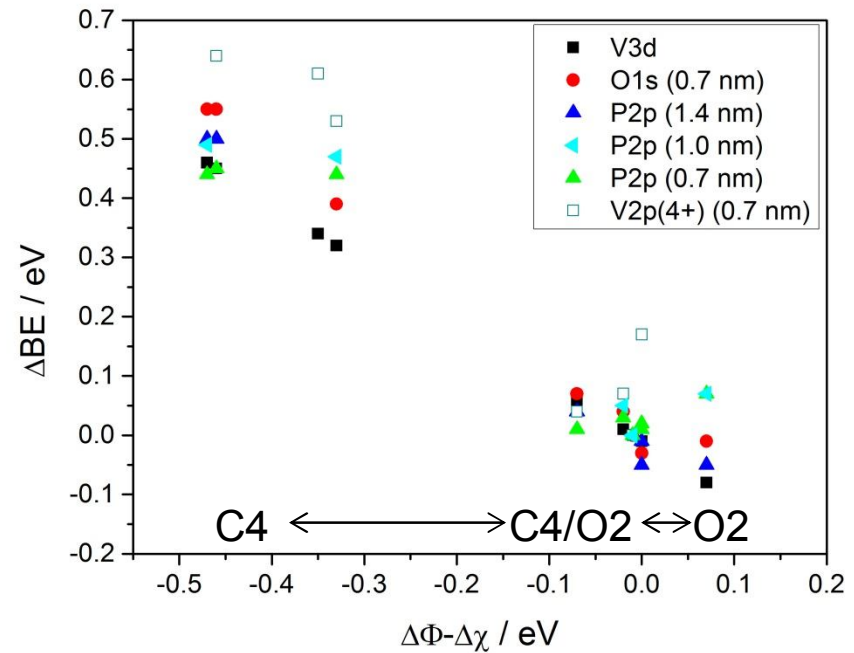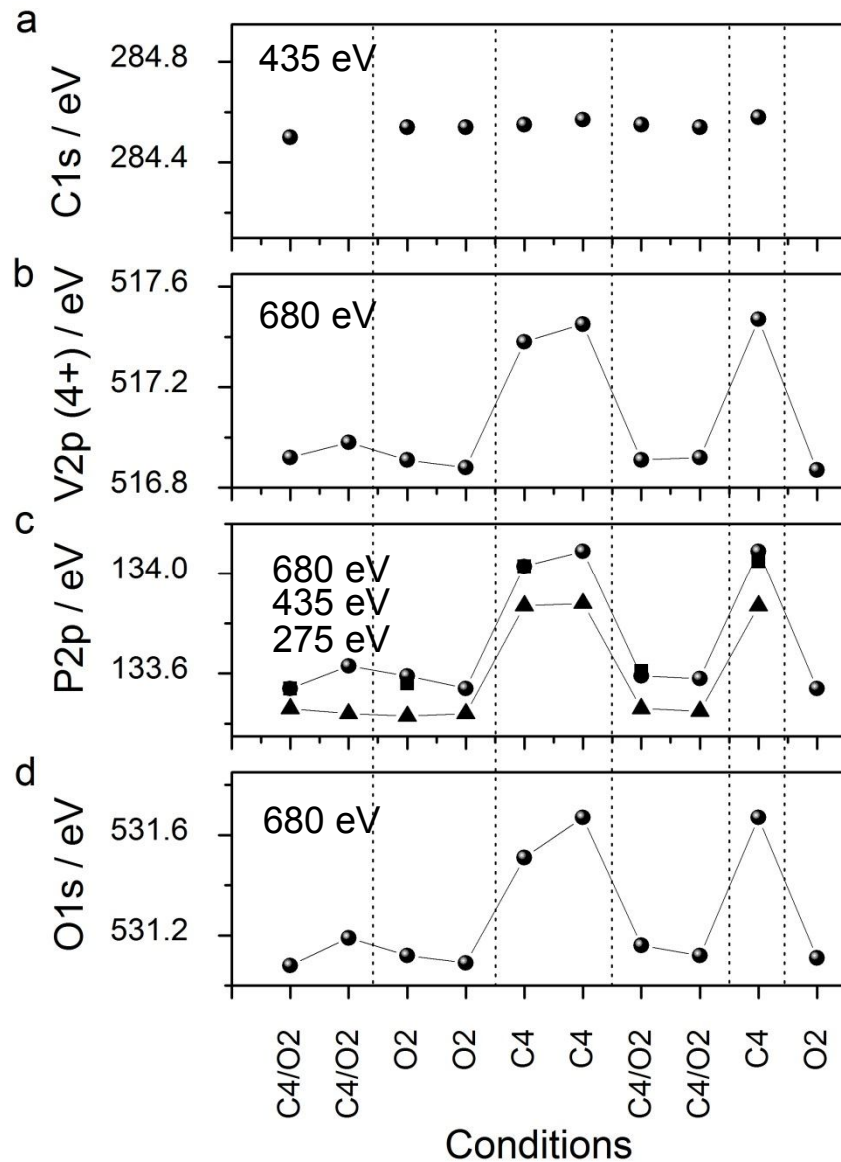
3. Surface states and space charge
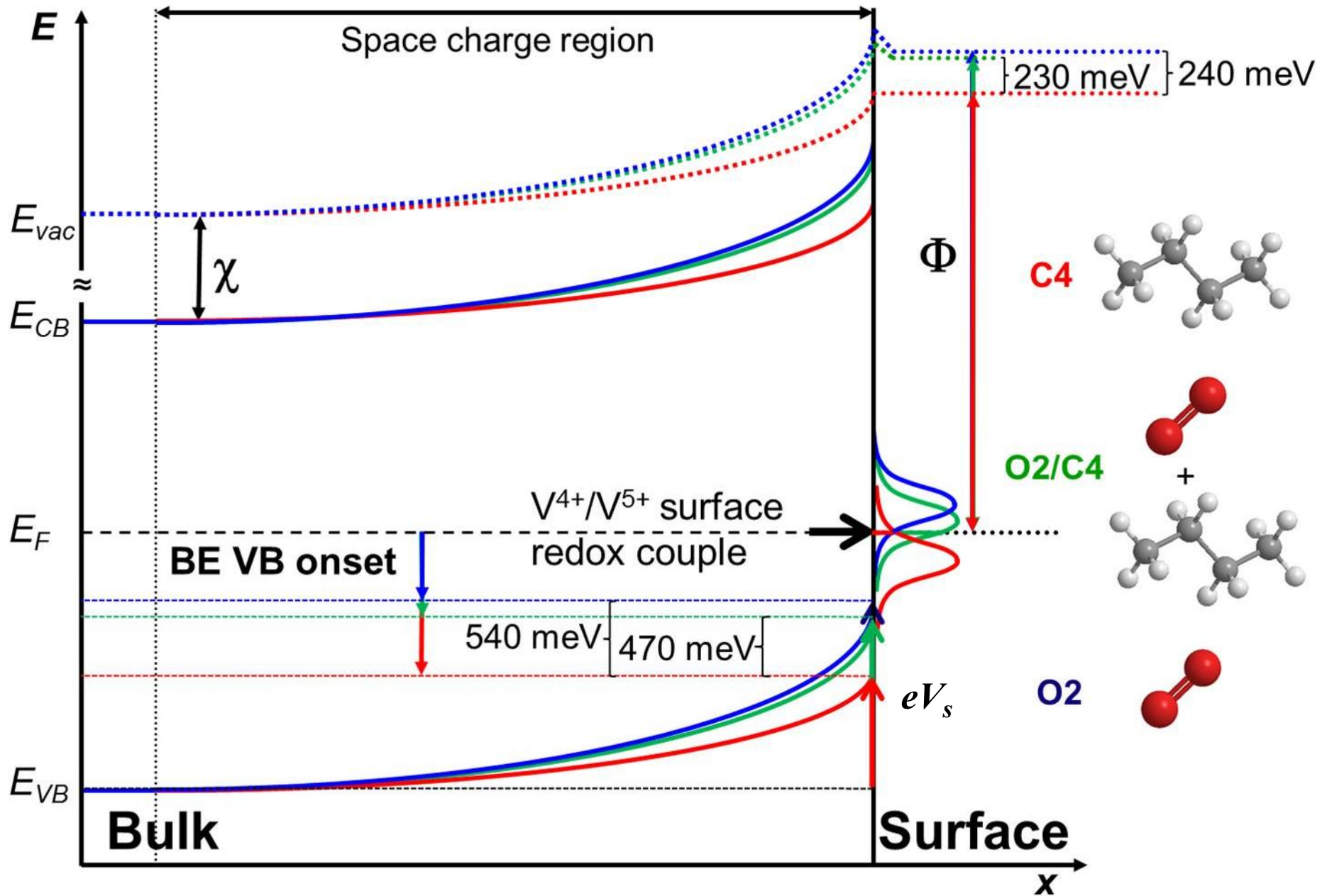
Electron and hole transfer between bulk and surface: The consequences of space charge regions for adsorption and catalysis

4. Bulk-surface charge transfer

Double layer

depletion layer

E

E_{vac}

$\Delta\chi$ (surface dipole)

χ

$e\phi_{WF}$

E_C

E_F

Ge Ge Ge
Ge P$^+$ Ge   O$_2^-$
P$^+$ Ge Ge   O$_2^-$
Ge Ge P$^+$ O$_2^-$

O$_2^-$ $\dfrac{d^2\phi_{sc}}{dx^2} = -\dfrac{\varrho}{\varepsilon\varepsilon_0}$

Space charge region

eV_s

$eV(x) = \dfrac{e(N_D - N_A)(x_0 - x)^2}{2\varepsilon\varepsilon_0}$

Number of surface charges per unit area:

Schottky model:

$N_s = -(N_D - N_A)x_0$

$eV_s = \dfrac{eN_s{}^2}{2\varepsilon\varepsilon_0(N_D - N_A)}$

E_V

x_0

0

x
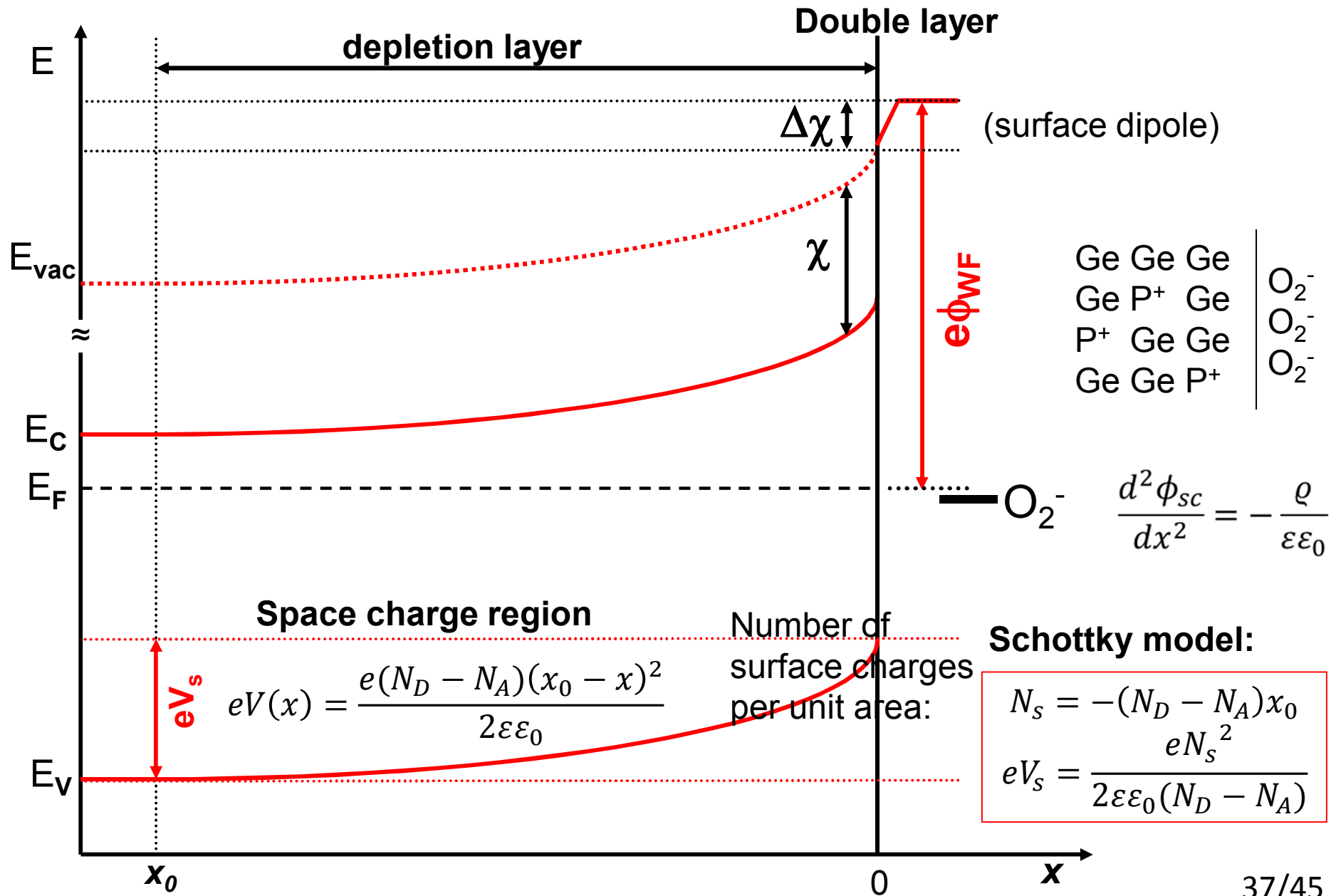
4. Bulk-surface charge transfer

Schottky model (example calculation):

V_s = 1 volt (typical surface barrier for adsorption)
Dielectric constant ε = 8

Very pure material: $N_D - N_A = 10^{20}$ m^{-3}
→ $N_s = 3$ x 10^{14} m^{-2} ; 1.5 x 10^{-5} monolayers (e.g. of O_2^-)

Heavily doped semiconductor: $N_D - N_A = 10^{25}$ m^{-3}
→ $N_s = 1$ x 10^{17} m^{-2} ; 5 x 10^{-3} monolayers (e.g. of O_2^-)

Schottky relation:

$$eV_s = \frac{eN_s^{\,2}}{2\varepsilon\varepsilon_0(N_D - N_A)}$$

Depletion layer limits surface coverage to about 10^{-3} – 10^{-2} monolayers of equilibrium ionosorption! (Weisz limitation)

4. Bulk-surface charge transfer

Fermi energy pinning by redox couples

Surface state additives can be used to control the surface barrier (pin the Fermi energy) of a semiconductor or insulator

e.g. $10^{18}/m^2$ (0.1 monolayer) redox couple deposition (e.g. 1 $FeCl_3$ / 1 $FeCl_2$) on n-type semiconductor

→ Weisz limitation: max. $10^{16}/m^2$ charges can be transferred to surface; only 1% of deposited surface states would change their electron occupancy
→ e.g. 3×10^{-4} monolayers converted from Fe^{3+} to Fe^{2+} induces change of surface barrier by 0.42 V

$$E_F = E_t + kT \ln \frac{[Red]}{[Ox]} \approx E_t$$

Fermi energy E_F is firmly pinned to surface state energ E_t

First approximation (ignoring local surface bonding of the adsorbate at the gas/solid interface) : E_t ~ redox potential of the couple

If gases react with redox couple, e.g. O_2 → adsorption/desorption of O_2 will control the surface Fermi energy

4. Bulk-surface charge transfer

depletion layer

E

E_{vac}

E_{vac}
E_C

$E_F \approx$

E_C

E_F

electrons

E_t *Surface state*

e.g. Fe^{2+}/Fe^{3+}

Flat band
Space charge region

E_v

eV_s

$eV_s = E_F - E_t$

E_v

Fermi level of the bulk
pinned to the energy of the
surface state (high density
of partially occupied
surface states)

x_0

0

x
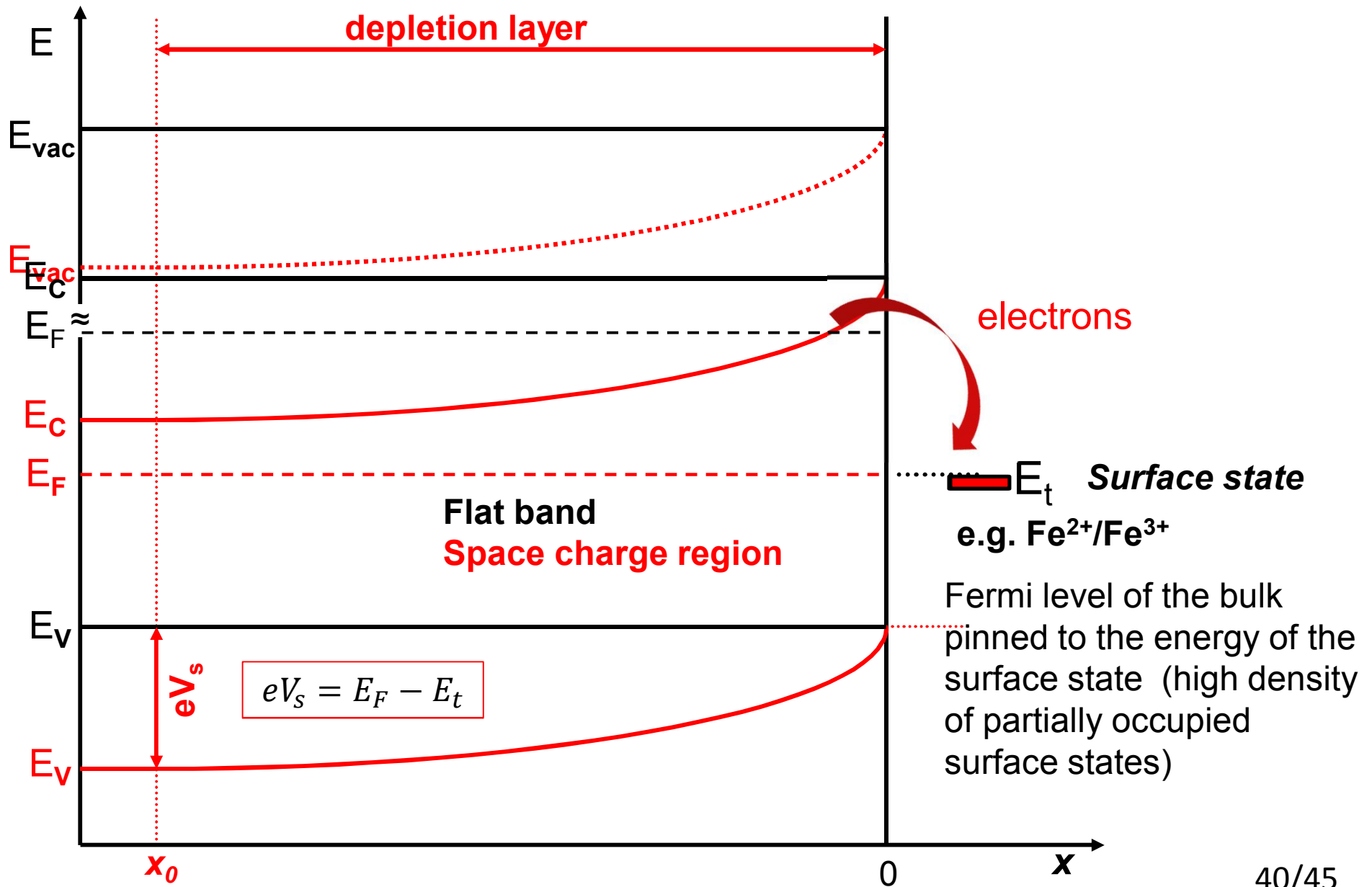
4. Bulk-surface charge transfer

Frank-Condon splitting of unoccupied (E_{t1}) and occupied (E_{t2}) surface states

due to changes in the local bonding interaction after an oxidation state change of the adsorbate

E_{t1} e.g. O_2 or V^{5+}

E_m

E_{t2} e.g. O_2^- or V^{4+}

Franck-Condon splitting in case of a polar medium: $E_{ox} - E_{red} = 2\lambda$

Electron transfer: $S_1 \cdot A^{n-} + e \rightleftharpoons S_1 \cdot A^{(n+1)-}$
Relocation ($\Delta G''$): $S_1 \cdot A^{(n+1)-} \rightleftharpoons S_2 \cdot A^{(n+1)-}$

Electron transfer: $S_2 \cdot A^{(n+1)-} \rightleftharpoons e + S_2 \cdot A^{n-}$
Relocation ($\Delta G'$): $S_2 \cdot A^{n-} \rightleftharpoons S_1 \cdot A^{n-}$
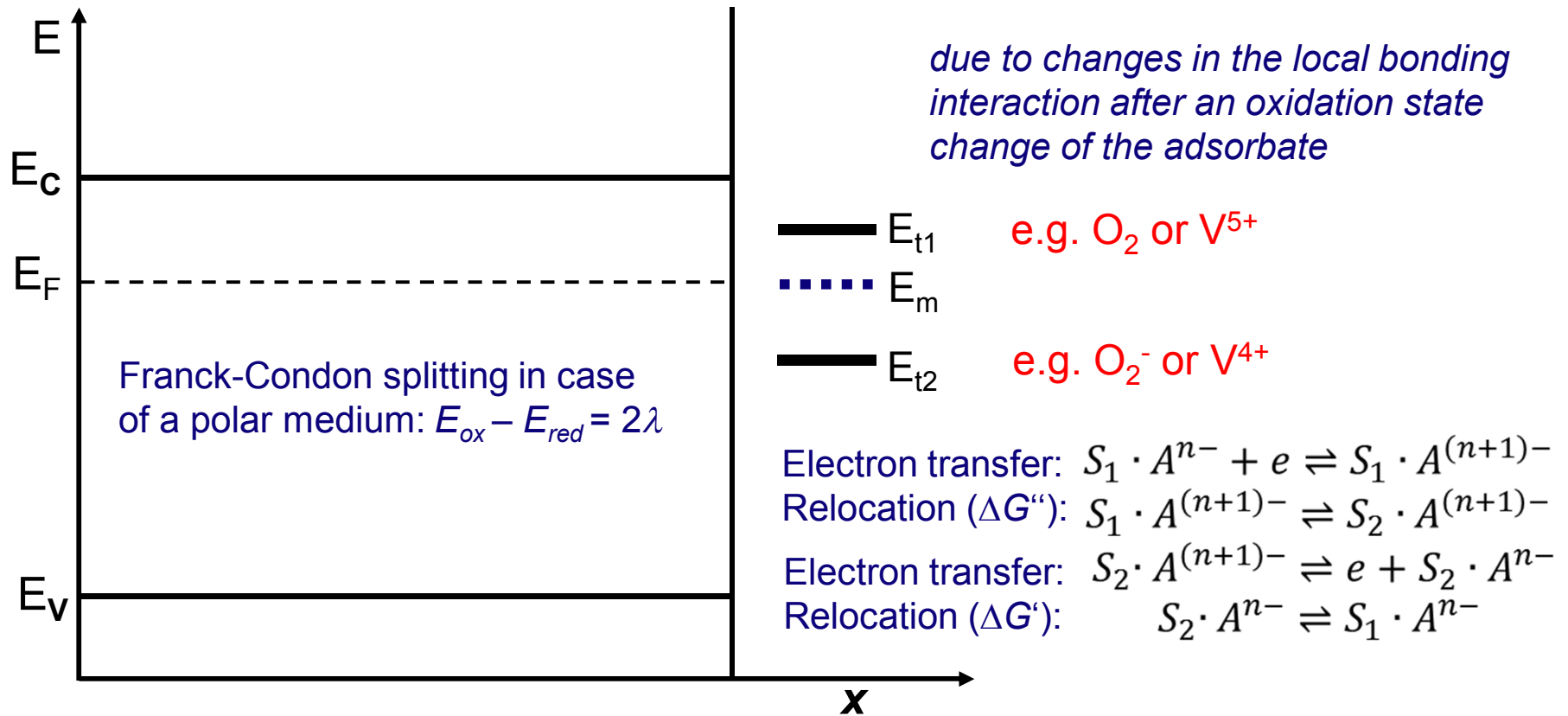
$$E_{t1} - E_{t2} = -(\Delta G'' + \Delta G')$$

$$E_F = \tfrac{1}{2}(E_{t1} + E_{t2}) + \tfrac{1}{2}(\Delta G'' - \Delta G') + kT \ln\left(\frac{[S_2 \cdot A^{(n+1)-}]}{[S_1 \cdot A^{n-}]}\right) \longleftarrow \frac{reduced\ species}{oxidized\ species}$$

$$E_m = \tfrac{1}{2}(E_{t1} + E_{t2}) + \tfrac{1}{2}(\Delta G'' - \Delta G')$$ (intermediate energy for an apparent single energy level)

4. Bulk-surface charge transfer

Role of space charge layer in controlling electron transfer
→ charge transport kinetics

3 models:

1) Low and constant surface states density (surface free of volatile species)

2) High but constant surface states density

3) Energy level of surface states fluctuates with time (Franck-Condon effects, Gerischer model)

4. Bulk-surface charge transfer
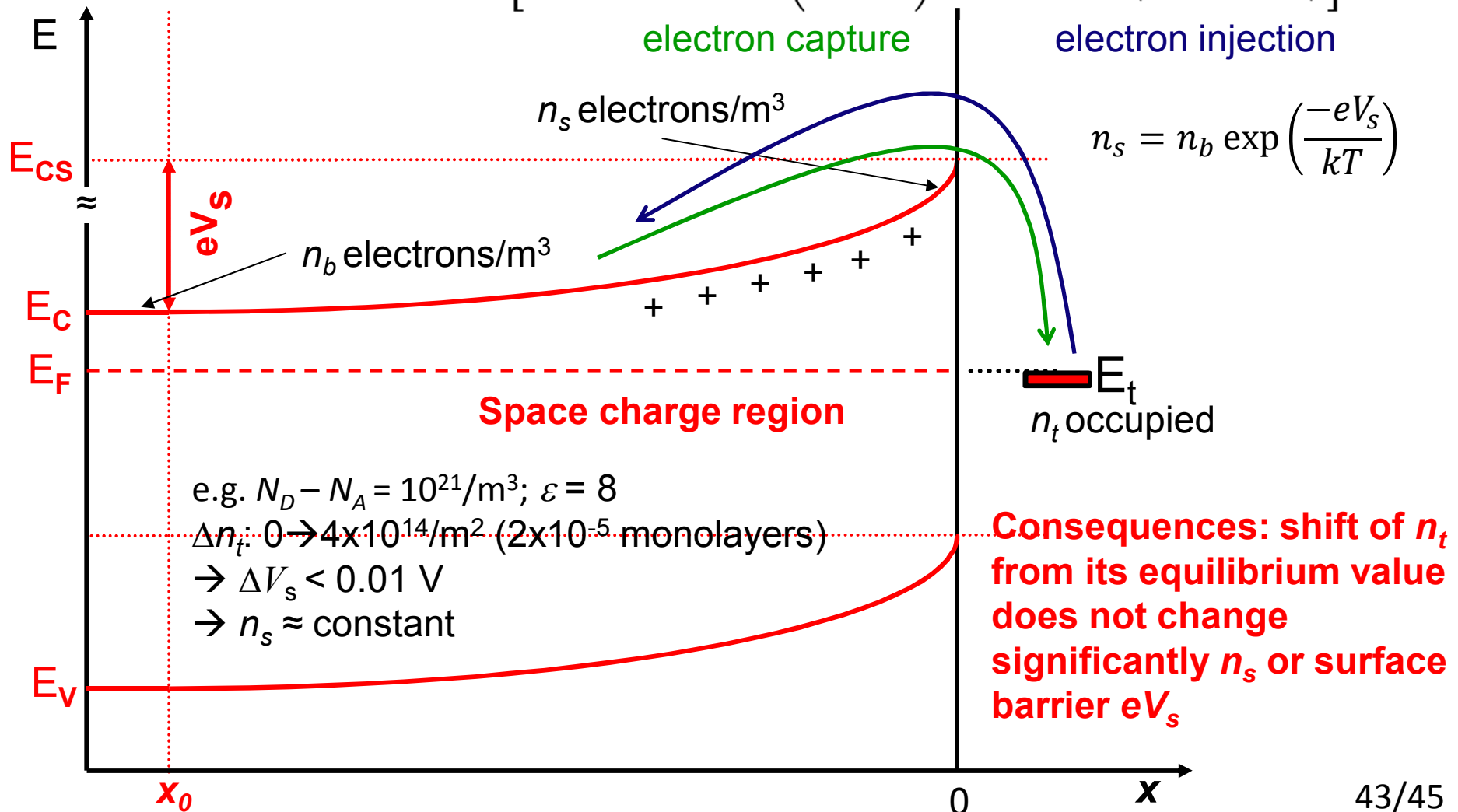
1) Low and constant surface states density N_t low ($< 10^{15}/m^2$)

$$\frac{dn_t}{dt} = K_n \left[(N_t - n_t)n_b \exp\left(-\frac{e\,V_s}{kT}\right) - n_t N_c \exp\left(-\frac{E_{cs} - E_t}{kT}\right) \right]$$

electron capture   electron injection

n_s electrons/m^3

$$n_s = n_b \exp\left(\frac{-eV_s}{kT}\right)$$

E

E_{cs}

eV_s

n_b electrons/m^3

$+$ $+$ $+$ $+$ $+$ $+$ $+$

E_C

E_F

Space charge region

E_t

n_t occupied

e.g. $N_D - N_A = 10^{21}/m^3$; $\varepsilon = 8$

Δn_t: $0 \rightarrow 4 \times 10^{14}/m^2$ (2×10^{-5} monolayers)

$\rightarrow \Delta V_s < 0.01$ V

$\rightarrow n_s \approx$ constant

Consequences: shift of n_t from its equilibrium value does not change significantly n_s or surface barrier eV_s

E_V

x_0

0   x

4. Bulk-surface charge transfer

2) High but constant surface states density N_t very high (> 10^{15}/m²)

$$\frac{dn_t}{dt} = K_n \left[(N_t - n_t)n_b \exp\left(-\frac{e\,V_s}{kT}\right) - n_t N_c \exp\left(-\frac{E_{cs} - E_t}{kT}\right) \right]$$

$$\rightarrow \frac{dn_t}{dt} = B' \left[\exp\left(-\frac{e\,V_s}{kT}\right) - \exp\left(-\frac{eV_{s0}}{kT}\right) \right]$$

V_{s0}: surface barrier at equilibrium
B': collection of constants

($N_t - n_t$ and n_t less sensitive to n_t than $\exp(-eV_s/kT)$)

$$\frac{dn_t}{dt} = B \left[\exp\left(\frac{-e\Delta V_s}{kT}\right) - 1 \right]$$

Rate of return
to equilibrium
for Δn_t:

$$\frac{d\Delta n_t}{dt} = B[\exp(-\beta\,\Delta n_t) - 1]$$

Rate decreases exponentially
with Δn_t

with $B = B'\exp(-eV_{s0}/kT)$
and β: constant

Consequences: a small change in surface state occupation induces a large increase of the surface barrier; electron transfer can be slowed to a negligible rate!

6. Literature

(Examples)

Adsorption/catalysis on semiconductors, e.g.:

- S. R. Morrison, "*The chemical physics of surfaces*", Plenum Press New York and London **1977** (semiconductor physics concepts of surfaces, includes chapter on heterogeneous catalysis)
- F. F. Volkenshtein, "*The electronic theory of catalysis on semiconductors*"; Pergamon Press **1963**.
- H. Lueth, "*Solid surfaces, interfaces and thin films*", Springer **2010**
- H. Lueth, "*Space Charge Layer*", Springer Verlag **2001**
- P. A. Cox, "*The electronic structure and chemistry of solids*", Oxford University Press **1989**
- R. Hoffmann, "*Solids and surfaces : a chemist's view of bonding in extended structures*" VCH **1988**

Fundamental textbooks, e.g.:

- N. W. Ashcroft, N. D. Mermin, "*Solid state physics*", Brooks/Cole Cengage Learning **2009**
- H. Ibach, H. Lueth, "*Solid-state physics : an introduction to principles of materials science*", Springer **2009**