Elementary Semiconductor Physics for Transition Metal Oxide Heterostructure

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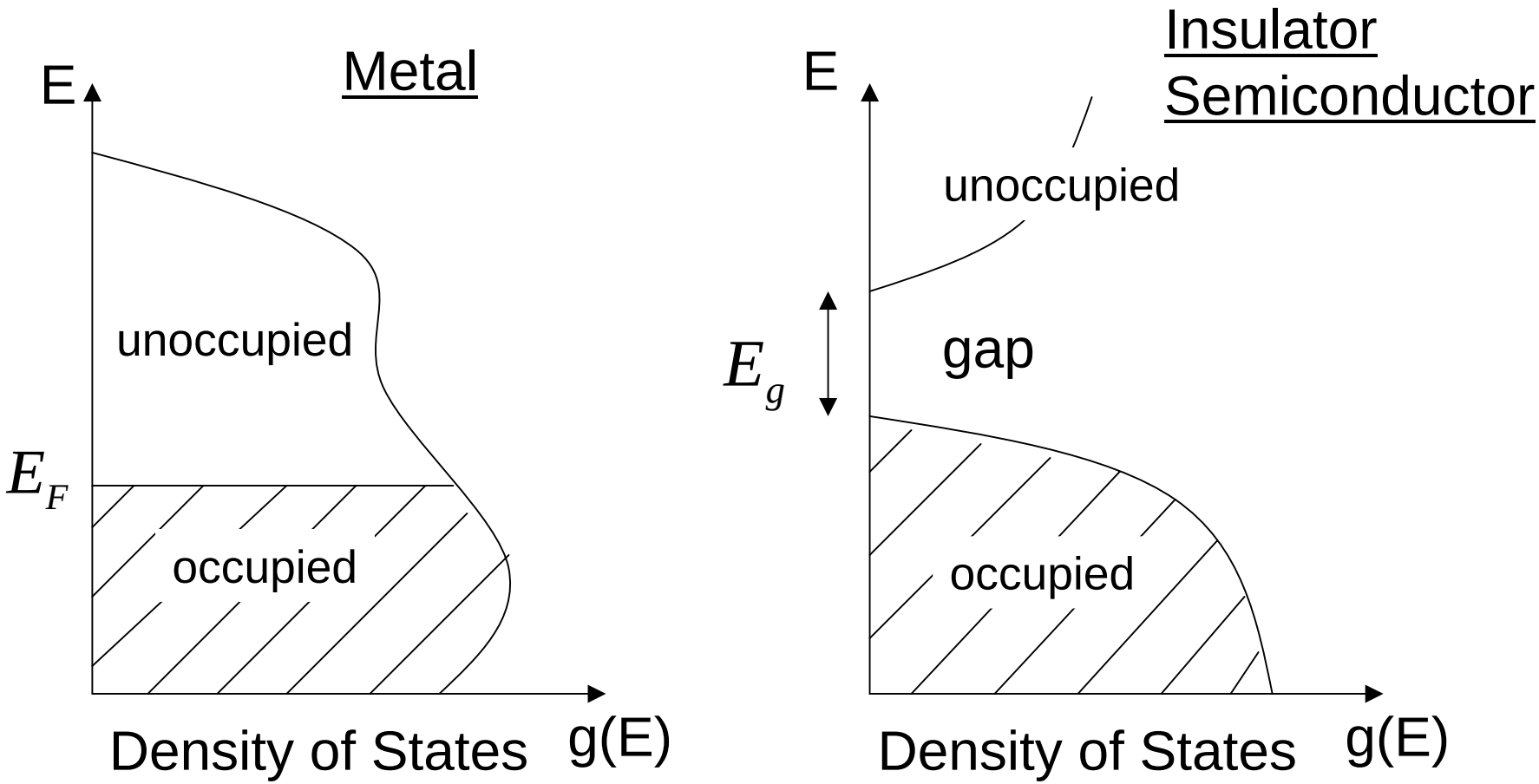
Content of lectures

- Homogenous semiconductors
  - Intrinsic (pure) semiconductors
  - Extrinsic (impurity doped) semiconductors
- Inhomogenous semiconductors
  - Homopolar junction (p-n junction, rectification, …)
  - Hetero junction (inversion layer, …)

See, for example, “Solid State Physics” by Ashchroft & Mermin

- Heterojunction made of correlated electronic systems

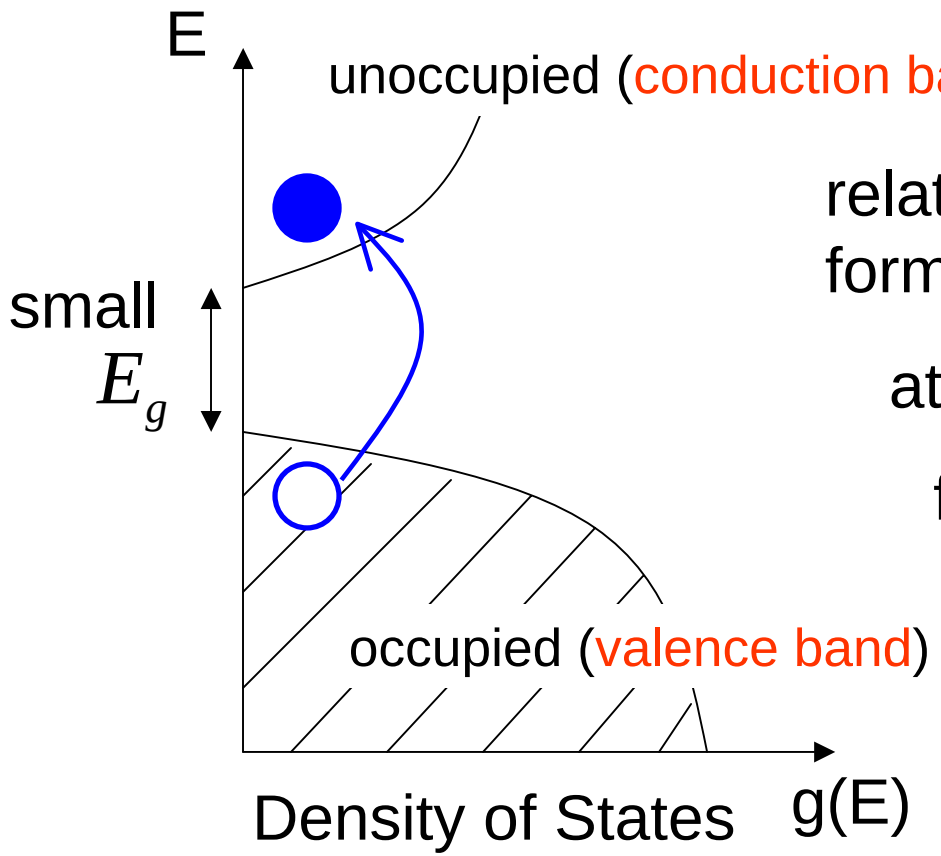
Metal, Insulator, and Semiconductor



Semiconductor: E_g relatively small (~1eV or less)

Insulator: E_g relatively large (~several eV)

Semiconductor: small energy gap



relatively easy to excite electrons form valence to conduction bands

at finite temperature (T)

finite amount of electrons in C.B.

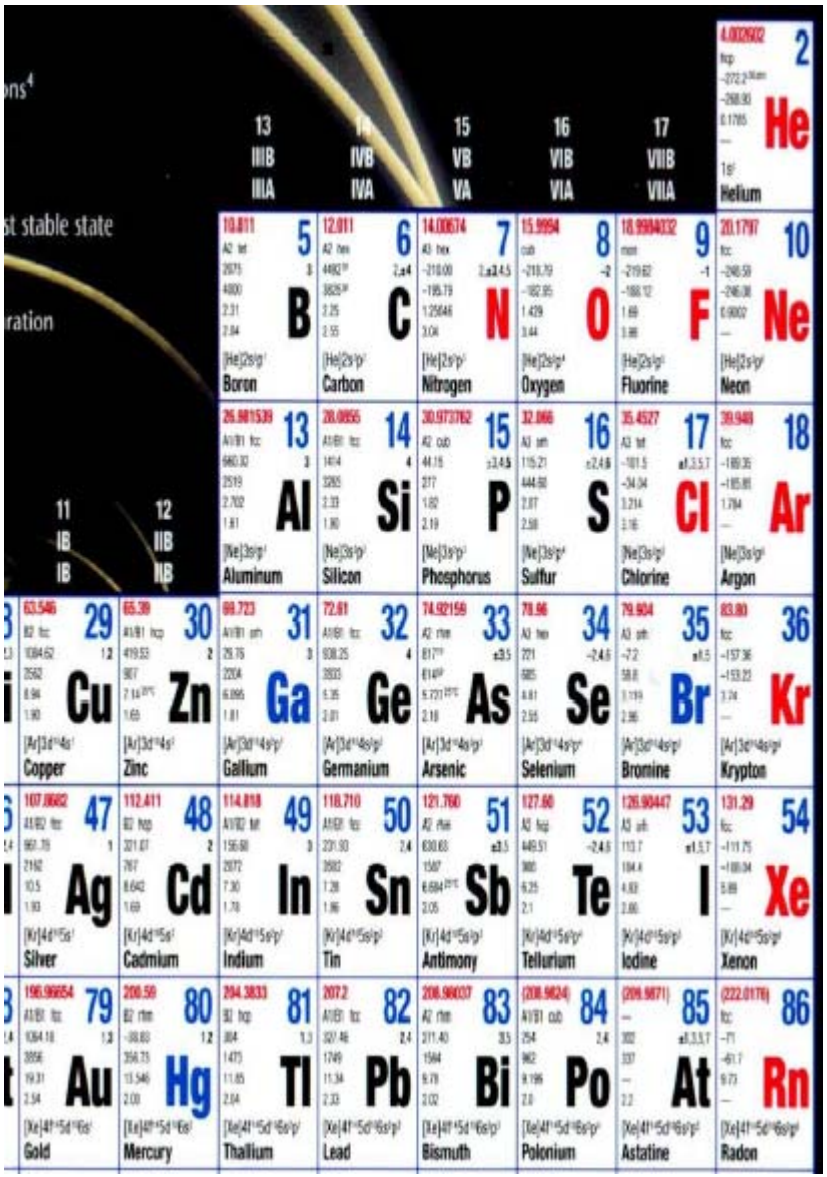
$$n_c(T) \sim \exp\left[-E_g / 2k_B T\right]$$

$\sim 10^{-2}$ $\left(E_g = 0.25 \text{ eV}\right)$

$\sim 10^{-35}$ $\left(E_g = 4.0 \text{ eV}\right)$

at room T $\left(k_B T \approx 0.025 \text{ eV}\right)$

Pure (Intrinsic) Semiconductor

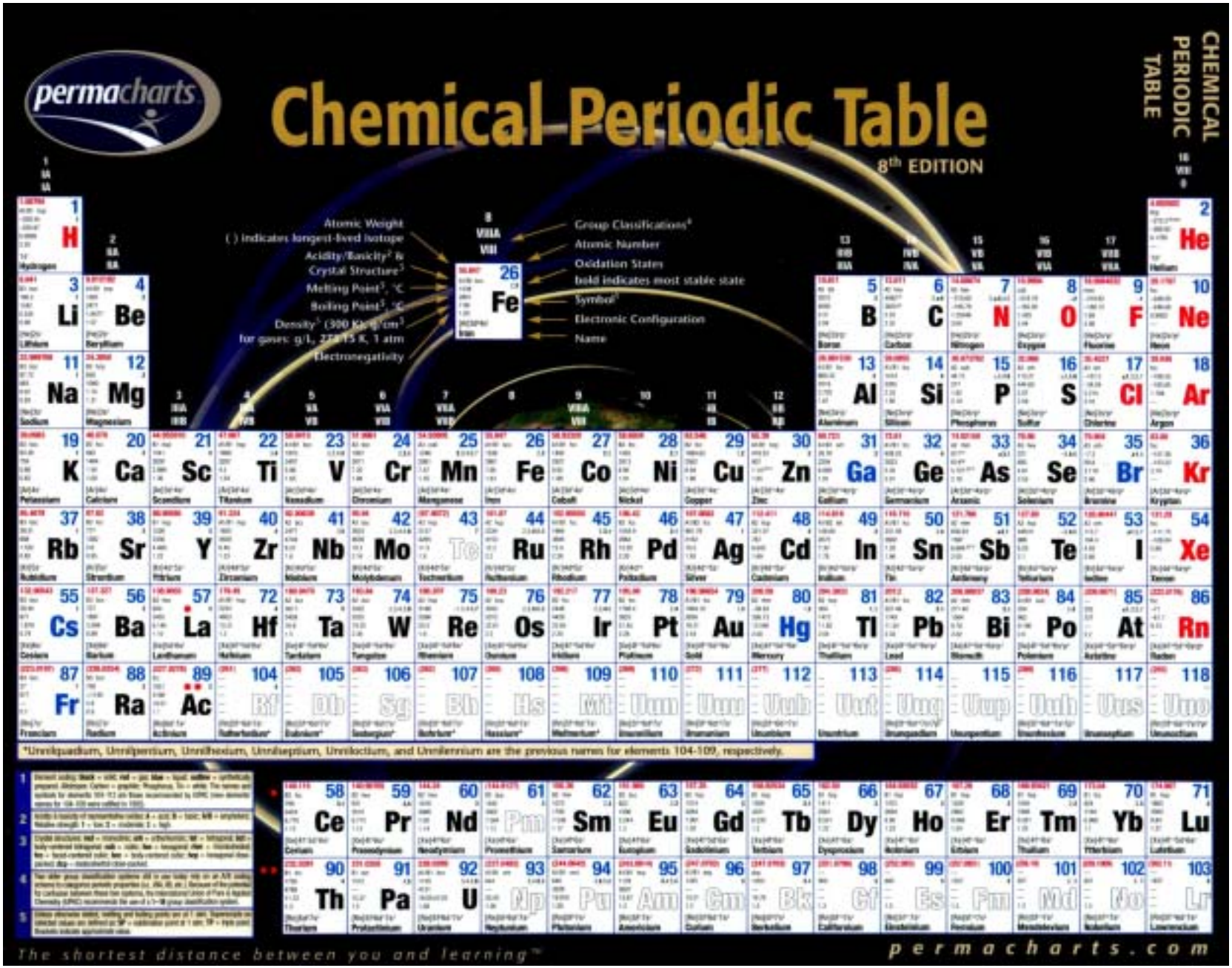


Semiconducting elements: IV

Si, Ge, …

Semiconducting compounds: III-V

GaAs, GaP, InSb, …


permacharts
Chemical Periodic Table
8th EDITION
CHEMICAL PERIODIC TABLE
Atomic Weight
( ) indicates longest-lived isotope
Acidity/Basicity[2] is
Crystal Structure[3]
Melting Point[3], °C
Boiling Point[3], °C
Density[3] (300 K), g/cm³
for gases: g/L, 273.15 K, 1 atm
Electronegativity
Group Classifications[4]
Atomic Number
Oxidation States
bold indicates most stable state
Symbol[5]
Electronic Configuration
Name
*Unnilquadium, Unnilpentium, Unnilhexium, Unnilseptium, Unniloctium, and Unnilennium are the previous names for elements 104-109, respectively.
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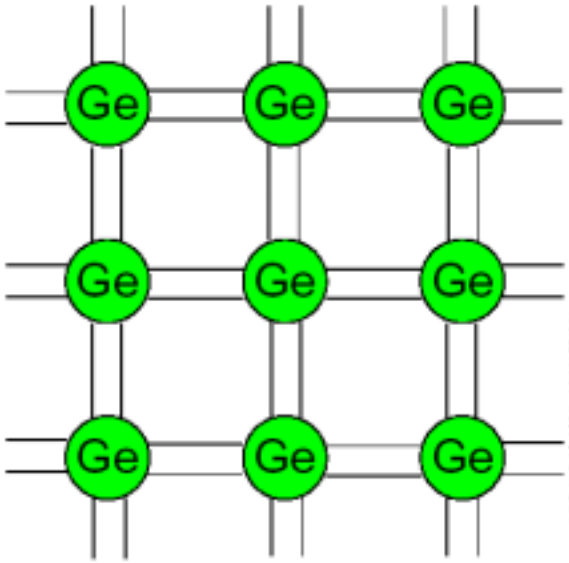
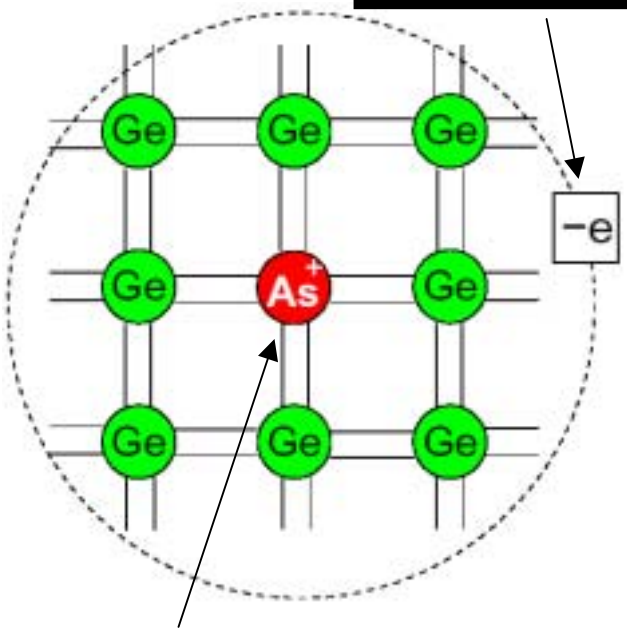
Extrinsic Semiconductor

Ge: $(4s)^2(4p)^2$



Covalent bonding

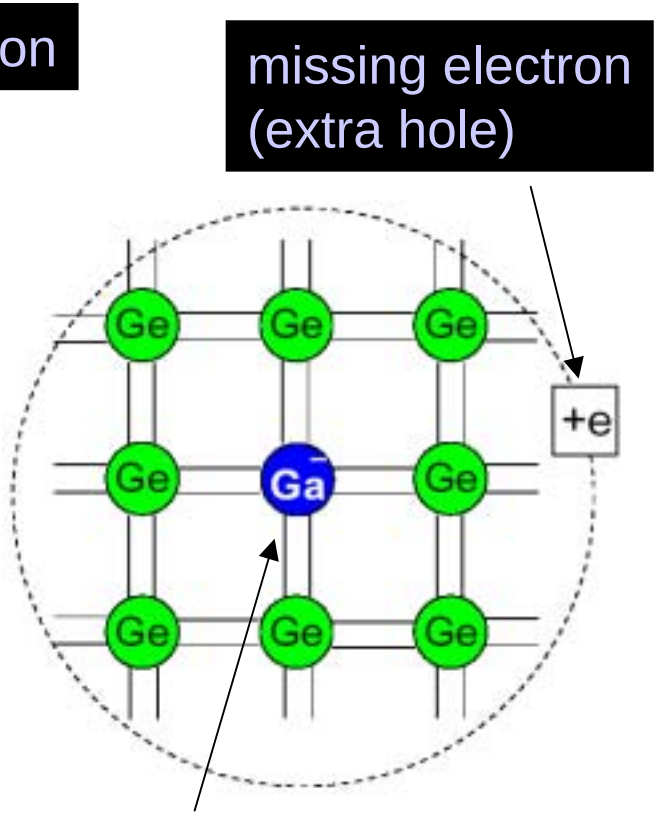
As: $(4s)^2(4p)^3$



extra positive charge

(donor impurity)

Ga: $(4s)^2(4p)^1$



extra negative charge

(acceptor impurity)

Very small binding energy

Hydrogen atom:

$$E_H = -\frac{me^4}{2\hbar^2} \sim -13.6 \text{ eV}$$ binding energy

$$a_B = \frac{\hbar^2}{me^2} \sim 0.5\times10^{-8} \text{ cm}$$ Bohr radius

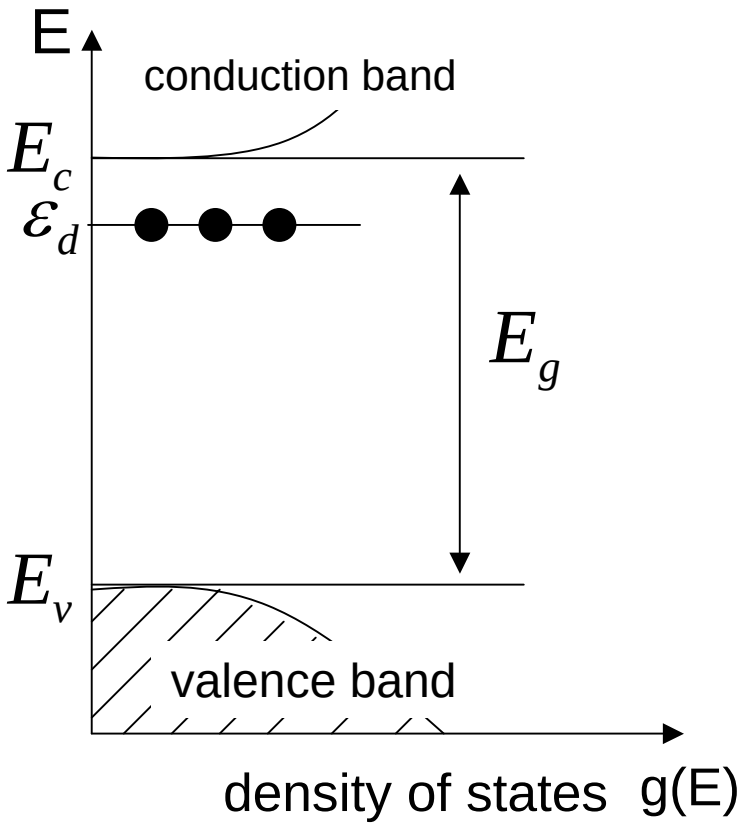
Inside solid: $e^2/r \to e^2/r\varepsilon$ screening $\varepsilon \approx 10-20$

$m \to m^*$ band $m^*/m \approx 0.1-1.0$

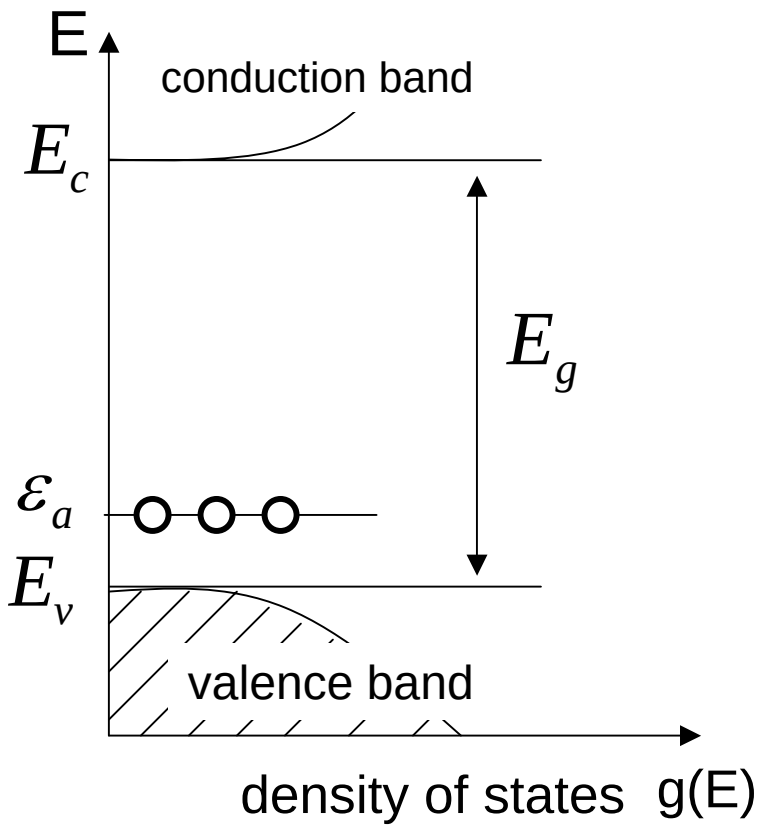
$$\begin{cases} E = \dfrac{m^*}{m}\cdot\dfrac{1}{\varepsilon^2}\cdot E_H \sim 10-100 \text{ meV} & \text{very small binding energy} \\ \langle r \rangle = \dfrac{m}{m^*}\varepsilon\cdot a_B \sim 100\cdot a_B & \text{very large radius} \end{cases}$$

Energy band for extrinsic semiconductors

As-doped Ge
(n-type semiconductor)



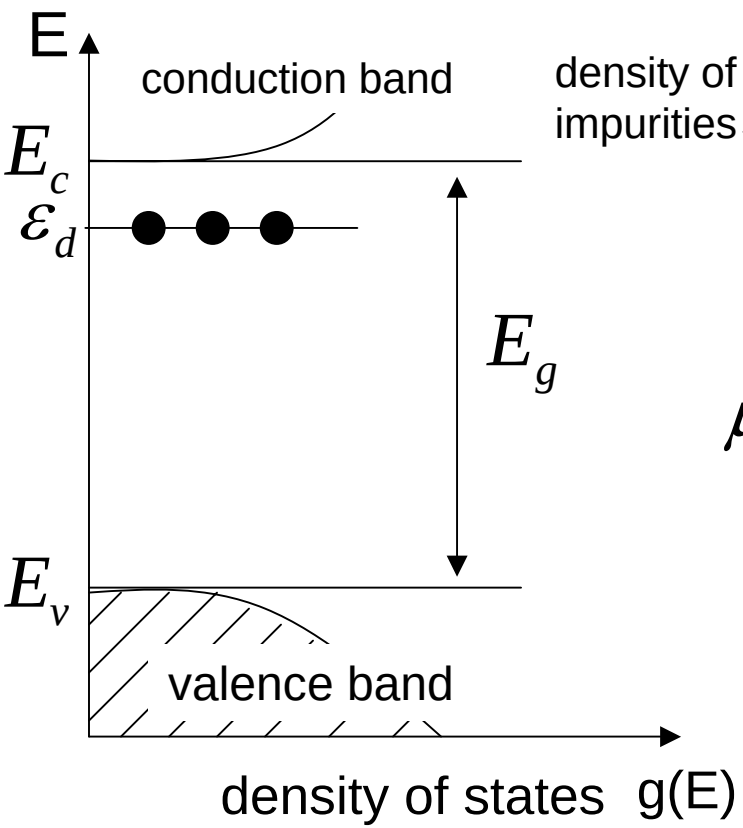
Ga-doped Ge
(p-type semiconductor)

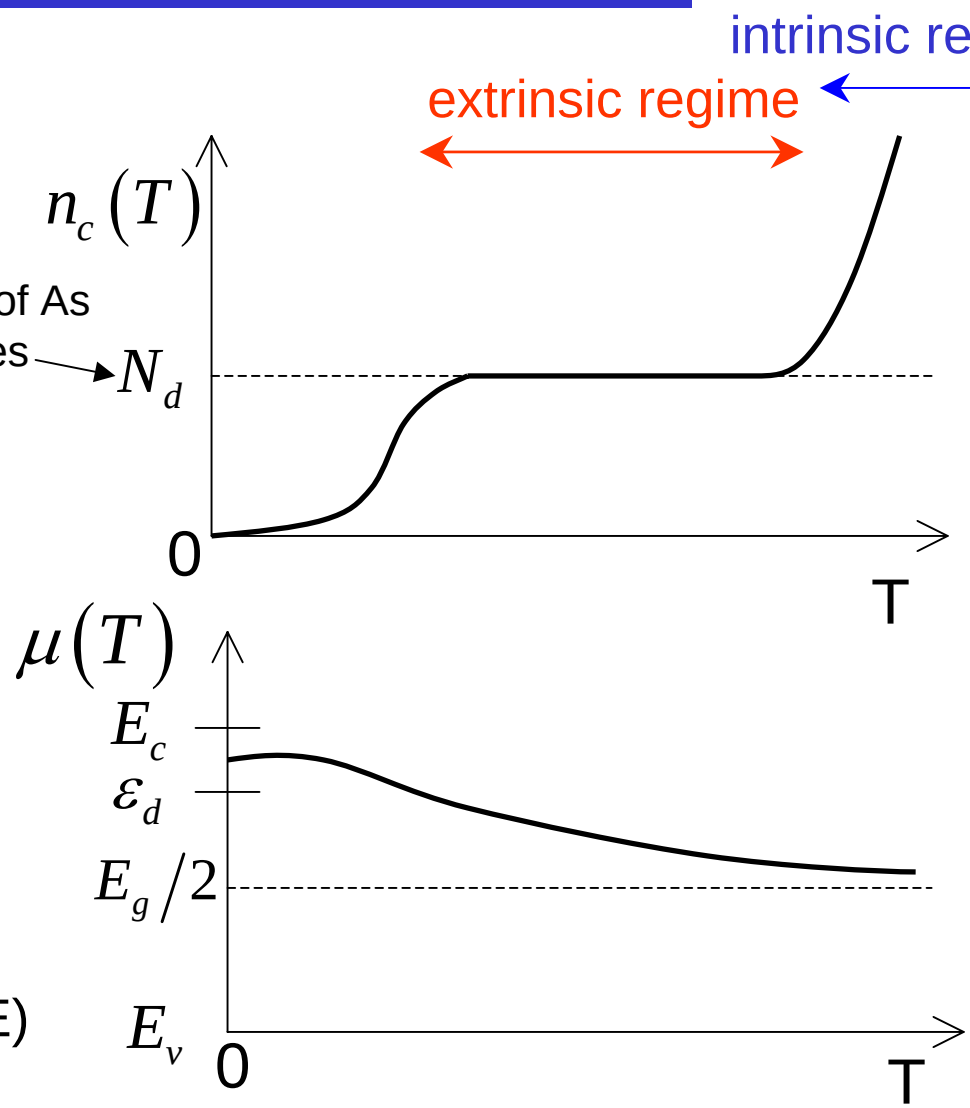


$$n_c(T) \sim \exp\left[-\frac{(E_c - \varepsilon_d)}{2k_B T}\right] \sim 1$$ at room T

of conduction electrons vs T

As-doped Ge
(n-type semiconductor)





Conductivity (metal vs semiconductor)

Drude formula:

$$\sigma = \frac{ne^2\tau}{m}$$

carrier density

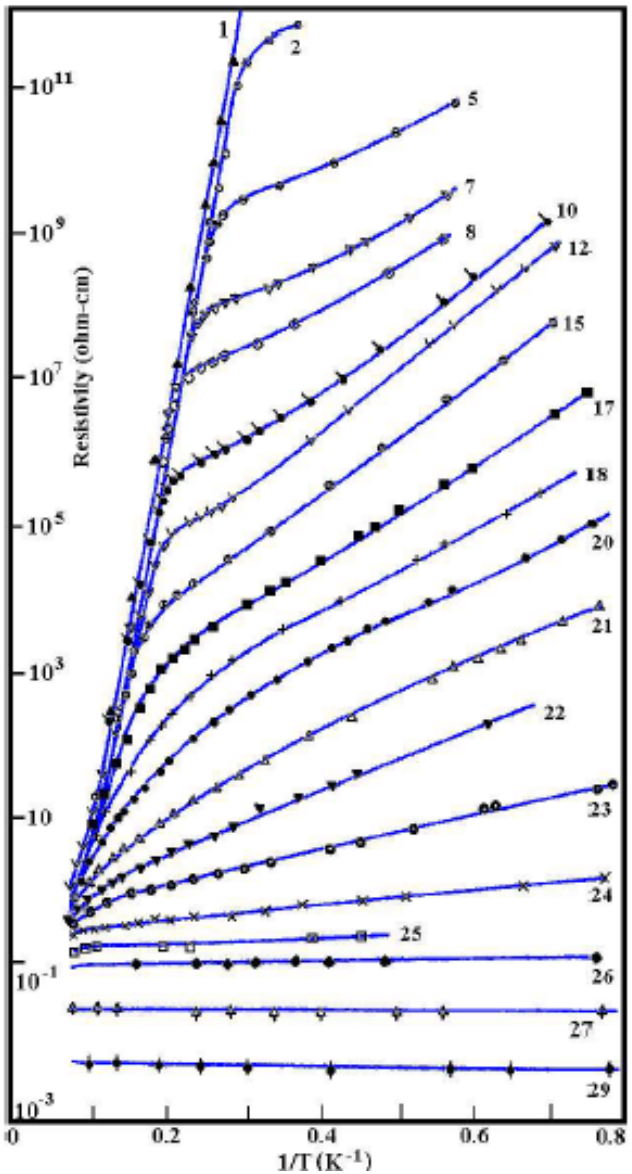
relaxation time

(effective) mass

Metal: $\tau(T)$ dominates

Semiconductor: $n(T)$ dominates

Antimony (Sb) doped Germanium (Ge)

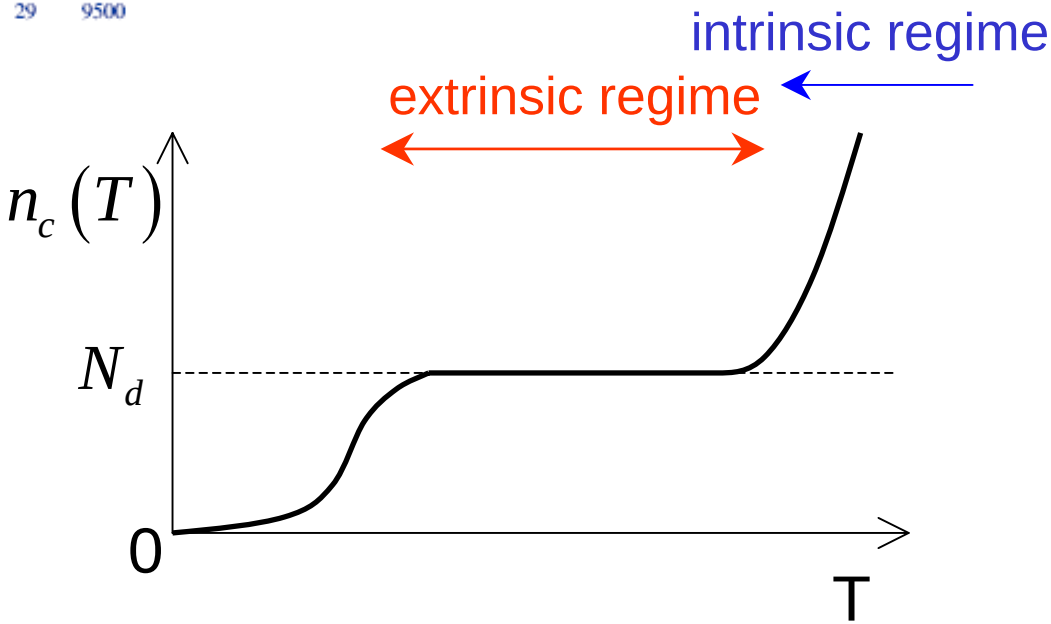


Specimen	Donor concentration x 10^{14} cm^{-3}
1	5.3
2	9.3
5	16
7	23
8	30
10	52
12	85
15	130
17	240
18	350
20	450
21	550
22	640
23	740
24	840
25	1200
26	1300
27	2700
29	9500

T-dependence of resistivity with varying impurity concentrations

H. J. Fritsche (1958)

n-type semiconductor



Inhomogeneous Semiconductors

- pn junction (pn diode): homopolar junction(↔heterojunction)

Ga-doped Ge | As-doped Ge

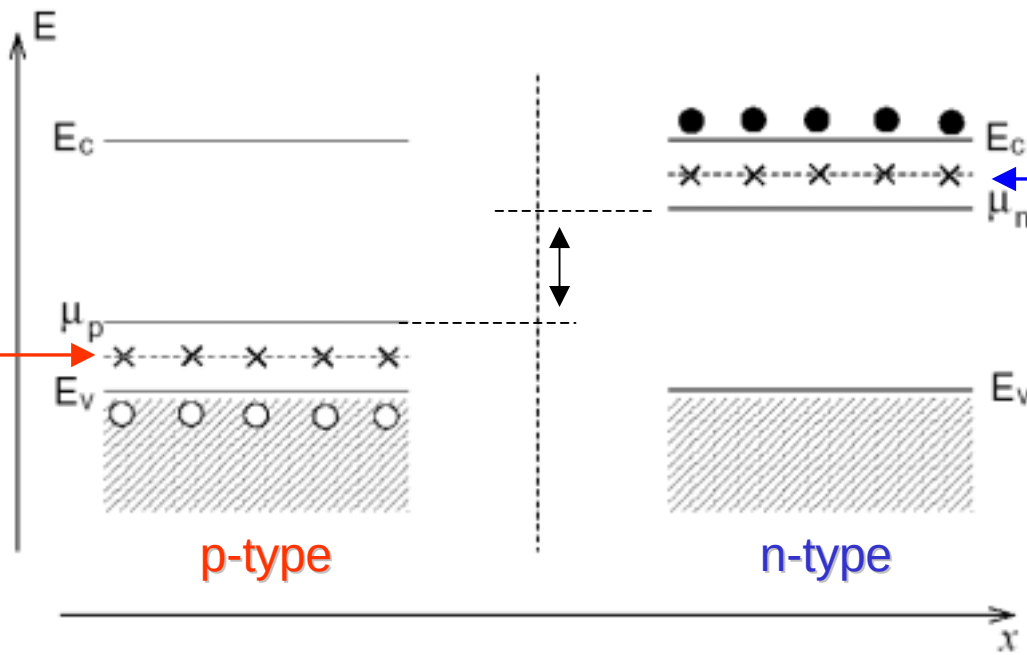
p-type semiconductor | n-type semiconductor

at equilibrium
(no current flow)

Schematic energy band (not yet in contact): saturation regime

free valence **holes** embedded in the back ground of immobile **negative ionized acceptors**

impurity ion charge: -e

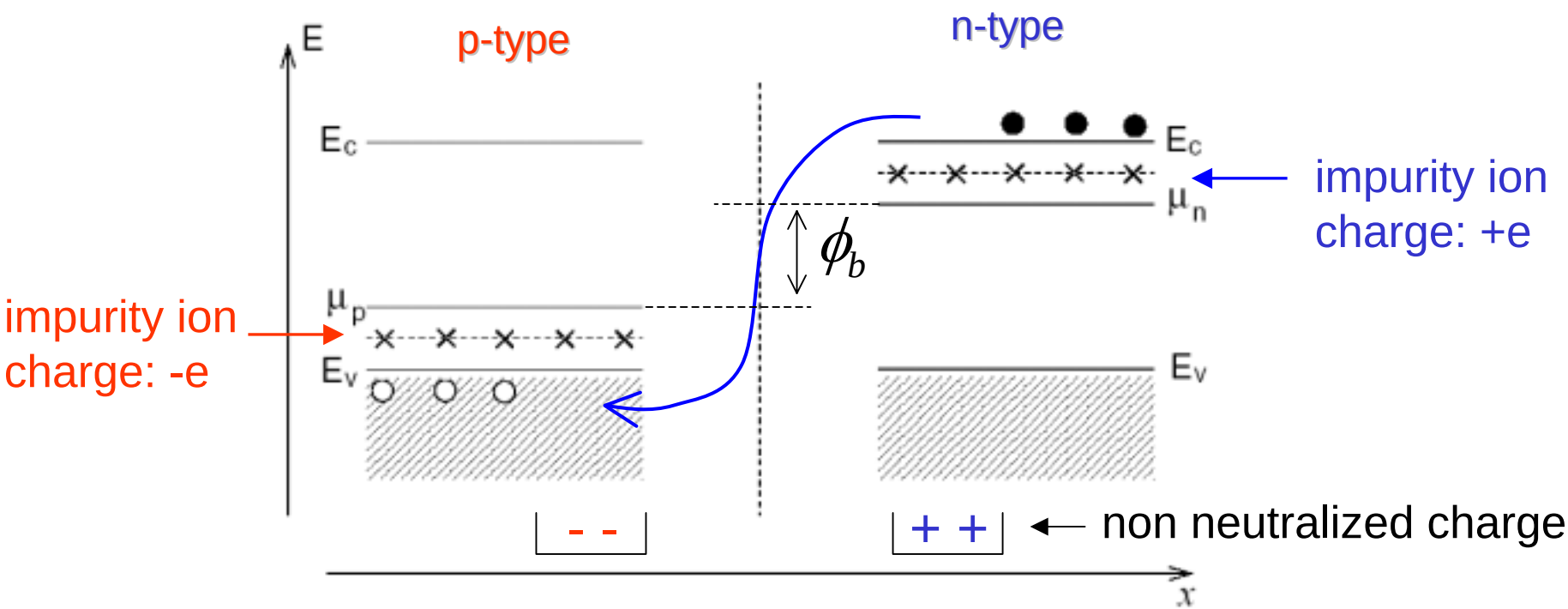


impurity ion charge: +e

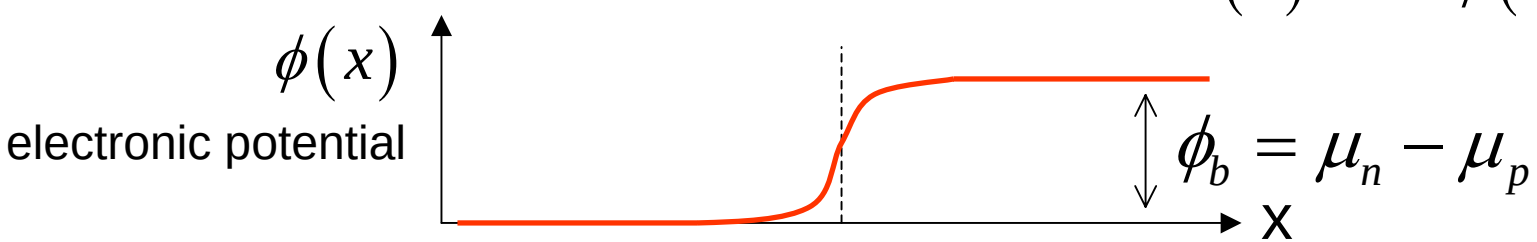
free conduction **electrons** embedded in the back ground of immobile **positive ionized donors**

pn junction

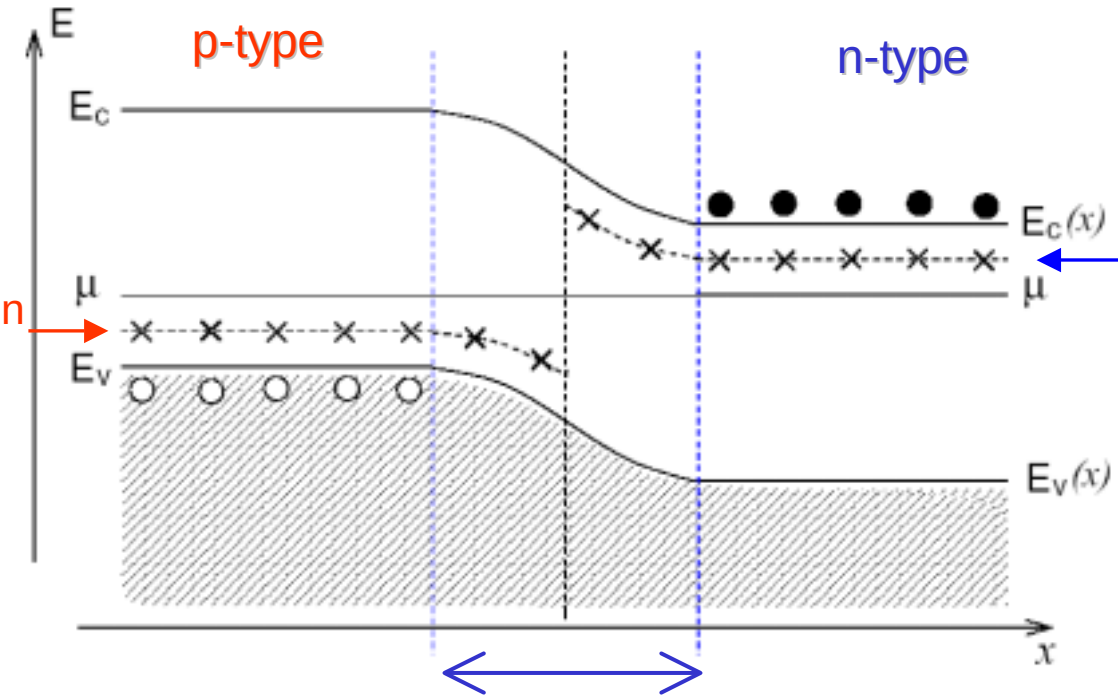
in contact ($\mu_p = \mu_n = \mu$ in equilibrium)



- ✓ electron redistribution
- ✓ non-neutralized charge regions
- ✓ finite electronic field E(x) only at the interface: $E(x) = -\nabla\phi(x)$



Schematic energy band of p-n junction



impurity ion charge: -e

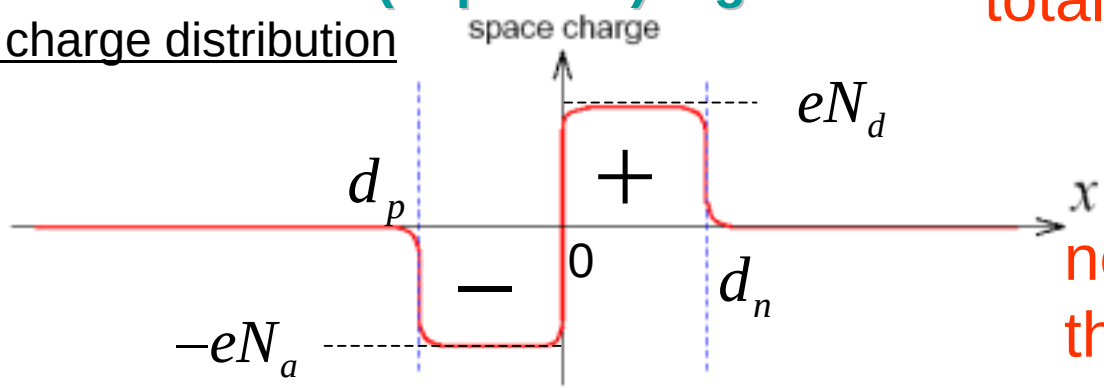
impurity ion charge: +e

$$E_c(x) = E_c - e\phi(x)$$

$$E_v(x) = E_v - e\phi(x)$$

space charge (depletion) region

space charge distribution



total charge neutral:

$$N_d \cdot d_n = N_a \cdot d_p$$

no free carriers in the depletion region

More quantitative treatment

Charge density:

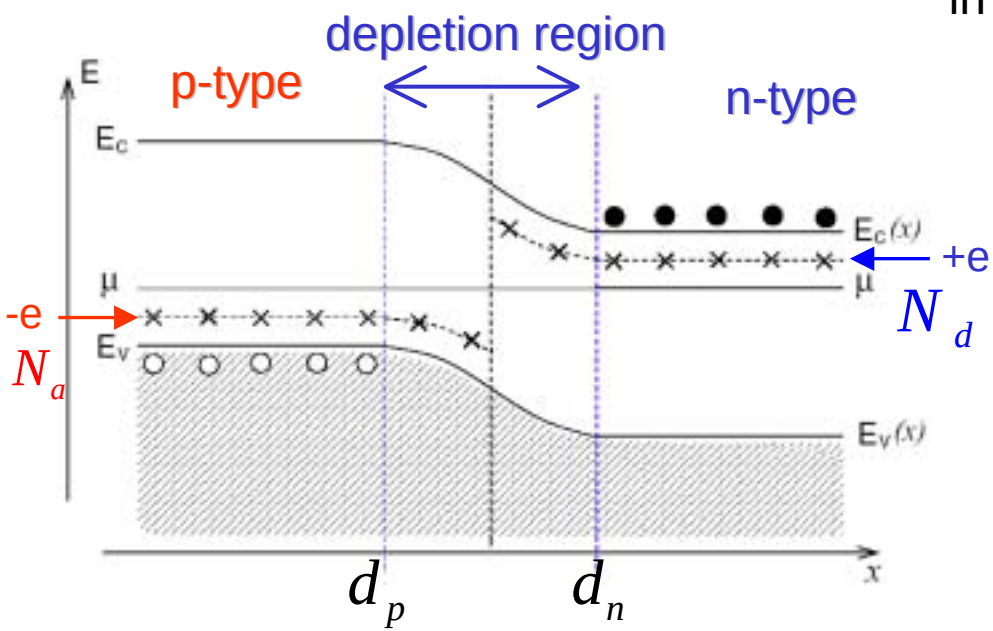
density of **electrons** in **conduction band**

density of **acceptor** impurities

$$\rho(x) = -en(x) + ep(x) - eN_a(x) + eN_d(x)$$

density of **holes** in **valence band**

density of **donor** impurities



non zero local charge distribution

→ finite electronic field

Poisson eq.:

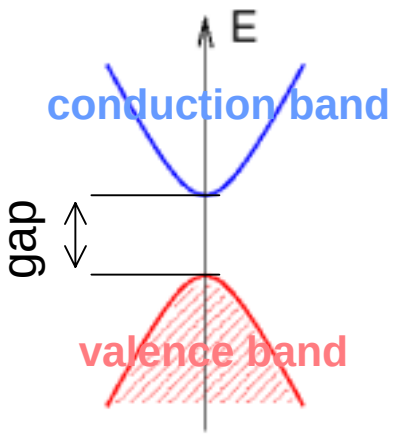
$$\nabla^2\phi(x) = -\frac{e}{\varepsilon}\rho(x)$$

static dielectronic const. (~10-20)

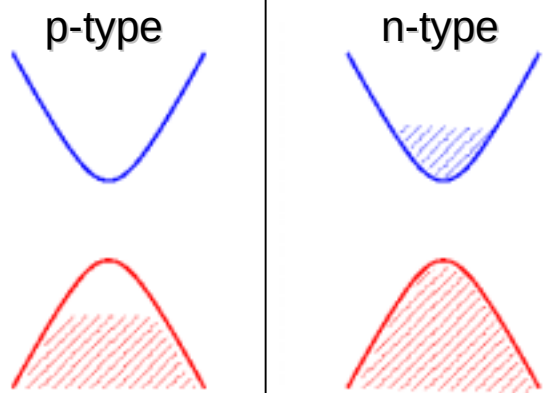
Numerical model calculations

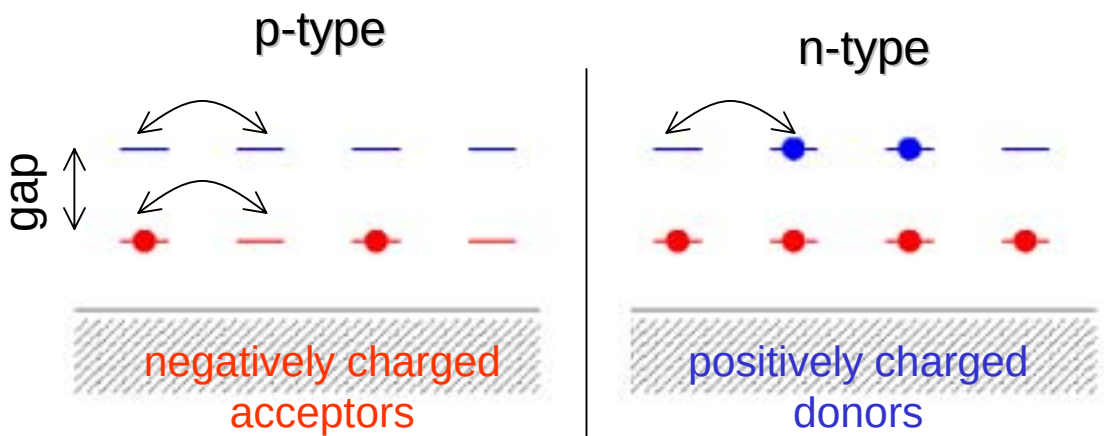
1d tight binding model

(instructive for model calculations of heterojunctions made of correlated materials)



- ✓ 2 band = 2 orbitals per site (unit cell)
- ✓ saturation region (all impurities ionized)





self-consistent calculation

$$\rho_{\text{in}}(x)$$

$$\nabla^2\phi(x) = -\frac{e}{\varepsilon}\rho_{\text{in}}(x)$$

Schrodinger eq.

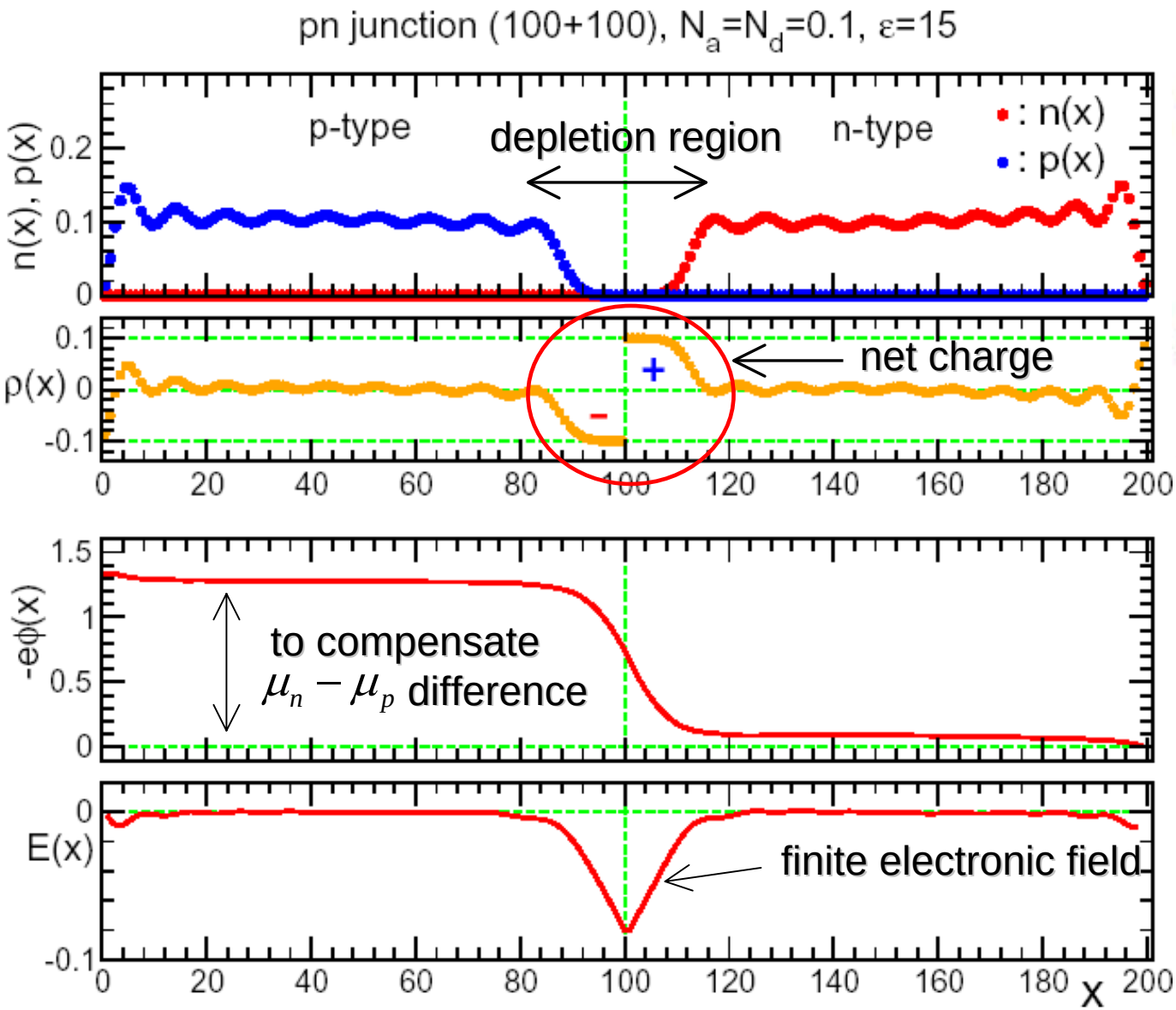
$$\rho_{\text{out}}(x)$$

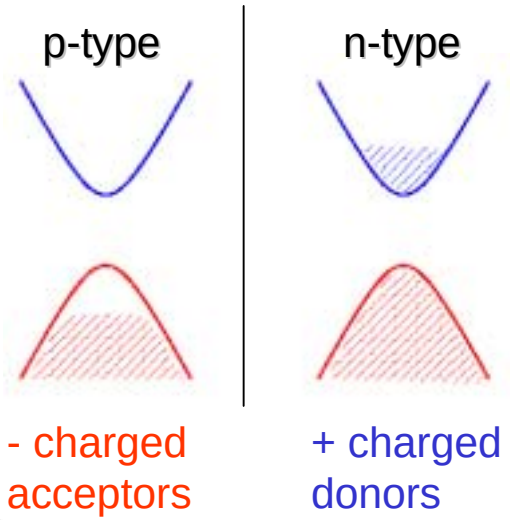
$$\text{if } \rho_{\text{out}}(x) \neq \rho_{\text{in}}(x)$$

1D 2 orbital tight binding model with Coulomb interactions

Numerical calculations: results

1d tight binding model

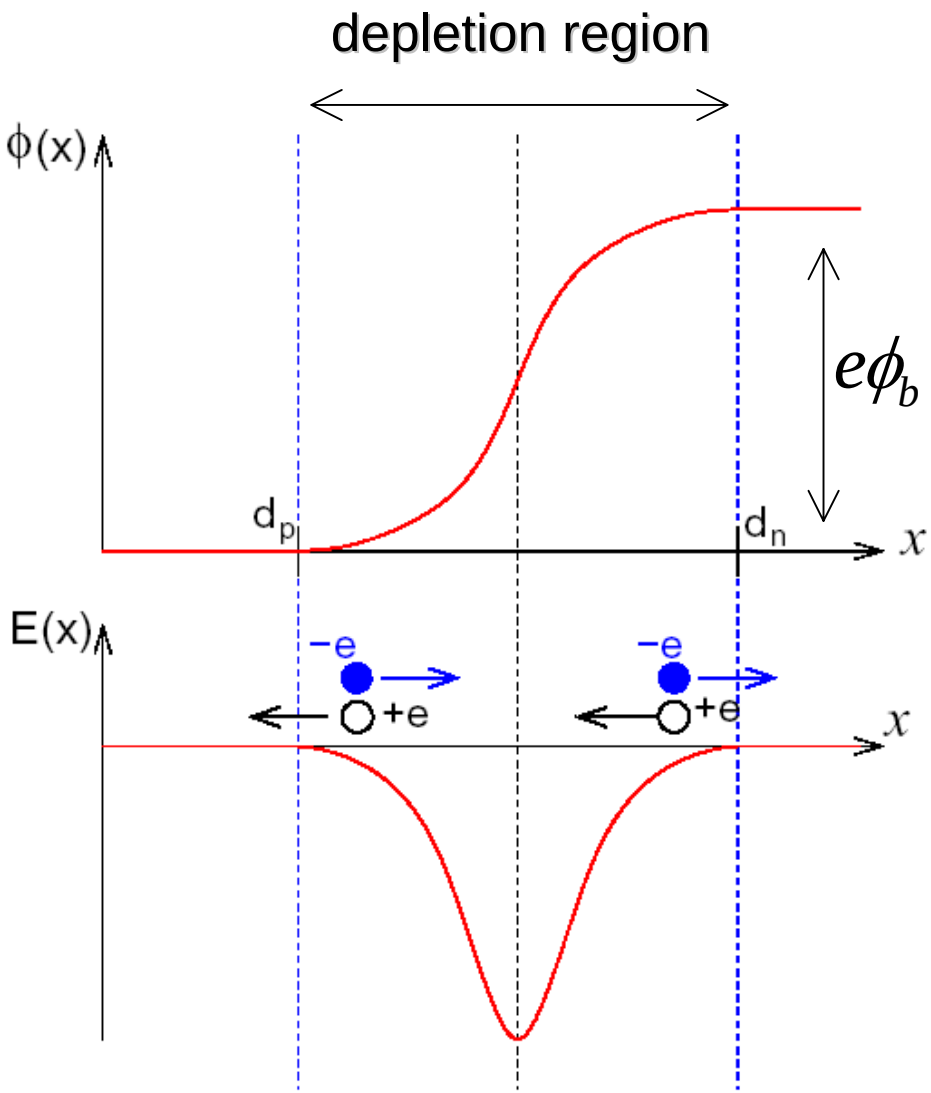


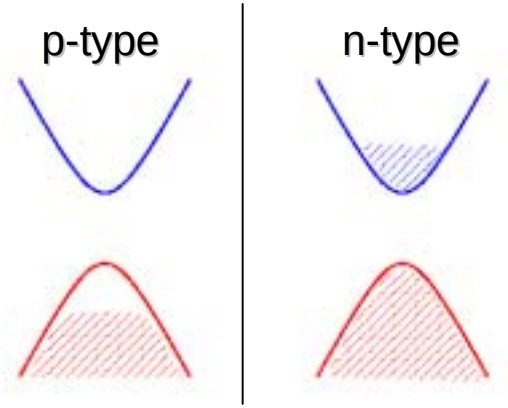


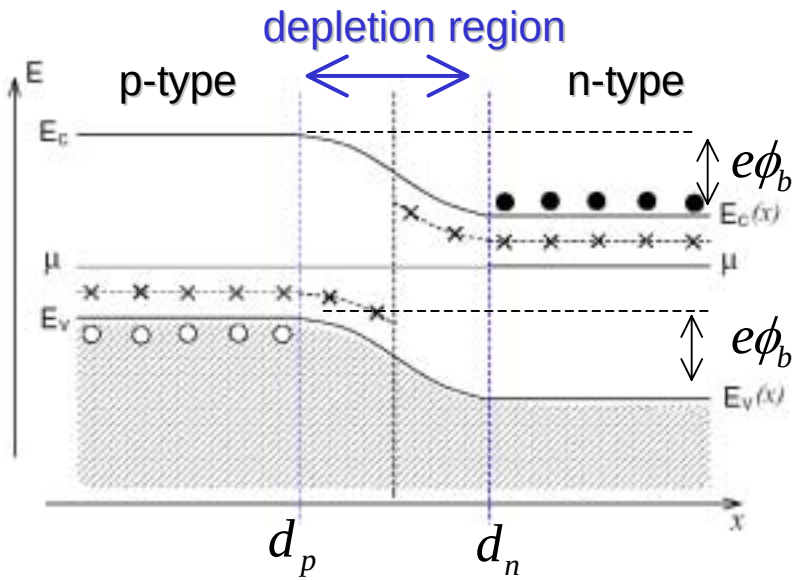
$$E(x) = -\nabla\phi(x)$$

Schematic picture

p-type | n-type







at equilibrium, no current flow

No current flow ??

at equilibrium, no current flow

- From Boltzmann eq.

mobility

diffusion coefficient

$$\mathbf{J}_{\mathrm{n}} = en(x)\mu_n \mathbf{E} + eD_n \nabla n(x)$$ for conduction electrons

$$\mathbf{J}_{\mathrm{h}} = \underbrace{ep(x)\mu_p \mathbf{E}}_{\text{drift current}} \underbrace{- eD_p \nabla p(x)}_{\text{diffusion current}}$$ for valence holes

(see Ashcroft & Mermin, p601)

- Exact cancellation

$$en(x)\mu_n \mathbf{E}(x) = -eD_n \nabla n(x)$$

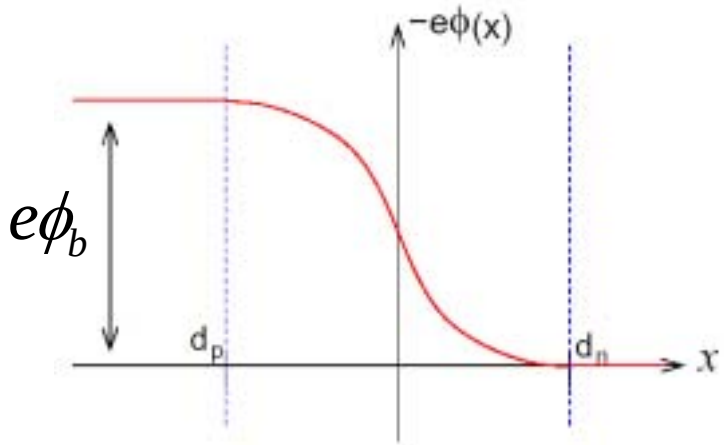
$$\mathbf{E}(x) = -\nabla \phi(x)$$

$$D_n = \frac{k_B T}{e} \cdot \mu_n$$

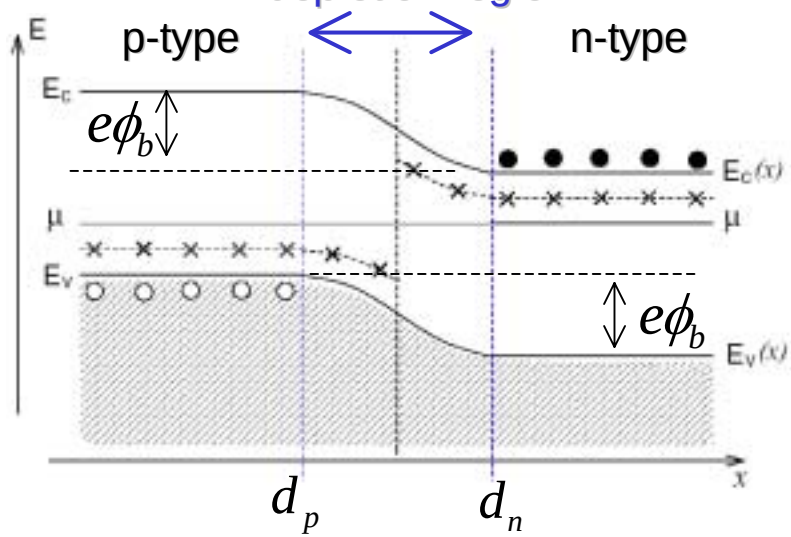
(Einstein relation)

Conduction electrons

$$n(x) = \text{Const.} \times \exp\left[-\frac{\left(-e\phi(x)\right)}{k_B T} \right]$$



depletion region



free electrons in conduction band in p-type semiconductor (minority carriers):

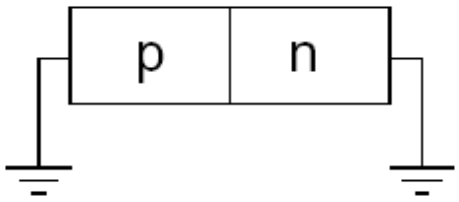
$$n(d_p) = n(d_n) \cdot \exp\left[-e\phi_b / k_B T \right]$$

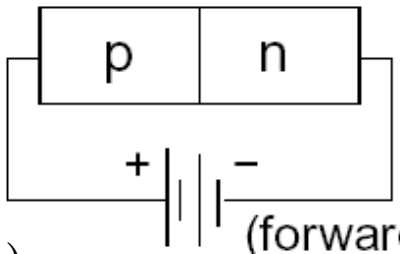
similarly, free holes in valence band in n-type semiconductor (minority carriers):

$$p(d_n) = p(d_p) \cdot \exp\left[-e\phi_b / k_B T \right]$$

I-V characteristic of p-n junction

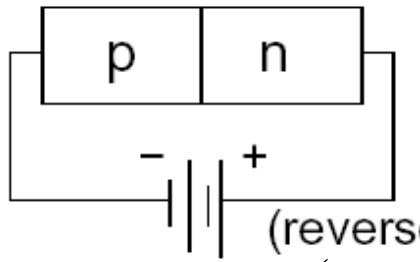
(rectifying response)





(forward)

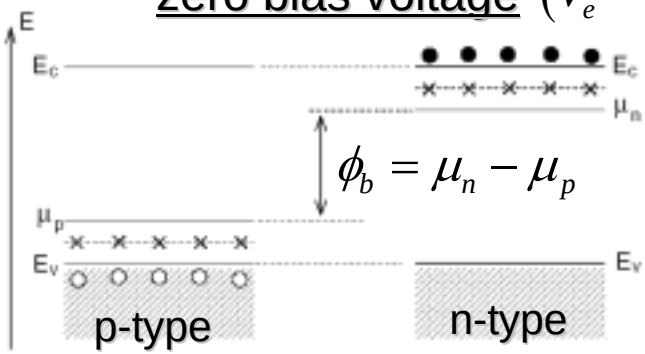
$(V_e > 0)$



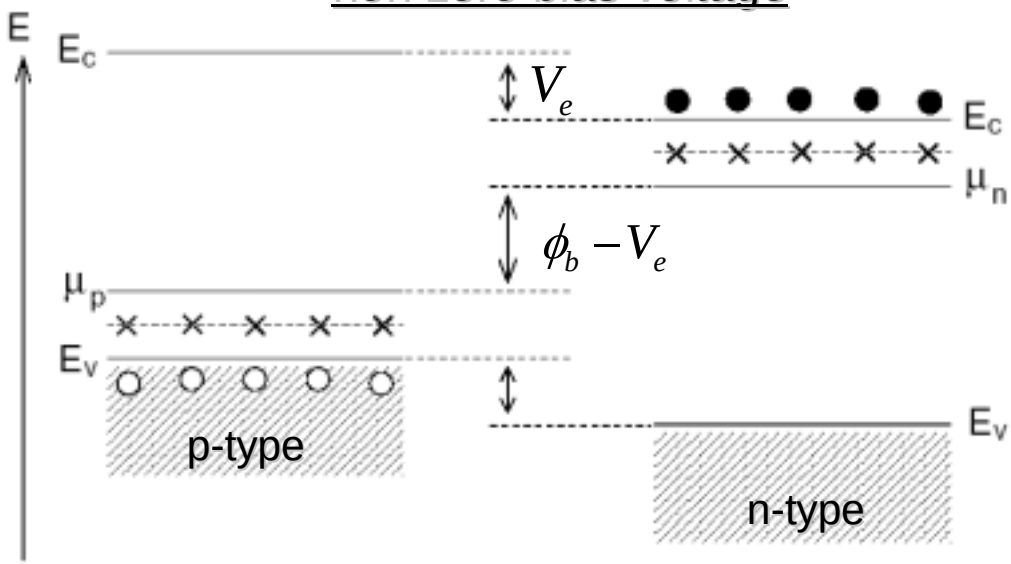
(reverse)

$(V_e < 0)$

zero bias voltage $(V_e = 0)$

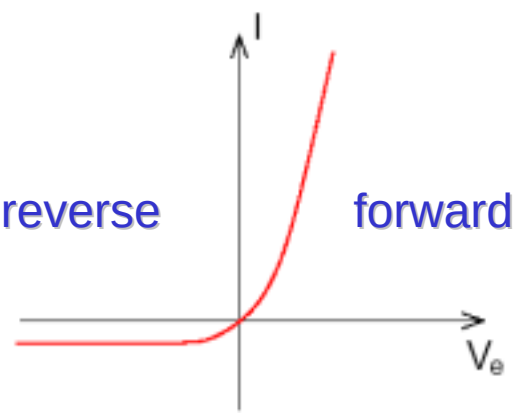


non zero bias voltage

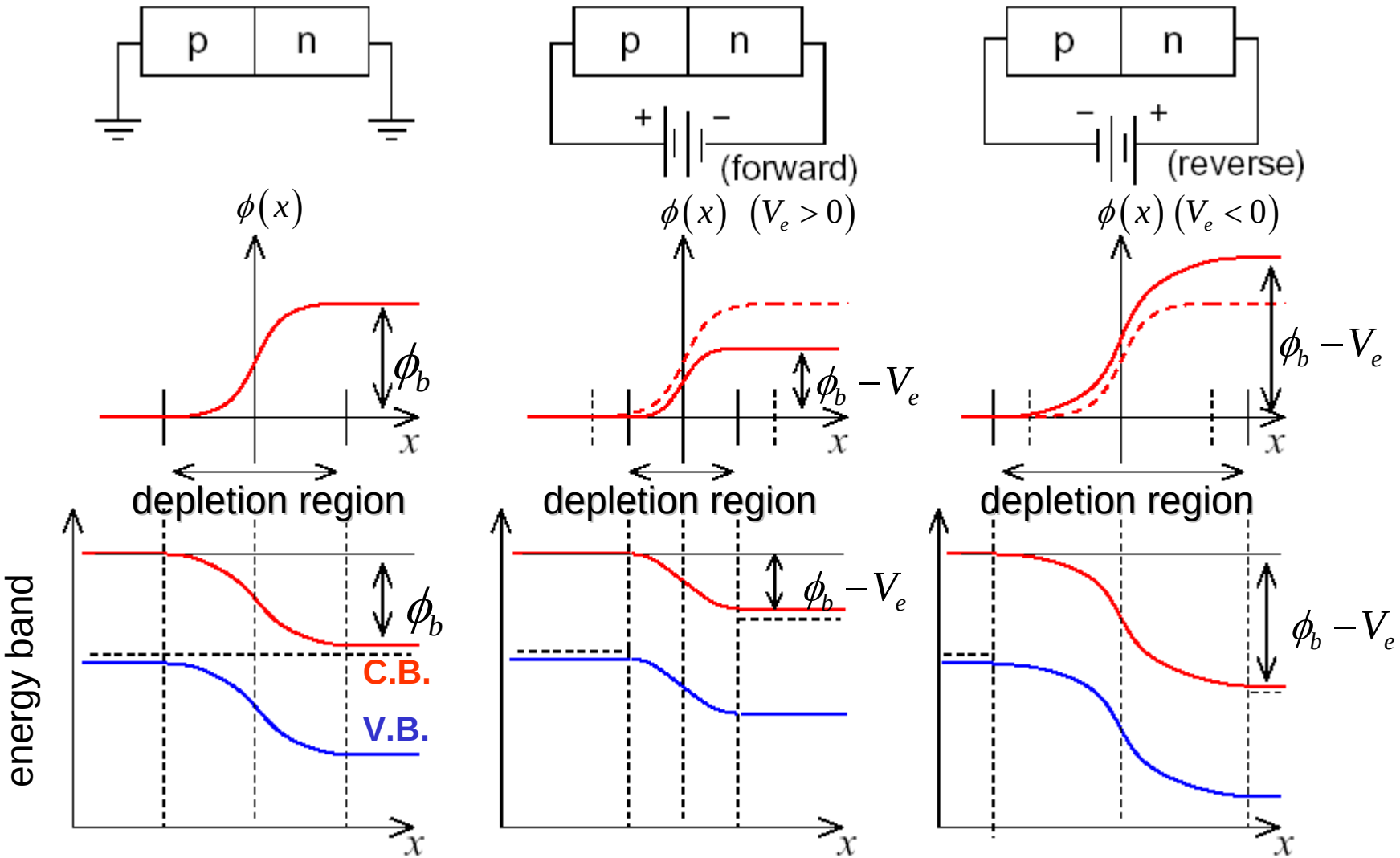


$V_e > 0$

non-linear I-V characteristic

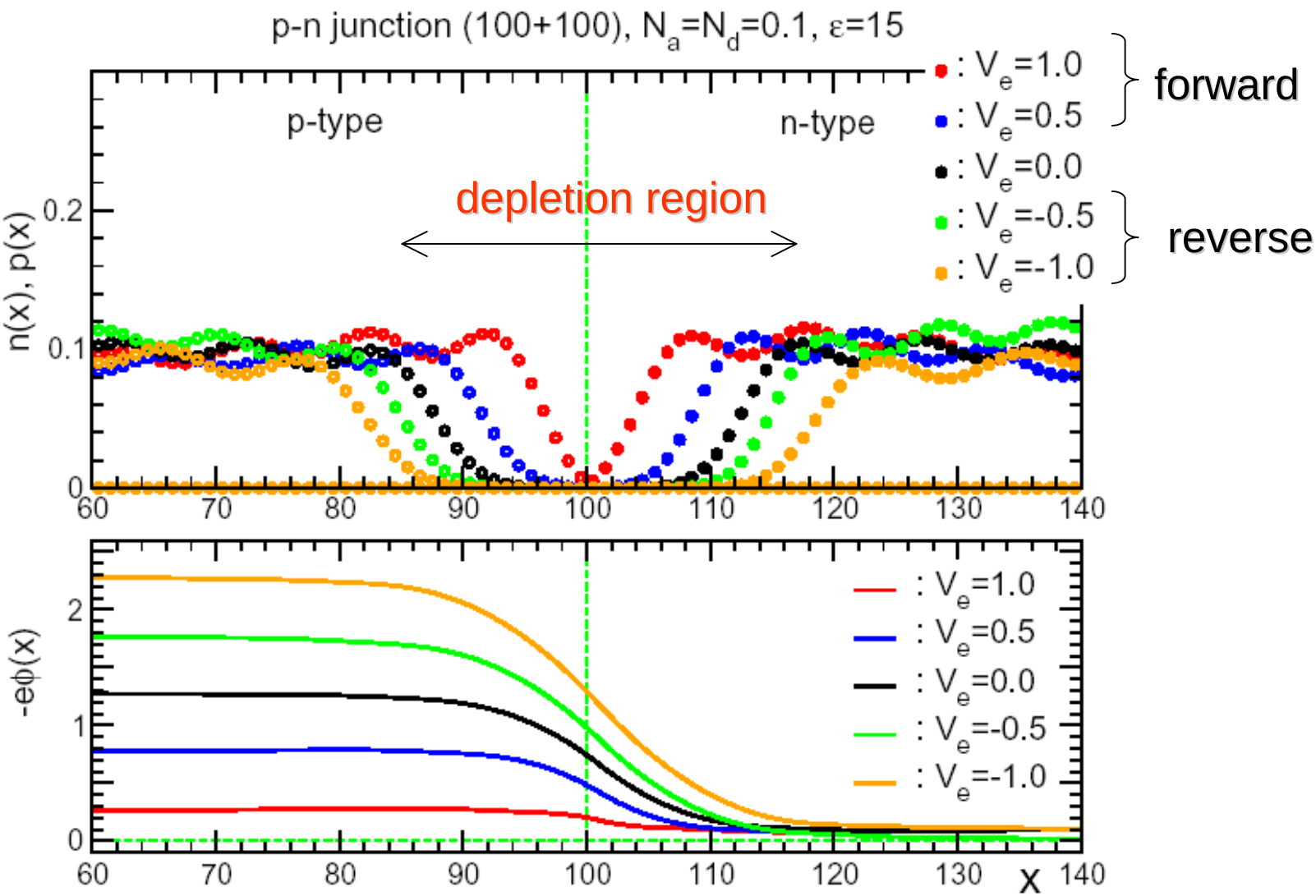


I-V characteristic of p-n junction



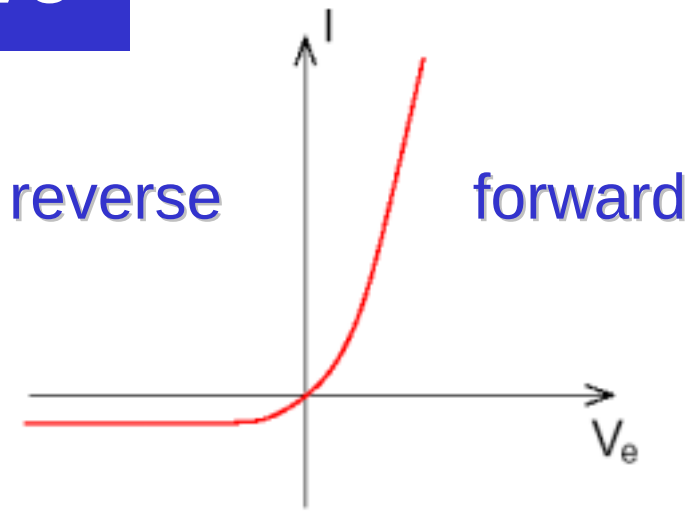
Numerical model calculations

1D 2 orbital tight binding



Rectifying feature in I-V curve

<u>"Oversimplified" understanding</u>



$V_e > 0$ increases

→ depletion region decreases

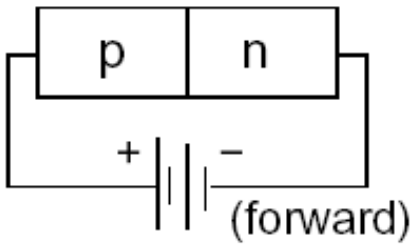
→ electronic potential decreases

$V_e < 0$ decreases

→ depletion region increases

→ electronic potential increases

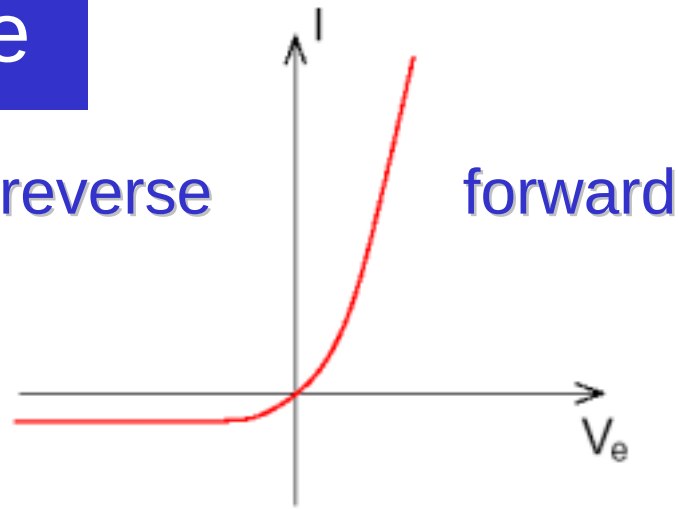
Rectifying feature in I-V curve

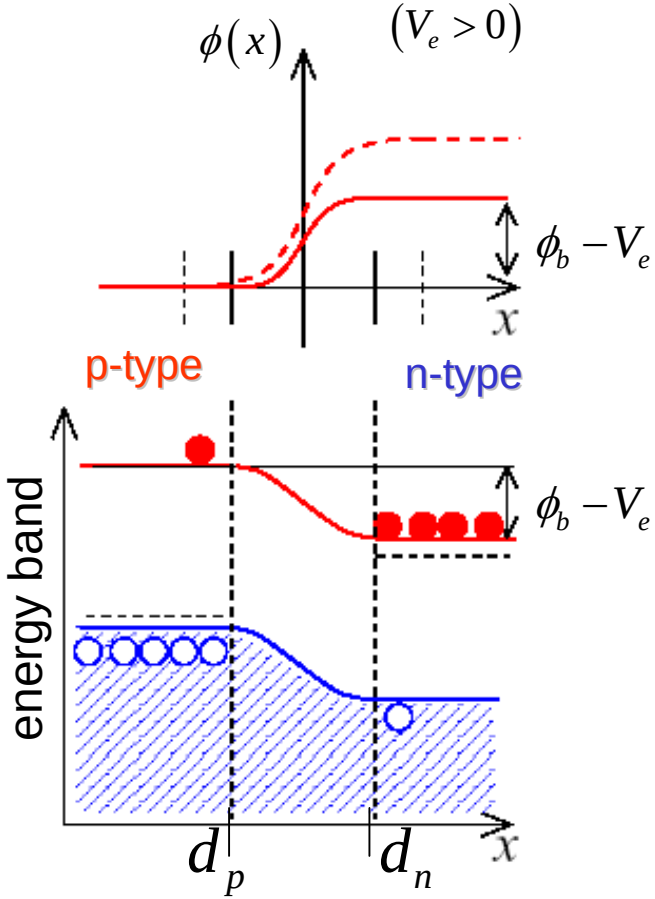


(forward)

$(V_e > 0)$

- ✓ # of minority carriers depends on Ve
- ✓ diffusion current





free electrons in conduction band in p-type semiconductor (minority carriers):

$$n(d_p) = n(d_n) \cdot \exp\left[-e(\phi_b - V_e)/k_B T\right]$$

→ # of electrons injected into C.B. in p-type semiconductor

$$\Delta n(d_p) = n(d_p) - n_0(d_p)$$

$$= n(d_n)\left[e^{eV_e/k_B T} - 1\right]$$

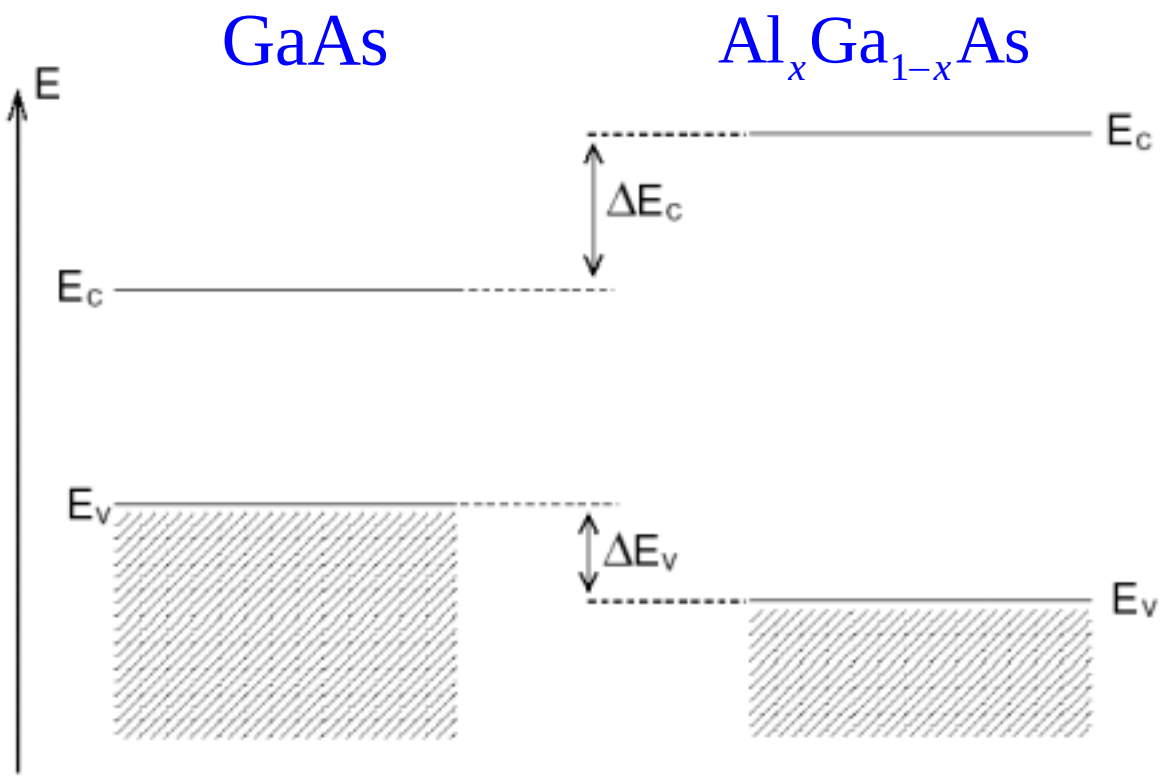
→ $$I \sim \Delta n(d_p) \propto e^{eV_e/k_B T} - 1$$

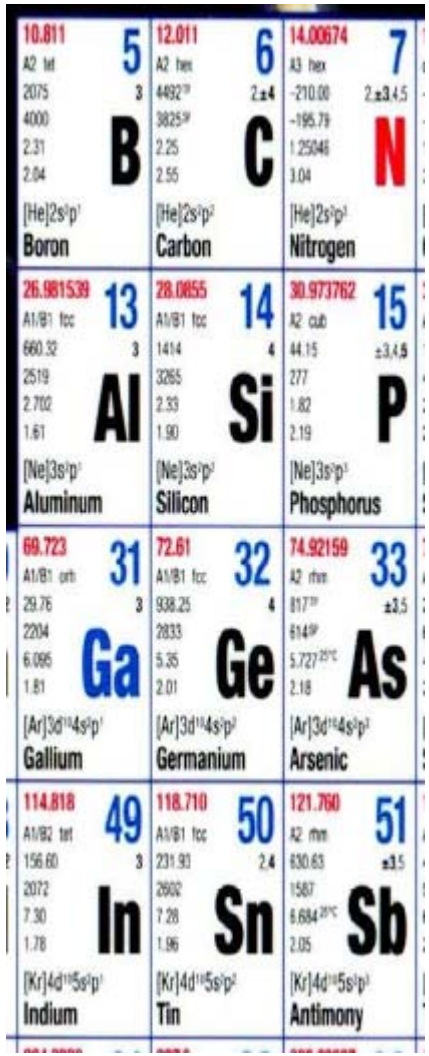
Semiconductor Heterojunctions

$\leftrightarrow$ homopolar junction

$$GaAs/Al_xGa_{1-x}As$$

gap: 1.42 eV 2.17eV (x=1.0)

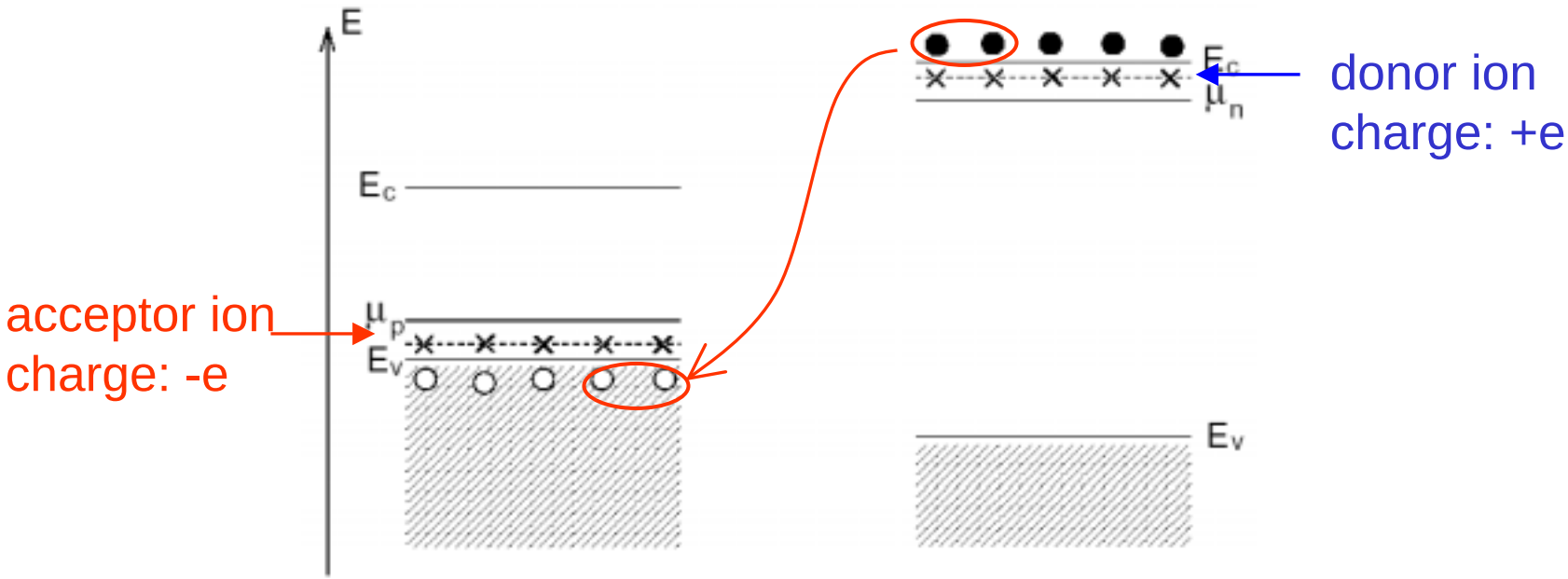




p-n junction made of $p\text{-}GaAs/n\text{-}Al_xGa_{1-x}As$

Schematic energy band

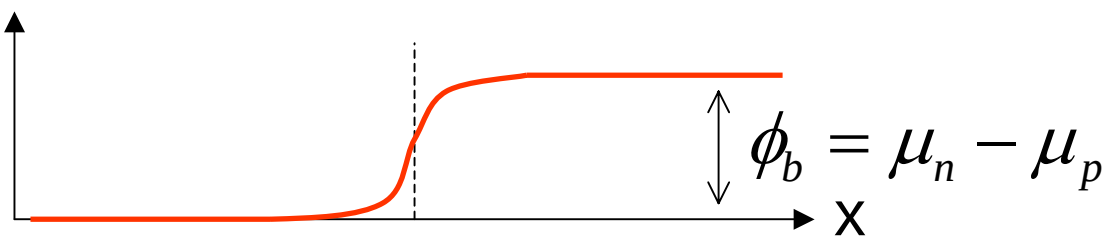
$p\text{-}GaAs/n\text{-}Al_xGa_{1-x}As$



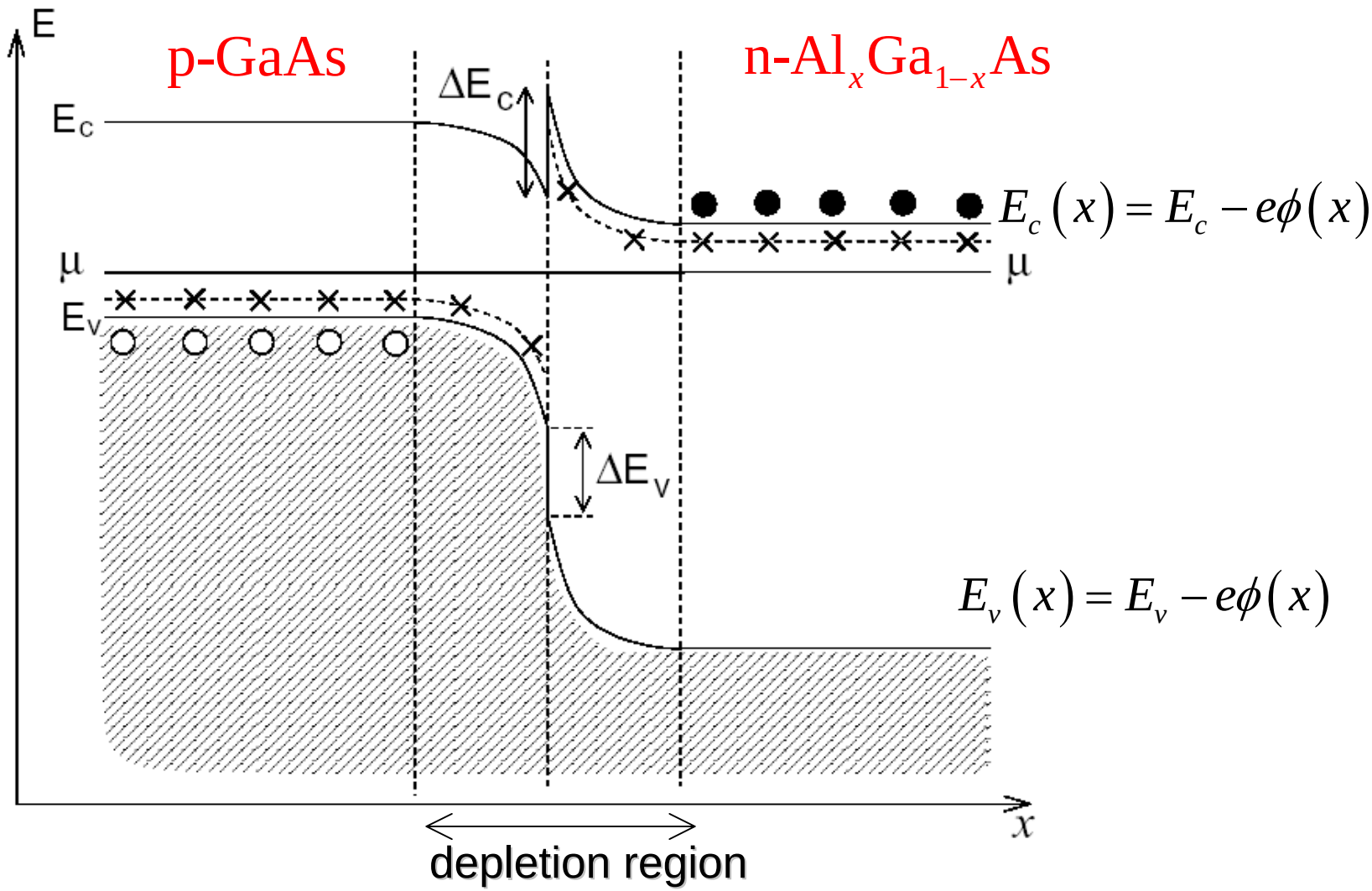
in contact → non-neutralized charge appears → finite electric field

$\phi(x)$

electronic potential



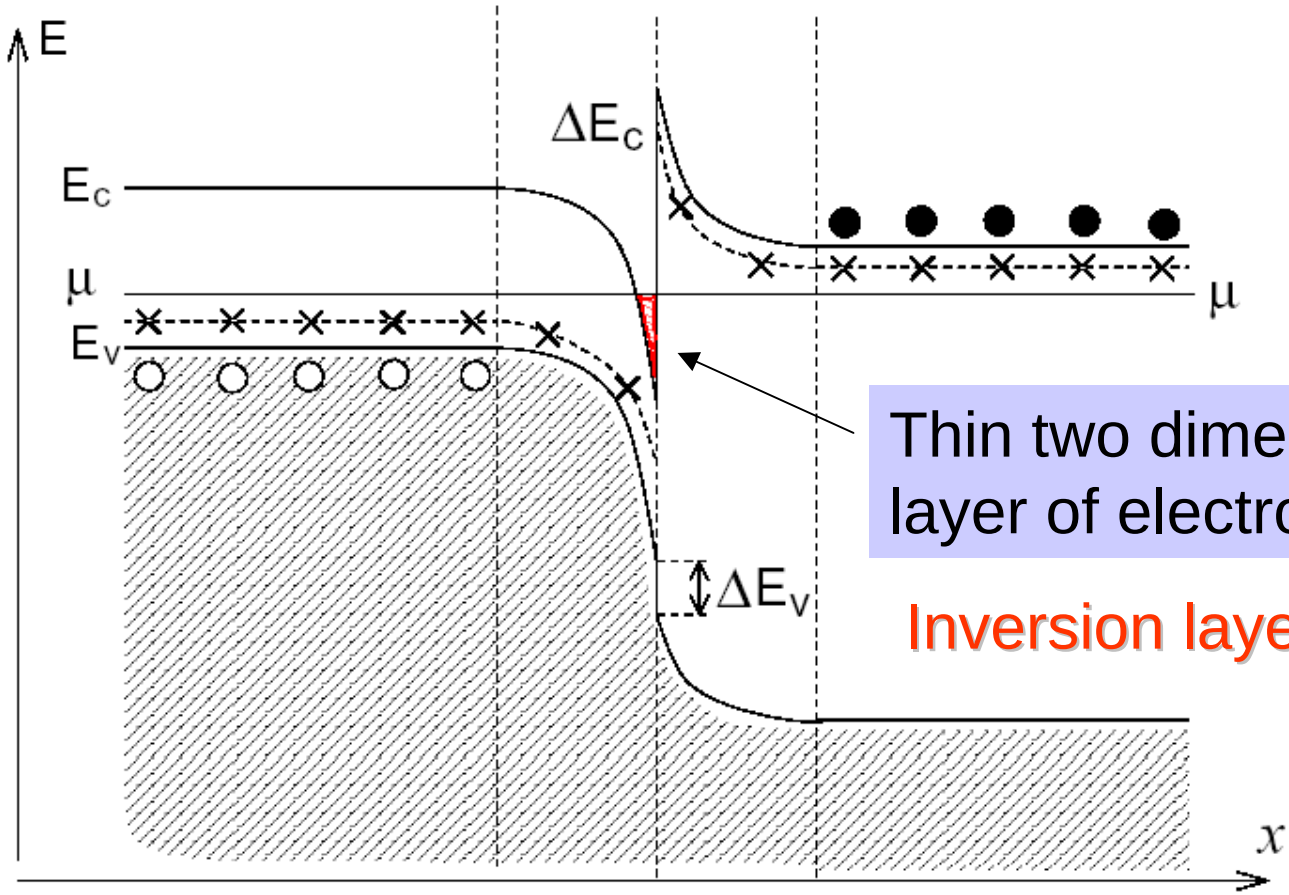
Schematic energy band (in contact)



Band discontinuity ΔE_c & ΔE_v preserved

Inversion Layer

By tailoring the band off set



Thin two dimensional layer of electrons

Inversion layer of electrons

Heterojunction made of transition metal oxides

- ✓ Rapidly growing, very promising new research field

  Many experimental groups (S. Pennycook, H. Christen, J. Shen, …) and a theory group (Dagotto) at UT and ORNL

  Good for your career

- ✓ Transition metal oxides (cuprates, manganites, …)

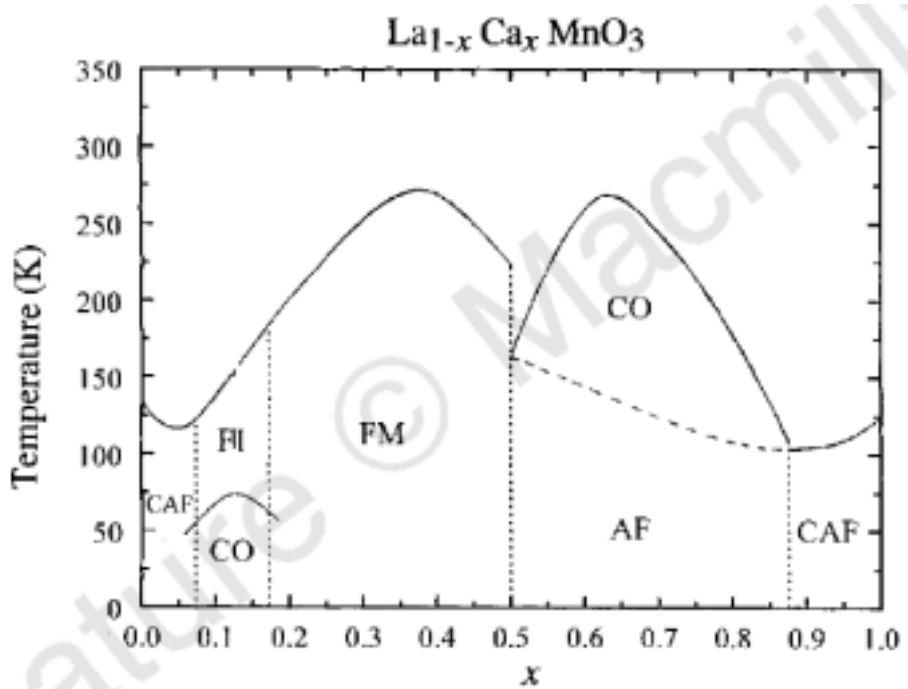
  Strongly correlated systems (Coulomb and electron-lattice interactions)

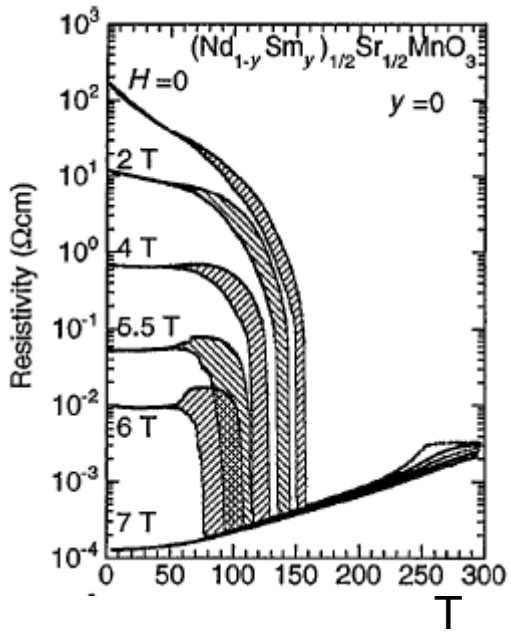
  Many degrees of freedom (charge, spin, orbital, phonon)

Heterojunction made of transition metal oxides

- ✓ Transition metal oxides (cuprates, manganites, …)

Complex phase diagram and large response





- ✓ Next generation electronic device with rich functionality

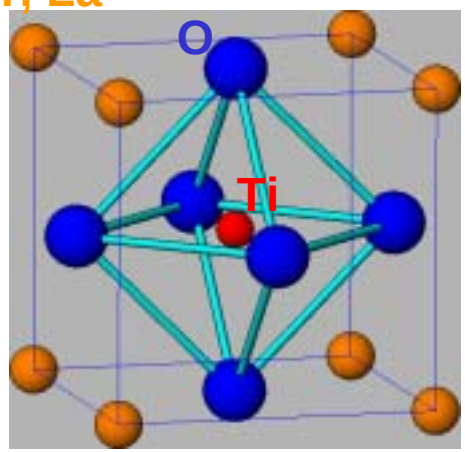
Oxide Electronics (Strongly Correlated Electronics)

A Simplest Example: Titanate Superlattices

(Ohtomo et al, Nature **419**, 378 ('02))

- ✓ $SrTi^{4+}O_3/LaTi^{3+}O_3$ superlattice film

Perovskite structure

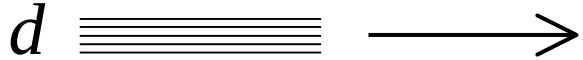


$Sr^{2+}Ti^{4+}O_3 : d^0$ → band insulator

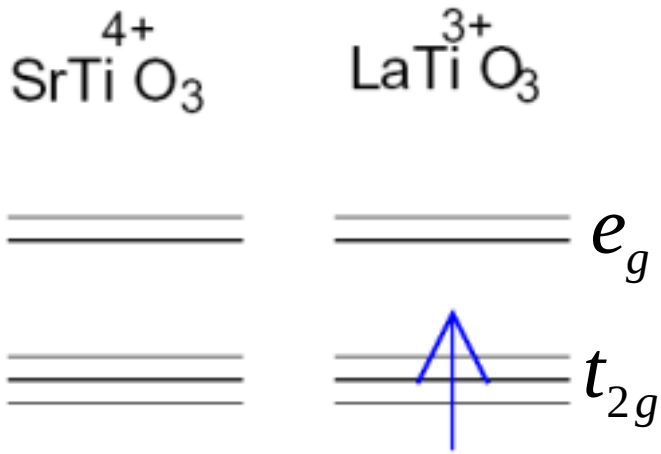
$La^{3+}Ti^{3+}O_3 : d^1$ → Mott insulator

$\text{Ti: } [\text{Ar}](3d)^2(4s)^2$

atomic d level



spherical symmetry



cubic symmetry (octahedral)

Titanate Superlattices

$SrTi^{4+}O_3 / LaTi^{3+}O_3$

(Ohtomo et al, Nature **419**, 378 ('02))

dark filed image (scanning transmission electron microscopy)

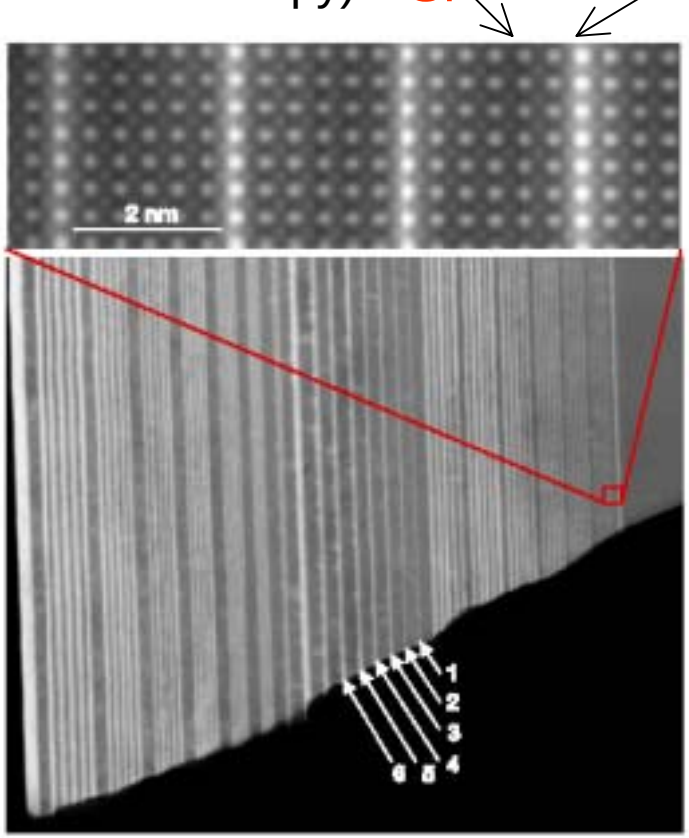
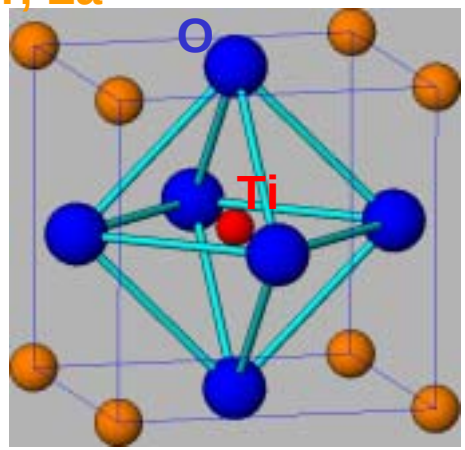


Figure 1 Annular dark field (ADF) image of $LaTiO_3$ layers (bright) of varying thickness spaced by $SrTiO_3$ layers. The view is down the [100] zone axis of the $SrTiO_3$ substrate, which is on the right. After depositing initial calibration layers, the growth sequence is $5 \times n$ (that is, 5 layers of $SrTiO_3$ and n layers of $LaTiO_3$), $20 \times n$, $n \times n$, and finally a $LaTiO_3$ capping layer. The numbers in the image indicate the number of $LaTiO_3$ unit cells in each layer. Field of view, 400 nm. Top, a magnified view of the 5×1 series. The raw images have been convolved with a 0.05-nm-wide gaussian to reduce noise.

Sr, La



atomic-scale fabrication

Insulator + insulator = **metal**

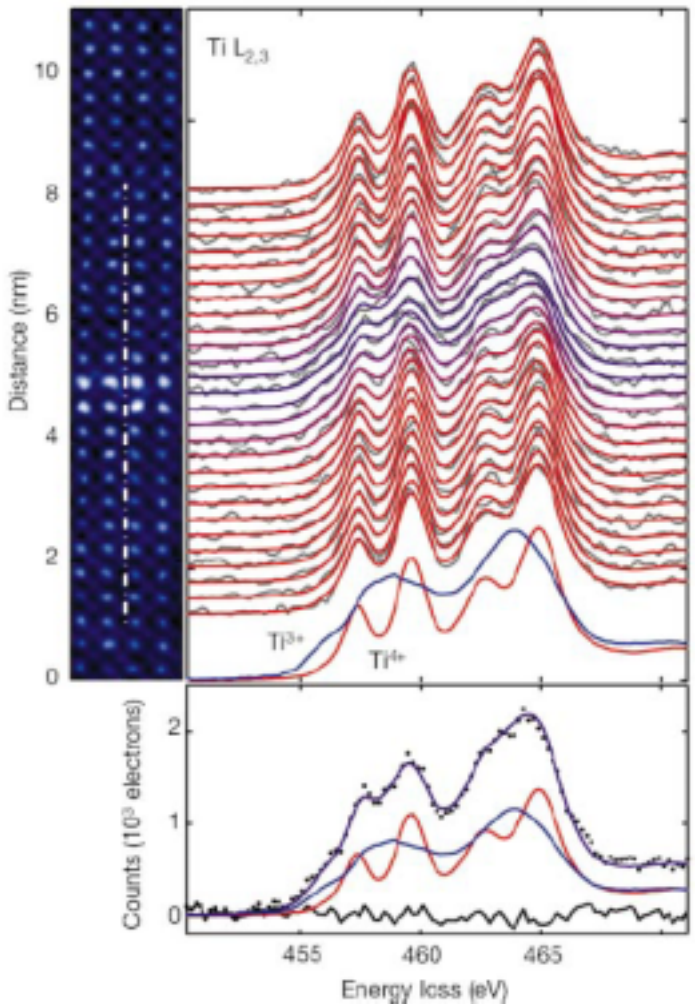
e.g., T^2 dependence of $\rho(T)$

Titanate Superlattices

$SrTi^{4+}O_3 / LaTi^{3+}O_3$

(Ohtomo et al, Nature **419**, 378 ('02))

electron energy loss spectra (EELS)
- atomic column by atomic column -



Ti $L_{2,3}$ edge spectra:

$$\text{Ti: } 2p \rightarrow 3d$$

How to analize data:

measured spectra depending on position

$$I(\omega) = \alpha I_{LaTi^{3+}O_3}(\omega) + (1-\alpha) I_{SrTi^{4+}O_3}(\omega)$$

reference spectra

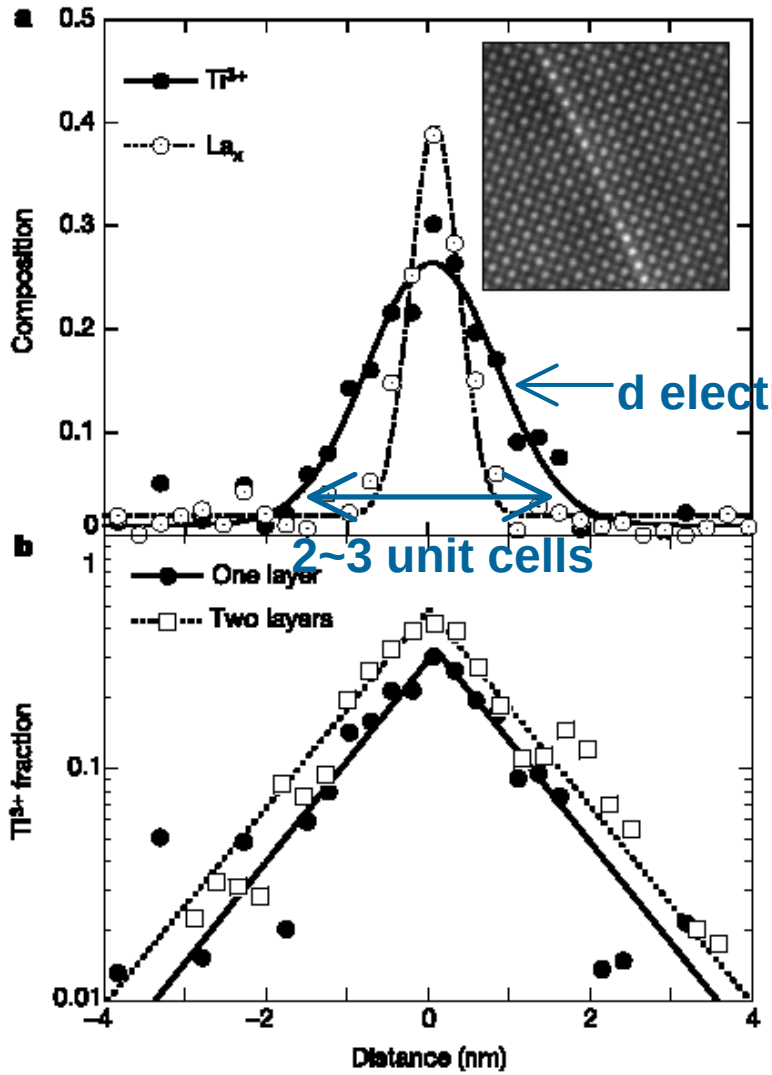
α → # of d electrons

Titanate Superlattices

$SrTi^{4+}O_3/LaTi^{3+}O_3$

(Ohtomo et al, Nature **419**, 378 ('02))

Ti^{3+} fraction = # of d electrons



d electron density

2~3 unit cells

# of d electrons < 1

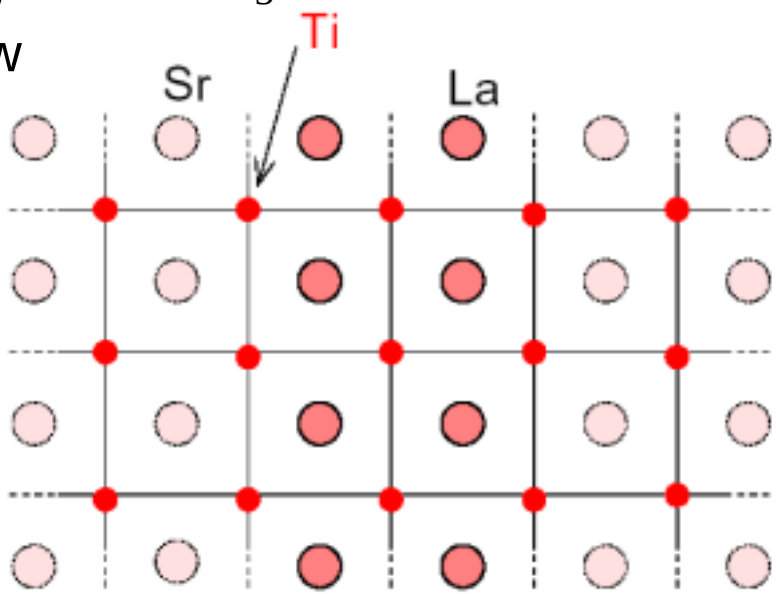
→ charge leakage

To recover the bulk valcue, at least 5 layers of La-ions are needed.

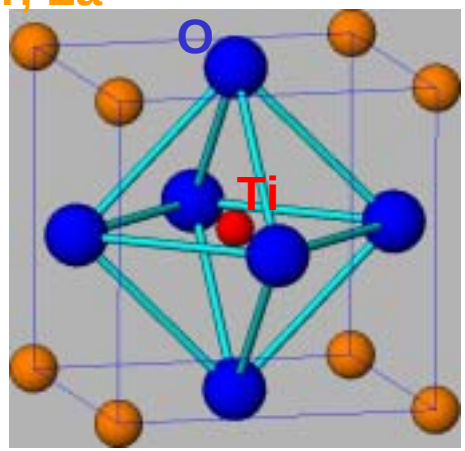
Model Calculations of Titanate Superlattices

$SrTi^{4+}O_3/LaTi^{3+}O_3$ superlattice

- Top view



Perovskite structure



$Sr^{2+}Ti^{4+}O_3: d^0$ = reference, $La^{3+}Ti^{3+}O_3: d^1$

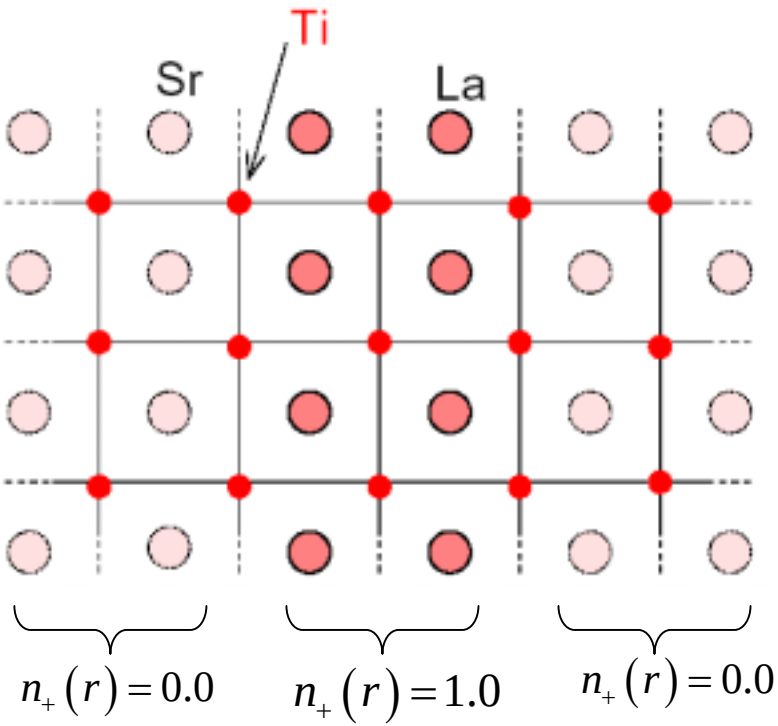
- Extra +1 charge on La site
  (positively charged back ground)
- # of total d electrons = # of total La ions
  (donor impurities)

} very similar to semiconductors

- Ti d orbitals: electrically active orbital

Model Calculations of Titanate Superlattices

$SrTi^{4+}O_3 / LaTi^{3+}O_3$ superlattice



$$H = H_{d-band} + H_{Hubbard} + H_{long-range}$$

where

H_{d-band} : Ti d-electron band (cubic lattice)

$H_{Hubbard}$: on-site short range electron-electron interaction (on-site U)

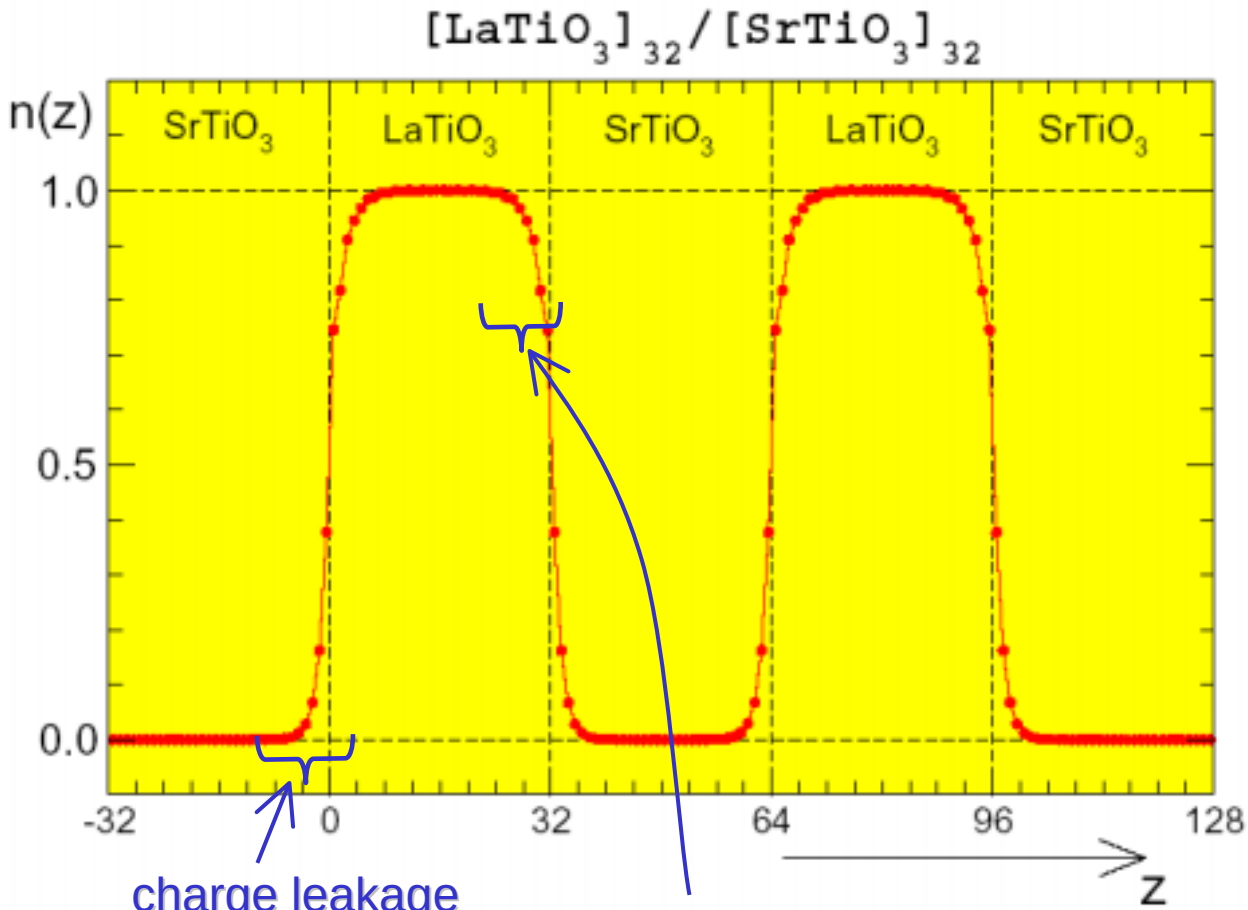
$H_{long-range}$: long-range Coulomb Interaction between electrons and electron-ion (positive back ground charge)

total # of d electrons = total # of La ions
= total # of positively charged back ground charge

self-consistent mean-field calculations

Oxide heterostructure interface: mean-field results

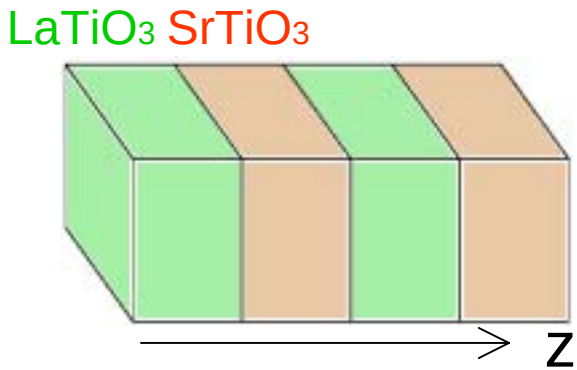
- $LaTiO_3/SrTiO_3$



dielectronic constant:

$$\varepsilon = 15$$

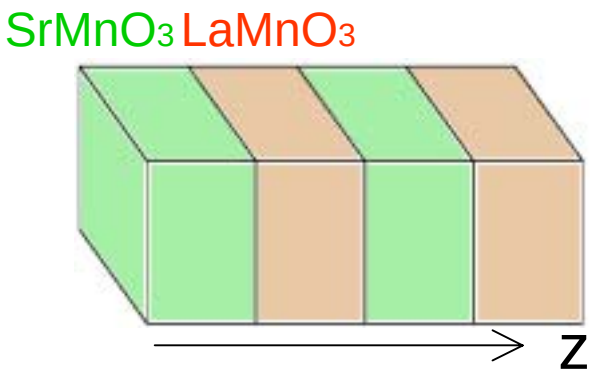
single band approximation

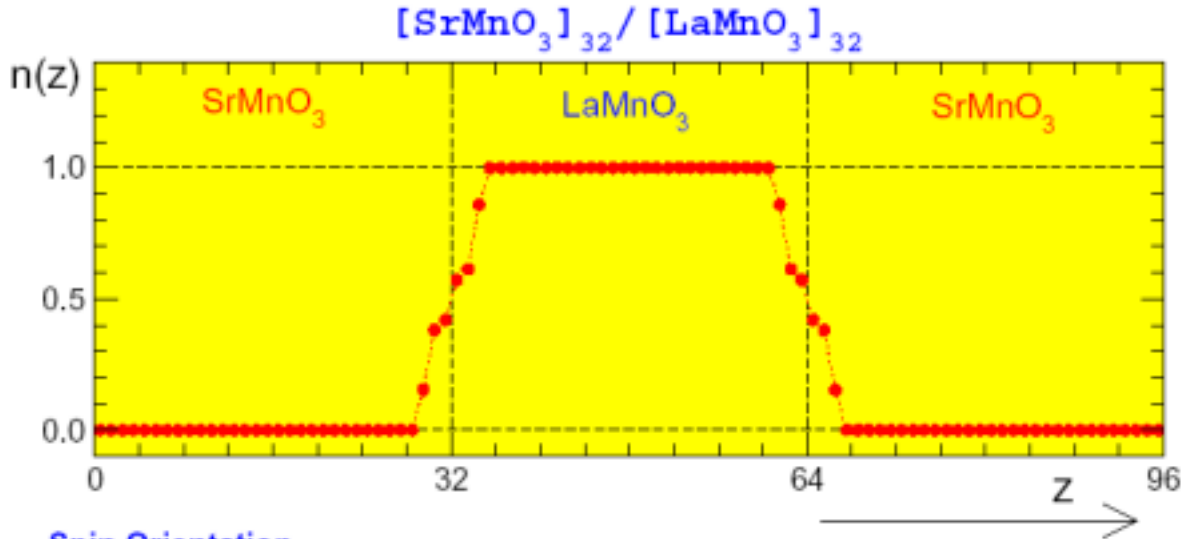


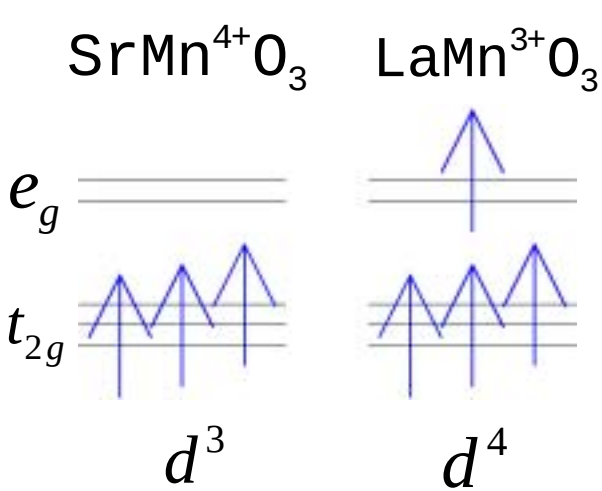
electron-positively charged ion interaction crucial to produce potential wells

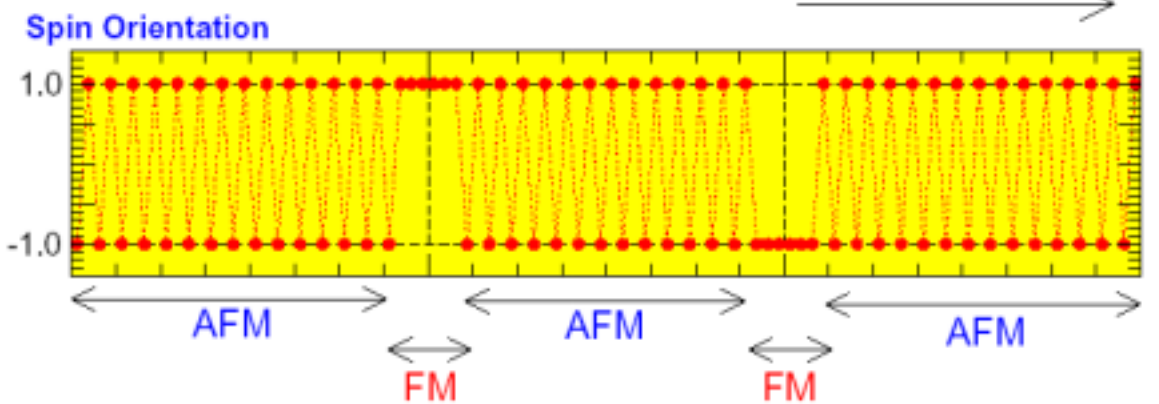
Oxide heterostructure interface

- $LaMnO_3/SrMnO_3$





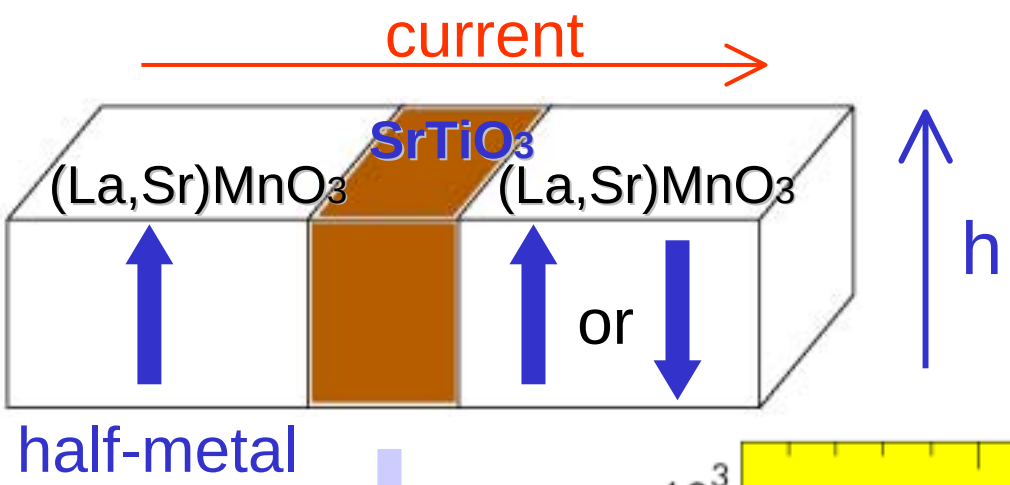




Ferromagnetic half-metallic interface

Oxide heterojunction: magnetic tunnel junction

- $La_{2/3}Sr_{1/3}MnO_3/SrTiO_3/La_{2/3}Sr_{1/3}MnO_3$

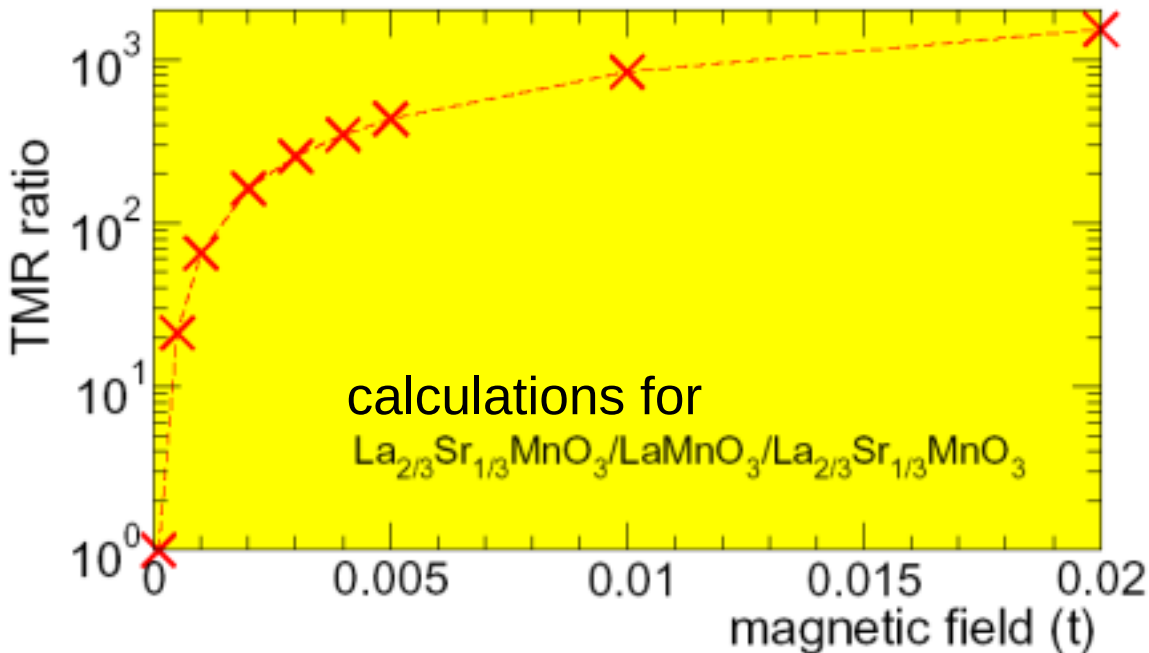


A. Fert's group (2003)

Tunneling magneto-resistance (TMR)

TMR ratio ~1800%

$$\rho(0)/\rho(h) = 1 + (\text{TMR ratio})$$



Summary:

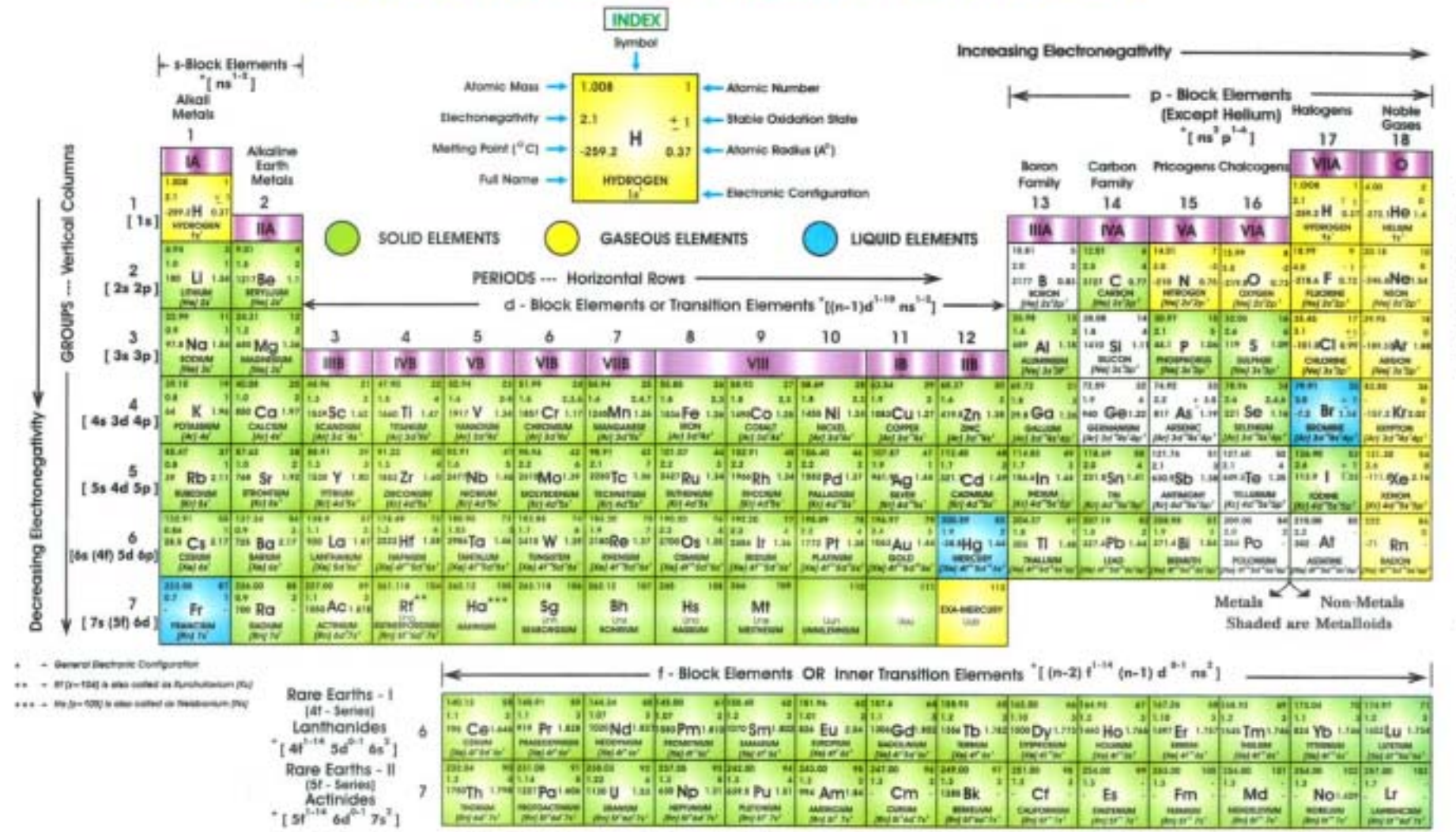
Transition Metal Oxide Heterostructure:

- Very promising new research field
- Next generation electronic devices

Oxide Electronics

- Emergence of new exotic quantum states in heterostructure interface

LONG FORM OF PERIODIC TABLE



Values are taken from Lange's Handbook of Chemistry
12th Edition, McGraw Hill Book Company, New York
Edited by: John A. Dean