

Elementary Semiconductor Physics for Transition Metal Oxide Heterostructure

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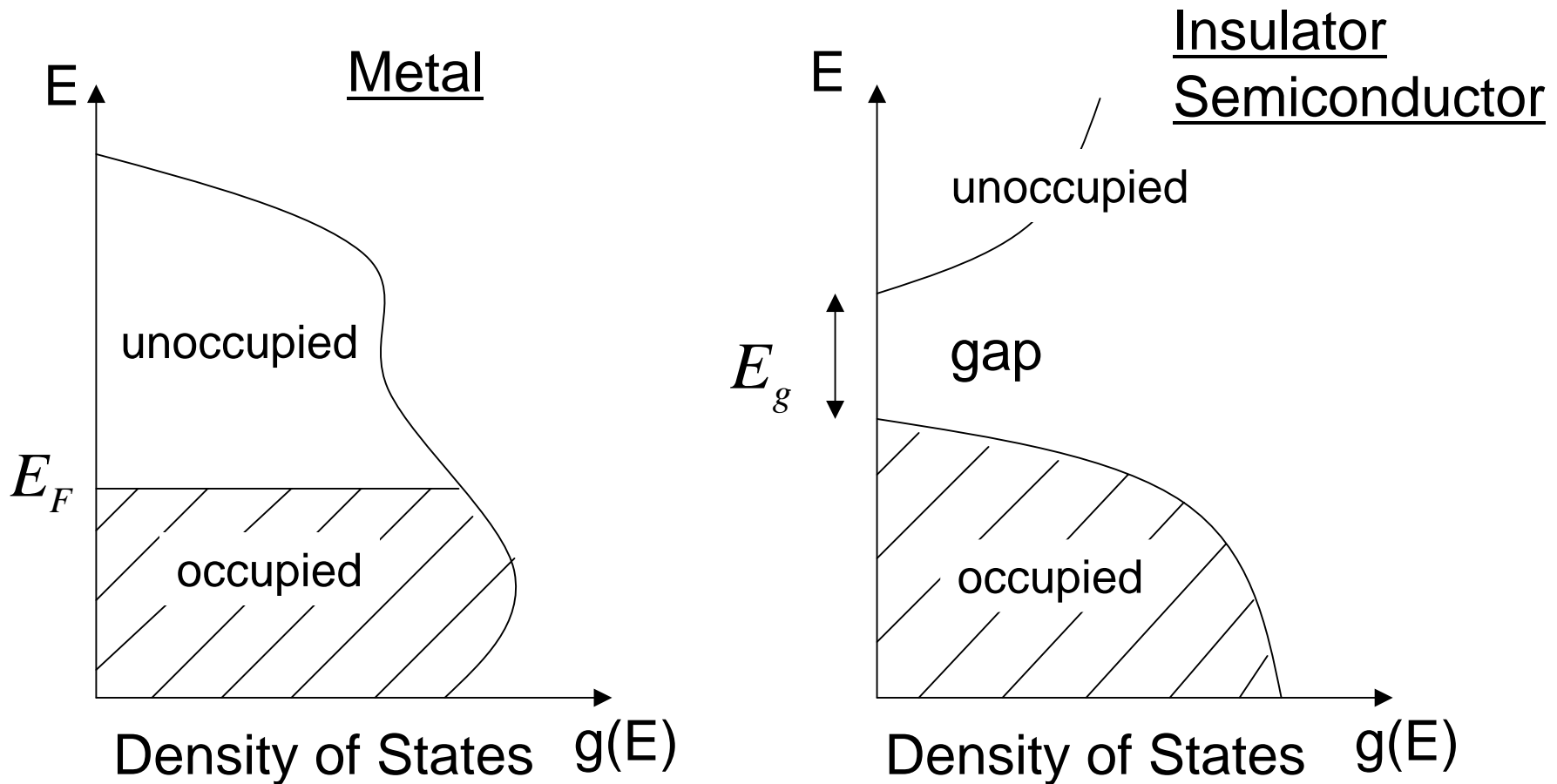
Content of lectures

- 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 Ashcroft & Mermin

- Heterojunction made of correlated electronic systems

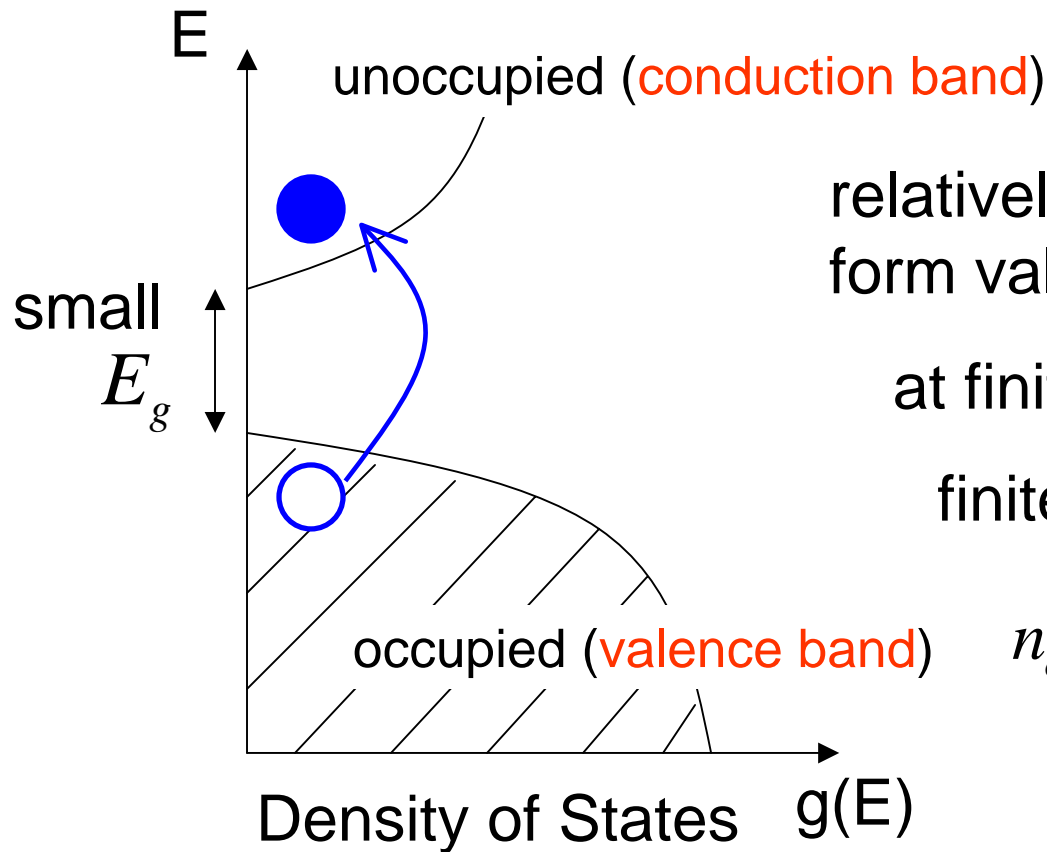
Metal, Insulator, and Semiconductor



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

Insulator: E_g relatively large (\sim several eV)

Semiconductor: small energy gap



relatively easy to excite electrons
from valence to conduction bands
at finite temperature (T)

finite amount of electrons in C.B.

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

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

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

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

Pure (Intrinsic) Semiconductor

13 IIIB IIIA	14 IVB IVA	15 VB VA	16 VIB VIA	17 VIIB VIIA	18 VIIIB VIIIA
13.8011 42 met 2071 4000 2.31 2.04 B (He)2s ² p ¹ Boron	12.011 42 met 4402 3525 2.25 2.35 C (He)2s ² p ² Carbon	14.00374 42 met -210.00 -195.79 1.25648 3.04 N (He)2s ² p ³ Nitrogen	15.9994 42 non -218.79 -192.95 1.429 3.44 O (He)2s ² p ⁴ Oxygen	18.9984032 42 non -219.62 -192.12 1.69 3.99 F (He)2s ² p ⁵ Fluorine	20.1797 42 noble -248.50 -248.36 0.0002 — Ne (He)2s ² p ⁶ Neon
26.981539 41 met 660.32 2519 2.702 1.81 Al (Ne)3s ² p ¹ Aluminum	28.0855 41 met 1414 3205 2.33 1.90 Si (Ne)3s ² p ² Silicon	30.973762 42 met 44.15 3205 1.62 2.19 P (Ne)3s ² p ³ Phosphorus	32.066 42 met 115.21 444.66 3.07 2.59 S (Ne)3s ² p ⁴ Sulfur	35.4527 42 met -101.5 -34.04 3.214 3.16 Cl (Ne)3s ² p ⁵ Chlorine	39.948 42 noble -189.35 -185.85 1.794 — Ar (Ne)3s ² p ⁶ Argon
63.546 42 met 1064.62 2562 8.96 1.90 Cu (Ar)3d ¹⁰ 4s ¹ Copper	65.39 41 met 418.1 419.52 967 1.65 Zn (Ar)3d ¹⁰ 4s ² Zinc	69.723 41 met 418.1 29.75 2204 1.81 Ga (Ar)3d ¹⁰ 4s ¹ p ¹ Gallium	72.61 42 met 508.25 3823 5.35 2.01 Ge (Ar)3d ¹⁰ 4s ² p ² Germanium	74.92159 42 met 817 3823 6.149 2.19 As (Ar)3d ¹⁰ 4s ² p ³ Arsenic	78.96 42 met 721 3823 4.81 2.59 Se (Ar)3d ¹⁰ 4s ² p ⁴ Selenium
79.904 42 met -2.2 58.8 1.119 2.96 Br (Ar)3d ¹⁰ 4s ² p ⁵ Bromine	79.904 42 met -2.2 58.8 1.119 2.96 Br (Ar)3d ¹⁰ 4s ² p ⁵ Bromine	83.80 42 noble -157.36 -153.25 3.74 — Kr (Ar)3d ¹⁰ 4s ² p ⁶ Krypton	83.80 42 noble -157.36 -153.25 3.74 — Kr (Ar)3d ¹⁰ 4s ² p ⁶ Krypton	83.80 42 noble -157.36 -153.25 3.74 — Kr (Ar)3d ¹⁰ 4s ² p ⁶ Krypton	83.80 42 noble -157.36 -153.25 3.74 — Kr (Ar)3d ¹⁰ 4s ² p ⁶ Krypton
107.8682 47 met 960.76 2142 10.5 1.93 Ag (Kr)4d ¹⁰ 5s ¹ Silver	112.411 48 met 301.07 767 8.642 1.69 Cd (Kr)4d ¹⁰ 5s ² Cadmium	114.818 49 met 156.60 2072 7.30 1.78 In (Kr)4d ¹⁰ 5s ¹ p ¹ Indium	118.710 50 met 221.90 3982 1.28 1.96 Sn (Kr)4d ¹⁰ 5s ² p ² Tin	121.760 51 met 600.63 1587 6.684 2.05 Sb (Kr)4d ¹⁰ 5s ² p ³ Antimony	127.60 52 met 449.51 380 6.25 2.1 Te (Kr)4d ¹⁰ 5s ² p ⁴ Tellurium
126.90447 53 met 113.7 194.4 4.83 3.80 I (Kr)4d ¹⁰ 5s ² p ⁵ Iodine	126.90447 53 met 113.7 194.4 4.83 3.80 I (Kr)4d ¹⁰ 5s ² p ⁵ Iodine	131.29 54 noble -111.75 -100.34 5.89 — Xe (Kr)4d ¹⁰ 5s ² p ⁶ Xenon	131.29 54 noble -111.75 -100.34 5.89 — Xe (Kr)4d ¹⁰ 5s ² p ⁶ Xenon	131.29 54 noble -111.75 -100.34 5.89 — Xe (Kr)4d ¹⁰ 5s ² p ⁶ Xenon	131.29 54 noble -111.75 -100.34 5.89 — Xe (Kr)4d ¹⁰ 5s ² p ⁶ Xenon
196.96654 79 met 1064.18 3556 19.31 2.54 Au (Xe)4f ¹⁴ 5d ¹⁰ 6s ¹ Gold	200.59 80 met -80.83 354.73 13.543 2.03 Hg (Xe)4f ¹⁴ 5d ¹⁰ 6s ² Mercury	204.3833 81 met 304 1473 11.85 2.04 Tl (Xe)4f ¹⁴ 5d ¹⁰ 6s ¹ p ¹ Thallium	207.2 82 met 307.46 1749 11.34 2.33 Pb (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ² Lead	208.98037 83 met 211.40 1584 6.79 2.02 Bi (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ³ Bismuth	208.98037 84 met 211.40 1584 6.79 2.02 Po (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁴ Polonium
209.98711 85 met 302 337 — 2.2 At (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁵ Astatine	209.98711 85 met 302 337 — 2.2 At (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁵ Astatine	222.0176 86 noble -71 -61.7 6.73 — Rn (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁶ Radon	222.0176 86 noble -71 -61.7 6.73 — Rn (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁶ Radon	222.0176 86 noble -71 -61.7 6.73 — Rn (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁶ Radon	222.0176 86 noble -71 -61.7 6.73 — Rn (Xe)4f ¹⁴ 5d ¹⁰ 6s ² p ⁶ Radon

Semiconducting elements: IV

Si, Ge, ...

Semiconducting compounds: III-V

GaAs, GaP, InSb, ...



Chemical Periodic Table

8th EDITION

CHEMICAL PERIODIC TABLE

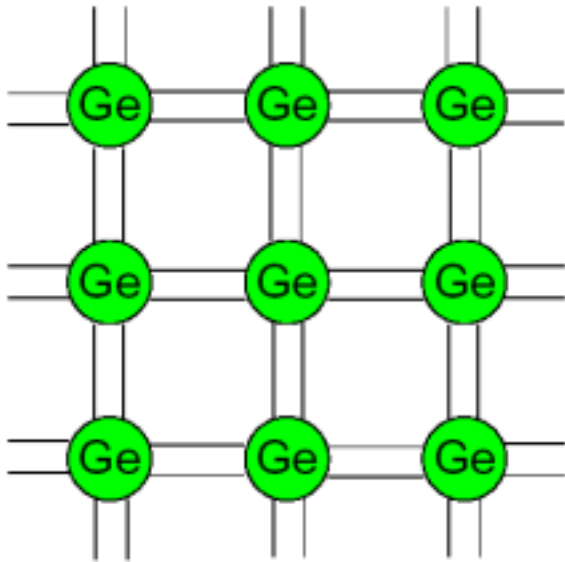
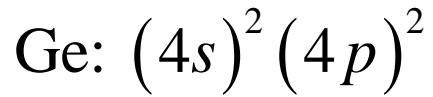
<p>Atomic Weight () indicates longest-lived isotope</p> <p>Acidity/Basicity² & Crystal Structure³</p> <p>Melting Point⁵, °C</p> <p>Boiling Point⁵, °C</p> <p>Density⁵ (300 K, g/cm³) for gases: g/L, 273.15 K, 1 atm</p> <p>Electronegativity</p>										<p>Group Classifications⁴</p> <p>Atomic Number</p> <p>Oxidation States bold indicates most stable state</p> <p>Symbol¹</p> <p>Electronic Configuration</p> <p>Name</p>									
<p>1 H Hydrogen</p> <p>2 He Helium</p> <p>3 Li Lithium</p> <p>4 Be Beryllium</p> <p>5 B Boron</p> <p>6 C Carbon</p> <p>7 N Nitrogen</p> <p>8 O Oxygen</p> <p>9 F Fluorine</p> <p>10 Ne Neon</p> <p>11 Na Sodium</p> <p>12 Mg Magnesium</p> <p>13 Al Aluminum</p> <p>14 Si Silicon</p> <p>15 P Phosphorus</p> <p>16 S Sulfur</p> <p>17 Cl Chlorine</p> <p>18 Ar Argon</p> <p>19 K Potassium</p> <p>20 Ca Calcium</p> <p>21 Sc Scandium</p> <p>22 Ti Titanium</p> <p>23 V Vanadium</p> <p>24 Cr Chromium</p> <p>25 Mn Manganese</p> <p>26 Fe Iron</p> <p>27 Co Cobalt</p> <p>28 Ni Nickel</p> <p>29 Cu Copper</p> <p>30 Zn Zinc</p> <p>31 Ga Gallium</p> <p>32 Ge Germanium</p> <p>33 As Arsenic</p> <p>34 Se Selenium</p> <p>35 Br Bromine</p> <p>36 Kr Krypton</p> <p>37 Rb Rubidium</p> <p>38 Sr Strontium</p> <p>39 Y Yttrium</p> <p>40 Zr Zirconium</p> <p>41 Nb Niobium</p> <p>42 Mo Molybdenum</p> <p>43 Tc Technetium</p> <p>44 Ru Ruthenium</p> <p>45 Rh Rhodium</p> <p>46 Pd Palladium</p> <p>47 Ag Silver</p> <p>48 Cd Cadmium</p> <p>49 In Indium</p> <p>50 Sn Tin</p> <p>51 Sb Antimony</p> <p>52 Te Tellurium</p> <p>53 I Iodine</p> <p>54 Xe Xenon</p> <p>55 Cs Cesium</p> <p>56 Ba Barium</p> <p>57 La Lanthanum</p> <p>58 Ce Cerium</p> <p>59 Pr Praseodymium</p> <p>60 Nd Neodymium</p> <p>61 Pm Promethium</p> <p>62 Sm Samarium</p> <p>63 Eu Europium</p> <p>64 Gd Gadolinium</p> <p>65 Tb Terbium</p> <p>66 Dy Dysprosium</p> <p>67 Ho Holmium</p> <p>68 Er Erbium</p> <p>69 Tm Thulium</p> <p>70 Yb Ytterbium</p> <p>71 Lu Lutetium</p> <p>72 Hf Hafnium</p> <p>73 Ta Tantalum</p> <p>74 W Tungsten</p> <p>75 Re Rhenium</p> <p>76 Os Osmium</p> <p>77 Ir Iridium</p> <p>78 Pt Platinum</p> <p>79 Au Gold</p> <p>80 Hg Mercury</p> <p>81 Tl Thallium</p> <p>82 Pb Lead</p> <p>83 Bi Bismuth</p> <p>84 Po Polonium</p> <p>85 At Astatine</p> <p>86 Rn Radon</p> <p>87 Fr Francium</p> <p>88 Ra Radium</p> <p>89 Ac Actinium</p> <p>90 Th Thorium</p> <p>91 Pa Protactinium</p> <p>92 U Uranium</p> <p>93 Np Neptunium</p> <p>94 Pu Plutonium</p> <p>95 Am Americium</p> <p>96 Cm Curium</p> <p>97 Bk Berkelium</p> <p>98 Cf Californium</p> <p>99 Es Einsteinium</p> <p>100 Fm Fermium</p> <p>101 Md Mendelevium</p> <p>102 No Nihonium</p> <p>103 Lr Lawrencium</p>																			

*Ununquadium, Ununpentium, Ununhexium, Ununseptium, Ununoctium, and Ununennium are the previous names for elements 104-109, respectively.

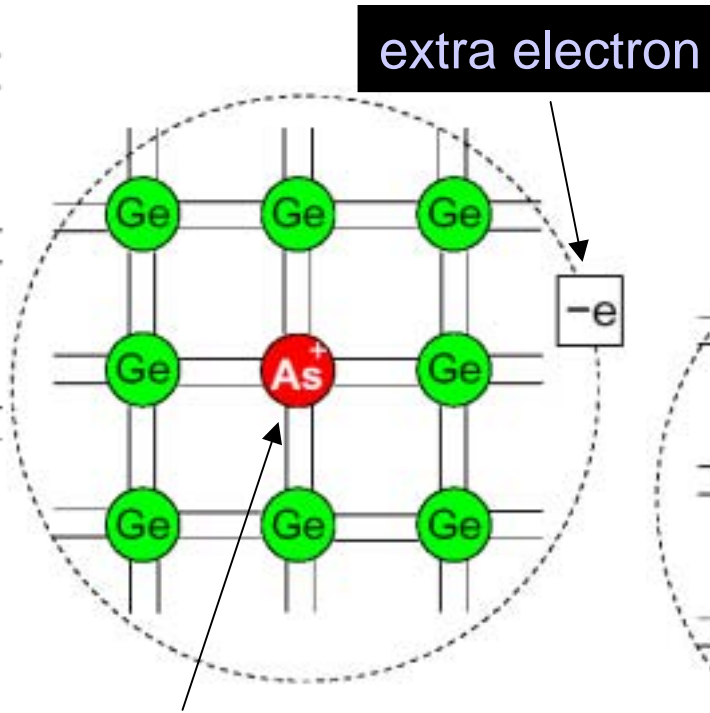
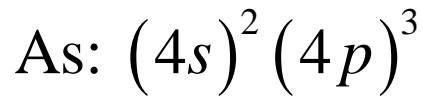
- Element symbol, name, atomic number, group, block, and oxidation state are indicated by color. The name and symbol for elements 104-110 are shown as examples by IUPAC. The names and symbols for 104-110 were revised in 2016.
- Atomic weights of elements are shown in bold. The atomic weight of an element is shown in bold. The atomic weight of an element is shown in bold.
- Crystal structure, acid-base character, and electronegativity are shown in bold. The crystal structure of an element is shown in bold. The acid-base character of an element is shown in bold. The electronegativity of an element is shown in bold.
- The color key for the periodic table is shown in bold. The color key for the periodic table is shown in bold.
- Element names, symbols, and atomic weights are shown in bold. The element names, symbols, and atomic weights are shown in bold.

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Extrinsic Semiconductor

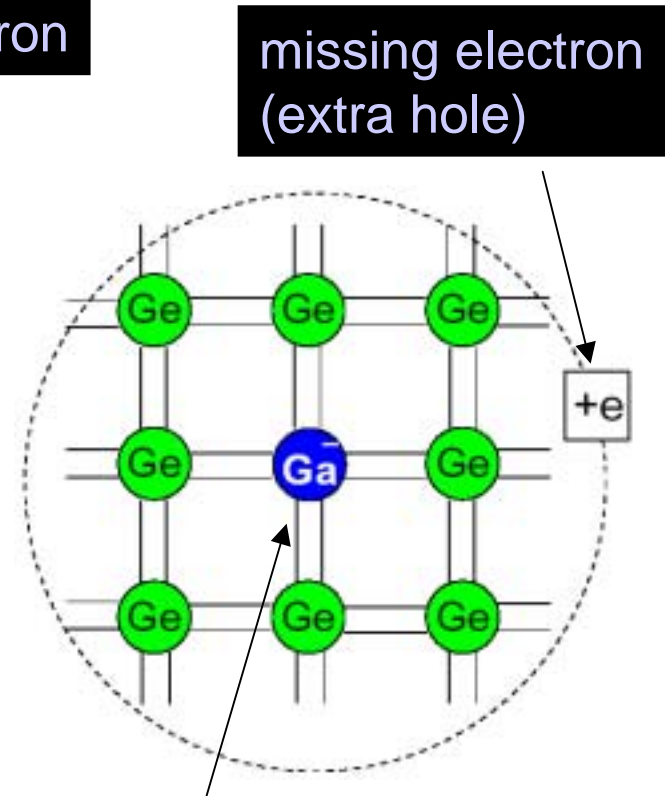
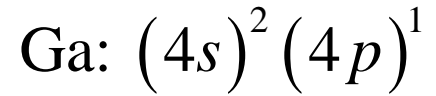


Covalent bonding



extra positive charge

(donor impurity)



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

$a_B = \frac{\hbar^2}{me^2} \sim 0.5 \times 10^{-8} \text{ cm}$ Bohr radius

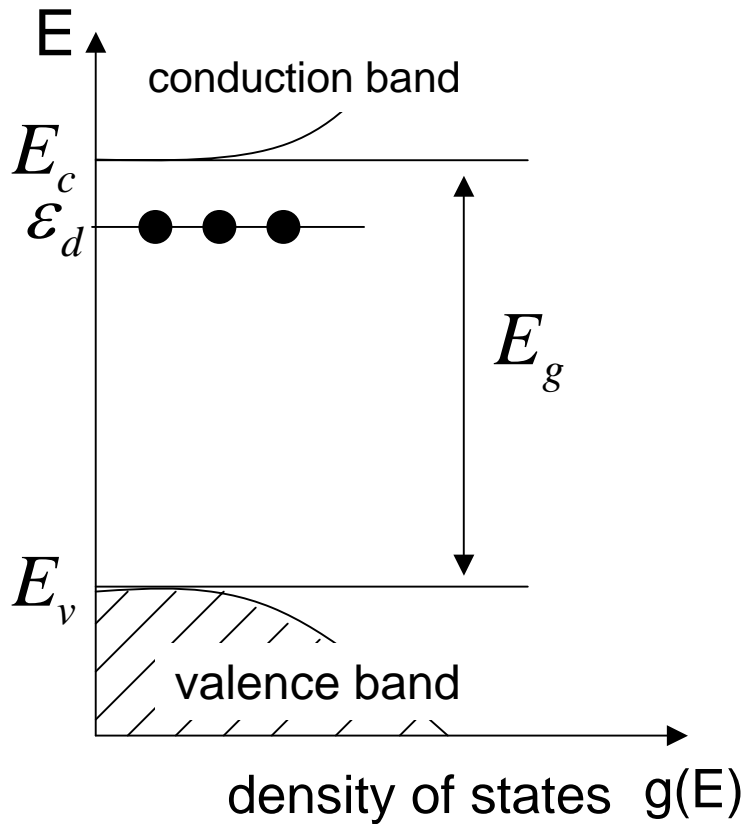
Inside solid: $e^2/r \rightarrow e^2/r\epsilon$ screening $\epsilon \approx 10 - 20$
 $m \rightarrow m^*$ band $m^*/m \approx 0.1 - 1.0$



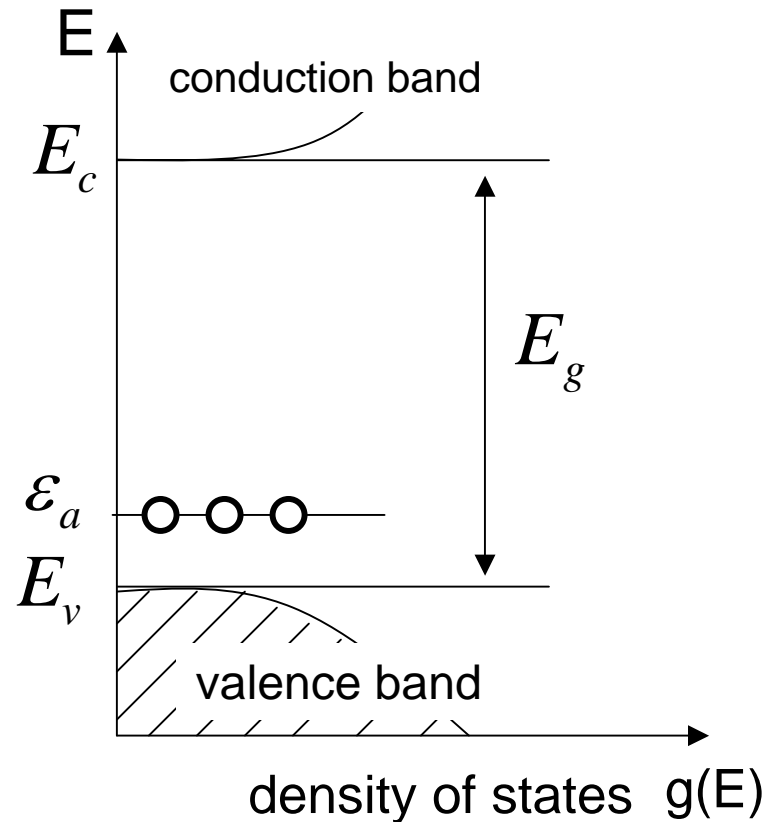
$E = \frac{m^*}{m} \cdot \frac{1}{\epsilon^2} \cdot E_H \sim 10 - 100 \text{ meV}$ very small binding energy
 $\langle r \rangle = \frac{m}{m^*} \epsilon \cdot a_B \sim 100 \cdot a_B$ very large radius

Energy band for extrinsic semiconductors

As-doped Ge
(n-type semiconductor)



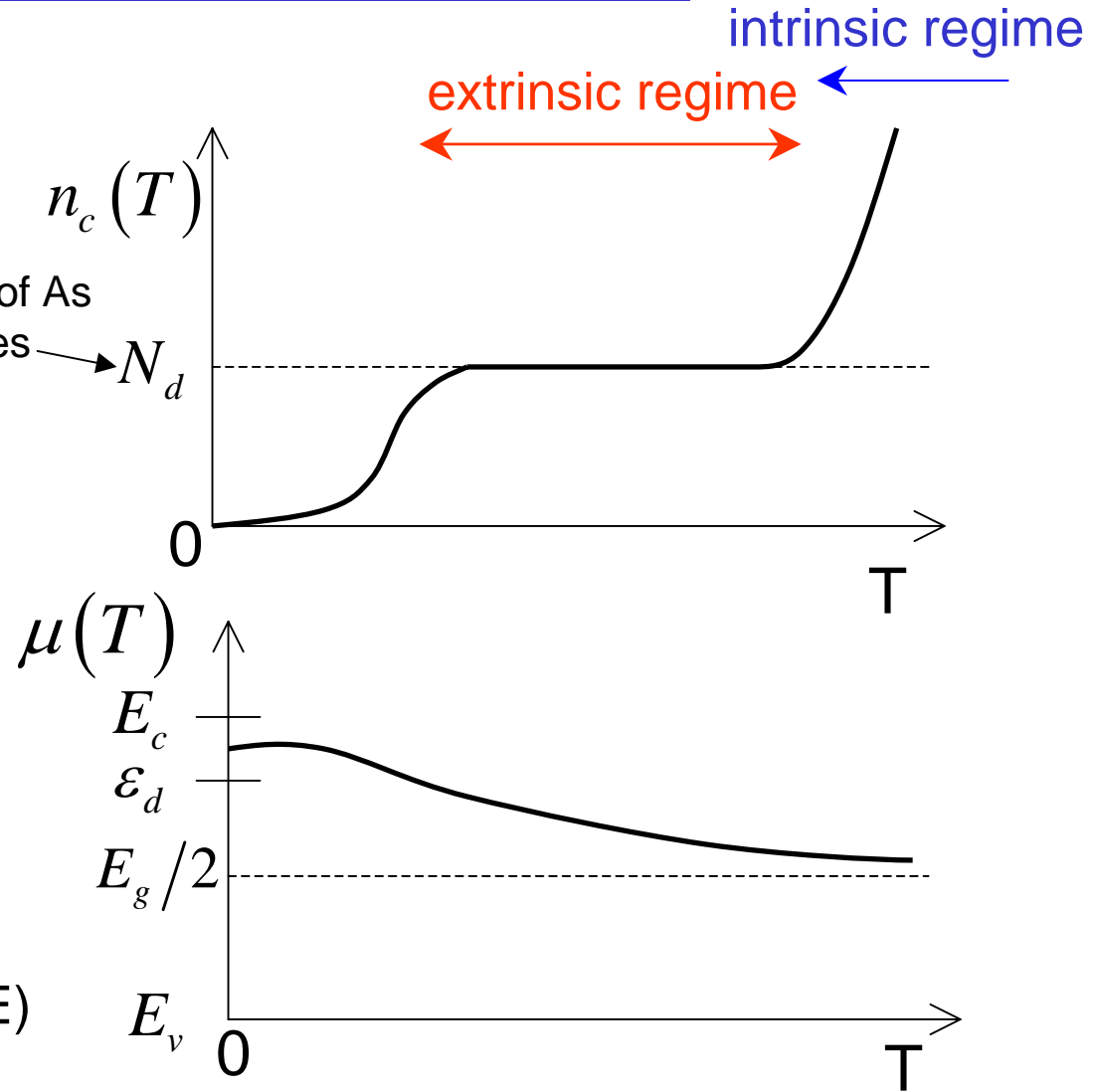
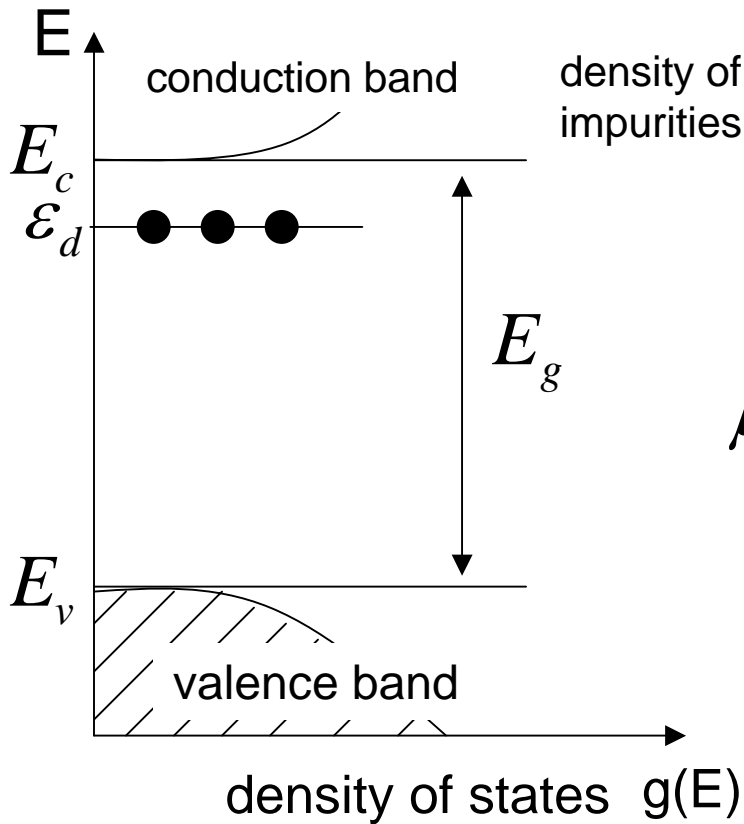
Ga-doped Ge
(p-type semiconductor)



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

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

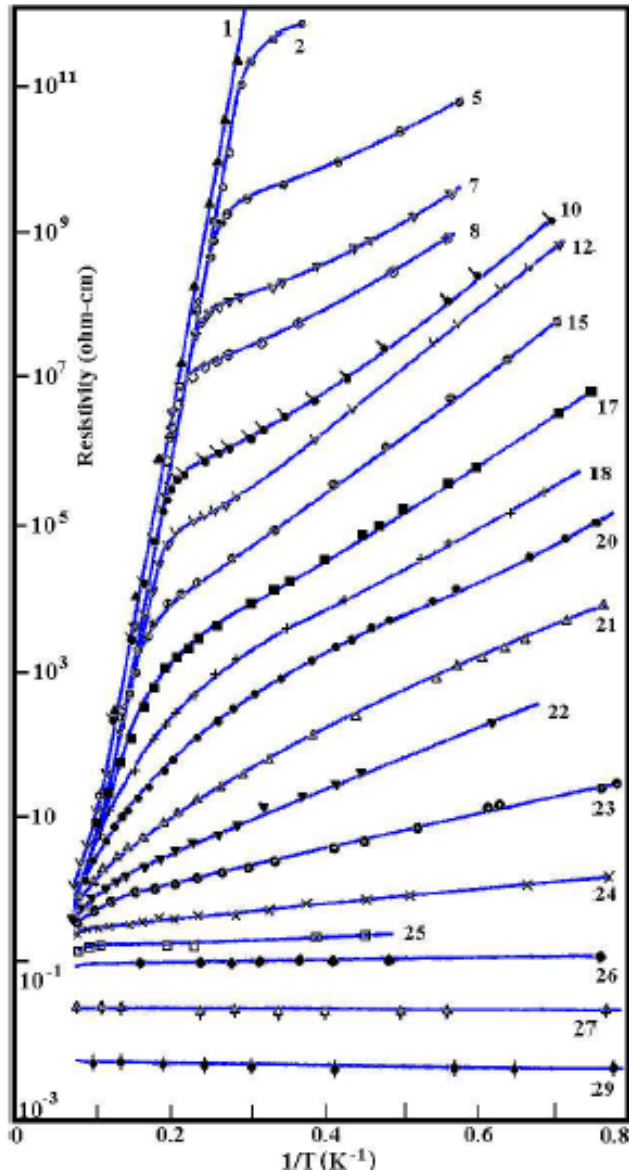
relaxation time

(effective) mass

Metal: $\tau(T)$ dominates

Semiconductor: $n(T)$ dominates

Antimony (Sb) doped Germanium (Ge)

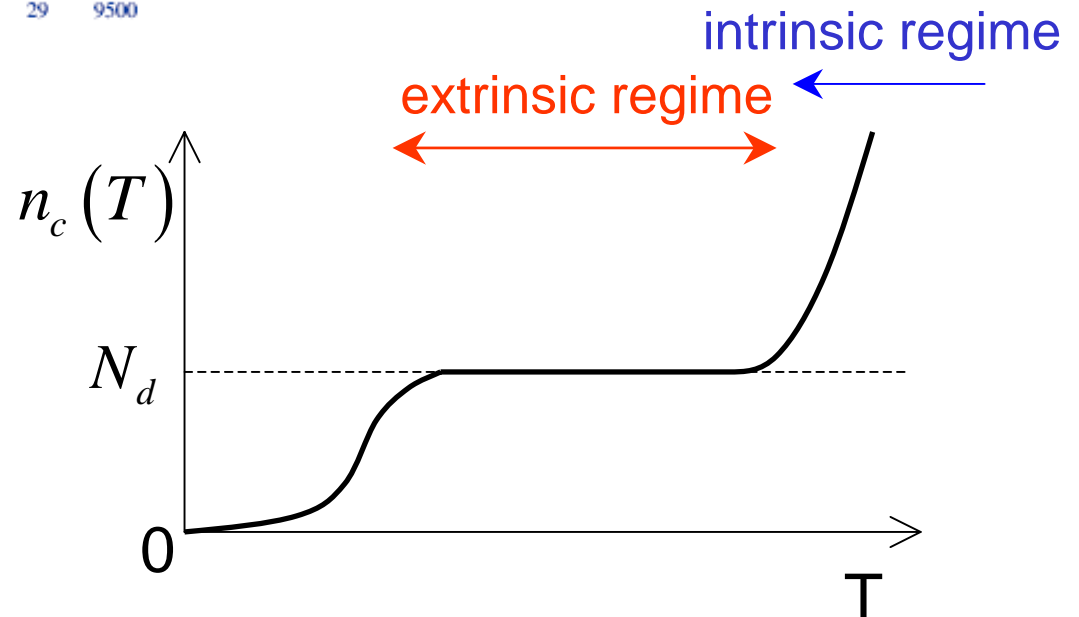


Specimen	Donor concentration $\times 10^{14} \text{ cm}^{-3}$
1	5.3
2	9.3
5	16
7	23
8	30
10	52
12	85
15	130
17	240
18	350
20	450
21	550
22	640
23	740
24	840
25	1200
26	1300
27	2700
29	9500

T-dependence of resistivity with varying impurity concentrations

H. J. Fritsche (1958)

n-type semiconductor



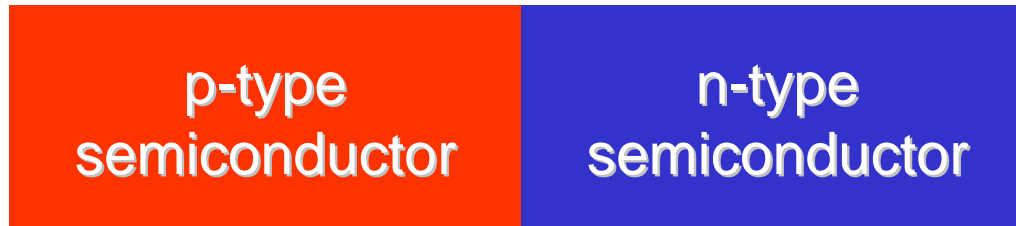
Inhomogeneous Semiconductors

□ pn junction (pn diode): homopolar junction (\leftrightarrow heterojunction)

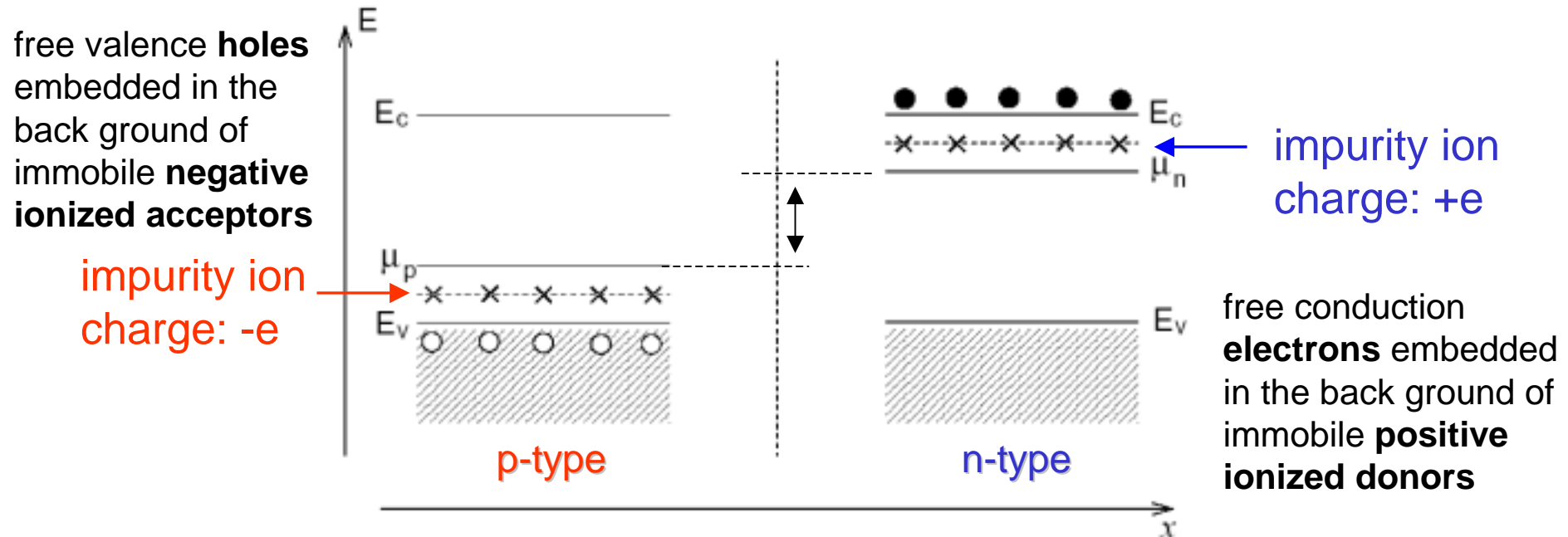
Ga-doped Ge

As-doped Ge

at equilibrium
(no current flow)

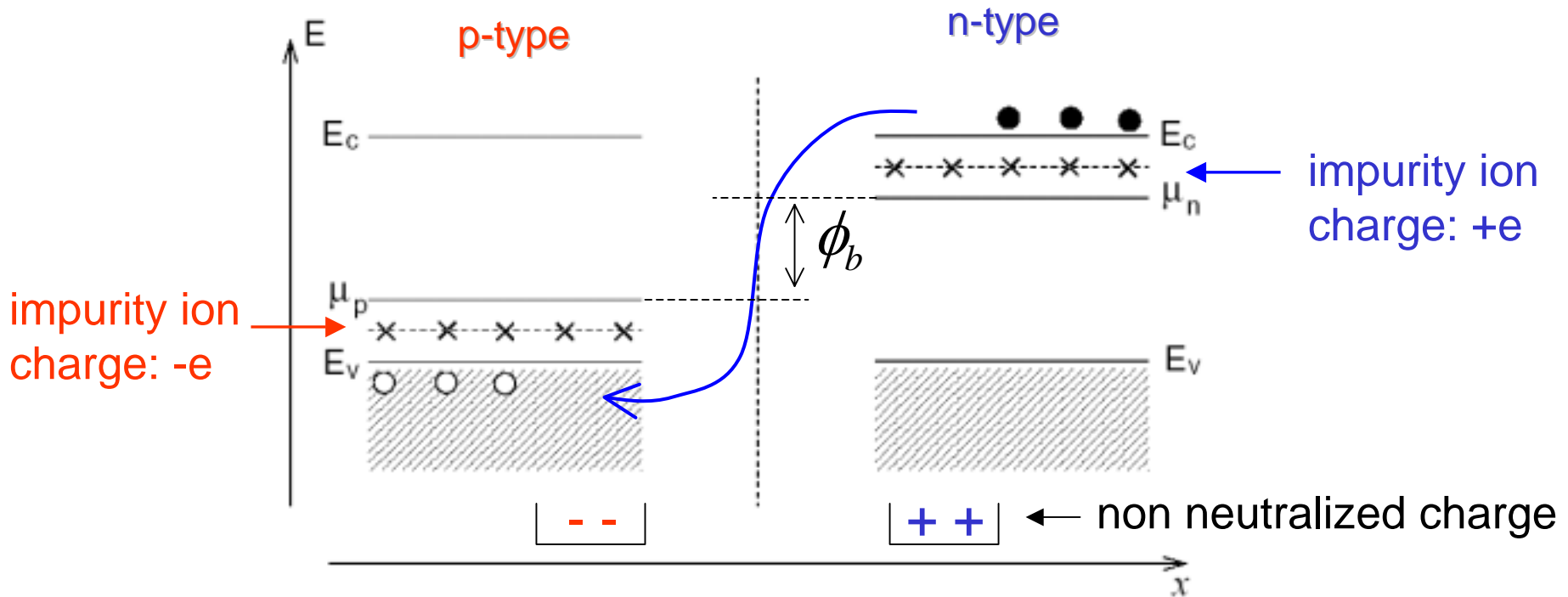


Schematic energy band (not yet in contact): saturation regime

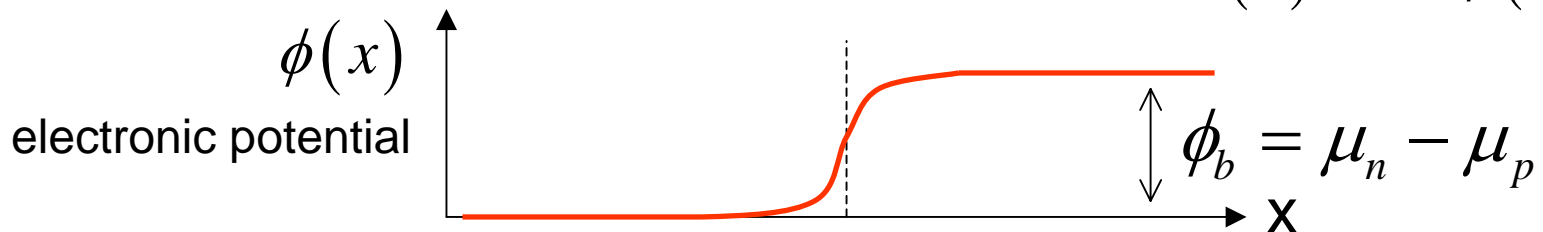


pn junction

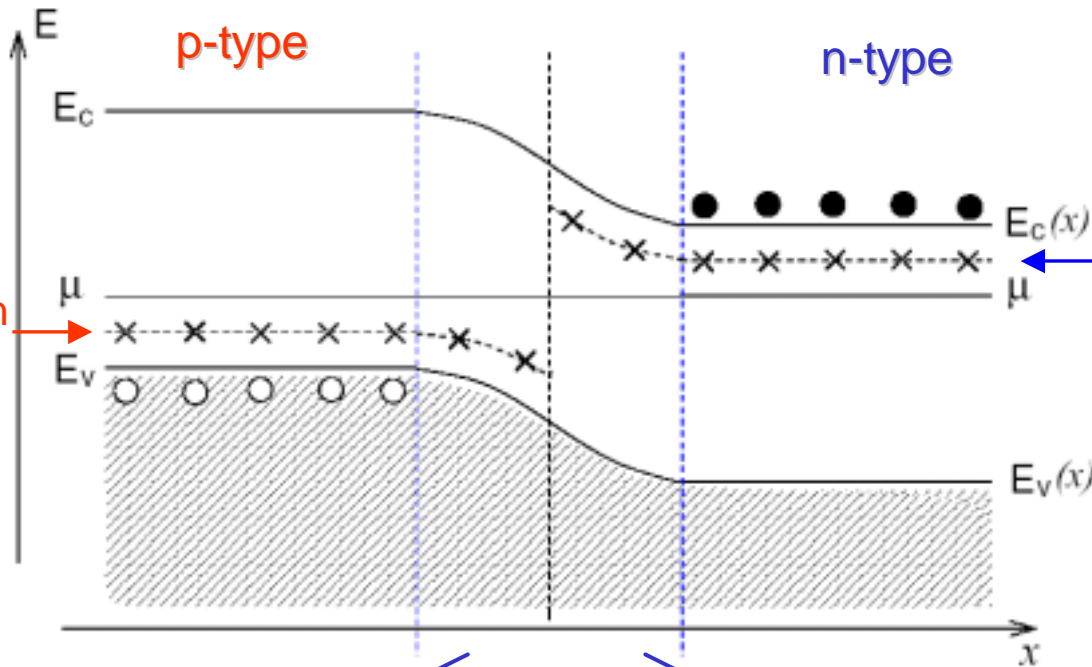
in contact ($\mu_p = \mu_n = \mu$ in equilibrium)



- ✓ 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



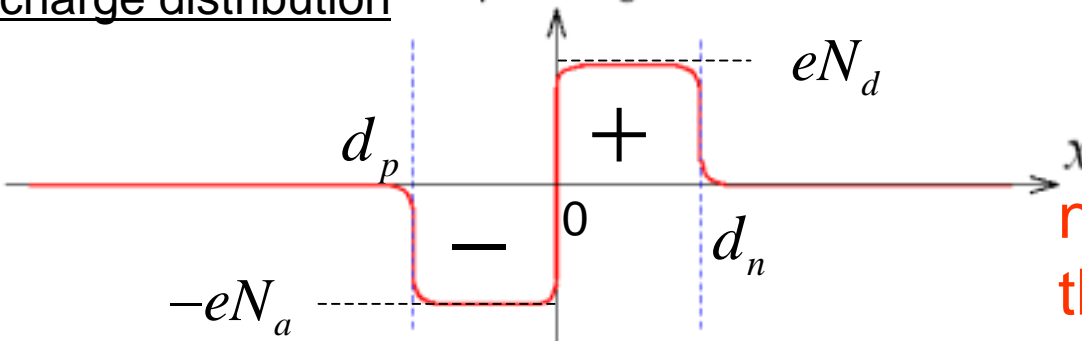
$$E_c(x) = E_c - e\phi(x)$$

impurity ion charge: +e

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

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:

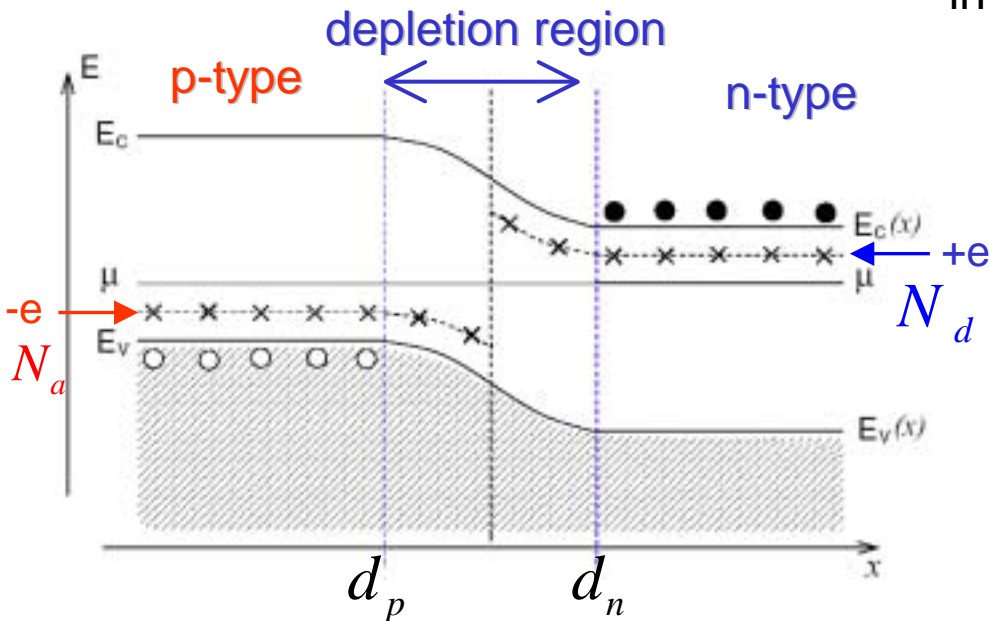
density of **electrons**
in **conduction band**

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.:

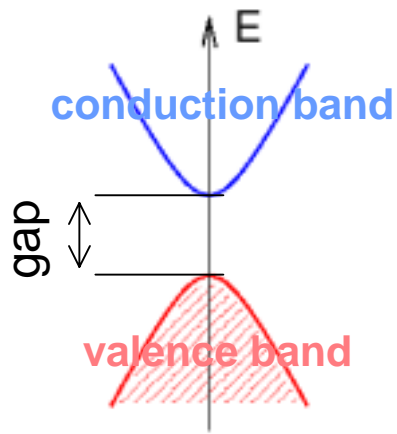
$$\nabla^2 \phi(x) = -\frac{e}{\epsilon} \rho(x)$$

static dielectronic const. (~10-20)

Numerical model calculations

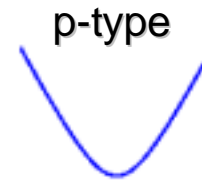
1d tight binding model

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

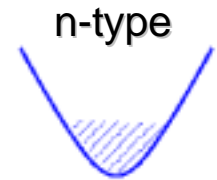


✓ 2 band = 2 orbitals per site (unit cell)

✓ saturation region (all impurities ionized)



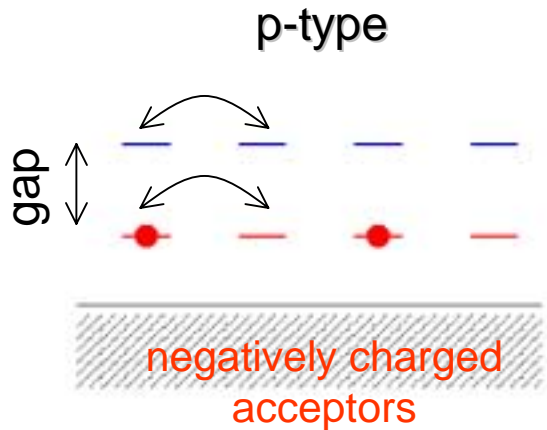
p-type



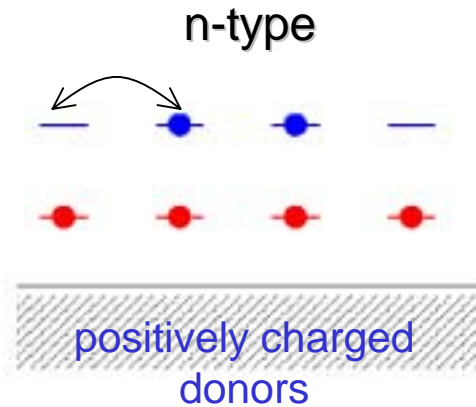
n-type

- charged acceptors

+ charged donors



p-type



n-type

self-consistent calculation

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

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

Schrodinger eq.

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

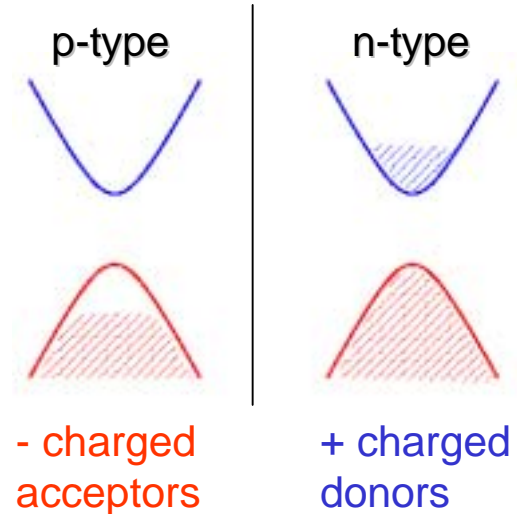
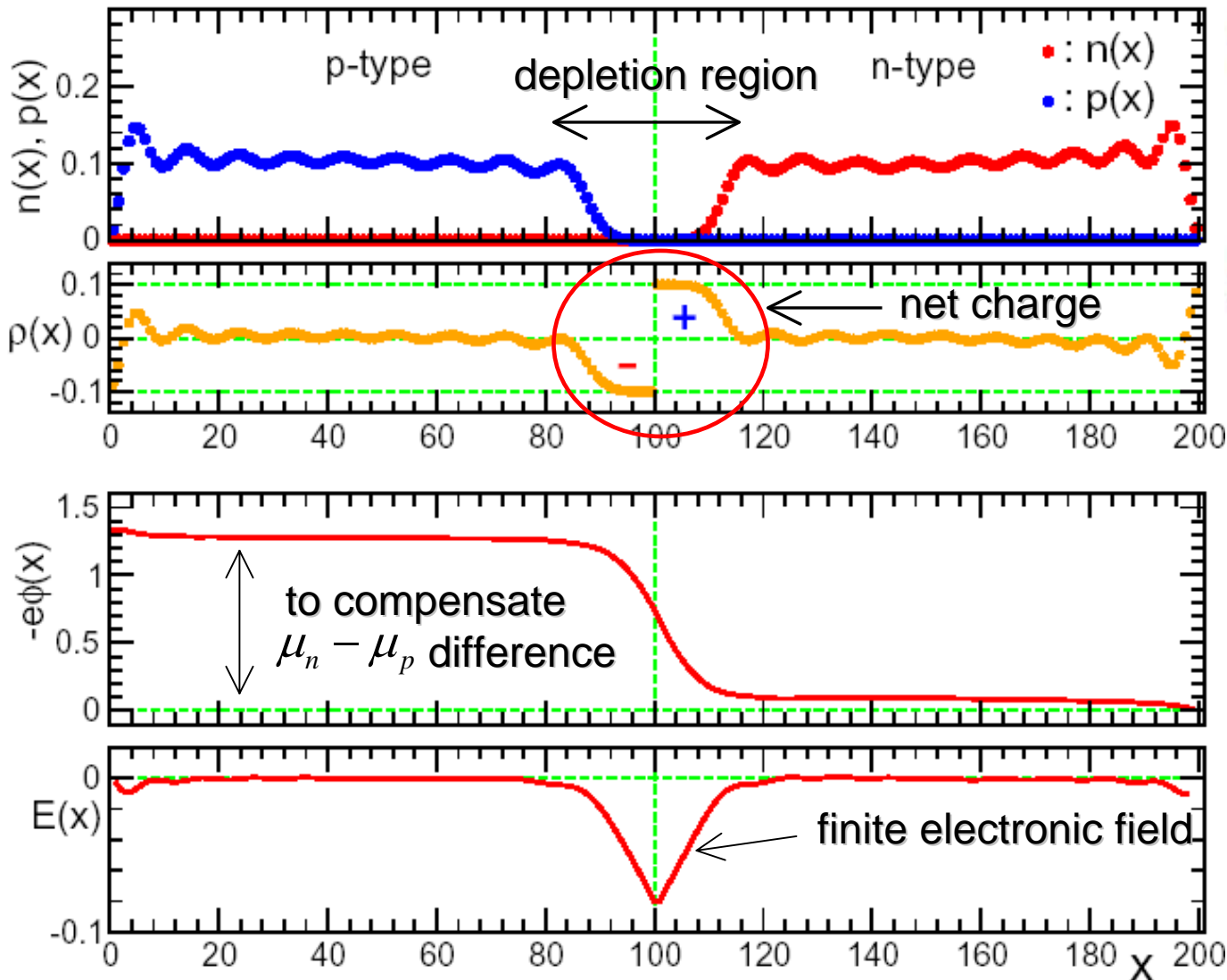
$$\text{if } \rho_{\text{out}}(x) \neq \rho_{\text{in}}(x)$$

1D 2 orbital tight binding model with Coulomb interactions

Numerical calculations: results

1d tight binding model

pn junction (100+100), $N_a=N_d=0.1$, $\epsilon=15$



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

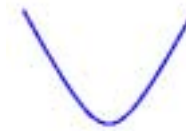
Schematic picture

p-type

n-type

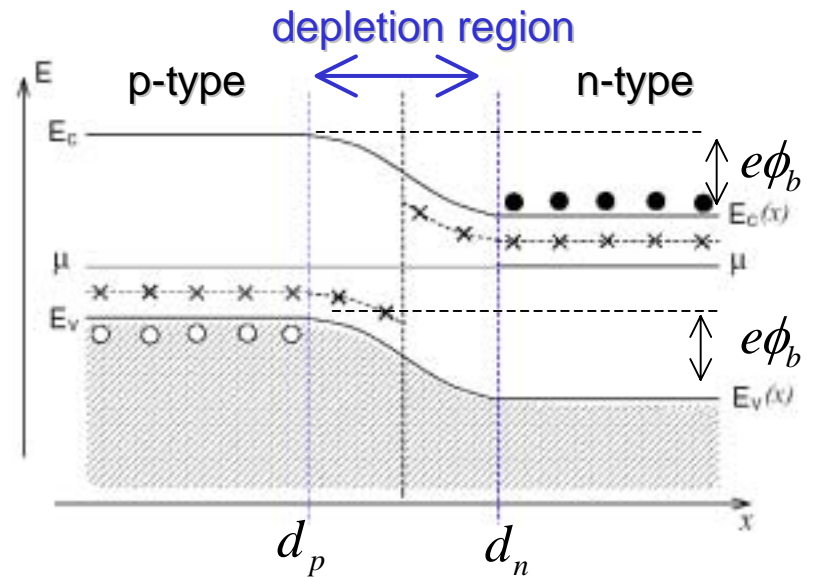
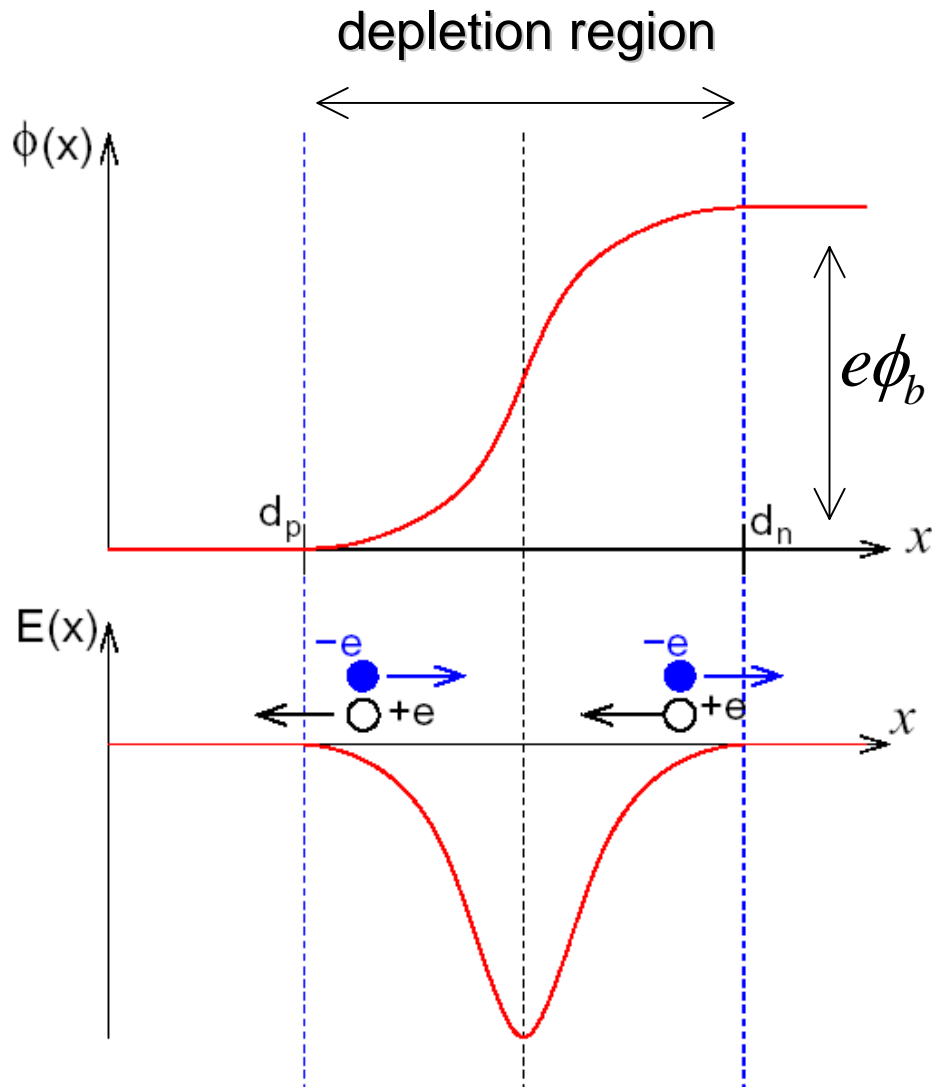
p-type

n-type



- charged acceptors

+ charged donors



at equilibrium, no current flow

No current flow ??

at equilibrium, no current flow

- From Boltzmann eq.

$$\mathbf{J}_n = en(x) \underbrace{\mu_n}_{\text{mobility}} \mathbf{E} + e \underbrace{D_n}_{\text{diffusion coefficient}} \nabla n(x) \quad \text{for conduction electrons}$$

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

(see Ashcroft & Mermin, p601)

- Exact cancellation

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

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

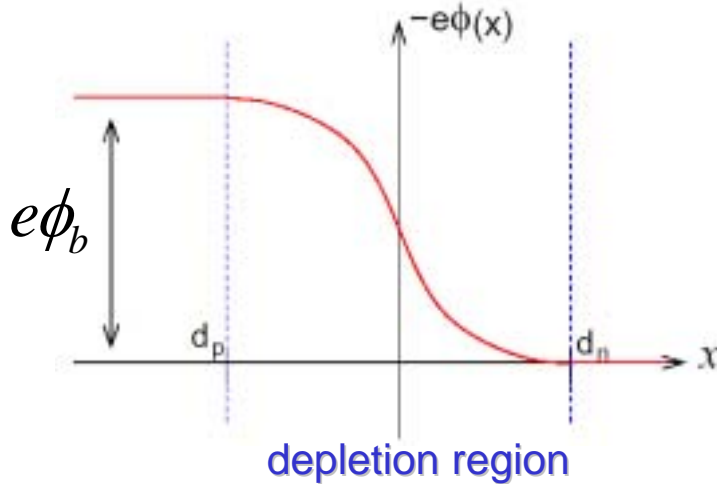
$$D_n = \frac{k_B T}{e} \cdot \mu_n$$

(Einstein relation)

Conduction electrons

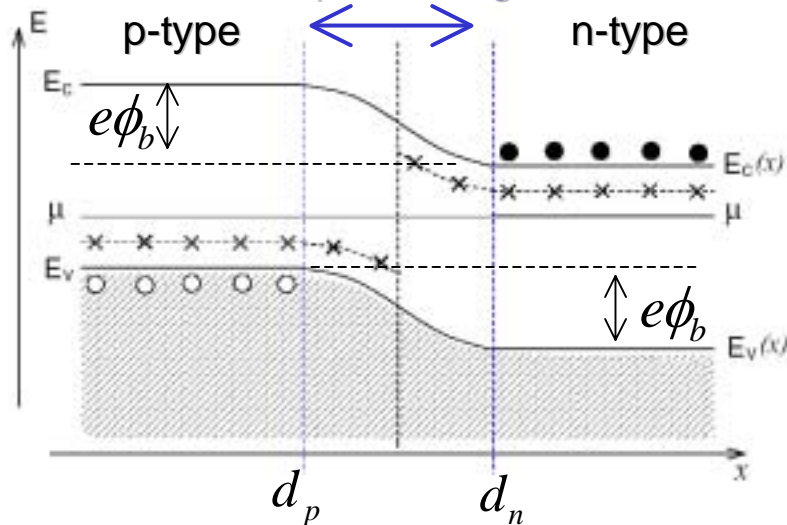


$$n(x) = \text{Const.} \times \exp \left[- \frac{(-e\phi(x))}{k_B T} \right]$$



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

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

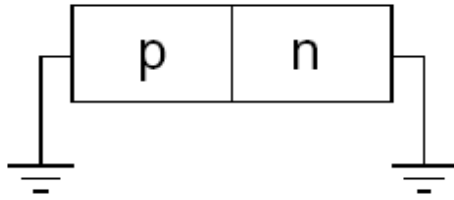


similarly, free holes in valence band in n-type semiconductor (minority carriers):

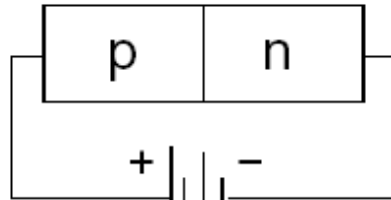
$$p(d_n) = p(d_p) \cdot \exp[-e\phi_b/k_B T]$$

I-V characteristic of p-n junction

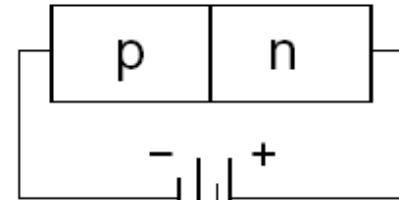
(rectifying response)



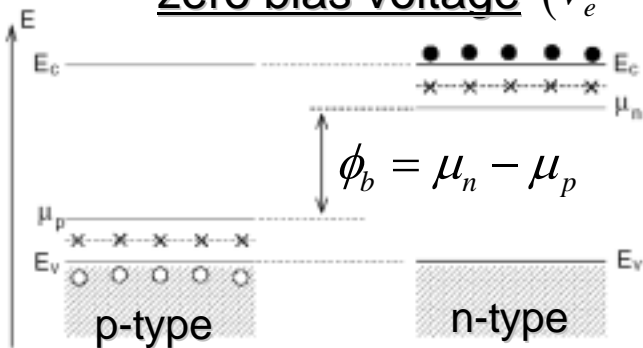
zero bias voltage ($V_e = 0$)



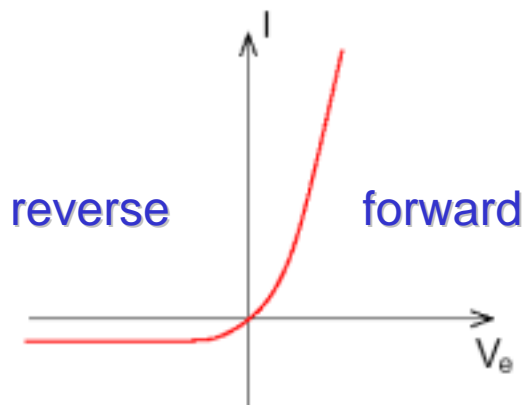
(forward)
($V_e > 0$)



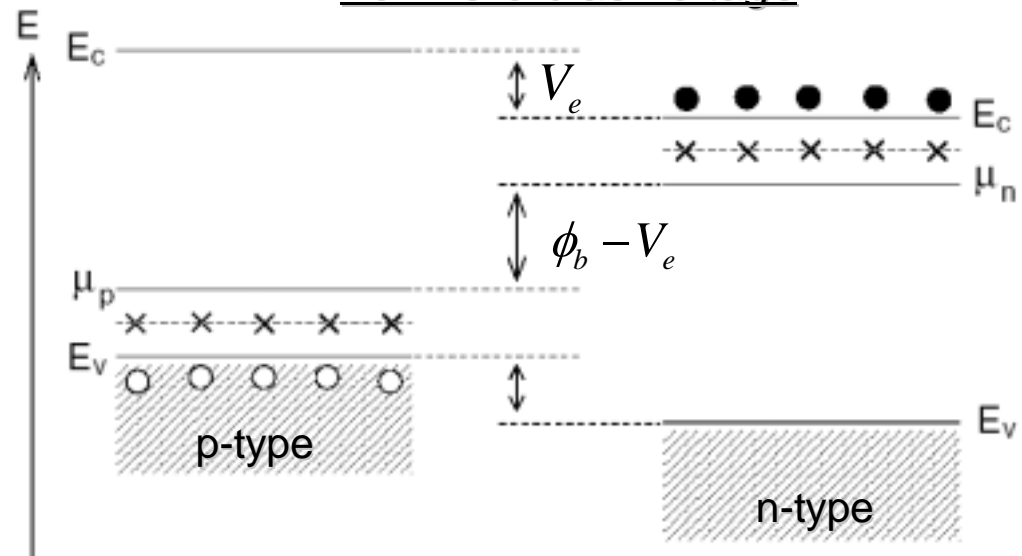
(reverse)
($V_e < 0$)



non-linear I-V characteristic

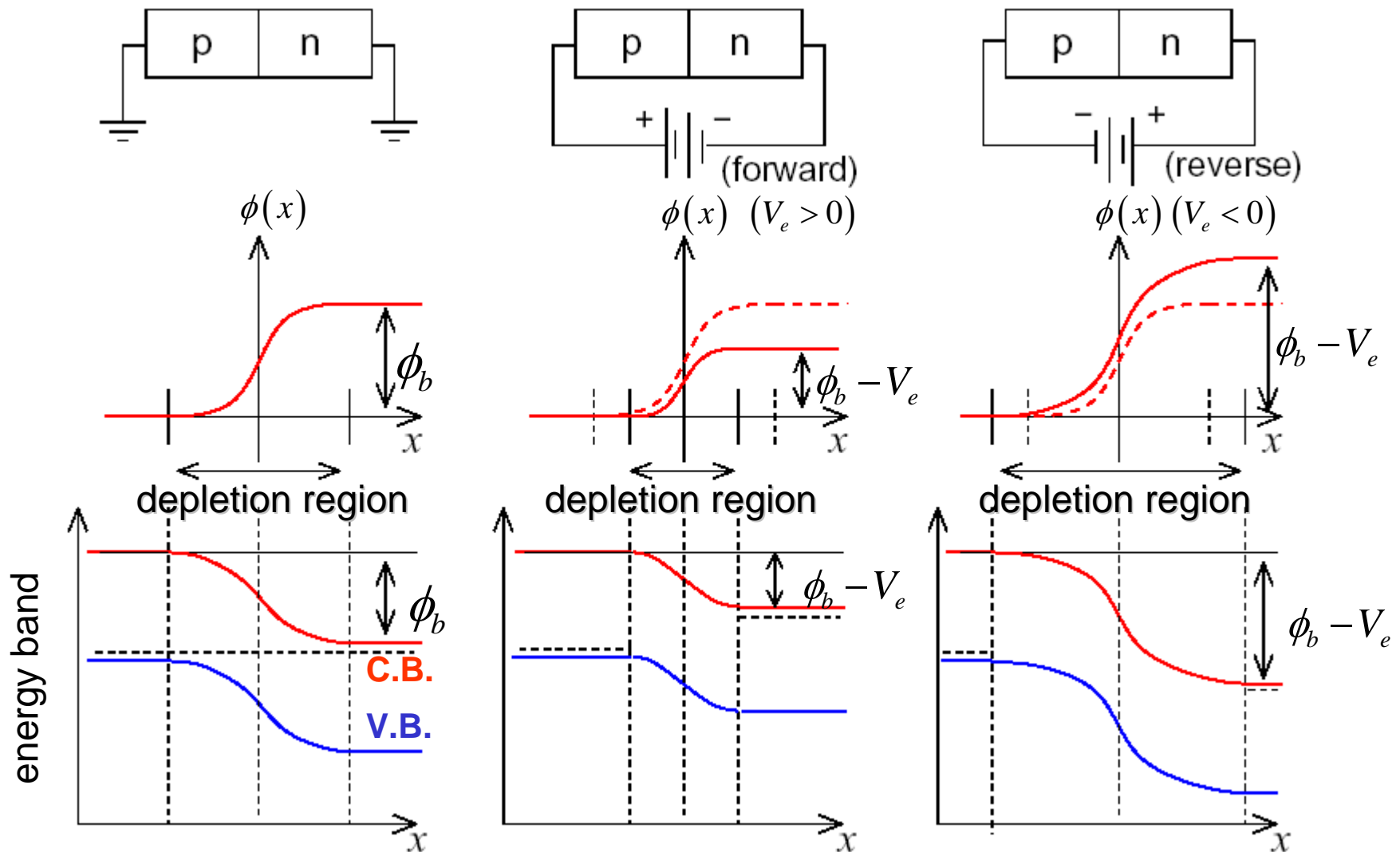


non zero bias voltage



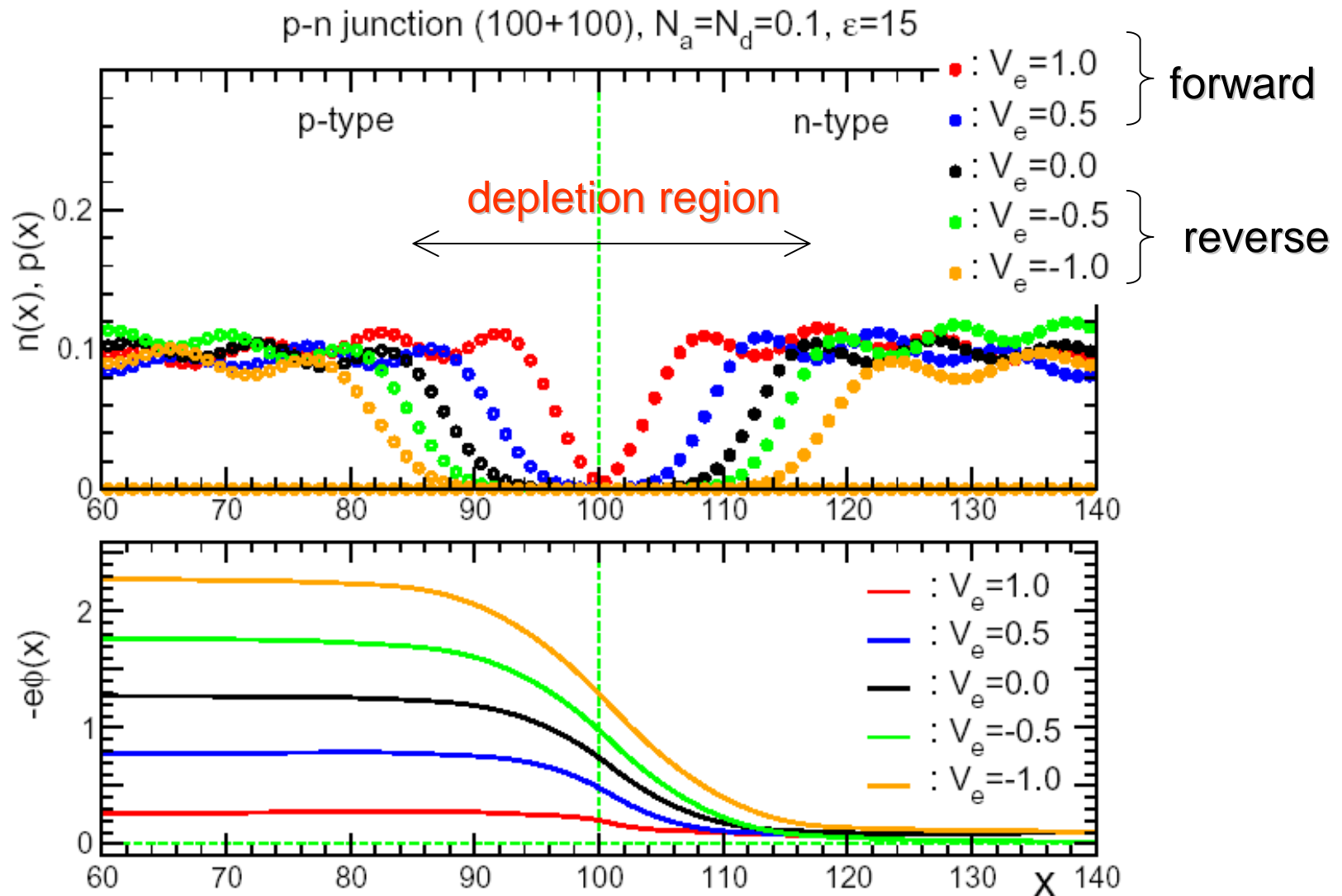
$V_e > 0$

I-V characteristic of p-n junction



Numerical model calculations

1D 2 orbital
tight binding



Rectifying feature in I-V curve

“Oversimplified” understanding

$V_e > 0$ increases

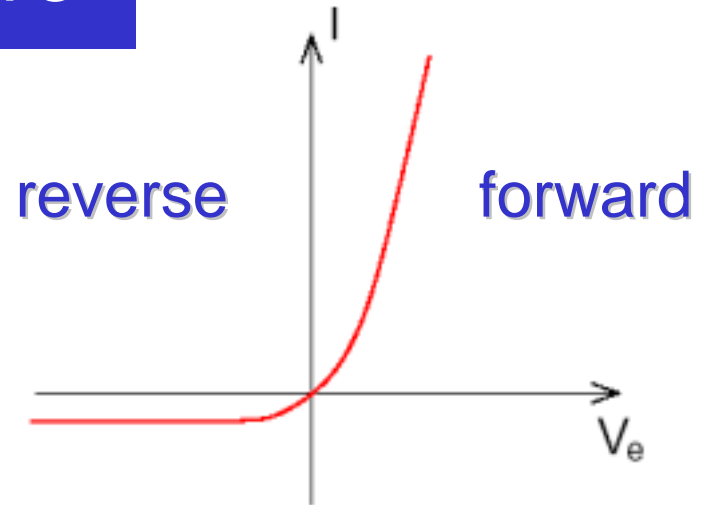
→ depletion region decreases

→ electronic potential decreases

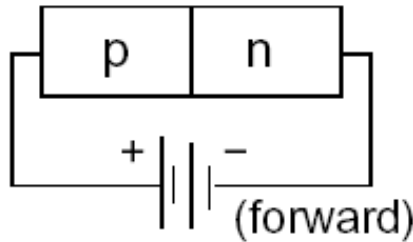
$V_e < 0$ decreases

→ depletion region increases

→ electronic potential increases



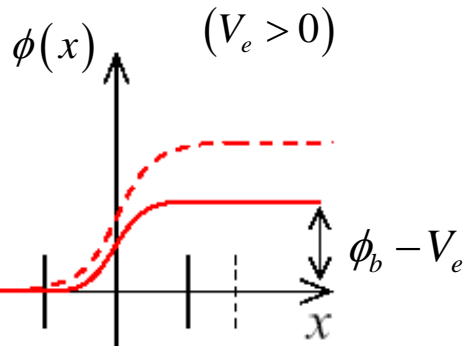
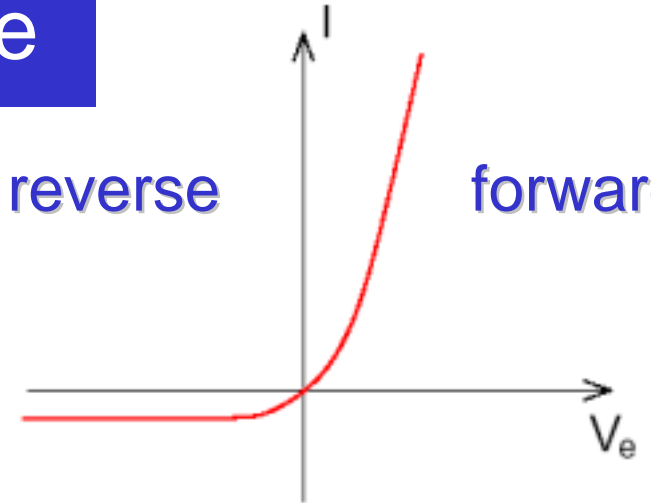
Rectifying feature in I-V curve



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

reverse

forward



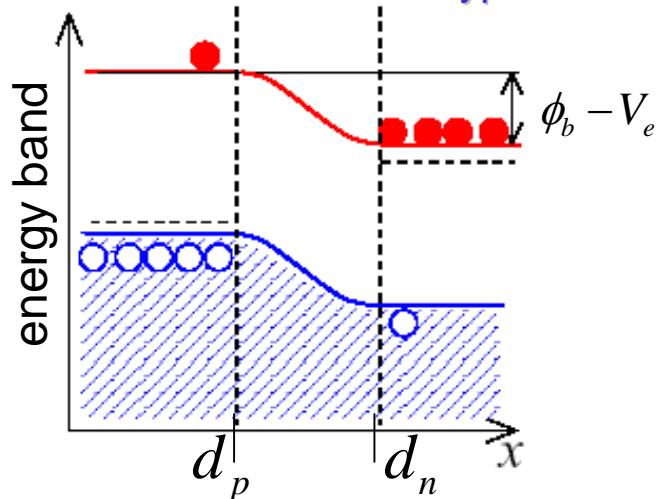
free electrons in conduction band in p-type semiconductor (minority carriers):

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

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

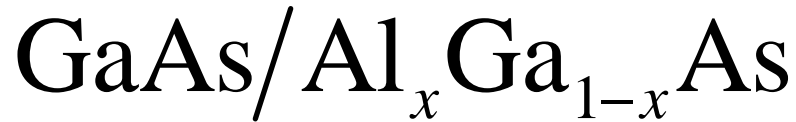
$$\begin{aligned} \Delta n(d_p) &= n(d_p) - n_0(d_p) \\ &= n(d_n) \left[e^{eV_e/k_B T} - 1 \right] \end{aligned}$$

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

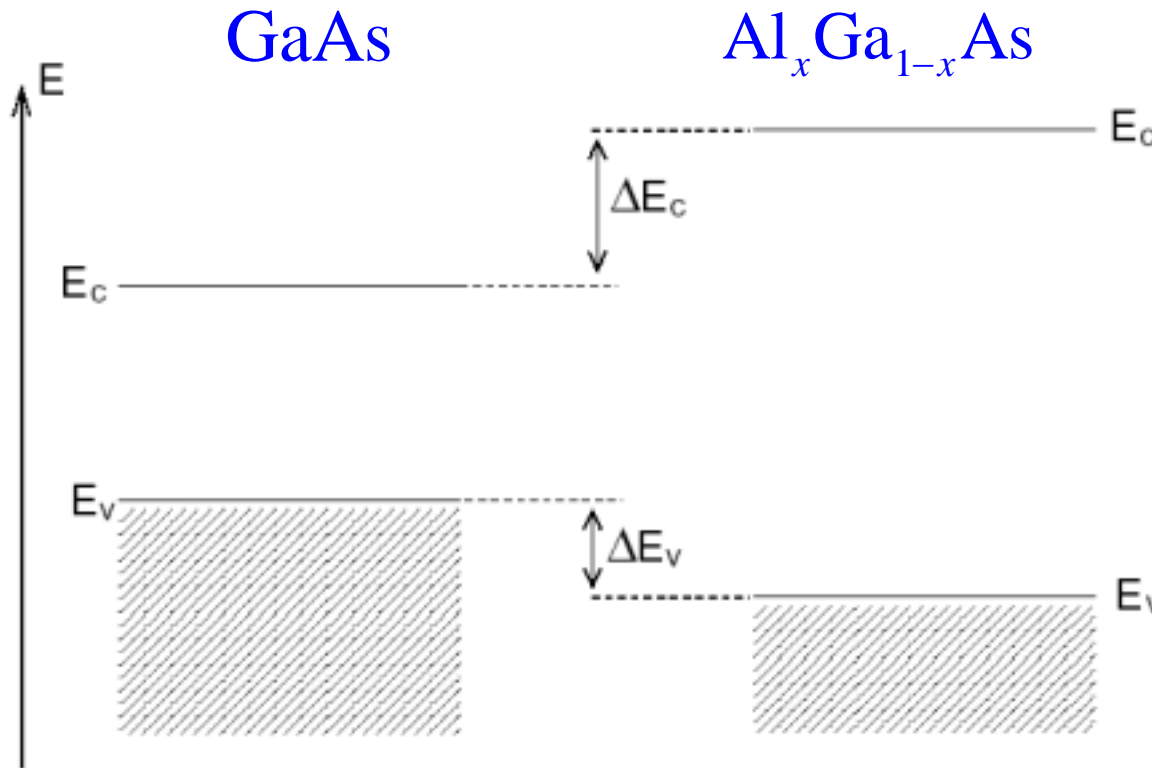


Semiconductor Heterojunctions

↔ homopolar junction



gap: 1.42 eV 2.17 eV (x=1.0)

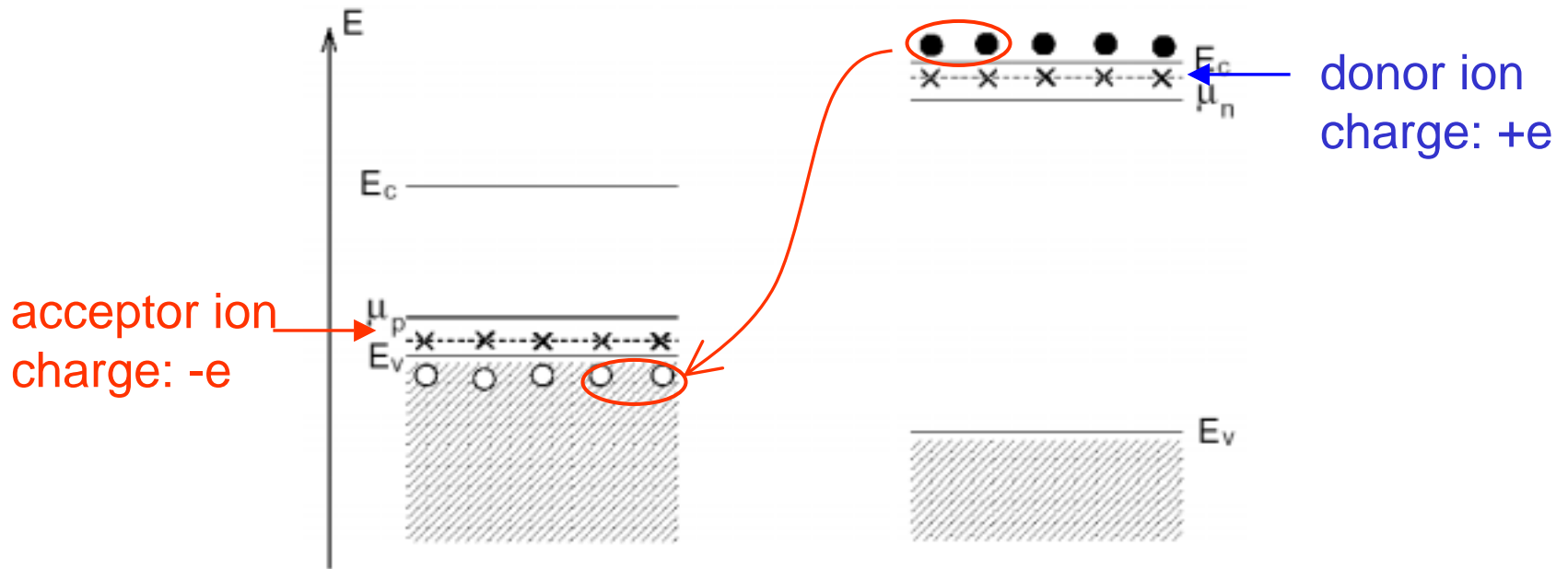


→ p-n junction made of p-GaAs/n-Al_xGa_{1-x}As

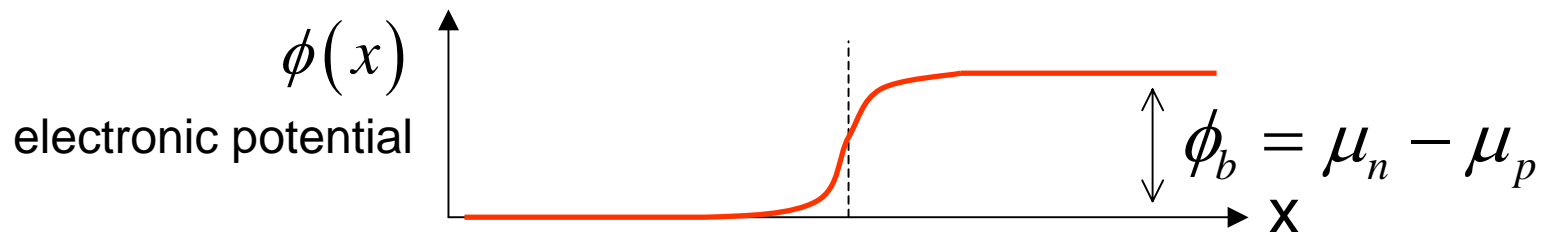
10.811 A2 tet 2075 4000 2.31 2.04 [He]2s ² p ¹ B Boron	5 3 B	12.011 A2 hex 4492 ⁰ 3825 ⁰ 2.25 2.55 [He]2s ² p ² C Carbon	6 2, 4 C	14.00674 A3 hex -210.00 -195.79 1.25046 3.04 [He]2s ² p ³ N Nitrogen	7 2, 3, 4, 5 N
26.981539 A1/B1 fcc 660.32 2519 2.702 1.61 [Ne]3s ² p ¹ Al Aluminum	13 3 Al	28.0855 A1/B1 fcc 1414 3285 2.33 1.90 [Ne]3s ² p ² Si Silicon	14 4 Si	30.973762 A2 cub 44.15 277 1.82 2.19 [Ne]3s ² p ³ P Phosphorus	15 ±3, 4, 5 P
69.723 A1/B1 orb 29.76 2204 6.086 1.61 [Ar]3d ¹⁰ 4s ¹ p ¹ Ga Gallium	31 3 Ga	72.61 A1/B1 fcc 938.25 2833 5.35 2.01 [Ar]3d ¹⁰ 4s ² p ² Ge Germanium	32 4 Ge	74.92159 A2 rhm 817 ⁰ 614 ⁰ 5.727 ²⁰ ⁰ 2.18 [Ar]3d ¹⁰ 4s ² p ³ As Arsenic	33 ±3, 5 As
114.818 A1/B2 tet 156.60 2072 7.30 1.78 [Kr]4d ¹⁰ 5s ¹ p ¹ In Indium	49 3 In	118.710 A1/B1 fcc 231.93 2902 7.28 1.96 [Kr]4d ¹⁰ 5s ² p ² Tn Tin	50 2, 4 Tn	121.760 A2 rhm 630.63 1587 6.684 ²⁰ ⁰ 2.05 [Kr]4d ¹⁰ 5s ² p ³ Sb Antimony	51 ±3, 5 Sb

Schematic energy band

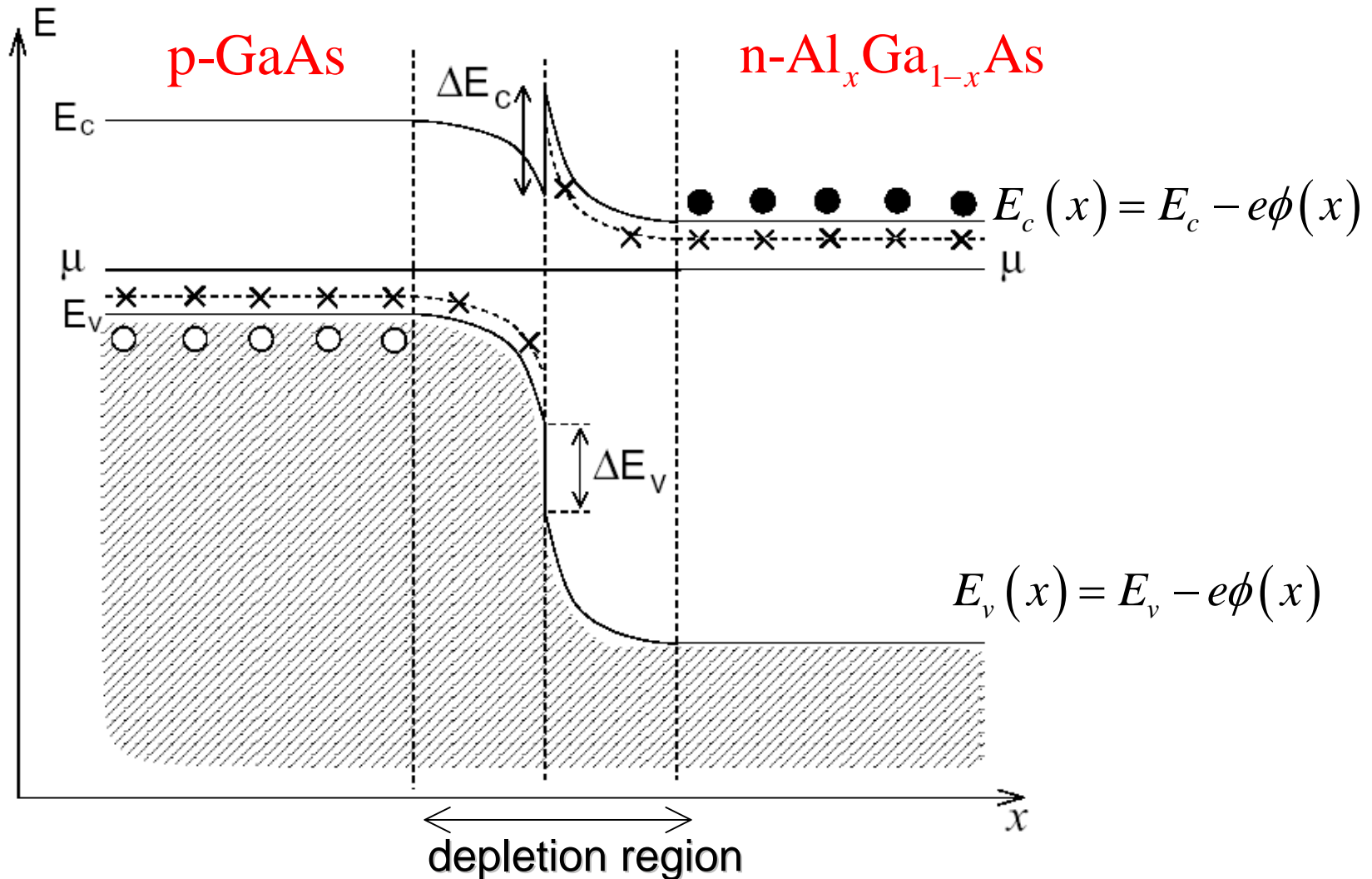
p-GaAs/n-Al_xGa_{1-x}As



in contact \longrightarrow non-neutralized charge appears \longrightarrow finite electric field



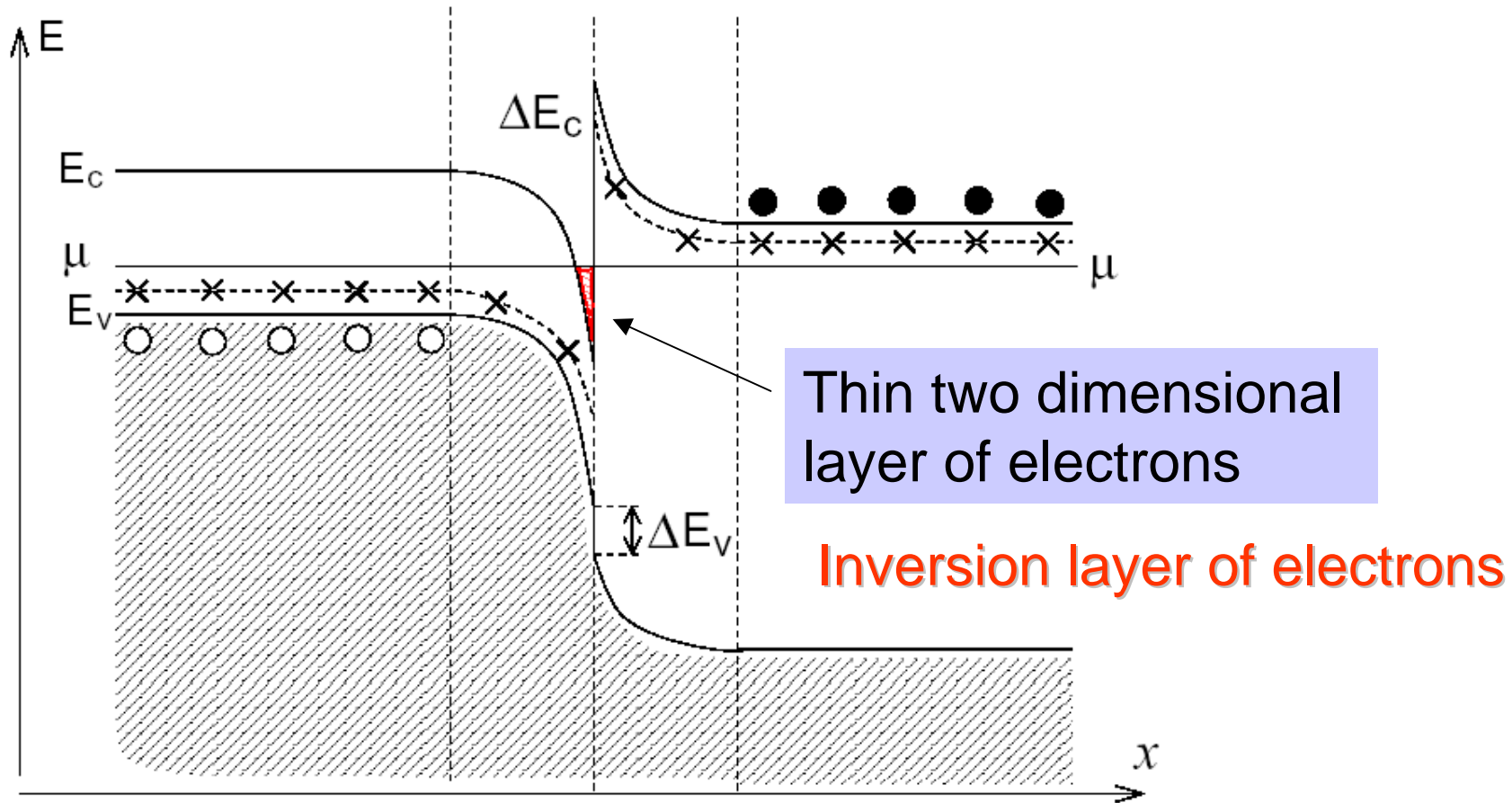
Schematic energy band (in contact)



Band discontinuity ΔE_c & ΔE_v preserved

Inversion Layer

By tailoring the band off set



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, ...)

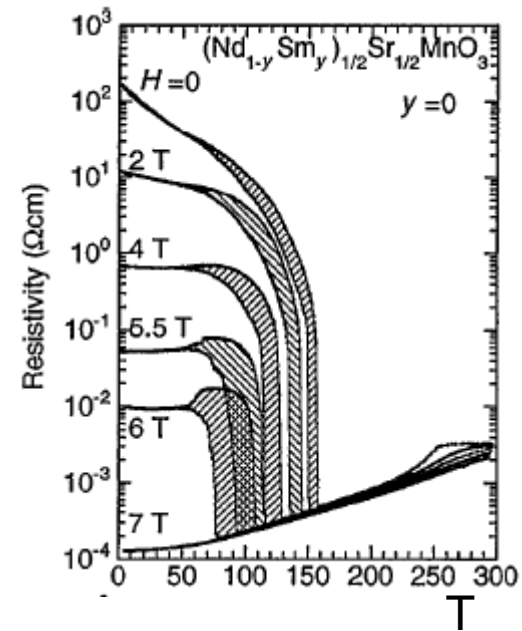
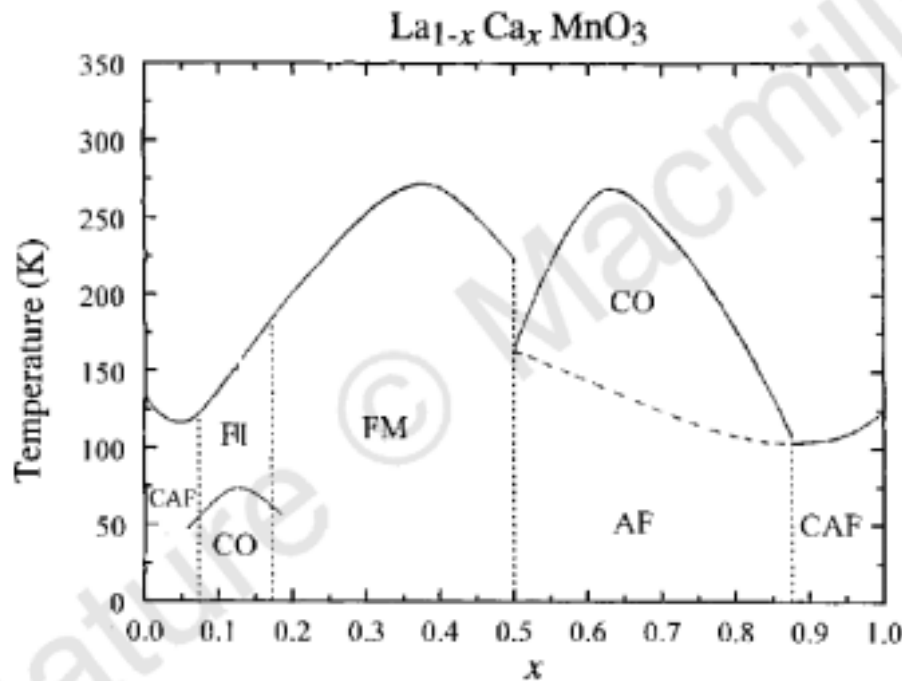
Strongly correlated systems (Coulomb and electron-lattice interactions)

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

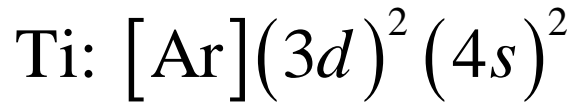
(Ohtomo et al, Nature **419**, 378 ('02))

✓ $\text{SrTi}^{4+}\text{O}_3/\text{LaTi}^{3+}\text{O}_3$ superlattice film

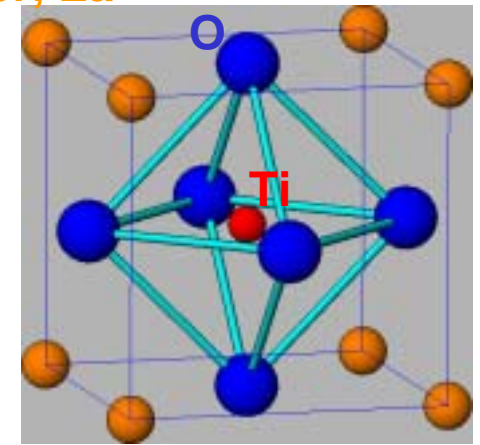
Perovskite structure

$\text{Sr}^{2+}\text{Ti}^{4+}\text{O}_3 : d^0 \longrightarrow$ band insulator

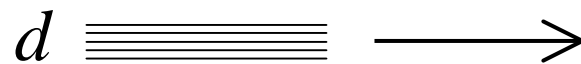
$\text{La}^{3+}\text{Ti}^{3+}\text{O}_3 : d^1 \longrightarrow$ Mott insulator



Sr, La

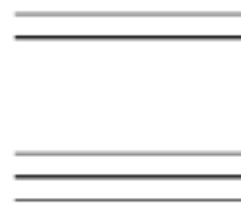


atomic d level



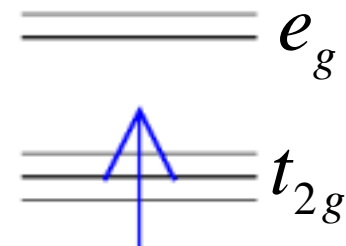
spherical symmetry

$\text{SrTi}^{4+}\text{O}_3$

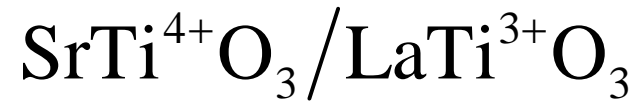


cubic symmetry (octahedral)

$\text{LaTi}^{3+}\text{O}_3$

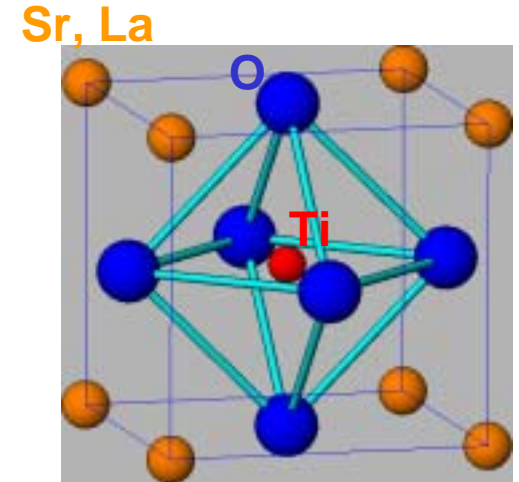
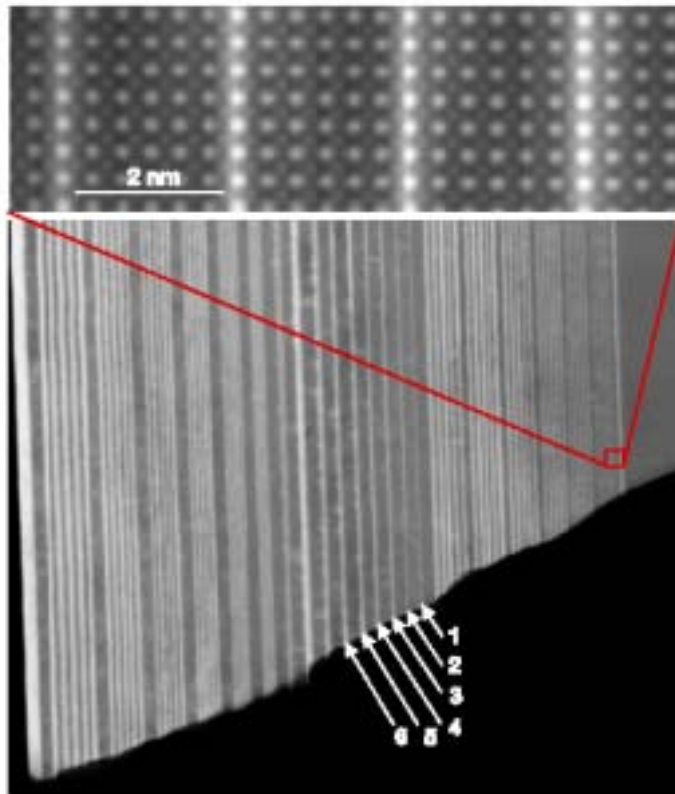


Titanate Superlattices



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

dark filed image (scanning transmission electron microscopy) **Sr** **La**



atomic-scale fabrication

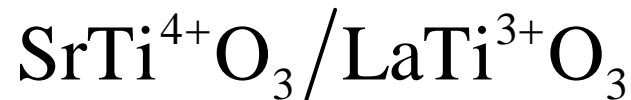


Insulator + insulator = **metal**

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

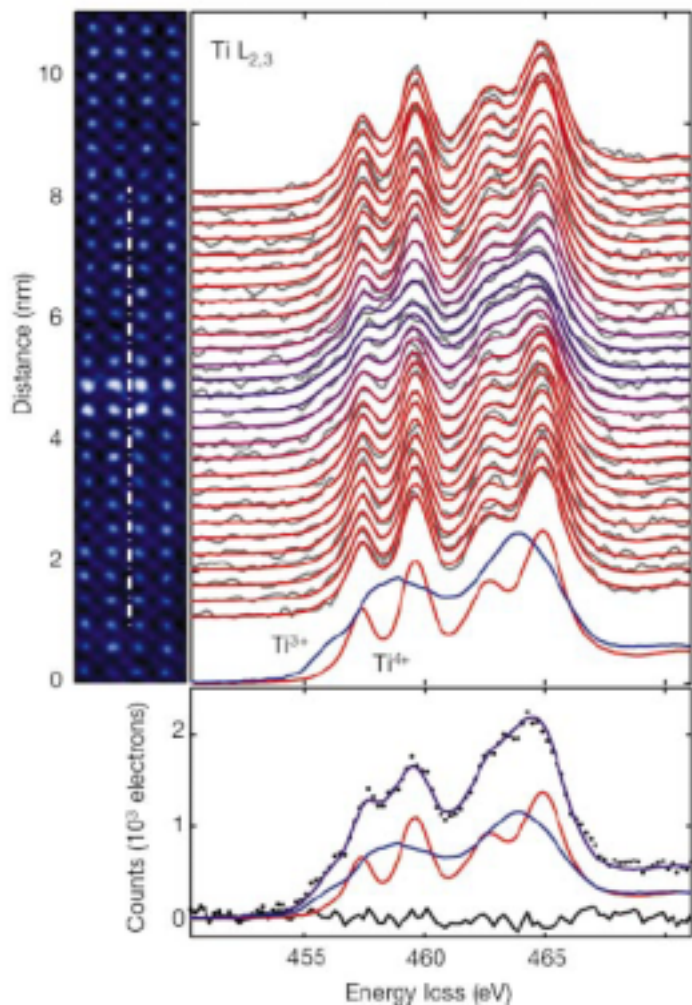
Figure 1 Annular dark field (ADF) image of LaTiO_3 layers (bright) of varying thickness spaced by SrTiO_3 layers. The view is down the $[100]$ zone axis of the SrTiO_3 substrate, which is on the right. After depositing initial calibration layers, the growth sequence is $5 \times n$ (that is, 5 layers 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.

Titanate Superlattices

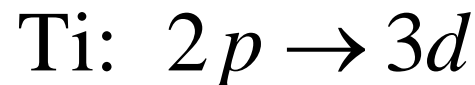


(Ohtomo et al, Nature **419**, 378 ('02))

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



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



How to analyze data:

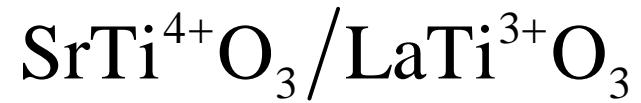
measured spectra depending on position

$$I(\omega) = \alpha I_{\text{LaTi}^{3+}\text{O}_3}(\omega) + (1 - \alpha) I_{\text{SrTi}^{4+}\text{O}_3}(\omega)$$

reference spectra

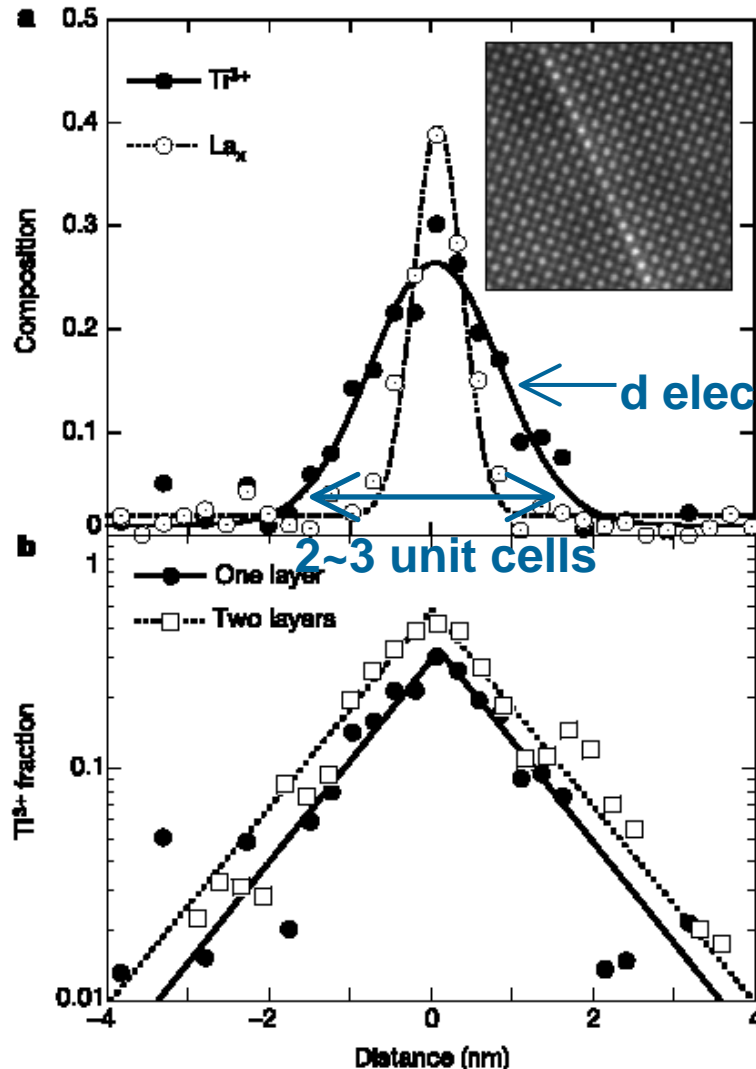
α ➔ # of d electrons

Titanate Superlattices



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

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



of d electrons < 1

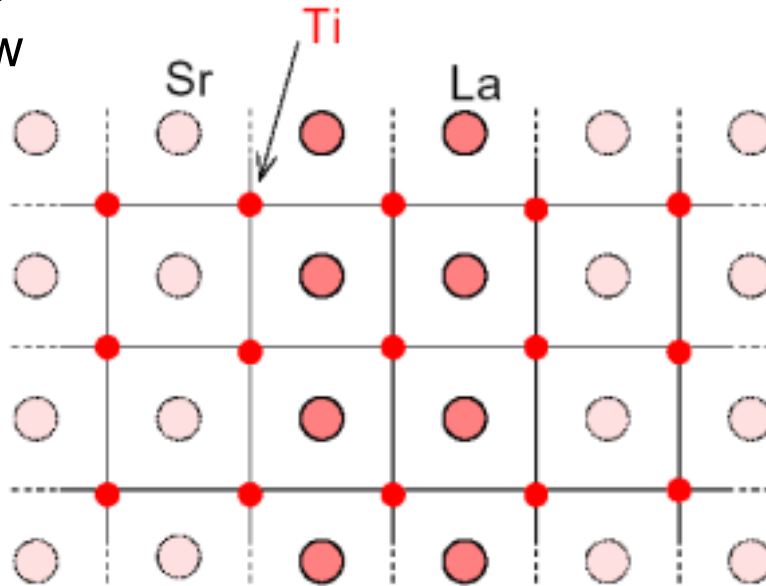
→ charge leakage

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

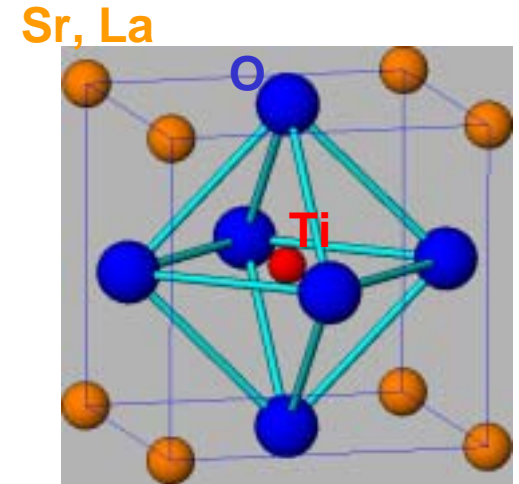
Model Calculations of Titanate Superlattices

$\text{SrTi}^{4+}\text{O}_3/\text{LaTi}^{3+}\text{O}_3$ superlattice

■ Top view



Perovskite structure

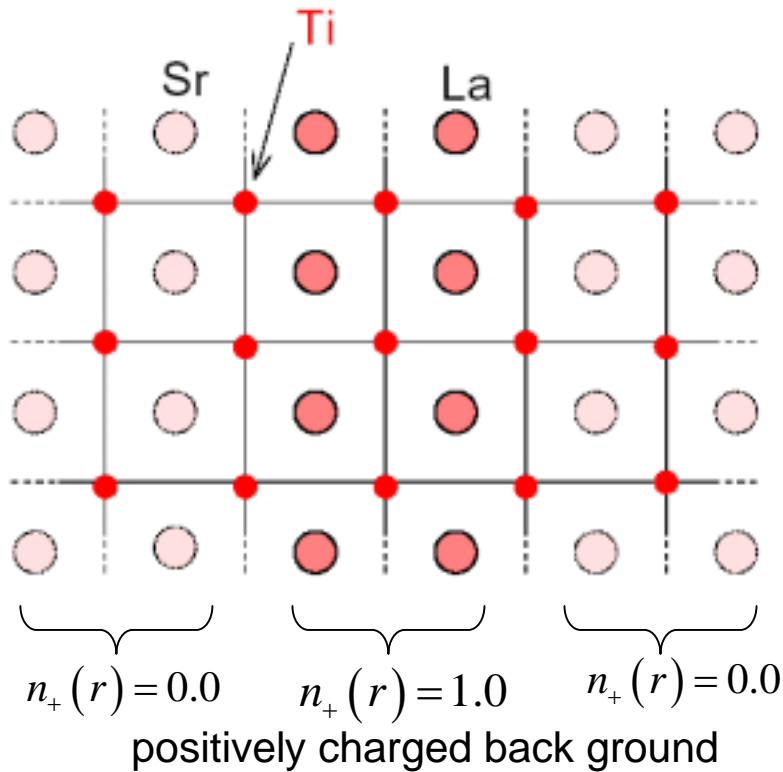


- Extra **+1 charge** on **La** site
(positively charged back ground)
- # of total d electrons = # of total La ions
(donor impurities)
- Ti d orbitals: electrically active orbital

} very similar to
semiconductors

Model Calculations of Titanate Superlattices

$\text{SrTi}^{4+}\text{O}_3/\text{LaTi}^{3+}\text{O}_3$ superlattice



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

where

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

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

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

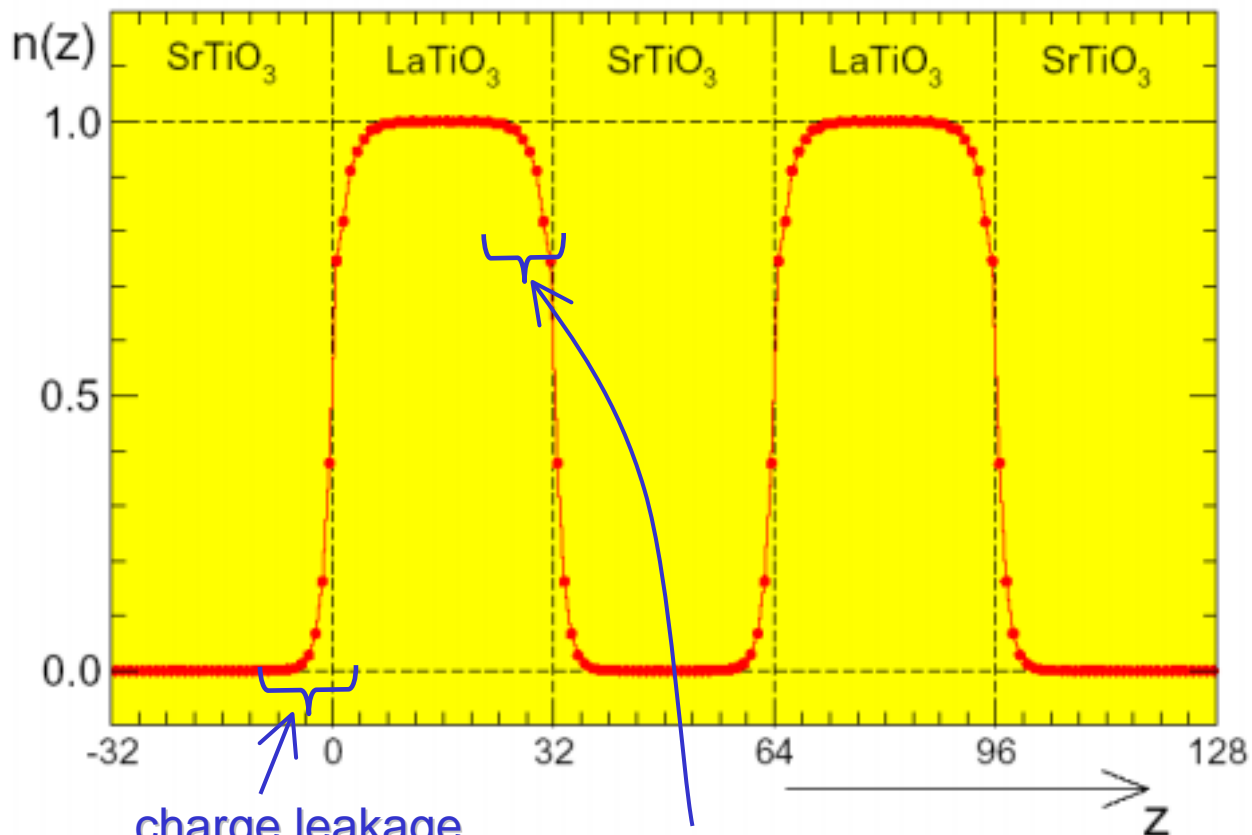
total # of d electrons = total # of La ions
= total # of positively charged back ground charge

self-consistent mean-field calculations

Oxide heterostructure interface: mean-field results

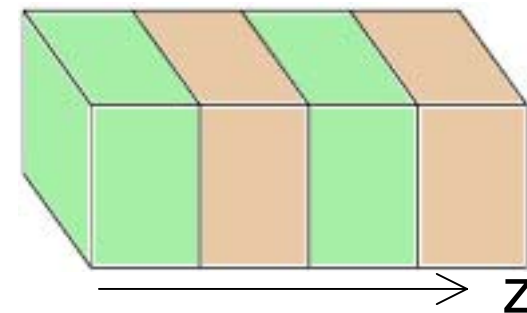
■ LaTiO₃/SrTiO₃

[LaTiO₃]₃₂ / [SrTiO₃]₃₂



dielectric constant:
 $\epsilon = 15$
single band approximation

LaTiO₃ SrTiO₃

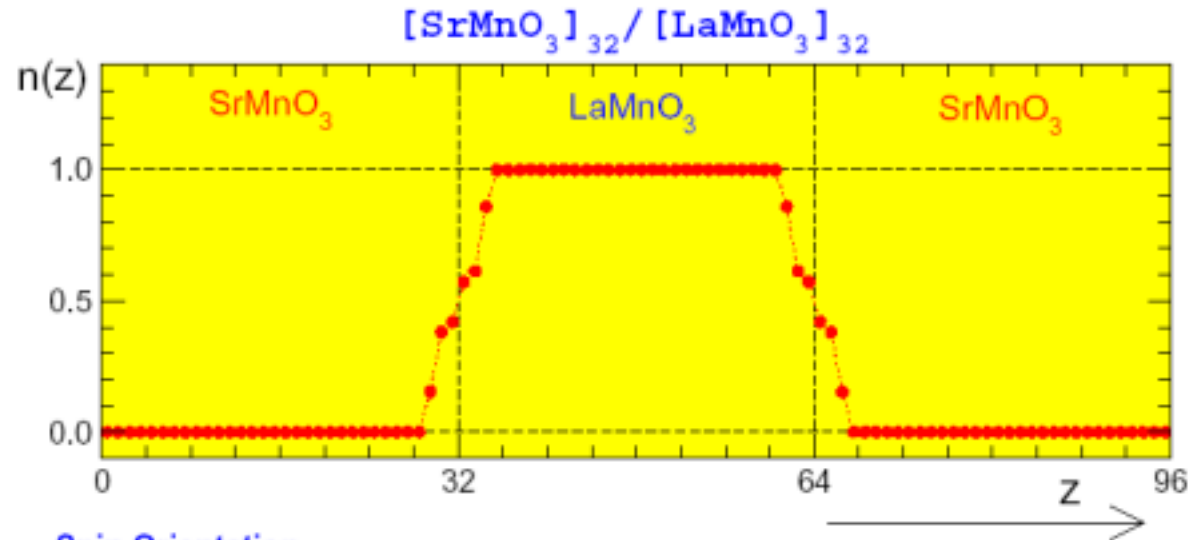
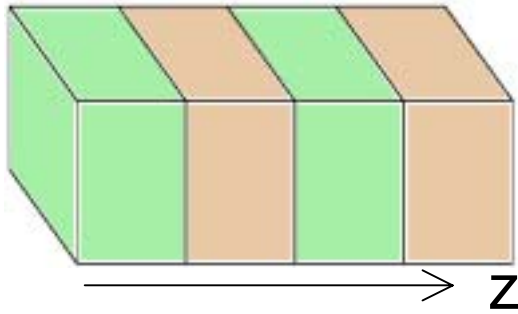


electron-positively charged ion interaction crucial to produce potential wells

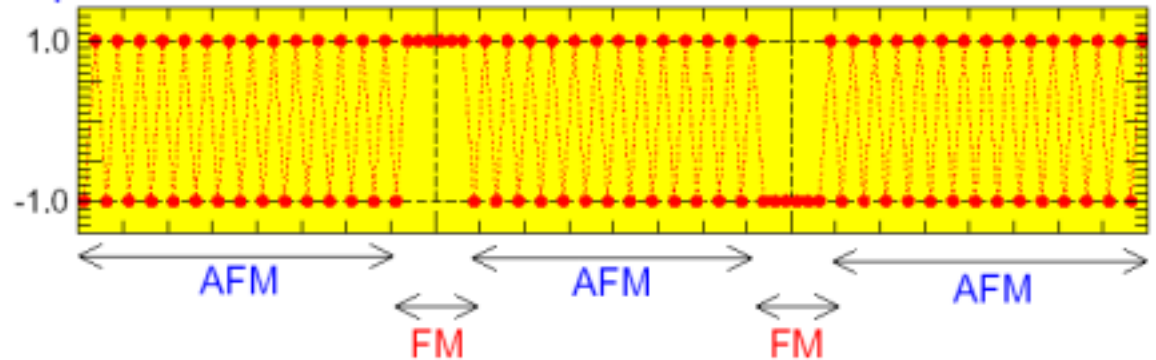
Oxide heterostructure interface

■ LaMnO₃/SrMnO₃

SrMnO₃ LaMnO₃

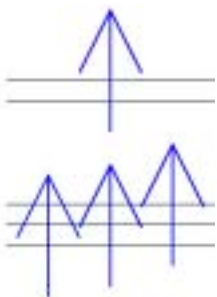
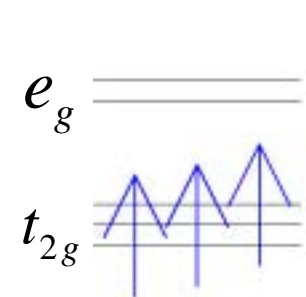


Spin Orientation



SrMn⁴⁺O₃

LaMn³⁺O₃



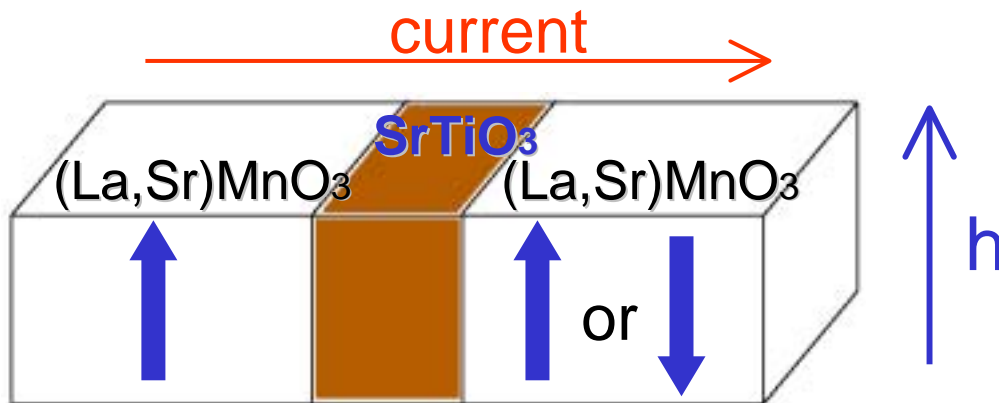
d^3

d^4

Ferromagnetic half-metallic interface

Oxide heterojunction: magnetic tunnel junction

■ $\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3/\text{SrTiO}_3/\text{La}_{2/3}\text{Sr}_{1/3}\text{MnO}_3$



half-metal

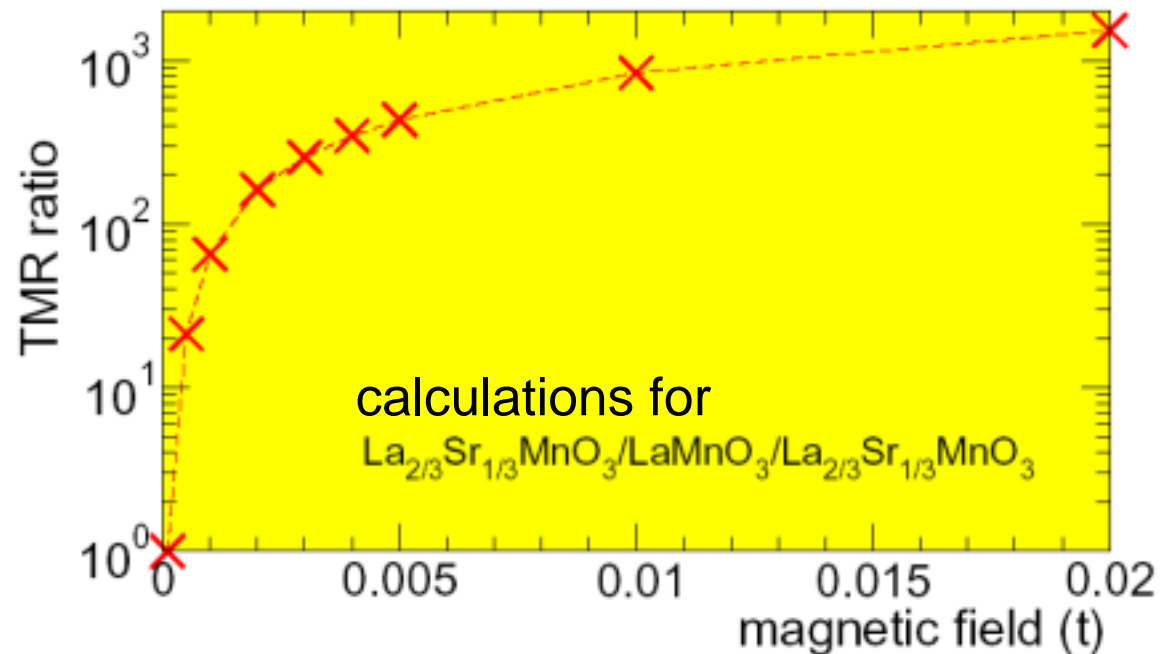
LaMnO_3

A. Fert's group (2003)

Tunneling magneto-resistance (TMR)

TMR ratio $\sim 1800\%$

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



Summary:

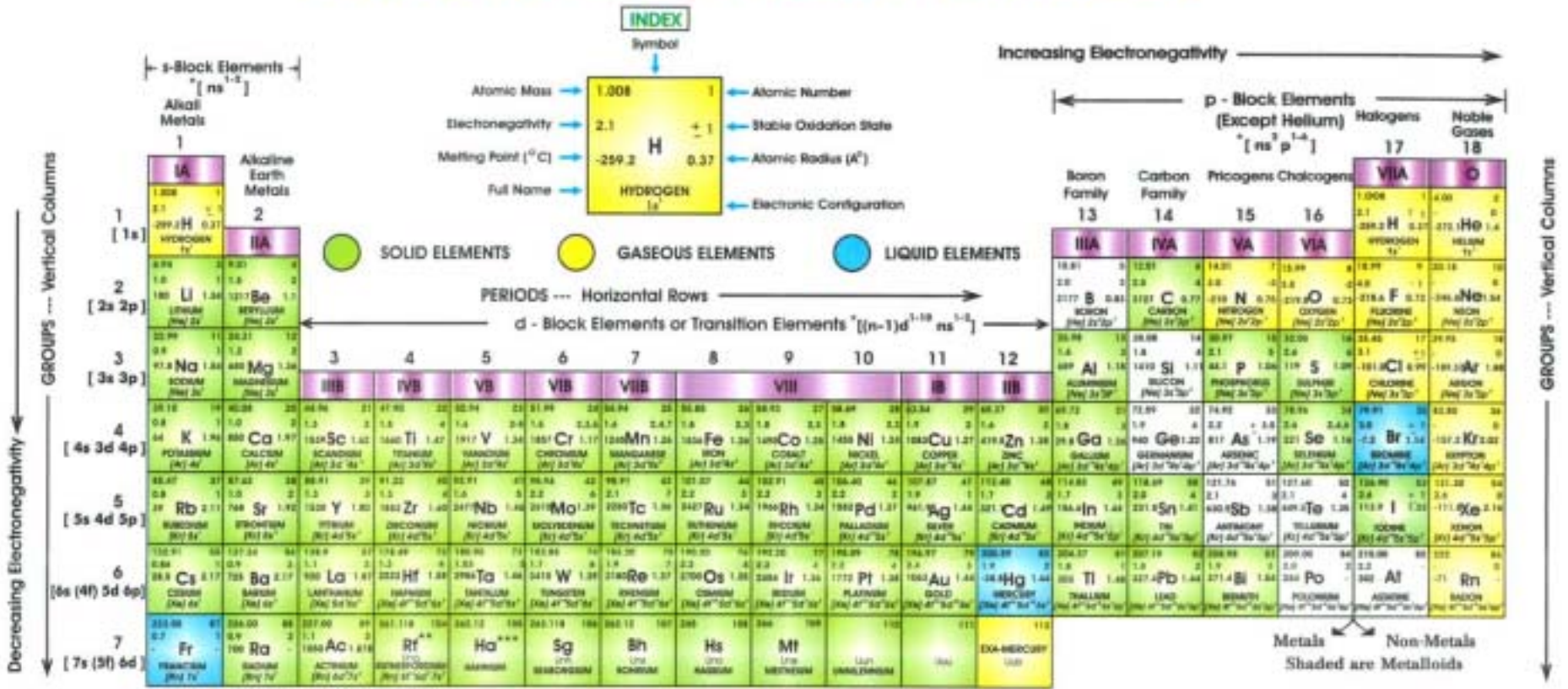
Transition Metal Oxide Heterostructure:

- 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



* - General Electronic Configuration
 ** - If (n-1)d¹⁰ is also called as Subshell (2d)
 *** - If (n-1)f¹⁴ is also called as Subshell (2f)

Rare Earths - I
 (4f - Series)
Lanthanides
 [4f¹⁻¹⁴ 5d⁰⁻¹ 6s²]
Rare Earths - II
 (5f - Series)
Actinides
 [5f¹⁻¹⁴ 6d⁰⁻¹ 7s²]

f - Block Elements OR Inner Transition Elements [(n-2)f¹⁻¹⁴ (n-1)d⁰⁻¹ ns²]

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

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