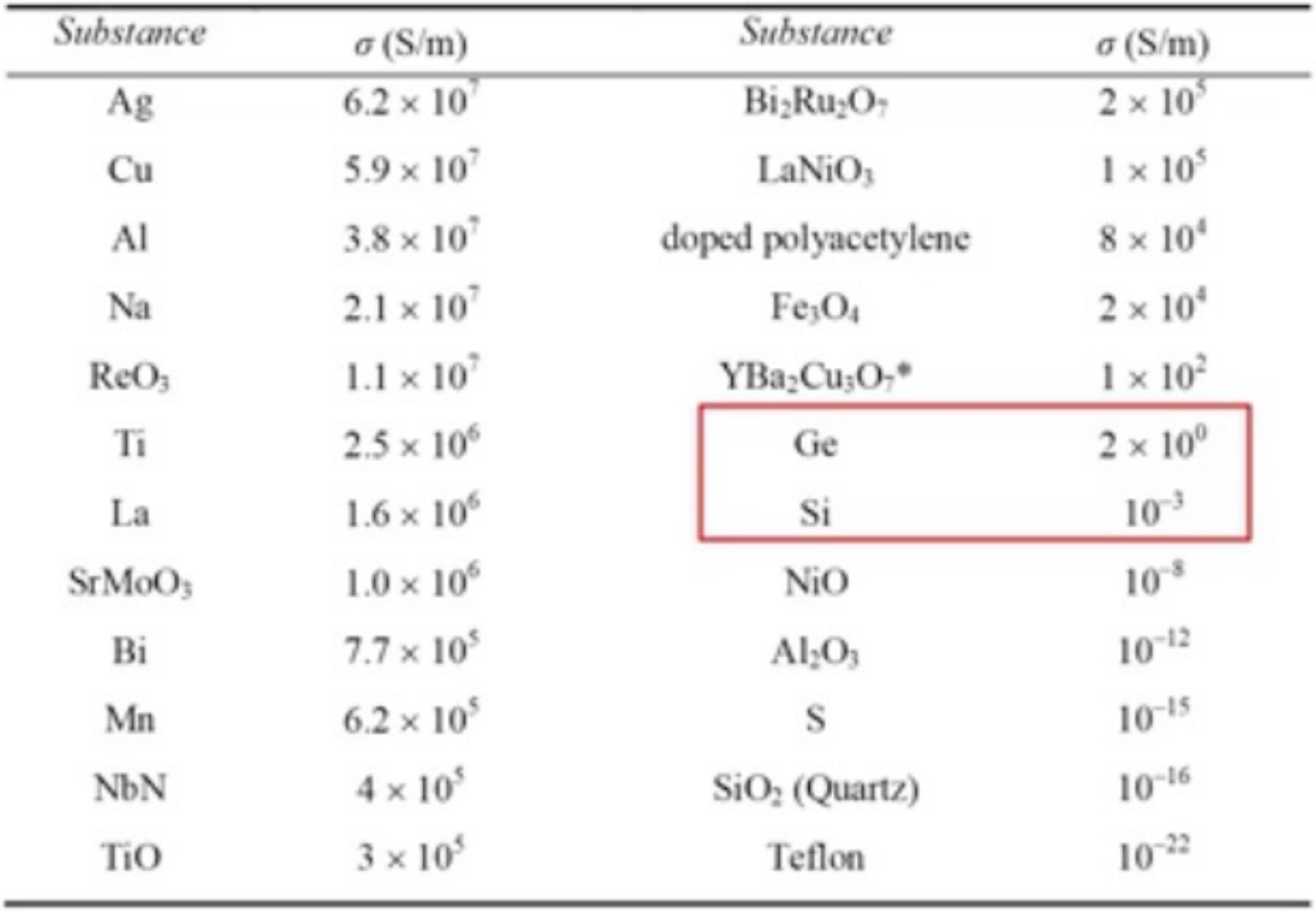
Learning Objectives

Semiconductors

By the end of this lecture, you will be able to:

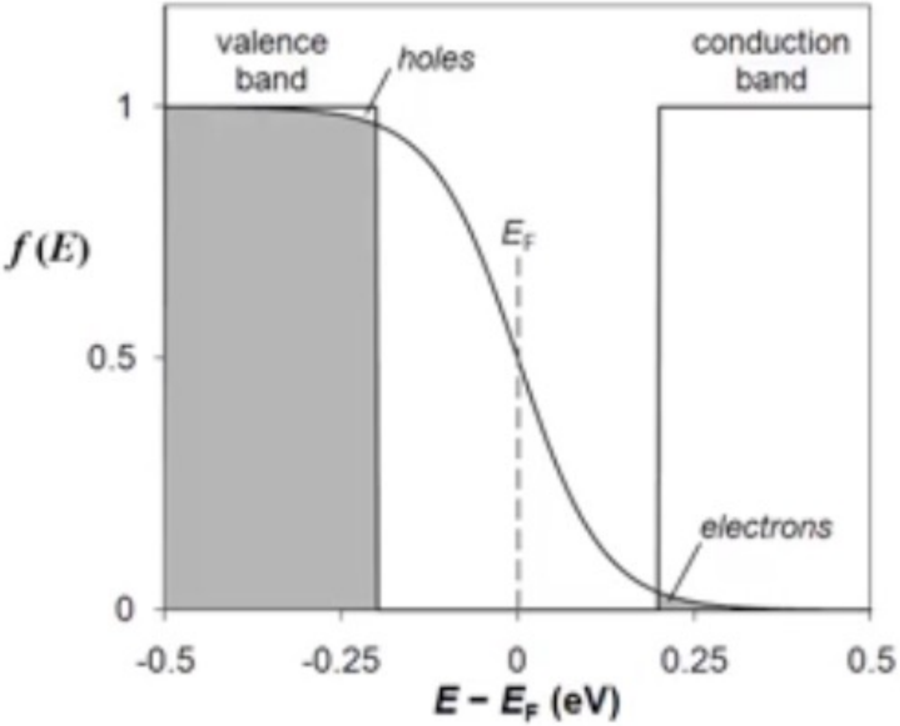
- Explain the origin of low conductivity in intrinsic semiconductors and the role of band gaps in limiting charge carrier concentration
- Describe donor and acceptor doping mechanisms and their effects on semiconductor conductivity through band structure modifications
- Understand the temperature dependence of semiconductor conductivity including freeze-out, saturation, and intrinsic regimes
- Explain P-N junction behavior including rectification, band bending, and the formation of depletion regions
- Describe practical applications: photovoltaic cells, light-emitting diodes (LEDs), and metal-oxide-semiconductor field-effect transistors (MOSFETs)

Conductivity of Select Materials



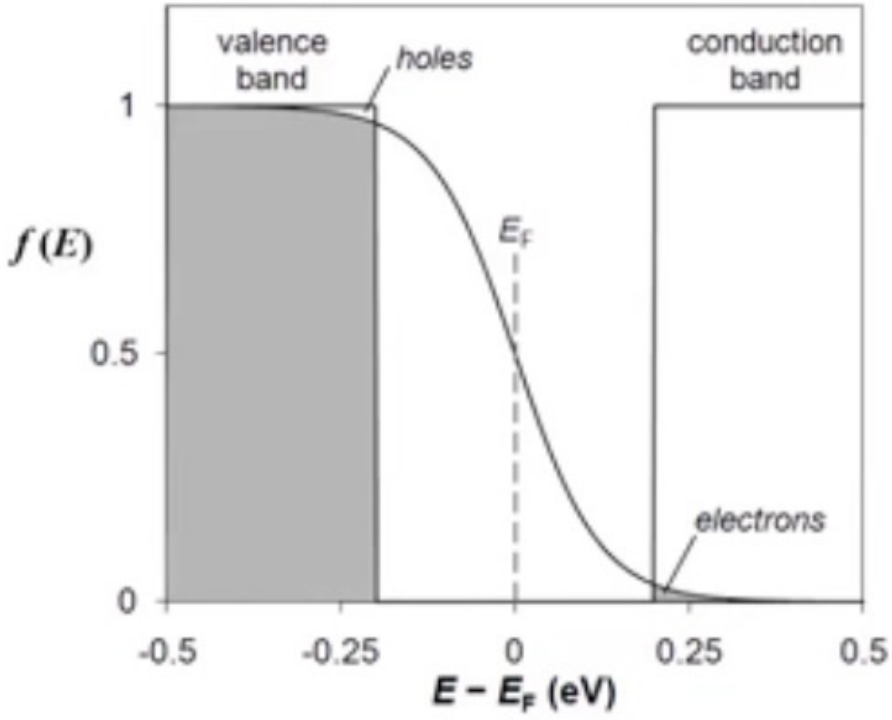
Substance	σ (S/m)	*Substance*	σ (S/m)
Ag	6.2×10^7	$Bi_2Ru_2O_7$	2×10^5
Cu	5.9×10^7	$LaNiO_3$	1×10^5
Al	3.8×10^7	doped polyacetylene	8×10^4
Na	2.1×10^7	Fe_3O_4	2×10^4
ReO_3	1.1×10^7	$YBa_2Cu_3O_7$*	1×10^2
Ti	2.5×10^6	Ge	2×10^0
La	1.6×10^6	Si	10^{-3}
$SrMoO_3$	1.0×10^6	NiO	10^{-8}
Bi	7.7×10^5	Al_2O_3	10^{-12}
Mn	6.2×10^5	S	10^{-15}
NbN	4×10^5	SiO_2 (Quartz)	10^{-16}
TiO	3×10^5	Teflon	10^{-22}

Fermi-Dirac distribution in a semiconductor



$$f(E) = \frac{1}{1 + \exp[(E - E_F)/k_B T]} \approx \exp[(E_F - E)/k_B T]$$

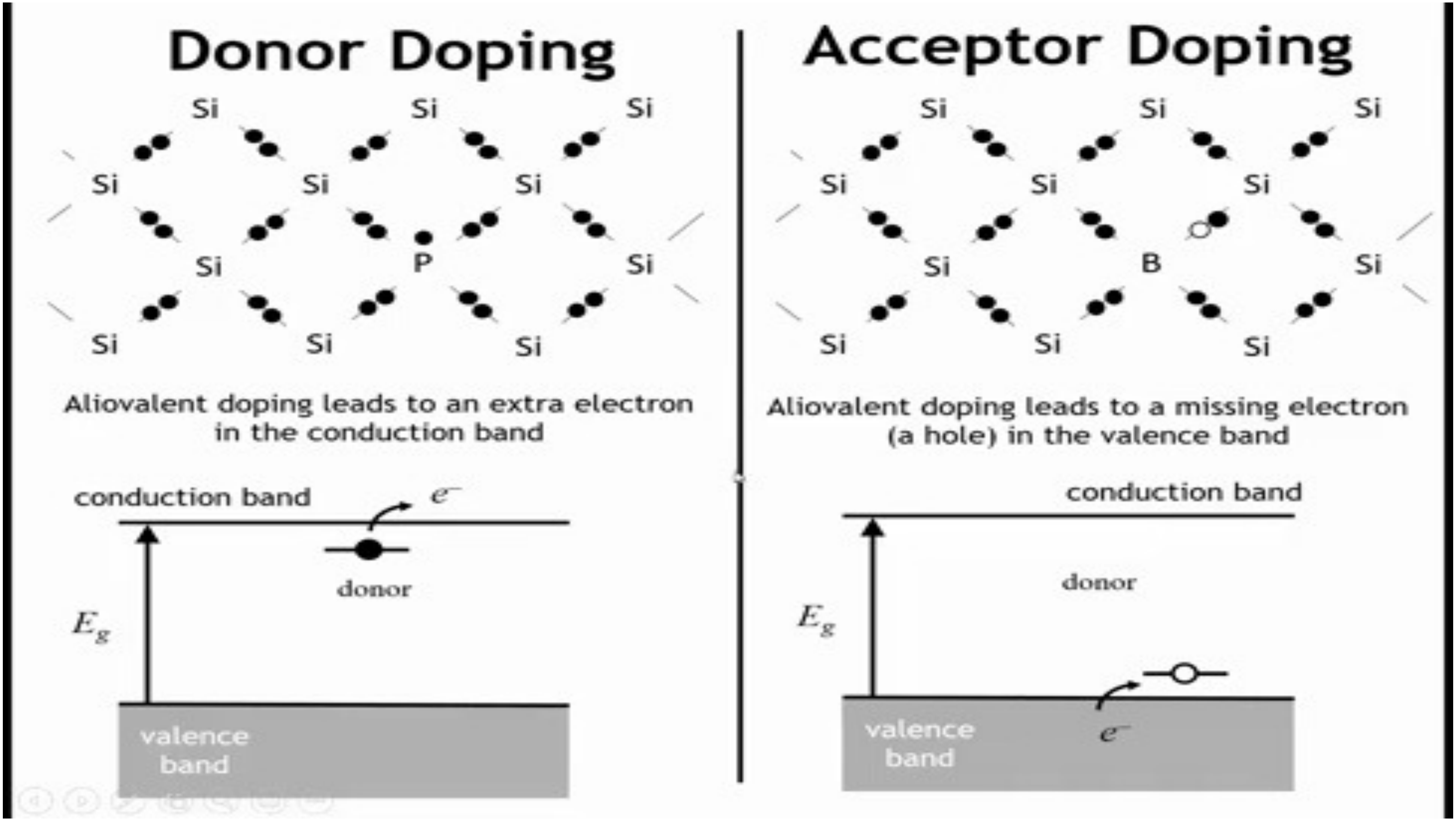
Fermi-Dirac distribution in a semiconductor



It can be shown that the concentration of electron carriers in an intrinsic semiconductor is

$$n \propto \exp\left[-E_g/2k_BT\right]$$

@300k, Si (Eg = 1.1 eV) has 1 electron per trillion atoms

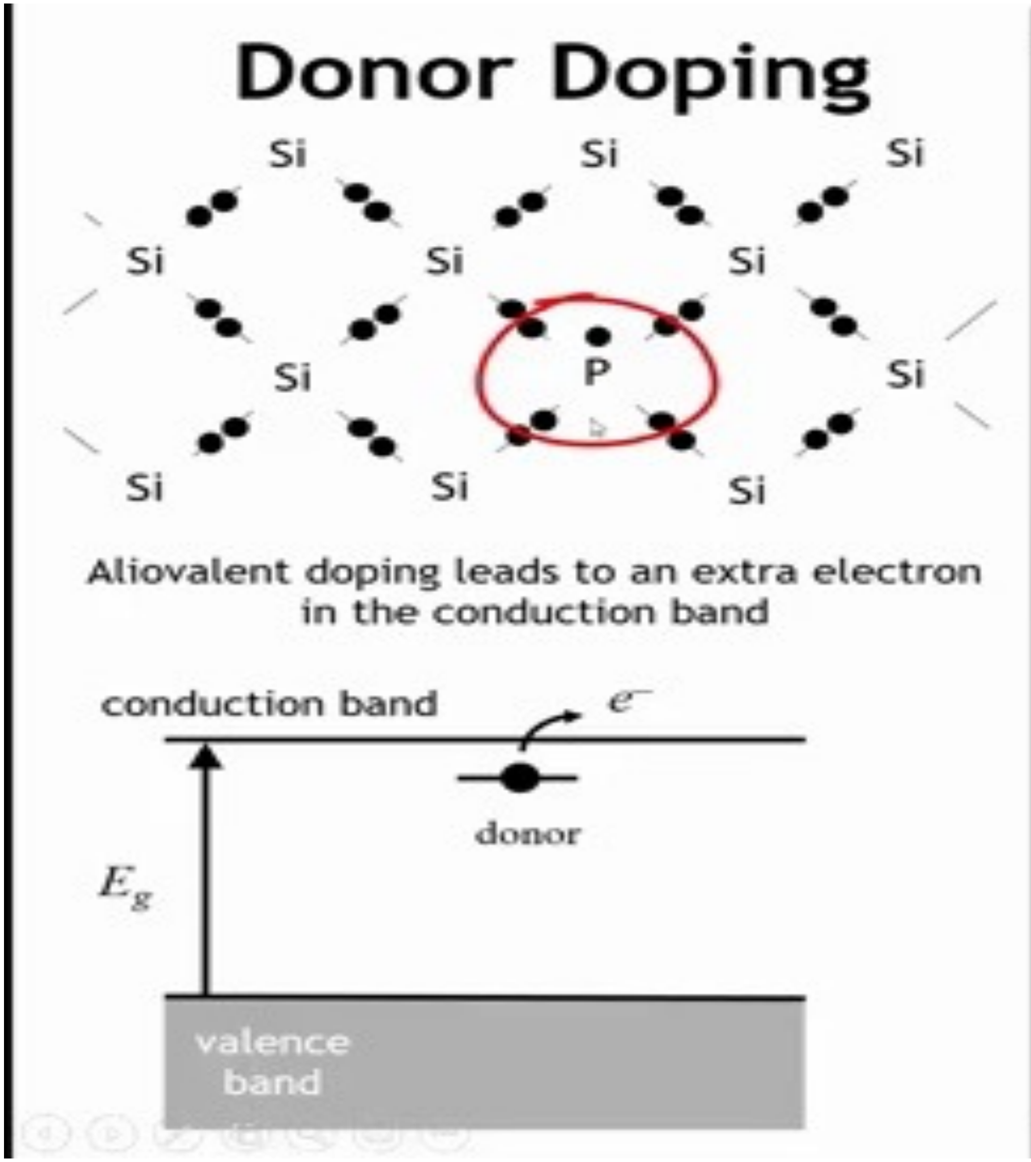


Donor Doping

Aliovalent doping leads to an extra electron in the conduction band

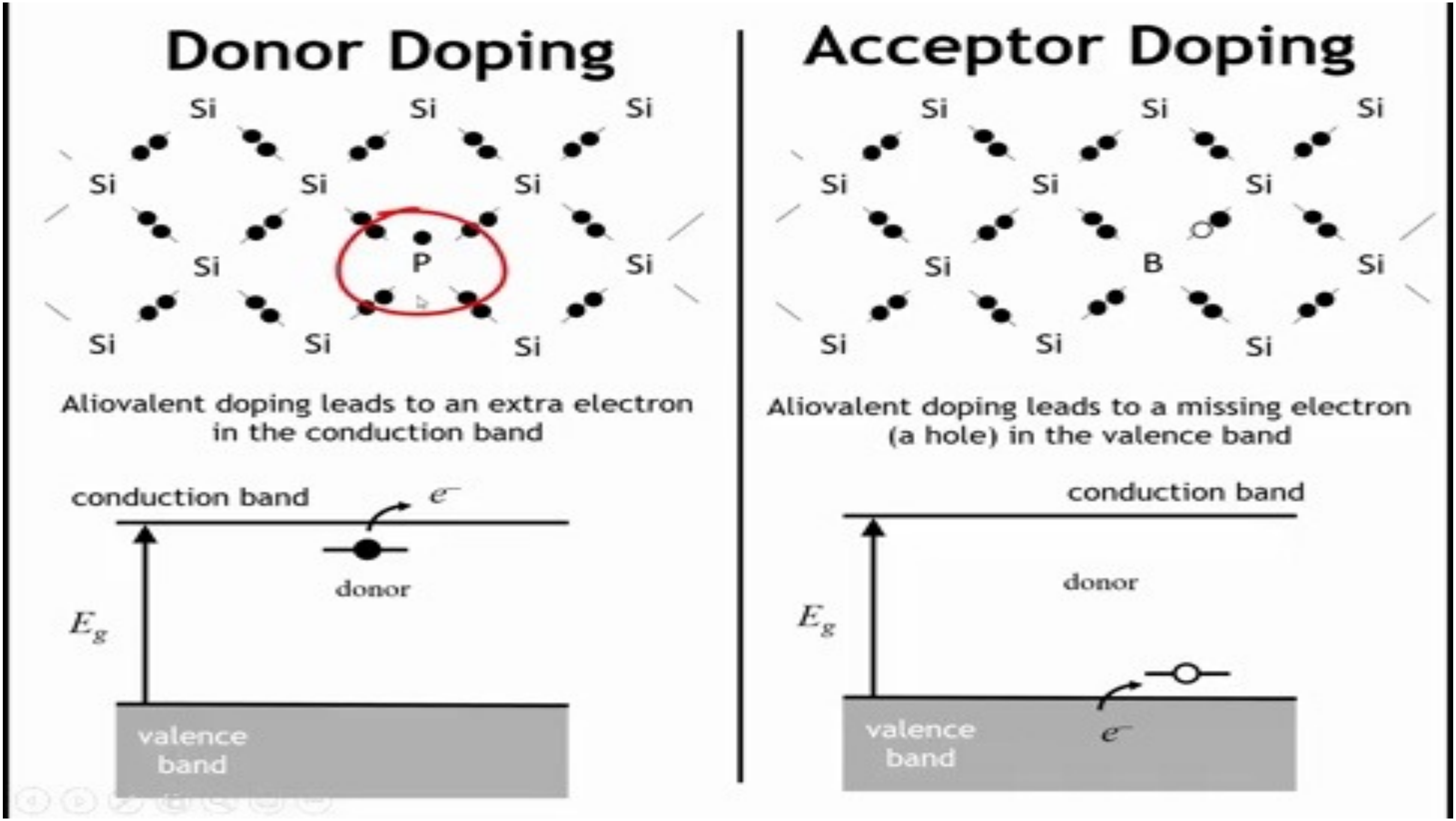
Acceptor Doping

Aliovalent doping leads to a missing electron (a hole) in the valence band



Donor Doping

Aliovalent doping leads to an extra electron in the conduction band



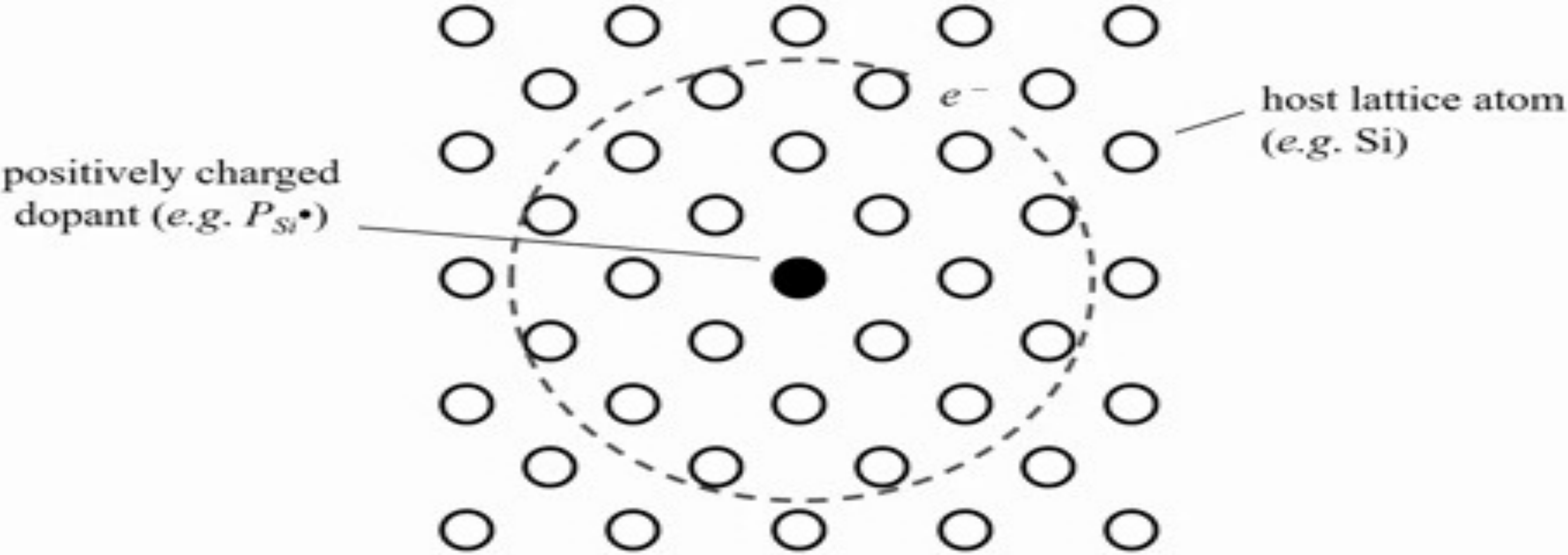
Donor Doping

Aliovalent doping leads to an extra electron in the conduction band

Acceptor Doping

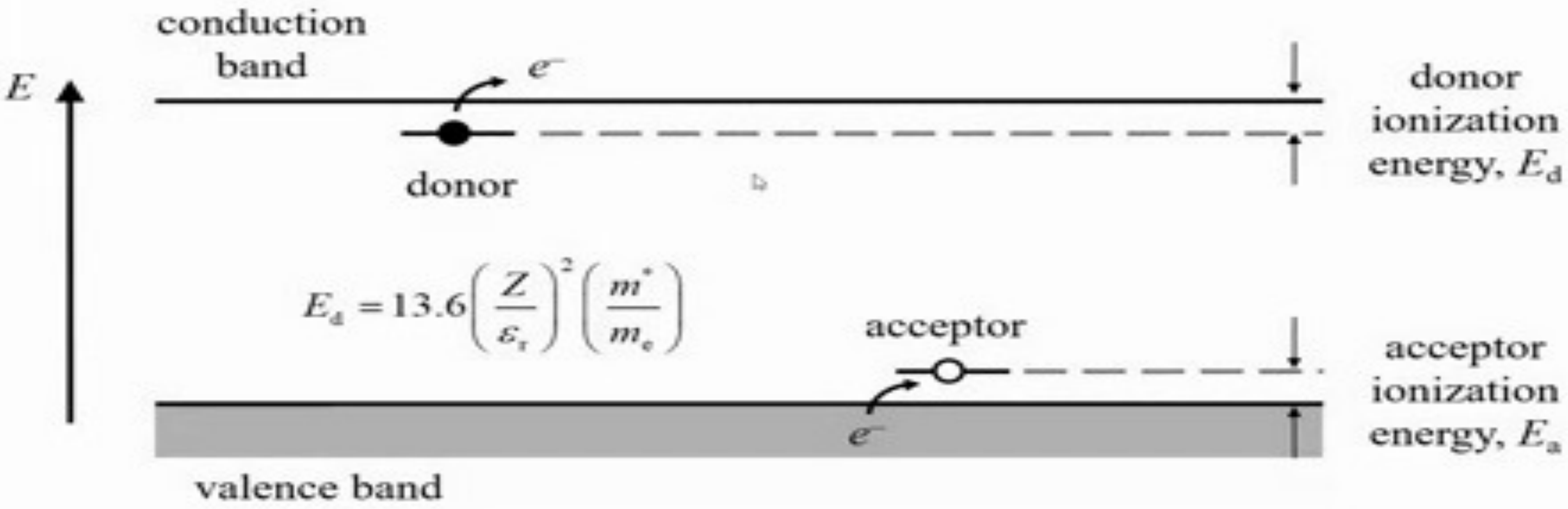
Aliovalent doping leads to a missing electron (a hole) in the valence band

Hydrogenic type orbital in a donor doped semiconductor



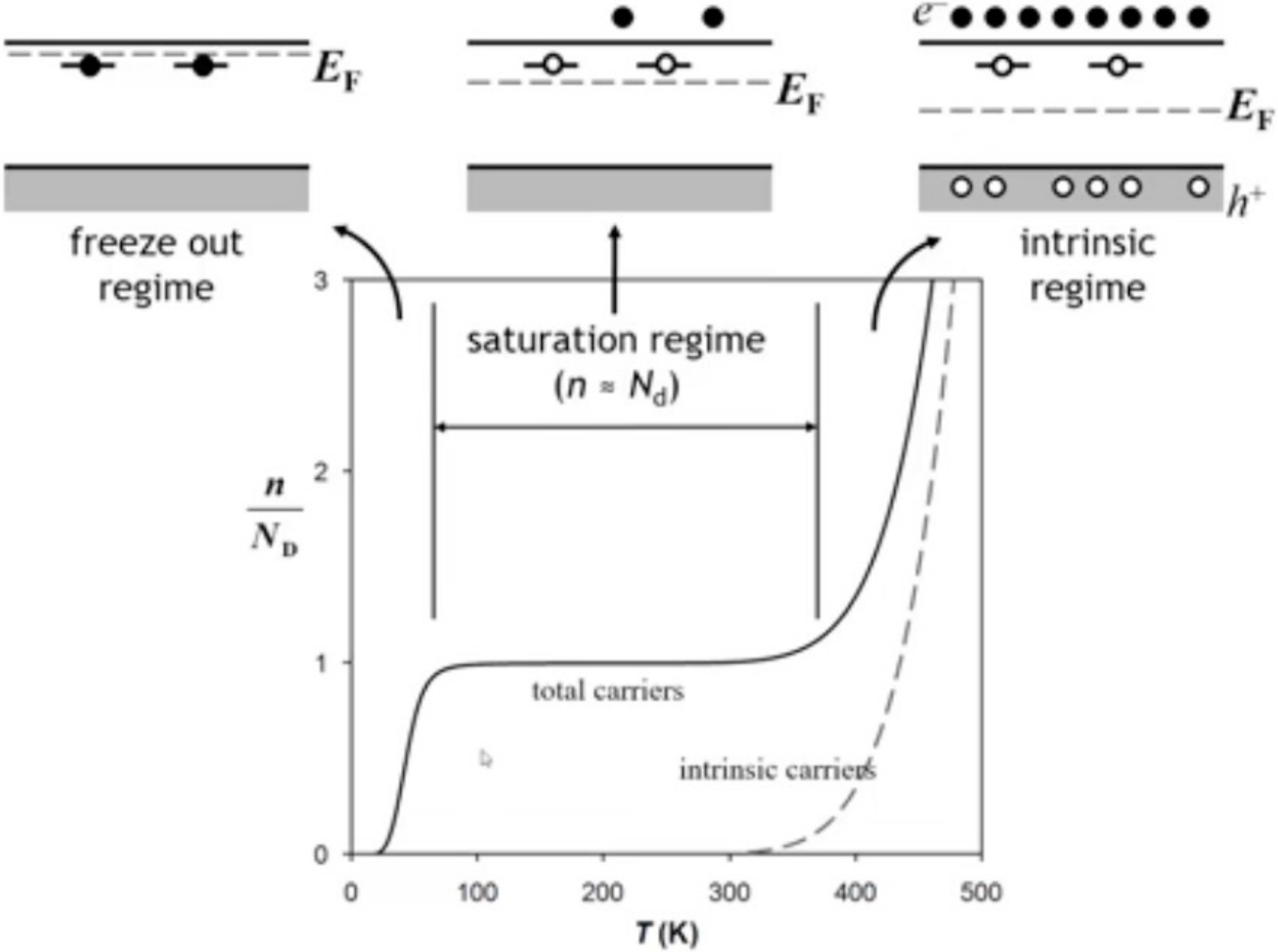
$$r_d = \varepsilon_r\,(m_e/m^*)\ 0.053\ \text{nm}$$

Energy levels in a doped semiconductor



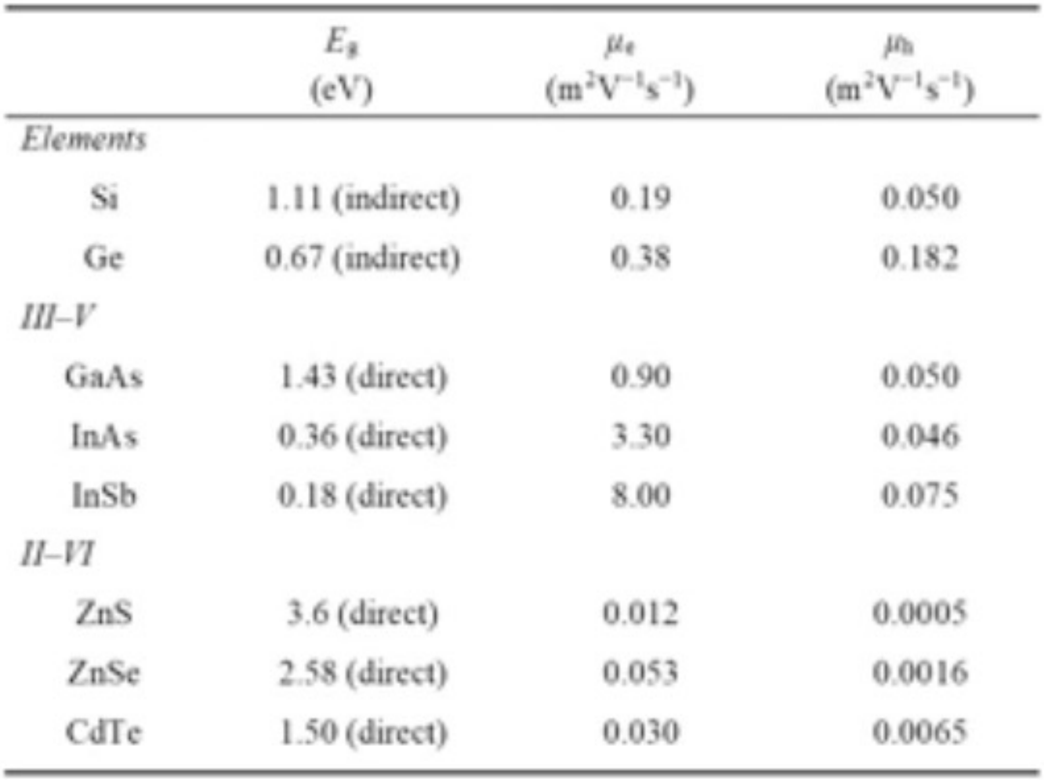
$$E_d = 13.6\left(\frac{Z}{\varepsilon_r}\right)^2\left(\frac{m^*}{m_e}\right)$$

Donors	Si	Ge	Acceptors	Si	Ge
P	0.045	0.013	B	0.045	0.010
As	0.054	0.014	Al	0.057	0.011
Sb	0.042	0.010	Ga	0.065	0.011



E_F
freeze out regime
E_F
saturation regime
($n \approx N_d$)
e^-
E_F
h^+
intrinsic regime
$\frac{n}{N_D}$
3
2
1
0
total carriers
intrinsic carriers
0
100
200
300
400
500
T (K)

Mobility and Conductivity



	E_g (eV)	μ_e ($m^2V^{-1}s^{-1}$)	μ_h ($m^2V^{-1}s^{-1}$)
Elements			
Si	1.11 (indirect)	0.19	0.050
Ge	0.67 (indirect)	0.38	0.182
III–V			
GaAs	1.43 (direct)	0.90	0.050
InAs	0.36 (direct)	3.30	0.046
InSb	0.18 (direct)	8.00	0.075
II–VI			
ZnS	3.6 (direct)	0.012	0.0005
ZnSe	2.58 (direct)	0.053	0.0016
CdTe	1.50 (direct)	0.030	0.0065

$$\sigma=\sigma_n+\sigma_p=n\mu_e e+p\mu_h e$$

See Gradescope Quiz 1

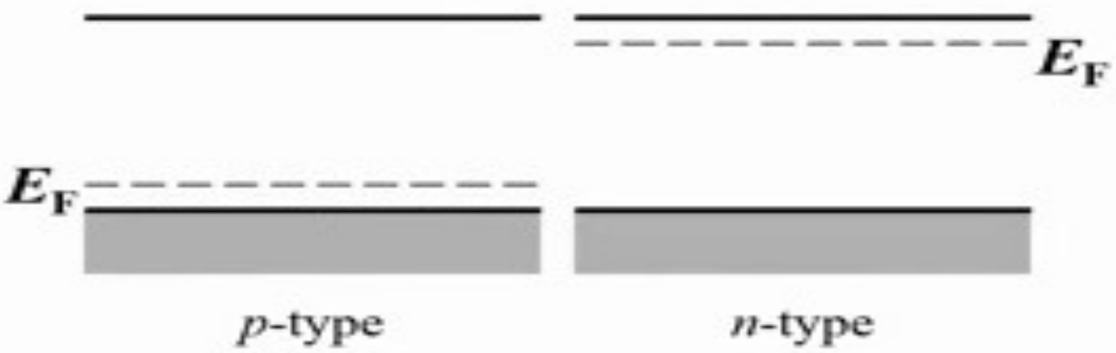
1. What is the primary reason for the low conductivity of an intrinsic (pure) semiconductor like silicon?

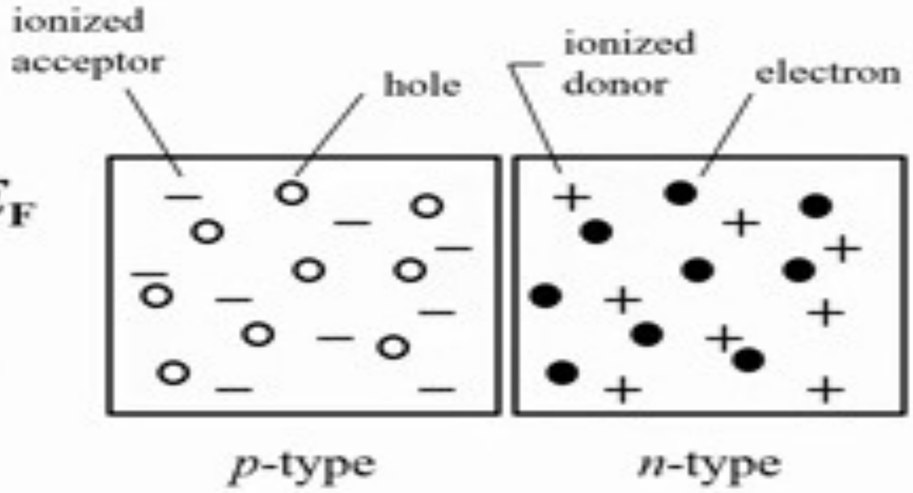
2. When an acceptor dopant like boron (which has one fewer valence electron than silicon) is added, what type of charge carrier is created?

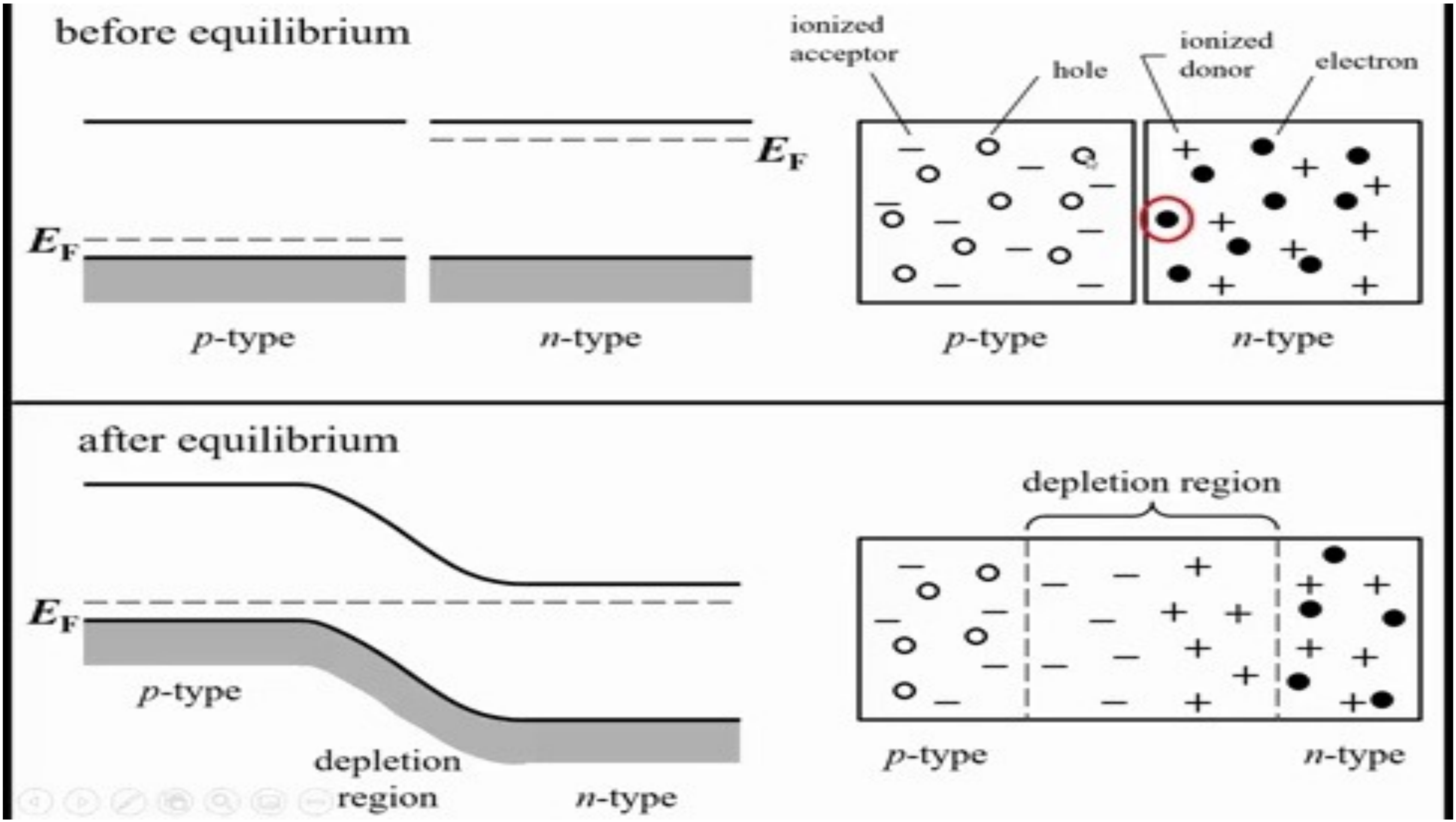
3. How does the conductivity of a semiconductor generally change as temperature increases (in the intrinsic regime)?

4.In a doped semiconductor, what is the "saturation regime"?

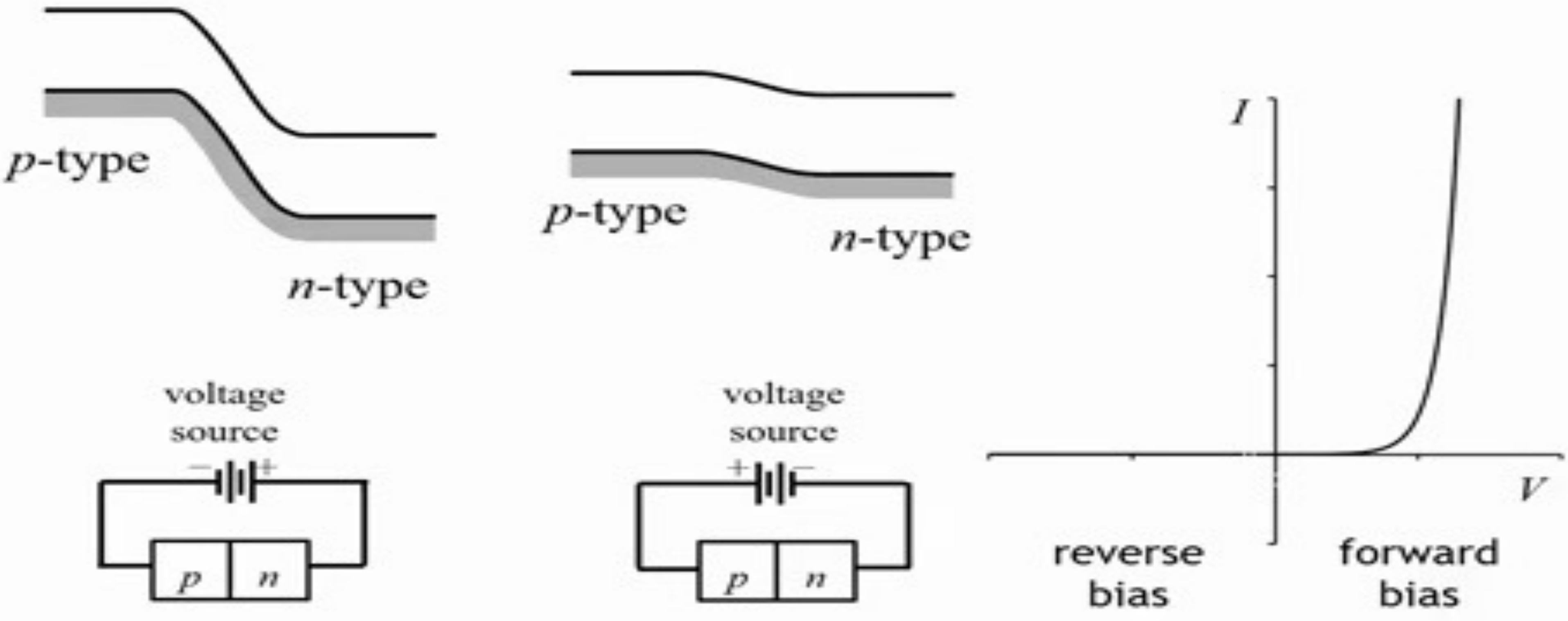
before equilibrium






before equilibrium
ionized acceptor
hole
ionized donor
electron
E_F
E_F
p-type
n-type
p-type
n-type
after equilibrium
depletion region
E_F
p-type
depletion region
n-type
p-type
n-type

p-n junction under bias

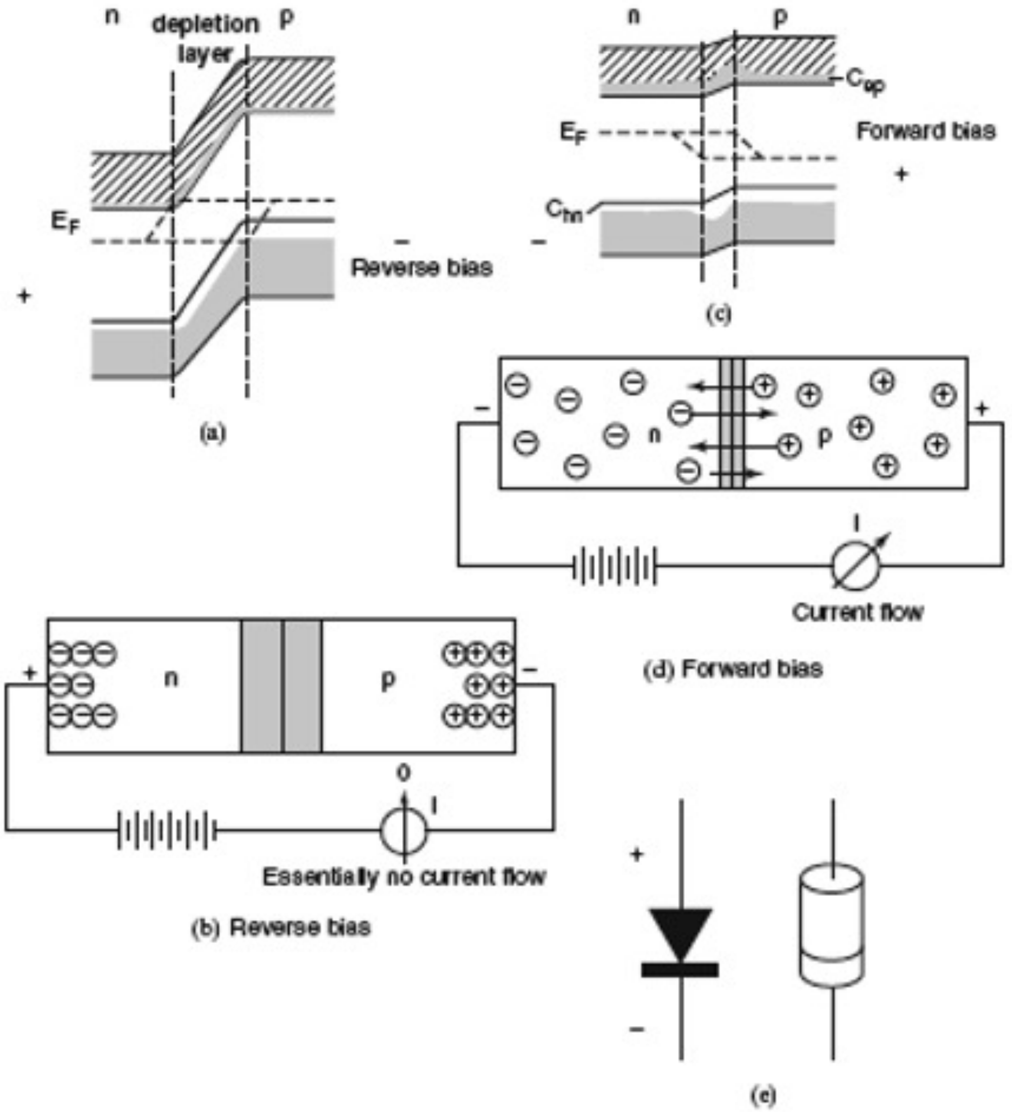


(a) reverse bias ($V < 0$)

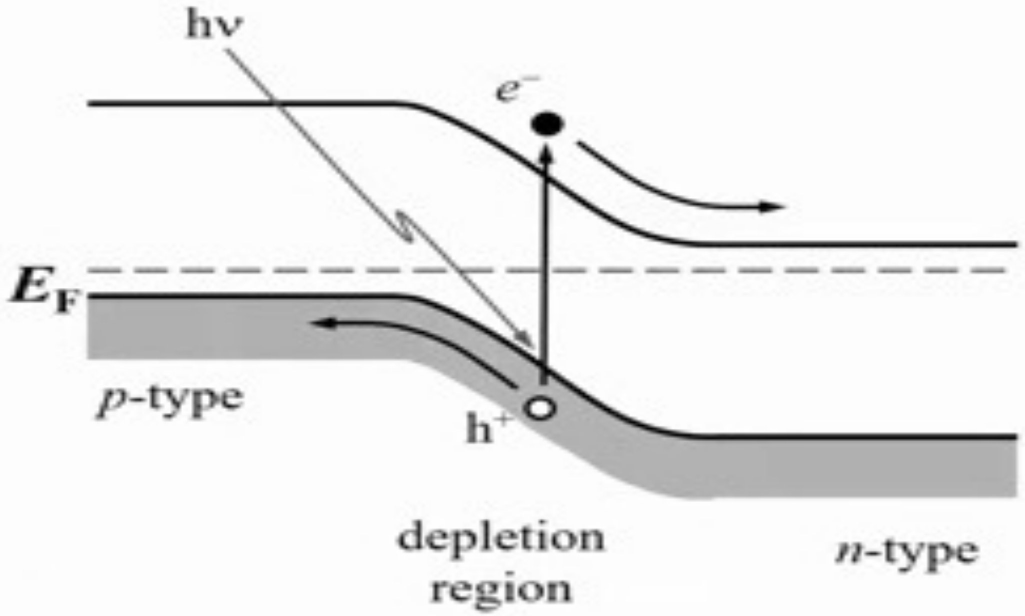
(b) forward bias ($V > 0$)

(c) current−voltage (I−V) curve

p-n Rectifying Junction



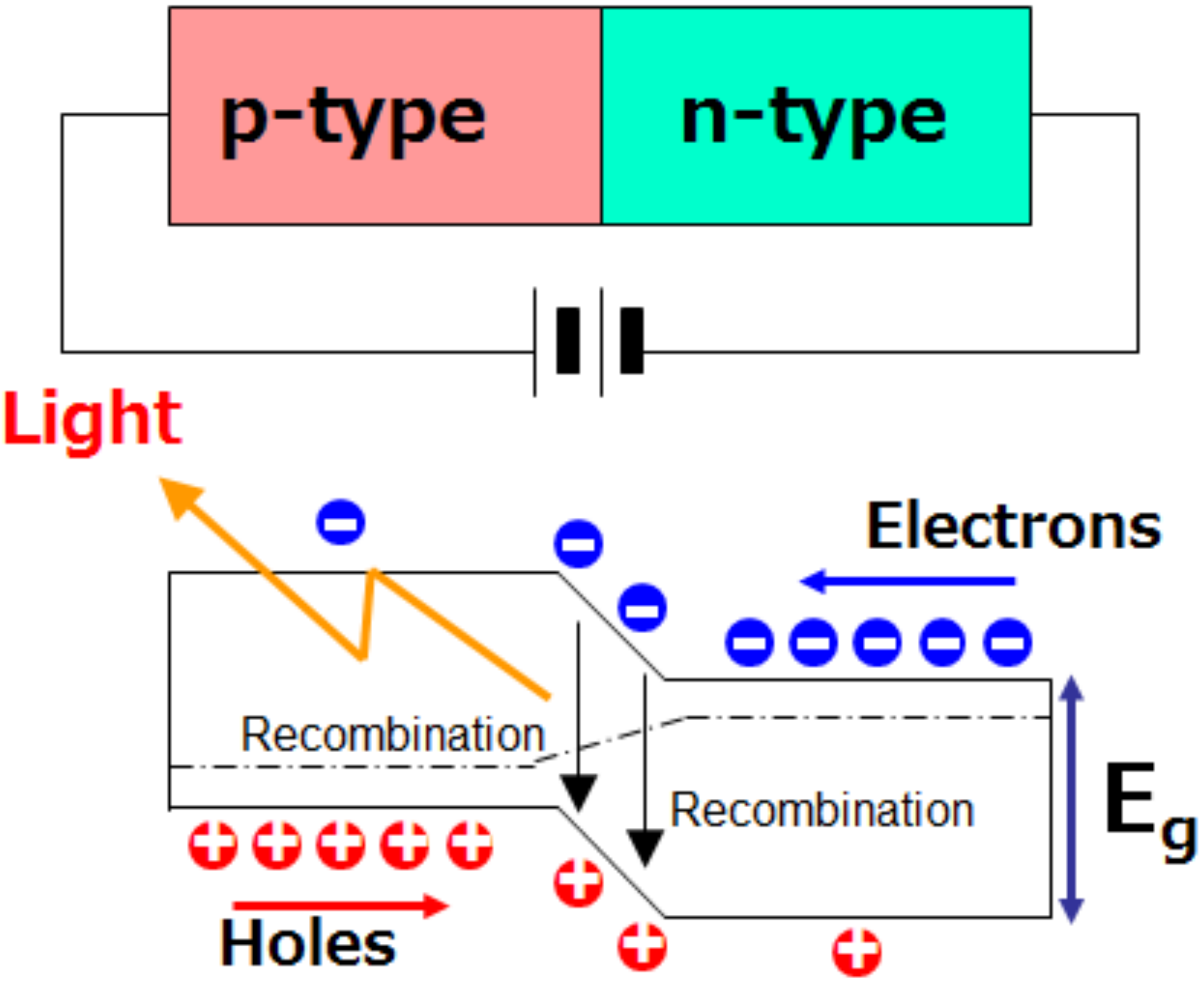
Photovoltaic cell

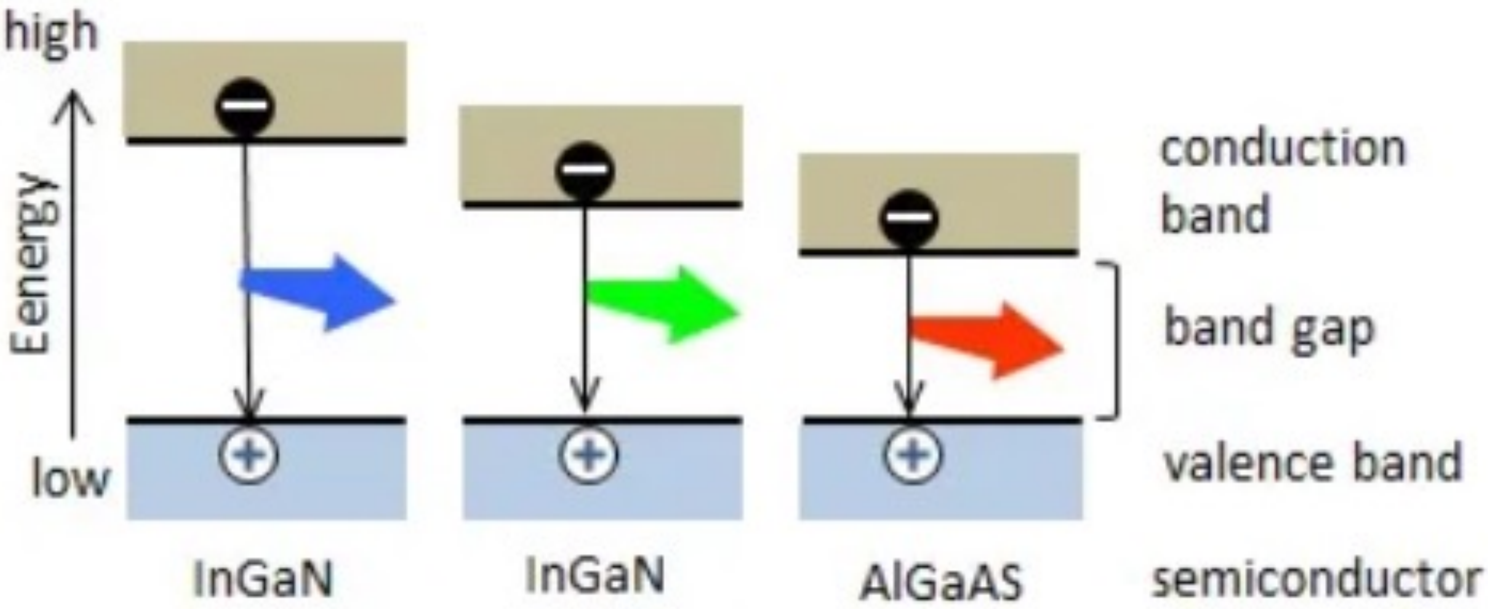


Photons that are absorbed in the depletion region contribute to the photocurrent.

- Small band gap = Large absorbance = Large current
- Large band gap = Large potential drop across depletion region = high voltage

High efficiency is a trade off between the two

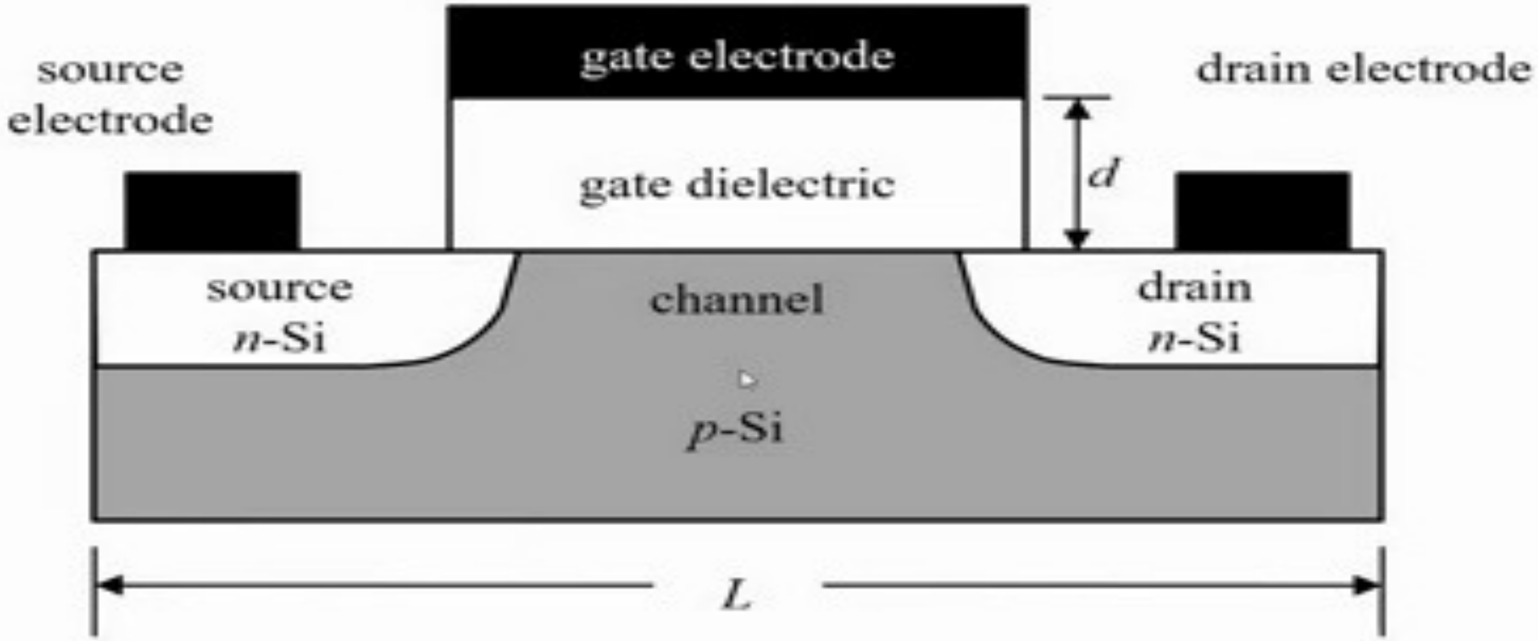

p-type
n-type
Light
Electrons
Recombination
Recombination
E_g
Holes



- Pure GaN → ~365 nm (ultraviolet)
- $In_{0.2}Ga_{0.8}N$ → ~450 nm (blue)
- $In_{0.3}Ga_{0.7}N$ → ~520 nm (green)
- $In_{0.5}Ga_{0.5}N$ → ~600 nm (orange-red)

- Pure GaAs → ~870 nm (infrared)
- $Al_{0.2}Ga_{0.8}As$ → ~750 nm (red)
- $Al_{0.4}Ga_{0.6}As$ → ~650 nm (orange)

Metal oxide field effect transistor (MOSFET)



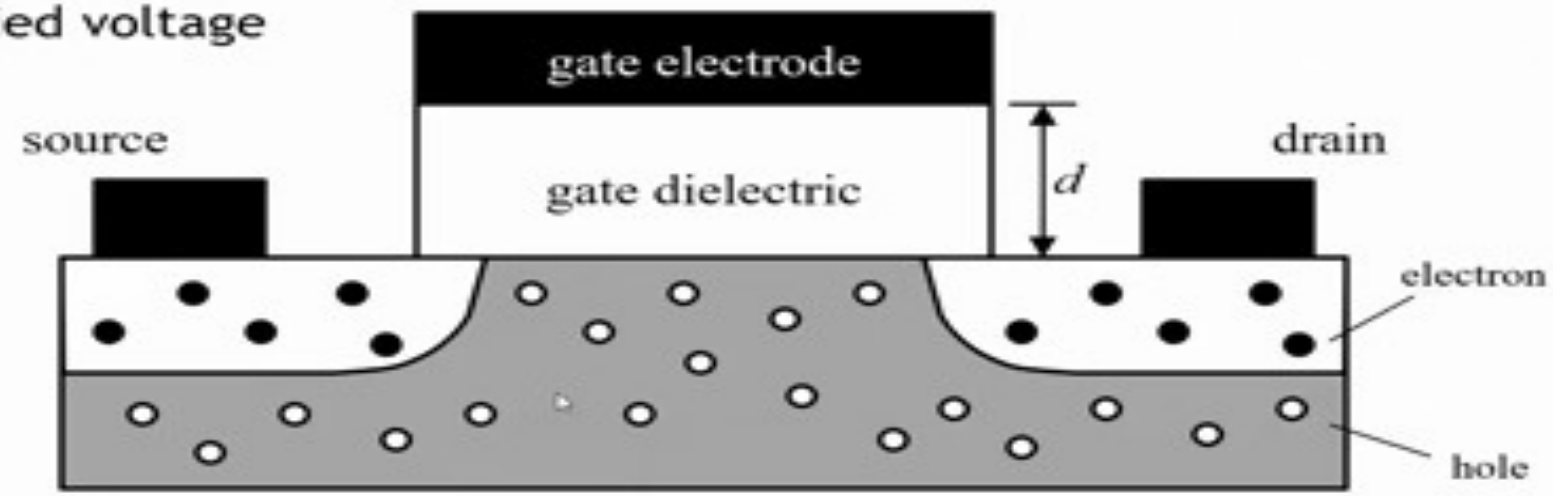
2006 MOSFET

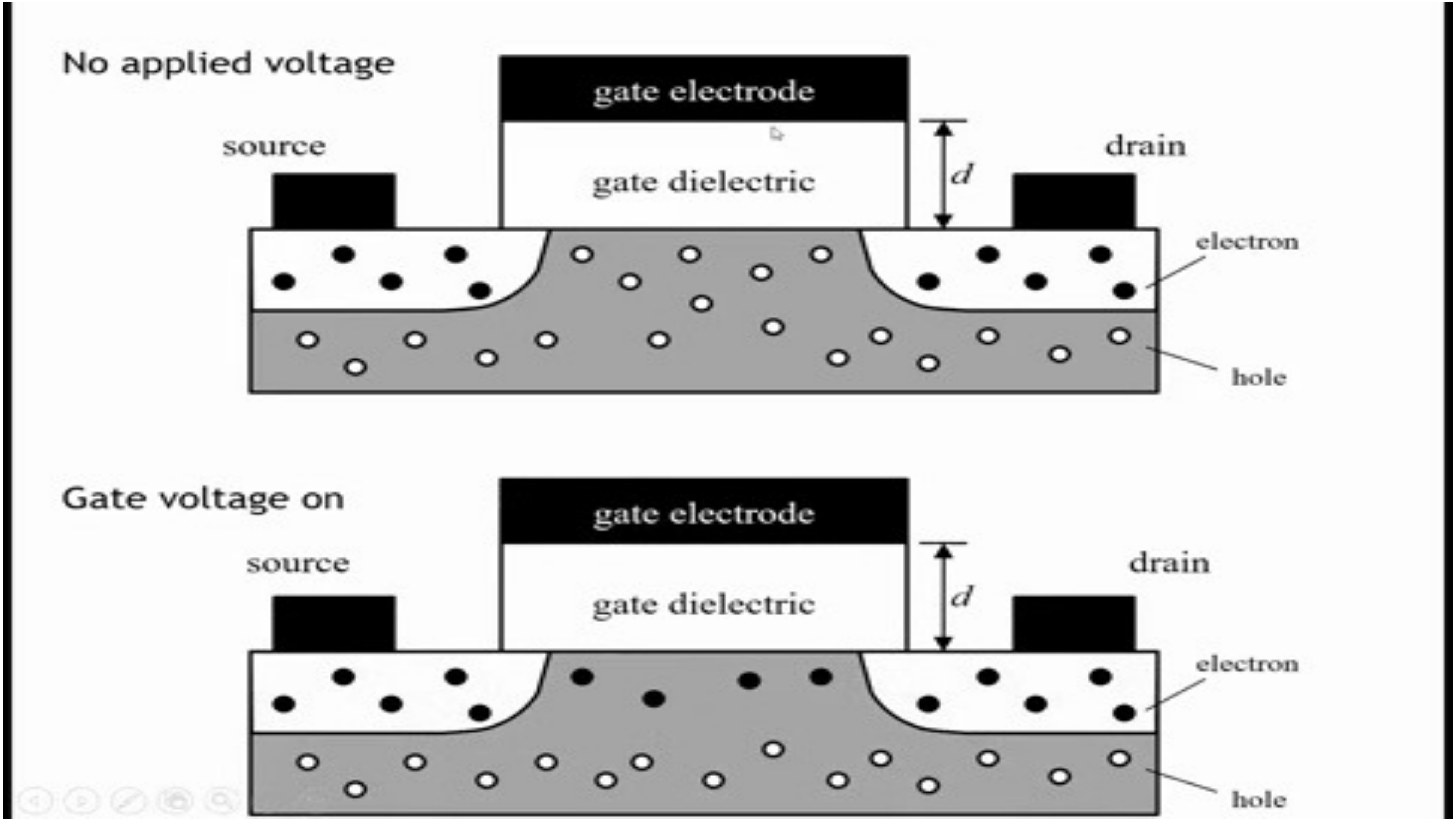
L = 65 nm
d = 1.2 nm
Gate dielectric: SiO_2 (ε_r = 3.9)
Gate electrode: n-doped Si

2010 MOSFET

L = 32 nm
d = ~7 nm
Gate dielectric: HfO_2 (ε_r = 30)
Gate electrode: TiN

No applied voltage

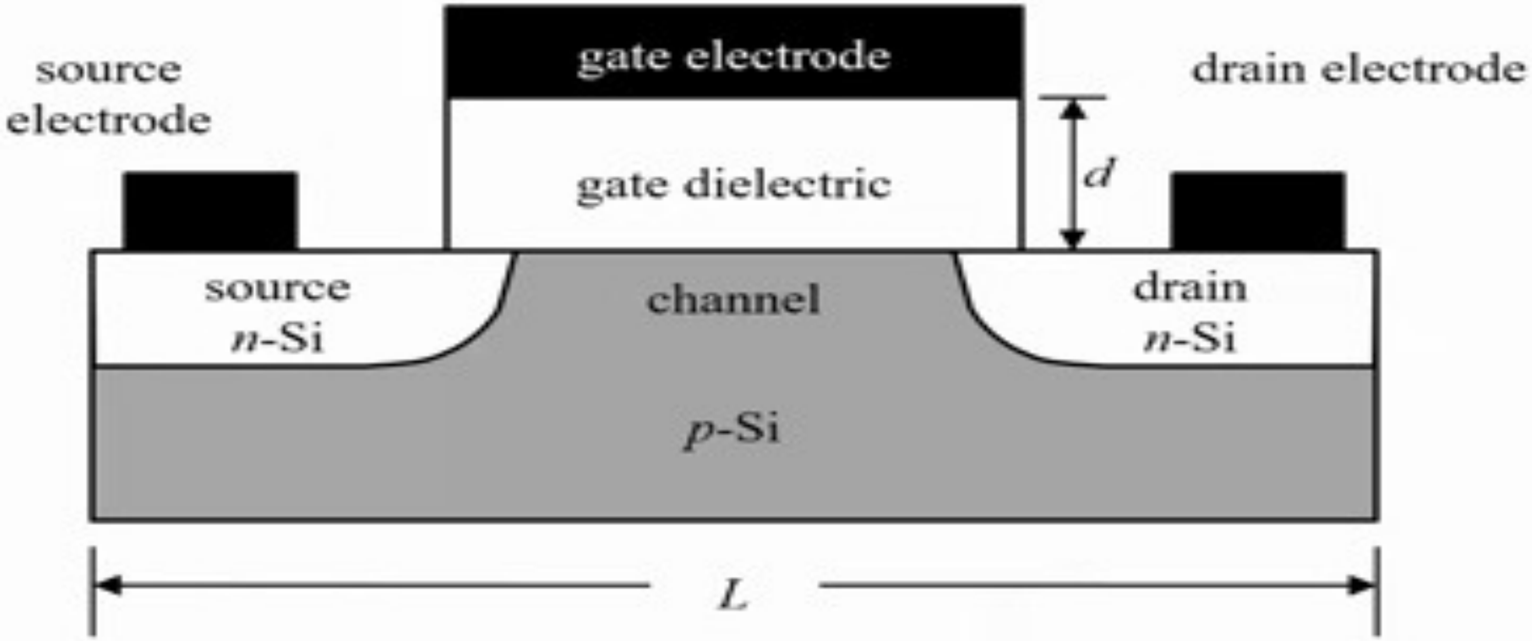




No applied voltage

Gate voltage on

Metal oxide field effect transistor (MOSFET)



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Bi	7.7×10^5	Al_2O_3	10^{-12}
Mn	6.2×10^5	S	10^{-15}
NbN	4×10^5	SiO_2 (Quartz)	10^{-16}
TiO	3×10^5	Teflon	10^{-22}

See Gradescope Quiz 2

1. In a p-n junction at equilibrium (no external voltage), what is the fundamental origin of the built-in electric field within the depletion region?

2. When a p-n junction is formed, the conduction and valence bands "bend" across the depletion region. What is the primary physical reason for this band bending?

3. Applying a reverse bias to a p-n junction (e.g., positive voltage to the n-type side) stops significant current flow. How does it accomplish this?

4. In an n-channel MOSFET built on a p-type substrate, how does applying a strong positive voltage to the gate electrode "turn on" the transistor?

5. Why was it necessary for the semiconductor industry to switch from silicon dioxide (SiO2) to a high-k dielectric like hafnium oxide (HfO2) for the gate?

Homework:
10.11-10.13

Learning Objectives

Conductivity of Transition Metal Compounds

After this lecture, you will be able to:

- Explain how electron-electron repulsions determine conductivity in transition metal compounds
- Apply the Hubbard model to predict metallic vs. insulating behavior by comparing bandwidth (W) and on-site repulsion (U)
- Identify Mott-Hubbard insulators and explain their origin
- Predict conductivity trends across rock salt structure oxides based on d-orbital contraction and metal-metal distance
- Analyze conductivity patterns in perovskite structures and explain differences between 3+ and 4+ oxidation states

Conductivity of Select Materials

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Ag	6.2×10^7	$Bi_2Ru_2O_7$	2×10^5
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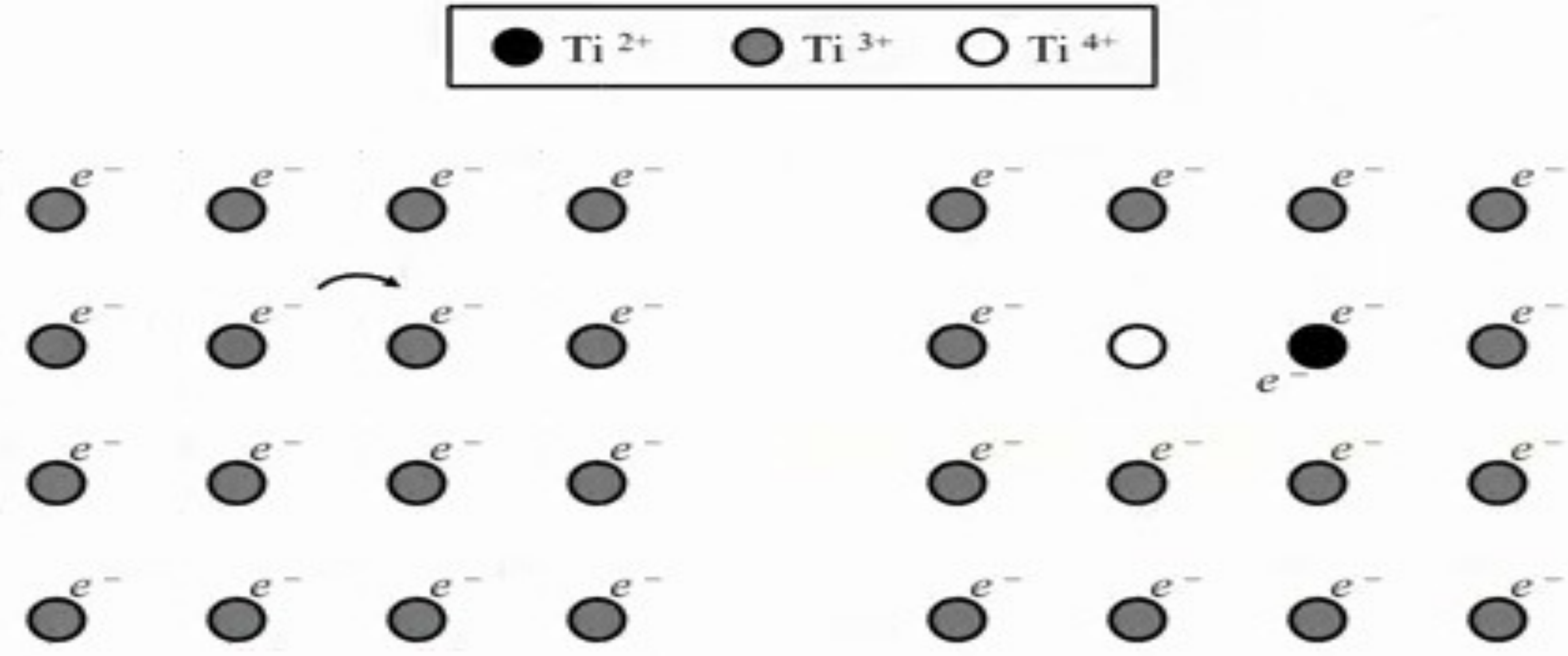
Al	3.8×10^7	doped polyacetylene	8×10^4
Na	2.1×10^7	Fe_3O_4	2×10^4
ReO_3	1.1×10^7	$YBa_2Cu_3O_7$*	1×10^2
Ti	2.5×10^6	Ge	2×10^0
La	1.6×10^6	Si	10^{-3}
$SrMoO_3$	1.0×10^6	NiO	10^{-8}
Bi	7.7×10^5	Al_2O_3	10^{-12}
Mn	6.2×10^5	S	10^{-15}
NbN	4×10^5	SiO_2 (Quartz)	10^{-16}
TiO	3×10^5	Teflon	10^{-22}

Conduction on a $Ti^{3+}(d^1)$ lattice



Hubbard U

The Hubbard model considers interactions (repulsions) between electrons on the same site, while neglecting longer range electron-electron interactions. The strength of the onsite electron-electron interactions is given by the Hubbard U, which we can estimate for gas phase ions.

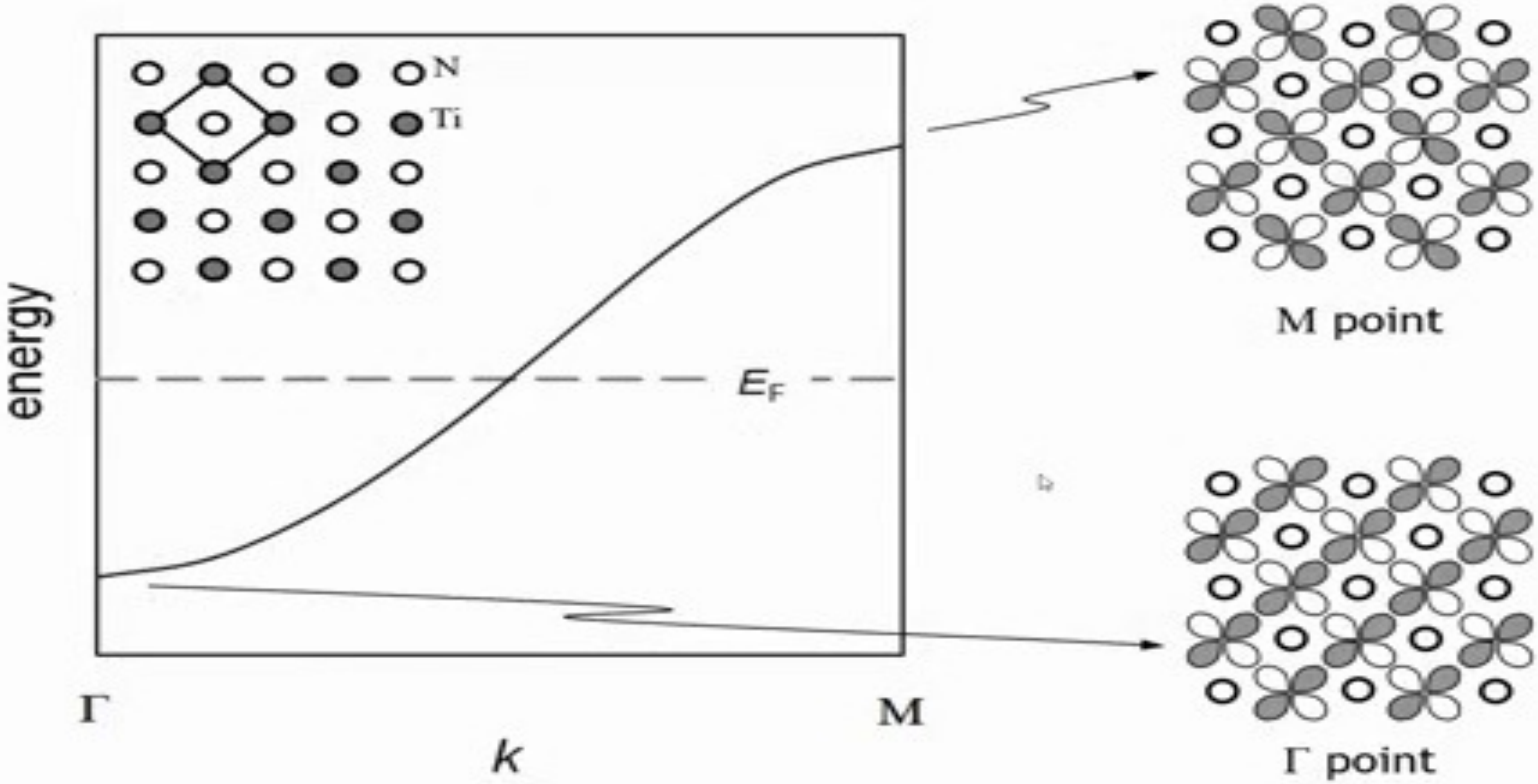
$\mathrm{Ti^{3+}}(g) \rightarrow \mathrm{Ti^{4+}}(g) + \mathrm{e^-}$	IE of $\mathrm{Ti^{3+}}$ = 4th IE of Ti = 43.3 eV
$\mathrm{Ti^{3+}}(g) + \mathrm{e^-} \rightarrow \mathrm{Ti^{2+}}(g)$	H_{eg} of $\mathrm{Ti^{3+}}$ = −(3rd IE of Ti) = −29.3 eV
$2\mathrm{Ti^{3+}}(g) \rightarrow \mathrm{Ti^{4+}}(g) + \mathrm{Ti^{2+}}(g)$	$U = IE + H_{eg} = 14.0$ eV

In a solid U is smaller (2-5 eV for 3d TM ions) because:

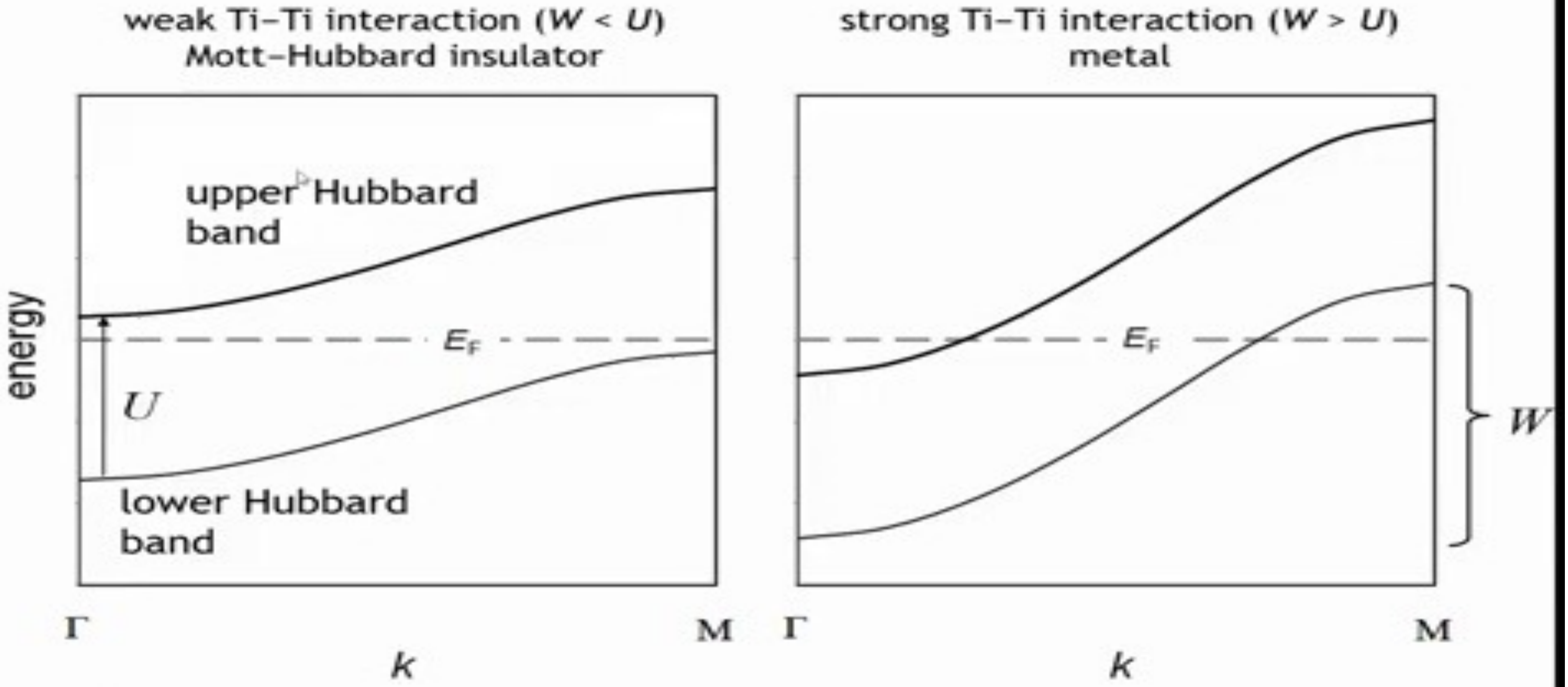
- the surrounding lattice is polarized by the charge of the site
- the electron wavefunctions are more spread out than they are on a gas phase ion

H_{eg} (electron gain enthalpy) is equivalent to electron affinity (with the opposite sign)

d_{xy} band in a square TiN 2D plane



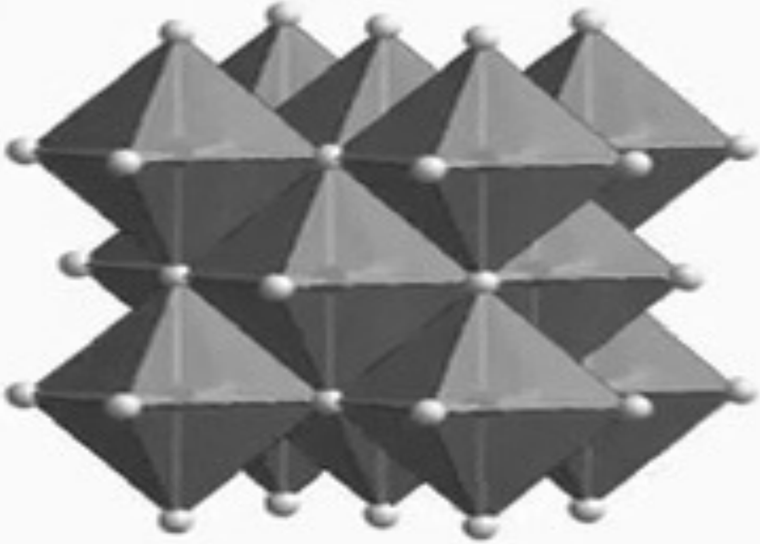
Mott-Hubbard Insulator

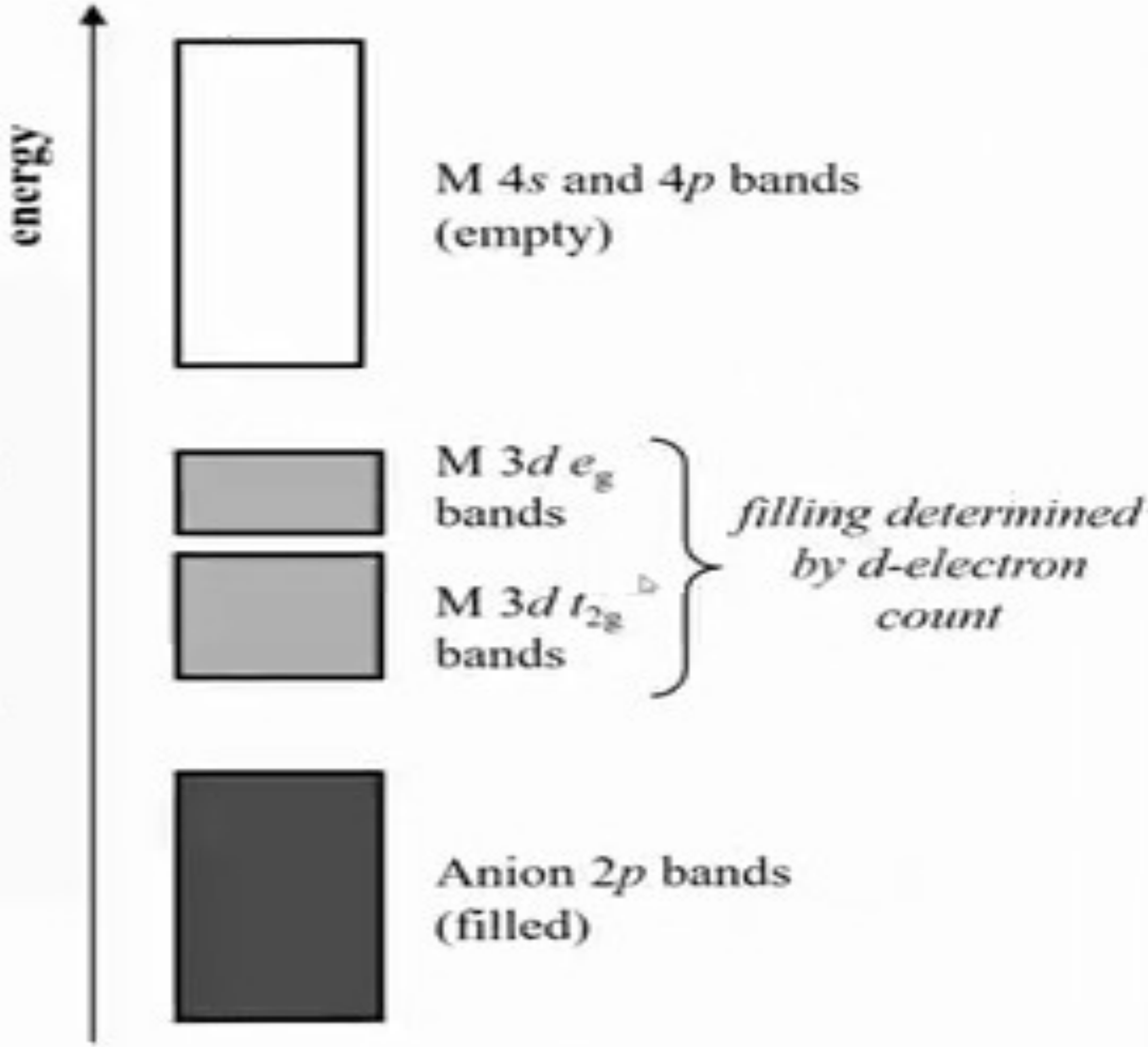


weak Ti–Ti interaction ($W < U$)
Mott–Hubbard insulator

strong Ti–Ti interaction ($W > U$)
metal

Rock salt type transition metal oxides





energy

M 4*s* and 4*p* bands (empty)

M 3*d* e_g bands

M 3*d* t_{2g} bands

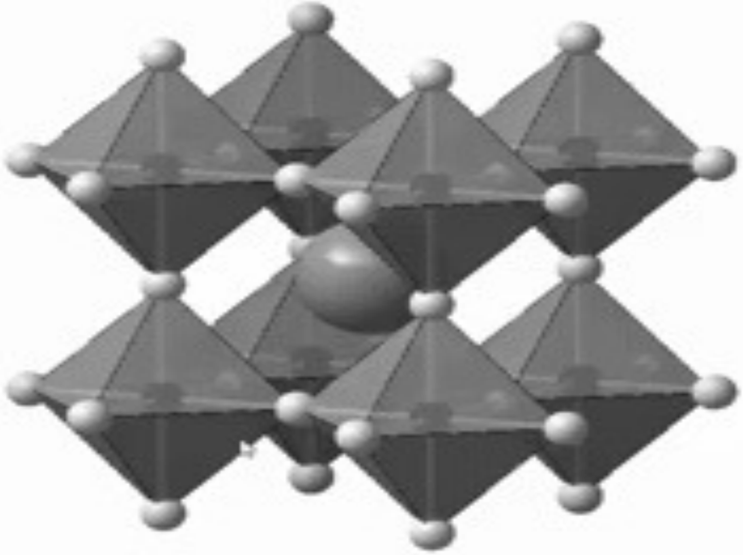
filling determined by d-electron count

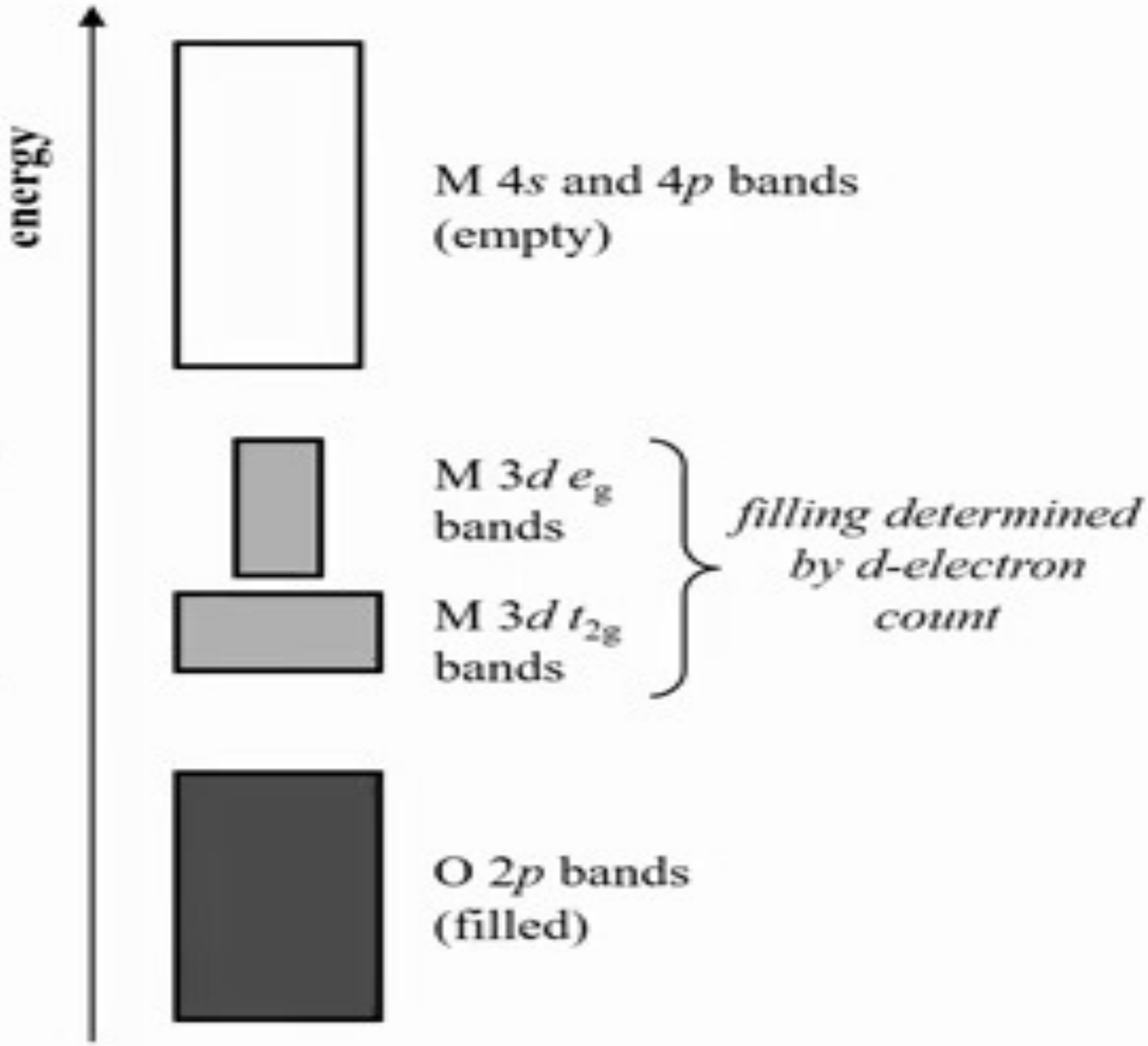
Anion 2*p* bands (filled)

Properties of MO Rock Salt Compounds

Compound	M–M *distance* (Å)	*d-orbital* $r_{\max}$ (Å)*	*Electrical properties*	*Magnetic properties*†
TiO (d^2)	2.94	0.53	Metallic	Pauli PM
VO (d^3)	2.89	0.48	Semimetallic	PM
MnO (d^5)	3.14	0.41	Semiconductor	AFM, $T_N = 122$ K
FeO (d^6)	3.03	0.38	Semiconductor	AFM, $T_N = 198$ K
CoO (d^7)	3.01	0.36	Semiconductor	AFM, $T_N = 293$ K
NiO (d^8)	2.95	0.34	Semiconductor	AFM, $T_N = 523$ K

Perovskite type transition metal oxides





energy

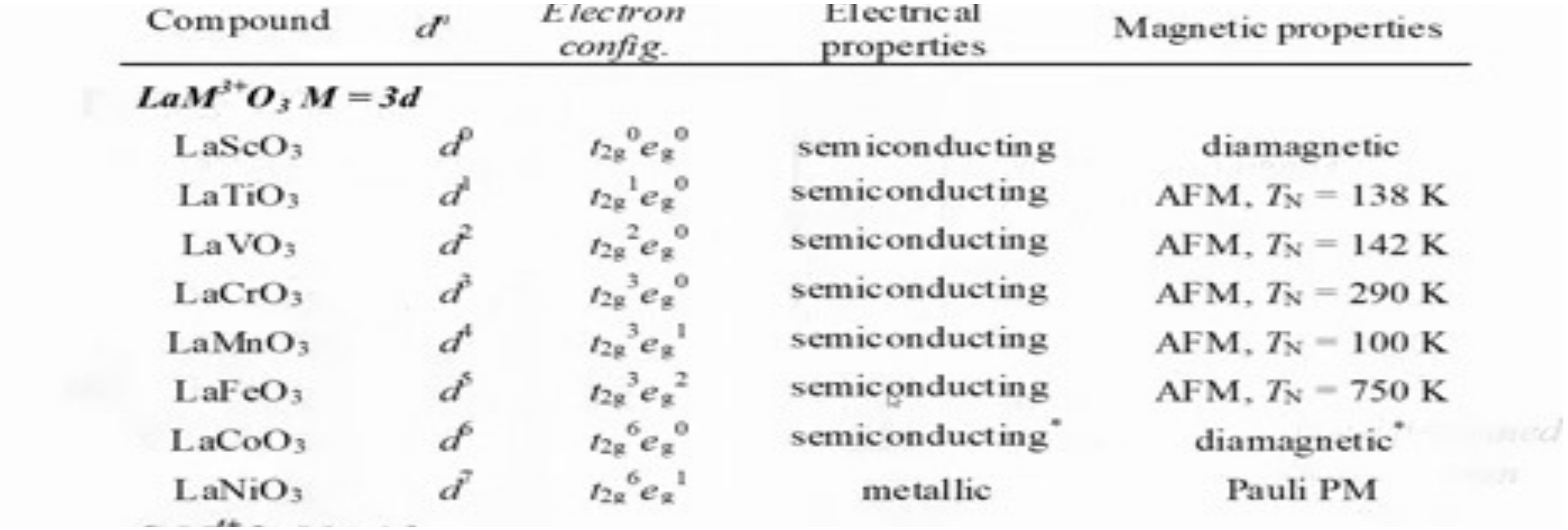
M 4*s* and 4*p* bands (empty)

M 3*d* e_g bands

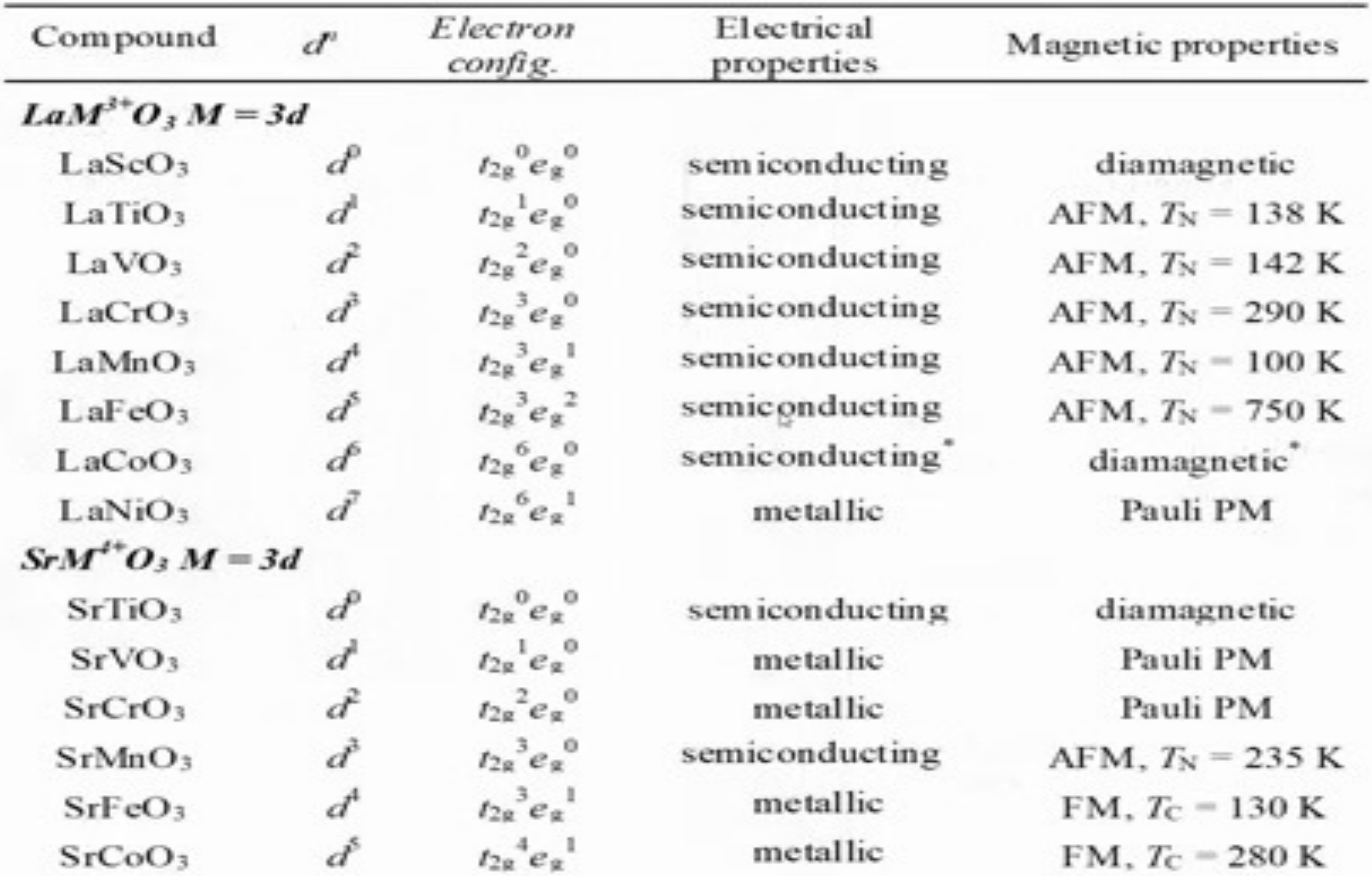
M 3*d* t_{2g} bands

filling determined by d-electron count

O 2*p* bands (filled)



Compound	d^n	Electron config.	Electrical properties	Magnetic properties
$LaM^{3+}O_3$ $M = 3d$				
$LaScO_3$	d^0	$t_{2g}{}^0e_g{}^0$	semiconducting	diamagnetic
$LaTiO_3$	d^1	$t_{2g}{}^1e_g{}^0$	semiconducting	AFM, T_N = 138 K
$LaVO_3$	d^2	$t_{2g}{}^2e_g{}^0$	semiconducting	AFM, T_N = 142 K
$LaCrO_3$	d^3	$t_{2g}{}^3e_g{}^0$	semiconducting	AFM, T_N = 290 K
$LaMnO_3$	d^4	$t_{2g}{}^3e_g{}^1$	semiconducting	AFM, T_N = 100 K
$LaFeO_3$	d^5	$t_{2g}{}^3e_g{}^2$	semiconducting	AFM, T_N = 750 K
$LaCoO_3$	d^6	$t_{2g}{}^6e_g{}^0$	semiconducting*	diamagnetic*
$LaNiO_3$	d^7	$t_{2g}{}^6e_g{}^1$	metallic	Pauli PM



Compound	d^n	*Electron config.*	Electrical properties	Magnetic properties
LaM^{3+}O$_3$ M = 3d				
$LaScO_3$	d^0	$t_{2g}{}^0e_g{}^0$	semiconducting	diamagnetic
$LaTiO_3$	d^1	$t_{2g}{}^1e_g{}^0$	semiconducting	AFM, $T_N = 138$ K
$LaVO_3$	d^2	$t_{2g}{}^2e_g{}^0$	semiconducting	AFM, $T_N = 142$ K
$LaCrO_3$	d^3	$t_{2g}{}^3e_g{}^0$	semiconducting	AFM, $T_N = 290$ K
$LaMnO_3$	d^4	$t_{2g}{}^3e_g{}^1$	semiconducting	AFM, $T_N = 100$ K
$LaFeO_3$	d^5	$t_{2g}{}^3e_g{}^2$	semiconducting	AFM, $T_N = 750$ K
$LaCoO_3$	d^6	$t_{2g}{}^6e_g{}^0$	semiconducting*	diamagnetic*
$LaNiO_3$	d^7	$t_{2g}{}^6e_g{}^1$	metallic	Pauli PM
SrM^{4+}O$_3$ M = 3d				
$SrTiO_3$	d^0	$t_{2g}{}^0e_g{}^0$	semiconducting	diamagnetic
$SrVO_3$	d^1	$t_{2g}{}^1e_g{}^0$	metallic	Pauli PM
$SrCrO_3$	d^2	$t_{2g}{}^2e_g{}^0$	metallic	Pauli PM
$SrMnO_3$	d^3	$t_{2g}{}^3e_g{}^0$	semiconducting	AFM, $T_N = 235$ K
$SrFeO_3$	d^4	$t_{2g}{}^3e_g{}^1$	metallic	FM, $T_C = 130$ K
$SrCoO_3$	d^5	$t_{2g}{}^4e_g{}^1$	metallic	FM, $T_C = 280$ K

Compound	d^n	*Electron config.*	Electrical properties	Magnetic properties
AMO_3 $M = 4d$				
$KNbO_3$	d^0	$t_{2g}^{0}e_{g}^{0}$	semiconducting	diamagnetic
$BaNbO_3$	d^1	$t_{2g}^{1}e_{g}^{0}$	metallic	Pauli PM
$SrMoO_3$	d^2	$t_{2g}^{2}e_{g}^{0}$	metallic	Pauli PM
$SrRuO_3$	d^4	$t_{2g}^{4}e_{g}^{0}$	metallic	FM, $T_C = 165$ K
$LaRuO_3$	d^5	$t_{2g}^{5}e_{g}^{0}$	metallic	Pauli PM
$SrRhO_3$	d^5	$t_{2g}^{5}e_{g}^{0}$	metallic	PM[†]
$LaRhO_3$	d^6	$t_{2g}^{6}e_{g}^{0}$	semiconducting	diamagnetic
$LaPdO_3$	d^7	$t_{2g}^{6}e_{g}^{1}$	metallic	Pauli PM

See Gradescope Quiz 3

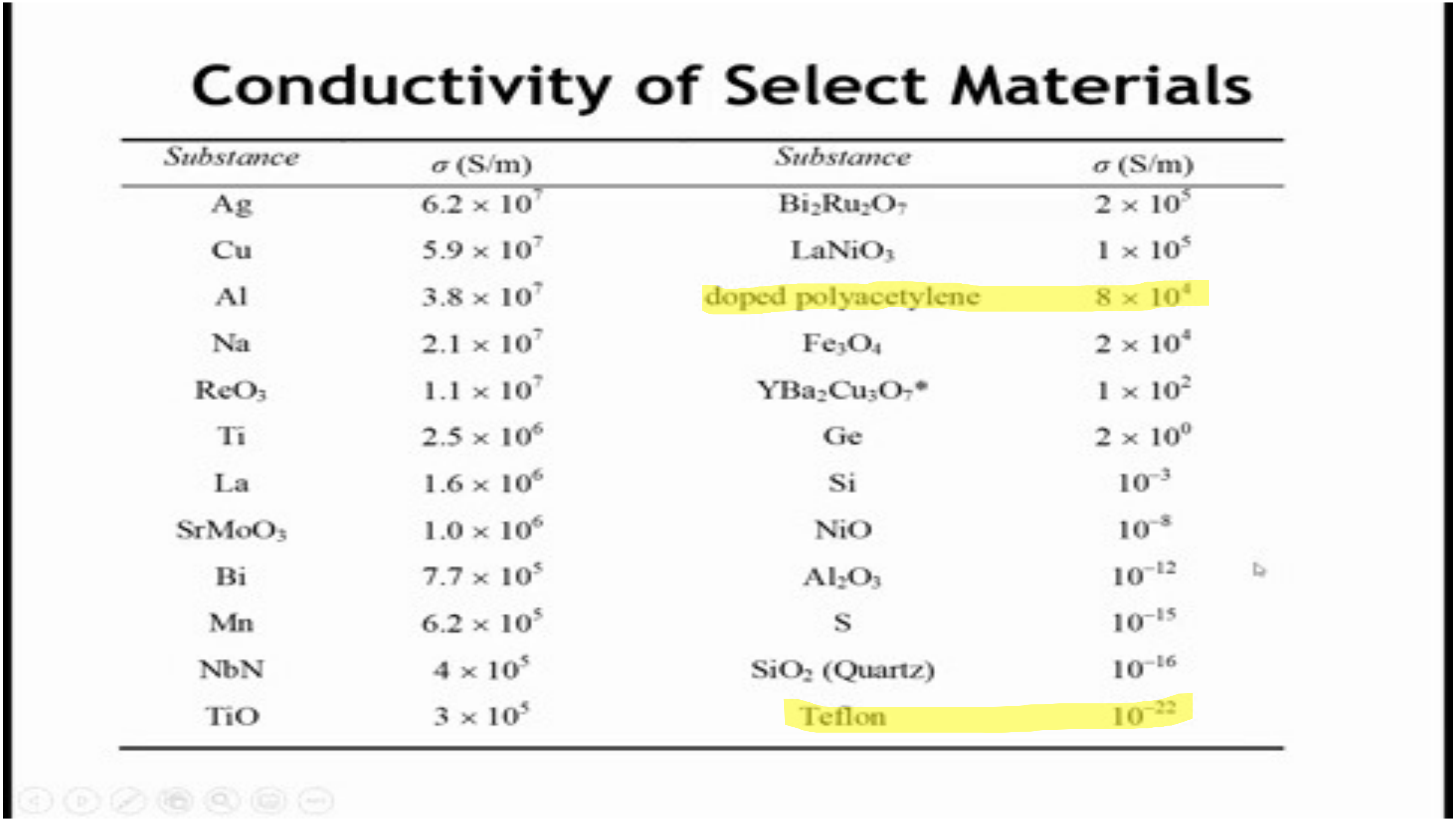
1. Which of the following best explains the dramatic difference in conductivity between NiO and TiO, despite both having the rock salt structure and partially filled d-orbitals?

2. In the context of the Hubbard model, which condition is most likely to lead to a Mott-Hubbard insulator?

3. Considering transition metal oxides with the rock salt structure (e.g., TiO, VO, MnO), why does the conductivity trend from metallic (TiO) to semiconducting (MnO) as we move across the period?

4. Strontium manganate (SrMnO3) is a semiconductor, even though other 4+ perovskites exhibit metallic behavior. This is attributed to a particularly large Hubbard U. What characteristic of the Mn4+ (d3) electron configuration contributes to this exceptionally large U?

Homework:
10.14-10.16



Conductivity of Select Materials

Substance	σ (S/m)	*Substance*	σ (S/m)
Ag	6.2×10^7	$Bi_2Ru_2O_7$	2×10^5
Cu	5.9×10^7	$LaNiO_3$	1×10^5
Al	3.8×10^7	doped polyacetylene	8×10^4
Na	2.1×10^7	Fe_3O_4	2×10^4
ReO_3	1.1×10^7	$YBa_2Cu_3O_7$*	1×10^2
Ti	2.5×10^6	Ge	2×10^0
La	1.6×10^6	Si	10^{-3}
$SrMoO_3$	1.0×10^6	NiO	10^{-8}
Bi	7.7×10^5	Al_2O_3	10^{-12}
Mn	6.2×10^5	S	10^{-15}
NbN	4×10^5	SiO_2 (Quartz)	10^{-16}
TiO	3×10^5	Teflon	10^{-22}