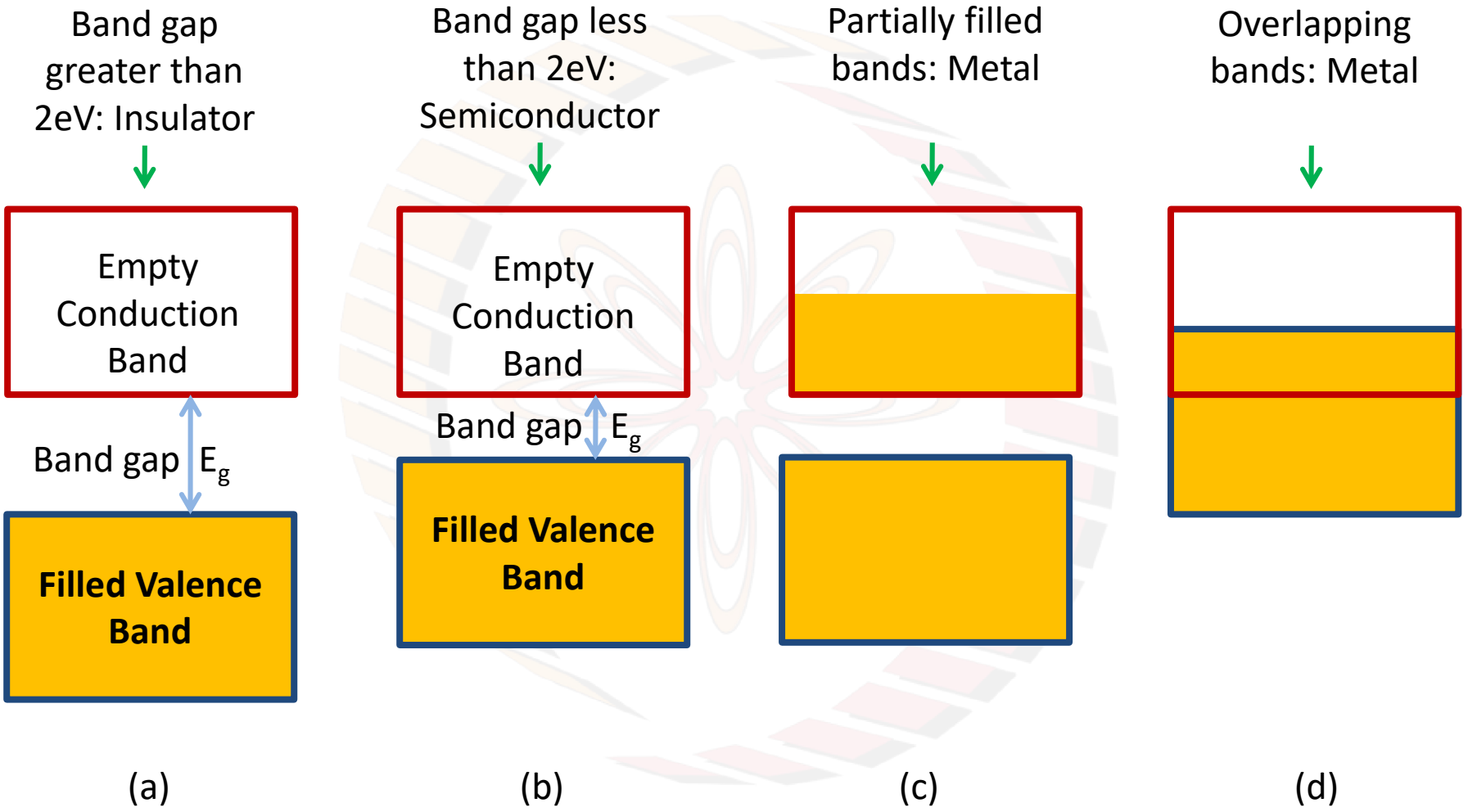
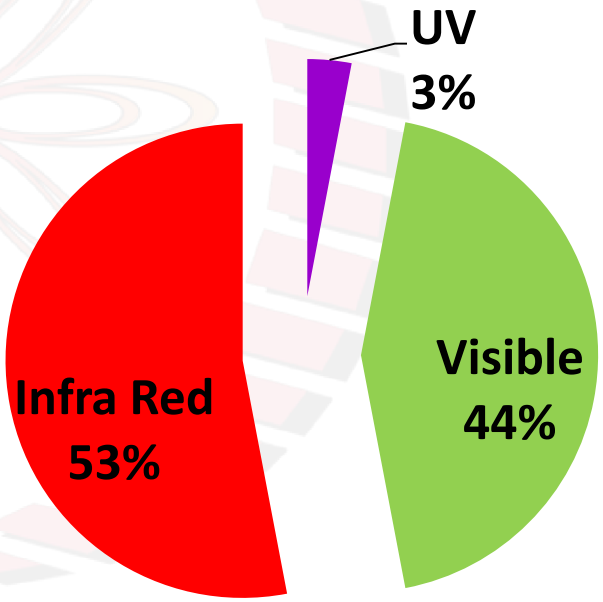
Solar Energy:
The Semiconductor

Learning objectives:

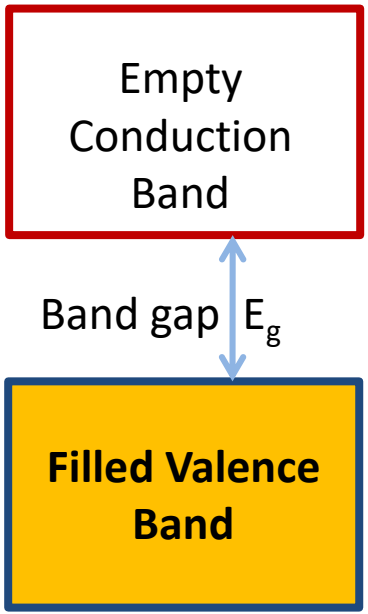
1) To plot the band diagrams of materials
2) To explain the interaction of bands with radiation
3) To understand the different ways in which band diagrams can be plotted.


Band gap greater than 2eV: Insulator
Empty Conduction Band
Band gap E_g
Filled Valence Band
(a)
Band gap less than 2eV: Semiconductor
Empty Conduction Band
Band gap E_g
Filled Valence Band
(b)
Partially filled bands: Metal
(c)
Overlapping bands: Metal
(d)

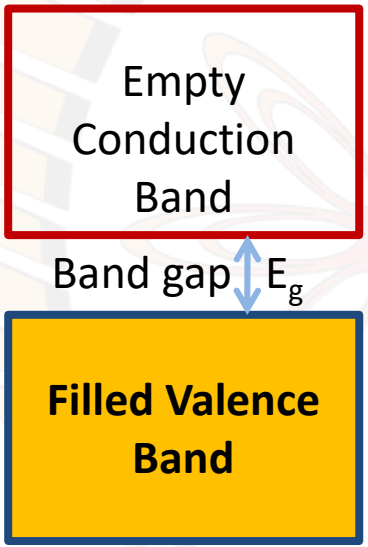
Visible Spectrum Wavelength:	400 nm (violet)	to	700 nm (red)
Corresponding band gaps:	3.1 eV	to	1.8 eV



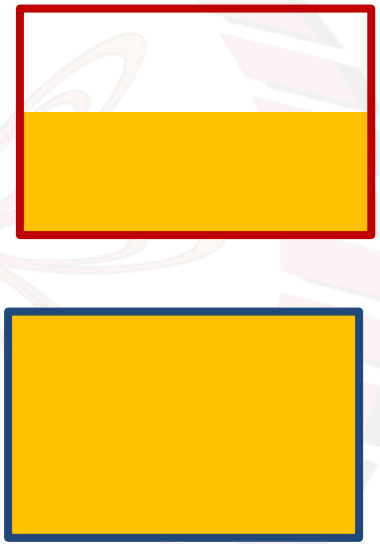
Band gap greater than 2eV: Insulator



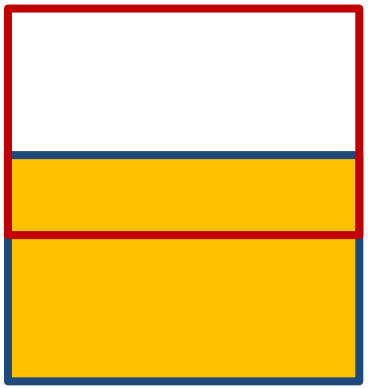
Band gap less than 2eV: Semiconductor



Partially filled bands: Metal

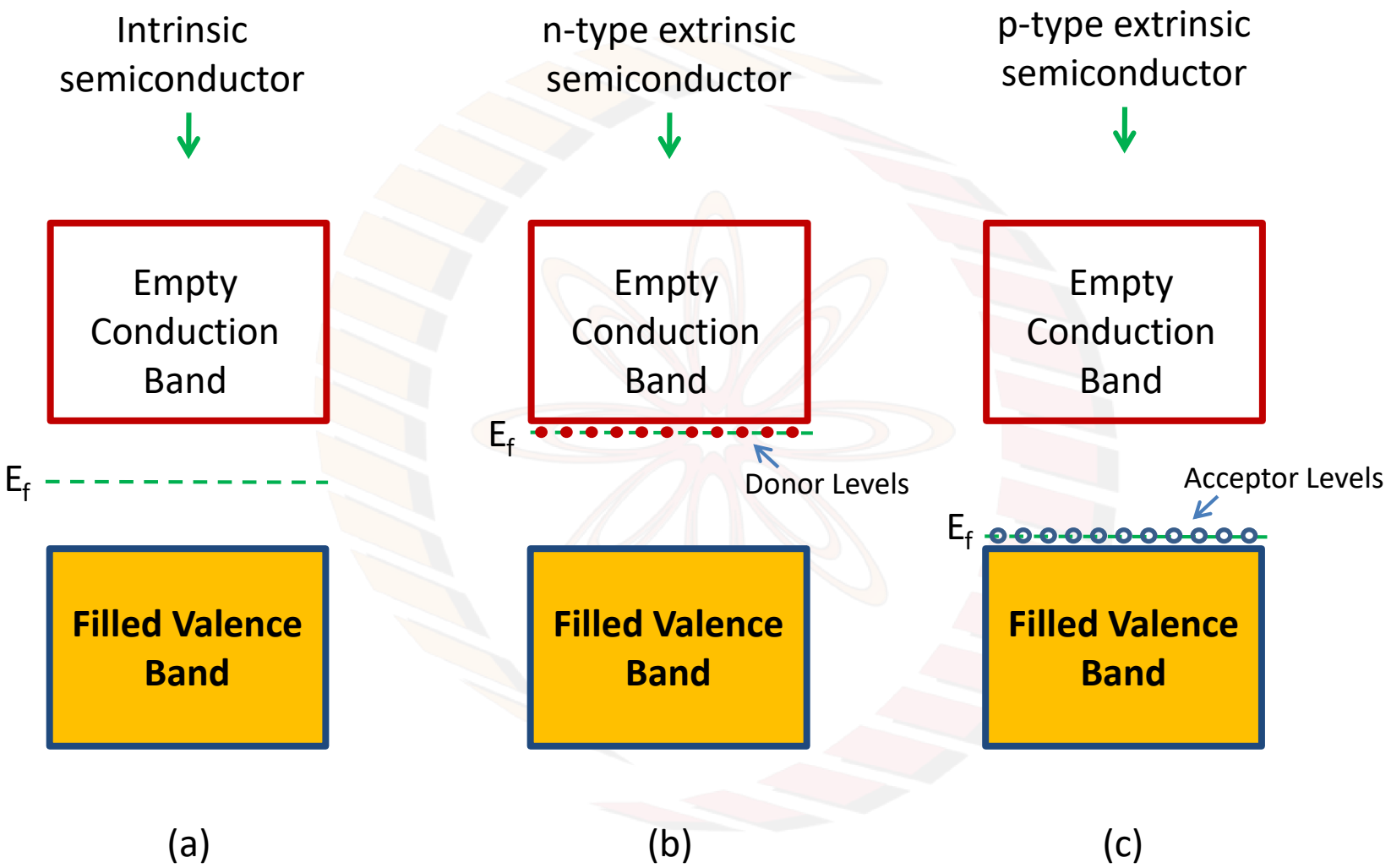


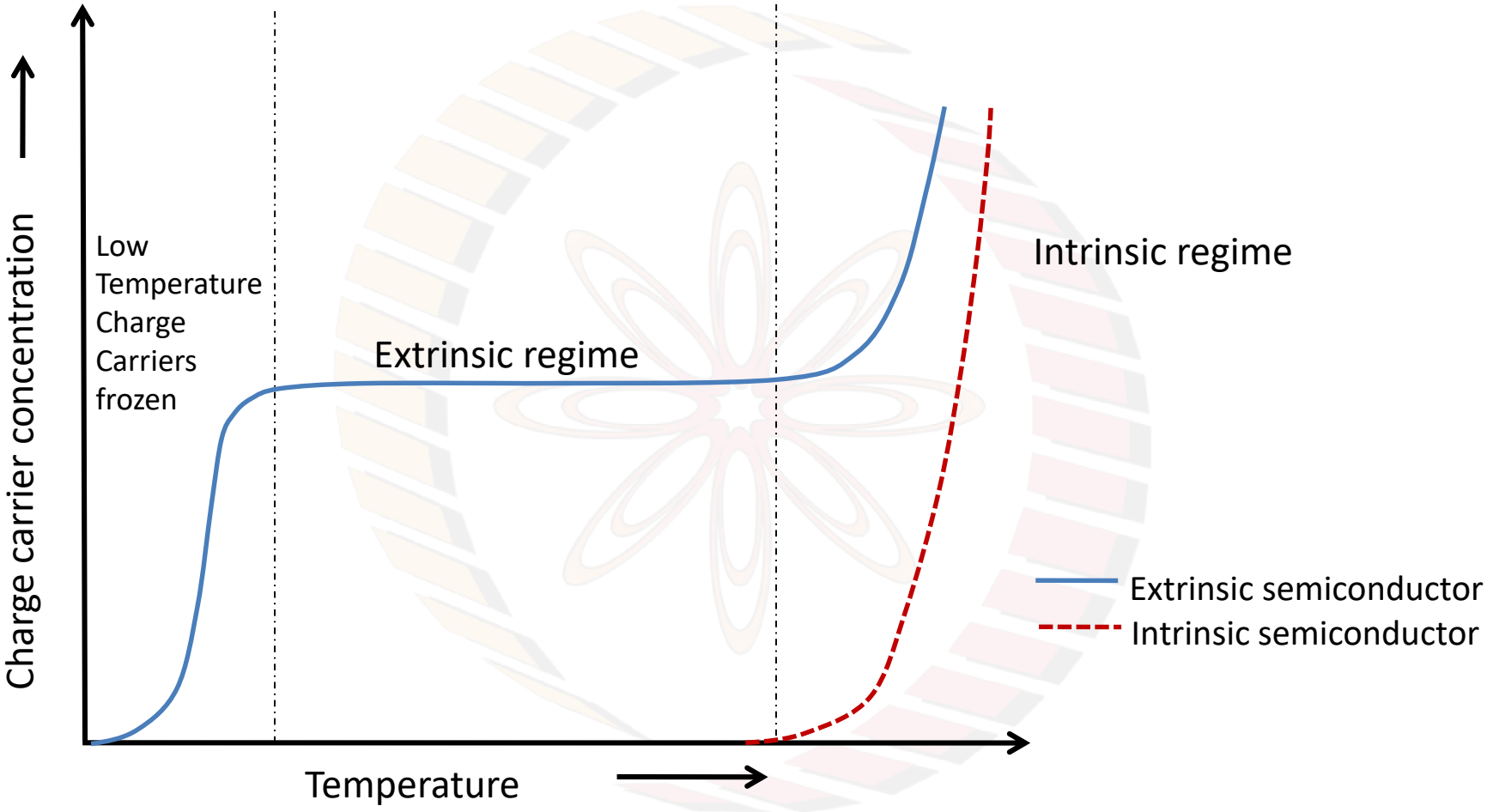
Overlapping bands: Metal



Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)

Corresponding band gaps: 3.1 eV to 1.8 eV


Intrinsic semiconductor
n-type extrinsic semiconductor
p-type extrinsic semiconductor
Empty Conduction Band
Empty Conduction Band
Empty Conduction Band
E_f
E_f
Donor Levels
Acceptor Levels
E_f
Filled Valence Band
Filled Valence Band
Filled Valence Band
(a)
(b)
(c)


Charge carrier concentration
Low Temperature Charge Carriers frozen
Extrinsic regime
Intrinsic regime
Extrinsic semiconductor
Intrinsic semiconductor
Temperature

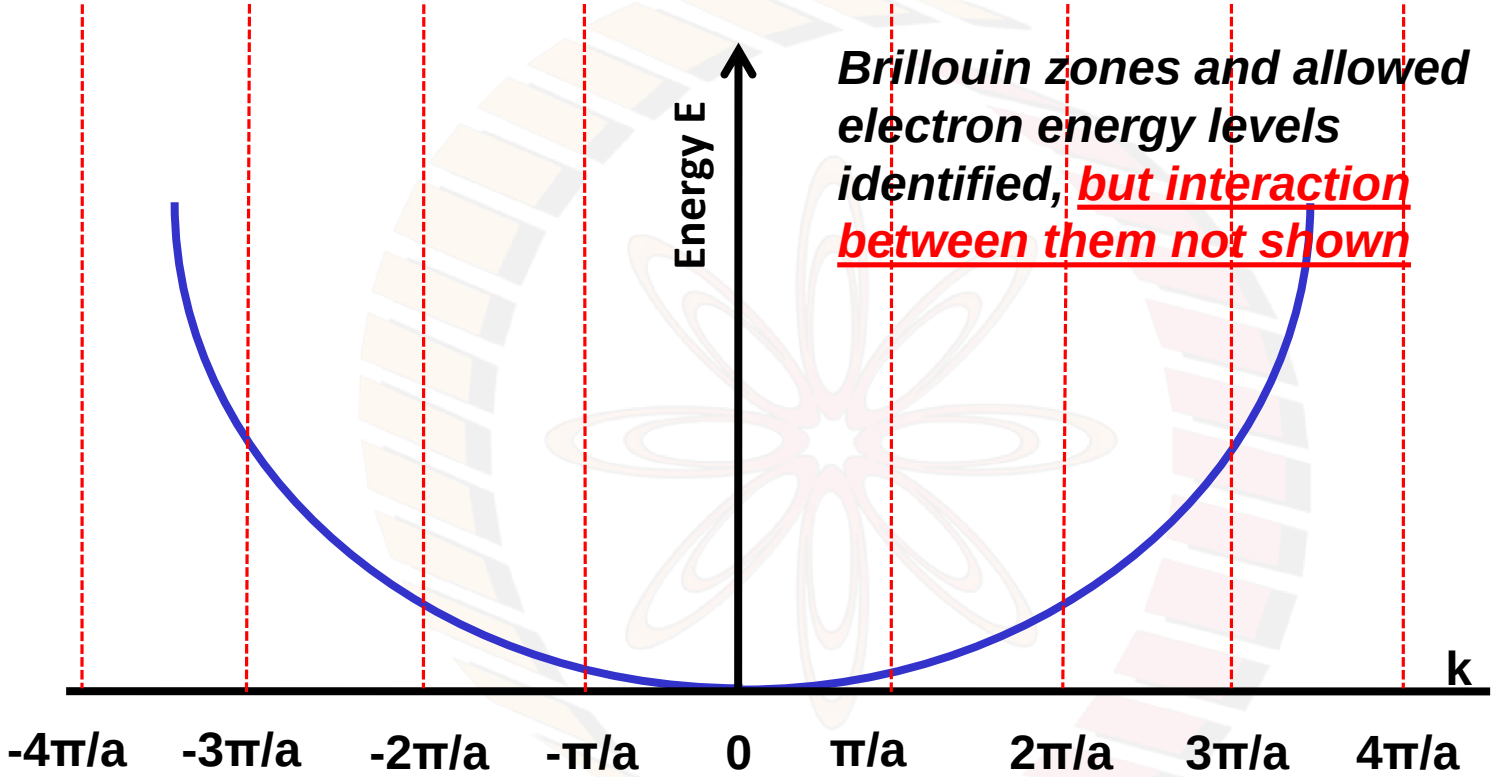
$E = h\nu$

Planck

$\lambda = \frac{h}{p}$

de Broglie

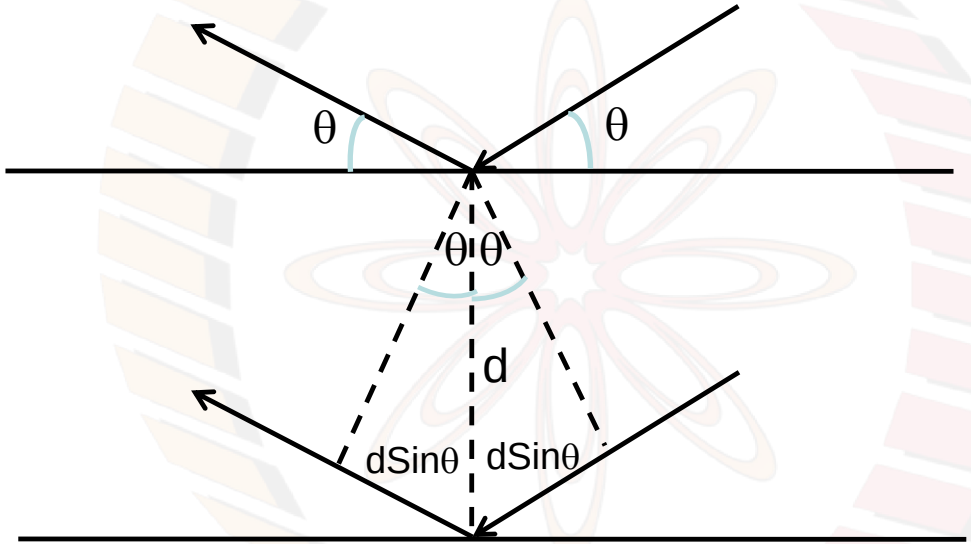
$$E = \frac{\hbar^2 k^2}{2m}$$

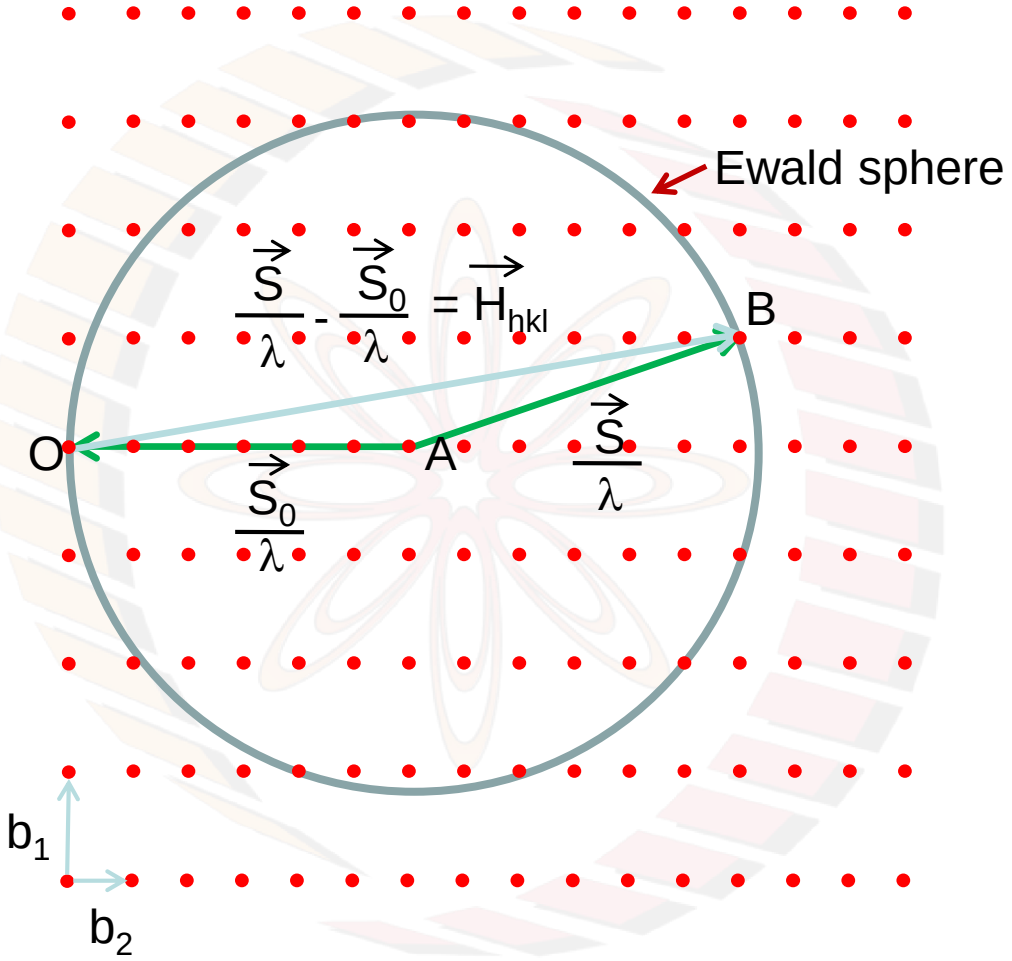


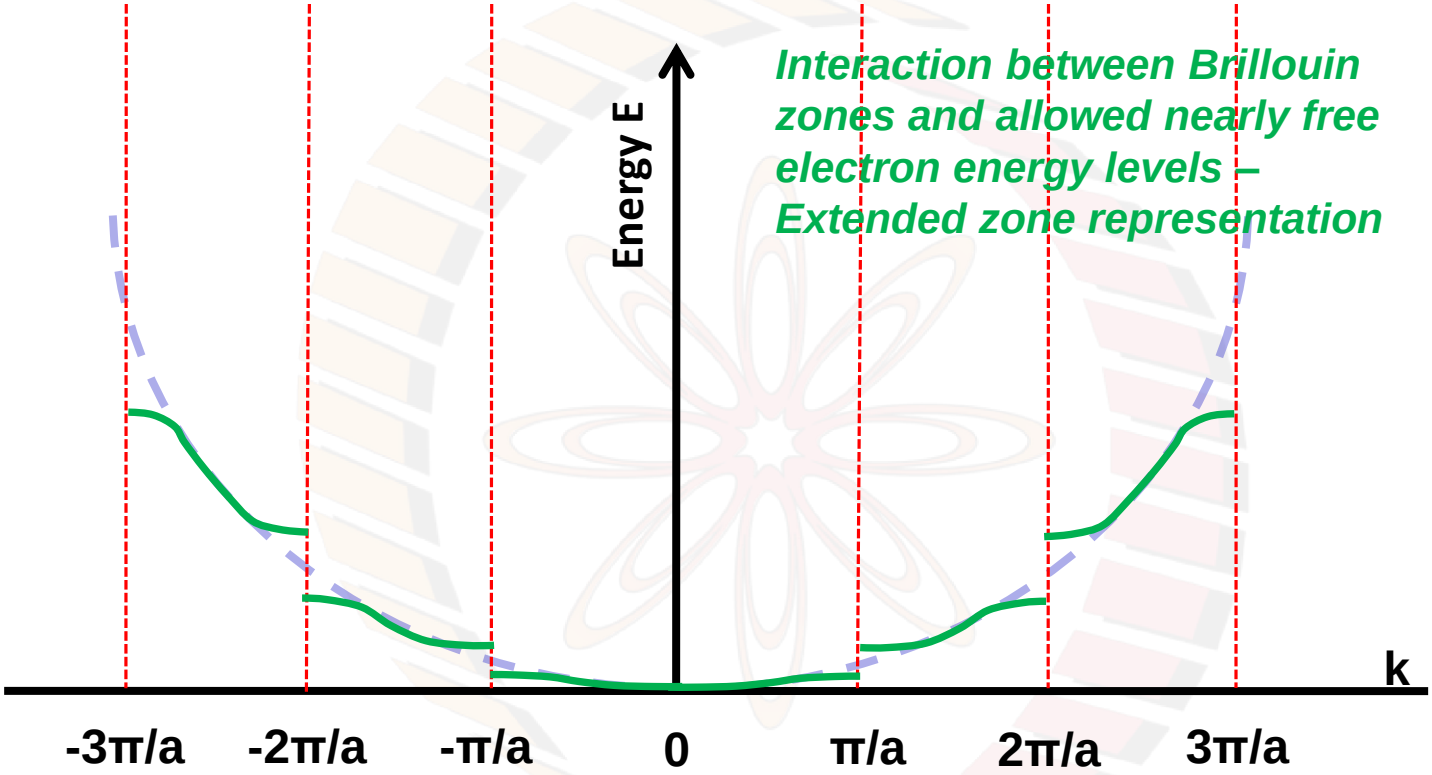
Brillouin zones and allowed electron energy levels identified, but interaction between them not shown

Allowed energy and wave vectors of nearly free electrons

Brillouin zone boundaries


θ
θ
θ θ
d
dSinθ
dSinθ


Ewald sphere
$\frac{\vec{S}}{\lambda} - \frac{\vec{S}_0}{\lambda} = \vec{H}_{hkl}$
B
O
A
$\frac{\vec{S}}{\lambda}$
$\frac{\vec{S}_0}{\lambda}$
b_1
b_2

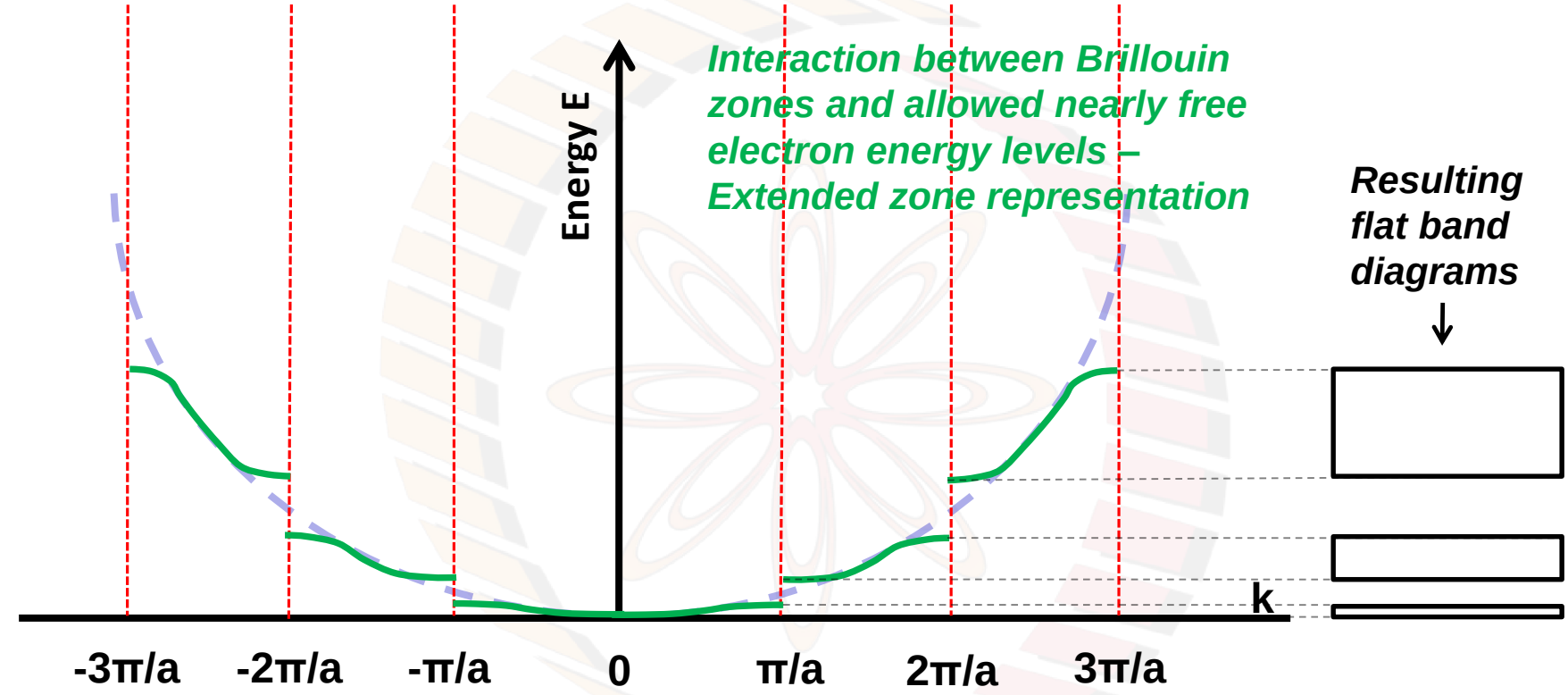


Interaction between Brillouin zones and allowed nearly free electron energy levels – Extended zone representation

E Vs k of nearly free electrons, without accounting for the Brillouin Zones

E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones

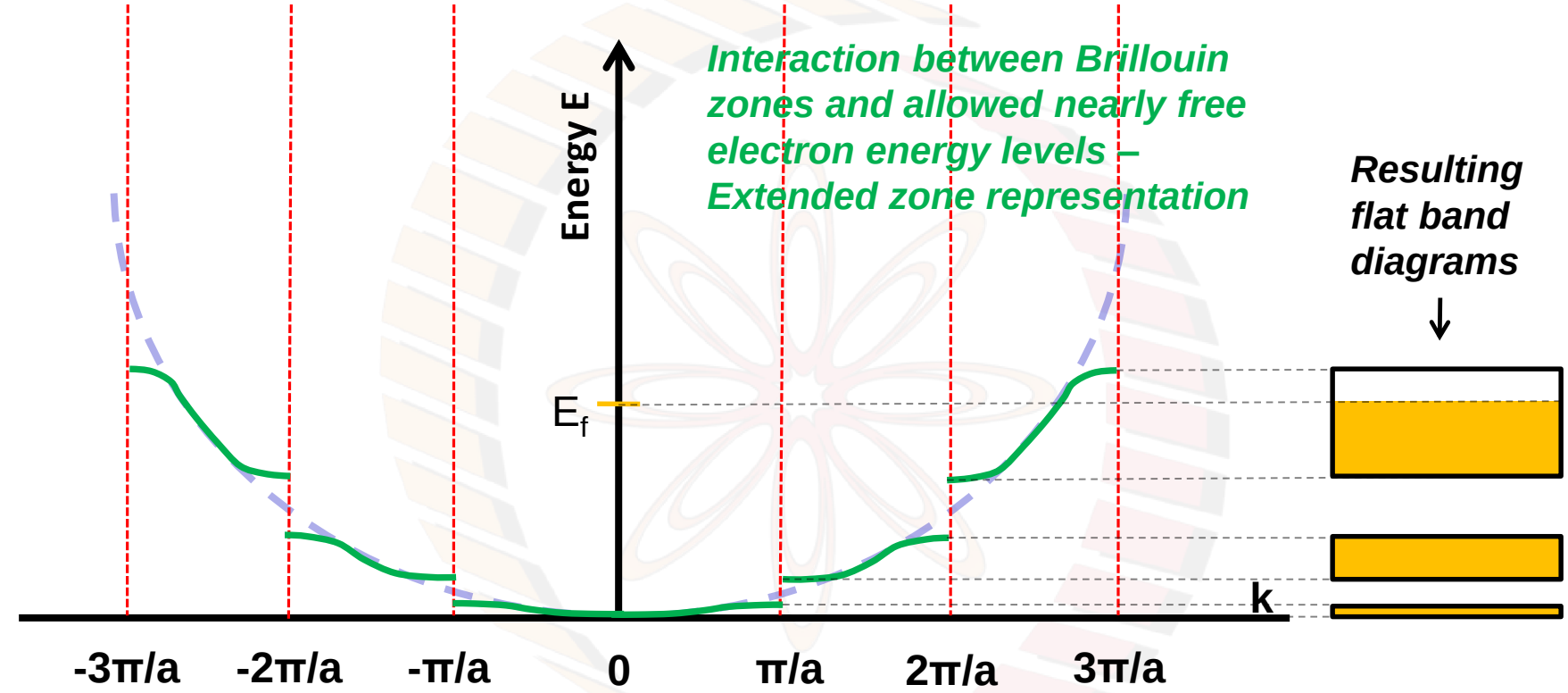
Brillouin zone boundaries



E Vs k of nearly free electrons, without accounting for the Brillouin Zones

E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones

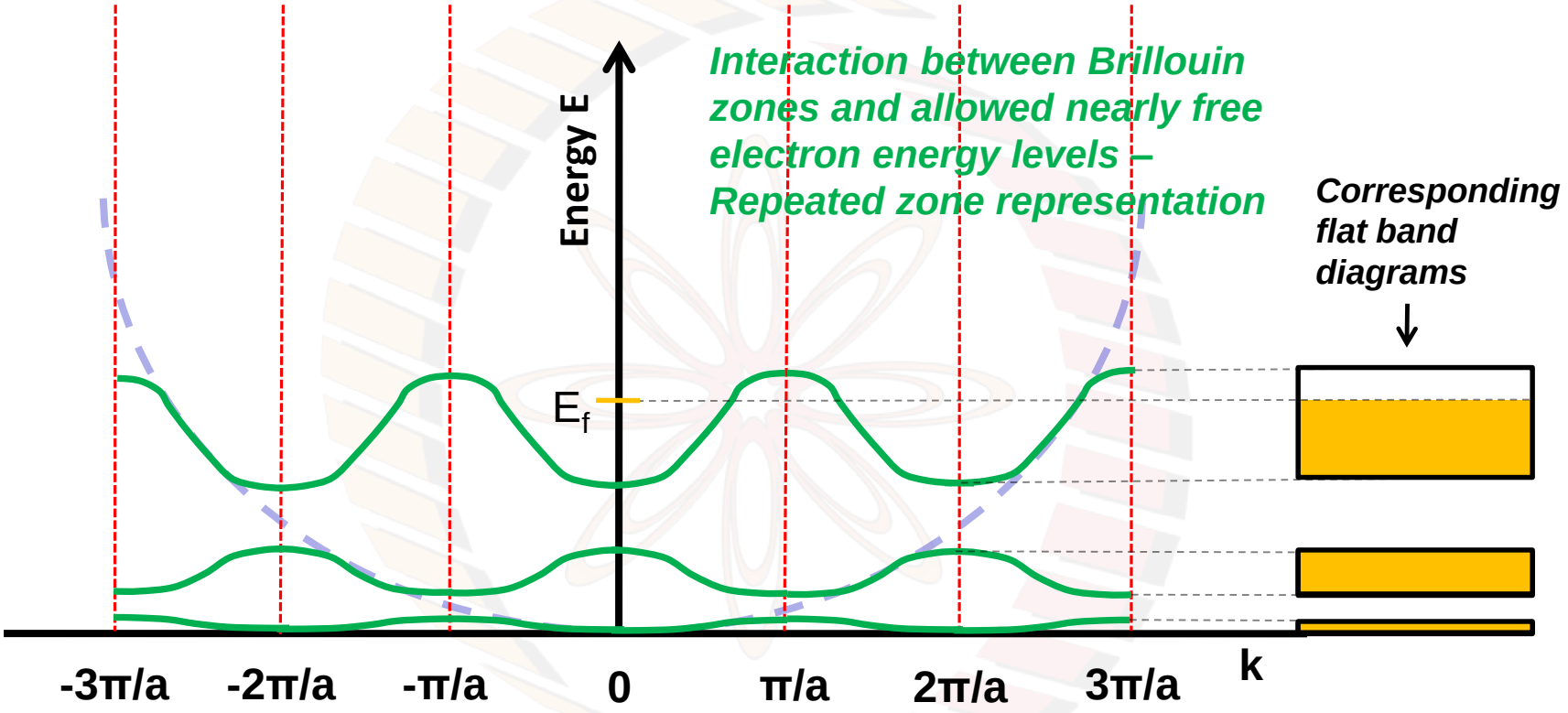
Brillouin zone boundaries

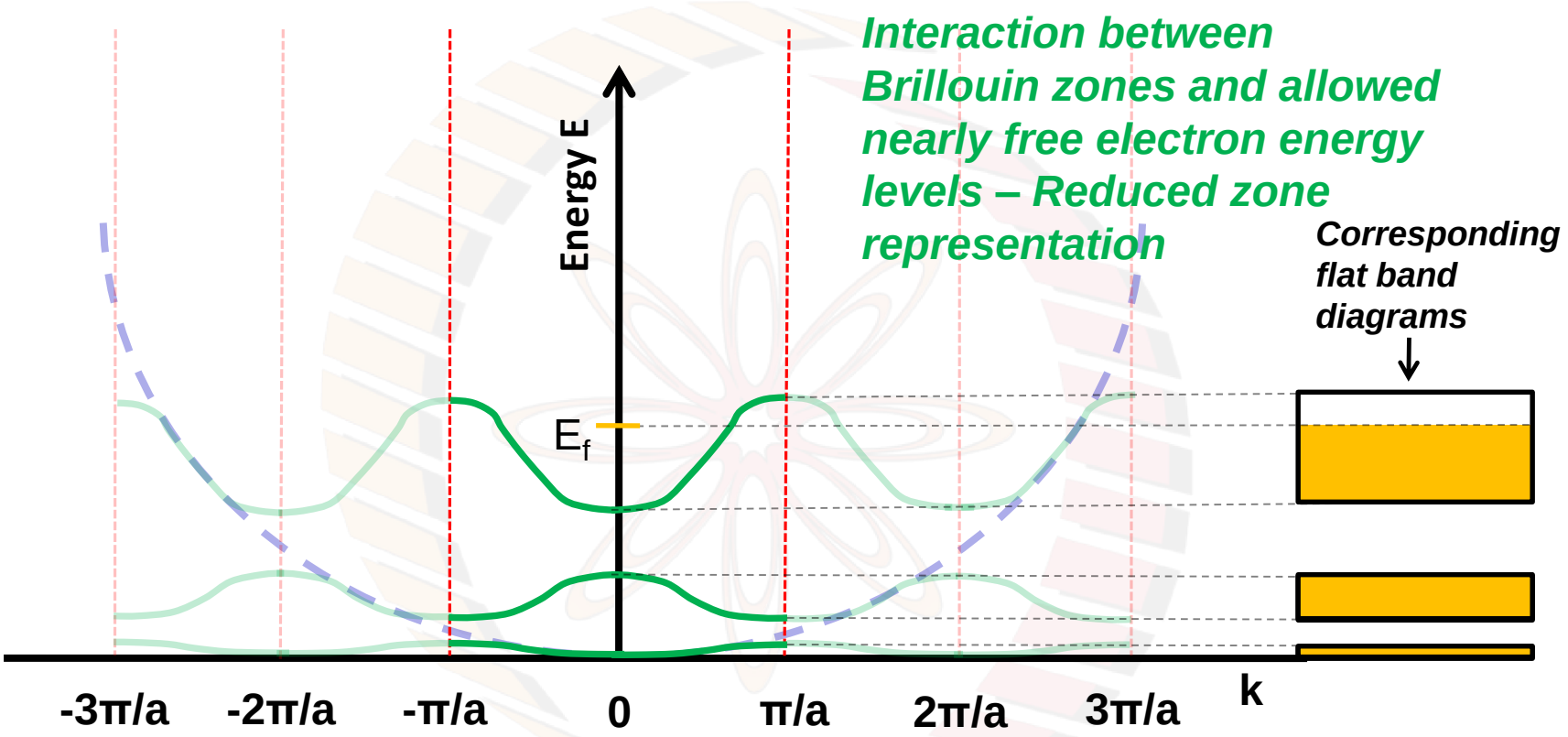


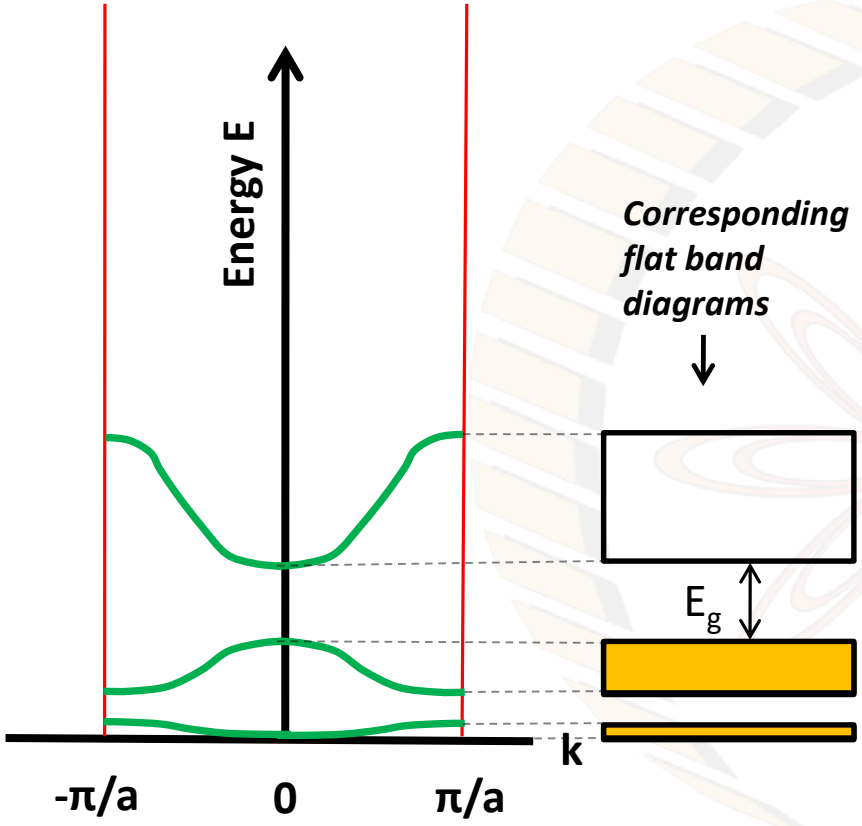
E Vs k of nearly free electrons, without accounting for the Brillouin Zones

E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones

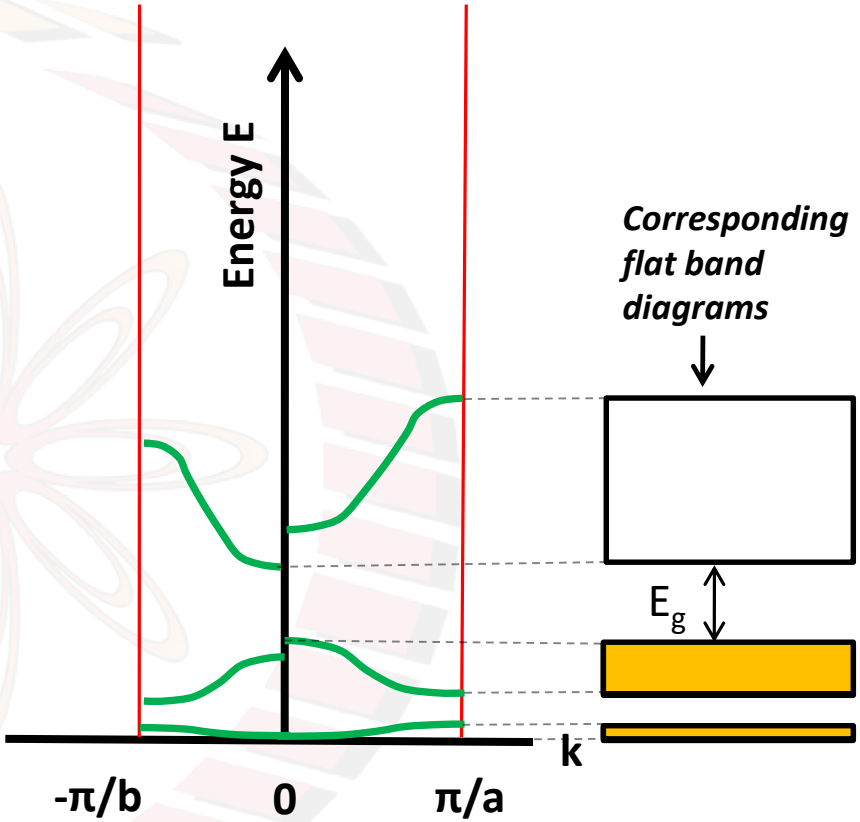
Brillouin zone boundaries


Interaction between Brillouin zones and allowed nearly free electron energy levels – Repeated zone representation
Corresponding flat band diagrams
Energy E
E_f
-3π/a
-2π/a
-π/a
0
π/a
2π/a
3π/a
k
E Vs k of nearly free electrons, without accounting for the Brillouin Zones
E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones
Brillouin zone boundaries

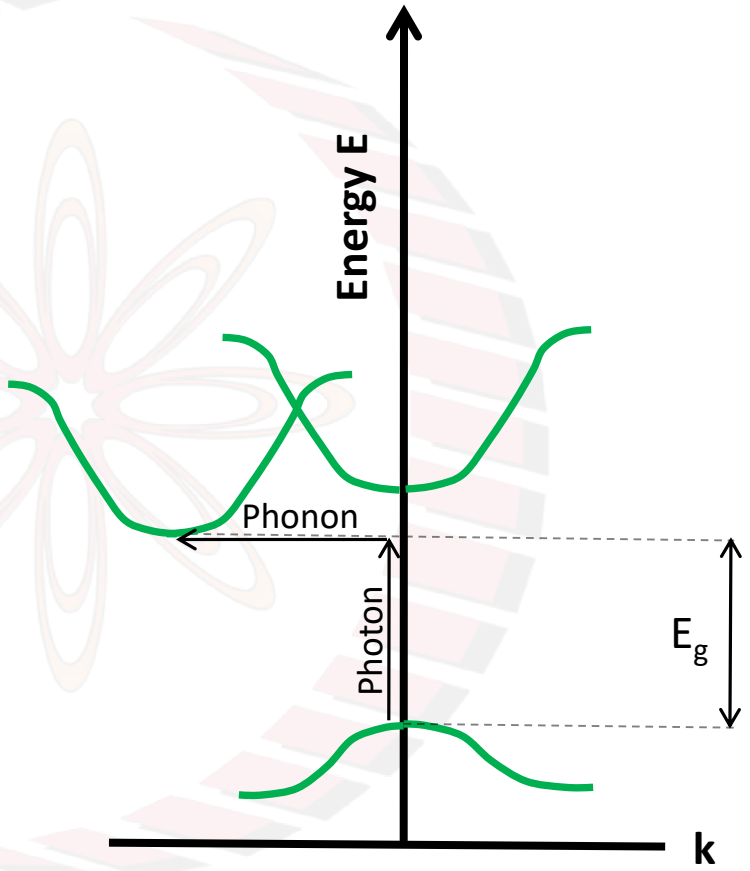

Interaction between Brillouin zones and allowed nearly free electron energy levels – Reduced zone representation
Corresponding flat band diagrams
Energy E
E_f
-3π/a
-2π/a
-π/a
0
π/a
2π/a
3π/a
k
E Vs k of nearly free electrons, without accounting for the Brillouin Zones
E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones
Brillouin zone boundaries



Direct bandgap semiconductor



Indirect bandgap semiconductor


Energy E
Phonon
Photon
E_g
k

Conclusions:

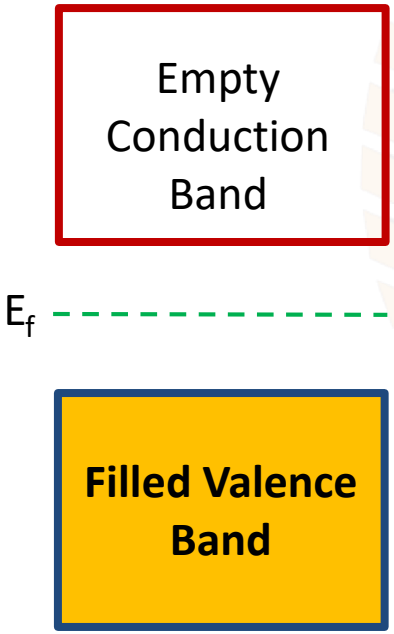
1) There is significant variation in the band diagrams of different types of materials
2) Interaction of a material with radiation depends strongly on its band diagram
3) Visible spectrum is a small fraction of solar radiation
4) There is a difference in the effectiveness with which direct and indirect bandgap semiconductors interact with radiation

Solar Energy: The p-n junction

Learning objectives:

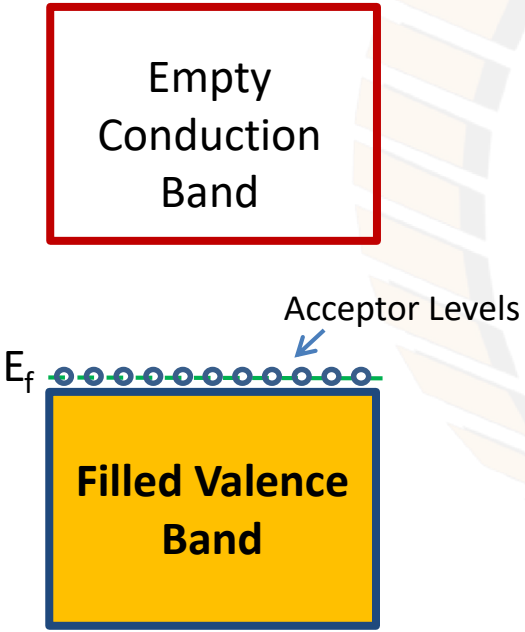
1) To describe the material features as well as characteristics of the p-n junction
2) To explain the functioning of the p-n junction

Intrinsic semiconductor



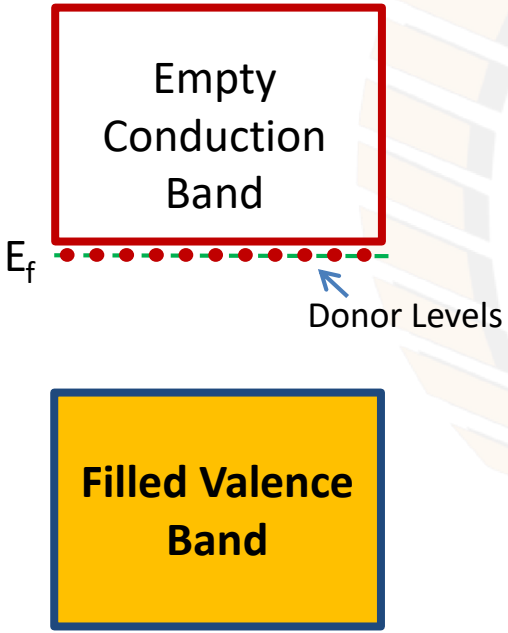
- Charge carrier concentration depends only temperature
- Conductivity depends only on Temperature
- Examples:
  - Elemental: Group IV A: Si (1.1 eV), Ge (0.7 eV)
  - Compound:
    - Group III A and Group V A (III-V)
      - GaAs, InSb
    - Group II B and Group VI A (II-VI)
      - CdS, ZnTe

p-type extrinsic semiconductor

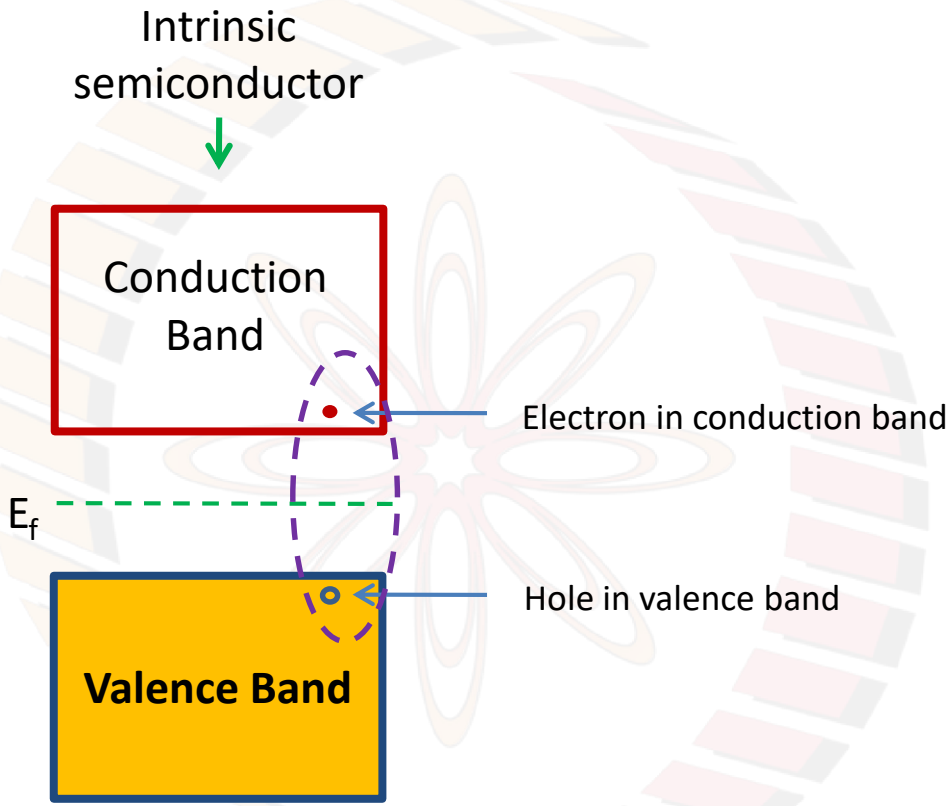


- Charge carrier concentration depends on dopant concentration
- Conductivity depends on dopant concentration
- Examples:
  - Group IV A elements doped with small quantities of Group III A elements: B, Al, Ga, In, Tl

n-type extrinsic semiconductor

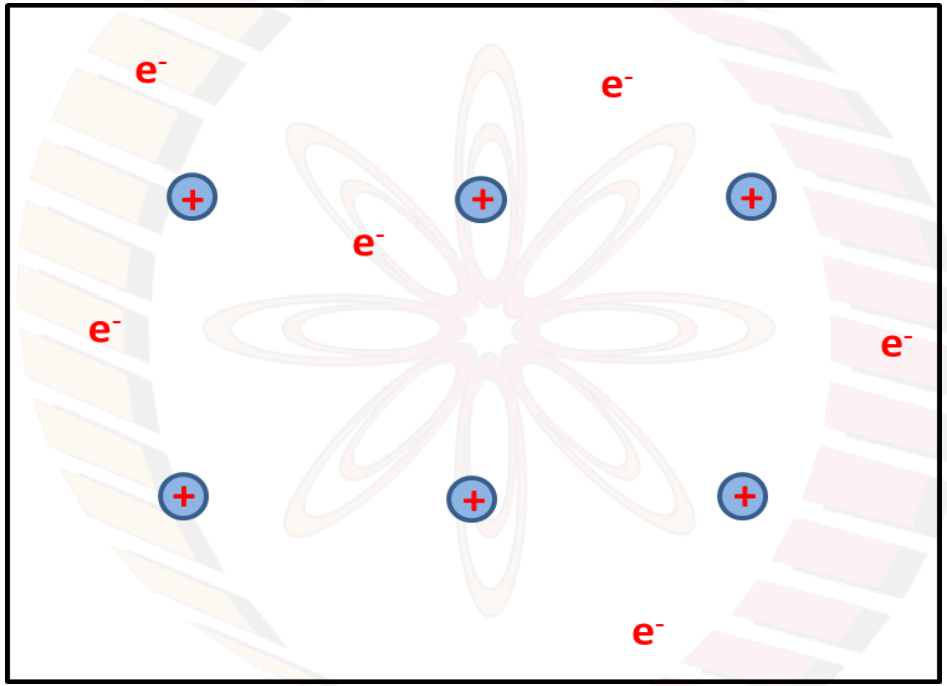


- Charge carrier concentration depends on dopant concentration
- Conductivity depends on dopant concentration
- Examples:
  - Group IV A elements doped with small quantities of Group V A elements: N, P, As, Sb, Bi

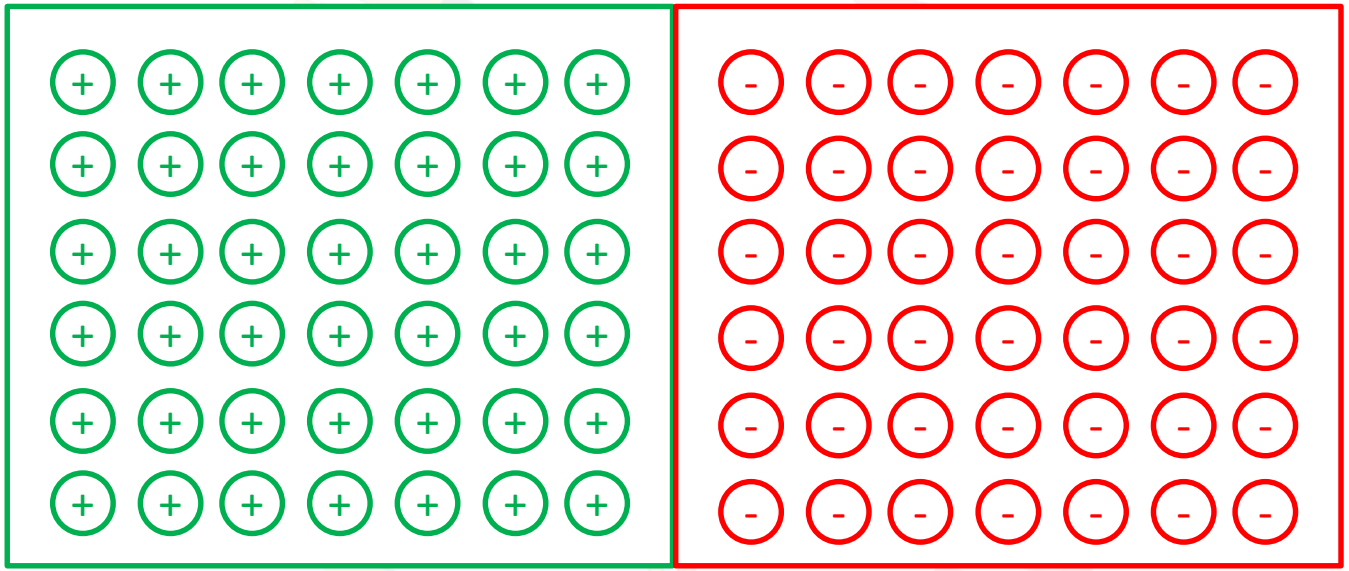


$E_g = hv$ Stability of electron-hole pair?

Metal



The p-n junction

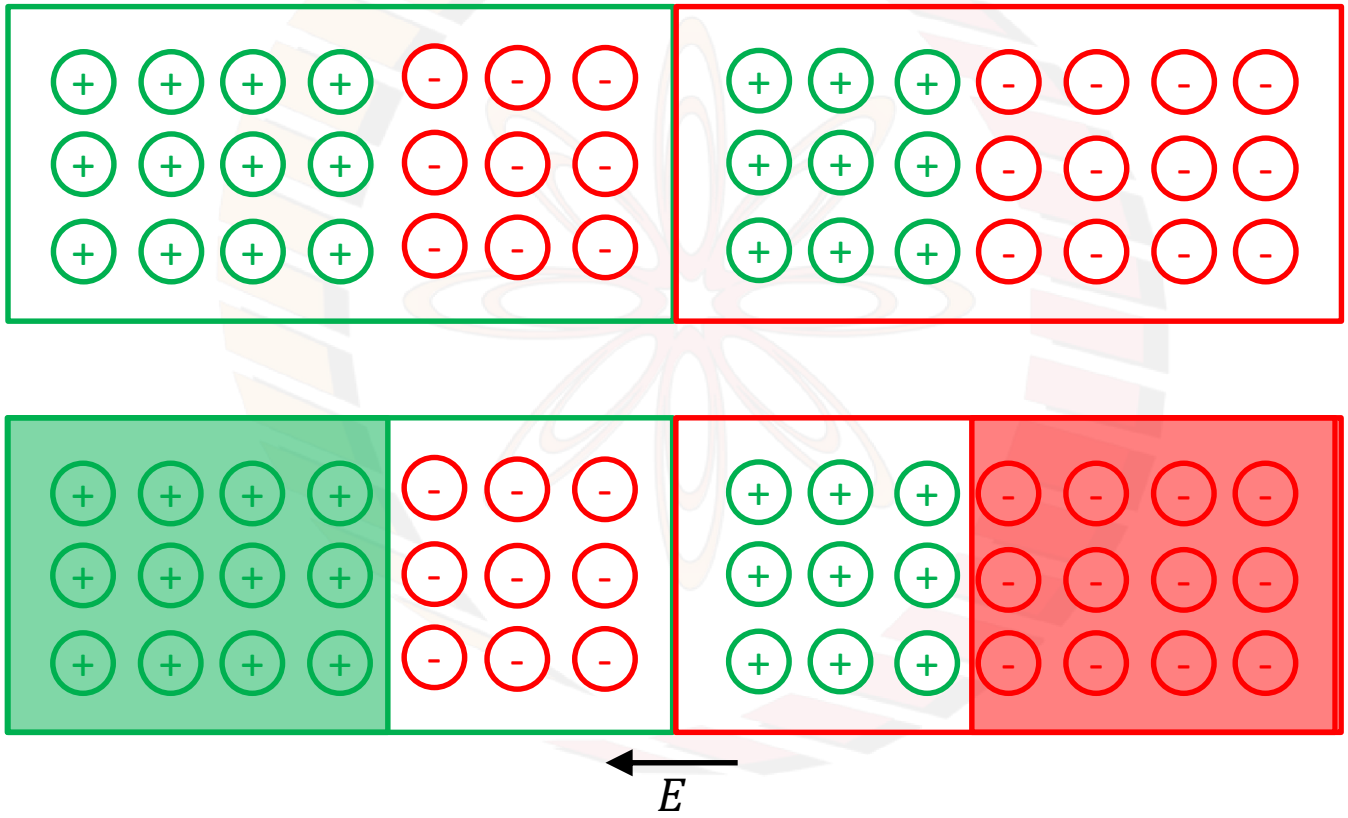


Si doped with B

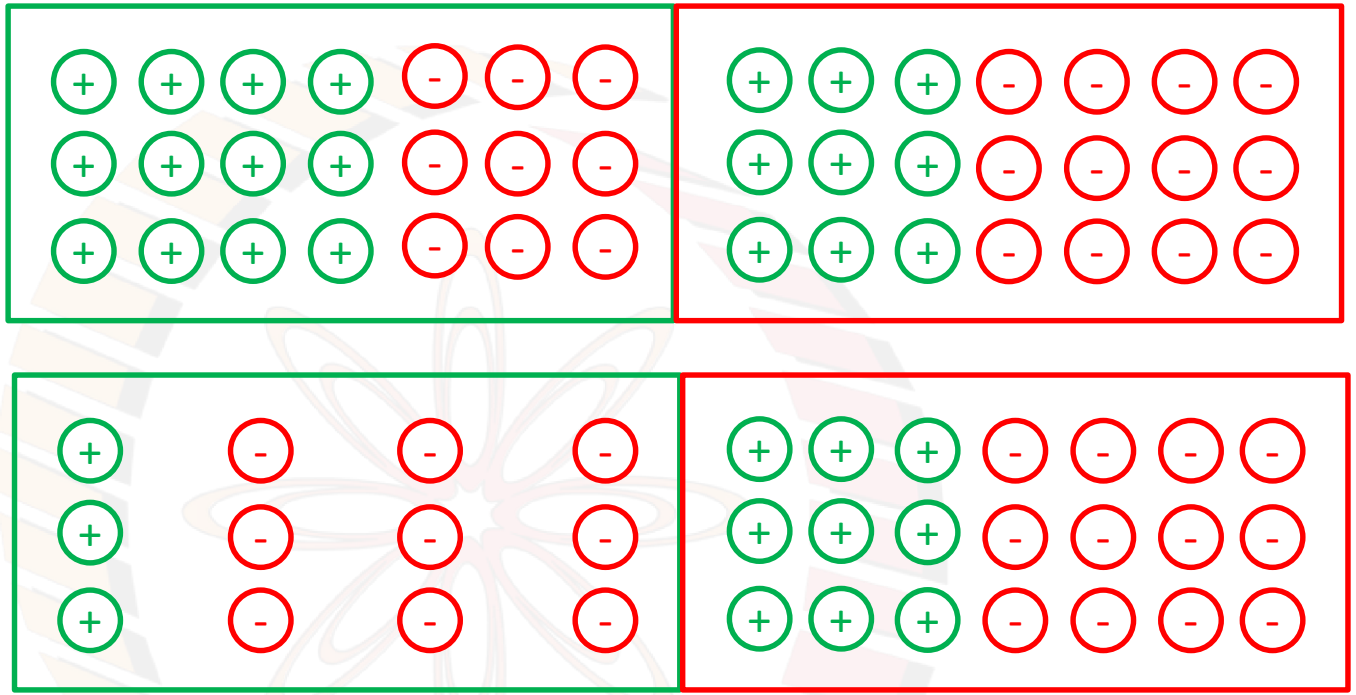
Si doped with P

$$\sigma = n|e|\mu_e + p|e|\mu_h$$

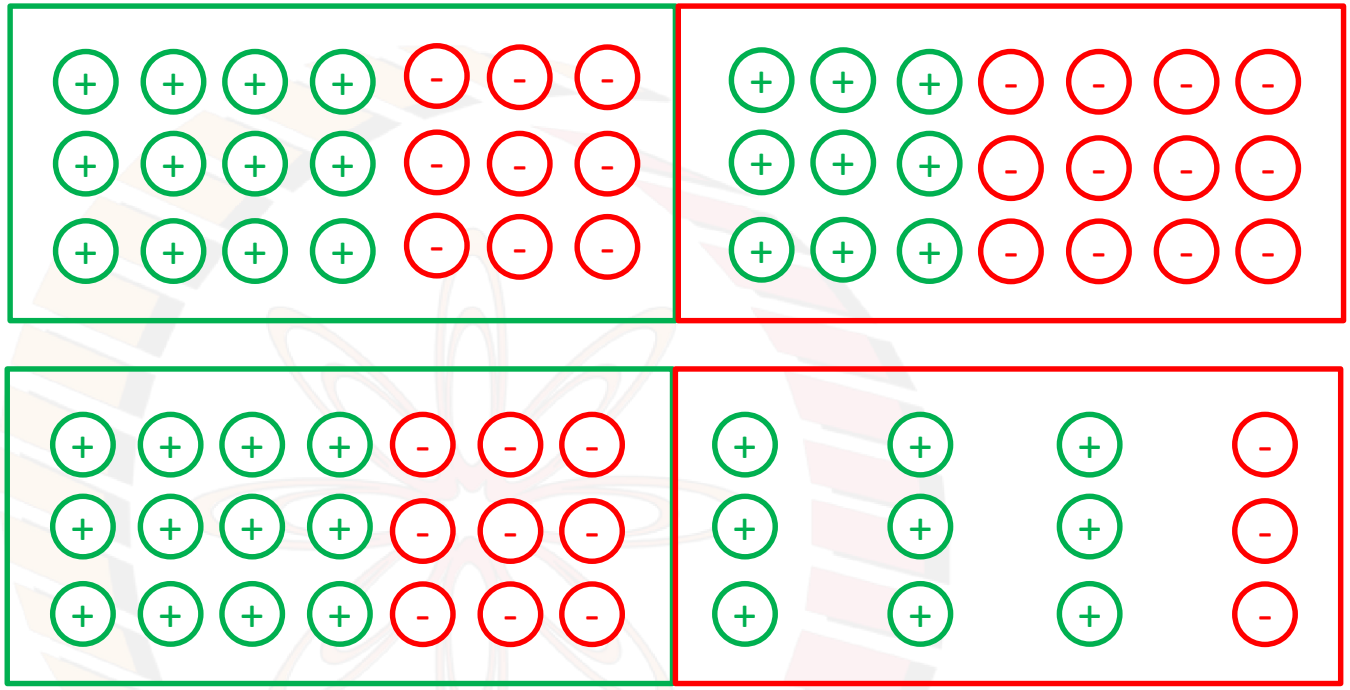
The space charge region
Depletion region

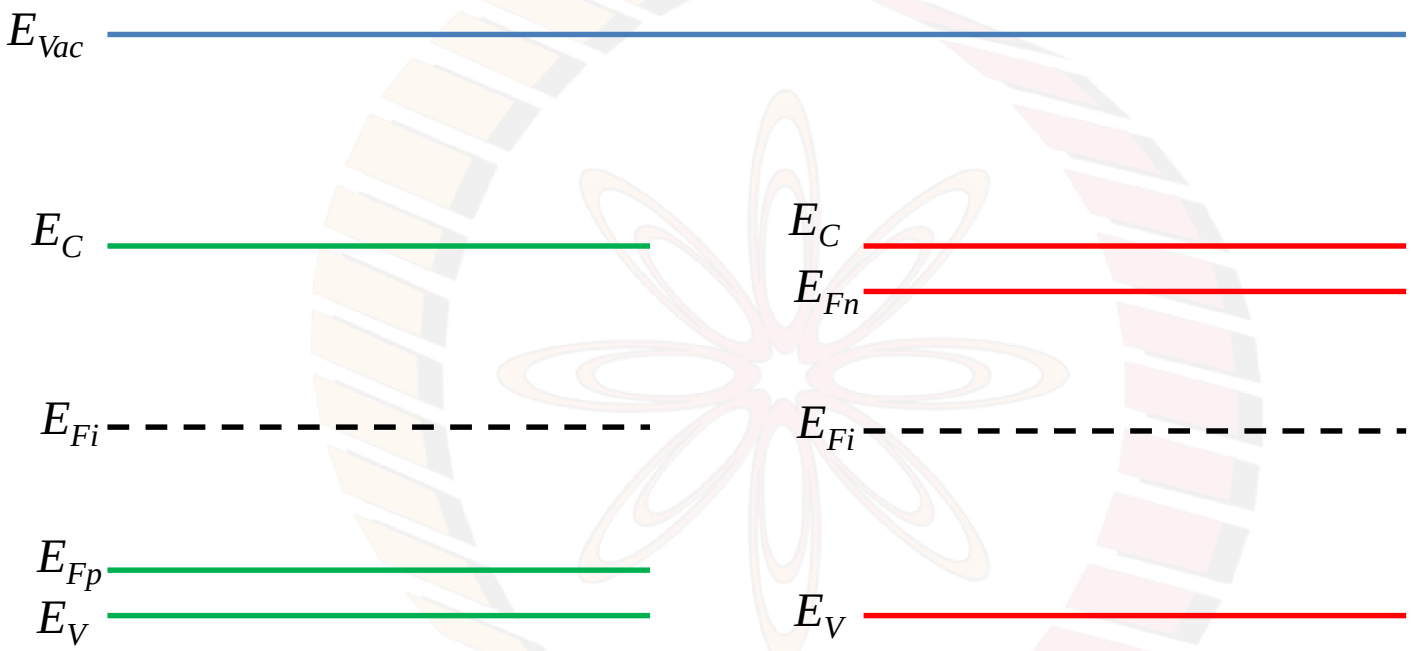


space charge region
depletion region



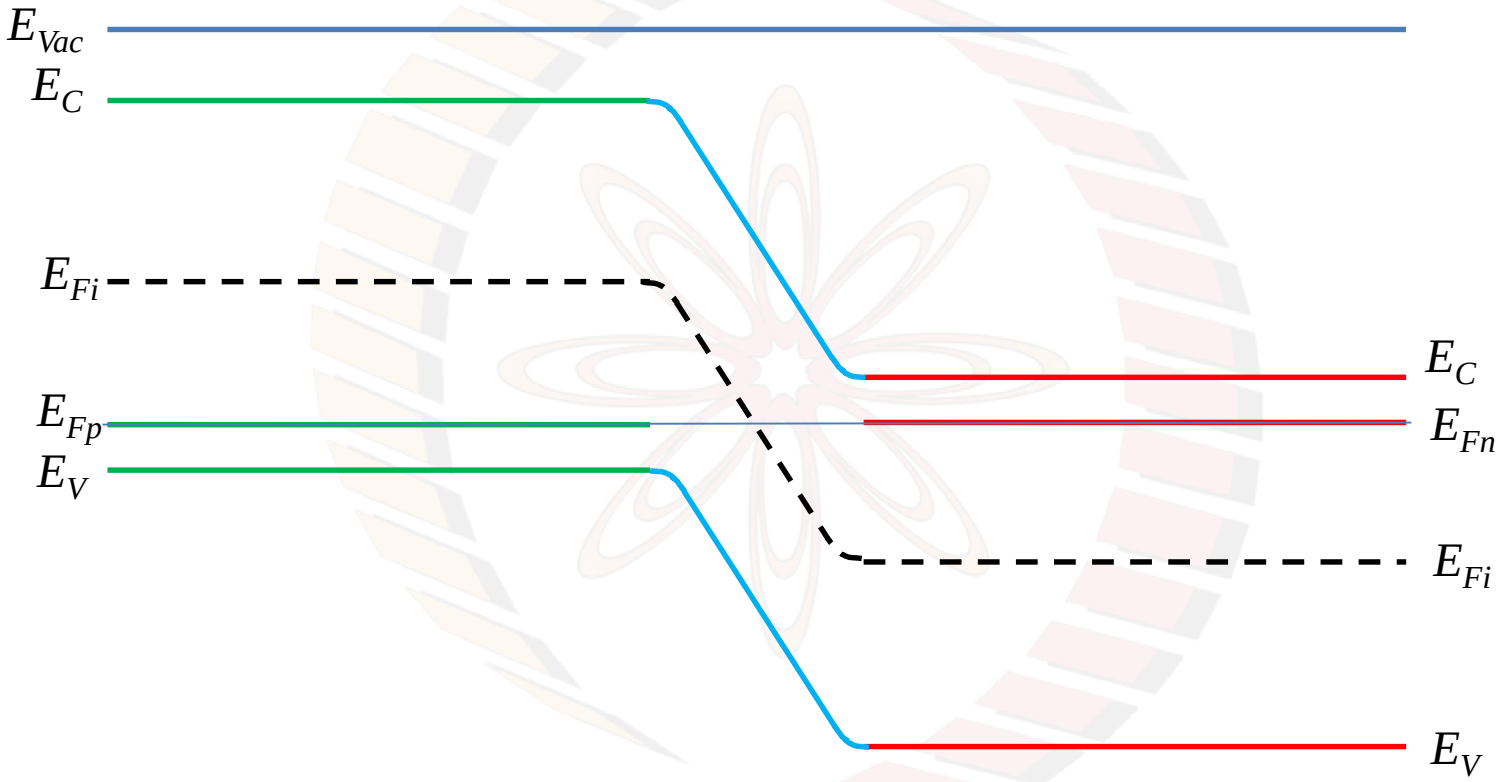
space charge region
depletion region



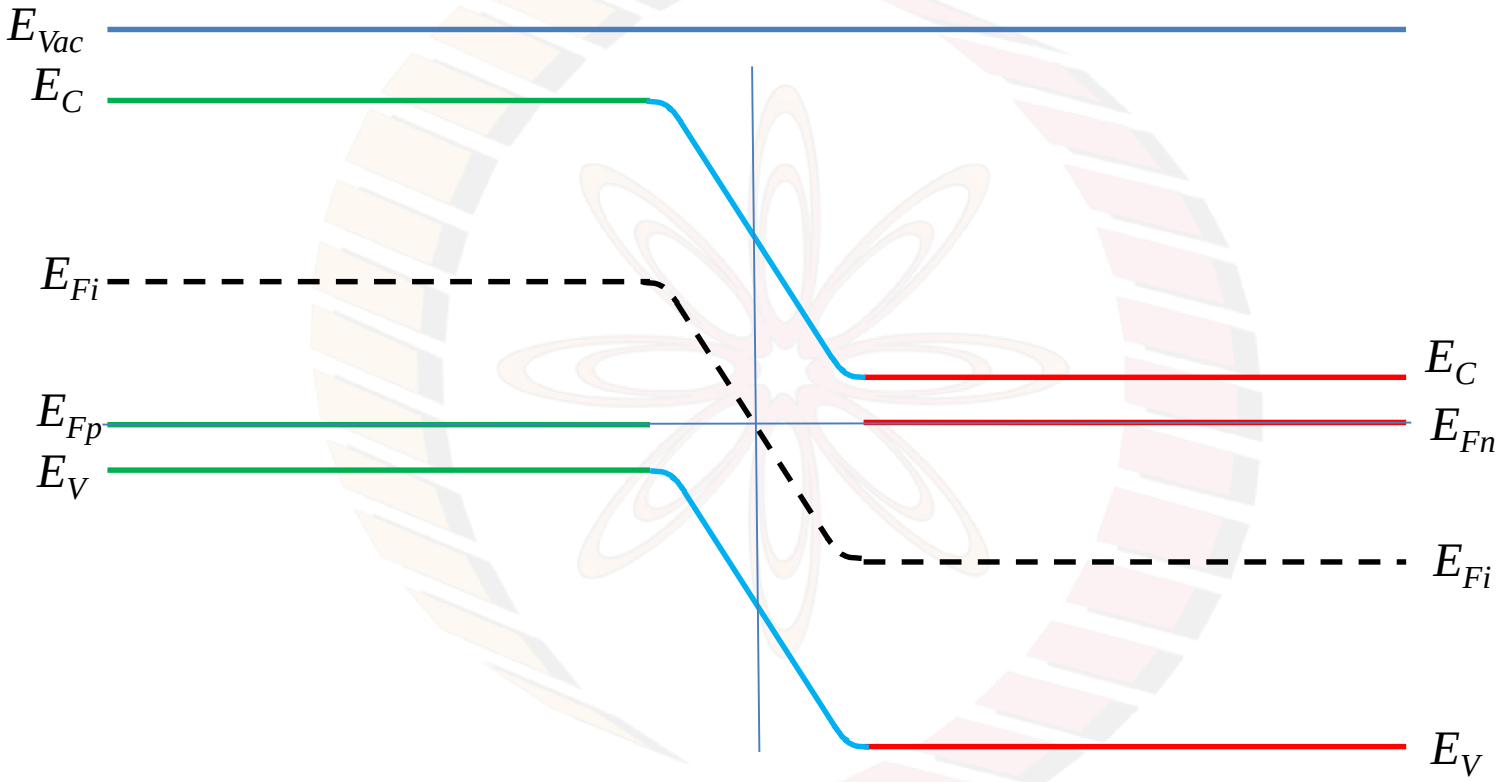


p- type

n- type

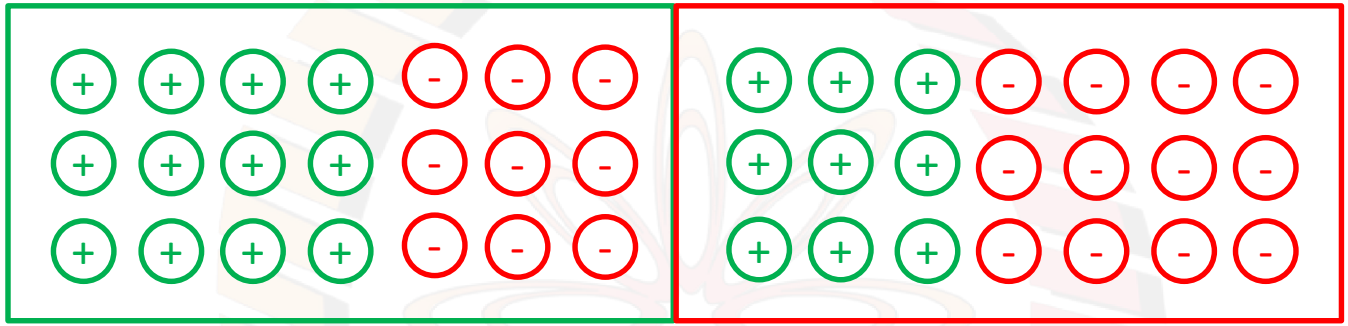


pn-junction

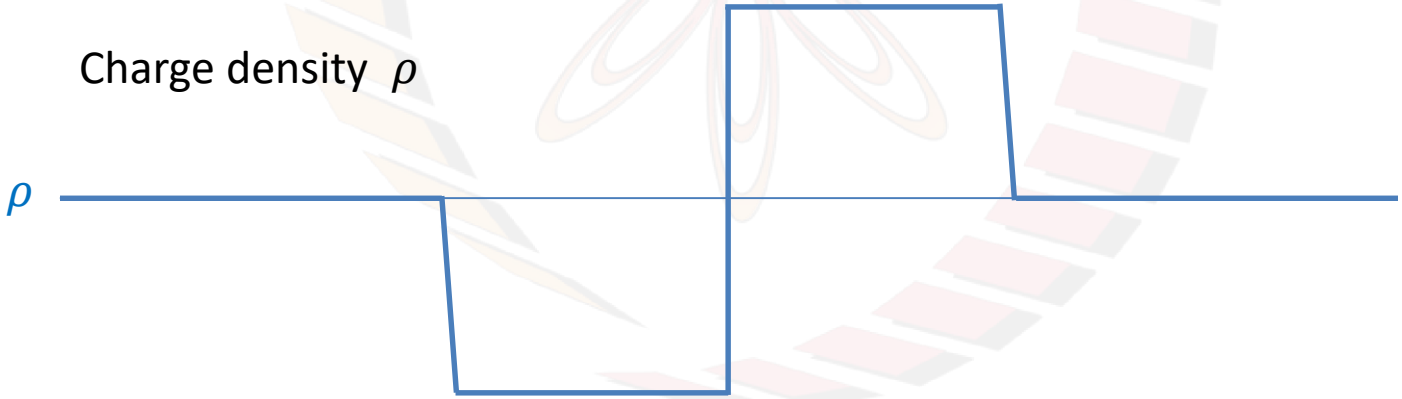


pn-junction

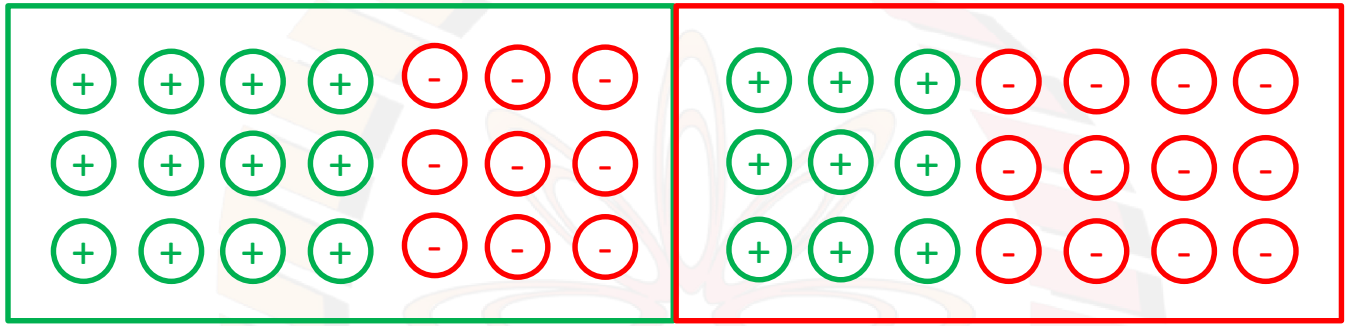
The space charge region



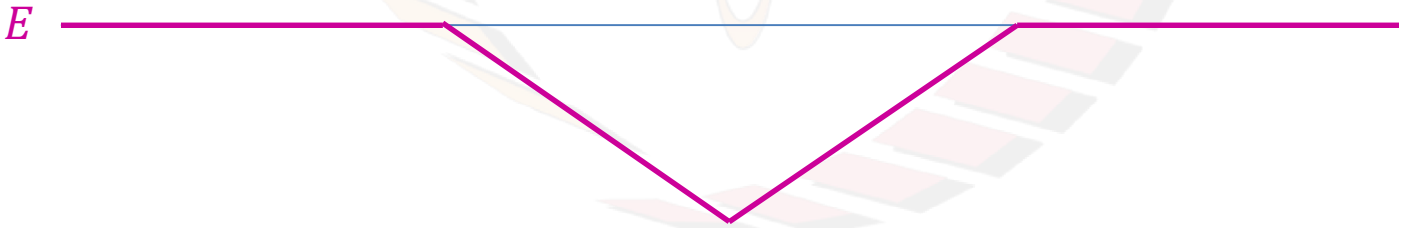
Charge density ρ



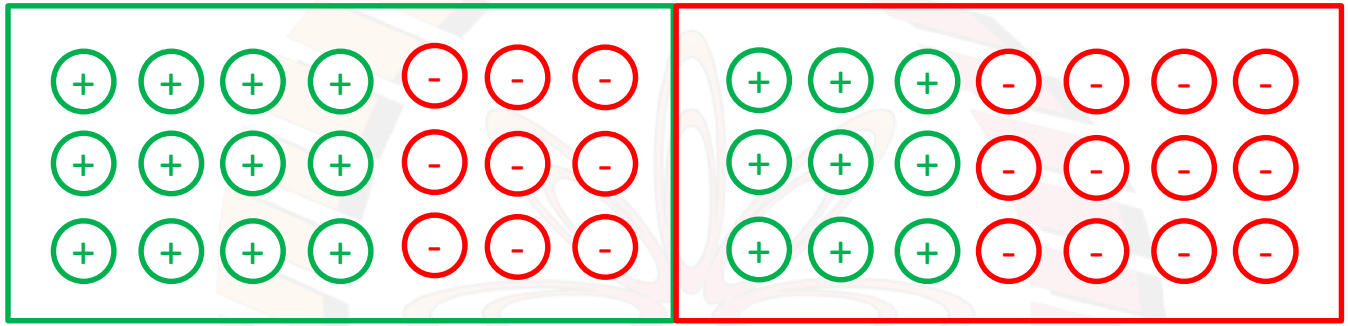
The space charge region



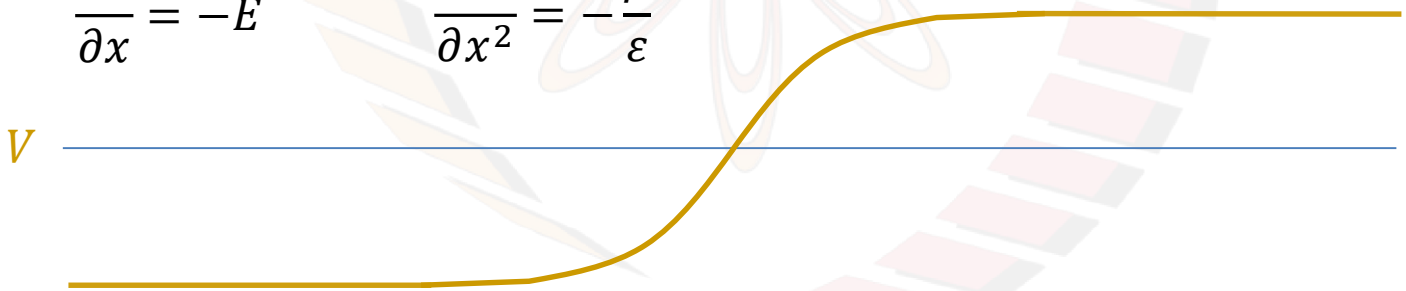
$$\frac{\partial E}{\partial x} = \frac{\rho}{\varepsilon}$$

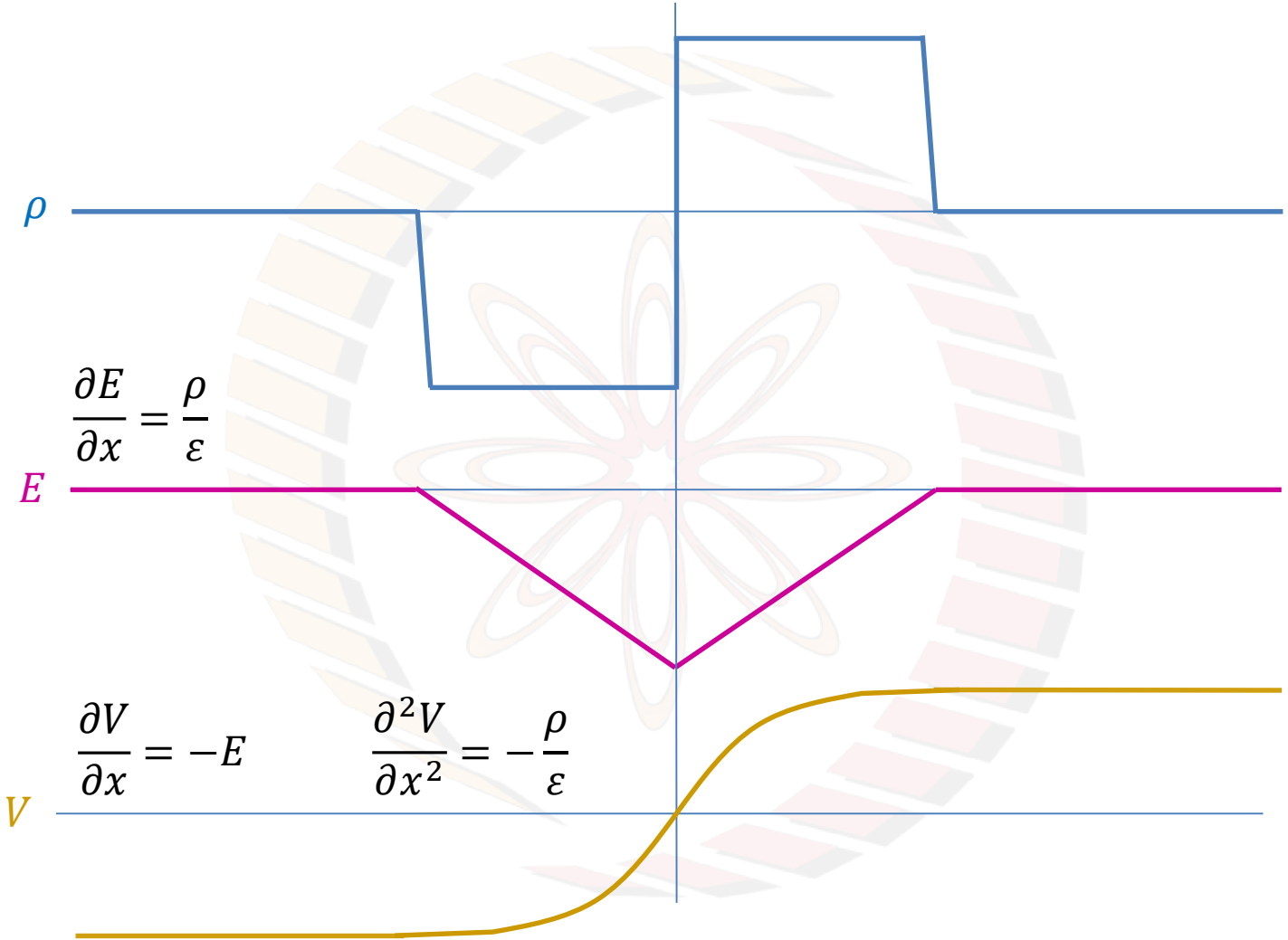


The space charge region

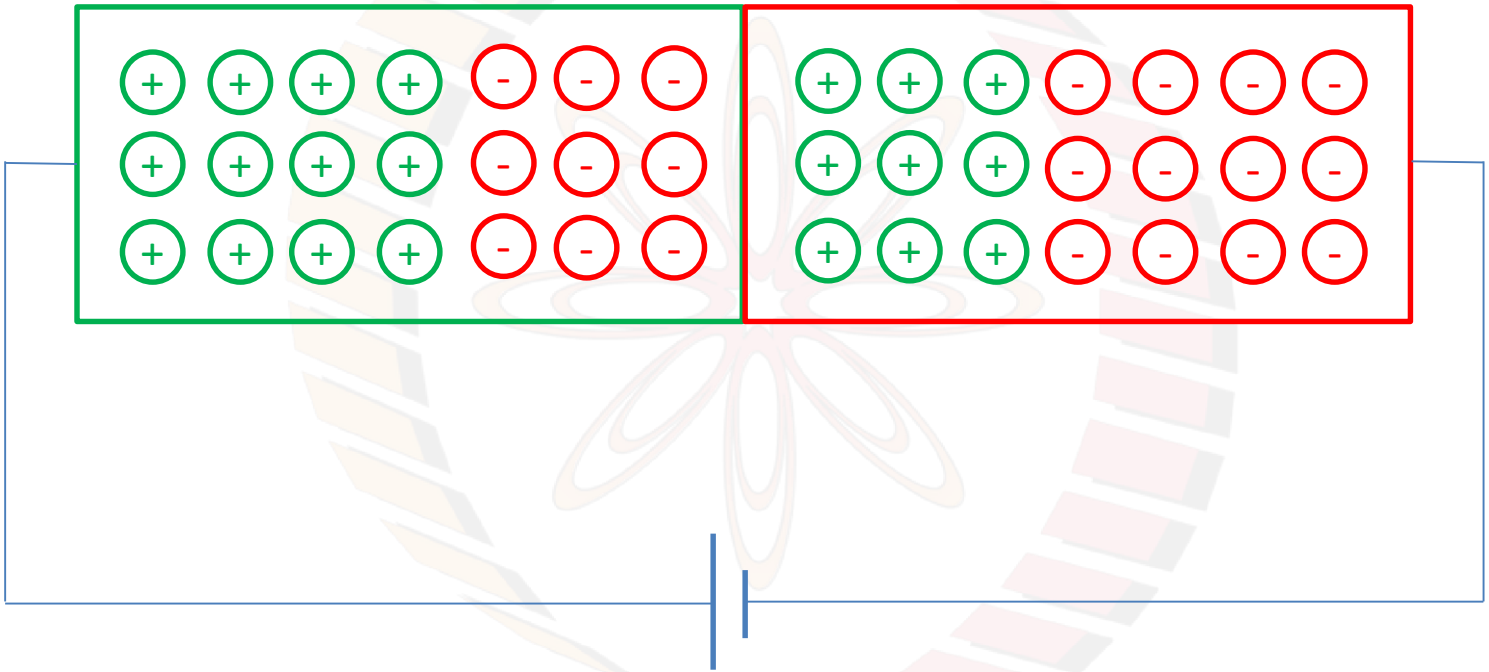


$$\frac{\partial V}{\partial x} = -E \qquad \frac{\partial^2 V}{\partial x^2} = -\frac{\rho}{\varepsilon}$$

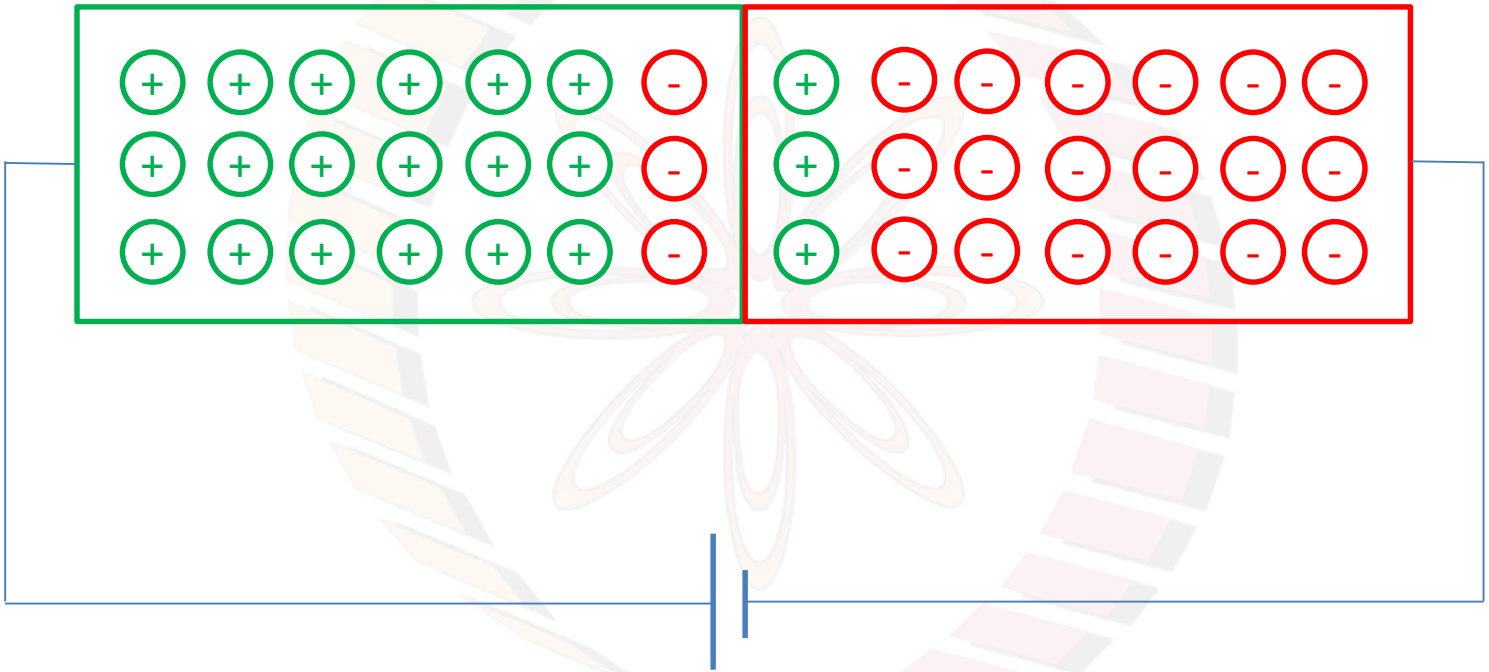



ρ
$\frac{\partial E}{\partial x} = \frac{\rho}{\varepsilon}$
E
$\frac{\partial V}{\partial x} = -E$
$\frac{\partial^2 V}{\partial x^2} = -\frac{\rho}{\varepsilon}$
V

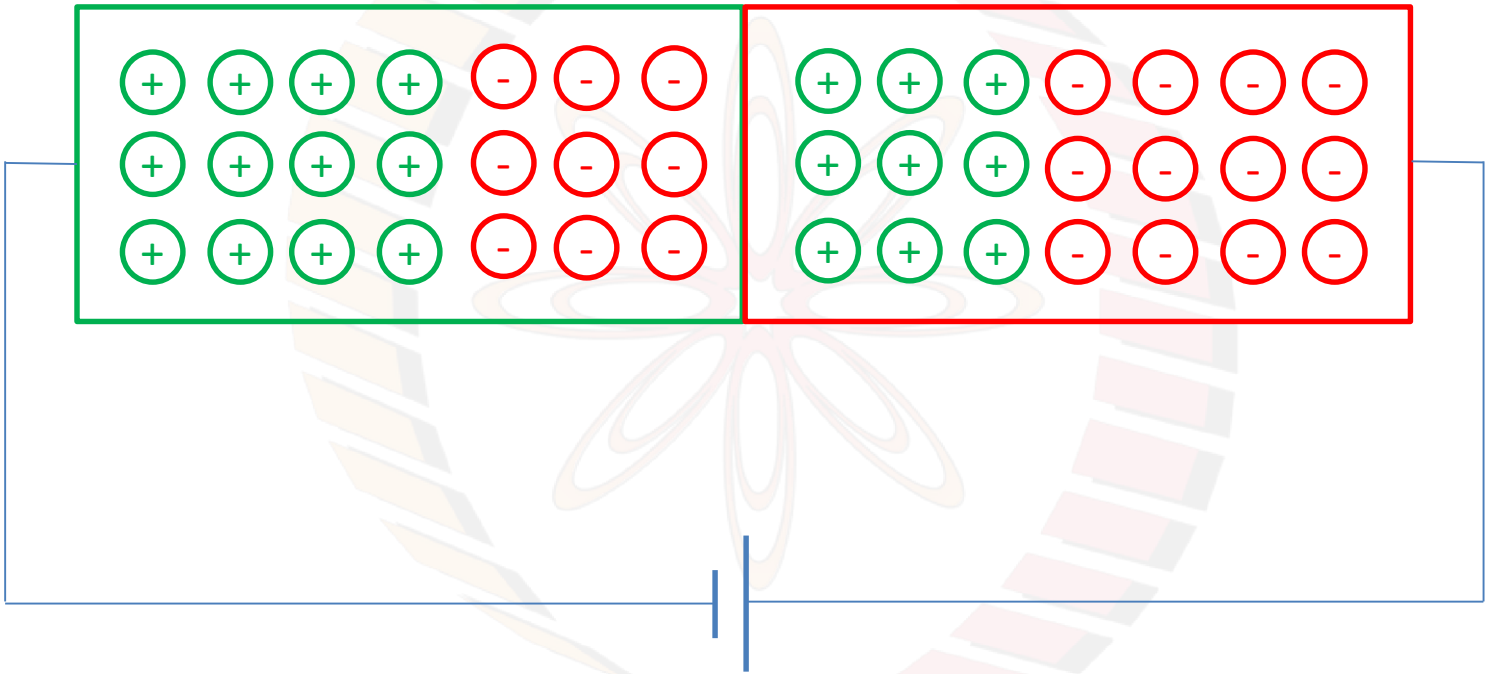
Forward bias



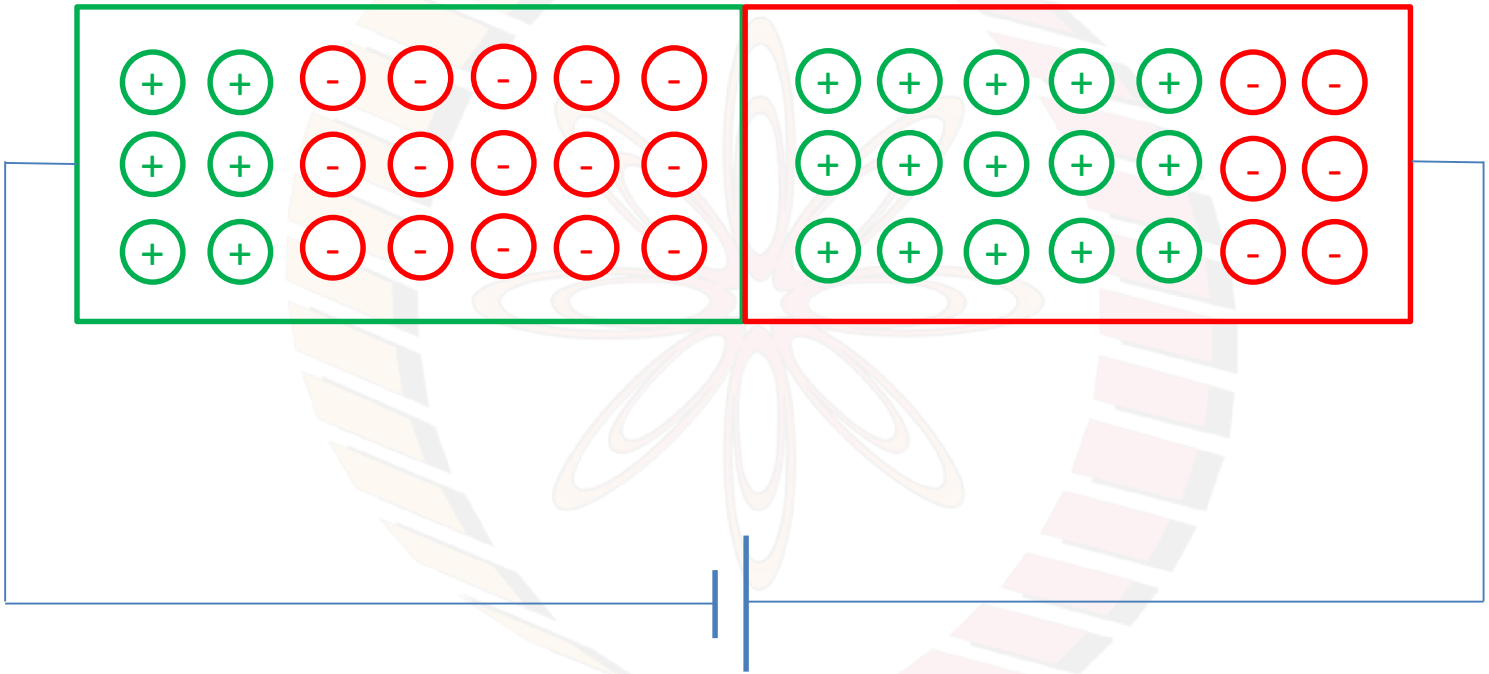
Forward bias



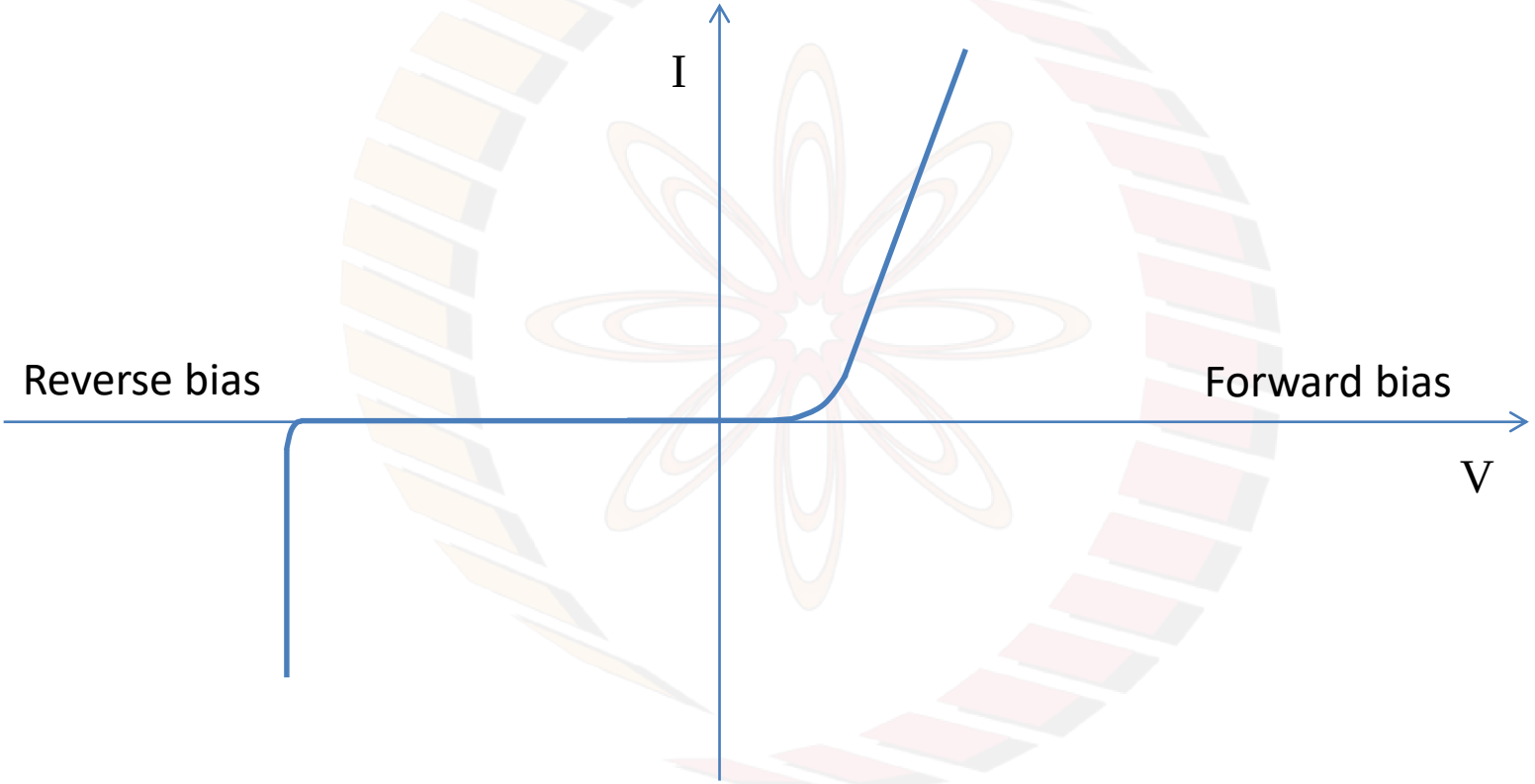
Reverse bias



Reverse bias



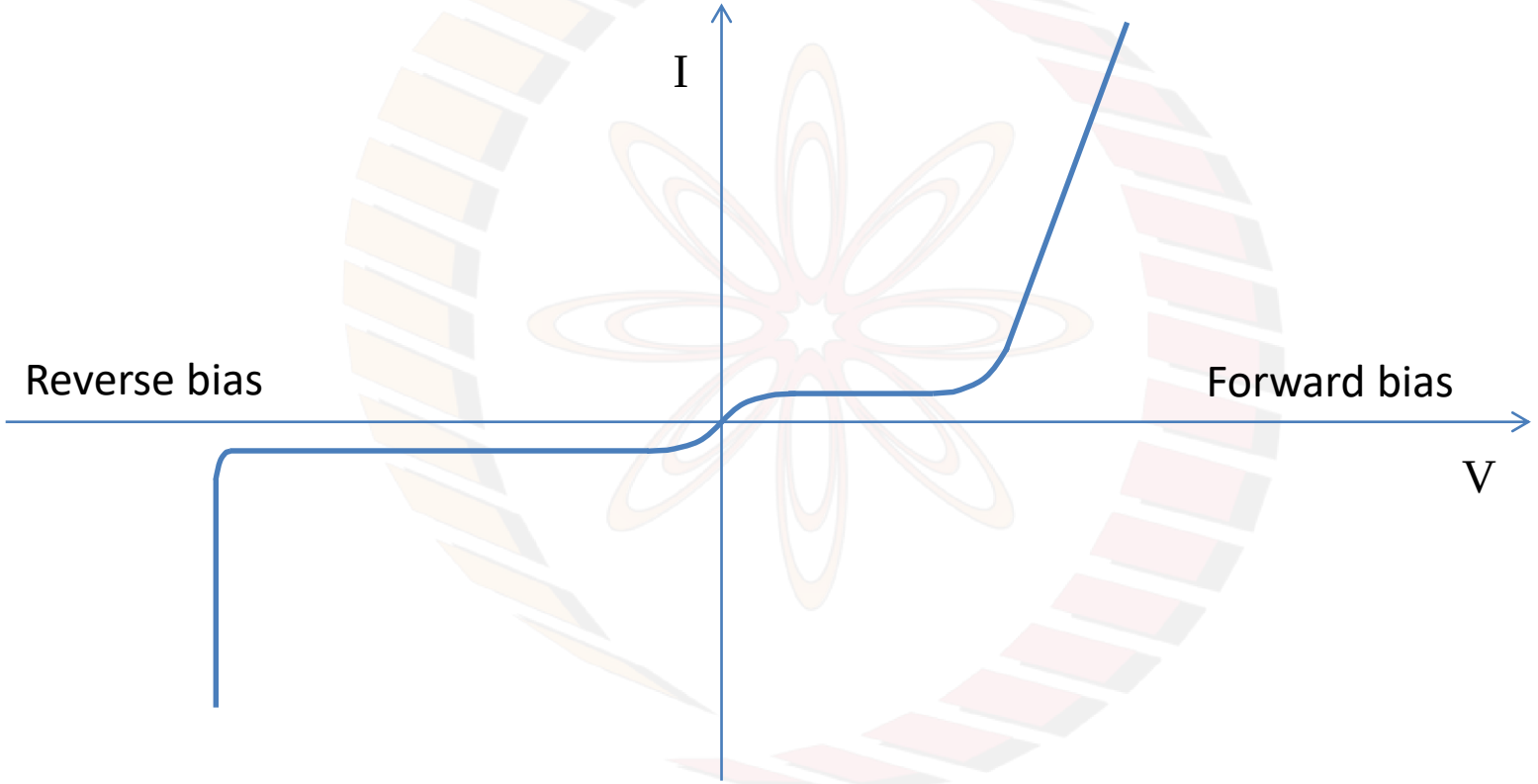
I-V characteristics



Conclusions:

1) A p-n junction can be formed using appropriately doped materials that are processed carefully
2) Charge, Field and Potential depend on the location in a p-n junction
3) A p-n junction has interesting I-V characteristics

I-V characteristics



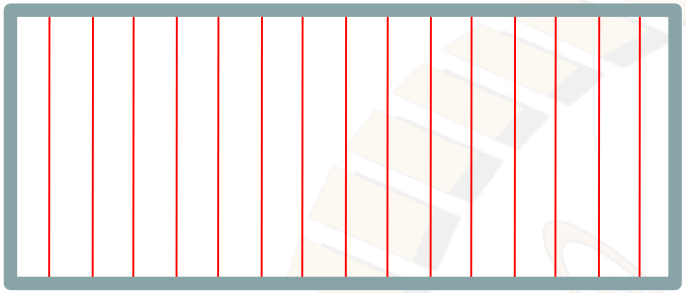
Solar Cell:
Growing the single crystal and making the p-n junction

Learning objectives:

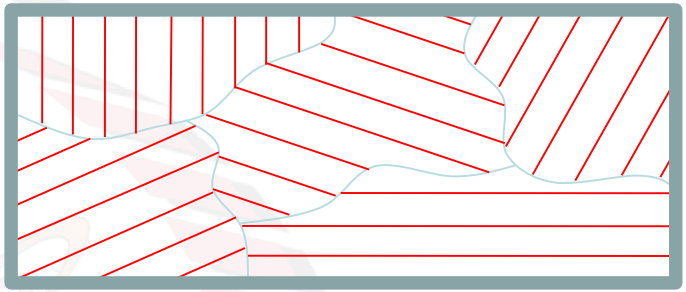
1) To become familiar with the techniques used to make single crystal as well as amorphous Si
2) To understand the method to manufacture the p-n junction

- Czochralski process
- Float Zone process
- Zone refining
- Cutting wafers
- Amorphous Si
- Manufacturing p-n junctions

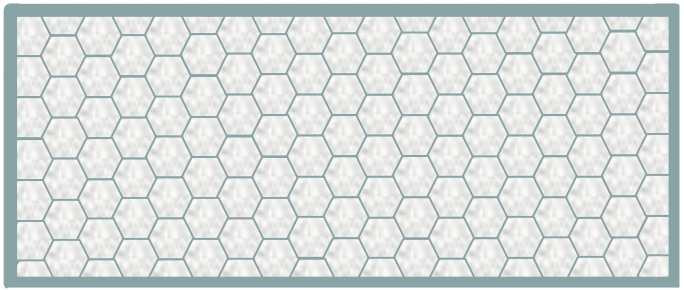
(a)



(b)



(c)



(d)

Quartzite (relatively pure sand) → Metallurgical Grade Silicon (MGS)

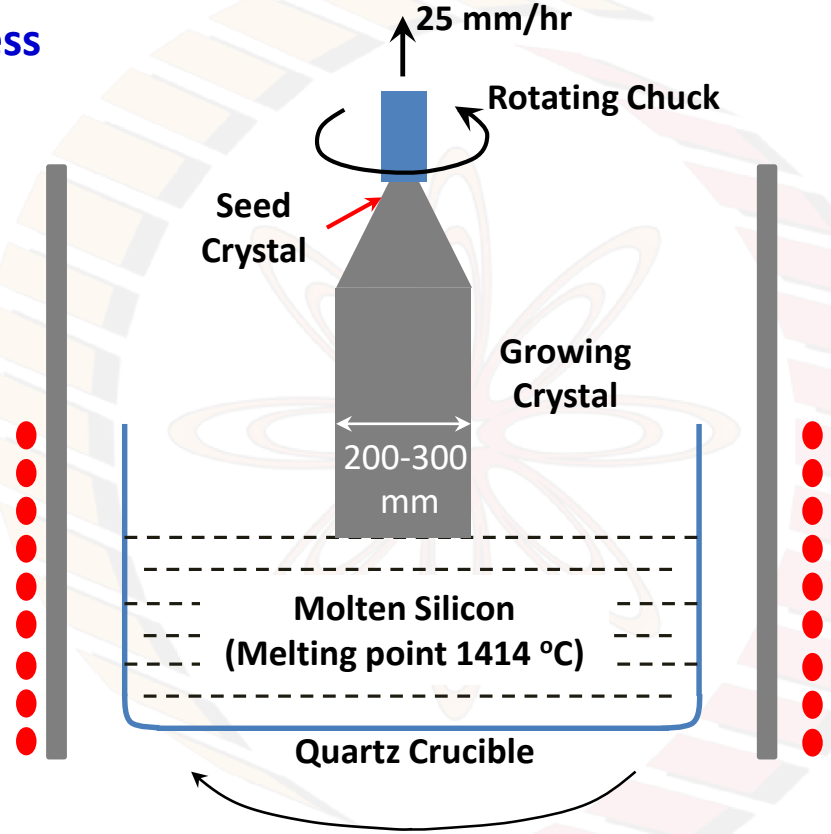
SiO_2 + Coke + Heat

Metallurgical Grade Silicon (MGS) 98% purity → Electronic Grade Silicon (EGS) ppm (C, O) to ppb (metals)

Si (solid) + 3HCl → $SiHCl_3$ (gas) + H_2

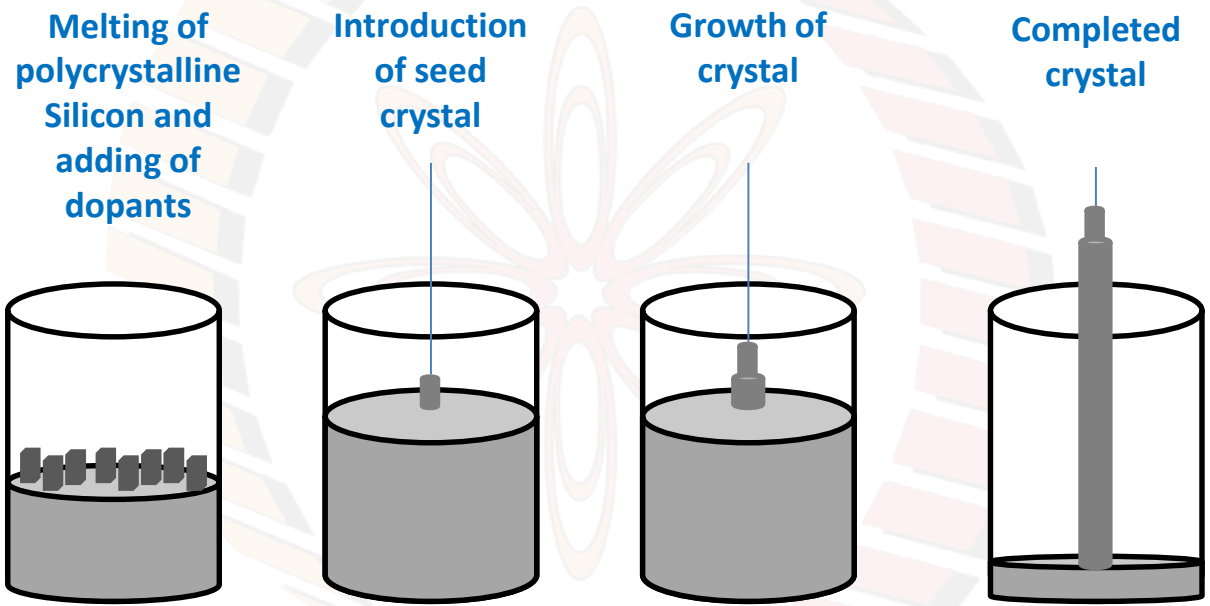
Si converted to Trichlorosilane, which is purified and reduced back to Si

Czochralski process



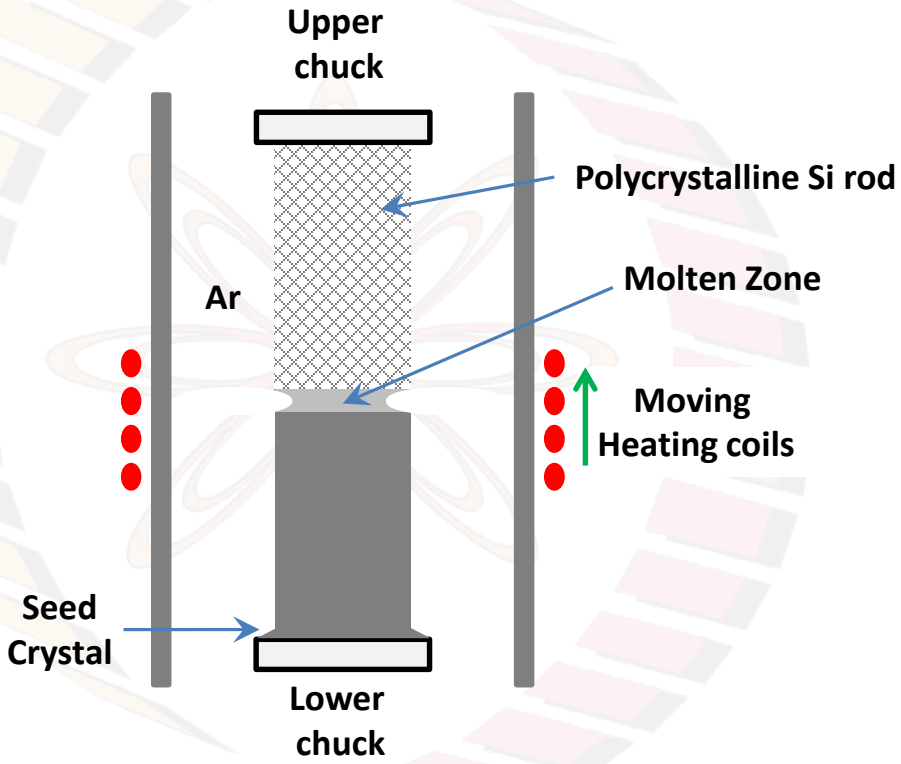
Semiconductor grade Silicon
Quartz (SiO_2) crucible (1670 °C)
Inert atmosphere of Ar
B or P added before melting

Czochralski process

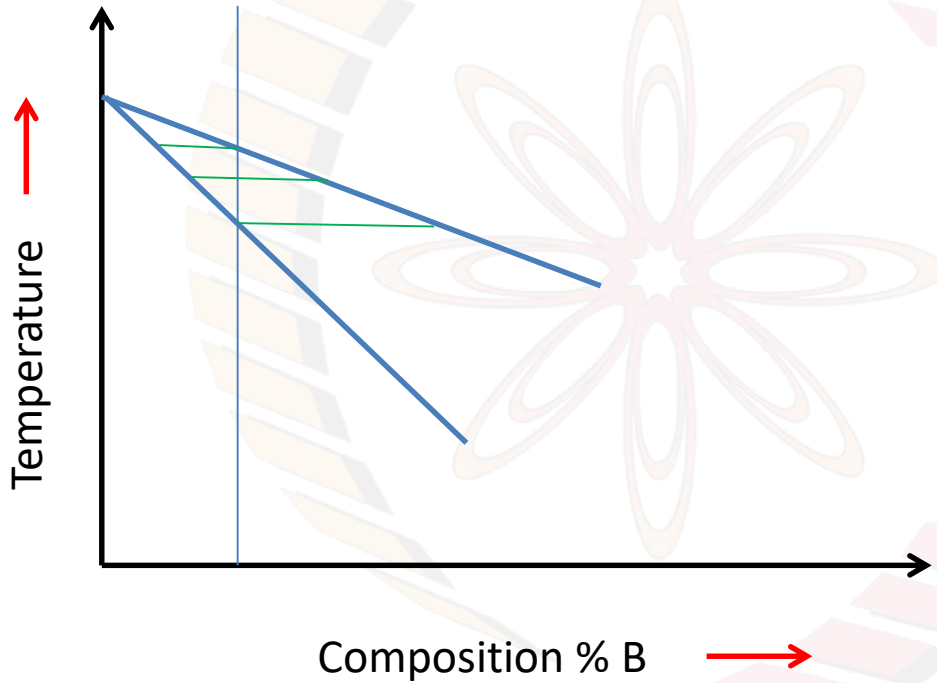


Float zone process

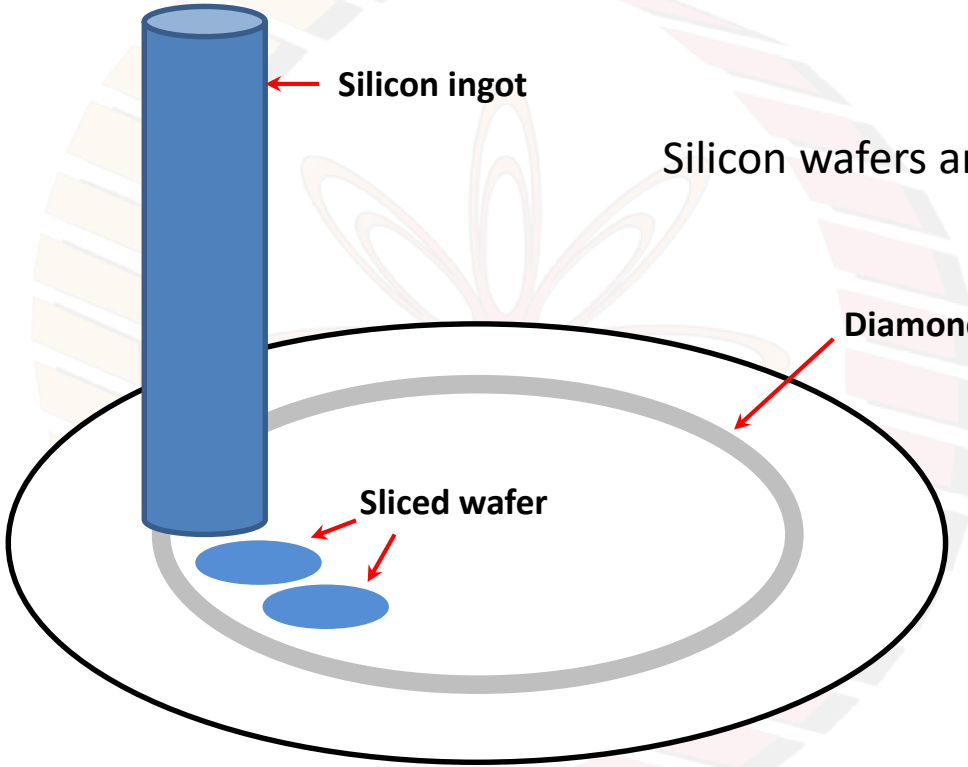
- Smaller diameter (150mm) due to surface tension
- Higher purity



Zone refining



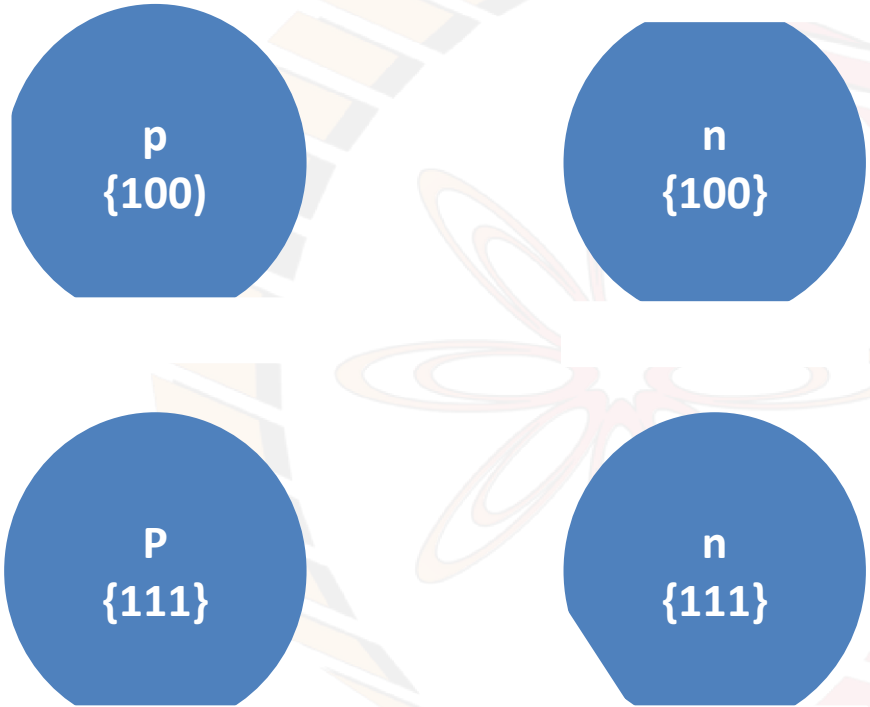
Inner diameter slicing of Si ingot



Silicon wafers are 0.2 to 0.75 mm thick

Can produce one wafer at a time

Wire saw uses fast moving thin wire with abrasive slurry, can cut several wafers at the same time



Notches typically used to indicate orientation and doping

Amorphous Si

CVD process

Has dangling bonds (defects)

Hydrogenated amorphous Silicon, a-Si:H by deposition from Silane gas SiH_4

p-n junction

- Ion implantation: Low temperature process, ionized dopants accelerated using electric fields. Annealing required
- Diffusion: Vapour phase deposition followed by high temperature diffusion
- Epitaxy: Under high vacuum, gaseous elements condense on substrate wafer

Conclusions:

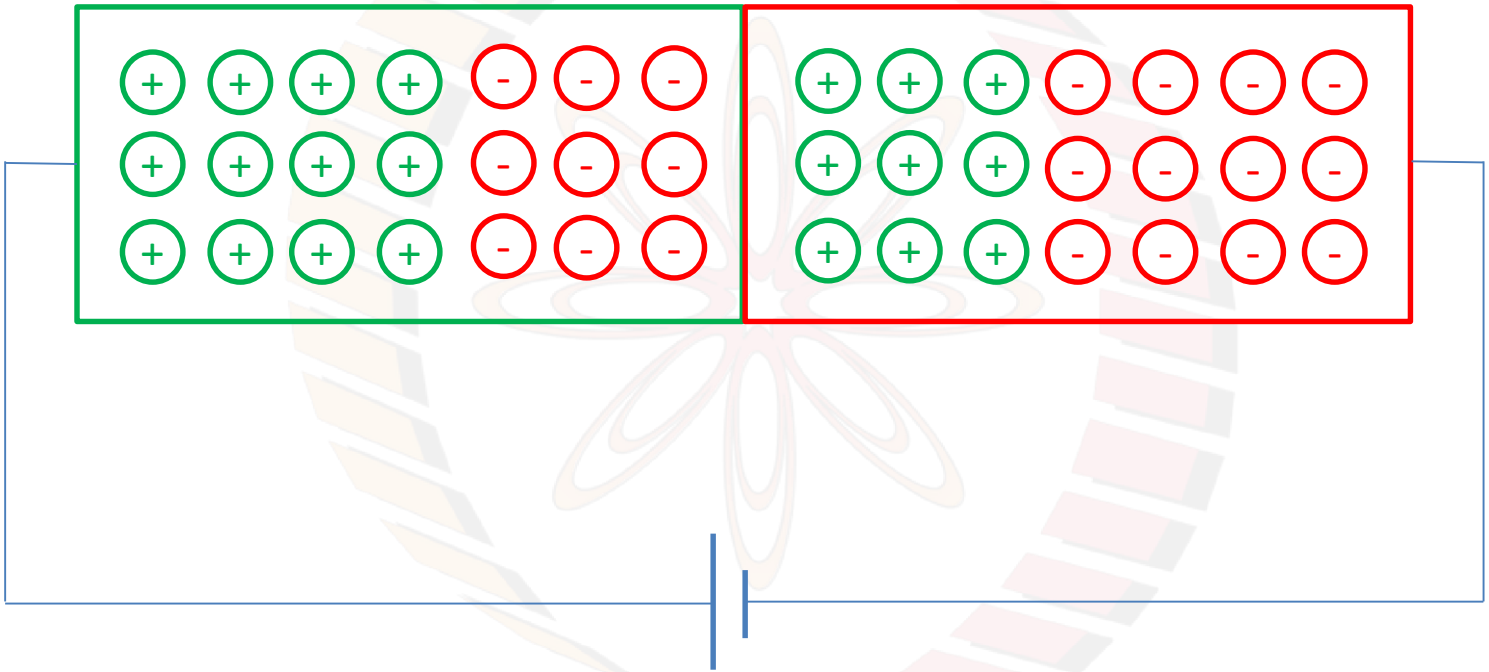
1) It is quite challenging to produce single crystal Si
2) Multiple process steps involved
3) Purity and dimensions can have significant impact on costs
4) Amorphous Si is an option

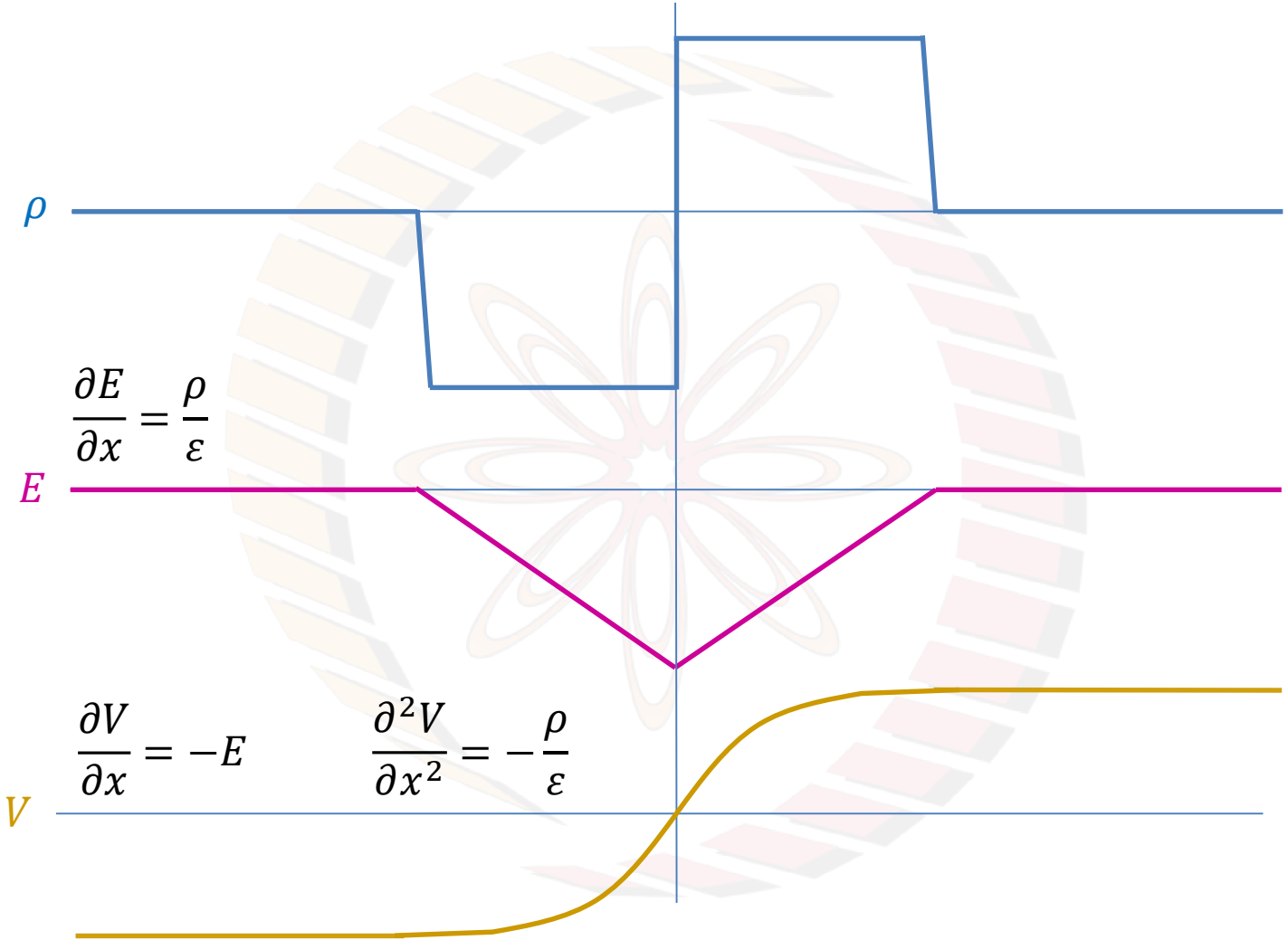
Solar Energy: Interaction of p-n junction with radiation

Learning objectives:

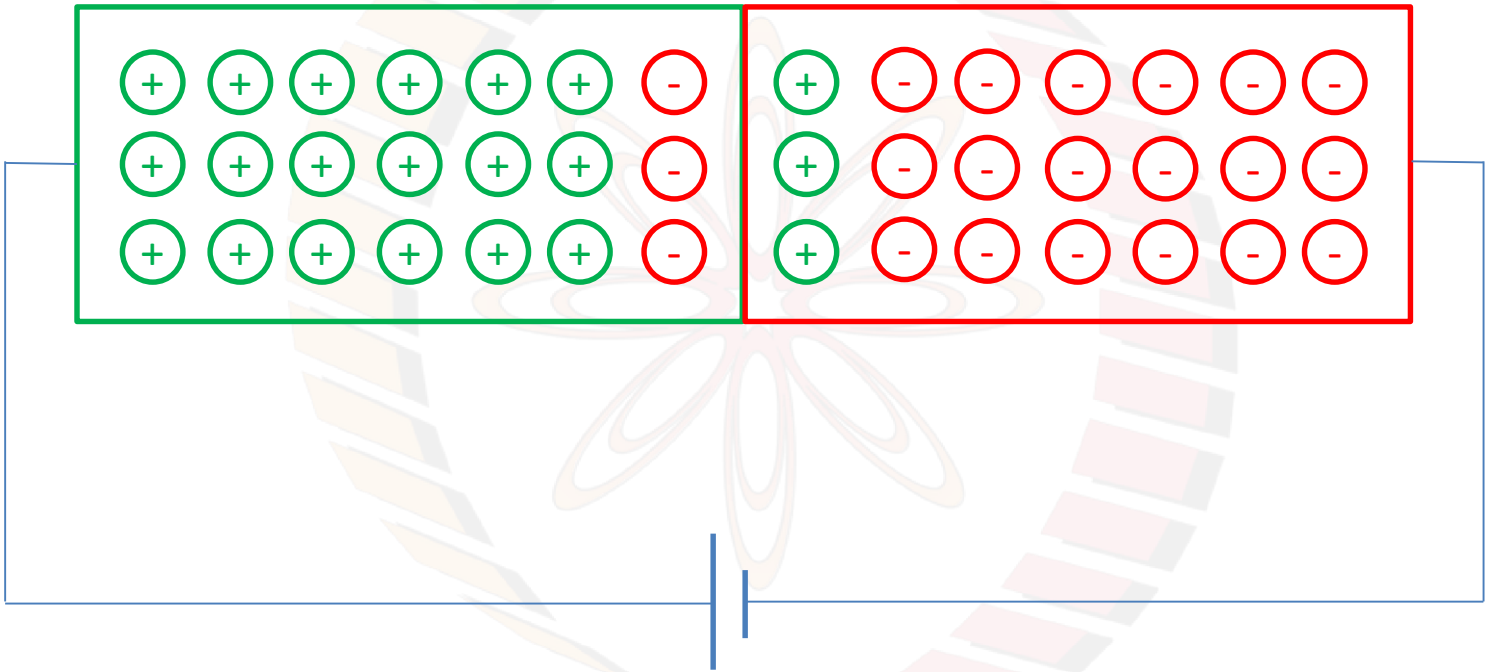
1) To describe the interaction of a p-n junction with radiation
2) To explain the functioning of the p-n junction solar cell

Forward bias

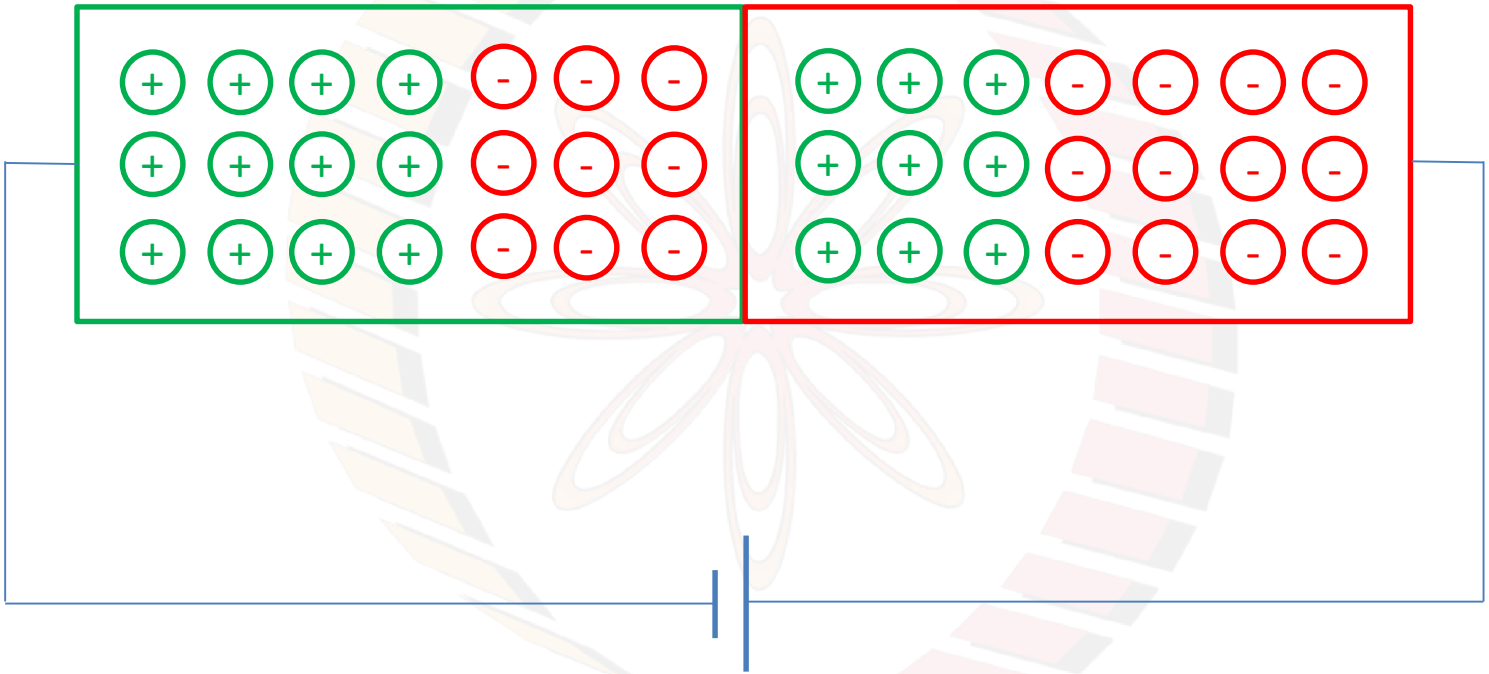



ρ
$\frac{\partial E}{\partial x} = \frac{\rho}{\varepsilon}$
E
$\frac{\partial V}{\partial x} = -E$
$\frac{\partial^2 V}{\partial x^2} = -\frac{\rho}{\varepsilon}$
V

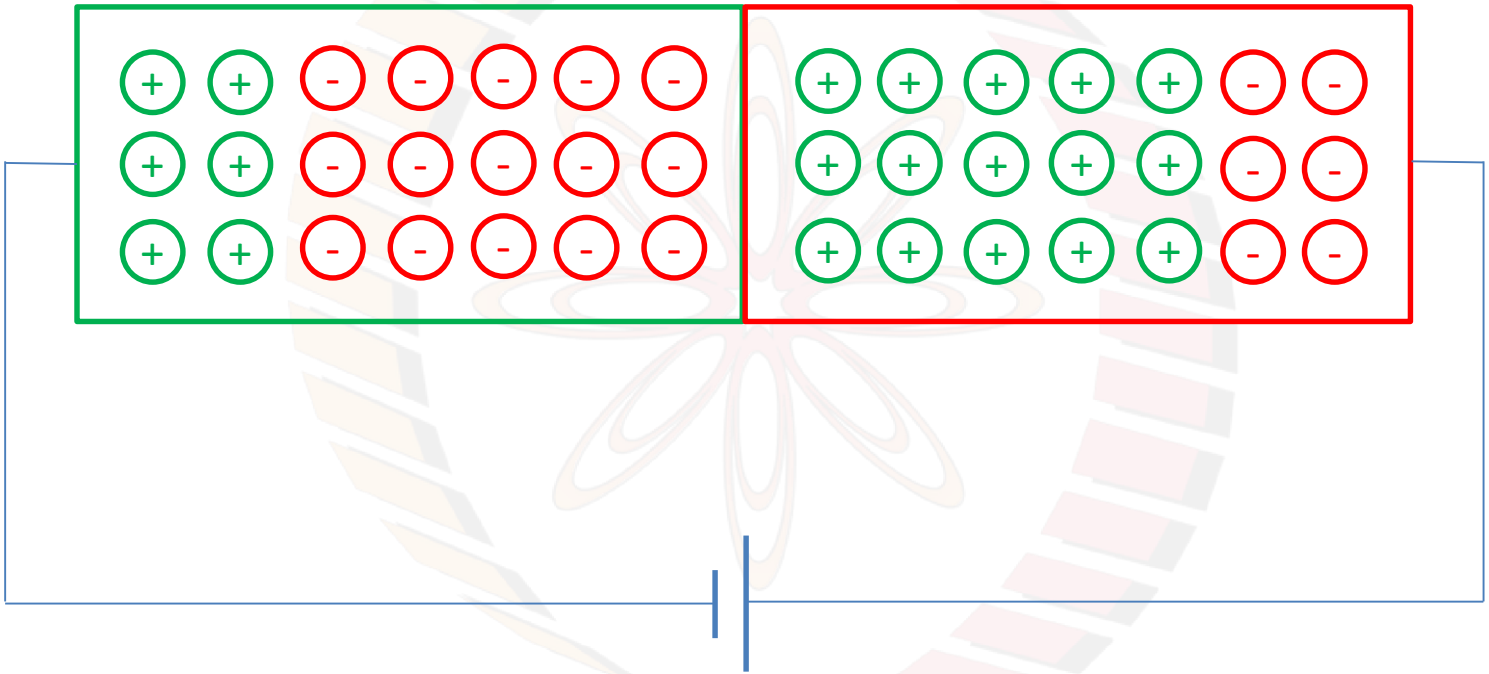
Forward bias



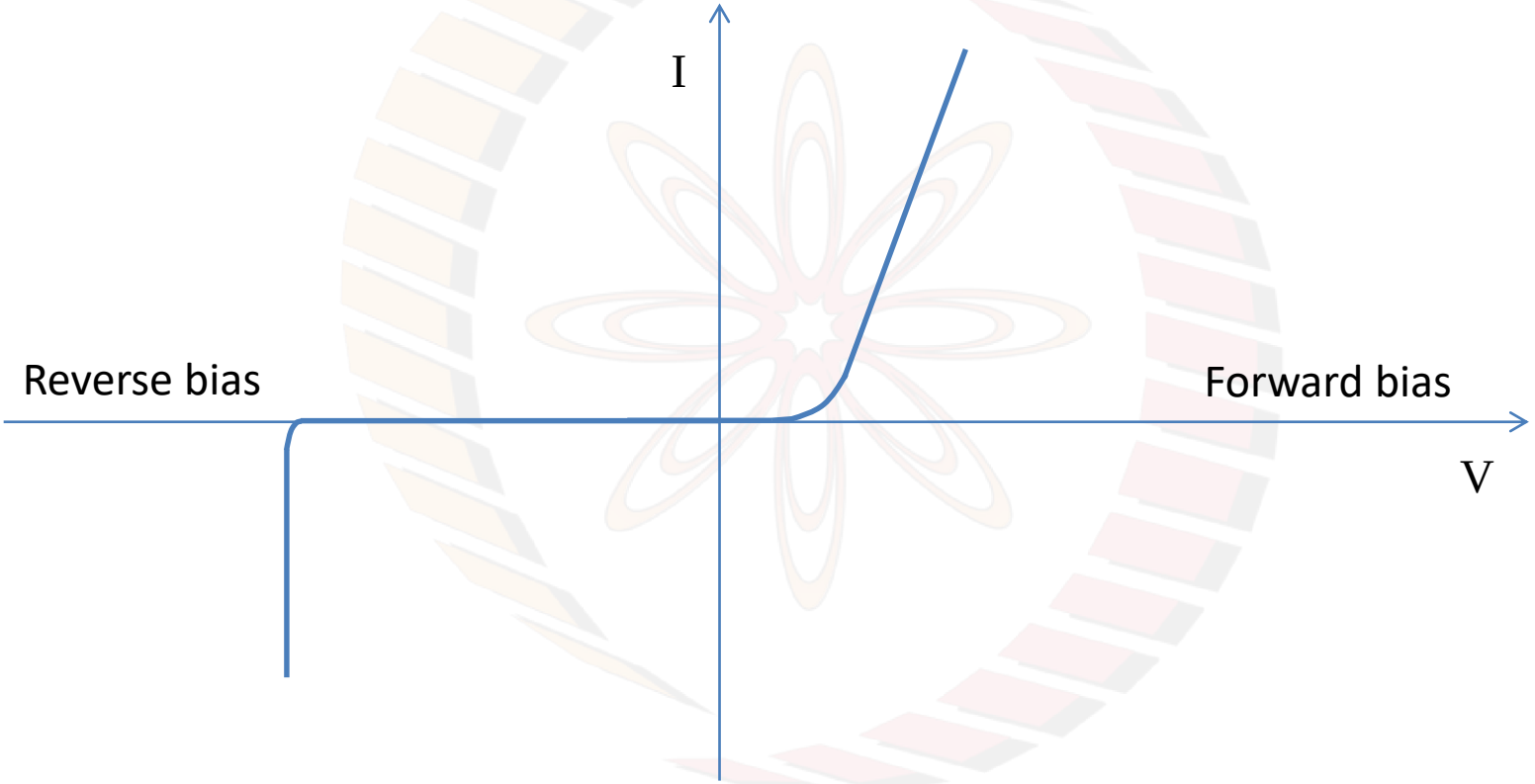
Reverse bias

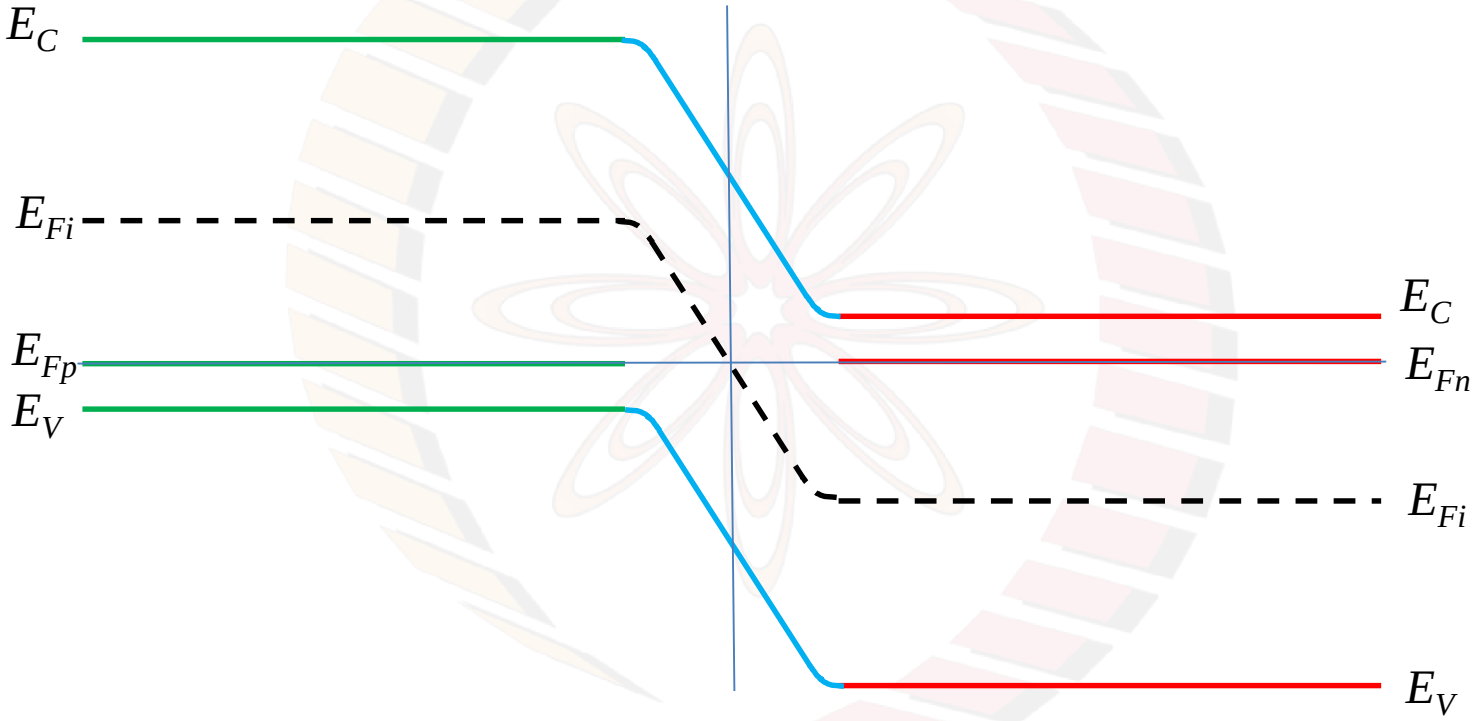


Reverse bias

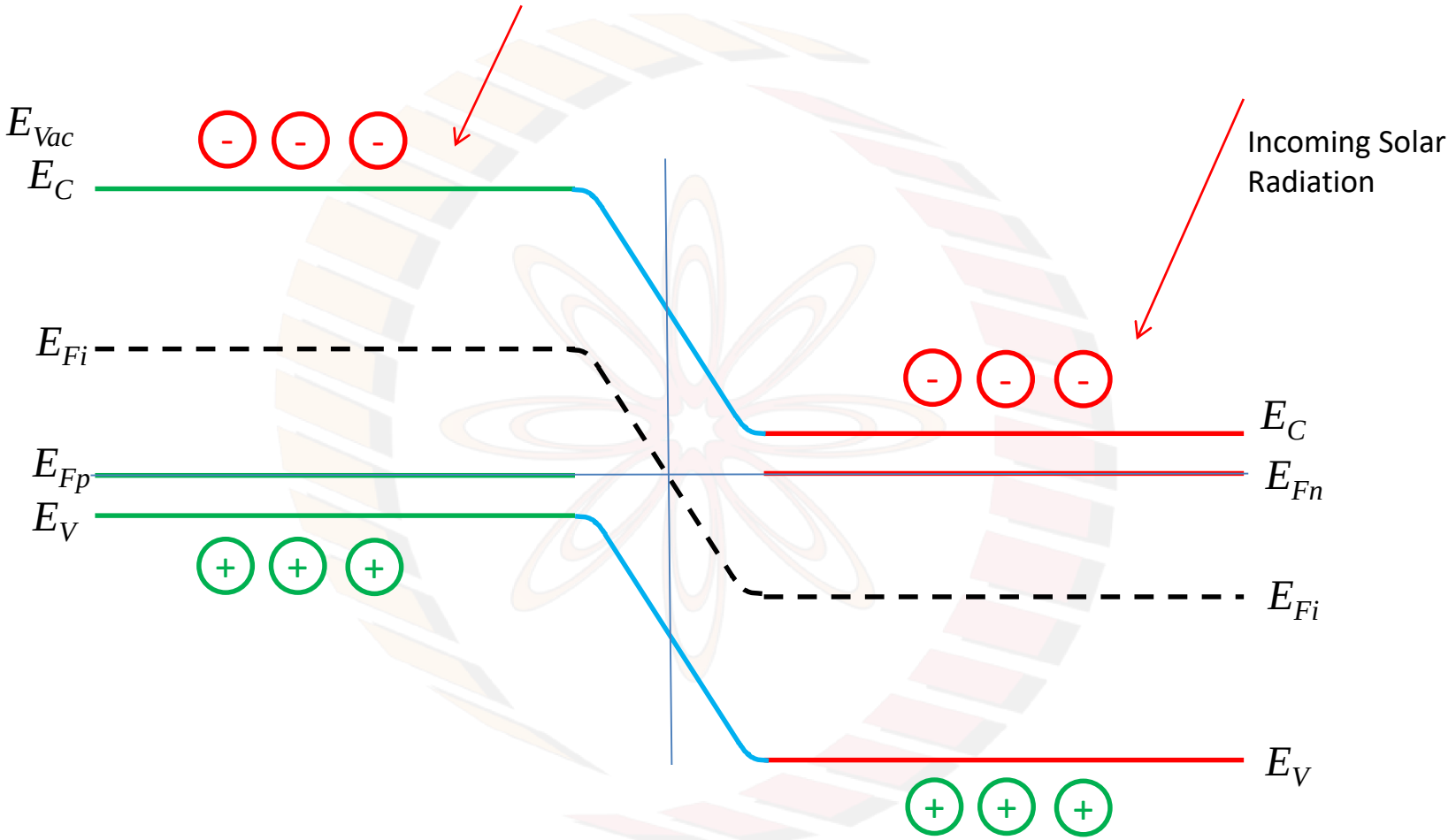


I-V characteristics

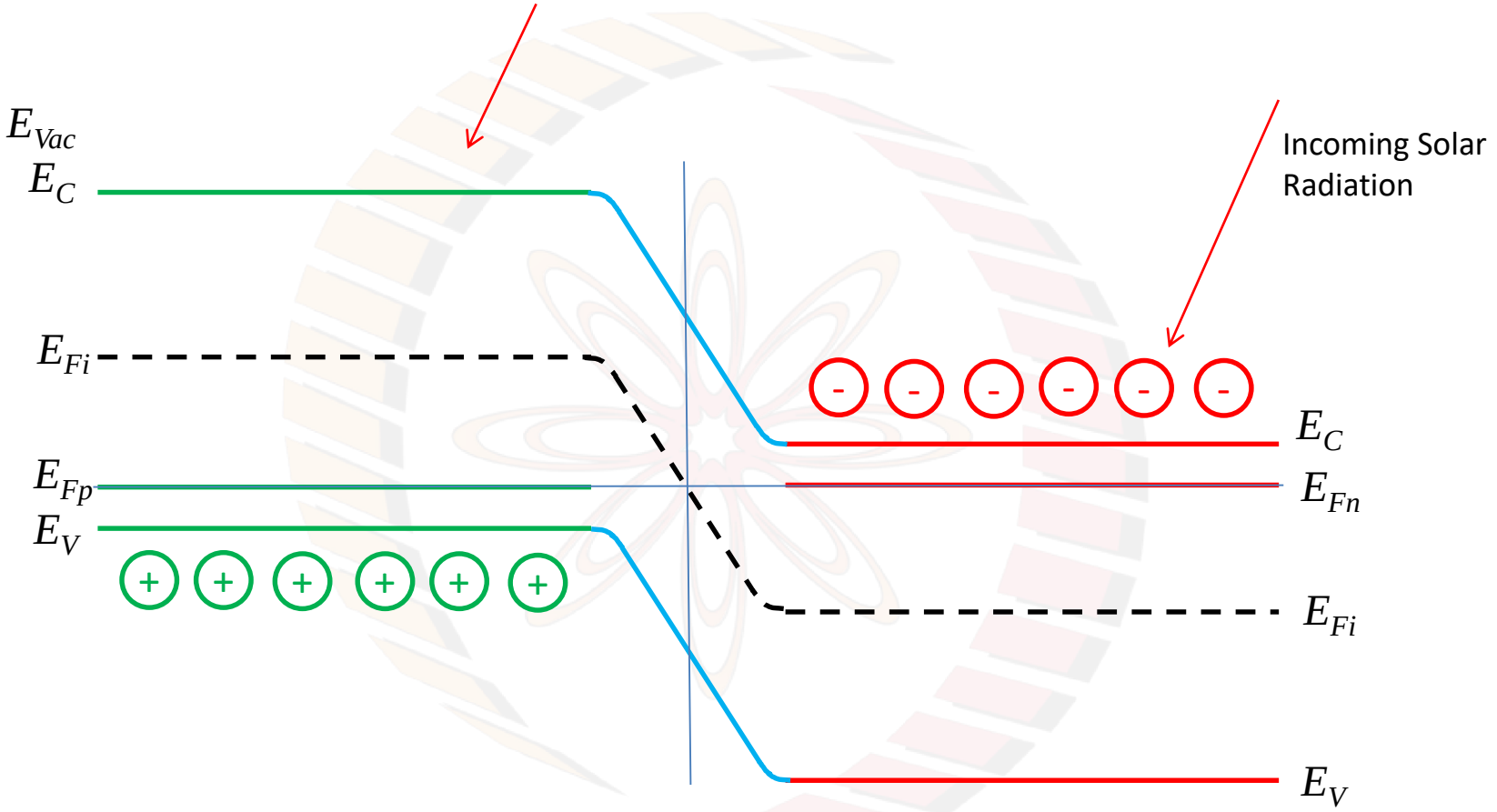




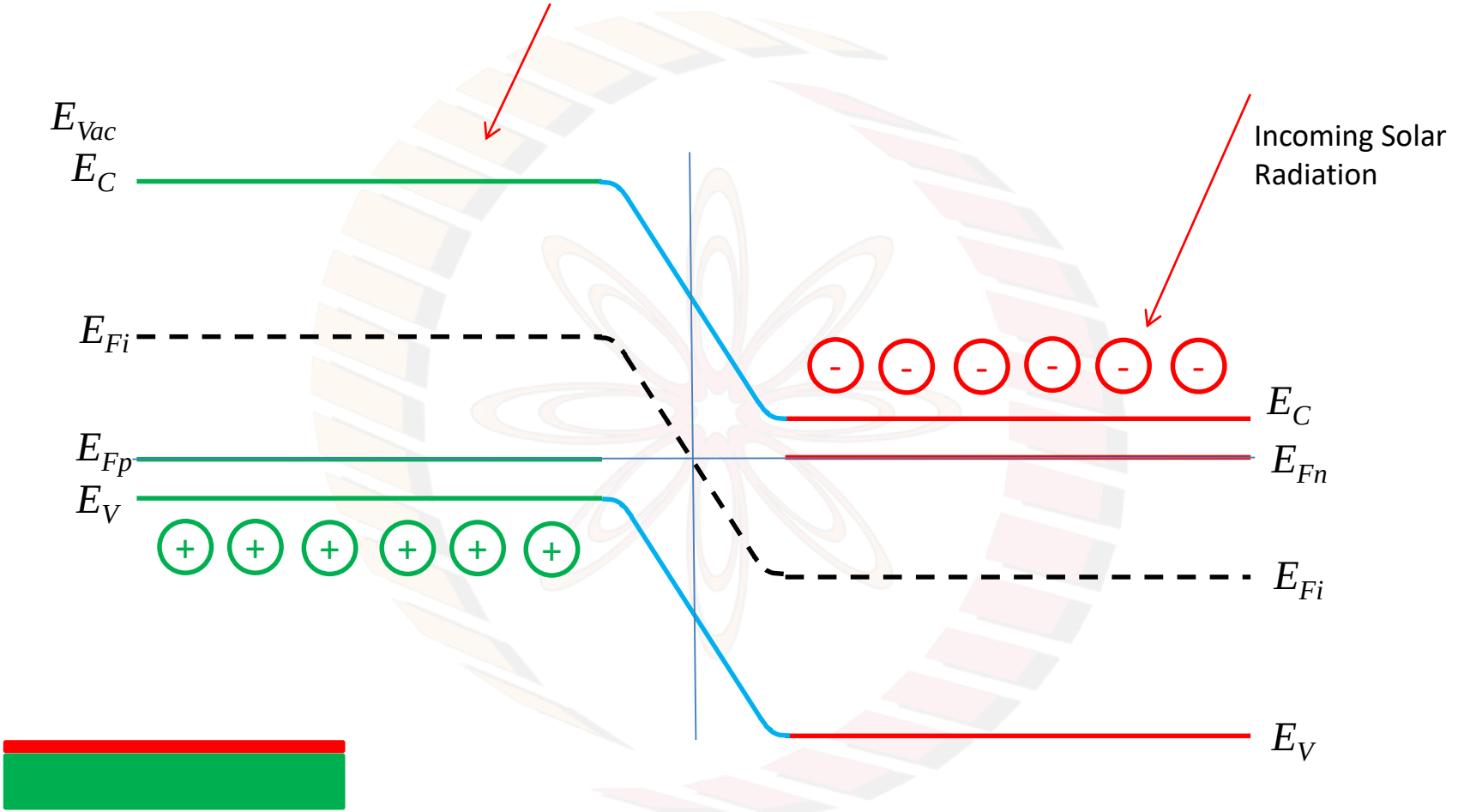
pn-junction



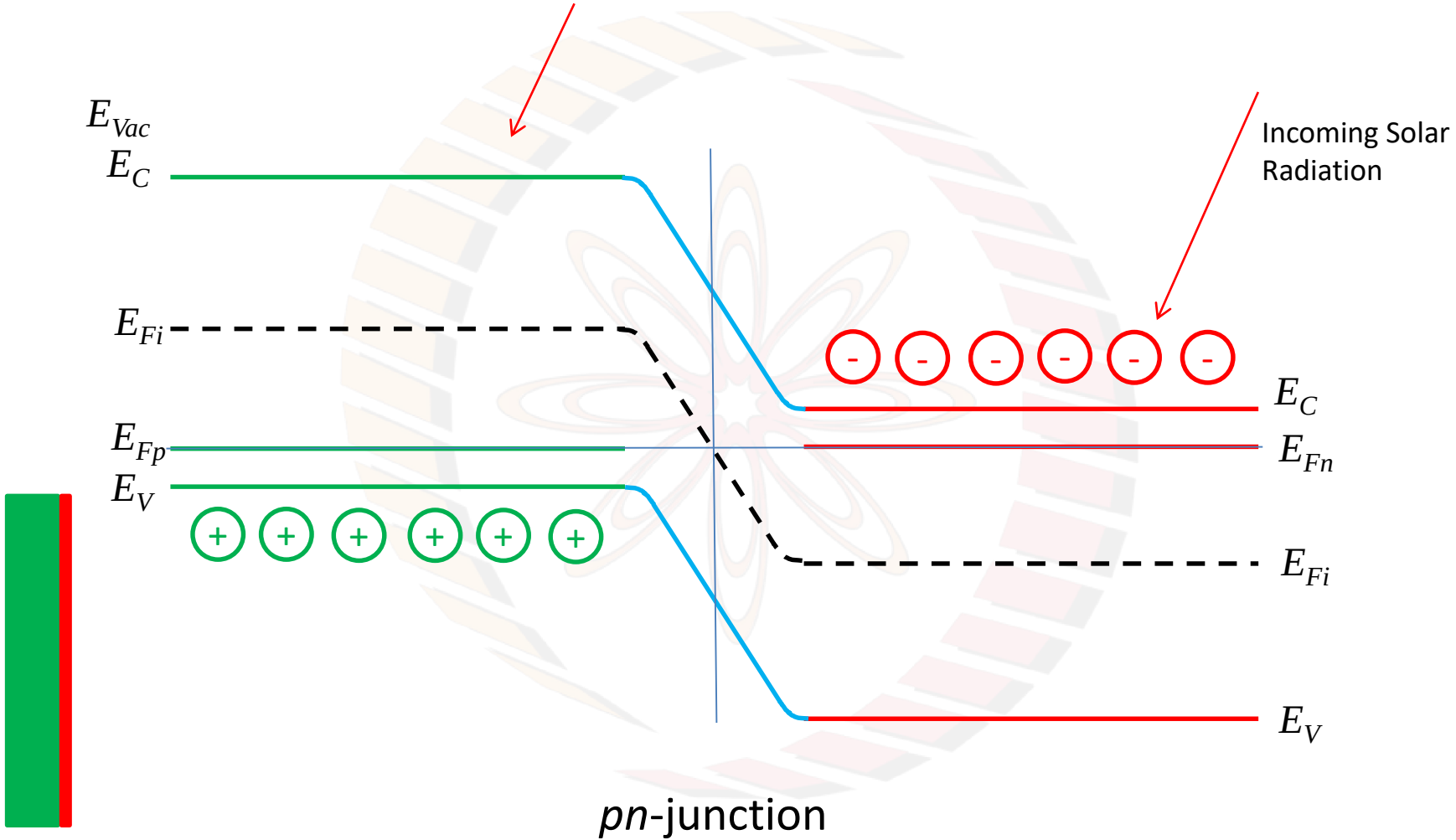
pn-junction



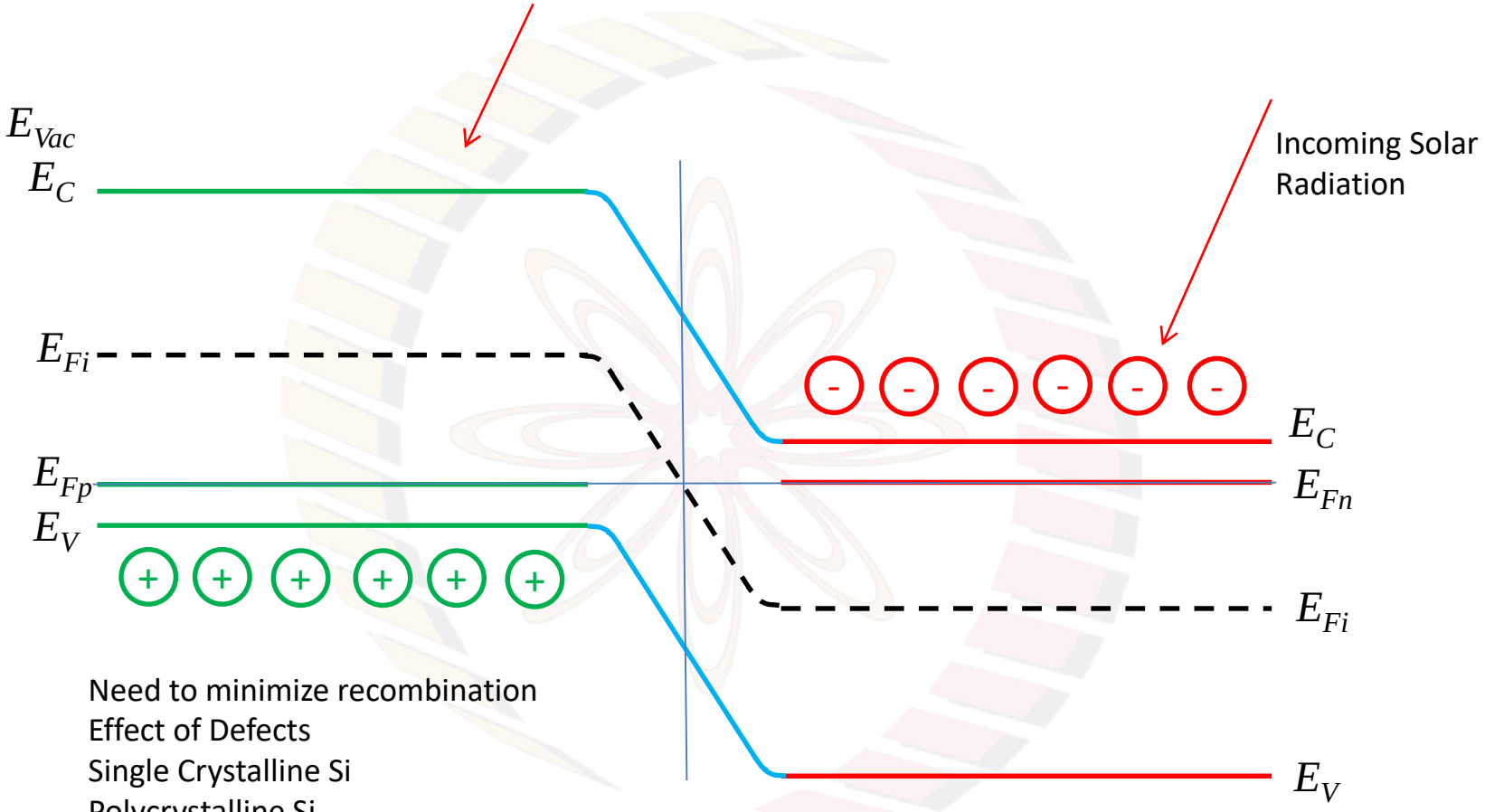
pn-junction



pn-junction



pn-junction



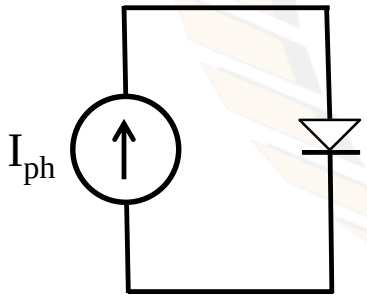
Need to minimize recombination
Effect of Defects
Single Crystalline Si
Polycrystalline Si
Amorphous Si

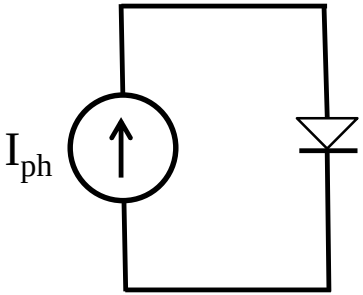
pn-junction

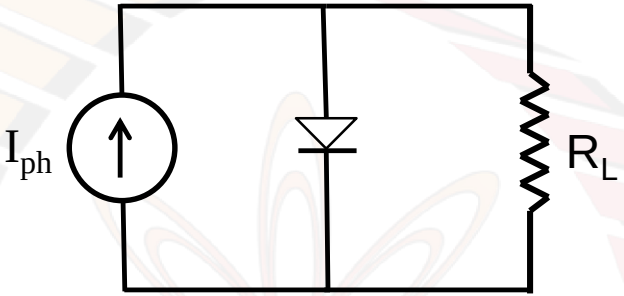
Trade off between cost and efficiency

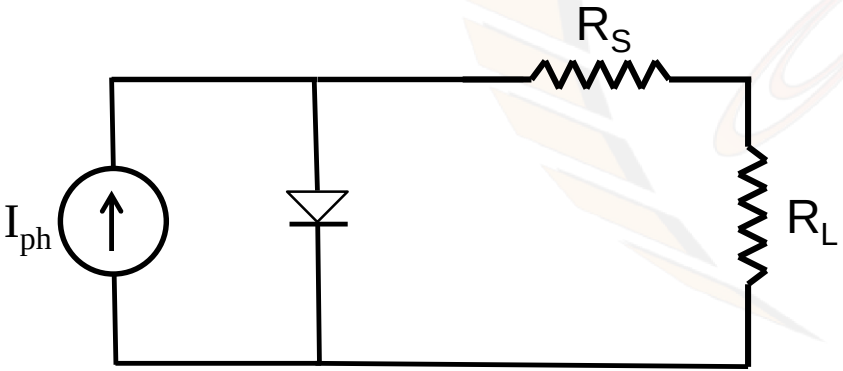
Solar Cell is a current source
Charge carriers created by sunlight received: Photocurrent I_{ph}

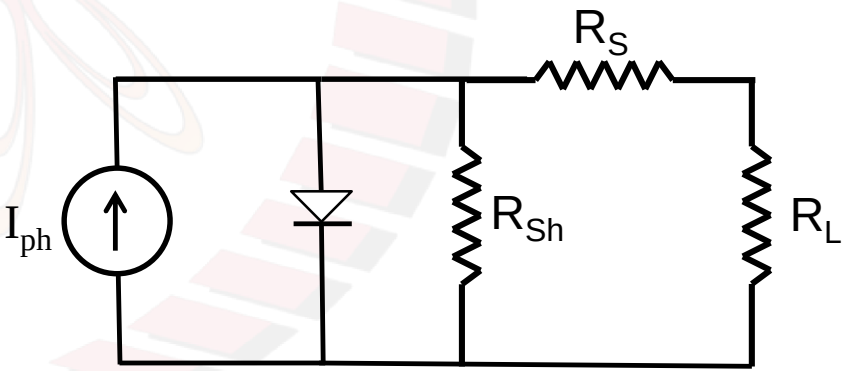
Without external load, the pn junction is forward biased, and internally shorts




I_{ph}


I_{ph}
R_L


R_S
I_{ph}
R_L


R_S
I_{ph}
R_{Sh}
R_L

Conclusions:

1)The p-n junction stabilizes the electron-hole pair
2)The p-n junction solar cell is a current source and has to be used accordingly

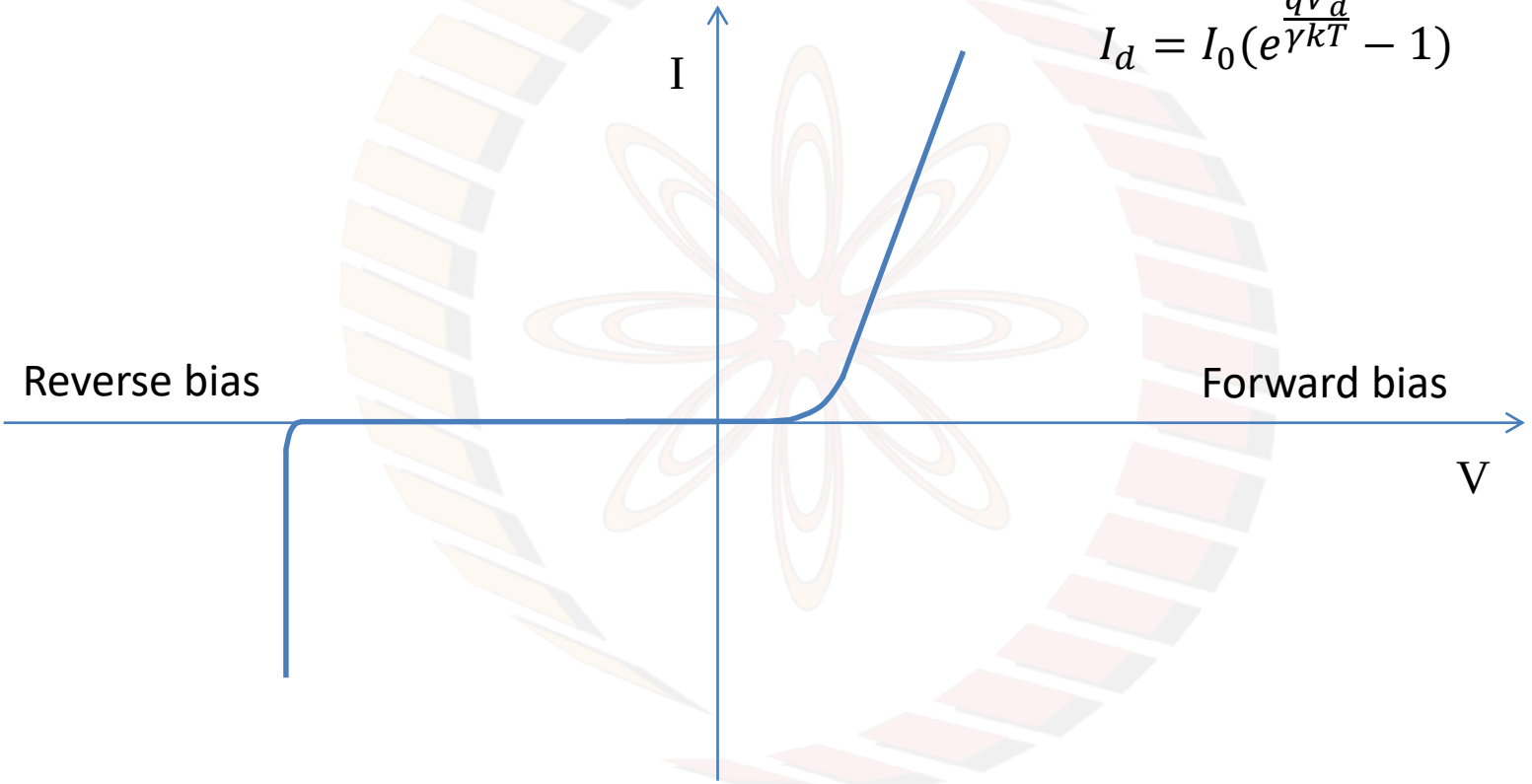
Solar Energy:
Solar cell characteristics and usage

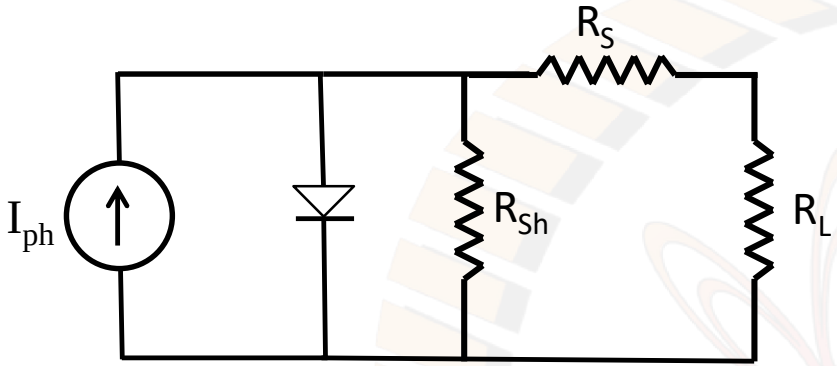
Learning objectives:

1) To determine the operational characteristics of a p-n junction based solar cell
2) To understand the best way to use the solar cell

I-V characteristics

$$I_d = I_0(e^{\frac{qV_d}{\gamma kT}} - 1)$$





(Assuming recombination current is low)

$$I_{ph} - I_d = I_L$$

$$I_d = I_0\left(e^{\frac{qV_d}{\gamma kT}} - 1\right)$$

$$V_d = V_L + I_L R_S$$

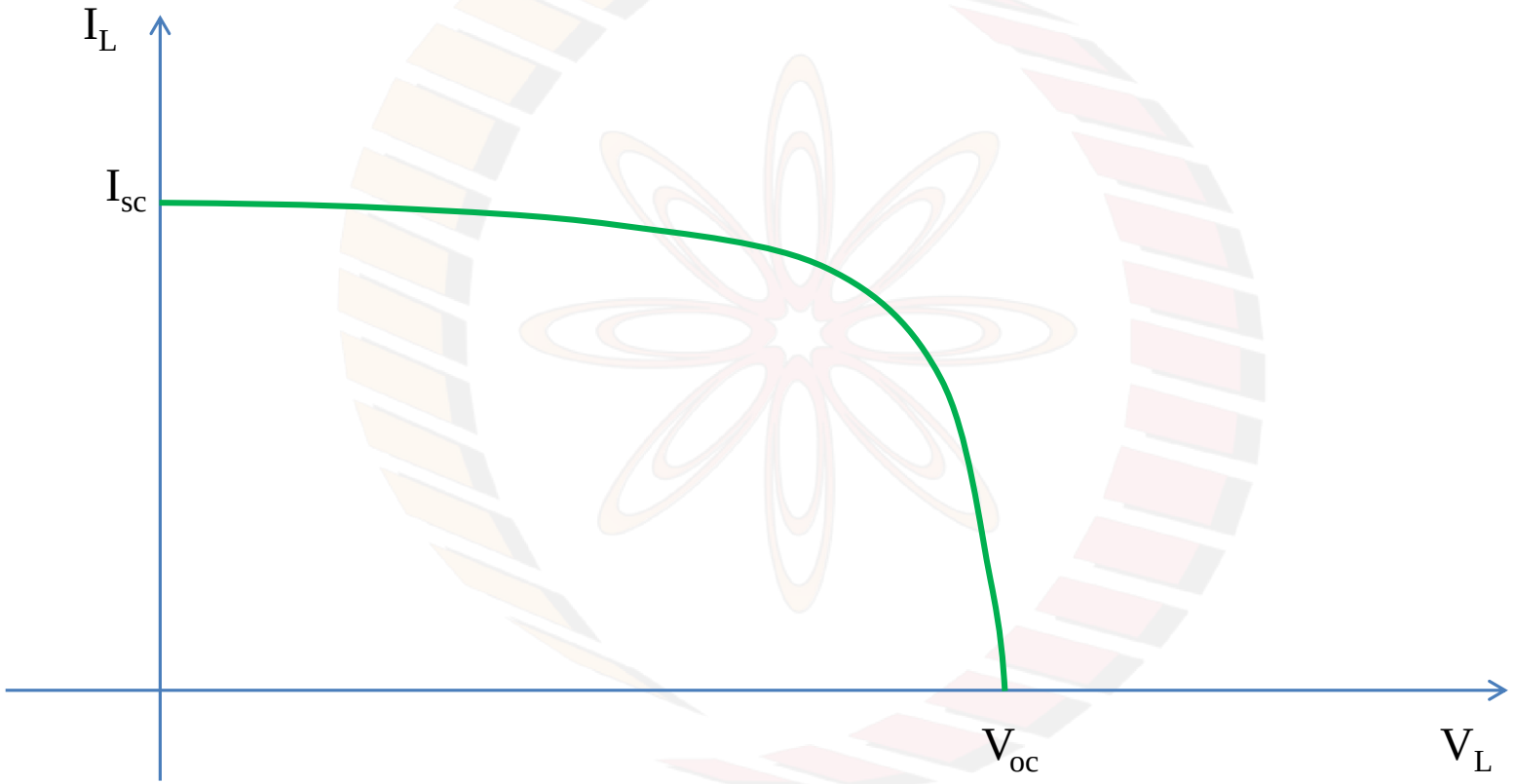
$$V_L = \frac{\gamma kT}{q}\ln\left\{\frac{I_{ph} - I_L}{I_0} + 1\right\} - I_L R_S$$

$$V_{OC} = \frac{\gamma kT}{q}\ln\left\{\frac{I_{ph}}{I_0} + 1\right\}$$

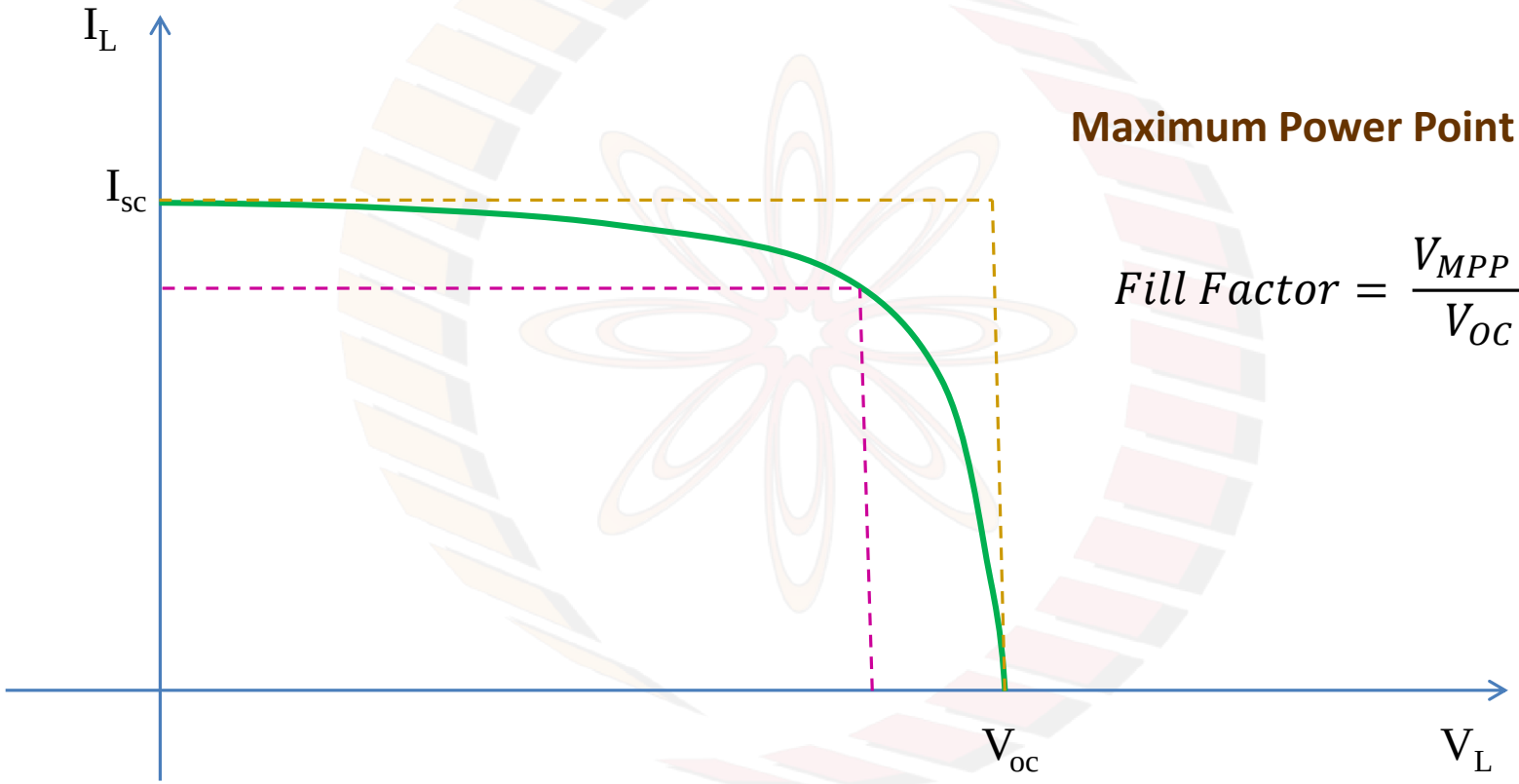
$$I_{ph} - I_d - I_{Sh} = I_L$$

$$I_L = I_{ph} - I_0\left(e^{\frac{q(V_L + I_L R_S)}{\gamma kT}} - 1\right) - \left(\frac{V_L + I_L R_S}{R_{Sh}}\right)$$

I-V characteristics



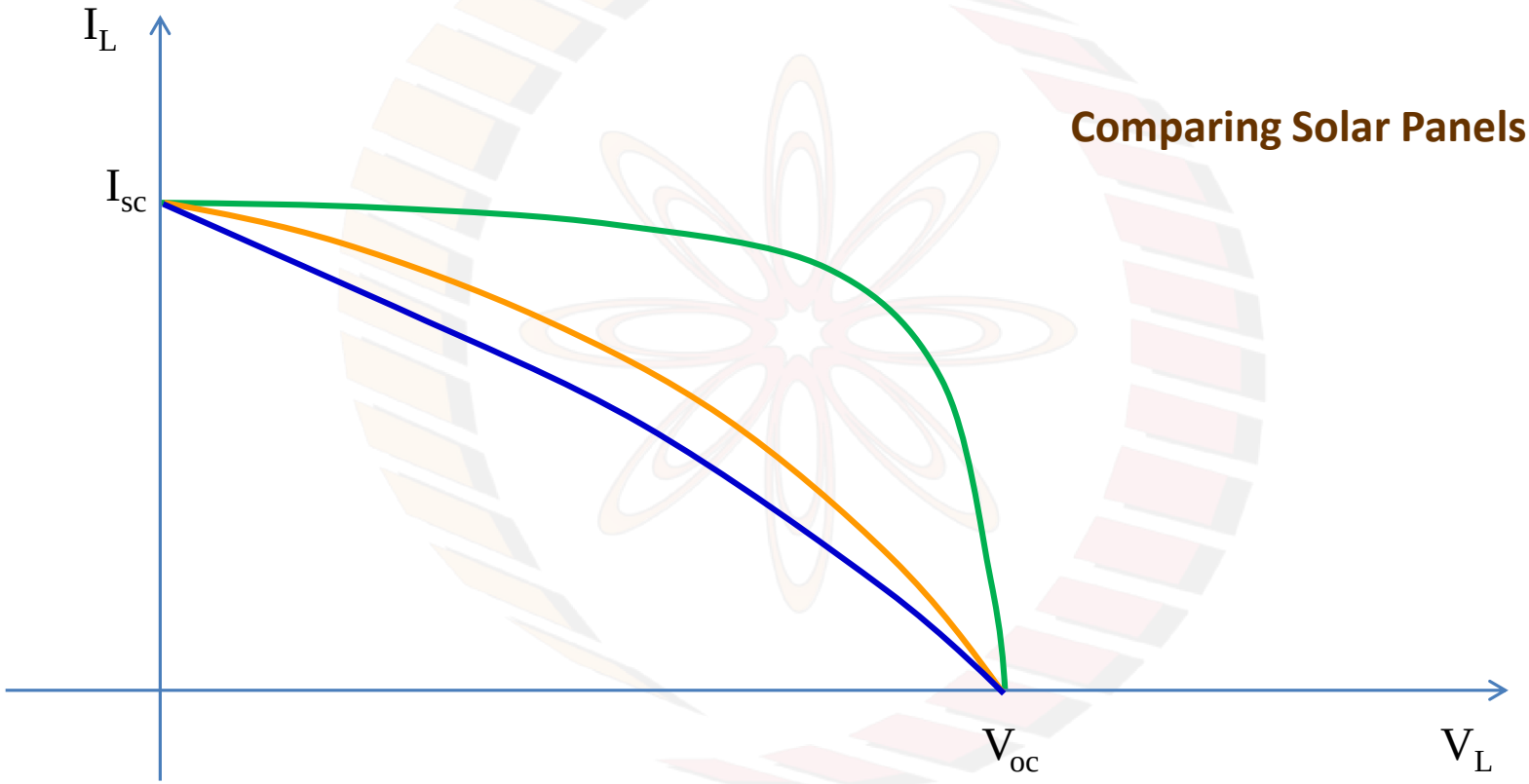
I-V characteristics



Maximum Power Point

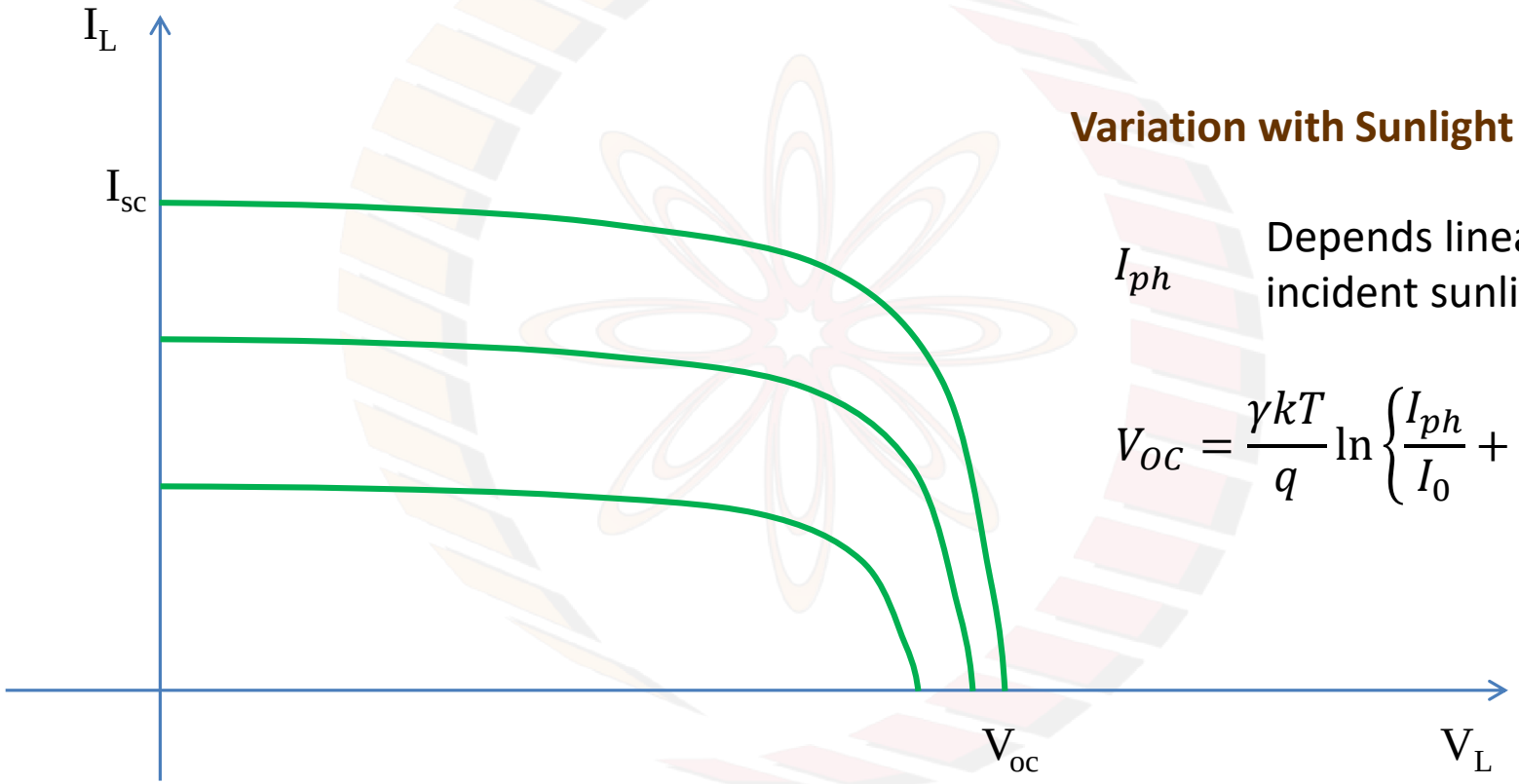
$$Fill\ Factor = \frac{V_{MPP} \times I_{MPP}}{V_{OC} \times I_{SC}}$$

I-V characteristics



Comparing Solar Panels

I-V characteristics

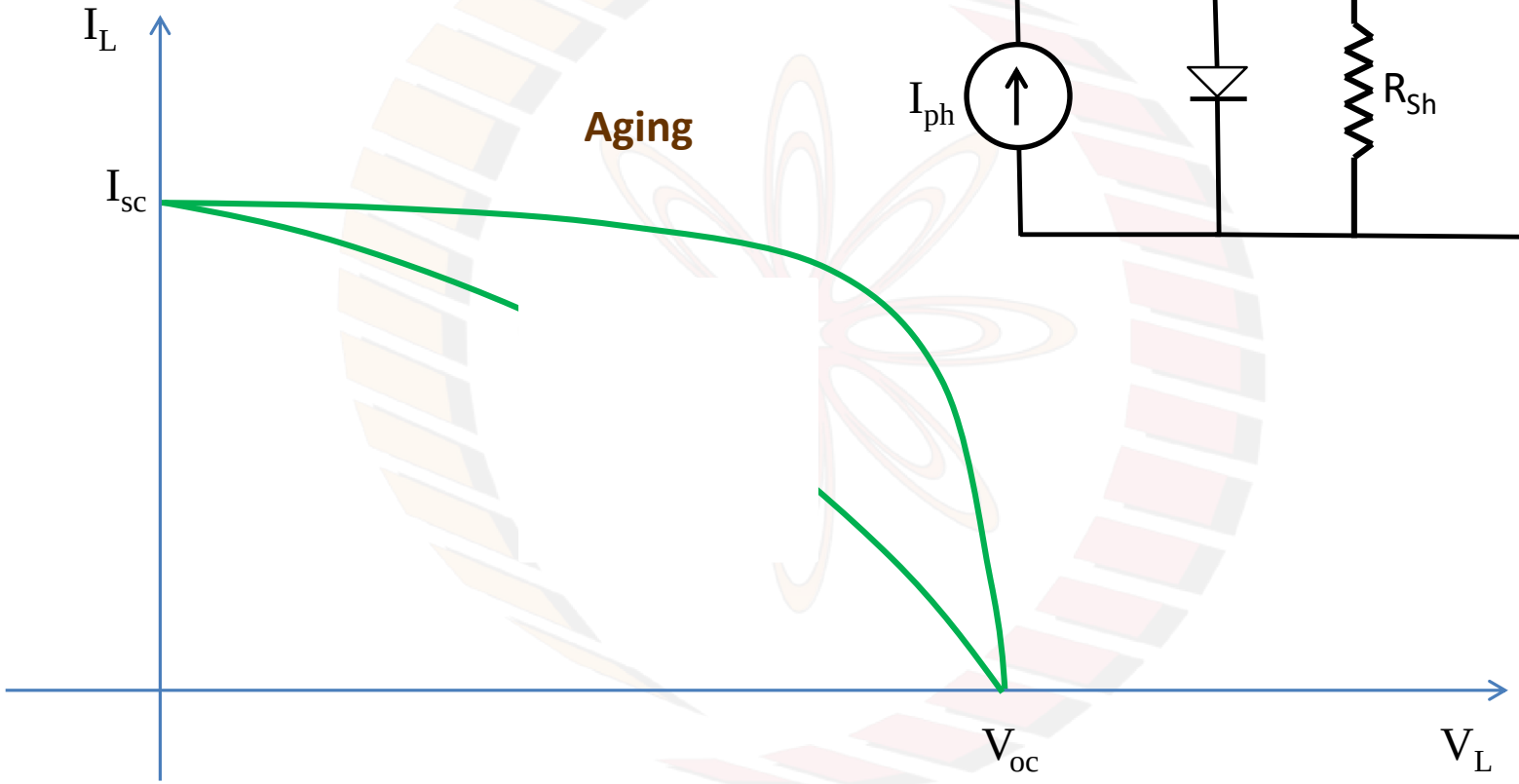


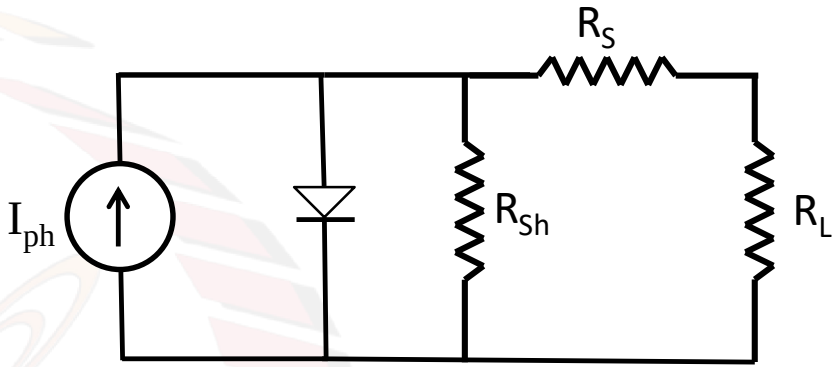
Variation with Sunlight

I_{ph} Depends linearly on incident sunlight

$$V_{OC} = \frac{\gamma kT}{q} \ln\left\{\frac{I_{ph}}{I_0} + 1\right\}$$

I-V characteristics





Conclusions:

1)The solar cell is a current source
2)I- V relationship is complicated
3)OCV is not the most important parameter
4)Fill factor of a solar cell is important
5)Solar cell must be coupled with an end use that utilizes the MPP

Solar Energy:
Solar cell construction

Learning objectives:

1) To indicate the limitations of single junction solar cells
2) To describe how solar cells are constructed
3) To describe the functioning of tandem solar cells

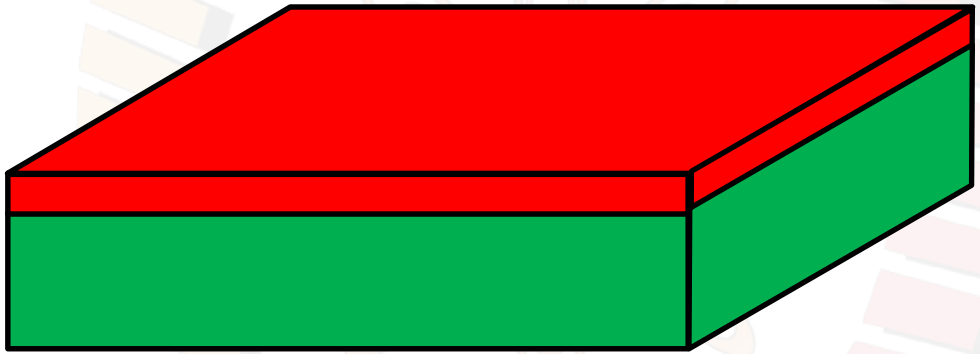
Shockley-Quiesser limit

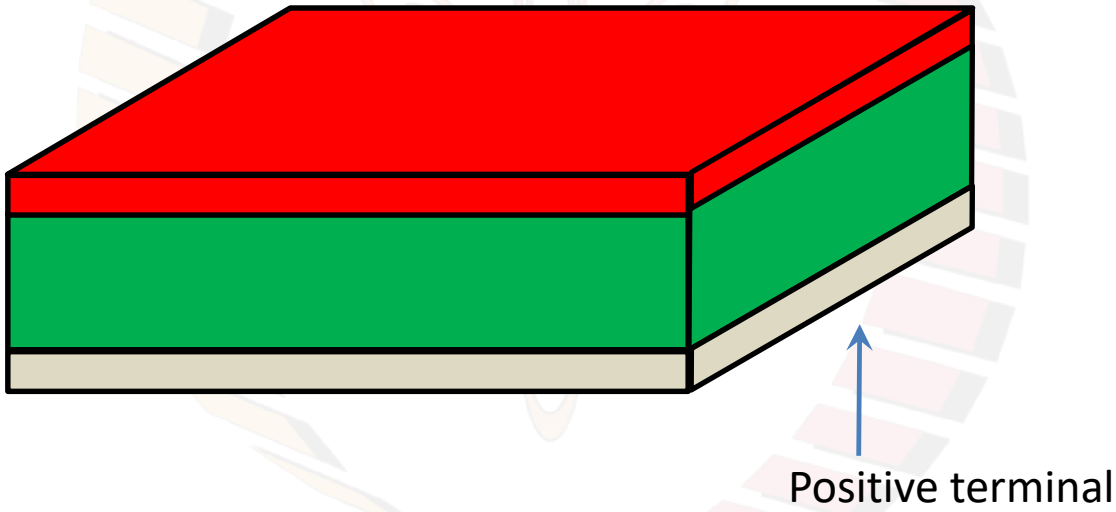
In unconcentrated, AM 1.5 Solar radiation with a band gap of 1.34 eV, 33.4 % efficiency is obtained

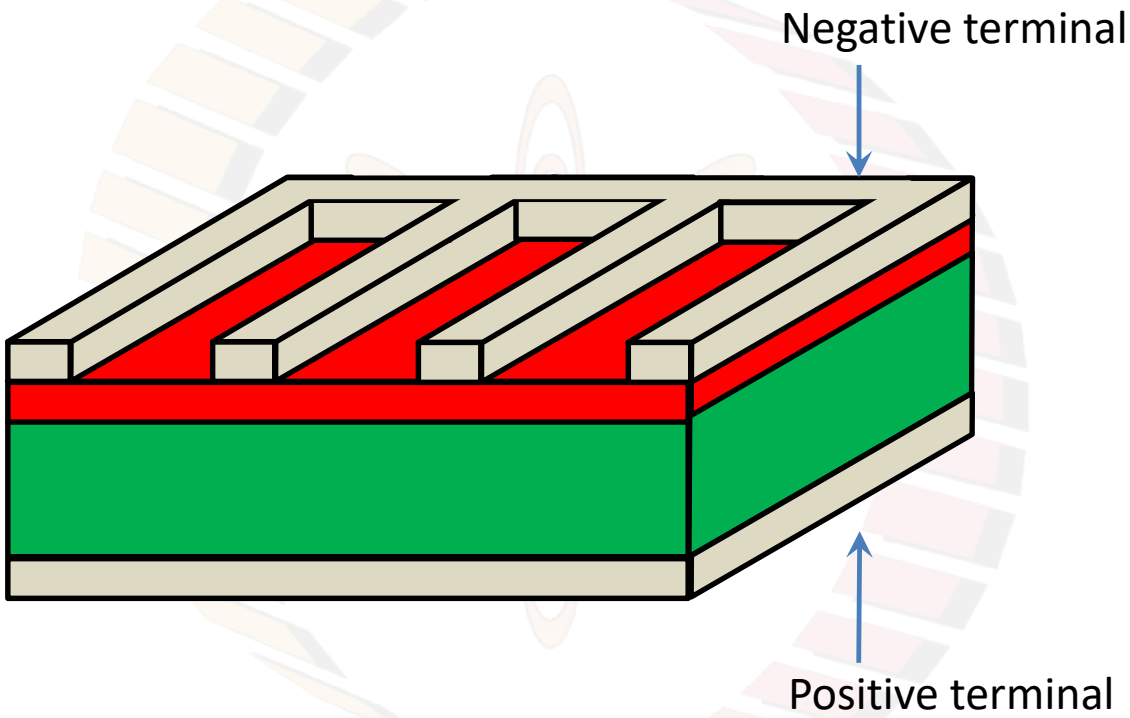
Si, 1.1 eV, 32 % efficiency is the best. Practically 24% accomplished

Air Mass Coefficient: Optical path length relative to path length vertically upward
AM 1.5 typically used for evaluating panels

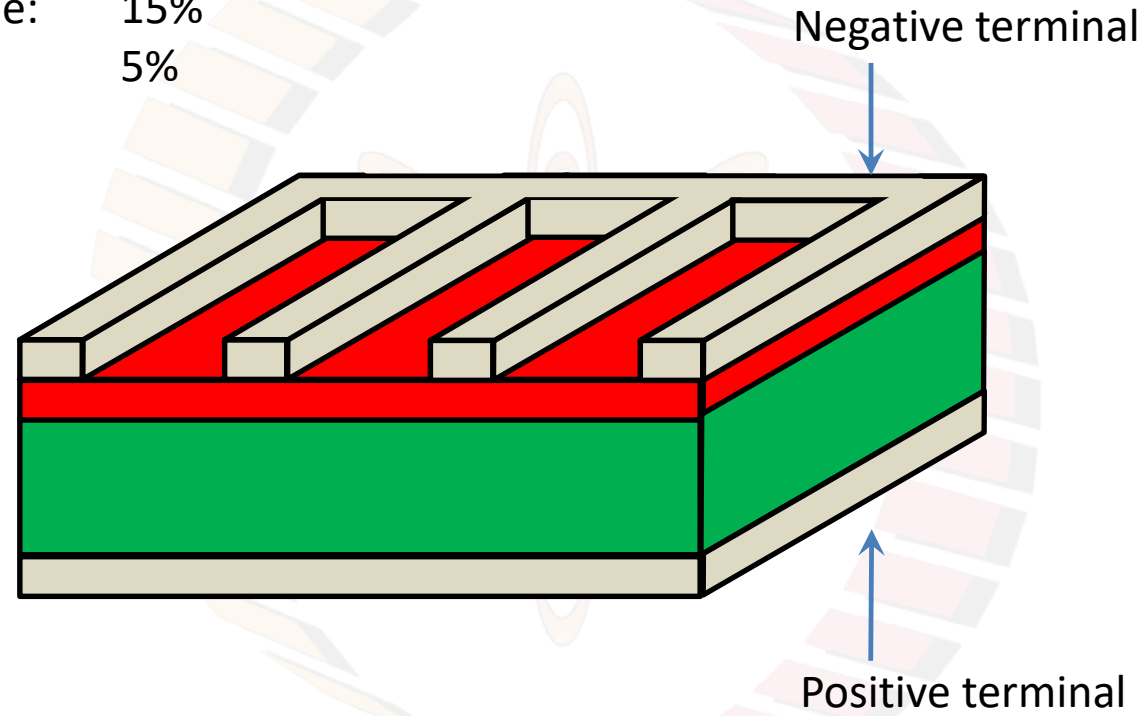
Blackbody radiation	7% (At room T, actual T~ 75 ^{o}C)
Recombination losses	10%
Spectrum losses	19% unabsorbed, 33% excess ν, total 52%



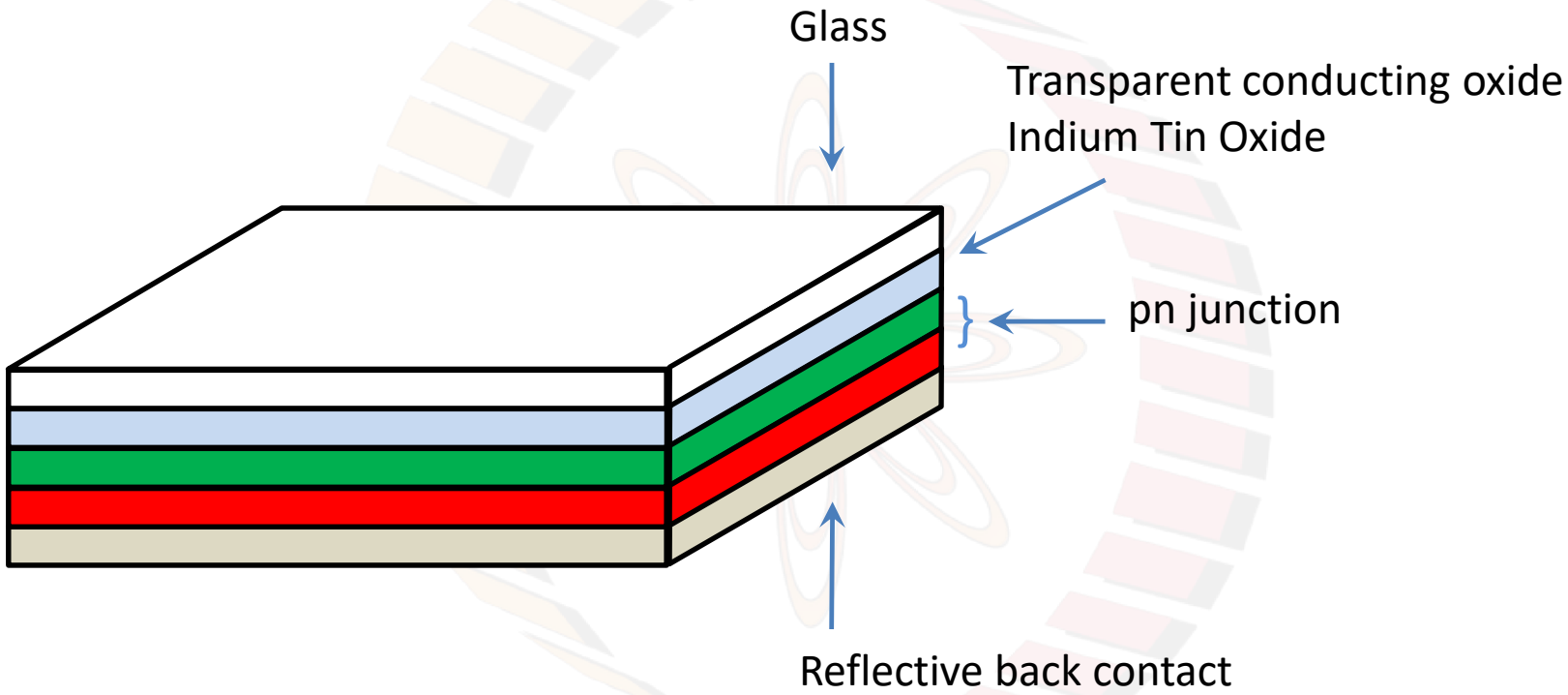

Positive terminal


Negative terminal
Positive terminal

Single crystalline: 25%
Poly crystalline: 15%
Amorphous: 5%



Amorphous Silicon Solar Cell



Anti-reflective coatings

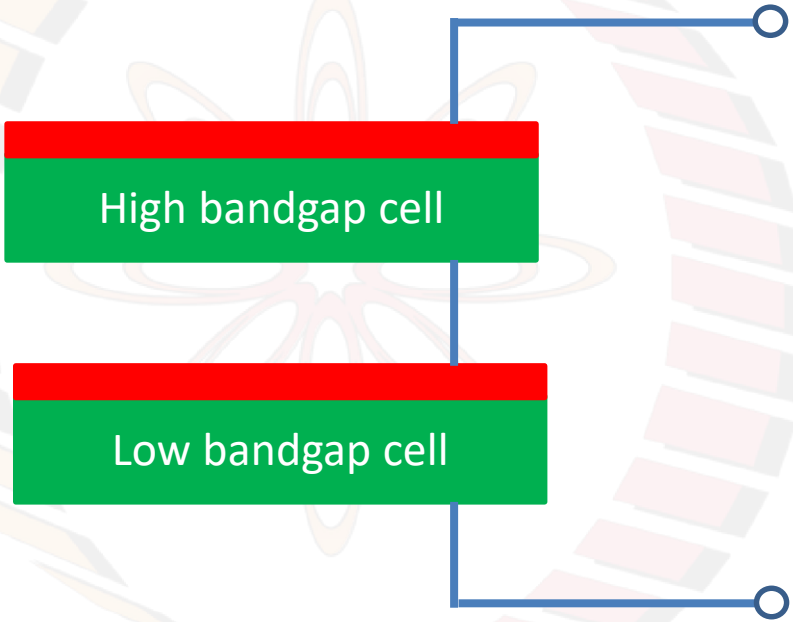
$$n_1 = \sqrt{n_0 n_s}$$

Glass n_s = 1.5

Air n_0 = 1

Film n_1 = 1.225

Tandem Cells



With several tandem cells and concentrated sunlight, theoretically > 80% efficiency possible

Visible Spectrum Wavelength:	400 nm (violet) to 700 nm (red)
Corresponding band gaps:	3.1 eV to 1.8 eV

PbS, a direct bandgap semiconductor

Bandgap of bulk PbS:	0.41 eV (3020 nm)
Bandgap of nanocrystalline PbS:	Can be varied to 4.0 eV

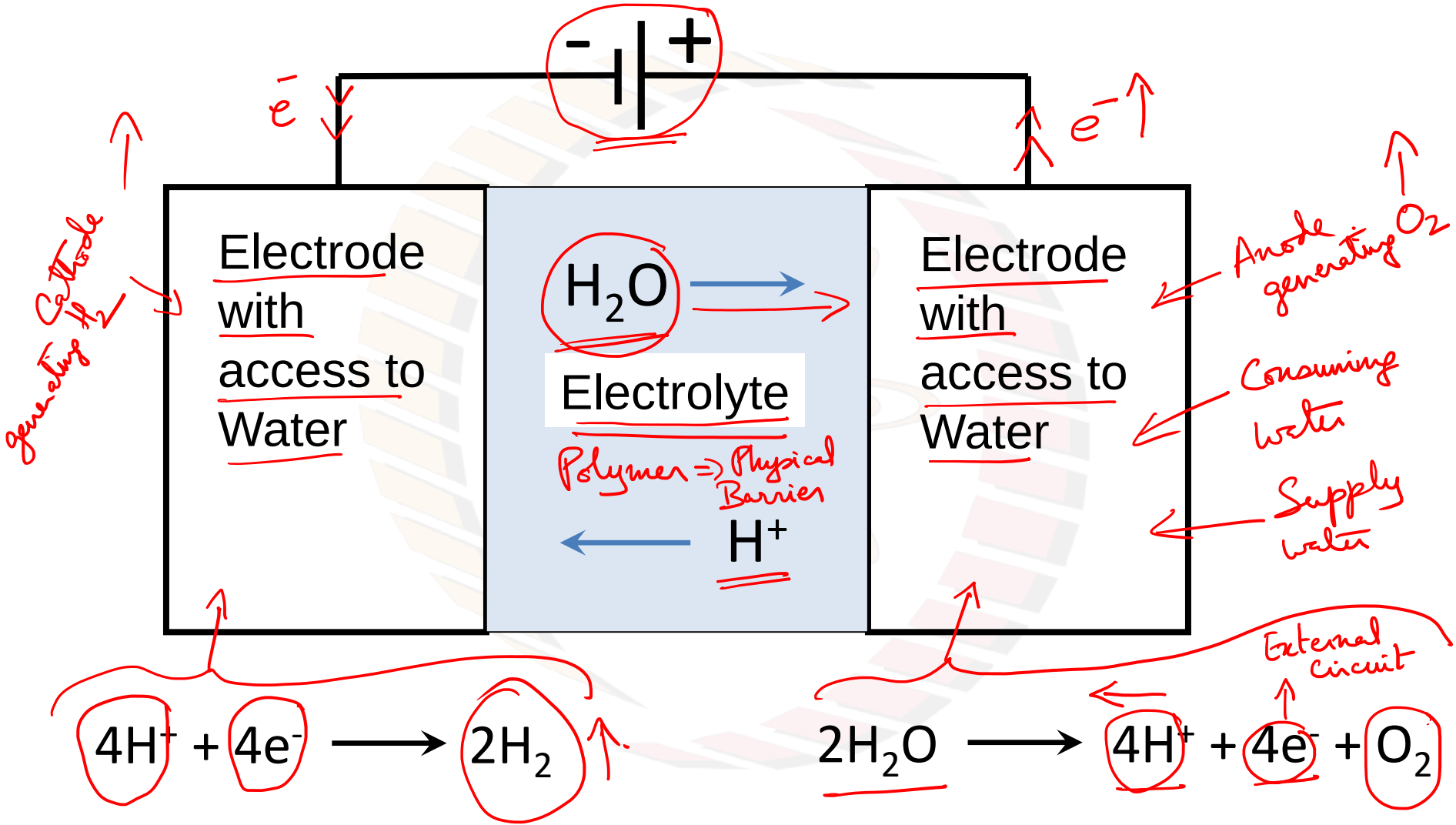
Conclusions:

1) Parts of a solar cell are designed to increase the efficiency of the solar cell
2) Shockley-Quiesser limit indicates the limitation of a single junction solar cell
3) Tandem solar cells can overcome these limitations

Solar Energy:
Solar photocatalysis

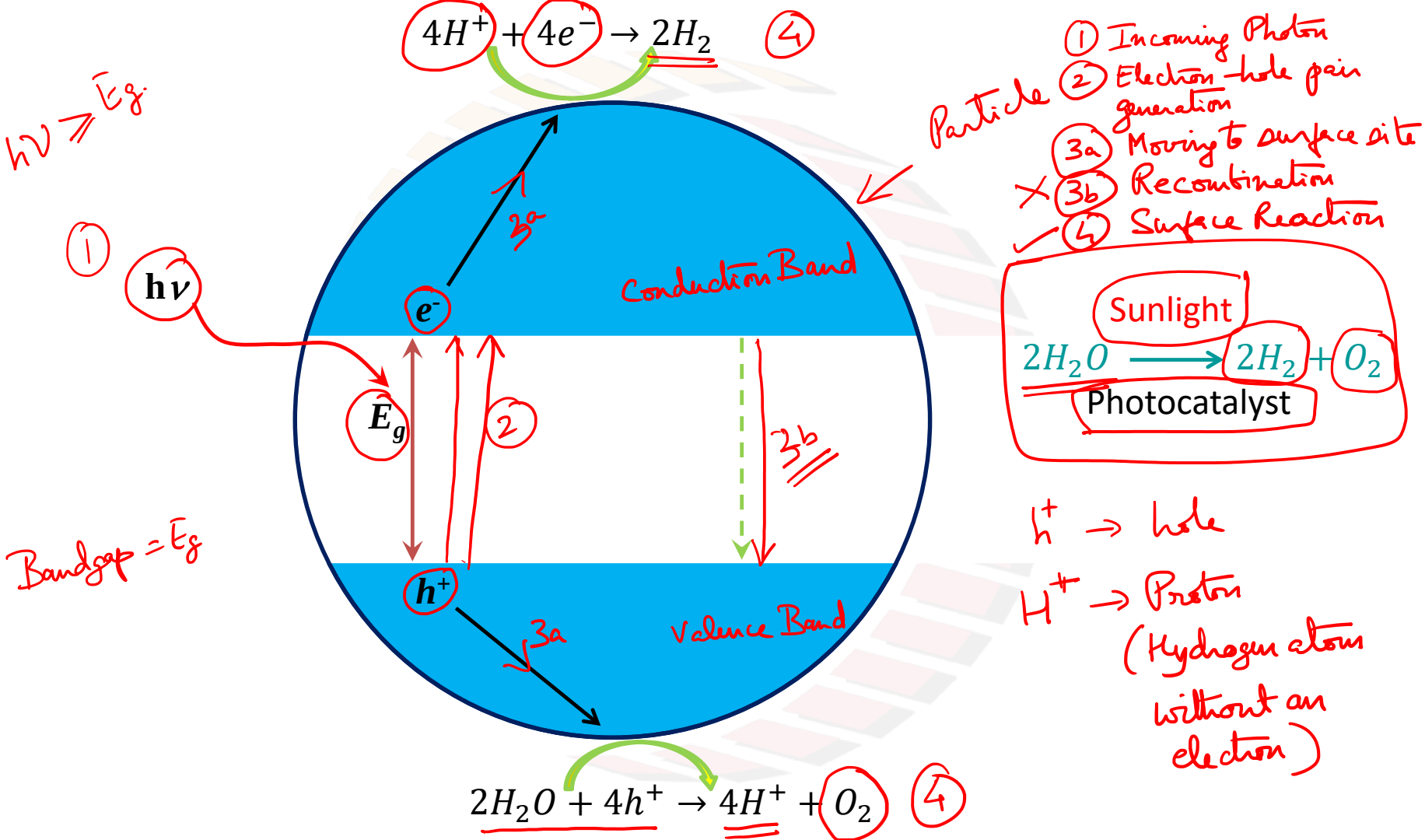
Learning objectives:

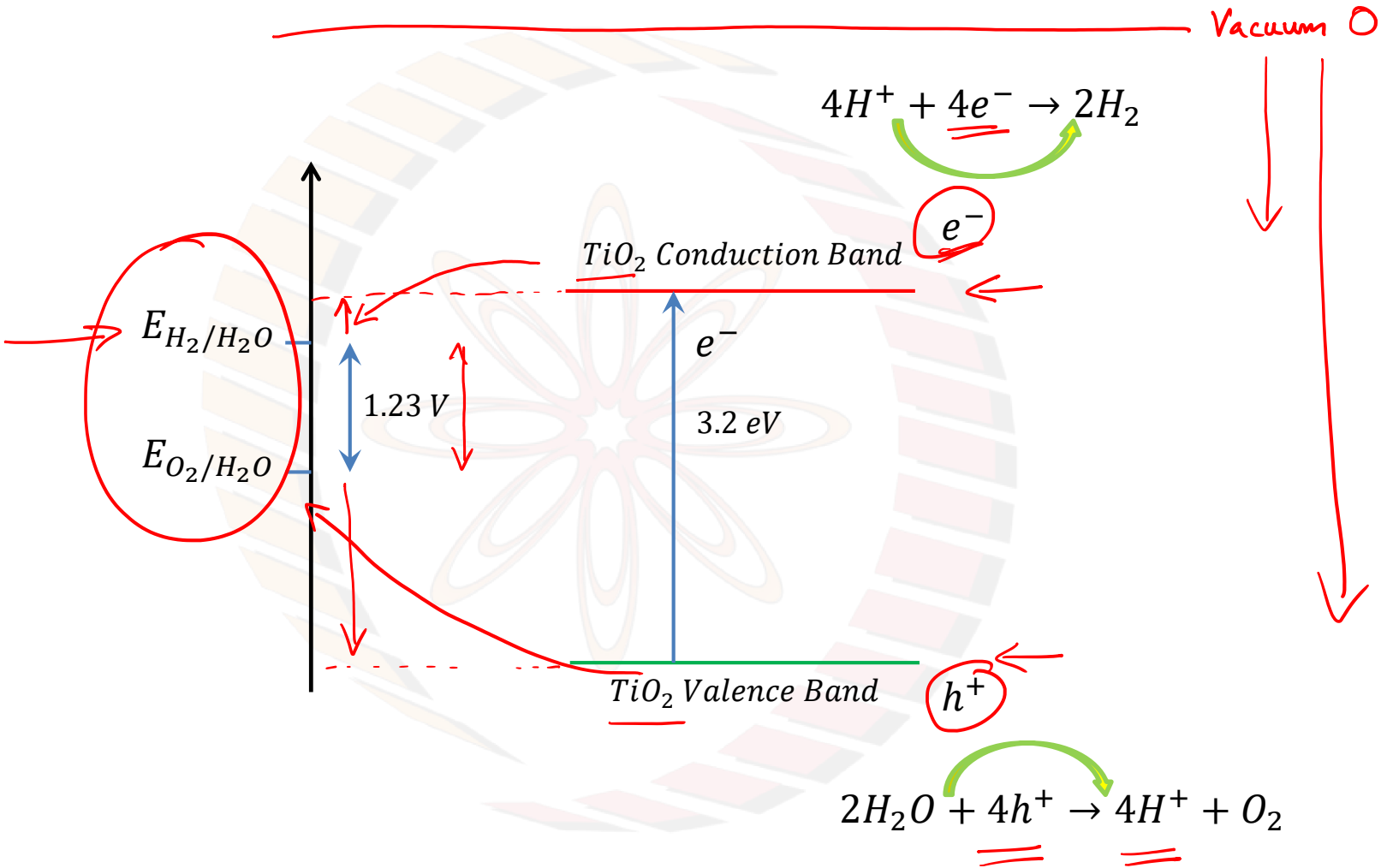
1) To describe the principle of photocatalysis
2) To indicate the various energy considerations associated with photocatalysis
3) To list important challenges that need to be address with respect to photocatalysis

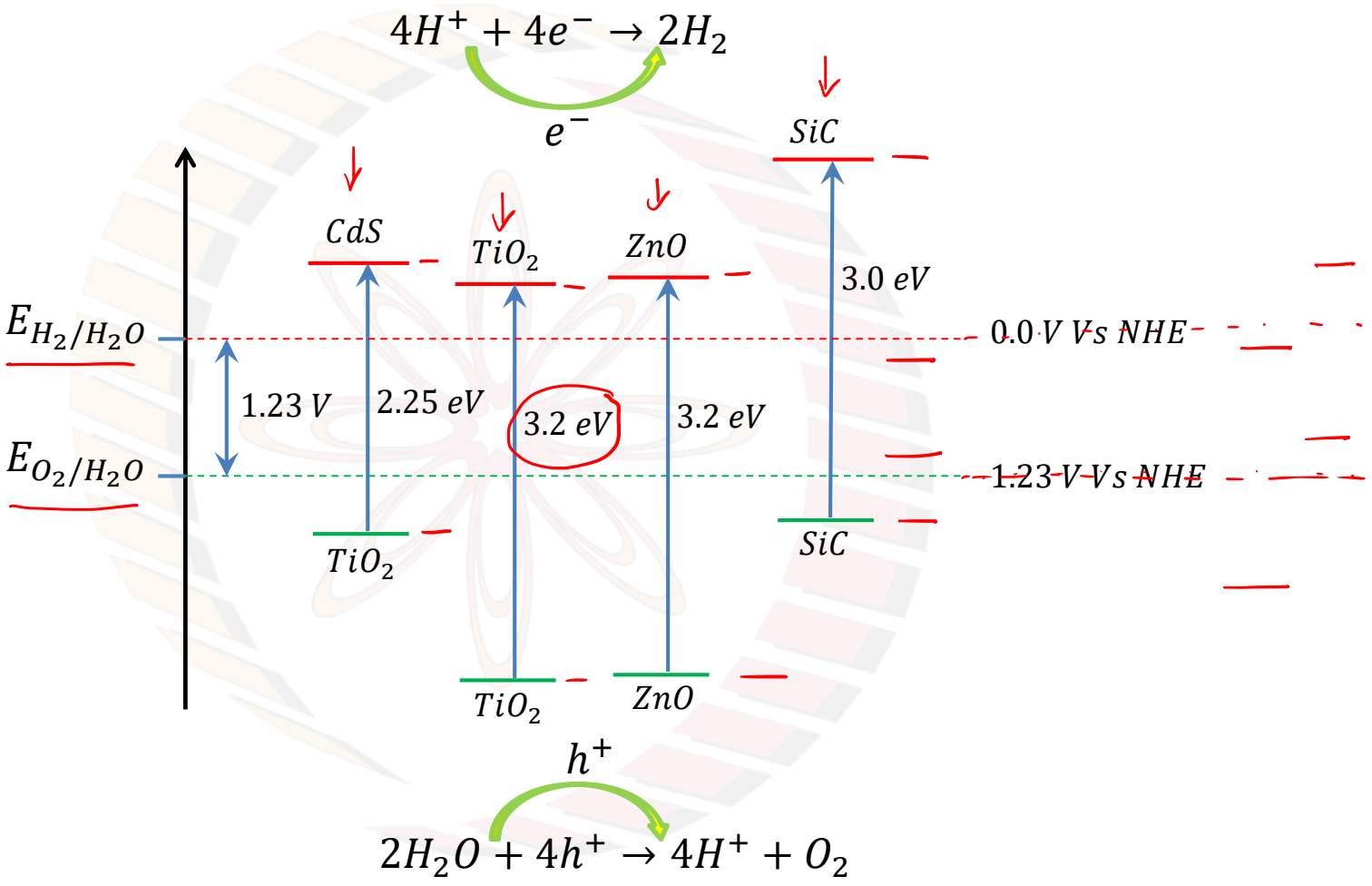

Electrode with access to Water
H_2O
Electrolyte
Polymer ⇒ Physical Barrier
H^+
Electrode with access to Water
Cathode generating H_2
Anode generating O_2
Consuming water
Supply water
External circuit
$4H^+ + 4e^- \longrightarrow 2H_2$
$2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

Photochemical: Light is directly used to enable the reaction

Photo-electrochemical: Photochemical reaction that involves the flow of current in an external circuit


$4H^+ + 4e^- \rightarrow 2H_2$
4
$h\nu \geq E_g$
Particle
1 Incoming Photon
2 Electron-hole pair generation
3a Moving to surface site
3b Recombination
4 Surface Reaction
1
$h\nu$
e^-
3a
Conduction Band
E_g
2
3b
h^+
3a
Valence Band
Sunlight
$2H_2O \rightarrow 2H_2 + O_2$
Photocatalyst
Bandgap = E_g
h^+ → hole
H^+ → Proton
(Hydrogen atom without an electron)
$2H_2O + 4h^+ \rightarrow 4H^+ + O_2$
4


Vacuum 0
$4H^+ + 4e^- \rightarrow 2H_2$
e^-
TiO_2 Conduction Band
E_{H_2/H_2O}
E_{O_2/H_2O}
1.23 V
e^-
3.2 eV
TiO_2 Valence Band
h^+
$2H_2O + 4h^+ \rightarrow 4H^+ + O_2$

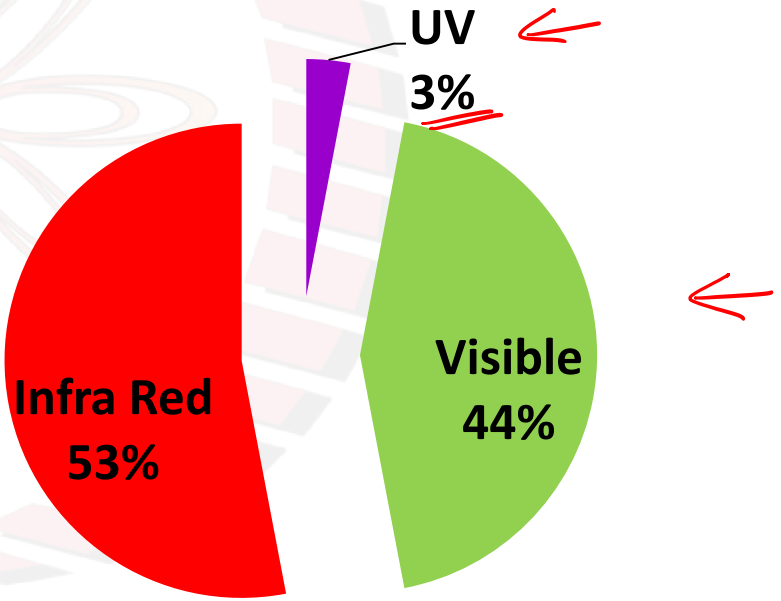

$4H^+ + 4e^- \rightarrow 2H_2$
e^-
CdS
TiO_2
ZnO
SiC
3.0 eV
E_{H_2/H_2O}
0.0 V Vs NHE
1.23 V
2.25 eV
3.2 eV
3.2 eV
E_{O_2/H_2O}
1.23 V Vs NHE
TiO_2
TiO_2
ZnO
SiC
h^+
$2H_2O + 4h^+ \rightarrow 4H^+ + O_2$

Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)

Corresponding band gaps: 3.1 eV to 1.8 eV

E_g for TiO_2 : 3.2 eV

97.1 Visible + IR



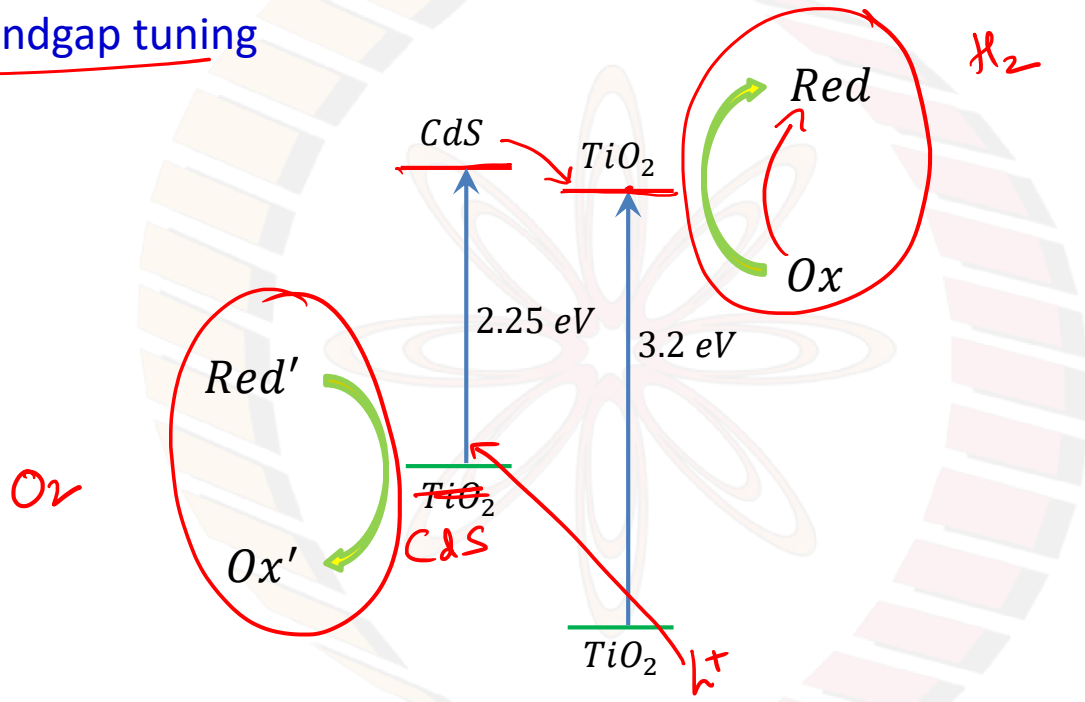
Limitations:

1) Only UV part of spectrum utilized
2) Electron hole recombination
3) Reverse reaction is easy

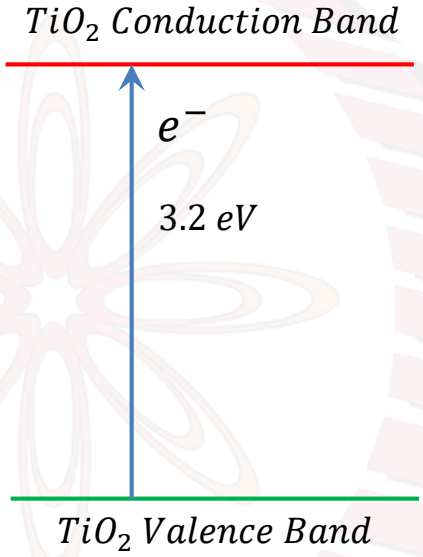
Approaches:

1) Bandgap tuning
2) Adding sacrificial agent, reduce particle size
3) Presence of co-catalyst

Bandgap tuning



Adding sacrificial agent to reduce recombination



$$4H^+ + 4e^- \rightarrow 2H_2$$

e^-

$14H^+ + 14e^- \rightarrow 7H_2$

Smaller particle size reduces chance of encountering a defect enroute surface

$$C_3H_8O_3 + 14h^+ + 3H_2O \rightarrow 14H^+ + 3CO_2$$

$$2H_2O + 4h^+ \rightarrow 4H^+ + O_2$$

Conclusions:

1) Photocatalysis can enable direct production of Hydrogen from water
2) Matching the bandgaps of materials to the voltage window needed for splitting of water
3) Separation of the generated hydrogen and oxygen has to be enabled effectively