Junctions and Contacts

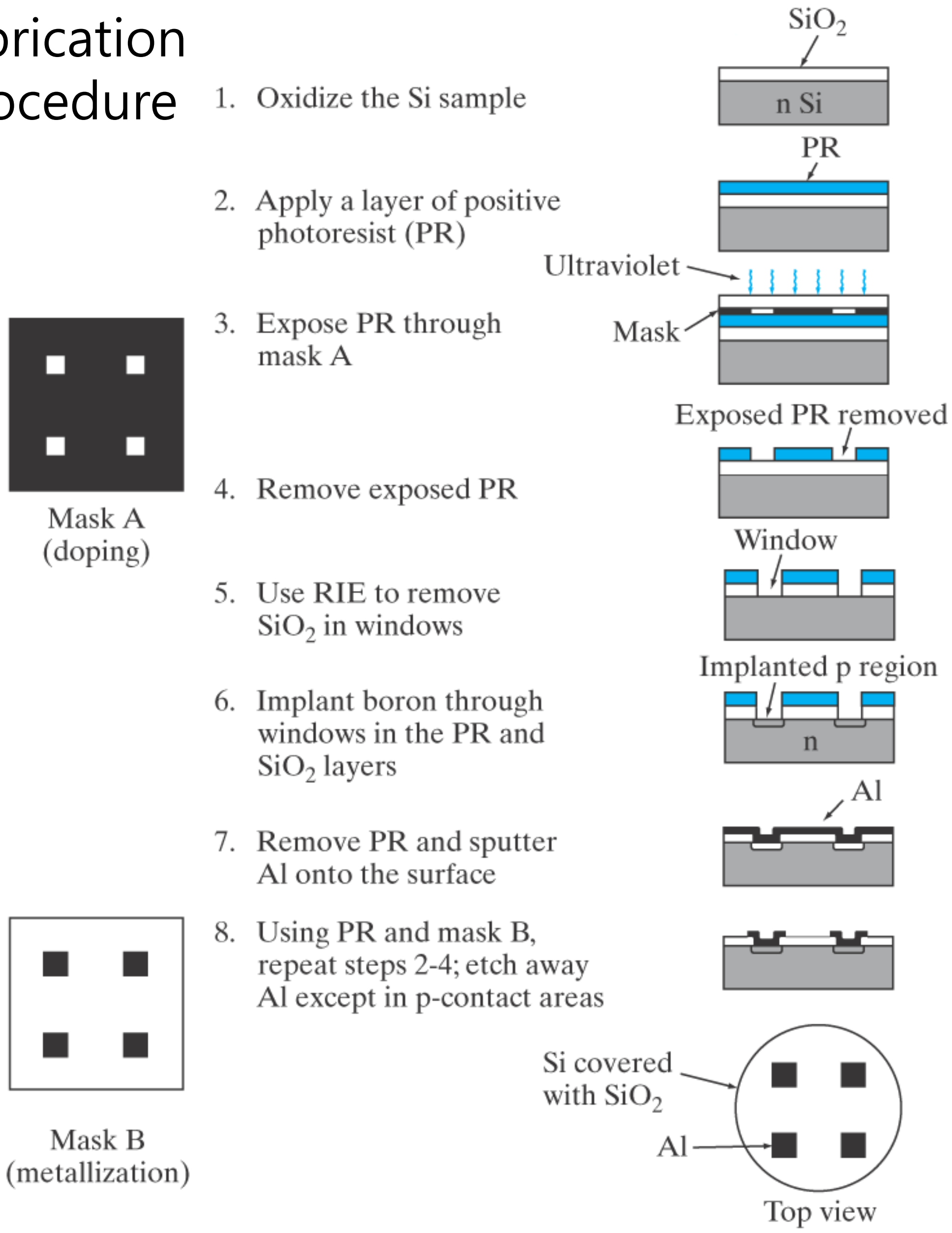
PN Junction is the simplest electronic device.

- Two PN junctions with a MOSCAP form a MOSFET (metal-oxide-semiconductor field effect transistor).
- Single PN junction using direct band gap materials can work as a LED (light emitting diode).
- Single PN junction (direct and indirect) can be a photodetector (diode) or photovoltaic (diode).
- All devices require metal contacts (metal-semiconductor junction) for interconnection.

Let’s try to understand the operation mechanism and structure of PN diodes and metal contacts.

PN Junction Fab

Fabrication Procedure



1. Oxidize the Si sample
2. Apply a layer of positive photoresist (PR)
3. Expose PR through mask A
4. Remove exposed PR
5. Use RIE to remove SiO_2 in windows
6. Implant boron through windows in the PR and SiO_2 layers
7. Remove PR and sputter Al onto the surface
8. Using PR and mask B, repeat steps 2-4; etch away Al except in p-contact areas

Wet oxidation, CVD deposition

Dry oxidation, Ebeam evaporation

Positive PR vs Negative PR

Mask alignment, UV exposure

Development using developer

Dry etching using CF_4 (SF_6, O_2, CCl_4)

Diffusion

Metal deposition

Thermal, Ebeam, Sputter

Metal etching

Top contact – p
Bottom contact – n
(n-type substrate)

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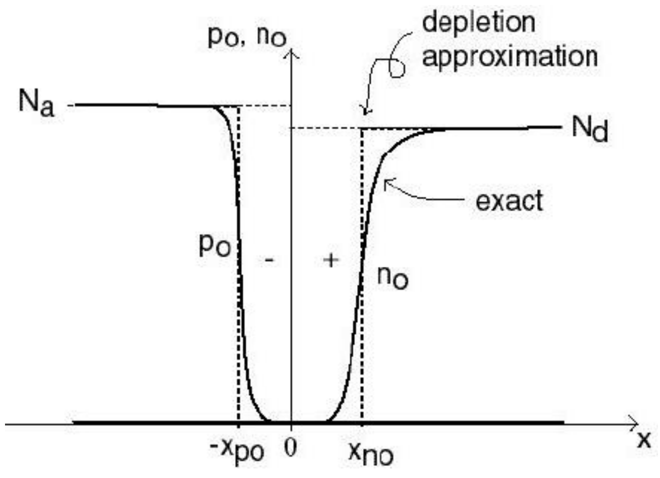
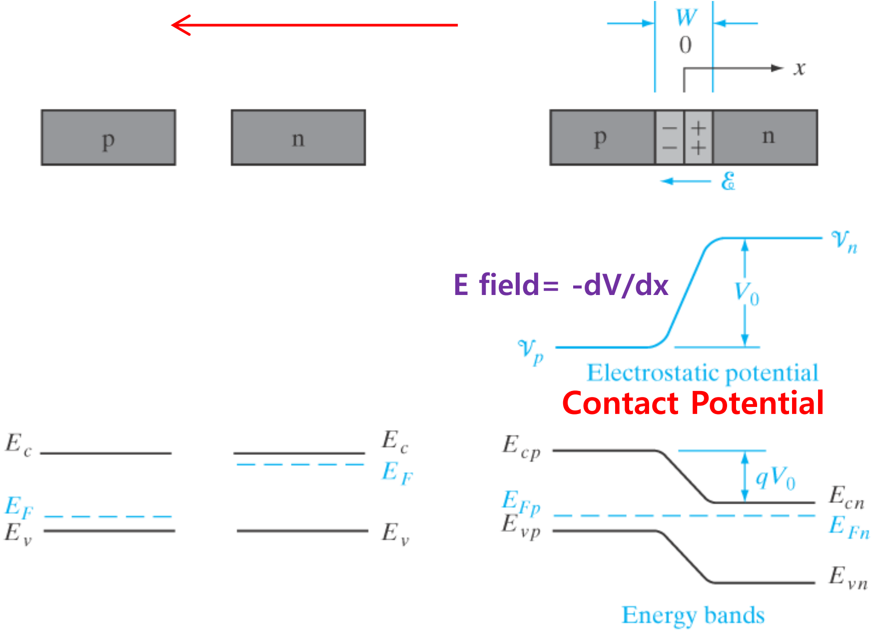


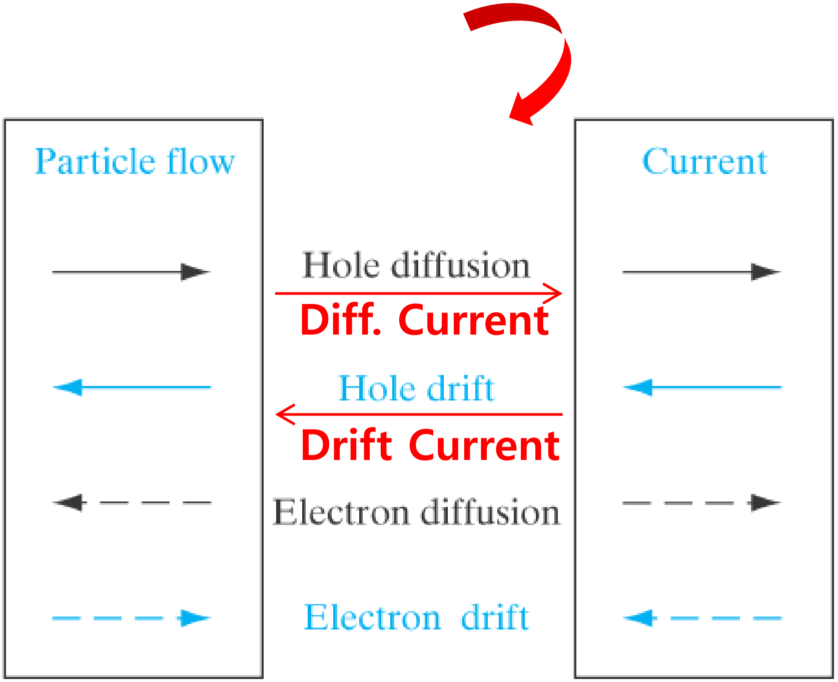
- The uncompensated doner ions (+) and acceptor ions (-) create positive space charge near n side region and negative space charge near p side region. The resulting electric field E, which is directed from n side to p side, cause the drift current with opposing direction to the diffusion current.
- The current flow is as follows:

Electric Field



E field= -dV/dx

Contact Potential



Diff. Current

Drift Current

Since no net current can flow at equilibrium, the drift current and diffusion current cancel out each other.

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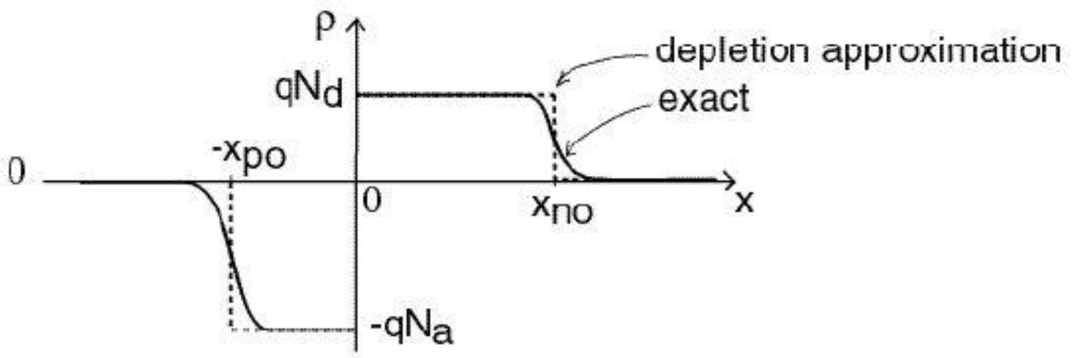
Space Charge



- There are very few carriers within the depleted transition region since the built in electric field sweeps carriers away. Therefore with a good approximation, we can assume that the only charges in space charge region are uncompensated doner and acceptor ions.
- The charge density within the space charge region (width of W = $x_{n0}+x_{p0}$) is in the above graph. Note that x_{n0} and x_{p0} can be different due to the doping concentration (low doping leads to larger depletion length). But the net charge amount in n and p region should be same, i.e. $qAx_{p0}N_a = qAx_{n0}N_d$
- The space charge region width W = $x_{n0}+x_{p0}$ is as follows:

$$W = x_{po} + x_{no} = \sqrt{\frac{2\varepsilon_s \phi_B \left(N_a + N_d\right)}{qN_aN_d}}$$

Where ε_s is permittivity of semiconductor and ϕ_B is the contact potential; If N_a and N_d increases, W decreases.

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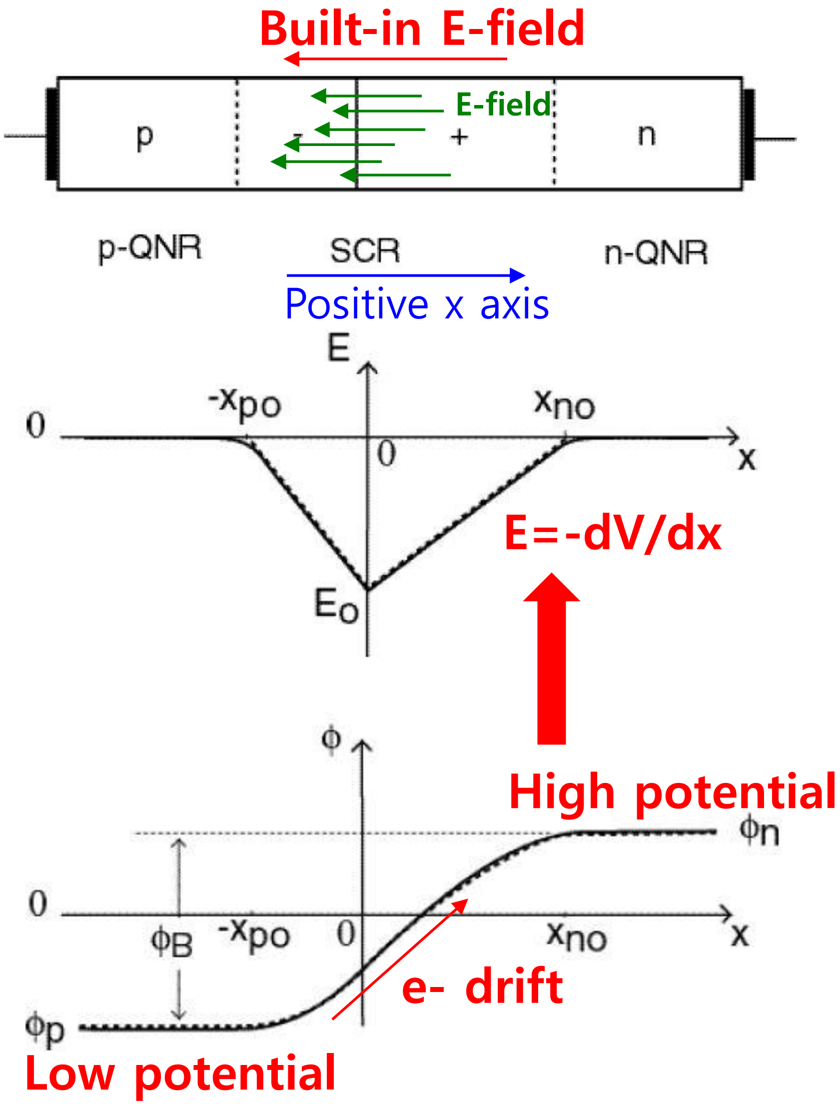

Built-in E-field

Positive x axis

E=-dV/dx

High potential

e- drift

Low potential

- The electric field E has two slopes. There is a maximum value of the field E_0 at x=0, since all the electric flux lines pass through x=0 point.

- E is negative everywhere in space charge region, since the E field direction is from n side to p side.

- The electric field goes to zero at the edges of the transition region. Therefore the shape of E field is like left graph (triangle).

- By integrating E field, the potential is calculated as the left graph. (E=-dV/dx, integrate from $-x_{p0}$ to x_{n0})

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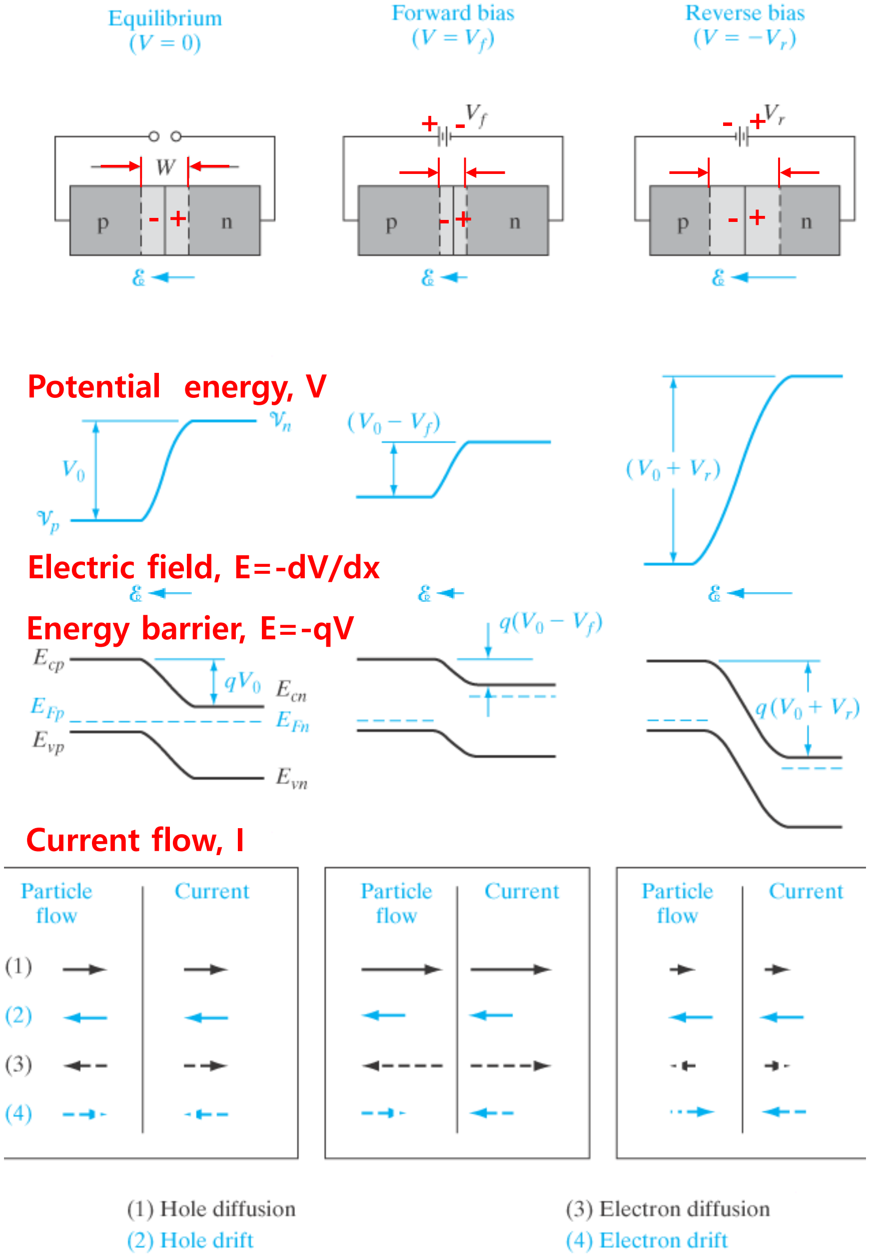
Junction with Bias

- Now let’s apply a bias over the junction.
- The applied voltage bias V appears across the transition region of the junction rather than in the neutral n and p regions, since the resistance is small in n and p region and only small voltage drop is maintained outside the space charge region.
- We shall take the applied bias V to be positive (forward bias) when the external bias is positive on the p side relative to the n side. Vice versa for reverse bias.
- Since the applied voltage changes the electrostatic potential barrier and thus the electric field within the transition region, we would expect changes in the various components under external biases, such as current, band structure and depletion region width at the junction.



- The electrostatic potential barrier at the junction (V_0) is lowered by a forward bias V_f from the equilibrium value V_0 to V_0-V_f, since forward bias (positive to p side (N_a^-) and negative to n side (N_d^+)) raises the potential of p side relative to n side.
- By applying reverse bias (positive to n side (N_d^+) and negative to p side (N_a^-)), the opposite happens and V_0 changes to V_0+V_f.
- The electric field E=-dV/dx changes accordingly with V change, smaller E with forward bias and larger E with reverse bias.
- From the change in E field, we can easily deduce the change in depletion width W, smaller W with forward bias and larger W with reverse bias.
- The energy band is a function of potential V. The “height of energy barrier” = q × “height of potential barrier”. (E=-qV)
- The Fermi level deep inside each neutral region is essentially the equilibrium value. (no current at equilibrium and flat Fermi level).
- Therefore shifting energy band under applied bias separate originally flat Fermi level (now we have current flow). Under forward bias, electron is supplied to n side, which raises Fermi level of n side, while the opposite under reverse bias.

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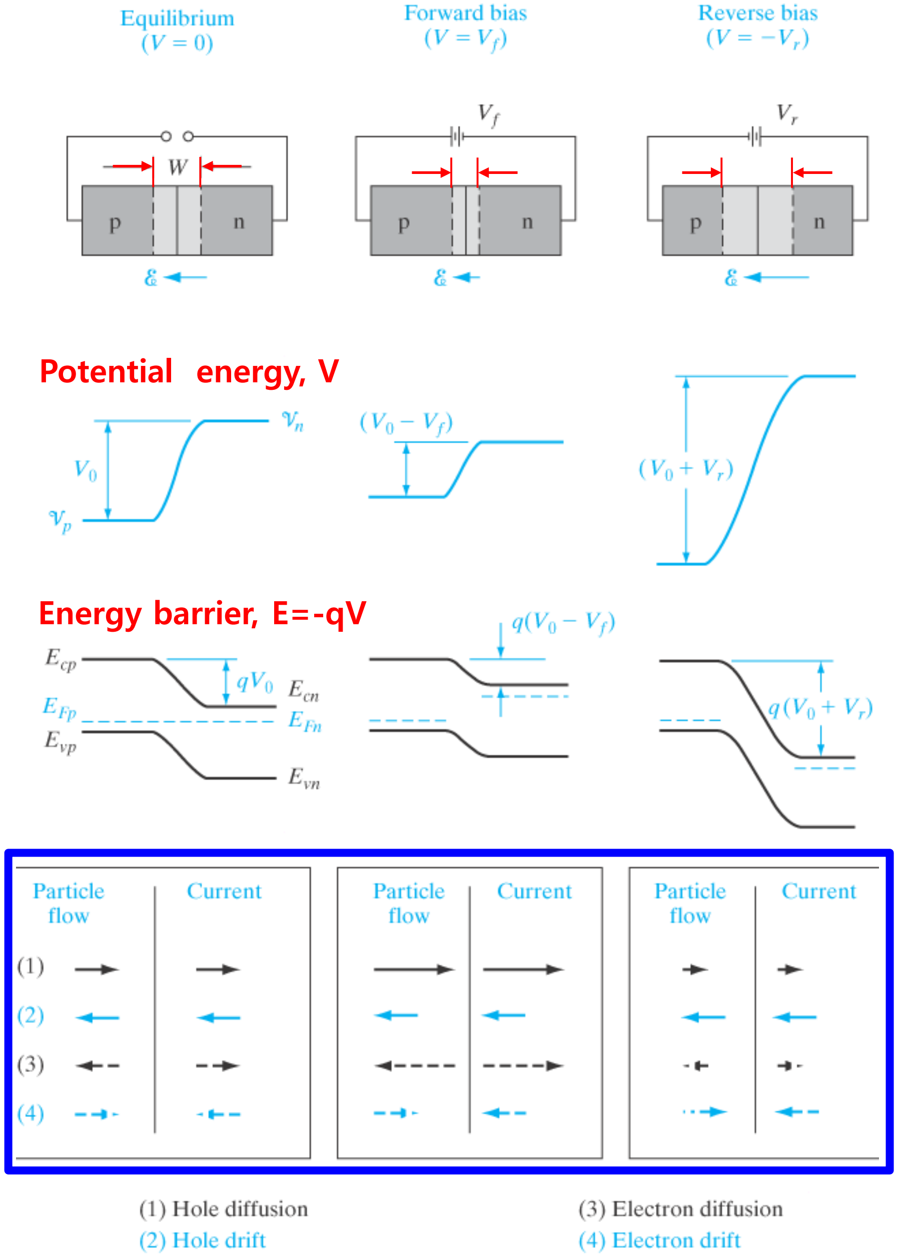

- The diffusion current is composed of majority carriers (electrons in conduction band on the n side and holes in valence band on the p side).
- With forward bias, the energy barrier is lowered, therefore more electrons in CB can diffuse from n to p side and more holes in VB from p to n side.
- With reverse bias, the energy barrier is raised and we will have less diffusion current.
- The drift current is relatively insensitive to the energy barrier. Even though higher electric field increases the possibility of carrier sweep, the bottle neck is in the generation of electron hole pair via thermal EHP generation. I.e. the drift current does not depend on how fast carriers are swept but on how many carriers are swept. Therefore to a good approximation, the electron and hole drift current are independent of applied voltage.
- To supply minority carriers for drift current, EHP should be generated in the p and n neutral regions within one diffusion length from the space charge region. Thermal excitation is not much. However optical excitation is much larger, which can work for the photodiodes (camera).

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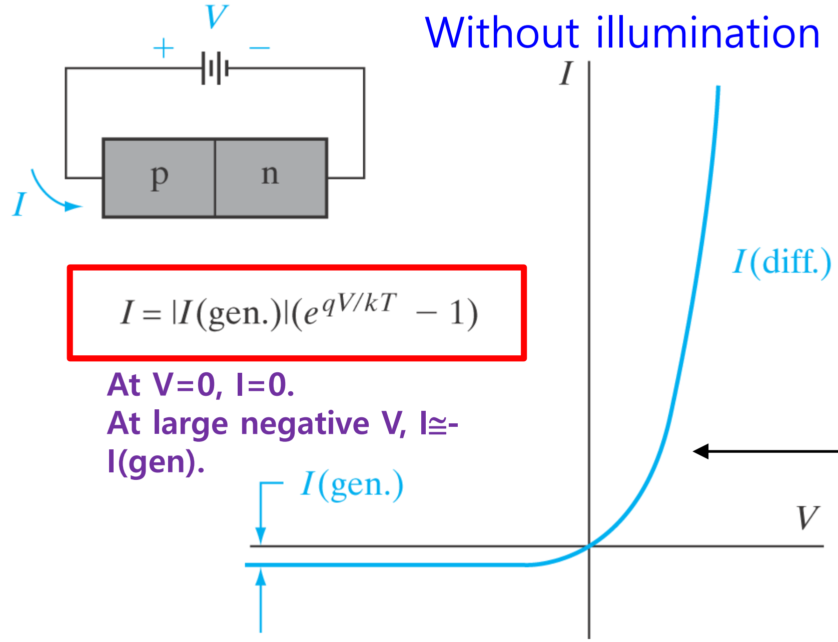
Optical EHP Generation

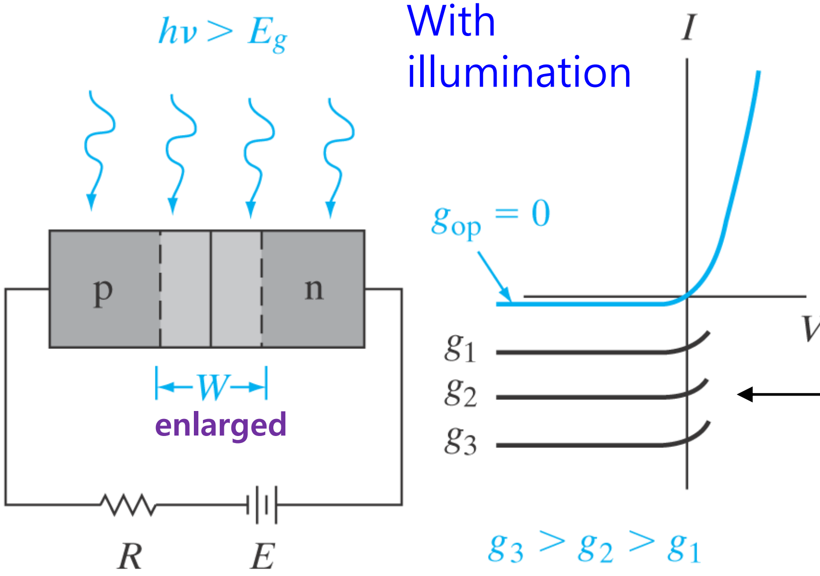
Without illumination



$$I = |I(\text{gen.})|(e^{qV/kT} - 1)$$

At V=0, I=0.
At large negative V, I≅-I(gen).

With illumination



- Total current crossing the junction is composed of the sum of the diffusion and drift components.
- The net current crossing the junction at equilibrium is zero (drift=diffusion current, cancel out) and the Fermi level is flat.
- Under reverse bias, both diffusion components are negligible due to high potential barrier and the only current is small generation current (thermal). Therefore the absolute current amount under reverse bias is very small, while the forward current is exponentially increasing with applied bias (lowering potential barrier).
- But applying external illumination that causes electron hole pair generation by photon absorption dramatically increases EHP amount. Therefore the reverse current increases with increased illumination, which can be used for photodetectors (photodiodes, camera).

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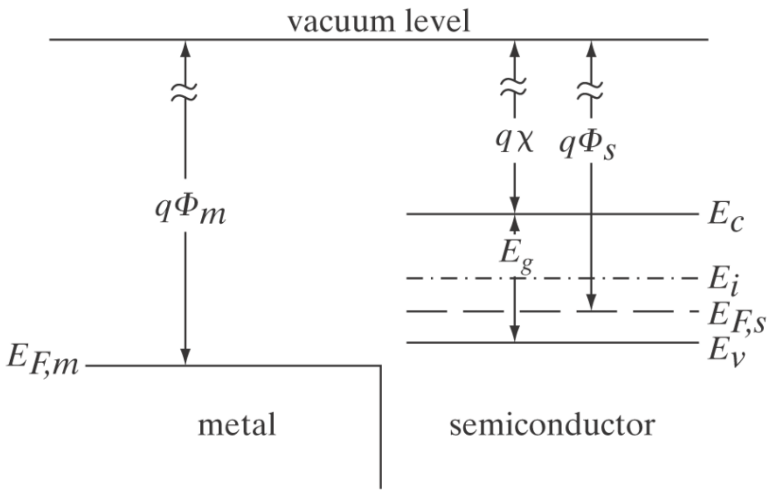
Work Function



- **The work function is the minimum energy (usually measured in electron volts) needed to remove an electron from the Fermi level of solid (ex, metal or semiconductor) to a point outside the solid surface (to vacuum level).**

- **The work function is a characteristic property of any solid.**

- **Depending on the work function difference between two materials of junction (semiconductor vs metal, usually), the contact becomes either rectifying (schottky) or ohmic.**

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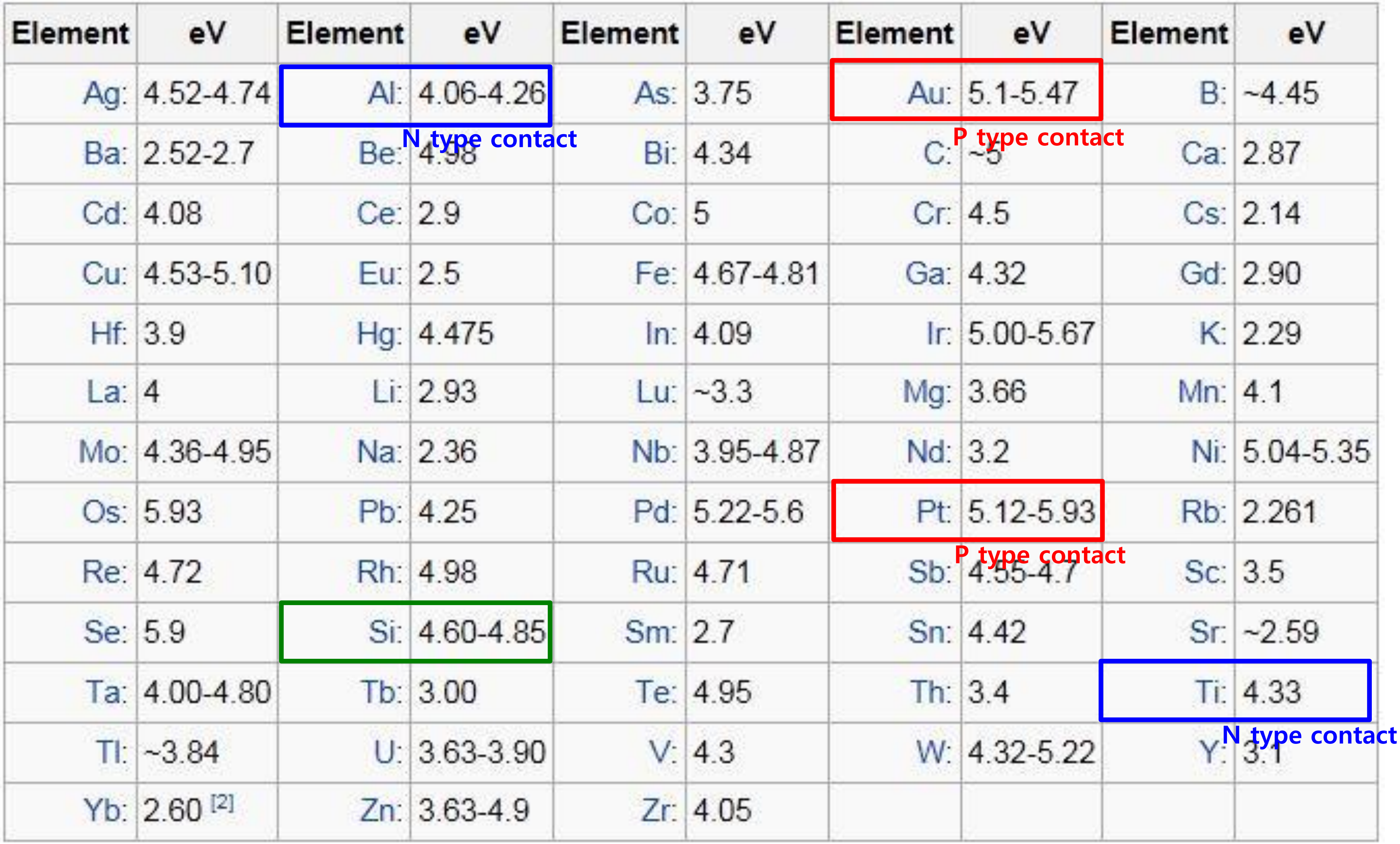
Typical value of work function



Element	eV	Element	eV	Element	eV	Element	eV	Element	eV
Ag:	4.52-4.74	Al:	4.06-4.26	As:	3.75	Au:	5.1-5.47	B:	~4.45
Ba:	2.52-2.7	Be:	4.98	Bi:	4.34	C:	~5	Ca:	2.87
Cd:	4.08	Ce:	2.9	Co:	5	Cr:	4.5	Cs:	2.14
Cu:	4.53-5.10	Eu:	2.5	Fe:	4.67-4.81	Ga:	4.32	Gd:	2.90
Hf:	3.9	Hg:	4.475	In:	4.09	Ir:	5.00-5.67	K:	2.29
La:	4	Li:	2.93	Lu:	~3.3	Mg:	3.66	Mn:	4.1
Mo:	4.36-4.95	Na:	2.36	Nb:	3.95-4.87	Nd:	3.2	Ni:	5.04-5.35
Os:	5.93	Pb:	4.25	Pd:	5.22-5.6	Pt:	5.12-5.93	Rb:	2.261
Re:	4.72	Rh:	4.98	Ru:	4.71	Sb:	4.55-4.7	Sc:	3.5
Se:	5.9	Si:	4.60-4.85	Sm:	2.7	Sn:	4.42	Sr:	~2.59
Ta:	4.00-4.80	Tb:	3.00	Te:	4.95	Th:	3.4	Ti:	4.33
Tl:	~3.84	U:	3.63-3.90	V:	4.3	W:	4.32-5.22	Y:	3.1
Yb:	2.60 [2]	Zn:	3.63-4.9	Zr:	4.05				

N type contact

P type contact

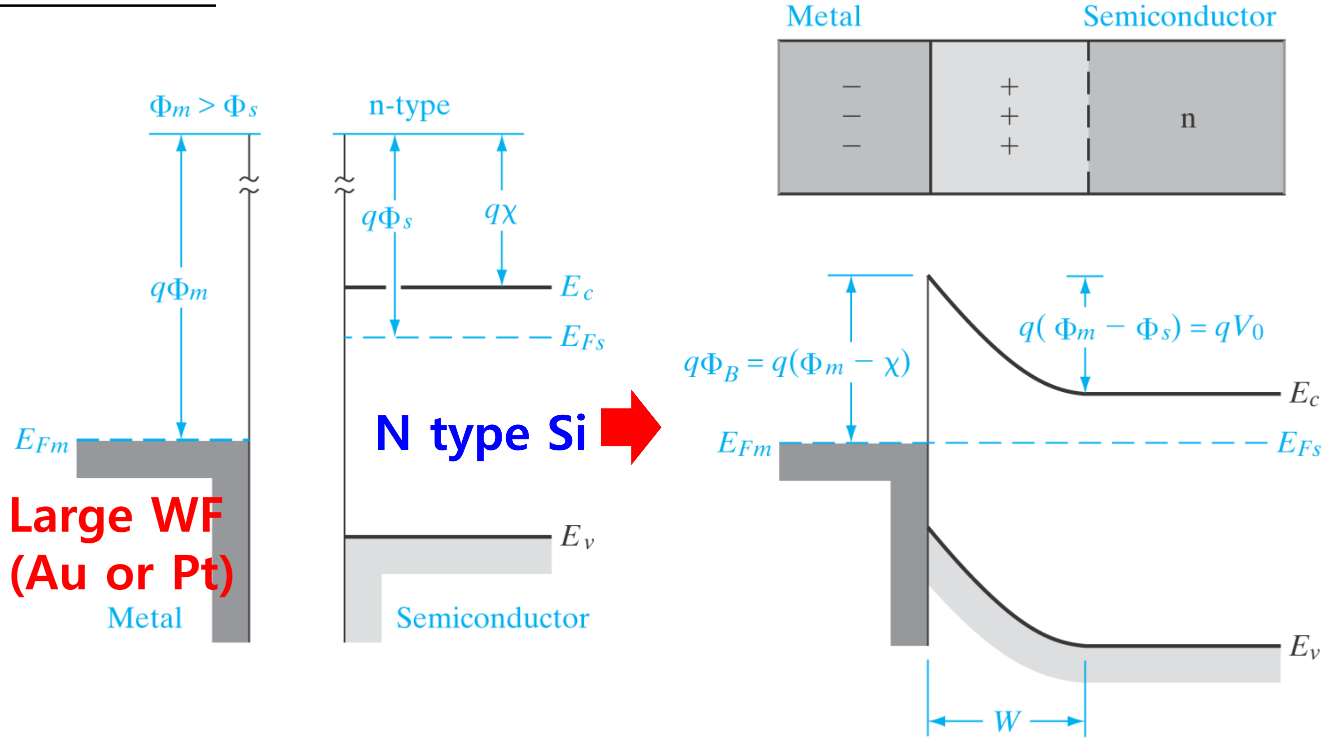
P type contact

N type contact

From wikipedia

Metal Contacts

Schottky Barriers I



Large WF (Au or Pt)

N type Si

- **When metal and semiconductor are contacted, charge transfers to align Fermi level.**
- **In above case, n type semiconductor and high work function metal is contacted. To align the Fermi level, the electrostatic barrier and depletion region W are formed.**
- **long W for low doping – schottky (next slide)**
  (cf. short W for high doping – ohmic by tunneling)

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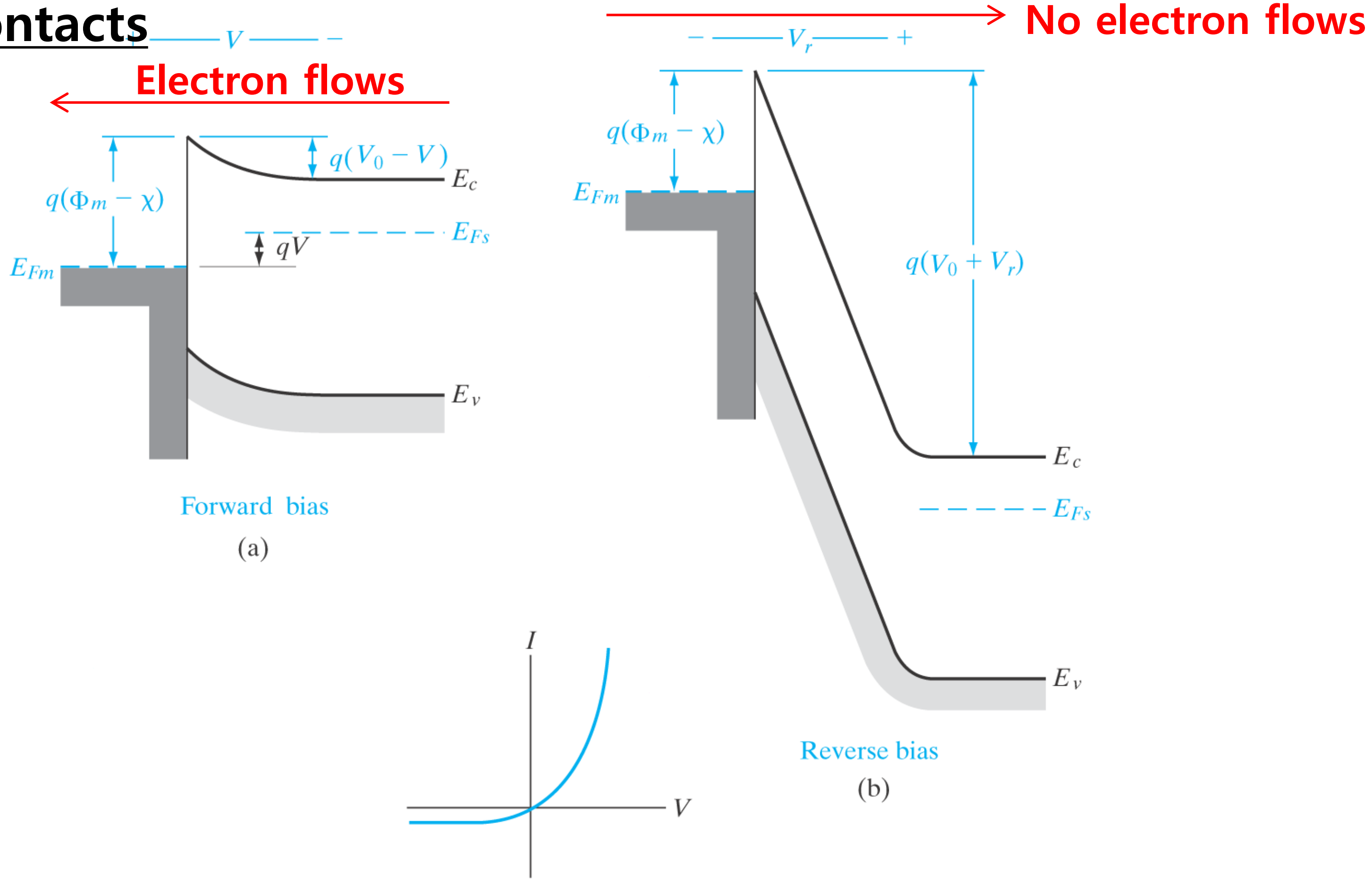
Rectifying Contacts



Electron flows

No electron flows

- By applying the forward bias (negative to n side and positive to metal), n side Fermi level is raised and energy barrier is reduced. Therefore current can flow.
- When the reverse bias (positive to n side and negative to metal) is applied, electrons from metal to semiconductor cannot get over the schottky barrier.
- These two show rectifying property.

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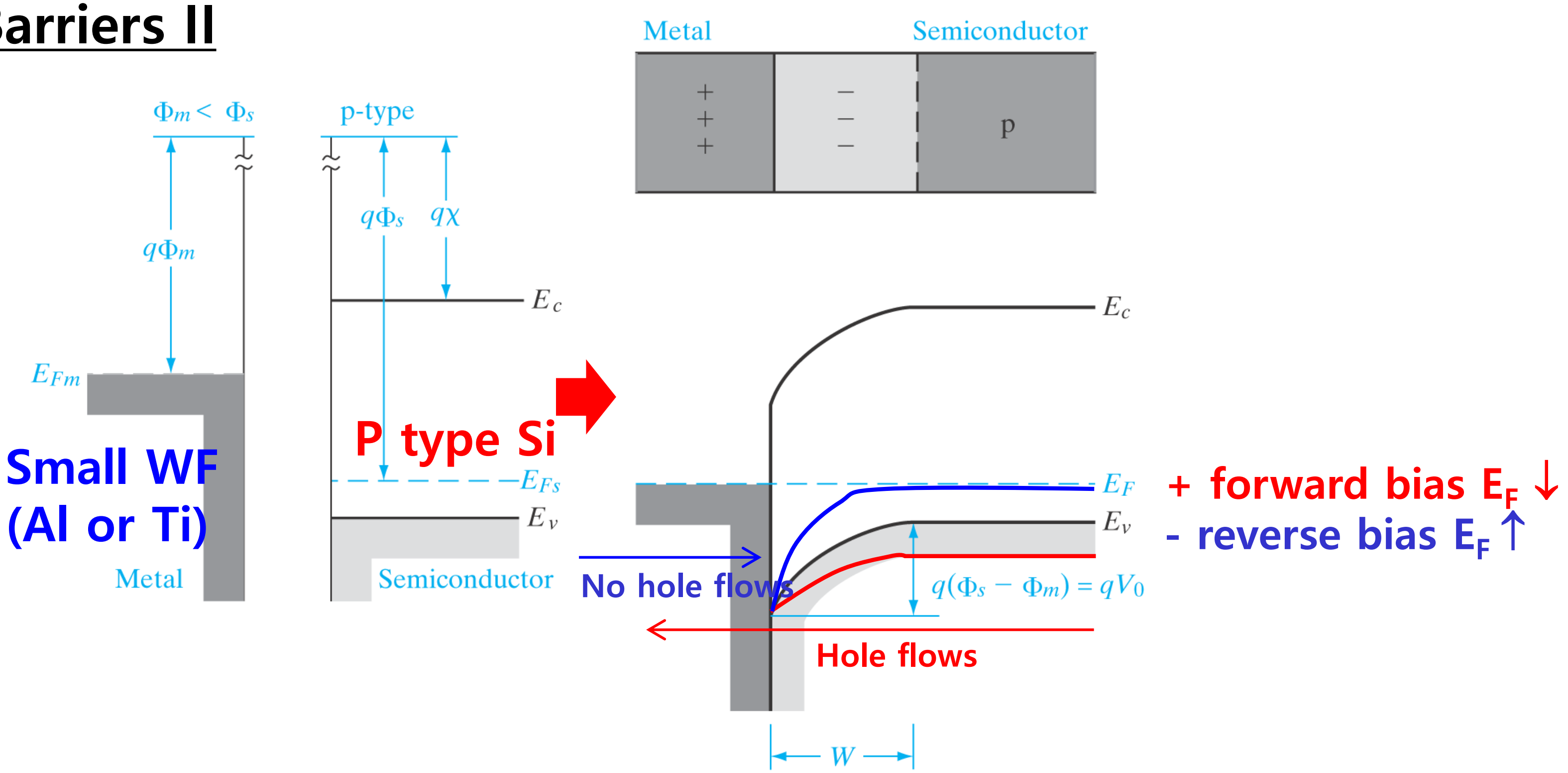
Schottky Barriers II



Small WF (Al or Ti)

P type Si

+ forward bias E_F ↓

- reverse bias E_F ↑

No hole flows

Hole flows

- **When metal and semiconductor are contacted, charge transfers to align Fermi level. In above case, p type semiconductor and low work function metal is contacted. To align the Fermi level, the electrostatic barrier and depletion region W are formed. (reverse of n type material)**
- **When forward bias is applied, holes in p type semiconductor flows over the lowered energy barrier. However, holes under reverse bias cannot go over the schottky barrier.**

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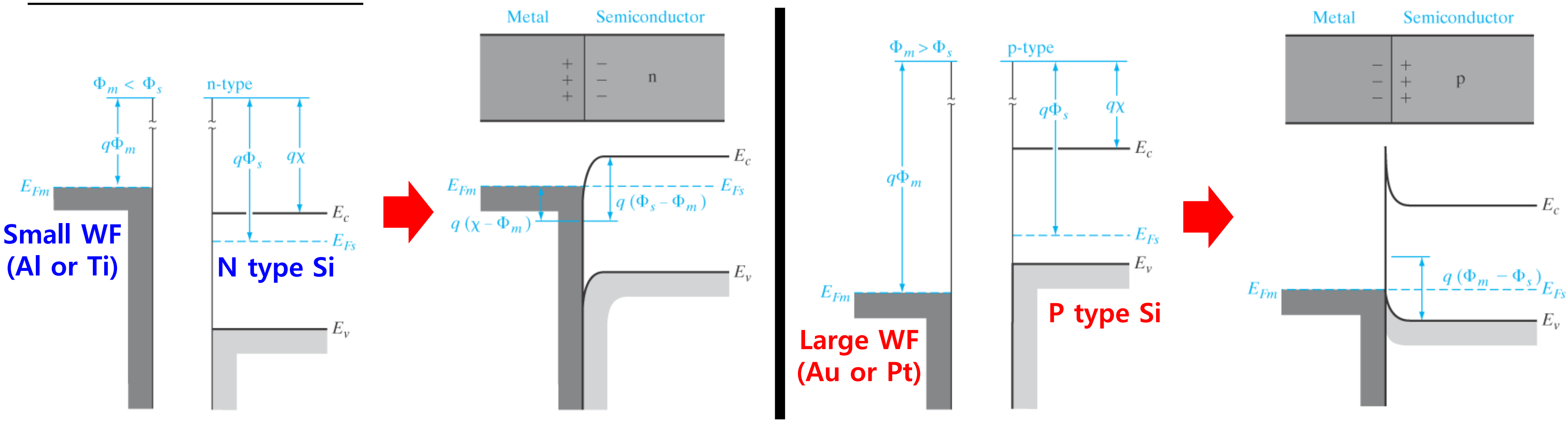
Ohmic Contacts



- In many cases, we want Ohmic metal-semiconductor contacts, which have linear IV characteristic for both forward and reverse bias conditions. (ex, TR)
- For Ohmic contacts, first, we can select a metal whose work function is similar with the semiconductor. For n type material, low work function metal, for p type material, high work function metal can be used (above diagram).
- Or, a commonly used, more practical method is to use heavy, degenerated doping of semiconductor. In this case, even though the energy barrier exists at the interface, the depletion width W is very small due to the heavy doping, which is enough to allow carriers to tunnel through the narrow energy barrier (See next slides).

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Optoelectronic Devices

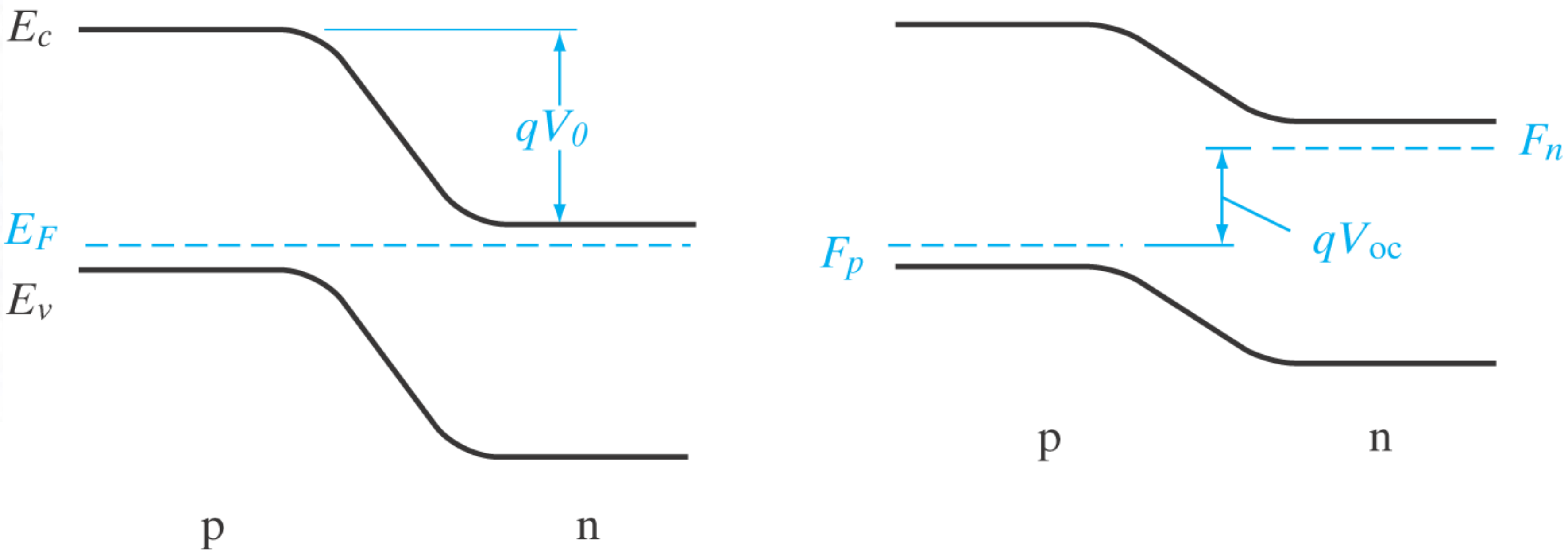
The PN Junction can be used for optoelectronic devices.

- **Three different devices, i) light emitting diode (devices as light sources that convert electrical energy into optical radiation; LED), ii) photodetector (devices that detect optical signals; camera), and iii) photovoltaic device (devices that convert optical radiation into electrical energy; solar cell) will be covered in this sub-chapter.**

$$\boxed{V_{oc} \simeq \frac{kT}{q}\ln\frac{g_{op}}{g_{th}} \quad \text{for } g_{op} \gg g_{th}}$$

And in terms of the band diagrams...

In open circuit (I=0, V_{OC}) and illuminated junction, forward bias-like potential is generated, an open circuit voltage, V_{OC}.



- In fact, it cannot increase beyond the equilibrium contact potential since the contact potential is the maximum forward bias that can appear across a junction.
  (since this is generated by minority carriers drifted by the E field formed by the contact potential)
- The appearance of a forward voltage across an illuminated junction is known as the **photovoltaic effect**.

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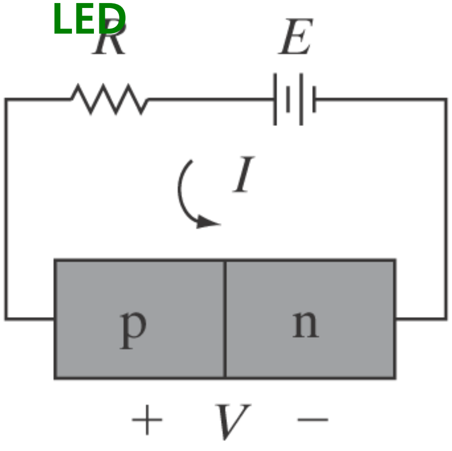
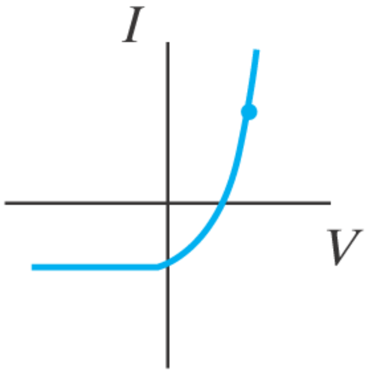
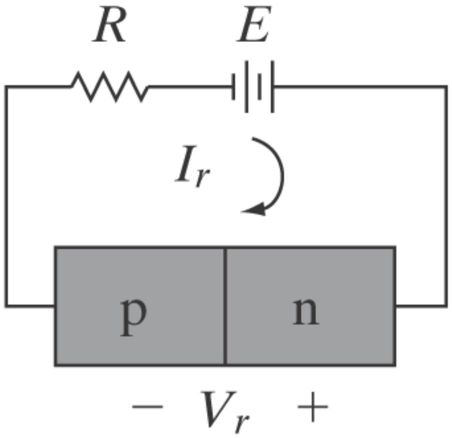
Forward bias, LED



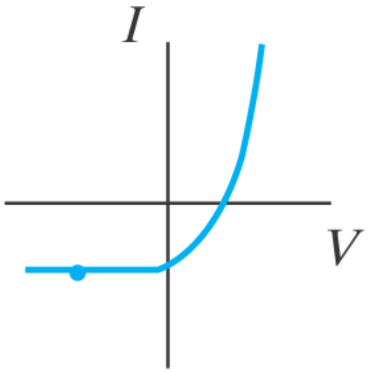
1st quadrant



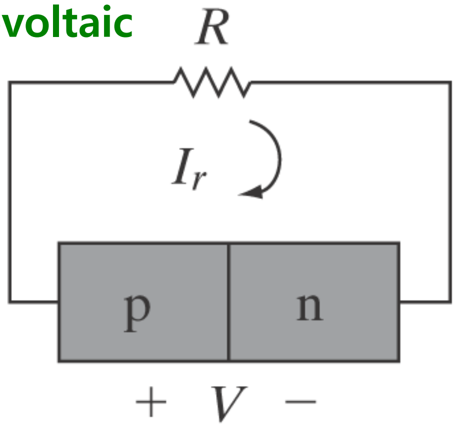
Reverse bias, Photodetector



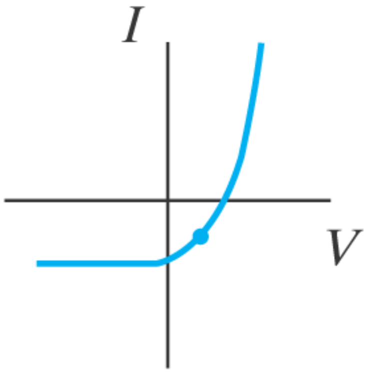
3rd quadrant



No external bias, but forward-like generated bias, Photovoltaic



4th quadrant



Power delivered from the circuit to the junction.

Power delivered from the junction to the circuit.

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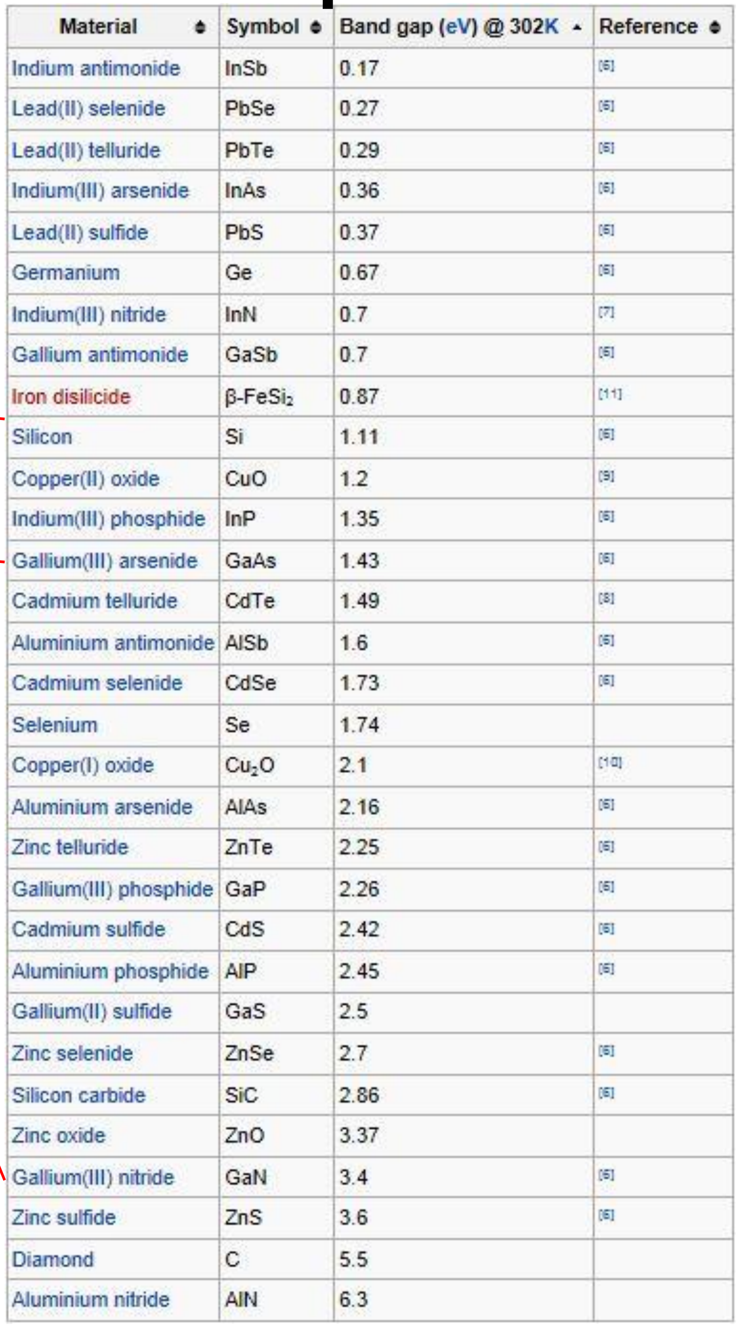
Band Gap of Materials

Each semiconductor material has different band gap

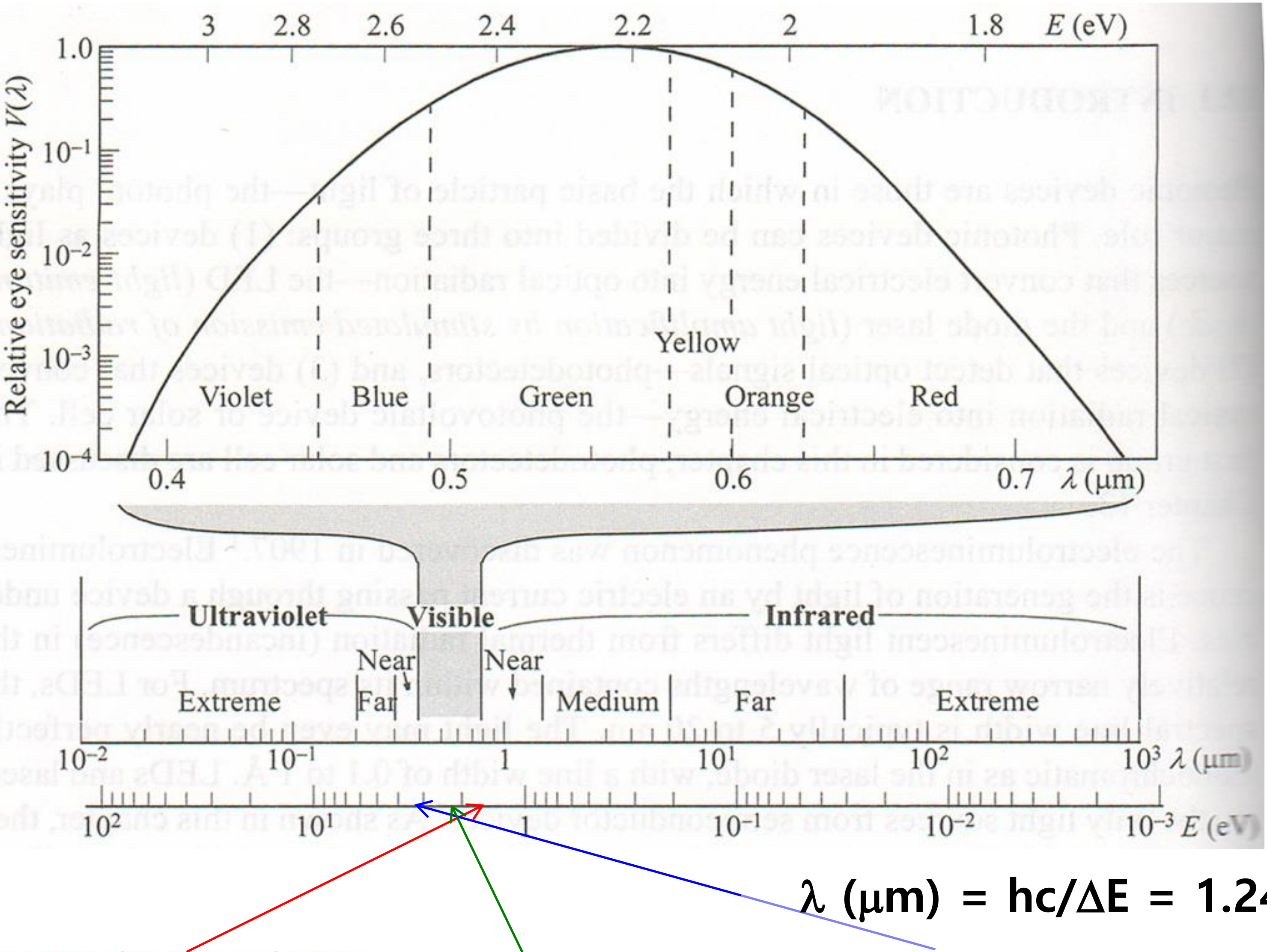
		(eV)
Silicon	Si	1.11
		Red
Gallium(III) arsenide	GaAs	1.43
		Green
Gallium(III) phosphide	GaP	2.26
		Blue
Gallium(III) nitride	GaN	3.4



Material ⬍	Symbol ⬍	Band gap (eV) @ 302K ▲	Reference ⬍
Indium antimonide	InSb	0.17	[6]
Lead(II) selenide	PbSe	0.27	[6]
Lead(II) telluride	PbTe	0.29	[6]
Indium(III) arsenide	InAs	0.36	[6]
Lead(II) sulfide	PbS	0.37	[6]
Germanium	Ge	0.67	[6]
Indium(III) nitride	InN	0.7	[7]
Gallium antimonide	GaSb	0.7	[6]
Iron disilicide	β-$FeSi_2$	0.87	[11]
Silicon	Si	1.11	[6]
Copper(II) oxide	CuO	1.2	[9]
Indium(III) phosphide	InP	1.35	[6]
Gallium(III) arsenide	GaAs	1.43	[6]
Cadmium telluride	CdTe	1.49	[8]
Aluminium antimonide	AlSb	1.6	[6]
Cadmium selenide	CdSe	1.73	[6]
Selenium	Se	1.74	
Copper(I) oxide	Cu_2O	2.1	[10]
Aluminium arsenide	AlAs	2.16	[6]
Zinc telluride	ZnTe	2.25	[6]
Gallium(III) phosphide	GaP	2.26	[6]
Cadmium sulfide	CdS	2.42	[6]
Aluminium phosphide	AlP	2.45	[6]
Gallium(II) sulfide	GaS	2.5	
Zinc selenide	ZnSe	2.7	[6]
Silicon carbide	SiC	2.86	[6]
Zinc oxide	ZnO	3.37	
Gallium(III) nitride	GaN	3.4	[6]
Zinc sulfide	ZnS	3.6	[6]
Diamond	C	5.5	
Aluminium nitride	AlN	6.3	

From wikipedia

Electromagnetic Spectrum



λ (μm) = hc/ΔE = 1.24/ΔE (eV)

Gallium(III) arsenide	GaAs	1.43	Gallium(III) phosphide	GaP	2.26	Gallium(III) nitride	GaN	3.4

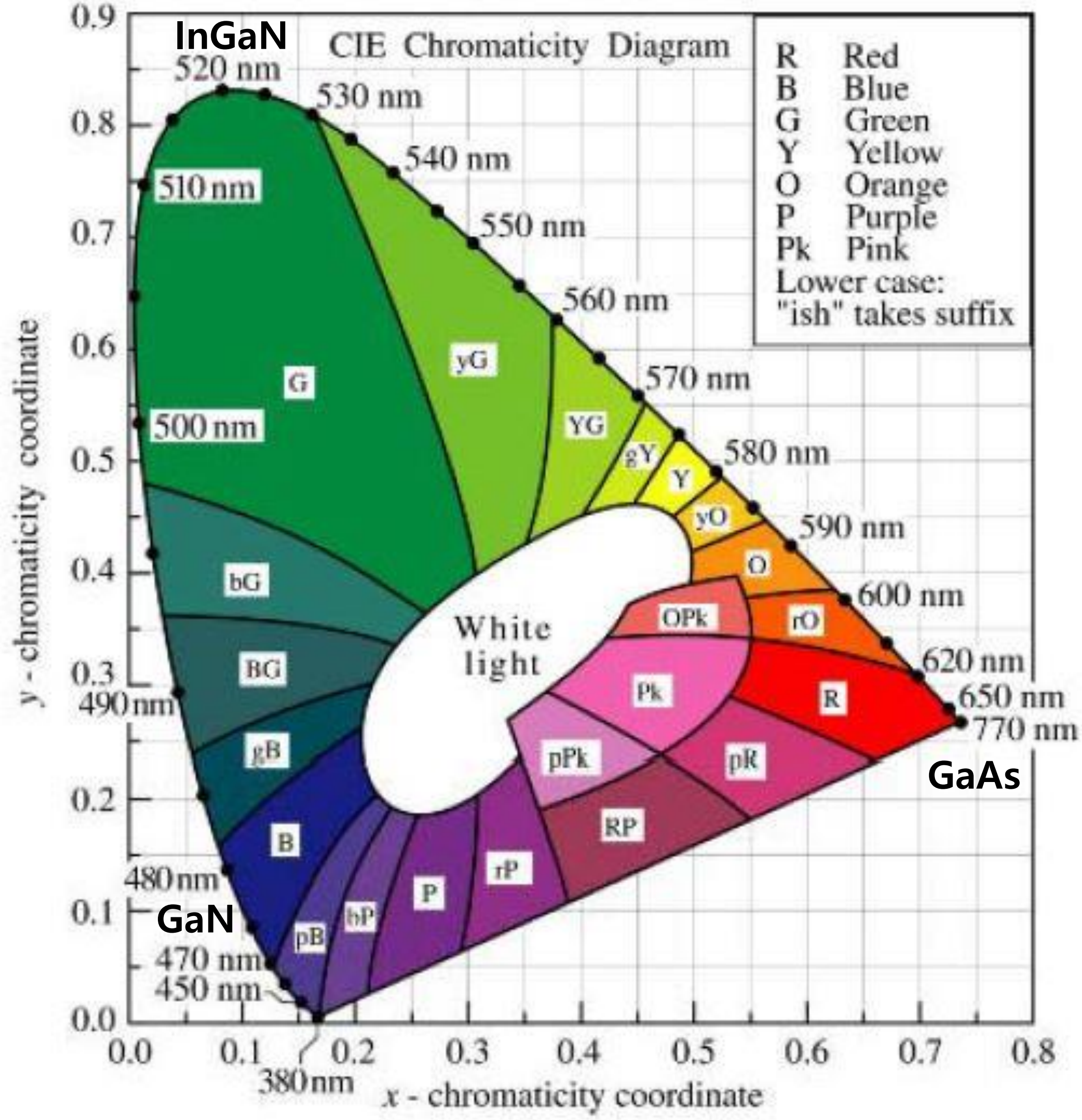
red

green

blue

We can choose a proper material for each color.

From wikipedia



CIE Chromaticity Diagram

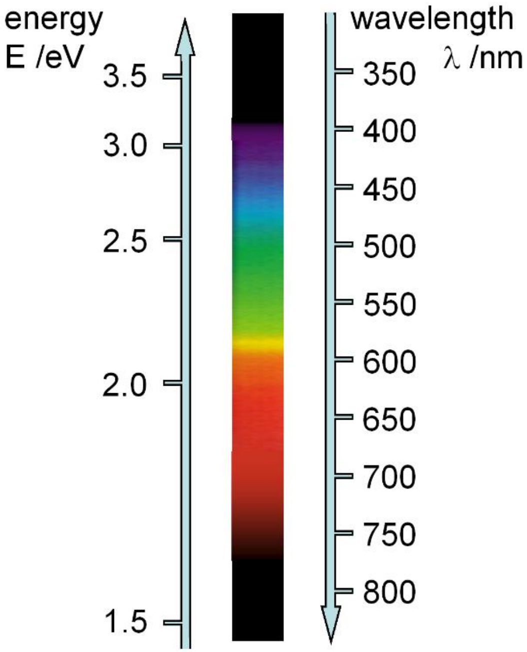
From wikipedia

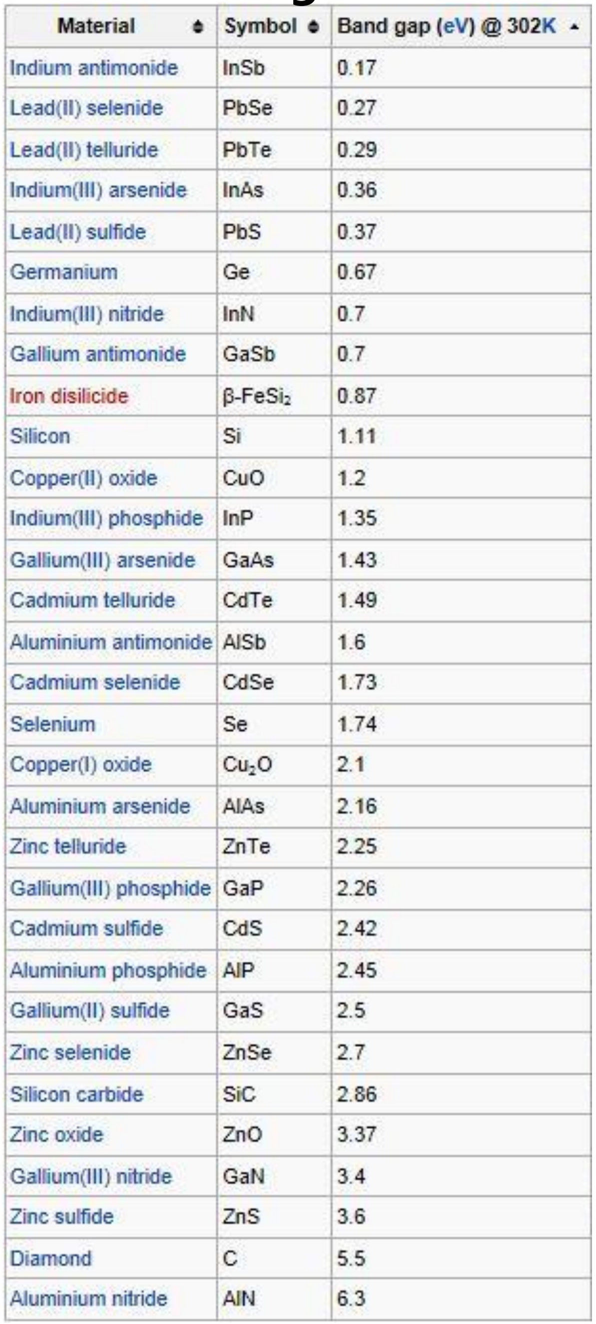
Solar Spectrum

- The intensity of solar radiation in free space has a value of 1353W/m^2. The atmosphere attenuates the sunlight, mainly due to water vapor absorption in IR, ozone absorption in UV and scattering by airborne particles
- Energy distribution: UV / Vis / NIR ~ 6.6% / 44.7% / 48.7%
- Therefore we focus on visible (~ 800 nm / ~1.3 eV) and NIR (~1.8 μm / ~0.8 eV) range for PV of "high efficiency / low cost". (and maybe little bit of high energy UV region..)

Each material has a frequency range of its own best absorption efficiency ~ Materials selection is important (Si ~ 1.1 eV, GaAs ~ 1.4 eV, Ge ~ 0.7 eV).

E_g for NIR and Visible





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Indium(III) nitride	InN	0.7
Gallium antimonide	GaSb	0.7
Iron disilicide	β-$FeSi_2$	0.87
Silicon	Si	1.11
Copper(II) oxide	CuO	1.2
Indium(III) phosphide	InP	1.35
Gallium(III) arsenide	GaAs	1.43
Cadmium telluride	CdTe	1.49
Aluminium antimonide	AlSb	1.6
Cadmium selenide	CdSe	1.73
Selenium	Se	1.74
Copper(I) oxide	Cu_2O	2.1
Aluminium arsenide	AlAs	2.16
Zinc telluride	ZnTe	2.25
Gallium(III) phosphide	GaP	2.26
Cadmium sulfide	CdS	2.42
Aluminium phosphide	AlP	2.45
Gallium(II) sulfide	GaS	2.5
Zinc selenide	ZnSe	2.7
Silicon carbide	SiC	2.86
Zinc oxide	ZnO	3.37
Gallium(III) nitride	GaN	3.4
Zinc sulfide	ZnS	3.6
Diamond	C	5.5
Aluminium nitride	AlN	6.3

From wikipedia

Air Mass (AM)

- The degree to which the atmosphere affects the sunlight received at the earth's surface is quantified by the air mass, Air Mass (AM).
- The Air Mass quantifies the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust.
- AM 0 represents the solar spectrum outside the earth's atmosphere.
- AM 1 is the incident directly from above, 90 degree ($\theta=0$).
- AM 1.5 (~1.414) is from 45 degree ($\theta=45$).
- AM 0, AM 1, AM 1.5 has the power of 1353, 925, 844 W/m^2, respectively.
- The AM 1.5 conditions represent a satisfactory energy-weighted average for terrestrial applications. We typically use AM 1.5 condition for PV characterization.

Materials of Solar Cells

Important parameters: energy gap (λ_c, V_{OC}), direct/indirect, photon-absorption coefficient, mobility/crystallinity, cost, etc.

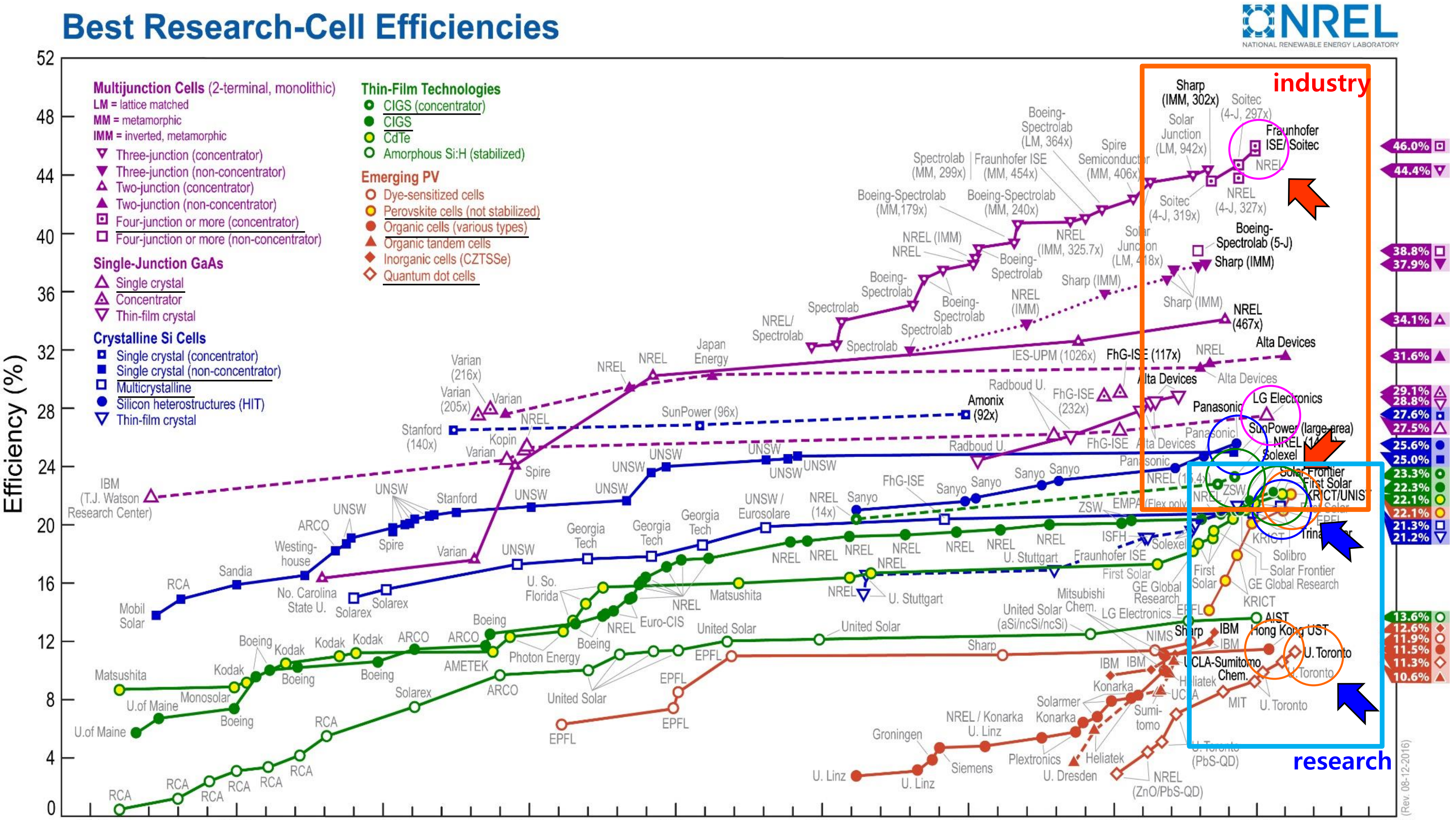
- **When the incident light with the intensity of I_0 passes through a medium, the original intensity decays into I. (if the material is thin. if it is thick, I decays to 0. If there is a photon-trapping structure, I can decay to 0.)**
- **α is the absorption coefficient of semiconductor materials.**
- **α is a function of the wavelength of light and also the property of the medium.**
- **Direct gap materials (GaAs, InP; photon only) are more efficient (can be thinner) than indirect gap materials (Si, Ge; photon + phonon), but more expensive.**

Materials of Solar Cells

- The conventional solar cell, typically a pn junction diode, has a single band gap E_g.
- A photon with energy less than E_g makes no contribution to the cell output. A photon with energy greater than E_g contributes an electric charge to the cell output, and the excess energy over E_g is wasted as heat.
- As E_g decreases, the photocurrent increases due to better absorption. But as E_g decreases, V_{OC} decrease (low voltage solar cell), which is smaller than E_g ($V_{OC} < V_O$). Therefore there is an optimum E_g for maximum power (=current×voltage).
- **For high conversion efficiency using single junction cell, the band gap should lie in the range of 0.7~2eV (NIR~visible) or 1~1.6eV for better efficiency (NIR ~ 1eV, Violet ~ 3eV).**
- GaAs (~1.4eV) shows the best efficiency (above plot), and Si (~1.1eV) is a famous material that shows high efficiency and relatively cheap cost.

- The diffusion length (before recombinatic $L_{\text{diff}} = \sqrt{D \cdot \tau}$) should be long in comparison with the absorption depth, which requires high quality crystalline structure with small defects (single crystal > polycrystal > amorphous).
- Amorphous silicon has a suitable band gap but diffusion lengths are too short compared to the absorption depth, while poly crystal or single crystal silicon have a much longer diffusion length due to its high crystalline structure and less defects.
- Silicon is indirect band gap material. Therefore even though the band gap is 1.1eV, the efficiency is low near 1.1eV since the energy is consumed by phonon vibration, while direct band gap material (such as GaAs) has sharp increase of absorption efficiency near its band gap.
- GaAs and InP has broad “high quantum efficiency range” that matches with solar photon flux density and therefore it show best efficiency among various materials.

Efficiency of PVs (Research)

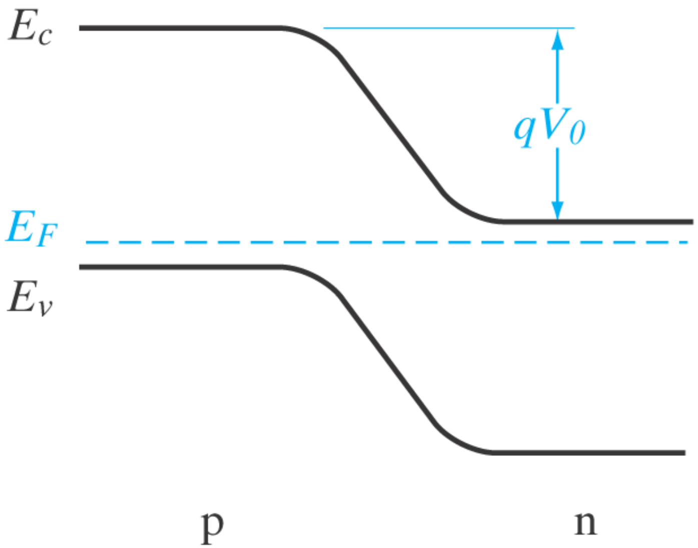


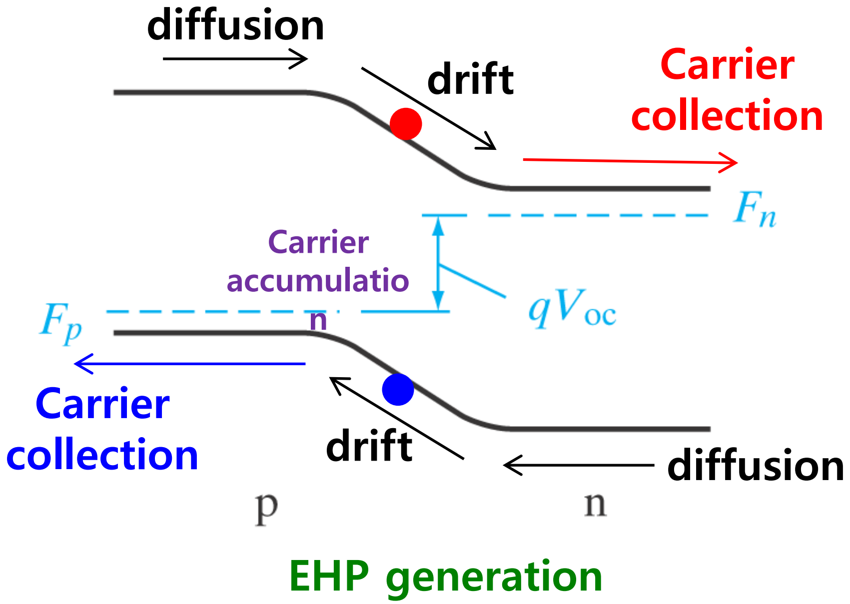
- Single crystalline (Si, GaAs) > Poly crystalline (Si, GaAs) > Amorphous (thin film)
- Direct gap materials (GaAs, CIGS, CdTe) > Indirect gap materials (Si)
- Inorganic (less defect, GaAs, Si, CIGS, CdTe, etc..) > Organic, DSSC / QDSC

Operation

- Four basic operation steps of a solar cell include followings:

- **generation of EHP, i.e. light-generated carriers, and separation of them by the built-in electric field**
- **collection of the light-generated carries at electrodes to generate current (I_{SC})**
- **generation of a large voltage across the solar cell (V_{OC}) due to accumulated EHPs**
- **dissipation of power in the load and parasitic resistances**





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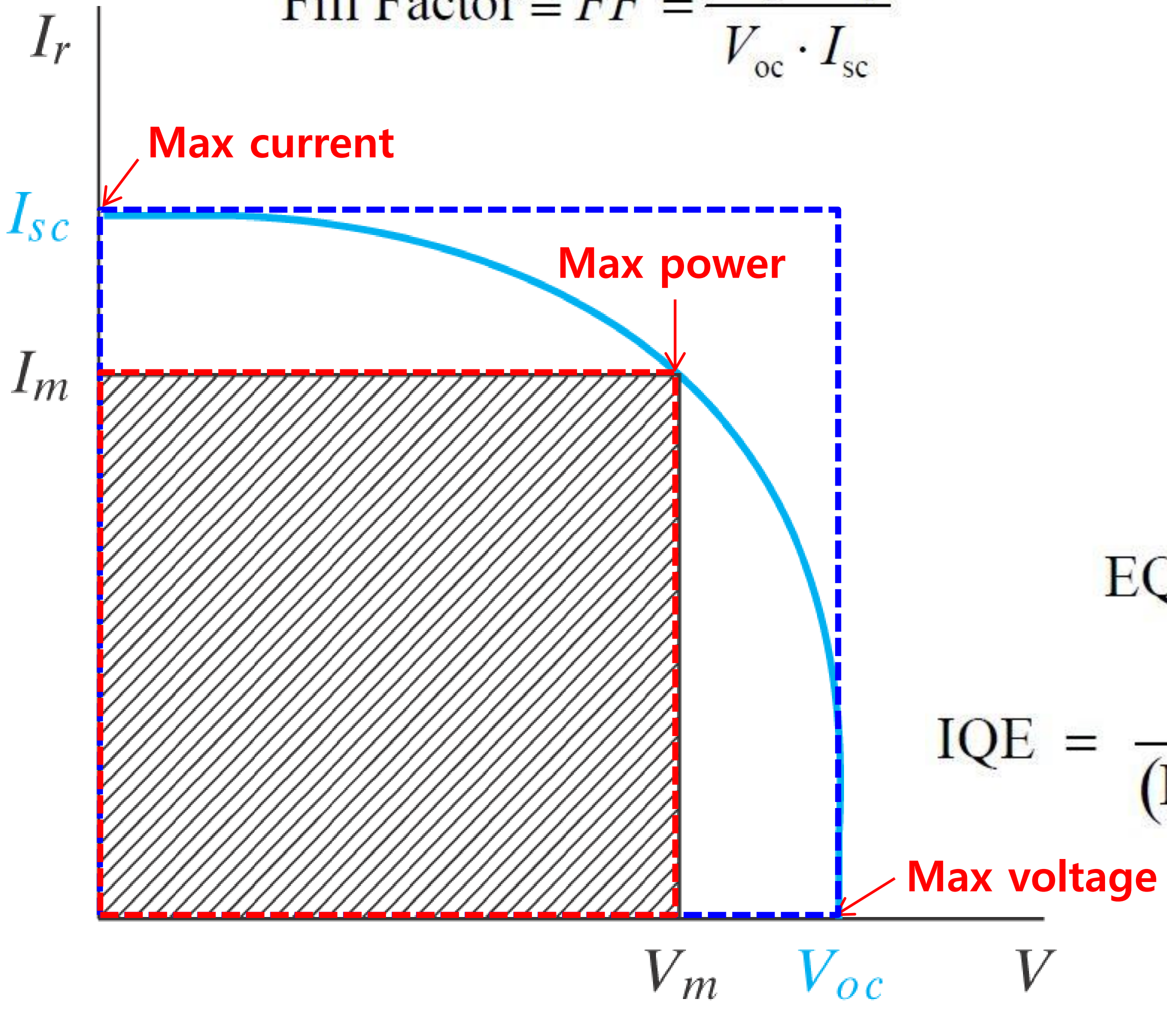
Efficiencies

$$\text{Efficiency} \equiv \eta = \frac{\text{Power Out}}{\text{Power In}} = \frac{V_{\text{mp}} \cdot I_{\text{mp}}}{\Phi}$$

Details in the next slide

$$\text{Fill Factor} \equiv FF = \frac{V_{\text{mp}} \cdot I_{\text{mp}}}{V_{\text{oc}} \cdot I_{\text{sc}}}$$



$$\text{EQE} = \frac{\text{Electrons Out}}{\text{Photons In}}$$

$$\text{IQE} = \frac{\text{Electrons Out}}{(\text{Photons In}) \cdot (1 - \text{Reflectivity})}$$

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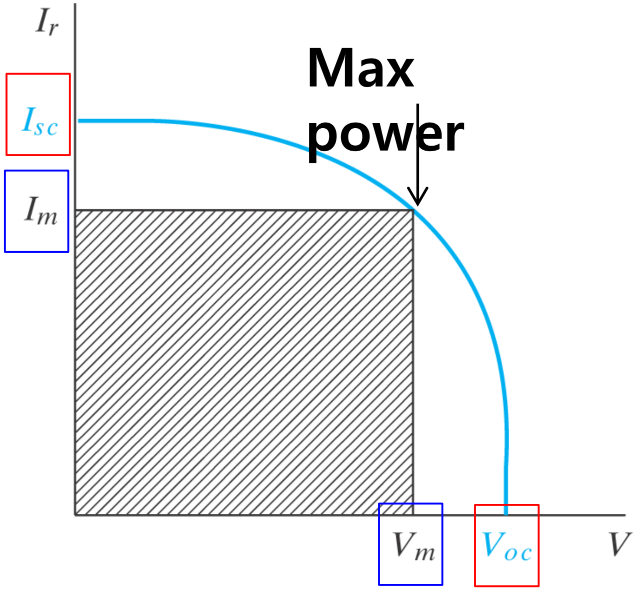
Efficiency and Fill Factor

(1) A solar cell's ***power conversion efficiency* (η , "eta")**, is the percentage of incident light energy that actually ends up as electric power. This is calculated at the maximum power point, P_m, divided by the input light irradiance (E, in W/m^2) under standard test conditions (STC) and the surface area of the solar cell (A_c in m^2).

$$\eta = \frac{P_m}{E \times A_c}$$

STC specifies a temperature of 25 °C and an irradiance with an air mass 1.5 (AM1.5) spectrum.
Maximum power $P_m = I_m \times V_m$ happens when product of IV is maximum under IV curve. This conversion efficiency tells the efficiency of power generation.



4th quadrant portion of IV
(plotted upward by convention)

(2) Another defining term in the overall behavior of a solar cell is the ***fill factor (FF)***. This is the ratio of the available *power* at the *maximum power point* (P_m) divided by the *open circuit voltage* (V_{OC}) and the *short circuit current* (I_{SC}):

$$FF = \frac{P_m}{V_{OC} \times I_{SC}}$$

This fill factor tells the resistance level of the solar cell system. If the resistance is large, the power loss by the resistance decreases fill factor.

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Collection Probability

- Collection of light generated carrier: If the photo-generated minority carrier reaches the edge of the depletion region (by slow diffusion), it is swept across the junction (fast drift) and become a majority carrier.
- Therefore the collection probability is the probability that a light generated carrier reach the depletion region and be collected, which depends on where it is generated. i.e. if the carrier is generated farther away than the diffusion length from the junction, the collection probability is low.
- Depth of the junction: If the junction location where the collection probability is high is too deep, the photon-absorption efficiency is low. Therefore the location of pn junction should be optimized depending on the diffusion length and photon-absorption efficiency of the material.

Quantum Efficiency

- **Surface recombination** can have a major impact both on the short-circuit current and on the open-circuit voltage. High recombination rates at the top surface have a particularly detrimental impact on the short-circuit current since top surface also corresponds to the highest generation region of carriers in the solar cell.
- **Lowering the high top surface recombination is typically accomplished by reducing the number of dangling silicon bonds (defects) at the top surface by growing a "passivating" layer (usually silicon dioxide or silicon nitride) on the top surface.**
- There are three kinds of recombination process (see next slide).

Recombination

- There are three basic types of recombination in the bulk of a single-crystal semiconductor.

- 1) Radiative recombination is the recombination mechanism that dominates in direct bandgap semiconductors. The light produced from a light emitting diode (LED) is the most obvious example. Space solar cells are typically made from direct bandgap materials (ex GaAs) and radiative recombination dominates. However, in most silicon solar cells (indirect bandgap semiconductor) radiative recombination is extremely low and usually neglected.

- 2) Recombination through defects, called Shockley-Read-Hall (SRH) recombination, does not occur in perfectly pure, undefected material (single crystal). SRH recombination is a two-step process: i) An electron (or hole) is trapped by an energy state in the forbidden region, which is by defects in the crystal lattice. ii) If a hole (or an electron) moves up to the same energy state before the electron is thermally re-emitted into the conduction band, then it recombines. The rate at which a carrier moves into the energy level in the forbidden gap depends on the distance of the introduced energy level from either of the band edges. Therefore, if a defect energy level is introduced close to either band edge, recombination is less likely as the electron is likely to be re-emitted to the conduction band edge. For this reason, energy levels near mid-gap are very effective for recombination.

- 3) Auger Recombination involves three carriers. An electron and a hole recombine, but rather than emitting the energy as heat or light, the energy is given to a third carrier, an electron in the conduction band. This electron then thermalizes back down to the conduction band edge. Auger recombination is important at high carrier concentrations (caused by heavy doping or high level injection under concentrated sunlight).

Device Configuration

- A typical schematic representation of a solar cell is shown in left figure. It consists of a shallow pn junction formed on the surface, front Ohmic contact stripes and fingers, an antireflection coating and a back Ohmic contact.

- The finger grid reduces series resistance, but at the expense of blocking some light, so there is a trade-off for the design. Some use transparent conductors such as ITO (See the next slide for more about TCO). But we need to consider both contact resistances and the cost of electrodes.

- To reduce the light reflection in addition to the antireflection coating, a textured surface, either on the front or back, has been used to trap the light. This uses reflection to enhance light input.

- Light incident on the side of a pyramid will be reflected onto another pyramid instead of being reflected backward. The reflectivity of bare Si is reduced from ~35% to 20% for textured surface.

Transparent Conducting Oxide

TCO: Typically oxide semiconductor materials that exhibit low electrical resistivity and high optical transparency (Band gap > 3.3 eV)

Undoped TCOs: Used for TRs, n-type semiconductors cadmium oxide (CdO), tin oxide (SnO2), indium oxide (In2O3), titanium oxide (TiO2), zinc oxide (ZnO)

Doped TCO: Used for electrodes, most well known example is indium tin oxide (ITO), fluorine doped tin oxide (FTO), and aluminum doped zinc oxide (AZO), which is a "degeneratively doped semiconductor" with metallic-type conductivity and high optical transparency

Operation of DSSC

- Excitation of dye by photon: $S+h\nu \rightarrow S^*$
- Excited electron injection by oxidation of dye: $S^* \rightarrow S^+ + TiO_2$
- Dye reduction by oxidation of electrolyte: $2S^+ + 3I^- \rightarrow 2S + I_3^-$
- Redox regeneration at the cathode (electrolyte reduction at cathode by electrons through the circuit): $I_3^- + 2e^- \rightarrow 3I^-$

- The CB of TiO_2 should be lower than LUMO of dye and the Fermi level of cathode should be higher than HOMO of dye.

- The basic element of a DSSC is a nanostructured material, an assembly of TiO_2 nanoparticles about 20 nm diameter, well connected to their neighbors.
- TiO_2 nanoparticle is the preferred material since its surface induces highly effective electron transfer from dye and it has large area surface where dyes can be adsorbed. (The use of TiO_2 nanoparticles by Gratzel group was the breakthrough in DSSC technology, whose efficiency was increased from ~1% to >10%. Also used in perovskite for the high efficiency over ~20%)
- However, TiO_2 only absorbs a small fraction of the solar photons (wide band gap, E_g~3.2eV). Molecular sensitizers (dye molecules, its color originates from absorption of visible range) attached to the semiconductor surface, are used to harvest a great portion of the solar light.

QD (Sensitized) Solar Cell

- Narrow-bandgap semiconductor QDs (such as CdS, CdSe, PbS, and InAs) have been the subject of considerable interest as promising candidates for photon absorption material.

- QDs can be directly integrated with electrodes for QDSC or can be attached to high surface area nanostructures (QDSSC), following the strategy of DSSC with replacement of dyes by QDs. The latter is called QD-sensitized solar cells (QDSSC) and working mechanism is similar with DSSC.

- The advantages of QDSC/QDSSC include:
- i) the bandgap of the QDs, and thereby the absorption spectrum, can be ***tuned by controlling their size*** to match the spectral distribution of sunlight,
- ii) semiconductor QDs have large extinction coefficients (how strongly a substance absorbs light at a given wavelength) due to the ***quantum confinement effect*** (like quantum well)

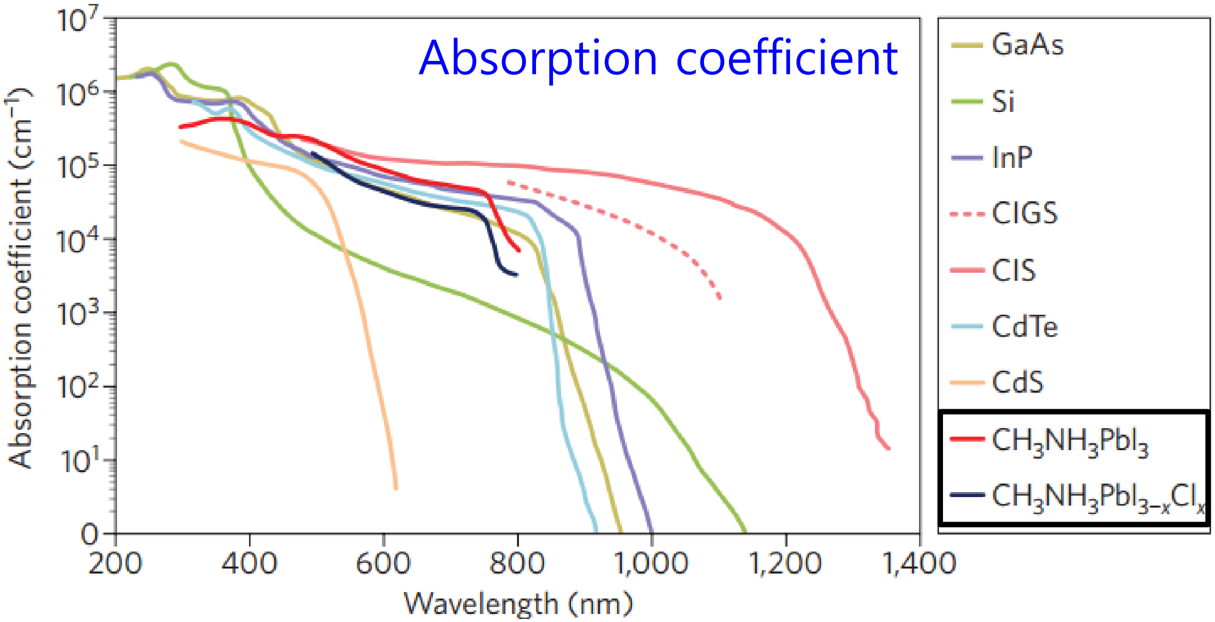
Perovskite Solar Cells (PSCs)

Perovskite structure (ABX_3)

$CH_3NH_3MX_3$: organometal halide light absorber (M = Pb or Sn) with ***high photon absorption*** with ***long diffusion lengths***

Efficiency of perovskite solar cell (~22%) is larger than that of Organic solar cell, DSSC, QD cells (~10%).

- The name 'perovskite solar cell (PSC)' is originated from the crystal structure of the absorber materials (ABX_3 :Perovskite).
- The most famous perovskite absorber is methylammonium lead trihalide ($CH_3NH_3PbX_3$: where X is a halogen ion such as I^-, Br^-, Cl^-), with a bandgap between 1.17 eV and 2.3 eV depending on halide/metal and their contents.
- This cubic perovskite structure stabilizes at the ambient temperature rapidly.
- A: cation, $CH_3NH_3^+$, edge of the unit cell
- B: heavy metal, Pb^{2+}, center of the unit cell
- X^-: anion, I^-, face-center of the unit cell



Perovskites exhibit **direct-bandgap** properties and **strong optical absorption**, which is the key to the excellent optoelectronic performance, reducing both the required thickness and the challenges in collecting photogenerated carriers.

(Nature Photon. 2014, 8, 506-514)

Structure of the PSCs

- Two types of PSC (TiO_2 Sensitized & Thin film type)

- Sensitized PSC: similar to the sensitization in DSSC, the perovskite material is coated onto a mesoporous TiO_2 scaffold. **The absorption coefficient of perovskite is > 10 times higher than molecular sensitizers**

- Thin film PSC: Perovskite layer acts as absorber and ambipolar charge-conductor (Perovskite has the balanced electron and hole transport properties)

- FTO: Transparent conducting oxide
- c-TiO_2: n-type contact (eletron transport & blocking layer)
- m-TiO_2: mesoporous structure (high temp. sintering of a paste-form)
- Perovskite: $CH_3NH_3PbX_3$
- Spiro-OMeTAD: p-type contact (Hole transport layer)
- Au: conducting metal

Operation of PSCs

- Perovskite has the well balanced electron and hole transport property.
- The electron and hole diffusion lengths are ~1069 nm and ~ 1213 nm, respectively. (Perovskite film can be thinner than 1 um due to its high photo-absorption)
- The electron and hole mobility are ~ 25 cm^2/Vs for both.

- In perovskite PVs, the interfacial properties mainly determine the performance.
- The desirable process:
  1. Efficient photoexcitation in perovskite
  2. Efficient electron transfer to the electron transport layer (ETL, ex: TiO_2)
  3. Efficient hole transfer to hole transport layer (HTL, ex: spiro-OMeTAD)
  4. Efficient electron transfer to conducting oxides (ex: FTO)
  5. Efficient hole transport to metals (ex: Au)

- Current issues:
  - Humidity/Air/Thermal stability, Hazard Pb^{2+} ions, Cost
  - **CH_3NH_3I is humid-sensitive, and the perovskite layer exhibit phase transition around 150 °C.**

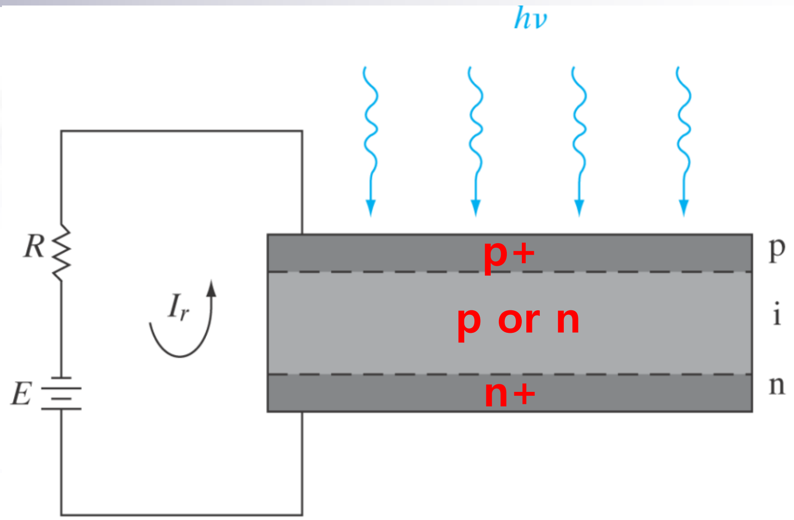
Choice of depletion width is a tradeoff between speed and sensitivity.

- Large W leads to a very sensitive device

High absorption coefficient is required for high sensitivity.

- But it also cannot be too large or the drift time will be excessive and lead to low speed.

High mobility semiconductor is required for fast response.



If we fix the material as a silicon, then..

- For high speed operation, the depletion region must be kept thin to reduce the transit time. On the other hand, to increase the quantum efficiency (the number of EHP generated per incident photon; sensitivity), the depletion layer must be sufficiently thick to allow a large fraction of the incident light to be absorbed. Therefore, there is a trade-off between the speed and the sensitivity.
- Since most photodiodes use band-to-band photoexcitation of carriers, the long wavelength cutoff (λ_c) is established by the energy band gap of the semiconductor. For wavelength longer than λ_c, the absorption is very small.
- For wavelength shorter than the short wavelength cutoff, the absorption efficiency is too high and the radiation is absorbed at the very near of the surface, where EHP recombination (surface recombination) is very likely. The photocarriers are recombined before they are collected by electrodes.
- Therefore, each material has a frequency range of its own best absorption efficiency.

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