# Lecture 2
# Electrons and Holes in Semiconductors

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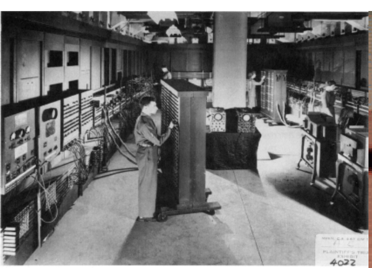
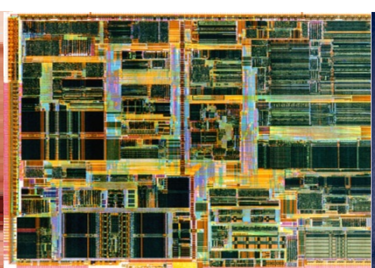
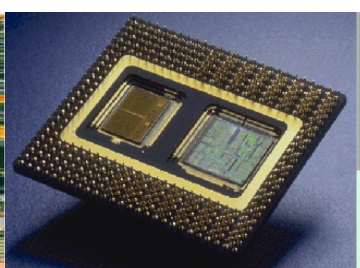
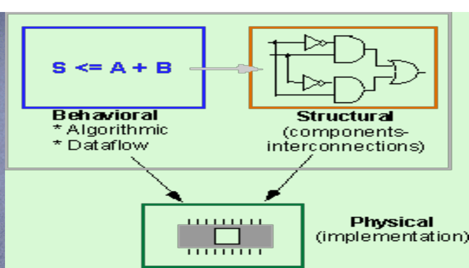
Adapted from Modern Semiconductor Devices for Integrated Circuits, Chenming Hu, 2010

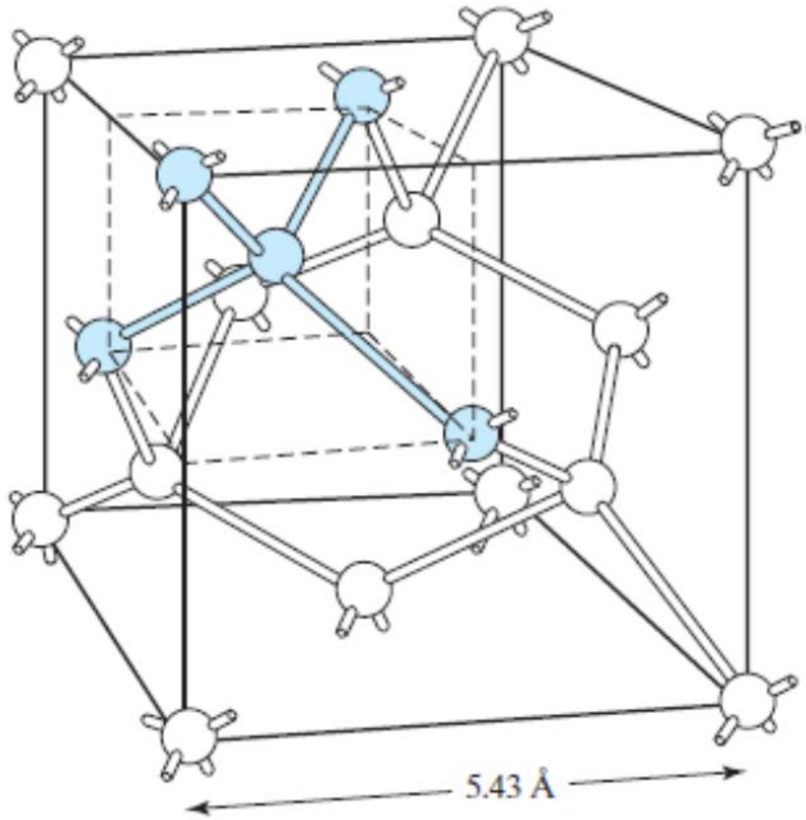


# Silicon Crystal Structure

- Most semiconductor materials used in microelectronics are crystalline

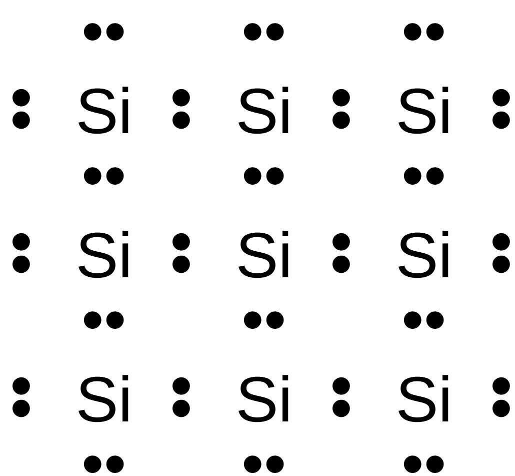
- Unit cell of silicon crystal is cubic
  - contains 18 silicon atoms arranged in tetrahedral (diamond) bonding pattern



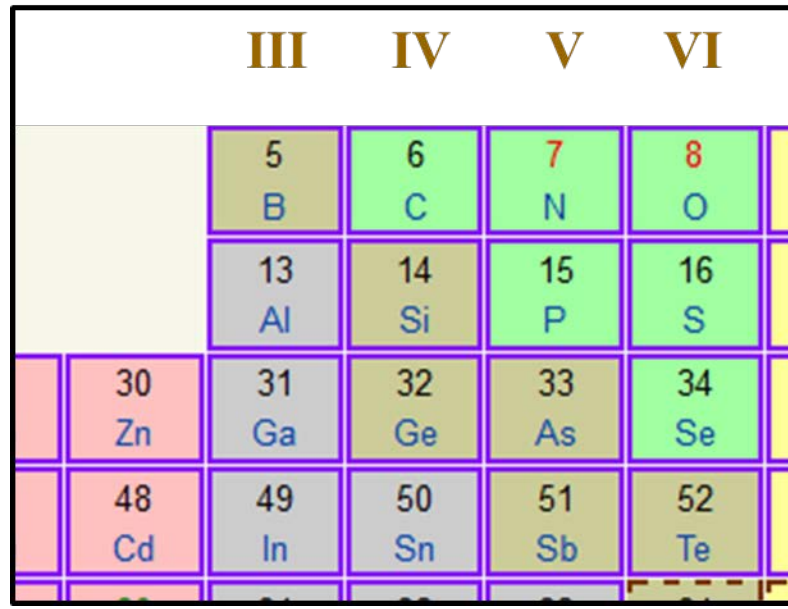

- Each silicon atom has four nearest neighbors

# Bond Model of Silicon Crystal

- Silicon is a Group IV material – 4 valence electrons
- Valence electrons shared with 4 nearest neighbors
  - each pair of electrons forms covalent bond
- At low temperature (≈ absolute zero) no free electrons to conduct electric current

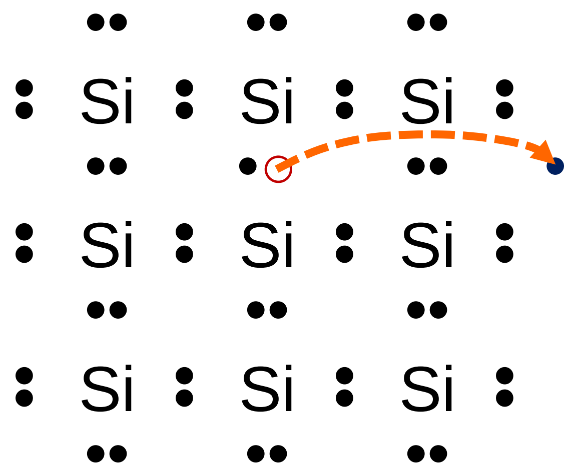



*2-D representation of crystal lattice*



# Conduction Electrons in Pure Silicon

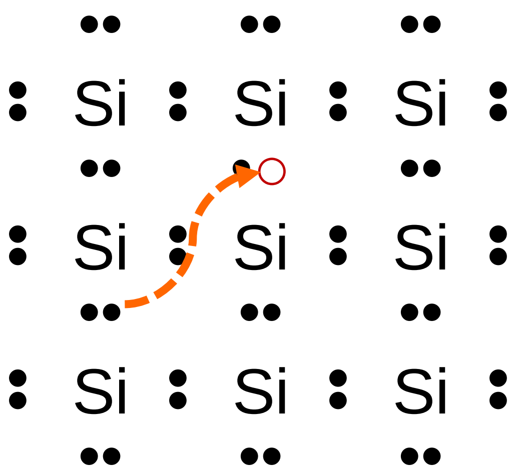
- At any temperature above absolute zero, electron has thermal energy $kT$
- Finite probability that an electron will break loose from its bond and become a conduction electron

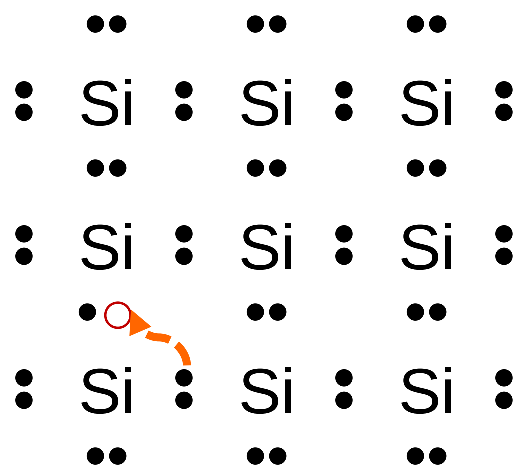



- Energy required to break loose ≈ 1.1 eV
- At room temperature (300°K), kT ≈ 26 meV
- Number that break free at room temp. is 1 in $2 \times 10^{13}$

# Holes

- When an electron breaks loose and becomes a conduction electron it leaves behind a vacancy called a hole
- Another valence electron may jump across to fill the hole
  - as a result the hole “moves” to another location
  - alternative way for electrons to move around and conduct current




- Hole can be viewed as a positively charged carrier
  - bubble in a liquid analogy
- In pure (intrinsic) silicon, # conduction electrons = # holes

# Other Semiconductors

*Germanium*
*(elemental semiconductor)*

: Ge : Ge : Ge :

: Ge : Ge : Ge :

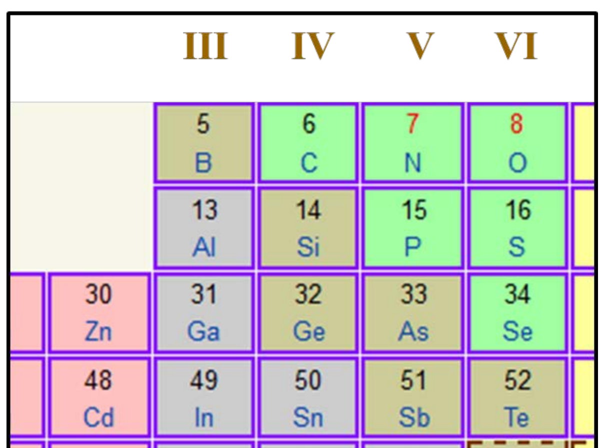
: Ge : Ge : Ge :

*Gallium Arsenide*
*(III-V compound semiconductor)*

: Ga : As : Ga :

: As : Ga : As :

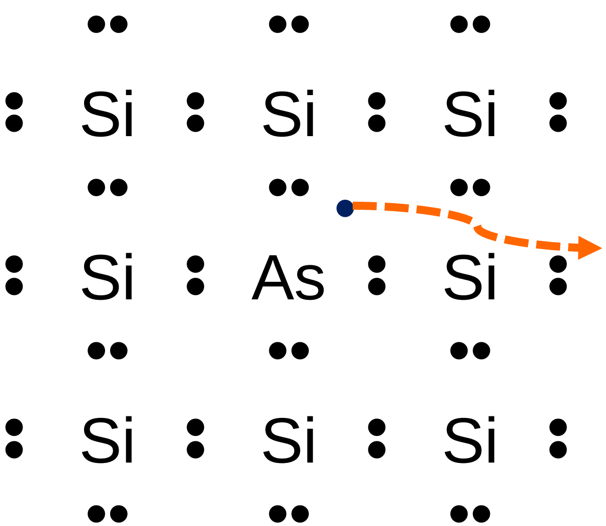
: Ga : As : Ga :

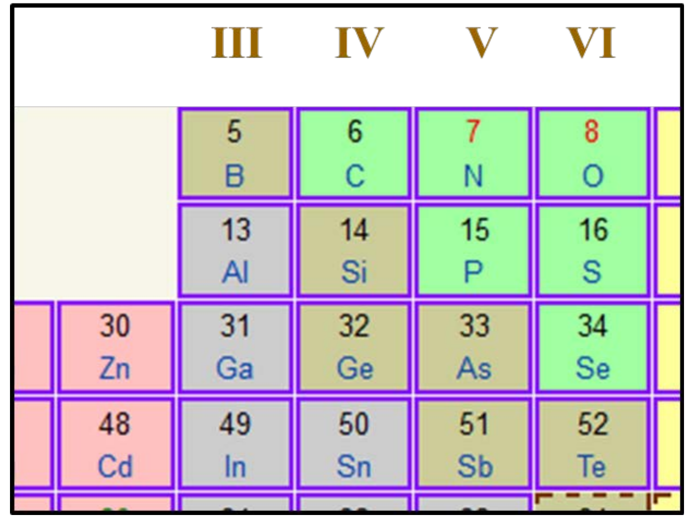


| | III | IV | V | VI |
|---|---|---|---|---|
| | 5 B | 6 C | 7 N | 8 O |
| | 13 Al | 14 Si | 15 P | 16 S |
| 30 Zn | 31 Ga | 32 Ge | 33 As | 34 Se |
| 48 Cd | 49 In | 50 Sn | 51 Sb | 52 Te |

# Adding Dopants: N-type Silicon

- Suppose we replace one silicon atom with an arsenic (group V) atom:

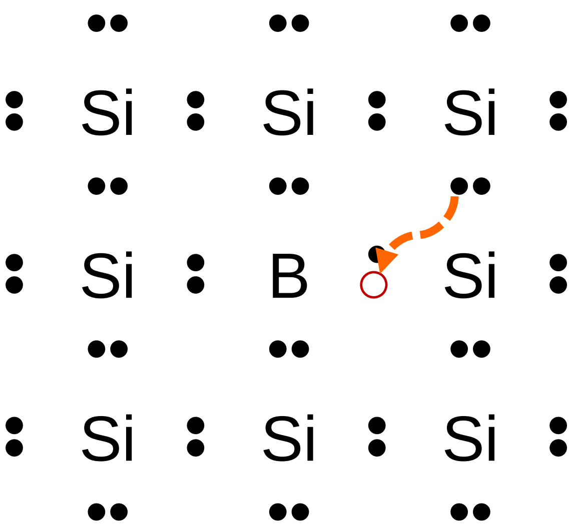


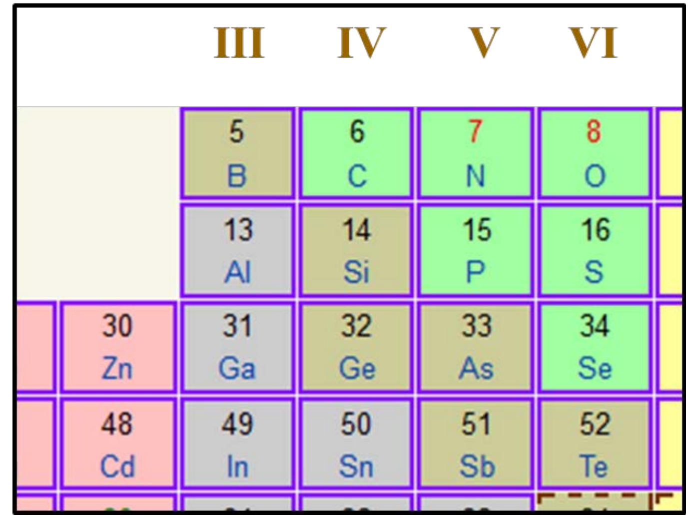




- Contributes one extra electron which is weakly held
  - energy to break loose (ionization energy) ≈ 100 mev
  - free to wander at room temperature (almost 100% ionization)
  - electron leaves behind a positive $As^+$ ion – <u>but no hole</u>
  - impurities (dopants) such as arsenic are called donors

# Adding Dopants: P-type Silicon

- Similarly, if we introduce a boron (group III) atom:

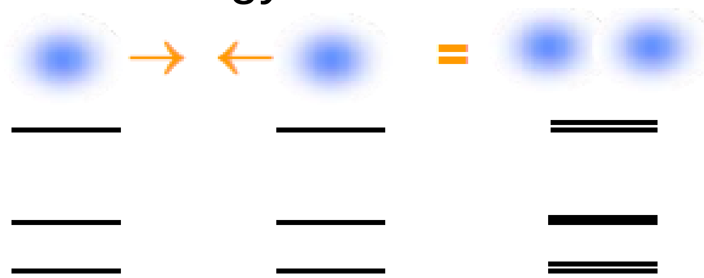


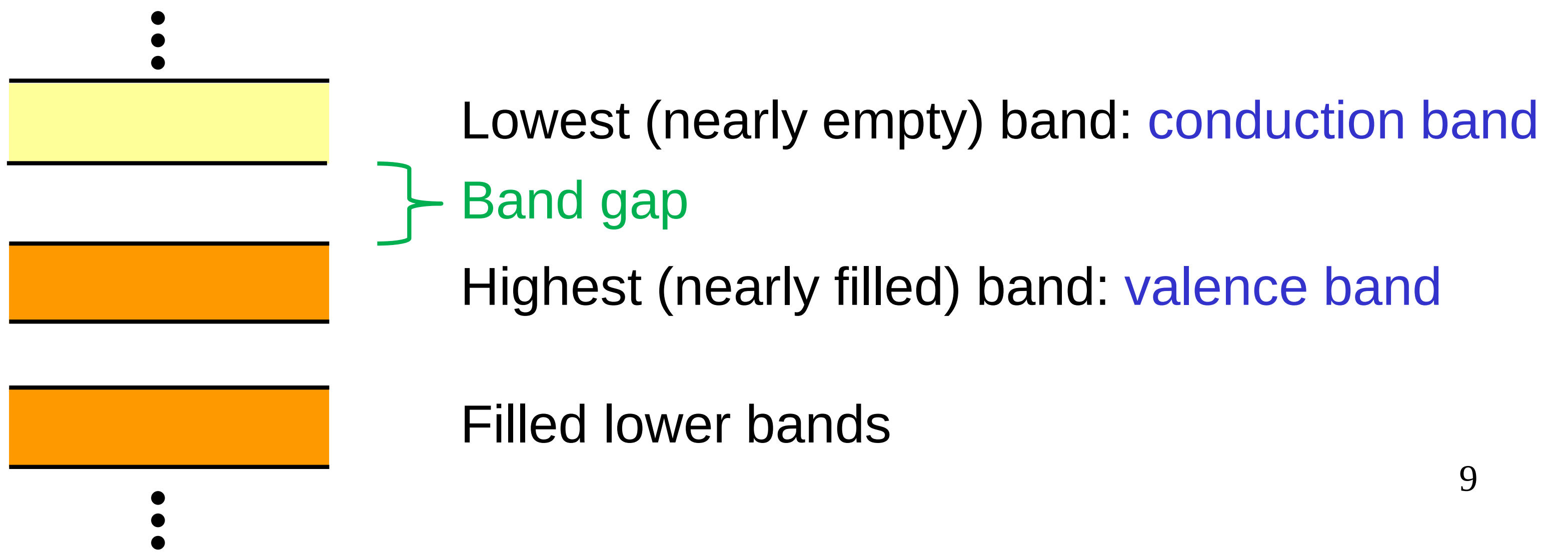

- Can accept an extra electron which creates a hole
  - leads to a negative $B^{-}$ ion – <u>but no conduction electron</u>
  - impurities (dopants) such as boron are called acceptors
  - if one in million Si atoms is replaced by an acceptor, number of holes available to conduct current increases by a factor of $5x10^6$ (same is true for donors and electrons)
  - property of semiconductors: large changes in conductivity through the addition of trace amounts of dopant material

# Energy Band Model

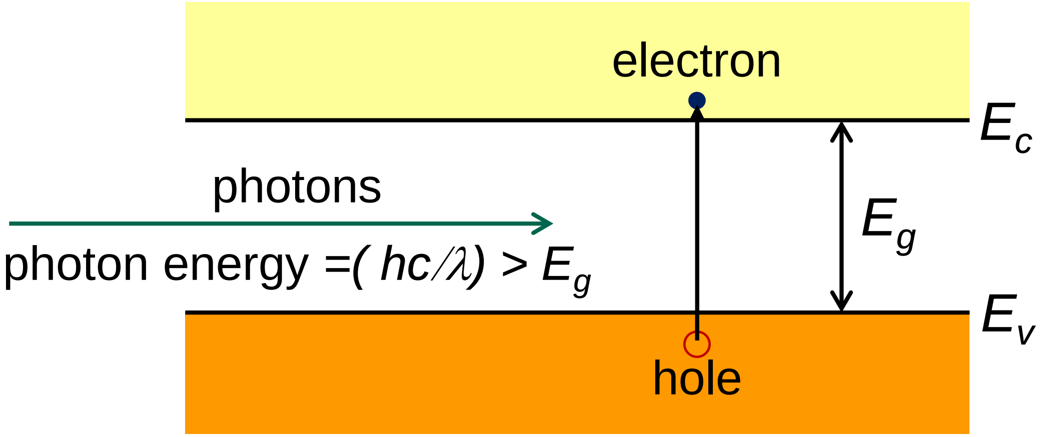
- When two atoms of silicon are in close proximity
  - splitting of the energy levels of the outer electron shells



- When many atoms are in close proximity
  - discrete energy levels are replaced by bands of energy states separated by gaps between the bands



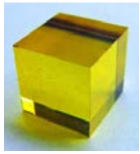
# Measuring Band Gap Energy



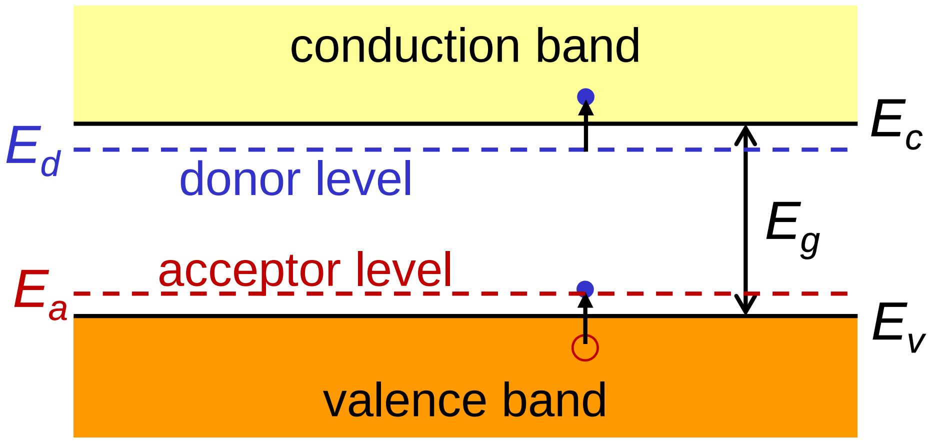

- When light is absorbed by semiconductor, electron-hole pairs are created - *conductivity increases*
- Photon energy must be greater than $E_g$
  - *at longer $\lambda$, photon is not absorbed and material is transparent*

| Material | InSb | Ge | Si | GaAs | GaP | ZnSe | Diamond |
|---|---|---|---|---|---|---|---|
| $E_g$ (eV) | 0.18 | 0.67 | 1.12 | 1.42 | 2.25 | 2.7 | 6 |
| $\lambda_{cutoff}$ (nm) | 6900 | 1800 | 1100 | 870 | 550 | 460 | 210 |





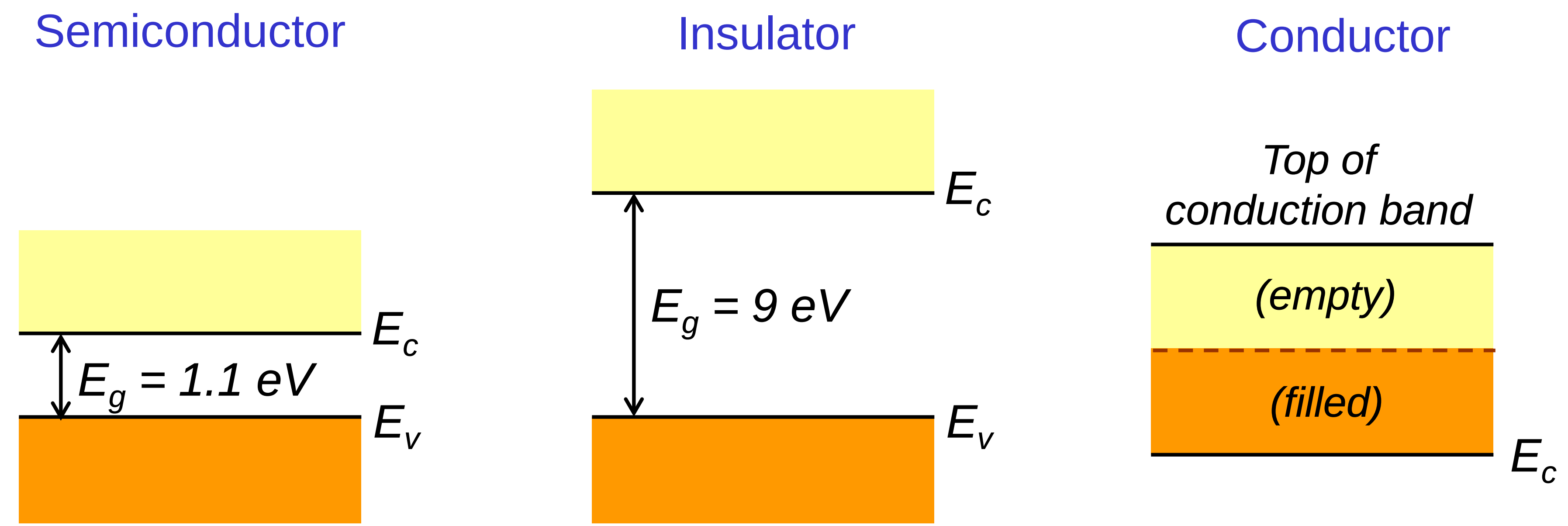

# Donor and Acceptor Levels




- N-type silicon has a donor energy level
  - Donor ionization energy = $E_c - E_d \approx 50$ meV
- P-type silicon has an acceptor energy level

| *Ionization Energy in Silicon* | Donors | | | Acceptors | | |
|---|---|---|---|---|---|---|
| Dopant | Sb | P | As | B | Al | In |
| Ionization energy, $E_c - E_d$ or $E_a - E_v$ (meV) | 39 | 44 | 54 | 45 | 57 | 160 |

# Conductors, Insulators and Semiconductors



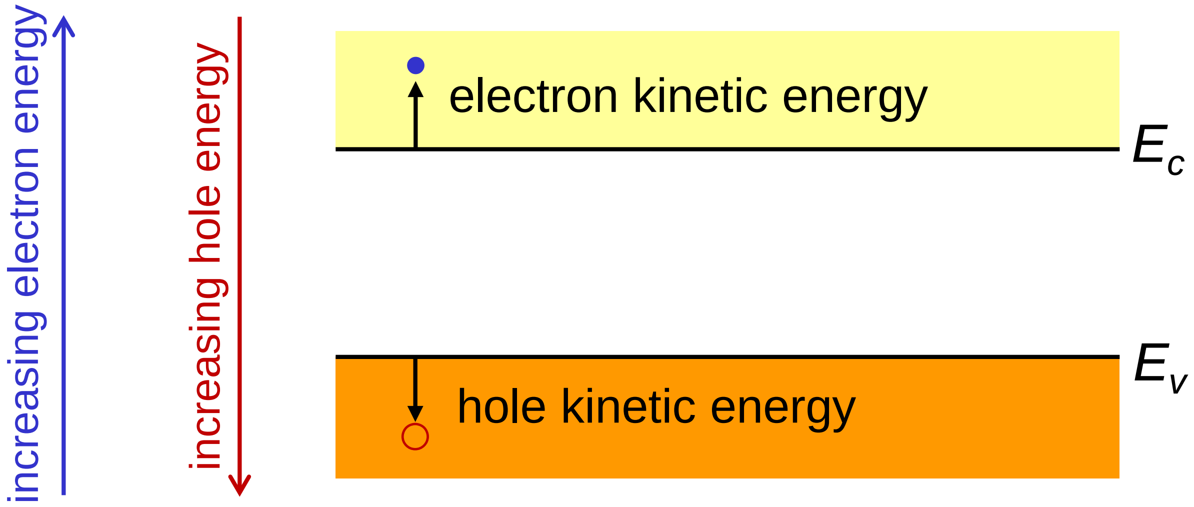

**Silicon**
$\sigma = 1.5 \times 10^{-5}\ (\Omega.\mathrm{cm})^{-1}$

**Silicon Dioxide**
$\sigma = 10^{-18}\ (\Omega.\mathrm{cm})^{-1}$

**Aluminum**
$\sigma = 3.5\times10^{5}\ (\Omega.\mathrm{cm})^{-1}$

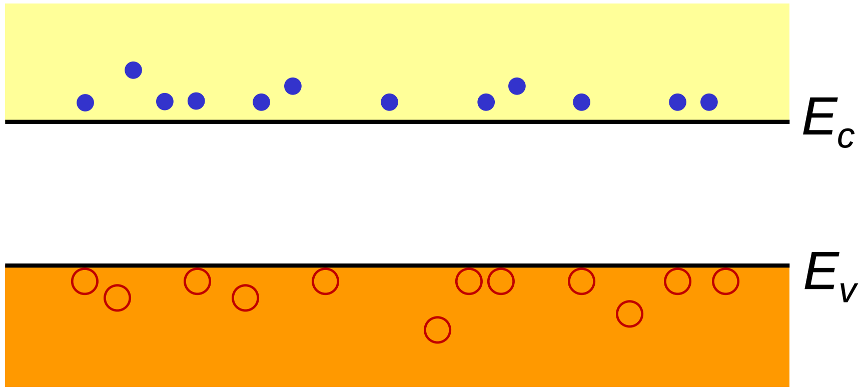
- Totally filled and totally empty bands do not allow current flow
  - Metal conduction band is half-filled
- Semiconductors differ from insulators in that:
  - they have narrower band-gap
  - conductance dramatically increased through impurity doping

# Energy of Electrons & Holes



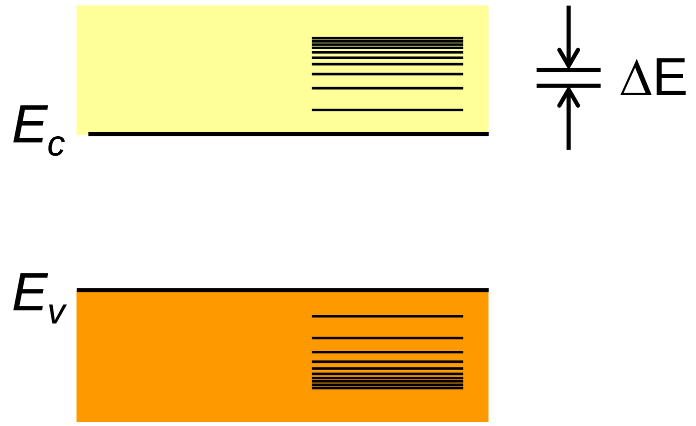

- Higher position in band diagram represents a higher electron energy
  - Minimum conduction electron energy is $E_c$
  - Any energy above $E_c$ represents electron kinetic energy
- Lower position in band energy represents a higher hole energy
  - Requires energy to move hole downward
    - equivalent to moving an electron upward
  - Minimum hole energy is $E_v$

# Distribution of Electrons & Holes




- Electrons & holes carry negative and positive charge (± q) respectively
- To determine electrical properties of a semiconductor we need to know number of electrons and holes available for conduction
- Quantum mechanics allows us calculate:
  - Density of energy states in the conduction and valence bands
  - Probability that a particular state will be occupied

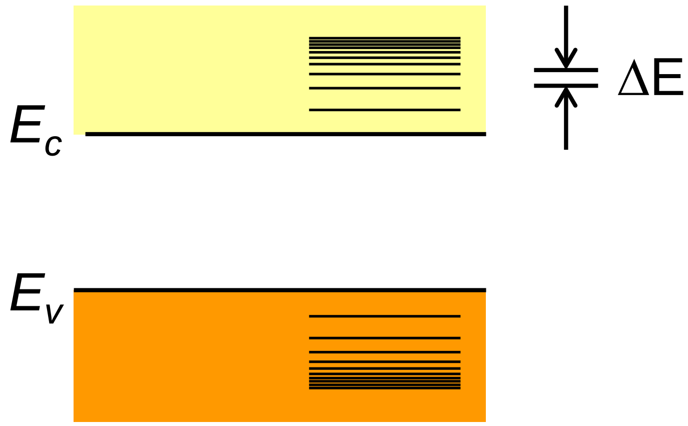
# Energy States

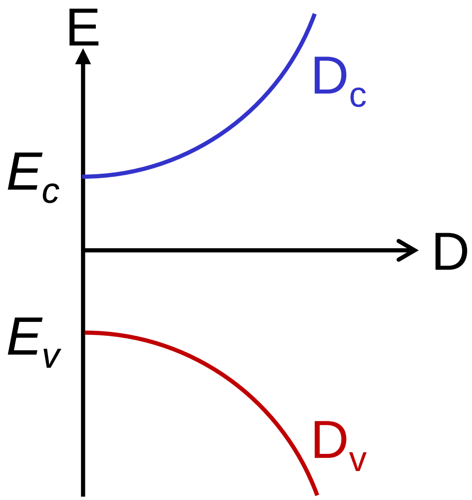



- Energy band is a collection of discrete energy states
  - each state can hold 0 or 1 electron (hole)
- If we count number of states in small energy range ΔE in the conduction band in a given volume of material:

$$D_c(E) \equiv \frac{number\ of\ states\ in\ \Delta E}{\Delta E \times volume}$$

# Density of States




- Analysis of available quantum states yields:

$$D_c(E) \equiv \frac{8\pi m_n \sqrt{2m_n(E-E_c)}}{h^3}, \qquad E \geq E_c$$

$$D_v(E) \equiv \frac{8\pi m_p \sqrt{2m_p(E_v-E)}}{h^3}, \qquad E \leq E_v$$

- Density of states increases as we move away from band edge

# Effective Mass of Electron (Hole)

$$D_c(E) \equiv \frac{8\pi m_n \sqrt{2m_n(E - E_c)}}{h^3}, \qquad E \geq E_c$$

- $m_n$ is effective mass of electron within the crystal lattice
- $m_p$ is effective mass of hole within the crystal lattice
- In silicon:

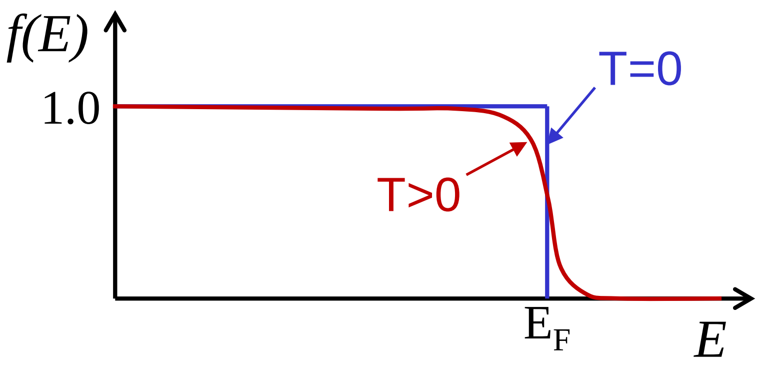
$$m_n = 1.08 \times m_0 \qquad m_p = 0.56 \times m_0$$

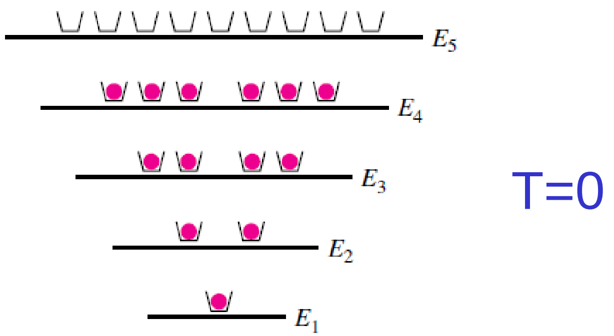
where $m_0 = 9.11 \times 10^{-31}\ kg$ is the rest mass of electron

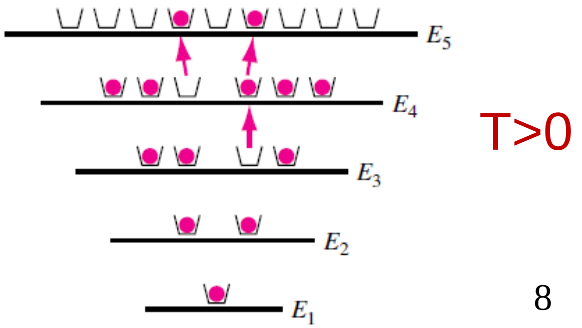
- <u>Note:</u> Any formula with a mass term in it, must be evaluated in full SI units (kg, meters, joules etc.)

# Distribution of Carriers in States

- Now need to determine distribution of electrons (holes) into these available states
  - i.e. probability of each state being occupied
- If there are N electrons (holes) in a system, then at T=0, the N electrons (holes) will occupy the N lowest energy levels.

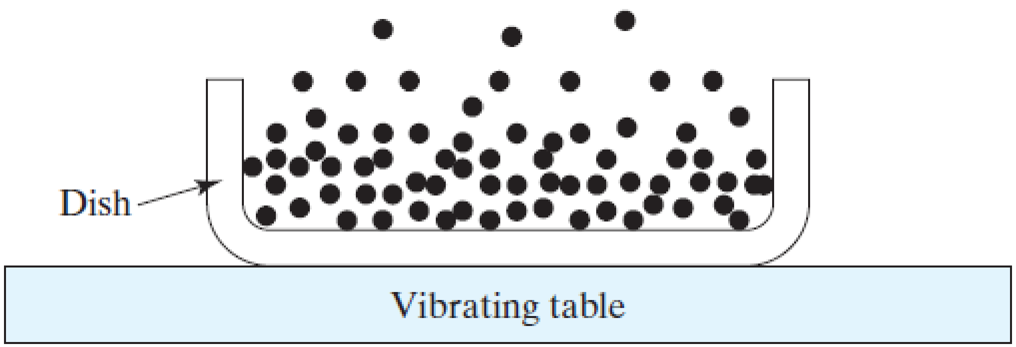



- For T>0, some electrons (holes) will move to higher energy states leaving vacancies at lower energy states

# Vibrating Sand Analogy




- Elevation of sand particles represent energy of electrons in conduction band under agitation of thermal energy
- At equilibrium (after constant shaking for a time), there is a finite probability that an energy state (i.e. height above table) will be occupied by a sand particle.
  - *higher the energy state (height above table) the lower the probability*
- Similarly, in silicon at thermal equilibrium, there is a finite probability that an electron will be elevated to a particular energy state
  - *higher the energy state, the lower the probability*

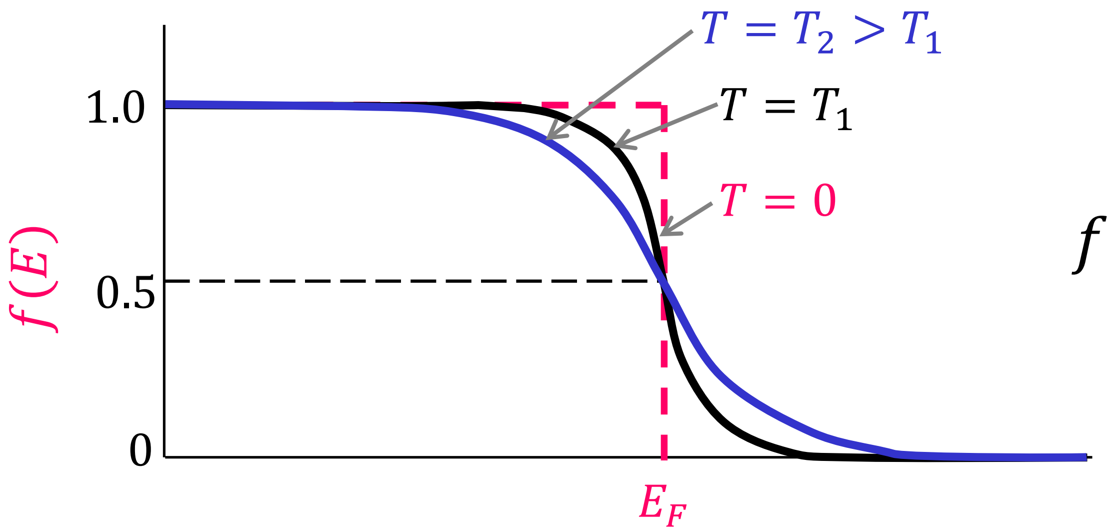
# Fermi-Dirac Probability Function

- If we have a system in thermal equilibrium, in which there are a large number of indistinguishable particles and at most one particle is permitted in each quantum state:

$$\boxed{f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}}$$

- $f(E)$ is the probability that a state at energy $E$ is occupied by an electron
- $E_F$ is called Fermi energy or Fermi level
- Note: There is only one Fermi level in a system at thermal equilibrium

# Fermi Function at Different Temperatures




$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

- For T=0:
  - $f(E) = 1$ for $E < E_F$
  - $f(E) = 0$ for $E > E_F$
- For T>0, non-zero probability that some energy states above $E_F$ will be occupied by electrons and some states below $E_F$ will be empty
- $f(E_F) = 0.5$ at all temperatures

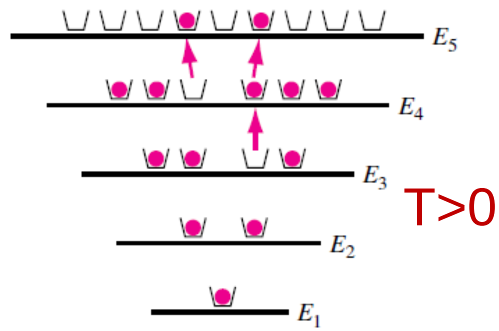
# Exercise: Where is the Fermi level?

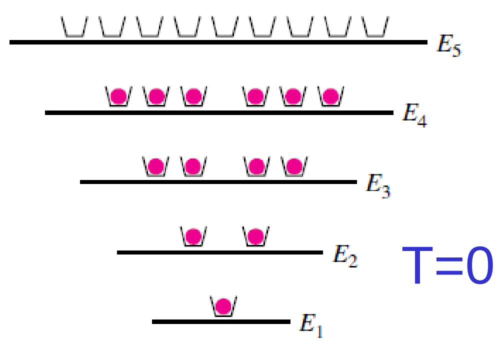
Suppose we have a one-electron system

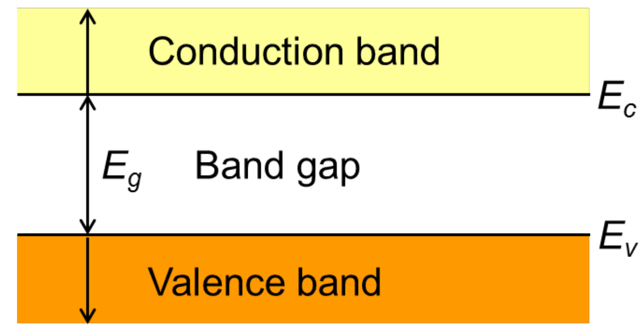
$E_3 = 0$ eV

$E_2 = -1$ eV

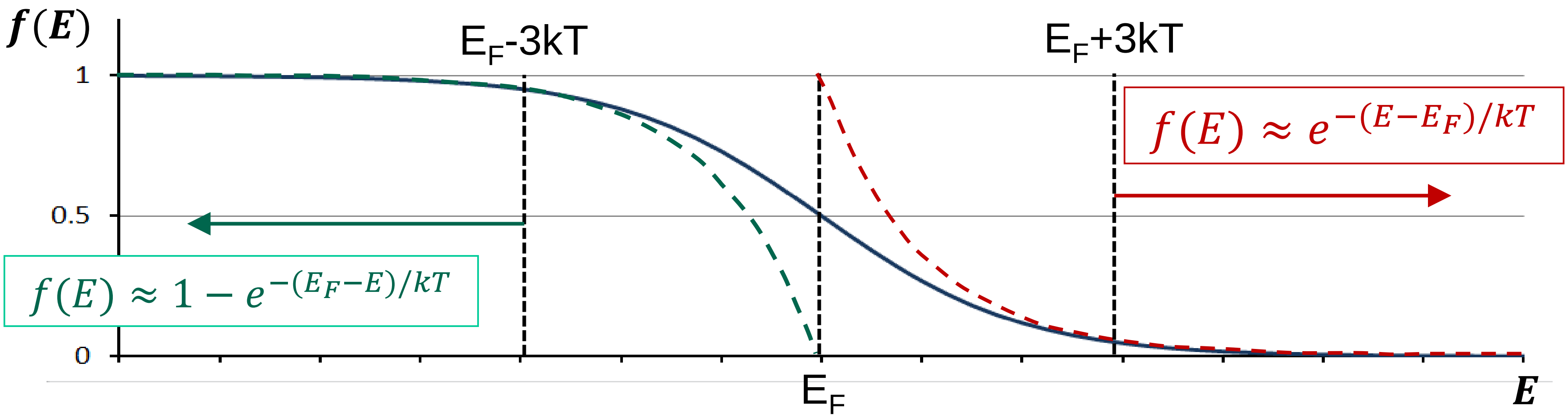
$E_1 = -4$ eV



# Boltzmann Approximation




$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$

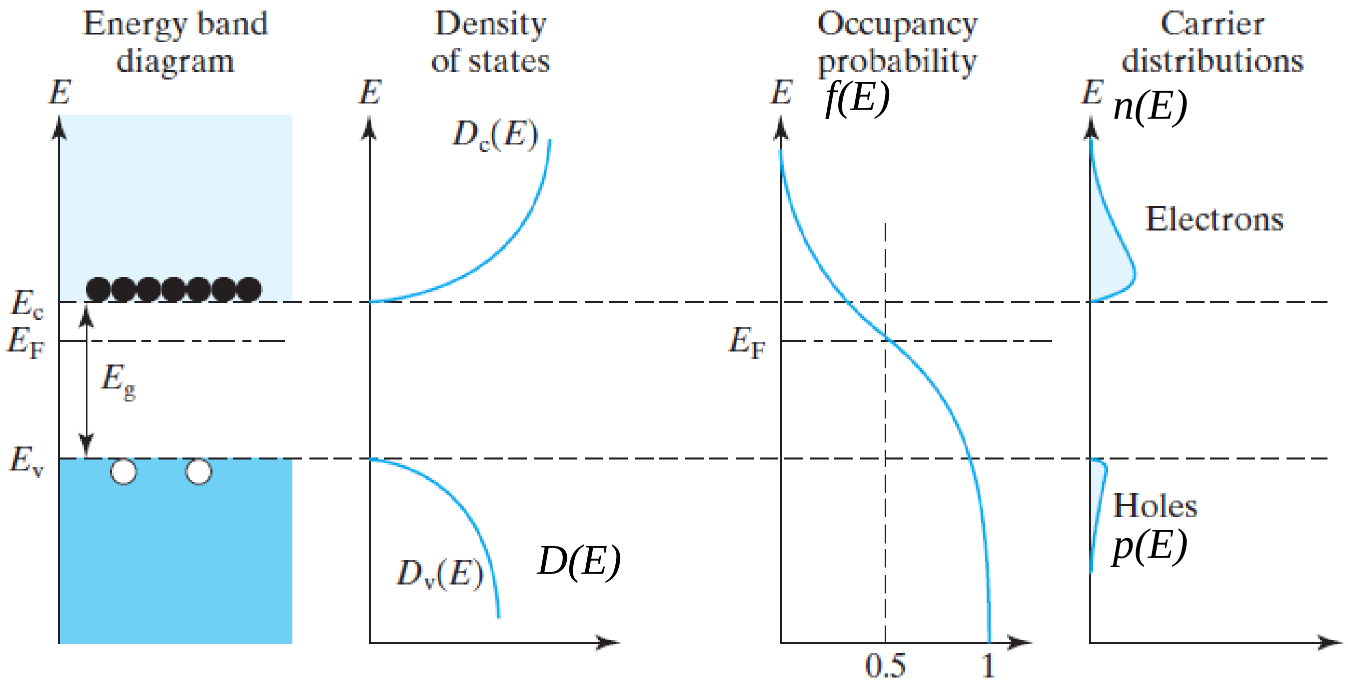
- For $(E - E_F) >> kT$: $f(E) \approx e^{-(E-E_F)/kT}$
- For $(E - E_F) << kT$: $f(E) \approx 1 - e^{-(E_F-E)/kT}$
- Approximation is within 5% accuracy for $|E - E_F| > 3kT$

# Electron & Hole Distribution

- Distribution of electrons in conduction band $n(E)$ is:

*(Density of states) x (Probability that state is occupied by electron)*

$$n(E) = D_c(E).f(E)$$




- Similarly, distribution of holes in valence band

$$\mathrm{p}(E) = D_v(E).[1 - f(E)]$$

# Total Electron Concentration

- Electron concentration *(n)* is total number of electrons (per unit volume) available for conduction

$$n = \int_{E_c}^{top\ of\ conduction\ band} D_c(E).f(E).dE$$

$$= \frac{8\pi m_n\sqrt{2m_n}}{h^3}\int_{E_c}^{\infty}\sqrt{E-E_c}.e^{-(E-E_F)/kT}\,dE$$

using Boltzmann approximation

$$= \frac{8\pi m_n\sqrt{2m_n}}{h^3}.e^{-(E_c-E_F)/kT}.\int_0^{\infty}\sqrt{E-E_c}.e^{-\frac{E-E_c}{kT}}\,d(E-E_c)$$

- Introduce a new variable: $x = (E - E_c)/kT$

and using $\int_0^{\infty}\sqrt{x}.e^{-x} = \sqrt{\pi}/2$ …

# Total Electron Concentration (cont.)

- We get:

$$\boxed{n = N_c . e^{-(E_c - E_F)/kT}}$$

- where $$N_c \equiv 2.\left[\frac{2\pi m_n kT}{h^2}\right]^{3/2}$$

- $N_c$ is called effective density of states of conduction band
  - as if there were a total of $N_c$ states in conduction band
  - all $N_c$ states existed at energy $E_c$

# Total Hole Concentration

- Similarly, we get the concentration of holes (i.e. number per unit volume) present in valence band:

$$\boxed{p = N_v . e^{-(E_F - E_v)/kT}}$$

- where $$N_v \equiv 2. \left[\frac{2\pi m_p kT}{h^2}\right]^{3/2}$$

- $N_v$ is called effective density of states of valence band
- For Si at 300°K: $N_c = 2.8x10^{19}\ cm^{-3}$, $N_v = 1.04x10^{19}\ cm^{-3}$
- Note: as $E_F$ moves up towards $E_c$, $n$ increases (while $p$ decreases); as $E_F$ moves down towards $E_v$, $p$ increases (while $n$ decreases)

# Fermi Level and Carrier Concentrations

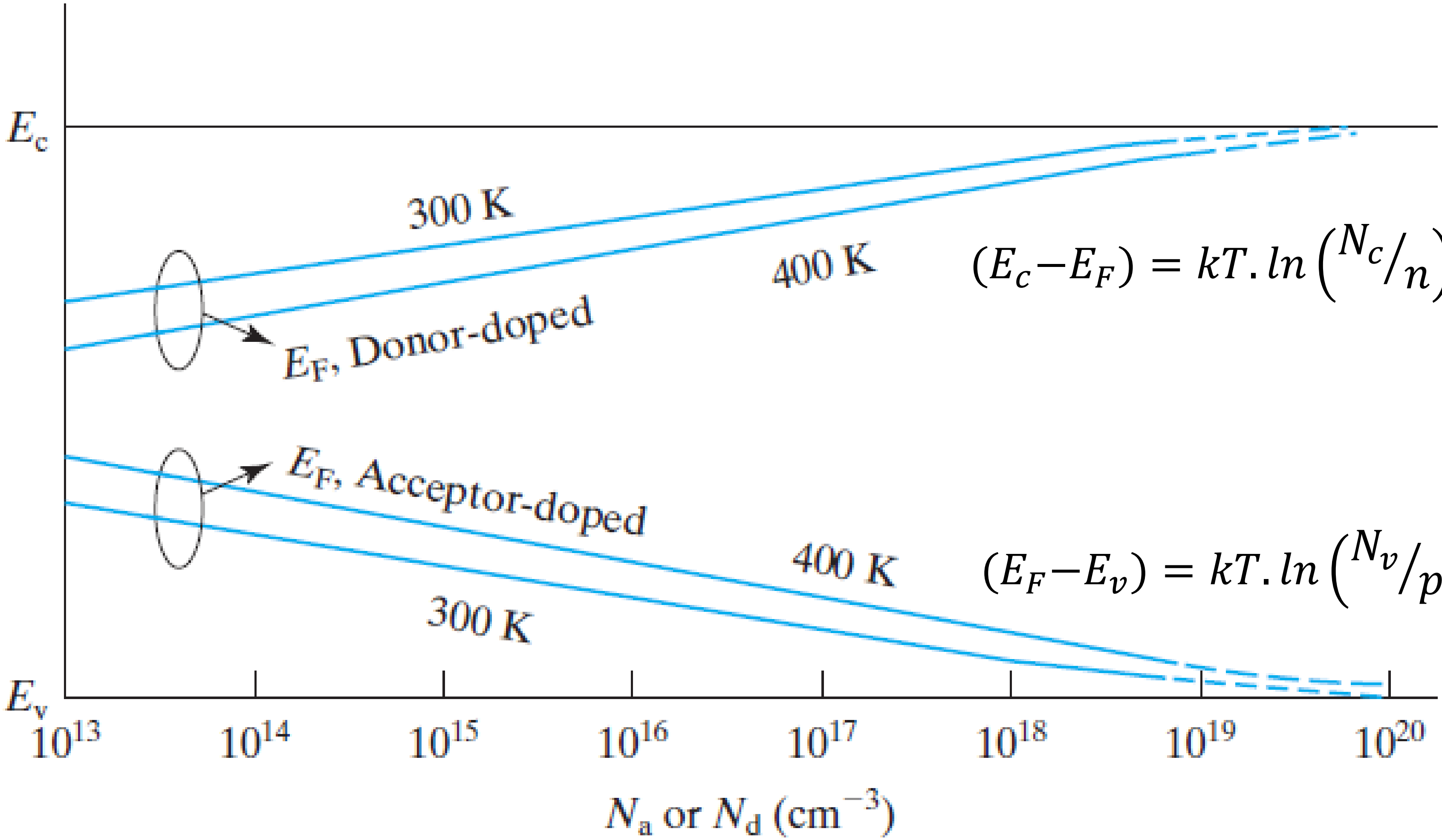
- These two equations tell us total carrier (electron or hole) concentration (*n* or *p*) (in thermal equilibrium) for a given Fermi level
- Can also use them to calculate the Fermi level given a carrier concentration
- If $n = N_c . e^{-(E_C - E_F)/kT}$

then $(E_c - E_F) = kT . ln\left({}^{N_c}/_{n}\right)$

- Similarly $(E_F - E_v) = kT . ln\left({}^{N_v}/_{p}\right)$
- Example: Where is $E_F$ if $n = 10^{17}\ cm^{-3}$ ?

  Where is $E_F$ if $p = 10^{14}\ cm^{-3}$ ?

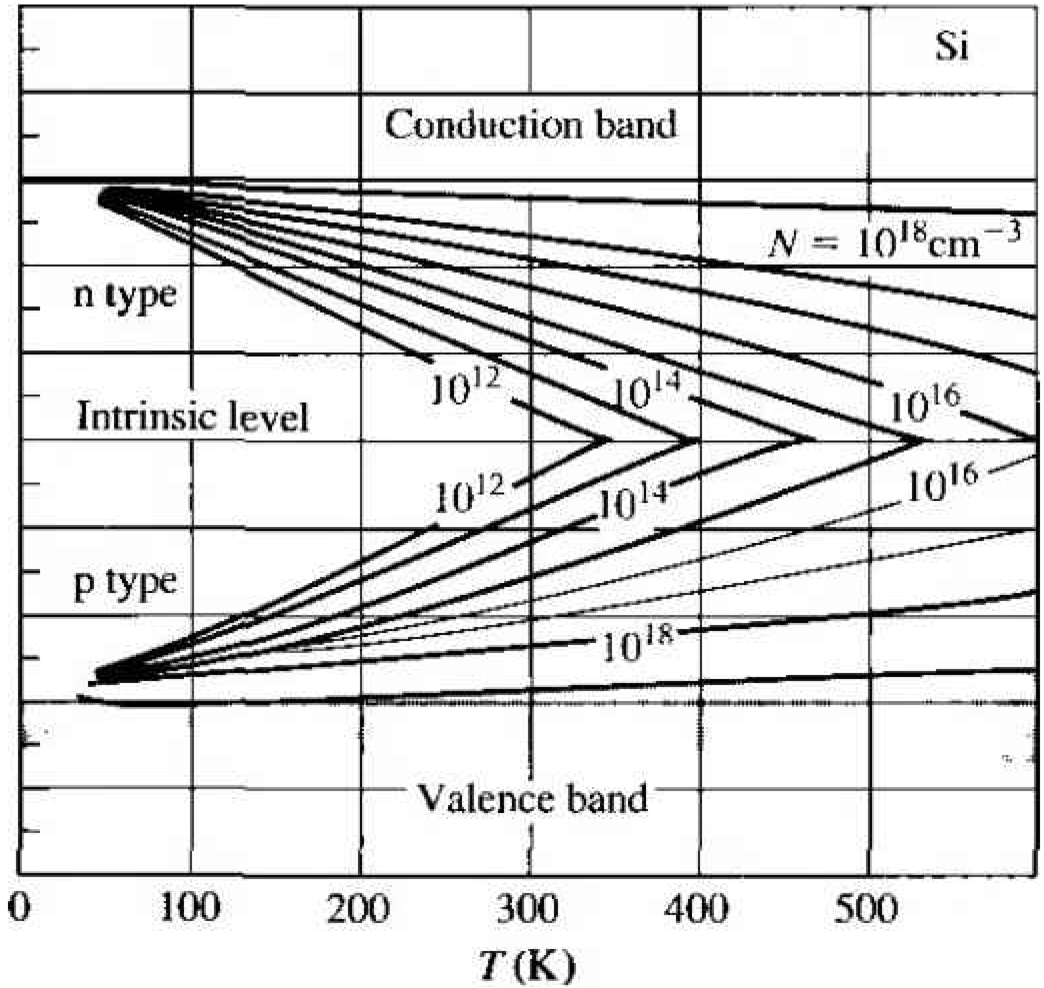
# Fermi Energy vs. Doping Concentration




$$(E_c - E_F) = kT.\ln\left({N_c}/{n}\right)$$

$$(E_F - E_v) = kT.\ln\left({N_v}/{p}\right)$$

# Fermi Energy vs. Temperature




$$(E_c - E_F) = kT.\ln\left({}^{N_c}/_{n}\right)$$

$$(E_F - E_v) = kT.\ln\left({}^{N_v}/_{p}\right)$$

# *np* Product & Intrinsic Carrier Concentration

- Note that $E_F$ can't be both close to $E_c$ and $E_v$
  - *n* and *p* cannot both be large numbers

$$n.p = N_c.e^{-(E_c-E_F)/kT}.N_v.e^{-(E_F-E_v)/kT} = N_c.N_v.e^{-E_g/kT}$$

- For a given material and temperature, *n.p* is independent of $E_F$ and therefore of dopant concentrations

- For intrinsic silicon (i.e. no dopants) we know $n = p \equiv n_i$

$$\boxed{n.p = n_i^{\,2}}$$

$$\boxed{n_i = \sqrt{N_c.N_v}.e^{-E_g/2kT}}$$

- In silicon: $n_i \approx 1.0 \text{ x } 10^{10}$ at room temperature

# Carrier Concentrations

- What are the electron and hole concentrations in N-type silicon at 300°K if donor concentration $N_D = 10^{15}\ cm^{-3}$ ?

  Assuming full ionization: $n = 10^{15}\ cm^{-3}$

$$p = \frac{{n_i}^2}{n} \approx \frac{10^{20}}{10^{15}} = 10^5 cm^{-3}$$

- With a temperature increase of 60°C:
  - $n$ remains the same
  - $p$ increases by a factor of 2300
  - because $n_i$ increases exponentially with temperature
- In N-type silicon, many more electrons that holes
  - electrons are called the majority carriers
  - holes are called minority carriers
  - in P-type, holes are majority carriers

# Intrinsic Fermi Level

- Where is Fermi level in intrinsic silicon?
- Since *n = p*, $(E_c - E_F) \approx (E_F - E_v)$
- Intrinsic Fermi level $E_i$ is approx. in middle of band gap
  - not exactly because $N_c \neq N_v$

$$E_i = E_c - \frac{E_g}{2} - kT.\,ln\sqrt{\frac{N_c}{N_v}}$$

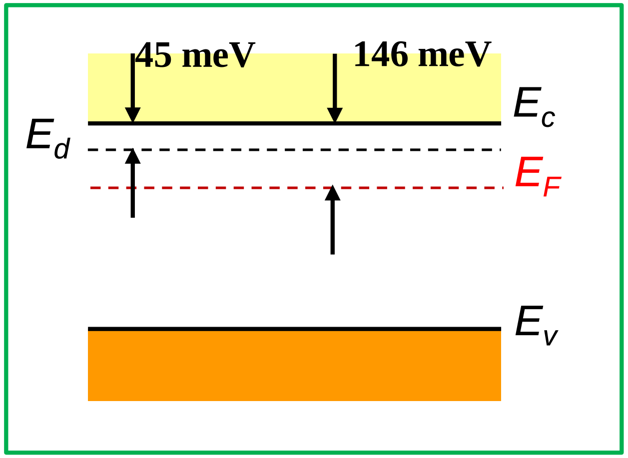
- For silicon, this last term is very small (≈ 12.9 meV)
- Normally assume $E_i$ is mid-gap in silicon

# Ionization of Dopant Atoms

- We have assumed that donor and acceptor atoms are completely ionized – *is this accurate?*
  - If $E_d$ is a few $kT$ above $E_F$, then donor level will be almost empty
  - If $E_a$ is a few $kT$ below $E_F$, then acceptor level will be almost full
- Suppose we have silicon doped with $10^{17}\ cm^{-3}$ of P atoms
- First assume all donors are ionized, i.e. $n = N_d = 10^{17} cm^{-3}$

$E_d$ is located 45 meV below $E_c$

$E_F$ is located 146 meV below $E_c$




So Probability of non-ionization =

$$\frac{1}{1+0.5e^{(E_d-E_F)/kT}} = \frac{1}{1+0.5e^{((146-45)meV)/26meV}} = 3.9\%$$

# Extrinsic Semiconductor

- *Extrinsic semiconductor is one in which controlled amounts of dopant atoms have been added to change the electron & hole concentrations from their intrinsic value*
- Potentially four kinds charged species :
  - electrons, holes, positive donor ions and negative acceptor ions
- Assuming complete ionization, charge neutrality requires:

$$n + N_a = p + N_d$$

- Substituting $np = n_i^2$ gives:

$$n = \frac{N_d - N_a}{2} + \left[ \left( \frac{N_d - N_a}{2} \right)^2 + n_i^2 \right]^{1/2}$$

$$p = \frac{N_a - N_d}{2} + \left[ \left( \frac{N_a - N_d}{2} \right)^2 + n_i^2 \right]^{1/2}$$

# Extrinsic Simplifications

- Very rarely is $N_a \approx N_d$
- For $N_d - N_a >> n_i$ (i.e. N-type)

$$\boxed{\begin{aligned} n &= N_d - N_a \\ p &= n_i^2 / n \end{aligned}}$$

- Furthermore, if $N_d >> N_a$, then $n = N_d$ and $p = n_i^2/N_d$

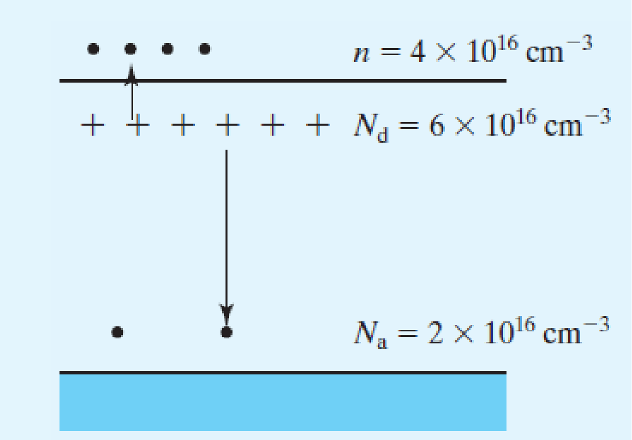
- For $N_a - N_d \gg n_i$ (i.e. P-type)

$$\boxed{\begin{aligned} p &= N_a - N_d \\ n &= n_i^2 / p \end{aligned}}$$

- Furthermore, if $N_a \gg N_d$, then $p = N_a$ and $n = n_i^2/N_a$

# Example: Counter-doping

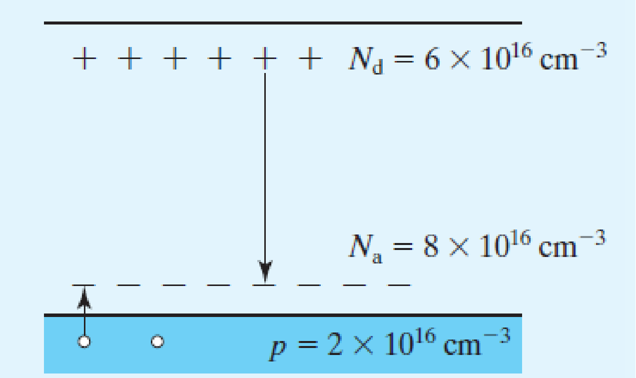
- What are $n$ and $p$ concentrations in Si with $N_d = 6 \times 10^{16}$ cm$^{-3}$ and $N_a = 2 \times 10^{16}$cm$^{-3}$ ?
- What if we add another $6 \times 10^{16}$ cm$^{-3}$ of acceptors?




(a)

*(a)* $n = N_d - N_a = 4 \times 10^{16}\ cm^{-3}$

$p = n_i^2/n = 10^{20}/(4 \times 10^{16}) = 2.5 \times 10^3\ cm^{-3}$




(b)

*(b)* $N_a = (2 \times 10^{16}) + (6 \times 10^{16}) = 8 \times 10^{16}$

$p = N_a - N_d = 2 \times 10^{16}\ cm^{-3}$

$n = n_i^2/p = 10^{20}/(2 \times 10^{16}) = 5 \times 10^3\ cm^{-3}$

# Example Problems

- How many silicon atoms are there per unit cell?
- How many silicon atoms are there per cubic centimeter?
- If Si atomic weight is 28.1 and Avogadro's number is $6.02 \times 10^{23}$ atoms per mole, what is the density of Si in $gm/cm^3$

- In silicon, $m_n = (1.08 \times (9.11 \times 10^{-31}))$ kg. Determine the number of quantum states per $cm^{-3}$ in silicon between $E_c$ and $(E_c+kT)$ at 300°K

- What is the probability that an energy level 3kT above the Fermi level will be occupied by an electron?

- Silicon at 300°K contains an acceptor impurity concentration of $N_a = 10^{16}$ $cm^{-3}$. Determine the concentration of donor impurity atoms that must be added to move the Fermi energy to be 200meV below the conduction band edge.