

# ECE606: Solid State Devices

## Lecture 7

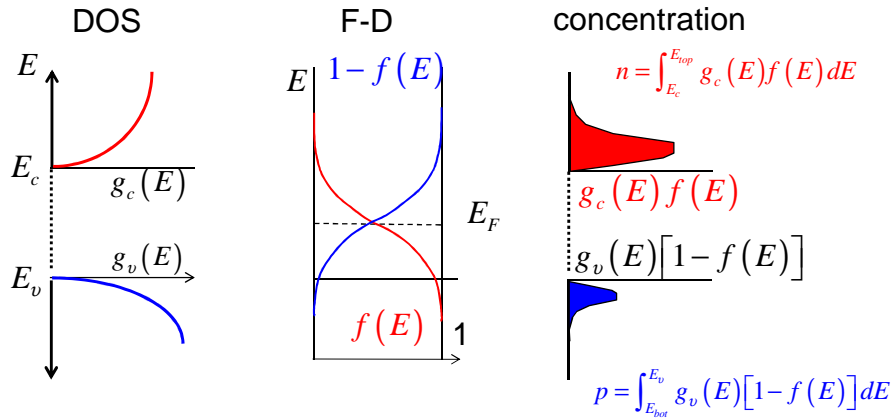
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- Intrinsic carrier concentration
- Potential, field, and charge
- E-k diagram vs. band-diagram
- Basic concepts of donors and acceptors
- Law of mass-action & intrinsic concentration
- Statistics of donors and acceptor levels
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- Temperature dependence of carrier concentration
- Multiple doping, co-doping, and heavy-doping
- Conclusions

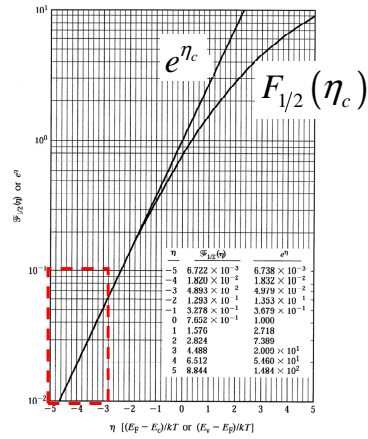
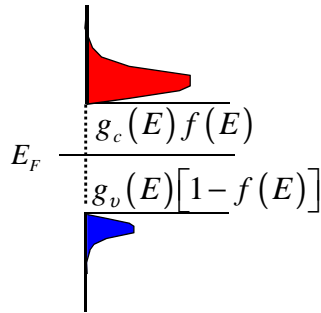
**Reference:** Vol. 6, Ch. 3 & 4



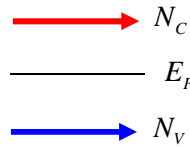
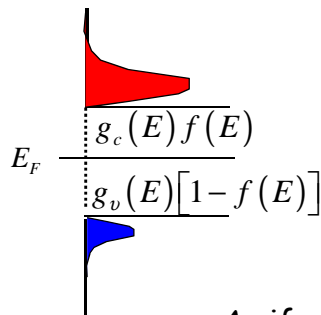


$$\begin{aligned}
 n &= \int_{E_c}^{E_{top}} g_c(E) f(E) dE \\
 &= \int_{E_c}^{E_{top}} 2 \times \frac{m_n^* \sqrt{2m_n^* (E - E_c)}}{2\pi^2 \hbar^3} \frac{1}{1 + e^{\beta(E - E_F)}} dE && \text{Include spin factor of 2} \\
 &\approx \int_{E_c}^{\infty} \frac{m_n^* \sqrt{2m_n^* (E - E_c)}}{\pi^2 \hbar^3} \frac{1}{1 + e^{\beta(E - E_c)} e^{\beta(E_c - E_F)}} dE && \text{Assume wide bands} \\
 &= N_c \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \quad \eta_c \equiv \beta(E_F - E_c) \\
 N_c &\equiv 2 \left( \frac{2\pi m_n^* \beta}{h^2} \right)^{3/2} && F_{1/2}(\eta) = \int_0^{\infty} \frac{\sqrt{\xi} d\xi}{1 + e^{\xi - \eta}}
 \end{aligned}$$

$$n = N_C \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \rightarrow N_C e^{\eta_c} \quad \text{if} \quad -\eta_c \equiv \beta(E_C - E_F) > 3$$



$$n = N_C \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \rightarrow N_C e^{-\beta(E_C - E_F)} \quad \text{if} \quad E_C - E_F > 3\beta$$

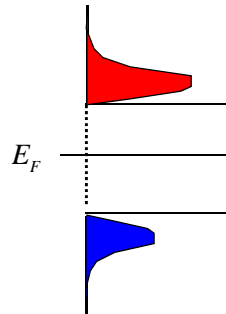


As if all states are at a single level  $E_C$

$$n = N_C e^{-\beta(E_c - E_F)}$$

$$p = N_V e^{+\beta(E_v - E_F)}$$

$$\begin{aligned} n \times p &= N_C N_V e^{-\beta(E_c - E_v)} \\ &= N_C N_V e^{-\beta E_g} \end{aligned}$$



Product is independent of the Fermi level!  
Very useful balance equation! Will use it often

$$n = p = n_i$$

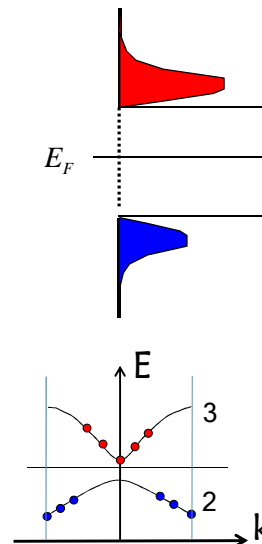
$$n_i^2 = N_C N_V e^{-\beta E_g}$$

$$n_i = \sqrt{N_C N_V} e^{-\beta E_g / 2}$$

$$E_F \equiv E_i$$

$$n = p \Rightarrow N_C e^{-\beta(E_c - E_i)} = N_V e^{+\beta(E_v - E_i)}$$

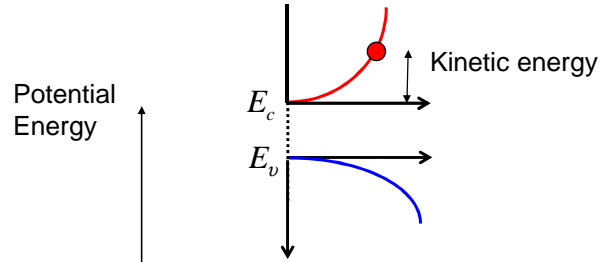
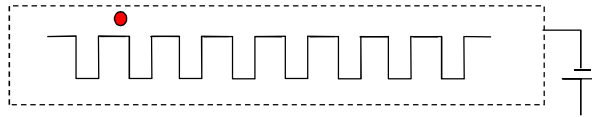
$$E_i = \frac{E_G}{2} + \frac{1}{2\beta} \ln \frac{N_V}{N_C}$$



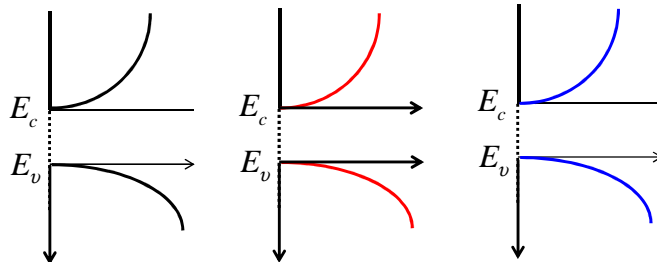
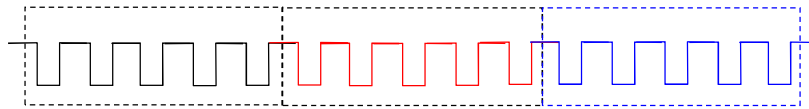
- We discussed how electrons are distributed in electronic states defined by the solution of Schrodinger equation.
- Since electrons are distributed according to their energy, irrespective of their momentum states, the previously developed concepts of constant energy surfaces, density of states etc. turn out to be very useful.  
=> will not discuss Schroedinger Eq. anymore  
=> everything is captured in bandedges and effective masses
- We still do not know where  $E_F$  is for general semiconductors ... If we did, we could calculate electron concentration.

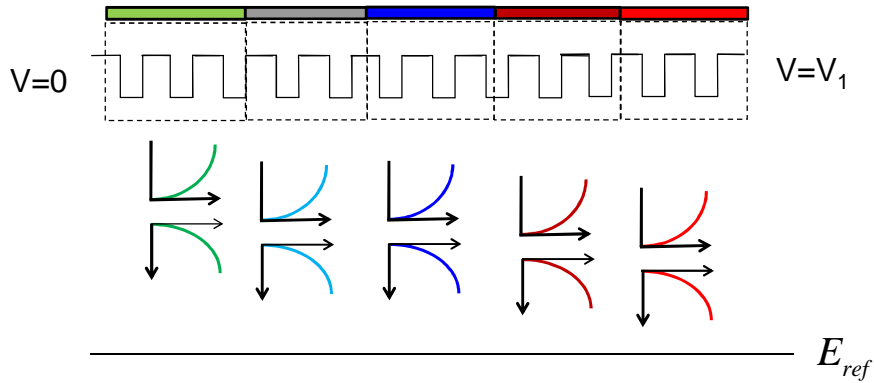
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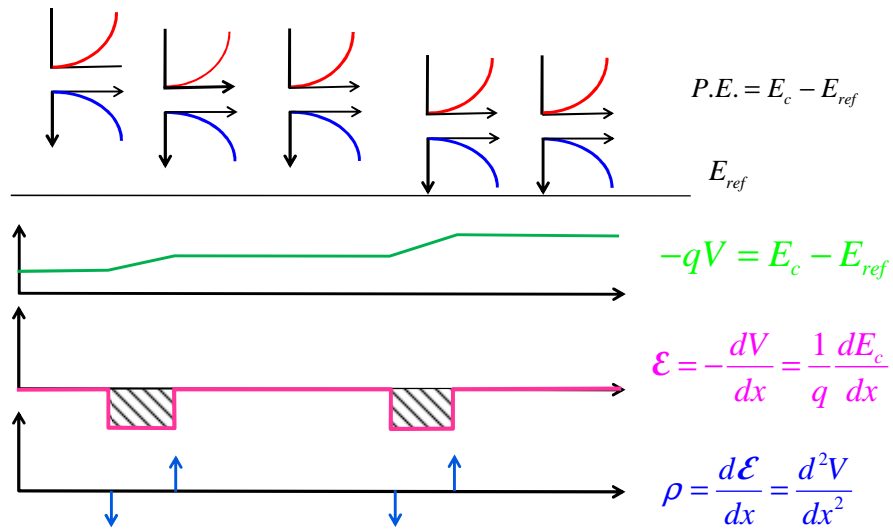


$$P.E. = E_c - E_{ref} = -qV$$





$$P.E. = E_c - E_{ref} = -qV(x)$$



$$P.E. = E_c - E_{ref}$$

$$E_{ref}$$

$$-qV = E_c - E_{ref}$$

$$\mathcal{E} = -\frac{dV}{dx} = \frac{1}{q} \frac{dE_c}{dx}$$

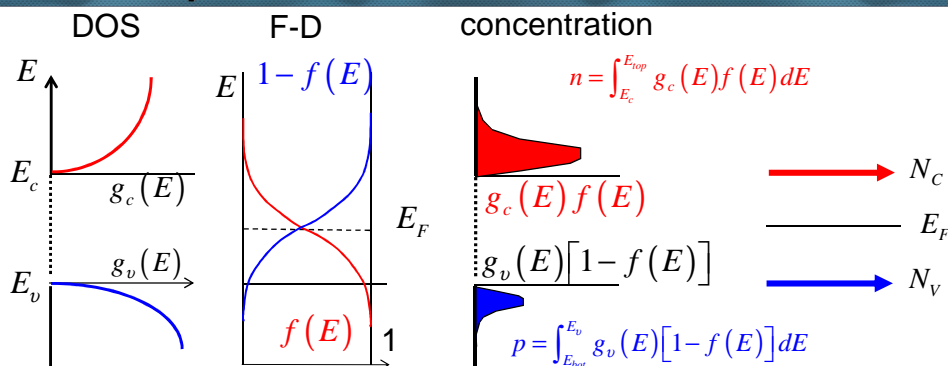
$$\rho = \frac{d\mathcal{E}}{dx} = \frac{d^2V}{dx^2}$$

In most practical cases start from charge and derive potentials!

PURDUE => Useful to learn "graphical" integration

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Critical items here;

Intrinsic semiconductor has VERY few active electrons

$n_i$  is of the order of  $10^{10}/\text{cm}^3$ . In  $10^{22}/\text{cm}^3$  atoms!

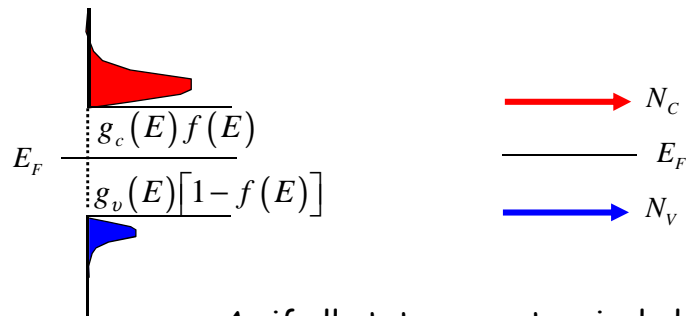
Do not include the coulomb interactions of individual free electrons

Often good enough to forget about the

Distribution of carriers in energy

=> Replace by delta functions at band edge

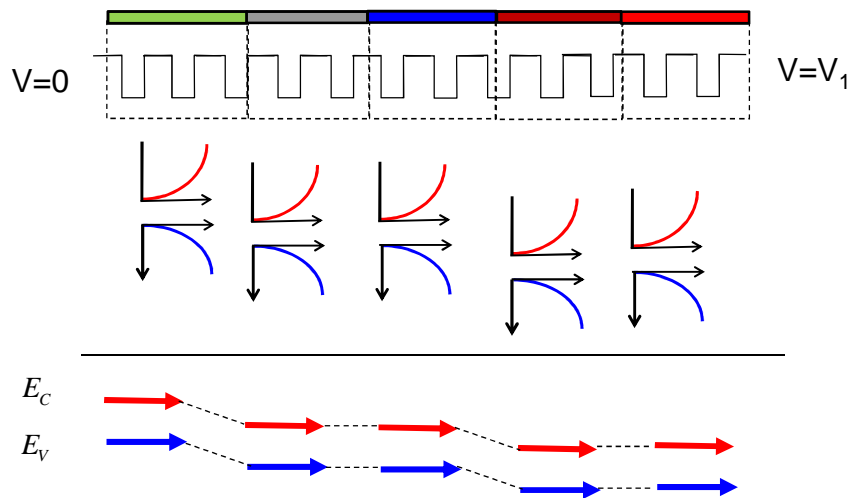




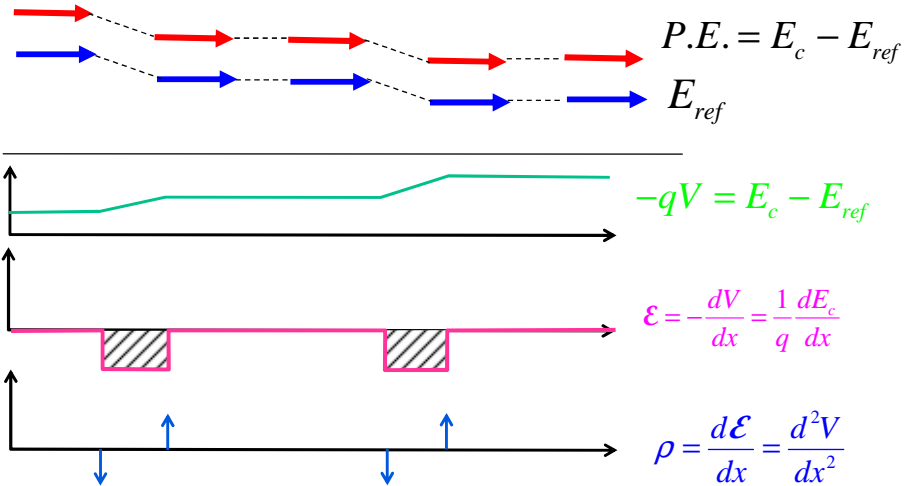
As if all states are at a single level  $E_c$

$$n = N_C \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \rightarrow N_C e^{-\beta(E_c - E_F)} \quad \text{if } \beta(E_c - E_F) > 3$$

Often good enough to forget about the  
Distribution of carriers in energy  
=> Replace by delta functions at band edge



All quantum mechanics is now hidden in a single point per band!



In most practical cases start from charge and derive potentials!

PURDUE => Useful to learn "graphical" integration



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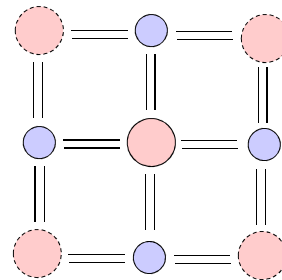
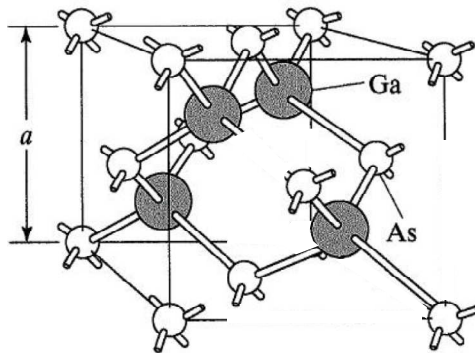
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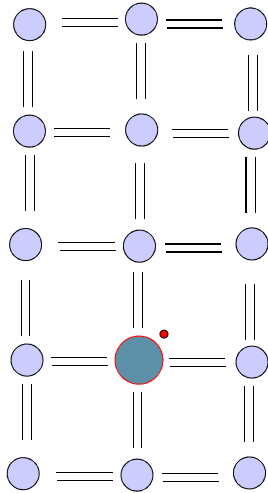


- Metal:
  - » Conducts electrons even at very low temperatures
  - » Fermi Level crosses multiple bands even at very low temperatures
- Semiconductor
  - » Very weakly conducting
  - » Si:  $E_g=1.1\text{eV}$   $n_i \sim 10^{10}/\text{cm}^3$  in  $10^{23}/\text{cm}^3$  0.1 in a trillion
  - » GaAs:  $E_g=1.42\text{eV}$   $n_i \sim 10^6/\text{cm}^3$  in  $10^{23}/\text{cm}^3$
  - » Ge:  $E_g=0.8\text{eV}$   $n_i \sim 10^{13}/\text{cm}^3$  in  $10^{23}/\text{cm}^3$  0.1 in a billion
- Insulator
  - » "Not" conducting
  - » SiO<sub>2</sub>,  $E_g=9\text{eV}$ ,  $n_i \sim 10^{-68}/\text{cm}^3$
  - ✓ The whole earth has about  $10^{50}$  atoms! If you made the whole world out of glass there would be not one electron conductive at room temperature!

$$n_i = \sqrt{N_c N_v} e^{-\beta E_g / 2}$$

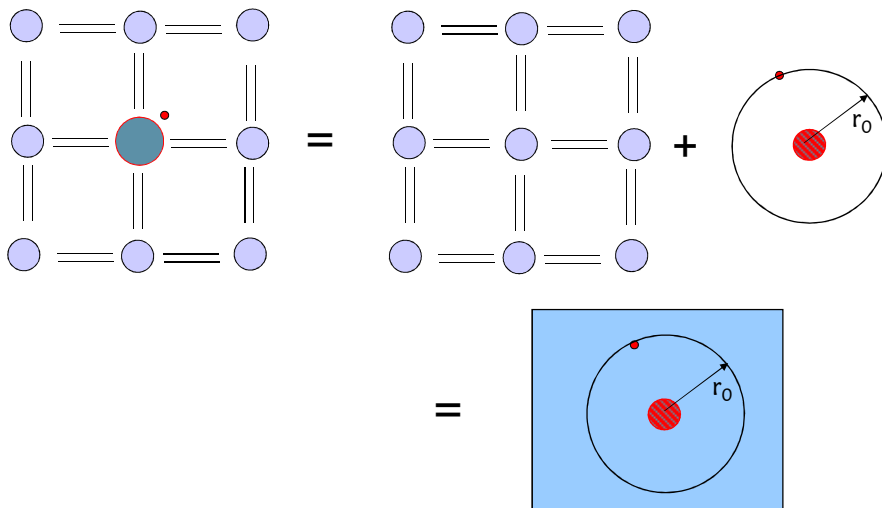
$$E_F \equiv E_i$$

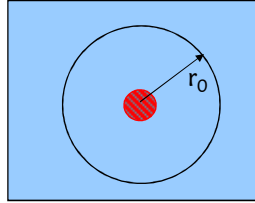




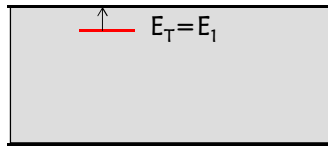
	II	III	IV	V	VI
4	Be	5 B	6 C	7 N	8 O
12	Mg	13 Al	14 Si	15 P	16 S
30	Zn	31 Ga	32 Ge	33 As	34 Se
48	Cd	49 In	50 Sn	51 Sb	52 Te
80	Hg	81 Tl	82 Pb	83 Bi	84 Po

Even with donors, material is charge neutral





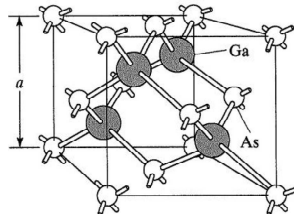
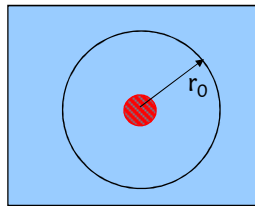
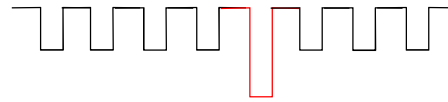
~10s meV



$$E_1 = -\frac{m_{host}^* q^4}{2(4\pi\epsilon_0 K_{s,host} \hbar)^2}$$

$$= -\frac{m_0 q^4}{2(4\pi\epsilon_0 \hbar)^2} \frac{m_{host}^*}{m_0} \frac{1}{K_{s,host}^2}$$

$$= -13.6 \times \frac{m_{host}^*}{m_0} \frac{1}{K_{s,host}^2}$$



$$r_{1,P} = \frac{4\pi\epsilon_0 K_{s,host} \hbar^2}{m_{host}^* q^2}$$

$$= \frac{4\pi\epsilon_0 \hbar^2}{m_0 q^2} \frac{m_0 K_{s,host}}{m_{host}^*}$$

$$= r_{1,H} \frac{K_{s,host}}{m_{host}^* / m_0}$$

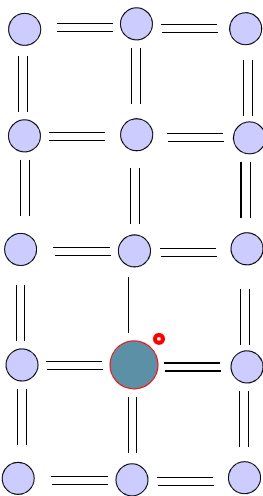
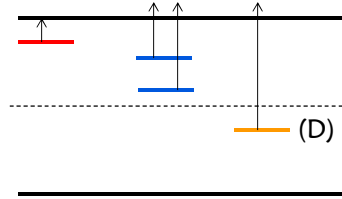
$$r_{1,P} = 0.53 \text{ \AA} \times \frac{12.9}{0.53} = 12.9 \text{ \AA}$$

$a \sim 0.5 \text{ nm} = 5 \text{ \AA} \Rightarrow$  hundreds of Si atoms

The number of donor atoms is much smaller compared to host atoms. Therefore, the electrons from one donor atom can go to the other donor atoms only via the conduction /valence bands of the host crystal.

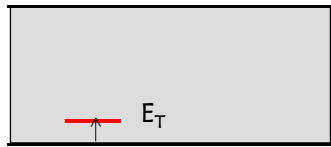
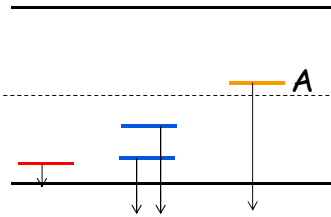
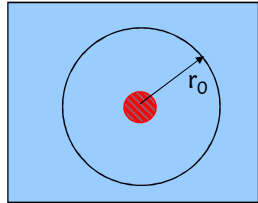
Just like a Hydrogen atom, it is possible to have multiple localized level for a given atom (see the blue levels).

Good donors live close to the conduction band, so that they can offer electrons easily. However, if they are below the midgap, the donor levels are marked with (D) to differentiate them from acceptor atoms (which live close to the valence band).



	II	III	IV	V	VI
4	Be	<b>5</b> B	6 C	7 N	8 O
12	Mg	13 Al	<b>14</b> Si	15 P	16 S
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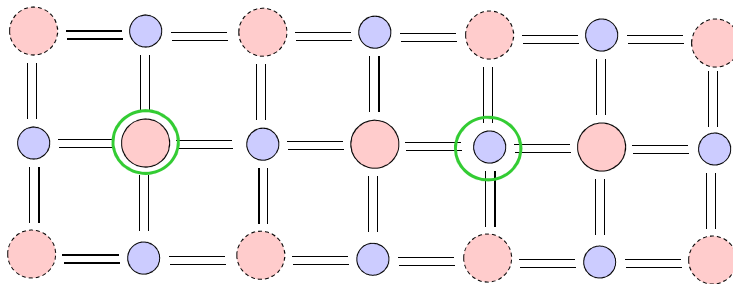
Even with acceptor, material is charge neutral



II	III	IV	V	VI
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Donor-type

acceptor-type





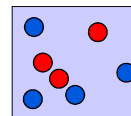


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A bulk material must be charge neutral over all ...

$$\int [p - n + N_D^+ - N_A^-] dV = 0$$

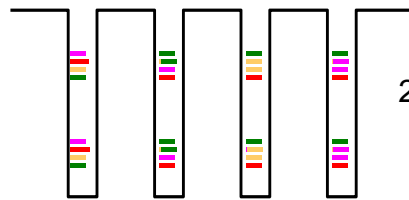
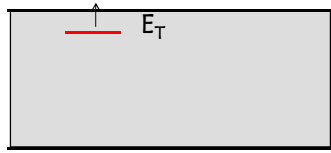
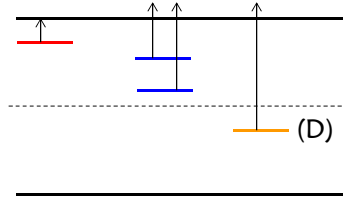
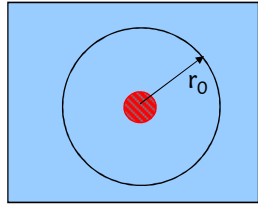


Further if the material is *spatially homogenous*

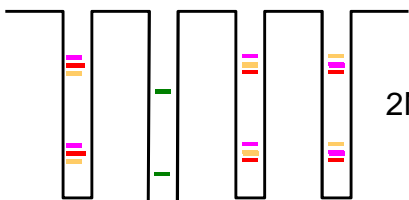
$$p - n + N_D^+ - N_A^- = 0$$

$$N_V e^{-(E_F - E_V)/k_B T} - N_C e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0$$

Let us see how the formula come about ...



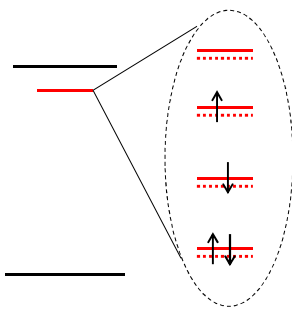
2N states/per-band (with spin)



2N-2 states/per-band (with spin)



$$P_i = \frac{e^{-(E_i - N_i E_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} \equiv \frac{e^{-(E_i - N_i E_F)/k_B T}}{Z}$$



$u/d$	$E_i$	$N_i$	$P_i$
0/0	0	0	$1/Z$

**1/1**   **x**   **x**   **x**   Coulomb interaction forbids this configuration



$u/d$	$E_i$	$N_i$	$P_i$
0/0	0	0	$1/Z$
0/1	1	1	$e^{-\frac{(E_i - E_F)}{k_B T}} / Z$
1/0	1	1	$e^{-\frac{(E_i - E_F)}{k_B T}} / Z$

Prob. that the donor is empty (charged)


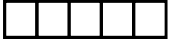

$$f_{00} = \frac{P_{00}}{P_{00} + P_{01} + P_{10}} = \frac{1/Z}{1/Z + 2e^{-(E_i - E_F)/k_B T} / Z} = \frac{1}{1 + 2e^{(E_F - E_i)/k_B T}}$$

Prob. that the donor is filled with at least one electron (neutral)

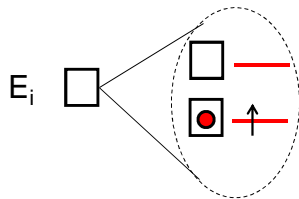
$$1 - f_{00} = 1 - \frac{1}{1 + 2e^{(E_F - E_i)/k_B T}} = \frac{1}{1 + \frac{1}{2}e^{(E_i - E_F)/k_B T}}$$

Note the extra factor ....

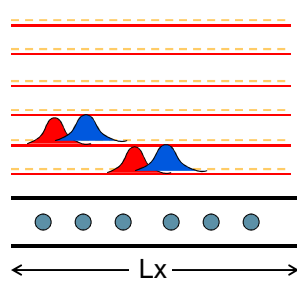


$E=4$  
  
 $E=2$  
  
 $E=0$  

$$P_i = \frac{e^{-(E_i - N_i E_F) / k_B T}}{\sum_i e^{-(E_i - N_i E_F) / k_B T}} \equiv \frac{e^{-(E_i - N_i E_F) / k_B T}}{Z}$$

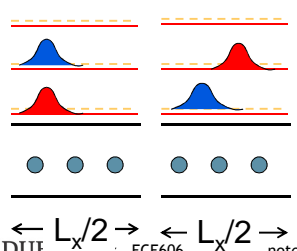


state	$E_i$	$N_i$	$P_i$
0	0	0	$1/Z$
1	1	1	$e^{-\frac{(E_i - E_F)}{k_B T}} / Z$



$E6 \leftarrow 12\pi/L_x$   
 $E5 \leftarrow 10\pi/L_x$   
 $E4 \leftarrow 8\pi/L_x$   
 $E3 \leftarrow 6\pi/L_x$   
 $E2 \leftarrow 4\pi/L_x$   
 $E1 \leftarrow 2\pi/L_x$

Two electrons (even with opposite spin) can not be at the same position and same energy because of electrostatic repulsion

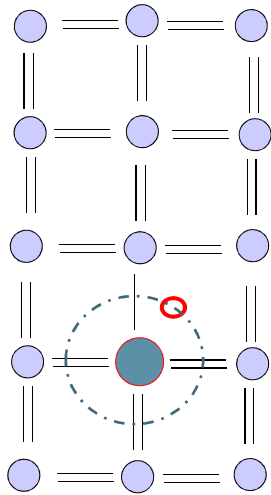


$E3' \leftarrow 6\pi/(L_x/2)$   
 $E2' \leftarrow 4\pi/(L_x/2)$   
 $E1' \leftarrow 2\pi/(L_x/2)$

Band electrons (with opposite spin) need not be at the same position, so they can share occupy same energy level.

When we divide space by a factor of 2, the number of states (e.g. 6 here) does not change.

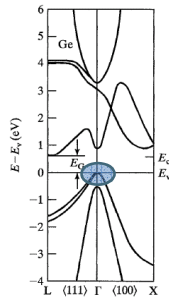
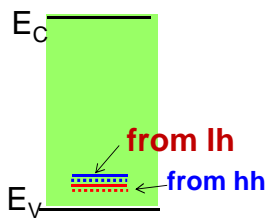




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80	Hg	Tl	Pb	Bi	Po

State [1] .... Hole present ... N-1 charges

State [0] ... Hole filled .... N charges



1. Each atom contributes 2 states (up & down spin) to a band, therefore a band has  $2N$  states.
2. Every time a host atom is replaced by a impurity atom, 2 states are disappear per a band and appear as localized states (sort of).
3. Therefore an acceptor atom close to hh and lh bands removes four states from those bands.
4. Because of Coulomb interaction only 1 hole can seat in these 4 states: the states are 0000, 0001, 0010, 0100, 1000.



0000    1000    0100    0010    0001
 
 4N-4 States  
 In HH/LH bands

- 1) [0000] is the charged state as it has N electrons, but N-1 protons.
- 2) Single hole configuration [0001] is uncharged, as we have N-1 electrons, and N-1 protons ... same is true for [0010], [0100], [1000] states.
- 3) Going from [0000] to [0001] states, the number of electrons goes down by 1 ( $N_i = -1$ ).
- 4) Going from [0000] to [0001] states energy goes down by  $-E_A$ , because one electron is no longer occupying the high energy level at  $E_A$ .



$$P_{0000} = \frac{e^{-(0-0xE_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} \equiv \frac{1}{Z}$$

0000    1000    0100    0010    0001

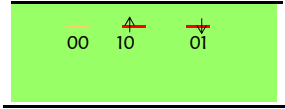
Steps 3 & 4

$$P_{0001} = P_{0010} = P_{0100} = P_{1000} = \frac{e^{-(-E_A - (-1)E_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} \equiv \frac{e^{(E_A - E_F)/k_B T}}{Z}$$

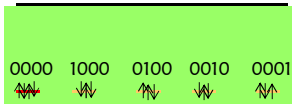
$$f_{0000} = \frac{P_{0000}}{P_{0000} + P_{1000} + P_{0100} + P_{0010} + P_{0001}} = \frac{1}{1 + 4e^{(E_A - E_F)/k_B T}}$$



2N-2 states



$$N_D^{empty} \equiv N_D^+ = N_D f_{00} = N_D \frac{1}{1 + 2e^{(E_F - E_i)/k_B T}}$$



$$N_A^{filled} \equiv N_A^- = N_A [f_{0000}] = N_A \frac{1}{1 + 4e^{(E_A - E_F)/k_B T}}$$

4N-4 States  
In HH/LH bands  
(Two holes can not seat together)



$$f_D = \frac{N_D}{1 + g_D e^{(E_F - E_D)/k_B T}}$$

Degeneracy factor ...

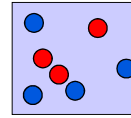
$$f_D = \frac{N_D}{1 + e^{\epsilon/k_B T} e^{(E_F - E_D)/k_B T}} = \frac{N_D}{1 + e^{(E_F - E_D')/k_B T}}$$

Effective donor level



A bulk material must be charge neutral over all ...

$$\int [p - n + N_D^+ + N_A^-] dV = 0$$



Further if the material is *spatially homogenous*

$$p - n + N_D^+ + N_A^- = 0$$

$$N_V e^{-(E_F - E_V)/k_B T} - N_A e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0$$



- Intrinsic carrier concentration
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- Temperature dependence of carrier concentration
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- Conclusions

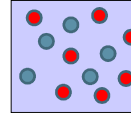
**Reference:** Vol. 6, Ch. 3 & 4





A bulk material must be charge neutral over all ...

$$\int [p - n + N_D^+ + N_A^-] dV = 0$$



Further if the doping is **spatially homogenous**

$$p - n + N_D^+ + N_A^- = 0$$

**FD integral vs. FD function ?**

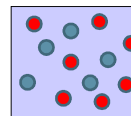
$$N_V \frac{2}{\sqrt{\pi}} F_{1/2}[\beta(E_F - E_V)] - N_A \frac{2}{\sqrt{\pi}} F_{1/2}[\beta(E_C - E_F)] + \frac{N_D}{1 + 2e^{\beta(E_F - E_D)}} - \frac{N_A}{1 + 4e^{\beta(E_A - E_F)}} = 0$$

$$N_V e^{-(E_F - E_V)/k_B T} - N_A e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0 \quad (\text{approx.})$$

Once you know  $E_F$ , you can calculate  $n$ ,  $p$ ,  $N_D^+$ ,  $N_A^-$ .



$$p - n + N_D^+ + N_A^- = 0$$



$$N_V e^{-(E_F - E_V)/k_B T} - N_C e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0$$

$$n - p = 0 \Rightarrow N_C e^{-\beta(E_C - E_F)} = N_V e^{+\beta(E_V - E_F)}$$

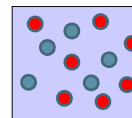
$$E_F \equiv E_i = \frac{E_G}{2} + \frac{1}{2\beta} \ln \frac{N_V}{N_C}$$



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In spatially homogenous field-free region ...

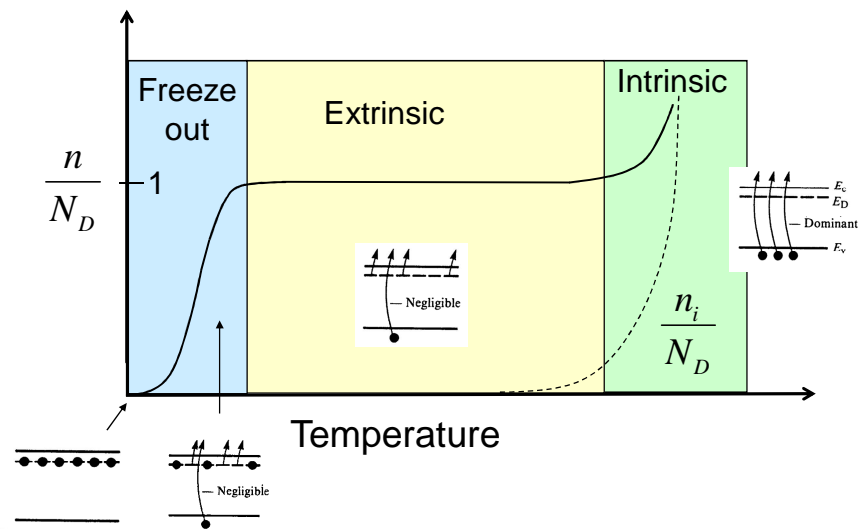
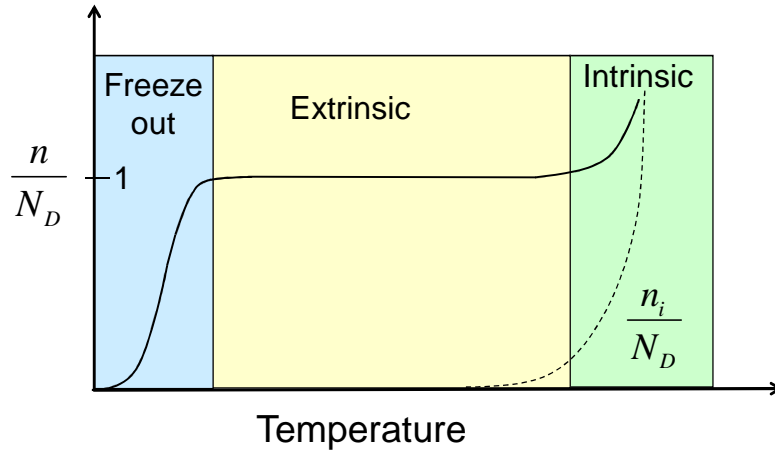


Assume N-type doping ...

$$p - n + N_D^+ + N_A^- = 0$$

$$N_V e^{-(E_F - E_V) / k_B T} - N_C e^{-(E_C - E_F) / k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D) / k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F) / k_B T}} = 0$$

$n$   
 (will plot in next slide)



$$n = N_C e^{-\beta(E_C - E_F)} \Rightarrow \frac{n}{N_C} e^{\beta E_C} = e^{\beta E_F}$$

$$N_D^+ = \frac{N_D}{1 + 2e^{\beta(E_F - E_D)}} = \frac{N_D}{1 + 2 \left[ \frac{n}{N_C} e^{\beta(E_C - E_D)} \right]} \equiv \frac{N_D}{1 + \frac{n}{N_\xi}}$$



$$p - n + N_D^+ = 0$$

$$N_V e^{-(E_F - E_V)/k_B T} - N_C e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} = 0$$

$$p \times n = n_i^2$$

$$\frac{n_i^2}{n} - n + \frac{N_D}{1 + \frac{n}{N_\xi}} = 0$$

No approximation so far ....



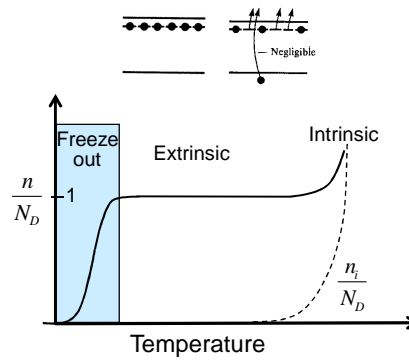
$$\frac{n_i^2}{n} - n + \frac{N_D}{1 + \frac{n}{N_\xi}} = 0$$

$$N_D \gg n_i$$

$$\Rightarrow -n + \frac{N_D}{1 + \frac{n}{N_\xi}} \approx 0$$

$$\Rightarrow n^2 + N_\xi n - N_\xi N_D = 0$$

$$N_\xi \equiv \frac{N_C}{2} e^{-\beta(E_C - E_D)} \quad n = \frac{N_\xi}{2} \left[ \left( 1 + \frac{4N_D}{N_\xi} \right)^{1/2} - 1 \right]$$

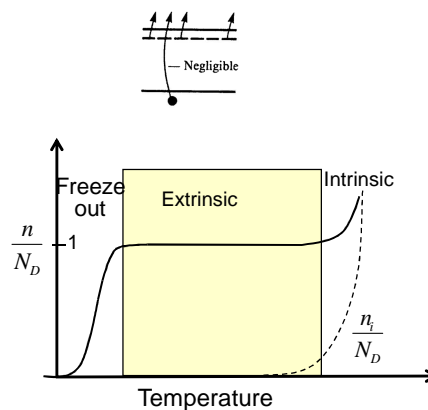


$$N_\xi \equiv \frac{N_C}{2} e^{-(E_C - E_D)/kT} \gg N_D$$

$$n = \frac{N_\xi}{2} \left[ \left( 1 + \frac{4N_D}{N_\xi} \right)^{1/2} - 1 \right]$$

$$\approx \frac{N_\xi}{2} \left[ \left( 1 + \frac{1}{2} \frac{4N_D}{N_\xi} \right) - 1 \right]$$

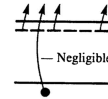
$$\approx N_D$$



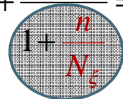
Electron concentration equals donor density  
hole concentration by  $n p = n_i^2$



$$N_D^+ = \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} \approx N_D \text{ for } E_F < E_D$$

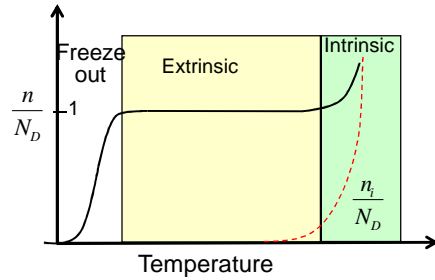


$$\frac{n_i^2}{n} - n + \frac{N_D}{1 + \frac{n}{N_D}} = 0$$



$$\frac{n_i^2}{n} - n + N_D \approx 0$$

$$\Rightarrow -n_i^2 + n^2 - N_D n = 0$$

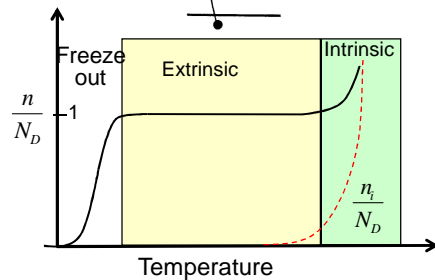
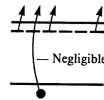


$$n = \frac{N_D}{2} + \left[ \frac{N_D^2}{4} + n_i^2 \right]^{1/2}$$



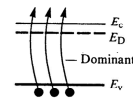
For  $N_D \gg n_i$

$$n = \frac{N_D}{2} + \left[ \frac{N_D^2}{4} + n_i^2 \right]^{1/2} \approx N_D$$



For  $n_i \gg N_D$

$$n = \frac{N_D}{2} + \left[ \frac{N_D^2}{4} + n_i^2 \right]^{1/2} \approx n_i$$



What will happen if you use silicon circuits at very high temperatures?  
Bandgap determines the intrinsic carrier density.



$$n = N_c e^{-\beta(E_c - E_F)} \Rightarrow E_F = E_c + \frac{1}{\beta} \ln \left( \frac{n}{N_c} \right)$$

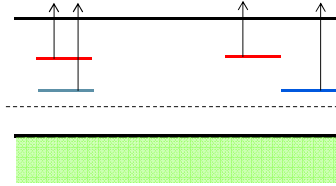
$$p - n + N_D^+ = 0$$

$$N_v e^{-(E_F - E_v)/k_B T} - N_c e^{-(E_c - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} = 0$$



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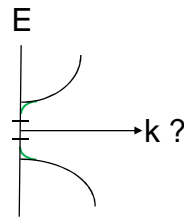
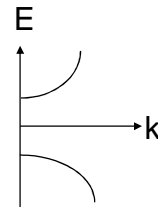
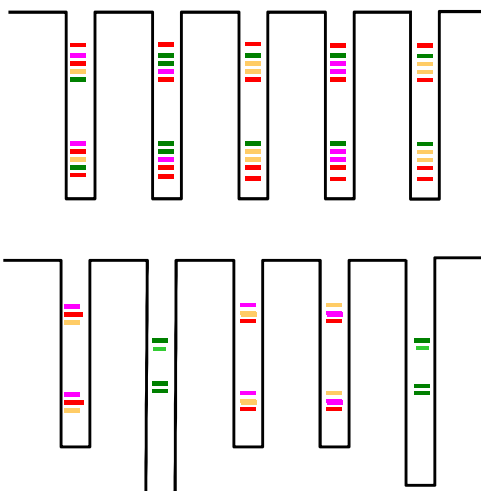


Multiple levels of same donor ...

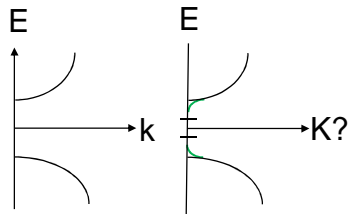
$$p - n + \frac{N_D}{1 + 2e^{(E_F - E_{D1})/k_B T}} + \frac{N_D}{1 + 2e^{(E_F - E_{D2})/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0$$

Codoping...

$$p - n + \frac{N_{D1}}{1 + 2e^{(E_F - E_{D1})/k_B T}} + \frac{N_{D2}}{1 + 2e^{(E_F - E_{D2})/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0$$







Bandgap narrowing

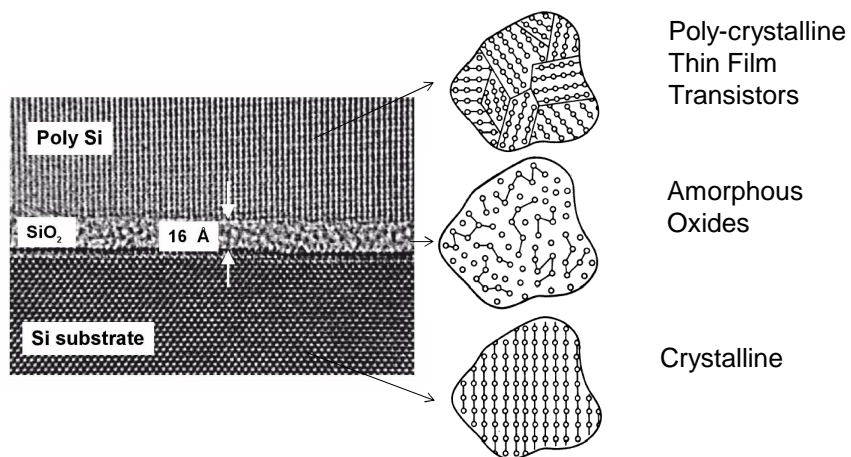
$$p \times n = N_C N_V e^{-\beta E_G^*}$$

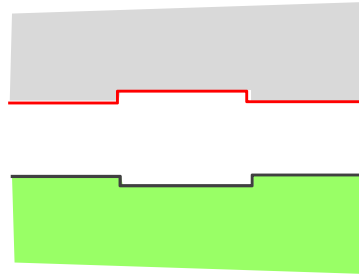
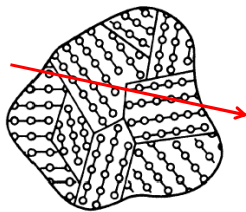
e.g. Base of HBTs



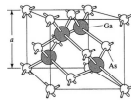
Band transport  
vs.  
hopping-transport

e.g. a-silicon, OLED

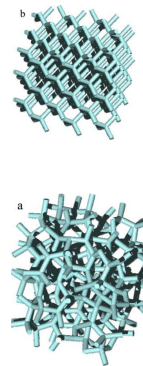
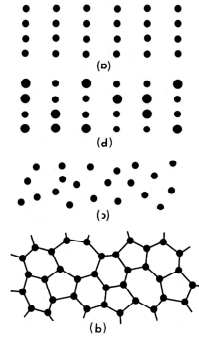




Isotropic bandgap and increase in scattering



PRB, 4, 2508, 1971



Edagawa, PRL, 100, 013901, 2008

Periodicity is sufficient, but not necessary for bandgap.  
Many amorphous material show full isotropic bandgap



1. Charge neutrality condition and law of mass-action allows calculation of Fermi-level and all carrier concentration.
2. For semiconductors with field, charge neutrality will not hold and we will need to use Poisson equation.
3. Heaving doping effects play an important role in carrier transport.

