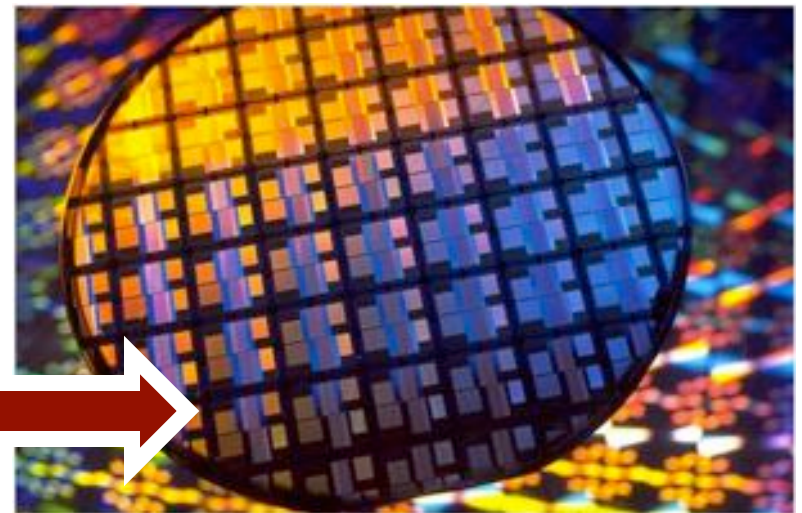


# Band Diagrams and Carrier Concentrations

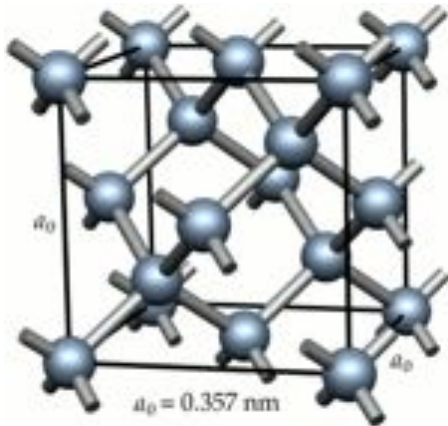


▶ LET ME BE CLEAR!

- (1) I will test, retest, and retest again this quarter to make sure you are SOLID on basics like recombination, what causes drift, what causes diffusion, band diagrams, etc.. **and, BJT'S, FETs, SOLAR CELLS, ETC. ARE ALL BASED ON DIODES!**
- (2) IF you have any trouble understanding these, ask NOW at the beginning of the quarter. There is NO excuse for not understanding these later in the quarter. You should FULLY understand everything in the 1<sup>st</sup> few lectures and the first homework. If not, ask!!!!
- (3) So pay attention now, like your life depended on it!
- (4) My main goal is to create 'unafraid' students... ...So what does that mean in terms of your learning, your job, your profession?

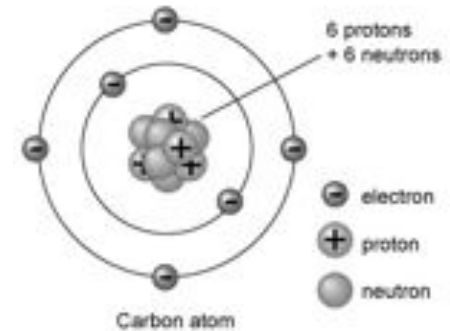


Inorganic (diamond).

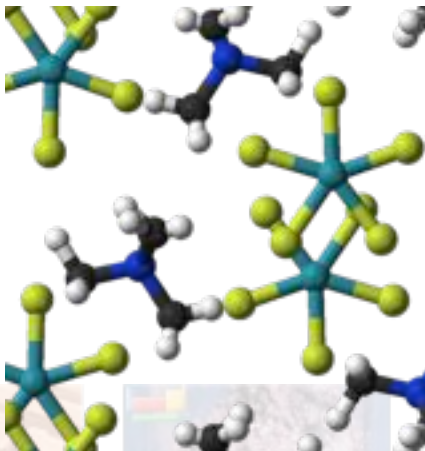


► Lets say we have some sort of material... any material, how do we get electrical conduction?

To make a material electrically conductive, we need some way to get charged carriers (like electrons) free from the atoms... So that if we apply E-field, they will start to drift in the E-field...



Organic (bunch of C-H bonds, like plastics)



► Obviously the charges for an atom are happy to stay with the atom, so how do we get them free? Bonding with other atoms!

**Metals (Al, Cu, Au...)** - Bond one or more types of atoms such that bond, share electrons, and favor freeing up a flood of electrons.

**Semiconductors (Si, GaAs, GaN...)** - Bond one or more types of atoms such that bond, share electrons, with a little energy (heat) can free up some electrons.

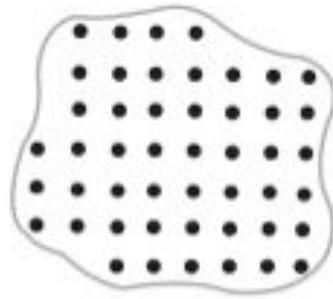
**Insulators (SiN, Al<sub>2</sub>O<sub>3</sub>...)** - Bond one or more types of atoms such that bonds share electrons, but it takes a lot of energy to free up electrons.



**Metals (Al, Cu, Au...)** – Energy to free up electrons is zero or so low that crystallinity not as important.

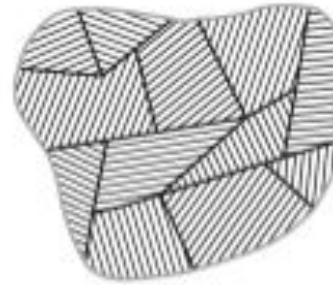
**Semiconductors (Si, GaAs, GaN...)** – Freeing up the electrons is more sensitive to crystallinity. You have just enough energy to free up a few electrons, crystal defects can kill (recapture) these electrons or make it hard to move them...

**Insulators (SiN, Al<sub>2</sub>O<sub>3</sub>...)** – Energy to free up electrons is so large that crystallinity not as important.



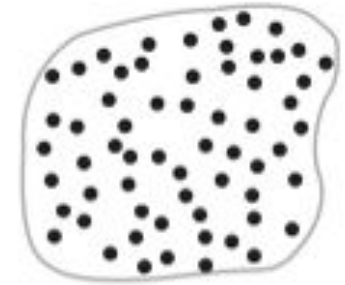
Crystalline.

Highest performance, highest cost for Si.



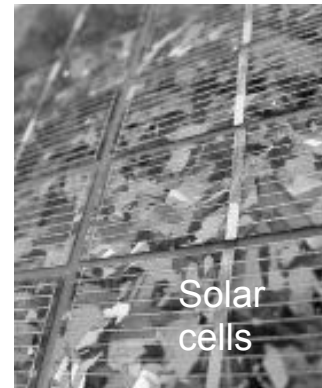
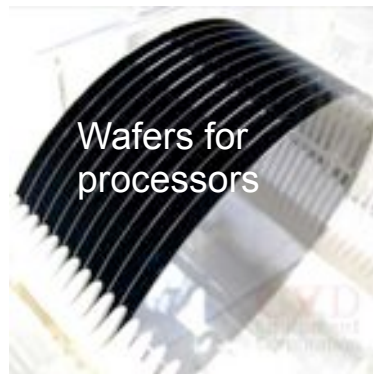
Polycrystalline.

Medium performance, medium cost for Si.



Amorphous.

Lowest performance, lowest cost for Si (low temperature fabrication).



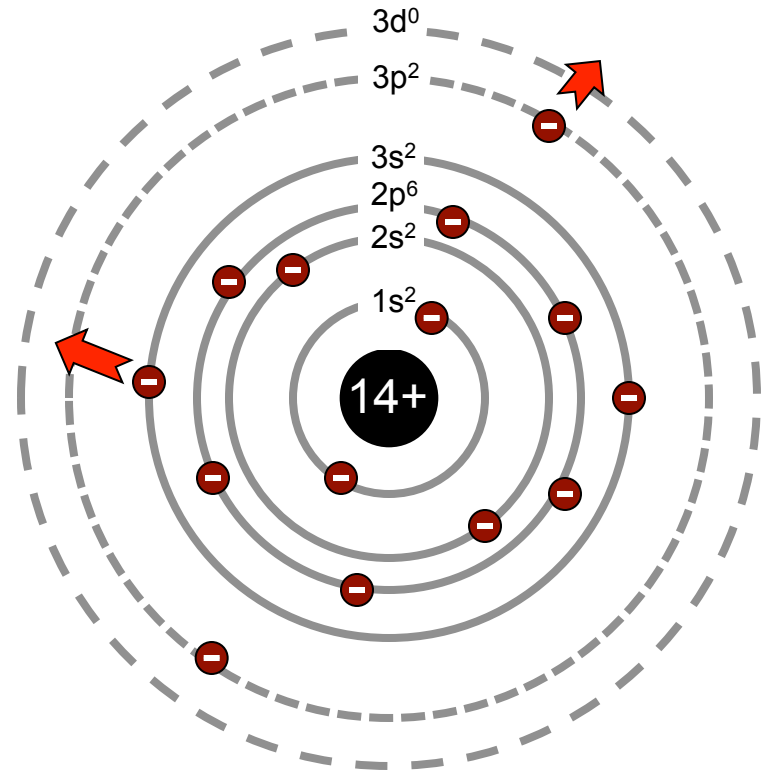
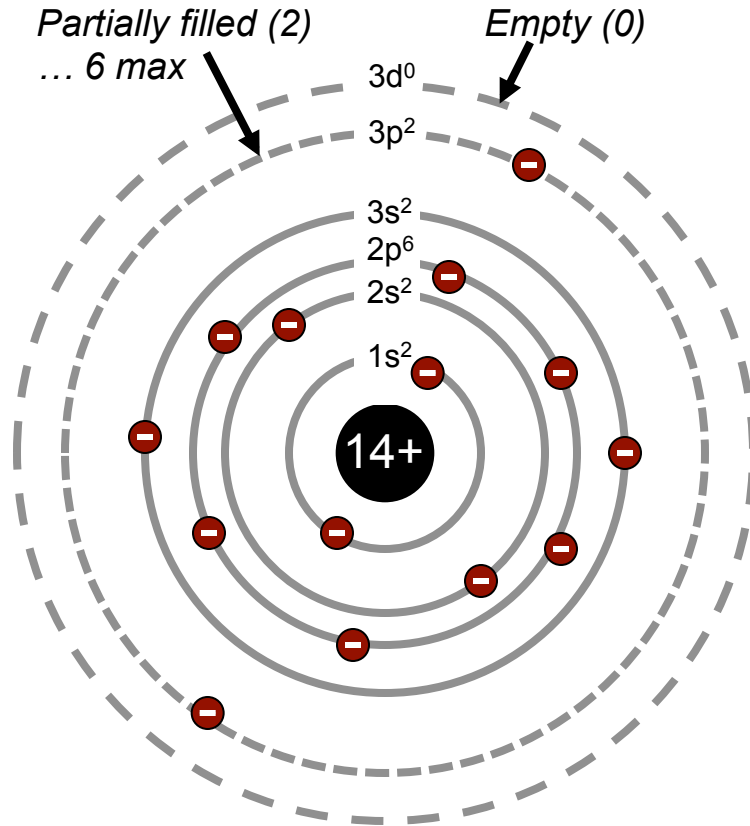
How make? See Fig. 1-10.



▶ Silicon atom (ground state)

▶ Pauli Exclusion Principle (only one electron per quantum state, n, l, m, s)

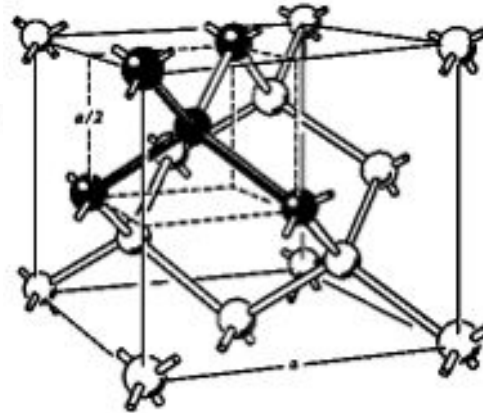
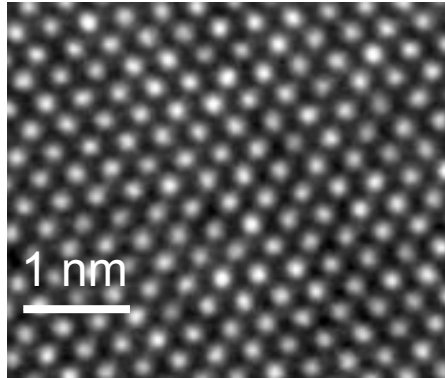
▶ Add a bit of energy (heat = vibration of atoms) to the Silicon atom, an electron could move to higher energy state...



► Si bonds in a ‘diamond’ style lattice (unit cell shown at right)

► Each Si atom covalently bonds with another Si atom (each sharing 1 electron) which effectively completes its outer shell...

► So they like to share electrons, but how do we free one up?



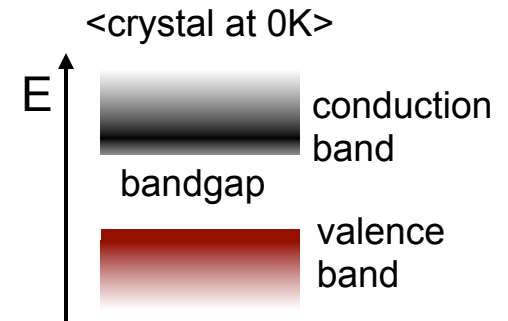
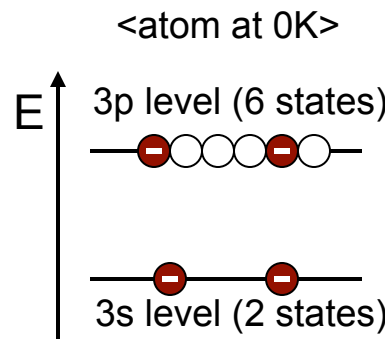
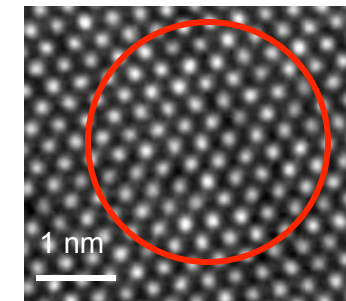
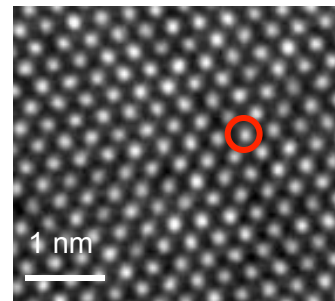
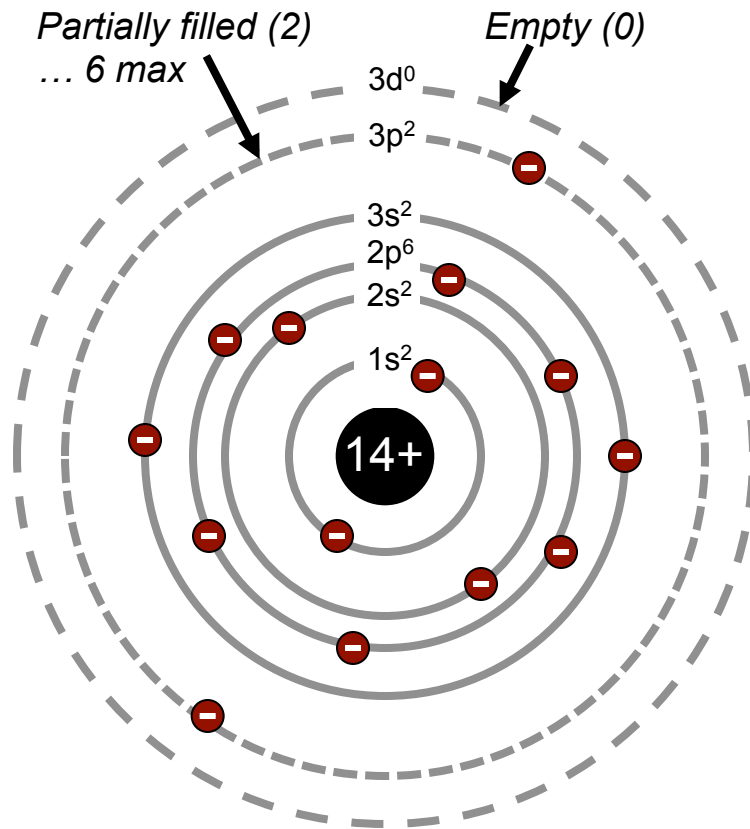
3 4 5 6 7 8

Periodic Table of Elements																		
1 H 1.00794																	2 He 4.002602	
3 Li 6.941	4 Be 9.0122															10 Ne 20.1797		
11 Na 22.98976928	12 Mg 24.304															18 Ar 39.948		
19 K 39.0983	20 Ca 40.078	21 Sc 44.955912	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938044	26 Fe 55.845	27 Co 58.933195	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90584	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 101.07	46 Pd 106.32	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.603	53 I 126.905	54 Xe 131.29	
55 Cs 132.90545196	56 Ba 137.327	57-70 * * * * *	71 Lu 174.967	72 Hf 178.49	73 Ta 180.94788	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.222	78 Pt 195.084	79 Au 196.966569	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.9804	84 Po 209	85 At 210	86 Rn 222
87 Fr [223]	88 Ra [226]	89-102 * * * * *	103 Lr [260]	104 Rf [261]	105 Db [262]	106 Sg [263]	107 Bh [264]	108 Hs [265]	109 Mt [266]	110 Uu [267]	111 Uuh [268]	112 Uub [269]						



- ▶ Silicon atom (ground state)
- ▶ Pauli Exclusion Principle (only one electron per quantum state,  $n, l, m, s$ )

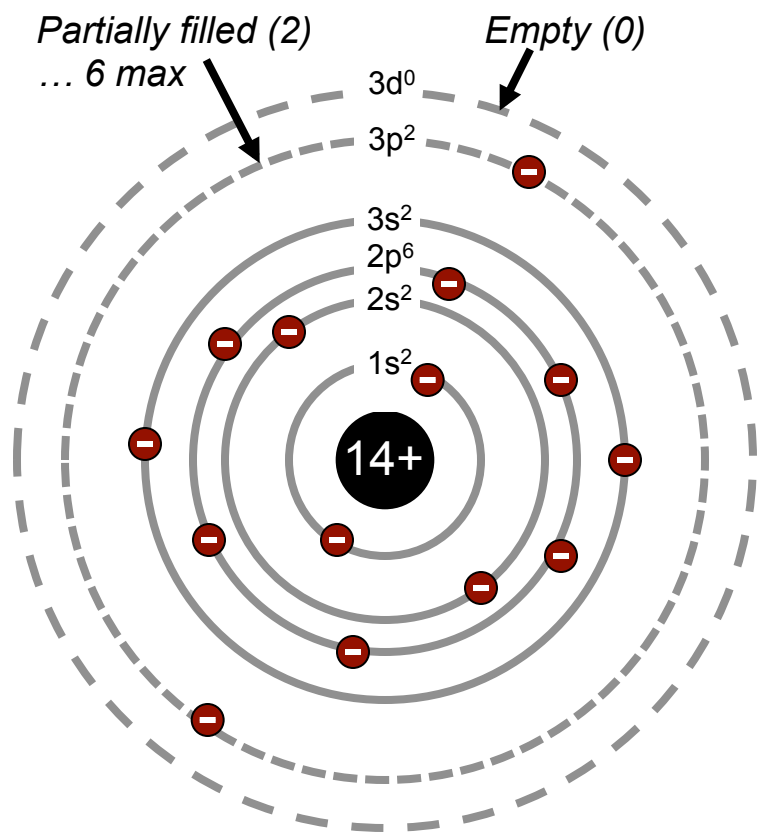
- ▶ We bring a bunch of Si atoms together, all w/ electrons in the same states... to prevent the end of the Universe as we know it, what must happen?



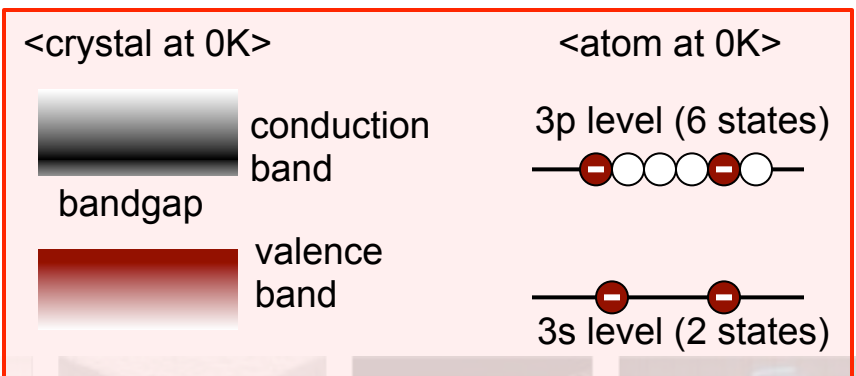
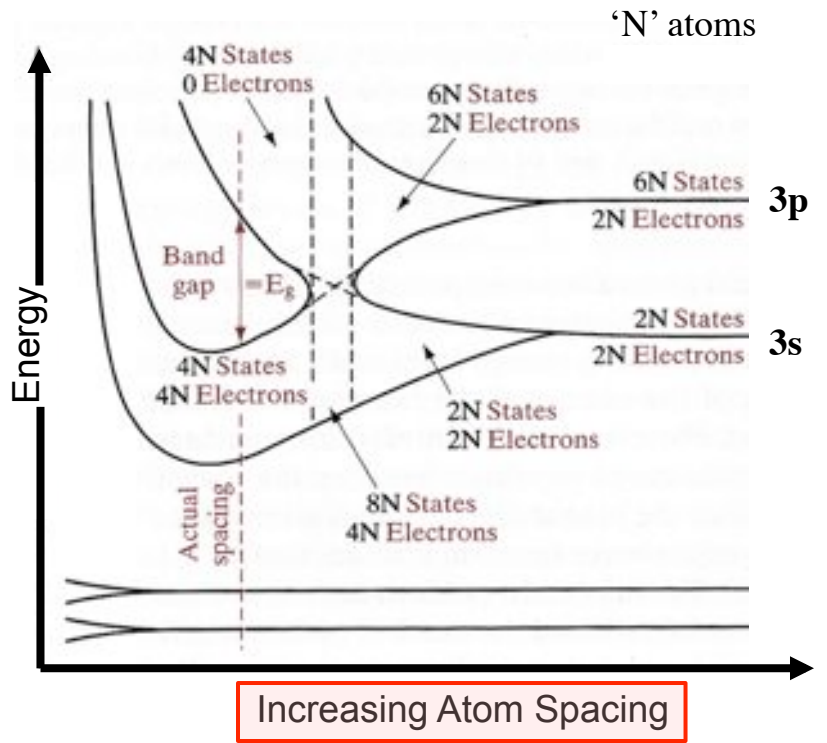
*Band diagram is a bit more complicated than broadening of 3p and 3s levels... (next slide)*



▶ As we bring the Si atoms closer, quantum mechanics (Pauli Exclusion Principle) starts to kick in... and two electrons can't occupy the same state.



*I will explain the importance of this plot on the next slide...*



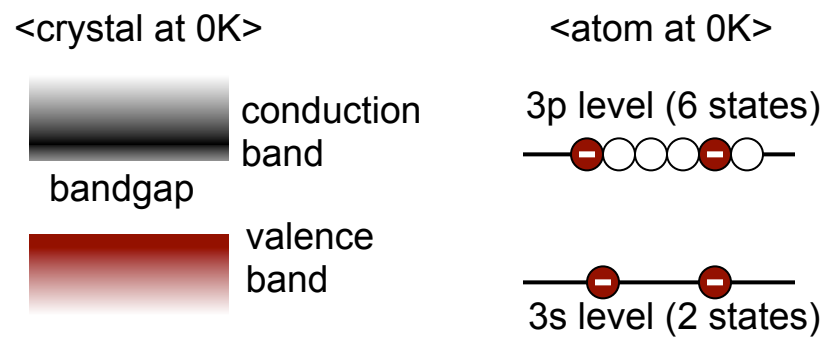
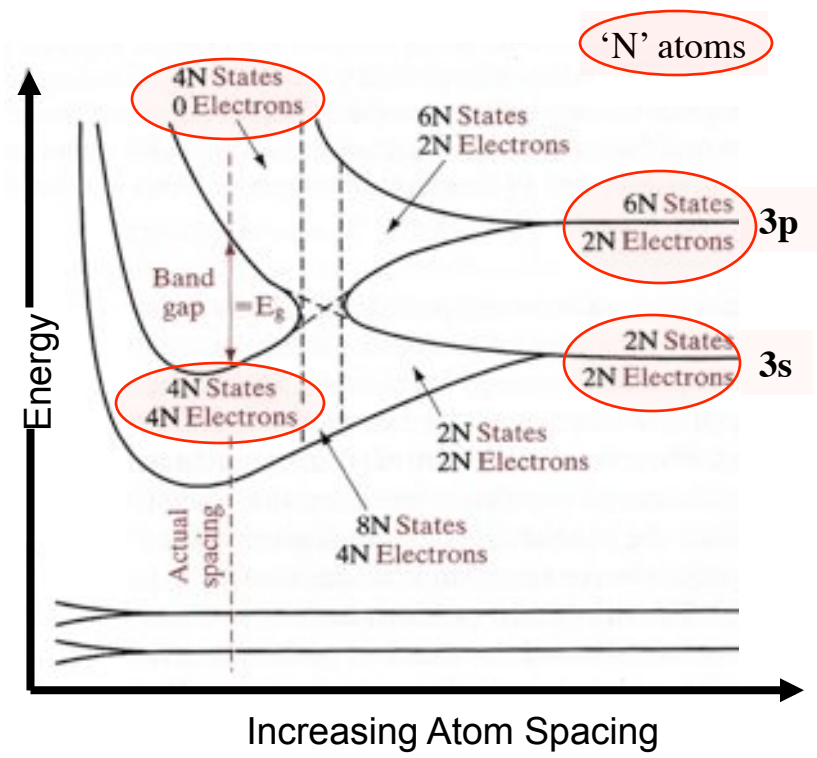


1) Notice for an individual Si atom, that we started with 4 electrons, 2 in the 3s level (maxed out), 2 in the 3p level (still 4 empty states)...

2) Notice for a crystal of Si, there are now 4 states in the 'valence' band (the lower band)...

- ▶ Question 1: at 0K, in what band are all the electrons?
- ▶ Question 2: okay, so why do we call this band the 'valence' band?
- ▶ Question 3: okay... these electrons in the valence band, can they move through the Si when E-field is applied?

▶ Question 4: next... we heat up the Si a bit (add some energy to get it to 300k), what will happen...?

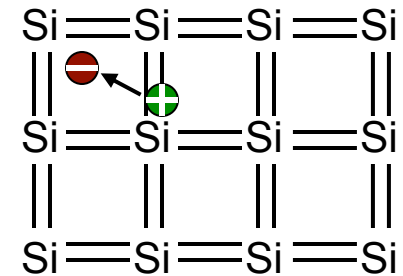
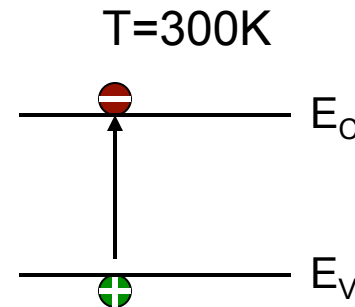
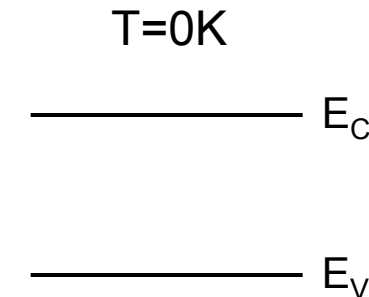
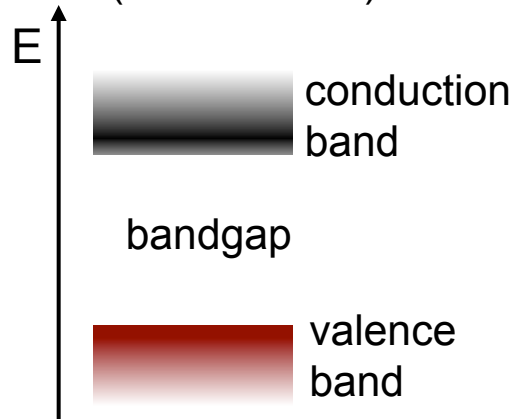


► Let's take a closer look at 0K, lots of electrons but they are all stuck with Si atoms... (valence band)

► At T=300K some electrons get enough energy to leave the valence band and make it to the conduction band...

Is a band  
(lots of states)

But we draw it this  
way for simplicity...

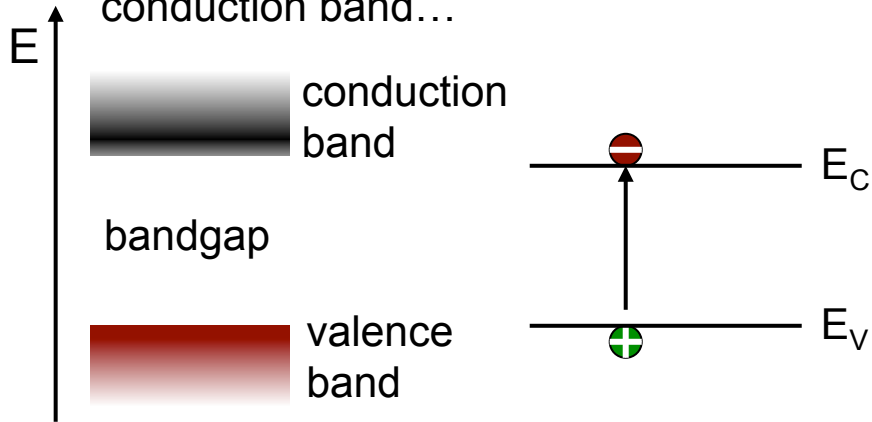


- Removing negative electron leaves behind a positively charged 'hole', a hole is the absence of an electron!
- At 300K, obviously this *thermal generation* of electrons and holes does not go on forever... electrons and holes have a *lifetime* after which they *recombine* with each other and disappear...
- AND, electrons can move freely through the lattice in electric field (conduction!)
- AND, holes can be traded between adjacent Si atoms (also conduction!)

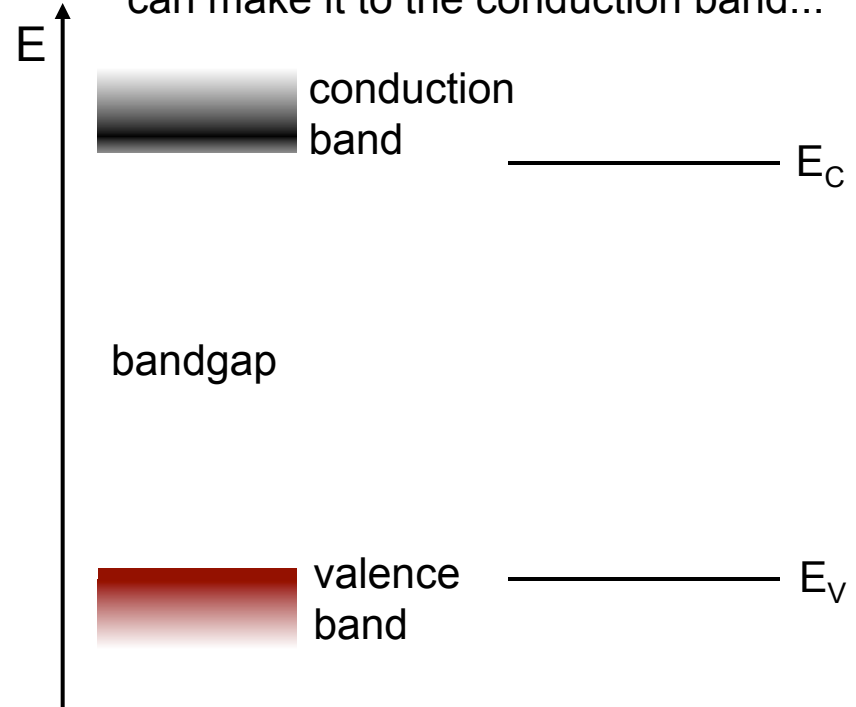
Which is easier... which type will have higher mobility typically? Think of a line of students and throwing a football from one end to other, or pass it one person at a time...

▶ Now, lets revisit the difference between metals, semiconductors, and insulators...

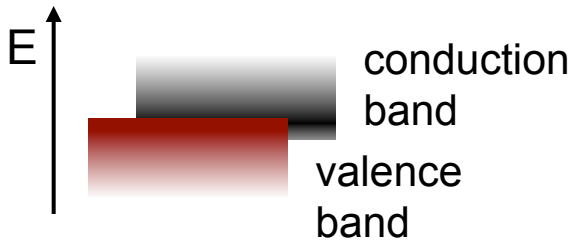
Semiconductor (Si, GaAs, etc..): at 300K some, but not all, electrons make it to conduction band...



Insulator ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ): energy bandgap is so large that at 300K almost no electrons can make it to the conduction band...



Metal (Al, Cu, etc...): at 300K some bands are so close or they overlap such that a flood of electrons are freed up...



Okay. Great! But for semiconductors how can we calculate how many electrons and holes we have?

▶ You will find that this entire course, even the more advanced devices, are built upon the physics of one type of device, what is it?

▶ Unlike a single Si atom which has only a few discrete energy levels, a Si semiconductor (many atoms together) has 'bands' comprised of numerous closely-spaced energy levels. What principle causes this to happen?

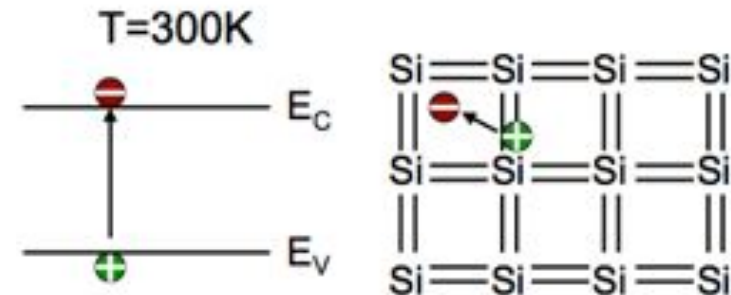
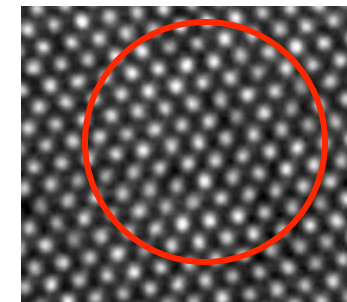
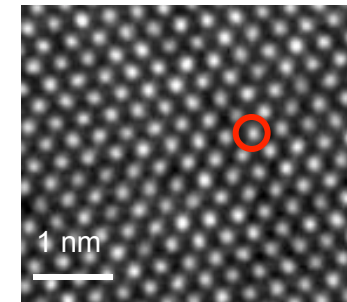
▶ True or false: an electron can be created by thermal generation which removes the electron from a Si atom.

▶ True or false: a hole is simply the absence of an electron at a Si atom, and therefore has opposite charge.

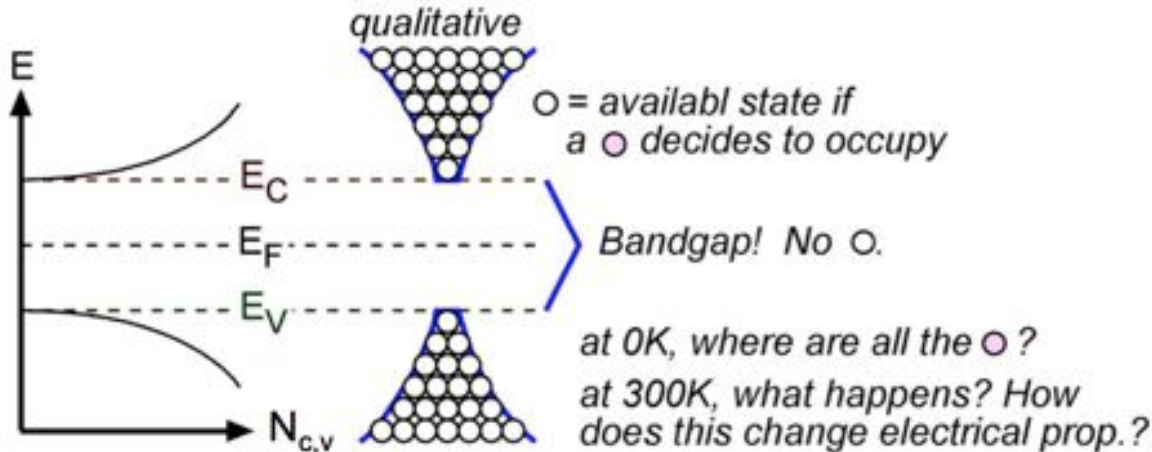
▶ Which band contains all the electrons that are thermally generated and able to move?

▶ Which band contains all the holes that are thermally generated and able to move?

▶ Thermal generation is happening all the time at 300K, so why don't we end up with infinite electrons and holes over time?



► **FIRST** – need to know how many energy states exist: Effective Density of States!

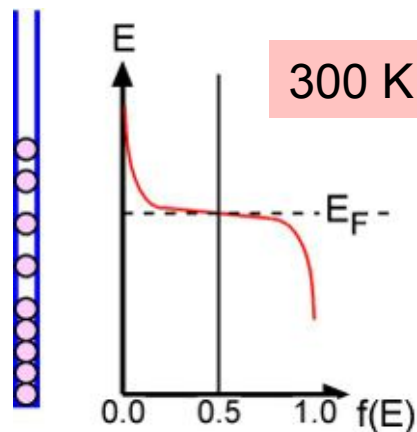
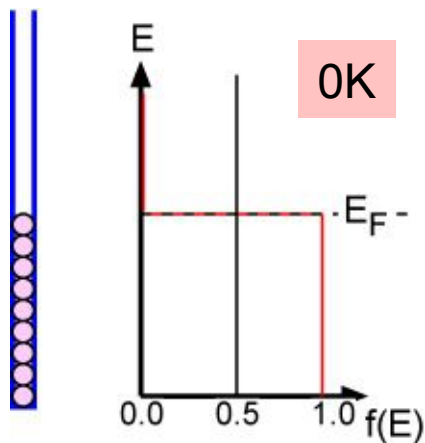


$$N_{c,v} = 2 \left( \frac{2\pi m_{n,p}^* kT}{h^2} \right)^{3/2}$$

Effective = a number, not a function of E.  
k = Boltzman's constant  
m = effective mass.  
h = Plank's constant.

► **SECOND**, we need the probability of filling a state: Fermi Distribution! That's all we need!

$f(E) = 1 / (1 + e^{(E-E_F)/kT})$  Analogy: ping-pong balls & E=mgh.

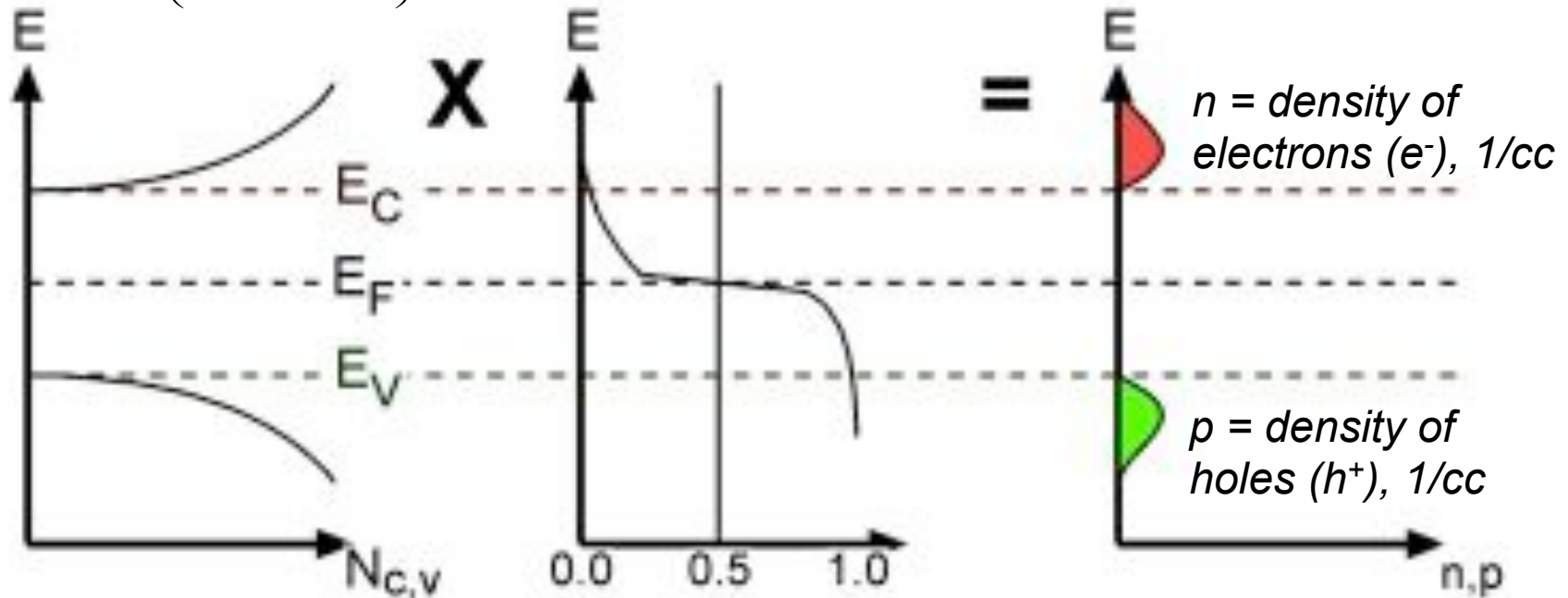


$f(E)$  simply gives the probability of finding an electron at an energy E:  
@  $E = E_f$  ... 1/2  
 $E_f$  is the 50% point  
@  $E \ll E_f$  ... 1  
@  $E \gg E_f$  ... 0  
k is the Boltzmann constant

*Effective Density of States*  $\times$  *Fermi Distribution* = *Carrier concentration (1/cc)*

$$N_{c,v} = 2 \left( \frac{2\pi m_{n,p}^* kT}{h^2} \right)^{3/2}$$

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



1) Question, what would this look like @  $T=0K$ ?, @  $T>300K$ ?, @  $T=500K$ ?, etc... Answer based on equation AND qualitatively please...

2) Are we done? No! This is for intrinsic semiconductor where the electron and hole densities are equal. Devices like pn junctions, BJTs, FETs, LEDs, require doped semiconductors...!

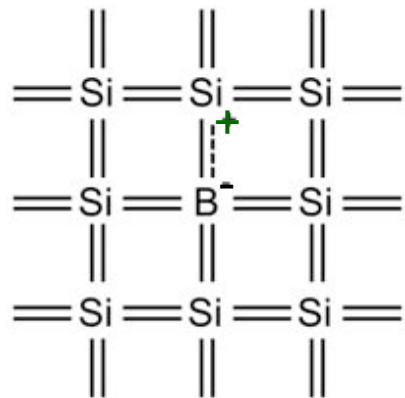
► Doping Si with other atoms allows us to create an excess of electrons (n-type) holes (p-type)

The periodic table shows elements B, Si, and P highlighted with colored boxes: B (green), Si (blue), and P (red).

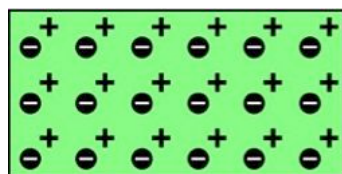
*B(III) takes an extra electron from Si (IV) to achieve '8', this creates a hole which can move from Si to Si.*

Si has 4 valence e' s, covalent bond with 4 Si atoms since desires a full outer shell of 8, and no more!

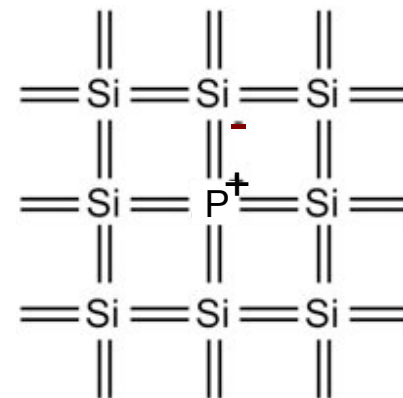
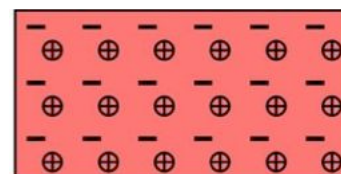
*P(V) gives up an electron to achieve '8'. Note how P atoms are 'circled' in diagram at left.*



p-type

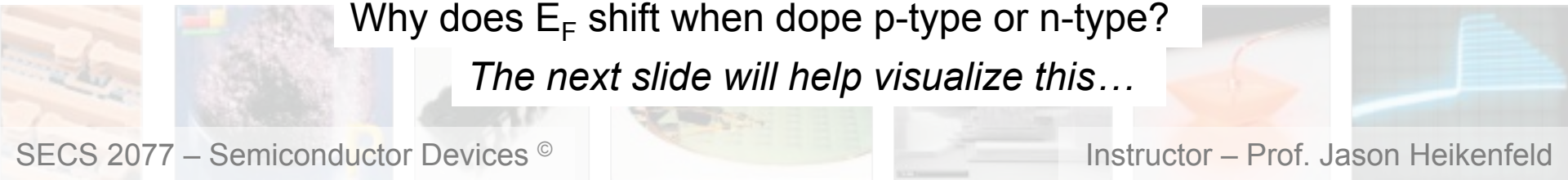


n-type



Why does  $E_F$  shift when dope p-type or n-type?

*The next slide will help visualize this...*



► Effective Density of States:

$$N_{c,v} = 2 \left( \frac{2\pi m_{n,p}^* kT}{h^2} \right)^{3/2}$$

► Fermi Distribution:

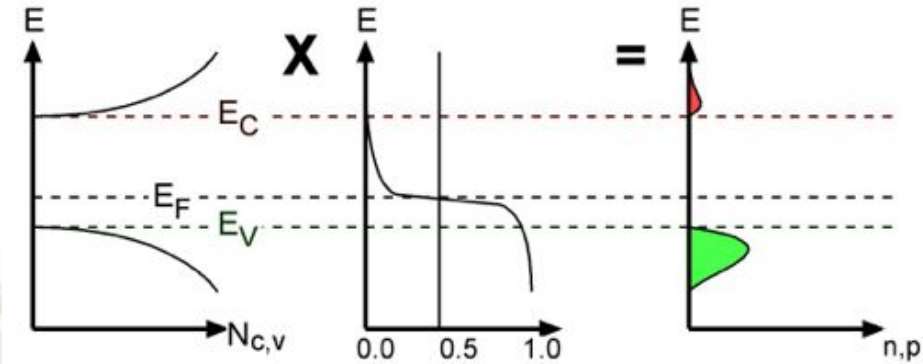
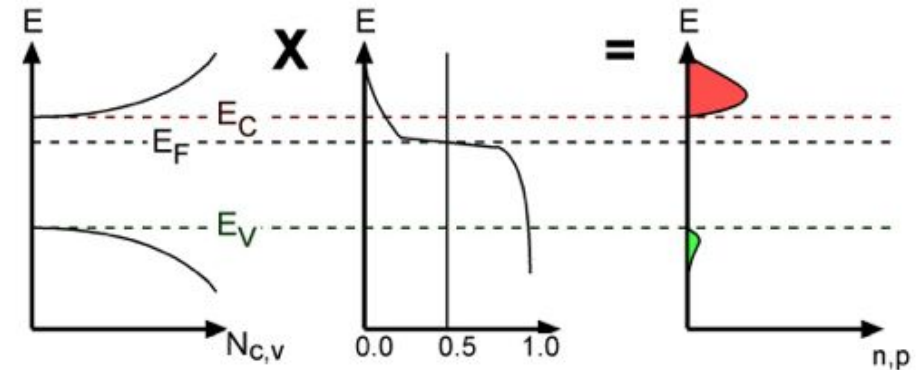
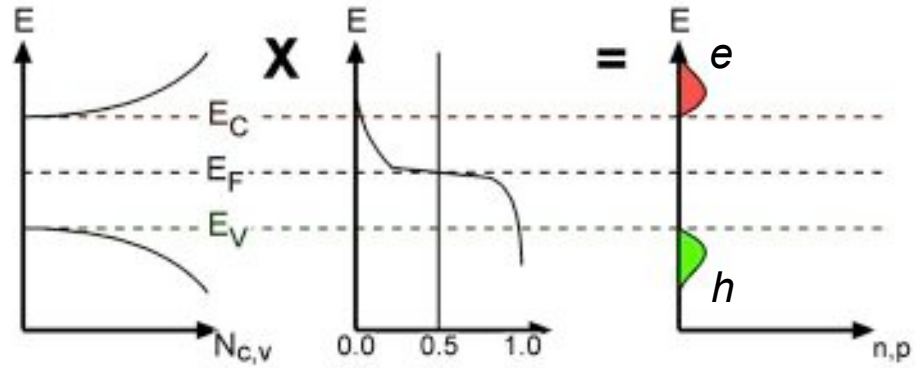
$$f(E) = 1 / (1 + e^{(E-E_F)/kT})$$

► Carrier Concentration:

$n_0, p_0, n_{0n}, p_{0n}, n_{0p}, p_{0p}$

'0' = thermal equilib.

Density of States X Fermi Dist. = Carrier Conc.

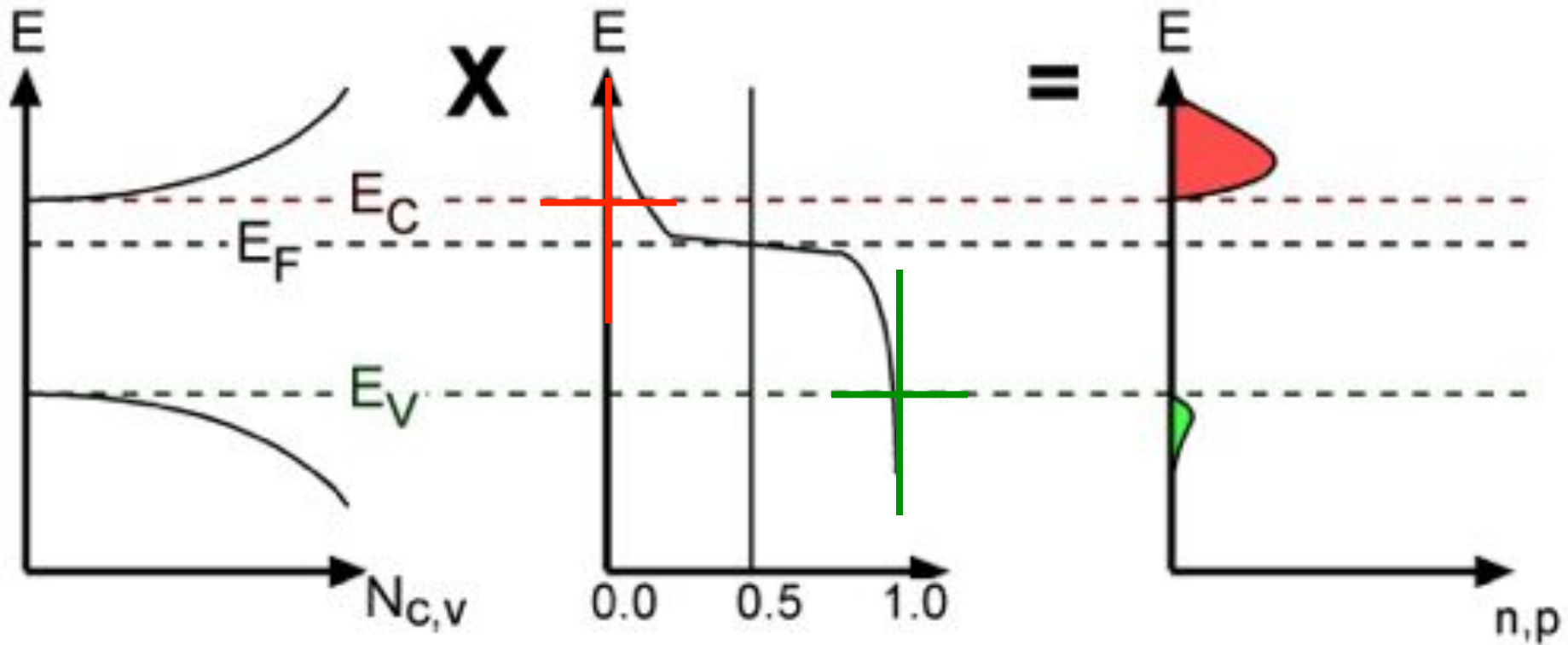


Notice how the majority carrier increases and the minority carrier decreases compared to intrinsic material... why? Has something to do with recombination...



▶ Again, doping level shifts the Fermi Level (which it should! right!)

▶ Again, notice the increased overlap of the Fermi Function with the density of states for conduction band, and reduced overlap with density of states for the valence band...



- ▶ So close to making the basic building block for all s/c devices (PN junctions...)
- ▶ Assume that the entire density of acceptors ( $N_A$ ), like boron atoms ionize at 300 K

▶ p-type material

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

$$p_0 = N_v e^{-(E_F - E_v)/kT} = N_A$$

$$\begin{aligned} p_0 &= N_A \\ n_0 p_0 &= n_i^2 \end{aligned}$$

The farther apart  $E_F$  and  $E_v$ , the smaller the hole concentration...

As  $E_F$  and  $E_v$  get closer you can approach  $N_v \sim 2 \times 10^{19} / \text{cc} \dots$

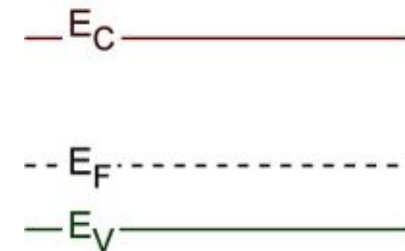
Simple terms:

p- Si (light doped)

p Si (normal doping)

p+ Si (heaving doping)

p++ Si (degenerate doping, act more like a metal than a semiconductor)



*Remember! There are still electrons in p-type material! Just less of them: as we increase the number of holes, the chance for electrons to disappear via recombination increases (higher rec. rate)*

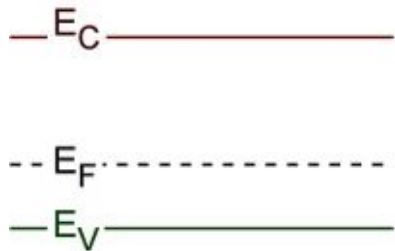
$$n_{0p} = N_c e^{-(E_c - E_F)/kT} = \frac{n_i^2}{N_A}$$

▶ Again, close to ready to make a PN junction.... few more topics next time, then we will join these two materials together!

▶ p-type semiconductor

$$p_0 = N_A$$

$$n_0 p_0 = n_i^2$$



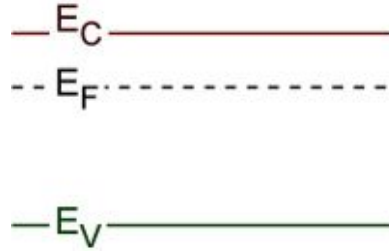
$$p_0 = N_v e^{-(E_F - E_v)/kT} = N_A$$

$$n_0 p_0 = N_c e^{-(E_c - E_F)/kT} = \frac{n_i^2}{N_A}$$

▶ n-type semiconductor

$$n_0 = N_D$$

$$n_0 p_0 = n_i^2$$



$$n_0 = N_c e^{-(E_c - E_F)/kT} = N_D$$

$$p_0 n_0 = N_v e^{-(E_F - E_v)/kT} = \frac{n_i^2}{N_D}$$

▶ example 3-5 from book:

Si doped with  $10^{17}/cc$  Phosphorus atoms.

(1) What is  $p_0$  at 300K?

$$p_0 = \frac{n_i^2}{N_D} = \frac{2.25 \times 10^{20}}{10^{17}}$$

$$p_0 = 2.25 \times 10^3 / cc$$

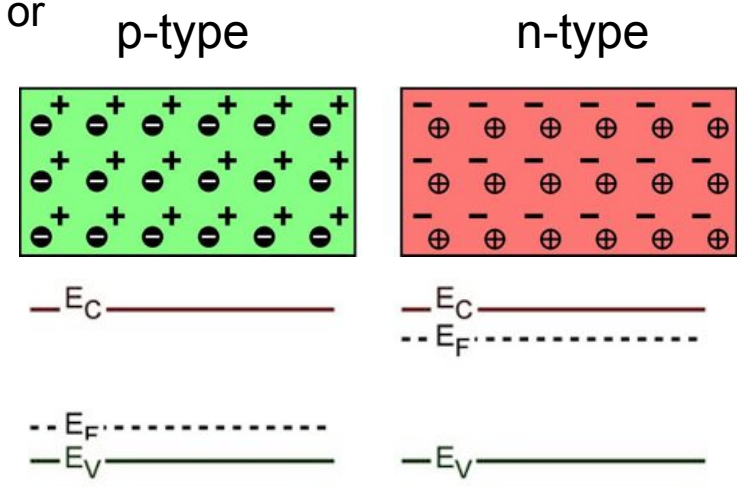
$$n_0 = 10^{17} / cc$$

(2) This is strong n-type doping, what % of the Si host is this?

$$\% = 100 * \frac{10^{17} / cc}{5 \times 10^{22} / cc} = 0.0002\%$$



- ▶ What are the circled things in the diagram at right with +’s or -’s in them? Can they move?
- ▶ What are the things in the diagram at right with +’s or -’s and no circles? Can they move?
- ▶ What is the net charge for either block of material?
- ▶ Why does  $E_F$  shift?
- ▶ Where do most of the carriers sit (what do the profiles look like on the energy band diagram, and why does it look that way)?
- ▶ Why does increasing one carrier type lower the other carrier type?
- ▶ What columns of atoms on the periodic table can I use for doping and why? At 300K, are they all ionized?
- ▶ Again, is the valence band given its name? *Note, this of course applies only to the host Si material, not its dopants.*
- ▶ Lastly, why at 300K do I have carriers even without dopants?



► Using MATLAB to plot  $f(E)$  vs.  $T...$ *Adapted from Pierret, Ex 2.3*

```
%Fermi Function Calculation, f(E-EF,T)
```

```
%Constant
```

```
k=8.617e-5;
```

```
%Computation proper
```

```
for ii=1:4;
```

```
    T=100*ii;
```

```
    kT=k*T;
```

```
    dE(ii,1)=-5*kT;
```

```
    for jj=1:101
```

```
        f(ii,jj)=1/(1+exp(dE(ii,jj)/kT));
```

```
        dE(ii,jj+1)=dE(ii,jj)+0.1*kT;
```

```
    end
```

```
end
```

```
dE=dE(:,1:jj); %This step strips the extra dE value
```

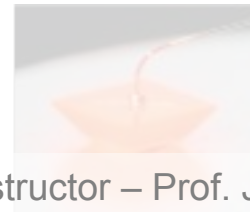
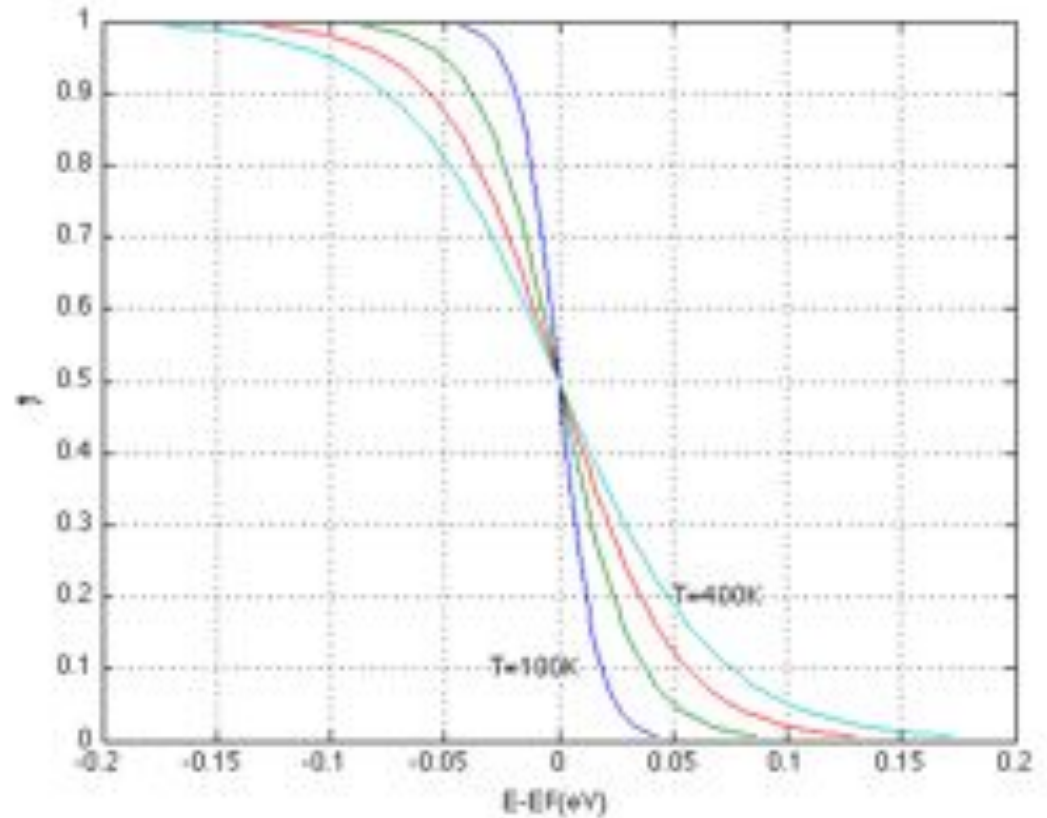
```
%Plotting result
```

```
Close
```

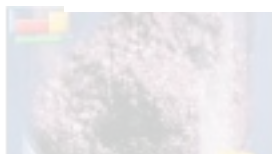
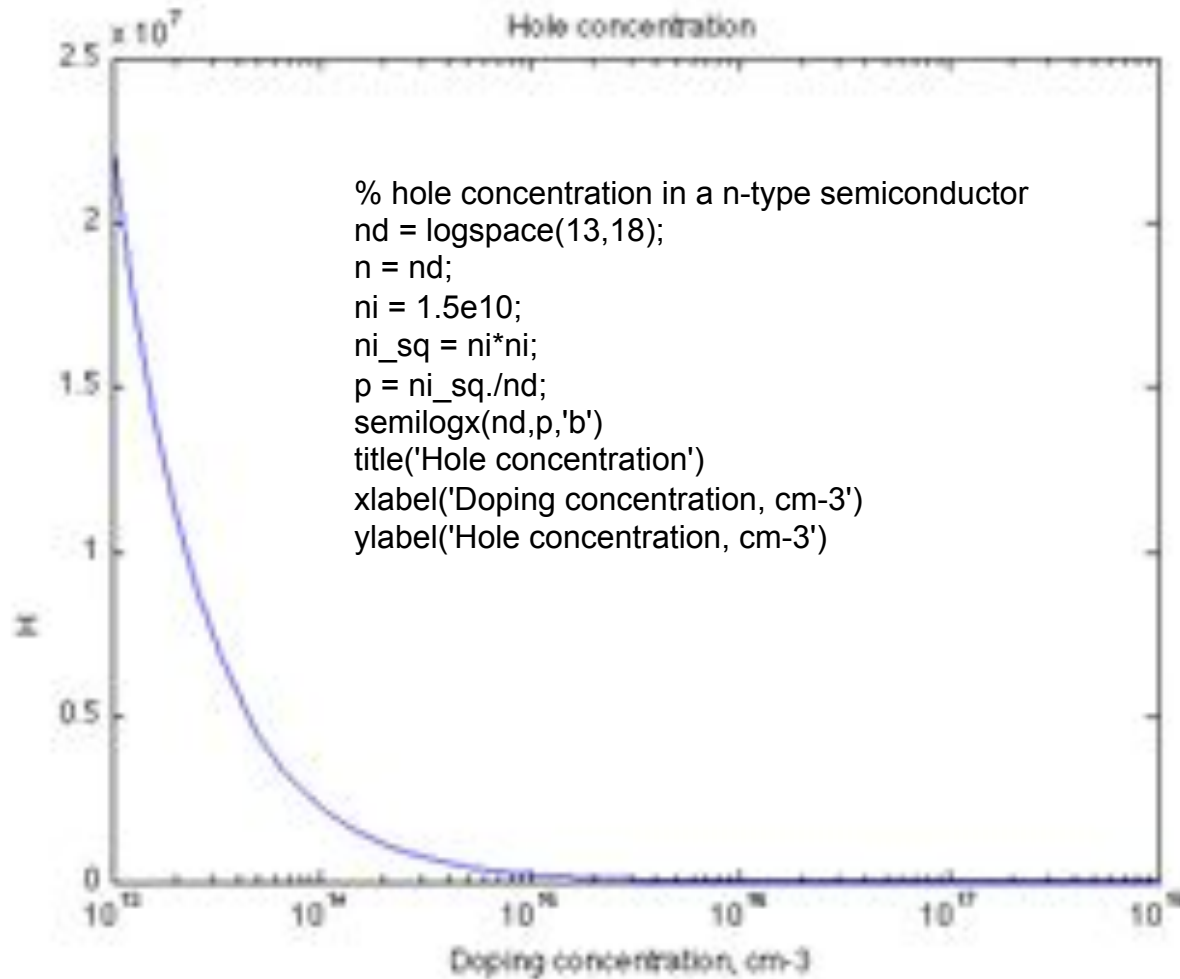
```
plot(dE',f'); grid; %Note the transpose (') to form data columns
```

```
xlabel('E-EF(eV)'); ylabel('f(E)');
```

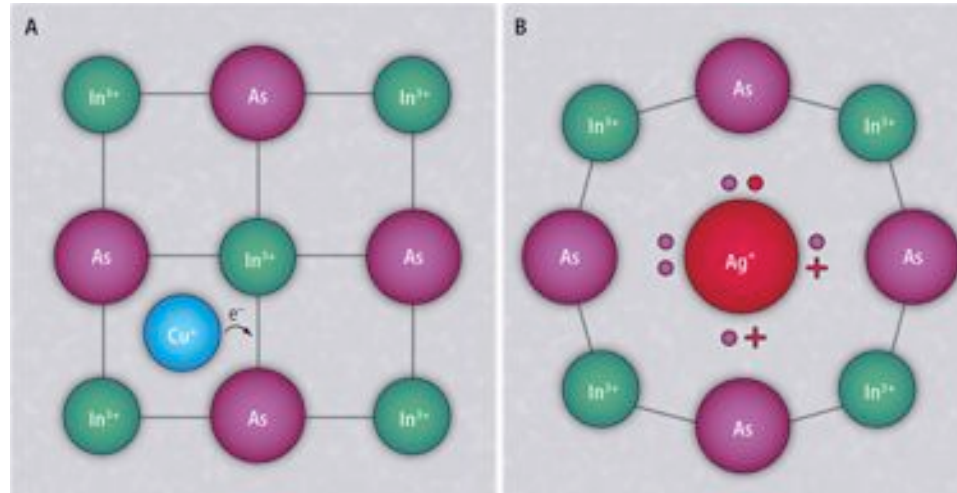
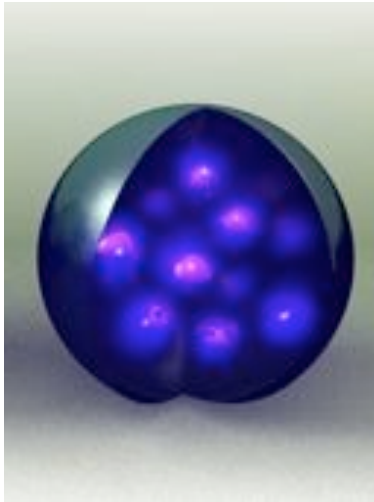
```
text(.05,.2,'T=400K'); text(-.03,.1,'T=100K');
```



## ▶ Using MATLAB to hole concentration in an n-type semiconductor



► Quantum Dots Get Doped (IEEE Spectrum, April 2011)



5 April 2011—At just a few nanometers across, quantum dots are tiny—so tiny that scientists attempting to insert new atoms into their structures have found that the atoms tend to quickly wander back out.

Now a team led by Uri Banin and Oded Millo of Hebrew University, in Jerusalem, and Eran Rabani of Tel Aviv University think they have found a controlled way to introduce dopants into quantum dots. To do so, the group made a solution containing 3.3-nanometer-wide crystals of indium arsenide and either silver or copper atoms. These atoms bounced around in solution due to the random jiggles of Brownian motion and eventually wandered inside the crystals. The copper atoms lodged themselves into gaps between atoms in the lattice, donating their extra outer electrons to the crystal to create an n-type nanocrystal. Although silver atoms diffused through the crystal at much the same speed, they instead dislodged indium atoms and took over their positions in the lattice. Because the silver atoms had fewer outer electrons than the indium atoms, they created p-type crystals containing electron-craving "holes."

The work could eventually pave the way for new flexible solar cells and LEDs, which would be built from the bottom up.

<http://www.mathworks.com/matlabcentral/fileexchange/25088-fermi-level>

