Semiconductor Devices - Hour 11  

Semiconductors Doped with Donors or Acceptors

Earlier we described "intrinsic semiconductors" where electrons & holes are created only by thermal promotion

**Last Time:** Introducing "extrinsic" semiconductors with added mobile charge carriers:

1) **Introduced more electrons by adding DONOR impurities**

Donors are atoms that have one MORE bonding electron than required for their crystalline site

Another way of putting it: In periodic table, they are one column to the RIGHT of atom they supplant

For Silicon semiconductor crystals it is easy to figure out which atoms they must be:

- Silicon = 4 bonding electrons = Column IV of the periodic table
- Donor atom in Silicon lattice = 5 bonding electrons = Column V or the periodic table

For example Phosphorus or Arsenic atoms

Tricker for compound semiconductors such as GaAs = alternating Column III and Column V atoms

- On the Ga Column III site, to act as a donor, need Column IV atoms, such as Carbon or Silicon
- On a As Column V site, to act as a donor, need Column VI atoms, such as Sulfur or Selenium

If you succeed in getting such a donor atom in place, it has an excess of bonding electrons

At room temperature, that extra electron is likely to wander off

Leaving the donor atom short one of its own electrons => It becomes a POSITIVE ION

Or looking at the donor atom only:

And concentrations:

\[
N_d^0 \leftrightarrow N_{d+} + n
\]

2) **Introducing more holes (electron vacancies) by adding ACCEPTOR impurities**

Acceptors are atoms that have one LESS bonding electron than required for their crystalline site

Another way of putting it: In periodic table, they are one column to the LEFT of atom they supplant

For Silicon semiconductor crystals it is again easy to figure out which atoms they must be:

- Silicon = 4 bonding electrons = Column IV of the periodic table
- Acceptor atom in Silicon lattice = 3 bonding electrons = Column III or the periodic table

For example Boron (or Aluminum or Gallium)

Again trickier for "compound semiconductors such as GaAs = alternating Column III and Column V atoms

- On the Ga Column III site, to act as an acceptor, need Column II atoms, such as Cadmium or Zinc
- On a As Column V site, to act as an acceptor, need Column IV atoms, such as Carbon or Silicon

If you succeed in getting such a acceptor atom in place, it has a deficiency of bonding electrons

At room temperature, it is likely to "accept" (steal) a bonding electron from another crystal atom

Giving the acceptor an additional electron => It becomes a NEGATIVE ION

Or looking at the acceptor atom only:

And concentrations:

\[
N_a^0 \leftrightarrow N_{a-} + p
\]

"Aren't you sort of beating this to death?"

Absolutely!! Because so many students remain confused about this through entire course

So do YOU really understand it now? Or do you want to talk about it some more?
Some more subtle points about donors and acceptors:

First, above assumed donors and acceptor atoms found their way onto normal crystal lattice sites

That is, that these are substitutional impurities (i.e. they substitute for semiconductor atoms)

How do you accomplish this? Nature will take care of this if:

1) Atom is not too different in size from the crystal atom it replaces
2) And you supply some heat to allow atoms to rearrange themselves

Comparable size requirement means donor or acceptor should be from nearby ROW of Periodic Table

So for Silicon:

<table>
<thead>
<tr>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>2e</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>N</td>
<td>O</td>
<td>1.56</td>
</tr>
<tr>
<td>B</td>
<td>P</td>
<td>Se</td>
<td>1.82</td>
</tr>
<tr>
<td>In</td>
<td>As</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td>TI</td>
<td>Bi</td>
<td>1.18</td>
<td></td>
</tr>
</tbody>
</table>

B and Al work well as acceptors

(but Ga has problem with SiO2)

In, Tl are so big they are less likely to assume crystal positions

P and As work well as donors

But Sb and Bi are so big are less likely to assume crystal positions

Second, concerning compound semiconductors like GaAs, you may have caught something strange above:

<table>
<thead>
<tr>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>2e</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>S</td>
<td>Si</td>
<td>1.37</td>
</tr>
<tr>
<td>Ge</td>
<td>Br</td>
<td>1.79</td>
<td></td>
</tr>
</tbody>
</table>

Impurity atoms from Column IV on Ga site are donors

For instance C, Si, or Ge

Impurity atoms from Column IV on As site are acceptors

For instance C, Si, or Ge

Make up your mind, are Column IV atoms donors or acceptors?

They really can end up being both in such a III-V compound semiconductor!!

For this reason, their use in such materials is often avoided

Unless crystal has been grown with more missing Column III or V atoms

As can be done, for instance, by growing with low or high Column V pressures

But how to quantify effects of adding donor or acceptor atoms to semiconductor crystals?

Now have total of FOUR possible charged species in the semiconductor, with corresponding equations:

\[ n_d(E_F) = N_c \frac{e}{k_B T} \]

Number of negative electrons in the conduction band

\[ n_p(E_F) = N_v \frac{e}{k_B T} \]

Number of positive holes in the valence band

\[ N_d^{plus}(E_F) = N_d_{total} \left[ \frac{1}{(E_F - E_d)} \right] \frac{e}{k_B T} \]

Number of donors that have donated (lost) an electron

Thereby becoming positive ions

\[ N_a^{minus}(E_F) = N_a_{total} \left[ \frac{1}{(E_a - E_F)} \right] \frac{e}{k_B T} \]

Number of acceptors that have accepted an extra electron

thereby becoming negative ions

How to deal with these possibilities:

1) Realize that in semiconductors, we don't make small changes (10%, 50%...)

   Instead change things by 10, 100, 1000, 100000! Only need to know which things dominate

2) Recall that charge imbalances quickly lead to HUGE restoring electric fields

   So semiconductors tend strongly towards: Charge Neutrality = Net charge per volume ~ zero

4) Four equations above cover all the ordinary charges All are functions of the Fermi level position

   Need to solve for the value of \( E_F \) that gives Charge Neutrality
Case 1: "Intrinsic Semiconductor" (one with ~ no donor or acceptor impurities)

Intrinsic Semiconductor

Na_total and Nd_total are things WE control: We decide how much impurity is put in crystal
If these values are zero (or very small) we have a pure or "intrinsic semiconductor"

Then, setting net charge in semiconductor crystal to zero:

Total positive charge = p
Total negative charge = n
Charge Neutrality requires these are equal

\[ p = n \]

or substituting in equations above:

\[ \frac{1}{k_B T} \ln \left( \frac{N_v}{N_c} \right) \]

plug this back into equations for n or p:

\[ n = p = n_i = \sqrt{N_c N_v e^{-\frac{E_g}{k_B T}}} \] (worked out in lecture 9)

Note the effect of that negative exponential:

Larger the bandgap of the semiconductor, \( E_g \), larger the negative exponential \( \gg \) smaller \( n_i \)

Yes! Larger bandgaps, less likely it is for electrons to jump out of bonds (i.e. make it to upper band)

Silicon's bandgap is 1.1 eV. Its "intrinsic carrier concentration" \( n_i \) at room temperature is \( 10^{10} / \text{cm}^3 \)

GaAs's bandgap is 1.42 eV. Its "intrinsic carrier concentration" \( n_i \) at room temperature is \( 10^6 / \text{cm}^3 \)

Larger the temperature (in denominator of the negative exponential), larger \( n_i \)

One of the reasons integrated circuits don't like high temperatures:

Intrinsic carriers become more important that carriers added by donors and acceptors

Case 2: Semiconductor "doped" with Donor and Acceptor Impurities

"Old" charges:

Valence band holes: \( p(E_F) = N_v e^{-\frac{(E_F - E_v)}{k_B T}} \)

Conduction band electrons: \( n(E_F) = N_c e^{-\frac{(E_F - E_c)}{k_B T}} \)

"New" positive donor ions:
Neutral donor V atom \( \rightarrow \) Positive donor ion

Electron lost, atom \( \rightarrow + \) ion

"New" negative acceptor ions:
Neutral acceptor III atom \( \rightarrow \) Negative acceptor ion

Electron gained, atom \( \rightarrow - \) ion

Corresponding donor energy diagram:

\( E_c \rightarrow E_d \)

Corresponding acceptor energy diagram:

\( E_v \rightarrow E_a \)

Concentration of donors that have ionized:

\[ N_d^{\text{Plus}}(E_F) = \left[ \frac{1}{k_B T} \ln \left( \frac{N_v}{N_c} \right) \right] N_d^{\text{Total}} - \frac{(E_F - E_d)}{k_B T} \]

Concentration of acceptors that have ionized:

\[ N_a^{\text{Minus}}(E_F) = \left[ \frac{1}{k_B T} \ln \left( \frac{N_v}{N_c} \right) \right] N_a^{\text{Total}} - \frac{(E_F - E_a)}{k_B T} \]

These new charged species must be incorporated into the net charge neutrality requirement:

\[ p + N_d^{\text{Plus}} = n + N_a^{\text{Minus}} \]

Before plunging in to algebra, notice what happens when we multiply together the n and p equations:

\[ \frac{1}{k_B T} \ln \left( \frac{N_v}{N_c} \right) e^{\frac{E_F - E_v}{k_B T}} \cdot \frac{1}{k_B T} \ln \left( \frac{N_v}{N_c} \right) e^{\frac{E_F - E_a}{k_B T}} = N_v N_c e^{\frac{E_F - E_v - E_a}{k_B T}} \]

\( E_F \) cancels out of product

further: \( N_v N_c e^{\frac{k_B T}{3}} = n_i^2 \) The carrier concentration we had in the pure semiconductor
n and p may no longer equal $n_i$ - but their product is still $n_i^2$

As one increases, the other decreases to precisely compensate

So can always eliminate one of our new unknown charges by using:

$$n = \frac{n_i^2}{p} \quad \text{or} \quad p = \frac{n_i^2}{n}$$

So going back to our impurity doped semiconductor case:

Charge neutrality requirement: $p + N_d^{\text{plus}} = n + N_a^{\text{minus}}$

If use $n = \frac{n_i^2}{p}$ get:

$$p + N_d^{\text{plus}} = \frac{n_i^2}{p} + N_a^{\text{minus}} \quad \text{or:} \quad p^2 - (N_a^{\text{minus}} - N_d^{\text{plus}}) + n_i^2 = 0$$

*Houston, we (still) have a problem!* Every single term (except $n_i$) depends on $E_F$ - see equations page 7

Only way out (other than iterative computer solution):

Remember that donor state is high in bandgap $\Rightarrow$ Will ionize (loose its electron) if $E_F$ is lower than $E_d$

Remember that acceptor state is low in bandgap $\Rightarrow$ Will ionize (gain electron) if $E_F$ is higher than $E_a$

Completely ionized donor (lost the electron) at $E_d$

Completely ionized acceptor (grabbed electron) at $E_a$

This assumption, THAT ALL DONORS AND ACCEPTORS IONIZE, is far from automatic.

We'll use it a lot in this class, because it yields only algebraic way of finding carrier concentrations

But it can and is VIOLATED FREQUENTLY in real semiconductors

WHEN are we likely to loose full ionization?

When add SO MANY donors, liberating so many electrons that $E_F$ rises to CONDUCTION BAND

When add SO MANY acceptors, creating so many holes that $E_F$ sinks to VALENCE BAND

Donors / Acceptors then cannot stay ionzed (so many carriers present, they come back!)

How many is TOO MANY? Rules of thumb (that come out of our earlier analyses):

Are heading for trouble when donor or acceptor concentrations approach $N_c$, $N_v$

Say what?

Trouble when donor or acceptor concentrations approach the band's "Lumped Density of States"

Those things we spent most of lecture 9 calculating!!

Trouble when donor or acceptor concentrations approach the band's "Lumped Density of States"

Those things we spent most of lecture 9 calculating!!

From that lecture (or book's Appendix B):

For Silicon, lose ionization as as approach $\sim 10^{19}/\text{cm}^3$ donors and acceptors

Different (often lower) number for other semiconductors

So, while in this class we will almost always make the assumption of full ionization, A WARNING:

A mean professor could easily set up a test problem where assumption of full ionization fails

A slightly less mean professor at least expects you to note (in writing) where you make this assumption

Professor's SHOULD BE OBNOXIOUS about this because in real-life devices assumption OFTEN fails

Compelling you to then use iterative computer solutions (or their tabulated results)

I.E. Assume position of $E_F$, calculate resulting $n$ and $p$

Recalculate $E_F$ based on calculated $n$ & $p$. Repeat until converges
SO ASSUMING, VIA MODERATE DOPING, WE DO STILL HAVE FULL DONOR / ACCEPTOR IONIZATION:

With this assumption, the charge neutrality condition becomes:

\[ p + N_d^{\text{plus}} = n + N_a^{\text{minus}} \implies p + N_d^{\text{total}} = n + N_a^{\text{total}} \]

Then depending on whether you eliminate \( n \) or \( p \) using \( np = n_i^2 \) get:

\[ p^2 - \left( N_a^{\text{total}} - N_d^{\text{total}} \right) p - n_i^2 = 0 \quad \text{or} \quad n^2 - \left( N_d^{\text{total}} - N_a^{\text{total}} \right) n - n_i^2 = 0 \]

Where only unknowns are \( n \) and \( p \)Simple quadratic solutions (picking physically realistic roots):

\[ n_o = \frac{N_d^{\text{total}} - N_a^{\text{total}}}{2} \quad \sqrt{\frac{N_d^{\text{total}} - N_a^{\text{total}}}{2} + n_i^2} \]

\[ p_o = \frac{N_a^{\text{total}} - N_d^{\text{total}}}{2} \quad \sqrt{\frac{N_a^{\text{total}} - N_d^{\text{total}}}{2} + n_i^2} \]

Have added "o" subscript to remind are in equilibrium

To check if you indeed have full ionization:

Have to solve for above value of either \( n_o \) or \( p_o \) plug that value into left side of:

\[ \frac{- (E_c - E_F)}{k_B T} \quad \text{or} \quad \frac{- (E_F - E_v)}{k_B T} \]

THEN solve for \( E_F \) and check to make sure it is several \( kT \) within the bandgap:

That is, result had better be that BOTH:

\[ E_v + 2kT < E_F < E_c - 2kT \]

Conduction Band

Valence Band

If condition is met: You are done

If condition is NOT met: Go back to full \( N_d^{\text{plus}} \) and \( N_a^{\text{minus}} \) equations

Put these monsters into charge neutrality requirement

Do iterative computer solution (or try to talk Mathcad into doing this)