ET3034Tux - 2.2.2 - Band Gap 2 - Electrons in Molecular Bonds

We have arrived to the question: how do molecular bonds determine the band gap?

We have discussed that the silicon atom has four outer electrons.

These four outer electrons play an important role in making the bonds with other atoms in a molecule or in a solid.

These electrons are the so-called valence electrons.

In a very cruel simplification a bond can be considered as the mixing of two orbitals of neighboring atoms.

One valence electron shares its orbital with the orbital of a valence electron of a neighboring atom.

This means that it takes two valence electrons to make one valence bond.

This resulting orbital is called a molecular orbital.

From nature we know that the orientation of a silicon bond is tetrahedral like.

Consider the lattice of crystalline silicon, which is a diamond cubic crystalline lattice.

Looking at a single atom in such lattice, the angle between all four bonds is 109 degrees.

However, if we look at the orbitals of the four valence electrons in the third shell of silicon, we don't recognize the tetrahedral coordination.

Their shapes do not match a tetrahedral coordination at all.

How are these states related to the orbitals?

To explain this we consider one electron in the 3s state and three electrons in the 3p state.

We now make a cocktail of orbitals, we will mix these four states.

In nature, it appears that these four states mix into effective four symmetric states.

The animation demonstrates the mixing.

The four resulting symmetric states are called the sp3 hybrid.

In nature the four valence electrons behave like they are in these four sp3 orbitals.

The orientation between these four orbitals corresponds to the tetrahedral coordination with an angle of 109 degrees between them.

Now, we can roughly understand the coordination of the lattice of crystalline silicon, but still don't understand the origin of the band gap.

For that we have to look in more detail to how a bond is made between two atoms.

Here you see two sp3 orbitals of two neighboring atoms, which are at a far distance from each other.

Both orbitals have one electron at a discrete energy level that resembles that of the sp3 hybrid.

To establish a bond, the two atoms have to approach each other.

The orbitals start to overlap and merge into one molecular orbital with its own shape.

Here again the Pauli exclusion principle starts to play a role.

Two identical electrons cannot occupy the same quantum state simultaneously.

Nature splits the original sp3 energy level up in two energy levels.

The lowest energy level is the bonding level and is lower in energy as the original two individual sp3 levels.

As a result both electrons prefer to fill this state, in which one electron has a spin up and the other electron has a spin down.

This bonding state represents the attraction between the Si atoms and the creation of a bond.

The energy level of the bonding level is lower than the original sp3 level and therefore more stable.

The second high energy level is called the anti-bonding level.

The energy level is higher than the original sp3 level and therefore electrons do not prefer to fill this state.

Another important aspect of bonding and anti-bonding levels is that the closer the two neighboring atoms are together the larger the energy splitting between the bonding and anti-bonding level will be.

This is demonstrated in the animation.

Let's consider the example of silicon again.

For silicon the far majority of electrons will fill up the lowest bonding state.

These lower bonding states reflect the valence band as introduced earlier.

The anti-bonding states correspond to the conduction band and is hardly occupied by any electron.

The gap between the bonding and anti-bonding states corresponds to the band gap.

If we look at the molecular orbital its bonding and anti-bonding states are discrete energy levels.

However, if we look at a solid like crystalline silicon, its network contains many silicon-silicon bonds.

All these bonding states do not appear as one single discrete energy level, but spread their energy levels continuously over a broader electronic band, like the valence band or conduction band.

Physicists in general use the terms valence band, conduction band and band gap.

Chemists might use different terms for the same concepts.

They might use the expression highest occupied molecular orbital (the HOMO) as the valence band and the lowest unoccupied molecular orbital (the LUMO) as the conduction band.

The HOMO-LUMO gap would be the band gap.

So far we have discussed the situation for silicon, which is an element with four valence electrons.

Carbon and germanium are elements, which have four valence electrons, as well.

Carbon has four valence electrons filling the second shell and germanium has four electrons partly filling the fourth shell.

Carbon, silicon and germanium all have tetrahedral coordination and form a diamond cubic crystalline lattice in its crystalline phase.

Silicon and germanium can be considered as IV-semiconductor materials, the IV stands for the number of valence electrons.

Why is carbon not a semiconductor as it has the same lattice?

To answer this question we have to consider the bond length between the atoms.

Or in other words to which extent the neighboring orbitals forming the molecular orbital are pressed together.

The bond length is in general expressed in terms of lattice constant.

What is the relation of the lattice constant and the bond length for a diamond cubic crystalline lattice?

In this figure the unit cell of a diamond cubic crystalline lattice is shown, the edge length of this cube is equal to the lattice constant.

In diamond crystalline lattice the lattice constant equals to 4 times the silicon-silicon bond length divided by the square root of 3.

In the next graph we plot the band gap of crystalline carbon, silicon and germanium versus the lattice constant.

Crystalline carbon is another name for diamond.

We indeed see that the band gap is very large for diamond, as diamond has the smallest lattice constant.

In a very simplified representation the larger band gap can be considered as a larger overlap of the original sp3 like orbitals of the neighboring atoms.

A larger overlap induces a larger splitting of the energy levels of the bonding and anti-bonding level.

Materials with semiconductor properties can be made from other materials than elements with four valence electrons.

Let's consider the so-called III-V semiconductor materials like gallium-arsenide (GaAs).

III-V semiconductor consists out of two elements, one element has three valence electrons, the other element has five valence electrons.

These materials can similar to silicon form a diamond cubic crystalline lattice.

In the crystalline lattice shown here the gallium are the blue atoms and the arsenide are the red atoms.

The difference with silicon is that every gallium atom is neighboring four arsenide atoms and every arsenide atom is neighboring a gallium atom.

Let's consider the III-V materials based on gallium, like gallium-phosphor (GaP), gallium-arsenide (GaAs) and gallium-stibium (GaSb).

Again, the larger the lattice constant of the material, the smaller the band gap will be.

Gallium-phosphor has the smallest lattice constant and therefore the largest band gap.

Another group of semiconductor materials are the so-called II-VI semiconductor materials like cadmium-tellurium.

II-VI semiconductor consists out of two elements, one element has two valence electrons, the other element has six valence electrons.

These materials can form a diamond cubic crystalline lattice as well.

In the crystalline lattice shown here the cadmium atoms are the blue atoms and tellurium atoms are the red atoms.

So, every cadmium atom is bonded to four tellurium atoms, and every tellurium atom is neighboring a cadmium atom.

Let's consider the II-VI materials based on cadmium, like cadmium-sulfur (CdS), cadmium-selenium (CdSe), cadmium-tellurium (CdTe).

Again, the larger the lattice constant of the material, the smaller the band gap will be.

Cadmium-telluride (CdTe) has the largest lattice constant and therefore the smallest band gap.

I hope you have become familiar with the important properties of semiconductors like the valence band, the conduction band and the band gap.

And I have shown that we have different semiconductor materials like silicon, germanium, gallium-arsenide and cadmium-telluride.

Important to remember is that all these semiconductors have different band gaps.

So how can we make semiconductor materials conductive?

Or in other words: how can we fill the conduction band with free electrons?

It is my pleasure to show that in the next block.