

### 5.1.3 Doping of Compound Semiconductors

#### Some Basic Considerations

- Essentially, the semiconducting properties of silicon stem from the  $sp^3$  hybrid bonds formed between electrically neutral atoms.
  - Two **Si** atoms donate one electron each to all four  $sp^3$  hybrid bonds, forming the familiar diamond type lattice.
  - Substituting a **Si** atom by a group **III** or group **V** element produces a mobile hole or electron *and* an immobile ion in the familiar way.
- All **III-V** compounds also form  $sp^3$  hybrid orbitals, but there is now a *big difference* to **Si** (or **Ge**, or diamond-**C**): The binding, which was *totally covalent* for the elemental semiconductors, now has an *ionic component*.
  - This is simply due to the fact that different atoms differ in their *electronegativity*, describing the affinity to electrons of the element. The numbers in brackets give the electronegativity quantitatively: The larger the value, the stronger the effect.

IIa, b	III	IV	V	VI
Be (1.6)	B (2.0)	C (2.6)	N (3.1)	O (3.4)
Mg (1.3)	Al (1.5)	Si (1.9)	P (2.2)	S (2.6)
Zn (1.7)	Ga (1.8)	Ge (2.0)	As (2.2)	Se (2.6)
Cd (1.5)	In (1.5)	Sn (1.7)	Sb (1.8)	Te (2.7)
Hg (1.9)	Tl (1.6)	Pb (1.6)	Bi (1.7)	Po (2.0)

- A more electronegative element will attract the electrons from the partner more strongly, become more negatively charged, and thus increase the ionic part of the binding.
- The percentage *p* of the ionic binding energy varies for the various compounds.
  - The difference in electronegativity of the atoms in a compound semiconductor gives a first measure for *p*.
  - To give some examples: For **Si** we have  $p = 0$ , for **GaAs** we find  $p = 0.08$ .
- Doping is still achieved by introducing specific atoms as *substitutional impurities*. But in contrast to elemental semiconductors, we now have more possibilities as can be seen by looking at the relevant part of the periodic table (the elements in yellow cells are never used for doping of *compound* semiconductors).
  - We can replace the group **III** elements by group **II** elements to produce *acceptors* and the group **V** elements by group **VI** elements to produce *donors* – in principle.
  - But we can also replace both the group **III** and group **V** elements by group **IV** elements which, however, may generate donor *or* acceptor levels in the band gap of some compounds – we have **amphoteric doping**.
  - We could also replace the atoms of the compound by an **isoelectronic** atom – group **III** elements by some other group **III** elements, and the same thing for the group **V** partner. In **Si**, this would mean replacing a **Si** atom by e.g. a **Ge** or **C** atom – which is not very exciting. In compounds, however, *doping with isoelectronic atoms* produces differences in the ionic part of the binding and therefore *local potential differences* with noteworthy effects as we shall see below.
  - We could even replace an atom of the lattice by a small molecule – isoelectronic or not – and achieve a doping effect.
- Well, in **Si** we could also use molecules and all group **III** or group **V** elements – but in reality only **B**, **As**, **P**, and sometimes **Sb**, **Ga** or **Al** are used.
  - In **Si**, we do not use the group **III** elements **In** and **Tl**, neither the group **V** elements **N** and **Bi**. The reasons are "technical": They may be difficult to incorporate in a crystal, their solubility may be too small, their diffusivity too high (or too low?), or their energy levels in the band gap not suitable.
- The same situation occurs with compound semiconductors.
  - There are *optimum solutions* to doping, depending on the type of semiconductor, the technology available or mandated by other criteria, and so on and so forth.
  - There are therefore no general rules for optimal doping, and here we will only discuss *amphoteric* doping and *isoelectronic* doping in somewhat more detail.
  - The [energy levels of some dopants](#) and other impurities in some **III-V** semiconductors are shown in an illustration module.

## Amphoteric Doping

- ▶ A prime case of amphoteric doping is the incorporation of **Si** into **GaAs**. If the **Si** atoms replace **Ga** atoms, they act as *donors*, and as *acceptors* if they occupy **As** lattice sites. How does this work?
- A **Si** atom has four electrons disposable for binding. If it replaces a **Ga** atom that had only three electrons, the **As** partner has to supply one electron less than before to make up for its "deficient" partner **Ga**, and the surplus electron will only be weakly bound – it will easily escape into the conduction band.
  - **Si** on a **Ga site** causes the release of an electron from the **As**, because the electrons are more strongly bound to **Si** than to **As** – thus, in this case **Si** acts as *donor* even so the electron is actually supplied by the **As**.
  - Contrariwise, if an **As atom** is replaced by a **Si** atom, the new twosome is now short one electron. It can therefore take up an electron from the valence band – **Si** now acts as an *acceptor*.
- ▶ While this seems to offer an elegant way for doping, the tough question now is: How do we *control* which lattice sites are occupied by **Si**?
- In other words: On what kind of lattice sites will we find the **Si** atoms after it was ion-implanted, diffused into the crystal from the outside world, or incorporated directly during crystal growth procedures, or thin film growth?
- ▶ This question cannot be easily answered from first principles. Two guidelines are:
- At *low* temperatures ( $T \leq 700 \text{ °C}$ ), **Si** will prefer to sit on **As** sites – it acts as an *acceptor*, with an energy level about **35 meV** above the valence band edge.
  - At *high* temperatures ( $T \geq 900 \text{ °C}$ ), it tends to sit at **Ga** sites and acts as a *donor*, with an energy level about **6 meV** below the conduction band edge.
  - If **Si** is incorporated into a **GaAs** melt, *large Si* concentrations tend to produce *donors*, *small* concentrations *acceptors*.
- ▶ More about amphoteric doping and its practical aspects will follow in the various chapters about specific compound semiconductors.

## Isoelectronic "Doping" and Bound Excitons

- ▶ If we introduce isoelectronic replacements in the lattice – e.g., a group-V atom (like **N** or **Sb** substituting a **P** atom), or a molecule (like **ZnO** substituting a **GaP** pair in the **GaP** lattice), or even a larger entity (like the **Li-Li-O complex in GaP**, with one interstitial **Li**, the other **Li** substituting **Ga**, and **O** substituting **P**) – we do not "dope" in the conventional sense of the word. We rather change the ionic component of the local binding.
- Since the introduction of isoelectronic elements is deliberate with a specific purpose in mind, we deal with it under the general heading "doping", keeping in mind that we do not change the carrier *density* in this way, but their *recombination behavior*.
  - Doping with isoelectronic elements may not do much in most compound semiconductors, but it can have pronounced effects in others by providing *new* radiative recombination channels due to an interaction of the isoelectronic dopant and electron–hole pairs called *excitons*.
  - The paradigmatic semiconductor for isoelectronic doping is **GaP**, an *indirect* semiconductor. It is used as a strong emitter of green light, however, by doping it with isoelectronic elements and using the *radiative decay of excitons bound to the doping elements*.
- ▶ How does this work? There are several crucial ingredients, all from rather involved solid state physics:
- First, we need *excitons*.
  - Second, we need to have the *excitons bound to isoelectronic dopants*.
  - Third, we need to have a *radiative recombination* of the electron and hole constituting the exciton – *despite the nominal violation of the crystal momentum*.
- ▶ A detailed treatment of these points (explaining, among other things, why this "works" in **GaP**, but not in many other compound semiconductors) is not possible in the context of this lectures course. We will only superficially look at the basics; somewhat more information is contained in an [advanced module](#).
- ▶ Again: What is an **exciton**? Imagine the generation of an electron–hole pair, e.g., by irradiating a semiconductor with light.
- If the photon energy is large enough to lift an electron all the way from the valence band to the conduction band in a direct transition, you now have a *free* electron and a *free* hole which move about the crystal in a random way.
  - Now imagine that the hole and the electron stay so close to each other (i.e. less than a [Debye length](#)) in *real space* that they feel the Coulomb attraction. They are then *bound* to each other with a certain binding energy  $E_b$ , and their coordinates in *r*-space are (nearly) identical, but still undetermined.

- Bound together like that, they behave like an individual particle, and this particle is called exciton (standard symbol:  $X$ ). Note that, since it consists of two fermions with spin =  $\frac{1}{2}$ , an exciton is a boson. Thus, in principle, arbitrarily many excitons can be present.

We already know a system where *one* negative elementary charge is bound to *one* positive one, forming a new "particle" – it is called "*hydrogen atom*". The only difference between an exciton and a hydrogen atom is that the mass of the hole is much smaller than the mass of the proton (and, of course, that our exciton can only exist in a solid).

- From a more advanced treatment of the hydrogen atom, where the electron mass is *not* neglected with respect to the proton mass, we can immediately carry over the solution of the relevant Schrödinger equation to an exciton. Of interest are especially the allowed energy states  $E_X$  of the exciton, for which we obtain

$$E_X(\mathbf{k}) = E_{\text{gap}} - \frac{m_{\text{red}} \cdot e^4}{8 \cdot (\hbar \cdot \epsilon_0 \epsilon_r \cdot n)^2} + \frac{\hbar^2 k^2}{8\pi^2 \cdot (m_e + m_h)}$$

- With  $n =$  quantum number = 1, 2, 3, ... and  $m_{\text{red}} =$  reduced mass (from  $1/m_{\text{red}} = 1/m_e + 1/m_h$ ). Although not written explicitly, always the relevant *effective* masses (of electron and hole) have to be used for the exciton.
- The first term simply accounts for the crystal energy, the second one is straight from the hydrogen atom (see below for details), and the third term is a correction if the two particles are not at the same place in  $\mathbf{k}$ -space (it is zero for  $\mathbf{k}_e = -\mathbf{k}_h$  or  $\mathbf{k}_e = \mathbf{k}_h = \mathbf{0}$  as it will be for most direct semiconductors), giving the kinetic energy of the exciton as a whole.

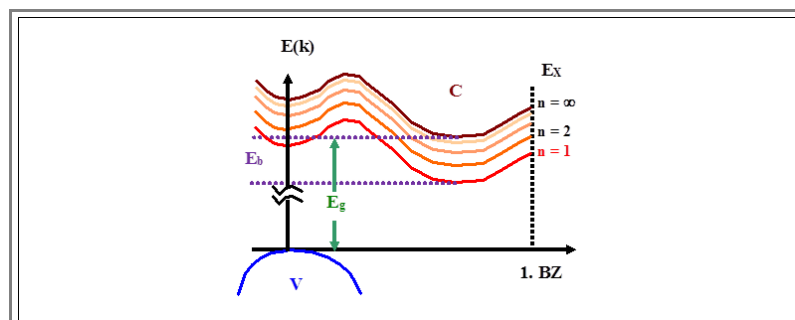
In total we have a system of energies *smaller than the band gap energy*, with the "deepest" level defined by the following energy difference relative to the band gap – which is just the exciton binding energy mentioned above (also known as the Rydberg energy of the exciton), being directly related to the standard Rydberg energy of the hydrogen atom ( $1 \text{ Ry} \approx 13.6 \text{ eV}$ ) as follows:

$$E_b = \frac{m_{\text{red}} \cdot e^4}{8 \cdot (\epsilon_0 \epsilon_r \cdot \hbar)^2} = \frac{m_{\text{red}}}{m_0 \cdot \epsilon_r^2} \times 1 \text{ Ry}$$

- To estimate the order of magnitude relevant for the exciton binding energy, we use  $0.5 m_0$  for both effective masses, giving  $m_{\text{red}} = 0.25 m_0$ , and a (static) dielectric constant of  $\epsilon_r \approx 10$ , resulting in  $E_b \approx 34 \text{ meV}$ .
- This is already a rather reasonable value. The actual exciton binding energy depends mainly on the effective mass of the respective semiconductor. As an example, a properly calculated value for **GaAs** gives  $E_b = 4.4 \text{ meV}$ , which is close to the experimental one.
- [More values](#) can be found in the advanced module.

Due to the exciton binding energy, it takes exactly  $E_b$  less energy to create an exciton than a free electron–hole pair. Since both creation processes start by exciting the electron from the top of the valence band, one commonly finds the picture of excitonic energy levels sitting in the band gap, close to the conduction band.

- This involves several fundamental misconceptions:
  - The symmetry between electron and hole, valid for the exciton, is lost since the hole is imagined to stay at the top of the valence band;
  - the excitonic energies do not represent usual electronic states of the crystal, because excitons are bosons.
- Nevertheless, for simplicity reasons we stick to this picture. In  $\mathbf{k}$ -space for **GaP** this looks like this:



- Since  $E_b$  for a free exciton – that moves about the crystal, transporting energy, but not charge – is just a few **meV**, similar to the typical energy difference from a donor level to the conduction band, it will not live very long at room temperature: The thermal energy then is enough to ionize the exciton, i.e. to remove the electron (or the hole; your choice – everything is rather symmetrical), and we are left with a free hole and a free electron.

● Even so the electron and the hole are almost at the same place, recombination is *not* possible without the help of phonons, so it is rather unlikely – *as stated before*. Excitons in most semiconductors therefore only make their presence known at low temperatures – and in the absorption of light, because you will already find some absorption for light with an energy slightly below the band gap energy!

Now imagine an *isoelectronic dopant in GaP*, e.g. **N** instead of **P**. It distorts the potential for electrons a little bit *and strictly locally*; and in **GaP** this will lower the energy of the electrons *locally* – inside a radius similar to the lattice constant.

● An electron thus may become bound to the isoelectronic dopant – i.e. it "revolves" around the isoelectronic atom. It may now attract a hole by Coulomb interaction and thus form a **bound exciton**. This is an easy, albeit oversimplified way, to conceive bound excitons.

The net effect of a binding interaction of an isoelectronic dopant and an exciton is twofold:

● The exciton energy levels move "down" from the free exciton level by an amount equal to the binding energy of the electron to the isoelectronic dopant; i.e.  $E_b$  *increases*. In some cases – naturally for **GaP** – the additional binding energy may be in the order of **10 meV**, and this pushes the exciton levels so far below the conduction band that the bound exciton is now *relatively stable* at room temperature.

● The exciton is now *localized* in space. This demands that its coordinates in  $k$ -space must be somewhat undetermined thanks to the *uncertainty principle* which requires that

$$\Delta(\hbar \mathbf{k}) \cdot \Delta \mathbf{r} > \hbar$$

● With  $\hbar \mathbf{k}$  = *momentum*. Since  $\Delta \mathbf{r}$  is in the order of the length scale of the attractive potential, i.e., a *lattice constant*,  $\Delta \mathbf{k}$  will be in the order of  $a/(2\pi)$ , i.e., a *Brillouin zone width*.

● In other words, the *bound exciton* can have *any* wave vector in the **1st Brillouin zone** with a certain, not too small probability.

This has an important consequence: *Recombination for bound excitons is easy!* It is still an indirect recombination that needs a phonon as a third partner. But in contrast to indirect recombination between free electrons and holes, which needs a phonon with a precisely matched  $k$ -vector, *any* phonon will do in this case because it always matches one of the  $k$ -vectors from the spectrum accessible to the bound exciton.

● If bound excitons exist (at room temperature), their recombination provides a very efficient channel for establishing equilibrium and thus a possibility to generate light with an energy given by the exciton energy, i.e., the bandgap minus a small exciton binding energy.

● This is essentially the mechanism to extract light out of the *indirect* semiconductor **GaP**!

You should now have a lot of questions:

● Why **GaP**? How about other **III-V** compound semiconductors?

● How about more exotic semiconductors, e.g. the **II-VI** system or organic semiconductors?

● Anything similar for elemental semiconductors? After all, putting **Ge** into **Si** also changes the potential locally.

● How about other defects, not necessarily isoelectronic? For example, ionized donors and acceptors also attract and possibly "bind" free electrons or holes, respectively?

Well, this is not an advanced solid state lecture course. And even there, you may not find all the answers easily. Some answers I would have to look up, too; some, however, you can work out for yourself – at least sort of.

Of course, there is another question looming large by now: How is doping actually *done* – at least for the more common non-**Si** semiconductors out there? What are particular problems and limits?

● Again, answering these questions in any detail would far exceed what is possible to do during this lectures course.

● We will, however, touch upon the subject in various and any places in the course of the following chapters.