5.1.4 Wavelength Engineering

We will now try to find some answers to our [fifth question](#): How can we change the wavelength of the light produced by radiative recombination?

- This question is to be understood in the sense of "changes beyond just choosing from given materials having different band gaps".

- The recipe coming to mind is: Mix two similar (direct) compound semiconductors with different bandgaps.

- Luckily, most **III-V** compounds are completely miscible in ternary or even quaternary crystals.

- In other words: From the **2** compounds **GaAs** and **AlAs** we can make ternary $Ga_{1-x}Al_xAs$ for $0 \leq x \leq 1$, from **GaAs** and **InP** we can produce quaternary $Ga_{1-x}In_xAs_{1-y}P_y$.

This gives a lot of options. What happens upon mixing, which changes of properties are useful, and which are not? Are there guidelines or do we have to try it out?

- Generally, all properties of interest as given in a [table in subchapter 5.1.1](#) will change while x and y run through the accessible range, but not necessarily linearly (or even monotonously) with the composition.

- Here we focus on just a few of the especially important properties:

  - *Bandgap magnitude*
  - *Bandgap type* (direct or indirect)
  - *Lattice constant*
  - *Thermal expansion coefficient*

- The two last properties will be of overriding technical importance as soon as we learn how to make heterostructures, i.e., combinations of two different semiconductors.

There are some standard diagrams showing major properties of the most important combinations.

- The first and most important one shows the *bandgap vs. the lattice constant* plus information about the gap type. It is shown below, with the **II-VI** compounds included for good measure:
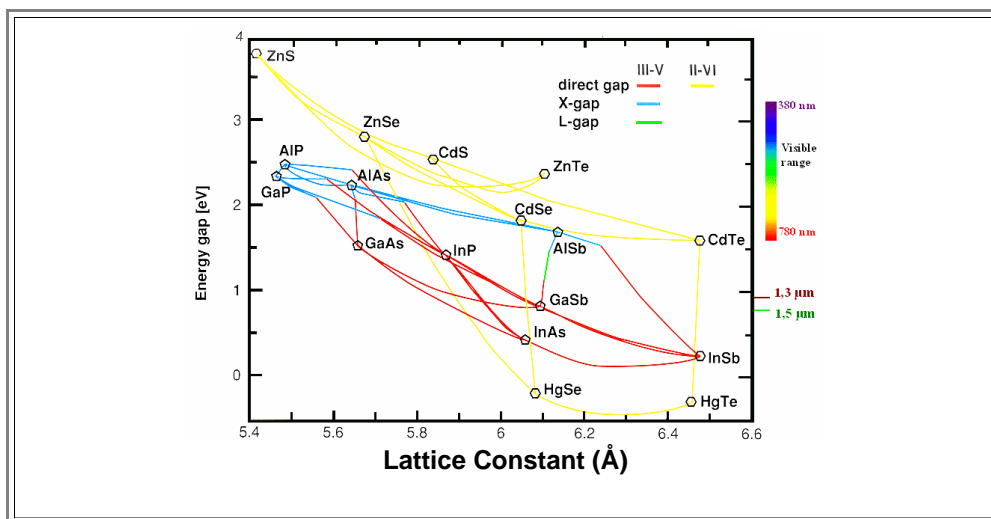

There is a tremendous amount of information in this diagram (note that "**X**-gap" and "**L**-gap" both denote *indirect* band gaps at the [respective positions in the band diagram](#)):

- Most **III-V** compounds radiate at wavelengths above the visible region, i.e., in the infrared. However, adding some **Al** to **GaAs**, producing $Al_xGa_{1-x}As$, will shift the wavelength into the red region of the spectrum – here are our red luminescence diodes and lasers!

- *Very fortunate*: **GaAs** and **AlAs** have almost the same lattice constant; we can thus combine (e.g., in a stack of layers) any mixtures of these materials without encountering mechanical stress.

- *Very unfortunate*: There are *no* **III-V** compounds in the diagram that emit *blue* light – which is a severe problem for many potential applications. While in the past, **SiC** could be used to some extent, it was only with the recent (early 1990s) advent of **GaN** that this problem was solved.

- **SiC** and **GaN** crystals, however, are not of the "[zinc-blende](#)" type common to all the **III-Vs** in the diagram but have a *hexagonal* unit cell. *They therefore do not easily mix with the others!* To grow **GaN** layers (bulk crystals can hardly be produced!) it is therefore favorable to use a hexagonal substrate as, e.g., **SiC**, Al_2O_3 (sapphire), or **Si(111)**, plus a special buffer layer.

- If we want to radiate at **1.3 μm** or **1.5 μm** – infrared wavelengths of prime importance for optical communications – we should work with combinations of **GaAs**, **InAs**, and **InP**.

- Most interesting: The **II-VI** compounds are *all* direct semiconductors and span a much larger range of wavelengths than the **III-V's**. The fact that they are not much used for products tells us that there must be big problems in utilizing these compounds for mass products (prominent exception: thin-film PV modules made of **CdTe**).

Here is another picture of the same thing including more materials:
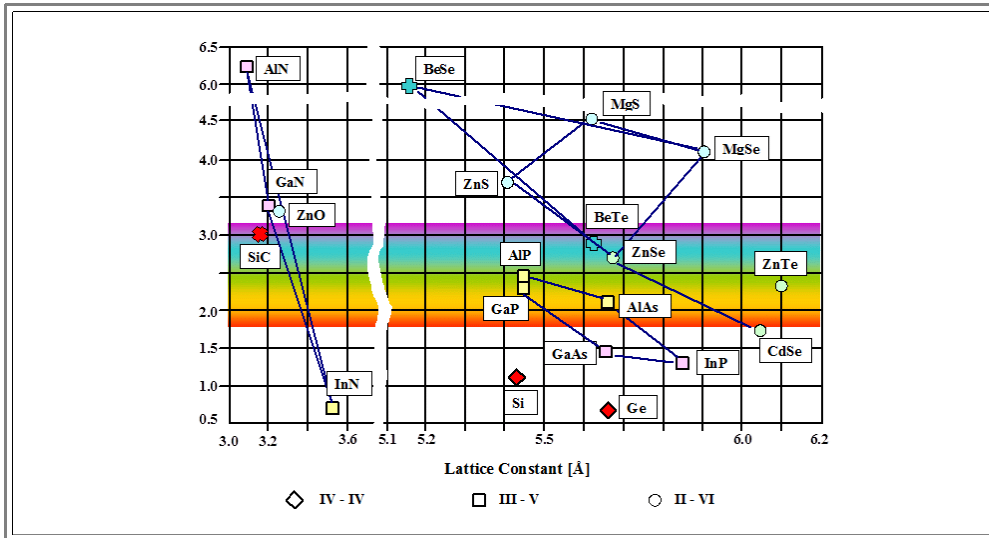
- In the left part, all hexagonal materials are shown; for them, the value of the in-plane lattice constant (i.e., the one perpendicular to the hexagonal axis) is used.

- The group-III nitrides **AlN**, **GaN**, and **InN** span an extremely wide range of band gap energies, thereby providing a plethora of design opportunities for devices. In the first two decades of the 21st century, there were a lot of activities in this field, and the development still goes on.

- The success in this field is mainly due to two basic achievements: First, to find out how *stable p-type doping* can be reached; second, to find out how the materials can be *grown with sufficient quality* regarding high purity and low defect density, especially dislocation density (that's one of the reasons the special buffer layer mentioned above is needed for).

- The first problem was overcome by Shuji Nakamura, the second one by him and by Isamu Akasaki and Hiroshi Amano. Together, they received the **2014 Nobel prize in physics**. The Nobel lecture given by Nakamura ("Background Story of the Invention of Efficient InGaN Blue-Light-Emitting Diodes") provides valuable insight into present-day semiconductor research and device development.

- **Zinc oxide** has already found many different applications, but only very few in the field of electronics. This is mainly hampered by the same difficulty originally also faced for the nitrides: Stable p-type doping is still a problem. Nevertheless, **ZnO**-related research and development in other fields of materials science is also very interesting; see, e.g., the relevant activities in the group of Prof. Adelung here at the TF.

- In addition, among the group-III nitrides there is also **BN**, showing some similarity to **carbon**: The most stable form is **graphitic boron nitride** (i.e., covalently bonded hexagonal layers kept together by van der Waals forces), whereas the cubic modification **c-BN** (having zinc-blende structure) is metastable, just like **diamond**. Graphitic BN has a band gap of 5.2 eV, it is mainly used as a lubricant (c-BN: 6.4 eV, used as abrasive).

Let us now look a bit more closely at some other properties for the technically more relevant systems.

- The following diagrams show the direct and indirect bandgap and the refractive index for **Ga$_{1-x}$Al$_x$As** as a function of **x**.
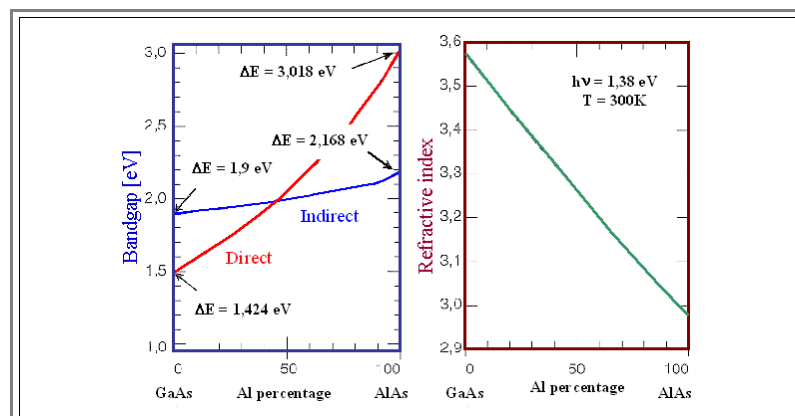
Mixing does not only affect the band gap and the lattice constant, but also the quantum efficiency of light production. The next figure shows the mixture **GaAs$_{1-y}$P$_y$**.

- The quantum efficiency decreases rapidly as the material approaches the indirect bandgap region.

● If an isoelectronic center – **N** in this case – is added, the **GaP** side obtains a strong radiative recombination channel via bound excitons and the quantum efficiency is two orders of magnitude larger.
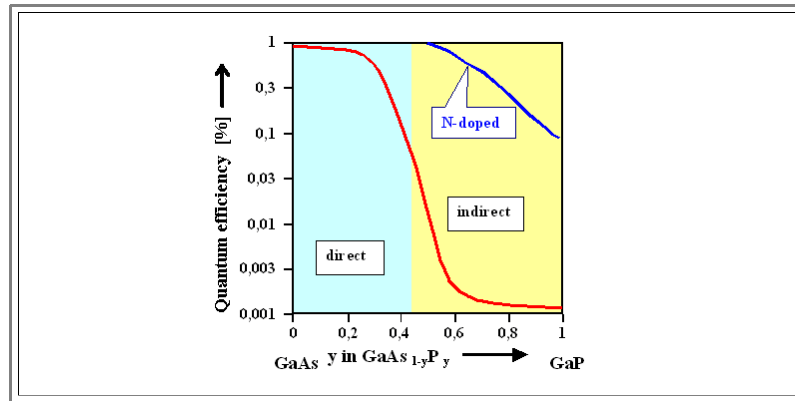
▽ Next the lattice parameters of various mixtures as a function of **x** are shown.

● This is easy to calculate; for complete mixing (no precipitation etc.), the lattice parameter changes linearly with the composition index **x** between the values for **x = 0** and **x = 1**.
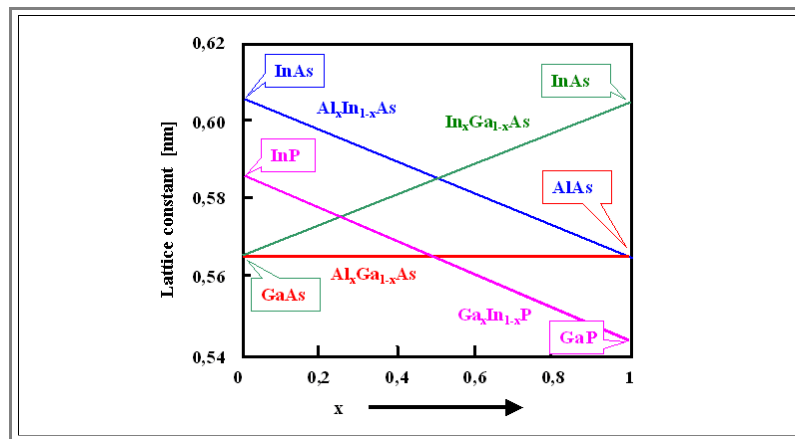
▽ Finally, the technically most important systems are listed together with some key properties:

● We see that all kinds of *ternary* and *quaternary* compounds are used, and that the *external* or total efficiency – the relation of light *out* to total power *in* – is relatively small in most cases. The external efficiency should not be confused with the quantum efficiency (relation of light *produced* to total power minus ohmic losses), since some of the light produced may never leave the device – remember the fourth question!

● Also remember that the total efficiency of a light bulb is just a few percent. The semiconductor values don't look so bad in this context, and that for **GaAs** we can get up to **30 %** in extreme cases (and beyond!) is encouraging. From that perspective, the blue emission efficiency of the group-III nitrides is beyond expectations. Note that the somewhat exotic exciton process can account for an efficiency of **15 %**!!

Material (Dopant)	Wavelength [nm]	Transition	External Efficiency [% of power]	Color
$Al_{0.60}Ga_{0.40}N$	265	band–band	2 - 10	UV
$In_{0.16}Ga_{0.84}N$	445	band–band	50 - 70	purple
SiC (Al, N)	480	defect-related (stacking fault?)	0.01 - 0.05	blue
GaP (N)	565	exciton	0.1 - 0.7	green-yellow
$GaAs_{0.15}P_{0.85}$ (N)	590	exciton	0.1 - 0.3	yellow-orange
$GaAs_{0.3}P_{0.7}$ (N)	630	exciton	0.4 - 0.6	orange-red

GaAs$_{0.6}$P$_{0.4}$	650	band–band	0.2 - 0.5	red
Ga$_{0.6}$Al$_{0.4}$P (N)	650	band–band	1 - 3	
GaP (ZnO)	690	exciton	4 - 15	
GaAs	870	band–band	0.1	infrared
GaAs (Zn)	900	band–acceptor	0.5 - 2	
GaAs (Si)	940	deep level	12 - 30	
In$_{0.73}$Ga$_{0.27}$As$_{0.58}$P$_{0.42}$	1310	band–band	1 - 2	
In$_{0.58}$Ga$_{0.42}$As$_{0.9}$P$_{0.1}$	1550	band–band		