Chapter 3

What is alloying?

To create a semiconductor with a specific lattice constant, effectively one must mix together different semiconductor components. This is called *alloying*.

For example, if we alloy AlAs and GaAs, depending on the ratios, one would get $Al_xGa_{1-x}As$, where x is the molar fraction.

What is a random alloy?

This is the chemical mix of two not-so random materials. Also 'random' due to the random probabilistic distribution of the type 3 constituents.

What is the virtual crystal approximation?

The VCA assumes that for an alloy such as $Al_xGa_{1-x}As$, one may treat the structural, electronic and optical properties as being due to a perfectly regular crystal, with As on the usual group V site and the group III site occupied by an imaginary (virtual) atom whose properties are a weighted average of those of Ga and Al, weighted according to the molar fraction x.

What is the expression for the potential due to the VCA?

$$U_{VCA}(r) = xU_{AlAs}(r) + (1 - x)U_{GaAs}(r)$$

What are the two requirements for the virtual crystal approximation to hold?

1. Based on the premise that the two constituent atoms are chemically similar. (Elements in the same group are chemically similar)

2. The material's structural and optoelectronic properties are based on an average across the material.

What is Vegard's law?

For alloy materials, they can be described to a good approximation using Vegard's law, once the VCA is valid.

If $P(x)$ is some property of the alloy as a function of molar fraction x, then $P(x)$ can be written as,

$$P(x) = xP(1) + (1 - x)P(2)$$

where $P(1)$ and $P(2)$ are the properties of the two constituent alloys.

Example:

The bandgap of $Al_xGa_{1-x}Al$ is described as:

$$E_g(Al_xGa_{1-x}As) = xE_g(AlAs) + (1-x)E_gGaAs$$

And similarly for the lattice constant:

$$a_{(Al_xGa_{1-x}As)} = xa_{(AlAs)} + (1-x)a_{GaAs}$$

What are the differences between direct and indirect bandgap semiconductors?

- Direct bandgap semiconductors are more efficient than indirect BG semiconductors for LEDs and laser diodes.

- For a direct BG, the minimum of the CB has the same k value (crystal momentum) as the valence band maxima. In an indirect BG, this is not the case.

- In a direct BG, the BG energy is lower than any other indirect BG.

- In an indirect BG, at least one of the indirect bandgaps is lower energy than the direct bandgap energy.

- Electrons congregate at the lowest E level possible, which leads to a predominant emission of light equal to that BG energy.

Give an explanation for the effect of 'bowing' for Vegard's law in reference to energy bandgap

Two effects associated with the bowing effect for energy bandgap:

1. *Intrinsic effects:* Even when the VCA is used in calculating the bandgap, many calculations find the bandgap violation is **not linear**. This is due to a number of effects, e.g. atomic electronegativity.

2. *Extrinsic effects:* In any finite volume of crystal there will be inherent statistical defects throughout the crystal leading to a different bandgap localised around a specific area. This causes local fluctuations of the measured value. If E_g is made over a small crystal volume, the measured E_g can have large deviation from $\langle E_g \rangle$.

Why do lattice spacings obey Vegard's law better than energy bandgap measurements?

In contrast to energy bandgap measurements, lattice spacings are measured using x-ray diffraction and are measured over a larger (macroscopic) volume. Therefore, measurements are less susceptible to error due to local deviations, etc.

Provide a description of quaternaries

These are alloys with more than 3 chemical constituents

Example: $In_{1-x}Ga_xAs_yP_{1-y}$

In and Ga in group III, As and P in group V.

The group III atoms will locate at the group III site, at a statistical probability of finding them at any particular site being either x or $1 - x$, respectively. The same can be said for the group V atoms.

Following the same logic as with the ternary molecules:

$$InAs = (1 - x)(y)$$

$$InP = (1 - x)(1 - y)$$

$$GaAs = (x)(y)$$

$$GaP = (x)(1 - y)$$

Hence, if $P(x, y)$ is some property of the quaternary alloy that is a function of x,y, it can be written:

$$P(x, y) = (x)(y)P(1, 1) + (1 - x)(y)P(0, 1) + (1 - y)(x)P(1, 0) + (1 - y)(1 - x)P(0, 0)$$

where $P(1, 1)$ is the property of the constituent alloy with $x, y = 1$.

Note: Having the ability to have 4 constituents allows one to tune both the bandgap and lattice constant, as required.