

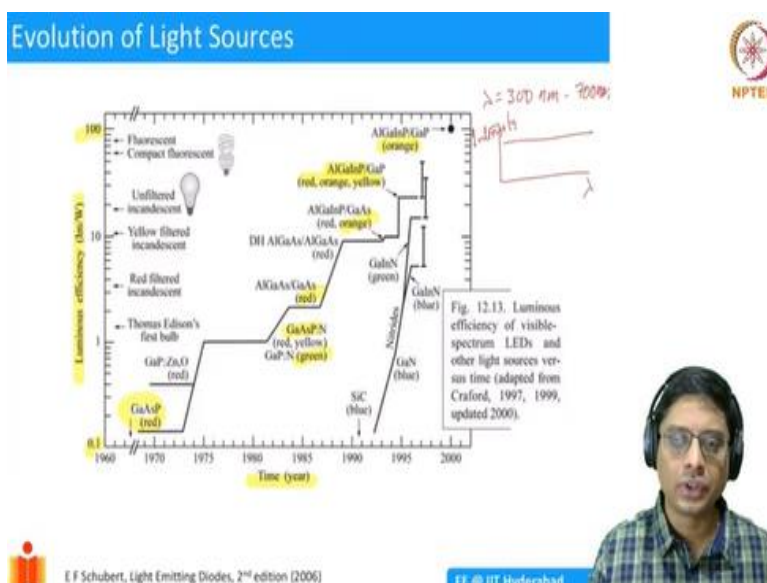
Introduction to Semiconductor Devices
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Lecture - 75
Materials for Optoelectronic Devices

This document is intended to accompany the lecture videos of the course “Introduction to Semiconductor Devices” offered by Dr. Naresh Emani on the NPTEL platform. It has been our effort to remove ambiguities and make the document readable. However, there may be some inadvertent errors. The reader is advised to refer to the original lecture video if he/she needs any clarification.

Hello everyone, welcome back. So, in this video we would like to talk about various optoelectronic materials. So, we have understood how the optical emission process happens. So, we would like to understand the materials in a slightly deeper fashion.

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So, to do that I want to start with this graph here this shows the evaluation of light sources over the last 50 to 60 years. So, here you are seeing time in the x axis and luminous efficiency in the y axis. So, essentially if you have a higher lumen per watt that means you have more efficient light source and its brighter source and if this is a logarithmic scale you are going from 0.1 to 100 lumen per watt.

So, what you see is the traditional you know the old incandescent bulbs the Edison's bulb and the incandescent lamp that you know it was used in 80s and 90s also actually. They are not very you know bright sources, but nowadays you know with in 2000s and 2010s in the last

decade you see that more and more CFLs and then LED lights are coming which are actually very bright.

So, on the logarithmic scale there is a significant improvement in the luminous efficiency. Also, if you look at the x-axis you know in the 1970s, we had red LEDs that were possible. The technology was just getting developed at that time and over time we started having various different materials and you see that the you know the efficiency is improving and also, we are moving towards you know green and orange and so on.

So, various combinations of lights are possible. So, if you look at the visible light you have the wavelength range of 300 nanometres to 700 nanometres. Let us say you want to simulate you want a light that simulates sunlight you want to have a white light. So, then you should have if you look at the spectrum of that you should have all the wavelengths possible. If I have let us say this is λ , this is intensity; ideal white light should be flat.

You have same intensity at all wavelengths but that is never going to be possible, even sun has a certain peak and then there is some variation in spectrum energy density. So, what we would like to do is you know have a source which emits at different wavelengths. But we already seen that for a particular material the band gap defines where the emission happens. So, is it possible to have a wide range of band caps in the same material?

Well, of course not we are not going to have that, so, we have to tune the band gap and that is essentially what is shown here, you see that in the beginning in about 80s you started introducing arsenic, this is a compound semiconductor. We have so far seen elemental semiconductors which are silicon germanium, we have seen gallium arsenide which is a compound semiconductor we call it a binary semiconductor binary compound semiconductor.

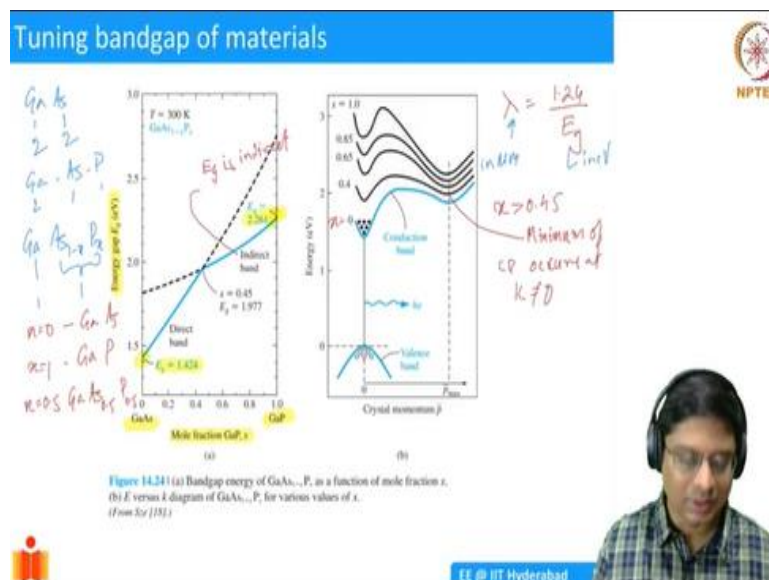
Because it has only two elements you could also have gallium arsenic phosphorus which is a tertiary compound semiconductor which has three elements or you could have quaternary compound semiconductor such as you aluminium indium gallium phosphide and so on. It will become clear why we want these structures in a short while. And the other important trend you see is that starting about 90s there is a very significant development of nitride semiconductors.

Starting with gallium nitride which actually has a band gap of 3.3 eV, so it can actually be tuned to give you emission in the blue spectrum and sometimes you know in the green spectrum. So, you can have this nitride which are giving you very strong emissions and they are significantly developing. So, a Nobel Prize was given for the invention of blue LED in the last you know in 2014, I believe.

So, there is a lot of improvement, so the trend over the last 50 years has been increase in the luminous efficiency and also various material combinations that are possible. So, we left the initial in uh you know gallium arsenide based devices and lot of different combinations are being used. So, you already understand why we need to go for compound semiconductors. Because silicon and germanium are indirect band gap semiconductors, they are not useful for light emission.

Because of that so, you need to have direct band gap semiconductors and the combinations this slide shows you various combinations that are used but to go back to the basic question, now what sort of band gap is good? What sort of band gap needs to be realized for a particular wavelength of emission?

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So, we know the relation between wavelength and band gap, so this is $\lambda = 1.24/E_g$ so this E_g is in eV and λ will be in micrometres. If you put λ in micrometres and E_g you will get, I mean for example a certain band gap let us, say 1 eV will give you a λ of 1.24 micrometres and so on. So, how do we change this how do you change the band gap?

Well, so far, we have only seen three materials germanium, silicon and gallium arsenide which have their characteristic band gap. Is it possible to get something in between and if so, how do we get that? And the way to do that is the approach is actually described in this slide. So, here on the left you see on the x axis we see mole fraction I will describe in a moment what mole fraction is, on the y axis you have energy gap.

So, we have two well-known materials which is the first one is gallium arsenide. Gallium arsenide has a band gap of 1.42eV, so I will put gallium arsenide at 1.42 eV, so here somewhere here E g of 1.42. You have gallium phosphide which is an indirect band gap semiconductor and which has a band gap of about 2.26 eV. So, I will take gallium phosphide I will put its band gap at 2.26 eV.

These are the common, these are the naturally occurring materials, I mean we can synthesize them and actually have a highly pure substrate with this. So, now what if I want to have a band gap in between them in between 1.42 and 2.26 is there a way to get it. It turns out that there is a way and the approach is actually to mix the semiconductors. How do we mix the semiconductors?

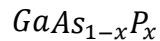
Well, what I can do is I can replace an arsenic atom with a phosphorous atom. If I do that, I will increase the band gap slightly but of course it never happens that you replace one atom you replace in a significant quantity. For example, if you take silicon, what is the atomic density of silicon? We saw that it was 5×10^{22} . Well, for gallium arsenide it might be something slightly higher than that but in the same order of 10^{22} .

So, now you replace about 0.5×10^{22} atoms and you remove 0.5×10^{22} arsenic atoms. And replace them with phosphorus, what do you expect? So, that process is known as you know mixing semiconductors and now the way we do that is let us say I have gallium and here you are having arsenic. I will take let me replace, for example you have gallium and arsenic. Let us say there are N atoms of gallium and N atoms of arsenic in your material.

But I mean you can think of this in terms of per unit volume. Now I will replace, let us say there are two arsenic atoms in the unit cell I will replace one arsenic atom with the phosphorus. So, what I will do is instead of N let me use 2. Let us say there are 2 atoms of gallium and 2

atoms of arsenic in a unit cell just for discussion purposes. So, now what I will do is? I will replace one arsenic atom with a phosphorus atom.

So, instead of this gallium will remain 2 but arsenic I will have one atom and phosphorus one atom. What did I do? Well, now I created a structure which has gallium and then arsenic $1 - x$ phosphorus x .



Where my x is a mole fraction, I call it you know if you sum up both $1 - x$ and x you get 1. So, this combination is going to be remain, 1 and this will be 1 anyway. So, the overall count of atoms is going to remain the same but some of the atoms you remove.

If in of course in a material you have huge number of unit cells. And in some of the unit cells you replace some of them you do not replace. So, essentially you can have a mole fraction which is changing from $x = 0$ to $x = 1$. So, what I can do is? If I make $x = 0$, what am I doing, well I am essentially having all arsenic atoms only so I have gallium arsenide. If $x = 1$ I am essentially having all phosphorus atoms, so it becomes gallium phosphide.

Now what if I do some combination what if I choose $x = 0.5$? If I do that gallium for every 2 gallium atoms there is 1 arsenic atom and 1 phosphorus atom that is what it means when I say mole fraction of gallium arsenic phosphorus 0.5 0.5 that means for every 2 atoms of gallium there is 1 arsenic atom and 1 phosphorus atom physically. So, why is this useful? Well, it turns out that we have seen already that band cap of gallium arsenide is 1.42.

On the other extreme you have gallium phosphate which has a band gap of 2.26. Now a combination of this as I change my mole fraction from 0 to 1 will have a band gap from 1.42 to 2.26. So, this is a very important, very interesting idea to generate various band gaps because naturally occurring you know good quality substrates are very limited. So, how do we overcome that? By this process.

What is actually happening in energy and diagram perspective well this is the E-k diagram. So, we know that gallium arsenide is a direct band gap semiconductor. So, the valence band maximum and the conduction band minimum will coincide. So, now if you excite you

somehow introduce electrons in the upper level and holes in to lower level they will recombine and give you a photon which is shown here.

Now this is at $x = 0$ and if I increase the mole fraction you know I increase x from 0 to let us say 0.2. What would happen? Or in this case 0.4 is shown. So, you have the valence band does not change so much but the conduction band changes in this fashion. So, there are two values one is this main value at , crystal momentum 0 and at some other point you have different k you have a different value.

So, now as you increase to 0.4 this gap is increasing, that is why the band gap is increasing. As x is increasing now if you cross $x = 0.5$ you know for x greater than 0.45 if you increase you know x beyond that what is happening is this peak is going much higher and then now the minimum of conduction band occurs at here at this point. The minimum of conduction band CV occurs at you know k not equal to 0, $k = 0$ is what we want because that is the direct band gap.

But now if you go for example take this 0.85 the peak is here but then the smaller peak in the lower peak is here. So, the band gap is going to be this minus this is going to be band gap and it is an indirect band gap not a direct band gap. Of course, there is always this direct band gap line which is there but finally the material the band gap we define is the minimum of the conduction band and the maximum of the valence band.

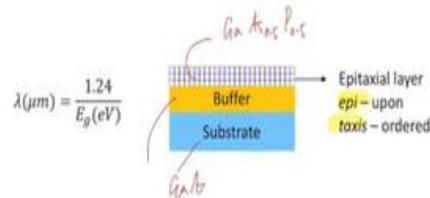
So, after this point here E_g is indirect below that it is a direct band capability conductor. So, this is how you can tune different tune materials to get various band gaps. It sounds quite simple, well conceptually it is simple but practically it is quite complicated.

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Substrates for optoelectronics



Important semiconductor substrates	
Silicon, Ge	Inexpensive, well-developed technology, up to 30 cm wafers
GaAs	Expensive relative to Si, but affordable, up to 12 cm wafers
InP	Expensive, up to 10 cm wafers, critical for optoelectronics and high-performance electronics
SiC, Al ₂ O ₃ , GaSb, etc.	Available in small pieces of a few square centimeters, very expensive



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And the way to understand that is; by this let us say these are various substrates for electronic devices. So, the reason I am discussing this is whenever you have semiconductor devices, we want very pure materials and large sizes. For example, silicon we can purify to 9n levels and then we can have wafers which are about 1 foot in diameter, 12 inches in diameter. And this is very well-developed technology it is relatively cheap nowadays.

So, silicon is easy and even germanium is actually available quite easily. It may not be the same diameter but you can get it quite cheaply. But gallium arsenide if you want gallium arsenide wafers are available but they are more expensive compared to silicon and also the diameter of the gallium arsenide wafer is much smaller. We can only typically get up to 4 inches in diameter that is about 12 centimetres.

So, if you have indium phosphide which is another commonly available substrate, this is even smaller diameter and it is much more expensive. But it turns out that indium phosphate is very useful for high performance electronics and optoelectronics. We cannot live without this so this is still used. These are some of the common substrates for semiconductors or optoelectronics.

In addition, there are various substrates like silicon carbide, aluminium oxide alumina basically. This is sapphire which is used for gallium nitride devices and gallium antimonite and so on. These are also available but you know you do not get large size crystals the crystals might be a few square centimetres. So, the whole reason why semiconductors became cheap is

that we are able to grow large crystals large and we can fabricate many, many devices at the same time.

The whole integrated circuits we can do. But if you have small substrates and you fabricate one or two devices it is not going to be economically viable. So, it turns out that there are these few substrates and if you want any other material for example gallium arsenic 0.5 and phosphorus 0.5 you cannot really make a substrate out of it. What we have to do is? We have to grow it on an existing substrate.

So, these are the three main substrates that we have and a few others. So, how do we grow them? The process we grow is called as Epitaxy, it is derived from the Greek word it is given here epi means upon and so on top of something, taxis means ordered. So, you maintain the same order same crystalline orientation that is what epitaxy means. So, an example would be, take a substrate you know.

I could take for example gallium arsenide, and then I grow a buffer layer this is for, growth reasons. Now you can just accept it some sort of combination, on top epitaxial layer I want gallium, arsenic 0.5, phosphorus 0.5. If I want that I need to have a small buffer layer and then I can grow this material. This sounds simple enough but in practice you need to satisfy a condition which is known as lattice matching to actually grow efficiently.

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The slide, titled "Lattice matching", illustrates the process of growing a thin layer on a substrate. It shows three scenarios: 1) Growth on a Si substrate, where a SiGe epitaxial layer is grown, leading to a lattice mismatch of 2.8% (10 nm). 2) Growth on a SiGe substrate, where a SiGe epitaxial layer is grown, leading to a lattice mismatch of 0.5%. 3) Growth on a Si substrate, where a Si epitaxial layer is grown, leading to a lattice mismatch of 0.5%. The diagrams show the atomic lattices of the substrate, epitaxial layer, and the resulting strained layer. A band diagram shows the conduction band (Ec) and valence band (Ev) for the SiGe layer. The NPTEL logo is in the top right. A video inset shows a speaker in the bottom right. Handwritten notes include "traps/defects" and "Ga As or P-As".

Image credit: Jasprit Singh, Electronic and Optoelectronic Properties of Semiconductor Structures, Cambridge (2003)

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So, this is a slide which is image which is taken from Jasprit Singh book I mean if you want you can go back and refer, but you do not need to do it for this course. So, what I am showing

you is three different scenarios. So, well you have an initial substrate this you know dots are representing the atoms and the lines are representing the bonds. So, you have a substrate and let's say your substrate is exactly having the same lattice constants as the material that you want to grow.

So, the same sizes right these two are, the one is dark and one is grey that is all. And if you grow them then you have what is known as perfectly lattice matched material. What we mean by that is? There is a same one to one correspondence between the substrate and the epitaxial layer. And this is really very hard to get if you have dissimilar materials. If I try to go grow gallium arsenide and gallium arsenide then I can get it.

If I try to grow silicon and silicon maybe I will get it. But if I want to grow germanium or silicon well it is not going to be perfectly lattice matched there are going to be some constraints. What are the constraints? Well, you know, let us say you want to grow silicon and silicon germanium, we saw that silicon germanium was used in the 90 and the 65 nanometre technology, in 2000 to 2003 time run two it was a five time frame, they introduced silicon germanium.

So, what we said was that is strain. How is the strain happening? Silicon germanium is going to have a slightly different lattice constant from silicon. So, you see that larger unit cell here. This is just a qualitative depiction it is by no means the actual physical thing it is much more complicated. So, this is a slightly larger unit cell and then you grow try to grow on this. What happens?

There is one possibility that is the lattice of the layer that you are growing tries to adjust itself to the lattice which is laying in the substrate. This is basically about 500 microns of wafer 500 micrometre wafer; it is a big bulk wafer. On top of it you are trying to grow a thin layer maybe 2 nanometres or 10 nanometres, it just depends you know what you want. And there is a whole procedure for this, it is called as molecular beam epitaxy.

It is quite detailed and we do not need to get into it in a technology course somebody might teach you that if you are interested you can learn by yourself. Well, what happens is? If you try to grow the silicon germanium on top of silicon you will see that on the x direction the lattice

has shrunk but in the y direction it has become stretched, so this is called a strain. We stretch it or compress it.

What happens if you do that? In the discussion, we said that it enhances the mobility and it can be used for example in the NMOS devices there was tensile strain applied and then in the PMOS devices compressive strain. If you do that the mobility was improved and that is how they managed to improve the drive currents in the 65 and 90 nanometre technologies. Something similar happens and you get a different material you are able to grow.

If you want to perfectly pure silicon germanium then you have to use entire substrate differently and if you try to grow very thick materials here invariably what happens is this will have some you know what we call as defects. What is that? Suppose if the strain is not happening, somehow the lattice configuration is such that let us say you are trying to grow gallium arsenide on silicon the lattice constants are completely different then it will not work.

What happens is? You have the substrate you have a epitaxy area you are trying to grow but instead of having one to one correspondence between the substrate and the epitaxial layer it will try to grow in whatever default you know its lowest energy state. So, it will try to maintain the same lattice constants. If that happens; you will see that some of the atoms are not bonded.

There is no one to one correspondence and some of them are stretched here like this. So, you can have a whole variety of defects that happen and because of that you see here that, now this is a picture again from the same book. So, you want to have a perfect neat you know lattice instead of that. Sometimes a particular lattice atom might be replaced by another atom which is called a substitutional impurity.

So, because of that the whole lattice around, it is distorted. Similarly, you can have an impurity in between the lattice sites. So, you saw that in a unit cell, the corners and those face centred and body centre and all that you have these atoms. Somehow a lattice atom goes and sits somewhere in between we call it as an interstitial impurity. So, that can happen or it can be an alien atom or it can be a same atom.

I mean it is just a whole lot of combination you can sometimes there might be a missing atom so, that is called as a vacancy. So, a how range of defects can occur and we do not like them.

The reason we do not like them is let us say you have a certain band gap, let us say this is your E_v and this is your E_c . If let us say there is a strap or this we call as traps or defects in the lattice.

If you have these defects they will end up as a level in between the energy band gap here. When you have energy levels in between the band gap then that will cause recombination. So, we are creating electrons and holes in the electron hole pairs and these electron hole pairs can recombine through the trap levels and because of that you can actually lose the functionality that you are trying to achieve.

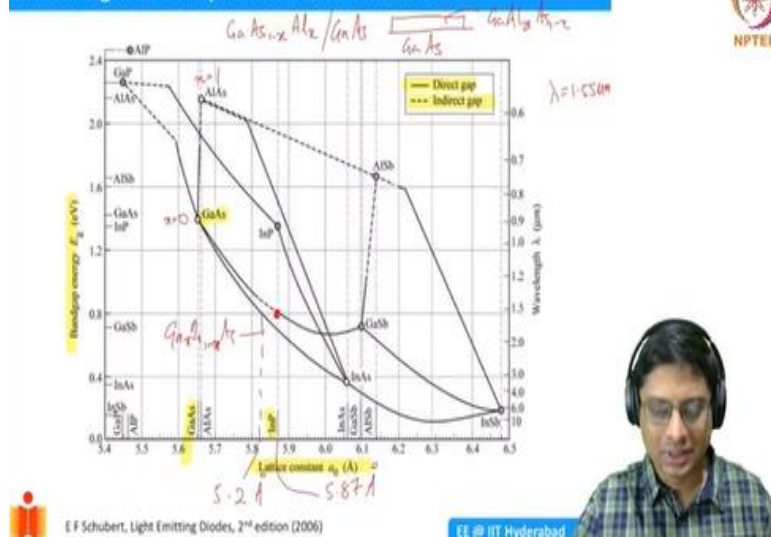
You already saw that recombination is proportional to the difference in energy inversely proportional rather if your energy difference is large then the recombination probability is small, same as generation just the inverse process. But now if you introduce a trap level you are actually having small, higher probability of this transition happening higher probability of this transition happening. So, the overall probability will increase.

So, this is a second order process but it is significant enough for us. And in optoelectronic devices it is absolutely you know undesirable because whenever electron recombines through this process it does not emit radiation that we like. It is emitting maybe it is just emitting as heat or it is emitting at a different wavelength which you still do not like. So, whenever you have defects in the lattice they sometimes show up as we call them colour centres, they give a different colour.

For example, if you have a defect in a sodium like sodium chloride lattice it will show up yellow and there are many, many things like that. Anyway, I am getting distracted, it is not necessary for right now. What I wanted to convey is? You have this lattice matching that is very important and this is not easy to achieve. You cannot arbitrarily grow any substrate, for example if I want I just today I dream that I want arsenic 0.35, phosphorus 0.65. Maybe I will grow it, maybe I will not be able to grow it, how do we decide that?

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Choosing the composition and substrate



Well to decide that we need to look at a diagram of lattice constant and energy band gap. This is the diagram that will help you to choose the composition of what we can achieve technologically. This is a very interesting diagram I like it very much because it explains the concept of lattice matching very well and you can spend a lot of time analysing this and you will automatically understand what is suitable.

So, in this picture you have the x axis as the lattice constant y axis is the band gap. So, now there are various materials on the x axis here gallium arsenide has a lattice constant of 5.65, indium phosphide has 5.85 angstroms and so on. Many different materials there are 6 to 7 materials here which have their lattice constants. And what are their band gaps? The band gaps are given in the dot here. So, for example gallium arsenide has a band gap of 1.42 eV.

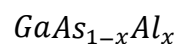
That the corresponding wavelength is given on the right side just the same the relation any way to convert. So, 1.42eV will correspond to 870 nanometres, 0.87 microns that is what you are seeing. Similarly, if you take indium phosphide, indium phosphide has a band gap of I think 1.34 eV and it has the emission around 920 nanometres so you see that. So, by looking at this you can analyse what are the band gaps and what are the wavelengths.

Another interesting thing is let us go back to the discussion we had about gallium arsenide and phosphorus that is the discussion we had initially. Let us go back so this was the combination, so we had gallium arsenide and gallium phosphide. Let us see what happens when you combine them. So, on this picture you have gallium arsenide here and gallium phosphide here.

So, when you combine them, you see that there is this line which is showing you that the band gap is increasing. And then aluminium arsenide it is going to gallium phosphate which is indirect band gap. So, this dashed line shows you indirect band gap and a direct band gap is a solid line. So, just as we; have explained in the using the band diagrams you have this line which is appearing.

Now can I grow that? For example, I want to grow this point you know gallium let us say arsenic x phosphorus 1 - x. We want to grow that; can we do that well it is going to be challenging the reason is there is no substrate available on which we can grow this material. On the x-axis you do not have a suitable substrate. So, how do we achieve emission in the red region of the spectrum?

Well, that is achieved if you come if you look at this particular line if you pay attention to this line. This is a combination of gallium arsenide and aluminium arsenide. Do not choose phosphorus, choose aluminium. So, what you should do is let us say this is to remove that so, instead of that instead I will say gallium arsenic 1 - x aluminium x,



I choose this combination. So, if I put $x = 0$, I get gallium arsenide, if I put $x = 1$, I get aluminium arsenide.

If I choose somewhere in between I get that different band gap. The interesting thing is gallium arsenide has 1.42 aluminium arsenide has 2.2 maybe 2.2 something 2.5 in between that you have this line. The beautiful thing is both of them have very close lattice constants. So, because of that there nearly straight line here and so it tells you that if I want to let us say grow this $x = 0$ to x equal to let us say maybe 0.5 or something here, you can grow it on top of a gallium arsenide substrate.

So, this has the same lattice constant as a gallium arsenide. So, I can grow this structure. By doing that you know basically I can take gallium arsenide wafer. On top of it I will choose this epitaxial layer of gallium aluminium x arsenic 1- x whatever you can do that. If you do that it is going to satisfy the lattice matching condition because they are in the same direction. So, whenever you have straight lines, you can grow those substrates; that is what we are looking for in this diagram.

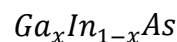
Let us take another example, let us say if you grow this essentially you get 700 nanometres light easily you can get. 700 to 800 nanometres you can tune it and you can grow various materials and we can get lasers and LEDs. Another wavelength of interest would be you know 1.55 microns. I told you that you know for telecommunications we use 1.55 microns wavelength.

And what is energy corresponding to that? Well, the 1.55 micron is here and this corresponds to 0.8 roughly 0.8 eV is a line. So, I want to grow this. What do I do? Well, when I look at this immediately it looks like you know I want to be on this substrate can I use indium phosphide. Indium phosphate looks to be a great material because it has the same lattice constant as the line that I want right vertical exactly on the same line.

But it turns out that indium phosphate's band gap is actually much higher, it is 1.34 or so on. So, we cannot use indium phosphide for if I am interested in any optoelectronic device at 1.55 micrometre. This is critical if you do not have it there is no internet because if you do not have it there is no fibre optics. You are sending this signal at 1.55 and you are laying fibres connecting continents and we are able to have instant communication.

So, this is so critical and you cannot use indium phosphide. So, the challenge for you is to think about what sort of combination can give for wavelength of 1.55 micrometres. So, the obvious choice seems to be you know the first choice seems to be, let me use this combination I will use a combination of gallium arsenide and indium arsenide. I will start replacing some arsenic, some gallium atoms with indium, can I get it?

Well, you can change the band gap it is beautiful. If you use this combination this is basically gallium x indium 1 - x arsenic.



So, you are having this sort of compound semiconductor tertiary semiconductor and it is always direct band gap. It is beautiful but the problem is at the substrate that at this point it is not having really the same lattice constant. So, if you want to use this material you could still try because you will if you grow it on indium phosphide you have to be somewhere here this one.

So, indium phosphates lattice constant is probably 5.87 angstroms and your gallium indium arsenates and its constant is going to be 5.2 angstroms. There is some amount of lattice matching. So, if you actually study this in greater detail, if you look at the mismatch you can try to predict how thick you can grow, that is for material science. So, it is possible to grow it and people have done it.

But it is still not ideal because there is we want to minimize this difference in the lattice matching. So, another option is to choose this particular point here on this line. But this is a very complicated thing because you have to use a whole combination of indium arsenide and antimonide and gallium arsenide and so on. So, if you try to go on this line you have to use maybe 4 compounds instead of 3 compounds.

And with that you can get a much better lattice matching with indium phosphide. So, this is challenging but scientists have done it with quaternary compounds they are able to help get very good emission at 1.55 micrometres. So, this is by no means simple I mean it is a very complicated process and I mentioned the Nobel Prize in for blue LED. The scientist was actually you know one of the scientists was Amano.

And he was actually a PhD student and he spent 5 years of his life also trying to develop the process and then later on after 10-20 years, he got a Nobel Prize for that. So, it is a very challenging work but scientists have figured it out and if you are interested of course, you can look at all the details later on. So, this is basically the quantitative picture. Now you could take another example, let us say I want to design a laser which has a wavelength of let us say 900 nanometres.

What do I do? You think about it 920 nanometres also you think about what can be done. Or rather you know I will leave it to your imagination 820 nanometres maybe something close to that. So, think about it and analyse this stop the slide here and spend a lot of time. The reference this is taken from this reference book again Schubert's book so you can go and refer to this and you will find a lot of material on LEDs and lasers in this book.

So, with that I would like to stop the discussion in this video. So, we looked at the various materials or material aspects of the optoelectronic devices. So, I will stop and then in the next

video we will talk about the LEDs the electrical aspects of it. Thank you so much, see you later,
bye.