Optoelectronic Materials and Devices
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Module - 3
Optoelectronic Device Physics
Lecture - 24
Optoelectronic Materials and Bandgap Engineering

In the last lecture we discussed various recombination and generation processes in a semiconductor. We also saw how generation processes are basically dependent on the electronic structure of the material. In this lecture we will discuss electronic structure of different materials and if we want how to change it? So, this is a more material specific lecture and we can discuss various topics in this lecture.

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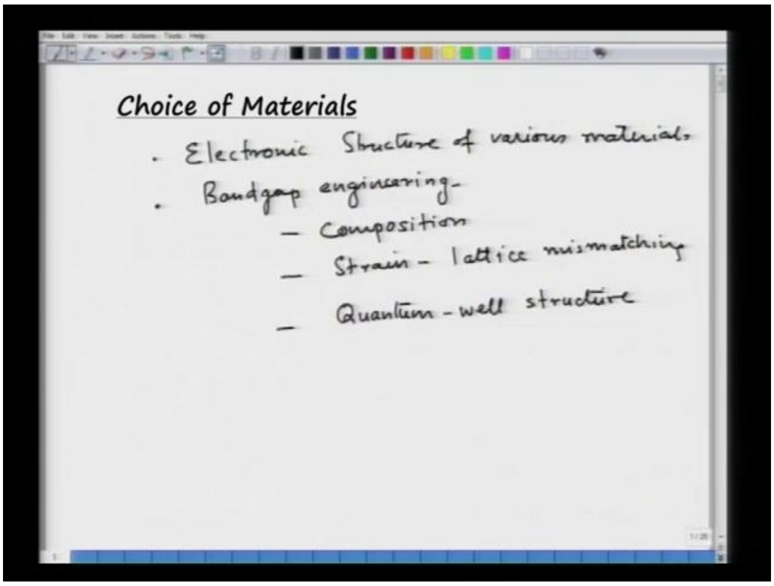

Choice of Materials

- Electronic Structure of various materials
- Bandgap engineering
  - Composition
  - Strain - lattice mismatching
  - Quantum-well structure
  -

Basically, related to materials choice and based on our last lecture we know that, any semiconductor can be used for devices which require light absorption, except that the structure of the device may be effected, whether it is a direct bandgap or indirect bandgap. But when we are looking for light emission, it is extremely important to know which semiconductor to use, because the light emission that we saw last time is at the bandgap energy. So, if I have a material which has the bandgap energy equivalent to the red light, then I will get only red emission. Hence, it is important to know how to choose my material or engineer my material, so that I can get different light emission from the material.

So, today’s lecture will cover basically materials choice, discussion on electronic structure of various materials. We will further have discussion on how to change the bandgap? One technique in this is to change the composition of 3 5 materials. So, composition is one way of changing bandgap, the other one would be through strain or lattice mismatching. Yet another technique that is available to here to us for changing bandgap is quantum well structure. To start our discussion we will talk about three five semiconductors so if we want to make a light emitting device of course,, the material of our choice is a direct bandgap semiconductor.

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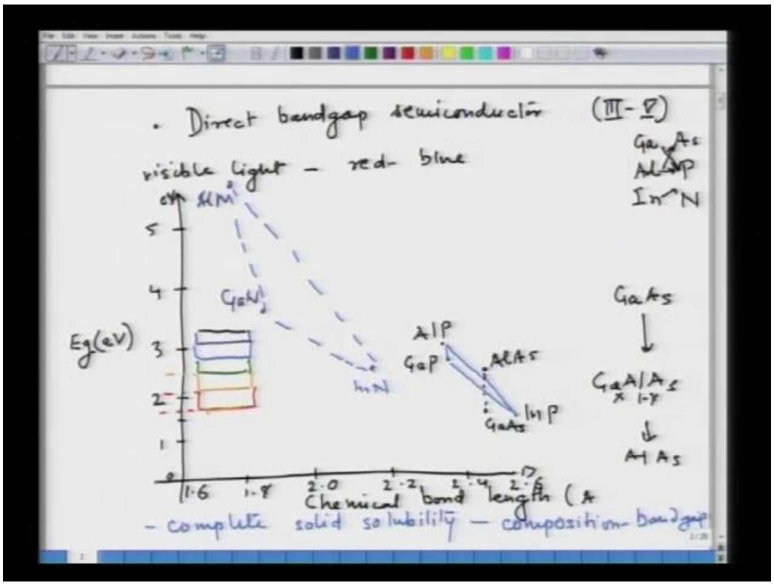

3 5 semiconductors are the ideal system for this material. Now, to before I continue our discussion, I would like to make sure we are on the same page. So, if I am looking to make to make an optical device, obviously I am talking about only visible light, because our eyes are only sensitive to the visible light. Hence, we are talking about visible light which is basically going from red to blue, the energy range in which we are talking about. If we go from 0 to bandgap of something like 7 e V the visible range.

So, this is the bandgap of the material, this is given in electron volts, the range of energy that we are talking about is which comes in the visible range is going to be from about above 1.5 e V to about 3.4 e V. So, this here is about red color, then we have yellow and we have green blue and violet. So, basically what this means is that if I want to make light emitting diode, which is an emitting in the red, then I need to have a semiconductor which has bandgap in this range. Similarly, for the other colors, if I want to make a diode which is yellow, then I must have bandgap in the yellow range and so on so forth.

If we look at the 3 5 semiconductors, they are extremely interesting system. If I plot their structure as a function of chemical bond length, which is given in angstrom, so the chemical bond length goes all the way from 1.6 to 2.6 for these systems. We have basically 3 5, which are arsenic based. So, gallium arsenide in the fifth, in the fifth group we have option of phosphor arsenide and nitride in the third group. We have the option option of gallium aluminum and indium, so we can do the mixing and matching in any of these combinations and that gives us our us the 3 5 system.

So, in this 3 5 system the, the first system which was used for making LED or gallium arsenide and if we look at the gallium arsenide, gallium arsenide has the the devalue closer to to this. It it gives emission in in red red or yellow gallium arsenide aluminum arsenide. It is a very interesting system, if you one looks at it all the way going from gallium arsenide to aluminum arsenide. Although, we are changing the aluminum to gallium atom the lattice parameter of this particular material does not change. This is a very good thing for device point of view which means, I can always make change the make a combination and make a material which is going to be gallium aluminum aluminum arsenide in a certain composition, when gallium is x and aluminum is 1 minus x.

So, I can go from all composition from gallium arsenide to aluminum arsenide and x will change over here x is 100 percent and here it is 0 percent. By changing this composition, I change the emission from this material all the way from being infrared to red region. So, it is a one full material for that and for the lattice matching, it has a very good lattice matching as we will see later. The lattice matching is going to be important for the material, it can change the bandgap of the material, if the material is not lattice matched. Let us look at the phosphide systems; the phosphide systems are slightly higher here. You have aluminum phosphide, it comes somewhere close to the green range and we have indium phosphide and gallium phosphide.

So, if I try to cover this triangle, what I have is once again the lattice parameter here is changing between 2.3 to 2.5, but the color that you can get from this system is all the way from blue to red. The another interesting thing about the 3 5 compound is that they have complete solid solubility in each other, which means I can change as I was describing in case of gallium arsenide. I can change the composition of gallium atom, all the way from 0 to 100 percent and get a new material and a new color. 3 5 system have this flexibility in the case of phosphide. We are able to get colors up to green and all the and red in gallium phosphide systems.

The nitride systems are a bit difficult, because they are of higher energy indium nitride is somewhere here and gallium nitride is above 3.4, aluminum nitride is even higher than 5 around 6. So, this triangle is for nitride system, so again in the 3 5 system, this is indium nitride. But as you can see the nitride systems are take care of the visible light in the upper lower higher energy or lower wave length. So, if we want to make blue LED's, we will like to go with the three nitride systems, but the problem with nitride system is obvious that there is a huge change in the lattice parameter. That creates a problems in create making good materials, because of this strain that come in, but this signifies the beauty of the 3 5 system, which have complete solubility.

Hence, they allow you to change composition and which changes the bandgap or the material in turn that you can get different color devices. Now, all although we talked about changing the bandgap of the material, it is not always necessary. That the 3 5 semiconductor is direct bandgap for all its composition gallium arsenide definitely is direct bandgap. The reason for that is that for different composition material may be different, for example in the case of gallium arsenide.

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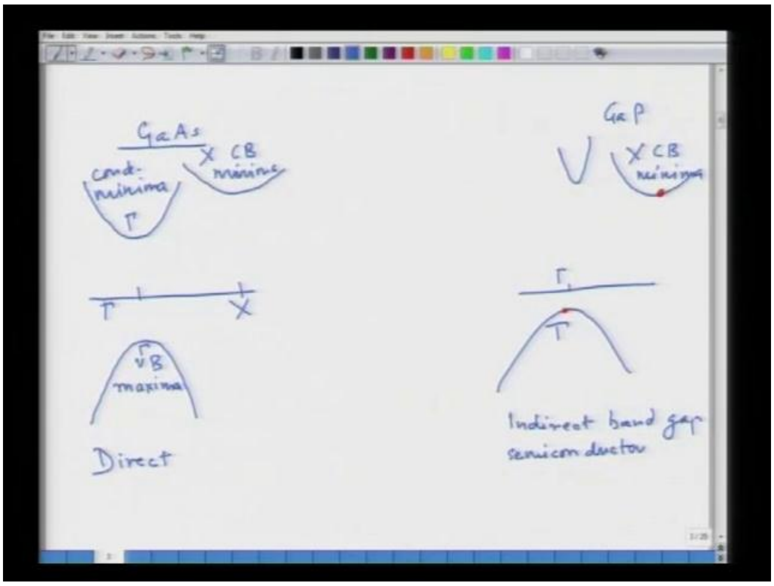

If you look at the electronic structure of gallium arsenide and look at the reciprocal high symmetry points, which are the tau and the chi, then what we find is that the for the valence band maxima, it occurs at the tau point. That is the valence band maxima in the gallium arsenide, which is the direct bandgap semiconductor. The conduction band minima also occurs at the tau point.

This is a conduction band minima and as we discussed, then this is a direct bandgap semiconductor, because the the minimum of the conduction band and the maximum of the valence band aligned. Hence, you have a very good probability for radiative emission and this is a wonderful material for light emitting devices, but we also have another minima at x point, which is also in conduction band. This is another conduction band minima and in some materials, which are variant of gallium arsenide this minima takes over and the material becomes indirect.

So, if we look at gallium phosphide, this is an indirect bandgap material and basically it has similar band structure. Only thing is that now with with change in from arsenic to phosphorus, what we find is the the x conduction band minima is the lower value while the maxima remains at tau. So, basically what we have is a situation where we have the minima of the conduction band and the maxima of the valence band do not meet at the same crystal momentum value. This is then becomes a indirect bandgap semiconductor.

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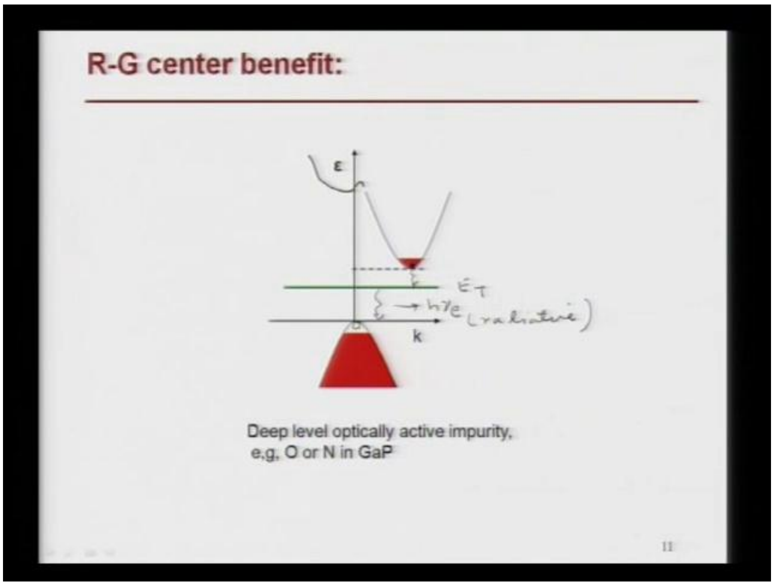

R-G center benefit:

Deep level optically active impurity,
e.g, O or N in GaP

But there are certain exceptions some indirect bandgap semiconductors, which are not good for general light emission can emit light through R G process. We will see an example, they can give radiative emission through a R D center. So, in general it is not good to have R D center recombination. Since, it is non radiative in nature, but in case of indirect semiconductors, it can help and can give sometimes radiative emission. Then let us look at another way of trying to recombine R G centers.

This is an example of the indirect semiconductor in which this is this electron is not able to recombine with the electron here for the reason, because the k the crystal momentum is very different. In order to compensate, that as we saw earlier you need to have a interaction with the phonon, but if we have a R G center, which is at some level E T. Then this electron can easily interact with the R G center and give you emission that would be in radiative. This is a case in case of an example is gallium phosphide material where oxygen and nitrogen impurities the R G center. They create can be used for changing an indirect semiconductor to a radiative semiconductor through this R G center. So, R G centers in general are bad, but sometimes they can be useful.

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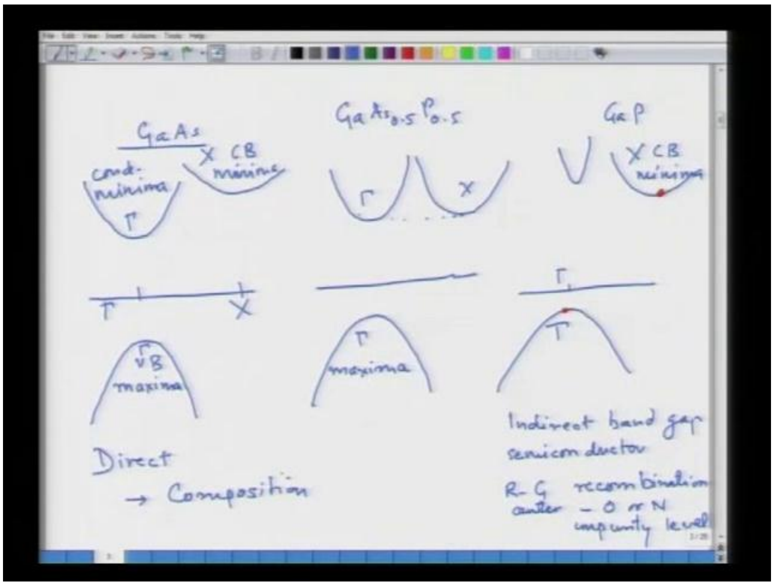

Position of gallium arsenide 0.5 and phosphide 0.5, which is in between the two composition for arsenic and phosphor. At that point there is a crossover, it starts it stays direct all the way up to point about 0.5. Then it becomes a indirect bandgap at the point of the crossover, we basically have a situation where you have the maximum of the valence band and the minimum of the conduction band. So, at this point, the conduction band minima are same for both tau and x point. Below this composition the material is direct bandgap and above this composition the material is indirect bandgap.

We as we have seen through some recombination process, we can sometimes even use the indirect bandgap semiconductor to get the light. So, this is one way of trying to change the emission one way of changing bandgap is the composition. 3 5 semiconductors are wonderful to allow this, because they have complete solid solubility in each other. So, you can change composition and go from all the way to 100 percent gallium to 100 percent indium or 100 percent aluminum change the bandgap and as well as the lattice parameter. Now, what are the other ways in which we can we can change the bandgap? The very important way that works is the lattice matching problem lattice matching or strain.

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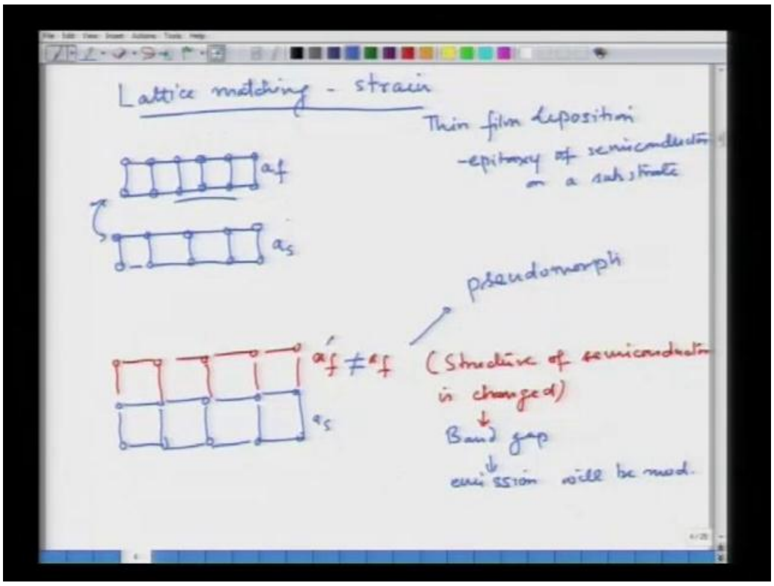

Lattice matching - strain

Thin film deposition
-epitaxy of semiconductor
on a substrate

pseudomorph

(Structure of semiconductor is changed)
↓
Band gap
↓
emission will be mod.

Now, as we have seen in earlier lectures that the the the lattice structure of that the material is important to decide, what would be the electronic structure? So, if I have a way or means by which I can change the lattice parameters, which means that I can change its electronic structure as well. This also has implications toward, how I process my semiconductor? Because when these semiconductor materials are deposited, they are actually deposited by using some thin film technology, thin film deposition technology, in which I do epitaxy epitaxy of the semiconducting material on on a substrate. Epitaxy basically needs growth of a single crystal on a substrate in this process depending on, how my material is going to lattice match with the substrate?

My material may have a different structure, it introduces strains in the material. So, in this process if I assume that the semiconducting material, which I am depositing has a lattice structure. I am drawing only a two dimensional lattice here. This is a semiconducting material, which I am going to use for emission. This is the active material and then I have a substrate which has a lattice parameter, which is slightly larger than than the semiconductor. Now, the lattice parameter for the material, let us say this is the film that I have is a f and this is a substrate which is a s. When I try to deposit this material on top of my substrate the atoms where they are going to match with the substrate are at a different length.

As a result what happens is, when I deposit this material I have two options; one is that the material joins without any change and if that happens I will have a structure. My films has to go on top of this substrate and it would try to take the shape of the of the substrate. So, this is a new parameter in which I have deposited my semiconductor on the substrate. Now, a f is not the same as a f prime is not the same as a f and which basically means that I have changed the structure of my material. If I change the structure, it is obvious that the bandgap will change. Hence, the emission will be modified.

So, one way of changing the band structure or the bandgap of the of the semiconductor is also to strain the material. The way the we process our semiconductor, it it can develop into structures, which are not its equilibrium structure, which are slightly strained. This particular film is under tensile stress and because of that a new structure is developed which is also referred as pseudomorph. This is a pseudomorph and it has a new bandgap and by this technique, we can change what kind of emission we are getting from our material? The other side of this process is that I I am going to have a substrate.

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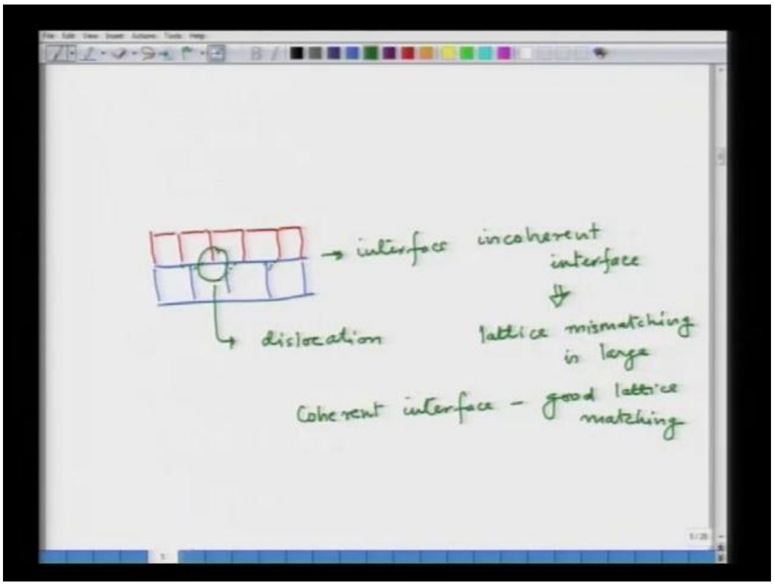

But the material that is deposited on it does not change its original crystal structure. In other words, there is no matching of the atomic rows in this structure. In this case, it normally ends up giving you defects like dislocations. This kind of interfere which is created between the semiconductor and the substrate is called an incoherent interface and the earlier is is is called the coherent interface. Between incoherent interface, this would happen only when the lattice mismatching is high and the coherent interface requires good lattice matching.

So, this is another way of creating strain material by that we create pseudomorph, which have different electronic structure and which have different in which has different bandgap. Will I mean different light and that is one way of changing doing the bandgap engineering. The next technique that is used to change the electronic structure of the material is quantum wells.

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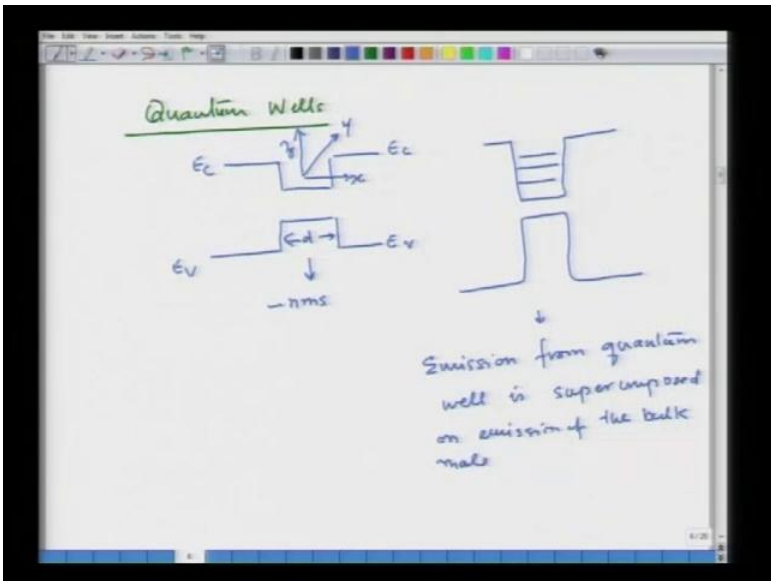

Emission from quantum well is superimposed on emission of the bulk mate

Quantum wells is again another technique, which is possible because of thin film processing. It is possible for us to sandwich one material between two different kind of materials of a different bandgap and that allows us to create structures, which will have a completely different electronic structure. So, what we are talking about here is we have a material which is going to be large bandgap. Then we make another material which is going to be low bandgap we are using the picture of the the band bandgap structure where large bandgap material is sandwich, sandwiching a low bandgap material.

Now, the emission properties of this particular material are going to be just like the bulk material as long as this thickness is large. But as we reduce this thickness in the range of nanometers, the property of this particular material becomes completely different. Then we have a situation in which in the x direction, the electron is confined in a well, but in the y and z direction, it is free to move. As a result that the y and z directional electronic structure does not change, but in the x direction, the electronic structure will get quantized.

Then it will introduce electronic states, which are quantized in the x direction and that change the emission of the light. Now, quantum well the quantum structure gets the quantum emission from quantum well is superimposed on emission of the bulk material. So, far what we have discussed is that we can change the bandgap of the material.

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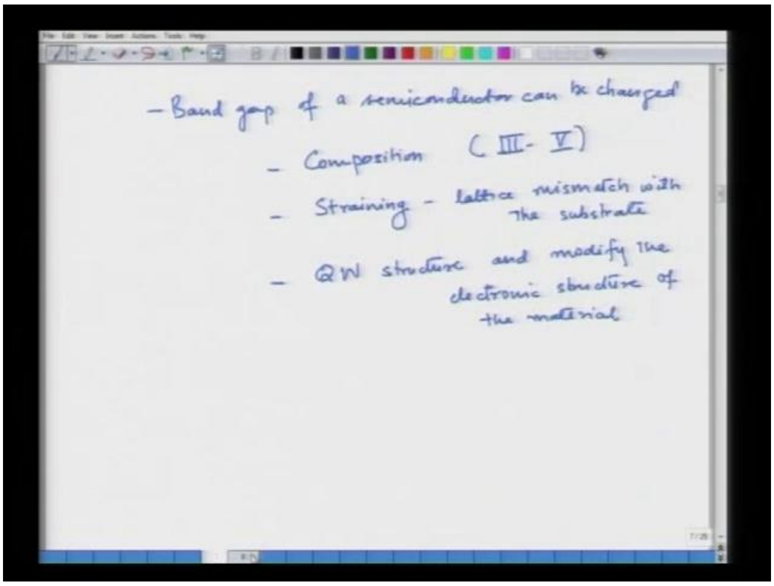

- Band gap of a semiconductor can be changed
  - Composition (III- V)
  - Straining - lattice mismatch with the substrate
  - QW structure and modify the electronic structure of the material

Bandgap of a semiconductor can be changed using different needs via changing its composition. 3 5 semiconductors provide the entire composition range. For this we can change its structure by straining. The material and this is possible in lattice; lattice mismatch with the substrate. Finally, we can create quantum well structures and modify the electronic structure of the material. If we look at materials for devices which require absorption of light, then things are completely different.

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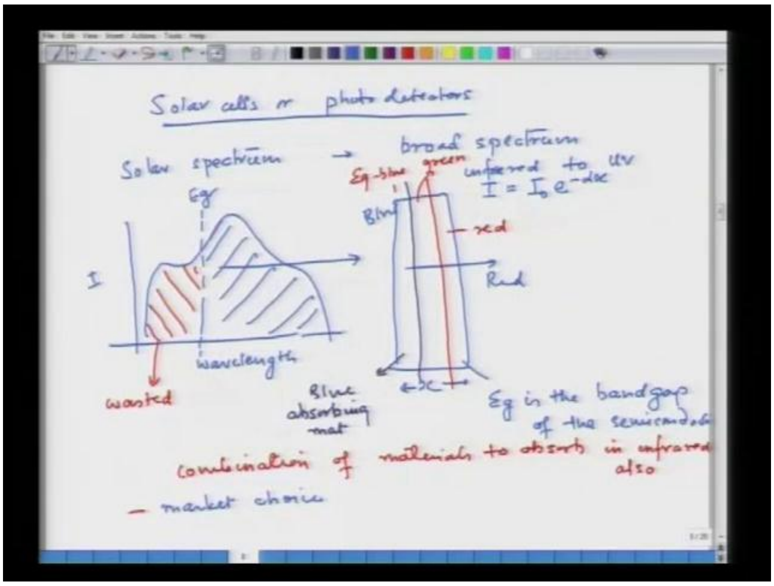

For example, we are talking about solar cells or photo detectors here, our aim is different. For example, in case of solar cell, we have a spectrum of solar spectrum which is a very broad spectrum all the way from infrared to UV. In order to absorb all of, all this light, if we plot intensity versus wave length and this is the the spectrum of light coming in and the device, and the material that we have of some thickness x material is going to absorb. This light only to the extent that for the light for which its E g is higher. So, the light which is going to be the solar light, which will be absorbed by this material is going to be only the amount, which is higher than the bandgap of the semiconductor.

So, E g is the bandgap of the semiconductor. Now, this is the problem here what we have is a situation where this amount of light is not absorbed. This is this is wasted. So, the choice here is to choose materials, which will absorb infrared visible as well as light which might be hidden in the UV region. Hence, we need to use materials which are going to have bandgaps need combination of materials to absorb in infrared also with the blue light also. There is a problem; the problem occurs because the amount of absorption in this slab as discussed earlier, is basically decided by the exponential. As we go towards higher energy, then the the most of the light gets absorbed in the near the surface, because the absorption coefficients are high. It it gets absorbed near the surface the light, which is of lower energy continues to go deeper in the material.

So, the blue light gets absorbed at the surface and the red light gets absorbed deeper in the bulk. As as a result what we want is we want a material, which is absorbing in the blue at the in front of the device. So, this should be a blue absorbing material, then something in between and so the first layer should be E g in blue, the second layer the e g should be in green and the third layer should be more red. This may be absorbed more, most portion of the solar cell. Now, which what would be the choice of materials in this case?

The choice here is mostly not that dictated by the bandgap, it is more of a market choice. Although, silicon in the terms of this absorption does not absorb most of the the solar light, but it is the easily and least costly material to make solar cell with. That is why people use silicon, but if we take some 3 5 compounds and make triple junction solar cells in which we use three different materials, we will be able to capture most of the solar light in this device. That will give us better efficiency. Similar thing is going to be true for photo detectors.

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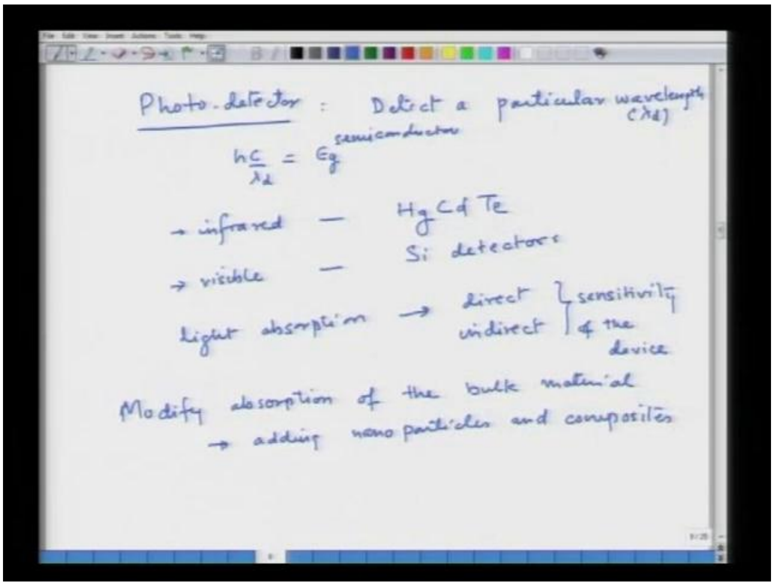

Photo-detector : Detect a particular wavelength (λ_d)

$$h\frac{c}{\lambda_d} = E_g^{\text{semiconductor}}$$

→ infrared — HgCdTe

→ visible — Si detectors

Light absorption → direct / indirect } sensitivity of the device

Modify absorption of the bulk material

→ adding nano particles and composites

For photo detectors, the application is basically to detect a particular light and whichever wave length you want to detect that wave length should have for detection. There should be equivalent to the E g of the semiconductor. So, once again the the problem is of materials choice, so if I want to detect infrared silicon is not the choice material. I will go for chalcogenides like mercury cadmium telluride. If I want to detect visible light which is higher than 1.1 e V, then I can go for silicon detectors.

Now, for the case of detectors again availability of a, the current after the after the light is absorbed in the material depends on whether it is direct bandgap or indirect bandgap? This will basically decide the sensitivity of the device and in order to improve the sensitivity earlier, the same bulk material that we had, we use to use that for making the devices. But now it is possible to change the material absorption properties. We can modify the absorption of a bulk material and that would, could be done by adding nano particles.

So, so far we have discussed various ways of modifying the electronic structure of the semiconductor, which can modify our properties. For different devices, we can get different specifications required only thing in this discussion. We have only focused on the optical properties and when we want a device to work, the electrical properties are also important. Hence, there is an optimization, because when we use all these modification normally the electrical properties take a hit. In order to make good devices we need to optimize both of them.

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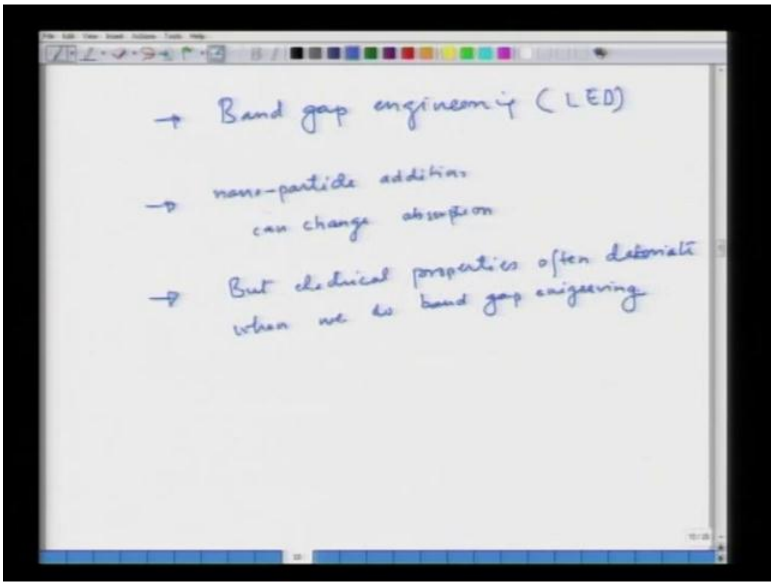

→ Band gap engineering (LED)

→ nano-particle addition
can change absorption

→ But electrical properties often deteriorate
when we do band gap engineering

Earlier we discussed the requirement for light emitting diodes and we talked about the bandgap engineering. Later we looked at how addition of nano particles can change the absorption behavior of materials? But point to remember here is that, while we are focusing on the optical properties electrical properties, often often deteriorate when we do bandgap engineering. Hence, there is a optimum that needs to be obtained in order to change the electronic structure of the of the device, without changing its electrical properties and modifying its optical properties.

So, optical properties and electrical properties are often are often against each other and you can have an improved absorption, but then it gives you very poor mobility of the carriers. Hence, the device will not work very well, so these two properties have to be optimized in order to get a good device. At the end of this lecture, I would like to look at various materials and and their bandgaps, and the their electronic structures has been discussed.

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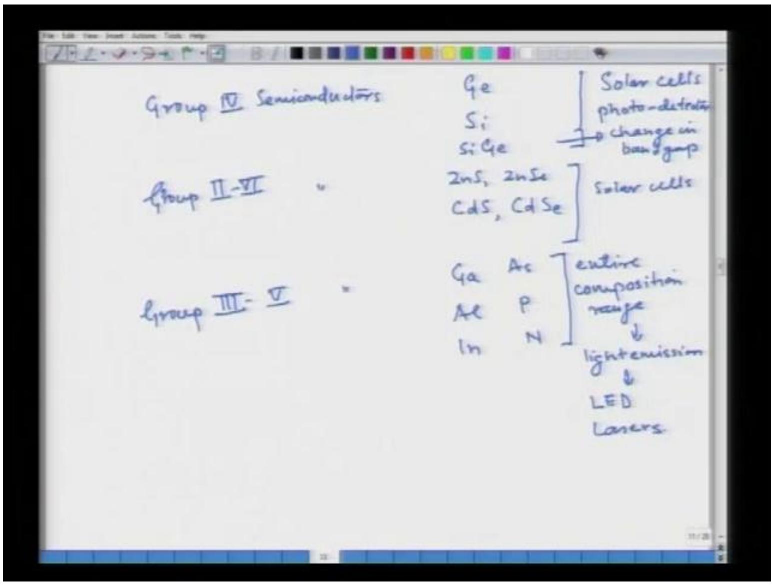

Group IV Semiconductors
Ge
Si
SiGe
Solar cells
photo-detecto
→ change in bandgap

Group II-VI "
ZnS, ZnSe
CdS, CdSe
Solar cells

Group III-V "
Ga As
Al P
In N
entire composition range
↓
light emission
↓
LED
Lasers

So, if we if we have if we take group four semiconductors, the most common one is germanium silicon. Then we have group 2 6 say semiconductor in which we have zinc sulfide, zinc selenide, cadmium sulfide, cadmium selenide, these are good materials for solar cells photo detectors. One also uses strain layer silicon germanium to change to have the change in bandgap. The 2 6 semiconductors are chalcogenides are also good materials for solar cells. Then we have group 3 5 materials, which are basically gallium aluminum, indium, arsenic, phosphide, nitrogen combination of these material. The entire composition range these are good material for light emission and light emitting diodes, and lasers.

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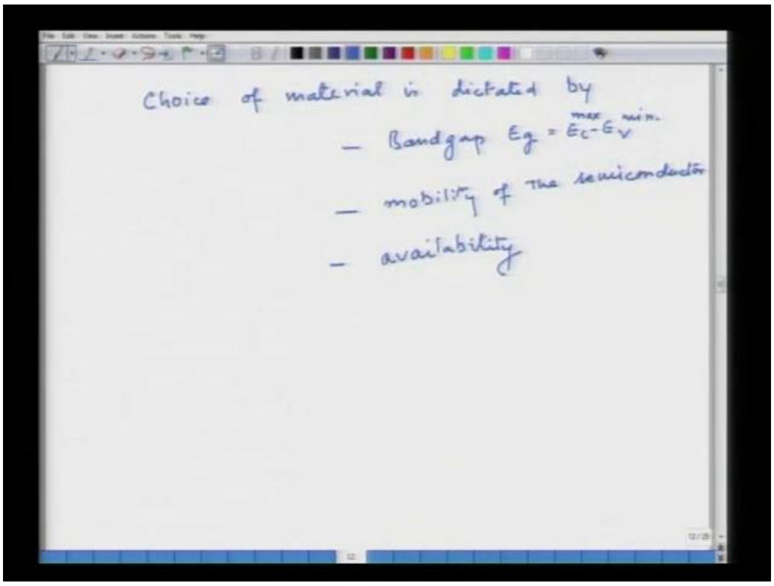

Choice of material is dictated by

- Bandgap $E_g = E_c^{max} - E_v^{min.}$
- mobility of the semiconductor
- availability

The choice for material is dictated by its electronics structure the bandgap E g, which is basically the difference between the conduction band and the valence band conduction band maxima, and the valence band minima. The choice of material also dictated by how electrical properties are dependent the mobility? Most important that becomes for various devices it is it is availability and this is reason for the popularity of silicon. Although, silicon is being indirect bandgap, it is a still more popular for many applications, because availability of silicon it is cheaper to obtain and use as well. With this I would like to summarize what we have covered in this lecture.

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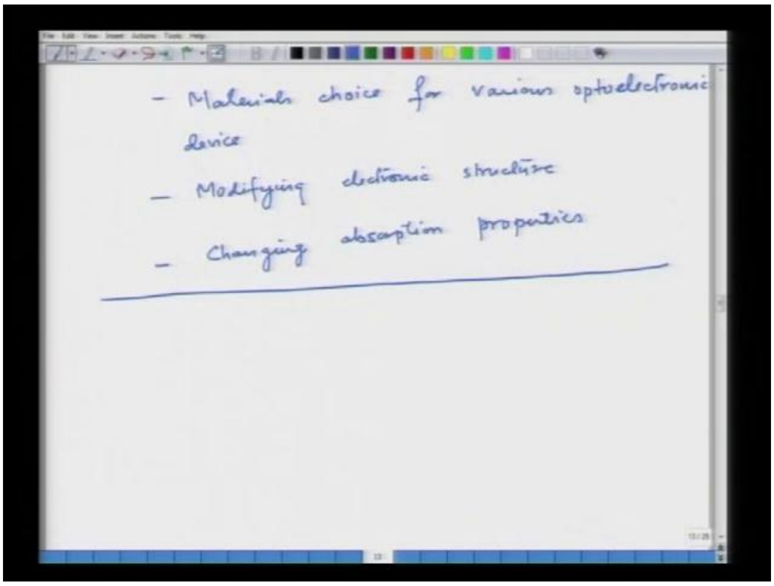

- Materials choice for various optoelectronic device
- Modifying electronic structure
- Changing absorption properties

We have looked at materials choice for various devices. We have looked at ways of modifying electronic structure and ways of changing absorption properties.