Non-conventional Energy Resources

Prof. Prathap Haridoss
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

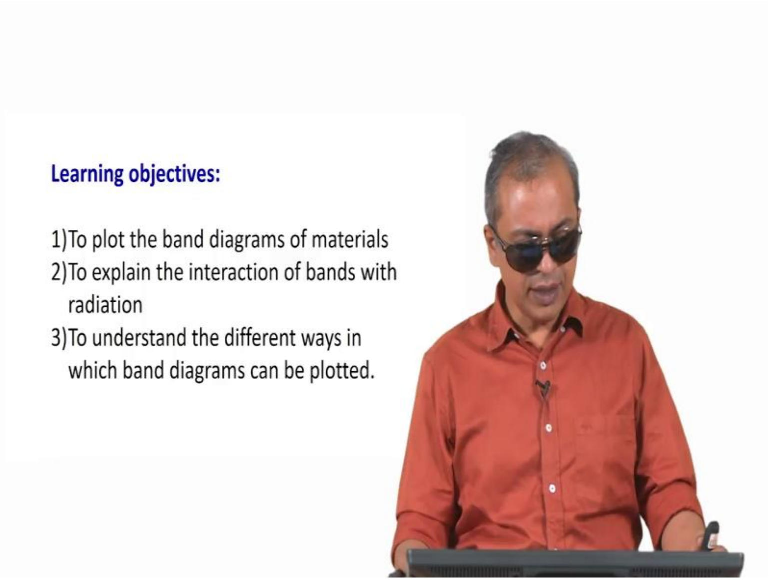
Lecture – 13
Solar Energy: The Semiconductor

Hello. In this class and in the next few classes we are going to look at the process of capturing solar energy using the photovoltaic approach. We have previously looked at how you can capture solar energy using the thermal approach where basically you are trying to concentrate the heat that comes from the sun and capture it in some kind of a heat transfer fluid and then use that for some application. Here it could either just be hot water at your home or it could be for running some turbines to generate electricity. So, we looked at you know the flat plate collector, we looked at the concentrators both the dish as well as the trough and that and that entire process we looked at we also looked at the possibility of using a solar tower and also the idea of a non imaging concentrator.

So, all of these things we looked at. We will now look in the next several classes on the possibility and how we go about capturing a solar energy directly in the form of electricity or in other words you capture it in a way such that the process creates electricity directly. You don’t need to use a turbine in the middle, you don’t need to generate steam and then run a turbine and then generate electricity you can directly get electricity.

So, that process is referred to as the solar photovoltaic process as opposed to the other process which we previously saw in the last two classes which was the solar thermal process. So, this is the solar photovoltaic process and central to the solar photovoltaic process is the use of a material which is a basically the type of material is the semiconductor. So, in this class we will look at the semiconductor and particularly we will see some of the basics of the semiconductor and some various aspects associated with it how it can you know be used and then build on those basics in the subsequent classes.

(Refer Slide Time: 02:08)



Learning objectives:

1)To plot the band diagrams of materials
2)To explain the interaction of bands with radiation
3)To understand the different ways in which band diagrams can be plotted.

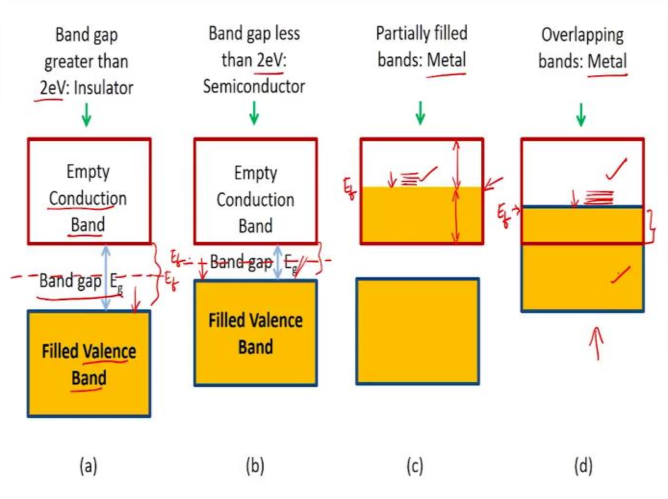
So, the learning objectives for this class are to plot the band diagrams for materials and particularly this is of interest because you want to get a good feel for how the different materials compare with each other with respect to their band diagrams and why a semiconductor is therefore, of interest to us okay. So, therefore, we will start by looking at by plotting the band diagrams of materials so that will be a learning objective for this class and we will then look at the interaction of these bands with any incoming radiation. So, we have band structure in the material and then there is incoming radiation.

So, there is going to be an interaction and through this interaction some energy gets absorbed and so that’s a process that we would like to get a better feel for. So, we will look at and try to explain the interaction of the bands with the radiation that is incident on the material.

And we will also look at in this class the different ways in which band diagrams can be plotted. This is very important because we traditionally through school and in fact, through most of college there is certain standard way in which band diagrams are plotted that most of us are familiar with. But when you look at the science of the material in much greater detail you will recognize that if you especially if you have say a physics background and you are looking at these materials in greater detail you will learn that there are there are different ways in which the band diagram can be plotted and some of those processes some of those approaches actually have a lot more detail in lot more information about the material in the band diagram. And therefore, the diagram that you are used to is actually an approximation and that's the point that I will try to highlight the diagram that you are used to is not necessarily wrong it is just that it's an approximation and therefore, it is not having some very important detail in it which is relevant from the perspective of application for capturing solar energy as in the form of a photovoltaic, cell capturing the solar energy.

So, since it is missing that information it is important to see how that diagram comes about and what is that additional information that is available in the diagram which is then being approximated by the kind of diagrams that you are familiar with? So so, these are the 3 learning objectives for this class and so we will go over this as we progress through the class.

(Refer Slide Time: 04:21)



So, in this slide you see the various types of materials that you are most often familiar with we have insulators, we have semiconductors and we have metals. So, these are at least from the perspective of electrical properties these are the 3 broad classes of materials that we are familiar with insulators, semiconductors and metals. So, if you look at it essentially from the perspective of a band diagram and again this is the kind of band diagram that we are more familiar with we are used to from high school days there is a valence band and there is a conduction band.

And so we typically explain the material properties using these two bands the valence band and the conduction band and it is at least when you look at insulators and semiconductors we talk of a filled valence band and then empty conduction band. So, this is the way in which we look at it and then there is a important parameter here called the band gap which you see here band gap band gap E g. So, there is a band gap there E g and that is a forbidden energy gap where there are no allowed energy levels for the electrons. So, electrons can either be in the valence band or they can be in the conduction band and typically in an insulator or a semiconductor especially if it's in a pure state, at 0 Kelvin this is the situation you will find where all the electrons are sitting in the valence band and the valence band is full and the conduction band is completely empty. So, this is how you will see.

So, the real difference between the insulator and the semiconductor is actually in the value of this band gap E g. So, if you see here I have put here if the band gap is less than two electron volts it gets referred to as a semi conductor and if it is greater than 2 electron volts it gets referred to as an insulator. Now, this is not a very hard and fast rule, but this is a guideline which is used. So, just for easy reference we are referring to roughly about two electron volts as being the cutoff if it is around 2 electron volts or less the band gap would be referred to as a semi conductor if it is more than 2 electron volts you refer to it as an insulator.

Metals on the other hand have a very different band structure here also you can think of various bands being present in the material, but the important thing is that in in a metal there is a half filled band. So, you can see here this band is partially full. So, within this band itself you have empty states and within the same band you have full states, filled states. So, within the same band you have both filled states as well as empty states or in this case which you see here on in this diagram here you have a band that is full this one and a band that is empty, but they are overlapping they are overlapping over a range of energies okay. So, you either have a, you either have an empty band and a full band that are overlapping. So, there is no band gap it is band gap is essentially I mean 0 in this case in fact, less than 0 if you want to just look at the idea that it's overlapping, but or in other case where in this case where the band is half full. So, that is what you are looking at out here.

So, the main difference is that since you have these there is no gap there is no forbidden gap that is just above the highest occupied level of electrons here, that’s the highest occupied level of electrons in a metal and there is no forbidden gap immediately above it. So, you still have continuous energy levels that electrons can occupy on both cases both sides both possibilities.

So, this is very critical to the behavior that the metals display, that there is no gap and therefore, the electrons which are on the top of this level are able to occupy energy levels that are immediately above them very easily okay. As opposed to semiconductors and insulators where if you look at the top most occupied level which is sitting here or here in this case immediately above the topmost level there are there is a forbidden gap and that gap is relatively large, it’s a fairly large gap that you see here right several electron volts is what you are looking at. Whereas, here you have virtually nothing in the metal you have virtually no gap it is a continuous set of energy levels that are there just above the highest occupied energy level that is the reason why metals behave very differently from semiconductors and insulators because these electrons have immediately available energy levels and so they are able to do certain things which semiconducting which electrons in semiconductors and in insulators are unable to do because they do not have that freedom of seeing those energy levels just badly above their highest occupied level.

So, this is the sort of the band structure of these materials that you see. Incidentally I kept referring to the highest occupied energy level in a metal at 0 Kelvin they give it a name it is called the Fermi energy level. So, this is E f the Fermi energy level, E subscript f Fermi energy level it is the highest occupied energy level for by electrons in a metal at 0 Kelvin and so here again would be E f. So, E f is there in these two cases I have just indicated the E f the highest occupied energy level in both these cases for a metal is the Fermi energy level.

In the case of semiconductors especially and insulators especially what are referred to as intrinsic semiconductors and we will talk about them in just a moment intrinsic semiconductor simply means it is pure, it does not have any impurities in it that have been deliberately added it is not a doped semiconductor it is a pure semiconductor. So, in those conditions you can still define something called a Fermi energy level and that definition is necessary because it helps us figure out certain other behavior of the materials which I will talk about in just a moment. But for insulators as well as for pure semiconductors which is the two band diagrams that I am showing you the Fermi energy level is exactly halfway between the top of the valence band and the bottom of the conduction band. So, if you can imagine energy level here and here. So, that would be the Fermi energy level for semiconductor and another Fermi energy level for the insulator that I have showed you.

So, of course, it is by definition it is like this and as you can see it is actually sitting in the forbidden energy gap. So, actually at that instant there is not going to be an electron sitting at that position, but that is how it is defined the Fermi energy level is defined there and in the middle of the gap. So, there is a variation in the definition for the Fermi energy level for metals and metals as well as the definition that is used for semiconductors and insulators. So, this is just something that you keep in mind we will use it later.

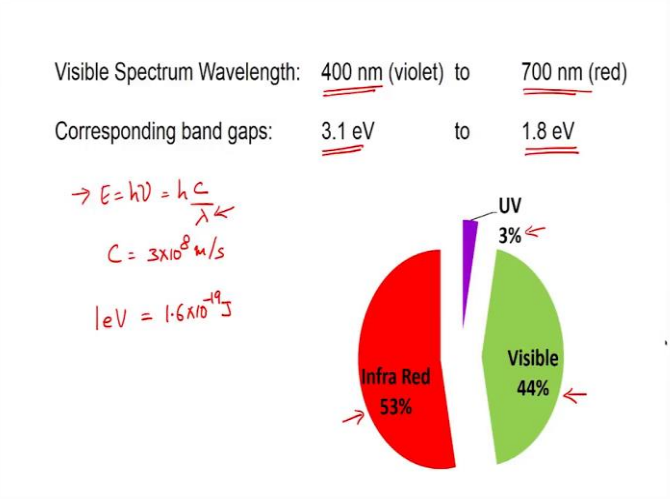
The Fermi energy level is actually very important when we look at all these materials because that is the electrons which are sitting close to the Fermi energy level are the electrons that interact with anything okay. So, when you put two materials together even when you make two materials come in contact it is the electrons that are sitting at the Fermi energy level that decide the behavior of the contact that is formed when those two materials come together and therefore, that energy level is important to at least know to know where is that energy level and then figure out what is going to happen when two materials come in contact it decides which direction electrons will flow from one material to the other when you put two dissimilar materials in contact.

In many ways you can think of it as the chemical potential of electrons if in thermodynamics they will talk of chemical potential of any you know species in a in a phase which basically is the amount of energy that is required to add a small delta extra of that material to that phase and essentially it represents the energy level of that that component in that phase. And therefore, when two know samples with the same component available at two different chemical potentials come together wherever it is at higher chemical potential it will start flowing into the other material okay. So, that is how diffusion occurs. Normally, we say you know something at high concentration comes in contact with something at low concentration if you put them in contact from high concentration the species will go to, the sample which higher where it is there in low concentration that’s our general deferred general way in which we describe it.

But concentration does not completely capture the detail of what is the driving force for the process. So, in some cases concentration works perfectly fine, but in many cases the correct term to use is a chemical potential if you are not familiar with it you can look up some thermodynamics book, but the idea is the same in some examples the chemical potential will be the concentration in some other examples chemical potential may have additional detail which will not be fully captured by the concentration. But the basic idea being if your concentration is different it flows same way chemical potential is different species flows and the Fermi energy is the chemical potential for electrons. So, if you say Fermi energy is high in a material then it’s the electrons are holding at higher energy in that material Fermi energy is low in another material it’s at a lower level when they come in contact the electrons will flow from wherever it is in high energy to wherever it is in low energy okay.

So, that is the reason why this Fermi energy is of importance to be aware of and to follow as you look at various materials. So, anyway, so this is the background for these materials and we will try to understand a little look a little bit more and how these materials will interact with radiation.

(Refer Slide Time: 14:18)



Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)

Corresponding band gaps: 3.1 eV to 1.8 eV

$\rightarrow E = h\nu = h\frac{c}{\lambda} \leftarrow$

$c = 3 \times 10^8$ m/s

$1 eV = 1.6 \times 10^{-19}$ J

So, if you look at the spectrum the spectrum that comes to us from the sun then we have some parameters that are of interest for us to see. So, the wavelength range for the visible spectrum is about 400 nanometers which is the violet end of the range to 700 nanometers which is the red end of the range. So, so this is in microns this is 0.4 microns to about 0.7 microns and you can ascribe an energy to it. So, you simply have to do E equals h nu and that is the same as h c by lambda this lambda is the wavelength that I am just referring to here on your screen you have the wavelength put down there and c is simply speed of light which is 3 into 10 power 8 meters per second. So, once and h is the Planck's constant. So, you can look up the Planck's constant. So, once you know the Planck's constant and you know the speed of light, if you know the wavelength of the radiation. So, its 400 nanometer, we convert it to, so 400 into 10 power minus 9 meters if you use that and you use this formula you will get the energy corresponding to it.

That energy will be in Joules I see I have shown I am showing you here energy in electron volts. So, that again is a simple conversion 1 electron volt is the amount of energy that is required to move 1 electron across 1 volt and an electron has a charge that is 1.6 into 10 power minus 19 coulombs. So, when you take 1.6 into 10 to power minus 19 coulombs and move it across a volt then the work done is simply 1.6 into 10 power minus 19 Joules. So, an electron volt is 1.6 into 10 power minus 19 Joules.

So, whatever energy you get when you do E equals h nu if you get it in Joules you can convert it to electron volts if you have a value in electron volts you can convert it to Joules. So, for example, I am showing you here band gaps of 3.1 electron volts and 1.8 electron volts you simply multiply that by 1.6 into 10 power minus 19 you will get this value same values in Joules. So, we just use the value that is convenient the value that is used in the literature often and so with that we work.

So, the corresponding band gaps for the visible range of the spectrum is 1.8 electron volts if you are talking of red end of the spectrum. So, red and red end of the spectrum is typically longer wavelength which is why you see 700 nanometers here. So, the longer the wavelength as you can see since the wavelength is in the denominator the energy is going to be less right. So, energy is inversely related to the wavelength. So, the longer the wavelength the energy is going to be less. So, 700 nanometers is 1.8 electron volts 400 nanometers which is a shorter wavelength gives you higher energy 3.1 electron volts this is the visible range of the spectrum.

Now, the energy that comes from the sun has ultraviolet rays it has the visible spectrum and it has infrared range of the spectrum. So, if you actually look at the total energy coming from the sun you see here a small pi chart here that tells you how it is distributed across all these different wavelengths. So, you see about 3 percent of the radiation comes as ultraviolet radiation 3 percent of the energy comes as ultraviolet radiation, 44 percent of the energy comes as visible part of the spectrum and 53 percent comes in the infrared. So, this is marked in red the visible spectrum, I simply marked in green just to follow it easily, but anyway. So, this is the way in which we get the spectrum.

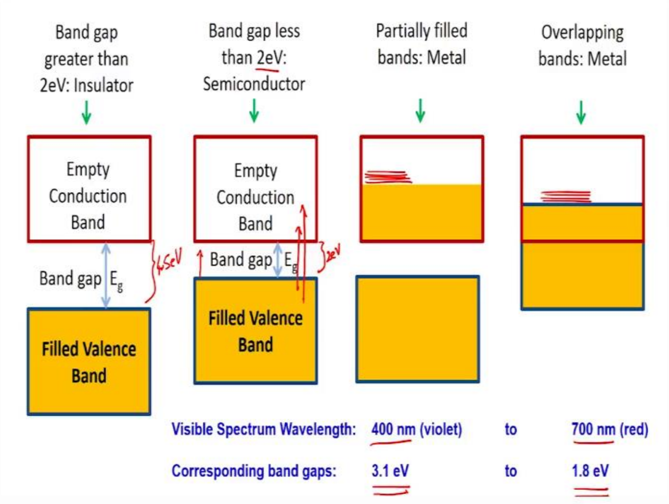
So, we keep thinking of the visible spectrum often you know when we see sunlight we look and think of the, you know light that comes from the sun that is actually just the visible part of the spectrum which is what our eye is sensitive to see and this is able to see. But you can actually see here more than just over half the energy that comes from the sun actually comes in the infrared part of the spectrum.

So in fact, when you design systems to capture solar energy this is a very important piece of information and that is the reason why we might need to know all this information in detail. So, when you design a system to capture solar energy it is important to see how best you can go about trying to capture the infrared as well. So, that you capture all the energy that is coming from the sun. So, it ideally you would like to capture all of this the infrared the visible and the ultraviolet. If you had to make a compromise I guess ultraviolet is only 3 percent of the energy. So, maybe if that’s a compromise that you have to do then that is something that you can accept, but generally it helps to capture as much of this as possible. There may be restrictions which may prevent you from capturing all of it we saw in fact, in the flat plate collectors and concentrators where we were looking at the thermal part of the spectrum we ended up actually doing more in the visible and ultraviolet we didn’t capture as much of the infrared.

So, some other you know engineering limitations may come implementation limitations may come and it is always interesting to actually see if there is a way to overcome those limitations so that you can actually capture the entire range of the spectrum. But in any case this is of interest to be aware of that this is the range of spectrum and these are the kinds of you know values associated with the time I mean the wavelengths associated with the incoming solar radiation and the energy is associated with them.

Now, if you take this information and you take it along with the band structure then it is interesting to see here how this radiation will interact with materials of different band structure.

(Refer Slide Time: 19:24)


Band gap greater than 2eV: Insulator

Band gap less than 2eV: Semiconductor

Partially filled bands: Metal

Overlapping bands: Metal

Empty Conduction Band

Band gap E_g

4.5eV

Filled Valence Band

Empty Conduction Band

Band gap E_g

2eV

Filled Valence Band

Visible Spectrum Wavelength: 400 nm (violet) to 700 nm (red)

Corresponding band gaps: 3.1 eV to 1.8 eV

So, we have here again we know as I said 400 nanometers to 700 nanometers or which comes to energy of 1.8 electron volts for the 700 nanometers radiation and a 3.1 electron volts for the 400 nanometer radiation. Now, there is something very interesting here we have a band gap E g. So, when radiation is incident on the material if the energy of the radiation is higher than the band gap then it enables a transition of an electron from the filled valence band into the conduction band.

So for example, if I say let's just use this value here we have a value 2 here, 2 electron volts okay. So, 2 electron volts I just assume that I have got a semiconductor with a band gap of 2 electron volts and let us say since we have this range of radiation I will take the 2 extremes of the radiation I will assume that I have photons arriving on the sample which have 3.1 electron volts energy and some other photons arriving at the sample which are 1.8 electron volts energy. So, let's say we have these options available to us. What will happen? Interestingly what happens is the higher energy radiation which is 3.1 electron volt radiation gets absorbed by the material because it is possible to do this transition this transition that I just showed you it is able to do. So, even though this is only 2 electron volts, the 3.1 moves the electron in into the conduction band because it has got lot more energy pushes the electron into the conduction band it takes it above you know starting point of the band. But and then maybe some other things will happen let us not worry about what happens at that point, but it will take an electron into the conduction band.

On the other hand the 1.8 electron volt photon that arrives at this material is unable to provide enough energy to clear this gap and therefore, the 1.8 electron volt photon is unable to do the transition. So, then what happens to the 1.8 electron volt radiation so in fact, these materials end up being transparent to that radiation okay. So, generally speaking they are transparent to radiation of wavelengths less than the band gap and therefore, interestingly normally you think that you know some low energy thing will get absorbed high energy thing will be able to you know pass through that’s the you know intuitive way we think of things. Here it is the other way around the high energy photon gets absorbed because it is able to cross the band gap, but the low energy photon is unable to cross the band gap. So, it just passes through the material without doing any transition. So it is, so, the material sort of is transparent to this radiation.

So, therefore in fact, if the insulator were let’s say for example, let’s say the insulator were just by looking at this let’s say its let I will just give a value of say 4.5 electron volts. So, 4.5 electron volts let us say the insulator has a band gap of 4.5 electron volts then it will be completely transparent to the entire visible spectrum. So in fact, ceramic materials which are you know of high band gap materials if you make them defect free if you make them you know single crystal that is defect free ceramic material. So, for example, zirconia if you take and you make a single crystal of zirconia that is defect free you will find that it is clear crystal clear you can look through it and it will be transparent. Transparent meaning the entire visible radiation is able to go through it without interacting with the material because then at that point its band gap will be higher than the value of the energies that are available in the visible part of the spectrum okay. So, this is how it works with respect to these materials.

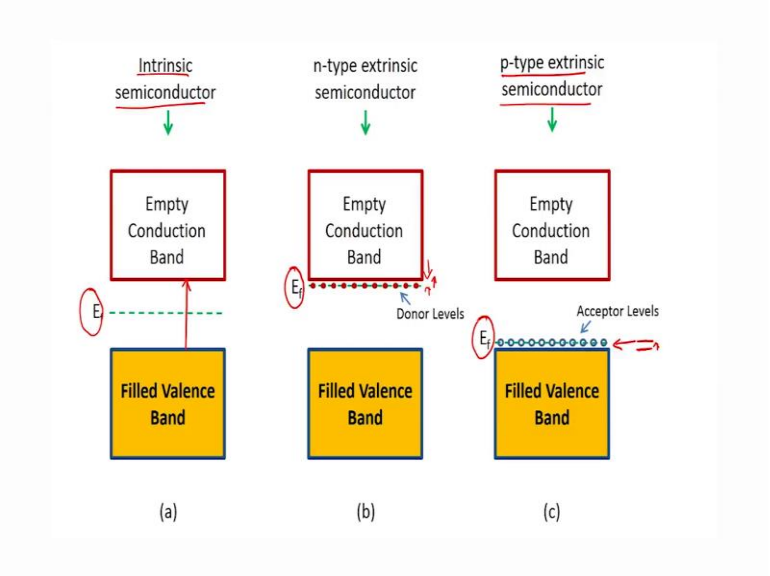
Now, what would happen with respect to a metal? With respect to a metal since you have continuous set of energy levels there is no gap here, you have continuous set of energy levels that are available just above this highest occupied energy level. So, therefore, for metals any radiation that is incident on incident on it can absorb and that is the reason why any metallic surface is opaque because no light goes through it no visible radiation goes through it. In fact, essentially no other radiation will go through or the values of energy levels that are just above it are so closely spaced that essentially it is a continuous band for all practical purposes it is a continuous band any radiation incident on it will get absorbed. So, that is the idea here.

But we have two things to do here if you use a metallic surface it gets absorbed heat gets absorbed and that is why we are using metallic surfaces for you know capturing the sunlight to pick up the heat and then use that heat or heating water or air or generating steam or a variety of things that we previously saw. But if you want to generate electricity you have to absorb the sunlight you have to get these charge carriers and you have to separate the charge carriers and then use those charge carriers in some external circuit. So, you have some process that is involved it and for that the metal then is not particularly useful to us because it just absorbs and it is all the electrons are all right there and you are not able to capture it as a separate electron that you can move into an external circuit at least not in this general layout. I mean a semiconductor there are ways in which you can know now pull off the electron and then take it to an external circuit.

So, as we look at this photovoltaic approach to dealing with solar radiation through our next few classes that is the idea that we will look at. How is it that we can use semiconductors to create the situation where you have these electrons that can be pulled off into the external circuit and then used in a you know as a power supply or a power source there which can then run something usefully. So, for that we need to understand all this idea of you know how these bands come about, where is this, what is happening is there some more detail in this band structure that we have not fully captured are various materials with is the same band gap exactly the same in terms of how they handle the solar radiation.

In fact, the answer is no there is some further finer detail here which decides which will tell you that some materials are actually better suited for solar cell application for photovoltaic applications than some other materials because there is some finer detail in the band structure which helps them in that idea. So, that’s sort of the thing that we will look at in this class.

(Refer Slide Time: 25:23)



So, we spoke about pure semiconductors and that is what we have listed here as intrinsic semiconductors. So, here there is no doping and it's a you know pure material and so there then we as I said the Fermi energy level E f is exactly halfway between the conduction band and the valence band and that's how it is defined.

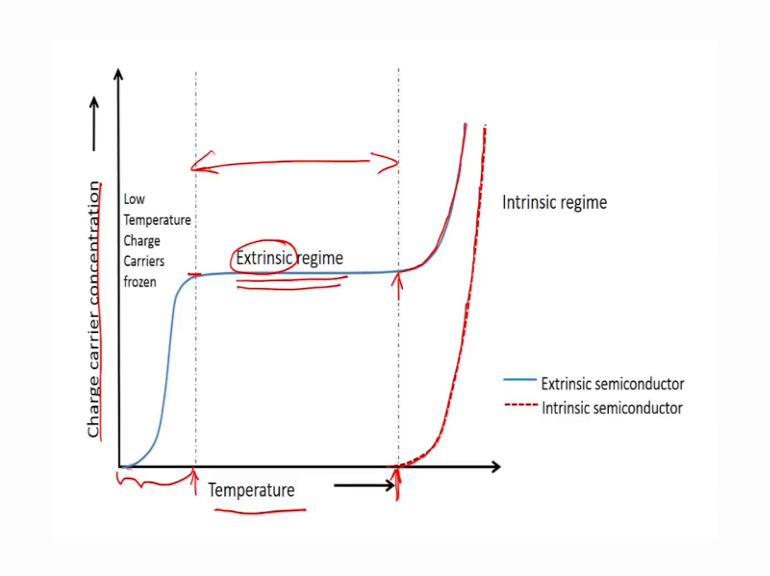
Now when you do any kind of doping n-type doping to a semiconductor or a p-type doping to a semiconductor you are essentially introducing an element into the material which either has an additional electron which can which it can put into the system or it has one less electron that it can put into the system relative to the base material. So, you can add dopants which you push we increase the number of electrons in the system or decrease the number of electrons in the system on average.

So, those that increase their number of electrons are referred to as the and create this semiconductor referred to as the n-type semiconductor, n being you know indicating the fact that it's now having this negative orientation with the negative charges and what it creates is, it creates set of donor levels which are very close to this conduction band. So, whereas, previously you had to if this were a pure semiconductor an intrinsic semiconductor you would have to move from here to here, in order to push the electron from the valence band to the conduction band in the n-type semiconductor you can actually you only have to do this small jump and you can get some you know conducting electrons. But that is only a limited number of conducting electrons if you want large number of conducting electrons, you still have to go down to the valence band and pull it up, but you get this limited set of electrons which are close to the conduction band which can get into the conduction band, and that gives the semiconductor some interesting properties and that is why we look at we more more often work with extrinsic semiconductors than we do with intrinsic semiconductors.

Analogous to that and I know you know in sort of a similar, but opposite manner we have the p-type semiconductor here you are putting in materials as dopants which have one less electron than the base material that is present. So, it creates a bunch of acceptor levels. So, here again the electrons which are on the top of this valence band can go into the acceptor level by just doing this small jump and it enables the material to start functioning in some interesting ways. So, this is the p-type extrinsic semiconductor and that’s the n-type.

For the with respect to the Fermi energy because it is you know integrated or intricately linked to the energy level of the electrons and the fact that that is where they are in a position to interact with their surroundings the Fermi energy level for an n-type semiconductor is essentially the very much the donor level energy level that is present there and the Fermi energy level for the p-type semiconductor is the acceptor level. So, so this is how the Fermi energy level is certified. And as I said this is important for us to understand this definition for the Fermi energy level and also the location of this Fermi energy level in the energy scale because that will tell you what will happen when you put these materials in contact and that is something that we are going to see subsequently. So, that is the reason why I am drawing your attention to Fermi energy level now we will use it progressively.

(Refer Slide Time: 28:46)



So, what happens when you look at these intrinsic and extrinsic semiconductors? Just to give you an idea of how they behave differently when you take both the semiconductors and then you look at the charge carrier concentration which is what is marked on your y axis here and you look at it as a function of temperature. At very close to 0 Kelvin all the charges are held within the you know their base energy level their lowest energy level which could be the you know the filled valence band or the acceptor level or the donor level it just sits there I mean nothing moves its basically just sitting at those values.

So, only when you start heating the material a little bit that the charges get a chance to start moving. Now, as I said because the n-type as well as the p-type semiconductors need very small amount of energy here as well as here to get those electrons into a position where they can move if you see here at relatively low temperatures this is a temperature scale relatively low temperatures for the semiconductors that are extrinsic. The charged carriers get into a position where they can start carrying charge and moving around and actually showing you some behavior corresponding to the existence of those charge carriers. So, at fairly low temperatures and in fact, this is if you this dotted line that I am showing you here is there would be even below a room temperature. So so, by the time you reach room temperature all those charge carriers are already in a position to participate in some process that you are trying to put them to use for.

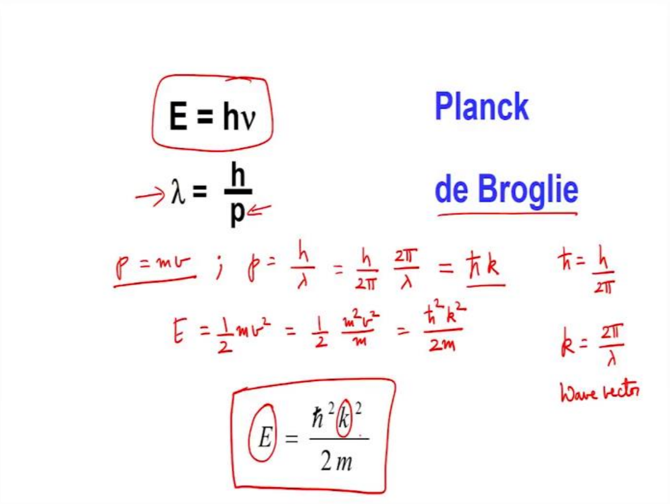
So, typically if you look at the charged carrier concentration in a fairly low temperatures you start giving energy and those charged carriers get into a position where they can start carrying charge and so they show up as part of the charged carrier concentration and then pretty quickly they max out at some value. That value will depend on the doping concentration based on how much dopants you put you may have a higher value or lower value, but essentially at a value, at a temperature below room temperature itself all the charge carriers become available and so that corresponds to some fixed charged carrier concentration which is in exactly in line with the doping concentration. So, they it will level often at that value.

And from there on for a fairly large range of temperature the charged carrier concentration will remain flat and this is the charge carrier at a concentration that you end up using for a variety of purposes when you are using a extrinsic semiconductor and so this is referred to as the extrinsic regime extrinsic regime of the semiconductor. If you go to very high temperatures significantly higher than room temperature then if you see here in addition to this transition from the donor level or from the valence band to the acceptor level in addition to the transition you will also enable transitions from the valence band to the conduction band. You will have this full transition also occurring in addition to the original transition that you did. So, that is why you start seeing this additional behavior here for an extrinsic semiconductor which is basically additional charge carriers which are now coming from the valence band.

If you had an intrinsic semiconductor that's completely pure then you have no extrinsic regime you only have it just tracks the x axis all the way up to this point and from there on it starts showing you this intrinsic regime. So, it only shows you the intrinsic regime it e doesn't show you any other regime it stays flat till the time and then shows you the intrinsic regime. Whereas, the extrinsic semiconductor which has dopants first shows you the extrinsic regime and it shows you the extrinsic regime for a wide range of temperatures which are of interest to us which is basically from below room temperature to a significant value above room temperature and only after that it starts showing you the intrinsic regime and so in fact, mostly we are operating in this temperature range. We tend to operate in this temperature to for most of the properties that we put the semiconductors to use for. So, this is something that you should keep in mind when you look at all these semiconductors.

So, even though we show you, I show you this intrinsic semiconductor initially and I compared it with you know insulators and metals and I also showed you where the Fermi energy for an intrinsic semiconductor is it and how it compares with extrinsic semiconductors you will you generally find that much of the discussion is mostly on extrinsic semiconductors. We don’t use intrinsic semiconductors as much as we do with extend as we use extrinsic semiconductors which are the doped semiconductors because of this interest these interesting properties it provides to us by this extrinsic regime that is present with which we actually operate the material.

(Refer Slide Time: 33:24)



$$\boxed{E = h\nu}$$

Planck

$$\rightarrow \lambda = \frac{h}{p} \leftarrow$$

de Broglie

$$p = mv \; ; \; p = \frac{h}{\lambda} = \frac{h}{2\pi}\,\frac{2\pi}{\lambda} = \hbar k \qquad \hbar = \frac{h}{2\pi}$$

$$E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{m^2v^2}{m} = \frac{\hbar^2k^2}{2m} \qquad k = \frac{2\pi}{\lambda}$$

Wave vector

$$\boxed{E = \frac{\hbar^2 k^2}{2m}}$$

Now, in the next few slides are after this small calculation that I am going to show you the next few slides may look a little complicated, but I am just going to show you some few highlights which help you understand why there is additional detail in the band structure which is not been shown to you so far. But in the end I will summarize it and the summary is what is more important for you to keep in mind, but I will walk you through a few slides which show you the detail before we reach that summary.

So, once we start talking of electrons in solids over the years it has been recognized that it is more appropriate to use quantum mechanical principles to talk about electrons. So, we will not go into great detail of the quantum mechanics and how it is developed, but the most important equations which we are in fact, familiar from high school days is all I am going to use here, but this is relevant for the next few diagrams that I am going to show you and that is why I am going to develop them for you.

So, Planck put this I mean was the first to discover this equation E equals h nu and that is considered as the you know the equation that originated that led to that that defined the discovery of quantum mechanics. And then de Broglie extended this idea and said that you know if any particle has a momentum p then you can associate a wavelength with it called the de Broglie wavelength lambda which is given by as h by p and p is basically mv that is the momentum mv the momentum right.

So, now, if you extend this a little bit and rearrange and extend things a little bit we have p equals h by lambda and then because of some notation that we use in physics instead of just using h the preference is to use h by 2 pi and similarly instead of just using lambda we use 2 pi by lambda you can see that if you multiply the 2 pi cancel out and it is the same as h by lambda okay. And this notation has some detail I mean names associated with it. So, this h by 2 pi is referred to as h bar, so in books in physics sometimes you will see h bar that's what they are referring to this is simply h by 2 pi Planck's constant divided by 2 pi and this 2 pi by lambda is referred to as k or the wave vector k equals 2 pi by lambda h bar equals h by 2 pi k equals 2 pi by lambda that's it okay. So, this is called wave vector okay.

So, this is what it is. So, now, if you if you keep this these quantities in mind. So, if you look at energy and how it relates to momentum energy we write as half mv square right. So, if I want to relate this to momentum and momentum is m v, so I simply play around a little bit to the numbers, so I have simply half m square v square by m. I have just multiplied the numerator and denominator by m. So, m square v square is nothing, but p square because p equals mv right p square and p itself is h bar k. So, instead of writing m square v square I can write h bar square k square. So, I will write h bar square k square right because p equals mv and p is also equal to h bar k k and I have p square here. So, I write h bar square k square by 2 m. So, energy is h bar square k square by 2m and that's the equation that I have got down here right.

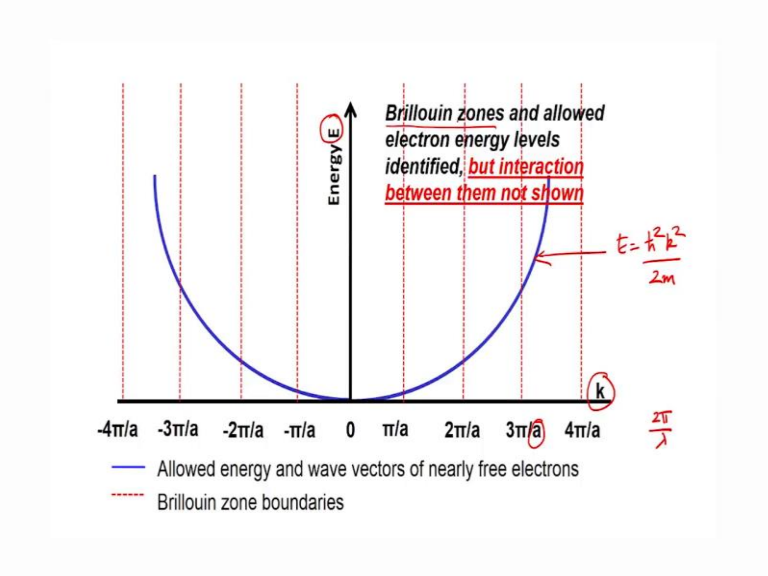
So, why is this interesting? So, this is an equation, this is the equation is related to quantum mechanical approach of looking at electrons in solids. So, this is the equation this is here the h bar is a constant. So, it's h by 2 pi is a constant, 2 is a constant of course, and m is the mass of the electron. So, that is also a constant. So, what do we have that is related here we simply have E here which is the energy and k here which is the wave vector which is 2 pi by lambda. So, when electron moves with different energies you have a different wavelength associated with it based on the momentum that it has and for each wavelength that you have associated with the electron you can find out the energy associated with it using this equation right. So, now, if you, I am going to now, this if you see if you plot E versus k. It is going to be a parabola.

So, k is a wave vector and it can have positive values or negative values which simply represents the direction in which the electron is moving. We will consider a one dimensional case. So, it can move in the positive x direction or in the positive or in the negative x direction and so I simply have plus k or a minus k and regardless of whether it is plus k or minus k E will be k square proportional to k square right. So, if you put E proportional to k square you will get a parabola right. So, this is called the free electron parabola it represents all the energy values that the electron can assume and the corresponding wavelength values that it will have right.

So, in the next few plots I am going to show you this parabola and then I am going to show you some distortions of the parabola and what is the significance of this distortion from the perspective of a band structure. So, that is the idea that I am going to pursue. So, you are going to see a few diagrams which show the parabola and then eventually the distortion of the parabola. There will be a few terms you may not be familiar with I will briefly tell you what those terms are as we go along.

As I said at the end of those slides I will summarize it with one key result which is a result that is of immediate relevance to us.

(Refer Slide Time: 39:08)



Brillouin zones and allowed electron energy levels identified, but interaction between them not shown

— Allowed energy and wave vectors of nearly free electrons

------ Brillouin zone boundaries

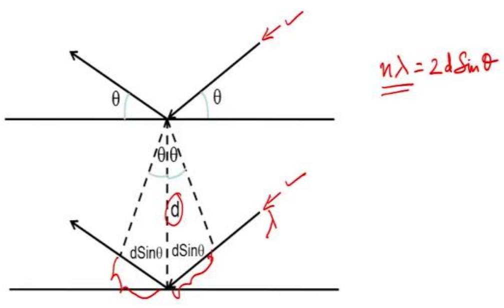
Okay so, this blue line that you see here is that free electron parabola which is essentially E equals h bar square k square by 2 m. So, I have plotted E as a function of k, k is here and energy E is here okay and I have this is this k is in the 2 pi by lambda various values of 2 pi by lambda are plotted here okay. So, now, so that is the blue curve that you see there. So, the basic idea is that the electrons are actually traveling in this material and they have various velocities associated with them therefore, they have various wavelengths associated with them.

Now, we know from general science that when you have radiation of some wavelength and it interacts with the material that has that it that has a periodic structure you have diffraction right. So, we realize that the typical metal or semiconductor that you have or an insulator that you have is typically crystalline material mostly we are discussing about crystalline materials they have some periodic structure. So, when when you have periodic structure and you have electrons within that material traveling with some wavelength associated with them they can interact with that periodic structure. So, we will briefly look at that that's essentially what we are going to look at the next few slides.

We will talk about this, I will briefly tell you what this Brillouin zone is. In this plot and in the subsequent plots that I am going to show you we are plotting 2 pieces of information. The first is this E equals h bar square by h bar square k square by 2 m which is that curve that you see and these dotted lines that you see represent that periodic structure of the material okay without and this a is from that it is a you know if you assume a one dimensional lattice of spacing a. So, you start at the origin at a there is a lattice point at 2 a there is another lattice point, 3 a that is a lattice point, etcetera, this a is that lattice spacing okay. So, it is simply since we are comparing it with 2 pi by lambda we are plotting here similarly a in the inverse notation okay. So, this is called reciprocal space notation not very critical for you to know that name. But the point is what is plotted on your x axis at those specific values where I am plotting those dotted lines represents the periodic structure of the material and you can see all the parameters here which therefore, indicate that.

So, there is a periodic structure for the material which is represented by those dotted lines and there is a free electron parabola which corresponds to the behavior of the electrons inside that material. In the few slides that we are going to see we are going to see how this periodic structure interacts with this parabola. And this periodic structure has this name called Brillouin zones and that's all you need to know about it, if you need to know more about it there are courses on physics of materials which discuss this in greater detail. But its sufficient for you to know that there is something called a periodic structure and one way to represent it is using this inverse notation where a gets represented as 2 pi by a and in that process you get this set of Brillouin zones at spacing of 2 pi by a. So, that's all you need to know, but just remember there is periodicity here wave information here both of them are here.

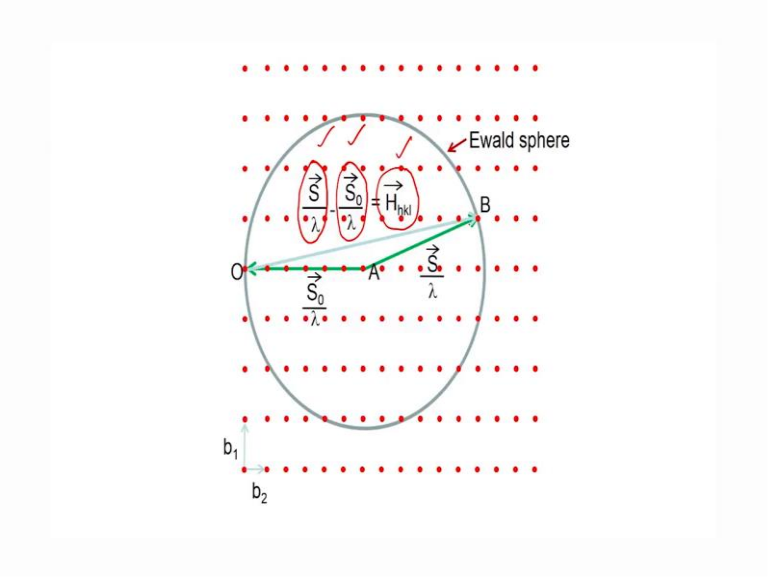
(Refer Slide Time: 42:13)



$$\underline{\underline{n\lambda}} = 2d\sin\theta$$

So, we know from Bragg's law that n lambda equals 2 d sin theta n lambda equals 2 d sin theta is one way in which we represent the diffraction condition in materials which is sort of what is shown in the plot here how it gets it derived. So, d is indicated here and you have some wavelength lambda coming in and d sine theta is the additional distance it travels here as well as the additional distance it travels here in which this wave here travels relative to this wave the additional distance that the second wave travels relative to the first wave. And if that spacing is an integral multiple of if the wavelength is an integral multiple of that 2 d sine theta then you have constructive interference right. So, that is how you get this Bragg law.

(Refer Slide Time: 43:12)

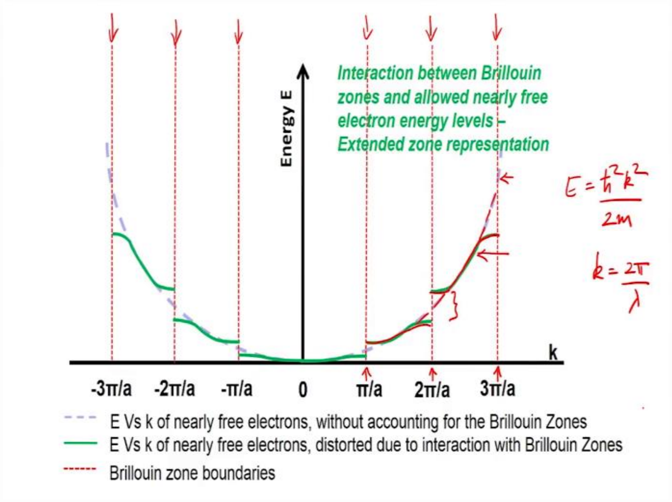


Now the same thing is also shown in another notation. It's a exact same idea here where these dots represent the periodic structure of the material and we are looking at the same radiation in inverse notation. So, again you need not know great detail of it, but they accept that there is an equation here which represents the this S naught by lambda here represents your incident beam this S by lambda represents the potential diffracted beam, could be, could be not we don't know. So, in that direction we are looking for a diffracted beam.

If it equals a reciprocal lattice vector for example, here I have OB it's a reciprocal lattice vector. So, if it equals ob if the vector difference between these two equals this vector here then diffraction occurs. It is analogous to this equation here where you have wavelength information here, you have spacing information here right this is the same thing.

In reciprocal notation you have wavelength information in the S by lambda and S naught by lambda and you have spacing information in H hkl that’s all you really need to know. So, what it basically means is that when you have specific wavelengths and those wavelengths result in this you know on touching of these reciprocal lattice points you get diffraction this is basically what what the whole idea is.

(Refer Slide Time: 44:29)



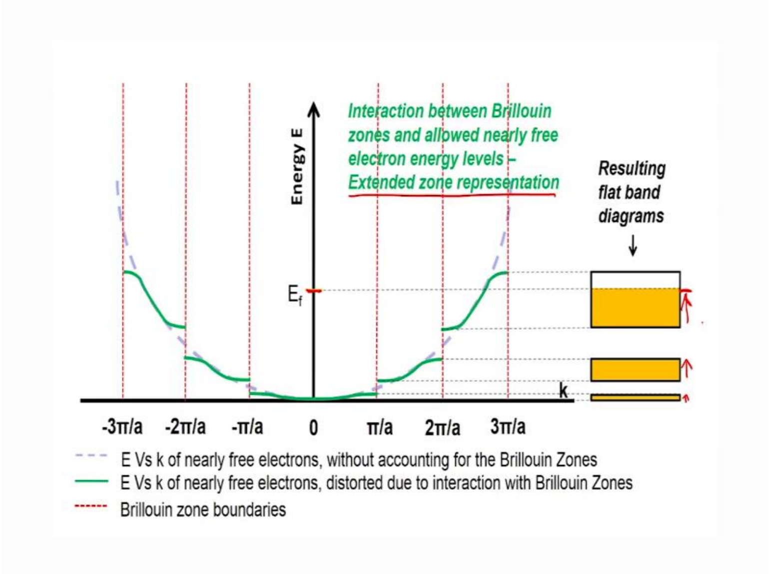
Now, at the Brillouin zones this is exactly what is happening. So, you have these boundaries these dotted line boundaries which represent this periodic structure that is present in the material. When a wavelength of corresponding wavelength touches that boundary diffraction occurs, so at these boundaries diffraction wherever the free electron parabola is touching these boundaries diffraction is the condition for diffraction is valid okay. So, what happens is this free electron parabola is represents as I said all the energies that the electron can possess all right. So, when it is free when it is not seeing a periodic structure when it is free to run around without any periodicity in the present in the material then it can assume all of those energy levels okay. So, there is no restriction on the energy level it can take. For every energy level there is a corresponding wavelength that it can have and you can do whatever it is possible with that free electron parabola.

When the same electron is put inside a structure that has a periodic lattice then it tries to do this free electron parabola it tries to assume all energy values that are consistent with that free electron parabola. So, E equals h bar square k square by 2 m. So, the electron tries to assume all values consistent with this E equals h bar square k square by 2 m where k is that 2 pi by lambda, but it finds that at values corresponding to pi by a corresponding to 2 pi by a when lambda equals pi by a lambda equals 2 pi by lambda equals 3 pi by etcetera.

It’s actually meeting or rather 2 pi by lambda equals 2 pi by a, pi by a, 2 pi by a, 3 pi by a 1 E whenever it meets those conditions it is actually satisfying the condition for diffraction. Because of this diffraction occurring at those values of wavelengths it actually creates some standing waves and it creates a small gap there is a way to calculate it, but it creates a gap where it is unable to hold those energy values. So, that is the reason this free electron parabola which is the dotted line that you see here gets converted to a distorted version of it which is this green line that you see here. So, whereas, you previously had a dotted line going this way at the boundaries there is a distortion of the dotted line and you see this curve that you see here and that is basically what you see here and so on.

So, now, what we have done, we suddenly find that this set of energy values here which are not allowed for the electron. This set of energy values that are not allowed for the electron is that band gap that you see okay. So, only when you go into the structure of the material in this level of detail do you understand where is this band gap coming from? Till now mostly you know simply heard that there is a band gap you have heard that there is a valence band there is a conduction band in between there is a band gap that’s all the information we have. But only when you get into this level of detail do you understand where this band gap is coming from, what is that interaction that is happening in the material that creates the situation, what, there is a set of energy levels that are forbidden? So, this is the origin of the bands, band structure in the material.

(Refer Slide Time: 47:29)

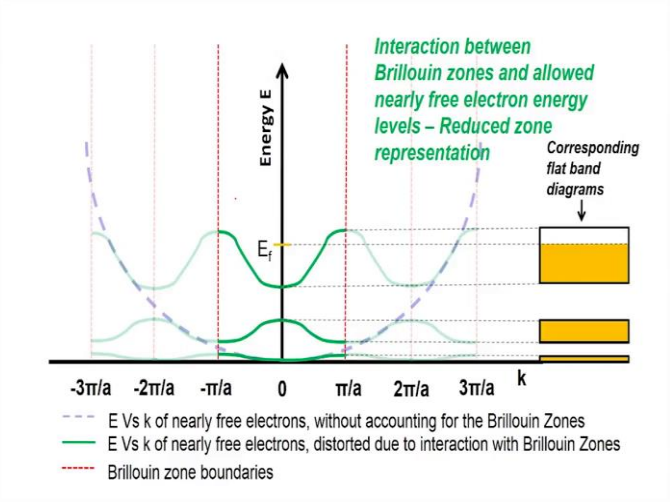


And to be more specific whatever you see here which is the allowed set of values becomes an allowed band and whatever is not allowed here becomes this band gap right. So, this is how you get and so in fact, the material you have many bands, you have a band right at the bottom then this a band gap here, another band here, another band gap here and there is a band here. If these two were the last two bands that were present in the material then yes we would call the topmost band as the conduction band and the immediately lower band which is full would then be referred to as the valence band.

So, this is the way in which the material begins to show itself. And the one additional detail that we need to add here which will complete the picture is the presence of the Fermi energy which is the highest energy level occupied by electrons. So, that could be anywhere. So, that is one value here. So, if this were the Fermi energy level up here it means that up to that electrons are full. So, this band is full here, this band is full here and this band on top is full up to this point and that is how you get the Fermi energy information also into this and you can see here and in this case, may have a example that I am showing you it is a situation where this is a metallic sample because the final band is already partially full. If you had a final band that was completely full and then there is a band gap and then there is another band that is empty then that would be a semiconductor on insulator depending on the band gap. So, this is called extended zone representation.

Just to show you a couple more representations before we begin we summarized this information. The same thing because the crystal is symmetric this is caught, this can be replicated at all those lattice locations based on the symmetry and, so for every a that you move correspondingly in this representation we would move by 2 pi by a. So, you can center this figure at 0 at 2 pi by a, at 4 pi by a etcetera and you can you are essentially creating the same situation. So, the next two slides will simply show you this in 2 3 slides will show you this no complete picture, but you will find that the band structure on your left on your right side of your screen will remain is essentially the same corresponding to this detail. So, you see that this is called extended zone representation which starts at 0 and then extends in all directions.

(Refer Slide Time: 49:38)



Interaction between Brillouin zones and allowed nearly free electron energy levels – Reduced zone representation

Corresponding flat band diagrams

E Vs k of nearly free electrons, without accounting for the Brillouin Zones

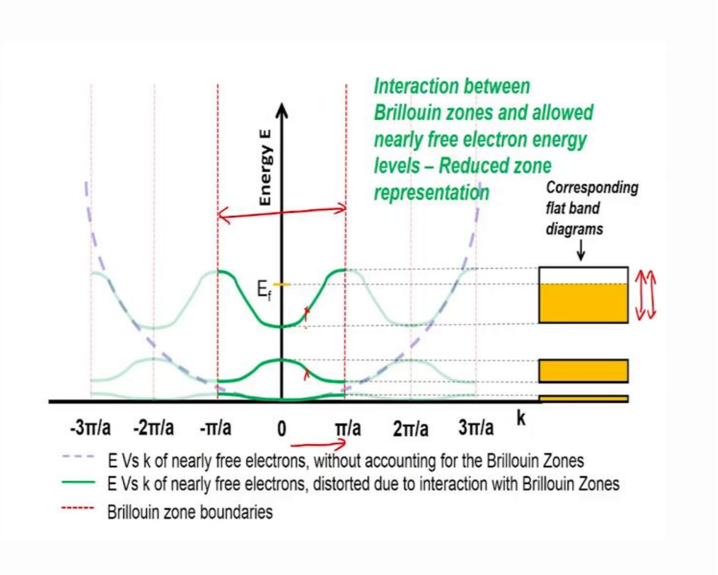
E Vs k of nearly free electrons, distorted due to interaction with Brillouin Zones

Brillouin zone boundaries

This is called repeated zone representation which is exactly the same representation you saw in the previous slide except that it has been replicated at each of those 2 pi by as locations. So, at 0 I centered this at 0 and got 1 curve I centered it at 2 pi by a and got one curve and similarly at 4 pi by a and so, on minus 2 pi by a, minus 4 pi by a and within the scope of the diagram I am showing you all those locations where you have allowed energy levels and non allowed energy levels, you see the band structure on your right hand side.

So, this is called a repeated zone scheme because it shows up at all the lattice locations and it helps you understand how the entire band structure exists in the material. And there is finally, one representation which basically takes into account the fact that whatever you see in this first zone as it is called because it is symmetric the same thing gets replicated everywhere else. So, it is sufficient that we see this full structure in the first zone alone, it is not necessary that we plot it for all the zones and so that is called this reduced zone scheme you can see that we are only looking at this consideration. We are considering only this part. The rest of the diagram is identical it is the same thing being replicated in many ways.

(Refer Slide Time: 50:31)

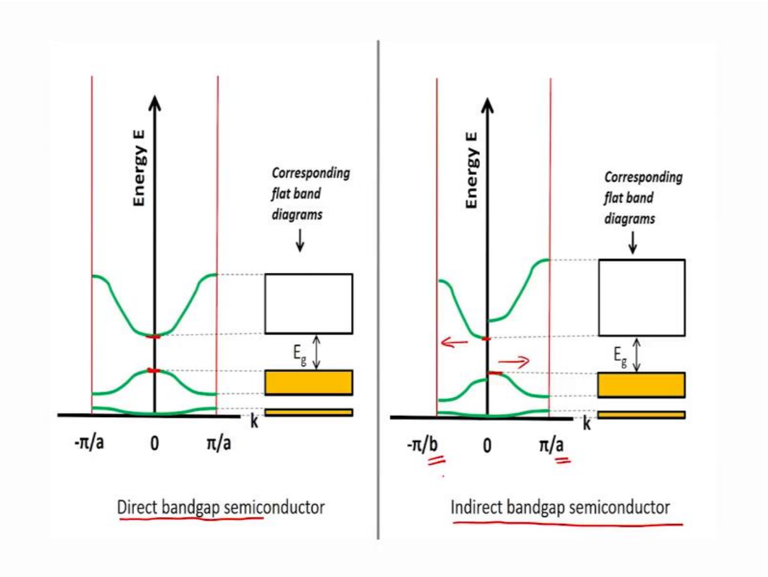


So, these are different ways in which you plot this information. But the most important point being there is the allowed energy level even though in this diagram we see a big band we see a solid band. So, that is called a flat band diagram because we just should draw blocks here it is a flat band diagrams, even though you plot it like that what you see in detail is that within the material based on the location in the material which is what that case space is it is got to do with the crystal structure of the material, location of the material, directions within that material based on the directions within the material there are specific values of energy level that the electron can have.

So, even though there is a band here the electron cannot assume all of these energy levels everywhere, the electron can assume these energy levels only at specific values of these energy levels it can assume at specific locations within that lattice and so at some other location it cannot assume that energy level.

Overall for the material as you step back and watch this there seemed to be a continuous set of energy levels it can occupy, but if you go to a particular location there may be only one particular set of energy or 1 or 2 if you come to this place you may have this allowed, this is allowed, this is a allowed right. So so, therefore, it is location dependent the band structure is location dependent which is not visible to us which is not clear to us when we look at the flat fat sorry flat band diagram. It is clear to us only when you look at this kind of a representation which is an E versus k diagram that is where you see this representation.

(Refer Slide Time: 52:07)



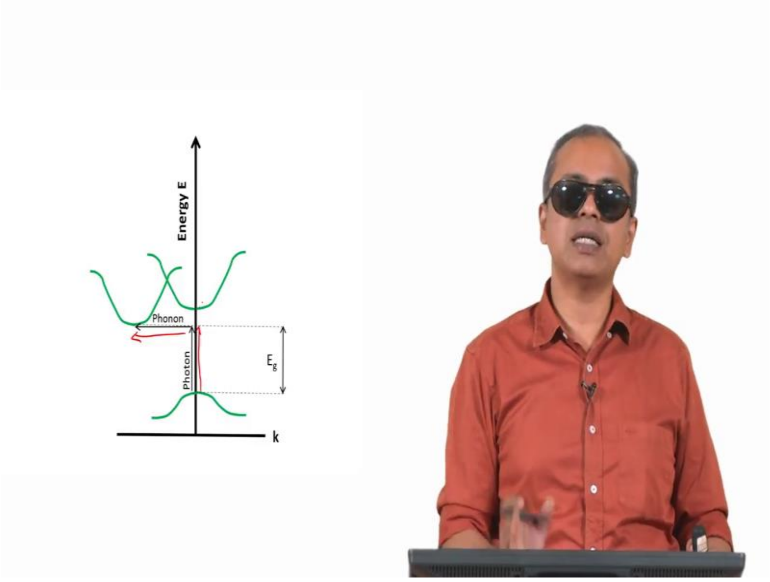
So, why is this important to us? This is important to us because I on your screen now we have two possible semiconductors which have exactly the same band gap E g, the E g for both the semiconductors is same right. So, on the left hand side of your diagram the diagram on your left hand side we find that the highest occupied energy level here is here and the next lowest unoccupied energy level is at the same location in k space, in other words in the same location at the crystal structure.

So, therefore, if you have an incoming radiation you can shift an electron from the highest occupied level which is the top of your valence band to the next lowest unoccupied level which is the bottom of your conduction band and the transition happens. So, that is where you do E g equals h nu and you are able to do the transition right. So, that happens.

Now, you look at another material on this side and so this first set of materials that I spoke to you about are called direct band gap semiconductors. Another material on your screen here is an indirect band gap semiconductor where what is happening is if you see here these are two different directions in k space. So, I have that is why I have marked this as b and this is a. So, I am going in a direction and if I am going from the origin to the right side and I am going to b direction if I am going from the origin to the left side and because of symmetry I am just showing you one you know one segment of it, but you can imagine that it is distributed. Now, you see that the highest occupied energy level is actually in the a direction right, but the next lowest unoccupied energy level is in the b direction in this direction this is in this direction.

So, therefore, if you now want to move an electron up you cannot just move it in the a location you have to go to the b location right. So, from a you have to move it up and then you have to move from the a direction at some location you move it up then you want to shift it to the b direction only then it can go into the conduction band. So, it’s like a two step process. Whereas, in the direct band gap semiconductor a single step you went from the valence band to the conduction band in the indirect band gap semiconductor you have to do a two step process only then you go from the valence band to the conduction band. So so, that is specifically different.

(Refer Slide Time: 54:14)



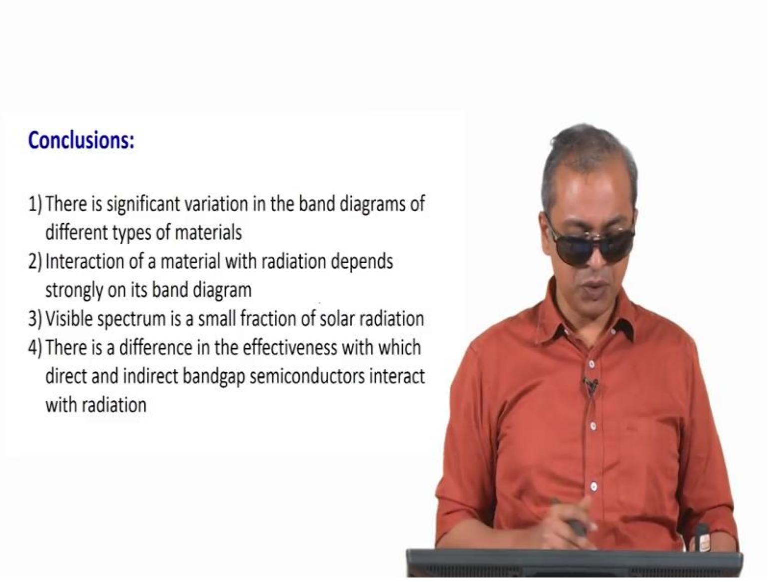
So, what happens within the material is that you now need end up requiring a two step process. I am showing you that I am just taking the indirect band gap semiconductor here and highlighting that. So, normally we would simply require E equals h nu to get your electron up into the conduction band, but we find that when you do E equals h nu and you bring the electron up there is no available site where it can go and sit. It is still sitting in a forbidden gap with respect to that direction in this example that you see. So, it has to move sideways and get to a location where it can now get accepted because the next available energy level is sitting there.

So, it's a two step process as I said. The incoming photon E equals h nu pushes it up in energy and then a lattice vibration which is referred to as a phonon pushes it to the other direction and that is how you get a transition to complete okay. And each is each of these are statistical there is no guarantee that once the h nu pushes the electron up something will automatically move into the available site there is a probability that the h nu will push the electron up. And there is another probability associated with the phonon being available at that exact instant to push the electron to that region.

So, you have two probabilities here. So, naturally by definition of probability is you know less than 1 and so when you multiply two probabilities that which are both less than 1, the total probabilities even lower than both of them okay. So, in a direct band gap semiconductor there is greater probability because it is a single event associated transition is greater probability of transitioning to the conduction band in an indirect band gap semiconductor there is less probability of transition to the conduction band.

So, as we look at photovoltaic materials we will recognize which is a direct band gap semiconductor, which is an indirect band gap semiconductor indirect band gap semiconductors are being used for solar applications, but they have limitation. This is a limitation that is there in the background that we should be aware of. And so, when some other materials are explored and you know greater emphasis is placed on some other materials this is one of the reasons why that emphasis is being placed. Even though you may see that you know band gaps you don't look terribly different, but inside this there is this detail that one is direct band gap the other is indirect band gap. So, better chance that it will absorb the solar radiation and do the transition that there is a lesser chance that it will absorb the radiation to do the transition.

(Refer Slide Time: 56:22)



Conclusions:

1) There is significant variation in the band diagrams of different types of materials
2) Interaction of a material with radiation depends strongly on its band diagram
3) Visible spectrum is a small fraction of solar radiation
4) There is a difference in the effectiveness with which direct and indirect bandgap semiconductors interact with radiation

To summarize conclusions from this wall that we discussed in this class is that there is significant variation in the band diagrams of different materials. We saw semiconductors, we saw insulators and we saw metals.

We also saw that the interaction of radiation with the material depends totally on the band gap and that is how you find metals being opaque because they absorb anything that falls on them, semiconductors and insulators are opaque to some wavelengths and are you know or in other words they absorb some wavelengths and they are transparent to some other wavelengths and interestingly lower energy wavelengths are able to go through because they are unable to do the transition.

The visible spectrum we also saw briefly only a small fraction or a certain fraction of it is the, of the overall solar radiation is the visible spectrum you do have a lot of parts of it which are not the visible spectrum you have in fact, a significant amount of it being in the infrared. And finally, we saw that there is a difference in the effectiveness with which material will absorb radiation based on whether it is a direct band gap semiconductor or an indirect band gap semiconductor.

So, that’s our summary for the class today. These are all parameters and know concepts that we should keep in our mind, as we look at the details of photovoltaic materials and how they function going forward.

Thank you.

KEYWORDS:

Capturing Solar Energy using Photovoltaics; Solar Photovoltaic Process; Band Diagram for Materials; Semiconductor; Drawing Band Diagrams; Band Gap; Conduction Band; Valence Band; Insulators; Conductors; Fermi Energy Level; Extrinsic Semiconductors; Intrinsic Semiconductors; Ultraviolet; Visible; Infrared; Wave Vector; Momentum; Quantum mechanical approach of looking at electrons in solids; Brillouin zone; Periodicity; Wave Information; Braggs Law; Extended Zone Representation

LECTURE:

Band Gap diagrams of materials like Conductors, Semiconductors & Insulators were illustrated. Importance of band gap and the interaction of radiation with this band gap was explained conceptually to understand the consequences. The usage of Direct and Indirect semiconductors n harnessing solar energy is discussed.