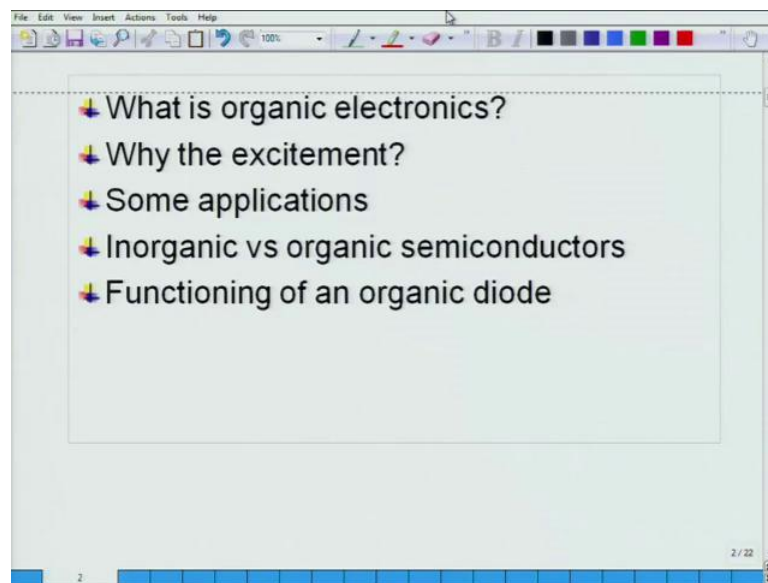


Optoelectronic Materials and Devices
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Module - 4
Optoelectronic Device Physics
Lecture - 38
Organic Electronics

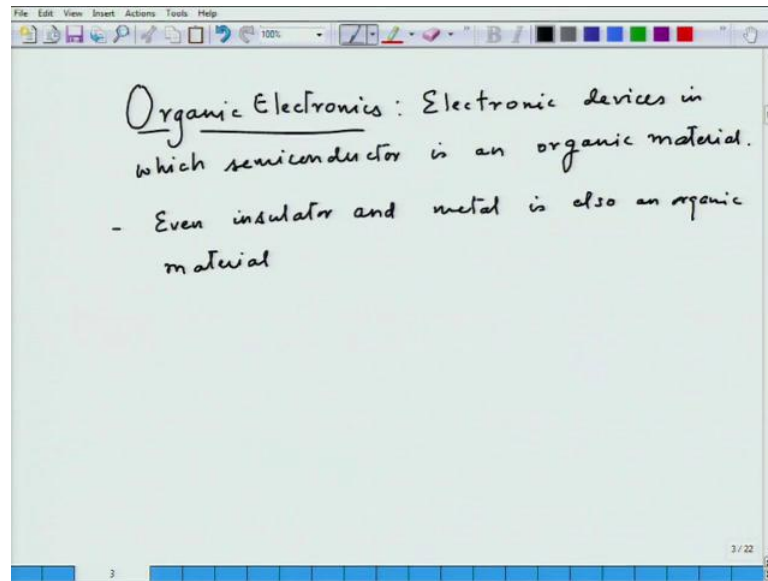
Today, we are going to talk about very new kind of material and devices. The topic of today's lecture is organic electronics. And the topics that I am going to cover in today's lecture is what is organic electronics, why the excitement about organic electronics, some applications that have already come out and some things which are under development.

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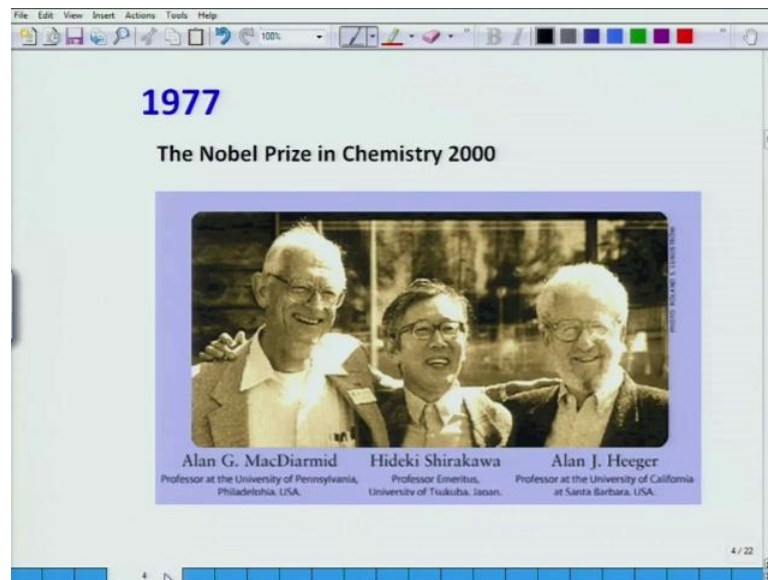
Then I will explain the difference because throughout this course you have been looking at the electronic structure, the carrier action in organic semiconductors. So I will point out the main differences between inorganic and organic semiconductors, and then I will discuss functioning of an organic diode. So, what is organic electronics?

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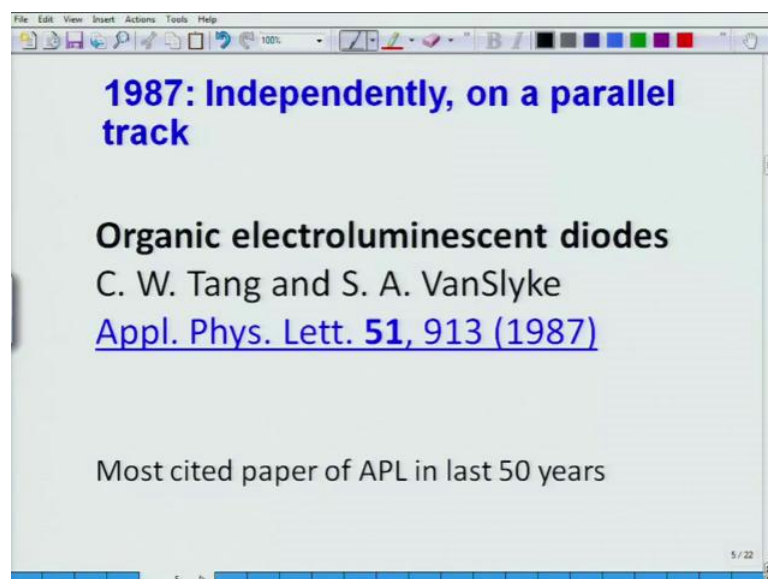
Organic electronics can be generally defined although there is no strict definition for it. It is electronic devices in which semiconductor is an organic material. And very often these days not only the semiconductor, we find that even insulator and metal is also organic, is also an organic material. So, at least in order to get qualified as a organic electronics in a device at least one layer should be made of organic material, mainly the semiconductor and then we would call that as organic electronics. The field is about 10 15 years old. The area is developed a quite a lot that today we even have a commercial product and that is what you will look at it. The story of organic electronics to some extent is incomplete without mentioning the two things in this area.

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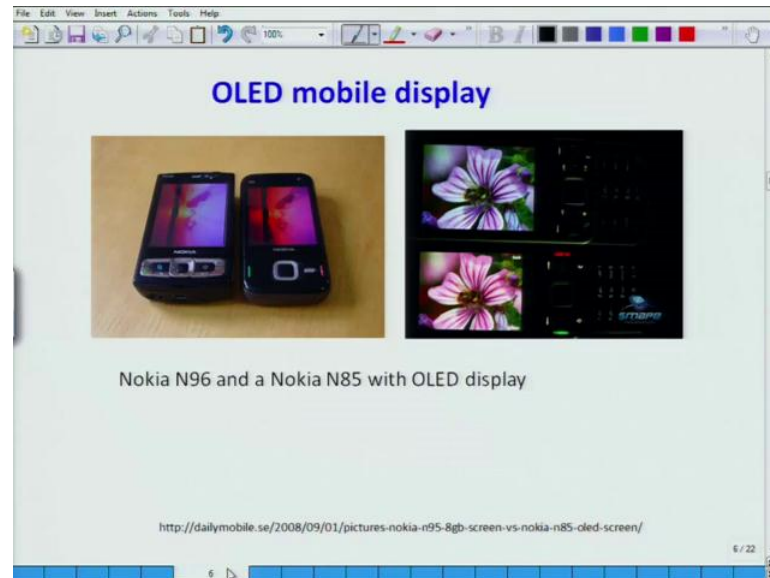
First one is a work of Alan MacDiarmid, Hideki Shirakawa and Alan Heeger in 1977 where they showed that polyacetylene which was known as a polymer, which is generally we expect it to be an insulator can be made very conducting and then they explained the behaviour how a polymer can be very conducting and later in 2000 they got noble prize for it and that opened the field of trying to see the semiconducting and conducting properties of the polymers and organic materials.

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In a very independent way C W Tang and S A VanSlyke in Kodak in 1987 started work on making devices out of these organic materials and their paper on organic electroluminescent device diodes in 1987 is highly cited paper in, it is the most cited paper of the applied physics letters in last 50 years and it has come to a point of being commercialized the ((Refer Time: 04:11)) that they have developed.

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Why do we talk about that they have been commercialized? I think even today most of you have heard the word O LED and this is what the organic electronics is. The O there stands for organic, this is the organic light emitting diode. I am bringing a very commercial application here where you see a Nokia mobile phone which display, their displays are made of organic light emitting diodes and not even just that mobiles.

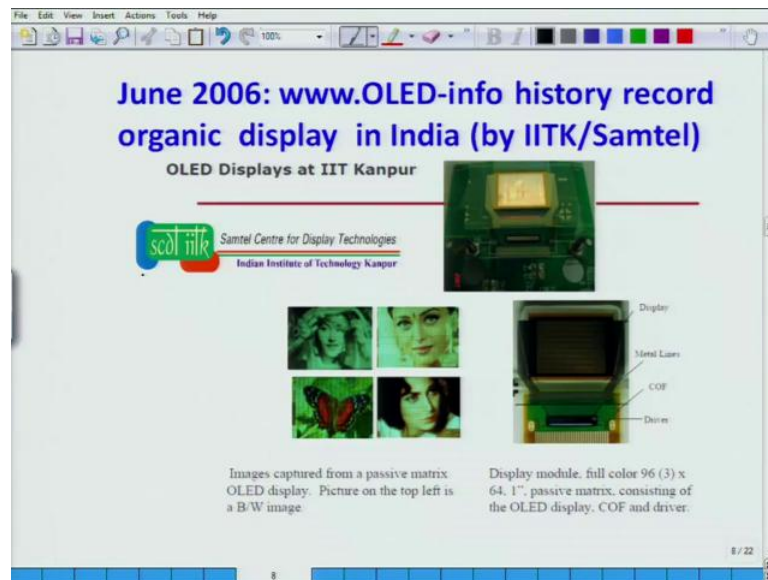
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Even in TV area you can see some of the big names which are going to use organic light emitting diodes for creating the display, information displays for their TV's. Here there is a image of a organic light emitting display from Sony compared with the liquid crystal display and these are were already available sometime back in 11 inch displays. LG also has prepared a O LED display which was, which is presented here. So, you can see that the, in the organic electronics field especially the light emitting diode has made its mark in the commercial applications in electronics.

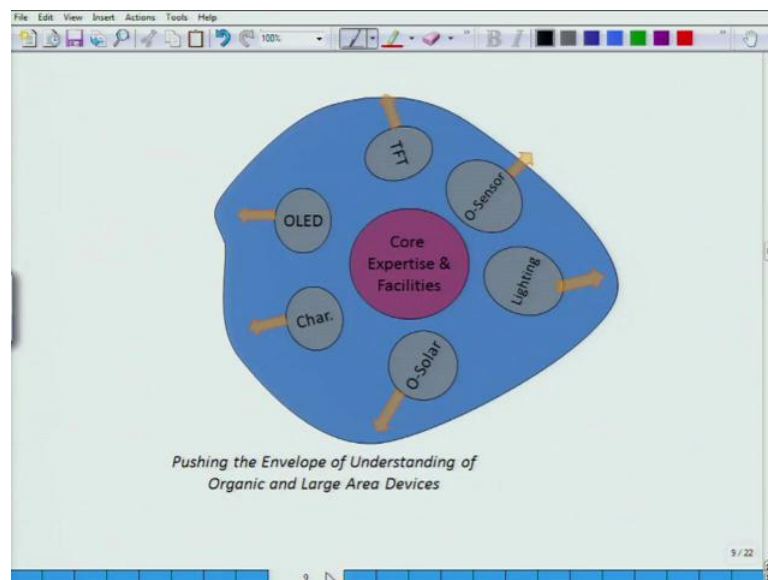
This field is very near to my heart because a research at IIT, Kanpur is group is existing which, where about 8 to 9 faculty are working in the field of organic electronics. In June 2006 this website which continues to update information on O LED info history recorded that organic displays in India were made which was an effort by IIT, Kanpur in collaboration with Samtel and these are the displays which are made at IIT, Kanpur at Samtel centre for display technology.

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So, we had started our effort and I already showed you that this product is already commercial.

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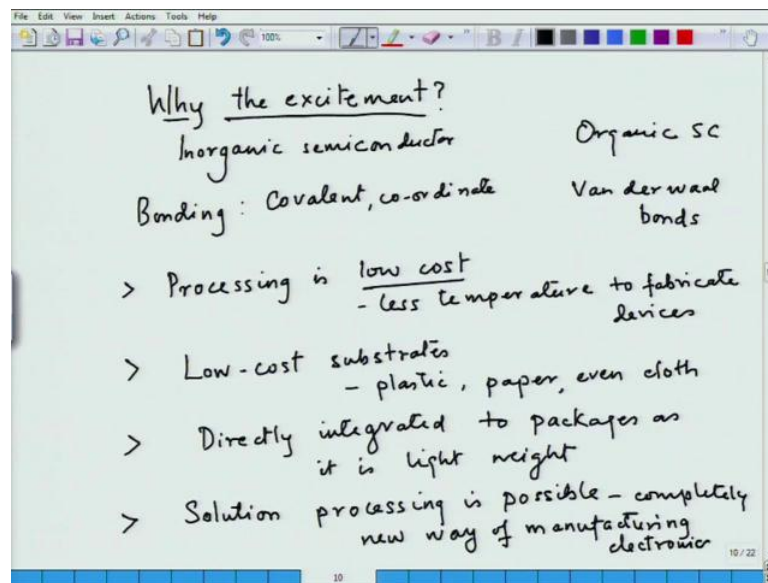


But organic electronics is just not organic light emitting diode. When the organic electronics basket we have organic light emitting diodes, we can make use of same organic material for making organic solar cells and we can use the same material for making thin film transistors which is variation of the MOSFET that we discussed in earlier lecture. We can make use organic materials for making sensors and same light

emitting diode can also be used for making white organic light emitting diode for the lighting application.

So, organic electronics in its basket has many applications that people are developing. We already saw that O LED display is already in commercial products. So, the field is very exciting and it is growing and I hope I will be able to convey some of the excitement in this lecture and why we should be doing it. So, the next question is why is there so much excitement about organic electronics?

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Why is the excitement? What is the difference between organic and inorganic? Most of the semiconductors that we have talked about so far are inorganic semiconductors. Silicon is an inorganic semiconductor and today we are talking about a organic electronics which choose organic semiconductors. The main difference in inorganic semiconductors is that these materials, the bonding is of the type for example, silicon silicon semiconductors, silicon silicon bonding is covalent or coordinate bonding.

They are basically primary bonding, primary bonds are made between the atoms of the material; while in organic semiconductor the basic entity is a molecule which is bonded by the primary bonds, but the materials itself is held by secondary bonds called Van der Waals, Van der Waal bonds. So, this brings the difference between the two areas what we discussed so far in the course. Inorganic semiconductors the materials are one which

require very high temperature to make changes into them because they are, they are made by primary bonds.

On the other hand organic semiconductor which are basically molecular in nature when we make materials out of them, they are bonded by the Van der Waal forces and require very little energy in order to make them. This is what is the reason for the excitement in organic electronics because it is very easy to process these organic semiconductors it makes it, the organic electronics is generally processing is low cost because less temperature is required to fabricate devices.

So, processing is expected to be low cost. So, these materials are going to be low, organic electronics is expected to be low cost. In addition to that since it requires very little energy to make these it is possible to process these materials on any substrate and that is the second a big advantage. They can be processed at low cost substrates such as plastic, paper and even cloth. So, now you can envisage a whole field of electronics which is going to be flexible.

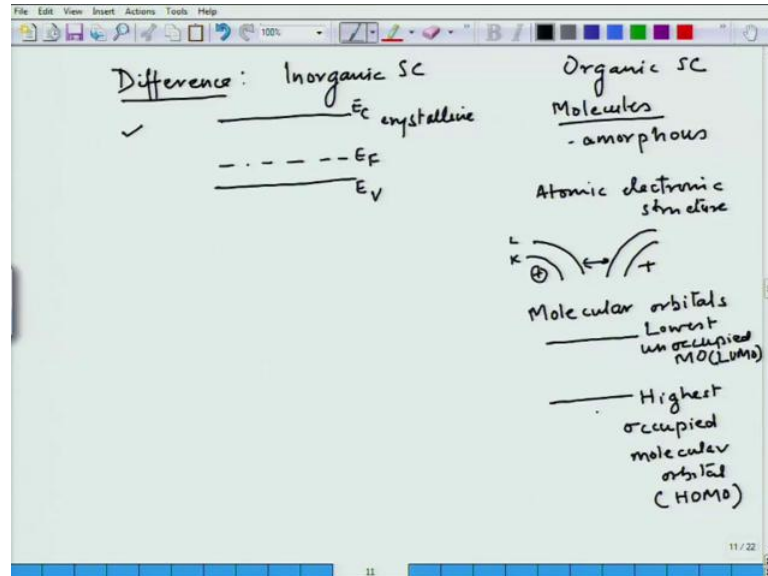
We can have may be solar photovoltaics which will be on our cloth and we will be walking around. So, that would be possible with organic electronics. It can be directly integrated to packages as it is light weight. There is a additional advantage of organic electronics and that comes from the fact that it opens the way for a very new paradigm for manufacturing semiconductors. It is possible to take organic semiconductor and do solution processing.

Solution processing is possible in organic electronics, which basically means that if I want to make a thin film for a silicon I will have to use very high cost evaporation techniques, but for organic semiconductor I can just take a solution, spin coat it on a substrate and get a thin film. Hence, the cost would completely come down because the manufacturing paradigm has completely changed. So, it the, this organic electronics changes the manufacturing technique for electronics.

The complete, completely new way of manufacturing electronics which is low cost, which makes it possible and this is the excitement about organic electronics. People think that once they can make these devices they can make them flexible, the devices can be flexible; they can be low cost and then that would bring electronics to everybody. So, now I hope we at this point you know what is the basic area of organic electronics and

why people are so excited about this field? The next question then that one needs to understand is what is the basic difference between organic and inorganic semiconductor?

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So, let us kind of review what all we know. So, the difference inorganic versus organic semiconductors. So, let us start from the beginning. The first thing that you learnt in this course was electronic structure of materials. What is the electronic structure of materials? In inorganic semiconductor we understood it as that; generally inorganic semiconductors are crystalline in nature. These are generally crystalline in nature. Their electronic structure which is important for devices can be represented by a conduction band and valence band and a Fermi level will define whether which kind of doping that we have put in the material or if it is intrinsic or extrinsic and I can change the character of the material from p to n type by doing a particular kind of doping.

Here I would like to point out that although when we developed the electronic structure of materials we took care that it is for crystalline materials, which are highly ordered and have a periodic arrangement of atoms, but similar structure will come out even if an inorganic semiconductor would be amorphous. And there are such cases although not possible to cover all these cases here and one such example is hydrogenated amorphous silicon which is an amorphous inorganic semiconductor.

On the other hand, organic semiconductor is a completely different electronic structure. Organic semiconductors are built of molecules which are, which are bonded using the

primary bonds and then when once we make the material most of the time these organic semiconductors are amorphous. Once again, it is not necessary that you cannot get crystalline state, you can get crystallization, but generally they will be amorphous and the electronic structure is going to be defined by the electronic structure of the molecules.

So, what is a electronic structure of the molecules? If you recall if we, when we form bonds we are going to form between two atoms. So, we have atomic electronic structure where we have different orbits and then each orbit, orbital will have different subgroups of orbitals which interact with the second atom and when a bond is formed between these two atoms then linear combination of these atomic electronic structure give rise to the molecular orbitals.

And these molecular orbitals are occupied by electrons using the required quantum mechanical rules and in these molecular orbitals the highest occupied molecular orbital and the acronym for that is HOMO is where up till which point the electrons are there in the, in the molecule. And the next level which is of the molecular orbital is called the lowest unoccupied molecular orbital and the acronym is LUMO. And so, this is the electronic structure of the molecule and the material is basically a amorphous collection of all these electronic structures.

So, there is no continuation of the band in case of amorphous or organic semiconductor. This particular HOMO level can be thought like the valence band of the inorganic semiconductor and the LUMO level can be thought as conduction band of the inorganic semiconductor. So, this is the basic difference between the electronic structure of inorganic and organic semiconductors. Because of this difference there are few things happened and which will affect the behaviour of these two semiconductors.

And that is rated next, one is that in the in the case of, in the case of inorganic semiconductors electrons are delocalized in the whole material. But in the case of organic semiconductors electrons are localized on the molecules. So, electrons will move from molecule to molecule in case of organic semiconductor while in case of inorganic semiconductors electrons in the conduction and the valence band move throughout the material as if they are free. So, that is the main difference between the electronic structure of the two materials.

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The whiteboard contains the following handwritten notes:

- Carriers: e^- and h^+
- Conduction mechanism: band conduction
- Diagram of scattering: An electron (e^-) is shown moving from left to right, then being deflected upwards and then downwards by a scattering center.
- R-G processes
- Mobility (μ_n, μ_p): $100 - 10^4 \text{ cm}^2/\text{V-s}$
- Polaron: A diagram shows an electron (e^-) interacting with a molecule, causing it to distort. The electron is then shown hopping between molecules.
- Hopping mechanism
- Equivalent processes exist in organic SC
- $\mu_n \text{ or } \mu_p$: $10^{-6} - 1 \text{ cm}^2/\text{V-s}$

The next difference between them is in the case of how, what are the carriers? In case of the organic semiconductor the carriers are electron and holes in the valence band which carry charge in case of inorganic semiconductor. But in case of the organic semiconductor the carriers, the electrons interact with the lattice and the carriers for charges what is called a polaron. Polaron is basically if I have a molecule which has a electron on it.

The electron interacts, it interacts with the lattice, it interacts with the molecule and thereby it changes the structures slightly. And that is why it is not a free entity and it has to move along with that distortion in the molecule that it has created. And so, there is again a difference between inorganic, organic. In inorganic electrons are basically free from the, from the atoms, but in organic the electron which is carrying the charge is associated with the atoms in the molecule and it carries the distortion along with it when it moves. So, the carriers in the organic semiconductors are polarons.

Now, what is the other difference? When we come to carrier action the conduction mechanism is very different in the two cases. In case of inorganic semiconductor conduction is band conduction, electrons are free and they move freely in the material. So, electrons move freely in the material or holes for that matter only when they see is scattering, then they get scattered, then they may see another scattering and get scattered again. So, this is a scattering center. Otherwise, they are free to move.

There is a band conduction. Once they, once they are in their band they are, they are free to move. On the other hand in case of organic semiconductor there is no band structure. Basically, you can think of the organic semiconductor as molecules which are next to each other and a polaron here, a electron with its lattice distortion in a molecule has to hop to the next molecule because it is not free, it has to hop to the next molecule. So, the electrons are moving in with the mechanism of hopping, rather than being free and moving around.

So, the hopping mechanism is operative in organic semiconductors. Next, we come to the recombination generation processes, R G processes that we discussed in inorganic semiconductor. We talked about recombination, generation, band to band or through traps, pretty much equivalent of all these may exist even in the case of equivalent processes will exist. There will be traps that will take, that will capture the electron or holes or there will be traps that would kill the luminescence of the material. So, equivalent processes exist in organic semiconductors also.

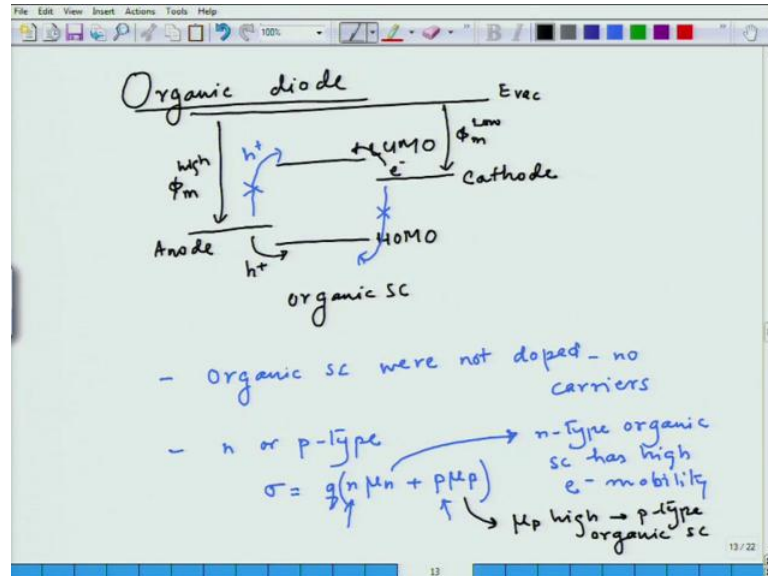
So, as you can see that from the point of view of electronic structure of the material and the mechanisms that take place the two semiconductors are quite distinct, but still we are able to use these two the organic semiconductors to make a very good devices. Another difference that these materials have is in terms of mobility of the carrier. Then in this case we have μ_n and μ_p and we, it is generally as we have seen the numbers are in the range of 10, 100 to 10^4 centimetre square per volt second, but because of all the differences in the electronic structure and the mechanism of conduction the mobility of carriers. Now, you may wonder that since there are no electron and holes how I can define electron and holes.

But since, there is a already a good physical base is existing for inorganic we still go on and define the mobility of μ_n or μ_p in case of organic semiconductor. Although, we know the conduction is taking place through a polarons and this is generally very low. Because you have to hop from one molecule to the other molecule and this generally in the range of 10^{-6} to 10^{-1} centimetre square per volt second and this again is a key difference in these two materials.

Organic semiconductor in terms of mobility, which decides the speed of the device can never replace a inorganic semiconductor in that aspect, but there the speed of device is

not important. In those cases organic semiconductor provide a low cost option for electronics. So, now let us see how we make a device using a organic semiconductor.

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So, I am going to show you functioning of a organic diode. So, earlier we talked about a diode in inorganic semiconductor in order to make the diode we have to make a p-n junction. So, we took a p type silicon and then process it to make a p-n junction and we got a built in field there, but in order to make a diode using organic material we will take the material and the electronic structure as we mentioned earlier will be given by HOMO and LUMO level of the semiconductor.

So, this is organic semiconductor and if you want to make p-n junction here, it is not possible. Why is it not possible? Because we do not have, although now people are able to do the p and n doping where electrons or holes can be given to the material, but for most of the part initially people did not know how to dope organic semiconductors. So, we, I will discuss that part only where we do not know how to dope it, but I want to make a diode from here.

So, I do not have the option of making p-n junction. So, what I do is I create a contact on the, on one side of this semiconductor using a metal. So, I make a contact using a metal and I call this as a cathode whose work function is low. And I make contact on the other side using a electrode whose work function is large and the idea here is that since the

barrier between the anode metal and the work function is being defined again in the same way using a vacuum level.

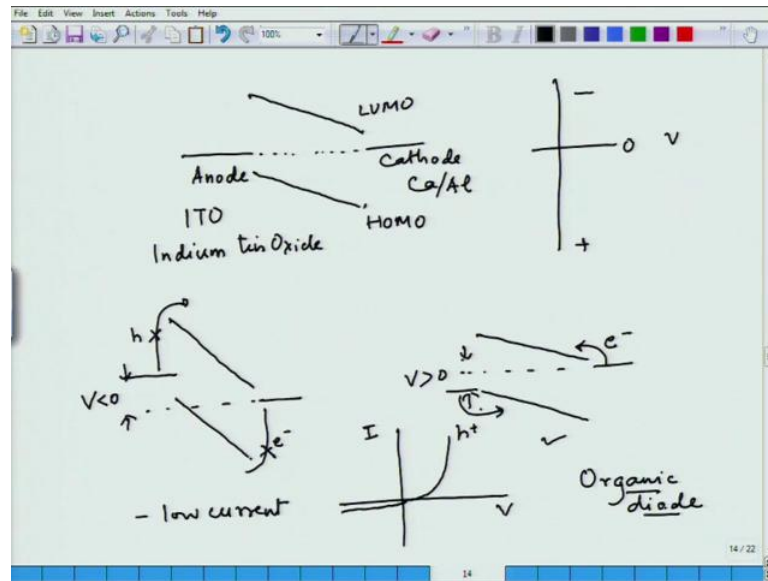
This is a low work function metal ϕ_m , low work function metal and this is a high work function metal. And we are bringing the, breaking a symmetry here is because the barrier is low it is easier for electrons to move in this direction. Once, we apply the bias and for holes to move in this directions. But it is not easy for these holes to be injected in the material. This is not easy or this possibility is not there. So, this brings the asymmetry of the diode in one direction when we will apply the bias it will be possible to conduct the electrons, in the other direction it will not be possible to conduct the electron.

Now, at this point I also want to mention since I already mentioned that in the initial period organic semiconductors were not doped. So, if you do not dope it is basically a intrinsic semiconductor which has electrons in the HOMO level, but no electrons in the LUMO level and this leads to basically no carriers which means that the device has to work the carriers have to be injected into the device. But still we define the organic semiconductor as n or p type semiconductor and the reason for that is because conductivity of the semiconductor if you recall can be written as $q n \mu_n + p \mu_p$.

So, in the case of inorganic semiconductor we could change this n n p, n n p by doping the material. But in case of organic semiconductor we define a material if its mobility, electron mobility is high then we call it n type. n type organic semiconductor has high electron mobility and if μ_p is high compared to μ_n then you will call it a p type organic semiconductor. So, the definition of n and p type is also very different in the case of organic and inorganic.

In the case of inorganic it was the carrier concentration that defined the n and p type material and in the case of organic semiconductor it is the mobility difference in the two material that defines the n or p type material. So, let us see how this device will work. So, let us first look at the device in a similar manner that we used to do earlier we will make the equilibrium structure.

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So, in the equilibrium structure it means that I must have the work function metal, the anode metal and this in general is ITO indium tin oxide. There are other materials which can be substituted and on the cathode side I have a low work function metal. These are generally one example is a combination of calcium aluminium is used and then I look at the equilibrium structure these two should align. So, if I see it here if this has to align with this particular one then I am going to have and the LUMO is for is here this is the built in potential inside the, inside the organic diode in equilibrium.

And since there is no Fermi level defined in the material we are not connecting that, but these two will align. So, this is the condition when I am applying no voltage. So, the applied voltage is 0. Now, I can go forward bias or a reverse bias. In reverse bias case I will apply a positive voltage to cathode. So, this would be the reverse bias case and forward bias case where I will, where I will apply the negative to cathode or positive to the anode.

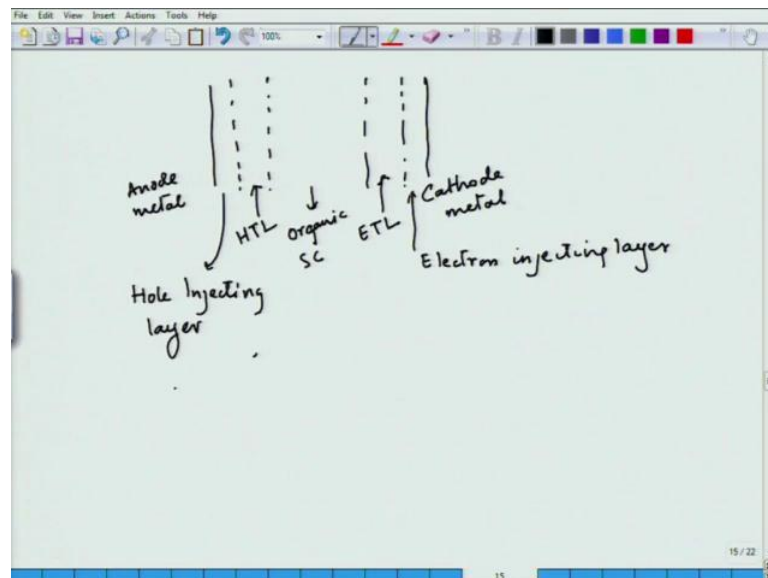
So, what will happen if I apply reverse bias in this case and a forward bias, I should then move the anode with respect to the cathode. So, in case of reverse bias the electrostatic potential of the anode is going to become less than that of the cathode. And in terms of electronic structure the energy level should move up. So, it is going to be like that and this would be the amount of applied reverse bias when V is less than 0. In that case I have increased the slope here due to the applied field and in the reverse bias I am trying

to take the electrons from the anode and the hole from the cathode and we can see that this is too much of barrier for electrons.

So, there will be no electrons and too much barrier for holes in this direction. So, there will be no holes. So, this would lead to a very low current. So, there should be no current in this direction and if I apply the forward bias then this is going to move in the opposite direction with respect to the cathode. This is applied forward bias and now we have, so it become a little too flat. We have a little less of slope or field in the material and it is easier for holes to electrons to go to the LUMO level and also very easy for the holes to go to the HOMO level. And this provides the forward current which is going to be very large.

So, if I would look at the IV characteristics of this O LED diode the voltage and current, I am going to find, in the forward direction I will have large current and the reverse direction I will have very little current. And that is how a O LED diode works, organic diode works. So, with this particular structure then we go on to describe a little more complex structure. What was then found was that these organic materials as we have already seen have very low mobility and if you want to make the device work.

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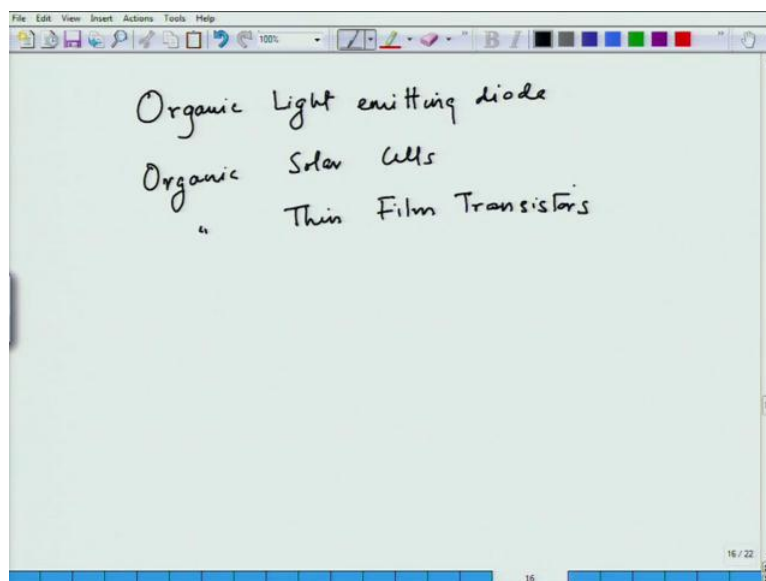
Generally, the structure of the device is going to be the anode metal which is injecting the carriers, the holes and the cathode metal which is injecting the electrons in the forward bias. And in between another layer of material is used which is referred as

electron injecting layer which further lowers the work function of the metal. And on this side one can use another layer which is known as the hole injecting layer. And after that we have the organic material in which we can divide by, we can have the organic semiconductor which is my active material.

And in addition to that in order to improve the conduction I will use a layer called hole transporting layer and on this side I will use a layer called electron transporting layer. So, you can see I can have many options for organic materials. In order to improve the device behaviour I can add other electronic materials to my device which will help the conduction and injection of the carriers. And this is another advantage of organic semiconductors.

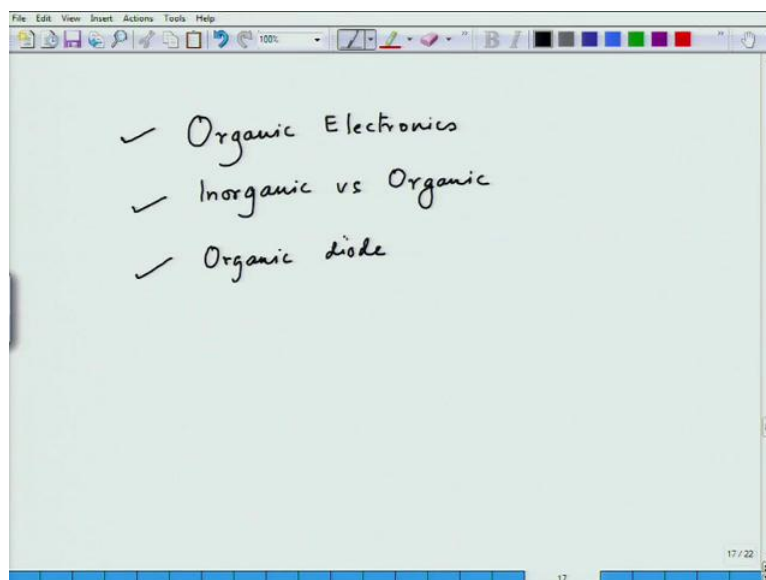
In inorganic semiconductors there are very few semiconductors that you can use. There you have silicon gallium arsenide, which dominate the discussion and there are few others which have very specialised applications. But in organic semiconductors there is no limit. One can use, one can change the molecule a little bit and there you have a new semiconductor and that is the another big drive for organic semiconductor because of this reason, because you can alter the chemistry and make new materials very easily. So, there are many options for organic semiconductors. Now, the same light emitting diode I can use a organic semiconductor to make either a light emitting diode or solar cell.

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So, now I will discuss in the next few lectures organic light emitting diode, organic solar cells and organic thin film transistors.

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So, in summary I hope to have shown you a very new area of organic electronics. The key people in this field which initiated the field and the development in the area, the main key differences between inorganic versus inorganic semiconductors. And a very surprising result that even though the organic semiconductor is not crystalline, it is amorphous in nature, they work equally fine. The only problem with the organic semiconductor is they are the mobility of the carrier is very low, because it is a hopping mechanism of conduction and hence we can never replace silicon. We looked at how we defined, how O LED organic diode works as opposed to a diode which is made of a p-n junction that we have seen earlier.