Solar Photovoltaics: Principles, Technologies and Materials

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Lecture - 38

Generation III Technologies: Organic Solar Cells

So, welcome again to the new lecture of this course on Solar Photovoltaics Principles Technologies and Materials.

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Recap

- Second Generation photo voltaic technologies
- Thin Film based devices
  - a-Si
  - CdTe
  - Cu(In Ga)Se_2
  - Multijunction

So, what we have covered in last few lectures is; so just it is going to be recap of last few lectures. So, we talked about second generation solar cells or second generation photovoltaic technologies, which were based on thin film based devices.

And the; in these category we mainly studied amorphous silicon solar cells, we studied cadmium telluride based solar cells, then copper indium gallium selenide based devices and then finally, we looked at multi junction. These are primarily 4 technologies that we talked about in the last few lectures.

So, now we will move on to the third generation technologies.

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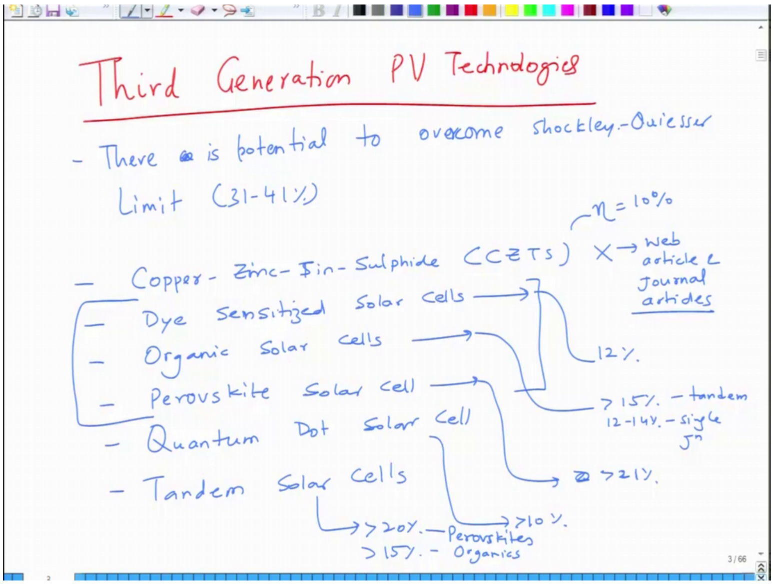

Third Generation PV Technologies

- There is potential to overcome Shockley-Quiesser Limit (31-41%)
- Copper-Zinc-Tin-Sulphide (CZTS) × → web article & Journal articles
  $\eta = 10\%$
- Dye Sensitized Solar Cells → 12%
- Organic Solar Cells → >15% - tandem
  12-14% - single J^n
- Perovskite Solar Cell → >21%
- Quantum Dot Solar Cell → >10%
- Tandem Solar Cells → >20% - Perovskites
  >15% - Organics

So, these are called as Third Generation PV Technologies and these are primarily because there is a potential to overcome Shockley-Quiesser limit. And that limit places efficiency rate about 31 to 41 percent and there is a potential in these technologies to overcome this limit.

The technologies of concern are to begin with a close cousin of CIGS which is Copper Cinc Tin Sulfide. We commonly call it as C Z T S, then we have dye sensitized solar cells, then we have organic solar cells. And off late in last few years we have perovskite solar cells and then another technology which is quite interesting is quantum dot solar cells. And of course, and these we can also add tandem because these devices are also coming in tandem solar cells.

So, tandem includes 2 G and 3 G it was also present in 2 G and it is also present in 3 G technologies. So, if time permits ah; so primarily we will look at dye sensitized solar cells, organic solar cells and perovskite because these are 3 distinct technology from the 2 G technologies.

Copper zinc tin sulphide is fairly similar technology to C I G S solar cells. So, we will not cover this in this lecture; however, if you are interested to read about it you can there are plenty of web articles and journal articles in which you can read about this technology. It is a potentially interesting technology with the efficiencies of the order of.

So, C Z T S has an efficiency of about 10 percent. So, this has efficiency of about 10 percent dye sensitized solar cells give you efficiencies of the order of about 12 percent.

So, roughly 12 percent organic solar cells; if you look at in tandem form then more than 15 percent and non; so this is for tandem and single junction will give you about 12 to 14 percent devices. Perovskite solar cells have exceeded 21 percent, then world record now stands at about 23 percent, quantum dot solar cells are at about 10 more than 10 percent. And tandem cells in these perovskites have crossed 20 percent whereas in organics they have crossed 15 percent.

So, we will look at the middle 3 technologies that is these 3 technologies in detail in this in the next couple of lectures. We do not have time to go through quantum dot and copper zinc tin sulfide, but if time permits I will cover them in a lecture or so.

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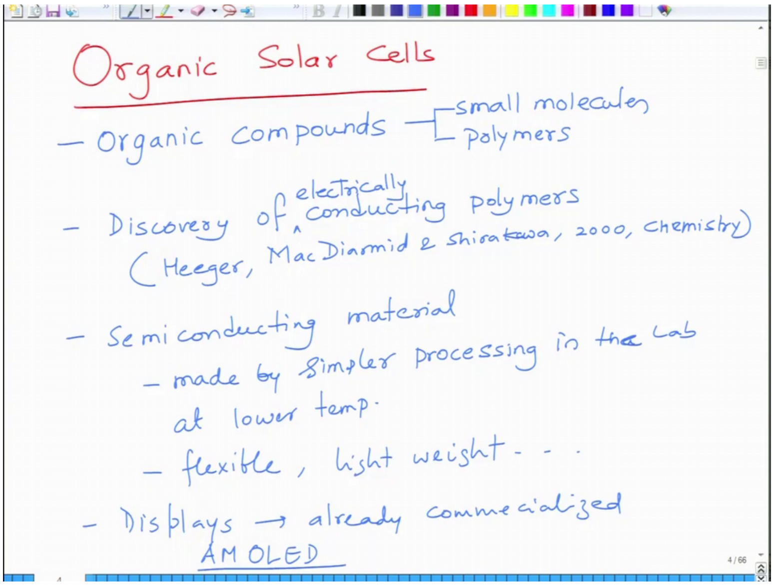

Organic Solar Cells

- Organic compounds — small molecules / polymers
- Discovery of electrically conducting polymers (Heeger, MacDiarmid & Shirakawa, 2000, Chemistry)
- Semiconducting material
  - made by simpler processing in the lab at lower temp.
  - flexible, light weight . . .
- Displays → already commercialized AMOLED

So let us look at first the organic solar cell technology to we will begin with the organic solar cell. Now these are this is an interesting technology because here we do not use inorganic materials; rather we use organic compounds which are called as either small molecules. So, these are organic small molecules or polymers.

So, basically their composition is consists of carbon, hydrogen, nitrogen, sulphur etcetera as is presence in these present in these materials. And these materials became prominent after discovery of by; so these becomes popular after discovery of electrically conductive polymers. So, we can say electrically not thermally, but electrically and this was this resulted in a Nobel Prize to Heeger Mac Diarmid and Shirakawa in 2000; this is Chemistry Nobel Prize.

This discovery although it was made a earlier it opens the floodgates for a different kind of electronics away from silicon electronics and this gave rise to these organic materials, polymeric materials which could conduct electricity. They were semiconducting materials; so, these are semiconducting materials which can be made by simpler processing in the lab nd that is their USP to make oxide you need to dig out things make them react to make telluride you need to have cadmium source, tellurium source and generally the processing of those materials is high temperature processing.

Silicon is made through high temperature processing, cadmium toroid is made through high temperature processing, cadmium indium gallium selenide is made high temperature processing. These can be made in the laboratory through simple processing at lower temperatures also these are organic materials, they are flexible. So, you can make devices which are on plastic substrates; they can be lightweight and so on and so forth.

One of their close cousins is already in application that is in displays; so displays are already commercialized. So, you have these OLED displays in mobiles, AMOLED displays in mobiles and TVs and all that Samsung and LG; they are competing with each other; they are already commercialized.

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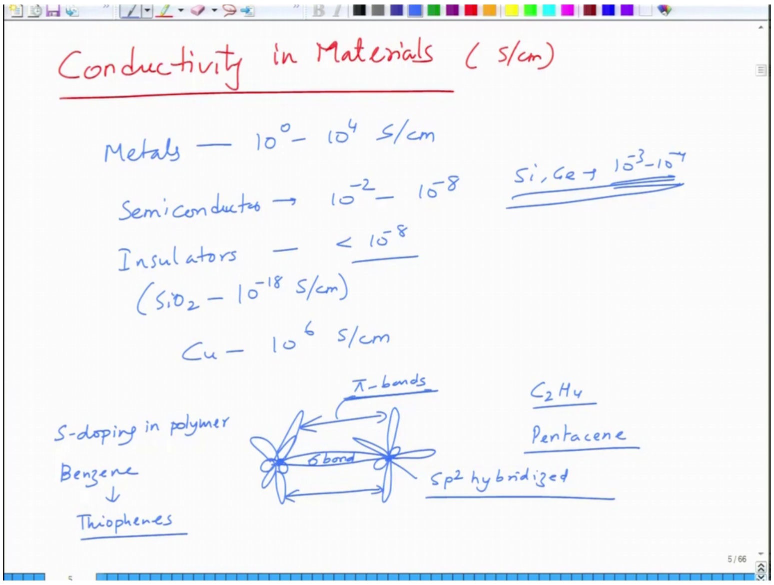

Conductivity in Materials (S/cm)

Metals — $10^{0} - 10^{4}$ S/cm

Semiconductors → $10^{-2} - 10^{-8}$

Insulators — $< 10^{-8}$

($SiO_2 - 10^{-18}$ S/cm)

Cu — 10^{6} S/cm

Si, Ge → $10^{-3} - 10^{-4}$

S-doping in polymer

Benzene

↓

Thiophenes

π-bonds

σ bond

C_2H_4

Pentacene

sp^2 hybridized

In this; in the present courses context we are going to learn about their use in organics in solar cells. So, these are materials which are which can be made potentially through low cost although right now the cost is very high because the processing is scale up has not been done. But there is a potential to lower the cost in terms of processing they are flexible they could be lightweight, they are also many of them also biodegradable and you can tune them you can tune their composition very easily they can be processed at lower temperature. So, these are certain advantages of using organic solar cells. So, if you look at the conductivity variation in materials and this is electrical conductivity by the way not thermal conductivity. So, and this is in Siemens per centimeter.

So, metals have a conductivity which is of the order of 10 to the power 0 to 10 to the power 4 Siemens per centimeter. Whereas, semiconductors have in the range of 10 to power minus 2; I do not know to 10 to power minus 8; whereas, for insulators it would be less than 10 to the power minus 8 ok. And generally your silicon and germanium will fall in the range of 10 to the power minus 4 or so; silicon and germanium will fall around minus 3 to minus 4 or maybe minus 5 depending upon the composition. So, if you look at quartz on the other hand Si O 2; this has a minus 18 Siemens per centimeter.

If you look at copper it has a value of 10 to power 6 Siemens per centimeter. So, you want polymeric materials to have conductivities which are in the order of semiconducting range. This was not possible earlier most of the polymers were insulating, they were you can see in electrical sockets and various other applications most of the plastics that we use are insulating.

However, the discovery of this by Ellen Heeger and Shirakawa and Mac Diarmid that opens the floodgates for designing compositions in organic materials which could be conducting. And this happens mainly because suppose you have an organic molecule and this has this. So, we have these atomic orbitals they let us say two molecules are making a bond. So, of course, it has these and so on and so forth.

So, between these pi lobes between these p lobes on that side; so there is a sigma bond here. So, let us say this is a; I do not know maybe you can take ethylene molecules alright poly or you can say; you do not know you can take pentacene molecule. So, in these things along the carbon chain you have a sigma bond which is a strong bond, but on the periphery we have pi bond and this double. So, you have this double bond here between the S p 2 hybridized carbons.

So, these carbons are S p 2 hybridized, but on the periphery we have this between the pi lobes we have pi bonds and these pi bonds are weaker in nature. And along these pi, along the outer periphery we there is a conduction that takes place for electrons; if you provide the composition if you have composition which is appropriate to make this happen and this generally happens by doping.

So, for example if you do sulfur doping in polymers; sulfur doping in polymers; for example, in benzene right this gives rise to what we call as thiophenes. This allows this pi pi transport along the pi channel. So, this; so it is not present in every polymer. It is present only when you dope it appropriately and this doping comes from the external elements other elements second elements like sulfur.

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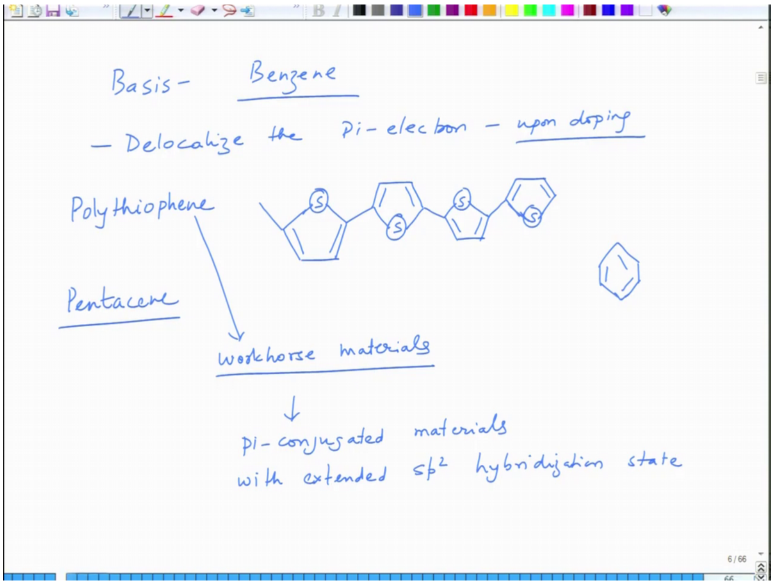

Basis - Benzene

— Delocalize the Pi-electron — upon doping

Polythiophene

Pentacene

workhorse materials

↓

pi-conjugated materials with extended sp^2 hybridization state

So, generally in many organic materials the archy type or the you can say the basis is benzene molecule. And when you start putting benzene molecules together then we start forming these compounds. So, basically what we want to do is that we want to the idea is to delocalize the; the pi electron. See pi electrons are present in other molecules as well, but they are not delocalized, they are localized and when the electrons are localized they do not they are not able to travel. So, you have to make them delocalized just like you have in metals to make them travel and to experience less force on them.

So, when you delocalize the pi electron upon doping these materials become conducting. So, these delocalized electrons are necessary for conduction to occur. So, basic and this does not happen along the sigma bond, it happens during the along the pi bonds because pi bonds are weaker as compared to sigma bonds. So, it is easier to delocalize the electron in the pi bands than in the sigma bands.

So, basically you; this happens in upon doping and this is where you have materials like polythiophene, we have pentacene which are conducting. So, if you look at polythiophene; polythiophene structure is something like this. So, you can see that your benzene ring otherwise is like this and it does not allow conduction because the electron is not localized.

So, by introducing these sulfur ions here in these rings you have made it delocalized. So, this is what you do in thiophene, polythiophene you also do it in pentacene and various other materials and polythiophene has been a back workhorse material in organic solar cells. So, when you dope these materials with elements like sulfur the molecules with extended S p 2 hybridization states become what we call as pi-conjugated materials.

So, these materials are also called as pi S p 2 hybridization state. So, S p 2 hybridization state is not localized, it is extended over a whole chain. So, as a result the these presence of these sulfur atoms here; it allows the conduction of electron to occur along the chain through the pi band.

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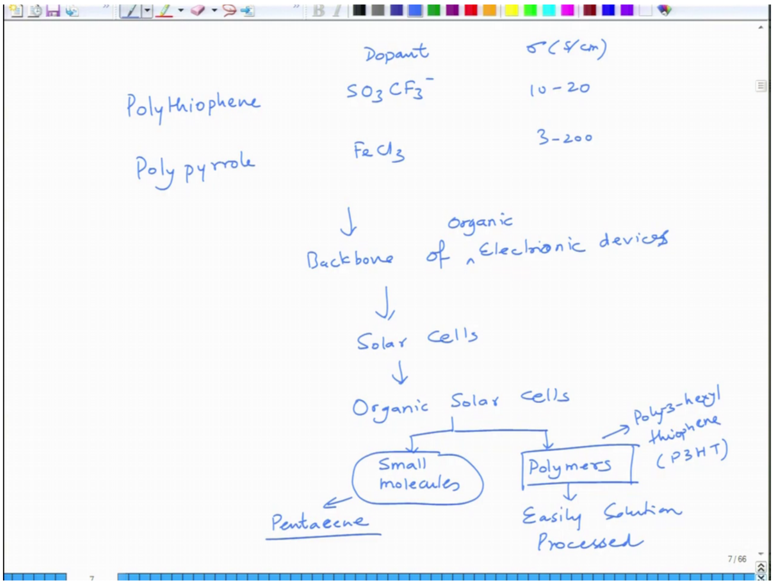

	Dopant	σ (S/cm)
Polythiophene	$SO_3CF_3^-$	10 - 20
Poly pyrrole	$FeCl_3$	3 - 200

So, if you look at conductivity comparison; so polythiophene for example, polythiophene has a; so, the dopant in this case is S O 3 C F 3 minus this is dopant and if you look at sigma values in Siemens per centimeter; it gives you a value of 10 to 20 ok; quite strongly conducting.

If you look at for example, polypyrrole; Fe Cl 3 is the dopant and you get conductivity variation between 3 to 200; so they become strongly conducting as against their undoped counterparts; which are strongly insulating. So, this is the power of doping in polymers which basically creates delocalized pi electrons which can conduct along the chain of the molecule giving rise to conduction.

So, these materials make the backbone of electronic; you can say organic electronic devices and this is and solar cell is one of them. So, materials which are based on these are called as organic solar cells. There are two kinds of materials which we generally use one is called as small molecules; small molecules are the materials which are materials of a small molecular weight.

They do not have extended chains smaller molecular weights and then we have polymers are of higher molecular weight. Generally polymeric solar cells are preferred because small molecules are difficult to be synthesized through solution processing root. They can be synthesized nowadays they can be synthesized through solution processing route, but small molecules are generally used in devices because they have very good evaporation capability.

So, you can evaporate them just like metals, but evaporation is a process which does not allow you to make large area devices. So, making large area solution large area devices is not very easy using small molecules. That is why most of the organic solar cell research has concentrated on the use of polymer because polymers can be easily solution processed. So, material like polythiophene poly; so it is called as poly 3 hexylthiophene which is called as P 3 H T ok. This is a polymer, but material like you know you can have a pentacene; pentacene is a; it is not a polymer it is a small molecule it can be evaporated easily.

So, we generally focus on polymers instead of small molecules and organic solar cell research. Although there is no discredit to small molecules community there are lot of good solar cells which have been made using small molecules using both evaporation and solution deposition, but we will mainly consider on polymer solar cells in this lecture.

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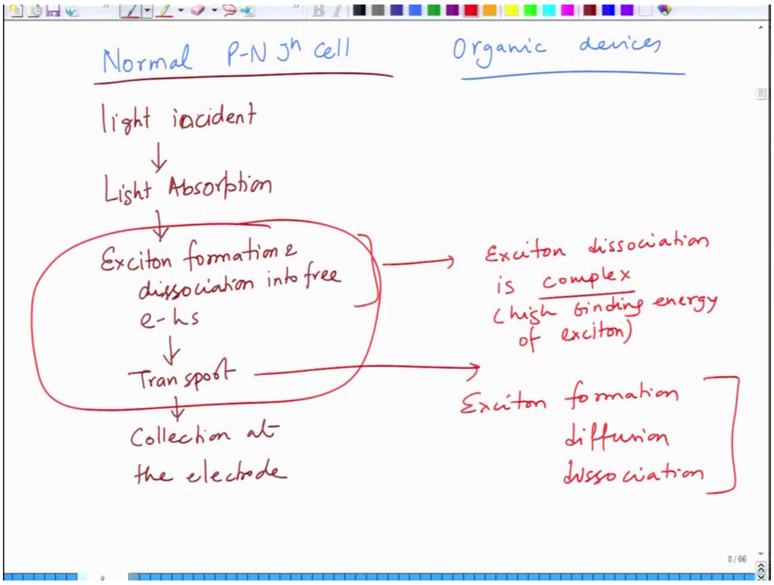

Normal P-N J^n cell

light incident

Light Absorption

Exciton formation & dissociation into free e-hs

Transport

Collection at the electrode

Organic devices

Exciton dissociation is complex (high binding energy of exciton)

Exciton formation
diffusion
dissociation

So, we know that in a solar cell what happens is that we have you know light comes on to the solar cell; then it you absorb the light. So, you know in a normal solar cell; so first step is you have light incident, then light absorption, after light absorption you have excitons formation and dissociation into free electron and holes after this we have separation of charge.

So, you have transport of charges and after transport, you have you have collection at the; in the normal inorganic p n junction solar cell these steps are relatively straightforward. The light comes, light is absorbed you form exciton, exciton has very low binding energy and it readily dissociates into electron free electron and free whole.

The free electron and free hole are swept away on either side of the junction through inbuilt electric field and this built in electric field and these transport carriers transport to the junctions to the electrodes and then they are collected. However, in an organic device while the steps remain the same in case of organic; this exciton dissociation is a problem; is rather complex because exciton binding energy of exciton and then again exciton transport, then carrier transport is also an issue because carriers have a smaller diffused that these excitons also have smaller diffusion length.

So, exciton must dissociate into small must dissociate into carriers before the carriers are recombined. So, carriers must find the electrode before they recombine and form the exciton again. So, these two steps exciton formation dissociation and transport; these steps are very really critical in case of organic solar cells and this is what has been the focus of behind the design of present architecture of organic solar cells.

So, in case of agri solar cells; exciton formation, exciton diffusion and exciton dissociation these are the things which are of utmost importance. So, exciton formation, exciton diffusion and exciton dissociation; these things are extremely important. And of course, you would like to minimize the recombination as well to back into excitons.

So, we will just mention the energies in excitons here; so exciton binding energy in case of in case of inorganic solar cell.

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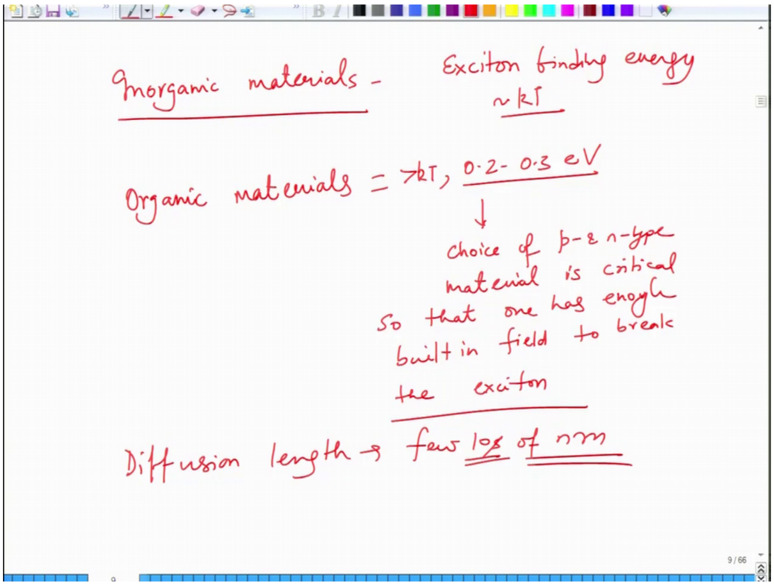

Inorganic materials - Exciton binding energy $\sim kT$

Organic materials $= > kT$, 0.2 - 0.3 eV

↓

Choice of p- & n-type material is critical so that one has enough built in field to break the exciton

Diffusion length → few 10s of nm

The exciton binding energy is of the order of k T; they get dissociated very easily using the thermal energy. In case of organic materials this energy is about 0.2 to 0.3 electron Volt much higher than k T; so it is higher than k T, it could be as high as 0.2, 0.3 or even 0.4 electron Volt; this energy has to be supplied from somewhere. So, that is why you need to create a junction in such a manner so that you have enough field electric field available to break this exciton and this has to come from the constituents of the solar cell.

So, that is why the choice of; choice of p and n-type material is critical so that one has enough built in field to break the exciton into electron hole pair. And then this exciton also has short diffusion length; the diffusion length of exciton is of the order of few 10s of nanometer. So, be exciton has to be broken away before this diffusion length. So, this creates a concern on the device design which means your device thicknesses of or also of the order of few 10s of nanometer if you have a single layer a bi-layer devices.

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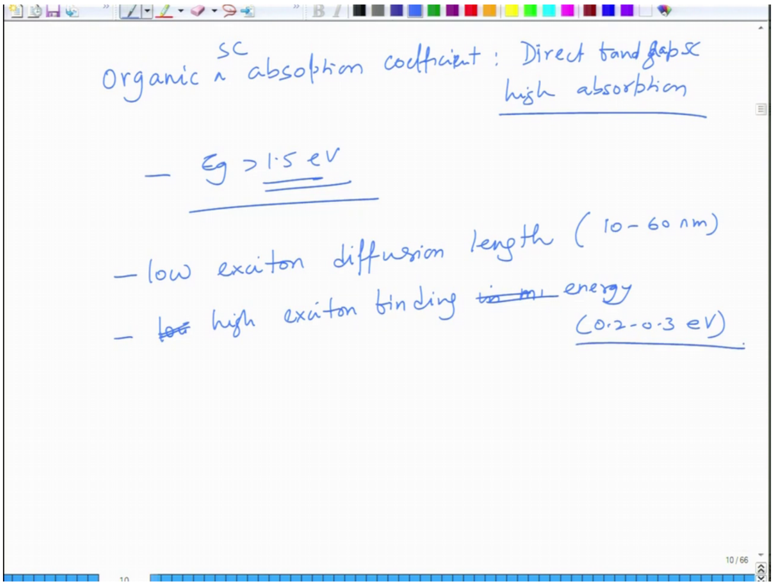

Organic $\overset{SC}{\wedge}$ absoption coefficient : Direct band gap SC
high absorbtion

- $E_g > 1.5$ eV

- low exciton diffusion length (10 - 60 nm)
- ~~low~~ high exciton binding ~~tio mi~~ energy (0.2 - 0.3 eV)

So, based on these two constraints; so there are three designs of solar cells which are possible here. When it comes to organic materials absorption coefficient organic semiconductor absorption coefficient; it is they act as a direct band gap semiconductor. And they have high absorption, but the band gap of these materials is generally higher than 1.5 e V ok.

So, their band gap is on the higher side, but they have good absorption coefficients. So, the if you; if you summarize these materials they are direct band gap semiconductors, they have relatively higher band gap, they have low exciton diffusion length. Before electron and holes recombine they this is the mini; this is the maximum length they can travel.

So, you can say about you know it could be anywhere between 10 to 60 nanometer and then they have high exciton binding energy. Keeping these constraints in mind, you need to design a binding energy of the order of 0.2 to 0.3 e V; keeping these constraints in mind you need to design a organic solar cell.

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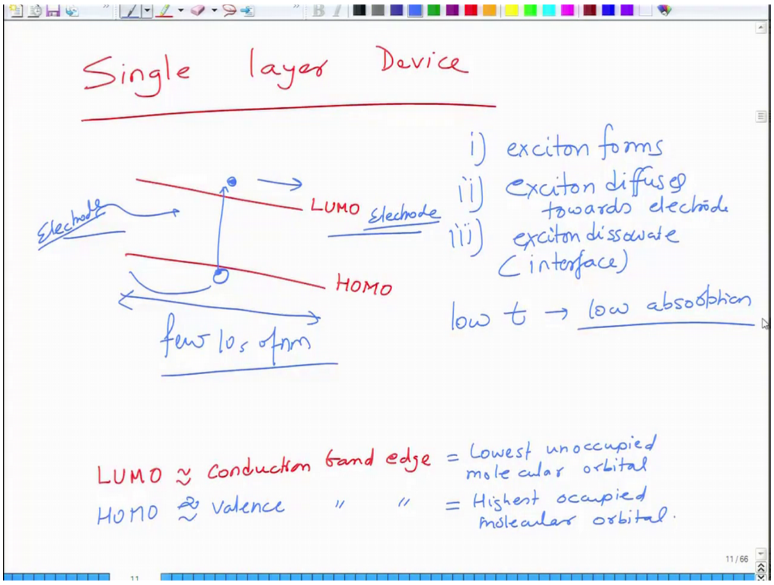

Single layer Device

i) exciton forms
ii) exciton diffuse towards electrode
iii) exciton dissociate (interface)

low t → low absorption

LUMO ≈ Conduction band edge = Lowest unoccupied molecular orbital
HOMO ≈ Valence " " = Highest occupied molecular orbital.

So, the first layer design of a solar cell is single layer jump device. So, what happens here is basically you have a single polymeric material like this; in case of polymer another thing that you will come across is instead of calling them conduction band and valence band, we call the band edges as LUMO and HOMO; where LUMO is equivalent to conduction band edge in organic in inorganic materials; it is not similar, but it is equivalent and this is basically called as lowest unoccupied molecular orbital.

See the thing is these are not ordered materials that is why the band theory result isn’t really applicable to these materials because they a periodic materials.

So, we talk here in terms of molecular orbitals instead of energy bands, but there are certain similarities which one can make. And then the lower one is called as HOMO which is similar to valence band edge in inorganic materials and this is called as highest occupied molecular orbital. So, in these materials when the light comes in there; the electron get excited from here to here, it goes here, later on and forms a hole.

However, until it is separated it remains a exciton; so now, this exciton will separate towards one of the electrodes. So, you have these electrodes on this side and this; so, they will diffuse to this side together and then the work function difference between the two metals and two sides will provide them enough energy so that they can dissociate. So that your hole will come; so first the exciton first what you will have is exciton forms.

Second step is exciton diffuses, third step is exciton diffuses towards electrode; one electrode one of the electrodes ok. And that depends upon the exciton where the excitons are created more whether on top or whether on the bottom. And then so diffusion gradient is going to move the exciton and then exciton dissociates and dissociation happens at the interface.

So, interphase must have some sort of energy to break this exciton. So, these are the three processes and as we said that exciton diffusion length is about few 10s of nanometers; the whole device thickness cannot be larger than few 10s of nanometer. If, so if your device thickness is controlled by this diffusion length which means your solar cell cannot be very thick.

If your solar cell is not very thick; so this is electrode you can say this is electrode metal electrode this is also electrode. So, you have to use two different metals so that you provide a there is a work function difference. So, one is high work function one is low work function metal. This creates a problem because now if you device thicknesses lower; you are not going to be able to absorb lot of light. So, low thickness means low absorption.

So, that is why even though you might absorb the light you might break the exciton; you simply do not absorb enough number of photons as a result your absorb efficiency is low. And this led researchers to make other architectures in the organic solar cells which we will see in the next lecture.

So, we stop here what we have seen today is in this lecture is about the organic solar cells, the introduction, what is the genesis behind them, what is the motivation behind them. We talked about excitons; why exciton is a problem in case of organic solar cell and how one needs to evolve a strategies to overcome this problem alright. So, we stop here.

Thank you very much.