Solar Photovoltaics: Principles, Technologies and Materials
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Lecture - 39
Generation III Technologies: Organic Solar Cells

So, welcome to this new lecture of Solar Photovoltaics course Principles, Technologies and Materials. So, we have been talking about generation III Solar PV technologies and we just initiated our discussion on organic solar cells in the last lecture.

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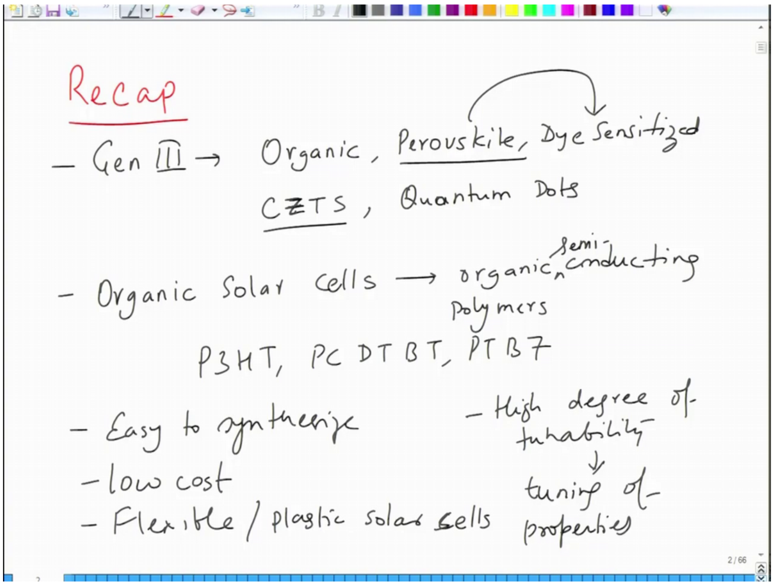

Recap

- Gen III → Organic, Perovskite, Dye Sensitized
  CZTS, Quantum Dots
- Organic Solar Cells → organic semi-conducting polymers
  P3HT, PC DT BT, PTB7
- Easy to synthesize
- low cost
- Flexible / plastic solar cells
- High degree of tunability
  ↓
  tuning of properties

So, let us just recap the last lecture. So, in the Gen III technologies, we have Organic solar cells; we have Perovskite solar cells and we have Dye Sensitized solar cells. And this perovskite is actually a direct extension of dye sensitized solar cells, it has evolved from the same technology just that it uses different materials.

You also have Copper Zinc Tin Sulfide CZTS and Quantum Dots solar cells in the same. So, if time permits we will discuss at least CZTS in this lecture. So, we were talking about organic solar cells. So, organic solar cells you use organic conducting polymers or the semiconducting polymers; polymers are generally insulating in nature and it was after a pioneering work of (Refer Time: 01:40) and (Refer Time: 01:42) viewer we are now having doped polymers which are semiconducting or conducting in nature. And polymers such as P3HT PC DT BT these are all thiophene or carbonyl or benzopyrene based materials. So, there are various formulas pretty complex formulas, but let us just like have a look at the acronyms PTB7 etcetera, they have emerged as choice of materials for these solar cells.

Now, these plastic based solar cells of certain advantages, they are easy to synthesize and in principle they can be low cost and they can also make flexible plastic solar cells which could be useful for certain applications. Another advantage of these is that they have high degree of tuneability; so, high degree of tuneability because they are synthesized in lab through chemical routes. So, this high degree of tuneability allows tuning of properties such as band gap. So, these are certain advantages and we were also talking about certain disadvantages.

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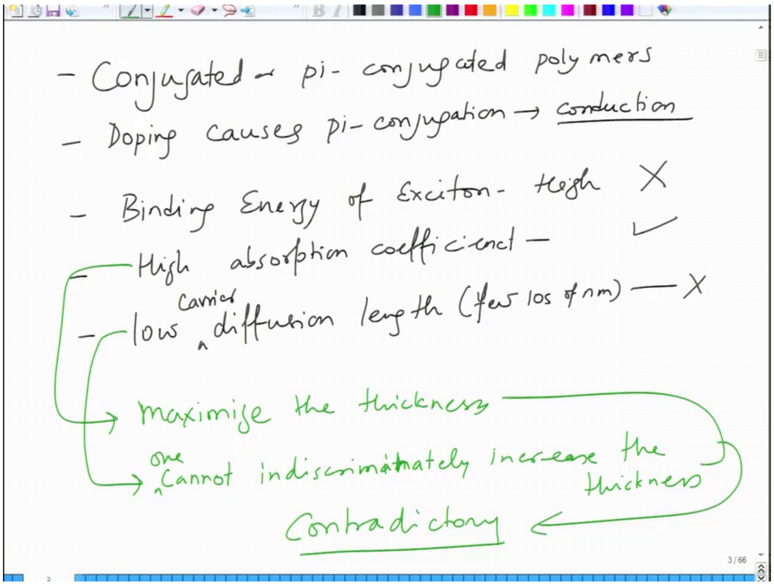

- Conjugated ~ pi- conjugated polymers
- Doping causes pi- conjugation → conduction
- Binding Energy of Exciton - High ✗
- High absorption coefficient — ✓
- low carrier diffusion length (few 10s of nm) — ✗

→ maximize the thickness

→ one cannot indiscriminately increase the thickness

Contradictory

These materials these materials are basically you can say conjugated or pi conjugated polymers ok, where conduction of electrons happens between pi pi's between the pi bonds or a pi backbone of the pi segment of the backbone and this happens by a doping. So, doping causes pi conjugation leading to conduction. So, conduction does not happen in sigma bands. It happens in the pi bands or pi electrons are the responsible for conduction.

So, we cannot go into details of how the conduction happens; it is just that you have to read more about organic semiconductors. There are plenty of literature available or organic semiconductors, but what they have something with us with the with regard to solar cells is that they have what we call as binding energy; exciton binding energy. So, binding energy of exciton in these materials is high. This is a drawback in these solar cells. So, this is the drawback. They have high absorption coefficient because they are nearly direct band gap semiconductors, since there are amorphous in nature or semi or semi crystalline in nature. They tend to have band structure which makes them almost like a direct band gap semiconductor. They have high absorption coefficient and they also have another problem that they have low diffusion lengths.

So, carrier diffusion length is low carrier diffusion lengths. This is of the order of few 10s of nanometer and this is also a problem. So, on one hand, you would like to maximize the thickness because of high absorption coefficient. So, that you are able to absorb maximum amount of light. So, on one hand, we have a conundrum that because of this we would like to maximize the thickness. But low carrier diffusion length cannot one cannot indiscriminately indiscriminate discriminately increase thickness because carrier diffusion length is lower.

So, these two factors are you can say they are contradictory and this poses a restriction on the thickness of material that one can use. So, as a result, there are various designs which have been proposed for making organic solar cells.

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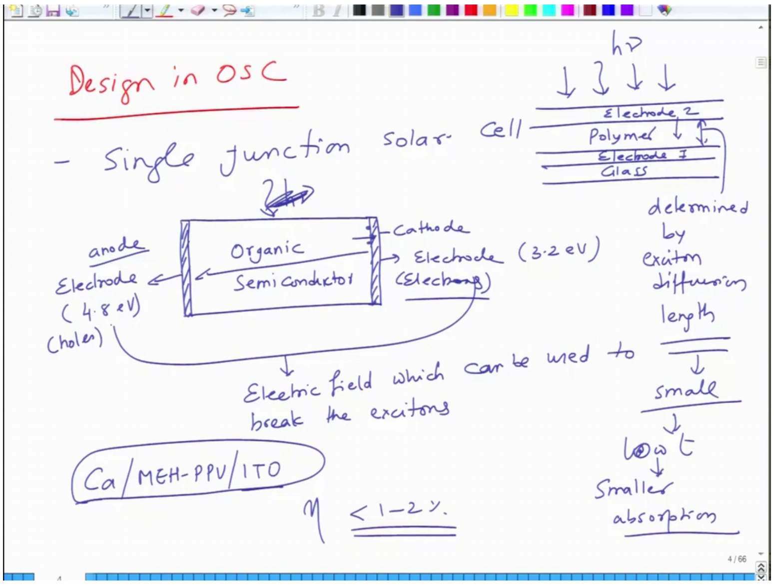

Design in OSC

- Single junction solar Cell

Electric field which can be used to break the excitons

Ca/MEH-PPV/ITO

$\eta < 1-2\%$

determined by exciton diffusion length → small → low t → Smaller absorption

So, we have three designs here; one is so designs in organic solar cell. So, generally initially people use to use Single junction solar cells. We were talking about that in the last class. So, what you have you have a metal on one side, then you have another, then you have a polymer in the middle, then you have another metal in the on the other side. So, this is metal 1; this is metal 2. So, for example, this metal 1 has a has a so this is semiconductor. So, you can say this is organic semiconductor and this is electrode 1 and this is electrode 2.

Let us say this electrode has a work function of 3.2 electron volt and this has a work function of 4.8 ev. These two have to have different work functions so that you have enough. So, they give rise to electric field which can be used to break the excitons ok. So, for as the light falls on it; as the light falls on it, the excitons are created, then excitons move towards 1 electrode. So, generally light will not come in this fashion, you device will be in this fashion. So, this will be substrate. This will be electrode 1; this would be polymer and this would be the electrode 2 so, light will come in this fashion.

So obviously, from the top excite there will be more excitons which are created in the top than in the bottom. As a result excitons will diffuse towards this electrode. So, when electron when exciton diffuse to. So,. So, that this thickness of this polymer is determined by determined by exciton diffusion length which is very small. So, as a result these devices are not very thick, they are very thin. So, since they are very thin they cannot absorb a lot of light. So, which means they cannot low thickness which means smaller absorption. So, as a result quantum efficiency of these devices generally lower because they cannot absorb a lot of photons. So, what happens here is when the exciton reach this interface let us say these excitons because of the built in electric field they get dissociated. So, one carrier will move here and another carrier will go there.

So, for example, in this case if you have; so, if you have this as a at 4.8 ev; this has 3.8 ev. So, this can be used as a cathode and this will be used as anode. So, holes will be collected here and electrons will be collected here. So, the main problem with this device is that this has lower. So, for example, materials like you can make a device between calcium MEH PPV which is a polymeric material. So, it is a phenalene phenalene vinylene waste material PPV; MEH PPV and ITO. So, ITO is one electrode; calcium is another electrode. So, ITO is has a work function which is higher as compared to calcium; calcium is a more reactive metal.

So, in these devices one can obtain one obtains the smaller efficiencies, but these are this is for example, one of the device efficient; one of the devices which have been used in these materials. So, efficiencies in these devices will be less than 1 to 2 percent generally, smaller efficiencies. People have demonstrated higher efficiencies, but getting higher efficiencies is not easy in these devices because of limitations of thickness. So, because of this problem in limitations in thickness then somebody came up with the concept of Bilayer Solar Cell.

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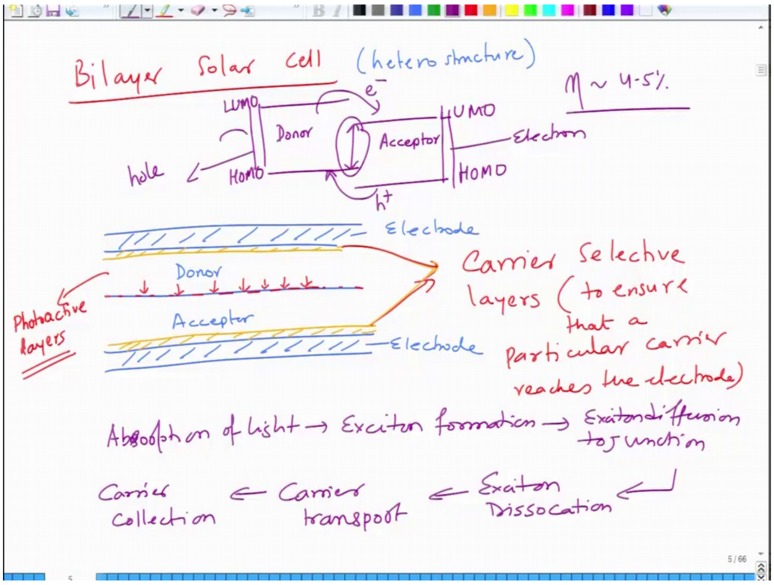

So, Bilayer Solar Cell is pretty much it is just like a just like it. So, it is basically a it is a you can say it is a hetero structure just like a p-n junction solar cell in 2 G devices. So, what happens here is you have a so basic structure is you have a Bilayer. So, you have a donor; you have acceptor and then, you have electrode 1 and then we have electrode 2. This is the basic structure.

In between you can also have sometimes carrier selective layers here and here. So, you can have these are carrier selective layers such as whole transporting. So, to ensure that so, let me just write in a darker color. So, this is to ensure that a particular correct carrier is reaches the electrode right. So, basically you can have electron selectivity and hole selectivity ok. So, these devices generally so what happens here is you provide a junction in between. This is the junction; this is the interface. So, you create excitons; excitons moved. So, generally the absorbing material in this case is donor ok. Donor is the you can say a photo active layer in most cases. Donors have better for better absorption for light as compared to acceptors. So, your light will fall here, you will create excitons, these excitons will move towards the interface and because of differences in HOMO and LUMO of the donor and acceptor, we will have an internal electric field which will break these exciton and so, free charge carriers which will then move and move towards the electrode.

So, what you will have is you will have so first is absorption of light. Then, you have exciton formation. Then, we have exciton diffusion to the junction and then, we have exciton dissociation which happens because of differences in the energy levels of donor and acceptor and then we have. So, just like you know you have differences in the fermi levels of p and n type, here we have differences in the HOMO and LUMO levels of these two semiconductors which so basically HOMO of one and LUMO of another forms the minimum energy gap and this provides a built in field.

So, exciton this dissociation; so what will happen is that you will have so this is the for example, donor. This is the acceptor. So, this gap; so, this is LUMO, this is HOMO; this is LUMO and this is HOMO. This gap provides the built in electric field bit to break the exciton. So, this is for example, donor and this is acceptor. So, once the carriers are broken they will move towards either side. So, as a result you will put a metal on both sides and they will get collected. So, exciton dissociation then you have we have carrier transport and then, we have carrier collection.

So, this is basically hetero junction concept in which we have a bilayer of donor and acceptor and these can give you fairly high efficiencies as compared to. So, these have given efficiencies of the order of 4 to 5 percent latest. So, for example, you can have a junction between one of the first junctions that were made was so on a glass substrate.

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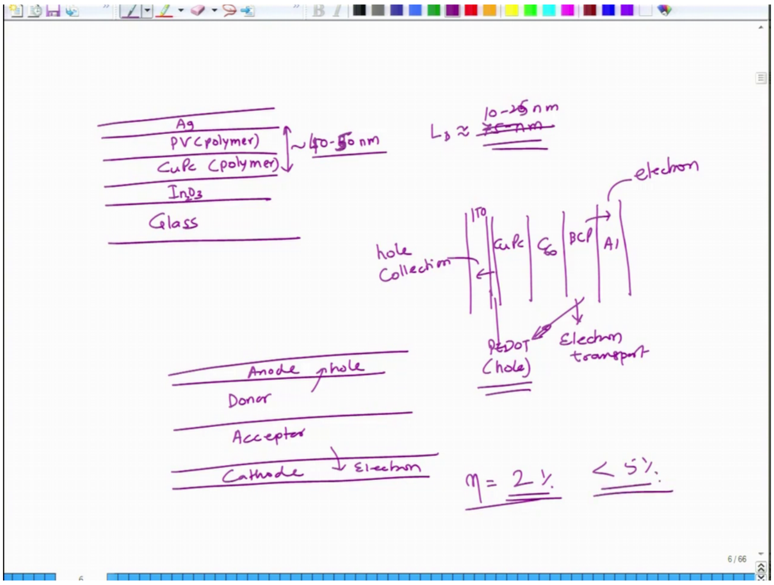

We have Indium oxide electrode and then we have what we call as Cu Pc polymer and then we have PV as another polymer or organic material and then we have silver as a electrode. So, when you have these devices, then silver acts. So, in these cases what happens is that you have so you can you can max. So, let us say if the device thickness in these cases can be about 50 to 80 nanometer; if your diffusion length is about let us say 75 nanometer or so. So, you can have sorry diffusion length is about 10 to 20 nanometers; sorry I am saying 10 to 20 nanometer and in this case so for either side of the junction you can have about 20 nanometers; we can have about 40 to 50 nanometer thickness.

So, roughly 40 to 50 nanometer thicknesses possible in these devices, so this can vary from 10 to 25 or so something like that. So, this can give you 10 to 25 nanometers of thickness. So, you have so on the donor side. So, this is for example, you can have a configuration like this. You can have donor; you can have acceptor; this is the junction. So, on the acceptor side let us say we have cathode and the donor side we have anode. So, you have hole collection on this side and electron collection in this side.

So, it depends about the energy levels of donor of anode and cathode with respect to HOMO and LUMO of the two. So, if you look at this configuration here. So, you will create electrons. So, electrons will go like this, they will get collected here and holes will go like this they will get collected here. So, this is electrons; this is holes. So, here you will have hole collection and here you will have electron collection. So, basically where will electron and where will hole go that will depend upon the matching of energy levels of metals both metals with respect to the HOMO and LUMO of the of the semi conductors.

So, this is a typical bilayer solar cell that is one can also make a. So, for example, a very nice structure is for instance we have Cu Pc. Then, we have C 60 fullerene and then, there is a layer of BCP which is basically a carrier selective layers and then, we have aluminum on this side and then, we have ITO on this side; on this side, we have a thin layer of PE dot. So, this is PE dot PSS. So, these are carrier selective layers. BCP and PE dot, they are carrier selective layer. So, this is for hole transport and this is for electron transport.

So, what will happen is that your energy levels and align in such a manner that hole and electron can move in either direction. So, this P dot will allow only the hole transport. So, you have hole collection on ITO and you have electron collection on aluminum. So, holes will be blocked by this layer ok, they will provide a energy barrier to the holes. In some cases what you may have is you may have both electron and hole towards either of the electrodes to prevent that you use these carrier selective layers which provide a barrier for whole electron entry to the respective electrode. So, if you have anode must collect only holes not the electron.

So, otherwise you will have loss of electrons. So, as a result PE dot is put in which is a hole conducting, but electron blocking. Similarly on this side, we put a layer of BCP which is a electron transporting, but hole blocking. So, this is a concept which is used in organic solar cells. So, for example, these kind of structures can give you fairly good efficiencies of about you know about 2 percent or so. So, these are generally lower than 5 percent efficiency devices; bilayer devices. So, the to improve this solar cell, what we had was because the device thickness is still lower in this case, device thickness the absorption coefficient is absorption of light is limited.

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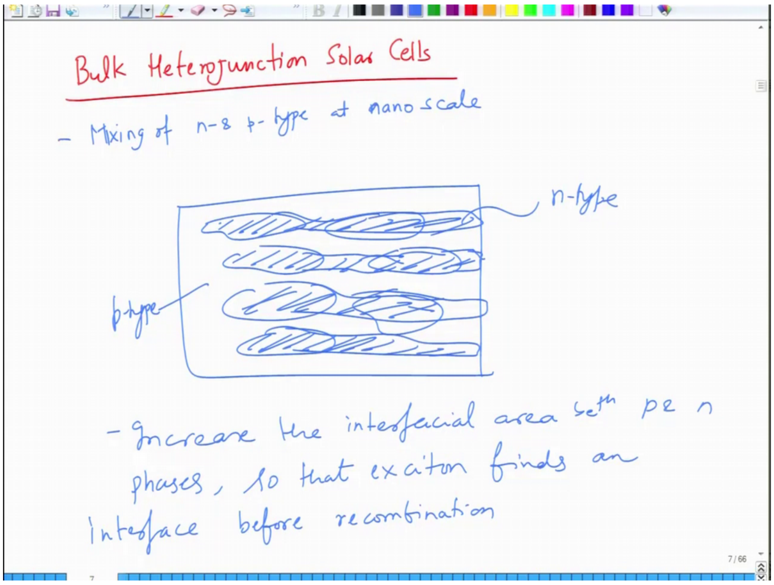

Bulk Heterojunction Solar Cells

- Mixing of n- & p- type at nano scale

- Increase the interfacial area betn p & n phases, so that exciton finds an interface before recombination

So, to overcome this, people came up with the concept of Bulk Heterojunction; Bulk Heterojunction Solar Cell. The concept is different here. The concept is if you cannot bring the carrier to the interface, you bring the interface to the carriers. So, what it was it was basically mixing off based on mixing of n and p typed acceptor and donor at nano scale. So, basically what it was? You mix these phases in such a manner. So, you have one as they have to be mixed in such a manner so that there is a continuous contact to the electrode ok; something like this.

So, let us say if this is this blue this is an n type material. This would be a p type material. So, wherever you create the exciton, it will always find the interface now in this composite form; provided the phases are distributed in such a manner so that n type phase so that one phase has so each of the two phases have continuous connection with the electrode. If you have broken paths, then carrier will not be able to reach the electrode.

So, this the requirement is so you basically what you do is that you increase the; increase the interfacial area between p and n phases. So, that exciton finds an interface because interface is the one which provides the built in field for it to break ok. So, exciton finds an interface before recombination; before it recombines and loses itself. So, excite. So, the idea is to increase the interfacial area the probability to find the interface within the diffusion length is higher because you have mixed donor and acceptor at the nano scale.

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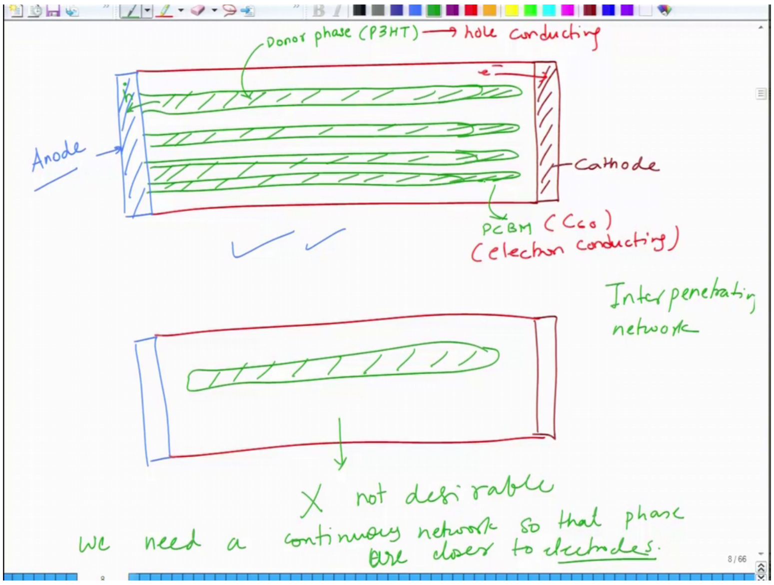

We need a continuous network so that phase are closer to electrodes.

So, this concept is very useful concept and this gives rise to; so, for example, the one schematic could be you have a electrode 1 metal and then, you have another metal on this side all right. This is let us say cathode and this is let us say anode and in between you have intermixing of phases in such a manner so that you have this phase at. So, this is the ideal morphology you would like to have; you have these nanostructures of. So, let us say this is the donor phase; let us say this is P3HT, poly 3 hexylthiophene and this is PCBM.

So, in such a manner your holes can; so, since you can create a lot of light the exciton will always find an interface, you have lot of interfacial area. The carriers, the holes will transport this way because this is the hole transporting material the it is a it has a better mobility for hole the donor phase whether is the acceptor phase which is the so these would be little longer than this and your. So, the holes will transport this way and your electrons will transport sorry they will go through here electrons will transport.

So, they have this narrow structure in which electron will move towards the cathode and holes will move towards the anode electrons will transport in the phases like PCBM which are acceptor phases. But they are electron conducting, you can say these are electron conducting, they have high mobility for electron and these are hole conducting phases.

Terminology is slightly different in as compared to normal p-n junction that donor phase is P3HT which is hole conducting and the acceptor phase is the one which is electron conducting PCBM phase of something like C 60 it is a fullerene. So, but the requirement is that the phases must make a continuous network. So, that there is a complete continuous path for electrons and holes you reach the electrode. If by chance you have a; so, this is a good structure to make.

Suppose, you have this structure on the other hand which is like this. So, suppose you have a phase which is present in this fashion, then you will create excitons; excitons will be broken. But carriers will not be able to reach because this phase has no contact with the electrode, this is lying isolated manner. So, this will reduce the performance. So, this is not desirable.

We need a we needed a continuous weed we need a continuous network so that phases touch; phases are closer to electrodes. That is how you will you would like to have you would like to have an Inter penetrating network. So, this is called as inter; what we require is Inter penetrating network. So, in reality you would like a structure like what is what it is shown here you would like a inter penetrating network like this ok. This is what you would require in practice; in theoretically, but what we get in practice is a little diffused kind of structure. So, what I will show you is that image of what we get in reality.

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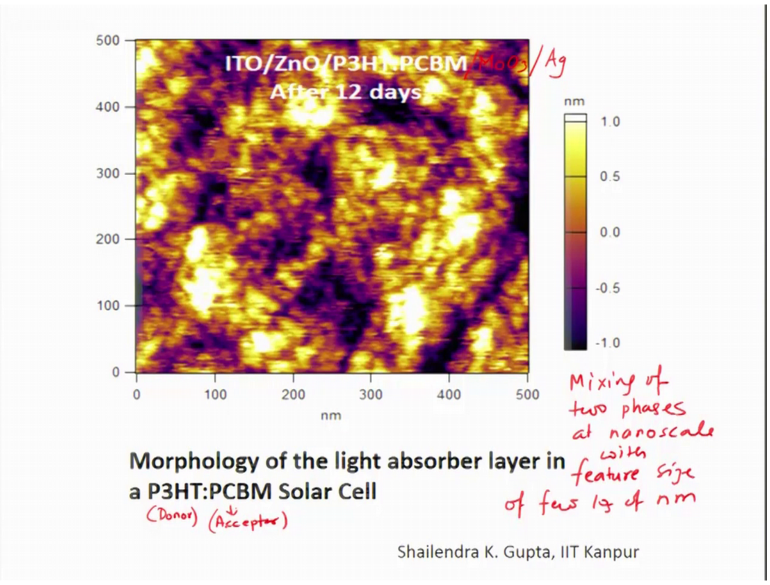

Mixing of two phases at nanoscale with feature size of few 10s of nm

Morphology of the light absorber layer in a P3HT:PCBM Solar Cell

(Donor) (Acceptor)

Shailendra K. Gupta, IIT Kanpur

So, in reality we will get a structure like this. So, this is basically a solar cell which is which uses the ITO electrode and zinc oxide is a electron transport layer P3HT PCBM as a donor acceptor layer and then, on top we have moly oxide as a whole transporting layer and then, we have silver as a top electrode. So, this is you can see there are there are there are different phases, they are dispersed at nano scale. You cannot see so this is a atomic force microscope image, you can see the whole image size is 500 nanometer.

So, the feature size here is of the order of you know about 20 nanometers or so. So, there is a there is a mixing of phases; two phases at nano scale with feature size of few 10s of nanometer ok. So, in reality this is the kind of microstructure that we obtain. So, this is what a P3HT PCBM. P3HT is donor poly three hexylthiophene; PCBM is a fullerene which is acceptor.

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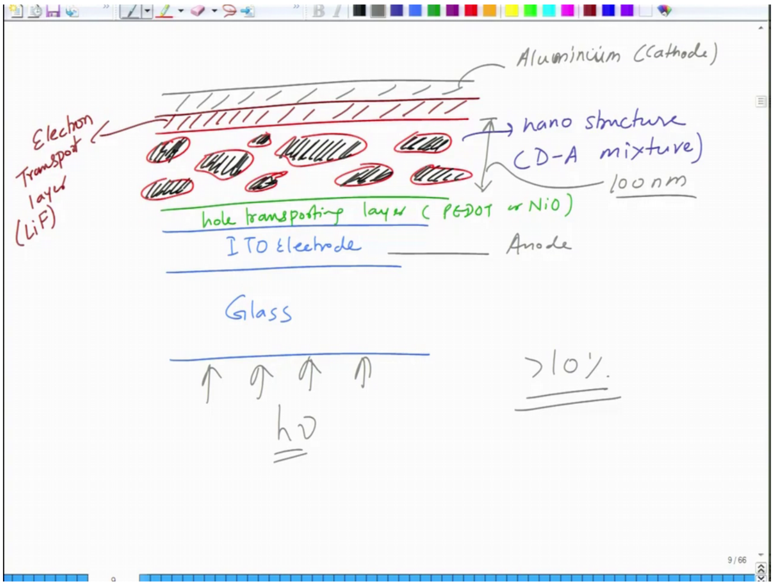

So, in reality what we get is I structure like this and if you if I give you an example of this solar cell. So, you can have things like you can have a glass substrate. On a glass substrate, we will have indium tin oxide electrode. Generally, we also have a hole transporting or electron transporting layer. Hole transporting layer such as a polymer called as PE dot or oxide called as nickel oxide which promotes the hole transport only so that on ITO electrode only holes are collected.

Then in between so we have this network of phases. So, you can say we have a nano nano structure nano structure. We can say donor acceptor mixture ok, then on top we have a. So, this is a electron transporting layer. This is only to ensure that only electrons cross through this layer. So, this could be something like you know lithium fluoride and then, on top we have electrode which is aluminum. So, in this case aluminum acts as a cathode, where electrons are collected ITO acts as a anode where holes are collected and that donor acceptor junction is separated by two carrier selective layers.

So, here the thickness is of the order of about 100 nanometers or. So, this thickness is higher than what you get for bilayer in single layer solar cells. As a result, they are better and on top, we have very thin layers of carrier selective layers which are of the order of 10 to 30 nanometers and on top and bottom we have 2 electrodes. So, light comes from the glass slide here and these if these solar cells, best solar cells nowadays give you more than 10 percent efficiency that are available.

So, we look at some of these in the next class.

Thank you.