

**Solar Photovoltaics:
Fundamental Technology and Applications
Prof. Soumitra Satapathi
Department of Physics
Indian Institute of Technology-Roorkee**

**Lecture-21
Organic Solar Cells**

Welcome everyone to our course today we will have 5th week and 1st module, now so far we have started discussing about generations of the solar cell. We discussed about first generation solar cell and you have seen there, we studied about single crystal silicon solar cell. And in second generation solar cell we talked about amorphous thin film solar cell, then we started the third generation solar cell.

In last few lectures we started one of the third generation solar cell namely dye-sensitized solar cell or DSSC devices and we have seen that how to fabricate a DSSC device in the lab. And what is the photo physics of the working principle behind the dye-sensitized solar cell. Now in this context we will today discuss about another very important variety of the third generation solar cell namely organic solar cell.

(Refer Slide Time: 01:22)



Now as you can see from this picture this is an example of an organic solar cell, now looking at this picture some of the facts which immediately come to our mind is that we can hold this

solar cell. So that means this kind of solar cells are flexible and also as you can see from the figure this is a transparent, so that means light can transmit through them. So, imagine we decorate our building in such a way, so that the every walls of our building is transparent.

But still we can do our indoor lighting using those transparent window which is now behaving as a solar cell. So, organic solar cells provides some of the advantages or benefits over the conventional solar cell in terms of flexibility, light-weight, compactness as well as the transparency. Now there are some important factors or important considerations has to be taken into account before we start about the organic solar cell.

Now our every day account to any kind of organic material, for example if we take a a water bottle a mineral water bottle. Now this is also made of some kind of polymer right, what kind of polymer may be some kind of polystyrene or crossed polystyrene. But if we touch this water bottle we know that we never get an electric shock why, because this kind of plastic does not conduct any electricity, but what will happen.

Let say if this water bottle which we use for drinking the water also contains electricity. So it is not long back the 3 Scientist namely (()) (03:12). So they discovered that there are some class of organic materials or some class of polymeric material more specifically they can conduct the electricity. Now this polymers they have alternative single bond and double bond in their back bone or structures.

This kind of polymers since they conduct the electricity they are called conducting polymer or conjugated polymer. Now once it was discovered that this polymer can also contained electricity or they can also conduct electricity. So then rapidly people were interested to see whether we can make any kind of optoelectronic devices using this polymer, for example whether we can make a solar cell or light emitting diodes using this conducting polymer.

Now obviously there are certain advantage of using conducting polymer over the inorganic materials, for example in any kind of organic material or conducting polymer we can tune their optical properties we can tune their electric properties and sometimes their mechanical properties

also. And also this conducting polymers are flexible, so you can make it on a flexible substance, inorganic semiconductors like silicon or gallium arsenide do not provide us this kind of opportunities.

So there usually we use some mechanical rigid substrate and we cannot make it on a flexible substrate and also tuning the optical properties is very difficult in inorganic semiconductors. So because of this advantage very soon organic materials take the phase and it replaced some of the important applications in modern days up to electronic devices and that begins the era of organic solar cells.

(Refer Slide Time: 04:57)

Organic Semiconductors

- Combine the virtues of plastics with those of semiconductors
- High optical absorption coefficients
- Properties tuned with flexible synthesis
- Low cost fabrication

The image shows a dark background with three rectangular panels in blue, green, and red at the top. Below them are several curved, flexible strips in various colors (red, orange, yellow, white, blue, cyan) that appear to be made of a material that can be bent into various shapes.

Organic semiconductors, this is a very special class of semiconductors which is made out of organic materials, now it combines the virtue of the plastic with those of the semiconductor. Now when you talk about plastic, so plastic has plasticity that means it can fold, it is flexible, so if the semiconductor has all the properties of a semiconductor. In addition to that if it is also flexible then it will be very very useful for making any kind of devices.

The second important properties of this organic semiconductor is high optical absorption coefficient. As you have seen that if the absorption coefficient is very high, so the light absorptions per unit length is also very high, third thing is that you can tune the properties with

flexible synthesis methods. As you can see in this figure we have a panel which contains 3 different films one is blue colour another is greenish another is the red colour.

These different films has made on a flexible transparent substrate and using the same material, same organic semiconductor. But by changing their synthetic protocol we can change their structure, we can change the side groups and that significantly change it is optical emission properties, that is why we see different colors here. For example here also we are showing like 4, 5 different varieties of the same semiconducting tune which emits a different colour.

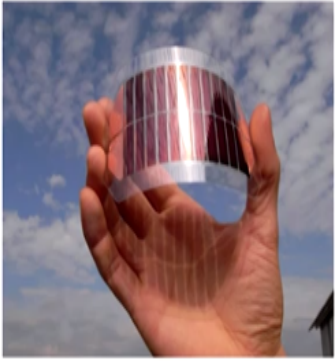
One is the red another is that yellow and another is that white something is blue. So, by tuning their optical properties by changing the synthetic protocol is much easier in this class of organic semiconductors, so this is one of the major advantage of organic materials. And also the fabrication cost is low, sometimes the precaution material is costly but if you look at the overall synthetic procedure in comparison to the inorganic semiconductor processing which always inverse very high temperature and the yield is very low.

These kind of materials can be synthesized at room temperature and at moderately low temperature also and end is moderate to high.

(Refer Slide Time: 07:12)

Organic Solar Cells :- Characteristics

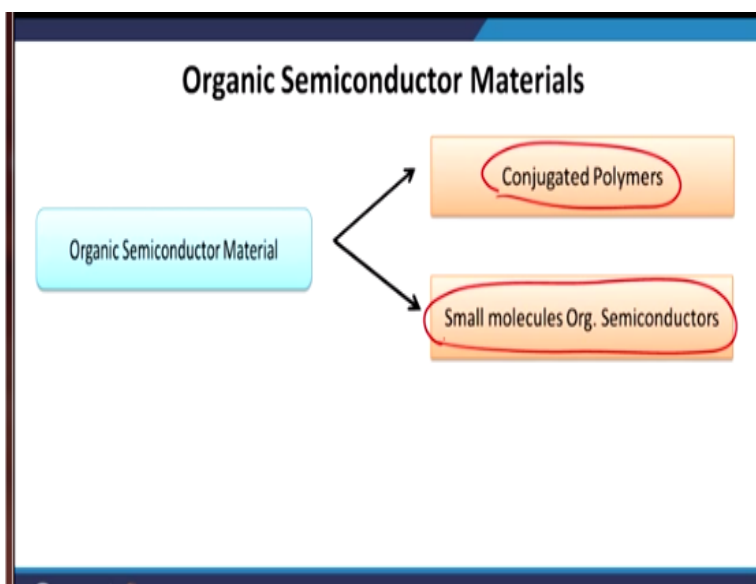
- Mechanical flexibility
- Lightness
- Low cost production
- High power generation efficiency
even under lower light intensities



Some of the other characteristics features of the organic solar cells are mechanical flexibility, as you can see in this figure we can hold the solar cell in our hand and we can bend it that means this is flexible. And we can put it in on any flexible substrate this are light weight, so these are compact devices, their cost of production is also low. And finally the power generation efficiency is also very high under the low light intensities, this is very important.

So especially because of this reasons these kind of solar cells are useful for indoor lighting like for the room decoration purpose or for any kind of small hall or stadium decoration purpose, this kind of solar cells will be useful. Now the power generation efficiency of this organic solar cells is of course not as high as the crystalline silicon solar cell, but it is improving by changing the geometry of the polymer by changing their absorption properties and also the synthetic protocol and the self assembly protocol of the device.

(Refer Slide Time: 08:21)



Now we can broadly classify the organic semiconductors into 2 different categories, first is the conjugated polymers. Conjugated polymers are a class of materials or a class of polymers we shows alternative single bond and double bond in their backbone and because of this kind of structure they can conduct electricity. Second example is the small molecule organic semiconductors.

So here the molecular weight of the organic semiconductor is small in comparison to the conjugated polymers. We will discuss about these 2 different types of the organic semiconductors in our lecture today.

(Refer Slide Time: 08:57)

The slide is titled "Organic Semiconductor Materials" and contains the following text boxes and diagrams:

- Text Box 1 (Blue):** Instead of C.B. and V.B. like inorganic semiconductors there are LUMO and HOMO levels are there in organic semiconductors.
- Text Box 2 (Red):** Charge carriers in organic semiconductors are called polarons.
- Text Box 3 (Purple):** Bound states of electrons and holes are collectively called excitons.
- Text Box 4 (Yellow):** Electrons are localized in the material.
- Small molecules section:** Shows chemical structures for Pentacene, Rubrene, and PC₆₁BM. PC₆₁BM is circled in red.
- Polymers section:** Shows chemical structures for poly(3-hexylthiophene), poly(p-phenylene vinylene), and polyfluorene. Handwritten notes include "P3HT", "Monomer (n=1)", "Oligomer (n=2,3,4...)", and "Polymer (n=5,6,7...)" with arrows pointing to the respective structures.

Now in this context let us introduce some of the terminology which we use in organic semiconducting material . In the inorganic semiconductor we use conduction band and valence band C.B and V.B but here instead of C.B and V.B like inorganic semiconductors we talk about the LUMO energy level and HOMO energy level in organic semiconductor. Now we already mentioned it earlier also, the word LUMO that is stands for lowest unoccupied molecular orbitals.

And the word HOMO that stands for highest occupied molecular orbital, so as you can understand the LUMO corresponds to the conduction band and HOMO conducts corresponds to the valence band. So the same thing as valence band and conduction band in an inorganic semiconductor is the HOMO energy level and LUMO energy level in an organic semiconductor. Charge carriers in organic semiconductors are called polarons, now this charge carriers they always generated in a bound state.

So the electrons and holes which are bound together but by some kind of force that are collectively called excitons. So in organic semiconductors we very often use excitons, exciton is

the bound electron hole pair, so I repeat exciton is the bound electron hole pair. Now since exciton participate in the charge conduction in this kind of material sometimes this class of devices are also called excitonic devices or excitonic solar cell.

And also electrons are localized in the materials unlike semiconductor unlike inorganic semiconductor like silicon where the excitonic binding energy is very very low and the charge carriers are free to move around or roam around inside the materials. So the electrons are delocalized inorganic semiconductor but because of the high binding energy of the excitons electrons are localized in this kind of material.

We have to provide some kind of external part of sun in terms of energy either by light energy or by thermal energy to dissociate this bound electron hole pair. Now on the right hand side we are showing some of the very popular structure of the small molecule and the polymer class. For example a small molecule which is used commonly in fabricating device is the pentacene, so penta stands for the 5.

So as you can see here there are 1, 2, 3, 4 5 benzene ring which are fuse together, similarly we have another common structure called rubrene and another very very commonly use small molecule for fabricating device is PCBM. Now C60 or fullerene which is also called buckyball that has a spherical football like structure like this. But the C60 if you remove this part from the compound PCBM the rest of the part is C60.

But the solubility of the C60 is not very high, so that is why if I wanted to make a film of the C60 what we have to do is that we have to deposit it by vacuum deposition technique. But let us say I wanted to make this C60 film by a solution based approach, so then we anchor or we conjugate a side group usually an alkyl group along on the fullerene moiety. And what we get is the PCBM, so the solubility of the PCBM and the absorptions of the PCBM is much higher than the C60.

And this is a common material of the choice as an acceptor material in organic solar cell. Now let us come to the polymers like there are different class of the polymer and the structure inside the

bracket that is the backbone or the moiety of the polymer. And depending upon the structure or the moiety the polymer nomenclature is done, for example this kind of structure where you can see that there are 5, 1, 2, 3, 4 and 5 coordination sites are there.

And there is a sulfur which has replaced this 5 kind of coordination site, this kind of unit is called a thiophene unit. Now in this thiophene unit we have put hexyl group as a side group, now this group inside this circle this is called the side group of the polymer and the main backbone or the main moiety of the polymer is this group. So the role of the side group is just to solubilize the polymer or to increase the solubility of the polymer in organic solvent.

So if I do not take the n , so what I will have, I have a thiophene backbone along with a alkyl group as a side group, this is an example of 3 hexylthiophene in monomer of this compound. Now if we put too many of them together then what I will write the formula a put a bracket and then I put the sign n , where n is a large number, then this kind of compound is called poly 3 - hexylthiophene, now depending upon the value of n like let us say if $n = 1$.

So then it corresponds to only one repeating unit of this structure, so that we call as a monomer, where $n = 1$. Now if $n =$ let us say 2, 3, 4 then it is not big structure but not also a single unit structure these kind of structure we call it as oligomer where the values of the n is 2 or 3 or 4 like until 5 like that. But if the values of the n is very very large like let us say n is greater than 50 then we have so many repeating units of this structure and that we call it as a polymer.

And it is interesting to know that in the case of the polymer the optical properties and the electronic properties pretty much repeats after $n = 6$ units. Now look at the other polymers called poly (p-phenylene vinylene) or PPV, here also there is a unit or the backbone which is inside the bracket. And if you make a many of this p-phenylene vinylene then you will get poly (p-phenylene vinylene) and similarly you will look at the next structure polyfluorene.

Here the structure inside the bracket this part that we call as a fluorine it is a highly fluorescence compound. Now if we make many of this fluorine unit then I put a bracket and I put the symbol n where n is a large number then we call it as a polyfluorene. Now all of this structure whether it

is a poly (3-hexylthiophene) or poly(p- phenylene vinylene) or it is polyfluorene, all of them has a conjugated backbone.

So it means that it has an alternative single bond and double bond, as you can see in this thiophene backbone first we have a single bond then we have a double bond, then we have a single bond then we have a there is a double bond. Similarly here we have an alternative single bond and double bond because of this kind of structures electrons are delocalized on this conjugated backbones and that helps them for the conduction of the electrons.


Now these compound poly (3-hexylthiophene) is also abbreviated as P3HT, this is a compound which is very very commonly used in fabricating solar cell along with PCBM. And this compound this P3HT is used as a donor polymer, whereas this PC60BM is used as an acceptor molecule. Now why you need this 2 different kinds of molecule that will discuss later on, similarly this poly (p-phenylene vinylene) this is also called PPV and polyfluorene this is also an example of a conducting polymer which is highly fluorescent.

Now we can use the pair of this polymer and the small molecule depending upon their energy level as a donor and acceptor material in this kind of solar cells.

(Refer Slide Time: 17:28)

Conjugated Materials

- Polymers generally insulating
- Alternating single and double bonds (conjugated)
- π electrons able to delocalize into clouds above and below the chain
- Band gap suitable for absorption of sunlight



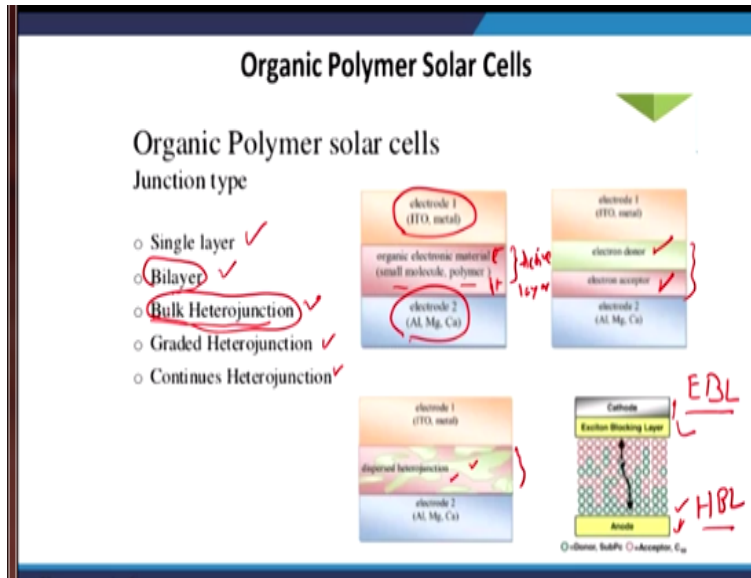
Now polymers generally insulating, if you touch your drinking bottle or your coca-cola bottle usually you do not get an electric shock why, because this kind of material does not conduct the electricity. But if you insert the alternative single and double bonds inside the polymer structure what you call it as a conjugated structure then the polymer will be able to conduct the electricity. For example you look at this structure here I have a alternative single bond then double bond, then single bond then there is a double bond.

So double bond is represented by this 2 line and the single bond is represented by the 1 line, this kind of structure is called a conjugated structure. So this is called conjugated structure and this kind of polymer is called conjugated polymer. Now what will happens in this kind of conjugated structures the pi electrons which looks like a dumbbell shape which is distributed over this polymer backbone, they are delocalized into the clouds above and below the chain.

So the pi electron density they distributed throughout the polymer chain above and below, so because of this conjugations this kind of polymer have a delocalization of the electron clouds or the pi electron clouds or π (18:46) electrons which is loosely bound throughout this chains. So if we wanted to calculate the probability of the electron, so the probability density is quite large in this kind of polymer and band gap is suitable for absorption of the sunlight.

So the band gap of this material is suitable to absorbs the light in visible regions or we can even tune some of the materials to absorb it near IR region or even in UV region.

(Refer Slide Time: 19:15)



Now if we cross section or if we look closely into the structure of an organic polymer solar cell. Then depending upon the junction type we can distinguish the organic polymer solar cell either as a single layer solar cell or a bi-layer solar cell or a bulk heterojunction solar junction solar cell or a graded heterojunction solar cell or a continues heterojunction solar cell. Now a single layer device as the name suggest there is only one particular kind of material is there either donor or acceptor material usually a donor polymer.

So as a donor polymer like for example you look at this structure of this devices where this is the sandwich type of geometry. I have 2 electrode, electrode 1 which can be a TCO transferring conducting oxide in ITO indium doped tin oxide or any kind of metal. And there is another electrode at the back which is electrode 2 which is usually made up any kind of metal like aluminum, magnesium and calcium and between these 2 electrode we sandwich the organic electronic material which can be a polymer or small molecule.

So whatever the charge carrier which have been generated here whatever the charge carrier that has been generated inside this organic polymer which is also called the active layer. They will be separated depending upon the voltage difference of the electrode 1 and electrode 2. So this kind of structure is a sandwich structure where we sandwich the active layer which is an organic polymer or a small molecule between this 2 electrode.

Now if you use only one particular kind of material it is a single layer device now if you use 2 different materials like here we are using 2 materials one is the electron donor and another is the electron acceptor both are organic materials. But one is electron donor, so that donor is the electron another is the electron acceptor which accepts the electron and the electrons will flow now towards the downward directions and hole will go to the toward direction.

So that is an example of a bi-layer devices but we can also mix the electron donor and electron acceptor throughout this active site. So instead of making this layer by layer we can also mix them together and we can make active layer out of this mixture and in this mixtures the donor and acceptor is distributed in a dispersed conditions. And that is an example of a bulk heterojunction solar cell, as you can see in the figure there are 2 different colour shade we are showing.

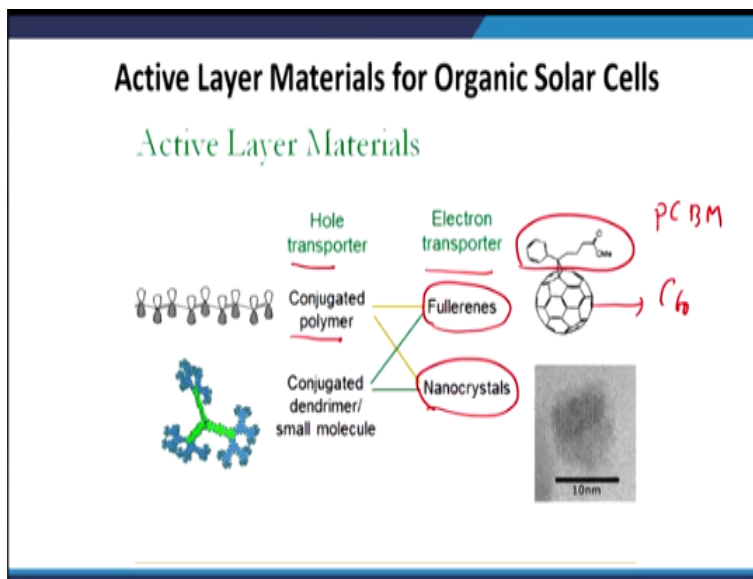
One is due to the donor another is due to the acceptor and this distribution is non-uniform and it is distributed throughout this active layer this is an example of a bulk heterojunction solar cell. Similarly we can have like a graded heterojunction like here like where you can see that a particular concentrations of the donor and a particular concentration of the acceptor gradually changing along the thickness.

And we can also further optimize this device by putting an electron blocking layer or a hole blocking layer. Now the electron blocking layer which is also called like EBL and the hole blocking layer which is also called HBL. The role of them is to block one particular kind of charge carrier and allow the other charge carrier. So basically they act like a filter, for example if you take an electron blocking layer, so the electron blocking layer or EBL layer that blocks the electron to flow on this site.

But allows the holes to flow on that site or the hole blocking layer or HBL that allows through hole to block and flow in this site and allows the electron to flow in this site. So the role of the EBL and HBL is to preferentially allow one particular charge kind of charge carrier over others things, so that helps to increase our short circuit current. So these are different class of solar cells.

Now there are 2 different class especially this bilayer devices and the bulk heterojunction solar cells they have been studied in details in organic solar cells.

(Refer Slide Time: 23:19)



Now we have talked about the active layer, now active layer is made of the active layer materials. Now what can be active layer materials, they are usually a hole transport material or an electron transport material, so as the name suggest the hole transport materials are those material which are have a good hole transport properties or their hole mobility is high, for example it can be a conjugated polymer like this.

You can see the example here or it can be a conjugated dendrimer or small molecule like this, so also this small molecules can comes together and can make a spherical kind of geometry which you call as a dendrimer. So it can be conjugated dendrimer or a small molecule, now electron transporter or electron acceptor, so basically these are the compounds which can accept the electron and whose electron mobility is very high.

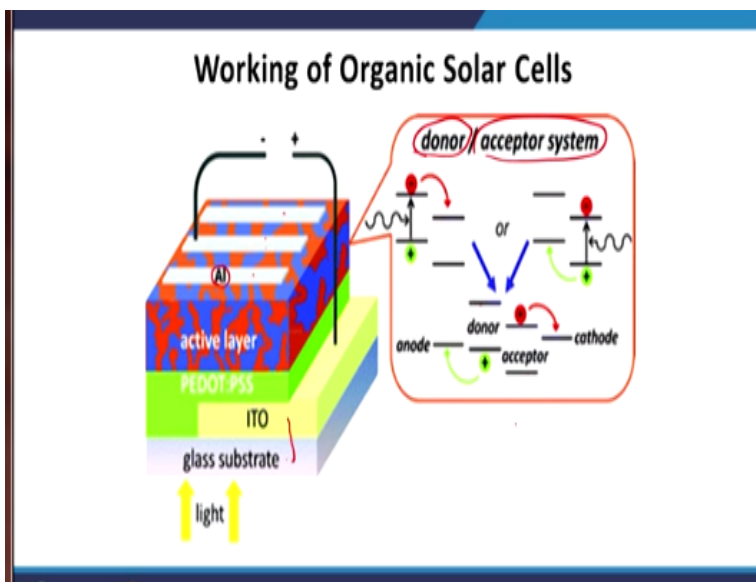
For example fullerene we just discussed about this fullerene, so fullerene is C₆₀, so as I said that if you remove this part from this structure, so this is C₆₀. And when I add this side group which is an alkyl side group then I call it as PCBM and why we put this side group here along this C₆₀

chain to make it solubilize, so that the solubility of this compound increase or even we can use different nanocrystals like metal nanocrystals or carbon nanocrystals as an acceptor materials.

For example we are showing and SM image of nanocrystals and you can see that we can find out each and single nanoparticles separately. And electron mobility of this nanocrystals is also very high. So when we make the device or when we make the active layer we have to mix the hole transport layer with the electron transport layer that means we have to mix the conjugated polymers with the fullerene or conjugate polymers with the nanocrystals.

Similarly we can make the conjugated dendrimers small molecule with the fullerene and conjugated dendrimers with the nanocrystal.

(Refer Slide Time: 25:21)



Let us try to look at the working principle of organic solar cells. Now as the organic solar cell just we have said that it is a sandwiched device, so basically we have 2 electrodes one is a transparent ITO substrate which is deposited on a glass substrate here. And then there is this metal electrode aluminum and you can see that we have put this metal electrode as a finger electrode to reduce the leakage loss and in between there is an active layer.

And we can use a hole blocking layer or electron blocking layer in between like in a we are using P.PSS which is again a polymer which hole mobility is very high. So it actually stops one kind of

charge carrier over other and another things PDOT:PSS does here is that it helps to weight the surface. So that the films on this substrate becomes very very uniform. Now if we load this active layer you will see that this active layer is made of 2 different compounds.

One is donor and another is the acceptor material, now we already said that as a donor we can use a conjugated polymer and as an acceptor we use a small molecule. Now what will happen, like this is the donor molecule ok and this is our acceptor molecule. Now when the donors when the light falls on it what will happen the light passes through here and the electrons they excited from the ground state or the HOMO to the LUMO level of the donors.

And that electrons now transfers to the acceptors, from there it goes to the cathode. So what it left at the donor is the hole molecule and it goes to the anode. So using the outside circuit it comes from the anode to the load and the electron which comes to the cathode using the outside circuit it comes to the outer circuit and you get a current in the output. So today we learn about what is the active layer or what is the some principle characteristics of an organic solar cell, how to fabricate organic solar cell.

And we have learn that there are certain advantage of organic semiconductor like flexibility, compactness, tunability as well as high efficiency over the inorganic semiconductor. And that is why organic semiconductors are prepared to make solar cells for indoor lighting or for flexible substrate base structures. And we have also seen that conjugated polymers and the small molecules they are used to make this organic solar cells.

And there can be different kind of solar cell like bilayer device or bulk heterojunction device or grade heterojunction device or continuous heterojunction device. Out of that bilayer device and grade heterojunction device this 2 are very very important class of this organic solar cell device. And in the next lecture we will discuss in details about this 2 different kind of solar cells bilayer solar cells and bulk heterojunction solar cells.

And we will also discuss about what kind of morphology and photo physics is optimum or required for getting maximum efficiency in this kind of solar cell thank you very much.