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

Lecture-26
Fabrication of Perovskite Solar Cells

Welcome everyone to our course, today we are having this 6th week lecture, so if you remember last week we have started with perovskite solar cell. Now perovskite solar cell as we have learned they provide us some of the advantage over the organic solar cell and also dye-sensitize solar cell. Like if you remember some of these excellent properties which we have discussed in the last class is that is perovskite material has a tunable band gap.

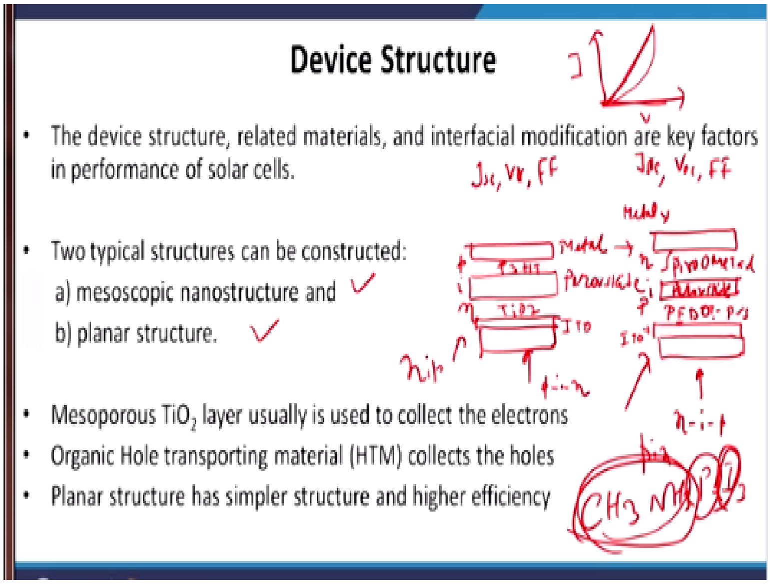
That means the same material by changing either the cationic component or by anionic component or by the metal ion we can tune the band gap over a wide range. Now this tuning the band gap actually tells a lot about the system because if you can tune the band gap, basically you can tune it is absorptions. So in the same material starting from the UV to visible to near IR the absorptions is possible now.

The next important thing with this material is that this kind of material has a very large absorption coefficient. So we do not need to make a very thick film for enough amount of light absorptions in the active layer. Moreover the processing cost of the perovskite is lower in comparison to the other third generation technology. Perovskite solar cell can be fabricated by a solution base approach where you can take the precursor molecule in a good organic solvent.

And then you dissolve it and then make a thin film out of it, you can tune or control the properties of this thin film. Similarly this perovskite material they have a large band gap variations simply by morphological variations of this structure they show a temperature dependent crystal structure orientations. So because of all of this thing or because of this all excellent up to electronic properties, it was the material of choice for solar cell devices. And we have seen from the efficiency graph that only within 5 to 6 years of research starting from a descent 3.8%.

The efficiency rise to 15% until 2015 and the present number of efficiency is 22% today and this number as I mention that increasing every day. Now in the last lecture we mention that we will learn about how to fabricate a perovskite solar cell or what are the different components of a perovskite solar cell. In today we will see that what are the different kind of geometry possible in this kind of solar cell or how you can make the perovskite solar cell in the lab.

(Refer Slide Time: 03:22)



Device Structure

- The device structure, related materials, and interfacial modification are key factors in performance of solar cells.
- Two typical structures can be constructed:
  a) mesoscopic nanostructure and ✓
  b) planar structure. ✓
- Mesoporous TiO_2 layer usually is used to collect the electrons
- Organic Hole transporting material (HTM) collects the holes
- Planar structure has simpler structure and higher efficiency

Let us take a look on the device structure, the device structure related materials and interfacial modification are key factors in performance of solar cells. So obviously like as I say that this efficiency in a solar cell is a product function it depends upon exciton generation. Now this exciton generation comes from the choice of material, if we have a material which have a low band gap then that material can absorb the light in a near IR range.

So the related materials is very very important, interfacial modification now when you make a device so a device is a sandwich structure where you put an active layer between the cathode and anode. Now many times very often you put blocking layers either in electron blocking layers or hole blocking layer to allow one particular kind of charge carrier to diffuse over the other. Now, so this interface modification plays a very very important role in determining the Voc and the field factor of the devices.

So all of this parameters needs to be optimized for devising a optimum performance of a solar cell, 2 typical structures can be constructed mesoscopic structure and planar structure, mesoporous TiO2 layer usually is use to collect the electron, organic hole transport material which we abbreviate as HTM they collects the hole. Planar structure has simpler structure and high efficiency.

So people have fabricated either a mesoporous nanostructure where you make a mesoporous layers with lot of bores inside the material or one can make a planar structure where there is no corrugation or no porous structure in the material. Now both of this structures have been tried in either PIN or NIP geometry and gives a different number of efficiency. Now what is PIN and NIP geometry these are the 2 very commonly used structural configuration in the perovskite solar cell.

So in the PIN geometry what happened here, let us say let we draw this thing this is your ITO which is coated on a glass substrate and then on the top you have your metal electrode right, so this is your metal electrode. Now you allow the light to pass through here, so one can put the active layer of the perovskite here, this is your active layer. Now I can put either titanium dioxide as an electron collection layer at the interface of the ITO and perovskite and some hole transport material like any conducting polymer.

For example P3HT as a hole collection materials at the interface of the perovskite and metals, so then so TiO2 is n-type semiconductor and P3HT is a p-type semiconductor. So between that I can think about an intrinsic layer of perovskite has been sandwich, so this kind of geometry is called NIP geometry. On the other hand let us look the other figure you have the same ITO here which we have deposited on the glass substrate.

And we have this top metal electrode this is metal electrode light is falling from here, in between I have a sandwich layer or perovskite yeah one important thing to mention here. So again I can put to 2 different blocking layer or charge collection layer at this 2 interface. If I put some hole conducting layer like PEDOT:PSS and on the top if I put something an electron collection layer like an common example is a small molecules spiro omitted or doped spiro omitted.

This is a small molecule which conducts the electron, so here I have a p-type layer, I have an n-type layer and the intrinsic semiconductor is sandwich between them. So now consider there are 2 different geometry one is p-i-n and another is n-i-p or I think is other way round this was n-i-p, this kind of configuration and here what we have drawn is the p-i-n. So in nip geometry we put titanium dioxide layer at the interface of the ITO and the perovskite.

And as a hole collection layer we use the P3HT or you can use any hole transport material any conducting polymer which has a very large hole mobility. Now this TiO_2 layer can be a mesoporous TiO_2 or can be a planar structure TiO_2. On the other hand in the pin geometry we put a PEDOT.PSS a conducting polymer layer at the interface of the ITO and the perovskite. And we put an electron collection layer, for example spiro omitted which is a small molecule at the interface between this perovskite and the metal contact.

So now in either of this 2 cases we will get the JSC, Voc and fill factor in both of these cases we will get JSC J short circuit VOC and fill factor. Now if we calculate the IV curve in the nip geometry of the same perovskite material and if I plot the IV curve for the efficiency measurement for the same perovskite material. Let say CH_3NH_3 lead iodide in the p-i-n geometry, what will see that if we do a voltage sweep from the negative to the positive voltage.

And comes back from the positive to the negative voltage in ideal case, the both that curve trace should be the same. So what I am meaning that if I have a current versus voltage graph like this and let us say my this is an arbitrary example although IV curves does not follow like lead cell like this way. So if the current or voltage graph follows like that when I do a voltage sweep like that and then again if I comes back, so in ideally it should follow the same curve like this.

So ideally it will trace back when I sweep back the voltage from this one to this one and then back to this point. But in realistic case what happens it does not trace the same path but it deviates from the path a little bit and this phenomena is called this deviation from the original path that phenomena is called hysteresis. And this is an intrinsic property of the perovskite material you remember, when you discuss about the barium titanate or calcium titanate.

And I said that in the earlier days the perovskite was mainly used for it is good ferroelectric properties. So perovskites shows a ferroelectric properties now in ideal case once I want to make a device I do not want to have any hysteresis in my device. Now it has been absorbed that between this pin and nip geometry one of the geometry let us say pin geometry shows a better hysteresis or less hysteresis, better hysteresis means here the less hysteresis in comparison to the nip structure.

Although the reason is not very clear, so if you do not want to have a lot of hysteresis in the circuit. So then we will prefer the pin geometry over the nip geometry now you might ask like you know what we are so much concerned about the hysteresis or what physical interpretation of the hysteresis. So basically later on we will see that hysteresis can be related to the stability of the devices.

Now one of the major problem of the perovskite although it is efficiency is very high is it stability. Now this perovskite material they are not very stable in the ambient condition, so that is why we need to have a very very control environment, like we need to control the humidity level and the oxygen level while fabricating this device. Now once you bring this device outside this controlled environment then it is efficiency drastically drops.

Now what is the reason behind is one of the reasons can be thermal degradations, one of the reason can be moisture sensitivity. So these all of the reasons which actually makes this device efficiency very very unstable. Now in apart from this factor like this temperature degradation or the thermal degradation or moisture sensitivity which is pretty much common in all most all kind of organic materials.

The perovskite materials in addition has another problem that is it is intrinsic photo instability. So when the light shines on this kind of material we mentioned in the last class when we talk about the crystal structure a perovskite material. For example you take this a common perovskite CH3NH3 lead iodide and we say that this is a cation and this is the metal ion. And this is the halogen and you also say that this cation can move along the structure of the perovskite.

So this is called the ion migration right, so because of the light exposure this emications spontaneously started movement along the crystal structure. And the 3D structures spontaneously disintegrates to a 2D structure, once we have a 2D then no longer tolerance factor ratio is precept. So no longer the perovskite crystal structure is precept, if it is not precept so we will not get the required photo physics as you require for getting a optimum device.

And that kind of instability due to the exposure of the light that is an intrinsic properties of the perovskite. Now once we talk about the thermal instability or once you talk about the moisture instability there are ways to prevent that. For example if you are too much concerned about the moisture instability we can put a barrier layer or encapsulant. For example a thin layer of the grapheme which is almost impenetrable by the moisture layer or any other kind of polymer layer which is highly hydrophobic.

We can make an encapsulant or barrier layer on top of the perovskite to prevent it from the moisture or there are ways like you know they are thermo polymers there are ways prevent it from the thermal degradations also. But finally we need to allow the light to fall on the device because these are solar cell, if there is no light there is no electricity. But once the light falls on it the device started degrading, so then how to prevent that.

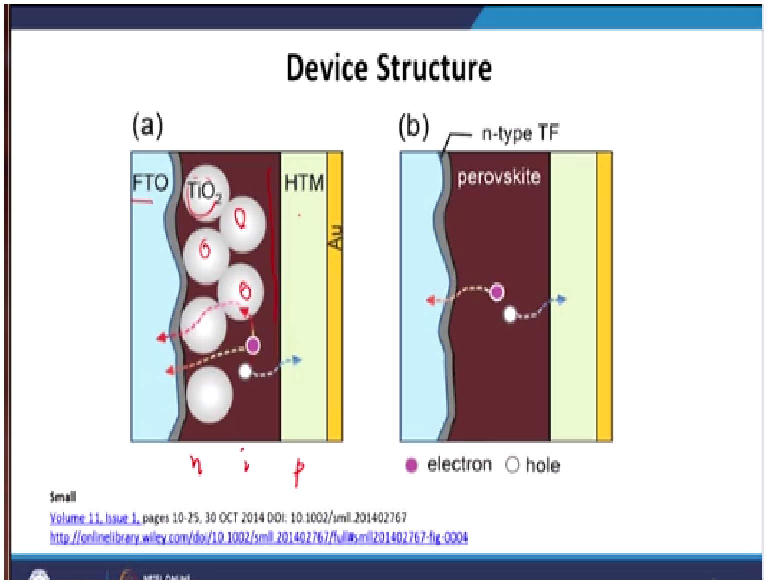
So that is one of the major reason the perovskite although having a very large efficiency it has not been rapidly commercialized into a product or technology. So that is why the major research in this field has been driven to find out a balance between the stability and the efficiency. So we want a perovskite solar cell which has a large stability as well as a moderate efficiency. So even the 10% efficiency will do our job provided this solar cell stable over 1 year or 2 years.

So that is done by this ion migration engineering and it is actually you can tune the properties of the material you can play around like for example here you can play around with the cationic group, you can play around with this anionic group to change the morphology or compositional or elemental compositions of this devices and get different documentary different structure a method called conformational mapping and that gives sometimes the better stability of the devices.

So for example instead of this methyl or emications, if I use a larger cation like FA cation, so then because of the steric hindrance those cations cannot move along the crystal structure. So then we can erase the ion migration probability, so that is one way of increasing the photo stability of the devices. So there are similar other aspects of it when you will discuss about the stability of the perovskite device we will discuss that in details.

But before that what we need to know that what are the different components and what is the role of that components in a perovskite solar cell right.

(Refer Slide Time: 17:14)



Device Structure

Small

Volume 11, Issue 1, pages 10-25, 30 OCT 2014 DOI: 10.1002/smll.201402767

http://onlinelibrary.wiley.com/doi/10.1002/smll.201402767/full#smll201402767-fig-0004

So let us take a look of a cross section of a perovskite solar cell, now as I said that there is this FTO which is a fluorine dot tin oxide coated glass substrate conducting photo anode. And on top of that we put the TiO2 layer, so titanium dioxide mesoporous titanium dioxide and there are this perovskite layer here, these are the perovskite layer. On top of that we put a hole transport material, for example a conducting polymer P3HT and on top of that we put metal contact like gold.

So basically this is an example of nip structure, so what will happens the charge carriers of the electrons and holes which will be generated here. Now using the TiO2 percolating network this electron can be rapidly transport towards the FTO and the hole can be rapidly collected by the HTM and transfer back to the metal electrode. And this electron using an external circuit comes back to the counter electrode and completes the circuit.

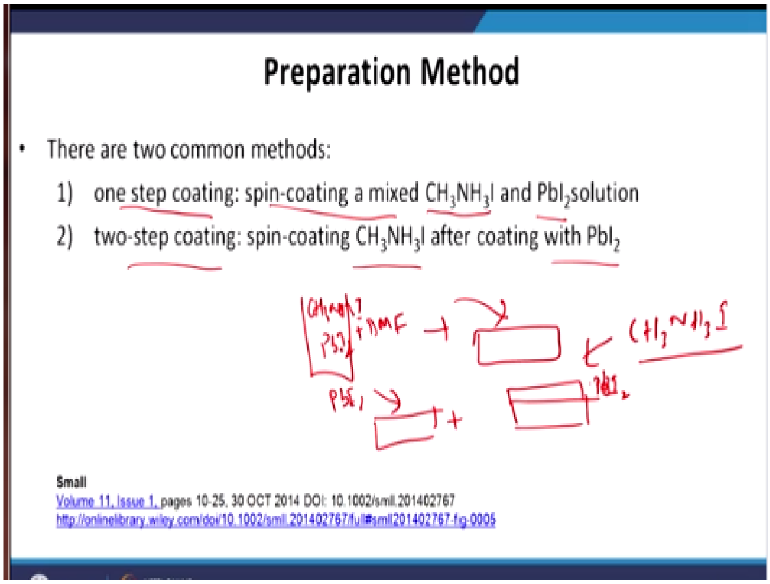
So that is what we have showing here if this is the electron the pink colour ball, so it goes to this direction and white colour ball the hole that goes to the hole transport material. So what is the role then of the hole transport material and the TiO2, so one of the role which is obvious to us is that TiO2 grab this electron, using this percolated network of the TiO2, so the electron transfer is now fascinated.

If I do not have the TiO2 still the electron can move depending upon the diffusion length of the electron depending upon the electron mobility of the perovskite. But if I put a additional TiO2 layer, so because of the energetics TiO2 will only allow or it will only filter out the electron to pass through it and it will block the hole to leave behind. Similarly the hole transport material because of the energetics they will only selectively allow the hole to transfer through them and block the electron what is the resultant effect, we reduce the recombination.

So in addition to the waiting the FTO substrate or giving a better surface contact between the FTO and perovskite, both of this layer, both of this electron transfer material and hole transfer material. They also acts like a filter layer which allows one kind of charge carrier to preferentially diffuse over the other charge carrier to prevent the recombination loss. So that is why in this kind of sandwich structure we always put a electron transport layer and hole transport layer in between the photo anode and photo cathode.

Now the fabrication method of the perovskite solar cell there are so many methods I mean it is important to mention that one can make perovskite solar cell either by vapor depositions method or by solution based approach. Today we will mainly discuss about solution base approach now in solution base approach the advantage is that you even can make it on a flexible substrate. Now even in solution based approach there are lot of different possibilities are there.

(Refer Slide Time: 20:51)



Preparation Method

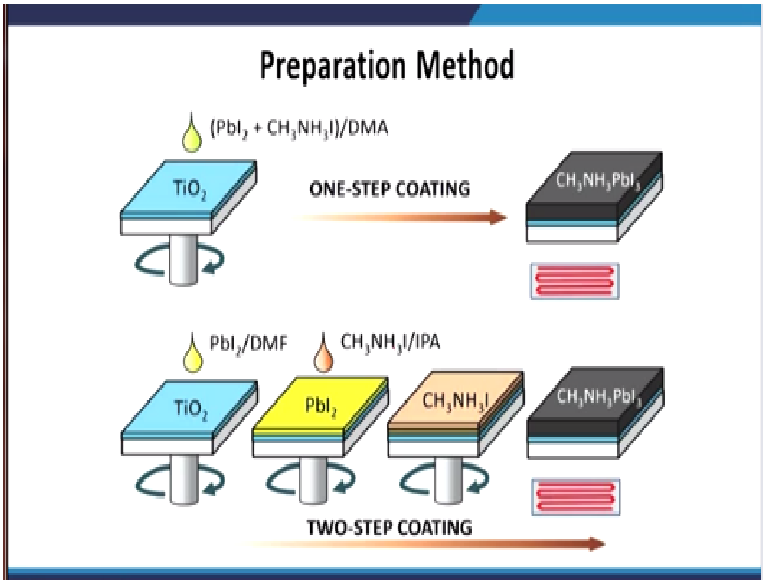
- There are two common methods:
  1) one step coating: spin-coating a mixed CH_3NH_3I and PbI_2solution
  2) two-step coating: spin-coating CH_3NH_3I after coating with PbI_2

Small
Volume 11, Issue 1, pages 10-25, 30 OCT 2014 DOI: 10.1002/smll.201402767
http://onlinelibrary.wiley.com/doi/10.1002/smll.201402767/full#smll201402767-fig-0005

Today we will discuss about 2 commonly used techniques for the fabrication of perovskite namely the one step coating, where you take the 2 different precursor CH3NH3I and lead iodide in one solution and spin coat from a mixture of them and two step coating, where you first coat a layer of lead iodide followed by a coating of CH3NH3I. So the 2 things is different, in one step method in a bigger you take both CH3NH3I and lead iodide let us say in a solvent DMF.

You mix them together well and then you spin coat the film, in another case and from this solvent you make the film. In the two step method first you put the lead iodide layer and then on the top of the lead iodide layer you put this CH3NH3I precursor. So now you allow this methyl ammonium this emi precursor to diffuse in the lead iodide structure. So the resultant morphology will be completely different if you make it by a one step or by two step method.

(Refer Slide Time: 22:07)



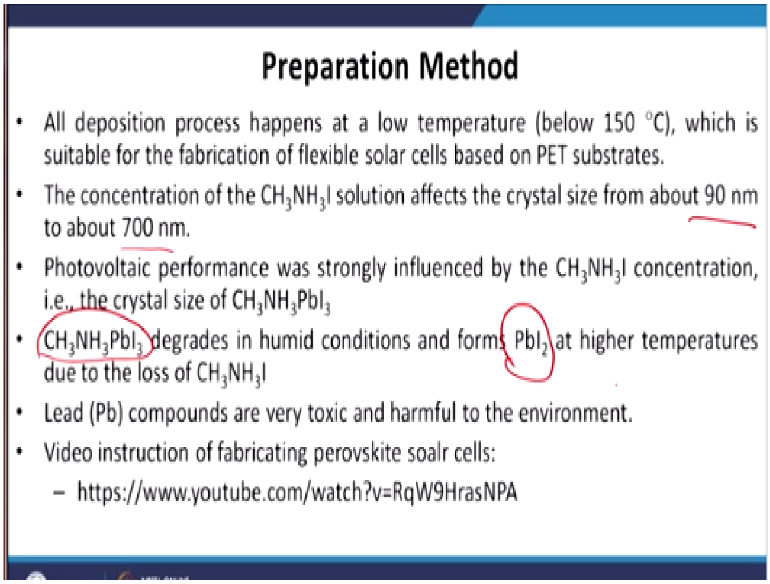
Preparation Method

For example look at this diagram of a one step coating as you mention that this is a spin coater we hold a substrate on the top titanium dioxide layer is on top of this substrate. And we take lead iodide and CH3NH3I in a DMA solvent and we spin coat it simultaneously the mixture of this 2 things and this is called the one step coating, whereas in the two step coating first we spin coat a layer up lead iodide from the DMF solvent on top of the TiO2.

So then on top of the lead iodide layer which is somewhat (()) (22:50) we put the CH3NH3I in the IPA solvent isopropyl alcohol. And then finally we heat the substrate to get a black colour CH3NH3 lead iodide, so finally we are allowing in both of the case lead iodide to react with CH3NH3I. In one case we are mixing them together and the reaction is happening simultaneously in a very rapid way.

In other case we are putting the pbI2 first followed by the CH3NH3I, now what is the difference between these 2 method, we will see later on that the morphology will be completely different if we do it in 2 different ways.

(Refer Slide Time: 23:33)



Preparation Method

- All deposition process happens at a low temperature (below 150 °C), which is suitable for the fabrication of flexible solar cells based on PET substrates.
- The concentration of the CH_3NH_3I solution affects the crystal size from about 90 nm to about 700 nm.
- Photovoltaic performance was strongly influenced by the CH_3NH_3I concentration, i.e., the crystal size of $CH_3NH_3PbI_3$
- $CH_3NH_3PbI_3$ degrades in humid conditions and forms PbI_2 at higher temperatures due to the loss of CH_3NH_3I
- Lead (Pb) compounds are very toxic and harmful to the environment.
- Video instruction of fabricating perovskite soalr cells:
  - https://www.youtube.com/watch?v=RqW9HrasNPA

All deposition process happens at low temperature below 150 degree Celsius which is suitable for the fabrication of flexible solar cell based on PET substrate yeah. So as I mention that If you like to mention or if you like to fabricate a silicon solar cell on a flexible substrate this is kind of not possible why. Because we have learned that the processing silicon always involves very high temperature but perovskite solar cell is made at a low temperature below 150 degree Celsius.

So even you have the possibility of fabricating it on a flexible substrate like PET ITO coated PET substrate. The concentration of the CH3NH3I solution affects the crystal size from about 90 nanometer to about 700 nanometer. Photovoltaic performance was strongly influenced by CH3NH3I concentration that is the crystal size of CH3NH3 lead iodide. CH3NH3 lead iodide in humid conditions and forms lead iodide at higher temperature due to the loss of CH3NH3I.

We already discuss that, so CH3NH3 lead iodide is a 3Dimensional crystal structure if you heat it what will happens CH3NH3I leads the crystal structure living only lead iodide in your sample substrate and one can experimentally prove that. So this materials are not every stable under the higher temperature, lead compounds are very toxic and harmful to the environment. Because it has been proved earlier that lead is neurotoxic and it is also nephrotoxic.

So there is a possibility of leaching the lead in environment and that is one of the concerns for the perovskite solar cell in addition to the stability. And there are lot of efforts have been devoted to replace the lead with some non-lead compound, for example bismuth or TIN or some other combination of that. Although the efficiency number which steel get very high efficiency in the case of lead base device also.

But still there are lot of ongoing research is going to replace the lead with some non-lead compound. In the next lecture we will discuss about the structural components of the perovskite solar cell and also how the morphology can be related to the photo physics and basic introduction to the photo physics of the perovskite solar cell thank you very much.