Solar Photovoltaic's: Principles, Technologies and Materials

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Lecture - 41
Generation III Technologies: Perovskite and CZTS Solar Cells

So, welcome to this new lecture of Solar Photovoltaic's course. So, this is probably the final lecture of this course.

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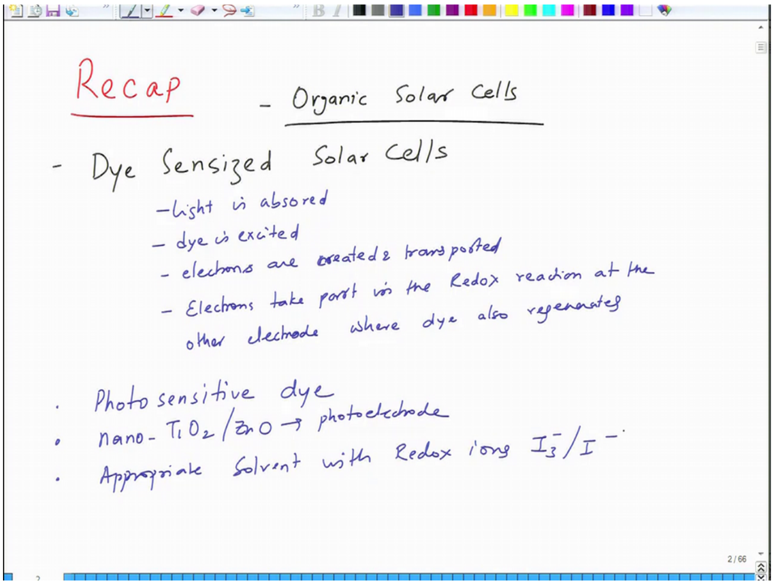

And we will just recap what we have done in the last lecture. So, in the last lecture, we talked about Dye Sensitized Solar Cells. We introduced dye sensized solar cells and we also looked at some other aspects of organic solar cells like degradation etcetera. So, in the dye sensitized solar cells, the concept is very similar; the concept is very simple that light is absorbed; dye is excited; electrons are created and then, created and then transported through that titanium oxide nanoparticles which are n type conducting materials and then, they go through the counter electrode through the circuit reach the other counter electrode.

And then the electrons are electrons take part in the Redox reaction at the other electrode, where dye also regenerates all right. So, the electrons which are created which moved through the circuit, they get absorbed in this Redox process and this Redox process also leads to creation of iodine ions which neutralized the excited dye to the normal truly to the regenerated dye. So, this is a simple process that happens in dye sensized solar cell. The key components in this solar cells were you have first is that photo sense sensitive dye.

So, the energy levels of this dye are very important so that you are able to excite this dye absorb the photons of appropriate wavelengths and excite the dye and then, we need to have nano Ti O2 or Zn O which is a photo electrode through which electrons are transported and a morphology is very important so that you have maximum interfacial area with the dye. Then, we need to have appropriate solvent with Redox ions. So, generally we have this I 3 minus I minus Redox couple, but we may have some other ions as well..

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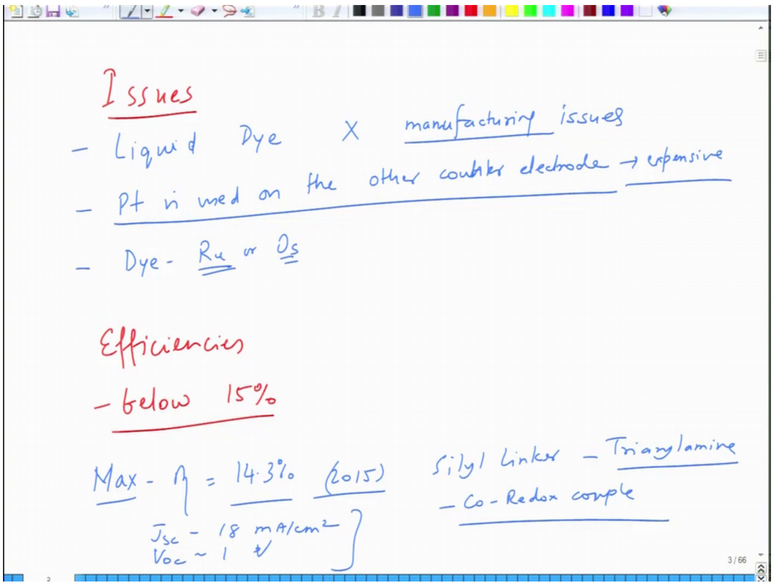

The issue with this solar cell is so we have the issues; issue with this solar cell is that it uses a liquid dye. A liquid dye is a problem because in ceiling an and it flows and as a result it is a problem in manufacturing solar cells manufacturing, good solar cells manufacturing issues. And then, we have what we call as we have we sometimes on the counter electrode on the other side towards the dye, platinum is used on the other counter electrode to improve the dye regeneration and Redox reaction; efficiency platinum is used as a sort of catalyst.

And this platinum is expensive ok. And then, we also have these dyes which are ruthenium based. Ruthenium is not a very you know this element is not very versatile or widely available element. So, it would be nice if we have dyes based on simple elements. So, they contain ruthenium or osmium which are sort of expensive elements. So, these are certain factors which are and the efficiencies have remained limited to right now efficiencies are below 15 percent. The maximum efficiency that is reported is about 14.3 percent in 2015 and this uses a silyl linker with triarylamine and it also uses a cobalt Redox couple. This gives a efficiency of around 14 percent in dye sensitized solar cells with Jsc of about 18 milli Amps per centimeter squared and Voc of about 1 volt.

So, this is something which is the status of this solar cell. There is a lot of work which is going on developing solid state dyes and efforts are also on to reduce the sealing issues. There is a effort towards reducing the cost of ruthenium containing dyes and use of platinum in the electrode and sometimes the electrolytes may also contain volatile and hazardous elements.

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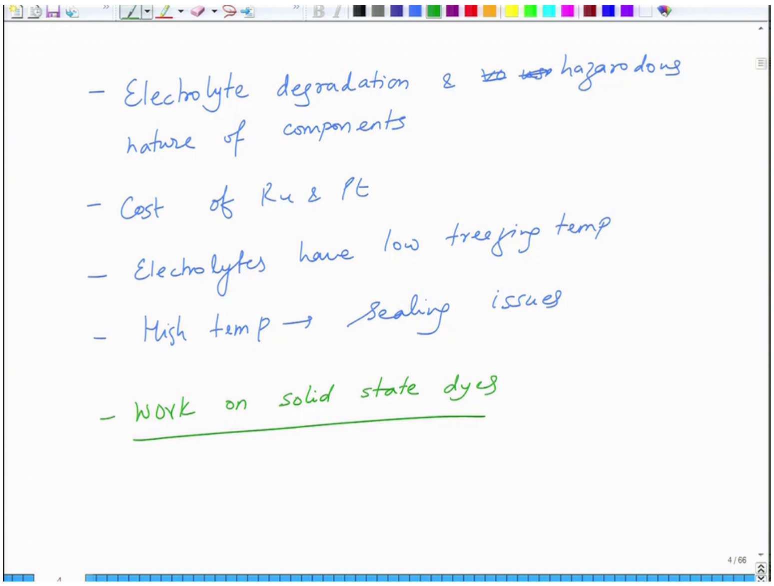

So, other issues are for example, electrolyte degradation and use of and hazardous nature of elements of components in it. Then, cost of ruthenium and platinum. Sometimes the electrolyte low freezing temperature; at high temperature sealing issues may come into picture because you have liquid dye. So, sealing is a issue. So, there is a work on solid state dyes and solid state dyes people are working tirelessly and there is a hope that these dye sensitized solar cell will be able to over overcome this barrier of fusing liquid dye with appropriate solid dyes and improve the efficiencies also.

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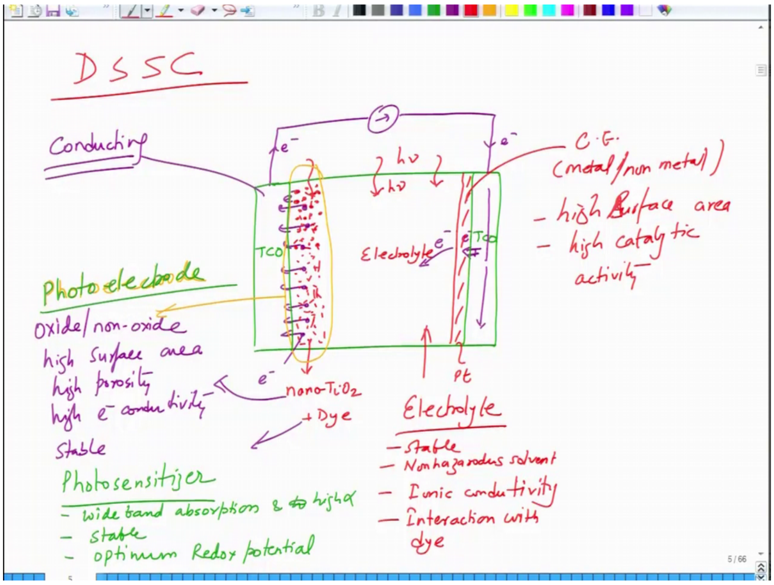

So, in summary what you require for a DSSC you have a; so you have a solar cell like this. So, you have a TCO on this side. This is the TCO another TCO on this side; then, somewhere here you have this nanostructure Ti O2 ok. So, this is you can say nano Ti O2 and this plus dye and this is in contact with what we call as electrolyte and here, it is possible to have a thin layer of platinum.

So, essentially the light is absorbed; the electrons are produced; the electrons are produced. These electrons are; so, these are electrons these electrons are transported to this side. So, these are electrons; the electrons then go to the other electrode and then, they go to this electrode and then, from this side the electron move to other side and then, we have transfer happening here so that they regenerate dye.

So, you have you can say that this is so there are various components here electrons are produced here and they are consumed here. This is the whole process and dye undergoes excitation as well as regeneration ok. So, basically you must have this side conducting; this is conducting side. So, conductivity of this side is important the working electrode on this side, this is this photo electrode; whatever is here this is the photo electrode ok. We call it a photo electrode.

This photo electrode is oxide. It could be a non oxide also. But oxides are more common like Ti O2. It must have high surface area, high porosity and high electronic conductivity right and should be stable. Then, we have dye photosensitizer, so, this is for this Ti O2; then we have dye. So, this photosensitizer is dye; photo sensitizer, this is photo electrode.

Photo photosensitizer should be it should have good absorption, wideband absorption and high wide and high right and high alpha. It should be stable and then, it should have optimum Redox potential. Then, we have electrolyte; electrolyte should be stable. It should have non hazardous solvent, ionic conductivity and interaction with dye. It should interact with the dye, then we have; then we have this counter electrode which could be a metal or nonmetal.

It should have high surface area and it should have high catalytic activity that is why platinum is preferred. So, these are certain attributes of dye sensitized solar cells in summary. So, this dye sensitized solar cell was a initiator for next generation technology that is perovskite solar cell.

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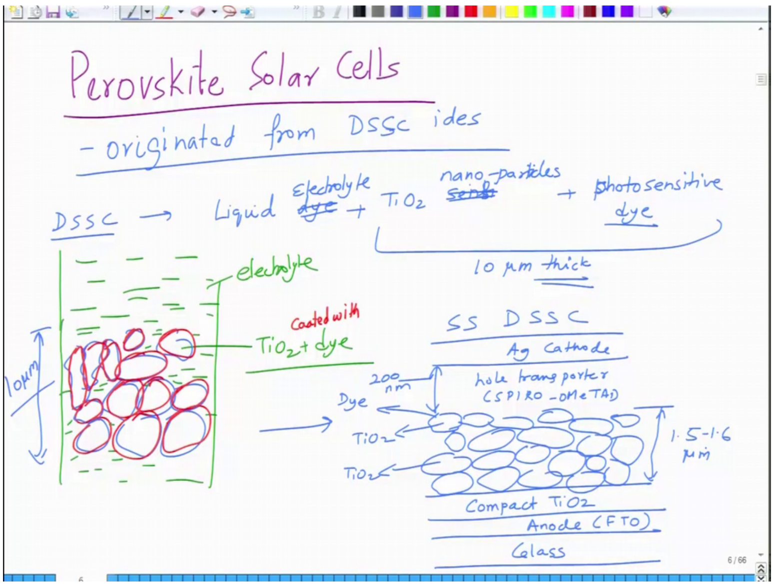

So, now we shift our gears to perovskite solar cells which is the hottest pv technology; a most exciting pv technology right now. So, the emphasis came from. So, it originated from DSSC ideas. So, in the DSSC initially we had you know the initially we have a liquid dye plus you know Ti O2 sensitizer; Ti O2 nanoparticles which has as a photo electrode plus a since photosensitive dye right. So, sorry liquid electrolyte plus Ti O2 nanoparticles plus photosensitive dye all right.

So, these made a device structure which was and this solid this thing was about 10 micron thick and the electrolyte was surrounding it all throughout. So, the electrolyte got impregnated into it because it was liquid. So, you made a sort of nanostructure like this; you had this nano structured which was interconnected like this and it had dye in contact with it. But in between it also had a so, if this was electrolyte all over the place. Electrolyte also got impregnated into this.

So, this is what mirror. So, this was electrolyte and this was Ti O2 plus dye ok. Now, Ti O2 was coated with dye because Ti O2 has remained in contact with the dye. So, dye was dyes were like this. So, these were dye molecules, they were made a they made a layer on top of it ok.

So, Ti O2 coated with dye, so, photosensitized Ti O2 nanoparticles. This changed this gave rise to a different geometry; people started working on solid state DSSC. SS solid state; so, what they had here was so this was about 10 micron here. This was about 10 micron. People started working on device, where people started using a silver cathode with a hole transporter such as CSPIRO. CSPIRO is a hole transporting material, CSPIRO OMeTAD and then, in contact we also had this Ti O2 nano structures. This was Ti O2 nanostructure and this was coated with dye. So, this was Ti O2 nanostructure with and on top, so, this is Ti O2 and this serf. So, this is Ti O2 on the surface we had dye.

And then, this was in contact with a compact Ti O2 layer and this is in contact with a anode which is let us say FTO Fluorinated Tin Oxide and this was on glass. So, this was sort of the solid state device dye where so the electrolyte was used as a hole transporting material instead of using a liquid electrolyte and this was about 200 nanometer and this was nearly 1.5 to 1.6 nanometer. So, the whole device thickness was much lower and it was solid state in nature.

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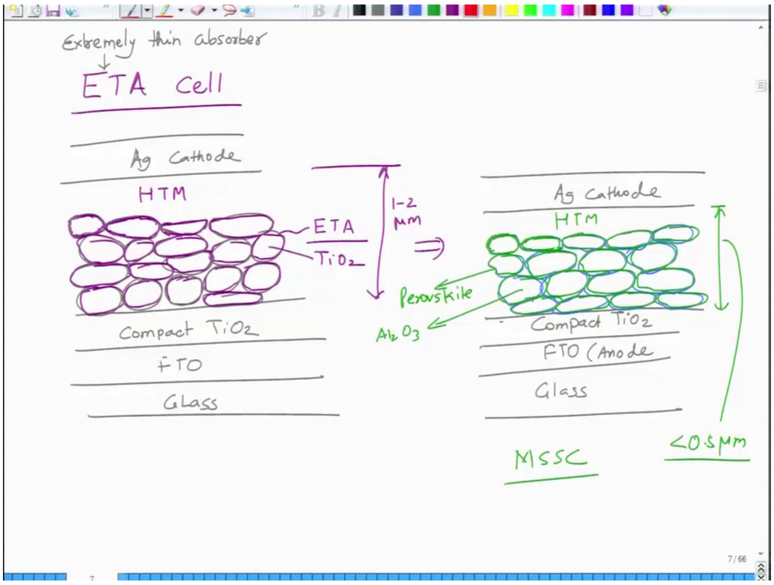

This gave rise to this design gave rise to what we now know as ETA cell. ETA cell is Extremely thin absorber layer. So, what we have here is we have a; so ETA is Extremely thin absorber. So, people started with silver cathode then we had a HTM and we had Ti O2 these nanostructure of Ti O2 and then this was put on in put in a in put on a compact Ti O2 and then, we had a FTO. We had a glass that the difference was that here we put a material which was not a dye, but a. So, this was ETA, extremely thin layer of a absorbing material concept is similar, but you change a material.

So, this is what is; so, all these particles were coated with this absorber layer ok. So, this is now ETA extremely thin absorber layer. These particles are again Ti O2 and this is HTM as we used earlier and this thickness is about 1 to 2 micron. So, the only difference with the previous design is that instead of using a dye using an absorber material and this gives rise to what we call as now the prescribed solar cell, where we have a glass; glass on top of that we have fluorinated tin oxide FTO which is let us say anode. On top of this we have compact Ti O2 and on top of it we have so it is started with this nanoparticles of alumina, but ok.

And then, on top we had HTM and then again, we had you can say silver cathode. So, this was here what we had here this is now a perovskite, the only difference is that this is again absorber, but a perovskite based absorber. So, basically you can say that development of solid state dyes, solid state DSSC was critical towards development of perovskite solar cell. So, this is the perovskite which is also absorber right. This is alumina particles and that is why the design is similar. Here, we have HTM and this thickness is about half a micron or even lower.

So, you can see that the only difference is it is a little thinner and instead of using a ETA the absorbing material, we have used perovskite which is excellent absorber of light and it has very good properties. So, this is what gave rise to what we call as a meso structured; this is called as MSSC by the way; meso structured meso super structured solar cell.

So, this gave rise to beginning of perovskite solar cell; perovskite the work started in 2009 and then 2011-12, oxford group and grazer group, they worked tirelessly to develop good quality perovskite solar cells and today, a lot of people are working on perovskite solar cells. So, there are so, essentially a perovskite solar cell is now essentially you can have multiple designs.

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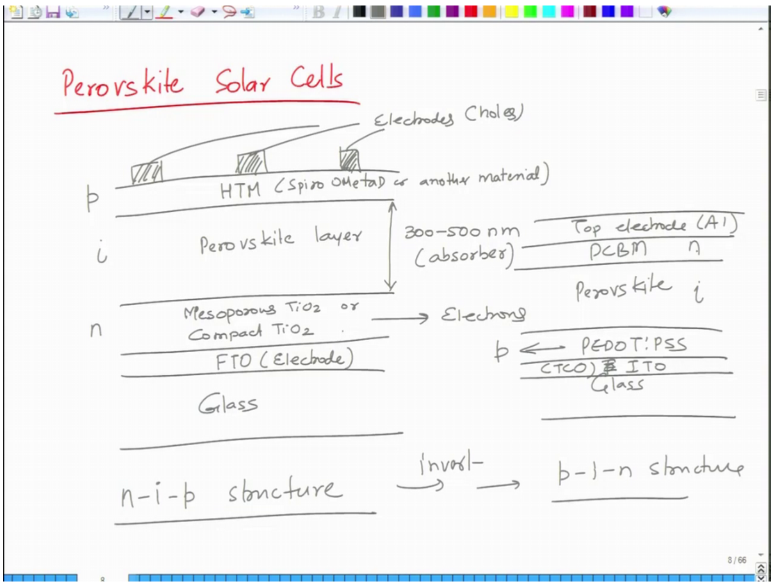

So, here we have, so, the in the previous case, we had this sensitization using a perovskite coating, but now we have moved away from perovskite sensitization what we have nowadays is as a is a hetero junction which is different. So, in the current context, we have a glass substrate and then we have a FTO which is a electrode and in this case we use FTOs. On top of this FTO, we have we can have a Ti O2 which is mesoporous Ti

O2 or a planer a compact Ti O2. So, this layer is either mesoporous Ti O2 or it could be compact Ti O2 right.

And then, what we have on top of it? What is the next layer? The next layer is perovskite layer which is of the order of 300 to 500 nanometer and then, on top of this perovskite, what we have is a HTM which could be CSPIRO OMeTAD or another material all right and then, we have electrodes. So, we collect holes on this side and we collect electrons on this side. So, this is basically you can say the structure of modern perovskite solar cells which uses a; so, it's essentially it uses a glass, followed by FTO, followed by a mesoporous or compact Ti O2, followed by a perovskite layer and then followed by a HTM.

And you can have 2 structures; this structure is generally called as a p-i-n structure. So, it is called as a p-i-n in this case it would be n-i-p structure right. So, you have n layer; you have i layer; you have p layer. So, this is n, this is i, this is p, just like amorphous silicon, where we had very thin layers of p and n type silicon on the two sides in between we had a intrinsic material absorbing. So, this perovskite is mainly the absorber layer. If you invert the configuration, then we get a if you invert it, then we get p-i-n structure ok. So, you basically start counting from the glass side from the glass side if n is first, then n-i-p structure; if its p first, then it is p-i-n structure.

So, this other structure would be glass. It could be the second layer of p DOT PSS which is a p type material, so, this is p. So, of course, you will have a FTO here or ITO. In this case ITO which is TCO right. Then we have perovskite; then we have PCBM; then we have top electrode and top electrode could be aluminium in this case. So, this is the p-i-n structure, so, this is p-i-n; this is n-i-p. These solar cells are basically based on a material called as Perovskite.

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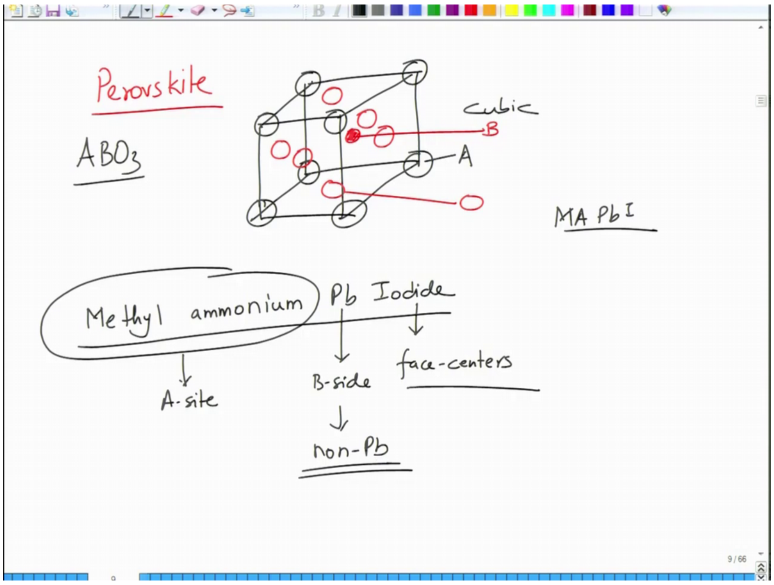

Perovskite structure material perovskite comes from ABO3 structured materials which make this kind of structure. It's a cubic structure where a cubic structure; so, where A ions occupy the corner. So, these are A ions and the B ions go at the sorry center of the unit cell. So, this is B and oxygen goes to the face centers.

So, this is oxygen. So, in this case it is basically you can say its perovskite dye which is commonly used is called as methyl ammonium. So, it is called as MAPbI right methylammonium lead iodide ok. So, you can say that here methyl ammonium molecules; so, methyl ammonium goes to the A-site, lead goes to the B-site and iodine goes to the face-centers.

So, this is what it basically makes the solar cell a perovskite structured material. So, this material is a very simple structure. However, there is a lot of work going on developing dyes which are non led because lead is a environmentally polluting. So, lead can be replaced by various other elements and lot of work is going on.

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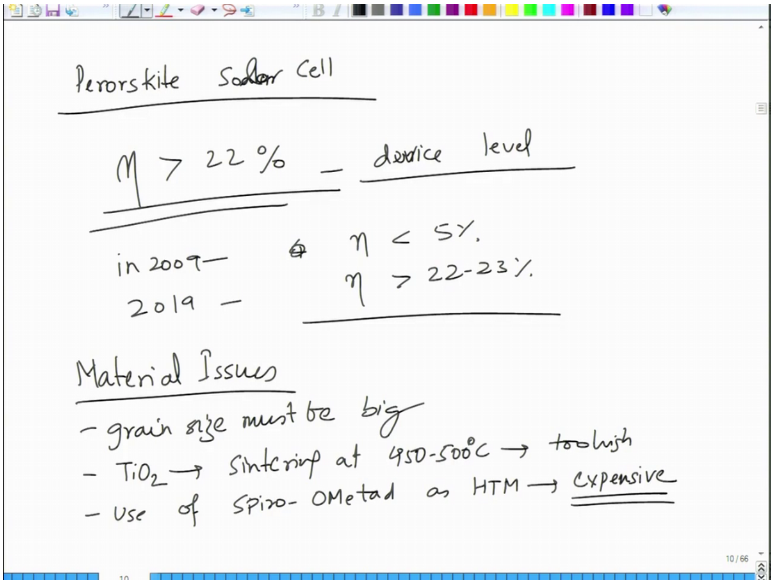

Now, this perovskite based solar cells right now, they have efficiencies of the order of. So, the efficiencies have exceeded 22 percent as of today and device level. So, in 2009, it started with the efficiency of less than 5 percent, 2019 we have more than 22 to 23 percent; huge jump in within past 10 years on this perovskite solar cells and right now, this is one of the most exciting technologies on which people are working upon. So, in this technology the microstructure of the device looks like this.

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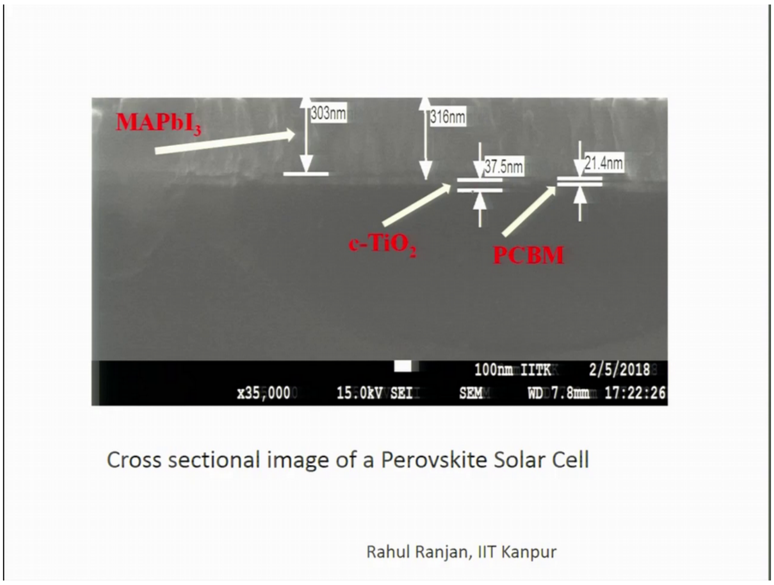

Cross sectional image of a Perovskite Solar Cell

Let me show you the microstructure how the. This is what the device may look like. You have a so this is the perovskite layer this is MAPbI 3. There is a work from our group about 300 nanometers thin which is in contact with the Ti O2 and a PCBM layer both together. So, the composite layer of c-Ti O2 and compact Ti O2 in PCBM which is the n type layer and this is in touch with the substrate which is on. So this is the perovskite layer which has a columnar structure.

What you require from the materials perspective is that so material requirements are material issues let us say. The grain size must be big generally big grain size is preferred so that grain boundaries are reduced and you have less recombination in the devices. Another issue in this is the use of Ti O2 and requires sintering at 450-500 degree centigrade which is too high. So, that is not a good thing and then use of CSPIRO OMeTAD as HTM is not good because its expensive. So, we want to avoid these issues in a device.

So, as a result lot of work is going on developing non lead freed non lead dyes, improving the grain size in the devices replacement of Ti O2 the materials which can be centered at lower temperatures and then use of other HTMs instead of CSPIRO OMeTAD which can be cheaper.

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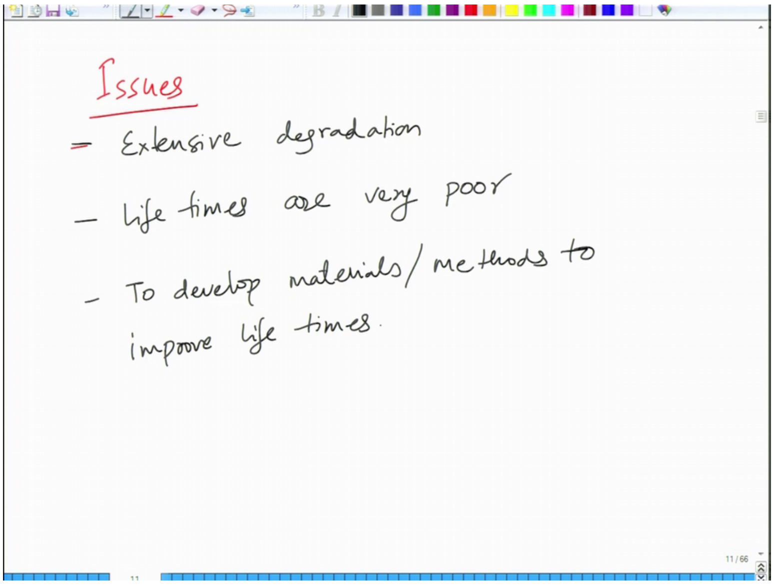

Another issue in this these solar cells is that they are extensively degrade. So, lifetimes are very poor. So, when you put a perovskite, solar cells in ambient the lifetime from 20 percent goes to less than 50 percent within no time, within 1 or 2 way depending upon the environmental condition the life times degrade.

So, what is important is that to develop materials and methods to improve life times. So, this is a short review of perovskite solar cells. These materials have shown efficiencies of the order of about 20-23 percent as of now. They have certain very good qualities, they have very good light absorption, they are easy to make, they are solid; so, basically this device a solution processable most of it.

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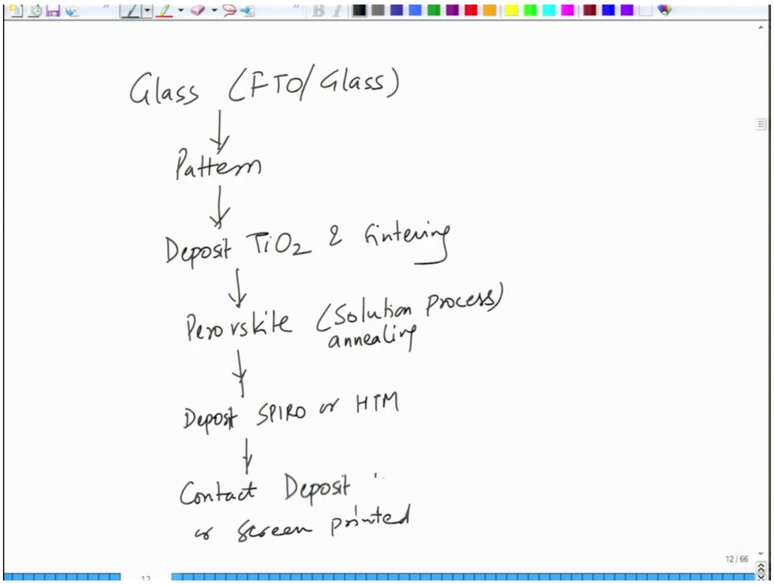

So, as just like organic solar cells when you make this device; so, manufacturing. So, you start from glass substrate FTO coated glass which is bought from the market, you pattern it, after patterning you deposit Ti O2; Ti O2 is deposited through solution technique, but it is centered at high temperature deposition Ti O2 and then sintering. And then we deposit perovskite which is again a solution based process. Solution processing you spin coat perovskite followed by a so annealing; then we deposit CSPIRO or other HTM which could be either solution processed or it could be evaporated and then, we deposit contact deposition. They can also be screen printed.

So, it is a very simple process to manufacture perovskite solar cells, but issues of degradation presence of lead and user expensive materials, it has to be brought under control, so, that we can make anything commercially out of this technology. So, finally, so, this is these are 3 third generation technologies that we have described and discussed I will briefly touch upon what CZTS. CZTS is basically Copper Zinc Tin Sulfide.

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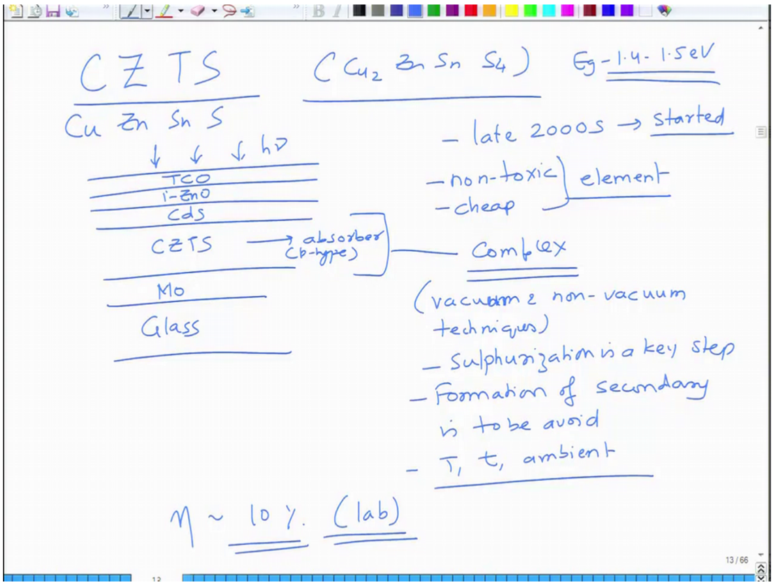

So, it contains copper zinc tin and sulfur in and the formula is C u 2 Z n S n S 4. This is a very simple technologies again based on CIGS. The device structure of this technology is like this. So, you start with a glass substrate, you have molybdenum as a back electrode. Then, we have CZTS as a active layer absorber layer which is in contact. So, this is absorber and its p type; then, we have cadmium sulfide layer. On top we put a thin layer of intrinsic zinc oxide and then we have top contact of TCO.

So, the light comes from this side. So, this is a very good technology the work started in late 2000 started. Primarily because it uses elements which are non toxic elements, cheap elements; copper is available, zinc is available, tin is available easily. So, this is where its a very exciting technology because it is very simple looking technology. How would the fabrication of CZTS is not trivial? It is a complex process because you have 4 elements present. So, as a result the fabrication of CZTS is a problem, it can be made by both vacuum and non vacuum techniques.

And so, again just like. So, very similar to CIGS technology, again in CIGS we do stalinization; here we do Sulphurization; sulphurization is a key step and formation of other phases has to be formation of secondary phases has to be is to be avoided. So, again time, temperature, ambient to form the phase is extremely important.

So, fabrication is a tricky thing and that is why this solar cell has not yet caught up. But it may catch up in the due course of time; given that the cost of these are very low and the efficiencies of these are about 10 percent as of now. So, roughly 10 percent have been achieved at the lab scale and this technology is supposed to remain exciting for at least some point of time some for some time.

The band gap of this material is about 1.4 to 5 eV. So, it is a ideally placed band gap and the absorption is also quite good. So, its a very good material and good very good technologies, but there are certain issues with respect to processing the particular phase and getting high efficiencies, but 10 percent have already been demonstrated in the at the lab scale and lot of work is going on in making this technology commercial.

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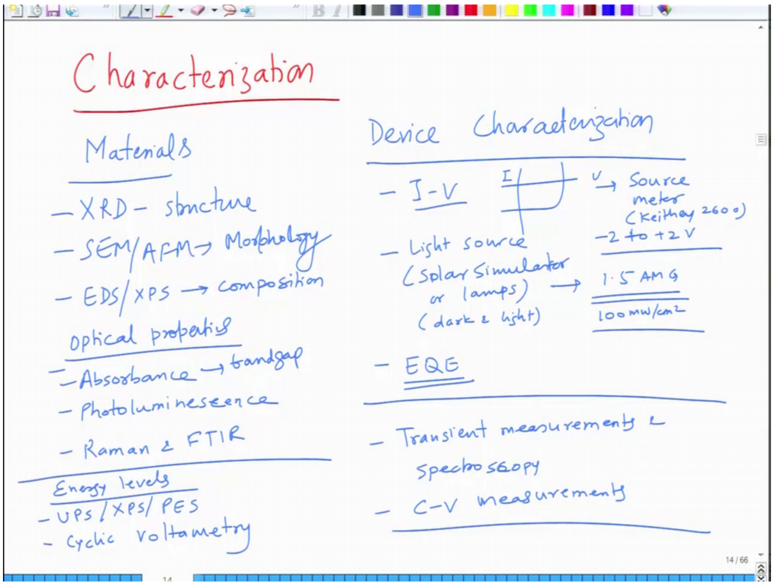

So, the last slide I will come to just the characterization part of solar cell. So, we have looked at; we have looked at Gen I, Gen II and Gen III technologies with the materials and device structures and in some cases processing issues also, processing methods also; how do you characterize these materials and technologies is important. So, there is one is called as materials characterization and then we have device characterization.

Materials characterization is done typically with techniques like X-ray Diffraction for a structure; scanning electron microscopy and atomic force microscopy for the morphology and then composition is done by either EDS or Energy Dispersive Spectroscopy or you can do XPS for composition. If you want to look at materials properties such as absorbance, optical properties you can say. For optical properties one needs to measure absorbance and one may also look at the photo luminescence, spectra. It may also be useful to look at Raman and FTIR spectra of these materials to look at the phase and type of functional groups that you have and things like that.

So, this is generally the material characterization that is done to characterize different materials X-ray diffraction can tell you what kind of phases you have, what is a grain size; scanning and scanning electron microscopy and atomic force microscopy can tell you about the roughness of thin films, the grain sizes, the presence of porosity and various other micro structural features.

Energy dispersive spectroscopy or X-ray photon and spectroscopy can tell you about the composition at local school as well as macroscopic scale as a little not macroscopic the scale of millimeter, but a scale of microns and nanometers. Optical properties like absorbance are necessary to be examined, you need to know the absorbance of the material, what wavelength range the material absorbs in and you can also determine the band gap from this for example.

So, band gap can be determined and then, photo luminescence measurements can also be done to look at the optical behavior where is the whereas, the where does the photons get quenched and whether where the photons are emitted; what kind of light is emitted in which frequency range that can be examined using photo limit cells which is useful for solar cell applications and then Raman are FTLR can be used to look at the molecular structure of materials.

Device characterization requires you to measure I-V characteristics to begin with and this I-V characteristics this plot. So, this is I-V, you require a source meter; you require a source meter. So, generally we have Keithley 2600 which is the most common commonly used source meter, but there are those meters available as well.

So, generally we should be able to measure between minus 2 to plus 2 volt for small devices and for bigger devices you will require different spectra. And you must have current compliance which is so you must know; what so you must know the equipment based on the current and voltage compliance of the device so that your current and level current and voltage levels are within the threshold measurement capability of the equipment.

Then, we require a lights light source and these light sources are called a solar simulators; simulators or one also uses customized lamps which mimic the solar spectrum or which can provide you certain spectral range within which you make the measurement. So, generally we make the measurement at 1.5 AMG, but you can make and you. So, this is equal to 100 milliwatts per centimeter square.

We also need to make EQE that is External Quantum Efficiency measurements. These are specialized systems which one can buy or one can fabricate, if you have sufficient expertise and if you want to do advanced characterization and then of course, I-V measurement, one needs to conduct in both dark and light conditions. And then look at the diode behavior what kind of current you get what kind of voltage you get what kind of fill factor you get and so on and so forth.

External quantum efficiency measurement is important to look at the quantum efficiency; what is the quantum efficiency at high wave lengths; what is the quantum efficiency at low wave lengths; what is in middle wavelengths? And if you want to do advanced characterization, you can look at transient measurements, time dependent measurements, transient spectroscopy. One can look at capacitance voltage measurements and so on and so forth. So, there are lot of things that one can do as far as materials characterization, if you want to measure the energy levels, then one needs to do Sorry.

Student: UPS.

So, one needs to do UPS or XPS kind of measurements. So, photoelectron, PES photoelectron spectroscopy, these measurements are useful for measuring the energy levels and then we also need to do cyclic voltammetry of certain materials to measure the homo lumo for example, in case of organic materials. So, these are the characterization methods which generally one needs to use. There are detailed discussions of detailed information of element various books on characterization, but this is a general guide to what kind of characterization one needs to do for solar cells.

So, this brings us to the end of this course. I hope that we have been able to learn about the principles of solar cells in terms of how. So, we started with solar radiation; what solar radiation is; how do you measure it? And then we learnt with semiconductors; what semiconductors are; what the electrical properties are; then, we move to junctions; a p-n junction is the backbone of solar cells. So, we learnt about operation of p-n junction in dark and light and then, we looked at different technologies; first generation, second generation, third generation technologies. With emphasis on the materials, the device structure and processing issues.

So, this is sort of an overview of photovoltaics in general. I hope you have been able to learn solar photovoltaics to some detail in this course. I have given you certain references to learn at every stage. So, the Gen III technologies you do not find too many books available. So, Gen III technologies are mostly good to learn from various review articles and periodicals which are available in literature. So, if you just Google it, you will find plenty of information available to as per this technology with regard to these technologies.

So, I hope you have enjoyed the course and if you have any questions you can always write back to me on the course portal and so, hope you find the; hope you find the course useful for doing research in this particular area working in this area.

Thank you very much.