

**Solar Photovoltaics:
Fundamental Technology and Applications
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**Lecture-20
Photophysics of Quantum Dot Solar Cells**

Welcome everyone to our course, today we will learn about quantum dot base solar cell. In earlier few lectures we introduced you the concept of first generation and second generation solar cell. In first generation solar cell we have discussed about single crystal silicon solar cell and what we learn that starting from the sand we can make a single crystal silicon and the single crystal silicon is further doped to make a p-n junction silicon solar cell.

Now many times due to the use of the excess heat and the low yield this process is very very expensive. In the second generation solar cell or amorphous thin film based solar cell, we get efficiency which is less than the first generation solar cell. But the manufacturing cost is much lower in comparison to the single crystal silicon solar cell that is why the most of the solar panels or solar modules that have been fabricated by this thin film amorphous silicon solar cell.

Now we introduced you the concept of the third generation solar cell also and we discuss that due to the discovery of different materials where are different varieties of third generation solar cell can be possible. Like if we new kind of dye or sensitizer molecule then we can fabricate dye sensitize solar cell. In one of our class we have explained the photophysics behind this dye sensitize solar cell and we have also demonstrated you how to fabricate this DSSC device in the lab.

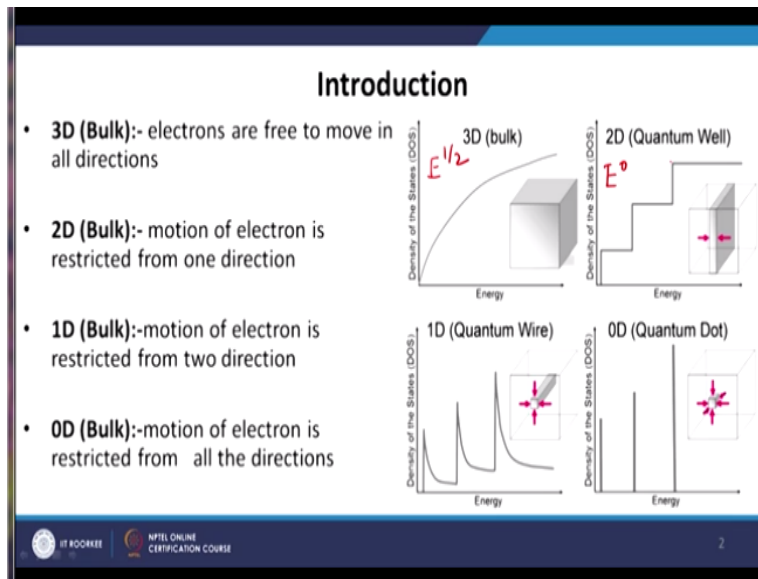
The fabrication of DSSC device that depends upon the choice of the dye and the electrolyte molecule. Similarly using the organic polymer we can make organic photovoltaics or organic bulk heterojunction solar cell. If we change the material from organic polymer to perovskite material we can fabricate perovskite solar cell. Now in this context another important category of this third generation solar cell is quantum dot base solar cell.

Now today first we will discuss about what is quantum dot how the quantum dot are made and then how we assemble this quantum dot to fabricate a quantum dot base solar cell. So before going to the quantum dot first let us see like which we have also discuss earlier about the density of state. If you remember the density of state is defined as the number of available energy states/unit energy/unit volume.

It tells you how many states are available from the charge carriers for occupancy. We also have learnt that there is a probability distribution function which tells that at a particular energy E what is the probability of occupancy of an energy state by an electron. And we have also seen that if we multiply the density of states with the probability density which we defined as a fermi distribution function and if we integrate it over all possible energy state.

Then we get the total number of electrons or total number of holes in the corresponding band. Now in the context of the density of state we have seen that when we change the dimension of the material the density of states change significantly. For example if you look here this 3D bulk material, here the electrons are free to move in all directions.

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And we have seen that the density of states in that particular case was proportional to E to the power half and if we plot density of states versus the energy then it looks like this graph. On the other hand if you look a 2 dimensional bulk material, for example 2 dimensional grapheme sheet.

Here the motion of electron is restricted from 3 dimension, so instead of 3 different dimension now electron are free to move in 2 direction.

So in the 2 dimensional system the density of states is constant, we can write it as E^0 because E^0 is constant. And if we plot the density of states first as energy for example in a case of quantum wire it looks like this (04:46). The third system in this category is 1 dimensional bulk system. So basically starting from a 3D bulk material we are reducing the dimension one by one.

You can take an example of a chalk and let us reduce the dimension of the chalk by reducing 1 dimension at a time and let us calculate what is the density of states corresponding to that particular dimension. Now in 1 dimensional bulk material motion of electron is restricted from 2 direction, so that means electron are now free to move in only one dimension. In that case the density of state is proportional to $E^{-1/2}$ or 1 over square root of E .

And if we plot the density of states first is energy for an 1 dimensional quantum wire it looks like this graph. Finally we have a 0 dimensional material where the motion of electron is restricted in all directions for example quantum dot. Now in here the density of states is a delta function and which can different values as you have plotted here the density of states is looks like a delta function.

Now this delta function kind of density of states that defines that at a particular position the value of the potential is infinitely high and at any other positions it does not exist. In the case of quantum dot which are very very small size particle usually in a dimension between 1 to 10 nano meter size. The effect of quantum confinement happens and because of that this kind of material shows a size dependant optical electrical and mechanical properties which usually why do not absorb in a bulk material.

That is an important features or characteristics of this quantum dot and this quantum dots has been use to fabricate different kinds of optoelectronic devices like light emitting diodes or solar cell, that we will see.

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Property/Phenomena	Specific Properties	Bulk State	Nano State
Structure	confinement	No confinement	Confine in zero, one, two and three dimension
	Surface to volume ratio(S/V)	(S/V) is small	Approaches 1, when all atoms are surface atoms
Electronic Properties	Band Gap	Constant value	Band gap is size dependent
Thermodynamic properties	Melting point	Metal have high melting point	Metal nanoparticle have low melting point

Now if we compare some of the important parameters or properties of the bulk material to the nano material. So we can see that in some case we get certain advantage over using an nano material over a bulk material. For example in this table you can look here, so we are comparing the first we are comparing is the structure. Now in the structure the specific properties is the confinement or surface to volume ratio, surface to volume ratio is also called aspect ratio.

Now in the bulk state there is no confinement, so electron is free to move in all 3 different direction. But in nano state like quantum dot here it is confined in 0 or 1 or 2 dimension and sometimes it is 3 dimension. So basically we can also make a nano particle where all the 3 dimension exist but the size is more than 10 nano meter. So anything like let us say we make a nano particle of 100 nano meters, so then we cannot say that it is the motion of the electron in this nano particle is only confined in 0 dimension or 1 dimension.

In this particular case the electron motion is confined or it is allowed in all 3 different directions. So the confinement have a freedom in the case of the nano state aspect ratio in the bulk material is small whereas in the nano it almost approach to 1 where all atoms are the surface atoms. Now if the aspect ratio is very high so that means the probability of contact of any external molecules to this kind of systems is much higher.

That is why the nano state materials are very very effective and useful for fabricating different kind of sensor material. Next important parameter is in terms of the electronic properties, now whenever we talk about electronic properties the first thing come in the mind is the band gap. Now we have learned that the band gap is the forbidden energy gap between the valance band and conduction band, in the case of the bulk material the band gap value is constant.

Whereas in the case of the nano material the band gap is size dependant, so what does it mean. Let us say I have a bulk zinc oxide so or bulk titanium dioxide the band gap value is 3.2 electron volt whereas if I make a titanium dioxide of 100 nano meter and if I make a titanium dioxide of 10 nano meter there will be a significant change in it is band gap. Similarly this quantum dot if I have a quantum dot of 2 nano meter or if I have a quantum dot of 4 nano meters their band value is different.

So we can have a tunable band gap in the same material system of course the experimental condition of fabricating this material has to be different. Now if the band gap is different obviously it is optical properties will also be different and some of it is electrical properties will also be different. Thermodynamic properties like melting point metals of high melting points but metal nano particles have low melting points. So in terms of melting points we do not gain much when you go from the bulk state to the nano state.

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Comparison of Properties of Bulk and low dimensional materials			
Magnetic properties	Magnetic effect	Bulk ferromagnetic material usually forms multiple magnetic domains	Small magnetic nanoparticle consist of only one domain and exhibit a super Para magnetism
Other Properties	Density of states	Directly proportional to the $E^{1/2}$	2D=constant ✓ 1D $\propto E^{-1/2}$ ✓ 0D- different for individual energy levels ✓

Now there are some other properties also we can compare for example magnetic effect, now bulk para magnetic material they usually for multiple magnetic domains. Whereas in nano magnetic particle they consist of only one domain and exist a super para magnetism. Density of states for a bulk materials is proportional to always E to the power half or square root of E whereas in the case of the nano material we can get either a 2 dimensional structure or a 1 dimensional structure or a 0 dimensional structure.

So density of states for a 2 dimensional material is constant for a 1 dimensional material it is inversely proportional to the square root of E . And for a 0 dimensional material it is different for individual energy levels and we have seen that it follows a profile of the delta function. Now since the density of states is different according to the different dimensions, now if we multiply with the fermi distribution function to get the number of electrons or holes in this system.

So it will be different from 2D to 1D to 0D from the same material system, for example let us say I have a carbon electrode, a carbon electrode of a 3 dimensional material, a carbon electrode of a 2 dimensional material and a carbon electrode for 1 dimensional and a carbon electrode of 0 dimensional material like carbon quantum dot. So in all of this cases the density of states will be different because although the material is made of carbon, the dimension of the material is different, starting from 3D it goes all the way to 2D to 1D to 0D.

Now if the dimension is different the density of states is also different, now if the density of states is different when we multiply even the same value of the fermi distribution function will get the different charge carrier concentration. So that is why we can see a significantly different value of the charge carrier dynamics and charge carrier concentration when you go from a 3 dimensional graphite to a 0 dimensional carbon quantum dot.


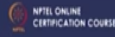
And because of that their optical properties as well as electrical properties is way different. Now the quantum dots actually was discovered a long back.

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History of quantum dots

- History of QDs begins with their first discovery in glass crystals in 1980 by Russian physicist Ekimov. Systematic advancement in the science and technology of QDs was driven after 1984, when Luis Brus derived a relation between size and band gap for semiconductor nanoparticles by applying a particle in a sphere model approximation to the wave function for bulk semiconductors.
- It finally catches up the speed by successful synthesis of colloidal CdX (X = S, Se, Te) QDs with size-tunable band-edge absorption and emissions by Murray et al.
- CdX is the most investigated QDs due to their excellent optical and electrochemical properties.

E_g d
 CdS
 $CdSe$
 $CdTe$



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History of quantum dot begins with their first discovery in glass crystal in 1980 by a Russian scientist Ekimov and who have a very very systematic advancement on the research of the quantum dot. And it also lead to the 1984 discovery by Luis Brus who derived a relation between the size and band gap for semiconductor nanoparticles by applying a particle in a sphere model approximation to the wave function for bulk semiconductor.

We can always find out a relation between the size of the nanoparticle and the band gap for semiconductor. For example let us say the quantum dot Cdse which is made out of cadmium and selenium and if we know it is band gap E_g and if we know it is dimension let us say d . So basically one can find out from the dimension what it will be the corresponding value for the band gap or other way round if I know the band gap we can find out the dimension of the particle.

So we have a tunability over the band gap that means you have tunability over the optical properties. It finally catches up the speed by successful synthesis of colloidal cadmium CdX , so colloidal cadmium based compounds like cadmium sulfide, cadmium selenide or cadmium telluride with (()) (13:48) structures, so a size tunable band is absorptions and emissions.

And because of that this kind of quantum dots has become very very popular over a very short amount of time. And this quantum dots can be made by solution based approach, CdX is the most

investigated quantum dot due to their excellent optical and electrochemical properties. In most of our experiment which still use cadmium based quantum dot it can be either cadmium sulfide, so we can write it as cadmium sulfide or we can write as cadmium selenide or we can write it as cadmium telluride.

So any of this combinations we can make it by suitably choosing the precursor materials and the reaction condition. And by changing the temperature of the growth we can also control the particle size of each of this quantum dot. So what is the definition of quantum dot then.

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The slide is titled "Quantum dots" and contains the following text:

- **Quantum dots (QDs)** are tiny semiconductor particles a few nanometer in size, having optical and electronic properties that differ from larger LED particles.
- Many types of quantum dot, when excited by electricity or light, emit light at frequencies that can be precisely tuned by changing the dots' size, shape and material. *cdse*
- Quantum dots are sometimes referred to as artificial atoms emphasizing their singularity, having bound, discrete electronic states, like naturally occurring atoms or molecules.

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Quantum dot which is also abbreviated as QD there the tiny semiconducting particle usually a few nanometer in size as I said usually less than 10 nanometer having optical and electrical properties or electronic properties that is significantly different from the larger corresponding bulk particle. Many types of quantum dot when excited by electricity or light, emit light at frequency that can be precisely tuned by changing the dot size, shape and material.

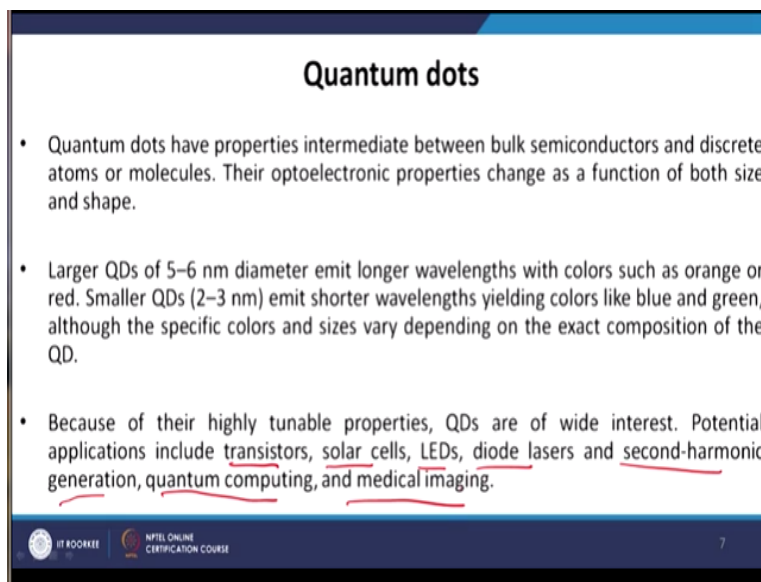
So what does it means is that let us say even if I have this material cadmium selenide, so by changing it is size or by changing it is shape we can change it is emission or photo emission properties. So that means we can make a light emitting diode as per our desired emission wavelength just by changing the size or shape of the cadmium selenide. Similarly if we go from

cadmium selenide to cadmium telluride or cadmium telluride to cadmium sulfide we can also change a tune it is optical properties.

So that is one of the biggest advancement the quantum dots provide us the tunable optical and electrical properties based on the size, shape and material. Quantum dot are sometimes referred to as artificial atoms, emphasizing their singularity having bound discrete electronic states like naturally occurring atoms or molecules. Now we know that in atoms or molecules we have discrete energy states.

Now in quantum dots the energy states are also discrete, so that is why sometime they are also called artificial atoms.

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Quantum dots

- Quantum dots have properties intermediate between bulk semiconductors and discrete atoms or molecules. Their optoelectronic properties change as a function of both size and shape.
- Larger QDs of 5–6 nm diameter emit longer wavelengths with colors such as orange or red. Smaller QDs (2–3 nm) emit shorter wavelengths yielding colors like blue and green, although the specific colors and sizes vary depending on the exact composition of the QD.
- Because of their highly tunable properties, QDs are of wide interest. Potential applications include transistors, solar cells, LEDs, diode lasers and second-harmonic generation, quantum computing, and medical imaging.

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Quantum dot have properties which are intermediate between bulk semiconductor and discrete atoms or molecules. Now if I have a single atom or molecule of a zinc oxide and if I have a bulk zinc oxide there is a huge difference in their properties. Now quantum dot has properties which is not similar in either one of them. Their optoelectronic properties changes as a function of both size and shape.

Larger quantum dots are 5 to 6 nanometer diameter they emit longer wavelengths with color such as orange or red, smaller quantum dot like 2 to 3 nanometer they emit shorter wavelengths

yielding colors like blue and green. Although the specific color and size they are very much depends on the exact compositions of the quantum dot. Now although this is a trend but we cannot generalize this statement usually what we see that this quantum dots with 5 to 6 nanometer size.

They emit something like orange or red color but the quantum dot which had like 2 to 3 nanometer they emits blue color. But this is not a very general statement it also depends upon what particular kind of quantum dot we are taking or what particular kind of quantum dot we are using for making our device. Because of their highly tunable properties quantum dots are of wide interest, potential application they are used very very extensively in fabricating transistors, solar cells, light emitting diodes, diode lasers.

And also second harmonic generation, second harmonic generation is a non linear optical effect. So here starting from one particular frequency we can generate different kind of frequency, different kind frequency means different kind of color. Quantum computing in area which has become very popular now a days and medical imaging. So since this quantum dot has a very strong degree of fluorescence emissions which is often quantified it by it is quantum efficiency of fluorescence and quantum efficiency of fluorescence for quantum dot is quite high.

So that is the reason this days are very potentially good candidate as a fluorescence probe or imaging probe in medical imaging. So not only in optoelectronics devices like solar cell LED or transistors or lasers they are also used in sophisticated applications like quantum computing and also in medical imaging.

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Synthesis of Quantum dots

- There are three main methods for the synthesis of quantum dots:-
- Lithography
- Colloidal Synthesis
- Epitaxy:- Pattern growth and Self Organised

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Now coming to the synthesis of the quantum dots there are 3 main methods we follow to make the quantum dot. The first method is a more physical based techniques called lithography, the second method is a solution base approach called colloidal synthesis, this is relatively easier to make in the lab. And then the third method is also another physical techniques called epitaxy, pattern growth and followed by the self organizations of this nanoparticle ok.

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Lithography

- The word Lithography comes from the Greek word Lithos, meaning stones and Graphia means to write. So it means literally writing on stones.
- Lithography (or patterning) refers to the series of steps that establish the shapes, dimensions, and location of the various components of the integrated circuits.
- For lithography processing, a hard copy of the pattern has to be first generated. This is called a reticle or mask.

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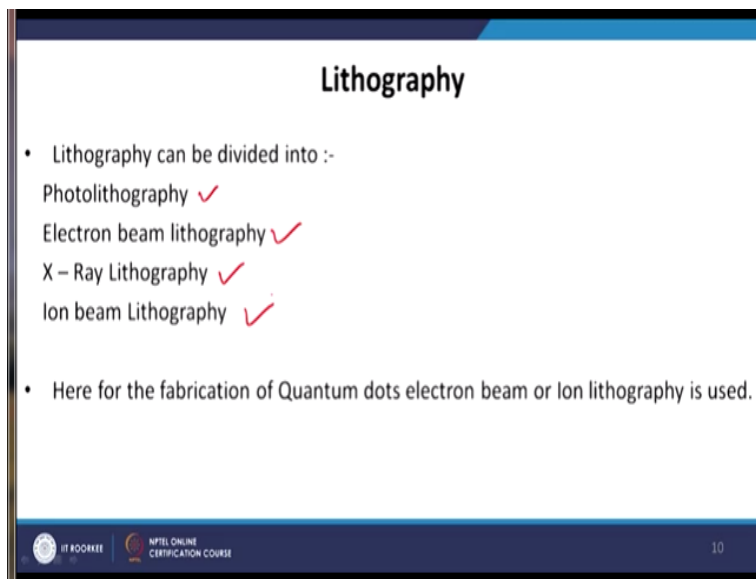
So let us come to the first procedure called lithography the word lithography that comes from the Greek word lithos, meaning stones and Grpahia means to write. So if you see that this word lithography they contains 2 different (()) (19:27) or they contains 2 different parts one is litho

which comes from the Greek word lithos and lithos means stones and graphy it comes from the Greek word Graphia which means to write.

So if we convert it a (()) (19:42) transition from the English to the Greek, so the meaning of lithography is literally writing on stones. So by the process of lithography we usually we mean patterning and patterning any particular kind of semiconductor substrate. So lithography or patterning refers to the series of steps that establish the shapes, dimensions and locations of the various components of the integrated circuits.

For lithography processing a hard copy of pattern has to be first generated, this is called a reticle or a mask. So for doing the lithography which can be electro-lithography or photolithography, so where in electro-lithography we use an electron beam to write the pattern. In photolithography we use an optical beam to write the pattern. But in either case to write the pattern we have to have some kind of structure or some kind of mould using which we can generate the patterns and that mould or structure is called mask or reticle.

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The slide is titled "Lithography" and contains the following text:

- Lithography can be divided into :-
 - Photolithography ✓
 - Electron beam lithography ✓
 - X – Ray Lithography ✓
 - Ion beam Lithography ✓
- Here for the fabrication of Quantum dots electron beam or Ion lithography is used.

At the bottom of the slide, there are logos for "IIT ROORKEE" and "NPTEL ONLINE CERTIFICATION COURSE", and the number "10" is displayed in the bottom right corner.

Lithography can be divided into photolithography, in photolithography we use light source or optical beam like laser light to write the structure. Electron beam lithography or EBM lithography where we use electron beam to write the structure, this sometimes comes with a

scanning electron microscope of SEM. Then X-ray lithography where we are using X-ray beam to make the structure and ion beam lithography.

Here we use the highly energetic ion beams to make the structure. Now for the fabrication of quantum dots we usually use electron beam or ion lithography ok.

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Lithography

- Quantum wells are covered with a polymer mask and exposed to an electron or ion beam.
- The surface is covered with a thin layer of metal, then cleaned and only the exposed areas keep the metal layer.
- Pillars are etched into the entire surface.
- Multiple layers are applied this way to build up the properties and size wanted.
- Disadvantages: slow, contamination, low density, defect formation

The diagram shows a six-step process: (a) A rectangular quantum well is covered with a polymer mask. (b) An electron beam is directed at the mask. (c) A thin layer of metal is deposited over the entire surface. (d) The metal layer is cleaned, leaving only the metal in the exposed areas. (e) Pillars are etched into the surface. (f) Multiple layers are applied to build up the structure, resulting in a quantum dot.

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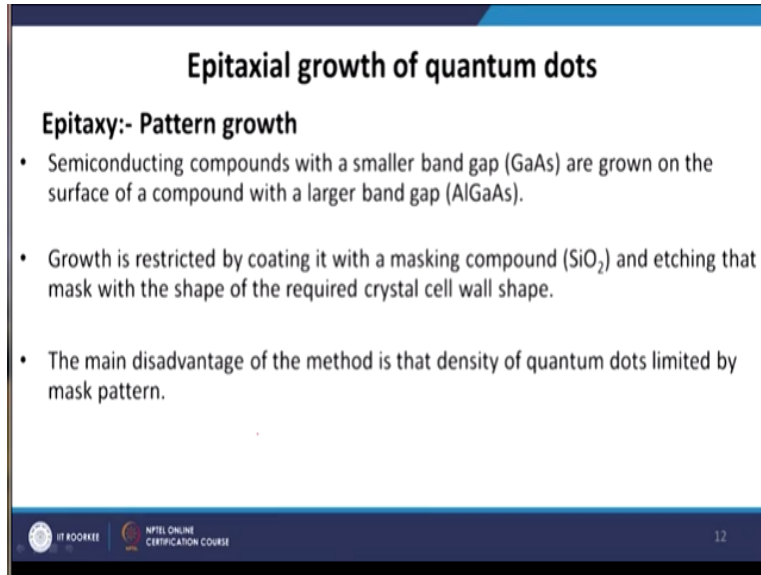
So in electron beam lithography like that is an ion beam lithography both are quite complicated process but we will try to see in a more simplistic fashion. For example quantum wells, so we start with a quantum wells and there covered with a polymer mask just like here you see this is a quantum well which is a 2 dimensional structure. And this quantum well has been covered with a polymer mask as shown in the beam here and an electron beam is falling from the top.

So quantum wells are covered with a polymer mask and expose to an electron or ion beam, so in this picture here there is a quantum well which have been covered with a polymer mask and on the top there is an electron beam is coming instead of electron beam one can also use ion beam. The surface is covered with a thin layer of metal then cleaned and only the exposed area keep the metal layers.

Now the next step is the you see there is only a thin layer of the metal which is only expose which you wanted to develop. Pillars are etched into the entire surface, multiple layers are

applied this way to build up the properties and size wanted. And there are some disadvantage associated with this process this method is slow this always inverse some contamination and the density of the material is low and sometimes we also generate defects or trap states while fabricating by this method.

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Epitaxial growth of quantum dots

Epitaxy:- Pattern growth

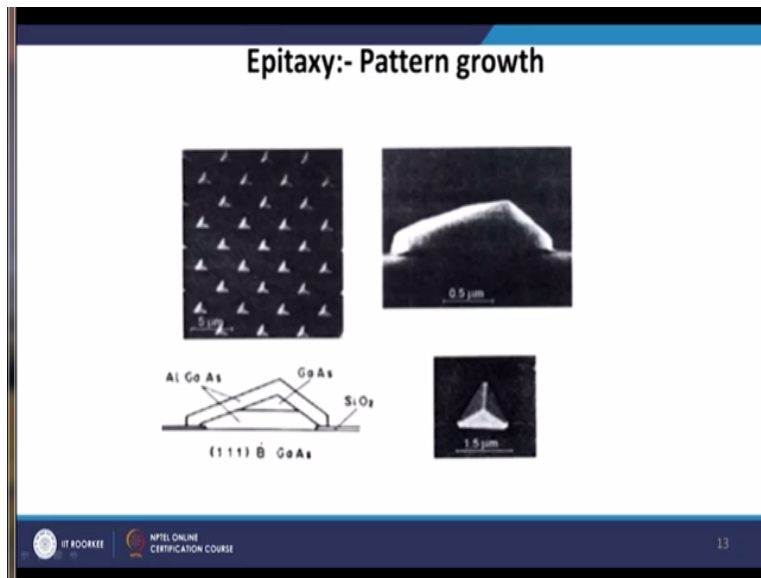
- Semiconducting compounds with a smaller band gap (GaAs) are grown on the surface of a compound with a larger band gap (AlGaAs).
- Growth is restricted by coating it with a masking compound (SiO_2) and etching that mask with the shape of the required crystal cell wall shape.
- The main disadvantage of the method is that density of quantum dots limited by mask pattern.

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The another important technique is the epitaxy or pattern growth. Semiconducting compounds with a smaller band gap for example gallium arsenide are grown on the surface of a compound with a larger band gap like aluminum gallium arsenide. Now growth is restricted by coating it with a masking compound, as a masking compound we usually use silicon dioxide and etching that mask with the shape of the required crystal cell wall shape.

The main disadvantage of this method is the density of the quantum dots limited by the mask patterns. So whatever the mask pattern we will generate that determines how many quantum dots we will be able to make in this process.

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For example in this figure we are showing that like you can see that on an indium gallium arsenide substrate we have put in a gallium arsenide substrate and then where etching it in the presence of the silicon dioxide.

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The slide is titled "Epitaxial growth of quantum dots". It has a sub-heading "Epitaxy: Self-Organized Growth" and a list of four bullet points:

- Uses a large difference in the lattice constants of the substrate and the crystallizing material.
- When the crystallized layer is thicker than the critical thickness, there is a strong strain on the layers.
- The breakdown results in randomly distributed islets of regular shape and size.
- Disadvantages: size and shape fluctuations, ordering.

Using a large difference in the lattice constant of the substrate here indium gallium arsenide and the crystallizing materials helps the epitaxial growth when the crystallization or the crystallize layer is thicker than the critical thickness there is a strong strain on the layers. The breakdown results in randomly distributed islets of regular shape and size. Some of the disadvantage associated with this method are size and shape fluctuations and the ordering of the material.

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Epitaxial growth of quantum dots

Epitaxy: Self-Organized Growth

- Uses a large difference in the lattice constants of the substrate and the crystallizing material.
- When the crystallized layer is thicker than the critical thickness, there is a strong strain on the layers.
- The breakdown results in randomly distributed islets of regular shape and size.
- Disadvantages: size and shape fluctuations, ordering.

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Now the third method which is popularly used in many of the research labs as well as in some of the industry process is the colloidal synthesis of quantum dots. One of the advantage of colloidal synthesis that in apart from the fact you can make it in a bulk amount you can also make it on a flexible substrate. Because you can print it or you can (()) (24:22) coat it on a flexible substrate in a roll to roll basis.

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Colloidal Synthesis of quantum dots

- The QD synthesis methodologies have progressed substantially in the past two decades, and various synthetic approaches have been developed for the synthesis of QDs, ranging from liquid-phase methods to vapor phase epitaxial growth.
- The liquid-phase methods have the potential to produce highly dispersed QDs in various solutions with less energy-demanding processes.
- A traditional approach for the synthesis of QDs relies on the heating of specific organic solvents and injection of semiconductor precursors, As the schematic diagram shown in figure.

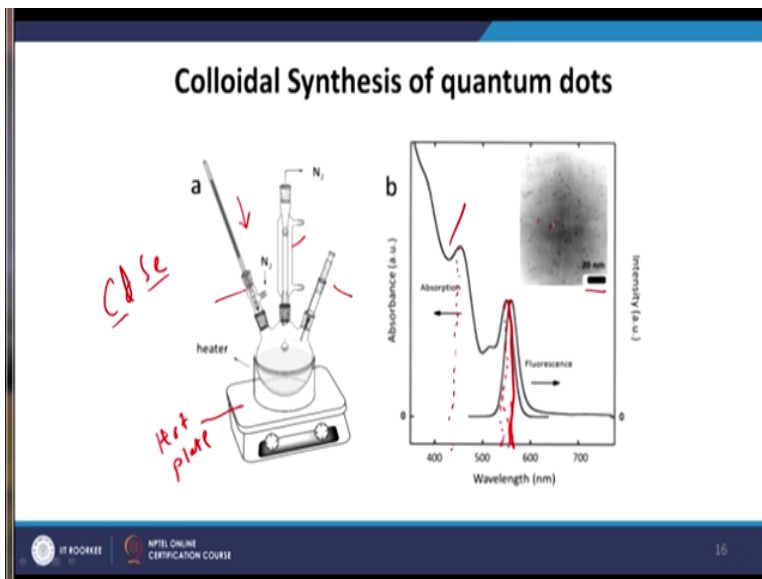
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The quantum dot synthesis methodologies have progressed substantially in the past 2 decades and various synthetic approach have been developed for the synthesis of quantum dots. Ranging from liquid phase to vapor phase epitaxial growth, the liquid base methods have the potential to

produce highly dispersed quantum dot in a various solutions with less energy demanding process.

A traditional approach for the synthesis of quantum dots relies on the heating of specific organic solvent and injection of semiconductor precursors as the schematic diagram shown in the next figure.

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So as you can see here like you know here we are showing a hot plate, so this is a hot plate and there are 2 knobs in this hot plate one is for the rotation and another is for changing the temperature. Now we have put a conical flask which has 3 neck you see here this is one neck this is the second neck and this is the third neck. So a 3 net conical flask has been put on a beaker which has been kept on a hot plate or a heater.

Now what happens like we purge from one of the neck or one of the inlets the nitrogen gas. And the precursor molecule is purged from the this inlet and we also substantially heat the material. So whenever like for example let us say I have to make a Cdse or cadmium selenide, so I have to choose a precursor for cadmium and I have to choose the precursor for selenium.

And this precursor materials are injected from one of this inlets and then nitrogen is bubbles and we precisely control the temperature by using this hotplate. And then within a certain interval we

take out the dispersions and cool it down and depending upon the time interval you allow the reaction to proceed you can have a different size distributions in the quantum dot. For example here like you know we are showing a particular size distribution for the quantum dot, the absorptions and fluorescence has been plotted in a same graph as a function of the wavelength.

The first graph this is showing the absorption spectrum and as you can see that this absorption is somewhat like you know around like you know 425 to 430 nanometer range. And which has also a tail which has an end here also like somewhat around 550 nanometer. And when you excite this quantum dot and it is absorption maxima at 420 nanometers, so it emits with a color which is equal to somewhat around 550 nanometers or yellow color.


Now SEM image high resolution SEM image has been picked up this quantum dot as you can see from this figure, the scale here is 20 nanometers and if you look that if this much is the 20 nanometer and it is quantum dot we are showing just by 1 1 dot. So the particle size hardly about 2 to 3 nanometers and again like this particle size can be always be tuned depending upon the experimental condition of the synthesis.

At what time we take out the particle or how much heat we are providing or how much precursors we are providing based on that we can even change the size and sometime the shape of this quantum dot.

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Colloidal Synthesis of quantum dots

- In a typical preparation approach of CdSe QDs, the Cd precursor and Se precursor solutions are first prepared by mixing Cd(CH₃)₂ and elemental Se in liquid tri-n-octylphosphine (TOP) solutions respectively, which are then rapidly injected into heated trioctylphosphine oxide (TOPO) solution under an inert atmosphere in a batch reactor (typically, a three-neck round-bottom flask).
- Here TOPO serves as the stabilizing agent and high boiling solvent, which allows the mixture to reach high reaction temperatures (up to 320 °C). A series of QDs with different sizes from 1.5 to 11.5 nm could be obtained over a period of a few hours by controlling the growth temperature.


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In a typical preparation method of cadmium selenide quantum dot for example the cadmium precursor and the selenium precursor solutions are first prepared by mixing cadmium CH₃ 2 and elemental selenium in liquid tri nitro octylphosphine TOP solutions respectively. So the precursors are here for cadmium it is Cd (CH₃)₂ and for selenium it is elemental selenium. And we take this 2 precursor in the presence of the TOP solutions which are then rapidly injected into the heated trioctylphosphine oxide r TOPO solutions under an inert atmosphere.

And the inert atmosphere is maintain by purging the nitrogens. In a batch reactor typically a 3 neck round bottom flask, so in the previous diagram we have shown that so the in there we are injecting through 1 necks this cadmium CH₃ 2 and the other neck elemental selenium in the presence of the top and the beaker already contains the TOPO solutions we have providing the heat and also maintaining the inert atmosphere.

Here TOPO serves as a stabilizing agent and high boiling solvent which allows the mixture to reach high reaction temperatures up to 320 degree centigrade. A series of quantum dots with different size from 1.5 to 11.5 nanometer could be obtained over a period of few hours by controlling the growth temperature. So as we said that by changing the temperature and by changing the time we can control the size of this Cdse nanoparticles.

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Applications

- Photovoltaic devices: solar cells
- Biology : biosensors, imaging
- Light emitting diodes: LEDs
- Quantum computation
- Flat-panel displays
- Memory elements
- Photodetectors
- Lasers

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Now what are the potential applications for this quantum dot for solar cell, like for example photovoltaic devices like solar cells. In biology this is been extensively use for fabricating biosensors and bio-imagings. For making light emitting diodes like LEDs, quantum computations, flat panel displays, memory elements, photodetectors and lasers. These are some of the potential applications where quantum dot has been used very very extensively .

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Quantum dot solar cells

- QDs have attracted considerable attention for PV applications due to their perfect crystallinity and unique optoelectronic properties which are defined by the particle size and can be controlled by the growth process.
- QDs with their characteristic of sharp absorption onset are excellent candidates as absorber materials in third generation PV cells such as QDSSCs
- In contrast to the large number of atoms in bulk material, the QDs consist typically of only 100 – 10000 atoms. The energetic structure of QDs changes dramatically with respect to bulk because of quantum confinement effects. In bulk the photo generated carriers can move freely throughout the material, whereas in QDs the photo generated carriers are confined in the three spatial directions of the QD volume.

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But our the syllabus that includes that quantum dot for fabricating solar cells, so we will discuss in detail how quantum dot can be use to make solar cell. Quantum dots have attracted considerable attention for photovoltaic application due to their perfect crystallinity and unique

optoelectronic properties which are defined by the particle size, shape and also controlled by the growth process.

Quantum dot with their characteristics of sharp absorption onset are excellent candidates as absorber materials in third generation photovoltaic solar cells such as quantum dot sensitized dye sensitized solar cells. While whenever we talked about dye sensitized solar cells we have said that when you choose a dye molecule or when you choose a sensitizer, the first thing we consider how good it is absorption or where does this material absorb.

Whether the material is good enough to absorb in the visible range and how much is this absorption coefficient. Now quantum dot does this job very well, it has a good absorption onset and its absorption coefficient is also quite high as comparable to other dyes. So that is why quantum dot is used to make a quantum dot sensitized DSSC device. In contrast to the large number of atoms in bulk material the quantum dot consists typically of only 100 to 1000 atoms.

So, usually 100 to 1000 atoms are there in a quantum dot, the energetic structure of quantum dot changes dramatically with respect to bulk because of quantum confinement effect. Now, the quantum confinement effect that is a very important effect which happens only in quantum dot and because of that they show size dependent optical properties. In bulk the photo generated carriers can move freely throughout the material whereas in quantum dot a photo generated charge carrier are confined in the 3 special directions of the quantum volume.

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Quantum dot solar cells

- Quantum dot (QD) solar cells have the potential to increase the maximum attainable thermodynamic conversion efficiency of solar photon conversion up to about 66% by utilizing hot photo generated carriers to produce higher photo voltages or higher photocurrents.
- The two fundamental pathways for enhancing the conversion efficiency (increased photo voltage or increased photocurrent) can be accessed, in principle in three different QD solar cell configurations; these configurations are shown in the figure:-

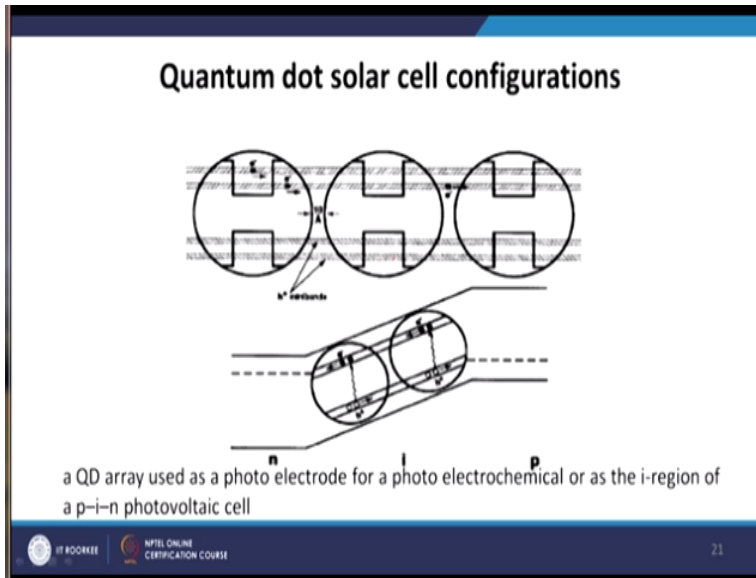
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Quantum dot solar cell have the potential to increase the maximum attainable thermodynamic conversion efficiency of solar photon conversion up to about 66% by utilizing hot photo generated carriers to produce high photo voltage or high photocurrents. Now in a single crystal silicon solar cell or in a single crystal solar cell there is a thermodynamic limit called quasi circular limit.

And according to quasi circular limit there is a particular limit of the efficiency we can get from a single junction solar cell. But when we use a quantum dot, so by using a thermodynamic conversion efficiency of the solar cell that can even bit the quasi circular limit it can reach up to 66%, how it does, it by using hot photo generated carriers to produce higher photo voltage or photocurrent.

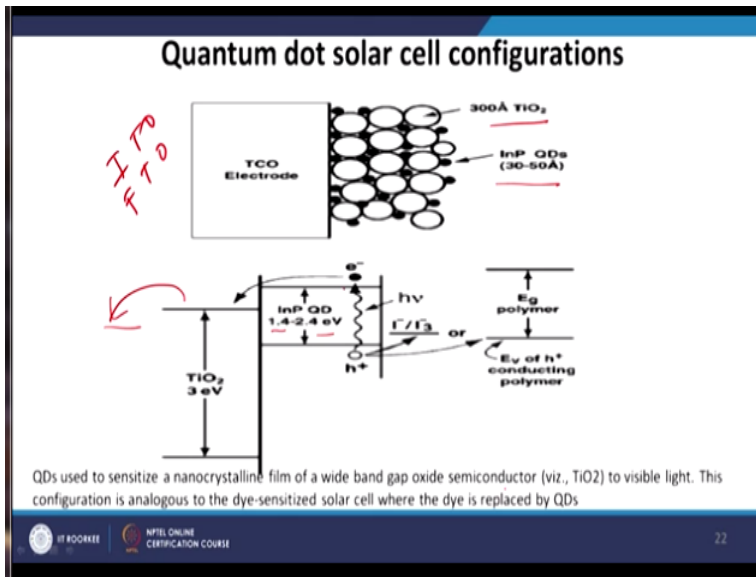
The 2 fundamental pathways for enhancing the conversion efficiency or increase photo voltage or increase photocurrent can be accessed in principle in 3 different quantum dot solar cell configurations, these configurations are shown in the next figure.

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As you can see here like you know where we are showing the 3 different configurations of the quantum dot solar cell. A quantum dot array used as a photo electrode for a photo electrochemical or as the i-region of the pin photovoltaic cells. So here this quantum dot is used as a i-region, so the intrinsic regions of pin junction device or pin solar cell.

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You see here on the left side I have a TCO electrode this is the transparent conductive oxide electrode. For example like an ITO indium dope tin oxide glass substrate or FTO fluorine dope tin oxide glass substrate any of them we can use as a TCO electrode. On top of it we have put a semiconductor titanium dioxide ok and the titanium dioxides now absorb this quantum dot and

what quantum dot we are using here indium phosphate, indium phosphate or InP is a quantum dot and we are using a dimension of 30 to 50 Angstrom.

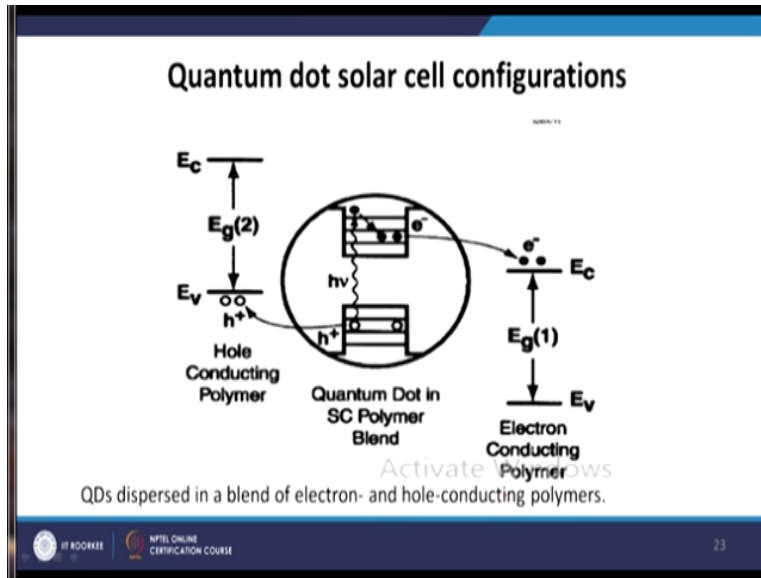
Now this quantum dot like you know they will go and sit inside the mesoporous of the titanium dioxides. Now what will happen now when the light falls on it, so the electrons will go from the ground state of the quantum dot to the different excited state of the highly higher excited state of this indium phosphate quantum dots. Now it has a band gap 1.4 to 2.4 electron volt what will happen like you know the electrons in the excited state, now it will be injected to the conduction band of the titanium dioxides.

And using the conduction band then again it will go from here to the TCO and it will come to the outside circuit. Now there is a hole in this process which is generated which is in the valance band now. Now to regenerate this hole we use a iodine, tri-iodide electrolyte a very similar recipe which we use in a DSSC device. Now the catch is here like you know here before of the quantum confinement effect we have a discrete energy band gaps, a tunable energy band gaps in the excited states.

So the excited electron can access any of the energy levels, so because of that the possibility of the electron excitement from the downstate is multifold or many fold. So we have more number of electron excitation possible in this kind of solar cell. For example here E_g the for E_g or the band gap for a polymer is showing here E_v of the h^+ conducting polymers it is showing in the right hand side.

Quantum dot use to sensitize a nano crystalline film of a wide band gap oxide semiconductor like titanium dioxide for absorbing the visible light. This configuration is analogous to the dye sensitize solar cell where we have replace the dye with the quantum dot molecule.

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Now as we have just explained that in a quantum dot in a Sc polymer blend like you know in a semiconducting polymer or in a conjugated polymer. Let us say I take a conducting polymer like polythiophene and I put some quantum dot in there. So what will happen like you know this is a hole conducting polymer and this is an all over electron conducting polymer. So now when the light falls on this quantum dot for example indium phosphate they absorb the light.

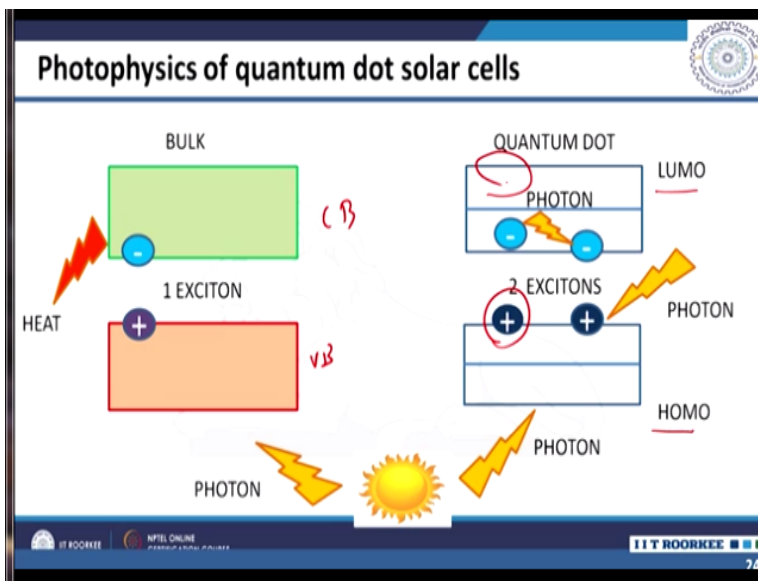
And the electron goes from the valance band to the conduction band right. And so there is a electron in the excited state and there is a hole in the valance band. Now usually for a charge conduction electron participate in the charge conduction. Now you see that I mean there are different discrete states due to the quantum confinement effect in the excited state of the quantum dot.

Now electron can jump in any of this excited states, from this state electron can jump to the nearest electron conducting polymers. Since the energy level matches with this electron conducting polymers but in it is never there is also a hole conducting polymer. Now this hole conducting polymer will be able to grab the hole from the valance band or from the lower energy states of this quantum dot, so in this process we are utilizing both electron and hole.

So whenever we are using a conducting polymer or a semiconducting polymer which is a hole conducting polymer and an electron conducting polymer junction with a quantum dot, so the

possibility of extracting electrons and holes are equal. Even if it is not equal, so at the same time we can extract the electron we can also extract the hole to some degree, so that contribute to the increase of the photocurrent.

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For example like you know this is a bulk material and you see that this is the valance band and this is the conduction band and sunlight is falling on both of this material where on my right hand side there is a quantum dot and in the quantum dot instead of valance band and conduction band we call it as a HOMO energy level and LUMO energy level. And we have learnt that HOMO stands for highest occupied molecular orbital whereas the word LUMO that stands for lowest unoccupied molecular orbitals.

So here in organic polymers or in quantum dots the organic polymers and in quantum dots the orbitals are define in terms of molecular orbitals. Now this is the highest occupied molecular orbital, so that is actually valance band at 0 Kelvin temperature. And this is the lowest unoccupied molecular orbital that is actually the conduction 0 Kelvin temperature. That is why these 2 energy levels are called HOMO and LUMO energy level.

Now I have 2 different system, let us say on the left hand side there is an indium phosphate bulk material on the right hand side we have an indium phosphate quantum dot. And here the light is

falling on both the material, so the electrons it will be going from the valance band to the conduction band.

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Here also there is a electron is there when photon falls on that, so electron goes from the valance band to conduction band, what you see they have separated the charge carrier. So electron is here and holes is in the valance band and this electrons they emits as a heat whereas in the second case same light is falling on the quantum dot. Let us have a look on this figure, now I have 2 electron in my ground state, photon waves falls on their electron 1 electron jumps from the valance band to the excited state or HOMO to LUMO level.

Leaving a hole in the HOMO energy level here and 1 electron here what happens to the next charge carrier before that the electron comes to the lowest unoccupied state and there will be a photon emission. Now the second electron that goes from the ground state to the excited state or HOMO to LUMO level leaving a hole behind. So here in the bulk case we have 1 exciton, here we have 2 excitons. So by similar approach here we get only one exciton but on the right hand side we get 2 excitons. So if I have 10000 quantum dots, so I gain $10000 * 2$.

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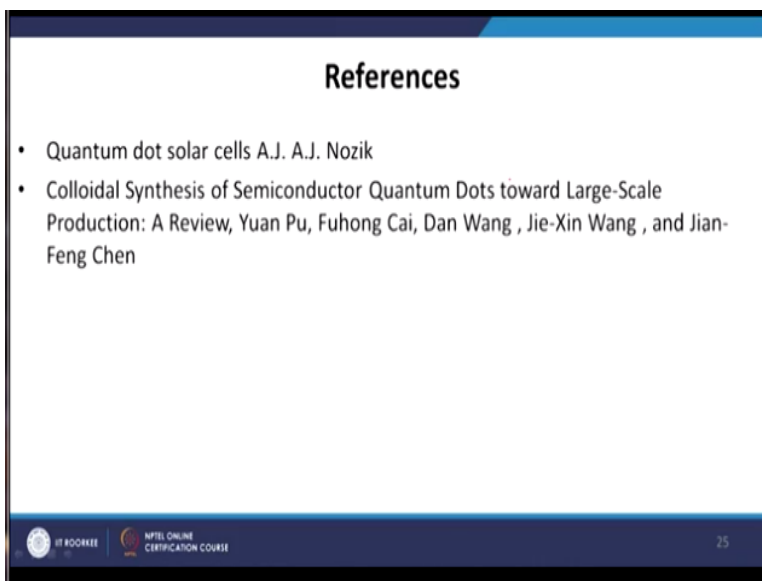
So I get two 20000 excitons in comparison to the 10000 excitons in a bulk case. So that is the advantage of using quantum dot sensitizer, so this was about our quantum dot based solar cells and as we have mention that here you can increase the efficiency of this device significantly. And even sometimes we can cross that thermodynamic limit by using to different kinds of polymers.

And quantum dot base solar cells are relatively easy to fabricate we can make it either by a physical methods like epitaxial growth or by photolithography or electron beam lithography or the most popular labile solution based or colloidal approach where we take the precursor molecules in a 3 neck conical flask which we put it on a beaker or and also the beaker is placed finally on a hotplate when you heat it.

And we add the precursor molecule in the presence of some kind of surfactant or some kind of stabilizing agents and we allow the growth of the quantum dot depending upon the temperature and the time interval the size and shape of the quantum dot is different. Now if the size and shape is different their optical properties and electrical properties also different. Now we can use this quantum dot either as a sensitizers or dye molecule in a dye sensitize solar cell or also we can use them along with some conducting polymer either with a hole conducting polymer or an electron conducting polymer.

And we have observed that in comparison to the bulk material the nano materials or the quantum dots they have an advantage of generating more kind of excitons or more hot charge carriers which can contribute to the larger photocurrents or larger photovoltaics in this kind of device. And that is why quantum dot based solar cells become very popular nowadays. Now for more reading and for a better idea you can also refer to some of the excellent text book.

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Like quantum dot solar cell by professor A.J. Nozik and colloidal synthesis of the semiconductor quantum dots towards large scale production a review paper by Feng Chen's group. And there are lot of excellent research papers and review papers are also available in this area. So you can also look for some of this to learn more about the quantum dot, thank you very much.