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

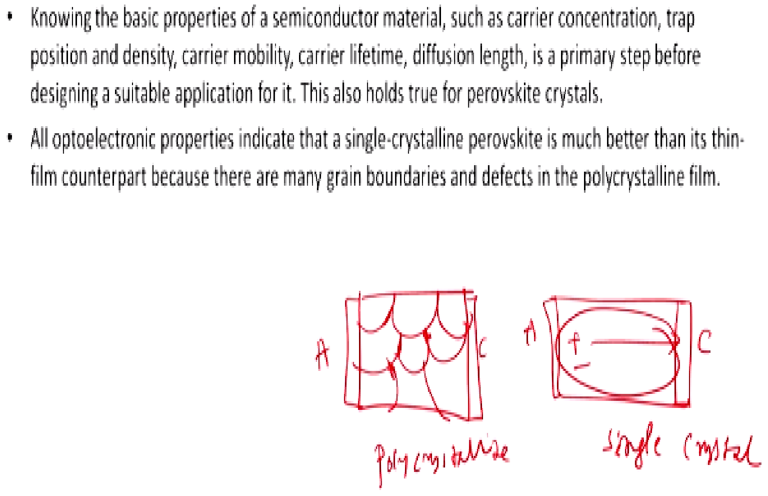
Lecture - 31
Photophysics of Perovskite Single Crystal Solar Cells

Welcome everyone to our solar photovoltaics course. Today we will have the seventh week. In today's lecture we will discuss about perovskite single crystal. Now when we discuss about the perovskite solar cell those perovskite material where a polycrystalline material, but one of the problem associated with the polycrystalline material is it is grain boundary and also the charge carrier recombination due to the defects states.

Now like inorganic crystal it has been found that whenever we go from a bulk counterpart to a single crystal material the number of defect state or number of the trap state reduce significantly in many cases and if the defect state or the trap state inside the system reduced that helps to lower the charge carrier recombination and that is always beneficial for solar cell application.

That is why the perovskite based single crystal solar cell has recently been popular as an alternative to bulk perovskite solar cell. Let us take a look about what are the advantage and what are the possible application of a perovskite single crystal.

(Refer Slide Time: 01:38)



- Knowing the basic properties of a semiconductor material, such as carrier concentration, trap position and density, carrier mobility, carrier lifetime, diffusion length, is a primary step before designing a suitable application for it. This also holds true for perovskite crystals.
- All optoelectronic properties indicate that a single-crystalline perovskite is much better than its thin-film counterpart because there are many grain boundaries and defects in the polycrystalline film.

Knowing the basic properties of a semiconducting material such as carrier concentration, trap position and density, carrier mobility, carrier life time, diffusion length is a primary step before designing a suitable application for it. This also holds true for perovskite crystal. So as I said that like whenever we choose the material for possible application in solar cell what are the properties we look for in the material?

First we look for its absorption property, how well the material can absorb or preferably we like to have a material which absorbs over a near IR range and that is related to the band gap of the material. Now second important property is absorption coefficient, that is the absorption per unit linked. Now the third important properties is that the charge carrier diffusion or charge carrier transport.

Now this charge carrier transport that depends upon the quality of the film or the morphology of the film. In most case we need a very continuous uniform almost defect or trap state free films for a very good charge carrier transport and if the mobility of the film is better that is also good for us. So all of this thing is related to the quality or the morphology of the film.

So just like it is valid in other cases similarly for a perovskite single crystal the number of defects state or the trap state is reduced that consequently lead to the less recombination and also the charge carrier mobility is high. All optoelectronic properties indicate that a single crystalline perovskite is much better than its thin film counterpart because there are many grain boundaries and defects in the polycrystalline film.

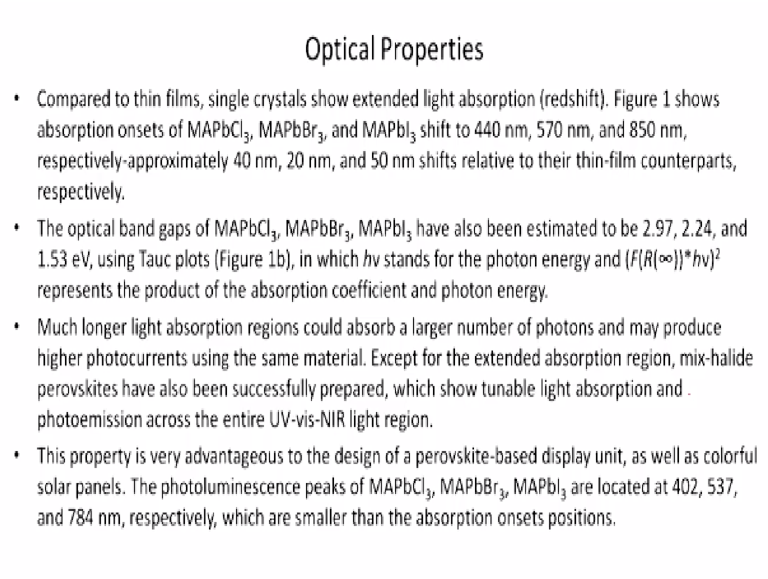
For example, if I draw this is a poly crystalline film and you consider this is the corresponding single crystal. Now in the same area if this is a polycrystalline film then we know that there are lot of these grains exist in the system. Now these 2 site are the electrodes. Now since there are lot of grains then there are lot of this grain boundaries are there. Like this kind of grain boundary.

Now this grain boundary they act like a source of the electron hole recombination. Because the potential energy minimum state exists there, but on the other hand you look a single crystal material. So here we expect to have only one domain or one grain which covers the whole material. So as usual this is your anode and cathode and let us say this is an anode and cathode.

This is a very primitive picture, this is your polycrystalline material and this is your single crystal material. So since there is only one grain here, so the charge carrier whatever has been produced here that will be directly moved to the electrode. Since it does not face any grain boundary or interfacial layer in between. So that is one of the advantage of having a single crystal material over the polycrystalline material.

Now since the number of grain boundary is less the possibility of the charge carrier recombination at those grain boundary is also reduced significantly. Although, I mean it is worthwhile to mention that in ideal case we expect that the grain boundary is as minimum as possible, but in reality when we grow a single crystal there can be some crystal grain boundary exist there.

(Refer Slide Time: 05:28)



Optical Properties

- Compared to thin films, single crystals show extended light absorption (redshift). Figure 1 shows absorption onsets of $MAPbCl_3$, $MAPbBr_3$, and $MAPbI_3$ shift to 440 nm, 570 nm, and 850 nm, respectively-approximately 40 nm, 20 nm, and 50 nm shifts relative to their thin-film counterparts, respectively.
- The optical band gaps of $MAPbCl_3$, $MAPbBr_3$, $MAPbI_3$ have also been estimated to be 2.97, 2.24, and 1.53 eV, using Tauc plots (Figure 1b), in which hv stands for the photon energy and $(F(R(\infty))*hv)^2$ represents the product of the absorption coefficient and photon energy.
- Much longer light absorption regions could absorb a larger number of photons and may produce higher photocurrents using the same material. Except for the extended absorption region, mix-halide perovskites have also been successfully prepared, which show tunable light absorption and photoemission across the entire UV-vis-NIR light region.
- This property is very advantageous to the design of a perovskite-based display unit, as well as colorful solar panels. The photoluminescence peaks of $MAPbCl_3$, $MAPbBr_3$, $MAPbI_3$ are located at 402, 537, and 784 nm, respectively, which are smaller than the absorption onsets positions.

Now optical properties, compared to thin films single crystal so extended light absorption or redshift. Figure 1, shows absorption onset of MAPbCl3, MAPbBr3 and MAPbI3 shift to 440 nanometre, 570 nanometre and 850 nanometre respectively. Approximately 40 nanometre, 20 nanometre and 50 nanometre shifts relative to their thin film counterparts respectively. So these 3 perovskite material.

One is this MAPbCl3 or like you know if you replace the chlorine with bromine or if you replace the chlorine with iodine so then you get this three different anionic combination of the MAPb family of the perovskite and there just by changing chlorine to bromine to iodine the onset changed from 444 nanometre to 570 nanometre to 850 nanometre and approximately this is a shift of 40, 20 and 50 nanometre relative to their thin film counterparts.

So what does it means like you know if we take the MAPbI3, a polycrystalline film and if we take a MAPbI3 single crystalline film and if we record the UV visible absorption spectrum of this two film we will see that there is a red shift in the absorption spectrum of the single crystal in comparison to their polycrystalline counterpart and that amount of shift is 80 nanometre or 50 nanometre in the case of iodine.

In the case of bromine it is 20 nanometre shift and in the case of chlorine-based perovskite it is 40 nanometre shift. So this shift one can attribute to the aggregations or one can attribute to the quality improvement in a single crystal film comparison to the bulk counterpart. The optical bandgap of MAPbCl3, MAPbBr3, MAPbI3 have also been estimated to be 2.97, 2.24 and 1.53 electron volt using the Tauc plots.

In which h nu stands for the proton energy and FR time h nu square represents the product of the absorption coefficient and photon energy. Much longer light absorption regions could absorb a large number of photons and may produce higher photo currents using the same material. Except for the extended absorption region mix-halide perovskites have also been successfully prepared which shows tunable light absorption and photo emission across the entire UV visible NIR light region.

Okay so just like when we have discussed about MAPbI3 or iodine base perovskite we said that by changing the iodine to chlorine to bromine we can change its band gap. Now not only the iodine to chlorine people have also used a combination of chlorine and bromine, a combination of bromine and iodine or a combination of chlorine and bromine that is called mixed halide perovskite.

And in the mixed halide perovskites the bandgap as well as stability is way different. So if we make a single crystal from the mixed halide perovskite then consequently the optical properties will be also be different. This property is very advantageous to the design of perovskite based display unit as well as colourful solar panels. The photo luminescence peaks up MAPbCl3, MAPbBr3, MAPbI3 are located at 402, 537 and 784 nanometre respectively which are smaller than the absorption on-set positions.

So the MAPbI3 a commonly used perovskite, the photo luminescence peaks happens at 784 nanometre, where as you remember its absorptions onset was around 850 nanometre. So the photo luminescence peak appears at a lower wavelength than the absorption onset.

(Refer Slide Time: 09:17)

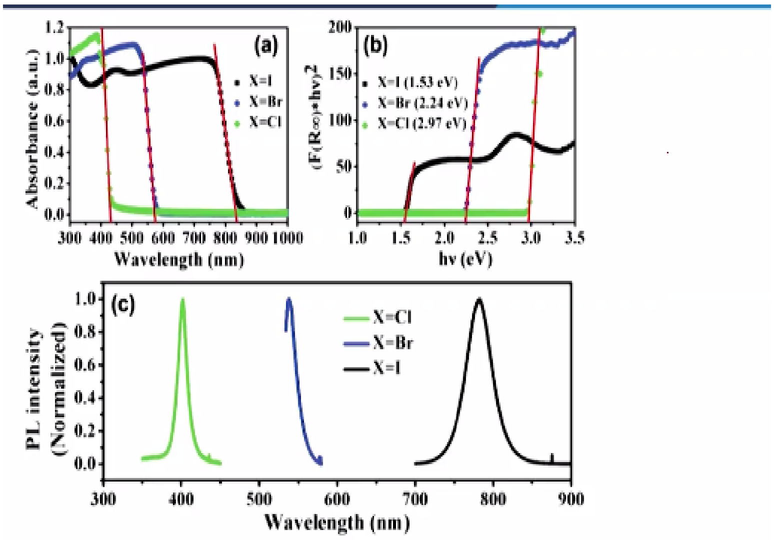


Figure 1. Light absorption and photoemission properties of single-crystalline perovskites.

Now if you look at this figures, the absorption versus wavelength here we are showing the x stands for the different halide compositions, the black curve is for the iodine and then the blue curve is for the bromine and the green curve is for the chlorine, y-axis is your absorption seen arbitrary unit and x axis is the wavelength and what we have plotted here is the tangent at the place where it is just turning.

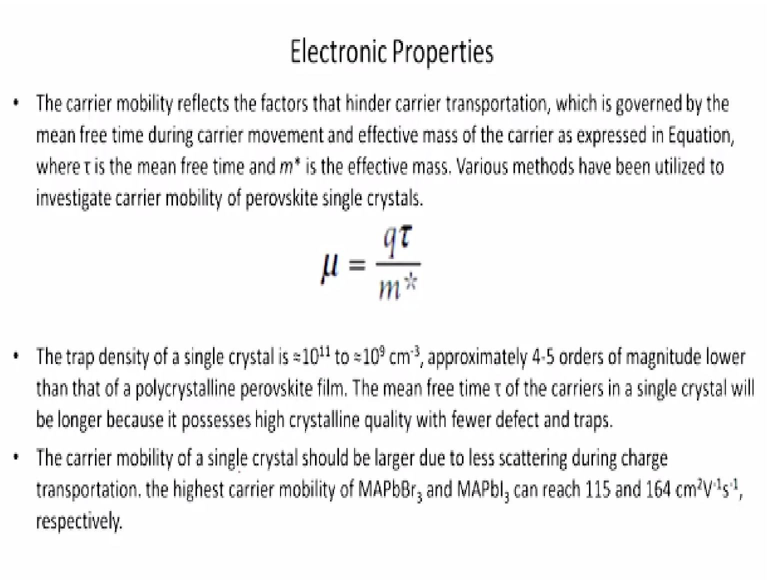
So to get the absorption on set. Now as you can see that in the case of iodine the absorption onset is happening here, the black curve, this is here, but whereas in the case of bromine the absorption onset is here and in the case of chlorine the absorption onset is here. So the absorption onset of the iodine is much higher than the bromine and absorption onset of the bromine is much higher than that for chlorine.

Or you can say that iodine greater than bromine greater than chlorine in the absorption onset. Now we can also put the photo luminescent properties here. When we excite the material in its absorptions maxima for example here. So we get the photo luminescence, the PL intensity which have been normalized here and the x-axis is your wavelength and you can see that when I take the iodine the photo luminescence is here.

And if you take the photo luminescence peak I can drop a perpendicular on the x axis so somewhere around here 780 nanometre, but you see the absorption onset for the iodine was around here that was 840 nanometre. So the photo luminescence peak has been blue shifted in comparison to the absorption peak, that corresponding to the less defects in the system. Similarly, for bromine this curve you can see the photoluminescence peak appears somewhat around here.

And for the case of chlorine if I drop a perpendicular it is happening somewhere around here. So this 2 plot is showing the absorption and photoluminescence properties of a perovskite single crystal when we vary the anionic position that means when we change the iodine to chlorine to bromine.

(Refer Slide Time: 11:33)



Electronic Properties

- The carrier mobility reflects the factors that hinder carrier transportation, which is governed by the mean free time during carrier movement and effective mass of the carrier as expressed in Equation, where τ is the mean free time and m^* is the effective mass. Various methods have been utilized to investigate carrier mobility of perovskite single crystals.

$$\mu = \frac{q\tau}{m^*}$$

- The trap density of a single crystal is $\approx 10^{11}$ to $\approx 10^{9}$ cm^{-3}, approximately 4-5 orders of magnitude lower than that of a polycrystalline perovskite film. The mean free time τ of the carriers in a single crystal will be longer because it possesses high crystalline quality with fewer defect and traps.
- The carrier mobility of a single crystal should be larger due to less scattering during charge transportation. the highest carrier mobility of $MAPbBr_3$ and $MAPbI_3$ can reach 115 and 164 $cm^2V^{-1}s^{-1}$, respectively.

Now what about the electronic properties? The carrier mobility reflects the factor that hinder carrier transportation which is governed by the mean free path during carrier movement and effective mass of the carrier as expressed in the following equation where the tau stands for the mean free time and m star is the effective mass. Now various methods have been utilized to investigate carrier mobility of perovskite single crystal.

Now the mobility of a perovskite single crystal is given by this equations where the term mu stands for the charge carrier mobility, q is the charge, tau is the lifetime, mean free time, m star is the effective mass. So basically the mobility is inversely proportional to the effective mass and it is proportional to the mean free time tau. Various methods can be adopted to measure the mobility of the perovskite single crystal.

Just like for a polycrystalline material we use various methods like time-of-flight method where we use the laser beam to excite the material and then whatever the time the electrons or holes take to travel from the bulk towards the electrode that we trace in an oscilloscope as a function of the voltage from there we can find out the mobility of the charge carrier that was the photo charge carrier mobility.

There are different methods for the mobility measurement. One of the very commonly used technique is called SCLC method, which is space charge limited current extraction method and similarly one can measure the mobility by field effect transistor FET method. FET method stands for field effect transistor method. So similarly all these methods can also be applied to the perovskite single crystal.

Whether it is an FET method, whether it is an SCLC method or whether it is a time-of-flight method all of these methods can be successfully applied to measure the mobility of the perovskite single crystal. Even we can do the mobility measurement as a function of the temperature. The trap density of a single crystal is 10 to the power 11 to 10 to the power 9 centimetre cube in verse.

Approximately 4 to 5 order of magnitude lower than that of a polycrystalline perovskite film. So the trap density of a perovskite single crystal value in unit volume of centimetre cube, it is 10 to the power 9 to 10 to the power 11 and this value of the trap is almost 4 to 5 order of magnitude lower than the perovskite polycrystalline film. So consequently the mean free time tau of the carriers in a single crystal will be longer because it passes high crystalline quality with fewer defects and trap states.

Now if the quality of the film improves if there are less trap states, if there are less defect states in the film, so obviously the charge carrier can now move without facing much obstacle or hindrance from the neighbouring charge carrier. So that leads to the higher value of the mean free path or mean free time tau in this material. The carrier mobility of a single crystal should be larger due to less scattering during charge transportation.

The highest carrier mobility of MAPbBr3 and MAPbI3 see can reach 115 and 164 centimetre square per volt per second respectively. So this amount of the charge carrier mobility what is

164 for MAPbI3 single crystal that is very high and almost comparable to a inorganic films mobility.

(Refer Slide Time: 15:10)

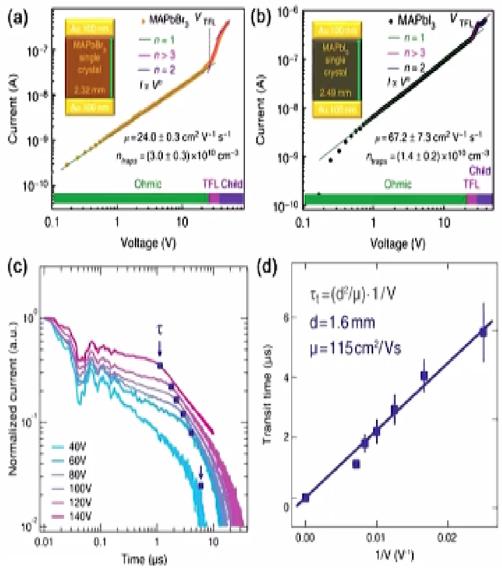


Figure 2.
a,b) trap density, carrier mobility, and carrier concentration of the crystal disclosed using the SCLC method;
c,d) TOF method and corresponding results revealing the carrier mobility of a single-crystalline perovskite.

In this figure we are showing in a and b, the trap density and carrier mobility and carrier concentration of the crystal disclosed using the SCLC method and in the figure C and D we are showing the time of flight in brief TOF method and corresponding results revealing the carrier mobility of a single crystal perovskite. So you can see here in SCLC method so what happens in both of this case we have been plotted current versus voltage.

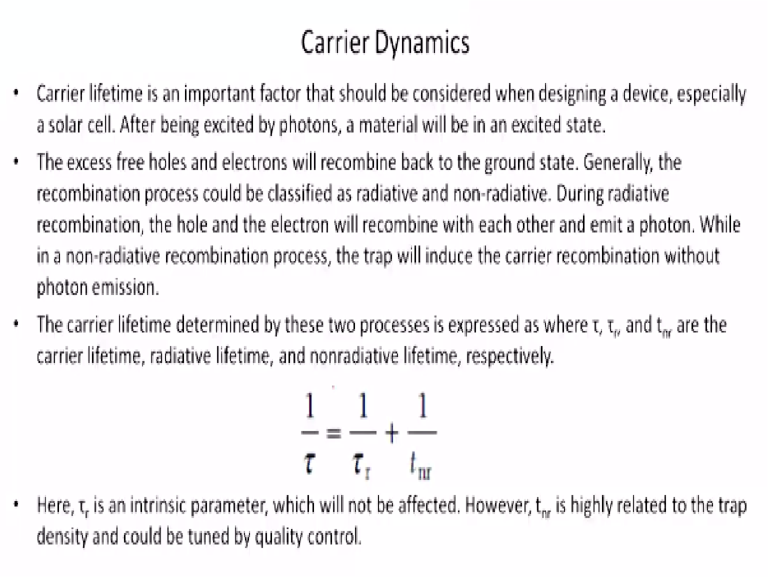
So the device structure is the following, we have this gold electrode of 100 nanometre on the both side and in between there is this perovskite single crystal MAPbBr3 2.32 millimetre single crystal which have been sandwiched between these 2 electrode. Now what happens like you know, I mean, we are changing the bias and the first region here that is the weak region where the current is proportional to the voltage.

But if we increase the voltage beyond that range then the space region dominates and we get area which is called the space charge limited current domain and that domain we measure the mobility. This was for the MAPbBr3. Now for MAPbI3 the corresponding curve is like this. So this area is the ohmic part and that is the non ohmic part or the space charge limited region.

In time-of-flight method so here the normalized current has been plotted against the time. So as I said that a laser beam usually nd at 532 nanometre laser beam falls on the material and that helps to dissociate the charge carrier and the charge carrier start moving and the flying time of the charge carrier that is measured as a function of the time for a different voltage.

For example, you look that we have applied different voltage 40 volt, 60 volt, 80 volt, 100 volt to extract the charge carrier and the corresponding current in the detector we are measuring as a function of the time and then when we plot the transient time verses 1/V from we get linear curve and the slope of the linear curve gives the mobility of the material. So these are the 2 methods and what we measure in these methods that is been shown in this graph.

(Refer Slide Time: 17:28)



Carrier Dynamics

- Carrier lifetime is an important factor that should be considered when designing a device, especially a solar cell. After being excited by photons, a material will be in an excited state.
- The excess free holes and electrons will recombine back to the ground state. Generally, the recombination process could be classified as radiative and non-radiative. During radiative recombination, the hole and the electron will recombine with each other and emit a photon. While in a non-radiative recombination process, the trap will induce the carrier recombination without photon emission.
- The carrier lifetime determined by these two processes is expressed as where τ, τ_r, and t_{nr} are the carrier lifetime, radiative lifetime, and nonradiative lifetime, respectively.

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{t_{nr}}$$

- Here, τ_r is an intrinsic parameter, which will not be affected. However, t_{nr} is highly related to the trap density and could be tuned by quality control.

Okay, the next important thing is the carrier dynamics. Carrier life time is an important factor that should be considered when designing a device especially a solar cell. After being excited by photons a material will be in an excited state. The excess free holes and electrons will recombine back to the ground state generally the recombination process could be classified as radiative and non-radiative.

During radiative recombination the hole and electron will recombine with each other and emit a photon. While in a non-radiative recombination process the trap will induce the carrier recombination without photon emission. So that we have also discussed earlier. So if I have a ground state and if I have an excited state let us say this photon beam falls on the material and electron absorbs this material this photon beam and goes from the ground state to the excited state.

Now it can stay in the excited state for some amount of time, but after some time it has to come down either by emitting the same amount of energy which can emit as the source of light which you call as a radiative emission or this amount of energy can be wasted as a heat or if there is any trap state is there then the electron can jump to the trap or defect state without emitting any life that is called non radiative emission.

So the emission always consists of the 2 part, one is the radiative part, another is the non-radiative part. So similarly or correspondingly the lifetime should have the 2 part, one is the radiative lifetime, another is the non-radiative lifetime and the total lifetime should consist of the radiative lifetime and the non-radiative lifetime. The carrier lifetime determined by these 2 process is expressed as where tau, tau r and tau nr are the carrier lifetime, radiative lifetime and non-relative lifetime respectively.

So 1/tau, where tau is the carrier lifetime that is equal to 1/tau r where tau r is the radiative lifetime plus 1/ tau nr, where tau nr is the non-radiative lifetimes. So 1/tau = 1/tau r + 1/tau nr. Here tau r or the radiative lifetime is an intrinsic parameter which will not be affected. Whenever the material is defined its radiative lifetime is already defined, why? because whenever we know the material we already know its homo energy level, we already know its lumo energy level.

And we also know how much time the electron can stay in an excited state. So that means this radiative lifetime is already fixed, but for example during the growth of the material somebody has introduced lot of trap and defect states. Let us say somebody has introduced 10 to the power 9 trap states and another person has introduced 10 to the power 11 trap states. So the second person has larger number of trap states than the first person.

So the probability of non-radiative recombination in the case of the second person is higher than the first person. So that means the lifetime due to the non-radiative part can change or can vary depending upon your crystal growth process. So tau non-radiative however tau nr is highly related to the trap density and could be tuned by quality control. So we cannot control tau r.

But we can control the tau nr, because it will depend upon how we have grow our material. So if we have a less trap state then this tau nr value will be something if you have a more and larger trap state since the tau nr comes from the trap assistant recombination so it will depend upon the value of the trap state, if you have a larger trap state then tau inner value will be something else.

So that is why we can tune the tau nr value, but we cannot tune the tau r value or otherwise tau r is an intrinsic properties of the material which we cannot tune, but tau nr which is not an intrinsic bodies of the material which depends on the trap state and which can be tuned.

(Refer Slide Time: 21:18)

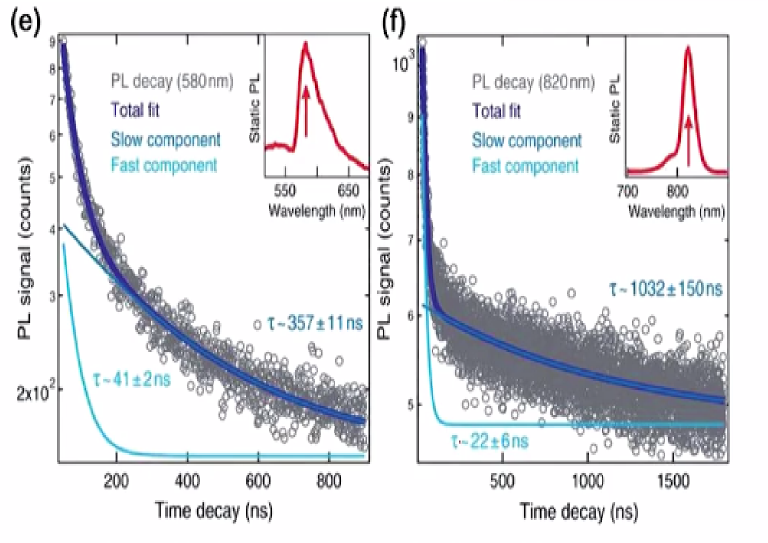


Figure 2. Photoluminescence decay; (e) $MAPbBr_3$ and (f) $MAPbI_3$

In this graph we are showing the photoluminescence decay for 2 different kind of perovskite namely MAPbBr3 and MAPbI3. I hope you always remember what is MA stands for. MA is CH3 NH3. So in brief instead of writing CH3 NH3 again and again, we have replaced this name by MA and MA stands for methyl ammonium. Now what will happen if I excite the MAPbBr3 perovskite film with a laser beam at its absorption maxima and then allow the film to relax.

So the electrons which will be in the excited state they will depopulate or they will de-excite the excited state for a certain amount of time. Now if we probe the relaxation of the electron or the charge carriers over a particular amount of time whether the timescale is very small then we get this so called time real spectroscopy data, where you get in the y axis is your PL signal and x axis is your time decay.

Now this decay curve or the fluorescence decay curve follows an exponential kind of decay. Now looking at this decay curve we can say that whether it is a germinate recombination or whether it is a non-geminate trap state recombination. So difference class of recombination that can be defined by looking at the decay curve. For example, like perovskite which has 2 different charge carrier electrons and hole.

So you see that we are looking it for the decay here and the decay has a first component and it has a slow component and if I take both the first component and slow component with their corresponding weight percentage and if we calculate the total lifetime it comes out like 357 +/- 11 nano second for the case of the bromide waste perovskite. Whereas if you look at the iodine based perovskite it is 1032 +/- 150 nanoseconds.

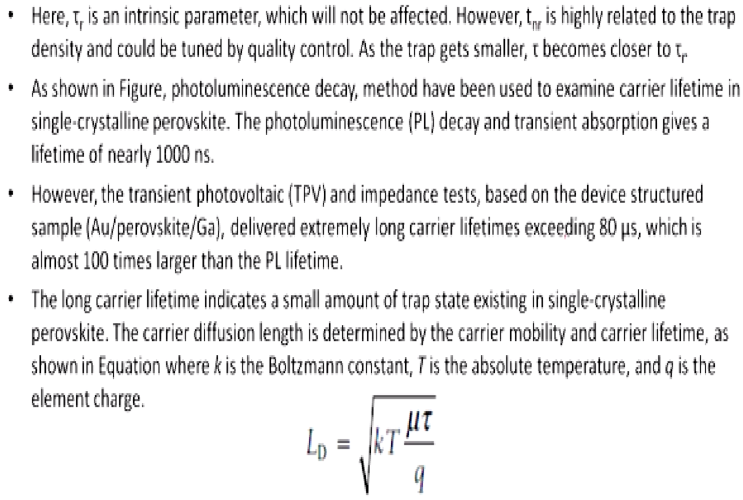
So that means the time scale over which the charge carrier relaxes that is different in the case of iodine based perovskite in comparison to the bromine base perovskite. Now one important thing to mention here is that in the time resolved spectroscopy what usually is done the material whether it is a perovskite bulk material or a single crystalline material that is first excited with the femtosecond laser beam.

Now femtosecond laser beam has a wavelength usually in a standard titanium sapphire femtosecond laser that has an wavelength of 800 nanometre and it has a, so femtosecond means 10 to the power minus 15 seconds. So that means it can send a train of signal at an interval of 10 to the power minus 15 second. So let us take a 100 to 150 like you know femtosecond.

One femtosecond titanium sapphire femtosecond laser okay which emits 800 nanometre light and we excite the material with that femtosecond laser what will happen the material will go from the ground state to the excited state and after some time it will de-excite to the ground state and we are following the de-excitation in a detector and that is the graph we are plotted here.

One is for the $MAPbBr_3$ and $MAPbCl_3$, in this case if we change the intensity of the laser beam then we will get different graphs, instead of that we will get different graphs, if we change the intensity of the exciting laser beam and from there by using some standard mathematical equation one can find out how many trap or defects stairs is there inside the system and we can also find out the location of these defects stairs.

(Refer Slide Time: 25:10)



- Here, τ_r is an intrinsic parameter, which will not be affected. However, t_{nr} is highly related to the trap density and could be tuned by quality control. As the trap gets smaller, τ becomes closer to τ_r.
- As shown in Figure, photoluminescence decay, method have been used to examine carrier lifetime in single-crystalline perovskite. The photoluminescence (PL) decay and transient absorption gives a lifetime of nearly 1000 ns.
- However, the transient photovoltaic (TPV) and impedance tests, based on the device structured sample (Au/perovskite/Ga), delivered extremely long carrier lifetimes exceeding 80 μs, which is almost 100 times larger than the PL lifetime.
- The long carrier lifetime indicates a small amount of trap state existing in single-crystalline perovskite. The carrier diffusion length is determined by the carrier mobility and carrier lifetime, as shown in Equation where *k* is the Boltzmann constant, *T* is the absolute temperature, and *q* is the element charge.

$$L_D = \sqrt{kT\frac{\mu\tau}{q}}$$

Okay, so just as I mentioned that tau r is an intrinsic parameter which will not be affected; however, tau nr is highly related to that trap density and could be tuned by quality control. As the trap gets smaller tau becomes close to tau r. So in principle of course and let us say somebody has made a perovskite single crystal with almost no trap or let us consider in an ideal hypothetical situation where there is no trap.

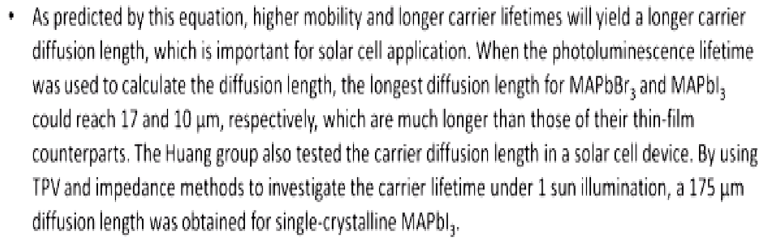
I know that is not possible in reality, so in that case, so there is no component due to the non-radiative part. So everything is coming due to the radiative recombination. A very ideal situation to have, but that is not possible in reality. As shown in figure, photoluminescence decay method have been used to examine carrier lifetime in single crystalline perovskite. The photoluminescence PL decay and transient absorption gives a lifetime of nearly 1000 nanosecond.

However, the transient photovoltaic TPV and impedance test based on the device structured sample like gold perovskite and gallium delivered extremely long carrier lifetimes exceeding 80 microsecond which is almost 100 times larger than the PL lifetime. The long carrier lifetime indicates a small amount of trap state existing in a single crystal perovskite.

The carrier diffusion length is determined by the carrier mobility and carrier lifetime as shown in equation where K is the Boltzmann constant, T is the absolute temperature and Q is the element charge. LD = square root of kT mu tau/k. So k is the Boltzmann constant here, T is the absolute temperature and as you can see mu is the mobility of the charge carrier, tau is the lifetime and q is the charge.

So one can find out also the carrier diffusion length by using this equation. So what you can see that the carrier diffusion length is directly proportional to the mobility and it is directly proportional to the lifetime. So as the lifetime changes the diffusion length changes and as the mobility changes diffusion length also changes.

(Refer Slide Time: 27:18)



- As predicted by this equation, higher mobility and longer carrier lifetimes will yield a longer carrier diffusion length, which is important for solar cell application. When the photoluminescence lifetime was used to calculate the diffusion length, the longest diffusion length for $MAPbBr_3$ and $MAPbI_3$ could reach 17 and 10 μm, respectively, which are much longer than those of their thin-film counterparts. The Huang group also tested the carrier diffusion length in a solar cell device. By using TPV and impedance methods to investigate the carrier lifetime under 1 sun illumination, a 175 μm diffusion length was obtained for single-crystalline $MAPbI_3$.

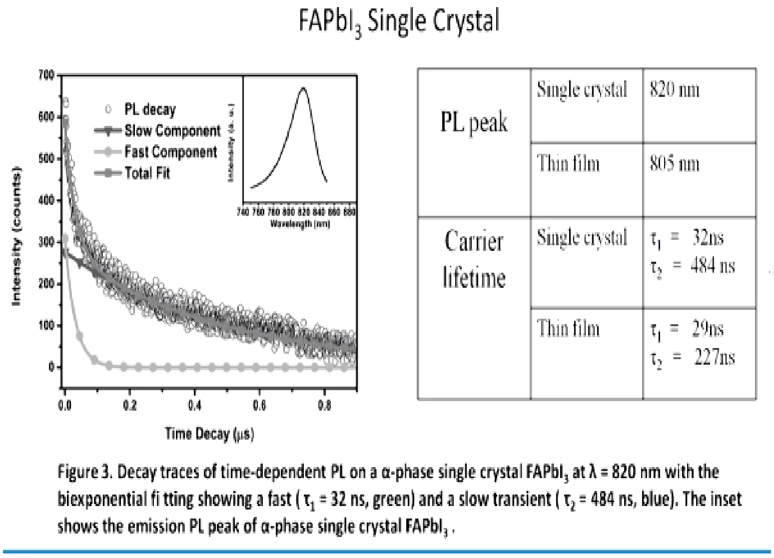
As predicted by this equation higher mobility and longer carrier lifetimes will yield a longer carrier diffusion length which is important for solar cell application. When the photo luminescence lifetime was used to evaluate or calculate the diffusion length the longest diffusion length for MAPbBr3 and MAPbI3 could reach 17 and 10 micrometre respectively, which are much longer than those of their thin film counterparts.

The Huang group tested, Huang group is a research group tested the carrier diffusion length in a solar cell device by using transient photovoltaics and impedance method to investigate the carrier lifetime under one sun illumination, a 175 micrometre diffusion length was obtained for single crystal MAPbI3. So see that 175 micrometre diffusion length is quite high that is almost comparable to the silicon.

So we can use the transient spectroscopy method which we just explained in the previous graph or impedance spectroscopy method which we will be discussing in our eighth module. So using either of these 2 techniques one can find out the charge carrier mobility and the carrier lifetime in the perovskite single crystal and if we know the mobility and the life time then we can find out the charge carrier diffusion length.

And it has been found that for example MAPbBr3 this CH3 NH3 lead bromide in this case the carrier lifetime is 175 micrometre that is very high almost comparable to the silicon.

(Refer Slide Time: 28:47)



FAPbI$_3$ Single Crystal

PL peak	Single crystal	820 nm
	Thin film	805 nm
Carrier lifetime	Single crystal	τ_1 = 32ns τ_2 = 484 ns
	Thin film	τ_1 = 29ns τ_2 = 227ns

Figure 3. Decay traces of time-dependent PL on a α-phase single crystal FAPbI$_3$ at λ = 820 nm with the biexponential fitting showing a fast (τ_1 = 32 ns, green) and a slow transient (τ_2 = 484 ns, blue). The inset shows the emission PL peak of α-phase single crystal FAPbI$_3$.

Now one of the important another class of the single crystal is FAPbI3 where FA as you have mentioned earlier that is a longer alkyl chain in comparison to the methyl ammonium or MA. See FA stands for the formamidinium lead iodide single crystal. So we are swaying the decay trace of time dependent PL on alpha phase single crystal FAPbI3 at lambda = 820 nanometre with the by exponential fitting shown as first tau 1 32 nanosecond and the slow transient tau 2 484 nanosecond.

The inset shows that the emission PL peak of alpha phase single crystal FAPbI3. So here just like so far we have been discussing with different anionic site, now we have changed the cationic site here. So you see that instead of MA we have used FA here and then this is the fluorescence or the photo luminescence curves of the FAPbI3. Now when we monitor the fluorescence decay so what we can see that it has 2 part.

One is the first component another is a slow component and the total fit is the biexponential fit which has 2 part. One is the first component tau 1 is 32 nanosecond, another is the slow component tau 2 is 484 nano second. Now if you compare the single crystal versus thin film you see that the PL peak for the perovskite FAPbI3 single crystal is 820 nanometre whereas for thin film it is 805 nanometre.

So what we have observed here, so there is a red shifting in the PL peak in a single crystal in comparison to the thin film. Similarly, for a carrier lifetime let us say a thin film tau 1 is 29 nanosecond right and tau 2 is 227 nanosecond, but a single crystal tau 1 is 32 nanosecond and tau 2 is 484 nanosecond, so this is way different from the thin film, the single crystal value.

Okay so today so far we have discussed about the perovskite single crystal and what are the advantages of the perovskite single crystal in comparison to the perovskite bulk pin in terms of its optical properties, in terms of its electronic properties and we have seen that whenever we go from a bulk perovskite to a perovskite single crystal since the number of defects state or trap state is significantly lower almost 4 times lower than the bulk counterpart we gain in the optical properties and the electrical properties.

The mobility is different, the charge carrier lifetime is different which changes the diffusion length and because of that this perovskite single crystal are useful for some emerging applications like for in solar cell, for in detectors as well as for lasers. In our next lectures we will discuss about in details about how a perovskite single crystal can be used for fabricating solar cell as well as for detector and also for the lasers. Thank you so far.