Optoelectronic Materials and Devices
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Module - 4
Optoelectronic Device Physics
Lecture - 39
Organic Light Emitting Diodes

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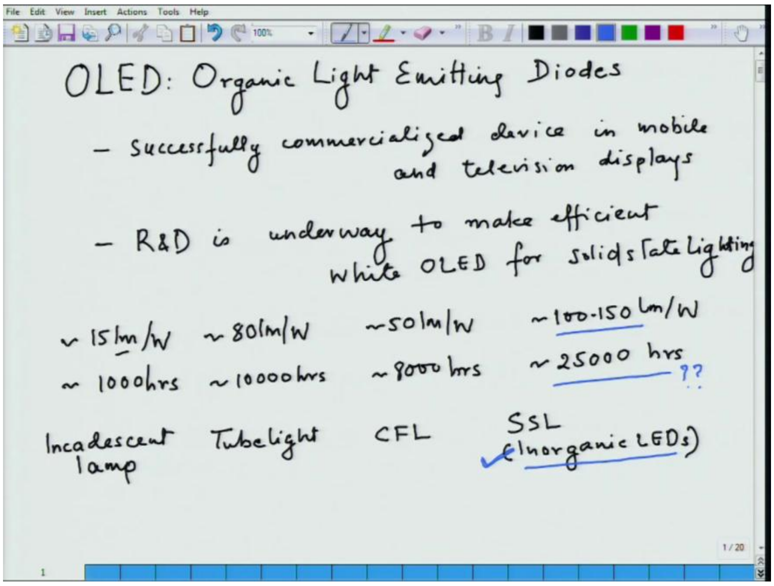

OLED: Organic Light Emitting Diodes

- Successfully commercialized device in mobile and television displays

- R&D is underway to make efficient white OLED for solid state lighting

~ 15 lm/W	~ 80 lm/W	~ 50 lm/W	~ 100-150 lm/W
~ 1000 hrs	~ 10000 hrs	~ 8000 hrs	~ 25000 hrs ??
Incadescent lamp	Tubelight	CFL	SSL ✓(Inorganic LEDs)

Today, we are going to talk about Organic Light Emitting Diodes. We introduced the device in the last lecture, we talked about a simple diode and today we will see if we want to get light out of this diode, what are the criteria's in by which we can get a more efficient device. So, I have already mentioned this to you that, OLED's are already successfully commercialized device in mobile and television displays, there are other applications as well in automobile, etcetera.

And there is also a substantial amount of R and D going on in this area, R and D is under way to use this particular device to make efficient white OLED for solid state lighting applications. Just to bring the motivation of this particular device, if we look at the lighting products that we are using or we have been using for last several decades, the one product which is very old is incandescent lamp.

It is the normal light bulb that we are very familiar with, if we look at the efficiency of this bulb, it is something like 15 lumens per watt. And here, I am introducing a new term for you lumens, lumens is the unit to measure the energy of the visible light. So, when whenever we are looking at lighting product, it we want to see how much of the electric power is converted into the optical light through which we see. So, that is the unit for measuring the efficiency of lighting products and if you look at the lifetime of the bulb, it is approximately 1000 hours.

The next improvement in a lighting product was tube light and this was substantially higher efficiency, the efficiency is 80 lumens per watt and even lifetime was comparatively improved, it was about 10000 hours. And then there was a long time gap before any a new lighting product was introduced and in recent years, you must have seen the compact fluorescence tubes, CFL as the lighting source and it is efficiency is generally in the range of about 50 lumens per watt.

But, there is a drive to replace at least incandescent bulb, which are much less efficient and even in some cases, tube light which has life much higher lifetime in this particular case. And then the current trend is to go towards solid state lighting especially, inorganic LEDs today, we can buy in the market, torch even the lighting products made of inorganic LEDs. These, as we discussed earlier are generally made of 3 5 semiconductors, gallium nitride and in in the efficiency, it is much better than any of the lighting products in the range of 100 to 150.

The one which are very highly efficient LEDs have much higher efficiency and lifetime is also expected to be much, much higher almost like 25000 hours. So, it has been seen that, if one looks at the usage of energy and today, the energy is a biggest concern of everyone. Then if we use higher efficient product lighting product, we can save substantial energy over the over the usage period and in LED, the usage period is very, very high.

And hence, thus, it makes more and more sense to go for solid state lighting to improve your energy consumption which means, to lower your energy consumption. And this is where, the organic light emitting diode the white organic light emitting diode comes, it is actually competing with the inorganic solid state lighting. If we compare the current state of the earth, it is possible to meet the people who have reported with the organic light emitting diodes, efficiency is in the range of at least 100 or even more.

The only problem with white organic light emitting diode is this lifetime, lifetimes for organics is generally lower so this is where substantial amount of work needs to be done. Hence, this is the motivation for the R and D that is going on currently worldwide that, we too improve the lifetime of the W OLED and even to get much better efficiencies of the W OLED for lighting applications.

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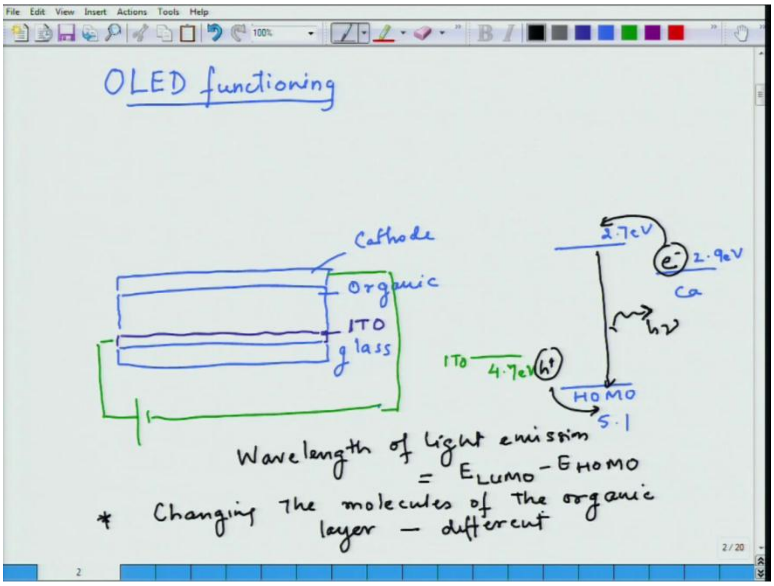

OLED functioning

Wavelength of light emission $= E_{LUMO} - E_{HOMO}$

* Changing the molecules of the organic layer – different

So now, let us look at, what is a how does a OLED work. So, OLED functioning and what are the processes which are important. So, if we review from last lecture, we said we will start with the glass substrate and we start with the glass substrate because the light has to come out. We cannot start up with the opaque substrate because of, purpose here in a LED is that, light generated in the device has to come out. So, we start with the glass substrate, you can also substitute it with some sort of plastics if needed.

And then on top of this, we are going to put a layer of a conducting transparent oxide as an electrode, which is typically indium tin oxide. And on top of that, we are going to put our organic layer, which is generally the source of emission in this LED and on top will be a cathode, which would be the electrode with the low work function. And this particular device then we will connect through a power source and apply forward bias to this device.

If I look at the electronic structure of this device, this device has indium tin oxide, ITO has work function with respect to the vacuum label 4.7 electron volts. And I am not plotting vacuum level but you know there is some vacuum level, with reference to that we are plotting these energies. And for the organic, the HOMO and LUMO come at highest occupied molecular orbital is at 5.1 and the lowest occupied one is around 2.7 and for the cathode, which is a calcium in this case, 2.9 electron volt.

So, when we apply the voltage to this device then electrons would be injected to the organic layer and on this side, holes will be injected to the organic layer. These electron and holes will recombine to produce light, so the electron will recombine with the hole to produce light in this particular case. And hence, you have the emission of a desired wavelength, so you can see the light the wave length of the light emission is related to, in the OLED is equal to the HOMO the the energy difference between the LUMO and HOMO of the organic material.

So, this is a way of trying to figure out how to get OLEDs of different color so by changing the changing the molecules of the organic layer by changing the molecules of the organic layer, one can get all colors from a OLED. And this is how, what is done in a display, you change the nature of the organic layer and you can get RGB red, green and blue emission which is then used to create the display.

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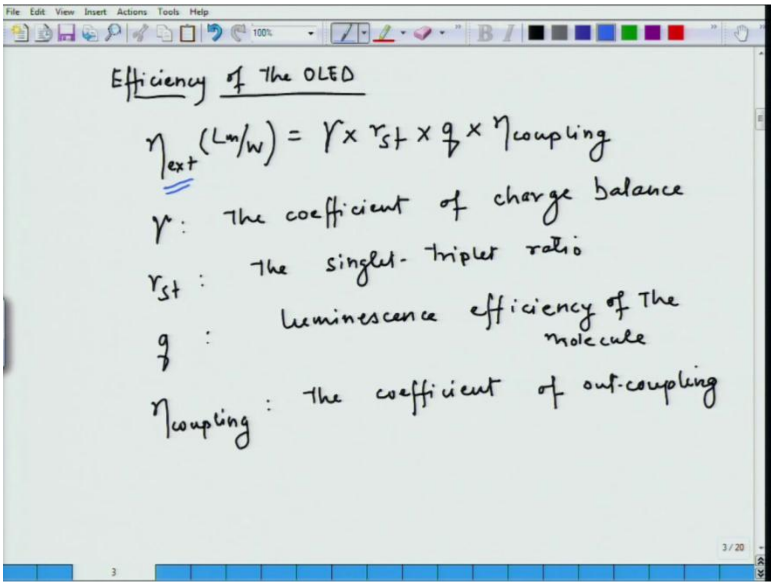

Efficiency of the OLED

$$\eta_{ext}(Lm/W) = \gamma \times r_{st} \times q \times \eta_{coupling}$$

γ : The coefficient of charge balance

r_{st} : The singlet-triplet ratio

q : luminescence efficiency of the molecule

$\eta_{coupling}$: The coefficient of out-coupling

Now, if this OLED is giving some light out and the quantity which is important for us is the light output divided by the electric power, that is given. So, when then we are interested in the efficiency of the OLED, efficiency of the OLED depends on number of processes. If I define efficiency of the OLED as the total light output divided by the electric power and we have been using the unit of lumens per watt here, it would first depend on the first process was injection of carriers.

And then the carriers had to move together, electron and holes had to move in order to create the exciton, which emitted the light. So, the the efficiency of that process will define if a exciton is created then the ratio of singlet to triplet and I will explain this a little later. We will define on, how many of those excitons are going to give you light out then finally, quantum efficiency of a exciton, whether the light is given as a emissive radiation or the non emissive radiation, as a radiative emission or a non radiative emission is going to decide the final efficiency.

And finally the efficiency of the coupling out coupling because whatever light is generated in that device, it has to come out of the device. So, each of this term gamma is basically, the coefficient it is the coefficient of charge balance in the device, r s t is the singlet triplet ratio because in normal fluorescent materials, only the singlets are the ones which give radiative emission. Hence, the triplet will be not not emitting hence, one needs to find out how many singlets are formed in a material. And q is the luminescence efficiency of the molecule and finally, eta coupling is the coefficient of out coupling. And now, let me explain each of this term and try to see, if I want to improve finally, my goal is to have as efficient a LED as possible then how would I improve each of these efficiencies.

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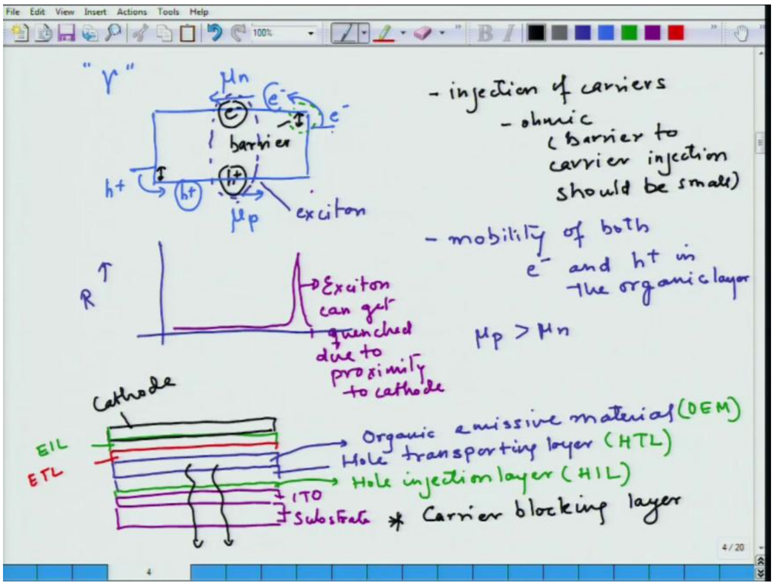

- injection of carriers
  - ohmic (barrier to carrier injection should be small)
- mobility of both e^- and h^+ in the organic layer

$\mu_p > \mu_n$

* Carrier blocking layer

So, let us first look at the gamma term, which is defining the charge balance in the device. So, if I am looking at this device in cross section where, electrons are coming from this side and holes, electrons are coming from the cathode side and holes from the anode side. The first process is injection of carriers so injection of carrier from the anode and cathode now, in order for efficient injection it is necessary that, this contact must be ohmic.

The contact is going to be ohmic when the difference between the the difference between the LUMO and the work function of the metal or in this case, HOMO and the work function of the anode is going to be small. So, this difference has to be this, what we call as the barrier to injection so barrier to carrier injection has to be small. Then next thing is that, this electron has to move, this electron has to move towards the anode and the hole will move towards the cathode.

And hence, the mobility of the electron and the mobility of the hole is important for, how they move with respect to each other and where, they come and combine to form a exciton so this is an exciton formation. So, the mobility of carriers is the second important parameter in charge balance, mobility of both electron and holes in the organic layer. Because, the desired result is that, each one electron which is injected into the organic layer from the cathode must form exciton with the 1 hole, which is injected from the anode.

So, in order to get the 100 percent efficiency, we must not lose any electron which is which goes from cathode to anode without forming the exciton, which means if we want 100 percent efficiency, we should have if we have 10 electrons being injected from the cathode and 10 holes being injected from the anode, then they should all recombine to form the exciton and emit the light. So, with this purpose, our charge balance should be the should be right in order to get good charge, good exciton formation e.

And so there is a problem here because normally in organic materials, the mobility mu p is much greater than mu n. Hence, what happens is that, if I plot the recombination rate in this particular device, what one finds at the recombination rate is all of the material recombine close to the cathode. Because, holes move much much faster compare to the electrons and they all combine close to the cathode and this is a problem because this these excitons then are quenched because of the proximity to the cathode.

Excitons due to proximity to cathode and that is why, it is required that, the the mobilities of the two carriers should also match in this particular device. So, what are the ways in which we can do that, we can do that by introducing in addition to the device that we have talked about, in which we had on the substrate. We had the ITO as the bottom electrode and if I want to improve the injection, very often I will add another layer on top of it, which we will call as a layer, which improves injection which is which would improve improve this barrier that is being caused, because of the difference in the work function and the LUMO level.

So, this is known as the hole injection layer and then it is also possible for me to add another layer on top of it, which is known as hole transporting layer. Then I have my organic emissive material, and I use certain acronyms here. So, this would be hole injection layer HIL, hole transporting layer and organic emissive material and on the the way, I am helping the holes to be injected from the anode side, I can do the same thing to the cathode side which means, I can add a electron transport layer.

And on that, I will add a electron injection layer and finally, the cathode so a single layer device, which we just talked about can become a very complex structure of a multilayer in order to improve this charge balance. And the the goal there is, to make sure that, whatever light is generated here is collected as much as this possible, is collected outside the substrate. So, these are some ways, in which one can improve the charge balance in the device.

There is one additional point here, I can if these carriers are getting coming from the anode and going to the cathode at a much faster rate, I can also add another layer here, which we call as the carrier blocking layer. To hamper the movement of the holes going towards the cathode and that helps better charge balance in the device. So, these are some of the ways, in which one can improve the OLED efficiency.

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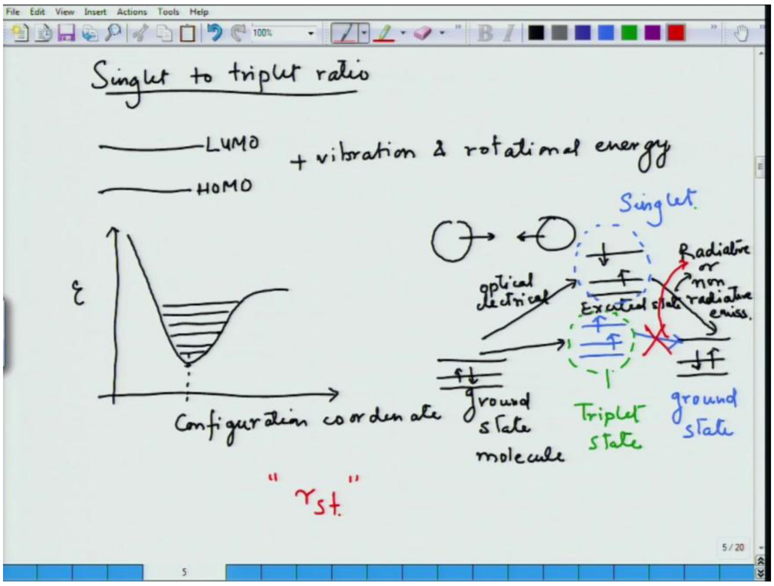

Now, let us talk about the singlet to triplet ratio, what is that, now before I describe this, I need to explain few more things. In the last lecture we discussed, what is the electronic structure of a organic molecule is and we talked about molecular orbitals. And we said that, organic molecules can be described in terms of the HOMO and LUMO level and this is a electronic structure of the material. But, in addition to this electronic structure of the molecule, we have in organic molecules the vibrational and rotational energy, which can be a significant part of the electronic energy.

So, in order to then include the effect of this vibrational and rotational energy is, in our discussion, we introduced a new concept which we called configurational coordinate energy diagram, which is basically representing the the the effect of the vibrational and rotational energy plus the interaction of the molecules with each other. So, we know if this is the distance between the molecule or we call it as configuration coordinate, it is very similar to as if, when we have a diatomic molecule, we have two atoms which are approaching each other.

So, very far off they have their independent electronic structure but if the atoms are approaching each other then this may can be considered as a distance between that atom. And we know the energy will be minimum at a at a distance equilibrium distance between these two atoms. Something similar we can talk about in the molecular configuration coordinate which means, when two molecules come together there is a minimum in the energy and as we take them either away or closer to to to that minimum energy.

We will have to add different modes of vibrational energy or rotational energy to the minimum minimum electronic energy. So, this we call as a molecular configuration configuration coordinate, which describes a lowest minimum energy plus it is possible to have the molecule in the excited vibrational states, which are higher than the lowest electronic energy. So, with this addition, we can then talk about, what is singlet and triplet.

So, when we say that, I have excited a molecule from ground state to the excited state and how do I do that, I can do it in many ways. I can let me say, if this is in my electronic structure, the ground state of the molecule and this ground state, I am representing by this configurational diagram. The ground state has a HOMO level, a LUMO level and the HOMO level may also have a state below it. But, in this HOMO level we have electrons, which in a particular level will have a opposite spins, because of the same spins are forbidden in the same energy quantum mechanical condition.

So, the ground state will have this configuration now, if I bring excite this molecule to a excited state and how can I do that, I can always shine light on the molecule. So, you can do optical excitation or like we do in the OLED, we can electrically bring electrons and holes, which will form the exciton. And now, the ground state will go to a excited state basically, we are saying that, one of this electron is going up to a higher energy and now, the molecule is in the excited state so this is the excited state in the electronic structure.

And then this molecule will emit this light and come back to the ground state so this is there can be a radiative or non radiative emission here by the molecule. And we know that, if we want a LED, we want radiative emission, there is another possibility in which this excited state molecule does not go to this excited state. But, goes to a second excited state, which is defined by the spins in the same direction which means, the spin symmetry has been changed during the excitation process, rather than having opposite spins in these two states, they have the same spin.

So, it is possible as we are doing the excitation in that process, that we get either this state or the second state. And again this state is can also either have radiative on or or non radiative emission and come back to the again the ground state. Now, in this configuration, this particular excited state is called a singlet state and the other excited state is called the triplet state. Now, for more information on, why these are formed and what are the reasons, certain molecules will form different ratios of singlet and triplet states upon excitation, one has to go back to quantum mechanics.

But here, it is important just to know that, depending on what is the nature of the organic molecule during excitation, you will form some singlet and some triplet states. And again depending on the nature of the molecule many times, this particular transition from triplet to ground state, which can also give rise to radiative emission or non radiative emission is forbidden. So, this is generally, forbidden and because this is forbidden which means, if I am exciting molecules from ground state to the excited state in a OLED then only the singlet the molecules which are in the singlet excited states can give me emission.

The ones which are in the triplet excited state will be wasted and that is why, we have this ratio of ratio of singlet to triplet, that we use in that particular equation. And now, let us get into a little bit more detail of, what is happening in the molecular structure.

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This is this is how normally, we talk about the electronic structure along with the vibrational structure of the molecules. So, we take from that configurational diagram and look at the ground state and then and the next vibrational rotational states in in this particular diagram. So, here is the ground state for the molecule, here is the first excited singlet state of the molecule, if the if I give enough energy and the electron goes to the next state.

This would be the second excited singlet state of the molecule then there is possibility of having the molecule in the triplet state. So, so first excited triplet state is going to be, in which this would be the first excited triplet state of the molecule. The second excited triplet state of the molecule is going to be, in which you have in this second energy level, this will be T 2 and the third one is going to be and this will be T 3.

And if now, I talk about different processes so first let us say, we can have optical excitation or we can have electronically molecules going from S naught to the first excited state. We can go from this vibrational state, they could be existing in the second vibrational state and go to the second level so this is absorption. For most molecule, absorption directly into the T 1 state is not possible, and so this absorption for most molecule is forbidden except for some, in which case the spin orbital interaction is existing.

And hence, the the the selection rules for excitation from a particular state to the next state are relaxed and those are important materials for us. Materials for which the selection rules are relaxed for optical absorption, these are known as phosphorescent materials. These phosphorescent materials are typically organic molecules with having a metallic molecule part of it and this particular case, the spin orbit coupling in the molecule relaxes the selection rule and it is possible then to actually directly absorb into the triplet state.

And then it also becomes possible to emit from the triplet state so you can see that, if you have a phosphorescent material, the ratio r s t is not important because this should this will become 1. Because, whether it is singlet or triplet, you would get emission and generally, it is the triplet because all the singlet excitations got get transferred to the triplet. So, once I have the molecules in the excited state then it is possible for me to also have inter internal conversion, in which the S 1 state, in this particular case the S 1 state is being inter system crossing to the T 1 state.

And vice versa is also possible that is from T 1, if the selection rules are if if the cross crossover is allowed then one can also go from T 1 to S 1 state. So, these this is the second process, which is possible in the electronic structure of the molecules now, once we have the molecule in the excited state, the next process is that, this this molecule from the excited state immediately loses it is extra energies and comes about comes down to the lowest electronic state of the of the second excited state.

And it will emit, come down to the ground state and it can come down in different configurations and this is this can be radiative emission. There is also possibility that, it does come down but it does not have radiative emission and it can also have non radiative emission and that brings us to our third coefficient in the efficiency, which is the quantum efficiency.

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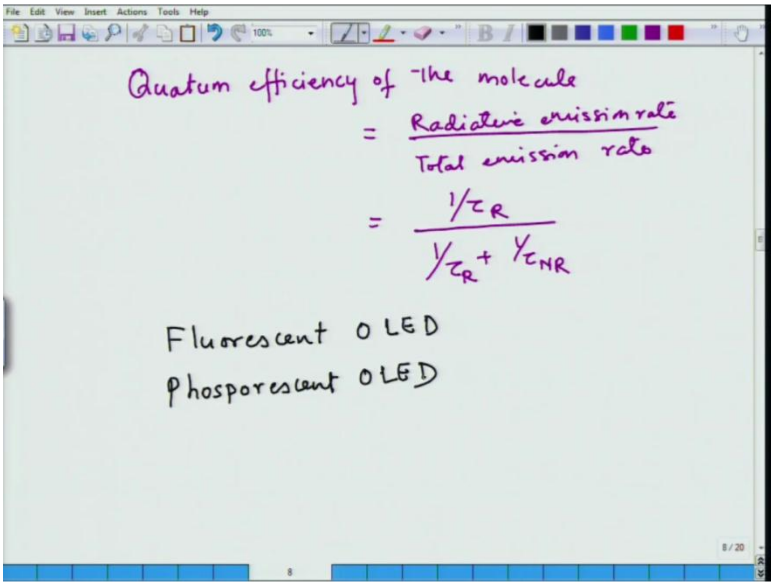

Quatum efficiency of the molecule

$$= \frac{\text{Radiative emission rate}}{\text{Total emission rate}}$$

$$= \frac{1/\tau_R}{1/\tau_R + 1/\tau_{NR}}$$

Fluorescent OLED

Phosporescent OLED

So, the quantum efficiency of a molecule is basically, the ratio of the molecule is is the ratio of radiative radiative emission rate divided by total emission rate and this is very similar to the discussion in recombination generation of inorganic semiconductor. This quantum efficiency is given by 1 over the radiative emission, decay constant for the molecule and 1 over the non radiative decay constant for the molecule.

So, if we have excited state, which is responsible for the emission in the OLED, we are going to have to have a higher quantum efficiency for molecules, for which this is a small that is, a loss in the OLED part. Now, molecules can get directly transferred, I have drawn these extra states here because it is also possible to directly have absorption in the higher states.

And this would also be possible for intersystem crossing in the higher T 3 states, from T 3 states one can have emission, which can be radiative or non radiative. And finally, from from T 1 once the rules are relaxed, one can have emission from from the phosphorescent T 1 layer and there is a emission can again be either radiative or non radiative. Now, it is typically that, when one has to go from the triplet state to the ground state, the spin has to crossover from being parallel to being antiparallel for the ground state and that is more difficult than singlet to singlet transition.

And generally then the decay constants, the time decay times are much much longer for the triplet to singlet transition. And these these materials in that case, it is possible that sometimes, when we go from triplet to S 1 state, we then have after this particular transition. We have and again emission from the singlet state and this is what, we called as delayed fluorescence.

So, there are three kinds of emission from this configurational diagram, first one is from excited singlet state to the to the ground state, which is a normal fluorescence of the of the molecule from the singlet state. There can be allowed triplet state and there will be emission from triplet to the ground state and this is generally, having a larger decay constant and this is known as the phosphorescent emission.

So, this would be a phosphorescent radiative emission, radiative emission is possible and and if we have a crossover back to the to the singlet states then we can have delayed fluorescence, which would even have a longer decay constant. Because there are two rates included in here, the transfer from singlet to triplet from triplet to singlet and then the emission of the the light, because of going from excited state to the ground sate.

So, depending on which molecule one chooses, one can have one can have fluorescent OLED which means that, the fluorescence emission was the dominating emission in that particular material. Or one can have phosphorescent OLED which means, the phosphorescent emission was the dominating emission in that particular material. So, we have basically, then described the first term charge balance on, how to improve it so far. We have described how the, what is a singlet to triplet ratio is and it depends on the type of the material on, how many singlet and triplet will be formed.

And also on the type of material, if this ratio will be 1 for phosphorescent materials and then we have also talked about the quantum efficiency of the material, which should be as high as possible in order to get the maximum light from a device. Now finally, the last term which is, once we have made sure that, each electron forms an excitons with the injected hole and then we are able to collect the light from that particular exciton. Now, this light has to come out of the device and this is where, the last part of this efficiency equation comes.

Because, it is not possible to collect all the photons, which are generated by the excitons created in the device and the reason for that particular loss is, this is eta out coupling and let me make a simpler device structure here. So, to be more realistic generally, a substrate is very, very thick in comparison to the rest of the layers in the device. So, if this is still schematic and then I have the thin ITO on top of it and I have organic layer.

This could be a single layer or as we discussed to improve the charge balance, this could be multilayer structure optimized to get the best charge balance in the device and then on top I will have the cathode metal. Now, let us think of points where, the light is being generated, it is going to be generated in all possible directions and we are looking at the light from this end in the LED. So, the light which is collected by the by the detector here or I side I here is, what is going to be defining the final efficiency of the device.

Now, it is going in all the direction and only a cone of this light is going to make it outside and assuming my detector is very, very far, I would be able to collect most of the light that comes out. So, what is happening to the rest of the light, what is happening to the rest of the light is that, when the light which is in a schematic form, which is at a cone in the cone. Outside this cone, when it comes to the interface between air and the substrate, because of the difference in the refractive index of the substrate and the air, this gets complete internal reflection similarly, on this side.

And hence, there will be a substrate loss due to the complete internal reflection, this is known as the wave guide mode. Similarly, some of the light is going to be lost at this ITO organic interface, again because of the change in the refractive index, you will lose some of the light in the wave guide mode at the organic ITO interface. This is the loss at organic ITO interface and then there could be some loss in addition to this, which is occurring at the reflecting cathode interface.

This is this could this loss could be due to surface plasmon of the cathode, the absorption in the surface Plasmon. Now, if we look at all these losses, the surface plasmon loss, the loss at the organic ITO and the substrate loss, it is almost amounts to about 80 percent of light generated in an OLED is lost inside the device. So, you can see, this is a huge factor in the efficiencies, only 20 percent of the light that we generate in a OLED is collected and this is a big there is a big room for improvement in trying to improve the, in trying to get the better efficiency of a OLED.

So, this these are the ways, in which one then tries to improve the efficiency of the OLED so how to improve. So, we will discuss some of the ways, in which one can do that so if we go back to our picture of our substrate, ITO organic layer cathode. Then first change that people have tried to do is, they have changed the interface from being flat to some sort of a graded interface or put lenses on top of it. What that does is, that the cone of light which we were collecting without the micro lenses becomes larger now, we should be able to collect even a larger cone.

So, micro lenses at the glass substrate, at substrate error interface, one can also improve this problem of the total internal reflection by going to graded refractive index. Then considerable amount of work is also done where, photonic structure is included or surface plasmons are manipulated to get to get to reduce a loss at this particular interface. So, in this way, there are are many optical techniques, by which one can try to reduce the loss and get more efficiency in these devices.

So finally, let us discuss, what is the what is another challenge that is there in the area of white OLED and the challenge in the white OLED is, how do we make white colour. So, the molecules, which are existing generally are creating pure colors which are either red, green or blue. And if you want to use these devices for lighting purposes, we are used to white color, which can be the warm white or a cool white.

How do we generate that and there are various ways to do that and first one is to mix different color molecules. So, we know that, if we take three primary colors, then that gives me a broad enough spectrum to give me a white emission. I can even take two complimentary to also get white emission and then there is work going on with designing the molecules, chemists are also trying to create molecules where, a single molecule gives broad white emission.

So, in this manner, once can see the possibilities with white OLED in terms of material choices are much more. In case of inorganic LED, normally our choices is gallium nitride or silicon carbide LED and from there, we use a phosphor to get the white light. While in white OLED, we have option of a very large number of molecules, which can be created to get the white color. And there is that is why, this field has lot of research activities going on to to find and get the best route to get the white emission.

So, in summary, let me recap on what all we have done today, I have looked at a OLED device. Why we should study organic light emitting diodes, how does a organic light emitting diode work, which is basically the charge has to be injected from the cathode and anode, there should be charge balance in the device and then finally, exciton should be created which emits the light. So, the material should be chosen such that, it has a high quantum efficiency and preferably, if you want higher efficiency material which where, the triplets are also allowed to emit by by relaxation of the selection rules.

And also then finally, the biggest challenge in trying to get the light, which is already lost in that device, almost 80 percent of it which is lost. And if we can cover all these options then a very high efficiency OLED is possible but the last challenge, which I mentioned in competition with the inorganic LED's. OLED has to come up with very techniques where, the life time of the OLED can become comparable to to LED or at least much better than, what it is right now.