Nano structured Materials-Synthesis, Properties Self Assembly and Applications

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Module - 4
Lecture - 7
Optical Properties – I

Welcome back to this course on Nano Structured Materials Synthesis, Properties Self Assembly and Applications, this is the 9th lecture of module 4. And today we are going to start our discussion on Optical Properties of nanostructures, previous lectures we looked at the magnetic properties of nanostructures of which we had 3 lectures. And now we start a three lecture part of a optical properties of nanostructures and in which we will discuss, what are the basic optical processes.

And how the banks are affected by decreasing the size of nanoparticles and how the variation in the banks and several other factors affect the absorption processes and the florescence and phosphorescence or luminescence in general. And other properties of the nanoparticles and how these optical properties can be applied for useful purposes, like in medical devices or for as sensors or for other optical encoding devices, several applications where nanoparticles having variation in there processes, optical processes due to the size and shape of nanoparticles will be discussed. So, today is the lecture 9 of module 4 and we are discussing optical properties.

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Use of gold nanoparticles with different optical properties

The Rose Window of the Cathedral of Notre Dame. The bright red and purple colors are due to gold nanoparticles.

Lycurgus cup: It appears green in reflected light, but appears red when light is shone from inside, and is transmitted through the glass.

So, the nanoparticles show variation in color with the size of the particle, this is now a very, very established fact and has been very attractive to students and practitioners of nano science and technology. Because of the large number of interesting colors, which can be generated with nanoparticles and people were making these nanoparticles long back, for example this window it is a glass window, but the glass has impregnated with gold nanoparticles.

Now, this is there in Cathedrale of Notre Dame, which is a very famous church and all the glasses have colors and those colors are due to gold nanoparticles, which we now know when it was made in the early years. Then it was probably not known why these colors are a being given by gold, now we know that when gold is made into small particles like nanoparticles, it can show you different colors.

So, many, many years ago in the 4th century AD itself, this kind of a cup was made where the glass has got gold nanoparticles impregnated. So, it is a glass where gold nanoparticles are there, today we know that they are gold nanoparticles and it shows red color when you have transmitted light. That means, when the light is either inside or coming from the other side and in reflected light, if you pass light on this direction and if you observe the reflected light, then it looks green and this is due to gold nanoparticles, which are embedded in this glass.

And these kind of structures were known thousands of years ago and give you an reflection of what optical properties of nano structured materials can be; and today people are analyzing these kind of information, which has been present for centuries with us. And this is only one particular application that you can have different colored glasses with nanoparticles of gold of different sizes, giving you different colors. And today we have gone ahead and made many new applications, whereby the optical properties are being used for applications.

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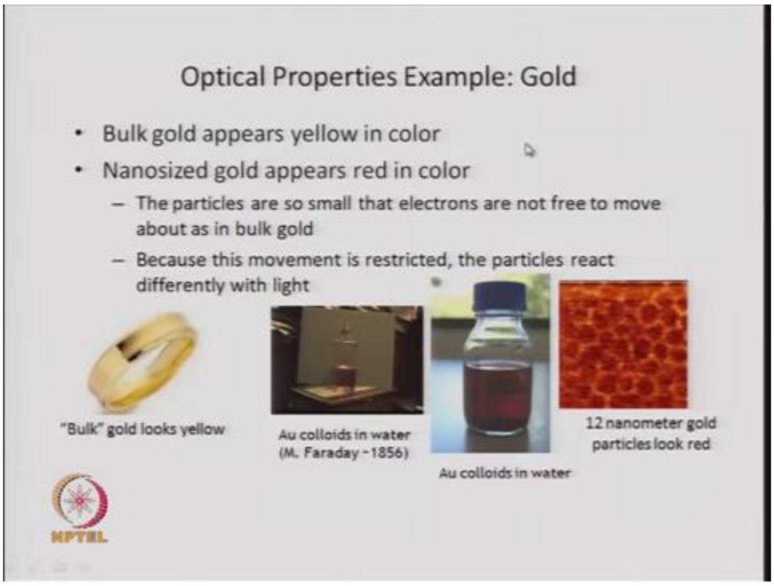

Optical Properties Example: Gold

- Bulk gold appears yellow in color
- Nanosized gold appears red in color
  - The particles are so small that electrons are not free to move about as in bulk gold
  - Because this movement is restricted, the particles react differently with light

"Bulk" gold looks yellow

Au colloids in water (M. Faraday ~1856)

Au colloids in water

12 nanometer gold particles look red

So, again gold is one of the most well studied materials, bulk gold is yellow in color all of us know, gold is yellow in color. But, when you make the particles of gold very small, it can have different colors, it can have red color, pink color, violet color and so the first time gold was made in a laboratory scientifically was by Michael Faraday, around 1856, 1857. And this is preserved even today this kind of light pink color of gold solution has nanoparticles of gold which Michael Faraday called at that time gold colloids.

So, this was the first scientific or laboratory synthesis of gold, but people had even much before 1000s of years before had made colored glasses using gold particles, which they did not understand at that time are due to gold particles. But, today we know that those kind of colored glasses are made of gold nanoparticles and of course, people have made using silver, cobalt, etcetera also. So, the area of the colors of nanoparticles is a very old area of course, the understanding was not there.

Today we understand why different size nanoparticles give different color and what other applications can be brought about by this variation of the optical properties of nanoparticles. So, to recap this gold slide, you have bulk gold looking yellow solution of gold looking pink made by Michael Faraday and this is a modern synthesis of gold colloids and water, and this is a picture where you can see the gold particles.

So, 12 nanometer particles can be seen in a micrograph and they look red in color in an optical micrograph, and which is the same thing as been shown here where you see the pink color. So, this color change of gold from yellow to a different color is due to the variation in the band gap of the material and that we will discuss in the next few slides.

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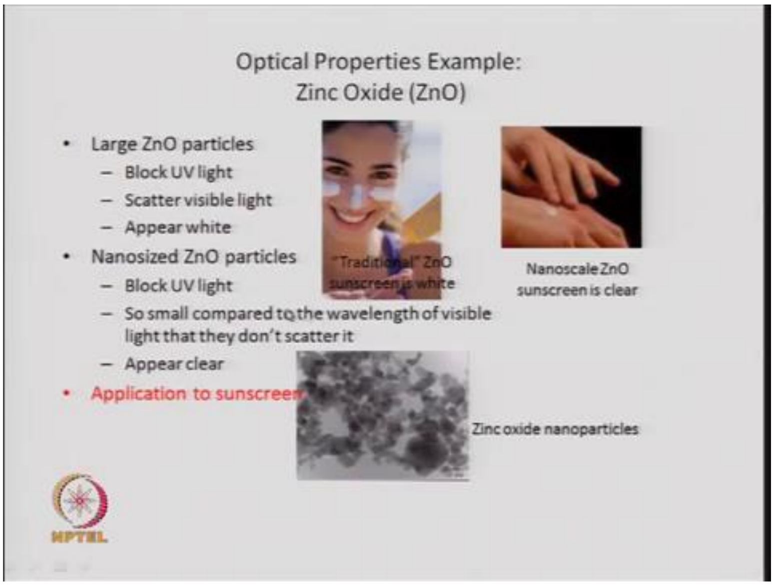

Optical Properties Example:
Zinc Oxide (ZnO)

- Large ZnO particles
  - Block UV light
  - Scatter visible light
  - Appear white
- Nanosized ZnO particles
  - Block UV light
  - So small compared to the wavelength of visible light that they don't scatter it
  - Appear clear
- Application to sunscreen

"Traditional" ZnO sunscreen is white

Nanoscale ZnO sunscreen is clear

Zinc oxide nanoparticles

Now, there are some other materials where you can see changes in the optical properties, like absorption or emission of these materials. And one of the examples, which peoples are using to a great extent for applications are kind of creams or lotions, where the material will reflect the U V light, because the normal rays which come from the sun, there is lot of U V radiation. And U V light is not good for human beings or any other animal and you want to protect yourself from ultraviolet rays.

So, one of the ways you can protect is put a sunscreen or a lotion, which does not absorb the U V radiation, so such things are like large zinc oxide particles. So, you make a kind of a suspension with zinc oxide particles and they will block the U V light and they actually scatter visible light and so it appears white in color. And the traditional zinc oxide sunscreen is white in color, because it scatters the visible light, when you make the zinc oxide particles smaller, it will also block U V light, this blocks U V light, the nanosized zinc oxide particles also block U V light.

But, the particles are so small that now they do not scatter visible light, because the particles are now smaller than the wavelength of the visible light. So, to scatter you must be of the order of the wavelength of the light that you are planning to scatter, when you make the size of the zinc oxide particles much smaller, then they do not scatter the visible rays. And hence, they will look transparent or like shown here it will not show this white color, which the large size zinc oxide particles were showing.

So, that is a change and it appeals to people, because in this kind of lotion which large size zinc oxide although you are protected, but your face is not no more original, you will have all these white patches on your body, whereas if you have a nanoscale zinc oxide, it is a clear solution. So, this is another example of how you can make nanoparticles, which can be tuned to absorb or scatter flow rays differently than the bulk sized particles or the large sized particle.

And this has been applied zinc oxide is a very, very important material, this tremendous amount of studies or zinc oxide and one of the applications of nanosize zinc oxide is in sunscreens or lotions. And this is the Tm picture of zinc oxide nanoparticles, which are basically present in a suspension or an emulsion and there are stable emulsion. So, that they do not precipitate out in the particle size is such that, it should not precipitate out or settle down in the bottom, so such material is of high demand for sunscreens.

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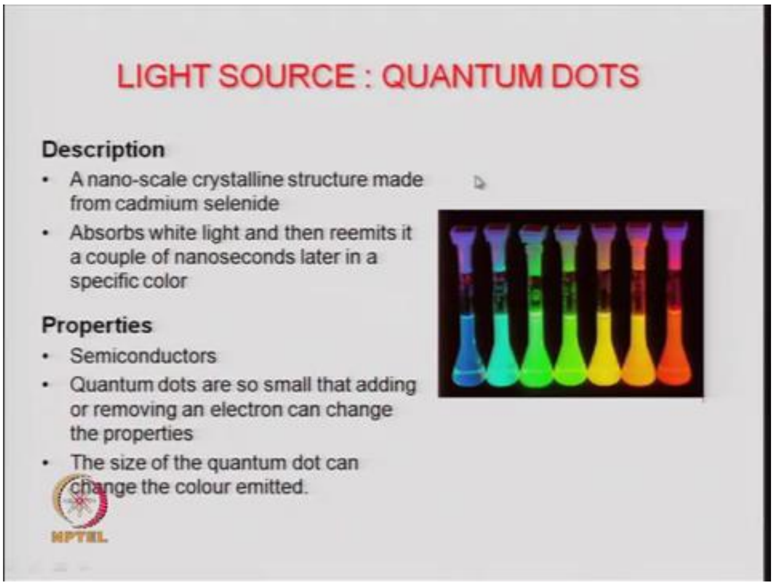

LIGHT SOURCE : QUANTUM DOTS

Description

- A nano-scale crystalline structure made from cadmium selenide
- Absorbs white light and then reemits it a couple of nanoseconds later in a specific color

Properties

- Semiconductors
- Quantum dots are so small that adding or removing an electron can change the properties
- The size of the quantum dot can change the colour emitted.

Now, coming to the other properties of nanomaterials showing variation in it is absorption or emission properties, this is a particular area which is called the area of quantum confinement. And one of the names, which is very commonly used in the nano science, nanotechnology area is the term quantum dots. So, what are quantum dots, from dots it basically means particles and since dots are spherical we are talking a spherical articles.

And why we call them quantum dots, because at the size of the particles which we are talking say around 4 nanometers, 5 nanometers etcetera, at that scale quantum phenomena becomes very important. And your energy levels, the band diagrams etcetera change and these are normally shown in this colored view graph, where you have solution of the same material; all the materials are having only the same cadmium selenide particles.

But, they are showing you different colors, the particle are the same chemical composition is the same, but they are showing you different colors. What is the reason, the reason is the optical properties have changed, because the size of the particles are different in different solution. So, all of them are crystalline cadmium selenide in the nano region, but their size some are 5 nanometers, some are 10 nanometers etcetera and with change with the size they give different colors.

So, they can be used as a light source of the different wavelengths, so normally cadmium selenide is a semiconductor, so these quantum dots are typically semiconductors and they are very small that you can by adding or removing one electron, you can change it is properties. Because, they are so small, there properties depend on few electrons and you can tune their properties very, very minutely, one of the ways that you tune the properties is by changing the size of this quantum dot and you can get a variation of these colors.

So, this is one of the most important or an simple property, which one can see in a nanomaterial, where there is a change in the optical properties as a function of size. And this is an example of cadmium selenide, where the color is changing as this size of the particle of cadmium selenide is changing. Now, why so much importance of course, this looks very nice and if you are a student of chemistry you enjoying seen colors and you can see all these bright colors, just by varying the size of the particle putting the same material.

So, it is very pleasing and enjoyable to see this variation of colors with the size of the particle, but what more can you do for an application, where it will be of use to mankind.

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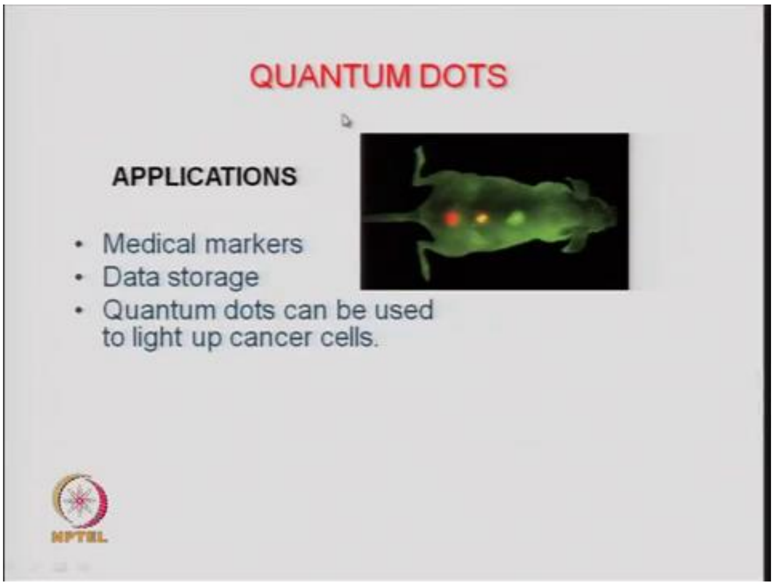

QUANTUM DOTS

APPLICATIONS

- Medical markers
- Data storage
- Quantum dots can be used to light up cancer cells.

So, that kind of an application shown here, where you have used quantum dots to be used as markers, so if you can find one particular quantum dot of a particular size going into one area and it is emitting red color, then you can identify that side. Now, another sized quantum dot goes to another site and shows a yellow color, and something shows a green color. That means, if you can use these quantum dots which are emitting different colors and if you can target them to different parts of the body, then you can illuminate different parts of the body.

And if which quantum dot will go where, you can identify that this part is having some kind of cells, because the red emitting quantum dots will only go there. And if green emitting quantum dot goes to another specific side, then we can identify easily that side, so quantum dots are being used as medical markers. So, in medicine in bio sensing applications, there is a tremendous importance of quantum dots and apart from that you can use quantum dots in data storage.

So, we have a earlier looked at data storage using magnetic nanoparticles, we mentioned that magnetic nanoparticles are used in DVD’s in CD’s etcetera now a days; and you can also use optical properties of nanoparticles. And optical encoding you can do and store data based on these optical properties of quantum dots, so that is another important area. But, the most important area I think is in bio sensing and as a medical markers to identify specific regions within organs or within a being, which can be identified by the specific emission of a particular wavelength of light by a particular sized nanoparticle.

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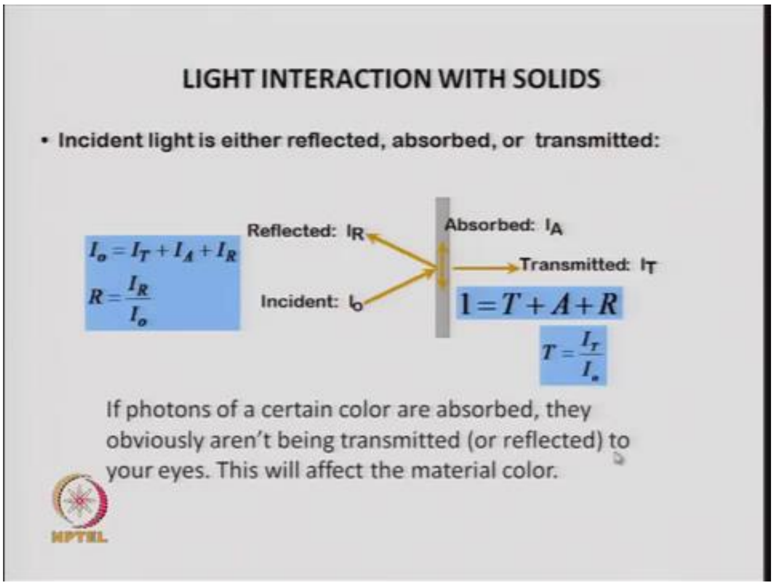

LIGHT INTERACTION WITH SOLIDS

- Incident light is either reflected, absorbed, or transmitted:

$$I_o = I_T + I_A + I_R$$

$$R = \frac{I_R}{I_o}$$

$$1 = T + A + R$$

$$T = \frac{I_T}{I_o}$$

If photons of a certain color are absorbed, they obviously aren’t being transmitted (or reflected) to your eyes. This will affect the material color.

So, what does light, because we are talking of optical properties, so we have to understand how light interacts with solids, because all optical properties you will involve some wavelength of radiation. So, light when it interacts with solids can reflect, so this is the incident beam, it can be reflected the light can be absorbed, so energy from the light can be absorbed, so photons can be absorb.

Photons are quanta of radiation and it can also be transmitted, so you can have reflection absorption and transmission, so I naught which is the incident beam should be equal to the some of the intensity of the reflected light plus the intensity of the absorbed light and the intensity of the transmitted light. So, if certain energy is absorbs or photons of a certain color are absorbed, they would not be seen in the transmitted beam they would not be seen in the reflected beam and hence, it will affect the color of the material.

Because, normally the color of the material, if you are observing from here depends on what is the beam, which is coming to your eyes, so if something is absorbed, then you will not see the exact wavelength, which is coming from the incident beam, because some wavelength is absorbed. And you will see a resultant wavelength minus this wavelength from the incoming beam, so you will see a different color, so this basically what happens when light interacts with solids.

And you look at the light either the reflected light or the transmitted light and that will be different from the incident light, because you have lost some radiation due to absorption of the material. So, you can write the total intensity as a sum of all these three and you can define what is reflectance by intensity, reflected upon intensity, you incident in say intensity. Now, if you have the total of the transmittance absorbance and the reflectance, the some total will be will be 1 and from that you can calculate what is transmittance, so this is reflectance and this is transmittance.

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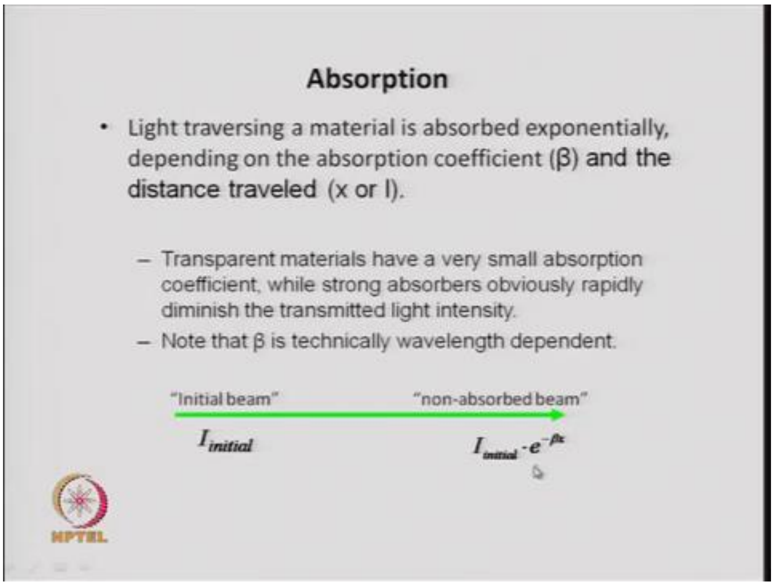

Absorption

- Light traversing a material is absorbed exponentially, depending on the absorption coefficient (β) and the distance traveled (x or l).
    - Transparent materials have a very small absorption coefficient, while strong absorbers obviously rapidly diminish the transmitted light intensity.
    - Note that β is technically wavelength dependent.

So, if light traversing a material is absorbed exponentially, then depending on the absorption coefficient, because different materials will have different absorption coefficients. If you have water it will absorb differently, if you have say you have a calcium chloride it will absorb differently. So, the material has some characteristic and the absorption, coefficient of the material beta depends on the material, apart from that it will depend on how much material is there.

So, how thick is the material, because the light has to travel through that material, since the material is very thick, very large. So, x will be large or l is large and so these two factors the absorption coefficient, which depends on the material and the atoms which make the material and the thickness of the material, both of them will affect the absorption intensity. So, normally transparent materials thinks which are transparent have very low absorption coefficient.

And things which are very strong absorbers will have a very high beta value, so low beta value means it has good transmittance, a high beta value means it has good absorption. So, if you have a initial beam which is I and that will be related to the beta, which is the absorption coefficient and the thickness, which is x using this relation that the transmitted beam, which is the non absorbed beam is equal to the initial intensity.

And then, a proportionality e exponential of minus beta x, because it decreases if you increase beta or x the transmitted beam intensity will decrease and so there is a negative sign here. So, the initial beam has an intensity I initial and the transmitted beam will have this intensity, where you will bring in a exponential factor depending on the absorption coefficient and the thickness of the material through, which the light is travelling.

So, one more thing is that the beta is actually wavelength dependent, so the beta value for a material will change, whether your shining U V radiation or you are shining visible light, it will change according to the wavelength of the incoming beam. But, for many purposes you can consider beta to be a constant, but in fact in reality beta is a function of the wavelength.

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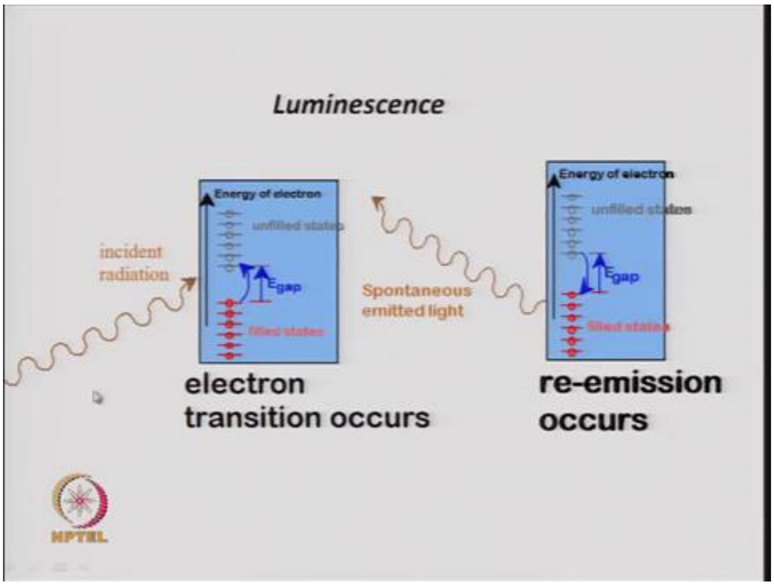

Luminescence

electron transition occurs

re-emission occurs

Now, looking a luminescence that is once radiation is absorbed, so you have incident radiation and these are the energy level in which the filled states are shown and then, there are the empty state and this is the gap, energy gap. So, if you shine light and there is an absorption of energy, then particles and electrons from here, the filled states will go to the unfilled states and this is what happen when light is absorbed.

Now, after some time that electron which was in the higher energy level, can come back or relax back to the empty sides, which was created when the electron went up and then, it gives out radiation and that is the spontaneous emission. So, you can have absorption and you can have emission when the electron comes back to the filled state.

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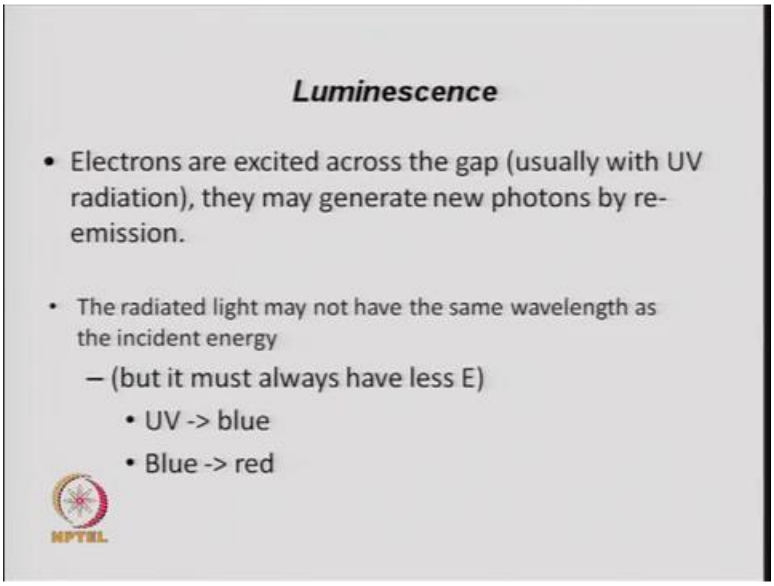

Luminescence

- Electrons are excited across the gap (usually with UV radiation), they may generate new photons by re-emission.
- The radiated light may not have the same wavelength as the incident energy
  - (but it must always have less E)
    - UV -> blue
    - Blue -> red

So, what is the luminescence, luminescence normally is that electrons which are excited and take up some amount of energy, but the electrons which come back to the lower energy level, they may generate at different energy, new photons by re-emission, that is due to the fluorescence or phosphorescence. So, in luminescence the radiated energy, that is the energy which is coming out, ((Refer Time: 24:05)) the energy which is coming out may or may not be equal to the energy being absorbed.

So, if it gives out the same energy, which it absorbed that is just emission, but if it has a lower energy or a higher wavelength, then the energy of the incoming beam, then that is called fluorescence or if it is delayed emission, then it is called phosphorescence. And both these types of emission with lower energy of photons compared to the incoming photons is together called luminescence.

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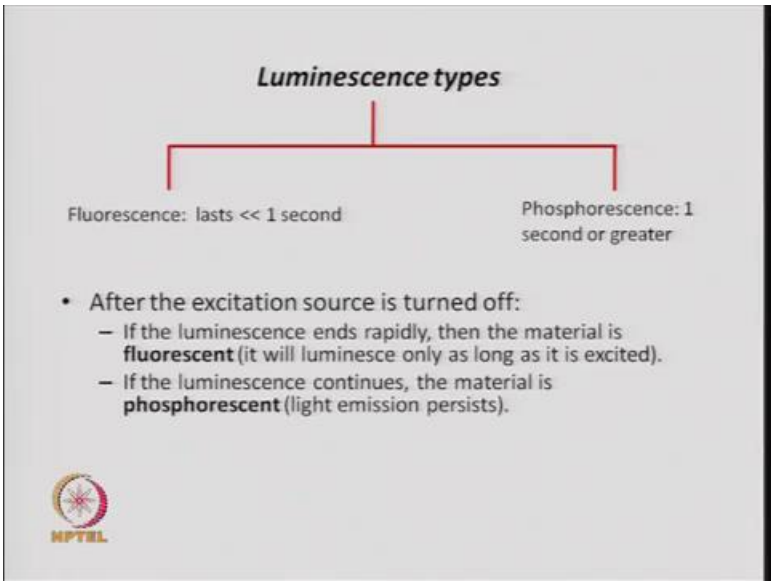

Luminescence types

Fluorescence: lasts << 1 second

Phosphorescence: 1 second or greater

- After the excitation source is turned off:
  - If the luminescence ends rapidly, then the material is **fluorescent** (it will luminesce only as long as it is excited).
  - If the luminescence continues, the material is **phosphorescent** (light emission persists).

So, in luminescence you can have phosphorescence, fluorescence which last for less than 1 second, it is very fast and when it is delayed that means, it is very slow, then the emission is called phosphorescence, where the photon which is emitted is coming out after 1 second, after it was a absorbed. So, there is a delay between the absorption and the re-emission, whereas in the fluorescence it last only very, very less than 1 second, within a 1 second everything is over.

So, typically if you shine U V light that means, your absorption is in the U V, the emission may be in the U V or it may be in the visible that means, it will always have less energy, the emission. And normally when you shine U V you will get blue emission, you can get blue or you can lower wavelengths, higher wavelength or lower energy, if you shine blue light then you would not get blue, if it is fluorescence or phosphorescence you will get red, that means lower energy light will be emitted in luminescence.

Now, so if the luminescence ends rapidly, then the material is fluorescent, because it luminescence only as long as it is excited, because the fluorescence is very fast. So, if you switch on the light and you are the material is having absorption of energy and it will fluores also immediately. So, if you remove that source of light, then fluorescence also will stop, but in phosphorescence if you shine on the material and after sometime you stop the light, then also you may see a glow of light coming from the material.

And that material is called phosphorescent material, because it is giving you a delayed radiation, so there is what is called a glow much after the light which was shining has been switched off. So, if the luminescence continues and the material is the phosphorescent; that means the light emission persists that differentiates it from fluorescence. So, these are two important things about luminescence, what is a phosphorescence and what is the fluorescence?

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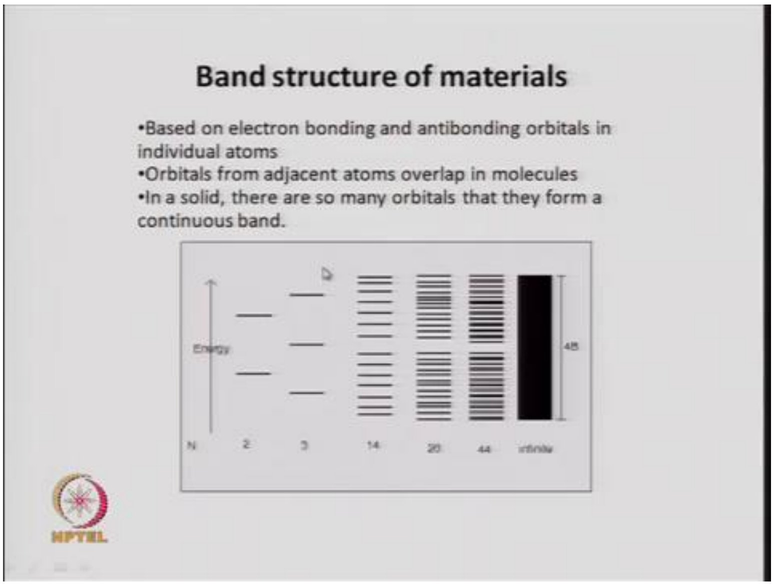

Band structure of materials

- Based on electron bonding and antibonding orbitals in individual atoms
- Orbitals from adjacent atoms overlap in molecules
- In a solid, there are so many orbitals that they form a continuous band.

Now, this difference between energy gaps is what causes different colors, so some material may have a large energy gap, some materials may have a small energy gaps, that is one thing. The other thing is the gap also changes with the size of the particles, because if you look at it from the atomic scale, if you have two atoms from simple overlap of atomic orbital that if you have 2 atomic orbitals overlapping, they will result in 2 molecular orbitals.

If you 3 atomic orbitals are overlapping, it will gives rise to 3 molecular orbitals, because the adjacent orbitals from nearby atoms will overlap, now that depends on number of atoms. Now, if you have a cluster of 20 atoms, then you will have 20 orbitals overlapping and the distance between the orbitals energies become smaller and smaller. As you see with the increase of number of atoms the difference between the two energy levels is becoming a smaller and smaller, till we reaches a stage when we have so many atoms that we call it an infinite solid.

Typically in solid there will be many, many millions of atoms, because as in 1 gram mole of any substance, you will have 10 to the power 23 atoms, so 10 to the power 23 is very large number, is a huge number. So, if you look at 44 atoms, if this is the situation think at what will happen at 4000 atoms or 40000 atom and when we are taking of millions of atoms, you will hardly be able to see any spacing between them. Because, the more the number of atoms, more will be these orbitals which are overlapping and then, we say that we have a continuous band.

Why we say it is continues band, because it tells you that any energy within this region, within this band is acceptable, here only 1, 2 and 3 energy levels are acceptable for this 3 atom system. Here, 14 energy levels are acceptable, you cannot put an electron in between these two levels, here 44 energy levels are acceptable, but in a solid there are so many energy level that are acceptable, that we say that all the energy level are acceptable within this energy and within this energy. So, this is called an energy band, this forms an energy band, this is important to understand.

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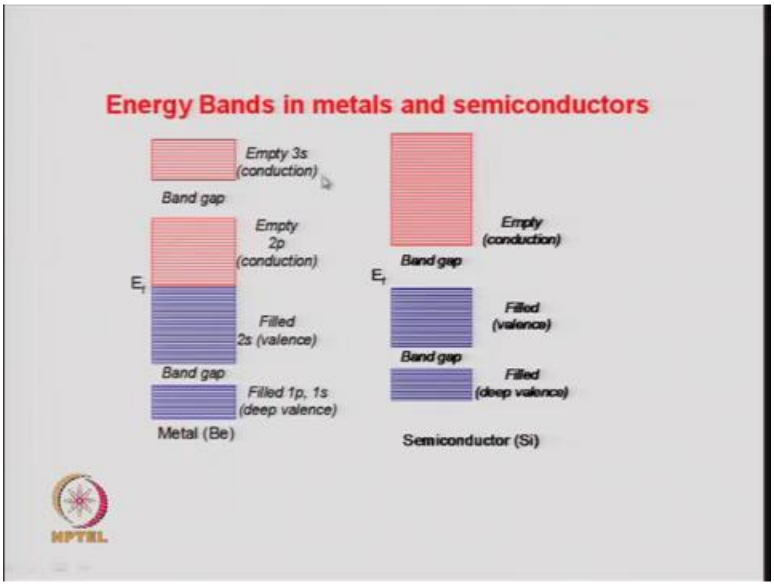

Energy Bands in metals and semiconductors

Now, so far in metal semiconductor what is the status with respective filling of electrons in these bands, now if you look at a semiconductor or a metal, you will have these two type of diagram, in a semiconductor you will have a band gap. That means, you will have a electrons this filled orbitals are blue in color as show, that the electrons are occupying this orbitals, so this is the filled valence band.

And then, these some valence internal band or the core band that is also fill, now when you go to the higher energy levels, there is a gap in energy where you cannot have any band, any electron, because there is no energy level available. So, this is a band gap here, there is also may be a band gap much lower, so where ever you have a set of orbitals or set of energies available, it forms a band and then, the next set of energies are available that forms a band and in between there are no energy levels available.

So, that is called the forbidden gap or no electron can occupy any energy in this region, so if you have an electron here, the next higher energy it can occupy is some where there. So, the electron has to jump from this energy to this energy, that is the band gap in a semiconductor, in a metal what happens that the conduction band, suppose this is conduction band and this above that also there is an empty band.

But, the conduction band is not full, there is some electrons in the conduction band and some electron can still come in the conduction band, where as in semiconductors there is no such band which is partially filled, so that is the difference. In a metal you have partially filled bands in a semiconductor, you do not have partially filled bands you have filled bands or empty bands and the difference in the energy is band gap.

In metals you do not have a band gap at the energy level at which electrons are presents, because there are available energy levels just above that. So, electrons can easily take this energy or this energy etcetera, so this is the difference between the metals and semiconductors.

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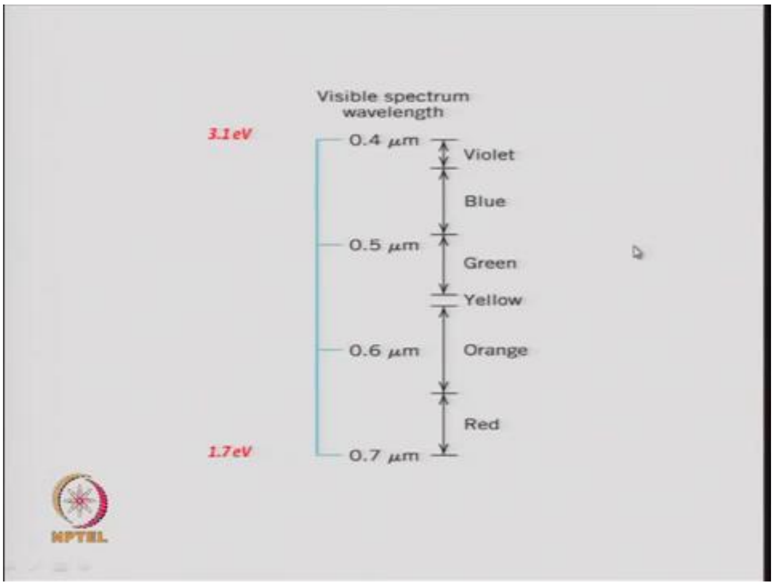

So now, when you change the size of a particles, you change the number of atom in the particle, so what will happen instead of having large number of available energy orbitals, you will have a less number of available energy orbitals, when you are decreasing the size of a particle from micron size to the nanosize. And from say 100 nanometer, when you are going to 5 nanometer you will have very few atoms and very few orbitals and so you will start getting a larger band gap, because the number of available energy levels will become lesser, and they will separate from each other and separate by larger distances. So, the band gap will change and if the band gap changes the color which you see will change in the visible region, if the light which is there in the visible region varies from say point 4 micron, there is a wavelength of radiation.

Then, it shows something like a violet color, if it is higher wavelength say 0.5 micron or lower energy this scale shows energy from 3.1 electron volt to 1.7 electron volt, which is the kind of the visible range of frequency or energies. And this scale 0.4 micron to 0.7 micron shows you the colors of the visible region, these are the wavelength, so the wavelength of the 0.4 micron or 400 nano meters is around violet, when it is 500 nanometers you are in the green.

And when it is above 600 it is orange and around 600 is orange and when it is around 780 or 680 nanometers, then you are in the red color. So, different wavelength are give you different colors and the wavelength range for the visible region of the spectrum is from around 400 to around 700 nanometers, which is point 0.4 to 0.7 micron. And corresponding energy is from 3.1 electron volts to 1.7 electron volt, so the band gap if the band gap is 1.7 electron volt, the color you may see is red color or it might have gone in to a lower color, which is the red.

Or if your 0.4 micron, which is 400 nanometers and suppose you go to lower wavelength of 0.375 micron that is 375 nanometers, then you may not see any color, because it is below the wavelength of visible light. So, then you have moved into ultraviolet radiation, so this the visible region and on this side you have ultraviolet at lower wavelengths and on higher wavelengths, you have the infrared radiation.

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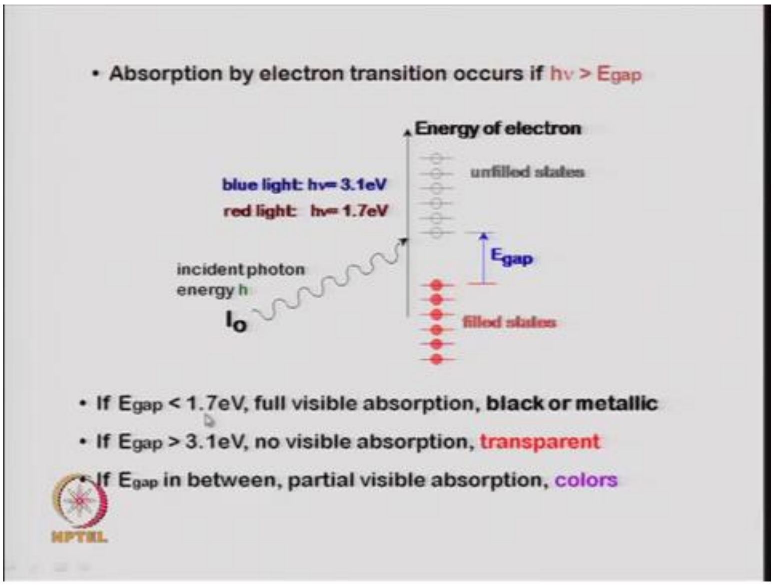

- Absorption by electron transition occurs if $h\nu > E_{gap}$

- If $E_{gap} < 1.7$eV, full visible absorption, **black or metallic**
- If $E_{gap} > 3.1$eV, no visible absorption, transparent
- If E_{gap} in between, partial visible absorption, colors

So, you can tune your band gap and you can tune the colors that you see, so if you apply an energy of h nu which is greater than the band gap or E gap, then you can the absorption. So, you have this incident beam and this is the energy gap and if the energy of this incidence beam is greater than this gap, then you will have electron, which are moving from the filled valence band to the conduction band.

And for example, if the energy gap is less than 1.7 electrons volts, then you can have absorption from entire visible region, because the visible region is starts from 1.7 to 3.1 electron volt. So, if the energy gap is less than 1.7, the entire visible can be absorbed and the materials looks black or metallic, if the band gap is smaller than 1.7 electron volt. If the band gap is greater than 3.1 electron volt, ((Refer Time: 37:26)) because we mentioned that 3.1 electron volt is the maximum energy within the visible region.

So, if you have a band gap, which is more than 3.1 electron volt, then there is no absorption in the visible, because the visible light is smaller than the 3.1 electron volt and so you will see a material will be looking like transparent material, it is not absorbing in the visible. And when it is less than 1.7 electron volt, all the radiation of the visible is absorbed and the material appears black or metallic in color, so that is the explanation of these colors.

And if in between that means, the gap is between 1.7 and 3.1, then you can see red color, blue color, green color, all the visible colors you can see, when you have a band gap in between 1.7 and 3.1, you will see all the possible colors from blue, yellow, green, red, violet, etcetera.

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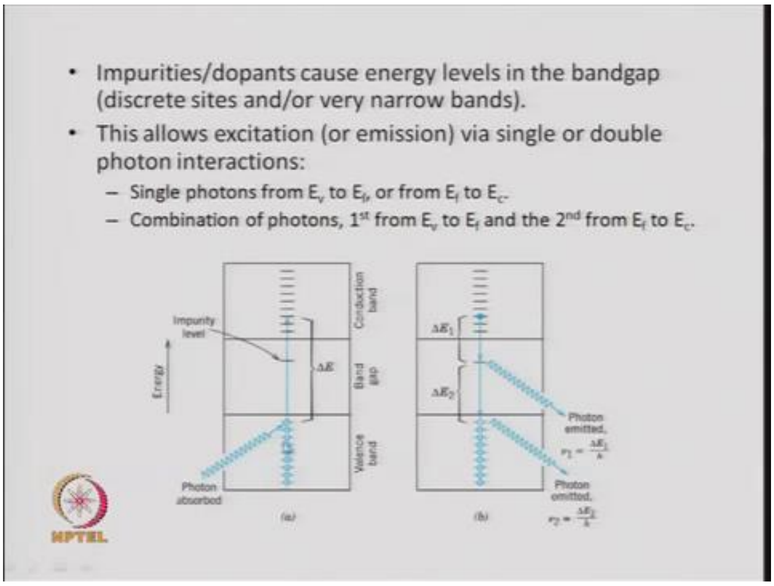

- Impurities/dopants cause energy levels in the bandgap (discrete sites and/or very narrow bands).
- This allows excitation (or emission) via single or double photon interactions:
  - Single photons from E_v to E_f, or from E_f to E_c.
  - Combination of photons, 1st from E_v to E_f and the 2nd from E_f to E_c.

Now, other than the valence band and conduction band, if you add impurities or dopants, then what happens, you have this valence band and you have this conduction band. If you add impurity, then you get some energy levels which are desecrate that means, there are not too many impurity atoms, so it cannot form a band, so they are like a energy level, but not too many energy levels in the vicinity.

So, it cannot form a band and there are one or two levels may be there, that too separated by some gap of energy, but if you can design your materials such that, you choose a impurity or a dopant such that, you introduce the energy level of the impurity in between the conduction band and the valence band. Then you can access this energy level that means, now you have ability to transfer an electron with less energy to this level, earlier you have to transfer an electron to the conduction band, that requires more energy.

When you transfer to this impurity level you need only this much energy, so with lower energy you can cause an absorption, so that is why sometimes this band gap is very high and you cannot see any color. But, when you add some impurity, then you starts seeing some color that is because you can have a transition, which is now in the visible, whereas the band gap is in the ultraviolent, so you can have that.

So, there are different types of absorption now possible, you can have one photon absorption from here to there, you can a have one photon absorption from here to the connection band, you can have two photon absorption that means, one from here, one from there, and they can also emit like this. So, one photon comes from here and then, you have this transition, electron comes down and you have a photon as a result of that emitted.

So, you can have this type of a one photon or two photon, combination of photons emitted due to the presence of impurity levels and how did the impurity levels come, the impurity levels came, because you took a solid and in that solid you have added some impurity atoms, so you add a very small amount of impurity atoms, so if you have a 100 percent solid.

So, you add 1 percent of some impurity material, so it is 99 percent of your original materials say zinc oxide, in which you add say 1 percent of europium or terbium or some such species, which has a energy level, which goes right in between or somewhere in between the conduction band and the violence band of the host compound. The host compound here we were discussing was zinc oxide, it can be some other oxide, some other chalcogenide etcetera.

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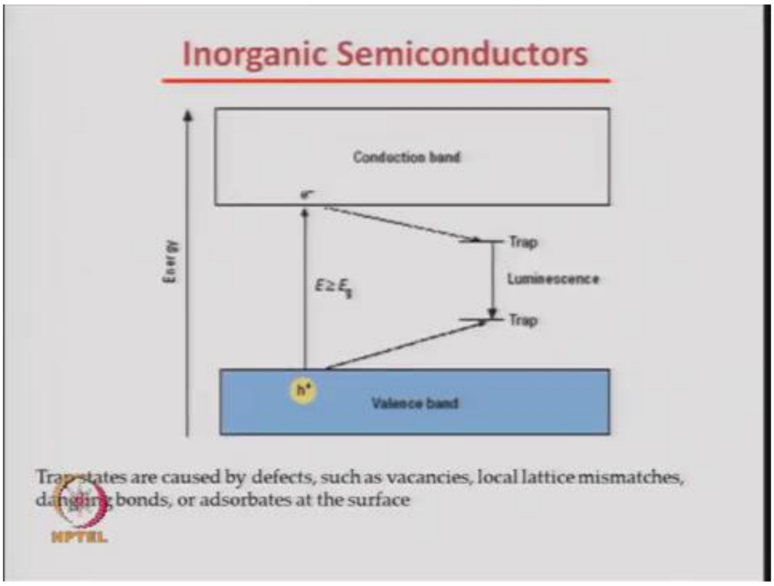

Inorganic Semiconductors

Trap states are caused by defects, such as vacancies, local lattice mismatches, dangling bonds, or adsorbates at the surface

Now, you can have in inorganic semiconductors, like you have a organic semiconductors are there, what we are discussing now is inorganic semiconductors a like zinc oxide or cadmium selenide, cadmium sulfide, cadmium telluride, they are all inorganic semiconductors, made of inorganic compounds. But, you can also have organic semiconductors made of carbon chains and may be having unsaturation etcetera.

So, in inorganic semiconductors what we discussed is that, you can have a violence band, you can have a conduction band, you can have these impurity levels, these are also called trap levels caused by defects. And when you cause an electron to go from the valence band to the conduction band, then you create a whole in the violence band, so this is also true that, whenever you have an absorption due to the a excitation of an electron from the valence band to the conduction band.

Then a hole is created in the violence band, a hole nothing but, the absence of an electrons, so if an electron goes away, electron has a negative charge, so what will it leave behind it will leave behind a positive charge, that is why the hole is a positively charge a unit. And you can have this kind of luminescence's between traps states, or you can have a emission from the conduction band to the valence band, depending on what kind of energy you are giving to the system.

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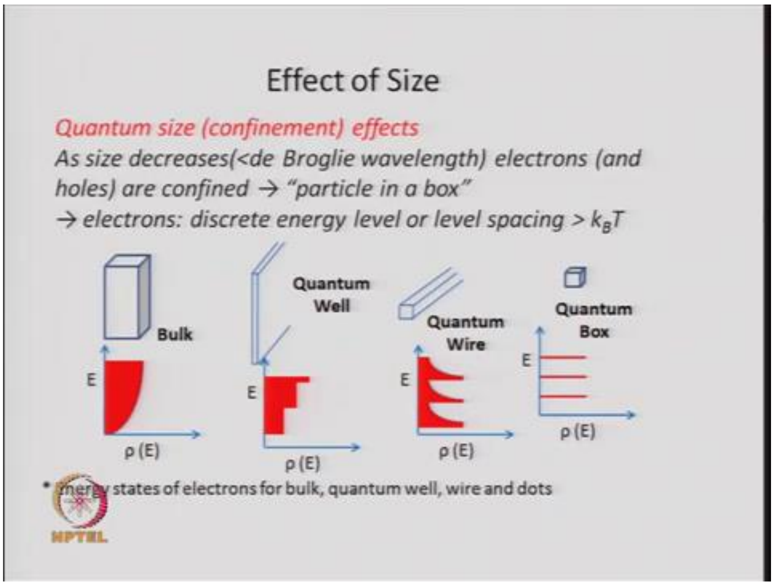

Effect of Size

Quantum size (confinement) effects

As size decreases(<de Broglie wavelength) electrons (and holes) are confined → "particle in a box"

→ electrons: discrete energy level or level spacing > k_BT

- Energy states of electrons for bulk, quantum well, wire and dots

So, typically in these materials a lot we discuss is about the effect of size, so we said in our earlier slides that you can have all kinds of colors for gold or you can have all kinds of colors for a cadmium selenide. And we showed you some 10 volumetric flasks field of solutions or field of colloidal solutions of cadmium selenide as a semiconductor. And why were the colors different all though in all of them, if you find out the materials, if you analyze the material using any technique.

A chemical technique or x-ray technique or any technique why which you can identify the material, you will find only cadmium and selenium in the ratio of 1 is to 1. Then what has changed the color, the color has been changed, because all though cadmium and selenium are there in all the flasks, volumetric flask and they show the red, green, let me show you that figure. ((Refer Time: 44:52)) So, this is the figure where you see all the flasks of cadmium selenide with different sized particles.

So, but we have not yet explained exactly why the colors are changing we have said that, because of particle size the colors are changing, if you change the particles size you will change the color. But, why because of particle size the color should change and that is a very, very important problem, which has been solved for long time using band gaps and that is the slide that we are discussing, where we show what happens when the particle size decreases.

So, this is say a bulk semiconductor that means, a semiconductor which has got large sized particles, so this is large size particle we call it a bulk. Now, if I reduce the size of the, it has got say a distance A, B and C, because this is a three dimensional solid, so you have three directions A, B and C and these are very large dimension say each side is 10 microns or something, so it is a bulk material.

Now, if I try to remove part of the material from this side, so I remove chop this particle like your chopping piece of cake, so you will make thin slices of this particle and you will get this kind of shape, now this kind of shape is like a plate. Because, it has two dimensions, one and two which are large, but the third dimension is very small and this kind of a plate like structure is called a quantum well in this kind of a nanosized objects.

So, in this quantum well what happens in terms of electrons and it is energy, in the bulk we know that the energy of the electron changes as the number density, this is called the number of electrons per unit change in energy or energy difference between E and E plus delta E. So, what is the electron density between a small change in the energy, so that is plotted here, that is call rho here is also called the density of states, it is the density of energy states.

That means, how many levels are closely packed that is the density is high or low it varies with the energy, so if you see for a bulk object, the rho of E or the density varies in this manner, it is like a parabola. Where the density is 0, rho E is 0 at zero energy and it changes and goes up the density increases till a certain value of energy, and after that the lines stops that means, there are no states above this value.

Now, this is true for a bulk where you have filled electrons up till this value and in that case, that will be called the fermi level, if you have electrons field up till this level, then that energy is called the fermi energy. And this is a density of states plot for a bulk material, which has got three dimensions A, B and C are large, now when the size decreases, now we are talking of confinement or quantum size effects.

When the size decreases from bulk, now you see you have made what we are calling it is a quantum well, because the property of the electrons and it is energy levels are going to be affected. So, how are they are going to be affected, the shape of this curve now has this step like feature, so in a quantum well, because you have one dimension very small, so you can say this is a nanomaterial, because one of the dimension is nanosized, the other two dimensions are not nanosized in a quantum well.

So, when this happens, the density of states is in a step wise manner, it does not vary continuously, like in a bulk solid you have a density of states of this value up till this energy, below that there is no density of states, below a certain energy. That means, electrons cannot have energy of this value, only it can have energy above this value, till this value you have a certain density of states, when you go to higher energy you have higher density of states.

And again for a small region of energy the density of states is constant, so density of state is constant from this energy to this energy, then density of states is constant from this energy to another energy. So now, this is called quantum confinement effects, because in the bulk density of states is not constant at all for any energy, it changes continuously, whereas here density of states is constant over a certain energy range and then, it suddenly changes and again becomes constant for another energy level.

This happens for quantum well where one dimension is nano dimension, when you go to a quantum wire where two dimensions are nanosized, this is nanosized and this is nanosized. And the third dimension is still long, then we call it a quantum wire and then, the nature of this density of states diagram changes again. So, here you have no variation in density of states in this energy region, there is a variation in the density of states in this region; and then, suddenly it jumps to another density of states and then, again there is a small variation.

So, this plot of density of states versus E is very characteristic, whether you have a bulk particle or a quantum well like structure, which is like a 2 D nano structure this is a 3 D bulk structure, this is 2 D nano structure like a plate, it is also called a quantum well. This is a quantum wire also called a one dimensional nano structure, because in one dimension this is long in the other dimensions it is small.

And if you reduce this to nano size in all three dimensions, one, two and the third one in that case it will become a quantum box or like a particle in a box in three dimensions. In all three dimensions it is now constraint, it is confined that is why we call it quantum confinement, because the electrons are not allowed to move outside this box, the dimension is so small, because the electron cannot go out of the particle and the particle is a nano particle.

So, the electron has to be within the nano particle, so you have got a quantum box or a 3 D quantum object, this is a 2 D quantum object, this is a 1 D quantum object and it is a 3 D quantum object, this is a 3 D bulk object. So, in this case you come back to your atomics structure, the energy levels are now discrete, there is no variation of the density of states, like in this case or in this case, the density of states one a particular energy is a varying.

But, the density of states cannot change with energy continuously or even in a small band it changes drastically, so it you have discrete energy levels. So, at one energy say E 1 you can have some density of states, at another energy E 2 you can have some density of states, but between E 1 and E 1 you cannot have any density of states. So, this is a quantum box, a 3 D quantum box and you have now electrons in discrete energy levels in this particular case.

So, what we talked about are these energy levels and the variation in the nature of the density of states versus energy plots, which calls all the changes in the optical properties of these systems. Because, what will happen to electrons when they are absorbed or moved from this level to this level, will be very different from shining light and pushing electrons between these levels and again it will be different in this case.

So, in all these cases, because the energy level diagram is different, because of the type or size of the particle and the shape of the particle, hence the optical properties will be different. And with that I will stop my lecture now and we will continue our applications, these were the basic properties of nanostructures with respect to optical properties that means, what happens when light is absorbed by different size particles, what happens how the colors change, and associated properties, which all depend on the energy band diagram and the spacing between the energy levels and the shape of the density of states plot as a function of energy. And now in the next 2 lectures, we will discuss on how these are applied to give you useful devices based on these variation of the optical properties in nanostructures.

So thank you very much and we will continue our lectures.