Nanostructures and Nanomaterials: Characterization and Properties

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Lecture - 25

1) Electrical, Magnetic
2) Optical Properties of Nanomaterials (C4)

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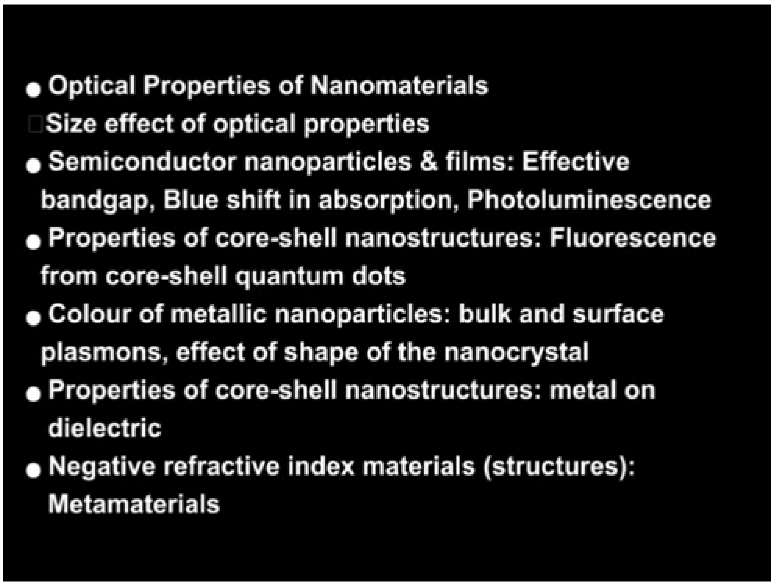

- Optical Properties of Nanomaterials
  - Size effect of optical properties
- Semiconductor nanoparticles & films: Effective bandgap, Blue shift in absorption, Photoluminescence
- Properties of core-shell nanostructures: Fluorescence from core-shell quantum dots
- Colour of metallic nanoparticles: bulk and surface plasmons, effect of shape of the nanocrystal
- Properties of core-shell nanostructures: metal on dielectric
- Negative refractive index materials (structures): Metamaterials

Now, let us go to optical absorption of nano materials, so to summarize the before we do that let us summarize the brief concepts so far. We have various phenomena in materials and various like reflection, refraction, and diffraction etcetera absorption. These phenomena give rise to colors and materials and they are also responsible for what you may call the overall optical response of the materials. Then we notice that we have to differentiate the optical behavior of metals where in there are free electrons, which give rise to plasmons.

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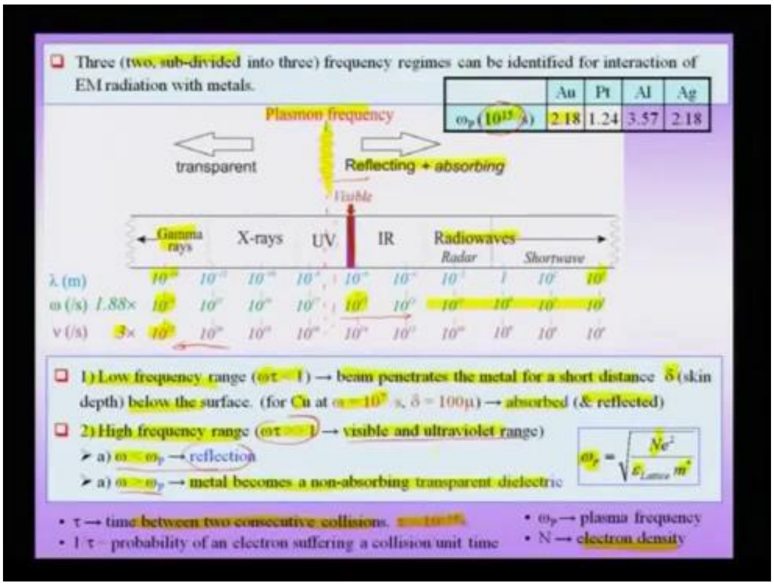

Three (two, sub-divided into three) frequency regimes can be identified for interaction of EM radiation with metals.

	Au	Pt	Al	Ag
ω_p (10^{15}/s)	2.18	1.24	3.57	2.18

1) Low frequency range ($\omega\tau \ll 1$) → beam penetrates the metal for a short distance δ (skin depth) below the surface. (for Cu at $\omega = 10^7$/s, $\delta = 100\mu$) → absorbed (& reflected)

2) High frequency range ($\omega\tau \gg 1$) → visible and ultraviolet range)

- a) $\omega < \omega_p$ → reflection
- a) $\omega > \omega_p$ → metal becomes a non-absorbing transparent dielectric

$$\omega_p = \sqrt{\frac{Ne^2}{\varepsilon_{Lattice} m^*}}$$

- τ → time between two consecutive collisions. [illegible]
- 1/τ → probability of an electron suffering a collision unit time
- ω_p → plasma frequency
- N → electron density

When we talk about and we have to talk about the frequency regime. That means the wavelength of the incoming radiation determines the response of the metal to the incoming radiations.

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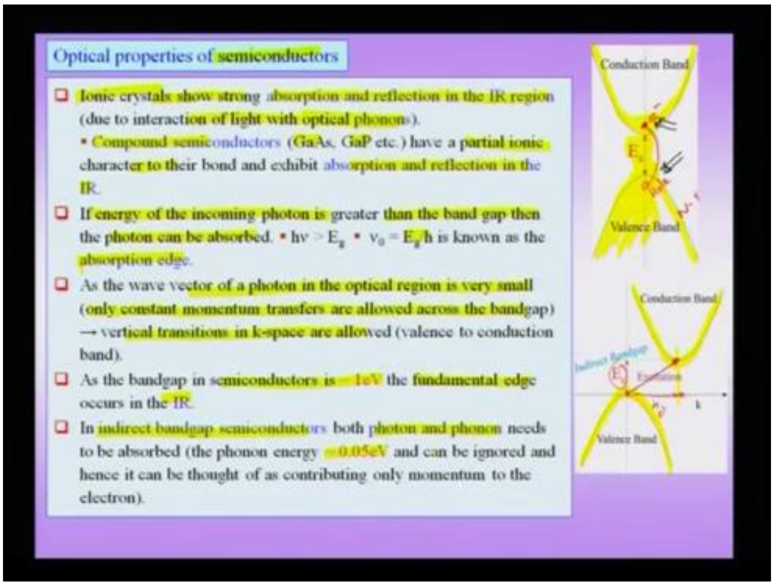

Optical properties of semiconductors

- Ionic crystals show strong absorption and reflection in the IR region (due to interaction of light with optical phonons).
  - Compound semiconductors (GaAs, GaP etc.) have a partial ionic character to their bond and exhibit absorption and reflection in the IR.
- If energy of the incoming photon is greater than the band gap then the photon can be absorbed. • $h\nu > E_g$ • $\nu_0 = E_g/h$ is known as the absorption edge.
- As the wave vector of a photon in the optical region is very small (only constant momentum transfers are allowed across the bandgap) → vertical transitions in k-space are allowed (valence to conduction band).
- As the bandgap in semiconductors is ~ 1eV the fundamental edge occurs in the IR.
- In indirect bandgap semiconductors both photon and phonon needs to be absorbed (the phonon energy ~0.05eV and can be ignored and hence it can be thought of as contributing only momentum to the electron).

In other words, a metal itself could actually becoming become somewhat transparent or it could be reflecting, depending on the frequency of the incoming radiation. We also noted that in the case of semi conductors we have to worry about the band gap and exciton. If I have to understand how the absorption of a semi conductor is going to be when a imposed an electromagnetic radiation. Therefore, and of course the important question that we are going to now ask is that when we go to nano materials, how is the behavior as compared to a bulk metal going to change or a bulk semi conductor going to change, when you have a material in the nano scale.

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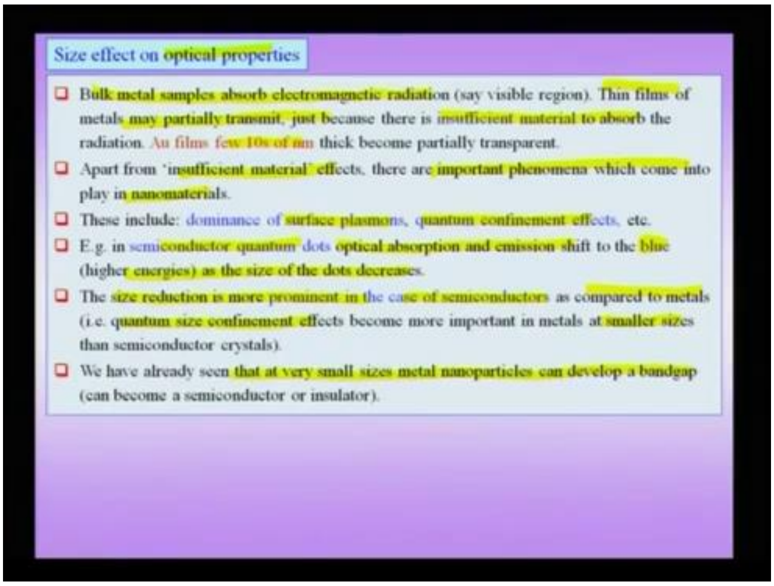

Size effect on optical properties

- ❑ Bulk metal samples absorb electromagnetic radiation (say visible region). Thin films of metals may partially transmit, just because there is insufficient material to absorb the radiation. Au films few 10s of nm thick become partially transparent.
- ❑ Apart from 'insufficient material' effects, there are important phenomena which come into play in nanomaterials.
- ❑ These include: dominance of surface plasmons, quantum confinement effects, etc.
- ❑ E.g. in semiconductor quantum dots optical absorption and emission shift to the blue (higher energies) as the size of the dots decreases.
- ❑ The size reduction is more prominent in the case of semiconductors as compared to metals (i.e. quantum size confinement effects become more important in metals at smaller sizes than semiconductor crystals).
- ❑ We have already seen that at very small sizes metal nanoparticles can develop a bandgap (can become a semiconductor or insulator).

So, when you are talking about size effect on optical properties, bulk metal absorbs electromagnetic radiations say in a visible region, thin films of metals may become partially transmitting. This is, because of the insufficient material effect as we pointed out. So, gold films about ten nanometer thick can become partially transparent. This is not something very what you might call unexpected. Apart from the insufficient material effects, there are other important phenomena, which come into play in nano materials, especially nano freestanding nano crystalline particles. These include the phenomena of surface plasmon and quantum confinement effects. So, we will take up these two important phenomena. We already talked about what is called the bulk plasmon, which is a longitudinal wave.

Now, we will take up the concept of a surface plasmon, because now we know in a nanostructure nano crystalline material or a nano material freestanding nano particles. You have a large surface to volume ratio, and therefore surface dominant effects like surface plasmon come into play.

In semi conductor quantum dots optical absorption and emission actually shift to the blue region of the spectrum, which means to the higher energies as the size of the dot increases. This we will see in detail, which implies that inherently, there is something changing in nano structured materials regarding the what you might call the electromagnetic structure or the band structure.

The size reduction is more prominent in the case of semiconductors as compared to metals. To see the effect of say quantum confinement in metals we have to go down to smaller sizes as compared to the thin semiconductor crystals. So, this effect becomes prominent at larger sizes in semiconducting crystals. Therefore, we will have a lot of examples of semiconducting crystals being described here.

We had also seen that at very small sizes metal nano particles can develop a band gap and can become a semiconductor or an insulator. So, this aspect we have seen that, because of dimensional confinement the density of states, we saw already changes between a bulk ready semiconductor normal metallic conductor to a 2 D kind of a system, where you get a stair case kind of a density of states.

Then we saw we got on to 1 D semi conduct 1 D metal, which actually develops a band gap. That means 1 D metal you talk to a material like copper, which is bulk metallic in the bulk and reduce its size. You saw that the density of states, now starts to behave like an e power minus half rather than e minus half in the bulk, we saw that you actually develop a band gap. In other words, the metal starts to behave like a semiconductor or an insulator in very small sizes.

Then we also saw the case when we go down to zero dimensional metal again metal in the bulk, then you actually start to the material starts to behave like an atom. That means you have discrete energy levels. So, all these possibilities we have already seen before for the case of a metal.

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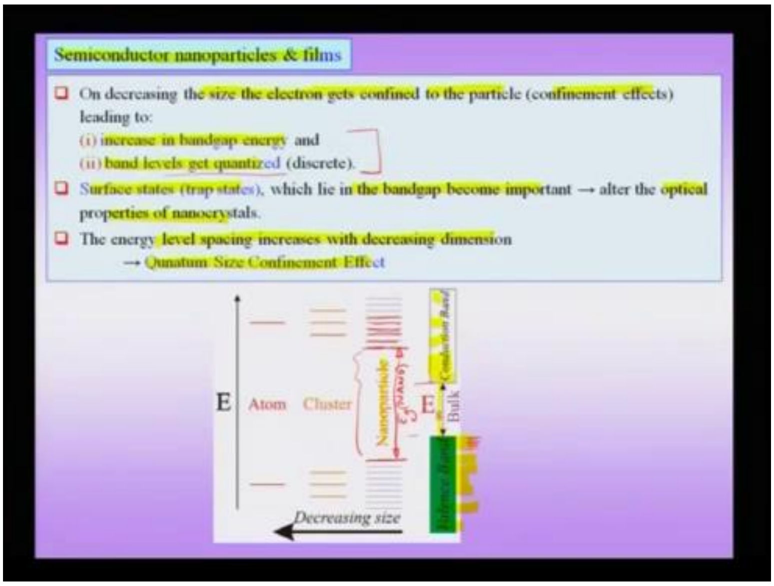

Semiconductor nanoparticles & films

- ☐ On decreasing the size the electron gets confined to the particle (confinement effects) leading to:
  (i) increase in bandgap energy and
  (ii) band levels get quantized (discrete).
- ☐ Surface states (trap states), which lie in the bandgap become important → alter the optical properties of nanocrystals.
- ☐ The energy level spacing increases with decreasing dimension
  → Qunatum Size Confinement Effect

Now, what happens in the case of semiconducting nano particles and films. So, these are very interesting things, which start to happen in the case of semiconducting nano particles and films and decreasing. On decreasing the size the electron gets confined to the particle and you confinement effects starts to dominating. What is meant by this confinement effect will become clear, when we discuss what is happening here. This leads to two important effects one is the increase in the band gap energy, this is very important. This is the heart of the blue shift we will be talking about the second is the band levels get quantized. So, you have a bulk semiconductor as shown schematically in the diagram.

So, you have the green region, which is now my schematic of the valence band. Now, you have the conduction band, which is separated by E g and this is not the bulk scenario. Now, when you make a nano particle you can clearly see two things are happening number one is that, when you look at the band gap originally this was my band gap. Now, the new band gap in a semiconductor in nano particle is this. So, the band gap has increased when you are talking about the semiconducting nano particle.

The second effect is that the band gap level gets quantized. Of course, this is an obvious effect, because now you in an nano particle. Even in a normal bulk material there are these discrete levels, but since they are placed. So, closely and when there are, because now there are now a mole of atoms or more. You can continue consider them to be a continuous stage, which is called a band. So, it is just a mere approximation, but when the number of particles in the system actually reduces. Obviously, there are not enough levels to make it what you might call a continuous or a semi continuous level. Therefore, you can see the discretization effect and you see that these levels start to become discrete.

So, there are two important effects that come into play when you reduce the size of a nano particle one is in the increase in the band gap energy. Number two is that the band gap levels, get quantized or start to discreteness of the levels starts to come above or get starts to be felt another important effect, which comes in semiconducting nano particles is the fact that surface states or trap states can form, which lie in the band gap and become important, because now the optical property of nano crystals is going to be dominated by the surface states. Therefore, there may be absorptions suppose I am talking about a surface state lying in the band gap.

This is my band gap this implies those surface states will absorb more strongly as compared to the inherent band gapage or what you might call the inherent E g nano. Therefore, those will stand to dominate the property optical properties of the semiconductor. So, the energy level spacing increases with decreasing dimension and this is called the quantum confinement effect.

So, we have now we talking about a semiconductor nano particle. We have to take in additional factors compared to the bulk. Number one is that you have insufficient material leading to discretization of the band into separate energy levels. Number two is a fact that there is a increase in band gap energy, which means now you have to supply a higher energy coming of course, through a electromagnetic radiation like photon to via photon to actually excite an electron. Third thing we saw is that surface trap states can also start to play an important role in the absorption properties of the semiconductor.

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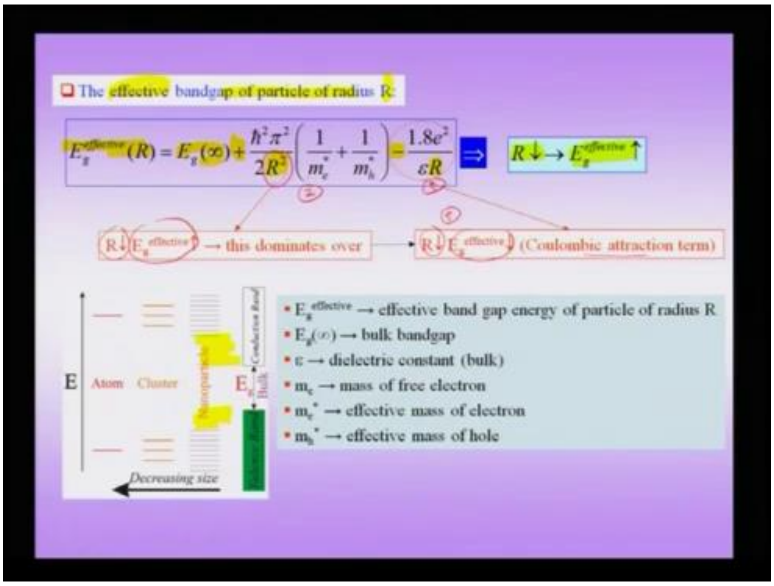

- The effective bandgap of particle of radius R:

$$E_g^{effective}(R) = E_g(\infty) + \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{\varepsilon R} \Rightarrow R\downarrow \rightarrow E_g^{effective}\uparrow$$

② ③

$R\downarrow E_g^{effective}\uparrow$ → this dominates over → $R\downarrow E_g^{effective}\downarrow$ (Coulombic attraction term)

- $E_g^{effective}$ → effective band gap energy of particle of radius R
- $E_g(\infty)$ → bulk bandgap
- ε → dielectric constant (bulk)
- m_e → mass of free electron
- m_e^* → effective mass of electron
- m_h^* → effective mass of hole

Now, how does the band gap or what you might call the effective band gap change with particle radius R, when you study this effect effective radius. Now, we have seen that the effective radius actually increases, so is these all originally were within the band, now become part of the band gap. Now, essentially we saw that we know that as r reduces the E g effective increases. So, we look at the formula of E g effective as a function of R. There is of course, the band gap energy of a bulk semi conductor the first term, but there are two more terms. One depends one is a positive term going as 1 by R square. There is second columbic term, which is coming from, which is a negative term coming as 1 by R, but since the 1 by R square term dominates over the 1 by R term. This implies that though given individual terms given the first term or the second term in that.

So, this my second term and this is my third term, the second term tells you that as the R decreases the E g effective has to increase. The third term tells you that as the R decreases the E g effective has to decreases the columbic attraction term, but as you can see this is R square dependence. Therefore, this term dominates and overall the band gap energy increases as you decrease the size or the as you confine the semiconductor. These are the terms in this are all constants, which we have dealt with before.

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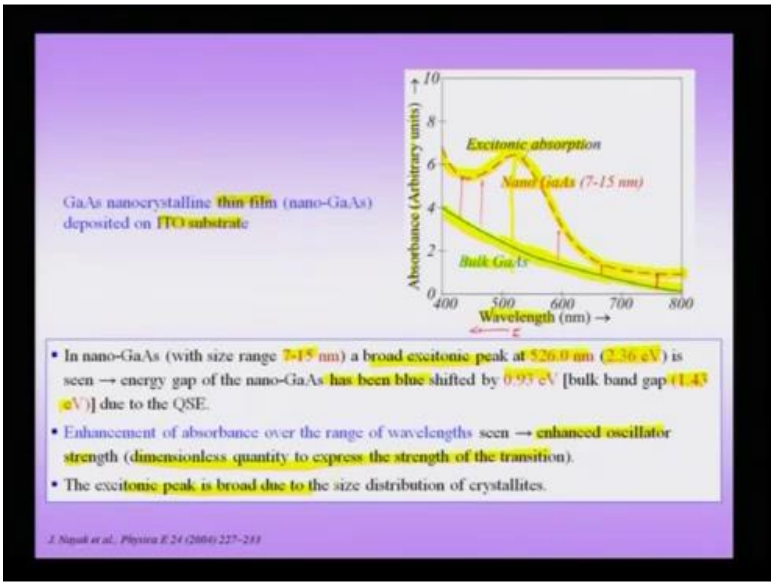

GaAs nanocrystalline thin film (nano-GaAs) deposited on ITO substrate

- In nano-GaAs (with size range 7-15 nm) a broad excitonic peak at 526.0 nm (2.36 eV) is seen → energy gap of the nano-GaAs has been blue shifted by 0.93 eV [bulk band gap (1.43 eV)] due to the QSE.
- Enhancement of absorbance over the range of wavelengths seen → enhanced oscillator strength (dimensionless quantity to express the strength of the transition).
- The excitonic peak is broad due to the size distribution of crystallites.

J. Nayak et al., Physica E 24 (2004) 227–233

Now, the signature of this increase of what you might call the band gap can be seen in this nice interesting example, where in Vijayalaxmi and co workers studied bulk gallium arsenide and compared it with nano crystalline gallium arsenide. Typically, they put this nano crystalline gallium arsenide as a thin film on a i to substrate and studies the absorption properties. If you look at the absorbance of this, now what you call the nano gallium arsenide visa be the bulk gallium arsenide. Here the x axis is the wave length you see that the bulk shows an increase in absorbance with wave length.

That means as the way decrease, that means as the wavelength increases the absorbance decreases. So, the wavelength is increasing in the right hand direction the energy is actually increasing on the left hand side direction, so this my energy, so with increase in energy we see a increase in absorption what is prominent in this absorption spectrum.

Of course, one of the things is that you do not find an exciton excitonic absorption. Because, this is now at room temperature experiment, where in you expect that the exciton has been disassociated. However, if you look at their paper they plot this nano gallium arsenide they actually plot a peak like this. They call it the excitonic absorption, now what is really and this nano gallium arsenide has size range about 7 to 15 nano meters size nano crystals. That means this is not a mono disperse system.

In other words I have to consider the size variations also into take into account. That means now I am not talking about a single band gap for this material those range of band gaps. Since, there is a range of band gaps I would expect absorption to take place over a range of energies. That is the reason and that is the reason that this peak is actually broader. It is not a very sharp peak as you would expect if you had a mono disperse crystalline size.

So, a broad excitonic peak occurs at about 526 nanometers. This is the range where it occurs and this corresponds the energy of about 2.36 e V. This is if you compare it with the band gap of the bulk gallium arsenide. It is about 1.43 e V. That means that the frequency is blue shifted. That means the band gap has effectively increased right the shift is 0.93 e V. It is not the net the net is 2.36 e V, that means now my band gap is 2.36 e V in the nano gallium arsenide while in the bulk gallium arsenide. It is 1.43 V, that means the effective band gap has increased. We already know that if we are talking about true excitonic absorption.

Then you would know that that has to lie in the band gap of the original semi conductor. Therefore, that would actually lead to a reduction in the reduction in the band gap. So, this we can understand as not as excitonic absorption though the terminology is used as, what you might call purely coming from confinement effect and increase in the band gap. So, to summarize this importance like you see that bulk gallium arsenide has a different absorption spectrum as compared to a nano gallium arsenide, in the nano gallium arsenide.

You observed that there is actually a very strong peak in the absorbance at 526 nano meters. This strong absorption peak corresponds to a band gap of about 2.36 e V. This is what you might call blue shifted with respect to the bulk gallium arsenide. That means now this happens at higher frequencies or in other words at lower wavelengths an additional fact.

That is seen from this curve is a fact that there is an overall increase in absorption, absorbance of the entire wavelength regime or the frequency regime in the case of the nano. That means the nano curve is shifted to higher absorbance values across the spectrum and this is coming. This is attributed to the enhanced oscillator strength an oscillator strength is a dimensionless quantity to express the strength of the transition.

Now, we are talking about the transition to the valence band to the conduction band. We have already noted that, the excitonic peak or the absorption peak is broad due to the distribution of the crystallite sizes. So, here we have a clear cut example of nano crystallite gallium arsenide film of an I T O substrate, which shows an absorption property, which is very different from that of the bulk gallium arsenide. The important thing to note is that the absorption peak is now blue shifted. That means it is occurring across a higher level larger band gap. There is a peak, where there was no peak in the case of the bulk gallium arsenide.

So, this is a very important difference between the optical property of what you might call bulk semi conductor visa V a nano semi conductor. We will take up some more examples in the coming slides to see the difference between, this what you might call bulk versus nano in the for semiconductors. After considering the example of gallium arsenide nano crystalline thin film…

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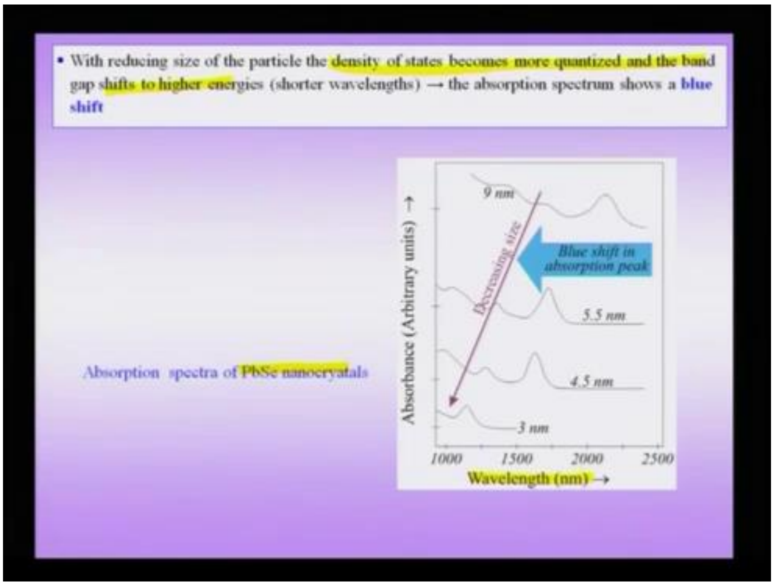

- With reducing size of the particle the density of states becomes more quantized and the band gap shifts to higher energies (shorter wavelengths) → the absorption spectrum shows a **blue shift**

Absorption spectra of PbSe nanocryatals

We take up an equivalent example the case of the P b S e nano crystals, where in again we see this dramatic effect of blue shift, which is coming from quantum confinement effects in these semi conductor nano crystals. Now, we have already noticed that the density of the state becomes more quantized. The band gap shifts to higher energies, which is the root cause for this blue shift in the case of the P b S e nano crystals. Again, we are plotting the wavelength as a function of the absorbance. We know of course, these curves have been shifted vertically.

So, that we can make a comparison and that is why the y axis is in arbitrary units. We note that dramatic change in the absorption peak as you go from say for an instance a 9 nanometer particles of P b S e to 5.5 nanometer particles to 4.5 and to the 3 nanometer particles. We will soon see a effect with respect to the surface plasmon absorbance in the case of metals, that there this effect of shift is actually negligible. It is actually small when you actually change the particle size.

So, here you see that there is actually a blue shift in the peak and you can see the big shifts to higher frequencies or in other words lower wavelengths. In other words the energy of the transition becomes high. Therefore, the material absorbs at higher energies, when you actually reduce the particle size. This particle size is only by a factor of about three from 9 nanometer to 3 nanometers. The wavelength you can see from absorbance shifts to something like about 1000, 100 nanometers from something more than something 2000 nanometers, so clear cut there is this quantum confinement effect in these nano crystals, which effects its optical properties, the counterpart side.

The other side of this absorbance is what is called photo luminescence. In other words if a material is put into an exited state, then it is going to relax at its ground state. In the process it may actually emit a photon in some cases. Of course, there can be radiation less transitions, but if there is a possibility here that the excited state will relax to the ground state by the emission of photons.

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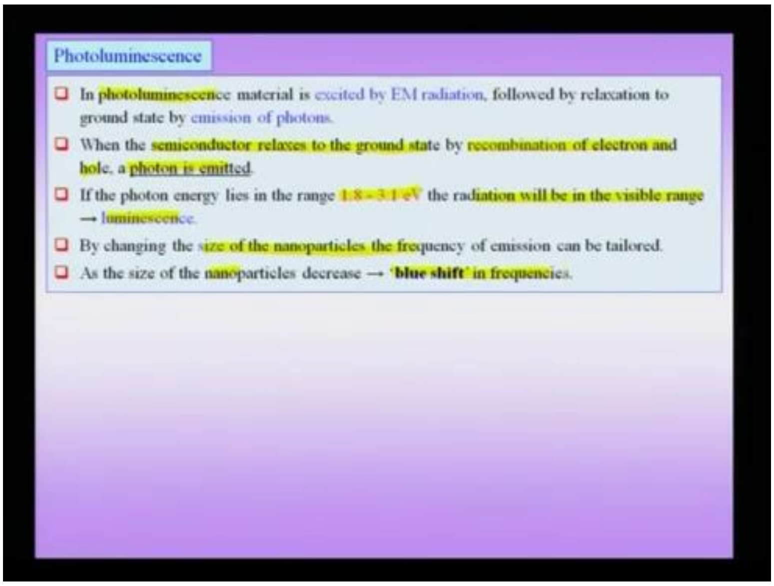

Photoluminescence

- In photoluminescence material is excited by EM radiation, followed by relaxation to ground state by emission of photons.
- When the semiconductor relaxes to the ground state by recombination of electron and hole, a photon is emitted.
- If the photon energy lies in the range 1.8 - 3.1 eV the radiation will be in the visible range → luminescence.
- By changing the size of the nanoparticles the frequency of emission can be tailored.
- As the size of the nanoparticles decrease → '**blue shift**' in frequencies.

This is the phenomena of photo luminescence and when this relaxation in a semiconductor takes place by recombination of electron and hole. The photon is emitted and if this emitted photon’s energy lies in the range of about 1.8 to 3.1 electron volts. Then the radiation will be in the visible range and often this phenomena is called luminescence. Now, by changing the size of the nano particles I have a handle on the band gap. Now, in other words in the bulk materials I just had one single band gap to deal with, but now I can tailor the band gap by actually changing the particle size.

Therefore, I can tailor the emission and in other words I get a handle on even on the color of the particle, which I see, which we will take up a startling example coming up soon. Even in these cases the emission case not unexpectedly you observe a blue shift of frequencies with reduction in particle size.

So, when we are talking about photo luminescence, which is the phenomena, which is called a other side of the coin of absorbance, which is the emission of a photon when a system is excited. In other words the recombination of electronic whole takes place and there is a emission of photon. This emission of photon can actually happen in the visible region in which case you call it luminescence. Of course, this need not always take place in visible range that depends on the band gap and the band gap happens to be about 1.8 to 3.1 volts. Then this will happen to be in visible region.

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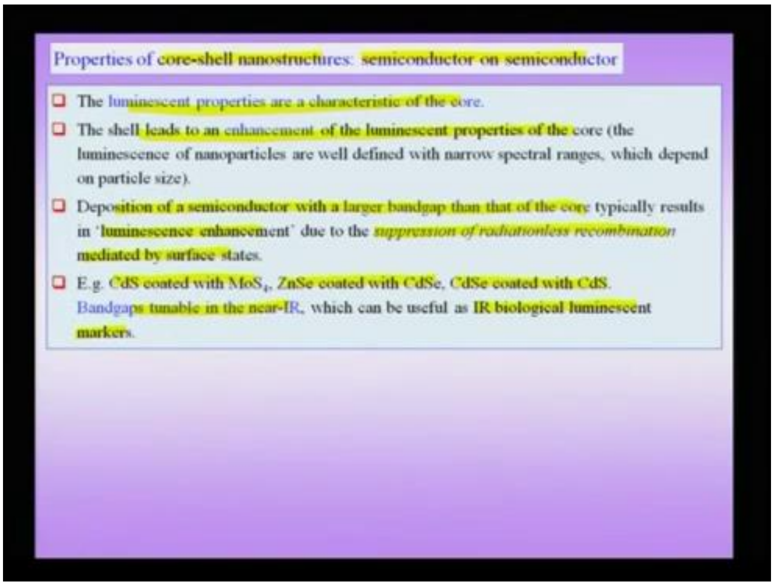

Properties of core-shell nanostructures: semiconductor on semiconductor

- The luminescent properties are a characteristic of the core.
- The shell leads to an enhancement of the luminescent properties of the core (the luminescence of nanoparticles are well defined with narrow spectral ranges, which depend on particle size).
- Deposition of a semiconductor with a larger bandgap than that of the core typically results in ‘luminescence enhancement’ due to the *suppression of radiationless recombination* mediated by surface states.
- E.g. CdS coated with MoS_4, ZnSe coated with CdSe, CdSe coated with CdS. Bandgaps tunable in the near-IR, which can be useful as IR biological luminescent markers.

The dramatic effect can be seen in what you might call the core shell nanostructures, where in there is one semiconductor as the core. Other semiconductor as the shell some examples of these are cadmium sulfide coated with most zinc selinide coated with C d S e, C d S e coated with cds etcetera. In this case we notice that the band gaps are tunable near the I R in which case they can be used as I R biological luminescent markers also. That means not only the emission can be in the visible region. It can also be in the I R region and you have a handle on the frequency of emission.

Therefore, you can tune what you call the frequency, which is emitted in such core shell structures the luminescent properties are typically, the characteristics of the core. We will take up an example and the shell actually leads to an enhancement of the luminescent properties of the core the shell. We said when we talked about the core shell structure in detail before we said the shell could actually be performing many roles. One of the roles could be one of mere passive layer, which is actually protecting the core from the environment, but we also pointed out that we will take up an example at some later stage, where we will talk about the enhancement of properties of the core.

This is a nice example, where in you will actually find that there is this enhancement of the luminescent property of the core. When you have a shell around it of a semiconductor. Now, typically the disposition of a semiconductor with a larger band gap than the core results in what you might call the luminescence enhancement. This occurs due to the suppression of radiation less recombination. This radiation less recombination is typically mediated by surface states.

So, if you had a raw semiconductor then you have the surface states, which lie in the band gap and the transition to these surface states may, sometime may not lead to luminescence. Therefore, having a shell layer enhances your luminescent properties of the semiconductor.

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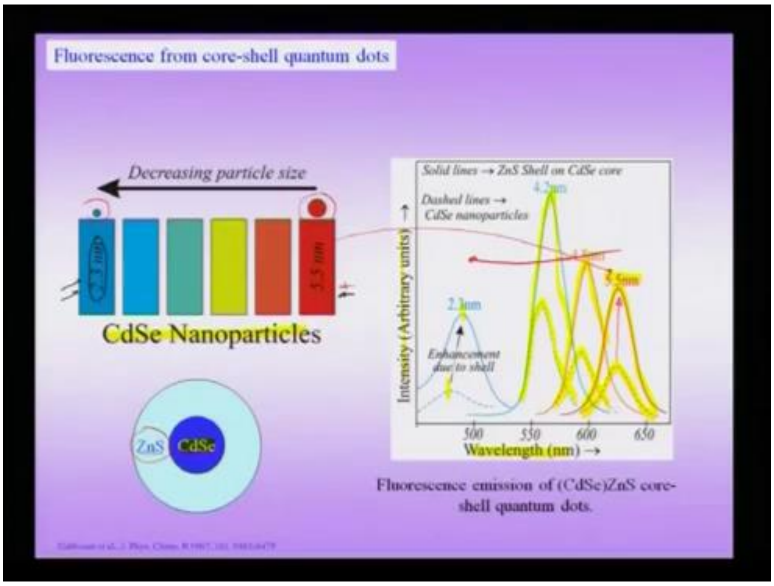

Fluorescence from core-shell quantum dots

Fluorescence emission of (CdSe)ZnS core-shell quantum dots.

The one of the beautiful examples available is the case of the C d S e nano particles. Now, we are talking about change in C d S e nano particles size from about 5.5 nanometers, which is on the right hand side a small nano particle to a size. So, this is my 5.5 nanometer to a size of about 2.3 nanometer particle a factor of about 2 to 3. Now, in these core shell nano structures of course, there is a shell of zinc sulfide. We will look at the properties of luminescence in the absence of the shell. Also, in the presence of the shell, so we have a case where there is no zinc sulfide. We will compare it to the properties, where there is actually a zinc sulfide shell.

The most beautiful unmarking, what you call characteristic signature of this change in size is the change in color of the colloid. This is cited as usually one of the beautiful properties emerging in nano structure, this is given as one of those what you may call the typical or the outstanding examples given. Where, in here I have schematically shown the change in color that on the 5.5 nano particle. On the left hand side you notice that you have emission or photo emission in the red region of the spectrum. When you reduce the size to 2.3 nanometer, which is on the right hand side.

You notice that the emission shifts to the blue color. Clearly, that is why the phenomena is known as blue shift. Because, now there is a change in color from red to the blue. That means from lower energy to higher energies. When you reduce the particle size, which again is coming from the phenomena of the quantum confinement, which is leading to a increase in the band gap.

Now, this is a very striking and startling example and if now if I plot the intensity versus wavelength. Now, this intensity is not the absorbing intensity, but the emission intensity. So, it is the other side of the coin of absorbance we just now saw. Now, again we are plotting it with respect to wavelength. So, when the particle size is 5.5 nanometer, which is a case corresponding to the figure on the right hand side.

So, this is the case the red case you notice that, there is an emission in the frequency wavelength region 60 to 600 to 650 in the red color regime. Now, the important thing is that in the absence of the shell you see that the emission has a certain intensity, but when you have a shell around it there is a clear cut marked enhancement in the intensity in the presence of the shell.

So, I can show that there is an enhancement in the presence of the shell. So, this is clearly you can see that an important effect of putting a shell around the core. Now, as you change the particle size, you can see that the frequencies are seeing a blue shift the peak is shifting to blue side. You can see that in each one of these cases the core shell structure has an higher emission as compared to the bare core or the bare core implying to the only core. The core is shown by the dotted lines the core shell structure is shown by the peak the overall peak of the emission, does not shift much.

So, there can be a small shift as you can see from the fact that the peak of the bare core lies slightly to what you call in over the shell at the slight red shift to this, but that is not a very significant effect the important effect is the enhancement in the intensity. So, there is a beautiful example here of a core shell structure, where in the absence of a core you still have a blue shift when you reduce the particle size.

There is an enhancement of the photon emission or enhancement in the fluorescence, when you have a shell around the core. This is as I said typically a beautiful example; there are beautiful nice pictures, where in they show that how this dramatic effect takes place, because of reduction in particle size. Here, again note that the particle size reduction is not too much, it is not an order of 92, it is only by a few factor of few.

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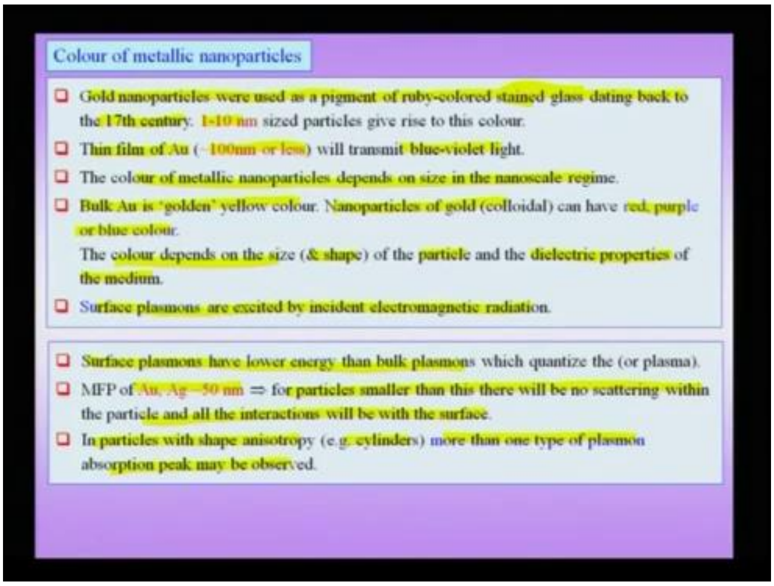

Colour of metallic nanoparticles

- ☐ Gold nanoparticles were used as a pigment of ruby-colored stained glass dating back to the 17th century. 1-10 nm sized particles give rise to this colour.
- ☐ Thin film of Au (~100nm or less) will transmit blue-violet light.
- ☐ The colour of metallic nanoparticles depends on size in the nanoscale regime.
- ☐ Bulk Au is 'golden' yellow colour. Nanoparticles of gold (colloidal) can have red, purple or blue colour.

  The colour depends on the size (& shape) of the particle and the dielectric properties of the medium.
- ☐ Surface plasmons are excited by incident electromagnetic radiation.

- ☐ Surface plasmons have lower energy than bulk plasmons which quantize the (or plasma).
- ☐ MFP of Au, Ag ~50 nm ⇒ for particles smaller than this there will be no scattering within the particle and all the interactions will be with the surface.
- ☐ In particles with shape anisotropy (e.g. cylinders) more than one type of plasmon absorption peak may be observed.

Now, if you look at on the other hand metallic nano particles. The metallic nano particles you will see we have pointed out the size does not effect, it is not. It does not have a very profound effect. Now, for instance gold nano particles have been used as a pigment, because of the ruby colored stained glass dating back to the old seventeenth century. So, if anybody has gone to an old church, where there is stained glass the color of the stained glass is coming from these nano gold particles. Typically, about 1 to 10 nanometer in size and we accept that this is this phenomena is coming this color is coming, because of surface plasmon resonance. We had also pointed out that the surface plasmon are transverse in nature as compared to the bulk plasmon, which are longitudinal character.

Now, we already noted that the thin films of gold can be partially transparent about a 100 nanometers or less. They will essentially transmit blue violet light now the color of these nano metallic particles depends on the size in the nano scale regime, but again now we have to see the larger size changes to see the change in color bulk gold is yellow in color nano particles of gold can have red purple or blue color. So, there is again a possibility of tuning the color of these gold nano particles by changing the size not only does the color depend on the size, but it also depends on the shape. In the next slide we will see that you will construct two types of particles one cylindrical particles and one spherical particles.

We will see how the shape actually affects the frequency of a emission or frequency of absorption not only does the particle shape and size play a role in this whole plasmon surface plasmon resonance, but also the dielectric properties of the medium. Because, as we said that in the case of the stained glass, this gold nano particles are embedded in a dielectric glass. You may also what you may call suspend this gold nano particles in the form of a colloidal suspension and in which case the dielectric property of the suspending medium plays an important role.

Now, in this case of this gold nano particles the surface plasmon are excited by the incident electromagnetic radiations. We few more points about that are in the next box surface plasmon have a lower energy than bulk plasmon. Now, when you have a gold or silver which has a mean free path of about 50 nanometers for smaller particles than this there will be no scattering within the particle. All the interactions will be on the surface, in other words when we have extremely small particles. It is the surface, which becomes important. That means we have to worry about the surface plasmon more than the bulk plasmon. In other words the bulk plasmon absorbance is going to be small.

It is going to be the surface plasmon, which are going to play key role in determining the optical properties of such small metallic nano particles. As we pointed out in particles with shape anisotropy. We are going to give an example of cylinder in the next slide more than one type of plasmon may be simultaneously excited. We may observe a absorption peak corresponding to both longitudinal and transverse plasmon. So, this is a beautiful example in this example, we have three kinds of objects.

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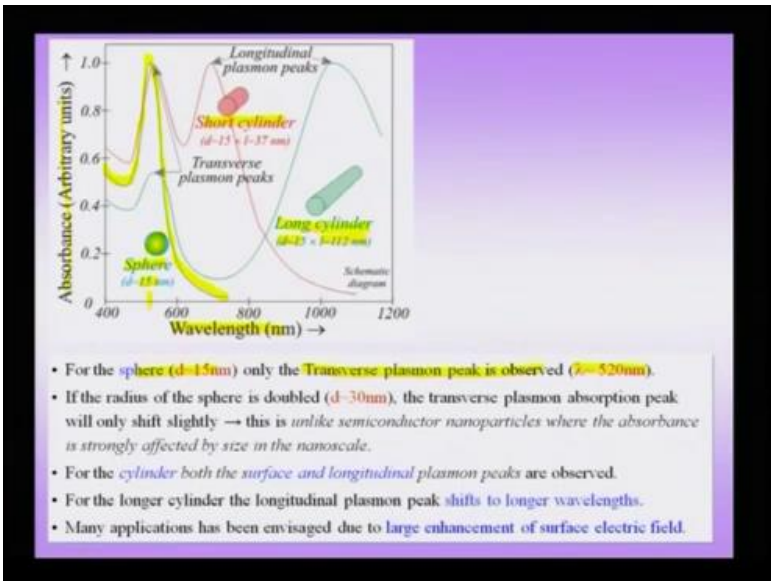

- For the sphere (d~15nm) only the Transverse plasmon peak is observed (λ~520nm).
- If the radius of the sphere is doubled (d~30nm), the transverse plasmon absorption peak will only shift slightly → this is *unlike semiconductor nanoparticles where the absorbance is strongly affected by size in the nanoscale.*
- For the *cylinder both the surface and longitudinal plasmon peaks* are observed.
- For the longer cylinder the longitudinal plasmon peak shifts to longer wavelengths.
- Many applications has been envisaged due to large enhancement of surface electric field.

One a sphere, one a long cylinder, which is marked in green. Also, the corresponding curve is also in green and one is a short cylinder. In other words sphere can be characterized by one dimension, which is just the radius of the sphere while on the other hand, if you have a long cylinder not only does you have to specify the diameter of the cylinder, but in addition you have to specify the length. That means two dimensions characterize a cylinder. This can be the sphere can be thought of as a quantum dot or a zero dimensional system. Of course, this is slightly large, but on the other hand a cylinder can be thought of as a one dimensional nano crystal.

Now, in some of the previous curves when we talked about semi conductors, we initially of course, we plotted what we might call the absorbance. Then we switch to when we switch when we talked about photo luminescence. We actually plotting the emission part that means how an excited system relaxes by emission of light. We use the term fluorescence for that, but here again we are going back to absorbance. That means what we are plotting here is absorption of wavelength or absorption as a function of the frequency of the electromagnetic radiation. Here, typically we are talking about visible regions.

Now, for a sphere of about 15 nanometer diameter and here this blue sphere, which is 15 nanometer diameter. Only transverse plasmon peak is observed at lambda approximately about 520 nano meter. So, if I look at this blue curve corresponding to my transverse plasmon absorbance. We see that it has a peak of about 520 nano meter, there is only one peak that is very important to note. This is coming from transverse plasmon in other words surface plasmon. So, this absorbance spectra of the sphere is dominated by a single quantity, which is now the absorbance of, because of sitting up transverse surface plasmon. So, that is the key phenomena here.

Now, as I pointed out there is one key difference between semiconductor particles and metal nano particles that is the size dependence the sensitivity to size. Dependence on this absorbance spectrum, we noted in the case of semiconductors that if I change the size…

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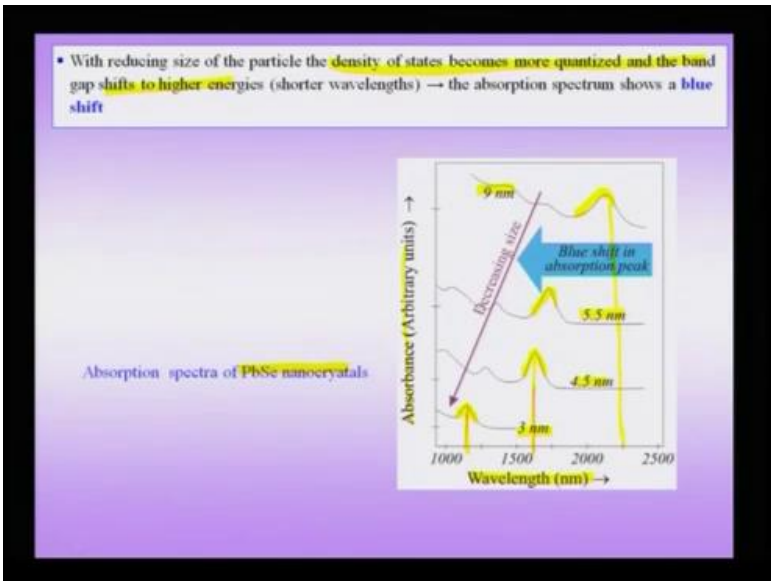

- With reducing size of the particle the density of states becomes more quantized and the band gap shifts to higher energies (shorter wavelengths) → the absorption spectrum shows a **blue shift**

Absorption spectra of PbSe nanocrystals

Just from 3 nanometers to 4.5 nanometer, which is about a 50 percent increase, You see that the peak shifts drastically. Another words for the 3 nanometer particle the peak is round about this may be considered 1200 in that range. This three nanometer particle is more than 1500. So, there is a drastic change in the absorbance peak, when you change the particle size in the nano scale regime, but when you are talking about metal nano particles, this is not the case. We have been talking about this previously. So, here is the right example to prove that point.

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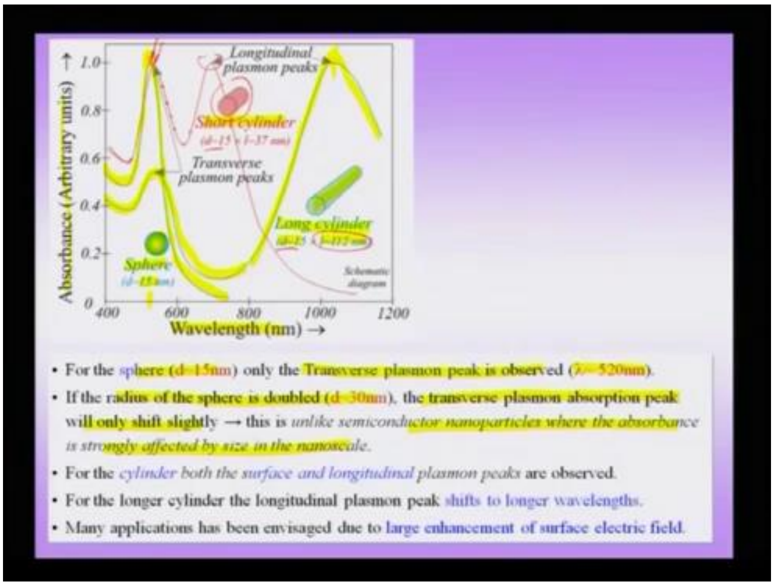

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Now, if I double the radius of the sphere I make it 30 nanometer the transverse plasmon absorption peak will only shift lightly I have not plotted it on this curve. Because, that will make it what you may call too much complicated there will be too many curves lying on top of the other therefore, but the shift is only slight, this is unlike semiconductor nano particles, where the absorbance is a strong function of the nano particle size. So, we see that if I make my sphere from 30 nanometer to 50 nanometer or 50 nanometer to 15 to 30. There is not much shift in the peak and this peak is now coming from surface plasmon resonance.

Now, the case of the cylinder is very interesting. Now, let me start with the long cylinder the 112 nanometer cylinder, in the case of the 112 nanometer cylinder you would notice that there is two peaks. In fact there are two peaks one peak in the low wavelength or the high frequency regime. The other one is in the longer wavelength regime these this longer wavelength is coming from the longitudinal plasmon, which is along the length of the cylinder of the along the length of the cylinder. The lower wavelength peak, which is here close to about maybe 5 slightly more than a board or close to 500 nanometers. This peak is coming from the transverse plasmon, another words based on the geometry of the cylinder.

Now, I got two peaks and these two peaks are coming from totally different mechanisms one from longitudinal plasmon. One is coming from surface plasmon, now if I make the cylinder short there is o b there is a shift in the longitudinal plasmon on peak. Because, that is along the length of the cylinder, which is what is sensitive while you can see that now for the short cylinder, this is the red curve. We can see that the red curve, so I have marked points on the red curve. The red curve the surface plasmon is in the same position, because now if you look at the D of the long and short cylinder, they are the same place.

So, the transverse plasmon peak appears at the same place as of the long cylinder, but then the longitudinal mode has actually shifted to shorter wave lengths. In other words higher frequencies, this shift this peak is coming from the longitudinal plasmon.

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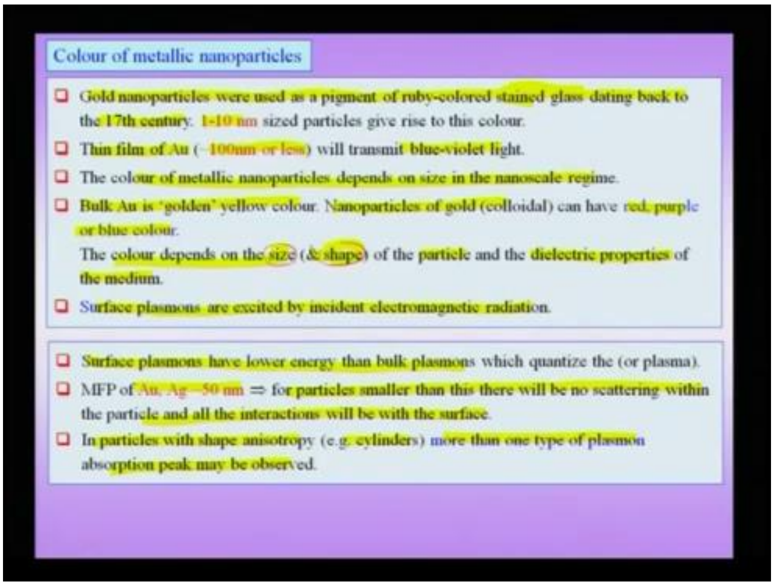

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In other words, now I have in the case of metal nano particles an important demonstration that the color depends on the size, obviously as we have seen and also on the shape of the particles. So, size and shape are the two important factors that we have seen in the previous graph, which is now going to determine my plasmon absorption. We have already seen that in the case of a shape the two peaks. We observe one is coming from that means the two peaks are from two different mechanisms. One is coming from a surface plasmon resonance ant the other is coming from the longitudinal plasmon. So, there is a nice example here of metal nano particles, which were in the size and shape are determining the absorption of the material.

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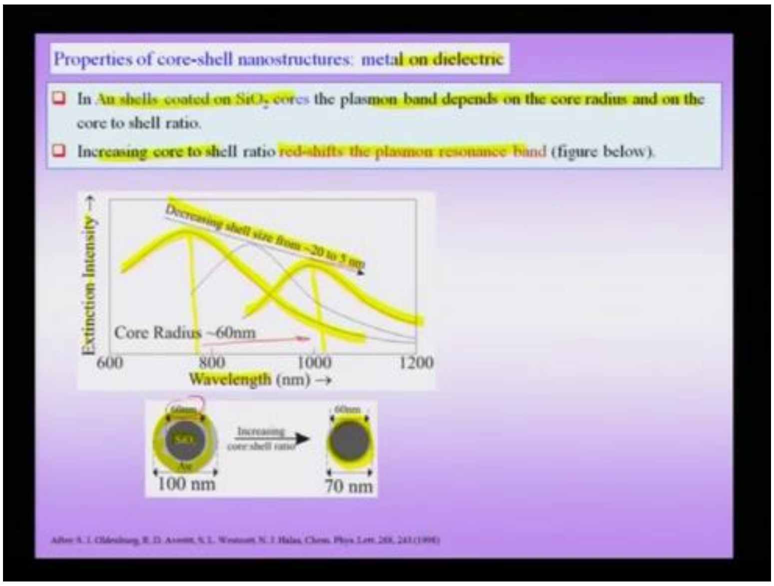

Properties of core-shell nanostructures: metal on dielectric

- ☐ In Au shells coated on SiO_2 cores the plasmon band depends on the core radius and on the core to shell ratio.
- ☐ Increasing core to shell ratio red-shifts the plasmon resonance band (figure below).

After S. J. Oldenburg, R. D. Averitt, S. L. Westcott, N. J. Halas, Chem. Phys. Lett. 288, 243 (1998)

Having said this, that we have to be careful, that we are comparing semiconductors with metals the mechanisms of absorption are obviously different, but after that we are comparing the sensitivity of two sides. We are definitely not saying that it is not size dependent. Obviously, we have seen the example that the absorption spectrum is size dependent, but it is not a sensitive function of size. That is the important thing we are saying, now we take up another of the core shell examples. In this core shell example we have a metal on the dielectric in the previous example of core shell structure.

We saw we considered a semiconductor on a semiconductor and we took up the example of zinc sulfide shell on a C d S e, which is a semiconducting nano particle. Now, we take up the example of a metal shell. In this case we have a gold shell as you can highlighting in a yellow here the gold shell on a silicon dioxide core S i O 2 core. So, the core is dielectric in other words, it is a non conducting material and the shell is our metal. We consider a case where we keep the core radius or the core diameter constant. The core diameter is 60 nanometers. What we do is we just change the shell size from about you can see that about 20 to 5 nanometers.

We keep on changing the shell size and we study the extinction intensity as a function of the wavelength. We note that in this case where you coat the gold on S i O 2 course the plasmon band shifts on changing the core radius. This depends on obviously the thickness of the shell, because we are keeping the core radius constant increasing the core to shell ratio, actually red shifts the plasmon resonance band. Because, I have taken up this example, because this is right opposite of what we have been talking, so far which is blue shift

In other words, here when I am reducing the metal thickness on this metal thickness of shell around this dielectric core. Then I am seeing that on decreasing the shell size I see that there is actually a red shift. That means that when you have a shell just thick, then the frequency peak lies close to about 800 nanometers, when I make the shell thin of about 5 nanometers. Then I see that there is a shift towards the red region. That means this is now towards the lower energy region. So, this shift is actually opposite to what we have been talking about, so far for the case of the semiconductor nano particles. So, this is a very interesting case of a core shell structure.

Now, we were when we talked about the refractive index. We said that there are very interesting class of materials known as materials with negative refractive index. So, meta materials or negative refractive index refractive index materials or otherwise, we meant to call them negative refractive index structures have a negative refractive index, when we say a negative refractive index.

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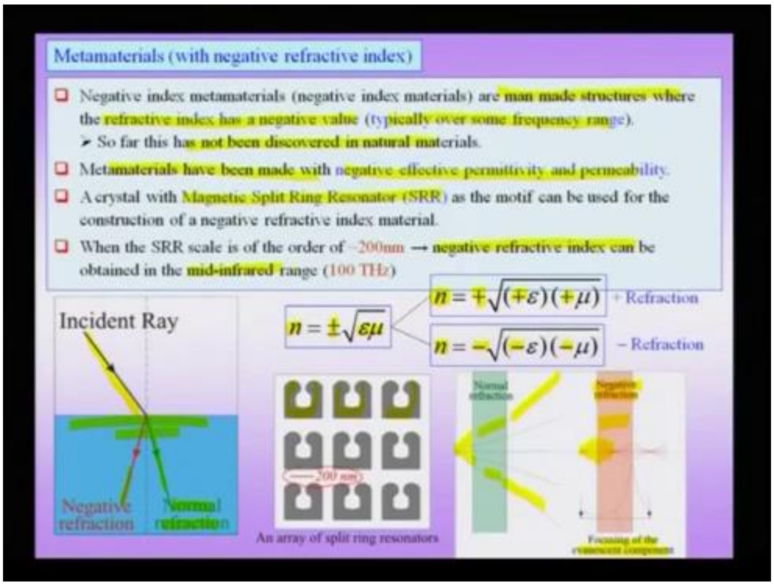

Metamaterials (with negative refractive index)

- ☐ Negative index metamaterials (negative index materials) are man made structures where the refractive index has a negative value (typically over some frequency range).
  - ➢ So far this has not been discovered in natural materials.
- ☐ Metamaterials have been made with negative effective permittivity and permeability.
- ☐ A crystal with Magnetic Split Ring Resonator (SRR) as the motif can be used for the construction of a negative refractive index material.
- ☐ When the SRR scale is of the order of ~200nm → negative refractive index can be obtained in the mid-infrared range (100 THz)

$$n = \pm\sqrt{\varepsilon\mu}$$

$$n = +\sqrt{(+\varepsilon)(+\mu)} \quad + \text{Refraction}$$

$$n = -\sqrt{(-\varepsilon)(-\mu)} \quad - \text{Refraction}$$

An array of split ring resonators

Suppose I am assuming ray we said coming from vacuum or air into a medium, which is colored blue here. Then we note that the refracted ray lies in the same side of the normal, as the incident ray unlike normal refraction, which is green line shown here, where in the refracted ray lies on the other side of the normal. Now, typically these are manmade structures where in the refractive index has a negative value. This refractive index and negative value typically over some frequency range and so far this has not been discovered in natural materials. These meta materials have a negative effective permittivity and permeability. Now, the refractive index we have noted before can be written as plus or minus epsilon into mu, where 1 is the permittivity and the other is permeability.

We have to note that, when we are talking about positive refractive index. Then we take the positive sign outside the square root and use the both positive of epsilon and mu. So, the negative refractive index structures use the negative sign outside the square root, use both the negative signs here an important property of the negative refractive index materials is shown in the figure below in normal refraction. What happens, suppose you have a divergent set of rays?

Then these rays of course, even after refraction will continue to be divergent within the medium, what you might call the angular regime of refraction may come down, but the rays continue to diverge, but in negative refraction you can see that, this is now my red material the refraction the refractive index material. The divergent rays will actually come to convergence in other words such a material can be used as a convergent lens.

Normally, we know that when we you are talking about a lens, which is converging like a double convex lens than, it is actually the shape of the lens, which alters what you might call the optical path length, which is leading to the convergence, but here you are seeing that this even a flat surface of negative refractive index can act like a converging lens. This kind of a negative refractive index material can actually be used for focusing what might be known as a evanescent component of the fields.

Now, what are the typical materials or structure, which show this kind of negative refractive index there are structures, which are known as magnetic split ring resonators. There is a schematic of such structures here all these grey regions in the figure below are these magnetic split rings detectors or split ring resonators. Now, there is a lattice of these structures. Therefore, I make a crystal of these and you note that if the scale of these structures happens to be a two of about 200 nanometers.

Then such a structure will show negative refractive index close to the visible range. That means if I change the scale of this structure, which I am making I can actually tune the regime in the electromagnetic spectrum, where in it shows what you might call the negative refractive index property.

So, if I make the structure even smaller then it will shift to the visible region, but if I make the scale of the structure larger. Then they will start to become negative refractive index only in the microwave or other regimes. So, these are what you might call very interesting materials, but the important thing to note from our course point of view, that if I make this structure in the nano scale about 200 nanometers are less. Each one of these what you might call these entities, in this is what is called a magnetic split ring resonator. Then this structure as a whole starts to behave like a negative refractive index structure.

So, people have been making various kinds of Kieran materials and various kinds of sculpted structures, which can actually give this kind of a property of negative refractive index, for that kind of negative refractive index to be in the optical regime. We have to note that the scale of the structure has to be about less the about 200 nanometers. So, these are again very interesting materials. People are interested in this area can investigate further with this we come to an end of this course. In this course, which Professor Kantesh Bilani and myself are the instructors.

We have tried to give you abroad flavor of what are nano materials, what are nano structures, what kind of properties can they have. Of course, briefly we have also been talking about the applications of these materials. In some cases we have gone into details of these classifications. Some of the properties we have considered in lot of detail like the magnetic properties, but in many other cases we have only made a cursory, what you might call a remark or a superficial consideration of many of these topics. So, students are expected to follow up these with further reading. Also there is an immense volume of material available in the literature.

Now, regarding the nano materials nano structures their properties one of the biggest what you might call the mammoth volumes is about… Now, initially there are ten volumes of the handbook of nano materials by Hari Singh Nalwa. Now, ten more volumes have been added. That means now you have twenty volumes as reference materials coming from a single handbook. There are many other such similar handbooks; there are beautiful review papers also available on any specific given topic. We are also being trying to give reference like for optics. We had cited a book, which you can refer. Similarly, we have talked about magnetism what books you can refer, but going through this course is…