# Nanomaterials and their Properties
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## Lecture - 27
## Optical Properties of Nanomaterials (II)

Students, we are going to discuss about Optical Properties in the lecture 27. And probably, this will be the last lecture on Properties of Nanomaterials. If anything is required to add it, I will do it bits and pieces. Otherwise, I will move into next things of the course.

So, lecture number 27, we are going to discuss about the Optical Properties of Semiconductors and Metallic Materials.

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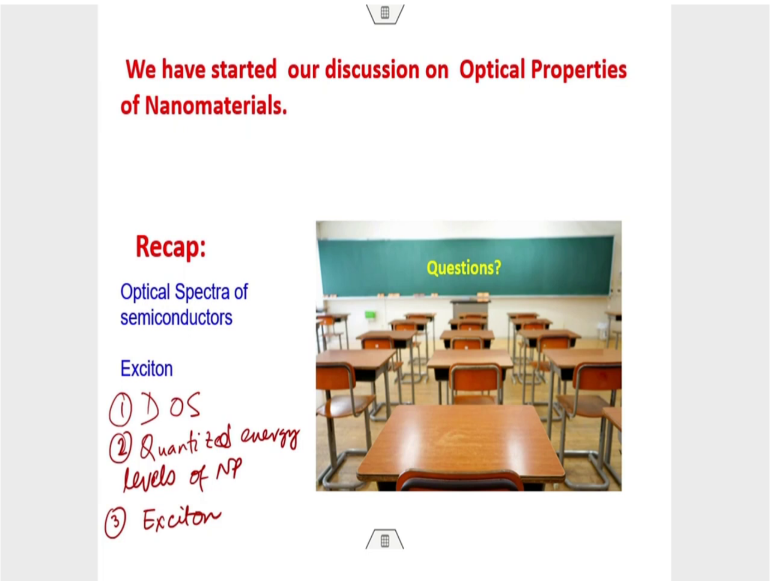

We have started our discussion on Optical Properties of Nanomaterials.

Recap:

Optical Spectra of semiconductors

Exciton

① DOS
② Quantized energy levels of NP
③ Exciton

You know this discussion we have started in the last lecture, and in the last lecture, we talked about optical spectra of semiconductors. I brought in a new concept called exciton which you have may not have heard earlier. Then tried to explain the optical spectra of the semiconductors using three important aspects. First, what is the important aspect we consider? First important aspect is the density of states, right. Density of states is the first important thing, which require discussing about the interaction of the lie to the electrons.

But you know density of states, the valence and the conduction bands also affected by the size, so that means, the quantized energy levels of the nanostructure nanoparticles, so nanostructures are going to be playing the predominant role in deciding the optical properties of the material. Third important thing is obviously, exciton.

So, remember, these three are the critical factors controlling the optical properties of different nanomaterials, right. But you know out of these things, density of states, where the electronic state levels in the valence and the conduction band plays the predominant role, at the same time exciton has an important role in the spectra optical absorption spectra coming at a higher wave planes, fine. So, that is what something which we did in the last lecture.

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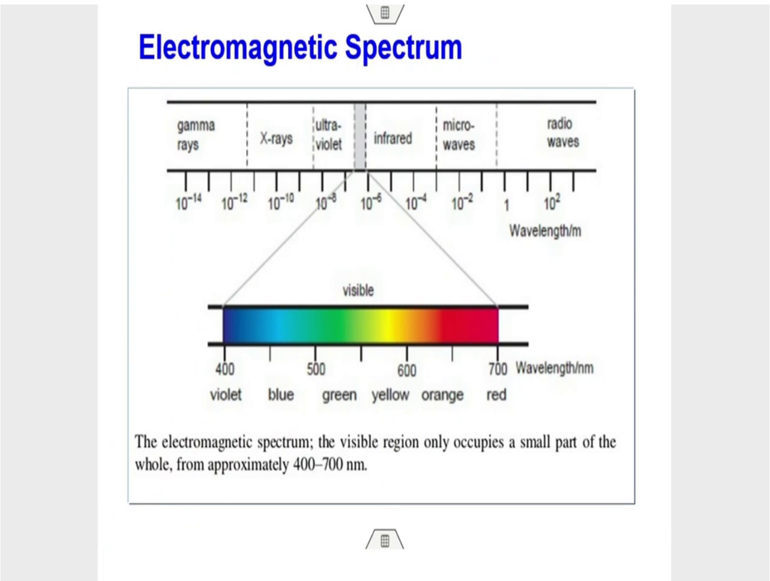

Electromagnetic Spectrum

The electromagnetic spectrum; the visible region only occupies a small part of the whole, from approximately 400–700 nm.

So, as you know electromagnetic spectrum is pretty large, starting from gamma rays on one side and then radio waves in the other sides. Gamma rays is a very very small wavelength of the order $10^{-14}$ to $10^{-12}$ meters. In addition, the other radio waves are like meter long, ok or couple of 100s of meters possible.

Light, actually comes with a very small energies electromagnetic spectrum that is between 400 to 700 nanometres. And by optical properties we are talking about this range of electromagnetic spectrum, right. So, therefore, you know the blue or the violet is on the lower wavelength side that is between 400 to 500 nanometres, red on the higher wavelength side that is about 700 nanometres. That is something which you should remember always in your life, right.

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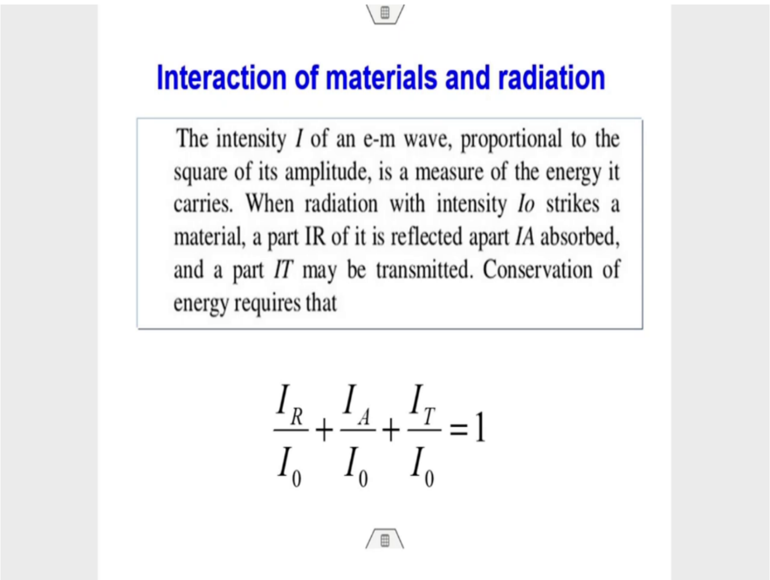
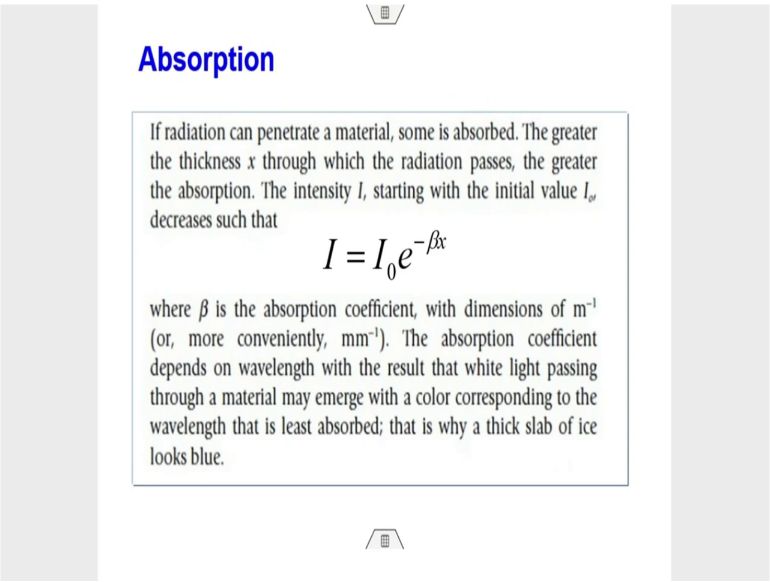


## Interaction of materials and radiation

The intensity *I* of an e-m wave, proportional to the square of its amplitude, is a measure of the energy it carries. When radiation with intensity *Io* strikes a material, a part IR of it is reflected apart *IA* absorbed, and a part *IT* may be transmitted. Conservation of energy requires that

$$\frac{I_R}{I_0}+\frac{I_A}{I_0}+\frac{I_T}{I_0}=1$$

Now, how does the radiation any radiation actually interact with material? The intensity of any electromagnetic radiation is I is obviously, proportional to the squares amplitude of the radiation and it has intensity $I_0$, then when it falls on a material, a part of it is reflected, part of is absorbed and part of it is transmitted, ok. So, therefore, if I have to do a conservation of this energy, then it will be $I_R+I_A+I_T=I_0$ or $\frac{I_R}{I_0}+\frac{I_A}{I_0}+\frac{I_T}{I_0}=1$ (Refer Slide Time: 04:16)



## Absorption

If radiation can penetrate a material, some is absorbed. The greater the thickness *x* through which the radiation passes, the greater the absorption. The intensity *I*, starting with the initial value $I_o$, decreases such that

$$I = I_0 e^{-\beta x}$$

where $\beta$ is the absorption coefficient, with dimensions of $m^{-1}$ (or, more conveniently, $mm^{-1}$). The absorption coefficient depends on wavelength with the result that white light passing through a material may emerge with a color corresponding to the wavelength that is least absorbed; that is why a thick slab of ice looks blue.

So, now question is absorption, that is very important aspect in optical spectrum. Radiation can penetrate on the material then it is absorbed, right. So, greater the thickness x through which the radiation can pass through greater is the absorption. And common understanding or the experimental understanding indicates that absorption varies like this $I=I_{0e}^{-\beta x}$, but β is the absorption coefficient.

Absorption coefficient, obviously, will depend on the wavelengths; also, it will depend on the type of material and thickness, right. So, obviously, these are the factors which controls.

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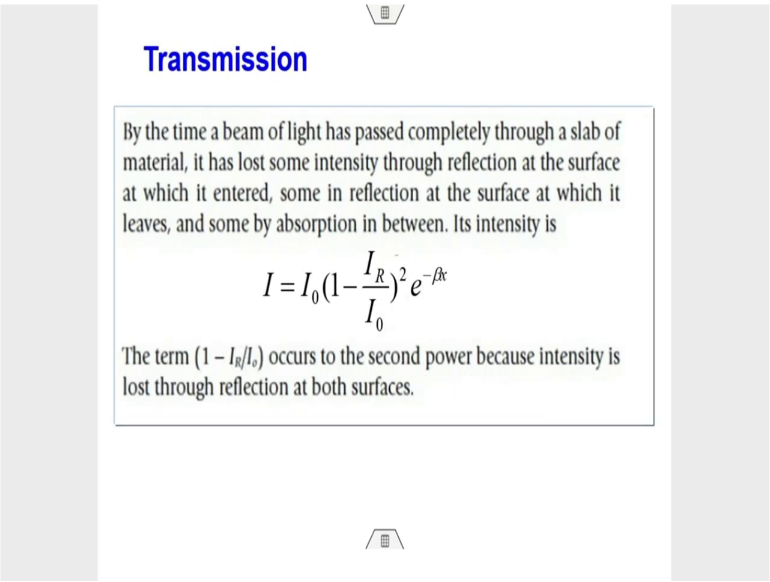

## Transmission

By the time a beam of light has passed completely through a slab of material, it has lost some intensity through reflection at the surface at which it entered, some in reflection at the surface at which it leaves, and some by absorption in between. Its intensity is

$$I = I_0 (1 - \frac{I_R}{I_0})^2 e^{-\beta x}$$

The term $(1 - I_R/I_o)$ occurs to the second power because intensity is lost through reflection at both surfaces.

Now, what is the next thing? Next thing is transmission. Transmission means what? The radiation must pass through a material. So that means, when it pass through materials, it will be lost some intensities will be reflection the surface, when it enters, and then rest is you know transmitted and absorbed. So, absorption is written like this, ok, $I=I_0(1-\frac{I_R}{I_0})^2 e^{-\beta x}$, and this term which is occurring $(1-\frac{I_R}{I_0})^2$ is because it is intensity lost a reflection from both the surfaces, ok.

That is why. So, that must be taken out. So, R transform stands for reflection, ok. So, therefore, transmission is intensity can be obtained simply by this equation.

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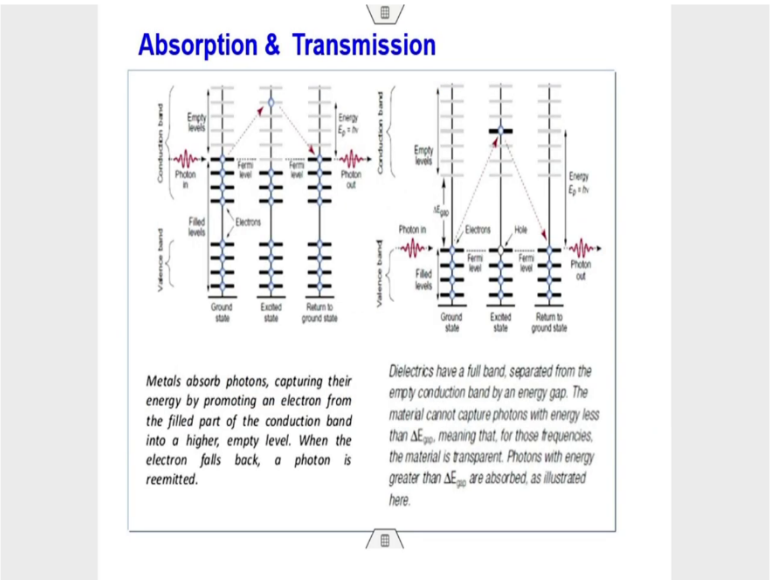

## Absorption & Transmission

*Metals absorb photons, capturing their energy by promoting an electron from the filled part of the conduction band into a higher, empty level. When the electron falls back, a photon is reemitted.*

*Dielectrics have a full band, separated from the empty conduction band by an energy gap. The material cannot capture photons with energy less than $\Delta E_{gap}$, meaning that, for those frequencies, the material is transparent. Photons with energy greater than $\Delta E_{gap}$ are absorbed, as illustrated here.*

Now, what is the third thing? So, yeah, before we go for that let us talk about let us little bit discuss of the absorption and transmission. This is basically nothing, but transition electronic transitions. Metal can absorb any photon and you know by capturing energy, in this way, from the photon electrons can go from the field part of the conduction band to higher entry levels or from the basically from metal that is what happens in metals conduction and valence bands are occupied with the metal electrons.

So, once the you know electron absorb the energy it goes to the higher empty energy levels, and when it comes back a photon is reemitted. This is the standard thing happens in a mostly metallic materials. But in case of you know dielectrics or I mean some semiconductors, what will happen? If its valence band is full and there is nothing in the conduction band, there is a energy gap as you see here E, delta E gap is written here. This is what is energy gap.

Now, therefore, if a material is you know material cannot absorb any energy, photon provides it can only absorb the energy, which is given by delta E gap. And when this much energy is available, the energy will be absorbed by the electrons, electrons go to the high energy level, and then again comes back to the lower energy level by transition and this will be followed by emission of a photon, right.

So, none the case, both the cases what you are having is a absorption and transmission taking place by the electronic transitions, whether it is a metal or a dielectric this happens in both the cases. Only way think difference is that the way it happens it is a metal is different from in case of dielectric.

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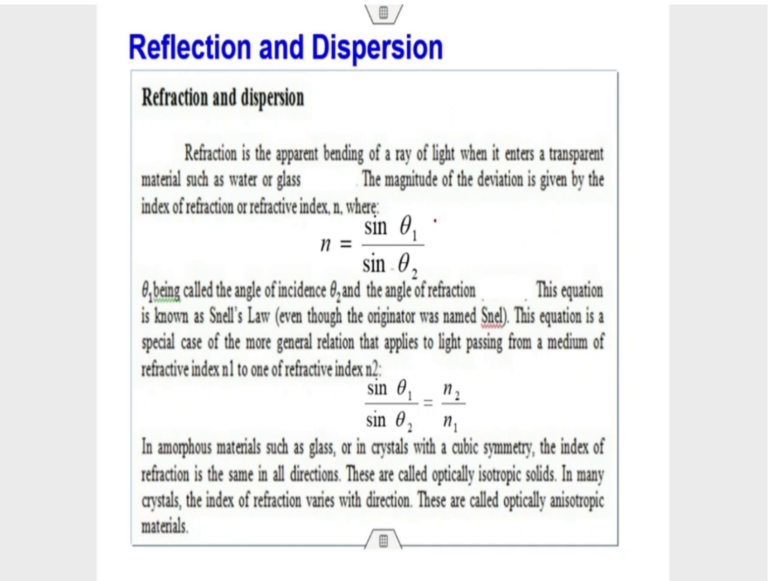

## Reflection and Dispersion

**Refraction and dispersion**

Refraction is the apparent bending of a ray of light when it enters a transparent material such as water or glass The magnitude of the deviation is given by the index of refraction or refractive index, n, where:

$$n = \frac{\sin\ \theta_1}{\sin\ \theta_2}$$

$\theta_1$ being called the angle of incidence $\theta_2$ and the angle of refraction This equation is known as Snell's Law (even though the originator was named Snel). This equation is a special case of the more general relation that applies to light passing from a medium of refractive index n1 to one of refractive index n2:

$$\frac{\sin\ \theta_1}{\sin\ \theta_2} = \frac{n_2}{n_1}$$

In amorphous materials such as glass, or in crystals with a cubic symmetry, the index of refraction is the same in all directions. These are called optically isotropic solids. In many crystals, the index of refraction varies with direction. These are called optically anisotropic materials.

Then, other than that you have some kind what is called reflection or refraction basically, not reflections. You can also have you know bending of lights because of the change of the media. And this is dictated by the Snell's law, ok.

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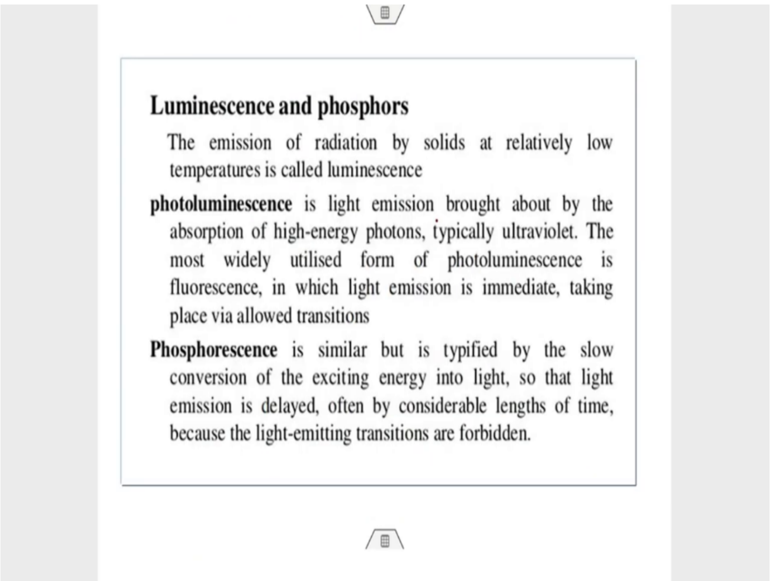

**Luminescence and phosphors**

The emission of radiation by solids at relatively low temperatures is called luminescence

**photoluminescence** is light emission brought about by the absorption of high-energy photons, typically ultraviolet. The most widely utilised form of photoluminescence is fluorescence, in which light emission is immediate, taking place via allowed transitions

**Phosphorescence** is similar but is typified by the slow conversion of the exciting energy into light, so that light emission is delayed, often by considerable lengths of time, because the light-emitting transitions are forbidden.

Well, and the last thing is what is known as a luminescence or photoluminescence. Luminescence is nothing but the emission of radiation by solid relatively low temperature is what is called as the luminescence. Photoluminescence is a light emission brought about by absorption high energy photons, typically ultraviolet. The most widely utilized form is photoluminescence is the fluorescence. All of you know fluorescence microscopes, wherein which light emission is immediate takes by the allowed transitions.

But you can also have photo phosphorescence in which slow a conversion the exciting energy into light happens, and that means, emission of light is basically delayed. And this is basically due to formatting transitions. So, you can have both photoluminescence and phosphorescence depends on what type of transition this is taking place. Your transition is fast and you know allowed, many times allowed then it will be photoluminescence whether it is if its forbidden and slow, then it you can term as a photo phosphorescence, ok.

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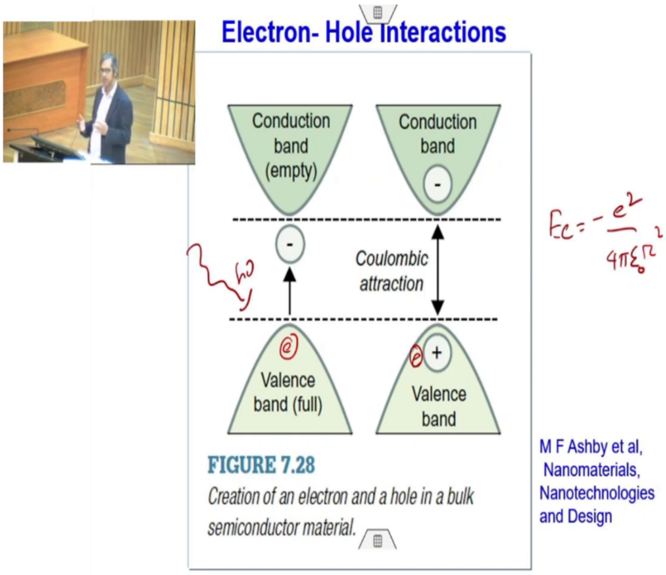

Electron- Hole Interactions

**FIGURE 7.28**

*Creation of an electron and a hole in a bulk semiconductor material.*

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$F_C = -\frac{e^2}{4\pi\varepsilon_0 r^2}$

So, now you know, but most important thing is that whenever you are you know what is called, whenever we are shining a light on the material, transitions electron transition do happens. And you know in case of most of the semiconductors, valence band is full conduction band is empty. So, therefore, if the photon falling on the valence band, electrons in the valence band will absorb the photon energy, and then if it can jump from photon to a valence to conduction band, then it will do that, provided the photon and sufficient energy to cross this barrier of the or the what is called as the you know energy gap.

Now, it can also happen that the this transition will lead to obviously, trans you know the electron movement from valence to the conduction band and then electron can come back also and lead to photon. That is we have discussed now. But what can also happen is that the because of the you know transitions, sometimes the electron can come back and electron on a hole can remain together. And this is what is known as exciton, ok.

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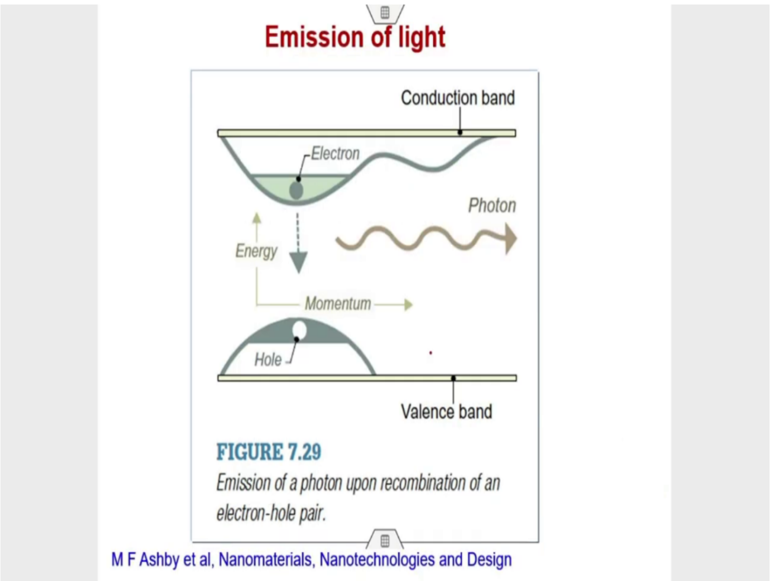

## Emission of light

**FIGURE 7.29**
*Emission of a photon upon recombination of an electron-hole pair.*

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That is something which is not happen always, but do happen. But I said emission of light is also possible, when you transport an electron whether or basically when you and an electron jumps from this valence band to the conduction band, and then it comes back because of energy reduction, photon can be emitted. And this is something which is we will be discussing a lot today.

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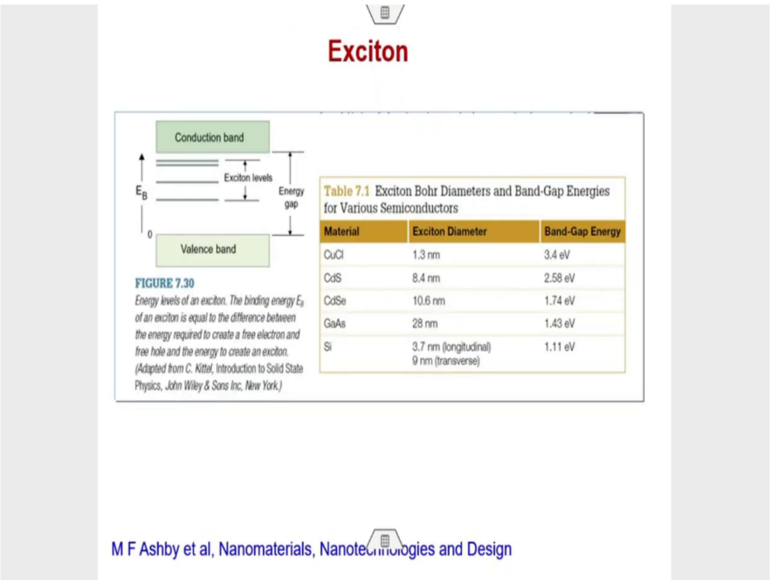

## Exciton

**FIGURE 7.30**
*Energy levels of an exciton. The binding energy $E_B$ of an exciton is equal to the difference between the energy required to create a free electron and free hole and the energy to create an exciton. (Adapted from C. Kittel, Introduction to Solid State Physics, John Wiley & Sons Inc, New York.)*

Table 7.1 Exciton Bohr Diameters and Band-Gap Energies for Various Semiconductors

| Material | Exciton Diameter | Band-Gap Energy |
|---|---|---|
| CuCl | 1.3 nm | 3.4 eV |
| CdS | 8.4 nm | 2.58 eV |
| CdSe | 10.6 nm | 1.74 eV |
| GaAs | 28 nm | 1.43 eV |
| Si | 3.7 nm (longitudinal)<br>9 nm (transverse) | 1.11 eV |

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By the way, so excitons are basically, very interesting thing excitons as you know, ok. So, what actually happens? Why do you think of excitation exciton actually? Let me explain again. You know at low temperature in the bulk semiconductors often show optical absorption just below the energy gap, just below this band gap actually.

And this is cannot be you know cannot be actually the case if you think of this is the band structure, ok. Here I have a photon energy coming into picture, if this photon has sufficient energy to drive the electrons from the valence to the conduction band, then only the photon will be absorbed, right. Otherwise, why the electron will absorb photon, if you cannot have a transition from valence to a conduction band.

But, in semiconductors, bulk semiconductors, what has been observed is that you know very simply at low temperature that this optical absorption can happen below the energy gap. So, this is very you know not easy to understand, why it will absorb an photon energy which are less than the energy gap. Because that will not allow the electron to have a transition from valence to conduction band.

So, that is why you know this process can be associated with you know something known as a exciton. What is that? Formation of the electron and a hole bound to each other. Electron is extracted, electron has absorbed the energy, but it could not have a transition from the valence of conduction band.

So, it stay together the hole which is there nearby, and they bound to each other. And this thing is called as exciton. That means, electron hole bound to each other, can be called as excitation exciton. As for any particle electrons excitons are basically mobile, right.

So, binding energy between electrons, and this hole is basically electrostatic. And that means, the columbic attraction actually dictates the binding between this exciton the electron and the hole. And that one can actually calculate it. It is nothing, but right $Ee= -e^2/4\pi\varepsilon_0$. That is what you know.

And why it is that? Because Coulomb's law tells you that energy is depends on 1 by r square, right. So, this is something which is very important. Now, what is the now what is the effect of these binding? How does it is going to change the you know kinetics of the whole thing?

Ok. That is can you know because of the electrostatic interaction between this hole and the electrons, the energy required for the excitation formation leads to electrostatic reduction interaction reduction, ok.

What does it mean? The compared to the unbound electron and the hole energy, the energy of this pair is much lower, ok. So, that means, what? The this electron which is at the valence band, energy compared to this energy of the electron this pair has low energy. So, if that is the case, if the pair has low energy, what will happen? That is nothing, but the electrostatic energy, this energy is reducing with energy gap actually.

So, that means, what? They can then easily if I shine a light, then easily absorb this pair can absorb the energy and move to the conduction band. That is what it is compared to a electron in the valence band. Well, and this is that means, we can think of change of Bohr radius. And therefore, we can always define a new Bohr radius, and this Bohr radius can will depends upon mass of whole, mass of electrons, and also the zero mass of electrons also as well as the radius of the Bohr, Bohr radius, ok. So, that I have only discussed in the last lecture.

Now, if you look at this Bohr radius or the Bohr exciton radius or exciton diameter is basically nanoscale. This value basically varies from 1.3 to about 28 nanometres, silicon it is about 3.7 nanometres, ok or 9 it was the or in case of gallium arsenide it is about 20 nanometres, ok. So, that means, what? Because this is a nanometric dimensions, so the confinement effects of the size as will affect it we have seen earlier cases.

So, that means, not only this density of states will undergo confinement because of the different class of nano material, as well as also this exciton will also undergo transitions. That is what something we discussed in the last lecture. And we said, that you see this is the values of the exciton diameters, so they are nanometric. So, therefore, they will be affected by the size because of the confinement effects.

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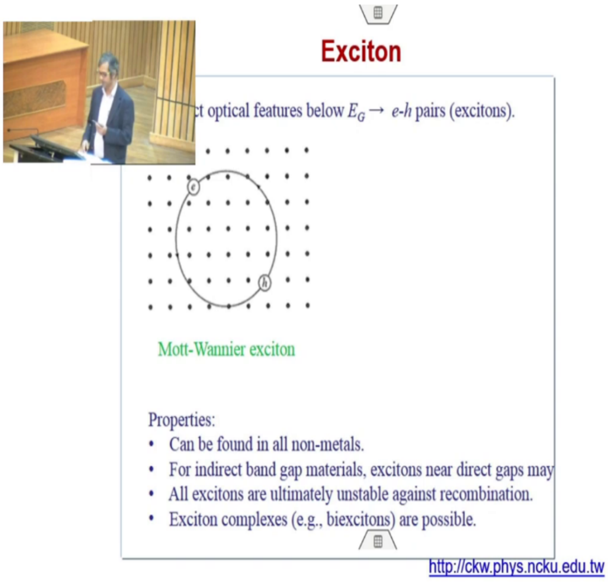

Exciton

t optical features below $E_G \rightarrow$ *e-h* pairs (excitons).

Mott-Wannier exciton

Properties:

- Can be found in all non-metals.
- For indirect band gap materials, excitons near direct gaps may
- All excitons are ultimately unstable against recombination.
- Exciton complexes (e.g., biexcitons) are possible.

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Now, we discuss further you know there are different types of exciton, what we have discussed in the Mott-Wannier type of exciton in which electron hole pair can remain together. And they can found in all my non-metals like semiconductors or you know or the you know dielectrics. For indirect band gap materials, excitons near the direct band gap may actually exist. All excitons are ultimately unstable against recombinations that is also true, they can be recombine and exciton complex complexes are possible, like there are can be 2 or 3 excitons can come together and complex also.

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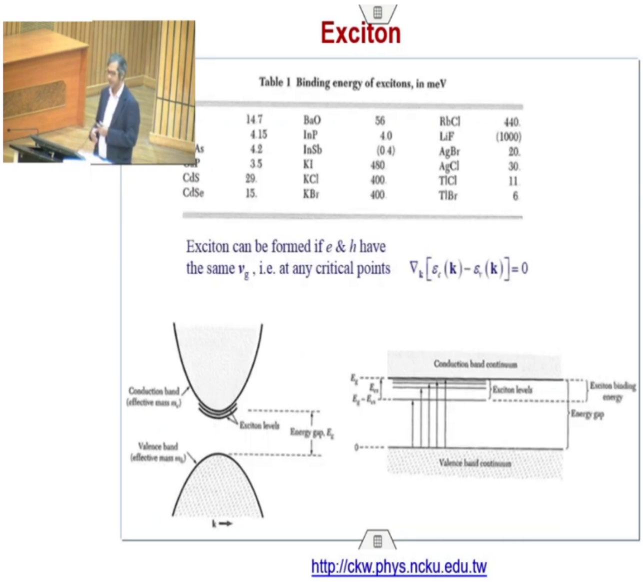

## Exciton

Table 1 Binding energy of excitons, in meV

| | | | | | |
|---|---|---|---|---|---|
| | 14.7 | BaO | 56 | RbCl | 440. |
| | 4.15 | InP | 4.0 | LiF | (1000) |
| As | 4.2 | InSb | (0.4) | AgBr | 20. |
| P | 3.5 | KI | 480 | AgCl | 30. |
| CdS | 29. | KCl | 400. | TlCl | 11 |
| CdSe | 15. | KBr | 400. | TlBr | 6 |

Exciton can be formed if $e$ & $h$ have the same $v_g$, i.e. at any critical points $\nabla_k\left[\varepsilon_c(\mathbf{k})-\varepsilon_v(\mathbf{k})\right]=0$

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So, not only that. So, what is the actual effect is this because the excitons are actually bind or bound by electrostatic force, so because of these then they can reduce this energy gap. As you can see, this is a conduction band these are the excitation exciton levels or there is a zone like this.

So, compared to the free electron which are there unbounded, here these energy levels are lower. So, that means, it can allow faster transitions because of the absorption of the optical photon or optical energy. Am I clear? So, that is something which you should remember.

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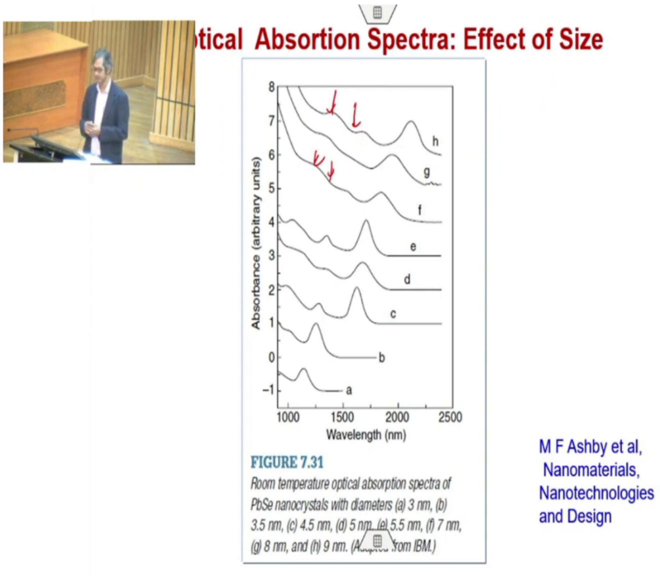

tical  Absortion Spectra: Effect of Size

**FIGURE 7.31**

*Room temperature optical absorption spectra of PbSe nanocrystals with diameters (a) 3 nm, (b) 3.5 nm, (c) 4.5 nm, (d) 5 nm, (e) 5.5 nm, (f) 7 nm, (g) 8 nm, and (h) 9 nm. (Adapted from IBM.)*

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And this we already discussed, ok. This kind of spectra which is coming from the lead selenide you know for different size of nanoparticles, the change of these optical spectra can be explained both in terms of nano size effect because of because of the confinements. That is the for this kind of low you know energy lower lengths peaks and the for high wilderness peak is mainly because of the exciton.

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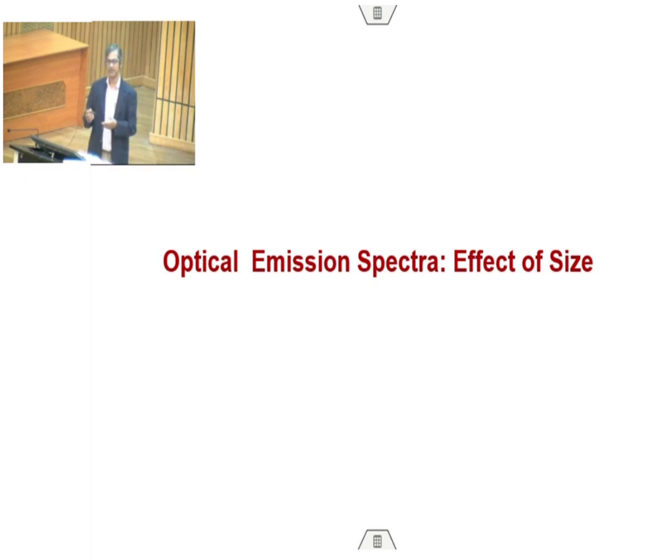

Optical  Emission Spectra: Effect of Size

Well, so that is about the last lecture we have discussed. Now, let us discuss about something about optical emission spectra. Those are absorption.

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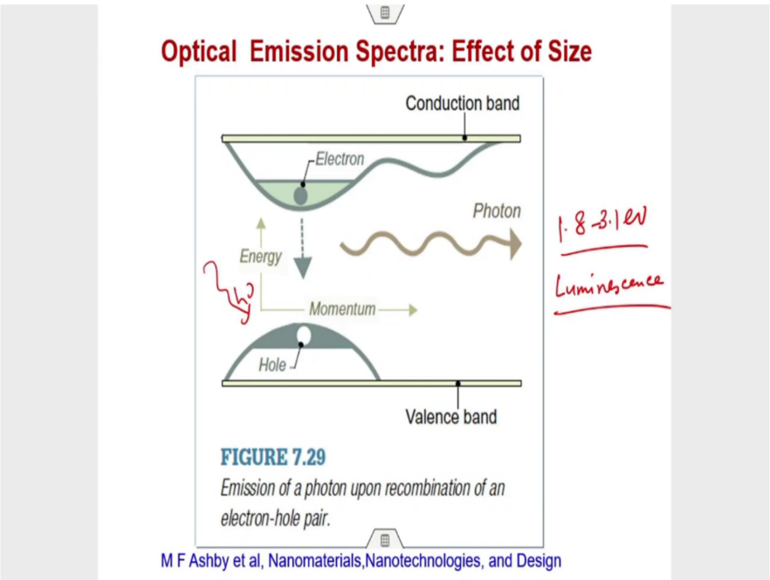

Optical Emission Spectra: Effect of Size

**FIGURE 7.29**

*Emission of a photon upon recombination of an electron-hole pair.*

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1.8-3.1 eV

Luminescence

Well, you know optical emission has already discussed about it. If we have valence and the conduction band, and if there is an optical you know photon falling on it and this electron absorb this photon, right, this for semiconductor actually, then it can move into the valence band to a conduction band because of these absorption by the photon energy, correct.

And subsequently, this electron then fall back to the valence band leading to release of energy in terms of photon. But this is something which is very easy. So, you know or this is basically one can tell that this is another kind of situations where exciton does not form, but electron hole, they combine. A recombine of electron hole can lead to, but in also optical spectrum.

So, the electron and hole, they combine, it can lead to optical spectra or optical emission only when energy released is within 1.8 to 3.1 electron volt. Then only, the radiation which will be emitted will be in the optical regime. Well, that is something which is very important and this is what is known as a luminescence, ok, luminescence.

We have discussed already, right. Because of the quantum confined nanomaterials the emissions of the visible light that can be tuned by varying the nanoscale dimension that is 1D, 2D, 0D, it can be varied. Not only that, it can also be varied by change the size in nanoparticle or nanomaterial.

Typical 10 nm is the shift of the emissions peak towards shorter wavelengths that is nothing but a blue shift, as the size of a nanoparticle decreases. This is what is normally found. But it can be tuned actually. That is a very important aspect of this.

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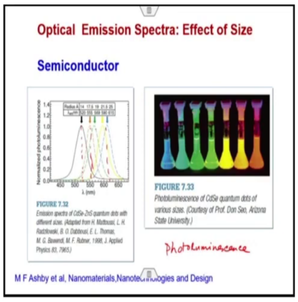

Optical Emission Spectra: Effect of Size

Semiconductor

FIGURE 7.32
*Emission spectra of CdSe-ZnS quantum dots with different sizes. (Adapted from H. Mattoussi, L. H. Radzilowski, B. O. Dabbousi, E. L. Thomas, M. G. Bawendi, M. F. Rubner, 1998, J. Applied Physics 83, 7965.)*

FIGURE 7.33
*Photoluminescence of CdSe quantum dots of various sizes. (Courtesy of Prof. Don Seo, Arizona State University.)*

Photoluminescence

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But you know not only that, another interesting phenomena, which can be observed in many of the semiconductors very interesting phenomena which people observe of light is that what is known as the photoluminescence, ok. Remember, this all we discussed. What is photoluminescence? Well, just let me discuss about these two plots, which are taken from different sources, but available in the Michael Ashby's book.

As you see here, on the left side of the plot what is shown is emission spectra of cadmium selenide, zinc sulphide, quantum, dots of different sizes, ok. Sizes means it can have 14 nanometres to about 25 nanometre sizes. What you see is a long big intense peak of normalized photoluminescence as a function of lambda. And these are the peak value of the lambda, you can clearly see where the radiation has picked, ok. And so, therefore, lambda max values are reported here 520 to about 565 nanometres, ok

So, not only that. So, smaller the land material size, shorter the wavelengths of visible light that is emitted, correct. That is what is on the right side. You can see from blue to the red depending on the particle size of cadmium selenide quantum dots, one can actually get photoluminescence in the whole spectrum. And this you must have seen it, many of you must have heard it from different books or different literatures. This is very common, ok.

So, what does it tell? Due to quantum confinement the shift from blue to red correspond to increase of nano particle size. In this regard, an issue of important is the use of homogeneous distribution nanoparticle because fluctuation size and composition can lead to illuminance spreading of the optical spectra.

So, we need a very very narrow distribution nanoparticle to see these effects clearly. That is what is done by Professor Don Seo from the Arizona State University. He has, he and his group has taken very narrow sides distributed nanoparticles of cadmium selenide quantum dots, and then once they irradiate with some kind of a you know radiation, these nanoparticles show optical emissions, ok. That is what is known as a photoluminescence. And it is very-very easy to understand why this thing happens. This is mainly because of this phenomenon, ok.

So, the moment you shine a light of a particular wavelength or particular energy which correspond to the energy gap between the conduction and the valence and the conduction band, these electron absorb this energy and goes to the conduction band. And then later on, the electron can come back or fall back to the valence band, and combine the whole and the process can generate a light.

This whole thing will depends upon basically the size of nanoparticle, ok and also the dimension of the nanoparticle, ok, because of quantum confinement effects, correct. Because electrons can only be staying in a particular; I remember go back to my discussion electron quantum confinement, electron can only stay in this different energy levels because of the confinement effects.

So, if you shine a light of that energy, it absorbs it and goes to the conduction bands and when it falls back to the valence band emission happens of the optical photon, ok. So, that is something which is easy to understand.

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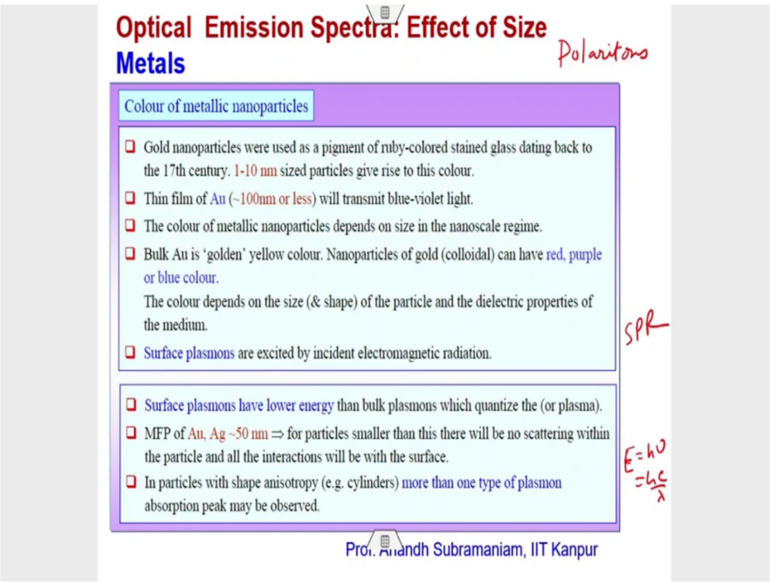

**Optical Emission Spectra: Effect of Size**

**Metals**

Polaritons

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.

SPR

☐ 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.

$E = h\nu$
$= \frac{hc}{\lambda}$

Prof. Anandh Subramaniam, IIT Kanpur

But what about metals? Metals are also equally interesting, correct. You know this is taken from Professor Anandh Subramaniam of IIT, Kanpur. Metals also show colours. Gold nanoparticles were used as a pigment of ruby-coloured stain glass dating back to 17th century. I have already discussed it, right in the very beginning of my course. So, 1 to 10 nanometre size particle gives rise to this kind of colour. And this was exploited heavily by the artisans in those days. They are exploited very heavily.

So, they show a very ruby colours or an actually they can show different colours. But the higher sides or the 10 nanometres and more, normally shows a ruby colour stained glass. Another thin film of gold which is obviously less than 100 nanometre can show blue-violet light. So, the colour of nanoparticles will depend on the size in nanoscale regime.

You know bulk gold is golden, that is why we like it, right. The yellow colour metal most of the woman in India wants to wear, wants to put on as a jewellery. But nano particle of gold will not be yellow, it can have different colours depending on size like red, purple, blue.

Colour depends on the size as well as shape and also dielectric properties of the medium in which you are kept.

Why this happens? This mainly because happens because of the surface plasmons. And the surface plasmon or plasma also the new concept to you. What is the Plasmon actually? You know let us first talk about that. Plasmon are nothing, but quantized waves, ok. And you may be thinking what is quantize. You know wave, right, waves light is a wave actually.

So, they actually quantize you, that means, their wavelengths are quantized, they cannot be any, they cannot have any wavelengths. They have only very few values of the wavelengths, ok. That is why they are called quantize. It is very easy to talk in terms of energy because energy is easily can be explained in terms of quantized facts, right from the quantum mechanics. So, wavelengths can be converted to energy, very easily. You know that, energy $E=h\nu=hc/\lambda$.

So, I can convert energy into a wavelength of energy, right. So, that means, this plasmons actually quantized waves, their quantized energy. And you know they propagate to the material very easily. And how they propagate? They propagate by the collection of electrons, which can be altered from the equilibrium positions, ok.

They, move from one part of the material to other part of the material by this collection of electrons, which are there. And these electrons you know can be altered, the energy can be altered or they can be alter from the equilibrium positions by these plasmons. So, plasmons are basically readily observed in noble metals like gold, silver, copper, even others, those who have d-electron bands or d-electrons bands, which are filled they can be thing like gold, copper, silver and also metals like magnesium, aluminium.

Plasmons can exist within the bulk as well as surface. Both it can exist. These are quantized waves moved because of the collection of the electrons in the material. So, in fact, photons can coupled with these plasmons, but important thing is the surface plasmons which actually leads to colour of the nanoparticles. That is what we will discuss more. What is surface Plasmon? Well, you know surface Plasmon have normally lower frequency than this Plasmon, which is then the bulk of the material.

And they can easily interact with the photons, ok. In fact, when photons coupled with the surface plasmons and that can lead to what is known as polaritons, ok polaritons, ok. This is nothing but coupling of photons to the surface plasmons. And this can lead to alternate regions of the positive and negative charge on the surface of the material.

The moment the optical or photon interacts with this surface plasmons, ok because the surface plasmon is also a wave, quantized wave. So, if you have a peculiar value a particular value of photon, incident proton, they can interact with the surface plasmons and that can lead to alternative surface charges positive negative on the material. And this can lead to a electric field, correct.

In the other words, this interaction between the surface plasmon and the optical light actually can be thought of, as you know light waves being trapped on the surface, ok. Light wave getting trapped in the surface of the material as a result of this interaction, ok. And this can be further emitted. Alternatively, I can actually need to give you more further descriptions of that, the surface plasmon resonance all of you heard, can happen when you know confinement of small particle size can lead to enhancements of the radiative properties of the nanoparticles, ok.

And this can lead to multi-moralities for the many applications. Like gold nanoparticles can be used for cancer research because of the first you know the surface modification capability, which allows them to bind with certain kind of proteins you know formed by this cancerous cell, and then one can actually tag this gold nanoparticle some drug.

So, whenever this gold nanoparticle like coming with the cancerous cell, this drug will be released and the cancerous cells can be killed. So, this is as very common we have been done in the medical sciences, ok. Another way, what is now to explain you further what is surface plasmon, let me just go to the this picture, ok.

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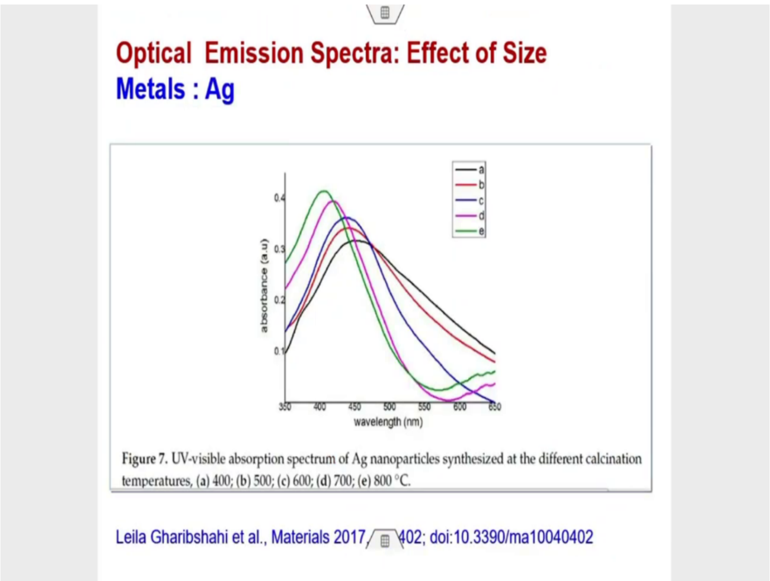

**Optical Emission Spectra: Effect of Size**

**Metals : Ag**

Figure 7. UV-visible absorption spectrum of Ag nanoparticles synthesized at the different calcination temperatures, (a) 400; (b) 500; (c) 600; (d) 700; (e) 800 °C.

Leila Gharibshahi et al., Materials 2017, 402; doi:10.3390/ma10040402

Before that let me tell you that, I will come back to it, do not worry. So, that means, what many of the metals like silver, gold, and all of them show surface plasmon and resonance are these kind of optical emissions spectra. As you see here, these are shown at different temperatures for silver 400, 500, 600, 700, 800, a stands for 400 and e stands for 800 degree Celsius temperature, and the peak shifts to the you know lower wavelengths as the temperature increases, correct.

And well this is something to do with not the temperature, but calcination temperature. So, this shift is basically because of size reduction. As the size is reduced there is a blue shift happens.

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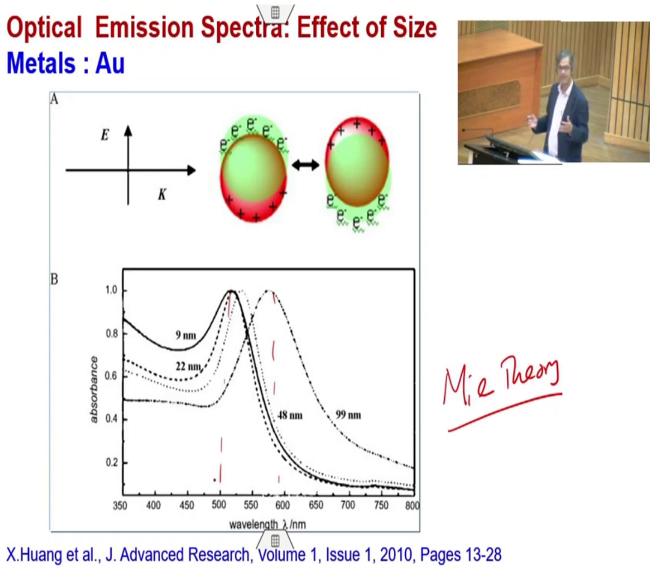

Optical Emission Spectra: Effect of Size

Metals : Au

Mie Theory

X.Huang et al., J. Advanced Research, Volume 1, Issue 1, 2010, Pages 13-28

Same thing has been seen because of gold also you can see, in a 99, 48, 22 and 9 nanometres, gold particles show strong optical emission spectra at wavelengths of different wavelengths 600, 500 nm or maybe even less, ok. This is very common. The question is why does it happen, ok. Let us talk about that.

So, when a metal particle is exposed to light the oscillating electromagnetic field of the light can induce the collective coherent oscillation of the free electrons, ok. As you know metal particle will have free electrons, right; metal has many free electron. The surface is covered as free electrons cloud.

Now, the moment light falls on these things, it can, it has is electromagnetic radiation oscillating electromagnetic radiation light has as you know that electric field and the you know magnetic field, they are alternative in case of light as which is a wave, ok. So, these can actually induce a collective coherent oscillations of these free electrons, ok.

Remember, collecting and coherent, collecting means many-many electrons actually can oscillate because of the interaction of the light with these, and it can lead to coherent. Why it will lead to coherent? Because energy will be not lost. That is why it is called coherent; emissions of these oscillations or the free electrons, correct.

And electron oscillation around the particle surface can causes you know charge separation with respect to the ionic lattice. What is it mean? Basically, what it leads to is that because of this interactions, electron you know particle surface can cause a charge separation from the ionic lattice; that means, from the basically core of the atom that is the centre of the atom, right.

So, it can lead to that form a dipole, ok. That is nothing but alternative electric field. That is what we discussed just now. Moreover, this dipole you know forming a dipole, which can oscillate along the direction of the electric field of the light, ok. You understand that. So, first thing is that light falls on the metal. It can interact with the electrons.

And the moment it interacts with electrons, it leads to formation of these you know charge separation, surface charges, positive, alternative positive and negative charges, because of the because, obviously, because electrons are actually a light is indeed inducing a collective coherent oscillation of the electrons, ok. And this oscillation of electron leads to positive and negative charges, ok. It is oscillating.

So, therefore, the parts where electron is not that will be positive charge, parts the electrons are there will be negative charge, and this alternative electron fields will be present on the material surface, correct. So, that means, what it will leads to dipole formation. In addition, this dipole can oscillate, oscillate between the along the direction of the electric field of the light. And amplitude of this oscillation will reach a maximum at a specific frequency called a surface plasmon resonance frequency, ok.

That means, what? This amplitude of you know oscillations of this dipole will be an interacting with the emitting light or the incident light and it can reach a maximum value at a certain specific frequencies, ok. And when it reaches that maximum value surface may receive what you see is nothing but a surface plasmon resonance, correct.

You must know about the resonance side and this a sphere induces a strong absorption of the incident light. And that can be easily measured by this individual spectroscope graphs which you are seeing in this pictures, correct. The sphere has and a band intensity and the wavelength, depends on the factors like electron Trans density, structure, composition of the material, size of the material many other things, right. I am not going to discuss about Mie theory, ok.

All of you; so, if you know little bit you know this theory can explain many of this. But I am not discussing about that. I was explaining how this kind of emission spectra could come up in the real sense. Now, one can actually control these emission spectra by shape of nanoparticle, structure of nanoparticles or even by you know what is known as a variation in the structure also. There are lot of many ways one can control that. So, the first thing you are seeing is the size of the nanoparticle altering this emissions wavelengths, ok a sphere wavelengths, ok.

So, from 600 to you can going down to about 500 nanometres. So, as the size decreases, ok, so that means, there is a blue shift happen as a side decreases for the SPS spectrum. This is something, which is very unique in metallic particles. And one can use this kind of concepts or this kind of measurement techniques to explain the presence of the, to rather know the presence of the particular metal nanoparticles of different size ranges. This is a very frequently utilized tool, ok.

So, I hope you understand what is surface plasmons, and how it can be used for various kind of purposes.

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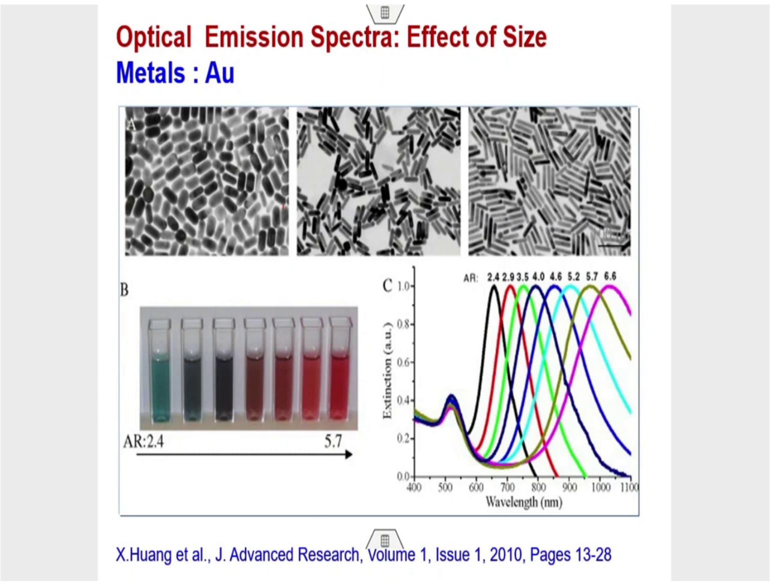

Optical Emission Spectra: Effect of Size

Metals : Au

X.Huang et al., J. Advanced Research, Volume 1, Issue 1, 2010, Pages 13-28

Well, so I am going to show you some more pictures. Let us talk about gold, ok or different types of gold, ok. And you know these different types of the gold as you see here, the can lead a can give us a tuneable property by changing the aspect ratio, right. You can have gold. It is a nanoparticle kind of a gold nano rod or you can see here this is like a rod here, ok. This is also rod, this is a rod, but the aspect ratios are different. Aspect ratio keeps on increases from left to the right side.

So, gold nano rods of different aspect ratios will exhibit different dimensions you know and different kinds of SPR, right. As you clearly see here the aspect ratio of 2.4 to 5.7, sizes may not be varying too much. However, aspect ratio can lead to different emission, correct. Why does it is happen so? It is again because of the surface plasmons interacting with the incident light, that is can change because of these different aspect ratios which is typically observed in here also. You can see these are all taken from a published literature, which is not very old, about 10 years old or so.

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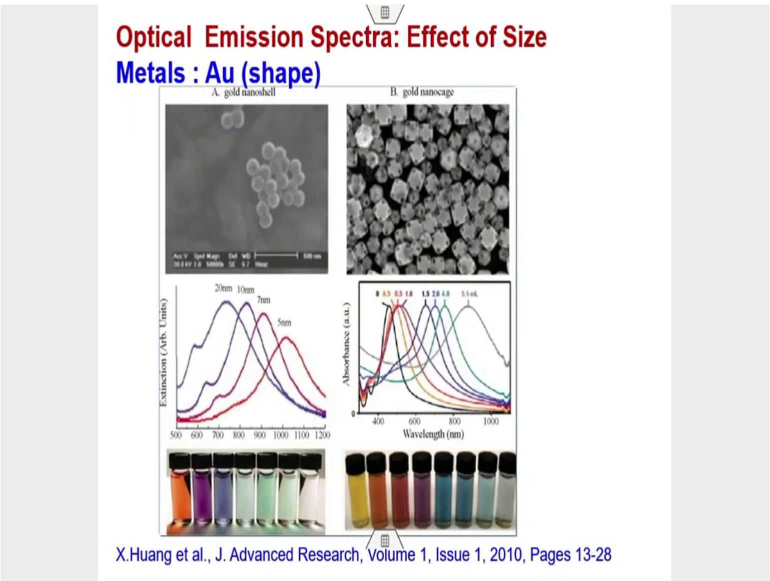
Optical Emission Spectra: Effect of Size

Metals : Au (shape)

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But you can also have you know issues like this. Beside this shape factor, optical tuning it is also possible by variation; you know as you can create core shell structure or you can create nano cage structure, right. As you can see here, left side is a core shell structure; right side is the cage structure, ok. These are the cage actually. You can see these are the gold nanoparticle within a cage, correct.

On the other hand, this is actually core shell structure, ok. And as you can see here basically that you know the by making it core shell or nano cage structure, one can change the optical emission spectrum very easily. So, not only the same, but also different kind of structure and size can lead to different types of optical emission spectra.

All are because of this you know surface plasmon resonance or the interacting of interaction of these surface electrons to the alternative field of light magnetic and the electrical field of light, which is very-very you know very clear and understandable, and cannot can be explained in different ways.

So, that is why this you know interaction between the photon and surface plasmon. Surface plasmon cannot be produced by the smooth metallic surfaces, ok when it can come in contact with the air. Mainly because you know when the momentum life is different from the moment of the surface plasmon. Therefore, to cause a change in the momentum a thin layer of metal can be placed above these particles, ok. So, that is forget about this.

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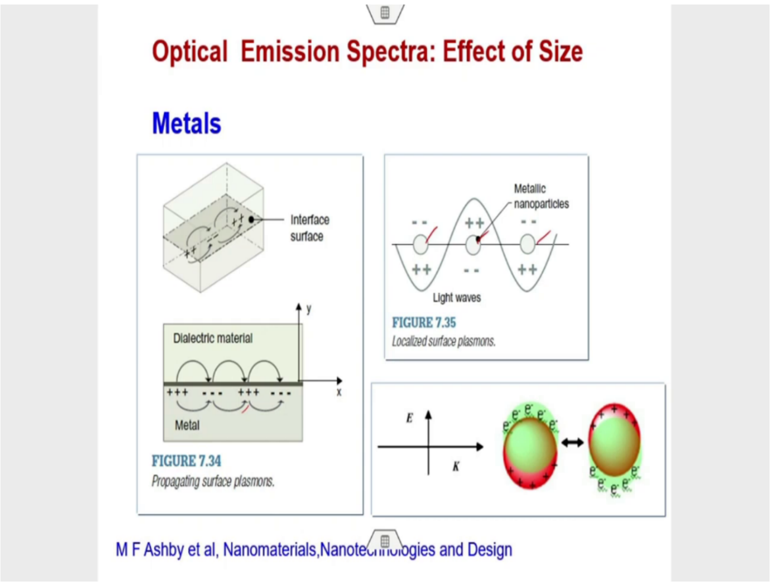

## Optical Emission Spectra: Effect of Size

### Metals

FIGURE 7.34
*Propagating surface plasmons.*

FIGURE 7.35
*Localized surface plasmons.*

M F Ashby et al, Nanomaterials,Nanotechnologies and Design

Another way of introducing, so that something which is shown here, ok. This is something will happen like this, you know how the surface plasmon actually propagates, correct. That is something, which we already discussed about it. However, you know another technique of introducing, inducing circular plasmon interaction is to roughen the surface, ok, by metal surface.

And this can be done in two ways, by creating a parallel linear features on the surface of the material or by randomly roughening the surface. Surface plasmon polar items can be used to cause external relatively transmission. And this is you know a phenomenon whereby metal thin films exhibiting a series of holes of surface specific size and periodicity can transmit more light at a certain energies than anticipated. That means, if you have holes series of holes in metal thin films, ok.

If you do that, these are the holes you see, ok. These are the different holes created here for the metal nanoparticles, and the thin films, you can do that. So, they can actually then transmit more into light than the other part of the thin film, ok. So, that is something which is can be; this basically you are creating a surface feature on the thin film. And this leads to the change of roughness of the material, correct.

So, this phenomenon is very widely used. Now, what is the reason behind that? Reason behind is basically resonance generated between incident light and the surface plasmon collateral in the incident side of the thin film. As you can understand by putting this metal nanoparticles, you can create alternative charges.

So, incident light can actually interact with these alternative charges and leads to formation of surface plasmons, ok. So, that means, we can create difference ways or different kinds of structures to induce surface plasmon. Not only the size, but also shape, geometry, roughness of surfaces can be altered to have optical emission from the metallic, ok.

So, if I have to put these things together, we discuss about semiconductors, optical emission, we discuss about metallic optical emission. A semiconductor metallic optical emission is pretty you know predominantly dictated by these electronic transitions from the valence the conduction band, and the recombination of these electrons and the hole, right. And this can be tuned simply by tuning the size.

And so, if you create different sizes of the semiconductor nanoparticles, like cadmium selenide, or lead selenide, or zinc sulphide, then you can see the whole spectrum of the electromagnetic light, the this whole you know visible spectrum by putting this size, different size particles into the solution, correct. And this can be used for various purposes, ok. Not only that, for not only the experimental things, but also technological aspects it can be used.

And second thing I discussed about this is a metal, ok. As you know many of these metals like, normal metals like gold, silver, copper, which has deep bands in the electronic structure field, they actually exhibit what is known as a surface plasmon resonance, ok.

And plasmons are nothing but a quantized you know waves which can propagate through material because of the collection of the electron, mobile electrons, ok. They are basically generated because of the interaction of the light with the electron leading to formation of the alternative charges on the surface of the nanoparticle.

And this, once this you know this charge is actually created on the surface of the nanoparticle, that is what we see, and these charges can lead to formation of the dipoles and the dipoles can oscillate in the electric field, the directional electric field of the light and this oscillation can lead to, this oscillation can be then you know can have resonance with the incident light at a certain wavelengths. And it can lead to huge emission. And that is what is known as SPR or surface plasmon resonance.

That is something, which is unique in metals. And, but this can be also alternatively created by making a roughness surface of the metal. This can be tuned by using different sizes of particle, different shapes of the particles, or different geometries, like cage structure, all these core shell structure can be done. That is very routinely done in the nano materials.

So, this I will conclude my discussions on the optical properties of materials, ok. And so, we have finished our 27 lectures. As you said that, I am going to wind up this course with 30 or 30, maximum 32 lectures or so. And you know this course is on both properties and the characterization of the nano materials.

So, I must spend about 5 lectures on nano, characterization nano materials. Characterization can be different types, ok. If I get some time, I will discuss about the carbon nanotubes and all these aspects, but that is may not be possible. If I take all the lectures, I wind up or rather I have to take more time to discuss about the characterization techniques.

With this, I stop the lectures today. I will get back to you with the next lecture on the Characterization of the Nanomaterials.

Thank you.