Materials Chemistry
Prof. S. Sundar Manoharan
Department of Chemistry
Indian Institute of Technology, Kanpur

Module - 6
Lecture - 3
Inorganic Phosphors I

In the last 3 lectures we have been looking at the photoluminescence properties in organic molecules. And we titled those lectures as the genie in molecule.

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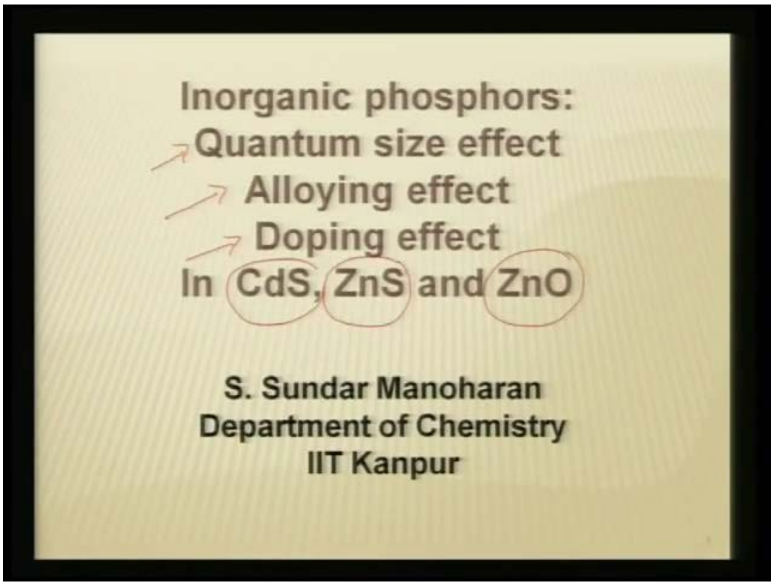

Inorganic phosphors:

Quantum size effect

Alloying effect

Doping effect

In CdS, ZnS and ZnO

S. Sundar Manoharan
Department of Chemistry
IIT Kanpur

When we look at the photonic applications not only the organic molecules have an edge over the inorganic phosphors, in terms of large area displays, in terms of economic viability. But, at the same time we cannot refuse the potential of the inorganic phosphors because in the last three decades the inorganic phosphors have controlled any sort of photonic displays, which has been in the market.

So, in today's lecture I am going to cover something about inorganic Phosphors, specially I would like to touch on three important issues, which has come to prominence in the last 5 to 10 years. One of the issue is of quantum size effect, which directly takes us to the issue of nano science and alloying effect in this phosphors, how do they effect the PL properties and then doping effect in these inorganic phosphors.

Notably, if we look at the market and the emerging trends and potential for applications, one would see that three compounds or choice phosphors, which can be used in a variety of environment, one is cadmium sulphide, zinc sulphide and zinc oxide these are emerging photonic materials. So, I am going to take you through a course of slides just to impress upon you, these three aspects and also tell why these phosphors still will hold the market. This is not to underplay the effect of inorganic phosphors, they are very established technology based compounds. But, nevertheless they will be competing with the organic molecules in the years to come.

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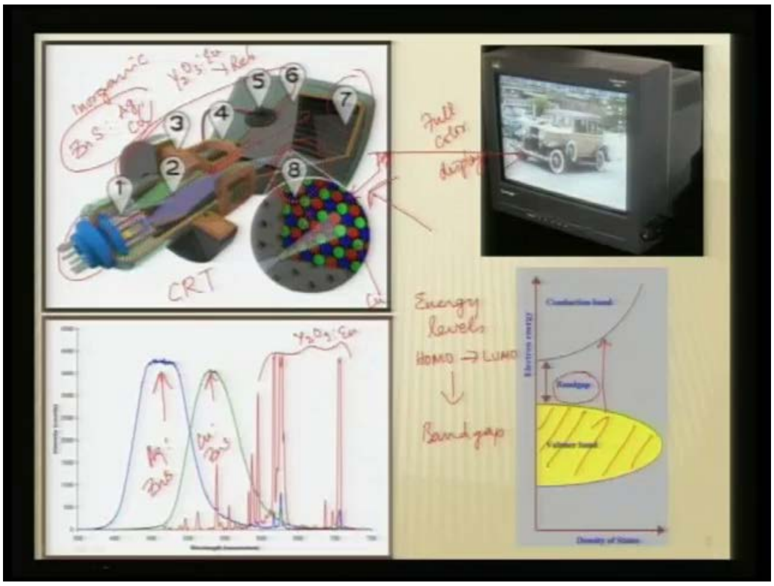

The first and foremost that we cannot deny the potential of this inorganic phosphors, is the application in a display material, what you see here is the CRT tube, Cathode Ray Tube. And in the cathode ray tube you have the cathode here and you have the anode here, anode is nothing, but your screen and this is typically how the old generation computers have performed. So, this is a typical CRT tube where cathode the electron gun goes from here all the way hitting here, I will not go into all these parts, because this a general description of a CRT tube.

But, quickly I want to take you to the item number 8 in this cartoon, 8 is nothing, but the florescent screen here glass, which is coated with the a graphitic layer a very thin graphitic layer. But, between the graphitic layer and the glass is coated the phosphors, and the phosphors are typically like this they are called triads of red, green and blue, red green and blue phosphors are coated in this fashion.

So, when you actually have the cathode ray going and hitting at this triads in different proportion, then you would get a continues image coming out of this screen. So, this is how a typical CRT works, but the issue of color is actually determined by inorganic phosphors and what are these phosphors, they are mainly zinc sulphide doped with the either silver or copper. If it is doped with copper, then you get the green color and if it is doped with the silver then you get the blue color, and yttrium oxide doped with europium is actually used for red.

So, you have the zinc sulphide based phosphors holding key for the CRT applications as you see, this is one of the very first TV's which came in picture, and this is a full color display. So, for full color display in our TV screens you essentially resort to inorganic phosphors, mainly those are zinc sulphide based ones and typically the spectrum is like this, you can see this is the silver doped Z n S, this is the copper doped Z n S and the these are the emissions coming from yttria or doped with the europium.

So, in essence all three phosphors together control the full color display in a typical CRT tube, and what is important here as I told you in the organic molecules we are talking about energy levels. And these energy levels are mostly to do with the HOMO to LUMO and the way the HOMO, LUMO spread and based on that you can tune the color this we have seen in the last three talks.

And in this lecture I would like to take you to the issue of band gap because in inorganic phosphors we are not talking about discrete energy levels, but we are talking about band gap. And this band gap essentially controls the sort of luminescence, as you know that valence band is always fully filled with electrons, and any absorption of radiation will put this electrons in the conduction band. And the way the electrons come back will determine how the combination recombination process occurs.

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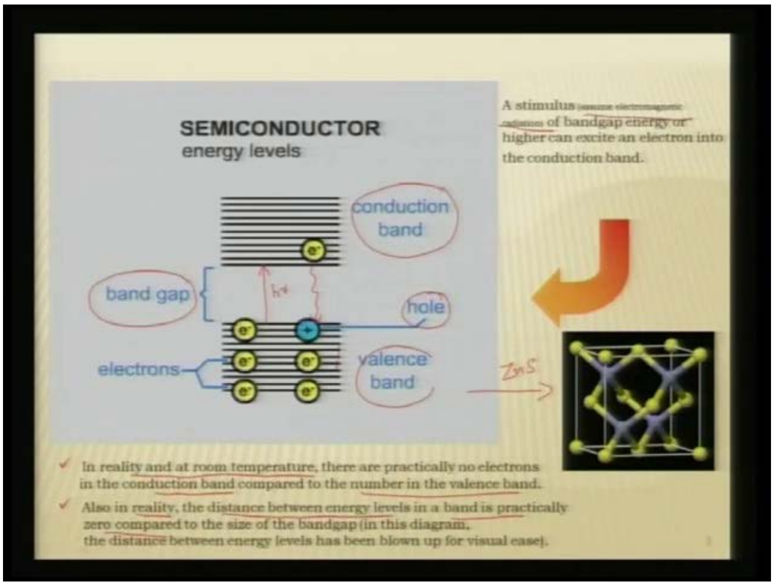

SEMICONDUCTOR
energy levels

A stimulus (assume electromagnetic radiation) of bandgap energy or higher can excite an electron into the conduction band.

- ✓ In reality and at room temperature, there are practically no electrons in the conduction band compared to the number in the valence band.
- ✓ Also in reality, the distance between energy levels in a band is practically zero compared to the size of the bandgap (in this diagram, the distance between energy levels has been blown up for visual ease).

Now, this is typically a semiconductor energy level that you see here these gap between these energy levels are exaggerated, just to make sure that we talk about this process with some clarity. Otherwise they are continues spread of this energy levels forming the valence band, and the conduction band. So, in reality and at room temperature there are practically no electrons in the conduction band compared to the number of electrons in the valence band, also in reality the distance between the energy levels in the band is practically 0, compare to the size of the band gap.

Now, what happens when you have a some light that is shining electrons can be ejected in the presence of light, and they can excite an electron into the conduction band as a result you get a hole. And there is a hole and a electron that is present in the valance band and conduction band, now this electrons cannot stay there it has to come back and that is what will control the emission process. And the band gap here, will control the recombination process and this is typical for all the semiconductors including zinc sulphide. So, this just to give you picture what is the photoluminescence, that we are talking about in this game.

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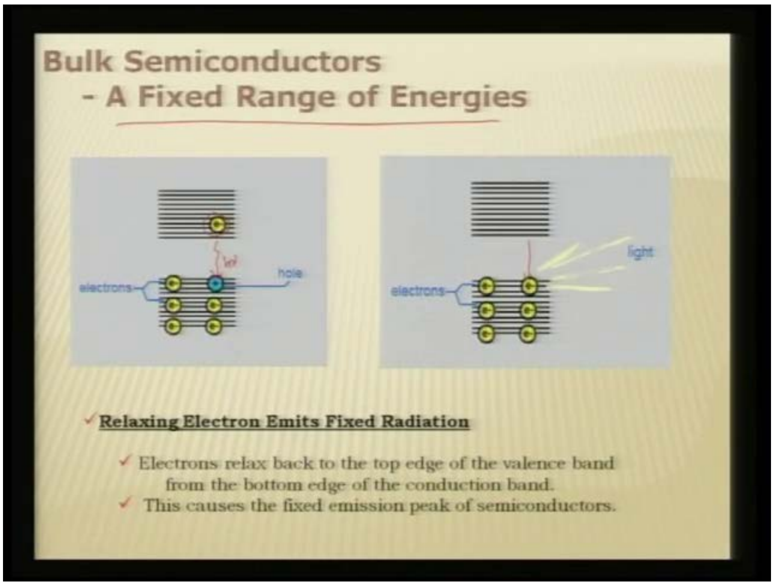

Bulk Semiconductors
- A Fixed Range of Energies

- ✓ **Relaxing Electron Emits Fixed Radiation**
  - ✓ Electrons relax back to the top edge of the valence band from the bottom edge of the conduction band.
  - ✓ This causes the fixed emission peak of semiconductors.

So, in bulk semiconductors we have a fixed range of energies we have hole, but the electron which has gone into the conduction band has to relax. So, the relaxing electron emits fixed radiation, so this has to come throwing out some light, so this causes a fixed emission peak of semiconductors. So, when the electron comes back then this is actually releases light and that is what we call it as phosphorescence or a florescence.

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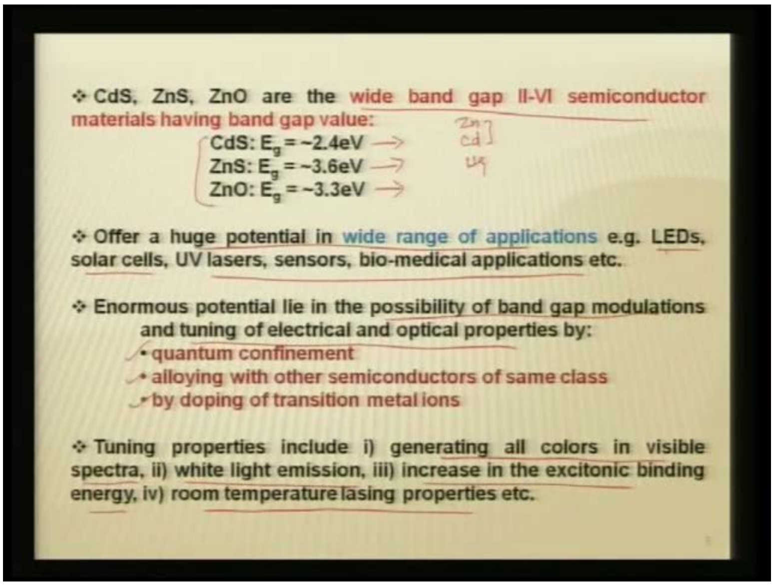

- ❖ CdS, ZnS, ZnO are the wide band gap II-VI semiconductor materials having band gap value:

  CdS: $E_g = \sim 2.4 eV$ →
  ZnS: $E_g = \sim 3.6 eV$ →
  ZnO: $E_g = \sim 3.3 eV$ →

  Zn
  Cd
  UV

- ❖ Offer a huge potential in wide range of applications e.g. LEDs, solar cells, UV lasers, sensors, bio-medical applications etc.
- ❖ Enormous potential lie in the possibility of band gap modulations and tuning of electrical and optical properties by:
  - quantum confinement
  - alloying with other semiconductors of same class
  - by doping of transition metal ions
- ❖ Tuning properties include i) generating all colors in visible spectra, ii) white light emission, iii) increase in the excitonic binding energy, iv) room temperature lasing properties etc.

Now, notably we can single out these three compounds which are of interest to us, cadmium sulphide is the low band gap semiconductor, and zinc sulphide is the wide band gap semiconductor. And in between these two zinc oxide also finds a interesting applications, so all this are classified as wide band gap 2, 6 semiconductor materials, so there are different possibilities that comes out because of the band gap one is we since zinc cadmium mercury they fall in the same group.

Now, we can think of cadmium zinc cadmium mercury, so we can think of solid solutions between zinc and cadmium as a result we can go for a new set of wide band gap semiconductors. Now, all this hold huge potential in wide range of applications as I already told LED’s, solar cell for back light purposes, most of this find very useful applications. And because of the possibility of tuning this band gap modulations, we can also tune the electrical and optical properties by means of quantum confinement or by alloying or by doping with the transition metal elements.

Tuning properties include generating all colors in visible, we can also produce white light emission, in this inorganic phosphors increase in excitonic binding energy and then room temperature lasing properties, all this can be realize in this group of compounds.

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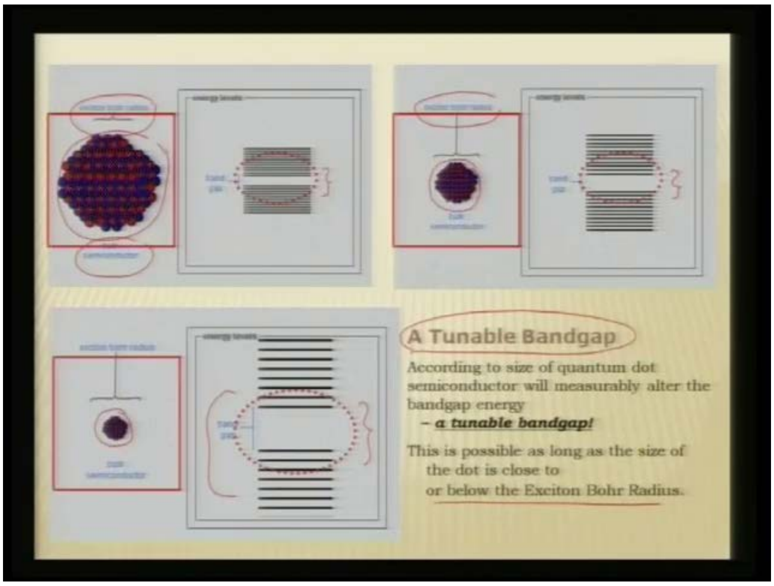

A Tunable Bandgap

According to size of quantum dot semiconductor will measurably alter the bandgap energy

– ***a tunable bandgap!***

This is possible as long as the size of the dot is close to or below the Exciton Bohr Radius.

So, if you control the size of your semiconductor particles which is actually equal or comparable to the exciton bohr radius, then depending on the size. Either it can be of this dimension or it can be less than even a exciton bohr radius or it can be much less than the exciton bohr radius, the bulk this is all in bulk semiconductor only. But, still if you can minimize on the size irrelative to the excitonic bohr radius, then you are actually manipulating or you are altering the band gap.

So, you if it is bulk and it is more than the bohr radius, the band gap changes are very minimal, in other words it could be as equal to the bulk value. But, if you make it comparable to bohr radius then you are opening a band gap considerably higher than what is found in bulk, But, if you go further down which is much less than the excitonic bohr radius, then you can see that you are opening up a band gap which is much, much bigger than what you see here.

So, what we are finally, ending up is a theme on tunable band gap according to the size of quantum dot semiconductor will measurably alter the band gap, which means a tunable band gap. This is possible as long as the size of the dot is close to or below the exciton bohr radius.

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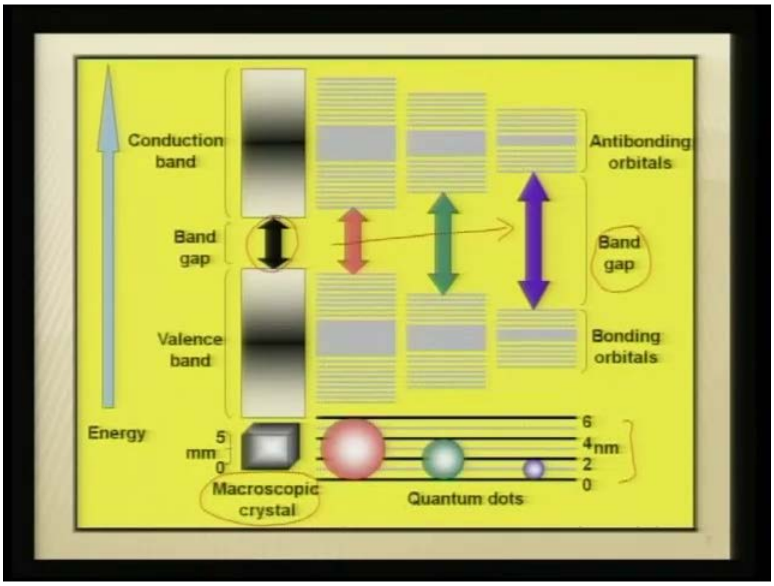

Now, this is the other picture just to drive home the point that you affect the band gap. So, this is a macroscopic crystal and this macroscopic crystal can be of the order of 05 millimeter, so such big crystal and the band gap is confined this way, now as you try to reduce this macroscopic crystal by some means. Either you can break it up or you can build it from the bottom to go to a optimum size, then you can see as you go down in the size say from 6 nanometer down to 2 nanometer, you are actually opening the band gap in this form.

As a result when the band gap is getting altered, you see the changes coming out both in optical properties, electronic properties as a result you can throw unique variety of applications or a variation in that properties, just by controlling the band gap. So, this becomes a challenge for both chemist as well as physicist, as to understand what is the correlation between the size and the properties.

So, in nano size or in quantum confinement you are throwing entirely a different gamete of properties, which are not true for the bulk materials.

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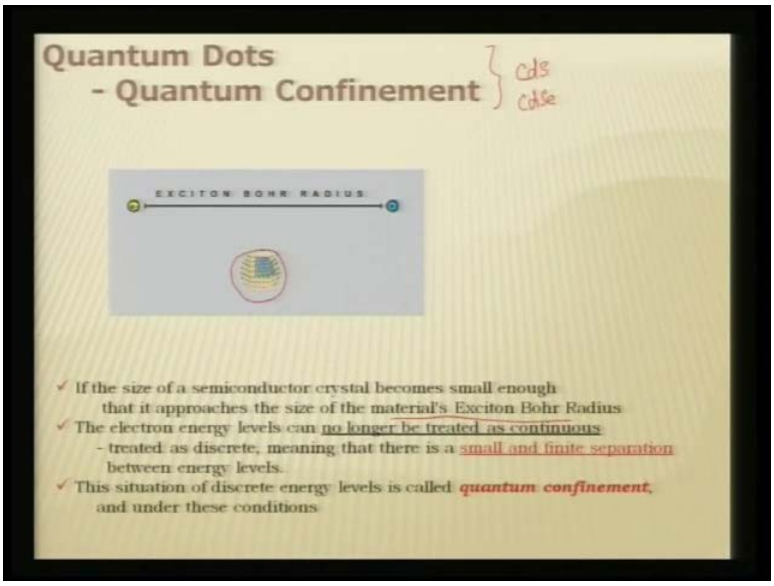

Quantum Dots
- Quantum Confinement } CdS CdSe

- ✓ If the size of a semiconductor crystal becomes small enough that it approaches the size of the material's Exciton Bohr Radius
- ✓ The electron energy levels can no longer be treated as continuous
  - treated as discrete, meaning that there is a small and finite separation between energy levels.
- ✓ This situation of discrete energy levels is called ***quantum confinement***, and under these conditions

So, in quantum dots which is another important issue specially with cadmium sulphide or cadmium selenide based compounds, you are talking about exciton bohr radius that is the distance between the electron and the hole. And this binding radius is what you call it is a exciton bohr radius, so this exciton bohr radius if it is like this and you are particle is much, much less than the exciton bohr radius. Then you are talking about a quantum confinement, if the size of a semiconductor crystal becomes small enough that is approaches the size of materials exciton bohr radius.

The electron energy levels can no longer be treated as continues, treated as discrete meaning that there is a small and finite separation. This situation of discrete energy levels is called the quantum confinement.

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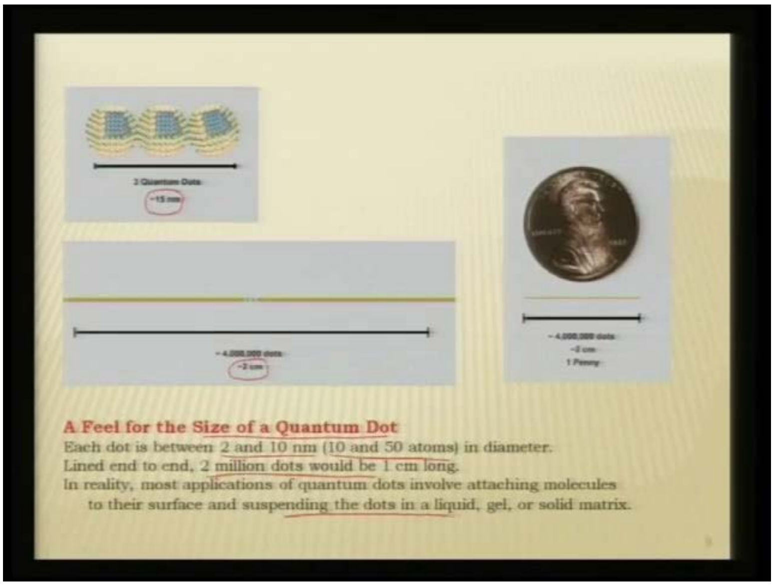

A Feel for the Size of a Quantum Dot

Each dot is between 2 and 10 nm (10 and 50 atoms) in diameter.

Lined end to end, 2 million dots would be 1 cm long.

In reality, most applications of quantum dots involve attaching molecules to their surface and suspending the dots in a liquid, gel, or solid matrix.

So, in quantum confinement what is that we are looking at, suppose you have three quantum dots then you are talking about 15 nanometer that is the size of range that we can simulate. If you are talking about several such quantum dotes to the order of say 40 lakhs or four thousands of thousand dots then such small array will only constitute to the order of 2 centimeters. So, so many quantum dots you can try to assemble in just two centimeters.

So, that is the quantum confinement that we can talk about a feel for the size of a quantum dot, each dot is between 2 and 10 nanometers or 10 to 50 atoms in diameter. Lined end to end 2 million dots would be one centimeter long, now this can come by suspending the dots in liquid gel or solid matrix. So, we can prepare it in many different ways.

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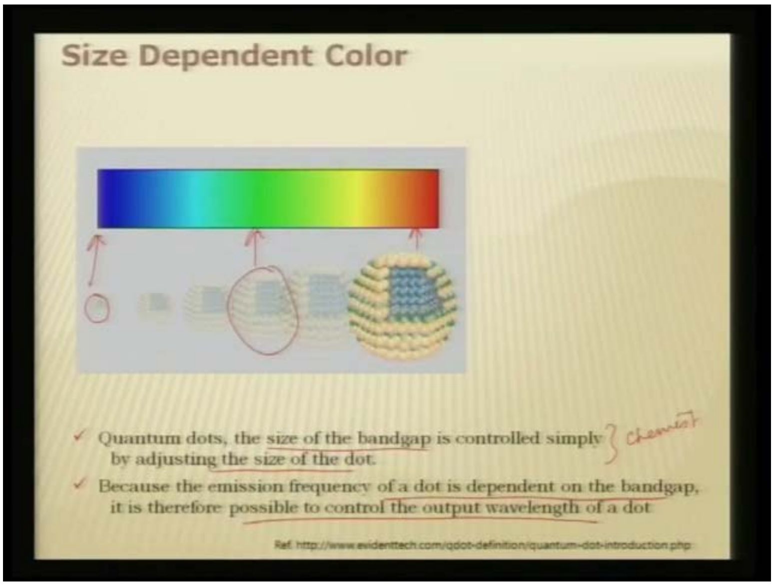

Size Dependent Color

- ✓ Quantum dots, the size of the bandgap is controlled simply by adjusting the size of the dot.
- ✓ Because the emission frequency of a dot is dependent on the bandgap, it is therefore possible to control the output wavelength of a dot

Chemist

Ref: http://www.evidenttech.com/qdot-definition/quantum-dot-introduction.php

So, the size dependent color also goes with the size as you see here, if the quantum dot is well below the excitonic bohr radius. Now; obviously, the color will be in blue, now if it is intermediate say around 10 nanometers are so you are talking something about green, and if it is beyond the excitonic bohr radius then you are talking about red emission. So, one single system, but if you are going to confine it in different ways, different sizes then you play round with the whole spectrum of emission.

So, quantum dots the size of the band gap is controlled simply by adjusting the dot, this becomes a challenge for chemist because chemist have n number of ways to produce this quantum dots. Typically the wet chemically routes and by which you can play around with the wide range of particles, which can affect the PL properties because the emission frequency of a dot is dependent on the band gap. Therefore, it is possible to control the output length of the dot.

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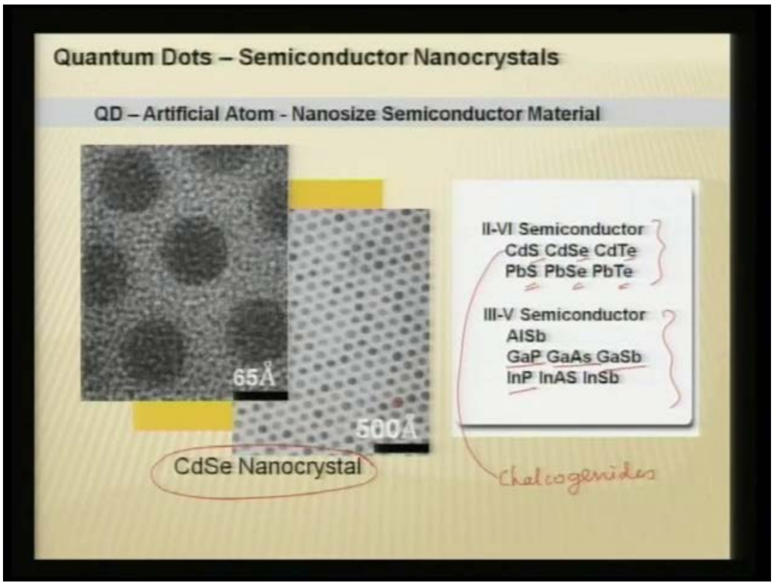

Quantum Dots – Semiconductor Nanocrystals

QD – Artificial Atom - Nanosize Semiconductor Material

II-VI Semiconductor
CdS CdSe CdTe
PbS PbSe PbTe

III-V Semiconductor
AlSb
GaP GaAs GaSb
InP InAS InSb

Chalcogenides

CdSe Nanocrystal

One of the classic example for such a quantum confinement is quantum dots, semiconductor nanocrystals and the notable once which are potential for this quantum confinement is cadmium sulphide selenide or telluride. This is also called as chalcogenides, chalcogenides are those which form compounds with sulfur, selenium and tellurium. So, cadmium base chalcogenides are a very candid material for quantum dot applications, so is led sulphide selenide and telluride.

And you also have this 3, 5 semiconductors like gallium phosphide, indium phosphide, gallium antimonide, gallium arsenide all these are essentially possible to be for quantum confinement. So, this is typically a viewgraph a TM picture of cadmium nano crystal, which can be prepared as you see here this is of the order of 15 nanometers, and each dot will be somewhere around 5 to 6 nanometers.

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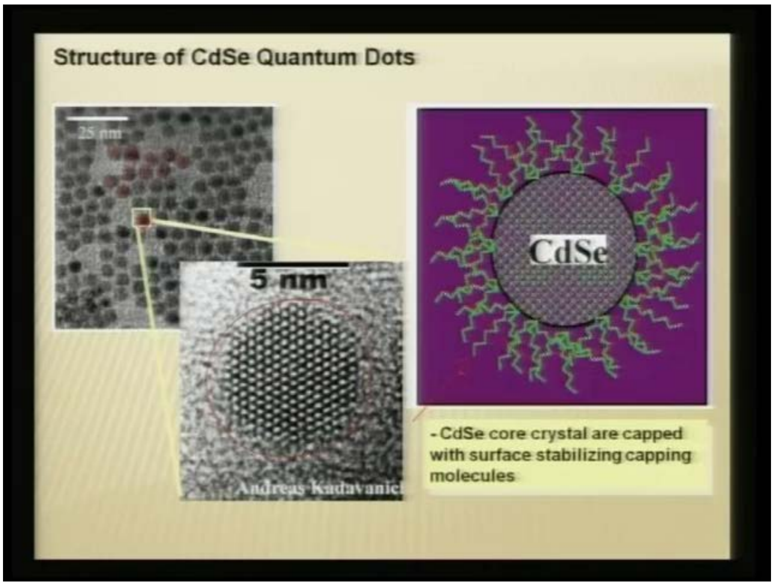

Structure of CdSe Quantum Dots

- CdSe core crystal are capped with surface stabilizing capping molecules

Structure of this cadmium sulphide quantum nano dots you can see in a matrix you can see how the a quantum dots can be arrange, if you just take a high resolution TM image of one of this crystal. Then you can see that this is clearly shows a well ordered quantum dot structure, and this quantum dots can be kept with surface stabilizing capping molecules. So, if you want to preserve this cadmium sulphide for specific applications the way that you can preserve it from getting agglomerated with another quantum dot is to cap it.

So, these are all the capping a molecules, so this capping molecules can actually isolate every single quantum dot from the other, in other words you can actually separate it out like this. So, each of this is a quantum dot in one sense because they are all kept with a capping molecule of this architecture. So, this is one way that you can keep it and most of these cadmium selenides are not isolated as solid products, they are actually as suspensions or collides. So, if you want to coat it you can actually take a collide or a suspension and a spin coat it you get a quantum dot.

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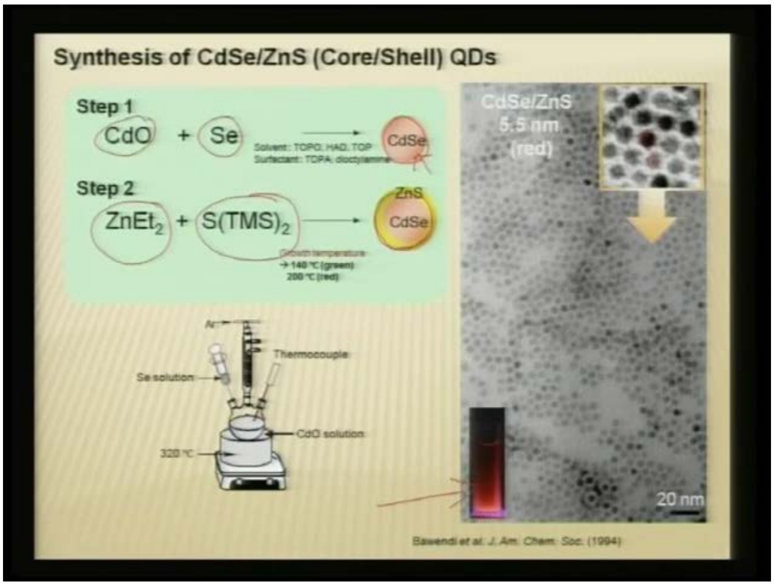

Synthesis of CdSe/ZnS (Core/Shell) QDs

Step 1

$CdO + Se \rightarrow CdSe$

Solvent: TOPO, HAD, TOP

Surfactant: TOPA, dioctylamine

Step 2

$ZnEt_2 + S(TMS)_2 \rightarrow$ ZnS/CdSe

Growth temperature

→ 140 °C (green)

200 °C (red)

Bawendi et al. J. Am. Chem. Soc. (1994)

So, that is the way to do it and typically in chemistry way you can make this quantum dots by a simple chemistry routes, you can take a cadmium oxide solution. And then you can put selenium solution seliniting agents, and if you can do it in argon atmosphere, cadmium oxide plus selenium will give you cadmium selenide quantum dots or if you want to cap this cadmium selenide, with zinc sulphide all you need to do is in situ as your generating cadmium sulphide, you will try to put zincating molecules and this is a sulfur source. So, you can actually try to coat this cadmium selenide with zinc sulphide.

So, this is another way which you call this is cadmium selenide core shell quantum dots, and typically you can see that this quantum dots are of the size. And it is well spread you can try to isolate it as a collide as a suspension, and the PL of such a compound shows a very strong red emission. So, this is reported by bawendi’s group.

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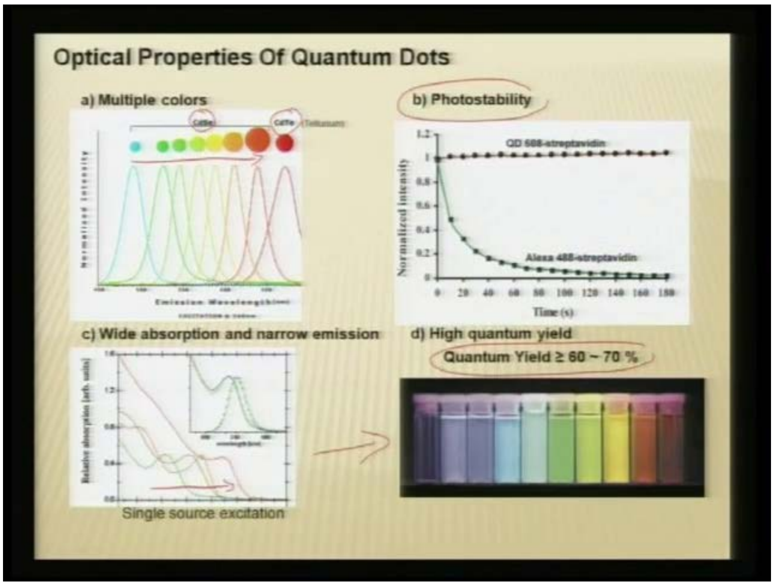

Optical Properties Of Quantum Dots

a) Multiple colors

b) Photostability

c) Wide absorption and narrow emission

d) High quantum yield

Quantum Yield ≥ 60 ~ 70 %

Single source excitation

So, several such molecules are possible, optical properties of this quantum dots you can fine tune like anything. So, if you talk about cadmium selenide, the candidates are mainly from blue to red, but if you want sharp red color then you can go for cadmium telluride. And you can see here that the band gap also changes, with the size or with the chalcogenides that you are talking about and because of that you can actually generate a widespread of PL emission, controlling the particle size.

And in most cases you see the absolute quantum yield is that of 60 to 70 percent. So, such highly luminousing suspensions of quantum dots can be acquired, and we can play around with several such systems, not only cadmium selenide, cadmium sulphide you can also play around with zinc sulphide base compounds.

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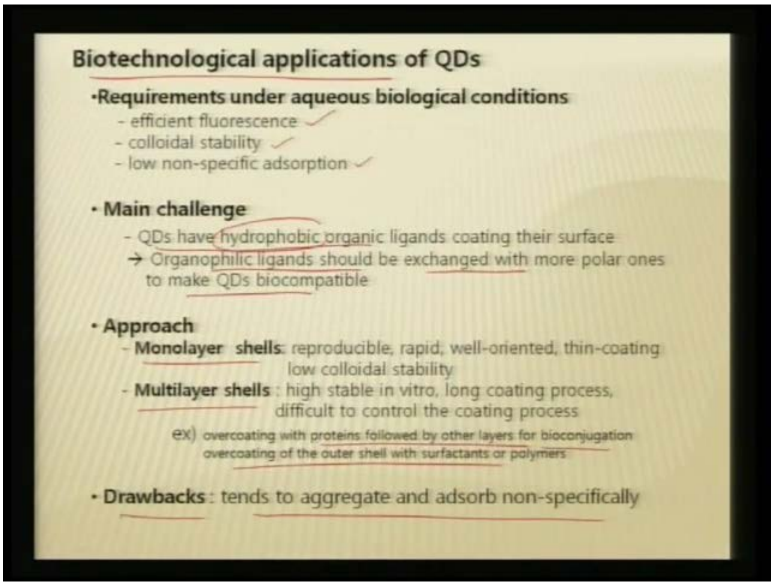

Biotechnological applications of QDs

- **Requirements under aqueous biological conditions**
  - efficient fluorescence ✓
  - colloidal stability ✓
  - low non-specific adsorption ✓

- **Main challenge**
  - QDs have hydrophobic organic ligands coating their surface

  → Organophilic ligands should be exchanged with more polar ones to make QDs biocompatible

- **Approach**
  - **Monolayer shells**: reproducible, rapid, well-oriented, thin-coating
    low colloidal stability
  - **Multilayer shells** : high stable in vitro, long coating process,
    difficult to control the coating process

    ex) overcoating with proteins followed by other layers for bioconjugation
    overcoating of the outer shell with surfactants or polymers

- **Drawbacks** : tends to aggregate and adsorb non-specifically

Now, the one of the prime application of this quantum dots is in the biotechnological applications, what are the requirements for bio applications one it is it should be efficient fluorescence, colloidal stability should be there and it should have low non specific absorption. So, if all three are taken care you can use this quantum dots specifically for biological applications, main challenge is when you try to surface coat with organic compounds. Then the surface becomes hydrophobic therefore, if you want to tag it with some other molecule, this hydrophobic nature will be reluctant to merge with another one.

Therefore, you need to do a another surface modification, so that you can tag it along. Organophilic ligands should be exchanged with more polar ones to make quantum dots biocompatible that way. You can actually make a monolayer shells or multilayer shells, and over coating with proteins followed by other layers of bio conjugation can also be achieved. in order to enhance the application prospects. Drawbacks tends to aggregate and absorb non specifically, specially when you try to play down on the surfactant then the issue of agglomeration comes into picture.

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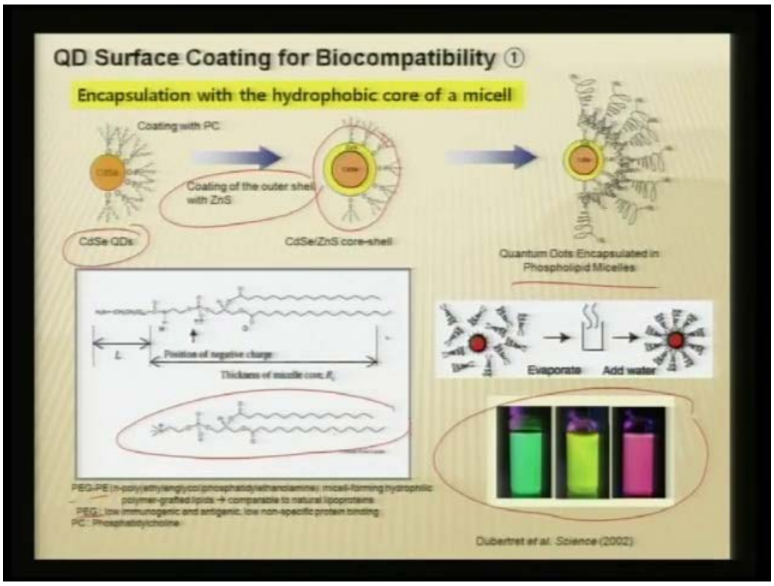

QD Surface Coating for Biocompatibility ①

Encapsulation with the hydrophobic core of a micell

PEG-PE (n-poly(ethylenglycol)phosphatidylethanolamine): micell-forming hydrophilic polymer-grafted lipids → comparable to natural lipoproteins

PEG : low immunogenic and antigenic, low non-specific protein binding

PC : Phosphatidylcholine

Dubertret et al. Science (2002)

So, quantum dots surface coating for bio biocompatibility usually goes through this, you can actually have this coating with the cadmium sulphide quantum dots, you can coat the outer shell with zinc sulphide. And then you can have the capping agent, so essentially this is one way encapsulating this with the hydrophobic core of a micelle, and these quantum dots are encapsulated with the phospholipid micelles. And depending on the range and the architecture of your core shell, then you can see different tag ends can be generated.

So, this is one way that you can increase the biocompatibility, and mainly the carrier that you would like to tag this compounds with are the PEG, PE or PEG these are polyethylene glycols. Because, these are biocompatible and they would form a micelle of these shells, so it is very easy then to drive it into the biological system.

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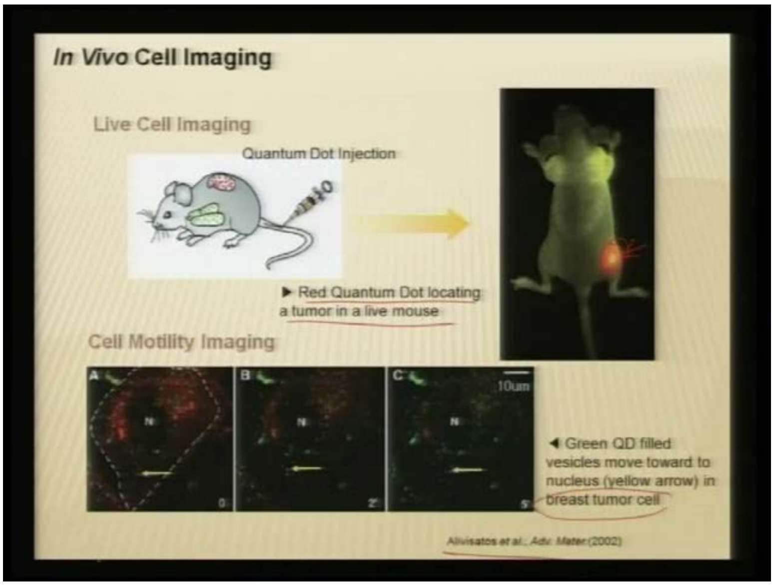

In Vivo Cell Imaging

Live Cell Imaging

Quantum Dot Injection

▶ Red Quantum Dot locating a tumor in a live mouse

Cell Motility Imaging

◀ Green QD filled vesicles move toward to nucleus (yellow arrow) in breast tumor cell

Alivisatos et al., Adv. Mater (2002)

Just to give a example whether this can be used in safe way, in vivo cell has cell imaging has been done, using this quantum dots for example, if you can take a live rat and or a mouse red quantum dot can be injected, which will go and target that tumor zone. So, it is possible to see, where the cancerous cells are, so it you can use this quantum dots in vivo to predict the malignancy. Also quantum dots can be use for breast tumors cells, here we have a green quantum dots filled vesicles which they move towards the nuclease to spot the areas where, breast tumor cells can be located. This was proved by alivisatos as early as 2002, since then these in vivo studies on quantum dots have been of a active interest.

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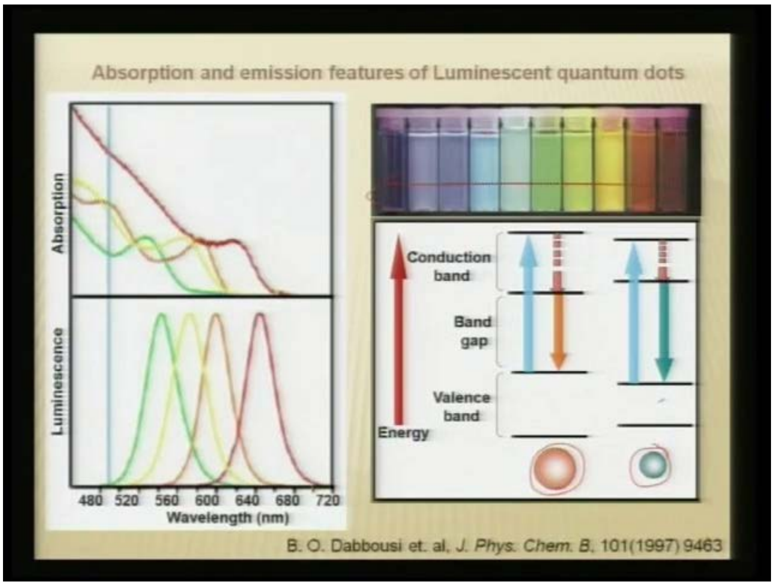

Absorption and emission features of Luminescent quantum dots

B. O. Dabbousi et. al, *J. Phys. Chem. B*, 101(1997) 9463

So, you can actually now play with any sort of compounds and all it needs it is a quantum confinement. So, you can actually modulate the band gap by moderating the size you can get a wide spectrum of colors, and the colors are also very specific, so if you want any combination you can go for such specific colors using quantum confinement.

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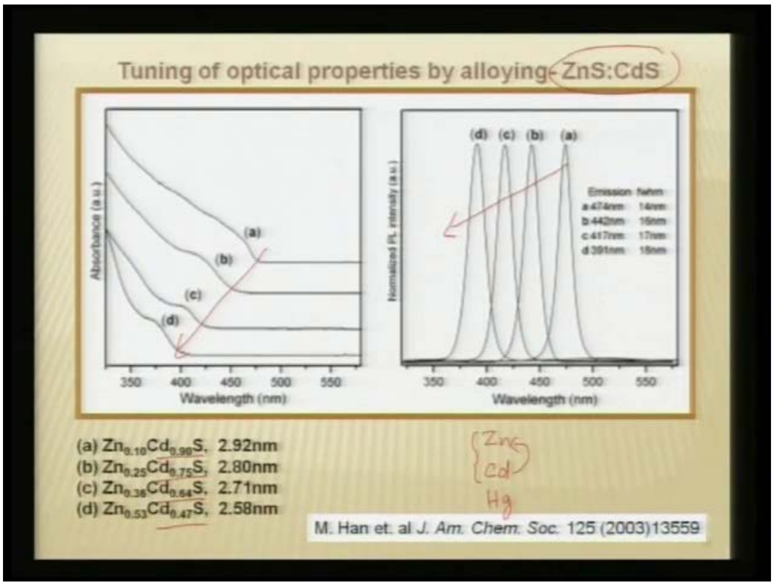

Tuning of optical properties by alloying ZnS:CdS

(a) $Zn_{0.10}Cd_{0.90}S$, 2.92nm
(b) $Zn_{0.25}Cd_{0.75}S$, 2.80nm
(c) $Zn_{0.36}Cd_{0.64}S$, 2.71nm
(d) $Zn_{0.53}Cd_{0.47}S$, 2.58nm

Zn
Cd
Hg

M. Han et. al *J. Am. Chem. Soc.* 125 (2003)13559

Now, another example of alloying that we have seen in the literature is that of zinc sulphide, cadmium sulphide this is not the quantum confinement issue, but this is another issue in phosphorescence that is alloying. So, you take zinc sulphide you put a low band gap suphide there what really happens, you can see here as you are doping the cadmium sulphide a is cadmium more. And as you decrease the cadmium content, you see that the absorption is going towards the blue color, and typically your emission also goes from red to blue.

So, from green to blue, so you clearly see with addition of cadmium 0.9 or 0.75, 0.64, 0.5 again you can see that the absorption edges changes, and it directly affects the photoluminescence. So, this is one way of a trying to tune the band gap and we call this alloying because zinc and cadmium they are in the same group and therefore, they are structurally similar, they crystallize in the same symmetry. And it is possible for you to keep on loading cadmium into zinc sites, so this is one way of alloying the phosphor.

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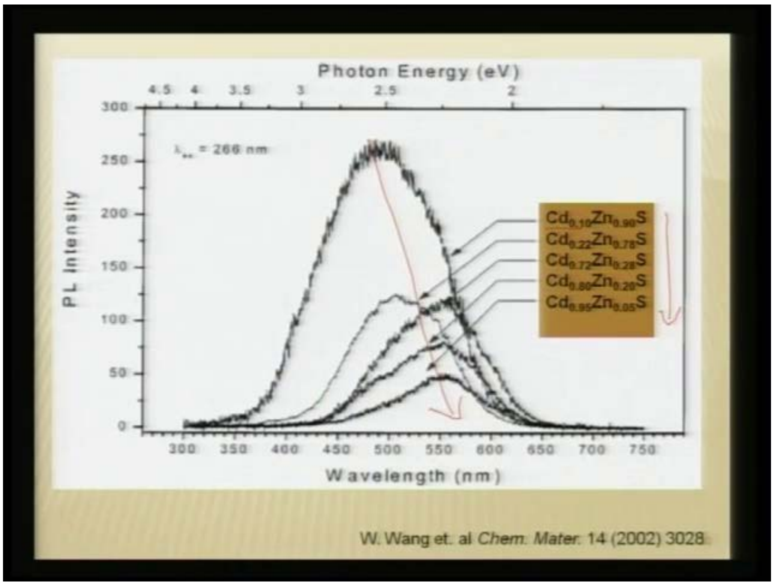

W. Wang et. al *Chem. Mater.* 14 (2002) 3028

This is another view graph that shows suppose you have cadmium instead of zinc, and you keep adding zinc what really happens. So, as you decrease the zinc content from 90 percent to 5 percent, you can clearly see that the PL intensity varies and also the maxima keep shifting from here to here, the maxima shifts to lower side as you keep doping in with more and more of zinc compounds. So, either way you can do reverse engineering, either you can try to blue shift it or red shift it depending on the size of the atom.

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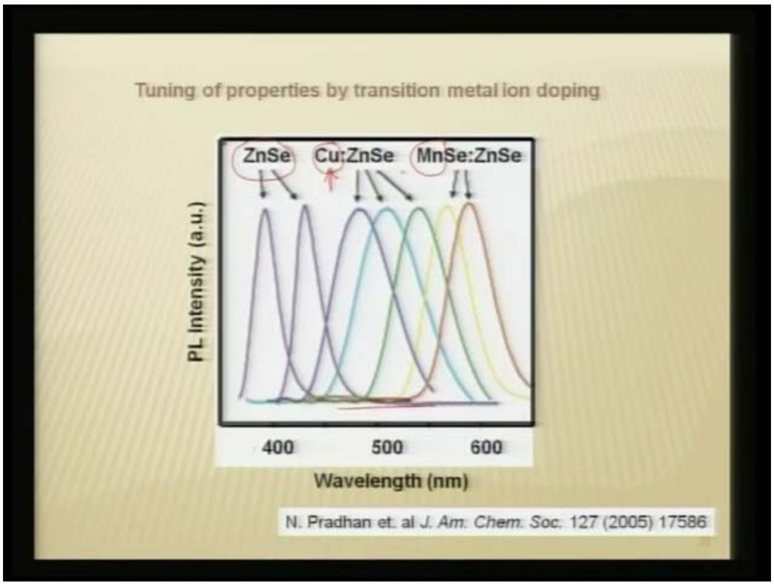

Tuning of properties by transition metal ion doping

N. Pradhan et. al *J. Am. Chem. Soc.* 127 (2005) 17586

And such tuning is possible, we can also tune the properties by going for metal ion substitutions for example, if you take zinc selenide, it shows emission in near blue region. So, if you start doping with transition metals these are all activators in this band gap, so depending on the nature of the transition metal that you doping, you can get specific colors. You can play around between 400 to 550 nanometer, if you are doping with copper, and specifically if I am interested in red then I would go for manganese doping. So, just by doping a particular transition metal you can actually play around with the color coordinates, and this was proposed as early as 2005 by pradhan and co workers.

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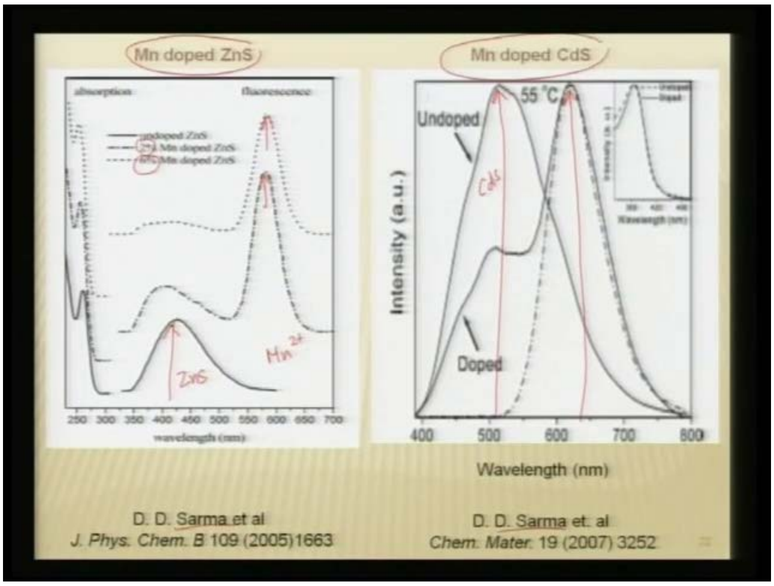

Mn doped ZnS

Mn doped CdS

D. D. Sarma et al
J. Phys. Chem. B 109 (2005)1663

D. D. Sarma et. al
Chem. Mater. 19 (2007) 3252

And another important thing is the photoluminescence is very sensitive to the crystal field environment, and as a result even if you are going dope just 2 percent of manganese or 6 percent of manganese. You can tune the band gap considerably D. D sarmas group, have reported quite a bit on this where, you dope manganese in zinc sulphide or doped manganese in cadmium sulphide, you can clearly see with this is the undoped zinc sulphide PL emission, which is centered around 450 nano metes or, so.

The moment you try to dope manganese, then you see the shift is more towards 600 and this is peculiar for M n 2 plus crystal field site. And therefore, you even with 1 or 2, 3 percent you can immediately shift the PL emission, same is true for manganese doped cadmium sulphide, this is the un doped PL of cadmium sulphide the moment you put manganese you can shift it to red region. So, manganese is very specific to this semiconductors.

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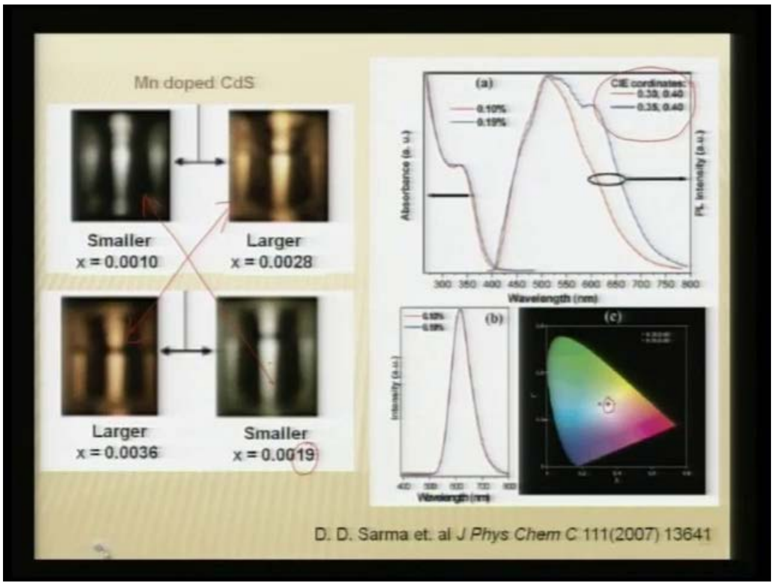

Mn doped CdS

D. D. Sarma et. al *J Phys Chem C* 111(2007) 13641

So, you can tune the band with minimum quantity of manganese doping, and this is what happens in both these cases you can see, when you have smaller ratios say 0.10 percent, 0.19 percent you can clearly change the PL compared to larger doping concentration. So, even with small amount of manganese we can fine tune, and in this case you can see each of this colors are specific to the CIE coordinates. So, if you want something near to white, you can see here for 0.10 percent or 0.19 percent, you can clearly get nearly white light emitting cadmium sulphide nano particles.

So, this is one way that we can tune the color.

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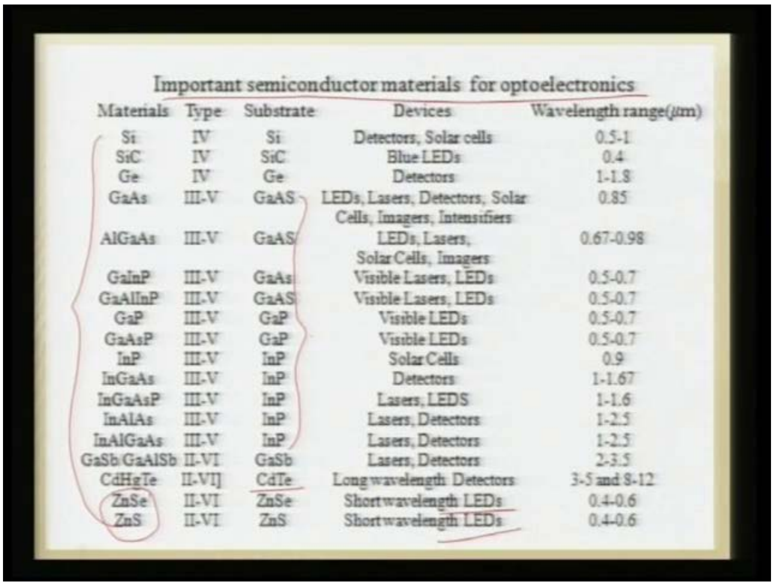

Important semiconductor materials for optoelectronics

Materials	Type	Substrate	Devices	Wavelength range(μm)
Si	IV	Si	Detectors, Solar cells	0.5-1
SiC	IV	SiC	Blue LEDs	0.4
Ge	IV	Ge	Detectors	1-1.8
GaAs	III-V	GaAS	LEDs, Lasers, Detectors, Solar Cells, Imagers, Intensifiers	0.85
AlGaAs	III-V	GaAS	LEDs, Lasers, Solar Cells, Imagers	0.67-0.98
GaInP	III-V	GaAs	Visible Lasers, LEDs	0.5-0.7
GaAlInP	III-V	GaAS	Visible Lasers, LEDs	0.5-0.7
GaP	III-V	GaP	Visible LEDs	0.5-0.7
GaAsP	III-V	GaP	Visible LEDs	0.5-0.7
InP	III-V	InP	Solar Cells	0.9
InGaAs	III-V	InP	Detectors	1-1.67
InGaAsP	III-V	InP	Lasers, LEDS	1-1.6
InAlAs	III-V	InP	Lasers, Detectors	1-2.5
InAlGaAs	III-V	InP	Lasers, Detectors	1-2.5
GaSb/GaAlSb	II-VI	GaSb	Lasers, Detectors	2-3.5
CdHgTe	II-VI]	CdTe	Long wavelength Detectors	3-5 and 8-12
ZnSe	II-VI	ZnSe	Short wavelength LEDs	0.4-0.6
ZnS	II-VI	ZnS	Short wavelength LEDs	0.4-0.6

Just before I go to specific examples from our own work I would like to list some of the important semiconductors which are already in market, there is a established technology already for the semiconductors. And these are the list of materials that we can see, which is already used in our optoelectronic applications for examples, we are talking now about zinc sulphide zinc selenide they are already in LED’s which they are used in the LED’s. And you also have cadmium telluride used in detectors, mostly you can see the gallium based, indium based ones which are traditionally used.

And this is one of the reason why organic molecules are challenging because these are very expensive routes to make LED’s. So, if you can use a rugged organic molecule for both large area displays, as well as for minimizing on the threshold voltage, then you can actually bring down the cost of this LED’s by orders of magnitude. So, this is one of the reason why organic displays are more prominent in today’s application.

But, nevertheless these are proven technology where the chemistry or the physics of the semiconductors are already understood. So, with this in view let me go to some of the examples from our own group, just to show that how the chemical routes can actually modify the sizes and depending on the size how the PL can vary.

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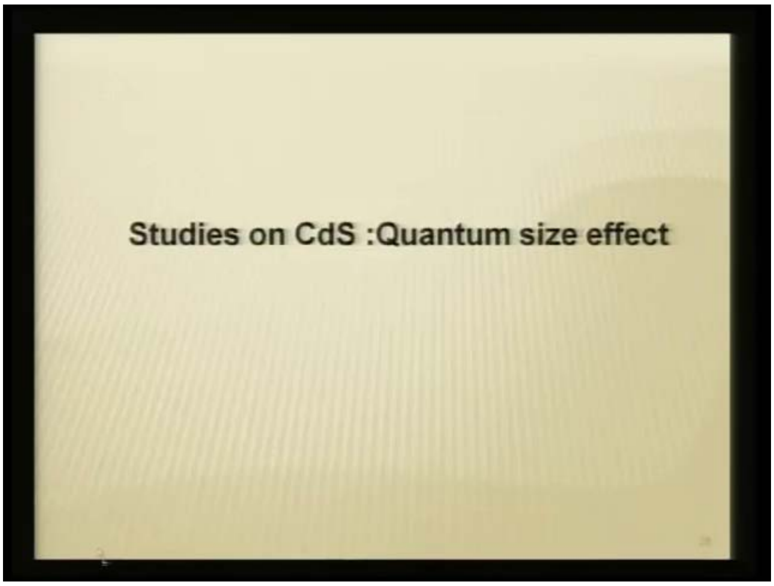

Studies on CdS :Quantum size effect

So, just one example on the quantum size effect.

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Sono-chemical Synthesis

$(CH_3COO)_2Cd + S \xrightarrow[Ar/H_2,\ 3hrs.]{DMSO\ )))))} CdS$

Li et al *J. Solid State Chem.* 172 (2003) 102

How we can make this sort of quantum dots without capping because once you cap it then you try to modify or you try to restrict the applications, you cannot use it as it is. So, one of the main thrust is to prepare uncapped cadmium sulphide, one of the way you can do that is using sono chemical synthesis. The principal of sono chemical synthesis I have already discussed in the first module on preparation.

Therefore, the simplest way to work on it is take a cadmium acetate, and a elemental sulfur in DMSO you can just sonicate it for 3 to 5 hours. You can get well dispersed cadmium sulphide and nano particles, how do we know that we have nano particles we can look at the properties.

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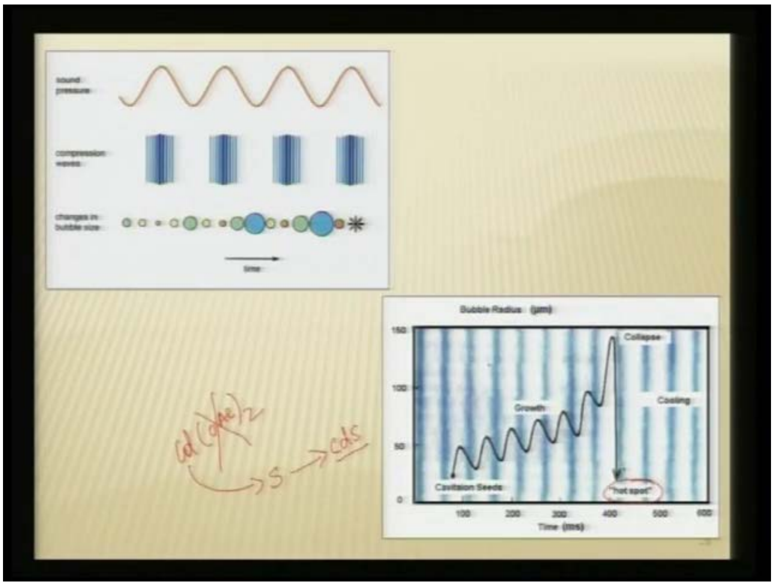

And how we can achieve this nano particles by simple cavitation technique, and this cavitation will break into a hotspot, and this hotspot will essentially will try to take out the organic moiety, it will sort of clear the organic moiety. And then it will release reactive cadmium, and this will react with your sulfur and from cadmium sulfur nano particles. So, this is a simple way one of the reason why we can resort to sono chemicals stuff is you do not have any side products that will affect, the cadmium sulphide nano particles, everything will go into the solution therefore, you can easily preserve it.

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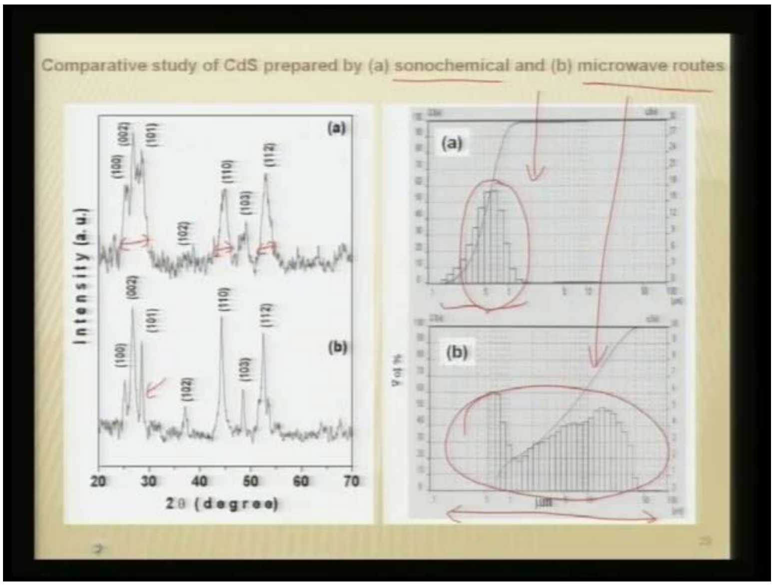

Comparative study of CdS prepared by (a) sonochemical and (b) microwave routes

A just to give a comparison between the properties of a cadmium sulphide prepared by two different methods for example, you can prepare it by microwave, where you take cadmium acetate and sulfur elemental sulfur expose it to microwave, you will get cadmium sulphide. You can also use it you sono chemistry to prepare, and just to give you a idea how they look, the particle size distribution of the sono chemically prepared one. Clearly shows the average agglomerate size is well below one micron whereas, in the microwave reaction you see a spread like this.

So, if you are actually looking for specific application it is not possible to use a cadmium sulphide particle, which has such a wide range you need to have a nano range. And in such cases you can see that the sono chemical approach is very selective, one of the way you can also answer this question whether it is nano or not or whether it is below 10 nanometers is from the broadening of the peak. You can see the x ray broadening of this peak, clearly suggests that they are in the nano range. Although this is also in nano range, but still it is much narrower compared to sono chemically prepared compound.

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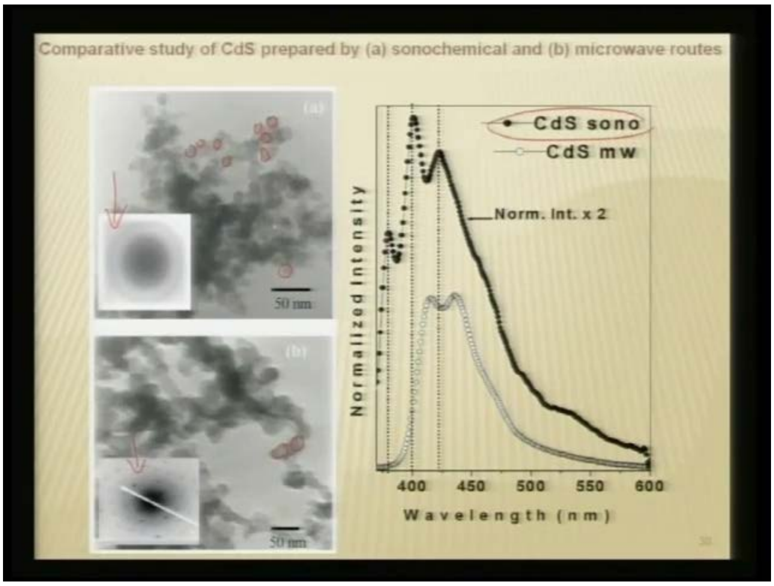

Comparative study of CdS prepared by (a) sonochemical and (b) microwave routes

And typically, if you look at the TM pictures you can see the clearly the variation, this is clearly in the amorphous range because you are electron diffraction pattern of cadmium sulphide, shows a blurred pattern which means it is amorphous. But, this one is crystalline the one prepared by microwave is crystalline, it gives a dark pattern and the size of the clusters are well below 10 nanometers. So, each of this are particles and if you look at this they are below 10 nanometers whereas, this is roughly around 20 to 30 nanometers.

So, depending on the preparative route you can actually prepare a wide size of range, and these ones although they are agglomerate you can see specifically they are individual particles, just fuse together without any capping that is important. And once we prepare a particles less than 10 nanometer, you can also see that they are blue shifted, so you can see there’s blue shift for cadmium sulphide, compare to the microwave prepared cadmium sulphide particle. So, another example of how we can modify this compounds by chemical route.

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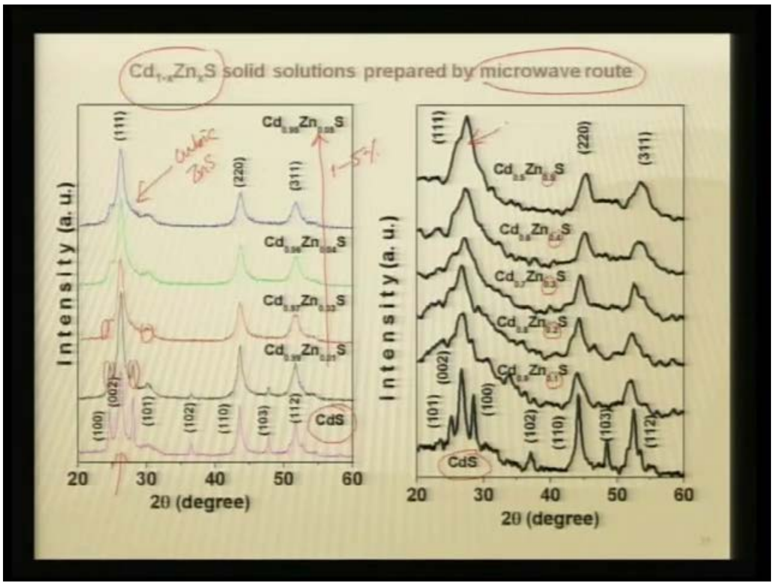

$Cd_{1-x}Zn_xS$ solid solutions prepared by microwave route

Let us take the microwave route and take specific example of cadmium sulphide which is doped with zinc. So, cadmiums if you keep on increasing from say, 1 to 5 percent of zinc you can clearly say even with the such low doping concentration, this is your cadmium sulphide typical hexagonal structure. And once you start doping with zinc, you can see that these x ray peaks are slowly coming down, and they fade and immediately transforms into a cubic phase which is typical of zinc sulphide.

So, from a hexagonal to a cubic pattern you can just simply transform in just with less than 5 percent of zinc doping. So, the fact that it affects the crystal structure, clearly shows that you can engineer this compound you can make solid solutions. Similarly, we do not have to confine just with the lower doping concentration of zinc, we can go 10 percent, 20 percent 30, 40 and 50 percent. You can clearly see compare to your parent cadmium sulphide, you can almost make amorphous or weakly crystalline zinc sulphide based cubic pattern, So, definitely using chemical routes we can successfully doped.

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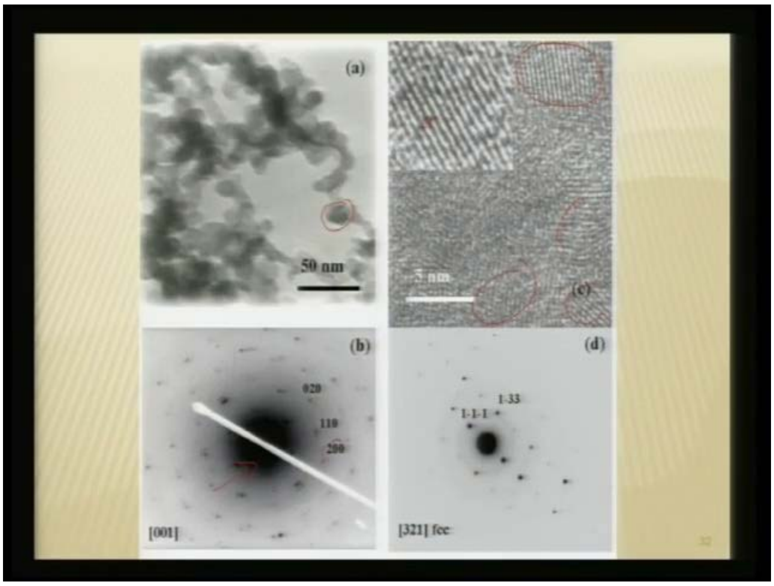

And this is the viewgraph of how the zinc sulphide, doped cadmium sulphide nano particles are and you can clearly see that these are all the embedded particles. And they clearly shows the crystallinity, and the lattice planer spacing’s are specific to the zinc concentration. And this is your SAD pattern showing that these are crystalline, and we can index that to specific planes.

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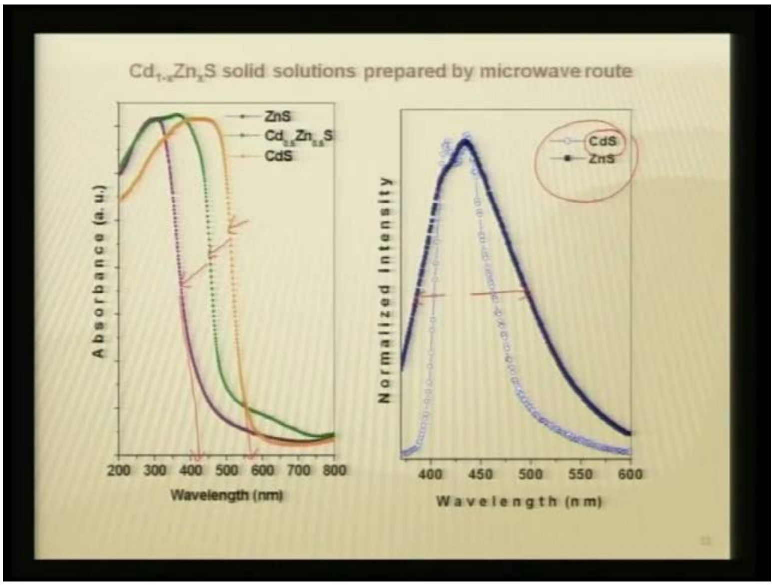
$Cd_{1-x}Zn_xS$ solid solutions prepared by microwave route

Now, when we look at the absorption spectra and the PL spectra, one can clearly understand how we can alloy this compound. And if alloying is rally true, then it has to show in the optical bandage, cadmium sulphide as I told you is low band gap material compared to zinc sulphide. So, if you actually dope cadmium sulphide with zinc, immediately you will see the shift in the absorption H, so typically you can see say from 550 it comes down to nearly 420 nanometers.

So, this is one way that you can understand whether your chemical doping or chemical process is really useful for fine tuning, your band gap and if that is, so then your PL spectra should also show changes. And you can see here zinc sulphide shows very large band width mainly because it is turning more amorphous, and it is a cubic in pattern and because of that you have a very broad PL emission, compared to cadmium sulphide. So, any sort of zinc incorporation will widen your PL emission, and this is noted in the emission spectra.

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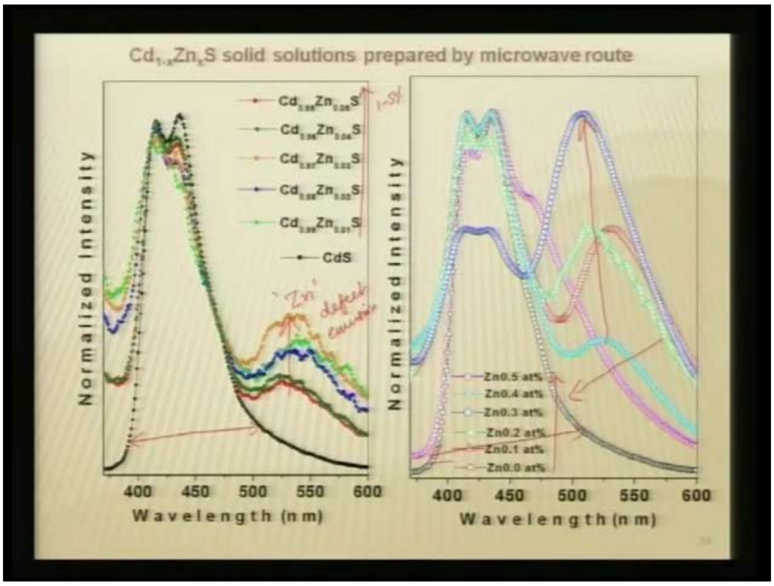

$Cd_{1-x}Zn_xS$ solid solutions prepared by microwave route

Now, we can also try to see how the zinc doping really affects, so you take the cadmium sulphide case, and start doping it with zinc. You can see as you go from 1 to 5 percent of zinc doping, you can notice that there is a peak that is propping up from zinc doped once, say around 550 nanometers, and this is typical for the influence of zinc on cadmium sulphide. So, this is your cadmium sulphide emission, and once you start doping with zinc you see this hump coming and this is mainly coming from defect emission.

Because, in zinc sulphide if you are sulfur concentration is less, then immediately it will induce a defect concentration. So, zinc seems to be more sensitive to sulfur deficiency or sulfur defects compare to cadmium sulphide, so this is one thing that you can note and also as you go further from 0 to 50 percent, you can see that the PL is shifting towards blue. And these defect induce concentrations or emission is more pronounced, as you keep on doping higher amount of zinc, and once you go more towards cadmium sulphide you can see that you almost get a defect free emission that is possible.

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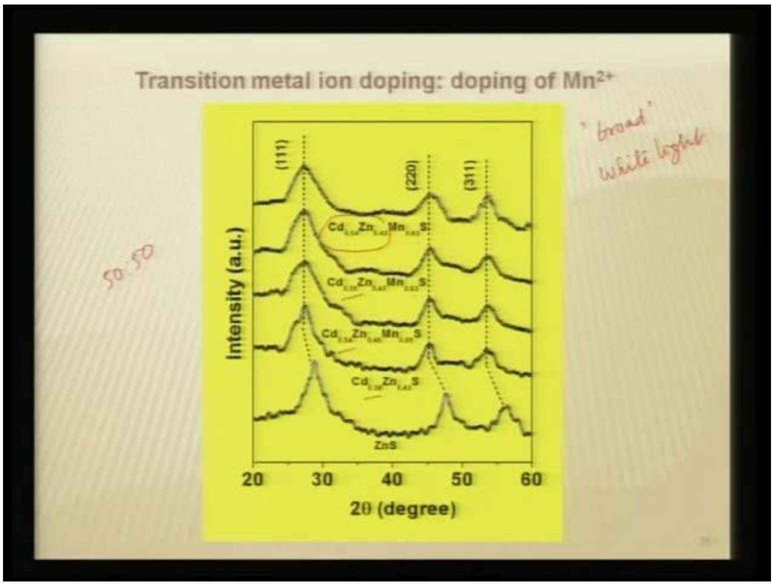

Transition metal ion doping: doping of Mn^{2+}

Now, if you have broad emission then one of the thing that we would like to do is see whether we can get a broad emission that would amount to white light emission. So, how can we do that, if we try to take this composition which is 50, 50 in other words those should be slightly cadmium rich compositions 0.54 or 0.51, 54, 58 always keeping cadmium slightly rich compare to zinc in other words they are nearly 50, 50. But, intentionally we keep cadmium on the higher side, then if you try to dope 1 percent, 2 percent and 3 percent of manganese we can try to see what is the influence.

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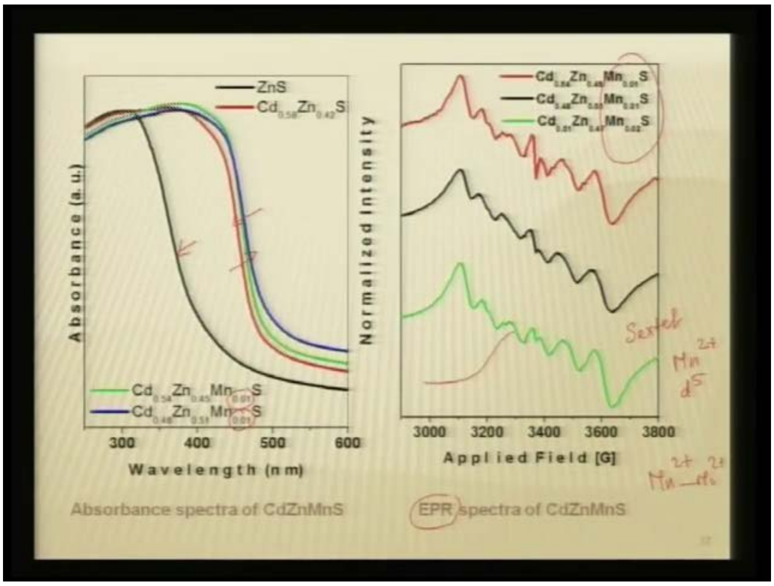

Absorbance spectra of CdZnMnS

EPR spectra of CdZnMnS

If you look at the absorption spectra, you can see that this is the zinc sulphide band gap and this is your cadmium sulphide band gap. And the moment you try to dope with manganese 1 percent in cadmium rich situation you can see that the bandage is immediately shifting to red. So, even with little incorporation of manganese it is very sensitive, so you can push this to higher band gap and how do we know that manganese is clearly doped in all these concentrations.

If you take the EPR spectra that is electron paramagnetic resonance spectra you will see this sextet that is that is six line spectra. So, this six line spectra is typical for M n 2 plus concentration why because this is a defy system, and this is supposed to show six lines. And you can clearly see that this six line spectra is pronounced, which means manganese is actually isolated.

So, you can selectively dope manganese in the zinc sulphide, suppose there is manganese, manganese two plus interaction this six lines spectra will not come it will come out as a broad spectra, which means manganese are clustering, together it is not doped clearly, so one can go for very elemental range of doping and precise way you can dope this co activators and you can fine tune the band.

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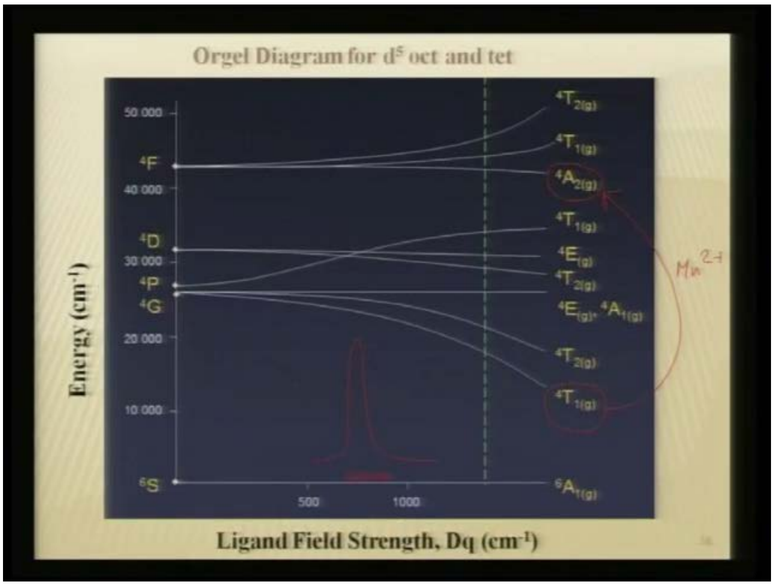
Orgel Diagram for d^5 oct and tet

Ligand Field Strength, Dq (cm-1)

The emission that is mainly responsible for this 600 nanometer emission comes from the manganese 2 plus concentration, and this is mainly because of the 4 T 1 g to 4 A to excitation. As a result you get this pronounced 600 nanometer peak that is coming, so if you see 600 nanometer peak it is purely because of the co activator that is responsible which is nothing, but your manganese ion. So, manganese two plus will induce such a selective emission.

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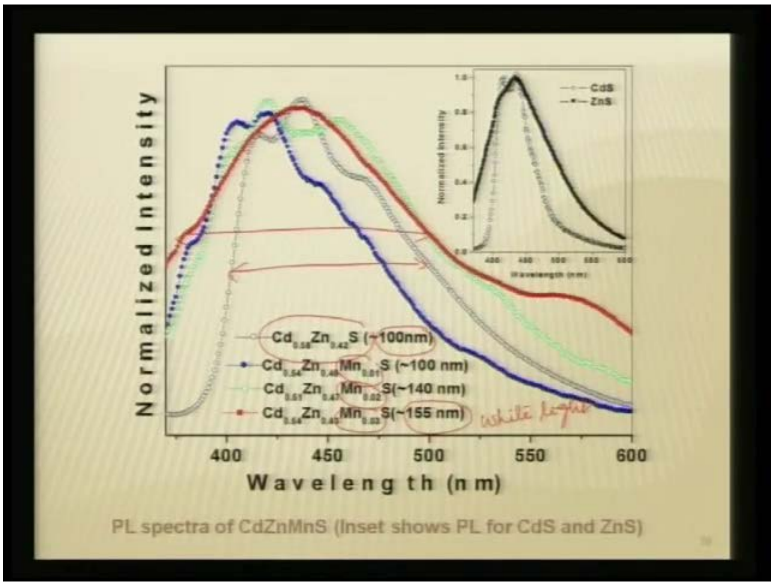

PL spectra of CdZnMnS (Inset shows PL for CdS and ZnS)

And that is what you see here, so I start with a cadmium sulphide, cadmium zinc sulphide, now you see here that this is your equiatomic nearly equiatomic composition. And in this case the broadening is of the order of 100 nanometer, now if you go to manganese doped ones 1, 2 or 3 percent, you can clearly see for a optimum of 3 percent concentration, which is your red one. You can see almost your full with that half maxima is 155, which means it is a very good candidate now for fine tuning white light.

So, what you essentially do is you try to stretch the emission both towards the blue, towards the red by just altering your composition with manganese. So, in other words you can actually use manganese for white light emission, this already I showed from one of the examples of D.D sarmas group that it is very specific, even if you put 0.10 percent or 0.4 percent. Then you should be able to bring about a candid change in the PL spectra. So, this one example by which you can fine tune to get a white light.

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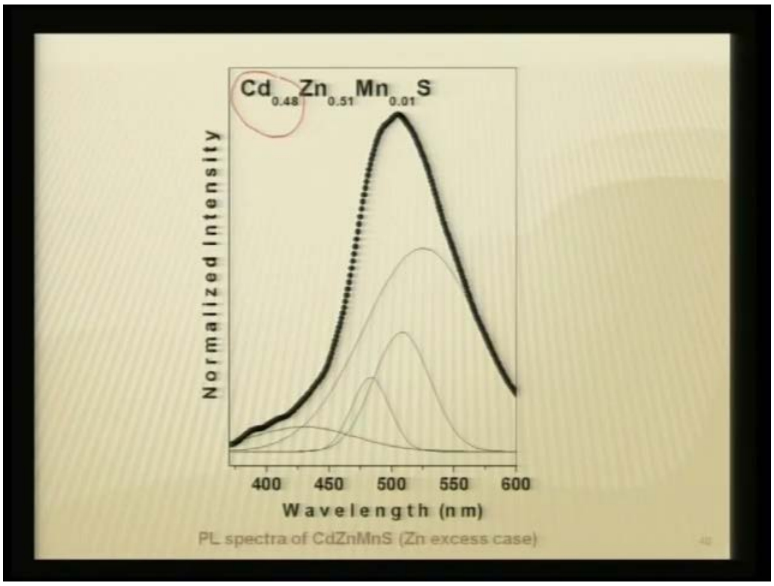

PL spectra of CdZnMnS (Zn excess case)

But, at the same time this is very specific, because instead of taking cadmium excess suppose I take zinc excess, in other words zinc is more in the equiatomic composition. Now, if I take zinc and still doped manganese immediately you see that broad emission what you see here, this broad emission immediately goes to a narrow emission. So, such is the sensitivity of your band gap you know, even if you put manganese there now it is only a green emission.

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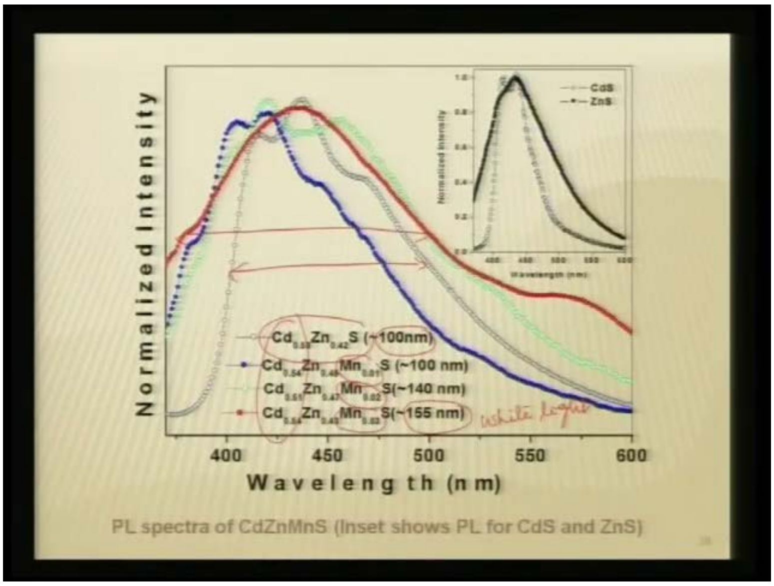

PL spectra of CdZnMnS (Inset shows PL for CdS and ZnS)

Because, it is the cadmium rich compositions which are important, so one thing is the host lattice another one is the guest lattice. So, your host lattice is as much important as your guest, so in other words here to sum it up we can say, cadmium rich once are good for broad emission. And zinc based ones are good for narrow emission, and you can fine tune that with manganese doping.

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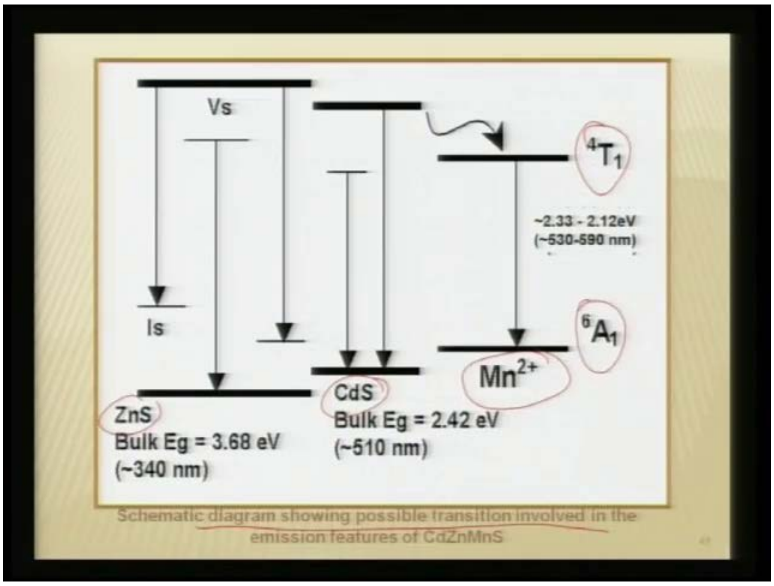

Schematic diagram showing possible transition involved in the emission features of CdZnMnS

So, this is one example that I wanted to show and this is how the band gap can be look at, you have a wide band gap zinc sulphide, and then you try to make a solid solution with your cadmium sulphide. Now, you are actually altering the band gap, and in between if you put co activator like manganese 2 plus you are essentially inducing a broad emission. So, this is the schematic diagram showing all possible transitions involved in the emission feature, as I told you we have this peculiar emission which is responsible for the broad emission.

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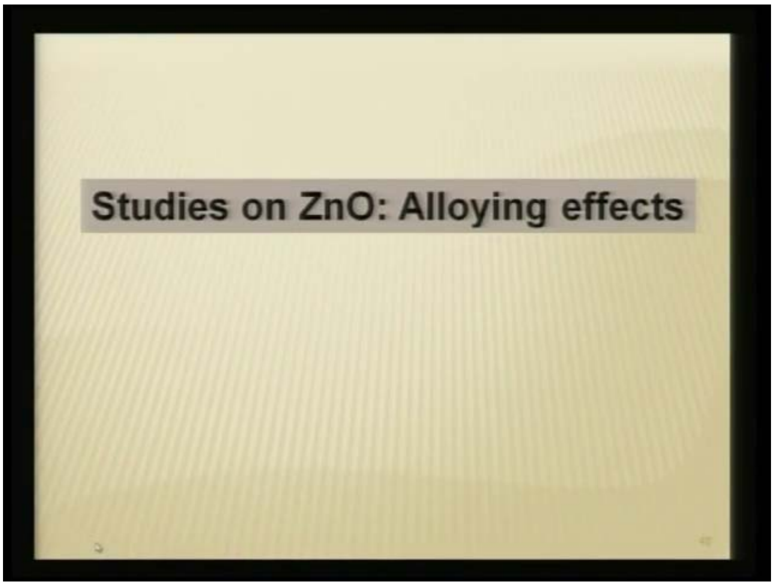

Studies on ZnO: Alloying effects

Now, I will try to show one more example of alloying effect in zinc oxide.

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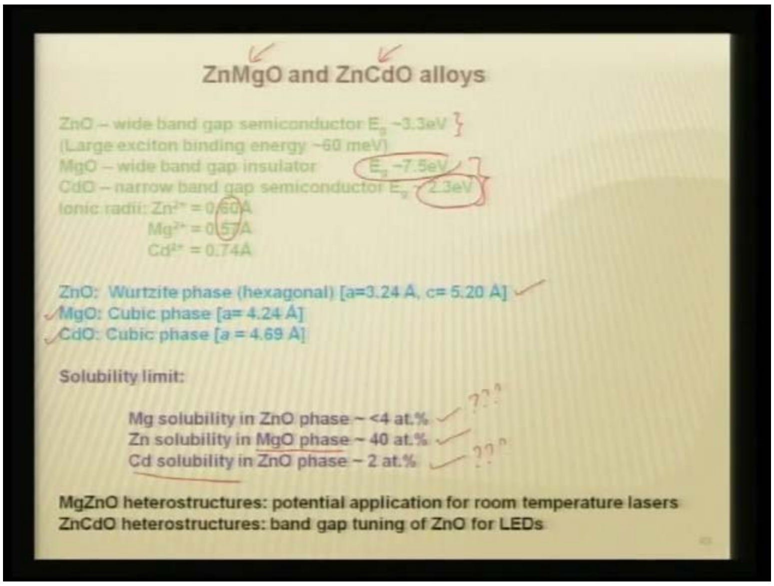

ZnMgO and ZnCdO alloys

ZnO – wide band gap semiconductor E_g ~3.3eV
(Large exciton binding energy ~60 meV)
MgO – wide band gap insulator E_g ~7.5eV
CdO – narrow band gap semiconductor E_g ~2.3eV
Ionic radii: Zn^{2+} = 0.60Å
Mg^{2+} = 0.57Å
Cd^{2+} = 0.74Å

ZnO: Wurtzite phase (hexagonal) [a=3.24 Å, c= 5.20 Å]
MgO: Cubic phase [a= 4.24 Å]
CdO: Cubic phase [*a* = 4.69 Å]

Solubility limit:

Mg solubility in ZnO phase ~ <4 at.% ???
Zn solubility in MgO phase ~ 40 at.%
Cd solubility in ZnO phase ~ 2 at.% ???

MgZnO heterostructures: potential application for room temperature lasers
ZnCdO heterostructures: band gap tuning of ZnO for LEDs

Zinc oxide is very interesting because it is used as a u V sensor, now if you want to alloy it you can try to do that either with manganese or you can try to do that with cadmium doping. So, typically the zinc oxide band gap is 3.3 E v, but you can actually dope it with the magnesium and cadmium, magnesium is a do pant which has a very high band gap that is 7.5, it is called a white band gap insulator. Now, cadmium sulphide is a low band gap stuff, so this is having 2.3.

And because they have comparable these two have comparable size, it is possible all though they have very high band gap variation. Still you can try to put as much of magnesium into zinc, so this is one way we can try to alloy this compound, and then what becomes important is, you cannot keep on doping magnesium there. Because, it will be restricted since magnesium oxide and cadmium oxide they through a cubic phase compare to wurtzite phase.

So, what is this solubility limit, so magnesium actually has a solubility limit of 4 percent, this has been widely suggested and one can actually try to put zinc into magnesium phase up to 40 percent. But, it is not possible to put magnesium into zinc phase which is very, very critical, so is it possible to increase the concentration of magnesium, by means of some other wet chemistry route, which can give a metastable phase. That is one question that we can try to answer cadmium solubility is only 2 percent can we increase it using any chemical procedures, so many studies I have gone through.

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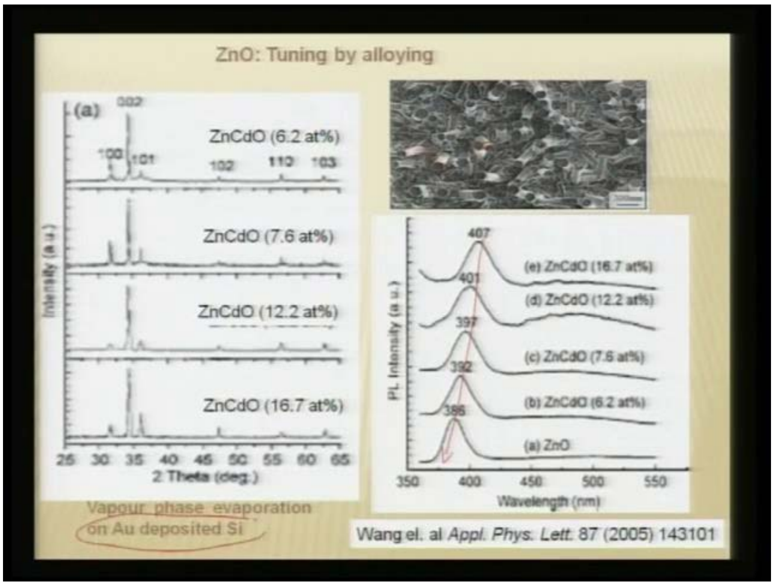

ZnO: Tuning by alloying

Vapour phase evaporation on Au deposited Si

Wang el. al *Appl. Phys. Lett.* 87 (2005) 143101

And I will just show some of our own results on this zinc oxide, this can be tuned by alloying up to 6 percent to 16 percent people have achieved it, by first depositing gold on silicon. And then over the gold layer you try to deposit it because of the mismatch in the lattice parameter, you can try to do that as you can see these are all the rods that you can grow, and the tip of the rod is actually a gold which will keep coming as a flux.

So, it is more like a surfactant your as you keep growing your zinc oxide the gold will come on the tip that is what you see here, the from this SEM picture. Now, is it possible to grow cadmium doped zinc oxide, you can clearly see that the bandage is shifting and the lambda max is also shifting. Therefore, by means of vapor phase deposition it is possible to dope cadmium this is proposed by Wang in 2005.

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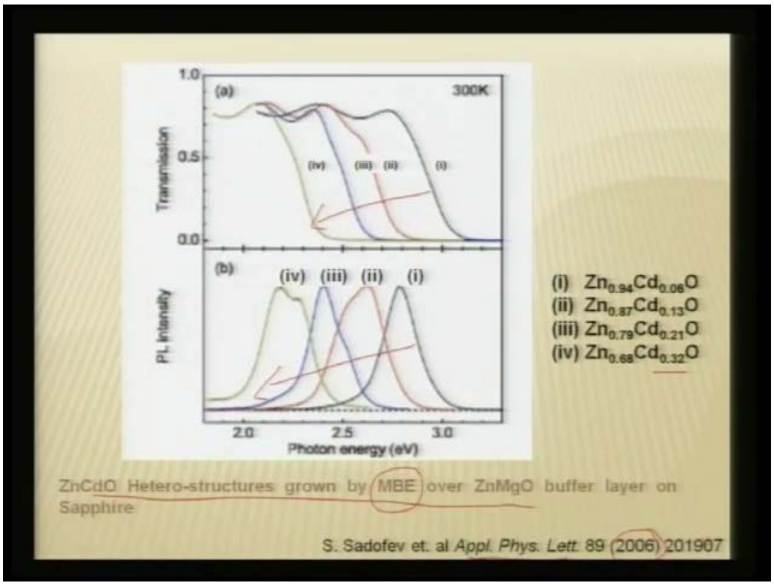

(i) $Zn_{0.94}Cd_{0.06}O$
(ii) $Zn_{0.87}Cd_{0.13}O$
(iii) $Zn_{0.79}Cd_{0.21}O$
(iv) $Zn_{0.68}Cd_{0.32}O$

ZnCdO Hetero-structures grown by MBE over ZnMgO buffer layer on Sapphire

S. Sadofev et. al *Appl. Phys. Lett.* 89 (2006) 201907

And if that is a case then what happens to the bandage, and to the PL you can see here in this case 30 percent cadmium, when you dope then it is shifting to a lower band gap. And the absorption also shifts to the lower band gap, so with increase in cadmium you can push this to a lower band gap emission. So, this is been done by MBE grown zinc cadmium oxide films, and this is reported in a PL in year 2006, so one can use MBE technique for making such hetero structures.

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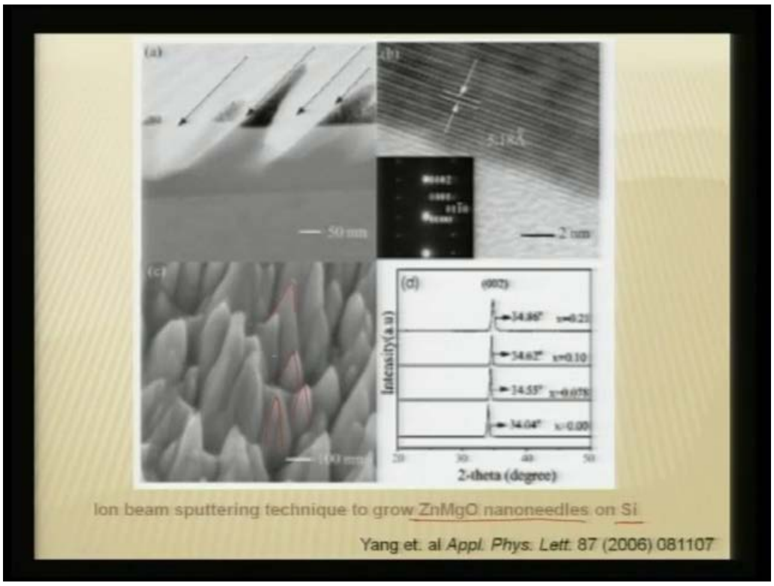

Ion beam sputtering technique to grow ZnMgO nanoneedles on Si

Yang et. al *Appl. Phys. Lett.* 87 (2006) 081107

And this is the viewgraph of your zinc magnesium oxide nano needles, which are grown on silicon, you can see these are the grown needles shaped structures of this zinc magnesium oxide that you can grow. And they clearly show the lattice fringes which is typical of the zinc magnesium oxide.

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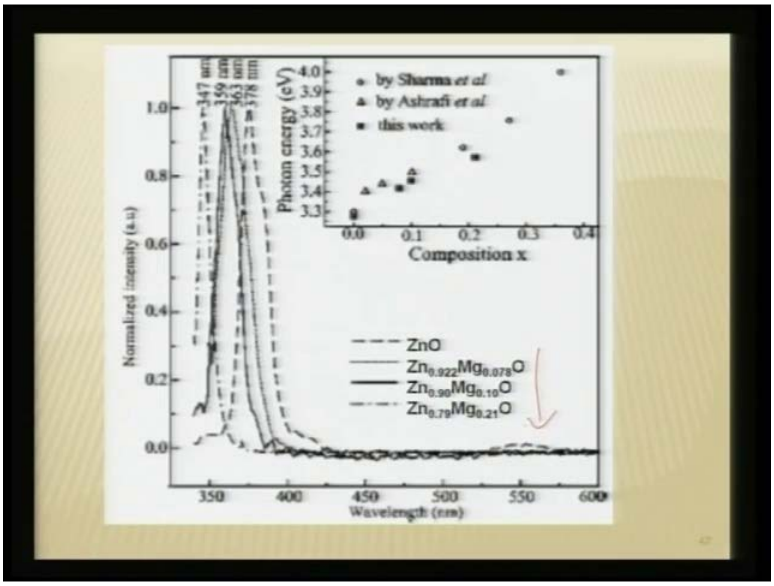

And as you would see here, with the different concentration of magnesium you can actually shift the PL emission. And therefore, it is possible for you to achieve in this case even up to 20 percent of magnesium can be doped skillfully.

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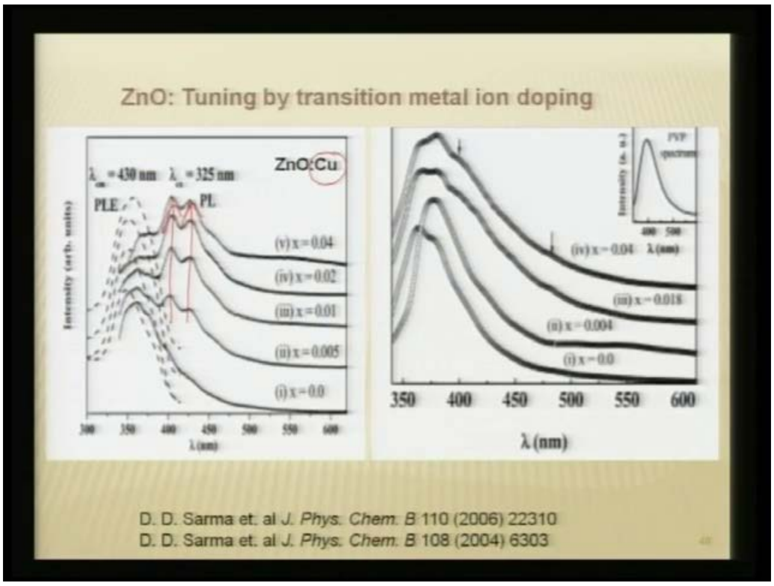
ZnO: Tuning by transition metal ion doping

D. D. Sarma et. al *J. Phys. Chem. B* 110 (2006) 22310
D. D. Sarma et. al *J. Phys. Chem. B* 108 (2004) 6303

We can also try to alloy it by doping it with copper, and in this case you can see how the PL varies, the maxima shifts towards the red and PL also changes considerably with copper doping.

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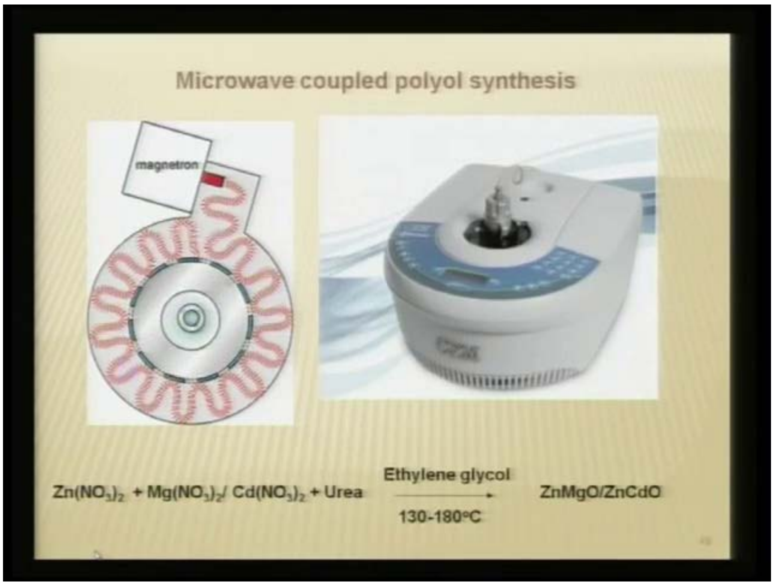

Microwave coupled polyol synthesis

$$Zn(NO_3)_2 + Mg(NO_3)_2/\ Cd(NO_3)_2 + Urea \xrightarrow[130\text{-}180^{\circ}C]{Ethylene\ glycol} ZnMgO/ZnCdO$$

One other way that we can prepare this compound is by using microwave polyol synthesis, which we will try to discuss in the next lecture.