Lecture - 36
Crystal growth and nanocrystals

Hello again, this is the next session of segment 3 of this course on Nanoelectronic Device Fabrication and Characterization.
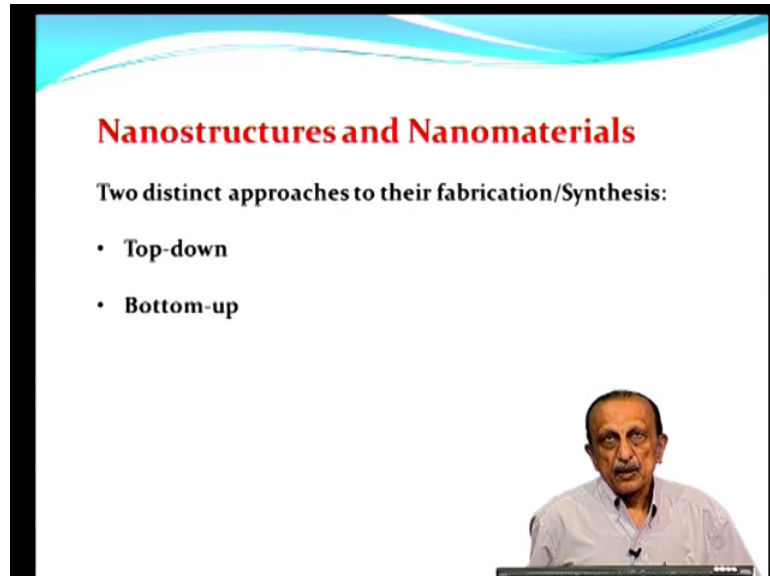
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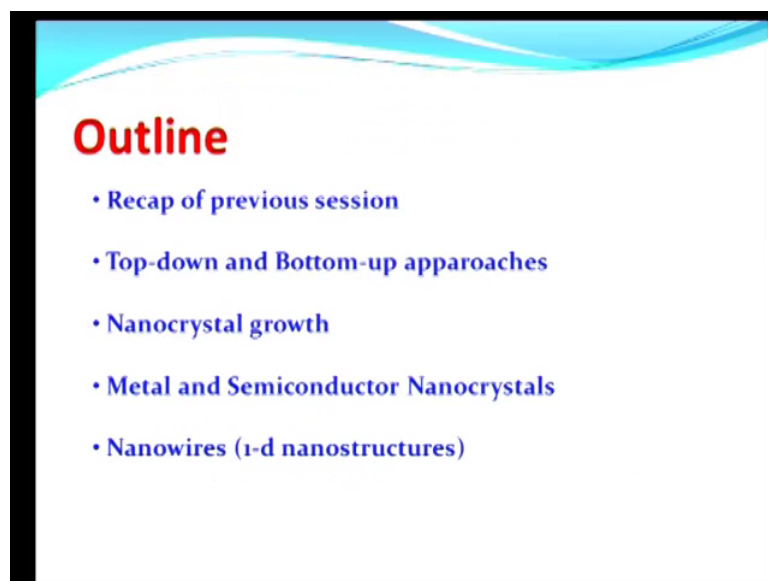
In the previous session we dealt with quantum wells and quantum tunneling, which led us to an understanding of the operation of the scanning tunneling microscope and then we began to consider ways of preparation of nanostructures and nanomaterials. As I pointed out there are 2 broad approaches top down and bottom up approaches for nanostructure preparation nanomaterial preparation, they are self explanatory as we already pointed out.

So, what we will do is to once again have a brief review of the top down and bottom up approaches, then we go on to Nanocrystal growth and then we come to specifically the growth of nanocrystals of metals and semiconductors and move on to the preparation of Nanowires which are one dimensional structures whereas, Nanocrystals would be
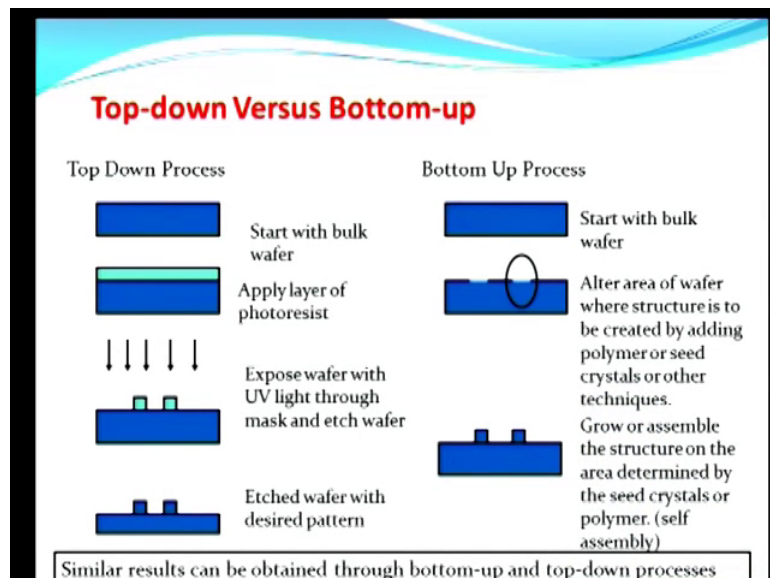
essentially 0 dimensional if they are very small. So, we will call them quantum dots for example, as we have said before.

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So, a 2 distinct approaches top down and bottom up.

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Now last time we reviewed the process of lithography which leads to top down preparation of various structures of very controlled dimensions and the bottom up process which would essentially start with atomic level components with which we

assemble in some way often through a chemical reaction nanostructures nanomaterials of various kinds. So, these are the 2 broad approaches.

Now, last time I dealt only with the lithographic approach as an example of the top down approach.

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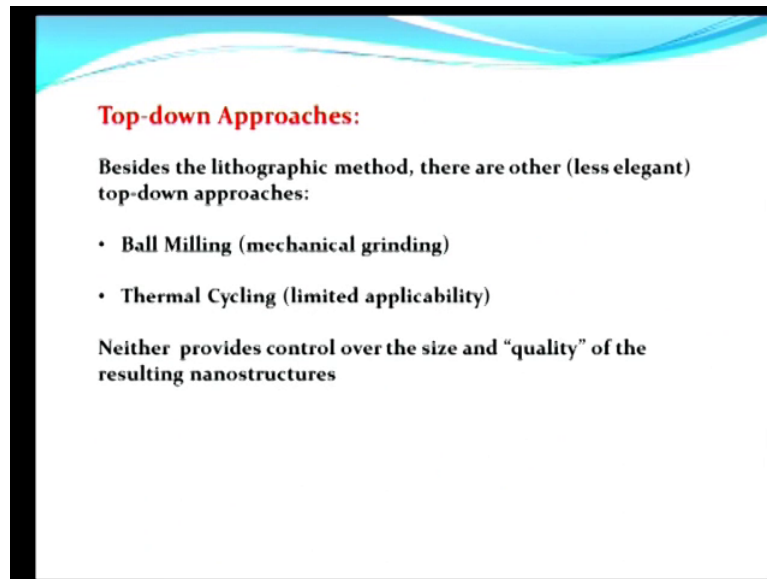
But it is important to note that there are other approaches besides the lithographic approach, although these other approaches are what might be called less elegant approaches. For example, there is his mechanical approach mechanical grinding or reduction through mechanical grinding so called ball milling whereby a material that we want to reduce to nano dimensions is continuously ground down using balls of substantial hardness. So, through this continuous attrition process in ball mills which spin at very high speeds for example, high values of G, then it is possible eventually to reduce particles from macroscopic dimensions starting with many micrometers 2 nanometers.
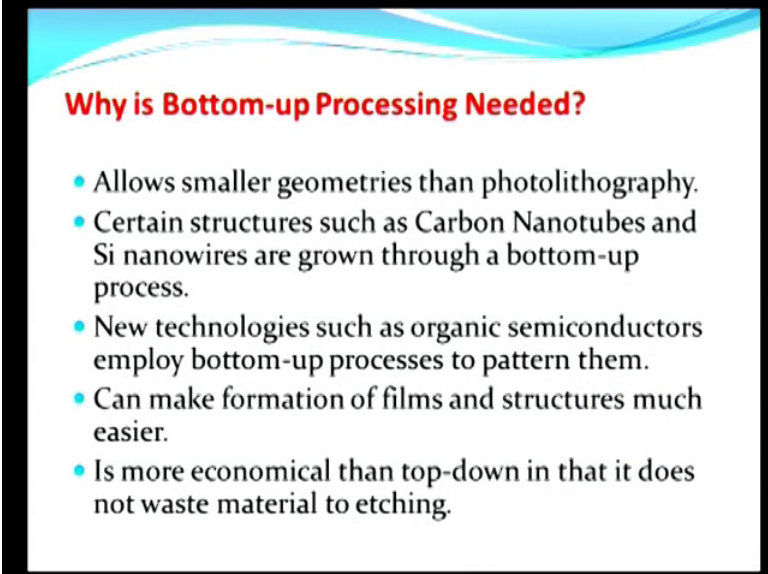
So, that is the that is one of the top down approaches, the other one is thermal cycling although it is of limited applicability whereby we one takes a material and cycles it back and forth in temperature many times and because of the thermal shock that the material suffers due to this cycling it essentially gets pulverized in the process and one can do this many times in order to continue this polarization into very small dimensions. It is a limited applicability because it depends on or rather it is applicable to materials, which

suffer thermal shock due to low thermal expensivity as a function of temperature whereas, ball milling even though it is more widely applicable has suffers from the disadvantage that this continuous pounding that the material receives mechanical pounding it receives even though it reduces the size the material progressively.

Generally it is difficult to control the size of the particles and there is a great distribution of sizes among the particles that we eventually obtained through these process nanoparticles that one might obtain through this process. Also because of the way the material is prepared through this attrition often the material is quite defective defective mechanically.

And defect defective in the electronic sense as well therefore, these 2 top down approach approaches although studied quite extensively are less applicable or less useful and provide material with fewer desirable qualities than the lithographic top down approach.

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Now, as we pointed out yesterday in the previous class the bottom up approach allows smaller geometries than photolithography; photolithography is limited eventually by the resolution of the lithography process which we discussed last time. And indeed certain very important structures such as carbon Nanotubes and silicon nanowires for example, are essentially made only through a bottom up process, it also turns out that new technologies new materials for new technologies such as organic semiconductors employ bottom up processes to pattern them.

Now, also a bottom up approach makes a formation of films and structures much easier, we mentioned yesterday processes such as molecular beam Epitaxy and MOCVD which are very useful for making high quality semiconductor layers of extremely small thickness. So, these really make a bottom up approach much more desirable and in fact, much more controllable. And as you already mentioned a bottom up approach is less wasteful of material, because in the top down approach as we already mentioned a lot of the material is H the way removed. After expensive the position or processing of some other kind a lot of it is removed to create smaller structures.
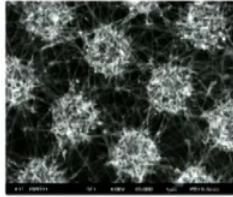
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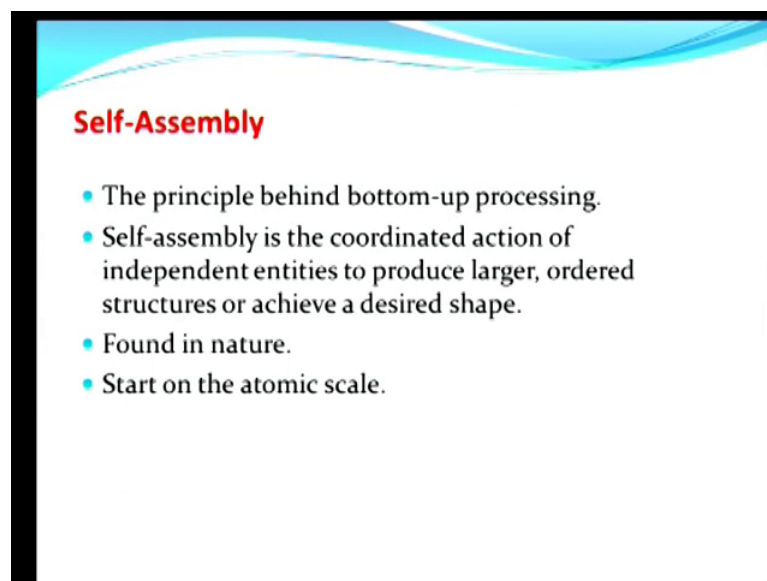
What would really be most desirable is as Self-Assembly process, that would be a bottom up process whereby through coordinated action of independent entities atomic and molecular and so forth. They produce larger ordered structures that desire achieve a desired shape, this is really what happens in nature in all kinds of biological growth and of course, these processes start. For example, if we were to mimic processes in nature they would start at atomic level and one would try to design processes that mimic processes in nature, that leads to self-assembly one of the desirable aspects of self-assembly that mimics a biological process also is that it can happen at a very simple set of conditions often at or close to room temperature although of course, it can be correspondingly a slow process, but self-assembly is a very desirable way to achieve nanostructures.

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Certainly if one were capable of bottom up processing that allowed self organization ourselves self assembly, then one would be able to as shown in this micrograph obtain silicon Nanodots or actually wires around certain specific pattern erase formation of Nanowires for example, as again shown in this view graph. So, called self assembled monolayers and what is being investigated extensively in the semiconductor fabrication business is to use carbon nanotubes as interconnects and in some way a kind of interest connects that happen in some sort of a self of self organized fashion.

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The ideas behind the bottom up approach of course, is as already mentioned the idea is borrowed from what happens in nature especially in biological systems; Cells, Crystals, are all assembled all kinds of living beings are assembled in a fashion as I said that under very modest conditions in terms of temperature and so on. And eventually they form extremely organized structures and great control of course, is possible as has been exhibited by nature herself. So, these approaches would be very desirable indeed we come now to do synthesis of nanocrystals.

Now, when we talk about nanomaterials we almost always mean at least in this segment of the course nano crystalline materials we mean crystalline materials although nanomaterials are a noncrystalline for example, certain polymeric materials which are in nano dimensions are certainly important and have been investigated or being investigated extensively what we generally mean is crystalline materials. Now the reason for that of course, is what we have dealt with in an earlier part of this segment namely that crystals can be described in a systematic fashion because of the ordered array of atoms the periodicity that is available in them and therefore, it is possible to deal with these as problems in quantum mechanics therefore, one can arrive of it for example, the energy band gap in such a system because of the periodic potentials available and so forth as we dealt with earlier in the in a previous session. So, we generally mean the synthesis of Nanocrystals.

Now, the synthesis of any crystalline material is really a process whereby the material somehow gets nucleated as the term goes you have nucleation and these nuclei of the crystal of the particular material. Let us say a semiconductor or a metal these nuclei then grow in order to make larger periodic arrays and we are of course, interested in such nano crystal crystaline arrays, we mean larger arrays to the extent of many nanometers of course, crystal growth goes on it can be continued on to produce very much larger crystals as for example, in the silicon semiconductor industry where one uses single crystalline wafers measuring 300 millimeters across. So, growing large crystals is very well understood, but our object here is to learn to make small nanocrystals in a controlled fashion that is what nanomaterials are about.

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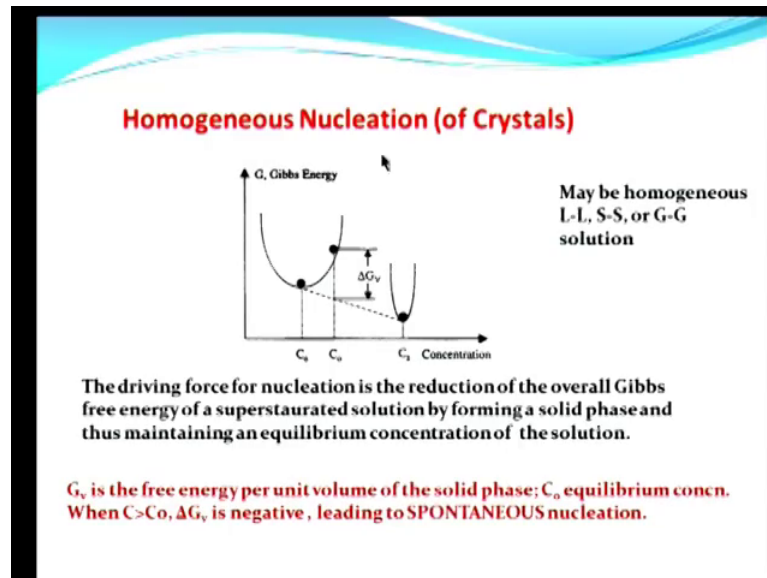
Now, let us begin with homogeneous nucleation of course, we mean nucleation of crystals. What is homogeneous nucleation we are talking about nucleation of crystals from either a liquid solution or a solid solution or it could even be a gas gas solution or vapor vapor solution. So, these are homogeneous ones in contrast with heterogeneous nucleation whereby for example, you can have nucleation occurring from the gas phase onto a solid phase as for example, in the chemical vapor deposition or CVD process.

Now what is shown here is a graph of the Gibbs free energy versus concentration when we talk about let us say we are talking about a liquid solution. So, we have a solvent and have a salute and therefore, we can talk about the concentration of the solute in the solvent. So, what is shown here is a variation of the Gibbs free energy as a function of concentration. Now what we really want is for this solute to be nucleated out of the solution to form a crystalline entity. So, that we can subsequently make it grow and obtain crystals presumably with control.

Now the driving force for nucleation is the reduction of the overall Gibbs free energy of a supersaturated solution. So, you have a solution and you go on progressively increasing this concentration of this solution that is you add more and more solute into the solvent. So, you eventually get a supersaturated solution. So, the driving force a nucleation is the reduction of the overall free energy of the supersaturated solution, by forming a solid phase and thus maintaining the equilibrium concentration of the solution.

So, we start with a point here in that in this curve which is really sort of schematic and hypothetical and because of the reduction in the Gibbs free energy delta G v, then we are able to come to the point where there is nucleation occurring. So, this reduction is the driving force and G v is the here in this J v is the free energy per unit volume of the solid phase, C o is the equilibrium concentration. When the concentration is greater than C o that is when you go here delta G v is negative and therefore, it leads to spontaneous nucleation. So, this is the general phenomenon of nucleation that is what one wants to achieve in a homogeneous fashion in a liquid liquid phase for example, for our consideration.

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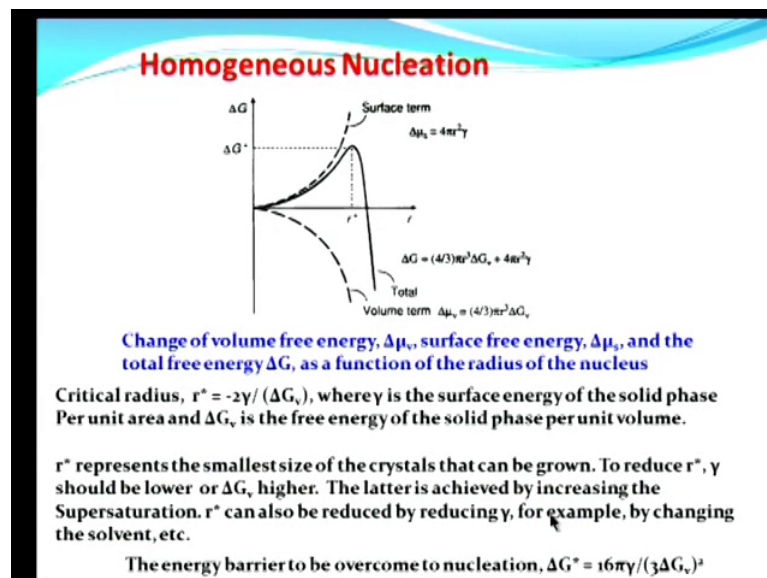
And what we want to then consider is a well known treatment of Homogeneous Nucleation were in what is plotted in this graph is delta G the change in the Gibb Gibbs free energy, as a function of r which is the radius of a presumably spherical nucleus. This makes consideration easier therefore; one considers a spherical nucleus formation of a spherical nucleus.

So, we have a plot of delta G versus r the radius of the nucleus. Now as the nucleation takes place there is a change in the volume free energy, as well as the surface free energy because now you begin to have the free energy due to the formation of the nucleus which has got a surface. So, there is a competition between the volume free energy and the surface free energy as shown here the surface free energy goes up like this the volume

term comes down like this and the summation of this is this graph over here, which then has a maximum at r star, which is called the critical radius. This critical radius is radius beyond which the nucleus is stable, below the critical radius suppose you form a nucleus that has a radius less than or prime or star then it will go back into solution and that particle nucleation would have been a failure. So, one wants to exceed this critical radius r r star in order to achieve successful nucleation from a in a homogeneous circumstance.

Now, therefore, r star represents the smallest size of the crystals that can be grown. Now to reduce r star, now r star is shown here to be given by minus 2 gamma divided by delta G v where gamma is this surface energy per unit area of the nucleated crystal. So, one has to either reduce gamma or increase delta G v in order to reduce r star. Now the reduction of gamma in the numerator that is the reduction of the surface energy can be achieved by changing for example, the solvent or adding other kinds of agents into the solution polymers surfactants and so forth.

So, one can manipulate the solution to reduce the surface energy. So, this is something that can be done often empirically to reduce gamma that way one can achieve a smaller r star. Another way is to increase delta G v and that can be done by increasing the super saturation.

So, by either changing the compositional solution that is changing the surface energy per unit area or changing for example, in super saturation increasing the super saturation which increases delta G v it is possible to reduce r star. So, that one can have nuclei that are stable that are smaller and smaller. So, this is a representation of the general hetero homogeneous nucleation the process.
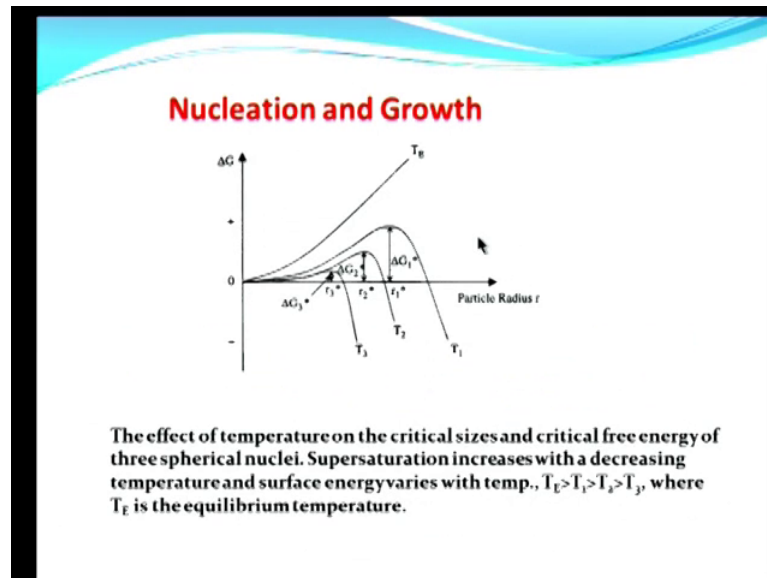
So, what is shown here is the effect of temperature on the critical sizes and critical free energy of 3 spherical nuclei that is we have 3 different temperatures T 1 T 2 and T 3? So, as the temperature is increased that is T 1 is greater than T 2 is greater than T 3 and T is equilibrium temperature. So, as the temperature is increased then the critical radius of a nucleus that can be obtained under those conditions is raised.

Now, when the temperature is reduced the super saturation increases and if the super saturation increases, as we showed in the you slide when delta G v is larger, than the critical size is smaller. So, as you can see here when the temperature is reduced the super saturation increases because the solubility of the solute in the solvent is lower at a lower temperature than at a higher temperature therefore, the super saturation is greater for a given solution when the temperature is reduced therefore, one gets a smaller critical size for the nucleus and by increasing the temperature one can everything else being equal when can give go to higher nuclei diameters.

So, these are the general approaches that one takes in trying to produce nanocrystals of different materials typically from a homogeneous liquid solution. So, we want to carry out the synthesis of nanocrystals of metals semiconductors oxides for example, and so on. Through such a solution process where we have a solvent and a solute and we want to produce nanocrystals of the solute and there are many ways one can manipulate the
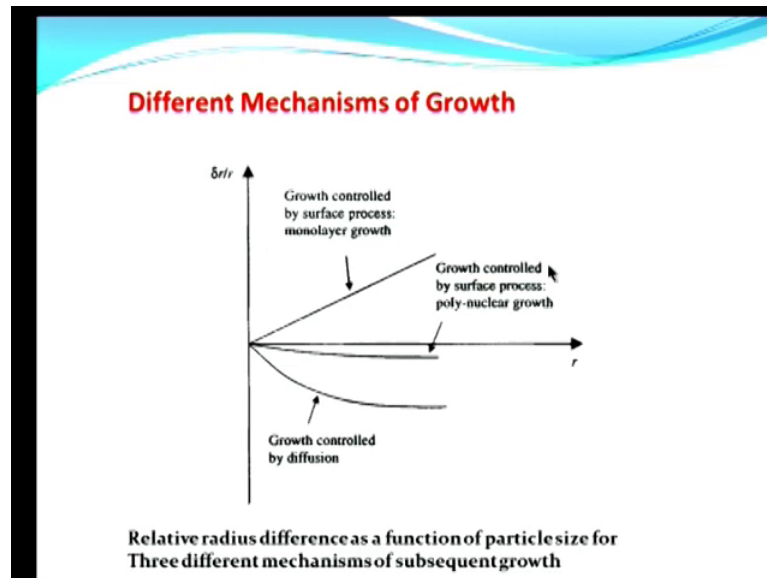
nucleation and growth process by changing the solution composition by changing and changing the concentration by changing the temperature and so forth.

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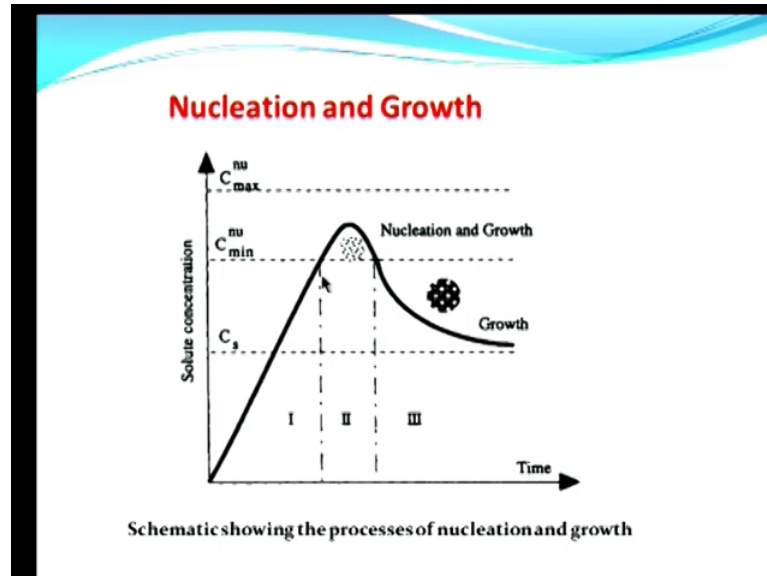
So, this is a general diagram that represents the process of Nucleation and Growth the homogeneous nucleation and growth process. So, what is shown here is solute concentration versus time? So, when the solute concentration is adequately high nucleation takes place and then if the process is continued then gradually growth takes place and one gets larger and larger crystals as a function of time as the growth process is continued. So, this is a general kind of an algorithm for the preparation of nanocrystals typically from a liquid medium.

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Different Mechanisms of Growth

Relative radius difference as a function of particle size for Three different mechanisms of subsequent growth

There are Different Mechanisms for Growth controlled by diffusion controlled by surface processes and so forth. All I want to point out is that the if you look at this graph here where there is control of growth through diffusion, what you can see here is that here in this case it is possible to get or that is a radius over here that we can control and is generally possible to have what is called monodisperse, that is a narrow distribution of the sizes of crystals that one obtains from such a case one can have monodispersed distribution of the sizes of the nanocrystal that one obtains under the diffusion controlled growth process.

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Gold Nanoparticles (Nanocrystals)

Various Potential Applications in Medicine:

• Drug Delivery

• Diagnosis and Sensing

• Treatment: Alzheimer's disease, Cancer

Now, a prototypical case of crystals is that of Gold Nanoparticles. As we mentioned I think at the outset of this segment of the course, world nanoparticles were prepared by Sir Michael Faraday more than 100 and 50 years ago through a colloidal solution. Now in the sense that the basic process is the same as what he used not much has changed, but on the other hand a great deal of work has been done to achieve control in a measurable way of the dimensions with gold nanoparticles, to get extremely small gold nanoparticles with extremely small size distribution, but extremely narrow size distribution that is monodisperse gold nanoparticles let us say measuring about 2 nanometers or 5 nanometers with an extremely small size distribution around 2 nanometers or 5 nanometers.

So, this has been achieved through a lot of work that has been carried out recently motivated by many applications, potential applications, in biology and medicine. In drug delivery diagnosis and sensing and in treatment of Alzheimer disease and Cancer and so forth and if time permits in a later part of this course we will deal with some aspects of this.

Now synthesis of gold nanoparticles as I said this has been done for a long time and the process by which it is done is not very different from what it was back in faradays days.
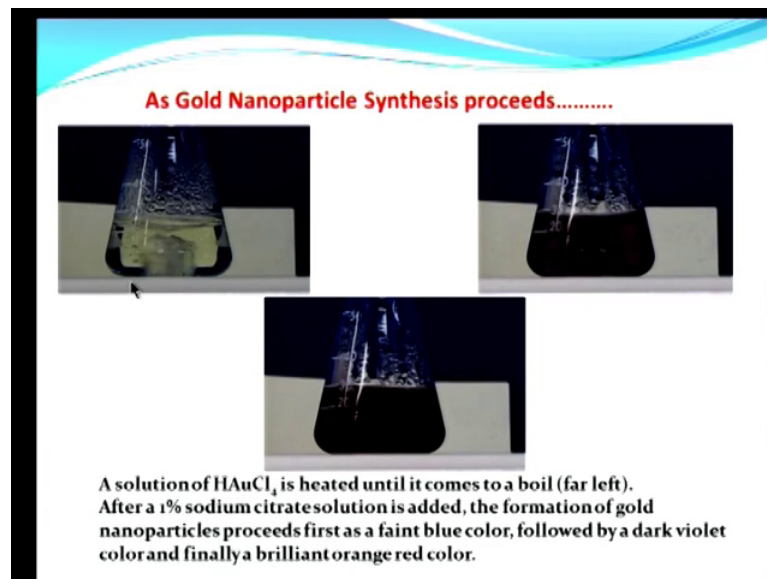
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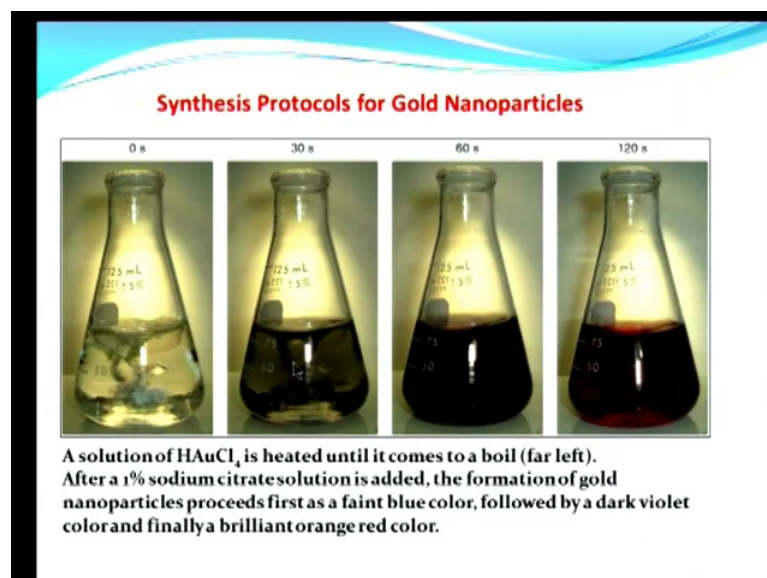
So, what is shown here is a series of images as a function of time when a certain synthesis protocol for gold nanoparticle synthesis is followed? A solution of Chloric acid

HAuCl 4 is heated until it comes to a boil, and then 1 adds sodium citrate into this solution and then you know a dilute solution that is 1 percent sodium citrate is added, sodium solution sodium citrate solutions are added to this boiling Oreck acid solution and the formation of nanoparticles then proceeds and you can see the change in the color of the solution as the process continues giving gold nanoparticles of progressively increasing size as time elapses 30 seconds, 60 seconds and 100 and 20 seconds and so forth.

So, finally, it begins to appear a brilliant red color gold as we know is yellow in color, but because of the size because of the so called Plasmon resonance in gold, it has colors that span from red to yellow depending on the size of the nanoparticles. Again this is something that we shall deal with in a later part of this segment of the course.

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So, as the Nano particle synthesis proceeds, as you can see here, there is a change in color, and what is also seen vividly here is that this layer of adsorbed citrate ions on the surface.

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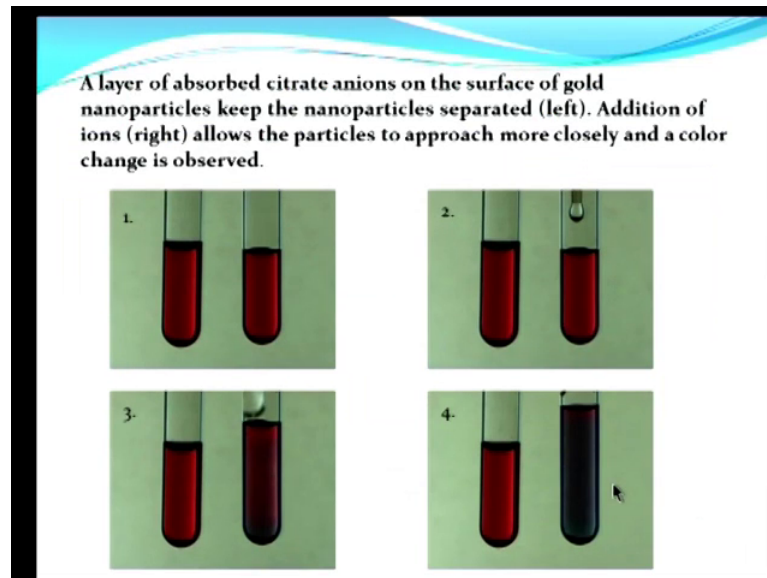
It this layer which is a charged layer and therefore, by electrostatics it keeps nanoparticles separated. Now the addition of ions for the addition of ion certain ions allows the particles to approach closely and the color changes therefore, what it means is that there is a change in color that also depends on the relative distance between gold particles in a colloidal solution. That is in addition to a change in color due to the size of the gold nanoparticles, it also matters what the relative distance is between the gold nanoparticles in the suspension.

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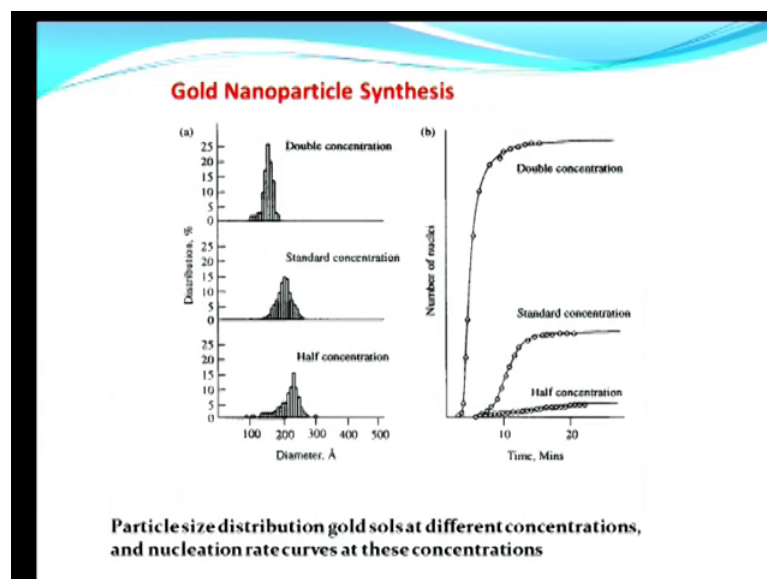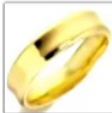
Now a lot of work has been done in time to control the sizes of gold nanoparticles prepared to such a process which is called as solve for example, this all of Chloric Acid. So, what is shown here is the size distribution of gold nuclei that are formed as a function of the concentration of the chloric acid in the solution?
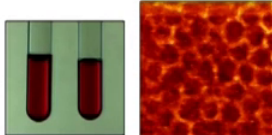
So, what you can see is that at a so called standard concentration, let us define that as some concentration we call it standard and then we how the concentration and we double the concentration. So, what you can see from this histogram on the left is that when the concentration is doubled then you have a narrower distribution of particles particle sizes as well as a smaller average size for the particles. So, what is done here is to enhance the nucleation rate and control it in such a way that what you have is a narrow size distribution, this is a wider size distribution around a larger average size and any one wider one. Therefore, by controlling for example, in this case the concentration it is possible to achieve control over the size reduce the size by increasing the concentration, as well as to have a narrower distribution of sizes in the resulting colloidal formation of gold.

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Optical Properties as we just mentioned we all know that gold in bulk appears appears yellow. Now, Nano-sized gold can appear blue or red in color, this is due to you know the particles are so small that electrons are not free to move about as in bulk gold this is the. So, called Plasmon effect as I said we will return to this bit later treat it more

formally therefore, because of this effect on the free electrons present in gold which is a metal because they are moving movement is restricted the particles appear differently with light. So, this is a an illustration of how 12 nanometer particle size of gold 12 nanometer crystals of gold let us remember these a crystals nanocrystals then it appears red in color as shown here.

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The color of nano-gold particles depends on the distance between the particles.
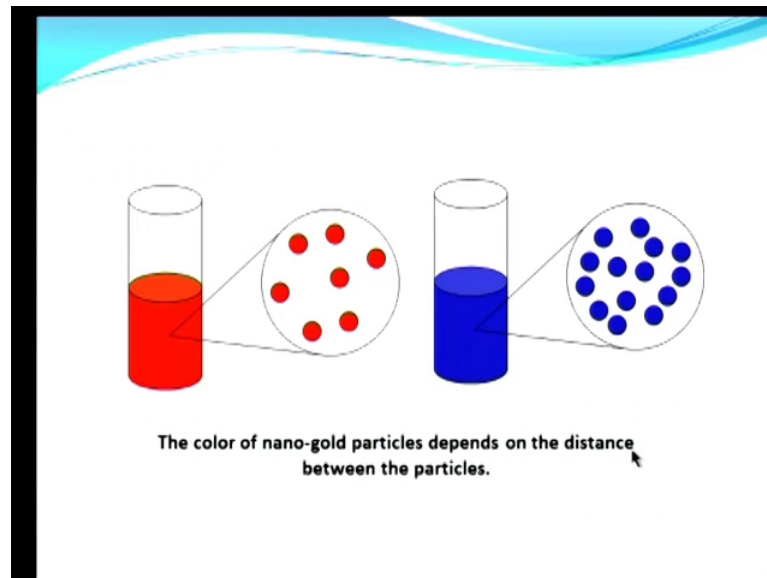
So, this is a cartoon that represents what I just said a moment ago namely that the color for a given size depends on the average separation between the gold particles in the colloidal suspension. So, when that is greater it appears reddish when there is when they are closer together it is more bluish.
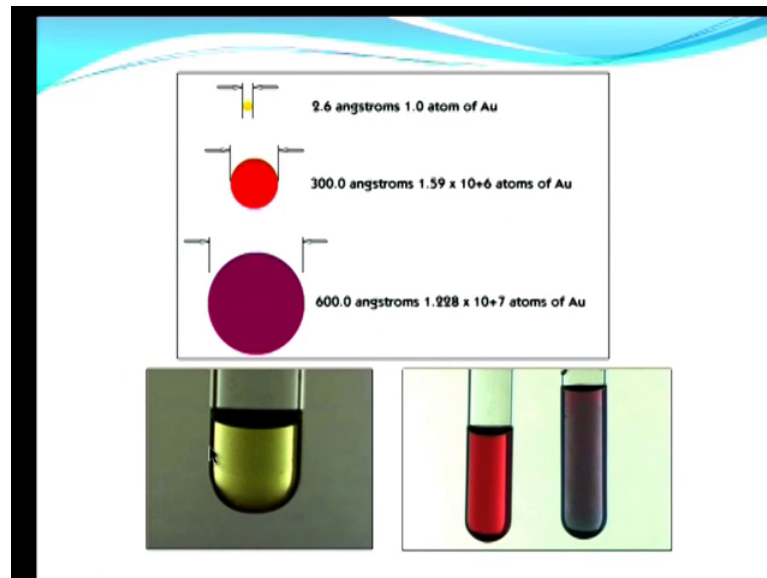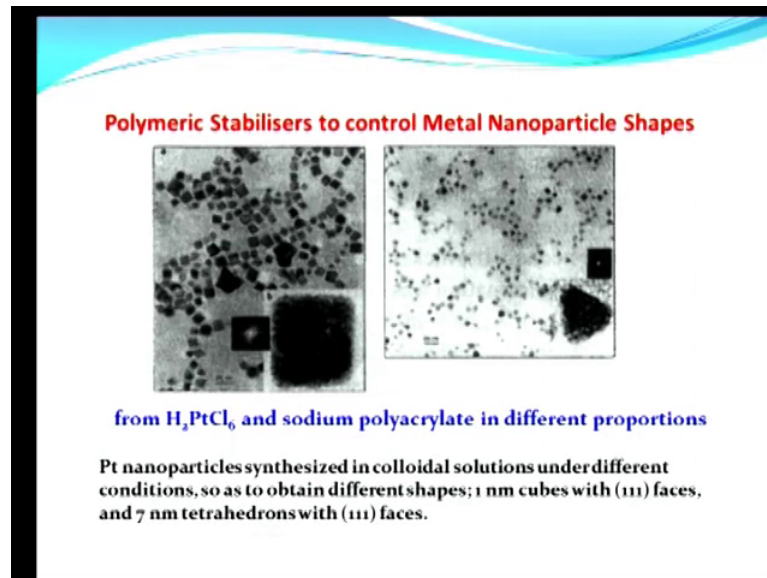
And again this is represented you know when you have a 30 nanometer gold nanoparticles, that is a suspension of 30 nanometer gold particles what you see is a reddish color and when you have 60 nanometer 600 angstroms. So, over here then you have this bluish color over here on the right.
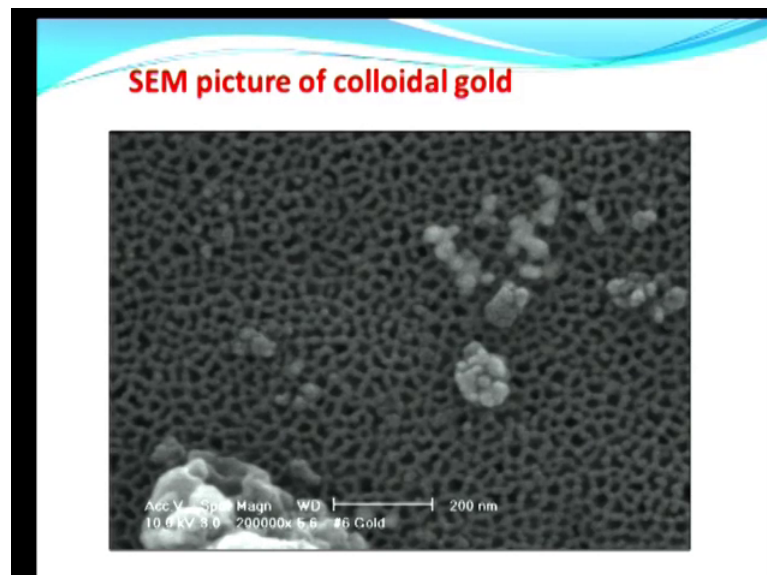
So, this is an SEM picture that shows the gold nanoparticles that are formed in a colloidal suspension and what you can see here is that there really are very very close to one another in size.

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Polymeric Stabilisers to control Metal Nanoparticle Shapes

from H_2PtCl_6 and sodium polyacrylate in different proportions

Pt nanoparticles synthesized in colloidal solutions under different conditions, so as to obtain different shapes; 1 nm cubes with (111) faces, and 7 nm tetrahedrons with (111) faces.

So, this is a monodisperse sample of gold. It is possible although gold nanoparticles are very important as I just said and I probably forgot to mention that the reason that gold is. So, important in medicine is because it is so unreactive and therefore, biologically safe. A lot of work also has been done on the nanoparticles of many other metals among which are platinum and silver for example, and platinum is obtained from platonic acid H 2 PtCl 6 and a an agent a polymeric agent called sodium polyacrylate and depending on the proportion of the platonic acid and the sodium polyacrylate. On the left what you have is a one is to one proportion of the platonic acid and the polymer on the right what you have is one is to 5 proportion.

So, therefore, you can see that a very substantial difference in the shape of the particles and the size of the particles occurs when one changes the composition of the solution. So, what you have here are cubic particles measuring one nanometer over here whereas, on the other side you have tetrahedral platinum particles or crystals I should say with what in both cases with 111 faces in both cases. So, here you are here you have one nanometer cubes with 111 faces here you have 7 nanometer tetrahedrons with 111 faces. So, this is actually these kinds of polymers and other additives to the solution are called structure directing agents.

So, through a careful choice of these structures structure directing agents is possible to change the shape of the nanocrystals that is to change the growth process in such a way

that one or the other crystalline phase is preferred or one or the other crystalline shape is preferred. So, these growth directing agents and the proper application of these growth directing agents is a very important aspect of nanocrystal formation especially for metals.

Similarly, silver nanoparticles have been produced and one of the great motivations for silver nanoparticles is that they are substrates very effective substrates for observing surfaced enhanced Raman scattering. Surface enhanced Raman scattering is a very powerful technique for detecting extremely small amounts of material minute amounts of material measuring in Nano Milords or Pico Molar quantities and silver and is a very good substrate for that and therefore, a lot of work has been done on synthesizing nanocrystalline silver with controlled size and shape.

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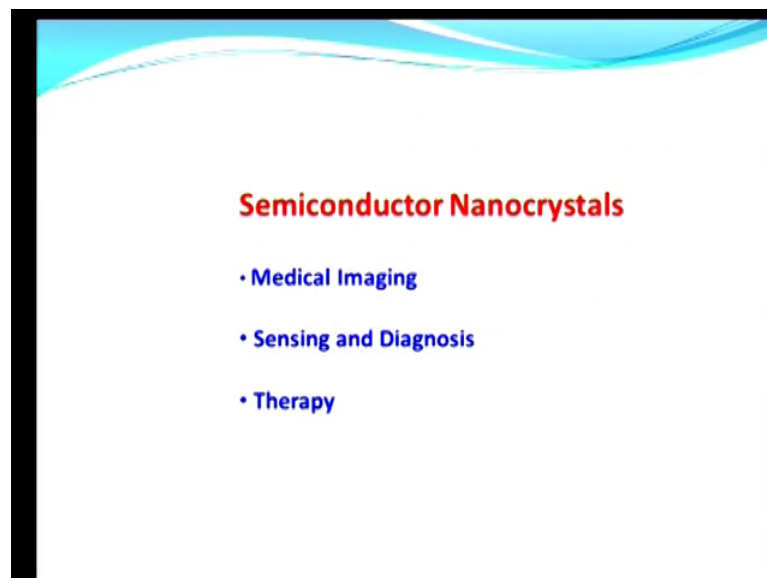
We now come to Semiconductor Nanocrystals; Semiconductor Nanocrystals we have already dealt with we have come across earlier and these are very important for Medical Imaging because if you recall Cadmium Selenide for example, can be produced in highly controlled sizes nanometric sizes leading to different band gaps therefore, they can fluoresce and at different wavelengths all the way from red to blue. So, by controlling by employing nanocrystals of cadmium selenide for example, it is possible to use them in imaging in of biological parts. By injecting that into a biological being for example, biological sample for sensing a diagnosis diagnosis of diseases and for therapy and so on.

So, formation of semiconductor nanocrystals with control over the size and shape is very important and therefore, has been investigated extensively I have shown you this particular week view graph.

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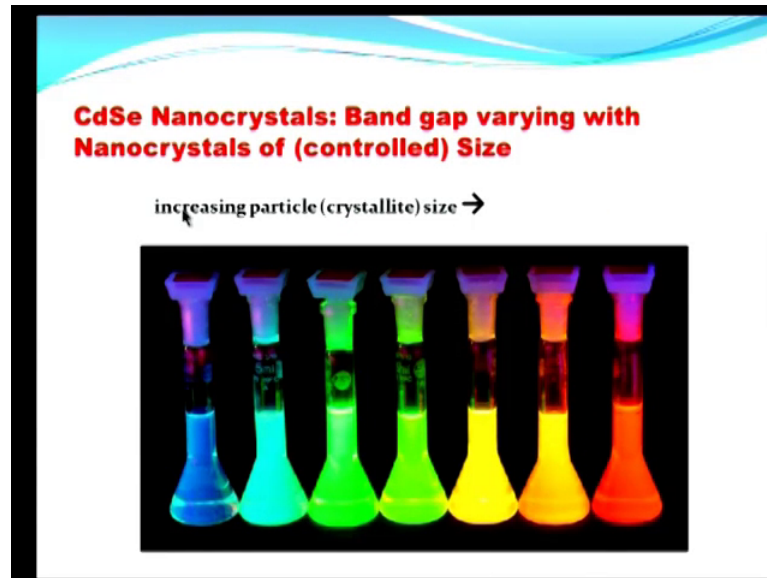
Where as a function of increasing particle size of cadmium cadmium selenide which is a direct Band gap semiconductor as one increases the size from about 2 nanometers or so to about 8 nanometers on the right hand side, the band gap is progressively reduced or as the size is diminished the band gap is progressively increased forming the blue shift that occurs due to quantization or quantum confinement.

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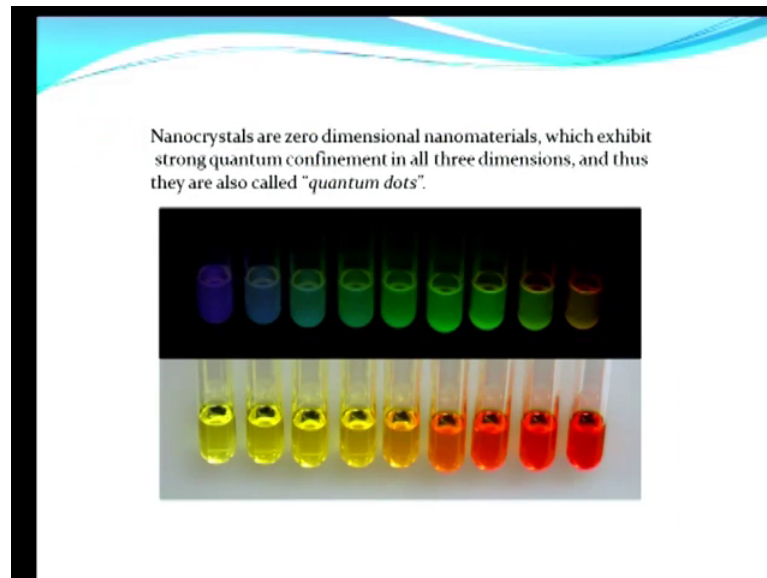
This is another image actually this is for I believe the one at the bottom is for zinc selenide. So, what this shows is that for different compound semiconductors in particular of the so called 2 6 family, that is one element from group 2 and another from group 6 cadmium selenide is one of those, cadmium is from group 2 selenium is from group 6. Similarly, you have zinc selenide zinc from group 2 and selenium group 6 so you have these compound semiconductors with direct band gaps with controlled sizes then giving rise to very vividly observable blue shift, that is band gap increasing as the average size of the crystals is reduced.

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Synthesis of carrot cadmium selenide nanocrystals. So, here is a kind of a protocol that one can find for cadmium selenide nanocrystal synthesis, one prepares a selenium precursor. So, selenium is one of the elements. So, I have shown here thirty milligrams selenium and 5 milliliters of Akhter dizzying and then one adds try up type Phosphine and so that the selenium is completely dissolved.

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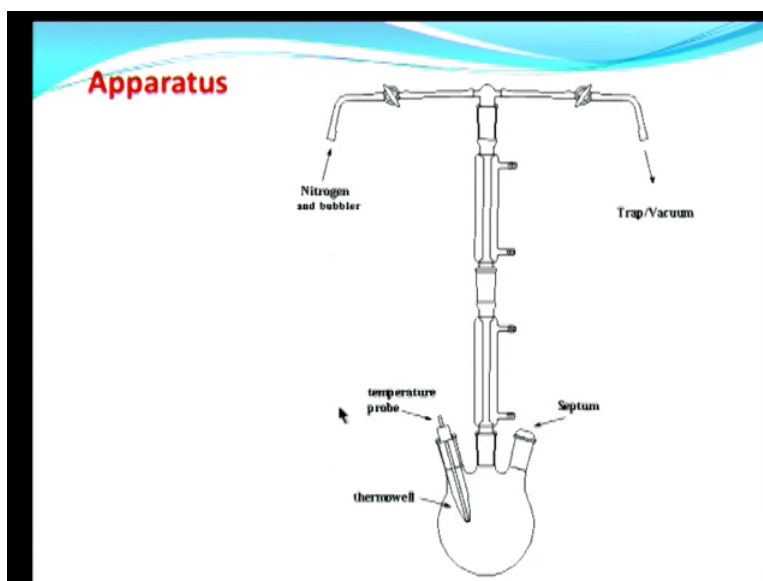
Now, let me jump ahead and show that these things have to be done in proper vessels under nitrogen that is under inert atmosphere. So, this sort of Apparatus which is really simple glass apparatus is sufficient to carry out this synthesis and what is shown here is really a very workable process for the synthesis of cadmium nano cadmium selenide nanocrystals.

So, we prepare a selenium precursor, then we prepare a cadmium precursor based on cadmium oxide and these solutions are properly heated and maintained and so forth. So, what is shown here is a protocol for synthesis of cadmium solenoid?

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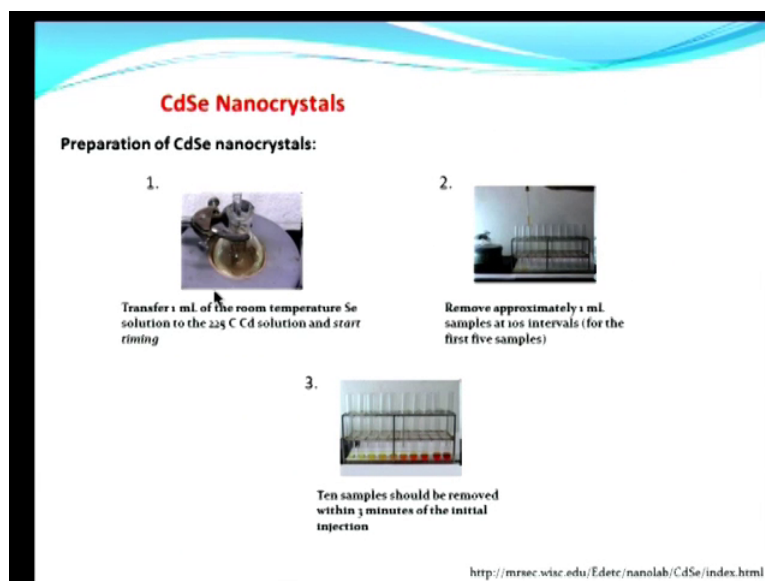
And then we transfer the cadmium solution we put them together and start timing that is we are doing this all these things at 225 Celsius, at a reasonably elevated temperature at which temperature the reaction occurs swiftly and therefore, in a controlled fashion one removes approximately 1 milliliter every 10 second intervals. That is we maintain the solution at 225 degree Celsius and we remove 1 milliliter of the sample every 10 seconds.

There are methods of the handling that the point is that as time elapses the nanocrystals of cadmium selenide grow therefore, one takes out samples of this solution in which the crystals are growing as time elapses in 10 second intervals, in order to obtain 10 samples in 3 minutes as shown here each with a different color meaning, each with cadmium selenide nanocrystals of a different dimension. So, these protocols are very well established and highly reproducible, take for these illustrate how well one can prepare nanocrystals of compound semiconductors with controlled sizes in a manner that is essentially a bench top experiment in a properly equipped laboratory.

This apparatus have already shown this is a simple one really and widely available. So, it is really possible is affordable to carry out these experiments in a typical laboratory.

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So, it is also possible to have temperature dependent growth what we have shown here is time dependent growth; you can have temperature dependent growth of cadmium Selenide.

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And you know really if one examines the spectral properties of a series of cadmium selenide quantum dots, that is we took out 10 samples in 10 second intervals. So, one can observe in a spectrophotometer peaks at different wavelengths or that correspond to the band gap of the respective particles. So, here you have 453 for a sample that was taken

out after 10 seconds, all the way to 546 for a sample that was taken out after 90 seconds for example. So, this is the blue shift we are talking about and this is the observed color of the suspension of the cab cadmium selenide colloid.

Similarly, one can produce Zinc Selenide Nanocrystals with appropriate precursors and the reference is given here. So, all of these really demand essentially the same kind of an approach. Now, what is also interesting is that you know these 2 are both compound semiconductors of the 2 6 variety, that is cadmium selenide and zinc selenide.

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So, what is possible is to produce a Coreshell structure, that is one produces cadmium selenide nanoparticles of a certain dimension, these are spherical let us say largely spherical and then one grows a shell of Zinc sulfide on that one, Zinc sulfide also is a 2 6 semiconductor. So, the protocols for making cadmium selenide well established the protocol for making Zinc sulfide well established and it is possible to grow Zinc selenide on top of cadmium sulfide saloni zinc sulfide on top of cadmium selenide nanocrystals. That is one prepares cadmium selenide nanocrystals and then uses the appropriate chemical agents and protocols to grow a thin layer of zinc sulfide on top of the cadmium solenoid nanocrystals, that way one obtains a coreshell structure of zinc sulfide cadmium selenide of a given dimension and all these are crystalline of course, nanocrystalline.

So, we talked so far about the synthesis of nanocrystals or quantum dots that is we are talking about essentially 0 dimension presumably it is 0 dimension crystals structures. So, if you have if you control the dimensions of a crystal to within a few nanometers you have essentially a quantum dot whereas, if you extend the crystals in one direction as shown here in these in this view graph what you have our so called nanowires.

So, each of these is a one dimensional crystal over here. So, I believe these are of zinc oxide I am not sure about it, but what this represents are the growth of individual nanocrystals which are one dimensional. So, each of these is a single crystal of zinc oxide, that is very small in diameter nanometric in diameter diameter, but much longer therefore, these structures have a high aspect ratio that is the length of these is much greater than the diameter. So, the high aspect ratio makes them essentially a one dimensional structure.

So, this should be a nanowire where the diameter is in the nanometric regime and the length can be much larger. So, you would have a confinement in these things along the length confinement of carriers along the length of the crystal. Now methods of nanowire synthesis how does one we learnt just now about making nanocrystals. So, how does one make nanowires. There are several methods the most well known and actually the oldest as old as 1964 is this VLS or the Vapor Liquid Solid method and there are several modifications of the vapor solid liquid method CVD laser ablation catalytic growth, low

temperature VLS method and so on. And more recently developed fluid liquid solid mechanism, solid liquid solid mechanism, oxide assisted growth and so on. So, these are all new avatars more recently developed for the preparation of nanowires which usually means nanocrystals that are one dimensional.

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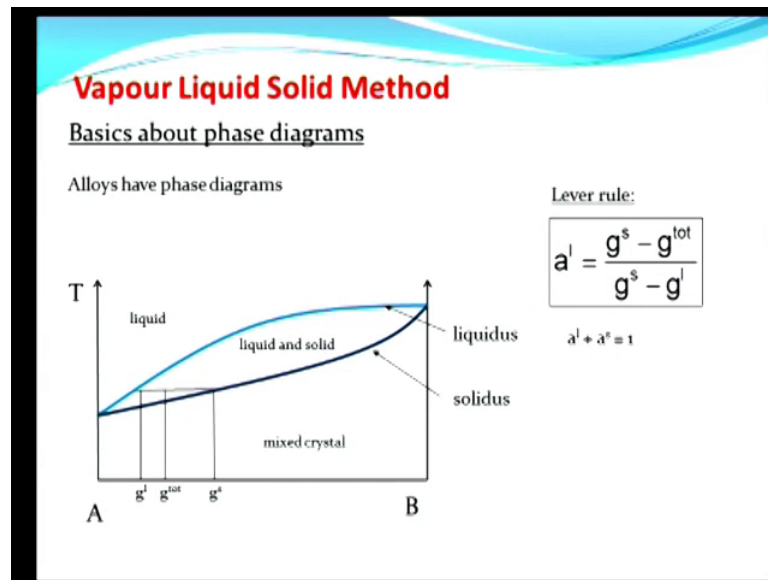
So, for this one starts with the basics of a phase diagram so you have an alloy phase diagram here. So, you have a component A and A component B and you have the liquidus and solidus and in this region over here and the vertical axis of course, is always temperature in the phase diagram and you have a region over here that is a liquid and solid coexisting under these conditions that is in this temperature range and at this composition and so forth. So, this is the phase diagram a simple phase diagram of a simple system and the so called lever rule gives us the composition and the melting point of these alloys is an alloy phase diagram.

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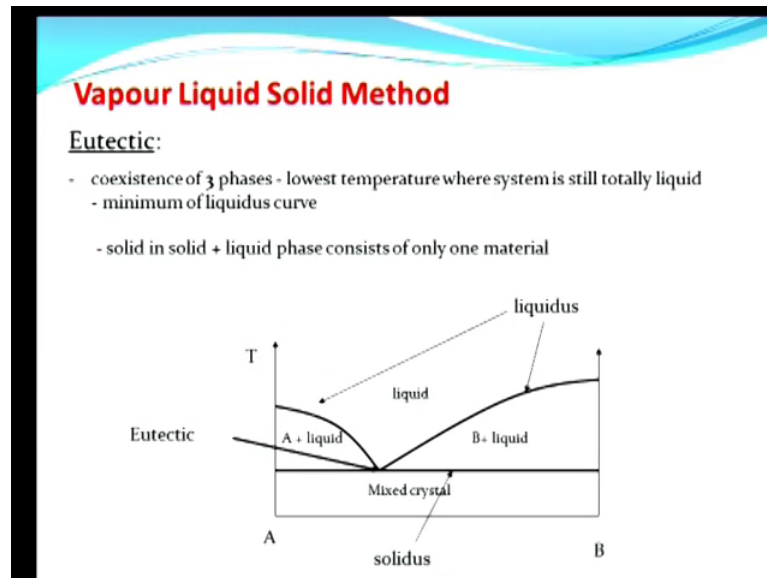
Now, why do we want it you want it because what we want is to have a eutectic that is the coexistence of 3 phases, liquid solid and the mixed crystal over here? So, we that is the point where you have the lowest temperature where the system is totally liquid over here so this is the eutectic point in this phase diagram. So, if you have 2 phases, if you have 2 components I should say A and B that can provide this kind of a Eutectic Diagram that have a eutectic eutectic phase diagram of this sort then it can form the basis of a nanowire growth through the liquid solid vapor liquid solid method VLS method.

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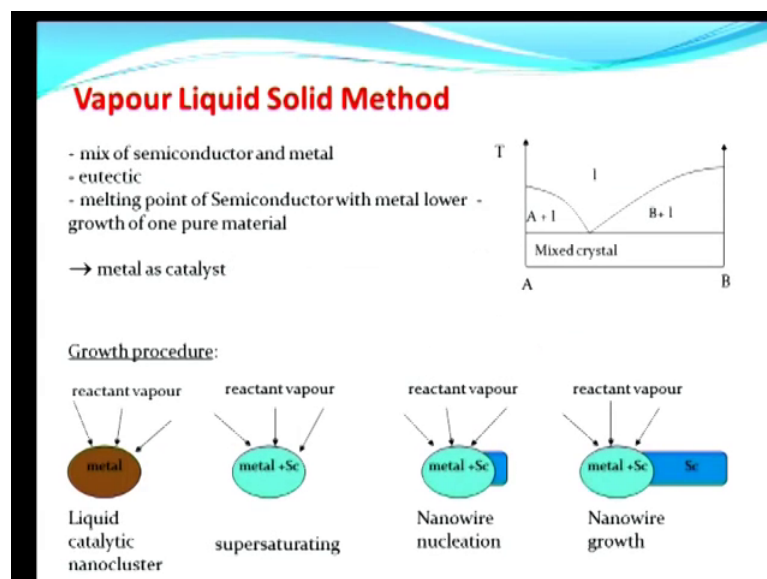
So, in particular you have a mix of semiconductor and a metal forming a eutectic therefore, the melting point of the semiconductor with the metal is lower and it allows the growth of one pure material from this eutectic mixture.

So, in practice what one has is a reactant vapor that is we have a liquid catalytic nanocluster, let us say gold actually and this vapor is that of Silane SIH 4 which would decompose at an appropriately elevated temperature into silicon elemental silicon and hydrogen and that silicon then that is the semiconductor hear it then forms a melt with the metal at an appropriately high temperature. And because of super saturation of this melt and the melting point of course, is lower because of the fact that we have a eutectic. So, out of this when the because of the super saturation the solute in this case which is the semiconductor that comes from the vapor begins to grow out of that melt into a crystal.

So, one has a gradual growth of a nanowire from this eutectic at an appropriate temperature as the flow of the reactant vapor is continued at an appropriate pace.

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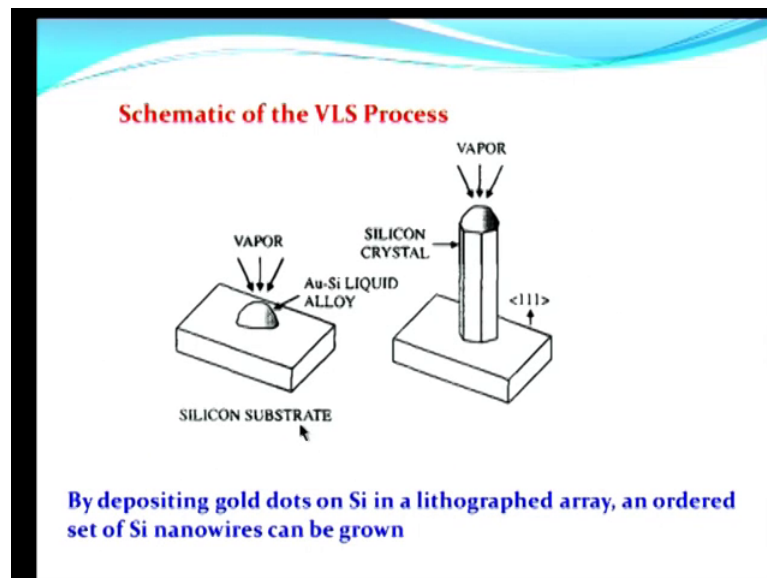
So, this is represented in the cartoon over here in particular one has a small island of gold on silicon let us say we evaporate gold onto silicon in a patterned fashion for example, So, we have a small island of gold and this substrate of silicon on which the gold is deposited is raised to an appropriate temperature appropriately high temperature. So, that the incoming vapor of silane SIH for decomposes into silicon and that silicon becomes a

part of the melt over here. And then as the flow of the nutrient namely SIH for continues then this silicon begins to grow from out of the silicon substrate, carrying with it the gold dot that is silicon is going out of the singlecrystal of silicon which is the substrate and the gold is raised. So, to speak the gold dot is raised and continuously takes in the silane or the silicon from the silane. So, that you have the feedstock for constant continued growth of the nanowire that comes out of the substrate of silicon through the vapor liquid solid process.

So, you have the vapor which is the silane vapor in this case you have the liquid which is the eutectic between the silicon and gold and then the solid which is the silicon wire that goes out of this out of this. And it is a nanocrystal if you make an island of gold that is sufficiently small and these things can be achieved very well through the lithographic process. So, that what one can do is to deposit gold dots on silicon by lithographic process in an array and if you hold this process if you conduct this process the VLS process, under these conditions what you would get is an array of silicon nanowires that is uniformly spaced and usually uniform in diameter because you have a lithographed array of gold dots of a suitable dimension nanometric dimension.

So, this is a very important part of the process for the growth of nanowires that is one dimensional nanocrystalline structures, which have significant device applications actually carbon nanotubes also are grown by a process that is essentially similar to that we will come to that in the next session. So, what we have learned today is about the growth of nanocrystals of metals and semiconductors from a homogeneous nucleation process in a liquid in a solution from a solution.

So, it is possible to obtain metal nanocrystals and in particular gold nanocrystals of very very fine dimensions, but is a very narrow size distribution it is possible also to control the shape and size of crystals of materials like platinum and silver through the use of appropriate growth directing agents in the solution from, which nucleation and growth occurs it is also possible of course, to grow as they have shown single crystals of cadmium selenide zinc sulphide zinc selenide and so on. Through appropriately appropriately designed processes that give us great control over the size of the particles of cadmium selenide zinc sulfide and so on.

We can go on to make cortical structures of one semiconductor over another nanocrystalline structures and then we have come to the consideration of the VLS process through which one dimensional crystals or nanowires of for example, semiconductors like silicon can be grown we will move on to the growth of other semiconductors and carbon nanotubes and so on in the next session.

Thank you.