Nanoelectronics: Devices and Materials

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Lecture - 37
Nanocrystals and nanostructured thin films

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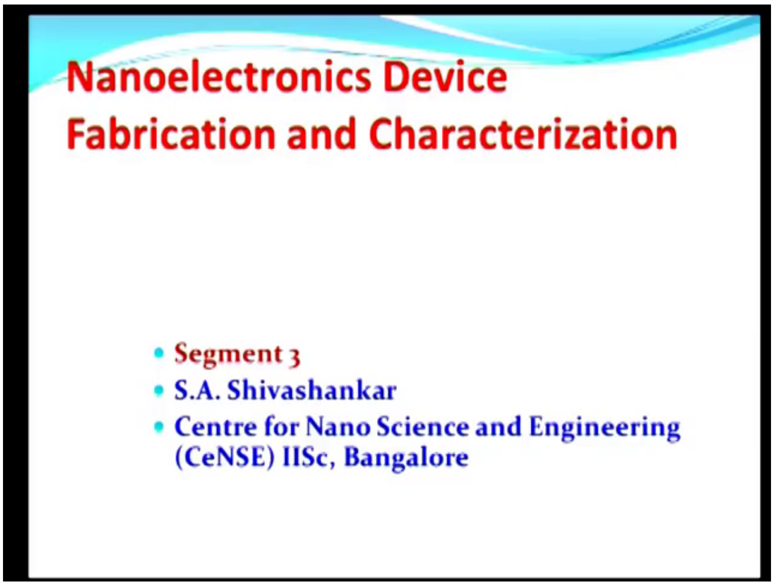

Nanoelectronics Device Fabrication and Characterization

- Segment 3
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Hello, this is the next session of this course or I should say the segment 3 of the course nanoelectronics device fabrication and characterization.

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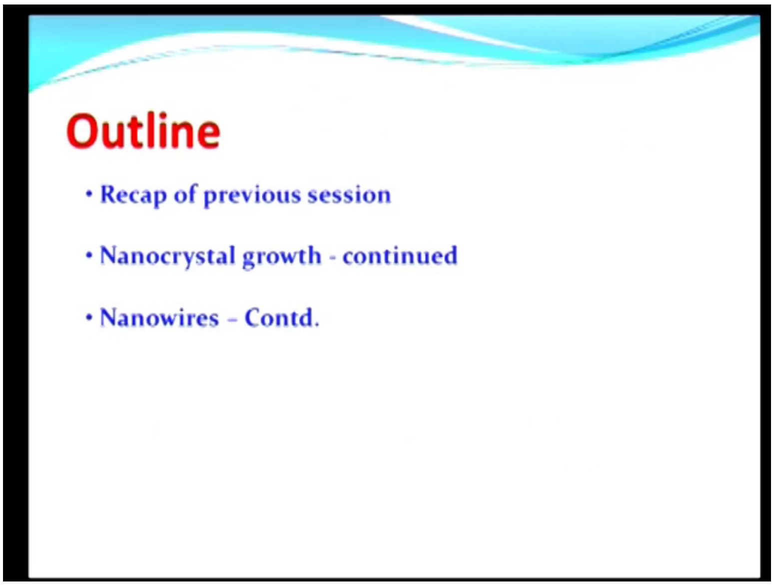

Outline

- Recap of previous session
- Nanocrystal growth - continued
- Nanowires – Contd.

In the previous session, we learned about the nucleation and growth of nanoparticles in a homogeneous medium such as a liquid and then we went onto consider the growth of nanocrystals of metals of semiconductors leading to the formation of quantum dots specifically of cadmium-selenide. And then we discuss the growth of nanowires through the vapor liquid solid or the VLS method. What we shall do is to continue to discuss the growth of nanocrystals and also of nanowires to touch upon certain aspects that are important because what we described last time especially regarding nanocrystal growth was really the protocols for doing so.

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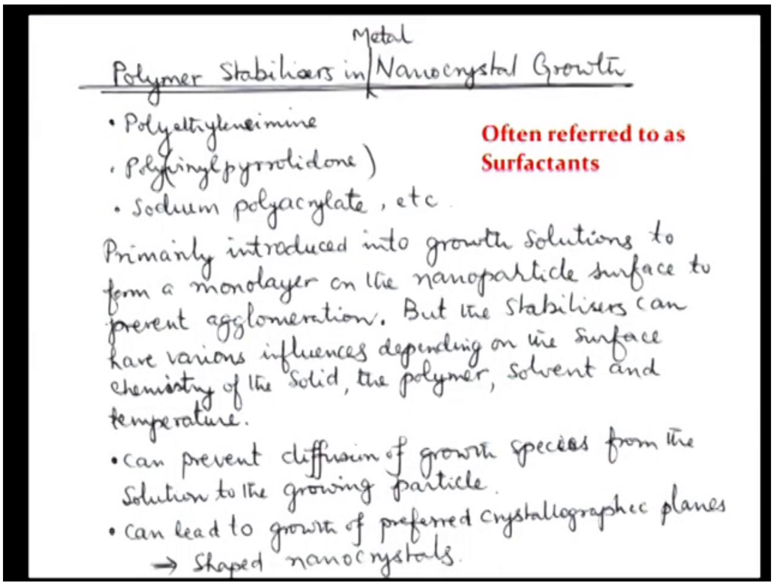

Polymer Stabilisers in Metal Nanocrystal Growth

- Polyethyleneimine
- Poly(vinylpyrrolidone)
- Sodium polyacrylate, etc

Often referred to as Surfactants

Primarily introduced into growth solutions to form a monolayer on the nanoparticle surface to prevent agglomeration. But the stabilisers can have various influences depending on the surface chemistry of the solid, the polymer, solvent and temperature.

- can prevent diffusion of growth species from the solution to the growing particle.
- can lead to growth of preferred crystallographic planes
  → Shaped nanocrystals.

I mentioned last time that crystals of metals nanocrystals of metals especially platinum which I give an example of was affected by the presence of polymers such as sodium polyacrylate, which gave us specific shapes depending on the extent of the polymer present in the solution from which nanocrystals or metals in particular that of platinum are grown. Now, these are known as polymer stabilizers and are very useful for the growth of I should say the controlled growth of nanocrystals in general, and specifically the nanocrystals of metals and semiconductors. There are a number of such polymer stabilizers polyethylenimine, polyvinyl pyrrolidone, sodium polyacrylate and so on.

These are introduced primarily into the growth solution to form a monolayer on the nanoparticle or the crystal that is incipient that is growing. So, it forms a monolayer and the surface of this growing nanoparticles. And the purpose of that is to prevent agglomeration that is we do not want these nanocrystals are formed to agglomerate into entities that are really not individual crystals, but they are really combinations of nanocrystals that are essentially sticking together. So, if one wants to have nanocrystals that are separate from one another that do not become agglomerates aggregates then the use of such polymer stabilizers which form a thin layer on the surface is growing nanoparticle is really very useful indeed essential.

Now, it also turns out that these stabilizers can be used and can have various other influences depending on the surface chemistry of the solid, the polymer under solvent together as well as the temperature. The presence of such polymer stabilizers can for example prevent the diffusion of growth species from the solution to the growing particle that is while we wish to prevent agglomeration, it can also have the effect of preventing growth of the nanoparticle which we may desire to a certain controlled extent. The presence of the polymer stabilizers can also lead to the growth of preferred crystallographic planes that is to the faster growth of certain planes and the relatively slower growth of some other planes, which can lead to shaped nanocrystals.

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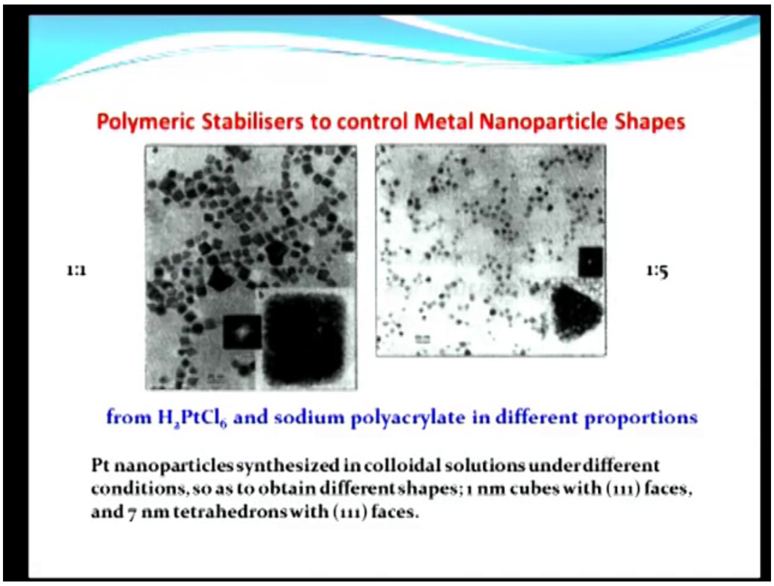

Polymeric Stabilisers to control Metal Nanoparticle Shapes

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.

This is what we saw in the growth of platinum nanoparticles in a solution that contained platinic acid H 2 PtCl 6 and sodium polyacrylates in different proportions. For example, on the left is the solution where the proportion of the two that is the platonic acid and the polymer stabilizer is one to one; and in the second case and right or images of nanocrystals of platinum formed when the sodium polyacrylate is in a much greater proportion that is the proportion is one is to five. So, what this illustrates is that one can actually control the shapes of nanocrystals that are formed using polymer stabilizers or polymer additives to the growing solution from which the crystals are grown in a controlled fashion in a control proportion. And also of course, very often the temperature at which these reactions are conducted that formed the nanocrystals through reduction, the temperature is also an important factor.

What is also an important factor as already mentioned is the solution from which this is grown that is you have H 2 Ptl 6 as well as sodium polyacrylate, these are solutes in a solvent. So, what is the solvent one uses? So, these are all factors that can influence the emergence of nanoparticles of different shapes and different sizes, controlled shapes and controlled sizes.

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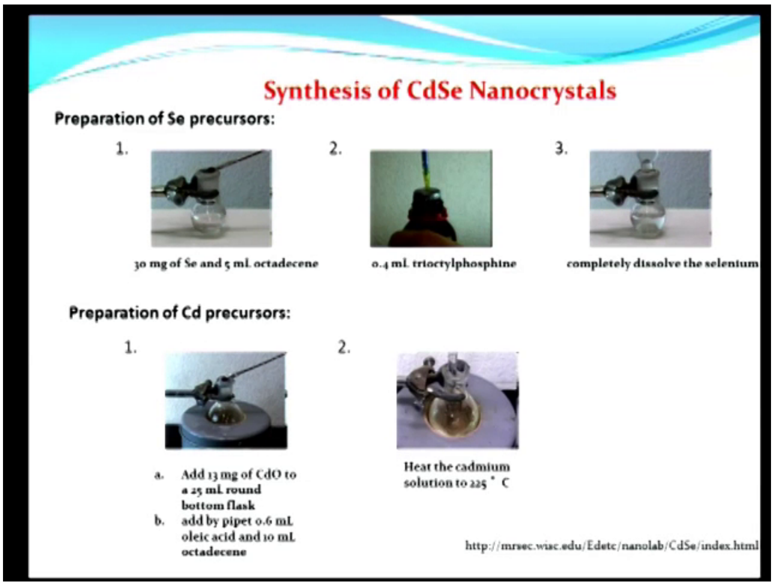

Synthesis of CdSe Nanocrystals

Preparation of Se precursors:

1. 30 mg of Se and 5 mL octadecene
2. 0.4 mL trioctylphosphine
3. completely dissolve the selenium

Preparation of Cd precursors:

1.
   a. Add 13 mg of CdO to a 25 mL round bottom flask
   b. add by pipet 0.6 mL oleic acid and 10 mL octadecene
2. Heat the cadmium solution to 225 ° C

http://mrsec.wisc.edu/Edetc/nanolab/CdSe/index.html

Now, we have referred to the synthesis of cadmium nano cadmium selenide nano crystal last time through protocols that prepare the selenium precursors precursor I should say through the addition of opted a scene triactol, phosphine. And then the preparation of the cadmium precursor which is the cadmium oxide; and then a anoleic acid the solution is prepared again with octadecene and so on.

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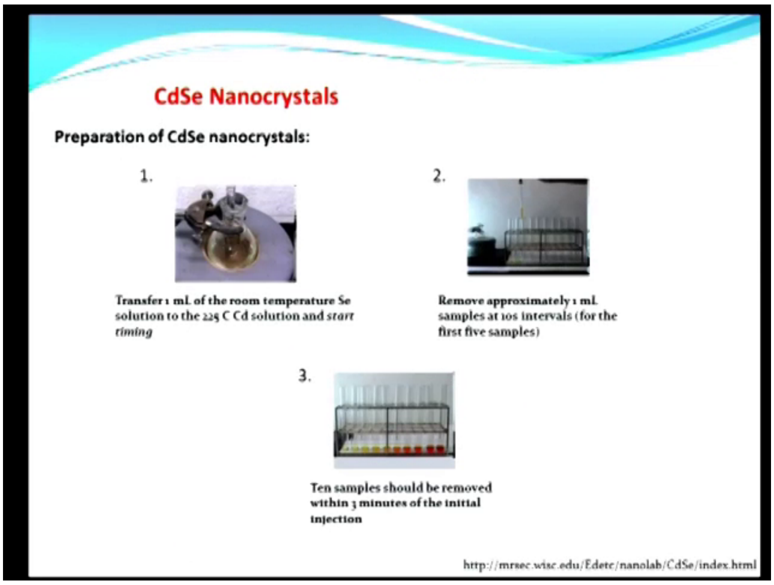

CdSe Nanocrystals

Preparation of CdSe nanocrystals:

1. Transfer 1 mL of the room temperature Se solution to the 225 C Cd solution and *start timing*

2. Remove approximately 1 mL samples at 10s intervals (for the first five samples)

3. Ten samples should be removed within 3 minutes of the initial injection

http://mrsec.wisc.edu/Edetc/nanolab/CdSe/index.html

So, these are subsequently mixed together and as I mentioned last time at an elevated temperature these are made to react so as to form cadmium selenide. And particles of different sizes separated by altering the reaction times that is to take out the solution at intervals of 10 seconds for example, each of those samples taken out at fixed intervals gives us cadmium selenide crystals of a certain size. And of course, the size increases as the reaction time increases.

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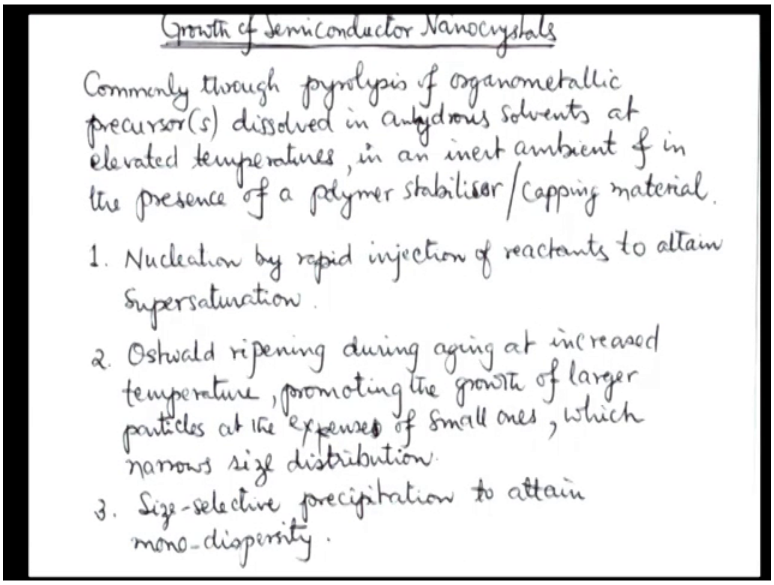

Growth of Semiconductor Nanocrystals

Commonly through pyrolysis of organometallic precursor(s) dissolved in anhydrous solvents at elevated temperatures, in an inert ambient & in the presence of a polymer stabiliser/capping material.

1. Nucleation by rapid injection of reactants to attain supersaturation.
2. Ostwald ripening during aging at increased temperature, promoting the growth of larger particles at the expenses of small ones, which narrows size distribution.
3. Size-selective precipitation to attain mono-dispersity.

Now, what is important to mention in the growth of semiconductor nanocrystals what is important to understand is that the growth of these nanocrystals which are really compound semiconductors occurs commonly through the pyrolysis of organometallic precursors as we have seen here. And unhrdro resolvents what is very important is that there is no hydration and also that there should be an inert ambient for these things. So, usually these are done in organ atmosphere or very dry nitrogen atmosphere or in a glove box, so that there is no possibility of oxygen in trace quantities being present neither should there be any moisture.

And a polymer stabilizer or a capping my so called capping material; in this case, we have occurred a scene for example so they need not be polymers for example, it is often called a capping material. What a capping material does is to literally cap the growth of the nanocrystals to a certain degree or after a certain extent of growth. What is involved in the preparation of compound semiconductor nanocrystals which are really quantum dots as we discussed earlier is that there should be nucleation of the nanocrystals of the compound semiconductor through rapid injection of reactants to attain super saturation. That is you inject them as we have shown last time it is rapidly injected into the solution how much growth takes place and by the rapid injection super saturation is induced. And then a phenomenon that is known as Ostwald ripening is at play during the growth and what Ostwald ripening really means is that as the growth takes place there is a distribution of sizes of these crystals that naturally occurs because some crystals grow larger at the expense of others. So, a certain degree of this growth that is these sizes then ripen Ostwald ripening is the growth of crystals at the expense of smaller one’s growth of larger crystals at the expense of smaller ones.

Now, because of such growth that is the larger crystals essentially eating up the smaller ones, what it does is to reduce these distributions of sizes that is it tends it leads us towards mono dispersity. So, as for rising ripening is a friend in the preparation of quantum dots that were mono disperse. So, Ostwald ripening is therefore, exploited to obtain mono disperse crystals of compound semiconductors and size selective decision precipitation is done as pointed out earlier in the protocol whereby we take out certain amounts of the solution of the growth medium, so that at different intervals we separate out crystals that are of different sizes. So, that is size selective precipitation to obtain mono dispersity which is aided by the phenomenon of Oswald ripening.

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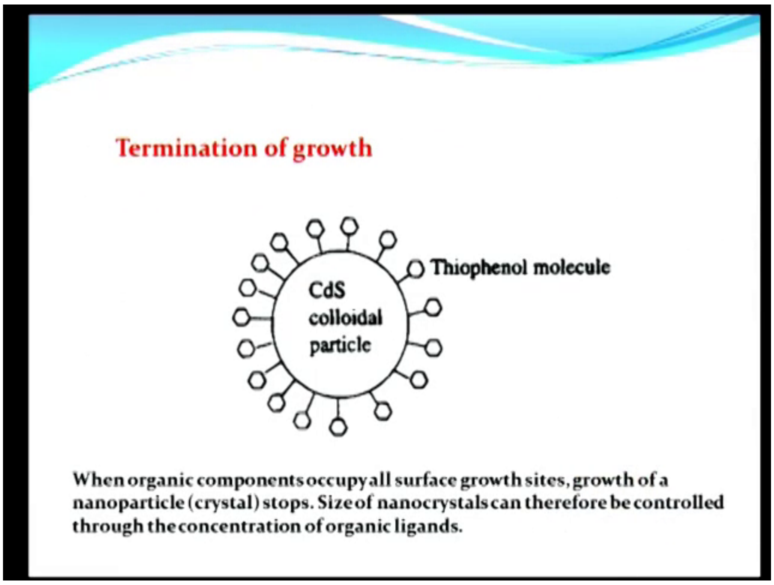

Termination of growth

When organic components occupy all surface growth sites, growth of a nanoparticle (crystal) stops. Size of nanocrystals can therefore be controlled through the concentration of organic ligands.

The termination of growth for example, you know we do not necessarily want growth to go on indefinitely we want to limit it and that can be achieved when the organic components are occupied the surface of the growth sides or covered by that is the growth surface is covered by an organic entity and the presence of such an organic entity as shown in this cartoon can then prevent additional growth. For example, something like this can be injected into the growth solution after the growth has proceeded for a certain interval. So, one can therefore, achieve the termination of growth at a desired stage.

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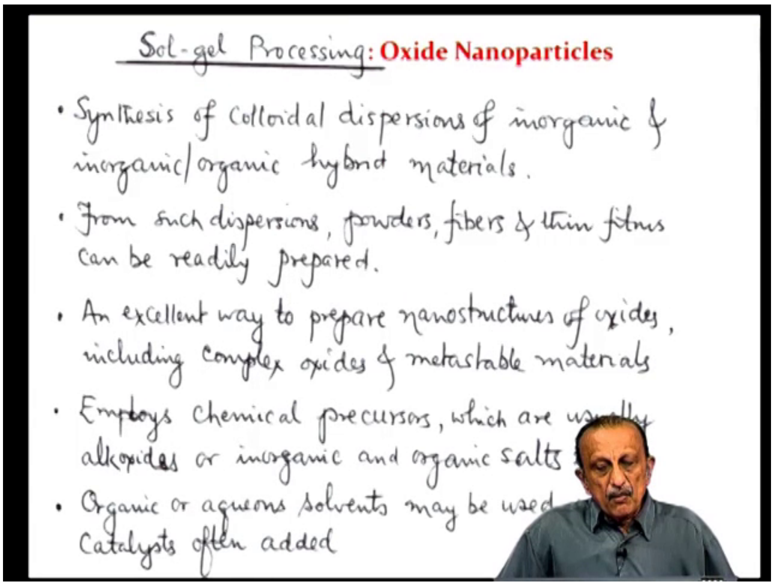

Sol-gel Processing: **Oxide Nanoparticles**

- Synthesis of colloidal dispersions of inorganic & inorganic/organic hybrid materials.
- From such dispersions, powders, fibers & thin films can be readily prepared.
- An excellent way to prepare nanostructures of oxides, including complex oxides & metastable materials
- Employs chemical precursors, which are usually alkoxides or inorganic and organic salts
- Organic or aqueous solvents may be used Catalysts often added

Now, so far, we have dealt with metal nanoparticles nanocrystals I should say all these are nanocrystals. Metal nanocrystals compound semiconductor nanocrystals and earlier we have dealt with nanocrystals in one dimension namely nanowires of semiconductors such as silicon. Many semiconductors are actually oxides often complex oxides and oxides are actually oxide and oxide nanoparticles, nanocrystals of oxides are potentially very important, they have significant applications for example, as catalysts. So, the growth of oxide nanocrystals is also worth looking into, but the method of growth for oxide nanocrystals is significantly different from the method of growth for either metals or compound semiconductors and a process known as sol-gel processing is often employed among other methods.

So, this soldier processing is the synthesis of colloidal involves the synthesis of colloidal dispersions of inorganic and organic hybrids. So, one can obtain inorganic materials like oxides, but can also obtain nanocrystals or nanomaterials of inorganic organic hybrids through such a process. And through this process one can also obtain fibers, powders, thin films and so on. So, it is a versatile method for the preparation of oxide primarily oxide materials or hybrids or contain oxides. As I said it is also an excellent way of making complex oxides such as peroxide, such as ferrite and so forth peroxides are AB O 3 oxides, ferrites are AB 2 O 4 oxides and so forth. And these have significant applications, for example, Ba T i O 3 a perovskite is a very important piezoelectric material. Sol-gel processing involves chemical precursors which are usually alkoxides or inorganic and organic salts. And it involves organic or aqueous solvents which may be used often with catalyst added to the solution to get the process going at a desired rate.

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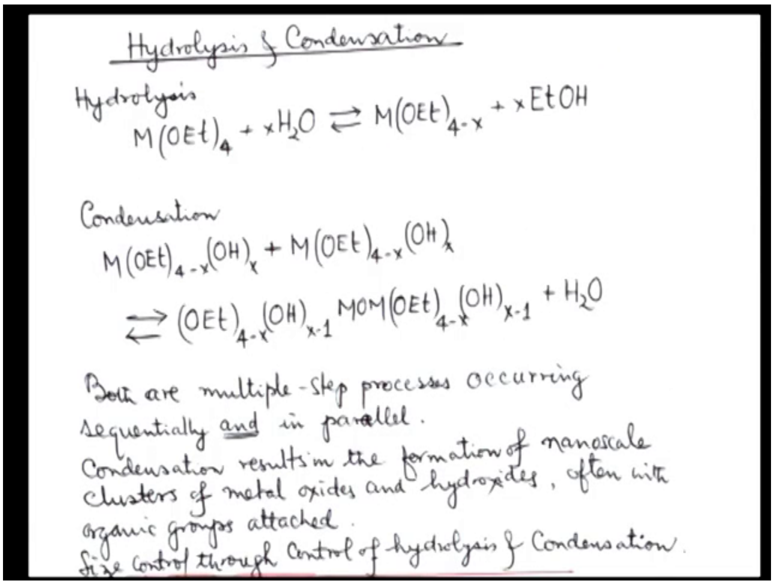

Hydrolysis & Condensation

Hydrolysis

$$M(OEt)_4 + xH_2O \rightleftharpoons M(OEt)_{4-x} + xEtOH$$

Condensation

$$M(OEt)_{4-x}(OH)_x + M(OEt)_{4-x}(OH)_x$$

$$\rightleftharpoons (OEt)_{4-x}(OH)_{x-1}MOM(OEt)_{4-x}(OH)_{x-1} + H_2O$$

Both are multiple-step processes occurring sequentially and in parallel.

Condensation results in the formation of nanoscale clusters of metal oxides and hydroxides, often with organic groups attached.

Size control through control of hydrolysis & Condensation.

The soldier process contains two steps two aspects so called hydrolysis and condensation. So, in the example shown we have a metal ethoxide OEt 4 is a Et stands for the ethyl group C 2 H 5. So, we have a metal eathoxide which is one of the alkoxides; alkoxides are very, very fond of moisture. So, they quickly take up water or moisture and form the kind of there is hydrolysis and the formation of a complex as I shown here where some of the water is taken up by the ethyl group. And then there is condensation, so this moiety over here that is shown this moiety takes up hydroxyl moieties and we have eventually the formation of this complex entity due to condensation. Both of these steps hydrolysis and condensation or multiple step processes pretty complex processes and they may occur sequentially, they may occur simultaneously depending on how exactly the process is designed. This condensation step that is shown here results in the formation of nano scale clusters of metal oxides and hydroxides as you can see here, this is an entity and depending on the aging of this how long one carries out this process one can obtain through this a metal oxide or a hydroxide often with an organic group attached to it and so on. So, this is the result of the condensation process which is then subsequently heat treated to obtain the desired oxide material oxide structures.

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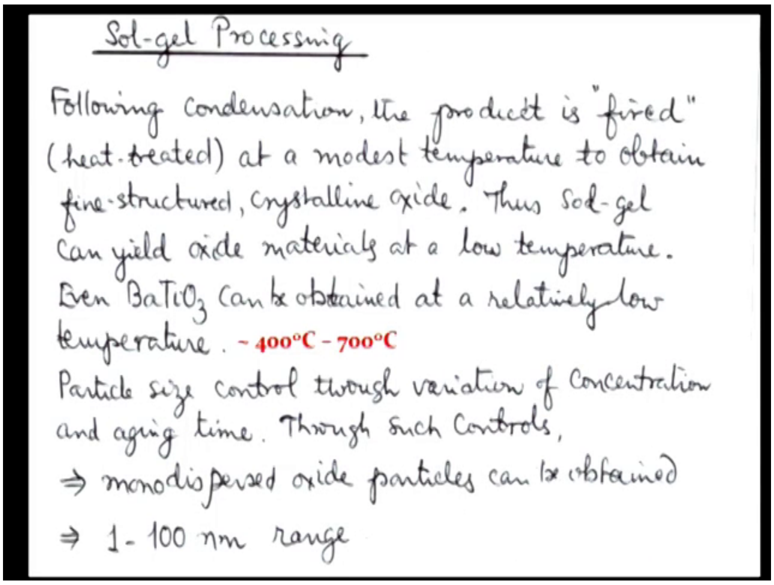

Sol-gel Processing

Following condensation, the product is "fired"
(heat-treated) at a modest temperature to obtain
fine-structured, crystalline oxide. Thus Sol-gel
can yield oxide materials at a low temperature.
Even $BaTiO_3$ can be obtained at a relatively low
temperature. ~ 400°C - 700°C
Particle size control through variation of concentration
and aging time. Through such controls,
⇒ monodispersed oxide particles can be obtained
⇒ 1- 100 nm range

So, following condensation the product is fired which means that heat treated to a modest temperature, modest by the standards of oxides, oxides often require high temperatures for formation, but the sol gel process reduces the temperatures that are required to obtain oxides and oxide nanostructures to a significant degree. And it also allows us to obtain as a result fine structured crystalline oxides nanostructured crystalline oxides for example, barium-titanate Ba Ti O 3 which I just mentioned a moment ago is obtained at a relatively low temperature of 400 to 700 degrees whereas, by a different process usually this, so called solid state reaction process the temperature is required for obtaining barium titanate is more than a 1000 degrees. So, a significant reduction in temperature is achieved by the use of sol gel processing.

And precisely because much lower temperatures are used it is positive it becomes possible to obtain much smaller sized crystals or nanocrystals. Size control of these particles is possible through the variation of concentration of the reactants. And by controlling these so called aging time how long one lets the sol gel process proceed., so it is possible through such controls to obtain mono disperse oxide particles in the range of 1 to 100 nanometers in size. A number of oxides can be prepared really there is no essential restriction on what kind of oxides can be prepared usually some kind of a metal complex or an alkoxide is possible for almost any useful metal.

Now, one important aspect that we should keep in mind over here which I think I probably did not mention earlier is that a way to restrict the size of crystals that is to limit them to the nanometric regime is to have processes design processes conduct processes of growth at a low temperature that is simply the kt so called k t factor. For crystals grow the species that are involved in the growth have to have sufficient energy to move about and therefore to have the energy to assemble together to become larger pieces, larger crystals. Therefore, when a when the temperature is low this energy is low and therefore, first of all the process is slow and secondly, because of the limited mobility of the growth species, the growth rate is low and therefore, becomes controllable. And often one can have very excellent control over the growth rates by controlling the temperature at which these reactions are conducted. And by limiting the temperature at which these reactions are conducted.

Another thing that one could remember one could one could note in this context is that one way to prevent crystallization essentially obviate crystallization is to go from a high temperature to a low temperature very rapidly that is through quenching temperature quenching. So, if you had a melt for example, and therefore you could take the melt from a relatively high temperature which is melting point to room temperature very rapidly by quenching then the kinetics are the process do not allow for crystallization to take place and one could end up with amorphous material, because no time is allowed for the relaxation of these growth species into equilibrium positions which they would occupy in their crystalline state. So, not only can one obtain nanomaterials through this kind of rapid cooling, controlled rapid cooling one can all together prevent crystallization from taking place to obtain amorphous materials, even metals which tend to crystallize very readily can be obtained in amorphous form through this quenching process.

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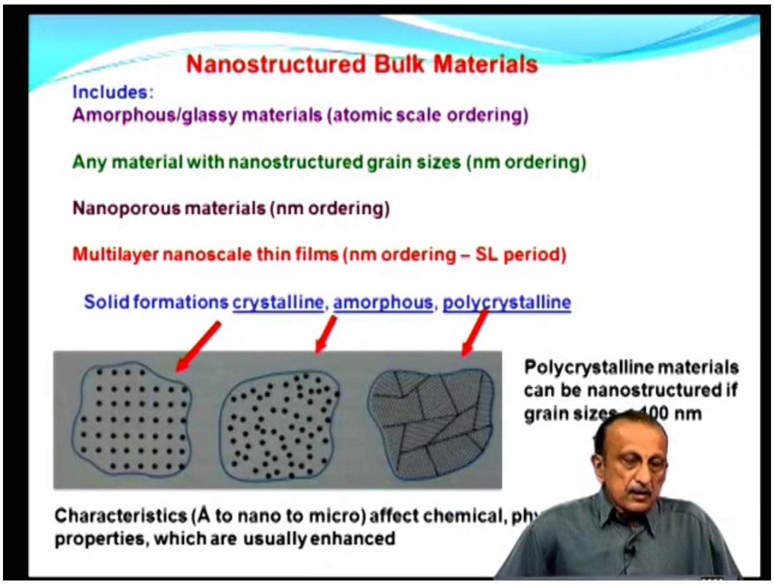

Nanostructured Bulk Materials

Includes:

Amorphous/glassy materials (atomic scale ordering)

Any material with nanostructured grain sizes (nm ordering)

Nanoporous materials (nm ordering)

Multilayer nanoscale thin films (nm ordering – SL period)

Solid formations crystalline, amorphous, polycrystalline

Polycrystalline materials can be nanostructured if grain sizes < 100 nm

Characteristics (Å to nano to micro) affect chemical, ph
properties, which are usually enhanced

It is also important to remember that not only can you have nanocrystals nanorods nanowires and so forth, but one can also have bulk materials that are nanostructured. I just mentioned amorphous and glassy materials, I just mentioned amorphous materials through quenching and one of these things is through quenching a melt from high temperature you would get amorphous a glassy material and that is nanostructured often altogether non-crystalline. So, that is an example of bulk materials which are very finely structured nanostructured if it is crystalline.

One can have nanoporous materials that is bulk materials with substantial macroscopic dimensions, but with porosity on a nanometer scale. So, these are for example, the zeolite materials I do not know whether we will have time to actually go through zeolites as a class of materials, but zeolites which are very important as catalyst materials are these porous materials mesoporous for example, or micro porous. So, that they have very large pores inside which act as sites for catalytic reaction promoting catalytic reaction. Multilayer thin films which we mentioned in passing at least last time where we discussed processes like molecular beam epitaxially and MOCVD, so that one can get multiple layers, multiple quantum wells super lattices and so forth, even though individual layers there would be nanometric in range you can have a stack of layers that together is substantial apart from having a relatively large area for each layer only the layer thickness is small, so that would be a nanostructured bulk material.

And such materials would behave like bulk materials for example, the band gap of gallium arsenide that is 3 nanometers thick or 10 nanometers thick that is grown by an epitaxial method is the same as the band gap of bulk gallium arsenide crystals because the way it is grown it is not a nanoparticle, but a nanometric single crystalline layer. Therefore, its behavior is that of a macroscopic gallium arsenide crystal, but we form quantum wells by alternately layering or sandwiching a gallium arsenide layer between gallium aluminum arsenide on either side laser only gallium aluminum arsenide on either side. So, all these are examples of nanostructured bulk material.

Now such nanostructured bulk material would for example, comprise nanocrystals that are compacted together. You can have nano composites where for example, you have individual components in the composite each of which is nanostructured, but then put together often through a process such as you know pressing them together and so on that results in a nanostructured bulk material it could be an alloy for example. So, in this case the nanostructuring of the material even though it is bulk, the nano structuring affects its chemical physical mechanical properties and often these properties are enhanced if the individual components are if the parts of the nanostructured bulk material or are the constituents are nanostructured. We have bulk material of which the constituents are nanostructured and as a result of it you have enhancement of certain properties depending on the nature of the come components nature of the constituents of such nanostructured bulk material. So, it is important to remember that we do not necessarily mean only quantum dots or nanowires and so forth when we talk about nanomaterials nanostructured bulk materials or an important aspect of nanomaterials.

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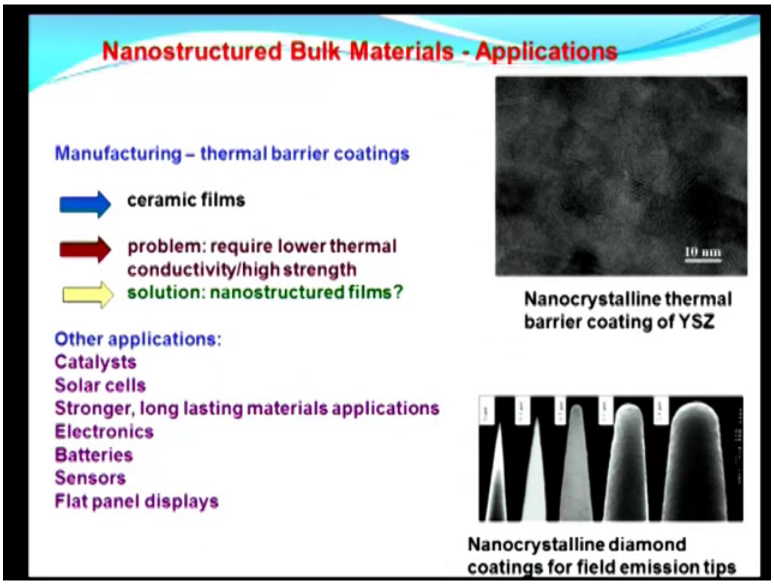

Nanostructured Bulk Materials - Applications

Manufacturing – thermal barrier coatings

- ceramic films
- problem: require lower thermal conductivity/high strength
- solution: nanostructured films?

Other applications:
Catalysts
Solar cells
Stronger, long lasting materials applications
Electronics
Batteries
Sensors
Flat panel displays

Nanocrystalline thermal barrier coating of YSZ

Nanocrystalline diamond coatings for field emission tips

Examples here you know for an important aspect of nanostructured bulk material or the so called thermal barrier coatings where you have nanostructured material as shown in this micrograph of yttrium stabilized zirconia over here where you can see nanocrystals regions of crystalline zirconia. And such materials are so called thermal barrier coatings which are able to withstand or which are able to support large thermal gradients for example, in the exhaust of jet engine. As an application include catalyst as already mentioned solar cells batteries and so forth. So, all these are examples of applications of nanostructured bulk material.

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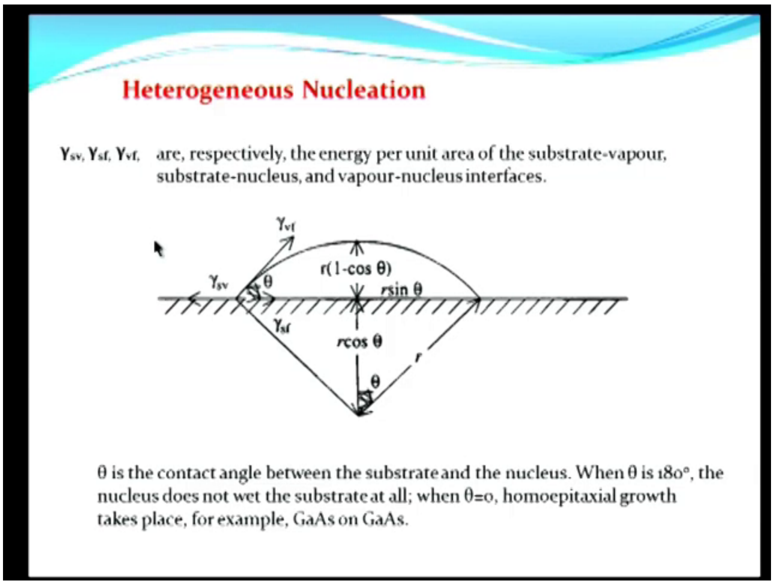

Heterogeneous Nucleation

$\gamma_{sv}, \gamma_{sf}, \gamma_{vf}$ are, respectively, the energy per unit area of the substrate-vapour, substrate-nucleus, and vapour-nucleus interfaces.

θ is the contact angle between the substrate and the nucleus. When θ is 180°, the nucleus does not wet the substrate at all; when θ=0, homoepitaxial growth takes place, for example, GaAs on GaAs.

Last time we mentioned homogeneous nucleation where we studied how nucleation is a result of the balance of energies, how the Gibbs free energy and the components of the Gibbs free energy then drive the formation of nuclei within the homogeneous medium. In heterogeneous nucleation, what you have is nucleation taking place for example from the liquid phase onto a solid surface or from the gas phase onto a solid surface. So, this is heterogeneous nucleation in the context of nanomaterials.

Now, what is shown here is a graph is a figure that sketches the formation of a nucleus on a flat surface that is shown here. So, you have a solid surface and a nucleus is formed over here that has this kind of a shape approximately a part of a sphere. In such a nucleation process then various energies surface energies surface energies per unit area at the different interfaces that are present play a role. Theta is the contact angle of this nucleus, theta is shown here there is a contact angle. And the different energies are gamma s v, gamma s f and gamma v f. These are the respective energy per unit area at the substrate vapor we have because we are nucleating from the vapor on a solid substrate. So, gamma s v represents the substrate vapor interfacial energy and then you have the substrate nucleus interfacial energy over here because the nucleus is forming on the substrate and then you also have the vapor nucleus interface.

So, you have 3 interfacial energies that are involved in the formation of this nucleus due to a heterogeneous process. If theta is 0 sorry let us begin with theta being 180 degrees that is this theta is 180 degrees. So, then what you have really you would have a sphere whatever sphere a droplet sitting on the surface not wetting the surface at all. So, no nucleation has taken place because really then you have nothing that is attached or bound to the substrate surface of the growth surface. Whereas, when theta equals 0 that is this one this this nucleus is making a zero-contact angle with the substrate surface, then you really have complete wetting of the substrate surface by the nucleus that is formed from the heterogeneous medium.

This for example, would be the case of homogeneous epitaxy or homoepitaxy where for example, gallium arsenide can grow on a crystal of gallium arsenide as simply an extension of the crystal that is suppose I have a nucleus a gallium arsenide and the substrate is gallium arsenide. Let us say the substrate is a single crystal of gallium arsenide. So, this nucleus then becomes simply an extension of the crystal that is underneath that is called epitaxial growth on top of epitaxial means on top of. So, this growth of gallium arsenide on gallium arsenide. So, it is one and the same material. So, that is the case where the contact angle is 0, so that is a sort of a simple case of heterogeneous nucleation.

But a very important part of it I mentioned this last time MOCVD metal organic chemical vapor deposition more accurately called OMVPE that is organo metallic vapor phase epitaxy that is a process whereby one grows a material like gallium arsenide or gallium aluminum arsenide on gallium arsenide itself. So, one grows a thin layer of gallium aluminum arsenide on gallium arsenide and that becomes possible because the lattice constant of gallium arsenide is substantially the same as the lattice constant of gallium aluminum arsenide. So, it is a case of homo epitaxy. And in that case, the vapor contains these species that are responsible for gallium arsenide on gallium arsenide. So, one brings in a species in this particular case a compound called a trimethyl gallium.

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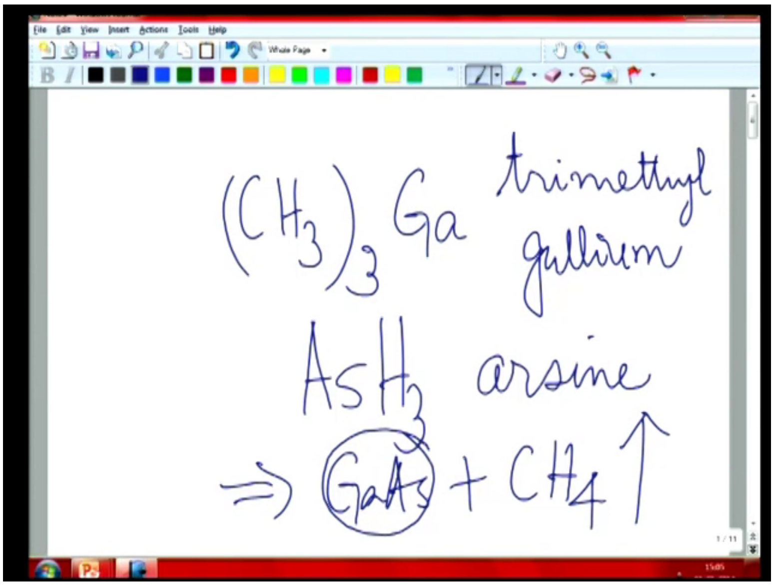

$(CH_3)_3Ga$ trimethyl gallium

AsH_3 arsine

$\Rightarrow \boxed{GaAs} + CH_4 \uparrow$

That is so you have tri methyl gallium and the vapor also brings in another component arsine. So, this is the arsine gas. So, this is trimethyl gallium. So, these two combined together on the substrate surface to give us gallium arsenide and they liberate methane which is a gas and escapes from the surface. So, this is heterogeneous nucleation of gallium arsenide on gallium arsenide and as I said in such a case there is zero contact angle and very easy growth of the film on the substrate.

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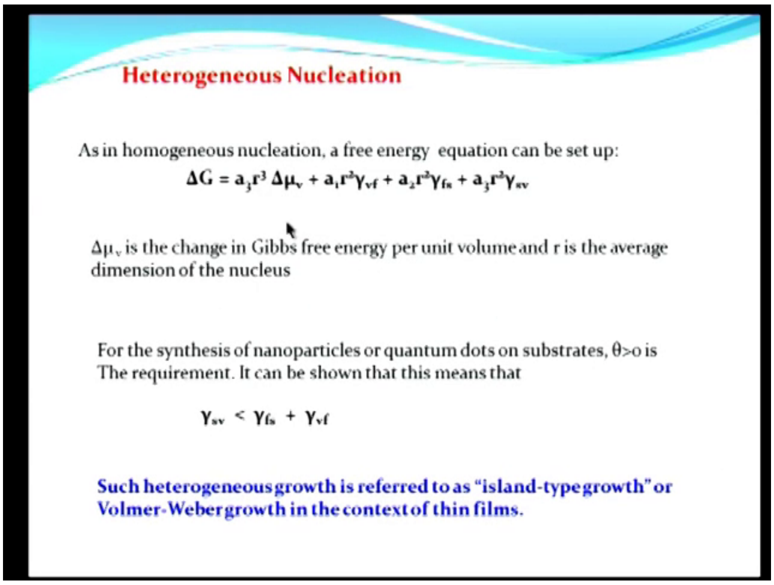

Heterogeneous Nucleation

As in homogeneous nucleation, a free energy equation can be set up:

$$\Delta G = a_3 r^3 \Delta\mu_v + a_1 r^2 \gamma_{vf} + a_2 r^2 \gamma_{fs} + a_3 r^2 \gamma_{sv}$$

$\Delta\mu_v$ is the change in Gibbs free energy per unit volume and r is the average dimension of the nucleus

For the synthesis of nanoparticles or quantum dots on substrates, $\theta > o$ is The requirement. It can be shown that this means that

$$\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$$

Such heterogeneous growth is referred to as "island-type growth" or Volmer-Weber growth in the context of thin films.

Now, again as in the case of homogeneous nucleation, one has to take account of the different components of the Gibbs free energy which are listed here the different surface energies or being the radius or being the radius of this nucleus average radius of this nucleus and delta mu v is the change in the Gibbs free energy per unit volume as a result of this nucleation. And the different components of this interfacial energy I have just described, so one sets up this delta G and of course, delta G has to be negative in order for nucleation to take place spontaneously.

Now, one can show through a detailed analysis that is why for example here in this diagram we have shown the contact angle and the different components and so forth. By using this diagram, one can write down the different terms over here in terms of or and the cosine theta and so forth. And one can arrive as a result of this analysis that if this gamma s v is less than the sum of the other two interfacial energies then in that case so called island-type growth takes place that is one gets islands of that is we get crystalline material formation due to nucleation on the surface that is one would get islands over here. For example, one would get crystals forming on the surface of the crystal of the substrate and these would be nanocrystals that is you now have nucleation of the nucleation on the substrate of the material of which for example, you may want quantum dots that is you want to grow nanocrystals due to heterogeneous nucleation on the surface.

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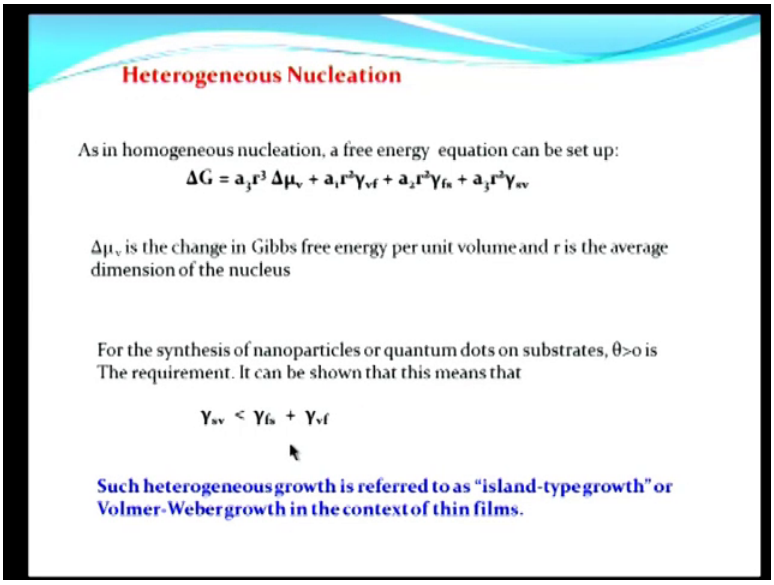

Heterogeneous Nucleation

As in homogeneous nucleation, a free energy equation can be set up:

$$\Delta G = a_3 r^3 \Delta\mu_v + a_1 r^2 \gamma_{vf} + a_2 r^2 \gamma_{fs} + a_3 r^2 \gamma_{sv}$$

$\Delta\mu_v$ is the change in Gibbs free energy per unit volume and r is the average dimension of the nucleus

For the synthesis of nanoparticles or quantum dots on substrates, $\theta > o$ is The requirement. It can be shown that this means that

$$\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$$

Such heterogeneous growth is referred to as "island-type growth" or Volmer-Weber growth in the context of thin films.

That is what happens when this condition is satisfied. So, one gets island type growth and is there is a name for it attached to two scientists is called the Volmer-Weber growth mode which is important in the context of thin film growth we shall come to that I think and in the next session. So, heterogeneous nucleation therefore leads to the formation under these conditions of quantum dots on this surface due to nucleation from for example, the vapor phase.

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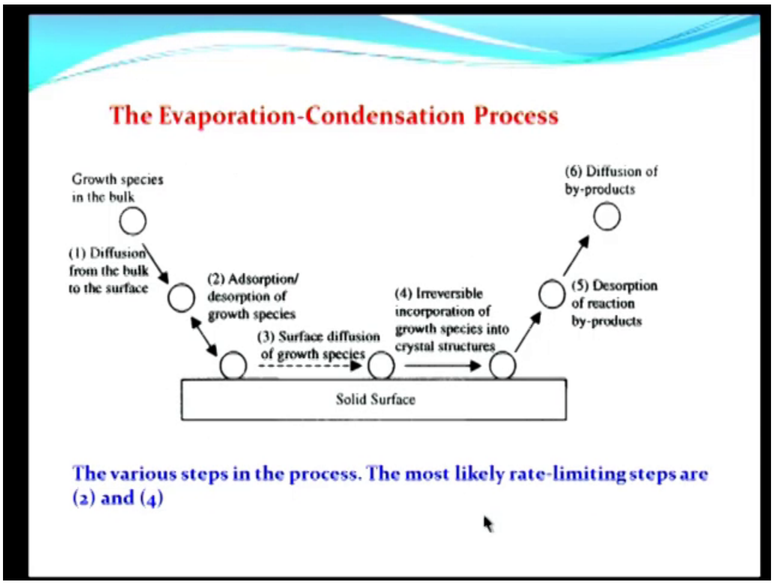

The Evaporation-Condensation Process

The various steps in the process. The most likely rate-limiting steps are (2) and (4)

Now, the context in which this becomes relevant is a so called evaporation condensation process that is you have a substrate or the solid surface on which you want to have nucleation to take place either to give you quantum dots or nanocrystals or give you a continuous film which may comprise calm quantum dots or which may really be an epitaxial surface of a very small thickness as we mentioned earlier. So, in this evaporation condensation process, clearly you have a heterogeneous growth process taking place you have evaporated think of evaporating some material and then collecting them or condensing them on a substrate surface. That process as shown in this cartoon is a multi step process in the bulk of the vapor let us consider this vapor. So, in the vapor phase, you have to create the growth species that you are interested in collecting on the substrate in a crystalline form.

Now, these have to diffuse from the bulk diffuse on the bulk on to the substrate surface of the growth surface where we want to have this heterogeneous growth taking place nucleation and growth taking place. So, they have to defuse on the bulk of the vapor on to this surface and then they have to get adsorbed onto the surface. They may get dissolved also you know without really having much of a dwell time on the substrate surface usually the substrate surface is at some elevated temperature not necessarily at a low temperature. So, usually this lands on a substrate that is reasonably at an elevated temperature, therefore adsorption is not guaranteed there can be enough energy for this growths specie to just get ejected out of the growth surface because the buccal surface is hotter. And those species that get adsorbed on the surface can have mobility all along the surface diffusion of the growth species.

Remember we are interested in the growth of crystals on this surface from the vapor phase. So, there is diffusion along the surface of the substrate. And then when this takes place that is when you have the chance of nucleation of a crystal and the growth of a crystal. What you want to have is irreversible incorporation of the growth species into a crystal structure to begin with of course, a nanostructure a nanocrystal. And this one as we just now described in the case of gallium arsenide you actually have a chemical reaction taking place. And if that is the case then you have the desorption of reaction byproducts such as for example, methane as I showed you just a moment ago.

So, you have the desorption of the reaction byproducts and then of course, really these byproducts such as methane that is in the vapor phase would get diffused out of this chamber this this vicinity. So, this process has to continue where there is diffusion of the growth species onto the surface it gets adsorbed on the surface is mobile on the surface due to diffusion gets incorporated into crystals and so on. So, this process has to continue for the growth of a crystal for the nucleation to occur and for the nucleation to lead to growth.

So, there are multiple steps this is a pretty complicated process actually of these six steps that are shown here it turns out that the most likely rate limiting steps that is the ones that control the rate of growth of the nanocrystal on the surface the ones that control the growth or the rate limiting step or step number two namely the adsorption of the growth species onto the growth surface. And then the incorporation of these growth species into a growing crystal. So, these two are usually the rate limiting steps.

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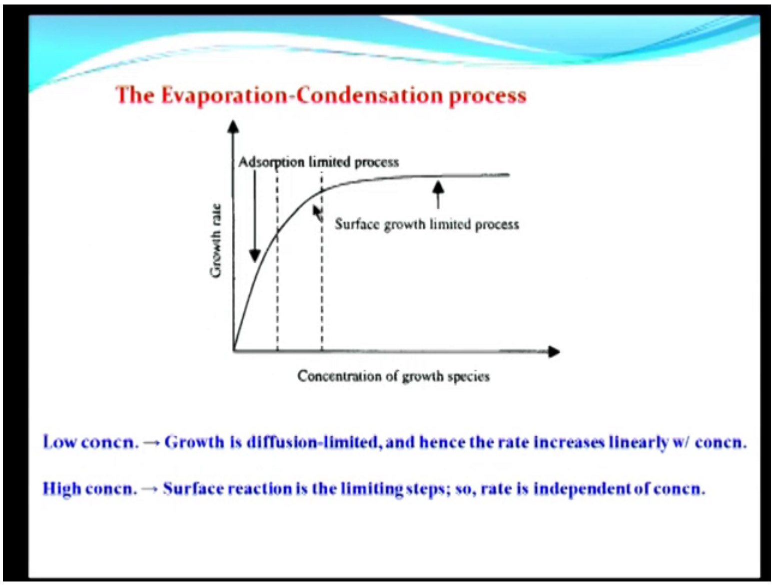

The Evaporation-Condensation process

Low concn. → Growth is diffusion-limited, and hence the rate increases linearly w/ concn.

High concn. → Surface reaction is the limiting steps; so, rate is independent of concn.

Now continuing if you have a low concentration of the growth species in the vapor remember the growth species is coming here in the vapor form because we have evaporated it in some fashion. So, these are coming through the vapor phase. So, if the concentration of the growth species in the vapor phase is low then the growth process is adsorption limited there is not enough of flux of the growth species onto the growth surface. Therefore, as at low concentrations what we have is growth rate of your crystal due to heterogeneous nucleation on the growth surface as a function of concentration of the growth species. So, at low concentrations on the left hand side, you do not have enough of flux onto the growth surface, therefore, the growth process is adsorption limited and essentially there is a linear increase in the growth rate as this flux of the growth species or the concentration of the growth species is gradually increased.

But when the concentration of the growth species is sufficiently high then what is happening is there is a lot of impinging of the growth species onto the substrate surface, but there is too much of that happening. Therefore, surface reaction namely the adsorption of the species and then the joining of the species into the growing crystal that becomes the limiting step because there is too much flux not enough time so to speak not enough room for the surface reaction to proceed therefore, that becomes the rate limiting step. Therefore, when the concentration is increased beyond a certain level concentration of the growth species in the vapor phase when that is increased beyond a certain level then what happens in the surface becomes the or what cannot happen I should say becomes the limiting step. As a result of it there is a saturation of the growth rate beyond a certain level of concentration of the growth species in the vapor phase.

So, this is a broad general description of heterogeneous nucleation process. And what I want to recall here is that this is a very important process for nanostructure growth both for example, in the formation of nanostructure nanocrystals quantum dots and so forth, and also in the formation of films on a substrate surface as I said we will probably return to this in the next session.

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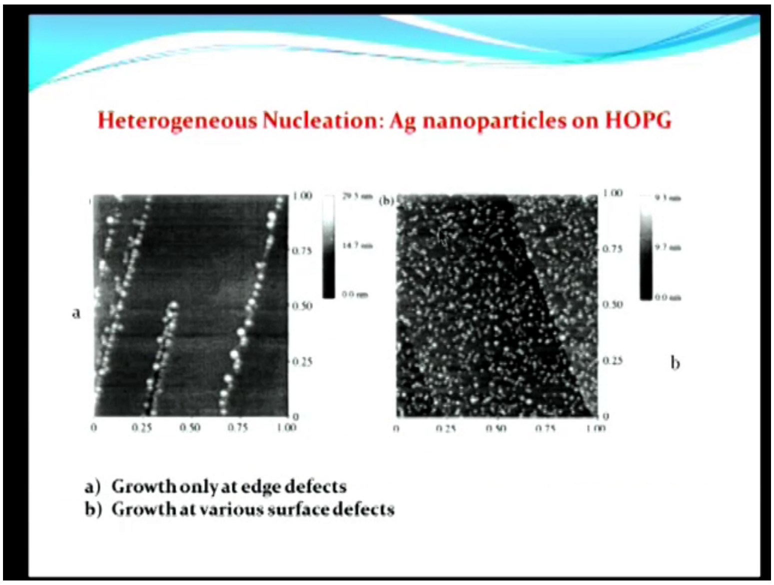
Heterogeneous Nucleation: Ag nanoparticles on HOPG

a) Growth only at edge defects
b) Growth at various surface defects

So, here are examples of heterogeneous nucleation, nucleation of in this case evaporated silver on highly oriented pyrolytic graphite substrate HOPG stands for highly oriented pyrolytic graphite. What you can see here is that on the in the image on the left you have a series of dots that are essentially in a line. So, what is happening here is growth is taking place at defects along an edge. So, these are so called edge defects. Defects often are the sites of nucleation that is where the conditions for nucleation are often more easily satisfied than in places where the crystallinity is perfect. So, defects in the HOPG edge defects then becomes they become the host for nucleation. On the right hand side is a case where you have a sample of HOPG with numerous defects on its surface and therefore, there is a more or less homogeneous nucleation of silver nanoparticles on the surface of the HOPG substrate from evaporated silver. So, these are specific illustrations of the formation of nanocrystals from the evaporation condensation process.

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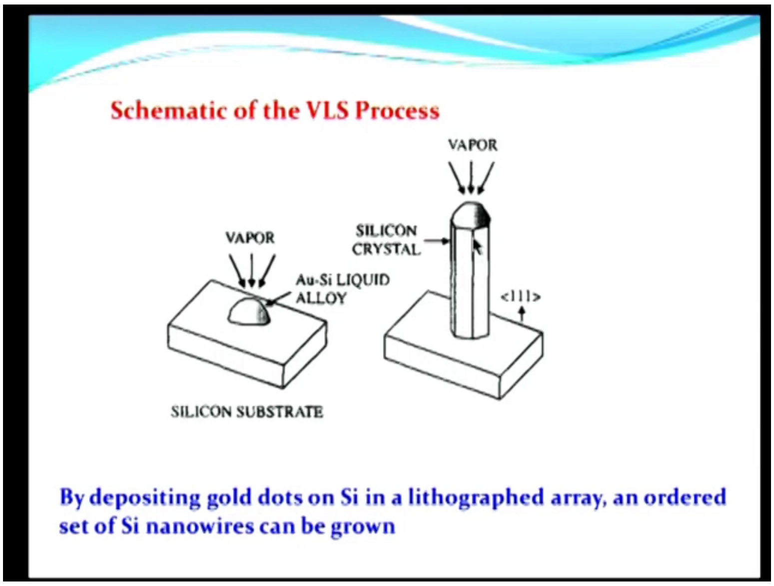

Schematic of the VLS Process

By depositing gold dots on Si in a lithographed array, an ordered set of Si nanowires can be grown

Then we return to the VLS process which we discussed last time, the vapor liquid solid process whereby nanocrystalline or other crystalline nanowires are nanorods of semiconductors or formed because of the formation of a eutectic in this case of silicon in gold. So, what we have is a goal droplet at an elevated temperature, and this is a very small droplet sized in nanometers. And at this elevated temperature, if you had for example flowing into this substrate if you had silane gas Si H 4, which decomposes into silicon and that silicon becomes a part of this eutectic over here and then this whole thing is sitting on a single crystal of silicon and progressively then there is the growth of or the crystallization of silicon from this eutectic and the gold droplets then gets gradually lifted due to the growth process. And the growth process continues because the vapor then continuously becomes a part of this eutectic solvent from which this nanocrystal gradually picks up the nutrient namely silicon to grow continuously with the orientation that is the orientation of the underlying substrate which is silicon 111.

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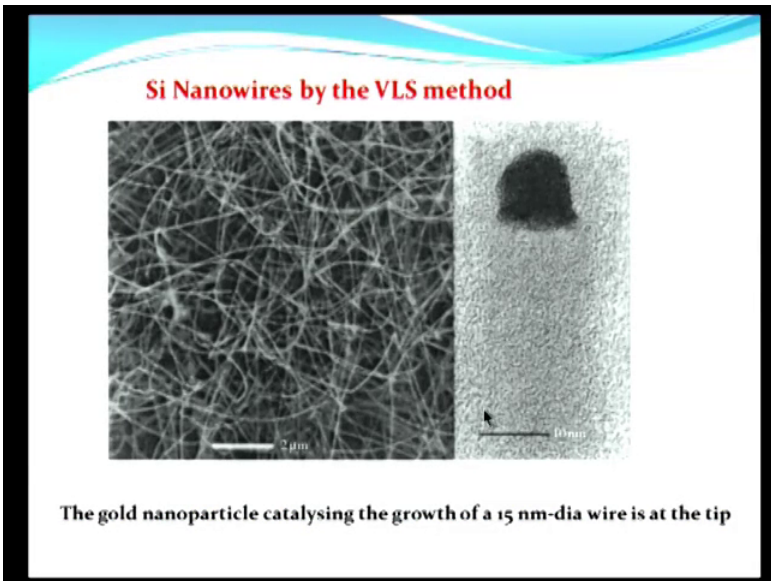

Si Nanowires by the VLS method

The gold nanoparticle catalysing the growth of a 15 nm-dia wire is at the tip

This is an example of silicon nanowires grown by the VLS method and what you can see here in a TEM micrograph transmission electron micrograph is the gold cap as we showed here this is the gold cap. This catalyst particle that is a part of the growth process so that gold cap is now at the top of this silicon nanowire which measures about 15 nanometers in diameter so that forms a tip of this nanowire. And you can see this forest of nanowires that on go on by the VLS method whereby one has gold nano dots that are in on a substrate. And in this case for example, those gold dots are not necessarily in a lithographed pattern gold dots are there and then there is a significant flux of silane that comes into it. And essentially this is an uncontrolled growth of silicon nanowires, but what this illustrates is that pretty long wires this scale is 2 micrometers. So, you can see that pretty long wires can be formed as a result of this process. So, high aspect ratio wires can be obtained in such a way as to define a one-dimensional crystal a nanocrystal one dimensional system.

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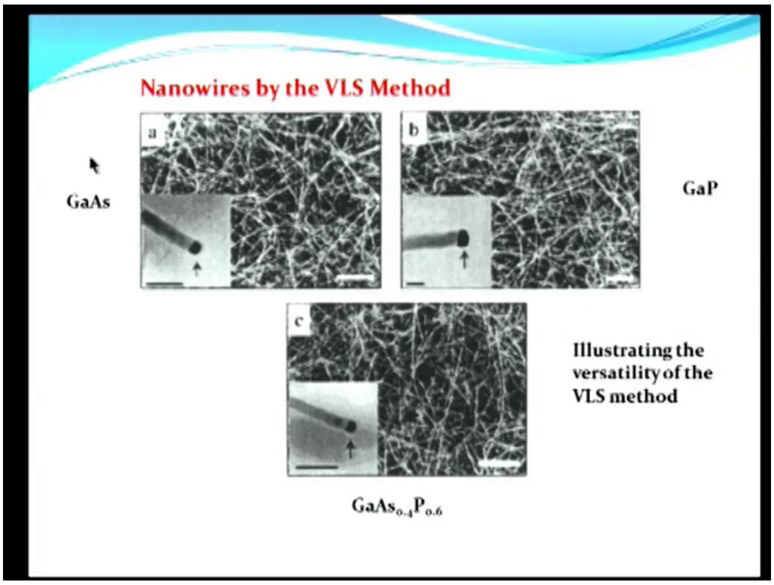
Nanowires by the VLS Method

GaAs

GaP

Illustrating the versatility of the VLS method

$GaAs_{0.4}P_{0.6}$

So, these are cases of or examples of gallium arsenide nanowires being grown by a similar method gallium phosphide and in this case gallium arsenide phosphide which is another compound semiconductor. The point is that these examples show that this method VLS method is a versatile method to obtain nanostructured crystals or nanowires of a variety of compositions.

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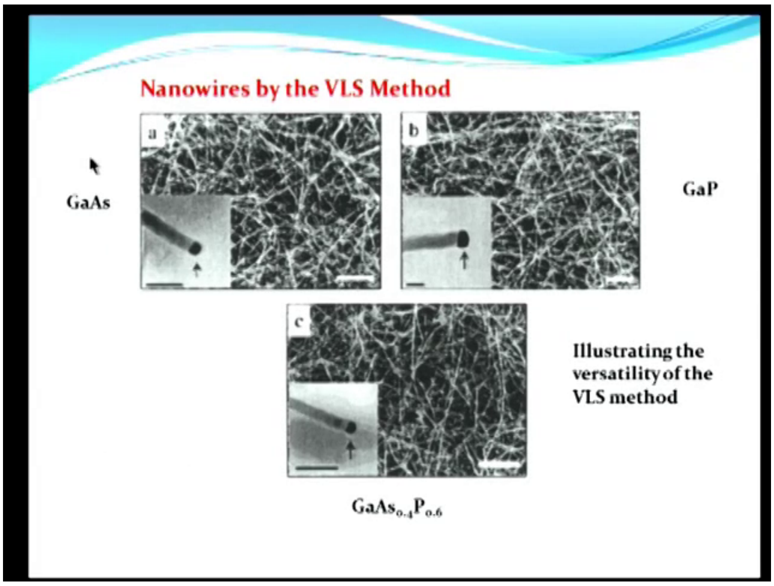
Nanowires by the VLS Method

GaAs

GaP

Illustrating the versatility of the VLS method

$GaAs_{0.4}P_{0.6}$

What this graph shows over here is the temperature variation of the growth rate of nanowires of silicon and germanium both the semiconductor. So, what has been done is to use silane vapor for silicon and germane Ge 4 vapor for germanium and the growth of nanowires by the VLS method is then that is the length of these wires is measured as a function of the growth temperature. That is the temperature at which the substrate respectively silicon and germanium or maintained. And these growth rates are found to depend on temperature and also on the catalyst employed it could be silver gold copper nickel palladium and. So, on. So, what you can see here is that there can be a sub let us remember that this is a So, called Arrhenius plot that is you have the logarithm of the growth rate versus inverse absolute temperature.

So, this is the so, called Arrhenius plot therefore, what we are seeing here is an activation energy is the slope of this each of these lines is the activation energy for growth under those particular conditions for that particular material. So, each of them has a particular activation energy and what you see are different slopes indicating different activation energies that are involved in the growth of silicon and germanium under different catalytic influences. And what you could also see is a very different rate of growth here and a rate of growth here that is you can substantially enhance the growth rate by changing the conditions under which growth is done. So, remember this is a log scale. So, here we have growth rates in the order of 0.1 micrometer per minute here you have growth approaching 100 micrometers per minute.

So, very substantial changes or increase in the growth rates can be obtained by adjusting the conditions of growth appropriately. So, what we have learned in this particular session is that the growth of nanocrystals can be controlled by polymer stabilizers which can actually also define the shape of metallic nanocrystals which allow us to get compound semiconductor crystals of very narrow set of dimensions that is monodisperse compound semiconductors. Semiconductor crystals and subsequently we learned about heterogeneous catalysis heterogeneous nucleation and how heterogeneous nucleation can lead to controlled nanocrystals on appropriate substrate surfaces. We will continue next time with the growth of nanowires in this case of carbon-carbon nanotubes and then move on to the growth of films through processes that lead us to nanostructures.

Thank you.