Nano structured Materials-Synthesis, Properties, Self Assembly and Applications
Prof. Ashok K Ganguli
Department of Chemistry
Indian Institute of Technology, Delhi

Module - 2
Lecture - 12
V-L-S Methods

Welcome back to this course on nanostructured materials- synthesis, properties, self assembly and applications. Today, we have the 10th lecture in module 2 and this lecture will be on the VLS method, where V stands for vapor, L for liquid and S for solid. So, as you can understand from that term, it is the vapor liquid solid method for the growth of nanostructured materials.

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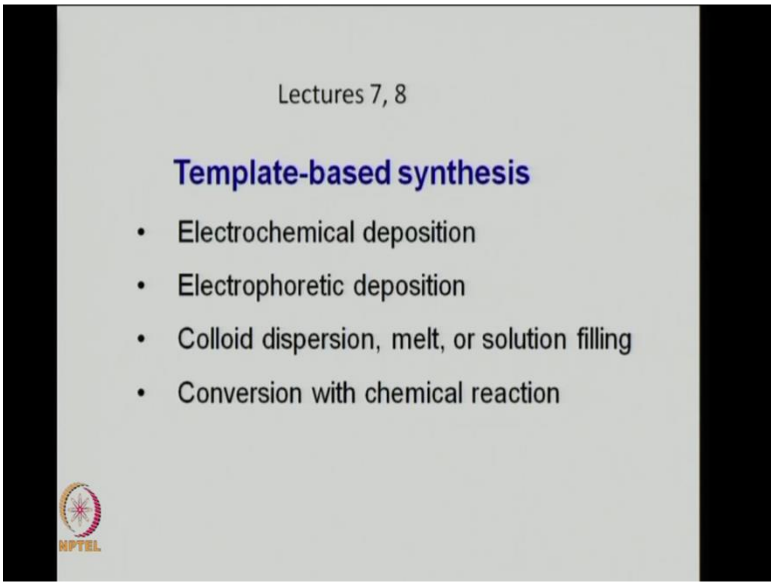

In the previous three lectures, let me just recapitulate. We looked at in lectures 7 and 8, we had two lectures on the template based synthesis of nanostructures where, we discussed electrochemical deposition, electrophoretic deposition, colloid dispersion that is making use of surfactant molecules and collides and also conversion with chemical reaction. Typically, in electrochemical deposition as you understand, you have an electrode and you have a electrolyte solution from which, you deposit on the electrode nanomaterials. In electrophoretic deposition, your particles which you make them charged and then you make them move and deposit.

In colloidal dispersion methods, you use surfactants and surfactant assemblies, which act as template, like, is the temporary structure in which you make your material and then you remove the template and get your nanostructured material. This template based synthesis; we discussed in the lectures 7 and 8.

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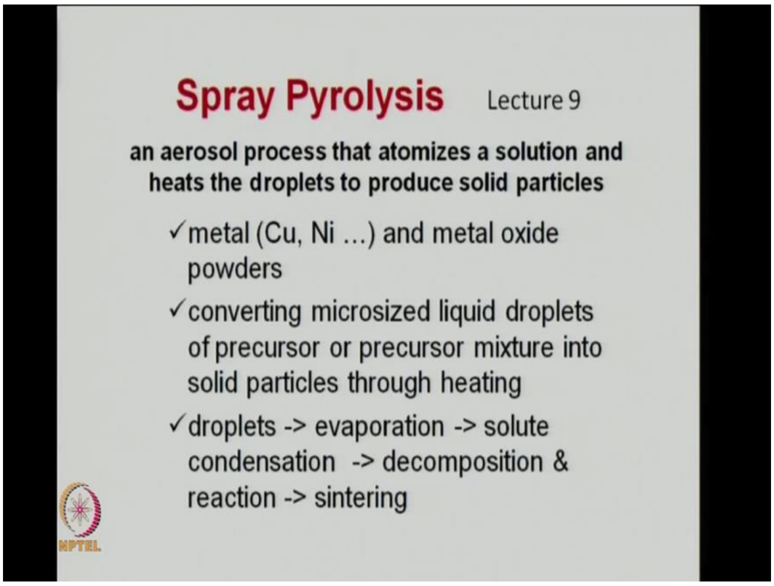

Then we discussed in the previous lecture that is, the lecture 9, we looked at another method of synthesis of nanostructured materials, using what is called the spray pyrolysis method. In the spray pyrolysis method, you basically use an aerosol, where you have these droplets of liquid in gas. You have a process that atomizes this solution and heats the droplets to produce solid particles. In a aerosol, you have these particles in liquid droplet and that liquid droplets, containing the solid particles is atomized and then you heat to get back the solid particles. You used this method to get fine powders nanoparticles of many metals, metal oxides and it has been used in a very big way to make nanostructured materials at industrial scale.

The process basically involves droplets, which have to be evaporated and then, the solute condenses and then decomposes, during a reaction and then you sinter if you want to increase the size of the particle. Today, we will start a new method of synthesis of nanostructured materials, which is the vapor-liquid-solid growth method and as you understand, that you go from the vapor to the liquid and a solid. All three phases are involved in this particular method.

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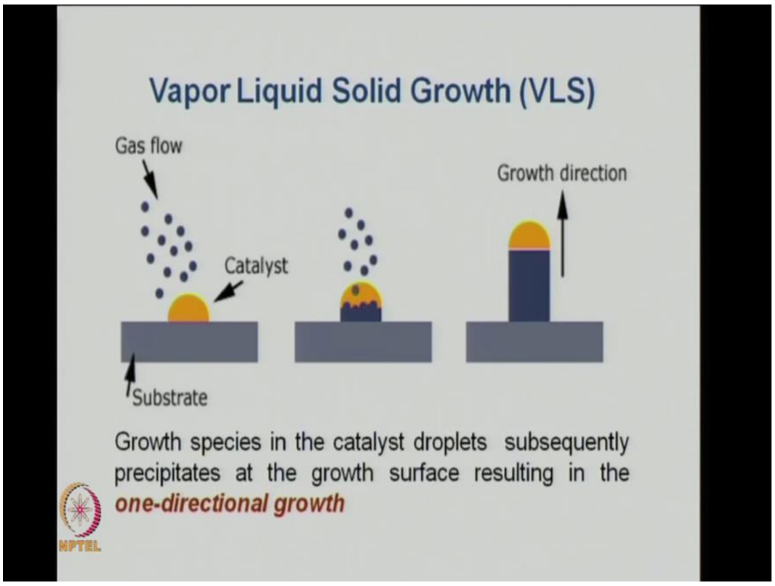

Diagrammatically, in one picture we can try to understand what is going on in a vapor liquid solid process or the VLS process. Here, what happens is you take the substrate to be the material, whose nanostructured you want to make. That material is used as a substrate and you have a catalyst, which is a impurity or some other material, other than the substrate material. What happens when you heat this substrate? You have particles of these in the gaseous state. So, the substrate which you want to make into a nanostructured material, you have it in the form of gaseous molecules.

These gaseous molecules then impinge on this liquid droplet, which is the catalyst or the impurity. We can call it a catalyst or an impurity, which is not the part of the substrate and which is not that material, which we want to make the nanostructure. We want to make the nanostructure of the material, which is in the substrate. And that is evaporated to give you these particles. These particles then fall on the liquid droplet or impinge on the liquid droplet like this, shown here. Then as the saturation; if the super saturation reaches, you get the precipitation at the interface of the solid and the droplet.

This is a solid. This is a liquid and this is a vapor. So, that is why this process is called the vapor liquid solid process. Because you have all the three things involved during this synthesis of the nanostructured materials. As more and more particles come here onto the liquid droplet and precipitate, the column starts moving. You start growing the nanostructured material in this direction. Note that at the tip you will always have the liquid droplet, which initially was on top of the substrate. So, the growth direction is controlled by the droplet. The droplet is always at the tip of this nanorod, which you can see here.

The growth species in the catalyst; which is this yellow colored particle shown here. It is a globule or a liquid droplet. They subsequently encapsulate these particles. So, the particles fall into this liquid droplet. These are gas molecules and then, they precipitate at the interface of the solid and the liquid. The liquid keeps moving in front. So, you get essentially, a one-dimensional growth of this substrate material. This particular methodology tends to give you nanowires on nanorods, if the dimension of this globule actually fixes the diameter of this rod. So, if you have a small diameter of this globule you get a thin nanowire. If you have a large diameter of this globule, you will get a thick nanowire. This is the overall process. Now, we try to understand by breaking it down, this whole process into small steps.

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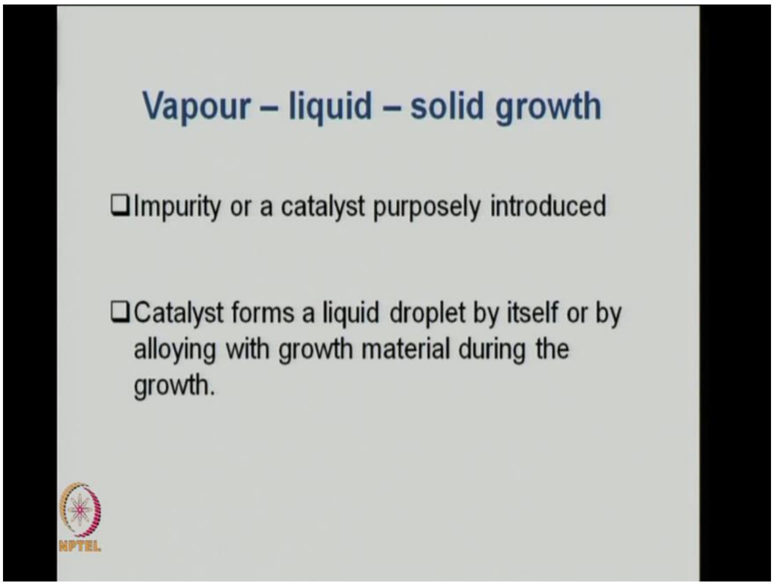

The vapor-liquid-solid growth; what are the key points? The key point is you have to have an impurity or a catalyst, introduced from outside. That is what we have introduced from outside. It is not a part of the substrate. So, you have to have an impurity or a catalyst purposefully introduced. The catalyst forms a liquid droplet by itself, as we have shown in the previous slide or it can form a droplet by alloying with the growth material, during the growth, which means that the catalyst can be forming the droplet involving this substrate also. Either alone or in alloying with this substrate, it can form a droplet. So, either of them is possible. These two points tell you that you need a catalyst and the catalyst will form a droplet on top of the substrate, either individually or taking some substrate molecules along with it to form the droplet.

The growth species, which is the species that you want to make the nanostructure, which is in the substrate is first evaporated. First, you have to evaporate the substrate such that, you have some substrate molecules in the vapor phase or the gas phase. That is important. The growth species has to be evaporated first, and then that diffuses and dissolves into a liquid droplet. So, the growth molecules evaporate and then dissolve in the liquid droplet and then precipitate.

This is what the sentence says, that first it is evaporated the species, which is in the substrate and then it diffuses in the liquid. After diffusing in the liquid it reaches the interface of the liquid and the solid and there, it precipitates. The catalyst acts as a trap for the growth species. The liquid catalyst or the droplet acts as the trap for the growth species. So, the growth species are basically vapor molecules, which come and sit on the liquid droplet surface and then they diffuse through. So, the catalyst is acting as a trap for the growth species. The growth species will then precipitate at the interface as mentioned earlier. After it diffuses through the liquid, this ultimately results in a one-dimensional growth. So, you get finally, the growth along one particular direction in which the liquid droplet is pointing.

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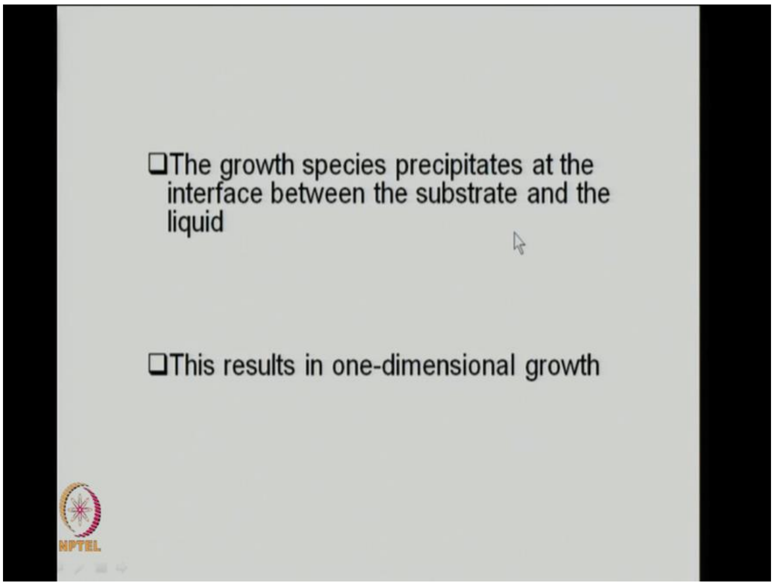

So, that is what, the end result of the vapor-liquid-solid process.

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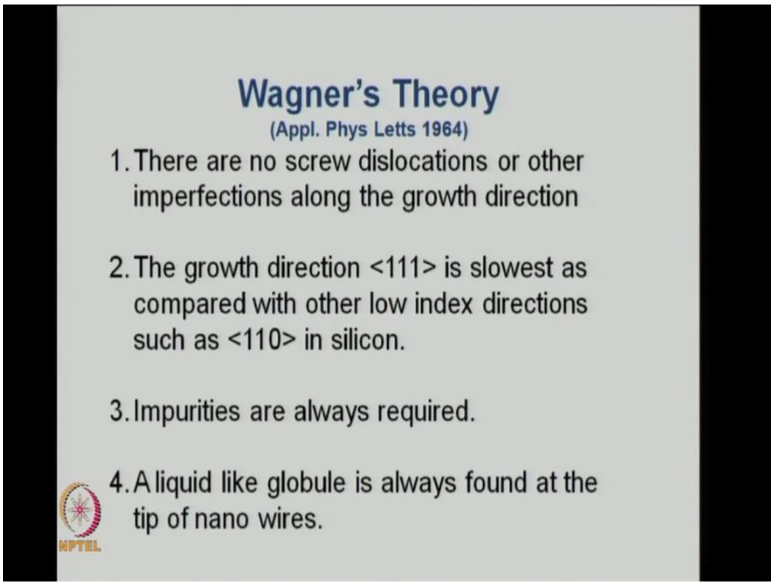

Now, to understand a bit more in detail, Wagner first tried to explain this growth of silicon nanowires and nanowhiskers. When, he could not explain the formation of nanorod or nanowhiskers, using the evaporation condensation method, which was known earlier. In 1964, he gave this theory, which is called the Wagner's theory for the VLS growth mechanism; for the vapor-liquid-solid growth mechanism. What are the characteristics and how do nanowires form using this vapor-liquid-solid mechanism? So, in this Wagner's theory, the key points are, that no screwed dislocations or any imperfection is required. Normally, when crystals grow they tend to grow from the substrate where there are some defects.

These defects are normally, what are called as screw dislocations. So, there are either screw dislocations or edge dislocations in crystals, which act as nucleation centers or growth centers, for subsequent growth of a compound or a particle. But, in this vapor-liquid-solid growth, there are no screw dislocations involved or any other kind of imperfection along the growth direction. You just have the molten globular kind of thing, which is the liquid droplet, which allows for the growth of the nanorod along the growth direction.

This is a key point where, it differs from the other growth mechanisms where, this kind of edge dislocations or defects of screw dislocations are required. The other thing is that the growth direction 111, which is slowest in a silicon, as compared with other low index direction, such as 110 in silicon. This has been explained by Wagner, that the growth is slowest along the 111 direction. If the rate is slow then, obviously, the facets that you see will be related to that direction. So, the 111 phase becomes very prominent in silicon.

Then, Wagner suggested that impurities are always required for the vapor liquid phase; vapor liquid solid method of synthesis of nanostructured materials. In 1964, when he gave this theory, it was not to explain so much about nanostructures, but to explain the growth of a particular material. It may be crystalline, amorphous or polycrystalline along a particular growth direction. Now, of course, we can apply it to the growth of nanowires and nanorod. So, impurities are always required in this method and that forms a molten globule or the droplet, and that molten globule or droplet is always seen at that tip of the nanowire.

As the wire is growing, if you are able to analyze or look at the nanowire, which is growing, then you will always see at the tip of the nanowire. You will see a liquid droplet kind of thing or a globular kind of thing, and that is basically the catalyst which is at the tip of the nanorod.

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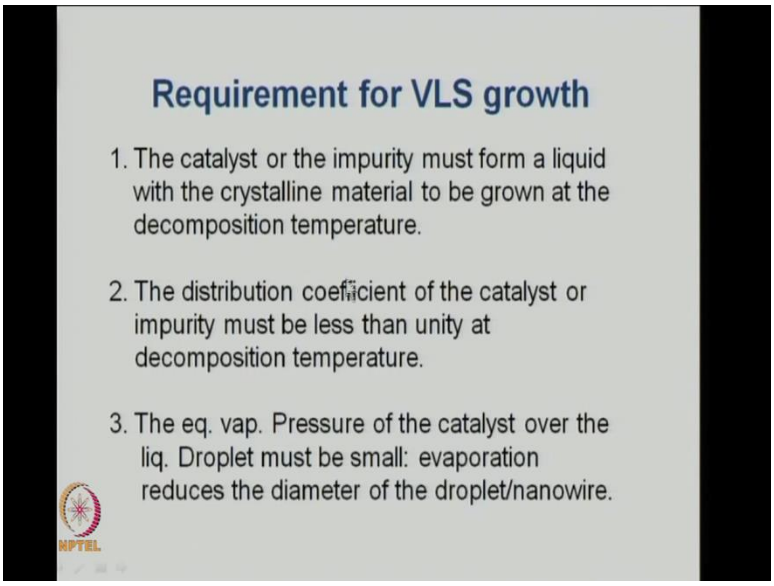

The requirements for a vapor-liquid-solid growth; the catalyst or the impurity must form a liquid, with the crystalline material to be grown at that decomposition temperature. So, this is an important point it has to be obeyed, if you want to grow using the vapor-liquid-solid method. That is, the catalyst must from a liquid with the crystalline material.

The distribution coefficient of the catalyst or the impurity must be less than 1 at the decomposition temperature. It tells you how the catalyst is distributed in the liquid phase. The distribution coefficient can be found out by doing certain experiments. For this you must choose a catalyst, which has a distribution coefficient, less than unity at the decomposition temperature. Then, the equilibrium vapor pressure of the catalyst over the droplet must be small; that means, the catalyst should not be evaporating very easily.

If it evaporates very quickly then, that catalyst will lead to reduction in the diameter of the droplet, which ultimately, will reduce the diameter of the nanowire or nanorod, which you are growing. Hence, you choose a catalyst, which has a small equilibrium vapor pressure and so less evaporation. If you have more evaporation, the liquid droplet size; the diameter of the droplet size will decrease and hence, the diameter of the nanorod or nanostructure or nanowire, which you are synthesizing, which is controlled by the diameter of the droplet will also decrease. So, equilibrium vapor pressure of the catalyst should be low. Distribution coefficient of the catalyst should be less than 1.

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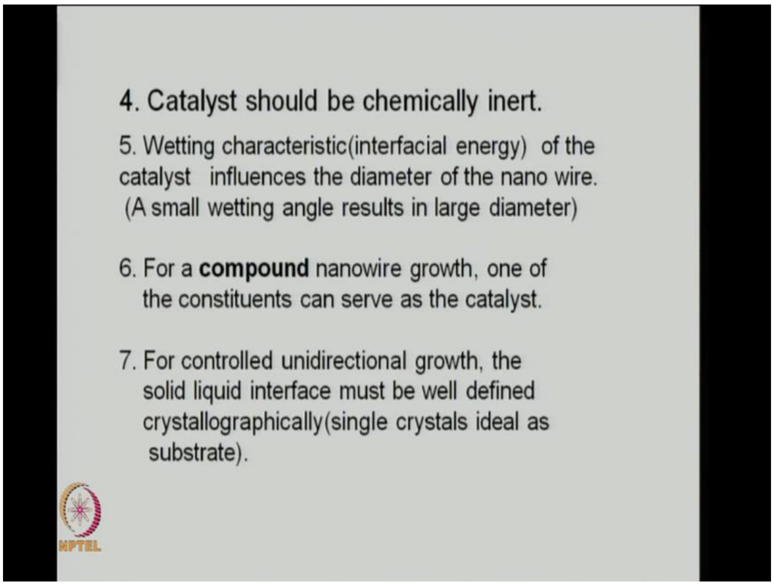

The catalyst should be chemically inert: the catalyst should not react with you substrate. It should be able to come out of that. Then, the wetting characteristics, which depends on the interfacial energy: the wetting character is like, when you have a droplet on a surface and if that droplet wets the surface very well then, you have a very low interfacial energy.

The interfacial energy or the wetting characteristic of the catalyst influences the diameter of the nanowire. The diameter of the nanowire can be related to the contact angle, which also depends on the interfacial energy of the liquid and the solid. A small wetting angle results in a large diameter. So, this is important and if you want to control the diameter of the nanostructure, or the diameter of the nanorod, you can control the wetting angle. Hence, you will control the diameter of the liquid droplet, which in turn, will control the diameter of the nanorod, which grows using the nano droplet at that tip.

If instead of a metal; suppose you want to grow a compound nanowire; that means, you have a material with two elements AB, then one of the constituents say, A or B can itself serve as the catalyst. If you are trying to grow only a monometallic compound; that means, which has only one element, like silicon, then you need another catalyst; another material as a catalyst, which may be gold or platinum or something like that. But, if you are going to grow a compound nanowire, then one of these two elements or three elements, which from the compound, can itself act as a catalyst.

That is what is mentioned here. For a compound nanowire growth, one of the constituents can serve as the catalyst. If you want to control the directionality; for unidirectional growth, the solid liquid interface must be well defined crystallographically. So, if you want to grow only say, silicon 111, you must have single crystals as substrates with proper orientation. If you have a polycrystalline substrate then you may not be able to grow a particular phase or a particular direction. So, the crystallographic orientation can be maintained, if you choose a single crystalline substrate, and then you can grow along some particular direction.

Although, it is, there are certain preferred directions in which, you can grow a single crystalline nanorod or nanowire. It is difficult to grow along other particular directions. For example, 111 may be easy to grow, but 110 may be difficult to grow. 100 may be difficult to grow. However, if you have a substrate of 100 or a substrate of 110, then maybe, it is possible for you to grow the nanorod, keeping that orientation along. So, you can grow unidirectionally or along a particular direction, if you have single crystalline substrates.

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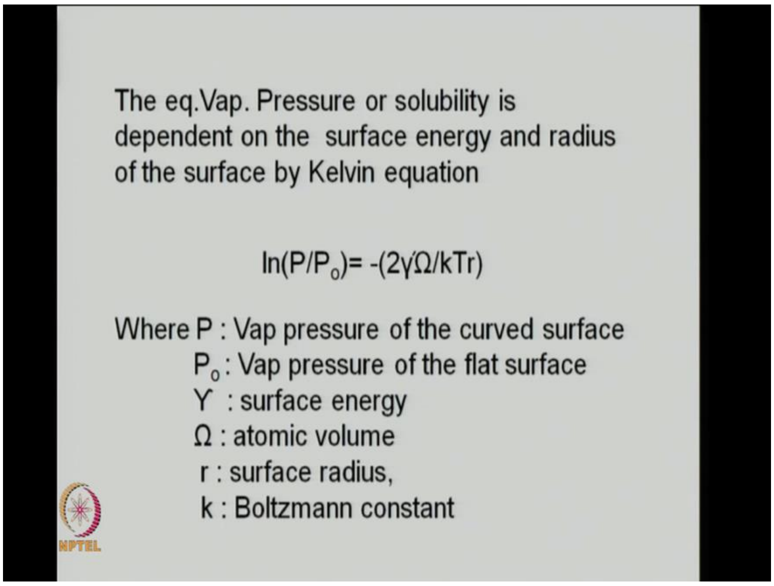

The other thing is, the equilibrium vapor pressure or solubility is dependent on the surface energy, and radius of the surface by the equation given here. It is also called the Kelvin equation. As you see that there are lot of parameters you can vary. You can vary the temperature. You can vary the surface energy, which are the two things and the radius; this radius at the surface of the liquid droplet. If you vary these, you can control the pressure- equilibrium vapor pressure or the solubility. So, you need these gas particles to be soluble in this liquid.

That will depend on the vapor pressure- equilibrium vapor pressure. And the equilibrium vapor pressure here can be controlled by controlling the interfacial energy on the surface tension, and the temperature, and the radius of this droplet. So, all that will contribute to the equilibrium vapor pressure. That will enhance or decrease the solubility of these particles in the liquid and hence, will ultimately control the amount of particles which are getting precipitated at this interface. Coming back to this equation, which is the Kelvin equation; by that you can calculate how, if you change the radius, if you double the radius then, what will happen to the equilibrium partial pressure, and how it will affect the solubility and ultimately, how it will affect the growth of the nanorod.

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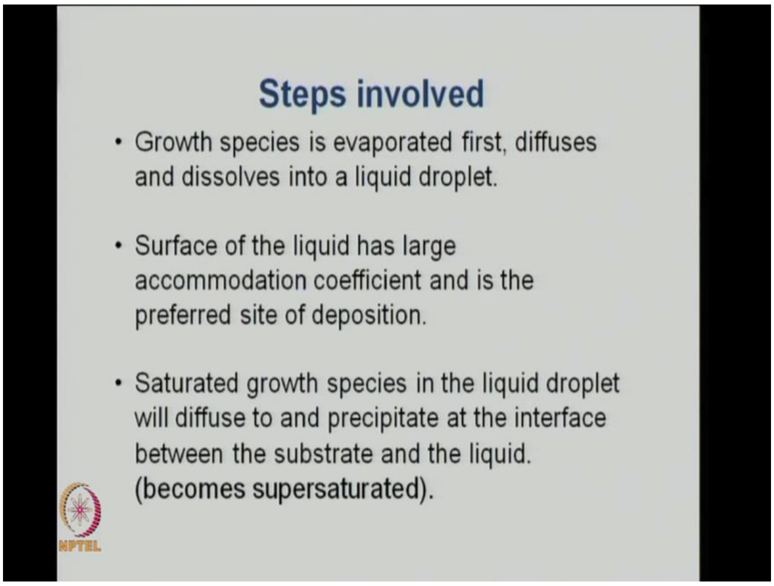

The typical steps involved; some of the steps we have discussed. If we go over some of them again, the growth species, which is in the substrate, is evaporated first, diffuses into the liquid and dissolves. Since, it is a liquid it has a large accommodation coefficient. If you try to absorb gas molecules on a solid surface, then as you know, on a solid surface there are some preferred sites, where the gas molecules can occupy. Like, in any heterogeneous catalysis reaction, if your surface is a solid surface then there are some sites where that gas molecules preferably occupy.

Since this is a liquid droplet, the number of every site can accommodate the incoming gas molecule. So, what we say is that the surface of the liquid has a very large accommodation coefficient and that; it has lot of preferred sites of deposition. The accommodation coefficient is high; means, there are lots of preferred sites of deposition. Hence, you can have lot of these gas molecules falling on that liquid, which can get accommodated. Then, once you saturate, the saturated growth species in the liquid droplet will then diffuse towards the solid liquid interface.

Once you saturate, that is you have lot of gas molecules into the liquid. Then in the liquid droplet, they will diffuse and slowly towards the liquid solid interface, and then precipitate at the interface, between the substrate and their liquid. This is when, it becomes super saturated, that is when the precipitation occurs. This step is very important and how you saturate the growth species by changing the equilibrium vapor pressure; you enhance the solubility; you enhance the saturation; and you force the diffusion to occur towards the liquid solid interface. Then, that forces the precipitation and then, the growth of the nanostructure.

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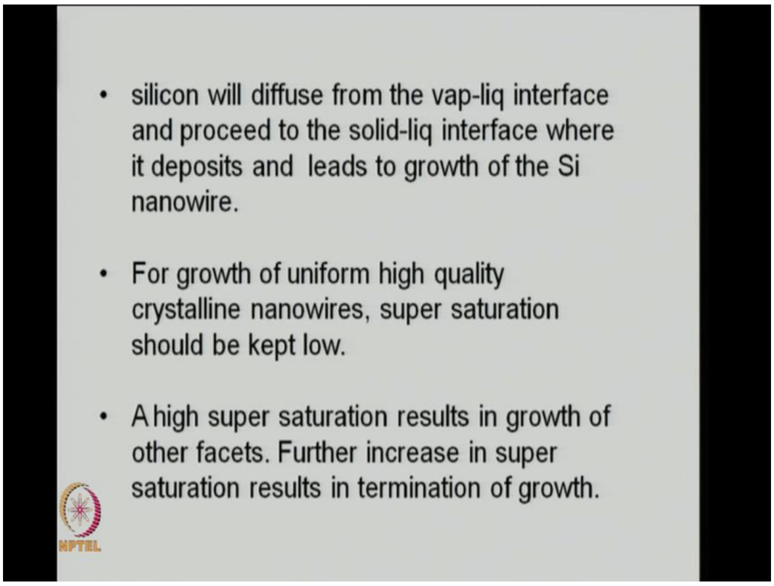

In the case of silicon, if you take silicon as the substrate, then silicon vapors will be formed. Then, silicon vapor molecules; the molecules in the silicon vapor will impinge on the liquid droplet, which is some catalyst, it maybe, gold or platinum. Normally, gold and platinum are used. Then, these silicon gaseous molecules, after solubilizing in the liquid, will diffuse from the vapor liquid interface and proceed to the liquid solid interface, where it will deposit and lead to the growth of the silicon nanowire.

This is a case of silicon, which was used as the substrate and you have some other element as the catalyst. For growth of uniform and high quality crystalline nanowires, the super saturation should be kept low. This is very important, if you want defect free high-quality crystalline nanowires; not amorphous; not polycrystalline. If you want crystalline nanowires then the super saturation should be kept low. It should not be very high, and then it will lead to polycrystalline nanorod formation.

The high super saturation results in growth of several facets, not one facet. If you want a crystalline nanowire, you want one facet or one direction to grow. If you have high super saturation, it results in growth of several facets. And further increase in super saturation; if you increase beyond a certain level, very high super saturation, then it will terminate the growth. It will lead to termination of the growth of the nanorod.

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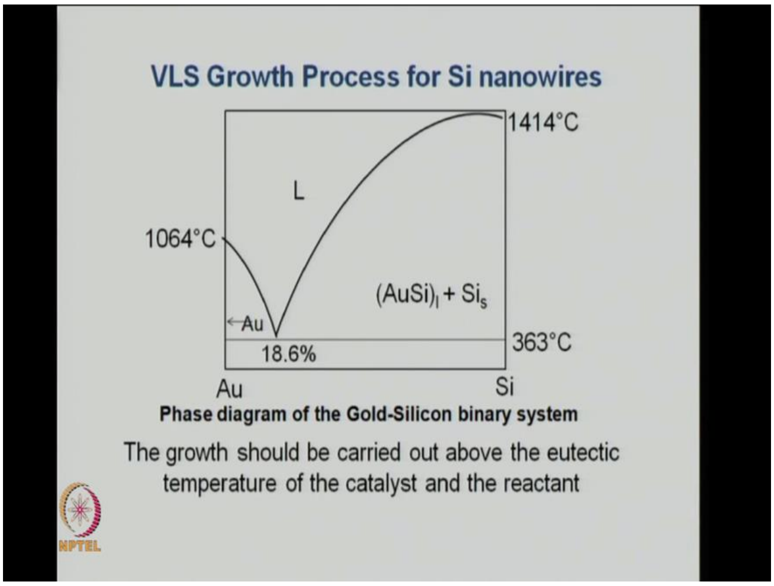

Typically, as we are discussing the growth of silicon nanowires, in silicon nanowires, we normally choose as we said gold or platinum as the catalyst. The phase diagram of gold and silicon is something, which one has to study before one starts to plan for an experiment of growing silicon nanowires, with gold as a catalyst or an impurity. See, if you look at gold and silicon, you see that the gold melts around 1064 degrees centigrade. This is called a phase diagram, where you are plotting temperature on this axis, versus percentage of silicon. Silicon here is 0 percent and silicon here is 100 percent. So, this is pure gold; 100 percent gold. This is 100 percent silicon and you see that, at 18.6 percent, you have what we call as the eutectic composition.

That means, when you take a mixture of gold, 18.6 percent and the remaining 83.4 percent is silicon. Then you have a composition which has the minimum melting point of 363 degree centigrade. So, that is called the eutectic temperature, which is 363 degree centigrade and 18.6 percent of gold is the eutectic composition. So, what does that tell you; this shows you a diagram which tells you that, if you heat at this composition above 363, you will get a liquid.

If you are somewhere here, that is, you are rich in silicon. There is more silicon than 18.6 percent and you are at say, 500 degree centigrade, then you will have a mixture of solid silicon and an alloy of gold silicon, which corresponds to this composition, which will be in the liquid form. So, you will have this liquid plus silicon. That is what is used, if you heat above 363, this substrate which has got silicon, on top there is gold. Then you will get droplet of gold silicon and you will get silicon solid.

However, if you are exactly at 18.6 percent of gold and silicon, then you will get only liquid gold silicon alloy, of that particular composition. Now, this phase diagram is used extensively for the growth of silicon nanowires, where gold is used as a catalyst. Silicon melting point is 1414 degree centigrade and gold melting point is 1064 degrees centigrade. But the eutectic temperature is 363 degree centigrade. You can use eutectic composition for that. The growth should be carried out above the eutectic temperature.

So, you have to do the reaction or you have to heat the substrate of silicon, which has got gold droplet on top, or the gold particle on top, above 363. When you heat you will get a liquid droplet, which will have the composition of gold and silicon in this ratio. That is what is used in vapor-liquid-solid growth of silicon nanowires, with gold as catalyst.

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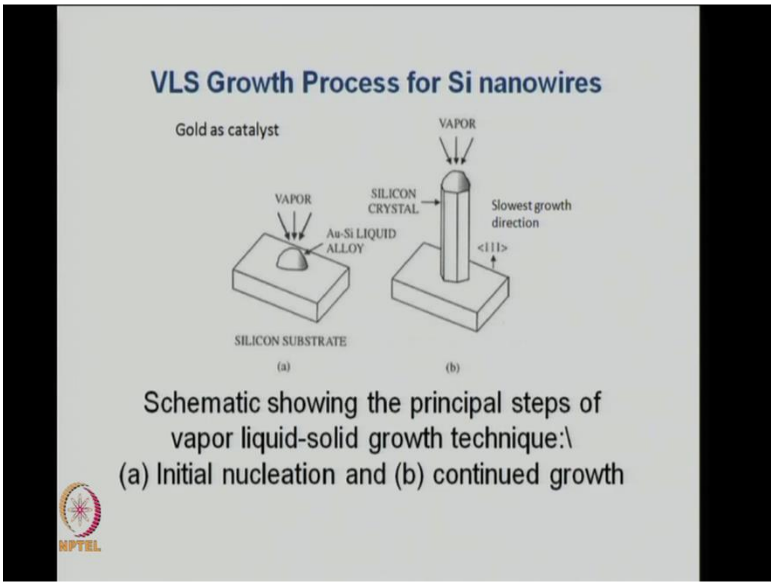

This is shown here. This is the vapor-liquid-solid growth process for silicon nanowires. Because, as you know silicon, is one of the most important materials in the industry; for semiconductor industry. Because, the entire IC industry; the integrated circuit industry, all kinds of chips are dependent on the silicon technology.

So, the technology for growth of silicon is being studied for a long time and this is a process, which has been developed long time back for the vapor-liquid-solid growth of silicon nanowires. You start with the silicon substrate and on top, you have a gold particle. Once you take the temperature above 363 degree centigrade, this gold particle will melt with the silicon substrate, which is this touching and will form a droplet of gold silicon liquid alloy.

The composition of this gold silicon, if you analyze, will be of the liquid. The composition of the liquid droplet will be 18.6 percent gold and 83.4 percent silicon. Because, that is the eutectic composition. Once you have that droplet, if further you heat, you will have vapor and that vapor will contain your silicon molecules. So, you will have silicon molecules in the vapor phase. Then, these silicon molecules will start impinging on the liquid droplet. Then, after enough gas molecules have been dissolved in this droplet, then it reaches the saturation value and then it precipitates at the interface.

When it precipitates, if this silicon is single crystalline then it also grows like a single crystalline rod. Here, what we have shown is that 111 direction growing; it is growing in the 111 direction; that means, this crystal, which is the substrate, is a single crystal silicon substrate, which is oriented with the 111 direction. You are getting the growth along the slowest growth direction, which is the 111 direction. So, that is the final face. If you cut this face, this plane will be the 111 plane.

The direction of growth is perpendicular to the face which you see. The 111 plane will be perpendicular to the growth direction and that is how a silicon crystal can be grown, using a silicon substrate and a gold catalyst on top of it. So, initially you have nucleation, when the first precipitate forms and then there is continuous growth, till you stop the growth either by increasing super saturation or by some other means.

This is typically, some images, the TEM images of a silicon nanowire. You can see the silicon nanowires. This is a scanning electron micrograph, where the scale as you see, is 2 micron; that means, this distance is 2 micron. These wires are a very long. They may be 5 microns, 10 microns long or even longer and the diameter is very small. The diameter may be of the type of 10 to 15 nanometers. It is around 15 nanometers. The reason, it is 15 nanometers is, if you look closely at one of the rods, then you will find at the tip of the rod, this liquid droplets. So, this is the liquid droplet of the gold silicon alloy, which is on top of the nanorod; of this silicon nanorod. This diameter of the droplet is around 15 nanometers because, the scale here as you see is 10 nanometers.

This is a high resolution transmission electron micrograph or we call HRTEM, in which you can see clearly, the tip of the rod with 15 nanometers diameter of gold silicon droplet and the silicon high resolution fringes can be seen below. This is not high resolution; this is a scanning electron micrograph. So, this is much lower resolution. It tells you more or less about how many wires are grown, how long are the wires, etcetera.

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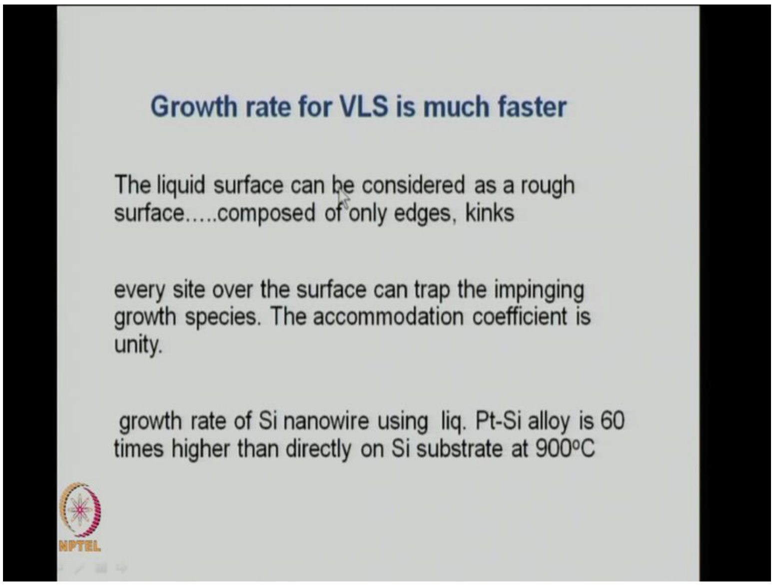

One of the things is that if you compare with other growth methodologies, the VLS method is much faster. This is because, in this case, we are using a liquid droplet as the catalyst. The liquid droplet as we discussed earlier, has all the surface for it to accommodate the incoming gaseous particles. Because, any point on the liquid surface is good for accommodating the gaseous molecules. That is not the case, if the surface is a solid. All points or all positions on a solid surface are not equally happy with the incoming gaseous molecules. There are some preferred sites, where the gas molecules will be accommodated. Hence, the accommodation coefficient in a solid surface will be much lower than in a liquid.

The liquid surface can be considered as a rough surface, composed of only edges and kinks. That means, every point can act to accommodate the incoming gaseous particle or gaseous molecules. So, every side over the liquid surface can trap the impinging growth species. The accommodation coefficient is 100 percent or unity and so the growth rate can be very high. This is the reason that the growth rate for the vapor-liquid-solid method of growing silicon nanowires, is much faster than other growth methods.

For example, in a silicon, if you use liquid platinum silicon alloy; that means, you have a platinum particle on top of a silicon substrate. You heat it and the platinum melts, forms a droplet with the silicon to form a platinum silicon alloy, like the gold silicon alloy, we discussed earlier. You can have a platinum silicon alloy. When you grow a silicon nanowire using this platinum silicon alloy, this is 60 times faster. So, the growth rate is 60 times higher than if you did not have platinum.

Suppose, you did the same synthesis on only the silicon substrate at 900 degrees centigrade and you compare it with the growth rate with same silicon substrate. But you have some platinum on top of the surface. Then the growth rate is 60 times faster for the case, where you have platinum on top of the silicon surface. So, growth rates for vapor-liquid-solid method of growing nanowire or nanorods is much faster than other techniques

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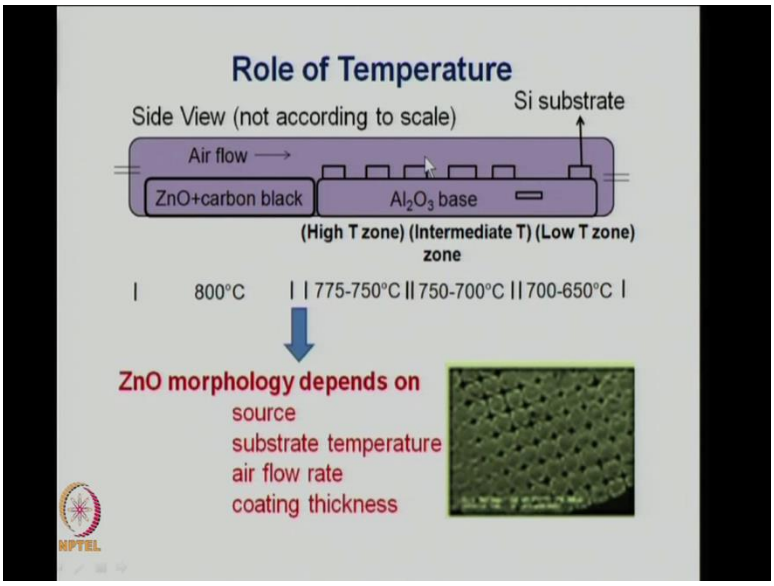

Temperature also has a role to play. The catalyst has a major role to play. The temperature has also a major role to play, as you know that in the equation of the equilibrium vapor pressure. In the equilibrium vapor pressure, there is a temperature here. The logarithm of this pressure is negative of the inverse of the temperature. That equilibrium vapor pressure can be affected by changing the temperature. That you can do and you can compare the growth in the same reaction. You have a furnace, where you can have different temperature zones; same furnace, but you can have different zones. So, one part of the furnace, you can keep at say, 800 degree centigrade. Another part of the furnace is at 750 to 775 and another part is 750 to 700.

And then, a low temperature zone; 700 to 650. You have a low temperature zone, an intermediate temperature zone and a high temperature zone and there is the edge of the furnace, is at much higher temperature than where that reaction is happening. The reaction is happening here. You have the silicon substrate here. In the lower temperature zone and in the intermediate temperature zone, you have the silicon and in the high temperature zone also, you have silicon, different substrates, all in the high intermediate and low temperature zones.

Now, you try to grow zinc oxide on that. You are trying to grow zinc oxide in this furnace. Depending on where the reaction is happening, if you take out the material from different zones; the zinc oxide which is forming because, you are keeping here some zinc oxide at high temperature. This zinc oxide along with the airflow, will go and deposit here on the silicon substrates. So, the substrate temperature is what is being controlled here; the silicon substrate.

And the zinc oxide is being volatilized from this part, which is at 800 degrees and is being carried to this part of the furnace, by airflow. There it will deposit on these and growth will take place. So, the growth or the morphology of the zinc oxide; what will be the shape of the particle of zinc oxide, will depend on the zone in which the reaction is happening and also, depend on the airflow rate and certain other thickness; coating thickness, etc. This is one picture of what you see here, of these silicon substrate on which zinc oxide is being grown. If you collect particles from the high temperature zone, intermediate temperature zone and low temperature zone after the reaction, you collect the zinc oxide and look under a scanning electron micrograph.

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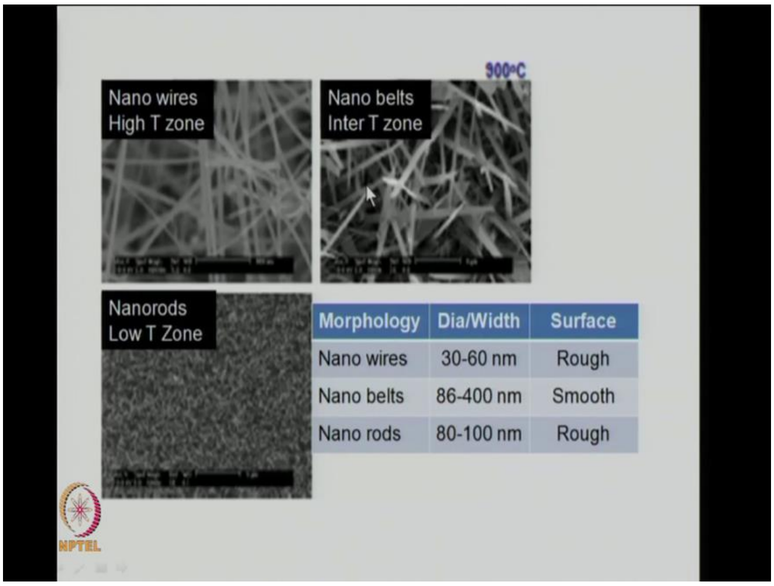

The high temperature zone shows nanowires; that means, the thickness of these wires is small. So, you get nanowires which have a diameter of around 30 to 60 nanometers; very fine wires at high temperatures. The substrate here is silicon and it is kept at high temperature around 750 to 775 degree centigrade.

If you go to intermediate temperature zone, that is this zone, where the temperature is between 750 to 700 degree centigrade, then you can see nanobelts. We call them nanobelts because, the thickness of these is much larger than the thickness of this. Here we call them nanowires. Here we are just calling them nanobelts because, the thickness is of the order of some 85 to 400 nanometers. Of course, we see that they are very smooth. They are smooth hence, we call them as a belt and these are rough. So, we call them wires. They are thin wires and here they are broad but, they are very smooth.

They we get the nanobelts. At that very low temperature zone, which is like 700 to 650 degrees centigrade, we get another morphology. So, you get different morphologies by doing the reaction at different zones of the furnace. Here we get nanorods again. Here we got nanowires. These are nanorods; that means, the thickness of the wires has increased. Here, you have very small diameter. Here the diameter is large, is 80 to 100 nanometers and the surface is also rough, which you can see from the SEM micrographs.

Basically, you are controlling the diameter of these nanostructures, as also the surface finish; whether that surface is smooth or rough, depending on the temperature of the reaction. This kind of furnace is called a multi zone furnace because; in the same furnace you are having different temperature zones. This is very useful for doing not only this kind of vapor-liquid-solid reactions, but vapor transport. You can do what is called the vapor transport mechanism, where you can see this kind of growth and this kind of change in the morphology of the zinc oxide nanostructures.

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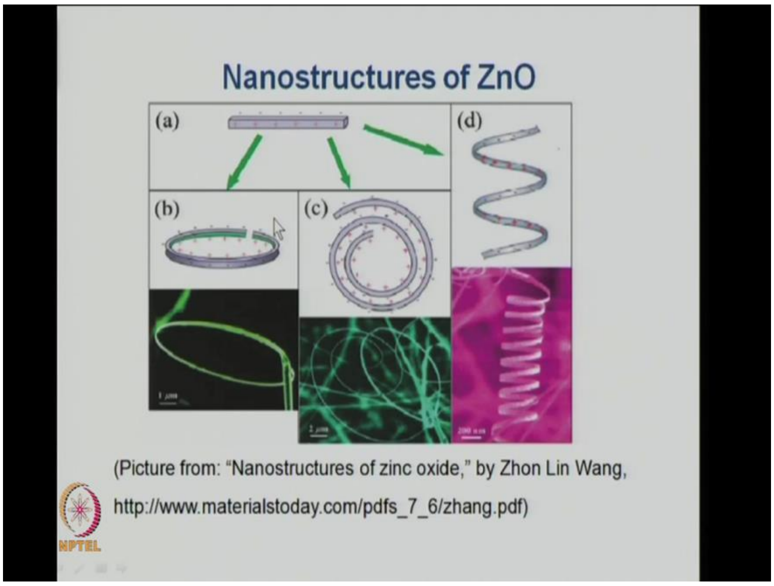

Many pictures are there in the literature that you can make nanostructures of zinc oxide. Like, a rod which is cuboidal in shape; this kind of helical tape like structures; or spherical tape like structures; or this kind of spring like structures; all of them are made up of zinc oxide. This looks like a spring, like, you know steel spring or a iron metal spring, but this is not made of iron. This is made of zinc oxide. All the structures are made of zinc oxide by controlling various features of substrate, airflow and the vapor transport, etcetera.

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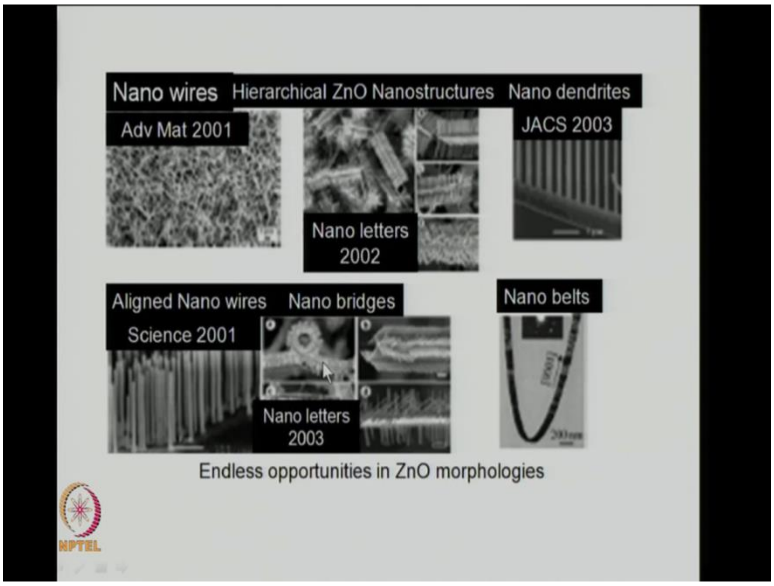

These are some other structures, taken from various sources in the literature as mentioned here. You can see nanowires of zinc oxide, hierarchical zinc oxide structures. Hierarchical structures imply that if you look at one nanorod, from a distance it looks like one nanorod. Then, when you look at it closely, you will see thousands of nanorods much smaller in diameter, like brushes, and then you take a look at one hair of that brush. Then it will have thousands of smaller brushes. So, this kind of wire inside a wire, that these kind of structures are called hierarchical structures.

It need not be a wire inside a wire. It can also be a sphere inside a sphere. That is also a hierarchical structure. Lot of such structures have been made in the laboratory in the recent past and these are all chemically, zinc oxide. You can get this kind of nano dendrites. You can get this kind of nanobelts, which is also in the shape like a garland. You can get nanobridges like, you have a shape like this; like a bridge shape. So, all kinds of shapes and alignments like this, all the wires in the same direction or in different directions is possible.

So, there are endless opportunities in making different kinds of zinc oxide morphologies. This can be extended to many other oxides. Not only in zinc oxide; this can be extended to several other types of oxides in which, people have interest. Although, lot of work has been done on zinc oxide because, it is a very cheap material; it is easily available and it has lot of potential for applications in photovoltaics, in light emitting diodes, etcetera.

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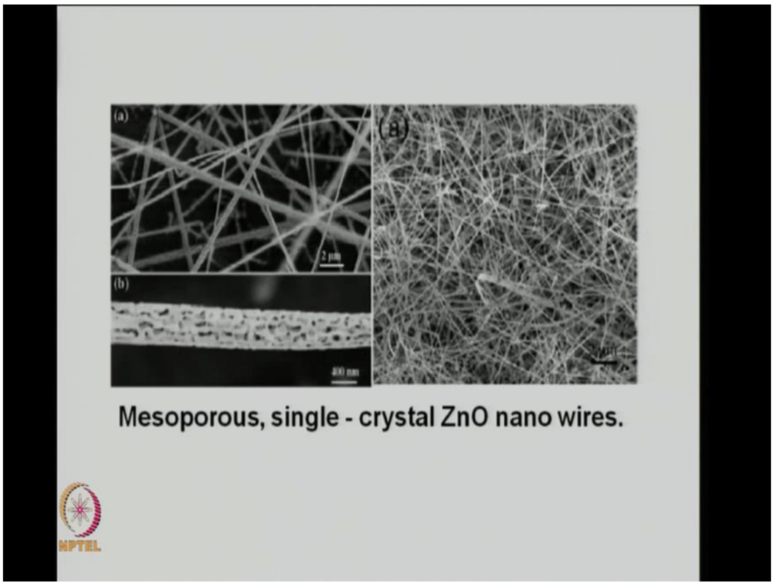

This is again a picture, a SEM picture of single crystalline zinc oxide nanowires. This is at a scale of 400 nanometers. This is zoomed in picture, we are looking closely at the nanowires. This is a low resolution picture of zinc oxide nanowires, where you can see like a jungle of nanowire; a mesh of nanowires; thousands of nanowires and this scale here is around 2 micron. So, this is a more closer picture of the same thing.

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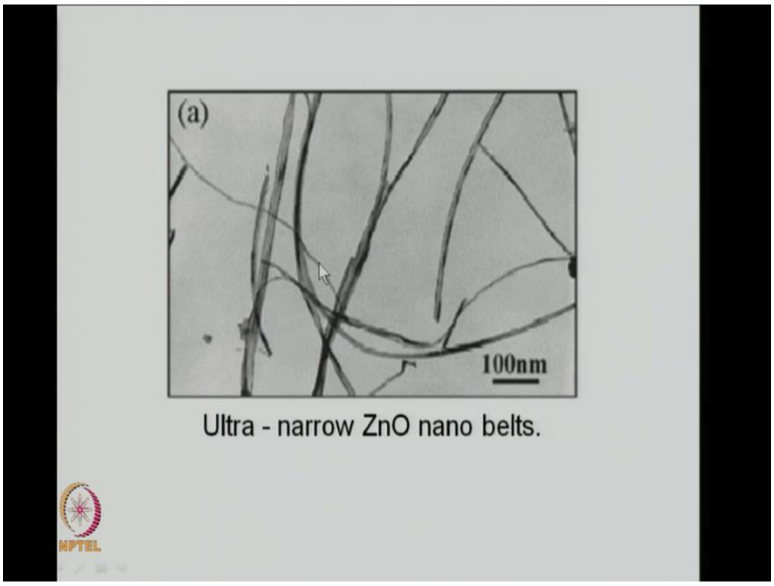

You can see ultra narrow zinc oxide nanobelts. This is again, a zoomed in picture. The scale here is 100 nanometers. So, this should be around 10 to 20 nanometers in dimension, and very long nanowires of the order of microns size; nanobelts of the order of micron size.

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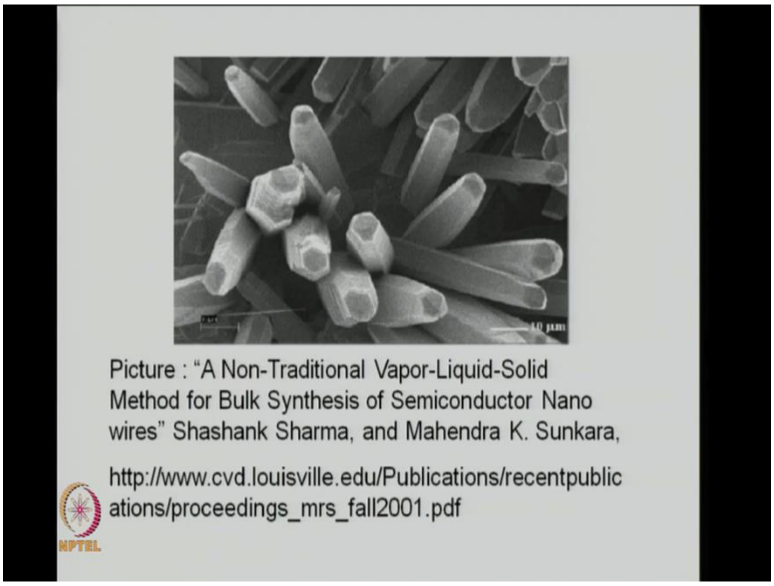

This is a special type of nanorod of zinc oxide. It is the title of this work, is called a nontraditional vapor-liquid-solid method for bulk synthesis of semiconductor nanowires. This shows facets very clearly. You are looking down these nanorods. Each nanorod, you can see a particular face right here. This is grown by the technique that we discussed, which is the vapor-liquid-solid method for the bulk synthesis of semiconductor nanowires. You can even see the facets on the sides. These are other planes. On the sides, you can see clear facets. The top facet, this belongs to certain plane.

So, these are single crystalline kind of nanorods of zinc oxide, which has been made using vapor-liquid-solid method. Large number of possibilities exist of how to control the morphology of these nanostructures, and you can change the diameter from 10 nanometers to several 100s of nanometers. The length from few 100 nanometers to a few microns is easily possible, using the vapor-liquid-solid method.

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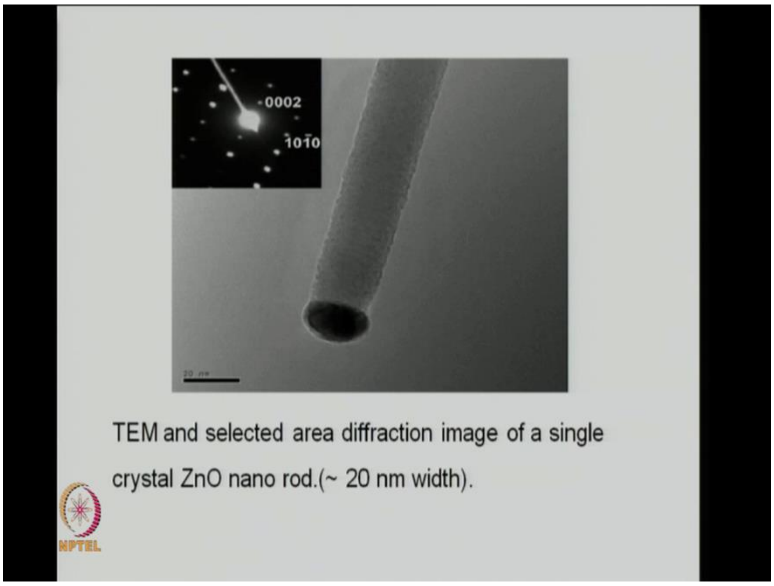

Very important, as you see in the vapor liquid solid method, we said that in the method you have a substrate; you have a droplet on top of the substrate of the catalyst. As the growth material, which has evaporated, falls into the liquid or solubilizes in the liquid, and then deposit itself on the liquid solid interface. The liquid droplet keeps moving on top of the growing rod and that is what is being seen here. This is the rod, which is growing. Actually the substrate is on this part and the rod is growing and at the tip of the rod, is your molten droplet or the liquid droplet, which is of the catalyst. If you continue growing, then this droplet will continue to move.

This is a TEM picture of a single nanorod, with the droplet at the tip. The dimension of the rod is around 15 nanometers, because the scale here is 20 nanometers. This is a TEM image or TEM, that is, a transmission electron micrograph of a nanorod of zinc oxide, and it is single crystalline in nature, with a particular growth facet or in particular growth direction. If you take the electron diffraction of this, then you can see the electron diffraction, is shown here. Then, you can index the growth direction. By looking at the electron diffraction pattern, you can tell about the growth direction. This is what we call the TEM image. It is in real space. This is the electron diffraction pattern of this nanorod and this is in reciprocal space.

What you are seeing are called the HKL indices. However, in most of the time, we have three indices. Here, as you can see; there are one, two, three, four indices. That is because, this is a hexagonal crystal system. Zinc oxide crystallizes in the hexagonal crystal system. In the hexagonal crystal system, instead of each plane using three indices, we can define certain planes with four indices. That is what has been done here. These are called the HKIL index and of course, if I know H and K, I can always find I. So, many times it is also called a redundant index. But, it is useful at times to use this HKIL or the four indices for hexagonal lattices, like, in zinc oxide to index the face, which is growing or the direction in which the rod is growing.

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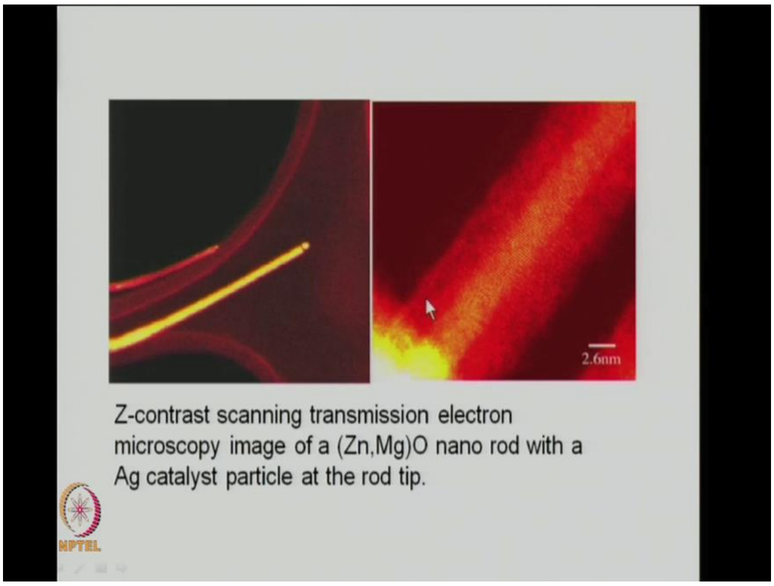

This is another picture, which is called the Z-contrast scanning transmission electron. This is called the STEM picture. So, you have, this is the TEM picture and earlier, we discussed is an SEM picture. You have the SEM picture, you have the TEM picture and this is a STEM picture. The scanning transmission electron microscope in which, you can see the tip of the nanorod, and the nanorod, which are growing. This is called Z-contrast because, the contrast is made by the atomic number. So, if you have a difference in atomic number then you will see a difference in contrast.

That can be seen in these pictures, which is called the Z-contrast STEM picture of a zinc mag oxide nanorod, where magnesium has been doped in the zinc oxide, and it is growing, and a silver catalyst is at the tip. This is a silver catalyst and this is the nanorod, which is growing on zinc oxide and this has been imaged by the STEM Z-contrast imaging system. This also clearly shows you that the mechanism that we discussed is correct, that you have a liquid droplet at the tip of the nanorod, which is growing to give you the ultimate nanostructure. That liquid droplet is of the catalyst. In this case, the catalyst is silver and the rod, which is growing is zinc oxide.

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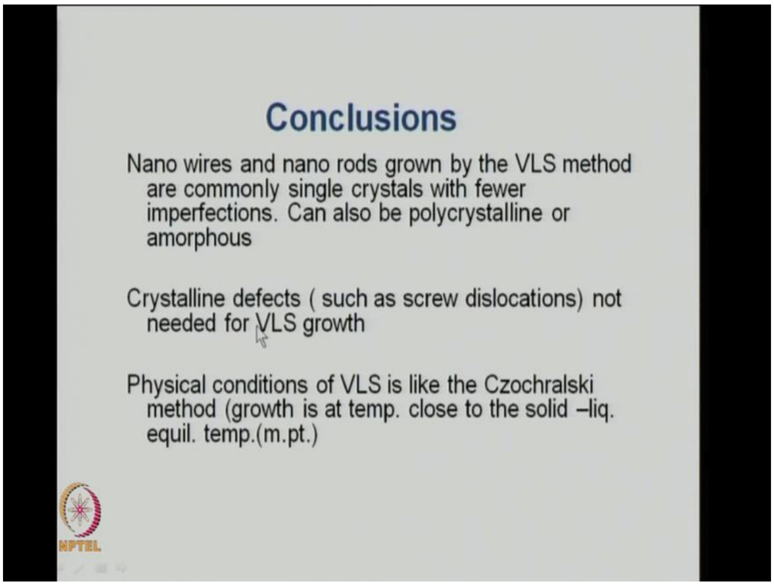

So, to conclude the vapor-liquid-solid method, we can easily grow nanowires and nanorods by the VLS method, with we do not need any defects and hence, the crystals that we grow also have less defects, because we do not start with any defects. Although, we grow single crystalline rods, we can also grow polycrystalline or amorphous rods using the VLS method. So, the most important thing is crystalline defects like screw dislocations, which is required in other methods of growth, is not required for the VLS growth mechanism. Then, the conditions of the VLS, that is, you are close to the melt; you have to melt the catalyst, is like, what is called the czochralski method, which is the common method of growing crystals. The czochralski method is close to the solid liquid melting temperature.

In the VLS case also, we are close to a solid liquid melting because, we have to melt the catalyst and make it, either into an alloy or the catalyst itself melts to remain as a molten globule. The conditions of VLS are little bit or quite close to the czochralski method of crystal growth. With that we come to the end of today's lecture of the vapor-liquid-solid method. By this lecture, we come to an end to the module 2 of this course on nanostructured materials. In the next lecture, we will start module 3. The first lecture of module 3 will be my next lecture.

Thank you and goodbye.