Nano structured Materials-Synthesis, Properties, Self Assembly and Applications

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Module - 3
Lecture - 19
Metal and Metal Oxide Nanowires – II

Welcome back to this course on nanostructured materials, today we will be having the lecture number 5 of module 3. In which we are discussing different types of nanowires other than carbon nanowires, which was the part of our discussions in the first three lectures of this module 3. So, in the previous lecture of module 3, which was the lecture number 4, we discussed various aspects of nano wires of metals and metal oxides, and their synthesis and properties.

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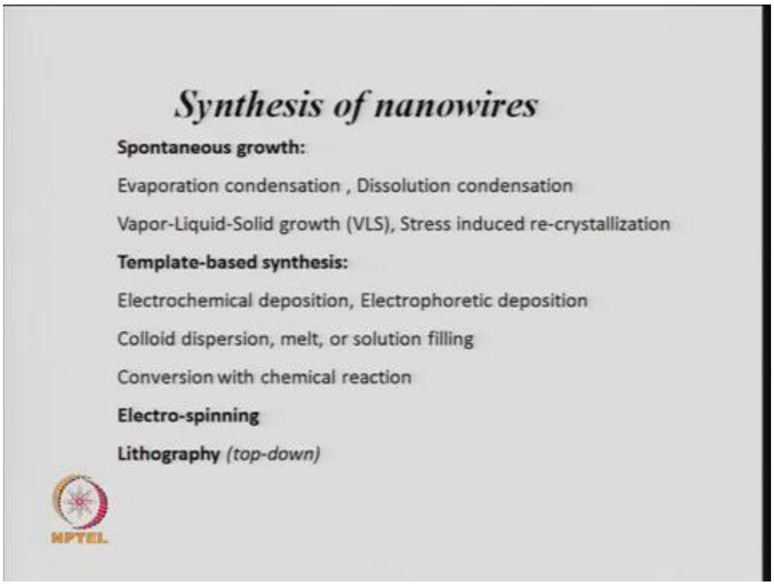

Today, we will continue on that aspect of the synthesis of nanowires. Basically the synthesis is based on spontaneous growth in which you have learnt in the previous lecture on evaporation condensation and dissolution condensation techniques of making metal nanowires and related nano wires. Some are oxide, some are alloys, and some are chalcogenides. And today we will look at some aspects of vapor liquid solid growth. Of course, there are other aspects like stress induced recrystallization, which we are not going to discuss in this course.

Then we will discuss how to make nano wires using templates and there are different types of template based synthesis. Predominantly large amount of work is done on the synthesis of nanowires using the electrodeposition or electrochemical deposition root. Typically, these are metallic nanowires while the electrophoretic deposition can be used for making metallic as well as nonmetallic like metal oxide nanowires. This is one of the most popular technique of making metal oxide nano wires, so for metal nano wires typically people go for electrochemical deposition routes and for metal oxide nanowires people use electrophoretic deposition.

Of course, there are other methods also, which we will not be discussing to large extent like the electro spinning method which is used a lot in the textile industry, where they draw fibers or nano wires of fibers which are used for textiles. There, electro spinning is a very popular root of making nanofibers and it can make very large amount of nano fibers in reasonable amount of time.

Then, people make nano wires with lot of precision, but of course much more expensive processes using the lithographic techniques or top down techniques. Our discussion mainly will be based on the evaporation condensation and dissolution condensation which we discussed earlier. Today, we will discuss the vapor liquid solid growth and the template based methods in which we will discuss mainly the electrochemical deposition route and the electrophoretic deposition routes.

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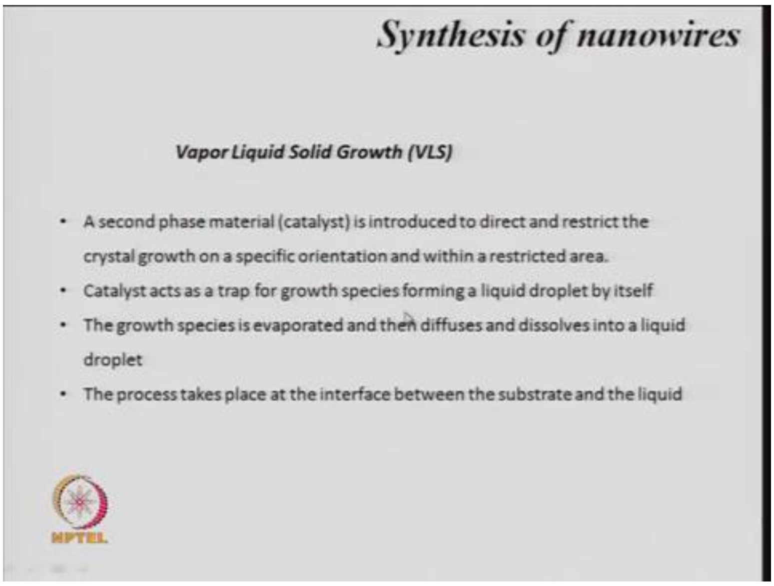

Now, what is this vapor liquid solid growth in some previous module, also we have introduced you to this subject of vapor liquid solid growth during typical our lectures on growth of nanostructures in general. There also, we showed how anisotropic nanostructures can be made using the vapor liquid solid growth and here since we are discussing nanowires which is of course an anisotropic structure.

Hence, it makes sense to discuss this method again giving examples for the synthesis of nanowires using vapor liquid solid method. So, what is this method, in this technique, a catalyst is normally used which we call a second phase material where as the main phase is the phase whose wire you want. So, that is the main phase, which may be a semiconductor wire, which you want, so it has to start from a semiconducting material along with that you have to add a second phase material which is the catalyst.

In this method, it can be restricted the crystal growth is restricted in a specific orientation and within a restricted area. So, that is the role of the catalyst, so wherever the catalyst forms a droplet there itself the growth takes place first the material is evaporated and then that evaporated material defuses through a droplet of a catalyst.

Wherever the droplet is present in only that area the growth of the nanowire occurs and then it moves in one direction, the catalyst acts as a trap for growth species. So, the catalyst basically traps the volatile, which whatever semiconductor species which you have converted to vapor and traps it forming a liquid droplet with the semiconductor material, which you have trying to grove nanowires.

The growth species as I mentioned which is suppose you want gallium oxide wire or some cadmium selenide wire then that growth species is your gallium nitrite or cadmium selenide and that has to be evaporated. Once it is evaporated then it defuses and dissolves into a liquid droplet which is the liquid droplet is basically made by the catalyst and this process takes place at the interface between the substrate and the liquid. So, there is substrate on which this droplet is formed as we will see in the subsequent slide and this process takes place at the interface between the substrate and the liquid.

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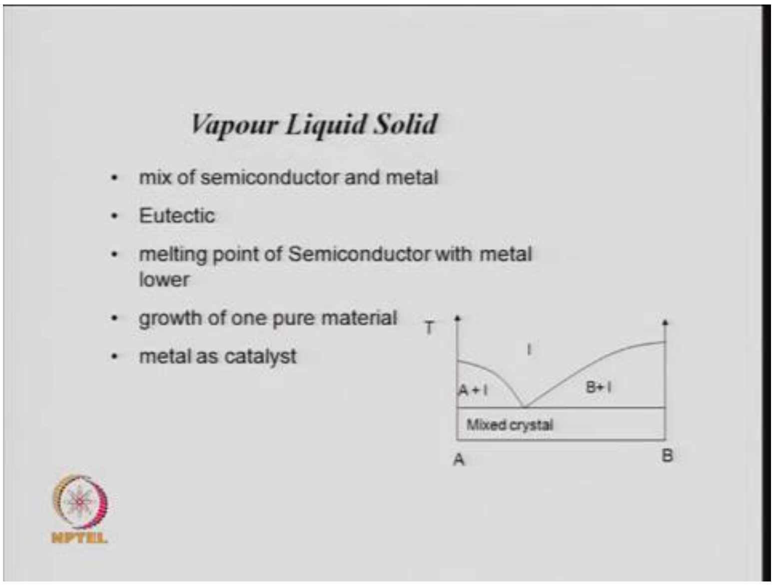

Before I show you the exact process in this vapor liquid solid, some basics of solid the phase diagrams of two materials, for example A and B are there. So, what happens if they mix, so you can draw phase diagram where you can define what the eutectic composition is, what is the eutectic temperature. As you all know the eutectic composition has the lowest melting point so anything below this temperature is a solid.

So, it is a crystal is the mixed crystal because it has components of both A and B here, A may be the catalyst and B is may be a semiconductor which you are trying to evaporate. Then, it re dissolves, so in the liquid phase you have this mixture of the catalyst plus the phase which you are forming and if you take the eutectic composition, what you are doing is you are lowering the melting point of the system.

So, suppose for A, the melting point is here for B the melting point is there where as for the catalytic composition, which is somewhere here the melting point is much lower than the melting point of A which is here and the melting point of B. So, such eutectic phase diagrams are important and most of the phase diagrams of semiconductors and these catalyst are known. If it is not known, then you have to work out the phase diagrams and find out these eutectic temperatures and eutectic compositions, because you have to use these temperatures and compositions for creating the droplets which you want.

So, when you take a mixture of a semiconductor and a metal and you get a eutectic and this eutectic has a melting point is which is lower. Then, the melting point of the semiconductor or metal and the growth of only one pure material takes place, so the growth of only the semiconductor which you want takes place and the metal is the catalyst and it is recovered.

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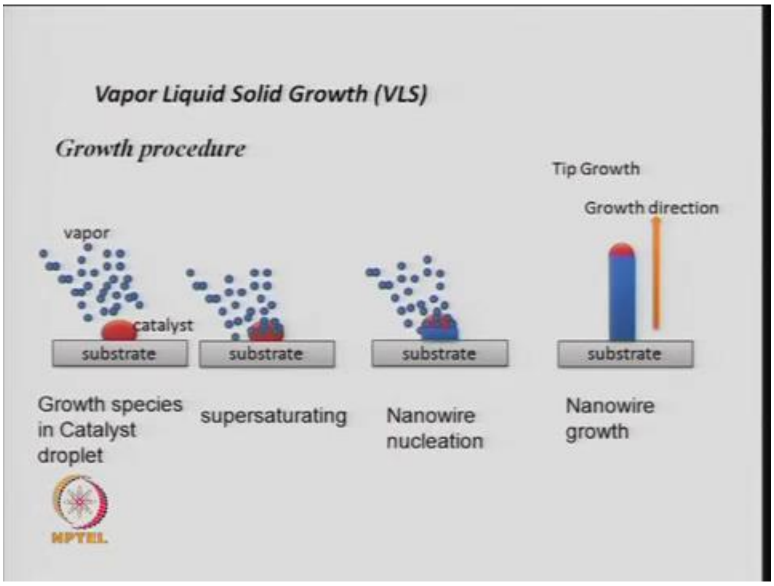

Now, this process can be shown in this as shown here, where you see that you have a substrate and you have a catalyst which has formed a droplet. So, you have heated it at a temperature where it is a droplet and this vapor phase that you have heated the semiconductor whose nanowire you want. So, this material is evaporated, so the vapor phase is present the catalyst is in the droplet or the liquid phase and this is the substrate. Now, at the substrate and droplet interface is where the actual growth, which will takes place.

Now, how will this takes place these molecules, which are in the vapor phase have to defuse through this liquid droplet that is what is being shown here that these vapor phase droplets or molecules get into the catalytic drop. Then, move towards the substrate once they hit the substrate, these vapor phase then becomes like a crystal or polycrystalline material depending whether you are growing is single crystalline nanowire or a polycrystalline nanowire.

So, the material that deposits on the substrate is the material which will grow into a nanowire and that is the material which you have evaporated and that is in the vapor state. So, this mechanism is called vapor liquid solid because you have all the three phases, you have this vapor and you have this liquid droplet and this solid nano rod is taking shape. As further reaction goes on, this blue color as you see is enhanced because these molecules which are shown in blue is this wire material for the nanowire.

That material keeps depositing here at the interface of initially the substrate and the droplet and then more molecules defuse and then deposit on the growing interface between the material for the nanowire and the catalyst droplet. So, the catalyst is always moving ahead and is at the tip of the nanowire and as you see the diameter of this droplet determines the diameter of the wire which will be resulting from this process.

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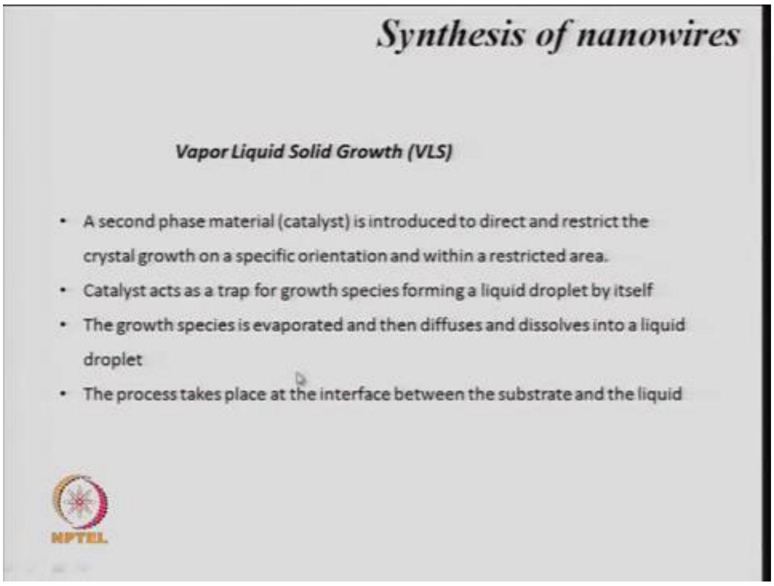

So, that is why it was said that the catalyst restricts the growth, so the crystal growth is restricted within an area and also the crystal growth is within along a specific orientation.

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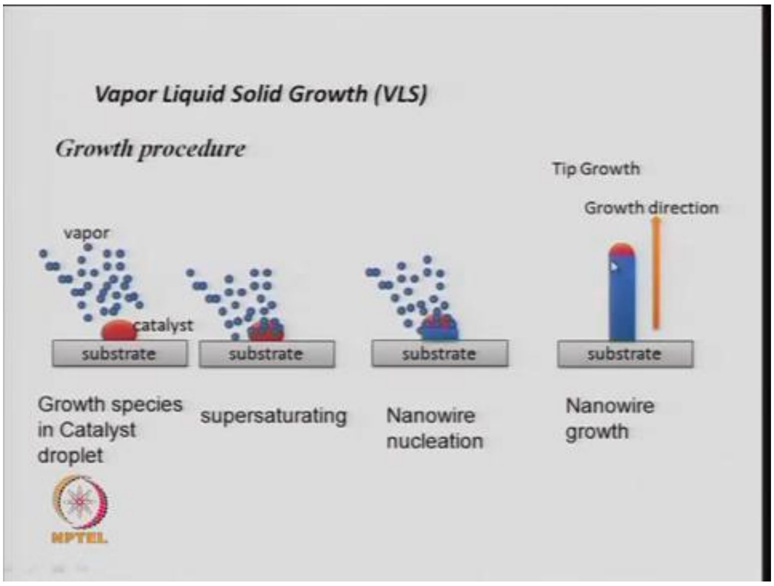

That is shown here that the area of cross section which will be a circle is defined by the diameter of the droplet if you have smaller droplet. The nanowire will have a smaller diameter and the growth is along this particular direction and this kind of growth is called the tip growth that means the catalyst is at the tip. The material which is to be grown is below it below the tip other than the tip growth we discussed in the growth of the carbon nanotubes.

You can also have what is called the route growth that means the growth is at the bottom, which means a catalyst is at the bottom. So, there are two types of growth in this particular case in the vapor liquid solid growth as we see here. This is the tip growth and the catalyst is at the tip and the nanowire keeps growing as more and more these vapor molecules are evaporated.

Once all the material, which is to be made into the nanowire is evaporated, then this growth will stop and you will get the result in nanowire. So, this is a schematic explanation of this whole process of vapor liquid solid in which you get the tip growth mechanism with the catalyst at the tip below which is the growing nanowire and below the bottom of the nanowire is the substrate material.

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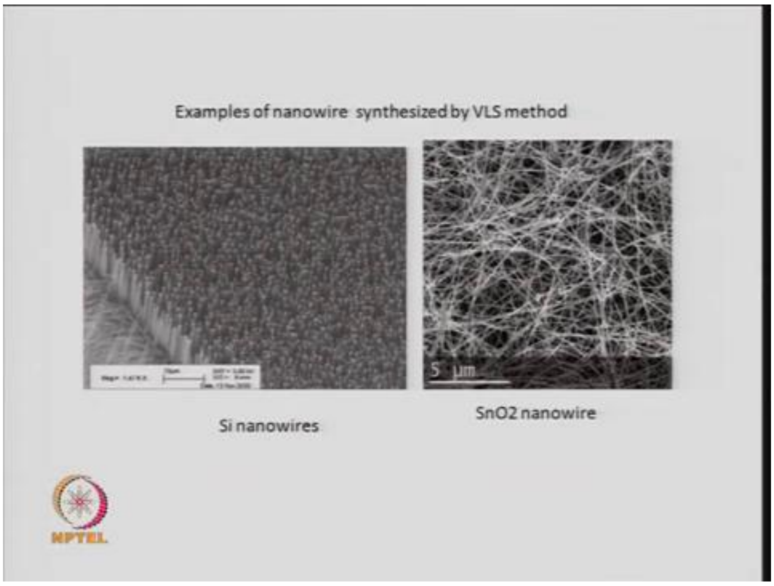

Now, these are examples of a nanowires grown by the VLS method that is the vapor liquid solid method. These are silicon nanowires, which as which are very well aligned as you can see and these are some tin dioxide nanowires which are of course not so well aligned. So, it depends on the material, it depends on the substrate it depends on growth conditions, what is the temperature etcetera that you can sometimes get aligned nanowires and sometimes you get nanowires in a bunch.

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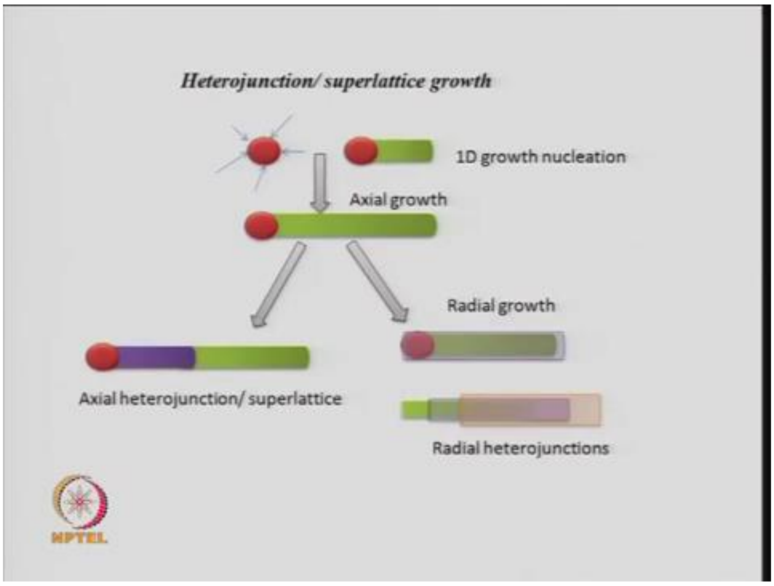

Now, you can also make junctions of nanowires that means two nanowires of different materials are interconnected. Now, such growth can be called heterojunction or super lattice growth and this is shown here you have this catalyst as discussed earlier a metal catalyst. You have one dimensional growth as discussed earlier, so this is the one dimensional nanowire growth and after that growth you have, this which is a one dimensional growth along one particular axis and so it is an axial growth.

Now, once you have an axial growth of a one particular material, now if you want to grow another material on that, there are two ways of doing it. One is you grow along the same axis another nanowire of a different material and that is called axial heterojunction or a axial super lattice. If you grow something around this nanowire that means radially you are growing another material, then that is a radial growth.

So, then the material which you originally had in your nanowire as shown in green has a another material on top of it like a jacket and there is a bluish kind of pinch shown here and that is radial growth. Now, this can be done several times, so once in the green nanowire, if you have a jacket of a blue nanowire and then you can couple with another nanowire which is growing outside radially. So, along the entire tube, then you have this kind of radial heterojunctions. Now, depending on the application you may like to synthesize a axial heterojunction or a radial heterojunction and these applications will be discussed later.

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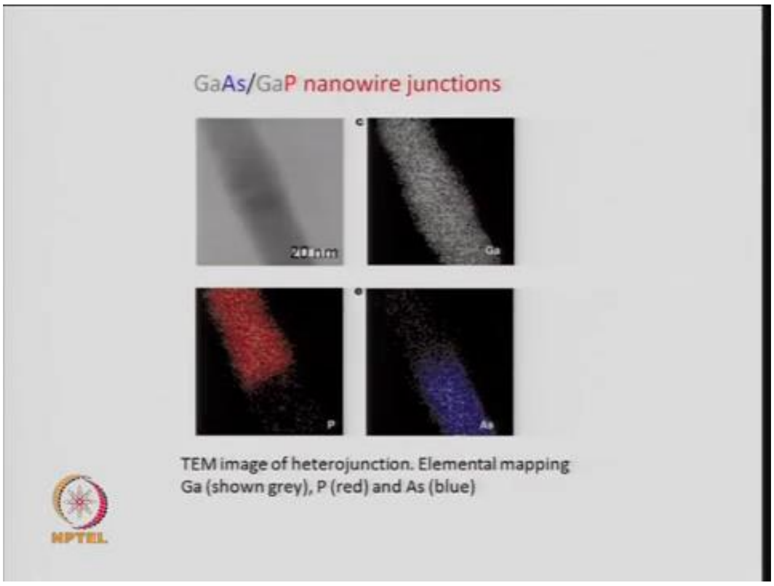

This is a an example of a growth of nanowire junctions, so this is an axial growth and this is a T E M picture where the gallium arsenide and gallium phosphide two semiconductors are connected along the same axis. So, it is a continuous axis where part of it is gallium arsenide and part of it is gallium phosphide, but in this simple T E M or transmission electron microscope. You cannot distinguish between the gallium arsenide and the gallium phosphide this is a low resolution T E M. If you want to see exactly where is your gallium arsenide and where is your gallium phosphide, then you have to do what is called mapping and in that as you see you color code different elements.

So, you do a what we call an edacs mapping, so it maps wherever one metal is there it is color coded with a one specific color. So, for example, wherever gallium is there, you have the gray color, so gallium is there in both gallium arsenide as well as gallium phosphide. So, gallium will be there in this part as well as in this part, hence the whole nanowire heterojunction which has got both gallium arsenide and gallium phosphide will be showing gray spots like this. It is showing the presence of gallium throughout this heterojunction, whereas if you map or look for only phosphorous or only arsenic, then you will see only half the nanowire being color coded.

So, for phosphorous if we choose the red color, we see only this half has got this red spots suggesting that this part of the heterojunction is made up of gallium phosphide where as if you take arsenic is color coded in the blue color. So, you see the lower half which is not showing anything other than gray no red spots will show now blue color here showing that this part of the heterojunction contains arsenic. So, this is the gallium arsenide part and the top part is the gallium phosphide, so you can exactly characterize very precisely the heterojunction nanowires as by edacs mapping as shown here.

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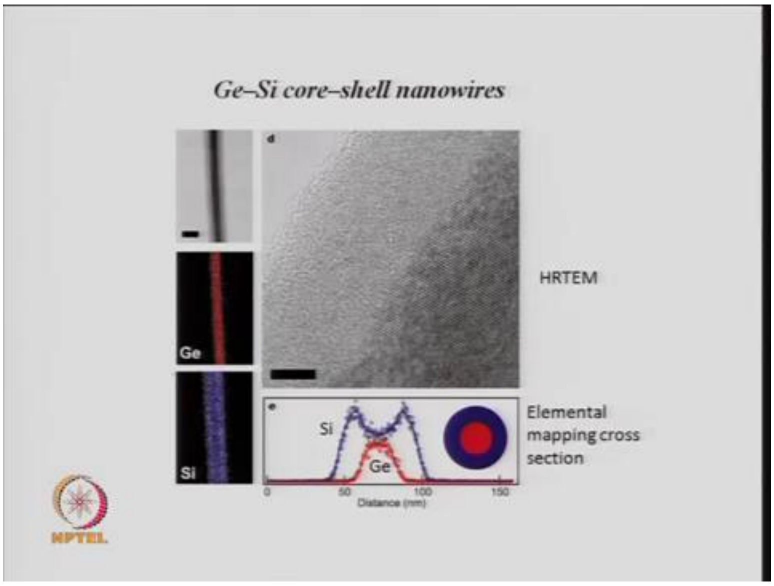

Now, this is another example of germanium silicon core shell nanowires, so you have one wire and then you have an outer wire. So, it is again like one wire growing on top of another wire, so one wire inserted in another wire or like coaxial cables you know, so if you look at this is this a T E M picture here also you can see the color the contrast.

So, you have a dark and lighted region and in the high resolution you can clearly see you have this high resolution part which has high a crystallinity and this has low crystallinity and if you do an edacs mapping like we discussed in the axial heterojunction. In the gallium phosphate and gallium arsenide case, you could see the two semiconductor nanowires, which are interconnected here the coaxial wires. Like inside, you have germanium and that is color coded red and you do not see any red color outside this.

When you looks for silicon, which is color coded blue silicon is all over the place because silicon is covering this entire germanium nanowire. So, it is on top of this wire on the side of this wire 2 and so the whole tube is color coded as blue. So, you can also plot this presence of silicon and gallium through this kind of cross section mapping elemental cross sectional mapping and you will see that at a the center this is center.

So, if you take the cross section of this wire at the center, you will have only germanium the red color and on the periphery which is a blue color you will have silicon. So, silicon will have maximum intensity, which is a way from the germanium maximum intensity and since it is covering the germanium it will be found on either side of the germanium peak. So, if you go away from the germanium center either on the left side or on the right side, you will find a intense silicon peak on both sides of the center of the circle, which is the cross section if you take the cross section of this coaxial core shell type of nanowires.

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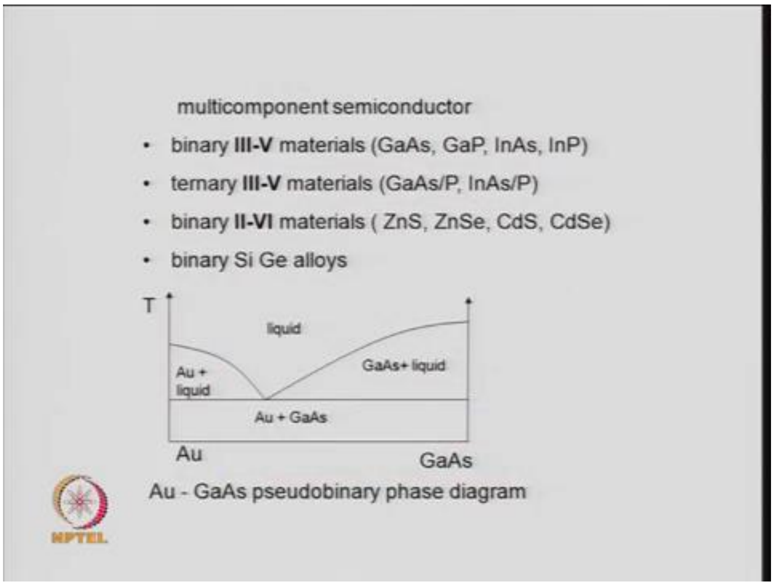

So, many of this kind of nanowires have been grown and again as we discussed phase diagrams play a very important role in the growth of this kind of VLS mediated growth of nanowires because you have this liquid phase interacting with the solid phase. This is a gold gallium arsenide pseudo binary phase diagram, where you will have this gold droplet in which gallium arsenide vapors will dissolve and form gallium arsenide nanowires. So, you can make using this kind of V L S method, many type of semiconductors like the 3 5 semiconductors. Like gallium arsenide phosphates, or indium arsenide phosphates even 2 6 semiconductors like zinc sulfide zinc solenoid cadmium sulfide cadmium solenoid.

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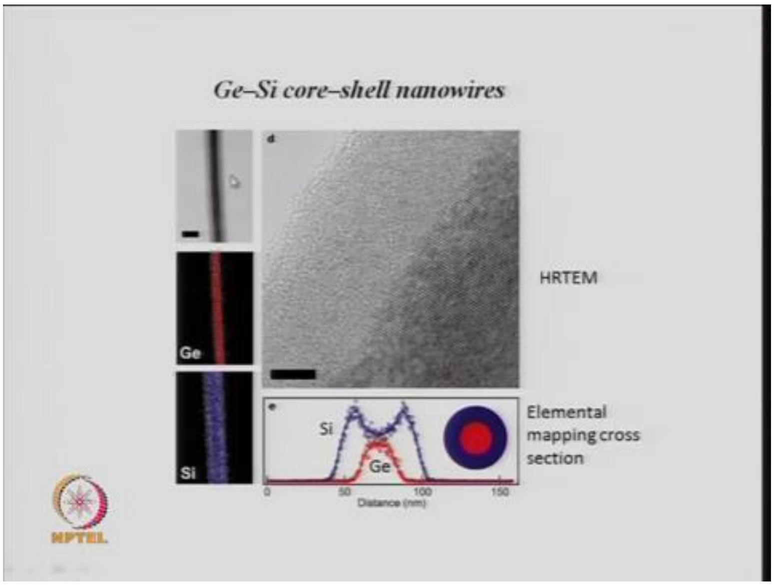

You can make binary silicon germanium alloys, which is the example shown here this is binary silicon germanium with the special core shell type of structure. Of course, you can also make alloys here in the previous slide, this are not alloy this are germanium nanowires covered with silicon nanowires, but you can also make silicon germanium alloy nanowires.

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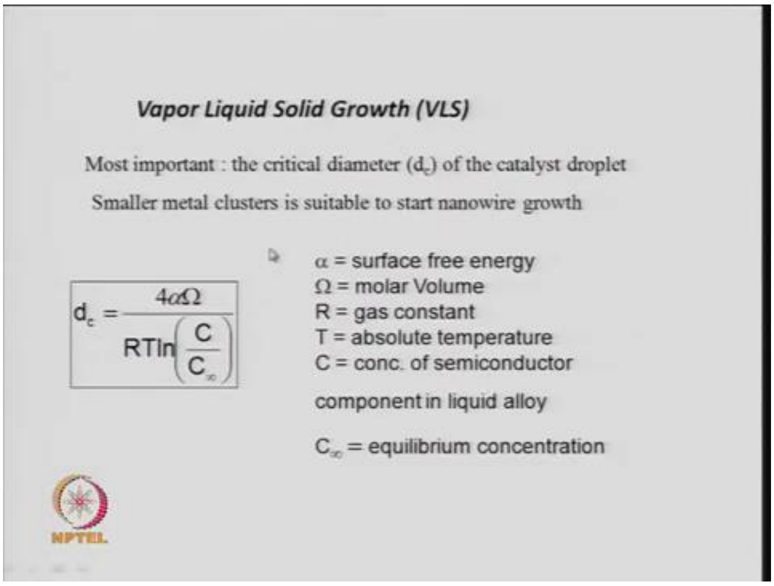

Now, typically the diameter of the nanowire is dependent on the diameter of the catalyst droplet and that is what is shown here that if you can make a small droplet of the catalyst. So, small metal clusters acting as then you can have good nanowire growths, so it is easier to grow nanowires when the diameter of the catalyst droplet is small. So, this is given by this relation the critical diameter d c of the catalyst droplet is related to the surface energy alpha and the molar volume.

So, it is directly relation related to this surface free energy, so to keep a small diameter for the nanowire, you need a small surface free energy and a small molar volume. Of course, you have other factors like the concentration of the semiconductor in the liquid alloy. So, in the liquid droplet what is the concentration of the semiconductor that also place a roll and this relation can be used to find out or optimize your conditions for suitable nanowire growth.

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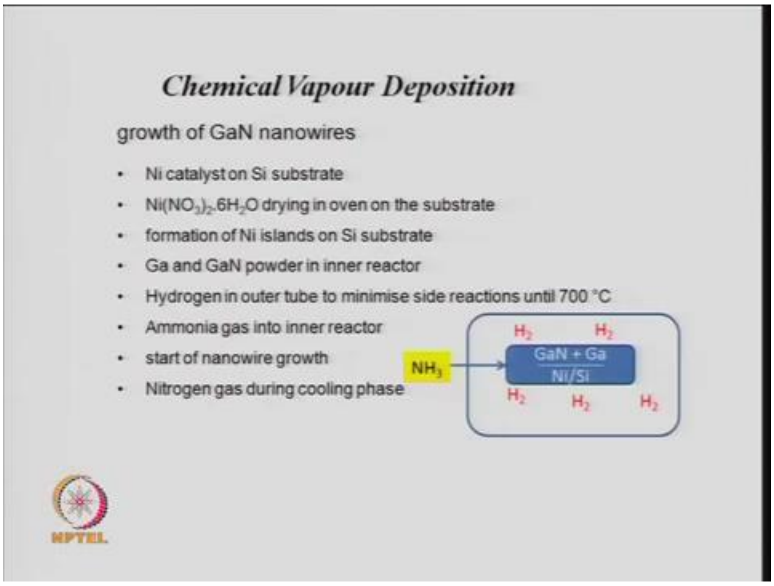

Now, other than the V L S method quick word on chemical vapor deposition this technique, we have discussed a in quite detail in our earlier lectures. I think in module one or I think in module two, we discuss the CVD technique of growing nanostructures to great detail. So, here we just discuss one case of how you grow nanowires using the CVD or the chemical vapor deposition technique. So, in the chemical vapor deposition technique from the term itself you can understand that you have to create a vapor using some chemicals and then you deposit that vapor to form the nanostructure material.

So, an example is given here of the growth of gallium nitrite nanowires is a very important material semiconductor and it has lot of applications in solid state lighting. So, gallium nitrite nanowires are very important and now how this has been grown using the CVD technique or the chemical vapor deposition technique is that you take a substrate and your substrate here is a silicon substrate.

So, you take a silicon substrate and you have to put a catalyst, so the catalyst here is the nickel and how you make this catalyst is you take a solution of nickel salt so that the salt commonly use is nickel nitrate. You put few drops of this solution of nickel nitrate over the substrate and then dried in an oven, so you will have some islands nickel islands on the silicon substrate and that is what is shown here.

So, you have this nickel on silicon substrate, now then you add gallium and gallium nitrate powder you are trying to make gallium nitrate nanowires and you start with the mixture of gallium and gallium nitrate powder. You put it in the reactor in which you have nickel catalyst on top of a silicon substrate. So, this is like double reactor vessel, so there is inner reactor and there is outer shell and this actually is housed within a furnace, where you can change the temperature.

Now, what you do is since you have this materials inside and you want the grow of nanowires now you pass ammonia gas through the inner chamber and where you have this gallium nitrate and gallium metal and this catalyst is there. You have to maintain some temperature, now normally they do reactions around 700 degree centigrade and due if you do not have a reducing atmosphere outside the chances are that the gallium will get oxidized to gallium oxide.

Hence, you have two a jackets, so you have an inner tube in which you have the reactants on with catalyst on the substrate and you have an outer jacket outer reactor, where you have hydrogen gas being circulated to maintain the reducing environment. The temperature is kept around in a 700 degrees at that temperature when you pass ammonia then reaction occurs and gallium nitrate wires start nucleating on the nickel catalyst and the growth of gallium nitrate nanowire occurs. So, the gallium nitrate which you added gets heated and there volatilizes and then re deposits on the nickel as a catalyst.

Then, the nanowires start going and then once the nanowires have grown, then this hydrogen is flushed out, the ammonia is passed only in the inner vessel and the hydrogen here which is actually it flows in and out. So, it is not a close chamber, where hydrogen is stored, but hydrogen is flowing through this around that chamber and out so once the nanowires have grown then you flush this with nitrogen and you cool the furnace. Then, then you take out your nanowires which grew in the inner chamber of this double chamber vessel inside a furnace, so that is how using CVD technique you can grow gallium nitrate nanowires.

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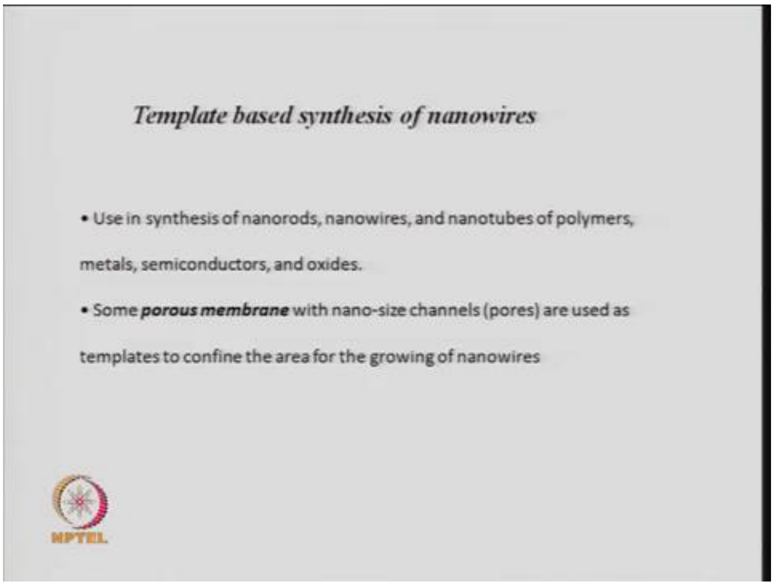

Now, coming to template based nanowires this is a very popular method and various kind of template based nanowires are there and these can be used for making thin nanowires or thick nanowires which are also called nano rods. So, the difference in the nomenclature of nanorods and nanowires basically going back to the aspect ratio. If the aspect ratio is very high, then normally we say they are nanowires and of course they should be the radius or the diameter of the wire should be very small.

When the diameter becomes large, then we call them nanorods and of course if this rods are wires or hollow, then we call them nanotubes and you can use this template based methodology for the synthesis of nanowires. Nanotubes and nanorods of all kinds of materials including polymerase metals, semiconductors, many of them will be oxides, some are also nitrates etcetera. Now, what many times this template is actually porous membrane, so what is this template most of the time it is a porous membrane with nano size channels or porous.

Within this porous, you want the growth of this nanowires, so the diameter of the nanowire is very closely linked to the diameter of the porous within this porous membrane because that restrict the growth of the nanowire in the radial directions. The growth can only be in the axial direction and so you get very long and thin nanowires.

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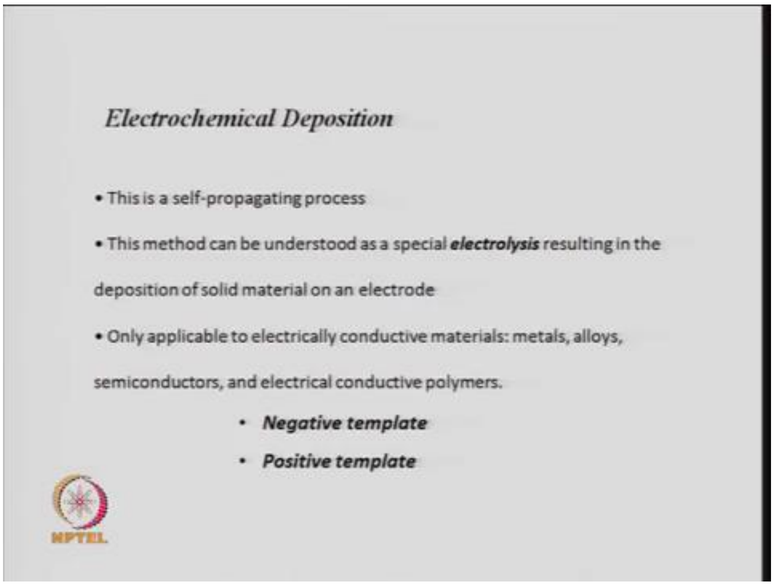

Now, when you use templates a common method is to apply an electric filed that is you do electric chemical depositions and this electrochemical deposition using porous templates is a self-propagating process. It can be understood as a special kind of electrolysis, we all know electrolysis in chemistry and in materials. That is the deposition of metals on electrodes when you apply an voltage and this can be consider to be a process which is similar to that where you have this porous templates on which deposition occurs. So, the deposition of this material is quite similar what to commonly what we call as electrolysis.

There is one major hindrance or one major drawback of this method that it can be applied only to electrically conducting materials like metals alloys and loop and gaps in semiconductors which or conducting polymers. They cannot be applied for insulators and many of the oxides and nitrates are insulators and in that case you cannot do the electro chemical deposition for the template method. So, the template base electro chemical deposition is mainly for conducting materials, now you can have two classes of this template method one is the negative template method and the other is the positive template method. So, we will go into some of this examples of where you are using a negative template to synthesis nanowires using electro chemical deposition and porous templates.

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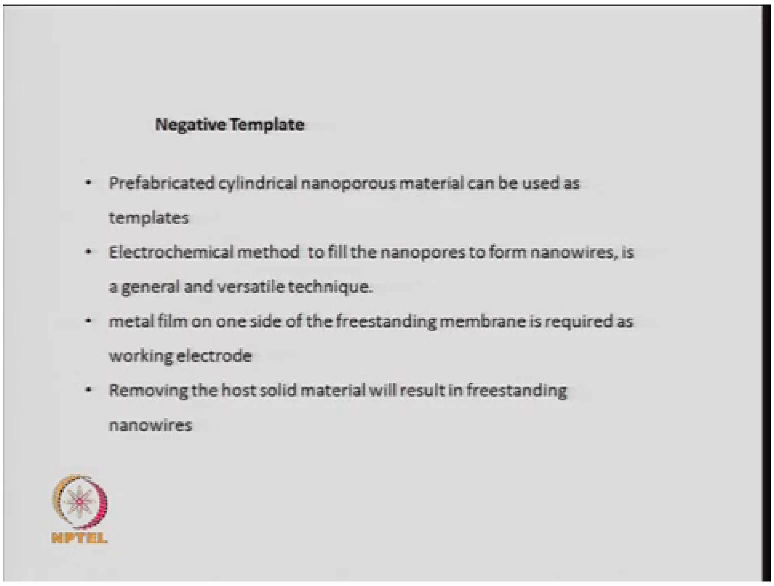

If the material grows on top of that template, then it is called a positive template, if the materials grow in the gaps within the porous template, then it is called a negative template. So, what are this negative templates prefabricated cylindrical nanoporous materials can be used as negative templates and many such materials are known. Using the electro chemical method, what you do is you fill this nano pores the material of choice or the normally metals or conducting polymers to form nanowires.

It is general, quite common and quite versatile you must have metal film on one side of the freestanding membrane which should work as an electrodes. So, it is the basically the working electrodes is a metal film on one side of the membrane and the host material when it is removed it will result in the free standing nanowires. So, you can you use a porous membrane and you have a metal as a working electrode or a metal film and once you fill the porous electrodes with material and then remove the solid host material, you get the nanowires.

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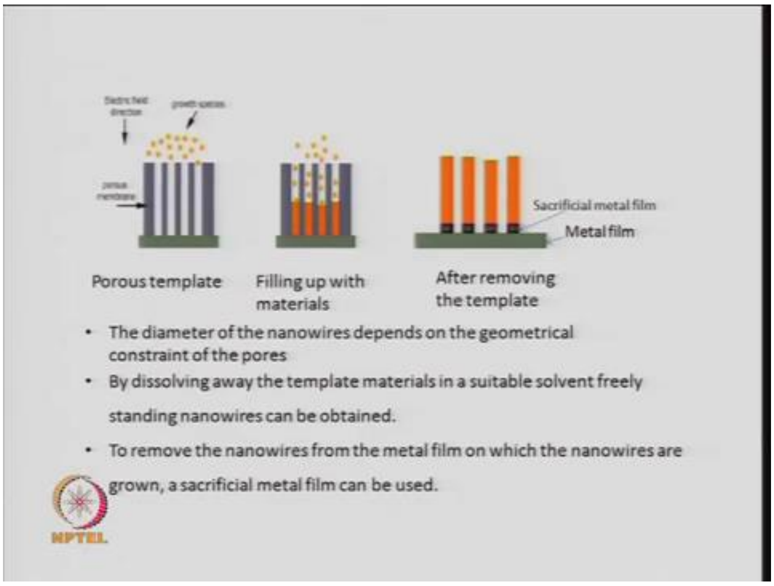

So, that is shown here, so you have this porous membrane shown here in gray color and this is the metal film which on which this molecule will deposit and form these nanowires. Once they are completed, then you remove this porous template, so the gray porous template can be removed and you get this free standing nanowires. Now, if you want to remove, disconnect from the metal, then in between the metal electrode, which act as the one working electrode you put a sacrificial layer. So, first you code this metal layer with the sacrificial layer, then the growth of this nanowire will not take place on the metal, but will take place on the sacrificial metal film once you have this then you can remove this metal film.

You will get free nanowires, so you have to apply an electric field in this direction in the electro chemical process the materials has to be conducting and you use a metal film to act as working electrode. The diameter of the nanowire as you see this diameter of the nanowire is dependent on the pore size, so whatever be the pore size will be the diameter of the nanowire. So, you if you have a choice of selecting the porous membrane or the porous material, then you have a choice of defining your thickness or the radios of your nanowire, the dissolving of the template material should also be easy.

So, if you have a porous material which cannot be dissolved easily or removed easily then that is not going to produce nanowires it is going to be difficult to get this free standing nanowires. The sacrificial metal film technique can be used if you on absolutely free nanowires, otherwise they will be always on this metal film at the bottom, which is being used as a working electrode.

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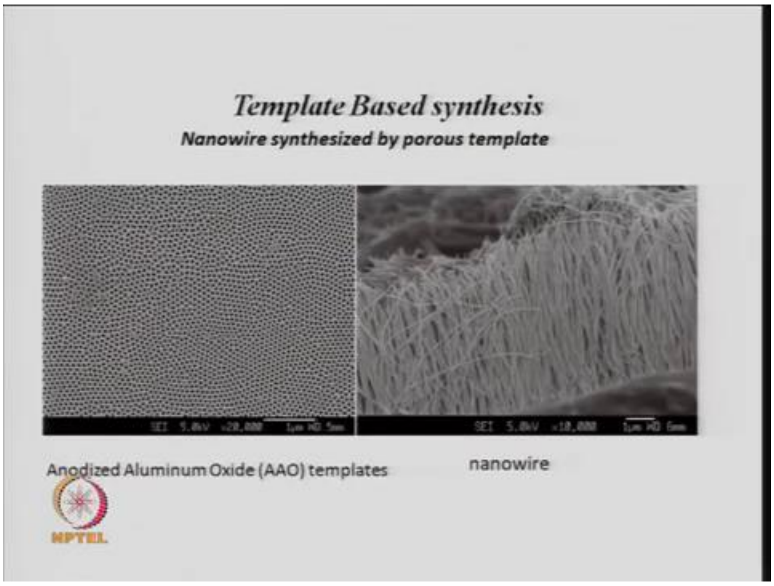

Based on such porous templates, you can grow a nanowires, so this is the template and this template is called anodized aluminum oxide a very popular template, which has a very uniform pore size as you see and the nanowire growth will be in this pores. Once you remove the template, then you can get these nanowires, which have grown in this porous templates this is an example of some metallic nanowires as shown here and this scale here is 1 micron.

So, the scale is one micron that then this nanowires are quite thin as you see compare to 1 micron, so they may be around 10, 20 nanometers in diameter. So, by this method you can grow depending on how big is your template you can grow very large scale nanowires using the electro chemical deposition with porous electrodes and here as you see the template is a negative template because you are getting the nanowires. Here, there was a pore, so the nanowire is not growing on this material, but is growing inside the pore of this material and hence this is called a negative template method.

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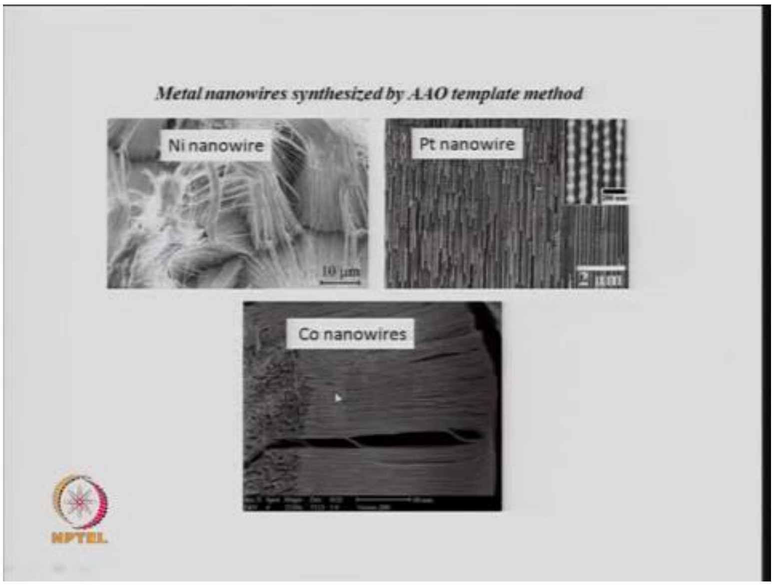

Now, there are many other examples like nickel nanowires platinum nanowires which have been grown by the anodized aluminum oxide template method the negative plate method.

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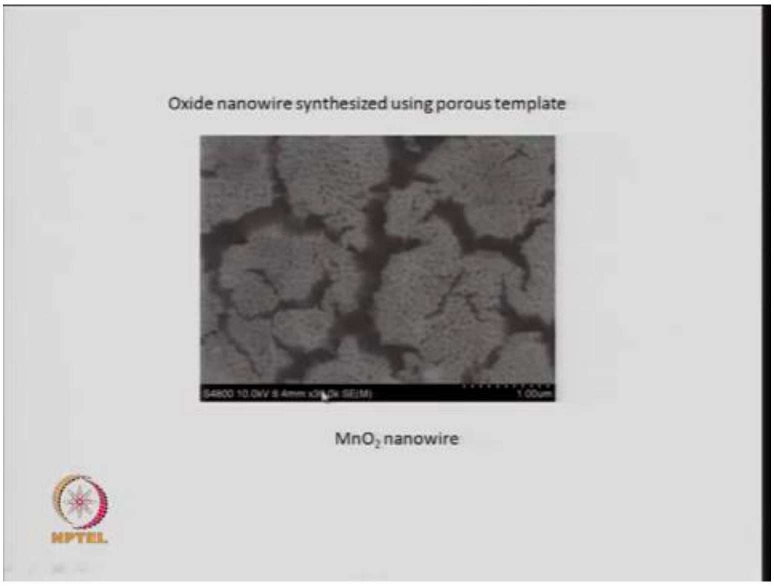

This is an oxide nanowire Manganese dioxide nanowire which has been synthesized using a porous template and a this manganese dioxide as you know is a slightly conducting, because it is manganese in plus 4 oxidation state. However, it would be difficult to make manganese nanowires, which are not so conducting, so which have high bang gaps, then you will not be able to make them using the electro deposition route.

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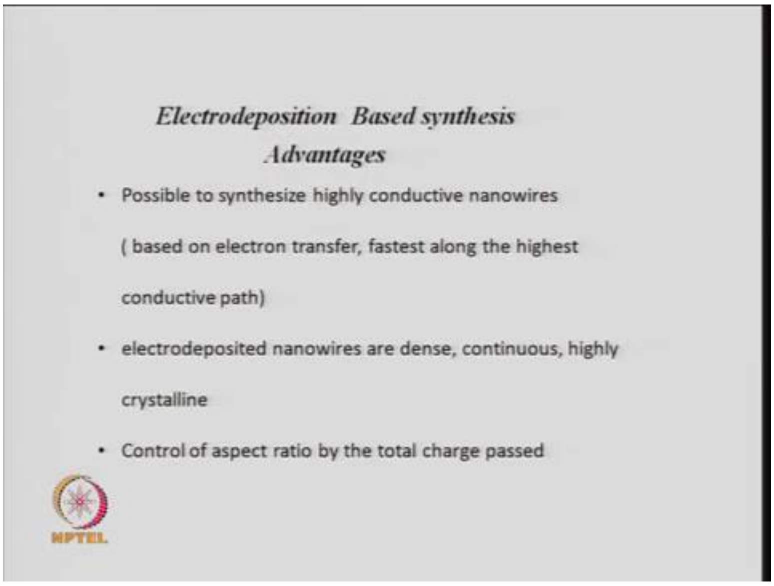

So, the electrodeposition route has certain advantages which we have been discussing the key advantage is you can synthesize highly conducting nanowires. You can make very quickly these nanowires because the growth occurs based on electron transfer and electron transfer is fastest along the highest conductive path. So, these wires can be made very quickly the electrodeposited nanowires normally are dense continuous and they are highly crystalline.

Another very important advantage of the electrodeposition method is that you can control the length of the wire why the amount of charge that you passed. So, in the electro chemical experiment, it depends how much charge that you passed because the growth occurs with electron transfer. So, it will depend on how much charge that is current here passing and so you can control the amount this charge and control the length of the nanowires that you are growing. That is a very big advantage using the electrodeposition method using porous templates.

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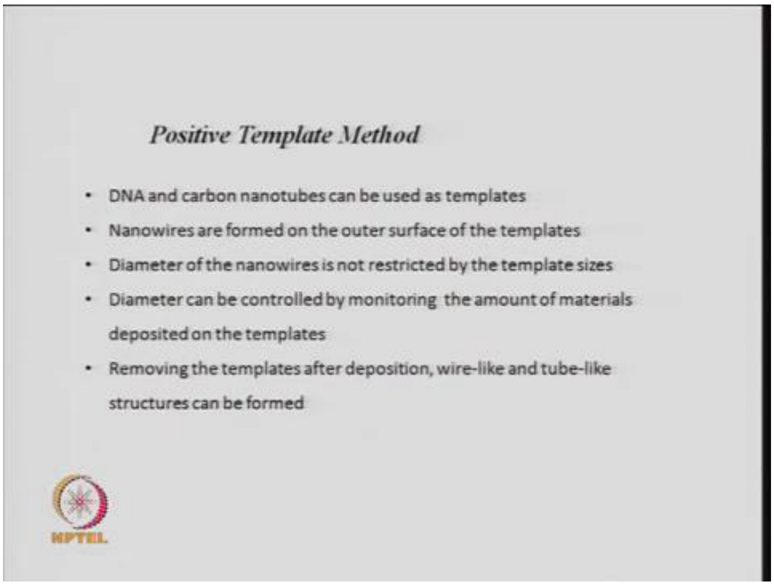

Now, so far we looked at negative template method, now we can let us discuss some examples of the positive template method. That is where you have a template and you grow your nanostructured material on top of the template not in the pores between the template material. So, in this case what are the templates very commonly carbon nanotubes have been used as templates. So, other materials have been grown on carbon nanotubes people have also used DNA, the biopolymer as all of you know the molecule of life and this DNA people have used other materials to be made on DNA.

So, the nanowires in a positive template method as mentioned or formed on the outer surface of the templates, whereas in the negative template method, the nanowires are formed inside the pores. The diameter of the nanowire here is not restricted by the template size, whereas the diameter of the nanowire in the negative template method is restricted by the pore size. So, the pore size is five nanometer you cannot make a nanowire of 6 or 10 nanometer using the negative template method. Using the positive template method, the diameter of the template does not control the diameter of the material or the nanowire that you are growing using, the positive template method.

So, that is a change or an advantage of using the positive template method the diameter of the material which you are growing a can be controlled by monitoring or controlling the amount of material being deposited on the templates. So, how much material you are flowing or making them a deposit will control the diameter not the pores, pore size not the template itself the removing the templates after deposition will result in wire like or cube like structure. So, you can get either nanowires or nanotubes by removing the templates as you have to remove templates both in the negative template method and positive template method, that is the definition of template you have to remove the template to get the final nanowires or nanotubes.

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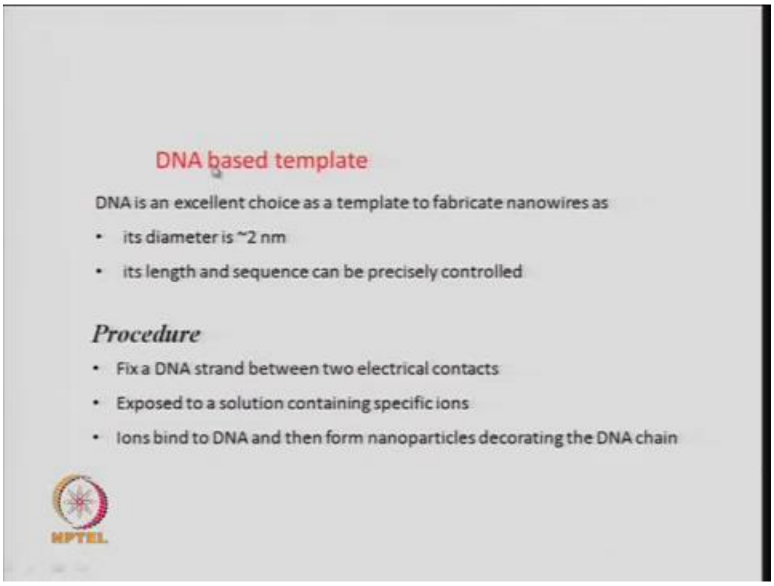

So, let us look at a d n a based template, so DNA is an excellent choice as a template in many cases a the diameter of a DNA is approximately 2 nanometers that is 20 angstroms and their length and sequence of the DNA can be controlled. So, you can have very long DNA fibers and the length you can control and DNA as you know are made of a sequence of amino acid and you can an control this sequence of various bases and amino acids which are nucleic acid which are making the DNA chain.

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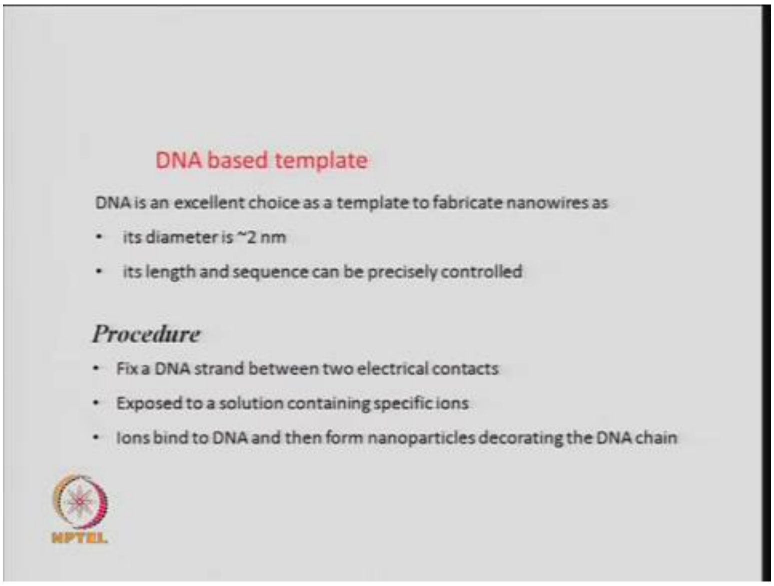

So, by controlling the length and the sequence, you can control the nanowire which are going to be deposited on the DNA chain, so the procedure is you normally take a DNA stand, which is a as we mentioned is around 2 nano meters thick. You connect this between two electrical contacts and then you expose this thread of DNA to a solution which contains the ions of the material you want to deposit. So, if you want a material of calcium phosphate to be deposited, you need calcium ions and phosphate ions in the solution.

So, these ions will bind to DNA and then form nanoparticles on the d n a chain, so why will the ions bind to DNA because DNA will have some charge. You can a give potential because you have two electrical contacts and then the opposite charge will then be a exposed to the charge which is on the DNA.

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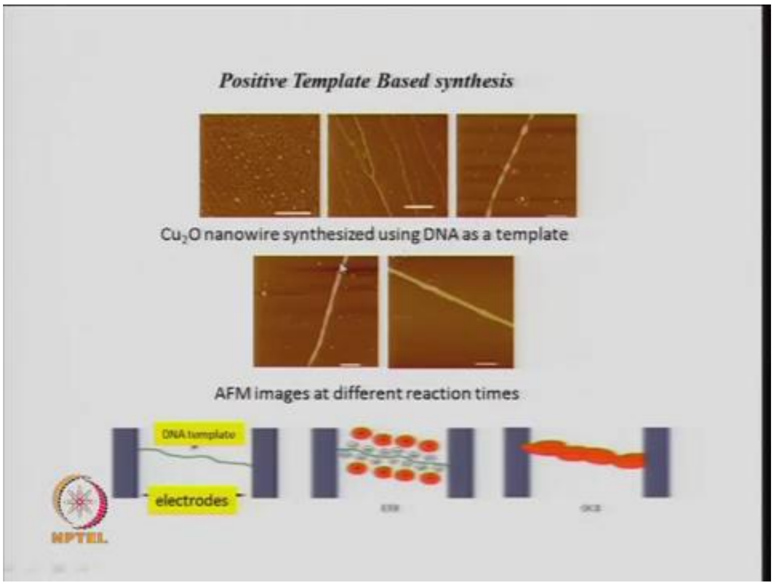

So, this you can see here in this example of growing nanowires on DNA, so which is a positive template based synthesis. So, copper oxide this is Cu 2 O, so this is cupric oxide nanowire synthesized using DNA as a template. So, these are the wires which you see with time actually this is growing with time, so these are the particle and this on the DNA fibers. These particles are growing like this and with time this is becoming thicker or more crystalline and this is the crystalline form of the a Cu 2 O, cupric oxide nanowire which has grown on the DNA, which you took as a template.

So, schematically you can show that you have to metal plate which are the electrodes and in between you have these DNA thread. So, this is a fine DNA fiber which is attached to the two metal contacts the diameter of this DNA fiber is around 2 nanometers which is like 20 angstroms. Then, you dip tin solution of particular ions and those ions which are oppositely charged to the charge on the DNA will come close and then you will have the particles on top of the DNA.

So, this is basically a positive template growth because the particles are on top of the original template and it takes the shape of the chain. So, the chain is in this fashion if it is zigzag, then you can have a zig zag form of the this material, so this is a positive template method using DNA wires on which cupric oxide material has been synthesized.

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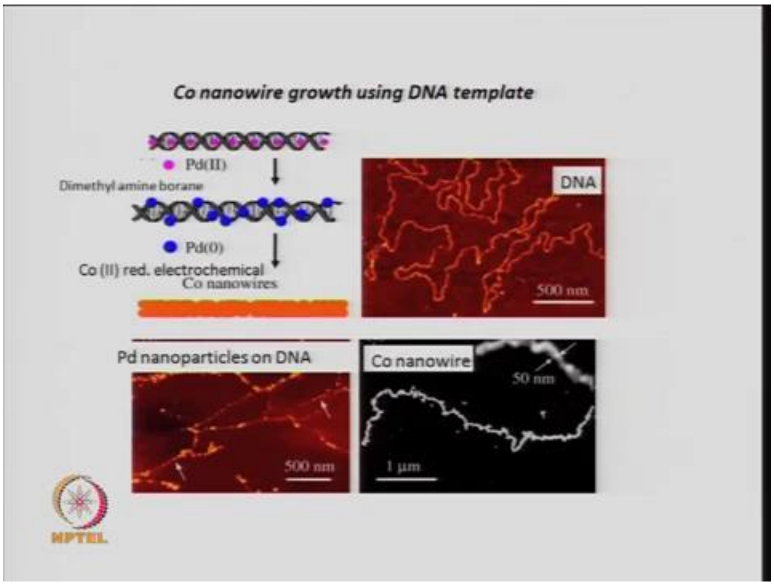

Now, this is another example of a cobalt nanowire growth on DNA as a template here, you use first a palladium, why palladium is used because it is a catalyst. So, you first dip the DNA stand in a palladium solution that contains palladium in divalent state, then you reduce that palladium divalent state to palladium metal particles. So, when it is these positively charged ions of palladium will be held within the DNA double standard DNA when it gets reduced and here a in this particular example dimethyl amine borane was used as the reducing agent.

This reduces the divalent palladium which is inside this chain helical chain when it reduces a 2 palladium 0, which is palladium elemental palladium or palladium metal. Then, these palladium metals is they have no charge, they come on the outside of outside the helix. Then, you dip tin cobalt two solution because we are ultimate aim is to make wire nanowires on the DNA template and since you cannot make them directly you are using palladium catalyst to deposit cobalt nanowires. So, once palladium metal is deposited on top of the DNA double helix, then you add the cobalt 2 solution and then you reduce it electrochemically to finally get the cobalt nanowires.

So, these cobalt nanowires are actually formed on the double helix of DNA using palladium 0 as the catalyst. So, this is an AFM picture of DNA and then you have palladium nanoparticles this stage on the DNA and then finally you have cobalt nanowire which is formed on the d n a template. So, using a the positive template a which is DNA, you can synthesize cobalt nanowires.

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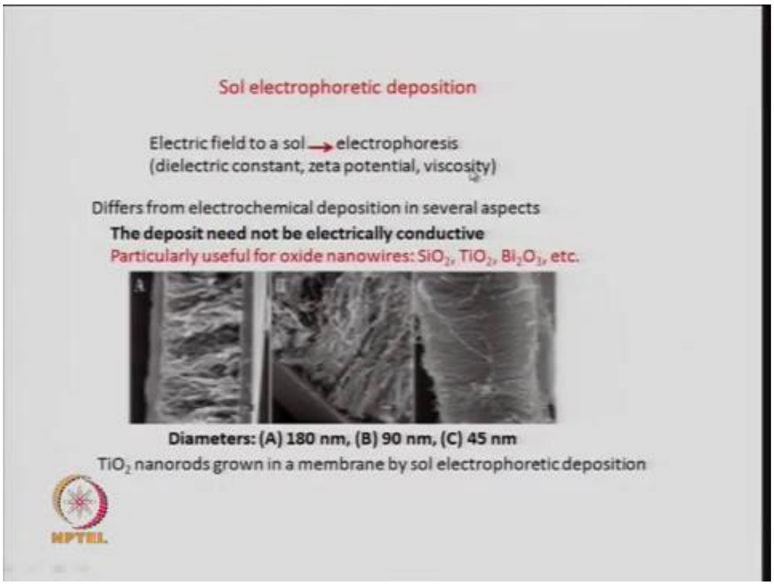

Now, the one of the disadvantage of the electrochemical method is that you need to a deposit they can only deposit conducting materials when you have non conducting materials like many oxides which have high band gaps. Then, what you do you go to another method which is called the sol electrophoretic deposition method here, you have a sol which is a sol is colloidal solution and you apply an electric field. When you apply an electric field to a colloidal solution or a sol there will be electrophoresis.

So, this is known and the electrophoresis depends on certain factors depends on a dielectric constant of the solution depends on zeta potential and it depends on the viscosity of the medium. So, all these parameters will control the electrophoresis, now the main thing is that you can use this technique to deposit materials which are not electrically conducting like silica titanium bismuth oxide which are very important materials.

These nanowires have lot of an applications, so then the sol electrophoretic deposition method becomes an ideal method to look at the deposition of such wires. Such examples are shown here with diameters in this case of around 180 nanometers 90 nanometers. These are very fine wires of these oxide materials of around 45 nanometers, so these are all examples of titeni at i 2 nano rods grown in a membrane by sol electrophoretic deposition. Here, you control the electrophoresis and you make the deposition is by moving the ions in the presence of an electric field. The movement of the ions in the charge particles in an electric field is controlled by the dielectric constant zeta potential and the viscosity, by controlling them you can control the deposition rate etcetera and so the thickness of the nanowire.

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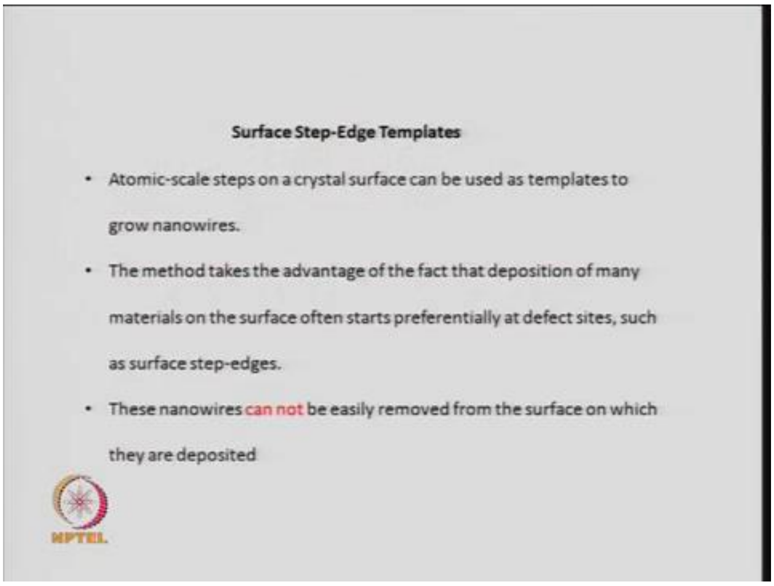

Now, there is another method by which people grow nanowires this is called the surface step edge template method, when you have crystal surfaces there are some steps or kings and these can be used as templates. We know that in many crystal growth text you may see nucleation occurs in this kings and steps and that knowledge is used to create nanowires on the steps. One disadvantage is of this method is the removal of the nanowires is not so easy compare to the methodology methods we discussed earlier.

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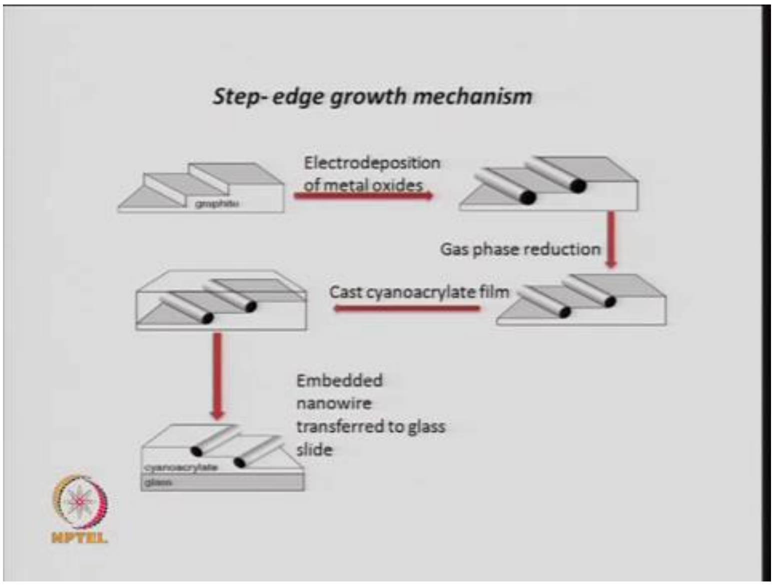

So, this is an example of a step edge growth mechanism, so they these steps are edges on graphite, this is highly oriented paralytic graphite or h o g p g and on that you deposit metal oxide. You get these wires and these wires are at these edges then you can remove these metal oxides by putting some films on top of it or you can reduce them and make metal nanowires. So, depending on whether you want oxide nanowires or metal nanowires you make a polymer film on top of this or top of that and then these nanowires come on to the film.

You can then transfer on to the glass slide, so this is another method by which people do make nanowires and this is an example of the growth of molybdenum nanowires by the step edge growth method. Here, you first make the wires on these edges and then you add a polymer like cyanoacrylate or a may be polystyrene or something an on that film this wires get attached. Then, you cast them on class, so with that we come to the end of today's lecture and we will continue this course on nanostructured materials.

Thank you very much.