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

Module - 3
Lecture - 16
Fullerences and Carbon Nanotubes – II

Welcome to this course on nanostructured materials- synthesis, properties, self assembly and applications. Today, we are going to go through the second lecture of module 3. We earlier have finished module 1 and module 2 and now we are in module 3. Today is the second lecture. The first lecture of module 3 we discussed about fullerenes, that is carbon based materials, C60 being the common fullerene and other fullerenes which were discovered for in 1985.

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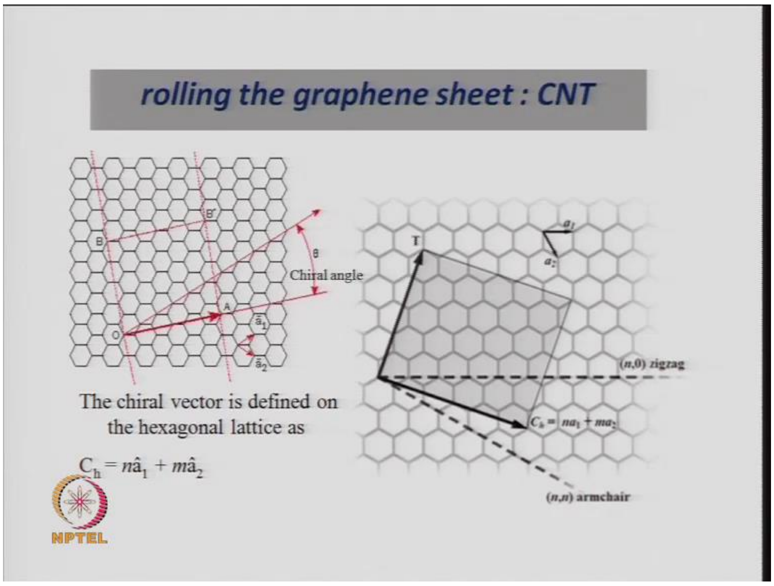

Today we will start on carbon nanotubes and how the carbon structure in C60, which is spherical. Now, we get cylindrical structures of carbon atoms by rolling a graphene sheet. The previous lecture, we saw a clusters of carbon like, c 60, c 70, c 80, c 82, etc. However, now we are going to discuss, how to get cylindrical objects, which are called carbon nanotubes and which has a relation to the c 60 structure. Basically, they are all made up of carbon and in c 60 structure, you had hexagons and pentagons of carbon forming a cluster. The number of pentagons are twelve in all carbon containing fullerenes, but the number of hexagons changes depending on the total number of carbons in the cluster, that is the total number vertices, this was given by the Euler's formula.

The discovery of c 60 lead to the noble prize to three people; Kroto, Curl and Smalley, which was given in 96. It was discovered in 85. The carbon nanotube was seen first by Ijima. Now, we will discuss, how you can actually get the carbon nanotube. Basically, you start if you think of a graphene sheet. If we roll the graphene sheet, we can get carbon nanotubes or CNTs. What is this graphene sheet? You must have heard of graphite. Graphite has layers of carbon hexagonally arranged carbons or hexagonal rings of carbons, forming layers or sheets, and these sheets are connected by van der Waals forces; weak forces to form a pseudo 3-dimensional structure, where the interactions are stronger in the 2-dimensional plane and weak in the 3-dimensional plane, that is graphite.

If you take only one layer of graphite, which is only having carbon; hexagons of carbon like, shown here, then that is called a graphene sheet. This graphene sheet if you take and you roll it say, assume that this graphene sheet is like a piece of paper and then you roll this graphene sheet, then you will get a cylinder, and that cylinder will then be called a carbon nanotube. But rolling the graphene sheet can be done in several ways. Depending on how you roll it you will get different types of carbon nanotubes. For example, we define couple of things like, what is the chiral angle; that means, if you are connecting, look one line here and you are rolling it at an angle, which is theta.

That angle is called the chiral angle and the chiral victor is defined using two unit vectors a1 and a2 like, which are shown here. If this is a1 and this is a2, based on hexagon, you can define these two vectors. Then, if you change the number of the coefficients, if n is say for example, 2, then the length of this victor will become twice of this vector. If m is 3, then m will be thrice of this vector and then you have to get the resultant vector. The chiral vector will be the resultant vector, which will be the sum of na1 plus ma2. So, depending on this numbers n and m, the chirality is defined. Here is an example. This is a general vector. The definition which we gave with is na1 and ma2.

But, if you take a particular value of n and m, for example, if you take m equal to 0; that means, this is the chiral vector C depends only on a1; that means, it will be in line or plainer to the a1 axis. In this figure a1 is denoted by this vector and a2 is denoted by this vector. If m is 0, then this a2 vector will not contribute to the overall chiral vector, C vector. The resultant will be always multiples of this vector a1. So, it will be parallel to this direction and that is what is shown here, that for a value, where n is non zero and m is zero, then the resultant vector will be along this direction, which is parallel to the a1 direction.

If this is your vector; that means, by this vector you are rolling the graphene sheet. The resultant carbon nanotube, that you will get, will be called a zigzag carbon nanotube. If you take a general vector, suppose, the m is non zero, then you will get some other chiral vector. Suppose, both n and m have the same value; that means, you take twice the amount of a1 and twice the amount of a2. So, the resultant will be like, shown here. The resultant will always go through the hexagon, to these vertices and the edges. When you roll this structure along this axis, then you will get what is called an armchair carbon nanotube.

These coefficients n and m are very important in understanding, what kind of carbon nanotube that you will get; whether you will get a zigzag carbon nanotube or a armchair nanotube or a chiral nanotube. Any other value for an armchair, the chiral angle is actually theta. If n and m are same, then always you will get an angle theta or the chiral angle will always be 30 degrees. For a zigzag carbon nanotube, the chiral angle will be 0. So, in between zero and 30 degrees, if you have any other any chiral angle between 0 and 30, you will have chiral nanotubes.

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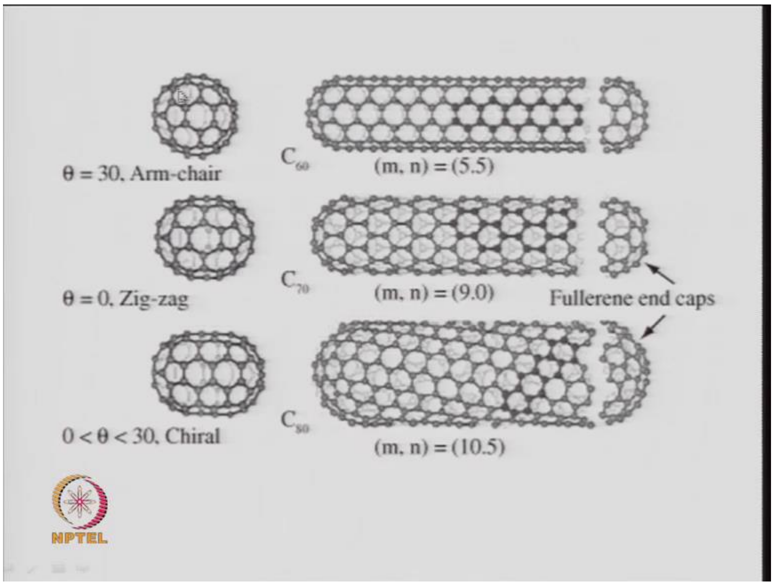

This is what is shown here, that if you have theta, the chiral angle is equal to 30. You will have the armchair kind of structure for the carbon nanotube. So, m and n both are same. So, it is (5, 5). So, one of the vectors a1 is 5 times a1 and the a2 has a coefficient, which is 5, and the resultant will be having this structure, which is called an armchair type of nanotube. If you want to close this nanotube, at the end, you must have a structure, which is related to the C60 structure. To close an armchair nanotube; that means, m is equal to n kind of a nanotube, you will have to close it with a half of a C60 molecule. So, half of the C60 is here. However, for other nanotubes, to close the nanotube, the structure has to be different. For example, this is a nanotube, where m and n are not same and n is equal to actually 0. So, the chiral angle is 0 and this is the zigzag form of the nanotube.

In this nanotube, to cap the end of the nanotube, you need a structure. You need a fullerene structure, which is not the C60 structure, but is actually close to the C70 structure. So, the C70 is this kind of molecule and if you take half of it, you can close the end of this nanotube. Depending on the type of nanotube, the type of the cap will also be different. This is a nanotube which is neither an armchair nanotube nor a zigzag nanotube; that means, the chiral angle lies between 0 and 30. So, the chiral angle will be the between 0 and 30, and this will be a chiral nanotube, and for a particular value of m n is 10 and 5. Neither they are equal to each other. So, it is not n n or armchair type of nanotube or neither one of the vectors has a 0 coefficient. So, it is not a zigzag nanotube, but this is a chiral nanotube. For this particular nanotube, to close the end of the nanotube, the structure that you need, is different than what you need for this nanotube and this nanotube. If you calculate, you will find out that this end can be capped by a fullerene, which has 80 carbon atoms, and if you get that fullerene and divide into half, then that heavy sphere, although it is not a true sphere, is a kind of, expand its sphere, that half of that will be capping this nanotube which is a chiral nanotube. So, depending on the n and m values, the coefficient of these two vectors by which you define your chiral vector, is very important to know, what kind of carbon nanotube, which will result from a particular kind of chiral angle.

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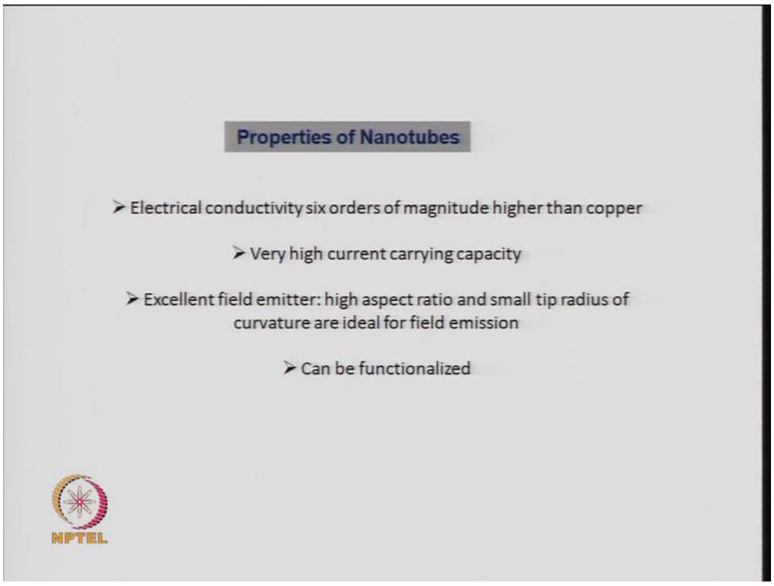

Now, what are the properties of such carbon nanotubes. They are very important and there are many kinds of properties, which are better than existing materials. For example, the electrical conductivity, that is the ability to pass current is six orders of magnitude higher than copper. All of you know that copper is very a good conducting material. So, we use copper wires in all our electrification and it has a very high conductivity; that means, very low resistivity. If the conductivity of copper is say, around 10 to the power 8 ohm meter, then the conductivity of carbon nanotubes will be 6 orders of magnitude higher; that means, 10 to the power 14.

So, it has tremendously high electrical conductivity compared to normal materials like, copper or aluminum, which are used to conduct electricity. Not only that, the carbon nanotubes can carry very high current; that means, if you compare a wire of unit cross section of copper and carbon nanotube, the carbon nanotube can carry much higher current than the copper nanotube. Another important property with respect to electrons is that if you apply a potential or a voltage to carbon nanotubes, you can get electron sort of it. It is called a field emitter; that means, if we apply our electric field you can get electrons out of the carbon nanotube.

There are other materials which show this effect and are used in many applications. These particularly there are compounds like, lanthanum hexaboride or tungsten metal, which are also field emitters; that means, if you apply electric potential, they will release electrons. So, they will emit electrons. Now, carbon nanotubes are excellent field emitters and that is because, they have very high aspect ratio. The aspect ratio of any wire or a rod, is the ratio of the length divided by the diameter. If you have a very high aspect ratio; that means, the length is very high and diameter is very small; that means, you have a very high aspect ratio, and you will have a very small tip radius of curvature.

Now, these facts, the high aspect ratio and small tip radius of curvature are very useful for field emission and hence, carbon nanotubes are very good field emitters. There is another property of carbon nanotubes, that you can functionalize them; that means, you can do some chemical reactions on the surface of these nanotubes like, you can put carboxyl groups or many of the groups, that you study, amino groups etc. on top of the carbon nanotubes. Once you functionalize them, you can do several other types of chemical reactions with carbon nanotubes. So, these are some of the very important key properties of carbon nanotubes.

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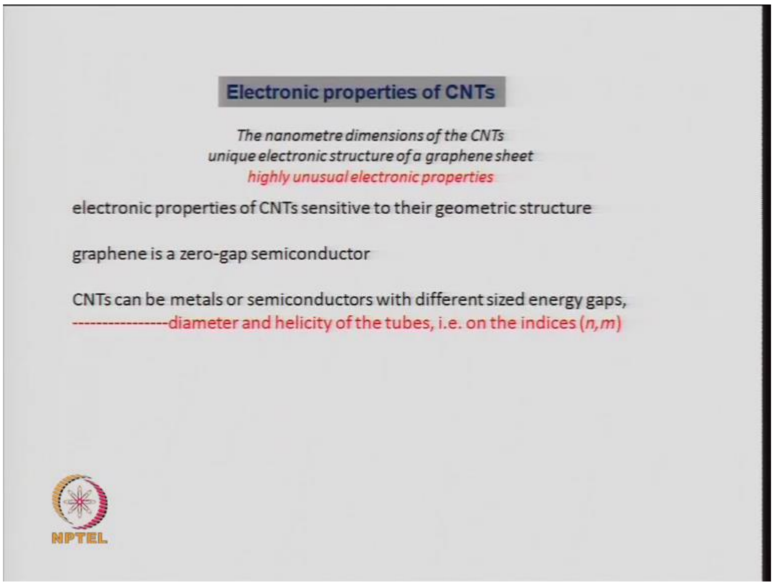

Coming again back to electronic properties, which we said that they are very good conductors. The reason is that it has nanometer dimension; the carbon nanotubes are having diameters in the nanometer region. Because, they are made up of a rolled graphene sheet and graphene itself has very unusual properties. We call that graphene is a dirac solid, it shows ballistic transport; that means, very high conductivity. Since, carbon nanotubes are made up of graphene sheets, which are rolled into cylinders, they have unusually high efficient electronic properties due to these two factors. The carbon nanotubes of course, will depend on their structure and their structure depends on the chiral angle.

So, the chiral angle and the coefficients of the vectors, which we discussed, the n and m value, will be very important to determine the electronic properties of the carbon nanotubes. We all know that graphene is a 0 gap semiconductor whereas, carbon nanotubes can be metals or semiconductors. They can be semiconductors with different energy gaps. So, they can have low gap, high gap. We can modify the carbon nanotubes by changing the diameter of the carbon nanotube, and also the helicity of the tubes. The helicity of the tubes depends on these indices, or the chirality, or the coefficients of the vectors, which are the n and m values. So, carbon nanotubes can vary as metals, semiconductors and semiconductors with different band gaps.

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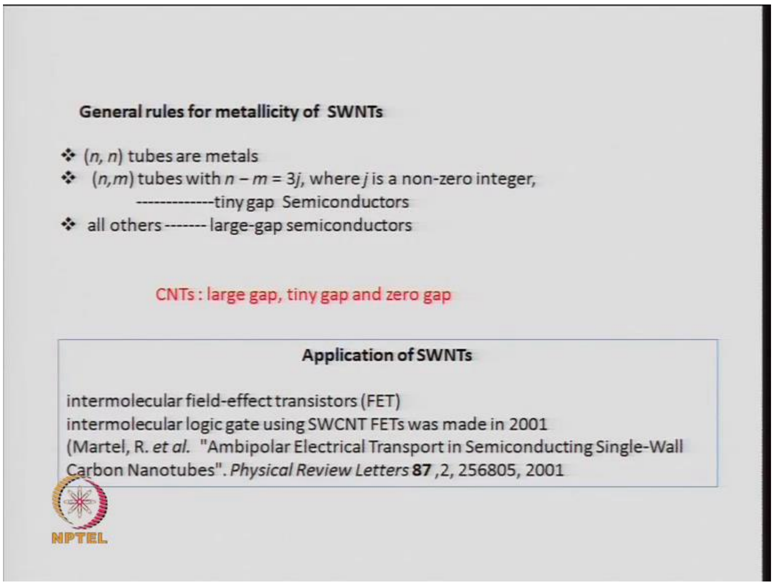

In general, if you look at single walled carbon nanotubes, which are called SWNTs. If you have the coefficients n and m, to be same for these nanotubes, then they have metallic conductivity. If you have the carbon nanotubes made with the chiral vector, where the coefficients of the two vectors a1 and a2 are n and m, and the difference between n and m is multiple of 3. It is like, 3j, where j is an integer, then the gap is very small. Although, it is a semiconductor, it will have a very small gap. If these values n and m are related, such that n minus m is equal to 3j, where j is an integer. If n minus m is 3 or n minus m is 6, then the carbon nanotube will be a semiconductor, but with a very small gap. For any other values of n and m, they will have much larger band gap.

So, depending on these values of n and m, you can have metals; small gap or tiny gap semiconductors; or large gap semiconductors. If you remember, you cannot graphene, are normally, zero gap semiconductors whereas, carbon nanotubes can have small gaps, large gap and they can also be zero gap semiconductors. Now, the applications of single walled nanotubes have already been shown. We have couple up them, were mentioned here. The intermolecular field effect transistor was discovered or made using carbon nanotubes in 2001. The logic gate, intermolecular logic gate using single walled carbon nanotube was made in 2001 by IBM. And the details of this are given in this reference here, where first time carbon nanotubes were used to form an FET, which is a very important part of the electronic industry. This has tremendous implications of making very small chips using carbon nanotube.

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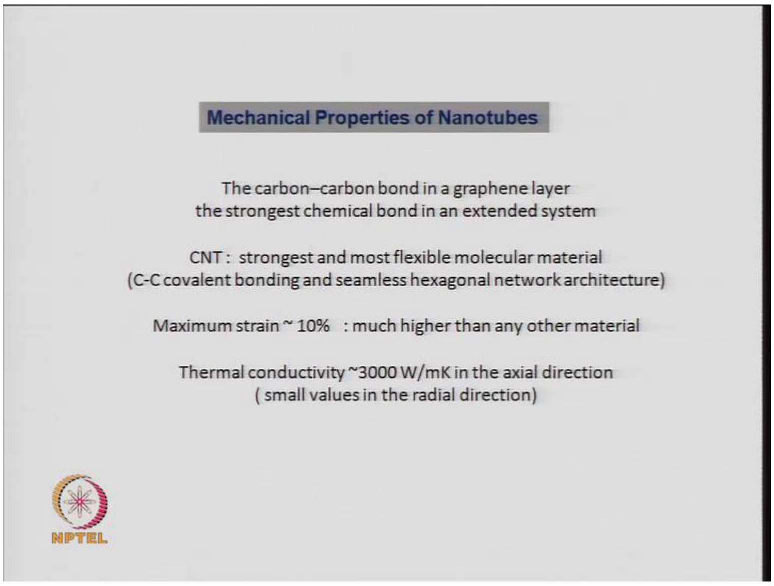

From electronic properties, if we look at the mechanical properties of carbon nanotubes, there are also excellent. The carbon-carbon bond in a graphene layer, have carbon-carbon bonds to form six membered rings, and then these six membered rings are then connected to other six membered rings, and it forms a layer or it forms an extended system.

In any extended system the carbon-carbon bond in graphene has the strongest bond. So, it this highest bond energy of any system, compared to any other system, is present in graphene. Since, the carbon nanotubes are based on rolled graphene sheet, this property or this strength of the carbon-carbon bond, in an extended system will also translate into the carbon nanotube. So, carbon nanotubes are the strongest and most flexible molecular material because, of this carbon-carbon covalent bonding, and seamless hexagonal network architecture.

It is one of the strongest and most flexible materials. The strain that carbon nanotubes can take is like, approximately 10 percent, which is much higher than any other material, the thermal conductivity, which is another property. You have the electronic conductivity which is very high for carbon nanotubes. The thermal conductivity is also very high. It is 3000 watts per mili kelvin in the axial direction; that means, in the long direction of the tube. However, in the radial directions, that is along the diameter of the tube, the value of the thermal connectivity is lower. But this value of 3000 is extremely high and this is present in carbon nanotubes.

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Mechanical properties of Engineering fibres

Fiber Material	Specific Density	E (TPa)	Strength (GPa)	Strain at Break (%)
Carbon Nanotube	**1.3 - 2**	**1**	**10 - 60**	**10**
HS Steel	7.8	0.2	4.1	< 10
Carbon Fiber - PAN	1.7 - 2	0.2 - 0.6	1.7 - 5	0.3 - 2.4
Carbon Fiber - Pitch	2 - 2.2	0.4 - 0.96	2.2 - 3.3	0.27 - 0.6
E/S - glass	2.5	0.07 / 0.08	2.4 / 4.5	4.8
Kevlar* 49	1.4	0.13	3.6 - 4.1	2.8

Let us look at a table, which gives you mechanical properties and compares the mechanical properties, of several engineering materials or engineering fibers. If you compare them especially, you compare the strength and strain of carbon nanotube with steel or other carbon fibers; polymers or glass; and Keylar, which probably, i even mentioned in my previous lecture. You see this value of carbon nanotubes has a strength of around 10 to 60 gigapascals and the strain is 10 percent, which we just mentioned. There is nothing comparable in any of these materials, which is close to what we have in carbon nanotubes. The extremely good mechanical properties compared to all known materials, which are used in engineering today.

So, carbon nanomaterials, carbon based nanomaterials especially, carbon nanotubes are better than other carbon based materials, which have been in market and polymers, like Keylar, which are already in market for bullet proof vests, etcetera. But you see carbon nanotubes has higher number even compared to Keylar.

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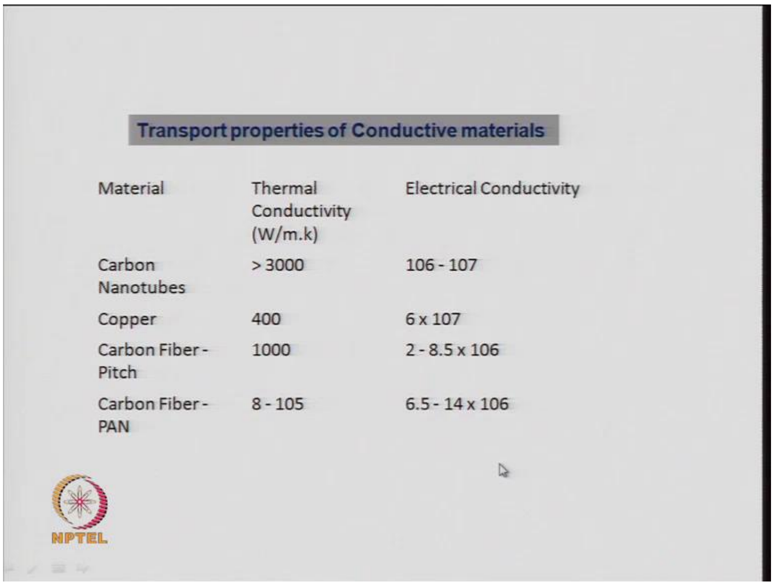

If we compare the electronic conductivity and thermal conductivity with other materials, together we can call them transport properties, because we are talking of, either moment of electrons or charged particles, or movement of what is called fonos, in thermal conductivity. If you look at carbon nanotubes, compared to other materials, like copper or other carbon fibers, you see this number of 3000 or greater than 3000 is 1 order of magnitude higher than copper, and 3 times that of a well known carbon fiber. The electrical conductivity is around 106-107, and of course this carbon nanotube, it is not 106. Actually, it is 10 to the power 6 to 10 to the power 7, and it is very high compared to many other materials. So, these are order of magnitude higher than other materials.

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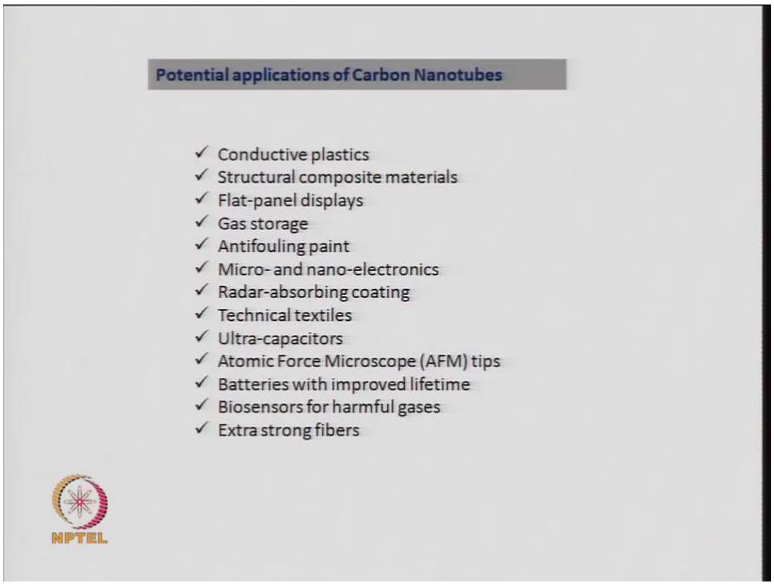

What are the potential applications of carbon nanotubes? Shown you several applications, but there are many other applications of carbon nanotubes, other than what has been shown here. Among them, you can see you can make conductive plastics, structural materials because, of its high mechanical strength. Then, because of it field emission properties you can make flat panel displays, and several other applications, which we will discuss in subsequent lectures. But the point is, one single material like carbon nanotube has so many applications, and this is also a very smallest.

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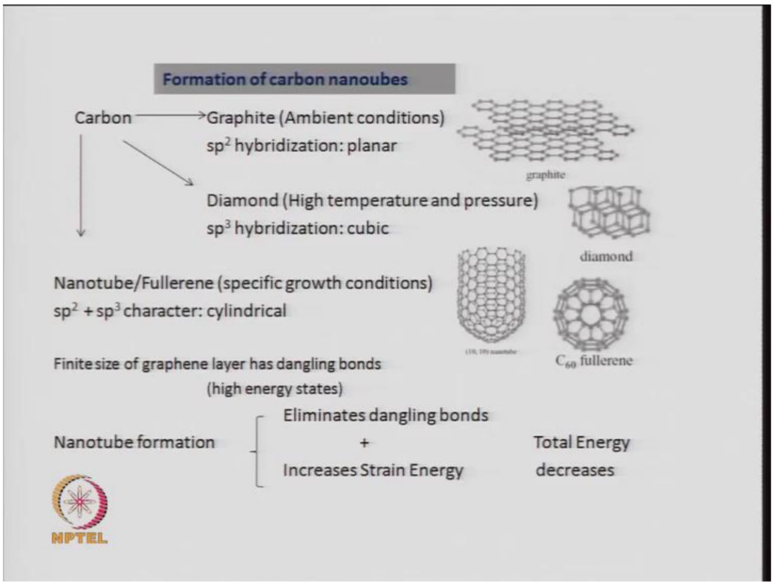

We will come to the applications later in our next lecture, but this was just to give you a brief idea, that there are many applications possible. Now, coming to the synthesis of carbon nanotubes. Normally, the other forms of carbon; the other allotropes of carbon that we know, like graphite, can be made using ambient conditions. In graphite, this is graphite, this is one layer of carbon with hexagons arranged, and this other layer of carbon is shown here. Like that there are many layers of these hexagonal layers, one above the other to form graphite. Here all carbons have sp2 hybridization to form these planar structures.

This can be obtained in ambient conditions; that means, under normal temperature and pressure, whereas, if you go to diamond, which is another allotrope of carbon, you need very high temperature and pressure. The structure is very different. You know graphite has this layered structure and diamond has this 3-dimensional structure, where each carbon is bonded to three or other carbons, and this each carbon is in a tetrahedral position. You can see, it is tetrahedrally coordinated to four other carbons and hence, each carbon has sp3 hybridization and this structure is of course, cubic. This is hexagonal.

So, you see graphite can be obtained in ambient conditions. Diamond can be obtained under high temperature and high pressure conditions. For nanotubes or C60 type of molecules, we need very specific growth conditions. In both nanotubes and other fullerenes like, C60, C70, etcetera, the carbons have both sp2 and sp3 character. Then we get this cylindrical type of structures as shown here. So, this is a cylindrical nanotube and this is an armchair nanotube, because you see n and m. Both are 10 and we know when n and m will be same, the chiral vector will show you, and you are rolling along that vector. You will end up with such a tube which is called the armchair nanotube.

In C60 of course, you know, we have this cluster like, the shape of a football and these require specific growth conditions. The finite size of graphene layer; that means, if you take a graphene layer and you are rolling it to form this carbon nanotube, why should it stabilize? That is one question. This graphene layer has several dangling bonds; that means, the carbons in the planar graphene layer, have some unsaturation. They want to take up some more electrons. So, they want to form some more bonds. Now, when you roll and make a nanotube from a graphene laye, that eliminates these dangling bonds.

That is a very kind of positive thing for lowering energy. When you are eliminating dangling bonds, you are stabilizing the system of course, because you are rolling the graphene layer. There will be an increase in the strain energy, but together, these two factors will lead to a energy decrease and hence, the nanotube is formed. So, formation of the carbon nanotubes is basically, driven by the need for the dangling bonds to find, to make some bonding, and help eliminate these free electrons or dangling bonds, which will then stabilize the system. However, there will be an increase in the strain energy, but overall the total energy will decrease.

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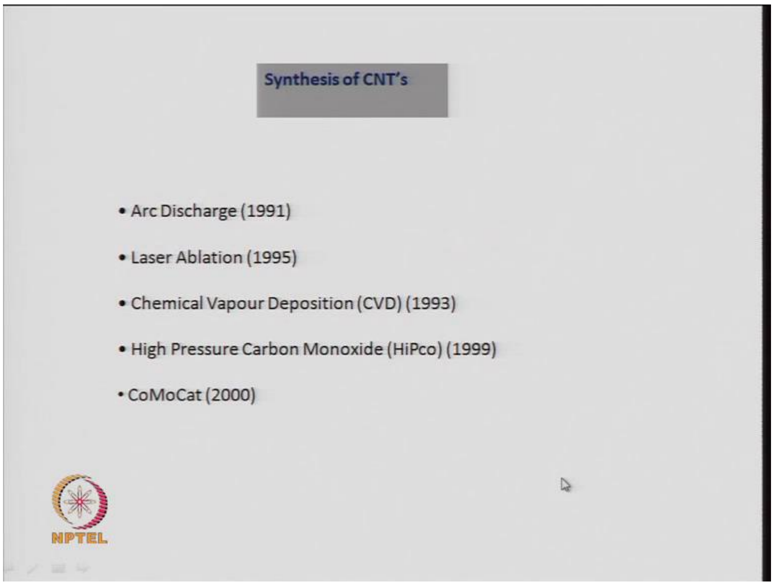

To synthesize carbon nanotubes, several techniques have been designed over the last 10 to 15 years. The earliest technique like the arc discharge method, it was discovered in 1991. It is also called the Kratschmer Huffman method. In the laser ablation method, where you use a laser on a target, a carbon based solid material. Then, you vaporize the carbon and then when it settles down, it forms carbon nanotubes. Then, later CVD technique, which is well known for other materials, was also applied to the synthesis of carbon nanotubes that was in 1993.

Then high pressure carbon monoxide based synthesis, which is also called the hipco method was discover in 1999. There is another method, which uses a cobalt molybdenum catalyst, and this technique was developed in 2000, for the synthesis of carbon nanotubes. The CVD technique is very popular, when we want very large quantity of carbon nanotubes.

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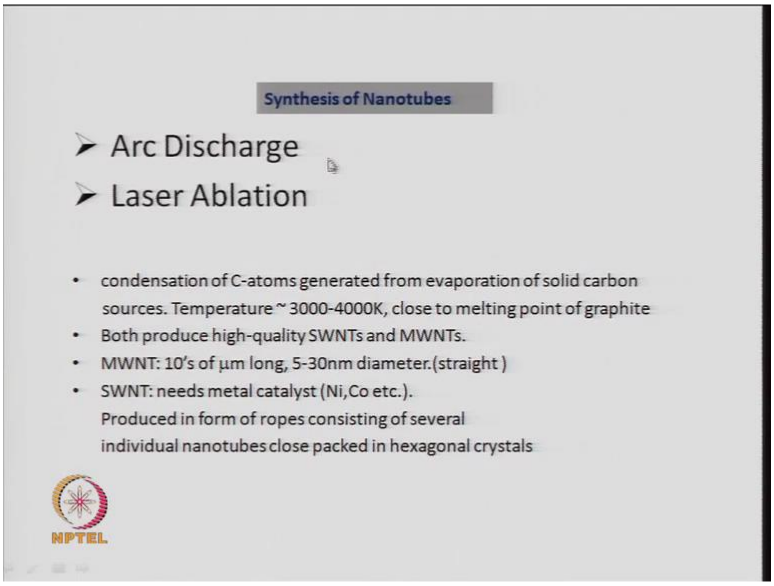

To describe the first two techniques; the arc discharge method and the laser ablation method; both involved condensation of carbon atoms, generated from evaporation of solid carbon. You take a solid carbon source and then you evaporate it, either using arc discharge or by laser ablation. Once the carbon atoms are evaporated from the solid carbon, then it condenses back to form this carbon based nanotubes. The temperature in these cases is close to 3000 to 4000 Kelvin, which is close to the melting point of graphite. So, it is a very high temperature process, but both produce high quality of single walled nanotubes and multi walled nanotubes. Multi walled nanotubes can be 10s of micron long and 5 to 30 nanometers in diameter.

They are normally the multi walled nanotubes are normally, very straight. Whereas, single walled nanotubes can be very curvilinear; that means, they need not be very straight and they are normally, produced in the presence of a small amount of a metal. This small amount a metal, when it is nickel or cobalt, acts as a catalyst. That allows the growth of single walled nanotubes; that means, you have only one graphene layer forming the nanotubes whereas, in the multi walled nanotubes, you have several graphene layers, one inside the other, forming several cylinders, one cylinder inside another cylinder of nanotubes. So, the single walled nanotubes normally, need a metal catalyst and are produced in the form of the ropes, where there are several single walled nanotubes. They are bunched together and weekly packed to Van der Waal forces. They form a rope like structure and they are also very curvilinear whereas, the multi walled nanotubes are normally very straight.

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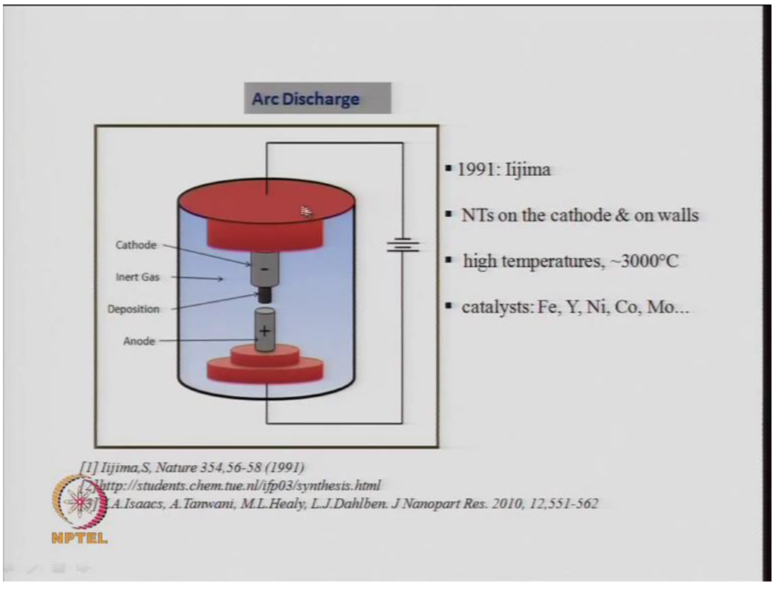

This is the arc discharge method, and this was the process shown here, as developed by Iijima. There, you see the nanotube, first observed by Iijima in 1991, in an electron microscope and it was made using this arc discharge method where, you have a cathode and an anode, and there is a deposition of the carbon nanotubes on the cathode. You have the nanotubes on the cathode and also on the walls of this, when you pass a high voltage on these two electrodes. Here also the temperatures are close to around 3000 degree Celsius. Several catalysts are used, as we discussed iron, yttrium, nickel, cobalt and molybdenum. Several catalysts have been tried and sometimes, mixture of catalyst are used and they appear to be better especially, when yttrium is used with some of the metals.

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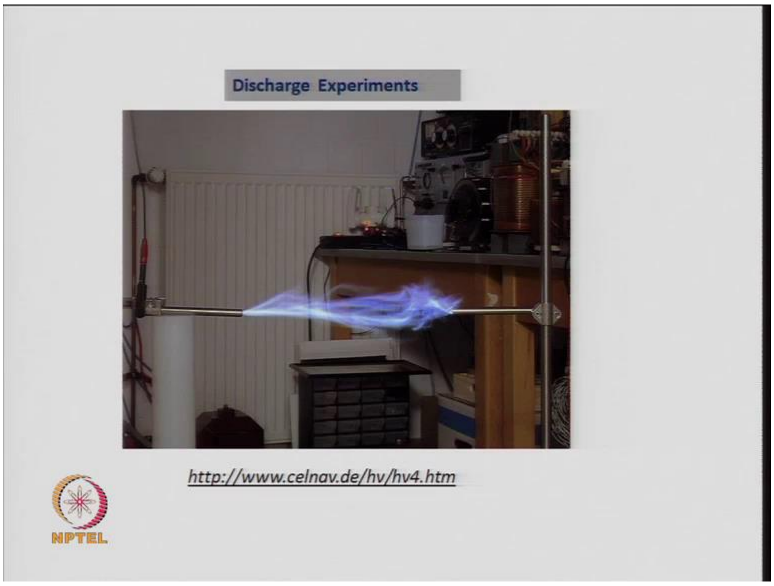

This arc discharge method, it is a high temperature method. This is a typical discharge which is taking place between the two electrodes, and during this discharge, which is between graphite electrodes you have, and then the deposit is on the cathode and from that deposit, you can extract the carbon nanotubes.

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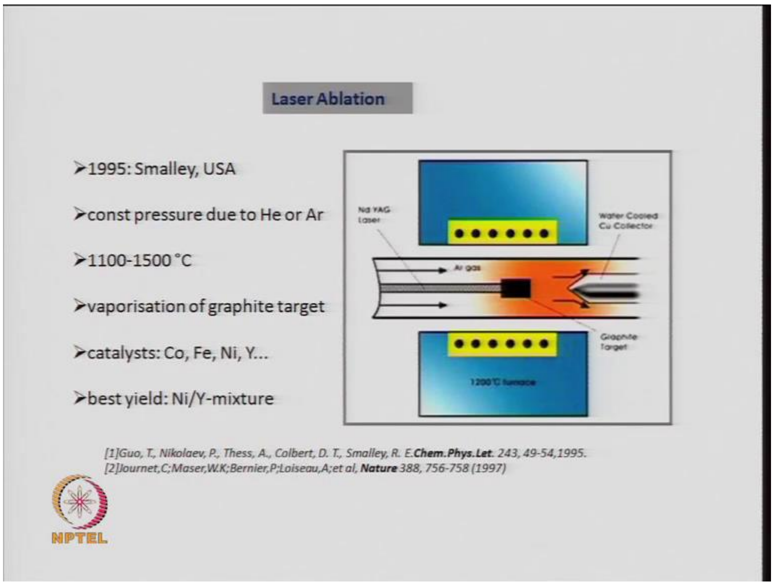

Using laser ablation which was developed by Richard Smalley, at tries university in Texas, USA in 1995. What he did was, he took this graphite target. You take a piece of solid graphite and you use a laser beam on top of the graphite target, which is heated by a furnace. So, the furnace is around it and it has a temperature of around say, around 1200 degree centigrade. When this laser beam hits this target, carbon atoms are vaporized and then, they condense on cold water, cold copper base and are collected, and carbon nanotubes deposit on this copper, which is cooled by water. So, this is the laser ablation technique like, the arc discharge method. This is also a high temperature technique although, here temperatures are like 1100 to 1500, whereas in the arc discharge method it was around 3000 degrees Celsius. The best yield you get is when you use catalyst like nickel and yttrium mix together, you get the best yield or quantity of carbon nanotubes, deposited on the copper collector.

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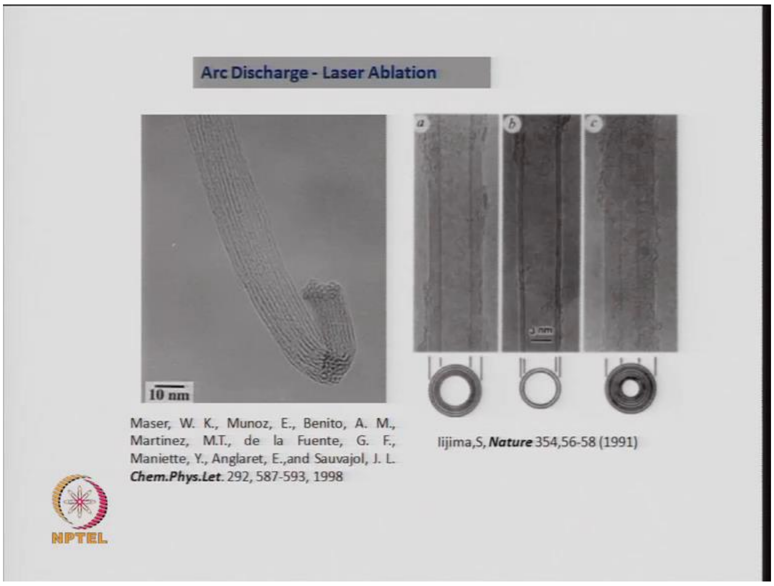

These are some of the pictures. These are transmission electron micrographs, taken on arc discharge and laser ablation methods. This is the paper of Iijima in nature, who first discovered the carbon nanotubes. As you see, there are multi walled carbon nanotubes and this is a single walled carbon nanotubes. There is only one carbon nanotube as drawn here, and these are the schematic diagram to show you. That is single layer, these are multi layer, multi walled carbon nanotubes. This is also multi walled carbon nanotubes, This is by another group, where you can see the single walled carbon nanotubes, which are connected to each other, through weak van der Waal forces. So, there are several, it is a bundle of carbon nanotubes, like a rope, they align themselves and this is a high resolution PEM picture of these carbon nanotubes.

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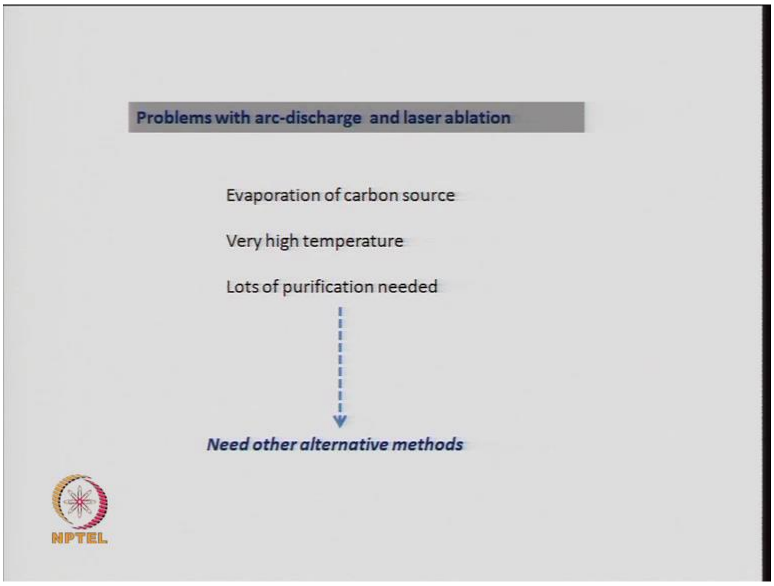

There are problems with these two methods. You always need to evaporate the carbon source, which requires high temperature. Then, when you get the material which is collected on the cold collector, like the copper collector, then you need to purify it by using particular type of solvents, and there is need for alternative methods. Hence, the chemical vapor deposition, the technique was already known for other type of materials, was developed.

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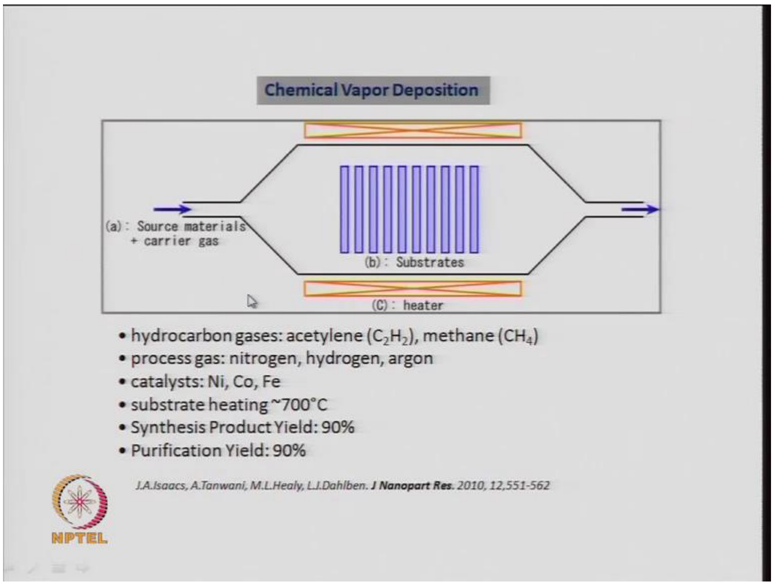

In the chemical vapor deposition, you use hydrocarbons, like acetylene or methane. It is passed through a chamber, where there is a substrate, on which you want the deposition to occur, and there is a heater to heat the substrates. So, the temperature of the substrate is around 700 degree centigrade. So, what you are passing, is the source of carbon here, is a gas which is a hydrocarbon and typically, you use acetylene gas or methane gas for the carbon to deposit on the substrate.

When the carbon deposits on the substrate, it deposits in the form of carbon nanotube, under these conditions, when have certain catalyst, like nickel, cobalt, iron and the temperature is around 700 degrees. The product yield is around 90 percent and they are pure to about 90 percent. This is a chemical vapor deposition technique, where the temperatures, as you see, has been brought down to 700 degrees centigrade. It was 1500 in the laser ablation method, and 3000 degree centigrade in the arc discharge method.

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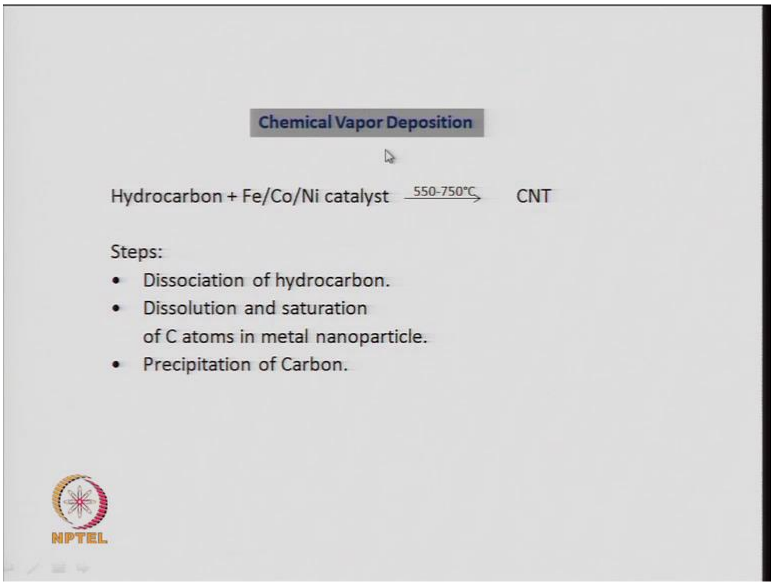

In a typical CVD method or the chemical vapor deposition, you have the hydrocarbon, you have the catalyst and around 700 degree centigrade, you get CNT. The steps which occur is, first, the hydrocarbon dissociates and then it dissolves on the metal catalyst, and then it saturates the carbon atoms in the metal nanoparticle and finally, you precipitate, reprecipitate carbon in the form of nanotubes.

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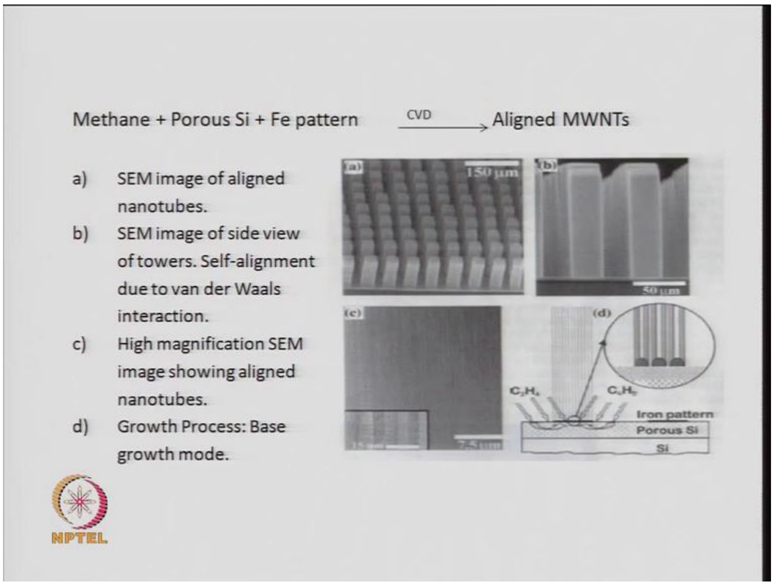

Here, you can see a picture of the CVD method on a substrate. The substrate is porous silicon and you are passing methane gas. You have iron pattern on it as a catalyst. So, these are your silica to the porous silicon and you can see the align nanotubes. This is the side of the towers and this is the SEM image to show the aligned nanotubes.

How do these nanotube form; these aligned nanotubes? So, you took a porous silicon; that means, there is a silicon which has got particular pores, and in that pores, you have this porous silicon, and below that of course, we have got the crystalline silicon and here, where you have got pores, you have got these gases, will go in and we have got this catalyst, which is iron which is patterned. The growth will take place from the catalyst particles. So, these are iron atoms. This is a blown up picture of this part, and you can see that, where the catalyst particle is there, the nanotube is growing from there. So, this growth of these nanotubes on the catalyst particle is shown here. You need this iron patterned on the pores silicon, to form these nanotubes.

So, wherever the iron is there, on top of that, carbon nanotube is grown. Whichever way the iron is patterned, ultimately, you will see a pattern of the nanotubes. So, that is how you get these aligned multi walled nanotubes, on an iron pattern, over a porous silicon substrate. So, this porous silicon is important for the gas, the hydrocarbon to go in, and interact with the catalyst, and then reprecipitate as carbon nanotubes. The carbon first forms and it dissolves in the catalyst, and then reprecipitates to form the carbon nanotubes. So, this is the growth process and this particular mechanism, where the catalyst particle is at the bottom and the nanotube is growing on top of the catalyst particle, is called the base growth model or the route growth model; that means, the catalyst at the base the base, and the tube is growing on top of the catalyst.

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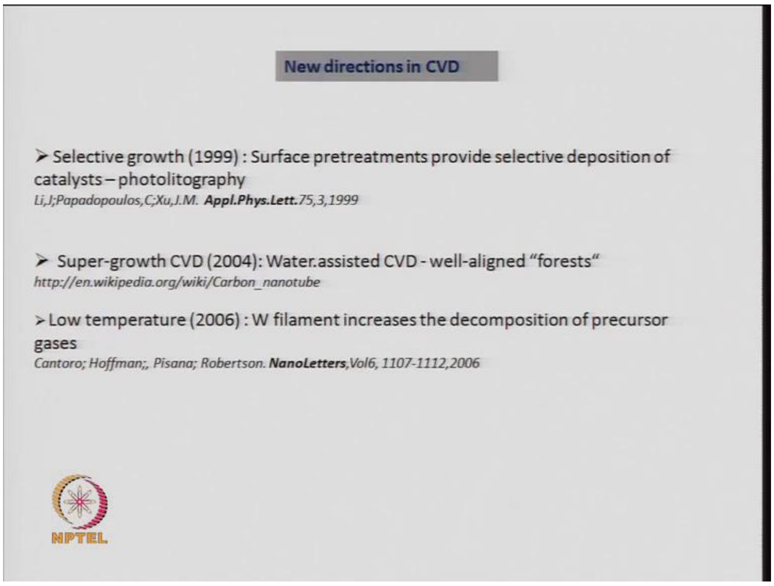

There are several other new directions, which have come about in the CVD process. We discussed the simple CVD. There are several new methods, where you can do selective growth of carbon nanotubes. For that you need to do pretreatment, to provide selective deposition of the catalyst, using photolithography. So, wherever you deposit the catalyst, you have to first modify the surface of the substrate by some pretreatment, by which you selectively deposit catalyst, and then the carbon nanotubes grow on that.

Then there is something called super growth CVD or water assisted CVD, to obtain well aligned forest. Here, we mean forest by, a forest of carbon nanotubes; it is not a forest containing tress, but is a forest containing well aligned; that means, each carbon nanotube is like a tree, and it is aligned to each other to form a very uniform looking forest. Then there are other low temperature methods developed, where you use a tungsten filament to increase the decomposition of the precursor gases. So, several new directions derived from the CVD or the chemical vapor deposition process, have been developed in recent years.

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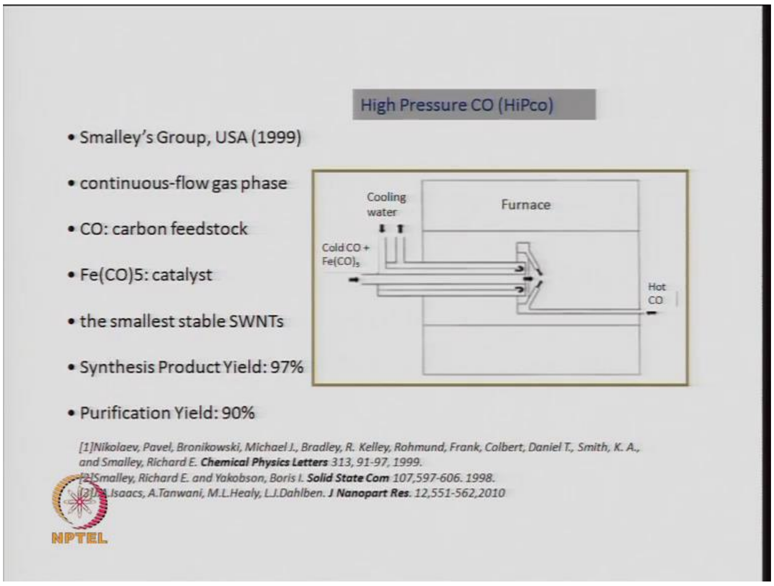

Now, coming to the next method, which is the high pressure or the hipco method, the high pressure carbon monoxide method, it was developed by against Richard Smalley's group in USA. Here, what you have is a continuous flow of carbon monoxide. You have hot carbon monoxide from here. This is a furnace and you pass cold carbon monoxide with a catalyst. This particular catalyst is what is called iron pentacarbonyl. So, it is a complex, a very well known complex of iron and carbon monoxide, and it acts as the catalyst here.

In all earlier discussions also, we mentioned that catalyst is important, but we were using metal catalysts like iron, cobalt, nickel or yttrium, etc. or mixture of metals as catalysts. Here, you are using a metal carbonyl as catalyst. Along with that, you are passing a cold stream of carbon monoxide gas. Here, there is cooling water to make it cooler and then here, have the furnace to heat this carbon monoxide. By this method, this is called the high pressure carbon monoxide. At high temperature carbon monoxide means, the pressure is higher and this will lead to these most stable single walled nanotubes, like, in other methods, the length of the nanotubes of single walled carbon nanotubes is a very large.

But to make small and stable nanotubes single walled, this technique is very popular. The yield is also very high. You get 97 percent yield and the purification yield is of course, again 90 percent; that means, from whatever material you make, the 90 percent of pure carbon nanotubes, single walled carbon nanotubes, you can obtain by this high pressure carbon monoxide route or the hipco route.

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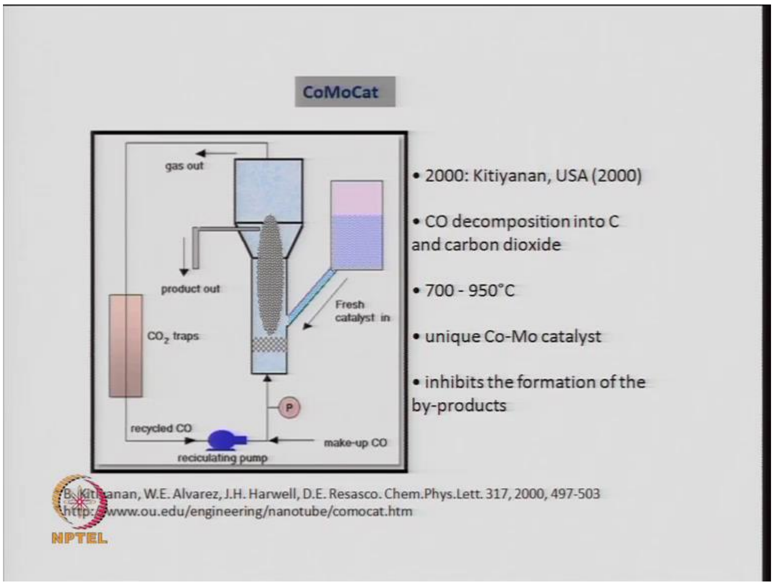

There is another method which is called CoMoCat method. This name comes because, you are using a catalyst. This catalyst is made up of cobalt and molybdenum; two metals, and this mixture of metal catalyst, if you take in this chamber and where, you are passing carbon monoxide. So, you are passing carbon monoxide and you pass the catalyst here, and then, it forms carbon dioxide. The carbon monoxide, in the presence of the catalyst, decomposes into carbon and carbon dioxide. The carbon dioxide is taken out and that carbon, which forms, deposits as carbon nanotubes. This is done at a temperature of around 700 to 950 degree centigrade. Now, this is also a very special method because, you use a very unique cobalt molybdenum catalyst, and this method is a good method because, it does not form too many side products. It gives you very uniform carbon nanotubes. This is what is called the CoMoCat process. So, we have discussed the various methods of synthesis of carbon nanotubes.

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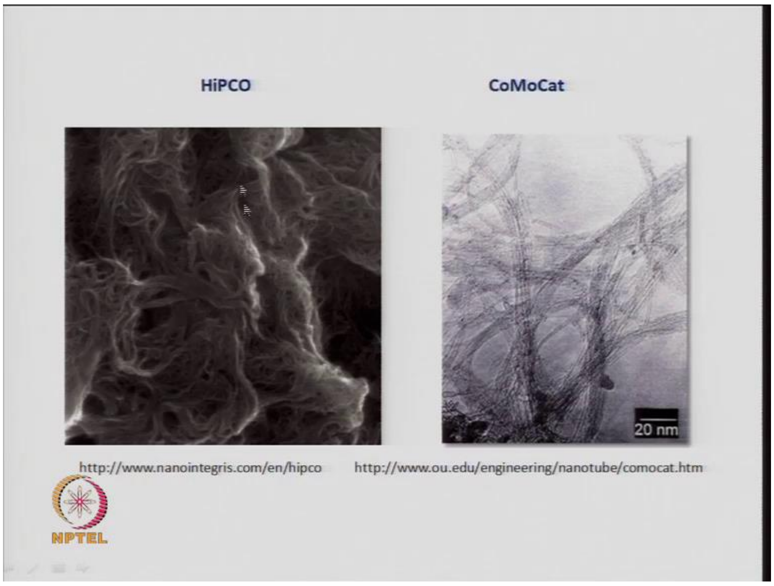

This is a TEM of the carbon nanotubes, made by the hipco method. You can see all these curvilinear form of carbon nanotubes. By the CoMoCat method, you can see much better quality of carbon nanotubes compared to the hipco method. Here, you are using a catalyst of cobalt and molybdenum and here you are using iron pentacarbonyl as catalyst.

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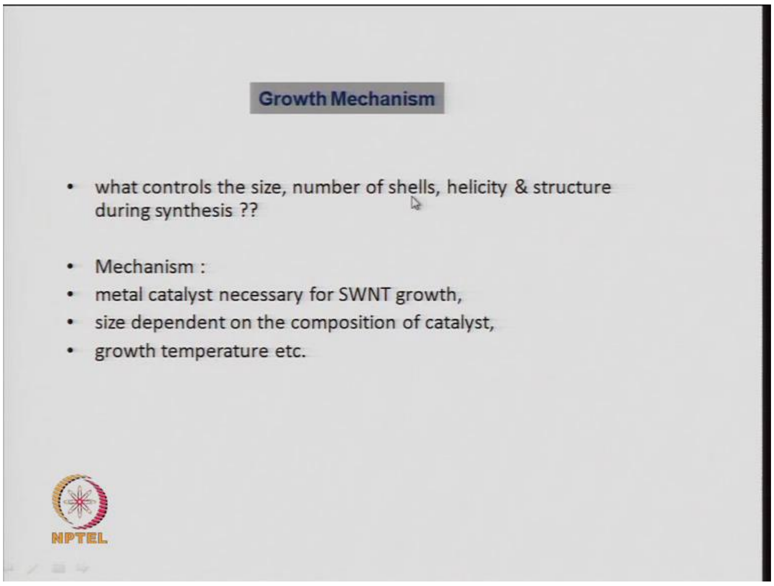

To understand, what is the growth mechanism; Because, we need to know how to control the size of these nanotubes? How to control the number of shells in this multi walled nanotube? The helicity; that means, the chirality and other structural aspects of the nanotubes; How do you control them during synthesis? To know these, we need to understand the mechanism. In the mechanism, what is necessary is the role of the metal catalyst. Because, it is important; a metal catalyst is important for single walled nanotube growth. Then, the size dependent on the carbon nanotube; the diameter, length of the carbon nanotube, depends on the composition of the catalyst that you use. The size also depends on the temperature of growth. So, these are various factors on which, the size and number shell, etc the helicity is controlled. The growth mechanism which is very popular is shown here. These two methods are given; the best growth method and the tip growth method

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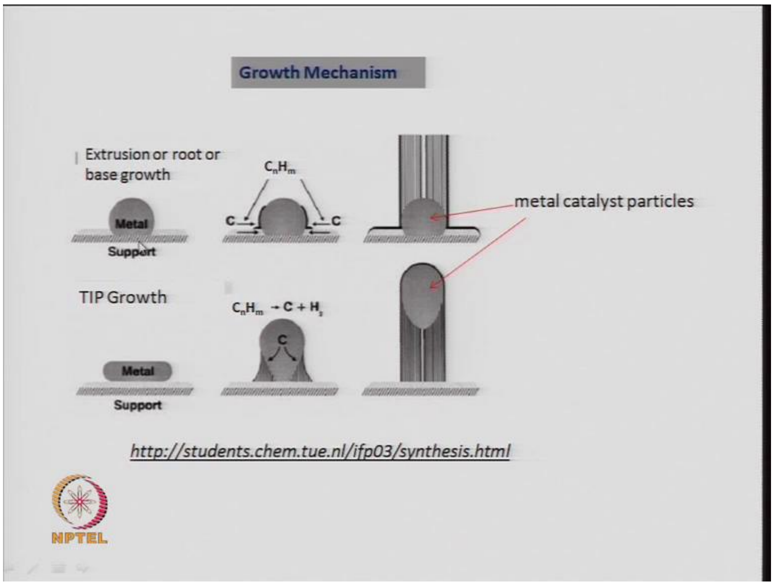

In the base growth method, you have the substrate of the support, on which you have the metal catalyst. Now, when you add the hydrocarbon, which is the source of the carbon nanotube or the carbon, the hydrocarbon decomposes, vaporizes and gives rise to carbon. This carbon, then forms or reprecipitates on top of the catalyst, and then starts growing on top of it, on the metal catalyst particles. This is the metal catalyst particle and the carbon is depositing on the surface and slowly, it will grow along this direction. Then you get the carbon nanotube. This is called the base growth mechanism because, the catalyst remains at the base. The tip growth mechanism is normally, shown here, you have the metal and the support.

Then, when the hydrocarbon decomposes to give carbon and hydrogen, and the carbon is dissolved in the metal particle, then when it reprecipitates, it precipitates at the bottom; at the tip of this, and not on top of this, like, it was doing here. When the carbon deposits here, at the tip, then the catalyst particle moves up. The catalyst particle keeps moving up and the carbon nanotube is formed here. This is called the tip growth mechanism because, the carbon nanotube is forming at the tip of the metal particle; the catalyst particle. As you see this, the tip of the catalyst particle and the carbon is precipitating here.

So, this tip will continue to move up and the carbon nanotube actually, will form on the substrate. The difference in the two, as you see, the nanotube here, is on top of the catalyst particle. Here, the nanotube is on top of the substrate and the catalyst is on top of the carbon nanotube. So, these are two very different growth mechanisms; the extrusion or route or base growth mechanism. There are various names for the same mechanism. The other mechanism is the tip growth mechanism; the nanotube is growing from that tip.

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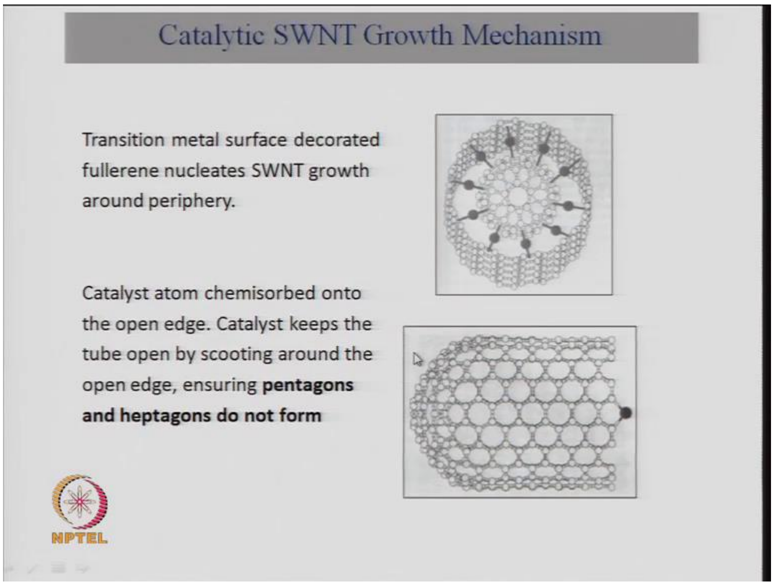

This is another way to show the same thing, that you have a metal, the transition metal surface here, and the carbon nanotube is forming outside, and this carbon nanotube is nucleating along the periphery. This is another picture to show you, that how the catalyst particle is at the periphery of the tube, and it allows the growth of the nanotube in this direction, by hopping from side to side, and not allowing the pentagon's and heptagons to form, because if the pentagon and heptagon form, then the tube will start getting closed. But, if only hexagons form, then the tube will continue to grow. So, the catalysts key role is not to allow a pentagon to close, by forming a bond there temporarily, and then, moving to another place, till a carbon comes and forms a hexagonal ring. The catalyst avoids making pentagons and heptagons. By avoiding formation of pentagons and heptagon it avoids closure of the tube.

Today, we will close here and will continue our lecture for the 3rd lecture of module 3, where we will look at the applications of carbon nanotubes in much more detail. Today, what we did is look at the synthesis of carbon nanotubes, the chirality of carbon nanotubes, the various types of catalyst that are used in the nanotube formation and the growth mechanism of carbon nanotube.

Thank you.