Nanotechnology Science and Applications
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Lecture - 23
Carbon

Hello, welcome to this class on Carbon. So, in this class we are going to look at the material carbon, which interestingly is just one element in the periodic table, but if you actually look at literature you look at articles that are there in journals and other magazines. You will find that there is significant amount of work that has been done on this material. So, although it is just one element in the periodic table, there are entire books written on this element carbon, there is even a separate journal which is titled the Carbon and that deals exclusively with research on this element.

So, therefore, it is considered very I mean the reason you see that kind of an emphasis is because a lot of people recognize it is importance, scientifically, and technologically, in a wide range of areas that we would use in the human a range of technologies that we end up using in our day to day life. So, therefore, there is a lot of emphasis on the sediment and that is why we will spend a few classes looking at the element carbon and in particular we will focus on the nanoforms of carbon. So, that is the general framework with which we will look at this element.

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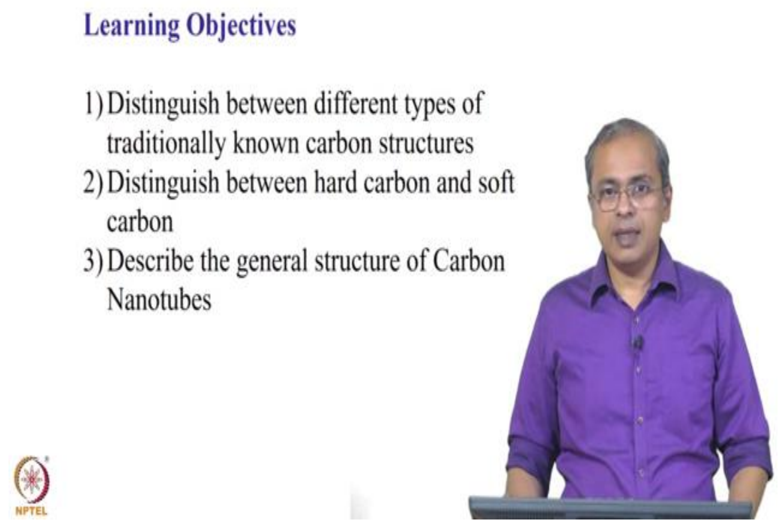

Learning Objectives

1) Distinguish between different types of traditionally known carbon structures
2) Distinguish between hard carbon and soft carbon
3) Describe the general structure of Carbon Nanotubes

So, our learning objectives for this class are to distinguish between different types of traditionally known carbon structures. So, this is something that you would have known from high school days, possibly also some time in which depending on the course that you took, somewhere in your college courses also you might have seen some elements of an information associated with this first point that we will look at which is distinguishing between different types of traditionally known carbon structures.

We will take that discussion a little deeper. So, that you can use that discussion to better understand the nanostructures of carbon that we will discuss in the subsequent classes. So, that is why we would like to set that framework and that is the reason why we would look at it. We will also look at how we can distinguish between what is known as hard carbon and something else that is known as soft carbon. So, again based on which book you read or which segment of the literature you read you will see some references to this.

They are actually a number of areas where carbon shows up in the literature you will find it associated with say energy-related materials, for lithium-ion batteries, for fuel cells. So, many of those places you see carbon materials showing up in different forms including the traditional forms as well as the nanostructured forms. You will also see it associated with creating composites for structural applications. So, in all these cases you see this element showing up. And, therefore, some understanding of what is hard carbon, what is soft carbon is relevant to our discussion. We will close this class by trying to describe the general structure of carbon nanotubes.

So, we will last we go further we will look at in 1 of our subsequent classes we will look at much greater detail of the carbon nanostructure or especially the carbon nanomaterial and nanotubes, but today we will certainly put some basic idea of the carbon nanotube on the table so, to speak. So, you begin to understand how the conditions come about. So, this is what we will do in today’s class.

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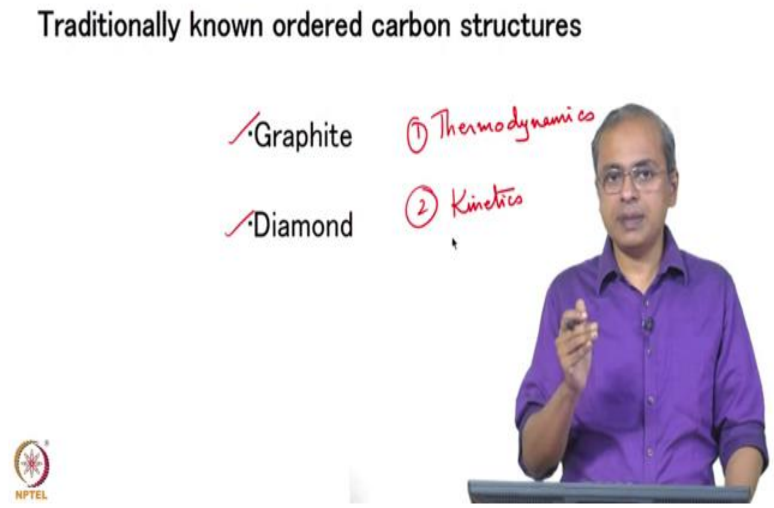
Traditionally known ordered carbon structures

- Graphite
- Diamond

So, the traditional forms of carbon are basically these two you have graphite and you have a diamond. So, for many years this was the form of I mean this was the knowledge of carbon, that they existed in that it existed in these two forms primarily graphite and diamond.

So, incidentally, the thermodynamical graphite is considered the most stable form. So, technically if you take diamond and you wait forever, you should end up arriving at graphite under the right circumstances. So, graphite is considered much more stable. So, you can see here that in fact, we say diamonds are forever is the kind of general public statement that is available, that is because how of how strong or how hard the diamond is, but thermodynamically it is the face graphite that is more stable so to speak.

So, incidentally so, why is it that you actually have it in different conditions, if I say that graphite is more stable, why does the diamond not abruptly change to graphite? Why do we even have a diamond? I mean so, so that is something that we should always keep in mind. So, that is got to do with the fact that in general any material that you take, the faces that you see are present due to a competition between two aspects; the first is the thermodynamics and the second is the kinetics. The thermodynamics tells us what is the stable face?

So, it tells us the face for which the free energy is the least and therefore, that that is the face towards which that element will tend towards. If you give it enough time it will move towards that face, but kinetically what happens is the kinetics is what tells us the rate at which that change happens. So, in all of chemistry you are essentially dealing with these two thermodynamics which tells us what will happen, kinetics which tells us at what rate that will happen?

So, many times you will see some face that is stable at room temperature that we see and we use industrially we use. So, therefore, it is actually available to us for extended periods of time in a very useful manner, which is actually not thermodynamically the most stable face? And, and the reason is that for it to become to transform to the most stable face, it will take 1000s of years because it is at room temperature in atmospheric pressure.

If, you put it under some other condition say very high temperatures, very high pressure so, some other variation of those conditions, you may find that it is transformation to the most stable thermodynamic face may occur very fast. But generally, many times you have created it under some circumstances and brought it kind of two-room temperature, and then atmospheric pressure, and then it sorts of stays for our purposes it appears stable indefinitely.

So, that is how you see the diamond appears very stable indefinitely and like with many things in chemistry, and metallurgy, and chemical engineering, it has got to do with the competition between thermodynamics and kinetics.

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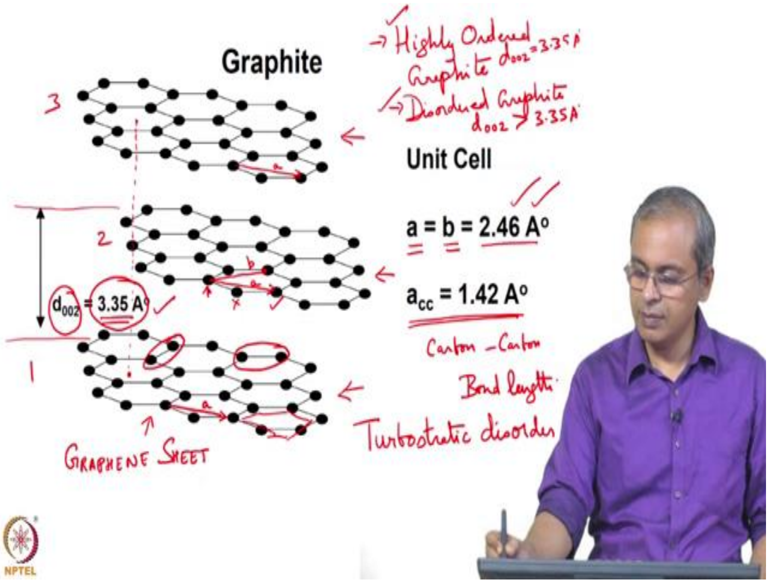

Graphite

→ Highly Ordered Graphite $d_{002} = 3.35$ Å

→ Disordered Graphite $d_{002} > 3.35$ Å

Unit Cell

a = b = 2.46 A°

a_{cc} = 1.42 A°

Carbon – Carbon Bond length

So, now look at the structure of these materials. And try to understand how they are relative to each other, what is fascinating about 1 structure relative to the other structure, what observations we can make in comparison. So, graphite, as we know, is a structure which has a very layered kind of set of aspects to it is structure. So, you have different layers each layer has a hexagonally bonded carbon atoms. So, you can see here. So, these are all hexagonally bonded carbon atoms that are sitting here, arranged in a hexagonal array and then you have layers.

So, this is 1 layer, this is a second layer, and this is the third layer, just for description sake we have put three layers together. They are sort of shifted with respect to each other you can sort of see that, say this atom here, sort of lines up to the center here, it also lines up with the center there. So, you can see that that is what happens we will sort of line up with this position. So, the central position there; so, the sheets are slightly shifted with respect to each other in a sort of a periodic arrangement, but between them they are all hexagonally bonded.

So, everywhere you see these hexagons and these sheets lined up on top of each other, parallel to each other. So, now, if you see the unit cell dimensions with respect to graphite, you see here I have written a=b=2.46 angstroms. So, now if you see the way the unit cell is defined for graphite the carbon-carbon bond length is not the unit cell vector. So, when you see here acc is 1.42 angstroms, this is the carbon-carbon bond length.

So, this number a_{cc}=1.42 angstroms is the is this distance, that distance or if you take this distance here, any of those distances that you take between two adjacent carbon atoms in the graphite structure, then you will see in the same plane of the graphitic structure, then you will get 1.42 angstroms. So, that is how we see the acc bond length? On the other hand the a=b, which is the unit cell vector so to speak is actually the vector that you would draw say starting from this carbon atom, not to the adjacent carbon atom, but to the 1 after that.

So, that you can call as say if you call that a and then this would then be b. So, you can see that it is not from the carbon atom to it is immediate neighbour, which is the carbon-carbon bond length, but then it is from the carbon 1 carbon atom to the 1 that is next to it is nearest neighbour. So, it is not the nearest neighbour. So, it is not this one, but it is this

1 starting from here. So, you start from there, you do not take the next one, but you take the 1 after that. So, that is you’re a=b kind of dimension and that is 2.46 angstroms.

So, when you look at graphite. So, this is the structure that we get and we also have 1 other dimension that we are interested in when we look at graphite, which is the c direction or called the so, these are called 002 planes the planes of carbon atoms that you see here the 3 planes of carbon atoms, that you see here are called the 002 planes. And, so, the distance between them is referred to as d_{002}, which is what I have got here d_{002} and that is 3.35 angstroms.

So, that distance is 3.35 angstroms it is basically the distance between the vertical distance between this plane of atoms and this plane of atoms. So, that is 3.35 angstrom. So, you have got a dimension which is 2.46, you have got b which is 2.46, and you have got c which is 3.35 angstroms. So, that is the set of parameters that help us define the graphitic structure.

Now, you will see in the literature or any regular book that you read to I mean kind of terms that are used with respect to graphite. So, they will say highly ordered graphite and you also have disordered graphite or description to this nature you will find a description that comes falls in this kind of category. So, what do they mean, when they say highly order graphite or highly I mean or disordered graphite. So, to understand the sense of order with respect to graphite, we have to look at these planes of carbon atoms. Now, each plane of carbon atoms is referred to as a graphene sheet. So, this is a graphene sheet. So, that is a graphene sheet.

So, now actually so, when we look at the research of in graphene that is essentially what they are referring to a single plane of carbon atoms that are hexagonally bonded, originally that was the definition for a graphene sheet. Today, when we talk of graphene, we have a little variation on this definition and there is a fair bit of discussion on exactly what should be called graphene, but if you look at the original definition, I mean every single plane of carbon atoms would be referred to as a graphene sheet.

So, when we discuss graphene we will look at this a little bit more on how those definitions can be modified a bit, but for the moment our definition of graphene is a single sheet of hexagonally bonded carbon atoms, such as the one that you suggest three layers that you see here. So, now what we refer to as highly ordered graphite is a graphitic sample where these graphene sheets are very large in extent. So, a very large area sheet is there and then there are several such sheets stacked in the c direction.

So, if you have 1000s of such sheets stacked in the c direction and each sheet is very large, I mean several microns large, maybe more maybe as centimeters large whatever it is some pretty large dimension relatively speaking? And, those sheets are stacked on top of each other, then that is considered highly ordered graphite. There is one more element of description here, which we have to be careful about and that is in addition to these sheets being stacked on top of each other, they have to also be oriented correctly with respect to each other.

So, you can have graphene sheets that are oriented exactly like this, you can also have graphene sheets that are twisted. So, you can have them twisted this way or that way, in which case the basically the a direction. So, if it if I take the a direction of this sheet, the a direction of the next sheet, and the a direction of the third sheet. So, I have just marked 3 A directions. So, we have the A direction in 3 different sheets that are shown here. So, if the a direction of sheet 1, sheet 2 is less it is called as 1 2 and 3 if the a direction of the 3 sheets lines up exactly with respect to each other.

So, they are all oriented in the exact same direction, then they are oriented, the sheets are oriented with respect to each other. But, if the a direction of 1 sheet is pointed this way, the a direction of the other sheet is pointed the other way, then the sheets are sort of twisted or rotated with respect to each other. So, this kind of existence of graphene sheets is possible inside some graphic graphitic samples.

So, you can get graphic graphitic samples, where the sheets inside the sample are not oriented in the same direction same with respect to a direction inside the sample. And, some others where they are oriented in the same a direction with respect to each other. So, if they are not oriented in the same a direction this is called a form of this is a form of the disorder that is present in graphite it is called turbo static disorder. So, that form of disorder is called turbostratic disorder. So, in a graphite example, if you want to say that it is highly graphitic, we want the graphene sheets to be large, we want several of those graphitic sheets to be stacked on top of each other.

And, we do not want turbostratic disorder, we want them all aligned in the same a direction. So, the a directions of all of them should line up exactly on top of each other.

If that happens it is called a highly ordered graphitic sample. And, if it is a highly ordered graphitic sample then the d_{002} comes to this value 3.35 angstroms. So, the d_{002} value comes to 3.35 angstroms. Now, when you have disordered graphite exactly the same three things that I just mentioned will not be present to the degree into the same amount of value.

So, for so, for example, the graphene sheets will be smaller, there will be less of them stacked on top of each other and then many of them will be twisted with respect to each other. So, you will have smaller sheets lesser number of stacking and turbo static disorder. So, if you have a combination of that then we call that disordered carbon, disordered graphite. Usually for disordered graphite what you will find is that if you did the x-ray diffraction of that sample or any other characterization like electron microscopy, and you find it is d_{002} value, you will find that it is d_{002} value is actually higher than 3.35 angstroms. Yeah so, for disordered graphite d_{002} greater than 3.35 angstroms.

So, here $d_{002}=3.35$. So, so that is how you see graphite you so, the general structure is that a layered structure, stacked on top of each other, you can have it in ordered form which means you have large sheets many of them stacked on top of each other a direction lined up correctly.

You can have disordered version is lesser number of sheets not stacked not many of them the smaller size sheets, not many of them stacked on top of each other and with turbostatic disorder. So, this is ordered and disordered graphite. Please keep in mind this value of the carbon-carbon bond length of 1.42 angstroms; we will get back to it in just a moment after we discuss the other traditionally known form of carbon which is diamond.

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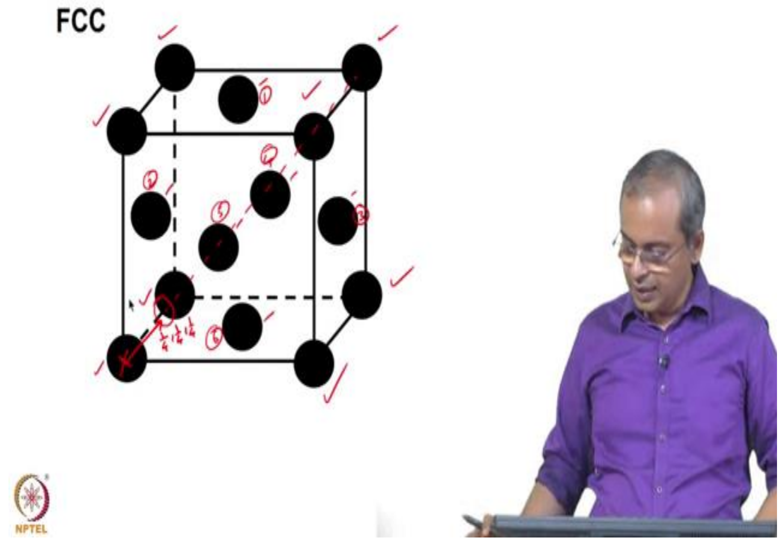

So, to look at the diamond structure, it is easy to visualize it by first looking at the face-centred cubic structure, which is basically a cube, which is what you see here and then so, these are the corners of the cube, this is the cube corner. So, 8 atoms at the cube corners and then you have a bunch of face-centred atoms. So, this one, this one also this is also a corner atom. So, this is a face-centred atom, face-centred atom, that is a face-centred atom and this is a face-centred. So, you will see here a 1 2 3 4 5 6 6 face-centred atoms present. So, that is put here 1 2 3 4 5 and 6, 6 face-centred atoms and the rest of them are corner atoms.

So, if you now take 1 more face centered array of lattice points. And, you merge the 2 such that the second cell that you are putting enters the first cell, but it is removed from this point, from this location, with from this location rather, from this location we shift it diagonally through the body diagonal.

So, what is the body diagonal? The body diagonal is this line here, which goes there. So, we shift it along the body diagonal, by one-fourth, one-fourth, one-fourth. So, if you shift quarter into that body diagonal and then place the first atom of the next face-centred lattice somewhere here, and then build the face-centred lattice around it, then what you will get is something like this.

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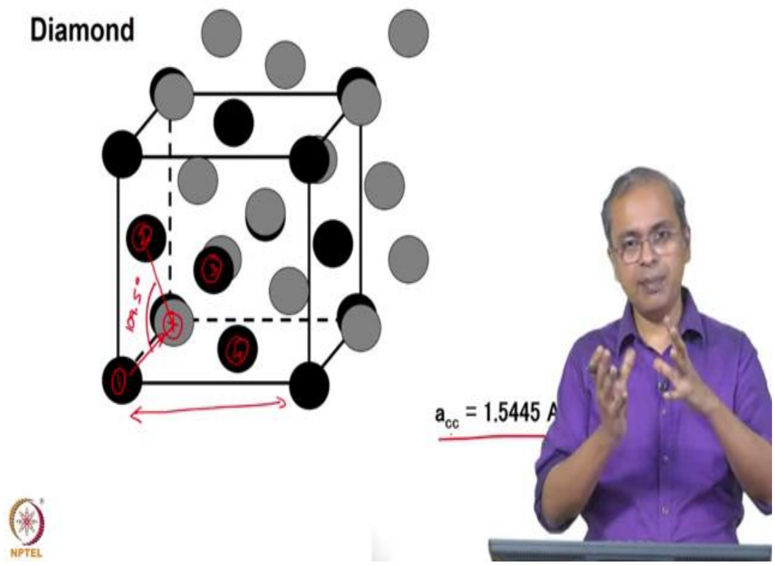

So, I have now got two face-centred structures which are which have sort of interpenetrated each other. So, they have penetrated each other and then they are shifted with respect to each other, by quarter, quarter, quarter, quarter of this distance. When, I say quarter it is one-fourth of this distance, one-fourth of the lattice length along the body diagonal. So, one-fourth of the lattice length along the body diagonal so, that is this distance. So, if you do that, then you will get this combination structure is called the diamond structure.

So, the diamond structure comes like this and it has it is own characteristics. So, so for example, the central atom here is now bonded to 4 different atoms here. So, this is 1, this is 2, this is 3 and 4. So, the central atom is now bonded to 1 corner atom which is which I have marked as 1 and then 3 face-centred atoms 2 3 and 4 of the 1 of the face-centred lattices. So, what it actually means is that the central atom here is tetrahedrally bonded to these 4 atoms. And, so, the bond angle here is some 100 and 9.5º.

So, that is the bond angle and that is how the diamond structure comes about? And, the carbon-carbon bond length here is 1.5445 angstroms. The diamond structure is very hard because of this three-dimensional network of bonding that exists within diamond. And, therefore, when you try to distort it in any manner, these bonds which are all covalent bonds are very strong bonds, they try to hold the structure rigidly in some position and that is why diamond is such a hard material. So, this is the structure of a diamond.

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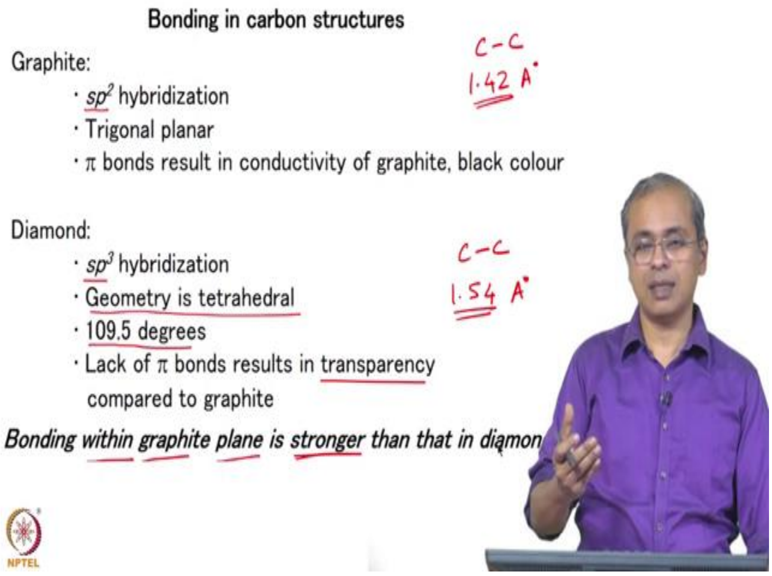

Bonding in carbon structures

Graphite:

- sp^2 hybridization
- Trigonal planar
- π bonds result in conductivity of graphite, black colour

C-C

1.42 Å

Diamond:

- sp^3 hybridization
- Geometry is tetrahedral
- 109.5 degrees
- Lack of π bonds results in transparency compared to graphite

C-C

1.54 Å

Bonding within graphite plane is stronger than that in diamon

So, if you look at the comparison, what you see is in graphite the carbon atoms are sp2 hybridized, which makes them distribute themselves in a planar structure and they are trigonal planar. So, that is why each carbon atom is now bonded to 3 other carbon atoms, 3 other adjacent carbon atoms, which is what you will see if you look at this structure here.

So, you can see every carbon atom here. So, for example, if I take that carbon atom here it is bonded to 1 2 and 3. So, 3 carbon atoms it is bonded to and so, that is trigonal planar, that is what you see here. And, the there is there are pi bonds which are above and below that the graphene sheet, where the electrons can relatively more easily move and that is what gives the graphite it is black color?

Diamond on the other hand and unlike this sp2 hybridization actually has sp3 hybridization. The geometry of the layout of those atoms is tetrahedral, which is what we saw in our previous slide the bond angle is 100 and 9.5^{o}, again I mark that on our previous slide, and there is there are no pipe pi bonds. So, there is so, these all the I mean all the bonds are covalent and there was there are no pi bonds. And, so, you in terms of band structure it ends up being such that there is I mean a significant band gap and it basically results in diamond being transparent whereas, graphite is black diamond is transparent.

So, now this is the summary of graphite versus diamond, but if you actually just go back a little bit, there is one interesting point we need to note, which is this a cc bond length. So, for diamond it is 1.5445 angstroms. And, if you go back a little bit, we note noted it down for graphite it is 1.42 angstroms. So, we have 1.42 for graphite and we have 1.54 for diamond. So, we will just put that here 1.42 angstroms and this is 1.54 angstroms. So, CC bond length.

So, this is what we have here? So, that is what we are? So, now, what does a bond length signified to us? A bond length basically indicates to us how strong the bonding is? The stronger the bond is the closer those atoms are going to be pulled together. So, that is an implication of so, it indirectly conveys to us which is this which is the material where the bonding is stronger. So, if you actually see, what you see is that the carbon-carbon bond length is actually lower in the case of graphite, then it is in the case of diamond.

So, this basically means that bonding within graphite, within the graphitic plane is actually stronger than that in diamond. So, that is a very non-intuitive result, because we always think of graphite as a soft material, that it can I know slide very easily many things can happen with respect to graphite. So, we always think of graphite is a soft material, we think of diamond as a very hard material.

In fact, that is one of the things that fascinates people about carbon and which is why so, many books are written about carbon, you can get it as one of the softest, faces present you can also get it as one of the hardest faces present within the scope of materials that are available to us. So, therefore, in diamond this is we find that actually if you look at the bonding the bonding in graphite is actually stronger than that in diamond.

So, that is a very interesting result to keep in mind and that tells us why there is so, much interest in a graphene sheets, there is so, much interest in carbon nanotubes and so on, you might think why not make everything out of diamond if you can theoretically make diamond in some form, but you see here that actually the graph graphitic material is actually stronger than the diamond material, which is not very intuitive. And, the reason diamond comes across as a strong material is because it has the 3-dimensional network of bonding and that makes the whole structure rigid.

Whereas graphite has this layered structure, where the layers can slide with respect to each other and that is why it comes across as a relatively weaker material. So, if you can utilize the strength the in within planar Intra planar strength of graphite in some form without having to worry about the sliding, then you have really captured or take an advantage of the extremely strong bonding that exists within each graphitic sheet. And, that is the basic idea with which a lot of people look at Nano-materials based on graphite our or some variations of graphite.

So, this is the basic idea with respect to the structures of the common materials graphite and diamond.

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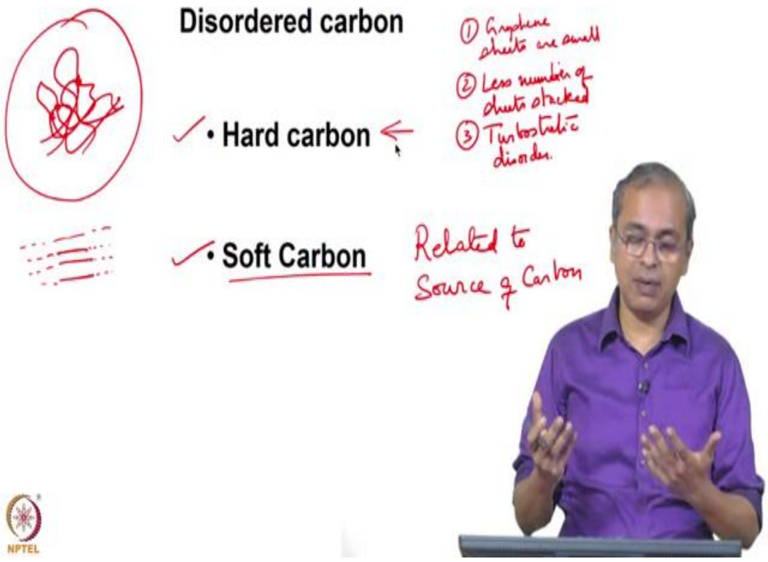

Disordered carbon

- Hard carbon
- Soft Carbon

① Graphene sheets are small
② Less number of sheets stacked
③ Turbostatic disorder.

Related to Source of Carbon

Now, amongst the disordered carbons as I said disordered carbon means the graphene sheets are small, and less number of sheets stacked, and turbostatic disorder. So, if you have that then you have a disordered carbon. Amongst the family of disordered carbons, you can have something called hard carbon and something else called soft carbon.

So, what is the difference? The difference is simply this if you take disordered carbon and say you take it put it in a furnace and you flow some inert gas you flow nitrogen or argon or something like that and you heat this sample.

So, some powder of this material you take, you heat the sample to say 800ºC 600, 700, 800ºC, you keep it in the absence of air with some inert gas flowing. You wait for a few hours you take it out and then you re analyze the sample for it is structural characteristics. You will find that some number of carbon samples are such that, if you do this process of heat treatment in the absence of air, for some few hours and then you cool it down and you look at the sample, you will find that what was disordered has become more ordered. And, if you do this heat treatment for a fairly long period of time it will become highly ordered.

So, it will start as a disordered carbon, if you keep doing this heat treatment, it will become more and more and more ordered eventually you will have highly ordered graphite. In fact, there is one version of it called highly oriented pyrolytic graphite, which is used as the standard for graphitic samples, but in general, you can move in that direction. So, graphitic samples which disordered graphitic samples or disordered carbon samples, which can be heat, treated and converted to highly oriented carbon samples are referred to as soft carbon materials.

So, if you can heat treat it wait for enough time and it becomes an oriented sample that is called a soft carbon. On the other hand, there are other forms of disordered carbon samples, where you can do exactly the same procedure take it to a 700 800ºc flow nitrogen or argon or some inert gas and you can wait indefinitely, nothing will happen. It will remain disorder, you will take it out, you do the analysis it will continue to remain disorder, you can put it back in the furnace wait for several hours take it out again analyze it remains disordered.

So, you will see that there is no improvement in order, that form of carbon which does not improve it is order when you do heat treatment is referred to as a hard carbon. So, that is the basic difference. So, when you see soft carbon what it means when you see hard carbon in some book or some discussion, you now know what it means, but the more fundamental question is why is hard carbon the way it is and why soft carbon the way it is. So, that difference comes simply due to the source of carbon.

So, for example, you can take many polymeric materials. So, for example, natural polymers is say sugar. So, you can take sugar and you can put it through a thermal treatment, say basically the absence of air you can heat it in do some thermal treatment, you will find that the sugar will basically disintegrate and you will end up with a carbon sample. All the carbon in that sugar will remain other constituents would leave and you will have carbon available with you a black carbon mass would be formed if you heat it under the right kind of conditions.

So, that is how you can get one form of carbon. So, what is the specialty of it the point is in a polymeric structure you have lot of cross-linking? So, you have a lot of cross-linking. So, the carbons are arranged in some three-dimensional form with lot of cross-linking that is present. So, you can think of it as. So, when even it becomes a carbon structure, when you have removed all the other constituents and you have remaining carbon structure, what it effectively comes across as is basically a graphitic structure a graphite sheet, which is no longer a flat graphitic sheet, but it is twisted in different ways and then bonded in all different direction.

So, in this kind of a hard carbon in soft carbon basically, you are having sheets like this, except that they a smaller number and they are turbostatically disorder. So, this they tend to grow in this direction and they start lining up. And, then you get more of them lining up and that is how the soft carbon starts off disordered and slowly becomes more and more ordered. Here, on the other hand, you do not have these flat sheets you have something like that, another sheet which runs like that and third sheet that runs like that and so on.

So, these already have bonding in all directions that are not the planar direction. So, you may have some bonding between the sheet that comes here and the sheet that comes here. So, here you may have a bond some other bond that is here so on. So, many of these junctions you will have bonds and those are not going to break down easily, they are as strong as the basic carbon-carbon bond.

So, unless completely disintegrate this material to individual carbon atoms, which require very high amount of energy, unless you would completely disintegrate this into individual carbon atoms and then reassemble it from there, you are not going to start with this material and end up with a graphitic structure.

So, this also has graphene sheets the disordered carbon also has the hard carbon also has graphitic sheets, except that they are not planar they are not flat they are coiled. So, basically you take a flat sheet you coil it, you twist it, you make it come and form a bond somewhere else and then in this complicated alignment it is present. And, so, far you will never be able to uncoil it, it is basically you made knots you have made knots of all sorts and you are not going to remove those knots, it is just completely coiled up and therefore, it does not respond to heat.

So, this is the hard carbon both of them have uses as so, hard carbon does get used in many electrochemical applications, it gets used in people try to people are investigating it is use, even in battery applications and so on same is true with soft carbon. So, it is not that any of these are useless they have their applications and there is a lot of research that goes on in them.

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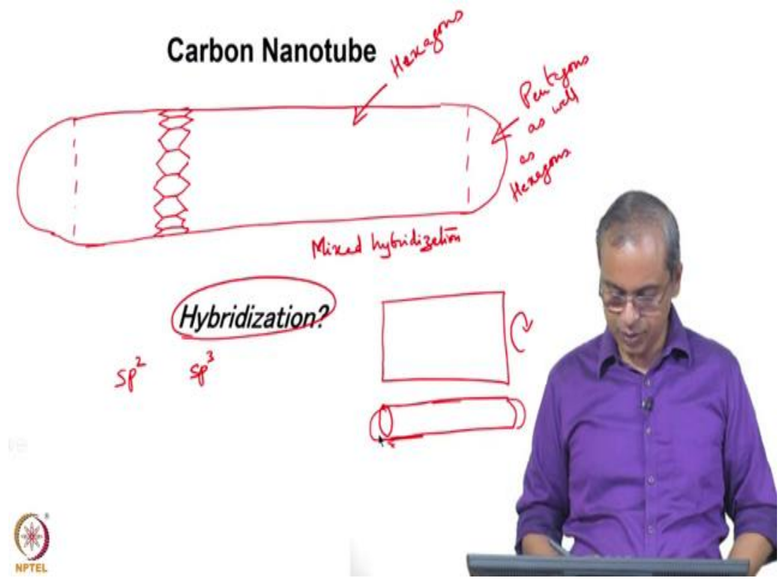

Carbon Nanotube

Hybridization?

So, then now we come to the carbon Nanotube. We have seen the traditional structures of a graphite and diamond we now come to a carbon nanotube. So, what does a carbon nanotube look like it is basically a tube as the name describes it is a tube? So, like I liked remove this. So, it is a tube capped on both sides with hemispherical caps and inside this, you have all the hexagonally bonded carbon atoms, and then, of course, it starts getting like that and then it continues that side.

So, you have you so, basically, you have you can think of it as a graphene sheet, that was a flat sheet flat graphite graphene sheet that you took and then you made a roll, you made a roll out of it. So, now, you have a tube. So, instead of a flat sheet you now have a tube. So, that is how you arrive at the graphene sorry the carbon nanotube structure. So, the one of the questions is to for us to understand what is the strength of the sheet, it is always nice to understand what is the hybridization in this sheet, and to understand that you have to see what is the structure of the sheet?

So, when it was completely flat it was sp 2 hybridization as you saw out here and then when it was in the 100 and 9.5º orientation and tetrahedrally aligned it was sp3 hybridization. So, on the other hand so, we have sp2 and sp3. So, what you see in a Nanotube is some is a structure that is neither flat nor it is completely at this 100 and 9.5º angle that is there. So, in fact, what we have is mixed hybridization it is called mixed hybridization. And, so, it is got a hybridization which is partly which shows partly sp 2 character, and partly sp 3 character, and that is how it relates to the two structures traditional structures of the graphite and diamond.

So, we will keep the thought in mind and as necessary we may need to revisit it. So, this is the way this structure is set up other two ends, you have hemispherical caps and this consists of a pentagons and hexagons. So, here you have only hexagons. So, hexagonally bonded carbon atoms, here you have pentagons as well as hexagons. Here also you can have disorder, you can have disorder on the tube which we will talk about later, but it is possible. The description I am giving you now is for a well-formed tube. So, the body of the tube only has hexagons and the end caps have an array of hexagons and pentagons which help you create those 2 end caps.

So, that is the structure that we have. So, those 2 end caps come here and here. So, that is how those end caps come.

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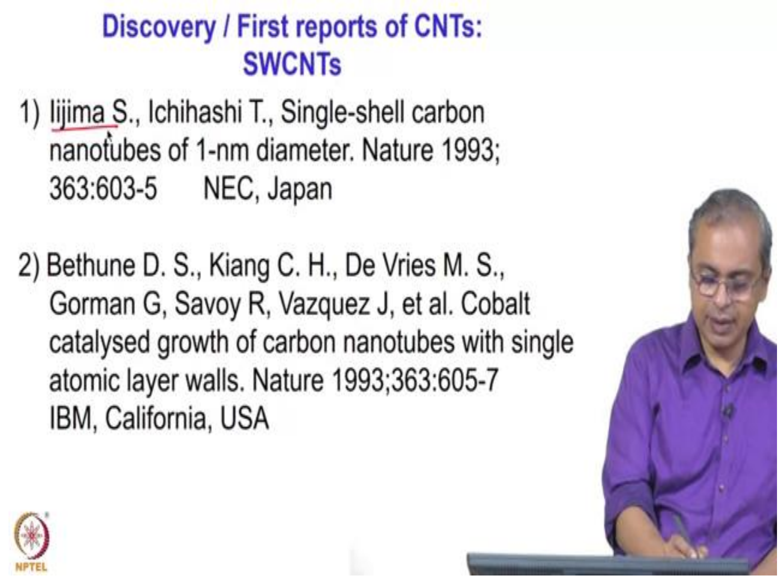

Discovery / First reports of CNTs:
SWCNTs

1) Iijima S., Ichihashi T., Single-shell carbon nanotubes of 1-nm diameter. Nature 1993; 363:603-5 NEC, Japan

2) Bethune D. S., Kiang C. H., De Vries M. S., Gorman G, Savoy R, Vazquez J, et al. Cobalt catalysed growth of carbon nanotubes with single atomic layer walls. Nature 1993;363:605-7 IBM, California, USA

So, if you look at the discovery of carbon nanotubes and the first reports of carbon nanotubes, it is interesting to know the history of it because that gives you some sense of perspective so, the credit for discovering single-walled carbon nanotubes. For example, is given to Iijima and so, if you see any paper associated with the carbon nanomaterial nanotube work. Invariably there will be a reference right at the beginning which says that the group of Iijima and coworkers discovered carbon nanotubes, and that is it is published in a in nature 1993. There was another group also which is published in the same journal and that is also listed there 1993.

But then I guess the subsequent pages this is 603 to 5 and this is 605 to 7. So, the general credit is given to this group here and that is considered by many to be a fair or a fair way of ascribing credit for the work that has been done. And, but the point you must remember here is something we are going to specify that as a single-walled carbon nanotube, we will talk about that exactly what it means a little later, but basically it means you just have one cylinder, you can also have concentric cylinders one on top of the other and that would be called a multi-walled carbon nanotube.

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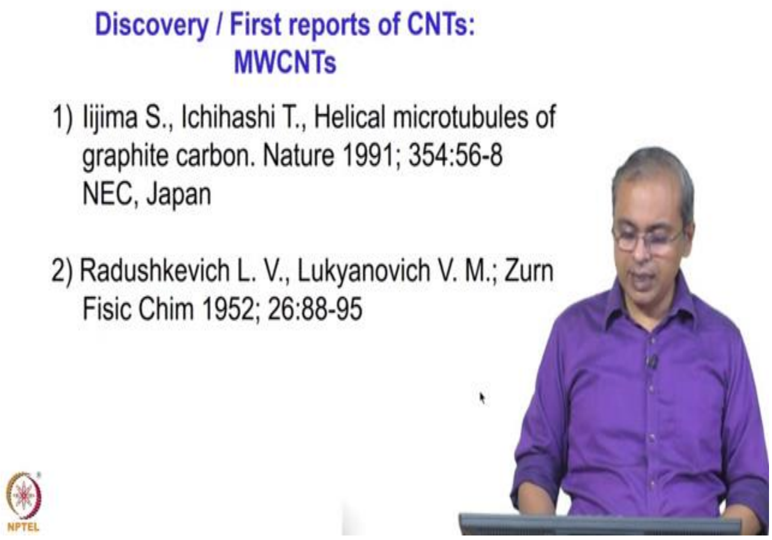

Discovery / First reports of CNTs:
MWCNTs

1) Iijima S., Ichihashi T., Helical microtubules of graphite carbon. Nature 1991; 354:56-8
NEC, Japan

2) Radushkevich L. V., Lukyanovich V. M.; Zurn Fisic Chim 1952; 26:88-95

So, for a long time actually, the multi-walled carbon nanotubes discovery was also attributed to Iijima to a paper 2 years earlier than the single-walled carbon nanotube paper that I previously showed you. So, that is sure in a nature publication in 1991 hm. So, but with a lot of people working beginning to work in this area, they looked at older literature and they found that much earlier; so, for example, in 1952 the earliest that they could find in 1952, they actually saw publications where there were electron micrographs, which showed structures which were essentially carbon nanotubes.

It is just that at that time they did not name it as a carbon nanotube. So, they just showed that carbon had that structure then they had that tubular structure.

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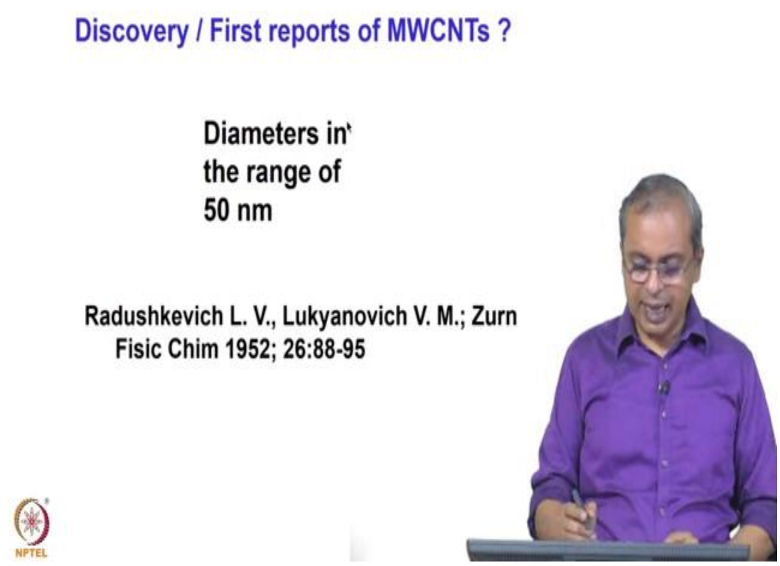

Discovery / First reports of MWCNTs ?

Diameters in
the range of
50 nm

Radushkevich L. V., Lukyanovich V. M.; Zurn
Fisic Chim 1952; 26:88-95

And, and so, for example, the diameters that they showed were in the range of 50 nanometers which is sort of an expected and this is in this 1952 paper. And so, today the way the credit is attributed is that the single-walled carbon nanotube work is indeed attributed to Iijima, but the general multi-walled carbon nanotube work is now open for debate on to whom you should describe it to and one place where it seems like it is a more reasonable way to describe it. It’s a much earlier reference so, to speak.

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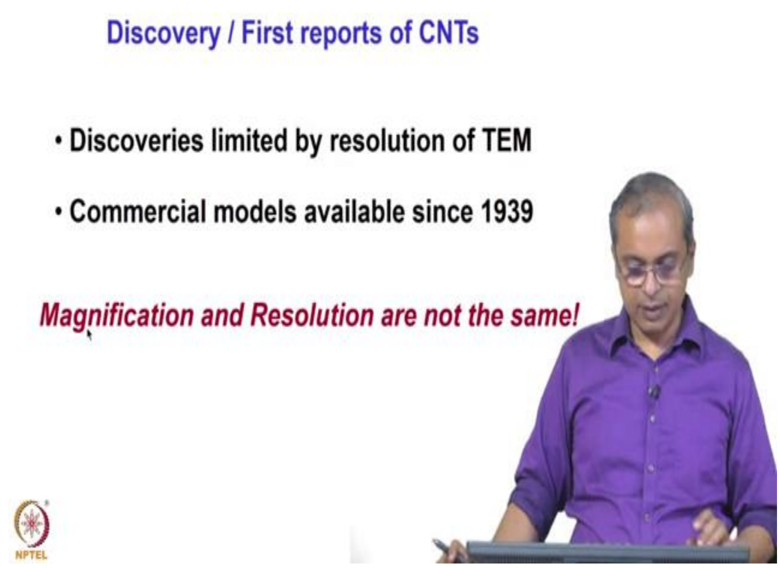

Discovery / First reports of CNTs

- Discoveries limited by resolution of TEM
- Commercial models available since 1939

Magnification and Resolution are not the same!

And, you will see in all these cases the discovery of carbon nanotubes and the reports of carbon nanotubes have been limited by the resolution of electron microscopes. So, actually, this is true for all nanomaterial work. The resolution of the electron microscope is what has made a significant contribution; improvements in the resolution have made significant contribution in the field of a carbon nanomaterial study and in the field of nanomaterials in general.

Commercial models have been available since 1939 into varying degrees. So, the electron microscope itself has been around now for 100 years and the commercial models have been around for about 8 years. So, to speak and continuously the resolution has been improving. And, also, we must understand from a general perspective, that normally when somebody says microscope we think of magnification.

So, we say higher the magnification you will get better image you can see smaller and smaller detail. So, that is the general impression, this is not really correct more important parameter is resolution. This is very important to understand that magnification and resolution are very different. So, for example, even in an optical microscope, you can put enough lenses and claim that you are having extremely high magnification.

But you will not see anything; you will see only a blurred image that is because the resolution is not high. And, a good way of understanding that is to see an image which shows you the difference between magnification and resolution.

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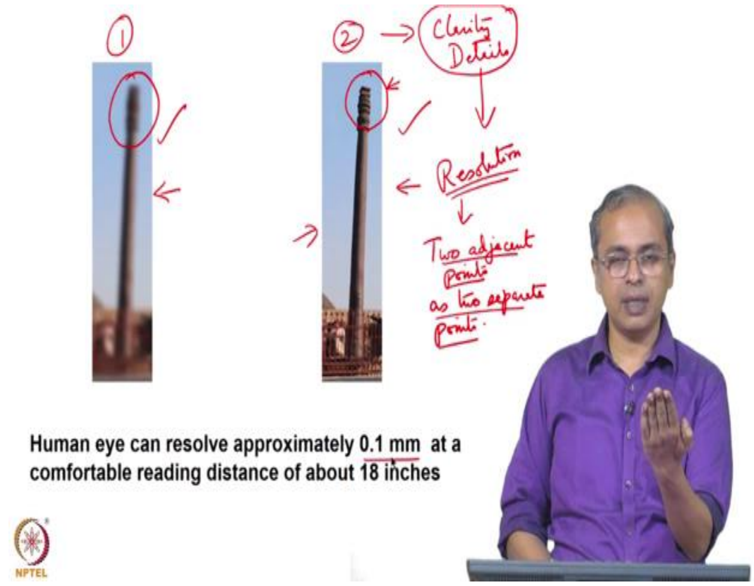

Human eye can resolve approximately 0.1 mm at a comfortable reading distance of about 18 inches

And for that I just have taken this famous pillar, which is there in Delhi, the Delhi iron pillar, this is not an electron micrograph this is just a regular photograph, but it conveys this idea quite clearly to you. So, you can see the size of this image here and the size of this image are roughly the same, which means the magnification. What is magnification? It is simply the actual object size and how it relates to the image size? So, image size divided by object size. So, if the object is 1 millimeter long and you have actually magnified it to 10-millimeter size, you have done a magnification of 10 x.

So, 10 times that size you are showing, showing the object. So, whatever is the actual object? So, this Delhi iron pillar, this rust-free pillar, has some size these two images are roughly the same size. So, both of them if you take the image size by the actual object size the magnification is the same. But you can see that in this image the details are very poor it is very blurred, blurred image you cannot really make out the details, on the other hand on this image you can make out a lot of designs here.

So, the so, in normal description we say clarity of this image is better. So, detail in this second image. So, the second image here, this is the first image we would say clarity is better or we will say. So, clarity is better details are better visible. So, this concept is what we refer to as a resolution. So, only if you have resolution you can see the detail in that object, that whatever it is that you have magnified. If you just see a blurred object you cannot make out anything, in this object I cannot say anything about what is the kind of pattern that is present in that region? What is the design that has been put in that region right?

So, if I were describing this in some paper, I cannot say anything I can simply say it is some cylindrical kind of structure, where towards the end of it there seems to be some additional work. Here, I can say much more in figure.2 I can say a lot more, I can say exactly what kind of designs I see on top in this region and how that differs from the rest of the pillar that is present. So, similarly for carbon nanomaterials or any other nanomaterials for you to start saying something about the structure of that material, it is not sufficient to have a highly magnified image of that nanomaterial.

You need a highly magnified image of that nanomaterial, which also shows sufficient detail. And, that idea of showing you sufficient detail is resolution; it is basically the ability to show two adjacent points as two separate points. So, supposing I have a spot in the image which is black in color another spot in the image which is grey in color. So, light grey in color.

So, now if the microscope helps, we see this black spot separately and this grey spot separately, I am able to say that I can see two spots. On the other hand, if it is creating an average dull grey spot across the entire region, I can only see one dull grey spot, I cannot see that I cannot say that there are two details available there. So, that is the idea of saying that two adjacent points the dark spot and the light spot are seen as two separate points, the dark spot and the light spot as opposed to one averaged point.

So, the lower resolution ones will take multiple points in the object and then bunch them together and give you one, averaged detail which from which you cannot make out much about the object. Higher resolution ones will take the same object and give you much finer detail. So, it is the same as what happens in your camera when they say. So, many megapixels camera and then you find one of the another camera which is even higher megapixels and so on the higher megapixels is adding more points to the same image.

So, therefore, increasing the detail so, human eye, for example, can resolve roughly 0.1 millimeter in a typical reading distance which is about 18 inches. So, you keep a book 18 inches from you and there are some drawing is there. If the in that drawing you have details which are 0.1 millimeter apart, you can still make them out, you can figure out that there is a white spot and there is a dark spot and so on. If it gets smaller than this you will only start seeing grey spot your eye will not be able to separate that as a dark spot and a light spot.

So, this is resolution very important for electron microscopy and very important for the field of nanomaterial’s and it has made a difference in many of the discoveries of a nanomaterials.

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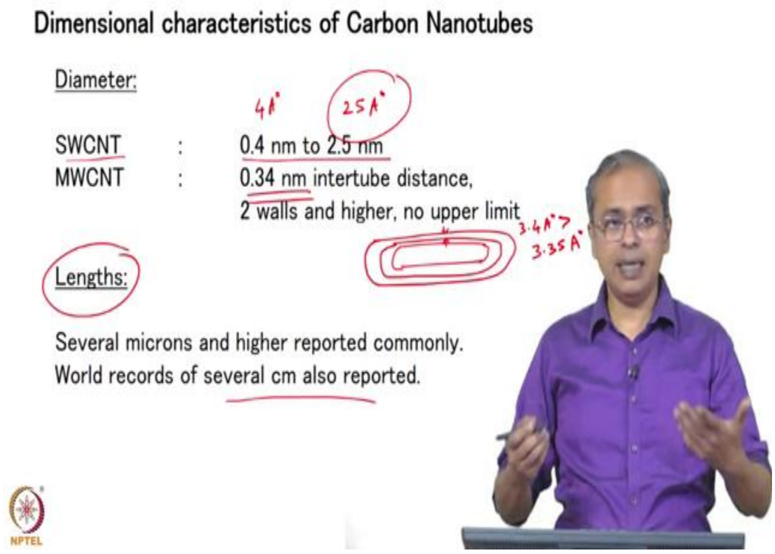

Dimensional characteristics of Carbon Nanotubes

Diameter:

4A° 25A°

SWCNT : 0.4 nm to 2.5 nm
MWCNT : 0.34 nm intertube distance,
2 walls and higher, no upper limit

3.4A° > 3.35A°

Lengths:

Several microns and higher reported commonly.
World records of several cm also reported.

So, with respect to carbon nanotubes, what we find is single-walled carbon nanotubes is they have dimensions our diameters of this range 0.4 nanometer. So, that is 4 angstroms to 25 angstroms. And, the reason why there is a limit is that if you make it smaller than 0.4 angstroms diameter, then you have to curve the curvature in the tube is too high, it causes a lot of the curvature and the tube is too high, it causes a lot of forces and strains in the structure, it is not able to sustain. So, it breaks up.

So, it stays up. So, only up to some point you can curve the tube. So, that is why you get 0.4 nanometer if you make it very large which is like these 25 angstroms. So, you have a diameter this large tube you can actually make larger tubes, but then it is unable to keep a circular cross-section, it collapses and forms like a ribbon, it forms this kind of a structure. So, you take a large paper you make a cylinder it collapse down on itself. So, that is the point in multi-walled carbon nanotubes you have multiple tube. So, so you have a tube and then around it you have the next tube, then you have the next tube and so on.

But this is a multi-walled carbon nanotube and the intertube distance here is the 3.34 angstroms I mean sorry 3.4 angstroms, which is slightly higher than the 3.35 that we indicated for highly graphitic sample. So, which is greater than 3.35 angstroms for highly graphitic sample; because this is not highly graphitic, because it's got curvature in it and so on. So, that is what we see and lengthwise people talk of very long lengths and so on, which are reported in literature several centimeters even larger lengths have been reported and so on.

So, you can make tubes of this nature. We will look at it in greater detail in our subsequent classes, even at this description of the carbon nanomaterial.

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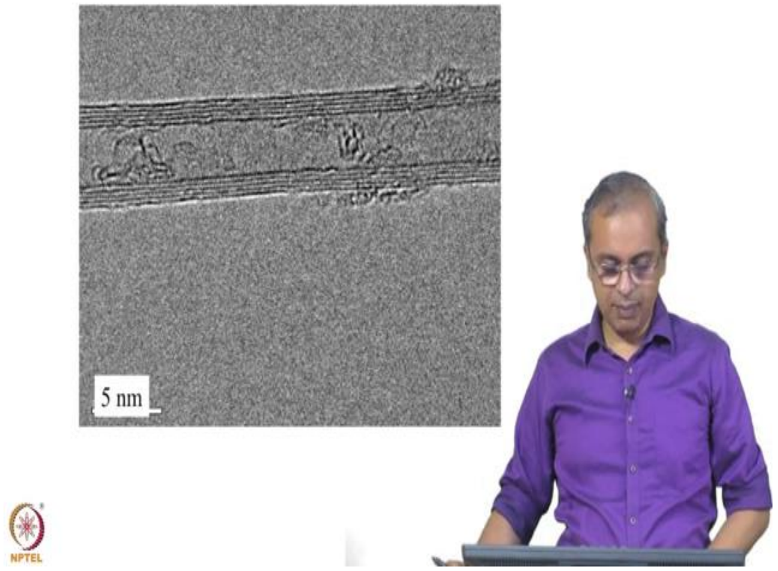

But basically, you can see here a magnified view of the nanotube; you can see here very various layers here, layer, layer, layer structure layer, layer, layer structure. So, these are concentric tubes that are around each other and that is how the tube is built and you get the overall tube, you can see this I mean we are having a 5 nanometer. So, this distance here is about 5 nanometers and that is basically what you see on the image.

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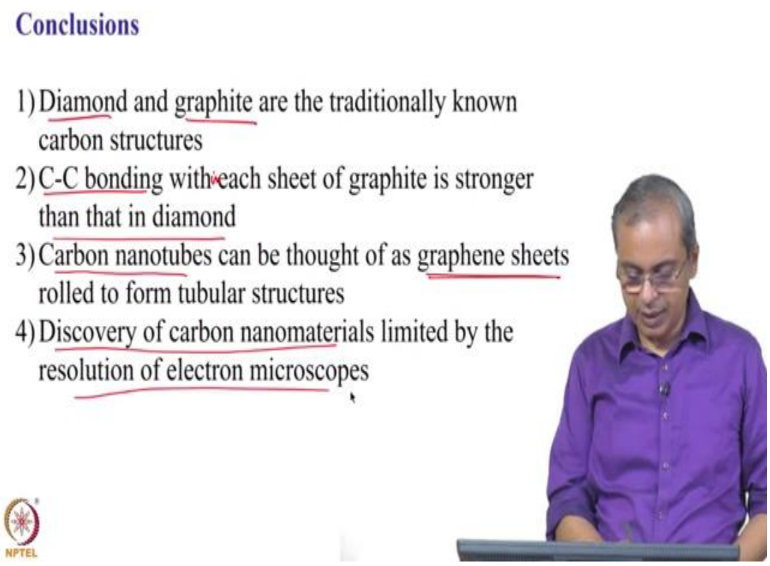

Conclusions

1) Diamond and graphite are the traditionally known carbon structures
2) C-C bonding with each sheet of graphite is stronger than that in diamond
3) Carbon nanotubes can be thought of as graphene sheets rolled to form tubular structures
4) Discovery of carbon nanomaterials limited by the resolution of electron microscopes

So, that is our sort of discussion on carbon nanomaterials, I mean to carbon at it is initial description and how it relates to nanomaterial's associated with the carbon. So, in our conclusions or summary of what we discussed today, we find that diamond and graphite are traditionally known carbon structures, we discussed how they relate to each other and how they are different from each other and which is more stable etcetera.

We found that interestingly the carbon-carbon bonding in within each sheet of graphite is actually stronger than that in diamond. So, within each sheet of graphite, it is actually stronger than that in diamond, but it is a 3-dimensional structure of diamond that gives us the appearance the diamond is stronger than graphite. And carbon nanotubes can be thought of as graphene sheets, which have been rolled to form a tubular structure that is not actually how they are formed, but that you can think of it that way. And, we also saw that the discovery of carbon nanomaterials has been limited by the resolution of electron microscopes, which have evolved over the years.

So, these are our major conclusions in our discussion or a initial discussion of carbon, we will look a lot more at the carbon nanotube in our subsequent classes we will re revisit some of the carbon nanotube structure and build on it. And, we will also see a lot of aspects of other carbon nanomaterials, which can also be thought of which have also be made and have been investigated.

Thank you.