Materials Chemistry
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Module - 5
Lecture - 7
The New Carbon Family II - Graphene

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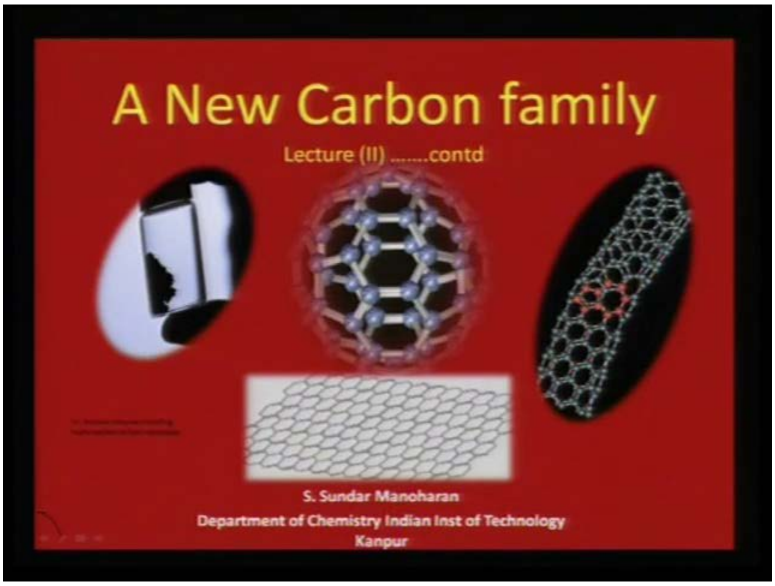

A New Carbon family

Lecture (II) ....contd

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We are looking at this New Carbon Family. And in yesterday's lecture, I specifically covered on the various aspects of this new carbons, which are identified the discoveries that underlies this new allotropic forms and also specifically we discussed about the chemistry of fullerenes. In today's topic, I would like to focus little bit more on the carbon nanotubes, because of it is application and then we will also look into the issues related to grapheme, the discovery and the properties related to graphene. So, just as a quick recap of, what we saw yesterday on carbon nanotubes, we said carbon nanotubes are those, which are confined in one dimension.

And the way, we roll these graphene sheets in different vectors determines, whether we get a zigzag carbon nanotube or a chiral or a armchair type. And depending on the way it is scrolled, it also alters the electronic property, and therefore you can look for a metal or a semi metal or a semiconductor. And the chiral vectors are also the ones, which decide the angle with respect to the CH vector and therefore, we can get different forms of carbon nanotubes.

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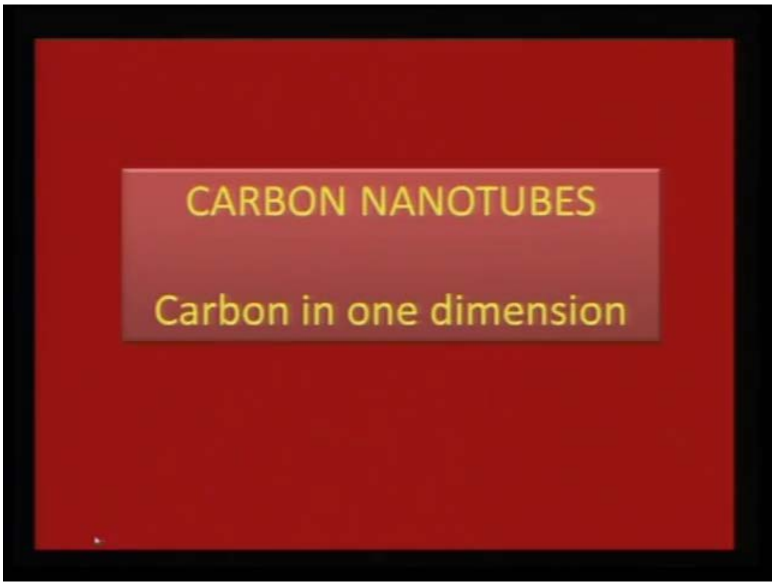

CARBON NANOTUBES

Carbon in one dimension

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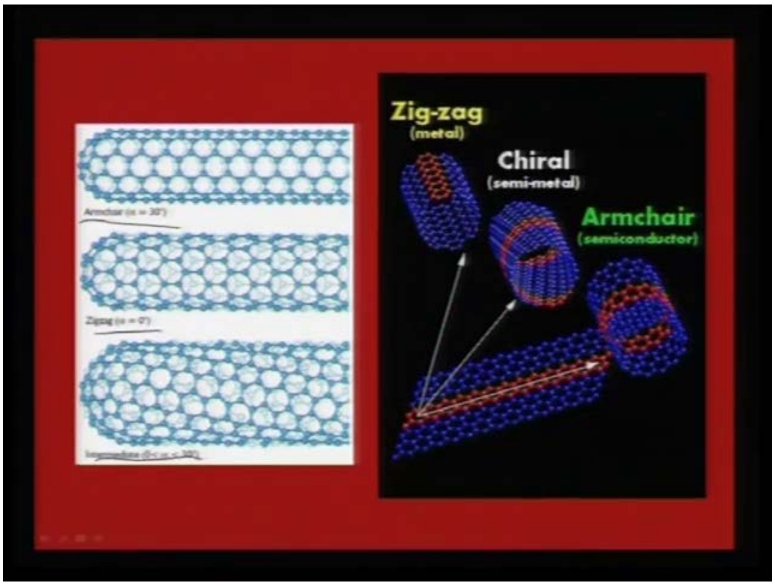

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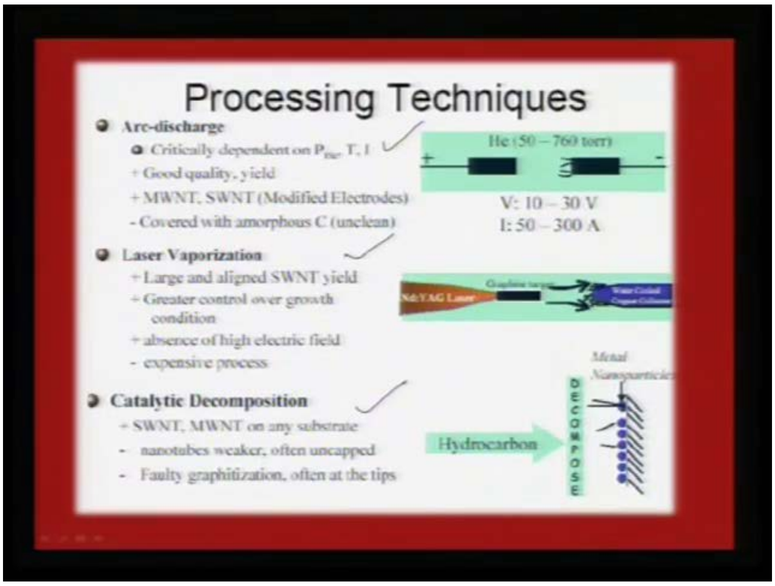

Processing Techniques

- **Arc-discharge**
  - Critically dependent on P_{He}, T, I
  - + Good quality, yield
  - + MWNT, SWNT (Modified Electrodes)
  - - Covered with amorphous C (unclean)
- **Laser Vaporization**
  - + Large and aligned SWNT yield
  - + Greater control over growth condition
  - + absence of high electric field
  - - expensive process
- **Catalytic Decomposition**
  - + SWNT, MWNT on any substrate
  - - nanotubes weaker, often uncapped
  - - Faulty graphitization, often at the tips

And we also looked at another view graph, where we said, there are three basic ways of preparing, one is CVD technique, another one is the arc discharge and also we have another technique using lasers. So, there are variety of ways, that we can realize this carbon nanotubes.

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Controlled Growth by CVD

Methane + Porous Si + Fe pattern ➡ Aligned MWNTs

a) SEM image of aligned nanotubes.
a) SEM image of side view of towers. Self-alignment due to Van der Walls interaction.
a) High magnification SEM image showing aligned nanotubes.
d) Growth Process: Base growth mode.

And one of the controlled way of growing this carbon nanotubes is to grow in one dimension as pillars. So, how do we do that, take methane and put that on porous silicon and porous silicon is actually kept with iron as nucleating centres. So, the carbon nanotube will actually get, will keep growing on the iron clusters, as you see here, these are the iron regions, iron patterns and this iron patterns will help the carbon nanotubes to grow in this fashion and what we see here in this view graph, is the oriented crystal growth.

So, if you can actually pattern your porous silicon in this way, as you see from the top then you can find out or you can realize such nanostructures growing in a preferred oriented form, so these are patterned way of growing silicon nanofibres. So, you do not necessarily need to get a bundle, but it can be streamline, the growth can be streamline. And therefore, the gross process is actually a base growth mode which means, it will only nucleate on a particular metal, where it is catalytically getting decomposed and it grows. And if you pattern the base then accordingly the growth of the carbon nanotube also proceeds. If you do not pattern then you get a bunch or like a forest it grows in one direction.

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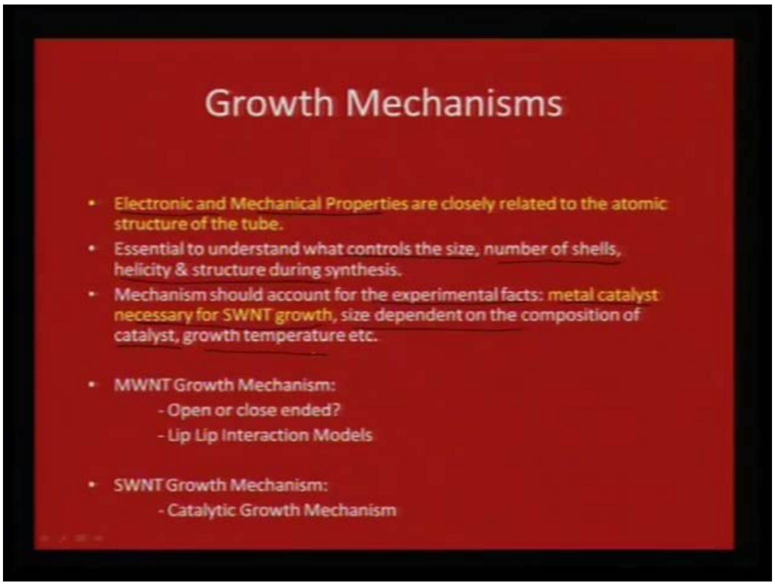

Growth Mechanisms

- Electronic and Mechanical Properties are closely related to the atomic structure of the tube.
- Essential to understand what controls the size, number of shells, helicity & structure during synthesis.
- Mechanism should account for the experimental facts: metal catalyst necessary for SWNT growth, size dependent on the composition of catalyst, growth temperature etc.
- MWNT Growth Mechanism:
  - Open or close ended?
  - Lip Lip Interaction Models
- SWNT Growth Mechanism:
  - Catalytic Growth Mechanism

So, the growth mechanisms are very important to understand the electronic and mechanical properties, because both are dependent on the atomic structure of the tube. What we need to understand is that, what are the parameters that control the size, number of shells if it is multiwalled and the helicity and structure during the synthesis. What has been proved and established is that, there is no way you can grow a carbon nanotube without a metal catalyst.

Therefore, that is much important for the synthesis of nanotubes and the size dependency comes with the nature of catalyst and the growth temperature, etcetera. Now, regarding the mechanism of a single walled growths or say multiwall, there are different models that are proposed to understand, because this happens in a very transient way. Therefore, one does not really know, what is the mode by which a multi walls propagate or single walls propagate, but there is some fair idea about, how the whole thing happens.

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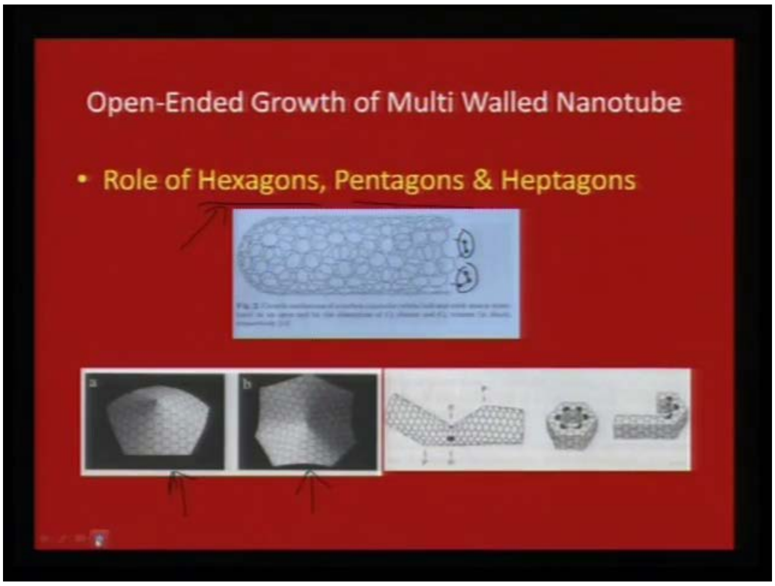

Open-Ended Growth of Multi Walled Nanotube

- Role of Hexagons, Pentagons & Heptagons

Open ended growth of multiwall nanotubes seems to occur mainly, because of the role of hexagons and pentagons, which played the important role in propagating this along one axis. As you see here, these are C 2 clusters, these are C 3 clusters and the way, they go and join to the nanotube, which is growing determines, whether it will be open ended or whether it will close or what will be their length scale of the growth process.

So, typically this sort of units do help in realizing, whether there will be a closing, because both sides can be open ended also, when it is growing along a preferred axis. But, in most of the cases, we see that the carbon nanotubes do close in one end to attain stability and why it happens, mainly because of the role of this hexagons and pentagons and the way, the carbon clusters keep on getting accumulated.

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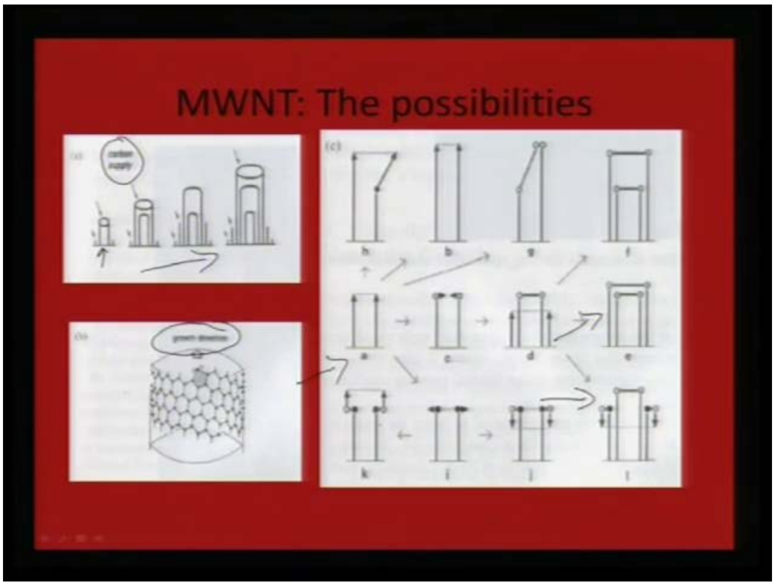

MWNT: The possibilities

When we come to multiwalled nanotubes, the possibilities are immense, and therefore there are very few ways that you can map to understand. As you see here, this is a single wall and as the carbon supply is coming, the second wall can actually grow as a open ended wall or this can close and the third wall can propagate. So, the way the multiwalls evolve, depends mostly on the way the carbon supply is and also it depends on the way the growth direction is.

So, this is a contour which tells, what are the different ways this multiwall structure is happening. As you see here, this can unfoil like this and again go for the third growth or this can actually go to close the second layer and so on. So, there are different combinations, which are worked out, but as far as the multiwall nanotube growth is concerned, two parameters are important. One is the way the carbon supply is and the growth direction that proceeds during the growth, so both are important.

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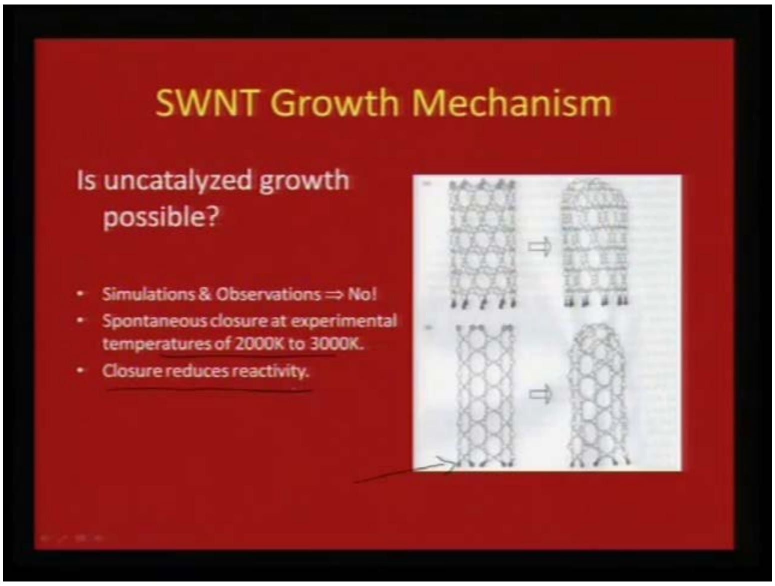

SWNT Growth Mechanism

Is uncatalyzed growth possible?

- Simulations & Observations ⇒ No!
- Spontaneous closure at experimental temperatures of 2000K to 3000K.
- Closure reduces reactivity.

Whereas, for single wall growth mechanism, it has also been tried theoretically through simulations to find out, if uncatalyzed growth is possible for single wall. And what has been found out is that, such uncatalyzed reactions are possible only at temperatures of 2000 K to 3000 K. Therefore, for single wall nanotube, definitely there is a much clearer mechanism than the multiwall. And what is implied here in this study is that, the nucleation through the metal centre is very, very important for single wall nanotubes. And the closure of this single wall nanotubes actually reduces the reactivity, in other words makes the tube stronger, therefore the closing also occurs.

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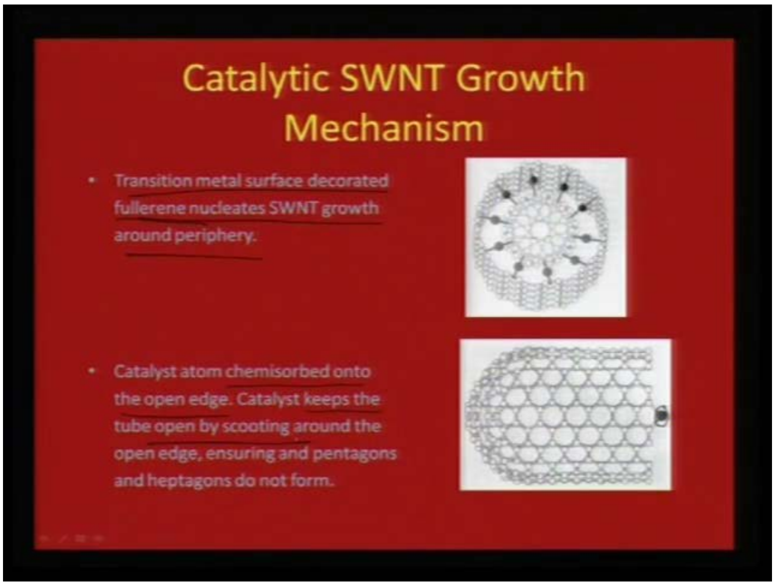

Catalytic SWNT Growth Mechanism

- Transition metal surface decorated fullerene nucleates SWNT growth around periphery.
- Catalyst atom chemisorbed onto the open edge. Catalyst keeps the tube open by scooting around the open edge, ensuring and pentagons and heptagons do not form.

And how does this happen, actually if you take a fluorine molecule and then the fluorine actually has this nucleation sides of the metal, of this metals lying in this direction then you can see the single wall nanotube is actually propagating through this links. So, this is one of the way, that we can visualize how a single wall can come compare to multiwall. So, transition metal surface decorated fullerene, they nucleate the growth around the periphery and what is the role of the catalyst there, catalyst keeps on coming out along with the growth.

So, this sort of catalyst atoms do stick to the edges of the carbon nanotube, so catalyst atom chemisorbed onto the open edge and this keeps the tube from scooting around the open edge. This will ensure that, pentagons and heptagons do not form, that is one of the reason, why a long chain single wall nanotube is possible with this sort of mechanism.

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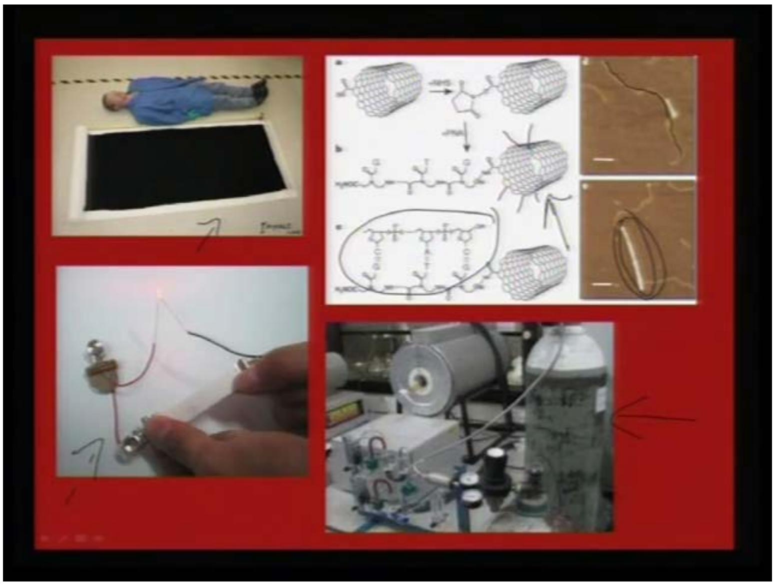

And if you really look at the way this field has grown with this basic understanding of how to make a single wall nanotube or a multiwall nanotube, sky is the limit. Because, the way people have mapped different derivatized single wall nanotubes or taking it through some functional applications, there has been a sky rocketing effort. And you can see here, some of this view graphs just to highlight, what all can happen, here this has been used for electrical applications and you can also spread this carbon nanotube like a screen to go for large area deposition.

And as you see, you can even roll it to 6 feet on a paper or plastic substrate, so processing of this carbon nanotubes to larger areas is possible. And here in this cartoon, you can find that the carbon nanotubes in the edges can be functionalized, when we say functionalized, you actually oxidize it and convert it into COOH, the terminal carbons and then you try to attach it to any material. As you can see here, you can almost simulate the sugar units here and CGAT pairs can be paired up, which is also seen very clearly from the AFM pictures.

So, when you substitute this carbon nanotube then they show a contrast here, these are the carbon nanotubes that you see in the AFM picture and those, which are highlighted here are the substituted ones. So, it is possible to go for a variety of substitutions on this single wall nanotube and if you want to make extensive substitutions then not just one, you can try to oxidize it. The more you oxidize it, the more you generate COOH groups in the terminal positions and then you can actually attach a variety of molecules to it. And the research has now reached to the extent, where you can actually do it in lab scale in a very defined way. So, this is one of the setup, where you can realize single wall nanotube preparation even on a lab scale.

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Quick and easy enrichment of metallic carbon nanotubes
Hiromichi Kataura and Yasumitsu Miyata
Enrichments of up to 80% can be achieved quickly and simply through the preferential oxidation of semiconducting nanotubes.
4 September 2006, SPIE Newsroom. DOI: 10.1117/2.1200608.0323

And the best part of carbon nanotube as I mentioned in the earlier slide, is the enrichment of this metallic carbon nanotubes. And we can also, not only enrich them, but we can go for preferential oxidation of this nanotubes to a larger extent. So, as you would see from this picture, that with more and more of selective oxidation, the color of this nanotube solution changes. So, these are those, which are oxidized which means, more and more of COOH groups are attached to the terminal carbon.

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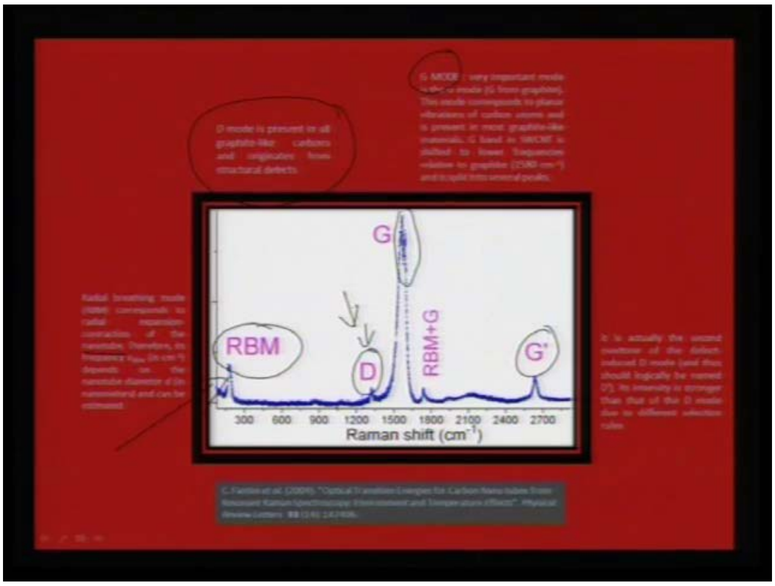

So, we can try to enrich that, but the best way to characterize, if you are able to really functionalize these carbon nanotubes or whether they remain as pure nanotubes, RAMAN spectra is one of the best way to analyze. And here are four important reflections that we should bear in mind, which gives us a clue, how to map the purity of it. The first one is your G mode, which is the very important mode, which is G from graphite, this mode corresponds to planar vibration of carbon atoms and is present in most graphite like materials.

So, this G band in your single wall nanotube is shifted to lower frequencies relative to graphite and is split into several peaks. So, this is the peak that you can map and if there are several splittings in this, as you can open this peak, you would see several splitting. Splittings really give the clue that these are single wall nanotubes, whereas the graphite will actually give a very intense single line.

So, this is one way to map the formation of single wall nanotube, another one is the radial breathing mode, which corresponds to the radial expansion contraction of the nanotube, therefore the frequency depends on the nanotube diameter and can be estimated. As I told in the previous lecture, that we can actually alter the diameter of these nanotubes, so this radial breathing mode is one measure, by which you can analyze the diameter.

Because, this is very sensitive and with the diameter of the tube, this radial mode would shift, so you can estimate, whether you have a preferred dimension or not. And another important mode is D mode, is present in all graphite like carbons and originates from structural defects. So, this is one important feature, which will give us clue, whether you have functionalized your carbon nanotube and this D prime is also called D prime. This G prime is nothing but your second overtone of D and the intensity of this will tell, whether you have functionalized the single wall nanotube or not.

For example, if you are treating this with nitric acid and then boiling it then this peak would actually be a measure, whether you have functionalized your nanotube or not. If this is really absent then you say that, it is a single wall nanotube. So, this is not only a measure of the defect structure in your carbon nanotube, but this also tells, whether you have functionalized it. So, this serves as a very good optimization for your single wall nanotubes.

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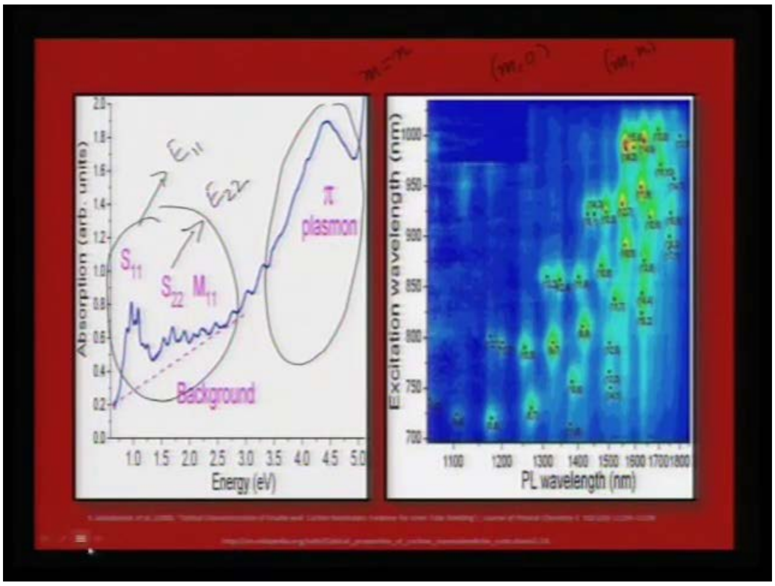

And when we come to the optical properties of single wall nanotubes, you would see a typical absorption peak for carbon nanotubes, where beyond 3 electron volt, this is due to Plasmon absorption. Whereas, there are peculiar reflections due to S 1 1, S 2 2, M 1 1, this S 1 1 or S 2 2 is actually to differentiate between metallic or semi metal carbon nanotubes. In semimetal zigzag nanotubes metallic, this will be more prominent, S 2 2 it can be called as E 2 2, if we do not know the metallicity or for the semi metals or semiconducting nanotubes, this is S 1 1 reflection.

So, these are two absorption peaks, which really play a very important role in mapping and here again, we see the profile of the excitation wavelength versus PL wavelength. As you would see here, these are plotted against the unit vectors m and n, so whatever numbers that you see here shows, that for m 0 repeats, you do not see any photoluminescence, neither for m is equal to n. So, the values in the parenthesis clearly tells us, what sort of mapping or what sort of orientation of the nanotubes, which are going to be effective for photoluminescence. But, the good news is that, carbon nanotubes show a very strong photoluminescence, but it is also dependent on the chirality. So, depending on that, we can map the photoluminescence response.

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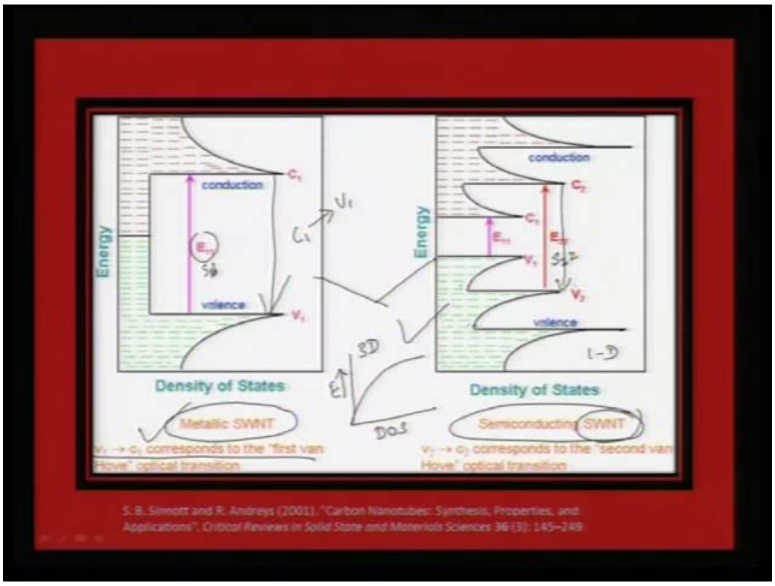

$v_1 \rightarrow c_1$ corresponds to the "first van Hove" optical transition

$v_2 \rightarrow c_2$ corresponds to the "second van Hove" optical transition

S. B. Sinnott and R. Andreys (2001). "Carbon Nanotubes: Synthesis, Properties, and Applications". *Critical Reviews in Solid State and Materials Sciences* 36 (3): 145–249

As I told you, this E 1 1 or S 1 1 is dependent on the metallic nanotube and this is for the semiconducting nanotube. So, if it is semiconducting then we mention this as S 2 2 specifically and if it is metallic, it is S 1 1 and this S 1 1 and which is nothing but E 1 1 in this diagram, is a transition from V 1 to C 1. So, when electron is getting excited to C 1 then a electron hole pair is actually formed, which by a phonon assisted process relaxes and then the emission comes out to be a C 1 to V 1 emission.

This is what is responsible in the case of metallic nanotubes and this is also called as first Van Hove optical transition, which talks about the transition that is responsible for the absorption. And in the case of semiconducting single wall nanotubes, you would see, that the density of states are slightly different from the metallic nanotubes. These are much more discretized and this sort of density of states, what you see here is nothing but the influence of your one dimensional structure, in one dimensional, you would not see a continuous density of states.

So, in a three dimensional material, for a 3 D, the density of states actually would correspond like this, but for a one dimensional nanotube, these are all discretized, and therefore you see this sort of pattern. And between the metallic and the semiconducting, you can clearly see, that the density of states differ very differently and these are the optical transitions, which are responsible for photoluminescence. And in the case of semiconducting nanotubes, it is C 2 to V 2 transitions, which are responsible.

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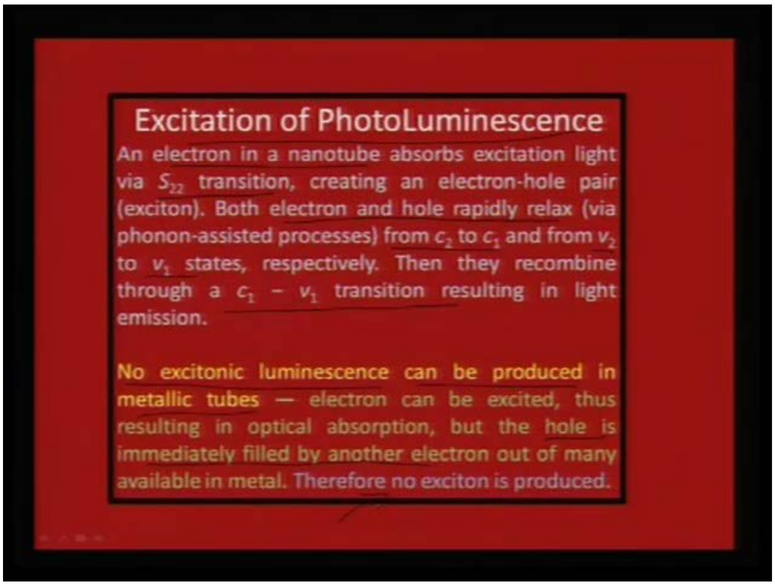

Excitation of PhotoLuminescence

An electron in a nanotube absorbs excitation light via S_{22} transition, creating an electron-hole pair (exciton). Both electron and hole rapidly relax (via phonon-assisted processes) from c_2 to c_1 and from v_2 to v_1 states, respectively. Then they recombine through a $c_1 - v_1$ transition resulting in light emission.

No excitonic luminescence can be produced in metallic tubes — electron can be excited, thus resulting in optical absorption, but the hole is immediately filled by another electron out of many available in metal. Therefore no exciton is produced.

So, excitation of a photoluminescence, an electron in the nanotube absorbs via S 2 2 transition, as I mentioned earlier. And the electron and the hole rapidly relax from C 2 to C 1 and from V 2 to V 1, and therefore the C 1 V 1 transition is actually responsible for the light emission. And one thing that we need to understand here is, the photoluminescence is not due to excitonic emission, this is quite different from the other PL situation, where PL emission usually is an excitonic influence.

But, carbon nanotube photoluminescence is not an excitonic luminescence and this because it cannot be produced in metallic tubes, the electron can be excited, thus resulting in optical absorption. But, in the case of carbon nanotube, the hole is immediately filled by another electron, because the electrons do keep coming. And therefore, no exciton is actually produced, which is responsible for photoluminescence, this is another thing that we should bear in mind.

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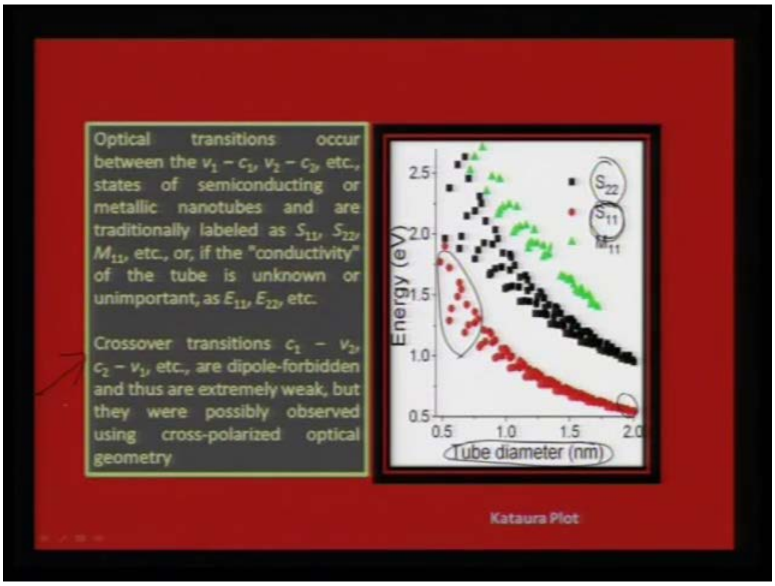

Optical transitions occur between the $v_1 - c_1$, $v_2 - c_2$, etc., states of semiconducting or metallic nanotubes and are traditionally labeled as S_{11}, S_{22}, M_{11}, etc., or, if the "conductivity" of the tube is unknown or unimportant, as E_{11}, E_{22}, etc.

Crossover transitions $c_1 - v_2$, $c_2 - v_1$, etc., are dipole-forbidden and thus are extremely weak, but they were possibly observed using cross-polarized optical geometry

Kataura Plot

So, critically, if you look at the photoluminescence behavior, the S 2 2 transition and S 1 1 transitions, which are for the metallic and semiconducting, are also dependent on the tube diameter. So, depending on the tube diameter, you can see the absorption or the energy gap will vary. And for, let us take the case of S 1 1 that is, for metallic single wall nanotubes, if the tube diameter is less than 1 nanometer then the band gap is much higher and the band gap becomes much much lower, when the tube diameter increases, so this is one thing that we should bear in mind. And also another important thing, where we should see is, a crossover transition from C 1 to V 1 and C 2 to V 1 is also possible, although they are dipole forbidden transitions, so all this do influence the photoluminescence.

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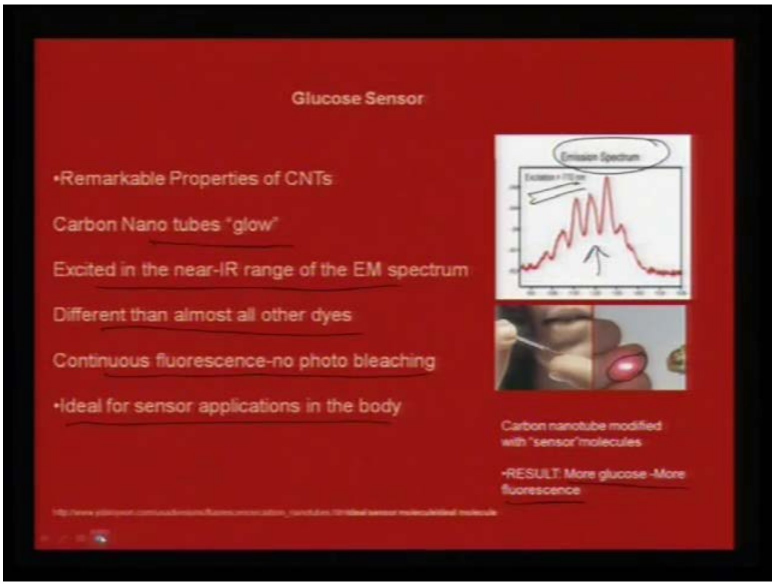

Glucose Sensor

- Remarkable Properties of CNTs

Carbon Nano tubes "glow"

Excited in the near-IR range of the EM spectrum

Different than almost all other dyes

Continuous fluorescence-no photo bleaching

- Ideal for sensor applications in the body

Carbon nanotube modified with "sensor" molecules

- RESULT: More glucose -More fluorescence

And based on this, several applications have been tampered, one is the use of carbon nanotubes as a glucose sensor, because carbon nanotubes glow, you can use this for mapping certain molecules or for mapping some study. The best part is, it is excited in near IR range of the electromagnetic spectrum, therefore it is safer to the cells. And the another point is, the glow that comes out is different from the other dyes, therefore it is very selective and continuous fluorescence also does not bleach the carbon nanotube.

Therefore, continuous radiation is also possible and it is ideal for sensor applications in the body and what you see here is a glucose monitor. If you have a glucose sensors kept with the carbon nanotube then you see that mapping can be or the glow can be much intense and rich. And more the glucose present in the in the blood then you will see very high luminescence, so that could be used as a mapping. And this is a typical emission spectra of your carbon nanotube, if you excite it at 770 then the emission actually comes at 1300 nanometer, so this is a typical spectrum for carbon nanotubes.

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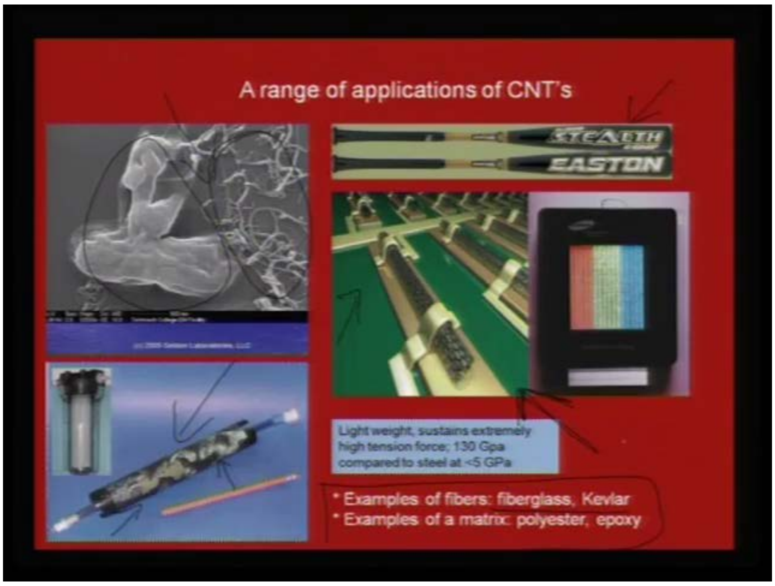

A range of applications of CNT's

Light weight, sustains extremely high tension force; 130 Gpa compared to steel at <5 GPa

- Examples of fibers: fiberglass, Kevlar
- Examples of a matrix: polyester, epoxy

Also there are range of applications for carbon nanotube already realized in the market and in the industry. This is a cartoon which tells that, it is having a very vivid antibacterial effect and you can see here, the influence of the carbon nanotube compared to uncoated or a region without carbon nanotube. Clearly you can see that, the bacterial presence can be removed using the presence of carbon nanotube and this is also acting as a very good filter, because of it is very high surface area.

And as you would see here, this is a filter that is currently employed in the US army, almost everyone is provided with a backpack, where these sort of filters are being carried by the soldiers for getting pure water. So, this has lot of advantage in filtering biological impurities and in the sports arena, people have also used this to improve the strength. It is used in tennis racket, it is used in baseball stuff and also there are other selective applications, where in AFM, tip carbon nanotube coated, AFM tips have been produced.

So, this is one of a very prime application, which is being currently exploited and also, this is being used in composite materials. As you would know, you have a matrix, which is polymer and then you try to reinforce with the some fillers like fiberglass or Kevlar. But, carbon nanotubes added to this matrix seems to enlarge the toughness and the strength of the material to a larger extent. One other application that we can see here is, in the use of displays, this is a map of your cathode ray tube, where you know that the electron guns impinch on the phosphorous and then you get a full colour spectrum.

But, you can get much sharper contrast and colour purity, if you are going to use carbon nanotubes in field emission process. Because, in field emission compared to the cathode ray operation, you see here, it is a blend of three electron guns mixing the colors. Whereas, in field emission displays, the important point is, behind each of the pixel, there is a electron that is generated. So, it brings color purity and sharpness to a greater extent and carbon nanotubes are able to improve on this contrast and it is also used in nano electronics now, carbon nanotubes can be used.

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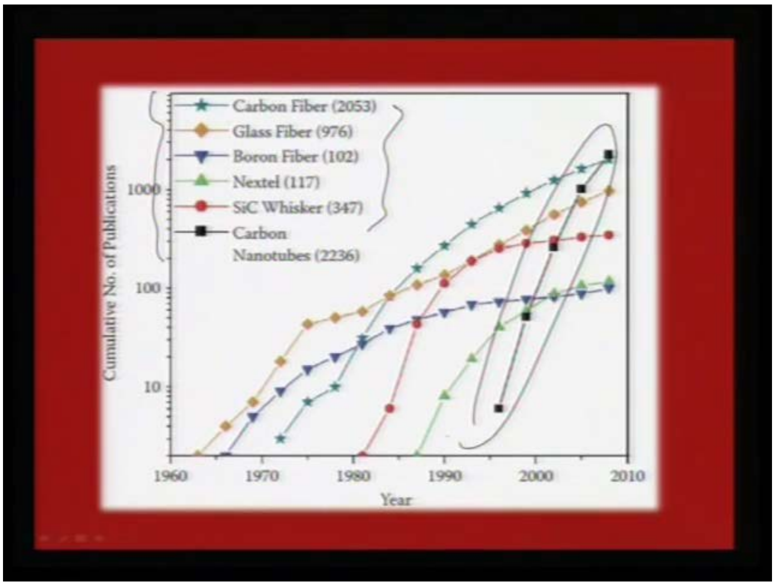

So, there are several applications, which are being realized for carbon nanotubes, I cannot go on showing more view graphs on the applications. But, just to highlight the interest that carbon nanotubes have generated compared to most of the composites that are currently being used, you can see the way carbon nanotubes have taken over is phenomenal. And specially, in the last 10 years, there has been marked changes happening and although, these are some of the fibre composites, which are still being used, but carbon nanotubes have certainly generated range of interest for applications.

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GRAPHENE

Material for all seasons

Carbon in 2-dimension

Next, I would like to go to graphenes, graphenes as I mentioned in the previous lecture, graphene is in two dimensional form and this is also by enlarge agreed as, a material for all seasons. As I told you, if we can really map how the 3 D is and 1 D and zero dimensional carbons are evolving, we found out in the previous lecture that, graphene can act as the base material, from which the folding can happen to realize either a buckyball or a single wall nanotube.

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Nobel Prize in Physics 2010

Andre Geim
Born: 1958, Sochi, Russia
Affiliation at the time of the award: University of Manchester, Manchester, United Kingdom
Prize motivation: "for groundbreaking experiments regarding the two-dimensional material graphene"

Konstantin Novoselov
Born: 1974, Nizhny Tagil, Russia
Affiliation at the time of the award: University of Manchester, Manchester, United Kingdom
Prize motivation: "for groundbreaking experiments regarding the two-dimensional material graphene"

So, just to highlight the importance, it was these two gentlemen who really did a pioneering work in getting graphene into prominence. And this is again a serendipity, because they gambled with the unusual ideas, so these two gentlemen, both of them are Russians by birth, but they both served as professors in the University of Manchester. Professor Andre Geim and professor Novoselov and both of them tried very unusual way of getting this graphenes to picture and this is what we would see for the next few slides.

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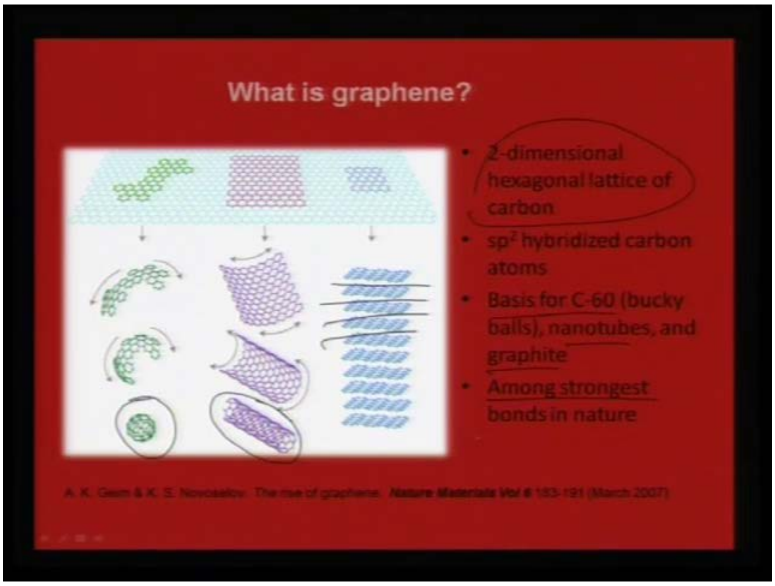

What is graphene?

- 2-dimensional hexagonal lattice of carbon
- sp^2 hybridized carbon atoms
- Basis for C-60 (bucky balls), nanotubes, and graphite
- Among strongest bonds in nature

A. K. Geim & K. S. Novoselov. The rise of graphene. **Nature Materials Vol 6** 183-191 (March 2007)

What is this graphene, the graphene as we pointed out, this is a two dimensional hexagonal lattice, from where we can either achieve this or this or we can actually get these layers of graphene. And this is the basis for C 60 for nanotubes and for graphite and among strongest bond in nature.

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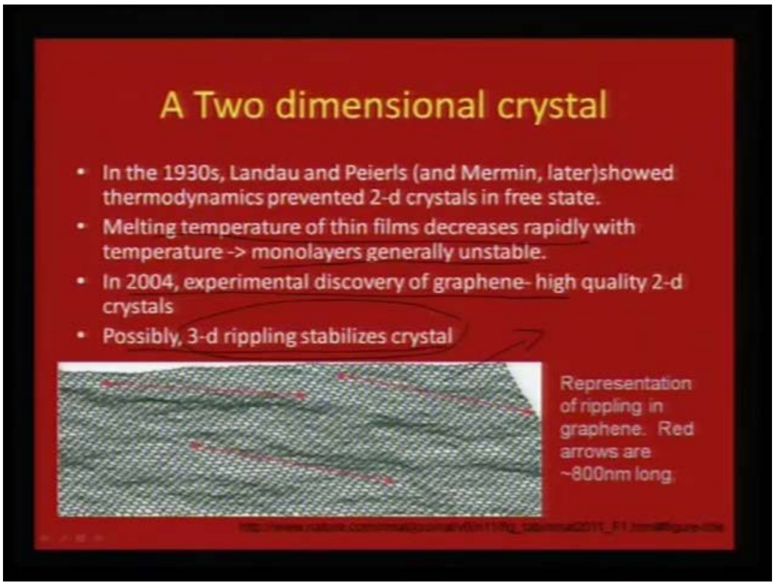

A Two dimensional crystal

- In the 1930s, Landau and Peierls (and Mermin, later)showed thermodynamics prevented 2-d crystals in free state.
- Melting temperature of thin films decreases rapidly with temperature -> monolayers generally unstable.
- In 2004, experimental discovery of graphene- high quality 2-d crystals
- Possibly, 3-d rippling stabilizes crystal

Representation of rippling in graphene. Red arrows are ~800nm long.

And if you really map this two dimensional crystal, you would find, that the melting temperature of thin films decreases rapidly with temperature. And therefore, monolayers generally are unstable, but in 2004, experimental discovery of graphene shows high quality 2 D crystals and this seems to be coming possibly, because of the 3 D rippling, which stabilizes the crystal. And if you actually find out, the representation of this graphene can even extent to 800 nanometres long. So, you can make such long stretches of graphene and the main reason why it stabilizes is, because of the 3 D rippling, which stabilizes a two dimensional platform.

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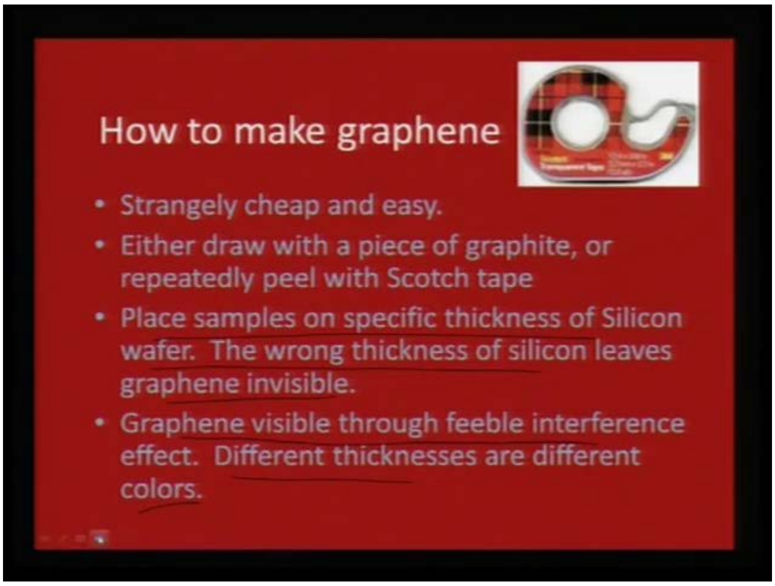

How to make graphene

- Strangely cheap and easy.
- Either draw with a piece of graphite, or repeatedly peel with Scotch tape
- Place samples on specific thickness of Silicon wafer. The wrong thickness of silicon leaves graphene invisible.
- Graphene visible through feeble interference effect. Different thicknesses are different colors.

How to make this graphene and this is how, the discovery of graphene emerged, strangely cheap and a easy. We can draw with a piece of graphite or repeatedly peel it of with the scotch tape and that is the first experiment, that was conducted by these two gentlemen. They just used a scotch tape, put in on graphite and keep on peeling it and what comes out is nothing but a two dimensional graphite. And it was almost thought, graphite cannot be broken up to such a measure and growing a two dimensional carbon was impossible, but this turned out to be the most simplest way, they could engineer.

So, place samples on specific thickness on silicon wafer, the wrong thicknesses as of silicon leaves graphene invisible and graphene visible through feeble interference effect, different thicknesses are of different colours. So, we can easily map from SEM, what is the thickness of the graphene layer that you have. Now, we can map it using optical microscope for a quick analysis, SEM and AFM can give you a proper idea.

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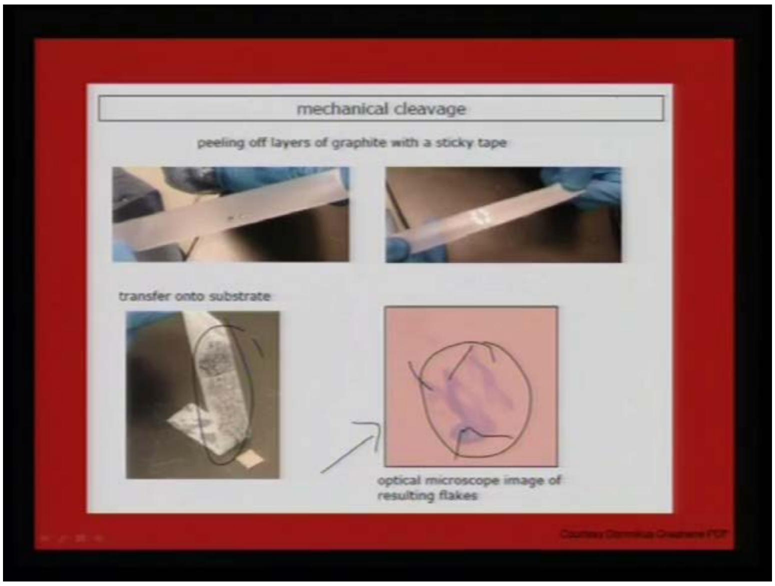

mechanical cleavage

peeling off layers of graphite with a sticky tape

transfer onto substrate

optical microscope image of resulting flakes

As you can see here, optical microscopy image of a resulting flake, which you can take from a sticky tape and then put in on graphite. Then whatever you peel it, would actually come out like a thick residue, which is sticking to the tape. And then you can actually put it back into a mica sheet or glass sheet, which will give you a thin film of graphene. So, we can actually use this graphene as metallic contact, in case if you want to study any electrical studies of some other metal.

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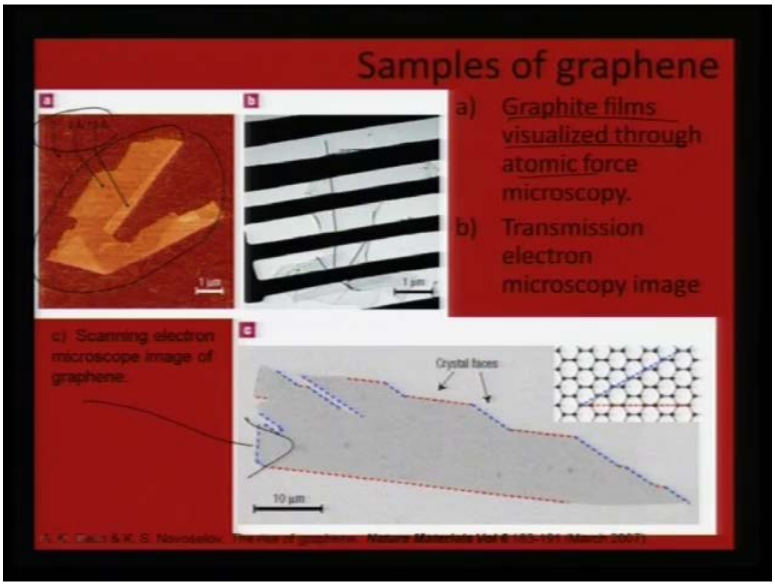

Samples of graphene

a) Graphite films visualized through atomic force microscopy.

b) Transmission electron microscopy image

c) Scanning electron microscope image of graphene.

A. K. Geim & K. S. Novoselov. The rise of graphene. Nature Materials Vol 6 183-191 (March 2007)

So, the graphene films are actually visualised by atomic force microscope and this is the way, it has been done. And as you could see here, the thickness of this graphene can be mapped using AFM and this is the TEM study, which clearly shows patches of graphene here. And here is the SEM micrograph of a graphene, which shows all the crystal phases of this film that is present, so it is possible to easily calibrate the thickness of graphite.

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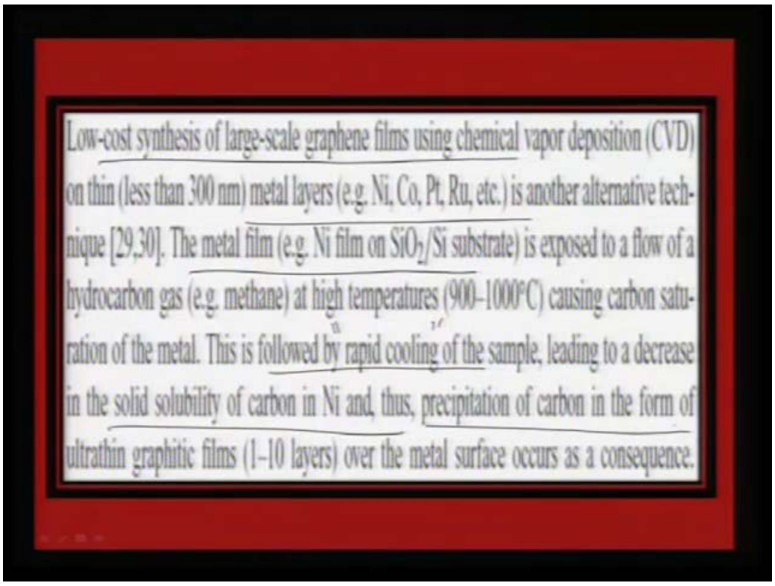

Low-cost synthesis of large-scale graphene films using chemical vapor deposition (CVD) on thin (less than 300 nm) metal layers (e.g. Ni, Co, Pt, Ru, etc.) is another alternative technique [29,30]. The metal film (e.g. Ni film on SiO_2/Si substrate) is exposed to a flow of a hydrocarbon gas (e.g. methane) at high temperatures (900–1000°C) causing carbon saturation of the metal. This is followed by rapid cooling of the sample, leading to a decrease in the solid solubility of carbon in Ni and, thus, precipitation of carbon in the form of ultrathin graphitic films (1–10 layers) over the metal surface occurs as a consequence.

Just one more mention of how we can make this graphenes, low cost synthesis of large scale graphenes can be attempted using chemical vapor deposition. And metal layers like nickel, cobalt, platinum, ruthenium is another alternative technique that can be employed. Metal films example, nickel on silica silicon dioxide is exposed to a flow of hydrocarbon gas, usually it is methane at high temperatures causing the carbon saturation of the metal, this is followed by rapid cooling.

This is the trick we need to adopt, not just heating, but once you do a rapid cooling here of the sample then there is a decrease in the solubility of carbon in nickel, which will come out as a graphene sheet. So, it is actually a precipitation process of carbon in the form of ultrathin graphitic sheets, which is nothing but your graphene layers. So, this is the way to realize using chemical vapor deposition.

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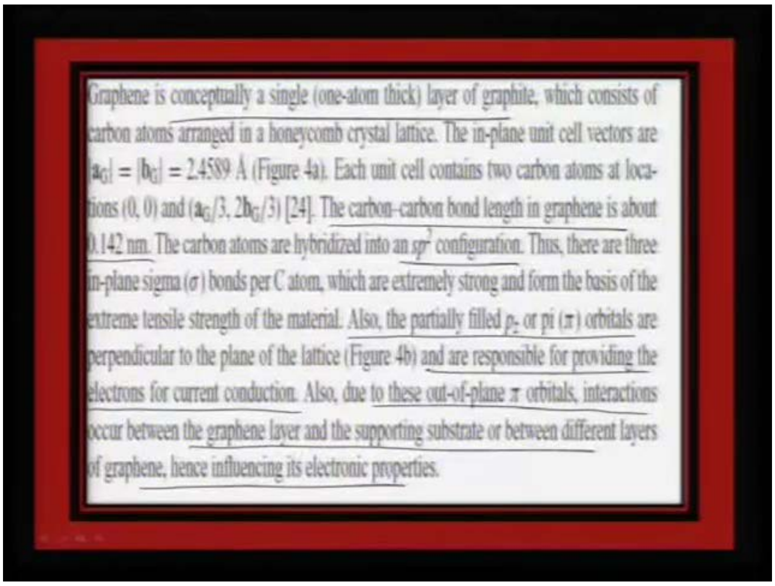

Graphene is conceptually a single (one-atom thick) layer of graphite, which consists of carbon atoms arranged in a honeycomb crystal lattice. The in-plane unit cell vectors are $|\mathbf{a}_G| = |\mathbf{b}_G| = 2.4589$ Å (Figure 4a). Each unit cell contains two carbon atoms at locations (0, 0) and ($\mathbf{a}_G/3$, $2\mathbf{b}_G/3$) [24]. The carbon–carbon bond length in graphene is about 0.142 nm. The carbon atoms are hybridized into an sp^2 configuration. Thus, there are three in-plane sigma (σ) bonds per C atom, which are extremely strong and form the basis of the extreme tensile strength of the material. Also, the partially filled p_z or pi (π) orbitals are perpendicular to the plane of the lattice (Figure 4b) and are responsible for providing the electrons for current conduction. Also, due to these out-of-plane π orbitals, interactions occur between the graphene layer and the supporting substrate or between different layers of graphene, hence influencing its electronic properties.

Graphene is actually a single layer of graphite, as we have seen and the carbon carbon bond in graphene is typically of this order and it is s p 2 hybridized. Actually if you see, we have partially filled p z or p pi orbitals, which are perpendicular to the plane of the lattice and these are responsible for providing electrons for conduction. So, it is more like a benzene ring, where your pi orbitals are perpendicular to the plane and your sigma orbitals stabilize the bonding.

And therefore, due to this out of plane orbitals, interaction between graphene layers and supporting substrates or between different layers, also influence the electronic properties. So, this is the way, we can try to engineer, the pi orbitals are the ones, which are responsible for any interaction with the substrates. So, this gives also a very good glue or adhesive property for the graphene to stick to a particular substrate.

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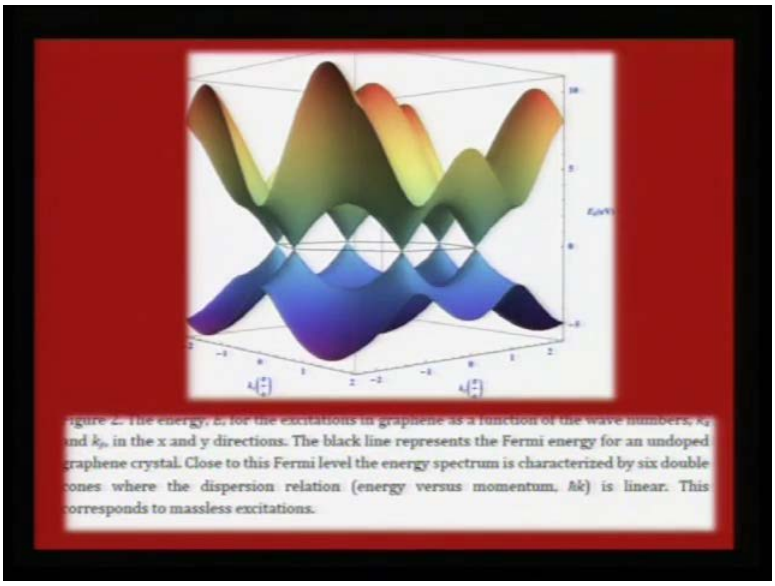

igure 2. The energy, E, for the excitations in graphene as a function of the wave numbers, k_x nd k_y, in the x and y directions. The black line represents the Fermi energy for an undoped raphene crystal. Close to this Fermi level the energy spectrum is characterized by six double ones where the dispersion relation (energy versus momentum, $\hbar k$) is linear. This orresponds to massless excitations.

When we look at the Fermi surface of this graphenes, this gives another different dimension to the understanding of electronic properties, because this is a two dimensional graphene. Therefore, the way the electronic property is defined in graphene is completely different from that of a 3 D metal. And as you would see, the Fermi surface of graphene, the plot of E K versus K, which is nothing but your wave numbers, gives us a different contour for your brillouin zone.

What you see here is the Fermi surface here, which is denoted by this black circle and against a conventional system, which is confined in 2 D dimension. Here we see, that there are 6 double cones and this is a hexagonal brillouin zone, which is mapped and this is your conduction band and this is your valence band. And they are actually separated by these six points and because of this, there is a linear behaviour between the E and K parameter. And therefore, both the electrons and holes at this point will have a zero effective mass, and therefore these points are actually called as Dirac points, because they behave like Dirac fermions having a spin of half.

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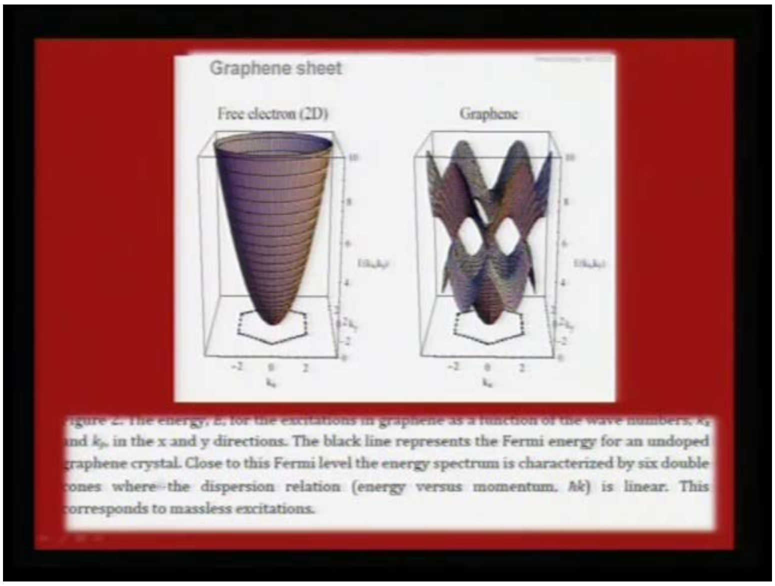

Graphene sheet

igure 2. The energy, E, for the excitations in graphene as a function of the wave numbers, k_x nd k_y, in the x and y directions. The black line represents the Fermi energy for an undoped raphene crystal. Close to this Fermi level the energy spectrum is characterized by six double ones where the dispersion relation (energy versus momentum, $\hbar k$) is linear. This orresponds to massless excitations.

And if you look at the typical 2 D surface of a material, which is confined in two dimensional space, this is how it should look like. But, for graphene, you have a very different brillouin zone, that accounts for the conductivity of this graphene sheets.

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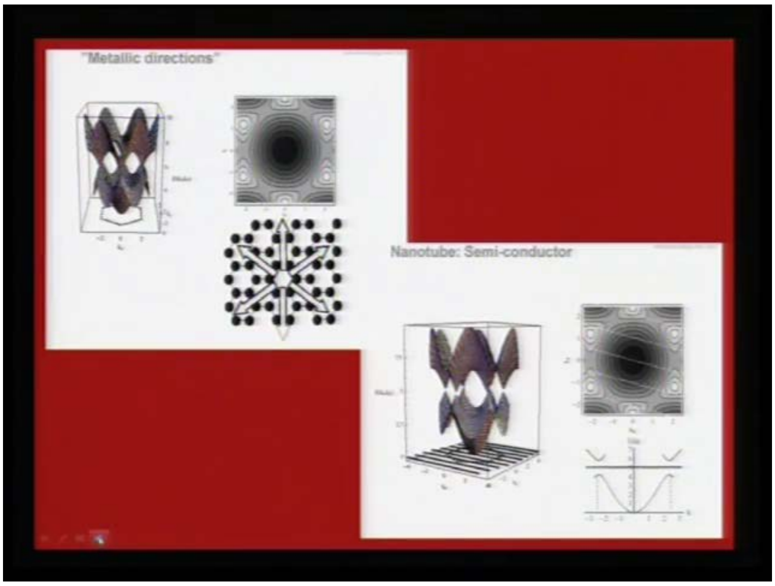

"Metallic directions"

Nanotube: Semi-conductor

So, if you take the metallic directions and you try to map it, these are the six metallic directions, in which the electrical conductivity is confined. And in case of semiconductor carbon nanotubes or the graphene sheets, you see an opening of this band gap coming across the Fermi surface between the valence and the conduction band.

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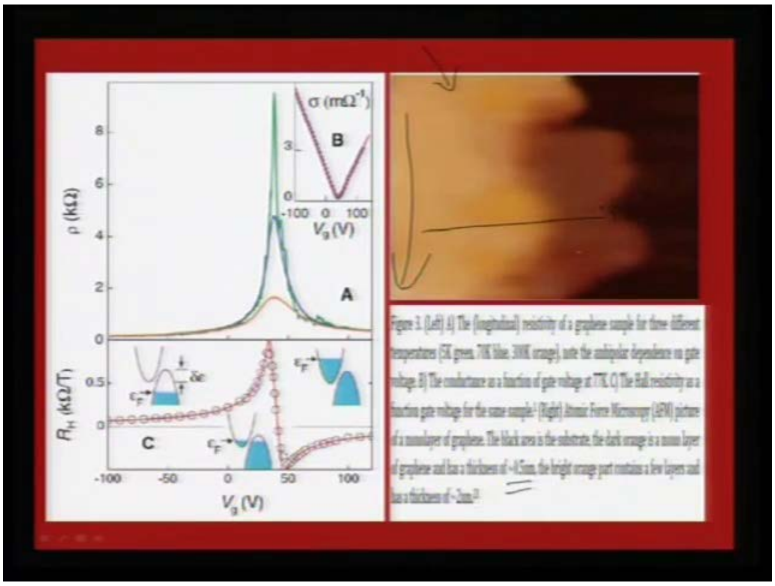

And typically if you map your resistivity as a function of gate voltage, you would see a very different picture compared to the other metals. So, if you make a plot of resistance as a function of gate voltage, you would see, this is mostly a ambipolar dependence that is observed for the gate voltage. Because, you can see the shift here towards one direction and this is for varying temperatures from 5 K to 300 K, you can see that there is a very clearer response for this graphene sheets against the gate voltage.

And also, the plot of this conductivity as a function of gate voltage, shows this ambi polar property and the hall measurement also gives the same feature, as that of the resistance. On the right side map, you have the AFM picture, which talks about the thickness that we can achieve in such samples. The lighter region what you see here, is nothing but the thinnest pass, which is roughly of 0.5 nanometre. And as you go towards the substrate, you can see that, it is varying from 0.5 to 2 nanometre.

When we consider the strength of graphene, it is much more interesting to observe, that the graphene can be more stronger than even steel, the stronger steel. Because, the strength is measured to be 42 Newton per metre and if you actually take 1 meter square of steel and try to calculate the breaking strength, it will only amount to 0.084 Newton per meter. Therefore, between graphene sheet and the steel, there is a tremendous increase in the mechanical strength.

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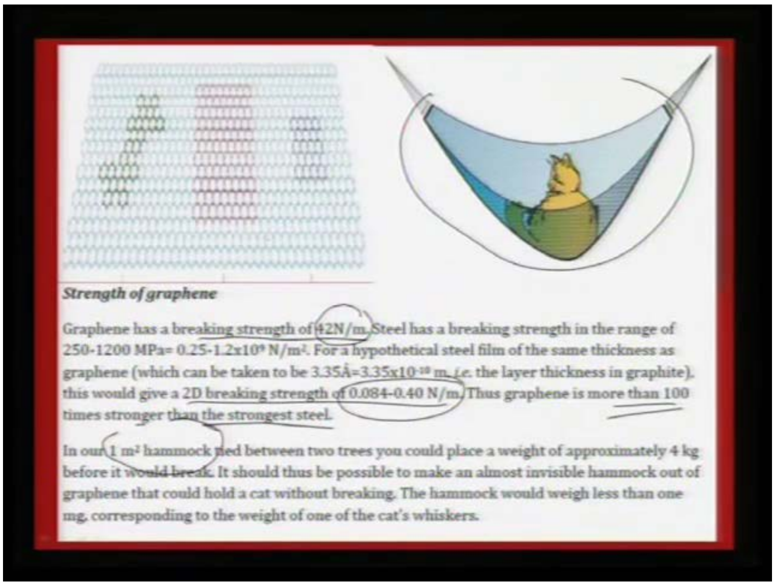

Strength of graphene

Graphene has a breaking strength of 42N/m. Steel has a breaking strength in the range of 250-1200 MPa= 0.25-1.2x10^9 N/m^2. For a hypothetical steel film of the same thickness as graphene (which can be taken to be 3.35Å=3.35x10^{-10} m, *i.e.* the layer thickness in graphite), this would give a 2D breaking strength of 0.084-0.40 N/m. Thus graphene is more than 100 times stronger than the strongest steel.

In our 1 m^2 hammock tied between two trees you could place a weight of approximately 4 kg before it would break. It should thus be possible to make an almost invisible hammock out of graphene that could hold a cat without breaking. The hammock would weigh less than one mg, corresponding to the weight of one of the cat's whiskers.

So, if you are actually going to spread 1 metre square of hammock like this, this is your hammock and if you are going to spread for 1 metre square, actually graphene sheet can take load up to 4 kg like putting a cat inside this hammock, so that much of strength can be derived out of graphenes.

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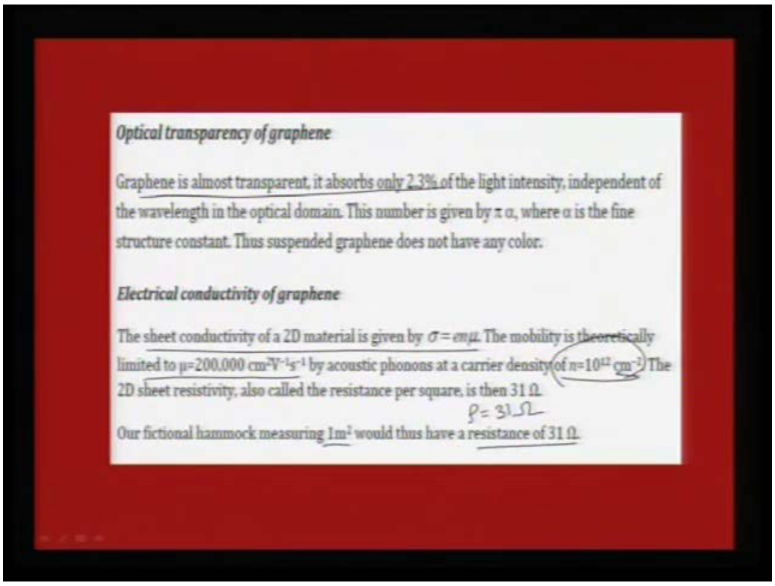

Optical transparency of graphene

Graphene is almost transparent, it absorbs only 2.3% of the light intensity, independent of the wavelength in the optical domain. This number is given by $\pi\alpha$, where α is the fine structure constant. Thus suspended graphene does not have any color.

Electrical conductivity of graphene

The sheet conductivity of a 2D material is given by $\sigma = en\mu$. The mobility is theoretically limited to μ=200,000 $cm^2V^{-1}s^{-1}$ by acoustic phonons at a carrier density of $n=10^{12}$ cm^{-2}. The 2D sheet resistivity, also called the resistance per square, is then 31 Ω.

$\rho = 31\,\Omega$

Our fictional hammock measuring 1m^2 would thus have a resistance of 31 Ω.

And therefore, it can be used for many mechanical applications, in terms of optical transparency it absorbs only 2.3 percent of light intensity. Therefore, a thinner graphene sheet say, 1 or 2 layers of graphene, almost will give you 90 percent transmittance, so it can be used as a transparent electrode also. The electrical resistivity of graphene is given by this form, sigma is equal to e n mu. If your charged carrier density, which is unusually large, which we can measure from hall resistance, your n is of the order of 10 power 12 centimetre square and the mu that is, your mobility is very huge. So, if you compare that and try to calculate your resistance, resistance comes to be around 31 Ohms. And for a hammock measuring 1 metre square that we showed, the resistance will typically be of 31 Ohm, which is very very less.

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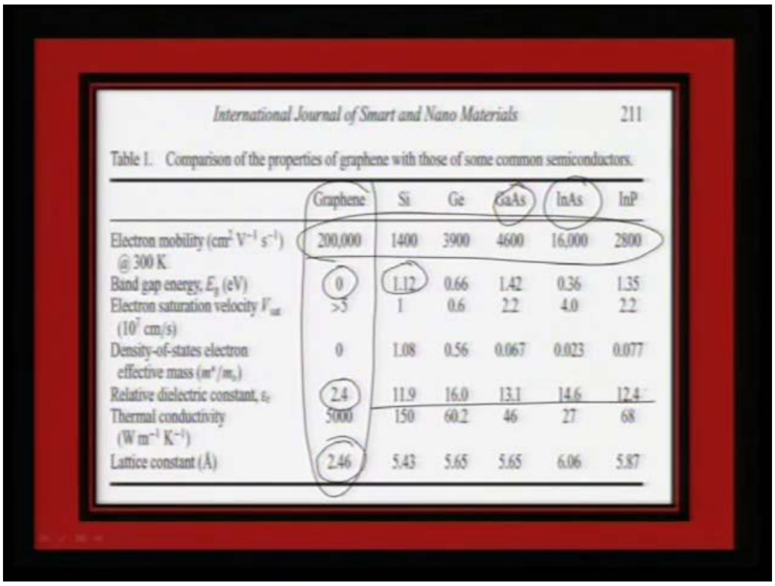

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Table 1. Comparison of the properties of graphene with those of some common semiconductors.

	Graphene	Si	Ge	GaAs	InAs	InP
Electron mobility ($cm^2 V^{-1} s^{-1}$) @ 300 K	200,000	1400	3900	4600	16,000	2800
Band gap energy, E_g (eV)	0	1.12	0.66	1.42	0.36	1.35
Electron saturation velocity V_{sat} (10^7 cm/s)	>5	1	0.6	2.2	4.0	2.2
Density-of-states electron effective mass (m^*/m_e)	0	1.08	0.56	0.067	0.023	0.077
Relative dielectric constant, ε_r	2.4	11.9	16.0	13.1	14.6	12.4
Thermal conductivity ($W m^{-1} K^{-1}$)	5000	150	60.2	46	27	68
Lattice constant (Å)	2.46	5.43	5.65	5.65	6.06	5.87

And therefore, if you make a comparison between graphene and other semiconductors like silicon or germanium or gallium arsenide, you can see here, that band gap is nearly a semimetal and compared to silicon. But, the point that we need to note here is, electron mobility is unusually very very high, and therefore this can find use in many of the applications compared to traditional semiconductors. As of now, the most preferred one for semiconductor applications is indium arsenide, because the mobility values are of the order of 16000.

But, the graphene mobility seems to even surpass indium arsenide and this also has a very low lattice constant. The dielectric constant also is very very low compared to any of the other semiconducting materials. And therefore, this makes it a very good candidate for semiconductor applications as well.

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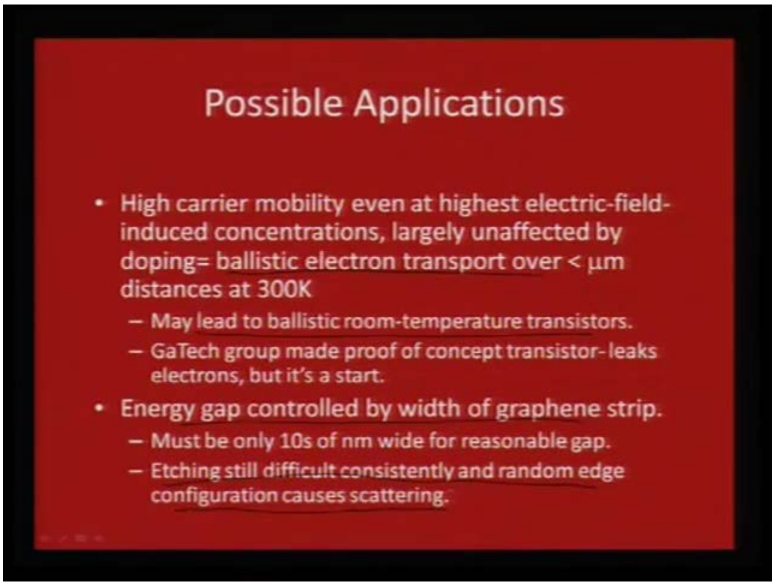

Possible Applications

- High carrier mobility even at highest electric-field-induced concentrations, largely unaffected by doping= ballistic electron transport over < μm distances at 300K
  - May lead to ballistic room-temperature transistors.
  - GaTech group made proof of concept transistor- leaks electrons, but it's a start.
- Energy gap controlled by width of graphene strip.
  - Must be only 10s of nm wide for reasonable gap.
  - Etching still difficult consistently and random edge configuration causes scattering.

So, what are the possible applications, high carrier mobility even at highest electric field, they largely are unaffected by doping, and therefore we can actually go for a ballistic electron transport over less than micron distances. And this can actually lead to applications in room temperature transistors and energy gap is actually controlled by width of the graphene strip. And therefore we can actually see, etching will be difficult consistently and random etch configuration causes the scattering, if you are going to modify the properties of the graphene strip.

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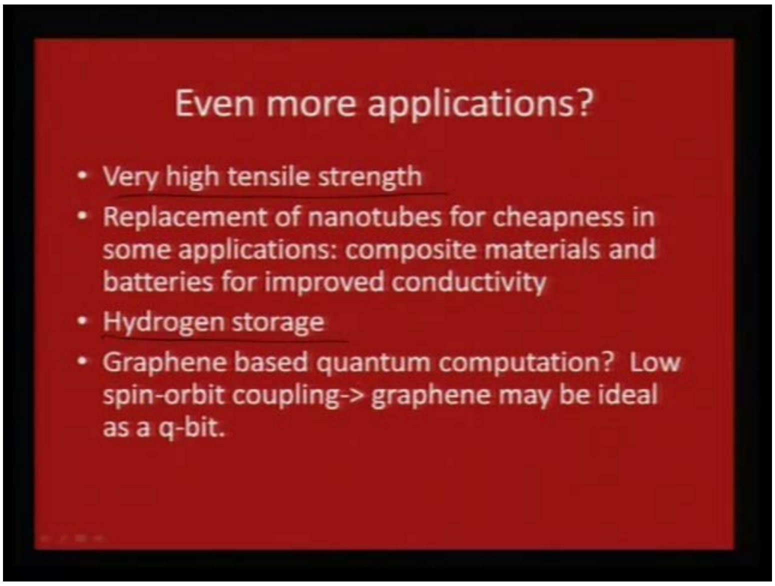

Even more applications?

- Very high tensile strength
- Replacement of nanotubes for cheapness in some applications: composite materials and batteries for improved conductivity
- Hydrogen storage
- Graphene based quantum computation? Low spin-orbit coupling-> graphene may be ideal as a q-bit.

In terms of other applications, we can look for very high tensile strength and hydrogen storage also has been noted to be remarkably high for graphenes. Graphene based quantum computation is another thing, which is being probed now. I will just take you through few applications, before I finish.

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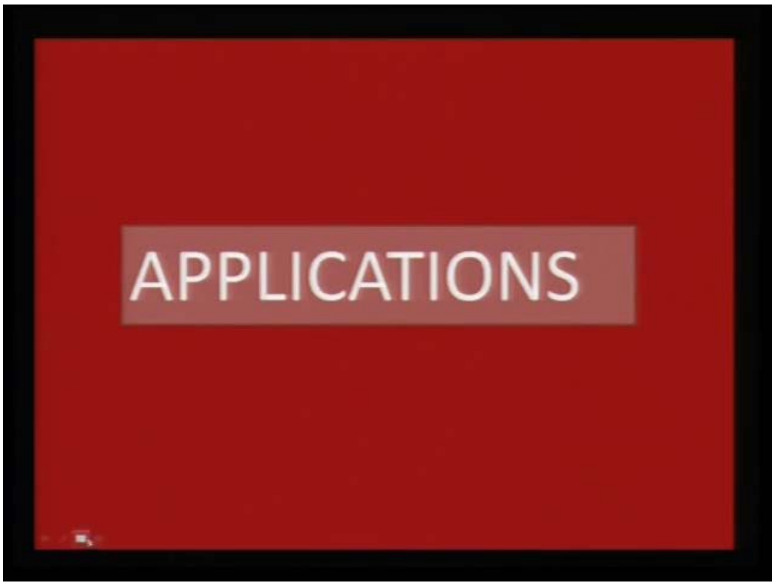

APPLICATIONS

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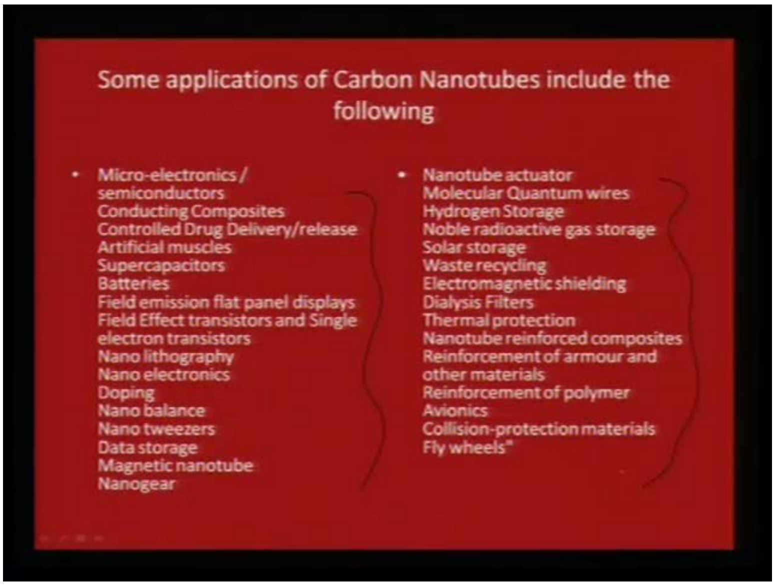

Some applications of Carbon Nanotubes include the following

- Micro-electronics / semiconductors
  Conducting Composites
  Controlled Drug Delivery/release
  Artificial muscles
  Supercapacitors
  Batteries
  Field emission flat panel displays
  Field Effect transistors and Single electron transistors
  Nano lithography
  Nano electronics
  Doping
  Nano balance
  Nano tweezers
  Data storage
  Magnetic nanotube
  Nanogear

- Nanotube actuator
  Molecular Quantum wires
  Hydrogen Storage
  Noble radioactive gas storage
  Solar storage
  Waste recycling
  Electromagnetic shielding
  Dialysis Filters
  Thermal protection
  Nanotube reinforced composites
  Reinforcement of armour and other materials
  Reinforcement of polymer
  Avionics
  Collision-protection materials
  Fly wheels"

Generally, for this carbon nanotubes and graphene and fullerenes, the spectrum of application is very wide. Carbon nanotubes in particular, has already been applied in all this areas, so I may not be able to run through all the applications. But, you can see here, it is from electronics to biological applications to magnetic storage, and also in several of our household applications, this has found a very useful candidate.

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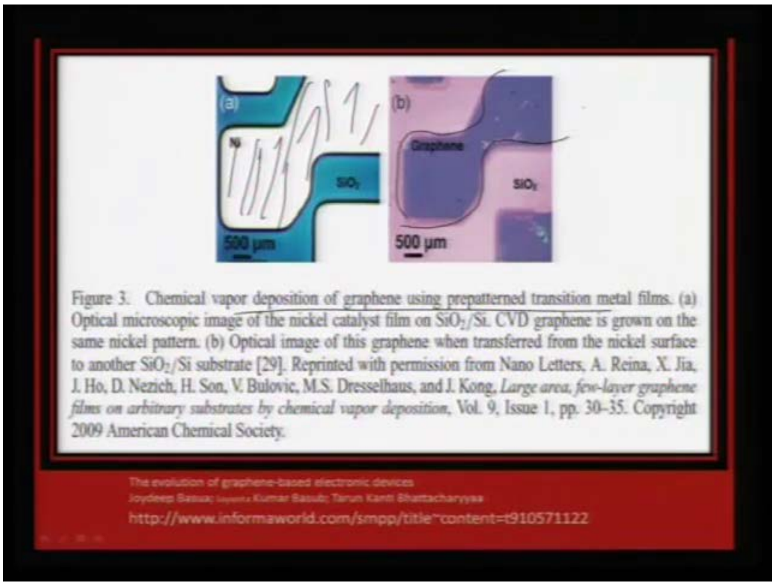

Figure 3. Chemical vapor deposition of graphene using prepatterned transition metal films. (a) Optical microscopic image of the nickel catalyst film on SiO$_2$/Si. CVD graphene is grown on the same nickel pattern. (b) Optical image of this graphene when transferred from the nickel surface to another SiO$_2$/Si substrate [29]. Reprinted with permission from Nano Letters, A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M.S. Dresselhaus, and J. Kong, *Large area, few-layer graphene films on arbitrary substrates by chemical vapor deposition*, Vol. 9, Issue 1, pp. 30–35. Copyright 2009 American Chemical Society.

The evolution of graphene-based electronic devices
Joydeep Basu; Jayanta Kumar Basu; Tarun Kanti Bhattacharyya
http://www.informaworld.com/smpp/title~content=t910571122

For example, when we try to pattern or make graphene sheets, it is easily possible to make a graphene sheet like this. If you pattern your nickel film of this form, we can selectively get a graphene sheet like this using a CVD process and this can be used for application, so patterning graphene sheets is not difficult.

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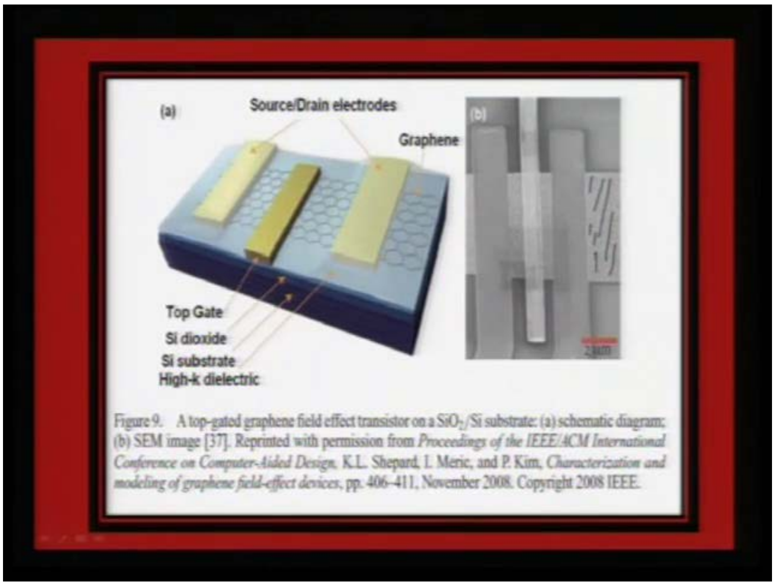

Figure 9. A top-gated graphene field effect transistor on a SiO$_2$/Si substrate: (a) schematic diagram; (b) SEM image [37]. Reprinted with permission from *Proceedings of the IEEE/ACM International Conference on Computer-Aided Design*, K.L. Shepard, I. Meric, and P. Kim, *Characterization and modeling of graphene field-effect devices*, pp. 406–411, November 2008. Copyright 2008 IEEE.

And graphene can also play as a very good metallic contact in transistors, field effect transistors. As you can see from this contour, you can easily make the graphite sheet, which is lying here. Graphenes can be made and then we can put a several electrodes for this transistor applications.

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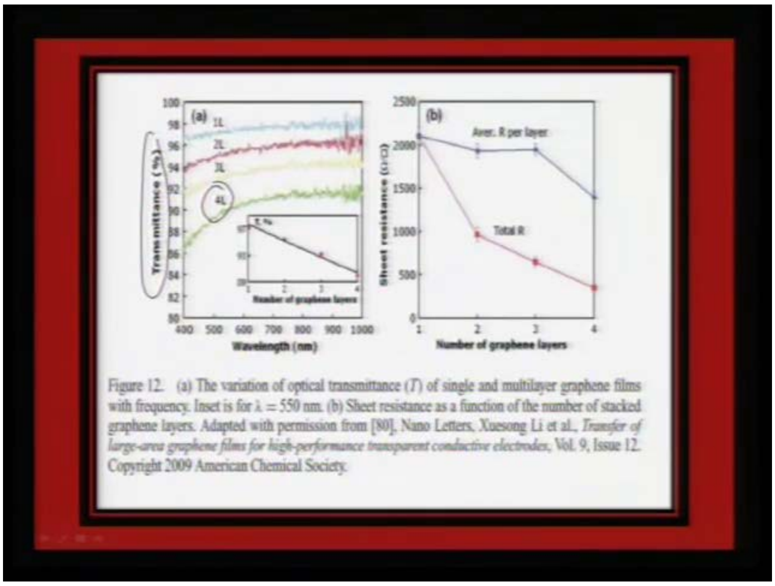

Figure 12. (a) The variation of optical transmittance (*T*) of single and multilayer graphene films with frequency. Inset is for $\lambda = 550$ nm. (b) Sheet resistance as a function of the number of stacked graphene layers. Adapted with permission from [80]. Nano Letters, Xuesong Li et al., *Transfer of large-area graphene films for high-performance transparent conductive electrodes*, Vol. 9, Issue 12. Copyright 2009 American Chemical Society.

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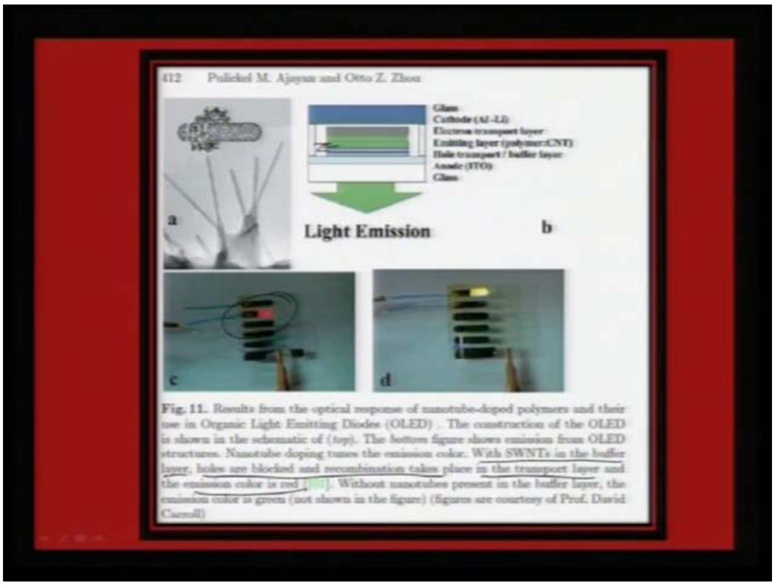
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Fig. 11. Results from the optical response of nanotube-doped polymers and their use in Organic Light Emitting Diodes (OLED) . The construction of the OLED is shown in the schematic of (top). The bottom figure shows emission from OLED structures. Nanotube doping tunes the emission color. With SWNTs in the buffer layer, holes are blocked and recombination takes place in the transport layer and the emission color is red [[illegible]]. Without nanotubes present in the buffer layer, the emission color is green (not shown in the figure) (figures are courtesy of Prof. David Carroll)

And as I pointed out to you, depending on the layer thickness, if it is one layer of graphene sheet then the optical properties are going to be very high of the order of 98 percent. But, if you are going to make a thicker graphene sheet then you can easily calibrate using the optical transmittance, it will fall down and therefore, we can have a precise control over that.

And it is also reported in OLEDs, if you are going to use carbon nanotubes then we can actually use this for tuning the colors. For example, if you put a single walled nanotubes in buffer layers here, which is in between, if you put buffer layers, holes are actually blocked and recombination takes place in the transport layer. And you can get selectively a red, but if you are not going to put carbon nanotubes then the emission will be green. So, this is mainly meant for modulating the charge carrier transport, and therefore the combination of the excitons can be mapped to come either in the transport layer or towards the conducting layer. So, you can actually fine tune the light emission by adding carbon nanotubes in OLEDs.

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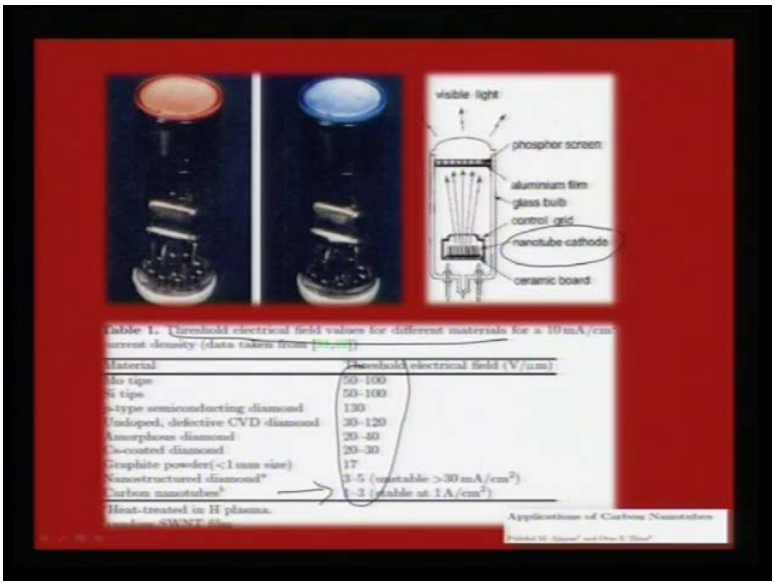

able 1. Threshold electrical field values for different materials for a 10 mA/cm
urrent density (data taken from [illegible])

Material	Threshold electrical field (V/μm)
Mo tips	50–100
Si tips	50–100
-type semiconducting diamond	130
Undoped, defective CVD diamond	30–120
Amorphous diamond	20–40
Cs-coated diamond	20–30
Graphite powder(<1 mm size)	17
Nanostructured diamond^a	3–5 (unstable >30 mA/cm^2)
Carbon nanotubes^b	1–3 (stable at 1 A/cm^2)

Heat-treated in H plasma.

Applications of Carbon Nanotubes

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Here also, nanotubes cathodes can be used for getting preferred colors and you can also see, that the threshold electric field for different materials are given. And carbon nanotubes seems to have a very low threshold electric field, therefore you can use this for display applications. And already a carbon nanotubes cathode has been experimented, which gives very sharp color feature.

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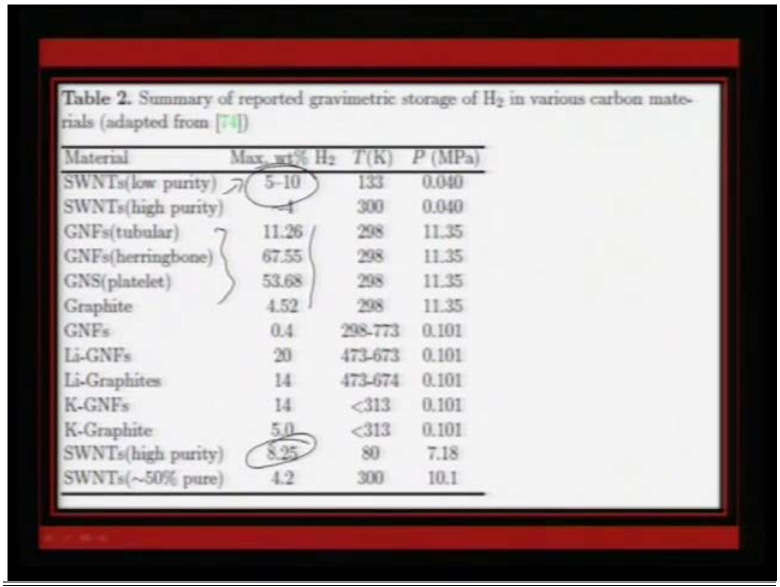

Table 2. Summary of reported gravimetric storage of H_2 in various carbon materials (adapted from [74])

Material	Max. wt% H_2	T(K)	P (MPa)
SWNTs(low purity)	5-10	133	0.040
SWNTs(high purity)	~4	300	0.040
GNFs(tubular)	11.26	298	11.35
GNFs(herringbone)	67.55	298	11.35
GNS(platelet)	53.68	298	11.35
Graphite	4.52	298	11.35
GNFs	0.4	298-773	0.101
Li-GNFs	20	473-673	0.101
Li-Graphites	14	473-674	0.101
K-GNFs	14	<313	0.101
K-Graphite	5.0	<313	0.101
SWNTs(high purity)	8.25	80	7.18
SWNTs(~50% pure)	4.2	300	10.1

And in hydrogen storage, carbon nanotubes, carbon materials have been explored. You can see, the single walled nanotubes with lowest purity giving hydrogen storage capability of 5 to 10 percent, those which are currently being used of this graphitic nanofibres and those are actually having a very high hydrogen storage capacity. But, single walled nanotubes also seem to have a appreciable amount of hydrogen storage and this is still being improvised for practical applications.

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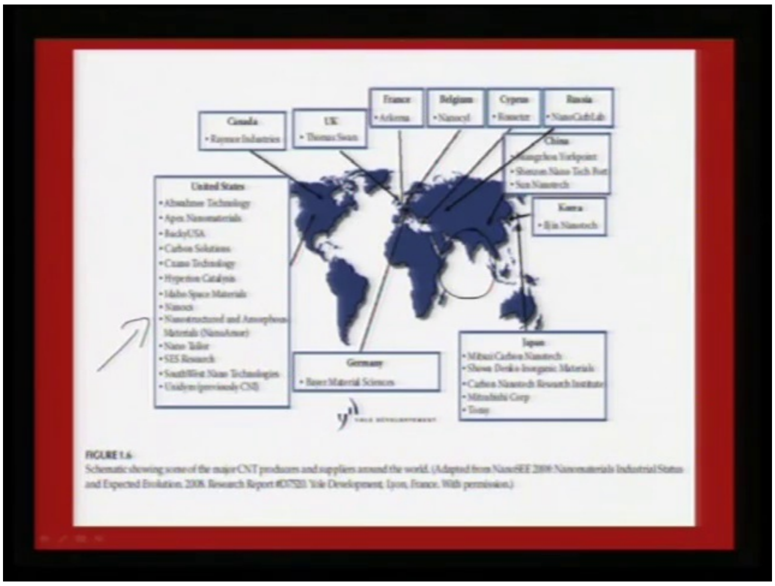

FIGURE 1.6
Schematic showing some of the major CNT producers and suppliers around the world. (Adapted from NanoSEE 2009 Nanomaterials Industrial Status and Expected Evolution. 2008. Research Report #D7520. Yole Development, Lyon, France. With permission.)

Lastly I just want to tell you that, this is not only a research effort, but this is become a business venture, as of now. And throughout the globe, we see many companies have started producing in larger scale and there is lot of activity. As you would map here, many companies are from US, which are already producing carbon nanotubes in a preferred way. And there are several activities going on in Europe, we also have isolated activities in South East Asia.

We do not have much activity both in South America, Africa and also in India, we do not have any carbon nanotube producing companies per se. But, the way the companies have evolved, this gives us a glimpse of, what is in store and therefore many things are going to happen.

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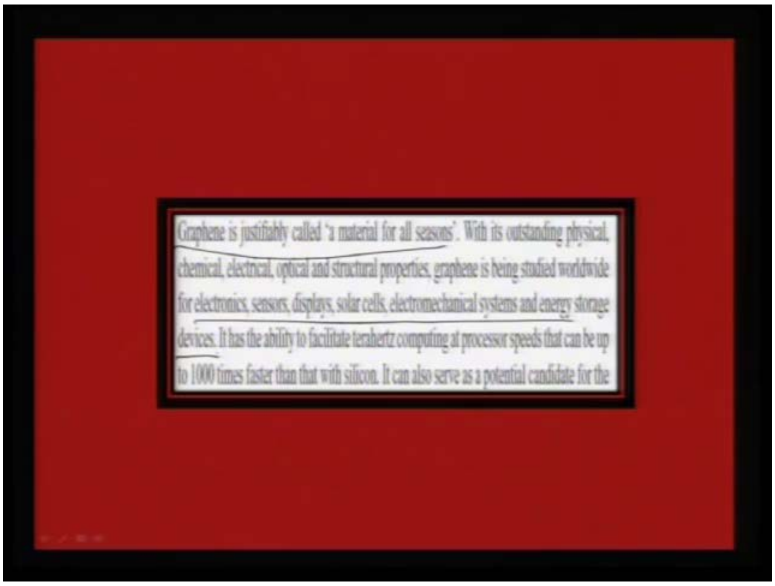

Graphene is justifiably called 'a material for all seasons'. With its outstanding physical, chemical, electrical, optical and structural properties, graphene is being studied worldwide for electronics, sensors, displays, solar cells, electromechanical systems and energy storage devices. It has the ability to facilitate terahertz computing at processor speeds that can be up to 1000 times faster than that with silicon. It can also serve as a potential candidate for the

And just to conclude, as I have already mentioned about graphene, graphene seems to be the basic material for all seasons. And if we can study further, get more insights onto the chemistry or the physics of graphene then more and more novel properties will generate. And this will have outstanding physical, chemical, electrical, optical and structural properties and for sure, these are going to find more applications in the days to come, in field of displays, solar cells and energy storage devices.

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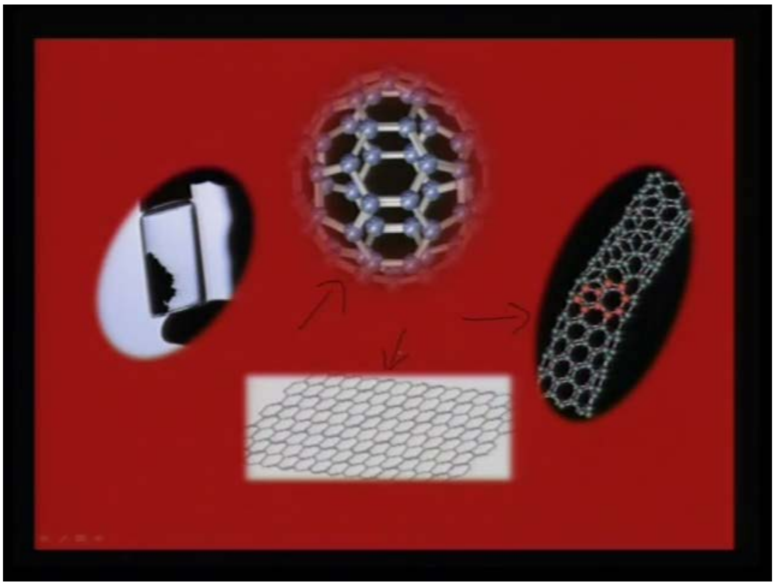

So, to conclude, we have actually seen three forms of carbon namely, buckyball then one dimensional carbon nanotube and also two dimensional graphene sheets.

Thank you.