Nanoelectronics: Devices and Materials
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Lecture – 39
Carbon Nanostructures and CVD

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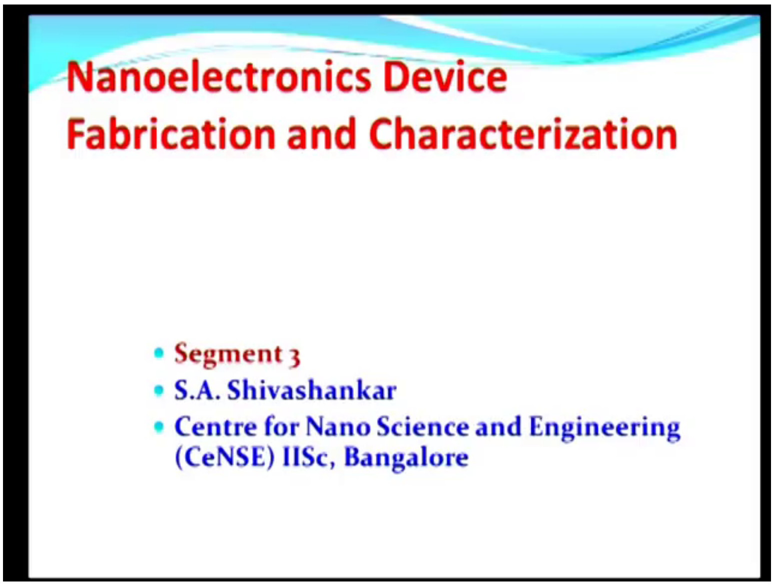

Nanoelectronics Device Fabrication and Characterization

- Segment 3
- S.A. Shivashankar
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Hello, again this is the next session of the course on Nanoelectronic Device Fabrication and Characterization and we have been discussing nano structures and deformation on nanostructures. And last time we went on to discuss the formation of nanowires by the vapor, liquid, solid method and followed by the solution, liquid, solid method. We also pointed out that there are variations of these methods that use for example, lasers to assist the formation of nanowires.

And then we went onto discuss the formation of nanowires and nano structures in general by the solution process where the assistance of microwave irradiation is used to obtain nano structures of high quality much more rapidly by the microwave assisted method done by other methods. What we shall do this time is to discuss some general aspects of nanomaterial preparation and then go on to nano carbon nanostructures and thin films we already discussed aspects of heterogeneous nucleation which is where they coming in the context of thin film deposition which are very important for nanotechnology in general device fabrication in particular.

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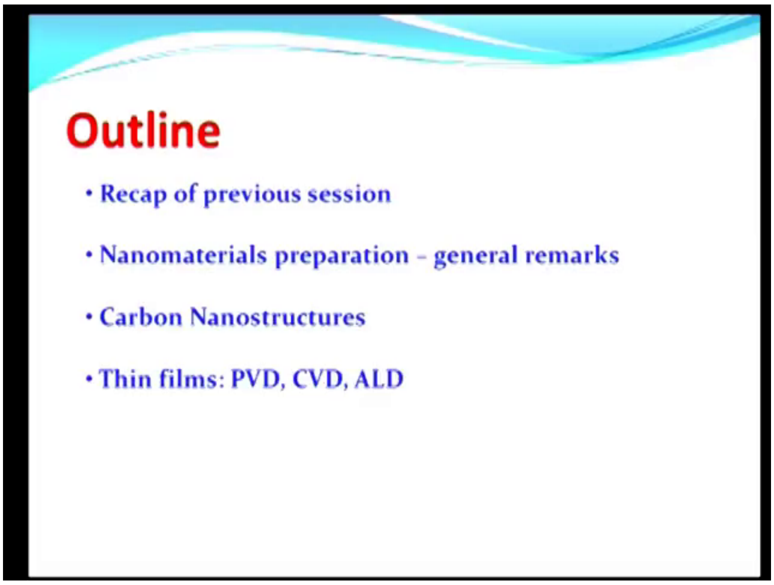

Outline

- Recap of previous session
- Nanomaterials preparation – general remarks
- Carbon Nanostructures
- Thin films: PVD, CVD, ALD

And then we will try to deal with the physical vapor deposition, chemical vapor deposition and atomic layer deposition.

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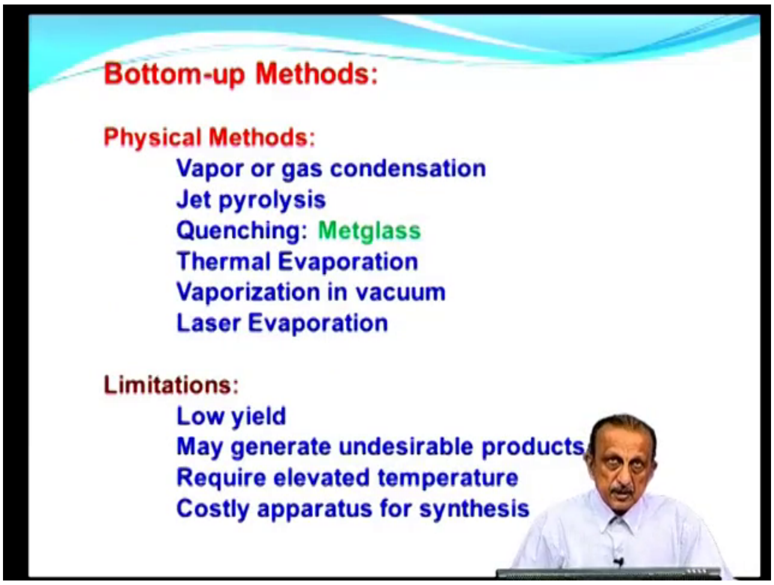

Bottom-up Methods:

Physical Methods:

- Vapor or gas condensation
- Jet pyrolysis
- Quenching: Metglass
- Thermal Evaporation
- Vaporization in vacuum
- Laser Evaporation

Limitations:

- Low yield
- May generate undesirable products
- Require elevated temperature
- Costly apparatus for synthesis

Now, some general comments we have discussed bottom-up methods and mostly so far we have confined ourselves to the discussion of different chemical methods that are bottom-up in their approach. It is useful to note that there are physical methods that are capable of producing nanoparticles and nanostructures as listed here. Vapor and gas condensation that is you have vapor, which generally involves high kinetic energies and therefore, correspondingly high temperatures and you suddenly subject them to a cooling condensation. And if you do not allow that condensation to take place or a relatively long period of time that is if you quench it then in the absence of time for these atoms in this condensate to relax into crystallographic position proper positions, you often get either nanocrystals very small crystals or you get amorphous material.

Jet pyrolysis is really much the same, you have jet a jet of particles moving at a high speed, which means high kinetic energy and high temperature, and then you suddenly cool it to obtain a condensate that will contain nano crystals or even amorphous materials as I just mentioned. The quenching of metal alloys to obtain glossy metallic materials known as metglass, which is actually an important part of technology for important part of materials technology that is a physical method where one obtains nanostructure material through quenching.

Thermal evaporation, we have discussed evaporation condensation. Again thermal evaporation of let us say metals or metal oxides or some such material in a vacuum system which is often the way to produce thin films of these materials. Suppose, you collect these evaporants including metals on a cold substrates, normally this is done on substrates that is at room temperature in a high vacuum on evaporates material and collects it on a substrate often held at room temperature. But suppose you deliberately cool the substrate then again these particles that are full of kinetic energy and therefore, correspondingly high temperature they get quenched and usually get thin films now with nano structured material.

Laser evaporation is also the same thing, lasers pump in a huge amount of energy into the target at which they are aimed, and therefore there is instantaneous evaporation of the top layer of the material when it is bombarded by the laser. And if one collects this material, and one collects it on a substrate that is not heated then once again one can get nanostructure material. Or even when it is heated by even the substrate on which this laser evaporated material is collected is heated even so it is possible to obtain nanostructure material. Indeed an important part of thin film technology a physical method of deposition of thin films known as pulsed laser deposition PLD is based on this laser evaporation technique.

Now, most of these techniques that are listed here except really that of the technology of metglass they are of low yield. So, you do not get much nanostructure material given the amount of material one starts with. They may require elevated temperature subsequently to obtain useful nanostructured material and often involve costly apparatus for synthesis. But all of these constitute physical methods that are bottom-up in nature. One of the things to remember which I am not sure that I alluded to earlier is that nano structured material nano crystalline material that is whether it is formed by a physical method or a chemical method as long as it is a bottom-up method as opposed to a top-down method. Where for example, one uses a ball milling to cut down material to very small sizes in such cases as we mentioned at that time defects are induced.

But if you consider nanocrystals of dimensions of the order of a few nanometers produced by let us say the solution based methods as in the case of metals or in the case of compound semiconductors the sol gel method and so on which we refer to or even the microwave assisted solution based processing. In all these methods, the crystals that are produced or of very high quality which means technically that they have a low density of defects. And that is in a way natural if you think about how atoms are progressively assembled into a periodic array.

If the array is large very large let us say you are talking about a crystal of the order of a you know let us say centimeter in size containing Avogadro number of atoms then as the assembly process proceeds as the atoms come together to form such a macroscopic crystal the chances of defect formation such as dislocations that is atoms in the wrong place wrong crystallographic phase. So, the chances of defect formation are increased when the total number of atoms that are assembled together is increased. So, in a crystal that has around the Avogadro number of atoms then naturally the chances of formation of defects is much greater than in the case of a nano crystal which might have let us say 10,000 or 50,000 atoms. So, in general given the scale of these crystals they have few defects much fewer. Therefore, nano crystals are generally more perfect than macroscopic crystals of the same material and that is important to keep in mind because it has consequences, we will come back to that.

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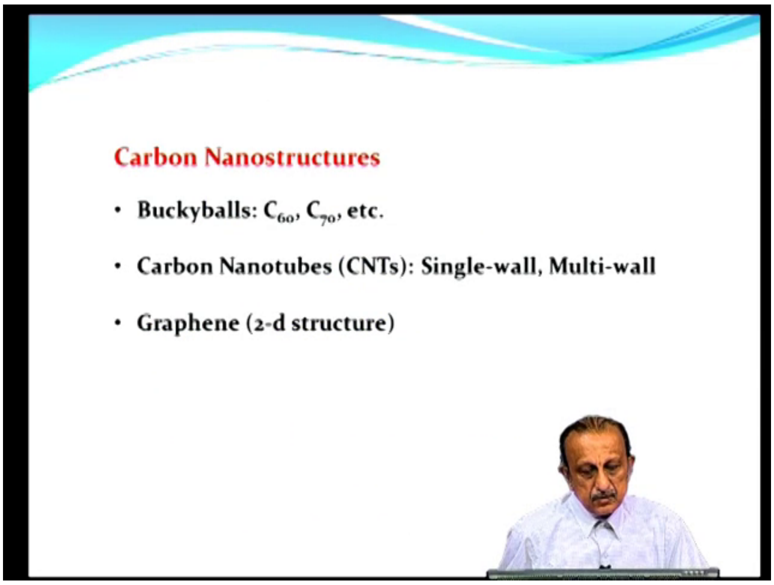

Carbon Nanostructures

- Buckyballs: C_{60}, C_{70}, etc.
- Carbon Nanotubes (CNTs): Single-wall, Multi-wall
- Graphene (2-d structure)

We come to carbon nanostructures. Carbon is a truly unique material as you know in terms of its chemical reactivity and ability to form compounds with virtually every element on the periodic table even. So, it has been even though it has been known for a very long time carbon has really thrown as surprises in the recent decades with the discovery of buckyballs, carbon 60, carbon 70, carbon 80 and so on. Carbon nanotubes soon thereafter and more recently the discovery of graphene a truly two-dimensional carbon structure. All of these are showing up to be very important technologically and certainly of course, there is been a very considerable amount of new science that has come out of these carbon structures, carbon nanostructures.

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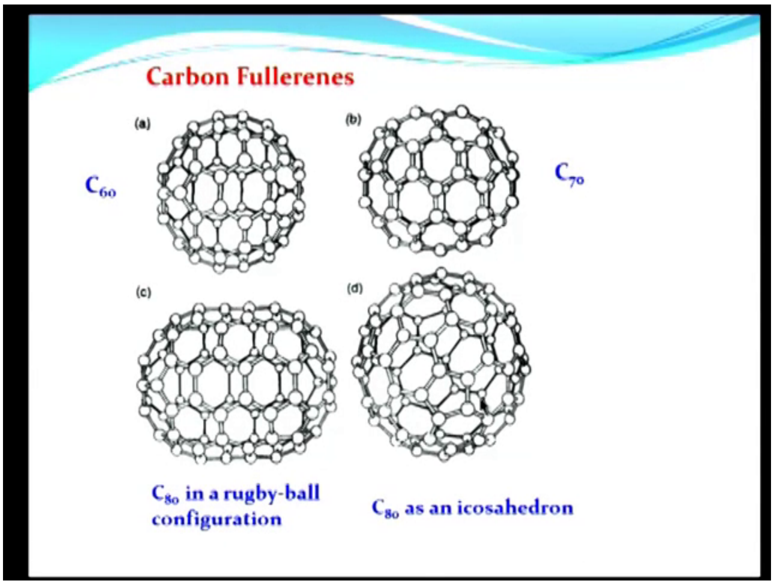

Carbon Fullerenes

Fullerenes first C 60, C 70 and polymer forms I mean polymorphs I should say polymorph C 80 one in so called rugby ball configuration, the other one in an icosahedron configuration. These are all molecules of carbon with a respective number of atoms. So, these are macromolecules of carbon. And this have been investigated for example, C 60 has had the surprising property that if there is a metal that sits at the center of this or within this C 60 shell then it becomes a superconductor and so forth.

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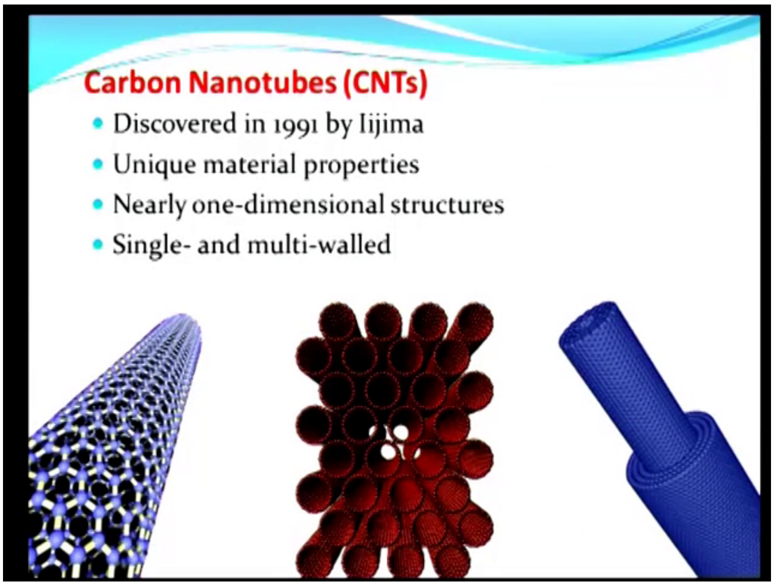

Carbon Nanotubes (CNTs)

- Discovered in 1991 by Iijima
- Unique material properties
- Nearly one-dimensional structures
- Single- and multi-walled

Carbon nanotubes really have been much more relevant technologically speaking, and these were discovered rather soon after carbon the buckyballs in 1991. And these are how unique material properties and they are in if it is a single walled carbon nanotubes because one can also have multi walled tubes as shown in this cartoon you know the one here is a multi walled tube you have concentric tubes. Whereas, you have in the center an array of single walled nanotubes. If it is a multi single walled carbon nanotubes as in the center over here, then it is as nearly a one-dimensional structure as one can practically have with diameters that can be as small as about a nanometer.

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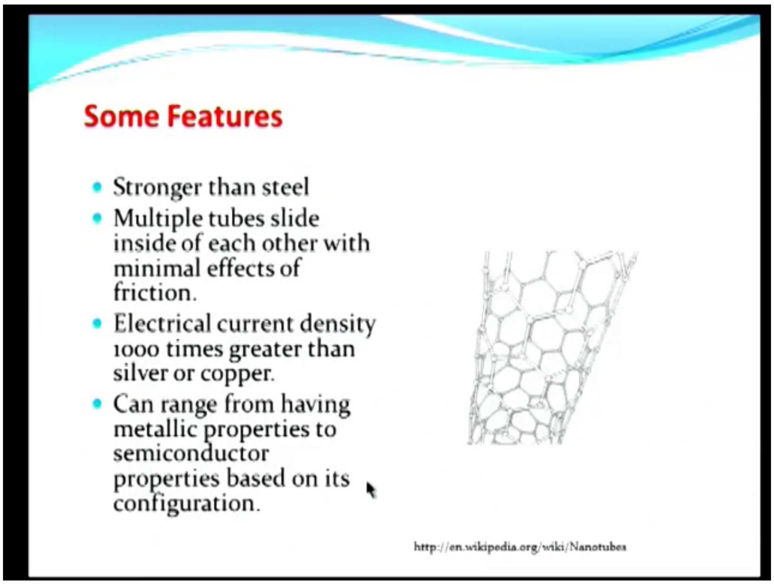

Some Features

- Stronger than steel
- Multiple tubes slide inside of each other with minimal effects of friction.
- Electrical current density 1000 times greater than silver or copper.
- Can range from having metallic properties to semiconductor properties based on its configuration.

http://en.wikipedia.org/wiki/Nanotubes

Some features of these carbon nanotubes is that you know mechanically it is stronger than steel, multiple tubes can slide inside of each other with minimal effects of friction. So, it can be a very good lubricant material, it can support electric currents of density one thousand times greater than silver or copper. And surprisingly it can have properties ranging from that of a metal to those of a semiconductor based on the configuration of the carbon nanotubes. So, these are some of the unique features of carbon nanotubes which are as I said especially if the single walled then you have a nearly one-dimensional structure.

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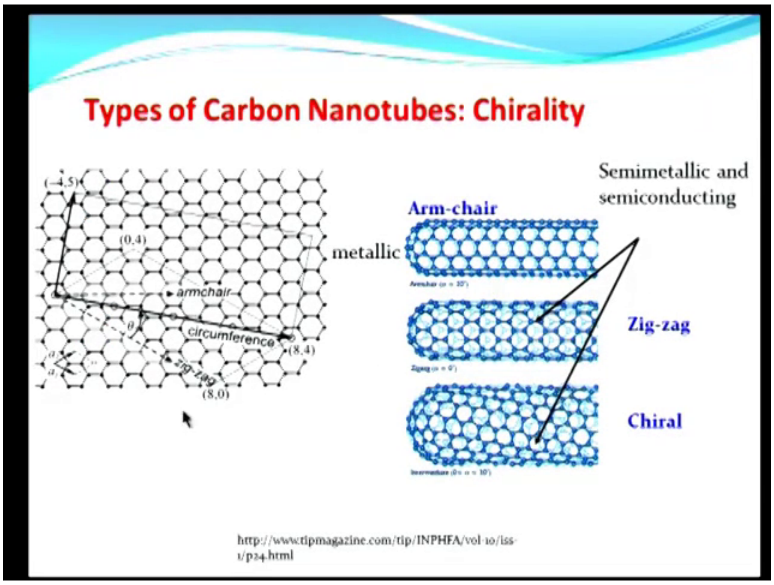

Types of Carbon Nanotubes: Chirality

http://www.tipmagazine.com/tip/INPHFA/vol-10/iss-1/p24.html

Now, what is shown on left here is the hexagonal graphene template this is the so called SP 2 bonded carbon that sits at each of these vertices of accidence over here. And what is shown on the right are three different configurations of carbon nanotubes that can be generated by folding this graphene sheet this is actually the so called graphene sheet that is graphene is a single layer a single two-dimensional layer of carbon. In fact, graphene is obtained by literally peeling off layers of graphite with an adhesive tape for example, there is a physical method of producing a graphene sheet. So, what is this, this is a graphene sheet. And by folding the graphene sheet along different directions with respect to the position of the atoms in this hexagonal lattice.

As shown here one can get you know if the axis of folding runs through the atoms then one gets this arm-chair structure of carbon nanotube which is closed at this end for example, one generally wants to think of carbon nanotubes which are closed at both ends. So, this end where it is closed easily half a buckyball. So, depending on the axis around which the graphene sheet is folded you would get an armchair configuration or a so called zig-zag configuration or a chiral configuration which lacks mirror symmetry. So, you have different configurations of carbon that can be derived quite readily by folding it along different directions of this two-dimensional lattice. And one can describe these things in terms of the basis vectors a 1 and a 2 as shown here basis vectors which will allow you to translate from any spot in the lattice hexagonal lattice to any other in terms of integral numbers of a 1 and a 2.

The remarkable thing is that carbon nanotubes of the metallic type or rather of the armchair configuration or metallic in character whereas, the other two configurations are semiconducting in character. So, it turns out that if one produces single walled carbon nanotubes, if one managed to produce them then about one-third of them would be of the armchair configuration and there four metallic and the rest would be semiconducting on the average. So, this is a remarkable property of carbon nanotubes that they can be of both the metallic and semiconducting types depending on the weight they are folded.

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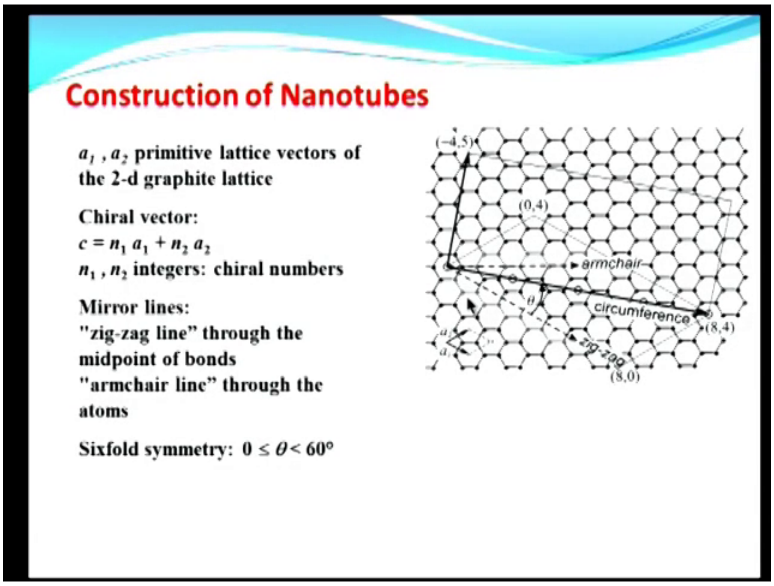

Construction of Nanotubes

a_1 , a_2 **primitive lattice vectors of the 2-d graphite lattice**

Chiral vector:

$c = n_1\, a_1 + n_2\, a_2$

n_1 , n_2 **integers: chiral numbers**

Mirror lines:

"zig-zag line" through the midpoint of bonds

"armchair line" through the atoms

Sixfold symmetry: $0 \le \theta < 60°$

So, this is a further demonstration of the construction on a nano tubes in terms of the primitive lattice vectors that I just described a 1 and a 2. So, as shown here you can have the zig-zag configuration by folding it along the line that bisects opposite faces of this hexagon. And then the arm-chair I have described and anything in between gives you the chiral symmetry.

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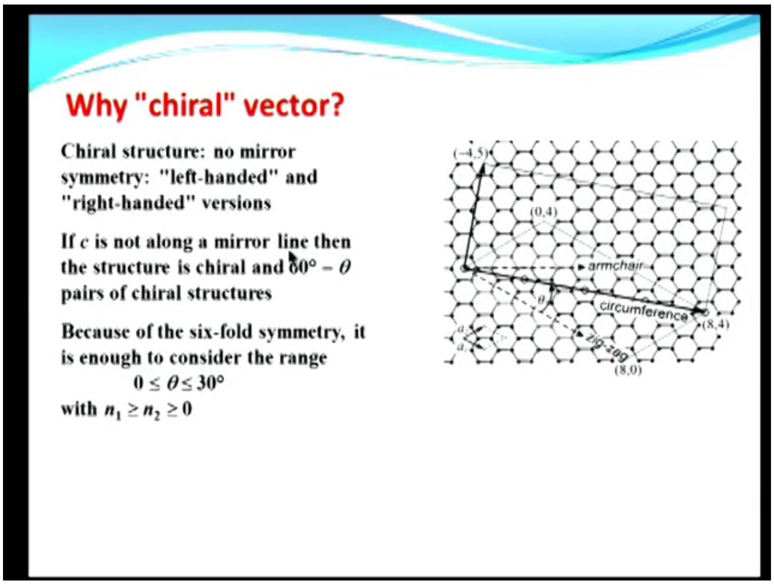

Why "chiral" vector?

Chiral structure: no mirror symmetry: "left-handed" and "right-handed" versions

If c is not along a mirror line then the structure is chiral and $60° - \theta$ pairs of chiral structures

Because of the six-fold symmetry, it is enough to consider the range

$0 \le \theta \le 30°$

with $n_1 \ge n_2 \ge 0$

So, therefore, this is the way one constructs the carbon nanotubes. And this is a further expansion of the same thing to tell us about the left handed and right handed versions because there is no mirror symmetry and that is the characteristic of folding the carbon nanotubes along a line that is between the armchair configuration and the zig-zag configuration. A great deal of work has been done on them on these things and these are now really textbook material.

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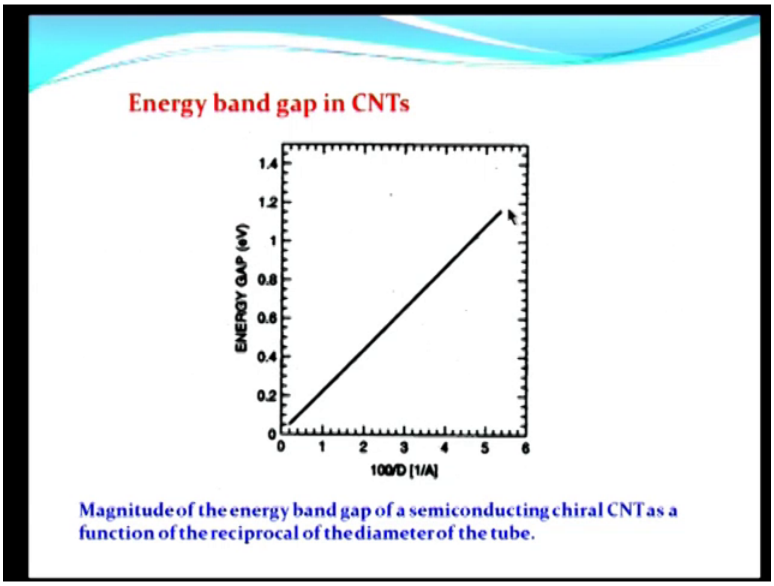

Energy band gap in CNTs

Magnitude of the energy band gap of a semiconducting chiral CNT as a function of the reciprocal of the diameter of the tube.

I mentioned that you can have semiconducting carbon nanotubes in this zig-zag and the chiral configurations. What is shown here is the energy band gap semiconductor have energy band gaps, so this is the energy band gap as a function of the inverse diameter. So, we are talking about the diameter is increasing this way because this is the inverse diameter. So, as the diameter is increased from low values to higher values, the energy gap falls from about 1.2 and approaches zero as the diameter of the carbon nanotube is increased. What it really means in terms of this folding is that if you have a for this vector for example, if n 1 and n 2 are large relatively large then you would have a relatively large diameter carbon nanotube because you are folding it with many more unit cells in them. Therefore, that will have a larger diameter and those ones with the larger diameter usually have a smaller energy band gap.

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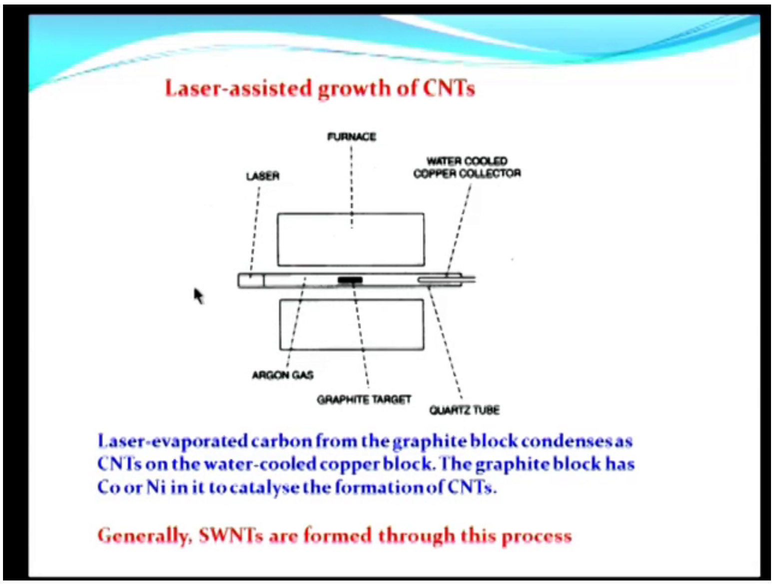

Laser-assisted growth of CNTs

Laser-evaporated carbon from the graphite block condenses as CNTs on the water-cooled copper block. The graphite block has Co or Ni in it to catalyse the formation of CNTs.

Generally, SWNTs are formed through this process

One of the earliest methods by which carbon nanotubes foreground is the laser assisted growth method. What is done here is to take a graphite piece in which either cobalt or nickel particles are embedded, small particles preferably nanoparticles of cobalt or nickel are embedded in this graphite piece. And this graphite piece is then bombarded with lasers. Remembering that the graphite piece itself is at a high temperature in a furnace and bombarded by this laser beam then the graphite is evaporated and then this evaporated graphite material is carried by the organ that is flowing through it as the carrier gas. So, this vapor of graphite that is evaporated is carried by the argon gas and it is condensed on a water cooled copper collector.

So, it is a rather simple method, direct method of a physical kind. When this process is conducted then it turns out that the copper collector collects single walled carbon nanotubes and it turns out that cobalt and nickel catalyze the formation of carbon nanotubes from this evaporated graphite material. So, this is an early method of producing carbon nanotubes single walled carbon nanotubes.

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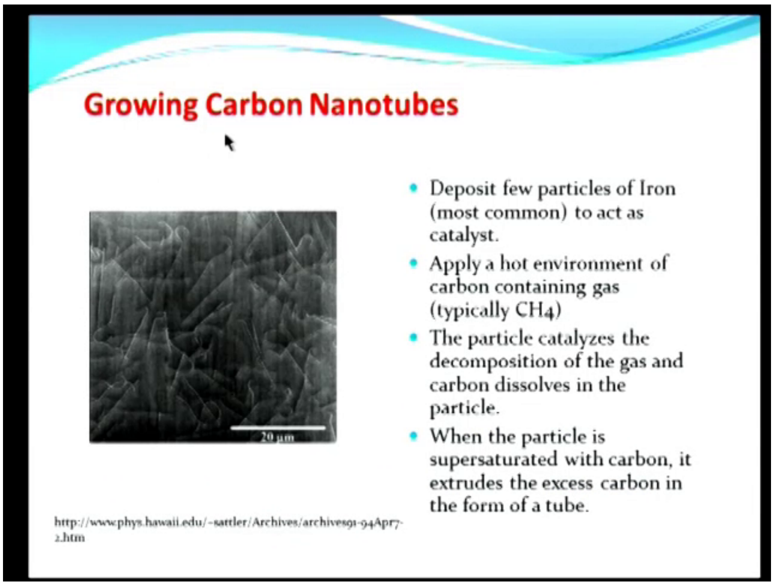

Growing Carbon Nanotubes

- Deposit few particles of Iron (most common) to act as catalyst.
- Apply a hot environment of carbon containing gas (typically CH_4)
- The particle catalyzes the decomposition of the gas and carbon dissolves in the particle.
- When the particle is supersaturated with carbon, it extrudes the excess carbon in the form of a tube.

http://www.phys.hawaii.edu/~sattler/Archives/archives91-94Apr7-2.htm

Subsequently chemical vapor deposition chemical methods such as CVD were developed to produce carbon nanotubes. Typically using a gas like methane as the precursor gas and it turns out that a catalyst such as cobalt d color ion is required to catalyze, the formation of carbon nanotubes from the decomposition of methane and the carbon that is obtained from that is then catalyzed into carbon nanotubes by these tiny particles of metals that are present. For example, on a substrate you can grow nanowires or rather nano tubes of carbon by spreading nickel or cobalt ion particles on let us say silicon substrate which is heated to a high temperature and methane gas for example, is then made to flow over that one.

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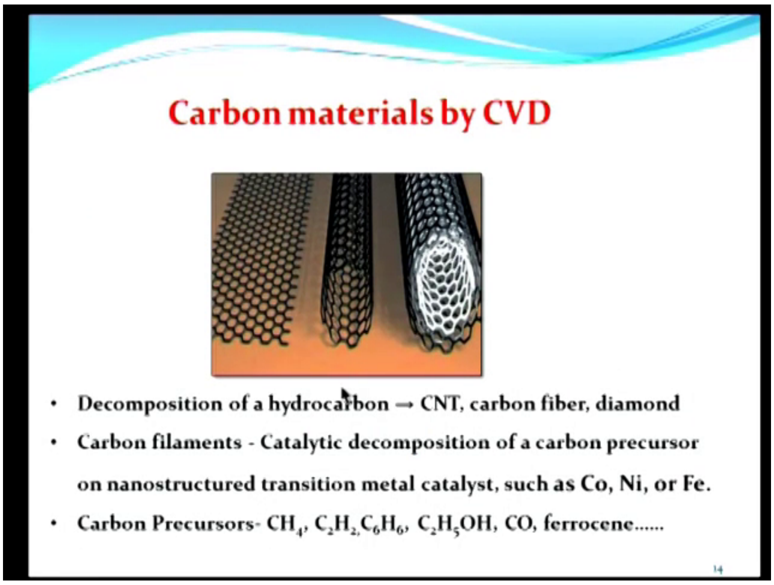

Carbon materials by CVD

- Decomposition of a hydrocarbon → CNT, carbon fiber, diamond
- Carbon filaments - Catalytic decomposition of a carbon precursor on nanostructured transition metal catalyst, such as Co, Ni, or Fe.
- Carbon Precursors- CH_4, C_2H_2, C_6H_6, C_2H_5OH, CO, ferrocene……

So, this is the general methodology. It turns out that what is seen here is the two-dimensional graphite lattice which is actually the graphene sheet, it turns out that graphene single-walled carbon nanotubes, multi-walled carbon nanotubes all of these can be produced by essentially the same chemical vapor deposition method using a variety of precursors that is it is possible to employ methane, acetylene, benzene, ethyl alcohol, carbon monoxide, ferrocene and so on. A variety whole variety of carbon containing vaporous compounds and then by slightly altering the methodology for decomposition and catalysis of these things into carbon nanotubes, it is possible to get carbon nanotubes multi-walled, single-walled and so forth by the general CVD method which works at around 700 to 800 degree Celsius.

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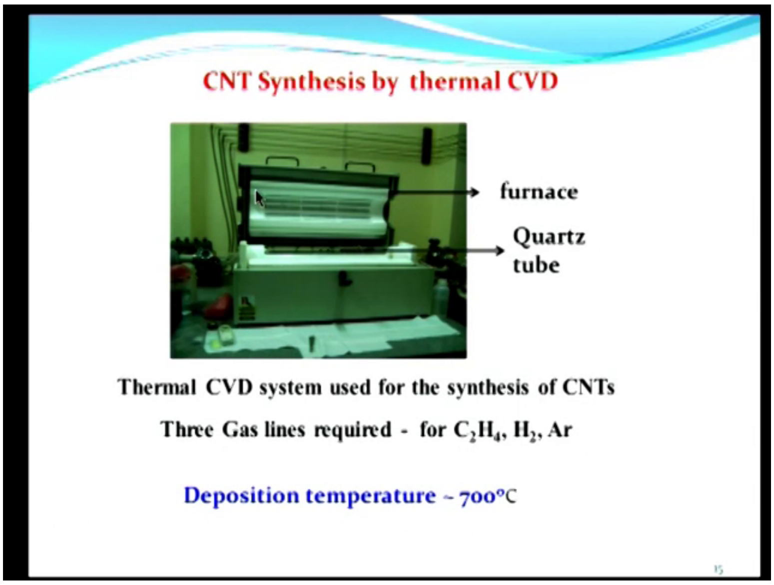

CNT Synthesis by thermal CVD

Thermal CVD system used for the synthesis of CNTs

Three Gas lines required - for C_2H_4, H_2, Ar

Deposition temperature ~ 700°C

This is actually a piece of apparatus a chemical vapor deposition reactor thermal CVD that is only temperature is used to conduct the reaction as opposed to anything like a plasma CVD, where a plasma is employed to accelerate the process typically. So, in this furnace one places substrate and then uses a gas for example, here ethylene C 2 H 4, hydrogen and argon. So, there are certain protocols over here that allows you to deposit carbon nanotubes on a substrate like silicon at a temperature of about 700 degree Celsius.

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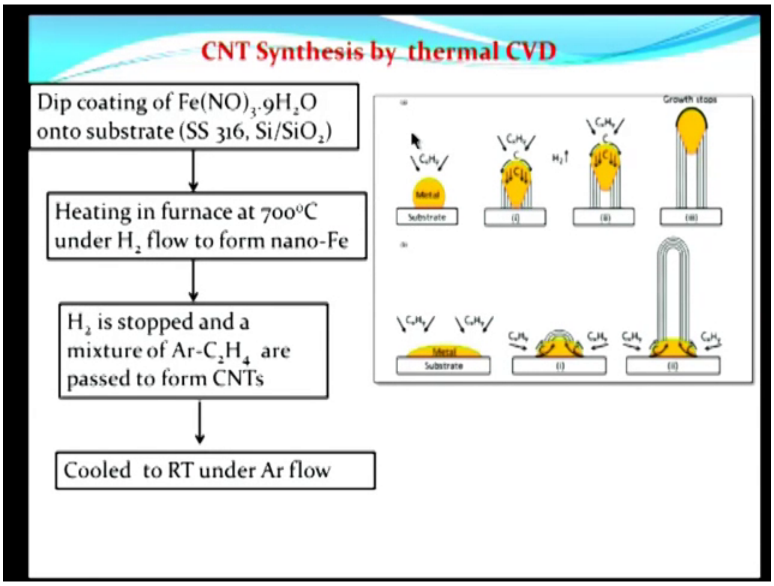

CNT Synthesis by thermal CVD

Dip coating of $Fe(NO)_3 \cdot 9H_2O$ onto substrate (SS 316, Si/SiO_2)

↓

Heating in furnace at 700°C under H_2 flow to form nano-Fe

↓

H_2 is stopped and a mixture of Ar-C_2H_4 are passed to form CNTs

↓

Cooled to RT under Ar flow

The formation of carbon nanotubes by thermal CVD is really quite analogous to the vapor liquid solid method that we discussed earlier except that this is not really of there is no liquid formation. What happens is that in the metal particles that we mentioned cobalt, nickel or ion, ion is really most effective, so this metal particle acts as the substrate initial surface on which the impinging hydrocarbon decomposes to produce carbon, elemental carbon that carbon dissolves in the metal without the metal itself becoming liquid. And the dissolved carbon then emerges as a carbon nanotube and the carbon nanotube grows out of this metal deposit.

So, in practice something like this is done one takes ferric nitrate and decomposes ferric nitrate to give ion particles on a substrate like that of silicon that is kept inside the furnace, so that is the first step you obtain a substrate and then you deposit or you obtain a substrate it is decorated with nanoparticles of ion that comes out of the decomposition of the nitrate. And then one goes through the process of chemical vapor deposition using an appropriate hydrocarbon and as a result of it typically at about 700 degrees one gets the growth of carbon nanotubes by a process and all goes to as I said the VLS process.

It turns out that in such a system one can conduct the reactions under an applied electric field giving rise to carbon nanotubes that are essentially perpendicular to the substrate. So, you can have a well-organized array of carbon nanotubes going on a silicon substrate by having an applied electric field during the deposition process.

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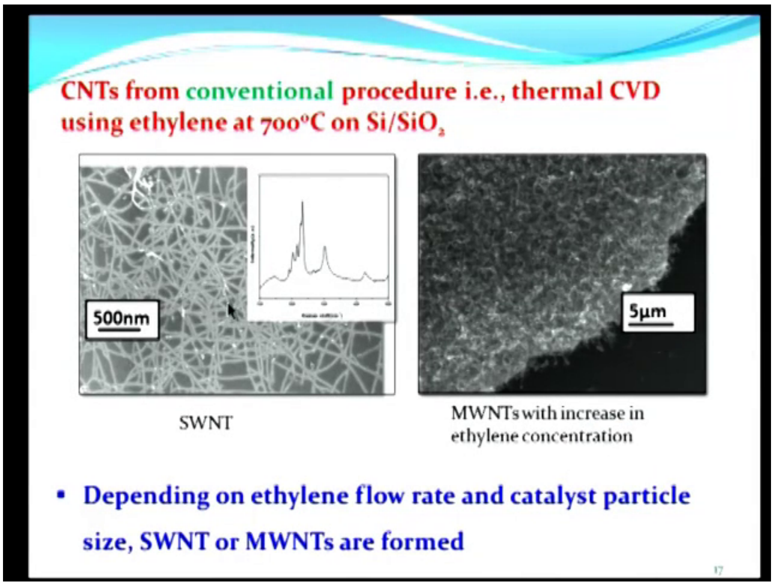

CNTs from conventional procedure i.e., thermal CVD using ethylene at 700°C on Si/SiO$_2$

SWNT

MWNTs with increase in ethylene concentration

- **Depending on ethylene flow rate and catalyst particle size, SWNT or MWNTs are formed**

So, what is shown on the left here is an array of carbon nanotubes produced by the process that was just described. And what is shown here in the inset is the Raman spectrum of the carbon nanotubes that are obtained and it turns out that this particular signature this particular spectrum is the signature of single walled carbon nanotubes. The multi walled carbon nanotubes have a slightly different signature. And therefore, from the Raman spectrum is possible to tell whether what you have got is single walled or multi walled carbon nanotubes through a CVD process.

Now, it turns out that depending on the flow rate of ethylene in the CVD process we described and the catalyst particle size that is employed in the process. Depending on that it is possible to obtain either single walled nanotubes or multi walled nanotubes. So, it is possible to control the nature of the carbon nanotubes that are obtained by tinkering with the process in a predictable manner as a matter of fact. So, what is shown here is a forest of multi walled carbon nanotubes that are obtained in the same chamber that was shown earlier in the same chamber by greatly increasing the ethylene concentration that is the precursor to carbon nanotubes by increasing ethylene in concentration it is possible to obtain a forest of multi walled carbon nanotubes.

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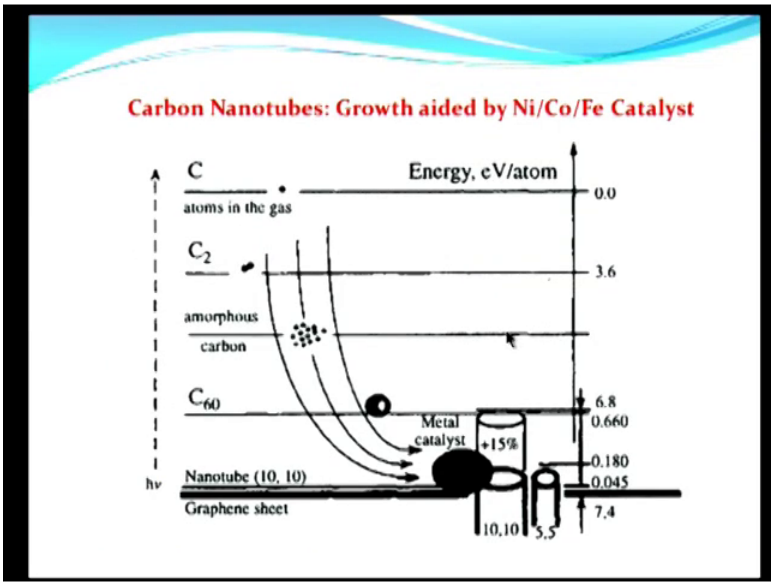

Carbon Nanotubes: Growth aided by Ni/Co/Fe Catalyst

What is shown here is a diagram that tells us how for example using a catalyst metal calculus, which could be nickel, cobalt or ion into which carbon of various types dissolve. For example, carbon atoms in the gas, carbon molecules in the gas amorphous carbon, buckyballs, all these things can go into the metal particle at an elevated temperature and then come out of this as carbon nanotubes under appropriate conditions. So, these really sort of a devouring of carbon different kinds of carbon to yield carbon nanotubes. What is noteworthy is that if one had buckyballs for example, then by a relatively small expenditure of energy 0.045 electron volts, it is possible to fold it into a carbon nanotubes, fold the carbon into a carbon nanotubes. Whereas, the energy required for doing the same thing with atoms in the gas is much greater several electron volts. So, if you had free carbon atoms then a great deal of expenditure of energy is required to produce carbon nanotubes from such disorder carbon.

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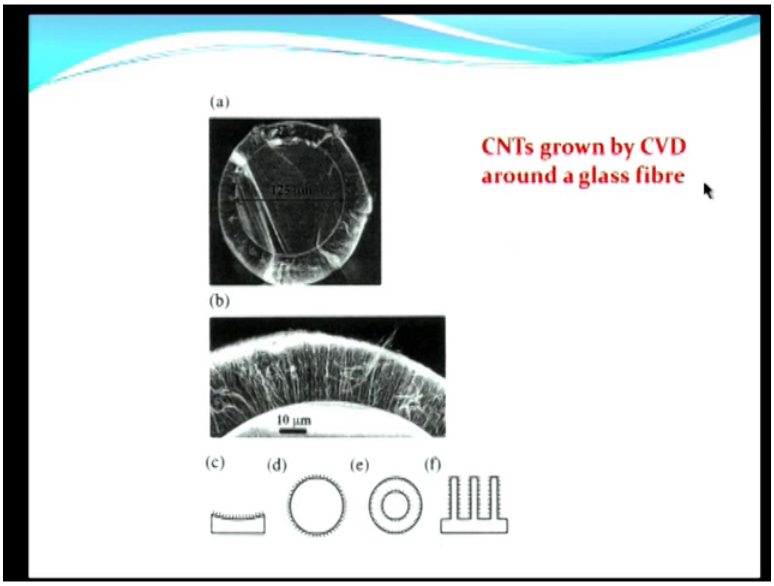

CNTs grown by CVD
around a glass fibre

What is shown here is how the CVD process allows you to grow carbon nanotubes around let us say a glass fiber in this case. What is in the center is a glass fiber, and you know all around that as shown in this magnified photograph carbon nanotubes have grown essentially perpendicular to the low to the glass fiber surface, so locally perpendicular. So, these things are done now quite can be done quite routinely quite predictably by the chemical vapor deposition process.

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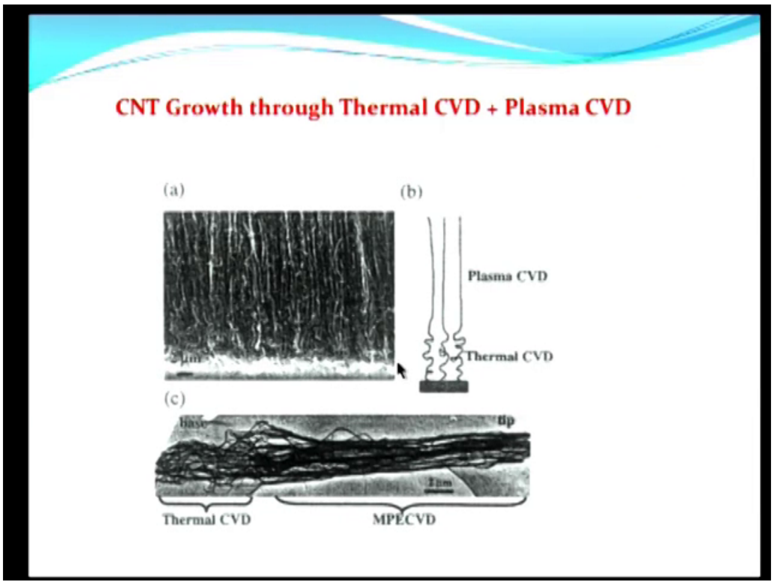

CNT Growth through Thermal CVD + Plasma CVD

What is shown here is how the process of CVD whether it is thermal or whether it is plasma assisted can alter the topology of the carbon nanotubes. So, what is shown here is that initially this process is conducted as a thermal CVD process that is only temperature is used to conduct the chemical reactions that result in the formation of carbon nanotubes, subsequently apply a plasma is turned down. Now, plasma CVD being a more rapid process would then pick it up and then allow you to grow this kind of a forest of nearly parallel carbon nanotubes at a pretty fast clip.

So, there are ways in which therefore, one can alter the process to obtain common nanotube structures, by the way these carbon nanotubes can be as long as several hundred micrometers in length with a diameter of the order of 10 to 20 nanometers. So, the aspect ratio of these things can be very high. In fact, there are reports of how millimeter long carbon nanotubes can be obtained by suitably altering the process.

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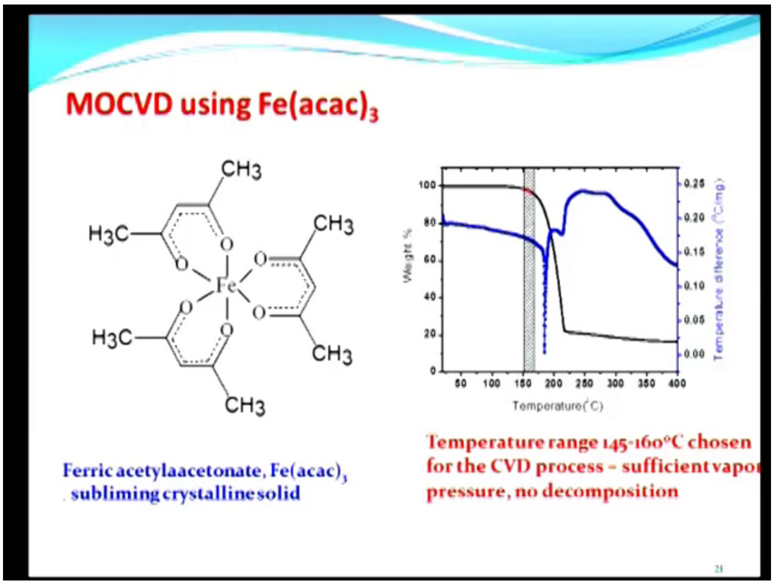

MOCVD using Fe(acac)$_3$

Ferric acetylaacetonate, Fe(acac)$_3$
. subliming crystalline solid

Temperature range 145-160°C chosen for the CVD process – sufficient vapo
pressure, no decomposition

So, far we have shown how using hydrocarbons, carbon nanotubes can be obtained. What is shown here is how a different kind of a starting material; in this case ferric acetylacetonate, I would like to recall to you that last time we used zinc acetylacetonate to produce zinc oxide nanorods from a solution under microwave bombardment MOCVD stands for metal organic CVD. So, this is a metal organic compound with ion at the core of it, and then methyl groups as terminations. Now, it turns out that this is a subliming crystalline solid and one can employ this as a CVD precursor, because it sublimes and produces vapor.

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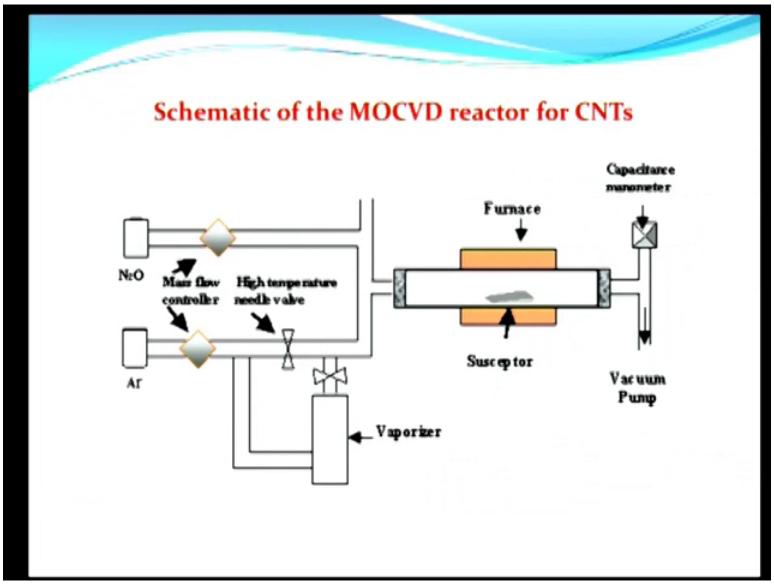

Schematic of the MOCVD reactor for CNTs

When that is done in a rather simple CVD reactor where you have a high temperature over here for the substrate and then you vaporize the ion compound, and you know carry it with organ vapor and so on. So, when this is done in an inert ambient that is argon and ion compound nothing else, no oxygen and so forth.

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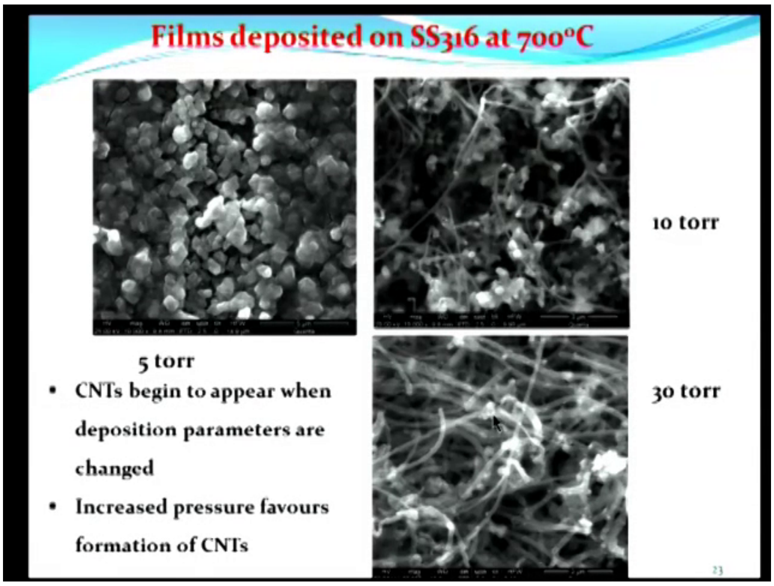

Films deposited on SS316 at 700°C

- CNTs begin to appear when deposition parameters are changed
- Increased pressure favours formation of CNTs

So, when it is when the ambient is inert then it turns out that depending on the pressure at which this reaction is conducted it turns out that it is possible to obtain carbon nanotubes as shown in the right hand micrograph simultaneously with ion oxide. So, what you get is carbon nanotubes that are interspersed with ion oxide in a composite material. Now, when the pressure is changed, it turns out that this is now carbon nanotube bridge. So, there is a smaller proportion of the oxide than of the carbon nanotubes. In other words, by using a different starting material all together not a hydrocarbon, it turns out it is possible to obtain carbon nanotubes along with in this case and oxide to form a composite which can be very interesting material.

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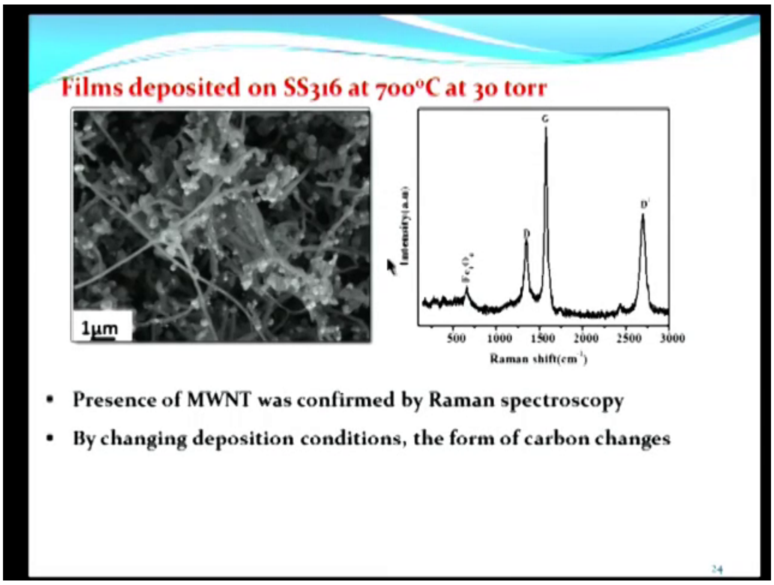

Films deposited on SS316 at 700°C at 30 torr

- Presence of MWNT was confirmed by Raman spectroscopy
- By changing deposition conditions, the form of carbon changes

Now, here is the Raman spectrum. And the Raman spectrum has signature of multi walled carbon nanotubes here and it also has his signature of ion oxide Fe 3 O 4 Fe 3 o 4 are these particles that are seen here. So, you have the simultaneous formation of Fe 3 O 4 and multi walled carbon nanotubes by this kind of a process.

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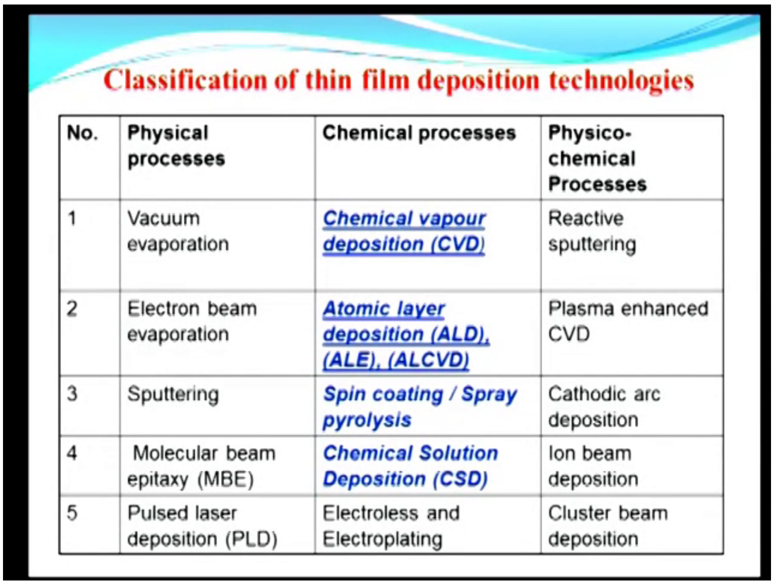

Classification of thin film deposition technologies

No.	Physical processes	Chemical processes	Physico-chemical Processes
1	Vacuum evaporation	*Chemical vapour deposition (CVD)*	Reactive sputtering
2	Electron beam evaporation	*Atomic layer deposition (ALD), (ALE), (ALCVD)*	Plasma enhanced CVD
3	Sputtering	*Spin coating / Spray pyrolysis*	Cathodic arc deposition
4	Molecular beam epitaxy (MBE)	*Chemical Solution Deposition (CSD)*	Ion beam deposition
5	Pulsed laser deposition (PLD)	Electroless and Electroplating	Cluster beam deposition

We move onto somewhat general discussion of thin film depositions because thin film formation is an important part of device technology including nano device technology. There are physical methods and there are chemical methods, we have just now gone through the chemical vapor deposition process. So, there are numerous methods like sputtering and plasma enhanced methods ion beam deposition and so on.

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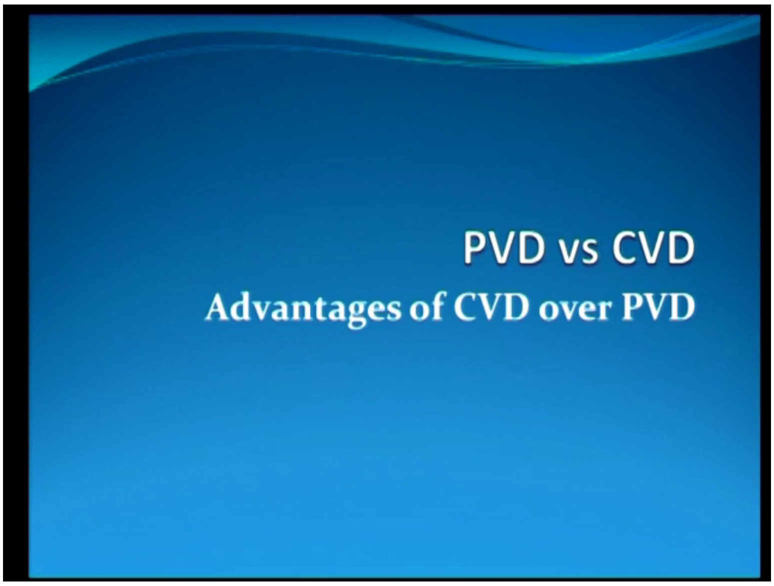

PVD vs CVD

Advantages of CVD over PVD

Now, there are PVD, CVD methods with advantages for CVD over PVD and PVD over CVD.

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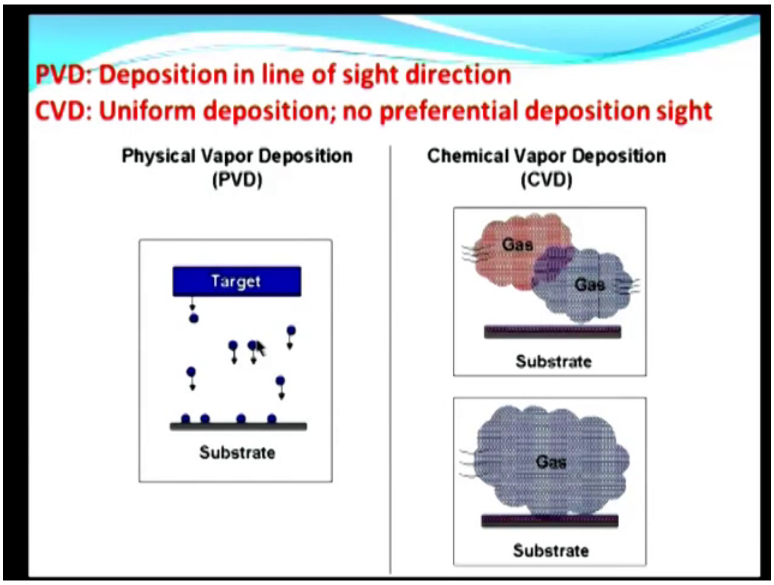

PVD: Deposition in line of sight direction

CVD: Uniform deposition; no preferential deposition sight

Now one general feature is that in physical vapor deposition you have for example, in sputtering a target from which material is knocked out by bombarding ions like argon ions and those particles of target material that are shot out of the target collect on the substrate to form a film. So, this is the physical vapor deposition method, where the material that forms the target becomes the material that forms the film. In the chemical vapor deposition process, you have some vaporous material including gases that flow through the reactor as we have shown in the case of the carbon nanotubes, and they react on the hot substrate surface and produce film of the material that is a result of the chemical reaction.

So, the material that is deposited is different from the material of which the vapors are allowed into the chamber, whereas here the material of these film is the same as the material of the target.

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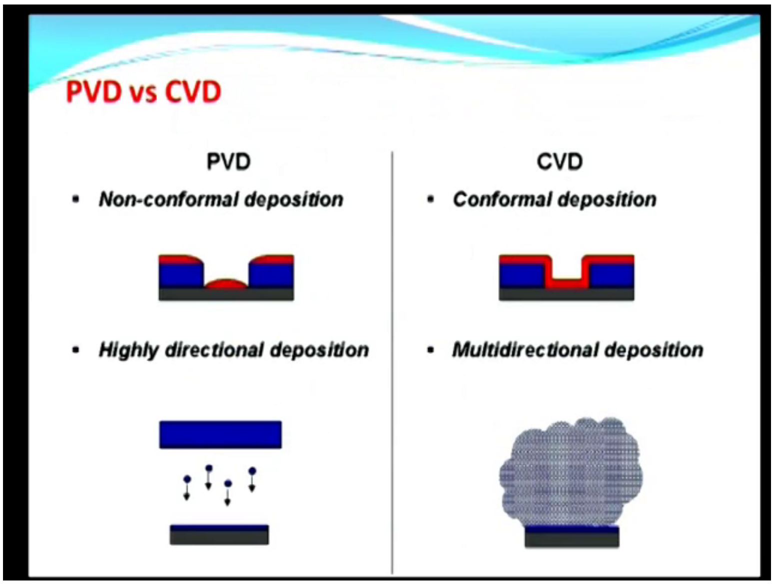

PVD vs CVD

PVD

- *Non-conformal deposition*
- *Highly directional deposition*

CVD

- *Conformal deposition*
- *Multidirectional deposition*

One of the important features of chemical vapor deposition is conformal deposition that is if you have contours on the substrate, which of course is a very important part of semiconductor fabrication, then chemical vapor deposition is capable of conformally covering that contour on the substrate that is usually a pattern contour that is you can have conformal coverage of all these features that are produced by patterning.

Whereas, in physical vapor deposition because it is a line of sight process you have direct deposition proper deposition on these surfaces that are normal to the flow of the vapor; whereas on these walls that are parallel to the flow the vapor, you can have little or no deposition. So, it is not conformal coverage in the case of physical vapor deposition. And as you well know from the earlier part of the course you need conformal deposition in order to be able to cover features in devices which are constantly becoming smaller.

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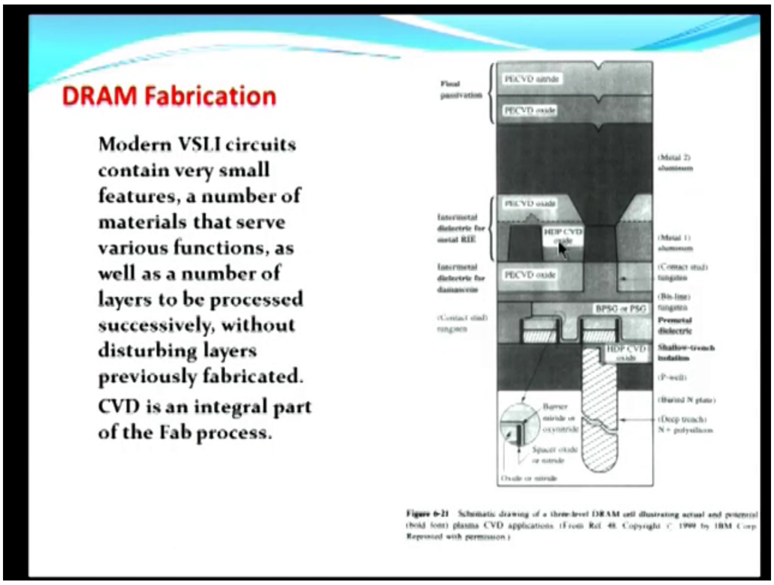

DRAM Fabrication

Modern VSLI circuits contain very small features, a number of materials that serve various functions, as well as a number of layers to be processed successively, without disturbing layers previously fabricated.

CVD is an integral part of the Fab process.

Figure 6-21 Schematic drawing of a three-level DRAM cell illustrating actual and potential (bold font) plasma CVD applications. (From Ref. 48. Copyright © 1999 by IBM Corp. Reprinted with permission.)

These are examples of where for example, you know here you have a high aspect ratio hole that you have to fill with a material and chemical vapor deposition turns out to be capable of doing so which normally physical vapor deposition processes are not capable of doing.

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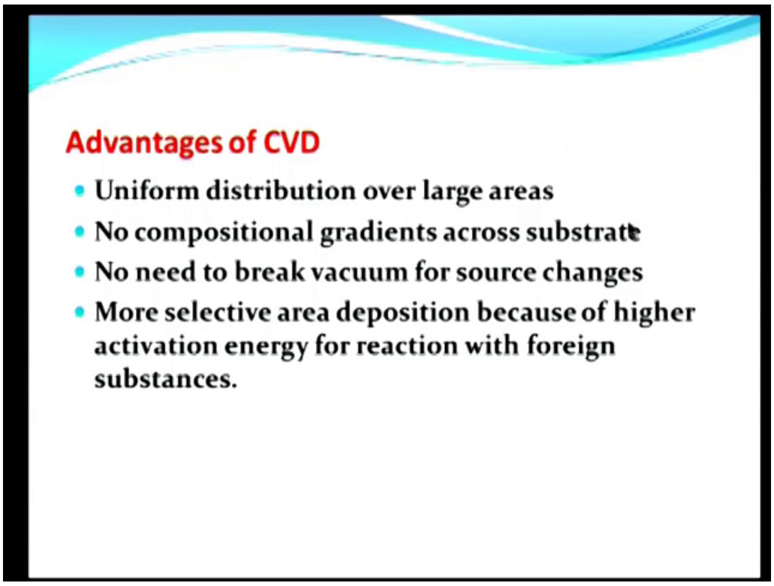

Advantages of CVD

- Uniform distribution over large areas
- No compositional gradients across substrate
- No need to break vacuum for source changes
- More selective area deposition because of higher activation energy for reaction with foreign substances.

So, CVD have advantage has advantages of uniform deposition over large areas and as we just said conformal coverage and usually high rates or deposition and so on, and therefore it is often the process of choice for VLSI fabrication especially where high aspect ratios are involved.

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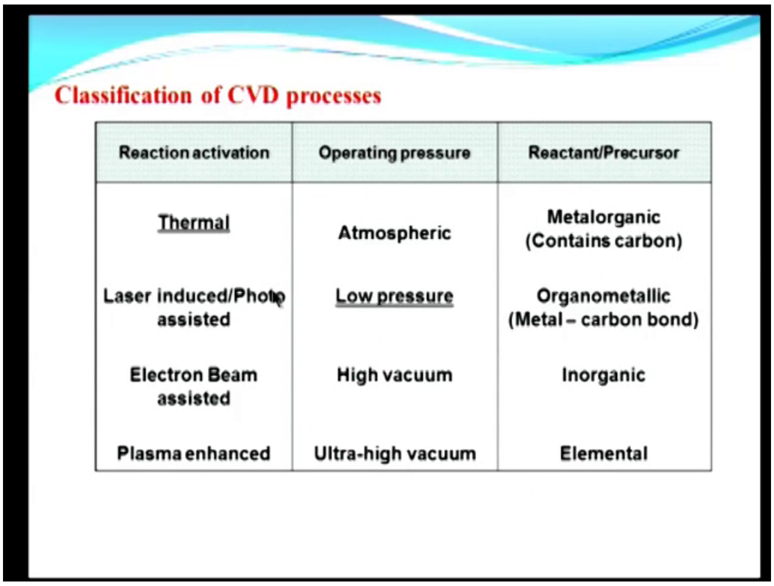

Classification of CVD processes

Reaction activation	Operating pressure	Reactant/Precursor
Thermal	Atmospheric	Metalorganic (Contains carbon)
Laser induced/Photo assisted	Low pressure	Organometallic (Metal – carbon bond)
Electron Beam assisted	High vacuum	Inorganic
Plasma enhanced	Ultra-high vacuum	Elemental

There are various kinds of CVD processes, thermal and low pressure and so forth high pressure and all that.

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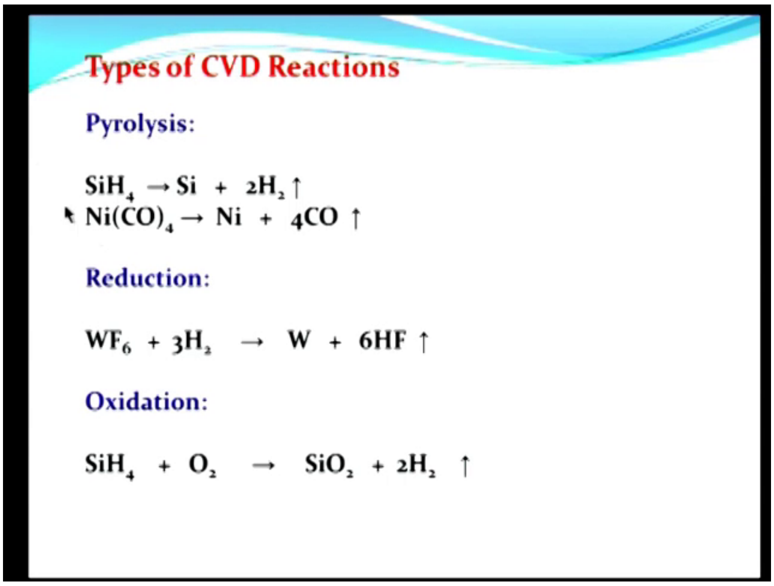

Types of CVD Reactions

Pyrolysis:

$$SiH_4 \rightarrow Si + 2H_2 \uparrow$$
$$Ni(CO)_4 \rightarrow Ni + 4CO \uparrow$$

Reduction:

$$WF_6 + 3H_2 \rightarrow W + 6HF \uparrow$$

Oxidation:

$$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2 \uparrow$$

Now the chemical vapor deposition process can be of various kinds can have different kinds of reaction, here is a decomposition of silane into silicon. Tungsten fluoride is reduced by hydrogen into tungsten which is again an important part of the tungsten plug process in VLSI fabrication. Silane is oxidized into SiO 2 and so forth. Now, all these are reactions that occur on hard substrates and the temperature is required depend on the kind of reaction. So, it can vary from a couple of hundred degrees to several hundred degrees. And each of these is a case of heterogeneous nucleation, so that reaction has to take place on the substrate surface and then of course, as we discuss in the other day regarding the formation of heterogeneous nucleation.

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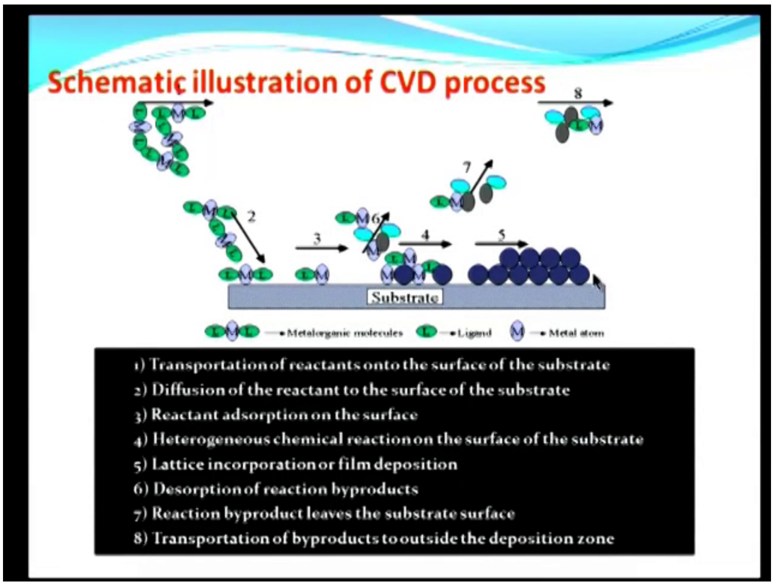

Schematic illustration of CVD process

1) Transportation of reactants onto the surface of the substrate
2) Diffusion of the reactant to the surface of the substrate
3) Reactant adsorption on the surface
4) Heterogeneous chemical reaction on the surface of the substrate
5) Lattice incorporation or film deposition
6) Desorption of reaction byproducts
7) Reaction byproduct leaves the substrate surface
8) Transportation of byproducts to outside the deposition zone

Much the same kind of a process is required. So, you have the diffusion of reactants and then the adsorption of reactants on the substrate surface, reaction taking place and then the mobility of the react the growth species on the substrate to form this film through nucleation and growth. And then the ejection of reaction by products into the chamber, so that they are pumped out and so on. Therefore, just as in the case of a physical heterogeneous nucleation process, which we discussed couple of days ago, this one also is a complex process that involves multiple steps.

One thing to remember in the context of nanomaterials is that this process can be slowed down by controlling the substrate temperature as long as the substrate temperature is high enough for the reaction to take place. If the substrate temperature is not high enough to allow the reaction to take place of course, then there is no nucleation, but usually these reactions take place over a range of temperatures and therefore, it could be possible to lower the temperature in order to get smaller crystals that are generated out of this heterogeneous nucleation process. So, one way to obtain a nano structured thin films is to lower the temperature of growth in a CVD process. As long as I said as long as the reaction takes place at that temperature. Another way is to choose the reactants appropriately.

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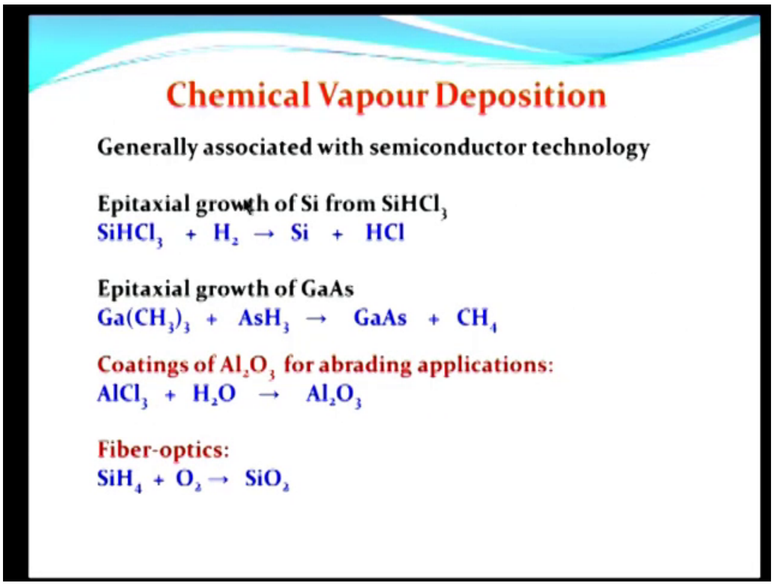

Chemical Vapour Deposition

Generally associated with semiconductor technology

Epitaxial growth of Si from $SiHCl_3$
$SiHCl_3 + H_2 \rightarrow Si + HCl$

Epitaxial growth of GaAs
$Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + CH_4$

Coatings of Al_2O_3 for abrading applications:
$AlCl_3 + H_2O \rightarrow Al_2O_3$

Fiber-optics:
$SiH_4 + O_2 \rightarrow SiO_2$

What I have shown here is you know there are numerous ways in which for example, one can obtain silicon, this is trichlorosilane. You can have as I showed in previous you can have silane directly giving the silicon you can have trichlorosilane giving a silicon. It is possible to alter these reactants, so that it allows us to alter the range of temperatures of the conditions over which reaction thing can take place and that way to control the structure the microstructure of the nano structure of the resulting film. Now, epitaxial growth of gallium arsenide gallium arsenide is a direct binding a semiconductor and we mentioned gallium arsenide and gallium aluminum arsenide in the context of formation of quantum wells for the formation of lasers for example.

Now, such an epitaxial layer is actually a single crystalline layer, but usually of a very small thickness, we mentioned thicknesses of the order of 1 or 2 nanometers, so they actually nano structured in that sense. So, epitaxial growth of gallium arsenide is possible by the CVD process by using tri methyl gallium and arsen to obtain gallium arsenide typically at about 600 degree celsius. So, one gets high quality crystalline layers of a controlled small thickness through such a process. So, this epitaxial growth is actually an important part of nanostructured materials, because these processes can be controlled with great precision to obtain let us say precisely 10.4 nanometers of thickness of gallium arsenide for example.

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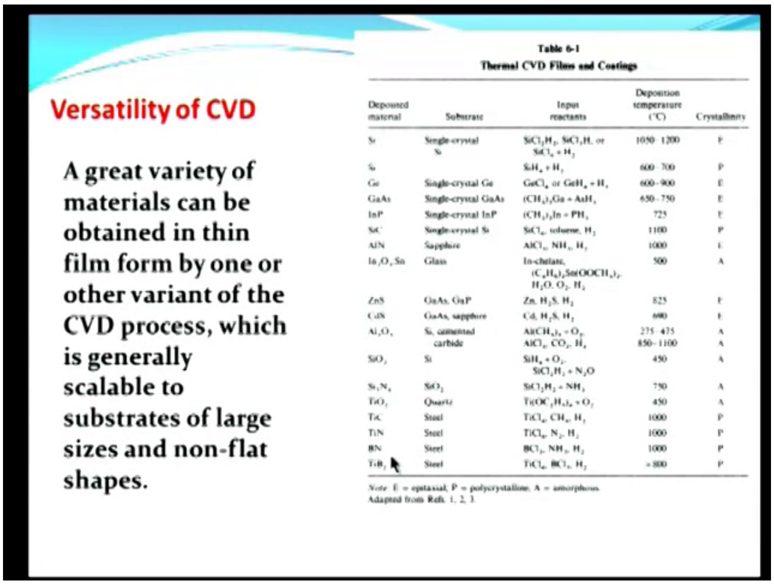

Versatility of CVD

A great variety of materials can be obtained in thin film form by one or other variant of the CVD process, which is generally scalable to substrates of large sizes and non-flat shapes.

Table 6-1

Thermal CVD Films and Coatings

Deposited material	Substrate	Input reactants	Deposition temperature (°C)	Crystallinity
Si	Single-crystal Si	$SiCl_2H_2$, $SiCl_3H$, or $SiCl_4 + H_2$	1050–1200	E
Si		$SiH_4 + H_2$	600–700	P
Ge	Single-crystal Ge	$GeCl_4$ or $GeH_4 + H_2$	600–900	E
GaAs	Single-crystal GaAs	$(CH_3)_3Ga + AsH_3$	650–750	E
InP	Single-crystal InP	$(CH_3)_3In + PH_3$	725	E
SiC	Single-crystal Si	$SiCl_4$, toluene, H_2	1100	P
AlN	Sapphire	$AlCl_3$, NH_3, H_2	1000	E
In_2O_3:Sn	Glass	In-chelate, $(C_4H_9)_2Sn(OOCH_3)_2$, H_2O, O_2, H_2	500	A
ZnS	GaAs, GaP	Zn, H_2S, H_2	825	E
CdS	GaAs, sapphire	Cd, H_2S, H_2	690	E
Al_2O_3	Si, cemented carbide	$Al(CH_3)_3 + O_2$, $AlCl_3$, CO_2, H_2	275–475 850–1100	A A
SiO_2	Si	$SiH_4 + O_2$, $SiCl_2H_2 + N_2O$	450	A
Si_3N_4	SiO_2	$SiCl_2H_2 + NH_3$	750	A
TiO_2	Quartz	$Ti(OC_2H_5)_4 + O_2$	450	A
TiC	Steel	$TiCl_4$, CH_4, H_2	1000	P
TiN	Steel	$TiCl_4$, N_2, H_2	1000	P
BN	Steel	BCl_3, NH_3, H_2	1000	P
TiB_2	Steel	$TiCl_4$, BCl_3, H_2	>800	P

Note: E = epitaxial; P = polycrystalline; A = amorphous.
Adapted from Refs. 1, 2, 3.

CVD versatile a whole host of materials can be deposited by the chemical vapor deposition process, elemental semiconductors, compound semiconductors, oxides, nitrides and so forth. All of these can be the microstructure of all of these things or should I say the nanostructure of all these things can be controlled by the controlling of the by choosing of the parameters of the CVD reaction. For example, microcrystalline silicon is an important part of technology under development. So, it is possible to obtain by the same CVD process not only single crystal silicon as shown here, but also micro crystalline silicon by choosing the appropriate conditions actually microcrystalline is generally speaking of nano crystalline dimension nanometric dimension. So, nano structures of a whole host of materials can be obtained in film forum by the CVD process.

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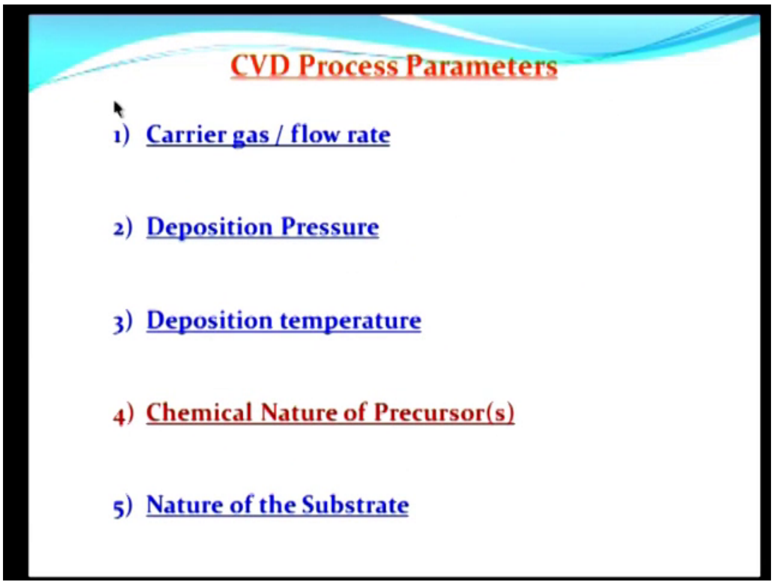

CVD Process Parameters

1) Carrier gas / flow rate
2) Deposition Pressure
3) Deposition temperature
4) Chemical Nature of Precursor(s)
5) Nature of the Substrate

the CVD process has various parameters which we control as I was just saying flow rates, deposition pressure, temperature, and the precursors themselves as I said there is usually a choice of these precursors. So, by choosing them, one can choose the conditions under which the reaction takes place which influences the structure of these materials, the crystalline structure of these materials. Therefore, all these give handles on obtaining film material by the CVD process with a highly controlled set of structures possible.

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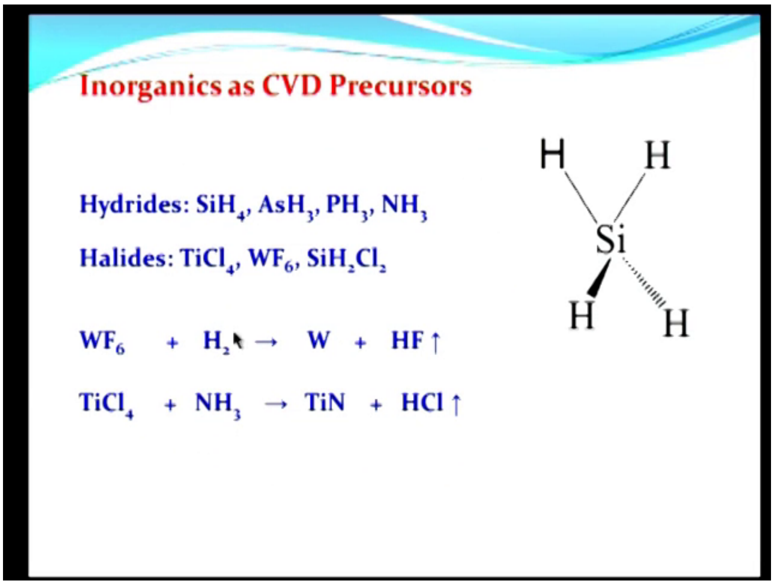

Inorganics as CVD Precursors

Hydrides: SiH_4, AsH_3, PH_3, NH_3

Halides: $TiCl_4$, WF_6, SiH_2Cl_2

$WF_6 + H_2 \rightarrow W + HF\uparrow$

$TiCl_4 + NH_3 \rightarrow TiN + HCl\uparrow$

A whole host of precursors are there and so forth. So, you know this is a kind of a laundry list of different precursors, inorganic precursors. The point is that one should have volatile materials as precursors that goes without saying because this is a chemical vapor deposition process. So, silane is really gas at room temperature tungsten hexafluoride is a gas at room temperature, titanium tetrachloride is a liquid at room temperature, but all of these have substantial vapor pressures which allow us to use them as precursor materials for CVD.

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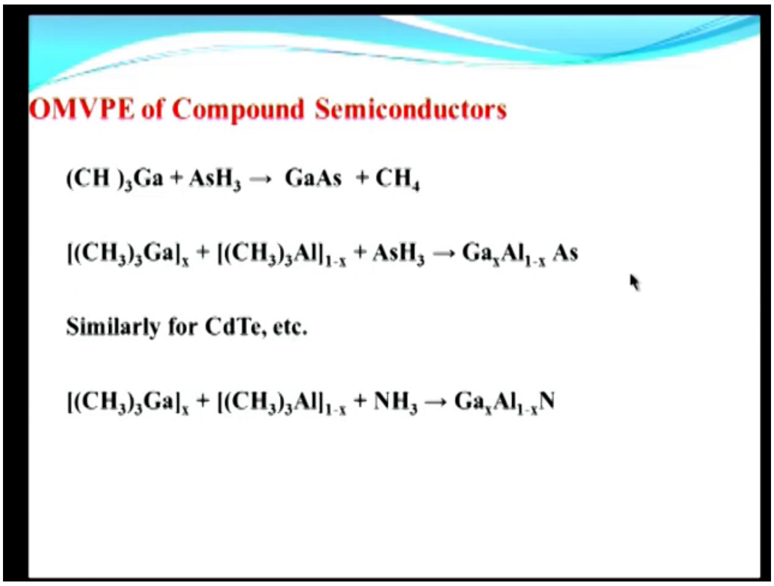

OMVPE of Compound Semiconductors

$(CH\ )_3Ga + AsH_3 \rightarrow GaAs + CH_4$

$[(CH_3)_3Ga]_x + [(CH_3)_3Al]_{1-x} + AsH_3 \rightarrow Ga_xAl_{1-x}As$

Similarly for CdTe, etc.

$[(CH_3)_3Ga]_x + [(CH_3)_3Al]_{1-x} + NH_3 \rightarrow Ga_xAl_{1-x}N$

So, these are all different precursors and one of the things I mentioned is the formation of gallium aluminum arsenide usually in epitaxial structures of nanometric dimensions that is just obtained by having an appropriate proportion of the gallium precursor which is try methyl gallium, aluminum precursor which is tri methyl aluminum. And then having the reaction with arsene at about 6 to 700 degrees to give us gallium aluminum oscillate of the chosen or desired composition. Similarly, nitrides which are now of course of great technological importance in the context of blue and green sources of light.

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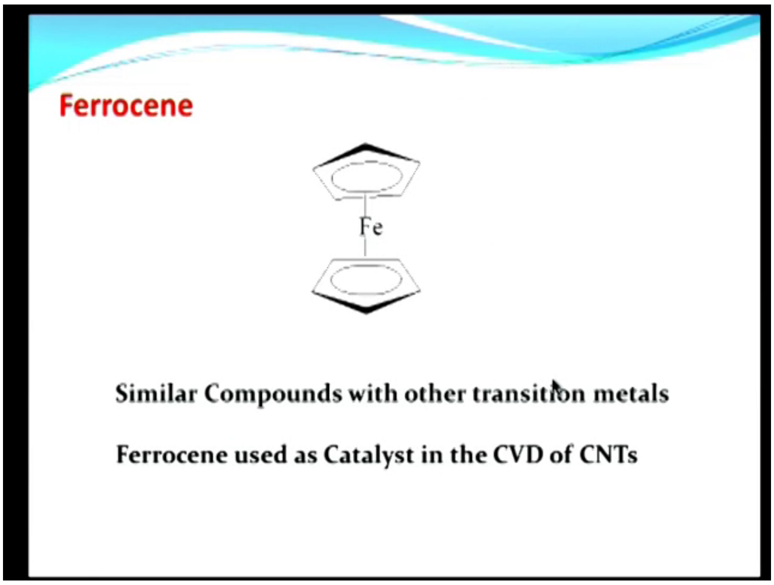

Ferrocene

Similar Compounds with other transition metals

Ferrocene used as Catalyst in the CVD of CNTs

Ferrocene is another precursor has been employed for the CVD of carbon nanotubes.

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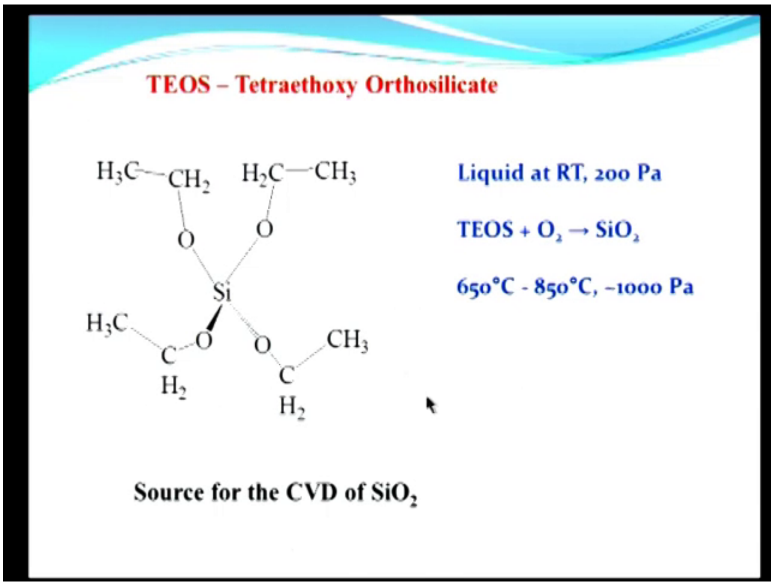

TEOS – Tetraethoxy Orthosilicate

Liquid at RT, 200 Pa

TEOS + $O_2 \rightarrow SiO_2$

650°C - 850°C, ~1000 Pa

Source for the CVD of SiO_2

This you know TEOS - tetraethoxy orthosilicate is widely employed in semiconductor technology to produce Si O 2.

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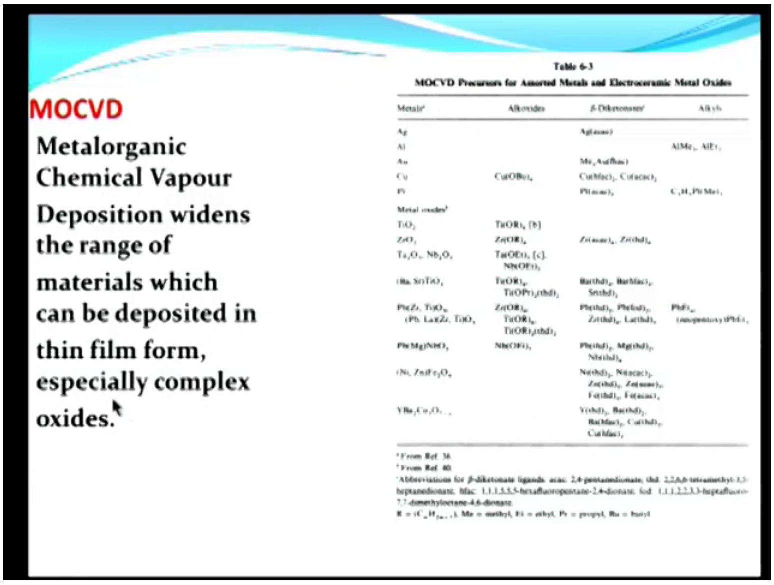

MOCVD

Metalorganic Chemical Vapour Deposition widens the range of materials which can be deposited in thin film form, especially complex oxides.

Table 6-3
MOCVD Precursors for Assorted Metals and Electroceramic Metal Oxides

Metals[a]	Alkoxides	β-Diketonates[c]	Alkyls
Ag		Ag(acac)	
Al			$AlMe_3$, $AlEt_3$
Au		$Me_2Au(hfac)$	
Cu	$Cu(OBu)_4$	$Cu(hfac)_2$, $Cu(acac)_2$	
Pt		$Pt(acac)_2$	$C_5H_5Pt(Me)_3$
Metal oxides[b]			
TiO_2	$Ti(OR)_4$ [b]		
ZrO_2	$Zr(OR)_4$	$Zr(acac)_4$, $Zr(thd)_4$	
Ta_2O_5, Nb_2O_5	$Ta(OEt)_5$ [c], $Nb(OEt)_5$		
$(Ba,Sr)TiO_3$	$Ti(OR)_4$, $Ti(OPr)_2(thd)_2$	$Ba(thd)_2$, $Ba(hfac)_2$, $Sr(thd)_2$	
$Pb(Zr,Ti)O_3$, $(Pb,La)(Zr,Ti)O_3$	$Zr(OR)_4$, $Ti(OR)_4$, $Ti(OR)_2(thd)_2$	$Pb(thd)_2$, $Pb(fod)_2$, $Zr(thd)_4$, $La(thd)_3$	$PbEt_4$, (neopentoxy)$PbEt_3$
$Pb(Mg)NbO_3$	$Nb(OEt)_5$	$Pb(thd)_2$, $Mg(thd)_2$, $Nb(thd)_4$	
$(Ni,Zn)Fe_2O_4$		$Ni(thd)_2$, $Ni(acac)_2$, $Zn(thd)_2$, $Zn(acac)_2$, $Fe(thd)_3$, $Fe(acac)_3$	
$YBa_2Cu_3O_{7-x}$		$Y(thd)_3$, $Ba(thd)_2$, $Ba(hfac)_2$, $Cu(thd)_2$, $Cu(hfac)_2$	

[a] From Ref. 36.
[b] From Ref. 40.
[c] Abbreviations for β-diketonate ligands: acac: 2,4-pentanedionate; thd: 2,2,6,6-tetramethyl-3,5-heptanedionate; hfac: 1,1,1,5,5,5-hexafluoropentane-2,4-dionate; fod: 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionate.
$R = (C_nH_{2n+1})$, Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl

I mentioned metal organic CVD, which is again a particular process of CVD particular version of CVD where metal organic precursors are used such as the acetyl acetonates and so forth that would give films or metals and metal oxides including complex metal oxide as listed here, it is a versatile process.

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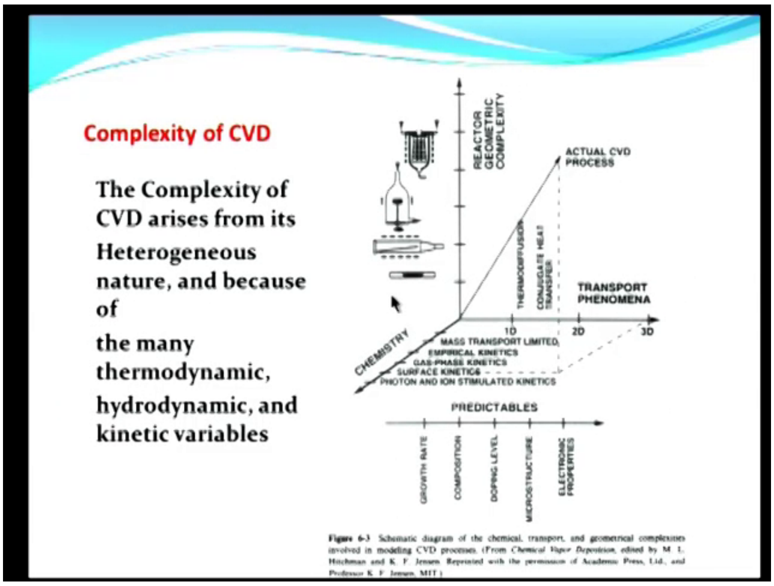

Complexity of CVD

The Complexity of CVD arises from its Heterogeneous nature, and because of

the many thermodynamic, hydrodynamic, and kinetic variables

Figure 6-3 Schematic diagram of the chemical, transport, and geometrical complexities involved in modeling CVD processes. (From *Chemical Vapor Deposition*, edited by M. L. Hitchman and K. F. Jensen. Reprinted with the permission of Academic Press, Ltd., and Professor K. F. Jensen, MIT.)

CVD is a complex process because transport phenomena are involved because gases are flowing, vapors are flowing, there is a whole variety of chemistry and often reactions on the in the gas phase may occur. So, the design of reactors and the geometry of reactors and so on are quite important for the successful execution of chemical vapor deposition to obtain the kind of material that one wants. So, there are thermodynamic factors because there are chemical reactions involved, hydrodynamic factors because there is flow of gases and vapors involved, kinetics involved both because of flow rates as well as because of temperature and the nature of precursors and so forth. CVD is a complex process, but fortunately, it is possible to control it well, model it also to obtain materials of the sort that one wants including very specifically nanostructure material.

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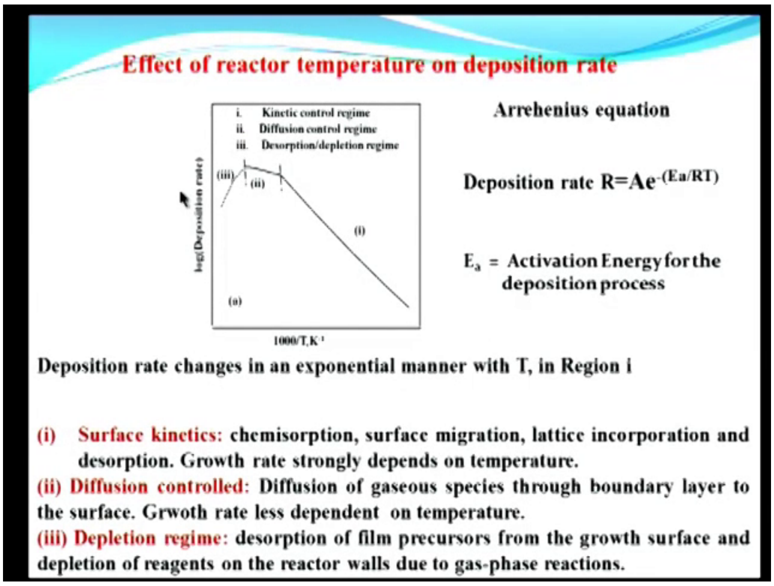

Effect of reactor temperature on deposition rate

Arrehenius equation

Deposition rate $R=Ae^{-(Ea/RT)}$

E_a = Activation Energy for the deposition process

Deposition rate changes in an exponential manner with T, in Region i

(i) Surface kinetics: chemisorption, surface migration, lattice incorporation and desorption. Growth rate strongly depends on temperature.
(ii) Diffusion controlled: Diffusion of gaseous species through boundary layer to the surface. Grwoth rate less dependent on temperature.
(iii) Depletion regime: desorption of film precursors from the growth surface and depletion of reagents on the reactor walls due to gas-phase reactions.

This describes the effect of temperature in an Arrhenius plot how the deposition rate of films in a CVD process varies with temperature, therefore you have because it is an Arrhenius plot you have inverse temperature. So, we are talking about low temperature here and high temperature on the left over here. So, as the temperature is increased, the growth rate increases linearly in this region over here. So, this is the kinetic region at a middle range of temperatures the growth rate is essentially independent of temperature. So, this is the region where one would like to operate the CVD process, where the growth rate is relatively insensitive to temperature.

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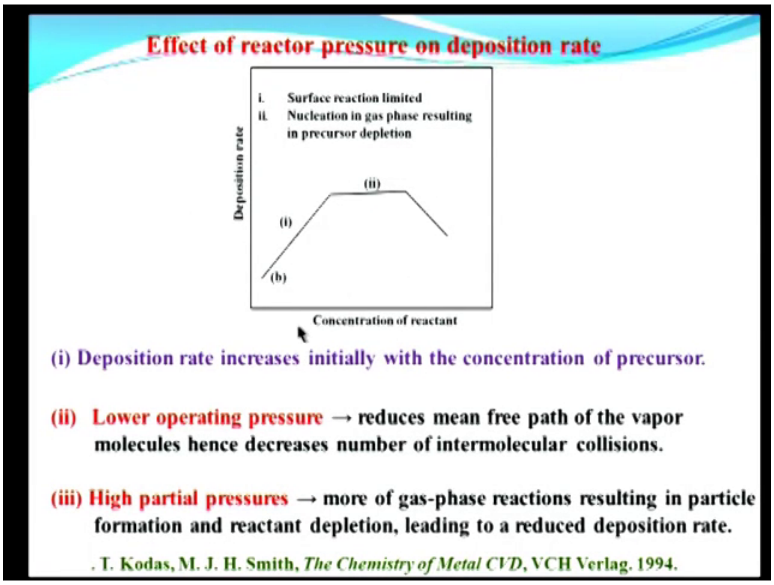

Effect of reactor pressure on deposition rate

(i) Deposition rate increases initially with the concentration of precursor.

(ii) Lower operating pressure → reduces mean free path of the vapor molecules hence decreases number of intermolecular collisions.

(iii) High partial pressures → more of gas-phase reactions resulting in particle formation and reactant depletion, leading to a reduced deposition rate.

. T. Kodas, M. J. H. Smith, *The Chemistry of Metal CVD*, VCH Verlag. 1994.

These are the concentration of the reactant, the vapor pressure of the reactant affects the CVD process. So, again over here where nucleation in the gas phase occurs, this is the region to avoid for the CVD process. One operates in this region, where the deposition rate depends on the concentration of the reactant in a linear fashion. So, since the concentration of the reactant can be controlled quite well, one operates along this region to get the deposition rate one wants in a given process.

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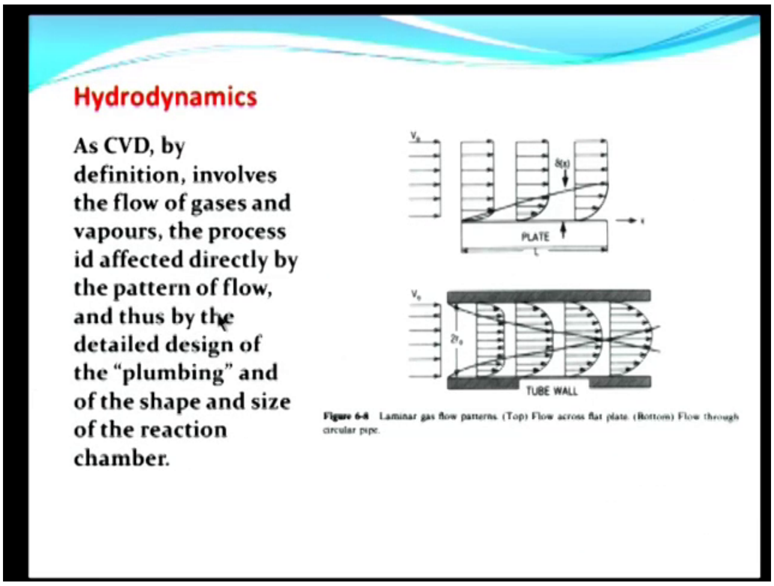

Hydrodynamics

As CVD, by definition, involves the flow of gases and vapours, the process id affected directly by the pattern of flow, and thus by the detailed design of the “plumbing” and of the shape and size of the reaction chamber.

Figure 6-8 Laminar gas flow patterns. (Top) Flow across flat plate. (Bottom) Flow through circular pipe.

Different types of reactors and the involvement of hydrodynamics and the analysis of the hydro dynamics of the reactors to obtain what one wants, and these all of this is very important for the semiconductor industry and gun done with a great deal of care.

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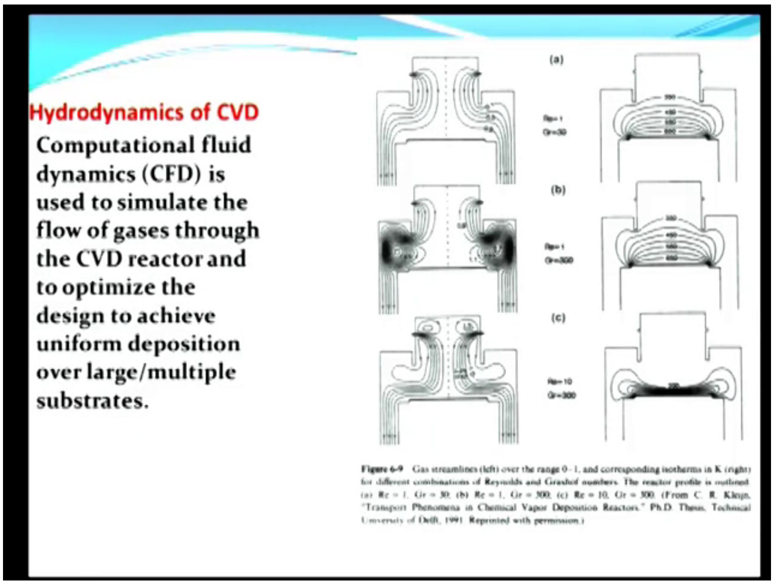

Hydrodynamics of CVD

Computational fluid dynamics (CFD) is used to simulate the flow of gases through the CVD reactor and to optimize the design to achieve uniform deposition over large/multiple substrates.

Figure 6-9 Gas streamlines (left) over the range 0–1, and corresponding isotherms in K (right) for different combinations of Reynolds and Grashof numbers. The reactor profile is outlined (a) Re = 1, Gr = 30; (b) Re = 1, Gr = 300; (c) Re = 10, Gr = 300. (From C. R. Kleijn, "Transport Phenomena in Chemical Vapor Deposition Reactors," Ph.D. Thesis, Technical University of Delft, 1991. Reprinted with permission.)

Again flow patterns and the visualization of flow.

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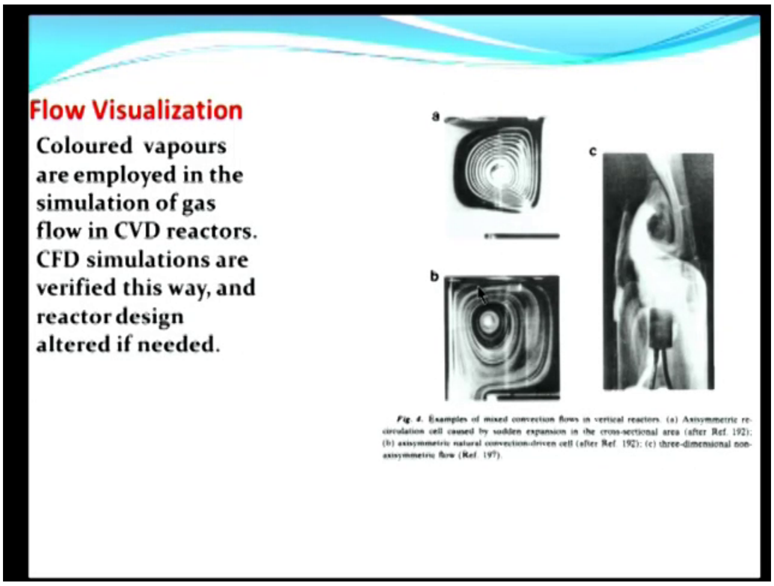

Flow Visualization

Coloured vapours are employed in the simulation of gas flow in CVD reactors. CFD simulations are verified this way, and reactor design altered if needed.

Fig. 4. Examples of mixed convection flows in vertical reactors. (a) Axisymmetric recirculation cell caused by sudden expansion in the cross-sectional area (after Ref. 192); (b) axisymmetric natural convection-driven cell (after Ref. 192); (c) three-dimensional non-axisymmetric flow (Ref. 197).

So, that one can design these things properly to obtain uniform films and so forth.

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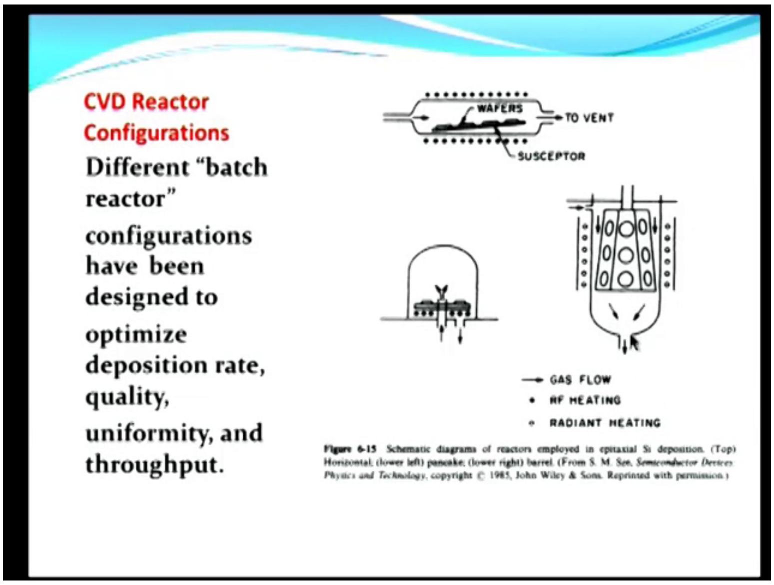

CVD Reactor Configurations

Different "batch reactor" configurations have been designed to optimize deposition rate, quality, uniformity, and throughput.

Figure 6-15 Schematic diagrams of reactors employed in epitaxial Si deposition. (Top) Horizontal; (lower left) pancake; (lower right) barrel. (From S. M. Sze, *Semiconductor Devices Physics and Technology*, copyright © 1985, John Wiley & Sons. Reprinted with permission.)

Different kinds of configurations to obtain multi substrate reactor over here and so forth, so these are all different versions of the reactor to obtain CVD films.

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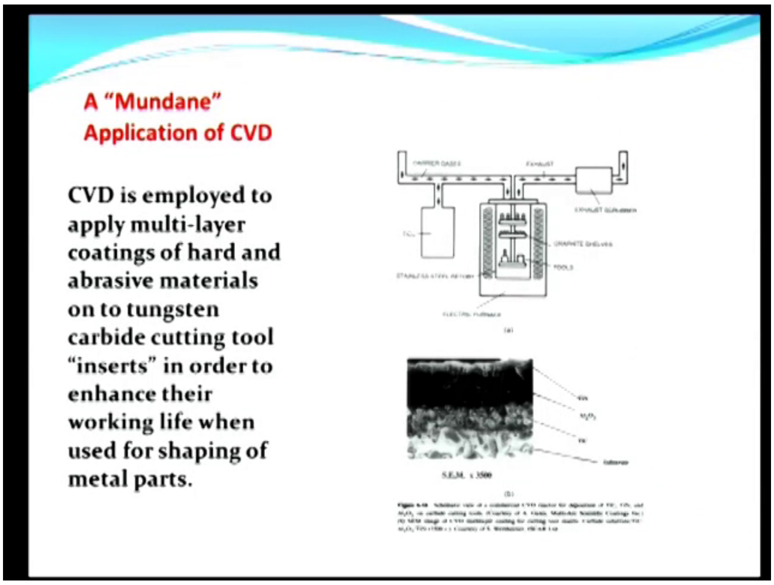

A "Mundane" Application of CVD

CVD is employed to apply multi-layer coatings of hard and abrasive materials on to tungsten carbide cutting tool "inserts" in order to enhance their working life when used for shaping of metal parts.

This is again a demonstration of the capability of CVD to provide us with conformal coverage. Now, so far we have dealt with CVD in the context of height technology applications, but CVD is also obtained used to obtain cutting tool coatings for the machine shop actually. So, it turns out CVD is very effective in obtaining multi layer coatings aluminum oxide and carbide and nitride and so forth to enhance the two life in cutting tool operations. So, CVD is used in such a much more mundane process as well.

We will conclude therefore, today. So, what you have dealt with today is to review some general aspects of nanomaterials by the physical vapor by physical methods. And then we went onto discuss carbon nanostructures, and how carbon nanostructures in particular carbon nanotubes and how carbon nanotube property is depend on the configuration carbon nanotubes. And the production of carbon nanotubes by the chemical vapor deposition process and then we went onto review the general aspects of chemical vapor deposition process, and how it has advantages of the physical vapor deposition process and certain applications of the chemical vapor deposition process both in high technology. And what we just mentioned at the end in mundane technology. We will continue with this discussion next time and then go onto discuss the analysis the characterization of nanomaterials by different methods.

Thank you.