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

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Module - 2
Lecture - 7
Synthetic Methodologies (Contd.)

Welcome back to this course on nano structured materials, synthesis, properties, self assembly and applications. This is the 5th lecture of model II. We have earlier done 4 lectures of model II in which we have looked at two synthetic methodologies using the Sol-gel method, and using the micro emulsion method. This lecture we will be starting with CVD technique which is chemical vapor deposition, where we will be using this method to make nano structured films.

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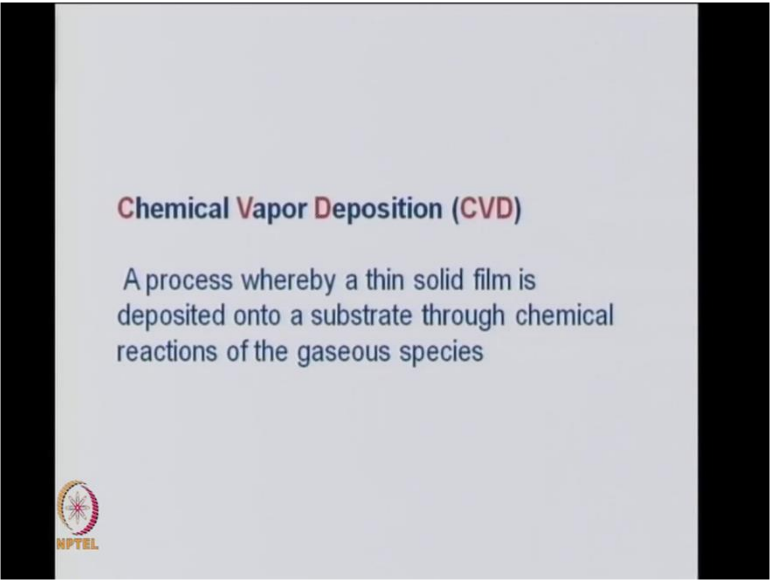

So, chemical vapor deposition is a process whereby a thin solid film is deposited onto a substrate through chemical reactions of the gaseous species. So, you have a substrate which is solid and you will have, you want to deposit a thin solid film starting from a chemical precursor from which you generate gaseous species, and they will condense onto a substrate and give you a thin solid for which is nano structured.

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So, why do we want to study thin films or deposition processes for thin films? It is because these single and multilayer films and coatings have a lot of applications. We want to synthesize nano layered materials, we want to synthesize optical films for transmission and reflection studies, you can make decorative films for various purposes.

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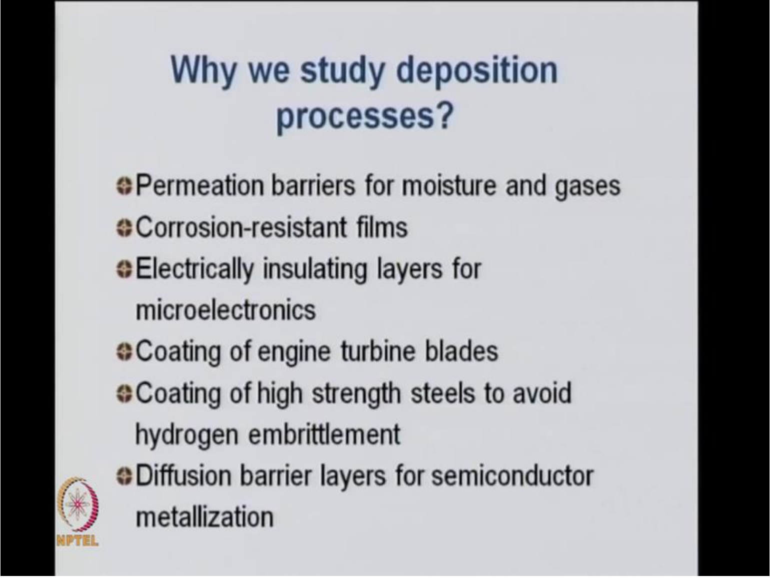

You can also make functional coatings which are having severe resistance or some other function. For all these type of films, we can use such deposition techniques like the CVD method. You can also make permeation barriers for moisture and gases, so that they do

not enter. Once you have this coating, moisture and gases cannot enter. You can have corrosion resistant films. For example, you can have some metals which normally get corroded in oxygen or in the presence of water vapor, and if you make a film which is resistant to corrosion, then you can protect those metals, you can make electrically insulating layers for microelectronics. So, you have electrical wires which you want to insulate from joining wires. You can make insulating layers, you can make coatings of engine turbine blades to enhance their longevity and life, you can coat high strength steels to avoid embrittlement using hydrogen. Normally, hydrogen needs that brittleness in the steels. So, you can avoid that by coating some material using the CVD technique. You can make diffusion barrier layers for semi-conductor metallization.

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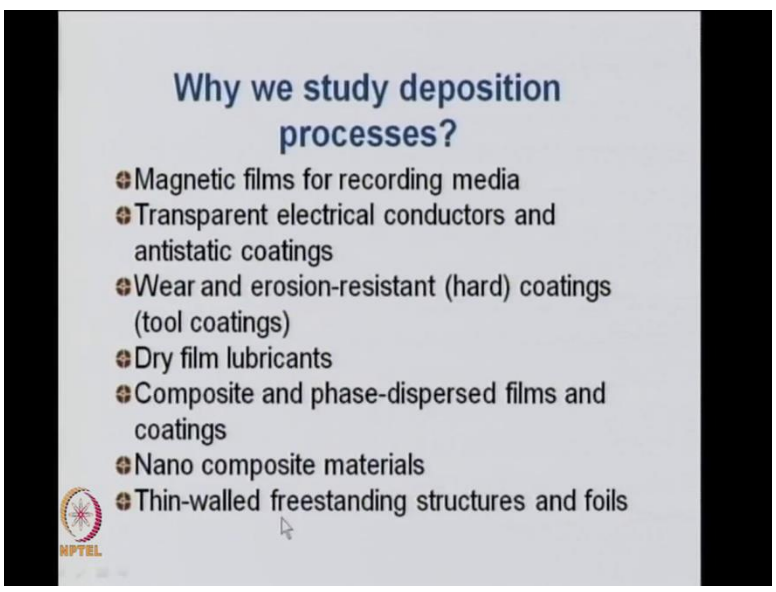

You can make magnetic films for various kinds of recording media like DVD's or many other kinds of regarding media. You need magnetic films and these can be processed using CVD technique. Transparent electrical conductors are required in several places and antistatic coatings are required. You can make as we discussed wear and erosion resistant hard coatings on tools.

So, the tools which are used for heavy duty work, they do not get warm. You can make coatings of certain materials on top of those tools. Then, you can make films which can act as lubricants. So, these are called dry films lubricants. Then, many other composite films, nano composite films can be made and thin walled freestanding structures and

foils which are to be used elsewhere which are very thin and can be made by the CVD technique.

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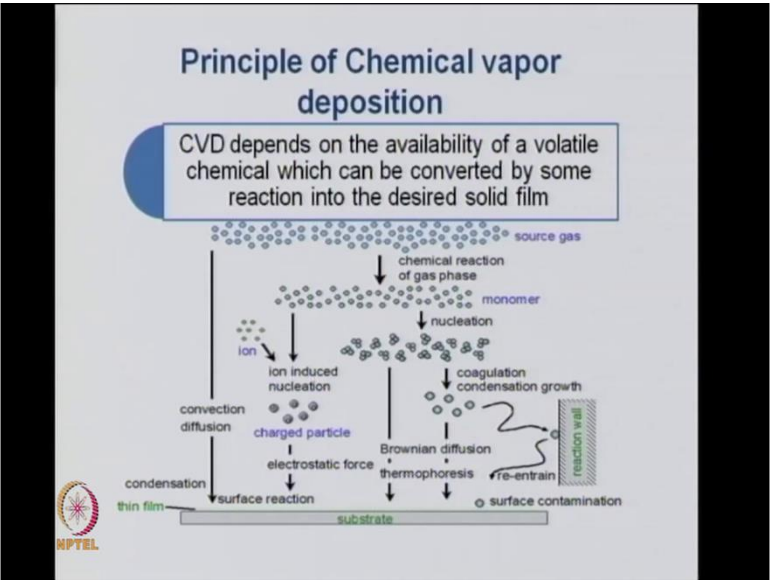

So, what is this CVD? A technique that is the chemical vapor deposition technique. What is the principal? So, typically CVD technique depends on the availability of a volatile chemical which normally we call the precursor, the chemical precursor. It is normally a liquid solution which can be converted by some reaction into the desired solid film.

So, ideally you have a source gas and the source gas undergoes a chemical reaction, and forms some monomers. These monomers nucleate to form some oligomers here, and this is one process where the oligomers can coagulate and condense become large particles and they undergo Brownian diffusion etcetera, and thermophoresis and then, fall on the substrate or they can be these monomers which form from the chemical reaction of the gaseous phase. This can be targeted using irons and that is called iron induced nucleation. So, you target these monomers which are formed from that gas phase which has been generated from your volatile chemical that if you bombard with irons, you get iron induced nucleation and this iron induced nuclear, nuclei are charged particles and then, you can apply an electrostatic force on the charged particle and direct them onto this substrate.

So, by that method also you can make coating. So, you have this substrate. A substrate can be a disc which is polycrystalline or which is single crystalline and on top of this substrate, these molecules will start adhering and condense and will result in a thin film.

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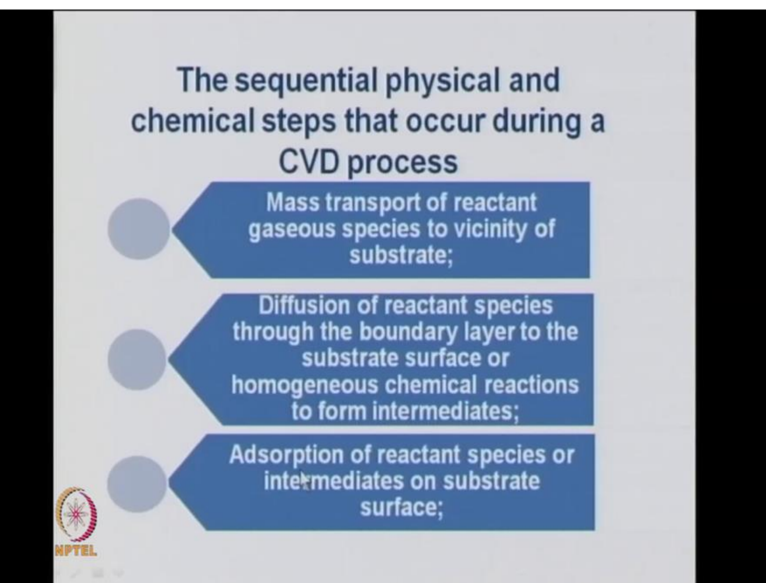

Now, the various steps that occur in a CVD process, both physical and chemical steps are as follows. You have mass transport of the reactant gaseous species, so that volatile precursor gives out gaseous species and these gaseous species are transported. So, there is mass transport near close to the vicinity of the substrate. So, that mass transport is important. We have to move these gaseous molecules which are coming from the precursor which may be liquid, where the liquid which normally liquid or solution and then, those gaseous molecules are transported close to the substrate. The next thing is diffusion of these reacting species through the boundary layer to the substrate surface or homogeneous chemical reactions to form intermediates. That is another part of the CVD process, and then absorption of the reactant species or intermediates on the substrate surface. So, these are mainly some of the key steps which occur during the CVD process.

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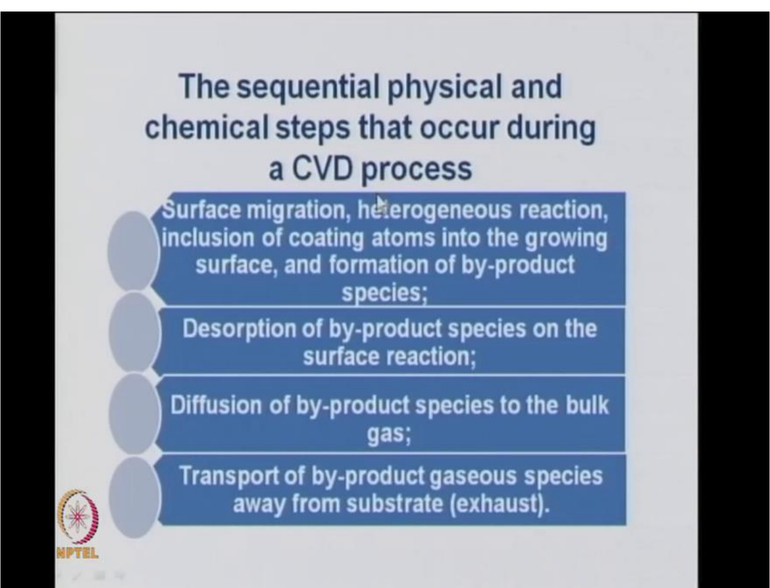

After that you may have surface migration. That means the clusters or monomers or our oligomers which are coming onto the substrate migrate on the surface of the substrate, they may undergo heterogeneous reaction. There may have inclusion of coating atoms into the growing surface and it may also form byproduct species. These byproducts species are then desorption from the surface, and then diffusion of the byproduct species to the bulk gas and transport of the byproduct gaseous species away from the substrate through an exhaust.

So, these are subsequent steps after the charge nuclei or neutral monomers or oligomers come onto the substrate surface. Then, the surface migration and subsequent reactions and desorption of the byproduct take place, and the byproduct has to be eliminated are transported away from the substrate.

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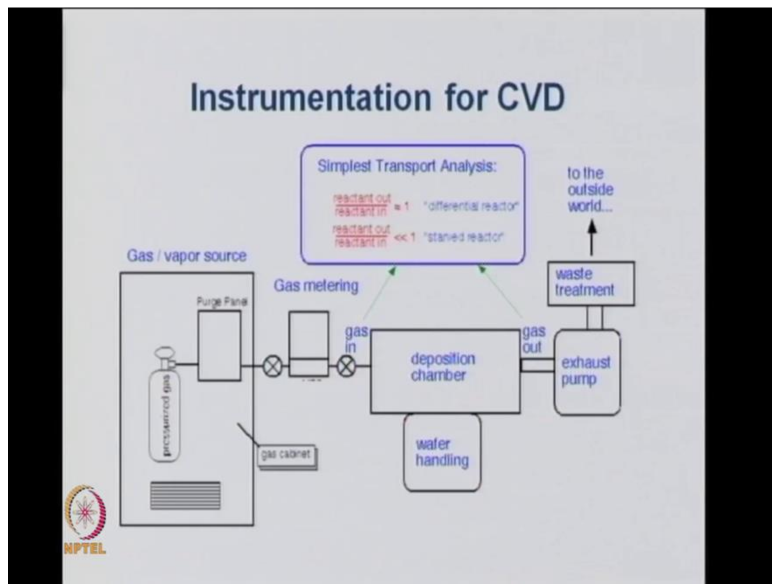

Now, if you look at the instrumentation required for chemical vapor deposition, you have the gas or the source for the vapor. So, it may be liquid or some source and there is a panel, where you use for purge, and then it goes to some meters where you can control the flow of gas in around.

So, there is this in and then, it is out and then, again the gas is sent to the final deposition chamber, where the substrate or the vapor. If it is a silicon substrate or a silicon vapor, we call it can be a quad substrate. There can be many substrates in this deposition chamber. So, the molecules have to come from the pressurized gas liquid which for if there is a liquid, then the gases molecules have to be generated and then, go through this various walls where you can control the flow of the gas inside the deposition chamber and typically, there are two types of transport analysis. One is when the reactant which is coming out and the other which is going in the ratio nearly 1 raise to 1.

So, that is called differential reactor. However, if the reactant coming out is much less, then what is going in is called a start reactor. So, this gas in and gas out the ratio of this leads to these two times. The differential reactor and the start reactor and the exhaust gases are taken out from the exhaust bomb, and if they are toxic, they have to be treated in the waste treatment before releasing less toxic gases outside. So, this is a schematic diagram of a typical chemical vapor deposition process, where you have the gaseous

source, the walls and the deposition chamber, the exhaust and the release of the waste gases.

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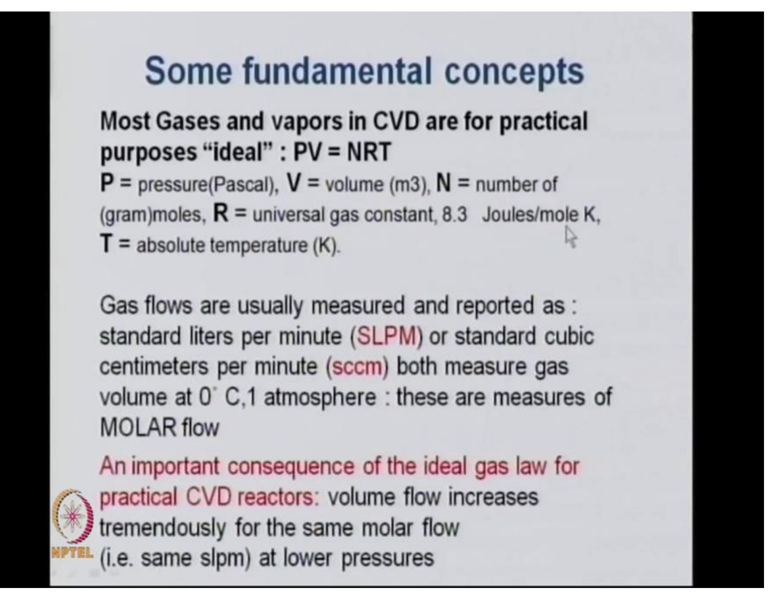

Now, to understand the physics and chemistry of the chemical vapor deposition, we have to undergo or understand some of the basic principles of physical chemistry or gas laws which are involved during this process of the gas molecules, going on top of the substrate, and what kind of nucleation or whether it is a homogeneous or heterogeneous nucleation and how the growth of the film takes place, etcetera. So, the basic concept in CVD starts from approximating the gases and the vapors that you use to be ideal. So, they obey the ideal gas law.

So, this is an approximation and ideal gas law as all of you know is PV is equal to NRT, where P is pressure, V is volume, N is number of moles the gas, R is the universal gas constant and T is the absolute temperature in Kelvin. So, the units are important. So, when you are taking volume in meters, the volume unit is meter cube and then, you have to take the R, the gas constant in SI units which is 8.3 joules per mole Kelvin. So, these are typical quantities one needs to know to apply the ideal gas law which is important for understanding CVD process.

The gas flow as you know will have to flow gases through these walls etcetera. So, there gas flow is very important and that gas flow are usually measured and reported as either standard liter per minute, which is SLPM or standard cubic centimeters per minute which

is sccm. So, these commonly you will find number. So, many slpm, so many sccm. So, these are units to tell you about the rate of flow of the gas going through the reactor. So, slpm and sccm, both are related to the gas flows and they measure gas volume at zero degrees celcius and one atmospheric pressure.

So, these are measures of the molar flow gases through the reactor. An important consequence of the ideal gas law is for CVD reactor is that volume flowing increases tremendously for the same molar flow at low pressures. So, volume flow will increase significantly at no pressure at the same slpm. So, if you have the same slpm, that is the same flow standard liters per minute same slpm, but when you change the pressure from high pressure to low pressure, the amount of volume flow will increase tremendously.

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USEFUL CONVERSIONS

1 atm = 760 Torr = 101,000 Pa, 1 Pa = 7.6 mT

1 cubic meter = 1000 liters = 1E6 cm^3, K = C + 273

1 mole = 22.4 liters at "STP" (0 C, 1 atmosphere)

1 liter = 0.045 moles at STP

1E6 = 1×10^6

1 cm^3 = 4.5E-5 moles @ STP

1 cm^3 = 6.4E-8 moles @ 1 Torr, 23 C

1 A/minute = 1.6E-10*(molar density) moles/(cm^2 sec)

1 SLPM = 7.4E-4 moles/second

1 sccm = 7.4E-7 moles/second

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There are some other useful conversions one needs to know which are normally available in text books or in all kinds of manuals, where CVD is discussed and these are present in many other text books of physics and chemistry or material science, and one needs to know these conversations, because many times you have to convert pressure safer from atmosphere to Torr or to pascals, and you need to know this conversion factor. So, this is for pressure volume and then, you have 1 cc is equal to stp.

Similarly, this rate of being suppose you have how many moles per centimeter square is falling in one minute, so that is this number one per minute. How many molecules or moles per unit area is falling per minute on particular substrate that is given by this

quantity, and what we just described the gas flow as 1 SLPM and 1 sccm, they arguing here and you see 1 SLPM and 1 sccm are different and they are one thousand times different. This is 1 SLPM is one thousand times 1 sccm.

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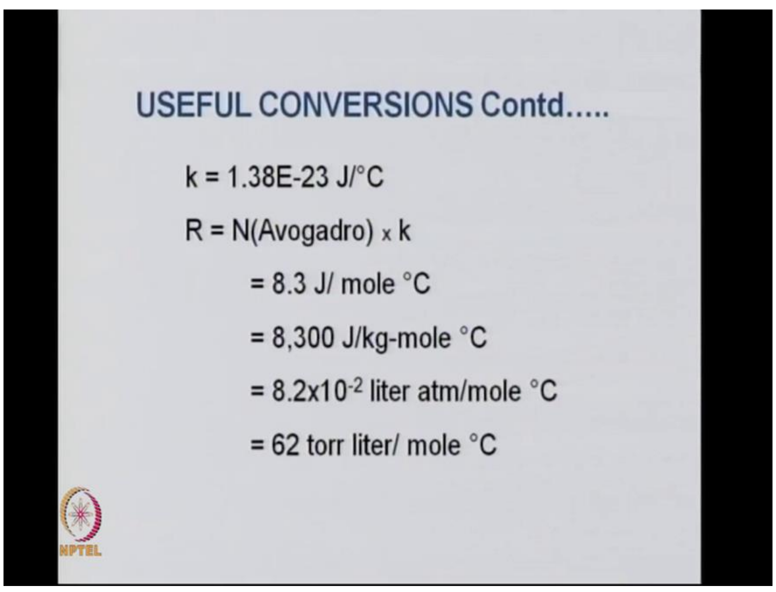

Now, some other useful conversions are between the Boltzmann constant k, and the universal gas constant r which can be written in several different units and one has to be careful when you are doing mathematical problems converting numbers from one unit to another unit. You need to be careful what to take the value of R. The value of R can be 8.3 or 62 depending on what units you are taking. So, these conversions are useful in doing some calculations with respect to pressure volume and basically, using the ideal gas law to understand the gas flows, etcetera. Now, the next thing that we try to understand because gas molecules will be flowing.

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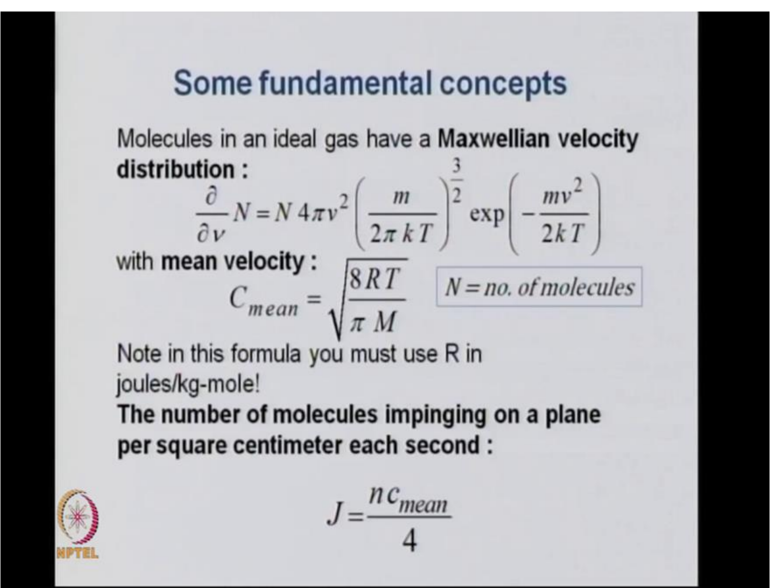

So, we have to understand the velocity of these molecules assuming that this is an ideal gas and hence, it will have Maxwellian velocity distribution. So, that is given by the rate of change of the number of molecules, where N is the number of molecules as with respect to velocity that is given by this quantity and as you see there is a term, where temperature to the power minus 3 by 2, and also there is an exponential with minus 1 by T. So, this is the Maxwellian velocity distribution and this will be the distribution of the gas molecules as assuming that it is an ideal gas, and from there we can calculate the mean velocity of these molecules which is given by C mean to be the square root of 8RT by pi M, and for this R must be in joules per kilo gram per mole.

Now, from this, then we can calculate the number of molecules which are falling on a plane which is say 1 square centimeter and in one second. So, that can be calculated as j which is the number of molecules impinging on a plane per square centimeter per second and that is given by this number c mean by 4, where the small n is the molar volume and c mean is the velocity. Here the mean velocity divide by 4 will give you the number of molecules which are falling on a plane per square centimeter per second.

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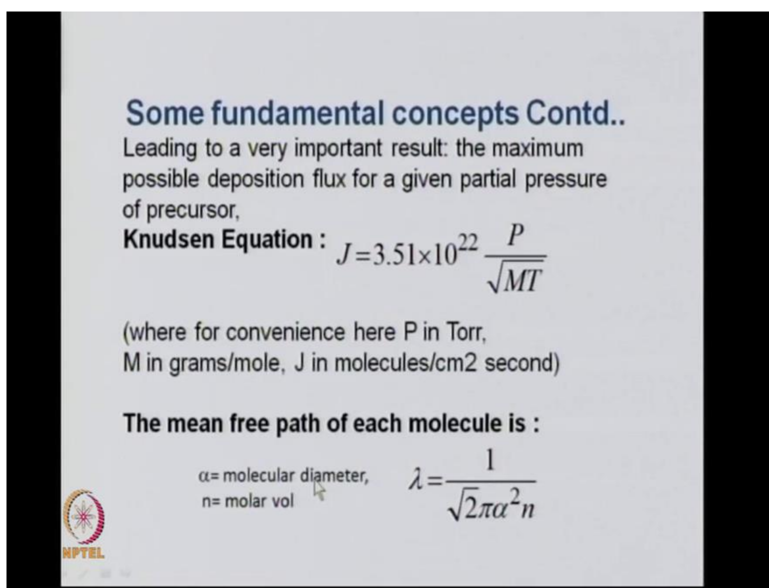

Now, from that we calculate something which is very important or which is the maximum possible deposition flux for a given partial pressure. So, given a partial pressure P, what is the maximum deposition flux that we can have and that is J is given by this equation. And you know at some pressure P and temperature T for a gas, where with the molecular weight M, which is given in grams per mole, you will have the J which is the maximum deposition flux by this equation.

Now, the another quantity which is important is the means free path of each molecule, that is the distance molecule travels before it is hit by another molecule. The means free path given by lambda is given by this equation, where the mean free path is now inversely proportional to the square of the molecular diameter and also, inversely proportional to the molar volume.

So, N is the molar volume and alpha here is the molecular diameter and the mean free path is related to it. That means, the smaller the molecular diameter. So, smaller the molecule where large will be mean free path. That means, the molecule will be moving without collisions for much longer distances if the molecule is smaller, right. Similarly, the molecule will be moving much longer distances if the molar volume of the molecules is smaller. So, lambda, the mean free path is inversely proportional to both molecular data and the molar volume.

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Some fundamental concepts

Pressure	Density	mean free path	mean velocity	flux to surface	"growth rate"
Torr	molec-ules/cm^3	microns	cm/sec	Molecul-es/cm^2 sec	microns/ minute
0.1	3.2E15	500	47,000	3.8E19	10
10	3.2E17	50	47,000	3.8E21	1000
760	2.5E19	0.07 (70 nm)	47,000	2.9E23	77,000

Now, from these we can now compare some situations like if you compare three different pressures for the same gas. You have a pressure of 0.1 Torr, 10 Torr and 760 Torr. So, if you assume these three pressures, we can calculate what will be the densities of this order and the mean free path at this pressure is around 500 microns whereas, at a higher pressure of 760 which is normal atmospheric pressure, you will have a mean free path of around 0.07 microns which is equal to 70 nanometers. So, as the pressure is increasing, the mean free path is decreasing. Similarly, the mean velocity is kept constant at 47000 at these pressures and you can calculate how many molecules will be impinging on a surface under these different pressures.

So, at low pressures, you will have less number of molecules impeaching per second which is say of the order of 10 to the power 19 whereas, at atmospheric pressure at 760 millimeter pressure of the seam gas keeping the mean velocity same, you will have 10000 times more molecules impinging on the surface. So, depending on the number of molecules which are falling on the surface per unit time if that is large, then the growth rate will be larger and that is seen here that their number of molecules falling on a surface per unit time here is much less than here, and you see the growth rate how much thickness the film grows per minute, that is the thicknesses in microns.

So, how many microns per minute does the film grow can be compared under these three conditions of 0.1 Torr of pressure. You have 10 micron thick film growing per minute. If

you increase the pressure to 10 Torr, this thickness goes up to 1000 micron per minute and at atmospheric pressure, it is an enormous number of 77000 microns per minute. So, you have kept the same mean velocity, but you have changed that pressure of the gas and the other parameters change and finally, what you require is the film and the thickness of the film you can control by controlling the partial pressure of the gas.

So, this slide shows you how some of these numbers change by changing the partial pressure of the gas. As you are going from low pressure to high pressure, you can change the thickness of the films which is the right control that you want on the growth of the film's using the CVD technique.

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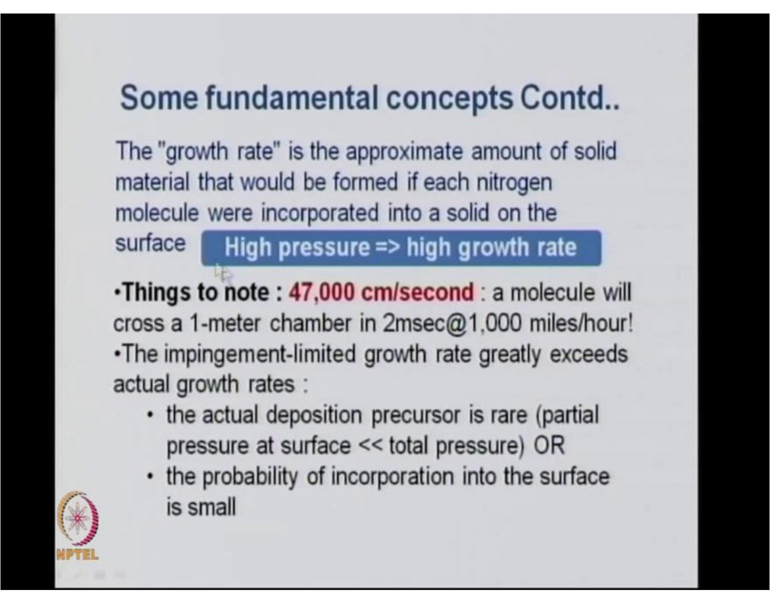

Now, the growth rate that we just now discussed shows this is the key point. It shows those numbers is that high pressure leads to high growth rate. So, at one thing what we have kept here is mean velocity of around 47000 centimeters per second. What it really means? 47000 centimeters per second means that a molecule will cross one meter chamber.

So, if you have one meter chamber in which you are doing this experiment, the molecule will be moving if you say at 2 meters per second. So, in 2 meters to millisecond, a 1 meter long chamber molecule will be moving into milliseconds at 1000 miles per hour. So, that will be the kind of speed. If you change the units here of 47000 centimeter per second to a mile per hour, you will get a speed of around 1000 miles per hour. So, this is

the kind of speed of molecules that you are talking when you are studying the impingement of gaseous molecules on the substrate or on the target.

Now, the impingement limited growth greatly exceeds actual growth rates. That means, whatever we have calculating is much larger. So, what we are showing here is 10 microns, but a minute this is the calculated growth rate. In reality, this will be lesser in actual experiment and the reason is that the actual deposition will not be the same because the partial pressure adds the surface will be less than the pressure inside, total pressure inside the gas. The other probability is that there can be the incorporation of the gases molecules on to the surface is small. So, there are two things. One is that the partial pressure what we are assuming for the total gas is not same, and the actual partial pressure at the surface is much lower or the probability of incorporation onto the surface of these gaseous molecules is small.

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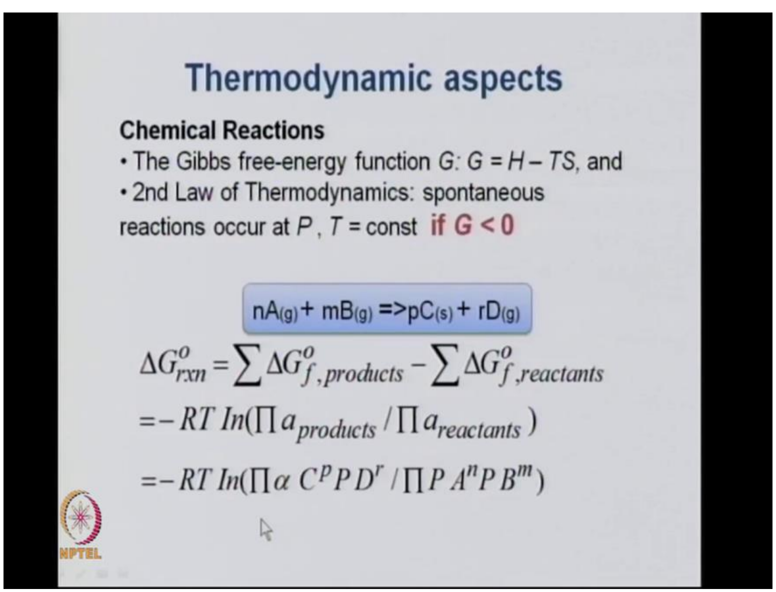

The other thing that we have to discuss, so we discuss some fundamental concepts using Maxwellian distribution of the velocities of these gaseous molecules, and assuming ideal gas behavior. Then, we also have to consider the power dynamic aspects. So, if some chemical reactions are going on, we have to incorporate the Gibbs free energy function which is G and is a function of enthalpy and entropy which is S and the relation between free energy enthalpy and entropy is given here, where T is the temperature.

By the second law of thermodynamics, a spontaneous reaction will occur at a pressure P and temperature T kept constant if the free energy is less than 0. So, this is a standard second law of thermodynamics. So, if you have any chemical reaction which is going to happen during the formation of the film, it has to obey this relation of free energy going to be less than 0 and the free energy calculation is done typically like this. For example, consider a reaction where a gaseous, the molecule of n moles of A react with m moles of another gaseous system B to give p moles of a solid say C which is the thin film which will form r moles of another gas say D.

Now, the delta G of the change in the free energy or the change of the free energy of the reaction is the free energy of the product minus the free energy of the reactants is a standard free energies. Delta G is not delta G naught and that can be equated to minus RT In. The product of the activities of all the products divided by the product of activity of all the reactants. So, if there are two products, it will be A 1 and A 2 multiplied and if there are two reactants say A 3 and A 4. So, this is A 3 multiply by A 4. That means the activity of 3 and activity 4 and that gives rise to a question like this. From here you come here because you have been given this reaction.

So, if A is water and B is ammonia, then accordingly you have to choose the concentration or activity of water and ammonia leads to the stoichiometric or the mole ratios in which they are reacting. So, here n moles are reacting. So, the activity of A will be raise to the power n, where n is the number of moles, A reacting with number of m moles B. So, here in the product of the activities, you will have B to the power m.

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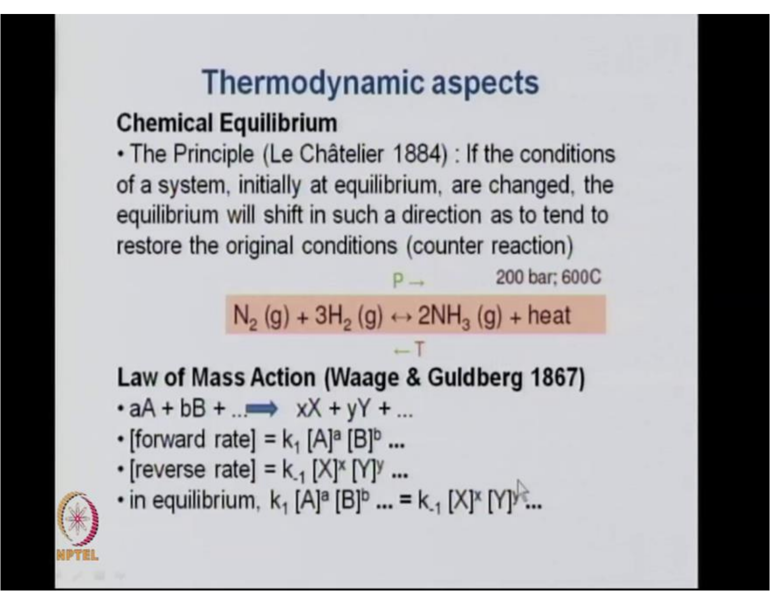

The other important thermodynamics aspect is well unknown. Chemical equilibrium principal given by Le Chatelier that if the conditions of a system initially at equilibrium are changed the equilibrium will shift in such a direction as to tend to restore the original conditions. So, what happens typically in reactions, where gaseous molecules are involved? You can assume this reaction which is well known reaction for the ammonia formation, where all three reactants and products or gaseous species. So, you have nitrogen gas, hydrogen gas and ammonia gas. This reaction at under high pressure moves the equilibrium towards the right side. At high temperature, it moves the equilibrium towards this side. So, that is basically Le Chatelier principle because it says that the equilibrium will shift in such a way if you change something.

So, you change pressure, you go from one pressure to high pressure, the equilibrium will shift and more of ammonia will be formed from nitrogen and hydrogen. If you lower the pressure or you increase the temperature, then some of the ammonia will dissociate to give nitrogen and hydrogen. That means the equilibrium is shifting to the left side. So, this is a very important principal given by Le Chatelier and is very important wherever gaseous species are involved to understand how the chemical equilibrium will shift in when you change pressure or temperature in a particular manner.

Now, you can write down these reactions which are the law of mass action for the forward reaction, and the reverse reaction and you can write down at equilibrium that the forward reaction will be equal to the backward reaction.

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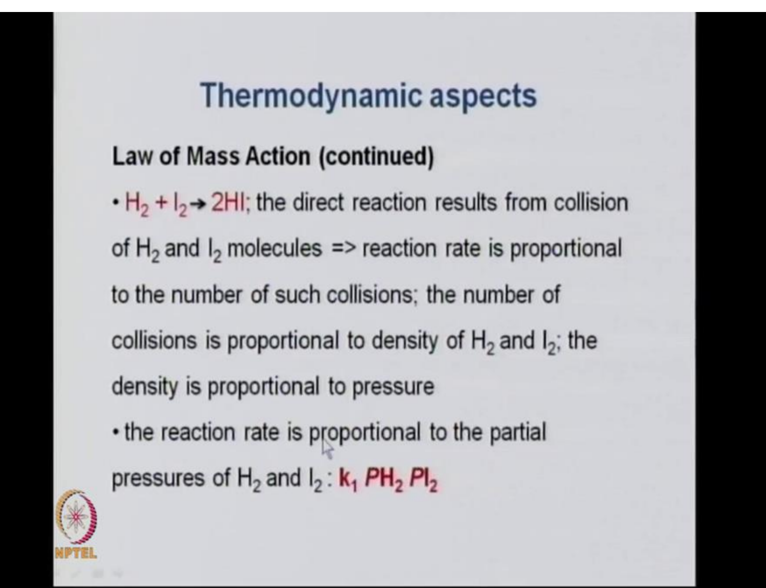

This is an example of that was the one we showed was nitrogen and hydrogen reacting to give ammonia, and these another reaction where hydrogen and iodine are giving you hydrogen iodine, and the reaction is basically due to the collision of hydrogen and iodine molecules and the rate of reaction. How fast the reaction will happen is proportional to the number of such collisions and the number of collisions is proportional to the density of the hydrogen gas and the iodine gas. So, the density is proportional to pressure and hence, finally it boils down to the reaction rate is proportional to the partial pressures of hydrogen and iodine.

This is the reaction rate, where the reaction rate is proportional to pressure. That means, you can write it as equal to constant k1 and multiplied by the partial pressure of hydrogen multiplied by partial pressure of iodine. That will give you the rate of the reaction. So, a partial pressure of the gaseous species is important.

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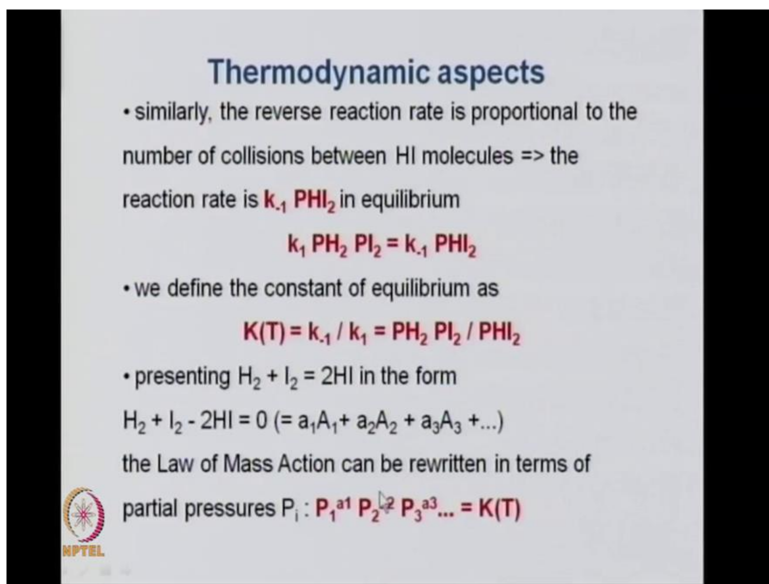

Now, similarly the reverse reaction rate will depend on the reverse constant k minus 1 and will depend on the partial pressure of HI which is in equilibrium. Now, we can define this just like redefined earlier the equilibrium constant which is a function of temperature taking a ratio of k minus 1 by k 1 and being shown by this, the partial pressures of the product and in the reverse reaction, the product is hydrogen and iodine gas divided by the partial pressure of the reactant gases. In this case, it will be hydrogen and iodinate.

So, you can write it down as this kind of reactions and find out the equilibrium constant of course which function of temperature is. So, at a particular temperature, you will have one particular equilibrium constant. Now, this law of mass action can be written in terms of partial pressures and the partial pressures of this particular reaction, where this is equal to one small a 1 multiplied by capital A1 plus small a 2 multiplied by capital A2. This can be rewritten as a product of the pressures raised to the powers of these coefficients a1, a2, a3, etcetera, and that product will give raise to the equilibrium constant at a particular temperature.

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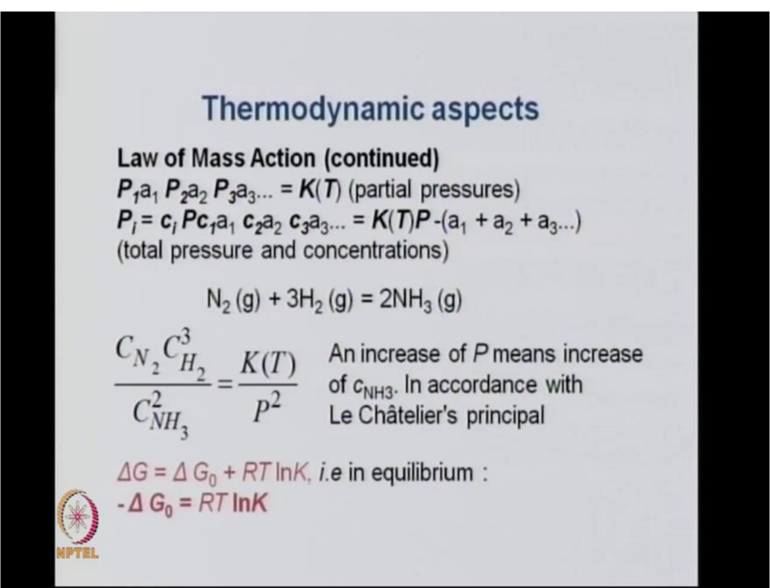

So, if you continue on this product which is equal to the equilibrium constant for ammonia, we can rewrite like this and from instead of activities, then we choose concentrations for certain cases where we can take the activity to be equal to the concentration. We can rewrite this equation in terms of concentrations, and you can find out that K is related to the concentration of the nitrogen and hydrogen and ammonia by P square. So, an increase of P here means increase of ammonia. So, if you increase P, the concentration of ammonia will increase, and this is in accordance with Le Chatelier principal. Ultimately delta g of course is given by minus RT InK or minus delta G naught is given by RTI and nK, these are very useful equation.

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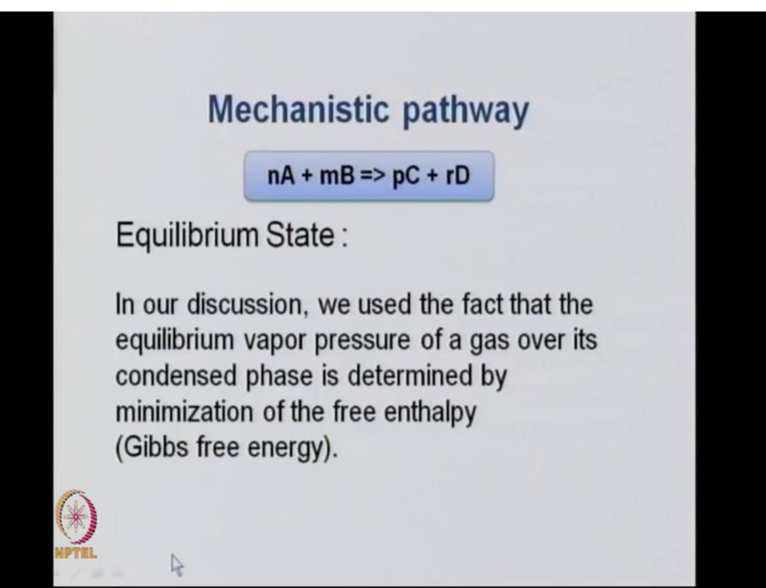

Now, to understand the mechanism at the equilibrium used, we understood this reaction of n moles of A plus m moles of B reacting to form p moles of C and r moles of D. We use the fact that the equilibrium vapor pressure of a gas over its condensed phase is determined by the minimization of the free enthalpy of the Gibbs free energy now.

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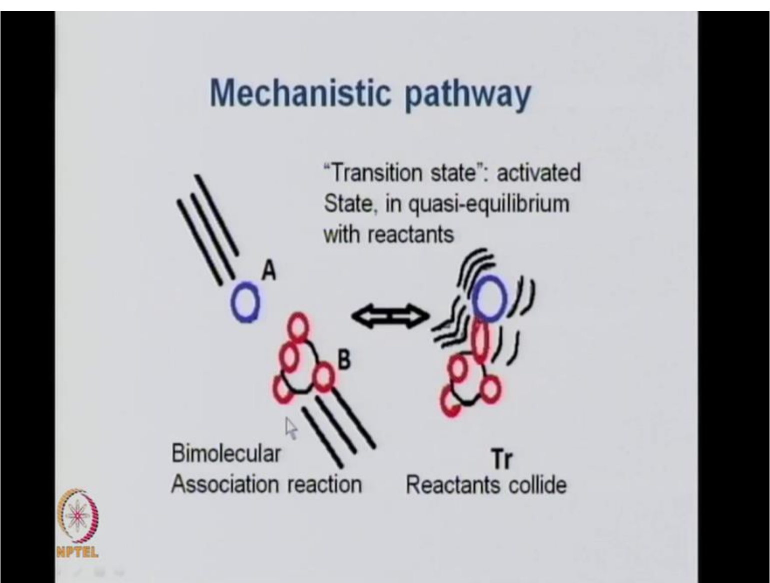

So, this can be shown in this way. This is the mechanistic pathway, where you have a molecule interacting with the molecule and it undergoes by molecular dissociation

reaction, and it forms a transition state which is in quasi equilibrium with the reactants. So, you have A and B forming this transition state, where A and B are collided.

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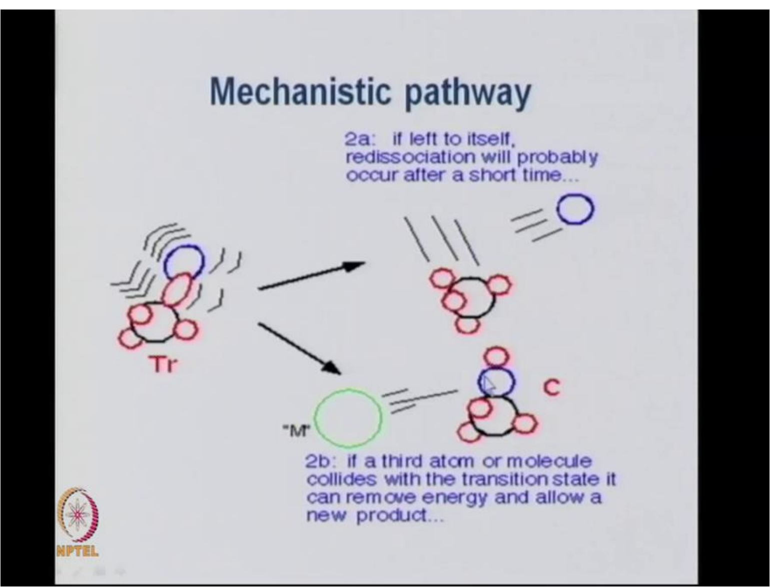

Now, the next step from the transition step, where A and B have collided that can be two ways that the reaction can proceed. One is it may dissociate back to give you A and b, or because this has some extra energy than A plus B, this can transfer its energy to some other molecule and the entire unit can remain as such which is C. So, the third atom which is m here can collide with the transition state and take away this excess energy and give back this new product, which is a combination of A and B or the other simple ways it falls back to the original state of energy with A and B dissociated. So, if you fall from the transition state, you can go back to the original reactant state or from the transition state, you can go to the product with a new molecule by the interaction through third molecule which takes away part of its energy.

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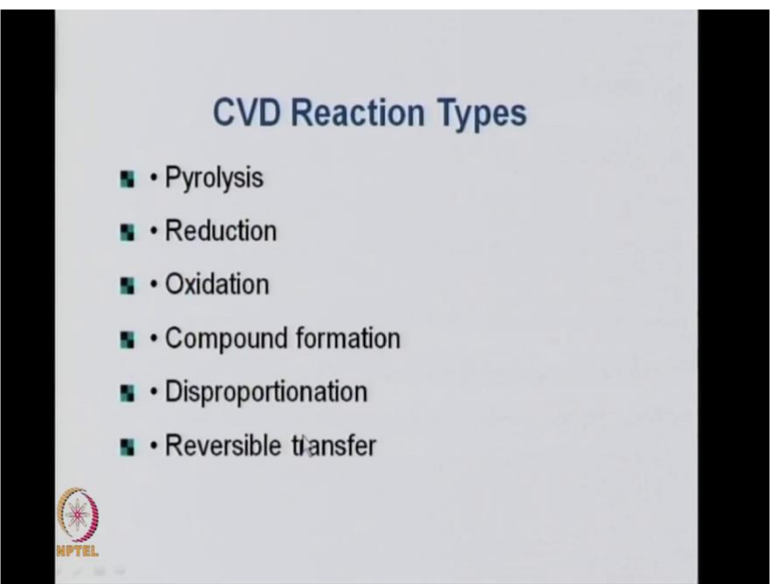

Now, there are various methods of doing CVD. One is the pyrolysis method and then, you have a reduction, then oxidation and compound formation. You can have disproportionation reaction or reversible transfer reaction. So, there are varieties of methods by which you can do these chemical vapor deposition techniques.

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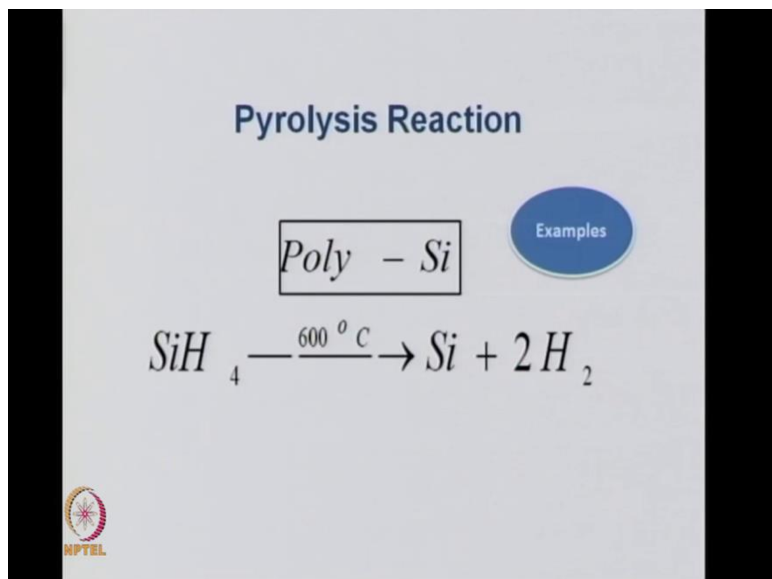

So, if you take the first case which we said the pyrolysis reaction. So, this is a typical pyrolysis reaction, where you want to make poly silicon. So, you take a gaseous species and this is called saline silicon. There are SiH 4 and when you heat it at 600 degree

celcius, then it will give rise to silicon and hydrogen. So, basically you are heating these gas molecules over a substrate and this decomposes to give you silicon which forms the film on the substrate and this hydrogen gas has to be taken out as an exhaust through the exhaust. So, this is a typical reaction, where pyrolysis is taking place. That means, breaking down of a compound under giving some heat. That means, at high temperatures, we are breaking this up to give you these molecules. These molecules will sit on and will be transported to the substrate and form the film. So, this is a CVD process which uses by pyrolysis reaction.

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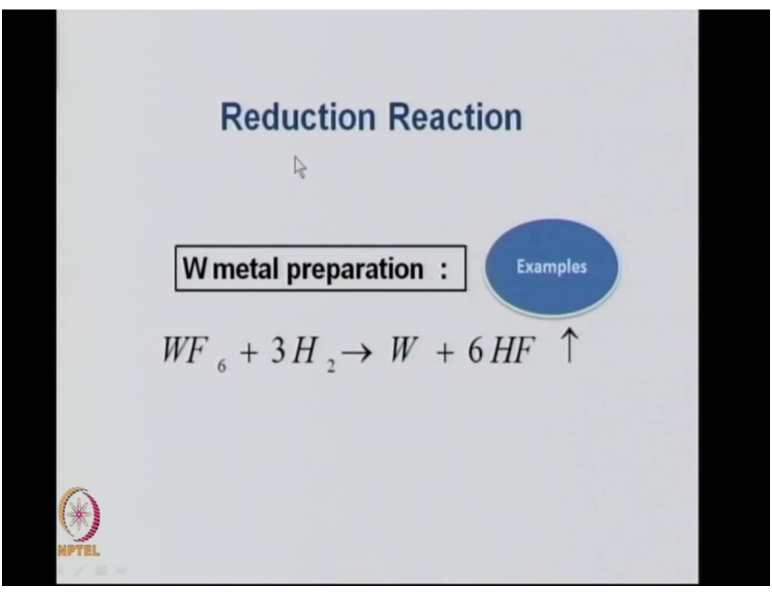

Then coming to an example for CVD, where reduction reaction is taking place can be seen in the case of tungsten metal preparation. So, double is the symbol for tungsten and you start from a gaseous species, hexafluoride tungsten and because this is a reduction reaction, the name you heat in the presence of hydrogen and you get tungsten which deposits on the substrate and HF forms during the reaction, and this hydrogen fluoride gas is then taken out through the exhaust. So, this is a reaction with is reduction of the reactant to give rise to the product which then is deposited as a thin film on the substrate.

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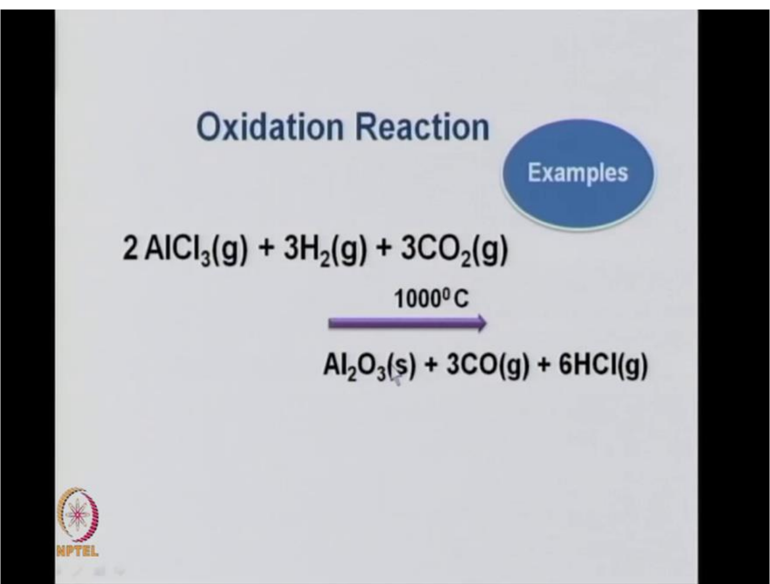

The third example where you are being an oxidation reaction to prepare film using the CVD technique and example here is of aluminum trichloride. You are using hydrogen and carbon dioxide to oxidize aluminum chloride of aluminum oxide and carbon monoxide and HCl gas have found. So, these two are gases and this is the only solid material. So, this will deposit on the substrate and give you the film. So, you are using an oxidation condition to make aluminum oxide or alumina films from aluminum chloride, and this is again a typical chemical vapor deposition process. Aluminum chloride molecules will be deposited on the substrate.

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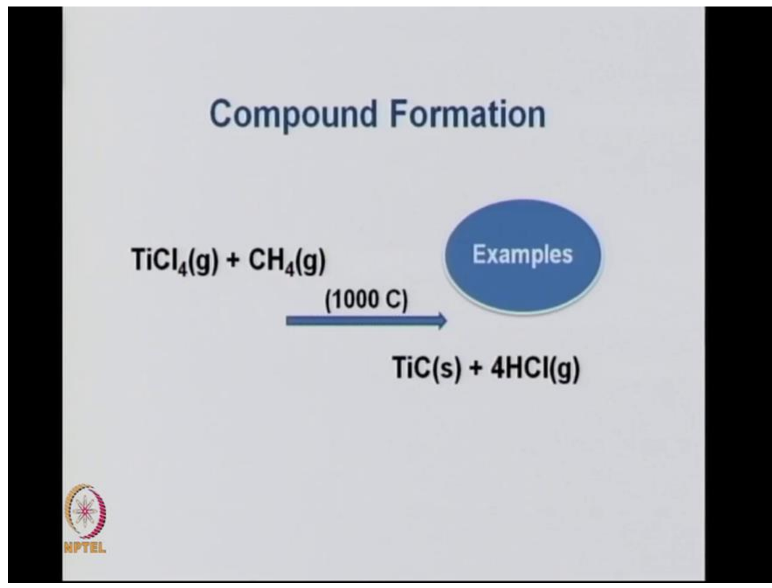

The next methodology is the compound formation methodology, where the example that we show here is of titanium tetrachloride reacting with methane. So, there are two gases, titanium tetrachloride and methane which is brought together near a substrate, and at a temperature of 1000 degree celcius and at that temperature titanium carbide which is a solid will deposit on the substrate and form a film. So, this is an example of CVD procedure. When you have a compound formation starting from two gaseous precursors and they interact and form a compound which deposits on the substrate, and forms a thin film of titanium carbide.

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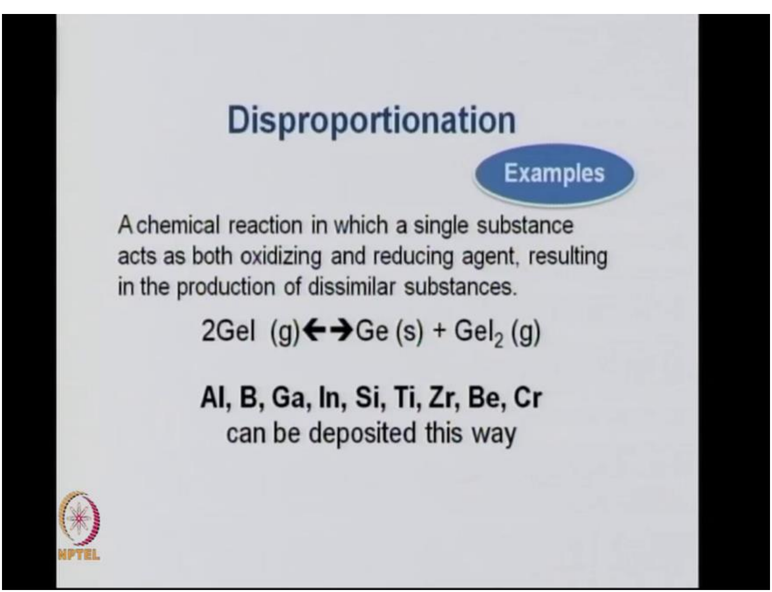

The next example is disproportionation reaction. As you understand from the word disproportionation means, it is breaking up. So, it is a chemical reaction in which the same chemical. From a more scientific point of view disproportionate reaction is basically the substance itself acting as both oxidizing and reducing agents. So, you start with two moles of germanium iodine. One of them oxidizes the other and other one reduces the other. So, GeI where geranium is in oxidation state 1 when 2 molecules of GeI come together in the gaseous state. They react and these GeI molecules then disproportionate. That means, one of them becomes higher or becomes oxidized. Ge2 plus and the other germanium get reduced to Ge0. So, here disproportionation the word is used because you are having a metal ion in a particular oxidation state. In this case, it is plus 1 oxidation state in germanium iodine molecule which disproportionate. That means, 2 molecules of geranium iodide both having plus 1 iron will give rise to 1 ion of

0 oxidation state which is a metal which deposits on the substrate and forms the film or geranium.

The other germanium from here becomes germanium plus 2 and the reactors with the iodine to form germanium iodide or diiodide, and these germanium diiodide in a gaseous species and is taken out of the exhaust. So, that is why this reaction is called disproportionate proportionation reaction because from 2 plus 1 species, we are getting 1 0 valence species and 1 divalence species, and it is the zero valance species deposits on the substrate and gives you a film of geranium on the sub state. So, this is CVD technique to make coat germanium films on several substrates. Similarly, you can coat aluminum, boron, gallium, large number of other metals and non-metals solid on substrates as films using this disproportionation CVD method.

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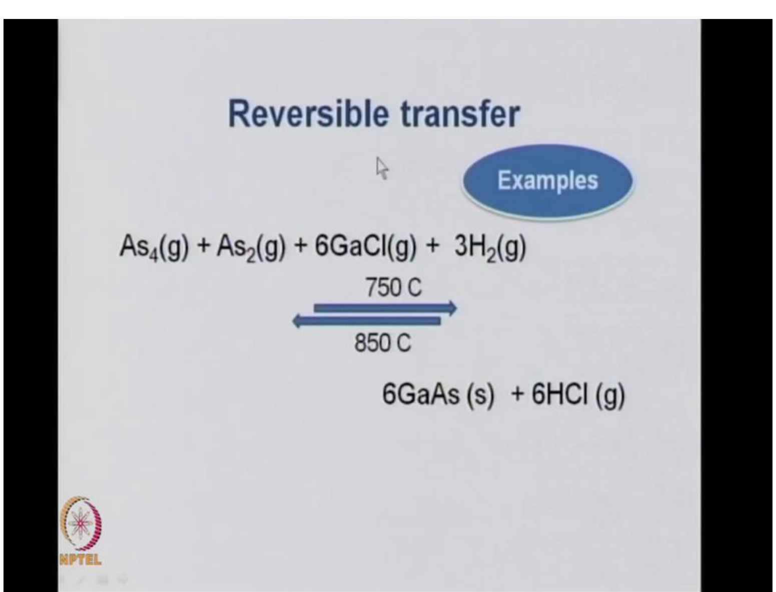

Then, this is an example of reversible transfer. So, here what we see is that you have a gas molecule. It is tetramer as 4 atoms of arsenic are there in this cluster, 2 atoms of arsenic are there in this cluster. So, it is a tetramer and dimer, and they react with a galium chloride, where galium chloride is here having plus 1 oxidation state and this gallium chloride in the presence of hydrogen at 75 degrees centigrade gives rise to gallium arsenide.

Gallium arsenide as you know is one of the most well known materials for semi-conducting devices, and has lot of applications and this technique has been used in the

CVD technique, where it is reversible transfer because if you use 750 degrees centigrade, you can go from the left side to the right side where you produce gallium arsenide on the substrate as a film say saline, and you get HCl gas. Now, if you start from this, ideal start with gallium arsenide and HCl and heat at 850 degrees, you will get back to the arsenic and the gallium chloride. So, that is why it is called reversible transfer reaction once a CVD technique, because you are starting from molecular precursors and ending up with a solid film on a substrate.

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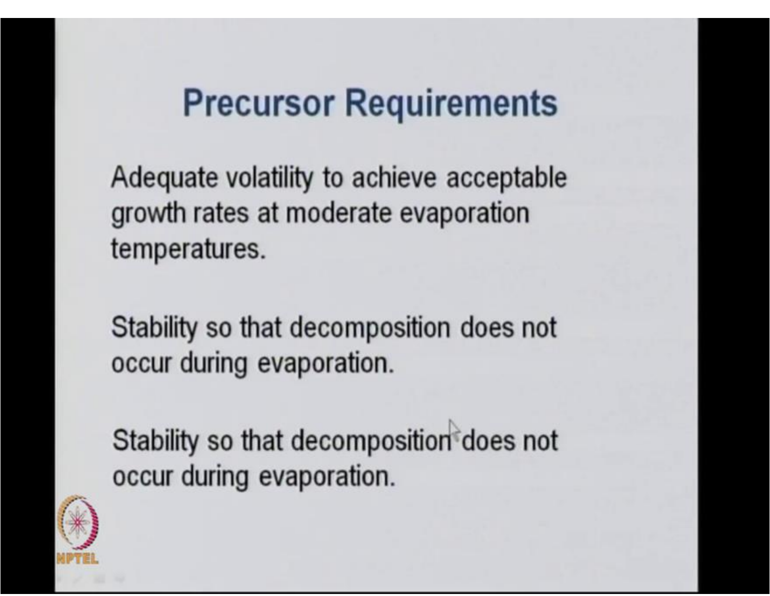

Now, we saw that there are lots of precursors which are used which are either gaseous molecule, they are gaseous which are pressurized into liquids and then, gas molecules come out of them and can be controlled before they are sent to the reaction chamber. Now, one of the important requirements for this precursor which is either the pressurized gas as a liquid are just the gas is. This should be sufficient volatility to achieve acceptable growth rates at moderate evaporation temperatures. That means, the volatility of that liquid to perform gas should be very high, otherwise you will need high temperatures to volatilize gaseous molecules from those liquids.

So, this is a very important requirement for the precursor that it should be very highly volatile or sufficiently volatility should be there to allow for gaseous molecules at moderate temperatures. You do not want to heat them at very high temperatures. Of course, you do not even want them to be very volatile that comes to the next point. This

should be stable, so that decomposition does not occur during evaporation. So, the molecules which are going should not decompose while moving close to the substrate, and they should be able to be transported without any decomposition from the point of entry to the reaction chamber to this vicinity of the substrate. They should be stable and should not decompose. So, this is the same thing as we are mentioning that the stability should be high and it should decompose.

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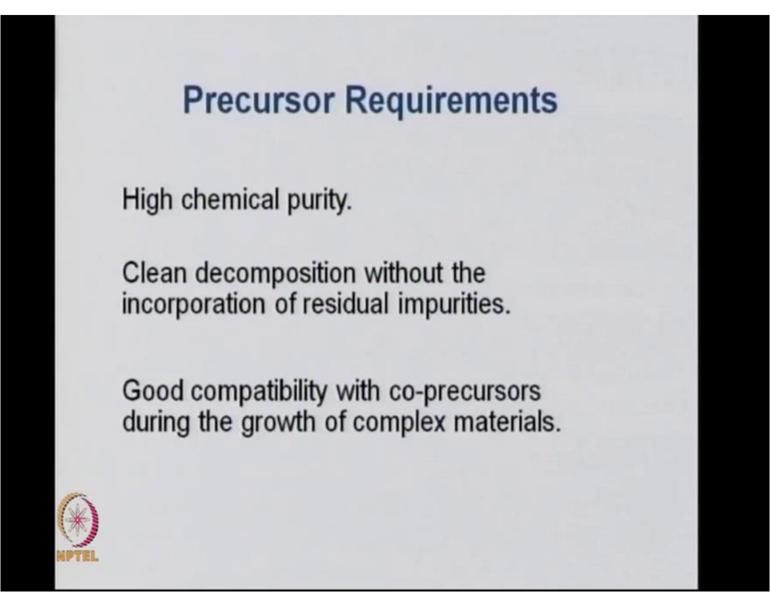

While evaporation some other requirements like this should be high chemical purity. They should be clean decomposition without the incorporation of residual impurities and there should be good compatibility with co-precursors during the growth of complex materials. So, this means that suppose you are trying to grow a bimetallic film, you have a precursor for one metal and you have a precursor for another metal. Then, that is called the co-precursors and during the growth of this complex metal film, there should be some compatibility with in these precursor molecules.

So, good compatibility with co-precursors during the growth of complex materials. Some materials which I have two metals or three metals or two metals and oxygen or carbon dioxide has to be injected to make a carbide or nitrogen for a nitrate. So, these co-precursors should be compatible among themselves. This is an important point of course. I mentioned about high chemical purity, and also the clean decomposition. There should be no other impurities which solidify on the surface of the substrate.

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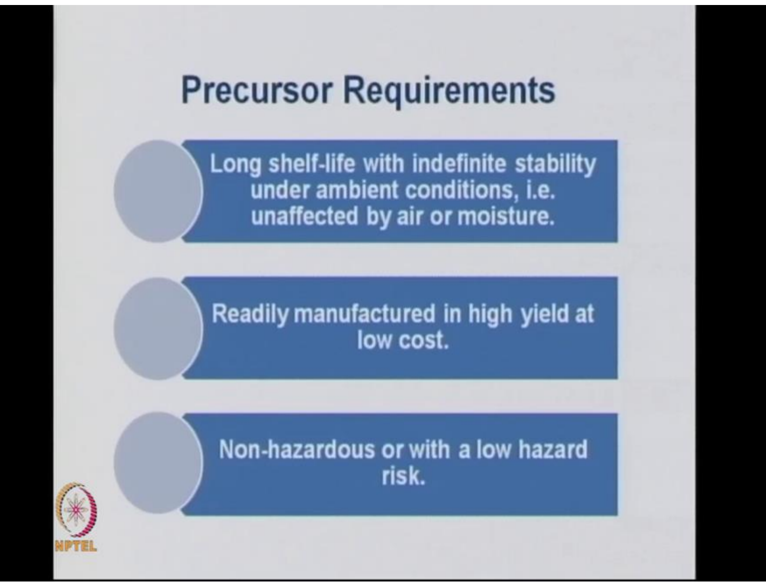

So, again talking of these precursors because is the most important thing in the CVD process. It should have a long shelf life with lot of stability at ambient conditions, and should not be affected by air or moisture. People should be able to manufacture them in large yield at a low cost and they should be in non-hazardous or with very low hazard risk. So, if you have to make an industrial process, you have to consider all these points for making CVD films using molecular precursors.

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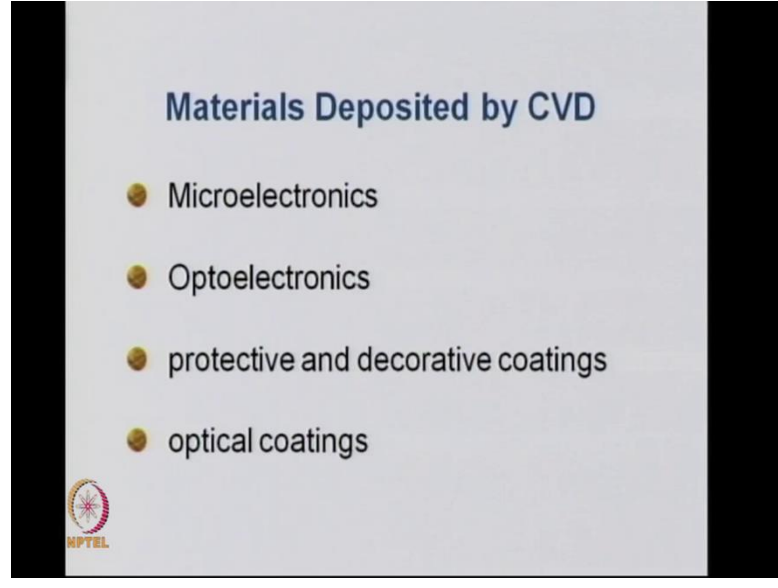

Now, the types of materials normally used for deposited by CVD techniques have applications in several areas of technology. Microelectronics is one of the most important areas, where CVD techniques are used, optoelectronics, protective and decorative coatings and optical coatings, all of them some time or the other people use CVD processes to make films which will be acting as components or devices, and many of these applications. With this I come to an end to the lecture 5, and we will be continuing our discussion about various methods of deposition of films, nano structured films by different methods in the coming lectures.

Thank you very much.