

Surface Engineering of Nanomaterials
Dr. Kaushik Pal
Department of Mechanical and Industrial Engineering
Indian Institute of Technology, Roorkee

Lecture – 13
Chemical Vapour Deposition (CVD)

Hello, today we are going to discuss about the Chemical Vapour Deposition process. In the last lecture we have discussed about the physical vapour deposition process. So, in this particular process we are going to discuss that how we are doing the coatings, how we are doing the modification of the surface, the only differencing between the physical vapour depositions and chemical vapour deposition is that in the physical vapour depositions just we had made certain kind of atoms or maybe the plasma and just we have deposited those on to the substrate itself. But here we are going to see that how we are making this kind of atoms or maybe plasma or any kind of gas which can react with the substrate itself and do the modifications. So, that is why it is called the chemical vapour depositions because there is certain kind of chemical reactions is relate with this process.

(Refer Slide Time: 01:25)

Introduction:

- ✓ In chemical vapour deposition (CVD) processes solid material is deposited from a vapour by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface.
- ✓ The resulting solid material is in the form of a thin film, powder, or single crystal
- ✓ Key factors in CVD system
 - Substrate Material
 - Substrate Temperature
 - Composition of Reaction Gas Mixture
 - Total Pressure Gas Flows
- ✓ Supports the growth of materials with a wide range of Physical, Technological, and Chemical properties.

Basic Principle of CVD

The diagram illustrates the basic principle of CVD. It shows a horizontal tube reactor with a substrate at the bottom. On the left, 'precursors' (represented by yellow circles) are introduced into the 'gas phase'. As the 'gas flow' moves to the right, it passes over the 'substrate'. 'adsorption & surface reaction' occurs on the substrate surface. This leads to 'film growth & release of volatile byproducts' (represented by red and green circles). The diagram is labeled 'Basic Principle of CVD'.

Here first we have to know that what is chemical vapour deposition means, so in chemical vapour deposition process, solid material is deposited from a vapour by a chemical reaction, occurring on or in the vicinity of a normally heated substrate. So,

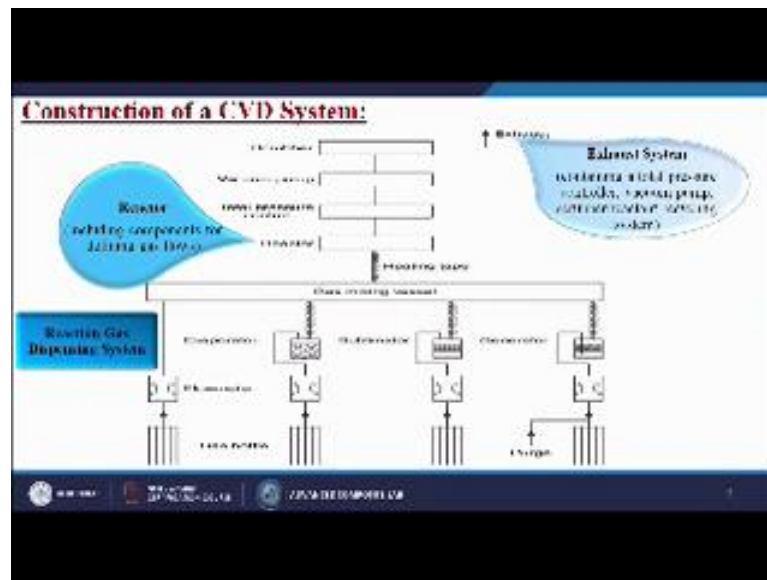
whatever I have explained already in the physical vapour deposition just we are creating certain of molecules, certain kind of atom, certain kind of plasma and then we are depositing those on to the substrate, but in chemical vapour depositions, we are making certain kind of gases or maybe certain kind of materials which will react with the substrate itself and make the coating. So, the resulting solid material is in the form of thin film powder or maybe the single crystal. So, we can get the modifications by these techniques or maybe, but by this way itself rather we can say.

What are the key factors in the CVD system? First one is called the substrate material which we are going to coat or maybe which we are going modify, next is the substrate temperature that what is the temperature it can sustain or maybe the what the temperature I can put my substrate so that it will not change its any kind of properties means like physical properties or maybe the chemical properties.

Next one is called the composition of reaction gas mixture. So, what type of gas I am going to used that either I can take a single gas or maybe I can take a multiple gases too so that they can mix together. So, they can form a new material that materials can react with the substrate and do the coatings.

And then last one is the total pressure gas flows. So, suppose the growth of materials with a wide range Physical, Tribological and Chemical properties. So, by doing this CVD process we can do or maybe we can change these properties on to the material itself. So, from this particular figure we can understand that there is certain kind of precursors which is reagent in gas phase, then the gas is flowing, then there is some kind of absorptions and surface reactions is taking place with the substrate itself and then at last the film is growing on to the substrate materials and release of volatile by products maybe some kind of toxic gases or maybe some kind of impurities in the form of gases, it can come out from the surface itself so that we are getting a begrime material coating on to the top of the surface. So, here it is a general idea that about the constriction of the CVD systems means chemical vapour deposition systems, what are these?

(Refer Slide Time: 03:50)



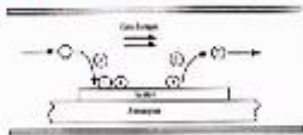
First we are having some reaction gas dispensing systems. So, after when the reaction will take place, all the products through these channels or maybe through these dispensing systems because we are having certain kind of flow meter, we are having certain kind of gas bottle, then we are having sublimator, we are having generator, we are having evaporator. The thing is that when the mixing is taking place, if there is any humidity, it can remove those humidity, if it is having some kind of impurity, it can substrate that impurities, not only that it can there is certain kind of flow meter by which we can control the flow of that particular gases on to the substrates itself then at last we have to purge it on to the substrate or maybe the on to the system.

Then we are introducing some kind of reactor which is including the components for defining the gas flow. So, by which we can put the gas into the system, we can do the mixing of the system, it is totally the automatic process, not only that we can control the percentage of mixing of the gases into that system, we can agitate the gases. So, just like it is the head of the family and another thing is that here we are having another exhaust systems containing a total pressure controller, vacuum pumps, scrubber reactant recycling system; that means, what type of the impurities or maybe the what type of the moistures or maybe the what type of the other means which is not required for this particular reactions that can be taken out and that can be thrown outside by this exhaust system.

(Refer Slide Time: 05:28)

Sequence of Gas Transport & Reaction Processes:

1. Transport of reactants by forced convection to the deposition region.
2. Transport of reactants by diffusion from the main gas stream through the boundary layer to the wafer surface.
3. Adsorption of reactants on the wafer surface.
4. Surface processes, including chemical decomposition or reaction, surface migration to attachment sites (such as atomic-level ledges and kinks), site incorporation, and other surface reactions.
5. Desorption of byproducts from the surface.
6. Transport of byproducts by diffusion through the boundary layer and back to the main gas stream.
7. Transport of byproducts by forced convection away from the deposition region.



The diagram shows a wafer surface with a boundary layer above it. Reactants (represented by circles) are transported from the main gas stream through the boundary layer to the wafer surface. On the surface, they undergo adsorption and surface reactions. Byproducts are then desorbed from the surface and transported back through the boundary layer to the main gas stream, where they are carried away by forced convection.

Next, we are having some sequence or maybe we are following some kind of sequence for the gas transport and the reaction process. What are those? First is that transport of reactants by forced convection to the deposition region. So here, this is our suscepter, then we are putting certain kind of wafer, that wafer is actually that the martial.

Then transport of reactants by diffusion from the main gas stream through the boundary layer of the wafer surface, absorption of the reactants on the wafer surface. So, the thing is that initially I am having one chamber in which I am putting my substrate which is known the wafer over here. Then I am injecting the reactive gases over there, but the problem is that, that reactive gases maybe directly not come into the contact on to the surface or maybe the wafer. So, that is why we are using certain kind of forced gases or maybe generally we are calling it as a carrier gases which will take those reactive gases with itself and then it will come, it will do the reactions and the roll of the carrier gases is to just to carry those reactive gases inside the chamber and take out from the chamber itself.

So, absorption processes of reactants on the wafer surface, surface process is including chemical depositions or reactions, surface migrations to attachment sites such as atomic level ledges and kinks, site incorporations and other surface reactions. Kinks means there is certain kind of maybe holes or maybe ports or maybe certain kind of scratches by which we can do the modifications.

Desorption or byproducts from the surface, transport of byproduct by diffusion through the boundary layer and back to the main gas stream, transport of byproducts by forced convection away from the deposit region. So, not only that carrier gas will help you to bring the reactive gases inside the chamber, sometimes whatever the byproducts, it will be created from the CVD chamber, it will take those byproducts means waste material from the chamber itself.

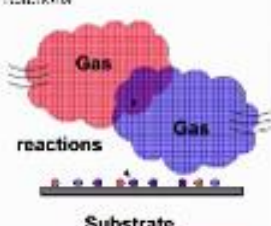
(Refer Slide Time: 07:33)

Physics of CVD:

- Reaction typically begins in the gas phase due to heating
- Reaction products are more reactive with substrate than with source gases.
- It is necessary to control both gas-phase and surface reactions

$$\text{Deposition Rate, } v \propto \frac{k_s k_g}{k_r + h_g}$$

k_s : surface reaction rate
 h_g : mass transfer coefficient
 If $k_s \ll h_g$, deposition is reaction limited
 If $h_g \ll k_s$, deposition is mass transfer limited



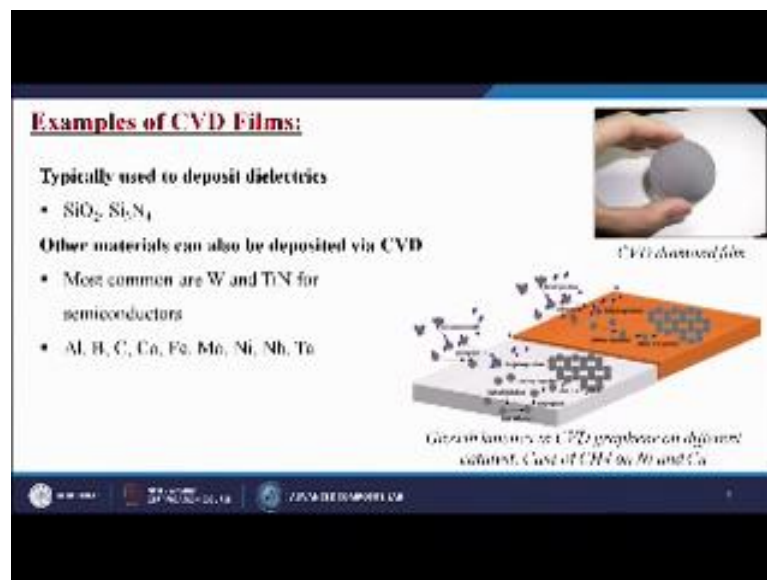
Next, what are the physics behind the CVD or maybe that chemical vapour deposition machines. So, the thing is that reaction typically begins in the gas phase due to the heating. Reaction products are more reactive with substrate than with the source gases. So, suppose you are having a single gas or maybe you are having a multiple gases, those gases you are mixing properly then those gases will directly will come into the contact with the substrate itself and do some kind of chemical reactions in between those reactive gases and the substrate and then they will form a some kind of powder or maybe fling on the substrate itself.

What are the deposition rates? So, deposition rate is generally denotes by these equations which is nothing but the k_s is known as the surface reaction rate, h_g is the mass transfer coefficient and if k_s is very very less then h_g , deposition is reaction limited and if h_g is very very less then k_s , deposition is mass transfer limited. So, that mean what about the deposition rate that also can be controlled from the outside itself, just increasing or

decreasing the volume of that gases you are injecting inside the chamber or maybe some kind of reactive gases you are putting not only that you can control the time over there so that the thickness of that particular coatings can be controllable by our self.

Here we can see that there are 2 gases which are mixing properly and this is the zone, this is the some reactive gases, it is forming over air which is directly coming into the contact with the substrate maybe this gas or maybe this gas as an independent, maybe they cannot react with the substrate itself. So, when they will mix properly then only these products maybe can be reactive to the substrate too. So, that is also the added advantage for the CVD (Refer Time: 09:31).

(Refer Slide Time: 09:41)



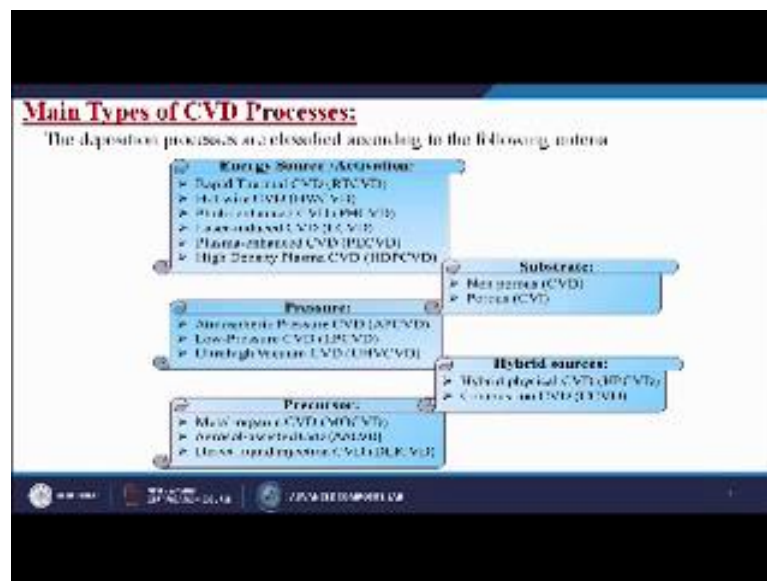
Next is the example, examples of the CVD films. So, typically used to deposit dielectric materials like silicon dioxide then Si_3N_4 , other materials can also be deposited by a CVD, most common are tungsten and titanium nitride for semiconductors then maybe aluminum, boron, carbon, kobold, iron, molybdenum, nickel, niobium, tantalum. So, these all are the different varieties of materials which we can put into the gaseous forms, we can modify those by this kind of materials or maybe rather we can coat this kind of materials onto our substrate too.

The thing is that here how the attachment is going on there are several mechanisms, chemical reactions is going on not only that when this molecules is coming from these materials directly, they are coming into the contact with the surface then they are doing

certain kind of chemical reactions in between the substrate and these molecules and then they are bonding together or may the addition is taking place. So, this is the growth kinetics in the CVD grapheme on different catalyst like case of CH₄ on nickel and copper.

So, now, we are going to discuss about the different type of CVD process, but the thing is that till now several scientist has given this kind of classifications based on maybe the substrate, based on maybe the gas, they are going to use best on that sources of energy. So, here just it is particularly, it is the thing is that we are trying to give this kind of classifications from our side itself. So, best on that whatever the energy we are going to use, best of the whatever the substrate we are going to use, how much pressure we are going to use, what is the sources we are going to use and what is the precursors are going to use. So just to generalize the classifications; just to make it simpler so that the audience can get it easily, it is totally our principles or maybe our logic to classify these CVD techniques into the different forms.

(Refer Slide Time: 11:44)



What are those? The deposition processes are classified according to the following criteria. So, first one is called the energy source and activations. So, rapid thermal CVD, in short form it is known as RTCVD, hot wire CVD, photo enhanced CVD, laser induced CVD, plasma enhanced CVD, high density plasma CVD. So, from this particular case, you can understand that all are coming under the CVD process, but only the energy

source is different, somewhere we are using the electron, somewhere we are using the laser, somewhere we are using the photo or maybe the light or maybe somewhere we are using the thermal sources over there.

Then next one we are coming to the substrate. So, non porous and porous, whatever the material where going to do, we are going to take for doing the modification, whether these material are porous phase or maybe that is nonporous or maybe the highly dense materials. Then whatever the pressure we are going to use, whether it is atmospheric pressure CVD or maybe the low-pressure CVD or maybe the ultrahigh vacuum CVD. So, based on the pressure is applying on that particular process, we are dividing the CVD process into 3 types.

Next one is called the hybrid sources, hybrid physical CVD, combustion CVD. So, it is a mixture of process means chemical vapour deposition in also with the attached with the physical or maybe the combustion. So, we are using certain kind of heat energy over there with the chemical vapour deposition process.

Next is called the Precursor, Metal organic CVD, Aerosol assisted CVD, Direct liquid injection CVD; that means, whatever the source material we are going to take. So, based on these source materials you can divide the CVD process into different parts. Next is called the types of CVD. So, now, little bit will going into the details of about different types of CVD processes, what are those?

(Refer Slide Time: 13:45)

Types of CVD:

Atmospheric Pressure CVD Reactors (APCVD):

- Processes at atmospheric pressure
- The reactor designs were simple, yet provided high deposition rates
- Typically at 400 °C, grew films in the 2000 to 3000 Å/min range.

Low-Pressure CVD (LPCVD):

- CVD in 0.25-2 Torr range (1 atm = 760 Torr)
- Operation in the surface reaction limited regime without lowering temperature
- Allows for stacking of wafers and higher throughput
- Typically performed in 500-900 °C range

First one is called the Atmospheric Pressure CVD reactors, APCVD. So, process at atmospheric pressure, from the name itself you can understand that we are maintaining the atmospheric pressure for doing this particular CVD process. The reactor designs were simple yet provided high deposition rates, typically at 400 degree centigrade, grew films in the fall of 200, 2000 to 3000 angstrom per minute range. So, that is the controllable limit over there and we can go up to the 400 degree centigrade. So, if our material is less than that then substrate is less than that temperature. So, you can easily do it from the normal to the 400 degree centigrade, but it is not go beyond that.

Next one is called the Low Pressure CVD process or maybe in short form it is known as LPCVD. So, CVD in 0.25 to 2 Torr range. So, this is the pressure actually. So, what generally we know one atmospheric pressure is 760 Torr. So, either 0.25 into 760 Torr atmospheric pressure so that from that 2, 2 into 760. So, that will be the range actually in the atmospheric pressure range generally we are going to use.

Here, operations in the surface reaction limited regime without lowering temperature allows for stacking of wafers and higher throughput and the typically performed in 300 to 900 degree centigrade range. So, here the temperature variation is little bit bigger actually.

(Refer Slide Time: 15:28)

Ultrahigh vacuum CVD (UHVCVD):

- Extremely high vacuum eliminates contaminants from reaching surfaces.

Aerosol-assisted CVD (AACVD):

- Precursors are transported to the substrate by means of a liquid/gas aerosol.

Hot wire CVD (HWCVD):

- HWCVD affords the capability to synthesize fluorocarbon and organosilicon thin films.
- It overcomes some of the processing constraints of having a directly heated substrate.

The slide also features a diagram of a reactor with a substrate and a schematic of a hot wire CVD system showing a hot wire, a substrate, and a gas inlet.

Next is called the Ultrahigh Vacuum CVD, UHVCVD process. So, extremely high vacuum eliminates contaminants from reaching surface. So, from this particular case you

can understand that we are using the vacuum pump over there, we are having some delivery rail, then we are putting the gas or maybe the purging the gas inside it, then the reaction is taking place inside and then through this delivery layers that gas is going and it is depositing on to the substrate itself.

Next called the Aerosol Assisted CVD or maybe the AACVD process, precursors are transported to the substrate by means of a liquid or maybe the gas Aerosols, here we are not going to use any kind of gases over there; carrier gases over there rather this is carried out by some kind of liquid or maybe the gas Aerosol. So, from the figure itself we can understand that the solution of precursors we are using then we are having some kind of atomizer then we are using the carrier gas; atomizer means nothing, just it will give a high pressure on to those liquids. So, that it will come into the it will make into the small small bubble form, they will make certain kind of small small bubble form, then that bubble will directly come into this substrate and then that will deposit on to the substrate itself and we are having some heating arrangements so that it can do the chemical reactions if there is any heat is required then they will make certain kind of film or maybe the coating on top of the surface.

Next one is called the Hot Wire CVD; HWCVD process, HWCVD affords the capability to synthesize fluorocarbon and organ silicon thin films, it overcomes some of the processing constraints of having a directly heated substrate. So, here we are going to use certain kind of heat so that is why it is known as the Hot Wire CVD process.

(Refer Slide Time: 17:35)

Photo-enhanced CVD (PHCVD):

- Based on activation of the reactants in the gas or vapour phase by electromagnetic radiation, i.e. short wave ultraviolet radiation.
- Selective absorption of photonic energy by the reactant molecules or atoms initiates the process.
- Low temperature (150 °C) needed to form films (e. SiO₂).
- Greatly minimized radiation damage.

Laser-induced CVD (LCVD):

- Allows local deposition of materials within the focus of a laser.
- LCVD allows one-step deposition of structures with lateral dimensions down to at least 1 μm.
- Three-dimensional structures of micron size is possible.

The slide contains two diagrams. The top diagram, labeled 'PHCVD', shows a cross-section of a substrate with a thin film being deposited. It includes labels for 'Pre-heated Gas (e.g. SiH₄)', 'UV Lamp', 'Substrate', 'Growth of SiO₂ film', and 'Purging Gas (e.g. N₂)'. The bottom diagram, labeled 'LCVD', shows a laser beam focused on a substrate. It includes labels for 'Laser source (e.g. Ar, CO₂, Nd:YAG, HeNe, etc.)', 'Substrate', 'Growth of SiO₂ film', and 'Purging Gas (e.g. N₂)'. The slide also features logos for IIT Bombay and IIT Madras at the bottom.

Then next one is called the Photo Enhanced CVD or maybe in short term it is called the PHCVD process. So, based on activations of the reactants in the gas or vapour phase by electromagnetic radiations, short wave ultra violet radiations generally we are using, selective absorptions of photonic energy by the reactant molecules or atoms initiates the process, low temperature generally 150 degree centigrade needed to form films like silicon dioxide, greatly minimized radiation damage. So, here you can see that we are using certain kind of UV lamp chamber, from where we are generating the UV source; ultraviolet source over there. So, that ultraviolet source it is coming then we are purging some kind of carrier gases then that carrier gases is reacting with that alpha ultraviolet, rays then they are forming certain kind of materials then that materials is going to deposit on to the substrate itself.

Next is called the Laser Induced CVD process or maybe the LCVD process. So, allows local deposition of materials within the focus of a laser, LCVD allows 1 step deposition of structures with lateral dimensions down to at least 1 micrometer, 3 dimensional substrates of micron size is possible. So, from this particular figure you can understand that we have given an example on CNT; that means the Carbon Nano Tubes. So, here we are putting the Carbon Nano Tubes over here then we are having some laser source maybe either it is carbon dioxide laser, maybe argon iron laser or maybe Nd Yag pulsed laser, maybe helium neon laser or maybe some kind of solid state or maybe the diode laser.

So, any kind of laser source, you can take over there and then that laser source you have put in then there is having so many inlet channels, where you are purging the carrier gas, where you are purging different gas which we can react properly then through these laser these gases will be agitated they will form certain kind of materials; new materials which will be deposited on to the Carbon Nano Tubes or maybe it can make that Carbon Nano Tubes more functionalized. So, you can make the fictionalization of the Carbon Nano Tubes by these techniques too.

(Refer Slide Time: 19:39)

Direct liquid injection CVD (DLICVD):

- Precursors are in liquid form (liquid or solid dissolved in a convenient solvent).
- Liquid solutions are injected in a vaporization chamber towards injectors (typically car injectors)
- Then the precursor's vapors are transported to the substrate as in classical CVD process.

Metal-organic chemical vapour deposition (MOCVD):

- Based on metal-organic precursors.
- Used to produce single or polycrystalline thin films.
- Highly complex process for growing crystalline layers
- Pressure: 10 to 760 Torr
- this technique is preferred for thermodynamically metastable alloys.

Next is called the Direct Liquid Injection process. So, here precursors are in liquid form; liquid or solid dissolved in a convenient solvent liquid solutions are injected in a vaporization chambers towards injectors typically like car injectors, then the precursors vapors are transported to the subtracting classical CVD process. The simple thing is that car injectors is nothing but that when the fuel is directly coming and it is injecting into the engine itself. So, we are using certain kind of injector over there. So, that is continuously injecting that of oil and air mixture and continuously the burning is taking place.

The same thing we are doing over here also. So, we are having some kind of pressure precursor tanks, where we are putting certain kind of gas pressure. So, due to that gas pressure the (Refer Time: 20:25) is taking place and directly that liquid; it is going into the atomization process and or maybe generally we are calling it as an atomizer. So,

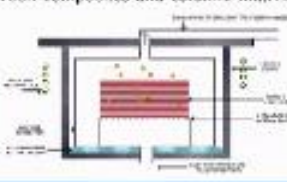
where this liquid is going, then a high pressure of air, we are giving due to that, that liquid is forming small small bubbles and then that small bubbles is directly coming as a vapour and then it is depositing on to the material surface and then rest of the vapour; it is going throughout the chamber. So, the thing is that here 2 things, first I said that we are putting the material in a bubble form and then also we are using certain kind of carrier gases. So, that carrier gases will carry those molecules to the substrate itself then those molecules will react with the substrate and rest the carrier gas will come out into the vapour form or maybe the in the gas formations.

Next one is called the Metal-organic Chemical vapour deposition or maybe the MOCVD. Based on metal organic precursors used to produce single or polycrystalline thin flames, highly complex process for growing crystalline layers, pressure is generally 10 to 760 Torr, this technique is preferred for thermodynamically metastable alloys. So, here generally we are using certain kind of metal precursors over there, then we need a high energy source over there, then the materials we are going to deposit is this one; M and here is the (Refer Time: 22:02) and (Refer Time: 22:04) is nothing, but the functional groups of that particular materials then they will react with the substrate itself then (Refer Time: 22:10) will release and only the metal irons will stick with the substrate itself.

(Refer Slide Time: 22:22)

CVI process

- Chemical vapour infiltration (CVI) is a ceramic engineering process whereby matrix material is infiltrated into fibrous preforms by the use of reactive gases at elevated temperature to form fiber-reinforced composites
- The earliest use of CVI was the infiltration of fibrous alumina with aluminum carbide
- CVI can be applied to the production of carbon-carbon composites and ceramic matrix composites
- A similar technique is chemical vapour deposition (CVD), the main difference being that the deposition process of CVD is on the bulk surface, while the deposition process of CVI is on porous substrates



The diagram illustrates the CVI process. It shows a chamber containing a fibrous preform. Gases enter from the left, pass through the preform, and exit on the right. The process is labeled with 'CVI process' and 'CVD process'.

Next is the latest technology that is called the CVI process that is known as the Chemical vapour infiltration process. This is also a latest technology. So, what means, the means is that Chemical vapour infiltration is a ceramic engineering process whereby matrix material is infiltrated into fibers performs by the use of reactive gases at elevated temperature to form fiber reinforced composite. So, not only that you can make the composites over there so here you cannot do the coating of the particular materials, you can do the coating of the particular composites too.

Here the earliest use of CVI was the infiltration of fibrous alumina with chromium carbide, CVI can be applied to the production of carbon-carbon composites and ceramic matrix composites a similar techniques is chemical vapour deposition process the main difference being that the deposition process of CVD is not on hot bulk surface, while the deposition process of CVI is on porous substrate too. So, that is basic difference in between that.

From these particular case you can understand that inlet, we are putting the chemical carrier gases and the reactant materials over there then the carrier gases is going through these fibrous materials and then that molecules is reacting inside and some molecules with the carrier gases is going out of the materials. That means, that carrier gases it can easily go inside the porous materials and then the molecules of that particular reactant materials can be absorbed inside the pores itself, some molecules maybe come out with the career gases. So, by this way we can do the CVI process, Chemical vapour infiltration. So, here we are doing the infiltration of particular molecules inside the material.

Next one is called the Hybrid physical CVD or maybe the HPCVD process. So, vapour deposition process that involves both chemical deposition of precursor gas and vaporization of solid source main difference between the HPCVD and other CVD means it is in the heating unit, both substrate and solid metal source and heated up a by the heating module.

(Refer Slide Time: 24:43)

Hybrid physical CVD (HPCVD):

- Vapor deposition processes that involve both chemical decomposition of precursor gas and vaporization of a solid source.
- Main difference between HPCVD and other CVD systems is in the heating unit.
- Both substrate and solid metal source are heated up by the heating module.

Rapid thermal CVD (RTCVD):

- Uses heating lamps or other methods to rapidly heat the wafer substrate.
- Heating only the substrate rather than the gas.
- Chamber walls help reduce unwanted gas-phase reactions that can lead to particle formation.

The slide also features a photograph of a reactor setup and a schematic diagram of the RTCVD process showing a substrate being heated by a lamp, with labels for 'Substrate', 'Heating Lamp', 'Gas Inlet', 'Gas Outlet', and 'Chamber Walls'.

Next one called the Rapid thermal CVD process; in the short form generally we are calling it as RTCVD. So, use of heating lamps or other method to rapidly heat the wafer substrate heating only the substrate rather than the gas, chamber walls helps reduce unwanted gas phase reaction that can lead to the particle formations. So, till now just we are agitating those materials, those reacted material, those gases.

But in this particular case just we are agitating our substrate. So, that it will make itself as a reactive. So, that it can react directly react with the gases and then form the any kind of layer or maybe the powder or maybe the coating on to it.

(Refer Slide Time: 25:25)

Plasma Enhanced CVD (PECVD):

- LPCVD with plasma source
- Ionized gas in plasma supplies energy to reactant gas
- Lowers deposition temperature to 200°-350 °C
- Good for deposition on multilayer films sensitive to temperature

High Density Plasma CVD (HDPCVD):

- PECVD with very high density plasma
- RF bias on substrate
- Lower deposition temperature of 20° - 150° C
- Much lower pressure needed: 1 - 10 mTorr
- Better quality films, with less voids

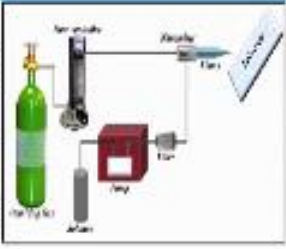
Next is called the Plasma Enhanced CVD process or maybe the PECVD, this also the latest techniques and that these equipment are very very expensive too. So, LPCVD with plasma source, ionized gas in plasma supplies energy to reactant gas, lower deposition temperature to 200 to 350 degree centigrade, good for deposition on multilayer films sensitive to temperature. So, this is all about the Plasma Enhanced CVD.

Next one called the High Density Plasma CVD or maybe HDPCVD. So, Plasma Enhanced CVD with very high density plasma so, here the density of plasma is more and then RF bias on substrate, lower deposition temperature; generally 20 to 150 degree centigrade much lower pressure needed journal 1 to 10 millitorr is required, better quality films with less voids, so this is the most sophisticated machines then the plasma enhanced CVD process.

(Refer Slide Time: 26:34)

Combustion CVD (CCVD):

- It has the ability to produce thin films in the open atmosphere using vapor precursors/inexpensive precursor chemicals in solution
- *Synthesis of coatings through the liquid solution route:*
 - I. Solution Preparation:** Starting precursors of materials are dissolved in suitable aqueous or organic solvents
 - II. Atomization:** The solution is delivered by means of a pump to a proprietary atomizer, where it is converted into submicron droplets
 - III. Combustion:** The submicron droplets are transported by a suitable gas to a flame where they are vaporized and combusted.
 - IV. Deposition:** Coatings are conveyed onto a substrate by sweeping through the flame plume, which causes the precursors to react or decompose to form the desired material



Then next one, we are going to discuss about the Combustion CVD or maybe the CCVD process. In this particular case, it is divided into 4 parts. So, it is the ability to produce thin film in the open atmospheric using vapour precursors or maybe inexpensive precursor in chemical in solutions. So, generally like a painting we are using this kind of techniques over there.

First one is called a solution preparations starting precursors of material are dissolved in suitable aqueous or maybe the organic solvent. So, here we are putting the solutions over there. So, these solutions to pump, it is going in particular nanomizer or maybe that gun which is going to spread those material into the surface itself. Then in the mean time we are using certain kind of filter maybe there is some impurities there maybe there is certain kind of humidity or may or maybe that there is certain kind of water molecules that can be absorbed directly. So, that the material the solution in a dry form; it will go directly to the nanomizer and here in this particular case we are doing the atomization of that particular gas, what is that atomizations on maybe atomizing gas? The solution is delivered by the means of a pump of to a proprietary atomizer were it is converted into sub micron droplets.

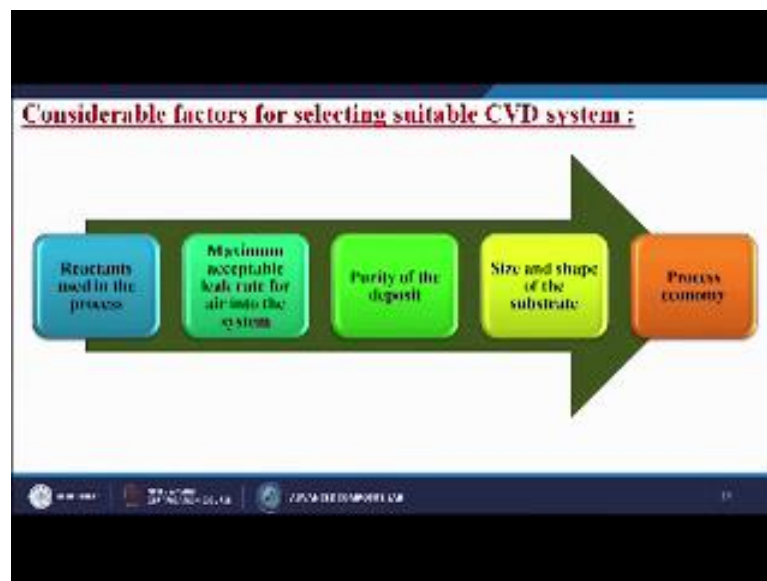
Here we are giving a high force of gases. So, through these gases, these solutions in the liquid form is coming into the small small bubble form, then directly through this film structure then it is giving certain kind of combustions of that particular juncture then that

film is directly falling on to the substrate and it is making the certain kind coating over there.

Combustion; the metastable droplets are transported by a suitable gas to a flame when, where they are vaporized and combusted. Deposition; coatings are converted on to a substrate by sweeping through the flame plasma which causes the precursor to react the component to form the desired materials. So, like this way like welding actually, we are having the flame, through that flame you are making solution and your gases is directly coming they are forming any materials then that flame directly we are putting on to your substrates and we are doing certain kind of coatings over there.

Now we are going to discuss, what are the considerable factors actually for selecting the different CVD process because till now I have given a brief discussion about different types of CVD processes. So, now first one is that reactant used in the process.

(Refer Slide Time: 29:00)



Next Maximum acceptable leak rate for air into the system, Purity of the deposits, Size and shape of the substrate and last one is called the Process economy; that means, why that the whole process is expensive or maybe it is cheap and not only that what type of substrate material you are going to use why that reaction in between your reactive gases and substrate material can be done or not, what are the condition inside the chamber you require? Whether you need a more pressure less pressure, then whatever the energy source you are going to use or maybe your material can sustain. So, depending of all

those things, we have to choose the better CVD mechanisms for your particular substrate.

(Refer Slide Time: 29:44)

Key Difference between PVD & CVD:	
PVD	CVD
Highly directional deposition	Multidirectional deposition
Non-conformal deposition	Conformal deposition
Uses physical processes only	Primarily uses chemical processes
Uses a pure source material	Uses a mixed source material

Next key difference between the Physical Vapour Depositions and the Chemical Vapour Depositions; first for the Physical Vapour Depositions we have seen that a highly directional deposition is taking place. So, we are having the target then directly the material is coming by using any kind of energy over there and then it is depositing on to the substrate over there, there is no or maybe any kind of chemical reactions is taking place, but from this particular figure we are getting that it is the multidirectional deposition rates. Means the coating is taking place all around or from all the sides over there.

Then it is a non conformal deposition is taking place over there, here we are getting a conformal deposition; that means, we are getting a homogeneous depositions in this particular case, then for PVD, we are getting uses physical process only here we are using the primarily the chemical process; that means, chemical reaction is taking place for the Chemical Vapour Depositions. Here used as a pure source material, here for the Chemical Vapour Deposition already have mentioned that we can use the single material maybe single gases or maybe there is a multiple gases, mixture of gases we can make the new materials inside the chamber and that new materials can be put on to the substrate itself.

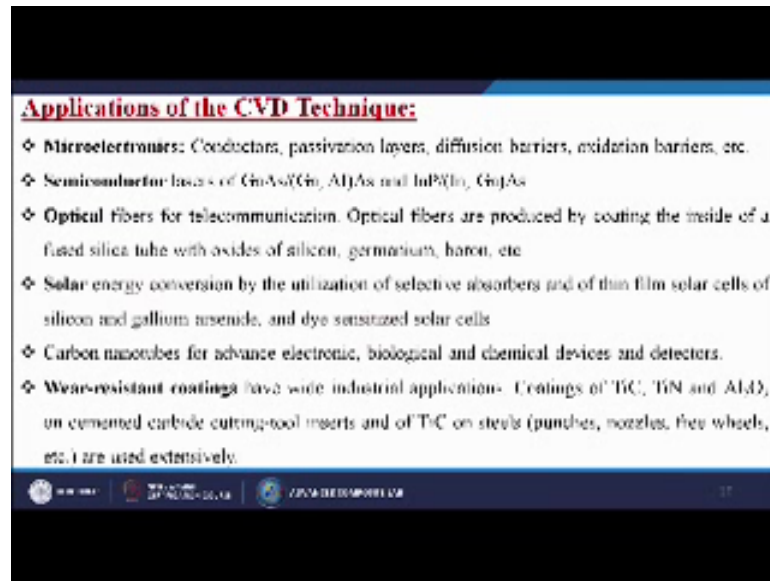
Next of course, each and everything there is certain kind of disadvantages, otherwise we cannot go forward. So, what are the disadvantages for this particular CVD process, first one is called the most involve safety and contamination that is the big problem over there that it can contaminate with the source, it can contaminate with the materials, it can contaminates the equipment.

Hybrids and carbonyls are poisonous especially Arsine. So, whatever the extract gases, it is coming out maybe that can be harmful for the environment that can be that harmful for the users or maybe the operators.

Metal organics are pyrophoric ignite in contact with the air, maybe it is generating some kind of flammable gases which can directly come into the contact with the air and can ignite, high cost for compounds with sufficient purity because the precursor is little bit costly if you go for some special kind of precursors over there, they are not possible for some materials means they simply is no suitable chemical reactions if that reactive gases will not directly do the reactions with your materials, it cannot do any kind of coatings over there, they are generally not suitable for mixtures of materials. So, generally sometimes we face certain kind of problems for particular composites where maybe one material is react with the reactive gases maybe, another material is not react with that reactive gases that is the one kind of disadvantages of the CVD process.

What are the applications of the CVD techniques? Generally we are going to use for the microelectronics purpose, conductors, passivation layers, diffusion barriers, oxidation barriers etcetera.

(Refer Slide Time: 33:32)

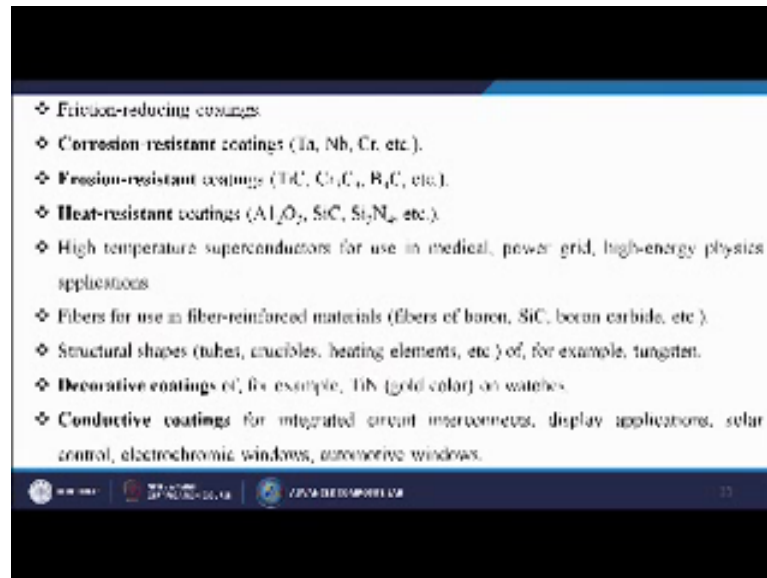


Applications of the CVD Technique:

- ❖ **Microelectronics:** Conductors, passivation layers, diffusion barriers, oxidation barriers, etc.
- ❖ **Semiconductor lasers** of GaAs/Gn, AlGa and InP/Gn, GaAs
- ❖ **Optical fibers** for telecommunication. Optical fibers are produced by coating the inside of a fused silica tube with oxides of silicon, germanium, boron, etc
- ❖ **Solar energy conversion** by the utilization of selective absorbers and of thin film solar cells of silicon and gallium arsenide, and dye sensitized solar cells
- ❖ **Carbon nanotubes** for advance electronic, biological and chemical devices and detectors.
- ❖ **Wear-resistant coatings** have wide industrial applications- Coatings of TiC, TiN and Al₂O₃ on cemented carbide cutting-tool inserts and of TiC on steels (punches, nozzles, free wheels, etc.) are used extensively.

Semi conductor lasers optical fibers for telecommunications optical fibers are produced by coating the inside of a fused silica tube with oxides of silicon, germanium, boron, etcetera, solar energy conversation by the utilization selective observers and of thin films solar cells of the silicon and gallium arsenide and dye sensitized solar cells, Carbon nano tubes for advance electronic, biological and chemical devices and detectors, wear resistant coatings have wide industrial applications coating of titanium carbonate, titanium nitrate alumina on cemented carbide, cutting tool inserts or titanium carbide on steels; punches, nozzles, free wheels, etcetera are used extensively, fiction reduction coatings corrosion resistant coatings like niobium, chromium etcetera.

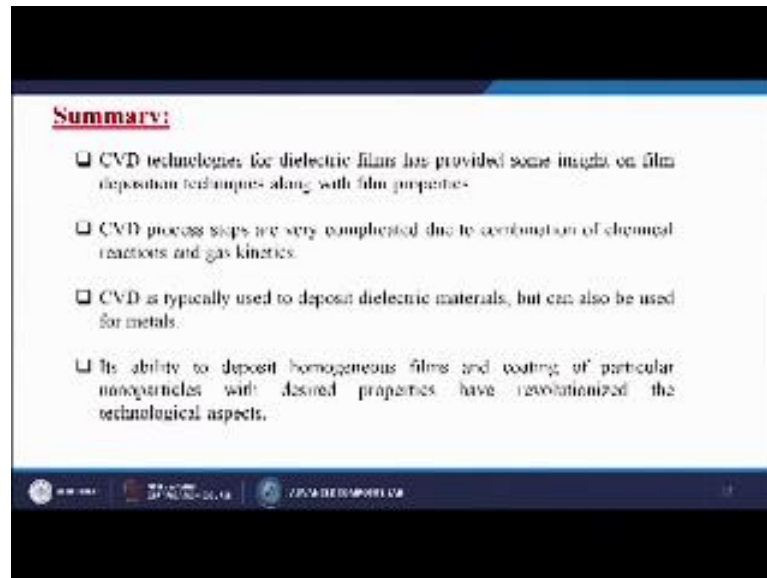
(Refer Slide Time: 34:18)



Erosion resistant coatings, heat resistant coatings like alumina, silicon, carbonate, high temperature superconductors for use in medical power grid, high energy physics applications, some kind of decorative coatings for example, titanium, nitride, gold color on watches, whatever we are calling it as a gold plating like my watch, then conductive coating for integrated circuit, inter connects, display applications, solar control, electro chromic windows, automotive windows.

Then at last, we have to come into the summery. So, fist in this particular lecture, I have discussed about the whole CVD process, what the CVD means, then I have discussed about the several types of CVD techniques, generally we are following or maybe we are using. Then I have already discussed that how we are going to use this CVD process, what are the selection criteria for different type of CVD process and at last we have disused about that different types of applications of that particular CVD process.

(Refer Slide Time: 35:25)



Summary:

- ❑ CVD technologies for dielectric films has provided some insight on film deposition techniques along with film properties.
- ❑ CVD process steps are very complicated due to combination of chemical reactions and gas kinetics.
- ❑ CVD is typically used to deposit dielectric materials, but can also be used for metals.
- ❑ Its ability to deposit homogeneous films and coating of particular nanoparticles with desired properties have revolutionized the technological aspects.

CVD is typically used to deposit dielectric materials, but can also be used for metals. Its ability to deposit homogeneous films coatings or particular nanoparticles with desired properties have reorganized the technological aspects. So, the whole general, I can say that it depends upon the substrate, it depends upon the environmental conditions, it depends upon the machine criteria or maybe our requirement we have to choose the proper CVD for proper modification types.

Thank you.