Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 47
Chemical Vapor Deposition (CVD)

Welcome to the 47th lecture of Surface Engineering. In the last couple of lectures we have discussed about physical vapor deposition and a special type of PVD namely the sputtering. In both the cases, we actually did produce, I mean both the methods are essentially mean for producing thin films typically few micrometers at the most may be few tens of micrometers. The essential commonality between the both the techniques was that the composition of the coating or the film, that we develop essentially, will be the same as that of the target.

So, either we vapor take the material in the vapor state by thermal evaporation; normally this is the basis of all PVD techniques or else we can use certain ions as projectiles to eject atoms neutral atoms from the target surface and deposit on a colder substrate and that is what, we do for sputtering.

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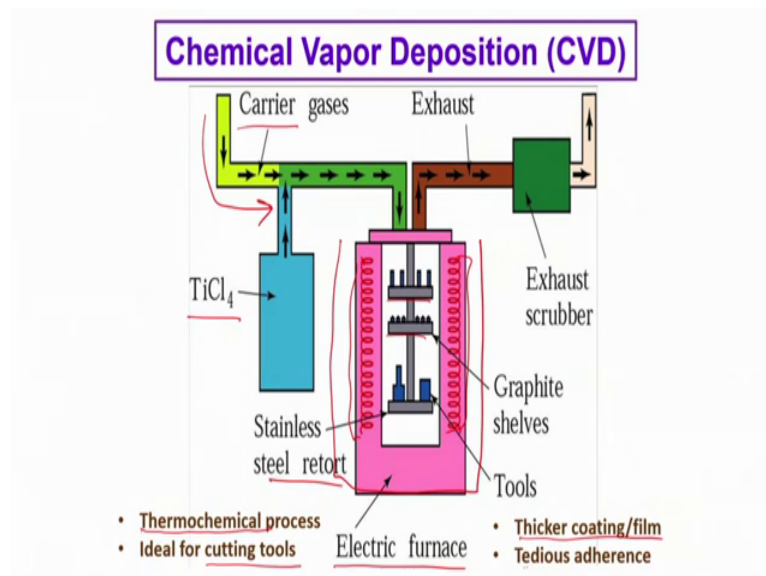

Now, compared to PVD and sputtering, we are now going to discuss chemical vapor deposition CVD, which essentially; is about the same technique we are thinking about low thickness deposits films typically few tens of micrometers or less than that in the

limit, we can also have we can create very thin layers few tens of nanometers in alternate sequence, but the difference is here; we actually, take recourse to some kind of a chemical reaction. So, the film that we deposit actually has a different composition than the precursors and we do not eject; we don’t do any thermal evaporation. We do bubble gases and we do use heating. Both heating of the precursor and as well as heating of the substrate, but most important thing is certain reactions take place in the vapor phase which gets deposited.

So, if you look at the overall scheme of the deposition process. So, you have a chamber you have essentially a chamber, which is. So, this is the chamber, that we have and this chamber is an enclosed chamber we have certain heating devices. So, these are the heating devices here and so we can maintain isothermal temperature over a certain temperature zone. Then, we have holders, which are essentially stainless steel or some kind of ferrous phase retorts. Now, we feed in carrier gas like this and we actually, when we feed in carrier gas the carrier gas does not react more acts more like a carrier agency and then, we also send certain precursor gas, which at the reaction chamber within the reaction chamber and the temperature dissociates and deposits on to the surface.

Now, after the reaction, we produce certain byproducts in some cases these byproducts are actually fairly toxic can be fairly toxic not always, but whatever it is; these byproduct gases actually come out and they are treated in an exhaust chamber by certain reactions we for example, in this particular case when we are using titanium tetrachloride as a precursor gas and we use some other carrier gas. So, they mix for example, hydrogen. So, they mix together and then, in the reaction chamber at that temperature they dissociate. So, hydrogen reacts with TiCl 4 and produces hydrochloric acid vapor and that, vapor goes into this chamber scrubber chamber, which is showered with water and then, the acid is collected and then, taken out or done the requisite treatment before disposal.

So, the essential components are that; the furnace the enclosed chamber the retort the stages on which the samples are mounted. In fact, it can be it is a batch process and you actually can feed in various sizes various dimensions of specimens the deposit composition is fixed, but the substrate can be varied may be steel, may be ceramic, may be certain other non ferrous metals this is.

So, essentially this is a thermo chemical process. So, we take the advantage of both temperature and chemical reaction and is ideal for manufacturing processes like cutting tools, but is also equally applicable to various semiconductor devices one can produce both thicker and thinner coatings and films. What is very important in case of the CVD compared to PVD is that, the coating that we develop; the film that we develop; actually is fairly adherent.

That is because, certain chemical reaction takes place and when the deposit or the film forms onto the substrate certain amount of inter diffusion, because of the high temperature takes place and there could be also a thin reaction layer;as a result of which the wettability is better or the adherence is better than the PVD or sputtering situations where the interface is always very sharp.

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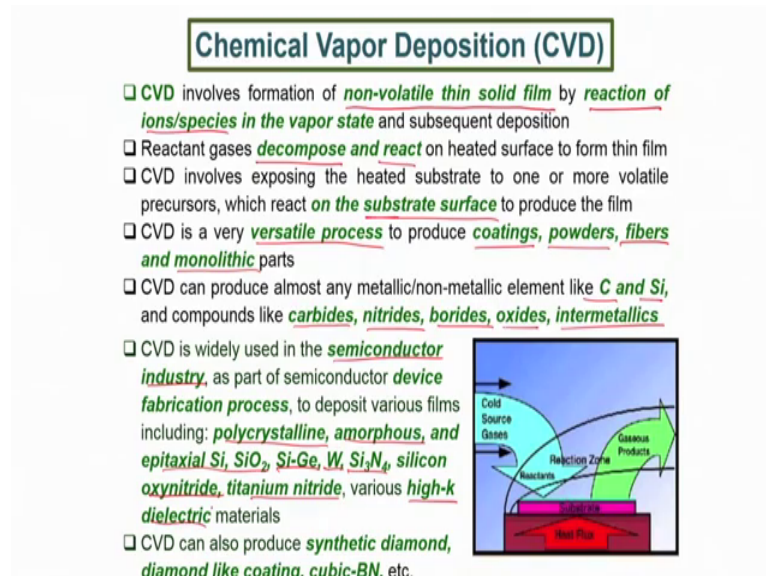

Now, so, we actually intend to produce a non volatile thin solid film. So that, deposit that we; it can be for example, it can be pure metal, it can be compound, it can be an alloy, but this film that we develop should be essentially a non volatile one. So that, at the reaction chamber it does not go back into the vapor state again and this film is produced by the reaction and the reaction through certain ionic species is that, we create into the vapor phase.

The reactant gases like we saw in the last example the titanium tetrachloride. They decompose and liberate certain species atomic species, which react with carrier gases and

what is important is the atomic species in neutral state deposit on to the substrate. Now, it can be atomic species, it can be even a compound, it can be a mixture or a composite; even we will we will learn, that in course of the lecture.

So, the reaction, that happens on to the substrate surface is very important. Because, this reaction makes the coating adherent and also this is where actually. So, the substrate actually in this case acts as kind of a catalyst, where the actual chemical reaction takes place. So, there is a fairly versatile process, because you can produce various kinds of coatings or films, you can make powders; I mean, freestanding powders, fibers the growth of very large aspect ratio fibers or even self standing monolithic parts can be produced.

So, compositionally apart from elemental coating like, carbon, silicon or titanium in some other cases, may be chromium. these are possible to be deposited, but also compounds like, various carbides, nitrides, borides, oxides, even intermetallic phases like, eliminates and silicides and so on. So, this is widely used in semiconductor industry; I already mentioned the possibilities of making tools on metallic or ceramic inserts; we can deposit in the poly crystalline form, in amorphous form, as epitaxial layer; for example, epitaxial, silicon or silicon dioxide layer on semiconductor wafers, silicon germanium wafers, pure metal like, tungsten; from say, tungsten WO 3. One can actually produce the pure tungsten layer onto the surface silicon nitride, silicon oxide nitride.

So, a complex compound, similarly titanium nitride t i n and even various high k dielectric materials. So, one can make a conducting coating, an insulating coating, create a dielectric coating and cover the entire surface or certain areas of the surface. One can also produce synthetic diamond to make extra hard layer onto the surface even diamond light coating or cubic boron nitride or various kinds of other ultra hard coatings on tool inserts or on components, which actually are supposed to experience very high wear and tear.

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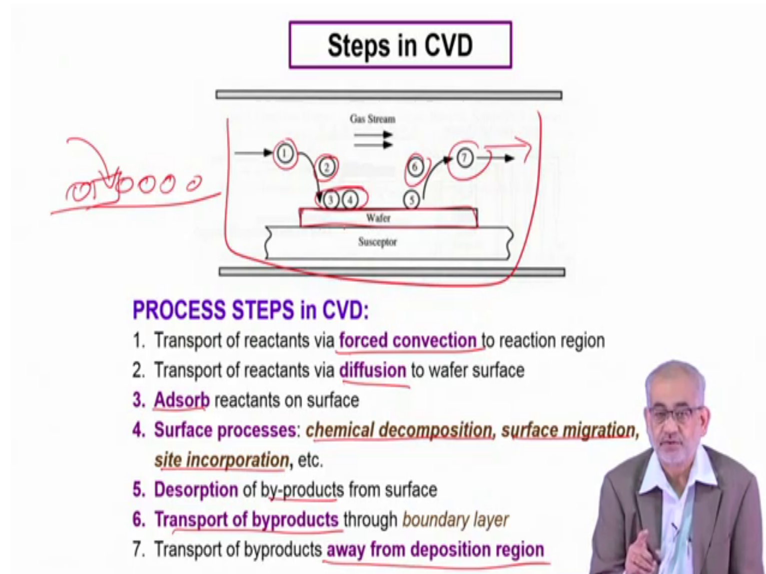

So, the process, basically follows certain steps let us say, a typical process like this, we will have initially, you have to feed in the precursor gases through force convection.

So, this is how the precursor gases come to the reaction chamber. Then, they undergo certain amount of diffusion onto the wafer or the substrate surface and then, they get adsorbed. So, this is where the reaction takes place and the desired species actually, they get adsorbed onto the surface, then the surface processes begin, which involves a decomposition surface migration and site incorporation; that means, the surfaces are known to have high density of defects typically, point defects like vacancies.

So, if you have more density of vacancies. So, free volume onto the surface, then those are the regions; where individual atoms can easily come and incorporate. So, if I have for example, certain surface atoms like this and I also have a vacancy. So, an individual atom coming here will find it easier to get incorporated onto the surface. So that, site incorporation; In fact, we also see side saturation through this process.

So, this 3 and 4 occur together and then, some desorption takes place, which is basically, desorption of the byproducts. Like, in case of titanium tetrachloride base power, that HCL forms and HCL molecules; they get dissolved; they eject out of the surface and they are transported as byproducts and then, these by-products are taken away through the pumping mechanism to a scrubber chamber then, we shower, we collect the poisonous gases or other by-products and then, dispose of through the usual mechanism.

So, this is the overall process. So, as you can see this is a batch process the substrate, which in this case is a wafer silicon wafer, but can be any other semiconducting compounds or a metallic component; may be a gear component, may be a some parts, which actually undergo mechanical forces under experience mechanical forces or relative motion or can be a tool insert and so on. In fact, always remember that, the coating that we develop here; since it is very thin;there are two things very important one is that, the surface topography has to be fairly smooth not rough and number two, the adherence with the substrate should be very strong.

So that, we do not lose the coating, that we develop and because, the composition wise this coating is different than the substrate fairly different, then the interface is supposed to be fairly sharp and that can lead to decuration. So, we need good surface integration. So, the heating is, as it is a chamber is it is a heated chamber even the substrate can also have an auxiliary heating system.

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Chemical Vapor Deposition (CVD)

- CVD is a technique for depositing thin films of materials on wafers or other substrates.
- Source gases are introduced into a reaction chamber and energy is applied through heat, high frequency high voltage (RF power), or other techniques that result in the decomposition of the source gas and reaction of the chemicals to form a film.
- Higher process temperature (600–1100 ºC) used in comparison to PVD

Various types of CVD:

Atmospheric pressure: APCVD

Low pressure: LPCVD

Plasma enhanced: PECVD

High density plasma: HDPCVD

Coating System

CH_4

H_2

Gas Inlet

H_2

H_2+TiCl_4

Liquid $TiCl_4$

Evaporator

Gas Outlet

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Now, so, we are depositing thin films on metallic or nonmetallic semiconducting or carbides or various kinds of ceramic substrates; even polymeric substrates fairly fairly flexible and soft substrates also can be given this kind of a CVD coating. So, as we saw that, we introduce gases into the chamber that is where the reaction takes place. The energy we supply through heat through isothermal temperature condition that we

mentioned; we actually can also apply high voltage in certain cases, where we want certain creation of plasma or some other conditions, that we want to create. So, we can use a radiofrequency coupled high voltage supply.

So, all these are essentially mean for decomposition of the gas, that we feed in and it is not just decomposition alone; once we decomposes, then it reacts either with the carrier gas or with the substrate surface and this reaction produces the film; thin film, that we intend. So, typically the temperature can be 700 degrees. I mean, easily above 500 degree centigrade and may be up to about 1000 degree centigrade in special cases may be 1200 degree centigrade. So, this process is this is where, it is different than the PVD. Normally, in case of PVD, you did not go anything more than 400, 450 degree centigrade. that is typically, to take the material of high vapor pressure into the vapor state.

So, like, I was saying that, you actually can produce a compound layer and you can feed in different kinds of gaseous mixtures like an hydro carbon and hydrogen together or even you can bubble titanium tetrachloride and hydrogen together. So, actually the substrate remains inside the chamber; the temperature and pressure conditions can be varied; what else can be varied? And that is what, make this whole process very versatile is the gas mixture that you feed in.

So, you can actually close the valve and then, say for example, you can close any of these valves or control these any of these valves and then, actually, control the flow rate you can even close altogether one particular gas for a particular period of time and hence, during that period you produce one film, which compositionally would be different than another film when you are feeding in different kind of gases.

So, the reactions can be varied and hence, the films composition of the films can be changed. Also the pressure plays a very important role. So, pressure wise, we actually can have an atmospheric plasma; we can have low pressure; just a few millibars or we can have plasma enhence, we can create a plasma by applying a chemical; sorry; electrical potential difference and so, we can take the help of the plasma to enhance the growth and adherence of the CVD film. We can even create a fairly high density plasma, where we actually intend to produce not only thicker, but also more complex films. So, all these variations are possible.

So, the variables wise, we certainly are talking about the temperature the composition the pressure and of course, the time. So, all these are major important parameters for the CVD process.

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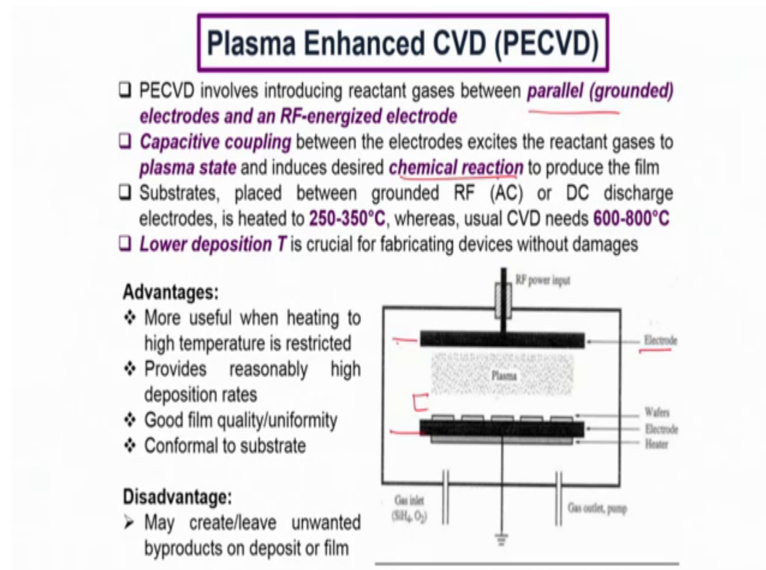

The in case of plasma enhance CVD what we actually need? Is to use two different electrodes and then, create a potential difference electrical discharge for electrical discharge and then you create this plasma. So, there will be a certain amount of dead zone here and these are the substrates, on which you want to deposit. So, once you create the plasma, then the deposition is controlled by the thickness of this plasma layer or the so called dead sheath that you have in between.

So, you need the substrates to be grounded and you need the other electrode actually, which will produce the plasma the capacitive coupling is essential is the reason ah; why the gases inside dissociate into the plasma state? And their chemical reaction, that follows. Actually, now can take place at as relatively lower temperature.

So, compared to the previous cases, where we did not have the presence of plasma, we saw that the CVD is typically held at about 500 degree centigrade or above, but because of the presence of these plasma the same reaction can now happen at a much lower temperature; compared to this is the normal CVD temperature range. So, this lower deposition temperature is actually very helpful if you are dealing with sensitive materials like, semiconductor device.

So, there will be very little damage; thermal damage to the substrate and yet, you can deposit the kind of film that you want, like a high dielectric or may be a conducting film, whatever you want. So, there are certainly distinct advantages, that we can see in case of plasma enhance CVD. So, we can restrict the temperatures.

So, we can conduct the deposition at a lower temperature. We can adopt fairly high deposition rate the film quality is known to be better and actually more adherent and overall the deposit that you form is much better or more conformal to the substrate meaning dimension wise, if they are contour wise, whatever you deposit you will exactly mimic.

So, if you have a flat surface, there is no problem, but if you have a rough surface, then also the deposit that you form will be fairly conformal to the substrate. Actually, the presence of plasma also helps to remove certain barrier layer, if at all it is present in the form of something oxide or some other reaction products, but there are certain disadvantages for example, this possibility of producing certain byproducts and which may get deposited along with the film the plasma produces certain chemical reaction.

You actually would like to deposit only the desired product, but there could be certain by-products due to the reaction taking place inside the chamber, which may get incorporated may be some complex interstitial compounds or intermediate compounds may get deposited.

But otherwise kinetically, this is much faster process.

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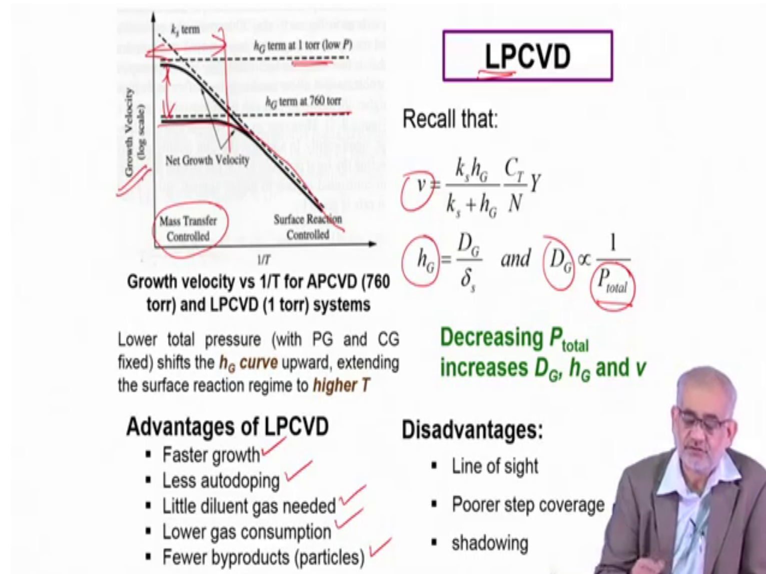

Now, in low pressure CVD, which is; where you actually a lot using fairly low pressure just a few torts compared to atmospheric pressure. So, you have fairly low pressure and because of this low pressure, the generally, the growth velocity is much higher at high temperature region. Now, typically in case of an atmospheric plasma; this would be the kind of growth rate. So, if you plot growth velocity as a function of reciprocal of temperature.

So, this is a high temperature region and this is the region, where you see that, the normal atmospheric CVD would give you a velocity profile, which will be high, but will not be extra very high, but then it drops as the temperature decreases. In case of low pressure plasma the reactivity is higher; the transport rate is higher as a result the velocity also will be higher. So, you have a fair amount of higher velocity at high temperature region.

So, this region; this provision is important, because this is where, the reaction is mass transfer controlled. So, we certainly have these advantages. We have faster growth, we have list auto doping; meaning, ejected atoms from the substrate or the chemical reaction getting doped or reaching the vapor phase and getting doped. So, this hazard is less, in case of low pressure CVD, the diluted gas or the carrier gas requirement is low, because already we are doing at very low pressure. So, scattering or resistance from within that atmospheric atmosphere within the chamber is less; the gas consumption is relatively

low and the by-products also low. Just because, the gas pressure is low so; obviously, the reactant concentration is low.

So, so, overall the velocity will depend upon the velocity will depend upon the various partition coefficient and the convection coefficient and convection coefficient in turn is dependent upon the layer thickness and the diffusion coefficient of the gas and division coefficient in turn is dependent upon the pressure, that we have in there. So, if you decrease the total pressure, then you increase the diffusion diffusivity; you increase the convection coefficient and also the velocity.

So, this is how the process, when you make it low pressure then, making it low pressure; helps in increasing all these major kinetic parameters and as a result of which, the growth velocity in general is higher at high temperature region. The on the other hand this process like any other CVD process is a line of sight process. The step coverage is low, because the velocity or the pressure the availability of the diffusion or the reactant is low and there is certain amount of shadowing effect which cannot be avoided.

So, for very small features; very sharp features, there will be certain difficulty.

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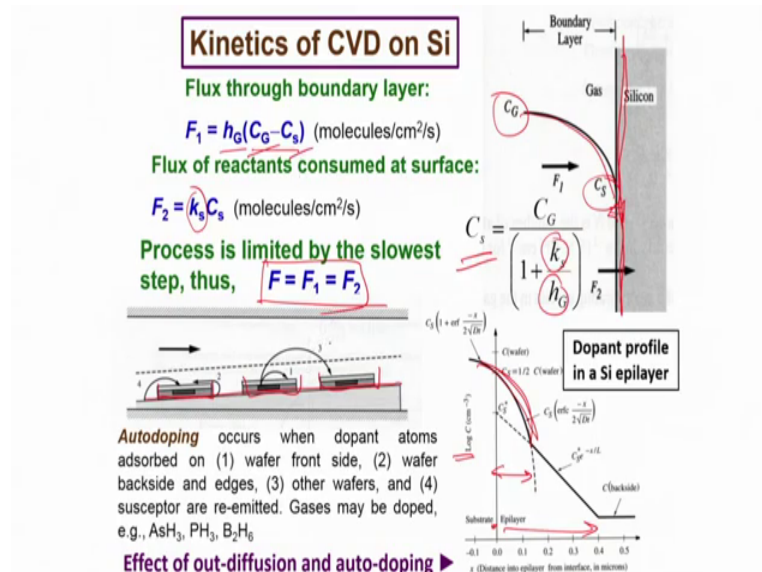

In fact, this for; when the substrate say for example, this is the stage on which, we have these samples these are the substrates and now, the flux of arrival of the of the deposits or the molecules or atoms of the deposit; they will be dependent upon the concentration

gradient; what we have in the gaseous phase and at the surface and of course and of course the coefficient of convection.

Now, this actually; at the surface, the flux that is available in terms of the molecules per unit area per unit time, will depend on the partition coefficient. So, what is the level of partitioning happening at the surface?

Now, So, the overall flux will be; when the when the situation is controlled very optimally, then the flux actually will be equal both in the away from the substrate surface and very close to the surface or on to the surface because, by then one of the steps, which could be due to partition coefficient or the convection or the concentration will actually make this condition valid, that the flux will be equal both for away from the boundary layer or at the top of the boundary layer or at the surface. So, this is what we want? And then finally, the profile known as the concentration profile varies like this; the concentration profile of the reactant species, which we want to be deposited.

So, away from the surface the concentration will be higher, but at the surface the concentration will be lower and this is dictated by this both by the partition coefficient and the coefficient of convection. So, this is how the CG decreases over a distance. Now, the diffusion the epitaxial layer that, we form basically. That the thickness of the of the species the concentration of the species always decreases with distance like this way.

So, this is how the. So, this is the surface and this is into the depth and this is where, the diffusion certainty is the maximum active; but then, and that is why the concentration is the highest, but the concentration decreases and then, below are certain level we will reach our saturation. The important point is that, this high concentration depth from the surface or this region from the surface.

So, this is the region which is very important and control of this can be a; thickness of this region can be controlled through the through meant through controlling the concentration turns and which in turn will be from the feed rate and of course, the temperature and other parameters.

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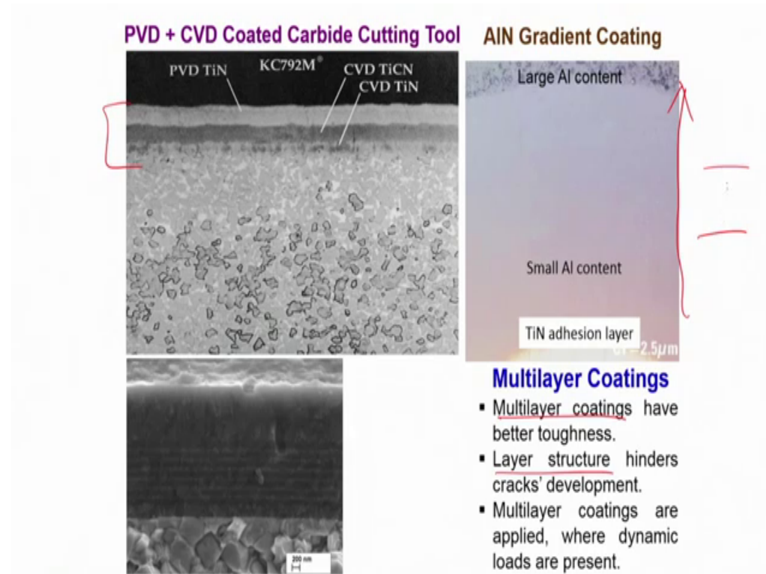

So, this is the example of certain coatings that we can develop maybe first you have a PVD coating and then, first you can have a CVD coating and then, you can have a final PVD coating. So, this is a kind of a composite coating, that you can develop, but what is important is that, in case of like; I was saying, in case of CVD. One can actually grade the coating from the depth to the surface or from the surface to the depth the coating can be graded and this is entirely depending upon what kind of gas you feed in? What is their flow rate concentration and other things?

One can actually change alternatively the feed gases and make multi layer coatings and can make layered structures and these kind of layered structures is very important, because if you make a very thick coating of a particular very high modulus material then, there is a possibility of greater chance of possibility of spallation or decohesion, because at the interface the mismatch is very large, but if the same coating may be a carbon nitride or a mixed nitride or a silicide if you do it in alternate thin layers very thin alternate layers; then the mismatch is actually accommodated nicely and the stress generated at the interfaces is minimized and as a result, you actually can make a much more adherent durable and mechanically stronger coating on top of the substrate.

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Points to ponder (recapitulation):

1. What are the distinctive features of CVD vis-à-vis PVD/sputtering and other coating methods from vapor/liquid/solid state?
2. Why is CVD considered more versatile than PVD or sputtering?
3. What are the main process parameters of CVD?
4. How does gas pressure affect CVD coating?
5. Why is adherence better in CVD than in PVD?
6. What are the main demerits of CVD?
7. What are the components usually subjected to CVD?

So, what did we discuss so far? We have talked about the mechanism the definition the mechanism and scope of CVD and we realize that, CVD distinguishes itself from other kinds of thin film coating techniques by the fact that, we are able to deposit a composition which is different than the precursor gases or the vapor that, we feed in and in fact, this is how it actually, differs from almost all other kinds of coatings either from vapor state or liquid state or solid state because; the compositional variation is possible here because of the chemical reaction that takes place.

So, it is obviously, much more versatile than all other vapor based techniques the process parameters we have discussed are mostly the composition the flow rate temperature the time substrate condition and so on and the gas pressure is very important because, we saw that, in case of low pressure CVD we actually can increase the kinetics of the process much faster and also the demerits like auto doping and so on can be avoided to a large extent the adherence in CVD is better.

Because of the possibilities of not only diffusion, but even thin chemical reaction layer at the surface which makes it more adherent. There are two merits; one of them is of course, the emission of the poisonous gases as by-products, which need to be handled carefully; also the entire chamber has to be hermetically sealed during the processing, because you are dealing with reactive gases like; hydrogen or certain hydrocarbons or even halide containing gases and so on.

So, leakage must be prevented at by all means and so, we actually also have to worry not only about the chamber, but also the also the pumping devices that we use either to feed in or to extract. All kinds of cutting tool inserts semiconductor devices ceramic components all moving parts which require a very thin hard high elastic modulus as substrates are ideal for such composite ideal for such coatings by chemical vapor deposition.

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References

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Thank you very much.