Surface Engineering for Corrosion and Wear Resistance Application

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Lecture – 45
Physical Vapur Deposition (PVD)

So, we have had discussions on coating by physical methods by diffusion control methods from the solid state or the vapor state. We also discussed a large number of techniques based on aqueous or molten bath including electrochemical deposition techniques. You also had various approaches of spray based techniques which are plasma or plasma based techniques for example.

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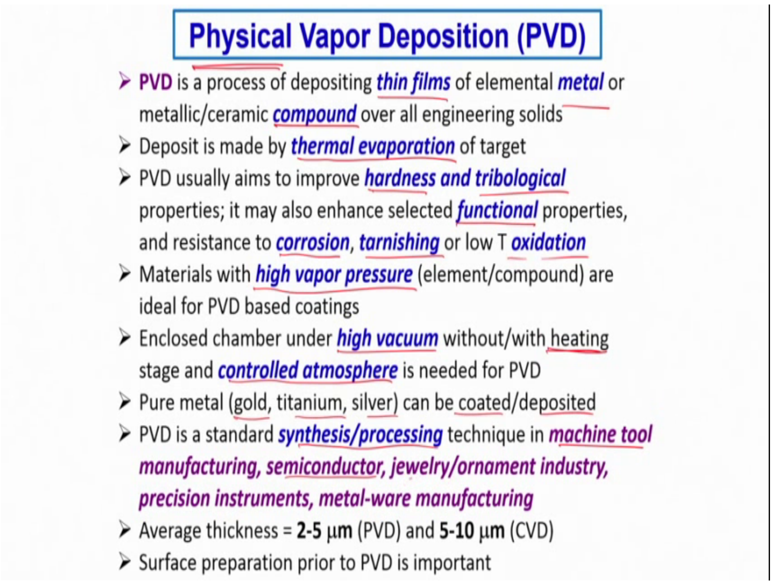

Physical Vapor Deposition (PVD)

- PVD is a process of depositing *thin films* of elemental *metal* or metallic/ceramic *compound* over all engineering solids
- Deposit is made by *thermal evaporation* of target
- PVD usually aims to improve *hardness and tribological* properties; it may also enhance selected *functional* properties, and resistance to *corrosion*, *tarnishing* or low T *oxidation*
- Materials with *high vapor pressure* (element/compound) are ideal for PVD based coatings
- Enclosed chamber under *high vacuum* without/with heating stage and *controlled atmosphere* is needed for PVD
- Pure metal (gold, titanium, silver) can be coated/deposited
- PVD is a standard *synthesis/processing* technique in *machine tool manufacturing, semiconductor, jewelry/ornament industry, precision instruments, metal-ware manufacturing*
- Average thickness = **2-5 μm** (PVD) and **5-10 μm** (CVD)
- Surface preparation prior to PVD is important

We are now going to discuss the this is going to be the 45th lecture and we are going to discuss the Physical Vapor Deposition.

As one of the possible methods of producing coatings, but for a difference these coatings are going to be thin, fairly is thin coatings usually in the tens of microns range; I mean at in special cases one can go to millimeter, but usually they are just a few micrometer thick coatings. So, that is why these coatings are typically called thin films, where not even coatings. So, as a name suggests Physical Vapor Deposition, the process requires only a change of state, physical state.

So, you can deposit a thin film of elemental metal or compound on any kind of engineerings solids for a small area or a larger area. The process is based on thermal evaporation; so, essentially you take the material to be deposited and evaporated by way of heating usually resistance heating. You would like to; you do this primarily to improve the hardness or all the most important tribological properties starting from friction to wear and erosion and other processes.

There could also be utility is based on improvement of functional properties, which can be anything from conductivity to reflectivity to; so, make it amenable to various kinds of other functional applications. Similarly, this also can impart resistance to corrosion resistance to tarnishing at room temperature degradation or even against oxidation. the difference as is mentioned already is in the fact that we are dealing with fairly thin films.

So, obviously we need materials in order to take to the vapor state we need materials with very high vapor pressure so that they can by heating we can easily take them into the vapor state and they can create a saturated vapor pressure around the material or component to be coated. The so, first we take the material that we want to coat and the component that we want to coat both inside and then, close chamber and then, evacuate and create fairly high vacuum over 10 raise to minus 5 millibar or even higher vacuum we may have arrangements for heating may not have arrangements for heating.

Heating separately, I mean ancillary heating processes for the substrate. We should also have a controlled atmosphere; we may create a controlled atmosphere, which could be simply verified chamber high vacuum or inert gas like argon or we can even have a reactive gas in some very special cases. But remember the evaporation is done by heating, but this heating here mainly refers to the possibility of heating the substrate, which actually you are getting coated.

So, you can coat pure metals like gold, titanium, silver in special cases may be chromium or nickel or materials which actually, but generally you choose metals which actually have fairly high vapor pressure. So, they can be coated or deposited and this actually also is a standard synthesis or processing technique for creating wire resistant coating or low friction coating on machine tool for machine tool manufacturing, for semiconductor industry creating various IC integrated circuits or various other kinds of components in jewelry and ornament industry; this is very popular.

It can be also very very useful for precision instruments to create and create a matching coating to match the coefficient of thermal expansion or friction coefficient and so on. Similarly, also is useful in metal ware industries. Typical thickness we are talking about is only 2 to 5 to 6 micrometer, not even 10 micrometer; whereas, in case of CVD one can go the chemical vapor deposition which, we will discuss after a couple of lectures; you can create slightly thicker coating.

So, here what we actually have to understand is that this is coming from the vapor state and if you build on a very thick coating the stresses at the interface is going to be fairly large, which is going to be harmful. So, we prefer to create a very thin coating, but we need to create; we need to clean the surface well, remove not only the any kind of oil or grease, but also any presence of thin oxide layer because that is going to then, not allow good adherence of the deposited film onto the substrate. So, surface preparation is very important.

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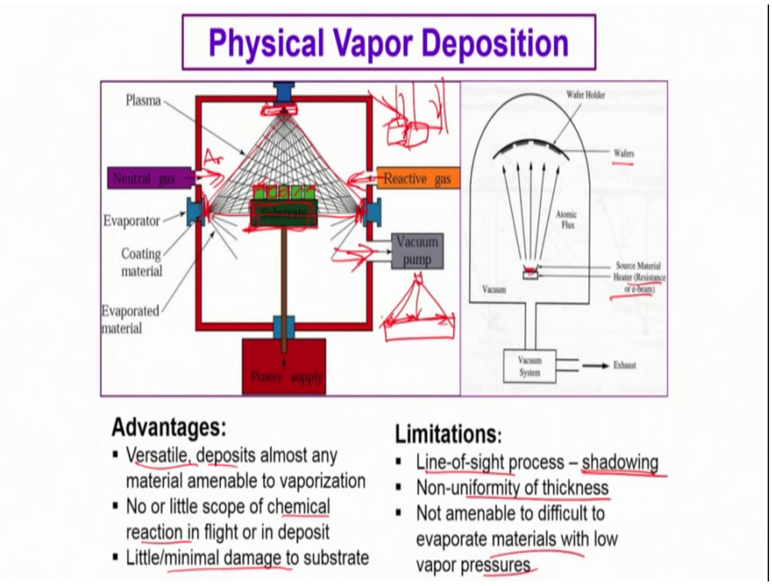

Physical Vapor Deposition

Advantages:
- Versatile, deposits almost any material amenable to vaporization
- No or little scope of chemical reaction in flight or in deposit
- Little/minimal damage to substrate

Limitations:
- Line-of-sight process – shadowing
- Non-uniformity of thickness
- Not amenable to difficult to evaporate materials with low vapor pressures

So, typically the chamber looks somewhat like this. It usually, it is like you would have seen bell top jar with a flat bottom. So that you actually can lift the bell and then, bring it back ah; otherwise, it can be simply a fixed chamber. You do not necessarily have to remove the bell or something; so, it can be a fixed chamber and you have evacuation process.

So, this is how you actually can evacuate and make it, make the inside the chamber extremely low pressure. You can backfill with neutral gas for example; argon or you can also feed in oxygen or nitrogen if you want certain reaction to take this.

But this is not very regular or usual, but feeding argon is fairly regular. Because once you evacuate then, when you feed in argon, argon remains neutral. And then, also creates a situation whereby, undue oxidation is avoided.

So, this is the substrate, the component that you want to coat or maybe this is the stage and on the stage you can place multiple components like here 1, 2, 3, 4 components. And now, once you actually create this high vacuum and apply high amount of current. So; now, you evaporate these materials and with the evaporation you actually create certain amount of vapor atmosphere of the component that you want to coat.

So, as you so this is let us say this is the may the component or the solid that you want to coat and as you as you evaporate and so this whole region gets completely filled with this vapor of the material. And this vapor atmosphere now covers the entire range of components that you want to coat. So, when you evaporate thermally say from these regions you actually can also create by way of applying certain amount of potential inside, you can create a plasma and that plasma actually can make the de polishing process more efficient.

So, for example, if you have heating process which can be either a resistance heating or through an external electron beam, which create which and you have your material to be coated kept in a tungsten boat or some other holding material, which can withstand very high temperature

And so, you can have a separate heating arrangement either by feeding current through this tungsten boat. Or you can allow the external electron beam to irradiate this place; and then, you create this atomic flux.

And this is where you keep all your components; for example, in this case this could be silicon vapor where, you want to for example, coat certain areas onto the surface, but not all. The areas where, you do not want to coat you cover them up with a certain mask and then expose the rest of the parts, which gets coated with the desired metal or the material.

So, you have multiple advantages. So, this is a very versatile process and the deposit you can deposit almost any material, which get goes to the vapor state; very little chance of chemical reaction. In fact, you can avoid completely chemical reaction in flight or in deposit and a very little damage to the substrate, because the substrate is at room temperature or near to room temperature.

The chamber inside gets heated up little bit, but not very high. So, when we evaporate from any of these evaporators and when, we want to coat these components we actually can immerse them. So, this is a line of sight, but at the same time this makes a very uniform coating because it is kind of immersed in the vapor, immersed in the vapor atmosphere.

Now, there are also demerits; for example, there is a line of sight process. So, you actually can cover only the surface that you are seen, the vapor is seen directly. So, there could be a process of shadowing. See, for example, if you have a component here and another component here and if the vapor is arriving this way a portion here may get shadowed.

So, we have to make sure that the vapor arrives uniformly from the top or from one of the sides so that you can cover the entire area. In fact, the area of the vapor actually should be wider than the components that we are coating.

Then, we can make sure that the component is very widely very uniformly covered. So, ah; so, we have to avoid these shadowing effect possible shadowing effect. There could be non uniformity of the thickness; see, for example, if you are coating wide area like this and if you have only a single evaporator here, you expect that the evaporation should actually cover the entire area like this uniformly, but the rate at which the species will arrive here will not be the same when, this region is fairly wide, fairly wider part.

So that coating thickness may vary from the center to the periphery. This is also difficult; for example, if you are thinking of coating tungsten itself; then, it is difficult because the melting temperature and the vaporization temperature is high. So, you would rather choose materials which are easy to evaporate, which has high vapor pressure and relatively low boiling temperatures.

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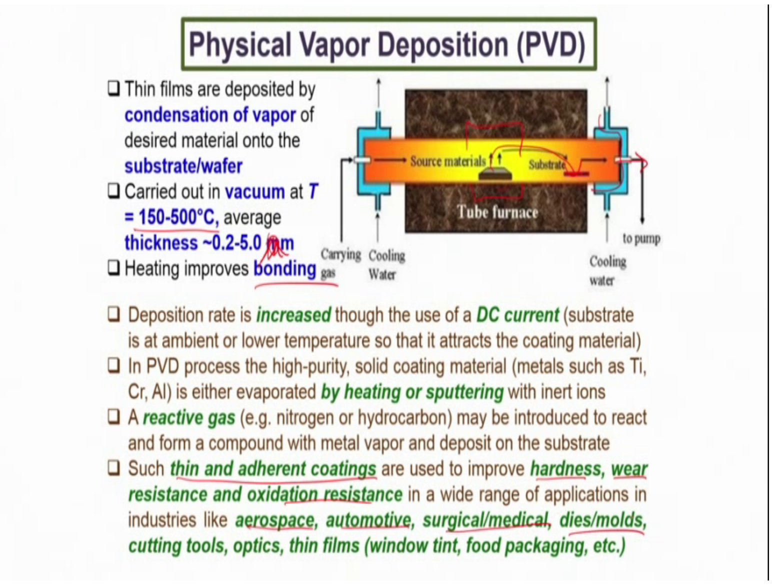

Physical Vapor Deposition (PVD)

- ❑ Thin films are deposited by **condensation of vapor** of desired material onto the **substrate/wafer**
- ❑ Carried out in **vacuum** at ***T* = 150-500°C,** average **thickness ~0.2-5.0 μm**
- ❑ Heating improves **bonding**

- ❑ Deposition rate is ***increased*** though the use of a ***DC current*** (substrate is at ambient or lower temperature so that it attracts the coating material)
- ❑ In PVD process the high-purity, solid coating material (metals such as Ti, Cr, Al) is either evaporated ***by heating or sputtering*** with inert ions
- ❑ A ***reactive gas*** (e.g. nitrogen or hydrocarbon) may be introduced to react and form a compound with metal vapor and deposit on the substrate
- ❑ Such ***thin and adherent coatings*** are used to improve ***hardness, wear resistance and oxidation resistance*** in a wide range of applications in industries like ***aerospace, automotive, surgical/medical, dies/molds, cutting tools, optics, thin films (window tint, food packaging, etc.)***

So, you can have instead of enclosing in a chamber like that you can also create of tube furnace like configuration; where, you can keep the holders cooled by flowing air, flowing water through these gaps. You can use these openings to pump out the gas inside evacuate it and this is the source material. And now, you can you heat it in a tube furnace.

So, instead of directed heating, instead of creating the I mean in the previous case if you see, we actually had a boat here and this boat usually is a tungsten boat, which can be heated to very high temperature. So, tungsten has the capacity of producing going up to very high melting temperature and in the process it has fairly high resistance, resistance increases with temperature; so, because of these kind of resistance heating.

The; whatever, powder you keep here they get evaporated. So, that is how we do and we expect the evaporation evaporated species to go all over. In fact, if we have evaporators surrounding the chamber then, of course, we can create a fairly uniform plasma inside or fairly uniform vapor vaporized atoms inside. On the other hand, we can make a relatively simpler process where, we can take a source material and simply place it inside a tube furnace and with enclosures airtight enclosure. So, we can evacuate make it very low very low pressure and then, we heat up the tube furnace; so that material from here gets evaporated.

And this is the colder portion of the furnace. So, maybe the heating zone is confined only here so that the material is heated and vaporized only in this region. And the vapor obviously, because of the temperature gradient will move towards the colder region and get deposited on to the substrate that you want to coat; so, that is also possibility. So, the temperature that we can heat up to inside the furnace is not very high maybe up to about 500 degree centigrade, but no actually this is micrometer. So, this can be fairly thin coating.

So, the deposit that we create should be thin and adherent. So, and we want to improve the hardness the wear resistance, the oxidation resistance and typical applications could be in industries like aerospace, automotive, surgical or medical in manufacturing using dies and molds and cutting tools in various kinds of optical devices; wherever, we you have use of thin films even on glasses for tinting for anti reflection for coatings photovoltaic layer and so on; for food packaging.

In various places we have these application of PVD. in rare cases PVD can also take the help of certain reactive gases like nitrogen or hydrocarbon and then, create reaction layer onto the substrate.

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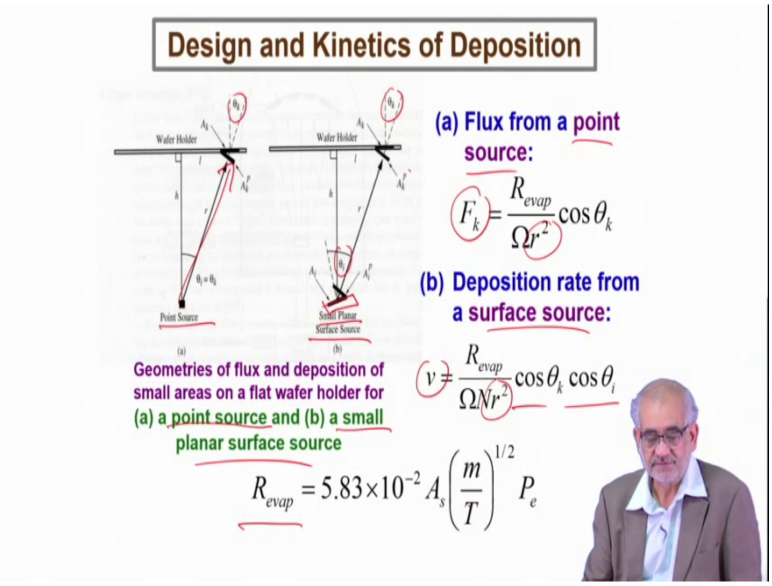

Design and Kinetics of Deposition

(a) Flux from a point source:

$$F_k = \frac{R_{evap}}{\Omega r^2} \cos\theta_k$$

(b) Deposition rate from a surface source:

$$v = \frac{R_{evap}}{\Omega N r^2} \cos\theta_k \cos\theta_i$$

Geometries of flux and deposition of small areas on a flat wafer holder for (a) a point source and (b) a small planar surface source

$$R_{evap} = 5.83 \times 10^{-2} A_s \left(\frac{m}{T}\right)^{1/2} P_e$$

So, the kinetics of the process will depend upon the configuration that we use. So, for example, we can use a point source or we can use a small planar surface source. So, the here the area is wider. So, we actually are able to cover wider area. Here, the area or the spot that we covered is fairly small; so, either a point source or a small planar source.

So, in case of a point source the flux will be inversely proportional to the radial distance. So, this radial distance, the same thing is true for a wider surface area the velocity in that case will be inversely proportional to the square of the radial distance, but in addition it will also depend; here, it primarily depends upon this theta k. Here, it depends both theta k as well as the theta i because of the points obviously cannot cover wider area, but planar if the source is not a point, but the source is of certain surface area; then, obviously it can cover a wide area and that is seen here. The overall evaporation rate of course, will depend upon the mass and the temperature of the material.

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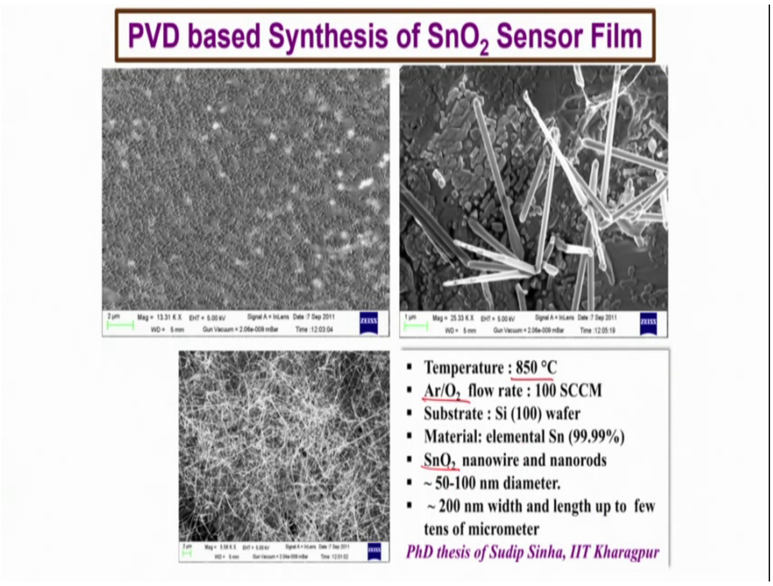

PVD based Synthesis of SnO_2 Sensor Film

- Temperature : 850 °C
- Ar/O_2 flow rate : 100 SCCM
- Substrate : Si (100) wafer
- Material: elemental Sn (99.99%)
- SnO_2 nanowire and nanorods
- ~ 50-100 nm diameter.
- ~ 200 nm width and length up to few tens of micrometer

PhD thesis of Sudip Sinha, IIT Kharagpur

Actually, you can create special conditions of maintaining a specific temperature and mixture of argon and oxygen to create certain oxide layer. So, you actually heat up tin and introduce very low amount of oxygen and allow certain reaction to take place and this reaction can lead to formation of a very thin tin oxide layer. And this tin oxide layer the beauty of it is that actually by controlling the process parameters you can change the aspect ratio very significantly.

So, you can make such very thin wires and rods. And in fact, you can have a completely a very thin wire mesh in the form of a wool. These kind of large aspect ratios where, the diameter is only a few tens of a nanometer, but the length can be easily a micrometer or close to a micrometer that can have very high applicability for sensing certain gases because a surface specific, surface area of these kind of shapes is extremely high.

So, normal tin oxide film will have one level of sensitivity whereas, if you can create such high aspect ratio the sensitivity would be much greater. And to create such exotic structures, you actually can modify the conventional PVD and change the process parameters and allow feed in a particular rate and way; so that you can produce such very thin layers with large aspect ratio structures.

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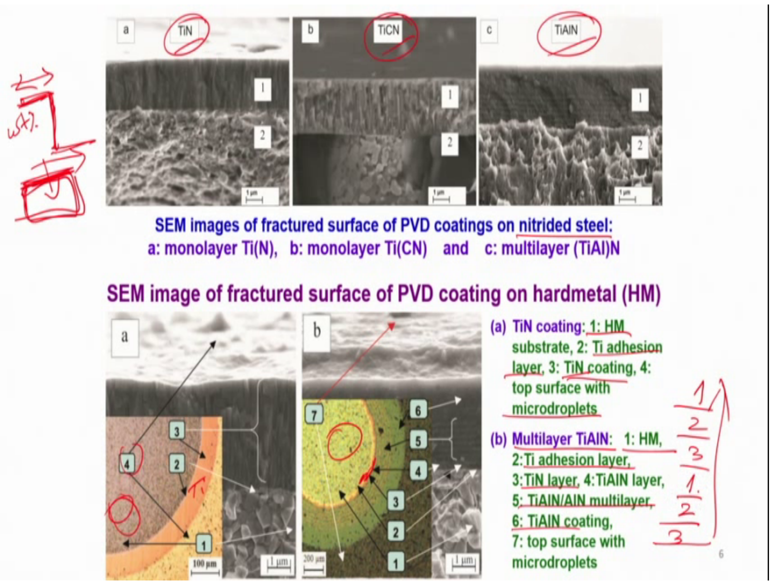

SEM images of fractured surface of PVD coatings on nitrided steel:
a: monolayer Ti(N), b: monolayer Ti(CN) and c: multilayer (TiAl)N

SEM image of fractured surface of PVD coating on hardmetal (HM)

(a) TiN coating: 1: HM substrate, 2: Ti adhesion layer, 3: TiN coating, 4: top surface with microdroplets

(b) Multilayer TiAlN: 1: HM, 2: Ti adhesion layer, 3: TiN layer, 4: TiAlN layer, 5: TiAlN/AlN multilayer, 6: TiAlN coating, 7: top surface with microdroplets

In fact, you can by way of reaction base PVD you can create for example, here you have a nitrided steel and on top of that this is where, in a you have created titanium nitride in b you have created titanium carbon nitride and in c you have created titanium aluminum nitride. So, you have created a single nitride, you can create the carbon nitride, you can create a combined nitride a mixed nitride. And this is possible not just.

It can be done in the same chamber; you simply have to move from one spot of heating to another. So, if you are heating by e beam you can switch the beam focus from one target to another and then, evaporate a different material. So, in this process say for example, you are seeing here that you can have; this is the hard metal that you have. So, this is the metal base metal that you have and on that you have the titanium edition layer; so, layer 2 is titanium and then, you have titanium nitride coating.

So, this is the; this is the layer which is titanium nitride and the titan nitride on the top surface will also show some micro droplets. Now, why does micro droplets home because of typically, because of the give some effect that you actually form very small deposits which, because of large surface area actually gets its melting temperature reduced. And as a result during deposition they tend to coagulate; they because of surface tension forces it into cognate and form a droplet.

So, this is not desirable. So, one has to make sure such that such non into format is avoided. we can also create the multi layer titanium aluminum nitride say for example, in this coating what you are seeing is that this is the base substrate as usual like we said here a base substrate is again some kind of a metal and on top of that we have a titanium adhesion layer which is this layer. Then, we have titanium nitride layer and this is, this the next layer.

Then, we can have multi layers. So, we can have multi layers of titanium aluminum nitride or aluminum nitride and so on. The point I am trying to make is that you actually in the same chamber without breaking the vacuum, without moving, without needing the sample to be taken out you can make multiple coatings. Now, in all these cases there is one point which I have not mentioned, but would now like to stress upon is the fact that whenever, you are creating these kind of vapor deposited coating maybe they are very thin film; yet the substrate coating interface is very sharp.

In other words, if this is the substance or substrate that we want to coat and this is the film that we have created if you go across at the coating in, coating substrate interface you see if this is the composition whatever you are saying and this is the distance; so, the coating will have one composition and the substrate will have another and the interface is fairly sharp. Now, this sharp because of this sharp interface you cannot afford to make this thickness of the coating very large because in that case you build up very high amount of stress at the coating substrate interface.

And which can lead to de cohesion during use. On the other hand, to have if you want a very exotic coating like titanium nitride or titanium aluminum nitride on top of and nitride it steel or some other cutting tool you do not need very high thickness coating; you would rather not have very thick coating because of the reasons that the mismatch will be substantial and this can actually lead to complete equation.

But this is the only way you can have such exotic coating created on top of a substrate; otherwise, you cannot think of a single manufacturing or synthesis process by which you can have a steel then, you nitride and then, you have other kinds of nitrides like titanium nitride or titanium carbon nitrides or titanium aluminum nitride these kind of combinations. So, in order to have such combinations and the beauty of these processes that you actually can have a multi layer; meaning I can have an alternate layer of. So, this is 1, this is 2, this is 3 and I can repeat this a number of times.

So, I can have such multi layer coating. And in the process I can make sure that the coefficient of thermal expansion miss match is minimized or marginalized and that would depend upon the relative thickness and their relative composition and obviously, the lattice parameter and other important physical properties. So, to have a very thick layer directly on top is very difficult, but if I can have such multi layers; then, the adherence is improved and such a thin film coating actually will perform better under any kinds of aggressive conditions.

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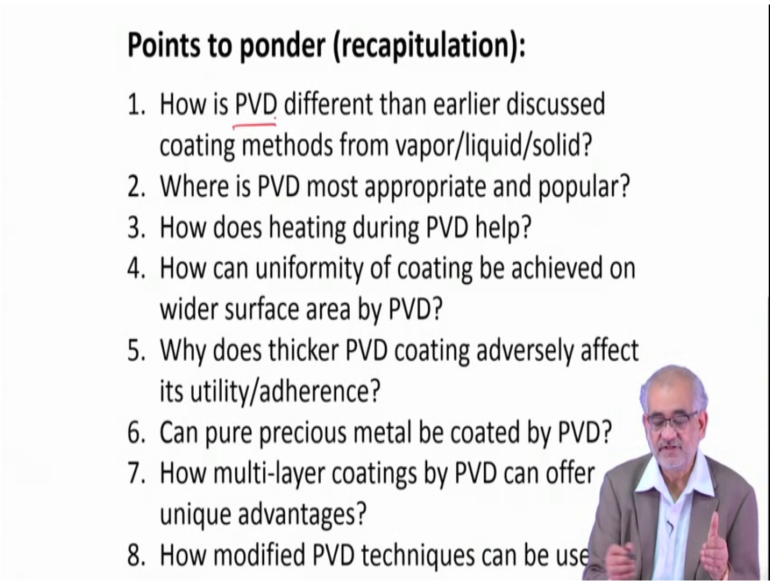

Points to ponder (recapitulation):

1. How is PVD different than earlier discussed coating methods from vapor/liquid/solid?
2. Where is PVD most appropriate and popular?
3. How does heating during PVD help?
4. How can uniformity of coating be achieved on wider surface area by PVD?
5. Why does thicker PVD coating adversely affect its utility/adherence?
6. Can pure precious metal be coated by PVD?
7. How multi-layer coatings by PVD can offer unique advantages?
8. How modified PVD techniques can be use

So, time to recapitulate. So, what all we have discussed. We said we first; now, are I have started discussing about thin film coating and this is one of the most versatile method would be Physical Vapor Deposition where, the process involves evaporation of very high vapor pressure material in the vapor state and then, allow them to deposit on any colder substrate, that cold substrate. In fact, if the vapor is allowed to go or to the chamber surface there also it gets deposited.

But we do not want that. So, we want, we create a certain trajectory; so that the component is placed on the path of the vapor the where, the vapor tends to move and on and at that part it could be a metal, it could be a silicon semiconducting material which gets coated.

So, there is no change in composition. This is where we are different than the previous methods that we have discussed. So, we exactly deposit what we have in the form of the target hm. So, PVD can be very very useful technique for semiconductor industry, for tooling industry, for precision measurement industry, meterological instruments industry; where, we want exactly 2.5 micrometer or maybe 200 and 10 nanometer and not 225 nanometer. So, it can be very precise.

The; if we have heating we do need to evaporate, but that is a separate one. But if you also heat the substrate during deposition; then, the interface that I was just talking about a few minutes ago which is usually very sharp may not be that sharp anymore. So, there could be some amount of diffusion and in the process there could be better bonding.

So, separate heating during the PVD process can be helpful. We actually can make sure that we are able to coat uniform by having multiple targets or having vapor zone much wider than the component that we want to get the coated. We also can make sure that the coating is more uniform by half creating a plasma inside by introducing certain amount for argon.

If you want to create a thicker coating then, we must be aware that this could lead to de cohesion because of the stresses generated at the interface. So, we can coat pure metal, we can coat compound, we can coat alloys. In fact, we can make a non stoichiometric alloy and rapidly solidify or simply blend different types of powders crush them, mill them and then, centre them together; create a target and use that target. The target probably should in that case be able to achieve a right composition and then, use that target as our target for deposition.

So, we are able to then deposit a very new and a very exotic and a non stoichiometric composition onto the component that we want to coat. We can make multi layer coatings as I was saying that we can make a, b, c, or a, b or we can vary the thickness of a, b, c sequentially; all by controlling the process parameters of PVD.

And we actually can make a modified PVD technique whereby, we introduce certain gases allow them to react and then, form a coating, thin film which is not pure say tin, but tin oxide or zinc not zinc, but zinc oxide and in the process we actually can create certain devices or certain sensors or other kind of applications with the microstructure which is very exotic and not possible by conventional techniques.

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So, we stop here now and then, in the next lecture we will discuss special technique of PVD called sputtering.

Thank you very much.