Surface Engineering of Nanomaterials
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Lecture - 12
Physical Vapor Deposition (PVD)

In this particular lecture we are going to discuss about the different types of physical vapor depositions. In the last slides or maybe the last lecture we have seen that there are several types of different deposition techniques or maybe the surface modification techniques which we have already discussed, but in this particular lecture we are going to discuss only about the physical vapor deposition in details. So, first, before going to start that let us know that what is the PVD or maybe in physical vapor deposition method actually tells us.

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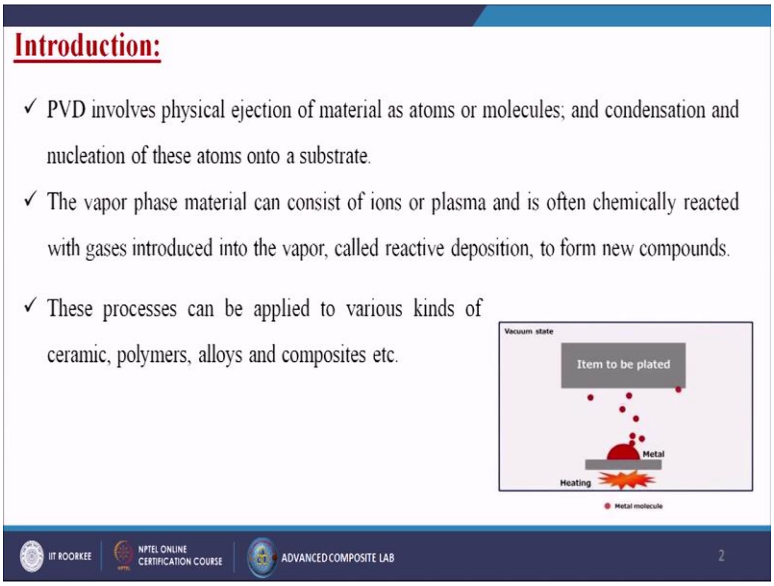

So, it is a one kind of methods by which physical ejection of materials and upon some molecules and convention and nucleation of these atoms onto a substrate; that means, from this particular line we can get that we are having certain kind of base or maybe that certain kind of materials we are agitating by maybe some laser or maybe some electron beam or maybe some current or maybe some thermal and that is releasing some kind of atoms or maybe the molecules or maybe the some kind of plasma materials. And then we are using certain kind of vapor gases may be or may not be then that materials or maybe that ions and that molecules can deposit onto the substrate which you are going to modify. So, in a basic term just simply we are doing the coating by using any kind of atoms or molecules or maybe the plasma into the vaporized conditions.

The vapor phase material can consist of ions or plasma and is often chemically reacted with gases introduced into the vapor called reactive depositions to form a new component. So, from this particular line we can understand that whatever the gas we are introduced maybe it can react with that ions or molecules or maybe it can simply the inert one to help the homogeneous coating of that particular material onto the substrate itself. Then this process can be applied to various kinds of materials like ceramics, polymers, metals, then allows, composites etcetera. So, here is the thing.

Now this is our material which we are going to substrate, which we are going to modify and this one or maybe that rather we can say it that as a substrate and this is the metal ions or maybe some kind of materials which we are going to put on top up to our substrate. So, here we are keeping our materials then either by giving the heating or maybe some kind of electron beam or maybe the laser beam or maybe some kind of other energy materials we are agitating these metal ions, so that these metal ions slowly, slowly it can deposit it on to the substrate itself.

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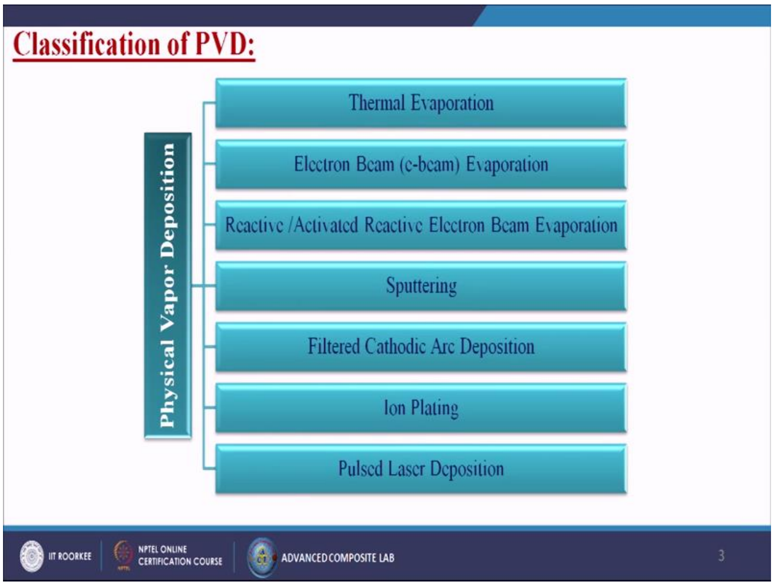

Then next slide we are going to discuss about the classifications of the PVD or maybe the physical vapor deposition process. So, there are several types of classifications are available in terms of that how we are going to modify those samples, how we are going to agitate the materials or may be how we are going to do the coatings or may be what terms of energy just we are using to agitate those materials and do the coating over the substrate.

So, first one is called the thermal evaporation methods, then electron beam or maybe the e-beam evaporation method, reactive activated reactive or activated reactive electron beam evaporations, sputtering, filtered cathodic arc depositions, ion plating and pulsed laser deposition. So, here we can see that total seven numbers of classifications are available regarding PVD method.

So, first we will discuss into details about the thermal evaporation. So, what the thermal evaporation means. So, from the name itself you can understand that we are giving certain kind of heat to the source material, so that it can agitate due to that temperature or maybe the heating and then it can release the atoms or molecules and directly that atoms and molecules can go onto the substrate an slowly, slowly it deposit on to top of that. So, here the beauty of these techniques is that it is totally the controllable one. So, what about the thickness we are going to achieve? Easily we can achieve those materials. So, a thermal evaporator users and electric resistance heater to melt the source material and raise its vapor pressure to a useful range. So, sometimes we are using certain kind of heating element or maybe the heating coil then that heating coil is giving a thermal environment by which your source is coming into the vapor form. And that vapor is depositing onto your substrate or maybe the metals or maybe the ceramics or maybe the polymers.

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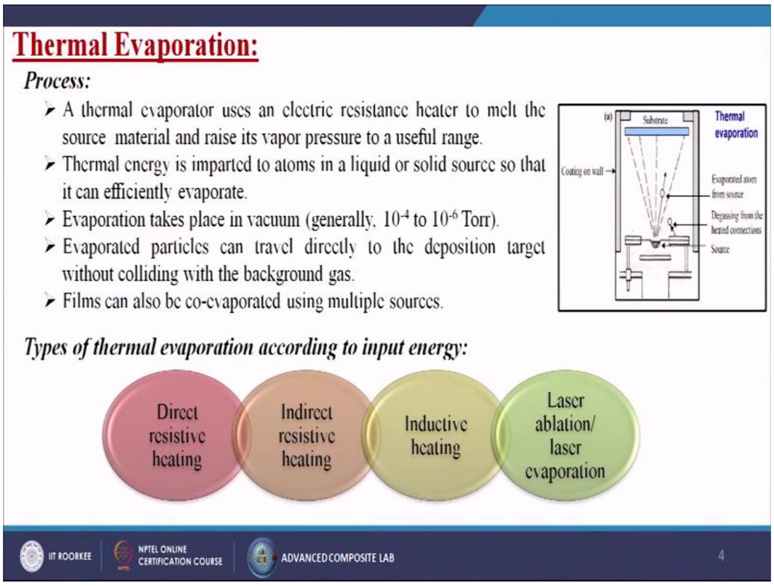

Thermal energy is imparted to atoms in a liquid or solid source, so that it can efficiently evaporate. Evaporation takes place in vacuum generally we are using the high vacuum because otherwise what will happen if we do not use the vacuum or maybe we do not use certain kind of inert gases maybe that vaporized materials can be reacted with the environmental oxygen or may be the moisture and it can form the newer materials or maybe the some un-useful materials.

Evaporated particles can travel directly to the deposition target without colliding with the background gas; films can also be evaporated using multiple sources. So, from this particular figure you can understand that we are having certain source over there then we are doing for the degassing we are having a coating onto the wall, so that that heat cannot go outside, this is our substrate material on which we are going to do the coating then we are agitating these materials by means of any kind of heater or maybe the electrical coil, so that this can be formed the vapor and that vapor directly can deposited on to the substrate itself.

So, now, from this we can see that there are several thermally evaporations according to the input energy first one is called the direct resistive heating, then indirect resistive heating, inductive heating and the laser ablations. So, as I already mentioned that there are different types of source or energy, it depends that how we are going to give the energy depending upon that we are doing the nomenclature of different heatings and different thermal evaporation methods.

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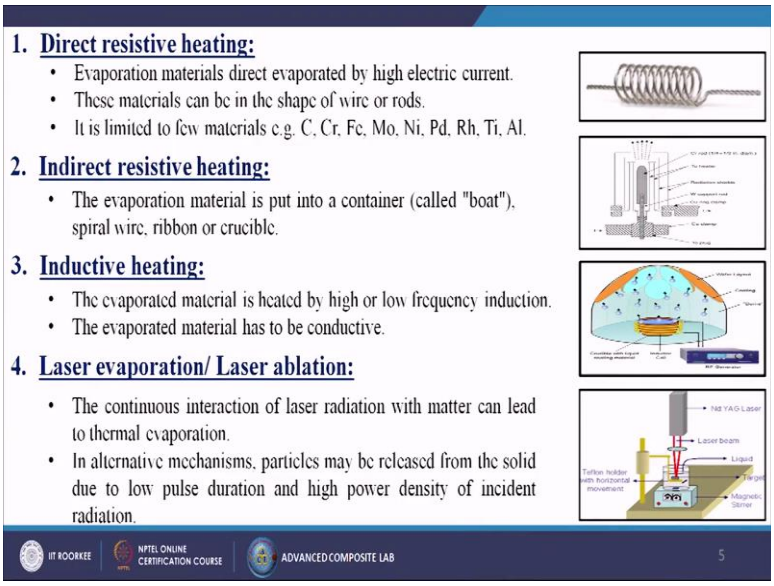

So, first we are going to discuss about the direct resistive heating. So, from this particular we can understand that we are giving the direct heat on to the source material itself. So, evaporation materials direct evaporated by high electric current. So, we are giving a high electric current it is a coil. So, we are giving a high electric current on to the source material by which it is coming into the vapor form. So, these materials can be in the shape of wear or rods, it is limited to few materials like carbon, chromium, iron, molybdenum, nickel, palladium, ruthenium, titanium, aluminum etcetera.

Then next one it is coming about the indirect resistive heating. So, in this particular case we are using certain kind of materials which is known as a boat its nothing, but the mid of my any kind of ceramic materials which can withstand the higher temperature too. It is like a small bowl type of materials which is known as a boat then some kind of spiral wire or maybe the ribbon or maybe the crucible which is means universally used in everywhere. So, in this particular case you can understand that we are putting the crucible over here then directly we are using certain kind of indirect heat onto those source materials, so that it can directly vaporize and that vapor can deposit onto your substrate

Then next one is called the inductive heating. So, the evaporated material is heated by high or low frequency induction method. So, here we are going to use the induction method that is why these techniques are known as the inductive heating the evaporated materials have to be conductive. So, there is no possible to do any kind of insulating material

Then laser evaporations and ably or maybe the laser ablations, from this particular we can understand that here the source of energy is the laser. So, simply we are applying the laser onto that source material, so that it can come into the vapor form and then that vapor can be deposited onto a material surface. Continuous interactions of laser radiation with matter can lead to thermal evaporation, in alternative mechanisms particles may be released from the solid due to low pulse duration and high power density of incident radiation. So, from this particular figure we can understand here we are using Nd:YAG laser, then it is coming the laser through there is a one lens then the all the source energy is coming into a single point, so that all the energy can be accumulated in a particular point, then we are putting the target over here and then we are having some kind of magnetic stirrer for the homogeneous coating of that particular material.

So, what are the advantages? First one is called the it is very very simple and cheap methods, less surface damage of the substrate excellent purity of the flames because there is some direct method, there is some indirect method. So, anyhow we are not going to harm our target materials. So, just we are giving the energy to the source material, so that source materials can come into the vapor form and simply deposit onto a target material or maybe the substrate material.

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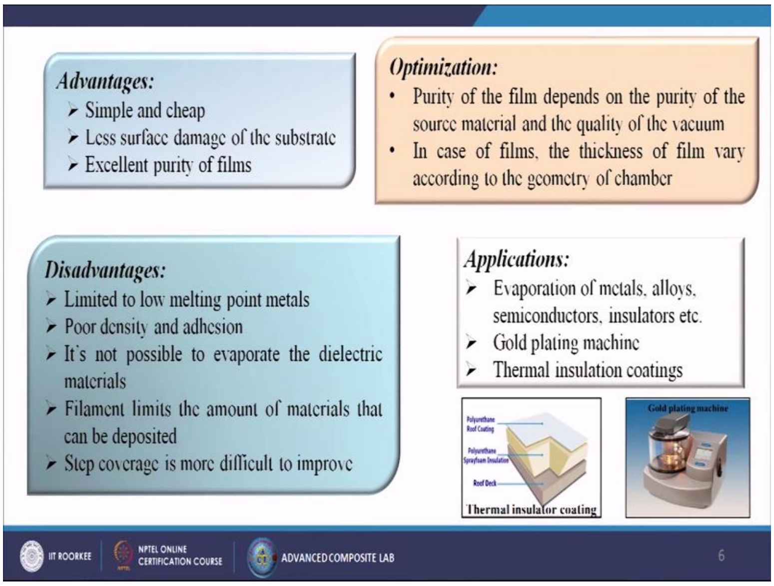

Then there is certain kind of disadvantages also limited to low melting point metals poor density and adhesions because we are giving a certain heat to that particular material. If the melting point of that precursor material is too high then it is very difficult to make them into the vapor form. Not only that the directly the gas is coming onto the substrate. So, it depends upon the surface chemistry of that particular target material. So, if the target material is little bit sticky or maybe there is some kind of oil or maybe the grizziness is absorbed, so automatically that material will deposit on to that surface of course, but there will not be any bonding or maybe the additions in between these two. Then it is not possible to operate the dielectric materials, filament limits the amount of material that can be deposited, step coverage is more difficult to improve. So, there are lots of disadvantages are possible.

Then optimizations purity of the film depends on the purity of the source material and the quality of the vacuum in case of films the thickness of films vary according to the geometry of chamber. The thing is that what about the source material or maybe the precursor materials we are going to take that depends upon the purity, if that material itself impure then with that material some impurity also come into the vapor form and that will deposit onto the substrate, so that will not get the exact properties whatever we want. Then in case of films the thickness of films varies according to the geometry of the chamber because it depends upon the vacuum. So, if the sample size will be more then automatically the chamber size will be more accordingly because we need certain constant vacuum for doing this kind of modifications. Then what are the applications evaporations of metals, alloys, semiconductors, insulators etcetera; gold plating machines; thermal insulation coatings. So, this is the common picture generally we can see in our lab where we are doing the coating of our materials for doing any kind of microscopical studies.

Then next one we are going to discuss about the electron beam evaporation. So, from the name itself we can understand that here we are using the electron and then that electron we are bombarding on to the source materials or may be the precursor materials and then that percussion a materials is releasing certain kind of ions or maybe the molecules or may the plasma, then that is directly depositing unto your base metals or may be the substrate.

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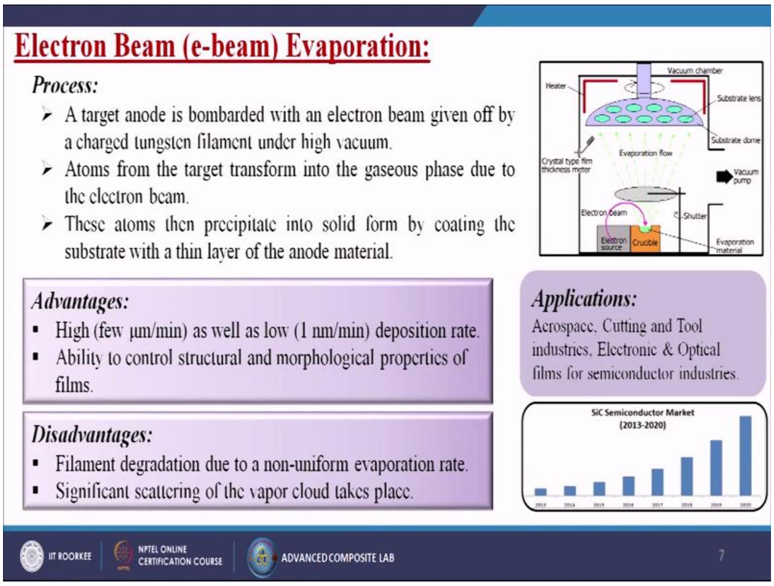

So, here it target anode is bombarded with an electron beam given up by a charged tungsten filament under high vacuum. So, here we are using one anode materials and other one is into the cathode materials. So, here the anode is the source or maybe the precursor and the cathode is our substrate. So, we are heating or maybe bombarding our anode materials by the electron then we are agitating those materials then they are releasing certain kind of atoms or maybe the molecules and that is depositing on to the cathode means our substrate.

Atoms from the target transform into the gaseous phase due to the electron beam this atom then precipitate into solid form by coating the substrate with a thin layer of the anode material. So, what are the advantages? High few micrometer per minute as well as low one nanometer per minute deposition rate means that is fully controllable depending upon the how much energy you are putting onto the anode material or maybe the onto the source, ability to control structural and morphological properties of the films. So, there are certain kinds of disadvantages too, what are those? Filament degradation due to a non uniform evaporation rate, significant scattering of the vapor cloud takes place. Yes maybe sometimes it cannot be the homogeneous thing coatings may be it may be the heterogeneous coating can possible.

What are the applications? Generally we are using this one for aerospace materials cutting and tool industries electronic and optical frames for the semiconductor industries. So, there is a chart that where we are standing today or maybe that in future means 20-20 what will be the market survey over there. So, you can see 2013 maybe it was very very less, but when we are talking about the 20-20 then almost it is 10 times more than the 2013 figures. So, you can see that how we are adopting this coating techniques and it is so easy and cheap also, so that it can be easily done not only that we can increase or decrease the thickness as per our requirement.

Then next one is called reactive and activated reactive electron beam evaporations. So, what is the purpose? Purpose of reactive and activated reactive electron beam: certain refractory oxides and carbide undergo fragmentation during electron beam evaporation resulting in stoichiometry which is different from initial material.

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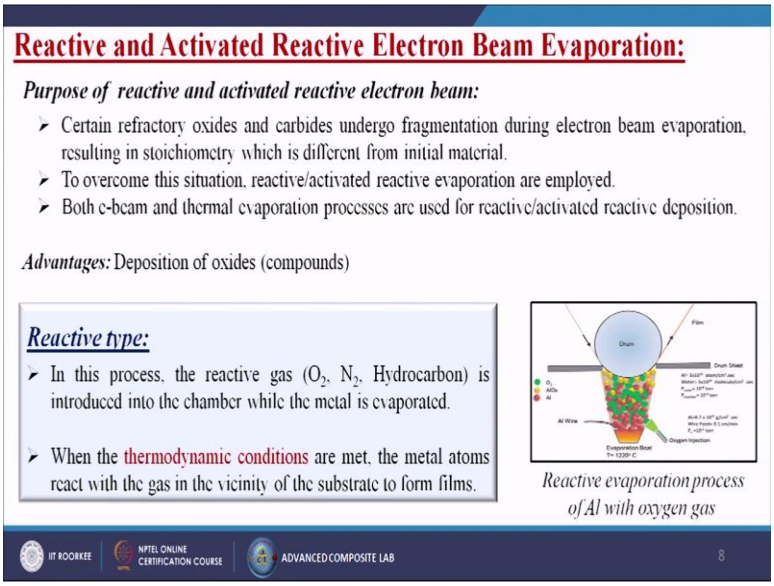

To overcome this situation straight to activate reactive operations are employed, both e-beam and thermal evaporation process are used to reactive and activated reactivity depositions.

So, first we have discussed about the thermal evaporation then we have discuss about the e-beam are may be the electron beam evaporations. So, these techniques is the combinations of the thermal evaporation as well as the electron beam evaporation right. So, when we are giving the material a high electron beam it is giving high energy to that material itself. So, while it is that source material is going into the vapor form maybe it can change its characteristics. So, whatever the material we are wanting as a coating material may be that properties can be changed. So, we are using the combinations of both the thermal evaporation process and e-beam operation process together in this reactive and activated reactive electron beam evaporation techniques.

What are the advantages? Deposition of the oxides, generally compounds we can do. What are the reactive types? In this process the reactive gas generally oxygen nitrogen hydro carbon is introduced into the chamber while the metal is evaporated; when the thermodynamic conditions are met, the metal atoms react with the gas in the vicinity of the substrate to form the films. So, here we are using the gas as well as the atoms together to do a coating onto the metal or maybe the substrate.

So, here is the techniques actually we are using certain kind of aluminum where over there then we are using the oxygen gas in over here. So, it is making the alumina oxide or maybe that Al 2 O 3, then that Al 2 O 3 is coating on to the substrate material. So, aluminum and the oxygen gas both are mixing together they are doing one kind of chemical reactions which is forming the Al 2 O 3 then that Al 2 O 3 is depositing on to the substrate.

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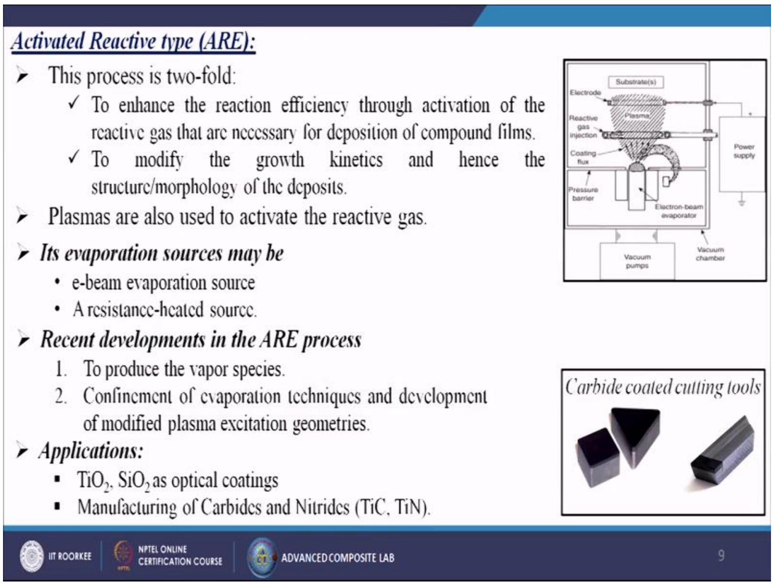

Next one is called the activated reactive type or may be the in short form we are calling it as A R E on maybe ARE. So, here this process is two-fold generally it is divided into two steps to enhance the reaction efficiency through activations of the reactive gas that are necessary for deposition of the compound films, to modify the growth kinetics and hence the structure morphology of the deposits, so that is why you are dividing into two parts. Plasmas are also used to activate the reactive gas. Its evaporation force may be either e-beam source or may be the electron beam or may be some kind of resistance-heated source. So, recent developments in the ARE process are to produce the vapor species, confinement of your operation techniques and development of modified plasma excitation geometries.

What are the applications? We can make titanium dioxide, silicon dioxide as optical coatings, manufacturing of carbide, nitrides means titanium carbide, titanium nitride which can be used for coating of the some kind of tool materials or maybe the cutting tool materials then here you can see some kind of inserts, generally we are using for the cutting tool because as we know that if we want to make the cutting tool by any kind of this kind of materials it will be very very expensive. So, what we do? Generally we are going to use the cutting tool made by the HSS; that means, high speed steel and the tip of sorry and the tip of the tool can be changed easily we are generally calling it as a inserts. So, that material is made by the titanium carbide or maybe that titanium nitride. So, when it will be (Refer Time: 19:21) no need to change the whole tool only you open the screws and take out that insert and put the new inserts over there.

Next is called a sputtering. So, it is a common method or maybe that it is easily available method and nowadays means we are extensively using these patterning techniques everywhere. So, steps for patterning process first you have to put a target material and the substrate is placed in a vacuum chamber.

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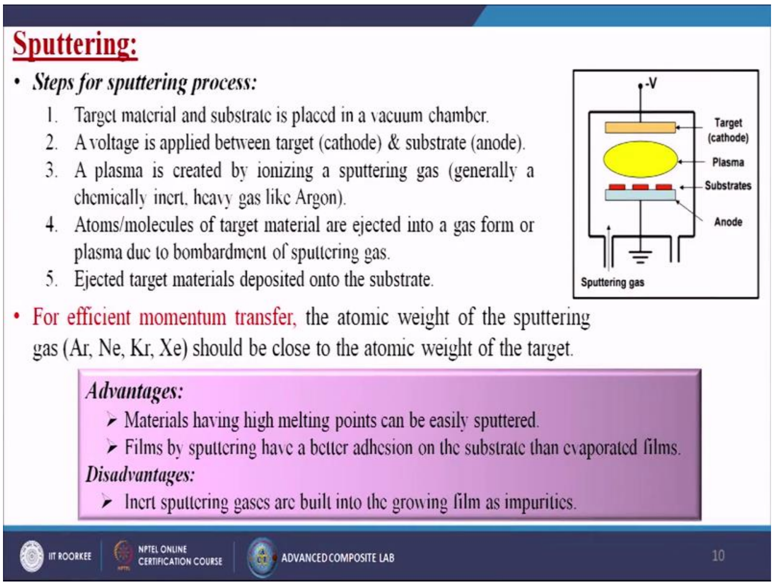

So, this is your vacuum chamber where you are putting your substrate. And then you are putting your target materials or may be the source materials over there then you are using certain kind of plasma over there if voltage is applied between the target and the substrate. So, there should be some kind of potential difference in between the cathode and in between the anode. So, plasma is created by ionizing a spattering gas generally a chemically inert heavy gas like argon. So, here we are using the inert gas like argon and then we are making this gas into the plasma form. Then that plasma actually it is depositing on to your substrate.

So, atoms or molecules of the target material are ejected into a gas form or plasma due to the bombardment of the sputtering gas, ejected target materials deposited onto the substrate itself. So, simply we are putting certain kind of potential difference in between the cathode and anode, then we are injecting certain kind of plasma over there which is nothing but the directly coming from using the argon gases then that plasma is directly hitting on to your target materials or maybe the source materials then due to that some kind of atoms or molecules it is directly coming from the source materials and it is depositing on to the substrate materials, so that is why it is called the spattering techniques. So, for efficient momentum transfer the atomic weight of the spattering gas like argon the neon chromium xenon should be close to the atomic weight of the target otherwise it is little bit difficult.

Then what are the advantages? Materials having high melting points can be easily sputtered; films by sputtering have better adhesions on the substrate than evaporated films. Disadvantages inner sputtering gases are built into the growing film as impurities. So, it can create certain kind of impurities too, but if we see the overall the sputtering techniques is good and it is cheap and it is less time consuming.

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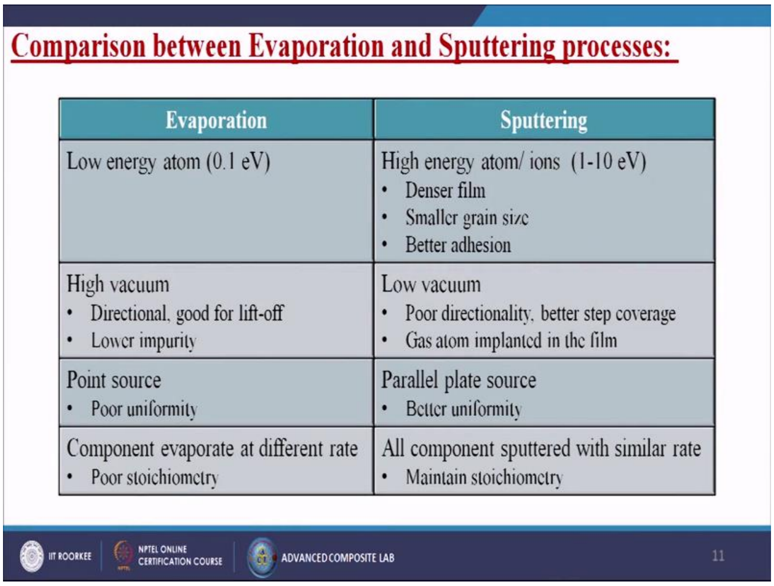
Comparison between Evaporation and Sputtering processes:

Evaporation	Sputtering
Low energy atom (0.1 eV)	High energy atom/ ions (1-10 eV) • Denser film • Smaller grain size • Better adhesion
High vacuum • Directional, good for lift-off • Lower impurity	Low vacuum • Poor directionality, better step coverage • Gas atom implanted in the film
Point source • Poor uniformity	Parallel plate source • Better uniformity
Component evaporate at different rate • Poor stoichiometry	All component sputtered with similar rate • Maintain stoichiometry

So, now we are going to make certain kind of comparison in between the evaporation and the sputtering processes. So, evaporations generally you are using the low energy atom its 0.1 electron volt, sputtering generally we are using the high energy atoms or maybe the ions sometimes we are using generally it is coming into the range of 1 to 10 electron volt, it is the denser film smaller gun size and better adhesions these all are the advantage over the sputtering techniques.

Then for evaporation methods we are using the high vacuum directional good for lift off lower impurity is possible then in the sputtering techniques we can do it by the low vacuum too. So, poor directionally better step coverage gas atom implanted in the film. Here generally for the evaporation it is the point source. So, poor uniformity here the sputtering is called the parallel plate source if you remember into the last slide that we are using two parallel plates over there. So, the surface area or maybe the sample size can be bigger in that particular case you can accommodate the bigger sample size too.

Component evaporate at different rate here the poor stoichiometry here all components parted with the similar rate. So, whatever the thickness you are achieving, so it is the same or maybe the homogeneous throughout the whole surface of your source of your substrate material. So, it maintains a constant stoichiometric over there.

Next techniques we are going to discuss is called cathodic arc deposition methods. So, first we have to know that what is the cathodic arc deposition methods.

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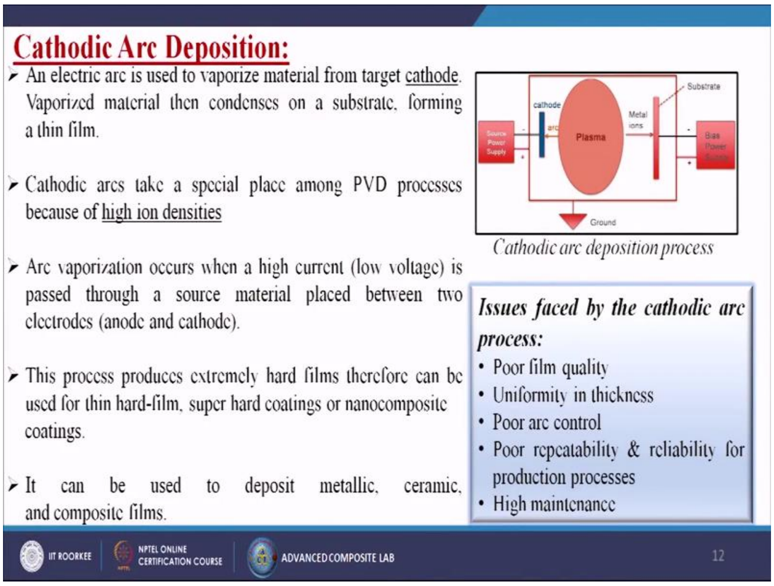

So, an electric arc is used to vaporize the material from target cathode, vaporized material then condense on a substrate forming a thin stream. So, here you are using some cathode materials over there then you are using the plasma then that plasma ions the arc is going to the cathode side and the metal ions it is going to the substrate side. So, here you are using some kind of potential difference by using some kind of power supply. So, you are using some kind of high potential difference in between your cathode and the anode material.

So, cathodic arc takes a special place among PVD processes because of high ion densities. So, the techniques maybe it can be matched 90 percent with the other techniques, but here the density of the ions whatever we are getting is more than the other process. So, here arc vaporization occurs when a high current low voltage is passed through a source material placed between two electrodes anode and cathode. This process produces extremely hard flames therefore, can be used for thin hard film super hard coatings or nanocomposite coatings. It can be used to deposit metallic ceramic and composite films. So, these techniques are more versatile than the others.

Here we can use so many materials we can use some kind of hard materials too. So, issues faced by the cathodic arc process poor film quality, uniformity in thickness, poor our control, poor repeatability and reliability for production processes high maintenance.

So, these all are the issues generally we can face while doing the cathodic arc deposition process

Next one is called the filtered cathodic arc deposition process. So, here from this name we can understand that it is the little bit modified versions of the previous one. So, here the filtered cathodic arc process is extensively used to deposit tribological and wear resistant thin films. Mainly it eliminates the macro particles that degrade coating performance. So, the small size particles or may be the same sized particles rather I can say that all the particles whatever it is depositing onto your substrate all particle size are more or less same. So, there should not be any mixture of the bigger particle and the smaller particle because as we know that if the particle size will be bigger it is very difficult to stick on to a substrate materials, and not only that its surface area will be less. So, there will be a less adhesions in between the coating materials and the substrate material.

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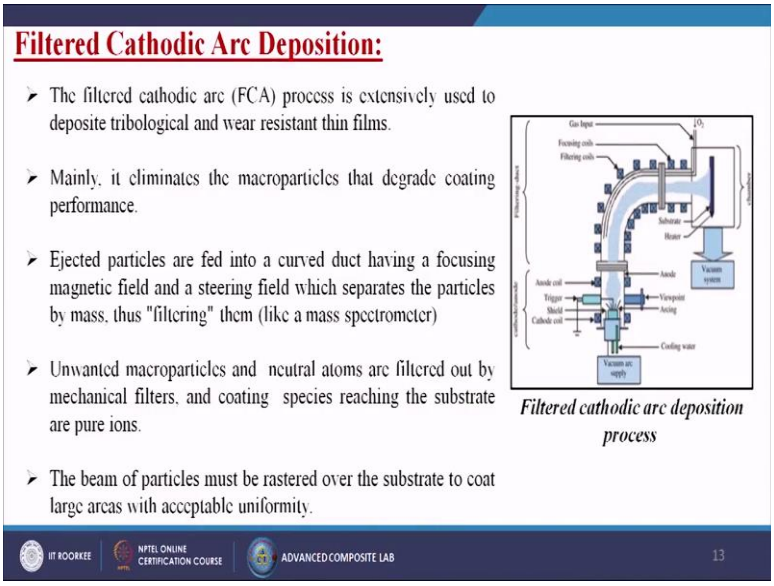

So, here ejected particles are fed into a curved duct. So, you can see there is a duct over there. So, through these duct your particles is going through and then it is falling onto your substrate materials, steering field which separates the particles by mass thus filtering them like a mass spectrometer. So, here there are several kinds of filtering coils which is absorbing the bigger particle size and only allowing the small particle size to go. Then unwanted macro particles and neutral atoms are filtered out by the mechanical filter and coating space is reaching the substrate are pure ions. The beam of particles must be rested over the substrate to coat large areas with acceptable uniformity.

So, here this is actually the movable one, so that it can cover up the whole area if the sample size will be bigger also, not only that here the purity of the coating materials is almost 100 percent and then it is very easy to take out the impurities from the coating materials too.

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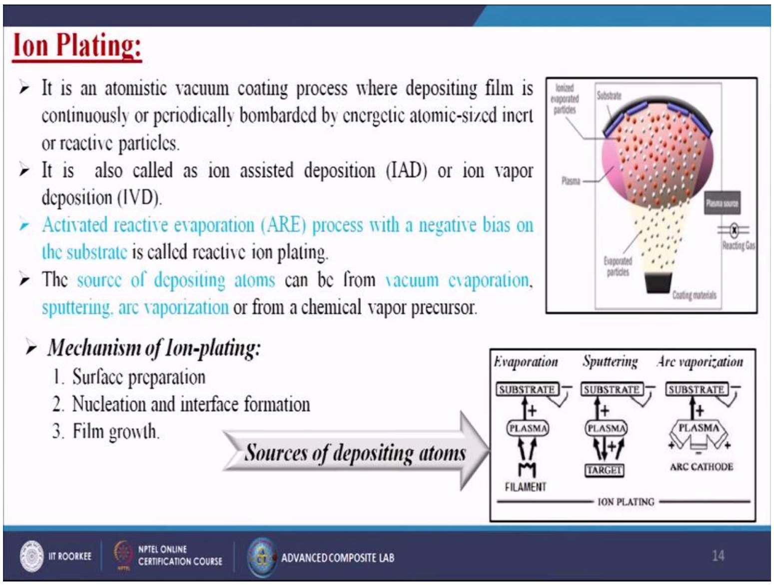

Next one is called the Ion Plating. So, it is an atomistic vacuum coating process where depositing film is continuously or periodically bombard by energetic atomic-sized inert or reactive particles. So, here we are not putting any kind of heat, we are not putting any kind of electron beam, we are not putting any kind of laser. So, here we are using certain kind of energetic atomic sized inert or maybe the reactive particles, we are bombarding on to the source materials and then we are doing the coating onto our substrate. So, it is also called as ion assisted depositions IAD or maybe the ion vapor deposition IVD. Activated reactive evaporations our process with a negative bias on the substrate is called the reactive ion plating. So, it depends upon the source how we are going to use different source. So, using the different source it is having different nomenclature. The source of depositing atoms can be from vacuuming operations sputtering arc vaporizations or form a chemical vapor precursor.

So, from this there is certain mechanisms are available. So, first one is called the surface preparations, then nucleation and interface formations and the film growth. So, here the source of depositing atoms, first in the evaporation techniques you are having the substrate you are using the certain kind of plasma, you are having the filament, then directly the material is depositing on to the substrate, heat over or on top of the substrate. But here you are using certain kind of target materials, so that target material is forming certain kind of plasma that plasma can heat the target materials, then from here some kind of atoms or molecules and directly go and it can deposit onto the substrate. And here directly you are using making certain kind of plasma by the arc cathode method and then that plasma itself is depositing onto your substrate materials. So, these all are the different techniques of the iron plating, first one is called the evaporation techniques, then sputtering techniques and the arc vaporization techniques.

Next we are going to discuss about the different types of the iron plating process. So, first one is known as the plasma based ion plating bombarding species are generally accelerated ion form a plasma then vacuum based ion plating bombarding species are accelerated ions from an ion source in vacuum chamber.

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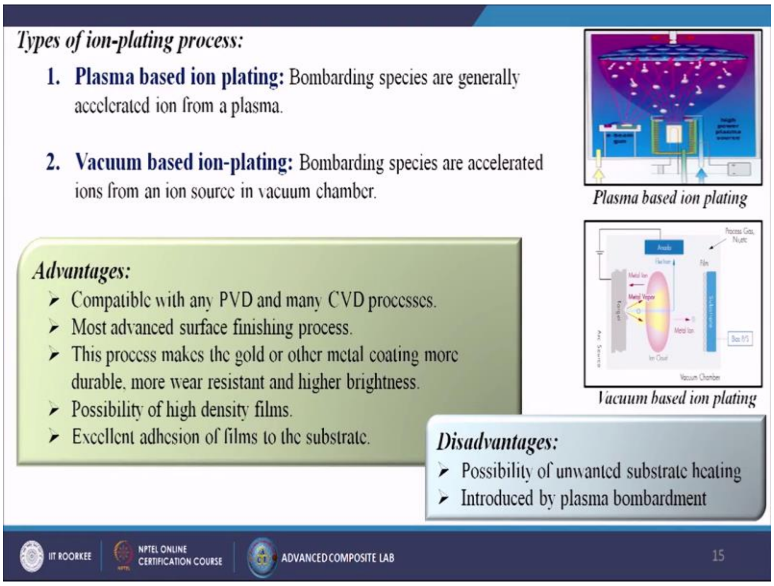

So, now, it actually divided into whatever the environment we are going to use. So, if you are going to use the plasma environment. Then that is known as the plasma based ion plating and if you are going to use into the vacuum chamber or maybe the vacuum environment then it is known as the vacuum based ion plating. So, what are the advantages? Comfortable with any PVD physical vapor depositions and many CVD process chemical vapor deposition processes. Most advanced surface finishing process; this process makes the gold or other metal coating more durable more wear resistance higher brightness generally we are using some kind of sophisticated materials, we are using for the ornaments or maybe any kind of plating with techniques or maybe the methods; possibility of high density films; excellent addition of films to the substrate.

But there are certain kinds of disadvantages too: possibility of unwanted substrates heating, introduced by the plasma bombardment sometimes it becomes little bit expensive.

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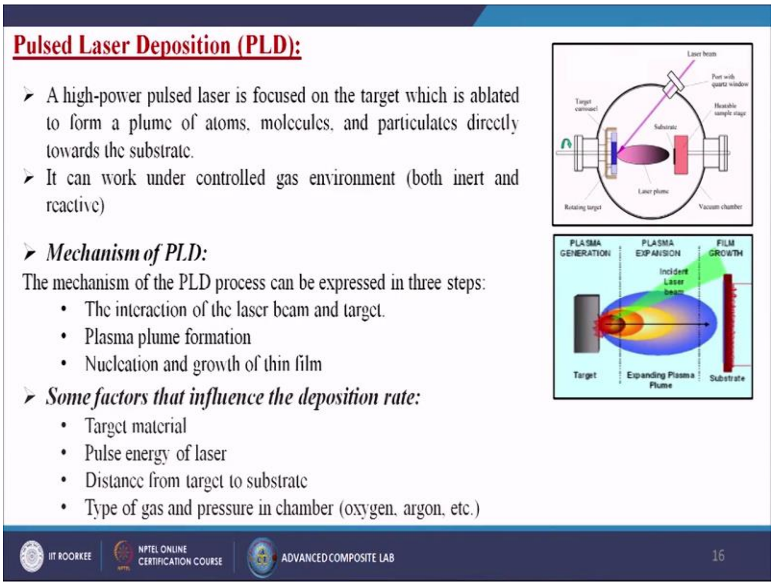

Next one is called the pulsed laser depositions or maybe the PLD process. So, a high-power pulsed laser is focused on the target which is ablated to form a plume of atoms, molecules and particulates directly towards the substrate; it can work under control gas environment both inert and the reactive gas. It depends upon which kind of material we are going to coat.

Mechanism of the PLD process, the mechanism of the PLD process can be expressed in three steps - first one is called the interaction of the laser beam and the target, plasma plume formations nucleation and growth of the thin films. So, simple till now we are discussing about different types of heating element may be electrical coil or may be certain kind of laser or may be certain kind of electron beam. So, here first we are putting the laser beam directly onto the target itself, then it is creating certain kind of plasma that plasma is directly depositing onto your substrate material, so that is why it is called the pulsed laser depositions.

Now, how you are going to control your laser depending upon that whether it is pulsed means there will be any on or off mechanisms or maybe they it will be the continuous one. So, it depends upon what type of source of energy you are going to use. Some factors that influence the deposition rate is called the target material, pulse energy of laser, distance from the target to the substrate, types of gas and pressure in chamber, oxygen, argon etcetera.

So, here first you are having the target, you are using certain kind of plasma over there then that plasma is directly hitting your target materials, then it is making certain kind of gases or maybe some kind of ions or maybe that some kind of plasma expansions over there, then that expanding plasma plume is directly depositing onto your substrate and it is doing the growth of that particular material. So, what are the benefits over other film deposition methods?

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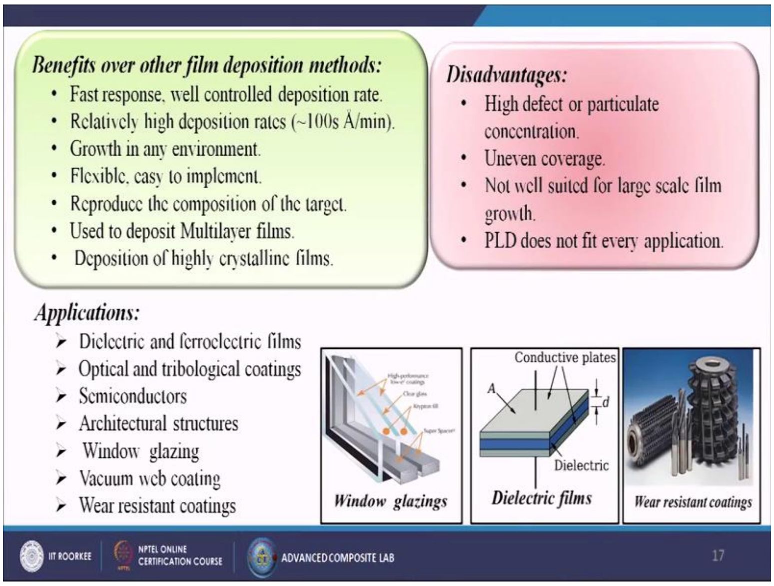

It is fast response well controlled deposition rate, relatively high deposition rates, growth in any environment can be possible either you can use certain kind of reactive gas or maybe you can use certain kind of inert gas, flexible easy to implement, reproduce the composition of the target, used to deposit Multilayer films, deposition of highly crystalline films. That means, you can make the sandwich structure also, so coating of one material then top of that you are using another material, then top of that you are going to use another material. So, it depends upon as per our requirement.

Then there is certain kind of disadvantages also: high defect of particulate concentrations, uneven coverage, not well suited for large scale film growth, PLD does not fit every application. So, what are the applications? Dielectric and theorem electric films we can make, optical and tribological coatings we can do, we can use it for the semiconductors, architectural structures, window glazing, vacuum web coating, wear resistance coating.

So, generally nowadays we are using onto the window maybe car window or maybe that our household window simply wear at the time of raining that water particle is not sticking with the surface of that particular glass, or maybe certain kind of electrical materials, some kind of semiconducting materials, we are using we are using certain kind of cutting tools where we are doing the coatings by the PLD process.

Then we are coming into our last slide of this particular lecture just to summarize up whole PVD process.

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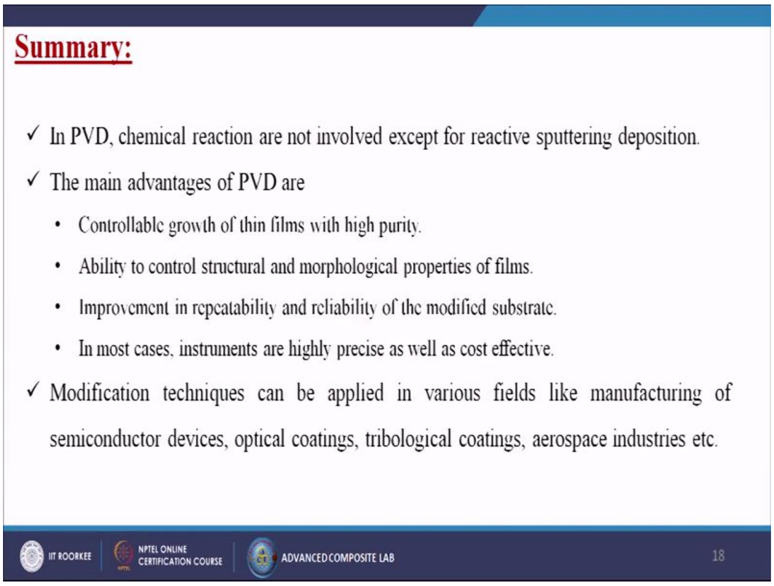

So, in PVD chemical reactions are not involved except for reactive sputtering deposition. So, here directly we are making any kind of gas or maybe the vapor then that is depositing onto the substrate.

The main advantages of the PVD are controllable growth of thin film with high purity, as I told already you can eliminate the impurities by using several kinds of methods and not only that you can use the controllable growth depending upon that how much energy you are going to put on your target materials or maybe the source materials. Ability to control structural and morphological properties of films, so easily you can make the material from hydrophobic to hydrophilic or not only that you can make the material which can withstand with high temperature or maybe it can be easily electrical conductive. So, whatever the properties you want you can do it by these methods. Improvement in repeatability and reliability of the modified substrate, in most cases instruments are highly precise as well as cost effective.

Modification techniques can be applied in various fields like manufacturing of semiconductor device, optical coatings, tribological coatings, aerospace industries, here we have listed a very few there are several applications are possible.

Thank you.