

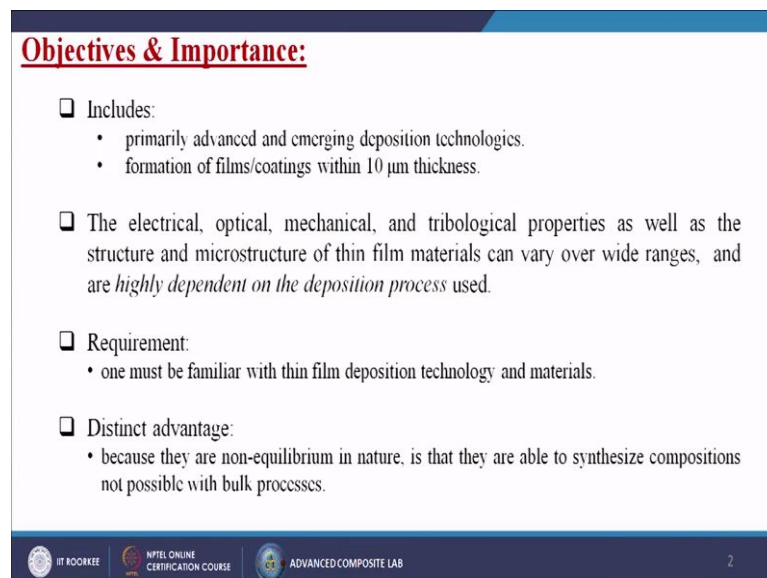
Surface Engineering of Nanomaterials
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Lecture – 11
Deposition and Surface Modification Methods

So, next lecture we are going to see what is the depositions and what is the surface modifications methods right. So, in our last lecture means module 10, we have discussed about the surface modifications on Nanomaterials, where we have seen that we have adopted several modification techniques in terms of physical, in terms of chemicals, in terms of bio and we have modified the Nano particles. So, now, in this particular topic we are going to discuss that there are several types of deposition techniques by which we can deposit the materials onto the base metals or maybe the base materials.

So, first before going to start we have to know that - what is the importance of that particular topic; why we are going to do this kind of surface depositions.

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Objectives & Importance:

- Includes:
 - primarily advanced and emerging deposition technologies.
 - formation of films/coatings within 10 μm thickness.
- The electrical, optical, mechanical, and tribological properties as well as the structure and microstructure of thin film materials can vary over wide ranges, and are *highly dependent on the deposition process* used.
- Requirement:
 - one must be familiar with thin film deposition technology and materials.
- Distinct advantage:
 - because they are non-equilibrium in nature, is that they are able to synthesize compositions not possible with bulk processes.

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So, it includes primarily advanced and emerging deposition techniques, formation of film coatings with 10 micrometer thickness. So, here we are going to deposit certain materials onto that metal surface or maybe the outer surface of that particular metal, onto up to 10 micrometer. The electrical, optical, mechanical, tribological properties can be enhanced

or we can enhance the mainly generally the physical properties of that particular material.

Next requirement one must be familiar with thin film deposition technology and materials. So, we should know about the thin film technology by which we are creating certain kind of thin film depositions onto the material surface. Distinct advantage because they are non equilibrium in nature is that they are able to synthesize compositions not possible with bulk processes these all are the distinct advantage. What are the classifications of deposition techniques? As I said already there are different types of methods can be obtained, but you have to choose as per your requirement which techniques will be best suit for our material or maybe for our substrate.

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Classification of Deposition Technologies:

- ❑ Basically, thin-film deposition is categorized into
 - purely physical, i.e., evaporative methods, or
 - purely chemical, i.e., gas- and liquid-phase chemical processes.

- ❑ A classification scheme is presented here, where we have grouped thin-film deposition technologies according to
 - Evaporative process
 - Glow-discharge process
 - Gas-phase chemical process
 - Liquid-phase chemical process

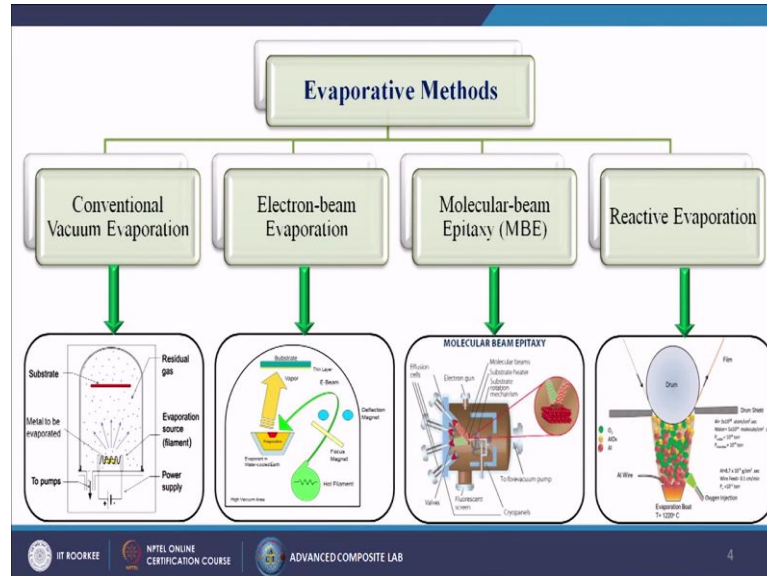
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So, first basically thin film depositions is categorized into purely physical; that means, evaporative methods purely chemical; that means, that means gas and liquid phase chemical processes, these two are the methods. Then a classification schemes is presented here where we have grouped thin film deposition technologies according to evaporative process, glow discharge process, gas phase chemical process, liquid phase chemical process.

So, here from this particular table we can see that there are several types of evaporative methods are available; one is called the conventional vacuum evaporations method, next

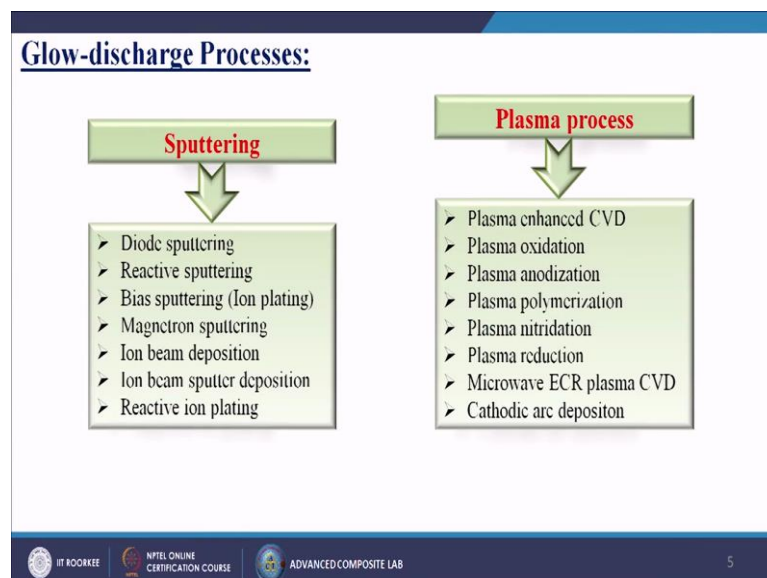
one is electron beam evaporations method, next Molecular-beam Epitaxy and last one is called the reactive evaporation methods.

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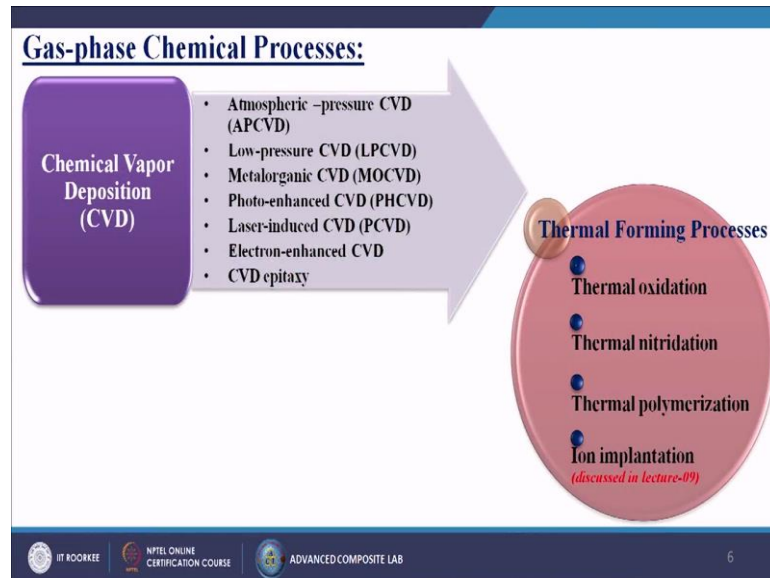
So, glow discharge processes, there are several types of glow discharge process also are available nowadays. So, what are those? Diode sputtering, reactive sputtering, bias sputtering, magnetron sputtering, ion beam depositions, ion beam sputter depositions, reactive ion plating; then when we are talking about the plasma process, there are also several types of plasmas are also available.

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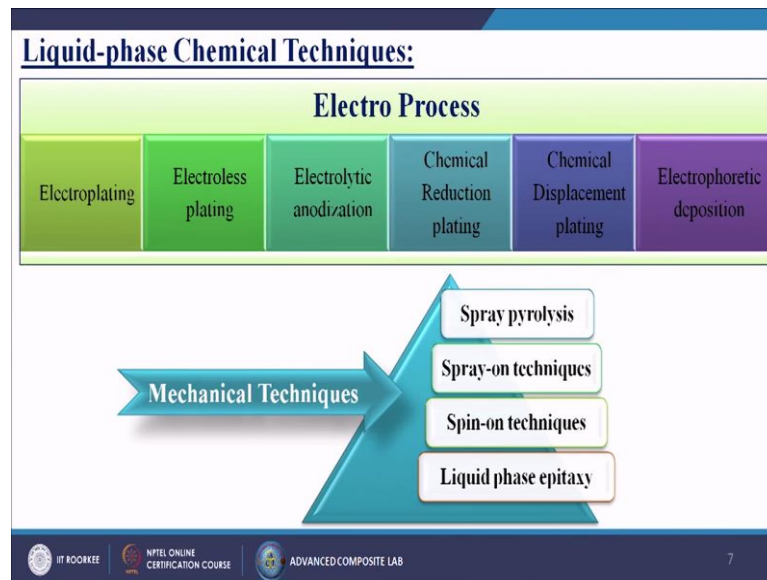
One is called the plasma enhanced, plasma oxidations, plasma anodizations, plasma polymerizations, plasma nitridations, plasma reductions, microwave ECR plasma CVD, Cathodic arc depositions; that means, from these particular slides we can see that depending upon the energy that how you are going to give the different energy and different you rather we can say the techniques that it varies into two parts.

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Next is called the gas phase chemical process also, here also we are using the chemical vapor deposition process, which is also divided into different types; one is called the atmospheric pressure CVD in short form it is known as APCVD, low pressure CVD that means LPCVD, Metalorganic CVD MOCVD, photo-enhanced CVD PHCVD, laser-induced CVD PCVD, electron enhanced CVD and the CVD epitaxy. What are the thermal forming processes are available over there? One is called the thermal oxidations, thermal nitridations, thermal polymerizations and the ion implantations which we have elaborately discussed in our 9th lecture.

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Next come to the liquid phase chemical techniques. So, first there are several types of process it is called the electro process. So, from the name itself you can understand that we are giving kind of electrical energy to that particular process or maybe there should be some kind of potential difference in between the process too. So, what are those? First one is called the electroplating, electroless plating, electrolytic anodizations, chemical reduction plating, chemical displacement plating and the electrophoretic depositions and there are certain types of mechanical techniques are also available, what are those? Spray pyrolysis, spray on techniques, spin on techniques and the liquid phase epitaxy. So, these are all the different techniques available.

Advanced deposition techniques: now because nowadays people are trying to modify the materials, people are making new composites, new alloys new base metals. So, all the conventional techniques which we were using in the past years or maybe in our old age, now these all have become obsolete. So, we have to adapt certain kinds of new techniques by which we can modify these composite materials or maybe the alloy materials too.

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Advanced Deposition Technologies:

- ✓ VPD and ALD have recently emerged as processes that can achieve molecular doping, polymer thin films and nanocomposites.
- ✓ Processes such as GLAD can achieve unique microstructures not possible with conventional substrate-source configurations and deposition processes.
- ✓ Films deposited by HPPMS have high density and excellent adhesion to the substrate, which makes them desirable for tribological, corrosion-resistant coatings, barrier coatings, and electronic applications.

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So, one is called the vacuum polymer depositions which is known as the VPD then atomic layer depositions which is called the ALD, next high power pulsed magnetron sputtering in short form it is known as HPPMS or maybe HIPIMS; next filtered cathodic arc depositions and the last one is known as the glancing angle depositions GLAD. So, now, little bit we will discuss into the details about these.

VPD and ALD are recently emerged as processes that can achieve molecular doping, polymer thin films and the nanocomposites. Processes such as glad can achieve unique microstructure not possible with conventional substrate source configurations and deposition processes, films deposited by HPPMS have high density excellent adhesion to the substrate, which makes them desirable for tribological corrosion resistant coatings, barrier coatings and electronic application, the same thing I am telling once again or maybe repeatedly that the depending upon our requirement that how much layer we need, how we are going to introduce the new material inside our base materials, how we are going to do any kind of doping inside our base materials, we are going to adapt any one of the method.

Unique features of deposited materials; there should be some unique features because when we are doing the depositions of that particular materials, what we are going to achieve or maybe what advantage is we are going to get?

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Unique Features of Deposited Materials:

Several features of materials can only be produced by vacuum deposition technologies, including:

- ❖ Extreme versatility of range and variety of deposited materials.
- ❖ Applied coatings with properties independent of thermodynamic compositional constraints.
- ❖ Ability to vary defect concentration over wide ranges, thus resulting in a range of properties comparable to or far removed from conventional bulk materials.
- ❖ High quench rate available to deposit amorphous materials.
- ❖ Controllable production of microstructures different from conventionally processed materials, e.g., A wide range of microstructures: ultrafine (superlattice, nanostructures) to single crystal films.
- ❖ Fabrication of thin free-standing shapes and foils, even from brittle materials.
- ❖ Ecological benefits with certain techniques.

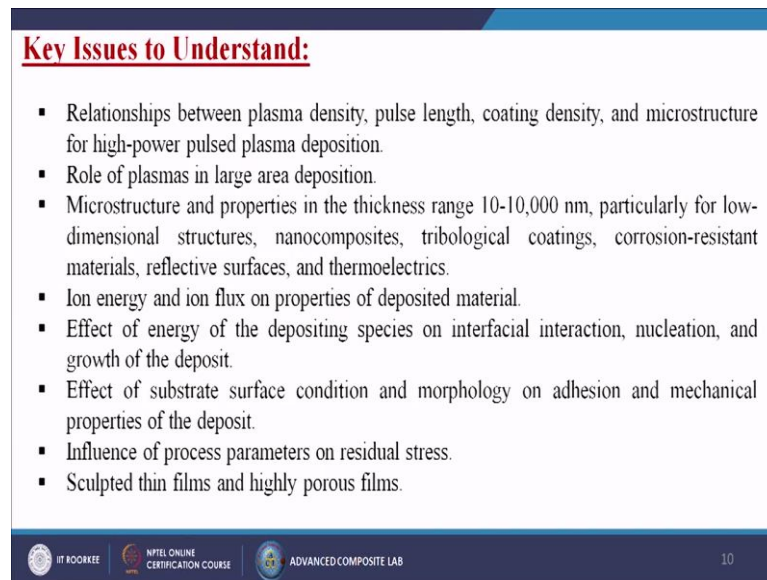
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So, several features of materials can only be produced by vacuum deposition technologies including extreme versatility of range and variety of deposited materials applied coatings with properties independent of thermodynamic compositional constraints, ability to vary defect concentration over wide range the resulting in a range of properties comparable to or far removed from conventional bulk materials. That means, you can change the material properties or maybe you can do certain kind of repairmen on the material surfaces or maybe that surface is totally behave abnormally you can change the material surface, so that it can be reactive or maybe it can be inert with the environment too.

High quench rate available to deposit amorphous materials; controllable production of microstructures different from conventionally processed materials, a wide range of microstructures ultrafine superlattice nanostructures to single crystal films; fabrication of thin free standing shapes and foils even from brittle materials ecological benefits with certain techniques. So, these all are the key features for depositing the materials onto the substrate.

Key issues; there are certain issues also, before going to do the depositions we have to know all these pros and cons about the deposition techniques.

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Key Issues to Understand:

- Relationships between plasma density, pulse length, coating density, and microstructure for high-power pulsed plasma deposition.
- Role of plasmas in large area deposition.
- Microstructure and properties in the thickness range 10-10,000 nm, particularly for low-dimensional structures, nanocomposites, tribological coatings, corrosion-resistant materials, reflective surfaces, and thermoelectrics.
- Ion energy and ion flux on properties of deposited material.
- Effect of energy of the depositing species on interfacial interaction, nucleation, and growth of the deposit.
- Effect of substrate surface condition and morphology on adhesion and mechanical properties of the deposit.
- Influence of process parameters on residual stress.
- Sculpted thin films and highly porous films.

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So, what are those? Relationships between plasma density, pulse length, coating density and microstructure for high power pulsed plasma depositions; role of plasmas in large area depositions; micro structure properties in the thickness range is 10 to 10000 nanometer particularly for low-dimensional structures, nanocomposites, tribological coatings, corrosion-resistant materials, reflective surfaces, and the thermoelectrics; ion energy and iron flux on properties of deposited materials.

That means before going to do we have to know that which material we are going to modify, what is the characteristics of that particular material whether whatever the energy I am going to input, whether that material can sustain that energy or not or maybe if I am dipping that material into some solvent, whether it should be chemically react or maybe it should be inert, not only that whatever the targeted gas or maybe the ion I am going to input on that substrate whether it will be acceptable by the base materials or not. So, there are n numbers of sub key factors or maybe key issues which we have to know prior to do the thin film deposition; effect of substrate surface conditions and morphology and adhesions and mechanical properties of the deposits, influence of process parameters on residual stress, sculpted thin films and the highly porous films.

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Current Applications:

Although there is significant overlap, current coating applications may be classified into the following generic areas:

- *Optically functional:*
Laser optics, Architectural glazing, Residential mirrors, Automotive rear-view mirrors and headlamps, Reflective and antireflection coatings, Optically absorbing materials, Low-e coatings, Solar selective coatings, Free-standing reflectors, Transparent conductive films.

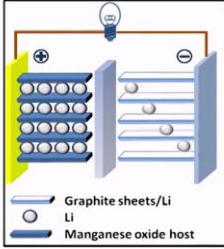
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Now, let us discuss about the current applications, where we are going to do this kind of thin film applications; what are those? Optically functional materials, Laser optics, Architectural glazing, Residential mirrors, Automotive rear-view mirrors headlamps, Reflective and antireflection coatings, Optically absorbing materials, Low-e coatings, Solar selective coatings, Free-standing reflectors, Transparent conductive films, where we are going to use certain kind of materials; say we are using certain kind of glasses, so that the harmful UV rays of that particular from the sun, it will give a resist to that particular from the sunlight itself.

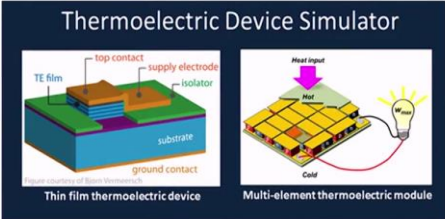
But still the sunlight can go inside our room, if there is any harmful element which it will resist for just to enter inside our room on may be the building or maybe there is a they are kind of certain kind of laser optics which can maybe transmit some lasers inside the materials or maybe reflect some material lasers from the surface of that particular materials, by changing the material properties we can train our material to act differently.

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➤ *Energy related:*
Thin film battery, Thin film fuel cell, Thin film solar cell, Thermoelectric thin films, Superlattice, Electrochromic coatings, Solar absorbers, Barrier coatings (oxygen and water permeation barriers), Transparent solar cells, Organic solar cells, Photocatalytic coatings.



Thin film battery



Thermoelectric thin films

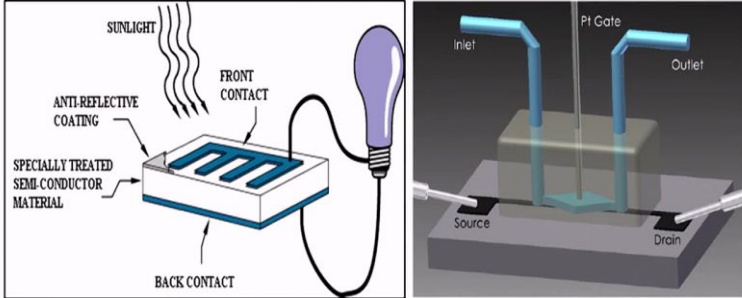
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Next energy related; so thin film battery, thin film fuel cell nowadays we are talking about the hydrogen fuel cell, lithium ion battery, super capacitor, flowable super capacitor, solar cell in the or maybe the solar cells in terms of peroxide solar cells or maybe die synthesized solar cells. So, there are n numbers of applications by where we can use this kind of thin film techniques.

So, Electrochromic coatings, solar absorbers, barrier coatings oxygen and water permeation barriers, transparent solar cells, organic solar cells, Photocatalytic coatings. So, where we can use from this particular figure we can understand that we are using for the thin film battery, where we are using some graphite sheets with lithium, then manganese oxide host materials or maybe its layer by layer techniques we are using, some kind of thermo electric thin films we are going to use. So, we are adapting it onto some substrates so that it can generate certain kind of electricity or maybe by applying the heat it can change into some other energy form formations. So, there are several types of applications where we can use this thin film deposition.

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➤ *Electrically functional:*
Electrical conductors, Electrical contacts, Semiconductor films, Active solid state devices, Electrical insulators, Photovoltaics, Transparent electrical contacts.



The diagram on the left shows a photovoltaic cell with layers labeled: SUNLIGHT, ANTI-REFLECTIVE COATING, FRONT CONTACT, SPECIALLY TREATED SEMI-CONDUCTOR MATERIAL, and BACK CONTACT. It is connected to a light bulb. The diagram on the right shows a transparent electrical contact device with labels: Inlet, Pt Gate, Outlet, Source, and Drain.

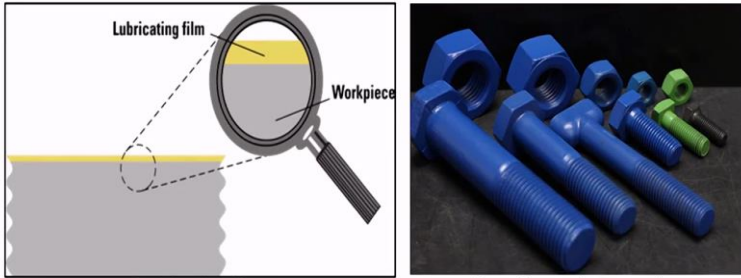
Photovoltaics *Transparent electrical contacts*

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Next one is called the electrically functional; so, electrical conductors, electrical contacts, semi conductor films, active solid state devices, electrical insulators, Photovoltaics, transparent electric contacts. So, these all are the different applications where we are using the depo thin film deposition techniques. So, here in this particular case we are using certain kind of things for the photovoltaic's applications and the right hand side we are using the transparent electrical contacts, so that the electrical energy can pass from one side to another very easily.

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➤ *Mechanically functional:*
Tribological coatings, Lubrication films, Nanocomposites, Diffusion barriers, Hard coatings for dies and Cutting tools, Wear and Corosion-resistant coatings, Biomedical coatings.



The diagram on the left shows a cross-section of a workpiece with a lubricating film on its surface, viewed through a magnifying glass. The diagram on the right shows a photograph of various blue and green corrosion-resistant coatings on metal parts.

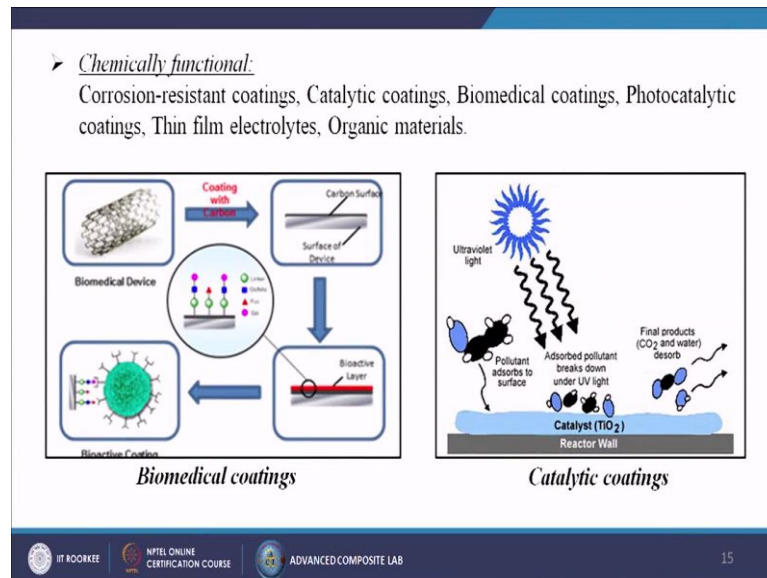
Lubrication films *Corrosion-resistant coatings*

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Next mechanically functional materials like tribological coatings, lubrication films, nanocomposites, diffusion barriers, hard coatings for dies and cutting tools, wear and corrosion resistant coatings, biomedical coatings. So, these all are the different applications where we are using the thin films. So, from this particular figure you can understand that on the top of the surface we are putting certain kind of lubricating films; so that any dust particle or maybe any contaminates from the air, directly it not come into contact with the base metals or maybe it will slight onto that surface on top of the film. So, that it will not directly come into the contact with the base metals. So, that there will not be any reactions, or maybe any kind of corrosions, or maybe any kind of frictions can generate at that particular point.

And also here you can see certain kind of fasteners in terms of nut and bolt arrangement. So, we are doing some kind of corrosion resistant coatings because these things we are using for the automotive parts or maybe maximum cases we are using for into the open air, so that there should not be any reactions with the moisture or maybe there should not be any reactions with the any kind of oxide formations or maybe the sulfide formations can be taking place.

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Next chemically functional material, corrosion-resistant coatings, catalytic coatings, biomedical coatings, Photocatalytic coatings, thin film electrolytes and organic materials. So, from this particular case you can understand that we are making certain kind of

materials, maybe with environment or maybe with some temperature or maybe with certain pressure that material can be activated and that can make certain kind of coatings onto to the surface of that particular material.

So, from this particular case here are the so many examples for the biomedical coatings. So, generally we are using for some implants, we are using for the stains or maybe we are using for some kind of transplantation cases where we are adopting this kind of materials; and right hand side here we are using certain kind of TIO 2; TIO 2 is titanium dioxide in various forms, either it maybe Nano flower or maybe TIO 2 flowers or maybe petals forms or maybe some different phases like anatine phases we can use this kind of materials as a die synthesized solar cells or maybe the solar cells applications or maybe some kind of catalytic coatings or maybe some kind of anti bacterial applications where we can use this kind of materials, when it will come into some controlled atmosphere, controlled temperature, automatically it will be activated and it will make a thin film onto the surface of that particular material.

Now, we have to know what is the selection criteria for selection of particular deposition process. So, as I told already. So, when we are taking certain kind of food, certain kind of drugs, first we have to know the characteristics of that food characteristics of that particular drug right and also we have to know about our body, whether that material will be accepted by our body or not or that will be rejected or maybe there will be some side effects with our body or not; same thing is happening for this techniques also. So, when you are going to do any kind of thin film depositions onto to the metal surface, whether that base material will absorb or maybe will attach with that particular material or not or maybe it will react with that particular material or not or maybe there will not be any reactions in between that so that detachment will be taking place. So, there are several factors we have to keep in our mind.

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Selection Criteria for Selection of Particular Deposition Process:

- ❖ Material to be deposited
- ❖ Limitations imposed by the substrate, e.g., Material, size, temperature stability
- ❖ Specific applications
- ❖ Deposition rate
- ❖ Adhesion of film to substrate
- ❖ Throwing power
- ❖ Purity of source material
- ❖ Availability of required apparatus
- ❖ Cost
- ❖ Safety considerations, e.g., Toxicity
- ❖ Process stability
- ❖ Manufacturing considerations, e.g., Batch size, throughput, process controls
- ❖ Abundance of source materials

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So, first is that material to be deposited; which material we are going to deposit, what is the characteristic of that particular material. Limitations imposed by the substrate material size, temperature stability; suppose I am having a soft material, I cannot go for the physical depositions because I cannot use certain load or pressure by which the material can be deformed. So, we have to search for some alternative methods or maybe I my material is electrical insulative material so that I cannot use certain kind of process where I have to generate certain kind of electrical field onto top of that, so that that process will be failed and then specific applications. What are the applications, why I am going to do this techniques?

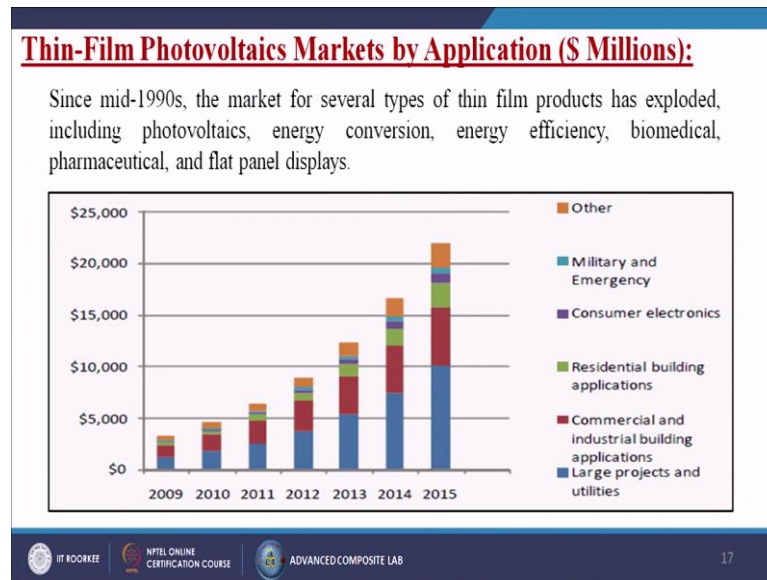
Then next one is deposition rate; how fast I am going to do these coatings or maybe the slow whether it is into the controllable manner or maybe uncontrollable manner, whether it should be homogenous or maybe it should be the heterogeneous.

Then adhesions of film to the substrate throwing power; how much velocity you are throwing that is your coating material on to that substrate, whether your substrate can easily accept that capability or not or it made some slow or maybe the faster.

Then purity of the source materials, availability of required apparatus what is the cost because nowadays we are talking about the expensive materials. So, we have to reduce the cost, so that it can be easily available to all the consumers; then safety considerations like toxicity, it is generating any kind of health hazards or not process stability,

manufacturing considerations like batch size, throughput process controls and the abundance of the source materials. So, there are several types of factors by which you have to choose the different thin film deposition techniques.

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Next thin film Photovoltaics; So, the here I am going to give you one examples that how it is going to effect in our daily life. So, since mid 1990s the market of several types of thin film products has exploded like Photovoltaics, energy conversions, energy efficiency, biomedical, pharmaceuticals and flat panel displays. So, these all are the normal things where we are adopting the thin film depositions, where the thin film depositions are the maximum we are going to use. So, from this particular figure he can understand that in the year of 2009, it was a near about 3000 to 4000 US dollar, but when you are talking about the 2015, it reached up to more than 20000 US dollar.

So, here the blue colour is giving the large projects and utilities where we are applying the thin films, then this orange colors is the others, then light blue or maybe the sky blue is giving the military and emergency, then the purple is giving you the consumer electronics, green is giving the residential building applications. So, here these all are the combinations of the different types of applications and if I go or maybe if I can see in wide spectrum, we can see that in 2009 it was around 4000; in 2015 it reached about 20000. So, 5 times multiplications have been occurred within this 7 or maybe 6 years.

Then this is the summarization of this particular lecture that we have to adopt the different coating techniques or maybe thin film deposition techniques based on the materials you are going to do, based on the applications you are going to choose or maybe the what type of use you are going to do.

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Summary:

- ✓ There exist a wide variety of deposition techniques.
- ✓ No unique method for classification of thin film deposition techniques. Depending on the viewpoint, the same process may fall into one or more classes.
- ✓ Each technique has its own advantages and disadvantages.
- ✓ Selection criteria for particular technique is mainly dependent on specific required applications and availability of resources.
- ✓ Hybrid techniques are becoming more widely used and available, i.e. Using more than one technique, simultaneously or consecutively, to deposit a given thin film material for microelectronics, bio-medical implants, etc.

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Next there exist a wide variety of deposition techniques already I have said it, no unique method for classification of thin film deposition techniques, depending on the view point the same process may fall into one or more classes. So, maybe you can see that for particular applications there are maybe 2 or 3 numbers of deposition techniques you can adopt.

Now, you have to go for the Costings, now you have to go for the requirement that in this particular case I need some specific atmosphere, for this particular case I need certain kind of specific temperature then choosing depend, you have to choose depending upon the availability of the equipment, depending upon the conditions available at that particular time or maybe which will be the less expensive, you can go for different types of coating techniques.

Each technique has its own advantages and disadvantages; a selection criterion for particular techniques is mainly dependent on specific required applications and availability of resources. Hybrid techniques are becoming more widely used and available because nowadays we are making different types of materials and we are

making more and more advanced materials, previously we are using some kind of virgin metals or maybe the virgin materials; nowadays we are using certain kind of alloys, certain kind of composites it is showing the various properties at a time, simultaneously it is giving in the higher mechanical properties, sometimes it is giving you the higher electrical properties along with the mechanical properties.

So, depending upon your requirement or maybe keeping those properties into the higher side, we have to adopt certain kind of techniques by which both the electrical properties or both the mechanical properties can be enhanced together or maybe the simultaneously. So, using more than one technique simultaneously or consecutively to deposit a given thin film material or microelectronics by material medical implants etcetera. So, by adopting several techniques, you can increase the several properties for a particular material or maybe the metal.

Thank you.