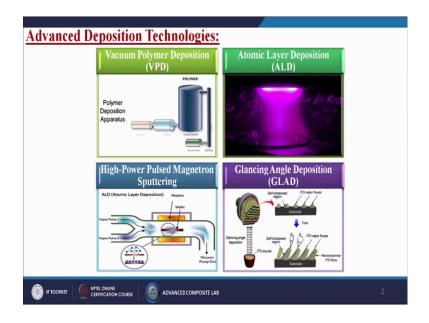
Surface Engineering of Nanomaterials Dr. Kaushik Pal Department of Mechanical and Industrial Engineering Indian Institute of Technology, Roorkee

Lecture – 14 Advanced Surface Modification Practices

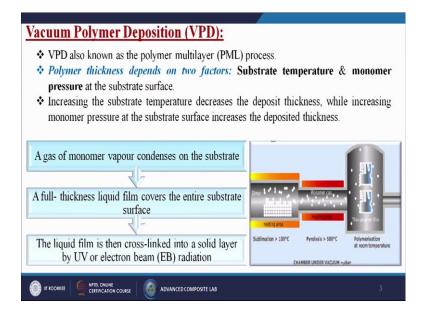
Hello, in this particular lecture we are going to discuss about the advanced surface modification practices. If you remember in my two last or maybe previous lectures I have discussed about the PVD process physical vapour deposition process and the CVD process chemical vapour deposition process. So, in this particular lecture I am going to discuss about the some kind of advanced surface modification practices rather than the PVD and the CVD.

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So, here in this particular lecture I am going to discuss about the 4 deposition techniques, one is called the vacuum polymer depositions in short form it is known as the VPD; next is called the atomic layer deposition process which is known as the ALD process then high power pulsed magnetron sputtering process and the glancing angle deposition or maybe the GLAD process we are calling it. So, these all 4 I am discussing into the details into the next subsequent slides.

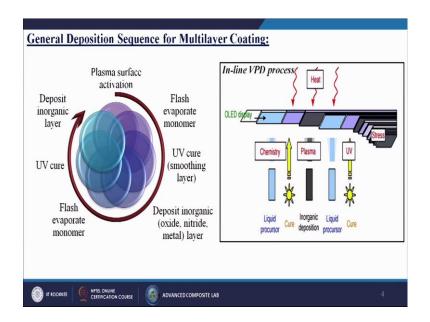
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So, first we will discuss about the vacuum polymer deposition process or maybe the in short forms the VPD process; first we have to know what the process is. VPD is also known as the polymer multilayer process or maybe short form we can call it as a PML process. Polymer thickness depends on two factors: substrate temperature and the monomer pressure at the substrate surface; increasing the substrate temperature decrease the deposit thickness, while increasing monomer pressure at the substrate surface increases the deposited thickness. So, from this particular you can understand that we can easily control the thickness of that particular coating, not only that we can increase or decrease the layers on that particular substrate.

So, a gas of monomer vapour condense on the substrate, a full thickness liquid film covers the entire substrate surface, the liquid film is then cross linked into a solid layer by UV or electron beam radiations. So, first like a pen. So, the thing is that we are having the substrate, we are doing the coating it is into the liquid formations then we are keeping into some conditions or maybe the into the environment by which it is forming some kind of reactions in between the substrate and in between that particular coatings and then it will be solid and it will acts as a layer on top of the substrate.

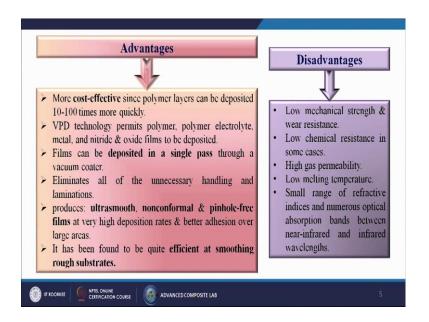
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General depositions sequence for multilayer coatings; here we can do the several types of coatings over there also depending upon our requirement, depending upon our applications. So, first is called the plasma surface activations, then flash evaporate monomer, UV cure or smoothing layer, deposit organic oxide nitride layer, flash evaporate monomer UV cure deposit inorganic layer. So, from this particular figure you can understand that we are adding so many materials layer by layer. So, just when are putting the one material onto the substrate, we are doing certain kind of curing over there. So, we are drying this materials then we are putting another materials then again we are doing the curing then we are putting another third material then again we are doing and so on we are making layer by layer depositions on top of the substrate

So, in line VPD process generally we are giving the heat over there onto the substrate itself, so we are using the OLED display. So, generally we are using it for the electronics purposes, here we are having the liquid precursor then first we are doing the coating of that liquid precursor, then again we are doing the curing, then we are using the plasma some inorganic depositions we are taking place, then we are using again the liquid precursor over there, then we are again we are doing the curing process. So, like this way we are doing the layer by layer depositions on to the material substrates

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What are the advantages? More cost effective since polymer layers can be deposited 10 to 100 times more quickly; VPD technology permits polymer, polymer electrolyte metal and nitride and oxide films to be deposited, films can be deposited in a single pass through a vacuum coater eliminates all of the unnecessary handling and laminations, process ultrasmooth, nonconformal and pinhole free films at very high deposition rates and better adhesion over large areas. It has been found to be quite efficient at smoothing the rough substrates; sometimes we can do this kind of modifications in a batch process too.

So, one the sample will enter then first we will do the curing, then we will do the one coatings then again we will follow the curing, then again we will do the another coatings. So, like this way continuously this process can be done or maybe we can put a single material and we can do the several coatings as a layer on top of the surface. There are certain disadvantages also, low mechanical strength and wear resistance, low chemical resistance in some cases, high gas permeability, low melting temperature, small range of refractive indices and numerous optical absorption band between near infra red and the infra red wavelengths. So, these are all the disadvantage of the VPD process.

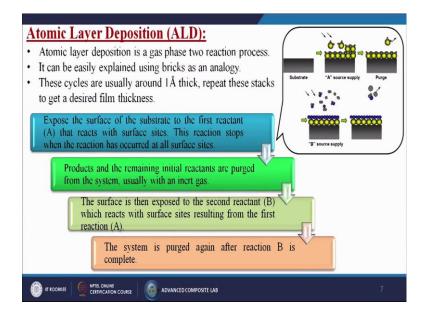
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What are the applications? Generally we can use these techniques for the Ultrabarrier materials, thin film lithium batteries, thin film photovoltaics or maybe the solar cells, light emitting polymers OLED device, multilayer optical coatings on flexible substrates, wear resistance coatings for any kind of mechanical fashioners, Nano laminate structures, thin film solar cells, an electroluminescent devices, radiation detectors, thin film capacitors and anti bacterial coatings, corrosions, contaminant resistance for fibers. So, here it is having a huge applications on electronics field, bio medical field, then physical field, physics site and not only that energy related field energy harvesting, energy storing all these.

Next we are going to discuss about the atomic layer deposition; before going to start let me tell you that ALD techniques is the latest techniques which we are going to use for modifications of our surface, the experiment the equipment is very expensive and not only that it needs utmost care and also it needs the proper maintenance and rectifications.

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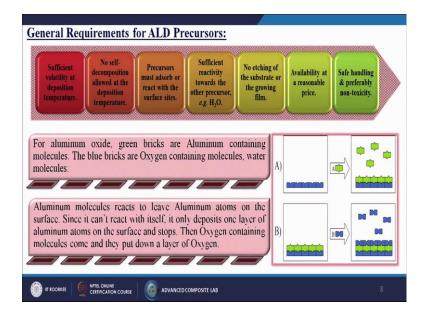


So, atomic layer deposition is a gap phase two reaction process; it can be easily explained using bricks as an analogy, these cycles are usually around one angstrom thick repeat these stacks to get a desired film thickness. So, form this particular case we can understand that we are having some kind of substrate over there, then first we are putting a source supply over there, then we are purging it, then we are doing a stack of coating then again we are doing that samples and then we are putting the another materials over there top of that. So, layer by layer techniques we can do this modifications onto the substrate itself.

So, here first expose the surface of the substrate to the first reactant that reacts with surface sites, this reaction stops when the reaction has occurred at all surface sites; that means, I am having the substrate which is in the virgin in nature, now I am putting some kind of reactive materials, it will react with the substrate and then it will do a coating over there, when there will not be any active sites are present on the top of the substrates total reaction will be stopped. Then products and the remaining initial reactants are purged from the systems usually with an inert gas, the surface is then exposed to the second reactant which reacts with surface sites, resulting from the first reaction A, the system is purged again after reaction B is complete.

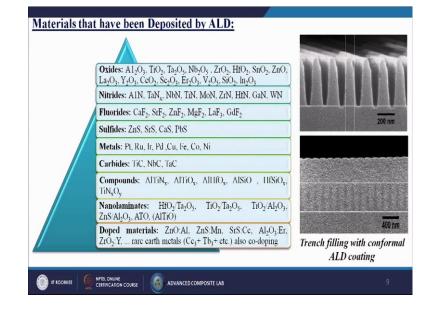
So, the thing is that on top of A I will put certain kind of materials or like a binder or maybe some kind of surfactants then I will put the whole material into some B reactive gases then that B reactive gases will do the reaction with the A material properly and then again will do the purging process, so that the whatever the impurities and whatever the gases it will directly come out from there. So, by this way we can do the layer by layer depositions on the material substrate.

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So, there are several types of requirements are required for the ALD precursors; first one is called the sufficient volatility at deposition temperature, no self decomposition allowed at the deposition temperature, precursors must absorb or react with the surface sites, sufficient reactivity towards the other precursors like water, no etching of the substrate or growing film, availability at reasonable price, safe handling and preferably non toxicity. So, these all are the requirements for the ALD techniques. So, for aluminum oxide green bricks are aluminum containing molecules, the blue bricks are oxygen containing molecules or maybe the water molecules so there. So, this is the blue one which is made of the aluminum, then when we are putting A gases over there or maybe the A reactive gases over there. So, it is attaching with the water molecules over there. So, aluminum it attached with the water molecules then we have to introduce the B once again.

So, aluminum molecules react to leave aluminum atoms on the surface. Since it can react with itself, it only deposits one layer of aluminum atoms on the surface and stops then oxygen containing molecules come and they put down a layer of oxygen. So, like this one by one reactions it can attach layer by layer.



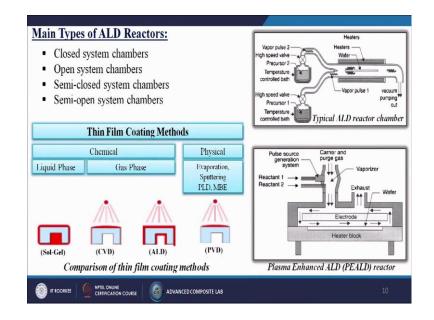
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So, what are the materials generally we are going to use by the ALD process? First one is called the oxides, generally the alumina, titanium oxide, tantalum oxide, (Refer Time: 10:36) oxide, tin oxide, zinc oxide. So, these all are the various materials vanadium pentoxide. So, these all are the several materials generally we are going to use for the ALD process, then we are using certain kinds of nitrides material: niobium nitride, titanium nitride, molybdenum nitride, zymphonium nitride. Some kind of fluorides material calcium fluoride, zinc fluoride, magnesium fluoride, caladium fluoride; sulfides generally zinc sulfide, then calcium sulfide, lead sulfide we are going to use; metals also can be done, carbides titanium carbides, then tantalum carbides; compounds like aluminum titanium nitrite, aluminum titanium maybe oxides or maybe some kind of other materials also can be done.

So, Nanolaminates also can be possible it s a mixture of different materials like titanium dioxide and tantalum oxides; doped materials like zinc oxide with aluminum, zinc sulfide with manganese or maybe that aluminum oxide with earthanium, some kind of rarer material like (Refer Time: 11:52) also can be done as a co doping. So, from these particular chart you can understand that we are doing or maybe we can use several

materials for the ALD process, it is having a huge (Refer Time: 12:08) on the applications. So, there is a whole range of materials that can be done for by these ALD process.

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Next what are the ALD reactors means, this is the total structure of that ALD techniques. So, closed system chambers, open system chambers, semi closed system chambers and the semi opened system chambers. By these four techniques we can use the ALD reactors either it can be open, it can be closed, it can be semi opened semi closed like this.

Then he here right hand side corner is the typical ALD reactor chamber have been shown over here. So, from this particular case you can see that here is one chamber either this can be open or maybe this can be closed, we are using certain kind of vacuum over there, now we are having two precursor over there: precursor 1 and precursor 2. So, form one material is going then it is attaching to the substrate itself, then here it is having some heater arrangement or maybe the heating arrangement by which it is drying, then from the material from the second precursor it will come and it will do the reaction over there. So, by these methods we can do the layer by layers coatings over there.

And here just we instead of heating or something like that, we have directly we are using the plasma. So, that is why it is called the plasma enhanced ALD or maybe the PLD reactor over there. So, we are having some purged gases, carrier gases over there. So, now, one reactant we are putting it is mixing with the purged gases or maybe the carrier gases, then directly it is coming and it is giving a coating onto the vapour itself. So, here the heating arrangement we are using as a plasma material, no direct heating or maybe the heat air we are going to use over here only the heat air we are going to use to dry the surface of that particular substrate.

So, thin film coating methods there are several types of techniques, if we go for the chemical it is divided into two parts, one is called the liquid phase, another one is called the gas phase and another one is called the physical like evaporation, sputtering, PLD, MBE. So, from this particular you can understand that how we can achieve the coatings by different methods, if we go for the sol gel methods if our substrate is like this shape like a sea shapes then the sol gel techniques it will coat the whole material over there. Somewhere it can hold the homogeneous layers or maybe the homogeneous thickness somewhere it is not, then when we go for the simple CVD methods, the CVD methods simply do the coatings on the top of that and also the thickness will not be the homogeneous.

When you will go for the atomic layer deposition methods, from this particular figure you can understand that we can do the coatings of all around and the coating thickness will be the homogeneous one at the corner also. It is not the confocal type and when we are going for the physical vapour depositions, it is only the top of the surface and also it is the confocal type and the thickness is not the homogeneous. So, in this slide we are going to discuss about the advantages for ALD processes.

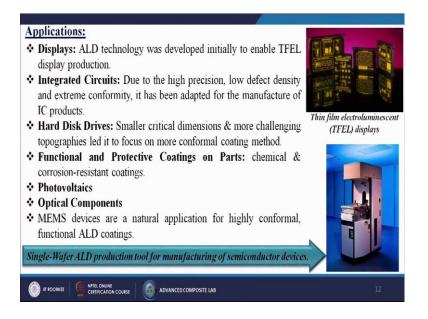
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Extreme surface conformity	<i>i.e.</i> nanotubes, nanowires, particles, diffractive optics, DRAM, 3D parts
Pinhole-free films	'Bottom up' growth of ALD is naturally pinhole free; excellent for passivation, barriers & insulators
Repeatability	Robust in production; without in situ feedback
Scalability	Processes based on robust ALD precursor chemistries straightforward to scale up for production
Ultrathin, dense, smooth films	One atomic layer at a time; gate oxides, tunneling insulators, <i>e.g.</i> for hard disc drives
Artificial materials	Digital control of ALD provides a way to create artificial materials; enables R&D innovations
	ighly uniform coatings over surfaces of three-

So, first we are going to discuss about the extreme surface conformity. So, by doing the ALD process we can achieve the extreme surface conformity for these materials like nanotubes, nanowires, particles, diffractive optics, 3 D parts; Pinhole-free films "Bottom up" growth of ALD is naturally pinhole free; excellent for passivation, barriers and insulators. So, actually the thing is that ALD technique is very very sophisticated technique, we can achieve so many things from here and it is having versatile applications. So, repeatability: Robust in production; without in situ feedback. Scalability process based on robust ALD precursor chemistries straightforward to scale up for production. Ultrathin, dense, smooth films: one atomic layer at a time; get oxides, tunneling insulators, or for hard disc drives.

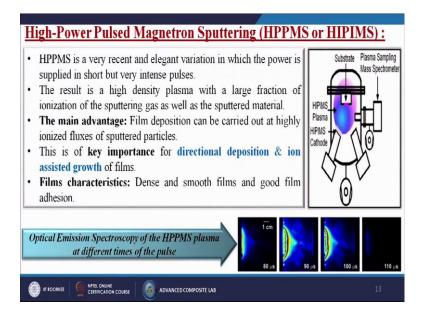
So, we can go for a single layer, we can go for different layer, we can minimize or maybe the increase the layer thickness. So, there are several kind of things we can do by this ALD techniques. Artificial materials like digital control of ALD provides a way to create artificial materials, enables R and D innovations. Growth of ALD provides highly uniform coatings over surfaces of three-dimensional parts via deep trenches, porous material and particles. So, it is having huge huge advantages and applications in recent days, not only that this is the whole ALD process, by this ALD process you can do the coatings homogeneously throughout the whole material and the thickness of that material you will be constant all over the substrate.

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What are the applications? Displays: generally ALD technology was developed initially to enable the TFEL display productions; integrated circuits: due to high precision, low defect density and extreme conformity, it has been adapted for the manufacture of IC products. Hard disc drives: smaller critical dimensions and more challenging topographies led it to focus on more conformal coating method. Functional and protective coatings on parts: chemical and corrosion-resistant coatings. Photovoltaics; optical components; it is having a numerous applications over there. So MEMS device are a natural application for highly conformal functional ALD coatings, single wafer ALD production tool for manufacturing of semiconductor device the machines is looks like this.

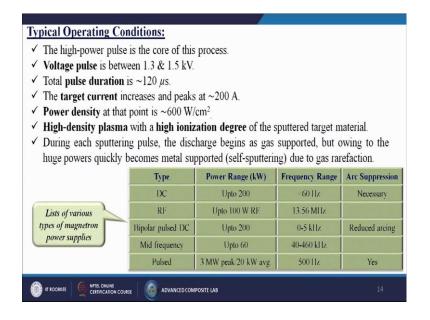
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Next is called the high power pulsed magnetron sputtering or generally in the short form we are calling it as a HPPMS or maybe that HIPIMS. So, HPPMS is a very recent and elegant variation in which the power is supplied in short and very intense pulse. The result is high density plasma with a large fraction of ionization of the sputtering gas as well as the sputtered material. The main advantage: film deposition can be carried out at highly ionized fluxes of sputtered particles, this is of key importance of directional depositions and ion assisted growth of films. Films characteristics: dense and smooth films and good films adhesions; so here we are keeping the substrate over here then we are using the plasma over there, we are having so many cathodes and then the plasma sampling mass spectrometer we are introducing in this particular cases. So, the film generation will be taking place into this particular juncture and it will deposit onto the substrate itself.

So, here we are showing certain kind of optical images, which we are getting for various samples during the HPPMS plasma process. So optical emission spectroscopy of the HPPMS plasma at different times of the pulse, if we increase or decrease the pulse; that means, for 80 microsecond, for 90 microsecond, for 100 microsecond and 110 microsecond, how much the thickness we are going to achieve or maybe the how the material is looks like.

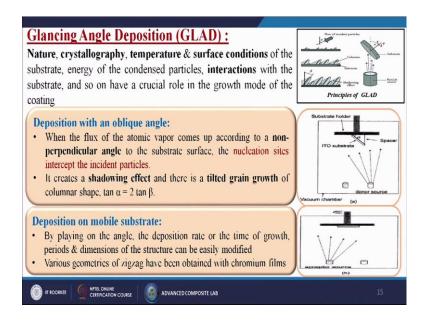
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Typical operating conditions: the high power pulse is the core of this process, voltage pulse is between 1.3 to 1.5 kilo volt; total pulse duration is generally up to 120 micro second, the target current increases at peaks at 200 ampere, power density at what point is at that point is 600 watt per centimeter square, high density plasma with a high ionization degree of the sputtered target material during each sputtering pulse the discharge begins as gas supported, but owing to the huge powers quickly because metal supported due to the gas fabrications.

So, what are the lists of various magnetron power sources generally we are using? We are using the DC sources; we are using the RF, bipolar pulsed DC, mid frequency, pulsed frequency. Power range in kilowatt generally it is up to 200 it is up to 100 watt RF frequency up to 200 kilowatt, up to 60 kilowatt, 3 megawatt peak to 20 kilowatt average. Frequency ranges generally its less than 60 hertz, 13.56 megahertz, 0 to 5 kilohertz, 40 to 460 kilohertz, 500 hertz. Arc suppressions it is necessary for this particular case DC case then by bipolar pulsed DC is new some reduced arcing and in the pulsed case of course, it is yes.

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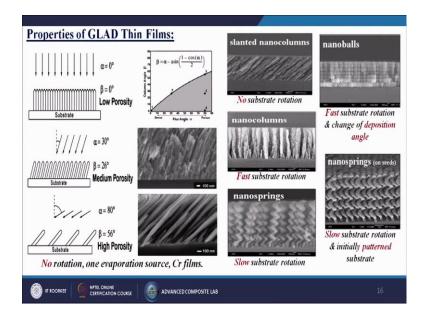
Next one is called the glancing angle deposition techniques or maybe then short form generally we are calling it as a GLAD, then generally nature, crystallography, temperature surface conditions of the substrate, energy of the condensed particles, interactions with the substrate and so on; have the crucial role in the growth mode of the coatings. So, we have already gone through this what are the natures of that particular material, what are the crystallographic structures, what are the temperatures we are applying, what is the surface conditions whether it is rough, whether it is hydrophobic hydrophilic. So depending upon that, you have to choose the different techniques over there.

So, depositions with an oblique angle, when the flux of the atomic vapour comes up according to a non perpendicular angle to the substrate surface, the nucleation sites intercept the incident particles, it creates a shadowing effect and there is a tilted grain growth of columnar shape tan alpha equal to 2 tan beta. So, from this particular case yeah till now we are discussing that when we are releasing that material directly it is coming and it is falling onto the substrate and it is doing the coatings, but here the thing is that a reactant gases or maybe that reactant molecules we are putting onto the substrate having a single angle. So, here from this particular figure you can understand that we are having the substrate, now we are throwing this incident particles into some angle itself and then here the column is also making angle over there the coating, the column of that

particular coating is also giving angle over there. So, it is not directly perpendicular with the substrate.

So, what are the reasons? Deposition on mobile substrate by playing on the angle, the deposition rate of or the time of growth, periods and dimensions of the structure can be easily modified. Various geometrics of zigzag have been obtained in the chromium films. So, in this particular case we can do the directional coating onto that particular materials depending upon our requirements, sometimes we can do the horizontal, some can would we can do the verticals, sometimes we can put certain kind of angular coatings also.

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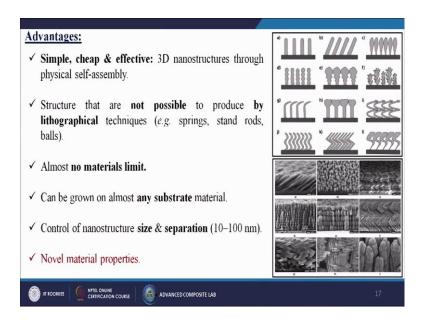
So, properties of the GLAD thin films. So, generally we are having the substrate. So, we can make it as a perpendicular also where alpha equal to 0 degree and beta will be the 0 degree. So, here this from this particular figure you are getting this kind of things. So, we are making the nanoballs, we are making the slanted nanocolumns then this type of nanocolumns, not only that we are making the nanosprings, some kind of spiral shapes over there, sometimes we are doing certain kind of nanosprings on seeds. So, all these having a different angle of deposition rate; when we are making try to make certain kind of porous materials, we are putting alpha around 30 degree, beta around 26 degree so that there will be certain angle columnar angle over there onto the substrate and when we

need the high porosity of material over there. So, we can make the alpha as 80 degree or maybe beta as a 56 degree, no rotations one evaporation sources chromium films.

So, these all are the FESM image, has been taken around 100 nanometer range. So, here the chromium films you can see that it is like a grass onto the field itself right. So, if some air has been passed, after that its looks like this and if there will not be any air it looks like some kind of straight things. So, it depends you can change the porosity of that particular materials by changing the angle of incident of that particular reaction reactive gases onto to the substrate itself.

So, if the known substrate rotations the shape will be like this, first substrate rotations and change of deposition angle you can get the this kind of shapes over there. So, substrate rotations and initially metal substrate you can get this one. So, first one is that how we are putting your substrate over there not only that whatever the angle you are following over there then you can make any type of directional coatings over there any kind of shift over there.

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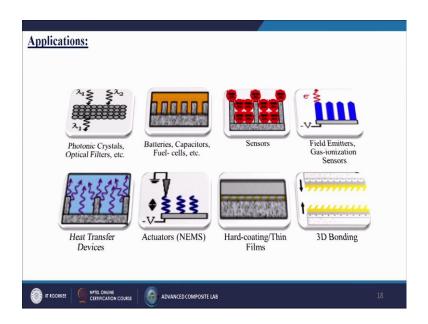


What are the advantages? Simple, cheap and effective: 3D nanostructures through physical self assembly, structures that are not possible to produce by lithographical techniques like springs, stand rods, balls almost no materials limit can be grown on almost any substrate material control of nanostructure size and separation generally 10 to 100 nanometer novel material properties.

So, from this particular you can understand or maybe you can see that depending upon our requirements, suppose I want to stretch my materials like this, so forgetting the maximum properties I can do the coatings in this direction means our columnar will be in the horizontal direction so that I can achieve the maximum properties. If I want to achieve the maximum properties into these directions then maybe I can do the coatings into these perpendicular directions so that I can do the maximum properties at this particular range.

So, from this particular figure you can see that any type of shapes of that particular structure, I can do on top of our substrate. So, we can achieve the different properties, we can make the material porous, we can make the material as a solid without any pores. So, any type of synchronizations can be possible on the top of the substrate.

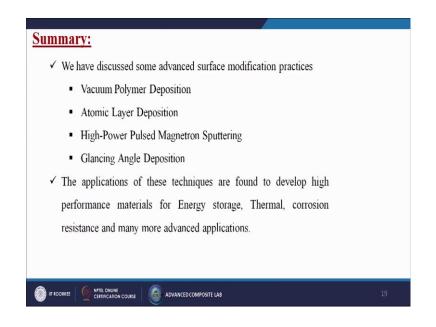
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What are the applications? Generally we can use these materials for the photonic crystals, optical filters, batteries, capacitors fuel cells, sensors applications, field emissions of gas ionization sensors, 3D bonding, hard coating thin films actuators NEMS or maybe the heat transfer devices. So, nowadays people are working on the different structural dimensions of different Nano fillers coatings are into the different directions and different shapes. So, by achieve, for achieving the better properties in terms of maybe that electronics, maybe that energy storage, maybe the sensors or maybe some kind of mechanical or maybe the thermal insulators or maybe the barrier materials.

So, in summary in this particular lecture we have discussed the 4 uncommon techniques; rather than the PVD process - Physical Vapour Deposition process and rather than the CVD process - Chemical Vapour Deposition process.

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So, one is called the vacuum polymer depositions VPD process, ALD process Atomic Layer Deposition, High-Power Pulsed Magnetron Sputtering and Glancing Angle Deposition process. So, these 4 processes we have gone through in details in this particular slide, the applications of these techniques are found to develop high performance material for energy storage, thermal corrosion. So, already I have mentioned it depends upon our requirement, it depends upon which properties we need more; we have to choose the proper coating techniques and the proper procedure we have to maintain.

Thank you.