

Introduction to Biomaterials

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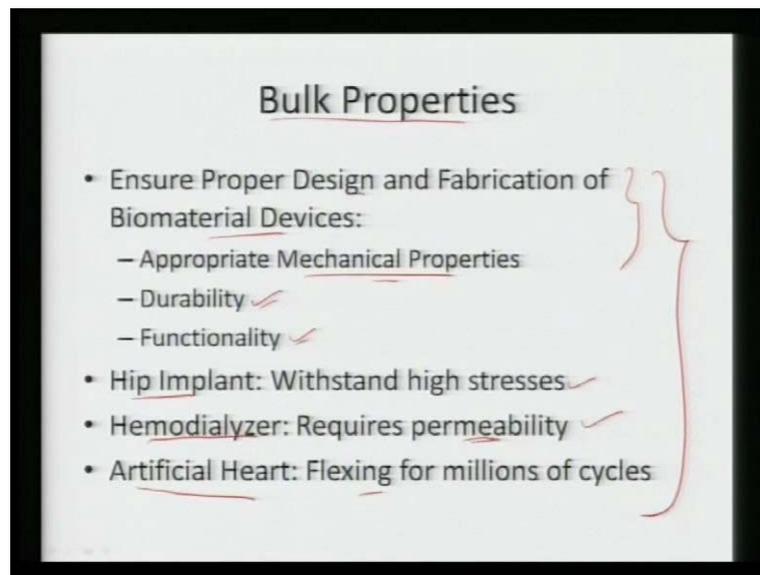
Module No. # 01

Lecture No. # 26

Thin Films & Coatings

In this lecture, we will learn about the thin films and coatings, how they have been applied on the surfaces of the bio **bio** implant devices and materials to enhance the cytocompatibility of all those devices, when once it is incorporated into the body.

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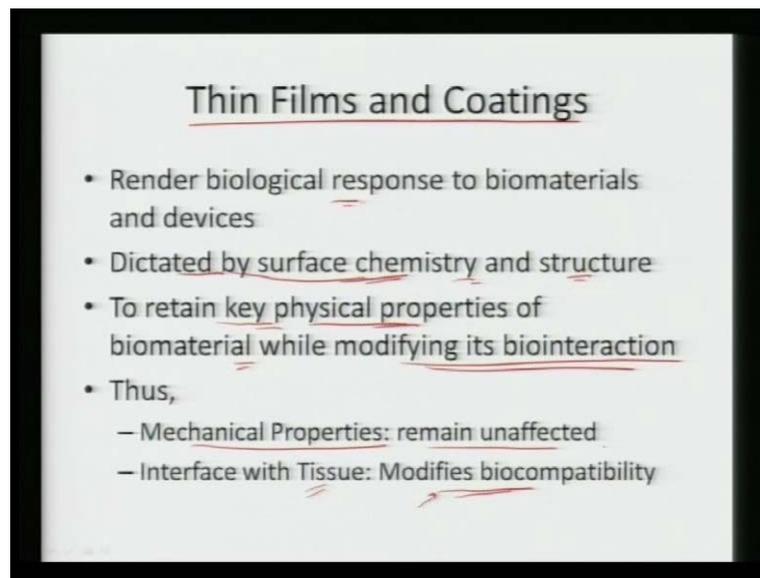


Generally the bulk properties of the device materials, they **they** are somehow design to ensure proper design and fabrication of biomaterial devices for certain applications, certain properties such as appropriate mechanical properties in terms of its durability; it can also incorporate the corrosion resistance, and even the functionality of that particular device. So, the bulk properties dictate the appropriate mechanical response, chemical response and the biological response, once there are inserted into the body such as Hip Implant - it has to withstand very high stresses that is sectional requirement;

Hemodialyzer - it requires very good permeability, and then again, that is again a fabrication requirement; and the Artificial Heart - it need flexing for millions and millions of cycles.

So we can see a variety of such requirement by Hip Implant, Hemodialyzer, Heart Implants, so in terms of withstanding either high stresses or high permeability or even flexing for millions and millions of cycles. So, we can see the bulk properties have been dictated by the functionality of the properties of the material itself, the bulk... The properties of bulk materials in itself; but once it has to interface with the biological entity, the environment, it has to be incorporated with certain surface layer, so in order that the overall bulk properties, they are maintained; at the same time, we enhance the interaction of this particular device with the surrounding material.

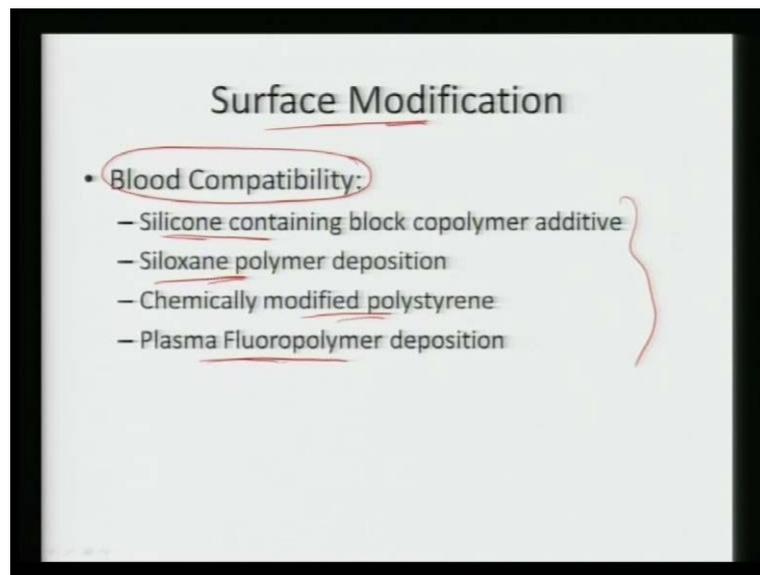
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So that is **that is** the reason - that is the critical reason that we require thin films and coatings. So this thin films and coatings they can render biological response to biomaterials and devices, while maintaining the mechanical and functionality of the device, which has been now placed into the body; so the thin films and device they get dictated by the surface chemistry, so the overall response of this device it gets dictated by the surface chemistry in the structure; and the idea of applying this thin films and coating to retain the key physical properties of the biomaterial, the bulk property are now being maintained, while modifying its biointeraction with the body.

So, in the process what happens we are applying thin films, it will retain the mechanical properties, they remain unaffected, but its interfacing with the tissues in the cells nearby, that is now being modified, because of these thin films and coatings; so we can see that thin films and coatings, they can render biological response to the biomaterials and the devices, which are placed inside the body; they dictated by surface chemistry and structure, so we can somehow tailor the surface chemistry and the structure in order to curtail or enhance certain response of this device with the surrounding tissues; and in the process, it retains the key physical properties of biomaterials, so it does not affect the mechanical properties in the functionality, but it modifies only the biointeraction (()). So in thin films and coatings they can render enhance cytocompatibility; so it can modify the biocompatibility while and... While maintaining the mechanical properties of the device.

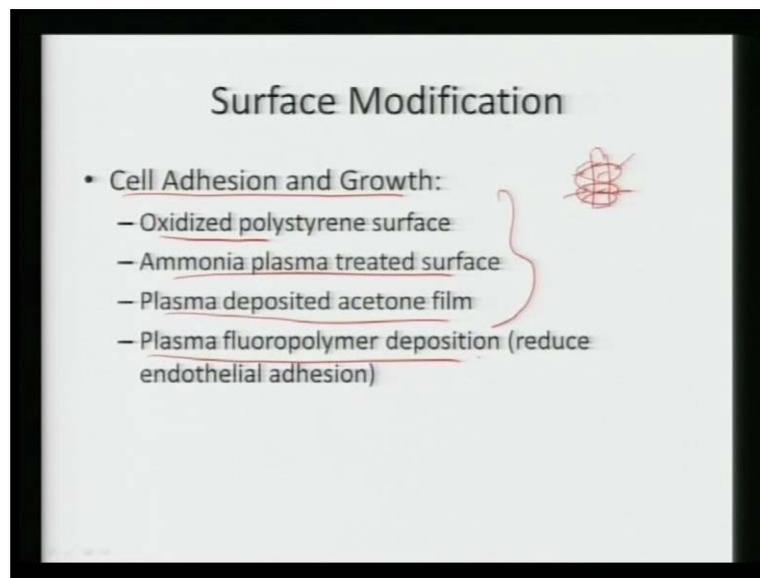
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Certain modifications are required such as it can be surface modification, so surface modification can include blood compatibility; so in certain cases, when we require the blood the blood comparability with the insert inserted device, we can utilize a silicon containing block of copolymer additives, so Siloxane polymer is a deposition chemically modified polystyrene and or Plasma Fluoropolymer deposition; so these are certain materials, which can be utilized for enhancing the blood compatibility with the device materials.

So these are being applied as a coating on to a device material to enhance the overall interaction and without letting the blood clot or inducing thrombosis in those particular regions; otherwise device can induce certain toxicity, it can also induce encourage thromboses near those regions, where the device has been inserted. So this induced induces the blood compatibility via certain materials such as silicon containing block copolymer, siloxanes or chemically modified polystyrene or even plasma fluoropolymer deposition.

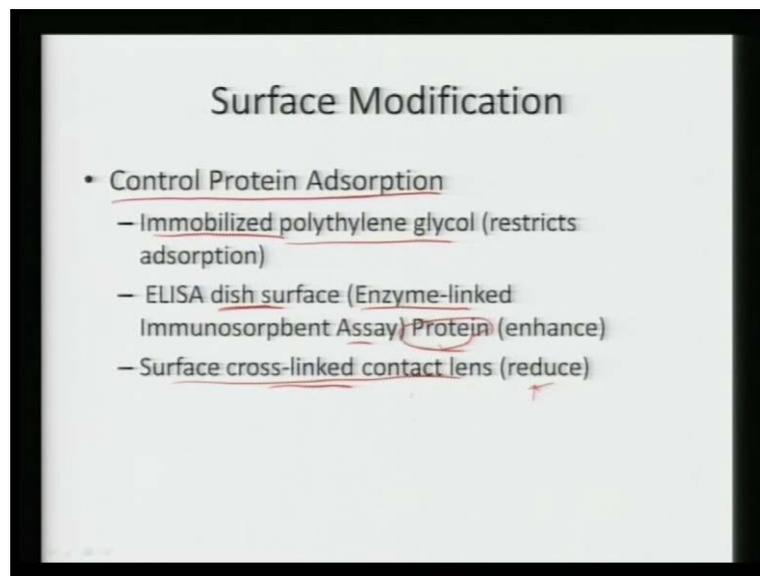
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And in certain cases, when we require cell adhesion and growth, so once we want the material, when the device is been inserted into the body, and we wanted to become an integral part of **the of** a particular organ itself, so it has now to be in cause in compose with the cell; so cell should adhere on the surface, and they should **get, they should** just basically inhale the overall entire machine for a nice anchoring, so cell adhesion and growth can be encouraged such as by oxidized polystyrene surface, ammonia plasma treated surface or plasma deposited acetone film; and these are all, which are required for enhancing the cell adhesion and growth, but in certain cases when we want to reduce the overall interaction of those cells with the entity, because in that case, we some time we want to remove that particular device or add something additional on the surface of the device that we do not want cells to damage surface of the device material.

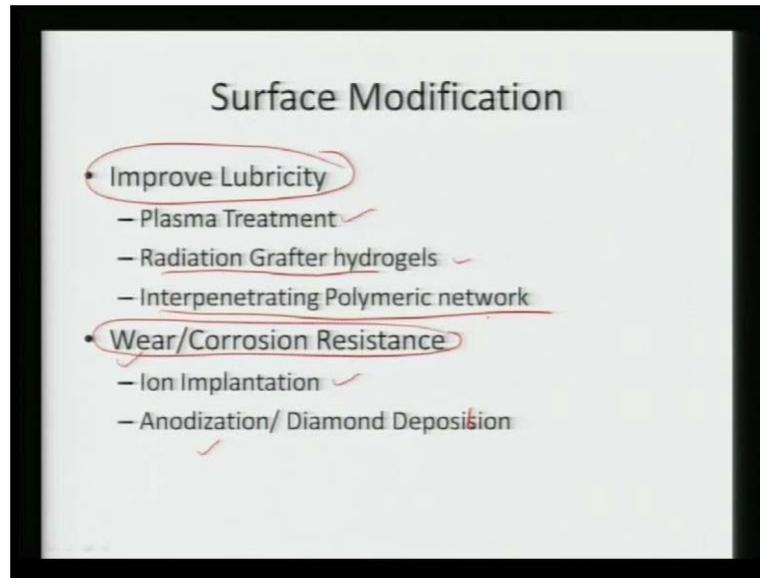
In case we want it to act as a sensor or retain there, so that we can analyze in the chemical composition of the nearby blood or even the pH value, so we want that particular surface to remain exposed for certain duration of time. So we do not want the cells to grow on to that particular region; so in those cases, we do not we want to reduce the cell adhesion on those surfaces, and we can utilize plasma fluoropolymer deposition again and certain cases; so we can either utilize certain techniques or certain composites, certain materials to impart that particular affect.

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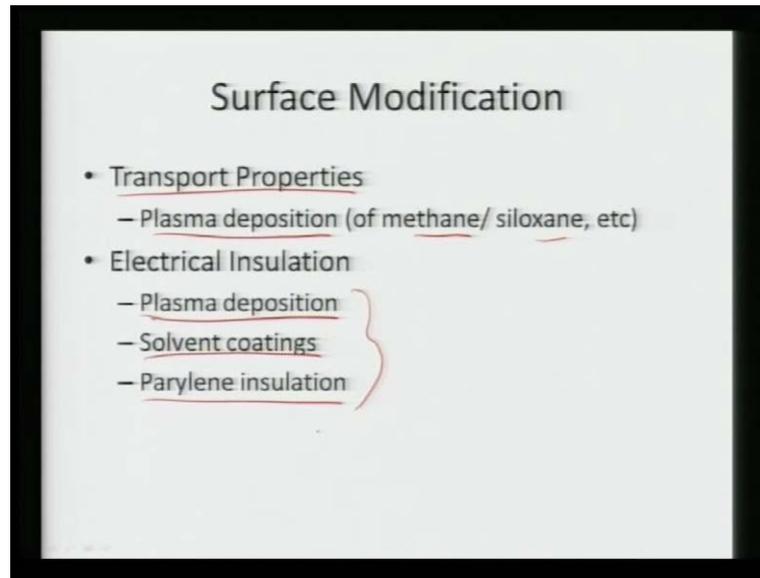
Again the surface modification can also be required in terms of controlling the protein adsorption. So if you want to incorporate or want to reduce the adoption, we can impart immobilized polyethylene glycol, we can also impart ELISA dish surface to enhance the overall protein adsorption, utilizing ELISA dish that is nothing but Enzyme Linked Immunosorbent Assay, so ELISA dish surface, it can **it can** impart enhance protein adsorption; again once we start cross linking the contact lens, it can again reduce the overall proteins adsorption, otherwise it will basically create a problem in terms of inter locking the surfaces, because protein, once proteins gets exhaust, then only the cell start coming on to the surface, and they adhere to the surface, and get adsorbed. So to eliminate the overall growth of cell or precipitation of certain cells on the surface of device materials, you want to control the protein adsorption, and that can be induced by surface cross **cross link cross** linking such for contact lenses.

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And in certain regions, we want to improve the lubricity; in case once we have certain joints, you want to enhance the lubricity, so that the meetings of undergo the minimum friction; so we can impart certain treatments such as plasma treatment, we can also induced radiation grafted hydro gels, we can also induce something called interpenetrating polymeric network, in order to supply **supply** nutrients or even to supply the lubricants for reducing the overall friction between the two meetings surfaces or adjoining surfaces; and in some cases, we also want to enhance the life of the particular device or in implant; we also want to **want to** improve its wear resistance and the corrosion resistance, that can be achieved by ion implantation or even doing the anodization or diamond deposition. So we can see by either by diamond deposition or anodization, we can enhance the wear and corrosion resistance of the implant or the implant of the device material.

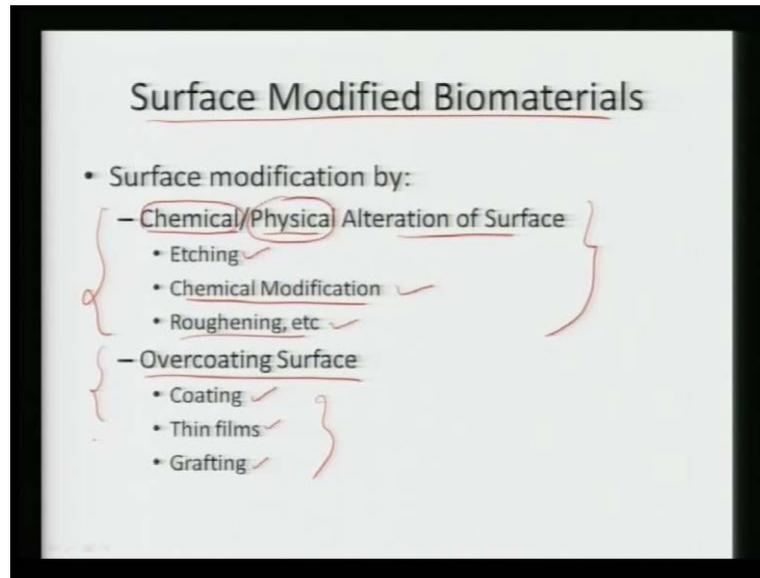
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And certain cases we want to improve the transport properties in order to enhance the drug delivery or a supply certain nutrients to certain location, we can do plasma deposition of successive methane or siloxanes; in some cases, we want **want** to have electrical insulation such as in the pumping hot region, so in that case, we want to when the leads are just coming out, we want to have them insulated so that they do not **they do not** really short circuit; so we can do something called plasma deposition, we can also apply solvent coatings or we can also apply parylene insulation in those regions.

So we can **see we can** apply certain techniques for either improving the wear resistance, corrosion resistance improving the transport properties, even inducing lubricity of providing electrical insulation; so this surface modification become very critical in terms of dictating the functionality or the overall surface interaction of the device with the nearby tissues or the environment or even the fluid around it.

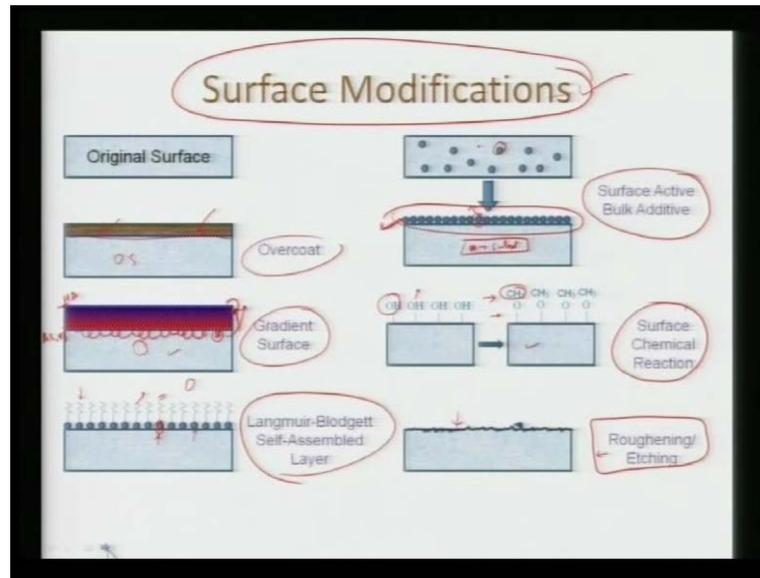
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And now there are certain techniques, which can be utilized for modifying the surfaces of the biomaterials; so once a biomaterial is being **induced** introduced into the body, the surface can be modified either by chemical or physical alteration of the surface. So either we take the inserted surface - inserted surface of the implant material of the device material, we somehow change the chemistry of the top layer, in that particular manner, we are changing the chemical **chemical** or physical nature of the surface of the implant directly, that can be done by either etching, so we apply certain chemicals to it, and then it is the surface to make it much more rougher; chemical modification again by changing in the chemistry via letting it react with some other species or even roughening in order to enhance the surface area, which comes in contact with the adjoining surfaces or the living environment.

So we can see that we can alter the surface of the device itself or the implant itself by altering its chemistry or by its physical nature; and the second technique, we can somehow coat or allow some different material to get deposited on the surface of the implant material, so we can either also do, we can also overcoat the surface of the implant material or the **or the or the** device material via certain coatings or by implanting certain thin films or by grafting; so we can see, we can have two kinds of techniques either we can go via chemical or physical alteration on surface, so we can also have an overcoating the surface such as by coating or introducing thin films and grafting.

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So they are certain techniques, so if we have original surface, so we can see this original surface is now very much proven for things like corrosion, wear resistance, even the cytocompatibility **becomes** can become an issue; it will also release certain ions and is found to impact certain functionality, if you want the tissues to get attracted or even the blood... We wanted to introduce the blood comparability, so (()) somehow modify the surface accordingly; the certain techniques: In first case, we can just overcoat the material; so we have this original surface, original surface and we then over coated with certain material to impart that particular functionality.

So in this case, we can apply just some material, which can protect this our underlying surface, this is nothing but the original surface, and impart certain functionality; in certain cases, we can also introduce a gradient surface, because this surface might be very, very inert, and if you want to impart certain functionality (()) say if you want to have much more cell comparability of the surface, but we also want to have the inter layer to be very, very strong and adherent, so we need to go gradually from this property of not allowing the cells to grow on to it to a very cell active surface, such as going from a very inert alumina **alumina** surface, aluminum oxide to hydroxyapatite surface.

So aluminum oxide to provide much more toughening, but hydroxyapatite will provide much more selectivity on the surface; so in that particular case, we want to go from 100 percent alumina 200 percent hydroxyapatite; so we have Al 23 100 percent and in this

case, we want to go for hydroxyapatite 100 percent. So in this case, we want to go gradually from 90, 80, 70, 60 percent of alumina to eventually come to 0 percent alumina; so we are providing nothing but a gradient surface, so that part also can be taken care by using certain surface modification.

And we can also apply certain self assembled layer, these are called Langmuir-Blodgett self assignment layers; so we can provide certain functionality to the surface, so we can either impact the... We can let polar head groups stick on the surface, and again so that can basically stick to the fluidic region, so polar region will be much more hydrofluoric in nature whereas, hydrophobic regions can stay outside, so that it will reduce the overall wetting of the surface; it can be done otherwise also we can let the hydrophobic region get attracted on the surface, then let hydrophilic region come on the top surface; so we can apply this Langmuir-Blodgett self assembled layers for again impart in certain functionality.

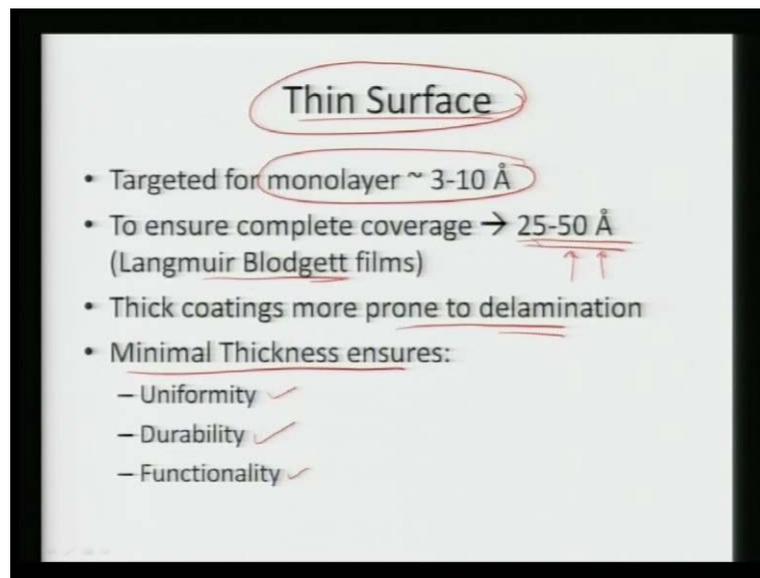
Then there is one more feature, we can also add some something called Surface Active Bulk Additive; in this case, we add certain material in the bulk of this particular original surface, and we play with the interfacial energies of that particular additive that it will have polar heads, it will also have certain tail region; and it happens that we can some somehow make these particular bulk additives to come and sit on the surface, just by playing with the interfacial energies of this additive on the original surface; so it can that will be dictated by overall difference between the interfacial energies of the additive, and that of a bulk material, and the difference between the interfacial energy of this additive with air, and difference between the interfacial energy of this additive with the substrate; so you should feel much more stable, once it is setting on the surface; so that interfacial energy has to be much lower than that of a additive on the substitute interfacial energy.

So in... So what we are doing which is reducing the overall energy of the system, by letting the bulk additive come and sit on the surface; so just by a single processing step we can allow this particular additive to come on the surface and impart certain functionality to the original surface. We can also introduce some something called surface chemical reaction; so once we have say OH group on the surface, we can some make it react, and make it a methyl CH₃ group, so from alcohol which we can go to with oxy-methyl group on the surface to impart certain functionality. So that is also

possible by inducing surface chemical reaction, and we can also introduce reactivity by enhance the reactivity on the surface by roughening it or etching it.

So once we have the surface, which was very smooth; and now we introduce surface roughness on the **on the** top of this particular surface, then we can **we can** still achieve enhance functionality or enhance surface area available for the reaction; so we can see we have certain **certain** modification techniques, we can either over code, we can apply gradient **gradient** layers, we can also apply Langmuir-Blodgett layers for impart in certain functionality, we can add bulk additives to the surface, we can impart certain chemical reactions or we can also enhance the surface activity by introducing roughness to the surface. So we can see these surface modifications in now possible by this all techniques.

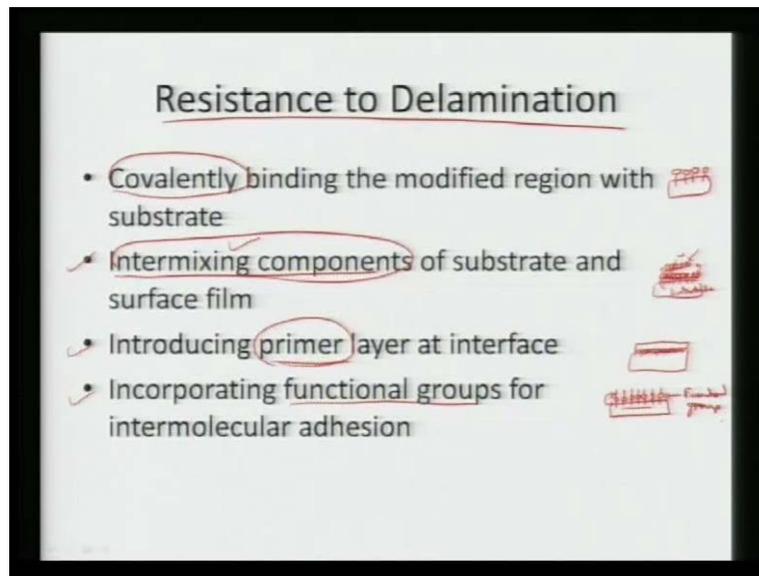
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And once we are coating thin surface, we are targeting a monolayer of around 3 to 10 angstrom in thickness; and basically to ensure complete coverage, we can go for up to 25 to 50 angstroms of Langmuir-Blodgett films, because we **want we** do not want any **any** part to remain unreacted or uncoated, so in that case, we may want to go for 25 to 50 angstrom, but what happens as we go for thicker and thicker coatings, though we are ensuring the complete coverage, but now, **but now** coatings become much prone to delamination, because as **as** soon as the coating start become a much and much thicker, it start incorporating certain stresses - residual stresses, and that might lead to its breakage.

So minimum thickness of this particular coatings, they ensure uniformity that it is nicely uniform, it is durable, and it is also highly functional; so we can see the thin surface, they are basically target in the range of 3 to 10 angstroms, and to ensure the complete coverage might even go for 25 to 50 angstrom thicker layer, but thicker coatings have problem of getting delaminate or getting crack, so that is the reason we want to go for thin films, which basically ensure the durability, uniformity and the good functionality of this particular surface.

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In order to reduce the overall delamination or enhance the resistance of delamination, what we can do? We can provide certain covalent binding of the modified region with the substrate, so instead of only VanderWaal's forces or electrostatic forces to cover the surface we can also impact certain chemical reactions; and induce certain chemical or covalent bonds with the surface, so we have surface bond with covalent bond to the applied coating, and then in the process it makes it much, much stronger, and we can also enhance the resistance to delamination **delamination** by intermixing components.

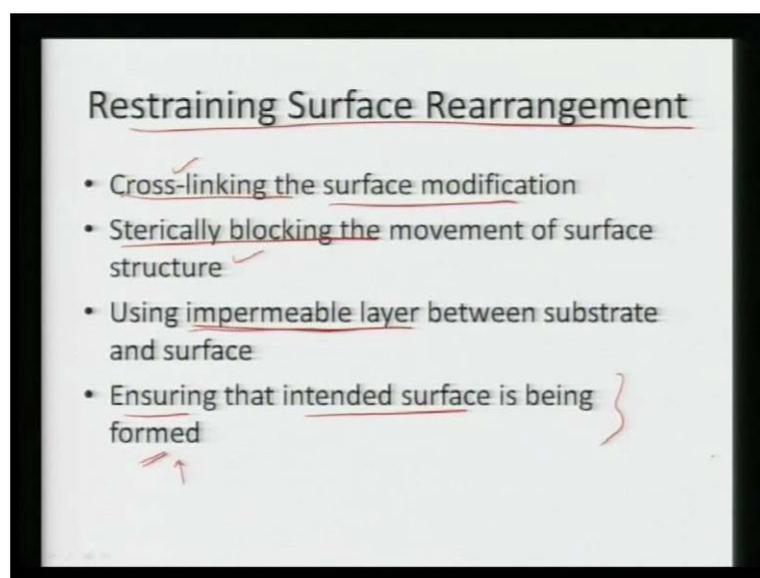
So in first case, we had substrate, which was no chemically bond to the outside or surface tissues; in this case what we do we do intermixing the components of surface substrate in a surface films; so in this case, it is more like a gradient layer; so we have just component it has now good affinity with itself, so we will provide some degree of bonding with the surface film; so in this case, we have substrate and other coating is

approximately of the similar material, then we coat one more layer, and then it is again of a different kind; so but in the process what we are doing we are intermixing the components, and by intermixing the components, we are inducing some sort of a interaction between the substrate and the surface film.

Third thing is we can also introduce some something called primary layer at the interface; primer layer at the interface is again mode like a glue, which can react again with the surface film to provide much more strengthening or resistance should delamination to the surface film. So, we can introduce the primary layer at the interface to again impact resistance to delamination. Additionally, what we can do? We can also incorporate functional groups; so if I have particular layer, a particular substrate, we can impact certain functional groups, which will bind strongly to the surface film.

So, in the process, this functional group **this functional group** can impart much more stronger bonding with the surface layer to the substrate by acting as an interlayer; so, we can see there are so many techniques of improving the resistance delamination; first we can bind the surface layer covalently with the substrate; secondly, we can also intermix the component of the surface and the substrate; or we can do something called primary layer to enhance the bonding; or we can also introduce something called functional groups to improve the bonding between the substrate and the surface layer.

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At the same time, once we are introducing a surface layer, we want to restrain that particular surface rearrangement; so the surface guides starts getting rearrange, it might even break, it might lose the structure, it might lose of functionality as well; so we want to retain the surface rearrangement, they way we wanted or the way we had plant. So first of all, we can reduce the movement or reduce the rearrangement part, but cross linking the modified surface or we can also sterically block the movement of surface; if we can allow, if we construct that change in such a manner that it is not the overall movements are not possible sterically; the overall the organization of the chain itself does not allow any further movement; so in that particular way also we can somehow block the movement of surface.

We can also introduce impermeable layer between the substrate in the surface, so again we can impart barrier between the substrate in the surface, so that the arrangement has been arrangement can be restricted, and again after we have done all that, we also need to characterize the surface, and ensure that the intended surface is really being formed; otherwise the overall device makes of no use, because we want to make sure that the internet surface is exactly its really forming.

It is not that it is getting rearranged to the different structure and getting damage; so we want to restrain the service rearrangement, and that we can do by cross-linking the surface, and somehow satirically blocking the movement of surface structure, so change the arrangement of chain itself can be in a such manner that it does not allow any rearrangement, or also introducing something called impermeable layer between the substrate and the surface in order to to minimize the movement, and after we have done that we want we also should ensure that it needs intended surfaces indeed being formed on the surface.

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The slide is titled "Methods of Surface Modification" and is enclosed in a black border. It contains a bulleted list of methods:

- Chemical Reaction: ✓
 - Reacts with atoms/molecules at surface
 - Do not overcoat with the reacting species
 - Can distribute different functional groups at surface
- Radiation Grafting Using
 - Co-60
 - UV radiation
 - High energy electron Beam

Handwritten in red ink on the slide is a diagram showing a surface with several vertical lines representing functional groups. A red arrow points from the text "Reacts with atoms/molecules at surface" to the diagram.

And the certain methods surface modifications; so we can see, we can modify the surface by something called chemical reaction; so we what in the chemical reaction what we can do? We can make the surface reacts with atoms or molecules at the surface; somehow we are now letting the surface items are setting on a surface of the particular device, let them react, and then form something else; so besides a OH group, we can make a reactive form OH CH₃ - OCH₃; in this case, it was much more a hydrophilic in nature, and once we start introducing CH₃ it becomes hydrophobic in nature; just like chemical reaction, we can change the overall contact angle on this particular surface, so in this case the contact angle will be much, much lower; in this case contact angle of the this thing will be **will be** very, very higher; we can see the contact angle is greater than 90 degree in this case, in this case contact angle is much less than 90 degree, so that is that can also be induced by utilizing chemical reactions.

And again the chemical reactions, they **are generally they** generally form monolayers, so they do not **they do not** overcoat with the reacting species, so we do not want if we are reacting it with certain spices, we do not wanted to settle down on this particular surface, but it just form a single monolayer on the top of it, and they should not overcoat with the reacting species. Again, we can distribute different functional groups at surfaces, so in some cases if you want to have a surface, which can take both hydrophilic as well as hydrophobic entities; we can impart functionality by introducing certain areas, which will be specifically hydrophobic, and other areas which will be specifically hydrophilic

in nature. So, we can see these areas can be totally hydrophilic, and another areas can be hydrophobic in nature; I will if you introduce some **some** surface, we feel any entity come over it, it will now be able to track both hydrophilic as well as hydrophobic entities on its surface.

So we can impart bi-functionality to the surface by somehow distributing different functional groups at the surface; so if water comes OH will be bonded when a polar region or **(C)** comes CH₃ might be bonded; so the chemical reactions, we can somehow react the atoms or the molecules they are sitting at the surface, and we can distribute different functionality by using these particular groups, but at the same time, we form only monolayers and we do not overcoat with these particular reacting species.

And there is an additional method of modifying a surface is by radiation grafting, so by radiation, in radiation grafting you utilize cobalt 60, and we impart UV radiation, and which is nothing but a high very high energy or we also utilize very high energy electron beam; in the process, they are doing nothing but breaking the chemical bonds, the bonding between the atoms or molecules can be easily disrupted by using **c 6** cobalt 60 or ultra violet radiation or even using high energy electron beam. So we can see we can somehow do the radiation grafting by breaking the bonding at the surface or by allowing either the gross thinking or even cleaning the surface or even inducing stability to the surface, we can utilize radiation grafting.

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Radiation Grafting

- Breaks chemical bonds of surface
- Reactive surface reacts with free radicals of introduced monomer
- Results good bonding with substrate
- Hydrophilic/hydrophobic ratio can be controlled on surfaces
- Can bond hydrogels to hydrophobic polymers

So, in radiation grafting, we can see it breaks the chemical bonds of the surface, so whatever bonding is formed on the surface, whether whatever it be, it can start damaging the bond structure, and it can basically break the chemical bond of the surface, and now that makes a surface highly reactive. Once the bonds have been broken, it makes the surface highly reactive, and all those reactive surfaces now can react with the free radicals and if you introduced certain monomer, now there is the free radicals will now interact with the introduced monomer.

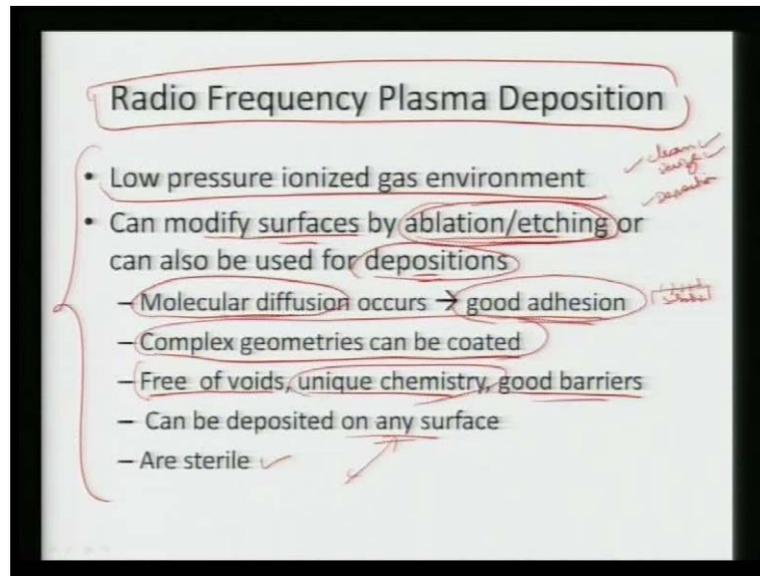
So the process we are activating the surface by breaking the chemical bonds, they start reacting with the monomer, which is now introduced in the system, and that now results a very good bonding with the substrate. So if you are able to activate the surface, let it react with the monomer, now it can bond very nicely or very strongly with the substrate; and again by radiation grafting as I said earlier, we can also control the ratio of hydrophilic or the hydrophobic ratio, it can be easily controlled. So we can always say which kind of specific ratio of hydrophobicity to hydrophilicity, we want to achieve in the system, and now we can make it react with the specifically to a certain entity biologically.

So we can attract a particular biological species with a particular hydrophobicity to hydrophilicity ratio, and then that can be achieved by utilizing the radiation grafting, because we can control the overall radicals, which are basically getting broken in the kind of monomer it is reacting with, so we can control the hydrophilic and hydrophobic ratio, we can make a surface coated with something, and we can **we can** exactly control the regions, where we are **where we are** breaking the bonds by directing it, and once we have done that we can let the monomer react to only those certain regions.

So in the process we have targeted the overall ratio of hydrophobic to hydrophilic content; and that is how we can really control the overall functionality or the reactivity of the system to the adjoining environment. Again, so in this process we can also see, it can also bond hydrogels to hydrophobic polymers. So we are seeing hydrogels, they contain much water; and hydrophobic polymers they are basically repellant to waters; so we can even achieve the bonding of this hydrogels to the hydrophobic polymers. So that is again a advantage, which you can achieve from the radiation grafting, because this is this can essentially utilize to break the bonds, and now control the exact reaction of that particular surface with any other chemical entity, it can be any monomer; and now we can change

the overall functionality of that particular surface, because of the radiation grafting, and we can even make hydrogels bond with the hydrophobic polymers.

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Then there is one more technique called radio frequency plasma deposition; and this is also called glow discharge; in this particular case, a low pressure ionized gas environment is maintained, and in this process, we allow high radio frequency to generate ionized gas; and now it can modify the surfaces by either ablation or by etching; and also it can be utilized for depositions. So in this case also we can either sterilize or we can clean the surface, we can even sterilize it or we can also utilize it for deposition. So we can see that radio frequency plasma deposition is also called the glow discharge process, it **may it** can be utilized for clean the surface, even sterilizing the surface or even depositing a different material on to that surface.

So it can easily modify the surfaces by either etching or ablation, what it does is it **it** allows molecular diffusion to occur, and once molecular diffusion is occurring, it can allow the penetration of this particular chemical species to go on to the substrate. So we have substrate, and this chemical entity now it can diffuse through the substrate as well; and once we have this sort of inter mixing, it will lead to a very good adhesion; so surface coating whatever is getting deposited on the substrate, it can impact very good adhesion with the substrate material.

One more advantage is that complex geometries can also be coated; it is basically doing nothing but we can also incorporate complex geometries, and also it is the coating itself is free of voids, it can have unique chemistry, it can also act as a very good barrier, and again it can be deposited on any surface that is one more advantage of this radio frequency glow discharge that we can utilize it for depositing on any surface, then also this radio frequency plasma deposition that also produces coatings, which are sterile in nature that is one more advantage of the radio frequency plasma deposition that whatever coatings we **we** are producing, they are sterile. So that is the advantage of this radio frequency plasma deposition.

So in this case, what we are doing? We are modifying the surface, we are also cleaning it, we can also etch or ablate the surface, we can also utilize it for deposition, and since it is it renders molecular diffusion, it can **it can** provide very good adhesion of the coating with the substrate; in this case, we can allow very complex geometries to be incorporated, and since they because of its higher energy, it can **it can** render very coating, which are free of voids, they can have very unique chemistry, they can also act as a good barrier films, and they can get deposited on any surface, and since it is utilizing again breaking the bond and utilizing radio frequency. The coatings which are produced they are sterile, so they can be directly used in any biomedical application, because they are already sterile in nature. So that is the advantage of radio frequency plasma deposition.

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The slide contains the following text and diagrams:

- Langmuir Blodgett Films
 - Highly ordered layer ✓
 - Polar head + non-polar region
 - High degree of order and uniformity ✓
 - Stability can be improved by cross-linking
- Self Assembled Monolayers
 - Spontaneously form as high order structures
 - Strong exothermic adsorption of anchoring chemical group → provides surface filling
 - Vander Waal attraction of alkyl chains due to close proximity → crystallization of alkyl chains
 - Good chemical stability ✓

Handwritten diagrams include:

- A schematic of a Langmuir-Blodgett film showing a substrate, a monolayer, and a second monolayer being transferred.
- A diagram of a self-assembled monolayer (SAM) showing molecules with polar heads and non-polar tails.
- A circled note: "Good chemical stability" ✓

Now there are certain kind of films, which are called Langmuir-Blodgett films, so in this case this basically form they are very highly highly ordered layer, so in this case, we introduced a particular a particular fluid, then we deposit certain species to it, and they tend to arrange very systematically on the top surface of it, but in this case, we need to keep the concentration of this particular species, much below below to that of a missile concentration; if it is above the missile concentration, then they go on they go to tend they tend to form missiles, it means that all the polar head groups will combine as one and the other hydrophilic tails will basically we rotating out.

So in order to maintain this particular geometries that they are aligned equispaced with each other, we need to to keep the concentration very, very low; and in process what we can do? If we have some sort of a barrier layer and we start pushing this particular regime, we can control the overall distance between the chains, and in process we can also control the porosity; thus porosity is nothing but the distance or the gap between the two, so if we somehow compress them we can reduce the porosity between them, and since it is nothing but the electrostatic attraction, we can electrostatic attraction, they will tend to organize very near to each other.

So that is the that is the reason it might imparted very high degree of uniformity, so we can see that Langmuir-Blodgett films, they have polar head, and they have a non-polar head, so polar head is basically out here, and non-polar head is sitting on the top; and again it provide a high degree of order and uniformity, and again stability can be improved by cross-linking; if you somehow cross link them, cross-link all these chains with each other, we can improve its stability; and if you want to coat it what we will do is we will just start pressing it and we start lifting its particular substrate. So in the process all this heads will start getting deposited, so we will have this head, this will start sitting on to it surface; so we start just compressing it, and lifting it, so that in process you can get a coating on this particular substrate, so we just have this substrate, and this is the overall coating, which will form on the particular substrate.

So Langmuir-Blodgett films, they are highly ordered layers, they are polar heads plus non-polar regions, they have they they can render very high degree of order in uniformity, and if you want to further improve its stability, we may just cross-link all of them, and then it will result a very stable Langmuir-Blodgett film. There is also called something called self assembled monolayers, and this monolayers they gets

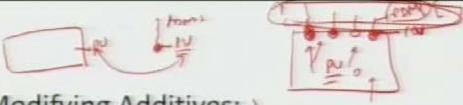
spontaneously form as very high order structures; they have very strong **strong** exothermic adsorption, once they get start anchoring, and that provides the surface filling, because they make the surface very, very stable, so as soon as the particular entity comes and sits, it will release certain heat, and this exothermic adsorption will now make then very, very stable.

Again there is second order of attraction that is called Vander Waal attraction between **those between** all those alkyl chains; and as soon as I start coming together, it is better they have some sort of attraction, and that makes them organized very strongly or very nicely and very nicely spaced and provide crystallinity as well. So we can **we can** also get very good crystallinity, if they have a very good Vander Waal attraction which is existent between those particular chains, so they can provide very good chemical stability as well.

So in the self assembled monolayer, it is more **more** or less **more or less** a chemical reaction what is happening on the surface, and they form they tend to form very high ordered structures, because they can excite, they can basically give out certain heat or exothermic adsorption. So once the anchor they release much energy, and they can become much more stable; secondly the chains, they themselves can have some sort of Vander Waal attraction of alkyl chains, and that brings then to much closer proximity, and leads to the overall nice arrangement or the or induces the crystallinity of the alkyl chains.

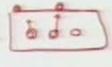
So, once they have good interaction between them, they can organize very nicely in very nice fashion, and it will lead **lead** to the crystallization of the alkyl chains, and in the process, it can give it out very good chemical stability, both because of chemical bonding and secondly because of the Vander Waal attraction force, which is predominated between the alkyl chains.

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• Surface Modifying Additives:

- Added in low concentrations in bulk to emerge at surface
- Mobility of additive in bulk decides rate of covering surface
- Interfacial energy with additive must be higher so the additive can be mobilized to reach surface
- e.g. PU (polyurethane) and PDMS (poly dimethyl siloxane) inserted in PU block will bring PDMS on surface.



In the second category of the surface coating or inducing thin films, we have something called surface modifying additives. So in this case, we add low concentration of this particular material in bulk, which now emergency at the surface; so such as in just given example, if you take a polyurethane matrix bulk, and we have certain chains which have polyurethane head and PDMS chain group, so we have polyurethane of head this material also is polyurethane.

So if you induce this particular material into the polyurethane matrix, we can expect polyurethane to have good compatibility with itself polyurethane; whereas, PDMS finds more suitability is it is now being hanging outside in the air or with certain entity. We can see either it can get merge out here, so this is nothing but PDMS **sorry** this one is polyurethane, which is the head groups of polyurethane and the tail groups are PDMS which are just basically hanging out of the polyurethane phase.

So now it can impart **hydrophilic** hydrophobicity to this **(())** surface, so we can see polyurethane it can now impart very high degree of **very high degree of** hydrophobicity on the surface; so in this case, we can see we are adding PDMS in very low quantity in bulk, which now automatically emerges at the top or the surface, because now p **(())** very high of a polyurethane, then process it have try to go to the surface, and now form surface with either air or the fluid around it. So in that case, it will try to reduce the

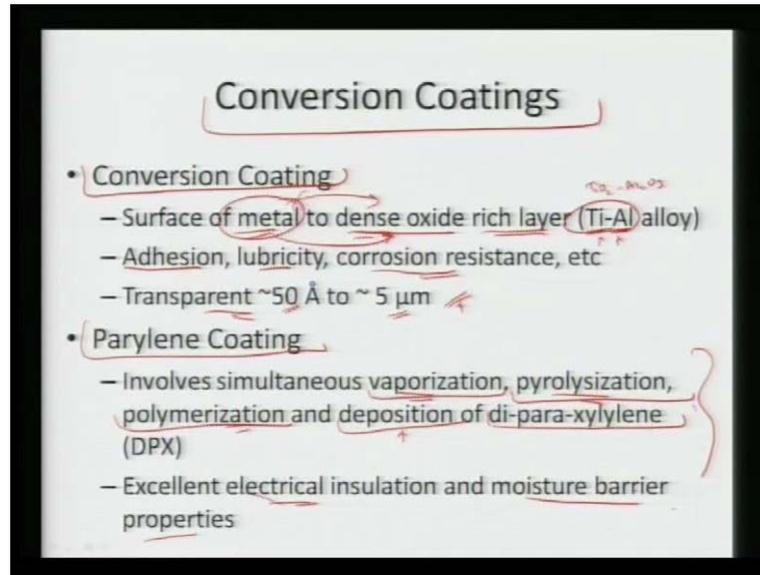
interfacial energy, and then the process it will also imparted in functionality to **to** the surface.

And the mobility of additive in the bulk is decided by the overall rate of covering the surface and also the interfacial energy regime, which is predominant between the polyurethane and the PDMS and PDMS and the outside environment, and again the interfacial energy with additive, must be higher. If it is not higher, then it will basically remain in the bulk, and it will not come to the surface, so that the additive can be mobilized to reach the surface so in the particular example, we are seen that polyurethane and PDMS, once they are inserted in a PU block will bring PDMS on the surface.

So in the surface modifying additives, we add particular entity in a **low** lower concentration in bulk, and in process it **it** the overall interfacial energy of the additive must be higher, so that it can be mobilized to reach the surface and imparts it in functionality and the mobility of additive in bulk, that decides the overall rate of covering or coverage of the surface; if mobility additive is very, very poor, the overall entire surface may not get covered properly.

So mobility of this particular entity is very, very slow it might happen that only a few will lead to reach the surface, and that is it **it** will not cover the surface, but if the mobility of this particular additive is very, very high, then only it will be able to cover the entire surface completely, and that interfacial energy with the additive must be higher, so that the overall additive can be mobilized nicely and then it can cover the entire surface and impart certain functionality to the surface. A good example is polyurethane and PDMS combination, once it is being inserted into the polyurethane block; it will bring the PDMS on the surface, and will cover the entire surface.

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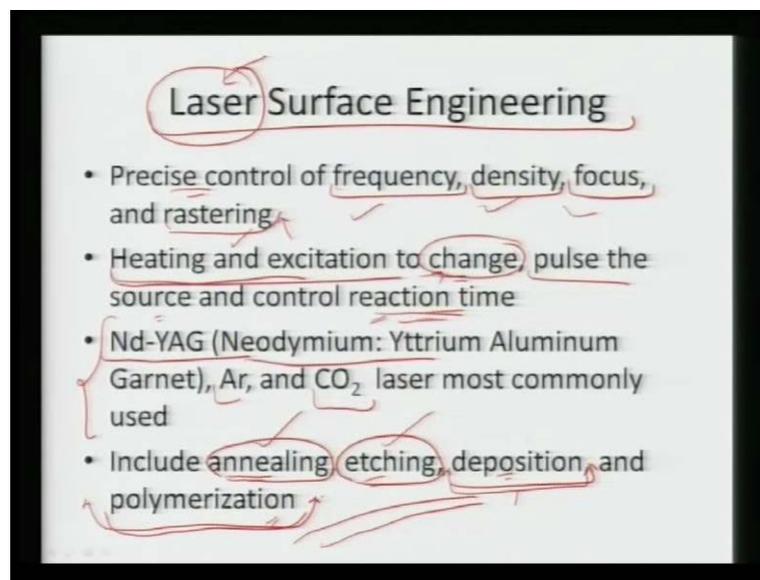
Again there are some class of coatings, which are called conversion coatings; and in conversion coatings, we can somehow introduce the we can somehow oxidize the surface layer, and the surface layer of a metal, and we oxidize it and form a oxide rich layer such as such examples are titanium and aluminum, which we start oxidizing them, we we can form TiO_2 or Al_2O_3 , and now these particular entities are very good in terms inducing either adhesion, introducing lubricity or providing corrosion resistance and these coatings are generally transparent once very, very thin up to 50 angstrom, they can be even made thicker, so up to even 5 micrometer, but as soon as we start increasing the thickness, it start it can even get damage or because of the stresses, which are induce between the self substrate and the generated coating, but in both the cases titanium and aluminum, this coatings are pretty thin, and they were adherent to the substrate surface.

So we can see in conversion coating, we let metal surface to get oxidized, so we form a very dense oxide, and dense oxide will acts as more like a barrier, and it it impart the resistance to the substrate material, it it can also induce some lubricity by in this particular manner, it can also induce some sort of a adhesion, and this coatings are generally transparent, when there are they can be even between fifty angstroms or 5 nanometer to 5 micrometer end thickness.

Then there is a last class of coatings, which is called parylene coatings, and these are more more or less like very good insulating coatings, and moisture barrier they have very

good moisture barrier properties as well. What parylene coating involves is it involves simultaneous vaporization, pyrolyzation and polymerization, and then deposition of this di-para-xylene; so we have this di-para-xylene, we do simultaneous vaporization, its pyrolyzation and its polymerization to finally deposit this particular coating, which are called parylene coatings, and they possess very good electrical insulation as well as good moisture barrier properties. So then so these are basically certain chemical coatings which are required to get the **to** which are basically deposited on the surface of a particular biomaterial or a device material.

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And again there is something called laser surface engineering; it utilizes laser light amplification by stimulated emission of radiation. So we utilize laser for somehow engineering the surface, and the advantage of laser is we can precisely control the overall frequency, the density, the focusing, and even the rastering; so we can select the particular regime with particular energy with particular density with **with** a particular focus to impart certain **functional** functionality to the surface.

So we can precisely control all these parameters of what all sort of energy we want to introduce, what all density we want to impact, whether it should be focused or defocused or even how do raster or **or** form certain geometries or certain surface... we can form certain surface contours to on this particular surface for providing certain functionality,

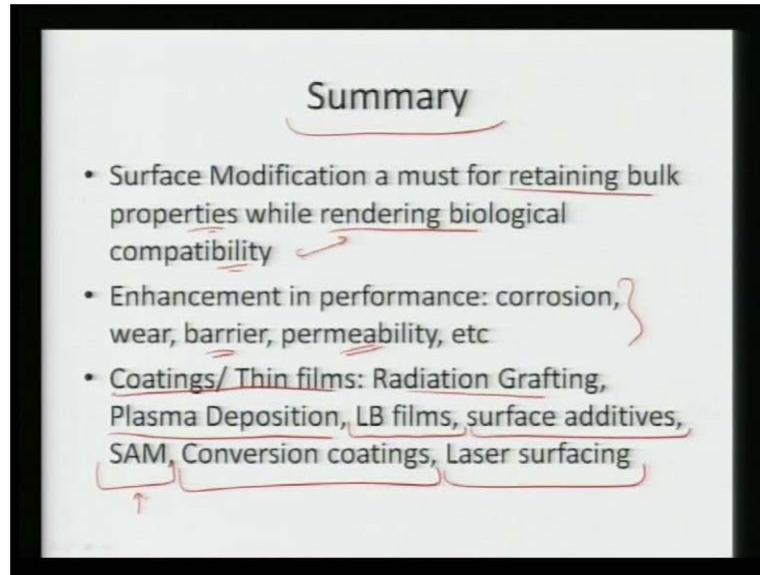
and again heating and excitation can utilize to change, we can pulse the source and control the reaction time.

So, we can we can provide certain heating and excitation for changing the chemistry, we can also pulse the source and control the reaction time, so we can precisely see in what time this particular reaction will go to completion. So what all chemistry is we want to retain on the surface, and what sort of functionality we want to provide to the surface; there are certain results which are very, very common, which are Neodymium-YAG which is called Yttrium Aluminum and Garnet laser, argon laser and CO 2 laser, and which are basically very commonly used; they also include they include annealing, etching, deposition and polymerization.

So, we can utilize laser for either annealing the surface, etching the surface out; so by etching we can provide certain contours and geometries to the particular material, we can also deposit certain materials or certain chemicals on the surface of the substrate. We can also induce cross-linking or polymerization by utilizing a lasers, so laser surface engineering has emerged as the **as a** wide tool in terms of precisely controlling the frequency, density, focus and restoring; so in **in** that particular manner, we can provide heating and excitation to the material for either changing the chemistry or controlling the chemistry for providing a particular reaction time.

So, we can exactly control the overall chemicals, which will be basically being retained on the surface or the kind of reaction, which should **which should be we should which we should should** be able to control so the overall reaction time can be controlled, a degree of reaction can also be controlled by properly engineering the laser surface by using by engineering the laser; and the certain lasers, which are very, very common neodymium, yttrium, aluminum, garnet, aluminum and CO 2 laser, carbon dioxide and they include all **all** the sort of things, we can now anneal the surface to remove the certain surface stresses, we can etch the surface to provide much more physical area to enhance the activity by **by** providing certain roughness to it, we can do deposition, so we can provide any coating or any sort of surface action to it, and then we can polymerize the surface or we can also induce cross-linking.

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So, in summary we can see that the overall surface modification, it becomes a must for retaining the bulk properties, while rendering certain biological compatibility. So surface modification is highly essential, because we want to retain the bulk properties or the bulk mechanical and the functional properties, but rendering the surface or the biological compatibility becomes essential, so we provide with a thin film coating or a grafting to improve the interaction of this particular device or implant material with the surrounding tissues or environment.

So, in process we are enhancing the performance of this particular device of the implant material, it can be in terms of wear corrosion, we can impart coatings of diamond, we can impart certain coatings - barrier coatings to improve the wear and corrosion resistance, we can also induce certain barrier performance, we can **we can** have some barrier layers, we can enhance the blood compatibility, we can also induce the permeability such as in homeodialysis we want the option to go through, but again the surface has to remain corrosion resistance, so we can **we can** impart certain functionality or improve the performance by incorporating the surface coating thin films and grafting.

Again, we can provide this coatings or thin films by technique such as radiation grafting. So we can either utilized cobalt 60 UV radiation or electron beam radiation to control the overall structure, we can clean the surface, we can sterile the surface or we can also do the deposition, utilizing all this techniques, we also have plasma deposition also called

the glow discharge technique. We **we** can also utilize Langmuir-Blodgett films, we can add surface additives which **which** are incorporated into the bulk of the material, and they tend to come on the surface, because of the mobility of this particular additive; since the energy the interface energy of this additive is much higher with the **with with the** bulk material. So it can have certain mobility, and it can come on the surface and impart certain functionality, then we have self assembled monolayers, we can also have conversion coatings, and we can also have laser surfacing.

So in the process, we are allowing the chemical species to come, interact the surface and provide very good bonding, while also inducing some sort of a interaction electrostatic interaction between the chains to stabilize the surface coatings, and make it very, very stable, we can have convergent coatings in which we can allow the oxidation of the surface metallic surface, and an induced much more corrosion resistance or barrier nature of the film, even up impart lubricity, and again we can have surfacing laser surfacing or laser engineering to coat the particular **to coat a particular** surface and somehow control the cross-linking or polymerization of the surface, and retain or provide certain gradient in terms of the overall functionality. It can be hydrophobicity, hydrophilicity or even certain barrier nature corrosion resistance even deposition of the films. So in the process, we realize that how important is the surface coating or thin films or grafting to impart the interaction between the device an implant material with the surrounding body, without hampering the overall mechanical functionality of the device or the implant material; thank you.