Nanostructures and Nano Materials: Characterization and Properties

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Lecture - 30
Self Assembly

In this lecture will learn about self assembly. It is nothing but organization of structure to form a high level structure. So, how do we do that? Will see upon this particular lecture.

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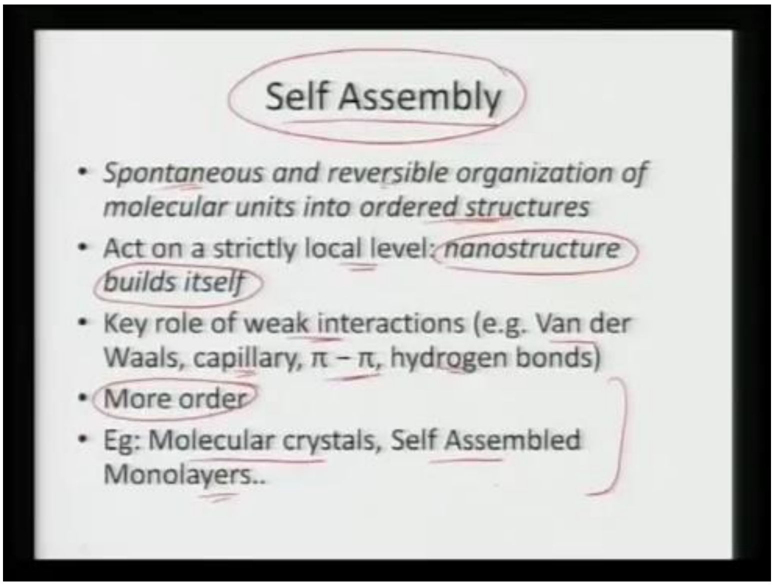

Self Assembly

- *Spontaneous and reversible organization of molecular units into ordered structures*
- Act on a strictly local level: *nanostructure builds itself*
- Key role of weak interactions (e.g. Van der Waals, capillary, π – π, hydrogen bonds)
- More order
- Eg: Molecular crystals, Self Assembled Monolayers..

So, we can see self assembly is nothing but spontaneous and reversible organization of molecular units into some ordered structures. So, there is some order which basically is incurred by these particular entities molecular entities, which is very spontaneous in nature and it is also reversible as well. Since it spontaneous and reversible, it also it is on a very localized level. So, in this case we are building nano structure, and it starts constructing itself or it builds itself. So, we see molecular units molecular units, they go on to forming certain organizations and it is self similar, it starts contracting itself.

The same time there is there is a key role of weak interactions, so weak interactions such as van der wall forces capillary action capillary forces or pi pi bonds or the hydrogen bonds. They tend to also provide secondary stability to the particular to particular organization to get high level of order and eventually goes on to forming such as molecular crystals, self assembled monolayer's and many other. So, we can see self assembly is nothing but spontaneous and reversible organization of structures in molecular units to form little bigger structure.

These are self sustaining and it means that it is constructing itself as it as the process goes on. There is very much key role of weak forces van der walls, hydrogen bonds capillary forces because they also tend to provide certain stability to the nano structure and it eventually goes on to forming more ordered structure such as molecular crystals self assembled and monolayer's and so on.

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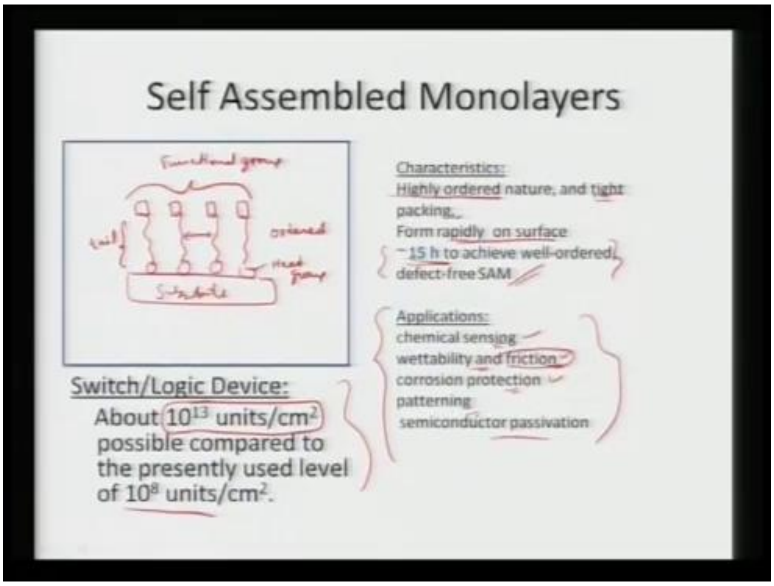

Self Assembled Monolayers

Characteristics:
Highly ordered nature, and tight packing.
Form rapidly on surface
~15 h to achieve well-ordered, defect-free SAM

Applications:
chemical sensing
wettability and friction
corrosion protection
patterning
semiconductor passivation

Switch/Logic Device:
About 10^{13} units/cm^2 possible compared to the presently used level of 10^8 units/cm^2.

So, seeing that self assembled monolayer's first of all they have highly ordered structures they are nature is highly ordered and it provides very tight packing and it forms very rapidly on the surface. To attain a particular order, it that is the time consuming step or that is the step decide the rate deciding step.

It may require up to fifteen hours to achieve a well ordered and a defect free self assembled monolayer its applications involve chemical sensing wet ability controlling friction corrosion protection even pattering or even semiconductor passivating. So, we can see that in self assembled monolayer we have substrate and that substrate is covered with certain head groups and which is a tail region. They go on to form becoming much more ordered, and they might have certain function grow on the top of their chain to order a to render a certain functionality.

So, we can see that this nothing but some sort of a functional grow, so we have a substrate over that we tend to deposit certain head groups that will attached itself to the substrate when it has, it has a tail region. It is the tail region, and then that tail is covered with again with certain functional group to impart certain functionality. So, we can that they are much more ordered in nature that they have very nicely ordered and that tightly packed. Also, they can form very rapidly on the surface, but to organize them into very ordered structure, it require much time because they have come.

Then, basically confirm to the forces which are acting a rounded to render a very ordered and a defect free self assembled monolayer. You can see that for switch or logic devices we need many functional units on the surface currently we had around 10 to power 8 units which are there on a per centimeter square area. Depending on this conformation, it can go 10 to power 13 units per centimeter square, so we have a possibility of increasing this number of this density of these functional changes by order of 10 to power 5. So, that is a logic we are talking about we can enhance it by 10 to power 5 times of 1 lakh times to render a certain density to this material and impact much more functionality to even logic devices or switch devices.

Their application also includes chemical sensing because if you have more number of such patterned surface on a on a particular substrate, then we can sense a particulars gas or a media or any chemical functionality to a very to very high level. So, we can even when there is a very small p p of a particular gas or chemical, we can sense it also utilize for either increase in the wettability or reducing the wettability for controlling friction.

If we can impact certain layers, which are much more resistance which can provide us lubrication or non reducing property, we can also provide corrosion protection to a surface we can have certain patterned structures. So, if we have certain functionality and that functional groups will come the hydro's will come and certain region. Then, we can achieve functionality to those functional groups by this particular mono layers and also require it can be utilized for passivating the semiconducting surfaces.

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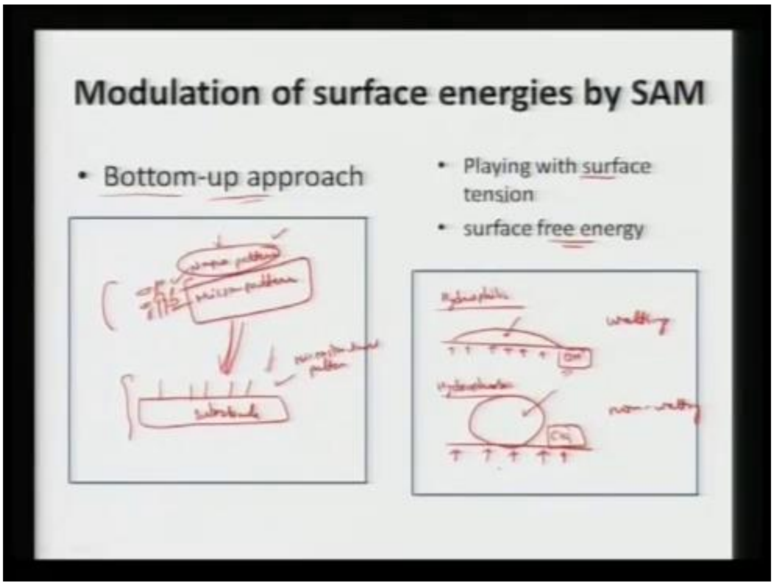

Modulation of surface energies by SAM

- Bottom-up approach

- Playing with surface tension
- surface free energy

So, again there can be two approaches first of all bottom up approach or the top down approach, but the overall idea in the bottom approach is we control something at a molecular level. Then, say if you have certain molecular level then we can apart certain micro structural pattern to it. Then, that micro structural pattern can again has certain nano structure pattern, so we have nano pattern over a micro pattern. So, we have substrate then we have micro structural pattern over it and this is a nano pattern, so if we are starting from a nano pattern, then we go on constructing a micro pattern.

Then, we deposit this micro pattern on a substrate, then we can basically we are going form a bottom approach. It means we are going we are combining couple of functional units molecular units go on to follow certain nano structures nano structures go on to forming a little higher level of micro pattern.

Then, that eventually getting deposit on a substrate this is useful in impacting certain functionality to do a material. So, if we have this sort of scalability or length scale associated with that, we basically going from nano structure from molecular structure to nanostructure to micro structure to impact certain functionality that is nothing but, bottom up approach. How can we utilize them? We play either with surface tension or the surface free energy.

So, in these case if we play with the functional group we can provide either complete writing so we can provide much more wetting to the surface or we can also provide non wetting those surface. So, if we can control the functional groups to be coming out to be yes say o h minus there renders very high affinity for water. Now, we make the mega surface hydrophilic in nature, but in another case, if you take if you take methyl grow then methyl grow try to repeal and because of that it can reduce much more non wetting or hydrophobicity. It will say that methyl a methyl can have hydro hydrophobic nature and that this alcohol OH minus can have much more hydrophobicity.

So, we can somehow we can if you are playing with the surface tension or surface energy we can we can impart a very different functionality of the surface. So, bulk is same, but only because of the functional unit, if it is alcohol group it will have much more hydro velocity. If it is methyl group, it can have much more hydrophobicity, so by playing with surface energy or the surface tension, we can somehow impart very different contrasting characteristic to a substrate. The substrate is the same, but only because its surface we can control the overall functionality of this particular surface or substrate.

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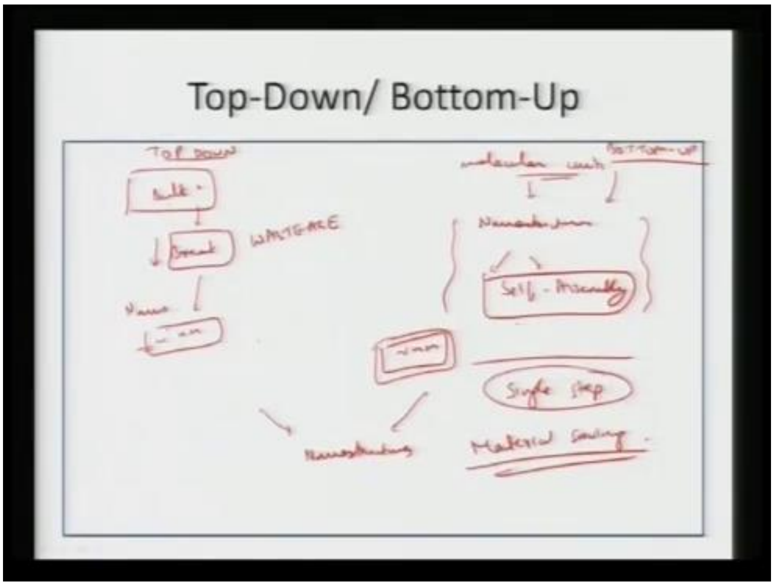

Top-Down/ Bottom-Up

So, we can again go by either top down approach or a bottom approach, so in top down we take a bulk and we start fracturing it until we reach nano. So, in this case, we are trying to break up the material, we break the material, so achieve a finally, nano structure which are approximately couple of nano meters and dimension. On the other hand, if you go from molecular units if we have molecular units they go on to forming certain nano structures, and this can be achieved by imparting self assembly. Now, we can get from molecular units, we can get microstructure and one unit, in this case we are breaking the material.

So, this much more wastage of material, but in this case, we achieve everything in single step because of the self assembly, so in the process what we are doing we are saving the material as well. So, in this case again we are able to reach couple of nano meter, but we are starting from molecular units which are sub sub nano meter in nature. Then, because of self assembly, we can get a structure, which are couple of nano meter, so what we are doing the final product is a same that we are achieving certain nano structures, but one is this is the top down approach, and this is a bottom up approach. We can say in top down approach, we take a bulk material, which is which is very big in size.

It can be couple of meters to that level and basically we are just breaking the structure and in the process finally get which is the nano entity, but in bottom approach, we go from molecular units will allow it to self assemble. Then, we get a final nano structure that is again nano meter is size is a single step, so we basically kind of saving the material because we are starting from entity which smaller than a nano meter. This gives us the advantage that we can also somehow control the overall assembly of this particular system from molecular units to a bigger structure.

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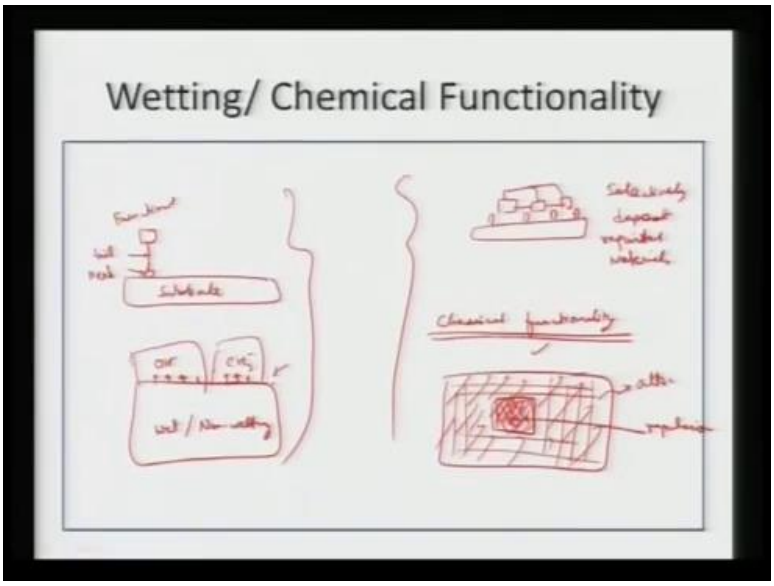

Wetting/ Chemical Functionality

So, we can see first of all we have a head group which is lying on a substrate, so we have a substrate, then we have a head group with certain tail and then a functional group. So, we have head this is a tail, this is also called as spacer, so depending on the length of this tail, we can somehow control the how this structure will come out to be, so in one case we can make the surface highly wetting or non wetting.

So, we can make either wet or non wetting surfaces just by controlling if it is alcohol or if it is methyl, so if we can somehow control this particular part we can control the major of wetting or non wetting. At the same time, what we can do? We can also play with the chemical functionality, so this case we can make it physically either attracted to water or repellent to water.

We can also make it make it sure, we can also utilize the certain chemical we can also utilize chemical functionality to impart certain characteristics to a material. So, we can somehow impart some chemical affinity only to a specified region a not to the remaining region that might be required in certain cases because in case we want to dual functionality. In one case, we might require its attraction with something in another case we might require its repulsion. So, we can chemical functionality we can achieve we can achieve duality or dual functionality from this particular arrangement, so we can see we can see that we can achieve this chemical functionality.

So, we can get either a deposition, so this particular layer is good for deposition of one entity and not for the second entity. So we can apply some sort of resist. So, this will not allow any entity to grown on to it where as other portion will allow the growth of the secondary unit and this might be required for constructing say certain chips or certain electronic circuits. So, in that part this functionality will be very useful. So, in certain cases we want to build up structure which goes a height.

We might require deposition along certain areas and not a long other areas and later we can go upon making something else over it and then somehow joining those series or a parallel or it can be any particular structure. So, this chemical functionality is very good because that will allows to selective selectively deposit required materials, so that is the advantage of controlling the chemical functionality or even controlling the wetting. So, it can allow us to achieve very low friction or to resist that deposition of water or any humidity on those surfaces of the electronic components when it is very high in the atmosphere. So, that is the advantage of this particular thing and depending on the spacer we can also somehow control overall nature of this self assembly.

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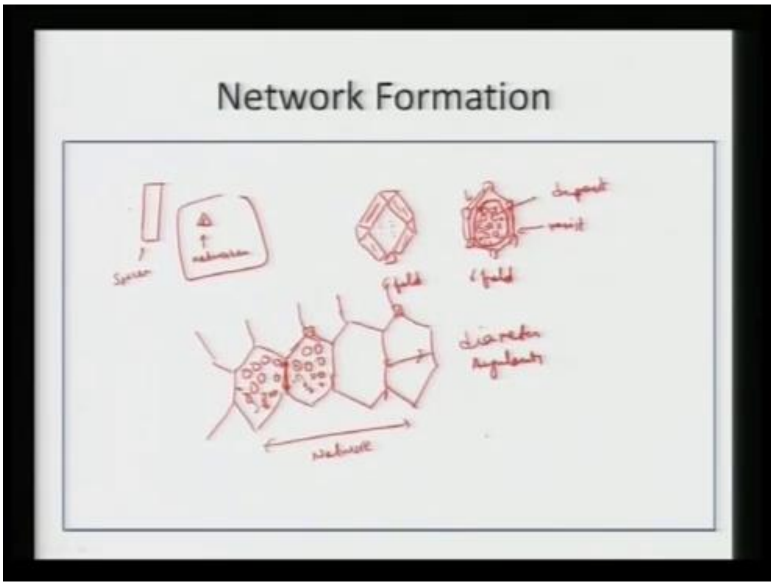

Network Formation

So, if we have this tail groups, a tail group is like this and then we have a functional unit which is basically trying to form the network. So, we have some something called a spacer, and then this is nothing but some sort of a joining or network networker. So, assembly of this one will lead to, so we can achieve certain structures, so we can achieve certain structures if the way we want it to or we can also get some other sort of structures depending on the our networker. If it requires a 6 fold 4 fold and so on, so we can get many different type of variety of these structures. So, the spacer width and height that will very critical, so that will decide what is the overall region which is available for us for deposition.

So, in one case we can have some sort of resist, this one can be resist, now we have certain region which is available for deposition. In this case, we can control the deposits, so once you are depositing something we can achieve which is called deposit, which is getting deposited on to this particular available region, and now this functionality. So, we have some sort of resist, now we getting deposit and this is now forming a structure within this particular pore. So, we have seen that somehow we are able to this is a nothing but network formation, so we are forming some sort of a network. So, depending on that, we can achieve a very nice arrangement of a, we can achieve a very nice network a how to here it can it can be self consistence or self propagating.

So, we can what we can get once we start another process. It can allow deposition only along this particular region and because its confined nature, we can control the overall diameter of this one also the angularity can also be controlled depending on this our network functional group. So, depending on that, it will provide the overall angle to it, and the length will be decided by the spacer or the tail group.

So, from that we can now achieve some sort of a network for which is required for the formation of nano structure. Now, depending on that we can also control the port if we control the overall the length of our spacer or the tail group, we can also control how thin or what will be the overall radius of that particular pore which can from.

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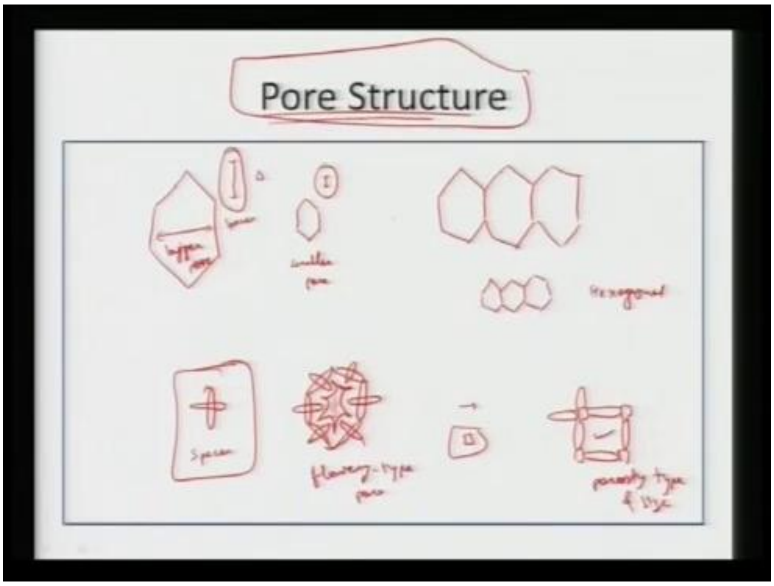

Pore Structure

If you have little longer space, we might get something like this, but if we restrict our spacer, we can also get pore, which are much smaller size. In this case, we get very bigger pore in this case and then we can also get a smaller pore when we have A. So, we can keep over networker the same, but in this case our length your spacer s this much, but in this case our spacer length is only this much. So, accordingly we can somehow control how much is the spacer length, and then what is the structure figure? So, in these in one case we can get structure which is more like this, in another case we will get something like this.

At the same time, if we somehow can control the overall geometry of our spacer, then again we can control the pore structure. So, if you want to provide much more surface to the pore we might require the pore to be very tortuous, so in that case we might require a different geometry of our spacer. So, spacer can be more like this, so we can have a spacer which can be more like this, so in that case, what we will get? In that case, we will get more like this. Now, we can see, now we have pore which is much more flowery kind, so that that is part we can see, so just by changing the geometry of our spacer, we can somehow control.

So, in this case we had a hexagonal pore, very symmetric pore, in this case we get more of a flowery type pore, which can be obtained and again the thickness of the pore the diameter of this pore can be alter depending on the spacer geometry. So, we can see the networker is the same in this case, we can again change the networker, we can we can make it square or something like that, we can also attain structures which are like this. So, depending on our networker we can also change the porosity type and size. So, that is the overall combination of over spacer or the spacer has to be what the geometry of spacer is and what is the how the networker will fight into the picture to give a resulted pore.

To achieve certain functionality or in order to achieve that, we enhance surface. The pore the surface area of the pore in order to trap certain signals for it or to allow a growth of certain entity into it or provide certain geometry or contraction to the newly deposited structure in to the pore the control of very essential. That can be controlled by playing around with the geo networker or the spacer so that is the one which makes this assembly much more useful to us.

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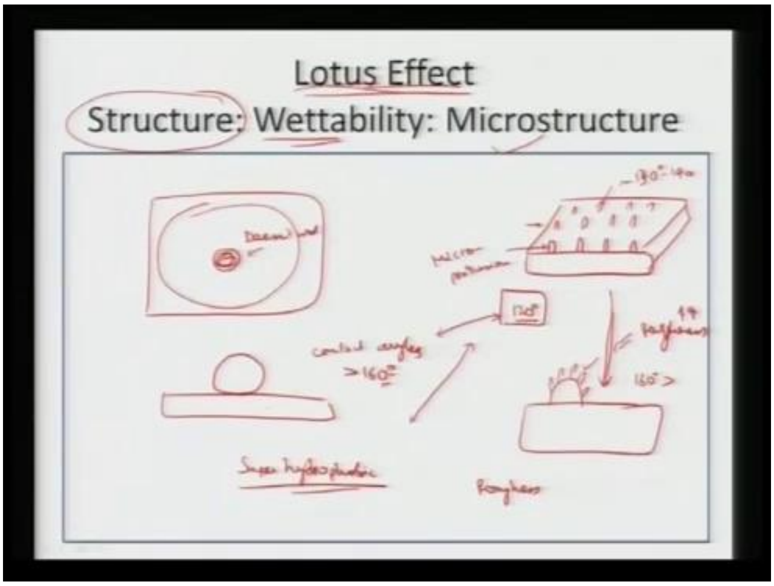

Lotus Effect

Structure: Wettability: Microstructure

Again, we can see in lotus effect is also controlled by the nanostructure, so we can see it can impact very high non wetting. So, wettability is one of the concern and that is governed by the microstructure. So, we can see if we have a lotus leaf if you if you lotus leaf and you drop out droplet of water if it sound to, it basically does not wet. So, we have the substrate of the lotus leaf, and then we have contact angels which are exceeding, which are exceeding around 160, 165 degrees. So, that makes the surface high super hydrophobic, so in this we have ah structure we have the overall lotus leave surface. Let us certain proto genus on the surface if you see the crosses ion of a, you will find there are certain micro pathogens, which are certain here and there.

So, these are nothing but micro pathogens generally the lotus leaves the non wetting on lotus leaf governed by the chemical composition or the epicuticular wax. This is present on the lotus leave surface, but it is apart from the non wetting nature of this epicuticular wax if had there be no roughness. So, the minimum surface energy of the surface will lead to a maximum contact angle of 120 degrees. So, maximum contact angle of only 120 degrees can be obtained if the surface as the least surface energy, but in lotus leaf we have seen contact angels in excess of 160 degrees. So, it means that chemistry of a surface is not in off on its own to govern the non wetting.

So, there has to be some extra feature which is governing the overall non wetting to increase the contact angle from 120 to 160 degrees. So, these micro pathogens are the first regions which basically enhance the wetting angle again contact angle, and then again there are certain nano hair, which are present on the reach of proto genus. Each of proto genuses will a certain nano hair, which is present on the surface so that in turn also increases the roughness back order of couple of times. This roughness is the one which either increases the wet wetting or non wetting depending on the inherent nature of the surface.

So, surface itself is non wetting non wetting, the degree of non wetting increases because of the micro roughness and then because of nano roughness and vice versa as well. If surface itself is hydrophilic in nature, it is water attracting the contact angel will go down drastically by adding roughness to it. So, roughness will either enhance wetting when inherent surface is itself is it is wet it is wetting characteristic or it will also increase non wetting. If the inherent surface is non wetting in nature, so because of that we have all the apparent contact angel is now increased because of our initial surface is epicuticular wax, it is hydrophilic in nature.

So, micro pathogens enhance this contact angle to a high degree, so it can go up to even a up to up to like 140 degrees and from there 130 to 140 degrees and then apparently the nano surface nano roughness enhances it further down to 160 degrees or higher than that. So, that is the overall role of nano structure, which are present on the surface of lotus to impact non wetting to lotus leave.

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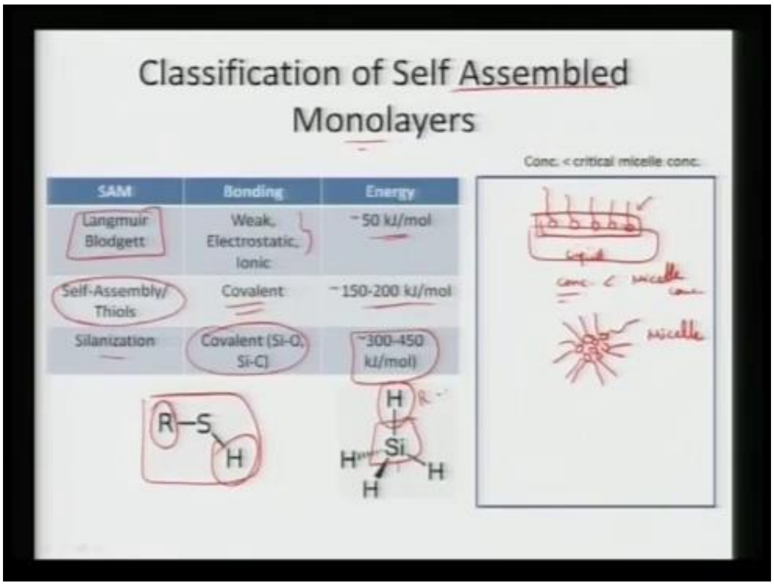

Classification of Self Assembled Monolayers

SAM	Bonding	Energy
Langmuir Blodgett	Weak, Electrostatic, Ionic	~50 kJ/mol
Self-Assembly/ Thiols	Covalent	~150-200 kJ/mol
Silanization	Covalent (Si-O, Si-C)	~300-450 kJ/mol)

Conc. < critical micelle conc.

There are then certain classes of self assembled mono layers, first we have Langmuir Blodgett films these are fond basically by the weak or electrostatic forces or certain ionic forces ionic bonding between the surface. Then, the film they have energy to the order of 50 kilo joule per mole a followed by thiols or they also called self assembled mono layers and they generally form covalent bonds. They have energy to the order of 150 to 200 kilo joule per mole, and then stalinization, which generally forms covalent bonds with silica, a silicon, a silicon oxide or silicon carbine. It has energy stability energy of or on 300 to 450 kilo joule per mole.

So, for Langmuir Blodgett we need to have a surface on which we have a tail group head group and then a tail group, which is basically head ring on to it, but again this tail group should have concentration. This can be again a liquid or it can be substrate, ideally the concentration of this particular entity the concentration of the film or the concentration of the secondary chemical should much less than that of a micelle concentration. So, concentration should be much lesser then micelle concentration, otherwise these all head groups will combine, and they will form a micelle concentration is very high, they will go on to forming a micelle structure.

So, this from a micelle when the concentration of this particular chemical much higher than the micelle concentration. So, the concentration of this particular entity or the Langmuir Blodgett will be the concentration of the chemical has to be much lesser than a micelle concentration. So, it can survive on a surface and get equally disturb dispersed to form a very regular or a structured layer on to the substrate. Then, again we have thiols this nothing but sulfur bonding with the functional group or the hydrogen at generally is a covalent bond with energy of 150 to 200 kilo joule per mole. Then, third one we have Stalinization or silicon, which is bonded with other 4 hydrogen atoms, so hydrogen atoms can again be replaced by certain functional groups later on.

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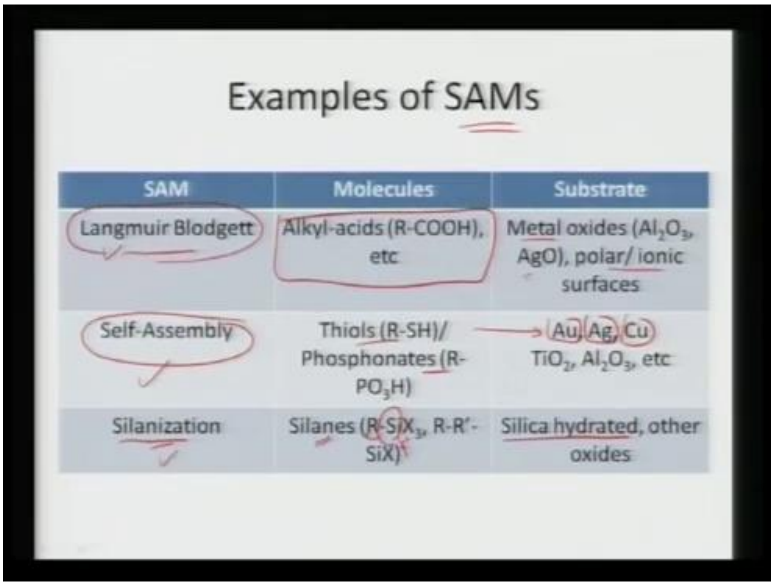

Examples of SAMs

SAM	Molecules	Substrate
Langmuir Blodgett	Alkyl-acids (R-COOH), etc	Metal oxides (Al_2O_3, AgO), polar/ ionic surfaces
Self-Assembly	Thiols (R-SH)/ Phosphonates (R-PO_3H)	Au, Ag, Cu TiO_2, Al_2O_3, etc
Silanization	Silanes (R-SiX_3, R-R'-SiX)	Silica hydrated, other oxides

So, we can see examples of self assembled monolayer’s, so we have Langmuir Blodgett, it generalize very prominent on the alkyl acids such as RCOH, it is predominant on metal oxide or polar or ionic surfaces, whereas thiols are self assembly. Self assembly retreated by thiol phrosphonates it has high affinity for materials such gold silver copper and so on and third is the Stalinization.

So, Stalinization is dominated by the silicon, so it has either functional group or some hydrogen or sanities which are available on the other site to complete four utilize for the silica hydrated or other oxides, it can form on silica hydrated or other oxides. So, we can see the three self assembled monolayer’s Langmuir Blodgett self assembly, which has nothing but thiols, and then Stalinization which can occur.

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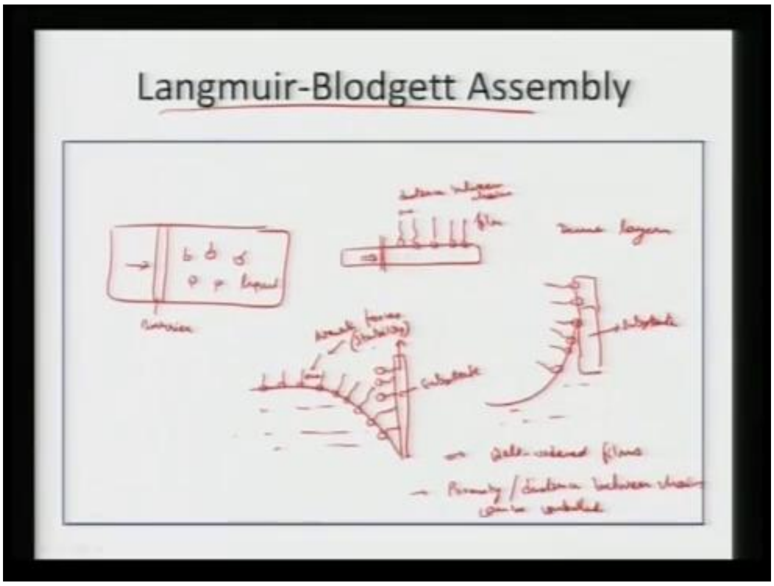

Langmuir-Blodgett Assembly

For the Langmuir Blodgett assembly, first of all we need to have concentration which is much below that concentration of the micelle. So, first thing is that we can first of all disperse this particular chemical, so we have some sort of a barrier which will not allow this. So, we have this head and tail group which are dispersed on to a liquid, and then we have some sort of barrier or traffilone barrier, which will not allow these particles come into. So, once you start quizzing it through, then these particular entities, they will start coming closer and closer and then they have, they will form like this, so we can see that there a certain molecules which are either amphiphilic or hydrophilic.

So, one entity will go on to this the particular fluid media, so we have film which is forming and then we start compressing it and a compression of this one will decide what is the distance between the chains. We can also do a secondary treatment, we can also somehow compress it, once we compress it, we can form very dense layers. If you want to coat it on certain entity, so we can somehow take it something like this we can let this molecules come like this, and then we can put our substrate out here and then we start pulling it up.

So, in the process if is if will start lifting at a, then what we get is deposition of all these entities on the surface of this particular substrate. We can also make it go like this to finally, deposited on to its surface in a process, we can deposit them, so we can see that we can deposit either the hydrophilic hydrophobic and to the substrate this is nothing but substrate, now what we are getting? We are getting very ordered cell, ordered cell which are basically getting deposited on to that, and these the overall substrate can also the films can also be controlled.

So, we can see that porosity or the distance between chains can be controlled. Now, the control of pore city is very critical in this particular aspect because that will decide what all chemicals what all chemicals can be can permitted through this particular. So, if you want to impact functionality that only hydrogen should be able pass through or only oxygen should be pass through or at only certain entities can pass through, we can control the overall porosity of this Langmuir Blodgett films. So, that can be detected by compressing or by applying low pressure lower compaction so that the tail all the chains are partially packed. So, in that case we can control the density of these particular amphiphilic or the hydrophilic entities all this change on a particular substrate.

So, that gives us a control that we can utilize this Langmuir Blodgett assembly to somehow play with the nature and the density of this particular film and impart particular permeability of to all this films. Again, the stability of this one this particular chain is also detected by the overall the hydrogen bonds or the van der wall forces. So, the weak forces also dictate the stability of films, so weak forces detect the stability of this film or the Langmuir Blodgett assembly to a provide much more or stability or ordered nature to the films.

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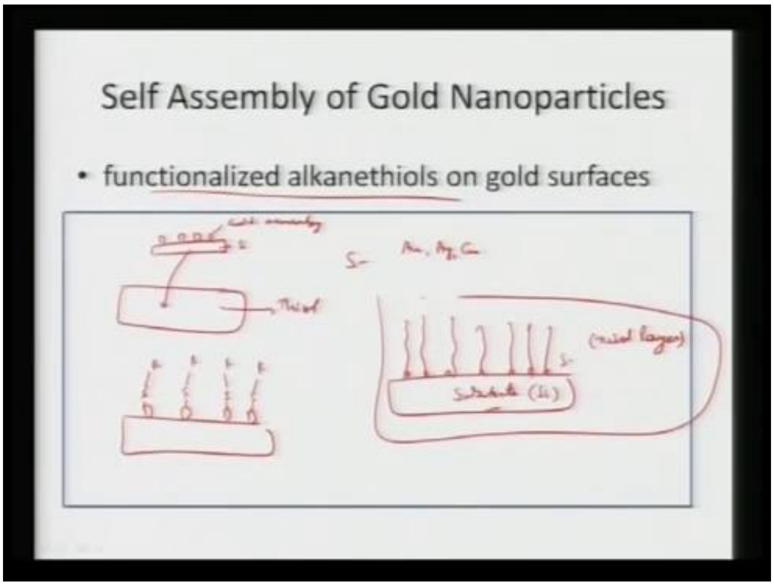

Self Assembly of Gold Nanoparticles

- functionalized alkanethiols on gold surfaces

The second part can again of self assembly, it can again be attained by this thiols, so we can get functionalized alkanethiols on the gold surfaces. So, we can have a solution, which is thiol solution and this sulfur group has high affinity for the noble materials such as gold silver copper and so on. Once we impart, if we can make certain structure, so we can electro deposit gold certain pattern of gold. So, we have silicon layer and over that we can provide certain construction of gold assembly by other spattering or any other technique and then deposit this structure into thiols solution. So, what we get a finally, is a certain structure of gold which is now thiol attached to it with certain functional group.

Now, eventually what we are getting we are getting a substrate is nothing but our silica silicon and then we have very nicely layered structure of thiol layer. So, we can get a very good monolayer, so we can get a self assembled self assembly of this particular structure or thiol on a gold on a silicon substrate, which again certain deposition of gold on the substrate. So, we can we can attain the self assembly by allowing the particular pattern deposition of gold on a silicon surface silicon surface.

Then, once we deposit that particular surface of silicon which has now gold in a certain pattern that particular pattern zone of gold will not attract the thiol group and thiol group with certain with certain functionality to it any carbonations change. It will now get attached to the gold particle to give monolayer of that particular chain, so in this particular case, now we are getting a self assembly of the sulfur on this particular chain.

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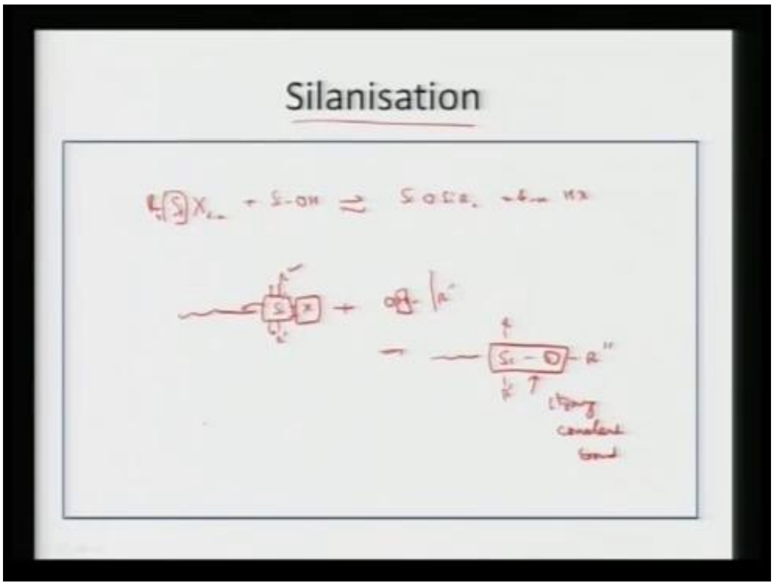

Silanisation

In Stalinization we utilizing particular functional group, so we have a some r and that is that is combined either hydrogen or ethanol, so we have to satisfy valiancy. So, for it is particularity and this will be four minus that particular ion and then what we are attaining silicon h x. So, essentially what is happening? We have chain, so we have silicon group, so if you have r here r here and say x here, and then we have OH, and then we have certain functional group. So, in this case we are moving this function not here, so what we are getting finally is a combination of silicon or oxygen and then r dash. Essentially, what we are getting? We are getting a strong covalent bond, so in this case that is that is what we are graying we have a functional group of r functional group of r dash.

Then, it combines to the third functional group of maybe say r double dash, so in that case we are getting we can get a certain very strong covalent bond of silicon with oxygen. Then, that can result a very strong a attachment of that particular silicon surface but, a problem with silicon is that has four arms. One arm has to go here, second arm here, third arm here, fourth arm here, so we can get four ordered kind of entity out here.

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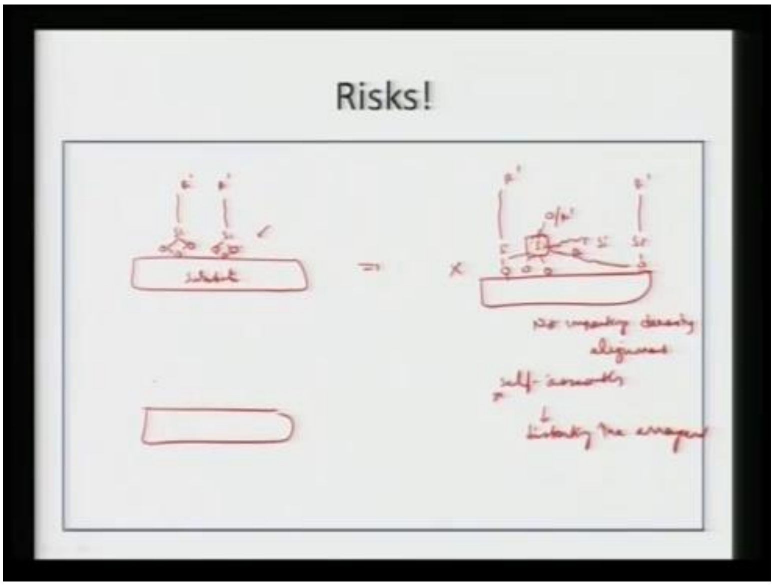

Risks!

So, the overall problem here basically occurs that we can ideally we should get a structure which is more like this, so we have substrate. Then, we should get three combination of silicon with say one oxygen, third one should has some r dash sort of a chain. So, we can get this structure oxygen and then some sort of r dash, but the problem that can happen is that instead combining the one oxygen here, it can break up. That break up that chain and instead it can combine with r dash out here, so it will lead to a chain, which is in another direction and not in the top direction. So, we can see oxygen it can have r on this side, and then it can again have oxygen or r on this side.

So, essentially we are getting a chain, which is now not a line to the other chains, but to some other to a different, so we can have r dash silicon oxygen r dash, but there certain other chain, which are now going in different directions. So, it is not imparting a much density or alignment, so the overall assembly the self assembly is now not distorting the arrangement. So, it is not a self assembly because it is not assembling on its own, so that can be problem associated with the silence. So, we can see that they have very strong bonding with the oxygen because of it because it is a covalent bond. So, it can give very strong alignment very strong deposition of all this particular entities.

So, we have oxygen, oxygen, oxygen and then we can have silicon which can combine with that. Then, it can impact r dash or some other entity, which is which it can provide a very nice layer but, it can also lead to a problem of distracting the overall geometry and then fracturing the overall concept of self assembly in this particular case.

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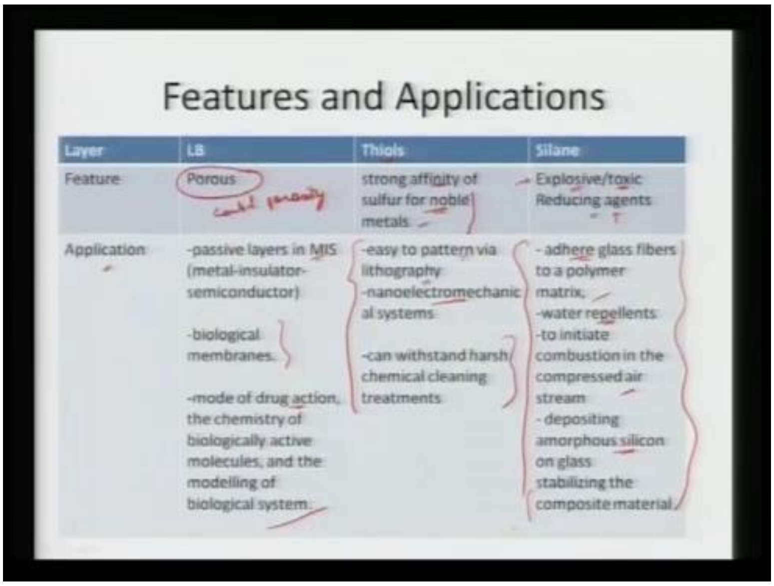

Features and Applications

Layer	LB	Thiols	Silane
Feature	Porous contl porosity	strong affinity of sulfur for noble metals	Explosive/toxic Reducing agents
Application	-passive layers in MIS (metal-insulator-semiconductor) -biological membranes. -mode of drug action, the chemistry of biologically active molecules, and the modelling of biological system.	-easy to pattern via lithography -nanoelectromechanical systems -can withstand harsh chemical cleaning treatments	- adhere glass fibers to a polymer matrix, -water repellents -to initiate combustion in the compressed air stream - depositing amorphous silicon on glass stabilizing the composite material

So, in comparison we can see Langmuir Blodgett films, they can be porous, so we can also control the porosity depending on the structure kind of pressure or the kind of structure we use as thiols. They have very strong affinity for sulfur for noble materials, so sulfur has a very high high affinity for noble metals. So, we can deposit on a gold copper or silver surfaces deposition. Then, we can control where the thiol has to come where as silence there tend to be give highlight explosive or toxic reducing agents because very high amount of hydrogen as well and the bond is also very strong.

So, in that in that particular process once the bond breaks it can release very high energy and make the thing explosive toxic. The application of Langmuir Blodgett films applies in metal insulator semiconductors biological membranes of drug delivery chemistry of changing chemistry of biologically active molecules and in the modeling of biological systems. Here, thiols are easy to pattern via certain techniques such as lithography.

They can be highly useful for the nano electro mechanical systems because it can also withstand very harsh chemical cleaning treatments. So, that is the advantage with the thiols that we can utilize them in micro electro electromechanical systems. It can also reduce the overall where or the harsh chemical environment that is that can predominate in such structures in the moving parts silence. They can adhere to glass fibers, so again it can also be utilized for water repellents coatings, it can also initiate combustion in the compressed air stream.

It can be also utilized for deposition of amorphous silicon on glass to stabilize the overall composite materials. So, there are certain applicability of the silence films as well, but they tend to be very explosive for toxic as well that again it requires a better control, but these films, they have very higher bond energy and they can be very stable as well.

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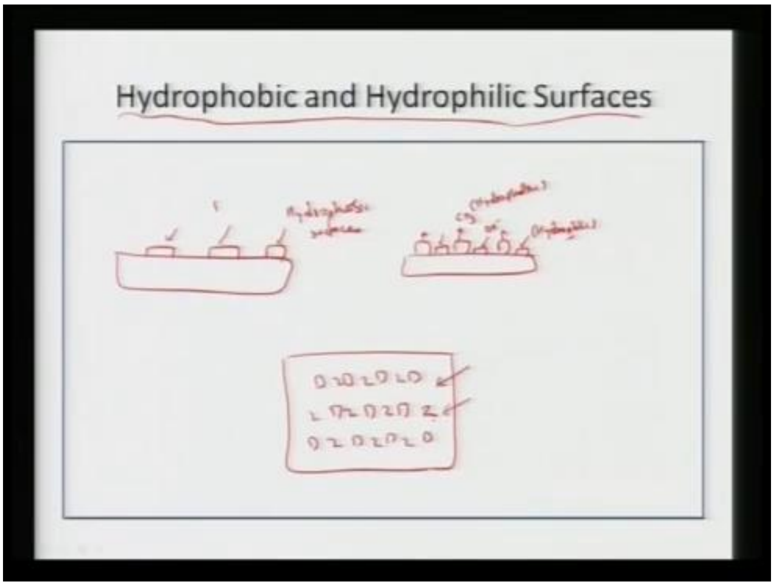
Hydrophobic and Hydrophilic Surfaces

In certain pattern also somehow construct selective hydrophobic and hydrophilic surfaces. So, if we if we select a particular entity, and let us deposit gold on to that and then if we can somehow control that. We want to deposit only hydrophobic surfaces, and then we can coat it again, and then we can deposit a pattern surface. Again, to deposit something else may be it is hydrophilic surfaces only on other regions, so we have phobic region, we can have c s three bond here we have OH bond.

So, this hydrophobic where as these surfaces are hydrophilic, so in case when you want to impart a dual functionality to a material you want certain regions to be hydrophobic and other region to be hydrophilic. We can impact that particular functionality, so we can have certain regions which are hydrophilic and hydrophobic. So, we can have certain regions, so not this particular material can be tail or accordingly that either we can want to capture hydrophobic or hydrophobic nature might be require. So, there is no contact of water on the surface where as hydrophilic can required to impact certain lubrication layer so that it did not under grow to that extent do not under go where to that extent.

So, you might require hydrophobicity or hydrophilicity on the same plat from, so the surface requires both these functionalities we can somehow tailor them and impart both of these features. So, if a particular material say for water drawplate falls on with on this particular substrate, it will stick because it has a localized hydrophobic hydrophilic regions. At the same time, it will still try to stick it because again you have certain empiphilic regions which are available on the particular pattern surface. So, we can achieve dual functionality or duality in a particular surface or if want to control it vice versa, we can also eliminate that particular part by controlling the hydrophobicity of amphiphobisity on the patterned surface.

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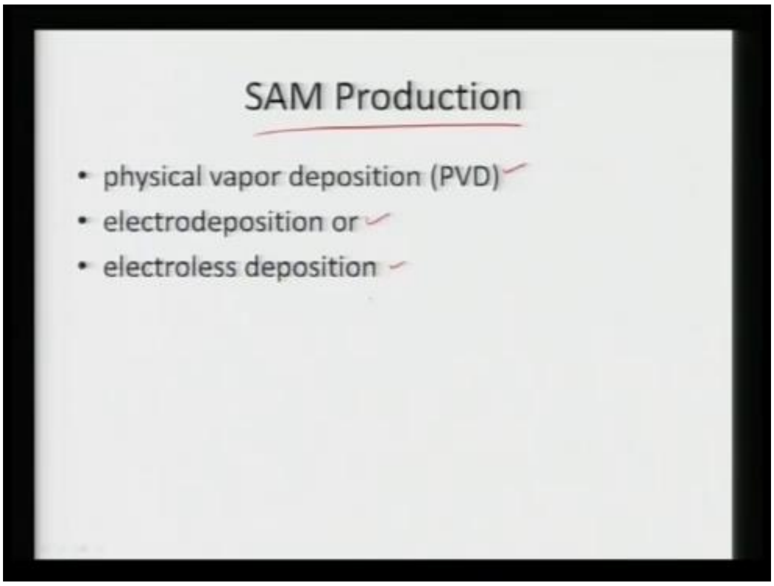

SAM Production

- physical vapor deposition (PVD)
- electrodeposition or
- electroless deposition

Again, SAM can be self assembly monolayer’s can be produce physical vapor deposition, electro deposition or even by electro less deposition many other techniques as well.

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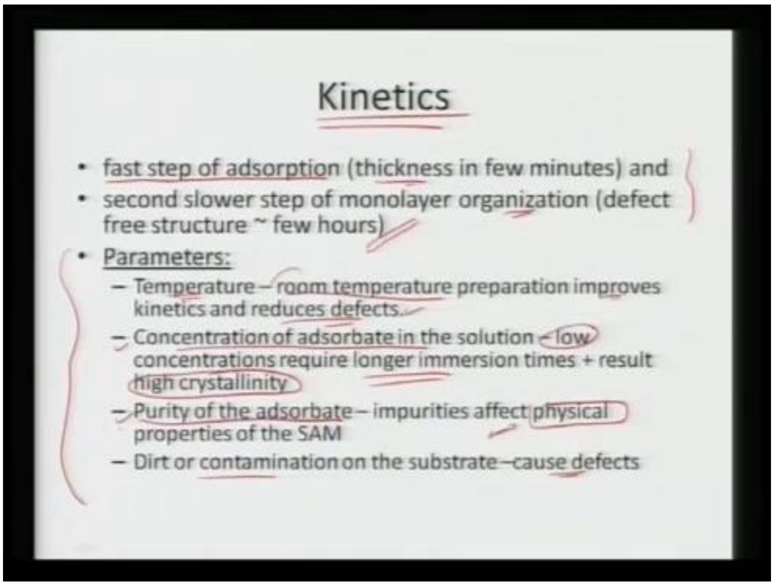

Kinetics

- fast step of adsorption (thickness in few minutes) and
- second slower step of monolayer organization (defect free structure ~ few hours)
- Parameters:
  - Temperature – room temperature preparation improves kinetics and reduces defects.
  - Concentration of adsorbate in the solution – low concentrations require longer immersion times + result high crystallinity
  - Purity of the adsorbate – impurities affect physical properties of the SAM
  - Dirt or contamination on the substrate – cause defects

The kinetics is basically detected that all these chains come to the surface very quickly, but the time it requires for organization. So, we can see it as a fast step of absorption thickness can be achieved in a few minutes. The rate deciding step is nothing but the organization of the particulars chain. It take particular time in terms of corresponding of basically acting towards the surface forces which are acting around these are first of all he ionic or the forces with this substrate. Second thing is the weak or the secondary bonding with the nearby chains that is that is what which requires very high time temperature. If we increase a temperature, it will try to basically form the coating or the layer at much rapidly it will have many defects.

So, if it deposit on room temperature, it will improve the kinetics and reduce the defects, so it will make very crystalline concentration of adsorbate in the solution. If you low concentration, it might require longer immersion time, but it will result high crystalline. So, that is current with the low temperature, if substrate is very pure, then the overall properties, physical properties of the SAM can be much better or much more predictable.

So, that can also lead to the confirmation to the coating certain requirement dirt or contamination on a surface on the substrate can also cause certain defects. So, we can see the characteristics basically detected by the rate in which the chains are organized and there certain temperature or pressure parameters. So, if we have a high temperature it might lead to formation rapidly, but then it will require it can create much more surface defects. So, low temperature preparation can may it much more crystalline in nature the characteristic basically will be comparable much though much lower, but still have very less lesser effect.

Lower concentration can again impart higher crystallite because now they can they will have enough time the overall deposition and an organization will be much quicker other entities. They can have enough time, because they are localization of these particular chains is much parallel from each other that tend become much more crystallite because they have now enough time available before. Next entity coming closer to them again high purity is also very much required, so we can predict what is the overall functionality that we can impart to the surface.

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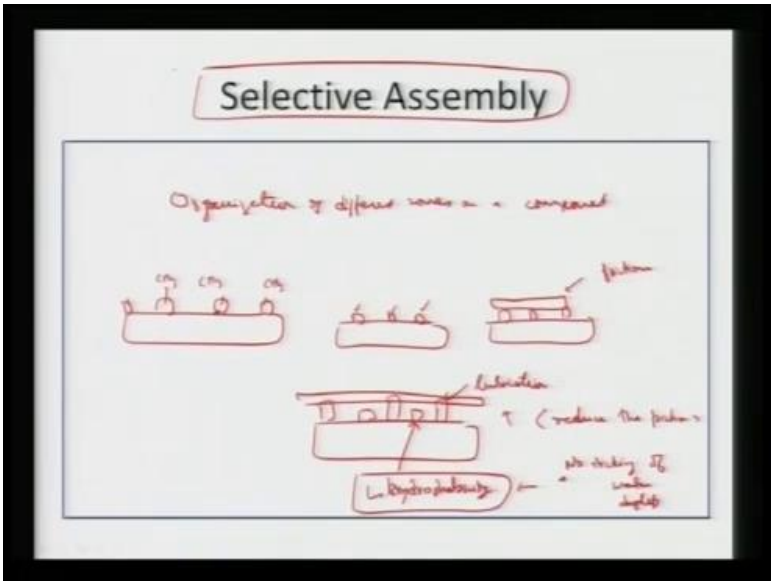

Selective Assembly

Again, we can have selective assembly; we can make it either highly hydrophobic or hydrophilic in nature, so we can have certain selective assembly. So, we can have organization of different parts on a component, we can organize different zones in a particular component. So, it is again nothing but, the extension of certain functionality, so we can see that we can attain a self assembly if start developing certain thiols and then start giving of functional chains say may be methyl on gold substrate.

If we can impart again thiols to do make it hydro hydrophobic in nature and then again we can somehow try to we can impart an assembly secondary level of assembly to this particular methyl group and if you can polymerize lubricant on to it. So, what you can make now a layer which can take care of the session and the remaining areas we can try to make it hydro folic.

So, we assembly self assembly of lubrication, and then this one will be part of impart us hydrophobisity. So, in this case we are assuming lubrication it will do nothing but it is the fiction of the moving parts and the hydrophobicity will not allow any no striking of water droplets. So, we can achieve multiple functionality or you can achieve a selective formally of combining various concerned of achieving more than one type of function to a particular component. So, particular component can be utilized in the vary condition in the even water so you have to impart lubrication by polymerizing a particular polymeric chain functional chain and then you can also impart non mating to the surface by applying layer. So, in that case you are able to achieve lower fraction as a super hydrofobisity or hydrofobisity on the same component that is nothing but the selective assembly by utilizing that you can achieve dual functionality.

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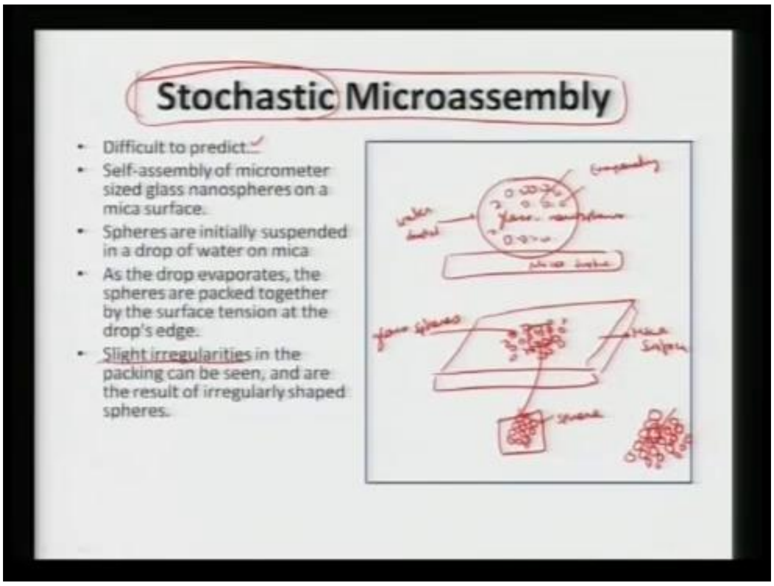

Stochastic Microassembly

- Difficult to predict.
- Self-assembly of micrometer sized glass nanospheres on a mica surface.
- Spheres are initially suspended in a drop of water on mica
- As the drop evaporates, the spheres are packed together by the surface tension at the drop's edge.
- Slight irregularities in the packing can be seen, and are the result of irregularly shaped spheres.

Then, the assembly also be took nature which is it means it is difficult to predict, so if you take a particular mica surface and then put a water droplet and then we disperse some glass nano sphere. So, you have many glass which are basically now which are there in on a particular fluid on water droplet. So, we have water droplet we have a mica surface and we depositing certain nano space of glass, so essentially once this particular water droplet starts evaporating. Then, you can see that these micro spears of silica, they start forming a structure on the on the mica surface. So, this is nothing but your glass spears, this is water droplet and this is your mica surface.

So, essentially what you will see you will see a very nice organization of this particular particles of this fears if it zoom it out here, it will look like this very nice organization of all this spears on this particular particles. It means that because of surface stantion between the particles because we are at some fluids layer and water layer on the on the glass surface glass spears. So, as soon as the water is not evaporating because of the capillarity action all these nano spears come in contact and they form certain organize layer. This is very difficult to predict which type of how it will basically develop because it has a similar probability in all the direction, but it will form a very nice dense organize layer that is called micro assembly.

Hence, this is difficult to predict it is called stochastic micro assembly again there can be slight irregularities can be. Basically, they can come into picture, but that will arise because of the non uniformity of the spherical particle of that because of no uniformity on the surface of the spears. It will again lead to certain distortion. So, once we surface it might lead to a it might lead to a different orientation of the particles. So, instead of coming like this, it might go something, so one particle is bad, so one particles are bad it will basically destroy the entire micro assembly.

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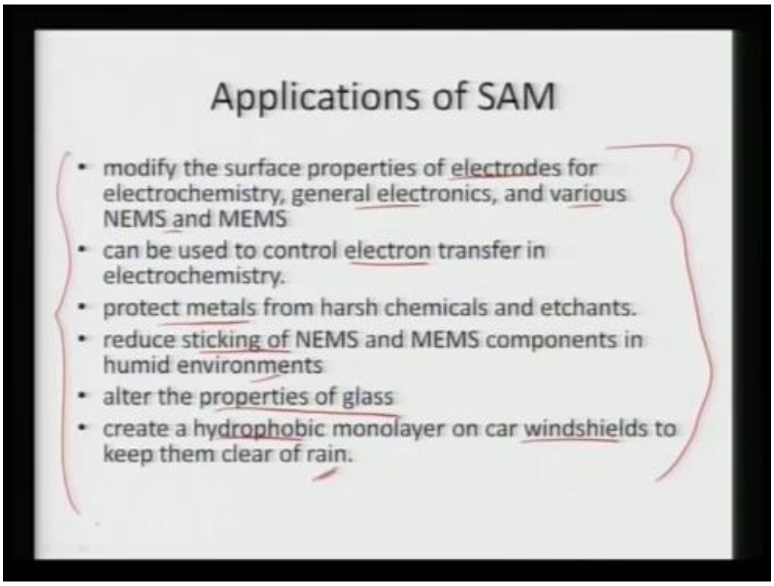

Applications of SAM

- modify the surface properties of electrodes for electrochemistry, general electronics, and various NEMS and MEMS
- can be used to control electron transfer in electrochemistry.
- protect metals from harsh chemicals and etchants.
- reduce sticking of NEMS and MEMS components in humid environments
- alter the properties of glass
- create a hydrophobic monolayer on car windshields to keep them clear of rain.

Again, application of SAM, they can go from chilling the surface properties of the electrodes we can enhance the properties of the electrodes we can enhance certain electronic properties. We can also utilize them NEMS and MEMS that is nano electro mechanical system, so macro electronic mechanical system can be utilize for controlling the electron transfer. So, by changing the functionality of the surface chain it can protect metals from harsh chemicals and etchants and thiols it reduce sticking of NEMS and MEMS and humid environment, it can alter the property of glass. It can create either hydrophobic or hydrophilic monolayer, it can also utilize for on the car windshields for keeping them clear of rain.

These are the various application of SAM we can take them from chemistry to electronics to even hydrophobic entities or even biological unit, where we can impart certain porosity or drug delivery using this particular monolayer. So, we can see that the whole application is not limited to any one entity it will go from married application.

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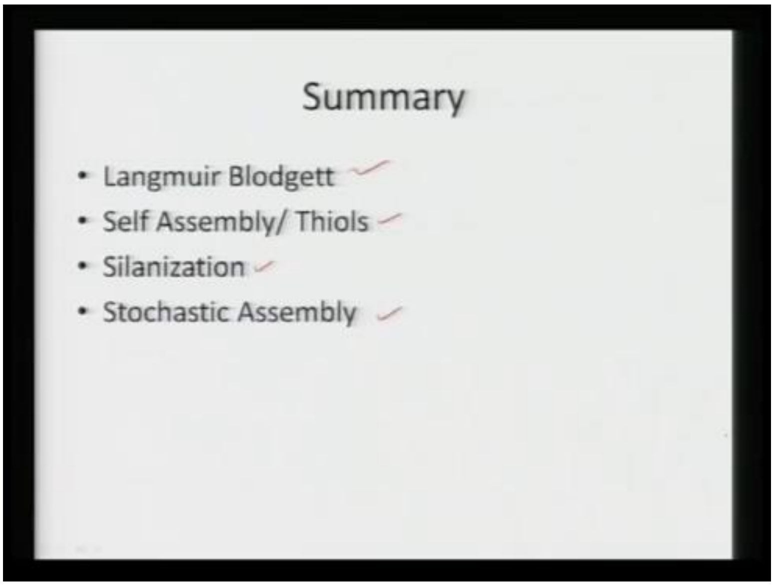

Summary

- Langmuir Blodgett ✓
- Self Assembly/ Thiols ✓
- Silanization ✓
- Stochastic Assembly ✓

So, in summary we have Langmuir Blodgett films which are nothing but the lower interaction lower forces interaction it is ironic and copper or hydrogen van der wall forces then we also saw that thiols have high affinity for precious matters. So, they tend to form a self assembly silanization, they have very high energy of the bonding. So, they can be very toxic or explosive if it is so, but they can form very strong layers, but the only problem with them is if they undergo breakage of any other direction, it can be lead to a non assembly or so. Then, we also learned about the stochastic assembly in this case we cannot predict how the assembly will occur, but it is self sustaining and construct to a very regular structure. So, in this I will end my lecture.

Thank you.