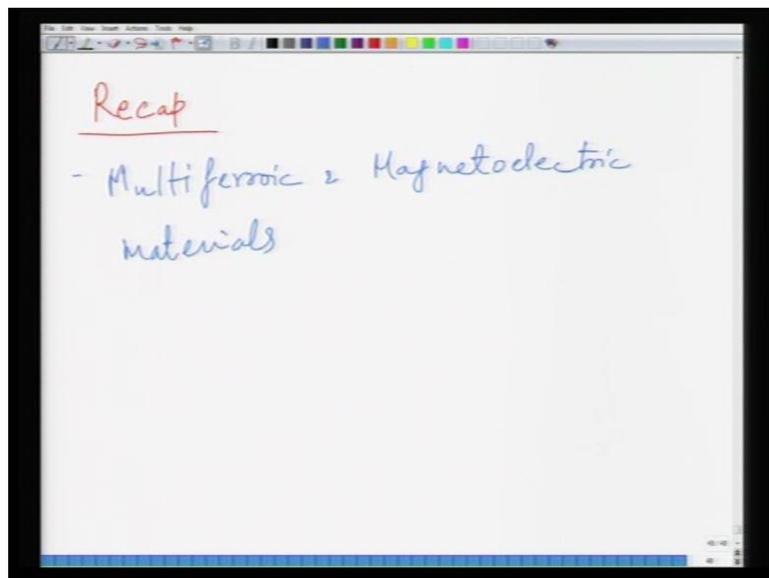


**Electroceramics**  
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**Lecture - 41**

So, we will again start a new lecture and first I will just go through the contents of last lecture just a quick recap, and then we will start the contents of this lecture. Present lecture is going to be essentially on synthesis methods, which are used for electroceramics; and we will look at both bulk and thin film methods, but we will just briefly review, what was the work that we did in last lecture.

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So, just a recap. So, in the last lecture we looked at what we call as multiferroic and magneto electric materials. These materials as the name itself suggests that multiferroic is a type of material which has more than one ferroic ordering in the single phase.

And magneto electric is a material which has coupling of electrical and magnetic properties, and not necessarily having ferroic properties in the single phase. Now, these materials as you can guess they offer a variety of exciting applications simply because they can afford more than one degree of freedom for the control of device operation and this is what makes them really important. And some exotic applications like you know spintronic transistors etcetera or spin walls which can be operated both electrically and

magnetically have been envisaged although nothing has come into real world as yet, but the research is going on these materials.

The difficulty is that these materials do not exist in nature. So, they have to be made in the laboratory and they are not easy materials, because the requirement what we are concerned with typically is co-existence of ferroelectric and magnetic ordering. Typically, what happens is that either the temperatures are low or material you know the ferroelectric temperature can be high, but magnetic temperature is low or vice versa or material is difficult to make because of impurities and many times these materials happen to be quite conductive; as a result you know ferroelectric applications are very badly hampered.

So, all these detrimental factors they make life of a researcher little difficult as well as challenging; and it is quite a challenge to make these materials in pure phase form and in the form that you want to use in some application. Physics of these materials is not really very well understood, because there are lot of conflicting requirements which are posed to fulfil both the criteria and as a result the physics is still being worked out. We looked at some physical aspects and which sort of some of them are necessary, some of them are not necessary, some of them are quite conflicting such as you know having a d ion with whether you have completely filled d orbital's ion or unfilled d orbital's ion and phase transition etcetera, because in ferroelectric form you require centre of symmetry to vanish whereas, in magnetic form Jahn-Taylor distortion and oxides prefers the centre of symmetry to exist.

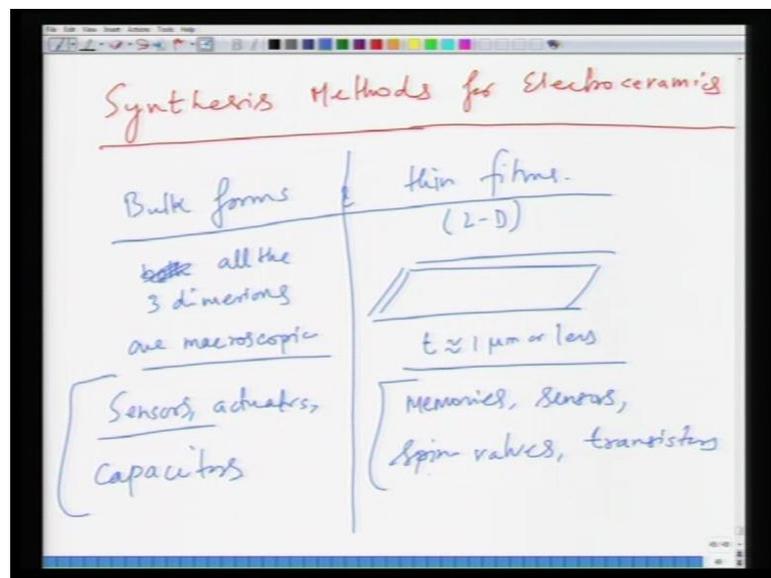
So, as a result these requirements are conflicting. So, at a moment the physics of these materials is not well understood; and on top of that then we discussed multiferroics. What are different kind of multiferroics? As we said, there are two kinds of multiferroics typically classified as type one and type two; type one are the materials where both the effects exist simultaneously, being independent of each other. So, one does not exist because of another.

However and as a result the magnitude can be large, but the coupling is relatively small. And then there is a type two multiferroic where Ferro electricity essentially cause of magnetism in the material. So, type one multiferroics were typically bismuth ferrite; probably the most researched multiferroic till date and then bismuth manganite etcetera,

then you have type two materials like you know T B M into 5 etcetera which are little more complex material, but they are exciting because they can give rise to fantastic property or strong coupling of magnetic and electric order parameters.

And then of course, you have composites where you do not have these two ordering in single phase, but rather you mix two phases having each of these orderings and then through either interface or strain you expect some coupling in these two properties. So, and this is what we discussed last time. So, what we are going to take up in this lecture which is probably going to be last lecture of this entire course.

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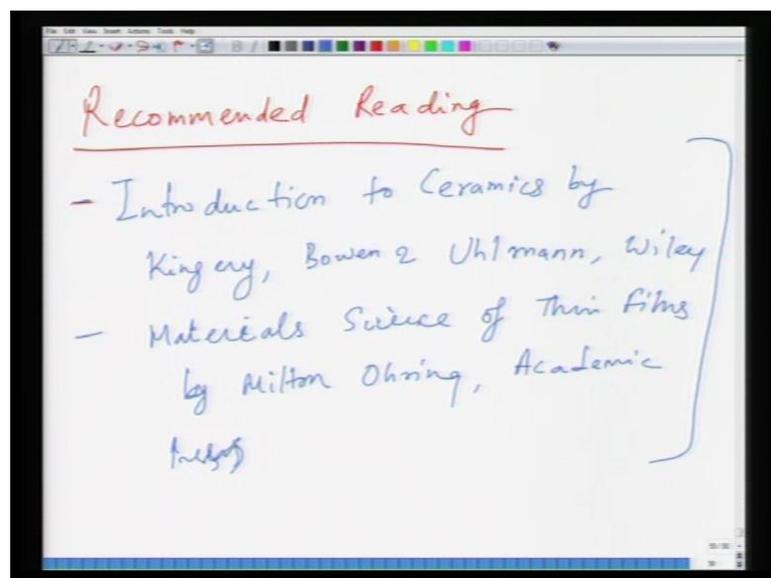
We are going to look at the synthesis methods for electro ceramics. Now, the requirement of synthesis methods or the understanding of synthesis methods is required, because these electro ceramics need to be used in both bulk and thin film forms.

So, for instance bulk form which is you know a palette form which is not a thin film form typically, how do you define? Bulk form and thin film form are differentiated on the basis of dimension. Thin film is a typically 2 dimensional stuff where it is deposited on top of a substrate using the processes that we will discuss. So, here the length and breadth are at macroscopic scale whereas the thickness of thin film is of the order of a micron or less. This is the definitions of thin film; where as in bulk form all the 3 dimensions are macroscopic which means you can measure them rather easily.

So, this is the critical difference between bulk and thin film form, and depending upon the application you might have to make ceramic in the bulk form or thin film form. In the bulk form there are variety of sensors like earlier sensors, actuators, capacitors; many of these devices earlier were made in bulk form; and in thin film form you have variety of fantastic devices modern devices like memories, again some sensors, then you have spin walls, transistors etcetera. So, all these are devices which require the electroceramic to be present in thin film form. So, you have to know both the processes and I will briefly discuss the processes to make both of these forms in this module.

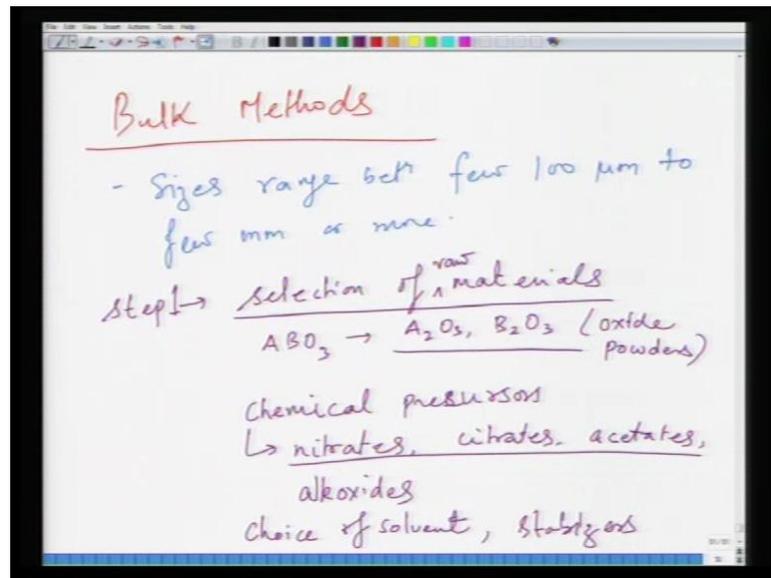
So, first we will take the case of bulk methods. Now, before we do that what I will do is that I will give you what is the recommended reading?

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So, you can through the books. Now, recommended reading first one can be you know introduction to ceramics by Kingery, Bowen and Ulmann, Wiley publication, and then you have material science of thin film by Milton Ohring. These are the two primary texts; there are variety of other texts and papers, and reviews which you can read through the internet or library and get an understanding, but this last book is from academic press. Most of these books are available in libraries as well as there could be e copies for which you have to pay probably and there are plenty of journals and journal review articles which give you information.

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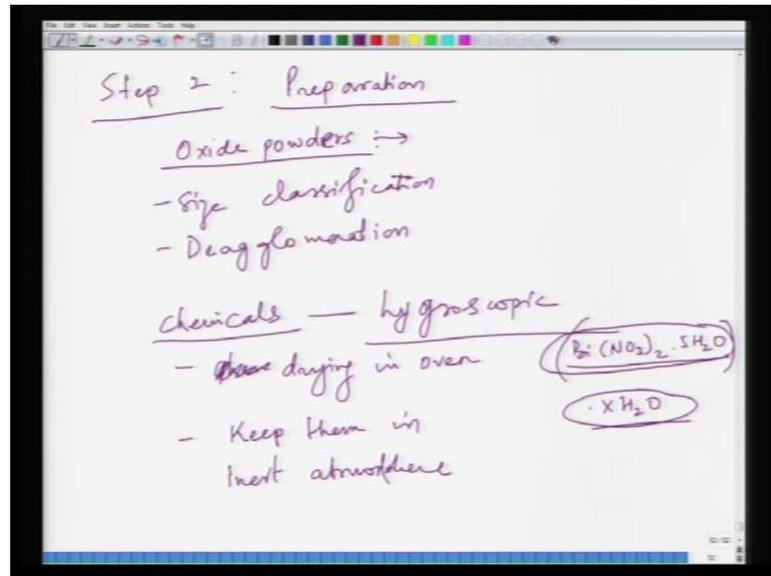


So, we will first look at what is called as bulk methods. Now, in case of bulk methods there are various steps. Now, the sizes that we are talking in case of bulk range between you know a few hundred microns to few millimetres or more. So, these are size ranges that we are talking about. So, a typical a method to make a bulk form would be to start with selection of materials. So, the first step in this whole process can be selection of materials. So, of course, you have to know about the materials, the raw materials that you are going to use; since the final phase is not available as a material itself, you need to choose precursors which means for resistance if you want to make an oxide  $ABO_3$  then you might be interested in choosing raw materials.

So, for instance the raw materials could be  $A_2O_3$  and  $B_2O_3$ . You have to mix them; you have to prepare them that we will see a little while. So, basically selection of materials for the desired end product. So, if your desired product was  $ABO_3$ , you could have  $A_2O_3$   $B_2O_3$  oxides; in some cases oxides may not be available. So, let us say oxide powders; in that case you look at chemical precursors. And these chemical precursors can be you know nitrates, citrates, acetates and alkoxides which are metal organic compounds, and all these nitrates, citrates, acetates they require dissolution in certain media, because these are all their salts. And similarly, alkoxides also require dissolution in certain media and then you have choice of solvent; sometimes you also have two solvent may not be stable. So, you need to think about stabilizers and solvents could be things like acetic acid, nitric acid or citric acid; stabilizers could be materials

like ethanolamine etcetera. So, step one is selection of materials; selection of let us say raw materials. Raw materials which are going to be mixed together according to the compositional requirement to yield the final composition.

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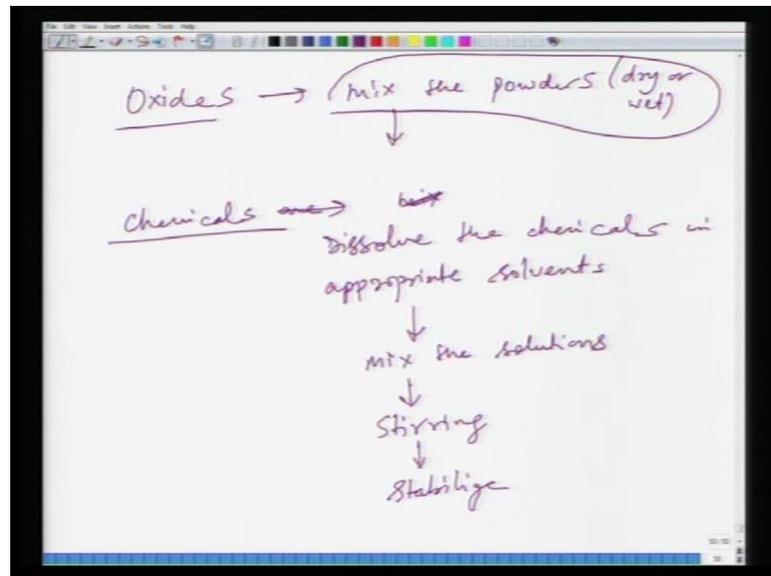


So, this is step one. Step two, in this process is now once you have identified these raw materials then preparation; now as far as preparation is concerned in case of oxide powders typically you may lead to oxide powders. Now, powders may be of different sizes. So, size classification may be required in order to have rather homogeneous size. You may have to deagglomerate them, because final particle size have tendency to agglomerate into lumps and as a result you might have to add surface active agents, and some surface treatment in order to get rid of these lumps.

So, variety of these processes need to be done to prepare these oxide powders. In case of chemicals like nitrates, citrates, acetates they tend to be hygroscopic. Now, what you mean by hygroscopic is essentially if they have this natural tendency to attract water molecules. Now, when you make calculations to mix them together then these water molecules which are attached to it; this is the formula, but this also has tendency to attract some other water molecules attached to it multiplied by  $X\text{H}_2\text{O}$ . Now, these can be get rid of just by a drying and this is necessary step, because you need to calculate the right amount of precursor according to through stoichiometry. So, drying in oven may be needed in order to get rid of excess water. Similarly, again you need to keep them in inert

atmosphere sometimes. So, that they do not react, if they have reactivity. So, these all these processes they come in the preparation.

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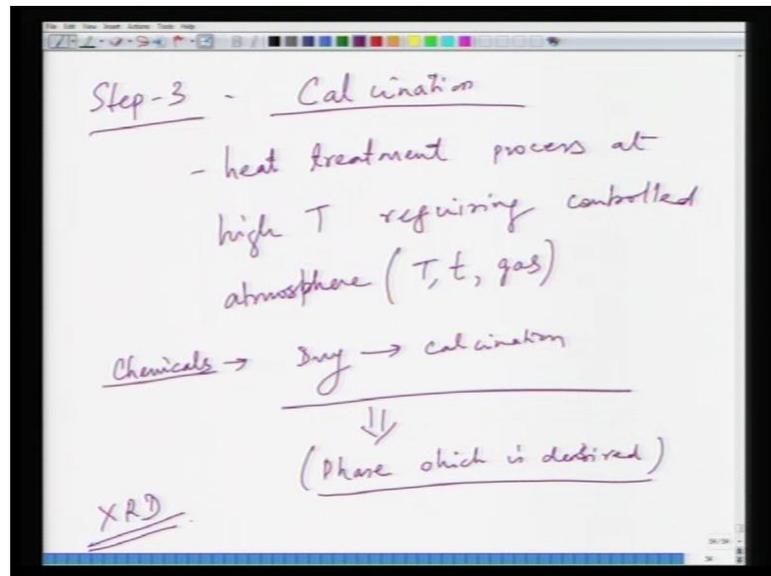
Now, preparation for bulk is simple; preparation for oxide powders is simple. Now, oxides typically mix the powders according to the stoichiometry followed by mixing you and this mixing can be done in pestle and mortar; if you have a small amount, it can be done in mixers which are commercially available and this mixing may be required to be done in a solvent or it could be dry mixing.

So, you can have dry or wet; and once the powders are mixed for a stipulated period of time then you need to heat treat them to form the phases. So, I will come to the heat treatment stage and now this is for powders. So, you mix the powders according to the stoichiometry either dry or wet. As far as chemicals are concerned first you dissolve the chemicals in appropriate solvents. Once you have dissolved them, it may be possible that you may require individual solvent for individual precursor. So, you may have to do the dissolution process individually for each of these salt according to their chemistry and then you may require to mix the solutions prepared from each chemical.

And once you got the mixing done, you need to stir it for long time; stirring and then stabilize. So, this is process for chemical root. Now, once you have prepared these

mixtures whether the oxide mixture or whether the chemical mixture then the next step comes is which is called as calcination.

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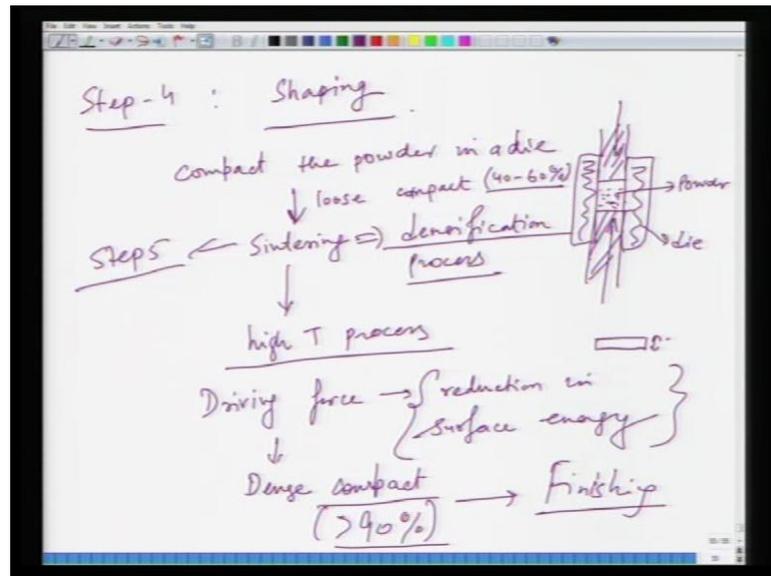
Now, this calcination is essentially a heat treatment process where powders or chemicals are subjected to high temperatures. So, that the constituents react with each other and they form the final phase. So, essentially it is a heat treatment process at high temperatures often requiring controlled atmosphere. Now, controlled atmosphere would mean essentially control temperature for a stipulate period of time and gas; whether you want to do it in air, whether you want to do in nitrogen, oxygen, hydrogen etcetera.

So, all these mixed powders and chemicals need to be calcined. So, in case of oxides, it is easy you just put them in the furnace and then calcine them in an appropriate crucible. So, the mixture does not react to the crucible and then calcine it for required period of time and temperature in a particular environment. In case of chemical solution mixture you may first need to dry it. So, the drying is different from calcination. So, in case of chemicals first you dry. So, drying may be done slowly. So, you get rid of all the solvents and then followed by calcination to achieve the phase formation. So, this calcination essentially this step gives rise to the phase which is desired.

Now, this process is very important because you need to optimize this process with respect to time temperature and environment. So, that you end up getting the phase

which you want and how do you know? What phase have you got? You need to characterize the powder by technique like x-ray diffraction which is called as XRD. So, you put your powder with the final calcined material in the XRD machine; take the spectra out; do the matching with the software standard patterns and find out whether you got your final phase or not.

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So, essentially the purpose of calcination is to obtain the phase which is desirable; and following this calcination process the step 4 is shaping. Now, once you have got this powder with the final phase that you require, you need to put it into a shape that you want.

And shaping is essentially a process in which you compact the powder in a die of appropriate shape that you want. So, compaction is done at room temperature and in dry state or wet state depending upon the type of powder, and for example, you can have a die like this. And if you just want to make a pellet, you have this bottom punch and then put your powder here, and then you put a top punch. So, this is your powder and this is die, and then you apply pressure through top punch; as a result of this pressure, the powder gets compacted and what you get is a pellet of this final thickness. So, this is simple process, you can have much more complicated process if your shape is complex.

So, you compact the powder in a die using mechanical pressure and once you get it compact which is brittle, but you must be able to handle it. So, that it does not break. So, once the compaction is done then you do what is called as sintering; and this sintering is a process which is you know step 5 of this whole scheme which is essentially a densification process. So, what you got at this stage is a loose compact and here you might have densities varying between 40 to 60 percent; density is very low. So, powders are essentially touching each other through mechanical or forces they are sort of welded with respect to each other, but the pores are not filled.

So, sintering what happens is it is a high temperature process. So, because of high temperature the mobility of atoms in the compact is higher. Now, the driving force for sintering essentially is the reduction in surface area, because you have porosity. So, you have lot of surface area and as you know surface energy is a positive energy which needs to be provided.

So, it wants to get reduced to reach on low energy configuration. So, driving force essentially is reduction in surface energy and this reduction in surface energy forces the loose compact to become a dense material by elimination of pores through diffusion of atoms via this driving force and curvature effects, and as a result you have a dense compact. So, you have a dense compact which you will have density typically greater than 90 percent and this is what is used in the final application, and then once you have achieved sintering then this is subjected to finishing.

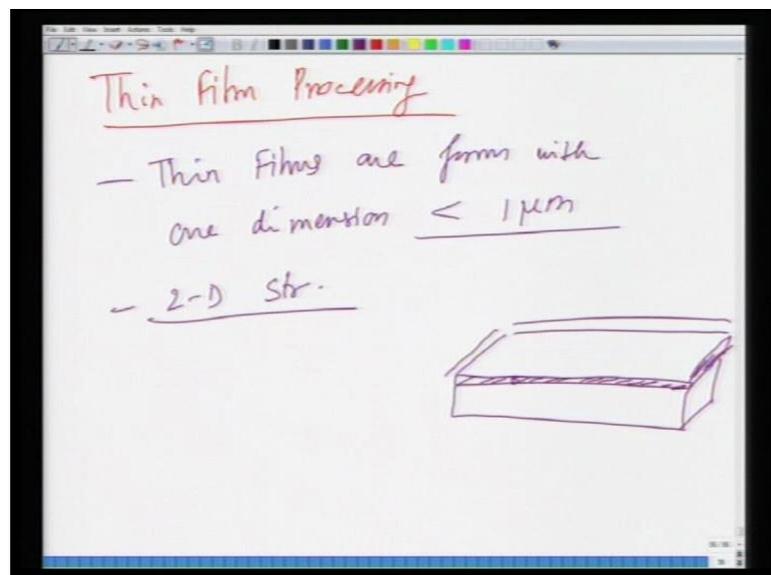
So, you just need to finish it to such as surface cleaning etcetera needs to be done to make the final product. So, this is what is the scheme of making a bulk material essentially from starting powders. Now, you must take some care in this whole scheme; the care essentially is taken at various steps and when you start with the step one let us say step one is powder selection, step two is preparation. So, first of all the choice of chemicals here is important; one must choose chemicals whose constituents are easy to evaporate which do not make complexes which are difficult to break or crack.

So, as a result choice of chemicals is very important and that also affects the preparation stage when you mix them together in variety of solvents. Then as far as the mixing is concerned in case of powders one must avoid agglomeration, because agglomeration of powders is a route to formation of secondary phases; because you will have non-

homogeneous distribution of initial phases. As a result the calcification will not be successful, because you know calcination requires high diffusion of atoms and diffusion is a high temperature process. As a result this solid state if you have compositional gradients all across the material that would be a deleterious to the final product which you do not want to the final phase formation. And similarly in chemicals, one must take care while mixing them and stabilizing them. So, here the process which are to be controlled are p H, viscosity and molarity. So, all these parameters need to be controlled in order to get a good solution.

And then of course, you have calcination step where time, temperature and environment is important and then shaping and sintering is important, because here the care must be taken. So, that you do not have cracking in the final product. So, the way you heat it, the way you cool it, the way you hold it at high temperatures, it is important that thermal gradients are taken care of and the heating process taken care also. So, that you do not you do not end up with cracking in the material.

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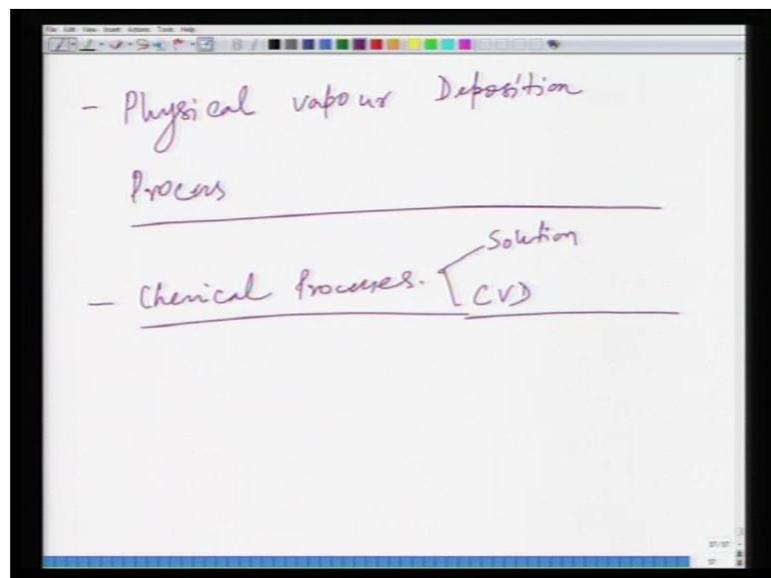


So, this is the complete scheme of bulk formation processes. Now, next stage is essentially thin film processing. Now, thin films are essentially are forms with one dimension smaller than a micron. So, it is essentially a 2D structure. So, as a result they have a large surface area and if this is a substrate on top of this you have a thin film; and of course, you have other dimension as well. So, you can see that these two dimensions

are large as compared to this dimension. So, there is a large aspect ratio; their length and breadth are much higher than the thickness of the film.

So, this is the thin film peculiarity. Now, thin film applications came into being as far as the oxides are concerned, the major impetus was came from ferroelectric and super conducting research. Because the devices that were envisaged were being made required; the material to be in thin film form and this required lot of advances in the technology, because thin film processing is essentially a technological marvel. Now, essentially how does a thin film grow? Now, there are variety of processes.

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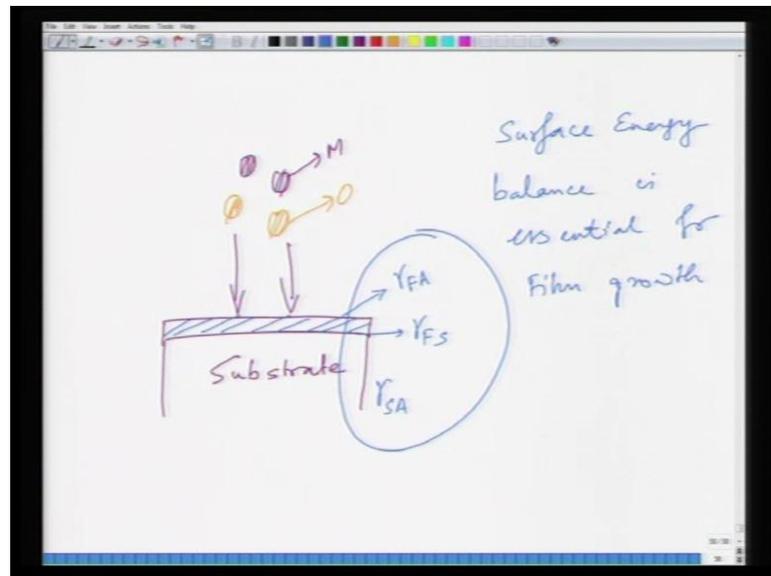


So, you have what is called as physical vapour deposition process and then you have chemical processes. Now, in case of physical vapour deposition process, material starts to grow essentially the process involves transport of atoms. So, material in the atomic form to the substrate surface and then it grows on top of the surface. There are variety of growth mechanism as well which I will briefly discuss and then in case of chemical process what you have is there are two processes; one is the solution processing and second is chemical vapour deposition.

In case of solution processing, you use solution spin coated on the substrate and then you have nucleation in growth. So, it is a rather different process as compared to physical vapour deposition process and in chemical vapour deposition you use precursors, and let

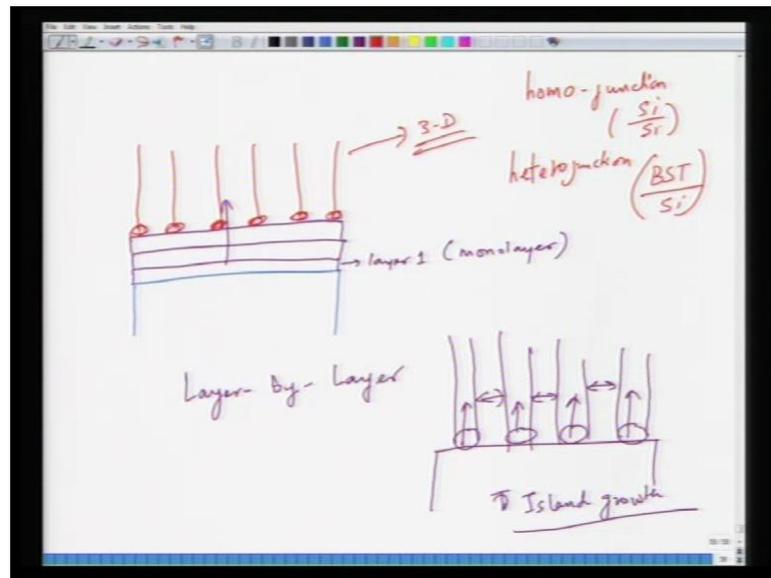
them react on top of the substrate surface, so that the final phase deposits on the substrates and completely different processes.

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Now, essentially how does a thin film grow? You have a substrate, the atoms arrive. So, these are your atoms; let us say this is an oxide  $M$ . So, there you have  $O$  and then you have  $M$  atoms, they arrive from some source and then they reach travel towards a substrate. Now, first requirement is that they must have an affinity towards a substrate which means the surface energy between the film and the substrate should be low. And the type and the energetics of this whole process which is surface energy process; the important energies are if you have a thin film here; the thin energies which are important are energy between the film and the substrates. So,  $\gamma_{FS}$ , energy between the film and the atmosphere  $\gamma_{FA}$  ambient, and then energy between the substrate and the ambient. So, you can say  $\gamma_{SA}$  the combination of these three energies is important to form a thin film. So, you can say surface energy balance is essential for film growth. So, you can do this thermodynamic analysis of surface energies and find out what is the requirement in terms of energy?

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So, when you have these atoms reaching on the surface they can grow in variety of mechanisms. You can have a growth mechanism like this in which the film grows this is layer one and this layer one is nothing, but your monolayer; monolayer is just one layer of atoms; then you have another layer. So, the process is essentially a layer by layer process; and then you have another process in which because of energetics what you find is that the film makes these islands and these islands grow vertically, and also horizontally.

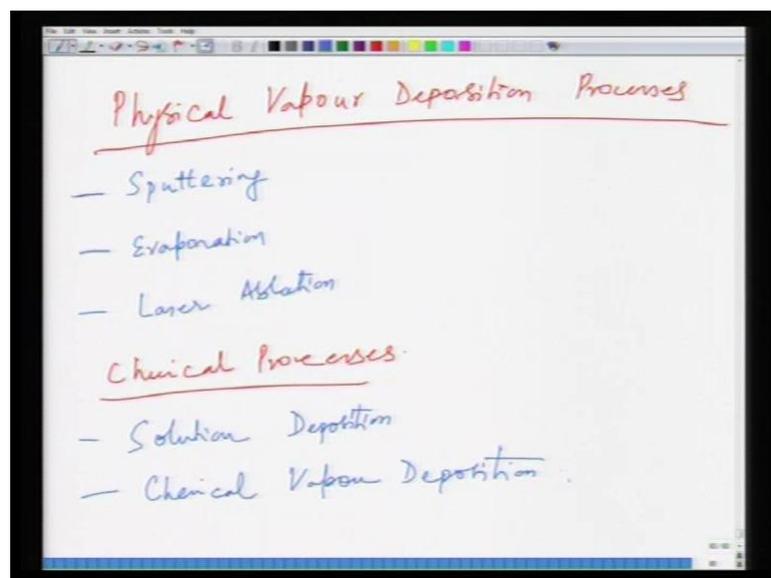
So, these islands grow vertically and then they merge into each other. So, this is called as island growth. And then you have another growth mechanisms in which you have a monolayer formation upto certain thickness followed by nucleation of island at certain places and then grows in this direction. So, this is called as 3 D growth mode which is called as stranskikrastanov growth mode. So, these growth modes which are dependent upon the balance of these surface energies and typically you would like for a very good quality; single crystal films you would like 2 D growth to be active; whereas, 3 D growth modes for a mode more like a randomised growth or that epitaxy is hampered in that case, but you cannot avoid that if you have some mismatch between the substrate and the film; you are always going to have because it is a hetero junction.

So, what you have is a homo junction which means two materials. So, silicon is homo junction; hetero junction would be you can have BST or BST is barium strontium

titanate growing on silicon. So, you have two different materials. So, in the first case silicon has same lattice parameters. So, you do not have any strain at the interface. So, the growth is likely to be of layer by layer type, but when BST grows on silicon they have different lattice parameters; they have different coefficient thermal expansion. As a result the stresses built in and these stresses give rise to a 3D growth mode.

If you want to read more about growth modes, you should read the book of ohring. There is a completely dedicated chapter to it; I will not go into details of this, but if you want to get fundamental understanding into this process; it is essential to read those. Now, as far as the processing is concerned, processing is done by as I said physical vapour deposition process and chemical processes.

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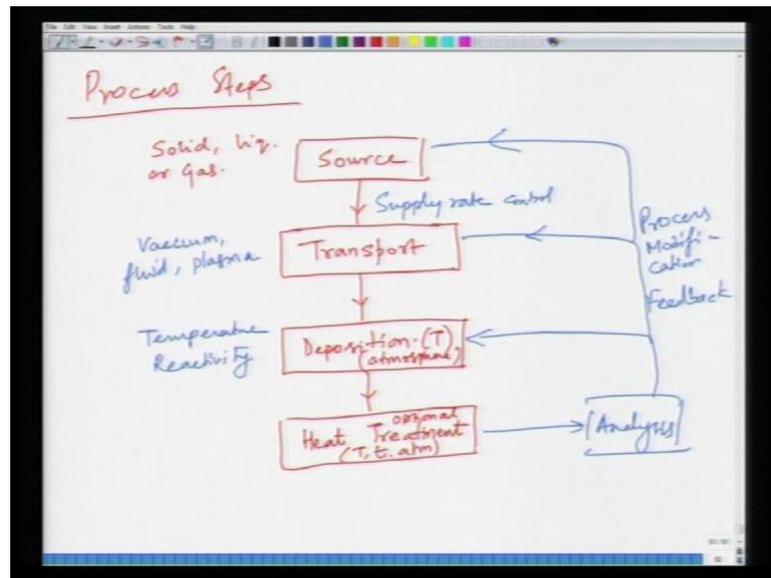


So, first we will look at the physical vapour deposition processes. Now, as the name itself suggests a physical vapour deposition process in which the material is in the vapour form in the atomistic state, then it moves towards a substrate and then all these atoms react together on top of the substrate, and then they make a continuous film.

So, this is what essentially a physical vapour deposition process and this happens in vapour state that is why the term vapour comes here. The processes which are included in this category are processes like sputtering, evaporation and laser ablation. There are some other processes as well which I am not going to discuss, but these are three

important processes which are adopted worldwide. And then you have chemical processes; chemical processes start and another thing about physical vapour deposition is you start without the use of any chemical, you do not require any carbon, nitrogen other solvents etcetera to represent; you may start right from the final phase as well. So, whereas, in chemical process you have solution deposition where you start from a solution and then you have chemical vapour deposition.

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So, we look at these processes individually, but essentially the process steps in thin film growth process is I will put the heading process steps. So, essentially you start with the source and this source could be you know solid, it could be liquid or it could be gas depending upon the type of the process. So, supply rate control and then the next step is essentially from the source the transport of material to the substrate.

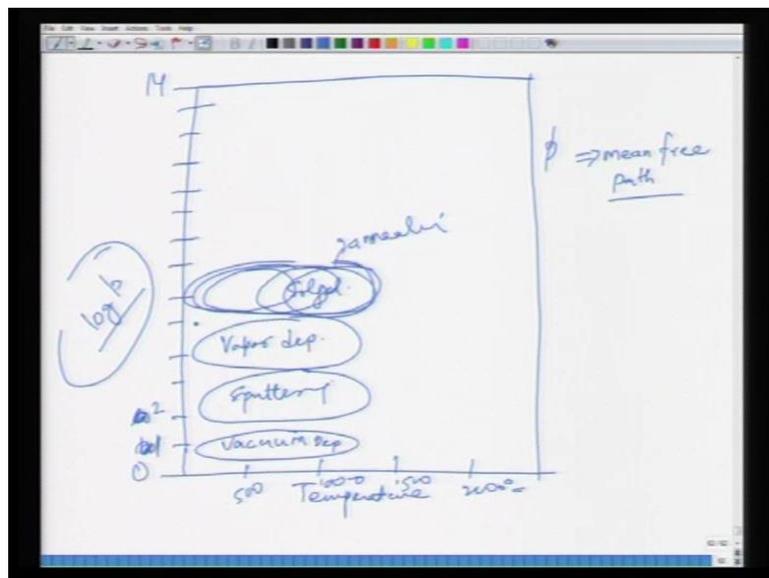
So, next fundamental step which is important is the transport and then after transport what is important is the thin film depositional growth, and then sometimes you may need a final step which is heat treatment. Now, this deposition may require certain temperature and heat treatment again is a temperature, time and this will also require atmosphere.

So, temperature and atmosphere need to be controlled; and here time, temperature and atmosphere need to be controlled. Now, this heat treatment process is of course, an optional process it depends upon type of material and type of deposition process that you

have done. And then essentially this transport can happen as I said it can happen in vacuum, it could happen in fluid form or it could happen in plasma form. Here as I said the important steps are temperature and then reactivity. And once you have made this thin film you need to do analysis and this analysis is done by techniques like x-ray diffraction, electron microscopy in order to get insight into the phase formation, and the feedback is then given to these steps. So, process modification feedback.

So, this is how a flow chart of a thin film growth process would appear. Now, another fundamental difference between thin film process and the bulk processes is the length scales or you can say the pressure which is related to length scales and the temperature.

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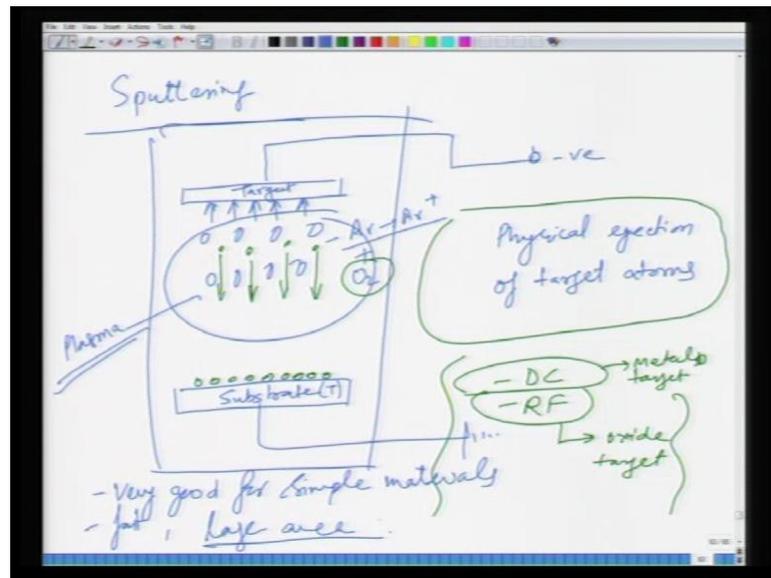
So, if I make a plot of temperature versus let us say log of some pressure, it could be background pressure, it could be oxygen pressure or whatever. Now, vacuum deposition typically happens at lower side. So, let us say these pressures are from 0 to somewhere around may be fourteen. So, you can divide this 1 2 3 4 5 6 7 8 9 10 11 12 13. So, you what you have is the temperature range of let us say 500, 1000, 1500 degree, 2000 degree centigrade's. So, vacuum deposition typically happens at very low pressures. So, you might have 10 to the power 1, 10 to the power 2, if you are writing in log then it is two and one. So, this is where vacuum deposition happens; sputtering takes place somewhere here; again the temperatures are fairly similar. The vapour deposition will be somewhere here and if you look at the sol gel process; sol gel process has happens at

atmospheric pressure and then you can have some other processes like CVD etcetera which may happen somewhere here you will have sol gel the temperature could be on the lower side. So, you can have you know this temperature higher temperature could be for annealing and these temperatures could be for the drying etcetera, lower temperature.

So, very broad range you can have in sol gel and then CVD typically a low temperature process, and the pressure will depend upon the type of precursor that you will use. So, this is the flow chart. Now, why I have put pressure? Because pressure is related to mean free path. The average distance which is travelled by the molecules or the atoms before they collide with each other. So, typically higher the pressure smaller the mean free path or vice versa lower the pressure, higher the mean free path. So, typically in vacuum deposition since you are depositing from a source and the atoms have to travel towards a substrate; you typically keep lower pressures. So, that lower pressure allows the larger mean free path in order to have a thin film growth and also lower pressure allows the conditions to sputter or to laser ablate the material, or evaporate the material from a source.

So, vacuum will help the lower evaporation temperature of materials like oxides in high temperature materials and if you want to evaporate them at high pressures, you will require much higher temperatures. And that is why lower pressures are typically used for vapour deposition. So, what we will do is that we will now look at some of the fundamental processes, we will look at sputtering.

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Now, sputtering is essentially a process in which you have a target and this target is biased. So, you have a substrate here; the substrate could be heated or unheated. This is target and substrate is typically grounded; target is you are biased. Typically, you are negatively biased and then you have this gas molecules here which are argon; and argon gas molecules under high biased they convert into argon plus.

And these argon plus molecules are attracted towards a target and they travel at very high speed, and they physically eject. So, physically eject the target atoms which fall towards a substrate. So, physical ejection of target atoms. So, simply by brute force the argon atoms eject all the target molecules and they reach towards a substrate. This substrate can be at certain temperature and typically this is all happening inside a vacuum chamber at low pressures; pressures could be as low as you know few Pascal's pressure.

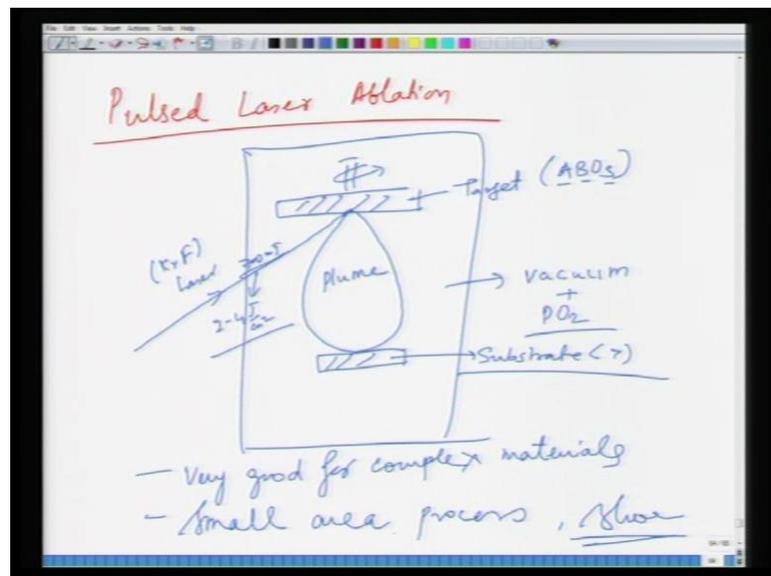
Now, here you might also want to have some gas like oxygen if you want to fabricate oxides, because typically you lose some oxygen as a result of vacuum. As a result of continuous pumping, you need provide some extra oxygen. So, the atoms which are coming down, they have sufficient oxygen in the atmosphere to form an oxide compound on the surface on which they can grow.

So, as a result you might want to have some extra oxygen in the atmosphere. So, essentially sputtering is a process which is nothing, but physical ejection of target atoms

by highly energetic ions or neutral gas like argon or krypton whatever. And there are variants of sputtering; there is DC sputtering, there is R F sputtering; in case of metals or conducting materials, you do DC sputtering. So, if you want to deposit oxide for metal target you need to have lot of oxygen in the ambient, but it can be done with D C sputtering. In case of oxide target since oxides are typically insulating, you may have to go for R F sputtering. So, these are the two variants of sputtering processes.

So, DC sputtering is typically for metals. From the metal target of course, make oxides by having oxygen as an ambient gas. So you can say metal target and R F is typically for oxide targets.

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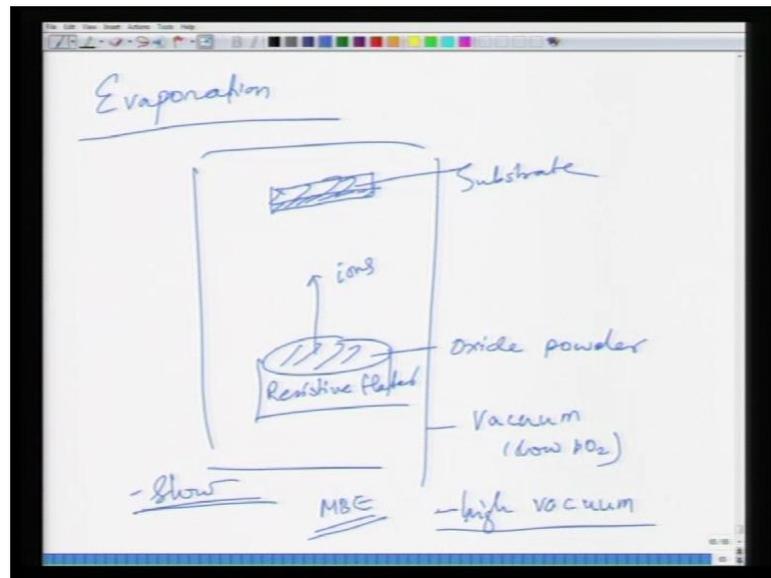
So, these are two variants of sputtering process. Another process which is important for physical vapour deposition is pulsed laser ablation. Now, what you have here is again you have a rotating target and you have a high energy laser beam coming. So, this is laser, it could be you know some gas laser or solid state laser either like n d r krypton fluoride laser and this laser hits the rotating target, and this laser let us say evaporates the material where it falls; it is a high energy laser. So, laser could be of the energy 700 milli joules which gives you energy of the order of let us say 2 to 4 joules per centimetre square; and this energy is sufficient to evaporate the material from the target in the form of a plasma which is called as plume. I forgot to mention that even in here you have a plasma.

So, this whole thing is a plasma and plasma is nothing, but a mixture of high temperature or high velocity positive and negatively charged ions. So, essentially it is a charged neutral thing in itself, but you have variety of atoms in there and which are at high energy. So, as a result plasma temperature can be quite high. So, here what you call as a plume and this plume is nothing, but a mixture of all the atoms which is coming from the target.

So, this is your target and this could be a complex material like  $A B O_3$ . So, you have A atoms, B atoms, O atoms and then of course, it is done in a vacuum chamber. So, you have some vacuum here which can have some background gas like oxygen. And this plume deposits on top of a substrate which can be at high temperature and oxygen of course, is provided in the background. So, that there is no oxygen deficiency.

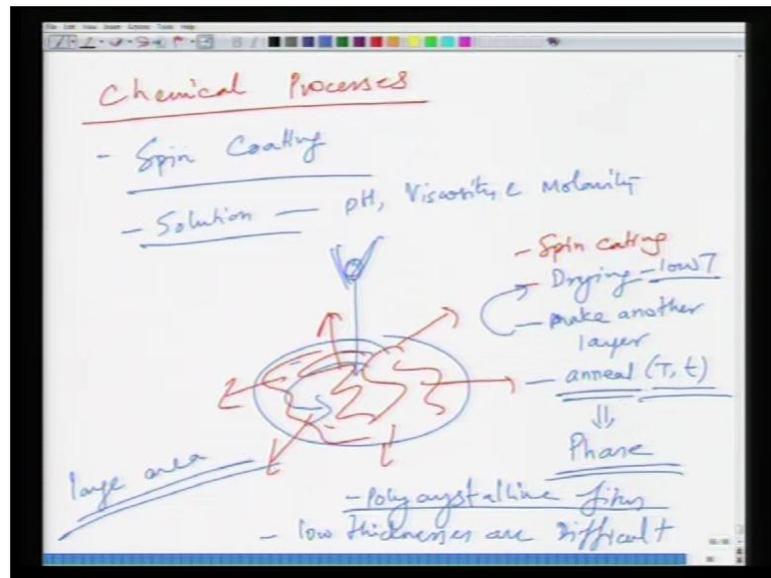
And this plume is like a plasma, and this plume deposits on top of a substrate at high temperatures; and this gives you a nice film. The advantage of pulsed laser deposition is it can completely replicate the target stoichiometry into substrate. So, very good for complex materials, but the disadvantage is it is a small area process. In case of sputtering, if you go it is very good for simple materials, fast and you can make large area. So, these are some of the advantages of sputtering. On the other hand, PLD can be pulsed laser deposition can be little slow as well. So, these are the two processes which are physical vapour deposition and of course, you have thirdly which is called as evaporation.

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So, in case of evaporation let us say a source containing oxide powder and this source is heated through resistive heating. So, you have resistive heater and this all action is happening in the vacuum. So, low  $P O_2$  as a result of low pressure, these are evaporated at reasonably low temperatures and these molecules travel towards a substrate. It is a low energy process as compared to sputtering, because in a sputtering you have very high energy ions ejecting the atoms here it is just natural evaporation. So, ions travel towards a substrate and make a continuous film. So, this is what evaporation is, it is a slow process. Another variant of this evaporation process is the molecular beam epitaxy which is done in ultra low vacuum or ultra high vacuum; you can have the vacuum of the order of  $10$  to the power of minus  $10$ ,  $10$  to the power minus  $12$  torque which is usually achieved through ion pumps. And that provides very slow growth rates, but very high quality; single crystal films can be deposited. So MBE which is called as molecular beam epitaxy is another variant of this process, but it is a slow process and high vacuum process.

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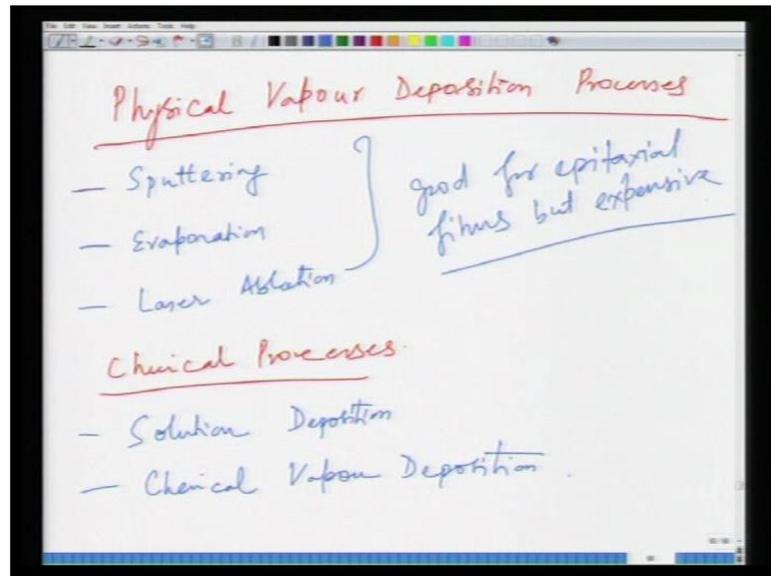


So, these are the three forms of physical vapour deposition processes and then you have chemical processes. In case of chemical processes, the first process is spin coating or chemical solution deposition. In this process what happens is that just like you prepare a solution in a similar manner as you prepare for bulk processing, control its p H viscosity and molarity and then you have a spinning substrate. So, you have a dispenser and from that you deposit a drop. So, you just spread this with the solution and then you spin coat it. And when you spin coat it, the excess solution goes out and what you have is a continuous layer, and the requirement here is the substrate should be prepared. So, that the solution is completely covering the surface. So, the surface should provide good addition to the solution which means it should be hydrophilic in most cases. So, you need to do some surface treatment for the substrate.

So, you have first process as spin coating; once you have a spin coated, the next process is drying before you deposit next layer and this drying is a low temperature process just to evaporate the solvent. And once you have achieved drying, you again make another layer then again dry and then again another layer. So, this process is cyclic and once you have a complete stack of films then you anneal it or heat treat it, and this annealing is a function of time and temperature in controlled atmosphere; and this heat treatment will give you what is called as a final phase. Typically, this process is a low temperature process, but it gives you polycrystalline films; whereas, physical vapour deposition processes evaporation, pulsed laser deposition and a sputtering are very good processes

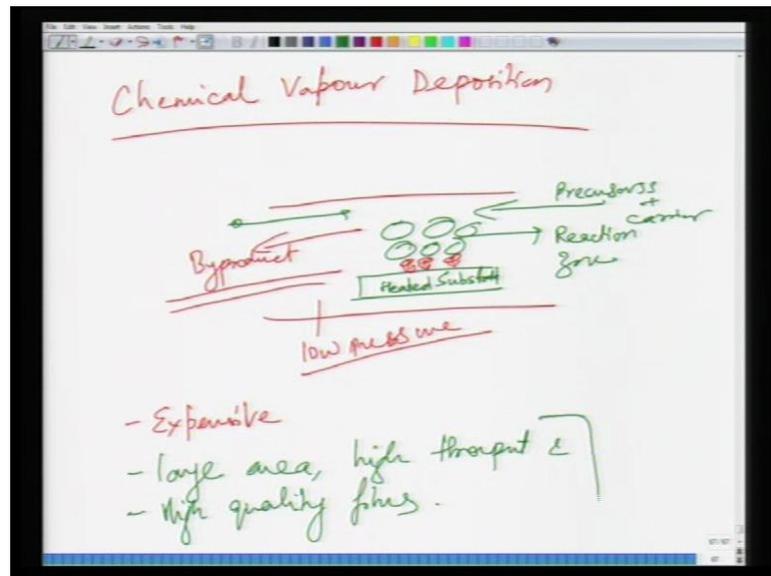
for making single crystal films, which are also called as epitaxial films. So, this gives you sort of polycrystalline films and low thicknesses are difficult. So, here you get polycrystalline films with slightly inferior morphology, low thinner films are difficult and advantage is it is a large area process. So, it is a large area process and it is a fast process; it is a cheap process, because you do not require any vacuum.

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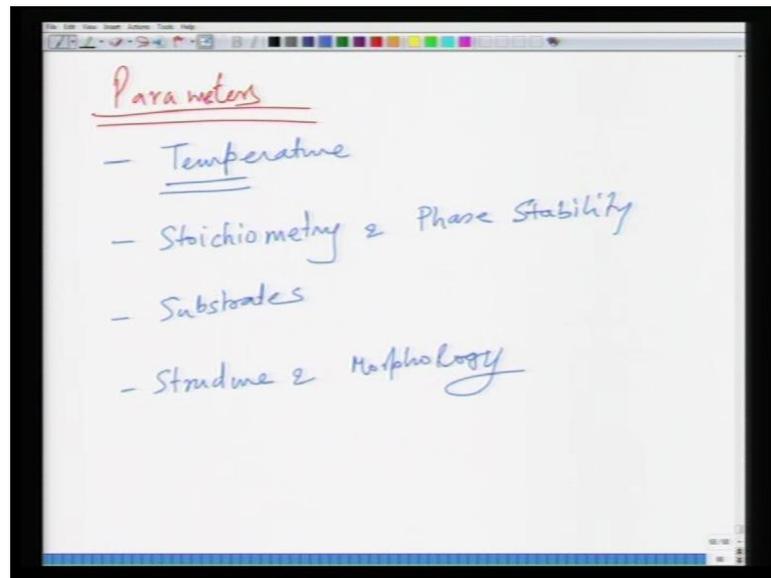
So, you do not have any massive instrumentation. In case of sputtering and laser ablation, all these three processes good for epitaxial films, but expensive; because you require extensive tooling to achieve low vacuum. And the final process after the spin coating is the chemical vapour deposition.

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And what you have here is essentially a chamber in which you have a heated substrate. So, precursors coming in plus carrier gases and these precursors come on top of a substrate and then they react. So, this is the reaction zone. So, final compound which is formed, it deposits on the substrate and the by-products go out. So, again this process requires quite a bit of tooling, because you have low pressure environment inside and since you handle with expensive precursors which also can be poisonous at times. So, the safety requirement is significantly high in chemical vapour deposition. So, it is an expensive process, but the good thing is it is large area, high throughput process and it can give you high quality films. So, there are some very good advantages of chemical vapour deposition process.

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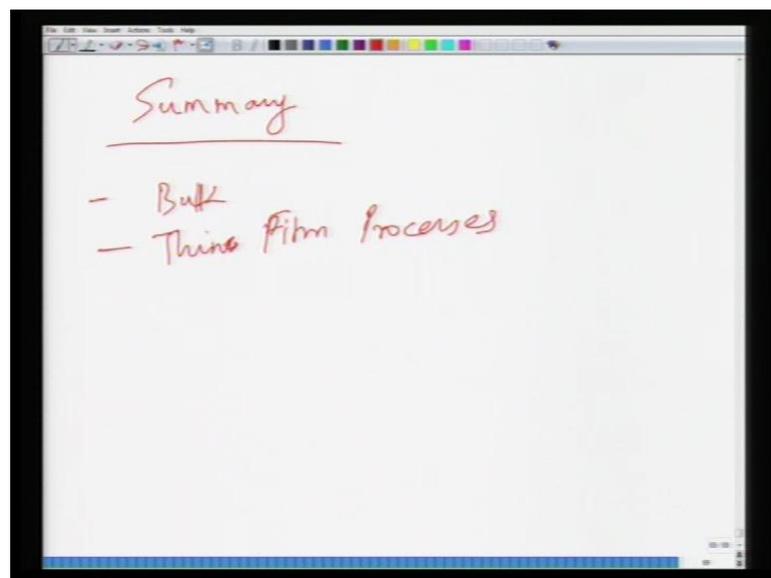
So, these are some of the processes which are used for thin film deposition of these electro ceramics. Now, the parameters which are of importance in chemical vapour deposition in basically thin film deposition processes. There are some of the important parameters which need to be understood. So, you need to understand what is the effect of temperature? Temperature is a very important parameter, because temperature is a process which affects the process of nucleation in growth and the final phase formation which is based upon the phase diagram as well. So, this temperature is selected according to variety of these things. Temperature is also useful in achieving single crystal films, because a higher temperature promotes the mobility.

So, typically epitaxy is promoted at higher temperatures while lower temperatures give more or less polycrystalline films. This is the general guideline in some cases by means of things like plasma and electric field to the substrate etcetera one can promote the epitaxy at lower temperatures, but by and large temperature promotes the epitaxial nature or single crystal nature of the film. Then you have then you need to worry about the phase stability and stoichiometry control. And this is a very important parameter, because most of the oxides are complex oxides. So, the cation ratios with respect to each other as well as to anions are very important, because as you know the defect chemistry can be quite tedious for most of these oxides and it can give rise to unwanted effects. So, one needs to maintain the stoichiometry well and stoichiometry also affects what is the final phase which is going to be formed?

So, control of stoichiometry is very important; some ions happen to be volatile. So, some like bismuth or lead they can be volatile. So, you may sometimes require to put extra bismuth and extra lead in the starting material. So, that you end up with the final desired composition and this will affect the phase stability of the desired phase. And this is particularly important for super conducting and ferroelectric oxides; and the third important part is substrate effects. Choice of substrate is very important; what kind of substrates you choose because substrate has very strong role in promoting certain phases, promoting certain kind of orientation and also any reactivity with the film. So, as a result choice of substrate is very important, it also affects what kind of atmosphere you can have inside the chamber whether you can have oxidative atmosphere or not; whether you can have a high temperature or not.

So, choice of substrate is important and then what is important is finally, structure and morphology. For many applications you require the structure and morphology to be as smooth as possible. So, objective is to choose conditions. So, that you end up with a 2 D growth then a 3 D growth; 3 D growth typically leads to higher roughnesses as compared to 2 D growth. So, these parameters need to be kept in mind in order to grow high quality films and the interplay of all these parameters is extremely important.

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So, essentially in this final lecture we have looked at bulk and thin film processes. And bulk processing is rather simple as compared to thin film processing; thin film processing

requires extensive tooling, because you need to control the dimensions and phase, and the transport of atoms. And as a result, physical vapour deposition processes which produce better quality films in general require extensive tooling in terms of pumping and in case of laser ablation also in laser. In case of chemical processes, chemical spin coating is a very efficient and very nice large area process, but there are some disadvantages such as it cannot make very good extremely thin films and morphology control can be little difficult; because it tends to give polycrystalline and rougher films.

On the other hand, chemical vapour deposition is a process, which is similar to physical vapour in terms of film quality, but again it is expensive, and it requires precursors, which can be sometimes toxic and undesirable. So, this is a sort of overview on thin film and bulk preparation of electroceramics. So, this is where we end this module as well as this course and there will be some questions, and some sort of references on the course website, where you can look at the required information or required reading which is required for this course.

So, I hope you have enjoyed this course. I certainly enjoyed teaching this course and if you have any questions or queries, you can post them online, which can be looked into, and which I can hopefully answer to your satisfaction.

Thank you.