Non - Metallic Materials
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Module - 08
Thin film growth and fabrication of devices
Lecture - 41
Thin film growth techniques, thermal evaporation, CVD, sputtering, CSD

Welcome to my course Non-Metallic Materials, and we are in module number 8, Thin Film Growth and Fabrication of Devices. This is lecture number 41, which will cover Thin Film Growth Techniques, Thermal Evaporation, Chemical Vapor Deposition, Sputtering and Chemical Solution Depositions.

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So, initially I will start with physical vapor deposition methods. And in the last lecture I have briefly covered the thermal evaporation technique. Then, we will cover chemical vapor deposition followed by chemical solution deposition, and finally, the characteristics of the substrates that is basically used for thin film growth.

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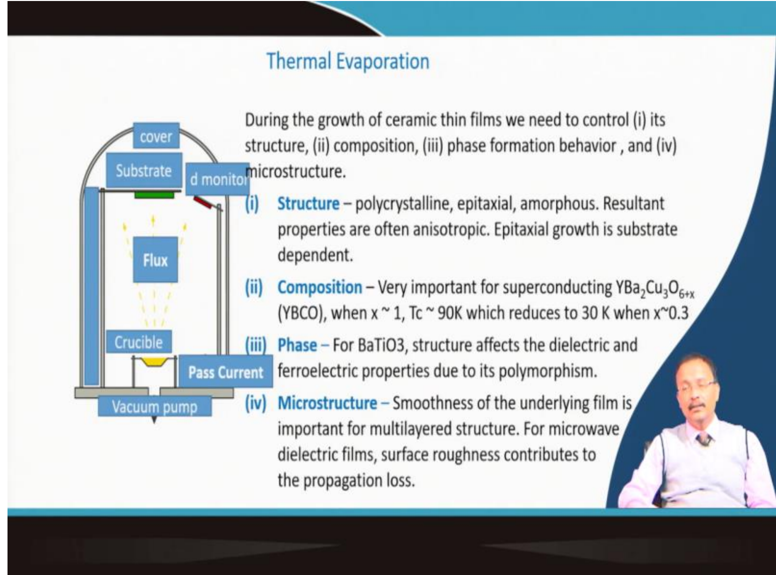

So, first we will talk about thermal evaporation in continuation of the last lecture. So, in case of this not only thermal evaporation, but for any thin film deposition technique we basically need to control 4 important parameters.

The first one is of course, a structure, structure of the thin film that is being deposited. And it should be similar or same as compared to the initial starting material. Then, composition, the translation of composition it should be stoichiometric in nature that also needs to be controlled.

And the phase formation behaviour also should be identical because there is a phase transition takes place. Initially, it is amorphous in nature, and then it transform into a crystalline structure. So, this phase formation behaviour is important. And finally, the microstructure plays a major role in controlling the thin film properties. So, microstructure control also is an important aspect.

So, as far as the structure is concerned, we were talking about whether it is a polycrystalline film, that you are interested in or epitaxial quality film or if it is preferred to remain amorphous the like the as deposited film. So, the resultant property of that particular film which we are depositing that is grossly dependent on this type of structure.

So, for example, if it is an isotropic in nature, then epitaxial growth is very much or even textured growth is also very much needed. And of course, this depends on the underline substrate. So, the substrate basically controls the nature of this textured whether it will be textured growth or it will be epitaxial type of growth the epilayer that is controlled by the substrate.

Composition sometimes is very important. As you know yttrium barium copper oxide is a very well-known super conducting ceramic material. So, oxygen and stoichiometry that is very very important in case of the grown film. And if the value of the oxygen this is given as 6 plus x and stoichiometry 7, so if x is nearly 1, then your transition temperature to the super conducting state it is 90 Kelvin. So, if it is 0.3 for example, then it goes much lower around 30 Kelvin.

For barium titanate as I have earlier described due to a polymorphism, its dielectric and ferroelectric properties are grossly dependent. So, it is important at what form the film is deposited, after annealing what structure it adopts. And accordingly its dielectric and lattice parameter, lattice parameter and its properties will be changed based on the phase that is present whether it is in tetragonal structure or whether it is in rhombohedra or orthorhombic structure.

So, microstructure plays a major role. Smoothness of the underlying substrate is definitely important and particularly in case of multilayer film, which is usually grown for antireflection coating as for example.

So, in case of the multi-layered film structure the not only film substrate interface, but followed by the other surface smoothness is important for the growth of the next layer. So, that basically for dielectric thin film also it is important, because this surface roughness that contributes to the propagation loss in case of microwave dielectric thin film like strontium doped barium titanate, BST.

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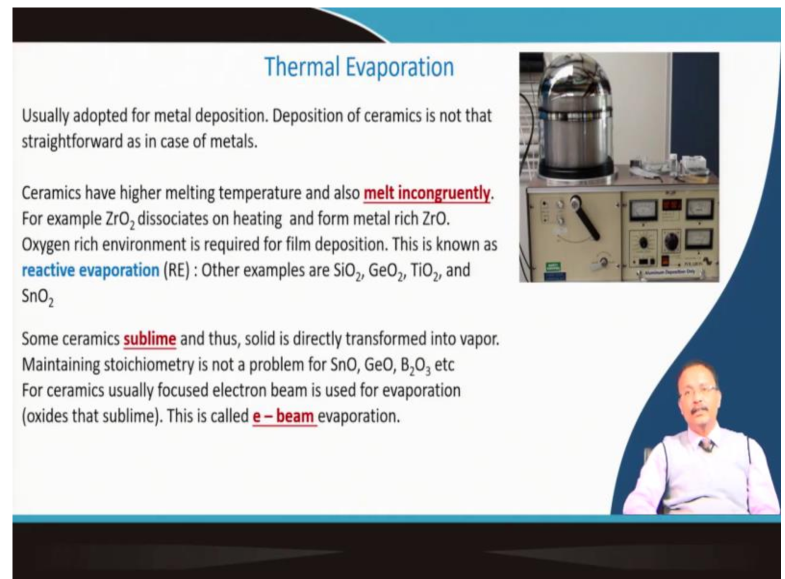

So, thermal evaporation is usually adopted for metal deposition and deposition for ceramic is not very straight forward because of the reason that many of the ceramic that melts incongruently.

The composition is very much different from the starting material. So, if you are taking for example, zirconium dioxide deposit it, although it is very difficult to evaporate zirconium dioxide ah. But instead of the thermal evaporation you can go by electron beam evaporation focus the electron beam into the crucible to evaporate it.

But the resultant film is metal rich zirconium monoxide forms. So, for that case you need to have a oxygen rich environment is required, so that the stoichiometry is maintained. So, this type of evaporation technique is called reactive evaporation technique. So, for example, silicon dioxide, germanium oxide, titanium oxide, tin oxide, all of them have this problem of incongruent melting. So, you need to have a oxygen rich ambient certain.

Ceramic material, they basically sublime from solid state directly it goes to the vapor state. So, the problem of maintaining the stoichiometry is not that apparent for this kind of film. For example, since tin monoxide, beryllium oxide, germanium oxide, bismuth oxide, I am not sure about beryllium oxide, but tin monoxide germanium oxide B_2O_3. So, those things are important they directly sublime.

For the ceramics which as I said they are having very high melting temperature. So, sometimes electron focused electron, beam, they are used and this type of deposition is called the electron beam deposition. A typical thermal evaporation technique is shown in this figure.

And as you can see once the metal, here in case aluminium was deposited it basically coats not only the substrate, but the throughout the bulgier it is coated internally. So, each and every time you will have to clean the bulgier after it particular deposition is over.

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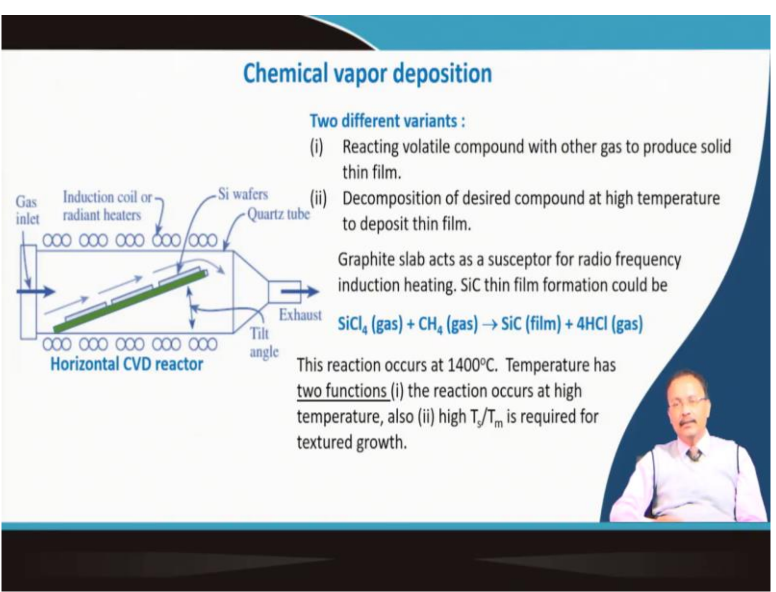

So, chemical vapor deposition that is unlike the physical vapor deposition, sometimes of this chemical vapor deposition is having distinct advantage. So, mostly two variants of chemical vapor depositions are there. So, one is the reacting the volatile compound with other gas to produce the thin film. So, that is one variety.

And other one is the decomposition of the desired compound at a very high temperature to form a film. So, you can see a graphite slab is used, a slanted graphite slab. There are various types of CVD reactor, but this one is very popular one. We call it is a horizontal CVD reactor. So, this graphite slab that act as a susceptor for the radio frequency induction heating.

And silicon carbide for example, I have taken the example of silicon carbide formation. So, silicon carbide is getting deposited on the silicon vapor and the gas that is initially used is $SiCl_4$, and it reacts with methane gas.

So, it is reacting the volatile component with the other gas to form silicon carbide and acid vapor is also produced in the process. Through the exhausts the gases are taken out and directly this reaction occurs at about 1400 degree Celsius.

And eventually, the temperature has two important effect, first this reaction is operative at that high temperature, and also in many of the instances as I have shown the module June 3, if you remember, from last lecture the substrate and melting temperature. In fact, the substrate temperature high substrate temperature is required for the textured growth. So, therefore, this high temperature is actually used.

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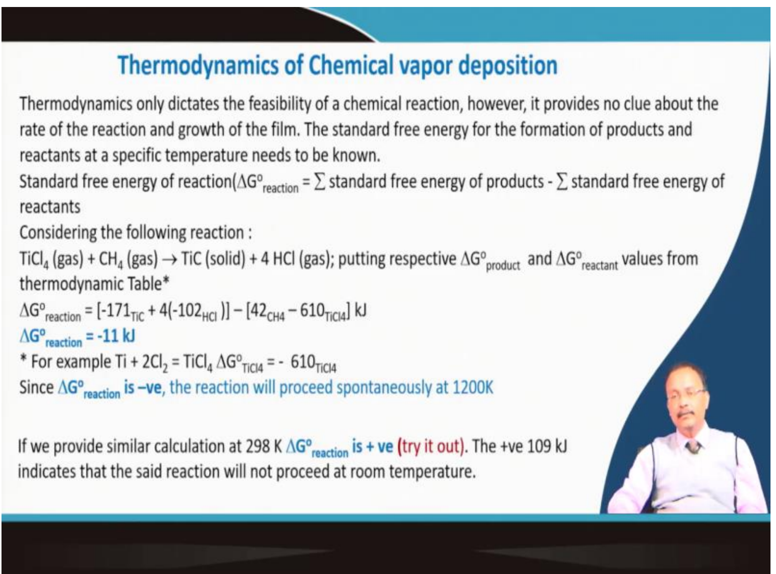

Now, the thermodynamics of this chemical vapor deposition that is pretty straight forward and basically the thermodynamics dictates whether this reaction is feasible. Otherwise, it cannot tell that whether if the reaction what is the time that we will required and what is the rate of the growth that will be there. So, thermodynamics is silent about this. But it will only tell you whether this reaction is feasible.

And this is the very standard method the to actually know whether this reaction is feasible. So, you need to know the standard free energy of the product and standard free

energy of the reactant. And that will give you some kind of idea that what are the temperature required for this reaction to occur.

So, the standard free energy of reaction that is the summation of the standard free energy of the product minus the summation of the standard free energy of the reactants. So, if you consider this reaction titanium tetrachloride in gaseous form is reacting with methane gas to form titanium carbide in thin film form with the acid vapor.

So, these values of standard free energies of this product as well as the reactants that is available from standard thermodynamic table. And for example, for this reaction titanium is reacting with chlorine gas to form $TiCl_4$. So, this is a feasible process with the standard free energy is about minus 610 kilojoule.

So, similar to that you have the free energies for all the reactant and the reactants as well as the product. So, you do this calculations. So, this is for the product and this is for the reactant. And then finally, it shows that this reaction is this standard free energy is negative, but at 1200-degree Kelvin, I have taken this standard free energy. So, this reaction is feasible at 1200-degree Kelvin.

But if you do the same calculation taking the free energy values at room temperature you will see that it is positive. So, check with a thermodynamic table and you will see that this is a positive value you will get about 109 kilojoule. And that indicates at the room temperature nothing will happen, so you need to heat the substrate temperature in order to make this thing feasible.

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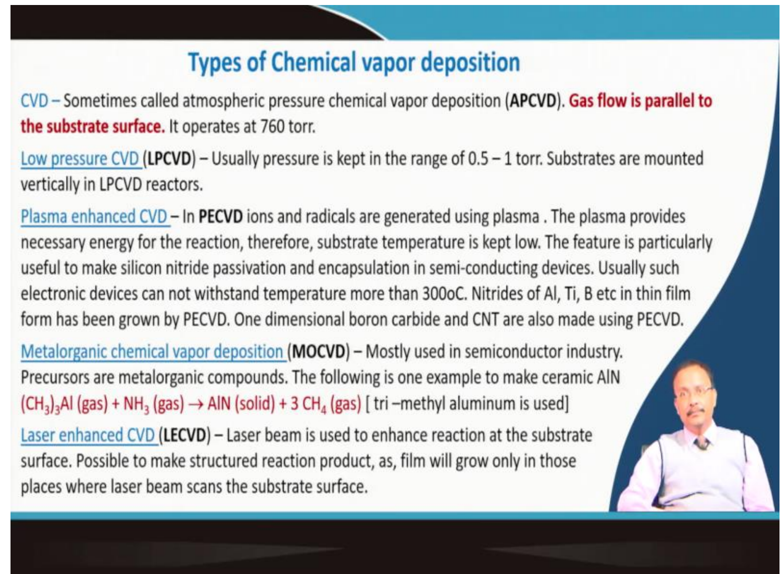

So, there are various types of chemical vapor deposition techniques and since the usually chemical vapor deposition is done at atmospheric pressure. We call it is atmospheric pressure CVD and gas flow here in this case is parallel to the substrate surface which are slightly in client and the reaction takes place and it deposits on the substrate surface. So, it operates at 760 torr.

Low pressure CVD, it is abbreviated as LPCVD. So, the usually the pressure is kept about 0.5 to 1 torr. And in this case substrates are vertically mounted during this LPCVD process. There is another variant which is plasma enhanced CVD. So, in PECVD, ions and radicals are generated using a plasma and this plasma. In fact, provides the necessary energy for the reaction to takes place and therefore, you can keep the substrate temperature low.

And this is particularly useful for silicon related fabrication because as you know that sometimes silicon nitride passivation layer is given in silicon circuitry. And there you cannot go beyond 300 degree Celsius otherwise it will degrade the substrate itself. So, here plasma enhanced CVD is important.

Nitrides of aluminium, titanium, boron, etcetera that all of them can be made by this plasma enhanced CVD technique. And sometimes one-dimensional structure for example, for boron carbide and also carbon nanotube they are also made by plasma

enhance CVD technique. And aluminium nitride for example, that is very good material because it has very high thermal conductivity. So, it dissipates heats very fast.

Other variants are metalorganic chemical vapor deposition, and that is also very grossly used in semiconducting semiconductor industry. And usually, the precursors is in the form of metalorganic. And I have cited one example to make this aluminium nitride which is an important ceramic material. And the precursor here is tri-methyl aluminium is used, it reacts with ammonia gas to form aluminium nitride and methane gas is a by-product.

Sometimes laser enhanced CVD abbreviated as LECVD that is also used. So, this laser beam is basically used to enhance the reaction rate at the substrate surface. And it is also possible to grow nanostructured material because you can scan the laser beam and you can make the product form at a very specific place. So, it is a nanostructured growth that is possible wherever the laser beam heat the substrate surface.

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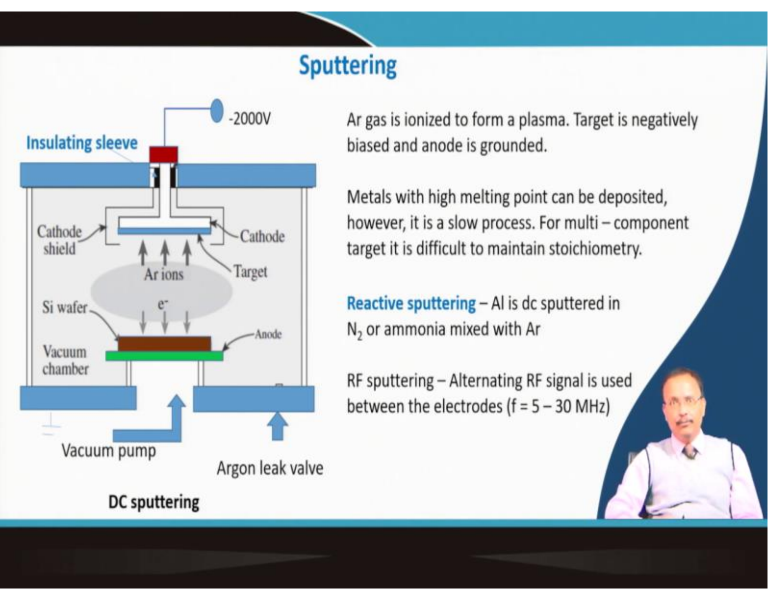

The next technique that I am going to cover is the sputtering technique, and this is a very simple technique. And particularly DC sputtering that is very routinely used for metal deposition.

So, here it is again a chamber is used and the chamber is first evacuated. So, all the air goes out. And you know that here you have the. So, called cathode where the target is

fixed, the metal that you want to deposit on the substrate is fixed here. And the substrate you keep at the bottom in this kind of geometry. And then you leak organ through this leak valve. So, organ is there and you bias this cathode with a very high negative potential, and substrate is used as anode, this plate is used as anode which is basically grounded.

So, organ gas is ionized and form a plasma, and then this organ is attracted towards the cathode plate. So, it basically bombards and then (Refer Time: 17:31) the metal atom and this metal atom is showered on the substrate it also coats the other surface as well. But basically you form a very thin layer of this metal.

So, the organ it is important for the organ gas to form the plasma and organ is positively ionised. So, the target will have to be maintained at a negative potential. And metals those metals which are having very high melting point like gold palladium gold palladium alloy those things can be deposited by this technique, but it is basically a very slow technique.

And if you have a multicomponent target not a single component and due one to translate the stoichiometry of multicomponent target here in the thin film it is relatively difficult. Sometimes reactive sputtering is also done, aluminium is DC sputtered in presence of nitrogen and ammonia that to that is mixed with the organ gas and it forms aluminium nitride, nitride ln film.

For ceramic usually RF sputtering is used. So, alternate RF signal is used between this two electrode the frequency is kept typically 5 to 30 megahertz. Because in metal film it is ah, ok, but in ceramic film there will be a charging affect, so you need to have a RF source and sometimes a magnetic field is also applied and those kind of deposition is called RF magnetron sputtering.

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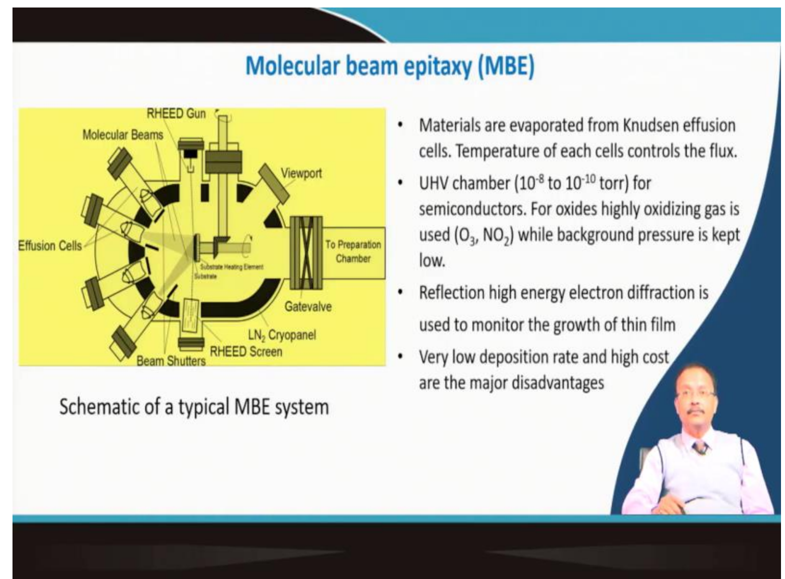

Molecular beam epitaxy is basically material is evaporated from this Knudsen effusion cells. And this temperature of each cell is controlled by current.

And so, the molecular beam forms and it gets deposited at the substrate. And usually, very very high vacuum is required in case of semiconducting film. For oxide usually oxidising gas is used the background pressure need not to be that low as tend to the minus 8 tend to the minus 10 torr.

And a reflection high energy electron diffraction this RHEED gun is equipped this MBE system is equipped with this that is to know to monitor the growth of the thin film. Problem of this MBE is its very low deposition rate and this systems are extremely costly.

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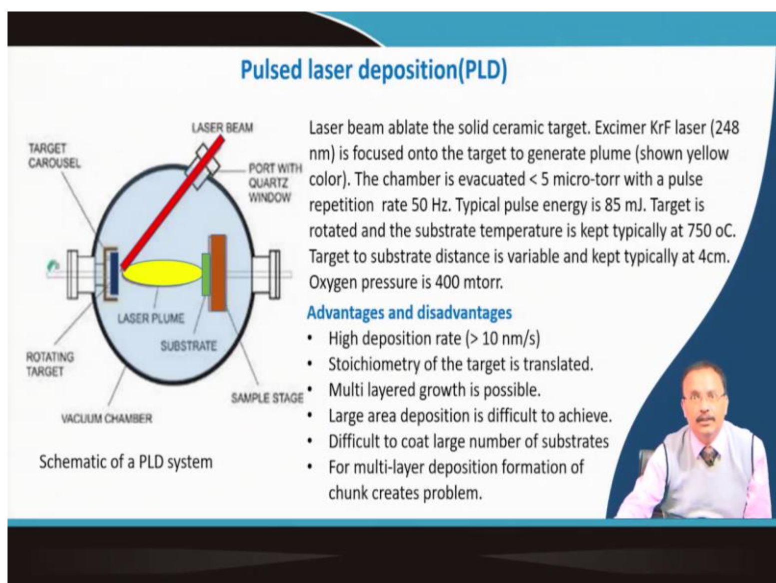

A suitable alternative of a high quality film deposition is pulse laser deposition. Here the laser beam basically ablets a solid ceramic target and this is particularly useful for ceramic thin film. Usually, excimer KrF laser with having a wavelength about 248 nano meter is focused on the target. The target is basically it is rotated for uniform deposition. And it generates a plume shown in this yellow colour.

Usually, a 5 micro torr pressure is sufficient and the pulse is applied. This laser is not a continuous, but it is a pulse is applied. So, that is why sometimes I mean all the time it calls a pulse laser deposition. Typically, the pulse energy is about 85 millijoule and the rate repetition rate the frequencies about 50 Hertz.

And substrate temperature is kept high because of this atom mobility surface diffusion in particular. And then when the film goes then the diffusion inside the bulk that is also possible to make a crystalline film from amorphous to crystalline phase transformation.

And target to surface substrate distance also can be manipulated and usually oxygen pressure is maintained here for the oxides and typically 400 millitorr kind of pressure is adopted.

So, the advantageous think of pulsed laser deposition it says high deposition rate and the stoichiometry of the target is rightly translated. That is another advantage it is otherwise difficult in RF sputtering, RF sputtered thin film for ceramic material.

You can have a multi-layered growth, you can have several targets like this which is equipped with a shutter. So, one after another you can change the target and on the substrate you can deposit layer by layer growth. For certain application it is very important to have for example, super lattice kind of growth that is possible by pulsed laser deposition ah. But the problem is that it is difficult to have a homogeneous film in a large area. So, coating is difficult.

And for multi-layer deposition formation sometimes the formation of the chunk from the substrate. So, it is not that smooth on the substrate surface, chunks are comes and that make the surface quite rough in nature.

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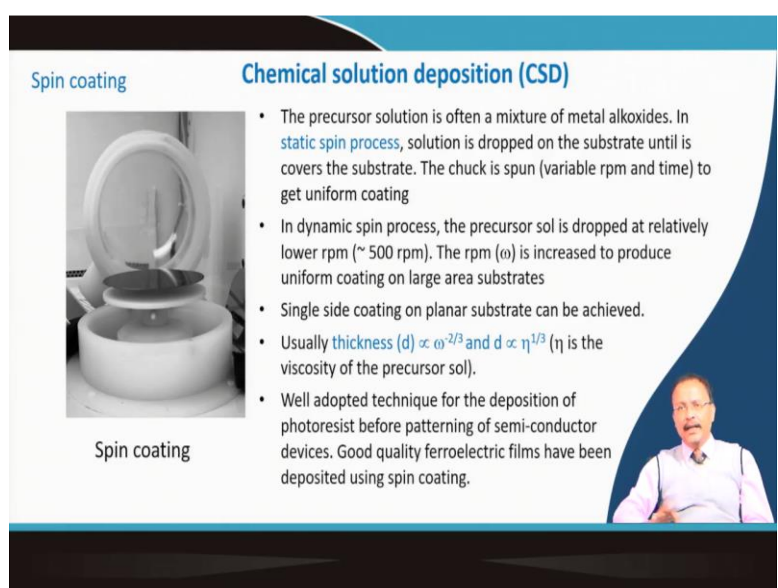

Cost effective deposition is this chemical solution deposition and spin coating is one of the technique. Here you can see the whole vapor of silicon that is kept on a chuck and you apply a vacuum here is to hold this substrate.

And then you can deposit your precursors sol and start to rotate this chuck with the substrate. So, the precursor sol evenly spread here to form a thin film.

So, there are two different way to do that, and usually we use alkoxide precursor for the oxide film deposition. Initially, the film is amorphous and it is baked at higher temperature to remove the organics, and still higher temperature for the annealing; that

means, crystallization of the film to take place. So, two step heat treatment is required for this kind of oxide film.

So, we have two process, first one is a static spin process where the solution is initially dropped here, then it spreads cover the surface and then you apply a very high rotational speed to spread it uniformly.

And the variation, slight variation to this process is a dynamic spin process where the precursor initially drop and then it rotates at relatively lower rpm, around 500 rpm. And progressively, this rpm is increased to produce a very uniform film on a very large area surface substrate. It is not otherwise possible to grow this kind of homogeneous film with perfect stoichiometry by other technique like PLD.

So, in that way this CSD deposition by spin coating technique, chemical solution deposition by spin coating technique is really attractive technique. And there are various empirical relations available to determine the film thickness and usually it is inversely proportional with the rotation speed. As you can see it goes with minus 2 by 3 with the omega rotational speed or it is also dependent on the viscosity of the precursor solution. And it goes with one-third of the viscosity of the precursor sol.

So, it is a very well adapted technique for the photoresist before patterning in the semiconducting device. And as I said good quality ferroelectric film that have been deposited using this spin coating technique.

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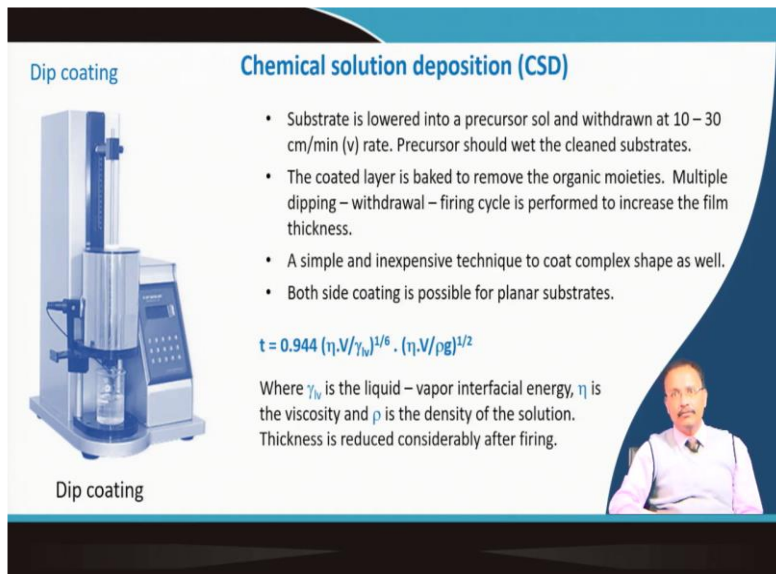

Other variant is dip coating and as you can see in case of a dip coater it is a commercial dip coating unit. You take the precursors sol here and substrate is hold in this vertical kind of holder and it is dipped at a certain rate. And then, withdrawal speed is controlled 10 to 30 centimeter per minute and this precursor of course, should wet the surface properly.

And then, this coating is gone through this furnace and the organic moiety is are baked to remove the organic moieties. And multiple dipping and withdrawal and also the firing it can continue to increase the film thickness. It is a very simple technique. Inexpensive as well, and unlike the spin coating technique here using dip coating you can coat complicated shape.

And it is also possible to coat both sides of the substrate. A typical empirical relation to control the thickness is given by this. So, you can see that this liquid vapor energy is important, viscosity is important, and density of the solution is important to control the thickness.

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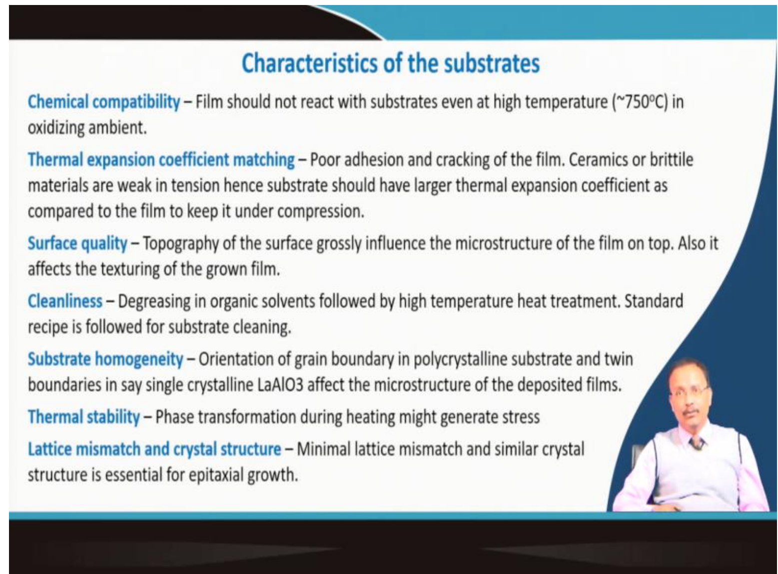

And this thickness is considerably reduced when you heat treat the film, so after it getting, after it gets crystalline, then the thickness is reduced in a considerable way.

Substrate characteristics is important and first it should be chemically compatible, it should not react with high temperature with the film material, then the substrate thermal expansion should be matched well. And as you can understand and I have covered it also in my earlier lecture. The ceramic is usually, they are weak in tension and strong in compression. So, you will like that your film should always be under compression.

So, substrate should have larger thermal expansion coefficient. So, during cooling it will shrink more, and so it should have a larger thermal expansion coefficient as compared to the film and film will be under compression as a result.

Surface quality of the substrate is important. The topography of the surface influence the microstructure of the grown film. It also affects as I have said texturing and epitaxial nature of the film. Usually, the cleanliness of the substrate is important. There are various recipe followed in different industrial practice that how to clean the substrate. So, that the precursor or the deposited film perfectly wets the surface and the degreasing is important.

Surface should be homogeneous as well, particularly for the single crystalline substrate. The twin boundary is one prominent defect and that controls the microstructure of the

film in; so, this orientation and the quality of the single crystal is important for a good growth of the film.

Thermal stability is important. It should not undergo any phase transition, because you know the when phase transition takes place it generate stress and that is translated into the thin film structure. So, that is important. So, there should not be any polymorphic phase transformation. And finally, lattice mismatch and crystal structure, they are so important for the epitaxial quality of the thin film which is grown on top of it.

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So, the study material is the from the book by Barry Carter chapter number 28, which covers thin film thin films and vapor deposition. Various kinds of thin film depositions are described there followed by the other book.

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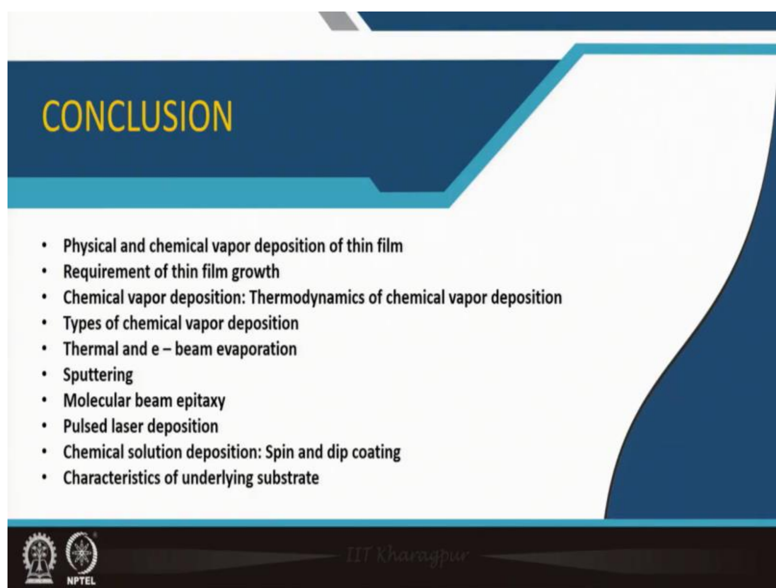

And in this lecture, we talked about physical and chemical vapor deposition of the film, and what is required for a ideal thin film growth. Then, we talked about chemical vapor deposition, the thermodynamics factor that control the chemical vapor deposition feasibility at a particular temperature. Then, we talked about various types of chemical vapor deposition, then we introduce thermal and e-beam evaporation concept followed by sputtering, RF sputtering, and DC sputtering was covered.

Then, we just touched the molecular beam epitaxy root, then we introduced the pulsed laser deposition and finally, chemical solution deposition, spin and dip coating, and then the characteristics of the underlying substrates are highlighted.

Thank you for your attention.