Surface Engineering of Nanomaterials
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Lecture - 30
Liquid Phase Techniques

Hello, in this particular lecture, we are going to discuss about the liquid phase techniques for thin film depositions on to the substrate itself. So, first we have to know that what is the liquid phase technique actually.

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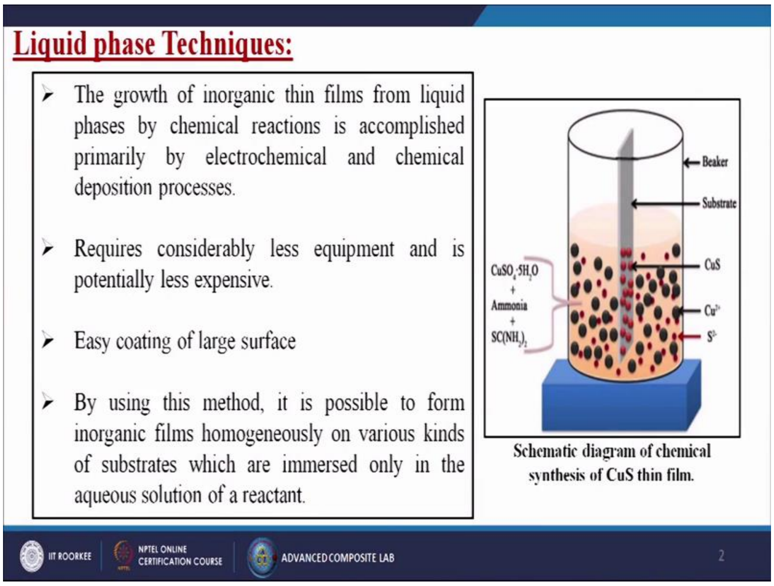

The growth of inorganic thin films from liquid phase by chemical reactions is accomplished primarily by electrochemical and the chemical deposition process. So, simply we are having some kind of solvents, we are dipping our substrate into that solvent inside the solvent then there is some kind of chemical reactions is taking place in between the taking place in between the substrate and to the solvent and they are following some new materials and that that new materials forming a coating on to the substrate itself.

Requires considerably less equipment and is potentially less expensive, easy coating for the large surface area only we have to check it out that our substrate should be fully immersed in to the solvent itself. By using this method it is possible to form inorganic films homogeneously on various kinds of substrates which are immersed only in the aqueous solutions of reactants. So, this is also a one kind of considerations. So, here simply you can see that we are taking some kind of substrate then we are having the beaker then when we are dipping in through are the solvent, the solvent is a mixture of copper sulphate with ammonia and with the thiourea then it is releasing some kind of copper ions and then the sulfur ions these copper and sulfur slowly slowly depositing on to the substrate itself and they are forming the copper sulfide. So, this is the overall diagram that how we are forming the copper sulfide on to the substrate material.

Next we are going to discuss about that why we are using these techniques, what are the advantages of these particular techniques. As we remembered that in our last several lectures, we have discussed about some kind of vapor mechanisms some kind of thermal mechanisms. So, here we are doing this kind of for the liquid mechanisms or maybe that liquid phase mechanisms.

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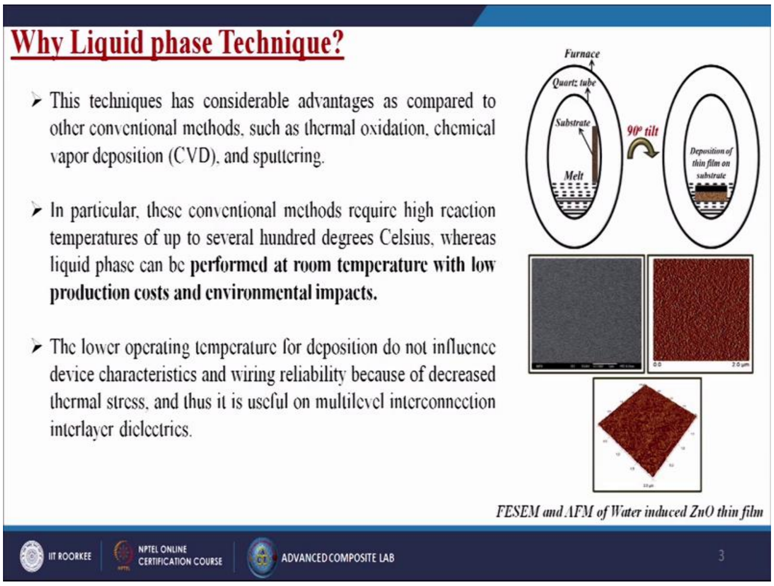

These techniques as considerable advantages as compared to other conventional methods such as thermal oxidations chemical vapor depositions and the sputtering techniques, in particular this conventional methods require high reaction temperatures of up to several hundred degree Celsius whereas, liquid phase can be performed at room temperature with low production costs and the environmental impacts.

Here we only we need the suitable solvent and we need that substrate simply we have to deep in to that the experimental cost is also very very less there is no need of any expensive equipment and this one also requires the less space and also it can be easily done and the costing of the solvent is also very very less sometimes of course, for some special cases maybe it will be expensive, but not up to that much level than other methods. The lower operating temperature for depositions do not influence device characteristics and wiring reliability because of decreased thermal stress and thus it is useful on multilevel interconnection interlayer dielectrics.

Here is the example. So, we are having the quartz tube, it is surrounded by the furnace then we are having the solvent and we are having the substrate. So, simply by rotating this one, we are putting this substrate into the solving solvent then chemical reactions is taking place by which we are forming the layer on the substrate itself and the below one is the FESEM and the AFM images that how we are you making that water induced zinc oxide thin films on to the substrate itself.

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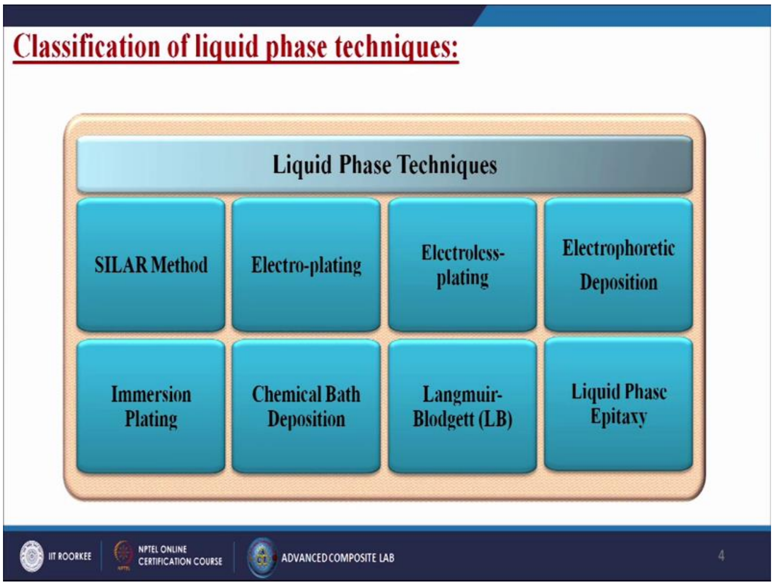

Now we are going to discuss these liquid deposition methods into more details. So, here we can see that there are a totally 8 methods or maybe that 8 techniques whatever we can apply for this liquid phase techniques. So, first one is called the SILAR methods, then Electro-plating, Electroless-plating, Electrophoretic depositions, Liquid Phase Epitaxy, Langmuir Blodgett, Chemical Bath Depositions and the Immersion Plating. So, there are a total 8 numbers of modifications techniques are available for this particular purpose.

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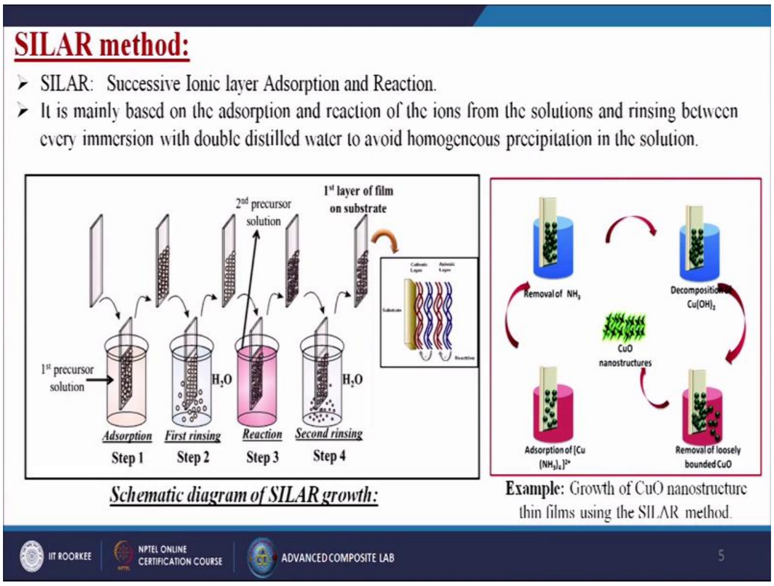

First one by one we will go in to the details. So, first we are going to discuss about the SILAR methods; SILAR, SILAR methods, the SILAR totally stands like successive ionic layer adsorptions and the reaction. So, SILAR is the short form of this sentence. Then it is mainly based on the adsorption and reactions of the ions from the solutions and rinsing between every immersion with double distilled water to avoid homogeneous precipitations in the solution. So, here from this particular line we can understand that we are following several steps in this particular reaction first you have to deep it then you have to take it out then you have to clean it then you have to deep it into the next solvent. So, by this way we can do the coatings of this particular process.

First we are taking the first precursor solutions. So, simply we are doing the adsorption process than we are taking in out. So, some precursor molecules is attached with that substrate itself then we are putting into the water. So, we are rinsing it then we are putting into some reaction a chamber where this solvent is reacting with the first precursor materials and then again we are deleting or maybe that rinsing it into some water and then we are getting the first layer of film on substrate.

Simply first we are initially doing the adsorption process then we are it is followed by the rinsing process. So, by this way we are doing the coatings on to the substrate itself. So, what are the methods? So, this is the very nice examples that growth of the copper oxide nanostructures thin films by using the SILAR methods. So, simply first we are taking the adsorptions of the tetramine copper to ion on to the substrate itself then simply we are removing the ammonia because when we are dissolving into some water molecules or maybe that water liquid water. So, simply that ammonia it is removing it then we are decompositions of the copper hydroxide once again then again we are removal of loosely bounded copper oxide and then finally, we are get the copper oxide nanostructures on to the substrate itself.

By these methods one is called the adsorption methods and then it is called the rinsing methods by applying these methods then again the reaction methods. So, by applying these techniques we are doing the modification surface modifications of our substrate.

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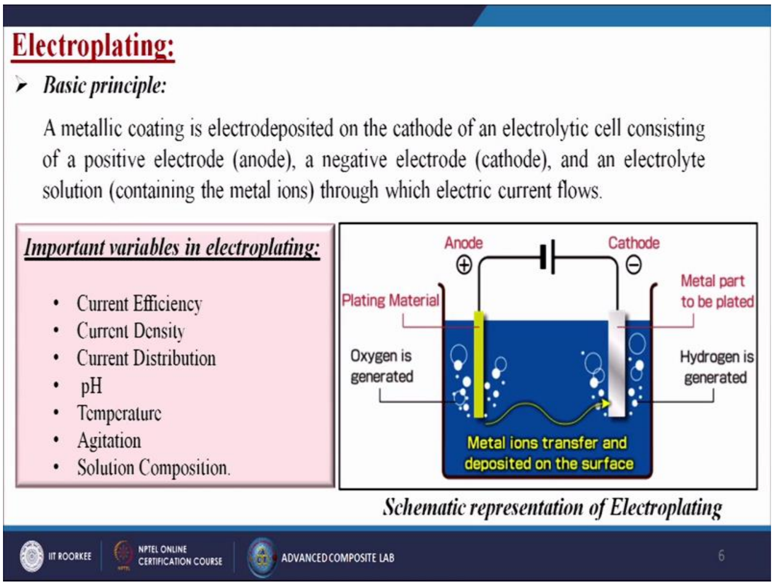

Next one is the electroplating techniques, it is not the newer one it is oldest methods still we are using this kind of methods for our normal samples because it is it can be easily done and it is also the less expensive methods and easy it can be easily controllable.

What is the basic principle a metallic coating is electrodeposited on the cathode? On an electrolytic cell consisting of a positive electrode which is known as the anode and a negative electrode is known as the cathode and then electrolyte solutions containing the metal ions through which electric current flows. So, from this particular figure we can understand that we are taking the anode we are taking the cathode then we are taking some kind of liquid which is nothing but the known as the electrolytic solutions.

So, here we have to keep our substrate on to the cathode part and whatever the materials we are going to deposit on to our substrate we have to keep that material into the anode part then I have we have to make certain kind of potential difference in between the cathode and anode so that these anode materials will release the ion and then that metal ions will transfer and it will deposit on to our cathode materials; that means, on to our substrate itself. By these techniques we can do the modifications so that is why here we are using certain kind of electrical energy. So, that is why it is known as electro plating techniques.

Here the important variables in electro plating techniques are current efficiency, current density, current distributions, then pH of that particular solution, temperature agitations and the solution combinations sorry compositions. So, these all are the different input variables for these electroplating techniques which can determined the efficiency for these particular purpose here right hand side is the figure already whatever I have discussed. So, this is the schematic representations of electroplating techniques.

Next we are going to discuss about the advantages and disadvantages of these particular techniques.

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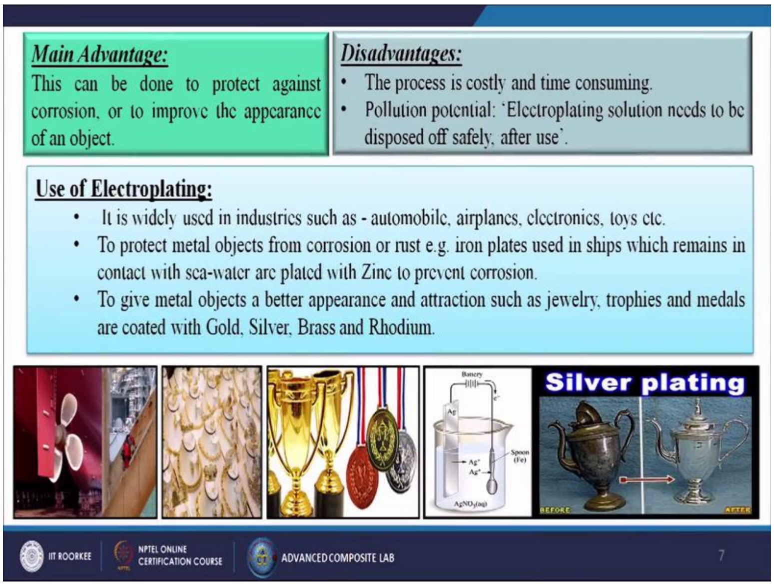

So, main advantage this can be done to protect against corrections or to improve the appearance of an object what are the disadvantages the processes costly and time consuming. Pollution potential electroplating solutions need to the disposed of safely after use because it is reacting it is one kind of solutions maybe sometimes it can be toxic or maybe some kind of it can be maybe the strong acid. So, after finishing the experiment we have to take care of these worst materials otherwise this can create some kind of pollutions to the environment itself.

Use of electroplating techniques; it is widely used in industries such as automobile, airplanes, electronics, toys, etcetera to protect metal objects from the corrosions or rust. So, simply we are doing some kind of stable material coating on to that substrate on to the substrate so that that stable material cannot react with some rain or may some moisture or maybe some other chemicals so that it can give protections on to our substrate materials to give metal object a better appearance and attractions such as jewelry some kind of mementos some kind of gifts some kind of trophies medals are coated with gold silver brass and the rhodium by this particular techniques. So, here we are doing the silver plating on to the cups or maybe the mementos this is before picture and this is the after picture we are doing it for some kind of jewelry we are use it some kind of medals mementos and all these kind of techniques.

Next we are going to discuss about the electroless plating. So, now, in our last lecture, we are discussing about the electroplating techniques where we are applying the current or maybe the voltage, but here this is known as the electroless plating. So, from the name itself here you can understand that here we are not going to use any kind of current or maybe any kind of voltage.

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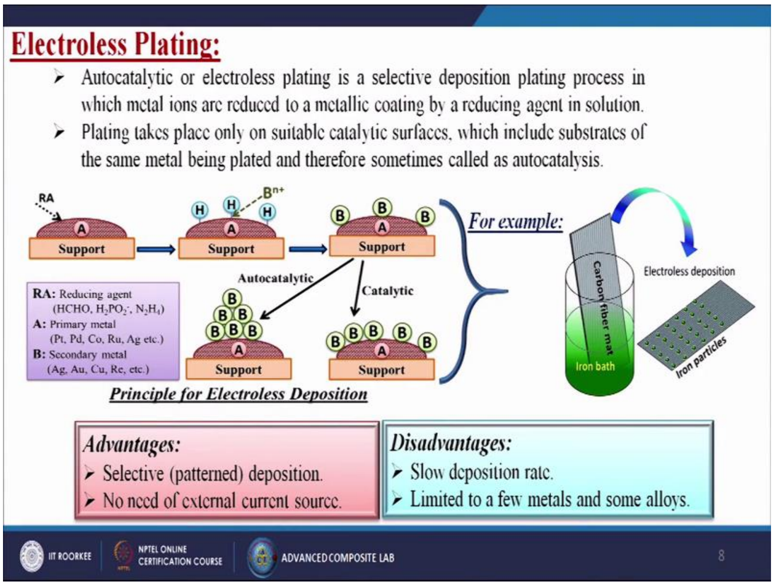

Simple autocatalytic or electroless plating is a selective deposition plating process in which metal ions are reduced to metallic coatings by a reducing agent in solution itself. Plating takes place only on suitable catalytic surface which include substrates of the same metal being plated and therefore, sometimes called as autocatalysis.

Whatever the materials we are going to take maybe sometimes the substrate of same materials or maybe some other materials and not only that, here we are not going to use any kind of current or voltage. So, that is why it is called as electroless plating and it is purely chemical reaction based techniques. So, from this particular figure we are going tell you that how you are doing or maybe how you are following this kind of techniques.

First we are having the support on top of that we are putting some kind of primary metals primary materials maybe anything that is platinum, palodium, copal, ruthenium or maybe the silver, etcetera then we are putting some kind of reducing agent on the top of that like HCHO, H 2 PO 2 or maybe N 2 H 4. So, we are putting then we are put a then creating that ions on that top of that primary metals then we are introducing the secondary metals like silver, gold, copper, then Re, etcetera and then it is reacting with the a materials and they are forming a layer on to the top of the a materials. So, either we can a do it by the autocatalytic methods or maybe the catalytic methods.

In the autocatalytic methods already I have discuss that which include substrate of the same metals being plated and therefore, sometimes called the autocatalysis. So, the same material we are applying on to that and for the catalytic metal maybe we can use the different metal also.

What are the advantages? Generally selective patterned depositions can be done no need of external current sources as already I have discussed. Disadvantages: slow deposition rate because this is the purely chemical based reactions it depends upon the solvent, it depends upon the solvent quantity, it depends upon the material which we are going to coat and then limited to a few metals and the some alloys this is not means it is applications is not the versatile.

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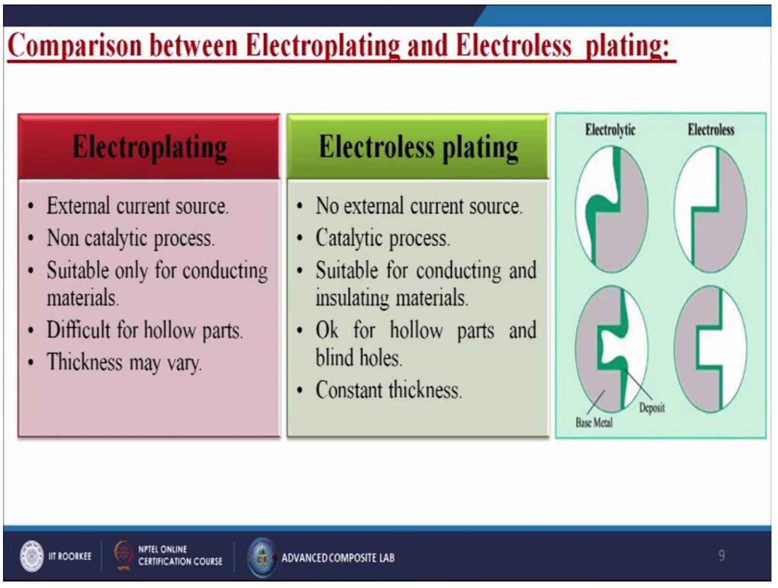

Then we are going to discuss about the comparison between the electroplating and electroless techniques. So, these are the techniques actually for the electroplating external current source we are using non catalytic process suitable only for conducting materials because we are giving the potential difference in between the anode and cathode. So, both the materials should be electrical conductive. Difficult for hollow parts; thickness may vary.

For the electroless plating no external current source we are using it as a catalytic process suitable for conducting and insulting materials for hollow parts and blind holes constant thickness these all are the thickness that whatever we are achieving by the electrolytic process and the electroless process. So, this is the, in the gray color it is showing the best metals and green one it is showing that deposition of the material from this particular figure you can get that for the electrolytic reactions we are not getting the homogeneous thickness on to the substrate itself, but for the electroless techniques we are getting the homogeneous thickness for our substrate material.

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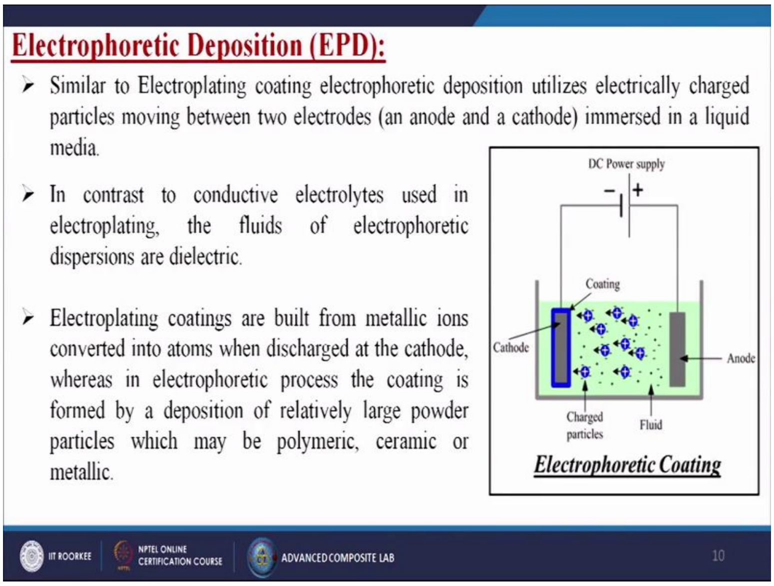

Next we are going to discuss about the electrophoretic depositions, in the short form we are calling it as EPD process, what the process tells similar to electroplating coating? Electrophoretic deposition utilizes electrically charged particles moving between 2 electrodes an anode and a cathode immersed in a liquid media the same thing over here.

Here we are using on some kind of charged particles over there we are using the fluid, fluid is nothing but some kind of electrolytic materials then we are applying the charge ions that charge ions is depositing on to the cathode itself. Then we here also we are using some kind of voltage and maybe the current in between the cathode and anode. In contrast to conductive electrolytes used in electroplating the flu the fluids of electrophoretic dispersions are dielectric. So, here we are taking from some kind of dielectric medium. Electroplating coating are built from metallic ions converted into atoms when discharged at the cathode where in electrophoretic process, the coating is formed by a deposition of relatively large powder particles which maybe polymeric ceramic or metallic these all are the advantages for these electrophoretic deposition process.

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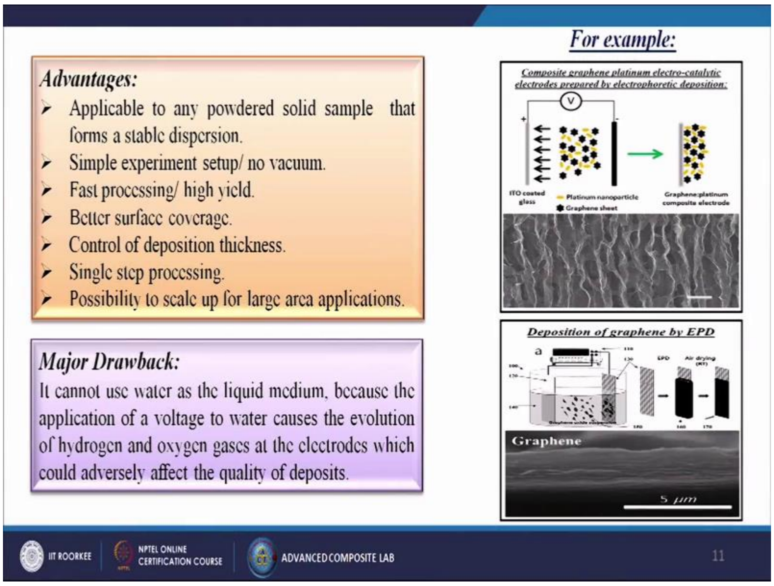

What are the advantages? So, applicable to any powdered solid sample that forms a stable dispersions simple experimental setup on no vacuum generally we are using, fast processing high yield means the output is more or maybe in large better surface coverage control of deposition thickness single step processing possibility to scale up for the large area applications.

There is certain kind of major drawbacks also. So, what are those? So, it cannot use water as the liquid medium because the application of a voltage of water causes the evolution of hydrogen and oxygen gases at the electrodes which could adversely affect the quantity of the deposits yes of course, because when inside the water we will apply some kind of potential difference it will generated the hydrogen on oxygen gas which will struck on to the cathode and anode materials and slower of the reaction rates. So, there are some few examples, whatever we are using by applying this process so composite grapheme, platinum, electro catalytic electrodes prepared by electrophoretic depositions.

We are having the ITO coated glass substrates, we are having the platinum nanoparticles and graphene sheet, simply they are mixing together and then they are forming that graphene platinum composite electrode on the glass substrate itself and below also the deposition of the graphene by the EPD methods. So, here also we are taking the graphene oxide a suspensions and then we are putting the EPO then we are air drying to the room temperature and there we are doing a graphene coating on to the substrate itself by this electrophoretic deposition techniques.

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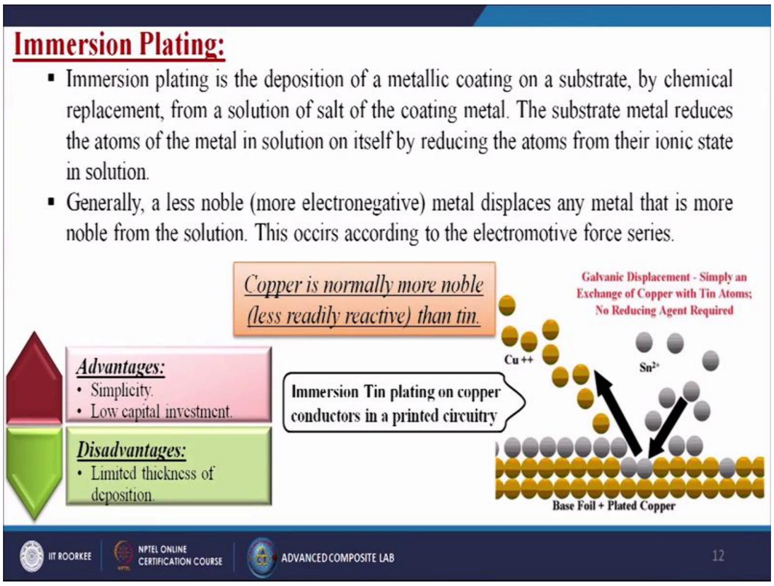

Next we are going to discuss about that immersion plating. So, immersion plating is nothing but it is also one kind of depositions of a metallic coating on a substrate by chemical replacement from solutions of salt of the coating metals. The substrate metal reduces the atoms of the metal in solutions on itself by reducing the atoms from their ionic state in solutions generally a less noble more electronegative metal displace any metal that is more noble from the solutions this occurs according to the electromotive force series.

Copper is normally more noble less readily reactive than tin. So, here the simple is that we are having a base foil with plus plated copper. So, simply we are taking this one into some tin solvent itself so that that copper ion by the galvanic displacement simply an exchange of copper with tin atoms no reducing agent is required. So, simply these copper ions are replaced by the tin atoms so like or maybe the tin ions. So by this way we are doing a coating on the tins on to our substrate materials. So, immersion tin plating on copper conductors in a printed circuit board generally we are doing like this. So, what are the advantages? It is very very simple methods low capital investment. Disadvantages: limited thickness of depositions can be possible by these techniques.

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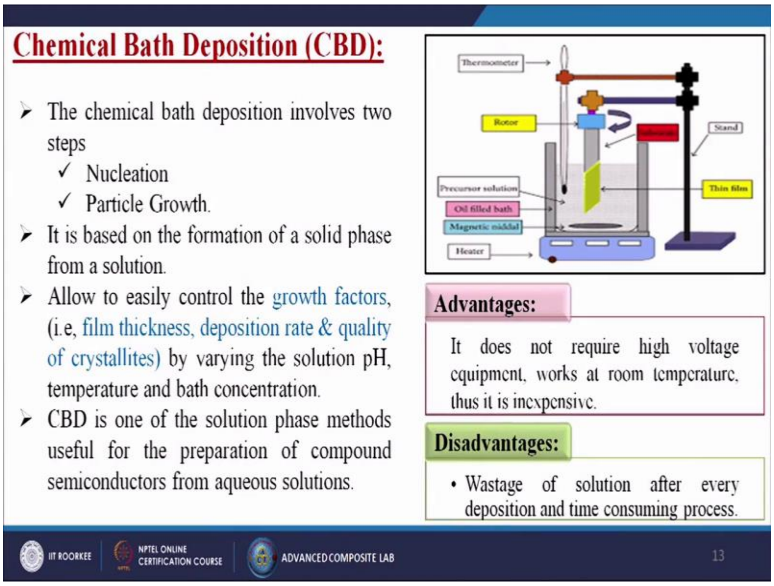

Next one is the called chemical bath deposition process, in short form it is known as the CBD process. So, the chemical bath deposition involves 2 steps, one is called nucleations, another one is called the particle growth. It is based on the formation of a solid phase from a solutions allow to easy control the growth factors, film thickness, deposition rate and quality of crystallites by varying the solution pH temperature and bath concentrations. CBD is one of the solution phase methods useful for the preparation of compound semiconductors from the aqueous solutions.

What are the advantages? It does not require high voltage equipment works at room temperature thus, it is less expensive. Disadvantages, wastage of solutions after every deposition and time consuming process because we have to allow to material for fully reactions and also the deposition rate is very very slow.

Then we are going discuss about the ultrasonic chemical bath depositions, only the thing is that here we are using some ultrasonic vibrations by which we can do the coatings onto our substrate itself.

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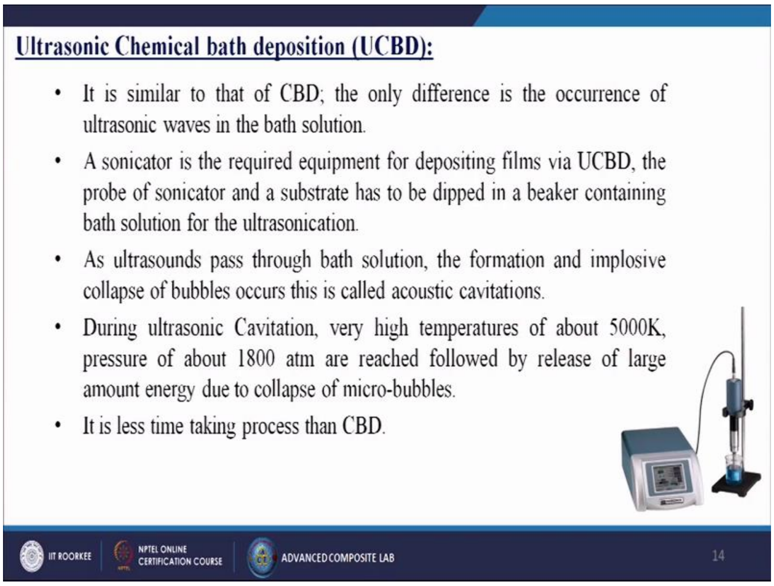

It is similar to that of CBD, the only difference is the occurrence of ultrasonic waves in the bath solutions a sonicator is the required equipment for depositing film via UCBD the probe of sonicator and substrate has to be dipped in a beaker containing bath solutions for the ultrasonications and ultrasounds pass through bath solutions the formation of and implosive collapse of the bubbles occurs this is called acoustic cavitations during ultrasonic cavitations very high temperatures of about 5000 Kelvin pressure of about 1800 atmospheric pressures are reached followed by release of large amount of energy due to collapse of micro bubbles. It is less time taking process than the CBD not only that it is more efficient than the CBD process.

Next we are going to discuss about the Langmuir Blodgett, it is also a one kind of techniques, the famous scientist is known as the Irving Langmuir and the Katherine Blodgett; they have invented these methods. So, just keeping their name, we have a given the name of the particular techniques is called the Langmuir Blodgett techniques.

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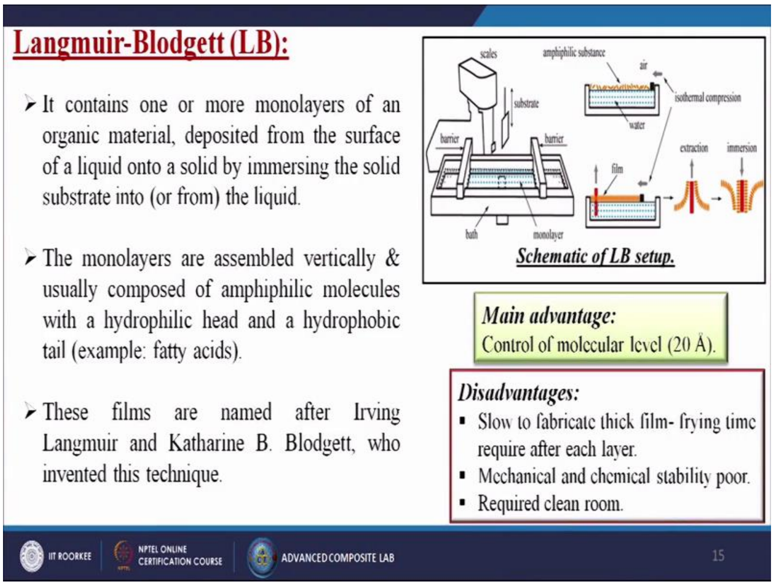

It contains one or more monolayers of an organic material deposited from the surface of a liquid onto a solid by immersing the solid substrate into the liquid form the monolayers are assembled vertically and usually composed of amphiphilic molecules with a hydrophilic head and hydrophobic tail examples the fatty acids. These films are named after Irving Langmuir and Katherine B Blodgett who invented these techniques so that is why we are calling it as a Langmuir Blodgett film or maybe that Langmuir Blodgett technique.

Here is the schematic diagram of the Langmuir Blodgett setups. So, we are having the substrate, we are having the barrier, we are having the scale and here we are having the bath in where we are keeping our monolayer’s materials. So, simply first instance we are dipping our substrate into that layer itself. So, generally we are doing it by the isothermal compression methods. So, simply we are dipping the film then first we are doing the extraction process then we are immersing process and like this way we are doing the coatings on to our substrate materials.

Main advantage: control of molecular level, around 20 angstrom. Disadvantages: slow to fabricate thick film- frying time require after each layer, mechanical and chemical stability is very very poor, required the clean room. So, these all are the disadvantages for these particular techniques.

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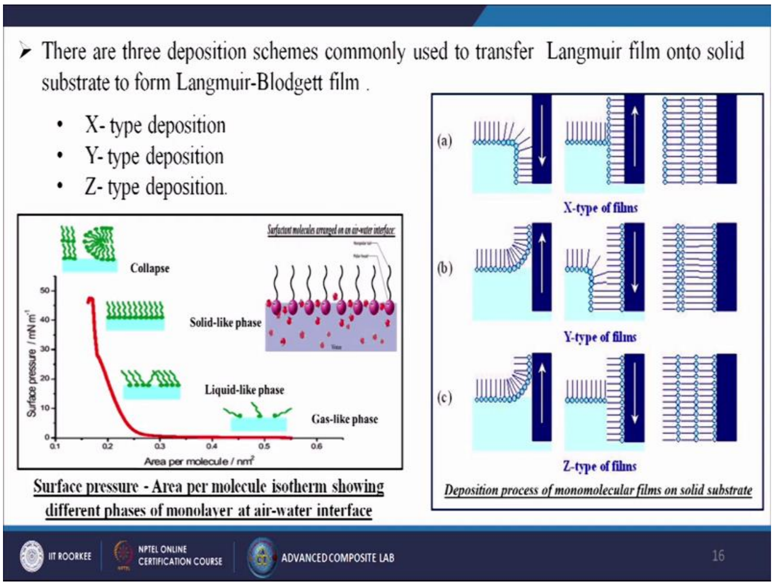

There are three deposition schemes commonly use to Langmuir film onto solid substrate to form Langmuir Blodgett film, first one is called the X type depositions then Y type depositions and the Z type depositions. So, from this particular graph we can see that first we are doing the collapsing then surface pressure we are keeping around 50 for first phases then for the second it is 20 then for the ground liquid like phases it is almost a barriers in between 0 to 10 and the substrate is looking like these. So, here it is a graph in between the surface pressure oblique area per molecule isotherm showing different phase of monolayer at air water interfaces.

So, this one is called the X type of films, Y type of films and Z type of films where we are seeing the different types of deposition process of mono molecular films on the solid substrate itself. So, here the how the attachment is taking place. So, by these methods we can see and we can see that how the film formation is taking place onto the substrate itself.

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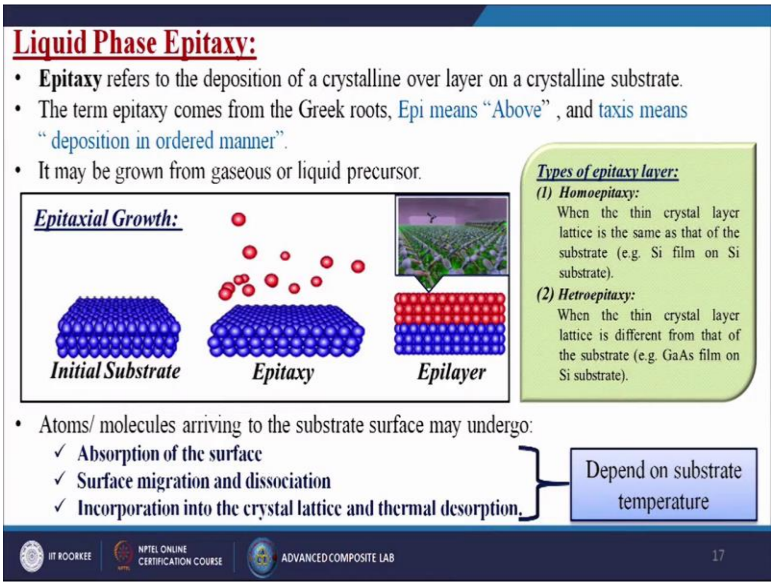

Next is called the liquid phase epitaxial method. So, epitaxial refers to the deposition of a crystalline over layer on a crystalline substrate. So, it is a layer by layer technique, the term epitaxy comes from the Greek roots Epi means above and taxis means deposition in ordered manner. So, one top of another so just layer by layer we are doing this kind of modifications so epitaxial growth, so generally we having that initial substrate then epitaxial growth is taking place and Epi layer is forming onto the substrate itself.

There are 2 types of epitaxial layer, generally it can form one is called the homoepitaxy, another is called the hetroepitaxy when the thin crystal layer lattice in the is the same as that of the substrate silicon film on the silicon substrate; that means, whatever the base metal we are going to use the coating material is the same. So, that is why it is called the homoepitaxy and hetroepitaxy is only the vice versa of the homoepitaxy; that means, here substrate materials and the coating materials is opposite or maybe the different, generally that gallium arsenic film on the silicon substrate.

Atoms molecules arriving to the substrate surface may undergo absorption of the surface, surface mitigations and dissociations incorporations into the crystal lattice and thermal desorption. These all are depending on the substrate temperature. So, by these methods we can do the liquid phase epitaxy onto the substrate itself

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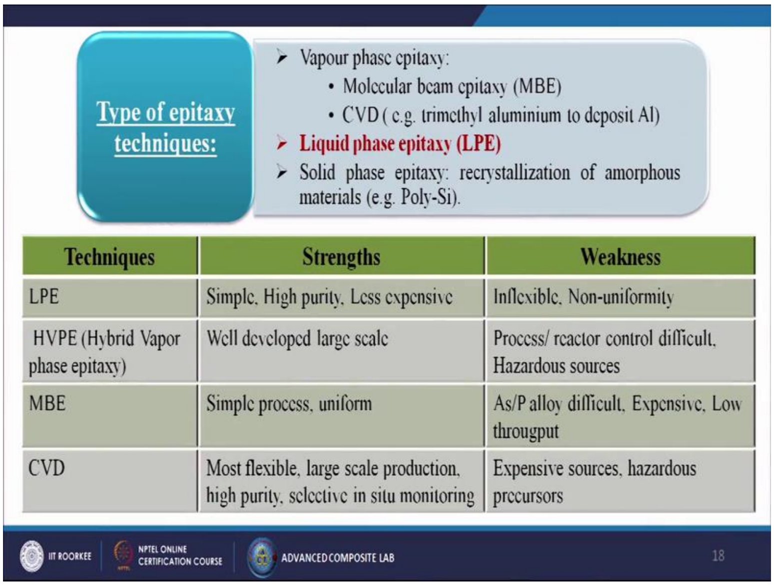

Now, there are several types of epitaxy techniques first one is called the vapors phase epitaxy molecular beam epitaxy, MBE methods, CVD, trimethyl, aluminum to deposit onto the aluminum. So, chemical vapor deposition methods then we are having that liquid phase epitaxy, LPE method, solid phase epitaxy recrystallization of amorphous materials like poly silicon then techniques LPE, what is the strength? Simply high purity less expensive weakness inflexible and non uniformity; when we are taking about the HVPE, hybrid vapors phase epitaxy, so its strength is well developed large scale process reactor control difficulty hazardous sources, when we are taking about the MBE, molecular beam epitaxy. Strength is simple process uniform as arsenic oblique phosphorous alloy difficult expensive low through put. When we are talking about the chemical vapor depositions most flexible large scale productions, high purity selective in situ monitoring, expensive, sources hazardous precursors. So, these all are the advantage and disadvantage for different techniques.

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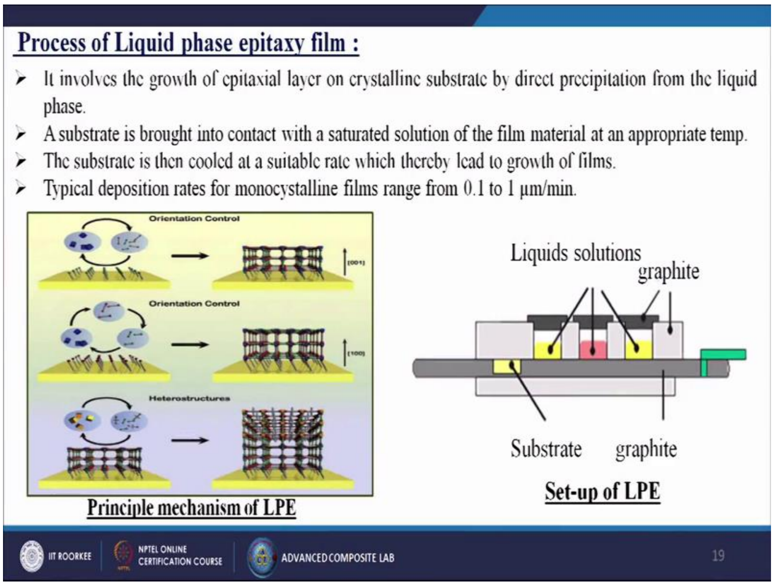

Now, this is called the process of liquid phase epitaxy film, whatever we are going to discuss. So, it involves the growth of epitaxial layer on crystalline substrate by direct precipitation from the liquid phase itself. A substrate is brought into contrast with a saturated solution of the film material at an appropriate temperature the substrate is then cooled at a suitable rate which there by lead to growth of films. Typical deposition rate for monocrystalline film range from 0.1 to 1 micro meter per minute, so simply I am keeping my substrate on to the solids on itself then after that we are picking in type. So, slowly slowly the deposition and is taking place onto the substrate itself by any kind of chemical reactions. So, here the principle mechanism of the LPE, liquid phase epitaxy is looks like this. So, first we can do the orientation control we can do it into the different orientations so that we can form the different crystal structure onto the substrate itself.

Here we are having several liquid solutions and we it is closing it by the graphite then we are having that substrate and then we are doing the coating onto the substrate itself. So, this is the simple type of liquid phase epitaxy. So, first initially, we are having the substrate then we are putting in to the different solvent and then thin films growing is taking place.

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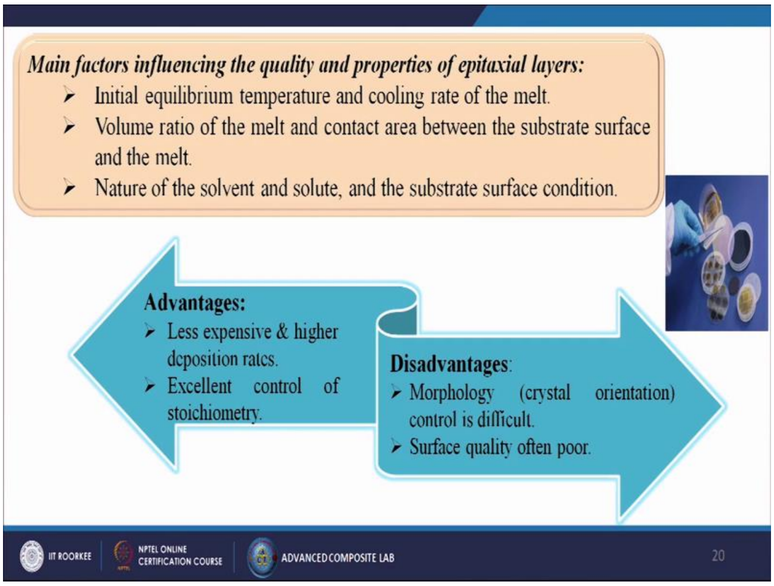

Main factors influencing the quality and properties of epitaxial layers initial equilibrium temperature and cooling rate of the melt, volume ratio of the melt and contact area between the substrate surface and the melt nature of the solvent and the solute and the substrate surface conditions. What are the advantages? Less expensive and higher deposition rates, excellent control of stoichiometry. There are certain kinds of disadvantages also morphology; that means crystal orientation control is very very difficult and surface quality often poor.

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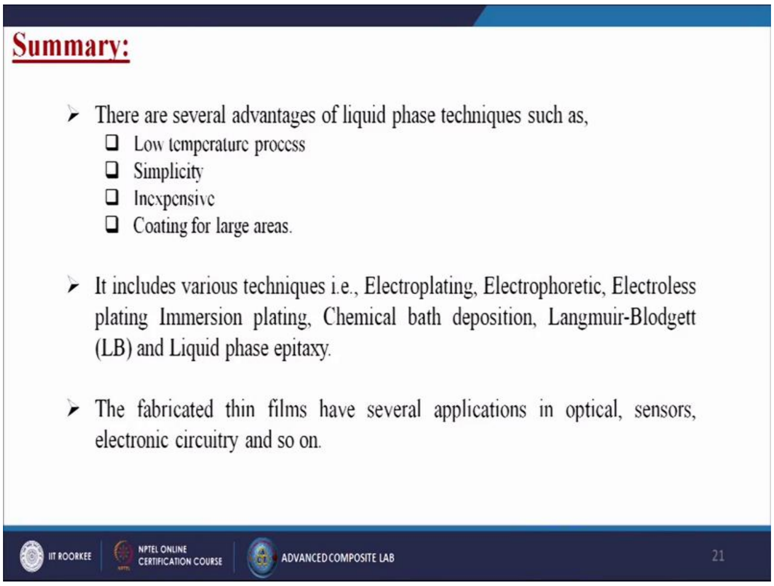

Now it is a time to summarize these lectures. So, we can summarize our lectures in this manner that we have already discussed that several advantages of the liquid phase techniques such as low temperature process, simplicity, inexpensive coating for large areas. So, these are all the advantages for these particular techniques. It includes various techniques like electroplating, electrophoretic, electroless plating, immersion plating, chemical bath depositions, Langmuir Blodgett films and the liquid phase epitaxy.

The fabricated thin films have several applications in optical sensors electronic circuitry and so on. There are numerous applications. So, depends upon the substrate, depends upon the materials, depend upon the condition we can choose any kind of liquid phase deposition techniques best on the applications.

Thank you.