Non - Metallic Materials
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Module - 08
Thin film growth and fabrication of devices
Lecture - 43
Processing of ceramics devices

Welcome to my course Non-Metallic Materials and we are in module number 8, Thin film growth and fabrication of devices and this is lecture number 43 in the last lecture I describe the fabrication of certain wide band gap semiconductor material and this lecture I will cover the processing of mostly insulating ceramic devices.

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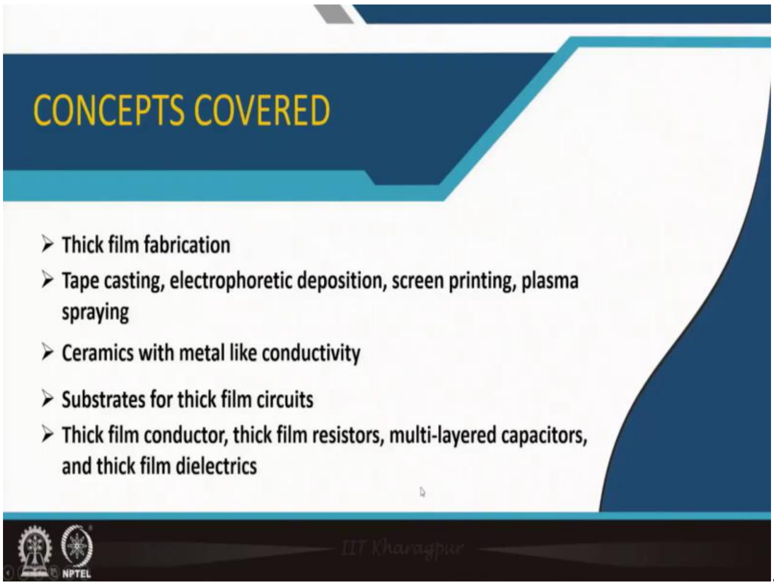

Now, I will cover the thick film fabrication techniques. Thin film fabrication already in one of the earlier lectures I described and this thick film fabrication will include tape casting electrophoretic deposition, screen printing, plasma spraying which are all important as far as the industrial practice is concerned.

And again we will come back to ceramics with metal like conductivity, what is done to fabricate various devices and how to make the substrates for thick film circuits for power electronics that will be described and then finally, thick film conductor, thick film register, multi layered capacitor, thick film dielectrics some basic idea you will get if you take this lecture.

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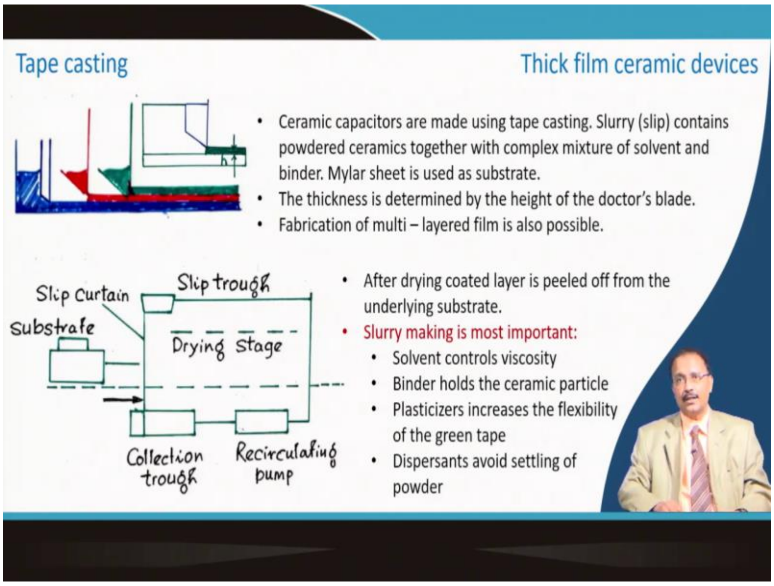

Now, the first thing that we usually do is tape casting when I was talking about the lithium (Refer Time: 02:07) battery in one of my earlier lectures, on the conducting electrode we usually deposit the active material using the binder and conducting material to form an ink which is coated on the current collector which is either aluminum foil or copper foil ah.

For thick film kind of ceramic something similar is done and this is actually done to make the capacitor ah. So, here your active material is not a battery, but a capacitor which is also energy storage device and this is this capacitors are made by tape casting. So, for that the slurry which call it slip which contain the powder the active material if you are using barium titanate, barium titanate is the active material which you give the capacitance, there is mixed with some kind of solvent a complex solvent and a binder.

So, usually we use a polymer sheet a Mylar sheet as a substrate and then we coat it coat this slurry on top of this substrate. The thickness is basically determined by the distance of the blade with the substrate. So, this is my substrate and this is the ink which has been coated by this doctor's blade.

So, it is something similar to this you have first film fill the bucket with your slurry and you have a blade here and this is moving. So, if it moves at a scan rate specific scan rate, then this doctor's blade they will put a thin layer on top of it.

So, the thickness will be basically controlled by the height of the doctor's blade from the Mylar sheet multi layer ceramic capacitor also you can make. So, this is another example you take three different materials. So, one top of another you can make multi layer film and not necessarily that all this three film will be of ceramic capacitor, you can coat it with conducting layer as well. So, it is a very versatile technique and at the later part of the lecture we will talk about a case study of a ceramic volatile fabrication.

So, they are also we use this kind of tape casting. So, here the tape casting is something similar to a rainfall kind of thing. So, here you know the slip the slurry that is pumped here to this trough and the material you need to put is on a rail here. So, this is a rail you put it here, then you slowly push it through this slip curtain. So, it is a rain drop kind of thing. So, it will coat on top of this surface and this is having drying stage different lamps are there.

So, the slurry will be dried on top of the material you want to coat and then you center it afterwards. So, this I will describe it in details when we will describe the case study for volatile fabrication. So, in this case once the ceramic is dried, they are peeled off from the underlying substrate. So, more important thing is to make the slurry because as you can understand the solvent that we use that control the viscosity, we use binder into it that holds the ceramic particle together.

We will have to also use a plasticizer that increase the flexibility of the green tape because the green tape should be flexible it should not break away into pieces and we also use dispersant to avoid the settling of the powders. So, while they are unstore, we need to have dispersant or deflocculating agent so, that the ceramic suspension that remains in the suspension it does not settle down.

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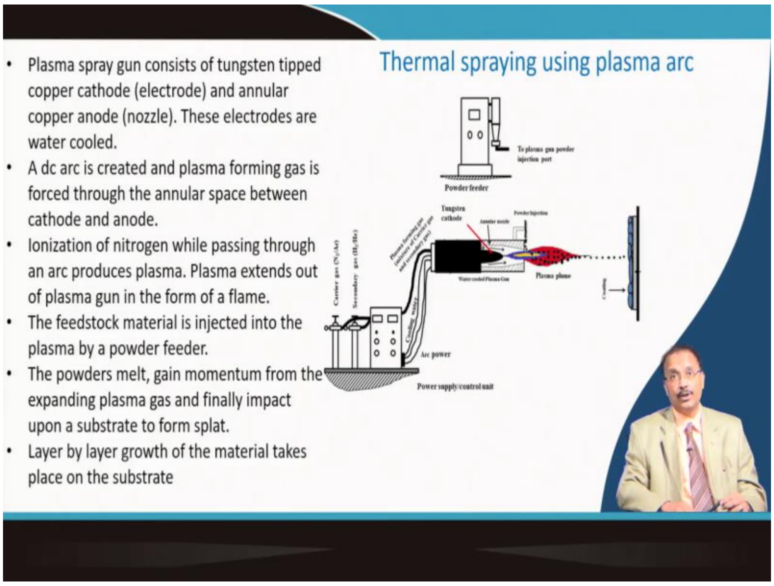

Another important thing to make this type of ceramic coating is thermal spray using plasma arc. So, for that we use this kind of plasma gun which consists of a tungsten tipped copper. So, this is the tungsten tip copper which we call a electrode and an annular type of copper anode we call its a nozzle and this electrode are water cooled. So, arrangement is there to water cool it this arrangement because a huge temperature will be raised and ceramic powder basically they are melt and then deposit.

So, after that a dc arc is created and the plasma is formed by a gas which is forced through the annular space between this electrode usually nitrogen is used nitrogen hydrogen carrier gas is used. So, when it passes through this through this nozzle which are kept at a potential, it produces plasma and this plasma is extended like this.

So, now you have a feedstock the ceramic powder which is feed into this plasma, the powders melt and they get momentum along with this expanded plasma and finally, impact upon the substrate and forms some kind of splat. So, layer by layer growth is possible using this type of thermal plasma spray.

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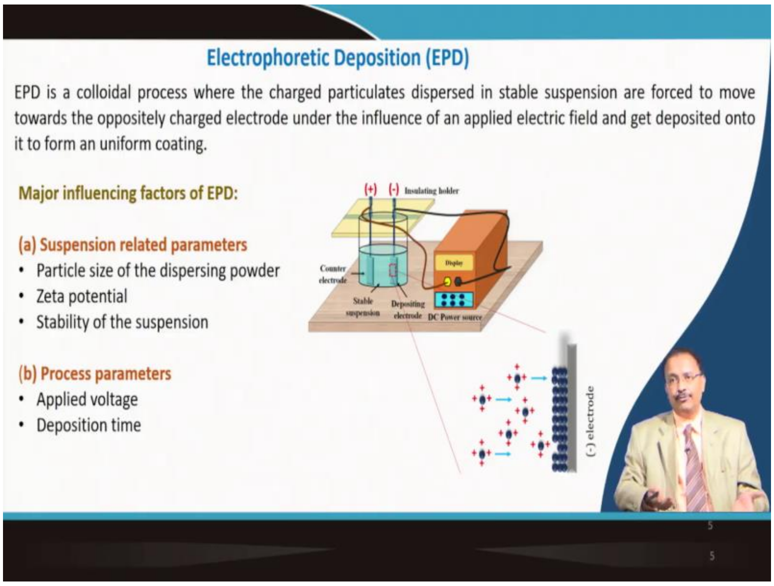

Another important technique which is used to make thick ceramic film, I did not define what is thick usually it is very difficult to define what is thin and what is thick usually anything around 1 micron we call it thick and anything which is above 50 micron, 50 to 100 micron 200 micron 150 micron we call it say thick.

Now, this thin and thick there is a gap and very few processing techniques are there which can fill up this gap. So, that is in between 1 micron to say 10 micron or 1 to 5 micron. So, other techniques are there, but that is not part of this course ah, but thick film means which is more than 50 micron thick.

So, this EPD is basically a colloidal process where you use the charged particle you want to deposit. So, here also you disperse and make it is a stable suspension and then with the application of electric field you force them to move opposite charge particle will be moved in the different direction as you apply the electric field and this will eventually get deposited to form an uniform coating.

So, the influencing parameter that is important is the particle size of the dispersing powder, zeta potential I will define what is exactly the zeta potential. So, that is important and of course, stability of the suspension is also related to zeta potential. So, both this factor together is important and process parameters they are very simplified either applied voltage or deposition time.

These two you can control to increase the film thickness. So, schematically this something similar to this is happening you see that electrode is kept under negative potential and your positive the particle is made positive potential around and they are forced to deposit in a nice way on the substrate.

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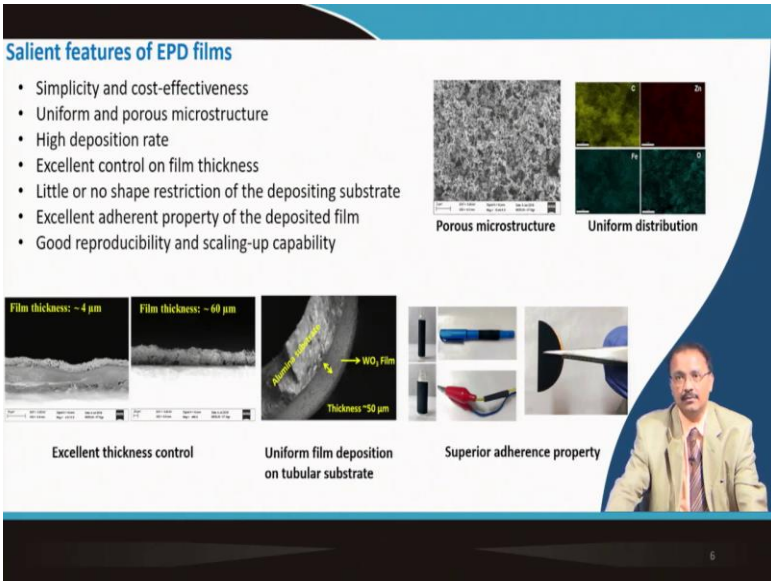

Now, the EPD is a very powerful technique because of its simplicity and also you can deposit porous layer uniform thickness porous layer you can deposit deposition rate is quite high and film thickness can easily be controlled and there is no shape restriction, you can coat it on flat surface you can coat it on the roll surface here is one of the examples you see that the film of tungsten oxide that is coated on a cylindrical surface.

Pretty good uniform thickness is achieved you can control the thickness from 4 micron to about 60 micron as has been shown.You can make the film quite porous for certain application and all the elements are eventually deposited by EDS spectra you know about EDS I have talked it in my ECM course ECM lecture.

So, you can control I mean you can have a uniform distribution and the layer is quite stable you can have this kind of deposition say on copper substrate you have a black colored coating and you can just rotate it, you see that it has been wrapped on a pen with a very small radius of curvature, but due to his adherent nature it will never come out of the substrate and it is a reproducible properties and one can easily scale it up. So, that is why industrially they are acceptable.

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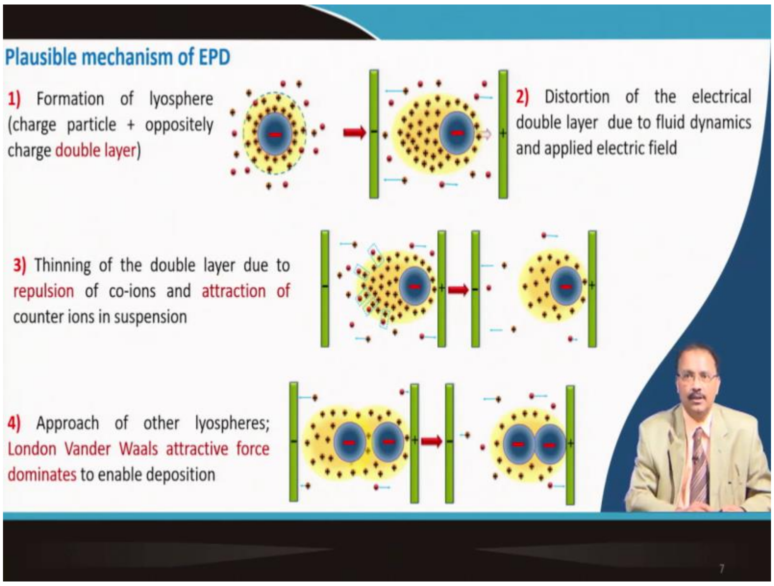

So, the mechanism is pretty straight forward the first a lyosphere; that means, a charge particle and oppositely charged double layer is formed and once you apply the field then there is a distortion of the electric double layer and you have counter ions along with the double layer.

So, then this counter ion actually force it to break. So, it is smaller in size. So, other charged particle can approach it and due to the London's Vander Waals force they get deposited on the substrate. So, this is the basic mechanism of EPD.

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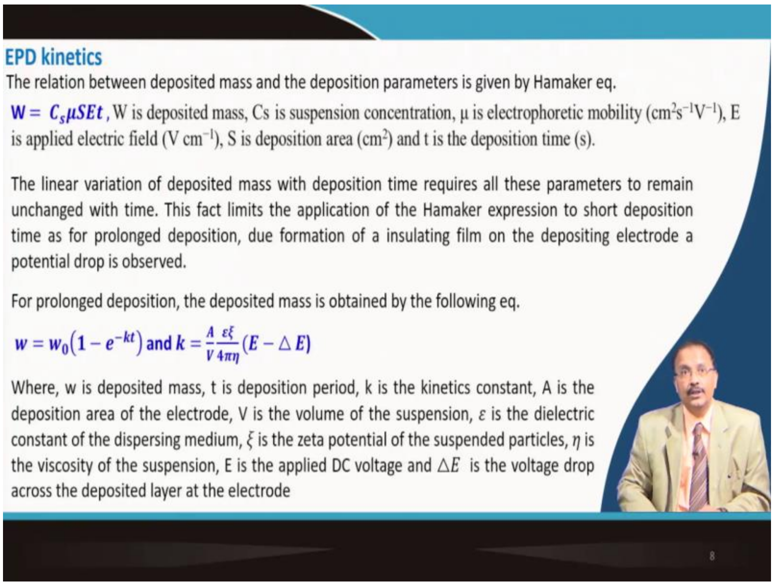

So, kinetics is pretty straight forward and it is the important thing is w the deposited mass and concentration of the suspension, then its electrophoretic mobility, applied electric field deposition area and the deposition time they are all processing parameter. So, as you can see its having a linear relationship with the time of deposition which is good.

So, ah, but once you deposit a conducting film then there you will be a voltage drop because otherwise you are depositing on a conducting substrate and insulating film. So, initially it is layer it is a linear type of deposition, but once the film attains certain thickness then the linearity is not maintained.

So, for prolonged deposition to get a thicker film this is a tentative equation which has been empirical equation which has been derived and this voltage drop must be taken into consideration if you want to make an uniform layer uniform thick layer. So, for smaller layer like 10 micron 20 micron its not a problem, but for larger film thickness it poses a problem.

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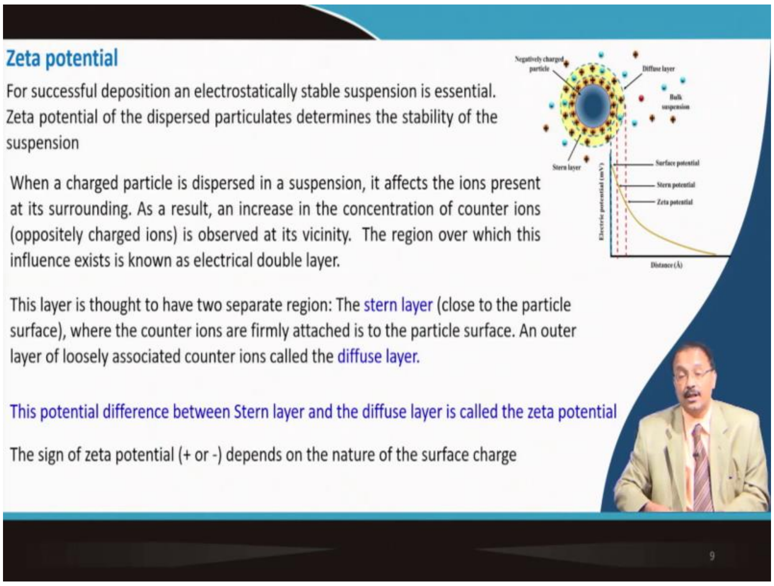

So, I was talking about the zeta potential that is a important factor that control the stability and it is related to the double layer formation. So, you have your particle here and which will acquire a charge and this is dispersed in a electrolytic media. So, the opposite charge will form a double layer and then once you are applying an electric field at some part this double layer will get detached. So, that particular hydrodynamic shear plane where from this double layer is getting detached that potential is called zeta potential.

Usually for a normal suspension, you can control the zeta potential by varying the p h. So, if you for example, in alumina you see that in most of the acidic range p h its having a positive zeta potential, but when the p h is about 9, then the zeta potential is 0. So, the zeta potential when it is 0, we call this is a isoelectric point or point of zero charge.

So, you have ah to maintain the zeta potential which is away from the isoelectric point so, that two similar type of charged particle will repel to each other and be stable inside the suspension. If you want to make a hetero coagulation if you might want to make a composite then one zeta potential positive another zeta potential negative you mix this two suspension together, they will form hetero coagulation ah. So, for processing this kind of concepts are taken into account.

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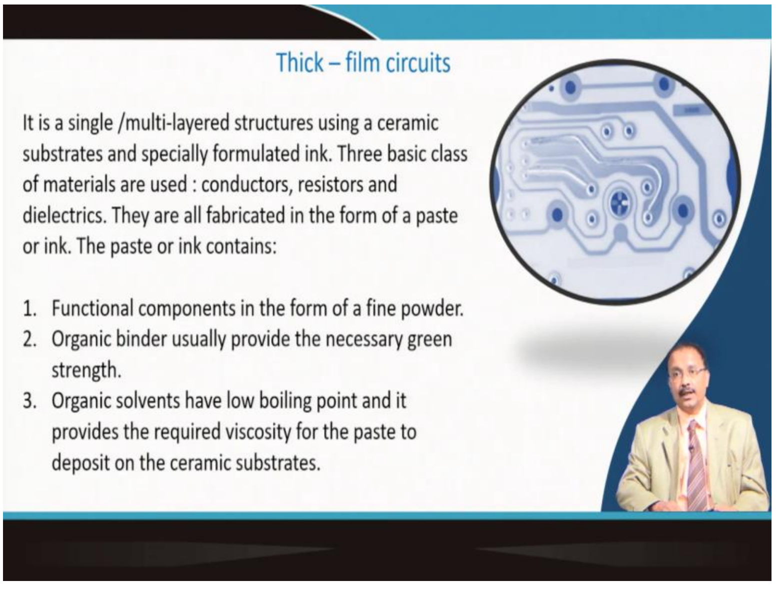

So, one can make the thick film circuit and this is for single or multi layered structure using ceramic substrate, using a specially formulated ink. So, three basic class of material is used for this one is conductor, another one is resistor and third one is dielectric for a particular simple circuit elements ah. So, they are all fabricated in the form of a paste and this paste contains the functional component that is the fine powder form.

So, if you want to make a resistor the functional component is a resistive ceramics, if you want to make a dielectric material it is a dielectric ceramic, barium titanate powder and if you want to make a conducting layer ruthenium oxide can be used. Organic binder they are usually provide the necessary green strength because up upon drying it should not crack an organic solvent have low boiling point and it provides the required viscosity for the paste to be deposited on the ceramic substrate.

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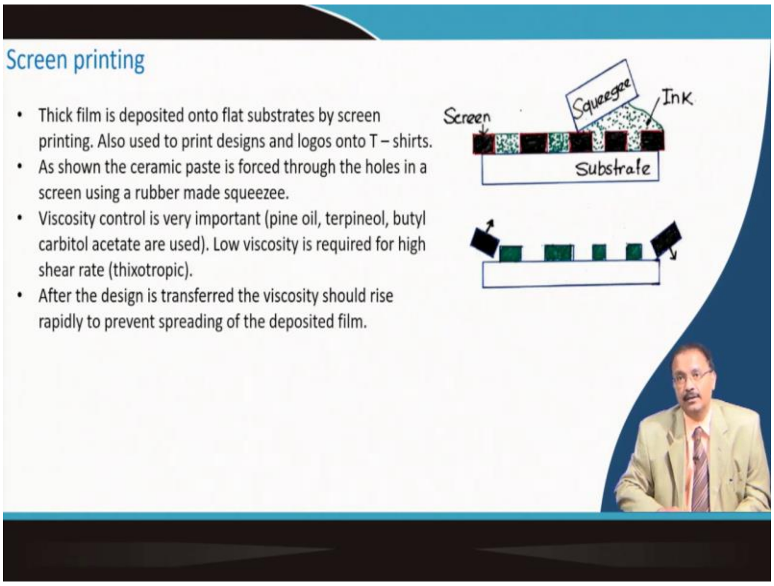

So, screen printing is one way to make a particular pattern on the substrate and this is usually done for the flat substrates you can use the screen print. So, here it is very common for designing the logo in the T shirt this screen printing is used.

So, this paste is forced through the holes in a screen using this rubber squeeze. So, first you put this ink here and then with the squeeze you can just squeeze the ceramic suspension, we call it a ink through this small holes and you can design this holes depending on your design.

So, the viscosity control is very important usually pine oil or terpineol or butyl carbitol acetate they are used and they make it thixotropic. So, once you apply a shear stress they become fluid and easily they transfer and when the shear stress is removed then again they the viscosity goes up. So, that is very important because after design is transferred, the viscosity must rise rapidly to prevent the spreading of the deposited film. So, various types of design one can make by screen printing.

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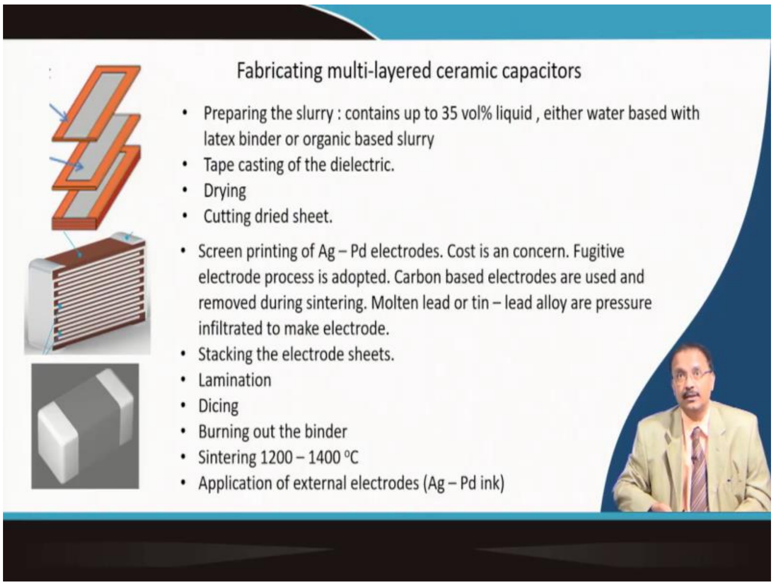

Now, one of the very important thing is to make a multi layer ceramic capacitor using the tape cast layer. We already talked about how to make the tape cast layer. So, first you prepare a slurry usually 35 volume percent liquid is used either it could be water based or it could be organic based with some kind of binder and then you tape cast on the Mylar sheet and you get this kind of brown tape.

You dry it should be flexible I told that we will have to add some kind of plasticizer to make it flexible. So, after drying it is flexible and then you can cut it you take it off from the Mylar sheet and you cut it in different shape, and then you screen print the silver palladium electrode which are conducting in nature.

Cost is a major concern you can use gold for sudden multi layer capacitor, gold was also used initially gold platinum or various types of alloys.

Now, base metals are used, but silver palladium is more or less ok as far as the cost is concerned sometimes you can use fugitive electrode process where carbon based electrode are used which are removed during sintering because remember this will have to be sintered so, that because otherwise it is a particulate coating and binder should be removed and you should get sintered.

So, during sintering this carbon goes out and then you infiltrate tin and lead alloy with pressure to make this electrode that is a much cheaper process then you will have to stack this electrode the way it is shown in between electrodes are there. So, you stack it and then you do the lamination the whole of it. So, all this is connected in parallel. So, the capacitor connected in parallel is will add up the capacitance value. So, you laminate it and then dice it according to the shape small shape and then apply electrode at this two end and lead also can be applied ah.

So, after dicing you binder removal takes place and then you will have to sinter it to get the final strength usually the sintering is done at 1200 to 1400 degree Celsius and that is why noble metal electrode is important otherwise those electrode will get oxidized. And then application of the external electrode as you can see to make a parallel plate capacitor, they are connected in parallel to get a huge capacitance in a multi layer ceramic capacitor is a huge market is there.

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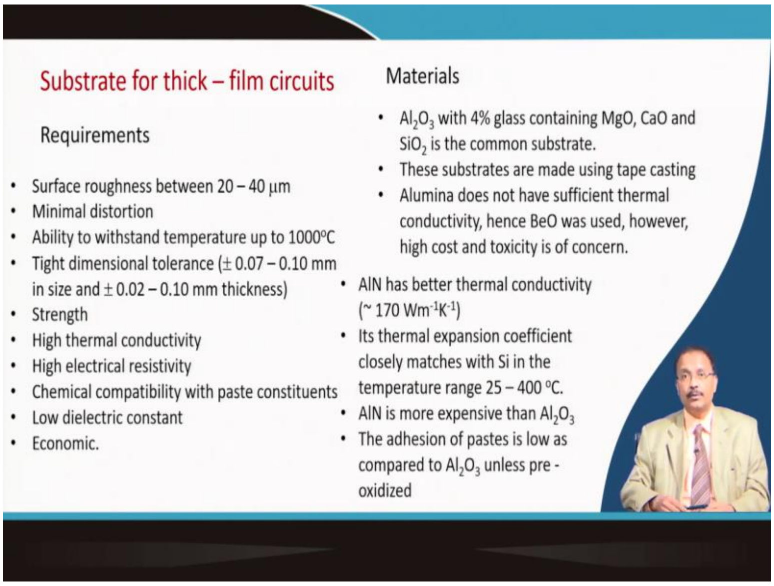

So, substrate is also used for thick film circuit. So, this substrate they should have roughness about 20 to 40 micron, they should not be distorted, they can they should withstand high temperature, dimensional tolerance will be pretty high, they should be strong have high thermal conductivity, high electrical resistivity so, that the electrical component will not get short.

Chemical compatibility with the ink that you are putting on top of it and low dielectric constant and finally, they should be economic. So, this kind of substrate is used for high power electronics where lot of heat is generated. So, normal PVC will not be used. So, this alumina based material is usually used and 4 percent glass containing material is used so, that the sintering is quite good to remove all the porosity.

And this substrate is used by making the tape cast layer which I already described, but alumina does not have sufficient thermal conductivity. Sometimes barium oxide was used, but that is toxic material and also cost is of another concern. So, aluminum nitride nowadays is being used it is having a good thermal conductivity about 170 Watt per meter per Kelvin.

The thermal expansion coefficient is also quite good match with silicon in the temperature range of 25 to 400 degree Celsius, but it is more expensive than alumina. So, the addition of paste is low as compared to alumina, alumina you can easily coat with the metal coated layer, but in order to do that in aluminum nitride you are supposed to oxidize the substrate and so, that this electrode layer is properly pasted.

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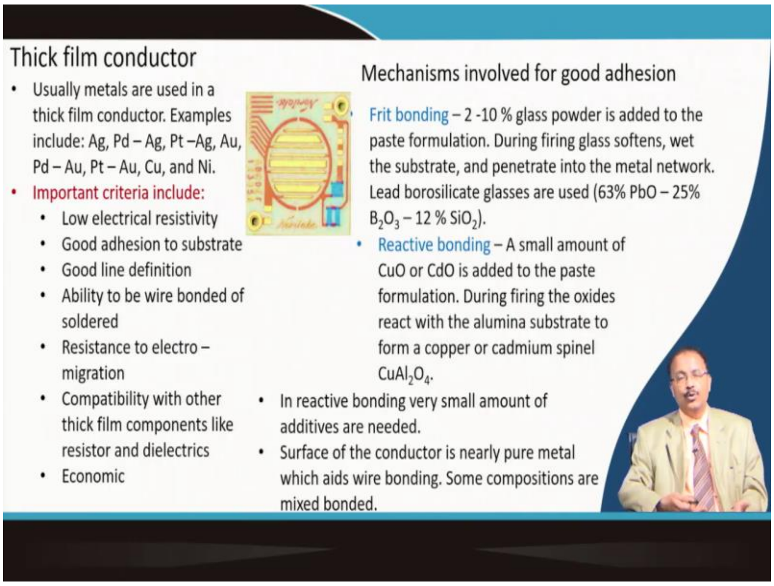

You can use a thick film conductor. So, usually metal is used here as a thick film conductor.

So, silver, palladium, palladium gold, palladium, palladium all those types of noble metals are used and they should have low electrical resistivity adhesion with the substrate should be quite good with alumina they have very good adhesion and then they can have different connectors and you see through the hole you can put the other component like filter or resonator you can put on top of it on this base and they should have compatibility with the other thick film kind of this thing.

So, the good adhesion is one thing which is very common. So, usually two types of thing is done first one is a frit bonding 2 to 10 percent of glass powder is added to the paste formulation and during firing this glass softens, wet the substrate and penetrates into the metal network and usually this composition is used lead oxide and boron oxide based composition along with little bit of silicon dioxide that is mixed with your conducting element ah.

So, this is a frit bonding. So, ceramic bonding is quite strong. So, it is good adhered on the substrate.

And sometimes reactive bonding is done. So, small amount of copper oxide or cadmium oxide if it is added in the paste then during firing this oxide they react with the underlying aluminum substrate to form some kind of spinel for example, in copper it forms copper aluminate spinel. So, if you are going for a reactive bonding between this thick film conductor and the underlying substrate then the amount of this material is pretty small.

And also the surface of the conductor nearly pure metal remains because if you are using a glass 2to 10 percent then the conductivity that is affected, but not in the reactive bonding materials.

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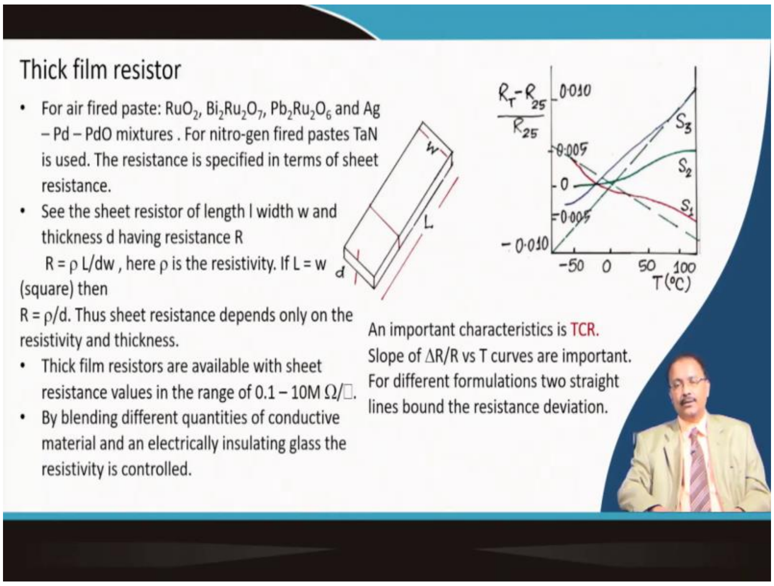

So, thick film resistor is also important for air fired paste we use ruthenium oxide which is highly conducting, bismuth ruthenate, lead ruthenate that is used, but you will have to control the actual resistivity. So, usually it is controlled by putting glassy material which is insulating in nature.

So, the property that is important is the sheet resistance. So, you see that R I defined as resistivity into L divided by the area d into w right. So, here if you just cut this in such a way. So, its a square resistivity. So, in case of square resistivity L and w is same. So, that term will cut from here L and w will cut. So, your sheet resistivity is only the function of sorry sheet resistance is a function of resistivity and the thickness. So, it is a pretty good way to handle this.

So, thick film resistor is usually having a sheet resistance sometimes in the range of 0.1 to 10 mega ohm per sheet and by blending as I said different quantities of conducting material electrical insulating glass the resistivity is controlled. So, it is purely metallic.

So, you need to have a little bit insulating material mix it in proper proportion and many of the instances the proportion volume proportion into respective conductivity that works quite well, the mixture rule and you can have this exact value of the resistor made for your purpose.

So, the important characteristics for this resistors are temperature coefficient of resistance. So, that is nothing, but this slope R T del R versus R. So, for variety of material you can see that the curve is something like this. So, once you increase the temperature usually resistance goes down for certain material depending on what type of metal you have used or metallic component, you have used you are you are having a positive coefficient as well.

So, usually for a particular composition this range is important. So, how much maximum and how much minimum that you are achieving out of this composition that is important. So, this two straight line they bound the resistant deviation and basically you are getting a straight line and you can easily calibrate the value of the resistance with temperature or you take the experimental value and then do a linear fit and achieve the same information.

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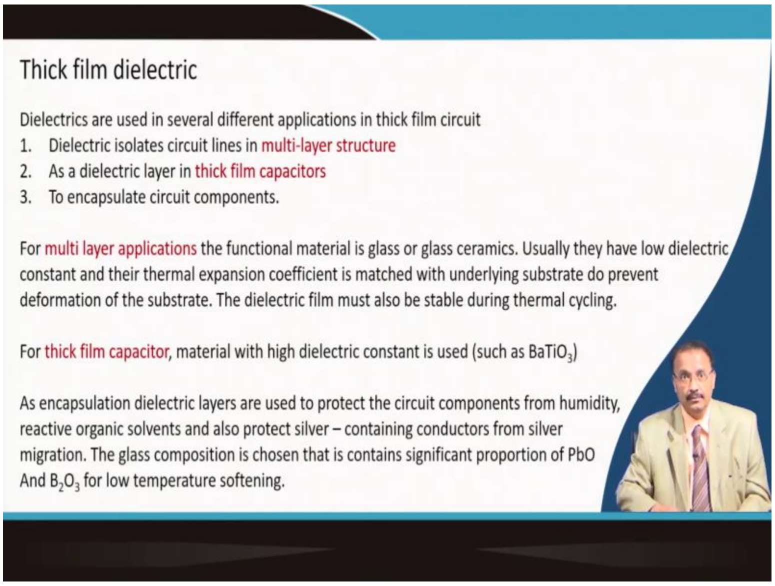

Finally, we talk about the thick film dielectric material. So, usually the dielectrics are used in several different types of applications in the thick film circuit.

So, first is this isolates the circuit in the multi layer structure remember when we will talk about the micro heater based sensor fabrication, then you have seen silicon nitride dielectric layer is used to separate one set of circuit with the other one. So, that is one application dielectric later dielectric layer can also be used as a thick film capacitor and also sometimes it is used to encapsulate the circuit component.

For multi layer application the functional material is glass or glass ceramics, there is a first here the multi layer structure usually glass and glass ceramics is used usually they are having low dielectric constant and their thermal expansion coefficient is matched with underlying substrate to prevent the deformation of the substrate otherwise the substrate will bow down.

The dielectric film must also be stable during the thermal cycling. So, that dielectric should withstand the temperature of the fabrication of the device.

For thick film capacitor which is used as a dielectric layer, the material with high dielectric constant like barium titanate is used. So, this is nothing, but a parallel plate capacitor and you have seen in multi layer ceramic capacitor not a single layer is used multiple layers are used and then they are connected in parallel configuration. So, the in a small area you get a huge capacitance using this material.

So, this concept of barium titanate and then your electrically conducting layer and then laminate it make a multi layer ceramic capacitor. So, you get a huge capacitance of this materials.

Encapsulation of dielectric layer that are used to protect the circuit from humidity reactive organic solvents, that also protect the silver containing conductors from silver migration you know sulphur is a problem otherwise the silver coating they will turn they will form silver sulphide and the conductivity will loss will be lost. So, this dielectric layer they protect it.

The glass composition contains significant proportion of lead oxide and boron oxide, that is basically for low temperature softening operation because ultimately will to cover the substrate well to protect the other electronic circuitry.

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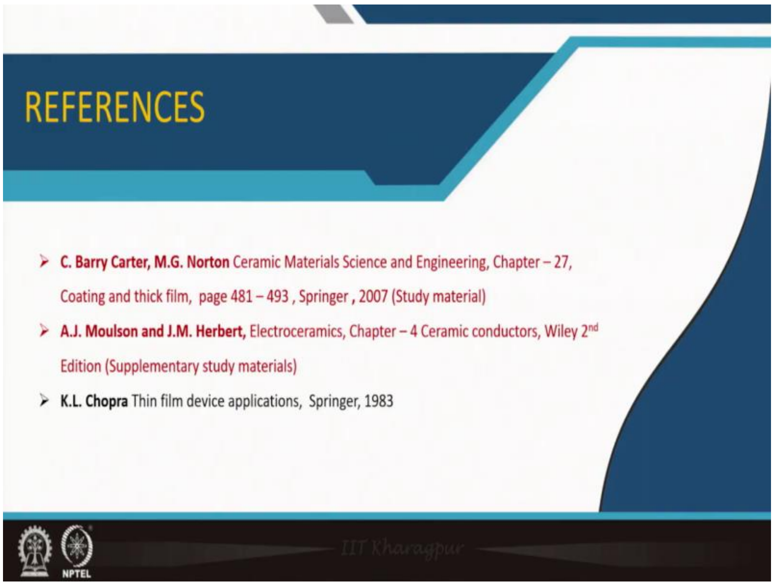

So, this part of the lecture is mostly taken by the book of Barry Carter chapter number 27 coating and thick film and also as a supplementary material you should read the book by Moulson and Herbert chapter 4 which is ceramic conductor.

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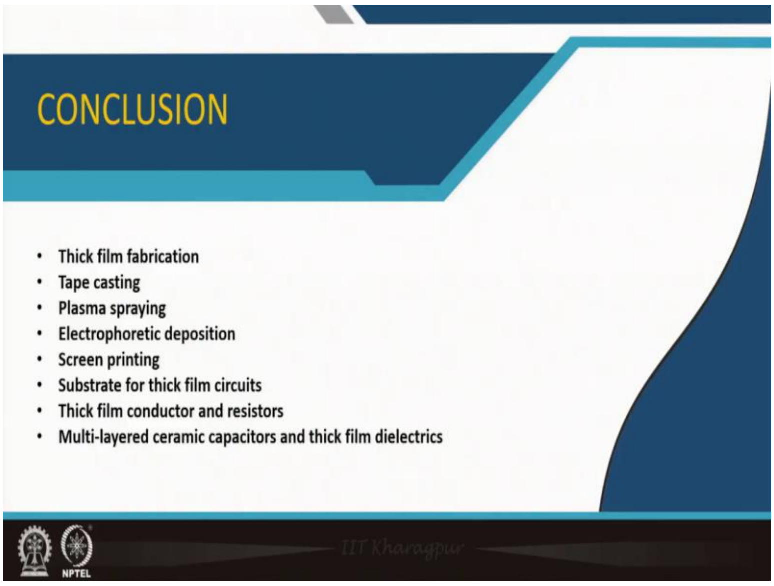

So, in this particular lecture we talked about thick film fabrication, then introduced the concept of tape casting, plasma spraying electrophoretic deposition, screen printing, then we talked about the substrate for thick film circuits thick film conductor and resistors we have talked about and multi layered ceramic capacitor and thick film dielectrics have been introduced.

Thank you for your attention.