Non - Metallic Materials
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Module - 10
Measurement of the mechanical electrical, thermal, magnetic and optical properties of non - metallic materials
Lecture - 51
Ferroelectric thin film: Synthesis and characterization

Welcome to my course Non-Metallic Materials. And we are in module number-10, Measurement of the mechanical, electrical, thermal, magnetic, and optical properties of non-metallic materials. And this is lecture number-51, where will we talking about Ferroelectric thin films: Synthesis and characterization.

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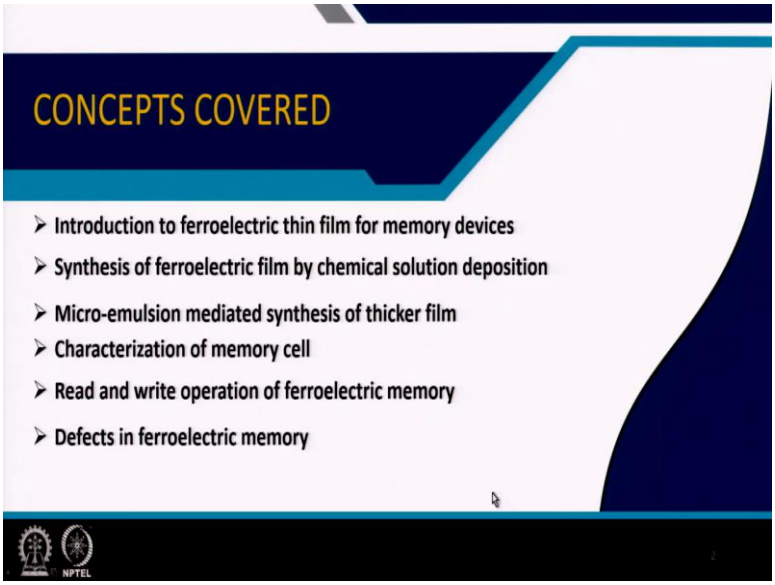

So, first I will introduce ferroelectric thin film. In part of my earlier lectures already we talked about ferroelectricity, origin of ferroelectricity, and it is a part of that lecture where exclusively ferroelectric thin film which is so important for memory devices that will be described, and how this films are synthesized especially using chemical solution deposition that we will be talked about.

And then a special technique micro-emulsion mediated synthesis of relatively thicker film. It is not as thick as the film that you deposit by tape casting or similar technique, but it is in between the so called thin film technique and the thick film the conventional

thick film that will be described. It is a very specific and special synthesis technique. And how this memory cells are characterized, and particularly read and write operations of the ferroelectric memory cell; and various types of defects in ferroelectric memory that we will be talking about.

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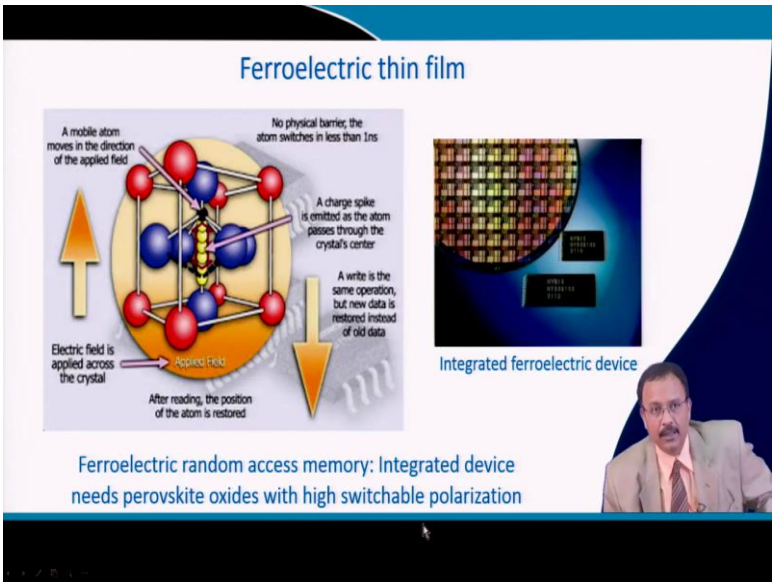

So, we will start from the perovskite crystal structure as you can see that already we have described it. So, there is a mobile cation here. So, this mobile cation moves in the direction of the applied field. So, if you have a positive field, then it if it goes up, then it is switchable. If you put a negative field, then this will be in the opposite direction, and there is no physical barrier for this kind of switches.

So, it can be switched very fast. And typically within 1 nanosecond, it can move from one polarization direction to other polarization direction. So, very fast memory unlike your magnetic memory, which are relatively slow; very fast memory one can make out of this ferroelectric material the switching time is in nanosecond order.

And once it switches, it gives a charge spike because this is a movement of a charge carrier. So, cation is moving. So, it gives a charge spike. So, you can stop the voltage, then it will the cation will be fixed either in this polarization state, or this polarization state. So, it is non-volatile in nature. So, at zero field, you can write something you can write some information in the form of a digital 0 or digital 1. So, it is non-volatile.

So, this ferroelectric random access memory they were very very lucrative in 90s in till 2000 that decade a lot of research used to be there. Now, it is still there, but it has been slowed up a bit because of certain problems in this memory. So, particularly when this memory switches from one polarization to state to another polarization state, there are associated defects in the memory cell we will be talking about it.

So, due to this fact, it is a bit retarded, but otherwise this technology is very very lucrative. And we call this as a non-volatile random access memory and which will eventually replace all existing memories conventional memory. So, integrated device is important.

So, this ceramic perovskite films will have to be deposited on a large silicon wafer to make this integrated device, and then in the form of this memory cells. And Ramtron is a company they usually commercialize this kind of memory, but as I said this is not yet in full fledge in the market.

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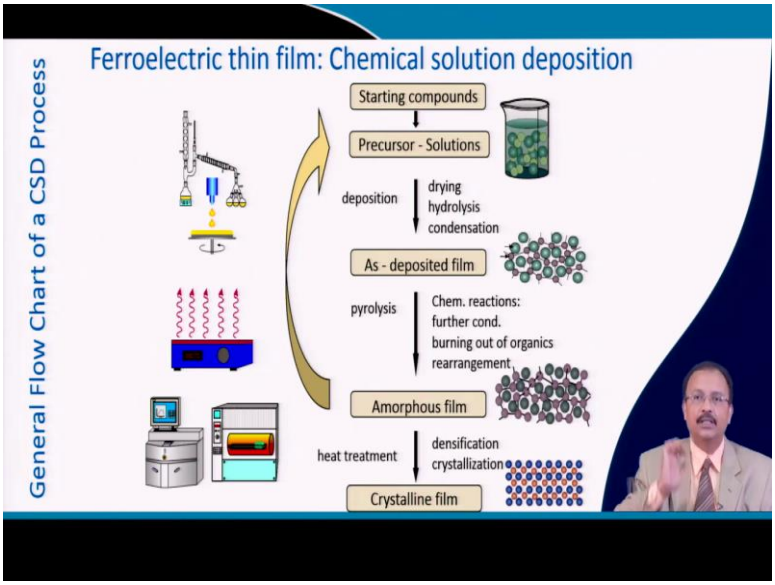

So, this chemical solution deposition I just briefly introduced in my earlier lectures, but again we are just taking it up just to refresh our memories. So, there are starting precursor - solution. So, once you want to make barium titanate or lead zirconate titanate or lead titanate or lead lanthanum titanate, then you will have to make a precursor solve so where all these chemical constituents are mixed in a molecular level.

So, if it is a soluble technique, so hydrolysis and condensation reaction that is important. And at this stage, at the precursor stage, you will have to deposit it and usually spin coating is used to deposit uniform film on the substrate material. So, as deposited film, it contains of course solvents inside and they are amorphous in nature.

So, you need to pyrolyze it, you need to bake it, so that during pyrolyzation this organic moieties, they are burnt out. And carbon should not be there, because these are basically oxide carbon you know that it is a reducing agent. So, if carbon is there, it can oxide; it can reduce this oxide in the form of metallic constituent which will increase the dielectric loss.

So, therefore, the carbon should be fully removed in this baking step. But still it is in amorphous state, and you need to do a heat treatment either in a conventional furnace or in a rapid thermal aniline furnace where the heat treatment rate the ramp is very high, so that it basically crystallizes.

And the phenomena nucleation and growth that is there it will densify the film, it will crystallize the film. And it will have a long range order, so that is the common way where the wafer is basically coated by chemical solution deposition. And 4 inch to 6 inch wafer can be coated by this technique.

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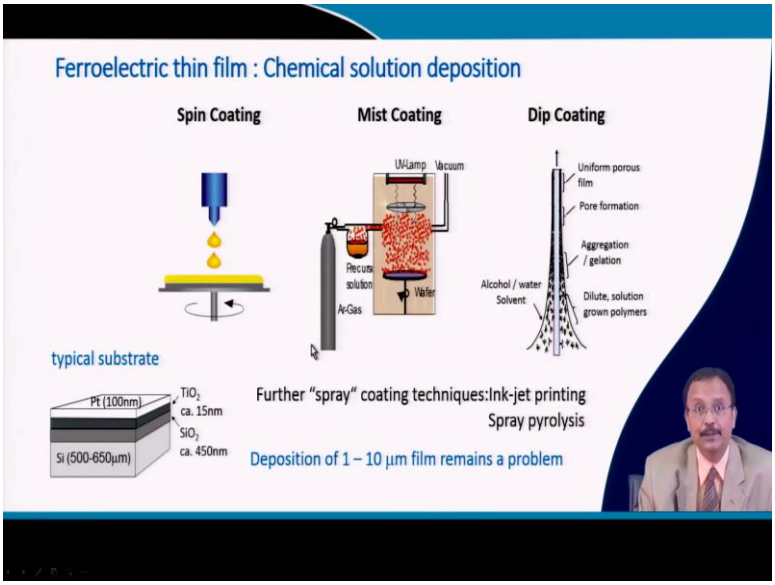

Other than that, other than spin coating, the mist coating that can also be used where the wafer is kept here, and it forms a mist by passing gases here, and it deposits. It can also be deposited by deep coating technique which already I described in one of my earlier lectures. So, ink-jet printing can also be done or spray pyrolysis is another thing to coat this substrate uniformly by this ferroelectric films.

So, usually the substrate that is used is silicon which is having a typical thickness of 500 to 650 micrometer. And then you have a native silicon dioxide layer, on top of it thermally oxidized. And then a glue layer in the form of titanium oxide that is given, so that the top layer the top conducting layer is platinum which is glued efficiently on this platinum layer. So, that is the substrate that is basically used for all this kind of deposition.

Now, it is a problem to make a film which is thicker than 1 micron. So, 1 to 10 micron that range is difficult to grow by any of this technique because once the film grows then it has a tendency to delaminate. So, delaminate from the substrate. So, thicker film deposition by using this spin coating or dip coating that is usually problematic.

So, some other thing need to be done. And also this 1 to 10 micron film that is too thin as compared to your tip casting or stuff like that or screen printing. So, I introduced earlier the electrophoretic deposition that also can be used, but there are very few techniques that is available which can grow film, which is in the range of 1 to 10 micrometer.

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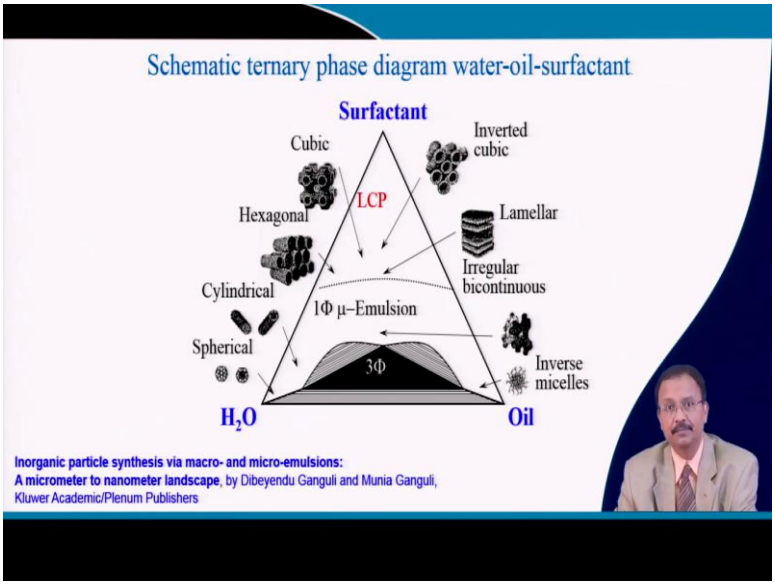

So, a special synthesis route has been adopted which we called micro emulsion mediated things. So, I am not going into the detail of the actual micro emulsion technique as such. If you are really interested, you can go through this book which is based on this technique totally dedicated on micro emulsion.

And basically you have a mixture of water and oil you do not you know that they do not mix to each other. So, either it will be a spherical water droplet inside an oil matrix or reverse is also true in oil droplet in water matrix. And you have surfactant which will basically protect this water or oil droplet to come in close proximity to have a bigger size.

Because you know that oil and water they will not mix with each other, but it is important to control their size, so that micro emulsion that reverse micro emulsion, the water droplet inside the oil matrix that is used that is used for this purpose. And there is a nice phase diagram that is available if you change the relative content of these constituents, then you can make different types of shapes of either oil and water inside the respective matrix.

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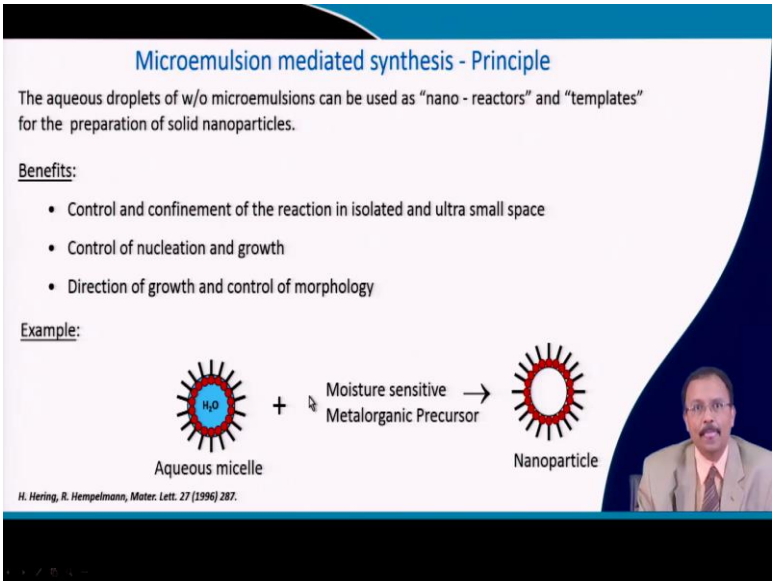

So, this concept was used this micro emulsion mediated synthesis. So, aqueous droplet water in oil, this micro emulsion that can be used as a nano reactors, and basically a template for the preparation of solid nano particle that was the idea to prepare a very small nano particles which will not scatter light. So, it will be a transparent solution, but

it will have a solid crystalline ferroelectric material embedded in your oil media. So, what is the benefit?

The benefit is to control the confinement of the reaction in a isolated ultra small space to grow nano crystalline powder material, and also to control the nucleation and growth inside that small volume. And in some instances, it is also possible to control the growth direction, and thereby the morphology of the particle that is being grown. So, here this is a typical aqueous micelle.

So, this water is there and you know that the surfactant which is hydrophilic that head is here, and hydrophobic the tail is in the other side in the oil part. So, this inside this water, if you can somehow mix the metal organic precursor the alkoxide I already talked about the soluble synthesis. So, if this kind of alkoxide the reaction, you can initiate inside this water they will hydrolyze. So, your condensation product will have a very, very uniform kind of particle size, so that was the idea.

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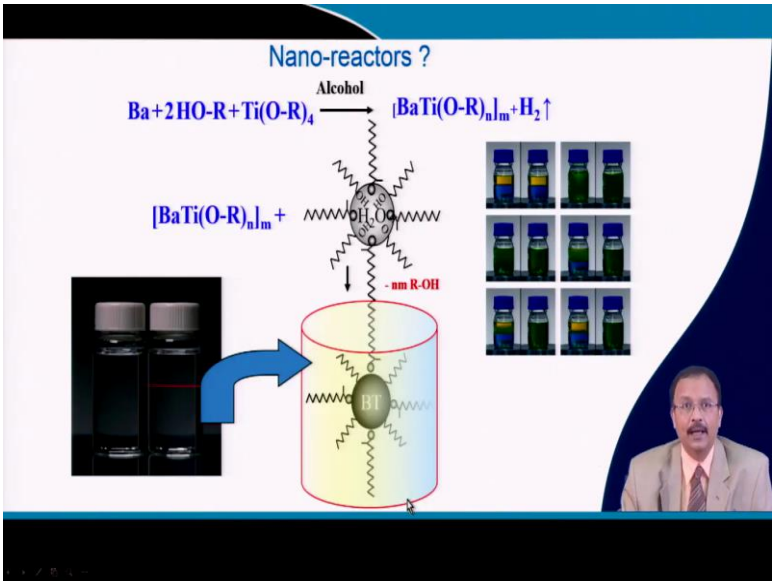

And it was for this particular example you can take the barium alkoxide that is prepared by reacting barium metal with alcohol. And you have titanium alkoxide, and it forms barium titanate, and this sole is injected inside the oil. So, basically you have inside this reactor that I call a nano reactor, this water will hydrolyze and eventually condense it to form barium titanic particle.

And this will be protected I mean dispersed by the use of this surfactant. So, lot of research is required to have a proper oil water ratio and to control the size of this nano droplet of water. So, if you change the oil and water, you can see that under certain condition they have mixed properly; otherwise they get separated.

So, lot of research is required to make a uniform particle size. And this is the example of the sole that is there you can see it is quite transparent in nature. And if you pass a laser light then the light is not scattering I mean this particle size is too small. And it forms something like this.

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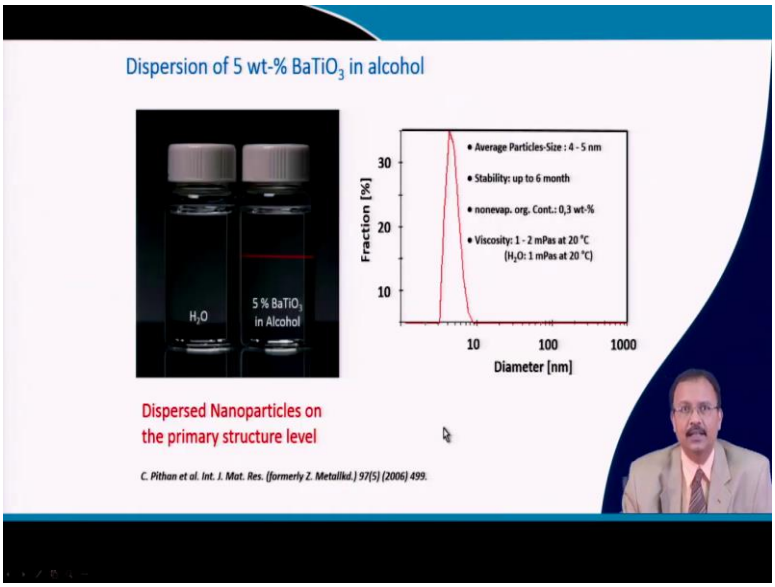

Then it was characterized to have a particle size which is less than, 10 nanometer. And you can see it is quite uniform particle size about 4 to 5 nanometer. And it is very stable up to 4 to 5 months this kind of particle inside the suspension, it is quite stable. And it is also not very viscous in nature. So, this dispersion typically this is 5 weight percent of barium titanate that is shown here.

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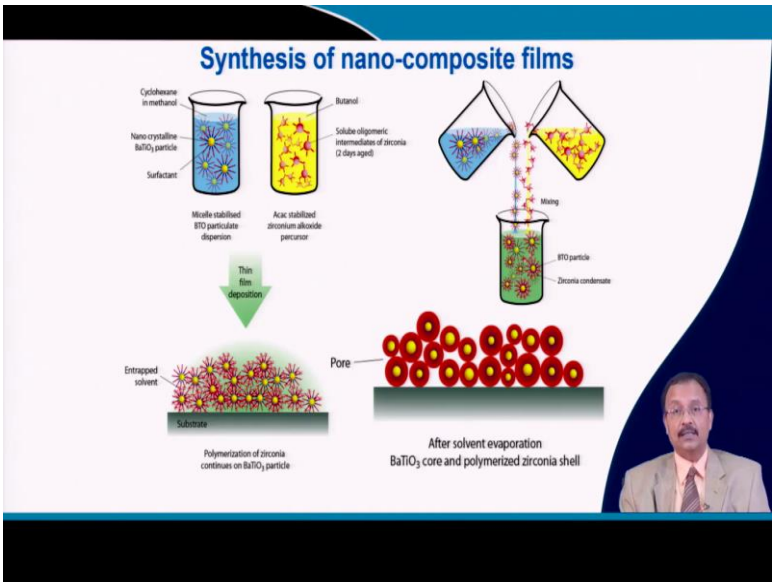

And this micro emulsion is has another effect that you can have two different types of material prepared in the same way. So, one is I have shown barium titanate here. And similarly zirconium alkoxide that can also be grown, and then they can mix together and deposit the film something like this. So, either you can deposit a single component film or you can make some kind of dopant or composite.

So, various possibilities are there. So, this particular example if you mix barium titanate with zirconium zirconium alkoxide, then eventually it will form a barium zirconate upon calcinations. But not on all barium titanate this core this will have zirconia layer in the form of this micelle of equal concentration. So, there will be a concentration variation. So, some eventually what you are doing that in barium titanate, you have several dopant content of zirconium.

And you know that barium titanate the Curie temperature can be changed by addition of the dopant. Strontium, the example I cited earlier, and zirconia also can do that. Now, if you have different types of dopant content, then the Curie temperature will not be sharp right. It will be broadened enough. So, that is one advantage that is used for this micro emulsion mediated synthesis.

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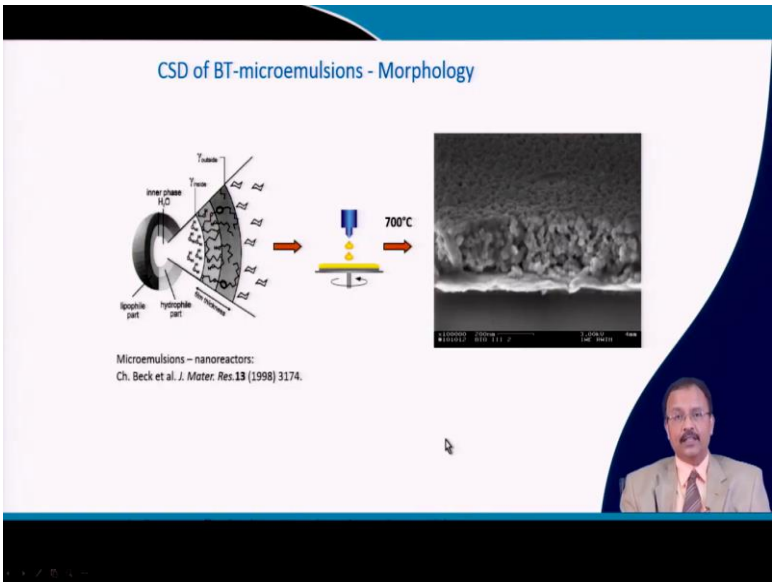

So, here it is shown that this is a core shell kind of structure, and that solution itself is spin coated and eventually annealed. So, you have a substrate, then you have metal, and then you have the thick film that is deposited there on top of it.

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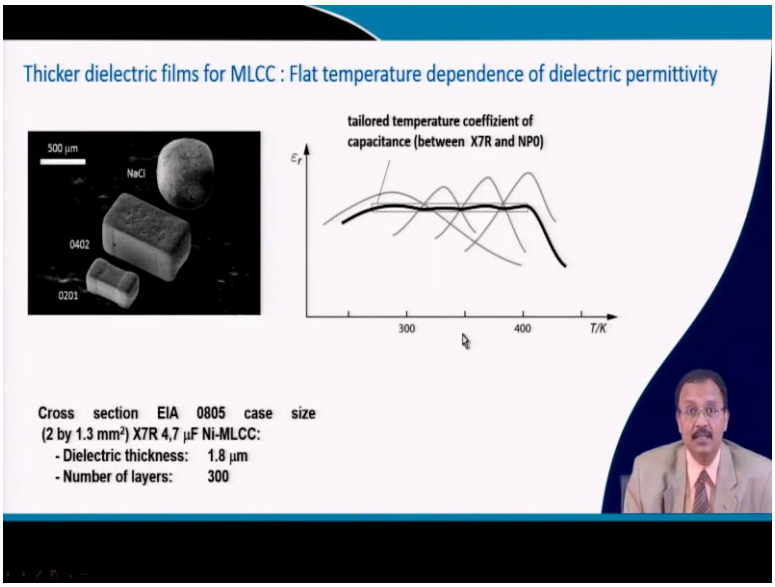

Now, this is due to the different coating layer of zirconia. The Curie temperature for each of this particle is different. So, once you do a temperature dependent dielectric measurement, then instead of a sharp dielectric maxima following the Curie transition, Curie law it is having a several of such peak and eventually it gives you a very flat kind

of profile which is required you know that you do not want that at a particular temperature, your dielectric constant will shoot.

You need that at room temperature it should have uniform, but higher dielectric constant. So, this is used to make the multi layer ceramic capacitor because now you can deposit a thicker film. And the thickness you know that the capacitance is dependent on thickness and area. So, by reducing the thickness, you can increase the capacitance thereby the dielectric permittivity.

So, eventually this technique is used to make the multilayer ceramic capacitor which is very small in size, but very high capacitive value. So, the density is many fold increase this is a comparison of this kind of MLCCs which are commercially available with respect to a salt grain. So, you can see that how small one can miniaturize to get a very high very high dielectric constant sorry capacitance, which is in the order of 4.7 microfarad in this small area for this particular device.

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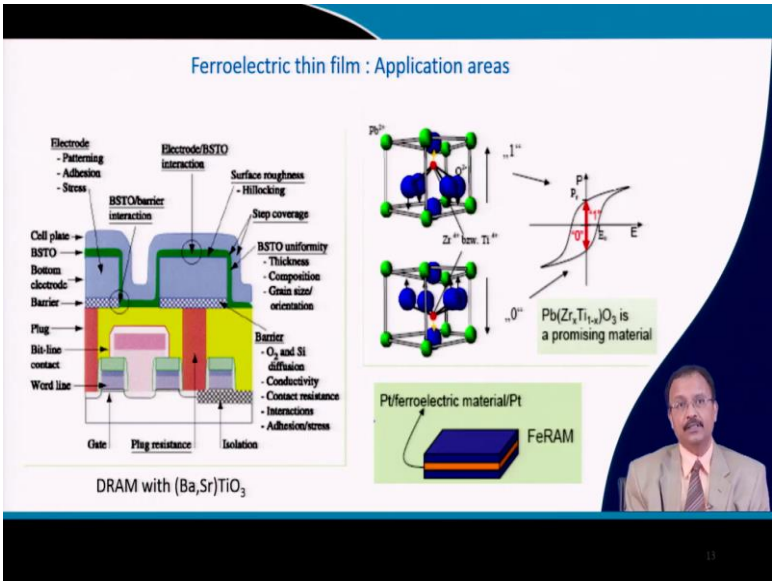

So, usually this ferroelectric thin film is used either as a dynamic random access memory which is I will not cover in this course. It is a simple dielectric and barium strontium titanate used for this, or you can have a memory non-volatile memory in the form of piezoelectric as well as ferroelectric PZT lead zirconate titanate, where the hysteresis in the hysteresis loop you can see that two different polarization is there. One is digital 0,

and another one is digital 1. So, this binary memory can be made out of this type of perovskite material. So, this is a typical device structure of a FeRAM.

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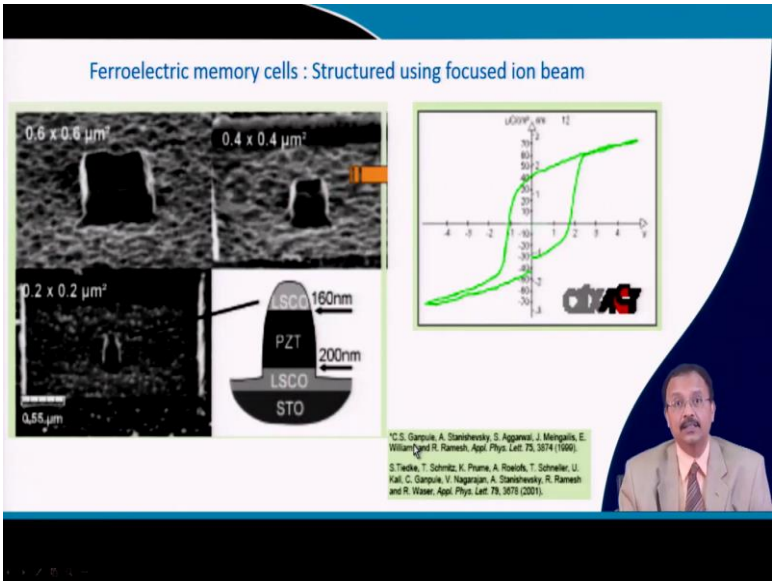

Now, it is challenging to make such a small device because the device should be very small in as far as the area is concerned. And you will have to measure that at each individual cells, they are ferroelectric in nature. It is really challenging. So, one thing that can be done is by focused ion beam. So, you can just itch the remaining part. And you have a device which is typically 0.6 into 0.6 micrometer square, then you can reduce it to 0.4 by 0.4, and 0.2 by 0.2.

So, here a typical structure that is used is PZT, it is having two different metallic layer. We talked about metallic metal like conduction. So, this is one example where exactly those metal like conductors are used. So, LSCO is metal like conductor which is deposited on strontium titanium oxide.

And PZT was deposited by chemical solution deposition have just cited the relevant literatures where they were used. And eventually they are focused ion beam. And on top of this, this cell you can have a good hysteresis loop and showing that they are indeed ferroelectric in nature.

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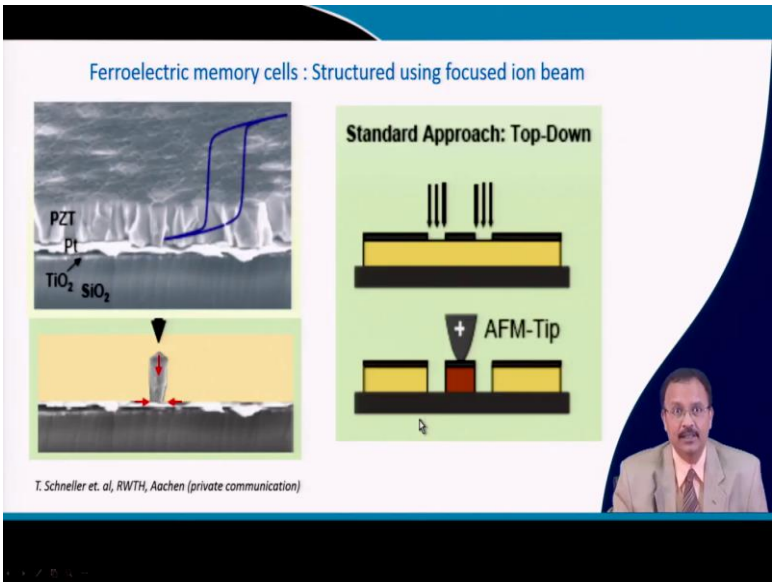

So, once the structure becomes very small – so smaller than this 0.2 by 0.2 micron, then by measuring with a normal ferroelectric tester, it is difficult. So, in that case, an AFM can be used. And this special technique I have not covered in this course, but this is known as piezo force microscopy the first by focused ion beam, and such structure is made. And then an AFM tip scans on top of each individual grain to see whether they are ferroelectric or not.

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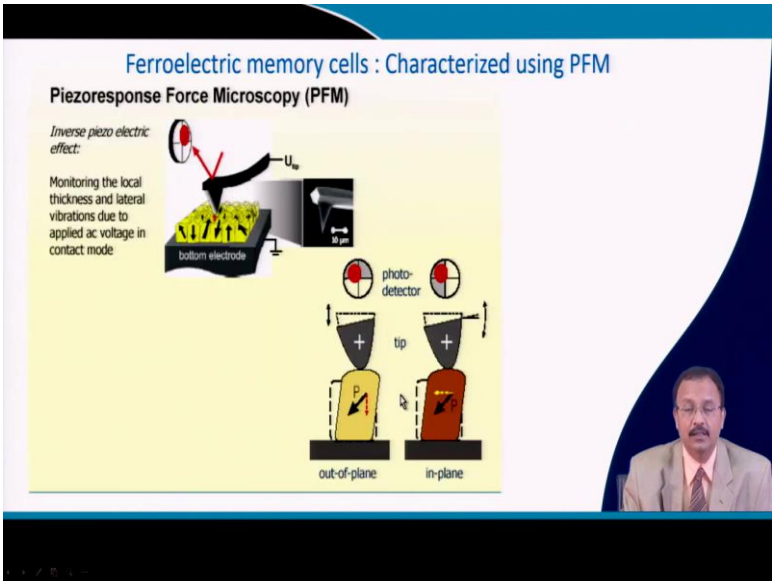

So, actually this polarization of each individual grain that interact with the AFM tip, and this is the signal of this AFM tip that is taken out, and that is the basis of piezo force microscopy. And you can basically trace the polarization state of each of this grain for a continuous film. And for a discrete very small ferroelectric memory cell, you can very well define the polarization state of each individual cell in a memory matrix. So, PFM – Piezo Force Microscopy can be used for this purpose.

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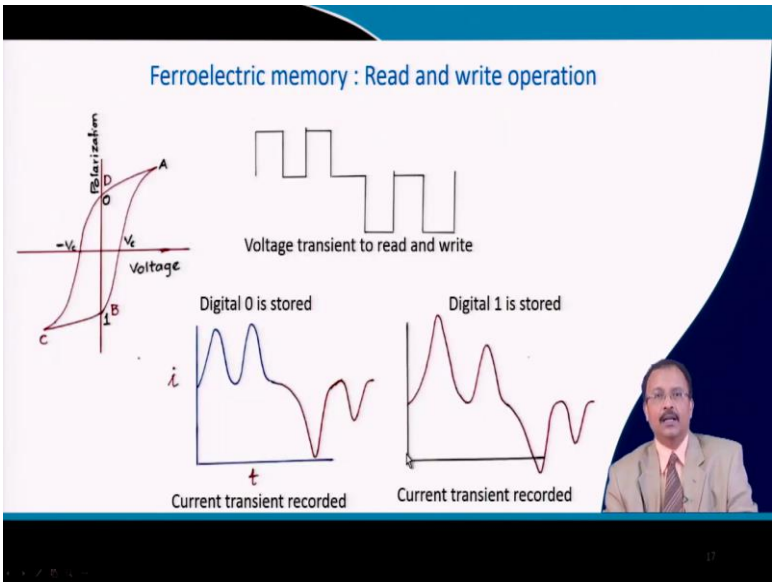

So, it is very interesting to know that how a digital 0 and digital 1 is first stored in the material that I will come later on, but more importantly what exactly is stored whether it is a digital 0 or 1 that can be identify by having this kind of voltage transient. So, as you can see the initial voltage transient is a positive up, then there is a delay here.

Then another positive up, then again there is a delay. Then negative – down, delay, and negative down. So, this kind of voltage strain that is applied in a ferroelectric memory individual memory, and say if you assume the digital 0 is stored, so once 0 is stored means it is somewhere here. So, if you apply this first positive pulse, then this memory this polarization will go here from here from D to A.

And then it will again come back to D. And second pulse it will go to D to A and again come back to here. So, if you as I told that it is a transition of the cation, and it will give you a current spike because it is a charge movement. So, the initial current spike and the

second current spike, they will be relatively smaller because it is only traversing this path.

Now, there is a delay and then a very then there is another voltage pulse which will which is negative in nature. So, it will just transient from here to here. So, there is a large change. So, therefore, the current pulse will be very large, and then there is a second negative pulse. So, it will be relatively small.

So, if you now read this current pulse corresponding to the voltage transient, so if you read the current transient, then you can easily see that for this type of voltage transient if this kind of current transient is there. So, a digital 0 is stored. If you compare it with a digital 1 storage, then first positive pulse will switch it.

So, there will be large current followed by a small current because second pulse will be from here to here only. So, there is a small pulse. Then the third pulse again it will get switched. So, again a large pulse and then followed by a small pulse. So, a large small, large relatively small, and again large relatively small that will tell that it is a digital 1 that is stored.

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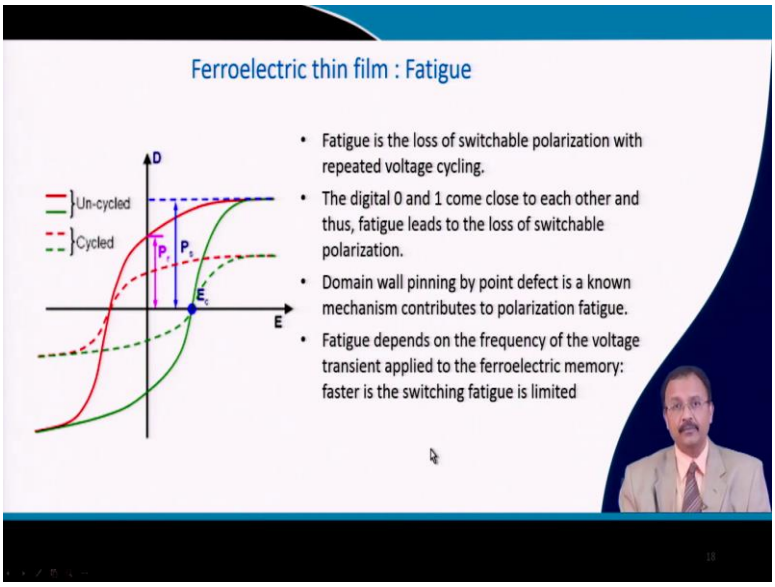

So, this is the operation. But if you want to do this read and write for several times, then actually the polarization drops. As you can see that this is this was the original hysteresis.

And then after repeated read and write cycle, you can see that the polarization drops down. And this is known as fatigue. And this is one of the major defects.

And people are yet to solve this puzzle that why exactly the fatigue takes place or how to get rid of this fatigue. And due to this reason, this is not yet in the market; otherwise you will have a very very fast memory in the market by this time. And so digital 0 and 1 will come to close to each other, and fatigue leads, therefore, leads to the loss of switchable polarization.

So, usually we as we understand that the domains as I explained in this kind of ferroelectric memorial that material that is pinned by the defect point defects. So, domain cannot switch, and therefore, it fatigues. So, progressively domain switching is retarded for the fatigue to take place. So, this is one prominent defect for the ferroelectric materials.

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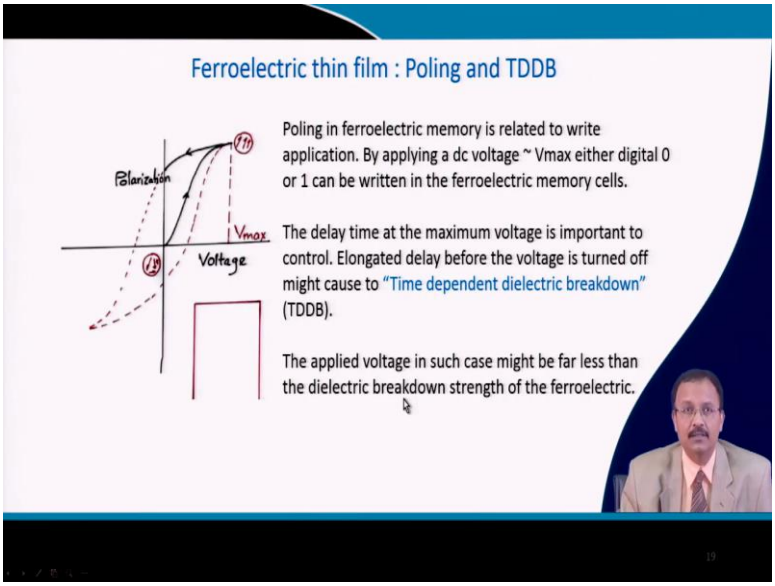

Now, in the virgin state you know that the domains are in all possible directions. So, if you apply a dc field something like that and there is a soaking period of this field, then and also this voltage is more than the cohesive voltage and very close to the maximum voltage which this film can withstand.

So, this operation is known as polling where from the random polarization state, it basically goes to one polarization state which is in the direction of the applied field. And

once the field is turned to be 0, then the either digital 0 or you can do it negative also. So, either digital 1 is stored, so that is poling.

Now, if you increase this duration while you achieve the maximum voltage, then even if this voltage is very small I mean very low as compared to the dielectric breakdown strength of this material, then also the material can fail, so that kind of failure is known as time dependent dielectric breakdown.

So, you apply one particular voltage for elongated period of time and the material fails. So, this is another defect of the ferroelectric memory and which is known as time dependent dielectric breakdown. So, remember this voltage is much less than the otherwise dielectric breakdown strength of this material. So, both this time dependent dielectric breakdown in a dc field and the fatigue which I explained in the last slide, they are detrimental for the life of the ferroelectric memory.

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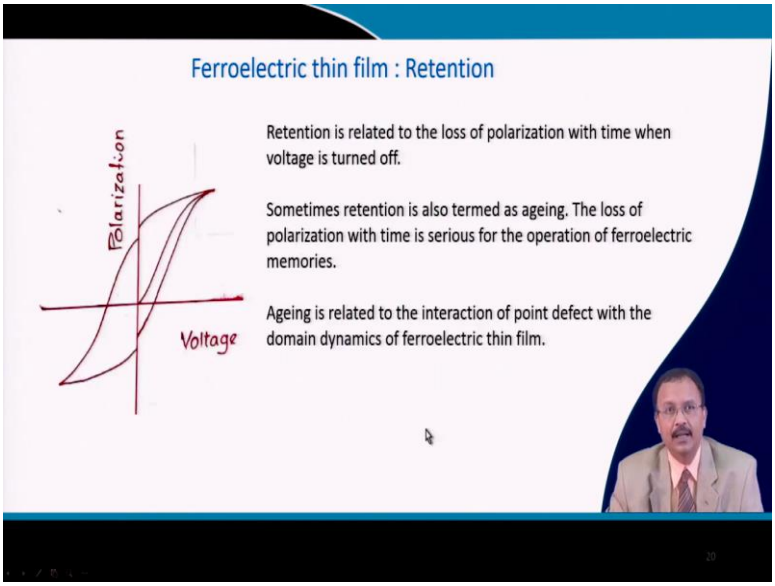

Another defect which is very important is called retention. You have written either 0 or 1 in the ferroelectric memory, and then you leave the memory as such then you will find that slowly there is a loss in the polarization. So, the polarization drops down here. Again you start to read it will start from this place instead of the original place.

So, this is known as retention failure, loss of polarization with time. Sometimes, it is also called aging effect of the ferroelectric memory. And defect and domain interaction plays a major role in this type of defect. So, this is the retention defect.

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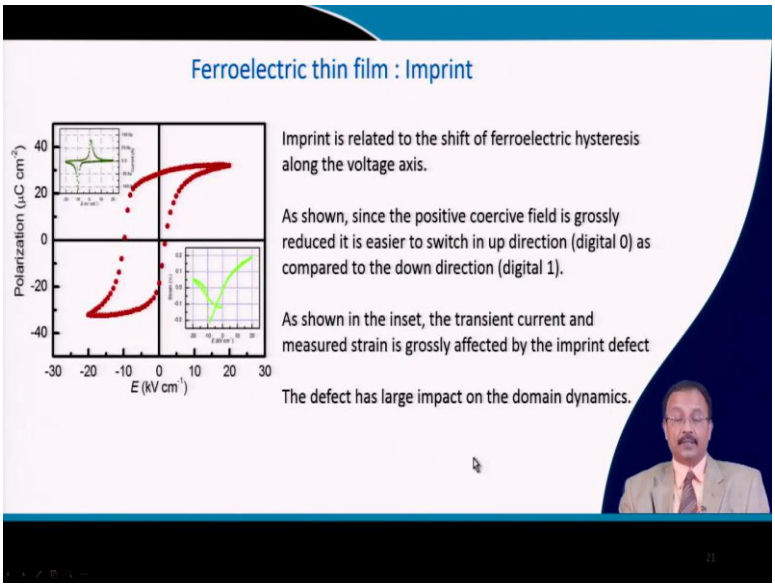

Another defect which is important which we called imprint. And this imprint is related to the translation of the ferroelectric hysteresis loop either towards positive x or negative x direction. So, it moves along with the voltage axis. As a result you see that if you want to switch this ferroelectric memory, you need a very small voltage if you go from positive up direction as compared to the negative down direction where you need a much larger voltage to switch it.

So, in other words, the coercive field changes. And it can easily be identified by the current pulse that I was talked I was talking about in couple of slides back. So, if you measure the current spike, then you will see that at one stage the current spike is relatively small in as far as the intensity is concerned as compared to the other one.

So that is a major defect the imprint needs to be solved. And since the ferroelectric is also piezoelectric in nature, this is also reflected if you measure the strain piezoelectric strain. We will talk about piezoelectric strain in my in as a part of my other lectures or some other interesting device. But this defect is also related to the domain dynamics interaction with the domain and the point defects inside the material.

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So, there is a two good books on ferroelectric thin film memory. They are basic. So, I am not giving any study material because I just wanted to introduce this important topic to you. So, there is not as such any study material. But if we are interested, these are two explain reference book on ferroelectric exclusively on ferroelectric memories. And people who are interested to do research in this area, they might find this book quite useful.

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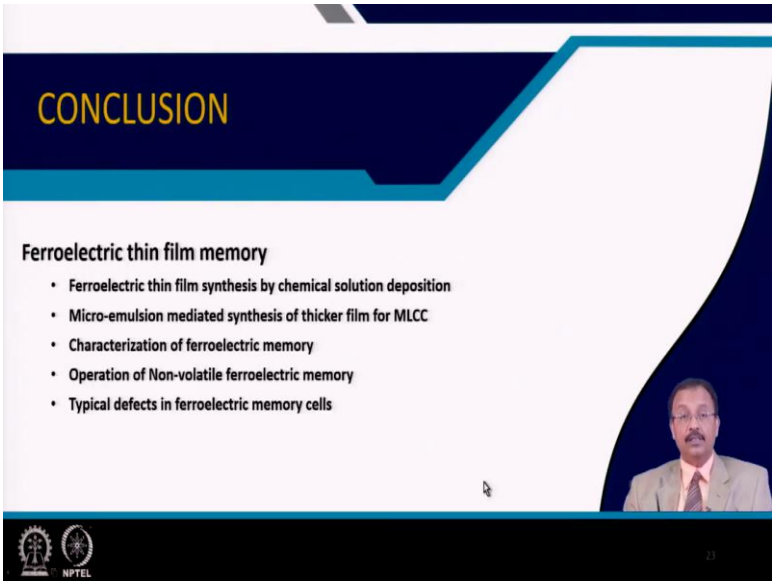

So, in this lecture, we talked about ferroelectric thin film synthesis and especially in the chemical solution deposition. Then we talked about micro-emulsion mediated synthesis of the thicker film for MLCC devices. And characterization of the ferroelectric memory, and how the non-volatile memory works how to determine the digital 0 and 1 from the measured current pulse. And finally, typical defects in ferroelectric memory cells.

Thank you for your attention.