# Fundamentals and Applications of Dielectric Ceramics

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## Lecture - 26
## Impedance Spectroscopy and Dielectric Breakdown

So welcome to the new lecture again for dielectric materials, fundamentals and applications of dielectric ceramics. So let us just briefly recap the last lecture.

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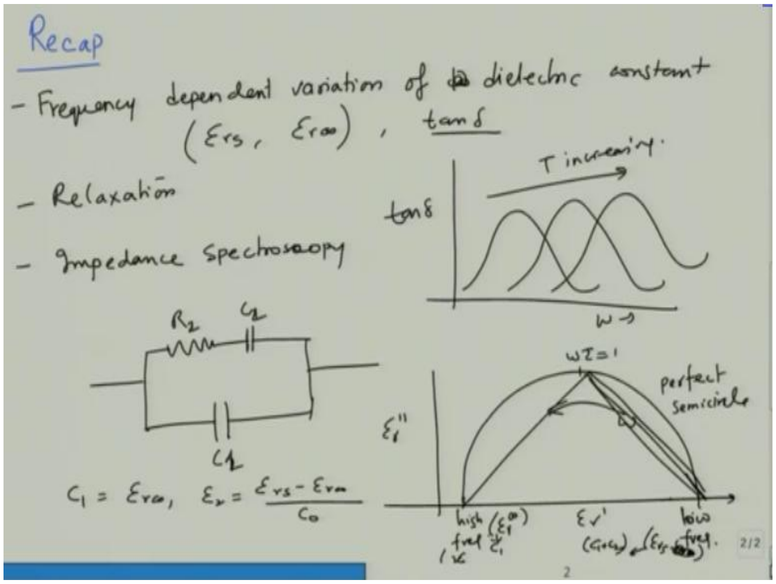

Recap

- Frequency dependent variation of dielectric constant ($\varepsilon_{rs}$, $\varepsilon_{r\infty}$), tan δ
- Relaxation
- Impedance Spectroscopy

$C_1 = \varepsilon_{r\infty}$, $\varepsilon_2 = \frac{\varepsilon_{rs} - \varepsilon_{r\infty}}{C_0}$

So in the last lecture, we basically talked about the frequency dependent variation of dielectric constant at low frequencies, okay. So we looked at essentially how the dielectric constant varies at lower frequencies. So it goes from a static, so basically we looked at $\varepsilon_{r,s}$, $\varepsilon_{r,\infty}$, and the difference between the two is the one that you observe at the lower frequencies and then we also looked at the variation of tan δ.

So this dipolar contribution is not resonance type of contribution rather it is a relaxation kind of behavior. So that is what we looked at and then there is also a temperature dependence as a result. Since it is a relaxation kind of phenomena, it is more like diffusive Arrhenius kind of behavior. There is an Arrhenius kind of relationship, so as the temperature changes, the change in the tan δ peak gets shifted to higher frequencies as the temperature changes.

So this is tan $\delta$, this is $\omega$ and the peak will shift to right as your temperature increases. So basically it requires lesser time for dipoles to respond and dipoles become weaker as increase in temperature and then we looked at the phenomena of impedance spectroscopy, because to analyse an electric material, it is often useful to model it in a circuit form. So we looked at one circuit.

For example, the device circuit through which you represented electric as a resistor and a capacitor in series and then you have, so this is $R_2C_2$ and then you have $C_1$, you can say $R_1$, that is entirely upto you. Let us just draw it a little. So this is, for what we did was, it was $R_1C_1$ and $C_2$. But it does not matter, means $R_1C_1$ and $C_2$ are entirely dependent upon your choice.

But what basically it means is that you will have for a perfect dielectric, when you plot $\varepsilon^{||}_r$ as a function of $\varepsilon^{|}_r$, you should obtain a perfect semicircle. It does not look like a perfect semicircle, maybe something like this. So this is perfect semicircle and as we saw that the peak of this is at $\omega\tau = 1$ and from this you can determine various characteristics.

So we looked at for instance, so this was actually $R_2C_2$, $C_1$ in the context of this. So essentially what we will have is, the frequency is increasing in this direction. So this your low frequency contribution and this frequency is, this is your high frequency contribution. So this is basically your $\varepsilon_{r,\infty}$ and this will be $\boldsymbol{\varepsilon_{r,s} - \varepsilon_{r,\infty}}$.
So that is what your contributions will be. So basically, what will happen is that if you work out $C_1$ and $C_2$, your $C_1$ will be $\varepsilon_{r,\infty}$ and $C_2$ will be $\boldsymbol{\varepsilon_{r,s}} - \boldsymbol{\varepsilon_{r,\infty}}$ divided by $C_0$. So if you look at the contributions here, this will be $\varepsilon_{r,\infty}$. This is basically $C_1$ corresponding to $C_1$ and this will be corresponding to, so this is $\varepsilon_{r,s}$. This will correspond to $(C_1 + C)$ basically. So this is what you should obtain, perfect semicircle.

And you can draw right angled triangle anywhere in this semicircle and you should get an equation of semicircle. Using this, this can also be modeled in the form of impedances, because we know that impedance is related to admittance. Admittance is related to your dielectric constant. This can be modeled in the form of impedances as well and we saw that when you measure impedance from an impedance analyzer.

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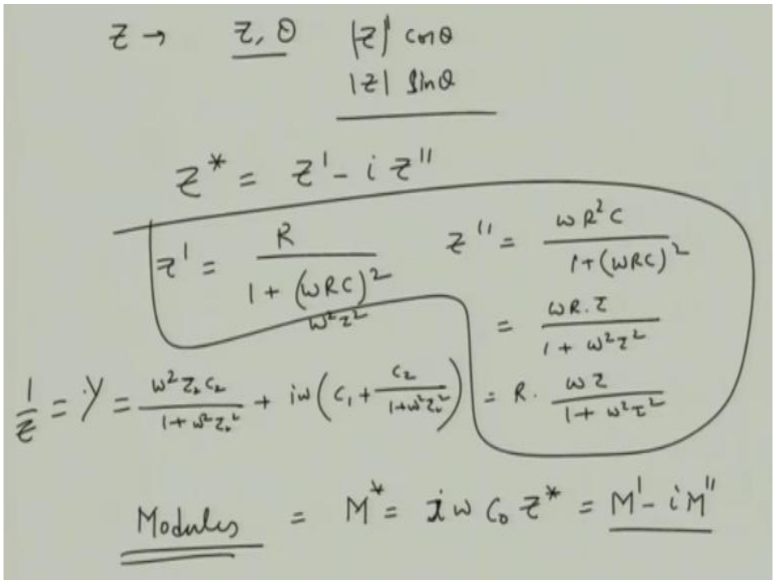

$Z \rightarrow \underline{Z, \theta}$ $\quad |Z| \cos\theta$

$|Z| \sin\theta$

$Z^* = Z' - iZ''$

$Z' = \frac{R}{1+\underset{\omega^2\tau^2}{(\omega RC)^2}}$ $\quad Z'' = \frac{\omega R^2 C}{1+(\omega RC)^2} = \frac{\omega R.\tau}{1+\omega^2\tau^2} = R.\frac{\omega\tau}{1+\omega^2\tau^2}$

$\frac{1}{Z} = Y = \frac{\omega^2 \tau_2 C_2}{1+\omega^2\tau_2^2} + i\omega\left(C_1 + \frac{C_2}{1+\omega^2\tau_2^2}\right)$

$\underline{\underline{\text{Modulus}}} = M^* = i\omega C_0 Z^* = \underline{M' - iM''}$

Basically you are measuring Z(θ), so real part of impedance will be |Z| cos θ and then you will have |Z| sin θ. So you can determine what are the real parts of impedances, what are the imaginary parts of impedances and they will allow you to determine, and we know that impedance is nothing but:

$$Z^* = Z' - iZ''$$

and Z prime can be modeled as:

$$Z' = \frac{R}{1+(\omega RC)^2}$$

And $Z''$ can be:

$$Z'' = \frac{\omega R^2 C}{1+(\omega RC)^2}$$

$$Z'' = \frac{\omega R\tau}{1+(\omega\tau)^2}$$

or,

$$Z^{\|} = R.\frac{\omega\tau}{1+(\omega\tau)^2}$$

So this is basically the variation of, so you can see that there is a frequency dependence of impedance and so frequency we saw earlier. So these impedances can be worked out as we know that Y was the admittance.

Admittance was worked out as:

$$\frac{1}{Z} = Y = \frac{\omega^2 \tau_2 C_2}{1+\omega^2 \tau_2^2} + i\omega\left(C_1 + \frac{C_2}{1+\omega^2 \tau_2^2}\right)$$

This is what we worked out earlier. Essentially from this Z, one can work out modulus as well. Modulus is given as:

$$M^* = i\omega C_0 Z^* = M' - iM''$$

The advantage of using this modulus and impedance spectroscopy together is that modulus tend to amplify the contributions of higher frequency, lower frequency contributions, but since you can see that $M^*$ is nothing but $\mathbf{i\omega C_0 Z^*}$, this tend to amplify the contributions at the higher frequency. So often you will see the semicircles at higher frequency are subdued in the impedance spectroscopy.

But when you do modulus spectroscopy, the contributions of high frequency contributions, they are more clearly visible in case of modulus. So they complementary of each other in the sense that they are not derived from something differently, they are all dependent upon each other, but is just that a different way of representing the two properties and also if we now make a table of the complex relationships, so let us say we make.

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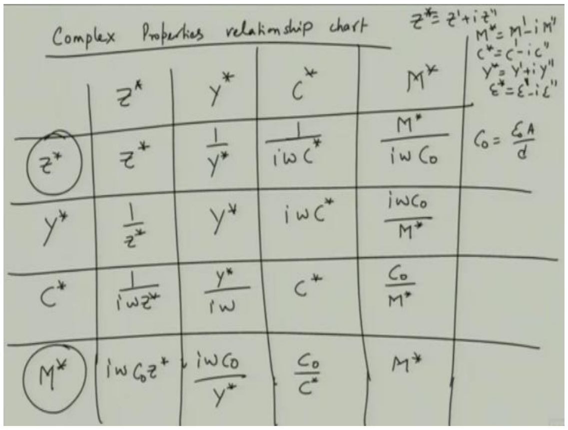

Complex Properties relationship chart

$Z^* = Z' + iZ''$
$M^* = M' - iM''$
$C^* = C' - iC''$
$Y^* = Y' + iY''$
$\varepsilon^* = \varepsilon' - i\varepsilon''$

| | $Z^*$ | $Y^*$ | $C^*$ | $M^*$ |
|---|---|---|---|---|
| $Z^*$ | $Z^*$ | $\frac{1}{Y^*}$ | $\frac{1}{i\omega C^*}$ | $\frac{M^*}{i\omega C_0}$ |
| $Y^*$ | $\frac{1}{Z^*}$ | $Y^*$ | $i\omega C^*$ | $\frac{i\omega C_0}{M^*}$ |
| $C^*$ | $\frac{1}{i\omega Z^*}$ | $\frac{Y^*}{i\omega}$ | $C^*$ | $\frac{C_0}{M^*}$ |
| $M^*$ | $i\omega C_0 Z^*$ | $\frac{i\omega C_0}{Y^*}$ | $\frac{C_0}{C^*}$ | $M^*$ |

$C_0 = \frac{\varepsilon_0 A}{d}$

Because we know that these are related to properties such as impedances, admittances, which are complex properties. So complex properties relationship chart can be made, which helps you in analyzing dielectric materials little better. So let us say, on this axis we plot. So here we have $Z^*$, here we have $Y^*$ and we have $C^*$ and we have $M^*$, right and again we say $Z^*$, Y, $C^*$ and $M^*$.

The above tables shows the following relationships:

$$Z^* = 1/Y^* = 1/i\omega C^* = \frac{M^*}{i\omega C_0}$$

$$Y^* = 1/Z^* = i\omega C^* = i\omega C_0/M^*$$

$$C^* = 1/i\omega Z^* = Y^*/i\omega = C_0/M^*$$

$$M^* = i\omega C_0 Z^* = i\omega C_0/Y^* = C_0/C^*$$

So this is how these complex properties are related to each other. Generally, we use Z and M for determination of various components.

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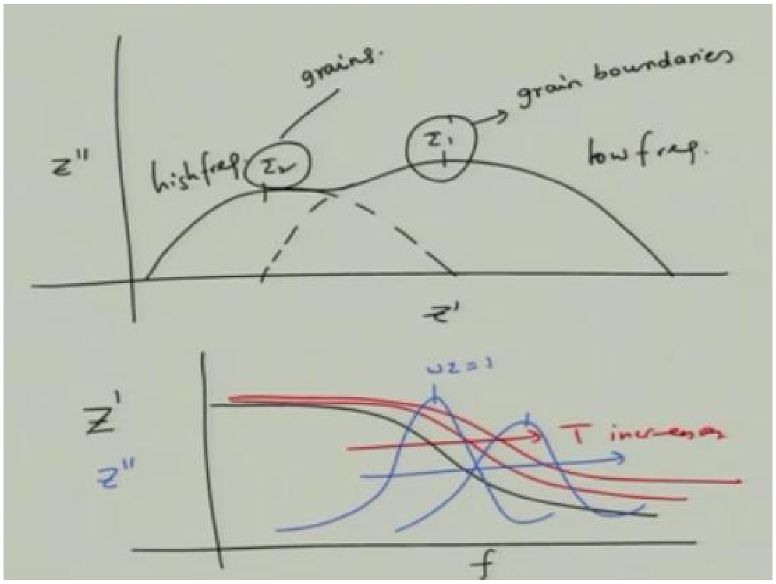

So what might happen for example is you might have a spectra like this. You may have spectra, which is like this. So this is let us say $Z''$, this is $Z'$. So basically we have two semicircles here, one is for low frequency and one is for high frequency. Both of them have $\tau_1$ and $\tau_2$. So as a result, what will happen is that the time constant for this semicircle belongs to one entity. So generally low frequency contributions in solids will come from grain boundaries.

Whereas the high frequency contributions will come from grains. So when you plot, let us say temperature dependence of these plots. How does the temperature dependence vary? So for example, if you want to plot $Z'$ as a function of frequency. So $Z'$ as a function of frequency might vary something like this. As we increase the temperature, the curve will shift to right. So temperature increases.

Similarly, the peak in the $Z''$, the $Z''$ will show correspondingly if you plot $Z''$, they will show corresponding peaks. These peaks will also shift towards right and these peaks correspond to basically $\omega\tau = 1$.

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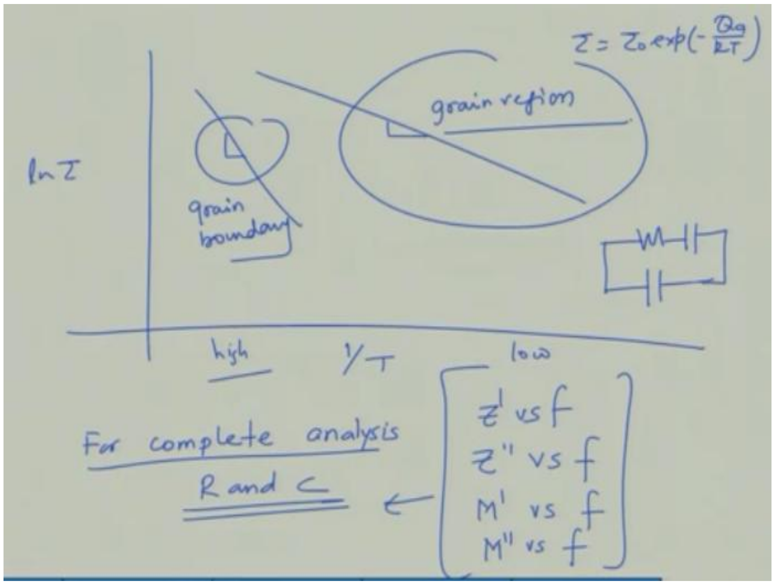

So what you do is that, when you plot 1/T and we know that:

$$\tau = \tau_0 e^{\left(-Q_a/k_B T\right)}$$

So when you plot ln τ, we get slopes like these for example. So you will get two distinct regions, in which you will have one slope and another slope. So this is for example at low temperature and this is at high temperature. So there is one entity, which has certain activation energy at lower frequency and certain activation at higher frequency.

So it might happen that you will have, this is for example it could be grain boundary region. This could be grain region. They also have different frequency dependence because the grain, for example this particular region on the right, this may respond at higher frequencies, whereas the region that you see on the left, which is for grain boundaries, it may respond at lower frequency. So the different type of peaks show different behavior in the evolution of Z and M.

So basically for complete analysis, you need to look at Z versus $Z'$ versus frequency, $Z''$ versus frequency, $M'$ versus frequency, $M''$ versus frequency. From these, you can determine R and C, the resistances and capacitances separately, because most of these entities have, so ideal device capacitor looks like this. This is your ideal device material, but in reality your material may look like.

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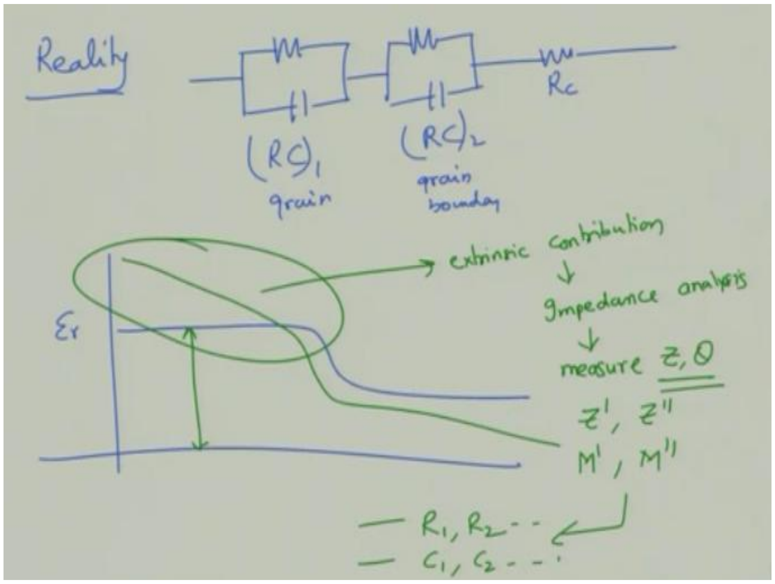

In reality, your material may be modeled like this and so on and so forth. So this is one RC circuit. This is another RC circuit, $RC_1$, $RC_2$, this could be for grain, this could be for grain boundary and then you have series resistance, which is, let us say contact resistance RC and so on and so forth. So reality may give you different resistances and capacitances and this happens especially in polycrystalline material or materials with lot of defects, where resistances and capacitances vary dramatically.

As a result, you need to separate out the resistive contribution and the capacitive contribution. So for example when you see dielectric constant variation as a function of frequency, ideally it should be like this, but in most cases you will obtain a behavior, which is like this. This decrease of electric constant suggests as a function of frequency that you have extrinsic contributions, which could be defects for example, which could be vacancies in the system, variety of defects.

So from this, from the blue plot, it is easy to measure what the dielectric constant is, because dielectric constant is, there is a contribution, which is frequency independent, but here you have a frequency dependence. So how do you separate out the real dielectric constant. What is dielectric constant is difficult to tell. So that is why you need to carry out impedance analysis, measure Z and θ from that, you work out what is $Z'$ and $Z''$.

Then you work out what is $M'$, $M''$. Then you work out what is different $R_1$, $R_2$, etc., different $C_1$, $C_2$, etc., then looking at the values of $R_1$ and $C_2$, you have to make a judgment. So generally you will find, how do you make a judgment then?

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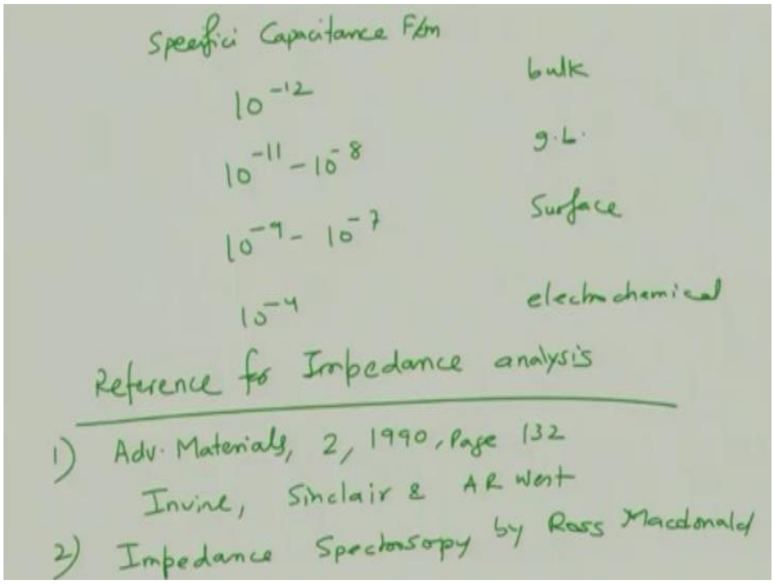

| Specific Capacitance F/cm | |
|---|---|
| $10^{-12}$ | bulk |
| $10^{-11} - 10^{-8}$ | g.L. |
| $10^{-9} - 10^{-7}$ | Surface |
| $10^{-4}$ | electrochemical |

Reference for Impedance analysis

1) Adv. Materials, 2, 1990, Page 132
Irvine, Sinclair & A R West

2) Impedance Spectrosopy by Ross Macdonald

So for example, if you look at, if you work out a specific capacitance, specific capacitance is given in farad per meter,or farad per centimeter let us say in this case. So generally, if the capacitance is of the order of $10^{-12}$, it is because of bulk. If it is a grain boundary, then it would be of the order of -11 to -8. So this would be grain boundary. If it is a surface layer, it would be -9 to -7 for surface layer.

And let us say if you have electrochemical reaction, it may be of the order of -4 for electrochemical reaction. So these values of capacitances will give you an idea about which entity are you talking about. Whether you are talking about bulk or whether you are talking of grain boundaries. So it is very important to know about what you are doing. So we will give you certain references that you may go through for impedance spectroscopy.

For example, there is a nice paper written by, there is book in Sheffield University, which has worked extensively on this. So let me give you the reference. If you look at reference for, so you can read this paper by, it is an *advanced materials general volume 2 1990 page 132*. This is by authors called as Irvine, Sinclair and A. R. West. It is a good paper that gives you some idea about the impedance spectroscopy.

Then, impedance spectroscopy, there is a book impedance spectroscopy by Ross MacDonald. It is a vast topic, impedance spectroscopy. We cannot talk about this in this course, but just wanted to tell you what you can do. The things that you can do is that, you can basically look at the microscopic mechanisms behind this capacitances and find out any resistances and separate out the resistive and capacitive contributions.

Work out the true value of electric constant, which is purely from the capacitive contributions, not from anything else by properly modeling the impedance data using these kind of circuits and this is helped by doing this impedance and modulus spectroscopy and measurement is basically measurement of impedance and angle, Z and θ, which is done on an impedance analyzer. So we will now stop this part of impedance spectroscopy and we will briefly now look at finishing this part of linear dielectric and dielectric breakdown.

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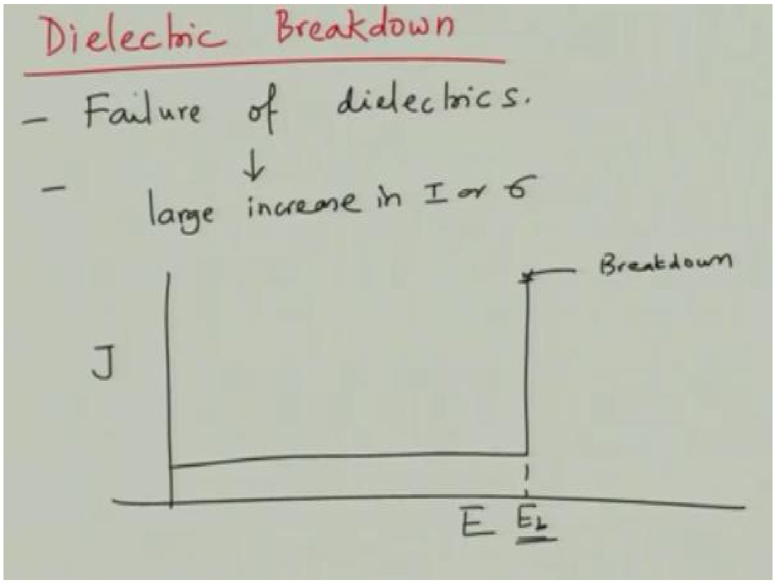

Dielectric Breakdown

- Failure of dielectrics.

↓

- large increase in I or $\sigma$

And this dielectric breakdown is basically about failure of the electrics. So dielectrics work under certain electric field when basically this top becoming dielectrics, that is when dielectric breakdown occurs and generally it is denoted in the form of large increase in current and conductivity of dielectric. So this is what basically dielectric breakdowns means. So essentially if you plot current density as a function of field.

For very large field, the current density will remain low and suddenly at some point the current density will shoot up. So this is where you will have breakdown and this field is denoted as $E_b$, which is the breakdown field. So essentially, this is what we mean by dielectric breakdown. So in many cases, the breakdown may not be sudden, it may be gradual, whereas in some cases it may be very rapid.

So if you look at the breakdown, the strength of certain materials, the most important material, something that we come across regularly is air.

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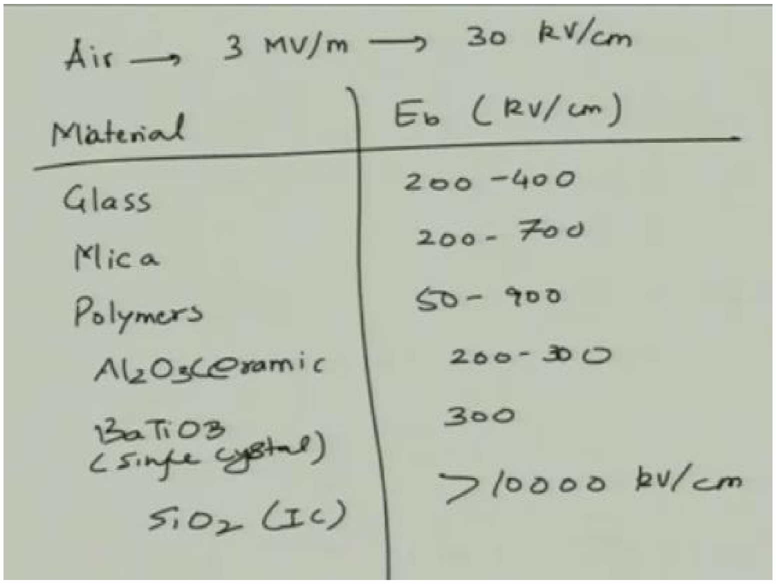

Air → 3 MV/m → 30 kV/cm

| Material | $E_b$ (kV/cm) |
|---|---|
| Glass | 200 -400 |
| Mica | 200- 700 |
| Polymers | 50- 900 |
| $Al_2O_3$ Ceramic | 200- 300 |
| $BaTiO_3$<br>(single crystal) | 300 |
| $SiO_2$ (IC) | $>$10000 kV/cm |

When you see sparking in the air right, sparking is basically ionization of air. Air has a breakdown field of 3 MV/m, which is about 30 kV/cm and now if you compare certain materials, so let us say we have materials and then we have $E_b$ and we compare this with the, so this is in kV/cm. So if you look for glass, glass has a value of 200-400. If you look at mica, mica has a value of about 200-700.

Look at polymers, they have a value ranging from 50-900. If you look at $Al_2O_3$ ceramic it has a value from 200-300. If you look at barium titanate it has a value of roughly 300 for single crystals and silicon carbide that is silicon oxide that is used in ICs, it has more than 10,000 kV/cm. So you can see that for most materials, the value of breakdown field is significantly larger than the value of breakdown field for air.

So if you now compare, for example on electric pole sometimes you see the sparking and that is mostly because of the failure of the capacitor that you have and the field in the capacitor becomes so high that the air molecules in vicinity, they get ionized. Also materials contain pores, within the pores you have entrapped air and when the field is applied, this air gets ionized and sort of it leads to blasting of the material or failure of the material. So there are various mechanisms because of which this failure occurs.

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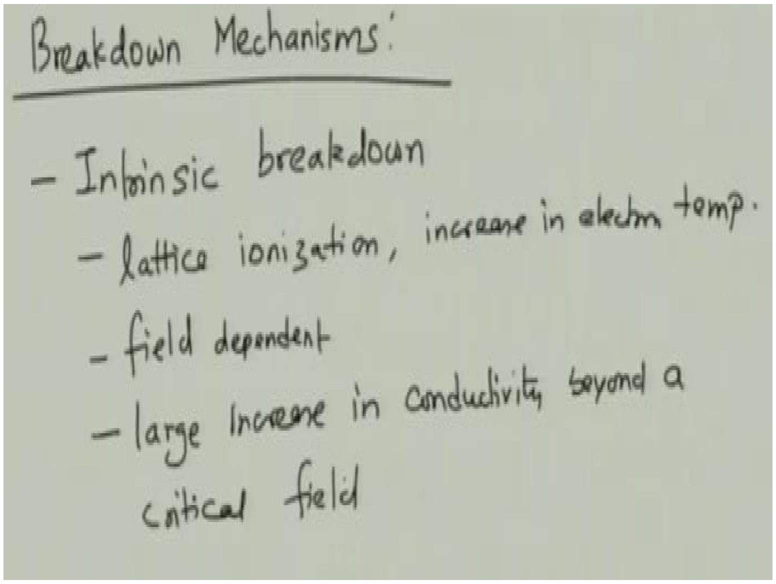

Breakdown Mechanisms:

- Intrinsic breakdown
  - lattice ionization, increase in electron temp.
  - field dependent
  - large increase in conductivity beyond a critical field

So the breakdown mechanisms are basically, so the first one is intrinsic breakdown. Intrinsic breakdown is basically based on lattice ionization and what it means is that there is a substantial increase in the electron temperature and this is basically a field dependent mechanism. When you apply very high field, the electron temperature rises. As a result, the materials it becomes very conducting, so field dependent. Large increases in conductivity beyond a critical field.

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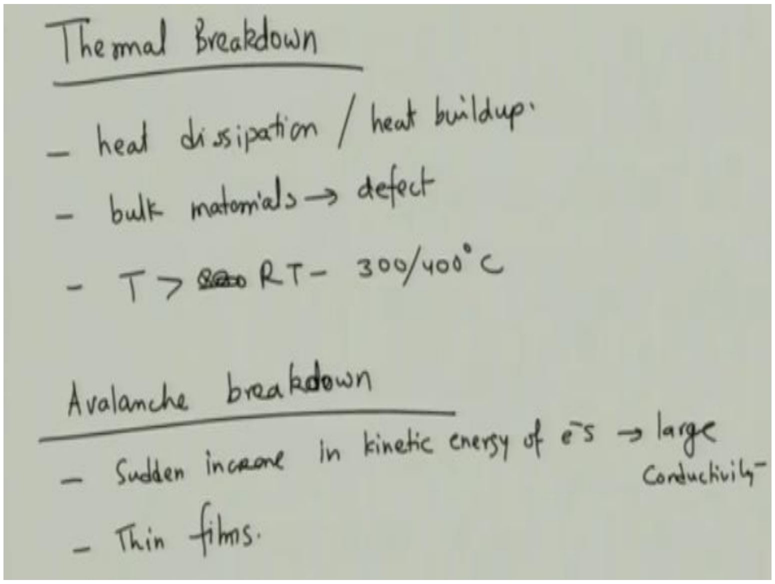

Thermal Breakdown

- heat dissipation / heat buildup.
- bulk materials → defect
- $T >$ RT – 300/400°C

Avalanche breakdown

- Sudden increase in kinetic energy of $e^-$s → large conductivity
- Thin films.

Then we have another mechanism, which is called as thermal breakdown. Thermal breakdown is basically because of heat dissipation. So materials have defects and various other reasons, which lead to increase in the temperature of the material and this is basically true for many of the bulk materials, which contain defects and they have intrinsic heating and this generally happens at temperatures, which is greater than room temperature upto about $300^0$-$400^0$C, something like that.

Basically, it can be, the process can be gradual. It can happen at various time scales and it may also be dependent upon the sample geometry. So this is thermal breakdown and then we have avalanche breakdown. Essentially, this is because of heat dissipation or a heat buildup and then we have, this is basically because of sudden increase in kinetic energy of electrons leading to large.

So any processes, kinetic processes which lead to multiplication in the electron density and electron velocities, they lead to large increase in the conductivity. So sudden avalanche, avalanche means deluge of electrons and that leads to a large conductivity. So this is another one and this generally happens in thin films and then you can have other breakdowns, such as you can have dielectric discharge.

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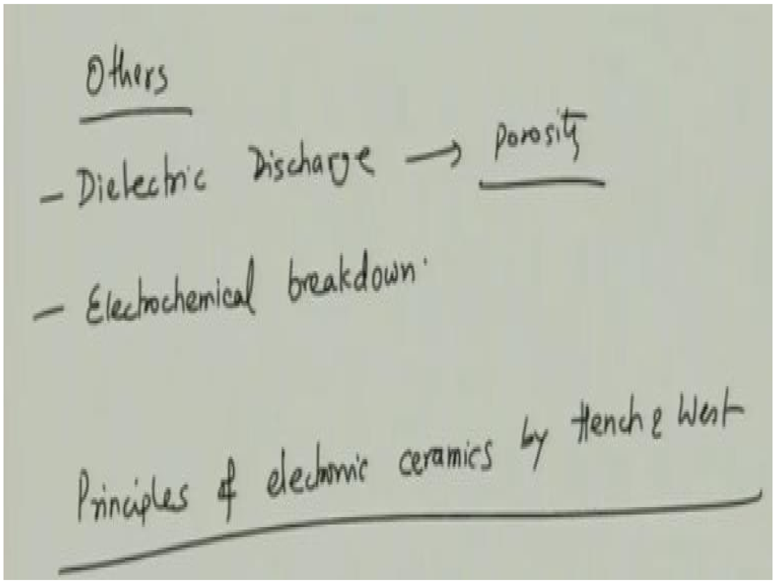

Others

- Dielectric Discharge → porosity
- Electrochemical breakdown

Principles of electronic ceramics by Hench & West

And dielectric discharge could be because of for example, porosity, if you have porosity or air entrapped in the air, the discharge is created inside the material, when you apply a field, the air gets ionized and which is basically electrical discharge and sort of leads to material ripping apart and then you can also have electrochemical breakdown, which could be because of transport of materials from one place to another within the same material.

So some species may transport one to another position and another species may transport to another position, which leads to change in the chemistry side or ionic defect chemistry leading to change in the conductivity. So if you want to read more about breakdowns, you can read this book, *Principles of electronic ceramics by Hench and West*. So this is sort of a short introduction to linear dielectric materials that we have given to you.

Basically, covering from fundamental dielectric materials, dielectric polarization, dielectric constant, mechanisms of polarization, what kind of polarizabilities that we have, with some analytical treatment of dielectric polarizabilities of ionic electronic and dipolar, looking at the macroscopic as well as the microscopic scale in terms of frequency dependence and finally we talked about device equations and impedance spectroscopy.

How to use impedance spectroscopy to characterize these materials and finally about the dielectric breakdown. So hopefully, this has given you a good idea about linear dielectrics, how do you work with them, how do you characterize them and in the next class, we will start our discussion on non-linear dielectric materials, which basically we will talk about some basics of piezo-electric, ferro-electric, and pyro-electric materials. What distinguishes them and individual physics and application of these materials.