Non - Metallic Materials

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Module - 08
Thin film growth and fabrication of devices
Lecture - 42
Fundamentals and processing conducting and semiconducting ceramic devices

Welcome to my course Non-Metallic Materials and we are in module number 8, Thin film growth and fabrication of devices and we are in lecture number 42, Fundamentals and processing of conducting and semiconducting ceramic device.

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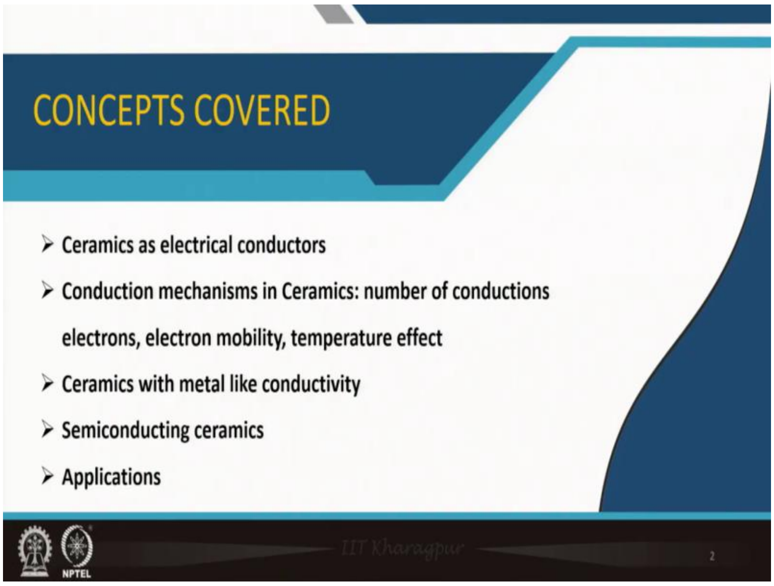

CONCEPTS COVERED

- Ceramics as electrical conductors
- Conduction mechanisms in Ceramics: number of conductions electrons, electron mobility, temperature effect
- Ceramics with metal like conductivity
- Semiconducting ceramics
- Applications

So, in this particular lecture, first I will introduce to ceramics as electrical conductors. Most of you know that ceramic is basically an insulating material, but certain ceramics they behave electrically they behave like electrically conducting way.

And, the conduction mechanism of ceramics will be introduced and that will include that how to estimate the number of conducting electrons, electron mobility and their temperature effect. Then we will introduce certain special ceramics which impart metal like conductivity, then we will talk about semiconducting ceramics which are having wide band gap as compared to the conventional ceramics and certain applications of this ceramics will be highlighted.

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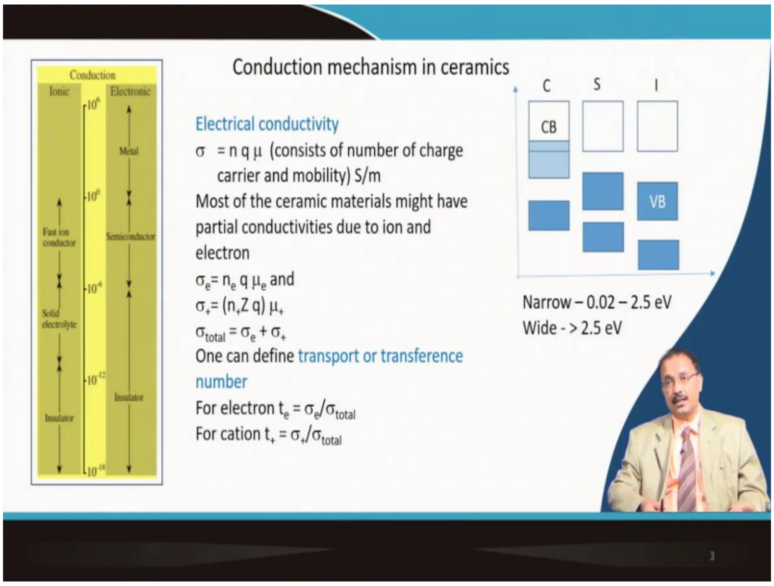

Conduction mechanism in ceramics

Electrical conductivity

$\sigma = n\,q\,\mu$ (consists of number of charge carrier and mobility) S/m

Most of the ceramic materials might have partial conductivities due to ion and electron

$\sigma_e = n_e\,q\,\mu_e$ and

$\sigma_+ = (n_+ Z\,q)\,\mu_+$

$\sigma_{total} = \sigma_e + \sigma_+$

One can define transport or transference number

For electron $t_e = \sigma_e/\sigma_{total}$

For cation $t_+ = \sigma_+/\sigma_{total}$

Narrow – 0.02 – 2.5 eV

Wide - > 2.5 eV

So, if you see the view graph the left one you can see that the conductivity based on the conductivity, you can differentiate metal you can differentiate semiconductor and there is a wide range of insulators. And, here the charge carriers are either electron and hole, apart from that you have ionically conducting solids and we have differentiated between fast ion conductor which partially I have covered in my earlier lectures.

Solid electrolyte concept that was also introduced in fuel cell as well as electrochemical sensors and some of them are perfectly insulator. It is not necessary that the same material will be both electronically as well as ionically conducting, there could be mixed conduction as well.

But, the basic conductivity that is given by this relation. So, conductivity depends on number of charge carrier and their mobility and associated charge and this is usually given by Siemen's per meter. So, most of the ceramic materials might have partial conductivity because both ion and electron they are the charge carrier.

So, you can have the situation that electronic conductivity that is given by this relation with the mobility of electron, density of the electron that has prominent role to control this conductivity and certain ions also can conduct.

So, here for example, cation is conducting. So, concentration of the cation, their associated charge Z q, and the mobility of the cation that will constitute this conductivity

– so, the total conductivity that will be both due to electron and ion. So, very often one can define a transport number that out of this total conductivity what is the fraction that is given by electrons and what is the fraction is given by the so called cation.

So, depending on that you can have the transference number which is defined as either t e or t plus. Now, this is a very basic band diagram as you can see in case of conductors the valence and conduction band they basically overlap; in case of your semiconducting material the band gap is relatively small about one electron volt or so. In case of insulating material they are relatively larger, more than 2 electron volt or could be 5 electron volt or higher.

So, we call it is a narrow band gap when the eg value the band gap value is in between 0.02 to 2.5 electron volt and we will define the ceramic as wide band gap semiconductor will not call it insulator. So, it is a wide band gap semiconductor when the band gap is more than 2.5 electron volt.

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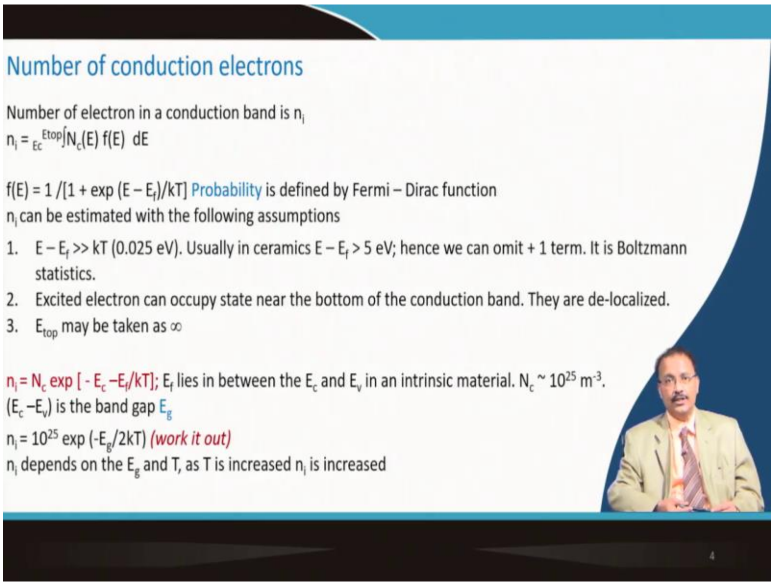

Number of conduction electrons

Number of electron in a conduction band is n_i

$n_i = {}_{Ec}{}^{Etop}\int N_c(E)\, f(E)\ dE$

$f(E) = 1 /[1 + \exp (E - E_f)/kT]$ Probability is defined by Fermi – Dirac function

n_i can be estimated with the following assumptions

1. $E - E_f >> kT$ (0.025 eV). Usually in ceramics $E - E_f > 5$ eV; hence we can omit + 1 term. It is Boltzmann statistics.
2. Excited electron can occupy state near the bottom of the conduction band. They are de-localized.
3. E_{top} may be taken as ∞

$n_i = N_c \exp [- E_c - E_f/kT]$; E_f lies in between the E_c and E_v in an intrinsic material. $N_c \sim 10^{25}\ m^{-3}$.

$(E_c - E_v)$ is the band gap E_g

$n_i = 10^{25} \exp (-E_g/2kT)$ *(work it out)*

n_i depends on the E_g and T, as T is increased n_i is increased

So, in order to get the conductivity first we will have to know what is their number of conducting electrons. So, we will borrow the knowledge of semiconducting materials and we know that for electron in the conduction band, if I define that concentration as n i intrinsic electrons that you can get if you integrate from the energy band of conduction to some level maybe infinity.

So, it is a top level of the conduction band, it is a flat band kind of approximation and this is given as N c density of state in the conduction band and the probability of finding an electron in that energy range. So, this probability is given by this relation and this relation is known as Fermi Dirac function.

So, if you have certain estimation assumption if you can make then it is possible for you to get the number of intrinsic electron in the conduction band. First approximation is quite straightforward. The difference between this energy E and E f it is much much larger than k T.

So, if you are considering t at room temperature, assume the value of k 8.865 into 10 to the power minus 5 electron volt per Kelvin then kT value is 0.025 electron volt. And, usually in case of ceramic this E minus E f is much larger than 5 electron volt for an insulator. So, you can omit the term which is this one and it is nothing, but Boltzmann statistics. This equation turns into similar to Boltzmann statistics.

Second assumption is that excited electron can occupy state near the bottom of the conduction band and once they are in the bottom of the conduction band they are delocalized. So, they can travel anywhere in the crystal and take part in the conduction. So, usually this E top of this equation that can be taken as infinity.

So, assuming this three assumption which is not very non real, we can have this n i is equal to density of state N c exponential of minus of E c minus E f by kT. So, it tells me that the Fermi energy level that lies in between the E c and E v, the conduction band and valence band of an intrinsic material and you can easily calculate the number of density states roughly it is 10 to the power 25 per meter cube.

So, the difference between E c and E v from the definition we know that it is a band gap. So, you can calculate you can work it out from this relation basically after you just put the relevant values it is nothing, but N c into exponential of minus E g by 2kT. So, that tells me that this intrinsic electron that depends on the band gap of the ceramic, the insulating material as well as temperature is also a function.

Usually, if you increase the temperature unlike the metal like conductor your intrinsic electron concentration increases.

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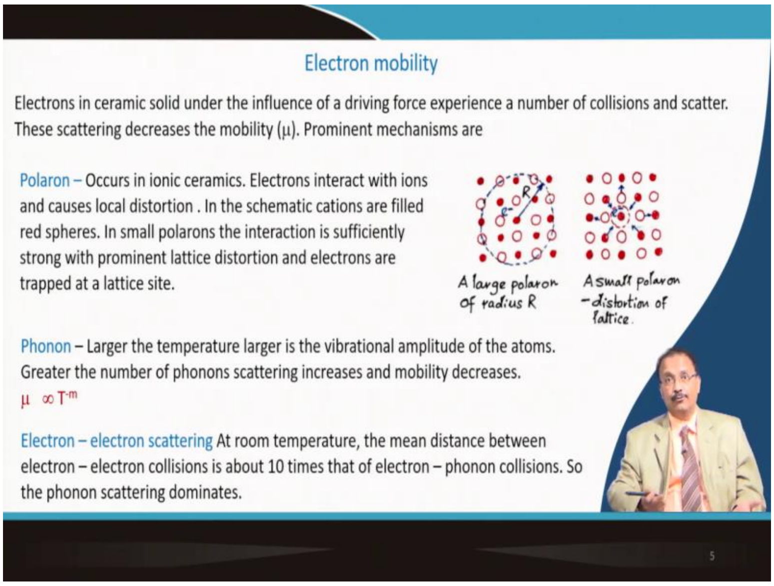

Electron mobility

Electrons in ceramic solid under the influence of a driving force experience a number of collisions and scatter. These scattering decreases the mobility (μ). Prominent mechanisms are

Polaron – Occurs in ionic ceramics. Electrons interact with ions and causes local distortion . In the schematic cations are filled red spheres. In small polarons the interaction is sufficiently strong with prominent lattice distortion and electrons are trapped at a lattice site.

Phonon – Larger the temperature larger is the vibrational amplitude of the atoms. Greater the number of phonons scattering increases and mobility decreases.

$\mu \propto T^{-m}$

Electron – electron scattering At room temperature, the mean distance between electron – electron collisions is about 10 times that of electron – phonon collisions. So the phonon scattering dominates.

Now, once the electron is there in the conduction band so, and they are under the influence of a some kind of driving force they could be electromotive force or temperature, then they experience a number of collision and they will start to scatter. So, your mobility term will be affected and if it scatters, then the mobility will be less.

So, there are three prominent mechanism which can affect your mobility. The first one is called this polaron and polaron is a new concept for you and it occurs only in ionic ceramic material. So, electrons will start to interact with ions. So, you can see that these are free electrons and you have ionic crystal, it will start to interact with the cation.

So, the cation is this red sphere and anion is the unfilled spheres. So, we call that is a interaction region and this is marked as a circular kind of thing it is a large polaron it is having a definite radius. So, this large polaron, that is, that can be there or more effectively there will be small polaron where the interaction is sufficiently strong.

Interaction between the electron and the cation of the material and this is so strong that the supportive the surrounding anion and cation they will come in close proximity to this. So, there will be a lattice distortion and sometimes this electron can be trapped here. So, if it is trapped then it is mobility is almost 0. So, this polaron first they affect the electron mobility.

Second one is the phonon you know the larger is the temperature, larger is the vibrational amplitude of the atom within a crystal that I have mentioned several times. So, greater the number of phonons scattering if it increases with temperature then the mobility decreases. So, roughly this mobility is proportional to T to the power minus m; m is a constant. So, as T is increased, your mobility will get reduced.

And third one is electron – electron scattering because electron can scatter with other electron as well. So, if you consider at room temperature, the mean distance of electron – electron collision that is quite large about 10 times as compared to electron and phonon collision. So, basically the phonon scattering, that dominates the mobility of this electron.

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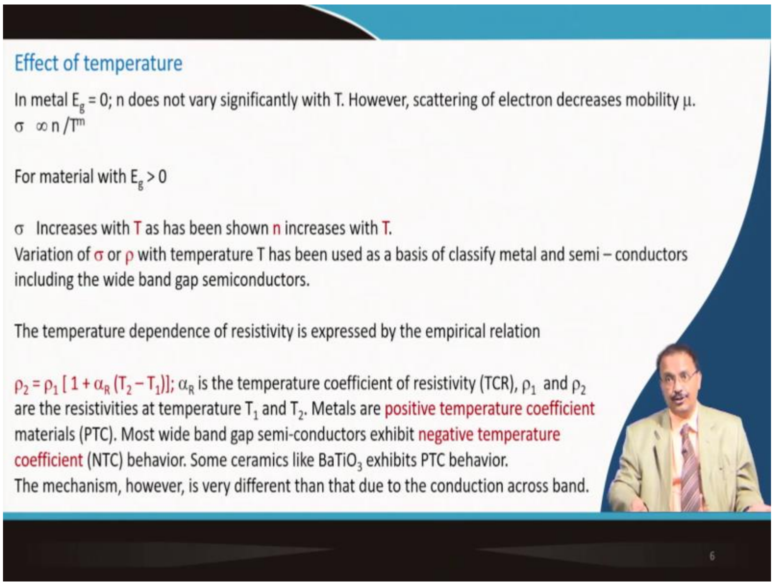

Effect of temperature

In metal $E_g = 0$; n does not vary significantly with T. However, scattering of electron decreases mobility μ.

$\sigma \ \infty n/T^m$

For material with $E_g > 0$

σ Increases with T as has been shown n increases with T.

Variation of σ or ρ with temperature T has been used as a basis of classify metal and semi – conductors including the wide band gap semiconductors.

The temperature dependence of resistivity is expressed by the empirical relation

$\rho_2 = \rho_1 [1 + \alpha_R (T_2 - T_1)]$; α_R is the temperature coefficient of resistivity (TCR), ρ_1 and ρ_2 are the resistivities at temperature T_1 and T_2. Metals are positive temperature coefficient materials (PTC). Most wide band gap semi-conductors exhibit negative temperature coefficient (NTC) behavior. Some ceramics like $BaTiO_3$ exhibits PTC behavior.

The mechanism, however, is very different than that due to the conduction across band.

Now, if you consider a metal, in case of metal your band gap is 0. So, n does not vary significantly with temperature, but the scattering of electron that do decrease their mobility. So, conductivity is basically controlled by n.

So, n does not change much with T because most of the electrons they are in the conduction band they are free to move but, it is inversely proportional to T. So, if you increase the temperature then the conductivity because of the phonon scattering they are actually reduced.

For material with band gap more than 0 so, either semiconductor or wide band gap semiconductor or perfect insulator sigma increases with T because n is a function of T that already I have shown. So, n increases with T. So, conductivity will also increase variation of sigma or the resistivity with temperature has been a basis of classifying the material the metal semiconductor.

So, based on that we can differentiate whether it is a metallic material or it is a semiconducting material. So, usually the temperature dependence of the resistivity, that is, defined by some kind of empirical relations so, we will more comfortable to define the resistivity.

So, the resistivity relation with temperature is with this simple relation where the constant alpha R; this is the temperature coefficient of resistivity is abbreviated as TCR and rho 1 and rho 2 are the resistivity at two different temperature T 1 and T 2. So, usually metals they have positive temperature coefficient with the increase in temperature the resistivity will increase. So, we call it is a positive temperature coefficient material.

Most of the semiconductor they exhibit negative temperature coefficient with a increase of temperature the resistivity they will drop conductivity will increase, some ceramic I will define later for example, barium titanate they do exhibit a positive temperature coefficient behaviour. But, the mechanism is very different and mechanism is basically controlled by the grain boundary.

So, that is a very different mechanism which is prevailing in this kind of PTC behaviour of barium titanate.

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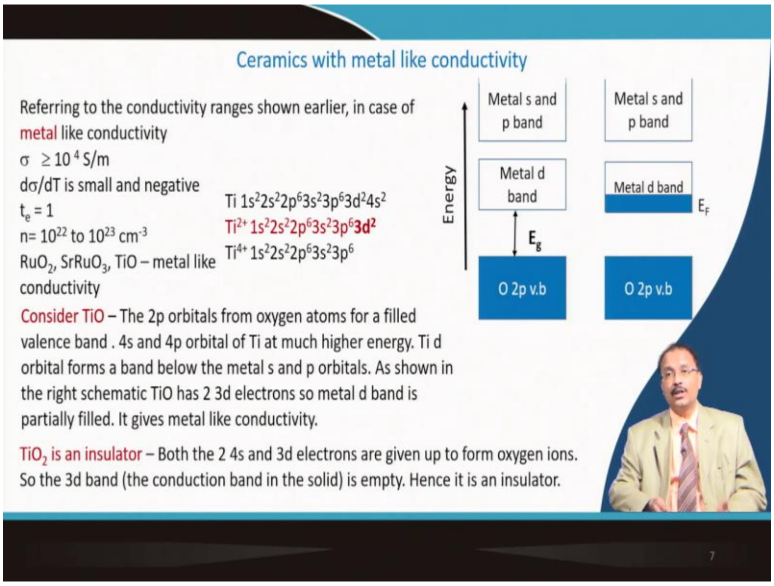

Ceramics with metal like conductivity

Referring to the conductivity ranges shown earlier, in case of metal like conductivity

$\sigma \geq 10^4$ S/m

$d\sigma/dT$ is small and negative

$t_e = 1$

n= 10^{22} to 10^{23} cm^{-3}

RuO_2, $SrRuO_3$, TiO – metal like conductivity

Ti $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$

Ti^{2+} $1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{3d^2}$

Ti^{4+} $1s^2 2s^2 2p^6 3s^2 3p^6$

Consider TiO – The 2p orbitals from oxygen atoms for a filled valence band . 4s and 4p orbital of Ti at much higher energy. Ti d orbital forms a band below the metal s and p orbitals. As shown in the right schematic TiO has 2 3d electrons so metal d band is partially filled. It gives metal like conductivity.

TiO_2 is an insulator – Both the 2 4s and 3d electrons are given up to form oxygen ions. So the 3d band (the conduction band in the solid) is empty. Hence it is an insulator.

So, certain material as I told that exhibit metal like conductivity. So, once I talk about metal like conductivity the conductivity range is more than at least 10 to the power 4 Siemens per meter. The deviation I mean that if you take a derivative of sigma with t that usually small and that is negative, remember we are talking about the conductivity now.

The value of n is usually in the range of 10 to the power 22 to 10 to the power 23 per centimetre cube. Certain oxide like ruthenium oxide, strontium ruthenate, titanium monoxide they behave like metal like conductivity. Now, it can be understood if you consider their pure metal what is their electronic configuration and in case of TiO where titanium is plus 2 valent what is their electronic configuration and in case of TiO_2 where titanium is plus 4 valent what is their electronic configuration.

So, if you consider that you can see that the 2p orbitals from oxygen atoms for a filled valence band and 4s and 4p orbital of titanium they are at much higher energy. So, titanium d orbital forms a band which is below the metallic s and p orbital that is shown in the right side schematic.

So, as you can see for titanium monoxide it is having 2 3d electrons. So, the metal d band is partially filled here. So, that partial fulfilment of the d band that actually gives you the metal like conductivity. If you consider TiO 2, then both the 2 4s and 3d electron. So, TiO_2 you have 4s and 3d electron they are given up to the oxygen to form this TiO_2 structure.

So, their 3d band is a conduction band that is empty. So, TiO_2 will behave as an insulating material, but TiO will have the metal like conductivity. Similar thing happens in ruthenium oxide as well but, here not the d electron, but the f electron is playing a major role and I am leaving it on to you to think that other oxides which are like nickel oxide, manganese oxide, FeO they do not behave like metal like conductor.

Now, just think on it maybe we will discuss it in a different forum that why this material unlike titanium monoxide they behave like an insulator. I am leaving it to you to think and it is related to the d orbital configuration and little bit more knowledge is required to understand it. Just think on it, may be we will come back to it at a later stage.

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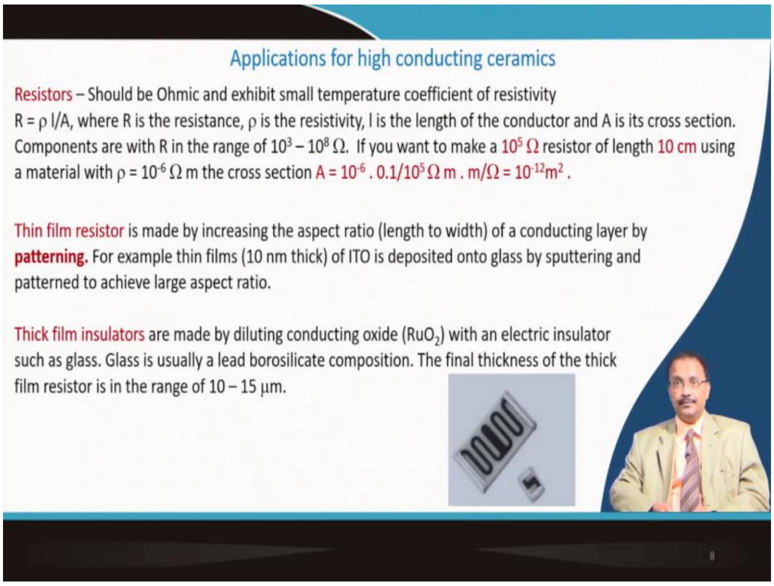

Applications for high conducting ceramics

Resistors – Should be Ohmic and exhibit small temperature coefficient of resistivity
$R = \rho\, l/A$, where R is the resistance, ρ is the resistivity, l is the length of the conductor and A is its cross section.
Components are with R in the range of $10^3 - 10^8\ \Omega$. If you want to make a $10^5\ \Omega$ resistor of length 10 cm using a material with $\rho = 10^{-6}\ \Omega$ m the cross section $A = 10^{-6} \,.\, 0.1/10^5\ \Omega\, m \,.\, m/\Omega = 10^{-12} m^2$.

Thin film resistor is made by increasing the aspect ratio (length to width) of a conducting layer by **patterning.** For example thin films (10 nm thick) of ITO is deposited onto glass by sputtering and patterned to achieve large aspect ratio.

Thick film insulators are made by diluting conducting oxide (RuO_2) with an electric insulator such as glass. Glass is usually a lead borosilicate composition. The final thickness of the thick film resistor is in the range of 10 – 15 μm.

Now, if you see the conducting ceramics, there are various use. The first use is as a resistor and it should be ohmic in nature and exhibit small temperature coefficient of resistivity. You know the resistance is proportional to the length of the conductor and inversely proportional to the area of the conductor.

So, the proportionality constant is the resistivity as you can see here. So, usually components with R resistance is not a material property. Whatever is in the range of 1 kilo ohm to 10 to the power 8 ohm; that means, point 1 mega ohm we call it is a resistor.

So, here I have shown an example that if you want to make a 10 to the power 5 ohm resistor using a ceramic material which is having a length of 10 centimetre and you know the resistivity of the material is 10 to the power minus 6 ohm meter, then you can calculate the cross-section of it is pretty small. The cross-section will be about 10 to the power minus 12 meters square.

So, that means, it is 1 micron by 1 micron. It is not very difficult to make 1 micron by 1 micron, but actually it is not very economically feasible to make this kind of resistor such a thin resistor. So, usually the thin film resistor is made by increasing the aspect ratio; that means, length to width ratio will have to be increase on a conducting layer by a technique called patterning. So, we will talk about patterning, briefly we will introduce

So, if you consider a thin film say about 10 nano-meter thick of indium tin oxide which is a conducting layer, you can deposit it in glass by sputtering and then you pattern to achieve this high aspect ratio different types of patterning is possible. In case of thick film insulator, we can also dilute it by conducting oxide.

So, RuO_2 is a conducting oxides very expensive. So, you can dilute it with a glass we call it flicked usually led borosilicate glass composition is mixed with RuO_2 and the final thickness of the thick film resistor is usually in the range of 10 to the 10 to 15 micrometer. So, one example I have shown is example of a thick film insulator made out of this so called conducting ceramics.

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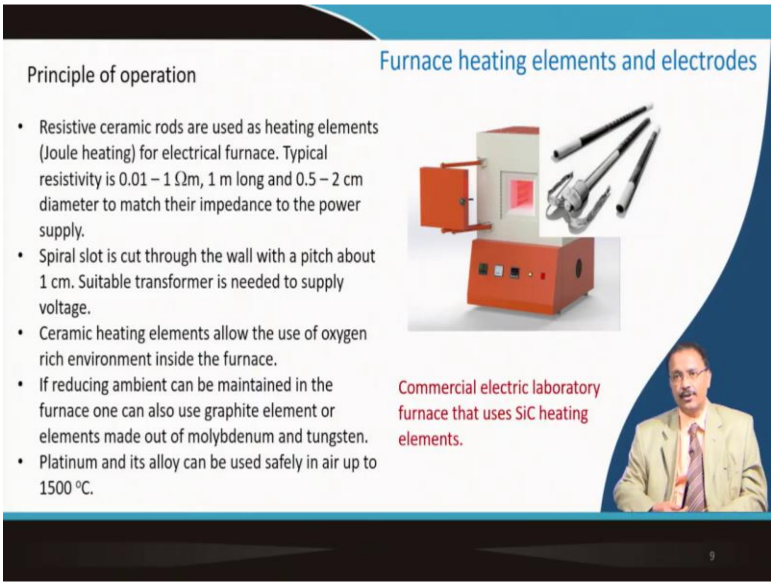

Furnace heating elements and electrodes

Principle of operation

- Resistive ceramic rods are used as heating elements (Joule heating) for electrical furnace. Typical resistivity is 0.01 – 1 Ωm, 1 m long and 0.5 – 2 cm diameter to match their impedance to the power supply.
- Spiral slot is cut through the wall with a pitch about 1 cm. Suitable transformer is needed to supply voltage.
- Ceramic heating elements allow the use of oxygen rich environment inside the furnace.
- If reducing ambient can be maintained in the furnace one can also use graphite element or elements made out of molybdenum and tungsten.
- Platinum and its alloy can be used safely in air up to 1500 °C.

Commercial electric laboratory furnace that uses SiC heating elements.

Another good use is to make the heating element for electrically heated furnace. So, resistive ceramic rods that are usually used as a heating element and usually you do a Joule heating I square R into t. So, depends on the current pass and it depends on the resistance to the power square and the time. So, we call it is a Joule heating.

Typical resistivity is in the range of 0.01 to 1 ohm meter, rods are 1 meter long and usually 0.5 to 2 centimeter diameter to match the impedance of the power supply. So, in order to engineer the resistance a slot spiral slot, it is not very clear in this view graph, but if you see it carefully you can see the slots are given here in order to manipulate the exact resistance whatever is needed.

So, this ceramic heating element one can use it in oxygen rich environment inside the furnace. Sometimes reducing environment is required if you change the heating element usually for normal use silicon carbide is used or you can use even metal like platinum can be used, graphite element can be used. So, platinum alloy they can heat the furnace up to 1500 degrees Celsius.

But, normal up to 1200 degree electrically heated furnace if you need then silicon carbide is the heating element that is a fuse.

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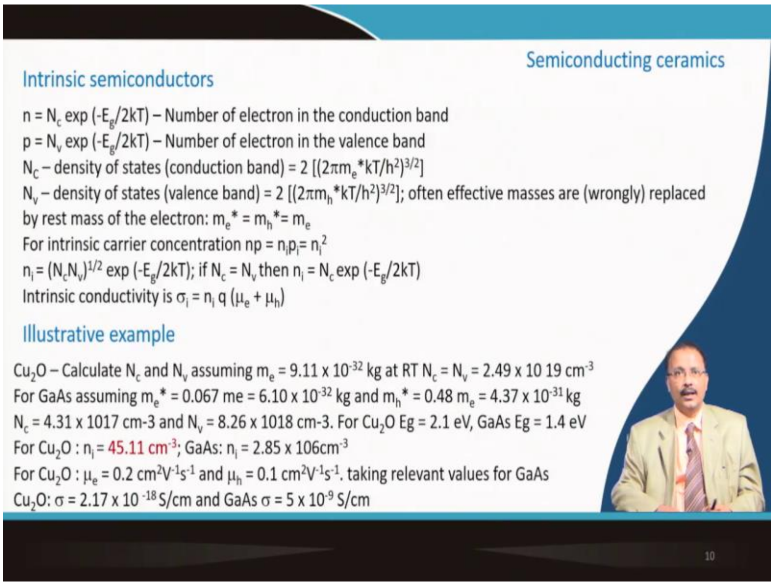

Semiconducting ceramics

Intrinsic semiconductors

$n = N_c \exp(-E_g/2kT)$ – Number of electron in the conduction band
$p = N_v \exp(-E_g/2kT)$ – Number of electron in the valence band
N_C – density of states (conduction band) = $2\,[(2\pi m_e^* kT/h^2)^{3/2}]$
N_v – density of states (valence band) = $2\,[(2\pi m_h^* kT/h^2)^{3/2}]$; often effective masses are (wrongly) replaced by rest mass of the electron: $m_e^* = m_h^* = m_e$
For intrinsic carrier concentration $np = n_i p_i = n_i^2$
$n_i = (N_c N_v)^{1/2} \exp(-E_g/2kT)$; if $N_c = N_v$ then $n_i = N_c \exp(-E_g/2kT)$
Intrinsic conductivity is $\sigma_i = n_i q (\mu_e + \mu_h)$

Illustrative example

Cu_2O – Calculate N_c and N_v assuming $m_e = 9.11 \times 10^{-32}$ kg at RT $N_c = N_v = 2.49 \times 10\ 19\ cm^{-3}$
For GaAs assuming $m_e^* = 0.067\ me = 6.10 \times 10^{-32}$ kg and $m_h^* = 0.48\ m_e = 4.37 \times 10^{-31}$ kg
$N_c = 4.31 \times 1017$ cm-3 and $N_v = 8.26 \times 1018$ cm-3. For Cu_2O Eg = 2.1 eV, GaAs Eg = 1.4 eV
For Cu_2O : $n_i = 45.11\ cm^{-3}$; GaAs: $n_i = 2.85 \times 106 cm^{-3}$
For Cu_2O : $\mu_e = 0.2\ cm^2V^{-1}s^{-1}$ and $\mu_h = 0.1\ cm^2V^{-1}s^{-1}$. taking relevant values for GaAs
Cu_2O: $\sigma = 2.17 \times 10^{-18}$ S/cm and GaAs $\sigma = 5 \times 10^{-9}$ S/cm

And, this kind of material not only silicon carbide, but super kanthal and various types of silicides they are also used as heating element for various uses in the furnace. So, now if you talk about the intrinsic semiconductor you know the intrinsic semiconductor the number of electron in the conduction band is given by this relation and number of electrons sorry, number of holes in the valence band.

So, it is not electron it is holes in the valance band it is given by this relation. So, N c is the density of state empirically you can derive N c by this relation where this is not electron rest mass. Sometimes we do use it the rest mass, but this is not it is basically the effective mass of electron and hole. So, sometimes as I have said that this effective mass is taken as the rest mass to aid the estimation.

And, intrinsic carrier concentration your mass action is balance. So, n into p that is equal to n i into p i and both are equal. So, n square n i square you can get out of it and then you just multiply these two equation you will come up with this relation. And, finally, if you know the concentration you know the respective mobility and the charge associated with the electron you can calculate the intrinsic conductivity.

You can compare it with copper oxide which is otherwise an insulating material. So, you can calculate N c and N v and here you assume because we do not have the correct data of m e star. So, you assume the rest mass of electron at room temperature. So, this value you will get for N_c and N_v.

Now, you take a semiconductor gallium arsenide here your rest mass if it is known then you can calculate the effective mass of this too. So, N_c can be calculated if you know from the earlier equation you need to know the band gap of course. So, band gap for Cu 2 O is much larger as compared to gallium arsenide.

So, you see this number of electrons is pretty low 45.11 and gallium arsenide it is 2.85 into 10 to the power 6 this is 10 to the power 6 per centimetre cube. So, you know the mobility for copper oxide and these are all they are in standard test textbook you can use this values and you can use the value of nu h and then you can calculate the conductivity of copper oxide, it is you see much larger as compared to the gallium arsenide behaviour.

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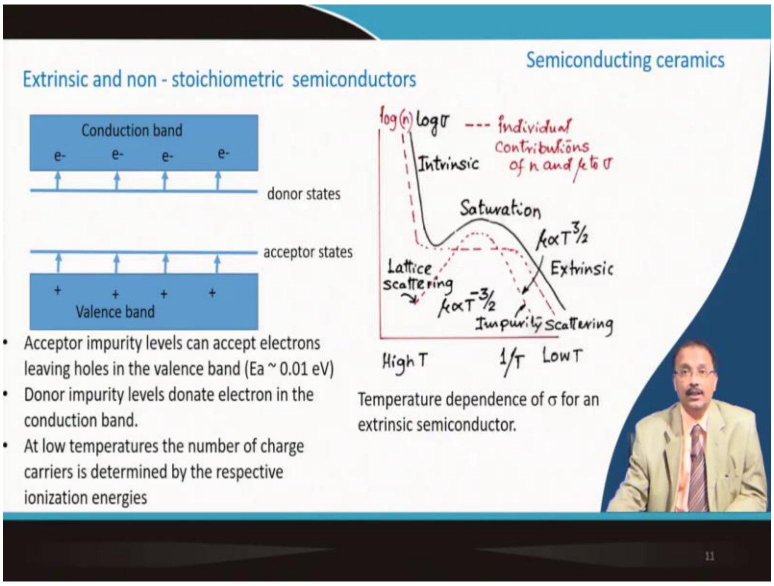
Semiconducting ceramics

Extrinsic and non - stoichiometric semiconductors

- Acceptor impurity levels can accept electrons leaving holes in the valence band (Ea ~ 0.01 eV)
- Donor impurity levels donate electron in the conduction band.
- At low temperatures the number of charge carriers is determined by the respective ionization energies

Temperature dependence of σ for an extrinsic semiconductor.

So, we can talk about the extrinsic non-stoichiometric semiconductor, we talked about the defect levels. So, once you introduce in the defect inside a semiconducting material the acceptor impurity that can accept electrons living hole in the valence band the typical energy for this is in case of donor and acceptor you can assume it is about 0.01 electron volt very close to the conduction and valence band electron.

So, the donor impurity level donates electron in the conduction band and at low temperature the number of charge carriers determined by the respective ionization energy. So, it will trap electron, but you need to know the ionization energy. So, if you plot it individually, you will see that at low temperature if you increase then at one stage it will get saturated because there are no more electrons to go to the conduction band from the defect levels.

And, then finally, it will be the intrinsic conduction band to band conduction it will take place and then along with that there will be mobility. So, the mobility initially with temperature it will increase, but at high temperature when the phonon is playing a major role, then the mobility will drop down. So, the actual plot for this log n versus temperature it shows that assume this kind of behaviour.

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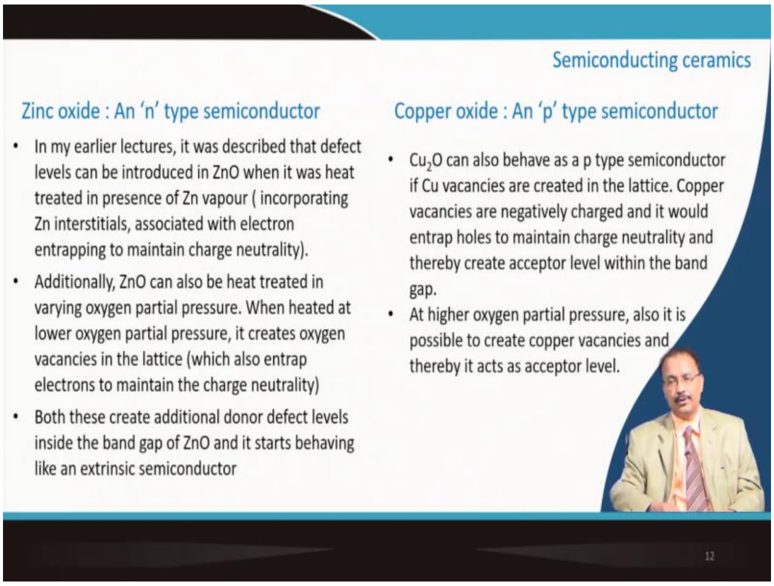

Semiconducting ceramics

Zinc oxide : An 'n' type semiconductor

- In my earlier lectures, it was described that defect levels can be introduced in ZnO when it was heat treated in presence of Zn vapour (incorporating Zn interstitials, associated with electron entrapping to maintain charge neutrality).
- Additionally, ZnO can also be heat treated in varying oxygen partial pressure. When heated at lower oxygen partial pressure, it creates oxygen vacancies in the lattice (which also entrap electrons to maintain the charge neutrality)
- Both these create additional donor defect levels inside the band gap of ZnO and it starts behaving like an extrinsic semiconductor

Copper oxide : An 'p' type semiconductor

- Cu_2O can also behave as a p type semiconductor if Cu vacancies are created in the lattice. Copper vacancies are negatively charged and it would entrap holes to maintain charge neutrality and thereby create acceptor level within the band gap.
- At higher oxygen partial pressure, also it is possible to create copper vacancies and thereby it acts as acceptor level.

So, zinc oxide is an n type semiconductor and both this I have already described when we talk about the defect once we talked about. So, in case of zinc oxide this is a n type of semiconductor either zinc oxide can be heat treated in zinc vapour. So, it will create interstitial zinc and it will trap electron or you can heat treat it at lower oxygen partial pressure, then oxygen vacancy will be created that will also trap electron.

So, likewise copper oxide is behaving as a p type semiconductor because of copper vacancy. So, copper vacancy will trap hole. And, higher oxygen partial pressure it is also possible to create copper vacancy and thereby it acts also as acceptor level.

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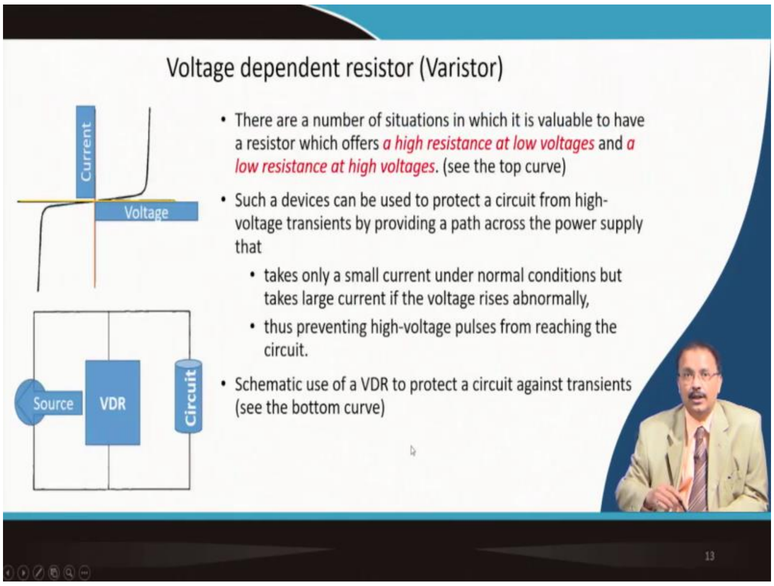

Voltage dependent resistor (Varistor)

- There are a number of situations in which it is valuable to have a resistor which offers *a high resistance at low voltages* and *a low resistance at high voltages*. (see the top curve)
- Such a devices can be used to protect a circuit from high-voltage transients by providing a path across the power supply that
  - takes only a small current under normal conditions but takes large current if the voltage rises abnormally,
  - thus preventing high-voltage pulses from reaching the circuit.
- Schematic use of a VDR to protect a circuit against transients (see the bottom curve)

So, the otherwise material which are insulating you can create band inside and they will start to behave as extrinsic semiconductor. So, you can use this as a voltage dependent resistor. This device you can see that at low voltage the current passes through it is very small. So, it behaves like a resistor and when a spark is there then suddenly the current increases.

So, if you put a VDR here, voltage dependent resistor, then when you have a higher resistivity then all the current will pass through the circuit. So, circuit will walk, but whenever it will sense a spark then all the current will flow through this. So, your circuit will be saved.

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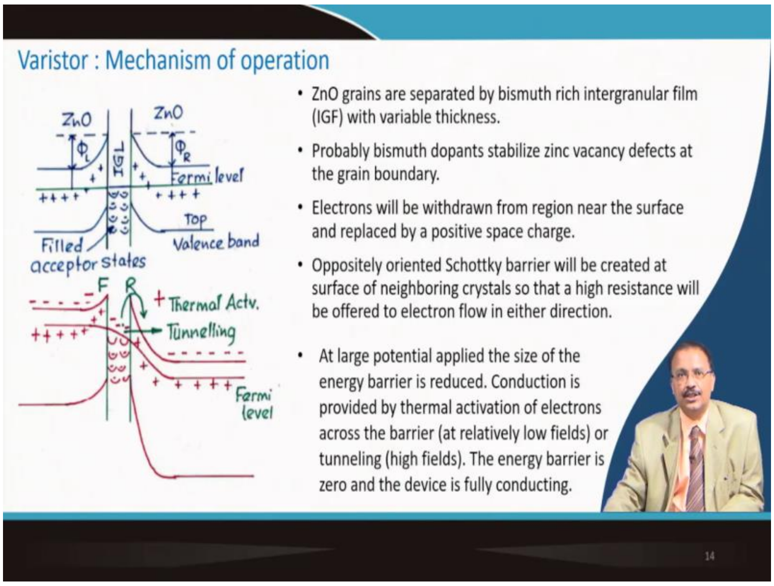

Varistor : Mechanism of operation

- ZnO grains are separated by bismuth rich intergranular film (IGF) with variable thickness.
- Probably bismuth dopants stabilize zinc vacancy defects at the grain boundary.
- Electrons will be withdrawn from region near the surface and replaced by a positive space charge.
- Oppositely oriented Schottky barrier will be created at surface of neighboring crystals so that a high resistance will be offered to electron flow in either direction.
- At large potential applied the size of the energy barrier is reduced. Conduction is provided by thermal activation of electrons across the barrier (at relatively low fields) or tunneling (high fields). The energy barrier is zero and the device is fully conducting.

So, this is due to a grain boundary phase and this grain boundary phase has a lot of acceptors site which can accept electron from the zinc oxide grain and both sides. So, you can see a positive charge barrier layer it is a just a Schottky barrier layer, it forms like this.

So, in normal condition electron cannot pass from here to here because it does not have sufficient energy to pass, but once a certain voltage it will see it will experience a spike voltage then the temperature will also go high. So, thermally activated electron can go from this area to this area it will start to conduct. So, it will behave like a conductor or some kind of tunnelling also when take place, direct electron can pass through this grain bond region and start to conduct.

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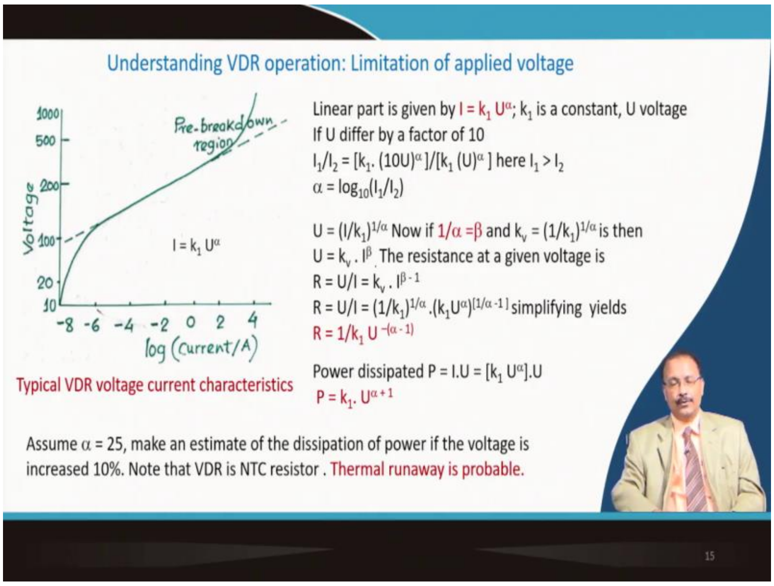

Understanding VDR operation: Limitation of applied voltage

Typical VDR voltage current characteristics

Linear part is given by $I = k_1 U^{\alpha}$; k_1 is a constant, U voltage

If U differ by a factor of 10

$I_1/I_2 = [k_1 . (10U)^{\alpha}]/[k_1 (U)^{\alpha}]$ here $I_1 > I_2$

$\alpha = \log_{10}(I_1/I_2)$

$U = (I/k_1)^{1/\alpha}$ Now if $1/\alpha = \beta$ and $k_v = (1/k_1)^{1/\alpha}$ is then

$U = k_v . I^{\beta}$ The resistance at a given voltage is

$R = U/I = k_v . I^{\beta - 1}$

$R = U/I = (1/k_1)^{1/\alpha} . (k_1 U^{\alpha})^{[1/\alpha - 1]}$ simplifying yields

$R = 1/k_1 U^{-(\alpha - 1)}$

Power dissipated $P = I.U = [k_1 U^{\alpha}].U$

$P = k_1 . U^{\alpha + 1}$

Assume $\alpha = 25$, make an estimate of the dissipation of power if the voltage is increased 10%. Note that VDR is NTC resistor . Thermal runaway is probable.

So, it is a very useful material and here if you plot voltage versus current usually it is showing a straight line behaviour here. So, you can calculate the value of the resistance and you can value you can calculate the value of the current and eventually you can estimate the power of this resistor P is equal to v into i.

So, with a simple calculation you can show that if the resistance is increased then there is a possibility of thermal runaway because huge current will pass. So, it will generate a lot of heat and this is a problem. So, the application of the voltage that should be very carefully controlled for this kind of device that is another thing one should be cautious about.

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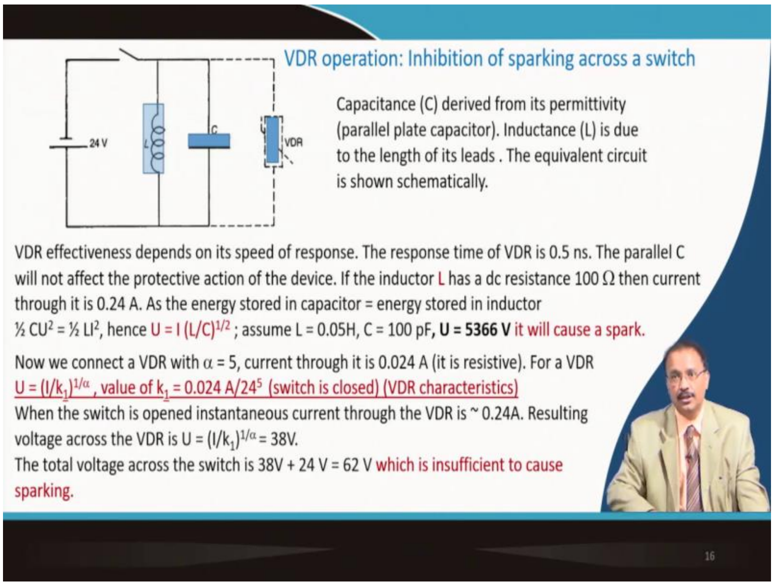

VDR operation: Inhibition of sparking across a switch

Capacitance (C) derived from its permittivity (parallel plate capacitor). Inductance (L) is due to the length of its leads . The equivalent circuit is shown schematically.

VDR effectiveness depends on its speed of response. The response time of VDR is 0.5 ns. The parallel C will not affect the protective action of the device. If the inductor L has a dc resistance 100 Ω then current through it is 0.24 A. As the energy stored in capacitor = energy stored in inductor $\frac{1}{2} CU^2 = \frac{1}{2} LI^2$, hence $U = I (L/C)^{1/2}$; assume L = 0.05H, C = 100 pF, **U = 5366 V** it will cause a spark.

Now we connect a VDR with $\alpha = 5$, current through it is 0.024 A (it is resistive). For a VDR $U = (I/k_1)^{1/\alpha}$, value of $k_1 = 0.024\ A/24^5$ (switch is closed) (VDR characteristics)
When the switch is opened instantaneous current through the VDR is ~ 0.24A. Resulting voltage across the VDR is $U = (I/k_1)^{1/\alpha} = 38V$.
The total voltage across the switch is 38V + 24 V = 62 V which is insufficient to cause sparking.

This type of material in a circuit where inductor and capacitor is there usually the charge stored by the in the capacitor and charge stored in the inductor if they start to resonate I have just shown a simple calculation here. So, if they start to resonate, then a huge voltage will generate at the switch whenever the switch will pass it will get spark.

Sometimes in your common application you experience this thing suddenly the electric power switch they spark, but if a VDR is attached to it then it will control the switch and here again from the voltage and current relation I have shown that here the applied voltage in the switch is about 5 kilo volt and that has been reduced with this VDR as low as 62 volt.

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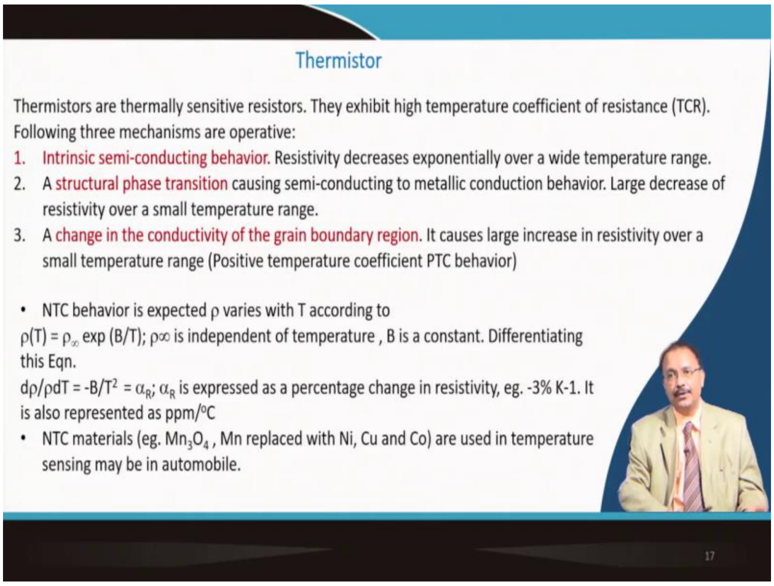

Thermistor

Thermistors are thermally sensitive resistors. They exhibit high temperature coefficient of resistance (TCR). Following three mechanisms are operative:

1. Intrinsic semi-conducting behavior. Resistivity decreases exponentially over a wide temperature range.
2. A structural phase transition causing semi-conducting to metallic conduction behavior. Large decrease of resistivity over a small temperature range.
3. A change in the conductivity of the grain boundary region. It causes large increase in resistivity over a small temperature range (Positive temperature coefficient PTC behavior)

- NTC behavior is expected ρ varies with T according to

$\rho(T) = \rho_\infty \exp(B/T)$; $\rho\infty$ is independent of temperature , B is a constant. Differentiating this Eqn.

$d\rho/\rho dT = -B/T^2 = \alpha_R$; α_R is expressed as a percentage change in resistivity, eg. -3% K-1. It is also represented as ppm/°C

- NTC materials (eg. Mn_3O_4 , Mn replaced with Ni, Cu and Co) are used in temperature sensing may be in automobile.

So, it is saving the circuit for any practical use. So, finally, we will talk about thermistor and thermistor is nothing, but temperature dependent resistor. So, as I have told you that it could be intrinsic semiconductor behaviour or it could be due to a structural change, it causes semiconductor to metal type of conduction behaviour or there will be a change in conductivity at the boundary region – all are possible.

So, here you can write the relation for the resistivity as a function of temperature and then you differentiate it and once you differentiate you will come up with this relation minus B by T square that is equal to alpha R that represent the percent change in the resistivity with temperature. Usually it could be minus 3 percent per Kelvin, sometimes it is defined as a ppm per degree Celsius.

So, popular NTC material is manganese oxide and manganese is sometimes doped with nickel and copper or sometimes in cobalt and they are used at temperature sensing particularly in the automobile the temperature sensor at the oil temperature what you see in the dashboard this kind of thermistor is used. And, this is calibrated with the temperature change the value of the resistance is calibrated so that you can read the actual temperature.

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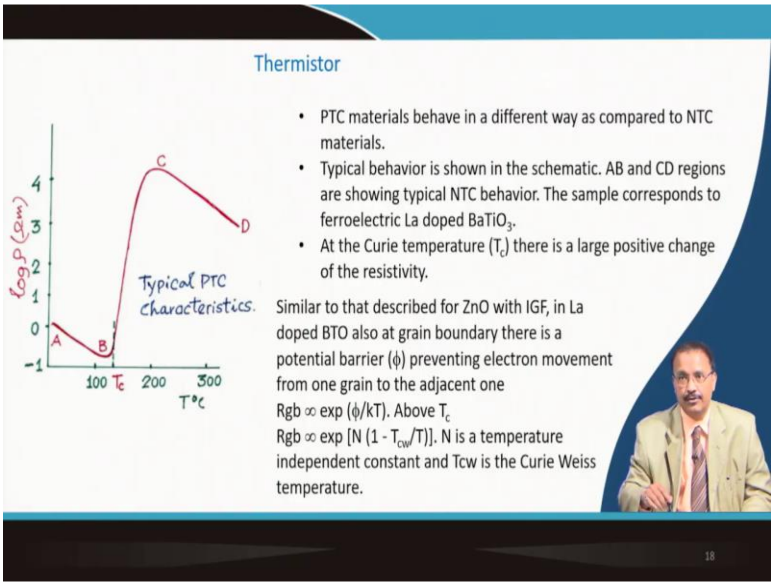

Thermistor

- PTC materials behave in a different way as compared to NTC materials.
- Typical behavior is shown in the schematic. AB and CD regions are showing typical NTC behavior. The sample corresponds to ferroelectric La doped $BaTiO_3$.
- At the Curie temperature (T_c) there is a large positive change of the resistivity.

Similar to that described for ZnO with IGF, in La doped BTO also at grain boundary there is a potential barrier (ϕ) preventing electron movement from one grain to the adjacent one

$Rgb \infty \exp(\phi/kT)$. Above T_c

$Rgb \infty \exp[N(1 - T_{cw}/T)]$. N is a temperature independent constant and Tcw is the Curie Weiss temperature.

There are other types of thermistor particularly barium titanate which undergoes this kind of phase transition which I was mentioning. So, barium titanate as I have told that it undergoes a phase transition at 120 degree Celsius. So, below and far above this temperature it behaves like an NTC material, but when it is exactly in this temperature zone that behaves like a zinc oxide.

So, it has an intergranular film particularly when you dope it with lanthanum. So, it creates a lot of valium vacancies vacancy in the A site and the potential barrier initially they prevent the electron movement from one grain to another. So, it behaves like a NTC.

So, after that this grain boundary take over so, the relation above T c it changes. You see the grain boundary is proportional to exponential of N; N is the temperature independent constant 1 minus this is Curie-Weiss temperature divided by the temperature of operation. So, when it is very close to Curie temperature, then the grain boundary resistance that actually decide the resistance so, the resistivity of the material.

So, very close to the Curie temperature there is a sudden jump of the resistivity for certain application this PTC behaviour used it is a purely grain boundary phenomena and very specific to this material which undergo this paraelectric to ferroelectric type of phase transition.

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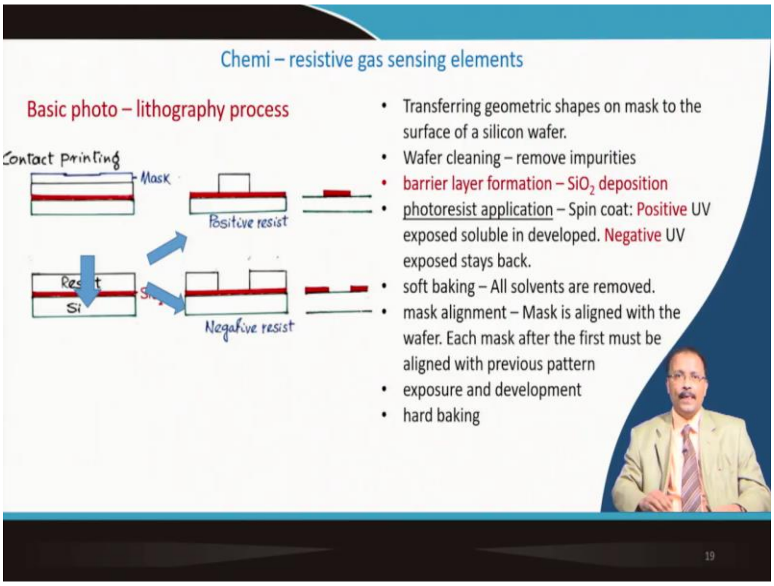

Chemi – resistive gas sensing elements

Basic photo – lithography process

- Transferring geometric shapes on mask to the surface of a silicon wafer.
- Wafer cleaning – remove impurities
- barrier layer formation – SiO_2 deposition
- photoresist application – Spin coat: Positive UV exposed soluble in developed. Negative UV exposed stays back.
- soft baking – All solvents are removed.
- mask alignment – Mask is aligned with the wafer. Each mask after the first must be aligned with previous pattern
- exposure and development
- hard baking

So, finally, we will talk about the chemi-resistive type of gas sensing element which one can make out of this semiconducting ceramics and usually they are built by photolithography process. So, in photolithography you have the silicon mask and then you put an oxide on top of it and then you put a photoresist and then the pattern whatever you want to transfer to this you can just put it here and shine it with UV light.

So, wherever the UV light is there, apart from those region, you can etch the other position. So, then we call this is a positive photoresist and when you expose it only that part will go out we call it is a negative resist. So, after you get this kind of structure you can repeat it by a suitable photo mask and mask aligner. You can built this type of circuitry.

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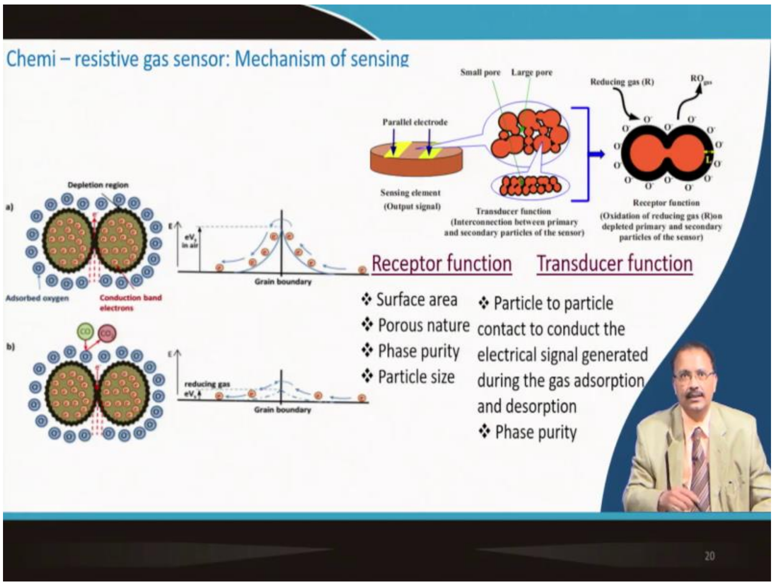

Chemi – resistive gas sensor: Mechanism of sensing

Receptor function

- Surface area
- Porous nature
- Phase purity
- Particle size

Transducer function

- Particle to particle contact to conduct the electrical signal generated during the gas adsorption and desorption
- Phase purity

And, exactly something similar is done in case of gas sensor where it is basically semiconducting material you heat treat it then it has a lot of electrons and oxygen in the ambient they absorb this electron forming a depletion layer, and they form a oxygen enriched layer at the surface.

So, whenever any toxic gas comes then this depletion layer is gone because this oxygen reacts with carbon monoxide to form this kind of carbon dioxide and this electron again drops back to the element itself. So, initially when oxygen is absorbed you can see that there is a potential barrier here and once you treat it in a gas, then this potential barrier is reduced so, electron will start to flow.

So, when you have a gas you can see the change in resistance here in this case resistance will get reduced. So, this schematic shows that this is the original particle which absorbed oxygen forming the depletion layer, then this are connected to each other. So, electron will transport from one end to another end and finally, from this electrode to this electrode.

So, the receptor function is the way the particle absorb oxygen and the transducer function is the way it transport the electron across it.

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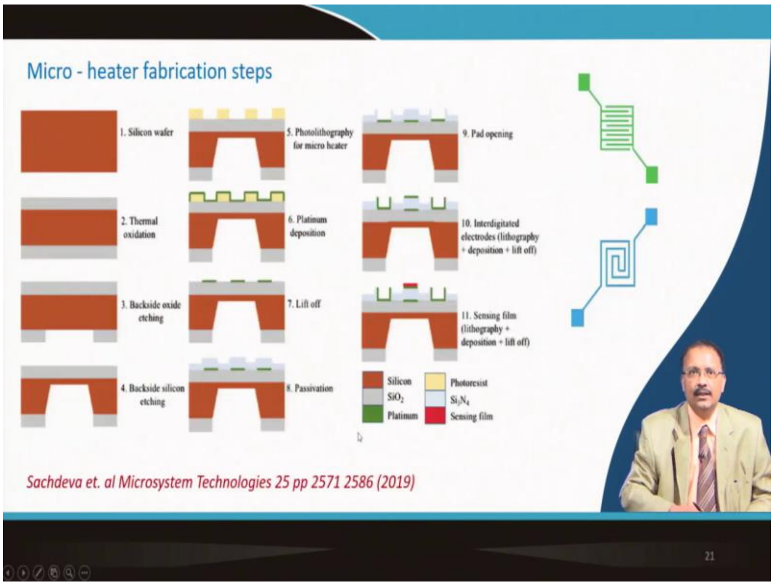

Micro - heater fabrication steps

Sachdeva et. al Microsystem Technologies 25 pp 2571 2586 (2019)

So, this material you can form in a thin film form usually the same procedure the photolithography is adopted starting from silicon you deposit with silicon dioxide and then follow this steps and also each the part of it at the back of the silicon to put this kind of heater these also are made by photolithography liftoff and etching. And finally, you get this kind of sensing element following these steps you can get this kind of sensing element.

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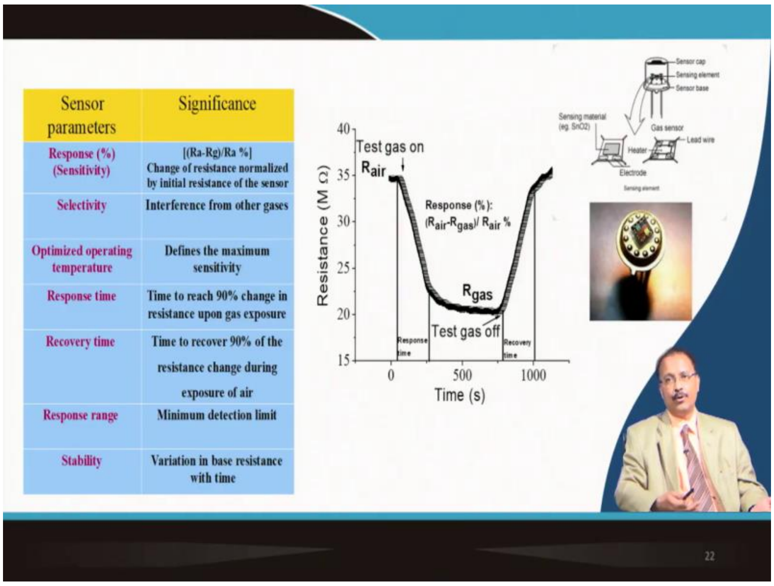

Sensor parameters	Significance
Response (%) (Sensitivity)	[(Ra-Rg)/Ra %] Change of resistance normalized by initial resistance of the sensor
Selectivity	Interference from other gases
Optimized operating temperature	Defines the maximum sensitivity
Response time	Time to reach 90% change in resistance upon gas exposure
Recovery time	Time to recover 90% of the resistance change during exposure of air
Response range	Minimum detection limit
Stability	Variation in base resistance with time

And, this sensing element they are actually where bond in this type of folder to make a gas sensor something like this. So, as I told that when it is in air that instance is pretty high, then whenever gas is on the oxygen reacts with this toxic gas and electron goes back to the depletion layer. So, the resistance drops down as long as the gas is there.

And, whenever you flush it with air or the gas is gone, then again the resistance comes back to it is base value because again oxygen is chemi raised chemi absorbed on the sensor surface. So, get this kind of resistance transient and you can define the response percent that is the change in resistance percent change in resistance.

Selectivity is something which is difficult to get from this kind of sensor because most of the sensor for all reducing gas behaves like this. So, I am not going into that that how to address the selectivity, there are ways to address it. Then the operating temperature is important that is the temperature at which the oxygen absorption is maximum and this reaction with the gas is also maximized.

So, that part is important. Response time is important how long does it take for you to actually detect the gas. So, from this part till it reduce its resistance up to 90 percent of its original value that is its response time. And, similarly from this part the time it takes to regain it is original resistance base value resistance that is recovery time. So, both are important, you need to detect the gas as fast as possible.

And, finally, the stability is the baseline resistance whether it comes back to its original value because the sensor you can use time and again. So, whether you can get back this value after repeated use that will tell that whether your material is stable or not.

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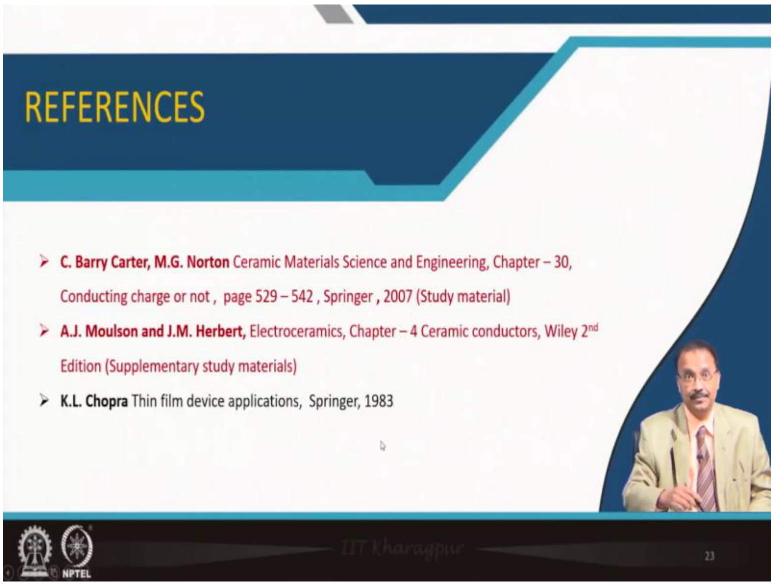

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- **A.J. Moulson and J.M. Herbert,** Electroceramics, Chapter – 4 Ceramic conductors, Wiley 2nd Edition (Supplementary study materials)
- **K.L. Chopra** Thin film device applications, Springer, 1983

So, the part that I have covered you can get it from the book by Barry Carter and also to some extent with A. J, Moulson, that is your study material.

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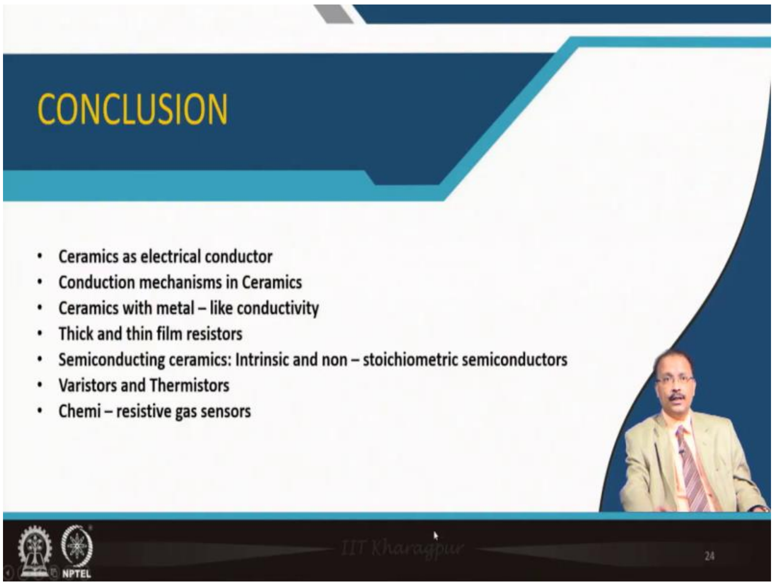

CONCLUSION

- Ceramics as electrical conductor
- Conduction mechanisms in Ceramics
- Ceramics with metal – like conductivity
- Thick and thin film resistors
- Semiconducting ceramics: Intrinsic and non – stoichiometric semiconductors
- Varistors and Thermistors
- Chemi – resistive gas sensors

And, in this lecture I talked about ceramic as electrical conductor, then very briefly we have introduced the conduction mechanism, the factor influencing the conduction mechanism, ceramic with metal like conductivity is possible.

Then we talked about thick and thin film sensor, thick film resistor, then semiconducting ceramics intrinsic and non-stoichiometric semiconductor we have introduced, application of a varistor and thermistor voltage dependent resistor and temperature dependent resistor we talked about and finally, the operation principle and fabrication of chemi resistive gas sensor is introduced.

Thank you for your attention.