Advanced Ceramics for Strategic Applications
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Lecture - 26
Ceramics Gas Sensor

Today's topic is a ceramic based gas sensors; obviously it is a very interesting application of ceramic materials, where ceramics, particularly oxides can be used for the purpose of sensing the presence, not only the presence or the even measuring the concentration of some of the specific gases at very low concentrations, may mostly less than 1 percent or even in the ppm range.

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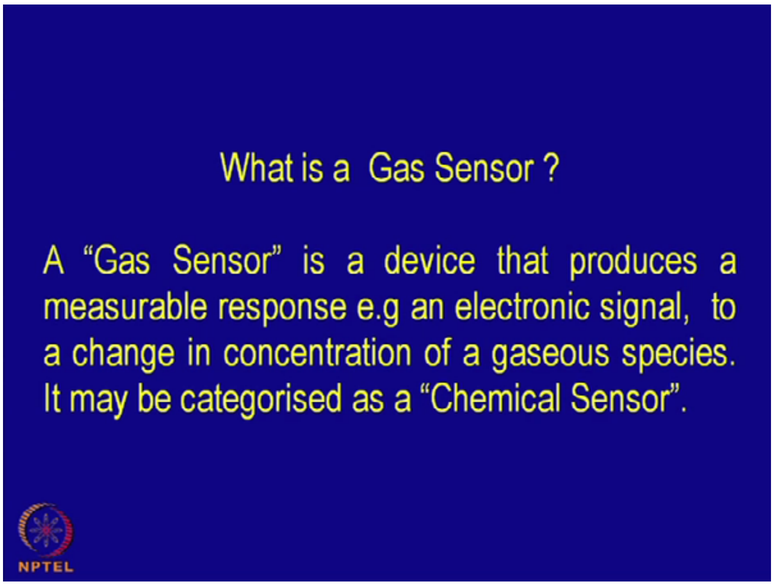

So, we will start with a definition, simple definition of course, I am sure it is quite known to everybody the gas, what is a gas sensor? Gas sensor is nothing but a device that produces a measurable response, normally it is an electronic signal to a change in concentration of gaseous species; it may be categorized as a chemical sensor. In fact sensors can be there be two major groups of senses, there are many different parameters, one can sense with various types of senses; one is basically physical sensor, another chemical sensor. Since, we are talking about a chemical species in this case, it can be categorized as a chemical sensor.

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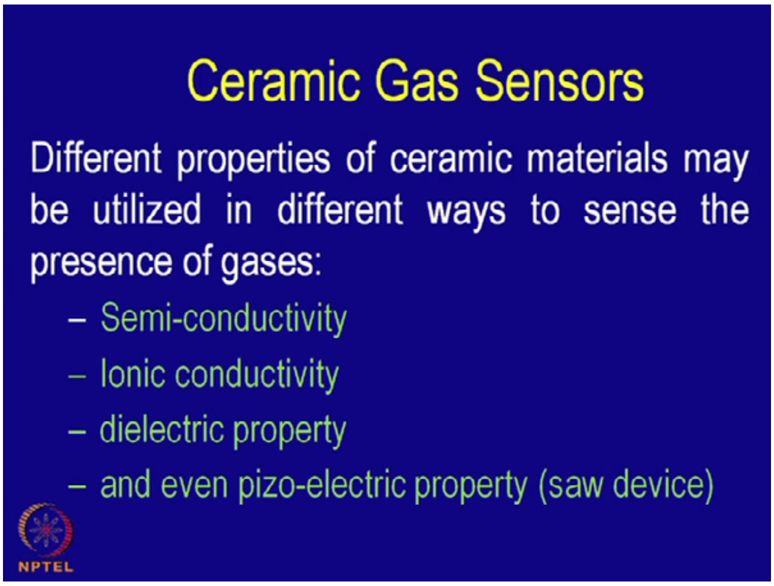

What are the different properties, on which a sensors are best? Different properties of ceramic materials may be utilized in different ways to sense. The presence or to measure the concentration of gases, in general we are talking about a electronic signal. So, the most convenient way is to utilized or exploit, the electrical conductivity of the oxides, as we know, there are many different kind of wide spectrum of properties available of the ceramic materials; some of them in semiconducting, some of them in metallic conductivity, there are ionic conductivity, dielectric property and even piezoelectric property; all these properties can be exploited, because there is a connection or there is a connectivity with the electrical properties.

Basically, there are many different kind of electrical properties can be utilized to sense, the presence of some gases, specific gases. In case of last one of course, will not be discussing much about here, because we have mention briefly, that piezoelectric property of the ceramic materials can be utilized to fabric at or saw device; and that saw device in the presence some of the gases, particularly moisture, the characteristics of this saw device changes and by monitoring the change, one can find out, what is the concentration of this moisture in presence of saw device?

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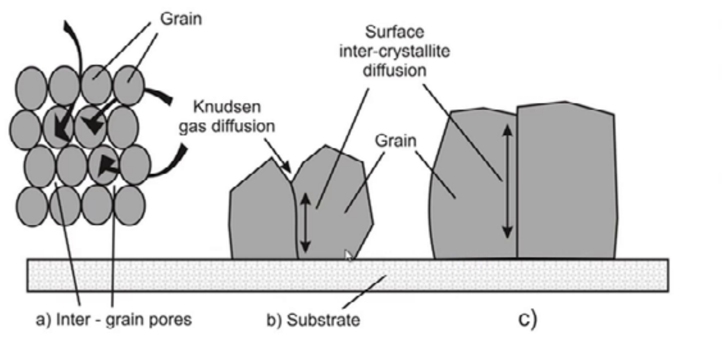

Schematic grain structures in thick (a) and thin (b and c) films of oxides and consequent gas diffusion models.

Well, if you look at the structure of ceramic materials in general, we have three situations in the left, you have a porous structure; basically ceramics are porous, their poly crystalline materials and they have a porous structure. So, you can have pores in between the material in between this sample, so you have not only the air outside but, also inside prison inside, the material inside the structure, so that is because of the pores structure. So, you have knowing presence of knudsen diffusion through to the knudsen diffusion.

Assuming the pores are continuous and open pores, what we call the open pores in ceramic terminology, that means there is a connectivity, from the internal pore to the outside ambiance, so these are, so the gas can go in through, the pores and in comes in contact with the surface of these individual crystals or individual grains.

So, this is one kind of structure. In fact, this is it is a very common structure in ceramics. Whenever you try to make a bulk ceramics, a thicker ceramics or even thick or thin ceramics, like thick films relatively thick, relatively thin several microns in thick in thickness, so but even then you have poor structures, so this is one kind of situation, this is of course a substrate, on which these materials can be deposited with across some kind of porosity.

There are other two situations here, these are basically relate to thin films; one can make thin film very dense thin films, they are also thin films can be porous but, normally thin films are not porous; they but, they may have polycrystalatinate; so they may not be single crystal or but, we have poly crystalline materials and in between, we have grains in between, you have grain boundaries.

So, these are the two grains and in between, there is a grain boundary; and grain boundaries are normally a defective structure. And, the diffusion even for the gases can take place much faster, so the activation energy for diffusion of the gases molecules or atomic gases, atoms are much faster along the grain boundaries, than through the bulk, so it is actually here also, the gases can come in into the material not to the pores like this, these are more molecular diffusion but, here it can be a atomic diffusion and in the form of some.

So, gases can come in either through the grain boundaries, primarily through the grain boundaries. So, the surface this is one kind of surface; this one kind of surface were, the surface is exposed to the atmospheric gas but, here this is also another surface inside internal of the internal to the material, and these also discontinuity crystallographic discontinuity. And, gas can diffuse in, so it can here there are two difference surfaces; one is the outside external surface and the other is called internal surface; in both this cases, one can have role of surface, where so for as the conductivity is concerned or the conduction mechanism is concerned now.

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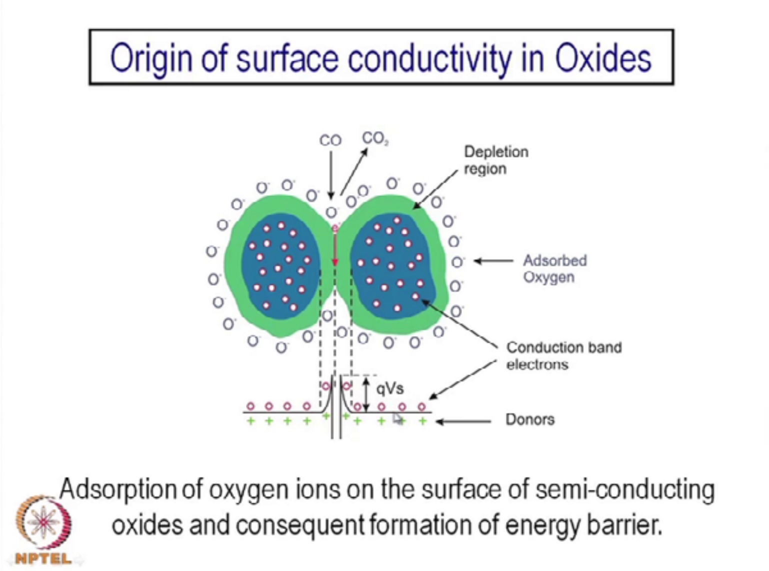

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How, this surface is particularly, we are talking to start with, we are talking of semiconducting property of the oxides and semiconducting oxides. So, how this surfaces can be different from the bulk of the bulk of the material. The in a semiconducting material, the electrons transfer is relatively easy compared to the insulating materials, so you have large number of electrons or holes available in this structure. And, all these materials have a inherent property; inherent property to adsorb, some of the ionic species, particularly oxygen and as you can see here, these are two different grains of a ceramic material; basically it is a semiconducting material, so these are actually the conducting conduction electrons, which has been just denoted here, that means initially these are a semiconducting material, so fairly large number of conduction electrons are already available, because of the defect structure, because of non stoichiometry and of course, because of the ambience ambience condition and so on.

So, a semiconducting oxide there maybe electrons, if it is a n type semiconductor, if it is hole conductor or a p type semiconductor, there are be holes. Now, if you have a electrons enough of electrons; electron will have certain of energy levels and that can be presented in the form of a band diagram, this is the so called conduction band of the electrons present here, and these are the donor levels close to the conduction band; so you have in the conduction band, you have already some electrons available, which are free to move under the application of the electric field, so these are the electrons already available. However, when there is a adsorption of certain species gaseous, species in particular here is been shown, that surrounding this grain.

You have a layer of adsorbed oxygen ion O minus is not O 2 minus is actually O minus, so oxygen atom has taken up an electron from this solid from this solid and so is become O minus, so it has been the electrons has been taken up from the outer surface. So, there is a creation of, what we call the depletion zone or depletion region; that means electrons are no longer there, so electrons, which was inside the crystal is still remaining but, because of the electrons as been picked up by the oxygen, which is available in the atmosphere, so that becomes as O minus and that electron is now attached, it is localized with the oxygen atoms and therefore, it is no longer free, it is no longer free.

So, there is an insulating layer, these green layers actually are the insulating layers, where the number of electrons free electrons as to very very less whereas, inside we have a conducting grain, so because of the presence of sufficient amount of oxygen, most of the time, which as basically it is an oxide and it is placed in anoxide environment or air environment. So, you have oxygen sufficient, oxygen atoms and they get adsorbed in the surface and during the adsorption process. If they pick up each one of the oxygen atom, picks up one electron from the surface layer as a result, the electron density, here is depleted and you get a insulating layer you get insulating layer surrounding all the grains.

So, if it is a whether, it is a porous material or a nonporous material does not matter, because there are still surfaces available the surfaces, available whether it is a free surface or a discontinuity in the crystallographic orientation, so that it like grain boundaries both acts as more or less the same manner and you get electron depletion zone surrounding, the crystals surrounding the grain boundaries, whether it is porous or nonporous, it does not matter right.

As a result of that, a insulating barrier is created and the band, the conduction band bends here, because you have a insulation barrier, so the electron cannot move, so easily from this point to that point, it has to cross a particular energy barrier, this because of the depletion zone, the band has bended here and you have a larger energy, so that electron if it go to from this side or this side to that side, then it has to go through a larger energy barrier and that can be calculated and it has been express at qVs charge into some amount of this height; this height is actually these expression.

So, the primary reason of the depletion zone is the adsorption that, which is inherent characteristics are all semiconducting oxides in presence of oxygen, so this is the characteristics and depletion zone and adsorbed oxygen ions, the conduction electrons; these are conduction electrons here as well as in the band here and these are oxygen negative sign, one negative sign, so O minus and that comes in that forms or automatically layer on its own, it does not need any external influence to create that now.

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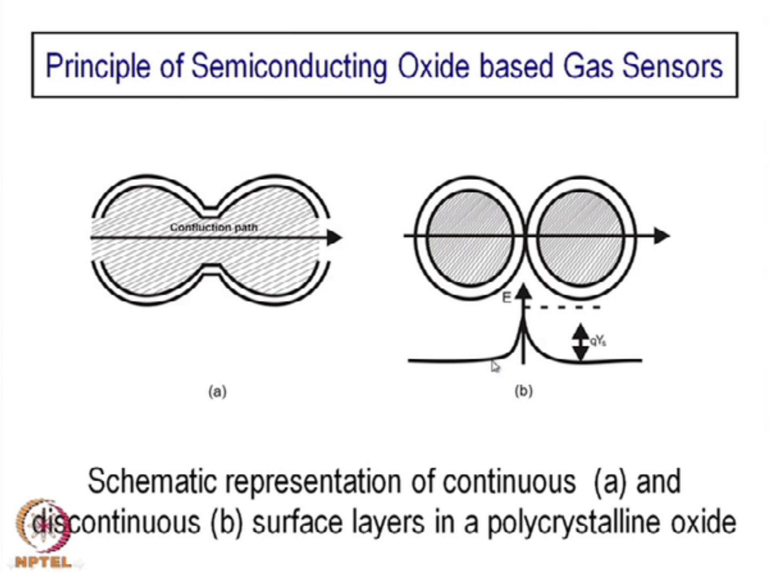

With this, one can have so, we have created or there is a presence of some surface layer a insulate, basically an insulating layer on adsorbed layer and that layer can be a continuous one like this, so the electron can move through this continuous phase, which is slightly insulating phase compare to the conduction phase, conductive conducting phases, which is the bulk of the grains, so it can be a continuous phase. If there is no boundary or even if the boundary there maybe another discontinuity here but, it may be a continuous phase, otherwise if the pores are there, then it can be a discontinuous phase, so it does not matter, whether it is continuous or discontinuous, there is a difference there is a difference in conductivity or the nature of conduction between this layer and the bulk of the material ok, so here this kind of barrier has been created, because it has been a discontinuous layer.

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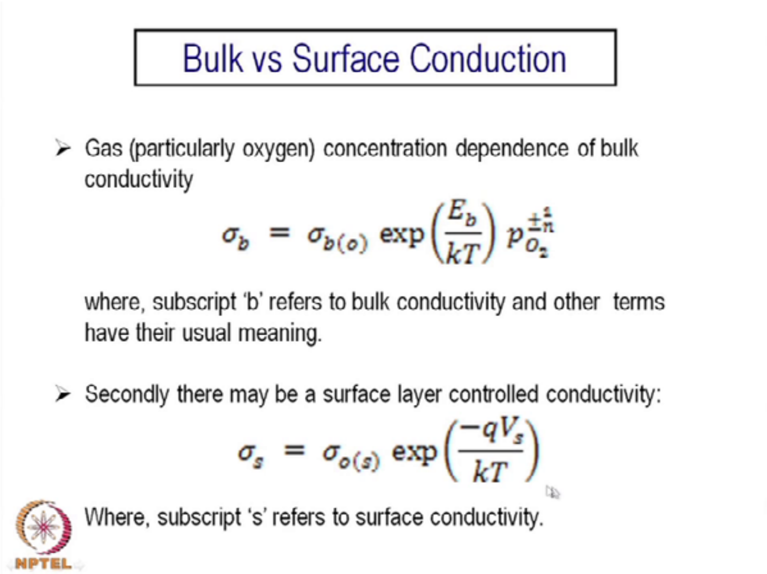

Now, the expression for conductivity, for the bulk and the surface conductivity are the barrier layer is different; this is a very common expression. We have seen earlier, that for any oxide, the defect concentration, the non stoichiometry changes with the kind of environment. It is exposed to because, there is oxygen in the oxide any oxide, and oxygen is also available in the environment, so there is exchange, there is a equilibrium of the oxygen concentration or oxygen partial pressure or in other or oxygen potential between these two solid.

And, the gas there is a solid gas exchange and you will always get a p o 2 dependence p o 2 dependence of the conductivity; so the conductivity particularly, when there non stoichiometric oxides, you will get a p o 2 dependence. That means conductivity is not only dependent on the temperature in this by this Arrhenius kind of equation but in addition you have p o 2 to the power plus minus 1 by n, so both p o 2 and temperature controls the conductivity, the particularly the bulk conductivity.

And, there is a equilibrium between the oxygen potential or oxygen concentration on the in the environment and the oxide, so there are plus minus, because depending on the situation it may be a either plus 1 by n or minus 1 by n. And, if one remembers that it depends on what kind of defect concentration, what kind of non stoichiometric the material has, if it is a oxygen deficient oxide, then it is a n types semiconductor and the conductivity increases with decreasing p O 2, so the minus sign applies, so minus sign applies for a oxygen deficient oxide whereas, plus sign apply with oxygen excess oxide or metal efficient oxide, so depending on the nature.

And, as we have a earlier discussed that, this is an inherent property of the semiconducting oxide, either it may be oxygen deficient or a oxygen excess oxide, so depending on that either the minus sign or the plus sign will be applicable. So but the most important aspect to note here is that any oxide or any oxide, there is a partial pressure dependence; so partial pressure is controlled by the environment. So, the oxygen potential is also controlled by the presence of other gases. In addition to the other oxygen well in air, you have only oxygen and nitrogen, so no other gases influence the p O 2. But if there is some hydrogen, if there is some reducing gases, the p O 2 will change will change the partial pressure, surrounding atmosphere and therefore, that is a bearing on the bulk conductivity of the oxide.

So, there is a direct relationship between, the oxygen concentration or oxygen potential of the surrounding atmosphere, to the conductivity of the oxide. So that, itself says that the conductivity will vary with the concentration of the gases and one can monitor the gas concentration, just by measuring the conductivity, so that is very the basic principle. But, so that is so far as the bulk conductivity is concerned, when we are not considering, the adsorbed layer or the surface layer.

If you are talking about the surface layer, then there is a band bending, as we have sent an and some surface states are created in the energy band diagram. And as a result, there is a enhanced barrier height; so the barrier height, there is a creation of a barrier height at the junction. And so, the surface conductivity is also exponential is exponential dependent on the surface on the barrier, what is created energy barrier, that is created these more or less the same expression, except that there is no p o 2 term. So, this is not dependent on there, it is basically dependent.

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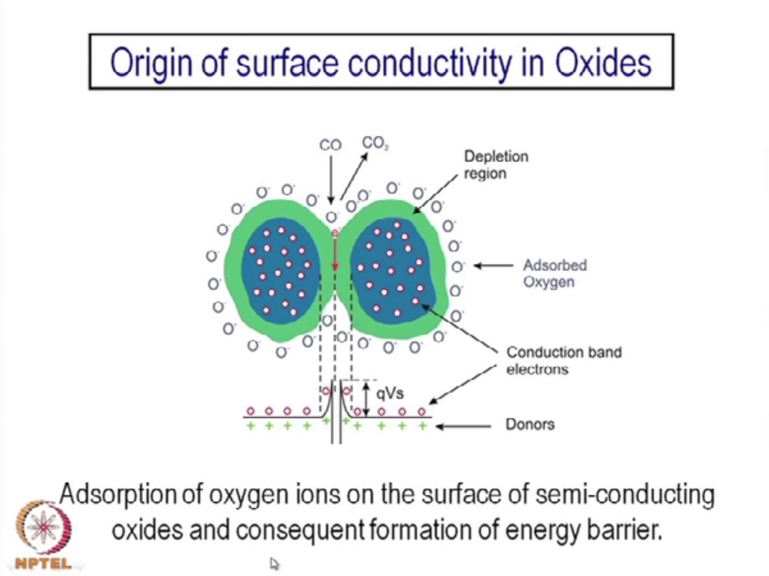

On as, we have seen earlier, it is on this adsorbed layer; once the adsorbed layer is formed, then it is in material, what kind of environment, it has particularly in terms of p, O 2. But it will certainly change it will certainly change, if the environment change but, we do not have that kind of a direct relationship like in case of a bulk conductivity; the relationship is slightly different.

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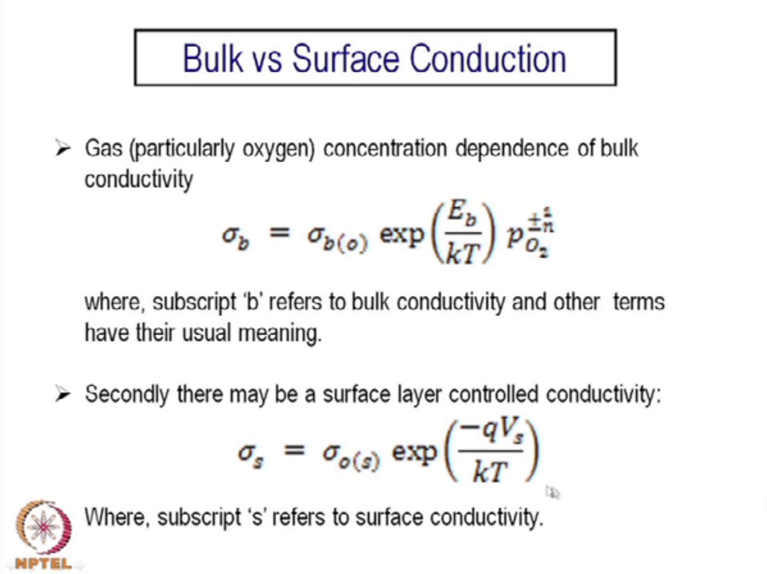

So, this is the conductivity of the surface, and that is the conductivity of the bulk material incident, all the conductivity this conductivity is relatively high magnitude of this conductivity. And, the same material, the magnitude on this conductivity is relatively high compared to this value, so whenever the adsorbed species on the surface, it is surface which predominates, so far as the conduction processes is concerned.

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Possible Sensing Mechanisms

- Adsorption of Oxygen on the surface:

$$O_2 = 2O$$
$$O + e' = O^-(ads)$$

- When exposed to a residual reducing gas in particular, interaction with surface chemisorbed oxygen in different ways:
  - $CO(g) + O^-(ads) = CO_2(g) + e'$
  - $CH_3CH_2OH + O_2 = CH_3CHO + H_2O$
  - $CH_3CHO + O^-(ads) \rightarrow CO_2 + H_2O + e'$

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What are the possible sensing mechanism? Then we have seen, there is a oxygen adsorption on the surface of the semiconducting oxides, and this is what happens, oxygen from the environment comes in has a contact as a molecule and then on the surface, it is actually atomized gets, a instead of molecules, it gets atoms atoms. So it is but through a catalytic process, so all oxygen oxide surfaces have some catalytic activity; and that catalytic activity leads you to the presence of oxygen atoms. Now these oxygen atoms, as mentioned earlier that, it takes up electron from the bulk of the material primarily from the close to the surface.

So, if picks up electron and then, becomes a monovalent or negatively charged oxygen atom or oxygen ion and that gets adsorbed, this is surface because there electrons there is a transfer of electrons from the solid and it picks up electrons from the solid and gets adsorbed to the, so it is getting localized at the surface. So, you have a layer, you have layer of oxygen adsorbed layer on the surface; now this oxygen layer, when exposed to a residual reducing gas, in particular the interaction with surface chemisorbed is chemisorbed oxygen layer, oxygen ion in different ways.

Let us say, we have a gas light carbon monoxide is a reducing gas, it is in the environment and then when it comes in contact with the surface, where already adsorbed oxygens are there, it will react with that and then, it will convert to C O 2, the oxidized gas and in the process, it will release this electron in this process; it will release this electron where it was taken from. So in the presence of oxygen, the electron gets picked up from the surface, however if there is a reducing gas then oxygen, what was adsorbed in the surface, it actually reacts with the carbon monoxide and oxidizes, it to C O 2 and there are electron, which was picked from the solid is given back to the solid. So particularly on the surface, that is what is has been shown in the pictorially.

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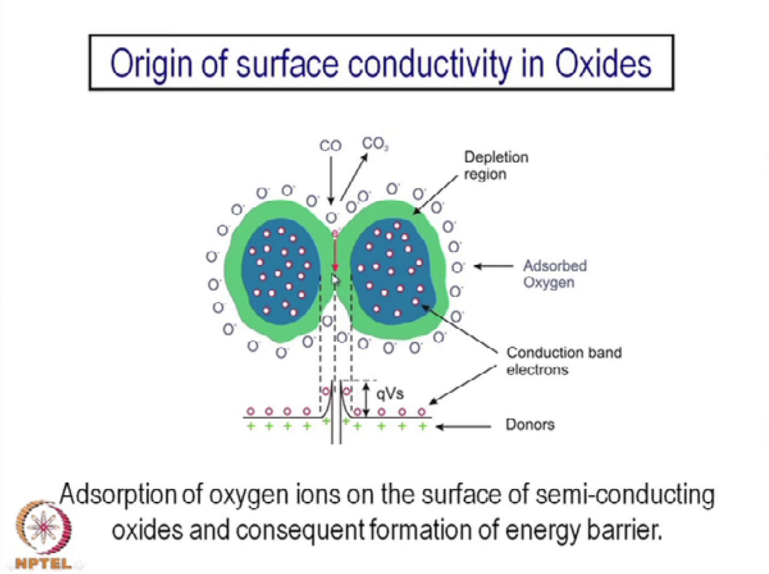

Here, again you can see, if carbon monoxide comes from outside and then reacts with this adsorbed oxygen ion, it becomes C O 2 and in the process, this electron gets injected into this systems, where it was picked up. So, as a result what would happen? what would happen, the this when carbon monoxide is not, there it was basically an insulating layer and then in the presence of carbon monoxide, this becomes again a conducting layer or relatively conducting layer, compare to the insulated layer, which was created.

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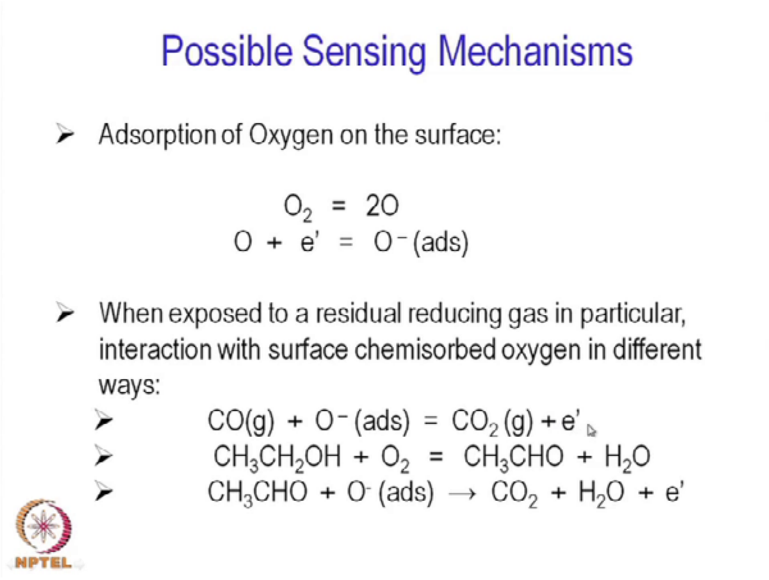

So, that is basically the simple mechanism by which, the electrical conductivity of the oxide, as a whole will increase, because it is injecting electrons similar thing happens. If there is some alcohols, and these are the kind of adsorbed oxygen ions, it sorry, it reacts with the oxygen and then it produces some absorbed oxygen ions, and its changes its changes to C O 2 H 2 o 1, once again an additional electron is generated, so by this chemical processes, whether it is a carbon monoxide or an alcohol? like this you can create, you can inject electrons, you can free electrons from the adsorbed sides or the adsorbed layers. So, this becomes free electron and it becomes conductivity increases, so that is the kind of very simple mechanism and adsorption as a very important role in the whole process.

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However, in case of oxidizing gases like NO_2, it can either be adsorbed on the oxide surface or can react with the pre-adsorbed oxygen ion as follows:

- $NO_2 (g) + e' \rightarrow NO_2^-$
- $NO_2 (g) + O_2^- + 2e' \rightarrow NO_2^- + 2O^-$
- Experimentally, it has been observed the presence of either O^- or O_2^- species on the surface of oxides like SnO_2 particularly > 200°C.

Well, it is not only the reducing gases, the oxygen or the conductivity can change conductivity certainly can change it is, so what we need, only a change its not necessarily one has to increase but, one can decrease also, change in conductivity, change in electrical signal, so that is what are change in current? What, which is the measure? Which can be measured? Which has the measure of the resistance of the material in case of oxidizing gases? like N O 2; it can either be adsorbed on the oxide surface or can react with the preadsorbed oxygen ion as follows on O 2 for example, in case of in place of c o, if you have nitric oxide, then it can pick up electron and instead of oxygen o minor o minus, this species can also get adsorbed; this species can also get adsorbed on the surface.

And, then this also can react with the oxygen ion, and by taking up two electrons, so it will pick up 2 electrons and then this will be adsorbed and it will create, another adsorption ion. So, you can see compared to the earlier one, here electron is not generated, electron is not actually injected in system but more electrons are being taken up more electrons are being taken up from the system. So the conductivity in this case will reduce well, any kind, anywhere, whenever particularly when there is a n type conductivity oxide, you will get that, the reducing gases will enhance the conductivity.

Whereas, oxides or oxidizing gases will reduce the conductivity, so that way experimentally, it has been adsorbed that presence of either o minus or O 2 minus species on the surface of oxides, like particularly like n o like S n O 2, the tin dioxide at 2000 degree centigrade, so the presence of this kind of species has actually been detected on the surface of semiconducting oxides like S n O 2; S n O 2, incidentally is a very common oxide, which is n type oxide and it is a oxygen deficient oxides N O 2 minus x actually, so there is a non stoichiometric, there and the you has a n type conductivity. So this is a very important oxide, which is been historically historically used used a gas sensing oxide. And particularly, it has been these are conjecture to a large extent, these are conjecture and it has been shown that, these are the species really gets adsorbed on the surface of a S n O 2, particularly at greater than 200 degree centigrade.

So, will come to that what is the temperature effect? there temperature of course, has a important role not only the gas concentration or the type of gases gaseous species but, the temperature also as a very important role, so far as the adsorption characteristics as concerned, and this adsorption characteristics is important for the detection of the gases, whether it is oxidizing gas or reducing gas incidentally ah, the oxidizing gas it is less sensitive whereas, reducing gas is much more sensitive. So, it can consume the electrons or this oxygen adsorbed oxygen, species and inject electrons, so reduction of resistance or enhancement in conductivity is much more significant, when you have a reducing gas or on the other hand, when you have oxidizing gas like this, the changes of conductivity are relatively small.

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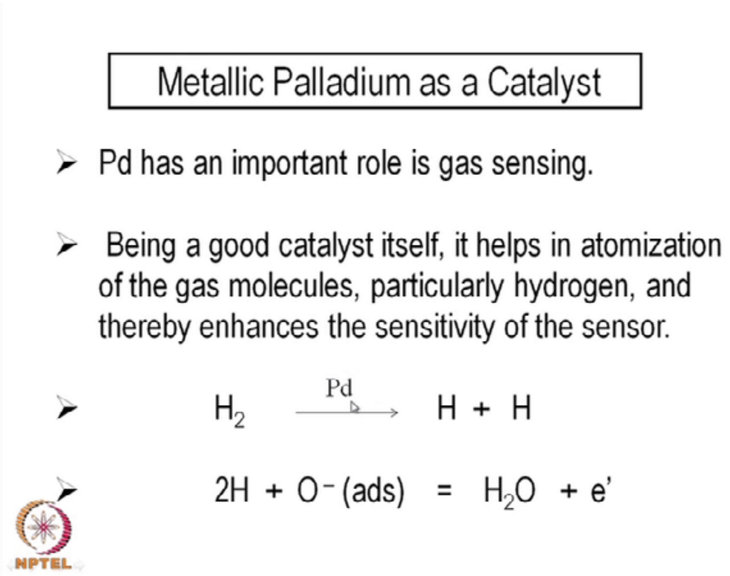

Well, since adsorption is one of the major species, a major phenomena on the surface, which gives rise to this kind of changes in conductivity, there is a very important role of catalysis, because initially we have seen that, first of all oxygen molecule has to get atomized by a catalytic process. And then that oxygen atom picks up an electron, so catalysis has also a very important role in determining the conductivity, and also in presence of the adsorption, in presence of sound, the gases in that context palladium has a very important role in gas sensing. So all the surfaces of the oxides are basically loaded with some amount of paladium palladium.

As, we know it is a it can adsorb hydrogen and it can also atomized hydrogen quite effective, so in this kind of situation happens being a good catalysis itself, it helps in atomization of the gas molecules not only hydrogen. But maybe hydrocarbons and there are many other gaseous species, which can be dissociated in presence of just in presence of paladium as a catalysts, at a relatively high-temperature, so palladium has a very important role.

Since, we are depending the total process is depending on the catalytic activity of that surface and the adsorption property of the surface of the oxide. So if you can, if one can load the surface with some very fine particles are fine islands of paladium metallic palladium. That helps in the catalysis and adsorption and in the process enhances the change in conductivity in presence of different gases. So this is what happens, it atomizes atomization reaction takes place and then atomized hydrogen reacts with the adsorbed oxygen ion, and produces H 2 O and electron.

Once again, the electron is liberated from this adsorbed surface and therefore, the overall conductivity increases, because this electron is a bound electron; this electron is very much there, it is locally bound the oxygen atom, so it is not available for conduction whereas, this electron is a free electron, once it is freed from the oxygen site, it becomes free electron, so by applying electric field, it can move and therefore, one can enhance the conductivity, so palladium has a very important role to play. So, whenever we talk about semiconducting oxides used for gas sensing, most of the time, we use a paladium dispersion on the surface of the oxide.

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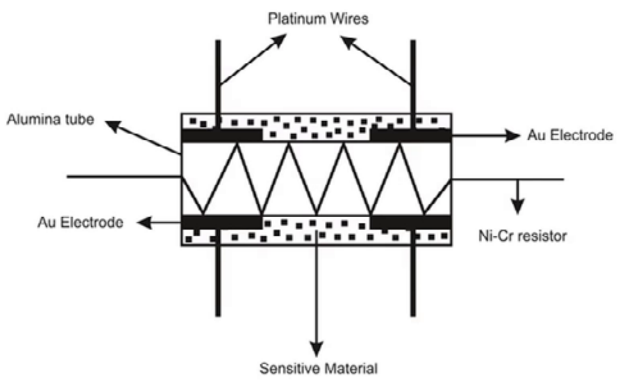

Schematic design of a gas sensor based on Semiconducting Oxide (e.g. SnO_2 and ZnO)

Next comes, what is the basic design? how you can, whatever disc you have discuss. So far, is the basic principal on which, a oxide can used as a gas sensor or for sensing or measurement of gas concentration in presence of this oxide. Here, how actual sensor looks like? how it is designed?

Of course, this design is a fairly relatively, old design and although, it is a standard design but, it is been a old design is will come to that, why it is an old and what are the new designs, one can have to start with, we have a small hallow tube; its alumina tube, a very small tube, oh the total diameter may not more than 2 to 3 millimeter in diameter and then on the surface, you coat one coats, the oxide it may be tin dioxide, zinc oxide may be other semi conduction oxides, one can certainly use but, these are the two most common oxides used for this purpose and incidentally both of them are n type semiconductors in S n O 2, it is oxygen deficient.

Whereas, this one is also oxygen deficient but, it has the defect is metal, interstitial here is the oxygen vacancy, when predominant defects here it is metal interstitial, that is zinc goes to interstitial side, so this is an example of both of them are oxygen deficient but, the defects are different, point defects are different; one is a oxygen deficiency, a sorry oxygen vacancy; and another is zinc interstitial.

So, this fine powders fine powders always a either, a S n O 2 or Z n O 2 is actually coated, is coated on the surface of the alumina tube. So this is the this is the actually active oxide, it is coated normally by different kinds some kind of a binder, just like one makes thick films with the use of some organic vehicles. So, one can make a paste with some organic vehicles and then coat it brass, it either brass it or screen print it on the surface. So, the overall thickness maybe about 25 to 50 microns. And of course, it is porous and porosity is important porosity is important, as we seen earlier, because the gas to come in contact with the surfaces of the particles, so control amount of porosity is important for this layer, so there is a porous layer of the active oxide.

And then of course, we have some electrodes; these are the electrodes to measure the changes in conductivity or resistivity. So, normally one can use the platinum leads, one can use but, for stability one can use gold layers or gold plated, otherwise because, it is they are nobel metals, so they dont change even in the presence of oxygen or different gases otherwise all other metals can either oxidize or make some compounds with this gases, which has to be measured. Another important aspect of this, it is not a room temperature sensing at room temperature.

The resistivity of the materials is very high, although we are talking about semi conductivity but, the resistivity may go of the order of mega home centimeter and so on. Therefore, it cannot sense it cannot sense at room temperature or the measurement becomes difficult. The impedance become electrical impedance, becomes difficult; so it becomes difficult to measure the resistive or the current; the current becomes, so low that one cannot measure therefore, it needs a heater, so this is the hollow part of the ceramic tube is actually used to house, a small coil, nickel chromium or nicrom coil, which actually heats up and the temperature of operation is normally above 150 and it can go up to 300 degrees, so you have to have a heater.

So, there is a source, there has to be a current source to heat this and then at the temperature in presence of gaseous species, the conductivity or the resistivity will change and you have to monitor that, so this is very simple mechanism or simple design, by which a gas sensor can be made. In fact, they have been made in huge numbers and their being commercial have already been commercialized; so there commercially available gas sensors and primarily developed in Japan and then of course, the other countries also can make it now, and there are very modified versions of this kind of sensors, the overall dimension as you can see, as I mention is only about 2 to 3 millimeter in diameter and the length not more than 5 to 6 millimeter, so that is and the coil, the heater coil has to be very very small my miniature of this coil. So, this is the basic design of a gas sensor, so it a self heated sensor.

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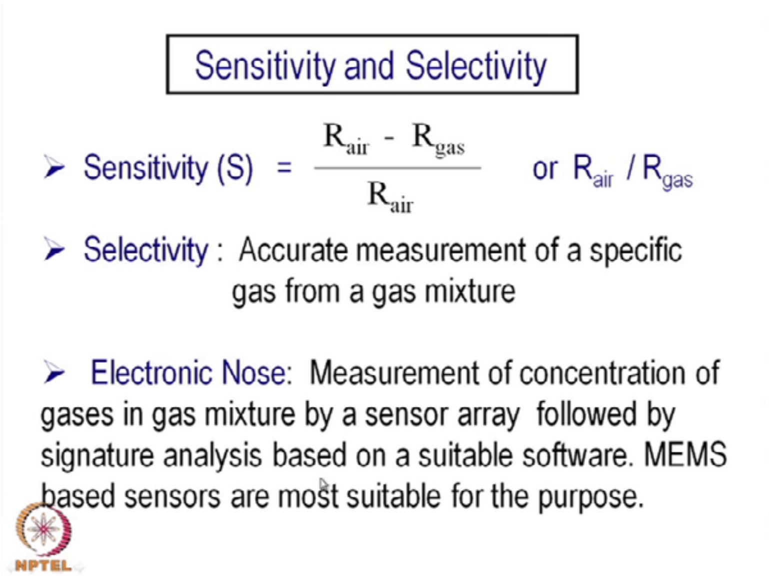

When you are talking about sensor one or two parameters are very important, how to express or how to know? what is the effectiveness of such a sensor? So, to measure the effectiveness, we have two or three parameter. We are normally used in sensor technology or sensor area, first of all the sensitivity well, there are one or two different ways of measuring, the sensitivity or make a quantitative measurement. This is the resistance initially, that is the stable resistance in air, so that is your reference; so air is the resistance and normally these resistance is higher than presence of gas.

If you are talking about primarily reducing gases, and many some of the reducing gases are combustible gases also, from that point of view resistance, in presence of the gas will be lower than that of the air resistance. And then you divide it by air resistance, so it becomes actually less than 1; it should be this will be lower and this be higher, so its normally less than 1 it may be greater also or sometimes it is also in some literature. You will also find there is just a ratio of resistance in air to resistance in gas, so that also is becomes a higher than 1 ratio; becomes higher than 1 in this case, so this is normally platted plotted either against time or again stages concentration to show, the sensitivity so that is the sensitivity of a sensor.

And, then selectivity; now selectivity of course, there is no quantitative parameter for that but, basically whether we are able to accurately measure, the specific gas concentration from a mixture of a gases, there may be different gases hydrogen, may be carbon monoxide, may be some other hydrocarbons and so on. So, whether we are able to distinguish between these different kind of gases, that is what we called the selectivity. And, in general in general as we have seen from the discussion in this lecture itself, that the selectivity of this kind of solid-state sensor or oxides base sensor is not very high.

So, whether it is a carbon monoxide or a hydrogen both of them are basically reducing and they will react more or less in a similar manner, with the adsorbed oxygen and therefore, enhance the electronic conductivity more or less in the same manner, one maybe little higher than the la other. But accurate sensitivity or the measurement of hydrogen separately, and carbon monoxide separately, becomes difficult; so this is one of the disadvantages; so this kind of sensors selectivity is relatively poor.

However, if somebody knows that, there is no presence of there is only one kind of reducing gases or one kind of oxidizing gases, then it becomes easier to understand, whether the gas concentration is increasing or decreasing? At what rate it is increasing and so on. And sometimes through a calibration processs, one can also find out the accurate measurement of the concentration of the gas of our interest. Now, in this context, I will come that in a minute before that there is another parameter.

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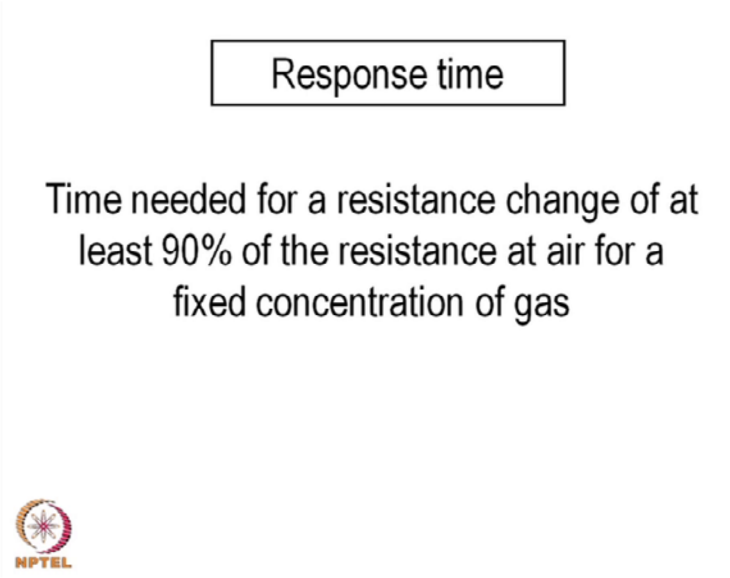

I think better introduce that it is the response time, how fast it can respond to a, to change in concentration. So that is another important parameter, and the response time has been basically defined, the time needed for a resistance change of at least 90 percent of the resistance at air, for a fixed concentration of gas. So, you introduce certain concentration of gas; and see, how much time it takes to change to that or to respond to that particular change. If we are changing the concentration from a 100 ppm tO 200 ppm, then 300 ppm that change may be instantaneous. But the sensor may not respond immediately, it may take some time, there may be a time lack to respond to the changes, what being introduced

And therefore response time is also very important, and in the process of response time or in the context of response time, there are two aspects; one is the response to the changes, it may be enhanced concentration or reduction in concentration, so you can withdraw the gas and see at what rate it is recovering? So one is response the time, another is also the recovery time. Mostly the response time is faster; that means the enhancement or the reduction in resistance is faster whereas, the recovery is slow, because there kinetically not a very fast process. So it is basically there is a need of mass transport and adsorption, desorption process; so all this process are relatively sluggish processes and therefore, although the response time is fast but the recovery time is relatively slow.

Now it can vary depending on the particular oxide, depending on the way, the samples have been prepared or the surface structure also these area of the surface, all these things are important, which we changes the different parameters like response time sensitivity, selectivity and so on. So, the response time may vary from fraction of a minute to more than a minute, a it is not in the range of milli seconds or micro seconds is not like that, it is relatively slow process but, certainly within a minute, one can respond very stable. So, the equilibrium can come within a minute at least sometimes. Of course, recovery can take little longer may be 1 to 5 minutes or so before that one cannot expect some accurate changes in the conductivity or the response behavior. So these are some of the parameters, one has to remember, while using a gas sensor of this nature.

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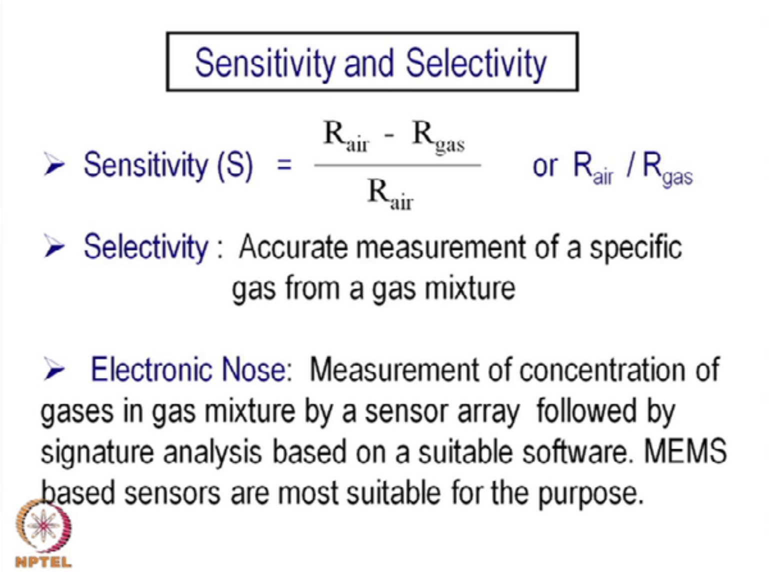

Coming back to the last point, which we mentioned here the electronic nodes, basically our nose senses various kind of automatic compounds, some smells and so on. These smells are nothing but the presence of certain gases, some gases actually produces some smell specific to the particular situation or fragrance and so on. Sometimes, smells are also there bad smells are also, there so even some rotten things produces some bad smells, so from that is basically generating certain very fine, very small quantities of gases, different kind of gases, that is the smell. So by measuring electronically by measuring the concentration of this gases or a mixture of gases, one can replace the human nose by an electronic instrument, and this is nothing but, what will call an electronic nose.

So, there are tremendous amount of development going on, it is a difficult task, no doubt because, when you sense a particular smell, it is not at specific gas or one gas, it is a mixture of various large number of gases of similar nature, maybe similar nature and distinguishing those gases, becomes quite difficult and therefore, if you want to really replace, human nose by a electronic instrument is not a very easy task.

Now, most of the cases, what we do? we do not use a single sensor but, array of sensor, large number of sensors with certain characteristics with certain different characteristics, so they have maybe sensitivity; one of the sensitivity gas a, another maybe more sensitive to gas b, another very sensitive little more sensitive to gas c, complete this distinction is difficult but, their relative sensitivities can be changed by manipulating some of the preparation techniques or the design techniques.

So, this can be, they will be array of such sensors and for making an array senses, it is better to have a miniaturize senses as small as possible as small as possible and from that point of view the senses, which are used in array of arrays are called name base sensor; they are actually miniaturize senses, micro electromechanical sensors and they are basically fabricated by the so called VLSI technology large-scale integration or chemical property position kind of techniques not thick film technique but, mostly thin film technology, so the fabrication techniques are little costlier but, one can get a miniature sensors of the order of, let us say few sometimes less than a micron of the less than a millimeter or 10 some microns, so such sensors can be placed by a thin-film technology on a substrates and each one of them.

The way, we have our micro electronics technology, each pixels in a display can be electronically connected, so here also of course, they are not as small as pixels of a display but, it is slightly larger but, they individually can be monitored and measure, so when a gas concentration comes in contact with all this array of sensors each individually. One can monitor, what is the response? what is the electrical signal from them? and then each one of them will have some kind of a differentiation for example, one can different sensors can be placed at different temperatures and by that process, one can differentiate their response times, the response to particularly gas and so on. So, for and there are catalytic activity can also be modify instead of palladium, you use maybe silver palladium, maybe gold palladium, and so on.

So, that different sensors senses, different gas within relative less or more importance and by that process, you get large number of signals; electrical signals, which can be then processed through a software and you can get a signature analysis signature analysis of all the signals; electrical signals coming from different maybe 100, different senses and then try to find out, what is the nature of that particular gas mixture, in fact there are many different, for many different things, people are using it, these sensors may be the quality, whether it is good press phases or rotten phases, that can be sensed in fact there is no not attempts.

Some instruments are also available in the market, fruit sensor; fruit freshness sensors can also be there and people, in fact there are some groups in this country working on this kind of senses, different kind of array of senses also and even the quality of t, because quality of t depends on the kind of kind of flavor it generates and that flavor again comes from a large number of aromatic compounds, several 10s or 100s of them are available. It is very difficult to identify them but as a collective measure, you can have a signature of different flavors. So by that one can by using this kind of a sensor a large number of sensor together, one can replace human nose and get an electronic nose, so that is one thing being tried even in this country several such groups are working in that area. That, we have discuss responses time

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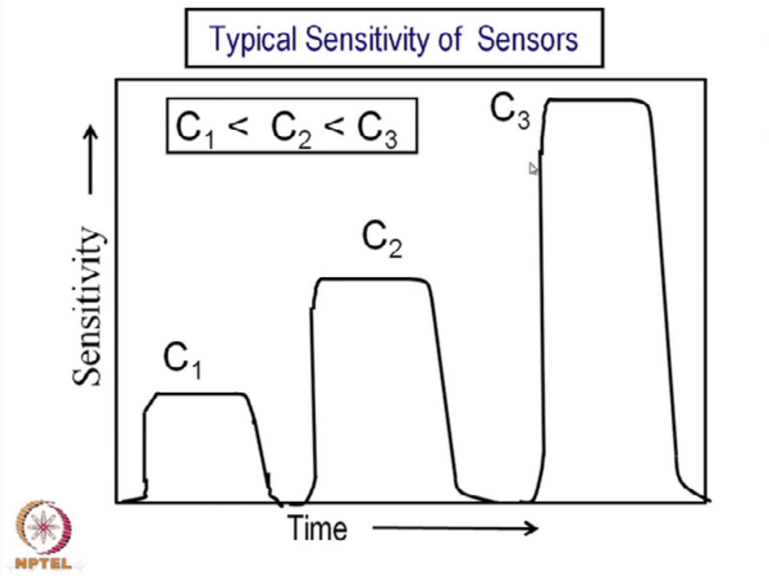

This is the last one for the time being, that is this kind of typical sensitivity of senses, while these are schematics only, these are schematic only, which what has been plotted here, as a time, sensitivity different concentrations of the same gas. Of course, this is not a mixture of gas, the same gas has been introduced at different times and see, how the response changes of the sensitivity changes or the signal changes, strength of the signal changes, so this is C 1 concentration, C 2 concentration and C 3 concentration of the same gas, maybe carbon monoxide, may be some alcoholic; one is less than C 2 and less than C 3, so this concentration is less, so the overall signal is intensity is less than…

In fact the resistance are changing, this less resistance, this sorry this high resistance, this the lower resistance, so lower resistance means larger current and still lower resistance or larger current, basically it is measuring the current; so it is proportional to current, and this is the your kind of response time; from in this is the time scale, so at this time it can be 0 time here, so how much time it takes to goes to the saturation, so that from this point to this point is your response time.

And, you can see the recovery, when it is withdrawn; this particular gas concentration withdrawn, it is coming back to 0 but it is a slower space, so this recovery time is slightly larger same thing happens. Once you a different concentration gas is introduced, once again it reaches a saturation, and then it continues, this is gas is withdrawn, it is coming down not because of anything else but because the gas is withdrawn. Here once again a different concentration is in introduced and the signal goes up and once again the C 3 concentration withdrawn and it takes some time before it comes back to its original position. So this is the typical response behavior of senses through the so we have sensitivity as well as response time and different senses response, different layer at different temperatures also. Temperature is another parameter by changing, by which one can change the response time as, where the sensitivity. Now one of the reason or one of the characteristics, one has to measure for any sensor, it is the linearity as a function of concentration in particular.

Since, we are related interested in concentration, so as a function of concentration are we getting a linear change, that is a very important issue well in some reason we do get linearity. But it is not always linear throughout, the concentration range some kind of calibration carbon always necessary and compared, if you are interested in a know specific concentration oh or a not a relative term but, absolute concentration is very interested in absolute concentration.

We need a calibration curve with respect to the concentration at different temperatures and try to find out, what is it is response and what is it sensitivity, so with this we complete this particular lecture, we will continue we will continue this discussion on ceramic gas sensors maybe in the next class so for the time being.

Thank you very much.