Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 63
Hydrogen Sensing Part - 1

Hydrogen, we know that it is flammable, it has a low flammability limit, it has low ignition energy and it is the smallest molecule; now that makes it much more prone to leak. So, it can leak from various joints, valves, fittings and from various equipments. So, as such sensing of hydrogen becomes very important. So, detection of hydrogen even in small traces is essential, at the same time monitoring the hydrogen concentration that is also required so, as to avoid any sort of hazardous situation.

Now, this hydrogen sensing is important in very small concentrations like ppm concentration, when it comes to identifying impurities present like hydrogen impurity being present or it is required to sense in concentration levels less than 4 percent such that it does not form a flammable mixture with air. And, it is required to sense in higher concentration, a wide range till say 100 percent when it is to be monitored or controlled for different applications.

Now, this sensing is important in various applications. It is not only related to hydrogen, it is definitely hydrogen sensors are required at the point of production, at the point of storage, transport, utilization. But, at the same time hydrogen sensors find their application in various other areas.

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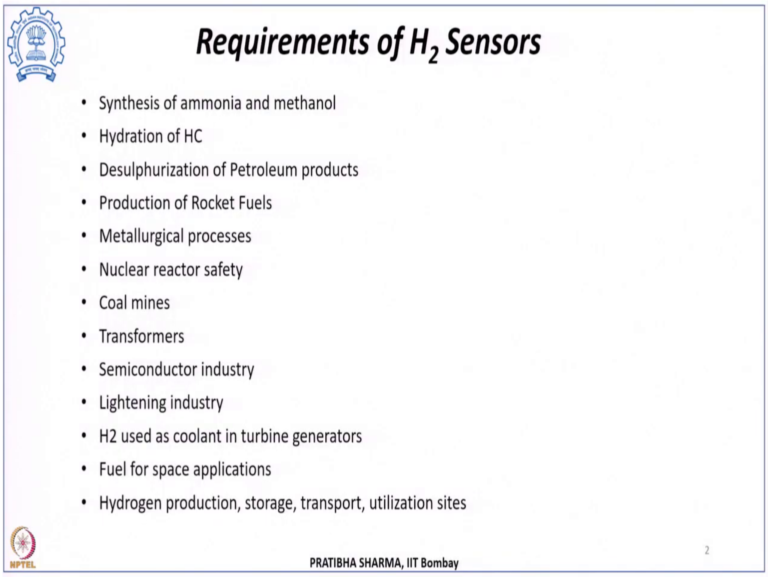

Like hydrogen sensors could be used during the synthesis of ammonia and methanol to identify any type of leak, hydrogen sensors are required at the process when the process is hydration of hydrocarbons or desulfurization of petroleum products, production of rocket fuels. For various metallurgical processes like galvanization or different types of other processes in the nuclear reactor safety.

While, fuel processing it is required to know the content of hydrogen, in the coal mines like if it is produced from say methane or from coal dust explosions. So, identifying the hydrogen amount, the concentration is very much essential. It is required that the hydrogen in very small amounts or traces to be identified from transformers that could result into an early fault detection in transformers. It is required to be sensed in case of semiconductor industry, in lightning industry where in the lightning industry it acts as a contaminant. So, we need to monitor that.

It also acts as a coolant in turbine generator. So, there if there is any hydrogen leakage that needs to be identified. We know that liquid hydrogen is used as a fuel in space applications. So, in this space application usage, if there is any hydrogen leak that needs to be identified. And, these are all above the top where indefinitely we require along the hydrogen value chain at every aspect of the hydrogen value chain.

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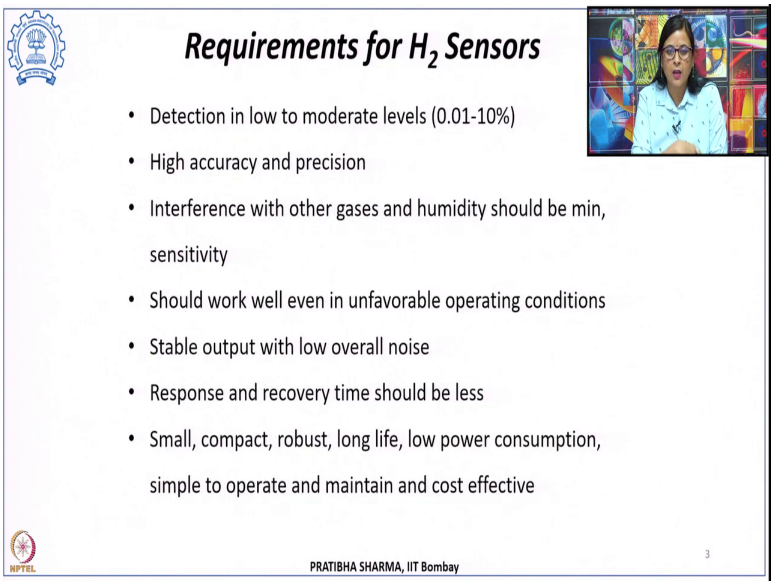

Now, when it comes to hydrogen sensors, there are several requirements that these sensors should meet. These should be able to detect hydrogen in a wide concentration ranges starting from low to moderate to high concentration levels. So, it could be like 0.01 percent to 10 percent. Like the low to moderate or even for certain application, this could be as high as 100 percent. The accuracy of these sensors which we use should be high and they should be very precise. There should not be any interference with any other gases other than hydrogen.

So, the selectivity or sensitivity towards hydrogen should be very high. Along, with that there should not be a cross sensitivity issues with the humidity being present. So, the interference from the other and the gases and the humidity should be as low as possible. At the same time these sensors are required to work well even in unfavorable operating conditions. By unfavorable operating conditions, we mean at high temperature or high pressures or gas chlorides.

They should show a stable output signal with very low noise; overall noise should be as low as possible. The response and recovery time with these sensors should be as low as possible, usually less than 5 seconds. Along, with all these requirements, they should be small, compact, robust, they should have a long life, they have a low power consumption, they should be simple to operate and maintain it and cost effective.

Now, the reason we have listed here hydrogen sensor to have all these requirements is because there are several other analytical equipments also which can be used for hydrogen sensing. Like, the well known gas chromatography or the mass spectrometry measurement techniques.

But, the these analytical equipments the major drawback that we could see is that they have a larger size, they have very high cost and the requirement is that they require very trained manpower, skilled person to operate those; the time of analysis is high, cost is very high. Then, the maintenance is the biggest challenge and then portability of those equipments are is a challenging task.

So, as such the sensor which is required to sense hydrogen to identify hydrogen to detect hydrogen or to monitor the concentration of hydrogen, they should be small and compact and easily operable and we should be easily able to maintain those and at the same time they should be cost effective. However, those analytical equipments that I mentioned, these are not good if hydrogen has to be continuously monitored. So, these are different sensors that are used for hydrogen sensing.

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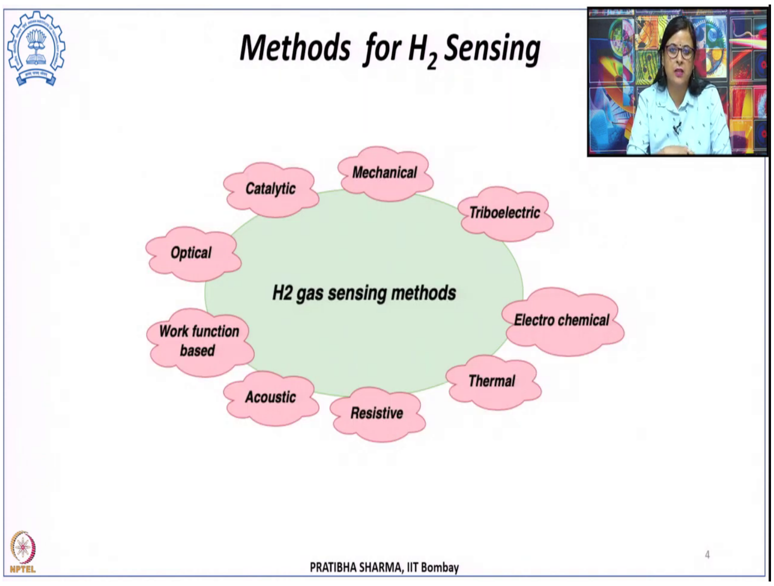

Now, based on the methods of hydrogen sensing, these can be classified into like mechanical sensors, triboelectric sensors, electrochemical sensors, thermal sensors, resistive sensors, acoustic sensors, work function based sensors, optical sensors and catalytic sensors. So, we will see very briefly these types of different sensors which can be used for hydrogen sensing.

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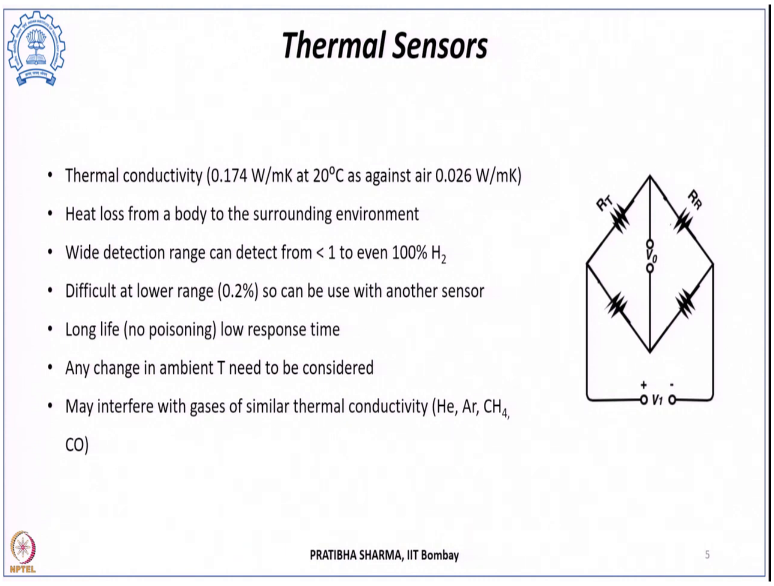

Now, the first type of sensor that we will see is a thermal sensor. Now, these thermal sensors are based on thermal conductivity. We know that thermal conductivity of hydrogen is higher than the thermal conductivity of air. Like, at 20 degrees centigrade, the thermal conductivity of hydrogen is 0.174 watt per meter kelvin and that of air is 0.026 watt per meter kelvin. So, the principle of these thermal sensors is based on heat loss from a particular body, that is the sensing element to the surrounding environment or the surrounding gas.

Now, the extent of heat loss from a sensing element will depend upon the thermal conductivity of the surrounding environment. For example, if there is more and more of hydrogen in the environment then the heat dissipation will increase because the thermal conductivity of hydrogen is higher. So, as such that correlation we can use to find the concentration of hydrogen in the environment.

Now, to understand that better this type of thermal sensors they usually consist of like there are two resistors; one is a target gas resistor and a reference resistance. So, these are two similar resistances and these are actually housed in a reference cell and a target cell. So, these are connected in a wheat stone bridge. Now, in case when there is no hydrogen in the environment, both these resistors are exposed to air.

So, here in the reference resistance or the reference cell, air is there in the reference cell. So, when there is no hydrogen both these resistors are exposed to air, as such there is the heat dissipation by both the resistances is same or there is no difference in the heat dissipation. So, as such your wheat stone bridge is balanced here. However, if there is a hydrogen in the surrounding environment that hydrogen enters into the target cell and the heat dissipation here changes.

Now, the difference in the heat dissipation between the target resistance and the reference resistance, that difference produces a signal in the wheat stone bridge and that signal in the wheat stone bridge can be calibrated to the gas concentration. And, using that calibration we can identify what is the concentration of hydrogen in the environment. Now, these particular type of sensors, the thermal sensors which are based on thermal conductivity they have a wide detection limit.

So, they have a wide detection range and they can detect from less than even 1 to even 100 percent hydrogen. By 100 percent hydrogen, we mean that there is no air or oxygen present, but the problem lies in the lower limit. So, we cannot detect below 0.2 percent and if we want to use, if the requirement is to detect below this range then we have to use another sensor along with this type of sensor.

Since, these type of sensor they do not get poisoned by the hydrogen or the presence of other gases. So, as such there is no poisoning effect and the life of these sensors is long, it is more than 5 years of operation. They have a very low response time, reported like 5 seconds even. But, the important thing that we need to remember or the disadvantage is that if there is any change in the ambient temperature that correction we will have to include.

So, that ambient temperature change need to be considered in a thermal sensor. Besides that, there could be interference from any other gas also, like any gas which has a similar thermal conductivity as that of hydrogen like the helium or the argon, methane or carbon monoxide. In that case, it will interfere with the sensing of hydrogen. So, that is the major disadvantage of the thermal sensors.

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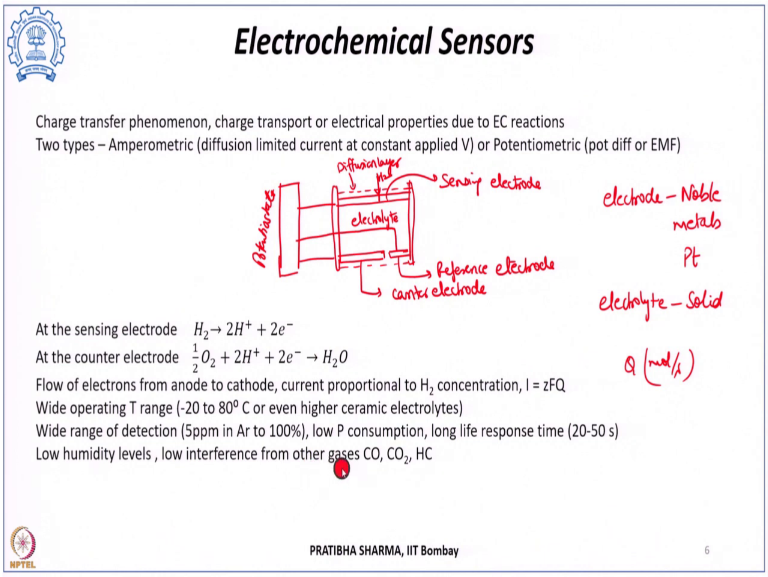

Now, the another type of sensor is electrochemical sensor. Now, these electrochemical sensors, they work on the principle of charge transfer phenomena. So, charge transfer taking place between the electrodes with an electrolytic medium. So, it is based on the charge transport or electrical properties which occurs due to the electrochemical reactions. So, these electrochemical sensors these are of two types, either amperometric sensors or potentiometric type.

So, in amperometric type of sensors, at a constant voltage the diffusion limited current is being measured. However, in potentiometric type of sensors, the potential difference or EMF is being measured. In a typical electrochemical sensor, there are two electrodes; one is a sensing electrode and another one is a counter electrode. Usually, a third electrode is also used which is a reference electrode.

Now, in order to keep the voltage constant, a potentiostat is connected and then there is a gas permeable layer. Now, this gas permeable layer or diffusion layer that limits the diffusion. Now, this gas permeable layer, it has multiple operations. One thing is that it permeates the annihilate, selectively allows the gas through it and limiting the other gases so, as to reduce the interference from the other gases, unwanted gases.

At the same time this diffusion limited condition is achieved using this diffusion layer. Along, with that it serves purpose that if like the there are two, these are the electrodes which are usually made up of noble metals. These are like generally made up of platinum, electrolyte could be either a liquid electrolyte or a solid electrolyte. Now, generally the solid electrolyte which is between these electrodes that is the nafion which is being used.

So, this diffusion layer, it prevents the electrolyte from drying and any sort of leakage from the cell it prevents that leakage. So, at the same time it prevents the diffusion of the unnecessary gases into the electrolyte. So, this a very simplistic diagram showing the arrangement of an electrochemical sensor. As hydrogen gas diffuses in onto the sensing electrode, the reaction that takes place is the hydrogen gets oxidized liberating 2 electrons.

Now, these electrons flow from the anode to the cathode and on to the counter electrode the oxygen gets reduced, reducing water. So, when these electrons flows from the anode to cathode, it produces current and that current produced is proportional to the hydrogen gas concentration that gets in. So, when these electrons flow from anode to cathode a current is produced and that is proportional to the hydrogen gas concentration.

Now, since the condition is diffusion limited, as such we can find out the current which is being produced by the Faraday's law $I = zFQ$, where I is the current, z is the number of electron transfer per molecule, F is the Faraday's constant, Q is the hydrogen conversion rate which is expressed in moles per second. Now, from here when we find out the current, that can be used to calibrate and find out the hydrogen concentration in the environment.

Now, these type of sensors they have a wide operating temperature range, ranging from minus 20 degree to 80 degree centigrade. But, only thing is that at this particular temperature, the electrolyte should not freeze that we have to take care of and even very high temperature range could be achieved with these type of sensors. So, like they can operate at even higher temperature and in that case, the electrolyte used could be ceramic electrolytes.

At the same time, they can provide a wide range of detection as well from say 5 ppm in argon to 100 percentage detection. They consume very low power and they have a response time which is little longer. However, some of the literature reports have even shown a lower response time. But, the major challenge here is that the requirement is that there these sensors should be subjected to low humidity levels and there should be low interference from the other gases like carbon monoxide, carbon dioxide and other hydrocarbons.

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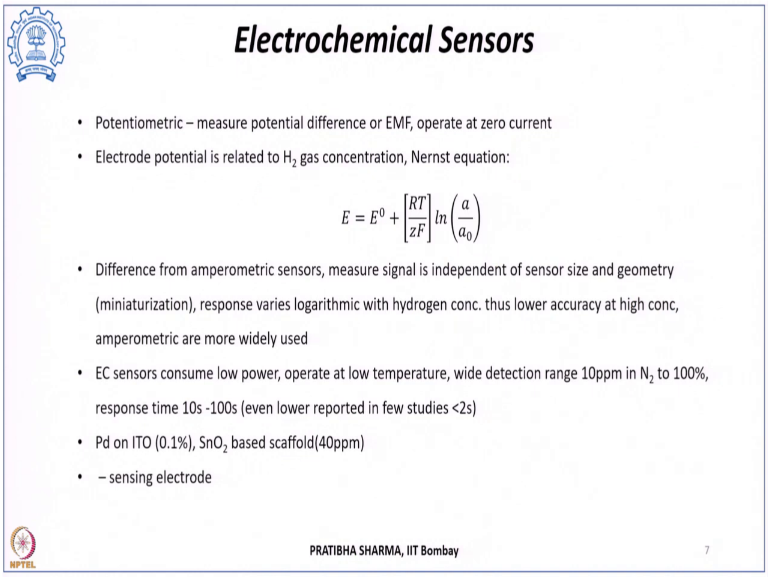

The other type of electrochemical sensor is potentiometric sensor. In this the potential difference or the electromotive force between the two electrodes is measured ideally under the conditions of zero current. Now, the electrode potential here which is being measured that is related or calibrated to hydrogen gas concentration. Now, in all these sensors that we are studying, the important thing is that the different types of sensors that I mentioned; here the certain property of the sensor changes and that property of the sensor has to be calibrated with the hydrogen concentration.

Now, these properties which changes that is in fact, tells us about the hydrogen levels. There is a transducer usually in the system and that transducer converts that change in property into an electrical signal. And, that electrical signal can be detected, monitored or analyzed so, as to find out the hydrogen concentration. So, that is the basic principle of the sensors; depending upon that property change we can find out what is the concentration of hydrogen being present.

Like in the case of potentiometric electrochemical sensors, the electrode potential that is related to the hydrogen gas concentration and a typical Nernst equation can be used to define that relationship. So, an electrode potential is E is equal to $E^0 + (RT/zF)\ln(a/a_0)$, where E is the electrode potential, E^0 is the standard electrode potential, R is the gas constant, T is the temperature, z is the number of electrons transferred, F is the Faraday's constant, a is the activity of the annihilate and a_0 is the activity of the reference.

Now, these activity is related to the hydrogen gas concentration. And, in this way we can by finding out the electrode potential, we can find out the gas concentration. Now, the major difference if we see between the amperometric and the potentiometric type of sensors is that in case of potentiometric type of sensors, the signal that we are getting; so, the structure remains same for both potentiometric and amperometric type of sensors.

The difference is in the potentiometric sensor, the signal is independent of the sensor size and geometry. Now, that makes an advantage in the sense if it is independent of the sensor size and geometry, we can reduce the size as low as possible. In that case, the miniaturization of such devices could be possible. But, the major disadvantage or the another difference that lies from the amperometric type of sensor is the logarithmic variation.

Now, this logarithmic variation with hydrogen concentration like the activity which is related to hydrogen concentration, that shows that there will be a low accuracy at higher concentration compared to the lower concentration. And, usually the amperometric sensors are more widely used compared to the potentiometric type of sensors.

Now, when it comes to electrochemical sensors, the advantages of electrochemical sensors are they consume lower power, they usually operate at lower temperature and they can have a wide range of detection ranging from like 10 ppm level in nitrogen to 100 percent detection.

At the same time the response time is faster like 10 seconds to 100 seconds. There are certain literature reports which have even shown that this response time could be as low as 2 seconds. Now, there are different materials which could be used in the electrochemical sensors like the palladium could be used on ITO and that has been found to have a limit of detection of 0.1 percent.

Tin oxide based scaffolds have been used and it has been found that they can operate at a higher temperature, at the same time they can have a limit of detection of 40 ppm.

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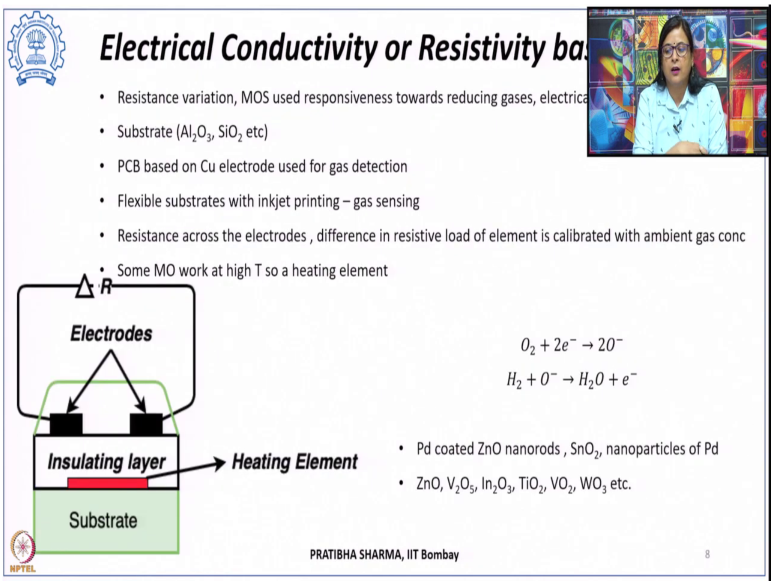

So, these are the general type of the electrochemical sensors which are used. Now, the another class of sensors is electrical conductivity or resistivity based sensor. So, as the name itself is suggesting, here in the electrical conductivity change or the resistivity change of the sensing element can be mapped to the hydrogen gas concentration. So, when there is a change in the resistance, that is measured as a reference for detection of the hydrogen gas.

Usually, these are metal oxide semiconducting type of structures. So, in these usually there is a substrate in the structure if we see. So, when these metal oxide type of sensors are used, actually these metal oxides have a higher responsiveness towards the reducing gases. And, as such that could be used for detecting hydrogen, the electrical properties changes. So, the now if we see the structure, the substrate is usually an aluminum oxide or silicon dioxide and then there is an insulating layer.

Sometimes, this heating element is used, this is particularly used when some of the metal oxides they operate at a higher temperature. So, this heating element is being provided. Then, there is a digitized electrode which is present and above that is a metal oxide layer which is being present. Now, the resistance between these two electrodes or the current between these two electrodes is being measured and this is calibrated. So, this change in the resistance is being calibrated as against the hydrogen gas concentration.

Now, there are different variations to this resistivity based sensors like the printed circuit board based on copper electrode, they can be used for gas detection or then there are like the future gas sensing electrodes could be flexible substrate which could be inkjet printed to detect the hydrogen gas. Now, the principle of operation remains that the resistance across these electrodes is being measured and the difference in the resistive load of the element, that is calibrated with the ambient gas concentration.

Now, if we see the operation of these resistivity based sensors, that is very simple and well known. The principle of operation is when in the metal oxide these sensors, when oxygen is adsorbed into these metal oxide, it diffuses into and it gets adsorbed. It takes up the free electron from the metal oxide and then the resistance increases or the conductivity decreases.

So, this is the usual phenomena, when oxygen adsorbs it takes up free electrons and the conductivity reduces or the resistance increases. Now, in presence of hydrogen the oxygen which is adsorbed, it combines to form water and then electron is liberated. In that case, the conductivity increases or the resistance decreases in n type material and resistance it increases in p type material.

Now, the typical example of these type of resistivity based sensors is like the palladium which is coated on zinc oxide nanorods or tin oxide or the nanoparticles of palladium. The different oxides that can be used include the zinc oxide, vanadium oxide, indium oxide, titanium oxide or tungsten oxide.

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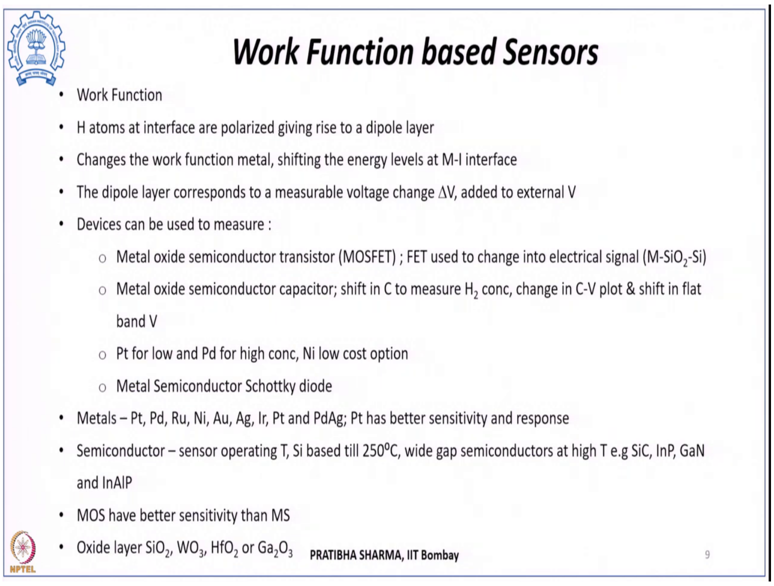

The another category of sensor is work function based sensor. Now, work function we know that it is the minimum energy required to remove an electron from a metal surface to infinity. Now, in these type of sensors, there are three layers in fact, a metal oxide and a semiconductor or it can be a metal and semiconductor layer. So, what happens is usually the metal layer is deposited onto the oxide layer or the semiconductor layer.

Hydrogen, it diffuses through the metal layer. This is the hydrogen sensitive metal which is deposited. So, it diffuses through the metal layer and it reaches the interface of the metal semiconductor or the metal oxide semiconductor. And, then at that interface the hydrogen atoms are polarized and that gives rise to a dipolar. Now, this results into a change in the work function of the metal and it also results into shifting of the energy level at the metal insulator interface or the metal oxide interface.

Now, this dipole layer which is being created that gives rise to a measurable voltage change. So, a voltage change is created and that adds on to the externally applied voltage. So, that change in voltage ΔV can be calibrated or can be used as a measure of gas concentration. Now, there are different devices that can be used which are based on the work function change like these devices could be metal oxide semiconductor field effect transistor.

So, MOSFET, now here in these MOSFETs, the FET the Field Effect Transistor is used to convert this ΔV, the change in the voltage into an electrical signal and that electrical signal can be calibrated with the hydrogen gas concentration. So, the typical arrangement which is a metal, then silicon dioxide and silica. It could be either a metal oxide semiconductor capacitor device, wherein the shift in the capacitance can be used to measure the hydrogen concentration.

And then correspondingly there will be a change in the C-V plot, there will be a shift in the flat band voltage and all that can be used to find out the hydrogen gas concentration. It could be even like the simple metals can also be used like the metal, for low concentration platinum could be used for hydrogen, a higher concentration palladium could be used. And, if we want to have a cost effective then nickel can be used or simply instead of having metal oxide semiconductor or metal insulator semiconductor, we can have a metal semiconductor short key diode.

Now, in these the metal that has to be used can be either platinum, palladium, ruthenium, nickel, gold, silver, iridium, platinum or palladium-silver can be used for the metal and the platinum has found to be the having the better sensitivity and a faster response. The semiconductor which is used here, this actually depends upon what is the sensor operating temperature and accordingly that semiconductor can be selected.

So, for a temperature operation in a range of say 250 degree centigrade, till 250 degree centigrade silicon can be used. However, if it has to be operated at a higher temperature then wide gap, wide band gap semiconductors can be used like silicon carbide or indium phosphide, gallium nitride or indium aluminum phosphide. But, the typically these metal oxide semiconductors, they have better sensitivity compared to the metal semiconductor schottky type of diodes. The oxide layer which is present that could be either SiO_2 or WO_3 or HfO_2 or gallium oxide.

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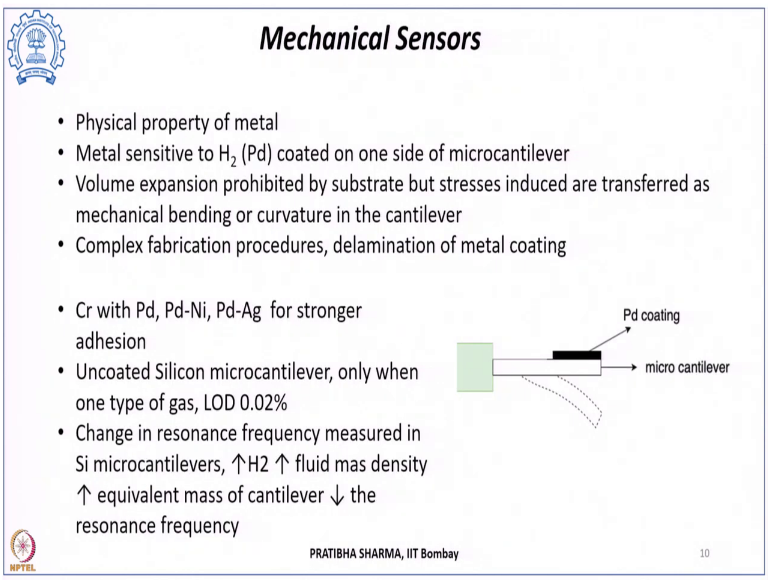

Now, the another class of sensors could be mechanical sensors and the sensing is done by the change in the physical property of the metal when it is subjected to hydrogen. For example, like if metal palladium is taken then palladium is actually coated on a micro cantilever.

So, the hydrogen sensitive metal is coated on a micro cantilever and we have already studied that in such materials the hydrogen it enters into the interstitial site. Now, when this palladium coating will be exposed to hydrogen, the hydrogen atoms will get into the interstitial locations and will cause an expansion. So, this volume expansion will occur in the palladium coating, but that will be prohibited by the micro cantilever.

So, as a result there will be stresses induced and that stresses will be transferred by bending of this cantilever. So, there will be a curvature which will be observed in the cantilever. Even this can be made porous so, as to have higher hydrogen diffusivity into the palladium coating thin film. But, the problem lies is like they have a complex fabrication procedure, at the same time subjected to several cycles of expansion and contraction when it comes to hydrogen absorption and desorption, the delamination of the metal coating, this palladium coating can take place.

Now, in order to improve the adhesion of this platinum coating, it could be either chromium with palladium can be used or palladium-nickel or palladium-silver could be used for stronger adhesion. Another possibility could be we can use uncoated Silicon Micro Cantilever, USCM. So, uncoated silicon micro cantilever can be used and, but the it will detect only one type of gas. And, the limit of detection for such cantilevers is restricted to 0.02 percent. So, the sensitivity is higher.

Now, in these uncoated silicon micro cantilevers, the principle of operation is that they are based on change in the resonance frequency which is measured in the silicon micro cantilevers. Now, as the hydrogen gas concentration increases, we know that the fluid mass density will also increase.

And, correspondingly there will be an increased equivalent mass of the cantilever and that will decrease the resonance frequency. Now, this decrease in the resonance frequency can be calibrated with the hydrogen gas concentration and that can be used for sensing hydrogen.

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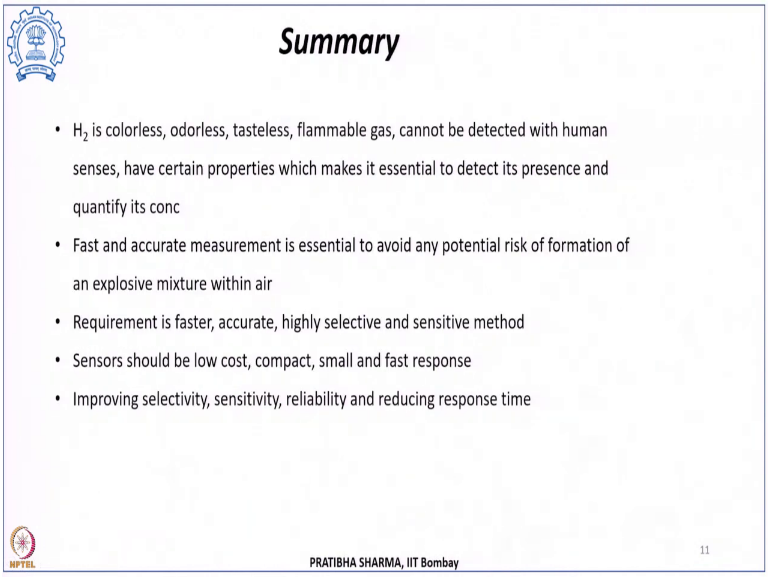

Now, to summarize this portion, we know that hydrogen is a colorless, odorless, tasteless, flammable gas and it is not possible to detect it by human senses. It also has certain properties like wide flammability limit, low ignition energy, certain auto ignition temperature. All that we have seen in the very first lecture and that makes it very much essential to detect its presence in to quantify its concentration; so, as to avoid any hazardous situation.

Now, it is required that a very fast and accurate method of such measurement should be there to avoid any potential risk of formation of an explosive mixture in the air. So, the required property for a sensor is they should sense fast, they should sense accurately, they should be highly selective and sensitive and there should not be any false signals from the other gases.

These sensors require to be low cost, compact, small and they should have a faster response. So, the research is dedicated towards improving their selectivity, sensitivity, reliability and reducing response times. The other type of sensors, we will see in the next class.

Thank you.