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A SURVEY AND ANALYAIS OF EXPERIMENTAL HYDROGEN SENSORS

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SUMMARY

In order to ascertain the applicability of hydrogen sensors to aerospace applications, a survey has been conducted of promising experimental point-contact hydrogen sensors and their operation has been analyzed. The techniques discussed are metal-oxide-semiconductor or MOS based sensors, catalytic resistor sensors, acoustic wave detectors, and pyroelectric detectors. All of these sensors depend on the interaction of hydrogen with Pd or a Pd-alloy. It is concluded that no single technique will meet the needs of aerospace applications but a combination of approaches is necessary. The most promising combination is an MOS based sensor with a catalytic resistor.

INTRODUCTION

The applicability of hydrogen leak detectors in aerospace applications, especially those involving hydrogen fuel propulsion systems, depends strongly on the operating parameters under which the sensor must function. Parameters such as sensitivity, ambient atmosphere, temperature, response time, and size, weight, and power restrictions vary considerably from application to application. In order to understand whether a given leak detection technique is applicable for a specific aerospace application, the detection mechanism of the sensor must be understood.

Previously, the behavior of commercially available point-contact hydrogen sensors has been discussed in operating conditions representative of aerospace applications (ref. 1). Four major categories were analyzed: catalytic combustion, electrochemical, semiconducting oxide sensors, and thermal conductivity detectors. Each sensor was found to be operational in a given range of applications; no sensor was found to be operational in a helium ambient environment at liquid hydrogen temperatures. This work concluded that in order to meet the needs of aerospace applications the development of point-contact hydrogen sensors beyond those commercially available is necessary.

The development of point-contact sensors has been a very active area of experimental research with a number of techniques being explored. A number of extensive reviews on hydrogen or gas sensing technology have been published which give an overview of this rapidly developing field as well as the detailed mechanism behind each type of sensor (refs. 2 to 8). Some of the more promising techniques include those based on metal-oxide-semiconductor or MOS structures, catalytic resistors, acoustic wave detectors, and pyroelectric detectors. These techniques are based on the reaction of palladium or its alloys with hydrogen. It is conceivable that one of these techniques or a combination of these techniques might meet all the needs of aerospace applications.

The purpose of this paper is to examine the mechanism of operation and range of applicability of experimental point-contact hydrogen sensors for use in aerospace applications. The question that is addressed is whether these detection techniques will be able to meet the needs of aerospace applications. First, a general overview of the most promising hydrogen detection systems is given with discussion of the mechanism of detection and sensor characteristics. For a more detailed discussion of each sensor type, an interested reader is referred to the references. The sensors reviewed are the MOS based systems, catalytic resistor sensors, acoustic wave detectors, and pyroelectric detectors. Next, an analysis is presented of the possible use of each sensor technique to the broad range of aerospace applications noted above and discussed in reference 1.

The major factor determining the applicability of each sensor to aerospace applications is the hydrogen-catalyst reaction and its effect on the sensing mechanism. The hydrogen-catalyst reaction rate depends on the environment, especially the ambient oxygen concentration and temperature. Determination of the oxygen concentration and temperature control is necessary to apply these techniques.

Each sensor type produces a signal from this reaction. MOS devices and catalytic resistors respond to a change in the Pd or Pd-alloy electronic properties upon the absorption of hydrogen while acoustic wave detectors respond to the change in the resonant frequency of an acoustic wave device. Pyroelectric detectors convert the energy associated with the hydrogen-catalyst reaction into an electric signal. However, the theory behind the operation of gas sensitive photopyroelectric detectors is still controversial.

Future development of these sensors for hydrogen detection in aerospace applications will likely involve changes in the catalyst and sensor structure as well as multiple sensors or sensor types in arrays with temperature measurement or control at each sensor.

It is concluded that, although these experimental sensors provide an expanded range of capabilities over those of commercial sensors, no single sensor type meets the needs of all aerospace applications. However, with continued development, a combination of techniques may meet these needs. I feel that the combination of MOS type sensors and catalytic resistors is the most promising combination.

SENSOR TYPES, OPERATION, AND CHARACTERISTICS

MOS Type Sensors

The operating mechanism of this type of sensor is based upon the interaction of hydrogen with a metal-insulator-semiconductor or MIS structure (ref. 3). MIS structures are composed of a thin layer of metal separated by an insulating layer from a semiconductor. The insulator is often an oxide leading to a metal-oxide-semiconductor or MOS structure. It is these MOS structures that we will discuss in this report.

The behavior of traditional MOS devices with respect to their current-voltage (I-V) and capacitance-voltage (C-V) characteristics is extensively discussed in the literature (refs. 9 and 10). A basic knowledge of the operation of these structures is assumed in the following discussion. A crucial property of MOS structures in most applications is their inertness to the surrounding environment. However, the use of MOS structures in gas sensing applications depends on the reaction of the structure with the gas to be sensed.

In gas sensing applications, each layer in the MOS structure performs a different function (ref. 3), as seen in figure 1. The metal layer reacts with the gas to be sensed in several possible ways. The results of these reactions include the modification of the metal layer work function and the introduction of a layer of field producing dipoles at the metal-insulator interface.

The thickness of the oxide layer determines whether current can tunnel through the oxide and thus whether the device can be used as a diode or a capacitor. An oxide thickness on the order of 50 Å allows tunneling. The role of the oxide layer in diodes may be to block chemical reactions between the conducting region and the semiconductor or affect the role of the metal/semiconductor regions in establishing a depletion layer in the semiconductor. The depletion layer is a region in the semiconductor in which the mobile charge carrier density is severely depleted. This affects the electronic characteristics of the MOS circuit. In capacitors, the oxide must block hole and electron transport between the metal and semiconductor regions.

The depletion layer of the semiconductor is sensitive to changes in the metal-oxide interface region. Changes in the depletion layer affect the I-V or C-V curves and can be correlated to the amount of reactive chemical species, e.g., hydrogen, present in the atmosphere. Thus, the MOS structure responds to changes in the gas composition. These structures may be used to measure hydrogen by themselves or as a part of a transistor.

The most common materials used in MOS devices for hydrogen detection are as follows. Pd or Pd-alloys are used as the metal due to the ability of Pd to catalytically disassociate and absorb hydrogen (ref. 11). The dominant insulator and semiconductor are SiO_2 and Si, respectively, due to their electrical and chemical properties as well as the vast amount of experience in processing these materials. A number of other materials and structures, including insulators that are not oxides, have been explored to improve the properties of these structures as hydrogen detectors: see, e.g., references 12 to 14.

The characteristics of hydrogen sensitive Pd-MOS devices, especially capacitors, have been discussed by Lundström (refs. 5 to 7). These devices can be sensitive to hydrogen concentration on the order of parts per million (ppm). Saturation of the signal is associated with the formation of a monolayer of hydrogen atoms at the metal-insulator interface. This limits use of this device, depending on the ambient, to hydrogen concentrations considerably less than 1 percent.

Since the working mechanism of the device is based on catalytic reactions on the surface, the surface state of the Pd is crucial. The response time of the sensor, on the order of a second depending on the Pd temperature, is dependent on the Pd surface state and can be affected by ambient conditions and catalytic poisons. For example, response rates have decreased by six orders of magnitude as a sputter cleaned sample is taken from a controlled environment into air (ref. 15). Structures kept in air for extended periods without exposure to hydrogen initially have a slow response to hydrogen due to the surface state of the Pd. Increasing the temperature decreases the response time by removing surface contaminants and poisons as well as increasing reaction rates. The discharge of hydrogen from the surface generally has a different time constant than absorption even at high temperatures of operation.

The presence of other gas molecules, which may take up sites on the Pd surface or react with hydrogen on the surface, affect the number of sites available to hydrogen and the sensor response. The most important of these gases is oxygen. Oxygen is adsorbed on the Pd surface and then combines with hydrogen to form water which may stay on the surface or evaporate off. In either case, this effect decreases the amount of hydrogen ions available to migrate to the SiO_2 interface for a given hydrogen partial pressure. Thus, the sensitivity of the device is different in an inert atmosphere than in an oxygen containing atmosphere. Further, recovery times are dramatically affected by the presence of oxygen in the ambient and its ability to draw hydrogen from the metal.

The disassociation and adsorption of hydrogen on the Pd surface as well as its possible recombination into water and removal from the surface is temperature dependent. Thus, these systems are often operated at temperatures above 50 to 150 °C to improve the speed of response as well as remove water molecules, contaminants, and poisons from condensing on the surface.

One of the most serious problems with this sensor type is long term instability, specifically that caused by hydrogen induced drift or HID. As a function of time, hydrogen may migrate into the oxide changing the response of the MOS structure. The time constants associated with the HID vary resulting in long term drift and slow recovery times. Thus, comparing the response of the sensor at a given time and hydrogen concentration to the baseline response becomes problematic (ref. 16). Changes in the composition of the oxide layer significantly affects HID (refs. 14 and 16).

A second concern with these sensors involves the phase change that occurs in Pd at higher hydrogen concentrations. The phase change from α phase to β phase is temperature dependent and occurs as hydrogen is absorbed into the Pd lattice (ref. 11). This phase change causes stress between the Pd and the other layers and may lead to spallation or bubbling in the Pd film (refs. 17 and 18). Alloys of Pd which have a phase transition at a higher hydrogen concentration or are more ductile may be used to address this problem. (See catalytic resistor section below.)

There are several major advantages to these types of sensors. They are highly sensitive to hydrogen. The same technology used in the semiconductor industry can be used to keep sensor size small allowing several sensors to be placed on one chip. This may allow an oxygen sensor or other hydrogen sensors of differing selectivities to be placed on the same chip. Heating the sensors is simplified since a heater and temperature sensor may be incorporated into the chip. The region to be heated may be made small which means the amount of heat necessary to heat the sensor may be kept relatively low.

Disadvantages include hydrogen induced drift which affects the long term stability of the sensor. Interfering gases, such as oxygen, affect the signal produced by the sensor. These sensors saturate with possible film damage at higher hydrogen concentrations limiting the application range of this sensor.

Catalytic Resistor Sensors

The operating mechanism of sensors of this type depends on the migration of hydrogen into the bulk of Pd or Pd-based alloys. Hydrogen in the bulk metal (shown in fig. 1 for a MOS device) acts as scattering sites and changes the electrical resistance of the material.

The magnitude of the resistance change depends on the hydrogen concentration in the bulk of the alloy. For low concentrations, the bulk hydrogen concentration, n, is given by Sieverts Law: $n \propto (P_{H2})^{1/2}$ where P_{H2} is the partial pressure of hydrogen. The proportionality constant depends on the alloy. The magnitude of the resistance change, ΔR, is approximately a linear function of n or $(P_{H2})^{1/2}$ but also depends on the ambient gas, especially the oxygen concentration (refs. 6, 19, and 20). Larger hydrogen concentrations induce the α phase to β phase transition leading to irreversible hysteresis and possible film damage (refs. 11, 17, and 18). This limits the use of Pd as a sensor material for higher hydrogen concentration applications.

The hydrogen concentration that induces the phase change depends on several factors. These include the temperature (ref. 11), film thickness for thin film resistors (ref. 21), and, most importantly, the alloy composition. Specifically, in Pd-Ni and Pd-Ag alloys, the α phase to β phase transition occurs at a higher hydrogen concentration than in pure Pd (refs. 18 and 20). For example, the α phase to β phase transition occurs at $P_{H2} = 7$ Torr for Pd and $P_{H2} = 2000$ Torr for $Pd_{15\%}Ni$ (ref. 20) near room temperature. Further, these alloys are more ductile than pure Pd which allows them to better withstand the stresses involved in the absorption and desorption of hydrogen. These alloys have greatly expanded the application range of this sensor type.

The response time depends on the amount of time for the bulk state to reach equilibrium with the surface states and for the surface states to reach equilibrium with the hydrogen in the atmosphere. The bulk states reach equilibrium with the surface states in less than 1 sec (ref. 15). Usually, the rate limiting step in the response time of these sensors is the hydrogen sorption on to the surface of the sensor. This is dependent on the metal surface state, temperature, and P_{H_2}. (See MOS type sensors discussion above.) The response time of this type of sensor can be on the order of a second.

The use of Pd-alloy resistors as hydrogen sensors usually involves a hydrogen sensitive resistor and a reference resistor. The reference resistor is often the same alloy as the hydrogen sensitive resistor but desensitized to hydrogen with a coating such as SiO_2. The output of the sensor is the difference in resistance between the sensing resistor and the reference resistor (refs. 19, 22, and 23).

Major advantages of the catalytic resistor hydrogen sensors, specifically Pd-Ni based resistors, is their ability to be microfabricated and, unlike the Pd-MOS based sensors, be able to respond to higher concentrations of hydrogen without saturation or hydrogen induced drift. Disadvantages include an insensitivity to low concentrations of hydrogen and drastic reductions in response time for contaminated surfaces. The production of a stable reference resistor to act as a temperature compensator is also necessary with this sensor type.

Acoustic Wave Detectors: SAW and Bulk

Acoustic wave detectors are based upon the ability of piezoelectric crystals to generate acoustic waves when coupled with radio frequency (rf) voltages. Surface Acoustic Wave (SAW) detectors make use of acoustic waves, usually Rayleigh waves, propagating on the surface of a piezoelectric material such as quartz or lithium niobate (refs. 2, 4, and 24 to 27). The waves are generated by rf voltages applied by metal interdigital transducer electrodes deposited on the piezoelectric material. The depth of these waves is localized to within a couple of wavelengths of the surface. Figure 2 shows one configuration with two SAW transducers. The frequency of the wave, which is in the MHz range, is dependent on the mechanical stress and electric fields present on the piezoelectric surface. It is also affected by an adsorbed film on the surface and changes in the mass of the film.

Gas detection using SAW resonators is depicted in figure 2. A SAW propagates along two paths and the resonant frequency to drive the SAW is measured for each path. One path is covered with a chemically selective film which selectively absorbs the gas to be sensed. The chemically selective film may be either a sputtered alloy or a chemically sensitive membrane. The second path is untreated or has a reference film. As gas flows over the surface of the SAW device, the selective film reacts with the gas to be sensed. The elastic properties and weight of the selective film change leading to a change in resonant frequency of the SAW. The resonant frequency change can be correlated to the amount of gas to be sensed in the ambient. A SAW gas detector can also be configured to measure the amplitude or phase shift of the wave. The results of all three of these methods are interrelated.

SAW detectors have been fabricated to detect a number of gases. The most important component of any SAW gas detector is the chemically selective film. The selective film used for hydrogen detection has been Pd (refs. 28 to 31). The results of this work suggest that SAW detectors are very sensitive, with achieved detection limits on the order of ppm and potential detection limits on the order of ppb. At room temperature, the response time depends on the gas concentration and for hydrogen, has been relatively slow: on the order of minutes. No information is available on the existence of a saturation hydrogen concentration.

Propagation of bulk acoustic waves in a piezoelectric quartz crystal microbalance is the basis of a second technique. A quartz crystal microbalance is a quartz crystal coated with a chemically selective absorbing film. The resonant frequency of the crystal depends on the mass of the quartz-film combination. In hydrogen sensing applications, Pd is often used as the absorbing material. As the hydrogen is absorbed by Pd, it changes the mass of the system which changes the resonant frequency. This change in frequency can be correlated to the hydrogen concentration.

Quartz crystal microbalances have been used in a number of applications to detect hydrogen and even characterize the phase transitions of Pd itself (refs. 2, 8, 32 to 35, and references therein). The response time is on the order of minutes with a sensitivity limit of a Pd-based sensor in flowing nitrogen on the order of 0.5 percent (ref. 35). Hydrogen concentrations of 100 percent have been observed with this technique.

The major advantage of the SAW sensors is their sensitivity. They probe the near-surface of the piezoelectric-chemically selective films combination at a high frequency leading to an extremely sensitive sensor provided the proper selective film is used. The crystal microbalance sensors, on the other hand, operate over a wide concentration range. Disadvantages of both of these sensors include their long response times, interference from other gases which may react with the Pd, and misleading signals if condensation occurs on the Pd surface. Temperature control will also be necessary to avoid stresses due to temperature gradients causing spurious signals. Microfabrication will be more difficult with these sensors than either the MOS or catalytic resistor sensors.

Pyroelectric Detectors

Pyroelectric materials generate a potential when there is a thermal gradient across their surface. Figure 1 schematically depicts how this property is used in a gas sensor. A pyroelectric substrate, $LiTaO_3$ in figure 3, is coated with metals on both sides. The side that faces the gas has two separate coatings: a hydrogen sensitive material, specifically Pd, in one area and a reference material, for example Au, on the other. On the opposite side, heat is generated forming a thermal gradient across the pyroelectric material. The voltage between the heated side and the Pd area, V_{Pd}, is monitored. The voltage between the heated side and the reference area, V_{ref}, is also monitored and the difference in voltages $V_{difference} = V_{Pd} - V_{ref}$ is the basis for the output of the sensor. When hydrogen reacts with the Pd coating, $V_{difference} = V_{Pd} - V_{ref}$ changes and this change can be correlated to the hydrogen concentration.

The heat generation has been accomplished with a dc resistive heater such as a NiCr film (refs. 8 and 35 to 38), and infrared absorption (refs. 2, and 39 to 41). The dc technique relies on the enthalpy of the reaction of hydrogen with Pd. The dc technique as presently configured is extremely sensitive. A number of environmental factors beside H_2 - Pd interactions can cause spurious signals and make it difficult to use except in very controlled conditions. Thus, this technique will not be discussed further here since this paper deals with a broad range of applications which are generally not highly controlled. An interested reader is referred to the references.

A second method of heat generation is infrared absorption of laser light. The light is produced by a laser diode and delivered to the heated side by means of fiber optic connections. The beam intensity is modulated to give rise to fluctuating heat generation and thus ac voltages across the piezoelectric material. The ac voltages are monitored by a lock-in amplifier synchronized by a photodiode monitoring the laser fluctuations. The signal monitored, V_{signal}, is the difference in voltages, $V_{difference}$, normalized with respect to the output of the photodiode. The result of the ac nature of the signal is that the sensitivity of this photopyroelectric technique does not depend on the heat of adsorption on the Pd surface. However, the exact mechanism by which the hydrogen changes V_{signal} is controversial and still being discussed. In fact, it has been shown that a pyroelectric material is not necessary for this technique to work (ref. 42).

Experimental results at room temperature suggest that this method has a lower limit of sensitivity of 40 ppm H_2 in N_2 with an ability to reproducibly respond to 100 percent hydrogen. The response time is flow rate dependent and on the order of minutes.

Advantages of this technique include its wide range of sensitivity with an ability to respond to 100 percent H_2. Disadvantages include its complexity, slow response time, and limited response to changes in hydrogen concentration in the concentration range from 10 to 50 percent. The future range of applications will, in part, depend on exactly what mechanism drives the sensor.

DISCUSSION

Each technique discussed in the previous section is currently being developed. The present stage of development does not necessarily determine the potential of these sensors for aerospace applications. The discussion that follows parallels that of reference 1 and will examine the applicability of each sensor type to aerospace applications given the physical principles and present trends of development of the sensor. Specifically, the discussion will address the range of aerospace applications for which each sensor will be applicable.

As discussed in the introduction and reference 1, the operating conditions present in aerospace applications span a wide range of parameters. Some general parameters relating to the gas environment and the sensors response can be identified.

The set of parameters related to the gas environment of the sensor are hydrogen concentration, ambient atmosphere surrounding the sensor, and temperature of the gas impinging on the sensor. The hydrogen concentration may vary from trace amounts of gas to 100 percent hydrogen. The ambient atmosphere surrounding the sensor may be air, nitrogen or helium purges, a vacuum, or mixtures of the above gases present from vacuum to at least atmospheric pressure. The temperature of the gas, which may be time dependent, can range from liquid hydrogen temperatures to room temperature and above.

The set of parameters related to the response of the sensor are its ability to detect hydrogen in a given environment and concentration level, the response time of the sensor, as well as the power requirement, weight, size, and complexity of the sensor. Of these, the most important attributes of any sensor are the first two: its ability to operate in a particular environment and give a meaningful signal in a period of time useful to the user.

The discussion will center on whether the sensor is operational in an appropriate amount of time to detect changes in hydrogen concentration in the broad range of gas conditions outlined above.

General Considerations

The mechanism of operation of all these sensors is based on the disassociation and/or absorption of hydrogen upon contact with Pd or a Pd-alloy. This mechanism does not need oxygen for its operation although recovery time is significantly decreased in the presence of oxygen. Therefore, operation in air, nitrogen, helium, or a vacuum is feasible. This is a significant improvement over commercial sensors which needed oxygen or were inoperable in a helium or vacuum ambient. However, the presence of oxygen does affect the Pd-H_2 reaction. In order to interpret the data, the oxygen concentration must be known or otherwise accounted for.

The sensor temperature is important since a catalytic reaction is responsible for the detection of hydrogen. The sensor temperature must be stable and at room temperature or above. Thus, in cryogenic applications, heating of the sensor is necessary.

MOS Type Sensors and Catalytic Resistor Sensors

These sensor types both rely on the change in electronic properties of Pd or a Pd-alloy upon the absorption of hydrogen. The hydrogen concentration at the Pd-insulator interface region produces the signal for the MOS type of sensor where the bulk hydrogen concentration is important for the catalytic resistor sensor. Both responses have been measured simultaneously for one sensor (ref. 15).

These sensors are complementary in their range of sensitivity given the proper alloy composition (refs. 5 to 7, 20, and 43). Generally, MOS sensors will be useful for hydrogen concentrations below 1 percent while catalytic resistor sensors will be useful for concentrations greater than 1 percent. Response times on the order of 1 sec are achievable given the proper sensor temperature. Each sensor individually would not have the sensitivity to meet all the needs of aerospace applications, but combined they do span the necessary range of hydrogen concentrations.

Both types of sensors may be microfabricated. This means that heating of these sensors for low temperature operation may be accomplished without heating a large area. This limits the amount of power necessary for overall operation of these sensors. Microfabrication is also an advantage in applications where weight and size of the sensor is a concern.

The actual use of these sensors in aerospace applications lies in the combined use of MOS and catalytic resistors (ref. 43) along with continued alloy development, elimination of such problems as hydrogen induced drift, and compensation for the presence of oxygen and other interfering gases. This compensation might be accomplished by the combination of several sensors of differing alloys and sensitivities to hydrogen and oxygen (ref. 43).

Acoustic Wave Detectors: SAW and Bulk

These sensors are different from the MOS or catalytic resistor sensors in that the area of the sensor which may influence the sensor response is much greater. For SAW sensors, both SAW propagation paths affect the sensor response while for the quartz crystal microbalance the response is effected by the whole crystal.

The use of these sensors in cryogenic applications implies that the sensor needs to be not only heated to room temperature but uniformly over an expanded area. Shielding must also be provided to the surface of the sensor to eliminate condensation since these sensors are also sensitive to any deposition which affects the mass of the sensor. In contrast, for a given ambient, the major effect of condensation for a given ambient for MOS sensors or catalytic resistor sensors is a decrease in the response time.

These factors increase the complexity of the sensor, the amount of power to drive it, as well the size and weight of the sensor depending on how the heating and shielding is accomplished. A second complexity related to the power needed to operate the sensor is that the power supplied to drive the sensor is high frequency rf voltages. This may complicate the sensor with the necessity for shielding of wires and monitoring for interferences.

The minimum hydrogen sensitivity for the SAW is nearly 88 times lower than that of the quartz crystal microbalance (ref. 2). The SAW hydrogen saturation concentration has not been discussed in the literature for SAW hydrogen sensors while concentrations up to 100 percent have been monitored with a quartz crystal microbalance. However, the response times, on the order of minutes, would limit the use of these sensors in aerospace applications where more rapid response is normally necessary.

Pyroelectric Detectors

This technique is still in its development stage. The photopyroelectric technique has many favorable qualities: it responds, although with a slow response, to a wide range of hydrogen concentrations. Heating, already part of the system as it is presently configured, would have to be uniform throughout the sensor. A drawback is that both fiber optic and electrical lines would be needed to drive the sensor. However, the major drawback of the system as it is presently configured is that the mechanism of operation, and thus possible sensor limitations, is poorly characterized. This approach may be of great interest in the future.

CONCLUSION

Several of the most promising experimental hydrogen sensing techniques have been examined for possible use in aerospace applications. All examined sensors are based on the interaction of hydrogen with Pd or a Pd-alloy. Each sensor has its own range of application: it will take a combination of sensors to meet all the needs of aerospace applications.

MOS and catalytic resistor sensors have a combined range from ppm to 100 percent hydrogen. They can be microfabricated with a temperature controller built into the chip. Future use of these sensors depends on improved stability of the sensors, continued alloy development, and compensation for the effects of oxygen and interfering gases.

Acoustic wave detectors as a group are capable of high sensitivity and able to detect hydrogen over a wide range. However, these detectors respond to any mass on the surface of the sensor and need to be thermally stabilized over a larger area than MOS or catalytic resistor sensors. Although photopyroelectric sensors offer a number of positive features, they are still in their early development stage and have a very complex structure.

Therefore, a single sensor type that meets all the needs of aerospace applications does not presently exist. Rather, a combination of techniques is necessary. The most promising and versatile combination is the MOS and catalytic resistor.

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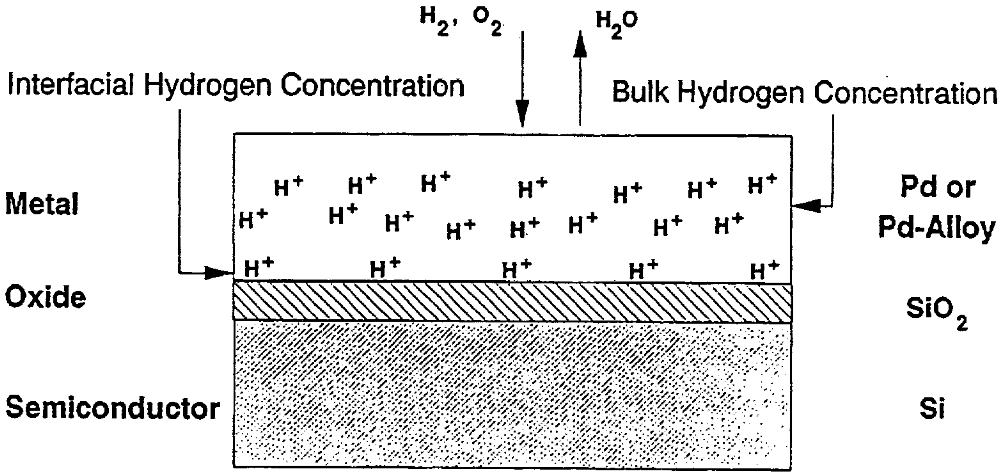

Figure 1.—The structure of a MOS device used for detection of hydrogen. Shown is each layer of the structure with the common material used for each layer. Hydrogne disassociates on the surface and dissolves into the interior of the metal. There is a equilibrium between the surface hydrogen cocentration, bulk hydrogen concentration, and interfacial concentration. The presence of oxygen affects these concentration by occupying sites and removing hydrogen in the form of H_2O.

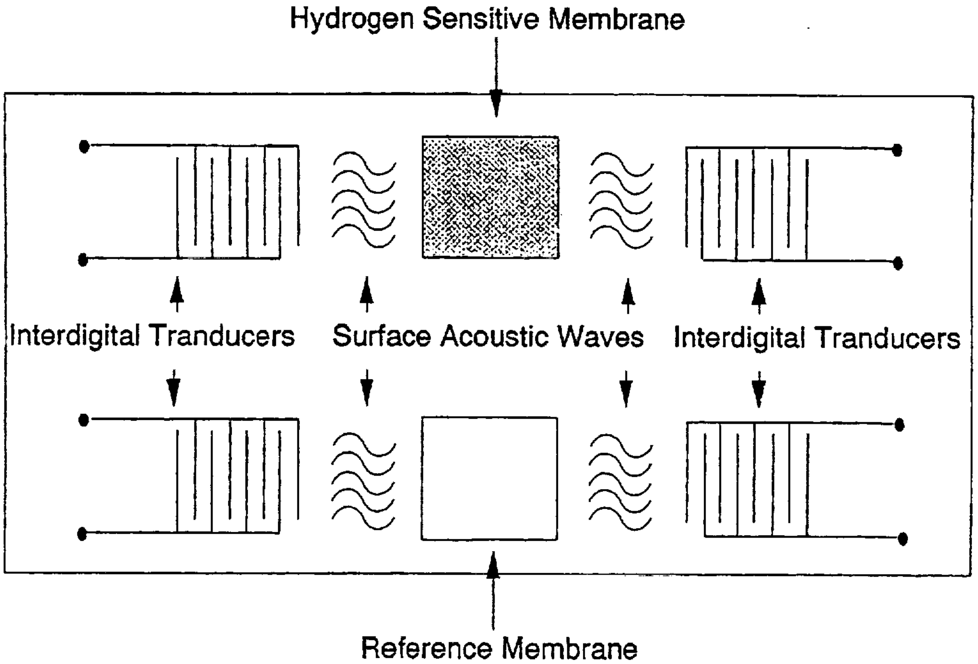

Figure 2.—The physical mechanism behind hydrogen detection in SAW devices. Surface acoustic wave are produced by inter-digital transducers and travel across the crystal to a second set of transducers. One wave interacts with a hydrogen sensitive membrane while the second interacts with a reference membrane. As hydrogen is absorbed on the hydrogen sensitive membrane, the difference signal frequency between the two waves changes depending on the amount of hydrogen absorbed.

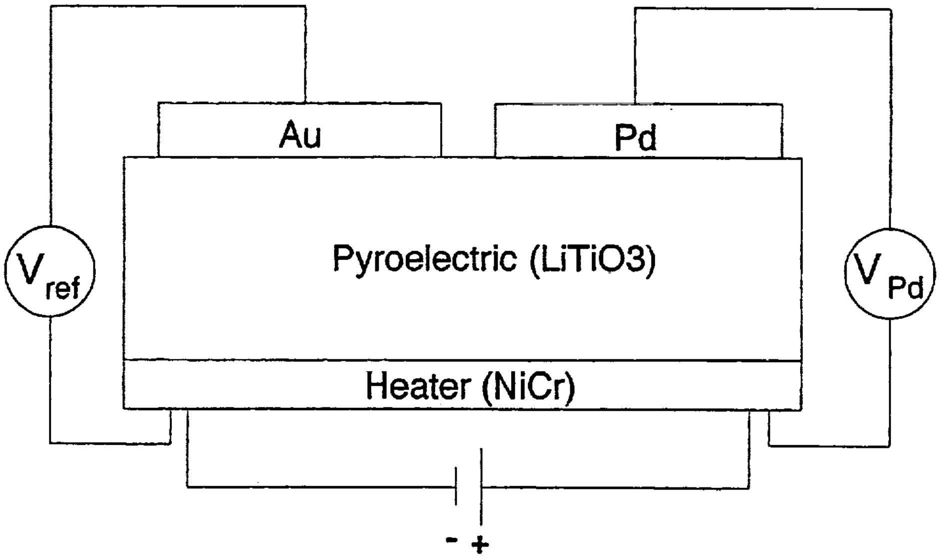

Figure 3.—Schematic of the general structure of a pyroelectric detector. Heat is generated by a NiCr heater forming a thermal gradient across a pyroelectric which generates a voltage. The difference in voltage between the Pd contact and the Au contact can be correlated to the hydrogen concentration.

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13. ABSTRACT ***(Maximum 200 words)***

In order to ascertain the applicability of hydrogen sensors to aerospace applications, a survey has been conducted of promising experimental point-contact hydrogen sensors and their operation has been analyzed. The techniques discussed are metal-oxide-semiconductor or MOS based sensors, catalytic resistor sensors, acoustic wave detectors, and pyroelectric detectors. All of these sensors depend on the interaction of hydrogen with Pd or a Pd-alloy. It is concluded that no single technique will meet the needs of aerospace applications but a combination of approaches is necessary. The most promising combination is an MOS based sensor with a catalytic resistor.

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