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ABSTRACT

Aeronautic and space applications require the development of chemical sensors with capabilities beyond those of commercially available sensors. Two areas of particular interest are safety monitoring and emission-monitoring. In safety monitoring, detection of low concentrations of hydrogen at potentially low temperatures is important while for emission monitoring the detection of nitrogen oxides, hydrogen, hydrocarbons and oxygen is of interest. This paper discusses the needs of aeronautic and space applications and the point-contact sensor technology being developed to address these needs. The development of these sensors is based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors. 2) The development of high temperature semiconductors, especially silicon carbide. The detection of each type of gas involves its own challenges in the fields of materials science and fabrication technology. The number of dual-use commercial applications of this microfabricated gas sensor technology make this general area of sensor development a field of significant interest.

INTRODUCTION

Aeronautic and space applications require the development of chemical sensors which operate in a number of environments. Two areas of particular interest are safety monitoring and emission monitoring. Each area of application has vastly different problems associated with the measurement of chemical species. However, the development of a common base technology can address the measurement needs in each area of applications.

In safety monitoring applications, detection of low concentrations of hydrogen at potentially low temperatures is important for applications involved with, for example, operation of the Space Shuttle. In 1990, the leaks on the Space Shuttle while on the launch pad temporarily grounded the fleet until the leak source could be identified. The method of leak detection used was a mass spectrometer connected to an array of sampling tubes placed throughout the region of interest. Although able to detect hydrogen in a variety of ambient environments, the mass spectrometer had a delay time associated with its detection of a leak and pinpointing the exact location of the leak was problematic.

In response to the hydrogen leak problems, NASA-endeavored to improve propellant leak detection capabilities during assembly, pre-launch operations, and flight. The objective has been to reduce the operational cost of assembling and maintaining hydrogen delivery systems with automated detection systems. In particular, efforts were made to develop an automated hydrogen leak detection system using point-contact hydrogen sensors. However, no commercial sensors existed that operated satisfactorily in this application. The reason for this is the conditions in which the sensor must operate.

The hydrogen sensor must be able to detect hydrogen from low concentrations through the lower explosive limit (LEL) which is 4% in air. The sensor must be able to survive exposure to 100% hydrogen without damage or change in calibration. Further, the sensor may be exposed to gases emerging from cryogenic sources. Thus, sensor temperature control is necessary. Operation in inert environments is necessary since the sensor may have to operate in areas purged with helium. Being able to multiplex the signal from a number of sensors so as to "visualize" the magnitude and location of the hydrogen leak is also desired. If a number of sensors are to be placed in an area, then size, weight, and power consumption for each sensor becomes an issue. Commercially available sensors, which often needed oxygen to operate or depended upon moisture (1), did not meet the needs of this application and thus the development of new types of sensors was necessary (2).

The development of a new class of sensors is also necessary for the monitoring of emissions from aircraft engines. The control of emissions from aircraft engines is an important component of the development of the

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next generation of these engines. The ability to monitor the type and quantity of emissions being generated by an engine is important in not only controlling those emissions but also in determining the status of the engine. Ideally, an array of sensors placed in the emissions stream close to the engine could provide information on the gases being emitted by the engine. However, there are very few sensors available commercially which are able to measure the components of the emissions of an engine in-situ. The harsh conditions and high temperatures inherent near the reaction chamber of the engine render most sensors inoperable.

A notable exception to this limitation in sensor technology is the commercially available oxygen sensor presently in use in automobile engines (3). This sensor, which is based on the changes in the properties of zirconium dioxide (ZrO_2) upon reaction with oxygen, has been instrumental in decreasing automotive engine emissions. However, comparable sensors for other components of the gas stream do not exist: monitoring of emissions of nitrogen oxides (NO_x), hydrogen, and hydrocarbons, is not presently possible in-situ with point-contact sensors placed near the engine. Even the traditional ZrO_2 based sensor has sensitivity limits as well as size, weight, and power consumption requirements which prevent its use in some applications.

In emission monitoring applications, the sensor must operate at high temperatures with exposure to low concentrations of the gases to be measured. Although the measurement of nitrogen oxides (NO_x) is important in these applications, the measurement of other gases present in the emission stream such as hydrogen, hydrocarbons and oxygen is also of interest. The measurement range depends on the gas and the engine but generally the detection of NO_x, hydrogen, and hydrocarbons may be necessary at sensitivities of less than 200 ppm with corresponding measurements of oxygen from less than 1% to near 20%. The sensors should be small so as not to interfere with the flow of gases in the engine or become significant projectiles if dislodged from their measuring site and emitted into the engine.

In order to meet the needs of these applications, a new generation of sensor technology must be developed. This paper discusses point-contact sensor technology being developed to address these needs. The development of these sensors is based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors. 2) The development of high temperature semiconductors, especially silicon carbide, to provide electrical components and sensors operable at the temperatures of interest. Using these technologies, point-contact sensors are being developed to measure hydrogen, hydrocarbons, NO_x, and oxygen. The detection of each type of gas involves its own challenges in the fields of materials science and fabrication technology.

This paper presents an overview of microfabricated chemical sensor technology and high temperature electronics. These technologies are used, where appropriate, to develop hydrogen, hydrocarbon, NO_x and oxygen sensors. A description is given of each sensor type and its present stage of development. The silicon (Si) based hydrogen sensor is at a relatively mature stage of development while the state of development of the other sensors ranges from the proof of concept level to prototype stage. The number of dual-use commercial applications make this general area of sensor development a field of significant interest.

MICROFABRICATION AND MICROMACHINING TECHNOLOGY

A significant number of silicon-based microfabrication processes have been derived from the advancements in the integrated circuit (IC) industry. Of the various processing techniques, lithographic reduction, thin film metallization, photoresist patterning, and chemical etching have found extensive chemical and biological applications, particularly in sensor-related development. These processes allow the fabrication of very small sensor structures. The ability to batch process these sensors using presently available semiconductor processing techniques significantly decreases the fabrication costs per sensor. However, these processes produce mainly two-dimensional planar structures, which have limited application. By combining these processes with micromachining technology, three-dimensional structures can be formed which have a wider range of application to chemical sensing technology.

Micromachining technology is generally defined as the means to produce three-dimensional structures using both bulk and surface micromachining techniques. The techniques used in micromachining fabrication include chemical anisotropic and dry etching, the sacrificial layer method, and LIGA (lithographic, galvanoforming, absorbing).

Chemical anisotropic etching is an etching procedure that depends on the crystalline orientation of the substrate. For silicon etching, potassium hydroxide (KOH) and tetramethyl ammonium hydroxide (TMAH) solutions are most commonly used as etching agents. Dry etching processes include ion milling, plasma etching, reactive ion etching, and reactive ion beam etching. These dry etching processes are not dictated or limited by the crystalline structure. However, although not many chemicals are required, the equipment cost of any of these dry etching processes is relatively high.

The sacrificial layer method employs a deposited underlayer that can be chemically removed. The sacrificial layer method has been used to create cantilever type structures for physical sensor and actuator applications. This technique can be used to make a chamber electrode structure to protect the integrity of the sensor element. LIGA techniques have been used to produce high aspect ratio multistructures. These microstructures can be used to define volumes as well as for microanalytical elements such as microcapillary structures.

For many applications, temperature control is necessary. Incorporation of a heating element and a temperature detector allows feedback control of the operating temperature. In these microstructures, a small thermal mass is desirable in order to minimize heat loss and heat energy consumption. This is accomplished by selective removal of the silicon substrate producing a suspension of diaphragm structure.

This processing is done using Si either as a semiconductor that is part of an electrical circuit or as a substrate on which a structure is built. If Si is used as a substrate, the temperature range of the sensor can be rather broad: from cryogenic temperatures to above 600°C. However, if Si is to be used as part of the electrical circuit, the temperature range is limited to below 300°C. Thus, for this and other applications, high temperature electronics must be developed. The most advanced high temperature electronic material is SiC. An overview of SiC-based high temperature electronics is given in the next section.

SiC-BASED HIGH TEMPERATURE ELECTRONICS

Silicon carbide (SiC) based semiconductor electronic devices and circuits are presently being developed for use in high-temperature, high-power, and/or high-radiation conditions under which conventional semiconductors cannot adequately perform. Silicon carbide's ability to function under such extreme conditions is expected to enable significant improvements to a far ranging variety of applications and systems. These range from greatly improved high-voltage switching for energy savings in public electric power distribution and electric vehicles to more powerful microwave electronics for radar and communications to sensors and controls for cleaner-burning more fuel-efficient jet aircraft and automobile engines (4).

Silicon carbide occurs in many different crystal structures (called polytypes) with each crystal structure having its own unique electrical and optical properties. The electrical properties of the more common SiC polytypes are compared to the properties of silicon and GaAs in Table I, which was constructed from data in references 5-12. In many device applications, SiC's exceptionally high breakdown field (> 5 times that of Si), wide band gap energy (> 2 times that of Si), high carrier saturation velocity (> 2 times that of Si), and high thermal conductivity (> 3 times that of Si) could lead to substantial performance gains, in spite of the low carrier mobility disadvantages.

Complex electronics and sensors are increasingly relied on to enhance the capabilities and efficiency of modern jet aircraft. Many of these electronics and sensors monitor and control vital engine components and aerosurfaces that operate at high temperatures. However, since today's silicon-based electronics technology cannot function at high temperatures, these electronics must reside in environmentally controlled areas. This necessitates the use of long wire runs between the sheltered electronics and the hot-area sensors and controls or the fuel-cooling of the electronics and sensors located in high-temperature areas. Both of these low-temperature-electronics approaches suffer from serious drawbacks, as the wire runs add a substantial amount of weight, fuel cooling has harmed aircraft fuel efficiency, and both have negatively impacted aircraft reliability.

	Si	GaAs	6H-SiC	4H-SiC	3C-SiC
Bandgap (eV)	1.1	1.42	3.0	3.2	2.3
Breakdown Field @ 10^{17} cm^{-3} (MV/cm)	0.6	0.6	3.2	3	> 1.5
Electron Mobility @ 10^{16} cm^{-3} (cm^2/ V-s)	1100	6000	370	800	750
Saturated Electron Drift Velocity (cm/s)	10^7	10^7	2×10^7	2×10^7	2.5×10^7
Thermal Conductivity (W/cm-K)	1.5	0.5	4.9	4.9	5.0
Hole Mobility @ 10^{16} cm^{-3} (cm^2/ V-s)	420	320	90	115	40
Commercial Wafers	12"	6"	1.375"	1.375"	None

Table I: Comparison of selected semiconductor room temperature physical properties.

A family of high temperature silicon carbide electronics and sensors that could function in hot areas of the aicraft would alleviate the above-mentioned technical obstacles to enable substantial aircraft performance gains. Uncooled operation of 300 - 600°C SiC electronics and sensors mounted in the aircraft hot areas would save weight and increase reliability by replacing hydraulic controls with "smart" electromechanical controls. SiC-based distributed control electronics would eliminate 90 % of the wiring and connectors needed in conventional sheltered-electronic aircaft control systems. This is extremely crucial given the fact that wiring and connector problems are the most frequent cause of propulsion maintenance action and downtime in commercial aircraft today. The U. S. Air Force has estimated that advanced SiC control

electronics implemented on an F-16 fighter would allow the aircraft to shed as much as 800 pounds of weight, operate with increased capabilities and fuel efficiency, and operate more reliably with less maintenance and downtime (13).

SiC electronics and sensors offer similar improvements to commercial jetliners, where increased fuel efficiency, weight savings, and reduced pollution carry particularly large economic and environmental payoffs over an aircraft's multi-decade operational lifetime. It has been speculated that the economic savings value will be in the millions of dollars per aircraft.

Therefore, silicon carbide electronics and sensors that could function while mounted in hot engine and aerosurface areas of an aircraft would enable substantial weight savings, increased jet engine performance, and increased reliability. Use of SiC electronics and devices in other applications such as in the fields of power distribution, automobiles, and communications and radar could have correspondingly significant effects on the operation of these systems.

SENSOR DEVELOPMENT

The needs of aeronautic and space applications require the development of new sensor technology to operate in environments which conventional sensors are inoperable or do not provide the required measurements. These applications require operation in a variety of conditions: from cryogenic temperature to above 600°C, from inert environments to corrosive engine conditions, and from the detection of one gas over a wide concentration range to the detection of several gases over more narrow concentration ranges. Combined with this is the desire to minimize size, weight, and power consumption as well as decrease the cost of the sensor. In order to meet these needs, a flexible approach is necessary. Microfabrication and micromachining technology as well as the use of SiC semiconductor technology can address many of the needs of aeronautics and space applications.

Microfabrication and micromachining allows the fabrication of a variety of structures. Size, weight, and power consumption are minimized by microfabricating the structure and micromachining allows complex shapes to be incorporated into a small region. A given structure can be tailor-made to measure different gases by changing, for example, the gas sensitive element. Batch processing using Si semiconductor technology can decrease cost per sensor and allow a large number of sensors to be produced in one series of processing. Silicon can be used as substrate or part of the electrical circuit. However, Si is not appropriate for sensor designs in which the substrate is an electrical component of the sensor and the sensor must operate at high temperature. Thus, the use of SiC is necessary in these applications.

The following reviews the application of microfabrication and micromachining technologies as well as SiC technology to develop sensors for the detection of a variety of gases. This work is done at NASA Lewis Research Center (LeRC) and at Case Western Reserve University (CWRU). The sensor design and sensing approach depends strongly on the application.

Si-Based Hydrogen Sensor Technology

One component of the sensor development program at NASA LeRC and CWRU involves the development of palladium (Pd) alloy Schottky diodes on silicon (Si) substrates. These sensors are designed to detect hydrogen in space applications. This type of sensor is based on metal-oxide-semiconductor (MOS) technology such as that used in the semiconductor electronics industry. The gas sensing MOS structures are composed of a hydrogen sensitive metal deposited on an insulator adherent to a semiconductor. This forms a Schottky diode in the case of a very thin layer of insulator. The most common MOS structure used for hydrogen detection is the Pd-SiO_2-Si structure. Hydrogen disassociates on the Pd surface and diffuses to the Pd-SiO_2 interface affecting the electronic properties of the MOS system (14). The use of pure Pd at near room temperatures as the hydrogen sensitive metal is problematic for several reasons. The most serious of these involves a phase change that occurs at high hydrogen concentrations which can lead to hysteresis or film damage.

Schottky diodes using Pd alloys as the hydrogen sensitive metal are presently being fabricated. The first generation of these sensors used PdAg. The use of PdAg in hydrogen sensing applications was pioneered by Hughes (15). Palladium silver has advantages over Pd. Palladium silver is more resistant to damage from exposure to high hydrogen concentration than Pd. Furthermore, the alloy has faster response times than Pd.

The sensor structure is shown in Figure 1. The structure includes a Pd alloy Schottky diode, a temperature detector, and a heater all incorporated in the same chip. The sensor is fabricated using a n-type silicon wafer on which approximately 50 Å of SiO_2 is thermally grown in the sensor region. The heater and temperature detector are platinum covered with SiO_2. Gold leads are applied by thermal compression bonding and the sensor is mounted on a TO5 header or on a ceramic flat package. The surface area of the Schottky diode is 6.1×10^{-3} cm^2 and the sensor dimensions are approximately 2.2 mm on a side. The power input is approximately 400 mW to heat the sensor to 100°C in a room temperature ambient. This power level can be decreased significantly to less

than 100 mW if the Si under the sensor region is micromachined to form a diaphragm.

The response of the Schottky diodes was determined by measuring the diode's reverse current. The sensor temperature was measured from the resistance of the temperature detector in a Wheatstone bridge.

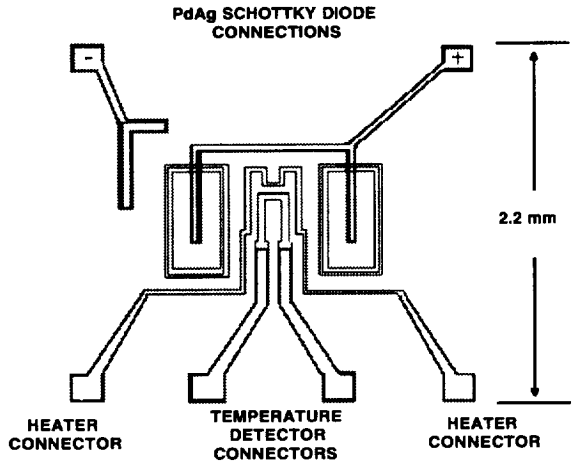

Figure 1. Schematic diagram of the Schottky Diode Hydrogen Sensor. The Pd alloy Schottky diode resides symmetrically on either side of a heater and temperature detector.

The response of the sensor to varying temperatures and hydrogen concentrations in a 90% N_2:10% O_2 carrier gas is shown in Figure 2. The sensor temperatures tested were 45°C, 60°C, 80°C, and 100°C. The sensor was first exposed to the carrier gas for 10 minutes, then, for 10 minutes each to 100 ppm, 500 ppm, 1000 ppm, and 5000 ppm H_2 in the carrier gas. The hydrogen flow was then stopped and the sensor recovered towards the baseline in the carrier gas. Figure 2 shows the sensor response on a linear scale, while the inset shows the first 30 minutes of the same test on a logarithmic scale.

The first sensor characteristic demonstrated by Figure 2 regards the magnitude of the diode's response throughout the temperature and hydrogen concentration range. After a response of nearly an order of magnitude to 100 ppm H_2 (Figure 2 inset), the sensor responds by a factor of nearly 100 to the subsequent factor of 50 change in the hydrogen concentration (Figure 2). Therefore, the sensor reverse current responds to changes in hydrogen concentration throughout the hydrogen concentration range from 100 ppm to 5000 ppm in oxygen containing environments and for sensor temperatures below 100°C.

Second, the magnitude of the response and the time it takes for the sensor to reach a stable value is temperature dependent. The higher the temperature, the larger the reverse current and the shorter the time until the reverse current stabilizes. However, the sensor response at 100°C and 5000 ppm hydrogen concentration is different from that at other temperatures. The reverse current reaches a maximum almost immediately upon the change from 1000 ppm to 5000 ppm hydrogen, then decreases with continued hydrogen exposure. This high concentration/high temperature behavior is explored further elsewhere (16).

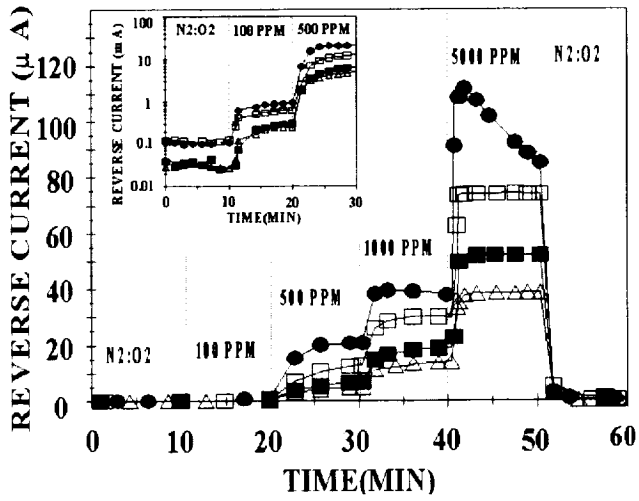

Figure 2. The response of a PdAg hydrogen sensor as a function of temperature when exposed for 10 minutes to the carrier gas 90% N_2:10% O_2, and then for 10 minutes each to 100 ppm, 500 ppm, 1000 ppm, and 5000 ppm of H_2 in the carrier gas. The inset shows the carrier gas, 100 ppm and 500 ppm response in a logarithmic scale. The temperatures are 45°C (Δ), 60°C (■), 80°C (□), and 100°C (●).

Other tests show that the sensor responds in an inert environment (no oxygen) to the presence of hydrogen. The presence of oxygen decreases the sensor response but the sensor is still sensitive to low concentrations of hydrogen (16).

Therefore, the properties of the PdAg sensor make it very useful for applications where sensing small amounts of hydrogen is necessary. The sensor response is large, rapid, and repeatable. If quick recovery is necessary, then the sensor should be operated in oxygen containing gases. If detection of the presence of hydrogen is required without rapid recovery, then this sensor can also be used in inert environments. The sensor responds to hydrogen across a wide concentration range with a signal and response time that is temperature dependent. This sensor can be used to monitor leaks in a multipoint leak detection scheme involving a number of these sensors. Further, this PdAg sensor has been shown to have a sensitivity and response comparable to that of a mass spectrometer (17).

Although the PdAg sensor showed excellent properties for a number of applications, its change in behavior and occasional failure at higher temperatures and higher hydrogen concentrations meant that its behavior needed to be stabilized if it was to be exposed to 100% hydrogen as in the Shuttle application. This led to the development of the next generation of sensor. This sensor, which uses PdCr as the hydrogen sensitive alloy, is in its later stages of development. A comparison of the response to 100% hydrogen at 100°C of the two types of sensors is shown in Figure 3. The PdCr sensor is much more stable than the PdAg sensor in these conditions. The PdCr sensor is presently under development for use on the NASA experimental vehicle, the X-33, in its hydrogen leak detection system.

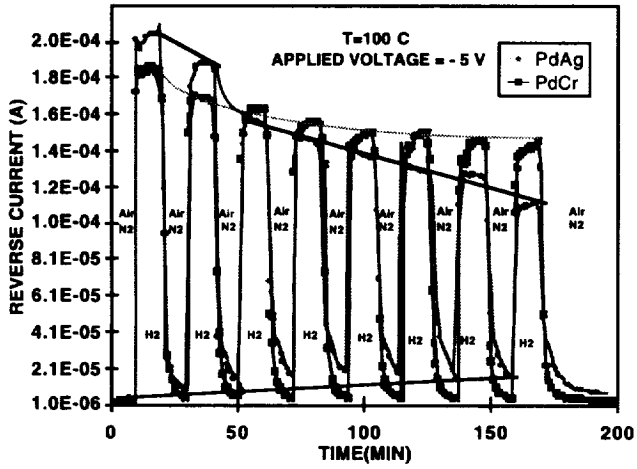

Figure 3. The response of PdAg and PdCr Schottky diode sensors at 100°C to repeated exposures of 9 minutes of air, 1 minute of nitrogen, 10 minutes of 100% hydrogen, and 1 minute of nitrogen. The PdCr diode shows a more repeatable baseline and a more stable response than the PdAg diode.

High Temperature Hydrogen and Hydrocarbon Detection

The development of high temperature hydrogen and hydrocarbon sensors for use in harsh environments has centered on the development of a stable SiC-based Schottky diode. A Schottky diode is composed of a metal in contact with a semiconductor (MS) or a metal in contact with a very thin insulator on a semiconductor (MIS). For gas sensing applications, the metal is often a catalytic film. The advantage of a Schottky diode sensing structure in gas sensing applications is its high sensitivity. This is especially useful in emission measuring applications where the concentrations to be measured are low.

The detection mechanism for hydrogen, as discussed in the previous section, involves the dissociation of hydrogen on the surface of a catalytic metal. The atomic hydrogen migrates to the interface of the metal and the insulator, or the metal and the semiconductor, forming a dipole layer. This dipole layer affects the barrier height of the diode resulting in an exponential change in the current or a quadratic change in the capacitance. The magnitude of this effect can be correlated with the amount of hydrogen and other gas species (especially oxygen) present in the surrounding ambient atmosphere. The detection of gases such as hydrocarbons is made possible if the sensor is operated at a high enough temperature to dissociate the hydrocarbon and produce atomic hydrogen. The resulting hydrogen affects the sensor output in the same way as molecular hydrogen (14,18-20).

The Schottky diode structure under development at NASA LeRC has begun with Pd on SiC MS structures (Pd/SiC). Direct contact between the catalytic metal and the semiconductor allows changes in the catalytic metal to have maximum effect on the semiconductor. Studies of this baseline system help determine limits of diode sensitivity, potential material interactions between Pd and SiC, and whether a barrier layer between the Pd and SiC is necessary for long-term sensor stability. The details of this work are reviewed elsewhere (19). The sensor detects hydrogen and hydrocarbons in inert or oxygen containing environments. The response to hydrocarbons is temperature dependent with a minimum temperature necessary for the hydrocarbon to be detected.

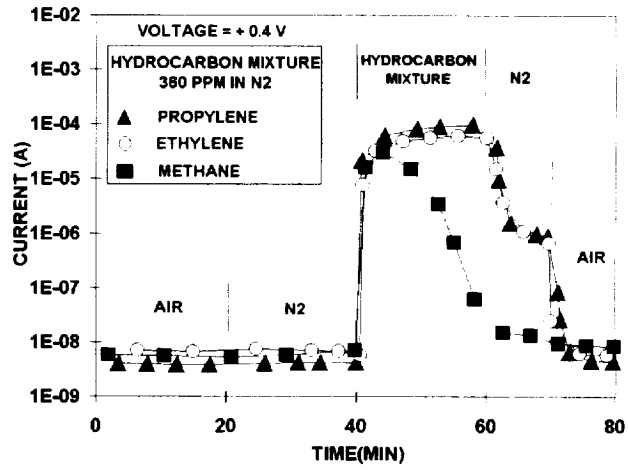

Figure 4. The forward current at 0.4V vs. time at 300°C upon exposure to propylene (▲), ethylene (○), and methane (■). The sensor response is large and depends on the class of hydrocarbon.

An example of the sensor's ability to detect hydrocarbons is shown in Figure 4. where the response of the Pd/SiC Schottky diode forward current at 300°C is shown for three different hydrocarbons. Two of the hydrocarbons, propylene and ethylene, are alkenes while the third, methane, is an alkane. Thus, this test involves

two different classes of hydrocarbons. The sensor is exposed to air for 20 minutes, N_2 for 20 minutes, 360 ppm of propylene, ethylene, or methane in N_2 for 20 minutes, N_2 for 10 minutes, and then 10 minutes of air. The sample preparation procedure is described elsewhere and contact is made to the sample using tungsten probes (19).

There are two points to note in Figure 4. First, the change in the forward current upon exposure to propylene and ethylene is very large: more than a factor of 1000. This demonstrates the high sensitivity of the diode operated in the forward current mode. Second, the sensor response to propylene is just slightly larger than that of ethylene. In contrast, the sensor response to methane is significantly different from that of propylene and ethylene: a short term increase in the current followed by a decrease back toward baseline. Thus, the sensor response depends not only on the hydrocarbon but also on the class of hydrocarbon.

The sensor response is affected by high temperature heating. Prolonged heating at 425°C has been shown to change the sensor properties and to decrease sensor sensitivity (21). Nonetheless, even after heating at 425°C in air for 140 hours, the Pd/SiC Schottky diode is still very sensitive to the presence of hydrogen: a factor of 1000 change in forward current is observed upon exposure to 1000 ppm hydrogen in He. The reason for this change in diode properties is likely due to reactions between the Pd and SiC at the interface upon heating. Attempts to stabilize this interface are continuing.

The Pd/SiC sensor response is also significantly affected by sensor packaging. Possible causes for the decrease in sensitivity upon packaging include: 1) The diode surface area in the packaged diodes is usually larger than that of diodes examined in the probe station. The presence of micropipes (4) in the SiC might dominate the current flow in a packaged sensor. 2) Processing the sensor for packaging may influence diode properties crucial to the sensors sensitivity. The stability of the sensor sensitivity after packaging is an area of continuing investigation. Micromachining of 4H or 6H SiC is under investigation to allow formation of, for example, diaphragm structures which decrease the sensor's thermal mass and power consumption in the same way as is done with Si structures.

Nitrogen Oxide (NO_x) Detection

Two approaches are being explored for sensitive detection of NO_x specifically NO and NO_2. First, the development of an MS or MIS SiC-based Schottky diode with a NO_x sensitive structure. The second is a sensor composed of tin-oxide as the sensitive element. Each approach is at a different stage of development.

The proof of concept of SiC-based approach is presently being demonstrated. There are two designs of the NO_x sensitive MS or MIS SiC-based Schottky diode. The first approach is to change the catalytic gate of the Schottky diode to a material more sensitive to the presence of NO_x. A prime candidate material is platinum (Pt). Changes in the Pt upon exposure to NO_x are thought to change the electronic properties of the diode. (22). These changes can be correlated to changes in the NO_x concentration in the ambient and thus be used to quantitatively measure the NO_x concentration.

The second SiC-based design incorporates a NO_x sensitive insulator into a Schottky diode structure. This approach allows the combination of SiC semiconductor technology with more traditional methods of NO_x detection such as the use of metal oxides. This would allow SiC to act as a platform for gas sensing over a range of temperatures which would not be possible with lower temperature and more reactive Si-based devices. For example, a thin insulating layer of tin oxide (SnO_2) can be placed between a porous catalytic gate and the SiC. Upon exposure to NO_x, it is surmised that changes will occur in both the catalytic gate and the insulating layer. The combined effect of these changes will yield a more sensitive sensor than changes in the gate alone. Prototypes of both these SiC-based systems are under development and the results of testing of these sensors is planned for a future publication.

The second approach to NO_x detection is to use a microfabricated and micromachined Si-based structure. In contrast to the SiC-based approach where the SiC is used as a semiconductor, the Si in this approach is not an integrated part of the electrical sensing circuit. Rather, the Si is used as a platform on which the structure necessary for the sensor is fabricated. This sensor structure, shown in Figure 5, includes a temperature detector, heater, and sensing element. The microfabrication process allows the sensor to be small in size with low heat loss and minimal energy consumption. Energy consumption is further reduced by etching out the backside of the Si wafer so that the sensor components (temperature detector, heater, and sensing element) are over a diaphragm region. This minimizes the thermal mass of the sensing area thereby decreasing power consumption for heating and decreasing the time for thermal equilibrium. The temperature detector and heater are doped into the Si substrate for operation over a wide temperature range. The sensing element is composed of interdigitated electrode elements across which is deposited SnO_2. Tin oxide, both doped and undoped, has previously been shown to be sensitive to NO_x (23-24). Changes in conductivity of doped SnO_2 across the interdigitated electrodes is measured and correlated to NO_x concentration.

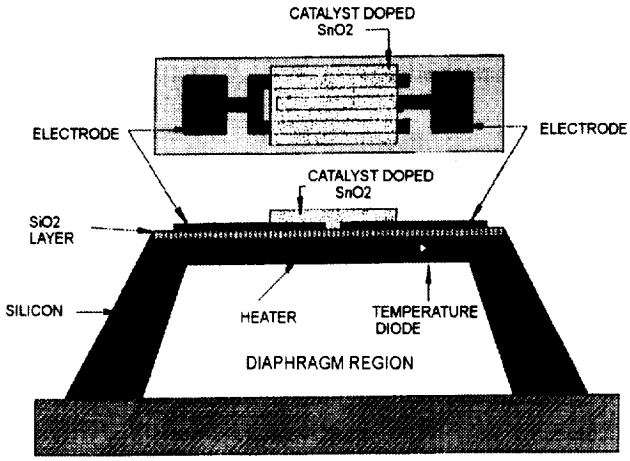

Figure 5. The structure of a tin-oxide NO_x sensor including temperature detector, heater, and sensing element. The electrode material is Pt and the sensor dimensions are approximately 300 microns on a side with a height of 250 microns.

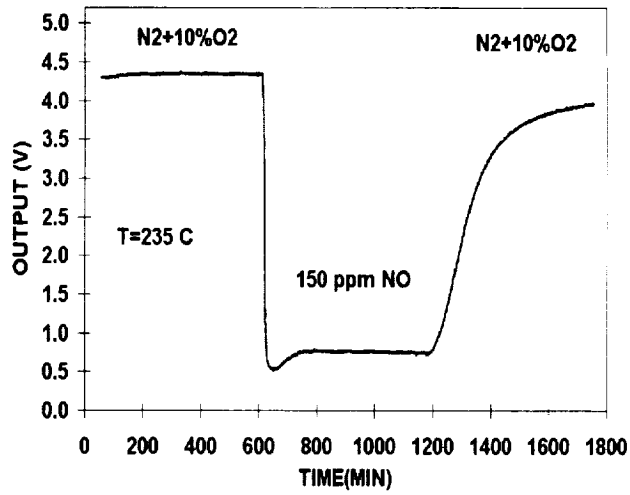

Figure 6. The response of a tin-oxide sensor to 150 ppm NO in nitrogen plus 10% oxygen at 235°C.

Several prototypes of these devices have been fabricated and evaluated. Figure 6 shows the response to 150 ppm NO of an undoped tin-oxide based sensor of the design in Figure 5. The sensor is first exposed to nitrogen plus 10% oxygen (O_2) followed by 150 ppm NO in nitrogen plus 10% O_2 at time t=600 sec, then nitrogen plus 10% O_2 at t=1200 sec. The sensor response at 235°C is large, rapid, and relatively constant during the NO exposure. Other tests have shown that the response is dependent on the temperature and the gas ambient especially the O_2 concentration.

A major component of this development work is to stabilize the SnO_2 for long-term, high temperature operation. Drift in the properties of SnO_2 with long term heating due to grain boundary annealing have been previously noted (25-26). This drift results in changes in the sensor output with time and reduces sensor sensitivity. In order to stabilize the SnO_2 structure for long term operation, attempts to fabricate nanocrystalline SnO_2 are under way. Nanocrystalline materials have several inherent advantages over conventionally fabricated materials including increased stability at high temperature (27-28). Further sensor development will include the deposition of nanocrystalline SnO_2 on the sensor structure of Figure 5.

Oxygen Detection

The development of a microfabricated O_2 sensor has been initiated for safety purposes in aerospace applications but, as demonstrated in the automotive emissions control example, significant applications exist in the area of aeronautics emission control. Commercially available O_2 sensors are typically electrochemical cells using zirconium dioxide (ZrO_2) as a solid electrolyte and Pt as the anode and cathode. The anode is exposed to a reference gas (usually air) while the cathode is exposed to the gas to be detected. Zirconium dioxide becomes an ionic conductor of $O^=$ at temperatures of 600°C and above. This property of ZrO_2 to ionically conduct O_2 means that the electrochemical potential of the cell can be used to measure the ambient oxygen concentration at high temperatures. However, operation of these commercially available sensors in this potentiometric mode limits the range of oxygen detection. Further, the cur rent manufacturing procedure of this sensor, using sintered ZrO_2, is relatively labor intensive and costly resulting in a sensor with a power consumption on the order of several watts.

The objective of this research is to develop a zirconium dioxide solid electrolyte O_2 sensor using microfabrication and micromachining techniques. As noted in the previous two sections, the presence of O_2 often affects the response of hydrogen, hydrocarbon, and NO_x sensors. An accurate measurement of the O_2 concentration will help quantify the response of other sensors in environments where the O_2 concentration is varying. Thus, the combination of an O_2 sensor with other microfabricated gas sensors is envisioned to optimize the ability to monitor emissions.

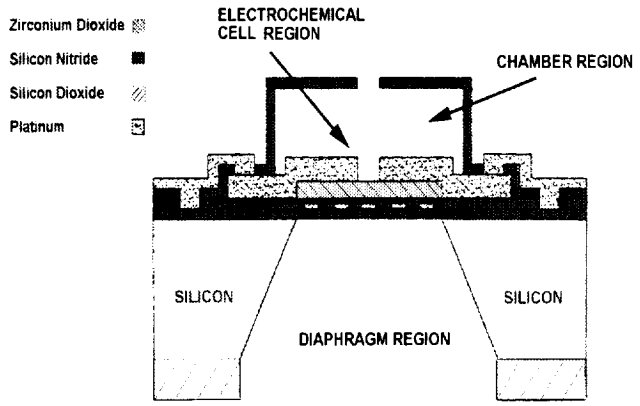

Figure 7. The structure of a microfabricated amperometric oxygen sensor. The dimensions of this sensor are comparable to that of the NO_x sensor shown in Figure 5.

A schematic of the sensor design is shown in Figure 7. As discussed in the NO_x detection section above, microfabricating the sensor components onto a micromachined diaphragm region allows the sensor to be small in size and have decreased energy consumption and time for thermal equilibrium. When operated in the amperometric mode, the current of this cell is a linear function of the ambient O_2 concentration. This linear response to oxygen concentration significantly increases the O_2 detection range of the sensor. A chamber structure with a well-defined orifice is micromachined to cover the sensing area. This orifice provides a pathway to control oxygen diffusion which is important in amperometric measurements. This orifice also protects the integrity of the sensing electrode from impinging particles. Performance tests of the temperature detector and heater are near completion and fabrication and testing of the complete O_2 sensor is planned in the near future.

COMMERCIAL APPLICATIONS

The gas sensors being developed by the Chemical Species Gas Sensors team at NASA Lewis are meant for aeronautics and aerospace applications but can be used in a variety of commercial applications as well. For example, the PdAg hydrogen sensors were developed for application on the launch pad of the space shuttle. These sensors were not completely developed for the space shuttle application due to the change in behavior at higher hydrogen concentrations. However, these sensors can be applied to an automotive application. GenCorp Aerojet Corporation, in conjunction with NASA Marshall Space Flight Center, has developed hardware and software to monitor and control the NASA Lewis/CWRU sensors. The system can be customized to fit the user's needs, e.g., to monitor and display the condition of the tank of a natural gas vehicle. Several of these systems have been purchased for use on the Ford Motor Company assembly line for natural gas vehicles (NGV). This complete system received a 1995 R&D 100 Award as one of the 100 most significant inventions of that year.

Likewise, the high temperature hydrogen, hydrocarbon, NO_x and oxygen sensors are being developed for aeronautics applications but can be applied in commercial applications. For example, the conditions in an aeronautic engine are similar to those of an automotive engine. Thus, sensors that work in aeronautic engine applications may be operable in automotive engine applications. NASA LeRC has interacted with the Partnership for the Next Generation of Vehicles (PNGV) program regarding possible use of SiC-based technology for the sensing of hydrocarbons in automotive emissions. Other possible applications include combustion process monitoring, catalytic reactor monitoring, alarms for high-temperature pressure vessels and piping, chemical plant processing, polymer production, and volatile organics detection.

SUMMARY

The needs of space and aeronautic applications require the development of sensors with capabilities beyond those of commercial sensors. These requirements include operation in harsh environments, high sensitivity, and minimal size weight and power consumption. NASA LeRC and CWRU are actively involved in developing this sensor technology using microfabrication and micromachining technology as well as SiC semiconductor technology. The combination of these technologies allows for the fabrication of a wide variety of sensor designs with behavior and properties that can be tailored to the given application. Several types of sensors have been described all of which have aeronautic and space applications. Some of the sensor designs are relatively mature while the development of others is ongoing.

Sensors designed for aeronautic and space applications also have significant commercial applications. One example is the use of the hydrogen sensor in automotive applications. This application involved a sensor not completely developed for a space application but with excellent properties for use in the automotive application. Further, given the similarities of aeronautic engine environments to those of automotive engine environments and chemical process monitoring, sensors developed for aeronautic applications also have a wide range of applicability. Although each application is different and the sensor needs to be tailored for that environment, the base technology being developed for aeronautic and space applications can have significant impact on a range of fields.

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Aeronautic and space applications require the development of chemical sensors with capabilities beyond those of commercially available sensors. Two areas of particular interest are safety monitoring and emission monitoring. In safety monitoring, detection of low concentrations of hydrogen at potentially low temperatures is important while for emission monitoring the detection of nitrogen oxides, hydrogen, hydrocarbons and oxygen is of interest. This paper discusses the needs of aeronautic and space applications and the point-contact sensor technology being developed to address these needs. The development of these sensors is based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors. 2) The development of high temperature semiconductors, especially silicon carbide. The detection of each type of gas involves its own challenges in the fields of materials science and fabrication technology. The number of dual-use commercial applications of this microfabricated gas sensor technology make this general area of sensor development a field of significant interest.

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