Chemical Gas Sensors for Aeronautic and Space Applications

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CHEMICAL GAS SENSORS FOR AERONAUTIC AND SPACE APPLICATIONS

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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 emis-
sions 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 tempera-
tures inherent near the reaction chamber of the engine
render most sensors inoperable.

A notable exception to this limitation in sensor technol-
ogy is the commercially available oxygen sensor pres-
ently in use in automobile engines (3). This sensor,
which is based on the changes in the properties of zirco-
nium dioxide (ZrO2) upon reaction with oxygen, has
been instrumental in decreasing automotive engine
emissions. However, comparable sensors for other com-
ponents of the gas stream do not exist: monitoring of
emissions of nitrogen oxides (NOx), hydrogen, and
hydrocarbons, is not presently possible in-situ with point-
contact sensors placed near the engine. Even the tradi-
tional ZrO2 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 con-
centrations of the gases to be measured. Although the
measurement of nitrogen oxides (NOx) is important in
these applications, the measurement of other gases pres-
ent in the emission stream such as hydrogen, hydrocar-
bons and oxygen is also of interest. The measurement
range depends on the gas and the engine but generally
the detection of NOx, 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 develop-
ment 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, es-
specially 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,
NOx, 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 elec-
tronics. These technologies are used, where appropriate,
to develop hydrogen, hydrocarbon, NOx and oxygen sen-
sors. 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 de-
development while the state of development of the other sen-
sors 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 proc-
essing techniques, lithographic reduction, thin film met-
alization, photore sist patterning, and chemical etching
have found extensive chemical and biological applica-
tions, 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 mi-
cromachining 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, galvanofoming,
absorbing).

Chemical anisotropic etching is an etching procedure
that depends on the crystalline orientation of the sub-
strate. 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 crys-
talline structure. However, although not many chemi-
cals 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 bandgap 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.

<table>
<thead>
<tr>
<th>Bandgap (eV)</th>
<th>Si</th>
<th>GaAs</th>
<th>6H-SiC</th>
<th>4H-SiC</th>
<th>3C-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Breakdown Field @ 10^12 cm^-1 (MV/cm)</td>
<td>0.6</td>
<td>0.6</td>
<td>3.2</td>
<td>3</td>
<td>&gt; 1.5</td>
</tr>
<tr>
<td>Electron Mobility @ 10^13 cm^-1 (cm^2/V-s)</td>
<td>1100</td>
<td>6000</td>
<td>370</td>
<td>800</td>
<td>750</td>
</tr>
<tr>
<td>Saturated Electron Drift Velocity (cm/s)</td>
<td>10^7</td>
<td>10^7</td>
<td>2 x 10^7</td>
<td>2 x 10^7</td>
<td>2.5 x 10^7</td>
</tr>
<tr>
<td>Thermal Conductivity (W/cm-K)</td>
<td>1.5</td>
<td>0.5</td>
<td>4.9</td>
<td>4.9</td>
<td>5.0</td>
</tr>
<tr>
<td>Hole Mobility @ 10^14 cm^-1 (cm^2/V-s)</td>
<td>420</td>
<td>320</td>
<td>90</td>
<td>115</td>
<td>40</td>
</tr>
<tr>
<td>Commercial Wafers</td>
<td>12''</td>
<td>6''</td>
<td>1.375''</td>
<td>1.375''</td>
<td>None</td>
</tr>
</tbody>
</table>

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 aircraft 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 aircraft 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-SiO₂-Si structure. Hydrogen dissociates on the Pd surface and diffuses to the Pd-SiO₂ 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 SiO₂ is thermally grown in the sensor region. The heater and temperature detector are platinum covered with SiO₂. 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 6.1x10⁻⁴ cm² 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.

The response of the sensor to varying temperatures and hydrogen concentrations in a 90% N₂:10% O₂ 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 H₂ 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 H₂ (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).

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.

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.

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, N₂ for 20 minutes, 360 ppm of propylene, ethylene, or methane in N₂ for 20 minutes, N₂ 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 after packaging is an area of continuing investigation to allow formation of, for example, a thin insulating layer of tin oxide (SnO₂) can be placed between a porous catalytic gate and the SiC. Upon exposure to NO₃, 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 SiC-based design incorporates a NO₃ sensitive insulator into a Schottky diode structure. This approach allows the combination of SiC semiconductor technology with more traditional methods of NO₃ 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 (SnO₂) can be placed between a porous catalytic gate and the SiC. Upon exposure to NO₃, 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 SiC-based approach to NO₃ detection is to use a microfabricated and micromachined Si-based structure. In contrast to the SiC-based approach, the Si 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 SnO₂. Tin oxide, both doped and undoped, has previously been shown to be sensitive to NO₃ (23-24). Changes in conductivity of doped SnO₂ across the interdigitated electrodes is measured and correlated to NO₃ concentration.
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 ($\text{O}_2$) followed by 150 ppm NO in nitrogen plus 10% $\text{O}_2$ at time $t=600$ sec, then nitrogen plus 10% $\text{O}_2$ 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 $\text{O}_2$ 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 underway. 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 $\text{O}_2$ 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 $\text{O}_2$ sensors are typically electrochemical cells using zirconium dioxide ($\text{ZrO}_2$) 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 $\text{O}^-$ at temperatures of 600°C and above. This property of $\text{ZrO}_2$ to ionically conduct $\text{O}_2$ 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 current manufacturing procedure of this sensor, using sintered $\text{ZrO}_2$, 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 $\text{O}_2$ sensor using microfabrication and micromachining techniques. As noted in the previous two sections, the presence of $\text{O}_2$ often affects the response of hydrogen, hydrocarbon, and NO$_x$ sensors. An accurate measurement of the $\text{O}_2$ concentration will help quantify the response of other sensors in environments where the $\text{O}_2$ concentration is varying. Thus, the combination of an $\text{O}_2$ 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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Chemical Gas Sensors for Aeronautic and Space Applications

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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.