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DEVELOPMENT OF HIGH TEMPERATURE GAS SENSOR TECHNOLOGY



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ABSTRACT

The measurement of engine emissions is important for their monitoring and control. However, the ability to measure these emissions in-situ is limited. We are developing a family of high temperature gas sensors which are intended to operate in harsh environments such as those in an engine. The development of these sensors is based on progress in two types of technology: 1) The development of SiC-based semiconductor technology. 2) Improvements in micromachining and microfabrication technology. These technologies are being used to develop point-contact sensors to measure gases which are important in emission control especially hydrogen, hydrocarbons, nitrogen oxides, and oxygen. The purpose of this paper is to discuss the development of this point-contact sensor technology. The detection of each type of gas involves its own challenges in the fields of materials science and fabrication technology. Of particular importance is sensor sensitivity, selectivity, and stability in long-term, high temperature operation. An overview is presented of each sensor type with an evaluation of its stage of development. It is concluded that this technology has significant potential for use in engine applications but further development is necessary.

INTRODUCTION

The control of emissions from aircraft engines is an important component of the development of the next generation of these engines. The ability to monitor the type and quantity of emissions being generated by an engine is an important step 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 (Logothetis, 1991). 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 hydrogen, hydrocarbons, and nitrogen oxides (NO_x) 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 use of the technology in some applications.

NASA Lewis Research Center (LeRC), in conjunction with Case Western Reserve University (CWRU), is presently developing a family of high temperature gas sensors for use in a variety of aeronautic and aerospace applications. The development of these sensors is based on advances in two areas of materials technology and processing: 1) The maturation of silicon carbide (SiC) as a high temperature electronic material. 2) Improvements in silicon processing technology to allow the production of microfabricated and micromachined devices.

The development of SiC as a high temperature electronic material (Neudeck, 1995) allows the fabrication of sensors and electronic devices which function in conditions where silicon (Si) based technology is inoperable. The device functionality of SiC is due to its wide bandgap and low intrinsic carrier concentration. Combined with other material properties, such as its superior mechanical toughness and high thermal conductivity, SiC is an excellent material for use in a wide range of harsh environments. In emission sensing applications, gas sensitive electronic structures such as Schottky diodes (Chen, 1996a, Hunter, 1995), or capacitors (Baranzahi, 1995a, Baranzahi 1995b, Baranzahi, 1995c) can operate at high enough temperatures to allow the detection of hydrocarbons or NO_x .

The ability to microfabricate and micromachine the sensor structure has significant advantages over traditional sensor processing. A microfabricated sensor can have minimal size and weight providing

the user flexibility in the quantity and placement of sensors at a given location. Microfabricating the sensor structure can also allow multiple sensor components to be placed in a small sensor package. Micromachining allows the formation of complex structures in a small area as well as the minimization of the sensor thermal mass. Finally, the use of Si-based processing technology allows mass production of the sensor thus decreasing sensor fabrications costs.

The purpose of this paper is to discuss the high temperature gas sensing technology under development at NASA LeRC and CWRU. We will first discuss the testing facility at NASA LeRC used to characterize the sensors. An overview is then presented of each of the sensor technologies with an evaluation of its stage of development. In particular, we will discuss the development of microfabricated point-contact sensors to detect low concentrations of hydrogen, hydrocarbons, and NO_x as well as the development of a microfabricated oxygen sensor. It is concluded that although further development work is necessary, microfabricated gas sensors have considerable potential for use in engine monitoring and control applications.

NASA LeRC GAS SENSOR TESTING FACILITY

The facility used for sensor testing at NASA LeRC is shown schematically in Fig. 1. The facility can supply a continuous flow of gaseous helium, hydrogen, hydrocarbon mixtures (mix), nitrogen, or air, either individually or as a mixture, to a chamber containing the sensor under test. (The testing of NO_x sensors is done at CWRU using a similar facility.) The temperature and pressure of the gas are measured as the gas enters the test chamber. The composition of the gas is monitored by a mass spectrometer. The mass spectrometer provides an independent measure of the relative concentration of the gases flowing into the test chamber as a function of time. The gas leaves the test chamber and can be sent through a flame before being

vented.

Gas flow into the test chamber at a range of flow rates is achieved using computer-controlled mass flow controllers. The helium, hydrocarbon mixtures, nitrogen, air, and one hydrogen mass flow controller are calibrated for flows from 0 to 4000 standard cubic centimeters per minute (sccm). A second hydrogen mass flow controller is calibrated for 0 to 20 sccm flows. A three-way valve allows the gas to bypass the test chamber and go directly to the vent. This feature allows the mass flow controllers to be stabilized without flowing gases through the test chamber.

Two types of test chambers are used in this work. One test chamber is designed for testing sensors mounted on integrated circuit (IC) connectors. The sensor is connected to an IC connector in the chamber which is in the flowing stream of the gas. The Si-based sensors with temperature detector and heater are tested in this type of chamber. The second chamber is designed for testing unmounted thin films or transistor chips at a range of sample temperatures. The sample is placed on a heated stage and tested by means of a probing station with tungsten probes. The SiC-based devices are tested in this chamber.

HYDROGEN AND HYDROCARBON DETECTION

The development of high temperature hydrogen and hydrocarbon sensors 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.

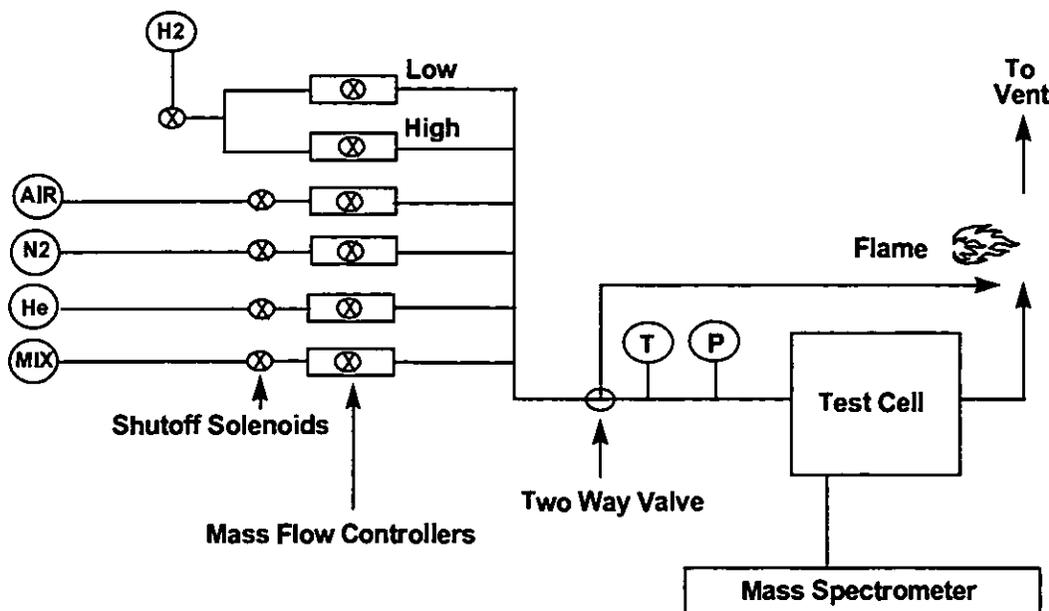


Figure 1. Schematic diagram of the NASA LeRC gas sensor testing facility. T and P represent temperature and pressure measurements.

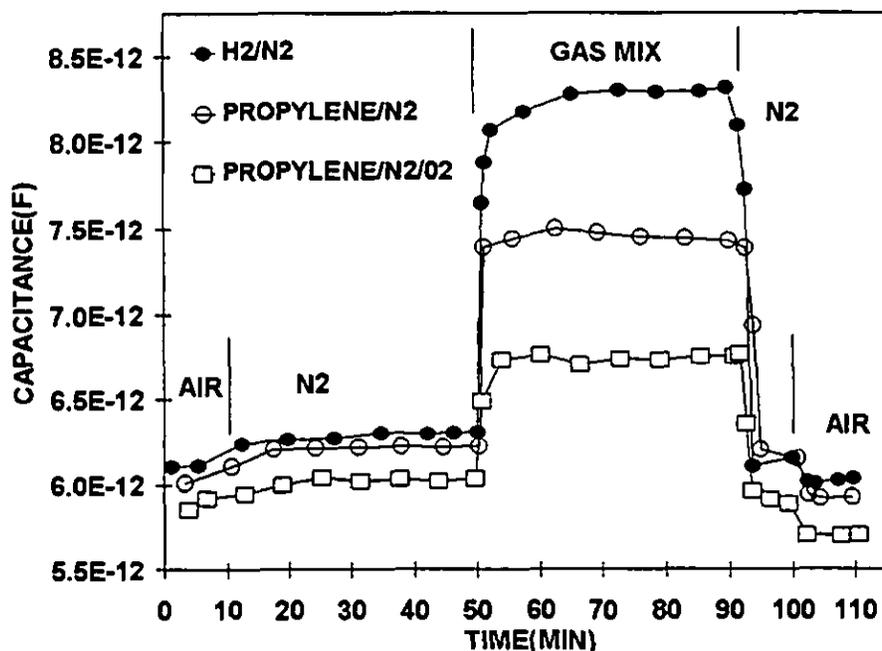


Figure 2. The zero bias capacitance vs. time at 400°C upon exposure to nitrogen plus 300 ppm hydrogen (●) or propylene (○), or nitrogen plus 300 ppm propylene plus 1% oxygen (□).

The detection mechanism for hydrogen involves the dissociation of hydrogen on the surface of a catalytic metal. The 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 hydrogen. The resulting hydrogen affects the sensor output in the same way as molecular hydrogen (Baranzahi, 1995a, Chen 1996a, Hunter, 1995, Lundstrom, 1989).

The Schottky diode structure under development at NASA LeRC has begun with Pd on SiC MS structure (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 (Chen, 1996a). In this section we will briefly discuss four major properties of the sensor's behavior.

First, the Pd/SiC Schottky diode detects hydrogen and hydrocarbons in both inert and oxygen-containing environments. This is illustrated in Fig. 2 which shows the capacitive response of the

diode at zero bias voltage to hydrogen and hydrocarbons at 400°C. The diode is first exposed to air for 10 minutes, nitrogen for 40 minutes, followed by 300 ppm of hydrogen in nitrogen (N_2/H_2) for 40 minutes and then 10 minutes of nitrogen and 10 minutes of air. The second and the third cycles are the same as the first except that the 300 ppm of hydrogen is replaced by 300 ppm propylene in nitrogen (N_2/C_3H_6), and then 300 ppm of propylene in nitrogen and 1% oxygen ($N_2/C_3H_6/O_2$) respectively. The sensor responds strongly to all three gas mixtures with the signal decreasing as the mixture is changed from N_2/H_2 to N_2/C_3H_6 to $N_2/C_3H_6/O_2$ respectively. This decreasing response can be explained by decreasing amount of atomic hydrogen available to migrate into the Pd film. The propylene releases less atomic hydrogen into the film than the molecular hydrogen and the presence of oxygen decreases the amount of available hydrogen even further. Nonetheless, this figure demonstrates that the diode can detect low concentrations of hydrogen and hydrocarbons and does not require the presence of oxygen to be sensitive.

Second, the sensor response to hydrocarbons at a given temperature will vary depending on the hydrocarbon. This is shown in Fig. 3 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.

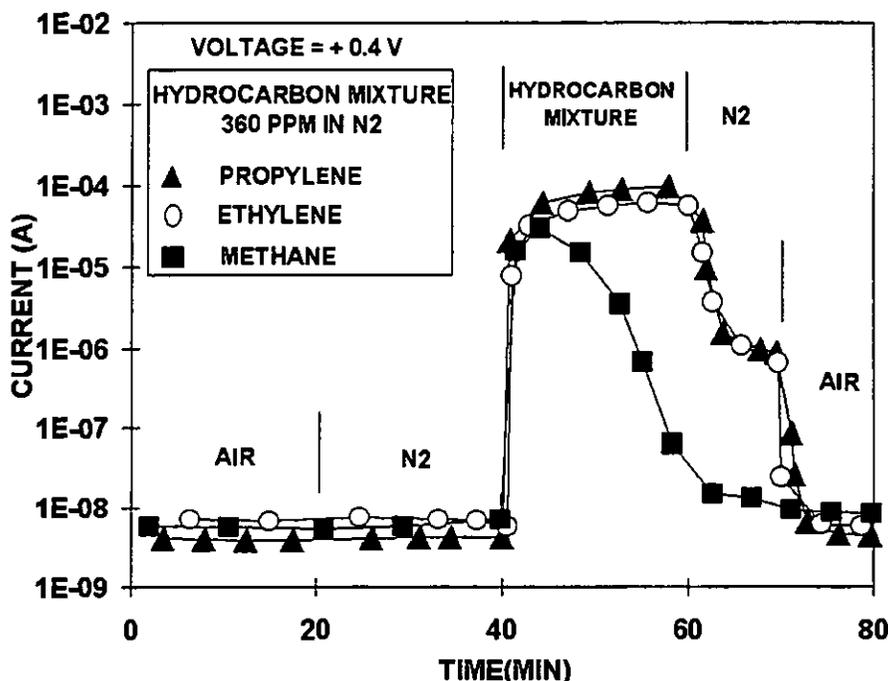


Figure 3. The forward current at 0.4V vs. time at 300°C upon exposure to propylene (▲), ethylene (○), and methane (■). The sensor response is large and depends on the class of hydrocarbon.

There are two points to note in Fig. 3. 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.

Third, 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 (Chen, 1996b). 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.

Fourth, the Pd/SiC sensor response is also significantly affected by sensor packaging. Possible causes for this 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 (Neudeck, 1995) in the SiC might dominate the current flow in a packaged sensor and decrease the effect on the sensor of changes in Pd work function. 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.

NITROGEN OXIDE (NO_x) DETECTION

Two approaches are being explored for sensitive detection of NO_x specifically NO and NO₂. 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. (Baranzahi, 1995b). 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 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 (SnO₂) 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.

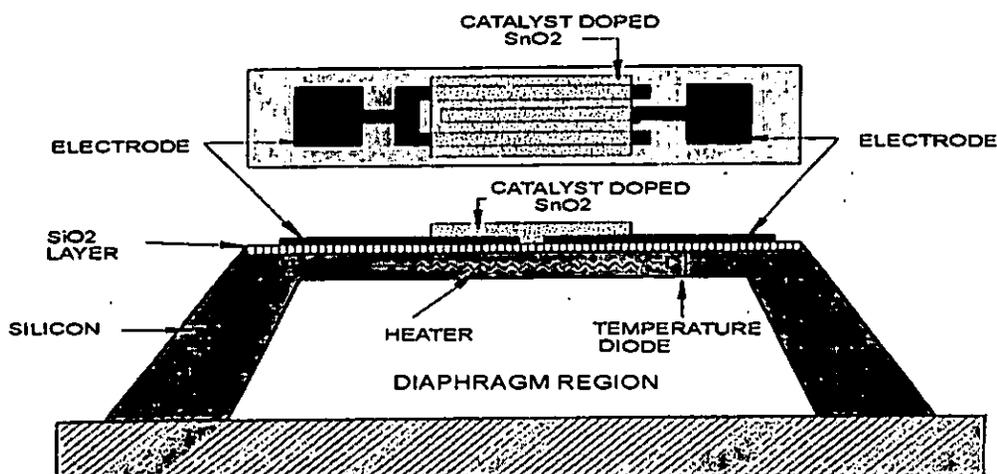


Figure 4. The structure of a tin-oxide NO_x sensor including temperature detector, heater, and sensing element. The electrode material is Pt and the sensor dimensions are approximately 300 microns on a side with a height of 250 microns.

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 Fig. 4, 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 (Chang, 1979, Sberveglieri, 1990). Changes in conductivity of doped SnO_2 across the interdigitated electrodes is measured and correlated to NO_x concentration.

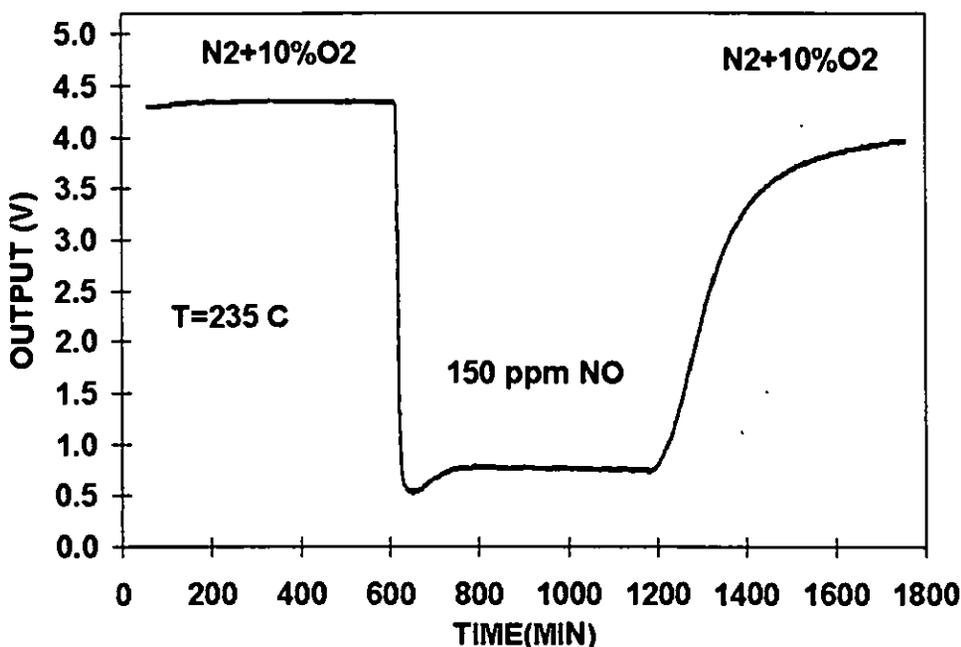


Figure 5. The response of a tin-oxide sensor to 150 ppm NO in nitrogen plus 10% oxygen at 235°C.

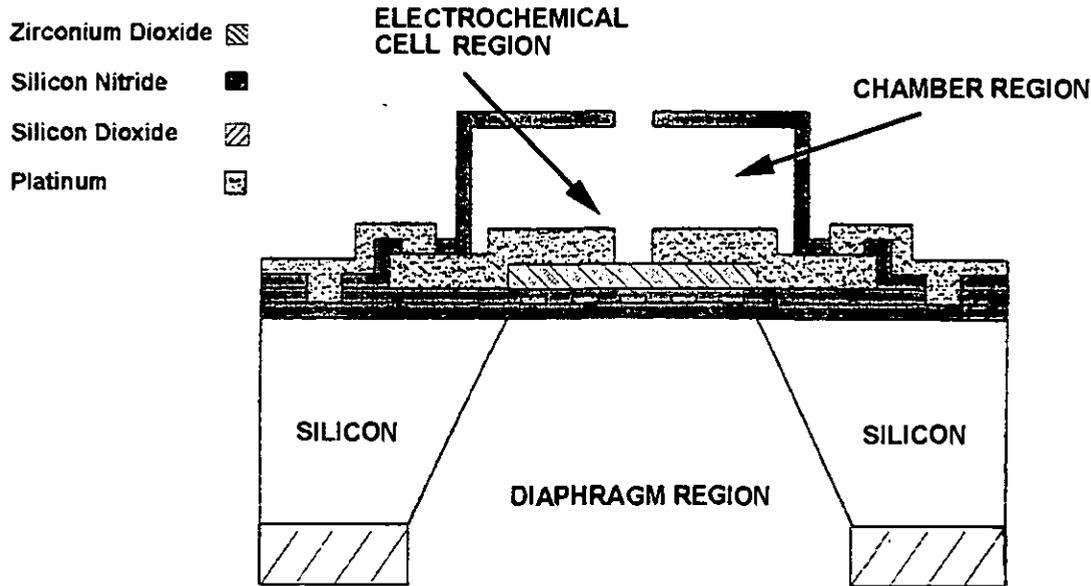


Figure 6. The structure of a microfabricated amperometric oxygen sensor. The dimensions of this sensor are comparable to that of the NO_x sensor shown in Figure 4.

Several prototypes of these devices have been fabricated and evaluated. Figure 5 shows the response to 150 ppm NO of an undoped tin-oxide based sensor of the design in Fig. 4. 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 (Ogawa, 1988, Xu, 1991). 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 (Vogel, 1994, Yoo, 1995). Further sensor development will include the deposition of nanocrystalline SnO_2 on the sensor structure of Fig. 4.

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^{2-} 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 current 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 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 at a given time 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.

A schematic of the sensor design is shown in Fig. 6. 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.

SUMMARY AND FUTURE PLANS

High temperature, microfabricated gas sensors are being developed for use in aeronautics and aerospace applications especially for use in emissions monitoring and control. The development of these sensors is based on SiC semiconductor technology and Si-based micromachining and microrfabrication technology. Hydrogen and hydrocarbon sensors composed of Pd/SiC Schottky diodes have been demonstrated to be highly sensitive at elevated temperatures. Stabilization of the sensor structure and improvements in packaging technology are required for long-term operation in engine environments. Nitrogen oxide sensors are being developed using both SiC and Si-based technology. The SiC-based approach is at the proof of concept level while the prototypes of the micromachined and microfabricated Si-based sensor have been demonstrated. Oxygen sensors using Si-based technology are under development and will complement the hydrogen, hydrocarbon, and NO_x sensor technology.

The successful development of this family of high temperature gas sensors will provide aeronautic engine designers with a new tool: the ability to monitor in-situ, and thus possibly control, engine emissions. The development of these sensors is an interdisciplinary project requiring contributions from several areas of technology including materials science, chemical engineering, and fabrication technology. These sensors can also be applied to a number of commercial applications including automotive emission control and chemical process monitoring. Parallel development of high temperature electronics and packaging will influence the ability to use high temperature gas sensors in aeronautic engine applications.

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