CHEMICAL GAS SENSORS FOR AEROSPACE APPLICATIONS

G. W. Hunter

NASA Lewis Research Center Cleveland, OH 44135

C. C. Liu

Electronics Design Center Case Western Reserve University Cleveland, Ohio 44106

9.1 Introduction

Chemical sensors often need to be specifically designed (or tailored) to operate in a given environment. It is often the case that a chemical sensor that meets the needs of one application will not function adequately in another application. The more demanding the environment and specialized the requirement, the greater the need to adapt exiting sensor technologies to meet these requirements or, as necessary, develop new sensor technologies. Aerospace (aeronautic and space) applications are particularly challenging since often these applications have specifications which have not previously been the emphasis of commercial suppliers. Further, the chemical sensing needs of aerospace applications have changed over the years to reflect the changing emphasis of society.

Three chemical sensing applications of particular interest to the National Aeronautics and Space Adminstration (NASA) which illustrate these trends are launch vehicle leak detection, emission monitoring, and fire detection. Each of these applications reflects efforts ongoing throughout NASA. As described in NASA's "Three Pillars for Success" [1], a document which outlines NASA's long term response to achieve the nation's priorities in aerospace transportation, agency wide objectives include: improving safety and decreasing the cost of space travel, significantly decreasing the amount of emissions produced by aeronautic engines, and improving the safety of commercial airline travel. As will be discussed below, chemical sensing in leak detection, emission monitoring, and fire detection will help enable the agency to meet these objectives. Each application has vastly different problems associated with the measurement of chemical species. Nonetheless, the development of a common base technology can address the measurement needs of a number of applications.

9.1.1 Launch Vehicle Leak Detection

In launch vehicle safety applications, detection of low concentrations of hydrogen (H₂), possibly at low temperatures, is important for applications involved with, for example, operation of the Space Shuttle. Hydrogen leaks can lead to explosive situations and, unless their locations can be rapidly identified, lead to hazardous situations, delays in vehicle launches, and significant costs. In the summer of 1990, 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. This leak detection approach was unable to adequately isolate the location of the hydrogen leaks leading to a delay in the Shuttle program.

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 an automated

detection system using point-contact hydrogen sensors. However, no commercial sensors existed that operated satisfactorily in this and other space related applications. The reason for this is the conditions in which the hydrogen 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 measurement and control is necessary. Operation in inert environments is necessary since the sensor may have to operate in areas purged with helium. Ability to operate in a vacuum is preferred. 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. Each sensor should have minimal size, weight, and power consumption to decrease vehicle weight and power requirements. Commercially available sensors, which often needed oxygen to operate or depended upon moisture (2), did not meet the needs of this application and thus the development of new types of hydrogen sensors was necessary (3).

However, hydrogen is not the only fuel which may be used in launch vehicle applications. Other potential fuels which may be considered include methane, ethanol, and hydrazine. Leak detection sensors for these fuels will need to meet many of the same requirements as the hydrogen sensor: sensitive detection of the fuel in possibly inert or cryogenic environments; sensor survival in high concentrations of the fuel; and minimal size, weight, and power consumption. Methane, which is a naturally occurring by-product of animal wastes, exists in small quantities already in the environment. This increases the difficulty of its measurement in some applications. Further, the detection mechanism

which may readily allow the detection of hydrogen may not work for methane [4] or ethanol. Hydrazine is known to be toxic which further adds complications to the leak detection process: not only must the gas be detected for reasons of explosion prevention but for health safety reasons as well. Just as there did not exist hydrogen sensor technology that met the needs of launch vehicle safety applications in 1990, there still does not exist comparable fuel leak detection systems for launch vehicles which use alternate fuels.

9.1.2 Aeronautic Engine Emission Monitoring

Development of a new class of sensors is also necessary for monitoring of emissions from aircraft engines. Control of emissions from aircraft engines is an important component of the development of the next generation of these engines. A NASA agency goal is to reduce emissions of future aircraft by a factor of three within 10 years, and a factor of five within 20 years [1]. A reduction of engine emissions can be achieved, in principle, if emissions of the engine are monitored and that information is used to modify the combustion process of the engine. This active combustion control also depends on the development of actuators to be able to control the combustion process as well as a control system to interpret the sensor data and appropriately change the engine parameters. Ability to monitor the type and quantity of emissions being generated by an engine is also important in determining the status of the engine. For example, by monitoring the emission output of the engine and correlating changes in the emissions produced with changes in engine performance, long term degradation of engine components might be monitored.

Ideally, an array of sensors placed in the emission's stream of 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 engine's emissions 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 used in automobile engines [5]. This sensor, which is based on the properties of zirconium dioxide (ZrO₂) 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: sensitive monitoring of emissions of nitrogen oxides, hydrogen, and hydrocarbons is not presently possible in-situ with point-contact sensors placed near the engine. Even the traditional ZrO₂ based sensor has sensitivity limits as well as size, weight, and power consumption requirements which prevent its use in some applications.

The environment in which a sensor must operate in emission monitoring applications varies drastically from the environment of launch vehicle 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 H₂, hydrocarbons (C_xH_y), carbon monoxide (CO), carbon dioxide (CO₂), and oxygen (O₂) is also of interest. The measurement range depends on the gas and the engine but generally the detection of NO_x, H₂, and C_xH_y, may be necessary at sensitivities of less than 200 ppm with corresponding measurements of O₂ 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. The sensor should have stable or at least predictable performance for extended periods of time. Given the limited number of appropriate sensors for this application, as well as the potential for a chemical sensor to be sensitive to several of the gases

simultaneously, development of new sensor technology is also necessary for this application.

9.1.3 Aircraft Fire Safety Monitoring

One of the most important factors in the vitality of commercial air travel today is the perception on the part of the public that air travel is safe. In the coming years, the number of commercial flights is expected to increase dramatically. However, if the number of commercial flights increases while the number accidents per flight (accident rate) remains the same, the overall number of accidents will increase. This may affect the public's perception of the safety of air travel. Thus, it is important to decrease the accident rate from a variety of sources. The agency goal is to reduce the overall aircraft accident rate by a factor of five within 10 years and by a factor of 10 within 20 years [1].

One source of accidents are those due to on-board fires. Although extensive and dependable fire detection equipment presently exists within the cabin, detection of fire within the cargo hold has been less reliable [6]. In aircraft where cargo hold fire detection is required, the fire detection equipment presently used in many commercial aircraft relies on the detection of smoke. These smoke detectors are either optically based or depend on ionization of the particles. Although highly developed, these sensors are subject to false alarms with estimated false alarm rates varying from 10:1 to 500:1. This issue is complicated by the fact that some cargo areas are inaccessible to the flight crew during flight. The presence of false alarms decreases the confidence of pilots in these systems and may potentially cause accidents as pilots react to reported fires that may not exist. These false alarms may be caused by a number of sources including: changes in humidity, condensation on the fire detector surface, and contamination from animals, plants, or other contents of the cargo bay.

A second, independent method of fire detection to complement the smoke detection techniques, such as the measurement of chemical species indicative of a fire, will help reduce false alarms and improve aircraft safety. Although many chemical species are indicative of a fire, two species of interest are CO and CO₂ [7]. Some requirements for these chemical sensors differ from those of leak detection and emission monitoring. The sensor must withstand temperatures ranging from -30° C to 50° C, pressures from 18.6 kPa to 104 kPa, and relative humidities from 0 to 95%. Different types of fires produce different chemical signatures [7]; the sensor must be able to detect the presence of a real fire and not be affected by the presence of gases common to the cargo hold or produced by contents of the cargo hold. The response must be quick, reliable, and able to provide relevant information to the pilot. All three applications discussed in this section share the common requirement that the sensor have minimal size, weight, and power consumption.

9.2 Emerging Sensor Technologies

In order to meet the chemical sensor needs of aerospace applications described in section 9.1, the development of a new generation of sensor technologies is necessary. Active development of chemical sensor technology to meet these needs is taking place at NASA Lewis Research Center (NASA LeRC) and Case Western Reserve University (CWRU) based on progress in two types of technology: 1) Micromachining and microfabrication technology to fabricate miniaturized sensors; and 2) Development of silicon carbide (SiC) to provide electrical components and sensors operable at high temperatures. This section will give a brief overview of these technologies while Section 9.3 discusses chemical sensor technology development and application.

9.2.1 Microfabrication and Micromachining Technology

Micorfabrication and micromachining technology (or MicroElectroMechanical Systems, MEMS, based technology) is derived from advancements in the semiconductor industry. An excellent review of microfabrication technology is given by Madou in reference 8. Of particular utility in chemical sensor development are the microfabrication techniques of lithographic reduction, thin film metallization, photoresist patterning, and chemical etching. These processes allow the fabrication of very small sensor structures. The ability to batch fabricate these sensors using 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 etching and the sacrificial layer method. Chemical anisotropic etching is an etching procedure that depends on the crystalline orientation of the substrate. The etching rate depends on the crystal plane of the substrate allowing etching to take place in a chosen direction. This technique may be used to selectively etch a silicon substrate producing a suspended diaphragm structure. This diaphragm structure underneath the sensing element, combined with a heater and temperature detector, is useful as a sensor platform when temperature control is necessary. A diaphragm structure etched beneath the sensing element, heater, and temperature detector results in a small thermal mass and minimizes heat loss and energy consumption. 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. In chemical sensing

applications, this technique can be used to make a chamber structure surrounding the sensor and protecting the integrity of the sensing element.

These processes allow the fabrication of sensors which have minimal size, weight and power consumption, can be tailored for a given application, and can be mass produced. This sensor processing is done using Si either as a substrate on which a structure is built or as a semiconductor that is part of an electrical circuit. 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 well below 300°C. Thus, high temperature electronics must be developed if semiconductor based sensors such as diodes or capacitors are to be used at temperatures significantly above 300°C. The most advanced high temperature electronic material is SiC. An overview of SiC-based high temperature electronics is given in the next section.

9.2.2 SiC-Based High Temperature Electronics

Silicon carbide based semiconductor electronic devices are presently being developed for use in conditions under which conventional semiconductors cannot adequately perform. Due to its wide band gap and low intrinsic carrier concentration, SiC operates as a semiconductor at temperatures significantly higher than that possible with silicon (Si) semiconductor technology. SiC is now available commercially and processing difficulties associated with its production are being addressed. [9]

Silicon carbide occurs in many different crystal structures (called polytypes) with each crystal structure having its own unique properties. In many device applications, SiC's exceptionally high breakdown field (> 5 times that of Si), wide band gap energy (> 2 times that of Si), and high thermal conductivity (> 3

times that of Si) could lead to substantial performance gains [9]. Combined with other material properties, such as its superior mechanical toughness, SiC is an excellent material for use in a wide range of harsh environments.

Silicon carbide's ability to function in extreme conditions is expected to enable significant improvements to a wide range of applications and systems. These include 1) greatly improved high-voltage switching for energy savings in public electric power distribution 2) more powerful microwave electronics for radar and communications, 3) electronics, sensors, and controls for cleaner-burning more fuel-efficient jet aircraft and automobile engines [9]. One potential major application of SiC as a semiconductor is in a gas sensing structure. How this is might be accomplished is discussed in Section 9.3.2.

9.3 Chemical Sensor Development and Applications

In order to meet the needs of aerospace applications, a new generation of chemical sensor technology needs to be developed. The sensor design and sensing approach depends strongly on the application but each application has common factors: 1) Optimally, the detection of gas should take place in-situ. Thus, the sensor must operate in the environment of the application; and 2) The sensor must have minimal size, weight and power consumption. Ideally, it should be readily multiplexed to allow a number of sensors to be place in a given region and the results of the measurement fed back to monitoring hardware or software.

This section will discuss the work at NASA LeRC and CWRU using microfabrication technology and SiC semiconductor technology to develop H_2 , C_xH_y , NO_x, CO, O₂, and CO₂ sensors. Three different

sensor platforms are used: a Schottky diode, a resistor, and an electrochemical cell. A brief description is given of each sensor type and its present stage of development. The 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.

9.3.1 Si-Based Hydrogen Sensor Technology

In order to meet the needs of launch vehicle leak detection applications to detect hydrogen, NASA LeRC and CWRU have developed palladium (Pd) alloy Schottky diodes on Si substrates. 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 hydrogen detection, the metal is hydrogen sensitive. The most common Schottky diode structure used for hydrogen detection is the Pd-SiO₂-Si structure. Hydrogen disassociates on the Pd surface and diffuses to the Pd-SiO₂ interface affecting the electronic properties of the diode [11]. Palladium alloys are more resilient than pure Pd to damage caused by high concentrations of hydrogen [12]. Although the sensor signal is affected by the presence of oxygen, the sensor does not need oxygen to operate.

The NASA Lewis/CWRU design uses a PdCr alloy due its ability to withstand exposure to 100% hydrogen [13]. The sensor structure is shown in Figure 1 and includes a PdCr Schottky diode, a PdCr resistor, a temperature detector, and a heater all incorporated in the same chip. The sensor dimensions are approximately 2.2 mm on a side. The combination of the Schottky diode and resistor results in a sensor with a broad detection range; the Schottky diode provides sensitive detection of low concentrations of hydrogen while the resistor provides sensitivity up to 100% hydrogen.

The PdCr sensor is presently under development for use on the NASA experimental vehicle, the X-33, in its hydrogen leak detection system. Hardware and software have also been included with the sensor to provide signal conditioning and control of the sensor [14]. An example of operation of the complete system with signal conditioning and temperature control is shown in Figure 2. The temperature is held constant at 70°C while the sensor package is exposed to hydrogen concentrations from 1000 ppm to 10%. The output is signal conditioned and presented in millivolts. The diode signal shows the highest sensitivity and quickest recovery times at lower concentrations while the resistor provides high sensitivity at higher hydrogen concentrations. This complete system is also scheduled for a demonstration flight on the Shuttle for the fall of 1998.

9.3.2 SiC-based Hydrogen and Hydrocarbon Detection

In order to meet the needs of leak detection and emission monitoring applications, hydrogen and hydrocarbon sensors are being developed using SiC semiconductors. Like the Si-based system discussed in Section 9.3.1, the SiC-based Schottky diode does not need oxygen to operate. In contrast to the Si-based system, the SiC-based diodes can operate at high enough temperatures to allow the detection of hydrocarbons. Further, SiC can operate at high enough temperatures as a semiconductor to be used without cooling in the engine environment in some emission monitoring applications. The development of high temperature SiC-based gas sensors for use in harsh environments has focussed on the development of a stable Schottky diode. 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. Given a fixed forward bias voltage, this dipole layer affects the barrier height of the diode resulting in an exponential change of current flow with the change in barrier height. The magnitude of this effect can be correlated with the amount of hydrogen and other gas species (especially oxygen) present in the surrounding ambient. The detection of gases such as hydrocarbons is made possible if the sensor is operated at a temperature high enough to dissociate hydrocarbons and produce atomic hydrogen. The resulting atomic hydrogen affects the sensor output in the same way as molecular hydrogen [4, 15-16]

Several SiC-based Schottky diode structures have been investigated. Two MS structures investigated are Pd on SiC (Pd/SiC) and PdCr on SiC (PdCr/SiC). Very sensitive detection on the order of 100 ppm of hydrogen and hydrocarbons in both inert and oxygen containing environments has been demonstrated. Although the Pd/SiC sensor response is affected by prolonged high temperature heating, the PdCr/SiC structure has been shown to be much more stable with comparable sensitivity [4, 17].

A third structure involves the incorporation of chemically reactive "insulators" into the SiC-based Schottky diode structure. A wide variety of materials, e.g. metal oxides such as SnO_2 , are sensitive to C_xH_y and NO_x at high temperatures. These materials could be incorporated as a sensitive component into MIS structures and, unlike silicon devices, SiC-based devices can be operated at high enough temperatures for these materials to be reactive to gases such as C_xH_y and NO_x . This structure has been demonstrated using tin oxide (SnO_2) to have improved stability and significantly different responses than the Pd/SiC structure [17]. Other research includes the development of complete high temperature packaging for the SiC-based sensor packaging to allow operation in temperatures greater than 300°C. The objective is to package the sensor, with connections to the outside world, for operation in engine environments. A prototype sensor package is shown in Figure 3. Thus, issues such as stable electrical contacts to SiC and the integrity of electrical insulation at high temperatures are of importance. Further, micromachining SiC is under investigation to allow formation of, for example, diaphragm structures which decreases the sensor's thermal mass and power consumption in the same manner as is done with Si structures.

9.3.3 Nanocrystalline Thin-Film Detection of NOx and CO

The detection of NO_x and CO is important for both emission monitoring and fire detection. NASA/CWRU have been developing a microfabricated and micromachined Si-based structure which uses a thin film resistor to measure NO_x and CO. In this approach, Si is used as a platform on which the structure necessary for the sensor is fabricated. This sensor structure, shown in Figure 4, includes a sensing element, temperature detector, and heater. 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 elements are over a diaphragm region. This minimizes the thermal mass of the sensing area thereby decreasing power consumption. 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. Changes in conductivity of the SnO₂ across the interdigitated electrodes is measured and correlated to the NO_x and CO concentration. A major component of this development work is to stabilize the SnO₂ for long-term, high temperature operation. Drift in the properties of SnO₂ with long term heating due to grain boundary annealing have been previously noted [18-19]. This drift results in changes in the sensor output with time and reduces sensor sensitivity. In order to stabilize the SnO₂ structure for long term operation, the fabrication of nanocrystalline SnO₂ is being investigated. The SnO₂ grains size shown in Figure 5 is approximately 10 nanometers. Nanocrystalline materials have several inherent advantages over conventionally fabricated materials including increased stability and sensitivity at high temperature [20-21]. Several prototypes of these devices have been fabricated and evaluated. The detection of NO₂ has been demonstrated down to the 5 ppm level at 360°C with the highest level of sensitivity in the lower ppm with a very stable response [22]. Similar results are seen with the detection of CO. Doping the SnO₂ is envisioned in order to improve the selectivity of the sensor to a specific gas.

9.3.4 Electrochemical Cell Oxygen Detection

The development of a microfabricated O_2 sensor has been initiated for aerospace safety applications but, as demonstrated in the automotive emissions control example, significant applications exist in the area of emission control. Commercially available O_2 sensors are typically electrochemical cells using ZrO_2 as a solid electrolyte and platinum (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 current manufacturing procedure of this sensor, using sintered ZrO_2 , is relatively costly and results in a

complete sensor package with power consumption on the order of several watts.

The objective of this research is to develop a ZrO_2 solid electrolyte O_2 sensor using microfabrication and micromachining techniques. As noted above, the presence of O_2 often affects the response of H_2 , C_xH_y , 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.

A schematic of the oxygen sensor design is shown in Figure 6. As discussed in the NO_x detection section above, microfabricating the sensor components onto a micromachined diaphragm region allows the sensor to have decreased energy consumption. 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. Preliminary testing of the complete O_2 sensor has been accomplished and further improvements on the design are planned.

9.3.5 NASICON-Based CO2 Detection

A combined CO_2/CO sensor is of interest not only for fire safety applications but for aeronautic combustion monitoring applications as well. The detection of CO_2 is, like the detection of oxygen, based on the use of a solid electrolyte. However, the CO_2 sensor will use NASICON (sodium super ionic conductor) as the solid electrolyte. NASICON is an ionic conductor composed of Na₃Zr₂Si₂PO₁₂ which has previously been shown to be sensitive for CO_2 detection. The preparation of NASICON will be performed using a sol-gel technique. The sensor structure will be similar to that of Figure 6: a microfabricated, miniaturized sensor structure which can be incorporated with other sensors such as the CO sensor.

9.4 High Temperature Electronic Nose Concept

Successful development of the individual high temperature sensors discussed above will allow the formation of a sensor array which will allow detection of a number of gases on a single chip. For example, the formation of an array of the sensors discussed in this paper will detect H_2 , C_xH_y , NO_x , CO_2 , O_2 , and CO_2 . Development of a such a microfabricated gas sensor array operable at high temperatures and high flow rates would be a dramatic step in allowing the monitoring/control of emissions produced by an aeronautic engine. This gas sensor array would, in effect, be a *high temperature* electronic nose and be able to detect a variety of gases of interest. Several of these arrays could be placed around the exit of the engine exhaust to monitor the emissions produced by the engine. The signals produced by this nose could be analyzed to determine the constituents of the emission stream and this information then used to control those emissions. Microfabrication of these sensors is necessary: a conventional bulky system would add weight to the aircraft and impede the flow of gases leaving the engine exhaust.

The concept of an electronic nose has been in existence for a number of years. Commercial electronic noses presently exist [23] and there are a number of efforts to develop other electronic noses. However, electronic noses often depend significantly on the use of polymers and other lower temperature materials to detect the gases of interest. These polymers are generally unstable above 400°C and thus

would not be appropriate for use in harsh engine environments. Thus, a separate development is necessary for a high temperature electronic nose.

9.5 Commercial Applications

The gas sensors being developed at NASA LeRC and CWRU are meant for aerospace applications but can be used in a variety of commercial applications as well. For example, an early design of the Pd-alloy hydrogen sensors, using PdAg, were adapted from space applications for use on 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 LeRC/CWRU sensors so the sensors can be used 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 to test for leaks in the valves and fittings of natural gas vehicles. 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 hydrocarbon, NO_x and oxygen sensors are being developed for aeronautic applications but can also 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. Other possible applications include combustion process monitoring, catalytic reactor monitoring, alarms for hightemperature pressure vessels and piping, chemical plant processing, polymer production, and volatile organics detection.

9.6 Summary

The needs of aerospace 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. Sensor technology is being developed to address these requirements 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. The combination of these technologies may allow the development of a high temperature electronic nose to provide complex chemical analysis in harsh environments. Sensors designed for aerospace applications also have significant commercial applications. Although each application is different and the sensor needs to be tailored for that environment, the base technology being developed for aerospace applications can have significant impact on a range of fields.

9.7 Acknowledgments

The authors would like to acknowledge the contributions of Dr. Philip G. Neudeck, Dr. Larry Matus, Dr. Jih-Fen Lei, Dr. Gustave Fralick, Dr. Herbert Will, Dr. David Larkin, and Dr. Daniel L. P. Ng of NASA LeRC, Dr. Liang-Yu Chen of AYT Corporation, and the technical assistance of Dak Knight, Drago Androjna and Carl Salupo of Cortez/NASA LeRC.

References

[1] "Aeronautics and Space Transportation Technology: Three Pillars for Success, available at http://www.hq.nasa.gov/office/aero/oastthp/images/3pillars2.pdf

[2] Hunter, Gary W., "A Survey and Analysis of Commercially Available Hydrogen Sensors", NASA Technical Memorandum 105878, November 1992.

[3] Hunter, Gary W., "A Survey and Analysis of Experimental Hydrogen Sensors", NASA Technical Memorandum 106300, October 1992.

[4] Chen, L.-Y., et al. "SiC-Based Gas Sensors", *Proc. Third International Symposium on Ceramic Sensors*, San Antonio, TX, 190th Meeting of the Electrochemical Society Inc., Oct. 6-11, 1996, pp. 92-105.

[5] Logothetis, E. M., "Automotive Oxygen Sensors," *Chemical Sensor Technology*, Vol. 3, N. Yamazoe, ed., Kodansha Ltd., 1991, pp. 89-104.

[6] "Nuisance Alarms in Aircraft Cargo Areas and Critical Telecommunications Systems: Proceeding of The Third NIST Fire Detector Workshop", Grosshandler, W. L., Editor, Dec. 1997, Gaithersburg, MD, NISTIR 6146.

[7] Grosshandler, W. L., "A Review of Measurements and Candidate Signatures for Early Fire Detection," NISTIR 555, Nat. Inst. of Stand. And Tech., Gaithersburg, MD, January 1995.

[8] Madou, M., Fundamentals of Microfabrication, CRC Press, Boca Raton, FL, 1997.

[9] Neudeck, P. G., "Progress in Silicon Carbide Semiconductor Electronics Technology", Journal of Electronic Materials, vol. 24, 1995, pp. 283-288.

[10] Cree Research, Inc., 2810 Meridian Parkway, Suite 176, Durham, NC 27713.

[11] Lundstrom, I., M. Armgarth, and L. Petersson, "Physics with Catalytic Metal Gate Chemical Sensors", *CRC Critical Reviews in Solid State and Materials Sciences*, vol. 15, 1989, pp. 201-278.

[12] Hughes, R. C., et al., "Thin Film Palladium and Silver Alloys and Layers for Metal-Insulator-Semiconductor Sensors", J. Appl. Phys., Vol. 62, 1987, pp. 1074-1038.

[13] Hunter, G. W., et al., "A Hazardous Gas Detection System For Aerospace And Commercial Applications," Presented At 31st Joint Propulsion Conference, Cleveland, OH, July 13-15,1998, AIAA-98-3614.

[14] Makel Engineering, 1028 Maurader Rd., Chico, CA, 95973.

[15] Baranzahi, A., et al., "Fast Responding High Temperature Sensors For Combustion Control", Proceedings, 8th International Conference on Solid-state Sensors and Actuators, and Eurosensors IX, Stockholm Sweden, 1995, pp. 741-744.

[16] Hunter, G. W., et al., "Silicon Carbide-Based Hydrogen and Hydrocarbon Gas Detection" presented at the 31st AIAA Joint Propulsion Conference, San Diego, CA, July 10-12, 1995 AIAA Paper 95-2647.

[17] Hunter, G. W. et al., "SiC-Based Schottky Diode Gas Sensors", Proceedings of International Conference on SiC and Related Materials, Stockholm, Sweden, Sep. 1-7, 1997.

[18] Ogawa, H., M. Nishikawa, and A. Abe, "Hall Measurement Studies and an Electrical Conduction Model of Tin Oxide Ultrafine Particle Films", *Journal of Applied Physics*, vol. 53, 1988, pp. 4448-4455.

[19] Xu, C., et al., "Grain Size Effects on Gas Sensitivity of Porous SnO₂-Based Elements, Sensors and Actuators, B, vol. 3, 1991, pp. 147-155.

[20]Yoo, D. J. et al., "Effects of Thickness and Calcination Temperature on Tin Dioxide Sol-Derived Thin-Film Sensor", *Journal of Electrochemical Society*, vol. 142, 1995, pp. L105-L107.

[21] Vogel, R., P. Hoyer, and H. Weller, "Quantum-Sized PbS, CdS, Ag₂S, Sb₂S₃, and Bi₂S₃ Particles as Sensitizers for Various Nanoporous Wide-Bandgap Semiconductors", *Journal of Physical Chemistry*, vol. 98, 1994, pp. 3183-3188.

[22] Hunter, G. W. et al., "Chemical Sensors for Aeronautic and Space Applications II" presented at Sensors Expo 98, San Jose, CA, May 1998.

[23] Gardner, J. W., and P. N. Bartlett, "A Brief History Of Electronic Noses", Sensors and Actuators, B, 18(1-3), 1994, 211-20.



۰.

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 resistor has been added to the PdCr based sensor design for high hydrogen concentration measurements.



Figure 2. Typical sensor response and recovery to step changes in hydrogen concentration for a temperature controlled PdCr Schottky diode and resistor. The diode and resistor response is shown to hydrogen in nitrogen from 100 ppm to 10%. Also shown is the accompanying temperature plot during this exposure. Courtesy of Makel Engineering [14]



Figure 3. Prototype SiC-based Gas Sensor



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.



Figure 5. Nanocrystalline SnO₂ after annealing at 600°C for 30 minutes.



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.