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NIST Special Publication 865

NIST Workshop on Gas Sensors: Strategies for Future Technologies

Proceedings of a Workshop Held in Gaithersburg, Maryland
September 8–9, 1993

Steve Semancik, Editor

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[1] At Boulder, CO 80303.

[2] Some elements at Boulder, CO 80303.

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Abstract

This Proceedings issue describes a Workshop on gas sensing held in Gaithersburg, MD, September 8-9, 1993. Future gas sensors with improved response characteristics, higher reliability, and lower cost can be expected to have increased application in diverse areas, including environmental monitoring, process control, and personal safety. This Workshop brought together gas sensor manufacturers, present and potential users, and researchers to explore ways to incorporate research discoveries and emerging technologies more efficiently into new, high-performance sensors. The Proceedings includes publications on invited and contributed presentations, reports on discussions of Emerging Technologies and Commercialization and Standards issues, and reports summarizing breakout sessions on gas sensing for Process Control in Manufacturing, Indoor Air Quality and Personal Safety, Outdoor Environmental Monitoring and Site Remediation, and Automotive and Other Transportation.

EXECUTIVE SUMMARY

NIST WORKSHOP ON GAS SENSORS: STRATEGIES FOR FUTURE TECHNOLOGIES

September 8-9, 1993
National Institute of Standards and Technology
Gaithersburg, MD 20899

Motivation

Advances in materials, electronics, microfabrication, and the understanding of transducing chemistry are creating opportunities for developing new generations of gas sensors with improved performance and lower cost. Such improvements can be expected to greatly increase the application of gas sensors in wide-ranging areas including personal safety, process control and environmental monitoring. While the market potential is large, workers in this field often recognize a time lag for incorporating new discoveries into sensing products. This Workshop, entitled Gas Sensors: Strategies for Future Technologies, was held as a timely attempt to identify and discuss the barriers connected with developing and commercializing new gas sensor devices suited to an expanding range of compositional monitoring applications. Most other forums on sensor development and use have centered around research conferences and highly specific application areas. A unique feature of this Workshop was that it provided an open environment with broad participation focused both (1) on promising technologies for creating reliable devices, and (2) toward exposing weaknesses in the chain of research, development, commercialization and application that can negatively impact domestic competitiveness in the field of gas sensing. Chemical gas sensing is at a relatively young stage in its development, especially in comparison with other technologies, such as integrated circuitry or even certain kinds of physical sensors (including accelerometers). While strategies for accelerating development were focused on, it was not the intent of this first NIST Gas Sensor Workshop to produce a detailed roadmap for the field.

Workshop Organization

To comprehensively examine various perspectives on relevant issues, this two-day Workshop encouraged direct interactions between gas sensor manufacturers, present and potential users, and researchers. The Workshop included a collection of 12 invited presentations selected to describe not only differing gas sensing technologies and measurement needs, but also to represent the viewpoints held at the various types of institutions and agencies in attendance. Contributed papers were presented in a poster session held on the afternoon of the first day. A special (off-site) poster session was also arranged for those who wished to display gas sensor product information.

Two types of discussion sessions were held during the second day. Cross-cutting, application-oriented Breakout Groups, of manageable size for interactive discussion, were held in 4 areas: Process Control in Manufacturing (Chaired by John Steichen of Dupont), Indoor Air Quality and Personal Safety (Chaired by Jarell Wenger of Johnson Controls), Outdoor Environmental Monitoring and Site Remediation (Chaired by Barry Wise of Batelle Pacific Northwest Laboratories), and Automotive and Other Transportation

(Chaired by Galen Fisher of General Motors Research and Development Center). Within these sessions various sensing approaches were compared for a related class of gas measurement problems. Participants were encouraged to move between the various sessions, and a significant fraction did so. The second type of discussion had more of a town-meeting format, and also served as the closing session of the Workshop. Two primary themes were focused on in the latter discussion: The Role of Emerging Technologies in Gas Sensing, and Commercialization and Standards Issues.

During the first day a representative of the Advanced Technology Program made an informal presentation outlining the operation and direction of this funding component of NIST. Attendees were also offered an opportunity to tour 8 sensor-related facilities at NIST. The Workshop was attended by approximately 135 persons from 30 states, as representives of small companies, large companies, federal agencies, government laboratories and universities.

Summary of Presentations and Discussion Sessions

The Workshop explored approaches for incorporating research discoveries and emerging technologies into the production of high-performance sensors (as distinguished from larger, more costly monitoring instruments). A variety of sensing schemes were presented, and their relative merits, suitability and shortcomings for certain categories of use were discussed. In considering benefits and limitations of various sensing technologies, markets, operational specifications, manufacturability, calibration and standards issues were addressed.

The invited speakers represented 2 small companies, 4 large companies, 2 agencies, 2 government laboratories and 3 universities. Among the gas sensor types discussed were thermal, surface acoustic wave, electrochemical, infrared, fiber optic, semiconducting oxide, catalytic gate and solid electrolyte. Existing commercial devices received attention as did novel concepts for new device development. In certain cases, instruments and sampling methodology were described in monitoring situations where sensors have not yet made inroads. Gas and vapor chemical monitoring problems were defined for 5 major areas including environmental testing and restoration, waste management, industrial safety, chemical processing and automotive emissions. Implications for these and other applications were addressed briefly when the first invited speaker discussed world market projections. Details for all of the invited presentations can be found in articles published in this volume.

The conclusions reached in the application-oriented Breakout Groups are summarized briefly below (and described more fully in the Chairpersons' reports found in the Breakout Groups section of this volume). While all Breakouts were given a base level of guidance for discussions, the Discussion Leaders and groups of participating individuals created a unique environment in each of the 4 areas. The open discussion of Emerging Technologies centered on new device concepts, micromachining, neural networks, and packaging and telemetry, while that on Commercialization and Standards was primarily concerned with a range of business, regulatory, and technical topics (see also articles in the text).

Process Control in Manufacturing

Discussion in this Group indicated that several factors have limited the use of sensors, thus far, for industrial process control applications. First, the area of process control is so diverse that it is difficult to define performance requirements. The level of secrecy that surrounds certain industrial processes further compounds the task of problem definition. Also, since chemical production lines cannot usually serve as test beds, sensors must be proven reliable before they will be applied. The importance of this point is underscored by the high installation cost that can occur for incorporating sensors into many types of chemical process lines, even if the sensors themselves are inexpensive. Once installed to serve process control functions, the sensors should have an extended life without significant maintenance.

The Process Control Group made a number of suggestions to guide sensor development for their field. Their primary suggestions included:

> concentrate on those measurements where traditional techniques are not available or reliable, or where there is a specific need for low-cost monitoring
>
> > Key areas identified:
> >
> > > rugged sensors for combustion and incinerator control
> > >
> > > sensing of fugitive emissions (not necessarily for "process control") of species such as methyl isocyanate, phosgene, vinyl chloride and HF
> > >
> > > real-time detection of low-level moisture
>
> involvement by NIST in coordinating and guiding sensor development through efforts aimed at:
>
> > > acting as a clearing-house to make available to the sensor community information on the "real" gas sensing needs and operating conditions for control of industrial processes
> > >
> > > creating, through increased funding, an effective development bridge between sensor researchers and sensor manufacturers
> > >
> > > effectively matching players to produce demonstrations of performance and payoff in real world applications

The Group agreed that this NIST-sponsored Workshop was an important first step in their recommended involvement for NIST in advancing sensors into process control applications. Additionally, members of the Group have been instrumental in helping to found a Process Chemical Sensor Forum, made up of industrial representives, which will meet periodically at NIST-Gaithersburg to voice measurement needs.

Indoor Air Quality and Personal Safety

This Breakout Group considered sensing issues relating to indoor air quality (IAQ), industrial hygiene and general health and safety. Unlike the Process Control Group, this Group indicated that attainment of low ($100's) or very low ($10's) cost sensors was critical to opening up extremely large commercial and residential markets in future years.

Minimal calibration and long term reliability were emphasized as essentially mandatory attributes.

Within this session, species and concentrations of gases to be monitored were identified in the areas of IAQ (including SO_2, CO, O_3, CO_2, radon, chlordane, SF_6, selected refrigerants and tobacco smoke), industrial environments (including O_2, CO, H_2S and freon) and hospitals, health and safety (including halothanes, NO, anesthesia gases, ethylene oxide and formaldehyde). The differing sensing situations presented for industrial hygiene and IAQ applications were described, respectively, as a case involving the detection of a (relatively) limited number of harmful compounds, compared to the measurement of hundreds of potential compounds, including volatile organics, at a 100-fold or higher sensitivity level. For certain applications, sensitivities ~ 10's ppb are required.

The Group felt that insufficient technological development represented the major impediment to sensor commercialization at this time. The exceptions which have seen significant deployment for IAQ are devices for monitoring CO_2, and more recently CO. It was indicated that integrated units measuring total volatile organics, CO_2, relative humidity and temperature could have a major impact in the heating/ventilation/air conditioning market, assuming they could be produced at a low enough price (estimates ranged from below $300 to $30). Other commercialization hurdles exist in these application areas, besides price. Reliability is extremely important and false alarms cannot be tolerated. Insurance issues and regulatory policies can also strongly influence acceptance.

The primary suggestions to accelerate sensor development in the Indoor Air Quality and Personal Safety area were:

> to increase investment in several technological areas (including surface acoustic wave and non-dispersive infrared) that hold higher levels of promise, in order to move across the "gap" from research scale to prototype products (while funding approaches such as the NIST ATP program were identified, it was felt that additional mechanisms for funding development might be required for small companies)
>
> to develop methods by which users could interact more directly with researchers to influence development directions and to help establish testing guidelines

Outdoor Environmental Monitoring and Site Remediation

The structure of this Breakout Discussion fell into 3 main sections relating to applications, specific issues for environmental sensing, and promising research directions. The Group identified and discussed stack emissions and fugitive emissions as 2 areas of major market potential. Environmental and safety concerns may dictate that detection for each of these classes could soon require continuous monitoring capabilities. The monitoring and cleanup of waste sites represents another sizeable challenge for sensor development. Volatile organics must be measured to screen sites and determine the effectiveness of remediation procedures. Hydrogen and other gases must be monitored in connection with nuclear waste storage and the identification of vapors above test-well water can be useful in locating groundwater contamination.

It was agreed that a number of important issues exist for environmental measurements. Among those expressed were (1) determining whether the measurement is for characterization, monitoring or screening, (2) protecting against the effects of fouling and corrosion, (3) dealing with unknown and uncontrolled backgrounds, (4) increasing efforts to develop properly-suited and reliable active coatings, (5) being aware that a wide range of sensor costs can be tolerated for varying environmental applications, (6) the shortage of reliable performance data in existence for environmental sensing systems, (7) developing methods for eliminating or correcting for sensor drift, (8) accomplishing sensor portability for the many applications that would require or benefit from this characteristic, (9) using concurrent engineering in developing cost-effective packaging, and (10) making reliable baseline data available for naturally-occurring chemicals in various environments.

The Environmental Breakout Group identified several research and development areas which should receive concerted efforts. The broad range of specific chemical measurements in environmental and remediation situations requires a significant materials research effort to develop and tailor selective coatings for marriage with existing and new detection schemes. Since response characteristics are often nonlinear, nonlinear and multivariate calibrations must also be developed by those working in chemometrics and pattern recognition. Widespread utility of new sensors will depend on their reliability, cost, and in certain cases, on their size. Efforts on developing streamlined manufacturing processes to reproducibly fabricate batches of integrated, miniature sensors could be rewarded by creating devices that would be accepted in the marketplace more rapidly. The Group also indicated that further development of fiber optic-based sensors would permit the power of spectrophotometry to be applied in many application areas and that biological sensors would also play an important role for certain environmental measurements.

The Group concluded that the largest barriers to environmental sensor commercialization related to:

insufficient development of active films

a lack of adequate support for the final development stage

uncertainty about potential market size for a given device.

Automotive and Other Transportation

Gas sensor needs for the automotive industry dominated the discussion in this Breakout Group. These needs are being imposed by the 1990 Clean Air Act as well as other new rules connected with the EPA and California Air Resources Board.

Current legislation was discussed which calls for auto on-board diagnostics (OBDs) by 1996. OBDs would make a driver aware when any component affecting emissions is not functioning properly. Monitoring of the catalytic converter, which converts hydrocarbons, CO and NO_x to CO_2, H_2O and N_2, is one of the sensing problems receiving considerable attention in this regard. A dual or multiple O_2 sensor approach is often used now, but a more direct method would be preferable. It was also pointed out that more stringent emission standards slated for the years ahead will probably make converter monitoring even more complex and require gas sensors of high sensitivity. The report of this Group includes a brief table on detection specifications for certain target gases and considerable attendant discussion dealt with the operational demands under which measurements must be performed. Among the conditions and requirements are operation over a wide temperature range, under-car spatial constraints, 12V DC compatibility, response times in the 10-20 second regime, and survivability (preferably without a service recalibration) for 100,000 miles.

Several proposed sensing solutions for the demanding task of automotive exhaust measurement were presented by representatives from 3 companies. Following the brief presentations, the Group debated the advantages and shortcomings of the various technologies. A dual calorimetry method was described for measuring CO, hydrocarbons, NO_x and SO_2 with response times of several seconds. It was pointed out that this approach requires sufficient oxygen to oxidize CO and hydrocarbons, and that CH_4 sensitivity may be low. A nondispersive infrared approach with a 10 m equivalent pathlength was presented as a possible low-cost method for monitoring hydrocarbons, CO_2, CO, NO_x, SO_2 and ozone. Concerns for this approach centered on stability and durability of the system under operating conditions. The third approach described in this session utilized a group of solid state and electrochemical devices, sometimes combined with selective membranes, in order to measure various oxidizing and reducing gases.

While considerable challenges exist for sensor developers in meeting the requirements for low, transitional-low and ultra-low emission vehicles (LEVs, TLEVs and ULEVs) in this country, it was explained that a somewhat lower level of interest in lean burn engines seems to exist elsewhere in the world. Many participants in the Group felt that considerable materials research to develop better sensing films will be paralleled by efforts aimed at improving catalytic converters in order to meet rapidly-approaching domestic emissions control deadlines.

General Comments

Participants at this first NIST Workshop on gas sensors felt it a rather unique and diversified forum which served a number of useful functions including defining a range of gas sensing problems, presenting a variety of existing and developing technologies and directly addressing problems encountered in commercialization (see also the Commercialization and Standards report in the Discussions section). The Breakout Sessions, while concerned with differing application areas, showed a high degree of commonality when it came to identifying barriers and challenges to successfully producing, marketing and using gas sensing devices. Each of the sections below indicates a major barrier, and then lists expressed actions for overcoming that barrier.

- ***Limitations in reliability and sensing function.*** Issues here go to the heart of the transduction process and require cross-cutting research on a number of fronts. Basic studies at NIST and other government laboratories and universities should provide foundational information on improved and new active materials, sensing mechanisms and new sensing concepts. To provide increased reliability and utility at acceptable costs, standard methods of (micro)fabrication and packaging should be developed and employed to the maximum extent. Schemes for low power operation are required for deployment in many applications. Effective signal processing routines must also be developed to provide recognition and calibration functions.

- ***Existence of a substantial "development gap" between promising research results and creation of a successful gas sensor product.*** The problem of connecting the research world and the real world is nothing new, but successful channeling between these sectors in the area of gas sensing is expected to be particularly fruitful. Contact and communication are key elements of a solution here, and the need to create effective mechanisms for researcher-manufacturer interactions and partnering was widely voiced. Cooperative research and development agreements (CRADAs) and guest worker and exchange programs should be continued and expanded. Funding sources targeted at such programs could catalyze increased inter-institutional activity.

- ***Product inertia and hesitance of sensor companies to invest into new technologies and markets.*** The push forward from existing product lines into new technologies and markets often ties considerable risk with the potential for substanial profit. In gas sensing, the costs of R & D, production scale-up and marketing can be larger than in other fields, and manufacturers often feel it necessary to share the costs of high risk development. Insufficient funding of the high risk development regime was among the problems most universally expressed at the Workshop. Attendees felt that a focused sensor competition through the NIST Advanced Technology Program could provide one important source of support for this area in the years ahead. The need for information on existing and projected markets in a range of application areas was also expressed.

- ***Uncertainty concerning the methods and value of existing sensor performance demonstrations.*** Manufacturers seek effective and rapid procedures for certification of their sensor products so that they can be used in regulated and personal safety applications. Users on the other hand, demand reliable performance specifications under conditions appropriate for judging whether a device will meet their particular monitoring need. Many participants indicated they now see the need for application-oriented test beds to properly evaluate sensing devices. They also expressed a potential role for NIST, possibly in an oversight position, in proving the capabilities of sensing technologies and in providing a nonbiased base of performance data.

It is worth noting that while it is unlikely that anyone would complain about using a small, reliable, low-cost sensor, there were a number of expressed situations where users indicated they could tolerate larger and considerably more expensive devices or systems. In those many cases where size, power requirements and cost are crucial, emerging technologies, such as micromachining (see also the Emerging Technologies report in the Discussions section), hold the potential to have great impact. A key element in developing future generations of high performance gas sensor devices is the well-coordinated integration of active materials with new structures and intelligent electronics. Well-matched active film/electronics combinations and the use of clever operating modes can amplify the inherent response characteristics of sensing materials and also make possible self-calibration and reset features critical for many applications that will require user-friendly sensors. Developers should therefore keep an eye to new enabling techniques and discoveries. However, they should also incorporate proven technologies, such as remote telemetry, in order to benefit in situations where harsh conditions or wide deployment are encountered.

Finally, gas sensor development was represented at this Workshop as an extremely broad technological challenge with the potential for great commercial and societal reward. Success, however, requires the assembly of varied resources and a mixture of talents. The National Institute of Standards and Technology heard the messages delivered by sensor users, developers and researchers during this 2-day meeting, and is reassessing its role in an effort to more effectively provide financial, technical, informational and partnering support in the field of gas sensing.

Acknowledgments

The organizers wish to thank all attendees for their participation in this Workshop. Special thanks go to the invited speakers, both for their excellent presentations, and for the camera-ready manuscripts they provided for this volume. Those who led discussions and took responsibility for developing reports on their sessions are owed a great debt of gratitude as well. The organizers also wish to acknowledge the assistance and support given by the Conference Program and Facilities staff at NIST in coordinating logistics for the Workshop.

Disclaimer

The views, conclusions, and recommendations expressed at this Workshop and those reported in this Proceedings are not necessarily those of the National Institute of Standards and Technology.

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Proceedings of the NIST Workshop on Gas Sensors: Strategies for Future Technologies

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I. Invited Papers

Solid-State Gas Sensors: World Markets and New Approaches to Gas Sensing

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A short review of the world market for solid state gas sensors is presented. It is pointed out that there is a sizable sensor industry manufacturing rather unsatisfying products. New approaches are urgently needed in the industrial world. Some new approaches are described. We report on new types of silicon and ceramic based amperometric electrochemical gas sensors. These new devices feature relatively dry and dry triple points resulting in very fast response times. The relatively dry triple point devices form a class of sensors having characteristics somewhere between a solid state sensor and a wet electro-chemical cell. The dry triple point sensors are truly solid state in nature and open up the new field of gas electrochemistry. Also attempts at introducing micromachining techniques in the construction of solid state gas sensors are analyzed.

World Markets for Solid State Gas Sensor Markets

Based on Schroder [1], Yamazoe [2] , Harmer [3] and Tschulena [4] the 1990 total sensor market was $15 billion and is expected to grow further to $36 billion by the year 2000. The US has a 39 % share of that market, Western Europe 38 % and Japan 23 %. The most details on the sensor market product make-up are provided by the Japan Electronic Industry Development Association [2]. This organization found the gas sensor share of the total Japanese sensor market to be rather small i.e. 6 % (66 million gas sensors were actually produced in Japan in 1989 (with a dollar value of $207 million)). Using this same percentage world-wide we estimate that the 1990 total gas sensor market was about $0.9 billion. Among the various types of gas sensors, zirconia based oxygen sensors, semiconductor type gas sensors and humidity sensors make up 90 % of the total.

Three major markets currently exist for solid state gas sensors: the toxic and combustible gas sensor market, the automotive market and the energy conservation market (e.g. all drying operations). True solid state gas sensors are not used in the biomedical arena and we have not included any biomedical market figures here. Each of the three identified markets accounted for over $100 million in sales for 1990 in the United States alone, including the sensors and the electronic systems such as signal processors, displays and alarms to which they are attached.

Toxic and Combustible Gas Monitoring. In the US solid state gas sensors are mainly used in environmental monitoring and control applications in industry. Applications for the home market are not yet wide spread. In Japan the home market is at least as big as the industrial market due to the prevalent use of gas, often piped into homes in outdated gas supply lines. This necessitated the mandatory use of domestic gas detection systems. The US gas sensor market is concentrated mainly around chemical sensors used primarily in the petroleum, petrochemical, mining, and semiconductor industries. In the first three industries, the most common gases monitored include hydrogen sulfide, carbon monoxide, chlorine, methane, and flammable hydrocarbons. The most important gases monitored in the semiconductor industry are phosphine, arsine, and silane. The prevalence of hazardous and combustible gases in the petroleum industry is so high and the danger for workers so great that the impetus to develop chemical sensors for monitoring their presence is strong. Government regulations have further stimulated monitoring requirements. Back in the 1960's semiconductor sensors were heralded as the replacement for electrochemical sensors for these type of applications; however the electrochemical gas sensor sales figures (some with a growth rate of 30 % /year) suggest the opposite. The latter is probably due to the slow rate of improvements in the selectivity of solid-state gas sensors and the superior selectivity of electrochemical sensors brought on the market by companies like Neotronics and City Technology [5]. With respect to true solid state gas sensors the major innovations under way are in the area of applying micromachining technology to their manufacture (see below) with the promise to improve the power requirements. The selectivity and sensitivity factors still lack detailed applications.

For the past few years the overall market for toxic and combustible gas sensors has been stagnant due to the collapse of oil prices and the current recession. The 1990 market for small solid gas sensors and sensor systems in the toxic and combustible gas arena is some $120 million in the United States. Broken down by product, the US market for these chemical sensors comprises about $25 million for hydrogen sulfide monitoring equipment, $20 million for total hydrocarbon monitoring equipment, $12 million each for carbon monoxide and oxygen deficiency monitoring systems, and small percentages for systems to monitor a myriad of other gases. When the oil business and the industry as a whole recovers, this market is likely to return to its previous 10% annual growth rate. New business developments in this area will probably wait until advances in sensor fabrication technologies lower unit costs to the point that home air monitoring is economically feasible.

Non industrial applicatons are only beginning to emerge, e.g. gas sensors for places where bottled gas is used (RV's, boats, mobile homes, etc.). The aspect of home safety, climate control in buildings and smart kitchens seems to be pursued much more agressively in Japan and Europe than in the US.

Automobile Combustion Control. The automotive market is another major development area for solid state gas sensors. Demand for reliable sensors in this business is quite high, which justifies the high development costs and the complex fabrication processes required to reduce unit costs. Once developed to the technical and economic specifications of the auto makers, these sensors are finding wider use in industrial applications which, by themselves, would not justify high development costs.

The chemical sensor of greatest interest to auto makers is the oxygen sensor, used to optimize the combustion process in the engine. The value of precise combustion control rose significantly after the price gasoline increased in 1974 and the US government began to regulate fuel efficiency in cars. As a result, a cheap oxygen sensor made from zirconia oxide was developed. Such sensors, commonly known as lambda sensors, are used in most automobiles sold today. They are extremely durable, long-lived, accurate and sensitive. Their major drawback is that they do not operate below 300°C, and therefore cannot be used for the many possible room-temperature applications of oxygen sensors.

The market size for automotive oxygen sensors is difficult to assess because most of them are produced captively by automobile manufacturers. Oxygen sensors (including some electronics) cost about $20.00 each; the total 1990 US market for automobile oxygen sensors alone was between $100 million to $120 million.

Several factors will make solid state oxygen sensors a very attractive business opportunity in the next few years; government regulations in California soon will require the installation of two oxygen sensors per car, amperometric and universal oxygen sensors i.e. a sensor measuring lean and rich gas mixtures are becoming industrially acceptable; and more and more countries will require the use of oxygen sensors in their cars.

Energy and Drying Operation Markets. Humidity sensors can make drying processes much more efficient. The energy savings generated by humidity sensors could be very large. Indeed drying was estimated to consume from 1.2 to 1.8 quads (1 quad $=10^{15}$ BTU) of energy per year in the US in 1980 (about 6 % of the total energy use in that year). The market for humidity sensing in the US is about the same size or larger than the total toxic gas sensor market ($120 million).

Of major significance is the fact that few of the solid state humidity sensors manufactured up to now satisfy the need for an inexpensive device. But industry makes do with what is available.

The situation depicted for the humidity sensors summarizes the state of affairs for solid state gas sensors in general (the zirconia oxygen sensor, being very reliable and robust, is probably the only exception); none of the current solid state gas sensors are very good but industry needs are so strong that application engineers make do with the rather imperfect devices available. Despite R&D

efforts world wide, no major improvements on any of the solid state gas sensors can be reported today. There is an urgent need for better sensors to be developed to break through this stagnation of the technology. In what follows we are illustrating some approaches attempted by the author over the last four years.

New Approaches to Gas Sensing

From Wet to Dry Triple Points

We have attempted to make faster responding gas sensors by innovative methods of exposing the triple points to gas media. The intent was to make the liquid path through which the gas must diffuse to reach the triple point as short as possible or even do away with it completely. We believed that in this manner it is possible to create gas sensors that combine some of the positive characteristics of both electrochemical and solid state gas sensors. Three sensors are described; two belong to a class we have called Back-cell™ (Figures 1 (a) and (b)) and one is a so-called gas electrochemical cell involving only air as the ionic medium (Figure 2).

-Relatively wet triple points: Two versions of the back cell sensors were investigated: sensors using a porous ceramic substrate and sensors based on a silicon substrate with micromachined pores. The ceramic alumina is a porous tile with average pore size of 3 µm (see Figure 1 (a)). The metal electrodes (sensing; Pt, counter; Pt and reference electrode; Ag/Ag_2O) are deposited onto the substrate by sputtering. Hence the electrodes are porous as well. A thin layer of Nafion™ or a hydrogel is then deposited over the metal electrodes and the gas to be detected is only allowed to reach the sensing electrode from the back of the porous ceramic. An alternative method of attaining a porous substrate is through silicon micromachining. A silicon micromachined substrate is shown schematically in Figure 1 (b). In this configuration only the sensing electrode is porous, consisting of several hundred micromachined holes. The details of the microfabrication procedure are explained elsewhere [6].

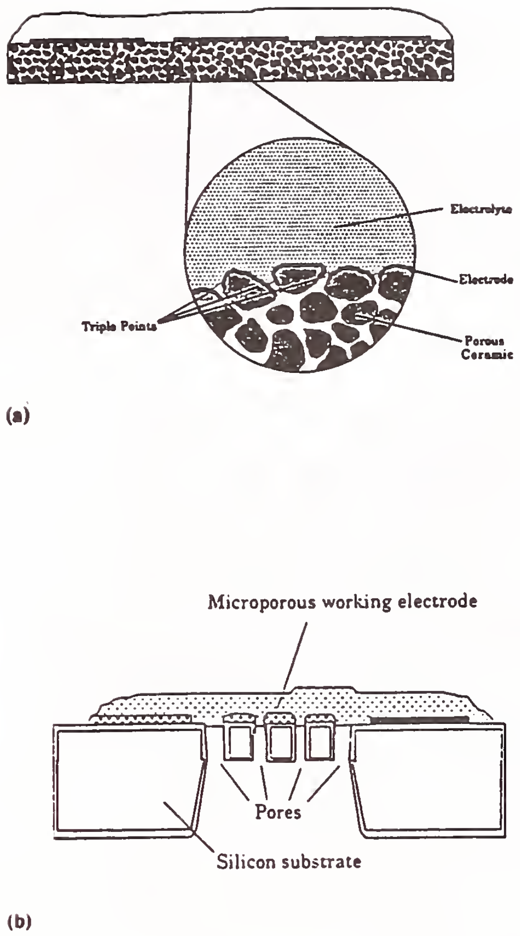

Fig.1 (a) Back cell sensor in the porous ceramic substrate; (b) Back cell with a silicon micromachined substrate

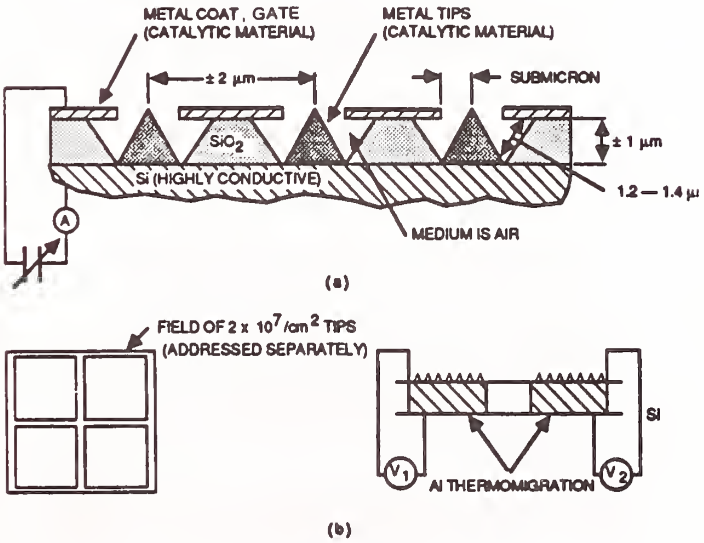

Fig. 2 Submicron gas sensor

Although the back-cell sensors are generic and can be used for a wide variety of gases, we shall only describe its use here as a fast oxygen sensor. Oxygen is detected amperometrically on the Pt sensing electrode by applying a potential more negative than -0.5 V vs. the Ag/Ag_2O reference electrode. At this potential , O_2 is electrochemically reduced at the sensing electrode according to the reaction

$$O_2 + 2H_2O + 4\,e^- \text{----------} 4\,OH^- \quad (1)$$

The response of this sensor to a step change in oxygen concentration from 0 to 100 % exhibits a 90 % response time of 300 msec. That response time is extremely fast compared to other amperometric sensors (typical response time 30 to 90 seconds). This fast response is due to the fact that a gas does not need to diffuse through a thick layer of electrolyte to reach the triple points where they react. In other words the triple point is almost dry (as water is involved in the reaction, gas probably still diffuses through a few monolayers of water to react at the metal). The recovery of the sensor back to baseline upon a step change in oxygen concentration from 100 % to 0 % is slightly slower than the initial response - 400 msec. We believe that recovery is slower because some O_2 dissolves into the Nafion electrolyte, and must diffuse out (a slower process than the diffusion into the pore) for the sensor to return to baseline.

The calibration curve of current vs. concentration for this sensor fits a linear least-squares fit with $R^2 = 0.993$. The reason for this linearity is unclear as there is no bulk diffusion through a liquid phase in this sensor, except possibly through a few monolayers of water right at the metal electrode. By varying the bias and the pore sizes we are attempting to understand the behavior of this sensor better.

In addition to fast response time, the back cell O_2 sensors demonstrated good reproducibility and reliability, and a reasonably long sensor life through the use of a water reservoir attached to the front side of the sensor. As the Nafion electrolyte requires water to be functional, this reservoir provides sufficient moisture.

- Dry triple points :

We also have been studying the detection of gases by ionization in a device made up of closely spaced metal electrodes (Fig. 2). The sensing electrodes are large numbers of field-emitter cones, all connected in parallel on a Si chip. Various steps are required to produce these cones initially produced for high-vacuum field emitters. Details on the fabrication of these field emitters can be found from reference [7]. A conducting layer very close to the cones, termed the "gate", was used as the counter electrode. In most of our experiments the cones and counter electrode had a Pt surface exposed to the atmosphere. Care was taken in keeping the sensors as dry as possible so that in this case we could truly speak about dry triple points.

Figure 3, curve 1, depicts a typical curve showing the current/voltage response for an array of about 10,000 cones in parallel where the cones (the tips) are biased negative in the presence of 1 torr HCOOH. No observable current is measured with the tip positive.

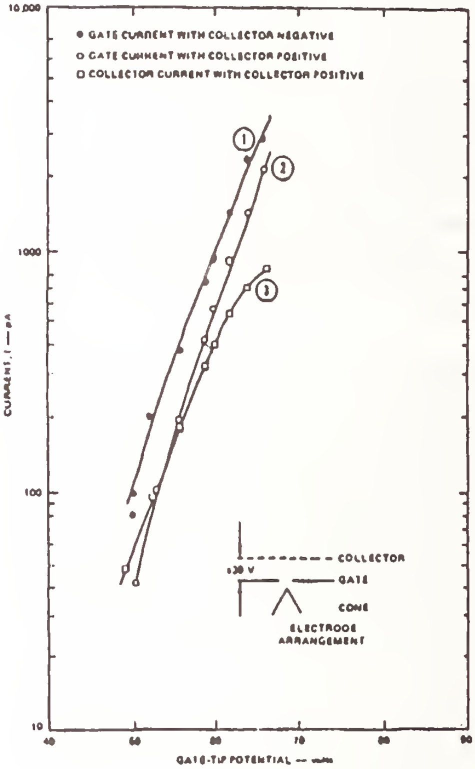

Fig. 3 Collector current and gate current as a function of tip potential showing formation of formate ions

We consider one experiment to be of particular interest. We introduced a screen as a residual charge collector about 2 mm over the gate and applied first a positive then a negative voltage between the screen (collector) and the gate. None of the current flowed to the screen with the screen negative; with the screen positive, a substantial fraction of the current flowed to the screen (curve 3). In other words, some of the charges normally attracted to the gate also found their way to the collector (actually the gate and collector currents, curves 2 and 3, add nicely up to curve 1). We interpret this phenomenon as follows: because only a positive screen bias can attract charges, the emitted charged species are likely to be dominantly negative electrons or ions. Moreover the screen experiment established that the observed currents are not leakage currents over the SiO_2 surface between the electrodes. Our contention is that negligible ionization occurs in the gas phase, and that we are observing ion production at the tip surface. These observations suggest the possibility of gas electrochemistry at dry triple points. This could lead to a new generation of sensors as well as a new generation of instruments with these cones as ionizers.

From thick to thin film and Micromachining in Solid State Gas Sensors

The use of a ceramic tube in a classical Taguchi sensor (Fig. 4) maximizes the utilization of the heater power, so that all the power is used to heat the tin oxide (as opposed to a flat configuration with the tin oxide on one surface, where some of the power is wasted). It also simplifies the form of the heater wire, which can be a coil inserted into the tube. The tin-oxide paste is applied on the outside of the ceramic body over thick film resistance measuring pads and is sintered at high temperature. The sintering stabilizes the intergranular contact where the sensitivity of the gas sensor resides. It is clear to some extent why the sensor is designed as it is. It is also clear, noting the messy procedures, how the problems with the Taguchi sensor arise.

The structure shown in Fig. 4 is a design ill suited for mass production as it involves excessive hand labor. Coating a cylindrical shape with a thick film paste is obviously more difficult than coating a planar structure. The problems with the thick film structure are mainly in the area of reproducibility : compressing and sintering a powder, the deposition of the catalyst (e.g., the size of Palladium crystallites and how close they are to the intergranular contacts), the use of binders and other ceramics (e.g for filtering) are all very difficult to control. It is obvious that the application of IC techniques could improve the state of the art dramatically here; if one could make a thin film with the same sensitivity as the thick film, one can be certain that micromachining the heater elements will further improve reproducibility and the absolute power budget needed to heat the thin film. In micromachined solid state gas sensors such thermal efficiency and a low power budget is obtained by thermally isolating the heater element.

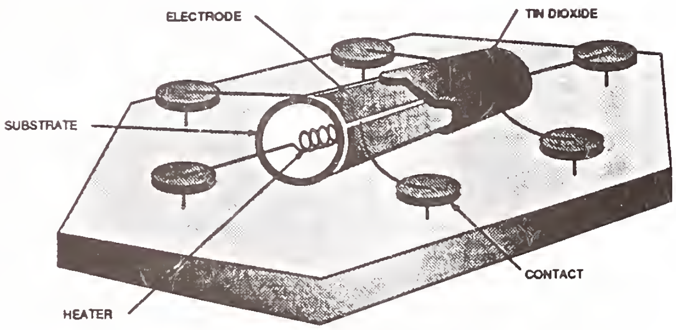

Fig. 4 Structure of a Taguchi gas sensor

The use of the intergranular contact potential as the resistance-determining parameter is required for maximum sensitivity. When making thin films, attention has to be paid to making the films thin enough for the extraction of electrons to have a significant effect on the overall film resistance (see Fig. 5). Obviously thickness control becomes a key factor here. In Fig. 5 the depletion region is shown , and the conductance is proportional to the thickness of the remaining conductive oxide. It has proven to be very difficult to make a thin film as sensitive as the ceramic type thick films.

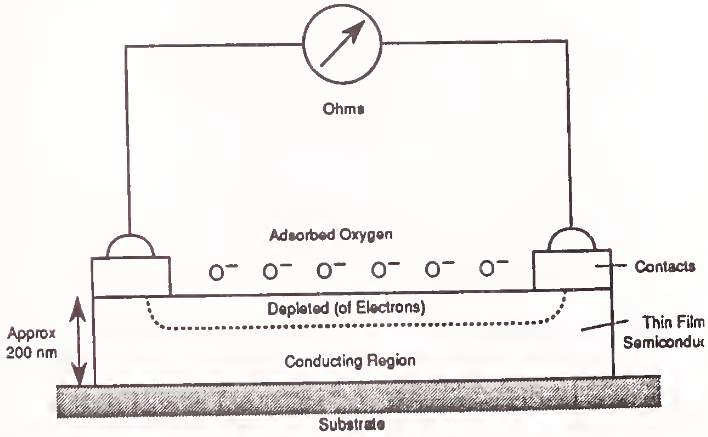

Fig. 5 Thin-film n-Type Semiconductor Gas Sensor

To retain the sensitivity of a thick film and the power efficiency of a micromachined device an ideal combination would be to put a thick film on a micromachined sensor structure. This author found it very difficult though to apply a thick film onto a thin, micromachined membrane without breaking the thin thermally isolated membrane substrates (only laboriously repeated applications of ink slurry drops and subsequent heating to drive of the solvent worked).

Thin-film are probably the only possible film that can be deposited on thin thermally isolated membranes without breaking them. A problem with thin film sensors is that the resistance often is not controlled by the bulk electron density, but by grain boundaries in the films. In principle grain boundaries should be avoided -- single crystal films should be used for easy interpretation. But thin (5000 Å) single crystals are not obtainable in the usual crystal growing techniques, and evaporated or sputtered films inevitably have grain boundaries. Again intergranular contact resistance is involved in determining the resistance of the film, and, because oxygen cannot directly reach the intergranular contact (as it does in the powder case) it must diffuse in and out at the grain boundary. This makes for long time constants. Blocking the grain boundaries completely (gold deposition was used in one attempt) is a solution if an effective block to O^- diffusion can be realized.

The major obstacle to more rapid progress with thin film micromachined sensors is that the sensitivity of thin films to gases is not yet very well understood. Except for the case of the thin-film H_2S sensors, micromachined Taguchi sensors have not yet replaced their commercially available counterparts. The currently available devices, already small and inexpensive, will only be replaced quickly when newer technology is improving upon the existing product in terms of :

>Reproducibility
>Cost
>Sensitivity
>Response time
>Concentration Range
>Specificity
>Reversibility
>Stability
>Power consumption

At this time the best course for progress in the Taguchi sensor area is to optimize thin film technology for the oxide semiconductor, use planar devices (reproducibility and cost) and concentrate on implementing less power-consuming microheater elements (power efficiency). The introduction of micro technologies could easily bring the power requirements down by a factor of 10 as we have seen. These devices will cost more that the planar ceramic devices but they will outperform them in terms of power needs and reproducibility.

From the above example it is clear that microfabrication cannot be pushed as a generic solution for obtaining all of the desirable characteristics in a sensor. For example, poisoning of metal oxide sensors, the humidity effect, or of sensors in general that depend on catalysis is a major issue that will not be resolved by implementing micromachining technology by itself.

Back-Cell^{TM} : Trade mark by TSDC
Nafion^{TM}: Trade mark by Dupont

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Gas Sensing for Industrial Safety and Health

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Sensors and instruments which are to be used in the industrial world must be capable of running without trouble for periods of many months. This means near zero maintenance, low zero drift with no false alarms, ruggedness, operation by workers with minimal training, along with many other criteria which may be specific to the particular application. Gas sensing technologies and instrument designs are discussed as they meet or fall short of these criteria, including electrochemical sensors, infrared, catalytic sensors, GC, IMS, semiconductor sensors, and portable and permanent instruments.

Introduction

Today's user of industrial gas sensing instrumentation is demanding much better performance. In the area of industrial health and safety, agencies like OSHA have insisted that gas sensing move out of the laboratory and into the work place. In the area of process control, much better gas sensing instruments are required to satisfy modern production needs. No longer are chemists alone performing gas analyses; rather, the average worker now has access to instruments which display gas concentrations automatically and tell him whether those concentrations are outside acceptable limits. Employers and employees alike are insisting that these instruments function reliably.

The ideal industrial gas sensing instrument should exhibit the following characteristics:

No false alarms. This is one of the most important criteria. No matter how good the instrument, it will not be in use very long if it is plagued by false alarms.

Near zero maintenance. An instrument which requires complicated or frequent maintenance will certainly be quickly replaced by on that does not.

Sensor life at least one year. Even two-year minimum lives are being demanded in some cases today.

Stable zero with no negative drift. Zero stability is required for user confidence and to prevent false alarms. Displays showing negative numbers for gas concentrations invite distrust of the instrument.

Fast response. Response times of less than two minutes are generally required for industrial safety and health measurements. Less than fifteen seconds is preferred.

Low span drift. Under a known concentration of gas, minimal drift of the output of an instrument with time is important, but less so than drift of the zero signal with no gas present. Users expect some drift in span which can be corrected by recalibrating, but are much less tolerant of zero drift.

Low Cost. Tolerable cost for a sensor is in the range of $100. Desirable cost for a simple instrument is $500. For a more complex instrument, users expect higher costs.

Fails gently with plenty of warning. Failures of sensor and instrument are tolerable, but the user should have plenty of warning. The user would like to see the instrument continue to operate after failure, with reduced specifications.

Rugged. The instrument must tolerate abuses typical of the industry to which it is sold.

No adjustment at turn-on. An unhappy user is one who must wait five minutes for the unit to warm up and then must adjust the unit before use.

Operable by untrained workers. It is usually not an instrument technician who will be operating most instruments.

Very fast calibration. Five minutes is a very long time for an instrument technician who must calibrate 300 instruments.

Easy sensor replacement with no adjustments. Complicated setup procedures after sensor replacement can lead to errors.

Highly selective or broad-band as desired. Normally the user wants to see only the gas in which he is interested without interference from other gases. At times a broad range is desired, i.e., for a class of chemicals.

Broad range of sensitivity. Desirable is a sensor which can accommodate several decades of change in concentration.

Stable over temperature, pressure and humidity. Sometimes a difficult task, but expected by the user.

Sensing Technologies

Some of the sensing technologies with which the authors have had some experience are:

electrochemical sensing for such gases as CO, H_2S, Cl_2, NO, NO_2, O_2, ethylene oxide, and HCN;

non-dispersive infrared for a variety of gases;

photoacoustic infrared;

pelement combustible gas sensors;

gas chromatography using photoionization and flame ionization detectors;

ion mobility spectroscopy for explosive vapors, drug detection, and chemical warfare agents; and

semiconductor sensors for a wide variety of gases.

Electrochemical sensors. An electrochemical sensor typically uses two or three electrodes, one of which, the sensing electrode, allows diffusion of the gas of interest to the sensing catalyst. In its simplest and most common form, the gas is oxidized or reduced at the sensing electrode and the resulting current is measured. This type of cell, an amperometric cell, produces a current which is directly proportional to the partial pressure of the gas outside the cell.

Another type of electrochemical cell is the potentiometric cell which produces a logarithmic signal, similar to a pH sensor.

An example of a common amperometric cell is the CO cell, which is used industrially at the rate of tens of thousands per year. It uses an acid electrolyte with a sensing, counter and reference electrode. A potentiostat holds the working electrode at a fixed potential with respect to the reference electrode. The following equations represent the reaction scheme:

$CO + H_2O = CO_2 + 2H^+ + 2e^-$ Sensing

$\frac{1}{2}O_2 + 2H^+ + 2e^- = H_2S$ Counter

$CO + \frac{1}{2}O_2 = CO_2$ Overall

Figure 1 shows the output of this sensor over the range of 0 to 1200 ppm CO.

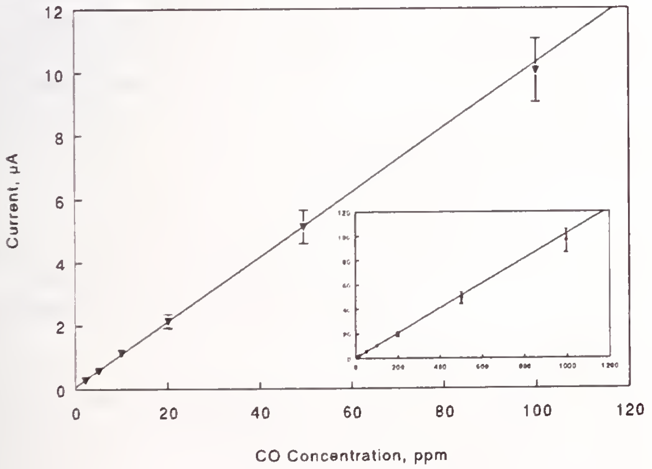

Figure 1. Linearity results for twenty 3-electrode CO cells. The solid line represents a least squares fit to the data. The error bars represent the desired goal of ±5% nonlinearity.

Figure 2 shows the response of a typical CO amperometric sensor. Fifteen seconds to 90% is quite good in most industrial applications.

Some advantages of electrochemical sensors include:

a two year life;
inexpensive;
fairly selective;
rugged;
fails gently;
can be compensated for temp.;
ppm sensitivity;
fairly stable zero;
stable span;
inexpensive; and
low power (microamperes).

Some limitations include:

liquid electrolyte; and
somewhat limited temp. range.

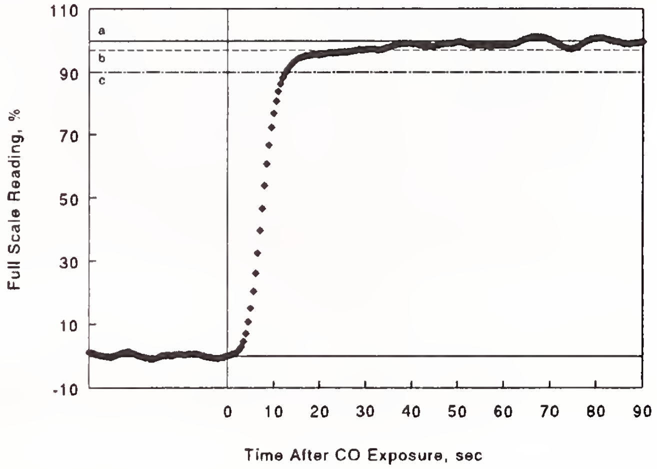

Figure 2. Typical response for a 3-electrode CO cell. (a) 100% of final value, (b) 97% of final value (25 ± 8 seconds) and (c) 90% of final value (15 ± 7 seconds).

Infrared Sensors. There are three types of infrared technology in common use for gas sensing: (1) dispersive infrared, (2) non-dispersive infrared, and (3) photo-acoustic infrared.

The most common dispersive technology in use today is Fourier transform infrared (FTIR). It is expensive, requires a technician, but is very selective and sees many compounds.

Non-dispersive infrared (NDIR) uses filters to select one wavelength for one compound. It is less expensive than FTIR, easy to use, but its sensitivity is limited to 10 or 100 ppm.

Photoacoustic infrared is similar to NDIR, but uses a microphone as a detector in a closed cell which is repetitively filled by a pump. Its sensitivity can be as small as 0.1 ppm, and it is characterized by a very stable zero. Its signal is generated as the gas in the closed cell is illuminated by a chopped, single-wavelength source; the gas expands, creating pressure waves at the chopping frequency which are detected by the microphone.

Some advantages of infrared instruments are:

- very selective;
- very low zero drift, especially photoacoustic;
- low span drift using source degradation compensation;
- wide range.

Some limitations are:

- high power(tens of watts);
- moderate cost ($2000-$10,000);
- can fail abruptly.

Pelement combustible gas sensors. Pelement combustible gas sensors use a hot wire covered by a high surface area ceramic impregnated with a catalyst. This sensing element is combined with a compensator element with no catalytic activity. The two are used in a bridge circuit at high temperature (typically >300C). As the sensing element sees a combustible gas its resistance changes, creating an imbalance in the bridge. The compensator corrects for differences in thermal conductivity and for shifts due to other gases such as water vapor.

Some advantages are:

- detects all combustible gases but doesn't discriminate;
- stable;
- long life (more than 2 years);
- wide temperature range;
- inexpensive (sensor $200, instrument $1000);
- generally fails gradually;
- rugged; and
- requires no maintenance.

Some limitations are:

- high power (several watts);
- typically narrow range; and
- signal first incrases then decreases with increasing gas concentration - cannot be used at high concentrations.

Gas Chromatography. This well-known technique uses a column to separate compounds which are detected by electron capture (EC), photoionization devices (PID), or flame ionization devices (FID).

GC can see many compounds very effectively when operated by a trained technician. It can also be configured to operate without an attendant for a few set compounds.

Its advantages are:

- versatility;
- high sensitivity; and
- certified technique for many gas analysis schemes.

Its limitations are:

- slowness;
- maintenance required;
- high power (tens of watts);
- high cost.

Ion Mobility Spectroscopy. IMS is the technique of choice for chemical warfare agent detection because of its high sensitivity (10^{-13} grams/cm^3). Compounds in the incoming air stream are ionized and these ions are then accelerated though a field. Ions are detected by an electrometer, and ion mobility in air is calculated by time-of-flight measurement.

IMS has been used for explosive vapor detection, for drug and drug precursor detection, and for industrial pollutants such as HCl.

Its advantages are its extreme sensitivity and speed.

Its disadvantages are its high power, expense, and its cross sensitivity to many compounds. In fact, a large response from compound A can be completely suppressed in the presence of compound B of much higher electron affinity.

Semiconductor Sensors. Semiconductor sensors use a film semiconductor such as polycrystalline tin oxide. Resistance change of this heated film is measured as gases adsorb on the surface.

Such devices are very inexpensive ($20), have good sensitivity for some gases (i.e. H_2S). They can see a very broad range of gases.

Semiconductor sensors use moderate power (ca. 1 watt), are not very selective (many see water vapor), and are limited in that the zero signal is not very stable.

Commercial Instruments

Some examples of commercial gas-sensing instruments are shown in the following photographs. The instrument labeled PASSPORT is a portable device which can accommodate up to five sensors. As shown it incorporates a combustible sensor, and three electrochemical sensors for O_2, CO and H_2S. Its rechargeable battery will run 10 hours. In is used in many confined-space applications.

The second photograph shows a disposable alarm for CO labeled CRICKET. It will operate for one year with only a weekly operational check. It has two gas alarm levels which are indicated by different audible alarms. It is used in steel mills and coal mines.

The third photograph is of a MODEL 6000 permanent instrument. It can receive inputs from multiple sensors, display them locally with alarms, and communicate with a central data collection console over a single twisted pair of wires. It is used in a variety of industries.

Figure 3. Portable gas sensing device.

Figure 4. Disposable carbon monoxide alarm.

Figure 5. Instrument for receiving, displaying, and communicating multiple sensor outputs.

Gas Sensor Needs in Environmental Testing

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The paper reviews the multiple roles EPA plays in environmental monitoring methodology, discusses a number of applications for innovative gas sensor technology in the environmental field, describes what EPA is doing to facilitate innovation and explains how companies and other organizations with new technologies can obtain EPA's assistance in commercializing their new products

With respect to innovation in environmental monitoring methodology, the Administration and the Agency are strongly committed to fostering and promoting innovation in monitoring technology. The Environmental Protection Agency (EPA) plays several key roles in this regard.

This paper will review the multiple roles EPA plays in environmental monitoring methodology, discuss a number of applications for innovative gas sensor technology in the environmental field, review what EPA is doing to facilitate innovation and how innovators can obtain EPA's assistance in commercializing the new products.

EPA'S ROLES IN ENVIRONMENTAL MONITORING METHODOLOGY

Evaluator

Many potential customers are wary of using a new technique without some assurance that the technology does the job it is marketed to do. EPA serves as a neutral evaluator of new technologies. The Agency conducts or oversees evaluation studies and publishes performance data that assist innovators in breaking down market place acceptance of new ideas and approaches.

Facilitator

EPA's regulations have, in the main, served as the driving force behind the development of the environmental monitoring marketplace in the United States. The air, water, and hazardous waste regulatory programs have, over the years, served as a catalyst for advancing the state-of-the-art in environmental monitoring technology. The regulatory programs have continually added new compounds to the lists of chemicals of concern, have lowered the levels of concern for existing compounds to reflect new toxicological information, and have issued many regulations establishing monitoring requirements. These requirements have had the effect of establishing a market for innovation.

A second manner in which EPA serves as a facilitator of new technology is by bringing the developer and user communities together. For example, EPA sponsors forums such as the annual Waste Testing and Quality Assurance Symposium that highlight new monitoring technology and serve as a way of both informing a large audience about new developments and encouraging them to use new, more cost-effective tools.

Innovator

As an innovator itself of innovative approaches to environmental monitoring, EPA has an active research program to advance the state-of-the-art not only at our three monitoring research laboratories but also at our regional laboratories. EPA conducts innovative research both on ideas generated internally, and through Federal Technology Transfer Act Cooperative Research and Development Agreements, assists outside organizations in bringing their innovations to market.

Enabler

The final role that I want to briefly highlight is that of an enabler. In several of EPA's regulatory programs, methods must have prior EPA approval before they can be used for complying with regulatory monitoring requirements. For example, the drinking water, ambient air, and certain parts of the hazardous waste programs have such requirements. In cases where EPA approval is needed, it is clear that EPA plays a critical and pivotal role.

In order to facilitate innovation in monitoring methodology, EPA is exploring changing its approach to methodology specification by moving to a system whereby EPA establishes performance specifications for the measurement rather than approving specific methods for conducting the analyses. Such a change would remove EPA from the approval business and allow people to use new methodology as soon as its becomes available. This does not mean that EPA would no longer publish monitoring methods. EPA would still publish methods, but the methods would serve as guidance rather than as requirements.

APPLICATIONS FOR GAS SENSORS IN ENVIRONMENTAL TESTING

Air Monitoring

Fugitive emissions

As part of the Agency's efforts to prevent or reduce air pollution, EPA regulations [1] require facilities to monitor on a monthly schedule pumps, tanks, valves, piping, and other potential sources of leaks of volatile hazardous air pollutants to detect product or raw material leakage. If such leakage is detected, then action needs to be taken to correct the problem. Current regulations require monitoring using EPA Reference Method 21. Method 21 is a procedure for using a portable VOC detector to screen for organic emissions. The method establishes performance standards rather than requiring a specific instrument of measurement technology.

Current approaches are to manually go from valve to valve, fitting to fitting, pump to pump and check for leaks. If rugged sensors could be developed that could be permanently install at each monitoring location with the sensors then being remotely interrogated by computer, several benefits would accrue. From an environmental protection standpoint, a much earlier indication of seal failure would be obtained. The facility would also benefit both from reduced product/raw material loss, and by eliminating the expensive labor involved in conventional monitoring.

For this application, it is necessary for the detector to be able to discriminate concentrations of 500 ppm higher than background levels. Thus one could attack the problem with either specific or nonspecific sensors. If compound specific sensors were developed, it might be easier to discriminate between source and background.

Odor monitoring

A portable odor meter is needed for evaluating potential air emissions from such facilities as dredging operations, wastewater treatment plants, and waste management sites. Often the Agency receives complaints from citizens about noxious odors that frequently do not show up on typical air monitoring equipment.

A field deployable monitor (i.e., ideally less than 10 pounds and less than 1 cubic foot) is needed that can sell for less than $5000. Such devices could then be set up around potential sources and used to monitor for odors. If such devices were available, it is conceivable that regulatory and permit officials might then establish objective standards for noxious odor emissions. Given the subjective manner in which odors are determined today, such standards have not been developed.

Mercury monitoring

Several states have found widespread mercury contamination in their water bodies and believe that the contamination results from mercury present in the ambient air. This appears to be an emerging problem and will require extensive ambient monitoring to resolve the issue. To cost-effectively conduct the monitoring necessary to resolve this issue, field deployable monitoring devices for use in monitoring ambient air for mercury are needed.

Spill monitoring

When an accident occurs and chemicals are spilled, on-site personnel require portable, quick response instruments to monitor what is happening. For these situations, we need rugged, easily used, easily deployed devices that can sit in storage (for example in a emergency response vehicle) and then be put into operation relatively quickly by the emergency response personnel.

It would probably be ideal if sensors for the more common volatile organics could be developed that could be plugged into a universal "counter". In addition, for screening purposes, sensitive, broad spectrum sensors would be needed.

The required sensitivity for the sensors would be a function of the specie's toxicity and hazard potential. EPA has a toxicological data base called IRIS [2] that can be used to determine an appropriate sensitivity for hazardous substances of interest.

Environmental Monitoring

In the environmental monitoring arena several applications for rugged, sensitive, low cost, species selective gas sensors come to mind.

Ambient Air Monitoring

Ozone formation in the troposphere poses a significant threat to human health and to the environment. Through the State and Local Air Monitoring Stations (SLAMS) and the National Air Monitoring Stations (NAMS) continuous monitoring is conducted for several species important to assessing ozone formation. These include:

- NOx
- VOC
- SOx

In addition, recent advances in continuous monitors are allowing EPA to expand the monitoring to include specific organic compounds which are known precursors to ozone. For further information on species and concentrations of interest see 40 CFR 58 [3] Monitoring, however, is expensive and the number of monitoring stations for which resources are available is much less than would be desirable. New types of stable, rugged, sensitive, selective gas sensors would thus find a ready market.

Mobile Source Monitoring

Automobiles, trucks, and busses comprise a major source of contamination to the air. Currently automotive emissions are controlled through a system of premanufacturing certification and periodic vehicle inspection and maintenance. The annual or semiannual inspections are time consuming and expensive. A problem can develop that leads to high emissions and the vehicle could operate for many months before its scheduled inspection. Alternative procedures under development can reduce the cost of testing but cannot operate in a real time mode. The vehicle still has to go to the detector. Onboard instruments for identifying out of specification performance can hold a key to this problem. Because of the need for such devices to be small, rugged, and inexpensive solid state sensors may be the ultimate solution.

Thermal treatment system monitoring

Thermal treatment is both a primary means by which toxic wastes are destroyed and by which resources, in the form of heat value, are recovered. However, incinerators, boilers, and furnaces pose a hazard if hazardous chemical emissions are not adequately controlled.

Many thermal treatment units operate in a batch mode or intermittent mode. Because of the constantly changing operating conditions, it is very difficult to ensure that emissions remain under established control limits. In order for the public to have confidence in thermal treatment as a means of waste disposal, continuous monitoring of stack emissions will be necessary. Proper sensors able to respond to mercury, organohalogen compounds, or polyaromatic hydrocarbons might serve as rugged, low maintenance alarms to alert the treatment unit operator to out of control conditions.

Underground Storage Tank Monitoring

Groundwater contamination resulting from leaking underground storage tanks (e.g., gasoline, fuel oil, solvents) has historically been a major source of environmental contamination. To prevent future problems, changes in tank design and monitoring have been instituted in recent years. Underground storage tanks are now equipped with double walls and interstitial zone monitoring for early leak detection. In addition, monitoring of the vadose zone around the tank is also used to detect leakage. Monitors for use in these applications need to be able to perform for many years without servicing while buried in the ground or between the tank walls. Sensors could either be ones sensitive to organic compounds in general or to specific products.

Site Characterization

EPA has looked at the issue of how to cost-effectively monitor to detect ground water contamination and has found that the presence of volatile solvents often serve as early indicators of contamination. When ground water becomes contaminated with volatile solvents, the volatile organics tend to move through the vadose zone. Therefore, monitoring the soil gas can serve as a convenient and effective means of monitoring ground water at contaminated sites.

The technology needed is akin to that needed for the underground storage tank problem with the exception that site monitoring might require a larger array of sensors than might a tank installation.

Personal Exposure Monitoring

Personal exposure monitoring for either worker protection or for exposure assessment studies are additional promising applications of sensors.

In the personal protection arena, compact, light weight devices that persons working in hazardous environments can wear to monitor exposure to toxic chemicals is one area that you might consider. A second, similar application, is exposure measurement. Here the issue is not whether a permissible exposure level is being exceeded. Instead, we need to be able to assess a person's exposure as they go about their normal activities as a means of determining risk.

In the personal protection application, multitoxicant sensitivity may be usable, while compound selective detectors might be needed for risk assessment detectors.

OPPORTUNITIES FOR COOPERATIVE DEVELOPER/EPA EFFORTS

For developers of new monitoring technology, dealing with EPA can be a daunting task. Many organizations within EPA have responsibilities in this area. For example, the various EPA regulatory program offices all have units who are responsible for measurement technology used in implementing the programs under their authority. The Office of Research and Development's three national monitoring research laboratories (i.e., EMSL/CIN, EMSL/LV, and AREAL/RTP) also play major roles in the method development and approval process. EPA recently issued a brochure that describes the method approval process used in each of EPA's regulatory programs and gives key contact persons. I have a limited number of these booklets with me and will be happy to give you one if you see me after the session.

In a nutshell, where you enter into EPA with new technology depends on the method's state of development. Those of you with technologies that are ready for the marketplace should contact the appropriate EPA office shown in the brochure.

If your product is in an earlier stage of development, then you have more options. The Office of Research and Development, our regional laboratories, and, in some cases, regulatory program offices may be able to help you develop and evaluate new monitoring technology. Cooperative Research and Development Agreements (CRADA) under the Federal Technology Transfer Act offer industry an effective mechanism for working with EPA scientists to speed up the development process. EPA can assist you with technical advice, can conduct joint research with you, and can help by in conducting field evaluations of new technologies. In this latter regard, EPA can often help in identifying appropriate sites for conducting real world tests of new monitoring method evaluations, can help ensure that the evaluation study is designed and conducted properly, and can therefore ensure the credibility of the resulting data.

The Agency's Innovative Technology Council (ITC) has issued brochures that describe which EPA organizations can assist with various environmental technologies and the procedures for entering into a working relationship with EPA. In addition to the previously mentioned **Monitoring Methods Approval Brochure** [4], the Council has issued **Accessing EPA** [5] which describes the interests and role of each major EPA office in encouraging the development of innovative technologies and lists the office's Innovative Technology Advocate. The brochure **Federal Technology Transfer Act Program** [6] presents an overview of the CRADA process. The Council is also developing a catalog which describes appropriate EPA organizations that are interested in establishing CRADA's with technology innovators.

In addition, the ITC is conducting a study to identify innovative monitoring technology needs and expects to issue a report within the next four months. This report will present information on monitoring problems for which innovative solutions are needed and for which the Agency feels a successful innovator will find a ready and profitable market. The report will describe the problem, likely users (i.e., purchasers) of the technology, and what properties the innovation will have to possess in order to be a commercial success.

Finally, it is important to mention the Administration's new Environmental Technology Initiative. In his State of the Union speech, President Clinton outlined a new initiative to accelerate environmental protection while strengthening America's industrial base. The focus of this initiative will be to harness the energies of EPA and other federal agencies to stimulate and accelerate the development, use, and export potential of innovative solutions to environmental problems. Environmental monitoring methodology is one of the areas that has been targeted for emphasis.

The Administration has proposed to allocate $36 million in FY 94 with a total of almost $1.8 billion over nine years to this initiative. Much of the money will be used to fund joint efforts with other federal agencies and the private sector. This program is designed to harness the expertise, facilities, and abilities of the DOE, the DOD and the other federal agencies to this effort. Therefore, you might want to consider establishing a three way partnership when your technology may also be of interest to these other agencies.

This paper covers a number of subjects in order to give you the reader:

1. an appreciation for EPA's multiple roles and responsibilities with respect to fostering innovation in environmental monitoring technology,

2. an appreciation for the variety of environmental monitoring problems for which gas sensor technology might offer a potential solution, and

3. a better understanding of how to approach EPA for assistance in helping you to commercialize innovative solutions to monitoring problems.

Time did not permit covering these subjects in detail. For further information on any of these areas, please contact the individuals listed in the brochures mentioned or, if you have a problem in finding the correct individual the author may be reached at 202-260-3535/FAX 202-260-4346.

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Gas Sensing in the Automotive Environment

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The task of meeting lower emission standards, achieving improved diagnostics of emissions and not impacting customer requirements for performance requires the development of improved emission gas sensors. This paper reviews the status of oxygen sensing, requirements for onboard exhaust sensing, and exhaust gas sensing needs.

INTRODUCTION

Many modern internal combustion engines are computer controlled to meet efficiency, performance and emission requirements. As an example, a typical Ford Electronic Engine Control (EEC) system contains these powertrain sensors:

Exhaust Gas Recirculation (EGR) Valve Position Sensor
Air Charge Temperature (ACT) Sensor
Crankshaft and/or Camshaft Position (CPS) Sensor
Mass Airflow (MAF) Sensor
Vehicle Speed (VSS) Sensor
Throttle Position (TPS) Sensor
Cylinder Knock Sensor
Heated Exhaust Gas Oxygen (HEGO) Sensor

The first six sensors are used in control of air, fuel and spark inputs, while the knock sensor and HEGO are used to determine engine response to these inputs. [1]

The HEGO primarily measures the equilibrium level of exhaust gas Oxygen. This equilibrium Oxygen level in the exhaust gas stream is used as an indirect measurement of air/fuel ratio.

EXHAUST GAS EMISSION

Because of the favorable emission reduction of Three-Way-Catalysts (TWC), most automotive control systems use stoichiometry (where all the carbon and hydrogen are combusted) for the feedback control reference point. Fortuitously, this corresponds to the "switch-point" of the HEGO sensor. The theoretical ratio of air mass to fuel mass for stoichiometry is 14.7 lbs. of dry air to 1 lb. of typical gasoline. The common term used in the automotive industry to denote normalized air to fuel ratio is lambda (λ). Lambda is defined as

$$\lambda = \frac{\text{air/fuel}}{\text{air/fuel at stoichiometry}}$$

Therefore, a λ of 1 denotes stoichiometry, a $\lambda > 1$ denotes a lean condition (excess air) and a $\lambda < 1$ denotes rich (excess fuel).

Air/Fuel Ratio Control

At the core of stoichiometric emissions control algorithms is the primary feedback gas sensor located in the exhaust pipe. This is the one sensor in the system in which it is imperative to have absolute accuracy. Adaptive routines in engine control strategies trim the output signal to compensate for drifts in the system, allowing for slight shifts in the feed forward sensors and actuators (intake air mass, fuel request vs. actual, engine and intake temperatures). These adaptive routines reference the emission gas sensor, and optimize the entire system to the exhaust gas sensor output. Our ability to lower emissions is limited by the accuracy of the feedback exhaust gas sensor.

The key to air fuel ratio control is the exhaust gas oxygen sensor. There are two basic types of oxygen sensors in use today; Zirconium Dioxide (ZrO_2) and Titanium Dioxide (TiO_2). [2]

The most common is the ZrO_2 sensor which consists of a thimble-shaped section of ZrO_2 with thin Platinum electrodes on the inside and outside of the thimble. The inside is exposed to atmosphere and the outer section to the exhaust stream. There is a voltage output proportional to relative partial pressure of Oxygen in the exhaust gas compared to that in ambient air. The potential difference is described by the Nernst equation,

$$E = \frac{KT}{2e} \mathrm{In} \, [P_{Ref} / P_{meas}]$$

where K is the Boltzman constant, T is the temperature in degrees Kelvin, e is the electronic charge and the respective Ps are the partial pressures.

The Titania sensor relies on the fact that the electrical resistivity of TiO_2 changes orders of magnitude upon exposure to Oxygen. The change in resistivity is dependant on the temperature and partial pressure of Oxygen.

The Oxygen sensor is used as an indicator of stoichiometry for controlling catalyst input for lowering emissions. Such a system can minimize the emissions of HC, CO and NOx.

The reason oxygen has been used is that these sensors are accurate, durable and a good indicator of the desired control point. These are the driving forces that now require the development of HC, NOx and CO sensors.

REQUIREMENTS FOR ONBOARD EXHAUST GAS SENSING

Meeting lower emission standards and achieving improved on board diagnostics of emission systems may require the development of improved emission gas constituent sensors. Emission challenges include meeting increasingly stringent governmental requirements designated Transitional Low Emissions Vehicle (TLEV) to Ultra Low Emission Vehicle (ULEV) levels. Constituents legislated in these phases include Hydrocarbons (HC), Carbon Monoxide (CO) and Nitric Oxides (NOx). Meeting these levels may require improved control of the air/fuel ratio and spark. To optimally achieve this control, sensors that can measure constituent gases may need to be developed.

There is presently a requirement in California that the driver be notified when his vehicle is exceeding emission limits and that the failed component be identified. Many states are considering similar legislation.

Exact sensor requirements to meet these regulations may vary based on individual powertrains and strategies. All such sensors will have to be durable over the life of the vehicle.

Durability Needs in Exhaust Gas Sensors

Exhaust gas sensor life is mandated by law to be 100,000 miles in the vehicle environment. This forms the basis for durability testing. Durability tests are not limited to temperature cycling, but add all environmental conditions which could occur during vehicle life. The sensor must survive abnormal system conditions such as extended rich or lean conditions due to failure of other emissions related components.

The preferred method to prove exhaust gas sensor durability is with engine dynamometer stand, because it delivers all potential causes of sensor failure. This system is capable of cycling all environmental variables, and can be semi-automated to facilitate the 2000+ hours required for full durability prove-out. Variables to be manipulated during such testing include, but are not limited to the following:

Gas Temperature: (200 - 900°C) Normal exhaust temp.
Gas Velocity: 10-40ℓ/min.
Air/Fuel Ratio Cycling: $.9 \rightarrow 1.1 \, \lambda$
  (normal control frequencies as well as extended exposure)
Excess Unburned Hydrocarbons and Oxygen:
  (by inducing engine misfire)
  consider as a full unburned cylinder, ½ℓ
Thermal Shock: 5°C liquid water in 350°C sensor
  (water condensation in exhaust stream during vehicle restart)
Pressure Shock: Peak 1000 K Pa
  (from induced engine back fire)
Gas Contaminants: Silicon, Sulfur, and trace Lead
  from multiple test fuels

Packaging integrity tests include contaminant entry into the sensor housing (ie. water) and exhaust/sensor sealing especially with designs requiring a reference chamber.

The other Major criteria for an exhaust gas sensor is selectivity.

Selectivity Criteria for Exhaust Gas Sensors

Exhaust gas sensors selectivity is especially demanding considering the multitude and magnitude of interference gases present in the exhaust stream. Before a single constituent sensor can be seriously considered for emissions control or diagnostic applications, selectivity tests would need to show promising results. Also when sensing reducing agents oxygen might be the limiting reactant. Externally supplied oxygen would increase the complexity and cost, reducing overall system viability.

Selectivity is tested by maintaining the concentration level of the measured constituent while ramping each interference gas through its vehicle exhaust range. The change in sensor output is considered its selectivity error due to the ramped interference gas at that particular signal level. Feedgas emissions levels corresponding to the relative air/fuel mass ratio (lambda) for a representative engine are shown below. Hydrogen is approximated at one-third the amount of Carbon Monoxide.

lambda	HC (ppm)	CO (%)	O2 (%)	NOx (ppm)	CO2 (%)
0.97	850	1.298	0.4192	1310	17.164
0.98	824	1.053	0.4903	1363	17.220
0.99	774	0.820	0.5539	1388	17.323
1.00	754	0.595	0.6733	1544	17.323
1.01	733	0.531	0.7519	1588	17.323
1.02	708	0.402	0.8496	1597	17.323
1.03	679	0.324	0.9496	1626	17.286

An example selectivity test for a hypothetical Hydrocarbon (propylene) sensor to Carbon Monoxide would be to monitor signal output for the following conditions:

HC (ppm)	CO	O2 (%)	NOx (%)	CO2 (ppm)	H2 (%)	(%)
754	1.298	0.6733	1544	17.323	3.90	
"	1.053	"	"	"	"	
"	0.820	"	"	"	"	
"	0.595	"	"	"	"	
"	0.531	"	"	"	"	
"	0.402	"	"	"	"	
"	0.324	"	"	"	"	

Other component characteristics that must be addressed are:

Accuracy
Repeatability
Time response
Component to component variability
Output stability

These requirements may vary depending on the particular system. All components will need to be able to be manufactured with a high volume robust process.

<u>Exhaust Gas Sensing Needs</u>

To continue to optimize the performance of automotive engines it will become necessary to measure the individual gases in the exhaust emission. In particular HC, NOx, CO levels will have to be known to optimize the emissions of internal combustion.

Many techniques [3] exist for gas sensing, including electrometric gas sensors (such as ZrO2 sensor), resistive gas sensors (such as TiO2 sensor), thermal conductivity cells, heat of combustion sensors, chemiluminescence, gas chromatography, absorption spectrometry, nondispersive infrared absorption and surface acoustic wave.

To date none, other than ZrO2 and TiO2, have been successfully adapted to the on vehicle environment. Some can meet the selectivity requirements (i.e. chromatography, spectrometry) but can not meet the environment. Others can meet the environment (i.e. resistive, surface wave) but can not meet the selectivity.

The successful implementation of any of these technologies will depend on developing the appropriate sensing element and package for the automotive environment. Packaging is the most crucial part of having a sensor that is capable of existing in the environment. Unfortunately, it is all too often the last thought in the development process. Most successful developers for the automotive industry realize that the package development must be developed simultaneously with the sensing element and the electronics.

The challenge is great and so are the rewards for those that can produce the next generation of exhaust gas sensors.

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Chemical Gas Sensors and the Characterization, Monitoring, and Sensor Technology Needs of the U.S. Department of Energy[†]

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The Office of Technology Development within the Dept. of Energy (DOE) has the responsibility of providing new technologies to aid the environmental restoration and waste management (ER/WM) activities of the DOE. There is a perception that application and judicious development of chemical sensor technologies could result in large cost savings and reduced risk to the health and safety of ER/WM personnel. A number of potential gas sensor applications which exist within DOE ER/WM operations will be described. The capabilities of several chemical sensor technologies and their potential to meet the needs of ER/WM applications in the present or near term future will be discussed.

In 1989, the U. S. Department of Energy (DOE) committed to rapidly bringing all operating facilities into compliance with applicable laws and regulations and to cleaning up the contaminated sites and facilities by the year 2019 [1]. The Office of Environmental Restoration and Waste Management (EM), within DOE, is responsible for fulfilling this commitment.

Within EM, the Office of Environmental Restoration (ER) has jurisdiction for an estimated 3700 hazardous waste sites at DOE facilities; the Office of Waste Management (WM) is responsible for management of approximately 100 million gallons of high-level radioactive waste in 327 tanks and more than 14 million 55-gallon drums of various waste forms including radioactive waste. The Office of Technology Development, also within EM, is responsible for providing new technologies to ER and WM, when needed, so the commitment can be fulfilled.

The current emphasis in ER is on assessment of the nature and extent of contamination so there is great interest in characterization, monitoring, and sensor technologies. In the future, these technologies will also be needed for remediation and post-closure monitoring. WM is focusing on ensuring adequate, permitted storage capacity for existing waste, much of which will have to be processed before disposal. Characterization, monitoring, and sensor technologies will also be required before and during the processing and following disposal.

Characterization and monitoring are typically accomplished by taking samples of air, water, soil, waste, and waste process material, and sending them to analytical laboratories for analysis. Although this practice is effective, it is expensive and time-consuming, in part because transportation and maintenance of sample integrity and identity are necessary. Some radioactive samples cannot be shipped off site. Because of the large size of the DOE commitment mentioned above and the projected enormous characterization and monitoring costs, there is a perception that application and judicious development of chemical sensor technologies could result in large cost savings and reduced risk to the health and safety of personnel.

Within the Characterization, Monitoring and Sensor Technology Integrated Program (CMST-IP), chemical sensors are defined as the components of characterization and monitoring systems that produce different, measurable, and reproducible responses when exposed to different levels of specific chemicals or classes of chemicals. In addition, the following criteria are believed to be applicable to chemical sensors:

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- Field deployable
- Selective detection of analyte
- Adequate sensitivity for application
- Capable of unattended operation
- Capable of long-term and continuous operation
- Real time response
- Inexpensive.

Activities to support the characterization and monitoring efforts of the DOE have been organized to focus upon five critical problem areas:

- Remediation of High-Level Waste Tanks
- Containment of Existing Landfills
- Characterization, Treatment, and Disposal of Mixed Waste
- Migration of Contaminants
- Decommissioning and Final Disposal

Table 1 summarizes the potential sensor applications within each of these problem areas.

Table 1

Remediation of High Level Waste Tanks

- Tank Safety Issues
  - Monitoring of Headspace Gas Concentrations
  - Hydrogen; N_2O; NH_3; Organics

Characterization, Treatment, and Disposal of Mixed Waste

- Waste Stream/Process Monitoring
  - Waste Streams During Processing
  - Waste Effluents (e.g. Off-Gas Monitoring for VOCs; PICs; Metals

Containment of Exisitng Landfills

- In Situ Determination of Contaminants Beneath Landfills
  - Organics; Metals

Migration of Contaminants

- Location, Type, and Concentration of Subsurface Contaminants
  - Chlorinated Hydrocarbons
  - Petroleum Hydrocarbons
  - Explosives; Pesticides; Herbicides

Decommissioning and Final Disposition

- Long Term, Post Closure Monitoring
  - Organics

Other applications for gas sensors may arise in response to needs for monitoring or characterizing a wide variety of chemicals in the air and in the headspace over different types of samples. Some of these needs may derive from legislative mandates such as:

Clean Air Act

Safe Drinking Water Act

Resource Conservation and Recovery Act

Clean Water Act

Toxic Substances Control Act

State and Local laws

Chemical gas sensors are not the only technology with the potential to meet DOE needs for characterization and monitoring. Currently large number of samples are collected in the field and sent to central laboratories for analysis. While this practice is expensive, it may be expected to continue indefinitely. It is also possible to build analytical laboratories into trailers which can be field deployed on site. Samples would still need to be taken, but sample transport and disposal would be simplified.

Field deployable instrumentation presents the strongest competition to chemical gas sensors. For example, conventional optical spectrometers, gas chromatographs, and mass spectrometers are all being adapted for field deployment. This route to field assay may be the most expeditious in the near future although the deployment of large numbers of these instruments may be cost prohibitive.

The chemical gas sensor technologies which have the potential to meet DOE characterization and monitoring needs may be classified into at least three categories:

Fiber Optic

Piezoelectric Mass

Electrochemical

Two reports discussing these categories have recently been produced under DOE sponsorship [2,3].

Fiber Optic Sensors

Chemical sensors that employ fiber optics exist in several forms [4-6]. The simplest types determine an analyte through observation of an intrinsic spectroscopic property of the analyte. In these sensor types, the optical fibers serve only as light guides. The spectroscopies commonly employed are optical absorption, fluorescence, Raman, and surface-enhanced Raman. Other spectroscopies beginning to be investigated for sensor applications include infrared, near-infrared, and ultraviolet reflection. Surface plasmon resonance is attracting commercial interest for biosensor applications.

A more sophisticated class of fiber optic sensors employs recognition chemistry. A chemical layer acts as a transducer or indicator in conjunction with an optical fiber. The layer may either be placed at the distal end or on an unclad portion of the optical fiber. The recognition chemistry may be reversible or irreversible. Presently these chemistries are deployed by coupling polymers, indicators, or combinations of the two, to detect such things as metal ions, ammonia, hydrogen ion, oxygen, carbon dioxide, and hydrocarbons. Sensors for all these analytes have been demonstrated with different levels of success and work is continuing. Enzymes can also be coupled to the chemical layers to provide additional sensitivity.

Sensors based on irreversible recognition chemistries use reagents rather than indicators. Such sensors respond only to a single analyte exposure unless additional reagent is released or otherwise delivered to regenerate the sensor. Such a reagent-based fiber optic sensor for trichloroethylene has already been field demonstrated.

Antibodies are also in the category of irreversible recognition chemistry. The highly selective binding of an antibody can be coupled with an optical sensing scheme to quantify the antibody/antigen interaction. Commercial immunoassay systems already employ such schemes. Fiber optic immunoassay techniques for clinical and other applications have been under development, for example, by Ciba Corning Diagnostics (Medfield, MA).

Considerable development work is in progress. Prototype systems that employ a variety of spectroscopic techniques are being evaluated for environmental monitoring, and commercial devices are available for selected applications. Issues of stability and selectivity remain to be solved. Internal calibration capability is a significant advantage of some fiber optic sensors [7]. Table 2 provides a rough indication of the current state of the technology.

Table 2.

Analytes	**Estimated Dynamic Range**
Trichloroethylene (TCE)	Low ppb to ppm
Polynuclear Aromatic Hydrocarbons	Tens to Hundreds of ppm
Hydrocarbons	Tens to Hundreds of ppm

There is a great need to develop improved recognition chemistries for fiber optic and other types of chemical sensors. The development of sensor coatings that have greater selectivity and sensitivity is expected to be a dominant research direction. For irreversible indicating chemistries, development of systems to continuously deliver reagents is possible and is presently an area of active investigation.

Specific sensors will become available for some priority analytes but the development of a large number of highly selective indicators or coatings is not likely in the near term. Development of sensors which can determine compounds as a class is clearly possible. Such sensors would indicate, for example, that a certain class of contaminants is present and could measure the total concentration. In the short term, it should also be useful to deploy sensors that are capable of indicating concentrations to only within an order of magnitude of the actual value for various chemical classes. Such sensors could provide valuable data on trends and significant concentration changes.

Among the recognition chemistries needed by DOE, but not yet available, are indicators for a variety of volatile organic compounds and some volatile explosives. If suitable recognition chemistries were developed, chemical sensors for these materials could be available in three to five years.

The establishment of an extensive field testing program is also needed. Too few field tests are currently being performed. An important aspect of such field testing is the packaging of the sensors for field use. A related issue is obtaining measurements that are representative of the material of interest. If a fiber is simply placed in the environment or material of interest, the sensor response depends on location. If the sensor is reversible, it can be moved to profile the environment. Otherwise, sensors must be placed at a number of different locations.

Piezoelectric Chemical Sensors

Piezoelectric chemical sensors are a special class of piezoelectric mass sensors, small electronic devices which quantitatively respond to the amount of mass deposited or sorbed on their surface. When such devices are coated with materials that selectively sorb a particular chemical or class of chemicals, they function as chemical sensors [8-10].

Piezoelectric chemical sensors currently exist as bulk acoustic resonators (BARs) and acoustic wave guides (AWGs). The BARs are made from thin piezoelectric crystals or thin layers of piezoelectric material on a supporting substrate. BARs operate with acoustic wave propagation perpendicular to the surface and are commonly referred to as quartz crystal microbalances (QCMs), thin film resonators (TFRs), quartz crystal resonators, and piezoelectric resonators. The AWGs are made from the same materials as BARs but involve acoustic wave propagation parallel to the surface. Various AWG types are surface acoustic wave (SAW), flexural plate wave (FPW), Lamb wave (LW), and shear horizontal (SH) acoustic plate mode (SH APM) devices.

Piezoelectric chemical sensors are under development at many laboratories; some are being commercially produced in limited quantities for a number of applications. A prototype system for VOCs is being field tested. Information on some known developers and potential suppliers of piezoelectric chemical sensors for various applications is given in Table 3.

Table 3. Developers and potential suppliers of piezoelectric chemical sensors.

Developer/Supplier	Application
Microsensor Systems Bowling Green, KY	SAW detectors with gas chromatographs, for industrial hygiene and environmental control
Femtometrics Costa Mesa, CA	SAW sensors for the measurement of ozone and detection of air borne particulates
Amerasia Technology Inc. Westlake Village, CA	Prototype SAW sensors for the detection of explosives such as TNT and RDX
Universal Sensors Metaire, LA	BARs with and without coatings for R&D use and for several sensing applications
Xsensor Delft, Netherlands	Manufactures SAWs, FPWs, and their support electronics in integrated circuit form
Vaisala Finland	SAW devices as dew point sensors
Ciba GeigySwitzerland	SAW sensors for internal process control applications
Sandia National Laboratories (DOE) Albuquerque, NM	SAW detectors, used with a gas chromatograph to measure VOCs
Ames Laboratory (DOE) Ames, IA	BARs and AWGs for gaseous species (combustion gases, formaldehyde)

Current piezoelectric chemical sensors can measure vapor concentrations (e.g. for VOCs) in the range of 10 ppm or higher; this sensitivity is thought to be adequate for many DOE needs. In selected applications, the sensitivity and/or selectivity of piezoelectric chemical sensors has been enhanced by the addition of a concentration and/or separation stage for treatment of sample material before it is exposed to the sensor. Such work is in progress, for example, at Sandia National Laboratories, Albuquerque, NM and Microsensor Systems, Inc., Bowling Green, KY.

The inability to selectively determine a single chemical in the presence of interfering chemicals is a current limitation of piezoelectric, and most other types of chemical sensors. Selectivity improvements are being sought through sample pretreatment to remove interferents and through pattern recognition analysis of the responses from piezoelectric sensor arrays in which each array element has a different coating.

At Iowa State University (Analytical Instrumentation Center and Ames Laboratory) thin film resonator (TFR) measurement systems are being developed in a field deployable form. Support electronics for the TFRs in the form of oscillator and mixer circuits have been developed as customized integrated circuits on a single chip. The small size and low power requirements of the TFRs and their support circuitry should make deployment of sizable arrays of these sensors quite feasible.

As in the case of fiber optic chemical sensors, major research will be directed to finding sensor coatings that will interact selectively with specific chemicals. Some coatings may be found via Edisonian experimentation based on known chemical interactions. Advances should also be made in the ability to predict interactions between coatings and species of interest via computational and other models founded on the rapidly increasing understanding of such interactions.

Additional development of arrays of piezoelectric chemical sensors, for which coating requirements are less demanding, is expected; new coatings and improved pattern recognition methods will also be sought. Also in the near term, efforts will be made to produce and couple more sophisticated sample treatment systems (chromatographs, etc.) with highly sensitive but not necessarily very selective sensors. Such chemical sensor systems would be both highly sensitive and selective.

Improvements in packaging for field deployment and optimization of the support electronics and noise reduction techniques are needed. Such improvements, addressed most efficiently by interdisciplinary teams of scientists and engineers, will certainly advance the application of piezoelectric chemical sensors.

Electrochemical Sensors

Electrochemical sensors determine analytes through measurements of their influence on the voltage, current, or conductance of an electrochemical cell [11-13]. For gas sensor applications, the most common types of electrochemical sensors are the semiconductor metal oxide sensor, which operates on the basis of changes in conductivity, and amperometric sensors.

Selectivity of response with semiconductor metal oxide sensors is obtained by mixing the oxide with a variety of dopants and by operation at different elevated temperatures. Amperometric gas sensors normally include a membrane where gases come into contact with the electrolyte of an electrochemical cell.

Electrochemical sensors exist and/or are under development for the measurement of gases such as CO, CO_2, H_2, SO_2, hydrocarbons, and chlorinated hydrocarbons. Improvements in selectivity and sensitivity may be required for many potential DOE applications.

Business Opportunities

A number of federal programs have been created to encourage private sector development of new technologies and the transfer of technologies developed in government laboratories. Cooperative Research and Development Agreements (CRADAs) require the private sector to provide in-kind matching funds to collaborate with government laboratories. Within the DOE, a program known as the Partnership for Global Competitiveness has been implemented to streamline the process of establishing CRADAs. Funding authority has been delegated to selected DOE contractors and the legal process has been standardized.

Three other programs provide grants for the development of commercializable technologies and do not require participation of government laboratories or contractors. These programs are:

Program Research and Development Announcements (PRDAs)

Research Opportunity Announcements

Small Business Innovation Research (SBIR) Program

These programs often focus on specific areas. Details and application procedures are published in the Federal Register and Commerce Business Daily.

The transfer of existing technology is encouraged by other programs as well. Within the Office of Technology Development of the DOE there is a Technology Integration Program designed for this purpose. Contact can be made via the following toll-free telephone number:

Technology Integration Program
Matt Cain
800 845-2096

A second program is the American Alliance for Environment and Trade. Its mission is to foster public/private partnerships for national technology development and applications. Contact may be made by calling:

American Alliance for Environment and Trade
Sheila Conway
303 279-2700

Finally, there is a mechanism for locating technology experts and special technical facilities within the federal laboratories. The Locator of the Federal Laboratory Consortium for Technology Transfer is the designated point of contact for all the federal laboratories. Inquiries can be made by calling:

Locator of the Federal Laboratory Consortium for
Technology Transfer
800 775-7445

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Thermal Microsensors for Environmental and Industrial Controls

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This review of thermal microsensors for gases focuses on the measurement of the physical state variables, physical gas properties, and concentrations of select species of interest. The impressive diversity of demonstrated sensing functions, the challenges of quantifying sensor stability, designing for low variability, and packaging for environmental ruggedness are discussed. The importance of thin-film stress control, metallization feature size selection, and characterizing the sensor environment as part of the specifications are pointed out, and quantified for several examples. The paper concludes with recommendations for the development of standard physical property data for thin films of common sensor construction materials and thermophysical gas-mixture properties so that the affordability of microsensors, their small size, and low power consumption can more predictably lead to successful applications and satisfied customers.

INTRODUCTION

To review all gas sensors for environmental and industrial control, within the frame of this workshop, would be a formidable task. This paper focuses instead on the discussion of the subset of thermal microsensor R&D and manufacture, from the points of view: (1) the needs we try to meet, (2) the opportunities offered by and recent progress of micromachined sensors, and (3) the challenges we are facing.

The purpose of the sensors R&D work at Honeywell Technology Center (HTC) is to serve the needs of Honeywell's three main controls businesses: Home and Building Control, Industrial, and Space and Aviation Systems. Stable and low-cost gas sensors are needed by all of them. Examples are sensors for flow, pressure, humidity, oxygen, VOCs (and "fugitive emissions" in general), CO, NO_x, and gaseous fuel properties as needed for combustion (stationary and automotive) and emissions control. One may group these sensors according to what they sense:

1. (Composition-independent) physical state, such as pressure, temperature, velocity, (i.e. flow) or even liquid level;
2. (Composition-dependent) physical properties, such as thermal conductivity, density, viscosity, specific heat, compressibility factor, and dew point (of hydrocarbons, water, . . .); and
3. Chemical species or groups of species, such as metal oxide sensors for O_2, CO, combustibles; NDIR/UV (nondispersive infrared/ultraviolet) sensors for CO_2, CO, H_2O, hydrocarbons, NO [1], and others.

The following limited discussion addresses the role of thermal microsensors within these groups and characterizes their performance and limitations.

DISCUSSION

The first set of thermal microsensors developed at HTC (and now manufactured at Honeywell's Micro Switch Division) were flow sensors (i.e. hot film microanemometers) featuring up- and downstream sensing elements that were separate from the heater. Heater and sensors were and are still positioned on a thin membrane of silicon nitride to enhance the sensor's sensitivity to about thirtyfold that of a solid silicon structure [2], while simultaneously reducing the power input to the heater to a few milliwatts.

Whether front-etched or back-etched, the thermal isolation provided by the membrane quickly led to a proliferation of sensors, as shown in Fig. 1. Their purposes range from the direct measurement of flow and differential pressure [2]; thermal conductivity and specific heat [3]; absolute pressure [4]; and of course, temperature, to sensing oxygen [5]; dew point; NO_x

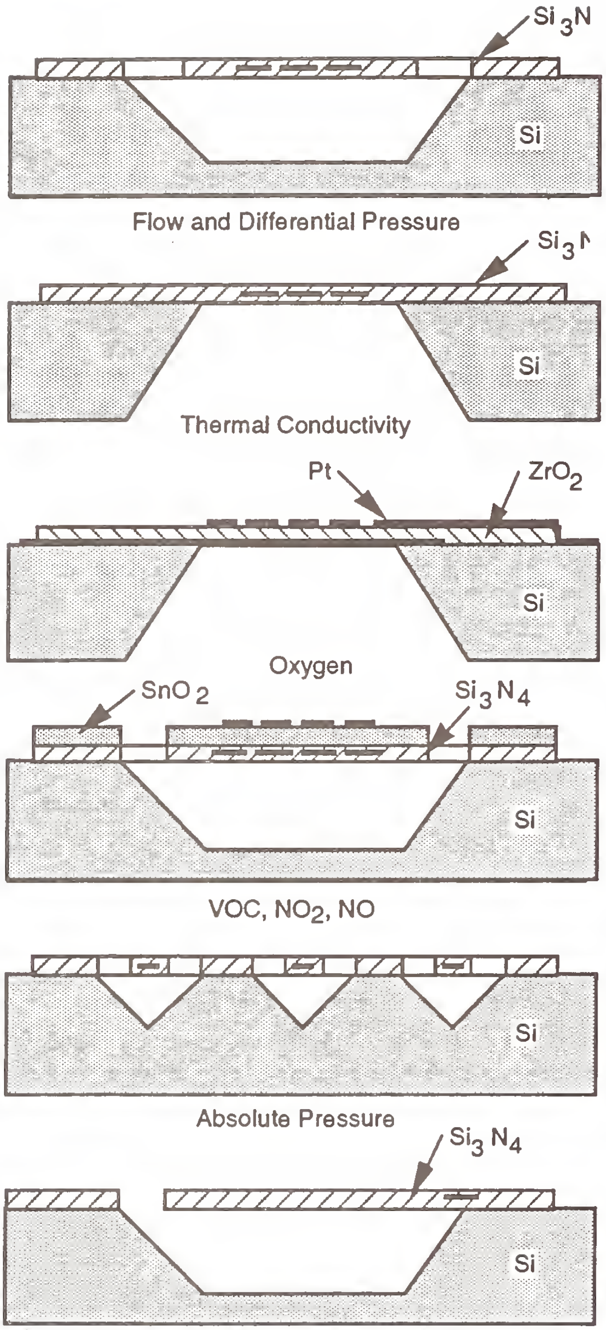


Fig. 1. On the microbridge sensor flexibility.

[6,7]; and combustibles by incorporating special films into the structure. For the first group, the permalloy or platinum thin films are fully passivated within layers of silicon nitride to suppress any possible chemical reactions between the metal film and the constituents of the surrounding gases. The structure of the second group of sensors is such that the environmental gases can react with either the special films (SnO_2 or WO_3 for NO_x or combustibles, or ZrO_2 for O_2) or with the metal catalyst directly (see Gall and others [8,9]).

The following subsections highlight the performance of some of these sensors (Subsection A), discuss generic challenges that are common to most (Subsection B), and review their use in correlation to further outputs of interest (Subsection C).

A. Performance of Some Thermal Microsensors

Thermal flow microsensors of the design described above feature at least 10 times greater sensitivity to low flows than conventional anemometers. Fig. 2 shows data of such a sensor taken for three different gases, stretching over three orders of magnitude. Compensation for the noticeable composition effect has been developed and consists of incorporating a correction factor into the output that depends on thermal conductivity, specific heat, temperature, and Prandtl No. [3]. The effect of the latter can be neglected in most applications.

Also, thermal conductivity, k, and specific heat, c_p, can be measured with such microbridge sensors, as outlined in Fig. 3. Each time after energizing the heater, k is obtained from the steady state signal, while c_p is obtained from a combination of the transient signal and k. Fig. 4 shows how well the sensor signals can be calibrated with known values of k(T,p) for various gases. Microconvection can influence those readings if not properly allowed or compensated for, as shown in Fig. 5 in which the plotted groups of 50 readings each were taken while holding the plane of the sensor membrane in one of the six possible orthogonal space orientations.

As an example to represent the special-film sensor group, Fig. 6 shows the results obtained with a thin film of tin oxide sensor [7] operated at about 200°C. The cross sensitivity of such thin film sensors to water

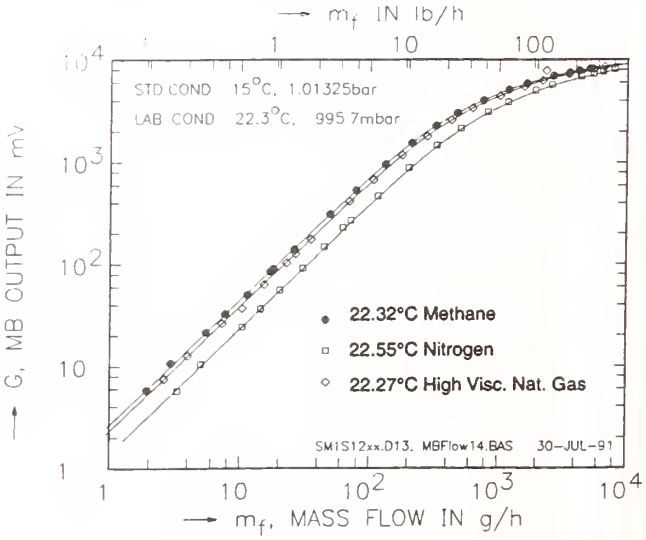
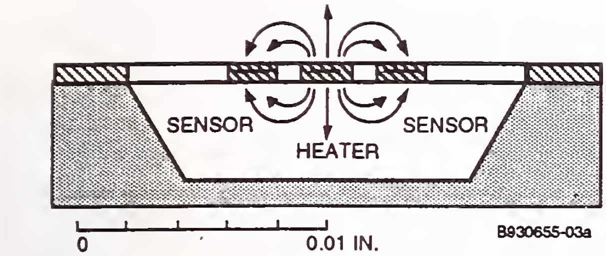
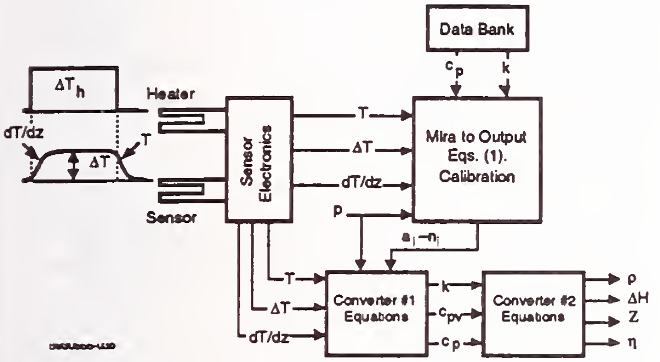


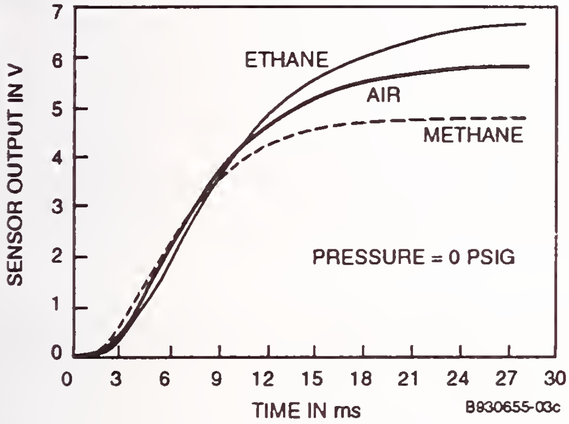
Fig. 2. Microbridge sensor output vs. mass flow for three gases.



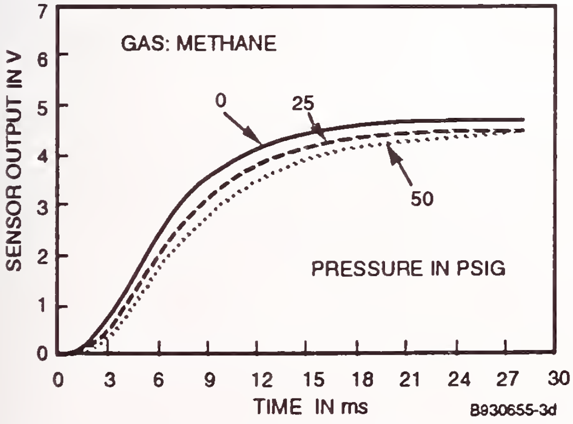
a. Sensor chip cross section



b. Electronics block diagram



c. Sensor output vs. time for three gases



d. Sensor output vs. time for three pressures

Fig. 3. On the measurement of k and c_p.

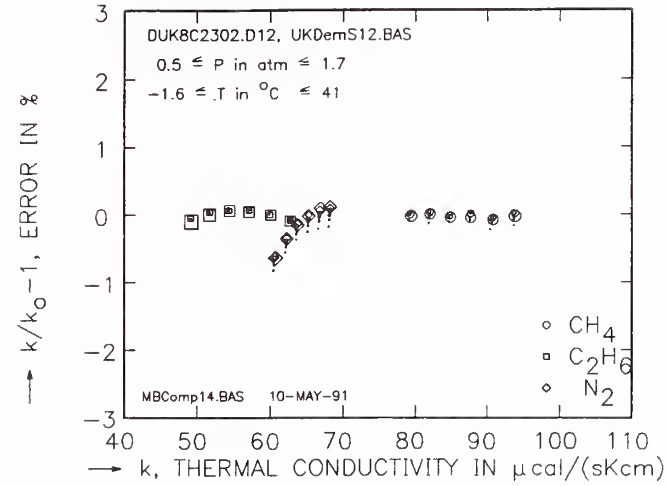


Fig. 4. Thermal conductivity determination error for several pressures, temperatures, and pure gases (std. error = 795 ppm).

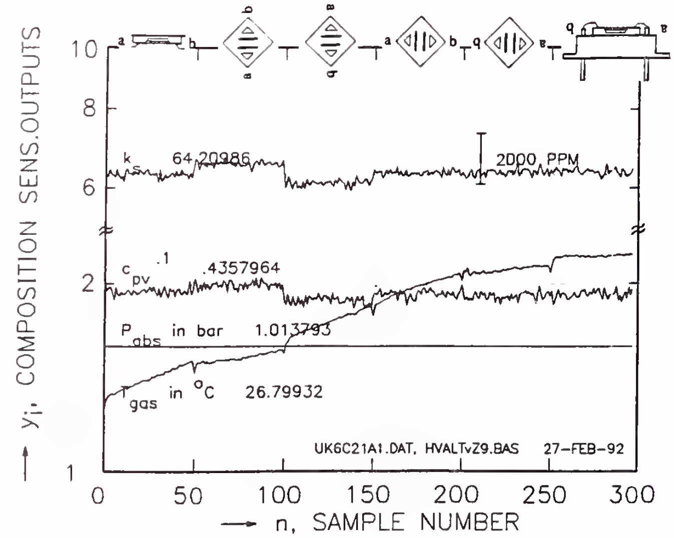


Fig. 5. Influence of sensor orientation and natural convection on output stability (y axis amplification = 100).

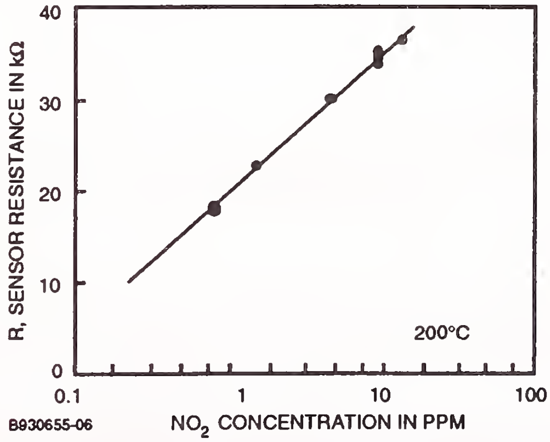


Fig. 6. Tin oxide thin-film sensor output sensitivity to NO_2 Concentration. in Air[7].

vapor is small relative to that of the traditional thick-film sensors, as pointed out by Schierbaum et al. [6].

B. Performance Limitations

To characterize the performance of thermal sensors, we suggest the following minimum set of parameters, which represent both challenges and limitations:

- Sensitivity to the parameter of interest, and quantified (cross) sensitivity to others;
- Noise level, in relative units of sensor reading (not full scale);
- Gravity-/acceleration-driven microconvection effects;
- Stability (low drift) under normal service life and/or during exposure to high temperatures (accelerated life test);
- Cost of trimming/calibration, electronics (monolithic, hybrid or separate), and packaging;
- Unit-to-unit variability.

The following paragraphs examine just three of these—stability, variability and packaging—still in the context of thermal microsensors

Stability—The importance of this aspect of sensor performance cannot be emphasized enough. Achieving stable operation requires materials selection to achieve satisfactory adhesion, stress control, and lack of solid-solid interdiffusion during high-temperature processing and/or operation. An understanding of the mechanism or mechanisms causing output signal drift is the first step in finding a solution or means of stability improvement. Figs. 7 and 8 provide a few examples of our experience with microbridge sensors.

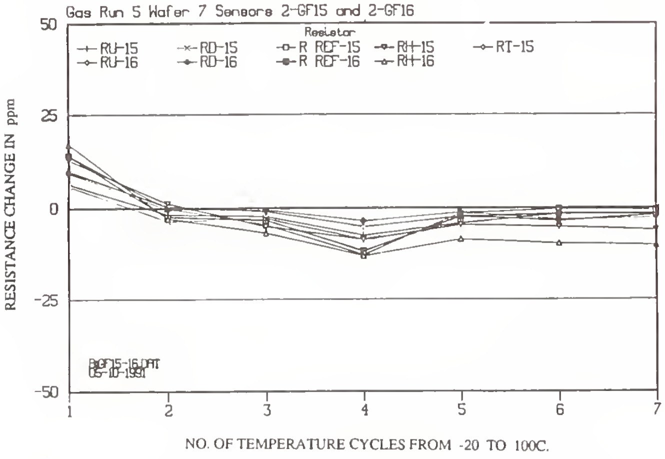


Fig. 7. Sensor resistance change due to temperature cycling, showing changes that are barely outside of the noise level.

Fig. 7 shows that the rate of change in the resistance element of the microbridge used slows with the number of thermal cycles, indicating a less than linear, possibly logarithmic, dependence on the number of cycles. Results of accelerated life tests of similar sensor structures support that view, as shown by the resistance change data plotted vs. log of time in Fig. 8 [3], where each point represents an average of ten samples. Similar log(time) dependencies are well known for the rate of mechanical stress annealing vs. time, and the depoling of piezoelectric ceramics (such as PZT (lead zirconate titanate)) vs. time. Both are based on the rearrangement of some grain or domain structure.

The challenge here is to elucidate the underlying mechanism. Thermal coefficient of expansion (TCE) mismatches clearly play a role. One might try to quantify that by postulating stable behavior (after annealing out residual fabrication stresses) if the thermal excursions the sensor is subjected to, do not cause the incurred strains to exceed the elastic limit of the weakest member, which often would be the thin film of sandwiched metal like platinum. Measurement of the resistance stability of a number of platinum thin-film-based elements of microsensors at 20°, 180°, 250°, and 350°C show, however, that not all sensors behave alike (Fig. 9), so that some allowance needs to be made for "individual" effects, beyond those one may identify as average behavior. There is clearly room for more study here.

Sensor Variability—Means to minimize variability may require some hard cost–performance tradeoffs. Cost reduction requires small feature and chip size, yet some of the low-power and low-cost (wafer real estate)

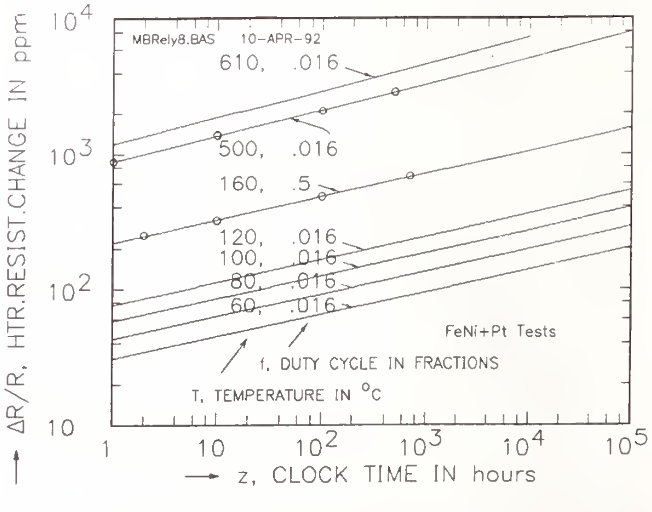
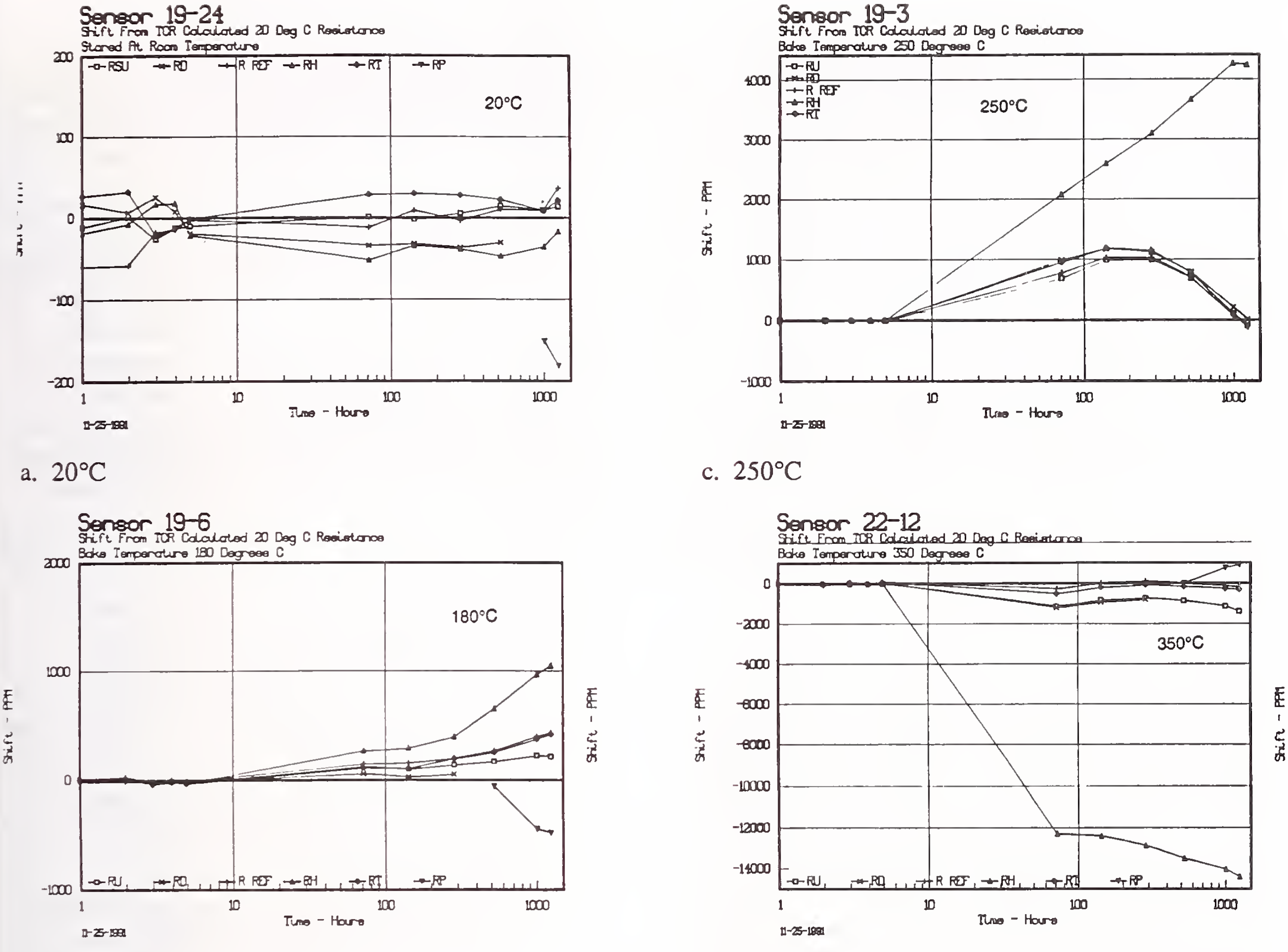


Fig. 8. Microbridge heater accelerated life test results.



a. 20°C

c. 250°C

b. 180°C

d. 350°C

Fig. 9. Sample of 1250-hour life tests with microbridge flow sensors at the indicated temperatures. Each graph shows data obtained for one chip with six different thin-film Pt elements.

benefits may entail unacceptable electrical variability, pressure dependence of thermal response due to nonuniform rather than uniform temperature field effects, high current densities (leading to electromigration), and heat transfer variability.

We recently measured sensor heater losses and electrical resistance of four bonded flow sensor chips vs. ambient temperature and heater temperature rise, see Fig. 10. The covered temperature range was 35° to 100°C for the heater rise and 20° to 73°C for the ambient temperature. The results showed an averaged one-standard deviation of ±0.357% to 0.358% for the resistance variability, but only ±0.08% to 0.11% for the thermal conductance variability. While the sample size was clearly not large enough for sweeping conclusions, the data do warrant a closer look to clarify why the electrical properties are about four

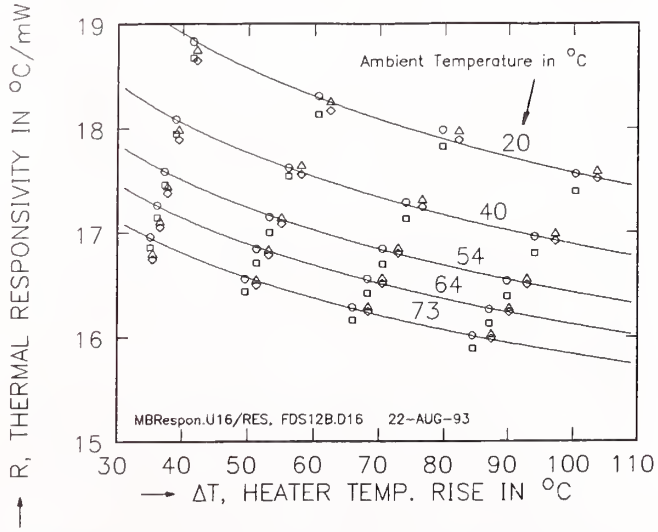


Fig. 10. Heat dissipation or thermal responsivity of microbridge sensors vs. heater input and ambient temperature.

times more variant than the thermal ones. The heater film width was 5 μm; in another sensor design, with a 2-μm heater film width, the resistance variability was measured to be ±12%. Feature size, rather than film thickness uniformity, may therefore be the governing influence here. Additional small-size penalties may surface in terms of reduced thermal responsivity.

Packaging—The concern about survival of such microsensors with thin (approximately 1 μm) membranes in a real-world environment needs to be addressed. In gas flow situations, encounters with particles more than 300 μm in average diameter is conceivable. Solutions we have found to be useful are based on either mounting the sensor in a protected (tortuous path) bypass [10] or trapping particles larger than a given size [11]. In both cases the sensors survived passing the specified load of particles representative of likely exposure during its specified service life.

C. Sensor Output Correlations

Having developed the capability to sense k and c_p, we explored the merits of using them to correlate with other gas properties of interest, Y_i, (indicated in Fig.3 as converter #2 equations, similar to those developed earlier[17]) such as density, ρ, relative density (= specific gravity), ρ/ρ_o, viscosity, η, higher heating value, ΔH, compressibility factor, Z, octane number of gaseous fuels, N_{MON}, critical compression ratio, R_{cc}, and others. Figs. 11 through 15 provide a few examples involving a set of over 70 natural gases, with a range of physical properties indicated in the caption og Fig.14. Fig. 11 presents the result of fitting relative density to k and c_p for the above set of gases, augmented by the addition of the corresponding set of peak shaving gases. The achieved correlation uncertainty was only ±0.33% or ≤±0.1%, with and without the set of peak shaving gases, respectively. Figs. 12 through 15 present error plots of viscosity, heating value, compressibility [12], and octane number [9], respectively.

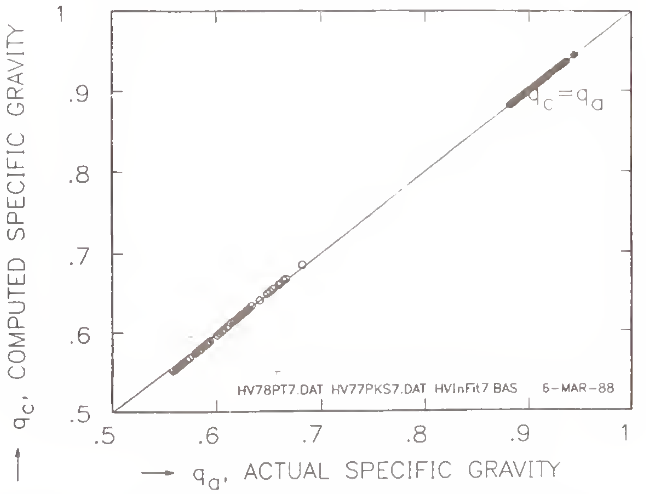


Fig. 11. Comparison between actual and computed specific gravity of 78 natural gases and 77 peak shaving gases (maximum correlation error = ±0.33%.

All these rely on the absolute accuracy of the k and c_p sensor calibration (e.g. with pure gases) and on accurate algorithms for the computation of the k and c_p of gas mixtures to develop the $Y_i(k,c_p)$ algorithm. For properties of gas mixtures that are nonlinear, the accuracy of the $Y_i(k,c_p)$ algorithm is compromised if such gas mixture properties cannot be predicted accurately (accurate measurement of a large set of gas mixtures is possible but expensive). Such gas mixture properties are being developed [13] but need further support.

CONCLUSIONS

From our experience with thermal microsensors, we conclude and might recommend the following.

- Stresses in microsensor thin films should:
  - Be kept within the elastic limits to minimize one source of sensor drift;
  - Be evaluated on the basis of the relevant phase diagram for possible phase changes.

    The study of possible phase change- and diffusion-driven changes in thermally stressed thin films, such as in thin-film ZrO_2-based O_2 sensors, should be supported to make such sensors available in microstructure versions.
- In striving for low-cost manufacturing, ways for reducing chip-to-chip variability —to the point where costly individual trimming and calibration

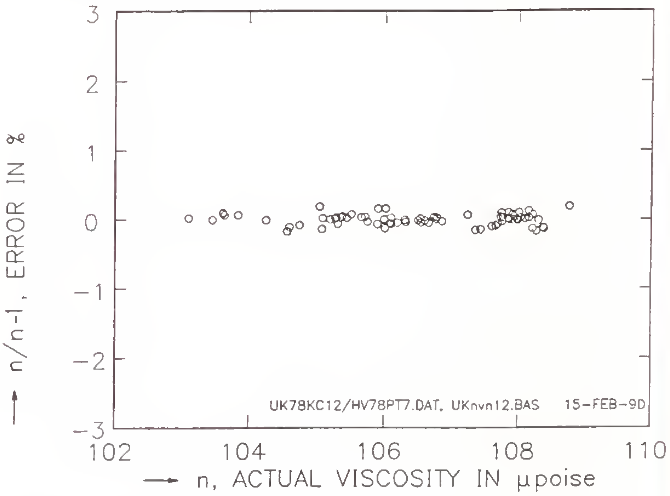


Fig. 12. Viscosity determination error for 78 natural gases (std. correlation error = 687 ppm).

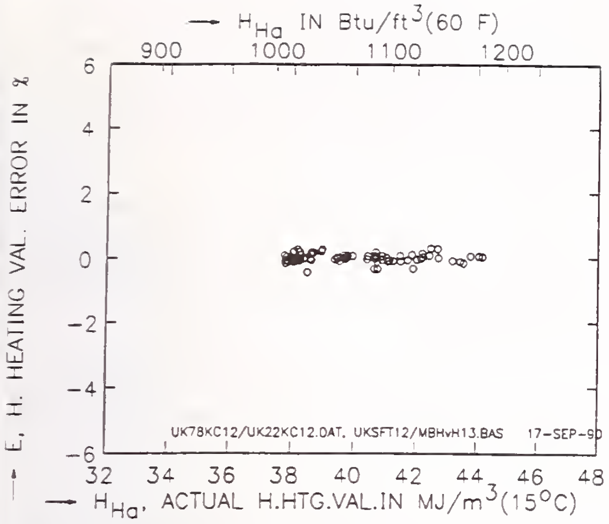


Fig. 13. Heating value determination error for 78 natural gases (std. correlation error = 0.13%)

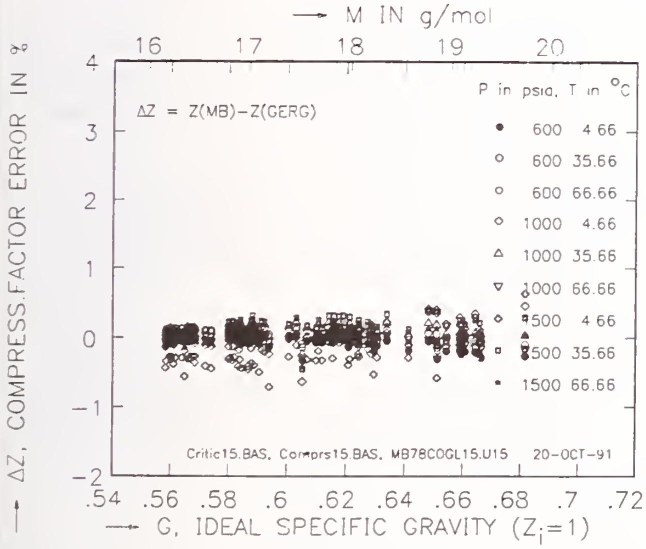


Fig. 14. Error in microbridge compressibility factor relative to the 13-component equation of GERG, using a two-pressure-term correlation (range of gases: ΔH: 17%; Δη: 7%; ΔM:20%;ΔCO_2, ΔN_2: 3%;Δp_{pc}: 2.3%).

can be eliminated—should be investigated. Required feature sizes should be established only after trading off performance,sensor and trimming costs, and variabilities.

- The accuracy and consistency of available thermophysical properties of gases, and especially of their mixtures, need to be improved. These are needed for calibration of sensors of k, c_p, η, ρ, Z and others.
- The use of exposed gold wire bonds for environmental gas microsensors may lead to unacceptable drifts, especially in harsh environments. Other, passivated means of contacting the sensor need to be developed.

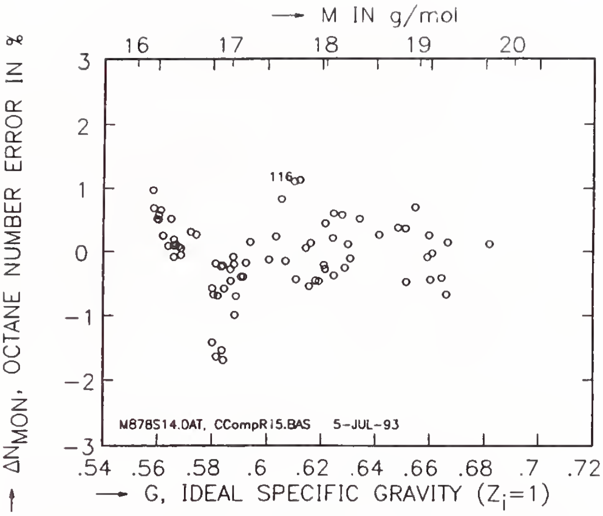


Fig. 15. Motor octane number (N_{MON}) error (std. correlation uncertainty = ±0.6%).

- Interesting gas sensors that might be reviewed at future workshops are those based on zeolites [14], thick-film O_2 sensors [15], and NDIR sensors based on selective, uncooled IR detectors [16].

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NIST Programs and Facilities in Gas Sensing and Related Areas

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Development of improved gas sensing devices requires research in a range of disciplines. Efforts within different organizational units at the National Institute of Standards and Technology (NIST) address a variety of key sensor-related issues. These include fundamental studies of sensing materials and concepts, device calibration, direct measurements in particular environments, and production of standard gas mixtures. This paper provides a brief summary of existing programs and identifies institutional contact points for those requiring more detailed information.

Research and development efforts in the area of gas sensing are being motivated by a wide range of identified application areas, such as environmental monitoring, process control, personal safety, and other areas which are being discussed in the Breakout Sessions of this Workshop. It is also generally believed that technological advancements that lead to the production of reliable, inexpensive, low-power sensors will create many new application areas for which current generation sensors are inadequate and analytical instrumentation is too costly. The discovery of new sensing materials and concepts and their incorporation into new devices requires a broad-based effort extending from basic research, to practical fabrication processing, to testing and performance demonstration in real world settings.

A number of different groups within NIST are involved in activities that support the required components of gas sensor development and testing just mentioned:

1. Gas sensing research efforts centered in the NIST Chemical Science and Technology Laboratory (CSTL) relate to developing several areas, including conductometric microsensor arrays and humidity measurement (and standards). There are also efforts in optical spectroscopic research and fiber optic-based sensing. (In addition, biosensing research occurs within CSTL.)

2. Development of techniques supporting production of well characterized gas mixtures as standard reference materials (SRMs). Such mixtures have direct application to gas sensor development and evaluation. These activities are also conducted in CSTL.

3. Issues associated with air quality in buildings are being investigated in NIST's Building and Fire Research Laboratory (BFRL). Additionally, research is underway on detection of gaseous species generated during the initiation of fires and the incidence of building fires.

4. Standards and measurement techniques for radioactive gas concentration are developed in NIST's Ionizing Radiation Division, Physics Laboratory (PL).

In this paper we provide summarized information on a number of these efforts. Those interested in greater detail than could be included here are encouraged to consult the references below or to contact the NIST Division where the studies are done. We begin by describing an overview of the NIST effort in solid state microsensor arrays.

Conductometric Microsensor Arrays

Background

The program aimed at developing gas microsensor arrays is centered in the Process Measurements Division of CSTL, but has involved a close collaboration with the Semiconductor Electronics Division of the Electronics and Electrical Engineering Laboratory (EEEL) at NIST. The objective is to develop the technology needed to integrate multiple active elements into a planar array configuration which can be used to provide compositional information on gas mixtures of varying complexity. The approach we use involves combining differing surface-active sensing films with micromachined-Si array structures that contain multiple elements which can be individually temperature controlled [1]. The type of platform produced is meant to be generic and tunable to a wide variety of applications. Many detection principles can be applied in solid state gas sensing (see also other papers in this section, and reference 1), and the selected method, in combination with the chemistry of the gases to be monitored, determines the types of active materials employed. Array devices reduce (or eliminate) the requirement of using *highly* selective films, and therefore permit the use of certain materials that are more robust.

While our group has investigated diode-based and surface acoustic wave devices, its research has been focused more heavily on conductometric microsensors that have active films of semiconducting oxides which are sometimes modified with surface-dispersed catalytic metal additives. These films, as well as the micromachined arrays, provide relatively durable devices able to operate in certain environments where, for example, polymeric materials would be ill-suited. Development efforts required for these conductometric microsensors include the study of improved films and interfaces, transduction mechanisms, fabrication and compatibility issues, response evaluation, and pattern recognition. The interactive combination of these research components is illustrated schematically in Figure 1.

Technical Approach

In our semiconducting oxide-based conductometric sensors, gas adorption can induce changes in the near-surface charge distribution and oxygen content that alters the conductance. Reducing gases increase the conductance and oxidizing gases lower it. The challenge is to instill a degree of selectivity or uniqueness into each of the multiple sensor elements so that the observed changes in conductance can be used to indicate the presence and concentration of a gas or gases. Two

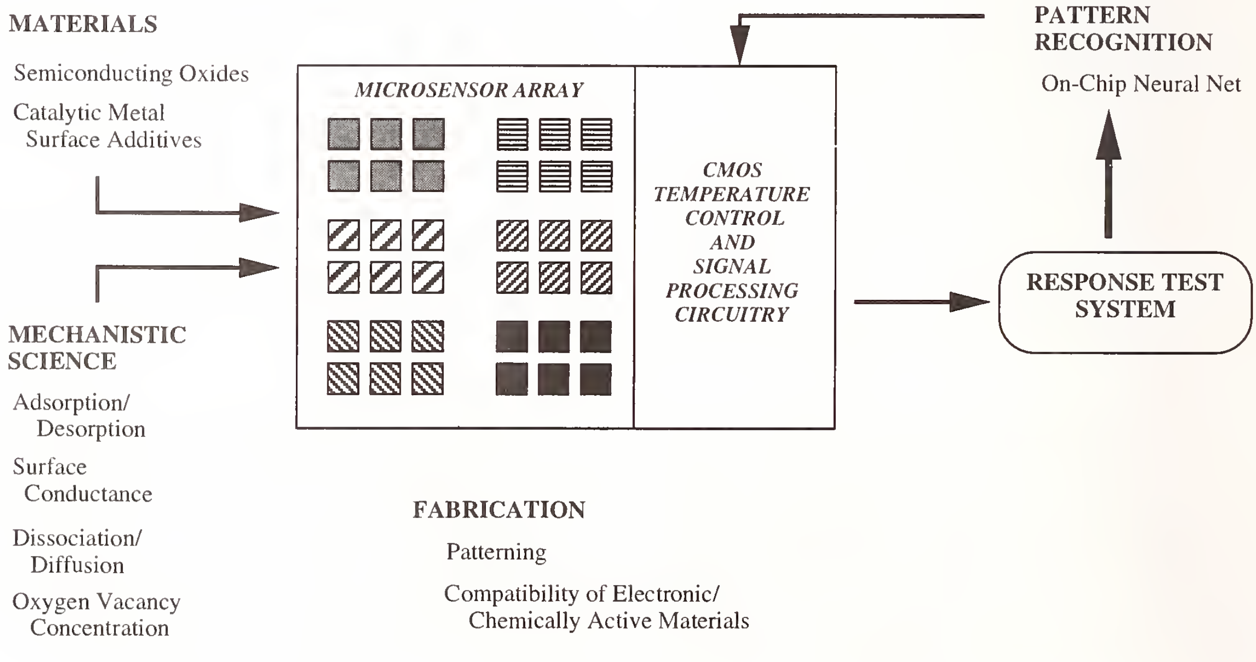

Figure 1. Schematic representation of the research components within the gas microsensor program in the CSTL at NIST.

selectivity-enhancing schemes, used in combination in our approach, involve (1) the variation of film (and surface) composition and microstructure of the active layers, and (2) the temperature-control afforded by the micromachined arrays, for each of the miniature elements in our devices.

Active films and interfaces can be varied in a number of ways. The use of differing oxide types such as SnO_2, ZnO, TiO_2, and WO_3 will, by the nature of their differing chemistries and electrical properties, cause variations in the gas-solid interactions and transduction processes. The microstructure, stoichiometry, and even the thickness of the oxide films can also be used to affect the response of the individual oxides. The action of the oxides can also be significantly modified by surface-dispersing catalytic metal additives in the monolayer coverage regime. Discontinuous overlayers of metal islands produce new adsorption characteristics and can create micro-Schottky barriers that influence electronic transport behavior. Discontinuous additive morphologies allow the interfaces to maintain semiconducting (rather than metallic) character, so that they have larger dynamic ranges of conductance response to adsorbing gases. The use of metal/oxide interfaces enhances selectivity and often lowers the operating temperatures of the conductometric sensors.

Temperature control has long been recognized as an important if not necessary feature of operation for gas sensors. For example, commercial Taguchi sensors [2], in existence for many years, use a heater to raise their active materials to elevated operating temperatures. Recently, the use of micromachining technology has introduced the possibility of much more versatile temperature programming to gas sensing structures. Other benefits include the greatly reduced power levels required to produce elevated temperatures for miniature sensor elements and the ability to fabricate reproducible planar devices cost-effectively through batch processing. The opportunity to incorporate on-board control and signal handling electronics also presents itself, and is most easy to achieve when standard methods are used to form the micromachined structure. The type of basic sensing element we have been developing for microsensor array technology is illustrated in Figure 2 [3]. Arrays of these "microhotplates" have been specially designed for fabrication at a Si foundry using standard CMOS -- complementary metal oxide semiconductor -- technology, (which facilitates the incorporation of on-board circuitry). The suspended microhotplate pixels are realized by a post-fabrication, anisotropic chemical etch of exposed Si. Each pixel is configured to serve as the platform for a planar, conductometric sensor film (variations can be used for applying other sensing principles). As indicated in the schematic, the microhotplate includes an integrated heater, thermal distributor/thermometry plate, and 4 top level contact pads. These electrically conducting structures are vertically separated by insulating SiO_2 layers. The suspended elements have typical lateral dimensions of 100-200 µm and masses of a few tenths of a µg. Their low mass and level of thermal isolation allow them be heated and cooled rapidly (1 ms time constant for heating to 500°C with a temperature/power coefficient of 8°C/mW).

This fast temperature modulation can be used to great advantage both in fabricating and operating the sensing elements [4]. For example, static or dynamic temperature control during or after deposition can affect the stoichiometry and microstructure of overlayer (oxide and metal) active

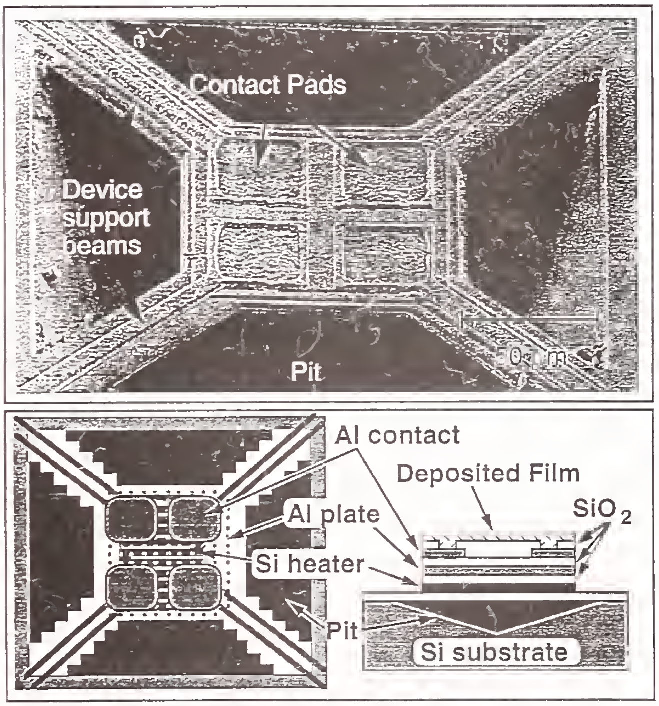

Figure 2. Scanning electron micrograph showing a suspended microhotplate structure with 4 top-surface contact pads for conductance measurements on an active film. Top and cross-sectional end view schematics (not to scale) are shown in the lower panel.

films. In certain processing, such as chemical vapor deposition (CVD), the microhotplates can provide an efficient means for selected area, maskless lithography to place multiple sensing films of differing composition on a set of elements. The use of temperature programming for sensor operation is illustrated below.

To demonstrate our conductometric microsensor technology, SnO_2 has been reactively sputter deposited on microhotplates so that the underlying contact pads of the elements can be used in monitoring gas-induced conductance changes. We have demonstrated that at a fixed temperature of 350°C, the pure SnO_2 shows opposite conductance excursions in response to the presence of oxidizing and reducing gases [3]. As a follow up to that study we have also taken advantage of the rapid temperature control possible with the microhotplates to examine pulsed mode operation. Figure 3 shows a simple example in which an SnO_2 film is being used to monitor on/off cycles of 0.1% H_2 injection in air. The microsensor temperature is pulsed to 400°C for 10 ms once every 1.0 s. Conductance is measured only at times where the film is not heated (so that only adsorption-induced changes in electronic transport are recorded rather than effects of thermal carrier generation). In this power-saving mode the energy requirement of the heater could be provided by a 9 V alkaline battery for almost 1 year.

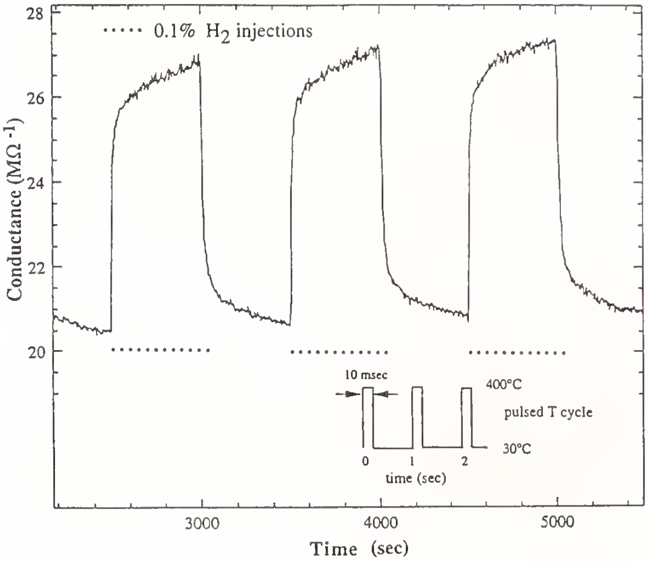

Figure 3. Conductance response of a SnO_2 film on a microhotplate using temperature pulsing (see inset) for a reduced-power mode of operation. Illustrated are 3 on/off cycles of the 0.1% H_2 in air test gas.

Further studies are underway with more sophisticated pulsed temperature cycling (both with and without catalytic additives dispersed on active oxide films). Initial results indicate that differing pulsed temperature schedules have considerable potential as a kinetic selectivity tool for distinguishing between similar gas and vapor species. These investigations generate information-rich response data sets as the detected analytes and temperature cycles are varied. A recently completed, fully-automated testing facility [5] is used in controlling test devices and monitoring their outputs. This system is critical for evaluating device speed and stability and for obtaining the large databases necessary for developing pattern recognition algorithms that will be required for gas mixture analyses.

Materials Studies

The sensing capabilities of oxide and additive metal films can be enhanced by the selection of special operating modes (e.g.- Figure 3) made possible when the active materials are combined in a compatible way with micromachined structures (e.g.- Figure 1). However the ultimate level of performance will be determined by the selection of film materials and their specific properties as fabricated in the sensing device. To explore and improve the active films that serve as the hearts of the sensors, our development program includes a parallel effort into the relationship between material properties and transduction mechanisms.

Two separate facilities have been constructed to study the fabrication, properties and interfacial sensing processes [5]. The Film Deposition and Characterization Facility is an ultrahigh vacuum-based system outfitted for depositing, modifying and characterizing films (thus far efforts have focused on semiconducting oxides and several metals) and exploring methods for producing new, microstructure-controlled materials. The Surface Analytical Facility is a multichambered system equipped for characterizing the chemical, structural, electronic, and electrical properties of the outermost 0.5 to 10 nm of sensing materials. These analytical capabilities are important for determining the detailed properties of fabricated materials and performing model studies of transduction mechanisms [6, 7]. Among the many factors that can be examined for sensing materials are sample purity, composition and stoichiometry, adsorption and desorption characteristics, the consequences of surface reactions, and the variation of electronic transport behavior [1].

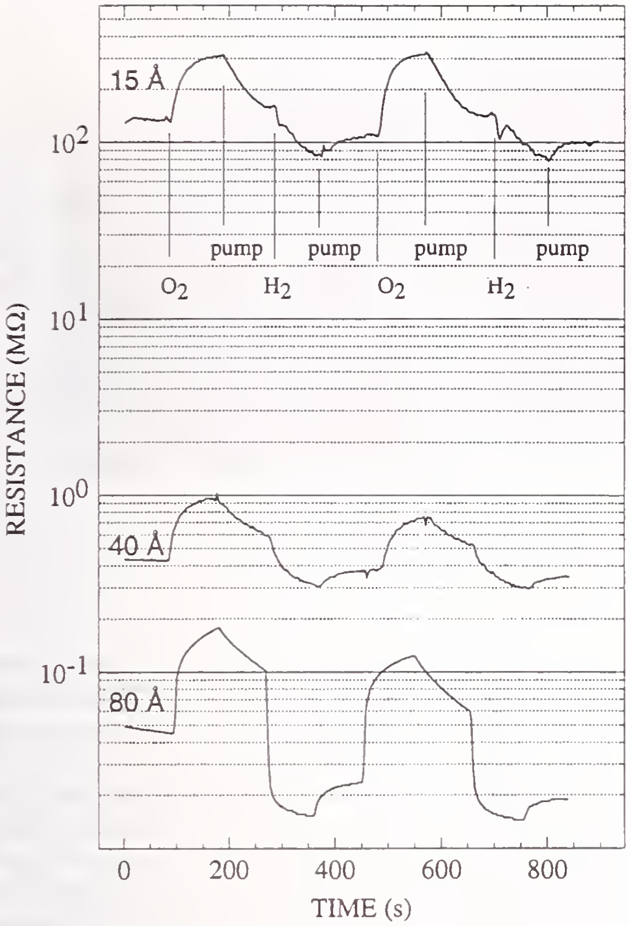

Figure 4. Resistance changes measured for O_2-pump-H_2-pump test cycles (gas pressures 10^{-3} Pa) on 3 ultrathin, epitaxial SnO_2 films on (0001) sapphire. The films, whose thicknesses are labeled (10 Å = 1 nm), have been activated with 1 monolayer equivalent of Pd and the responses were measured at 300°C.

A portion of our research program has involved examining highly ordered forms of oxides as improved sensing materials. Uniformity of factors such as particle size, crystalline orientation and atomic-scale structure can reduce the complexity of molecular adsorption phenomena in addition to producing more coherent and inherently stable base electrical properties. These benefits can be expected to occur for uniformity across the continuum of structure from the single crystal end toward the amorphous end. As one example of this work, we have developed procedures for the heteroepitaxial growth of SnO_2 on sapphire. The films grown have only a single, substrate-dependent orientation, with x-ray diffraction measurements showing that SnO_2 (101) forms on sapphire ($1\bar{1}02$) and SnO_2 (100) forms on sapphire (0001) [8]. Scanning probe measurements and low energy electron diffraction have indicated that the heteroepitaxial films are extremely smooth and that atomic ordering extends to the surface through a process of layer-by-layer growth [9]. The processing we have developed can therefore be used to produce continuous, ultrathin SnO_2 samples. The ability of such ultrathin oxide films to sense when they are modified by the addition of 1 monolayer equivalent of Pd is illustrated by the cyclical model responses shown in Figure 4 [10]. One noteworthy aspect in these results is that a sensing response is observed for an epitaxial film that is only 5 atomic layers (1.5 nm) thick. Efforts are being planned for incorporating epitaxial oxides into redesigned versions of our microhotplates.

Scanning tunneling microscopy (STM) characterization can define interfacial morphological and structural features which are critical to sensor performance. Figure 5a shows a STM image taken from a pure, 8.0 nm ultrathin SnO_2 (101) film. Islands of Pd that form when 0.5 and 7 monolayer equivalents are dosed onto this film are presented in Figures 5b and 5c [11]. Gas adsorption-induced, localized effects occurring near island structures similar to those shown in Figure 5b are collectively responsible for producing macroscopic sensing responses (related to those in Figure 4). In the years ahead, STM imaging and spectroscopy will become increasingly important as tools for understanding existing (and new) sensing mechanisms and guiding development of atomically engineered materials with improved sensing characteristics.

Before closing this section, it is important to note that device structures, such as the microhotplates discussed above, are playing a key role in materials research and development. For example, efficient surveying of relationships between materials processing, properties and performance can be achieved by using differing temperature schedules for the multiple microsubstrates present in a micromachined array. In addition, properly designed, systematic cycles of dosing and thermal schedules can be used to produce valuable information on surface adsorption [12] and reaction effects. In essence, these experiments seek to "invert" the device to examine the specific interfacial processes by which the it will operate as a sensor.

The remainder of this paper briefly addresses several other efforts at NIST.

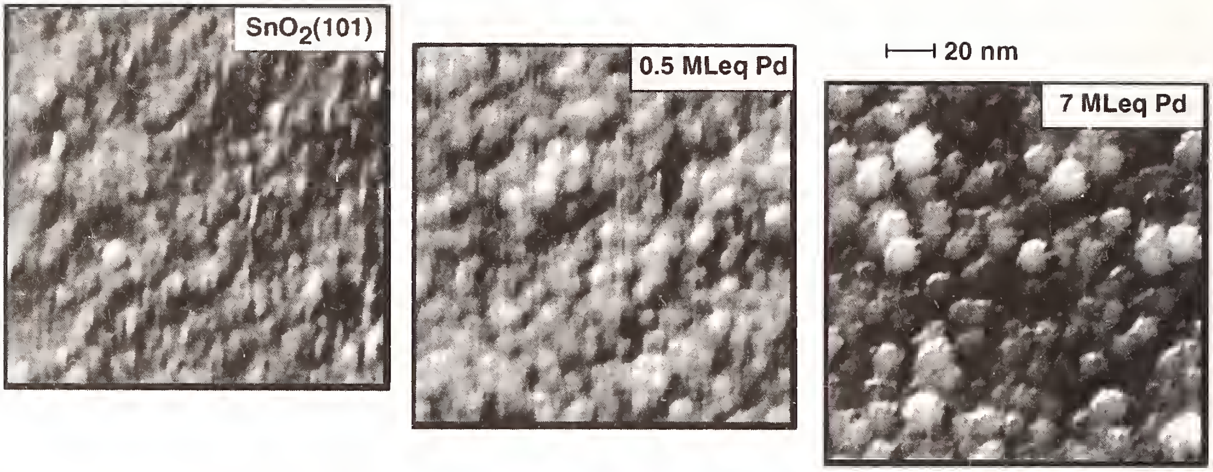

Figure 5. STM images obtained from (a-left) a pure, epitaxial SnO_2 (101) film, and the same film dosed with (b-center) 0.5 and (c-right) 7 monolayer equivalents (ML eq) of Pd.

Calibration Gas Mixtures for Sensor Development and Evaluation

Gas standards are developed by the Organic Analytical Research Division of NIST's Chemical Science and Technology Laboratory. These are binary and multi-component gases issued as part of the NIST Standard Reference Material Program. Approximately 90 gas SRMs are available ranging in concentration from 5 ppb to 21%. Inorganic, reactive and non-reactive species are available including organic halogenated and non-halogenated compounds. These SRMs may be obtained through NIST's Standard Reference Materials Program [13]. In cases where customer needs differ from available SRMs in species or concentration, research gas mixtures may be obtained through direct interaction between NIST staff and interested parties.

NIST is initiating a new facet to the program in gas standards to produce cylinders of gases known as NIST Traceable Reference Materials (NTRMs). This program utilizes the expertise and capabilities of the specialty gas industry to manufacture mixtures and relies upon NIST's analytical capabilities to analyze the mixture for species concentration. In this case the end user interacts directly with the specialty gas supplier(s) to obtain gas cylinders containing gases with species concentration assigned by NIST.

Optical Methods for Gas Compositional Measurement

Several research efforts within the Analytical Chemistry Division [14] of CSTL relate to the use of optical methods for compositional measurements. One project is aimed at evaluating the feasibility of doppler-free spectroscopy in the infrared spectral region as a means of monitoring for gaseous oxygenated hydrocarbon species. Development of such a capability could provide a new tool for real time automotive exhaust analysis. Fiber optic-based interferomery studies are also underway in the Analytical Chemistry Division. Thus far, this work has been focused in the area of immunoassay biosensors, but aspects of the detection and signal handling technology being developed could also impact related optical schemes for monitoring gases.

Gas Species Sensing for Fire Detection

Detection of gaseous species associated with fires is being pursued in the Fire Science Division [15] of the BFRL. Sensing requirements are the following:

Species of Interest:

CO_2, CO, H_2O, CH_4, H_2, Light Fuels

Oxygenated Hydrocarbons, HF, HCl, NO_x, HCN, O_2, & Carbonaceous Particulates

Concentration ranges:

10^{-7} - 10^{-1} mole fraction of gases

10^{-8} to 10^{-5} vol. fraction of particulates

Temp. Range: ambient to 1500K
Sensor Response Time: 10^{-3} - 10 sec.

Research activities are directed at investigation of fire phenomena under well-controlled conditions. Particular emphasis is placed on building fire phenomena. This research utilizes a large fire test facility that includes several types of energy-release measurement equipment based on calorimetric methods.

Standards and Measurement of Radioactive Gas Concentration

Development and maintenance of the National Primary Standard for Radon Concentration Measurement is one of the responsibilities of the Ionizing Radiation Division [16] of the PL. The standards and measurement technology developed are used in support of EPA and DOE environmental measurement programs, and for the U.S. Geological Survey. Calibration of working standards is offered.

Measurements and Standards for Moisture Concentration in Gases

The development and maintenance of national standards for moisture in gases is a responsibility of the Process Measurement Division [17] of the CSTL. Primary and secondary standards are developed and maintained. Secondary standards are precision humidity generators used to provide calibration services for humidity measuring instruments and sensors Operating ranges and uncertainty estimates are given in the table below for the NIST Two-Pressure Humidity Generator used to dessiminate calibration services.

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[2] The mention of commercial sensors based on the Taguchi design is included only for the purpose of example and is in no way meant as an endorsement of such products.

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[4] U. S. Patent No. 5,345,213.

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[13] For information, telephone 301-975-6776.

[14] For information, telephone 301-975-3108.

[15] For information, telephone 301-975-6864.

[16] For information, telephone 301-975-6090.

[17] For information, telephone 301-975-2609.

NIST Two-Pressure Humidity Generator, Mark 2, Range and Uncertainty

Humidity Parameter	Parameter Range		Uncertainty
Mixing Ratio (g water vapor/ kg dry air)	0.0015	0.005	1.5% of value
	0.005	0.1	1.0% of value
	0.1	0.3	0.5% of value
	0.3	515	0.3% of value
Volume Ratio, V (ppm$_v$)	3	10	1.5% or value
	10	170	1.0% of value
	170	500	0.5% of value
	500	820,000	0.3% of value
Dew-Point temperature, T_d (°C)	-70	-35	0.10
	-35	+80	0.04
Relative Humidity, RH, at Specified Test Chamber Temperatures			
$-55 \leq T \leq -40$ °C	3	98	0.8% RH
$-40 \leq T \leq -20$ °C	3	98	0.8% RH
$-20 \leq T \leq -0$ °C	3	98	0.4% RH
$-0 \leq T \leq 40$ °C	3	98	0.2% RH

*The expanded uncertainty with a coverage factor of two.

Gas Sensor Technology at Sandia National Laboratories: Catalytic Gate, Surface Acoustic Wave and Fiber Optic Devices

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Sandia's gas sensor program encompasses three separate electronic platforms: Acoustic Wave Devices, Fiber Optic Sensors and sensors based on silicon microelectronic devices. In this paper we review some of Sandia's research for the fiber optic and acoustic wave sensors and give some detailed new results for the new catalytic gate "robust" sensor. Performance of this sensor for reversible hydrogen detection is given for gas samples both with and without oxygen present and the effect of relative humidity is also discussed.

Sandia's gas sensor program encompasses three separate electronic platforms: Acoustic Wave Devices, Fiber Optic Sensors and sensors based on silicon microelectronic devices. A review of most of these activities was presented recently in a article in Science under the title "Chemical Microsensors" [1]. The focus of the program has been on understanding and developing the chemical sensor coatings that are necessary for using these electronic platforms as effective chemical sensors.

Fiber Optic Micromirror Sensors

The principles of operation of the fiber optic micromirror have been given in [1]. A special gas sensitive coating on the end of the fiber (50 μ diameter) changes its optical reflectivity in the presence of the species to be sensed. Recently an H_2 sensor using a Pd film was reported [2] and films sensitive to volatile organic compounds and nerve agent simulants are being tested [3]. The very light system weight for the micromirrors led to its being selected for an instrument package for the Mars94 lander. An array of micromirror fibers with different coatings will look for oxidants in Martian soil.

Acoustic Wave Sensors

Surface Acoustic Wave (SAW) devices use piezoelectric quartz as a substrate; they operate in the 100-MHz regime. SAWs rely on an identical pair of interdigital transducers to launch and detect a wave that travels from one end of the device to the other. Each transducer is comprised of many pairs of photolithographically defined fingers, each finger only a few micrometers wide.

The SAW is even more sensitive to tiny mass changes than the Quartz Crystal Monitor (QCM), detecting 100 pg/cm^2: less than 1% of a monolayer of carbon atoms. But the nature of the SAW's motion leads to extreme damping by liquids, so applications focus on gas-phase sensing and thin-film materials characterization in the absence of liquid contact.

The SAW device responds to changes in surface mass and other thin-film properties with a change in its velocity and, often, its attenuation. Measuring both these properties simultaneously helps to determine the nature and cause of the sensor response. Considerable effort has gone into the measurement of volatile organic compounds (VOC's) with the Sandia SAW devices [4]. Recently a new kind of chemically sensitive film based on a very thin self-assembled monolayer was reported [5]. It gives quite selective response to simulants of nerve agent compounds.

Catalytic Metal-Based Silicon Sensors

There are significant unmet needs for point sensors to detect H_2 and other oxidizing and reducing gases. The presence of H_2 can indicate corrosion or leaks and explosion and fire hazards exist for H_2 mixed with oxidants. There is considerable literature on the use of catalytic metals, particularly Pd thin films, for fabrication of microsensors for H_2 detection [6]. We recently reported a significant development of the "Robust, Wide Range H_2 Sensor"[7] in which some of the new research results on alloys of Pd were incorporated into a manufacturable sensor module which have been produced in large numbers in the Sandia Microelectronics Development Laboratory (MDL). A baseline radiation-hard CMOS 1.25 micron technology was used and the main deviation from standard IC processes was the deposition of the catalytic metal itself. This sensor has power transistors for chip heating and 9 p/n junctions for measuring temperature at various places on the chip. An analog feedback circuit keeps the chip at any desired operating temperature up to about 200°C. It can maintain the surface temperature even if cold gas flows are directed on the chip [8].

There are two kinds of gas sensors on each chip: a catalytic metal gated field effect transistor for low H_2 concentrations and a chemiresistor of the same catalytic metal for higher concentrations. We have found that sputtered films of about 10%(atomic)Ni and 90%Pd are providing outstanding sensor performance. The alloy does not undergo the hydride phase transition up to 630 Torr of H_2 at 25°C (pure Pd goes at about 10 Torr). This allows reversible detection from about 1 ppm to 100% (pure) H_2. In this article we would like to show some detailed performance data for the robust sensor in two real world situations. One involves the issue of detecting H_2 concentrations around the lower explosive limit(LEL) with and without the presence of O_2. The other concerns the effect of humidity on the response of the robust sensor.

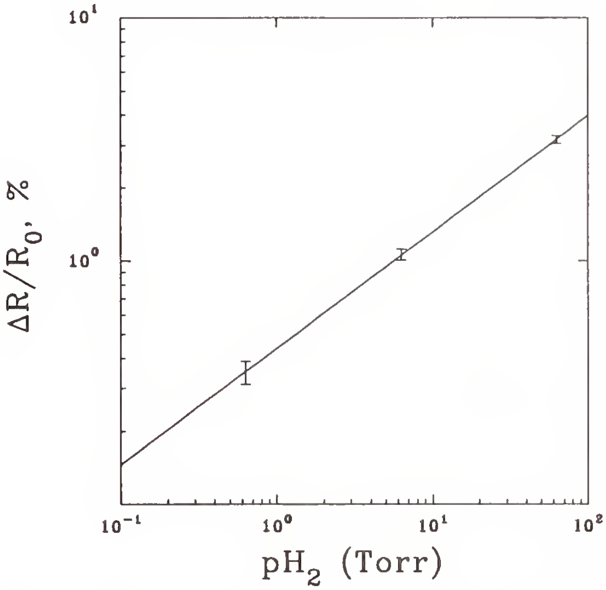

Figure 1. The response to pulses of H_2 of ten different robust sensors from the same wafer lot. The log-log plot shows the power law nature of the response.

Fig. 1 shows the response of the chemiresistors on ten separate robust sensors from the same wafer to pulses of H_2 ranging over two decades, from 0.63 Torr to 63 Torr (1000 ppm to 10%). The sensors were all operated at 50°C and were plugged into the same DIP socket, using the same read-out and temperature control circuit. The H_2 concentrations were provided by computer controlled flow controllers mixing the proper amounts of H_2 and N_2 to give the selected concentrations. The sensor head was placed in a Lucite fixture for exposure to the gas flows, which were kept at a constant 1 standard liter per minute (SLM). The error bars in Fig. 1 show the spread in raw data values among the ten sensors. The excellent die to die uniformity means that a minimum of calibration will have to be done with these batch produced sensors and shows one of the virtues of tightly controlled microelectronic batch processing.

The data in Fig. 1 are plotted as a log-log plot because of the power law response of the chemiresistors over a wide range in H_2 concentration: from about 100 ppm to 100%. For these sensors at 50°C, the power law in units of % change in resistance, is:

$$\Delta R/R_0 = 0.43(pH_2)^{0.48}\ (\%)$$

where pH_2 is the partial pressure of H_2 in Torr.

Fig. 2 shows how Sandia's Robust, Wide Range Sensor performs in both inert atmospheres like H_2 in N_2 and in the presence of an oxidant like oxygen. An oxidizing atmosphere is <u>not</u> required to sense variations in the levels of H_2 around the lower explosive limit (4%) on a time scale of a few seconds.

The sensor was put in a purged state at the beginning of the run by annealing at 140°C in air; the chip was held at an operating temperature of 80°C for the entire run. A pulse of 10% H_2 in N_2 (63 Torr) was delivered to the sensor in a flow cell at a measured flow rate of 1 (SLM). The fast response of both the FET and chemiresistor are seen. The gas composition was then changed to a much lower 0.1% H_2 in N_2 by introducing flow from another tank. The purge pressure of N_2 was not allowed to fall below 1 SLM to insure that no air backfilled the flow chamber. There are two seconds between data points and it can be seen that the sensor signal confirms a purging gas stream below the 4% explosive limit in less than 4 seconds. The actual sensor response is faster than this since it takes some time to purge the higher concentration out of the tubing and sensor holder volume. In less than 20 seconds the resistor sensor is reading the correct value for the mixture, 0.1% H_2 (1000 ppm). The FET only shows a small change, but it also gives the correct value for the 0.1% mixture. The next pulse to 10% H_2 shows the speed and repeatability of the sensor and is followed by a purge from a tank with 0.01% H_2 (100 ppm). It takes less than 20 seconds for the sensor signal to fall below the level for 0.1% and only 50 seconds to reach the steady state value for 0.01%, which is close to the

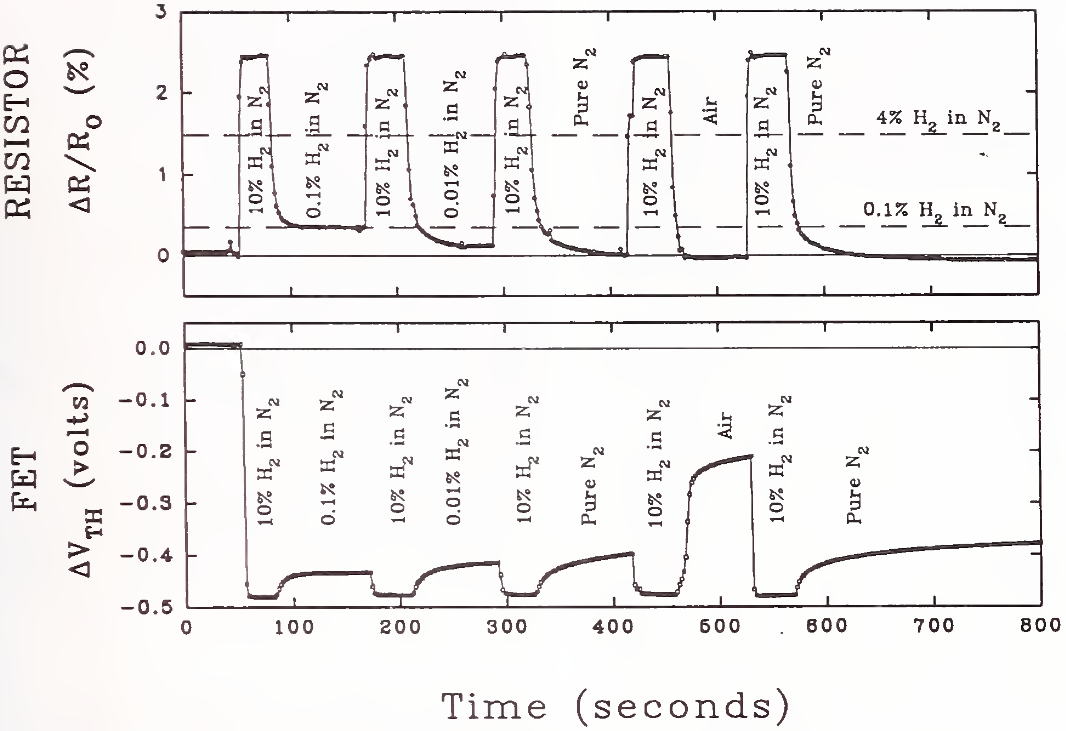

Figure 2. Raw data output from one of the Robust Sensors from a series of pH_2 pulses of various concentrations. The top trace is for the chemiresistor and the bottom trace is for the FET. The data from the two sensors is taken simultaneously and the sensor chip temperature is maintained at 80°C.

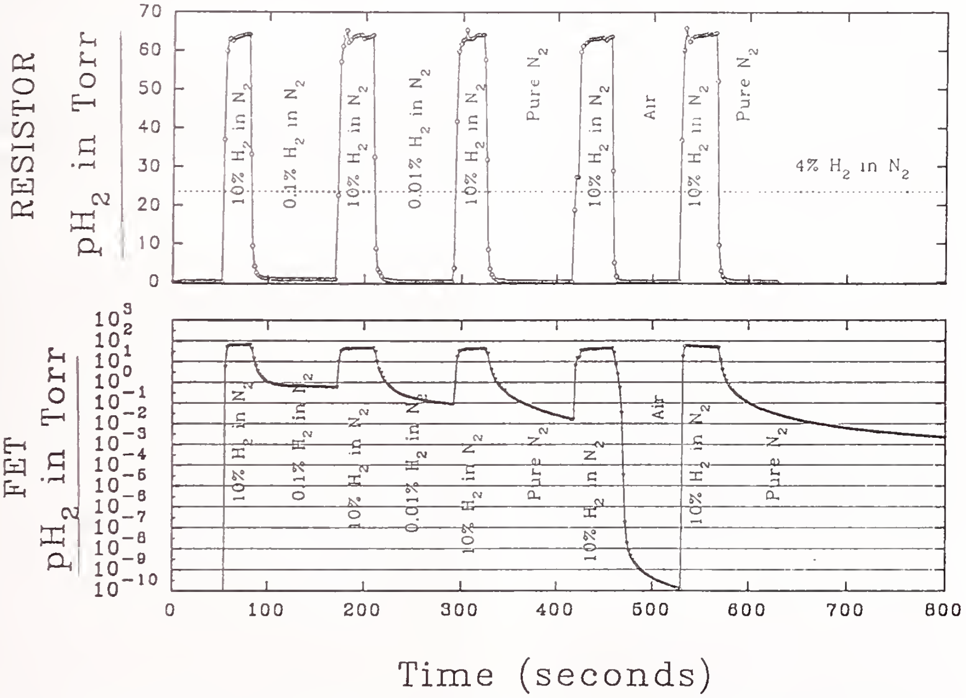

Figure 3. The same data set as Fig. 2 with each point converted to a pH_2 value the the calibration curves give text.

baseline for the resistor. A third 10% pulse is followed by a pure N_2 purge. It would be difficult to ensure from either sensor whether the H_2 has fallen below 0.01% (100 ppm) in the 100 second time scale. The purge for both the FET and the resistor is faster in air as shown following the 4th pulse of 10% H_2.

Figure 3 shows the same data set as Fig. 2 with every data point converted to a pH_2 value by the calibration formula for each sensor:

1) for the chemiresistor:

$$pH_2 = 9.4\,(R)^{2.08},\ \text{(a power law from ref.[9])}$$

2) for the FET:

$$pH_2 = \exp((\Delta V_{th}{*}1.813-.78)/0.0217),\ \text{(a Temkin isotherm from ref.[9])}$$

The deviations in the resistor signals for 63 Torr are not noise, but small changes in the actual pressure caused by attempts to fine tune the flow rate to 1 SLM by hand.

It may seem surprising that the FET has such a huge dynamic range, but this effect has been discussed by several authors [6, 9]. It occurs because the occupation of surface sites on a "dirty" Pd (or Pd/Ni) surface follows a Temkin isotherm. This probably means that there is a wide variation in the energy of adsorbed species; the deeper sites are occupied at low pressures and the shallow ones at the highest pressures. The ability of the FET in the real world to give accurate readings of the H_2 concentration is limited by the rate at which the deeper sites approach equilibrium with a given pH_2 value. Thus it can be seen from Figs 2 and 3, that for pH_2 above about 0.6 Torr both sensors give rapid reversible readings whether O_2 is present or not. For the purge of the FET in air (around 500 seconds), the actual value of pH_2 is zero, but the steady state value of the sensor signal for low pH_2 (say 10^{-5} Torr) mixed with 140 Torr of O_2 would not give an accurate reading of pH_2. If the pO_2 is known fairly accurately from a separate O_2 sensor, then we have found that the pH_2 can be fairly accurately determined down to about 0.01 Torr if time is allowed for steady state to be reached.

From the calibration formulas it would seem that all the necessary information about pH_2 could be obtained from the FET alone. In theory this would be true since the surface sites giving the FET threshold voltage shift are thought to be in equilibrium with the bulk sites that give the resistance change. In practice it turns out that drift in the baseline of the FET and the logarithmic response make it less reliable in determining the accurate value of pH_2 in the higher ranges. It should be remembered that both the surface sites and the bulk are in thermodynamic equilibrium with the gas phase pH_2, but they can independently change calibration and/or signal size because of materials changes in the surface properties or grain boundaries or other as yet unspecified changes in the metallurgical properties of the thin films.

Summarizing Figs. 2 and 3, the Sandia Robust, Wide Range Sensor has response times of less than 2 seconds for detecting H_2 leaks and less than 20 seconds for detecting large variations in the H_2 concentration around the 4% explosive limit including purge information down to 0.01% (100 ppm), more than a factor of 100 lower than the LEL. Most users will not be interested in fast, accurate measurements between 1 ppm and 100 ppm, but this can be accomplished by operating the FET sensor at 140 °C.

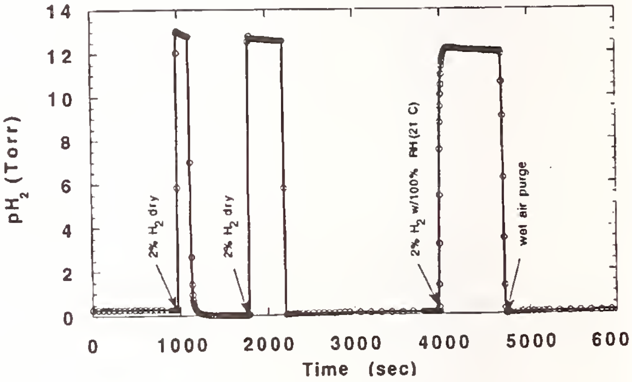

Figure 4. Response of a chemiresistor on the robust sensor to 2% pH_2 pulses followed by air purges. The third pulse has 100%RH at 21°C mixed with the gas stream. Operating temperature is 50°C.

The data presented in Figs. 1-3 were taken with 0% relative humidity (RH). In real world situations, even when O_2 is purged from a large structure by He or N_2, water vapor will probably be present. In a pending publication[10] we show how higher levels of RH slowed the response of a Pd/Ni chemiresistor operating at room temperature. The response for the heated robust sensor is much improved, as shown in Fig. 4. This data set has had every data point converted from the $\Delta R/R_0$ value to the calibrated pH_2 value by the calibration formula shown above. The first two pulses of H_2 were "dry" 2% (pH_2 =13 Torr). The first pulse was performed on a fully annealed robust sensor (140°C in air) and is slightly different from subsequent pulses. Each pulse of pH_2 is followed by a dry air purge at the operating temperature of 50°C. Before the third pulse the gas stream was routed through a water bubbler to bring the stream up to 100% RH (at 21°C). This adds about 19 Torr of water vapor to the stream. The gas mixture was then again changed to 13 Torr pH_2. The data points were taken 5 seconds apart and it can be seen that the presence of 19 Torr of water vapor slows the response of the sensor. The steady state value is only slightly lower than from dry pH_2 pulses. The purge with "wet" air is also somewhat slower. The operating temperature of 50°C was chosen because less power is consumed than at 80°C and the signal is somewhat larger. Higher operating temperatures, like the 80°C shown in Figs. 2 and 3 show faster responses and even less perturbation by water vapor. It should be noted that the partial pressure of the water vapor is determined by the temperature of the water in the bubbler; the actual RH on the sensor surface at 50°C is by definition lower. The partial pressure of water vapor in some very hot and humid parts of the country could be even higher than the 19 Torr employed here for the test.

ACKNOWLEDGEMENTS

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Microchemical Sensing Based on Temperature-Programmed Methods

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This paper describes a silicon batch-fabricated gas detector formed by an ultra-thin metal sensing film supported on a selectively-micromachined dielectric window. A 5µm-thick boron-diffused bulk-silicon heater under the window permits the film temperature to be varied from ambient to over 1200°C with heating efficiencies in air and vacuum of 6°C/mW and 20°C/mW, respectively. The window area is $1mm^2$ with an active sensing area of $0.12mm^2$. The heater has been optimized to produce a simulated temperature uniformity over the film area of better than ±0.5% while interleaved temperature-sensing resistors permit the average temperature to be measured to better than 1°C. The detectors are realized using a simple six-mask process in a die size of 2.8mm x 2.8mm. All process steps are foundry compatible. A custom VLSI control chip contains all the required interface circuitry for the simultaneous operation of four such detectors. Window temperature is set digitally with eight-bit accuracy. Film conductivity (magnitude and phase) is measured from dc to 2MHz for full-scale film resistances from 5 ohms to 1.3Mohms. The interface chip utilizes an eight-line bus interface, allowing the implementation of a multi-chip analyzer as a smart peripheral. The control chip is implemented in an eleven-mask 2µm CMOS process in a die size of 4.4mm x 6.6mm. This sensor structure can be operated in a number of modes depending on the requirements for selectivity, sensitivity, and time response. Examples illustrating monolayer sensitivity for oxygen, reversible adsorption of oxygen, and detection of oxygen in the presence of CF_4 are presented.

INTRODUCTION

Solid-state gas sensors have been the focus of considerable research during the past decade and are in high demand for automotive, medical, environmental monitoring, and process control applications [1-4]; however, substantial performance problems remain in such devices, including slow response, low sensitivity, poor selectivity, long-term drift, and high input power. In contrast to detection methods based on spectroscopic techniques or gas chromatography, conductivity-based gas detectors rely on chemical interactions between the gas molecules and a surface film to produce a detectable output signal. Such devices are promising candidates for many applications because of their low potential cost and suitability for batch fabrication; however, the significant amount of research that has been invested in improving these sensors has met with limited success due to the unforgiving nature of the films involved and the complexity of the associated surface chemistries [5,6].

Recent research on gas sensors at the University of Michigan has focused on silicon-based conductivity-type gas detectors based on ultra-thin (<4-6nm) metal films supported on selectively-heated micromachined dielectric windows [3-4,7-8]. Since the film conductance depends significantly on gas adsorption as well as on the window temperature, conductance changes at a known temperature can be used as an indicator of the type and quantity of gas present. Because in this case the film is very thin, surface effects are much more significant in determining the film conductivity than in thicker films, where bulk reactions and diffusion effects dominate [8]. Gases that chemisorb on the film surface will substantially affect the film conductance by changing the number of charge carriers or the mobility of charge carriers. On the other hand, inert gases such as helium or CF_4 do not chemisorb under typical operating conditions. Therefore, they do not change the resistance of the sensing films. The resulting devices are relatively fast (<1s), and initial measurements showed them to be stable over repeated temperature and gas cycling. For example, when operated at 150°C using 35Å/65Å Pt/TiO_x sensing films, such detectors responded chemically to oxygen from 10^{-7}Torr to 10^{+3}Torr with negligible drift and hysteresis, and the detection of sub-ppm oxygen levels in CF_4 was demonstrated [4,8].

This paper describes a second-generation detector [3] intended as a vehicle for further device characterization and as a prototype in-line sensor for gas purity in semiconductor manufacturing applications. The new detector offers substantially-improved temperature uniformity over the sensing area, more accurate sensing of the window temperature, and improved thermal efficiency. It is also compatible with use in a multi-element monolithic gas analyzer [4,9], allowing the detection of gaseous mixtures by using several windows, each programmed with a different sensing film.

The ability to precisely control film temperature is being exploited in various ways. Pretreating the film by heating it to temperatures in excess of those expected during subsequent operation has been found to play an important role in determining gas sensitivity. The use of temperature-programmed desorption (TPD) in these detectors should also provide increased selectivity and specificity in analyzing gaseous mixtures. By tracking the conductivity shifts as the window temperature is ramped through characteristic desorption thresholds (where the gas molecules have sufficient energy to escape from the surface), the type and amount of gas present can, in principle, be determined. At higher temperatures, TPD can also be used to "reset" the film by desorbing all gases, allowing a time analysis of the film reactions and disposing of gases that interfere with detection.

DETECTOR STRUCTURE

A cross-section and top view of the new gas detector are shown in Fig. 1. A stress-relieved dielectric window [7], composed of a sandwich of thermally-grown silicon dioxide (300nm), low-pressure chemical-vapor-deposited (LPCVD) silicon nitride (250nm), and LPCVD silicon dioxide (700nm), is used to support the sensing film as well as a set of four electrodes for measuring the film conductivity. The window stress is determined by the ratio of these layer thicknesses and has been adjusted to provide a stress-relieved window over the normal operating temperature range of 200-500°C. A boron-doped silicon heater is located under the window, allowing the upper surface of the chip to be highly planar. This is particularly important due to the very thin nature of the sensing film and the associated continuity problems over any surface steps. Contacts to the film and the heater are made with Ir/Ti metallization (200nm/25nm), which is stable at high temperatures on the windows [8]. The heater contacts are positioned away from the heated area of the detector so that they do not see the full window temperature. Two boron-doped silicon temperature-sensing resistors (shown black in Fig. 1) are used to monitor the chip temperature within its active area and are interleaved with the heater to provide high thermal coupling and temperature uniformity. The thin sensing film (e.g., Pt/TiO_x) is deposited at wafer level and is defined photolithographically using a lift-off process. For films that are not compatible with the final silicon etch used for window formation and die separation, a silicon micromachined shadow mask technology has been demonstrated at wafer level to allow the use of virtually any material that can be vacuum deposited.

DETECTOR FABRICATION

Figure 2 summarizes the process flow for gas detector fabrication. Processing is performed on <100>-oriented double-side-polished silicon wafers. First, a 1.4μm-thick silicon dioxide layer is thermally grown and patterned to act as a mask on both the front and back sides of the wafers during the following deep boron diffusion. Backside alignment is performed using an infrared aligner, with an aluminum pattern added to the front side as an alignment aid. The Al pattern is self-aligned with the front oxide and does not require an additional mask. After oxide patterning and removal of the aluminum, a 5μm-deep boron diffusion is performed at 1175°C for 2.5 hours in order to create the supporting rim, heater resistor, and temperature sensing resistors. In order to form the dielectric windows, the wafers are now thermally oxidized to about 200nm, and layers of silicon dioxide (100nm), silicon nitride (250nm), and silicon dioxide (700nm) are deposited using LPCVD.

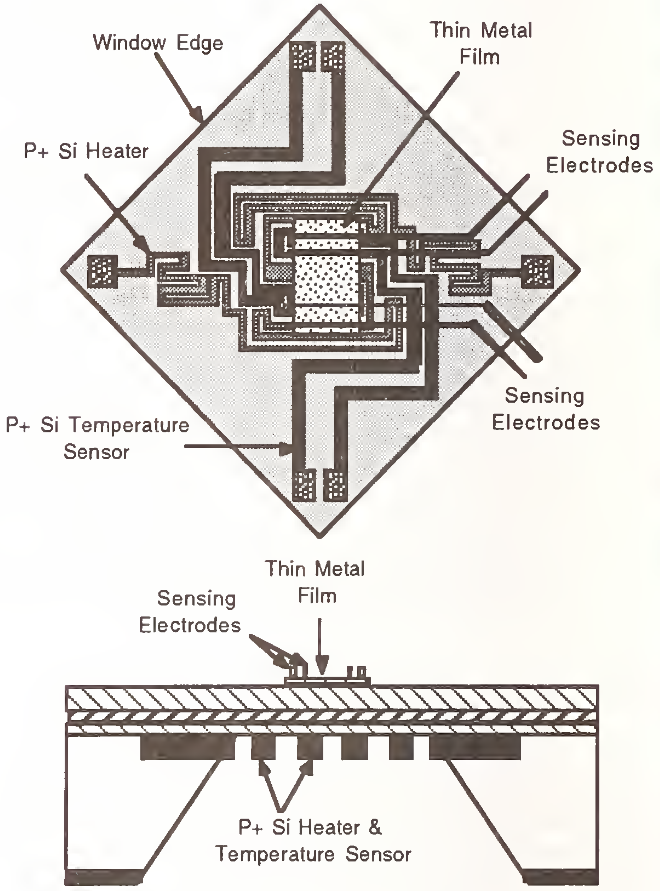

Fig. 1: Basic structure of the thin-film gas detector

Next, the heater and temperature sensor contacts are patterned and opened through the dielectric window using a combination of wet etching and RIE. After stripping this resist layer, the wafers are patterned again, and 5nm of Ti and 3nm of Pt are evaporated and lifted off to define a typical sensing film. The sensing electrodes and connections to the heater and temperature sensors are next formed by sputtering 25nm of Ti and 200nm of Ir onto the wafer using a second lift-off process. Finally, the silicon wafers are etched in ethylenediamine-pyrocatechol-pyrazine (EDP) in order to form the windows, heaters, temperature sensors, and separation lanes between the individual detectors on each wafer. The EDP anisotropically etches the lightly-doped silicon but does not significantly attack the areas that have been heavily doped with boron. Figure 3 shows a perspective view of the dielectric window, heater, and contacts after the completion of the fabrication sequence. All of the individual process steps are standard in the microelectronics industry and, in fact, similar process flows are now being run commercially. For individual detectors not containing electronics, the double-sided process could be eliminated and a deep boron-diffused rim could be formed from the front as in recent thermal detectors [10]. This would eliminate one masking step along with the infrared alignment and most of the slow EDP etch at the end of the process.

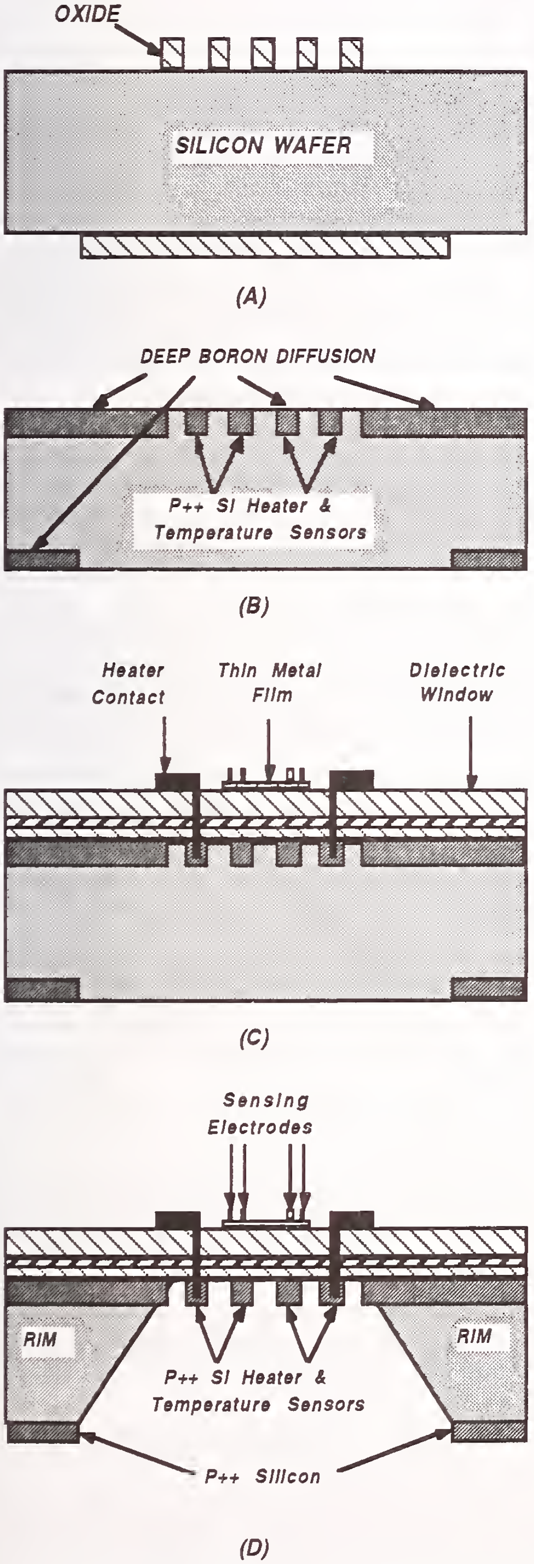

Fig. 2: Overall process flow for the monolithic gas detector.

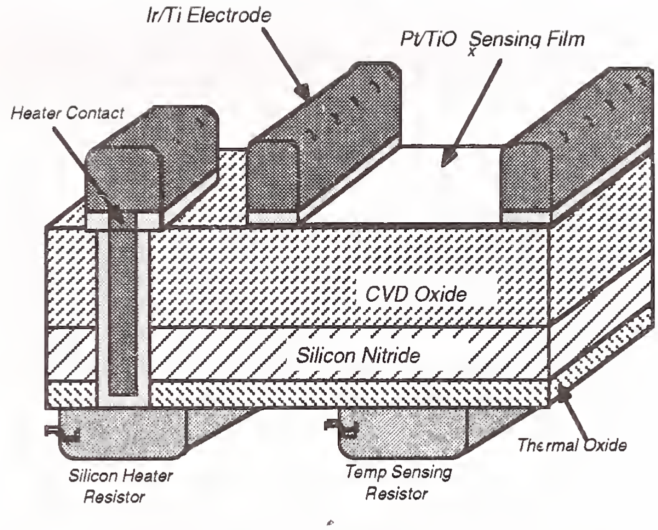

Fig. 3: Cross-section of the completed window area of a micromachined gas detector.

ELECTRICAL DETECTOR CHARACTERIZATION

Figure 4 shows a photograph of a typical detector chip. Both circular and rectangular heater and sensor geometries have been explored. The heaters have nominal resistances of 750 and 1000 ohms, while the temperature sensing resistors have a resistance of 350 ohms and temperature coefficients (TCRs) of 1800ppm/°C. The thin sensing films in the case of Pt/TiO$_x$ are deposited during the batch wafer processing and are defined using photolithography (lift-off). As noted above, they can also be defined using shadow masking.

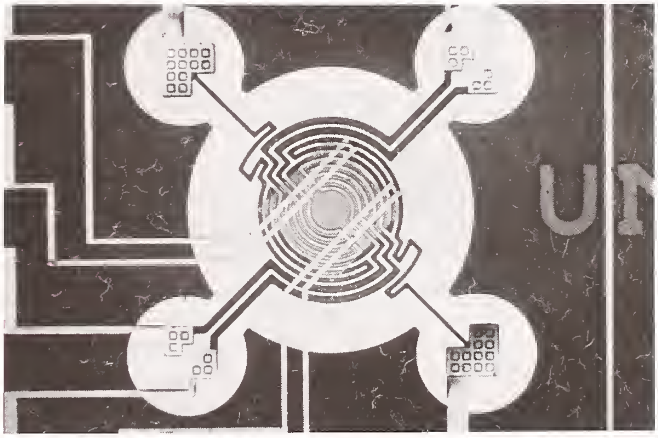

Fig. 4: Top view of a typical detector chip. The circular window has a diameter of 1mm.

Figure 5 shows the simulated window temperature distributions for both the first- and second-generation detector designs through the middle of the window. The new design provides a much more uniform temperature and the generated heat is restricted to the area under the thin film, resulting in a more efficient heater. The film temperature uniformity has been improved by more than an order of magnitude and is better than ±0.5% over the active area of 0.12mm^2 (350µm x 350µm). The total window size here is 1mm x 1mm.

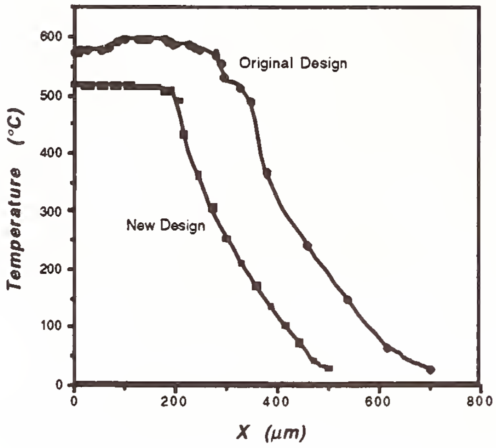

Fig. 5: Simulated window temperature distribution along a line from the center of the window to the window edge (x-direction). The input heater current is 10mA at room ambient pressure (maximum convection).

Figure 6 shows the response of the dielectric window to input power in both in room air and in vacuum. The slopes correspond to efficiencies of 6°C/mW and 20°C/mW, respectively. In vacuum, temperatures well above 1200°C can be achieved. At the anticipated operating temperatures for gases of interest (200-500°C), a long operating life is expected for the devices so long as the gases are not reactive with silicon. In the case where the gas of interest would react with silicon dioxide, a silicon nitride outer coating on the window could be used.

INTERFACE CIRCUIT DESIGN

In order to form a full gas analyzer, an array of these detectors is needed along with control circuitry for setting the window temperatures and sensing the film impedances. While in this research, the readout/control chip has been added as a hybrid to form a full analyzer, the basic gas detector process is compatible with the use of on-chip CMOS circuitry [11]. The only significant change introduced into the CMOS process when merging it with the detector process is to perform the etch-stop diffusion as part of the p-well drive-in procedure. For the present, however, the detector and its control circuitry have been kept separate in order to simplify fabrication of the many detectors needed during on-going characterization studies.

Figure 7 shows a block diagram of the control chip [3] and its connections to a corresponding detector. The chip consists of three principal blocks: the heater controller, the conductivity sensing circuitry, and the control/interface unit. The chip communicates over an eight-line interface [12] to either an embedded VLSI microcontroller (forming a smart sensing node) or to a remote processor. The desired set point for the heater is entered serially and latched in an eight-bit digital-to-analog converter (DAC). This DAC generates a reference voltage for an MOS comparator which drives the heater. Temperature feedback is derived from the sensing resistor on the window and is used to limit the comparator drive at the appropriate level. This window temperature can also be read out.

The film conductivity can be measured at ac or dc using the circuitry in the sensing block. Two eight-bit DACs can be set using serial input data to select the appropriate current level and frequency of the measurement. Magnitude and phase information is sensed and fed off-chip, again using the eight-line interface. The chip has been designed to operate with films having resistances (full scale) from 5 ohms to 1.3Mohms, allowing it to be used with a wide variety of different film types. This control chip employs over 4000 transistors and was fabricated at MOSIS using a 2µm p-well double-poly double-metal CMOS process in a die size of 4.4mm x 6.6mm.

The control chip has been tested and found fully functional with performance at or near the design targets. The heater drive voltage is separate from the logic supply to allow higher temperatures to be reached for special situations. (The temperature saturates at the higher DAC input codes if the heater back voltage exceeds the supply.) At 5V, the windows reach an operating temperature of about 150°C in air and about 350°C in vacuum, increasing in the latter case to 540°C at 7.5V and 700°C at 10V. The film conductivity measurement uses a film interrogation current that is set over an eight-bit range in amplitude and can be used from dc to 2MHz. The I/O interface logic also functions as required.

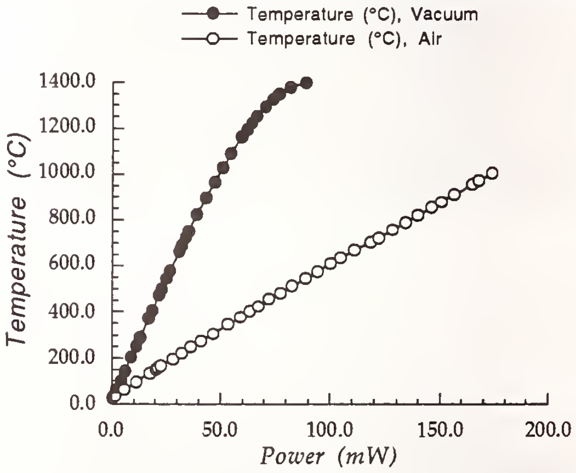

Fig. 6: Measured response of the dielectric window to input power delivered to the heater in vacuum and in air.

SENSOR OPERATING MODES

Several operational modes are available using this thermally-compensated multi-element sensor structure which emphasize various aspects of the chemical and physical sensitivity and selectivity of these devices.

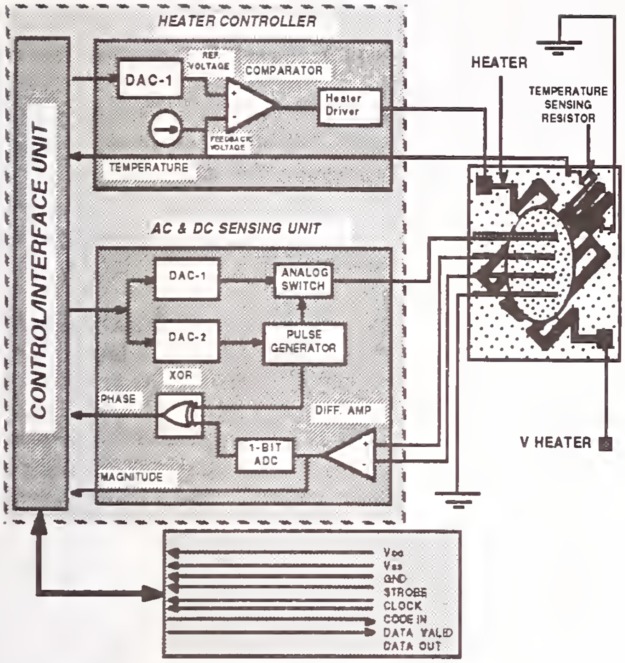

Fig. 7: Block diagram of one of the four circuit blocks of the gas analyzer control chip.

Thermally-uncompensated mode: When the film is not thermally compensated, the sensor resistance changes are dominated by heat transfer to the gas phase, making the device a pressure and temperature sensor.

Thermally-compensated isothermal adsorption/desorption mode: Accurate thermal compensation makes it possible to operate the sensor in an isothermal or temperature-programmed mode. In this mode of operation the sensor response is dominated by changes in resistance caused by chemisorbed gases. The ability to operate the sensor over a wide temperature range allows us to optimize the sensitivity and selectivity of the active film to specific gases by selecting a temperature where high surface coverages are observed. A reversible response can be achieved by operating in a temperature regime where reversible adsorption/desorption occurs.

Thermally-compensated isothermal reaction mode: One of the major problems in the field of chemical sensing is the need to reset the sensor surface after irreversible adsorption. This problem can be overcome by using chemical reactions with gases such as oxygen or hydrogen stored in adjacent, thermally-activated chemical reservoirs. For a specific film/adsorbate system, the adsorbed species will show a characteristic reactivity at a specific reaction temperature.

Thermally-compensated temperature-programmed desorption mode: For situations where rapid desorption is not feasible, adsorbed species can be removed by ramping up the temperature and monitoring the desorption of surface species. The temperatures where adsorbed species can be removed depends on their strength and nature of bonding to the surface. There is a characteristic temperature where the chemical bonds between film and adsorbed species break, releasing the adsorbate into the gas phase. By monitoring this change we can often differentiate between various types of molecules.

Thermally-compensated temperature-programmed reaction mode: Chemical reactions can also be used to remove adsorbed species. The reactivity of adsorbed species on particular catalytic surfaces depends on the structure of the adsorbed species and the chemistry of the active film. Therefore, for a specific film/adsorbate system, the adsorbed species will show a characteristic reaction temperature with typical "cleaning gases" such as hydrogen or oxygen. By monitoring the response, we can often classify the nature of the adsorbed species.

Multi-window sensing structures for enhanced selectivity: Enhanced selectivity or reactivity modes can be accomplished by combining several sensor windows into an array, where each window is independently temperature-controlled. The multiple windows can be equipped with different films to optimize selectivity for classes of molecules or for storage/release of reactive species. In these configurations, more than one of the above modes of operation can be easily accommodated on a single chip.

CONDITIONING OF SENSORS PRIOR TO USE

Stabilization of the active films is accomplished by repeatedly exposing them to chemical and thermal environments which are more severe than those expected under normal operating conditions. We have found experimentally that treating Pt/TiO_x films in vacuum vs. oxygen at temperatures in the range of 500-700°C results in films with unique but stable chemical sensitivity.

Films pretreated at 700°C in vacuum show resistances which are substantially smaller than those of analogous films exposed to oxygen at the same temperature. The temperature coefficient of resistance for vacuum-treated films is positive, a property characteristic for metallic films. The behavior of oxidized films is much more complex and often indicative of semiconducting behavior. Once stabilized, the sensing films show reproducible behavior for operation at temperatures below 500°C, independent of the chemical environment the films are exposed to in RIE applications.

SENSITIVITY AND SELECTIVITY OF Pt/TiO_x GAS SENSORS

Response to low-pressure oxygen and hydrogen dosing using the thermally-compensated temperature-programmed desorption mode:

We have demonstrated monolayer sensitivity by observing significant and surface-coverage-dependent resistance changes for both hydrogen and oxygen in a pressure regime of 10^{-7} Torr. These experiments have been performed in UHV on both hydrogen and oxygen pretreated films.

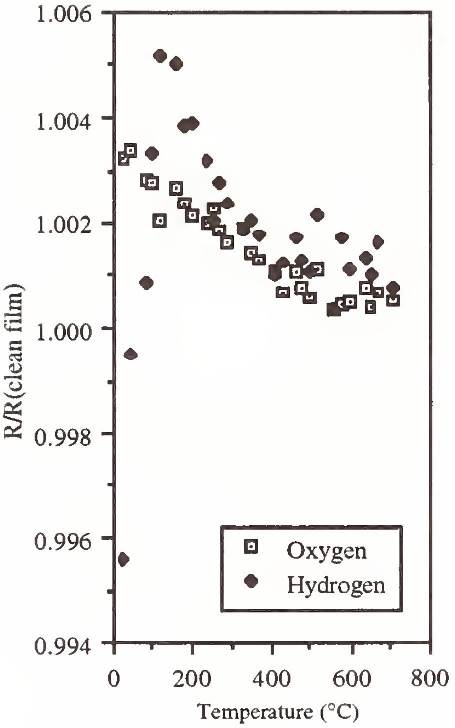

Fig. 8: Resistance change of a Pt/TiO_x sensing film during TPD following adsorption of 10L of O_2 or 5L H_2, respectively. (1 Langmuir, L, corresponds to exposure to 10^{-6} torr gas for 1s).

On adsorption of 5L of H_2, the film resistance R decreases compared to that of the clean film, R(clean film). When the temperature is raised into the regime where hydrogen is known to desorb from Pt surfaces, the resistance returns to that of the clean film. Exposure to 10L of O_2 initially increases the resistance compared to the clean film, and during temperature-programmed desorption the resistance slowly returns to the starting point of the clean film (Fig. 8).

Reversible response to oxygen using the thermally-compensated isothermal adsorption/desorption mode:

Figure 9 shows the response of a vacuum-activated Pt/TiO_x film exposed to 4.5×10^{-4} Torr of oxygen at 400°C. When oxygen is removed from the reactor chamber, the resistance of the film returns to its initial value in less than two minutes, demonstrating the reversibility of the response.

Response to oxygen and perfluoromethane mixtures at 10^{-3} Torr:

Films operated isothermally do not respond to pure CF_4, while small additions of O_2 in the ppm range lead to resistance changes characteristic for oxygen. Figure 10 shows a rapid increase in resistance when 6μTorr of oxygen is added to a flow of 10μTorr of CF_4 at 300°C. When the oxygen flow is stopped, the resistance of the film gradually decreases, indicating that the desorption of oxygen into the CF_4 stream is slow. Addition of 1μTorr of hydrogen rapidly removes the remaining oxygen, and the film resistance drops to the low value characteristic for a hydrogen-exposed film.

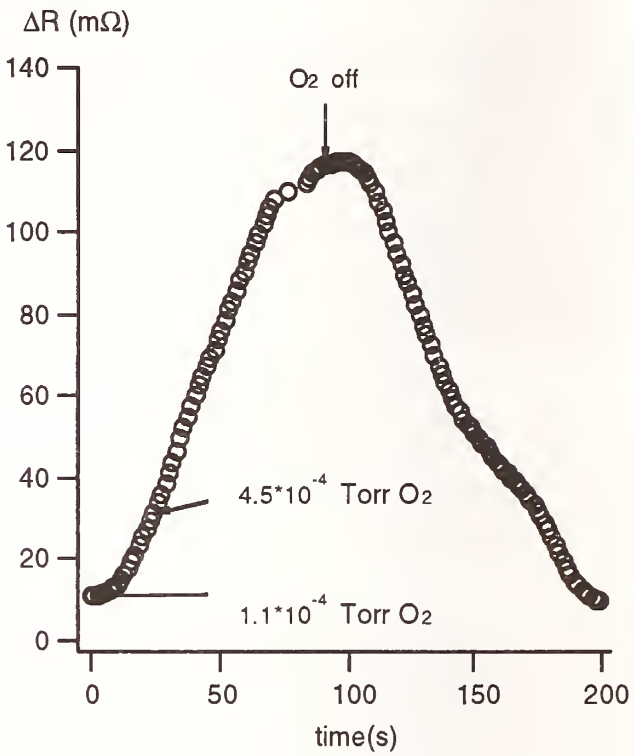

Fig. 9: Response of a Pt/TiO_x sensor operating at 400°C to changes in oxygen partial pressure. Oxygen was bled into the system during the first 89 seconds, followed by pumping down of the system.

CONCLUSIONS

This paper has reported a second-generation conductivity-type gas detector. The structure is suitable for use with both conventional sensing films (e.g., tin oxide) and with ultra-thin metal films. The upper surface of the detector structure is highly planar to eliminate the step coverage problems associated with polysilicon heaters. Single-crystal boron-doped silicon sensing and heating resistors are formed underneath the dielectric window from the wafer bulk. The heater design results in a temperature uniformity over the sensing area of within ±0.5 percent and allows measurement of the operating film temperature to within 1°C. A monolithic CMOS interface chip allows four such detectors to be operated simultaneously using digital input commands received over an eight-line bus. Window temperature can be set with eight-bit accuracy over the range from ambient to over 1200°C, while film conductance is measured over a broad range in both magnitude and frequency. This sensing structure can be operated in a number of modes depending on requirements for selectivity, sensitivity, and time response.

Monolayer sensitivity for oxygen and hydrogen has been recently demonstrated for a Pt/TiO_x sensing film operating at room temperature in the temperature programmed desorption mode. Reversible response to oxygen has been demonstrated for this same film operating at 400°C. The thermally-compensated isothermal reaction mode has been illustrated using oxygen in the presence of CF_4 and removing the oxygen by reaction with hydrogen. Detailed chemical characterization of these devices is underway in a variety of gaseous environments.

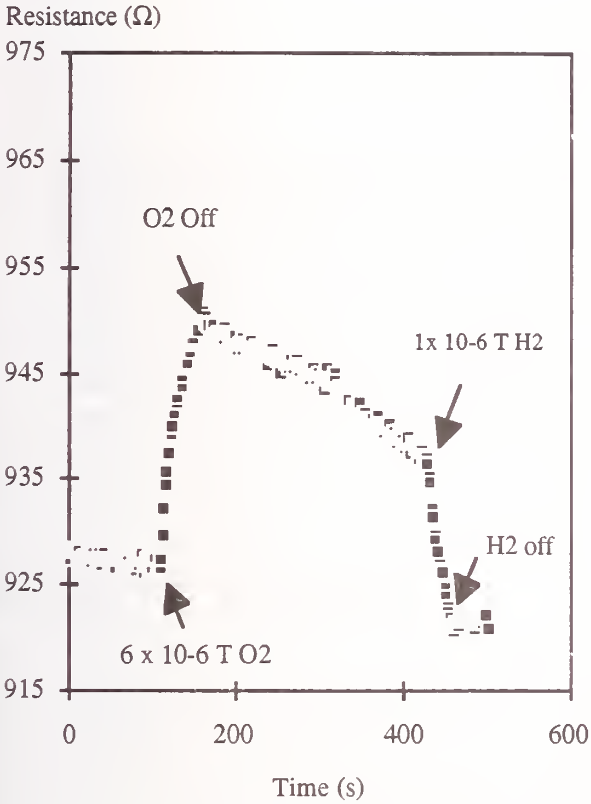

Fig. 10: Response of an integrated gas detector in 10μTorr of CF_4 to the addition of 6μTorr of O_2, followed by removal of oxygen and exposure to H_2.

Acknowledgments

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Amperometric Electrochemical Gas Sensors: Description and Applications

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The amperometric gas sensor can and does provide industry with a sensitive and often selective measurement for toxic gases. These devices are relatively simple and low cost, consume only mW of power and need no consumable supplies to operate. Gases measured include O_2, CO, H_2S, NO, NO_2, SO_2, O_3, HCN, HCl, NH_3, H_2CO, and many others at the ppm and ppb level. Applications include environmental, health, safety, industrial hygiene, medical, military, analytical instruments, field research [e.g. volcanology], and process control applications. Future devices will be improved and address new industrial markets like stack gases and space station controls.

AMPEROMETRIC GAS SENSORS

This manuscript presents a brief description of the amperometric gas sensor and is based upon several recent reviews [1,2]. The focus of this discussion is sensors of the type with which the author has been most extensively involved. There is not attempt to slight other electrochemical sensors be they excellent examples of amperometric, potentiometric, or conductimetric sensors. This review is limited for practical reasons. This work would not have been possible without the tireless support of my many collaborators and colleagues [whom are indicated in the citations and references therein].

The low power, small size, and other logistical characteristics of electrochemical detectors make them an attractive technology and commercial amperometric gas sensors are very successful [1,2]. The sensitivity of these electroanalytical methods is often impressive. For example, an NO_2 sensor, even in a flowing gas stream, can easily detect about 4×10^{-12} G/sec and this corresponds to a detectable concentration of less than 2 ppb in the 200 cc/min gas sample flowing through the sensor cell. The typical limit of detection in these systems is not the detection of the reaction since the reaction produces significant electric currents even at extremely low concentration. Rather, detection using electrochemical gas sensors is limited by the ambient background currents, interferences, drift, and amplifier noise all of which degrade the S/N (signal to noise ratio) of the amperometric sensor in a particular application. Therefore, we expect improvements in the sensitivity of amperometric gas sensors to come not from increasing the magnitude of the analyte signal but rather from the reduction or elimination of the background currents and by employing sensor electronics and pneumatics that can distinguish the signal over the background, noise, and drift. Investigation of novel solid electrolytes, new electrocatalysts, and microsensor structures with unique geometries have produced gas sensor systems with exceptionally fast response and improved signal to noise ratios. But these new gas sensor systems appear to contaminate easily.

The electrochemical gas sensor has been used to measure many industrial compounds including CO, H_2S, NO, NO_2, H_2CO, N_2H_4, H_2, SO_2, HCN, mercaptans, NH_3, HCl, and others. In principle, any compound that is electrochemically active [i.e., can be electro-oxidized or electro-reduced] can be measured with this approach. In practice, sensors are most useful for compounds with significant vapor pressures and functional groups that are easily reacted to form gaseous products. Problems occur if the analyte forms residues or contaminants that are deposited in the sensor or dissolved in the electrolyte.

Classical electroanalytical chemistry offers the tools to characterize gas sensor reactions. However, there have not been many scientific investigations of the electrochemical reaction mechanisms that occur in these gas sensors. There is however, a relationship between the structure of the sensor and the observed electroanalytical performance [advantages and limitations]. One of the most well characterized gas sensors is the classical Clark-type oxygen sensor and I suggest a review of this work for anyone interested in a basic understanding of the parameters involved in the construction and application of amperometric gas sensors [1,2].

STRUCTURE

The amperometric gas sensor is a device that allows a gaseous analyte to reach the surface of an electrode that is also in contact with an electrolyte. At this triple point of solid electrode, gaseous analyte, and liquid electrolyte, an electrochemical reaction [i.e., one involving the transfer of charge] can occur. If the electrolyte is a solid, the triple point is solid-solid-gas. The structure of this triple point is typically fabricated using a porous body that allows gas penetration from one side and electrolyte contact from the other. However, many variations of this porous body are possible and are only limited by the imagination and ingenuity of the sensor scientist.

A schematic of the amperometric gas sensor is presented in Figure 1.

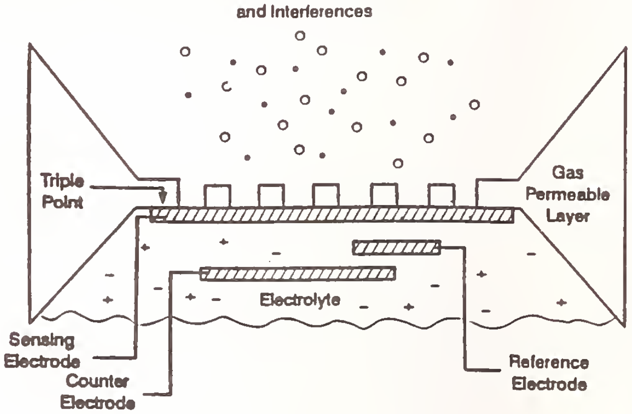

Figure 1. Schematic view of an amperometric gas sensor illustratin contact among analyte, electrode, and electrolyte.

Amperometric gas sensors have three major constituents: a gas permeable layer to allow gas to get into the electrochemical cell, electrodes at which to perform the electron transfer, and electrolyte to provide ionic contact among the electrodes. The geometry of the structure to house the electrochemical cell can have a profound influence on the rate of the electrocatalytic event and on the ultimate performance specifications of the sensor. An electrolyte is a material capable of ionic conduction. Typical examples are illustrated in TABLE 1. In a gas sensor, the electrolyte must solubilize the analyte in an appropriate form for reaction, be stable in the potential region [and T, P, RH] being used for the analyte reaction, and be inert to the electrode and other cell components so as not to cause corrosion [or stray currents] to occur. For the electrolyte system, it is important to consider the conductivity, liquid range, vapor pressure, dielectric constant, viscosity, stability [chemical and electrochemical], purity, ability to solubilize analytes and products, effect on reference electrodes, and spectroscopic properties (if a spectro-electrochemical experiment is planned). The best choice of electrolyte will depend upon the application of the sensor.

TABLE 1.

COMMON ELECTROLYTES

AQUEOUS ELECTROLYTES	Acid: Sulfuric, Perchloric, Phosphoric Base: NaOH, CsOH, LiOH, KOH Neutral: KCl, LiCl, LiBr, $NaHCO_3$
NON-AQUEOUS	Solvents: Propylene carbonate, DMSO, DMF, Acetonitrile, Ethylene glycol, Dichloromethane, (with salts e.g., LiCl or $LiClO_4$ for the electrolyte)
SOLIDS, POLYMERS, and MIXTURES	Nafion/water, PEO•LiX, PVA/H_3PO_4, PVA/CsOH, $AgRb_4I_5$, AgI,....

The sensor also contains a sensing (working),counter, and reference electrode. These are typically chosen from the noble metals such as Au, Pt, and composites like Pt/TFE. The electrode material must be compatible with the electrolyte. Silver and Nickel electrodes have been used in basic (and non-aqueous) electrolyte systems and (glassy) carbon electrodes are popular in acidic and basic media. The electrode material and the potential of operation are chosen to engineer sensitivity, stability, and selectivity into the gas sensor.

The gas permeable membrane can be a Teflon-bonded diffusion electrode (TBDE) of the kind used in fuel cells or a simple thin film material. A thin 0.5 mil solid film of Teflon will allow permeation of oxygen and is used in the Clark O_2 sensor as a barrier to keep out unwanted interferences in the sample. The TBDE is, typically, a thin 5-10 mil Teflon film, that is porous [1-10 micron pores], to which an admixture of Teflon particles and electrocatalyst particles [e.g. Pt black] have been bonded by heat and/or pressure methods. This unique structure is very rugged, convenient to make and use, and extremely efficient at maintaining a very high surface area triple point. Gas access is fast and the electrode-electrolyte interface is of very high stability and surface area. Gas sensors with high sensitivity are made with this approach.

APPLICATION NOTES

The essential components of a sensor (Figure 1) are always the same but the electrochemistry, geometry, and size differ greatly. There is an integral and an important relationship among the materials of construction, the specific cell geometry, and the analytical performance of the sensor for a particular application. This can be appreciated by consideration of sensor response to specific analytes and the wide variety of sensor systems that are available commercially and that have been reported in the past. A thin polymer film planar microsensor can have a response time measured in mSec while a large TBDE sensor for CO may take seconds to respond. The use of planar structures for both the sensor and the electronics offers significant possibilities for future sensor design. It may be possible to design and construct low cost sensors with the increased precision and reliability of silicon fabrication technology and also improved analytical performance.

Chemical differences also have a profound effect on the sensor performance specifications. Sensors with aqueous acid electrolyte (battery acid freezes at about -40°C) can be used at low temperatures but the solid polymer Nafion uses liquid water and freezes at 0°C losing much of its conductivity and preventing low temperature use of the sensor. Basic electrolytes produce well behaved signals for analytes like NH_3 or hydrazines while acid electrolytes produce drifting irreproducible responses. This is because the hydrazines are protonated in acid solution but remain in molecular form in basic solution. The electrochemistry of these two species (protonated or molecular) is very different. When the sensing electrode is made of high surface area Pt, it will provide a good response to CO, but when it is made of Au powder, it will not respond well to CO. Yet a gold electrode will respond to H_2S very well. Therefore, Au is the electrocatalyst of choice to make an H_2S sensor that can be used even in the presence of CO [i.e., a selective H_2S sensor].

Choice of electrochemical conditions is also important to sensor performance. If a gold catalyzed electrode is operated at a potential of about 0.8 V vs. SHE (the standard hydrogen electrode), then NO_2 can be electro-reduced but NO cannot be reacted (oxidized or reduced). Therefore, the selective detection of NO_2 in the presence of NO is possible with an amperometric sensor operated with potential control at 0.8V vs SHE [using a potentiostat circuit].

The above discussion provides only a few brief examples of choices that one can make for structure, materials, geometry, and method in a sensor. The point is that these are the parameters that profoundly effect sensor sensitivity, response time, selectivity, and stability. The overall performance of a sensor is a direct consequence of these choices.

CONCLUDING REMARKS

The amperometric sensor is a complex and interactive system of metallic and non-metallic components. The entire device must be chosen as a system in order to obtain good analytical performance for a specific application. The structure and geometry of the system is important as is the selection of appropriate materials. Our understanding of the electrochemistry within these geometries and their relationship to sensor performance currently limits applications engineering.

This brief essay has been intended to highlight some of the attributes of the amperometric gas sensor. There are many more systems that must be discussed to appreciate the intricate and fascinating variety of sensors that have been constructed. The reader is directed to the references for a more complete review of what has been accomplished to date by the many scientists and engineers who contribute to this field. Be assured that the future will bring even more creative devices that will find their way into the mainstream of our lives in the next ten years.

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Gas Phase Sensing in the Chemical Industry: Today's Practiced Technology

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The application of analytical techniques for on-line measurements termed process analytical chemistry is a rapidly growing area of technology attracting a growing commercial interest. Within the chemical industry, the majority of process analyzers utilize more conventional analytical methods than the technologically recent 'sensor' systems. Some reasons are given for this trend. A number of example process analysis approaches including sampling methodology are examined. The potential for gas sensor arrays in process analytical is discussed.

The evolution of chemical analysis in the chemical processing industry continues to move away from traditional off-line analysis, in which samples are removed from the process environment and taken to a laboratory, towards on-line analysis with sophisticated integrated sampling and analytical instrumentation systems. This integration of analytical techniques to on-line analysis is now recognized as a sub-discipline of analytical chemistry known as process analytical chemistry (PAC)[1]. Within the field of PAC, gas phase analysis is an area that perhaps can attest to being the most rapidly developed for on-line use.

The example applications cited in this paper are intended to give a representative accounting of how gas analysis is performed in the process environment within Dow and perhaps the chemical industry in general. This paper will highlight aspects of several applications successfully implemented for on-line or in-situ gas analysis at Dow. These applications were selected to emphasize how the major techniques can be implemented. These cases, in turn, can typify the types of challenges that gas 'sensors' must meet if they are to be utilized for on-line use in the process environment.

It is interesting to note that despite the tremendous advances made in micro-electronics and materials processing technology that has prompted the development of a myriad of gas 'sensors', these devices are in general, not widely used for on-line gas phase analysis. Rather, most of the advances in on-line gas analysis have resulted from the integration of the relatively mature analytical techniques such as gas chromatography, mass spectrometry, and optical spectroscopy.

There are several significant factors that contribute to the lack of gas 'sensors' being widely used for process measurements. First, the process environment requires an instrumentation package that provides higher reliability with lower maintenance than laboratory counterparts. As mentioned above, the relatively mature and proven laboratory analytical techniques for gas analysis have been easier to re-engineer to meet process analytical instrumentation specifications. Second, because the processes requiring gas analysis vary greatly, instrument vendors have found it difficult to generate multi-purpose or generic platforms on which to base the process instrument package. Third, by their very nature, gas 'sensors' generally respond only to a small range of compounds, while the detection schemes used in gas chromatography, optical spectroscopy, and mass spectrometry are far more versatile for examining the large variety of gases and vapors in the chemical processing environment. Because of this, many of the advances made in process gas analyzers were generated by industrial scientists with years of experience applying these techniques in many on-line applications.

While lagging behind in being utilized for on-line process applications, by no means are the use of gas 'sensors' absent from use in the chemical industry. As in many industries, sensors are utilized heavily for ambient air monitoring. In this arena, O_2 and CO comprise the most numerous applications with metal oxide and electrochemical based sensors performing the majority of the work. Within the field of industrial hygiene, in addition to the use of traditional off-line analysis, a number of gas sensors in the form of dosimeter badges are used for area and personal monitoring for toxic or noxious gases.

Gas 'sensors' are also used routinely for fugitive emissions measurements. Here, the portability of these sensor-based instruments are often the enabling feature. Some instruments used for this purpose within Dow are based on photo-ionization and thermal conductivity.

Gas Sampling

Critical to most process analytical methods is the means of obtaining and introducing a sample from the process to the instrument. An obvious way of improving sensitivity towards an analyte is to provide some means of preconcentrating it prior to analysis [2]. An excellent means of performing this task is with a membrane based technique. Figure 1 illustrates a typical hollow fiber membrane extractor. In this device, a pressure differential across the membrane acts as a driving force to push vapors across the membrane, while the membrane material properties determine the relative rates of diffusion for the various gases. Different diffusion rates (which are temperature dependent) leads to enrichment of one species over another. Table 1 gives a listing of enrichment factors for a variety of organics that can be obtained with a silicone membrane.

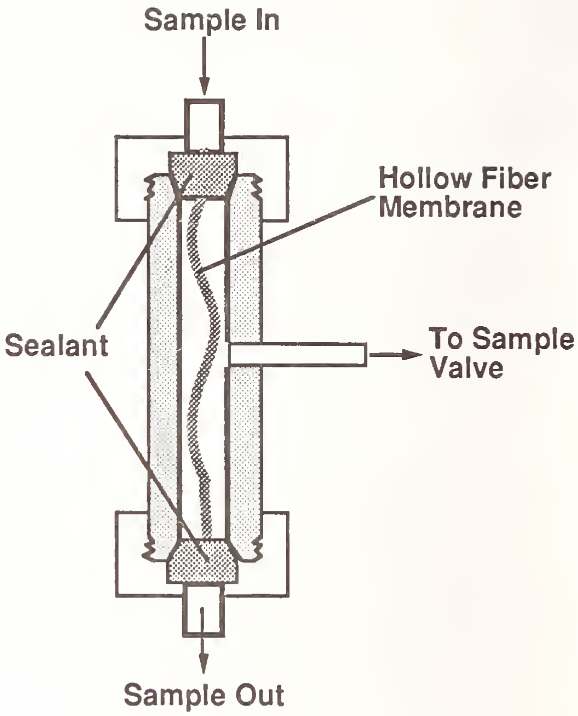


Figure 1. Diagram of a hollow fiber membrane extractor.

COMPOUND	Relative to N_2		Relative to H_2O	
	26° C	45° C	26° C	45° C
Chloromethane	40	27	---	---
Dichloromethane	48	33	1900	1100
Chloroform	91	58	2100	1100
Carbon Tetrachloride	110	74	1800	1100
Chloroethene	37	26	---	---
1,1-Dichloroethene	57	35	3300	1800
Trichloroethene	140	81	970	530
Tetrachloroethene	310	180	600	360
Dibromomethane	84	50	190	100
Bromoform	320	170	570	330
Benzene	170	110	2600	1400
Toluene	380	230	2300	1300
Ethylbenzene	450	280	2200	1200
Chlorobenzene	550	330	1300	730
1,3-Dichlorobenzene	520	350	470	300
1,2,4-Trichlorobenzene	780	400	450	390

Table 1. Enrichment factors for various organic species over nitrogen and liquid water.

As can be seen from Table 1, several orders of magnitude of preconcentration can be obtained. When used to extract organic vapors from aqueous streams, membranes also eliminate solids and dissolved ionic species from being sampled. This can reduce the problems of these compounds fouling or plugging sampling lines [1].

Another commonly used technique to sample dissolved organics from aqueous streams is to sparge with a non-interfering gas. Figure 2 illustrates a typical arrangement.

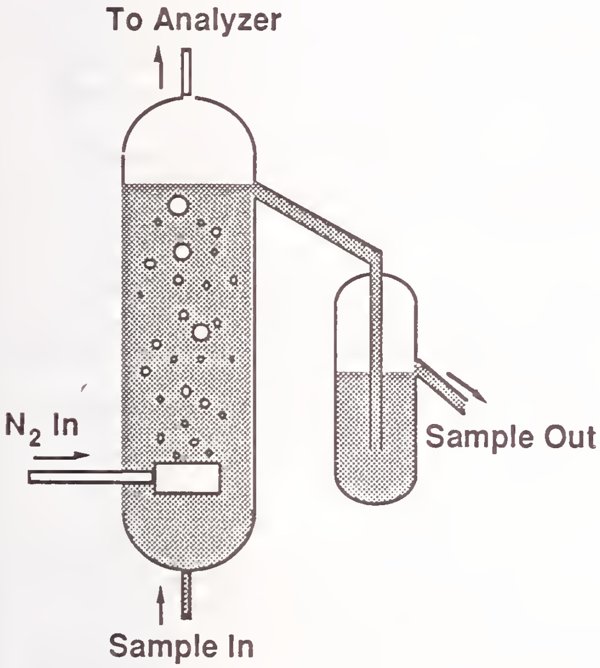


Figure 2. Sparge technique used to purge dissolved gases from liquid samples.

However, systems which utilize a sparging arrangement can be plagued by foaming when a small amount of surface active agent is present in the sample stream [1]. A better technique in these instances has been developed by Kozlowski et. al. [3], termed 'thin layer head space'. Figure 3 shows a thin layer head space apparatus for purging volatiles from liquid samples. In this device, the liquid sample is introduced into a coiled glass tube which has a sparging gas flowing counter current. Surface tension of the aqueous stream forces a thin film of liquid to flow via gravity down the inner surface of the coiled tube. The volatiles are purged from the liquid sample stream provided enough surface area to the sparging gas is available.

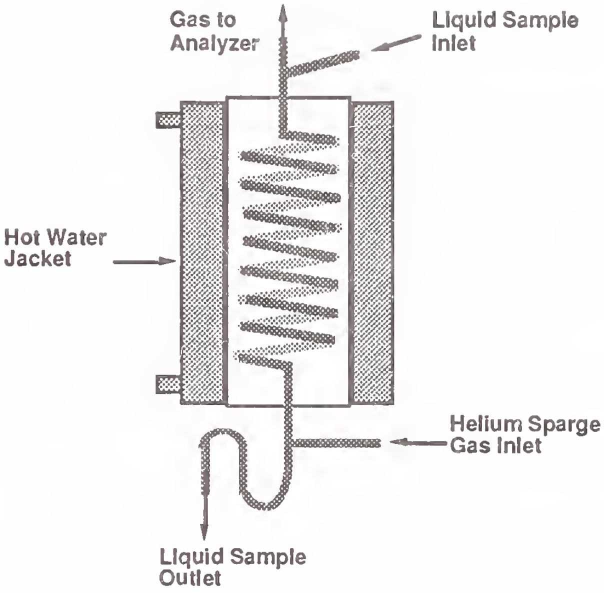


Figure 3. Schematic of Thin Layer Head Space sampling apparatus.

SELECTED CASE STUDIES

A. Multi-Point Sampling/Mass Spectrometry

When faced with a task of monitoring a large volume, area, or a large number of sampling points, two basic strategies are used. In one case, a process mass spectrometer is used to check for process leak detection. The requirements included low ppb sensitivity to the compound of interest and a relatively fast analysis time so that greater than 50 points could be sampled with a reasonable time. In this case, a specially built 64-way sampling valve was used to direct sample(s) from the various sampling positions to the process mass spectrometer. The process analyzer was used to alarm a process computer when the analyte exceeded 20 ppb. Expected mean time between failure(s) is greater than 1 year.

In another application, a small portable mass spectrometer was used to evaluate the concentration uniformity of an agricultural product in an exposure salon. Figure 4 gives a diagram of the case studied.

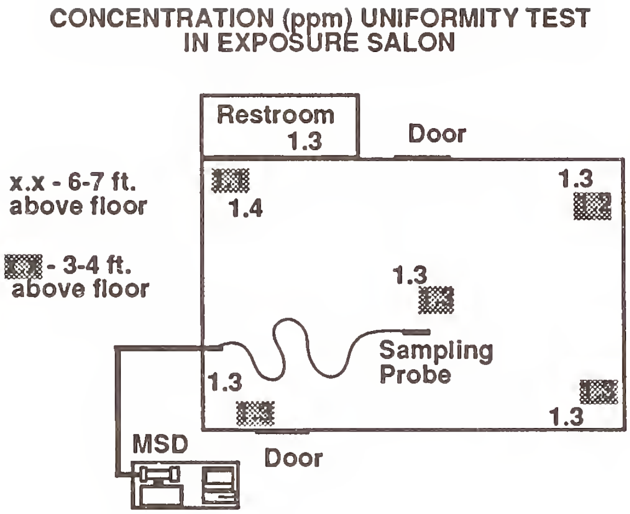


Figure 4. Sampling ambient air from multiple locations in an exposure salon.

In this study, participants were exposed in a controlled test to an agricultural product to determine product uptake in the body. For safety, the exposure level was monitored in the salon with a mass selective detector. In this case, a single sampling point physically moved to various sampling points proved an adequate solution.

In yet another case, a sampling station in the form of a tethered island was used to sample the evolved gases from a waste water treatment plant. The long tether contained a sampling probe which retrieved the sample to a process mass spectrometer. This sampling scenario provided a means to sample locations immediately above the water's surface without requiring a human to collect and retrieve samples.

B. Process Gas Chromatography

Perhaps the most widely utilized technique for process analytical is gas chromatography [1,4]. Strengths include versatility and low detection limits. Process GC also maintains perhaps the best product support, with a number of process GC's now commercially available in addition to the laboratory GC's which share many parts.

The method of sampling a process continues to be where a significant amount of development time is spent. In applications requiring a large number of points to be sampled, multi-point sampling can be employed (as mentioned earlier). However, if short cycle times are required, a conventional GC may be too slow.

A relatively new development is the micro-GC. Complete chromatograms can be obtained in under 1 minute with this technology. A micro-GC from MicroTechnologies Inc. has been incorporated into a process analyzer package employing two different columns with thermal conductivity detection. This instrument was utilized for vent stack analysis as required for the EPA. Figure 5 gives an example chromatogram illustrating the rapid multi-component analysis capability of this instrument.

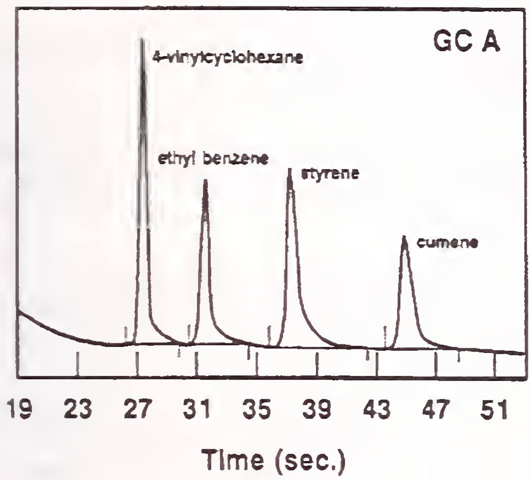
Currently, the micro-GC is limited to the analysis of gas samples only, since they lack a vaporization chamber. Additionally, care must be taken with this technique to avoid condensation of vapors inside the sampling lines.

C. On-Line FT-IR

A substantial amount of work incorporating FT-IR (also, NIR and Raman) into process analytical applications has been performed as evidenced by a recent extensive review of the subject [1]. Strengths of the technique include, low detection limits (with the use of long-path cells), improved flexibility with the use of optical fibers, the simultaneous determination of multiple species, and excellent reliability. These instruments for on-line use often exceed a mean time between failures of greater than 1 yr.

In an example application, an FT-IR has been in used in closed-loop process control for 8 years. In this application, a hot (170°C) process stream is interrogated via IR using a specially designed sample cell as shown in Figure 6.

A Module = 4m x 0.1mm ID, DB-5 0.25μ



B Module = 6m x 0.1mm ID, OV-1701, 0.5μ

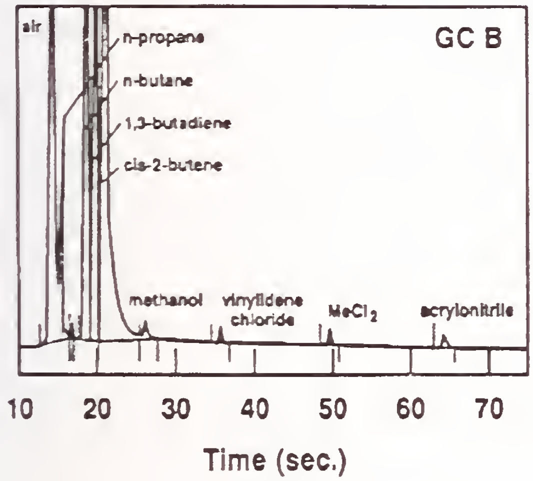


Figure 5. Example chromatograms taken on a micro-GC used in vent-stack analysis.

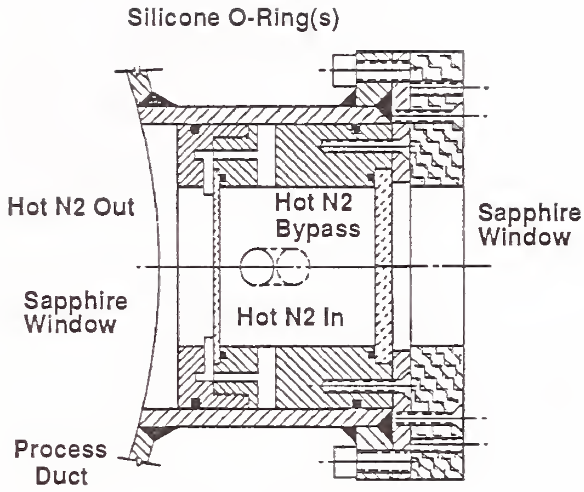


Figure 6. Special FT-IR cell with heated sapphire windows to prevent condensation from a hot sample stream.

An analysis is performed every 50 seconds and feedback given to a process control computer. In applications involving closed looped process control, reliability is essential.

In another application, a custom designed long path (22 meter) FT-IR process analyzer is being used to determine organic vapor break-through from a carbon filter bed. In this application, instrument resolution was sufficient to simultaneously determine 8 organic vapor species. Cost of the hardware components was on the order of $60K.

DEVELOPING GAS SENSOR ARRAYS FOR VOC'S

In an entirely new way of performing gas analysis (particularly in the process environment), the use of arrays of gas sensors has emerged as a 'hot' area of research. The approach, often termed "electronic olfaction" relies on a pattern recognition approach for gas analysis [5]. While not in current use for process measurements, research is underway at Dow (and many other institutions) to examine the utility of arrays of gas sensors for volatile organic compound (VOC's) determinations.

Currently, commercially available metal oxide gas sensors have been utilized in a flow injection arrangement for the identification and quantitation of 10 organic vapors. Provided that the sensor array can provide a pattern that can be mathematically distinct from other responses, complex mixtures can be identified as easily as single compounds.

The use of sensor arrays offers a means of providing 'state of condition' information within the process. This can be very useful in functioning as process alarms. Also, independent operating sensors placed throughout the process may prove useful in correlating sources of process upsets via chemometric analysis (i.e.. building an intuitive model of the process via sensor array feedback).

CONCLUDING COMMENTS

It has been reported that providing an adequate sampling systems consumes 90% of the effort in making a process analyzer functional [4]. Because the approach taken to determine the best method to implement is driven by the process requirements, a large number of methodologies will have to be supported. In the near future, process analytical methods will continue to be largely implemented with the traditional analytical methodology. The trend of having many of the advances in process technology being generated in-house is likely to continue until instrument companies better align themselves to these opportunities [1]. Improvements are also being generated by alliances between industry and academic and government laboratories. A large part of the research effort to improve process analytical technology will certainly be focused on integrating the advances in computers, electronics, materials, sensors, and chemometrics into process analyzers. In particular, as parallel processing technology improves, the use of pattern recognition techniques should heighten the interest in arrays of sensors used for process analysis.

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Development of Differential Mode and Solid Electrolyte Gas Sensors

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Chemical and gas sensing can be accomplished using tin oxide based, Schottky diode, calorimetric and electrochemical sensors. In recent years, the application of microfabrication and micromachining techniques has led to the development of these sensors into low mass, low energy consumption devices. Furthermore, an array of identical sensors can be fabricated permitting the sensors to be operated in the differential mode. In the differential mode of measurement, a pair of identical sensors are used, with one consisting of an electrocatalyst for the chemical or gas of interest, and the other serving as a reference. This operation enhances the selectivity and sensitivity of the sensor. For electrochemical sensors, solid oxide and solid polymer membranes have been used as the electrolytes, particularly for oxygen sensors. A comparison of the performance, limitations and applications of these two types of oxygen sensors will be given. We believe that microfabricated and micromachined sensors will contribute significantly to the development of chemical and gas sensors.

Over the years, it has been demonstrated that gas and chemical sensing can be accomplished using tin oxide based, Schottky diode, calorimetric and electrochemical sensors. For practical applications, solid state electrolytes are often incorporated into these sensing devices. In recent years, the desire to produce low mass, low energy consumption sensors has led to the application of microfabrication techniques in the research and development of chemical and gas sensors. The advancement of micromachining technology provides a new venue for fabricating these sensors to meet the needs. However, the selectivity and sensitivity of these microfabricated sensors need not be compromised.

Conventional chemical and gas sensors are operated using a single device for absolute measurement. This mode of measurement is considered practical, for the commonly used sensor is large in size and relatively costly. However, there are circumstances in which interference by other chemical species, the signal-to-noise ratio and/or the selectivity and sensitivity of a single sensor are less than desirable. It is feasible to employ a differential mode of sensor operation to overcome these weaknesses. In the differential mode of sensor operation, two identical sensors are used, with one sensor as the active device, and the other serving as a reference. The active device may incorporate an electrocatalyst or gas reaction promoter, whereas the reference sensor does not. While these two sensors are exposed to the same sensing environment, the active sensor will be more sensitive and selective to the gas or chemical of interest, due to the effect of the electrocatalyst. On the other hand, the reference sensor may detect only the background gases and chemicals in the testing environment. Consequently, the difference between the two sensor outputs can be used to quantify the detecting species. The reference sensor, in this case, nullifies the background contribution, enhancing the overall sensor selectivity and sensitivity. This approach is very similar to the well-accepted differential thermal analysis concept. A similar concept for electrochemical analysis has also been proposed, such as differential pulse voltammetry for enhancing detection sensitivity.

It is obvious that a sensor operating in the differential mode, if properly designed, can provide improved performance. However, over the years, the application of the differential mode of measurement in practical sensor development has remained elusive, and the potential for this mode of sensor operation has not been fully realized. This is due to the difficulties in fabricating highly reproducible, geometrically well-defined, modest cost sensor pairs on a relatively small structural substrate. The advancement of microfabrication and micromachining technology provides a new venue in the development of the differential measurement mode of chemical and gas sensors. Our laboratory has been engaging in this type of research, and examples will be used to illustrate the merits of this approach.

As mentioned, solid state electrolyte has been employed in electrochemical sensors for gas and chemical sensing. Among these solid state electrolytes, both solid oxide and solid polymeric membranes have been used, particularly for oxygen sensing. In our laboratories, a voltammetric sensor for oxygen detection is developed; one version of the sensor uses a yttria stabilized zirconium dioxide as the electrolyte, and the other employs a solid polymeric electrolyte (Nafion). The applications and characteristics of the oxygen sensors using these two different solid state electrolytes will be compared and discussed in this research.

Examples of Chemical Sensors Operated in the Differential Mode

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Calorimetric Sensors for Combustible Gases

Detection of combustible gases is highly important in gas sensing. A common sensor for gas detection is the catalytic combustible gas sensor. Oxidation of the combustible gas in the presence of a properly chosen catalyst results in the production of heat (heat of oxidation). If a temperature sensing element such as a resistance thermometer is used to measure the temperature rise due to the heat generated in calories, this rise in temperature can be used to quantify the combustible gas present. This type of calorimetric gas sensor is often described as a pellistor [1,2].

A pellistor can be a platinum coil which acts both as a heating and temperature sensing element and is coated with an electrocatalyst such as platinum black or palladium or others. This catalyst-coated pellistor is the active sensing element, and a non-coated pellistor serves as the reference. When this pair of pellistors is heated to a desirable operating temperature, e.g., 350° C, the oxidation of the combustible gas at the catalytic sensor surface will produce heat, resulting in a temperature increase. This temperature increase may be only in the order of degrees or tenth order of degree, but this increase is measurable and can be used to quantify the combustible gas present. The differential mode of measurement between the outputs of the two pellistors is well suited to this detection.

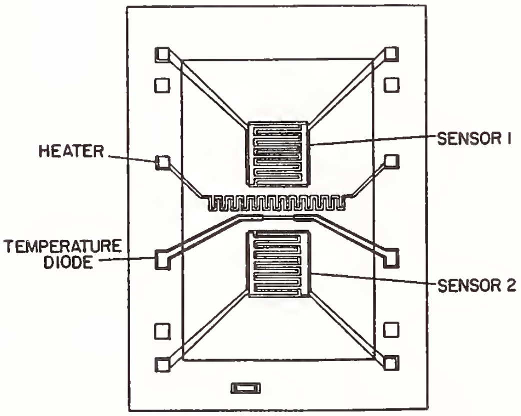

Figure 1: Schematic of a two-sensor array.

In our laboratory, silicon-based microfabrication and micromachining techniques are used in the development of a combustible gas sensor operating in the differential mode. Figure 1 shows the schematic structure of a two-sensor array combustible gas detector.

Sensors 1 and 2 in Figure 1 are two identical platinum resistant temperature sensing elements. They can also be used as resistant heating elements. Chemical anisotropic etching is used to selectively remove the silicon substrate upon which the sensors are formed. This results in a cantilever structure of the platinum resistant film, minimizing any mass heat loss due to the silicon substrate. Experimental results show that the power requirement for heating both sensors is very minute. Figure 2 shows that both sensors can be heated up to 400° C at approximately 80 milliwatts. With this "generic" sensor structure, various electrocatalysts can be incorporated forming different combustible gas sensors. The advantages of producing a sensor of low mass, low power consumption and differential mode of operation can be realized by these micromachined sensors.

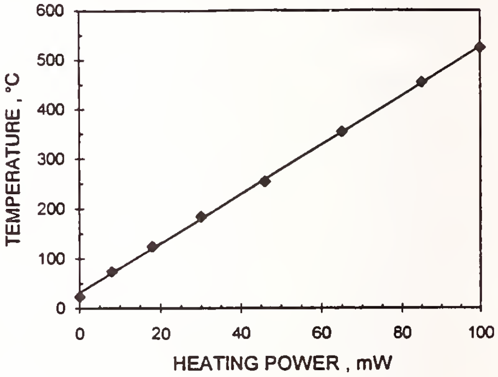

Figure 2: Heating power and temperature relationship of a two-sensor array combustible gas sensor.

Tin Oxide Based Gas Sensor

Another group of chemical and gas sensors used extensively is the tin-oxide based sensor, pioneered by Taguchi [3] and Seiyama et al. [4]. Tin oxide sensors were constructed using sintered tin oxide beads or bars. In recent years, silicon based microfabrication technology has been employed to produce tin oxide sensors. The selectivity of tin oxide sensors for gas sensing can be enhanced using various catalysts. Furthermore, in many cases the sensor needs to be operated at an elevated temperature. Hence, the incorporation of a heating and a temperature sensing element to the tin oxide sensor is desirable. In our laboratory, a tin oxide sensor integrated with an on-chip heater and temperature sensor has been fabricated using microfabrication and micromachining techniques. A doped silicon resistance heater, p-n junction diode for temperature sensing and platinum resistance heater and temperature sensor have been used in this development depending on the temperature and heating range required. Figure 3 shows the basic structure of the micromachined tin oxide sensor. The details of this sensor and its fabrication processes have been given elsewhere [5]. In order to minimize any mass heat loss and to provide stable operating temperature control, the back side of the silicon substrate is selectively removed by anisotropic etching. Consequently, this leads to a low mass, low power consumption device. Similar to other chemical sensors, tin oxide sensors cannot be totally free of interference by other species. The use of catalysts enhances the selectivity and sensitivity of the tin oxide based gas sensors, and Yamazeo and his associates [6] have reported the results of this improvement. We believe that further enhancement can be accomplished by using a pair of tin oxide sensors, with one having the chosen catalyst for the detecting gas, and the other does not. This pair of sensors operates in the differential mode, and the difference in sensor output between the two sensors is then used to quantify the detecting gas. Figure 4 shows the experimental results of a tin-oxide based H_2S gas sensor operating in the differential mode. One of the tin oxide sensors is doped with CuO which is known to catalyze the oxidation of the H_2S reaction, whereas, the other tin oxide sensor does not contain any CuO. The results showing that the sensor operates in the differential mode are very desirable.

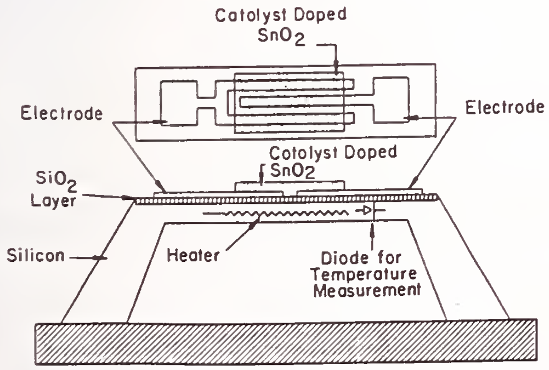

Figure 3: Basic structure of a single micromachined tin oxide gas sensor.

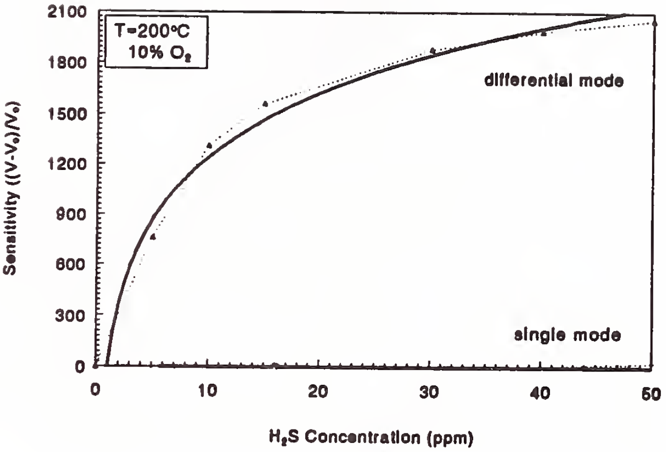

Figure 4: Characteristics of a Cu0-doped tin oxide sensor operated in differential mode.

OXYGEN SENSORS USING DIFFERENT SOLID STATE ELECTROLYTES

Electrochemical sensors, both potentiometric and amperometric modes, have been used for oxygen detection. Either mode of operation has its merits and limitations, but the amperometric type of electrochemical sensor, in general, provides better sensitivity and detectable ranges than the potentiometric one. A solid state electrolyte is used in these oxygen sensors. For high temperature gas sensing, calcia- and yttria- stabilized zirconium dioxide have been used for the monitoring of O_2, CO, H_2 and others. At ambient temperature, solid polymeric electrolytes (SPE) have been used for gas sensing. Among the SPE, Nafion is commonly used. In our laboratory, oxygen sensors using yttria stabilized zirconium dioxide and Nafion are fabricated, and each of these sensors has its own merits which will be discussed as follows.

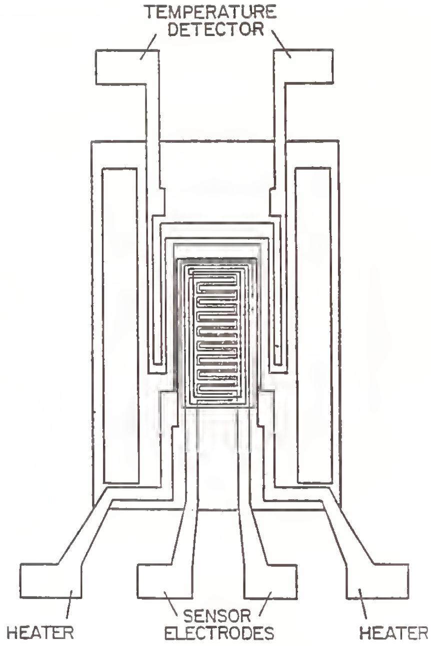

Figure 5: Schematic structure of a solid oxide oxygen sensor.

Figure 5 shows a schematic structure of the solid oxide electrolyte oxygen sensor. This device is fabricated using microfabrication and micromachining techniques. The amperometric mode of operation is used, and both working and reference electrodes are platinum films.

A heating and a temperature sensing element, both platinum film, are incorporated into the device. The backside of the sensor is selectively removed by chemical anisotropic etching. This also results in low mass-heat loss. Initial testing shows that the sensor can be heated up to 700° C at less than 2 watts. Further reduction in energy consumption is feasible by changing the sensor structures to a cantilever form.

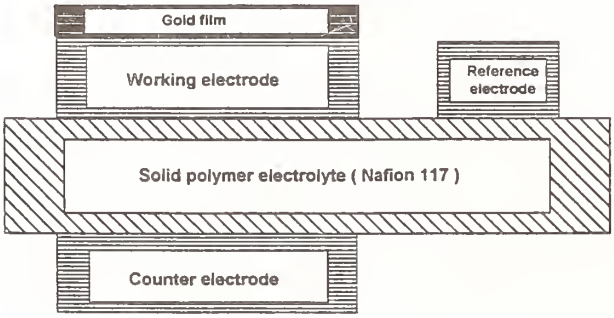

Figure 6: Schematic structure of a solid polymer electrolyte oxygen sensor.

Figure 6 shows the schematic of the solid polymer electrolyte (SPE) oxygen sensor. Nafion is used as the SPE and the substrate on which the electrode elements are deposited. This oxygen sensor operates in the voltammetric mode. All working, counter and reference electrodes are platinum film, and the reference electrode is, in fact, a pt/air reference. The deposition of these platinum films is accomplished by electroless chemical deposition. A thin gold layer ~ 2500 Å thick is deposited by ion-beam coating technology defining a diffusion barrier layer for the oxygen. This sensor demonstrates long-term stability when operated in an ambient environment. However, the sensor cannot be operated in an extremely dry environment, and can be affected by the humidity of the testing medium. This sensor has a relatively fast response time. A 90% response time is 5 seconds, and shows good long-term stability.

In summary, microfabrication and micromachining techniques are well suited to develop practical gas and chemical sensors for various applications.

Acknowledgment

Support of this research by the Edison Sensor Technology Center, Department of Development, State of Ohio, and by the NCRR, NIH Grant No. RR02024 are gratefully appreciated.

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[1] A. R. Baker, British Patent #892,530 (1962).

[2] J. G. Firth, A. Jones and T. A. Jones "The Principles of the Detection of Flammable Atmospheres by Catalytic Devices." Combustion and Flame 21 (1973) 303-311.

[3] N. Taguchi, Japan Patent No. 45-38200 (1962).

[4] T. Seiyama, A. Kato, K. Fuji and M. Nagatani "A New Detector for Gaseous Components Using Semiconductive Thin Film." Anal. Chem. 34 (1962) 1502-1503.

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II. Poster Summary Abstracts

SURFACE ACOUSTIC WAVE SENSOR (SAW) SYSTEM TECHNOLOGY

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During the 1980's small chemical sensors based on microelectronic devices emerged as the leading technology for a variety of chemical detection problems. A number of these sensor technologies have been developed and investigated at the Naval Research Laboratory, including optical waveguide chemical sensors, chemiresistors, and surface acoustic wave (SAW) vapor sensors. Both the SAW and chemiresistor chemical microsensors are capable of detecting organic vapors with high sensitivity. Selectivity is substantial but can be improved dramatically through the use of arrays of sensors whose responses are analyzed using pattern recognition algorithms. SAW sensors are readily adapted to such sensor array systems because of the great flexibility in tailoring the chemical selectivity of the individual sensors, and our in depth understanding of their reversible response mechanisms. As a result, SAW vapor sensors have become a leading microsensor technology for chemical vapor detection. Smart sensor systems based on arrays of SAW sensors and pattern recognition are being investigated for chemical agent detection and as intelligent fire detectors. The SAW devices, the analyte and its influence on selecting chemically selective coating materials, pattern recognition, and sensor system design and integration into a field system are current topics of investigation. The key features of our current system are an array of four SAW vapor sensors, temperature control of the vapor sensors,the use of pattern recognition to analyze the sensor data, and an automated sampling system including thermally desorbed preconcentrator tubes. Organophosphorus analytes were detected at concentrations as low as 0.01 mg/m^3 in 2 minutes, and an organosulfur analyte was detected at 0.5 mg/m^3 in 2 minutes. Pattern recognition algorithms correctly classified these analytes at these concentrations and discriminated them for a variety of other organic vapors[2].

1. Geo-Centers, Inc., 10903 Indian Head Highway, Fort Washington, MD 20744
2. "Smart Sensor System for Trace Organophosphorus and Organosulfur Vapor Detection Employing a Temperature-Controlled Array of Surface Acoustic Wave Sensors, Automated Sample Preconcentration, and Pattern Recognition", Jay W. Grate, Susan L. Rose-Pehrsson, and David L. Venezky, Analytical Chemistry, 1993, 65, 1868-1881.

Surface Acoustic Wave Gas Sensor Technology at Sandia National Laboratories

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Sandia National Laboratories, an 8500+ person, multiprogram research and development facility operated for the U.S. Department of Energy, has over 400 research, development and applications scientists and engineers working on sensor technologies. We describe here some of Sandia National Laboratories research and development activities using surface acoustic wave sensor devices coated with chemically sensitive films to sense gases and vapors. The coated SAW device, typically a SAW delay line structure, is configured in a resonant circuit so that the frequency and amplitude of oscillation of the circuit change when the film on the SAW device changes. When these SAW sensors are exposed to a gas of interest, the film changes mass and/or elastic properties through a chemical sorption process or other chemical-film interaction. These changes can be monitored and calibrated for each surface film and each chemical species anticipated.

We have developed SAW sensors to detect vapors from volatile organic compounds (VOCs), small inorganic molecules, humidity, organophosphonates, styrene, and a variety of other compounds. We have applied these sensors to such diverse applications as the monitoring of cleaning chemical concentrations in industrial process effluent streams and the monitoring of contaminant concentration levels in ultrapure process gases. For one application, a SAW sensor using a thin film of chemically absorbing polyisobutylene, demonstrated 400 ppb (part per billion) sensitivity to trichloroethylene (TCE). The application required the continuous real-time monitoring of TCE and d-limonene emitted into a fume hood exhaust duct at a printed circuit board cleaning station. The SAW-based real-time monitor tracked the emissions of volatile organic compounds from this industrial process. By implementing a solvent substitution from TCE to d-limonene and providing the cleaning station operator direct feedback on the solvent vapor emissions during the cleaning process, VOC emissions were reduced by over a factor of 40. Part of the reduction was directly attributable to the operator adjusting the air-solvent mixture going into the nozzle and the nozzle aim based on the SAW sensor output.

New research projects have been initiated to address SAW sensor specificity issues which are determined in part by the chemical characteristics of the transducer film. Since most films respond to several chemical vapors of interest, we and others are developing arrays of SAW transducers in which each SAW device is coated with a different film. Although no single film will have absolute selectivity, analysis of the array output using pattern recognition techniques will enable these systems to resolve different species in a gas mixture.

This work was performed at Sandia National Laboratories and supported by the U.S. Department of Energy under contract No. DE-AC04-76P00789.

Selection of Polymer Coatings for SAW Chemical Microsensors

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The choice of polymeric coatings for use with surface acoustic wave (SAW) chemical sensors is an important factor in the development of a successful operating sensor system. We have based the selection of coatings, for different vapors, on the use of a new solvation equation.

Gas-liquid partition coefficients, K, have been obtained by inverse gas-liquid chromatography for 20 to 70 solute analytes on 14 polymers at 25 °C. The polymer can then be characterized through a solvation equation, where Log K relates to a series of solutes on the same polymer:

$$\text{Log } K = c + r.R_2 + s.\pi_2^H + a.\alpha_2^H + b.\beta_2^H + l.\text{Log } L^{16}$$

The explanatory variables are solute parameters, R_2 indicates the polarizability contribution from n and π electrons, π_2^H the dipolarity/polarizability, α_2^H and β_2^H the hydrogen-bond acidity and basicity, and Log L^{16} where L^{16} is the K-value on hexadecane. The regression coefficients then characterize a polymer, the most important being "s" the polymer dipolarity/polarizability, "a" the polymer basicity, "b" the polymer acidity, and "l" which reflects the ability to discriminate between a homologous series of solute vapors. The coefficient "r" reflects the polarizability properties of the polymer and "c" is the constant resulting from the regression. The size and relative magnitude of the coefficients are used to identify polymers with high selectivity and sensitivity as coatings for chemical sensor applications. A term-by-term investigation of Log K values shows the solubility interactions that lead to sorption of a solute by a polymer.

The selection of polymer coatings for SAW chemical microsensors can be made based upon the relative magnitude of "r," "s," "a," "b," and "l" and the solubility properties of the vapor of interest. To illustrate this process a specific example is described for detection of a vapor with hydrogen-bond basic solubility properties in the presence of gasoline vapor. Dimethylacetamide (DMAC) is strongly dipolar and hydrogen-bond basic, octane is non-polar and has no hydrogen-bonding properties. In order to match the solubility properties of the polymer and DMAC the sorbent coating will be dipolar and exhibit maximum hydrogen-bond acidity with minimum hydrogen-bond basicity. Out of the 14 polymers studied, SXFA (fluoroalcoholpolysiloxane) best matches these solubility properties. The solvation equation at 25 °C for SXFA is:

$$\text{Log } K = -0.08 - 0.42.R_2 + 0.60.\pi_2^H + 0.70.\alpha_2^H + 4.25.\beta_2^H + 0.72.\text{Log } L^{16}$$

Solute Parameters	**R_2**	π_2^H	α_2^H	β_2^H	**Log L^{16}**
DMAC	0.36	1.33	0.00	0.73	3.72
n-octane	0.00	0.00	0.00	0.00	3.68

The calculated Log K values are 6.35 (± 0.12) for DMAC and 2.57 (± 0.12) for octane. This means that for equivalent vapor concentrations DMAC will partition into the SXFA polymer coating much more strongly than octane. In fact for every one molecule of octane collected in the polymer coating, approximately 6,000 molecules of DMAC will be reversibly absorbed.

The selection of polymeric materials used for coating SAW devices can be rationalized and quantified by using the solvation equation as described, and arrays designed for SAW sensor systems.

McGill, R. A., et al., *Choosing Polymer Coatings for Chemical Sensors*, CHEMTECH 1994, 24(9), 27-37.
Abraham, M. H., et al., *Hydrogen-bonding. XXIX. The characterisation of fourteen sorbent coatings for chemical microsensors using a new solvation equation*, submitted to J. Chem. Soc. Perkin Trans. 2.

Real-Time Neural Network Analysis of Chemical Sensor Arrays: One Step Closer to Artificial Olfaction

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Phone: 510-790-8222 • Fax: 510-790-0925

Neural network implementations of nonlinear pattern recognition algorithms have been combined with arrays of sensors to identify and selectively measure gases. These networks are shown to provide good generalization, they are able to estimate errors on computed concentrations, and they are parsimonious in their calibration requirements.

Many promising chemical sensors are limited by their unselectivity and nonlinear responses. These drawbacks may be remedied by coupling sensor arrays to chemometric analysis for selective quantitation. Neural networks provide a useful implementation; they partition the analysis into a computation-intensive training phase and a faster run-time computation. Consequently, microprocessors can calculate the run-time solution in real time at the sensor site.

Unfortunately, although neural networks perform well for pattern classification they often fail when used for the continuous, high-resolution mappings needed in chemometrics. Additionally, they usually require long training times, their solutions are often trapped in suboptimal minima, and they are so demanding in their requirements for calibration data as to prevent their practical implementation.

We have developed optimized network topologies and training methods that overcome many of these problems, resulting in artificial neural systems well suited to chemometric analysis. These innovations include:

- Biasing the network's solution toward preconceived internal representations well matched to the nature of the chemical sensor responses. This is done by choosing the internal nonlinear functions on the basis of the sensors' expected functional behavior. In contrast to general purpose transformations, these exhibit nonsaturating monotonic behavior which prevents oversensitivity to noise and amplification of back-propagation training errors.

- Designing the network topology and training method to constrain the number of independent data pathways in the network. These constraints ensure that the network forms an internal representation of the sensor-to-gas mapping that uses a minimal number of nonlinear principal components. The hidden units are chosen to model physically significant features including gas concentrations, temperature, humidity, and historical behavior.

- Using signal-to-noise criteria and cross validation to sequentially build optimal data flow paths through the network. This avoids the chronic overtraining that is characteristic of back-propagation networks and assures the predictive ability of the learned transformations.

These techniques have significantly reduced training times compared to the standard back-propagation algorithm, while dramatically improving the network's predictive ability. Using optimized network topologies and training strategies, we have trained feed-forward networks that efficiently convert sensor responses into analyte identities and measurements. These techniques are demonstrated using arrays of MOS sensors; two examples are provided:

- A multi-layer autoassociative perceptron is used in conjunction with a five sensor array to resolve mixtures of three gases with widely varying compositions. The network computes analyte concentrations and their expected errors, and, in conjunction with a Bayesian classifier, identifies dominant gases and detects outliers or phantom analytes. It has also achieved robust identification of a library of gases using small MOS sensor arrays.

- A feed-forward functional link network uses a minimal number of MOS sensors for interference-free measurement of CO and methane.

This research is part of a broader program at Mosaic Industries aimed at the development of low cost implementations of artificial olfaction. Efforts are now focused on more efficient training algorithms so that all calibration functions can be incorporated in a small microcontroller tightly coupled to the sensors.

Application of Olfactory Neural Networks to Processing Sensor Information

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ABSTRACT

The nose has a truly remarkable ability to detect and then accurately classify an odor based upon being exposed to minute amounts of a chemical. If such an ability could be duplicated artificially, then there would be numerous, significant practical applications. There is also the possibility of discovering completely new engineering algorithms for handling sensor information and for classification. This paper presents preliminary results on using olfactory neural nets to process sensor information, and discusses potential applications of such networks.

We have been studying the use of olfactory neural net models coupled with various sensors to detect fires. The problem of detecting fires is one of pattern recognition. A recent paper by Okayama illustrates the ability of two tin oxide detectors to discriminate between smoke from smoldering fires and ordinary odors from organic compounds, when the sensors were coupled with a neural network. Okayama used a standard backpropagation type neural network. In our work alternative neural network architectures, based upon modeling the olfactory system, are being studied for their ability to enhance fire detection. In addition to detecting fires there are other potential process applications of our approach. One application involves hazardous emissions from manufacturing plants. Tighter and tighter emission standards are being set for industry, and it is unclear how these standards will be met. If an olfactory chip could be developed to combine thin film sensors and signal processing (an artificial nose), then it could be placed at strategic locations around a plant to warn of emissions. Olfactory computation may also be useful for fault detection using standard plant sensors. In this way one would artificially "smell" a process fault. An approach that couples 12 thin film sensors and a neural net has also been reported for following the progress of a brewing process. The purpose of this paper is to give an overview of olfactory neural networks and how these networks might be applied to solve process problems.

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Second Order Devices: The Coming Revolution in Sensors

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Abstract

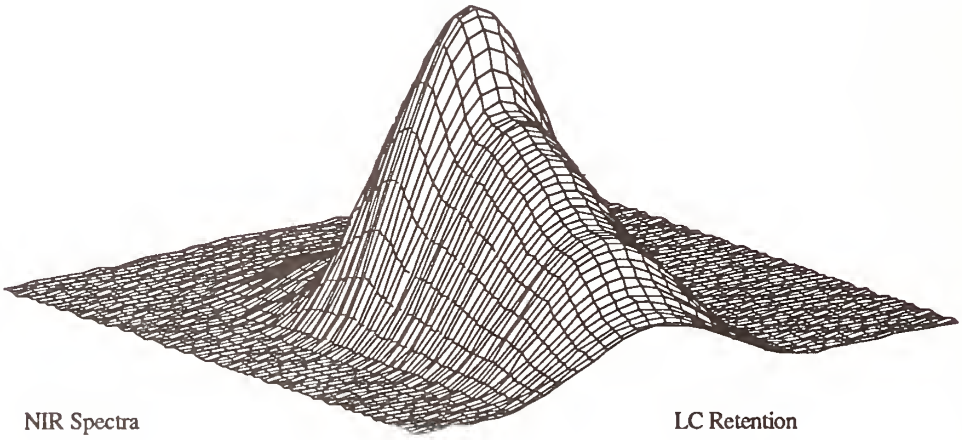
Analytical instruments can be classed by the dimensionality or "order" of the data they produce. For instance, a pH probe, which produces one datum per sample, is zero order. A spectrometer, which produces a vector (first order tensor) of data for each sample, is first order. Many modern analytical instruments, such as the hyphenated techniques like GC-MS, produce a matrix (second order tensor) of data for each sample and are, therefore, second order instruments. There are inherent advantages to higher order devices. In a zero order device, the presence of an interferent species cannot be detected. Correct quantitation is lost and no indication of a problem is given. In a first order device, the presence of interferents can be detected, but quantitation is still mathematically impossible. In second order systems, however, it is possible to achieve correct quantitation in the presence of interferents that were not included in the original calibration matrix. We refer to this quality as "the second order advantage."

Recently, researchers have begun to devise single sensors that produce second order data. These sensors are potentially much more robust to interferent species. This will be an especially important advantage in environmental sensing where the background matrix is often unknown.

Simulated liquid chromatography/near infrared spectroscopy (LC-NIR) data is used as an example of how second order calibration works. In LC-NIR an absorbance is measured as a function of retention time (the first order) and wavelength (the second order) producing a response such as the one shown in the figure. Given the response to a pure analyte and an unknown mixture possibly containing the analyte, the Generalized Rank Annihilation Method (GRAM) can be used to determine the amount of analyte in the unknown mixture, even without information about the interfering species. This capability is a revolutionary advance in calibration and analysis.

There are several possible strategies for developing second order sensors. A sensor array, e.g. a SAW device with different chemically selective coatings, can be coupled with a separation step such as LC or even a chemically selective membrane. It is also possible to develop a second order sensor "on a chip" by controlling the time-temperature profile of array elements. This approach is being actively pursued at PNL for detection of hydrogen in the presence of VOCs.

Response to Analyte #1



SENSOR TECHNOLOGY FOR ADVANCED COMBUSTION CONTROL AND MONITORING INSTRUMENTATION

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ABSTRACT: With increasingly stringent environmental legislation, there is a growing need for low cost instrumentation for combustion control and emissions monitoring. While low cost is necessary, advanced instrumentation also must be simple to operate and calibrate, require minimum maintenance, and give stable, reliable data. Combustion of fossil fuels leads to formation of CO, NO_X, SO_2, and other pollutants depending on the fuel and the combustion conditions. We will describe catalytic heat flux sensor technology and instrumentation based on these sensors for the quantitative measurement of CO, NO_X, and SO_2. Various strategies for control of emissions and for maximum fuel efficiency based on these measurements will be presented.

The 1990 Amendments to the Clean Air Act require tighter control of the emissions released during the combustion of fossil fuels. The new legislation is now targeting small industrial and commercial size combustion processes such as heaters, boilers, and stationary IC engines. Continuous Emissions Monitoring (CEM) systems capable of monitoring the major fossil fuel combustion emissions, NO_X, SO_2, and CO, have been used for over ten years on utility size boilers and large gas turbines. However, the prohibitively high cost of these systems, as much as \$150,000, is too high for smaller combustion processes. Sonoxco has developed a line of sensors to measure the stack gas levels of NO_X, SO_2, and CO on coal-, oil-, and gas-fired processes. The sensors are low cost and easily configurable into monitoring and control instrumentation.

The Sonoxco CO, NO_X, and SO_2 sensors are catalytic heat flux devices. Each sensor is comprised of two temperature sensitive elements, one active and the second a reference. The active element is coated with a highly selective catalyst that promotes an exothermic reaction of the component to be measured. The temperature difference between the active and reference elements is directly proportional to the gas concentration. As an example, the CO sensor operates by catalyzing the reaction of CO with oxygen as follows:

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \qquad \Delta H_{600K} = -67.6 \text{ kcal/mol}$$

Resistance temperature detectors (RTD) are used for the temperature measuring elements for the three sensors. Because the RTD resistance is proportional to temperature, the corresponding difference in resistance between the active and reference elements is linear with gas concentration. A bridge circuit can be used to produce a 0-5 Vdc signal that is directly proportional to the gas concentration as shown in Figure 1 for the CO sensor. The designs of the NO_X, CO, and SO_2 sensors are identical with the exception of the proprietary active catalyst coatings.

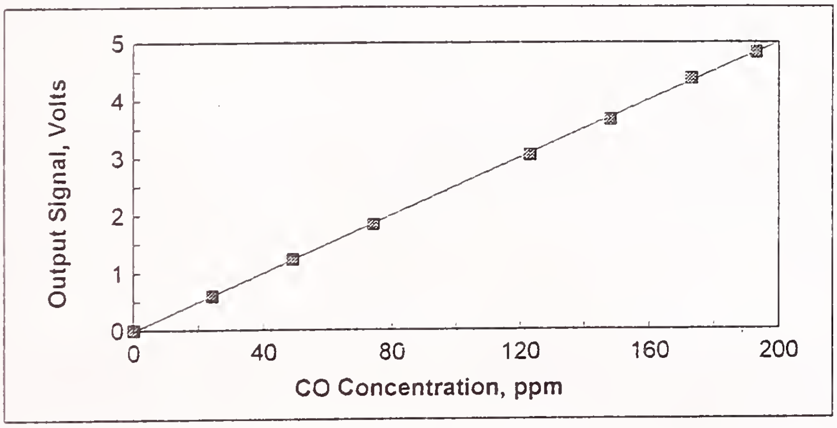

Figure 1. Signal linearity of the Sonoxco CO sensor.

NEW SEMICONDUCTING MIXED OXIDE-BASED SOLID-STATE GAS SENSORS FOR CARBON MONOXIDE AND HYDROGEN

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Solid-state gas sensors based on semiconducting metal oxides have been widely used for the selective detection and metering of reducing gases (such as carbon monoxide, hydrogen, hydrocarbons, etc.) in the flue gas streams of combustion furnaces and in the automobile exhaust systems. High-temperature application oriented new carbon monoxide gas sensors based on MoO_3 and the anatase phase of TiO_2 have been developed and their sensing characteristics such as selectivity, sensitivity, threshold detectable gas concentration and response time were investigated. It was found that MoO_3 thick films could be used as an ON/OFF type detector, whereas those based on the two-phase mixture of MoO_3 and ZrO_2 could be employed for measuring the concentration of CO in the flue gas stream. Significant enhancement in the sensitivity of these sensors in terms of the magnitude of the signal as well as the response time, was achieved by the addition of small amounts of palladium catalyst. In the TiO_2-based sensors, experiments showed that pure titania is a very good but nonselective sensor (responds to both CO and H_2 gases). Remarkable change in the sensing characteristics of the anatase modification of TiO_2 was observed when admixed with an insulating second phase, such as a-alumina or yttria. In the case of titania-alumina sensor, the response was found to be exclusively dependent on the hydrogen concentration alone; the presence of CO and/or CO_2 did not affect the sensitivity. On the other hand, the sensor based on titania-yttria showed increased sensitivity to CO and decreased sensitivity to H_2; the sensitivity was immune to the presence of NO and/or NO_2. Addition of elemental iron, in small concentrations, to the two-phase mixture of titania and yttria seemed to further improve the sensitivity to CO gas. X-ray and XPS (ESCA) studies, together with the experimental dc measurements and the reversibility characteristics, were used to elucidate the possible sensing mechanisms operative in these sensors. The danger of rather easy oxidation of the elemental iron present in small amount in the titania-based devices was circumvented by replacing iron with high activity noble metal. This chemistry variation resulted in higher stability and longer shelf-life of the latter, without affecting the sensitivity.

In order to understand the sequential contributions of grain boundaries, grains and two-phase mixtures, ac electrical data in the frequency range $5\text{ Hz} \leq f \leq 13\text{ MHz}$ were acquired at the ambient as well as elevated temperatures ($400\,^{\circ}\mathrm{C} \leq T \leq 900\,^{\circ}\mathrm{C}$). These were used to establish the role of microstructures on the resulting electrical behavior in these polycrystalline materials. The ac data, when analyzed utilizing the lumped parameter/complex plane analysis (LP/CPA), reveals several contributions from simultaneously operating mechanisms to the terminal admittance of the grain boundary. While the room temperature impedance spectra offers the lumped response alone, at high temperatures two semicircular relaxations observed in the impedance plane, are attributed to the low-frequency related grain boundary and high frequency related grain response. The grain boundary response, however, is still difficult to quantify even at elevated temperatures via LP/CPA and dc measurements. The electrical path homogeneity is examined via the presence of the depression angle which remained nearly invariant in the range of measurement temperatures.

The nature of electrically conducting paths is suggested via an equivalent circuit representation incorporating the underlying mechanisms in a systematic manner. The transformation of the room temperature equivalent circuit into that at high temperatures is shown in the light of experimental observations.

Research and Technology for Tin Oxide Gas Microsensor Arrays

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Gas microsensor arrays offer many potential advantages over discrete sensor devices. A fundamental feature of arrays is the improved selectivity obtained by taking advantage of pattern recognition algorithms to deconvolute signals from overlapping responses from different sensors in the array. By using batch fabrication methods to produce the arrays, lower cost and improved reliability can be expected. Miniaturization also permits operation at lower power, and therefore greater portability of instruments that use microsensors. To achieve these goals, improvements in fabrication technology and sensor materials, as well as improved understanding of how these devices operate, are required. Results are presented here in two areas: microhotplate technology and growth of epitaxial tin oxide.

A microhotplate is a micromachined structure with the ability to produce a wide temperature range We have fabricated microhotplates using a CMOS-compatible method which is described elsewhere[1]. The design used for a tin oxide gas sensor consists of a four element array, where each element contains a polysilicon heater, an aluminum hotplate/temperature measuring layer, and aluminum electrical contacts. The devices have a thermal efficiency of 8°C/mW, a temperature range of 0-550°C (limited by the aluminum layer), and a thermal time constant of 0.6mS. Tin oxide was deposited on top of the electrical contacts while the heaters maintained elevated deposition temperatures. Sensing action at 350°C to hydrogen and oxygen was demonstrated. Microhotplates were also used as a substrate array for materials processing. An array of 36 elements, with a temperature range 0-1000°C (no aluminum layer) was used to examine the microstructure of tin oxide as a function of deposition temperature. Subsequent scanning electron micrographs of the array elements showed an increase in grain size with deposition temperature. Such temperature processing by arrays can be an efficient way to optimize a materials process, as well as provide thermal conditioning for gas sensor elements.

A limiting factor in the performance of thin film sensors is the instability of the interfaces between grains in the film. Bulk sensors are usually sintered, creating "necks" between the grains, which are relatively stable. We have developed a method for producing epitaxial tin oxide films[2], which have properties closely related to single crystal tin oxide and may provide improved stability for thin film sensors. Films were deposited on sapphire substrates which are produced commercially for silicon-on-sapphire technology. The deposition method was reactive sputter deposition using a pure tin target, argon and oxygen sputtering gas, and a substrate temperature of 500°C. X-ray diffraction showed single orientation films which were (101) on sapphire $(1\bar{1}02)$ substrates and (100) on sapphire (0001) substrates. Atomic force microscopy showed 400 Å films to be atomically flat with steps from the underlying substrate still visible as steps in the top tin oxide layer. This form of tin oxide is capable of producing a sensor response at thicknesses of only 15Å.

[1] J. S. Suehle, R. E. Cavicchi, M. Gaitan, and S. Semancik, IEEE Electron. Device Lett., vol. 14, no. 3, p.118 (1993) and references therein.

[2] R. E. Cavicchi, S. Semancik, M. D. Antonik, and R. J. Lad, Appl. Phys. Lett. vol. 61 no. 16, p. 1921 (1992).

Micro-Hotplate by CMOS Technology With Application for Gas Sensors

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We have developed the design and fabrication methodology for a silicon micromachined micro-hotplate that is manufactured using commercial CMOS foundries with additional post-fabrication processing. The device can be considered "generic" in that we foresee a host of new applications that can be implemented with this structure as a basic element. The methodology for the fabrication of this device is based on prior work on commercial CMOS-compatible micromachining. The novel aspects of this device are in the design, choice and layout of the materials layers, and applications for the device.

Figure 1 shows a SEM micrograph of the suspended micro-hotplate structure after the deposition of a SnO_2 film. The composition and placement of the various material layers are shown in the inset. The thermal charcateristics of the device are shown in Figure 2 which plots the temperature of the micro-hotplate versus input power. The thermal efficiency of the device was determined to be 8 °C/mw.

This device has the advantage over other similar devices by its manufacturability in a standard CMOS process which leads to low cost and easy integration of VLSI circuits for drive, communication, and control. Also, this device can be easily incorporated into arrays of micro-hotplates, each with individualized circuits for control and sensing for independent operation.

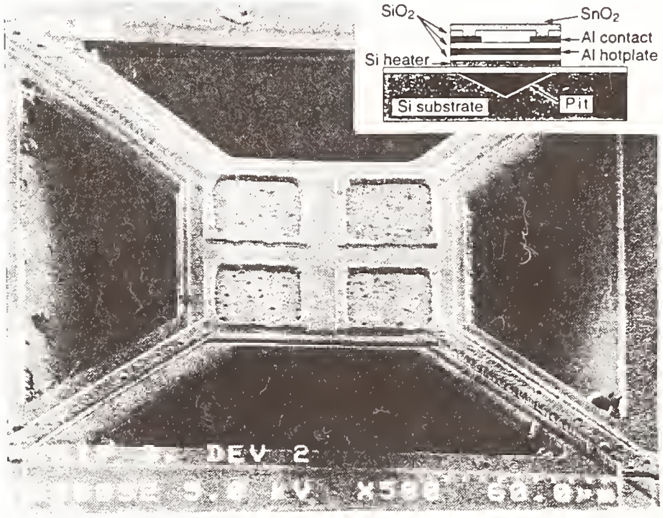

Fig. 1. SEM micrograph of suspended micro-hotplate structure with SnO_2 film coating. The inset shows a schematic illustrating the various layers comprising the structure.

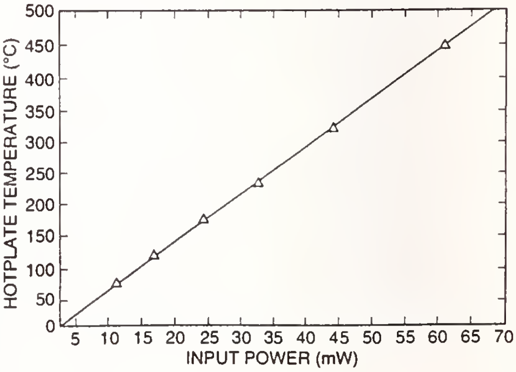

Fig. 2. Plot showing increase of micro-hotplate temperature over ambient versus input power applied to polysilicon heater.

Properties of Ultrathin SnO$_2$ Gas Sensors

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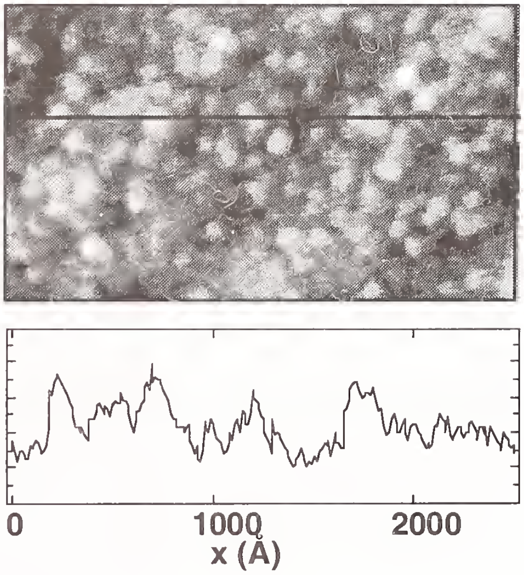
Many commercially available, conductance-based gas sensors use compressed powder tin oxide (SnO$_2$) active elements. In developmental sensor research, however, there is a move toward sensors using thin film active elements.[1] This move is motivated by the enhanced compatibility of thin films with microelectronic fabrication technology. Microelectronic-based integrated sensors[2] have the advantages of lower power consumption, higher manufacturing throughput, and greater miniaturizability. Moreover, integrated sensors can be fabricated in arrays to provide chemical selectivity and can be fabricated with on-board control and signal processing electronics. SnO$_2$ sensors operate by ambient gas-induced variations of the surface chemistry that lead to changes in the sheet resistance. For example, reducing gases can create surface oxygen vacancies. These vacancies act as donors and increase the sheet conductance. One source of error in the sensor response is the variation in surface stoichiometry due to migration of bulk oxygen atoms to the surface. This migration occurs at around 700 K and leads to an undesirable slow drift in the baseline conductance. Our group theorized that this source of error may be suppressed or eliminated by minimization of the bulk material. To this end, tin oxide films, 1.5, 4.0 and 8.0 nm thick, were grown on elevated-temperature sapphire $(1\bar{1}02)$ and (0001) substrates by reactive sputter deposition. The structural, chemical, and electrical properties were investigated by scanning tunneling microscopy (STM), low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), and 4-point conductance measurements. LEED data suggested that the SnO$_2$ films grown on sapphire $(1\bar{1}02)$ were crystalline with the [101] axis parallel to the growth direction. In contrast, for films up to 80 Å thickness grown on sapphire (0001), no long range order was evident in LEED images. STM images of the SnO$_2$ films grown on sapphire $(1\bar{1}02)$ showed atomically flat terraces separated by regularly spaced single atom steps. XPS measurements indicated that the only SnO$_2$ film impurity was carbon. This was probably deposited on the film surface from the laboratory air while transporting the samples from the deposition chamber to the analysis chamber and was subsequently removed by exposure to an oxygen plasma. Gas sensing measurements were carried out on films activated with 1 monolayer of vapor-deposited palladium. STM measurements indicated that the Pd forms 3-dimensional particles, roughly 100 Å in diameter, which do not completely cover the surface. The STM image on the right shows 2 monolayer equivalents of Pd deposited on a thin film of (101) oriented SnO$_2$. The extremely low surface roughness is evident in line scan below the image. Sensing response measurements were carried out in UHV by exposing the films to cycles of H$_2$ and O$_2$ gas at $1 \mathrm{x} 10^{-3}$ Pa while measuring the film conductance with an *in-situ,* collinear, 4-point probe. A sensing response was achieved for all the film thickness studied. The initial experiments suggest that the 1.5 nm thick film shows less hysteresis and less drift than the thicker films. This indicates that elimination of the bulk material does, indeed, result in improved sensor response characteristics. Experiments are underway to determine the sensing response of these films at more realistic gas pressures.



[1] M.J. Madou and S.R. Morrison, Chemical Sensing with Solid State Devices, Academic, San Diego, (1989).

[2] V. Demarne and A. Grisel, Sensors and Actuators, **13** 301 (1988).

Solid State Sensors Based on Semiconducting Metal Oxides With Surface-Dispersed Metal Additives: Modeling of the Mechanism of Response Formation

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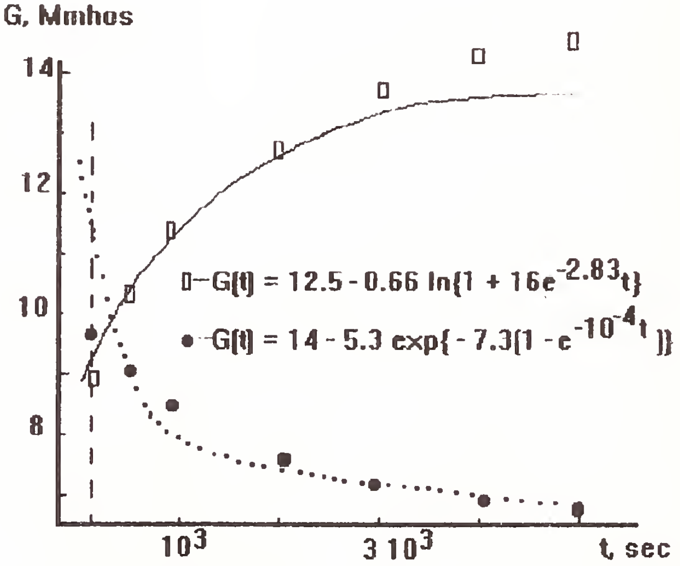
Solid state sensors based on metal oxide semiconductors with surface dispersed metal particles are characterized by strong sensitivity to definite gases which in some cases do not cause the conductivity response of pure metal oxide adsorbents. To understand the mechanism of such sensor response we investigated the adsorbent conductivity behavior under metal deposition and surface metal cluster formation. We considered Pd dispersions on nearly stoichiometric thermally oxidized and oxygen-rich plasma-oxidized SnO_2 (110) for coverages ranging from 0 to 10 monolayers-equivalent. The results were interpreted using a model that includes oxidation of metal species, formation and slow-filling of surface states, and the effects of overlapping depletion regions that result from the Schottky barriers formed around each particle. It has been shown that in all cases the measured G(t) kinetics was the adsorbent electroconductivity relaxation caused by a disturbance in the adsorbate-adsorbent electronic equilibrium. A comparison of experimental data for the conductivity relaxation kinetics of the thermally oxidized SnO_2 and theoretical dependencies is shown in the figure.



The possible mechanism of adsorption-induced response formation due to the breakdown of the overlapping of the space charge regions of adjacent surface metal clusters has been described. The existence of definite deposited metal concentration and adsorbent thickness ranges characterized by the biggest value of adsorbent conductivity response has been predicted.

Gas Sensor Research Facilities in the NIST Process Measurements Division

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Special research capabilities are required for the detailed study of sensing materials and transduction mechanisms as well as for the fabrication and performance evaluation of prototype sensing devices. Three custom research facilities have been constructed in the Process Measurements Division of the Chemical Science and Technology Laboratory at NIST in order to support development of optimized materials and concepts for next-generation sensors. These facilities are the (a) Film Deposition and Characterization Facility, (b) Surface Analytical Facility, and (c) Sensor Response Test Facility. Specific objectives for research using this equipment include:

- Determining the basic properties of active materials
- Developing practical methods for fabricating microstructure-controlled, planar gas sensor structures
- Understanding the molecular scale gas-solid interactions that lead to macroscopic responses
- Modeling the performance characteristics of prototype sensors to efficiently optimize devices
- Developing databases for use in constructing pattern recognition schemes for gas sensor arrays

A brief description of each facility follows.

FILM DEPOSITION AND CHARACTERIZATION FACILITY. This facility is a dual chamber, ultrahigh vacuum (UHV)-based system used to develop procedures for fabricating oxide and metal films of controlled microstructure. Oxide films (1-1000 nm thick) are deposited by reactive sputter deposition and ultrathin metal overlayers (monolayer regime island structures) are deposited by evaporation. The films can be characterized, in situ, using 4-point conductance measurements and their structures can be studied by low energy electron diffraction (LEED) and reflection high energy electron diffraction (RHEED).

SURFACE ANALYTICAL FACILITY. This multi-chamber UHV-based system is equipped with a complement of analytical hardware for characterizing the outermost regions of samples (0.5-10 nm). In order to perform thorough examinations of sensor material properties, instrumentation is included for performing chemical, structural, electronic and electrical analyses by x-ray photoemission spectroscopy (XPS), Auger electron spectroscopy (AES), thermal desorption spectroscopy (TDS), secondary ion mass spectroscopy (SIMS), energy loss spectroscopy (ELS), ion scattering spectroscopy (ISS), low energy electron diffraction (LEED), electron stimulated desorption (ESD), scanning tunneling microscopy (STM), ultraviolet photoemission spectroscopy (UPS), measurement of work function change and four-point conductance measurements. A variety of sample preparation and surface modification hardware (ion guns, evaporators, gas sources, quartz crystal monitors, etc.) critical to tailoring sensor materials is also mounted on the three chambers of this system.

SENSOR RESPONSE TEST FACILITY. This fully-automated facility operates under computer control to mix gases in desired ratios and flow them, at specified rates and pressure, to up to eight samples mounted within the test chamber. Electrical characteristics from the test devices are computer recorded with an update rate of up to 100 Hz. Efficient studies of adsorption/desorption kinetics and response functions of customized films can be performed in order to optimize active sensor interfaces. Prototype array devices can also be examined to acquire databases for development of pattern recognition/neural net algorithms.

Calibration Mixtures for Gas Sensor Development and Evaluation

Gerald D. Mitchell and William D. Dorko, NIST

The NIST produces many gas standards which are used for the calibration of analytical instruments and procedures employed to perform measurements for regulatory purposes. These same calibration mixtures can be used to determine the performance of gas sensors during their development and subsequent evaluation. Most of the standards are binary gas mixtures contained in cylinders and are Standard Reference Materials (SRMs). These gas SRMs are stock items which can be purchased from the NIST Standard Reference Material Program (SRMP) at any time. There are approximately 90 gas SRMs and the analytes or gases of interest include CO, NO, CO_2, Propane, Methane, O_2, SO_2, NO_2 with the balance or matrix gas being either nitrogen or air. There are some multicomponent SRMs, one contains 18 volatile organic compounds some halogenated and some not, while another contains 15 non-methane organic compounds non of which are halogenated. The concentrations of the analytes in the gas SRMs range from 5ppb to 21%. The NIST analyses each analyte in each SRM cylinder which is sold accompanied by a certificate describing the certification process and uncertainty in the concentration value. Most of the gas SRMs are certified to 1% relative, some to 5% relative, and two series of carbon dioxide SRMs are certified to 0.1% relative.

Another type of standard is the Research Gas Mixture (RGM). These are mixtures containing components or concentrations outside the range of the SRM program. RGMs can be requested by the private sector or government organizations. NIST determines the feasibility and then performs research to develop an analytical procedure or primary standards to analyze the requested mixture(s). The work is reimbursed by the requesting organization which is supplied with the mixtures along with a certificate of analysis when the work is completed. This program will enable NIST to be responsive to standards needs. Whereas it may take two years or more to develop an SRM, it is feasible that an RGM can be concluded in three to five months.

The third type standard is the NIST Traceable Reference Material (NTRM). NTRMs are mixtures similar to SRMs but are produced and distributed by the specialty gas industry. A company produces a "lot" of ten to twenty identical cylinder mixtures and analyzes each mixture against several gas SRMs after which the data are sent to NIST. NIST selects two or three cylinders to be sent to its facility and these are analyzed for concentration value assignment. NIST then combines its data and the producers data to assign a concentration to each cylinder in the lot. A certificate for each cylinder is supplied to the producer by NIST. This program allows the specialty gas industry to determine end user needs and respond to them but still maintaining NIST traceability.

NIST Humidity Standards and Calibration Facility

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NIST strives toward more accurate, uniform measurement of humidity by providing humidity calibration services and supporting these services through development and maintenance of humidity standards.

Hygrometers calibrated by NIST are subjected to moist air produced by the NIST Two Pressure Humidity Generator. Within the generator, a continuous stream of CO_2 free air at constant temperature and pressure is saturated with water vapor over a plane surface of pure water or ice. The moist air is then expanded isothermally into a test chamber maintained at atmospheric pressure. Moisture content of the test gas is determined based on the measured temperatures and pressures within the saturator and test chamber. The NIST Two Pressure Humidity Generator produces test air with moisture content ranging from 3 to 80100 PPM_V at flow rates from 28 to 280 standard liters per minute.

Humidity standards under development at NIST include a new primary standard hygrometer and a low frost point humidity generator that will extend NIST calibration capability to part per billion concentration levels.

The new primary standard hygrometer separates test gasses produced by a humidity generator into water and dry gas. Desiccant filled collection tubes extract the water from the gas. Weighing the tubes before and after a test yields the mass of water contained in the test gas. The carrier gas is collected in one of two glass prover tubes. Its volume is obtained by measuring the displacement of lightweight, mercury sealed pistons within the prover tubes, using laser interferometry. Once a prover tube is filled, pressure and temperature within the tube are measured, allowing calculation of the mass of the collected gas. The prover tubes are alternately filled and emptied until sufficient water, approximately 0.6 grams, is extracted from the test air.

The low frost point humidity generator under construction at NIST features a new saturator design that eliminates the large temperature controlled baths and cryogenic cooling previously required for saturation of air under constant temperature and pressure conditions. The saturator, a cascaded series of massive copper plates with internal spiral passageways, will be maintained in a vacuum, thermally isolated from the laboratory environment. Thermo-electric coolers will maintain the saturator at operating temperatures between -40 and -100 degrees Celsius by pumping heat to isothermal heat removal plates. Liquid refrigerant supplied by a remote refrigeration system, expanding within the isothermal plates, will remove the heat from the vacuum environment. The new generator will generate humidities as low as 14 PPB_V using air, argon, oxygen, hydrogen, or helium as the carrier gas. It is expected to be operational by late 1994.

III. Breakout Group Reports

Gas Sensors for Process Control in Manufacturing

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This paper summarizes the breakout session on using Gas Sensors for Process Control in Manufacturing that was held during the NIST Workshop on Gas Sensors. This study group examined the barriers that limit the application of new gas sensor technologies in the process control industry such as the lack of clearly defined performance requirements in a multifaceted market. Other barriers include a reluctance to apply new, non-plant-proven sensors, the high cost of sensor installation, and the lack of proven reliability for new technologies. The session participants then suggested several mechanisms that NIST might develop to assist in promoting new sensor devices for process control including having NIST become more active in sensor development, in addition to its current role in sensor research, by incorporating commercialization plans into internal funding proposals for research and development. NIST might also carry its involvement further down the commercialization path and broker technologies to the marketplace, identify common industry application needs including lists of analytes and specifications, provide forums for industry groups to collaborate on special sensing needs, and arrange for collaborative demonstrations of new technologies in manufacturing plants.

A breakout session on Gas Sensors for Process Control in Manufacturing was held during the NIST Workshop on Gas Sensors: Strategies for Future Technologies. A group of about 25 individuals representing the chemical, nuclear, and electronic processing industries, national laboratories, and universities attended this session. Most of the members of this group were familiar with sensor developments over the last 20 years. The primary question addressed was, "Why have recent, major efforts in sensor development not produced any measurable impact on industrial process control?" The group identified many barriers to the practical application of gas sensors in process control and proposed ways in which NIST could facilitate the process control application of the new and developing sensor technologies.

Barriers To Using New Sensor Technologies in Process Control

There are a number of barriers that limit the application of new sensor technologies in the process control industry. Primary among these is a lack of clearly defined performance requirements. Because the process control market is so diverse, there is no single view of sensor needs. Although the sensor requirements of the markets listed in Table 1 vary substantially, manufacturers in these areas share a reluctance to accept new, unproven technologies. When added to the other perceived barriers listed in Table 2, it is not surprising that the new sensor technologies have found limited industrial control acceptance.

Table 1
Process Control Industry Segments

1. Chemicals and Petrochemicals
2. Polymers and Fibers
3. Semiconductors and Electronics
4. Food and Drug
5. Combustion and Waste Incineration

Table 2
Barriers to the Application of New Sensor Technologies

1. Market diversity and the lack of a clear set of sensing requirements.
2. Reluctance to apply new sensors which have not been proven in plant applications.
3. Few vendors offer the new technologies.
4. Analytes often evaluated by researchers in developing new technologies are of little interest to most plants.
5. High cost of applying sensors and analyzers, regardless of the sensor cost.
6. Reliability and predictable maintenance requirements of new sensors not demonstrated.
7. Safety requirements for hazardous areas.
8. Secrecy surrounding industrial process information.

An additional barrier to the deployment of new technology in process control markets is the misunderstanding in the sensor development community that sensor cost is a major impediment to acceptance. In fact, there is a minimum expense in installing any sensor which will be part of a control system. Since control points are selected for their impact on overall process yield and quality, the sensor must be carefully installed. Issues of safety, maintenance, and good engineering practice must be considered. Typical sensor installation costs are listed in Table 3 which shows a minimum expense, excluding the cost of the sensor, of about $60,000 for an installation on a gas or liquid stream in an existing Class I, Division 2 area. Clearly, in most sensor/process control programs, the reduction of sensor cost is a secondary issue, since the total installed cost is very high.

On the other hand, because the installed cost of adding a measurement and control point is so high, the justification often used in the present economy is a payback of much less than one year. When such returns are expected, the risk associated with the installation must be low. If a plant administration is willing to install a new technology sensor to improve their operating costs, then the risk associated with that installation should not be technical, but rather market related. It was the perception of the breakout session attendees that the reliability of many new sensor technologies has yet to be demonstrated.

Device packaging requirements necessary to meet the physical, reliability, and safety constraints of the plant environment seem to be poorly understood by sensor development researchers. The gulf between a developed sensor technology and plant-ready devices seems to be very wide. Because of the expense and real risks involved in experimenting with on new technology for plant control, few manufacturers are willing to turn their operating lines into "testbeds for new technology." On the other hand, sensor development researchers often do not have access to "real life" applications for testing their devices. There seems to be no formal mechanism for establishing a "track record" for new sensor technologies.

Opportunities for NIST to Facilitate the Application of New Sensor Technologies to Process Control

Because of new Federal and/or state environmental regulations, plants are now frequently required to monitor their emissions more carefully. Again, reliability of the measurement is of paramount importance. Because these regulations permit the monitoring system to be out of operation for only brief periods, often less than one percent of the total operating time, the failure of a sensor can be extremely costly. Therefore, most plants will rely on traditional, often more expensive technologies, since the risk associated with the new approaches is too high.

It was the opinion of the session participants that the efforts in new technologies should be focused into areas where traditional technologies have not performed reliably, are not available, or where lower cost sensors are needed. Table 4 lists several such applications. Although not necessary for control, many plants now elect to measure fugitive emissions rather than calculate them from process variables, since the regulated limits for calculated emissions are much lower than those for measured emissions. The sensing of fugitive emissions represents an opportunity for new, low-cost gas sensor technologies. If reliability were demonstrated for at-line measurement of these emissions, then plants would become more secure in applying the same measurement to in-line control of a process. Several fugitive emission analytes of interest identified during the session are listed in Table 4.

Table 3
Typical Process Control Analyzer Installation Costs*

Engineering, Installation, and Training Costs	
Installation Assessment and Engineering Estimates	5,000
Piping	10,000
Electrical, DC Loops	5,000
Procedures, ISO 9000 Review	10,000
Control Algorithm	10,000
Training	20,000
Subtotal [Not Including the Sensor/Analyzer, Sampling System, or Certification]	**60,000**
Analyzer/Sensor Costs	
Photometer	20,000
NIR/FTIR	60,000 to 100,000
Oxygen	10,000
Emission Certification	20,000
Sampling System	5,000 to 30,000
Total Sensor/Analyzer Installed Cost	**75,000 to 210,000**

*Assumptions: Class I, Division 2 area classification; Process measurement is a process control point within an existing facility.

Table 4
High Value Applications for New Gas Sensor Technologies

1. Fugitive Emissions
   - Driving force is tightening of environmental regulations.
   - Example Analytes:
     Methyl isocyanate
     Phosgene
     Vinyl chloride
     Styrene
     HF
2. Semiconductor and Chemical Manufacture Contaminants
   - Low-level water is the critical analyte.
3. Combustion and Stack Scrubber Control
   - Analytes are related to various combustion optimization and pollution abatement schemes.
4. Incinerator and Stack Scrubber Monitoring
   - Analytes are related to the incineration of hazardous wastes.

Traditional analytical techniques have not worked well for water measurement in the low part-per-million region and below. On the other hand, the need for measuring such low water levels has expanded particularly in semiconductor, electronic, refining, and chemical industries. The need for real-time low-level water determinations is great enough that many plants would be interested in any new technology which offers the promise of making such moisture measurements, even if a performance track record had not been established.

In several areas, such as combustion and incinerator control and monitoring, current sensing technologies are hard pressed to provide the desired information. New methods are needed, but such devices would have to be very rugged to survive and operate reliably under very demanding conditions.

NIST has played an important role in the development of sensor technologies in the past and should continue to do so in the future according to the breakout session participants. It was the view of the group that the NIST involvement should be aimed toward better defining the industry needs and then aiding in bringing the new technologies into actual use. Some members of the group voiced their displeasure with several of the process analytical consortia which, although they provide good research, have failed to transfer any technology into plants.

A substantial effort should be mounted to bridge the gap between sensor research and sensor deployment. The attendees felt that in many cases sensor research has become an end in itself and, while the results new technology research can be valuable, the real payback is not realized until devices are commercially available. More effort should be expended to make newly developed transducers into sensors, new sensors into measuring systems, and new measuring systems into industrially hardened prototypes.

NIST should become more involved with this development process and carry its current research efforts much further toward commercialization. NIST could act as the needed forum and catalyst in getting researchers, developers, system integrators, and industrial users together. Furthermore, NIST's Advanced Technology Program (ATP) is particularly well suited to provide funding for the missing link in the new sensor development cycle. NIST should continue to encourage those involved in sensor development to apply for such funding.

In certain areas, special sensing needs are pushing the envelope of existing technology. One example is the semiconductor industry need to measure extremely minute concentrations of contaminants. Through one-on-one industrial Cooperative Research and Development Agreements (CRADAs), NIST-sponsored or NIST-organized industrial consortia and other joint ventures, NIST can help the industry spread out the costs and risks of developing new technology to meet these needs. Again, ATP funding could be appropriate for some types of these joint ventures.

Since there appears to be no formal mechanism for establishing "track records" for sensing technologies, and since the lack of such credentials is often cited as a reason for not using newly developed sensors, it was suggested that NIST establish some means for matching industrial users with researchers, developers, and system integrators to demonstrate new technologies in real plant environments.

Many attendees felt that much of modern sensor research did not address their sensing needs and that analytes being studied were of little interest in process monitoring applications. It was suggested that NIST help identify the real gas sensing needs of the industrial control community namely what analytes are important, what concentration ranges must be sensed, what operating conditions must be met, and what reliability concerns must be addressed to make sensors for the plant environment that is, after all, very different from the laboratory.

Many members of this breakout session felt that NIST had taken the first step in improving the gas sensor technology development process by sponsoring this workshop and most expressed their desire to reconvene in the future to assist in defining specific process measurement and control needs, to review new technology proposals, and reports, and to plan in-plant evaluations.

Indoor Air Quality and Personal Safety

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This report is a summary of the discussions of the Indoor Air Quality and Personal Safety breakout session of the NIST Workshop on Gas Sensors. The application areas discussed in this session were indoor air quality, industrial hygiene and general health and safety. Specific discussion topics included contaminants to be sensed, required sensor capabilities, sensor market potential, promising emerging technologies and commercialization issues. The lack of proper technology development was identified as the major impediment to wide scale commercialization of gas sensors for these applications. Required features for commercialization that require development efforts include very high sensitivity for IAQ applications, robust compound-specific sensors for IH and H&S applications, and long term reliability with minimal required calibration for all applications. Unit costs must be driven down to low levels to allow deep penetration into commercial and residential IAQ markets.

Introduction

This report summarizes the discussions of the Indoor Air Quality and Personal Safety breakout session of the NIST Workshop on Gas Sensors. To stimulate discussion, the session started with short presentations on contaminants of concern for indoor air quality (IAQ), industrial hygiene (IH) and general health and safety (H&S) applications. These themes were carried throughout the session, with distinctions made for the characteristics of the separate applications as necessary. An additional short presentation discussed application of an array of non specific gas sensors to IAQ sensing. To further stimulate discussion, specific questions were posed to participants including contaminants to be sensed, required sensor capabilities, sensor market potential, promising emerging technologies and commercialization issues.

Introductory Presentations

Andy Persily of NIST discussed contaminants of interest for IAQ. ASHRAE Standard 62 was noted as a reference for contaminants and relevant concentrations, including the National Ambient Air Quality Standards for SO2, particulates, CO, and O3 as contaminants of outdoor air used for ventilation. The standard also lists maximum allowable indoor concentrations for CO2, radon, chlordane and O3. Maximum allowable concentrations for additional contaminants, mainly organic chemicals, are listed in appendices to the standard, taken from Canadian and the World Health Organization exposure guidelines. Other IAQ sensing needs identified were: tracer gases such as SF6, selected refrigerants, odors, contaminant mixtures such as environmental tobacco smoke, temperature and relative humidity.

Alan Schnieder of MSA discussed Contaminants of Interest for Industrial Hygiene and General Health and Safety, building on his plenary talk on a similar topic. Primary IH sensing requirements for O2, CO and H2S were outlined and ammonia and freons were identified as other general needs. Specific applications such as the plating industry have typical needs. Hospital H&S needs include the sensing of halothanes, NO, anesthesia gases, ethylene oxide (at half of the action level), formaldehyde, and Sidex (a liquid sterilizing agent). Contaminants that are not well covered by the existing sensor market are anesthesia gases and general IH contaminants; the entire ACGIH book of threshold limit values (TLVs) for example.

Jarrell Wenger of Johnson Controls presented a strategy for sensing IAQ contaminants using an array of gas sensors. A distinction was made between IAQ and IH contaminants in that IAQ contaminants consist of hundreds of compounds that appear to start causing problems at 2 to 3 orders of magnitude lower concentrations than the limited number of compounds that are typically found in an industrial workplace. In the short term, IAQ exposure to individual contaminants does not generally pose a health risk, suggesting that individual compounds need not be monitored. Using advanced pattern recognition techniques, signals from an array of sensitive but non specific gas monitors have been correlated with a measure of human response. Reasonably good predictions of the odor perception of a trained panel of humans were obtained.

Discussion Topics
The following summaries are paraphrased from the discussion that followed the posing of specific questions.

1. What substances should be sensed? Building on the short introductory comments, it was suggested that IAQ contaminants be split into 2 categories: contaminants that impact people, and contaminants that impact equipment and building materials. The latter category would include particulates, VOCs and strong oxidants such as ozone. While many of the same contaminants would be included in each category, allowable concentrations may differ. Another type of environment is a submarine, where sophisticated analysis can be used to characterize the contaminants from the ship, the crew and the crew's belongings. Real-time sensing systems could then be devised. If the air cleaning systems on the ship can not remove these contaminants, the sources must be removed. The environments in battleships and carriers are more similar to buildings since contaminants can be exhausted and ventilation can be provided with outdoor air.

Air cleaning systems can potentially generate contaminants that are "worse" than the inputs. Breakthrough sensors for such devices are an emerging need. This concept can be taken to the point of installing sensors inside of respirators to monitor real-time performance.

Required levels of detection were also discussed. CO monitoring for a fire detection application requires a detection threshold of about 30 ppm, but high accuracy and resolution are required above that. For IH, sensors must be able to detect compounds at the TLV (or somewhat below, to allow control decisions to be made). Since suggested total VOC concentrations for IAQ are typically sub-ppm, detection levels for groups of compounds or individual compounds must be tens of ppb or better.

2. What sensing capabilities are currently available? Other than carbon dioxide, virtually no sensors that are currently available are adequate for the IAQ application.

Relatively good CO sensors based on several technologies (electrochemical, infrared, tin oxide) are available for other applications. Sensors cost as little as $100, have a life of more than 1 year, and require little calibration (although it is performed every month in some applications such as mining). A $50 CO sensor that meets UL 2034 guidelines is scheduled to be released for the home market soon. Absence of calibration requirement (or use of automatic calibration) is seen as essential for residential (and to a lesser extent, commercial) applications. For environmental monitoring to protect electronic equipment, reliability is more important than an ultra-low detection limit and a low first cost. For some other applications, even the $20K ion mobility spectrometer can be a cost effective sensor because of its high performance.

3. What sensing capabilities are needed; what are the current gaps (substances and performance parameters)? For IAQ, the key need is for devices with lower limits of detection (tens of ppb) for VOCs and some inorganics. For electronic equipment environments, even sub-ppm total VOC would be

useful. A radon gas sensor would be useful in the residential market, where real-time instruments are very expensive; such a sensor could be used to operate radon control systems on an as-needed basis. Multi-sensor strategies have applications for IAQ and IH, because of flexibility for general monitoring purposes; such systems can potentially be tailored for the classes of contaminants found in specific applications.

A good, inexpensive ammonia sensor is a current need for IH applications. Some VOCs such as vinyl chloride are toxic in very low concentrations and a sensor with an appropriate detection limit and sensitivity would be useful. Sensors and electronics that are immune to RF interference are also needed. Sensors and systems that are self-monitoring, self-healing and self-calibrating are highly desirable for all applications. Maintenance costs can be much higher than first costs, or as in residential applications, maintenance simply will not be performed. For high precision or high risk applications, periodic calibration with test gases may be necessary, but it can be simplified with calibration cocktails or automated calibration systems. Sensing mechanisms can be exploited to perform calibration; infrared CO sensors can potentially be calibrated with the much more benign CO2. Reference channels can be built into instruments for calibration checks. Barriers to such innovative calibration strategies may be more regulatory than technical.

4. What is the market potential for IAQ, IH and general health and safety sensors? Market potential will obviously depend on cost. At high prices, market penetration into IAQ and residential applications will be limited, but as costs drop, markets will expand. The IAQ market for example, is potentially huge if sensors are inexpensive enough to be applied in each thermostat zone. A large potential market exists for inexpensive (integrated) sensors for total VOC, CO2, temperature and relative humidity. Calculations performed by an HVAC control company indicate that integrated sensors for demand controlled ventilation must sell for less than $300 per building zone to achieve an adequate payback for customers through energy savings. Another control company estimates that selling price must be closer to $30 to achieve wide scale application. If residential sensors can be developed to have a 20 year maintenance free lifetime, $5 to $20 sensors would penetrate most of the market.

Wiring can be very expensive and cost-effective telemetry may be an additional required feature. Standard interfaces are another feature that would help convince customers to apply environmental sensors; the ability to easily plug in alternative sensors from different manufacturers would be attractive.

Systems engineering, modeling and control strategy development can not be ignored; complex strategies are required to balance control of thermal comfort, acceptable IAQ and energy costs in a wide variety of systems. Yet, inexpensive, high performance, properly applied devices still may not be sufficient. Experience with smoke detectors suggests that regulation and insurance incentives were the final steps necessary to achieve deep market penetration.

5. What are promising emerging technologies (in the research pipeline)? The Naval Research Lab is looking at SAW (surface acoustic wave) devices for environmental applications. These sensors exhibit good sensitivity and low detection levels, but stability over their lifetime is unknown. Current tin oxide detection levels are inadequate. Atomic force microscopy and scanning tunneling microscopy are possible sensor transducers that can be micro machined; these technologies have been used for studying antibody-antigen interactions.

With more sensitive detectors, NDIR sensors have the potential for detection levels in ppb range. Higher detection level for CO2 have potential to drop to $30 per device in large quantities. Ion mobility spectrometers exhibit very good performance, but it is unlikely that sensors could drop below $1000 each.

6. What are commercialization potential/pitfalls/resources required? The question was raised of why some of the promising emerging technologies of 5 years ago, such as SAW devices, remain promising emerging technologies rather than commercial products. One potential manufacturer spent substantial sums of money testing several new technologies including SAW and micro machined sensors, and could not get them to work.

Commercial devices must be reliable; false alarms are as undesirable as outright failures.

Some of the commercialization pitfalls are the hard to meetuser wish© lists of price and performance without regulations creating a firm market. As a counter argument, it is difficult to put regulations into place before the required technology is available, and once in place, compliance withregulations can still be slow. One alternative is to provide choices in regulations, such as the ASHRAE Standard 62 IAQ procedure, which can not be met now, but keepsoptions open for creative applications as technology becomes available.

One barrier to commercialization of new sensors is a lack of communication between researchers, potential manufacturers and potential users. Presentations from more users would have been a useful addition to the research results presented at this workshop. Many researchers do not appear to be targeting their work for the real world; micro devices are very popular in research, yet macro devices are more appropriate for many customers in IH (more robust). Perhaps more research should focus on monitoring electronics; production SAW sensors will be of negligible cost, but signal monitoring electronics can be prohibitively expensive.

User groups could potentially interface with researchers if the prohibitive proprietary issues and intellectual property concerns could be addressed. Users could develop testing standards to guide research testing under realistic conditions. The gap between researchers and users appears to be in the development area, reflecting general trends in US business. Hitachi spent $20 million to develop an electronic nose without success, but is ready to invest again with a suitable US partner. Government CRADAs can help small companies through development, but some past agreements have had intellectual property problems. The NIST ATP appears to be better suited to large consortia rather than small businesses, and for research rather than development.

7. Open discussion

Market potential and possible pitfalls are illustrated by the telecommunications industry; 34,000 buildings have sensing needs, but any sensing system must be entirely fail safe because false alarms can not be tolerated. Totally automated HVAC systems are the wave of the future, and automated diagnostics for controlled systems and control systems are needed.

Conclusions

The most significant impediment to wide scale commercial application of gas sensors for IAQ, IH and H&S is the lack of proper technology development. Promising technologies in the research pipeline are not emerging into the commercial arena, yet rapid commercialization of current research technologies is probably not the answer. Unless the investment is made in proper development of these technologies, critical user requirements will not be met. These requirements include very high sensitivity for IAQ applications, robust compound-specific sensors for IH and H&S applications, and long term reliability with minimal required calibration for all applications. Development efforts and high volume manufacturing will be required to drive unit costs down to the levels that allow deep penetration into commercial and residential IAQ markets. Most of the required technology improvements are not mutually exclusive between these applications, or versus process control, outdoor environmental monitoring and automotive applications. Substantial sharing of development efforts between applications should be possible.

Gas Sensors in Outdoor Environmental Monitoring and Site Remediation

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A special session on sensors in outdoor environmental monitoring and site remediation was held as part of the NIST Workshop on Gas Sensors. This manuscript summarizes the main points of the workshop. Application areas, issues of concern, and potentially fruitful areas for further research and development were discussed. The main conclusion of the group was that the problems and potential solutions to problems in environmental monitoring were common to other application areas of sensing as well. Of particular concern to the group were the many barriers to final development and commercialization of sensors. Barriers included lack of information on potential markets, lack of support for development, (as opposed to more basic research), and difficulties in developing the final packaging for a device. The characterization and development of chemically selective materials for sensor coatings was viewed by the group as a particularly important area for future research.

Introduction[1]

A special "breakout group" session on gas sensors in environmental monitoring and site remediation was held as part of the NIST Workshop on Gas Sensors. The breakout group had ~35 attendees, who were about equally divided between academic institutions, industry and government laboratories. The discussion was broken into three topics: application areas, important issues in environmental sensing, and promising areas of research. Highlights of the discussion follow. It should be noted that the topics discussed most likely reflect the particular biases of the group and that a somewhat different group may have different concerns.

Applications of Environmental Sensors

The group was polled concerning the areas of application of sensors in environmental monitoring. Two application areas in particular stood out as having a great potential for eventually being a very large market. The first of these was monitoring of stack emissions. While large chemical and power plants can afford fairly expensive equipment for monitoring emissions, smaller plants will have to rely on less expensive alternatives. It has also recently been found that in many urban areas, such as Los Angeles, the major contributors to air pollution are non point

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[1] Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

sources such as dry cleaners and bakeries. Small businesses such as these cannot support expensive equipment for monitoring emissions, yet it is clear that if progress is to be made in improving air quality, these small sources must be monitored.

Another area with a potentially large market is the detection of leaks of volatile and highly volatile organic compounds from valves and fittings in chemical plants. Current regulations require frequent testing of these systems, but it is entirely possible that continuous monitoring will eventually be required. This application will require distributed monitoring systems where the sensors are located far from power sources and may have to report to a central location. Sensors will also face the additional requirement of explosion safety. Related areas include the monitoring of chemical storage tanks for fugitive emissions and the monitoring of oil rigs.

Environmental monitoring and site remediation efforts being addressed by the Department of Energy constitute a wide variety of applications for gas sensors. A major area is the monitoring of the vadose zone in soils for volatile organic carbon compounds. This needs to be done both as a screening procedure in order to determine appropriate remediation measures and continuously as a worker safety measure during remediation activities.

Gas monitoring is also an important concern in nuclear waste storage and processing for remediation. The vapor head space in some nuclear waste storage tanks must be monitored for hydrogen and other gases. Gas formation in process pipelines is also an issue.

Another application is the monitoring of test wells for groundwater contaminants. These contaminants can often be detected in the vapor space above the well water. As an example, there are several thousand wells at the Hanford site alone that must be checked at least yearly, with many of them requiring testing more often than that. Sensing technology that would eliminate sampling of the wells and transport of the samples to testing laboratories would greatly improve the efficiency of the monitoring effort. There are many other specific needs within the DOE complex.

National security needs for gas sensors include monitoring to detect the production of chemical weapons and the detection of chemical warfare agents themselves. In the former case, it is generally the precursors to chemical weapons that must be detected, and are often present at only the part per billion level. A particular problem in this area is that many of the precursors are similar to relatively common pesticides in structure and chemical behavior. Thus, specificity is of concern, since it is very important in this area to not have any false alarms. Detection of warfare agents has been of concern to the military for some years. Here the cost of false alarms is less severe and quantitation is not required. However, ruggedness and portability become very important issues in these applications.

Issues in Environmental Monitoring

In the paragraphs that follow, the issues of concern to the group are discussed. These follow in no particular order, though the issues thought to be of greatest concern are noted.

A representative from the Environmental Protection Agency pointed out the differences between characterization and monitoring. Typically, sensors will be more suitable for the monitoring problem, where you already know what you are looking for, while more extensive analytical procedures are often required for characterization. Sensors can also be used in "screening" applications where a yes/no question about the presence of contaminants of interest must be answered, *e.g.* is analyte y present in the samples at concentrations greater than x? Unfortunately, screening techniques, which in practice can be very reliable for answering relevant environmental questions, have suffered a bad reputation due to the term "screening," which seems to imply highly uncertain results. It was noted that the most important requirement for screening tests is a reliable zero level.

Fouling and corrosion of sensors in outdoor environments is a concern. This is particularly true in applications where moisture levels are high and where there is the possibility for biological fouling of sensor surfaces.

Making measurements in an uncontrolled environment presents special challenges. Often, the background matrix is both unknown and variable. In the face of varying background matrices, a single sensor system must be totally selective for the analyte of interest. On the other hand, a sensor array, producing a vector of data for each measurement, need not have any sensors that are totally selective; however, the variable background matrix must be included in the calibration of the array so that a combination of sensors not affected by the background variation can be determined. Recent developments in second-order sensors, those that produce a matrix of data for each sample, where sensor response is a function of two parameters, hold the promise of quantitation in the presence of varying background that were not included specifically in the calibration matrix.

It was generally agreed that more work needs to be done in material science in order to achieve better understanding of the way that analytes interact with sensor coatings, both at the surface and in the bulk material. An example of this is the development of polymeric coatings for surface acoustic wave devices. A thorough understanding of the way analytes interact with the polymers is critical to a full understanding of the way that SAW devices operate. Many new materials are on the horizon, and the ability to grow surfaces through epitaxial and other methods will certainly impact the development of sensors. These techniques also hold the promise of enhancing the understand of the interactions of the materials because of the very well characterized nature of the materials. This is in contrast to the way much sensor development has occurred in the past, when materials were simply tested in applications and the underlying reasons for their behavior was not of concern. It has been demonstrated that understanding of materials is especially critical in the development of sensor arrays where a variety of coatings are used. Fundamental understanding of the materials is essential in determining how to best combine sensors to achieve selectivity of the analytes of interest in the presence of background matrix variation.

The cost of sensors was of widely varying concern to the group. At one extreme are the national laboratories responsible for environmental monitoring critical to safety and the prevention of further environmental contamination. In these instances, it is not unusual to spend hundred of thousands, or even several million dollars developing a device for an application that occurs only in a small number of instances. At the other extreme are the automobile manufacturers, which may require millions of copies of a single device but are only willing to pay a very small sum for each copy.

The lack of information about the performance, cost, and availability of systems for environmental monitoring is a hindrance to their integration into the marketplace. This results in some confusion in several areas. Often, it is difficult to sort out the claims of vendors and achieve a reliable estimate of the performance expected of a device in a particular application. There is a real need for unbiased, real-world testing. Often, sensor users are not aware of working technologies for particular applications and either purchase a suboptimal system or embark on unneeded development of a new device.

Concerns about sensor drift appeared to correlate with the complexity of the device under consideration. It was pointed out that many of today's single sensor systems include automatic zero and span set features. With more complex arrays, however, it is more difficult to correct for changes in the sensitivity and baseline of the instrument.

Portability of sensor systems is of some concern in environmental monitoring and site remediation applications. Often instruments must be taken "into the field" to remote locations. The physical size and weight of a system can be a factor in how widely it is used. Power supply is often an issue in remote locations.

There appears to be a need for more streamlined methods for developing cost effective packaging for environmental sensors, as well as sensors in other applications. Several remedies to this problem were suggested. For instance, would it be possible to develop some generic packages for sensors that could be used to house a variety of devices? Also, the need for concurrent engineering was noted. The development of a package must not lag too far behind development of the transducer itself.

A side issue in environmental monitoring is the lack of a reliable baseline for naturally occurring chemicals. Such a baseline would be useful for both regulatory purposes and in the development of sensors for specific applications. Knowledge of the background matrix is critical in the development of most sensor systems.

High Potential Areas for Research and Development

As noted above, materials science was seen as a critical research area with regard to the development of environmental sensors. Advances in the understanding of materials and improvements in our ability to tailor make materials for specific applications will have a great impact on the development of selective environmental sensors. Chemically sensitive films is an especially important area in the general field of materials. There is a great deal of variety in sensitive films, including polymers, catalysts, chemiluminescence, etc.

Many sensors have a nonlinear response to chemical and physical changes in their surroundings. Research in chemometrics, particularly in the area of nonlinear multivariate calibration, will be an important aspect of making nonlinear devices practical. A wide variety of nonlinear methods exist but more work needs to be done to make these methods more accessible to the nonexpert user. Research in second-order calibration methods may be particularly important.

While many second-order analytical instruments produce well behaved "bilinear" data, many second order sensors are expected to produce the more challenging "nonbilinear" data. Methods for dealing with these data types are still in their infancy.

The group agreed that fiber optic based sensors will be an important area for further development. The potential richness of the data produced by such devices, essentially the same as spectrophotometric methods, allows for selective sensing in many applications provided that suitable calibration matrices can be obtained. Furthermore, it is possible to combine fiber optic sensors with other technologies, such as chemically selective membranes, to form the basis for the second-order devices discussed above.

Miniaturization of sensors will continue to be an important research area, particularly to the extent that the transducers and electronics of these devices can be integrated for form robust packages. Arrays of sensors will also be important as they can be combined to operate as first or second-order devices. Research into the processes required to build such devices is important. Streamlining the manufacturing process is an important step in the commercialization of any sensing device.

The development of biological sensors may be important, particularly for the detection of biologically active analytes.

Conclusions

Many of the problems involved with using and developing sensors for environmental monitoring and site remediation appear to be common to other areas of sensing. There are a few exceptions, including an increased emphasis on the ability to obtain a quantitative reading in the presence of an unknown and possibly varying background matrix, and the importance of a stable zero reading.

Barriers to the commercialization of environmental sensors was one of the major concerns of the group. Often the size of a potential market is not known, nor are the prices that the market segment would be willing to pay. While support for research, particularly in the national laboratories and other government laboratories appears to be adequate, support for the final development is often lacking. This, in part, may be due to the fact that individuals prefer to work in the more glamorous domain of research rather than the more tedious area of development. A related issue is the packaging of sensors. It was noted during the main workshop program by a representative from Ford Motor Company that a complete sensor includes the package and connectors, not just the transducer. Often, it is development of the package that slows down final development. It was noted that concurrent development, or holistic design can alleviate the packaging problem.

The group did not appear to be concerned over transducers themselves. It appears that the variety of transduction mechanisms is adequate for most needs in environmental monitoring. More attention needs to be paid to the coatings for transducers, which is generally the only chemically active part of the sensor. One researcher noted that this is "where the rubber meets the road."

Gas Sensors for the Automotive and Other Transportation Industries

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Abstract

The needs for and results of a workshop session on gas sensors in the transportation industries are reviewed. Regulations calling for the on-board diagnosis of vehicle emissions performance provide the main motivation for sensor development. Because of difficulties with the present method adopted for monitoring catalyst performance, several more direct sensors of hydrocarbon conversion efficiency were discussed, including dual-element calorimetry and non-dispersive infrared measurements.

Introduction

This session was intended to examine the needs and technology for chemical gas sensors for the automotive and transportation industries. The 27 attendees represented users and suppliers of gas sensors and independent research and development institutions including government, academic, and private organizations. They considered both short and long term needs as well as technology available at present and in the foreseeable future. Because the needs of the automobile industry were well-defined, well-represented, and of large economic impact, these needs dominated the discussion of the full session.

The session was initiated by introductions and brief statements of interest by all participants. This was followed by a statement of purpose by the co-chairs which was prompted by a participant. Dr. Galen Fisher, one co-chair, specifically stated the need for identifying problems and coming up with solutions for onboard diagnostics for automobiles. Dr. Kenneth Kreider, the other co-chair, described NIST's role as a facilitator to bring the key participants together to address the technology of gas sensors and contribute to bringing these technologies into commercial use.

The workshop session then turned to the definition of the sensor needs of the auto industry followed by presentations of proposed solutions, a lively discussion of the advantages and shortcomings of these solutions, and a discussion of some of the broader issues related to the needs, such as research needs and usefulness of standards. The statement of the need for the automotive sensors which will be a result of the 1990 Clean Air Act was made primarily by Galen Fisher of the General Motors Research and Development Center. Supporting remarks were made by others, including Dr. Jaco Visser of the Ford Scientific Research Laboratories.

Gas Sensors Needed For Transportation Applications

The needs of the transportation industry for gas sensors are manifold, but there are a few new challenges that are receiving considerable attention. Among the most acute needs are those caused by recent changes in automotive emissions control regulations. In addition to the more stringent emission standards which new vehicles must meet in the 1990's (summarized in [1]), The California Air Resources Board and the Environmental Protection Agency have promulgated rules which require automakers to incorporate comprehensive on-board diagnostics for emissions control systems nationwide by 1996. In California vehicles from several manufacturers have them in 1994 model year vehicles. The intent of these regulations is to ensure that drivers are made aware, when any component of their vehicle which affects emissions is not functioning properly, by means of a dashboard malfunction indicator light. Among the monitored systems is the catalytic converter which converts gas phase pollutants consisting of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x, mainly NO), to the more benign species carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2).

It is difficult enough to monitor species in the exhaust at all because of the high temperatures and hydrocarbons and water present, but to do it for the life of the vehicle is even harder. At the same time the emissions standards are also becoming more stringent. This has led to the development of new methods to meet hydrocarbon standards. Strategies include having multiple converters, some closer to the engine so that they warm up faster to become active. With these new standards, the level of hydrocarbons that must be detected in exhaust will also fall during the 1990's. All in all it makes for a very difficult problem, to diagnose the HC conversion efficiency of possibly several converters in cars that are designed to convert almost all of the hydrocarbons.

The current approach to monitoring catalytic converters is called the dual or multiple oxygen sensor approach. Its rationale of operation is that there is a relationship between the oxygen storage of a catalyst, measured by the oxygen sensors, and the HC conversion efficiency [2,3]. This method has been found wanting from a fundamental point of view, since there is no clear causal connection between oxygen storage and HC conversion efficiency and the available data show a very non-linear relationship [1,4]. Particularly for close-coupled converters, it has been shown [5] that this method detects the loss of oxygen storage that occurs during the aging of converters, even though the HC conversion efficiency remains very high. This could lead to the unnecessary recall of good converters.

These problems with the present method have aroused considerable interest in other methods of measuring hydrocarbon or related emissions that are more direct. A method is needed that will detect the malfunction of the first catalyst in a system defined as the point when its HC conversion efficiency falls below 50%-60%. The regulations are actually expressed in terms of non-methane organic gases (NMOG) emissions. Methods that have been discussed include non-dispersive infrared, calorimetric methods, resistance measurements, zirconia-based sensors, and other approaches. Whatever the method, the diagnostic exhaust gas sensors should satisfy certain requirements. The first goal would be for a direct measurement of one or more of the three regulated constituents; HC, CO, and NO. If the sensor output involves an inferred relationship with, for example, HC concentration, then the relationship must be robust, well-established and documented. Table I sets approximate targets that are necessary for these measurements as generally agreed upon by the On Board Diagnostics II (OBD II) Catalyst Monitoring Committee of the USCAR Low Emission Partnership made up of representatives of General Motors, Ford, and Chrysler.

Table 1. Approximate targets for detection of hydrocarbons, carbon monoxide, and nitric oxide by a sensor for OBD II catalyst monitoring. Only HC measurement is called for by current regulations.

Constituent	Range	Minimum Detectable Resolution	Threshold
HC (NMOG)	0 - 1000 ppm (0.1 %)	25 ppm	25 ppm
CO	0 - 10000 ppm (1 %)	500 ppm	500 ppm
NO	0 - 1000 ppm (0.1 %)	25 ppm	100 ppm

In addition to the above measurement capabilities for HC, CO and NO_x, the sensor system will have to survive and perform for at least the order of 100,000 miles (160,000 km) in a very hostile environment, automotive exhaust. A minimum service interval would be 50,000 miles (80,000 km). A sensor in the exhaust, behind an engine, will see temperatures that can vary from -40°C to 800°C with spikes above that possible; the normal ambient temperatures may be between -40°C and 120°C. The sensor will also be exposed to a range of gases in these approximate proportions by volume: 10% CO_2, 10% H_2O, 1% O_2, 1% CO, 0.3% H_2 and 0.1% HC, nitric oxides (NO_x, mainly NO), and SO_2. There are also trace amounts of phosphorus (P) and silicon (Si). The balance is nitrogen (N_2). The flow rates are generally between 10-30 g/s and can be as high as 150 g/s.

A few other associated requirements occur for automotive applications. The entire device with its packaging must fit under the body of the vehicle. The devices should be totally interchangeable, with no calibration required and should be compatible with a 12 V dc system. The device should have characteristics that make it easy to carry-out self-diagnosis. Response times should be on the order of tens of seconds in the worst case; it does not need to respond to individual cylinder events. The test of this diagnostic and the others on the vehicle will all have to occur at least during the time of the Federal Test Procedure (FTP) for emissions performance.

Gas Sensors Proposed for Automotive Needs

After the discussion of sensor needs, the breakout session went on to cover a number of gas sensor technologies. Three interesting approaches, mainly for HC gas sensing, were presented to the workshop to solve the catalyst monitoring problems. They were presented by

Mike Richard of Sonoxco, Atul Shah of Cerametal, and Jacob Wong of Telaire Systems, and by other participants whose devices were under research and development.

One proposed solution, discussed by Dr. Richard, consists of a dual calorimeter comparing the signals from catalyzed and non-catalyzed elements. It can have the capability of measuring CO, HC, NO_x, and SO_2 depending on the selection of catalysts. Devices typically can be produced with a response time of seconds by conventional manufacturing processes. The catalytic process requires sufficient oxygen to oxidize CO and HC's; these devices have lacked sensitivity to CH_4. A newly developed microfabricated version of the sensor may have a faster response time and less dependence on flow rates. The complex technology of preparing these devices for automotive applications would require partnerships among the sensor producers and automobile manufacturers. The discussion at the workshop covered the sensor's capability to meet the measurement criteria stated above and its durability.

A second solution, presented by Dr. Wong, uses a non-dispersive infrared sensor for detection of HC, CO_2, CO, NO_x, SO_2, and/or ozone. The selectivity of the sensor depends on narrow band pass filters limited to an absorption band of the molecule of interest. The design presented had a simple IR source (a light bulb) powered by a pulsing waveform and a unique waveguide which, by design, simulates the 10 m pathlength normally needed for adequate sensitivity in measuring IR signals. The designer claimed that the IR sensor complete with the pyroelectric detector could cost less than $15 and require only 1.5 W of power. Questions were raised concerning the stability and durability of the device when exposed to 160,000 km of automotive exhaust.

The third approach which was discussed related to various solid state and electrochemical sensors, including ZrO_2, SnO_2, ZnO, and $SrTiO_3$. The zirconia sensors used on present vehicles would be improved and combined with selective membranes to measure oxidizing species. Zinc oxide sensors would be used for reducing species such as CO and hydrocarbons. There was considerable hesitancy to disclose information on the mechanisms of operation or even the transducing materials in these sensors, but it was clear that numerous organizations were interested in this billion dollar market.

The international competition was discussed as well as the techniques that would be used to meet the need for low emissions vehicles. Worldwide there is much interest in lean burn engines. A lean exhaust technology also is available for diesel engines and the new 2-stroke engine technology. In addition, a discussion of new, improved catalysts took place, primarily those for NO_x, possibly using zeolites. These technologies all depend heavily on the quality of the fuel and it was the consensus of the automobile manufacturers that improvements in fuel quality, especially as it relates to sulfur content, are needed. Since the primary job of the sensors is and will be to monitor catalytic converter performance, there was extensive discussion about converter technology. It was also apparent that research on the behavior of catalytic and sensor materials is still important to the development of this technology, since many questions remain on material behavior and stability. New approaches to these general problems were discussed including the consortium approach (i.e. Chrysler, GM, Ford Low Emissions Partnership within USCAR) and government programs, such as the Advanced Technology Program.

Summary

Our automotive sensor breakout session featured a lively discussion focussed on the near-term needs of the auto industry to meet requirements of the EPA and California Air Resources Board (CARB). These needs have been further defined by the USCAR Low Emissions Partnerships. They include responses to CARB's "Low Emission Vehicles" (LEV's), transitional LEV's or TLEV's, and ultra LEV's or ULEV's. They require extensive on-board diagnostic systems, which means an extensive market for automotive sensors in the near future. The workshop participants included knowledgeable representatives from automobile manufacturers, sensor manufacturers, and members of the R & D community. Although interesting solutions to the sensor requirements were proposed, the extremely stringent requirements for performance and durability indicate intense activity in improving the technology will be needed. The interaction at the workshop was an excellent way to further communication between the principals of this technical activity.

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IV. Discussion Sessions

THE ROLE OF EMERGING TECHNOLOGIES IN GAS SENSING

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Advances in a number of diverse technologies are converging to make possible a new generation of gas sensors with improved selectivity, sensitivity, portability, and reliability at lower cost. These advances range from improved sensing materials and new transduction methods to new computational techniques for analyzing multi-sensor data. It is the challenge to the sensor community to rapidly synthesize developments from these diverse areas and produce marketable sensors and sensing instruments. Each competing new technology brings both a new set of benefits as well as new limitations for application. In this field, competing technologies for a given sensor application may lie outside the realm of one individual's expertise. It is, therefore, the purpose of this session to highlight important developments in varied fields that can be expected to have an impact on gas sensing technology in the next 5-10 years.

Micromachined Devices

Microfabrication of electronic devices is a mature technology with well-defined procedures for film deposition, materials processing, lithography, and packaging to produce reliable devices. These methods are now being applied to create micro-machined structures on the length scale of 10 µm to 1 mm. The majority of micro-machined devices are based on Si wafer processing, partly because of the maturity of this technology, and partly because of the suitability of Si for micro-machining. Sensors based on micromachining may include miniature Taguchi (semiconducting oxide) sensors, pyroelectric devices, sensors using electro-osmotic pumps for fluids, and possible tunneling transducers. These devices offer the potential for integration into arrays of sensors with integrated electronic devices, as well as capabilities for self calibration and self-regeneration.

Some micromachined devices are created through process equipment which, while similar to commercial electronic device fabrication technology, requires special process steps, such as back-side wafer etching and wafer alignment, which are not part of the standard electronics manufacturing protocol. Facilities devoted specifically to micromachining technology offer the greatest flexibility for device design and material selection. Drawbacks to this approach mainly involve longer commercialization times due to the large capital expenditures for such facilities, and untested reliability issues. There are also efforts to adapt commercial electronics processing rules to form micro-machined devices. Dr. Michael Gaitan (NIST) described the use of existing CMOS (Complementary Metal Oxide Semiconductor) foundry operations to produce micro-hotplates and other devices. In this methodology, circuit and layer sequence designs are submitted through the MOSIS (Metal Oxide Semiconductor Implementation System) wafer-sharing service of ARPA (Advanced Research Projects Agency) to commercial foundries for device fabrication. Returned chips require only simple process steps such as etching or low resolution lithography to produce the micro-machined structures. Advantages are the reproducibility and reliability of the commercial process, the ability to integrate electronics onto the same chip, and low start-up costs. In this approach, however, there are limited materials and layer sequences available, as the designs must conform to the CMOS device fabrication rules.

Multi-variate Analysis and Neural Networks

The ability to fabricate sensor arrays presents new computational problems for the real-time analysis of sensor data. If the individual sensors in the array are not perfectly selective, many of the array elements may produce a response for a single gas. For example, the carbon monoxide sensor in an array may produce a response in the presence of a hydrocarbon. The patterns of responses generated by the array in the presence of different gases at different concentrations may, however, be used to correctly produce a gas-specific analysis. Computational methods that address these problems are found in fields such as character recognition and process chemometrics. A key requirement for all analytical algorithms, however, is calibration models and calibration sets that are well chosen.

The methods of multi-variate analysis were discussed by Dr. B. M. Wise (Pacific Northwest Labs). A key problem in sensor instrumentation is correctly compensating for drift and interfering signals from species other than the target analyte. It was noted that 0th order (single sensor) instruments are unable to detect drift or interfering signals ; 1st order (array sensors) instruments can detect drift and interfering signals , but cannot compensate mathematically; and with 2nd order instruments multi-variate analysis can correct mathematically for the effects of drift and interfering signals . Examples where second order instrumentation is used include combined gas chromatograph-mass spectrometer analytical techniques and combined liquid chromatography-infrared spectroscopic systems. Mathematical techniques used to deconvolute these data to detect drift and interfering signals can also be used in sensors. One example is fiber optic sensors with distal tip membranes, where the analyte diffuses into a membrane. Here the first order is the transport time and second order is response as a function of wavelength. A second example is microfabricated array sensors in which the first order results from varying the materials on each sensor and the second order uses temperature programming to give a matrix of data. It was noted that the multi-variate methods are computationally intensive, which therefore will place demands on instrumentation that uses arrays of gas sensors.

Alternative algorithms for coping with large quantities of data from only partially selective sensors are based on neural networks. Prof. Tom McAvoy (Univ. MD) noted that the nose performs such operations rapidly and can distinguish specific odors from a complex mixture. He has developed models based on a nonlinear chaotic oscillator that operates in an unstable state. When a stimulus is detected, the neurons are "kicked" into a new state. i.e. they jump to a new "strange attractor". This built-in instability gives speed and amplification of the detection process. Computational algorithms that mimic this process are being developed which can use existing sensors.

The need for computational capability interfaced to sensor array architectures is being met with instrumentation of decreasing size and increasing computational power. One method, discussed by Dr. Paul Clifford (Mosaic Industries) incorporates partial least squares data analysis with neural nets, allowing partitioning of the problem into learning and application. This model is incorporated in a small computer which analyzes responses from several Taguchi sensors.

Packaging and Telemetry

Key aspects of gas sensing technology that is often neglected by researchers are the problems of packaging the transducer and sending the signals from the transducer to the user. In automotive applications, the package is usually the most expensive part of the sensor system, due to the requirements for ruggedness in a harsh environment. Sensors for hazardous environments face similar issues. For signal transmission to remote or dangerous locations, radio-frequency transmission methods used in cellular telephone technology are being used, as are fiber optic systems, which provide immunity to electrical noise and can be combined with optical sensors. Remote sensors, for example, that will be used for space applications will require very low power operation and will be interfaced to other solar powered instrumentation. For array sensors that would have hundreds of sensing elements, signal communication will also a problem. Circuitry for multiplexing, controlling, and amplifying sensor signals will have to be integrated in the sensor design.

New Device Technologies

A number of approaches for improving gas sensors are being demonstrated. These approaches can be expected to expand the application areas for sensors.

Optical detection methods continue to advance. Fiber optic sensors exploit the interaction of light which travels down the fiber to interact with the sampled gas at the distal end. Light traveling away from the distel end carries with it spectroscopic information about the sampled environment. Advantages of optical fibers are the long transmission distances possible, enabling the remote sampling of inaccessible or hazardous environments with immunity to electrical interference. Dr. Jacob Wong (Telaire Systems Inc.) discussed an optical sensor which uses nondispersive infrared technique. The gas to be tested is sampled using a sampling chamber which is positioned between an IR source and a detector. Narrow band interference filters are used to achieve selectivity. Multiple sensors can be integrated into a single instrument. The device has been used for smokestack monitoring.

Surface acoustic wave (SAW) devices have long been of interest for use as gas sensing devices. These devices are incorporated into a resonant circuit and operate by measuring the change in resonant frequency when a gas is adsorbed on the device. Chemically selective films are used to provide selective detection of gases. A new development in this technology, described by Dr. James Wiczer (Sandia), takes advantage of the recent advances in creating self-assembled monolayers (SAM) on metallic and semiconducting surfaces. A SAM consists of an ensemble of long chain hydrocarbon molecules, in which one end of each molecule is designed to bond strongly to the substrate and the other end is tailored to produce a desired surface property. For example, thiol molecules have a sulfur group at one end which bonds strongly to gold. For sensor applications, the surface end group can be designed to be selective to the species of interest. The work at Sandia has involved the development of sensors for chemical warfare agents with a sensitivity of 100 ppb using a carboxy terminated long chain alkyl with a Cu^{2+} chelating agent. Differential measurements between a chemically selective SAW and a blank SAW are used to enhance sensitivity and compensate for drift. The sensors can be fabricated into arrays. For array devices, a method for patterning SAMs is required. Dr. Michael Tarlov (NIST) described a new patterning method for SAMs. Ultraviolet irradiation is used to photooxidize an exposed thiol region to create thiolate ions which can then be replaced in solution of another thiol with different chemical selectivity.

SAMs are one example of new materials systems being used for sensors. Other new materials which may find use in gas sensors include fullerenes, mixed semiconducting oxides, zeolites, sol gels, conducting polymers, and chemically selective membrane materials. Dr. Steve Semancik (NIST) described work at NIST to produce epitaxial semiconducting oxide films which could be used in Taguchi type sensors. Inhomogeneities in microstructure and orientation in polycrystalline-based sensors may be responsible for drift and slow response times in these devices. The atomically smooth, single-orientation epitaxial films may result in faster, more reliable sensors.

The invention of scanning tunneling microscopy has spawned the creation of many transducing instruments with position-sensitive detection at the sub-angstrom level. Dr. Gregory E. Poirier (NIST) discussed the possiblities for using this position sensitivity to create a gas partial pressure-mechanical displacement transducer. Micro-machined physical sensors (such as accelerometers) based on tunneling are being developed by Dr. William J. Kaiser et al. at JPL (Jet Propulsion Laboratory). There is also work to create micro-machined tunneling instruments in Prof. Noel MacDonald's group at Cornell University. Technological challenges for this approach include the development of chemically selective films that will alter the distance between the film and the tunneling tip, and vibration isolation.

Commercialization and Standards Issues

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Commercialization and standards issues related to sensor technology development involve both private sector and governmental activities. The private sector is largely responsible for development and evolution of commercial products. Federal government efforts impact the commercialization process through standards and regulations , Cooperative Research and Development Agreements, and licensing of government-owned technology, i.e., patents.

Commercialization - The Government Role

Government supports sensor technology development and commercialization through its research and development activities, patent licensing, and cooperative research efforts with private industry. The patent process is the only way government can protect intellectual property developed by government institutions. Government research efforts support generic sensor technology and attempt to transfer such technology to the U. S. private sector. As a result of their research activities, governmental agencies hold patents. These may be licensed by U.S. companies. The conditions of the license are negotiated for each agreement. NIST actively seeks to license technology patented by NIST research efforts through its Office of Technology Commercialization. Other government agencies pursue similar programs.

U. S. industry can utilize government research and development expertise in several ways. Agreements between individual government laboratories and private sector firms are a primary method used. This is facilitated through cooperative research and development agreements (CRADAs). CRADAs provide protection of both intellectual property developed during collaborative efforts and propriety information that may be divulged to the government. On a larger scale, consortia of private firms may interact with government laboratories in joint efforts that involve industry-wide issues. NIST and other government agencies encourage CRADAs and consortia for effective technology transfer methods of government research and development efforts. Additionally, various mechanisms are in place that provide access to government research capabilities by the private sector. At NIST these include both formal and informal agreements where NIST staff and staff of private companies perform collaborative research efforts. Formal agreements include Guest Researcher agreements, where an employee of a private sector firm would work at NIST in a collaborative effort with NIST staff. Recently NIST has established a mechanism where NIST staff are encouraged to spend up to a year's time at a private sector company working on a collaborative effort. Informal contacts are an important way in which NIST and other government laboratories work together on topics of mutual interest.

Commercialization - The Private Sector Role

The private sector brings sensor technology to market engaging in the spectrum of associated business activities. It protects that technology through use of the patent process where possible. Identification and determination of technologies with good potential for commercialization is a critical phase of the development cycle. In bringing sensor technologies to market a variety of issues must be addressed to make such efforts successful.

Standardization

Standardization efforts in the U.S. are led by private industry through several organizations, e.g., ANSI (The American National Standards Institute), ASTM (American Society for Testing, and Materials), ISA (Instrument Society of America), NEMA (National Electrical Manufacturers Association). ANSI bears the responsibility for coordination of U.S. standardization activities internationally. Government supports these efforts in the following ways:

- Acts as a neutral third party in technology assessment to evaluate performance claims.
- Provides measurement standards that support uniformity in measurements, both nationally and internationally.
- Participates in international standards activities by facilitating communication between participants, particularly where direct government-to-government interactions are helpful. This becomes an important function in those cases where standardization activities of other nations are the province of the national government. Such efforts are generally undertaken in partnership with ANSI.

An important aspect of participation in standardization activities is addressing non-tariff trade barrier issues in international commerce. These barriers, at times, take the form of standards compliance as a requirement for access to markets outside the U. S. The impact of such trade barriers on measurement-related technology has become more important in recent years. In addition, standardization activities may provide a forum for information exchange on a variety of related topics.

Discussion Topics

Discussion during the session involved a number of issues confronting both users and developers of sensor technology products. Several categories of concerns were identified during the discussions. These are given below and include various comments from workshop participants.

- *International Standards:* particularly in the European Economic Community (EEC), impact not only suppliers of measurement and sensor equipment, but also users of that equipment. Efforts of various U.S. standards bodies were identified as being pertinent. Concerns were raised that results from on-going activities should be freely available because their impact could be significant.

- *Performance of Measuring Instruments*: both short and long term. It was suggested that performance testing by NIST would be of use to the user community. (NIST staff noted that NIST, and NBS before it, has avoided this type of testing due to the potential for implied product endorsement.) Several in the user community noted that some of the round robin testing sponsored by private testing organizations was much too slow in reporting results.

- *Regulatory Compliance for Measuring Instruments:* Discussion focussed primarily on regulatory requirements for environmental emission measuring instruments. Issues not directly related to sensing were the driving force. Participants were especially concerned with requirements by various government agencies (federal/state/local) for reporting of results, and the potential for differing interpretations resulting in disputes between regulatory agencies and private sector users.

- *Risks in Commercialization:* Utility of marketing surveys and identification of sensing applications categorized by the manufacturing sector was desired. Discussion of this topic left unresolved the identification of an entity to perform this task.

- *Installation/Use Protocols and Requirements:* The requirements for installation in many user facilities, particularly manufacturing plants of significant size, are not well recognized by the sensor manufacturing community. This is particularly the case for small instrumentation companies because they do not usually have ready access to the knowledge. At one point in the discussion, a representative of a major chemical manufacturer noted that the cost of installation of a single instrument in a plant approached $60,000. Issues relating to safety requirements are usually not well understood by smaller instrumentation developers. It was suggested that a method be developed to address these areas. This would also be advantageous to the user community because much of the innovation in sensing/measurement technology is currently found in the small instrumentation companies.

V. Appendices

Appendix A —Final Program

NIST Workshop on Gas Sensors: Strategies for Future Technologies

National Institute of Standards and Technology
Gaithersburg, Maryland
September 8-9, 1993

All meetings will be held in the Green Auditorium of Building 101 at NIST, except as noted.

Wednesday, September 8, 1993

8:00 am - 8:30 am	On-site check-in/coffee
8:30 am - 12:40 pm	Morning Session Moderator: Dr. Steve Semancik Process Measurements Division, NIST Welcoming Remarks Dr. Hratch Semerjian, Director Chemical Science and Technology Laboratory, NIST Invited Presentations
8:50 am - 9:30 am	Solid State Gas Sensors: World Markets and New Approaches for Gas Sensing Dr. Marc Madou Microfabrication Applications
9:30 am - 10:00 am	Gas Sensing for Industrial Safety and Health Dr. Alan Schneider Mine Safety Appliances
10:00 am - 10:30 am	Gas Sensing Needs of the Environmental Protection Agency Mr. David Friedman Environmental Protection Agency
10:30 am - 10:50 am	Break
10:50 am - 11:20 am	Present and Future Gas Sensors for Automobiles Mr. Joseph Giachino Ford Motor Company
11:20 am - 11:50 am	Gas Sensor Needs and Technology at the Department of Energy Dr. Glenn Bastiaans Iowa State University

11:50 am - 12:20 pm	Thermal Microsensors for Environmental and Industrial Control Dr. Ulrich Bonne Honeywell
12:20 pm - 12:40 pm	• Introduction of Breakout and Discussion Session Chairpersons • Breakout Group Sign-up • Survey Material Distribution
12:40 pm - 1:30 pm	Lunch
1:30 pm - 5:00 pm	Afternoon Session Moderator: Dr. Kenneth Kreider Process Measurements Division, NIST
1:30 pm - 2:00 pm	NIST Advanced Technology Program Dr. Stanley Abramowitz ATP Program
2:00 pm - 2:30 pm	NIST Facilities and Programs in Gas Sensing Dr. James Whetstone, Dr. Steve Semancik Process Measurements Division, NIST
2:30 pm - 4:00 pm	Technical Poster Session (with refreshments) Employees' Lounge
	Invited Presentations (continued)
4:00 pm - 4:30 pm	Gas Sensor Technologies at Sandia National Laboratory Dr. Robert Hughes Sandia National Laboratory
4:30 pm - 5:00 pm	Microchemical Sensing with Temperature Programmed Methods Dr. Kensall Wise, Dr. John Gland University of Michigan
5:15 pm	Bus to Gaithersburg Hilton
6:00 pm	Product Poster Session (with cash bar) Gaithersburg Hilton
7:00 pm	Dinner at the Gaithersburg Hilton

Thursday, September 9, 1993

8:20 am - 12:40 pm	Morning Session Moderator: Dr. Richard Cavicchi Process Measurements Division, NIST
8:20 am - 8:40 am	Instructions for Breakout Groups
	Invited Presentations (continued)
8:40 am - 9:10 am	Amperometric Electrochemical Gas Sensors Dr. Joseph Stetter Transducers Research, Inc.
9:10 am - 9:40 am	Gas Sensors in the Chemical Industry: Today's Practiced Technology Dr. Kevin Hool Dow Chemical Company
9:40 am - 10:10 am	Development of Differential Mode and Solid Electrolyte Gas Sensors Dr. Chung-Chiun Liu Case Western Reserve University
10:10 am - 10:30 am	Break
10:30 am - 12:40 pm	Breakout Group Meetings (rooms assigned at 8:20 am)
	A. Process Control in Manufacturing Chair: Dr. John Steichen, Dupont Co-Chair: Dr. Gary Kramer, NIST
	B. Indoor Air Quality and Personal Safety Chair: Mr. Jarrell Wenger, Johnson Controls Co-Chair: Dr. Andrew Persily, NIST
	C. Outdoor Environmental Monitoring and Site Remediation Chair: Dr. Barry Wise, Batelle Pacific Northwest Laboratories Co-Chair: Dr. Frank Guenther, NIST
	D. Automotive and Other Transportation Chair: Dr. Galen Fisher, General Motors Research Laboratories Co-Chair: Dr. Kenneth Kreider, NIST
12:40 pm - 1:30 pm	Lunch

1:30 pm - 4:20 pm	Afternoon Session Moderator: Dr. Gregory Rosasco, Chief Process Measurements Division, NIST
1:30 pm - 2:30 pm	Reports on Breakout Groups Breakout Chairpersons of Groups A, B, C and D
	Discussion
2:30 pm - 3:40 pm	• The Role of Emerging Technologies in Gas Sensing Co-Chairs: Dr. Steve Semancik and Dr. Richard Cavicchi, Process Measurements Division, NIST
3:40 pm - 4:20 pm	• Commercialization and Standards Issues Co-Chairs: Mr. William Lyndon, Office of Technology Commercialization, NIST and Dr. James Whetstone, Process Measurements Division, NIST
4:00 pm - 5:00 pm	Lab Tours (see sign-up sheets)
4:20 pm - 5:00 pm	Executive Meetings for Breakout and Discussion Chairpersons

Appendix B —Participants List

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September 8-9, 1993
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Appendix C —Laboratory Stops

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1. Sensor Surface Processes Process Sensing Group, CSTL Bldg. 221, A-310	S. Semancik
2. Ultrathin Film Deposition Process Sensing Group, CSTL Bldg. 221, A-314	R. Cavicchi
3. IC Compatible Processing IC Technology Group, EEEL Bldg. 225, B-365	J. Suehle
4. Calibration Gas Standards Gas Metrology Group, CSTL Bldg. 222, B-332	W. Dorko
5. Humidity Calibration Process Sensing Group, CSTL Bldg. 221, B-353	P. Huang G. Scace
6. Fiber Optic Waveguides Sensors and Automation Group, CSTL Bldg. 222, A-332	S. Choquette L. Brown
7. Field Monitoring of Indoor Air Quality Indoor Air Quality and Ventilation Group, BFRL Bldg. 226, A-312	A. Persily
8. Large Scale Fire Test Facility Large Fire Research Group, BFRL Bldg 205*	E. Braun W. Grosshandler

* transportation required

Appendix D —Advanced Technology Program

Advanced Technology Program

U.S. Department of Commerce

Technology Administration

National Institute of Standards and Technology

Overview

Begun in 1990, the Advanced Technology Program at the National Institute of Standards and Technology invests directly in the nation's economic growth by working with industry to develop innovative technologies with strong commercial potential—technologies which, if successful, would enable novel or greatly improved products and services for the world market.

The ATP concentrates on promising, but high-risk, enabling technologies that can form the basis for new and improved products, manufacturing processes, and services. It accelerates technologies that, because they are risky, are unlikely to be developed in time to compete in rapidly changing world markets without such a partnership of industry and government. It does not fund product development.

Essential Features

The unique mission of the ATP—support for civilian technologies in the nation's economic interest—requires some special features, which have become hallmarks of the ATP and major factors in its success.

The ATP has a broad mission to promote large economic benefits for the nation.

The legislative mandate of the ATP is to promote "commercializing new scientific discoveries rapidly" and "refining manufacturing practices." This offers tremendous scope. The objective of some projects is to develop technologies that enable lower cost, higher quality, or faster-to-market products. The ultimate objective of others is to develop the know-how to provide new-to-the-world or radically improved products and services. The ATP has a high potential impact on U.S. economic growth because, unlike other federal technology programs, it makes investments explicitly for this reason rather than for some other national goal.

The ATP works as a partner with industry.

While government provides the catalyst, industry *conceives, partially funds, and executes* ATP projects. Management of projects is geared to ensure that the work performed is what industry believes should be done and is what it can do best.

The ATP relies on the substantial involvement of industry to define and implement its R&D programs. ATP research directions are selected based on suggestions from industry and developed in consultation with industry. Specific R&D projects are selected from proposals developed and submitted by industry. All awards are made through announced competitions.

The ATP emphasizes cost sharing—ATP recipients on average pay more than half the total costs of the R&D. This helps ensure that companies have a vested interest in the success of projects and in timely commercialization. At the same time, participation by small companies and start-ups is not precluded, because the single-applicant requirement for cost sharing is that the company cover its indirect costs. Since most start-ups and small companies have low indirect cost rates, this requirement is not prohibitive.

The ATP also takes an active role in helping to ensure the success of the projects it supports. ATP program managers work to build close, cooperative relationships with their counterparts in industry.

Projects are selected on the basis of both technical and business merit through a fair and rigorous competition.

Each proposal is reviewed thoroughly by scientists and engineers expert in the subject area—a common procedure for government technology programs. But ATP proposals that score well in this technical review go on to a *further* evaluation of potential economic impact, evidence of significant commitment to the project on the part of the proposer, and other business-related factors affecting the likelihood that successful results will be commercialized.

The scientific and technical reviewers are primarily federal and academic experts to avoid conflict-of-interest problems and protect proprietary information. Business reviews are conducted primarily by business experts from the private sector who agree to avoid conflicts of interest and abide by non-disclosure requirements. Semifinalists receive in-depth oral reviews. Proposals are ranked according to published selection criteria, and funding is awarded on the basis of the ranking. This merit-based selection process has been fully tested and refined and is essential to the effectiveness of the ATP.

The ATP provides direct support to for-profit companies of all sizes.

Commercial firms know best how to commercialize a promising new technology. With this in mind, the ATP funds for-profit companies. Small, medium, and large companies, and joint ventures led by two or more companies, are eligible for direct funding. Successful ATP project sponsors range in size from start-up companies with a handful of employees to major industrial firms with international scope. Universities, federal laboratories, and non-profit independent research organizations participate in many ATP projects, but as subcontractors or as members of joint ventures (non-profit independent research organizations may *administer* joint ventures).

The ATP has a comprehensive plan for monitoring and evaluating its performance.

From the start, the ATP has strongly embraced program evaluation and considers it critical to the development and operation of a results-oriented, efficiently run program. Early on, an evaluation plan was developed and measurable goals were identified against which to track performance.

ATP Competitions

The ATP conducts competitions each year to select R&D projects for support. Only project proposals submitted in response to a formal competition are considered. (Competitions are announced in the *Federal Register,* in *Commerce Business Daily,* and by direct mail, among other channels.)

Projects are evaluated against a list of criteria, including:

- the scientific and technical merit of the proposal,
- the potential for broad-based economic benefits to the United States,
- the quality of the proposer's plans for eventual commercialization of the technology—the ATP does not fund product development, but the proposer should have plans for capitalizing on a successful project,
- the level of commitment of the proposer and the adequacy of their organizational structure, and
- the experience and qualifications of the proposer.

Since 1994, the bulk of ATP funding has been applied to focused program areas—multiyear efforts of approximately $20 million to

$50 million per year, targeted at specific, well-defined technology and business goals. Often, these involve the parallel development of a suite of interlocking R&D projects. By managing *groups* of projects that complement and reinforce each other, the ATP can have the greatest possible impact on technology and the economy.

In addition to focused program competitions, which are open only to projects relevant to the program topic, the ATP sponsors at least one "general" competition each year, open to all technology areas. Past general competition awards have covered a broad spectrum of technologies in agriculture, biotechnology, microelectronics and electronics manufacturing, machine tools, advanced automotive manufacturing, advanced materials, information and communication technology, chemical processing, and other areas.

Regardless of whether a project is selected as part of a program or a general competition, awards to individual companies are limited to $2 million over 3 years and can be used only for direct R&D costs. Awards to joint ventures can be for up to 5 years, and joint ventures must provide more than 50 percent of the resources for the project.

Industry Input

The process of selecting program areas to focus ATP support is critical to success. Ideas for possible focused program areas come in from all sources, but particularly from industry: individual companies, trade associations, and professional societies. Universities and federal laboratories also have submitted "white papers" proposing possible ATP program areas.

Setting research priorities is a constant, ongoing process, beginning with submission of a program idea. If there appears to be sufficient industry interest in a particular program, the ATP generally hosts a public workshop to discuss and further refine the program concept. Other mechanisms for getting industry's input include:

- advice from senior industry technical and business managers;
- input from industry associations, trade groups, and professional societies; and
- analysis of proposals submitted to ATP in previous competitions.

Since every program has a fixed lifespan, there will be a constant turnover of programs as some are completed and others started.

"PROJECTS" VS. "PROGRAMS"

Make sure you understand the distinction between an ATP *project* and an ATP *program*!

An ATP Program:

- describes a major research direction for the ATP, with technology and business goals that generally involve a broad range of specific technology development tasks;
- may be proposed to the ATP at any time;
- involves multiple projects by single companies and joint ventures;
- provides a framework for one or more ATP competitions to solicit project proposals in support of the program goals—programs are not funded, projects are:
- involves no legal agreements between the proposer(s) and the ATP; and
- involves no proprietary information.

An ATP Project:

- is a specific research project;
- is proposed *only* in response to a formal ATP competition;
- receives ATP funds;
- involves a legal agreement between the proposer(s) and the ATP; and
- generally involves sharing proprietary information (which is legally protected from disclosure) with the ATP.

Each idea for a focused program is evaluated against four key criteria:

- the potential for a significant impact on the U.S. economy, including the credibility of the program's proposed pathways to economic growth, the importance of the existing or potential sector(s) affected, and the probability of subsequent commercialization;
- good technical ideas that are "cutting edge," high-risk, strategically important, and based on sound scientific and technical concepts;
- a strong industry commitment to participate, including breadth and depth of interest and willingness to share costs and to work with the ATP and other partners; and

- an opportunity for the ATP to make a major difference by supporting work that is unique or complementary to other industrial and government efforts, that offers timely and significant acceleration of research progress, and that requires a critical mass of funding that the ATP can provide.

Economic Returns

Early results indicate that the ATP is successfully improving the capability of the nation's businesses to capture economic returns from scientific and technological innovations. Two independent studies of projects funded in FY 1991 revealed substantial, early beneficial impacts on participating companies, including:

- expanded R&D activity, particularly the ability to engage in high-risk, long-term research with high-payoff potential;
- cost and time savings, improved productivity, and other benefits from industry-industry, industry-government, and industry-university collaborations;
- improved competitive standing;
- formation of valuable strategic business alliances;
- improved ability to attract investors;
- assistance in converting from defense to commercial applications; and
- acceleration of technology development, leading to improved market share.

Additional independent studies of the results of early ATP projects are under way.

New Strategies

Since FY 1994, the ATP has worked to reinforce its impact on the U.S. economy with several new strategies:

The ATP is taking a more active role in building cooperative programs among businesses, universities, and government agencies. Because of its global view and broad sources of information, the ATP is in a unique position to spot potentially advantageous alliances and bring them to the attention of its industrial partners. For example, the ATP might bring to the attention of a joint venture an outside company whose proposed work appears to mesh well with that of the joint venture. Or the ATP might suggest a strategic alliance between a single-company applicant proposing to develop a new technology and a potential end user of that technology, if such an alliance would increase the chances of a project's success.

Although the final decisions about such alliances will always lie with the companies, recognizing such opportunities gives the program an additional tool to increase the chances of success for its projects and to exploit promising opportunities that emerge.

The ATP will assist interested companies in planning for future commercialization and in developing linkages with investors. Many of the companies participating in the ATP—particularly small companies—are stronger in their R&D planning and implementation of the R&D plan than they are in their business planning and implementation of that plan. The early-stage, preliminary business plans developed by these companies often lack sufficient detail to provide the clear path to commercialization required by the ATP and may jeopardize many highly promising projects. The ATP will contract with private firms to provide business development support to ATP-funded companies that need such assistance.

The commercialization assistance program will be run initially on a trial basis. Several awardees have expressed interest in working with the pilot program. Its performance will be monitored and evaluated, and, if successful, it will be continued and expanded to serve all companies that wish to participate.

The ATP is intensifying its outreach efforts. While most of the larger technology-oriented companies in the United States are familiar with the ATP, the program is less well known or understood by thousands of small, entrepreneurial companies that play a critical role in technology development and might benefit from its programs. To remedy this, an intensified outreach program has been started to increase awareness of the program. The outreach program will be coordinated closely with state and local economic development organizations that are in a good position to identify small companies that might have an interest in the ATP.

Planning for success. President Clinton has proposed major increases in ATP funding to increase the number of awards made each year and the breadth of cutting-edge technologies covered. The expansion will allow the program to have a truly national impact on economic growth. The program's ultimate success will depend on an expanding relationship with U.S. industry to ensure a steady supply of good technical ideas and willing research partners to transform those ideas into successful new technologies with ATP support.

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Periodical

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