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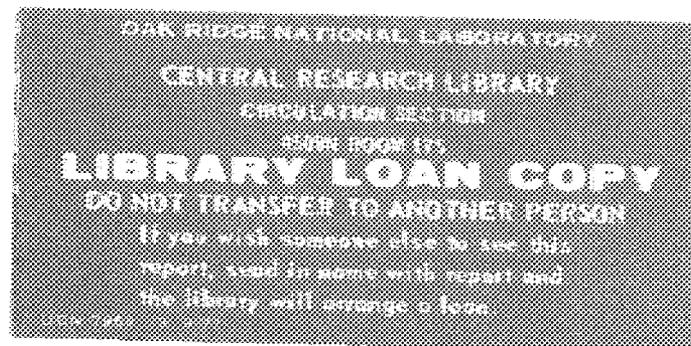


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An Intelligent Thick-Film Gas Sensor: Development and Preliminary Tests

R. J. Lauf
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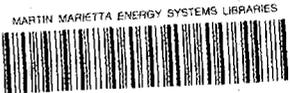
AN INTELLIGENT THICK-FILM GAS SENSOR:
DEVELOPMENT AND PRELIMINARY TESTS

R. J. Lauf
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C. A. Walls

Date Published: May 1987

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CONTENTS

ABSTRACT	1
INTRODUCTION	1
DESIGN AND FABRICATION	6
SUBSTRATE LAYOUT	6
SENSOR MATERIAL	9
INTERCONNECTIONS	14
SENSOR FABRICATION	16
EVALUATION AND TESTING	17
THEORY OF OPERATION	17
TEST APPARATUS	18
TEST RESULTS	21
THERMAL GRADIENT	21
DISTRIBUTED CATALYSTS	31
DUAL-GRADIENT APPROACH	36
FUTURE WORK	36
CONCLUSIONS	36
ACKNOWLEDGMENTS	37
REFERENCES	37

AN INTELLIGENT THICK-FILM GAS SENSOR: DEVELOPMENT AND PRELIMINARY TESTS*

R. J. Lauf, B. S. Hoffheins, and C. A. Walls

ABSTRACT

Thick-film techniques were used to create a gas sensor that has a semiconducting oxide surface whose catalytic activity varies from point to point. An integral heater causes the oxide film to react with combustible gases; the electrical resistance of the oxide film is mapped through an array of electrodes to yield a "signature" that depends on how a particular gas reacts to each of the different areas on the sensor. The catalytic activity can be varied by establishing a thermal gradient across the sensor, by distributing different catalysts in different areas, or by a combination of both effects. For simple cases, the signature can be related to the functional groups present in the gas. As an example, using a uniform distribution of platinum and a thermal gradient, alcohols, ketones, and alkanes have distinctly different signatures.

INTRODUCTION

It is well known that the reversible chemisorption of reactive gases at the surfaces of certain metal oxides can be accompanied by reversible changes in electrical resistance.¹ This effect is attributed to changes in the conduction-band electron concentration caused by charge exchange with the chemisorbed species. Because the resistance change can be large and reasonably linear over many decades of gas partial pressure, much work has been devoted to the creation of sensitive, inexpensive gas sensors and alarms.

A typical commercial gas sensor² (Fig. 1) consists of a small ceramic tube coated with tin(IV) oxide and a suitable catalyst. A heater coil maintains the temperature at 200 to 500°C so that the tin oxide can react

*Research supported by Cabot Corporation under Work For Others contract ERD-85-491 with Martin Marietta Energy Systems, Inc.

with combustible gases. The electrical resistance of the tin oxide is measured between two electrodes at opposite ends of the tube. The entire assembly is packaged in a protective housing with an open area (covered by wire mesh) to allow gases to enter.

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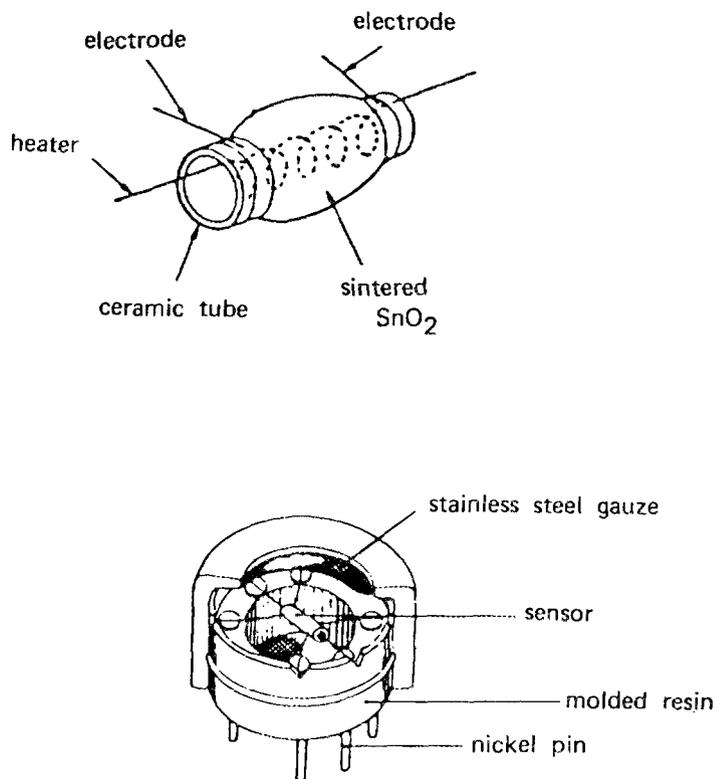


Fig. 1. Design of the Figaro Engineering TGS[™] gas sensor.²

Conventional tin oxide gas sensors as described by Taguchi³ can be made more sensitive to specific gases (e.g., methane or carbon monoxide) by the choice of catalyst applied to the oxide surface. For example, platinum enhances the sensitivity to light hydrocarbons such as butane, whereas palladium increases the sensitivity to hydrogen and carbon monoxide. Figure 2 shows the characteristic responses of two different Figaro gas sensors to various gases. Unfortunately, one can see from the figure that any one sensor cannot distinguish between high concentrations

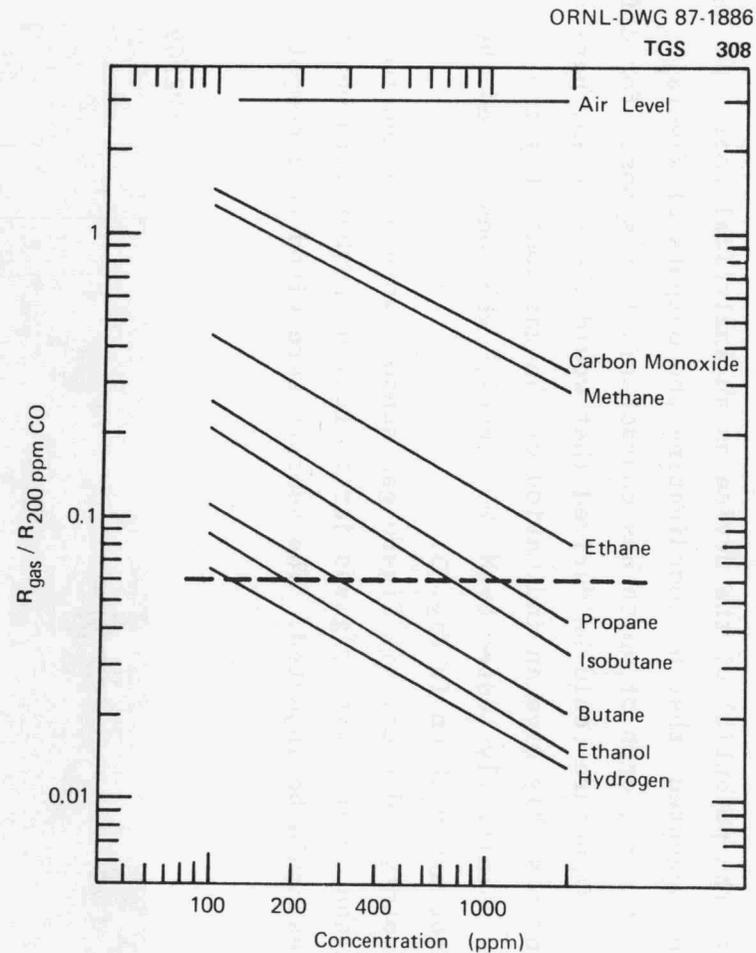
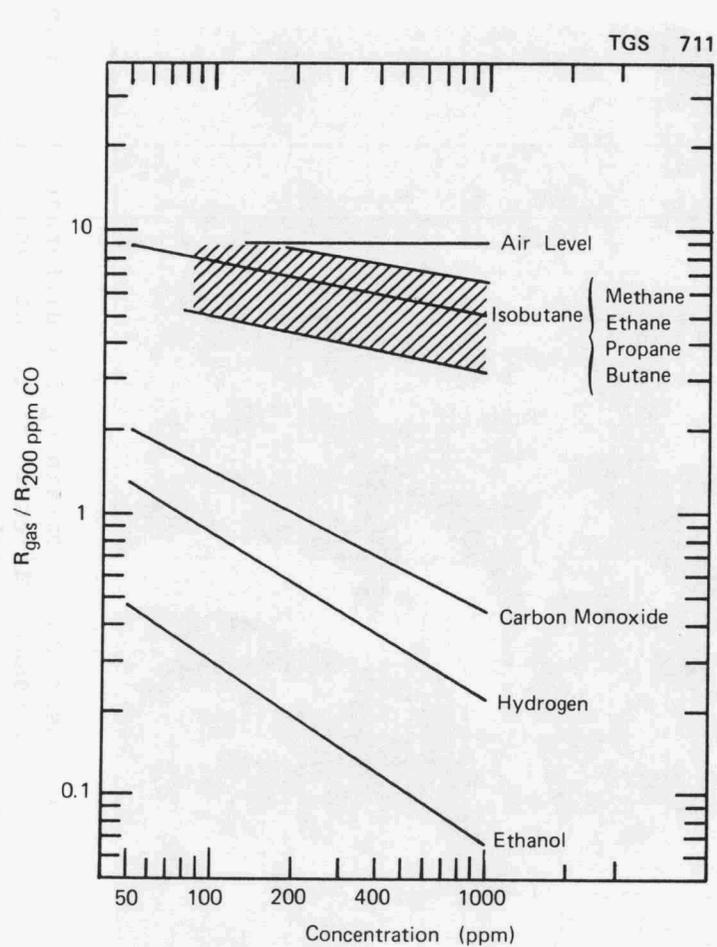


Fig. 2. Characteristic responses of two Figaro TGS™ gas sensors vs concentration of various gases in air. For each case, the sensor's resistance is normalized to its resistance in air containing 200 ppm carbon monoxide. It can be seen that any one sensor exposed to an unknown atmosphere gives a single reading (as an example, the dashed line shown above) that does not contain enough information to determine the identity or concentration of an unknown species.

of a less reactive gas and low concentrations of a more reactive gas. For many applications, this "cross-sensitivity" or lack of selectivity severely limits the potential of the device as an analytical tool. It has therefore been suggested⁴ that by coordinating the outputs of several different gas sensors, each of which has characteristic responses for different gases, a signature could be derived that would identify any particular gas and possibly give an indication of the gas concentration. This concept was initially tested by M. W. Siegel,^{*} who constructed the prototype sensor array shown in Fig. 3.

In the prototype device, six Figaro gas sensors were attached to a bakelite disk and covered with a glass jar to form a chamber into which the gas samples could be injected. The sensors were wired to a computer

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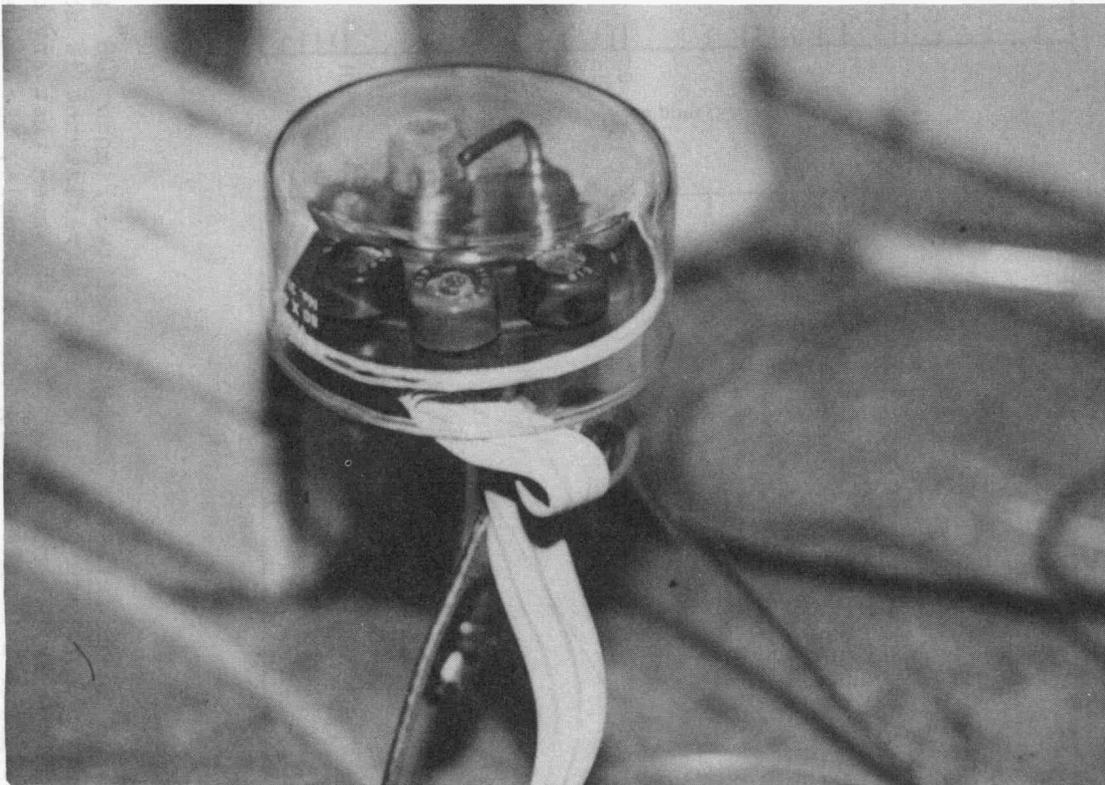


Fig. 3. Prototype sensor array containing six different gas sensing elements whose differential sensitivities to different gases could form the basis of an intelligent system. (Photo courtesy of M. W. Siegel, Carnegie-Mellon University.)

^{*}The Robotics Institute, Carnegie-Mellon University.

interface so that the "signature" of a known gas could be measured and stored for later comparison with the signature of an unknown sample. In its simplest form, the signature would consist of the steady-state resistance of each of the sensors in a constant flow of the test atmosphere. Greater complexity could be introduced by examining the transient response of the sensor array to changes in gas composition, temperature, etc.

A natural outgrowth of this bulky, multisensor device was the idea of integrating many sensors on a single substrate by varying the catalytic properties of the tin oxide layer, either by distributing different catalysts or by varying the temperature in the different reactive regions on the chip. We have achieved a dramatic increase in functional density by using thick-film circuit technology to create an array of closely spaced electrodes on a refractory substrate so that the equivalent of up to 25 different sensors could be fabricated on an area of about 2 cm². The resulting device is a small, intelligent sensing element, the Integrated Gas Analysis and Sensing (IGAS) chip, that plugs into a 20-pin, dual in-line IC socket, but has enough complexity for a microprocessor to resolve the gas responses into unique, identifiable signatures. The chip represents a significant advance in the development of a "smart" chemical sensor. Although conventional thick-film technology was used to develop this new gas sensing device, some of the design requirements dictated the formulation of nontraditional thick-film inks. The thick-film technique is an inexpensive, reliable manufacturing method, which provides much flexibility to accommodate design modifications as development progresses.

This report covers the first year of an ongoing program to conceive, develop, and demonstrate a miniature, intelligent gas sensing element. During this period, hybrid circuit methods have been exploited to produce a functional, rugged, and relatively inexpensive sensor. Several designs were built and tested under steady-state conditions. In a related program, workers at Carnegie-Mellon University (CMU) will study the sensor's response to transient conditions and develop the software needed to apply the sensor to specific analytical problems. The results obtained at CMU will be published elsewhere.

DESIGN AND FABRICATION

The IGAS chip was designed to meet the following requirements:

1. The active area must consist of a semiconducting oxide film [tin oxide (SnO_2), zinc oxide (ZnO), iron oxide (Fe_2O_3), etc.] whose catalytic properties vary from place to place on the surface. The response to various gases should be rapid and reversible and should cover a large dynamic range. The baseline resistance of the oxide film in air should not be too high to conveniently measure (realistically, less than about 10^6 ohms).

2. A large number of electrodes must be arranged so that the electrical responses of all the different areas of the sensor can be quickly mapped by addressing the electrodes in pairs.

3. The interconnection between the electrodes on the chip and the measurement equipment should be rugged, inexpensive, and compatible with standard circuit components.

4. An integral heater must be able to keep the sensor at a sufficiently high temperature for reaction with the sample gases. The heater should be available in either of two configurations, depending on whether a uniform temperature or a thermal gradient is desired.

5. The entire sensor should be stable with respect to thermal cycling and thermal aging. Specifically, mechanical incompatibilities such as poor adhesion to the substrate, spalling, etc. must be avoided.

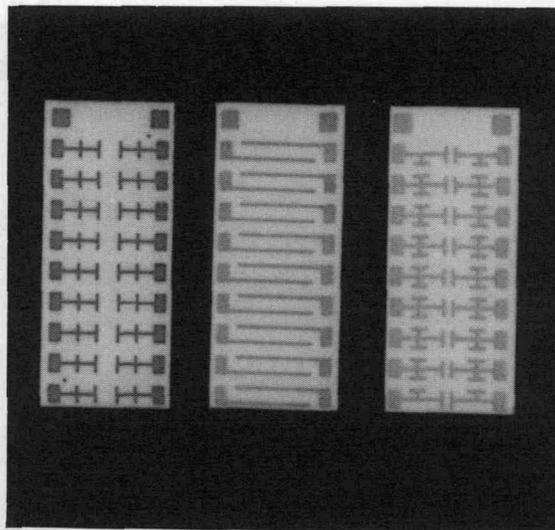
Although the present sensors have evolved with all of these considerations in mind, it is important to remember that the concept is quite general and that many alternative designs can be imagined for specific applications.

SUBSTRATE LAYOUT

Several electrode patterns were used, as shown in Fig. 4. The first pattern (top left) provides for measurement at nine points along the length of the chip by addressing opposite pairs of electrodes. The second pattern (top center) provides for measurement at 17 points, giving potentially greater resolution and a more complex signature. The third

pattern (top right) gives 25 measurement points and is conveniently arranged so that three strips of different sensor materials (e.g., with different catalysts applied) can be laid out along the thermal gradient. In each case, the photo masks were designed so that eight sensors are printed at once on a scored alumina substrate. The conductor material was a commercial gold-palladium frit-bonded thick-film composition, printed and fired according to standard practice.

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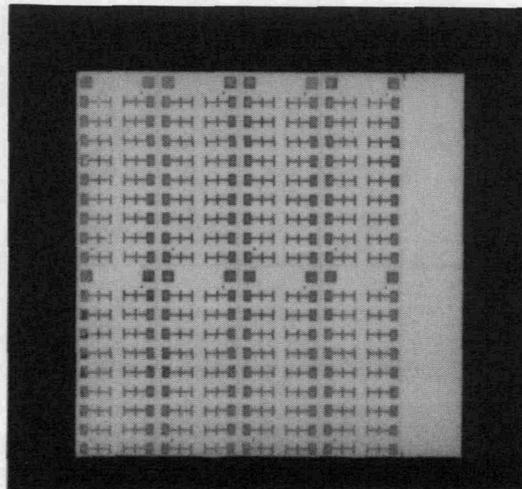


Fig. 4. Electrode patterns developed for the IGAS chip. Top: Three different patterns as described in the text. Bottom: One complete substrate, as printed, having eight individual IGAS chip substrates (approximately actual size).

Heater configurations are shown in Fig. 5. The heater material was a commercial ruthenium oxide (RuO_2) resistor composition. Although the heaters were not originally designed to be used together on the same substrate, the masks for the large heater can be rotated by 180° , allowing power for the large heater to be applied across pins 10 and 11 while power to the small heater is applied across pins 1 and 20. The possible benefit of a two-heater configuration is more precise thermal management and less thermal stress on the small heater.

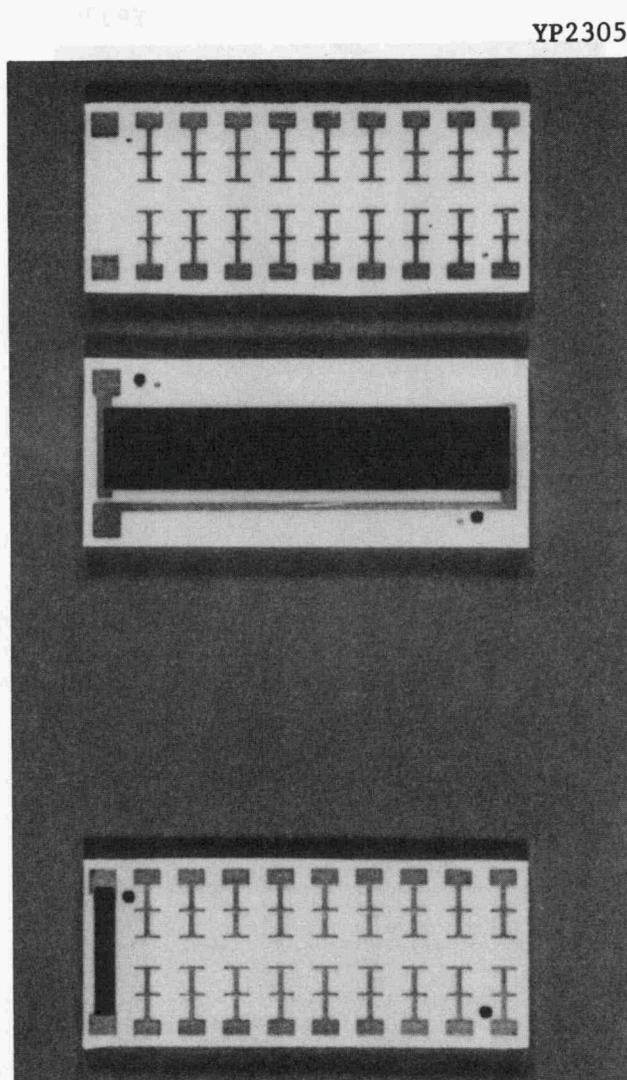


Fig. 5. IGAS substrates showing printed thick-film heaters (black strips). The large resistor (top) heats the chip uniformly, whereas the end resistor (bottom) provides a thermal gradient along the length. In each case, power is applied to the heater through the first pair of electrodes. (The small dots are alignment marks to aid in the printing steps.)

SENSOR MATERIAL

After the electrodes and heaters are fired onto the substrates, the semiconducting oxide layer can be deposited by either of two techniques. One approach involves in situ decomposition of an anhydrous tin chloride/stearic acid mixture. The other method involves the formulation of printable inks that can be applied and fired by traditional thick-film practice.

The stearic acid method, as described by Taguchi,³ involves the following steps. Anhydrous tin(IV) chloride, a clear liquid, was mixed with powdered stearic acid and warmed on a hot plate until the stearic acid dissolved. Upon further heating, the mixture became dark brown. At that point, the mixture was painted on the substrate and fired at 700°C in air. This process had to be repeated several times to build up an adequate film thickness on the substrate. The organic component was intended to be burned off, creating desired porosity in the tin oxide layer. On top of the tin oxide layer, one or more alcohol solutions of precious metal chlorides were then painted on selected areas and fired 5 min at 700°C in air. Films with sheet resistances in the range of 5 to 30 kΩ per square were deposited by this technique.

Figure 6 shows the active layer of one sensor made by this method. The tin oxide has a crenulated surface with a distribution of fine ruthenium catalyst particles. It will be shown later that this type of sensor is fast and quite responsive to many organic compounds. However, the stearic acid method had several important shortcomings. First, it was difficult to control and reproduce in the laboratory (although the technique can, of course, be used reproducibly with specialized manufacturing equipment). The tin oxide layers were not sufficiently uniform, and the stearic acid mixture tended to liquefy readily in the initial firing and partially overlap the heater strip, occasionally rendering the first measurement point on the chip unusable. Second, the strength and adhesion of the tin oxide layer was quite poor, and its initial resistance varied greatly from point to point on the chip.

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Fig. 6. Scanning electron micrograph of TOS-3. A tin oxide layer was deposited by the stearic acid/tin chloride method and fired at 700°C in air. The process was repeated approximately five more times, then the surface was doped with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ /ethanol which was painted on and fired at 700°C in air.

Third, the distribution of catalyst was difficult to control; it is likely that the sensor layer shown in Fig. 6 contains many times more precious metal than necessary.

To overcome these difficulties, it became clear that printable compositions were needed. Our proprietary sensor inks contain three major components: a metal oxide, which is the active agent; glass frit, for adhesion; and organic vehicles that burn off during firing. The catalyst can either be applied after firing, as before, or incorporated directly into the ink.

To conduct a preliminary study of the effect of ink composition and firing parameters, four master inks (SnO_2 , ZnO , Fe_2O_3 and glass) were formulated, as shown in Table 1. The same binder, dispersant, and solvent were used in each, so that the three batches could be blended in any desired proportion. The inks were formulated by the following procedure:

Each powder was milled in isopropanol to produce a fine particle size. The oxide powders were milled in a vibratory mill, in a plastic jar with zirconia medium, to break up agglomerates. The glass was pulverized in a steel mortar, ball-milled 16 h with alumina medium, and screened to -325 mesh ($<44 \mu\text{m}$). The powders were dried in air at 100°C .

Table 1. Thick-film master compositions

	Tin oxide	Zinc oxide	Iron oxide	Glass
Powder, g	47	56	52.4	25
Powder analysis, %	99.9 SnO_2	99.8 ZnO	99 Fe_2O_3	75 SiO_2 12 Na_2O 8 CaO 5 MgO
Binder, g	3.4	5	5	5
Solvent, g	13.5	20	20	20
Dispersant, cm^3	0.5	0.5	0.5	0.12

To maximize the sensitivity, it is important for the oxide layer to be porous. Therefore, we formulated the inks with more organic vehicle than a normal commercial thick-film composition. To achieve a target of about 30 vol % solids in the ink, an amount of solvent equal to twice the theoretical volume of the powder was added along with a small amount of a proprietary dispersant. The mixture was initially quite dry and was therefore blended by hand with a spatula until the dispersant was well

distributed and the mixture became semifluid. The slurry was then liquefied with an ultrasonic dismembrator for 1 min at about 180 W of power.

The binder (a commercial acrylic resin) was added to the liquefied slurry in the form of small beads as supplied by the manufacturer. The mixture was stirred well, covered, and placed in an oven for several hours at 60°C to dissolve the resin completely. Each ink was thoroughly mixed again before each use.

Because of the lower volume fraction of solids, our inks were somewhat less viscous than typical commercial thick-film compositions, but each of the inks had a suitable viscosity range for screen printing onto alumina substrates. They were mixable in all proportions. A trial printing of the glass master composition fused to the substrate after 15 min at 925°C. Higher firing temperatures (950 and 975°C) gave slightly smoother films, indicating greater fusion of the glass frit, as expected.

Tin oxide and zinc oxide inks were each formulated with three different nominal glass contents (11, 20, and 33 vol %, solids basis). These inks were printed on a standard resistor test pattern that included several resistor geometries ranging from 1×1 mm to 1.5×4 mm. The test pieces were leveled, dried, and then fired at 925, 950, and 975°C. Sheet resistivities of the fired tin oxide layers were measured at 125 and 200°C (Table 2). Resistivities of the zinc oxide specimens were measured only at 200°C (Table 3). Because the test pattern contains many sizes and shapes of resistors, we believe that the standard deviations of the sheet resistivities given in Tables 2 and 3 mainly reflect edge effects (such as interactions with the gold electrodes) rather than intrinsic variations in the printed films themselves.⁵ The samples were exposed to acetone vapor as a crude measure of their relative sensitivities. Resistivities changed rapidly and reversibly by as much as a factor of 14. Initial response to the gas took a few seconds and recovery took about a minute.

Table 2. Electrical characteristics of printed tin oxide inks

Glass content (%) ^a	Firing temp. (°C)	Sheet resistivity (MΩ/square) at 125°C	Sensitivity ^b at 125°C	Sheet resistivity (MΩ/square) at 200°C	Sensitivity ^b at 200°C
11	925	8.2 ± 4	1.5	1.7 ± 0.8	1.3
11	950	81 ± 56	3.6	6.5 ± 3	13
11	975	40 ± 12	2.1	13 ± 3	10
20	925	40 ± 14	1.3	5.3 ± 2.6	14
20	950	18 ± 7	1.3	1.6 ± 0.9	2.9
20	975	10 ± 4	1	1.7 ± .6	3.3
33	925	11.9 ± 5.6	1	2.4 ± 1.5	3.1
33	950	27 ± 7	1	1.2 ± 0.5	3.1
33	975	27 ± 7	1	1.6 ± 1	2.9

^aNominal vol % of glass master ink, balance tin oxide master ink.

^bResistivity in air divided by resistivity in acetone vapor, with no catalyst applied.

Table 3. Electrical characteristics of printed zinc oxide inks

Glass content (%) ^a	Firing temperature (°C)	Sheet resistivity (MΩ/square) at 200°C	Sensitivity ^b at 200°C
11	925	36 ± 10	4.0
11	950	0.8 ± 0.4	2.4
11	975	3.1 ± 0.8	1.8
20	925	93 ± 70	12
20	950	1.0 ± 0.15	3
20	975	2.5 ± 2	1.3
33	925	100 ± 49	2.0
33	950	1.7 ± 0.7	1.5
33	975	19 ± 7	1.7

^aNominal vol % of glass master ink, balance zinc oxide master ink.

^bResistivity in air divided by resistivity in acetone vapor, with no catalyst applied.

Figure 7 shows typical examples of our sensor inks printed and fired according to standard practice. Note the improved uniformity as compared with the tin oxide film deposited by the stearic acid method. Note also the fine porosity and correspondingly high surface areas of the printed compositions.

One can see from Tables 2 and 3 that the sheet resistivities of the printed sensors were quite high. The resistivities and sensitivities of the tin oxide samples were strongly temperature dependent, as expected. The tin oxide compositions were generally more responsive to acetone vapor than were the zinc oxide compositions, suggesting that tin oxide has greater intrinsic catalytic properties than zinc oxide with respect to the oxidation of acetone.

Because of the high resistivities of these compositions, the soda-lime glass frit has now been replaced by a more conductive frit. Experiments with these newly developed inks will be reported at a later time.

INTERCONNECTIONS

Connector pins for our substrates are a commercial product, DuPont Connector Systems* 75503-003 pre-plated brass stock, with a tin-lead solder coating. The connectors are supplied on a continuous roll and are designed to clamp onto the edges of the substrate, providing a mechanical bond to supplement the adhesive or solder joint. Initially the pins were joined to the thick-film electrodes with silver-filled polymer adhesives (Ablebond† 943-1 and 71-1). We found that the strength of these adhesives was inadequate to withstand repeated handling of the sensors, and there was evidence of deterioration at the high operating temperatures. As a result, vapor phase soldering was later chosen as the preferred method of attachment.

*Formerly Berg Electronics.

†Ablestik Laboratories, Gardena, California.

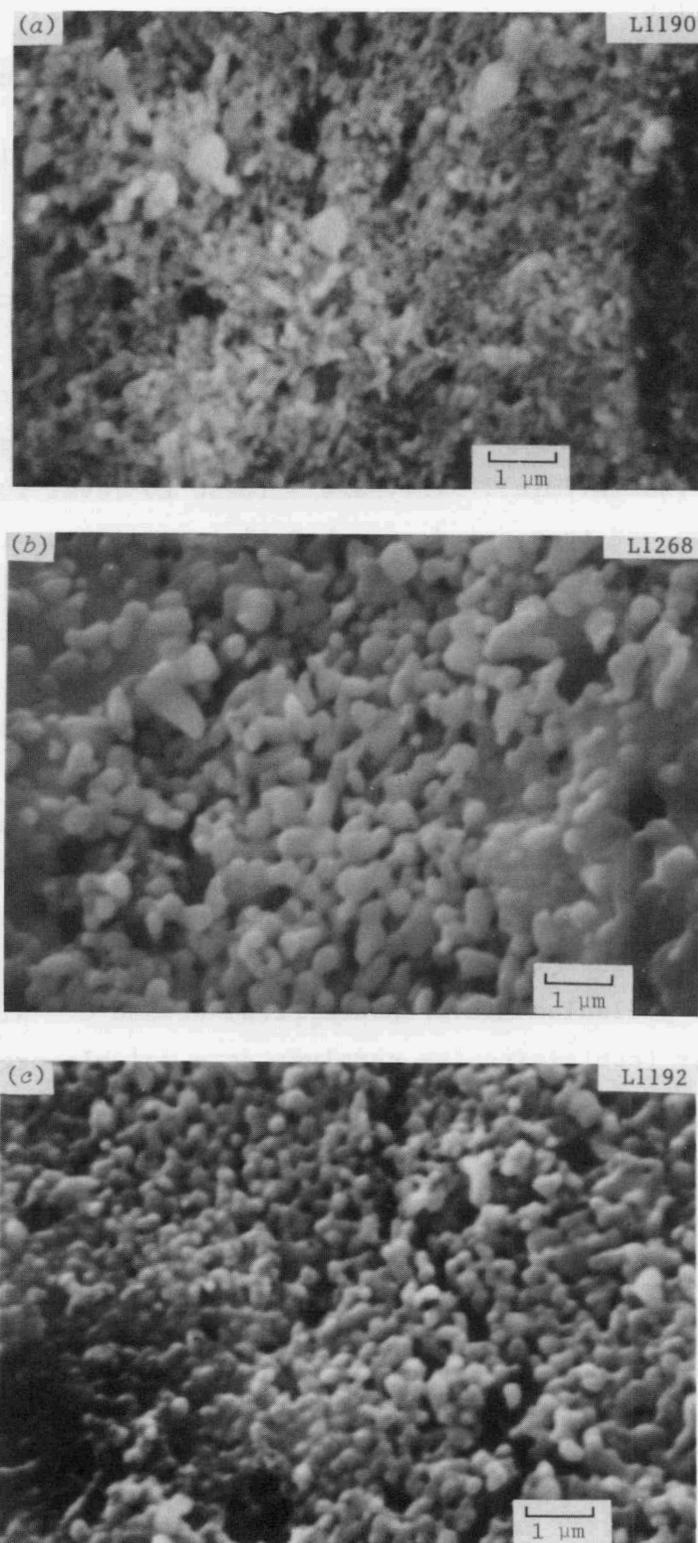


Fig. 7. Scanning electron micrographs of three thick-film sensor materials, screen printed and fired in air at 925°C. (a) SnO_2 + 11% glass. (b) ZnO + 11% glass. (c) Fe_2O_3 + 11% glass.

SENSOR FABRICATION

The entire fabrication process is summarized as follows:

1. Substrates are prepared for printing by boiling in a cleaning solution* for 5 to 10 min.
2. The substrate is placed in the screen printer and aligned with the mask, which is formed on a 200-mesh stainless steel screen. Standoff is adjusted to approximately 1 mm (0.040 in.).
3. Electrodes are printed with DuPont 9910 (gold) or 9985 (platinum/gold) thick-film conductor compositions at a squeegee speed of about 2.8 cm/s (65 in./min). They are allowed to level for 10 min at room temperature and then dried on a hot plate at 100 to 150°C.
4. Firing is done in air using a belt furnace. The speed is set to give about 10 min at a peak temperature of 925°C. Total time in the furnace is about 1 h.
5. Heaters are printed with DuPont 1711 resistor composition, leveled, dried, and fired as in step 4.
6. The liquid tin chloride/stearic acid mixture is brushed on and fired in air at 700°C for 5 min. This process is repeated several times to build up an adequate film thickness. Alcohol solutions of precious metal chloride are then brushed on, dried, and fired in air at 700°C except that the palladium mixtures are fired at 800°C. Alternatively, our proprietary inks (containing the catalyst as a soluble organometallic compound) are printed on and fired as in step 4.
7. Electrode pads are cleaned with a small fiberglass brush.
8. Leads are attached with conductive adhesive (silver-filled polyimide) and baked for 30 min at 150°C followed by 30 min at 275°C. Alternatively, leads are soldered using 63/37 tin-lead solder cream, reflowed by a fluorocarbon vapor-phase soldering unit (temperature of fluid is 216°C).

*Crystal Clean, Aremco Products, Ossining, New York.

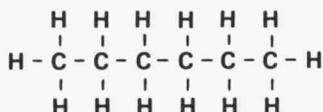
EVALUATION AND TESTING

THEORY OF OPERATION

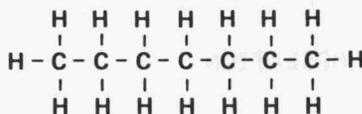
The reactions occurring in the IGAS chip are the same as those in the commercial sensors. The active material, tin oxide or some other semiconducting oxide, becomes reduced by combustible gases, and the resistance of the oxide decreases. When the gas is removed, the active layer is re-oxidized in air and its resistance should increase to its original value in a matter of minutes, depending upon humidity, etc. More information can be extracted from the IGAS sensor than from the conventional tin oxide sensor, however, because of the multisensor effect created in the manufacture of the IGAS chip.

The test program was intended to check the proposition that by varying the catalytic activity of the sensor material in the different areas on the chip, different gases would yield different, recognizable signatures. Several organic compounds were selected for testing, based on the following criteria. First, we need to have a set of molecules with some structural similarities as well as some structural differences, in order to determine the uniqueness of the signatures that each chip develops. Second, the molecules should be relatively simple, so that their behavior with respect to catalytic oxidation can be understood. Third, the compounds should be volatile enough to generate a steady source of vapor at room temperature, should represent important industrial materials, and should be relatively nonhazardous. Seven compounds were chosen for initial work; their structures are shown in Fig. 8. In addition, limited tests were made with water vapor and ammonia.

NORMAL HYDROCARBONS

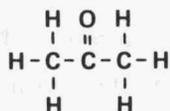


HEXANE

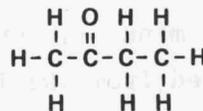


HEPTANE

KETONES

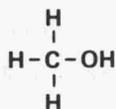


ACETONE

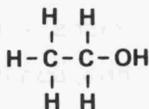


METHYL ETHYL KETONE

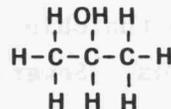
ALCOHOLS



METHANOL



ETHANOL



ISOPROPANOL

Fig. 8. Organic compounds used to test the IGAS chips.

TEST APPARATUS

The test chamber for evaluating steady-state response of IGAS sensor chips to specific gases consists of a glass cell mounted to a glass-ceramic base (Fig. 9). The base supports a 20-pin chip receptacle, which provides two power feed-throughs for the chip's heater and 18 connections to a terminal box to measure the electrical resistance between any two electrodes on the chip. Power is supplied to the heater from a controlled dc power supply.

The top of the glass cell is fitted with a stopper that secures the gas intake and the gas exhaust tubes. The intake tube is bent to the side of the chamber to avoid a direct flow of gas across the chip, which would tend to cool it. This tube opens about 1 cm above the base of the test chamber and provides a slow, diffused flow of the test atmosphere around the chip to the gas exhaust near the top of the chamber.

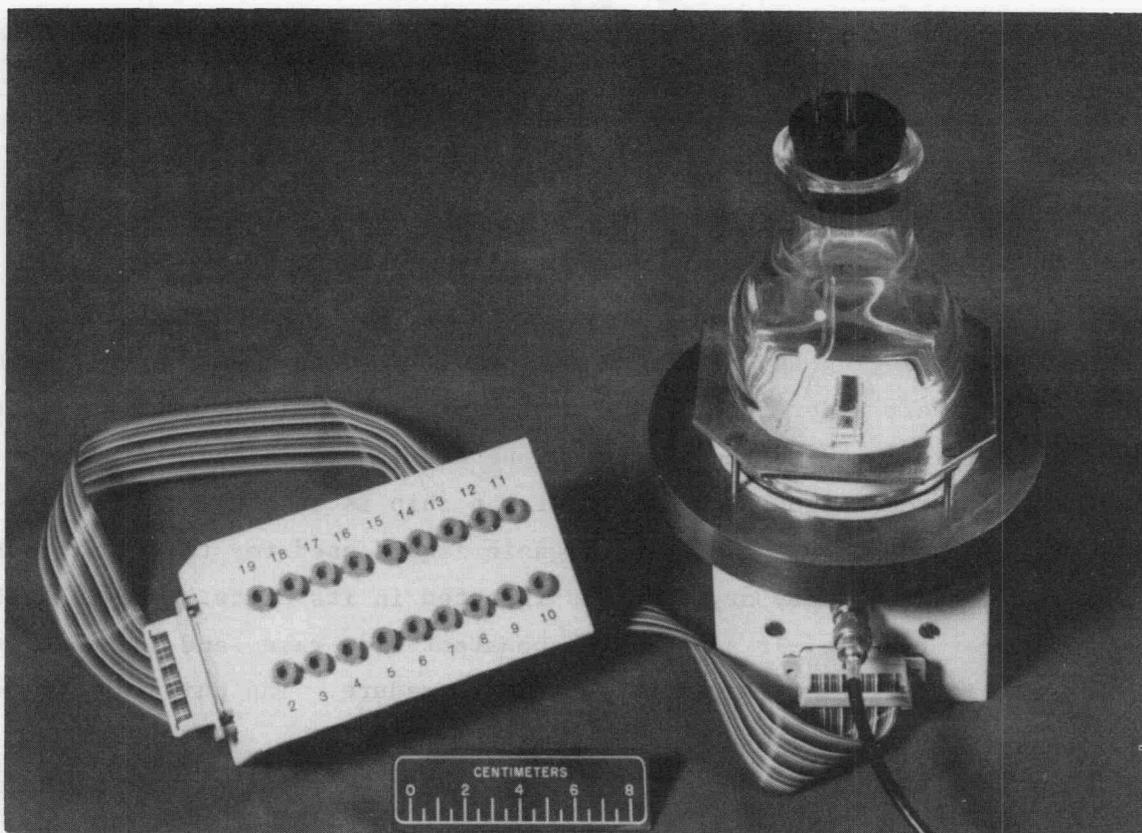


Fig. 9. Test cell for evaluating steady-state response of sensors to particular gases. The electrical box allows us to measure the resistance between any two electrodes on the chip. Power is supplied to the heater through the coaxial cable (lower right) from a controlled dc power supply. Gases from a vapor generator enter through the tube at the top of the flask.

The intake air, which constantly feeds through the chamber during testing, passes through a dry, empty flask to establish the baseline resistance of the different areas of the chip in air. This flask is removed and replaced with one containing a pure organic liquid at room temperature. The air picks up the organic gas that vaporizes from the liquid phase and carries it to the test chamber, exposing the IGAS chip to the test gas.

To begin testing, the IGAS chip is mounted in the test chamber under an air flow rate of 1.1 L/h. A potential of 15 to 20 V is applied to the heater on the chip, and the chip is left overnight to reach thermal equilibrium and come to chemical equilibrium with the air. The electrical resistance of the tin oxide between pairs of opposite electrodes is then measured with a digital ohmmeter by addressing the appropriate points in the terminal box.

Introduction of the test gas to the IGAS chip is accomplished by placing a flask of pure organic liquid in line with the air intake, thereby causing the air to pick up the test gas and transport it to the chip without changing the flow rate of the air into the test chamber. The IGAS chip is left under flowing air with test gas for 5 min to allow it to come to equilibrium with the test atmosphere. The resistance between opposite electrodes along the length of the chip is then measured.

The flask containing the pure organic liquid used for the first test is removed, and an empty dry flask is inserted in its place. The IGAS chip is left under flowing air at the same constant flow rate, and the power to the heater is left on throughout the test procedure. The chip is left for about 30 min to return to equilibrium with air.

The resistances at the various locations on the IGAS chip are measured after this 30 min recovery period, before the next sample gas is introduced and the test procedure is repeated.

The plot of the resistance in the test atmosphere divided by the resistance in air alone, measured between opposite points along the length of the chip, is recorded for each gas tested. These "signatures" are compared to show how well each IGAS chip can differentiate between various similar gases (e.g., alcohols) and between gases of greater diversity (e.g., alcohols vs ketones).

No attempt was made to determine the absolute gas concentrations, but it is likely that relative concentrations reflect the vapor pressure of each species at room temperature.

TEST RESULTS

As mentioned earlier, there are two ways to vary the catalytic activity across the surface of the IGAS chip, namely, by establishing a thermal gradient along the surface or by distributing different catalysts in several different areas.

Thermal Gradient

In some of the sensors, such as that shown in Fig. 10, the heater strip is located at one end to establish a thermal gradient along the length of the chip. The reactivity of a particular gas should dictate how far down the thermal gradient the reaction can occur. For relatively simple organic compounds, the reactivity will be determined by the most active functional group, so that similar compounds (e.g., methanol, ethanol, and isopropanol) would be expected to give similar reactions. To test this hypothesis, sensor TOS-2 was exposed to each of two ketones (acetone and methyl ethyl ketone).

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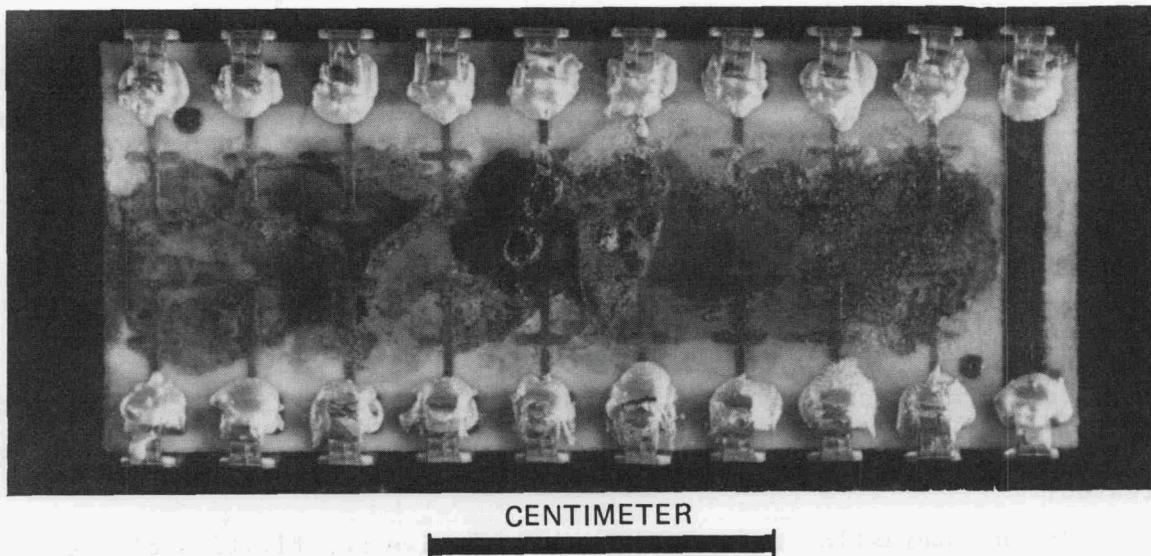


Fig. 10. IGAS chip Model TOS-2, showing thick-film resistor (on left) to provide a thermal gradient along the length of the chip. The active layer, covering most of the surface, consists of tin oxide deposited by the tin chloride-stearic acid method. The platinum catalyst was applied by decomposition of a solution of chloroplatinic acid in ethanol.

In the first set of exposures, the heater was operated at 2.2 W. Then a second set of exposures were made with the heater power at 4.3 W. (At this power level, the temperature across the chip ranged from approximately 160°C at the hot end to about 60°C at the cold end.) Resistances were measured for each exposure between pin pairs across the chip. These were compared with the resistances between the same points in air with the same power applied to the heater. The resistance of the oxide while exposed to each gas divided by the resistance of the oxide in air alone is plotted against distance with temperature decreasing from left to right. Notice that a stronger reaction leads to a smaller value of the resistance ratio. The reaction to each gas decreases toward the cooler end of the chip (Fig. 11).

We observed that, as the absolute temperature is increased on the chip, the shape of the curves for both ketones remains qualitatively the same but the reaction, following the thermal gradient, proceeds farther along the chip, as expected.

To examine the response to different organic compounds, sensor TOS-2 with approximately 2.5 W of applied power was then tested with seven gases: methanol, ethanol, isopropanol, hexane, heptane, acetone, and methyl ethyl ketone (MEK) (Fig. 12). In each case the reaction is strongest at the hot end of the chip, with the most reactive gases being the alcohols (methanol, ethanol, and isopropanol). Note that the alcohol curves are similar in shape and essentially differ only in magnitude of the reaction. The difference in magnitude is probably a concentration effect due to vapor pressure differences. The least reactive compounds were hexane and heptane, which showed a reaction only at the hottest end of the chip. The ketones (acetone and MEK) are slightly more reactive than the alkanes but less reactive than the alcohols. Each gas type forms signatures that are distinctly different from those of the other two types tested.

It is interesting to note that the relative reactivities of the compounds on sensor TOS-2 are in agreement with what we would expect based on the fact that alcohols are more easily oxidized than normal hydrocarbons.

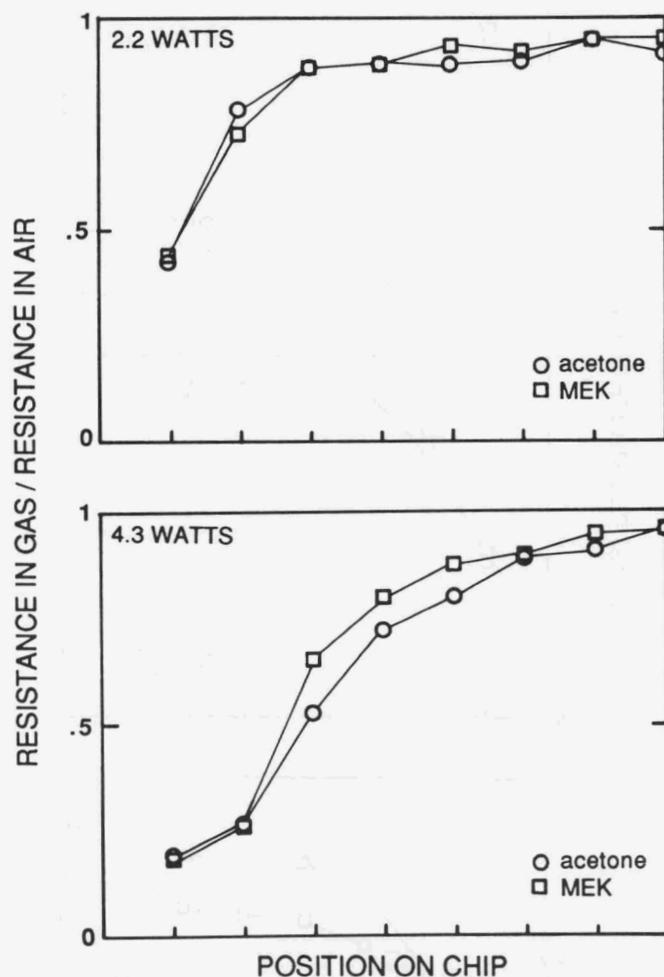
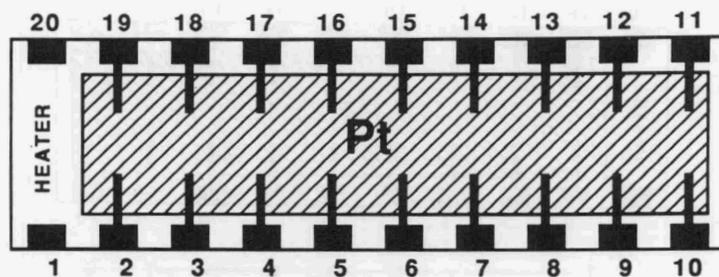


Fig. 11. Response of sensor TOS-2 exposed to acetone and methyl ethyl ketone (MEK). The responses along the length of the sensor indicate that the reaction is more readily catalyzed by platinum at the higher temperatures. As heater power increases, the reaction proceeds farther down the length of the chip. The two ketones show virtually identical temperature dependence, suggesting that the thermal gradient can produce a characteristic "signature" for a particular class of compounds. (Note that the first pair of electrodes could not be used, because the tin oxide layer had overlapped the heater. This difficulty with the stearic acid method is discussed in the text.)

ORNL-DWG 87-1888

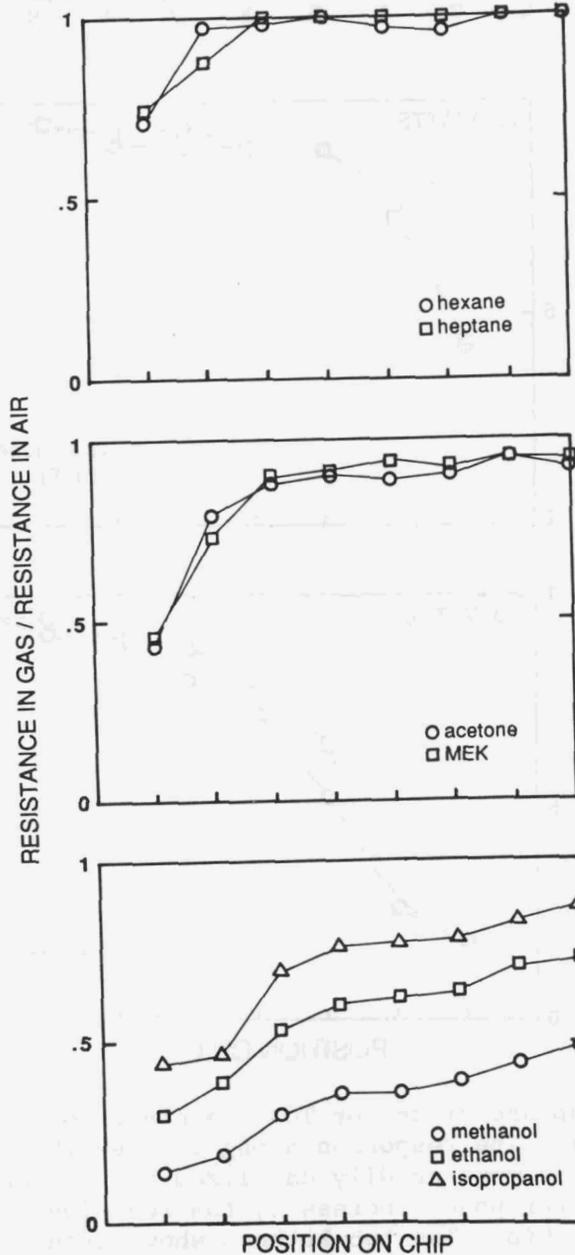
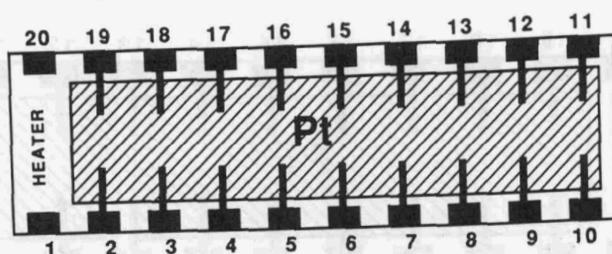


Fig. 12. Response of sensor TOS-2 exposed to seven different gases. Heater power was kept constant at about 2.5 W. Similar compounds have similar signatures, suggesting that the behavior is dominated by the most active functional group on the molecule and is relatively insensitive to chain length.

The interaction of the organic moiety with the catalyst works as follows: A transition metal, by definition, contains unfilled *d* orbitals. The strength of the interaction depends on the amount of electron density the organic species can donate to the metal. Electron donation from sigma bonds is not as facile as donation from lone electron pairs, because sigma bonds are tightly localized between the two nuclei. The normal hydrocarbons contain only sigma bonds, whereas alcohols and ketones contain a lone electron pair on the oxygen atom. Thus, the metal has a higher affinity for oxygen-containing organic compounds. Electron density flows from the oxygen atom to the metal. This is partially compensated by a flow of electrons from the carbon atom to the oxygen. The result is that the carbon-oxygen bond is weakened, which significantly lowers the activation energy for oxidation. Because ketones contain a carbon-oxygen double bond, this bond would be weakened less than the carbon-oxygen single bonds of alcohols. Thus, one would predict that alcohols are more reactive than ketones, and that normal hydrocarbons are least reactive.⁶

Another significant result is that related compounds have very similar signatures, which implies that the hydrocarbon chain length is much less important than the presence of active functional groups such as =CO or -OH.

Sensor TOS-4 had a uniform distribution of ruthenium and a thermal gradient along its length. The active layer on this sensor was made by the stearic acid method. The ruthenium was deposited from a solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol. After firing at 700°C in air, the area doped with catalyst was a blue-gray color. It is possible that the ruthenium was present in a partially oxidized form; the small size of the catalyst particles precluded a definitive analysis. The performance of sensor TOS-4 (Fig. 13) is qualitatively similar to that of TOS-2 discussed earlier. To get good separation of the signatures, TOS-4 was operated with 3.4 W to the heater. The major differences are that the ruthenium-based sensor has a slightly larger response to the alcohols and ketones, due mainly to its higher temperature, but has virtually no response to the alkanes.

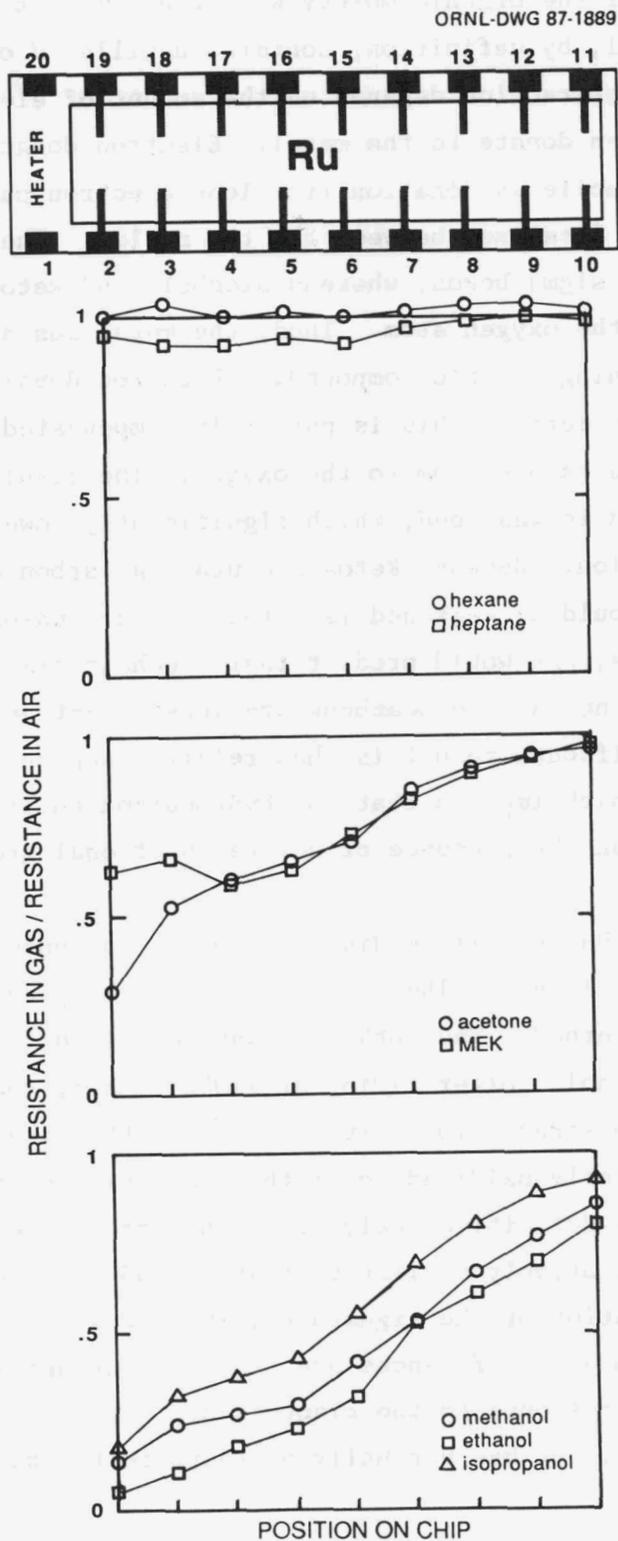


Fig. 13. Response of sensor TOS-4 to seven different gases. Note that there is little or no response to the normal hydrocarbons hexane and heptane. Applied power to the heater was 3.4 W.

Sensor TOS-5, also using a thermal gradient to vary the catalytic activity along its length, had palladium as the catalyst. The tin oxide was again applied by the stearic acid method; the palladium was deposited from a solution of PdCl_2 in acetone, fired in air at 800°C . It is doubtful that the palladium compound was reduced to the metal, because the as-fired sensor had a red-brown color where the catalyst was applied. After testing with the organic vapors, the brown area had become gray at the hot end of the chip (Fig. 14). For the seven gases used in this study, sensor TOS-5 was somewhat less sensitive (Fig. 15) than the two previous units. Naturally, for other gases, such as hydrogen and carbon monoxide, it is possible that the palladium-doped sensor would have a greater response.

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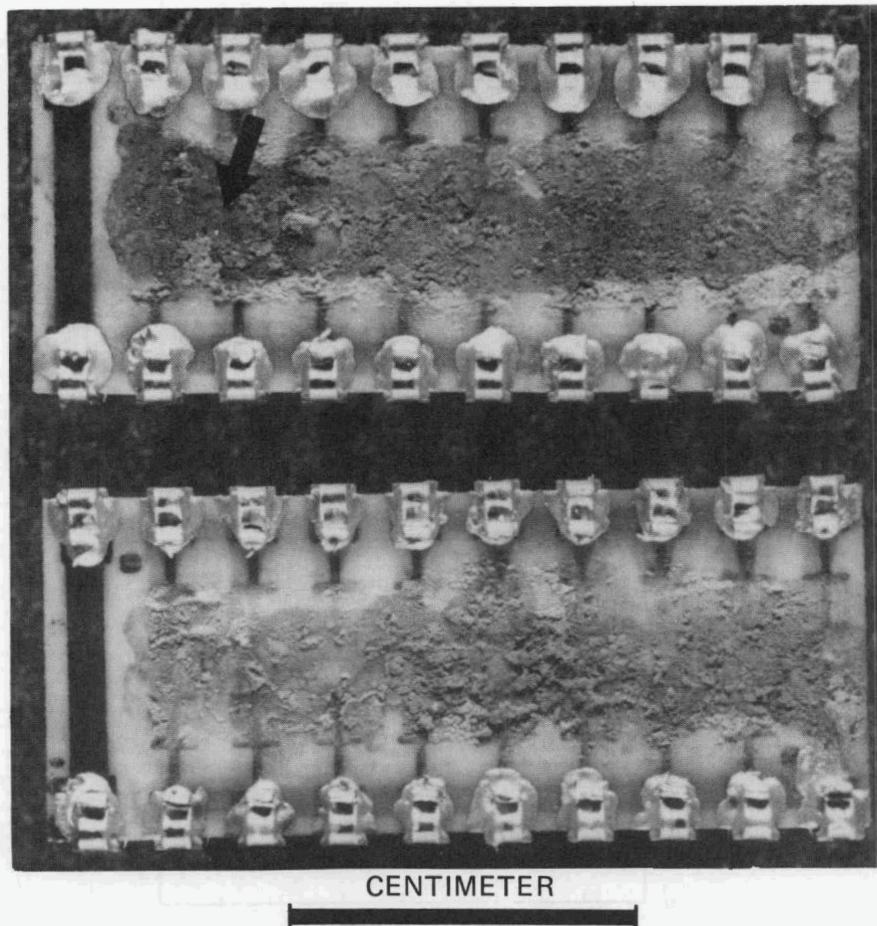


Fig. 14. Sensor TOS-5, showing alteration of the palladium-doped area (presumably caused by reduction of some palladium compound by the test gases). Top: after exposure; note discolored area near heater. Bottom: as-fired sensor.

ORNL-DWG 87-1890

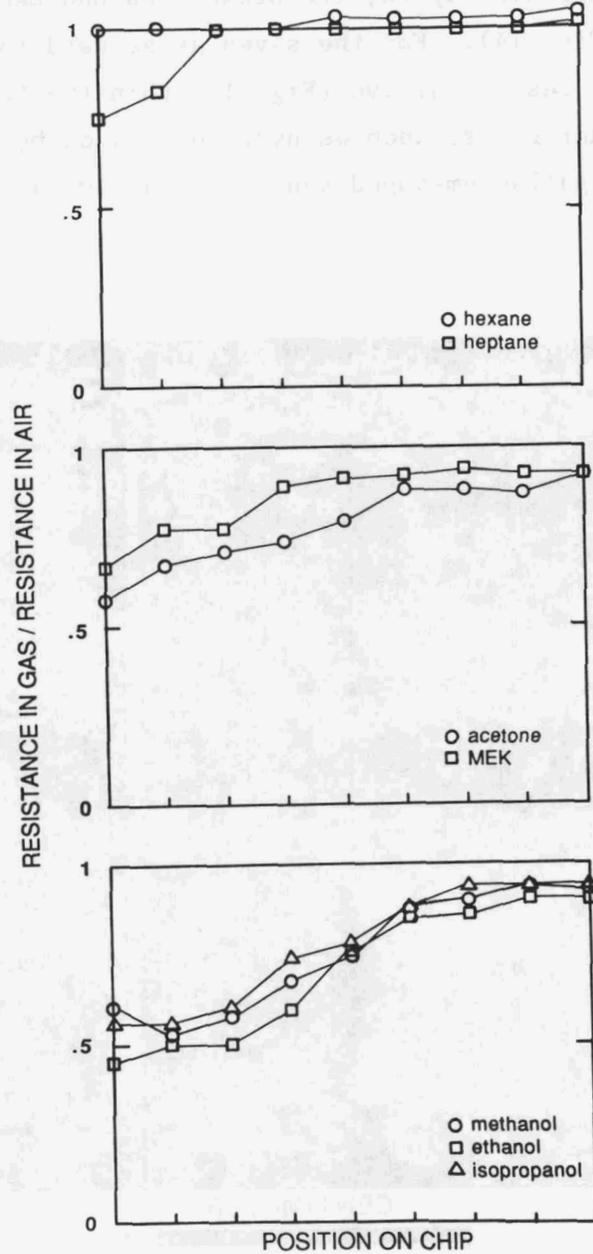
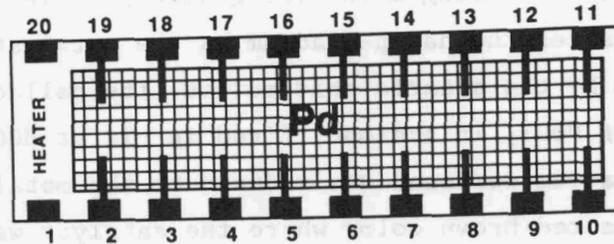


Fig. 15. Response of sensor TOS-5 to the seven test gases. The behavior is qualitatively similar to those of TOS-2 and TOS-4, but the overall response to these particular gases is somewhat weaker. Applied power to the heater was 2.4 W.

Two sensors whose active layers were made by screen printing our original thick-film compositions were also tested. Because of the high resistances of the early compositions, data could only be taken at the hot ends of the sensors. (Recall that the active material is a semiconductor whose conductivity increases strongly with temperature.)

Sensor TOS-9 was made using ink blended from our master inks to achieve a target composition of SnO + 11% glass. Palladium catalyst was added to the ink in the form of palladium resinate solution.* This ink was printed and then fired at 925°C in air. The limited data (Fig. 16) showed a significant difference in the response to ethanol vs hexane.

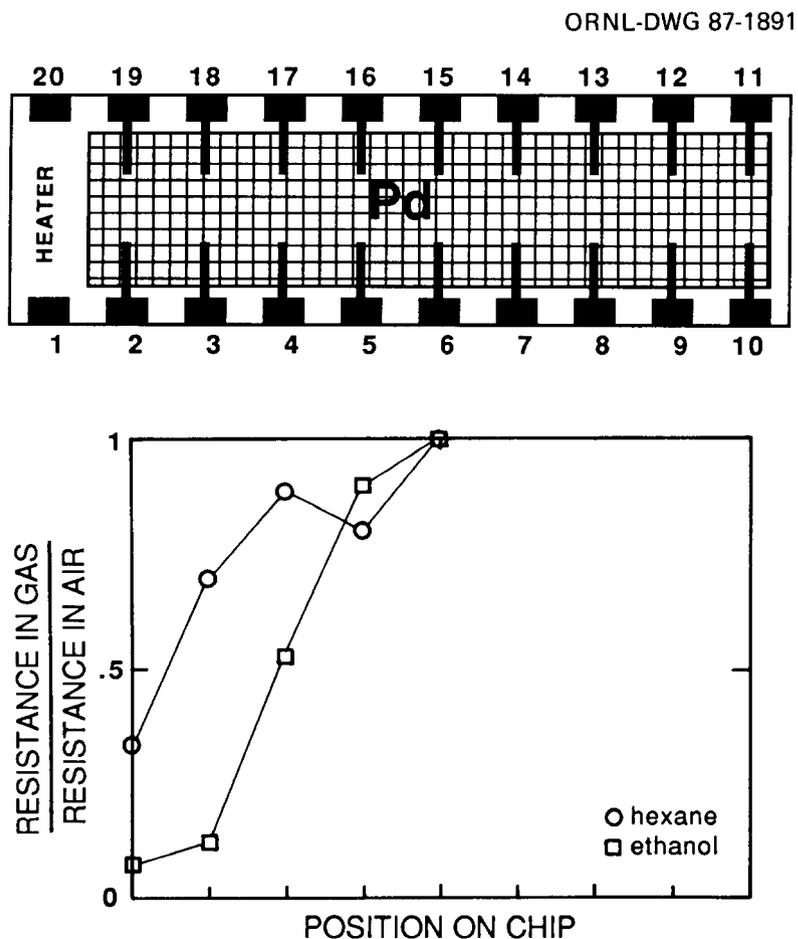


Fig. 16. Response of sensor TOS-9 to ethanol and hexane. The high resistance of the screen-printed oxide precluded measurements at the lower-temperature end of the chip.

*Englehard Specialty Chemicals Division, East Newark, New Jersey.

Sensor FOS-1 was formulated to a target composition of Fe_2O_3 + 11% glass. Platinum catalyst was incorporated into the ink as platinum resinate solution, and the ink was printed and fired as before. The response of sensor FOS-1 to hexane, ethanol, and acetone is shown in Fig. 17. Again, results are limited because of the high sheet resistivity of the early screen-printed sensor materials. Nonetheless, the different compounds have somewhat different responses. It is interesting to note that on this sensor, acetone is more reactive than ethanol, perhaps implying significant catalysis by the iron oxide itself. Sensor FOS-1 demonstrates that our design concept is not limited to sensors based on tin oxide.

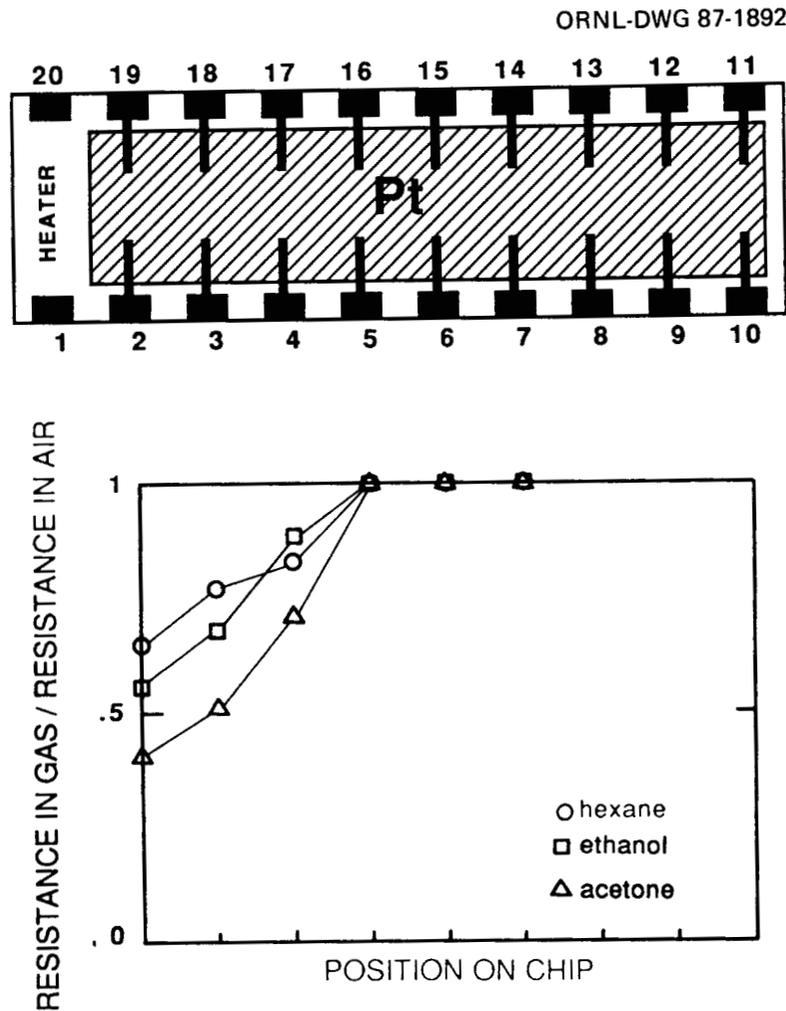


Fig. 17. Response of sensor FOS-1 to hexane, ethanol, and acetone.

Distributed Catalysts

As an alternative to the thermal gradient approach, heat may be distributed uniformly on the chip and the catalytic activity can be altered in different locations by doping the different areas with various catalytic materials. Again, a particular compound will be more reactive to one region than another, depending on how the individual catalysts affect the important functional groups in the gas. Several different sensors were constructed to test the effectiveness of the multicatalyst approach.

Sensor TOS-3 was made by the stearic acid method. It had three different areas, shown schematically in Figs. 18 and 19. One area had platinum catalyst, deposited from H_2PtCl_6 in ethanol; one area had ruthenium, deposited from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in ethanol; and one area had no catalyst added. The response of this sensor to eight gases (the previous seven organics plus ammonia) demonstrated several things: First, platinum is a more effective catalyst than ruthenium with regard to oxidation of the organic compounds studied here. Second, there is some catalysis by the bare tin oxide in the center of the chip. Third, the response increases with temperature (comparing Figs. 18 and 19), and the difference between the areas with and without a noble metal becomes more pronounced. Fourth, ammonia differs from the organics by reacting more strongly in the area catalyzed by ruthenium than in the platinized area. Sensor TOS-6, with three catalysts (Pd, Ru, and Pt) again demonstrated (Fig. 20) that palladium is a very weak catalyst for the alkanes. Alcohols are readily oxidized by all three catalysts. Ketones are intermediate in their reactivity.

Sensor TOS-7 had six catalysts (Pd, Ru, Pt, Rh, Os, and Ir) applied so that there were some areas of overlap. The response of this sensor to each of the test gases (Fig. 21) is consistent with the previous results. Note that osmium and iridium appear to be the weakest catalysts, and in that area of the chip there could be some contribution from the catalytic properties of the tin oxide itself. A test chip with areas of only osmium and iridium and bare tin oxide would be useful to clarify the potency of osmium and iridium, as catalysts in this system.

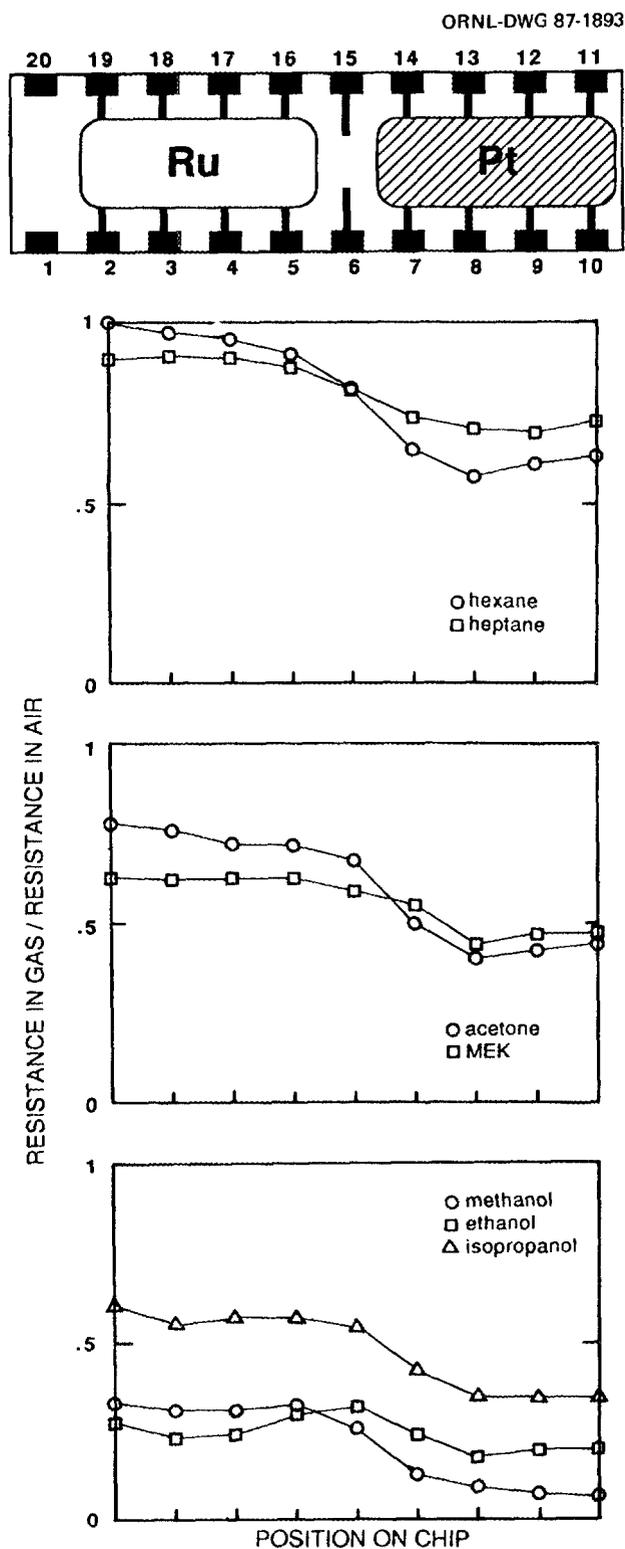


Fig. 18. Response of sensor TOS-3 to seven gases. The sensor was heated uniformly with 2.3 W applied to a large resistor on the underside of the substrate, so the different signatures arise from differences in the way each gas interacts with the separate catalysts.

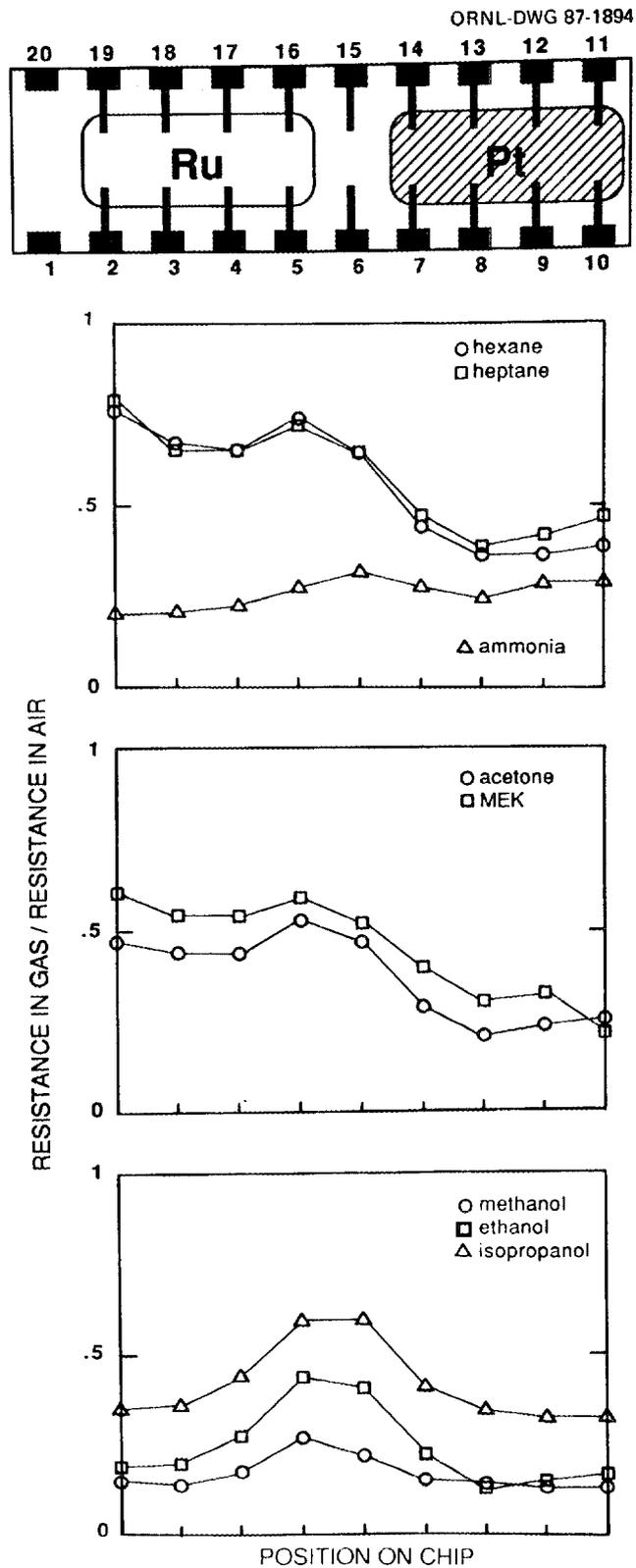


Fig. 19. Response of sensor TOS-3 to eight gases when heater power is increased to about 4.2 W.

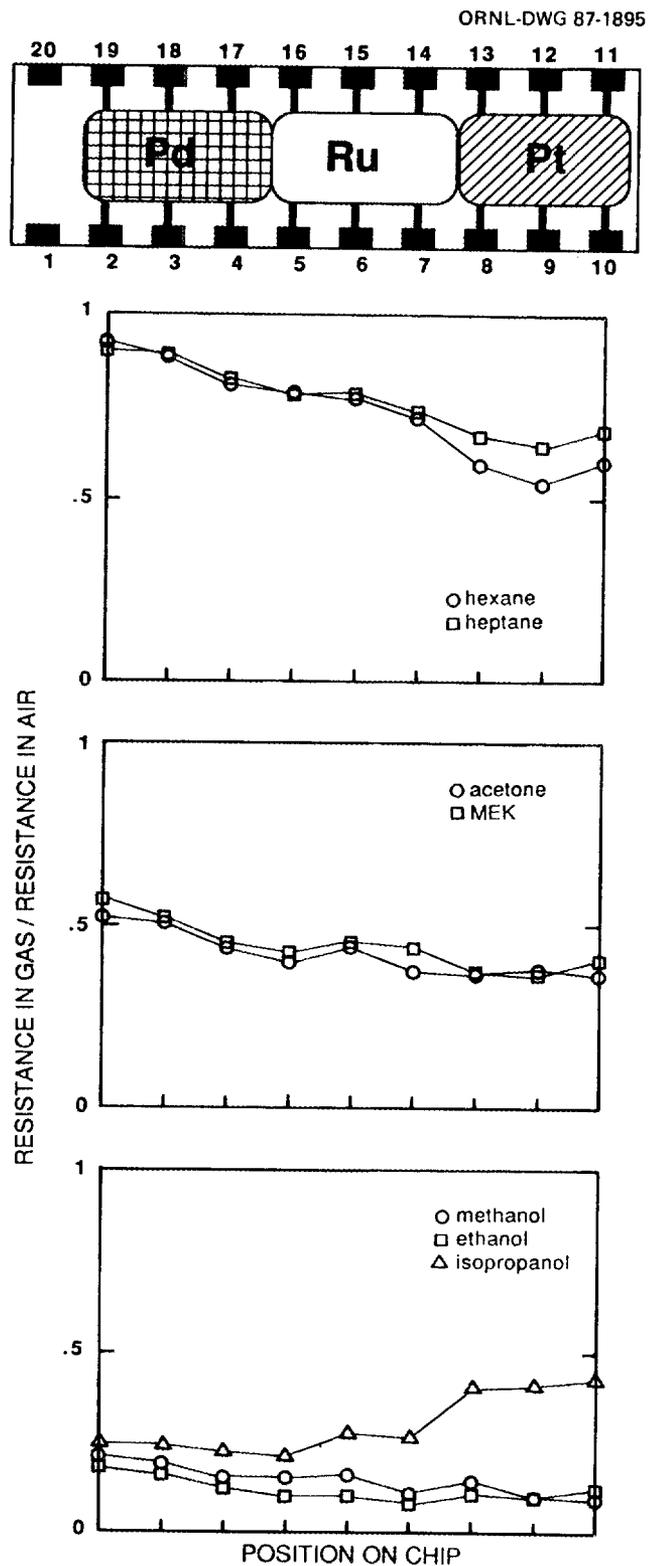


Fig. 20. Response of sensor TOS-6 to seven gases. Heater power was 4.0 W.

ORNL-DWG 87-1896

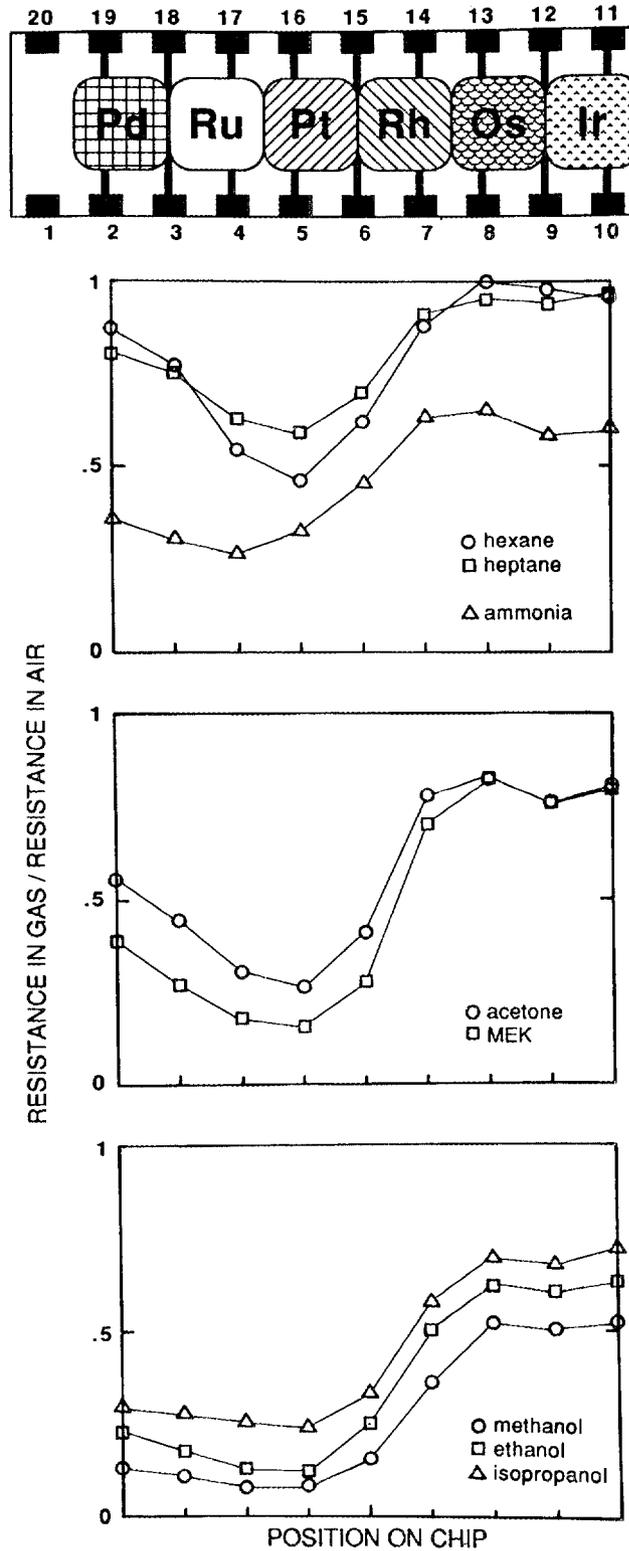


Fig. 21. Response of sensor TOS-7 to eight different gases. Heater power was 3.9 W.

Dual-Gradient Approach

A substrate has been designed and fabricated that will allow us to use distributed catalysts and a thermal gradient on a single chip (see Fig. 4). This design will be tested after the printable sensor materials have been optimized. With variations in both temperature and catalyst distribution, the complexity of the signature is further enhanced, potentially increasing our ability to discriminate between similar gases.

The integrated sensor concept is quite general, and by proper choice of catalysts and thermal gradients, the chip can be tailored to specific classes of gases and control applications.

FUTURE WORK

Further materials work at ORNL will focus on ink development, thermal management, packaging, and long-term stability of the sensing element. Signal processing research at CMU will emphasize the application of artificial intelligence to the collection and interpretation of the sensor output. Dynamic measurements will be performed in an effort to increase the information content by including the time response of the sensor to changes in temperature or gas composition.

CONCLUSIONS

1. A continuous gas sensing film with varying surface catalytic properties can produce electrical signatures that are characteristic of particular gases.
2. Variations in catalytic properties from point to point on the sensor can be achieved by establishing a thermal gradient, by distributing several different catalysts, or both.
3. In sensors examined thus far, the resulting signatures were similar within the functional group, i.e., the ketones exhibited similar responses, which were distinct from those of alcohols and normal hydrocarbons; likewise, the hydrocarbons and alcohols had similar responses within their groups.

4. The behavior of a given class of compounds is more strongly influenced by the presence or absence of reactive groups such as =CO or -OH than by the hydrocarbon chain length.

5. An active layer can be deposited by several methods, including screen printing of fritted oxide mixtures or the decomposition of tin chloride.

6. The relative effectivenesses of the catalysts with respect to oxidation of organic compounds studied here, in decreasing order of effectiveness are: platinum, rhodium > ruthenium > palladium > iridium, osmium. For some organic compounds, the oxide itself (e.g., Fe₂O₃), has some catalytic effect

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