

Semiconducting-Oxide Chemical Sensors

by S. Roy Morrison

Researchers discovered in the early 1950s that changing the composition of a gas that surrounds a semiconductor, changes the semiconductor's conductivity. With the single crystals of germanium studied at the time, the sensitivity was low. But although the resistance changes were small, they were quite measurable. Sensing a gas with a semiconductor was obviously possible, but non-reproducibility of results was a major problem. The sources of this problem were not clear at the time. Looking back, one might postulate that the processes responsible were slow oxidation of the germanium, hydration of the oxide, and other irreversible chemical reactions.

Semiconductor sensors are now on the market. They have much better stability than their predecessors, but some problems remain, particularly those involving reproducibility. The most popular sensors avoid the oxidation problem to a great extent by using semiconducting oxides as their active elements. The material is, one hopes, fully oxidized when produced. The current generation of sensors avoids the sensitivity problem by using a compressed powder. The intergranular contact resistance in these powders is determined by adsorbed species on the surface, and this contact resistance dominates over the bulk resistance of the material. Despite their drawbacks, however, these sensors are very low in cost and perform well enough to meet many user requirements, and millions are sold each year.

The dominant device is the Taguchi sensor, which is based on a powdered form of the n-type semiconductor SnO_2 . The sensor

is sensitive to combustible gases such as propane, methane and carbon monoxide. Other oxides such as Fe_2O_3 are under intensive development.

It is difficult to discuss semiconducting-oxide gas sensors without emphasizing their drawbacks, which should be balanced against the devices' low cost and simple signal output. Their economy and simplicity allows every user to install them in homes, boats, and trailers for detecting CO, propane or natural gas. Indeed, they will be extremely cost-effective in critical industrial monitoring applications, where sensors may be placed every few feet. In summary, even with their limitations, semiconducting-oxide gas sensors are already very useful.

Forms of Metal-Oxide Sensors

The commercialized Taguchi sensor is mounted on a small ceramic tube having an outer diameter of 1 mm and a length of 3 mm. Inside the tube there is a heater, and gold electrodes are deposited on the outside of the tube to measure the resistance of the semiconducting oxide. A slurry is prepared that contains SnO_2 powder, a binder, palladium as a catalyst, and (usually) other materials known as promoters or adsorbents to modify the response. This mixture is coated onto the ceramic tube and fired to induce mechanical stability and modest sintering of the SnO_2 particles.

In operation, the heater raises the temperature of the sensor to between 300°C and 350°C , which is high enough for the catalytic oxidation of most combustible gases on the catalyst. The operational mechanism is simple in principle. Oxygen from the air adsorbs on the SnO_2 and removes electrons from the SnO_2

conduction band near the surface (Fig. 1). The removal of electrons from the surface of each grain produces an insulating region that dramatically increases the contact resistance between powder grains. In pure air, the resistance between the gold electrodes is in the tens of kilohms. If a small concentration of combustible gas, say CO, appears in the atmosphere, the Pd catalyses the reaction of the CO with the adsorbed oxygen. The product CO_2 is liberated and, most important, the electrons that were bound to the oxygen, return to the semiconductor. With the electrons restored, the contact resistance lowers, and an observer knows that a combustible gas is present. About 100 ppm of combustible gas can change the resistance of the sensor by a factor of 10, so the sensor is adequately sensitive.

Reproducibility is a serious problem with this system. Compressed powders aren't noted for their predictability. Slight changes in particle size, intergranular contact area, adsorbed impurities, and which crystal face is dominant, produce changes in the initial relationship between resistance and the combustible-gas pressure. A typical sequence of processes in preparing the paste makes obvious the opportunities for variation in the final properties (Fig. 2).

Stability is another problem. Both the bulk and surface properties of SnO_2 powder can change with time at elevated temperature. One stability problem that has been turned into an advantage involves the adsorption of combustible gases as the sensor is cooled to room temperature, a temperature too low for catalytic combustion. All the molecules that are adsorbed when the device is turned off



The inexpensive and ubiquitous gas sensor improves steadily

accumulate, and then react in the first few minutes after the heater is turned on. As a result, the device indicates that the atmosphere is contaminated even when it is not. Once this behavior is understood it can be an advantage because the signal shows the device is working and, when the signal does disappear in a few minutes, one can be sure the atmosphere is clean. To obtain the greatest possible accuracy and stability, the devices should be calibrated and used only after the heater has been kept on for several days.

Thick-film sensors, in which the semiconducting oxide paste is deposited by silk screen printing (or a similar technique), offer opportunities for better mass-production techniques than are possible with the Taguchi type. However, the technical problems remain unchanged. Thin film sensors, in which the semiconductor oxide is prepared by evaporation or sputtering, have been studied extensively, and it seems that they present even greater problems in reproducibility because in thin films, the resistance is dominated by grain boundaries. This is even harder to control than resistance variations arising from intergranular contacts.

In our laboratory, we have tried to circumvent these problems by producing a modified thin-film sensor based on oxygen absorption rather than oxygen adsorption. The sensor is made with evaporated bismuth molybdate, which has a very high diffusion constant for oxygen vacancies. The combustible gas we wish to sense extracts lattice oxygen from the bismuth molybdate; atmospheric oxygen restores the lattice oxygen. Because the oxygen vacancies move rapidly in the material, the bulk stoichiometry (i.e., metal/oxygen ratio) follows the surface



stoichiometry and controls the resistance. Bismuth molybdate films are stable and, as prepared, are highly sensitive to alcohols (Fig. 3).

All the sensors we've mentioned are designed for detecting combustible gases. Presently, there is no accepted semiconducting oxide sensor for oxidants, except (perhaps) for TiO_2 , which is of potential interest for determining the air/fuel ratio in auto exhausts. Workers have studied phthalocyanine sensors for many oxidants, but the problems with these sensors have not been reported. For example, the lifetime of the sensor at 175°C (the temperature needed for fast response) has not, to our knowledge, been explored.

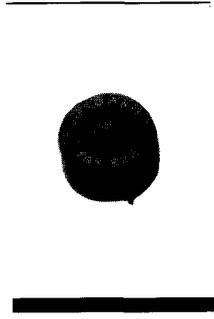
Improving Selectivity

Metal-oxide sensors are sensitive to all combustible gases, but with varying sensitivity. For many applications, selective sensitivity is desirable. In some parts of the world, sensors for the detection of CO and gas leaks are required by law in many homes. But a detector may frequently be turned off by a resident, because the sensor is sensitive to alcohol, and alarms sound at inconvenient times. Here, selectivity *against* alcohol would be highly desirable.

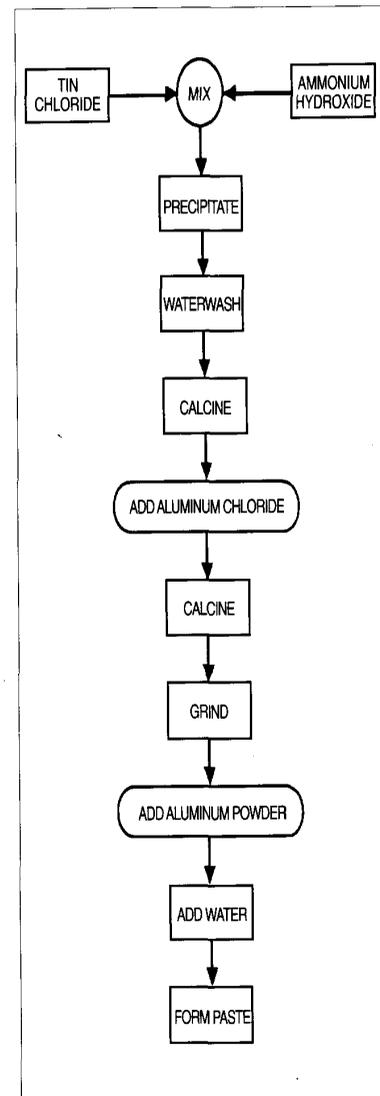
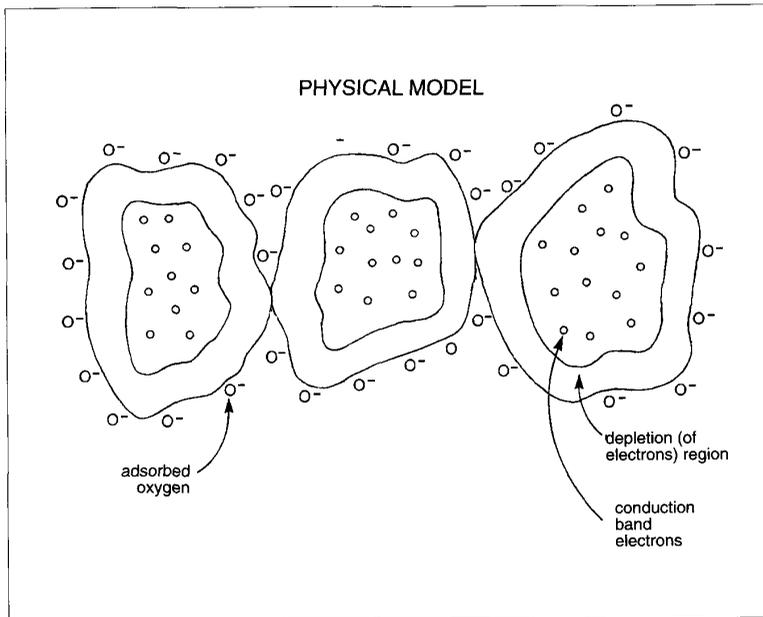
There are several ways to impart some selectivity to these sensors. One is the use of filters to remove some gases and allow others to reach the sensor. Silica and zeolites have been reported to be of value as filters, and silica is used in one commercial sensor. Another way to incorporate selectivity is to vary the sensor's temperature. Methane, for instance, requires a high temperature before catalytic oxidation begins, while CO oxidizes readily at a low temperature. It is possible to cycle the temperature and note conductance peaks at temperatures associated with a particular combustible gas. A third approach is catalytic oxidation of easily oxidized gases before they reach the sensor.

Beyond these techniques, there is always the possibility of varying the catalyst and the promoter. Tens of thousands of articles in the catalytic literature describe selectivity in catalysis. Unfortunately, they do not provide the information needed for designing sensors. In the usual catalytic reaction, one has a pure feed stream and wants to encourage a certain product over all others. But in catalysis for gas sensors, one has an impure "feed stream" and does not care what the product is as long as the desired combus-

1. The operational mechanism of the Taguchi sensor is simple in principle. Oxygen from the air adsorbs on the SnO_2 and removes electrons from the SnO_2 conduction band near the surface. The removal of electrons (shown as small circles) from the surface of each grain produces an insulating region that dramatically increases the contact resistance between powder grains.



2. A flow chart of a typical sequence of processes for preparing tin-oxide paste (the sensing medium of semiconducting-oxide gas sensors), makes obvious the many opportunities for variability in the final product.



tible gas in the feed stream reacts. If you want to sense CO, for instance, you need a catalyst-promoter combination that combusts only CO. If there is, let's say, propane in the atmosphere, the catalyst-promoter combination must ignore it. Thus, we need extensive new research in catalysis before we can develop this potentially useful class of sensors.

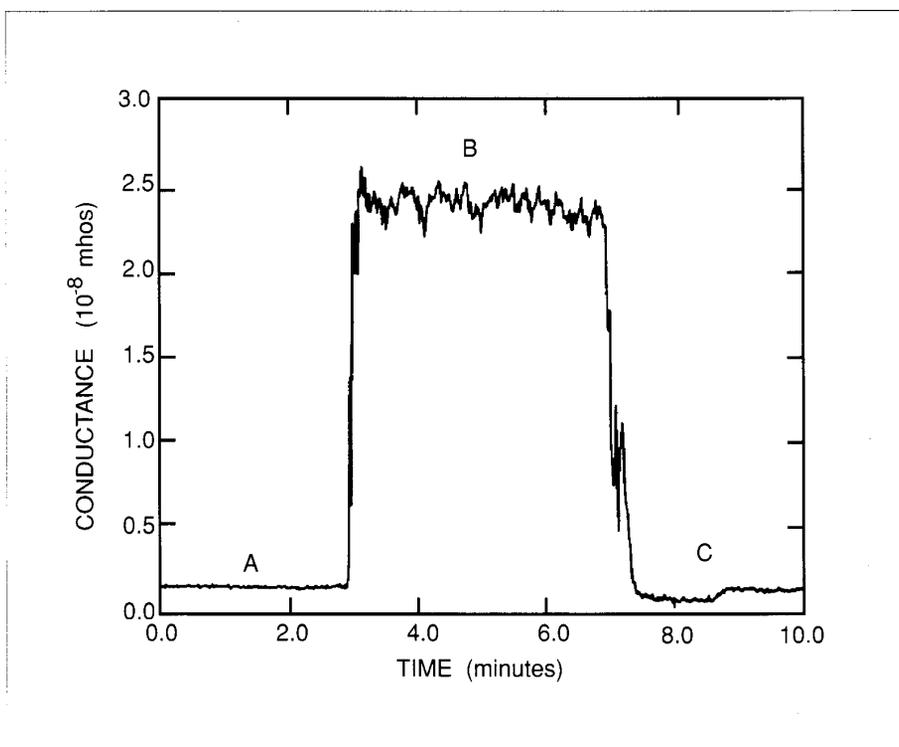
The Electronic End-Run

Sometimes, you can use electronic circuitry to circumvent inherent sensor problems. Consider the case where a sensor for propane triggers an alarm when there is 100 ppm or more propane in the atmosphere. If you measure the resistance

of ten Taguchi-type sensors in air containing 100 ppm propane, you will observe ten different resistance values. The external circuitry can (and must) be calibrated for each sensor individually to standardize the alarm signal. The current through the SnO_2 , for instance, can be adjusted so that with 100 ppm propane present the voltage across the sensor is at a specific desired value.

Such calibration adds to the labor cost, and the required labor is substantial. The coating of the paste onto the ceramic, the mounting of the sensor for several days so it can "burn in" after the heater is turned on, the transfer of the sensor to a controlled atmosphere (say, 100 ppm propane) and the calibration of the sensor all require human

3. The evaporated thin-film bismuth molybdate sensor is sensitive to 200 ppm ethanol vapor, a value that indicates over-indulgence if present in a person's breath. "A" is the sensor's response to laboratory air; "B" is the response to 200 ppm ethanol; at "C" the test chamber was vented.



attention. Given this cost, it is easy to understand why even the most primitive "mass-production" approaches, such as thick-film sensors, seem so attractive.

Calibrating the sensors is a problem in other ways. If the circuitry is adjusted to standardize the output of 10 sensors with 100 ppm CO, the 10 outputs will not be the same for 100 ppm propane. If accuracy is required, the sensor must be standardized specifically for the gas of interest. This is not trivial, particularly when sensors must be

calibrated for a noxious gas. Sensor-system manufacturers may not have the facilities or know-how for calibrating sensors in the more noxious gases.

When One is Not Enough

One goal for the future is that semiconducting oxide sensors become sufficiently selective and stable to permit the fabrication of arrays that will provide "perfect" selectivity. One should be able to use N sensors, each with a different characteristic response,

to determine the concentration of N gases in the atmosphere. Then, a simple chip could be designed to indicate which gases were present. For a simple example, let's look at an array of two sensors a and b exposed to two gases with concentrations x_1 and x_2 . We could have:

$$G_a = a_1x_1 + a_2x_2$$

$$G_b = b_1x_1 + b_2x_2$$

where G_a and G_b are the conductances, and the a 's and b 's are the sensitivities to the gases x_1 and x_2 . When one knows the sensitivities a_1 , a_2 , b_1 , and b_2 , it is easy to calculate the concentrations x_1 and x_2 . In principle, an array of this kind can provide perfect selectivity. Sensors are now available with the required differences in selectivity, but more research is needed before we

can attain the stability required for such an approach.

Biography

Dr. S. Roy Morrison is Professor of Physics at Simon Fraser University, Burnaby, British Columbia, Canada. **CD**

Supplementary reading

M. J. Madou and S. R. Morrison, *Chemical Sensing with Solid State Devices* (Academic Press, 1989).