DUAL GRADIENT THICK-FILM METAL OXIDE GAS SENSO

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ABSTRACT

We describe the technology and characteristics of a family of thick-film gas sensors as simple to manufacture as a one-element sensor, but whose signal can be as rich as that of an array of twenty-five or more discrete sensors. This sensor design is particularly well adapted to using pattern recognition and related methods of analyte identification and quantitation based on the co-interpreted response of multiple sensors. Our prototype sensors are constructed on alumina Snapstrates(TM) intended for 20-pin DIP hybrid circuit substrates. A printed precious metal alloy electrode pattern provides pin connection pads, electrodes for mapping the gas-sensitive resistance of the overprinted metal oxide thick-film, and connections to an overprinted ohmic heater. Gradients in one or two different catalytic properties can be imposed *across* the short dimension and *along* the long dimension of the film. Each gradient can be continuous, for example a catalyst concentration gradient across or along the film, or discrete, for example three stripes across or nine stripes along the film, each of different but uniform catalyst concentration and composition. Depending on the electrode pattern used, the resistances of up to twenty-five usefully distinct surface regions can be measured. While these regions are effectively separate sensors, they share an identical history, and in operation share an identical environment. Thus differential effects from region to region can be attributed with certainty to differential responses to the same sample. Several electrode patterns and thick-film formulations have been investigated. Measurements to date confirm the validity of the design, and suggest directions in which evolution of the fabrication technology might be directed. Future possibilities include making essentially continuous surface-location-resolved measurements, adding gradients in the third spatial dimension, and using temporal as well as spatial gradients.

INTRODUCTION

Metal oxide semiconductor resistor gas sensors, which typically are fabricated from bulk n-type (and sometimes p-type) metal oxides, are generally sensitive to many combustible or otherwise reactive gases and organic vapors, including hydrogen (H_2), hydrocarbons (HCs), methanol (CH_3OH) and other alcohols, acetone (CH_3OCH_3) and other ketones, carbon monoxide (CO), and ammonia (NH_3). The detection thresholds of commercial n-type tin oxide (SnO_2) sensors[1] to H_2, CO and ethanol (C_2H_5OH) vapors can be in the part-per-million (ppm) range.

The bulk electrical conductivity of a semiconducting metal oxide is primarily determined by its oxygen coverage. The effect of a reducing gas in the surrounding atmosphere is mainly to reduce the surface density of adsorbed oxygen molecules by mechanisms such as competition for surface sites and consumption by oxidation-reduction reactions[2]. The sensitivity of a metal oxide semiconductor resistor gas sensor to a particular reducing gas is related to the adsorption rates of the oxygen and reducing gas, and the chemical reaction rate between these two reactants in the adsorbed state. In the absence of added catalysts, these reactions are typically impeded by high activation energies. The competition between the reducing gas and oxygen for surface sites is then the dominant mechanism for reducing the oxygen coverage, and thus the sensor resistance. According to the classical adsorption isotherm of Langmuir[3], the surface coverage of each adsorbed species is directly proportional to its partial pressure. Without some additional amplifying effect, the sensitivity of these devices would thus be low.

CATALYSTS

The necessary amplification is provided by catalysts, typically precious metals or transition metals. Catalysts generally enhance chemical reaction rates by providing an alternative reaction path, involving different activated complexes, with a lower activation energy than the uncatalyzed mechanism. When a suitable catalyst is incorporated in a metal oxide semiconductor resistor gas sensor, the gaseous reactants adsorb onto the surface of the catalyst with an exothermic heat of adsorption equivalent to the amount by which the activation energy is lowered[4]. For n-type semiconductor metal oxides such as zinc oxide (ZnO) and SnO_2, surface adsorbed oxygen stabilizes in a negative ion state[a]. Free electrons in the bulk material are electrostatically inhibited (by the already adsorbed surface oxygen negative ion charge layer) from combining with newly arriving oxygen molecules. Oxygen coverage can thus be self limiting to a very low value, perhaps less than 1% of a monolayer, while the coverage of the reducing gas can become very high despite a large disparity, in the opposite direction, of oxygen and reducing gas partial pressures. As the chemical reaction rate is catalytically increased, the oxygen coverage in the presence of even traces of reducing gases can fall rapidly to near zero. The corresponding increase in bulk electron density, manifested as a decreased bulk resistance,

[a]The negative ion state is variously postulated as O_2^- or O^-, or even O^{2-}. In the first case, each adsorbed oxygen molecule would capture one bulk electron, exoenergetic by 0.44 eV (the electron affinity of O_2). In the second case, each adsorbed oxygen molecule would capture two bulk electrons, endoenergetic by 2.2 eV (the dissociation energy of O_2 less twice the electron affinity of atomic oxygen). In the third case, each adsorbed oxygen molecule would capture four bulk electrons, with uncertain endoenergeticity. Appropriate experiments, *e.g.*, coupled mass transport and amperometric measurements might resolve the issue.

can make for a very sensitive gas detector.

Nitta *et al* have found that palladium (Pd) catalyzes SnO_2-based gas sensors in the detection of H_2, CO and isobutane (iso-C_4H_{10}) about equally, but that the addition of thoria (ThO_2) and silica (SiO_2) preferentially enhances the sensitivity to CO over HCs[5]. Doping with transition metals such as niobium (Nb), vanadium (V), titanium (Ti) or molybdenum (Mo) could modify the relative sensitivities to CO, H_2 and HCs[6]. The effectiveness of catalysts at improving the selectivity of metal oxide semiconductor resistor gas sensors is thus a function of the changes of the adsorption, desorption and reaction properties of the gases or vapors of interest when the catalyst is added[7]. It is interesting to speculate that since the coverage of oxygen is much higher in p-type metal oxide[8], such as titania (TiO_2), than in n-type such as SnO_2, catalysis might be even more advantageous with p-type materials.

SYNTHESIZING SELECTIVITY

Despite this seemingly encouraging picture, a well known practical limitation of metal oxide semiconductor resistor gas sensors is that within large groupings of potential sample species they exhibit little or no selectivity. Thus the effect on sensor resistance of a less reactive gas in higher concentration cannot be distinguished from the effect of a more reactive gas in lower concentration. Much effort has been devoted to improving selectivity, by filtering[9] the sample gas, by varying gross composition[10], by doping[11, 12], and by surface preparation[13, 14]. Although these efforts have been partially successful in improving the sensitivity of some sensors to some specific gases, selectivity enhancement has not been satisfactorily reduced to a systematic discipline capable of producing on demand a sensor matched to a particular application.

An alternative approach to selective detection with metal oxide semiconductor gas sensor resistors is to use several elements of this type simultaneously, each element having a unique (although not necessarily exclusive) sensitivity to at least one of the anticipated species. For example, Clifford[15] has reported a now generally accepted physico-chemical response model to which he coupled a simultaneous equations solving approach to identifying and quantifying the species comprising a gas mixture, provided that the individual species have been anticipated, each of the sensors has been calibrated at least to each species, and in general to binary and higher order mixtures as well. This is recognized as an implementation in the spirit of chemometrics. While its power in principle is easily recognized, there are nevertheless technological hurdles to overcome. An important one is that its efficacy and economy depend on the precision of a potentially time consuming calibration step. Engineering concerns include the potentially unpredictable physical coupling among the elements. Finally, if constructed of discrete sensor unit packages the assembly might not be as small as desired, while if constructed of multiple sensor units in a single package or on a single substrate, yields might be low, and fabrication costs correspondingly high.

The dual gradient gas sensor which is the subject of this paper is a potential answer to some of these objections. It also provides a family of flexible devices that are well matched to the demands of empirical research in gas sensor materials development and evaluation. As a commercial device, it be manufactured about as simply as a conventional single element sensor, but it could provide a signal as rich as twenty-five or more discrete sensors with either a continuum or some discrete steps in absolute and differential sensitivity.

The essential departure of this sensor from conventional practice is a *large area* thick-film semiconductor deposited on an inert substrate with integral printed ohmic heaters. A metallization pattern for mapping the film resistivity is printed onto the substrate before the gas-sensitive semiconductor layer is overprinted. Figure 1 shows several examples of patterns we have used.

Figure 1: Examples of several metallization patterns used.

One or more spatial gradients are created by systematically varying the concentration of a single catalyst species, the concentration ratio of two or more catalyst species, or by design of the heater shapes. The catalyst is, in a production scenario, best added before firing the ink. But an alternative, especially well suited to the gas sensor research scenario, is to build stock uncatalyzed "blank" sensors, hand dope them with experimental catalysts, and evaluate catalyst efficacy before developing recipes for incorporating them in the inks. Figure 2 is an example of a "production" sensor, printed with three long stripes of inks containing different precious metal catalysts. Figure 3 is an example of a "research" sensor, spotted after firing with six different catalysts.

Figure 2: Three catalysts incorporated in ink, gradient heater. Catalysts, from top to bottom, are Rh, Pt, Pd.

Figure 3: Six catalysts spotted after firing, uniform heater. Catalysts, from left to right, are Pd, Ru, Pt, Rh, Os, Ir.

The art employed is that of hybrid circuit packaging. However the finished device differs from conventional encapsulated hybrid circuits in that the sensor ink is intentionally reactive, and it must remain exposed to air to perform its sensing function. The design requirements for the thick-film inks are atypical mainly in that the resulting layer must be porous and reactive (but stably so), whereas conventional thick-film resistor compositions are formulated to produce dense, inert layers that are stable and unreactive over as wide as possible a range of chemical and thermal environments.

FABRICATION

Three generations of prototype gradient sensors have been evaluated. The first generation was prepared according to the recipe disclosed by Taguchi[16]. The second generation, fabricated with a newly developed doped ink family, had resistances that were too high (larger than 30 MΩ at approximately 300 C) to be usable in the computer controlled precision sample delivery and measuring apparatus (discussed below). Offline experiments with a single channel electrometer based ohmmeter demonstrated that these devices responded sensitively, although not verifiably reproducibly. The third generation was fabricated very recently, incorporating both new ink compounding techniques that lower their resistance to a usable range, and a new electrode pattern with an aspect ratio that results in a lower resistance for a given resistivity. However, thermally-induced mechanical instabilities precluded obtaining data in time to include them in this report. Thus all the data reported in this paper were obtained using the first generation sensors made essentially according to the Taguchi recipe.

All three generations consist of a layer of SnO_2 deposited on an alumina (Al_2O_3) substrate, with an interposed precious metal alloy pattern of measuring electrodes and contact pads. A resistive strip is deposited on the substrate as the heater. Two heater patterns were produced: one covering the back of the substrate, producing a nominally uniform temperature, and one at one end of the front of the substrate, producing a nominally linear temperature gradient[b]. Neither the heater material nor the leg attachment method, both subsequently improved, could tolerate temperatures as high as we know to be desirable. The experiments described were therefore restricted to a maximum temperature of about 250 C. Response and cleanup are both sluggish at these temperatures, and sensitivity, while high, is lower than that anticipated at higher temperatures.

In detail[17], eight sensors are made on one GE Ceramics type 614 or 860 alumina Snapstrate(TM) substrate. Each unit is 25.4 x 10.7 mm (1.00 x 0.42 inches), compatible with attaching leads that plug into a 20-pin DIP socket. The fabrication sequence is to print precious metal alloy conductor paths, then the resistor pattern that forms the heater, then the sensing layer. The heater is an ohmic thick-film made from commercially available ink compositions (DuPont 9910 and 1711) by firing in a belt furnace according to the manufacturer's instructions. The heater strips have a nominal resistance of 70-100 Ω. After applying the active material, detailed below, leads are attached, initially with a conductive epoxy used for hybrid circuit packaging, and more recently using vapor phase soldering.

The first generation "ink," following Taguchi[16], was a mixture of tin chloride ($SnCl_4$) and stearic acid ($CH_3(CH_2)_{16}COOH$) that was painted on the substrate and fired at 700 C in air. This process was repeated several times to build up an adequate thickness. Firing burned off the organic component, leaving behind a porous SnO_2 layer. This uncatalyzed layer was the base material for fabrication of several sensor types. In each case, an alcohol solution of one or more precious metal chlorides was painted in selected areas and fired at 700 C in air. Thick-films with sheet resistances in the range of 5 to 30 KΩ per square were deposited by this technique. Two examples of the Taguchi-type sensors are shown in Figures 4 and 5.

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[b]The experiments have taught us that *both* "baseline" and "gradient" heaters are needed. The next fabrication generation will incorporate both, at the acceptable expense of two resistance measurement pins.

Figure 4: Taguchi-type sensor with uniform catalyst (Pt) and a temperature gradient.

Figure 5: Taguchi-type sensor with uniform temperature and two (slightly overlapping) catalysts regions, Ru on the left and Pt on the right.

While it provides an important baseline for comparison with later design generations, the stearic acid method has several obvious shortcomings. It is difficult to control and reproduce on a laboratory scale (although the technique could, we believe, be done reproducibly with specialized manufacturing equipment). Because the starting mixture liquefies during the initial firing, the gas-sensitive layer often partially overlapped the gradient heater, rendering the first measurement pair unusable. The strength and adhesion of the sensitive layer was poor, and its surface resistance varied greatly from point to point on the sensor. Worse, thermal cycling caused irreversible cracking, and permanent resistance changes. Finally, the distribution of catalyst was difficult to control, and obtaining a reasonable coverage everywhere required using many times more precious metal than would be necessary with a more uniform dispersal technique.

Printable ink compositions were developed to address these shortcomings. Our inks contain three or four major components

- metal oxide powders
- organometallic catalyst precursors (if desired)
- glass frit
- organic solvent vehicles

In contrast to conventional formulations, our ink contains only about 30% solids by volume. The glass, about 10% of the fired deposit, provides strength and adhesion, but contributes to the higher than desirable resistance. Firing burns off the organic vehicles, leaving a highly porous thick-film.

An example of the third fabrication generation, catalyst in ink, vapor-phase-soldered leads, and an electrode pattern matched to a high resistivity sensing surface is shown in Figure 6. This pattern is also the most suitable one to use for evaluation and optimization, since the individual resistors are much better isolated than in the other designs.

Figure 6: Third generation sensor.

EXPERIMENTS

Experiments were conducted in a test chamber to which we could deliver a pure air flow containing calibrated concentrations of one or two vapors derived by dilution of air flow through bubblers. The concentration of the vapor was calculated by combining tabulated values of the solvent vapor pressure at the measured operating temperature, the measured flow rate of the air bubbling through the liquid, and the ratiometrically-mass-flow-controlled mixing of the saturated vapor with a main stream of carrier gas, usually air. Electrical connections to the sensor were made through a 20-pin socket in the machinable glass-ceramic baseplate of the chamber. A commercial Taguchi sensor is also installed in the test chamber for comparison. The sensor was allowed to stabilize at operating temperature in a flowing pure air environment. Usually this took about a day at an operating temperature (at the hottest end, for the gradient devices) around 250 C.

The pressure of the test chamber was generally kept at just over one atmosphere by venting the outlet to the atmosphere through a tube long enough to prevent back diffusion of the laboratory atmosphere. The steady state and response state of the gas-sensitive layer was mapped by cyclically measuring the resistance between selected pairs of electrodes. The data were collected by data acquisition and control units on an IEEE-488 bus under the control of a computer workstation. The valves, heaters, mass flow controllers, auxiliary sensors, *etc*, were also controlled by the computer over the bus. All data were processed by the workstation, or sometimes during method development, by uploading to a mainframe computer.

Response to a variety of simple gases and vapors, primarily organic solvents, has been tested. The results are in essential agreement with literature reports of comparable observations on similarly fabricated unitary devices. We have paid particular attention to two organic vapors, C_2H_5OH and heptane (C_7H_{16}), (or sometimes gasoline, a mixture whose major component is C_7H_{16}) since there are several potential practical applications in the automobile industry for identifying and quantifying these two substances and their mixtures in air.

TYPICAL DATA

Figure 7 shows the resistances, along the length of the sensor, vs. time, when the Taguchi-type sensor shown in Figure 5 was exposed to a transient concentration of C_2H_5OH vapor. The vapor was introduced into the test chamber at the time marked t_1, and was cut off at the time marked t_2, where the elapsed time (t_2 - t_1) was about one hour. The response of the sensor to C_2H_5OH is seen to be relatively fast (equilibrium is reached within a few minutes), while it takes substantially longer (over an hour) to recover. This particular sensor was doped with two catalysts, Ru and Pt, the former covering the region from R1 to R5, and (with some overlap) the latter covering the region from R5 to R9. Clearly the Ru-doped region recovers significantly more rapidly that does the Pt-doped region. This is tentatively attributed to different desorption rates for adsorbed sample molecules. A similar effect of the same sign was also observed when the sensor was exposed to C_7H_{16} vapor.

Figure 7: Response of the sensor shown in Figure 5 to a transient sample of C_2H_5OH.
The interval t_1 - t_2 is about 1 hour.

In Figure 8, the near steady-state resistances of different regions of this same sensor are plotted parameterized by concentration of C_2H_5OH and C_7H_{16} vapor. To compensate for spatial nonuniformity, each resistance is independently normalized against its value in air. The Ru and Pt-doped regions clearly exhibit markedly different sensitivities. The Pt-doped sensitivity to both C_2H_5OH and C_7H_{16} than the Ru-doped sensitivity. This observation seems to agree with the conclusions of the previous experiment: the catalyst that recovers more quickly, presumably because of a higher sample desorption rate, exhibits the lower sensitivity.[c].

Figure 8: Near steady state response of the sensor of Figure 5 to various concentrations of C_2H_5OH and C_7H_{14}. Approximate concentrations (ppm) are (A) 20, (B) 53, (C) 82, (D) 138, (E) 333, (F) 58, (G) 72, (H) 245, (I) 261, (J) 268.

INTERPRETATION METHODOLOGY

The general curve fitting, pattern recognition, or chemometric, approach to synthesizing selectivity given a set of fundamentally universal chemical sensors is to

- enhance the differential response, or selectivity, as much as possible (without too much regard for sensitivity, but emphasizing preservation or enhancement of stability) by inducing physical (such as grain size), chemical (such as doping catalyst), or thermal set points;

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[c]If this is indeed a general principle, it may suggest a degree of futility in trying to make metal oxide semiconductor sensors that are both highly sensitive and briskly responsive.

- use various parameter matching criteria to construct a summary representation of a calibration data set (or a "training set") of the samples of interest;

- discover, by automated means, or more commonly by iterative interaction between the computer and a human, how to segment the space spanned by the responses of the collection of individual sensors into distinct generalized volumes corresponding to species or mixtures of interest;

- classify unknowns according to the region of this space into which their collective response to the set of sensors falls;

- quantitate the concentration by a set of methods designed to maximize the signal-to-noise available via optimal weightings of the individual sensor responses (in the noise-free idealization, once *identification* has been accomplished, via the previous step, any single sensor that has *some* response to the identified species provides quantitation)

- analyze mixtures, in contrast to samples that can be assumed *a priori* to be single species (albeit unidentified) or canonical mixtures (e.g., gasoline, lemon oil, etc.) contained in the basis set, by vector decomposition.

The difficulty in implementing curve fitting, pattern recognition, or chemometric approaches is that they assume smooth, hysteresis-free sensor behavior. They break down when one or more sensors exhibit response vs. concentration behavior that is not single valued, or that exhibits switching behavior, *i.e.*, sharp jumps between otherwise well behaved regions. We suggest that in these situations a knowledge-based approach, in an automated system taking into account context, *i.e.*, stored physical knowledge about what is and what is not within the realm of the reasonable, and historical knowledge about the path the sensors have taken to their present state, will permit us to overcome hysteresis.

FUTURE POSSIBILITIES

The gap between our concept and the development art and technology that will enable its successful execution is undeniably wide. Nevertheless several ideas for future amplification of the gradient sensor concept already come to mind.

The possibility of making measurements at very high spatial density along one or two continuum gradients might be realized by exploiting a surface resistivity mapping technique that did not require mechanical contact. For example, optical means of monitoring resistivity, *e.g.*, by exploiting the resistivity dependence of optical phase or polarization upon reflection, could make very high density maps possible. The well known gas sensitivity of the resistance of γ-Fe_2O_3 pellets and layers suggests the possibility of a parallel chemically dependent effect on the magnetic properties of this material. Thus we can imagine the possibility of a "chemi-magneto-optic" effect in which spatial gradients were induced either thermally or by doping. At sufficiently high chemical "pixel" densities, the vast arsenal of feature extraction tools in use by the computer vision community potentially becomes available to the chemical sensing field.

Three dimensional gradients, with a volumetric rather than areal electrode matrix, are another possibility. In this case differential sensing properties would be set up through the film thickness, or the film would include several differently sensitive layers. As in the architecture of color photographic film, specific layers might have either detecting or filtering functions, or both.

Finally, it may prove advantageous to leave the spatial domain and enter the temporal domain, *e.g.*, by exploiting temperature differences in time rather than in location. The idea of operating a single chemically sensitive resistor at different temperatures at different times is not new; indeed, some commercial instruments operate in thermal cycles of a few minutes for cleanup and conditioning. However it has not to our knowledge been previously suggested that especially useful information might become available via substantially faster thermal cycling, *e.g.,* as fast as the sensor's thermal time constant (ratio of heat-capacity to heater-power) will permit. Analysis of the difference between the ballistic resistance change of an impulse heated gas-sensitive resistor in pure air and in impure air might be be a powerful way to separate the surface effects we have been discussing from the slower bulk effects that may account for at least part of the drift for which metal oxide semiconductor resistor gas sensors are notorious.

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