Microfabricated Amperometric Gas Sensors

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Abstract—A series of Nafion-based amperometric gas sensors have been constructed using microelectronic fabrication technology. These sensors use a gold sensing electrode in the shape of a square grid. In this study, three different grid densities were employed. In order to ascertain the optimal design parameters for such sensors, the response characteristics of the various microfabricated sensors were compared to each other and to a conventional “macro” amperometric sensor. The critical performance criteria considered in this study were sensor response time, structural integrity under operating conditions, selectivity, and sensitivity to the analyte vapor. The response time of the miniaturized sensors was over an order of magnitude faster although they had a lower sensitivity than conventional sensors. The sensitivity of these sensors was dependent upon the total length of the gold–Nafion interface. A model that rationalizes this dependence is presented.

I. INTRODUCTION

AMPEROMETRY is a method of electrochemical detection in which the output current is proportional to the concentration of analytes. The reaction of interest occurs at the working electrode (or sensing electrode) surface. The first modern amperometric gas sensor was the Clark electrode for the measurement of oxygen [1]. During the next few decades, many improvements were made to this device so by the 1970’s, a wide range of amperometric sensors had been developed for many gaseous compounds [2]–[7]. Typically, amperometry can detect gases at parts-per-million to percent concentrations. Detection has been achieved, however, at parts-per-billion-level sensitivity for such analytes as H₂S [6] and NO₂ [7]. A detector chemistry rich in possibilities awaits the microfabrication of the versatile amperometric gas sensor, but in order to successfully produce a wide variety of micro-electrochemical sensors, new chemistries have to be interfaced to existing microelectronic fabrication techniques.

The decided advantages that are obtained through microfabrication of such sensors include reduced cost, reduced size, reduced sample volume, and faster response time [8]. In addition, it should be possible to obtain much greater control of the device structure with the application of microelectronic technology. These advantages, however, must be obtained without degradation of the signal-to-background ratio as the sensor size is reduced.

Progress in the development of microamperometric gas sensors has been slow. Micropotentiometric gas sensing devices abound [9], [10], but few examples of practical microfabricated amperometric devices are evident. Most of the microamperometric systems that have been reported consist only of microfabricated electrodes on a suitable substrate, and these electrodes are then dipped into the liquid electrolyte solution that also carries the sample [11], [12].

The purpose of this study is threefold: 1) to isolate and evaluate the structural characteristics important to sensor performance, 2) to provide a preliminary characterization of the analytical performance of microamperometric sensors, and 3) to ultimately develop techniques for the fabrication of complete amperometric gas sensors using a microfabrication approach. In order to accomplish this goal, several solid-electrolyte sensors having well defined sensing electrode geometries were constructed using microfabrication technology, and the analytical performance of each sensing electrode design was critically evaluated.

Nafion® was chosen as the substrate and electrolyte for the electrode/sensor structures described above. This proton conducting electrolyte is a solid polymer and can provide a sensor that is suitable for the detection of H₂S, NO₂, NO, or SO₂ [5]. Nafion has been used for many years in practical macro-amperometric sensors for these vapors [13]. In addition, such solid polymer electrolyte materials would be more likely to be compatible with integrated microsensor fabrication processes (e.g., electrode and electrolyte) than liquid electrolytes such as sulfuric acid and propylene carbonate.

II. EXPERIMENTAL

A. Types of Sensors Fabricated

Two configurations of test sensors were fabricated and compared in this study:

1) A “standard” sensor was constructed in which an existing amperometric gas sensor design was used [13]. These sensors utilized a gold mesh/gold powder working electrode (W.E.) in conjunction with a platinized platinum counter electrode (C.E.) and a platinum-air reference electrode (R.E.). The three electrodes were pressed into 1/16-in-thick Nafion as illustrated in Fig. 1(a). The performance of these “macro” sensors is known and can be
used for comparison to the microelectrode structure studied herein [13].

2) Several different sensors having microfabricated working/sensing electrodes were built. The counter and reference electrode designs were identical to those in the standard sensor described above. The working electrodes were vacuum evaporated onto sheets of 1/16-in-thick Nafion in a square grid structure (Fig. 1(b)). Three grid densities were used as described below. Since the C.E. and R.E. were identical, differences in the sensor performance can be attributed to the W.E. fabrication process and geometric configuration.

Measurement and analytical characterization of each sensor were performed to evaluate the relative reactivity of each sensing electrode design to be measured.

B. Sensing Electrode Design and Fabrication

A vacuum evaporation system containing both e-beam and thermal evaporation capability was used to deposit gold for the working electrode structures. Photolithographically etched evaporation masks for the sensing electrodes shown in Fig. 1(b) were prepared with three different perimeter-to-area ratios (P/A ratio). The three masks were fabricated from thin copper foil by etching a number of uniformly spaced parallel rectangles, each 6 mm long and with respective widths of 2.0 mm, 0.55 mm, and 0.125 mm. The spacing between electrodes was the same as the width. After the first evaporation of 3500 Å of gold, the masks were rotated 90° and a second evaporation of 3500 Å was performed to obtain working electrodes in a grid pattern.

Each working electrode design occupies a 6 × 6 mm region and has 0.5-mm-wide 2-cm-long runners to act as electrical leads from the structures. The grid patterns are defined by the grid line width, grid spacing, number of holes, and the thickness of the electrodes. Parameters that can be used to characterize an electrode design are the total perimeter, the area of the gold electrode, the ratio of the gold electrode perimeter to area (P/A), and the dimensionless ratio P^2/A. The specific dimensions for the three masks are given in Table I. The perimeter includes both the outer perimeter (24 mm) and the inner electrode perimeter, which is calculated by taking the perimeter of each "hole" in the grid electrode and multiplying by the number of holes. The total geometric area of electrode in contact with the electrolyte was approximately the same for all three designs.

Since the overall dimensions of each sensor were the same, each could be exposed in identical gas sample chambers and signal intensities could be compared under identical dynamic gas exposure conditions. Observed differences can then be related to differences in the working electrode structure.

C. Electroanalytical Protocols

The sensor structures were enclosed in a housing that allowed the electrolyte to be activated by exposure to water and the gases to be exposed to the working electrode in a convenient manner. The commercially available analytical-grade gases were obtained premixed in cylinders and, when required, were diluted to the appropriate concentration using a dynamic dilution system. A PAR Model 273 potentiostat was used for control and amplification of sensor signals. The electrodes were biased to +300 mV versus a Pt-air reference electrode (approximately 1.3 V versus the SHE). The gas mixture was pumped over the working electrode at a constant flow rate that was sufficiently fast (100-200 cc/min) to purge the approximately 0.25-cm³ exposure chamber rapidly. The signal from the sensor was recorded continuously during background measurements and when the analyte gas was present.

III. RESULTS

A. Structural Considerations—Adhesion Between the Gold and Nafion Sheets

The surface of the Nafion sheet electrolyte contains small pits, hillocks, and cracks that cause the gold coating to be irregular. The adhesion properties and structural
characteristics of the vapor-deposited gold thin-film electrodes on the dry Nafion sheet are illustrated in Fig. 2(a). The Nafion expanded 10 percent when wet causing ruptures in the microelectrode film (Fig. 2(b)). Although the resistance of the electrode increased due to the cracks, the electrode structure adhered and generally retained a resistance sufficiently low that the electrode continued to operate. Repeated wet/dry cycles can lead to flaking off of the gold and catastrophic increases in resistance.

B. Sensor Analytical Performance— "Standard Design" versus Sensors with Microfabricated Working Electrodes

The observed current density from each of the three microfabricated working electrode geometries (described in Table I and illustrated in Fig. 1(b)) and the standard sensor (Fig. 1(a)) differed by over an order of magnitude when first tested. The initial sensor response signals ($S$) and background ($B$) levels are summarized in Table II for selected gases under identical operating conditions. The sensitivity of the sensor is exceedingly dependent upon the structure of the sensing electrode. No significant sig-

| GAS MIXTURE | SENSOR SIGNAL (S) | standard Sensor ---
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<tr>
<td></td>
<td>Medium Grid**</td>
<td>Fine Grid**</td>
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<tr>
<td></td>
<td>$S$</td>
<td>$S$</td>
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<tr>
<td>DAY 1:</td>
<td></td>
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<tr>
<td>1% ppm NO/NO</td>
<td>0.29</td>
<td>0.30</td>
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<tr>
<td>99 ppm HSO/NO</td>
<td>1.8</td>
<td>0.25</td>
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<tr>
<td>DAY 2:</td>
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<tr>
<td>1% ppm NO/NO</td>
<td>0.077</td>
<td>0.1</td>
</tr>
<tr>
<td>99 ppm HSO/NO</td>
<td>0.19</td>
<td>0.1</td>
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<tr>
<td>0.1 ppm SO2/air</td>
<td>0.08</td>
<td>0.1</td>
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<tr>
<td>20 ppm SO2/air</td>
<td>0.30</td>
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<td>100 ppm SO2/air</td>
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* The sensor was operated at a constant potential of +100 mV versus the Pt/electrode. The "standard" porous gold electrode sensor was tested for comparison with the micro-electrodes.
Fig. 3. Comparison of the response induced by 83 ppm of H$_2$S on the fine-grid sensor and the medium-grid sensor (see Fig. 1(b) and Table I) as measured three days after fabrication. The bias potential was +300 mV (versus a Pt-air reference electrode) and the gas flow rate was 100 cc/min.

Fig. 4. Same as Fig. 3, but the analyte gas was 92 ppm of NO.

Fig. 5. Normalized response (to 83 ppm of H$_2$S) of the standard sensor (Fig. 1(a)) and the medium- and fine-grid sensors (Fig. 1(b)) to the indicated vapors. The actual current responses are summarized in Table II. The medium- and fine-grid sensors were three weeks old at the time of testing.

The relative signals obtained for three sensors and several gases are compared in Fig. 5. These results have been normalized to the strongest signal. The similarity of the results indicates that the electrochemistry is essentially the same for all of the gold electrodes. Thus, the structural differences are primarily altering the kinetic processes on the electrode surface.

IV. DISCUSSION

The background current in the sensor will be approximately proportional to the total geometric area of the electrode that is in contact with the electrolyte. This area was held approximately constant for all the microfabricated electrodes studied (see Table I). The sensor response (or output current during electrocatalysis) is influenced by various factors including both the active surface area of the sensing electrode and the specific activity of the catalytic sites that are available for reaction with the gas of interest. The morphology of the gold film would be expected to affect the activity of the sensing electrode, but that effect was not investigated in the experiments reported here.

Although the geometric area of the gold surface was nearly identical for the sensors, the signal magnitude was...
quite different for the different sensor structures. Such an observation indicates that the sensitivity of the device depends upon not only the chemical nature of the surface (which is gold and nearly identical for all sensors in this experiment) but also on the specific structure of the electrocatalytic surface and the interface created by gas/electrode/electrolyte.

It is reasonable to assume that the faradaic or analytical current is preferentially generated along the perimeter of the electrode where the gas, electrolyte, and electrocatalyst (the electrode) meet. This triple-phase boundary at the electrode edge should be the most catalytically active area for several reasons including:

1) edges, steps, and other defects are more catalytically active than flat surfaces,

2) the gas must diffuse through the Nafion over a longer path in order to react at the center of the electrode rather than to react at the edge, and

3) the electric field intensity is inversely proportional to the radius of curvature of the electrode and, therefore, much larger at the edge than along the flat surface.

To extend this discussion in a more analytical manner, let us assume that the geometric dependence of the signal-to-background ratio \( S/B \) for the microsensor is a function of only the total perimeter \( P \) and the area \( A \) of the electrode (i.e., the differences observed are assumed to be structure dependent since the chemistry of all the systems is constant). The ratio of the signal to background \( S/B \) is a dimensionless quantity and, therefore, \( S/B \) may be expressed as a function of \( P^2/A \), which is the only independent dimensionless quantity that can be formed from \( P \) and \( A \). In the simplest case, \( S/B \) would be directly proportional to \( P^2/A \)

\[
S/B = K \cdot (P^2/A)
\]

where \( K \) depends on the gas detected. Based on this hypothesis, all circular solid electrodes, or all square solid electrodes, or all electrodes that can be obtained from each other by only a change in scale will have the same \( P^2/A \) and therefore the same \( S/B \) for a given species. For example, all circular electrodes have \( P^2/A \) equal to \( 4\pi \) and all square electrodes have \( P^2/A \) equal to 16, which is the minimum value for a rectangle. The optimum design for a rectangular electrode occurs when one side is much longer than the other side. In this case, the \( P^2/A \) and \( S/B \) is proportional to the ratio of the sides, which is much greater than 1.

Based upon these geometric considerations and dimensional arguments, the \( S/B \) ratio for the fine-grid sensor is expected to be about 11.6 times greater than for the medium-grid sensor as shown in the last column of Table I. This is confirmed by the observations. The theoretical prediction assumes that the reactivity is proportional to the ratio of the square of the perimeter to the area. The \( S/B \) values for several of the measurements are given in Table II. The ratio of the \( S/B \) for both NO and \( H_2S \) initially after sensor assembly. This agreement between the theoretical prediction and the measured values is excellent and gives support to the hypothesis that the reactivity depends on the geometry of the electrode and is proportional to \( P^2/A \). The importance of edge effects on electrocatalyst was substantiated with recent experiments using an ultrafine-grid sensing electrode in which the analytical signal exceeded that observed for the standard sensor [16].

For comparison, consider a hypothesis congruent with a catalytic site model. Assuming that the signal depends linearly on the area and on the perimeter

\[
S = aA + bP
\]

and that the background depends linearly on the area

\[
B = cA
\]

where \( a \) and \( b \) are proportional to the catalytic activity per unit area and per unit length, respectively, and \( c \) is a background constant per area. For the fine- and medium-grid sensors, the area is approximately fixed, which implies that the maximum possible value of \( S/B \) would be \( (P/A)_{\text{fine}}/(P/A)_{\text{medium}} = 3.49 \). This value is much less than the experimentally observed value of 11.6. Note that this case occurs when \( a = 0 \). For \( a > 0 \), the ratio \( (P/A)_{\text{fine}}/(P/A)_{\text{medium}} \) would be less. Thus, a theory that predicts a linear dependence of the signal on \( P \) and \( A \) does not adequately represent the data.

After 21 days, the \( S/B \) value for the fine grid exhibited slight improvement (i.e. from 8.5 to 12 for NO), while the \( S/B \) for the medium grid made dramatic improvement (i.e. from 0.77 to 8.5 for NO). This reduced the ratio of \( S/B \) to 1.4, much less than the 11.6 originally observed. No explanation for this instability of response can be found, although the physical appearance of the fine grid appeared to degrade upon use (expansion, contraction, dry, and wet conditions appear to cause cracks and imperfections in the gold electrode surface). It is not unusual for electrocatalysts (and catalysts in general) to degrade with time.

Further analysis of the relative signals for the medium- and fine-grid sensors reveals additional insights into the structural effects upon sensor performance. Table III gives a summary of the \( S/B \) values for the fine- and medium-grid sensors normalized to the value for \( H_2S \). Note that, immediately after assembly (day 1 results), the microfabricated electrodes had precisely the same relative sensitivity to NO and \( H_2S \). The fine-grid sensor’s relative sensitivity does not change with time. However, the proportional response to NO for the medium-grid sensor has increased by a factor of 3.3 and is beginning to look more like the standard-type sensor. The standard sensor’s \( S/B \) ratios, however, are the same order of magnitude as the fine-grid electrode as shown in Table II.

Although the signal for the fine-grid sensor dropped by a factor of 1.4 from day 1 to day 21, the \( S/B \) actually improved by a factor of 1.4 (and it was exactly 1.4 for both NO and \( H_2S \)). The \( S/B \) can be viewed as a measure...
of the relative catalytic activity (or effective number of sites per unit surface area) of the gold working electrode surface. This has important consequences in sensor design because it means that surrogate gases or even absolute methods of device calibration may be possible by control of the electrode geometry and the measurement of sensor signals for surrogate gases.

The difference in initial responses of the fine- and medium-grid microfabricated electrodes is largely determined by differences in the electrode geometry. The intrinsic background signals for the several sensors are approximately equal, as is the total gold electrode area. Both the fine- and medium-grid sensing electrodes initially had the same relative response to NO and H₂S. This may be due to the initial similarity in electrode design, the difference being primarily that of scale. As time progresses, the swelling of the Nafion layer and other weathering effects cause the medium-grid sensor to fracture and become more like the porous composite electrodes (standard electrode). The fine-grid structure may be stronger and, therefore, retain its integrity as an electrode and its characteristic catalytic activity longer.

V. Conclusions

Several new amperometric electrochemical sensor structures were fabricated and the analytical characteristics of the resultant sensors were compared. The results lead to several important conclusions and consequences.

1) Methodology can be developed to fabricate integrated amperometric electrochemical sensors (including the electrolyte) using microelectronic device technology. Physical structures containing the entire sensor were fabricated using microfabrication technology with the resulting amperometric sensor being only a few millimeters square and a few micrometers thick.

2) Electrochemical responses were obtained for microfabricated working (sensing) electrodes. This means that the different structures fabricated have significant electrocatalytic activity and the structural effects can be isolated from the thermodynamic effects.

3) The qualitative response of the sensor appears independent of geometry while the quantitative response characteristics are clearly dependent upon the geometry.

4) The response time as well as signal-to-background ratio of the microsensor can be substantially improved over existing amperometric sensor geometries.

5) Sensor characteristics may be "engineered" by selection of the electrode design, fabrication technology, and precise control of the sensor geometry. Careful selection of materials of construction and the process can alter the electrocatalytic properties.

It is possible to use microfabricated structures to study response as well as to improve the sensor's analytical characteristics. It should be possible to build precise structures with exceptionally high reproducibility, engineered sensitivity, and selectivity for a given application. A complete theory and validated sensor response model cannot be constructed from the limited amount of experimentation that was presented here. Characterization of more structures will be required to develop additional quantitative relationships between electrode structure and sensor reactivity. Additional work is planned to understand the fundamental causes of the structural effects in the electrocatalysis and in gas sensor response.

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REFERENCES


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