Project ID: **65421**

Project Title: **Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature-Programmed Gas Microsensors**

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DoE Progress Report **June 15, 1999**

Project Title: Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature-Programmed Gas Microsensors

Principal Investigator: Dr. Steve Semancik

Period Covered by Report: October 1, 1998 to May 31, 1999

Recipient Organization: Process Measurements Division
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Anticipated Unexpended Funds at NIST for 1st Budget Period (10/1/98 to 11/30/99): approximately $10,000

Introduction

This Report discusses progress and accomplishments during the initial 8 months (October 1, 1998 through May 31, 1999) of a 3-year project. Work is being performed through a collaboration between NIST and the Institute for Systems Research at the University of Maryland (PI: Professor T. J. McAvoy

This three year project has a goal of producing a scientific database for conductometric sensing materials and using this information to advance gas microsensor technology. The technology will use arrays of miniature solid state devices in which adsorption of target analytes produces measurable and quantifiable changes in conductance on a suitably-chosen collection of sensing materials. Microsensor development evolving from this work would allow monitoring devices to be tailored for a range of Department of Energy hazardous waste sites (and for other applications). The primary project objectives for this three year program, summarized below, have not changed from those described in our proposal document. The key overall objectives are:

- **Fabrication** of microhotplate arrays as highly efficient platforms for film growth studies,

- **Surveying** the fabrication and properties of sensing films and relating sensing performance to oxide microstructure and additive metal loading and nucleation,

- **Providing data** on the adsorption/desorption/reaction characteristics of gases on sensing films, and relating conductance changes to adsorbate type and concentration,

- **Analyzing** gas composition using multi-element and temperature-programmed gas sensors operating on a basis of neural network modeling and pattern recognition.

Graduate Student Involvement

Two students from the University of Maryland are currently involved in this project: Mr. Balaji Panchapakesan is a doctoral student in the Department of Mechanical Engineering, and Mr. Junhua Ding is a doctoral student in the Department of Chemical Engineering. Both students perform experiments on a regular basis at NIST. There are also two NIST staff members involved in the project, Mr. Michael Carrier and Ms. Maria Aquino-Class, who are continuing their undergraduate and graduate studies, respectively.

Progress and Results on Objectives for First Budget Period (Year 1 and beginning of Year 2, the 14-month, defined by DoE Program Officers -- 10/1/98 to 11/30/99)

Progress on the first four tasks of this project, through 5/31/99, is described in this Report. These tasks, which are foundational to the entire project, are concerned with development of microplatforms, screening of materials, surface studies of interfacial structures, and equipment construction for desorption array experiments. We have been able to make rapid progress on microstructure control of materials and on the data-based modeling of sensor performance using existing (4-element) microhotplate arrays. The work is significant in that we are developing, for tin oxide thus far, relationships between microstructure, sensitivity, chemical selectivity, and long-term stability. The interfacial and thermal desorption studies will be making use of new microhotplate structures. During the current reporting period, these devices have been designed using CAD tools and the designs have been sent to a silicon fabrication foundry. Preparation for the desorption array experiments is proceeding, with the vacuum system and surface analytical tools designed and under assembly.

The labels on the subheadings below represent task elements in our original proposal (Y1.1 is Task 1 in Year 1, and so on).

Y1.1. Microplatforms

Micromachined structures are a critical part of this program. They are used both as platforms for fabricating solid state gas sensors, and as research tools. Figure 1a shows a micrograph of a 2 x 2, 4-element microhotplate array. Existing devices like this have been employed in our initial materials screening reported below. New platforms have

been designed for this project to be used as research tools for performing larger "growth/performance" studies, and for characterizing surface interactions. Some of these new platforms are shown in the micrograph and schematics of Figures 1b-1d. The micrograph in Figure 1b shows the structure of a 16-element array being developed for enhanced sensing film processing and performance studies. (On-chip control electronics consisting of multplexing, sample-and-hold, and amplification circuits for running the microhotplates are being included as part of our design submission to a silicon foundry in early June.) The use of more elements enables a more efficient means of examining sensing materials combinations and film processing. The increased number of elements also allows the incorporation of multiple sensing materials, varied modes of operation (fixed temperature and temperature-programmed), and system redundancy for reliability.

To learn more about the surface properties and interactions related to gas sensing, we are developing platforms tailored for the requirements of surface analytical tools. One such platform, shown in Figure 1c, is a 340-element array for adsorbate coverage and desorption studies (see also Y2.1 below). The large sample area is needed to generate enough desorbing molecules for mass spectrometer detection, while the small size of each element preserves the fast thermal speed needed for temperature pulsing. This structure will provide the first data that correlate transient electrical conductance measurements (measured with a number of on-array electrical contacts) in a sensor with thermally desorbed species. A second device, shown in Figure 1d, is a large (600 micron), flat single microhotplate element, which will provide the large, uniform surface needed for spectroscopic techniques such as x-ray photoemission spectroscopy, Auger spectroscopy, and secondary ion emission spectroscopy. We expect these tools to yield chemical state and composition data on sensing films both after fabrication and after exposure to analyte gases (see also Y1.3 below).

We have been developing methods to etch (micromachine) and pattern gold (for electrical contacts) on 16-element arrays, obtained through MOSIS (Metal Oxide Semiconductor Implementation Service - a silicon foundry). Challenges related to performing photolithography on the small, highly-contoured chips containing 16-element arrays have been overcome in this reporting period. A data acquisition system for controlling 16-element arrays, and for handling output signals has been developed. Work has also begun on processing 48-element devices with on-board multiplexers, for addressing element inputs and outputs. Second generation devices (including 16, 48 and 340 element arrays) are expected to be shipped to us from MIT Lincoln Laboratories during June. These devices will be processed (at MIT) with chemical mechanical polishing (CMP) to produce flatter device topologies (expected to improve microsensor reliability and simplify analytical studies on the sensing films). Once the Lincoln Laboratory wafers are received, we will develop the protocols for micromachining the devices within them.

Y1.2. Screening of Materials

Sensing material types and microstructures must be optimized for particular monitoring applications. All studies of materials processing and the performance of these materials in the microsensor format have been done, to date, using 4-element arrays. In order to find an optimal form for oxide base materials, we have developed/examined a variety of methods for depositing SnO_2, each of which leads to its own characteristic type of

microstructure. Previously, we have published descriptions of a self-lithographic CVD process which uses thermal activation to achieve selected-area deposition on microhotplates. During the beginning of this project, we extended the processing for SnO_2 to evaluate films produced by reactive sputter deposition, and by drying sol-gels and nanoparticle suspensions (see also reference 1). Films fabricated by seeding the SnO_2 CVD growth with small metal particles have also been studied. Films prepared with seed layers and nanoparticle suspensions have reduced grain size, leading to enhanced gas sensitivity and more stable operation, and hence are front-runners for more general studies as the project continues. Further details on the seeding results are provided in reference 2, and in the auxiliary report provided to DoE by the University of Maryland. A second CVD system is being commissioned in order to do parallel deposition research on a number of other semiconducting oxide materials.

We have also begun screening the performance of various surface-dispersed catalytic additives (on seeded SnO_2 films). The catalysts were deposited by evaporation to several equivalent monolayer thicknesses, and then the microhotplates were heated to affect the formation of a noncontinuous layer of catalyst particles on the SnO_2 surface. The array studies simultaneously examined three catalytic metals, Pt, Pd and Cu. Initial results correlating sensitivity to the type and dispersion of the catalytic additive are being investigated further to establish reproducibility (see also Y1.3).

Improvements to sensor testing hardware have been made in order to increase the volume of data associated with the larger number of samples to be tested. A second test system has been constructed and put into operation and a variety of target analytes in air (dilute concentrations of acetone, ethanol, benzene, methanol, and toluene in air) have been procured. New software has also been developed for automated switching of concentrations and analytes in our testing equipment. In connection with these efforts, we have initiated preliminary testing of sensitivity and stability as they relate to neural net training and predictive model development (a collaborative activity with the University of Maryland).

Y1.3. Interfacial Structures

Interfacial characteristics dominate the initial sensing interactions and are critical to understanding the overall transduction mechanism. Efforts at elucidating interfacial processes in conductometric sensing have proceeded on two fronts. As discussed in Y1.2 above, array studies of the controlled deposition (and annealing) of low coverages of Pt, Pd and Cu catalytic additives (onto SnO_2) have been carried out. In sensing methanol in air, Pt/SnO_2 was found to produce higher sensitivity than supported Cu or Pd, but it was also more susceptible to fouling in operation. This observation points up the need for planned studies of the best overall temperature range for sensor operation with each type of catalytic additive.

A “macrosample” stage has also been constructed so that the same processing methods used on microhotplates can be used to produce samples ~ 1 cm x 1 cm, a size more suited to various structural and compositional analysis techniques. This stage has been tested in oxide film deposition experiments in our CVD Facility, and can be applied for low coverage catalytic metal deposition, as well. Spectroscopic portions of the interfacial

studies of metal/oxide interfaces will also proceed when the microplatforms designed for surface analysis, mentioned in Y1.1 above, come on-line.

Y2.1. Desorption Array Studies

Temperature-dependent adsorption/desorption phenomena are the basis on which temperature-programmed sensing is built. A specially-outfitted vacuum system is required for the desorption studies will correlate electrical changes to adsorbate coverages for sensing films. Two types of experiments will be done: one involving a static-mode gas dosing followed by pulsed desorption from a 340-element microarray; and, one that will explore dynamic features with microelement temperature pulsing, beam dosing to examine elevated pressure regimes, and differential pumping. Construction of this system is underway. The vacuum chamber and a mass spectrometer have been procured, as have the multiple pumps for the system. Drawings for the static mode (macro) sample holder, beam doser and differential pumping stage have been submitted to the NIST Shops. Catalytic metal samples to be used in first tests of the system have been selected. The 340-element microarray platforms being fabricated to allow electrical characterization and coverage measurements are expected to arrive from Lincoln Laboratories in June, and will allow studies of varied metal/oxide samples.

Y2 and Y3 Preliminary Modeling Efforts

In the proposal timeline, the major modeling effort is scheduled to be carried out in the second and third years of the grant (Year 2-Items 3 and 4, Year 3-Item 2). As a precursor to that work, we are investigating certain critical issues. First, we have used chemometric techniques to determine the level of a single component in air. (A paper based on this work, listed below, has been accepted for the SPIE Conference to be held in Boston, in September 1999.) Secondly, we have studied the long-term stability of microhotplate gas sensors, which is of considerable significance for the practical use of sensors, and for developing training sets for modeling.

Significance of Findings

Results to date have: 1) provided demonstrations of the use of micromachined platforms for developing materials processing routines, both for semiconducting oxides and low coverage catalytic metals; 2) shown a number of deposition approaches to be viable with the microhotplate elements -- these methods allow for convenient fabrication of materials combinations (metals over oxides) that will be examined in the continuation of the project; 3) observed higher sensitivities for oxide films with fine microstructure, including those produced by seeding and nanoparticle processing; 4) observed catalytic metal enhancement of sensing for oxide films in 4-element array studies of different metals and dispersions; 5) demonstrated the utility of response screening protocols for correlating sensing film types with detection of target analytes, and for establishing device stability; and, 6) indicated how new microarray designs, including 16 and 48 elements, will amplify the value of array research studies – the implications can be expected to reach beyond gas sensing to other technological areas.

Manuscripts for the Period*

1. R.Walton, C. Kendrick, B. Panchapakesan, D. DeVoe, R. Cavicchi, S. Semancik, "Processing Methods for Selected Area Film Deposition and Preparation on Microsensor Platforms Using Thermal and Potential Control", *Digest 10th International Conference on Solid-State Sensors and Actuators*, Sendai, Japan, Vol. 1, June 1999, pp. 676-679.

2. B. Panchapakesan, D. L. DeVoe, R. E. Cavicchi, R. M. Walton and S. Semancik, "Micromachined Array Studies of Tin Oxide Films: Nucleation, Structure and Gas Sensing Characteristics", Proceedings of the MRS, Spring 1999 (in press).

Presentations (Completed or Accepted)*

1. "Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature Programmed Gas Microsensors", Environmental Management Science Program - Tank Focus Area Workshop, Richland, WA, 11/17/98 [R. E. Cavicchi]

2. "Micromachined Array Studies of Tin Oxide Films: Nucleation, Structure and Gas Sensing Characteristics", MRS Spring National Meeting, San Francisco, CA, 4/7/99 [B. Panchapakesan]

3. "Processing Methods for Selected Area Film Deposition and Preparation on Microsensor Platforms Using Thermal and Potential Control", 10th International Conference on Solid-State Sensors and Actuators, Sendai, Japan, 6/7/99 [R. M. Walton]

4. "Microarrays as Platforms for Gas Microsensor Development and Efficient Materials Research", accepted for presentation at the ACS National Meeting, New Orleans, 8/24/99 [S. Semancik]

5. "Modeling Microhotplate Gas Sensors", accepted for presentation at the ACS National Meeting, New Orleans, 8/24/99 [T. J. McAvoy]

6. "Microhotplate Gas Sensor Arrays", accepted for presentation at the SPIE International Symposium on Environmental and Industrial Sensing, Boston, MA, 9/17-22/99 [R. E. Cavicchi]

7. "Solid State Gas Microsensors for Environmental and Industrial Monitoring" accepted for presentation at the SPIE International Symposium on Industrial and Environmental Sensing, Boston, MA, 9/17-22/99 [S. Semancik]

8. "Quantification of a Single Component Gas in Air with a Microhotplate Gas Sensor Using Partial Least Squares Techniques", accepted for presentation at the SPIE International Symposium on Industrial and Environmental Sensing Boston, MA, 9/17-22/99 [J. Ding]

* funding includes that provided by DoE, and by NIST

Figure 1 on next page

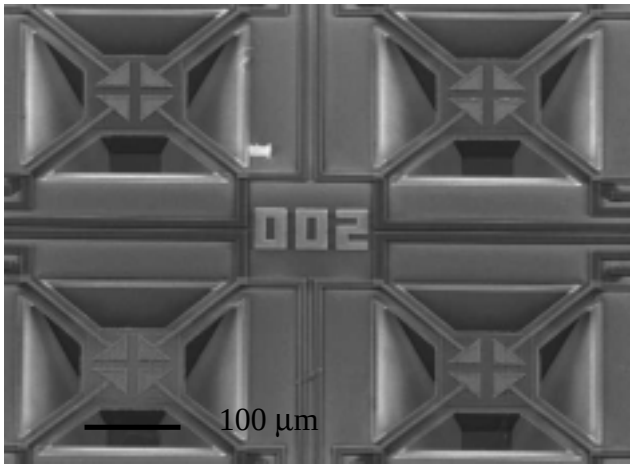

Figure 1(a) 4-element microhotplate array used for initial materials studies and microsensor tests.

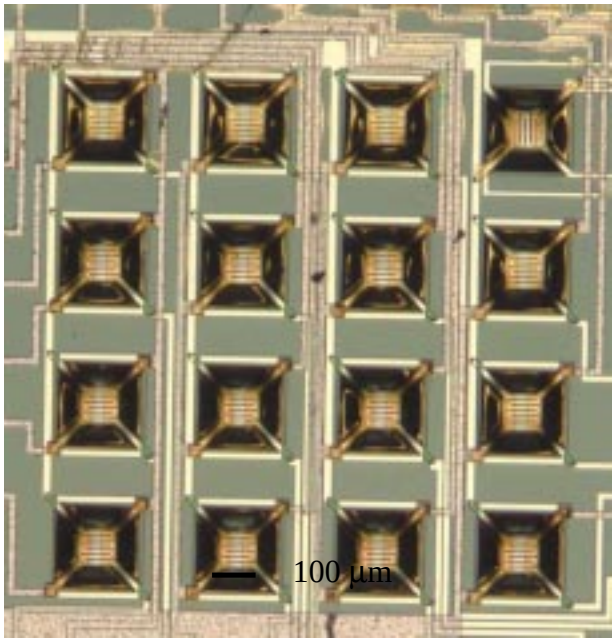

Figure 1(b) 16-element array developed for more effective process-performance studies.

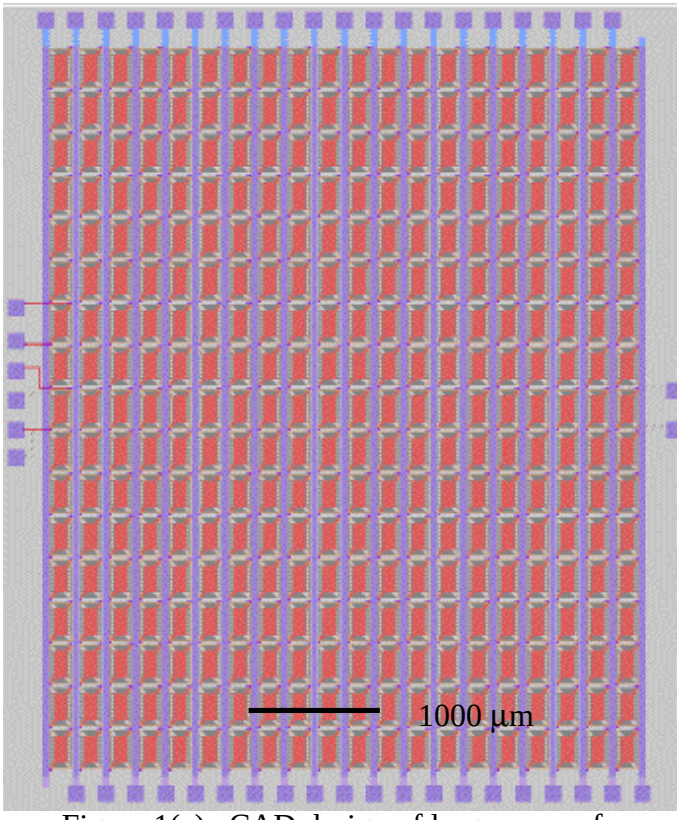

Figure 1(c) CAD design of large array of microhotplates for correlating adsorbate coverages with electrical changes.

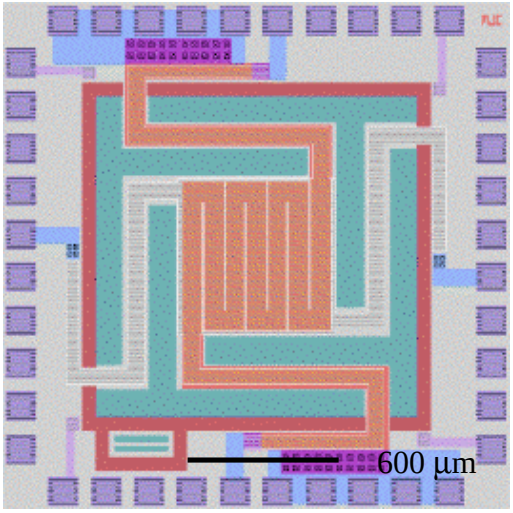

Figure 1(d) CAD design of large (600µm) microhotplate for surface analytical studies .