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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Number of Graduate Students and Postdoctorates Involved:
2 doctoral thesis students in Chemical Engineering and Mechanical Engineering from University of Maryland; also, 2 NIST staff members who are continuing their undergraduate and graduate studies

DoE Problems Addressed:
The primary DoE problem area impacted by this project is subsurface contamination, although potential also exists for use of our findings in the tank focus area. These studies of oxide-based gas sensing on micromachined platforms provide new insights into chemical sensor principles, particularly involving thermal control of analyte-surface interactions. Enabling technology and information on sensing materials are being developed for rapid waste characterization, and for monitoring spatial variability and transport in the vadose zone for analytes with sufficiently high vapor pressures.

Research Objective:
This research project seeks to produce, and demonstrate the utility of, a scientific database for oxide conductometric sensing materials that relates materials performance (sensitivity, selectivity and stability) to composition, microstructure and temperature. This information and the capabilities derived from it would be applied to developing a robust, low cost and application-tunable chemical monitoring technology based on micromachined platforms.

Research Progress and Implications:
The Report summarizes progress through the end of February, 2000, representing efforts for the first 17 months of a 3-year program. This program is creating the scientific and technical basis for gas and vapor sensors that work on a conductometric principle (adsorbed gases produce a change in electrical conductance) using low power, micromachined device platforms. In order to develop oxide-based microsensor arrays that can be tuned by choice of sensing film and temperature programming, we have worked in four parallel project areas: 1) development of advanced MEMs structures and arrays (platforms) with appropriate chemical and diagnostic functionality, 2) study of the process/property/performance relationships for semiconducting oxide films and metal/oxide interfaces, 3) mechanistic studies that examine temperature-dependent detection phenomena by relating changes in sensing film conductance with transient adsorbate coverages, and 4) combining mechanistic information and response databases with signal processing methods. More generally, this project has important implications relating to the use of microarrays and combinatorial methods in materials research, and in the examination of fast transient techniques to relate surface chemical and surface electronic phenomena.

Platforms *Micromachined structures are a critical part of this program. They are used both as platforms for fabricating solid state gas microsensors, and as research tools in efficient studies of materials*. Our original sensing device structure consisted of four individually-addressable and thermally isolated "microhotplates" (100 micron x 100 micron), which could be temperature controlled between 20°C and 500°C (8°C/mW and 3ms time constant). New platforms with flat surface topology (produced by chemical mechanical polishing) have been designed, fabricated and micromachined for this project. Arrays with 16, 36 and 48 elements are being employed as research tools for performing larger "growth/performance" studies, and for characterizing surface interactions. These new platforms include a 16-element array with on-chip control electronics, consisting of multiplexing, sample-and-hold, and amplification circuits, for running the microhotplates. An external data acquisition system used for controlling 36-element arrays, and for handling output signals has also been developed. The use of more elements enables a more efficient means of examining sensing materials combinations, film processing, and reproducibility. 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 is a 340-element array for adsorbate coverage and desorption studies (see 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 speed needed for rapid 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. Another new device, a 600 micron, flat, single microhotplate element, is being developed to provide the large, uniform surface needed for spectroscopic techniques such as x-ray photoemission spectroscopy and Auger spectroscopy. We expect these tools to yield chemical state and composition data on sensing films both after fabrication and after exposure to analyte gases.

Array Studies of Materials Processing and Performance *Sensing material types and microstructures must be optimized for particular monitoring applications. Microhotplate arrays provide a very efficient platform for temperature-dependent film deposition and temperature-dependent response measurements.* During the first year of this project, studies of oxide film growth/performance were done using 4-element arrays. In recent months we have amplified the efficiency of our studies on microstructure controlled oxides by moving to 36-element arrays. A variety of methods for depositing SnO_2, each of which leads to its own characteristic type of microstructure, has been examined. These methods included self-lithographic CVD (using thermal activation to achieve selected-area deposition on microhotplates), reactive sputter deposition, drying sol-gels and nanoparticle suspensions (see also reference 1). Films fabricated by seeding the SnO_2 CVD growth with small metal particles (Ni, Co, Fe, Cu, Ag) have also been studied with 36-element arrays. Film reproducibility, as judged by SEM and sensing response, was investigated by making whole columns of films by the same recipe. Films prepared with seed layers and nanoparticle suspensions have shown reduced grain size, leading to enhanced gas sensitivity (for a number of gases in air). A second CVD system has been 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) using 36-element arrays. The catalysts are being deposited by evaporation to varied (1-7 nm) thicknesses, and then the microhotplates are heated to affect the formation of a noncontinuous layer of catalyst particles on the SnO_2 surfaces. As for the oxide response evaluations, these samples will be studied in a collection of gases (including dilute concentrations of acetone, ethanol, benzene, methanol, and toluene, in air) to develop temperature-dependent sensitivity data. Improvements to sensor testing hardware have been made in order to increase data handling to the level required for larger numbers of samples in the larger arrays.

Mechanistic Studies *Temperature-dependence of adsorption/desorption, reaction, and other phenomena are the basis on which temperature-programmed sensing is built.* A specially-outfitted vacuum system is required for the desorption studies which will correlate surface 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 now complete. The vacuum chamber, mass spectrometer and multiple pumps have been put through initial tests involving desorption from macrosamples (~ 1 cm2). High resolution and rapid thermal imaging has been used to examine the temperature uniformity of the microhotplate array elements. Sample preparation on 48-element and new 340-element arrays are now underway.

Since rapid thermal modulation is used in the temperature programmed operation of the microhotplate sensors, experimental measurements were made (in collaboration with the University of Maryland) to determine the role that trap states might play in the measured electrical responses following purposeful thermal transients. To establish a non-chemical (no analyte) environment, measurements were made in an argon background, and an air background. Modeling of these data with shallow trap states provides good agreement with the measurements.

Signal Processing *Signal processing studies of the rich data content from temperature-programmed individual microsensors and array elements are critical for proper analyte recognition and quantification.* The major modeling effort (a collaborative activity with the University of Maryland) is scheduled for the latter two-thirds of this project, when multi-element, temperature dependent databases are available. As a precursor to that work, we have initiated preliminary testing of sensitivity and stability as they relate to neural net training and predictive model development. Preliminary findings on several types of films show trade-offs between sensitivity, stability and selectivity. We have also used techniques based on earlier work with temperature programmed sensing to recognize a single analyte in air and estimate its concentration (reference 5).

Planned Activities

In the remainder of FY00, efforts will focus on:

- Platforms - development of improved metallization for the microdevices and research arrays
- Materials Studies – measurements on 36-element arrays producing temperature-dependent databases of sensitivity for metal/oxide film combinations for a spectrum of analytes in air; critical studies to establish stable microdevice operation and acceptable sensitivity and selectivity (required for signal processing work)
- Mechanistic Studies – initial measurements from 340-element arrays directly correlating conductance changes with desorbed species
- Signal Processing – selection of stable films for training experiments and development of models for single analytes (in air) within acceptable analyte concentration ranges; interactive experimental design from database results to guide temperature programmed operation

Activities to be Emphasized in FY01:

- Design of one or more demonstration problems (with DoE input)
- Selection of candidate films for demonstration arrays, and investigation of level of film reproducibility
- Evaluative studies of devices and signal processing in demonstrations involving analyte mixtures
- Exploration of methods to enhance long-term operation

Information Access

• Published Papers

1. R.Walton, C. Kendrick, B. Panchapakesan, D. DeVoe, R. Cavicchi and S. Semancik, "Processing Methods for Selected Area Film Deposition and Preparation on Microsensor Platforms Using Thermal and Potential Control", *Digest of the 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) Vol. 574, pp. 213-218.

3. R. E. Cavicchi, S. Semancik, R. M. Walton, B. Panchapakesan, D. L. DeVoe, M. Aquino-Class, J. D. Allen and J. S. Suehle "Microhotplate Gas Sensor Arrays", Proc. SPIE International Symposium on Industrial and Environmental Sensing (Boston, MA, 9/17-22/99) Vol. 3857, pp. 38-49.

4. R.Walton, R. Cavicchi, S. Semancik, B. Panchapakesan, D. DeVoe, M. Aquino-Class, J. Allen and J. Suehle, "Solid State Gas Microsensors for Environmental and Industrial Monitoring", Proc. SPIE International Symposium on Industrial and Environmental Sensing (Boston, MA, 9/17-22/99) Vol. 3853, pp. 254-261.

5. J. Ding, T. Mc Avoy, R. Cavicchi and S. Semancik, "Quantification of a Single Component Gas in Air with a Microhotplate Gas Sensor Using Partial Least Squares Techniques", Proc. SPIE International Symposium on Industrial and Environmental Sensing (Boston, MA, 9/17-22/99) Vol. 3856, pp. 162-170.

• Presentations:

14 presentations, on work that was funded by DoE, and by NIST

• Web Access: Information relating to our microsensor program can be found at http://www.nist.gov/chemsensors