

FINAL REPORT

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

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3. Executive Summary

The spectrum of chemical monitoring problems faced by the Department of Energy (DoE) at its hazardous waste sites is formidable. It is likely that a variety of existing types of instrumentation will be applied in the years ahead, with varying degrees of practicality and success. A tremendous impact could be realized, however, if instrumental methods could be supplemented by a low-cost, reliable sensing technology for continuous monitoring of a range of species, including, for example, volatile organics, chlorinated hydrocarbons, ammonia, and hydrogen. To meet the diverse gas and vapor monitoring needs at DoE hazardous waste sites, the sensing system must offer, inherently, an adaptability to match the wide variety of analytes and environmental conditions that will be encountered (in tank vapor spaces, and at locations with contaminated soil or groundwater.) The purpose of this project was to investigate scientific and technical concepts that could enable a MEMS-based chemical sensing technology (developed in its foundational form at NIST during early and mid 1990's) to be made **tunable** for multiple target analytes in differing types of backgrounds relevant to DoE waste storage and remediation.

The basis of our sensing approach involves using arrays of “conductometric” microsensor elements, which undergo measurable changes in their electrical conductances as gases absorb, react, and desorb from their surfaces. Tunability was to be introduced by employing sensing films of varied composition within the arrays, and operating them at different fixed or time-varying temperatures. However, matching the appropriate sensing materials to the varied analytes and background atmospheres of interest, and then selecting operational temperatures which can provide the necessary analytical information, produces a challenging combinatorial problem.

Several key accomplishments contributed to the realization of our goal of demonstrating a tunable, MEMS chemical sensing technology. The first major accomplishment of this 3-year project was the development of a systematic research infrastructure that allows one to efficiently optimize the properties (composition, microstructure, thickness, additive loading, etc.) of sensing

films for varied monitoring problems. Our approach has been demonstrated on (but is not limited to) semiconducting oxides (such as SnO₂ and TiO₂), with and without surface dispersed metals (including Pt, Pd, Ni, Cu, Au, etc.). We chose this class of conductometric materials because they are not only sensitive in many instances, but are also robust for deployment in the kinds of aggressive environments sometimes present at DoE sites. Specialized microscale research tools were developed for our studies based on the same micromachined “microhotplate” device structure which has been used in fabricating prototype microsensors. 16-element and 36-element arrays were designed to conduct parallel experimentation on multiple samples in order to establish processing-performance correlations, for tuning sensor arrays, in an efficient manner.

Our second major accomplishment involved applying the multielement microhotplate approach to produce temperature-dependent **databases** on sensing materials responses to suites of gas phase analytes. This data was collected as microhotplates were operated in both fixed-temperature, and dynamic, temperature programmed sensing (TPS) modes, in which rapid (~10 ms) temperature excursions were used to purposefully alter gas-sensing film interactions, and create response “signatures”.

The mechanistic basis of the high information content possible in the TPS mode of sensing was investigated in greater detail through the development of another type of specialized microarray platform that included 340 microheaters, with an ability to elevate the temperature of sensing samples at 10⁶ °/s (with real time temperature measurement). Our third major accomplishment was demonstrating the utility of such platforms for examining the nature of adsorbate transient phenomena. This ability was realized following the construction of a custom ultrahigh vacuum chamber fitted with an apertured mass spectrometer, which was used to analyze the gases evolving under pulsed temperature control from 340-element “transient” arrays. Information from these mechanistic studies provided important insights for guiding our data collection in the TPS sensing mode.

Our overall goal of demonstrating the use of single and multiple conductometric microsensors as tunable chemical monitoring devices was realized in the third year of the project. It was at this point that all the component efforts reached a level of maturity which allowed us to fabricate microsensor arrays from different types (different processing) of films (some more sensitive, stable, and selective than others), and to collect databases that were then subjected to analyses by chemometric and neural network methods. These analyses demonstrated an ability of differing materials and differing temperature schedules for recognizing and quantifying analytes including trichloroethylene, dichloromethane, benzene, methylbenzene, formaldehyde, acetone, toluene, methyl ethyl ketone, butanone, ethanol, methanol, carbon monoxide and hydrogen, in air.

Even as progress continues on remediation techniques for the DoE waste sites, continuous analysis of the site chemistry will remain a critical need for decades to come. The primary DoE problem areas impacted by this project are monitoring of subsurface contamination and waste storage tanks. The technology described here is a low-cost, robust, miniaturized, and field-deployable alternative for chemical monitoring. It is readily adaptable to cone penetrometer and other probing hardware. It consists of a generic device platform with sensing materials and operating modes that can be tuned for multiple DoE measurement needs. The MEMS-based approach also allows the sensors to be operated at low power levels compatible with powering by batteries.

It is important to note that while our efforts were directed toward developing tunable microsensor devices, certain components of our work have more far-reaching implications. For example, we demonstrated methods of microarray combinatorial science, and developed microscale deposition and processing techniques for thin films. We also developed a new technique for studying oscillatory reactions, and used it to investigate microscale crosstalk effects. The fast adsorbate transient methods we developed, involving mass spectrometry electrical probing of

surface properties, are critical to understanding gas sensing mechanisms, but they also can contribute to basic understanding in other fields of surface and interfacial science.

This project was centered in the Chemical Science and Technology Laboratory at NIST where most of the research was carried out. However, important contributions were made by researchers from other institutions in various technical component areas. MIT-Lincoln Laboratories performed foundry runs to produce wafers of our microdevice designs. The University of Maryland contributed on studies of basic thermal response properties and microstructure engineering of oxide microsensors, as well as to signal processing sensor data by neural networks. Arizona State University used chemometric signal processing to analyze microsensor responses, while work of a Guest Researcher from the Israel Atomic Energy Commission focused on neural network modeling of our fixed temperature and dynamic temperature databases.

There was considerable student involvement in this project. One B.S. level student and one M.S. level student, both employed by NIST, were active in the project. In addition, two full doctoral theses and a portion of a third were connected to work on this project. The participating students, along with their thesis title, and academic institution follow:

- J. Ding, "Signal Processing and Dynamic Modeling of Microhotplate Sensors," University of Maryland (2000).
- B. Panchapakesan, "Nanoparticle Engineering and Control of Microhotplate Gas Sensor Performance," University of Maryland (2001).
- B. Dable, "Optimization and Validation of Multidimensional Chemical Analyses," Arizona State University (May, 2002).

Copies of these theses are (or will be) available through University of Michigan / Bell and Howell Thesis Service (Web availability at www.lib.umi.com).

This project reached its overall goal. The tunable sensing technology, which we describe in greater detail in the remainder of this document, is now poised for field testing at one or more DoE sites. The findings of the study also directly enable further efforts of other microscale temperature-controlled functions (such as reactive filters and preconcentrators) which can be combined with our microsensor “detector” to form microanalytical systems with even broader analytical capabilities.

4. Research Objectives

It is well known that a variety of gas- or vapor-induced property changes can be employed in developing solid state chemical microsensors [1, 2]. For example, one can sense by monitoring a given sensing material for changes in mass [3], temperature [4, 5], electrical conductance [6-8], ionic conductance [9-12], capacitance [13-17], or optical properties [18-21]. Each method employs an associated material suited both to the analytes being measured and the physical property being recorded. Our efforts in this project have been directed toward microdevices that monitor electrical conductance changes caused by gas adsorption, reaction and desorption. Primary research objectives, related to producing and demonstrating the utility of, a scientific database for oxide conductometric gas/vapor sensing materials, included:

- establishing temperature-dependent databases for the adsorption/desorption/reaction characteristics of gases on sensing films, and relating measured interfacial conductance changes to adsorbate type and concentration
- utilizing adsorption/conductance databases with chemometric and neural network modeling as the basis for designing multielement and temperature programmed gas sensors, with a microhotplate-based sensing demonstration
- demonstrating the utility of micromachined, microhotplate arrays as highly efficient platforms for surveying the fabrication and properties of sensing materials
- establishing the quality and potential of sensing performance as a function of oxide microstructure and additive metal loading and nucleation

Creation and analysis of materials-dependent and temperature-dependent databases is critical to developing a robust, low cost and widely deployable chemical monitoring technology. The technology we employ uses miniature solid state devices in which adsorption of target analytes produce measurable and quantifiable changes in conductance on a suitably-chosen collection of active 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.

Monitoring capabilities in our approach are centered on a generic, micromachined (MEMS) device structure, called a “microhotplate”. These devices have lateral dimensions $\sim 100 \mu\text{m}$, can measure conductance of active sensing films (with integrated microelectrodes), and also control their temperature on a very fast time scale ($\sim 1 \text{ ms}$) [22, 23]. Leading into this project, and during its course, other sensor groups, world-wide, have begun working on spin-offs of the NIST microhotplate technology [24-27].

The core of this research program involves experimental measurements to produce a direct correlation of interfacial conductance changes with the interfacial adsorption phenomena from which they result. Target analytes to be employed in our database development and sensing technology demonstrations included trichloroethylene, dichloromethane, benzene, methylbenzene, formaldehyde, acetone, toluene, methyl ethyl ketone, butanone, ethanol, methanol, carbon monoxide and hydrogen. To introduce selectivity, and an ability to analyze gaseous mixtures, we use microhotplate elements in an array format, which is illustrated schematically in Figure 1. Tunability of our conductometric microsensors, a key aspect of the study, occurs when one selects different sensing films for the elements of the array, and operates them under different fixed and time-varying temperature programs. We have limited our investigations here to semiconducting oxide films (SnO_2 , TiO_2), with and without surface-dispersed metal additives (including Pt, Au, Fe, Ni, Pd and Cu); these are robust materials that can stand up better to harsh DoE environments than most other sensing materials (eg. – polymers). The conductometric response information obtained from multiple sensors operating at different temperatures serves as the input stream to chemometric and neural net signal processing tools.

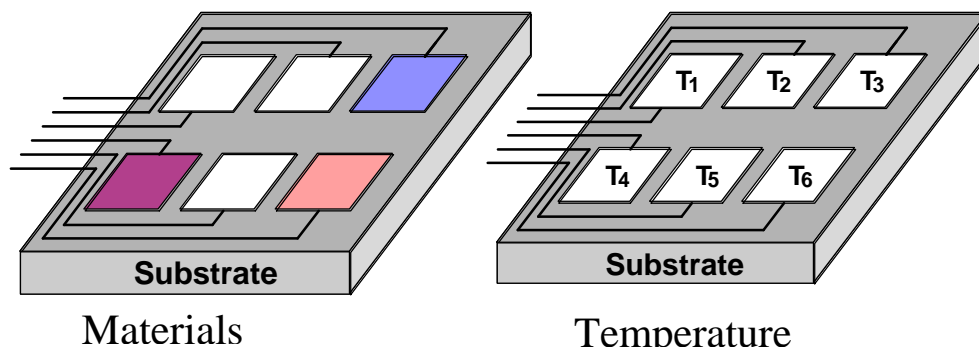


Figure 1. Schematic representation of arrays with elements that have different types of sensing films and different temperatures to provide response data for analysis of chemical mixtures in different monitoring problems.

A number of research hurdles in the areas of 1) device platforms, 2) thin film processing, 3) data collection and analysis, and 4) mechanistic studies, must be cleared to realize success in this project. Certainly, one must have reliable platforms for fabricating prototype sensors. As will be made obvious in Section 5, the microhotplate elements used in our prototype devices can also be adapted to create novel microscale research tools [28]. For example, we used arrays with up to 48 elements (considerable more elements than in our sensor prototypes) to perform highly efficient studies of materials processing and performance. The larger arrays allowed both parallel deposition and then temperature-dependent evaluation of all sensing microsamples, which was especially important in our database development. This approach is far more efficient than single material, deposit-test serial protocols, which are still widely employed by sensing researchers to discover new or suitable sensing compositions, microstructures, thicknesses and surface modifications [29]. The “simultaneous” aspect of our microarray methodology not only saves time, but assures that all samples see the same testing environment. However, the use of sample microsubstrates does create challenges when one attempts to locally deposit sensing materials, by different methods, onto the elements of a prototype or research array.

The matching of materials and their properties to the target analytes of different monitoring applications essentially produces a combinatorial problem. While this problem is well suited to our multielement array studies, there are large amounts of results to be dealt with in collecting and analyzing databases for chemical sensing. In our work we have also added the “amplification” of temperature dependence, which provides important inputs for analyte recognition and quantification. Data is typically collected in an automated way by incrementing through a collection of fixed temperatures, and by operation in high information content temperature programmed sensing (TPS) modes [30]. Efforts to understand the temperature-driven adsorbate transient effects created by surface adsorption, desorption and reaction phenomena that occur during TPS operation also present a challenge. These effects are studied using a newly constructed ultrahigh vacuum system (built for this project), which allows fast desorption phenomena from another newly-designed research tool, the 340-element adsorption/desorption/reaction microarray, to be measured with mass spectroscopic methods.

There are many innovative aspects to this project which produce opportunities for equally innovative results (these are described in greater detail in Section 5). The devices operate on very low power (because of the small mass of the sensing platform). The small size and thermal isolation means that heating rates $\sim 10^6$ °C/s can be attained in microdevice sensing prototypes and research tools, in order to utilize and explore effects of fast thermal switching. This capability is of value not only for sensing science and surface science, but also for materials science and other fields, including bioscience. The use of multielement arrays with individually addressable elements offers the ability to perform combinatorial, temperature-dependent experimentation, that is further supplemented by the ability to probe samples with integrated microelectrodes. The microscale control of temperature also presents methods for depositing small amounts of material onto tiny devices in a localized way.

5. Methods and Results

The research work performed during this 3-year project was broad-ranging and multidisciplinary. Efforts were aimed at creating a scientific and technical basis for an application-tunable microsensor technology based on conductometric effects that occur following gas adsorption on semiconducting oxides. Methods and results are discussed here within a four topic framework: MEMS Platform Development; Microscale Processing of Sensing Materials; Sensing Response Databases and Signal Processing; Research on Operational Effects and Detection Mechanisms.

5a. MEMS Platform Development

Micromachined structures were a critical part of this scientific and technological development program. They have been used both as platforms for fabricating solid state gas microsensors, and as research tools in studies of materials and interfacial phenomena.

The basic MEMS sensing device structure, developed at NIST in the early 1990's, is a temperature-controllable "microhotplate", illustrated in Figure 2a [22]. The pictured device is a single suspended microhotplate, which has been produced by surface micromachining the Si on which the device was fabricated. This microhotplate structure, created by using multiple patterned masks produced with CMOS design rules, includes functionality for conductometric gas and vapor sensing. The component layers are shown in Figure 2b). Local heating is made possible by a polysilicon resistive heater. Temperature measurement can be done by calibrated resistance measurements on either the polysilicon heater or the heat distribution/thermometry plate, and used as feedback input. The accessible temperature range is 20 °C – 500°C (with heat distribution/thermometry plate) and 20°C – 750°C (without the plate). Time constants are on the order of 1-5 ms, and heating rates can be in excess of 10^6 °C/s, so pulsed temperature operation is not only convenient, but can be realized over a wide frequency range. The top surface microelectrodes contact films deposited on the microhotplates and can be used to measure electrical characteristics of the films during or after growth (to monitor deposition processes and sense gases).

Replication of the microhotplate design to produce arrays of elements is straightforward. Figure 3 shows the kind of 4-element microhotplate array, which we have used extensively in developing sensor prototypes for DoE monitoring problems.

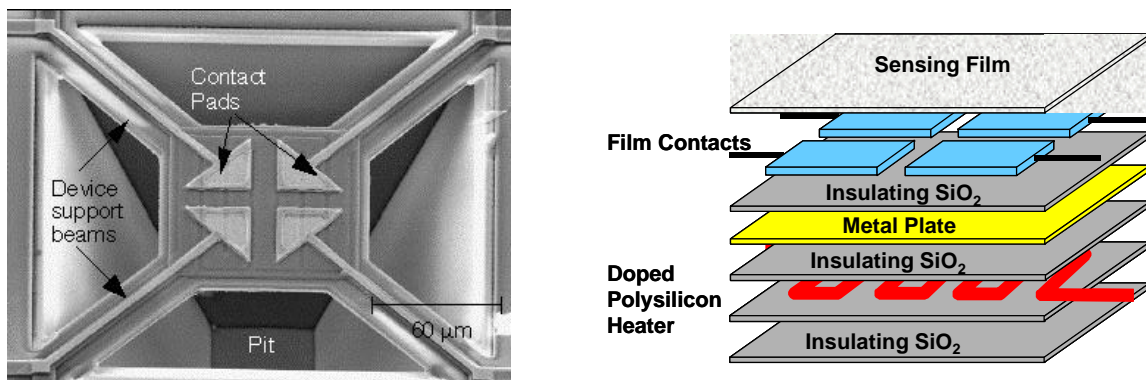


Figure 2. a) Micrograph of a microhotplate element used in conductometric gas sensing. b) Schematic of the vertical structure of the suspended device.



Figure 3. 4-element microhotplate array used to develop prototype gas

The microhotplate elements, as well as other structures with related microheater configurations, have characteristics that are particularly well-suited for developing tunable microsensors [23] and performing microscale research studies [28]. The lateral size of the suspended hotplate can be easily varied from 25 μm to 200 μm . The low mass of the suspended platform ($\sim 0.25 \mu\text{g}$ for a 100 μm device) allows each microhotplate to be thermally isolated (significant temperature gradients exist along the suspension legs). Elements within an array can be individually addressed for

temperature control and film electrical measurements.

Over the course of the project, we examined three different methods for surface micromachining our MEMS devices; they employed the chemicals xenon difluoride, ethylenediamine pyrocatechol (EDP) and tetramethylammonium hydroxide (TMAH). The tetramethylammonium hydroxide method was found to have the advantage of being easily tailored to protect exposed metal surfaces. Our generic tetramethylammonium hydroxide etchant solution contains silicic acid and forms silicates with exposed metal surfaces. The etch rate of metal silicates is extremely slow as compared to the etch rate of silicon in TMAH so exposed metal surfaces remain well protected. The TMAH solution is filtered through a 1750 x 1750 mesh screen to remove particles that would otherwise end up in the etch pit or on the hotplate itself. After copious water washes, the device is submerged in a gentle alcohol stream until it is positioned under a moderate nitrogen flow in order to dry the chip. Microhotplate surfaces are extremely clean prior to subsequent sensing film deposition.

A number of different contact materials have been tested for the microhotplate elements, including Al, Au, W, TiW, and TiN. Desirable features of contact materials are resistance to oxidation at elevated temperature, compatibility with the silicon etch process, and having a thermal coefficient of expansion match to the SiO_2 -based microhotplate. Additional details connected with die layout, contact materials, micromachining etchants and packaging of the devices are given elsewhere [28].

While we had already completed initial demonstrations of the value of such MEMS devices as platforms for advanced chemical microsensors prior to 1998, a considerable portion of this project was based on the realization that microhotplate arrays can play important roles as research tools, as well. The rapid thermal characteristics and the ease with which devices can be replicated into arrays with large numbers of elements are particularly relevant to opening up unique research opportunities. Such opportunities become possible because one can readily modify and adapt microhotplate structures for a variety of studies on temperature-dependent processes. A new set of 20 different microhotplate structures was designed at NIST and fabricated at MIT-Lincoln Laboratories for this project. The overall 13 mm x 15 mm die design is presented in Figure 4. Approximately 75 such die are fabricated on a 6-inch wafer. The designs included 4-element arrays with 50 μm and 100 μm elements, new contact structures (varying geometries, sizes and separations), larger arrays (16-, 48-, and 340-element arrays), and devices for probing new methods of chemical measurements (micromachined calorimeters, "chemical communication" devices for investigating reaction and proximity effects). There were also special structures with

microheaters for studying adsorbate transient effects. The configuration and utility of many of these platforms will be discussed in the subsections that follow (see Figures 9, 26, 32 and 34). Based on our microdevice and microarray work during the first two years of the project, we have also designed a new die and examined new fabrication routes with our MIT-Lincoln Laboratory collaborators. This die will be discussed further in Section 13.

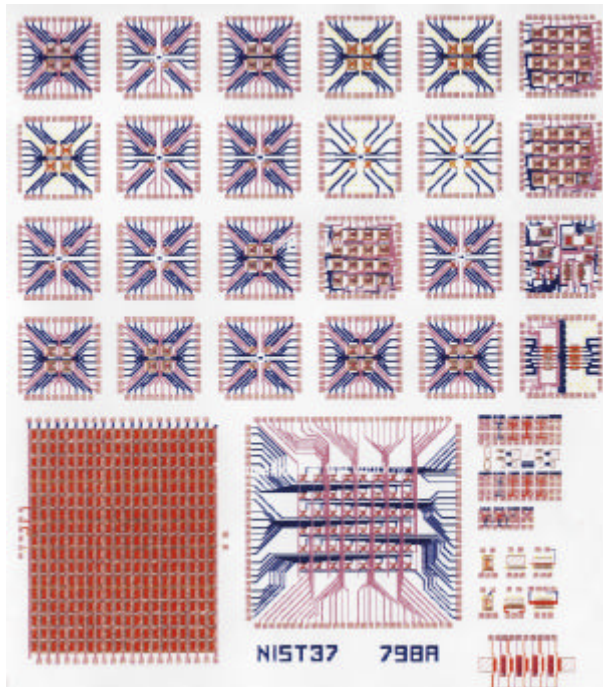


Figure 4. Design layout of a 13 mm x 15 mm die with a variety of microscale devices for sensor development and microanalytical research. The die is reproduced across a 6-inch wafer at a Si foundry.

5b. Microscale Processing of Sensing Materials

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, but methods must be developed to process the microsensing films.

Sensing materials must be capable of responding to the analytes of interest. Often the environment will contain multiple components. Typically for DoE problems, one deals with air backgrounds (with variable humidity levels) and one or more undesirable analytes. The properties of the sensing films must also be optimized to provide suitable response characteristics, which will often be a function of attaining the proper (bulk) composition, microstructure type, and coverage of surface additives.

The focus in this project was to concentrate on semiconducting metal oxides, with and without catalytic additives. These materials have been successfully used in discrete chemical sensing devices, for example, home carbon monoxide monitors. These sensing materials are more robust than polymeric sensing films, for example, a point which can be important both for operation in certain atmospheres, and for device longevity and film cleaning. Data to date has

been acquired on tin oxide and titanium oxide, with metal catalysts including Pd, Pt, Ni, Fe, Ag, Cu, Co, and Au [31].

Deposition Methods Developed

In order to perform sensing research on these pure and modified oxides, one needs to deposit them on the types of microplatforms described in the last section. This is necessary to form microsensors and study their operation, but also for performing novel microarray-based investigations of film growth and interfacial phenomena. The first issue we summarize here is the variety of methods we developed to effectively deposit oxide and metals materials of controlled microstructure on the tiny ($\sim 50 \mu\text{m}$ to $200 \mu\text{m}$), suspended microhotplate structures.

A method we developed and used extensively involves chemical vapor deposition (CVD). By selecting precursor and reactant gases that form the desired oxide (or additive metal) through a thermally-activated process, localized deposition can be made to occur on a desired microhotplate that is heated to an appropriate temperature [32, 33]. Figure 5 illustrates the results of a self-lithographic CVD deposition of SnO_2 onto each element of a 4-element array in which the devices were sequentially heated to 450°C in tetramethyltin and oxygen. We have also used a similar procedure to sequentially deposit SnO_2 and ZnO (from diethylzinc and oxygen), and SnO_2 and Pt (from trimethyl[cyclopentadienyl] platinum and hydrogen) within the same array [23]. The surface electrodes on each microhotplate can be used to monitor the film growth by measuring conductance changes for the oxide films once they become continuous.

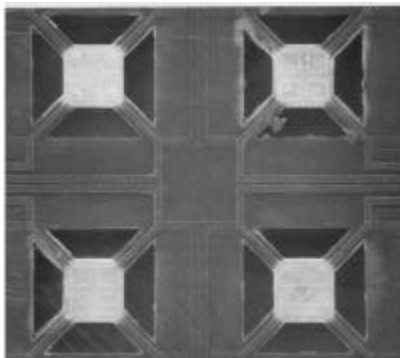


Figure 5. Micrograph showing SnO_2 films locally deposited on the elements of a 4-element array by thermally-activated CVD processing.

Our main (existing) CVD system was employed primarily for producing SnO_2 samples. However, during the course of this project a second CVD system was commissioned in order to do parallel research on developing new sensing materials from a variety of precursors.[34].

One of the most important aspects of how a material responds in a gas sensing application is the microstructure of the material. Fine-grain structures present high surface-to-volume ratios (and necked electron transport paths) resulting in high sensitivities. On the other hand, larger grains present a more limited range of

transducing surfaces, providing different chemical selectivity at the expense of sensitivity. While CVD is an elegant method for localizing films on the microdevice platforms, we sometimes found it necessary to use seeding techniques to reduce oxide particle sizes, and attain higher sensitivities. (An example of using seed particles to modify oxide nucleation is given below; see Figure 11).

Although the microhotplates are small, 3-dimensional structures within an array, we have also succeeded in depositing (sensing) films onto them by other methods [35]. Other processes that utilize the localized heating aspect of the microhotplates include the “fixing” and drying of sol-gel and nanoparticle solutions that are spun onto the surface [36], heated on selected microhotplates, and then rinsed from the other areas.

Sol-gel tin oxide was explored as a sensor material because we found that it could have small particle sizes and high gas sensitivity, with conductance changes ranging from a factor of 50 to

750 for (100 ppm) methanol (whereas CVD films often showed conductance changes of 1.5 – 5). The discrepancies in the sol-gel sensitivities can be attributed, in part, to the challenge of reproducibly depositing sol-gel films on the microhotplates. The SEM images in Figure 6 illustrate this point. The image on the left shows a relatively crack-free film of a sensor that gives a conductance change of 750 in methanol, while that on the right is a highly cracked SnO_2 film that

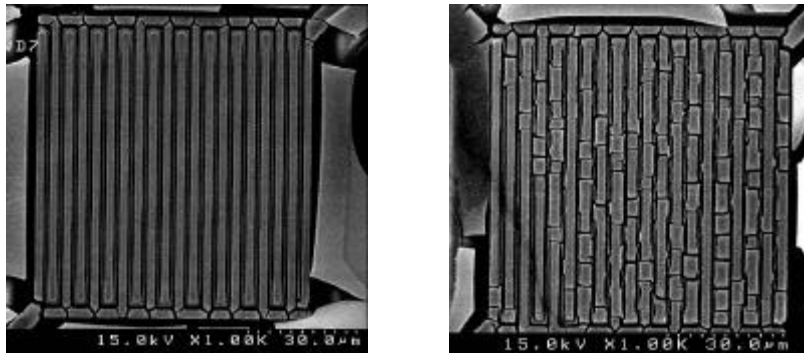


Figure 6: SEM images of two microhotplates after being coated with sol-gel SnO_2 by spin coating. The one on the left was 15 times more sensitive than that on the right to 100 ppm of methanol.

gives a much lower conductance change. The potential of these locally deposited sol-gel sensing films certainly warrants further work.

In another approach, a colloidal suspension of SnO_2 was deposited onto an array of microhotplates [36]. Tin oxide films prepared this way retained nanophase microstructure (Figure 7), showed high sensitivity (as illustrated in Figure 14 in the next Section 5c), and more importantly, exhibited stable operation to repeated exposures of test gases (Figure 15, Section 5c). These films also function well in a temperature-programmed sensing mode (repeated cycles of a linear ramp of temperature pulses).

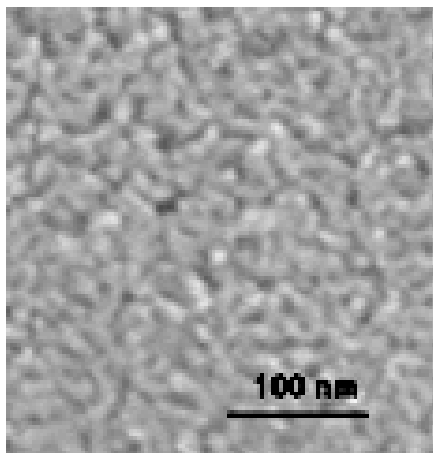


Figure 7. SEM image of nanoparticle film showing ~10 nm particles.

The suspended nanoparticle film was fabricated by spin-coating the solution over an array of micromachined hotplates and annealing. Thermolithographic processing of deposition windows, discussed in the next subsection, assisted localized deposition of sol-gel and suspended particle films.

Electrochemical deposition is another technique that can make use of the ability to individually address microhotplates in an array to localize films. In one realization, a polypyrrole film was deposited on a microhotplate designed with interdigitated top electrodes using electrochemical processing at 0.1V in a solution of anhydrous acetonitrile, 0.1M LiCl_4 and 50 mM polypyrrole. After the deposition step,

the electrode potential was set to -0.5V to expel LiO_4 anions [37]. This has not yet been applied to oxides, but will be in the future.

Microscale Patterning Methods

Thermal addressing of individual hotplates can also be used to define windows for deposition within “thermal resist” films [35]. In addition, the localized heating can be applied after deposition to post-process films, as one might do, for example, in creating a particulate film from a continuous metal overlayer. One lithographic technique with general applicability involves the use of an array element’s microheater to volatilize a nitrocellulose coating that has been spun on an entire array. A sensing film can then be applied, for example, by spinning on a solution or sol-gel. Lift-off by dissolution of the nitrocellulose layer leaves only the film on the selected hotplate(s). This method of volatilizing a coating also has potential applications as a protective coating for sensors in harsh environments, which would only be removed just prior to use.

Patterns of organosilane monolayers have also been successfully made on microhotplates. Organosilanes, such as (tridecafluoro-1,1,2,2-dihydrooctyl) trichlorosilane readily react with surface hydroxyl groups that are present on the surface of the microhotplate arrays. By heating specified microhotplates, the silane monolayer can be removed in a localized area [38]. Secondary Ion Mass Spectrometry (SIMS) can be used to characterize microhotplates both with the organosilane monolayer and after the silane monolayer has been removed. Figure 8 shows SIMS images of F^- concentration on the surface of two microhotplates. The unheated hotplate on the left has F^- present everywhere, while the hotplate on the right, which has been heated to 450 °C, shows a drastic decrease in F^- due to removal of the monolayer. Studies with x-ray photoelectron spectroscopy both confirmed these changes in silane monolayer coverage with sufficiently elevated temperatures, as well as at lower temperatures, but increased heating time. The organosilane monolayer is hydrophobic, so the patterning of the silane with temperature results in a mask of a hydrophobic region over the entire array, except on microhotplates that have been heated. These are hydrophilic. Future work will explore using this mask to selectively deposit metal oxides on the hydrophilic regions in order to make arrays that have different materials on each microhotplate.

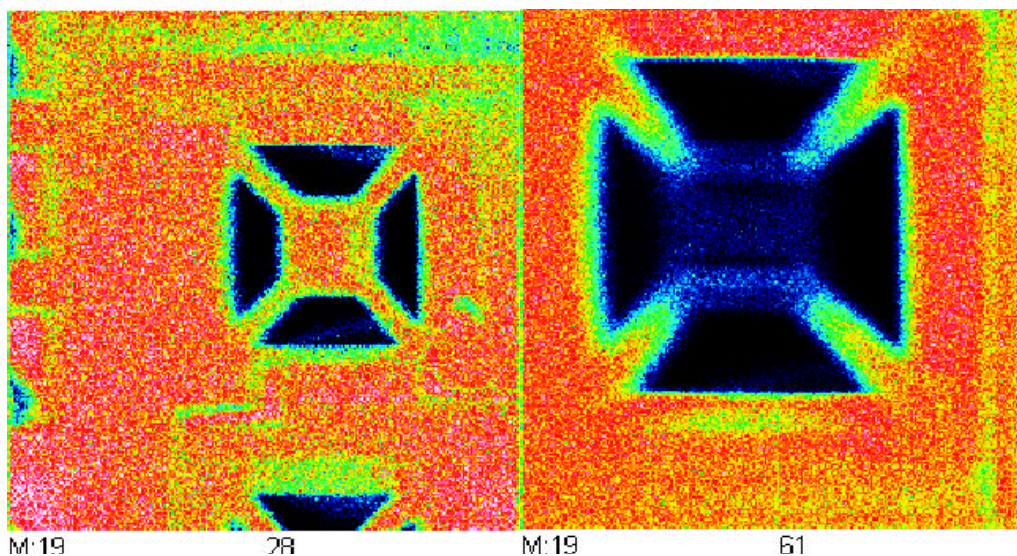


Figure 8: SIMS images of microhotplates with organosilane monolayer before heating (left) and after heating at 450 °C (right). The images show variation in the concentration of F^- .

Masking can also be effective for producing films on microhotplates by physical deposition methods, such as evaporation or sputter deposition. Lithographic methods can be used to create metal shadow masks (available commercially) with apertures of $\sim 50 \mu\text{m} - 100 \mu\text{m}$ which match to the configuration of the microhotplate arrays. Serial processing, with selected blocking of apertures, is required to attain a variety of film compositions within the array. We have utilized this approach to study the sensing effect of different surface-dispersed, low coverage metals on SnO_2 -based films [31]. Finally, for liquids that are not too viscous, one can also consider the use of micro-pipetting (without or perhaps with a mask) to place small volumes of materials on the microhotplate. Precision alignment methods must be used for locating a mask, or aligning a pipette dispenser to the microarray.

Combinatorial Studies of Sensing Materials

Selecting sensor materials that are properly matched to the analyte(s) for one or more specific applications, and then optimizing parameters (e.g. - microstructure, thickness, additive loading) for films of these materials, will create an inherently combinatorial problem. During the first year of this project, studies of oxide film growth/performance were done using 4-element arrays. During the second and third years, we amplified the efficiency of our studies on microstructure-controlled oxides (in a planned way) by moving to 16- and 36-element arrays. Micrographs of these devices are shown in Figure 9. We have applied the larger arrays to study various processing conditions and the final film characteristics for the oxide-based sensing materials. It is worth noting that the methodology can be applied to other types of sensor-related materials, such as catalytic metals in filters, and high area materials for preconcentrators. The approach can also be used even more broadly in other technical areas.

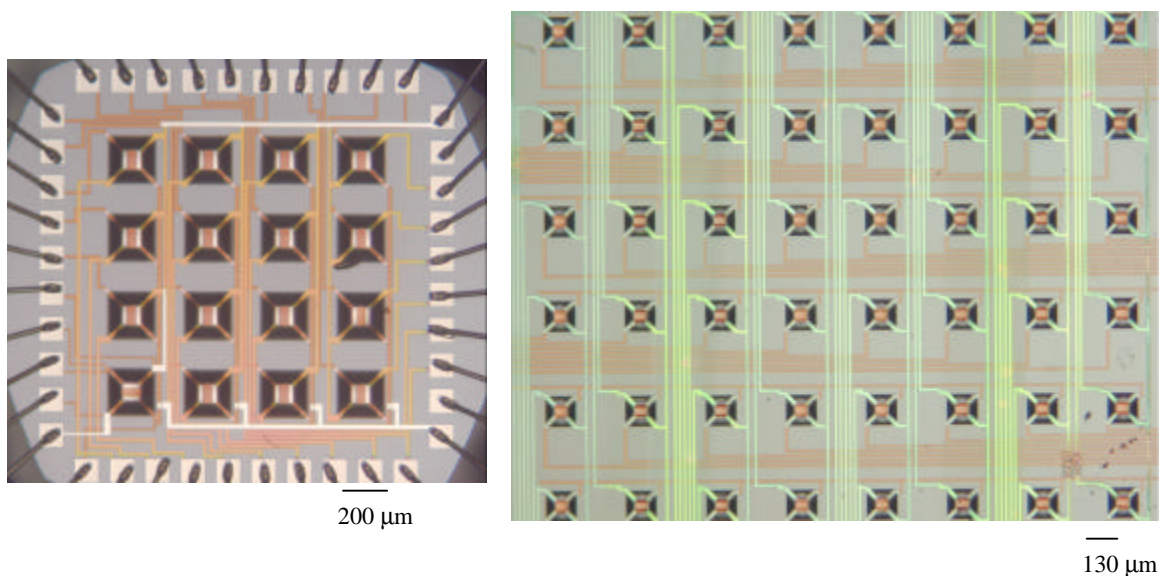


Figure 9: a) 16-element microhotplate array, b) 48-element microhotplate array.

In one example using 16-element arrays, microhotplate platforms were used to study temperature-dependent microstructures in CVD processing of titanium dioxide using titanium (IV) nitrate (TN) [34]. This precursor is capable of depositing titanium oxide that is free of residual carbon without the use of an external oxidant [39]. Upon receipt, the titanium(IV) nitrate was ground under inert atmosphere using an agate mortar and pestle prior to transferring it to the precursor vessel. In these experiments the precursor was maintained at 35 °C. High purity argon was used as the carrier gas with a one sccm flow rate. Reactor pressure was typically 500 mTorr to 650 mTorr. Microhotplate heaters were calibrated for temperature *in situ* with the carrier gas flowing through the bypass line. Following calibration, carrier gas flow was diverted into the precursor vessel, and after stabilization, the microhotplate was turned on to begin deposition. Experiments were carried out under fixed-temperature conditions. Deposition times were 5 minutes for each sample. The 16-element arrays were used for deposition temperatures up to ~ 450 °C. Micrographs of the resulting films are shown in Figure 10. Films deposited above 170 °C were of the same approximate thickness, while those deposited below 170 °C were considerably thinner, consistent with reaction-limited growth. As the deposition temperature increases (175 °C to 250 °C), the large grains seem to subdivide along a particular crystallographic direction resulting in a plate-like microstructure. This plate-like microstructure may be explained by migration of adsorbed precursor more rapidly in some directions than in others, causing anisotropic growth. Increasing deposition temperature further causes these plates to subdivide into smaller grains. This may be the result of a shortened diffusion length prior to desorption or reaction. Microstructures obtained below 400 °C exhibit large voids, indicating a relatively low surface mobility of the surface adatoms during film growth. The parallel (processing/performance) study of multiple samples has allowed us to uncover certain TiO₂ specimen that exhibit switching of response polarity (direction of conductance change) which can occur dependent on film composition, microstructure, and temperature or analyte concentration [40]. The switching behavior can be very useful for clear analyte recognition.

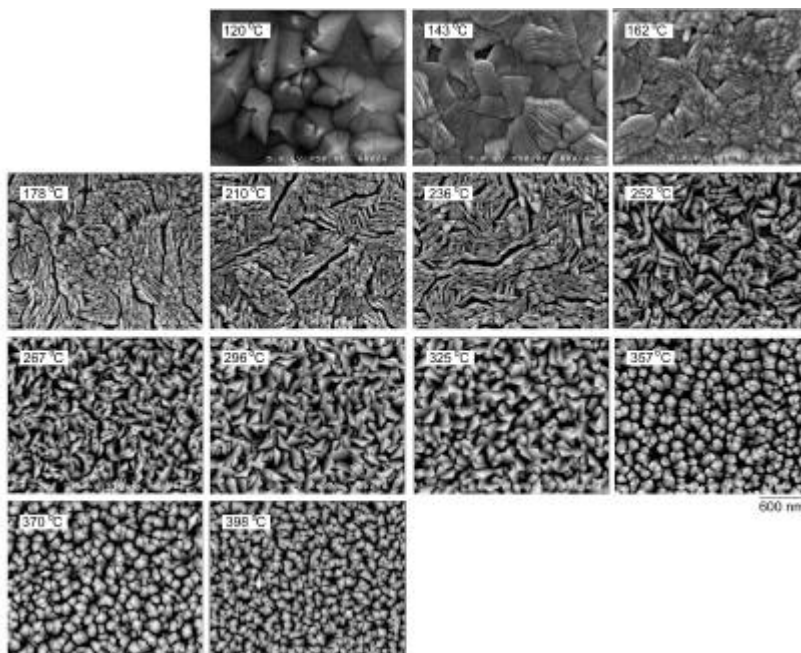


Figure 10. SEM images from a 16-element array in which TiO₂ was grown by CVD with each element held at a different temperature. All images are at the same magnification.

Films fabricated by seeding the SnO₂ CVD growth with small metal particles (Ni, Co, Fe, Cu, Ag) have been studied with 36-element arrays. Film reproducibility, as judged by SEM and sensing response, was investigated by making columns of six films in the array using the same recipe. The seed layer provides a larger number of distributed sites for nucleation, resulting in more rapid film growth with a finer grain microstructure [41]. We have found that SnO₂ films prepared with seed layers of different composition result in different microstructures [42, 43]. Representative microstructures, shown

in Figure 11, appear to correlate with the melting temperature of the seed layer metal: low melting

point materials like Ag were able to move around on the surface and produce larger but fewer nucleation sites, resulting in larger grains, while higher melting point metals like Fe and Ni produced a larger number of small stabilized nucleation sites, producing very fine (~ 30 nm) grains. While the fine microstructure generally enhanced the sensitivity to a wide range of gases, the different microstructures produced by using different seed layers also yielded sensor films that had different selectivities to the set of gases that were used for testing (see also Section 5c).

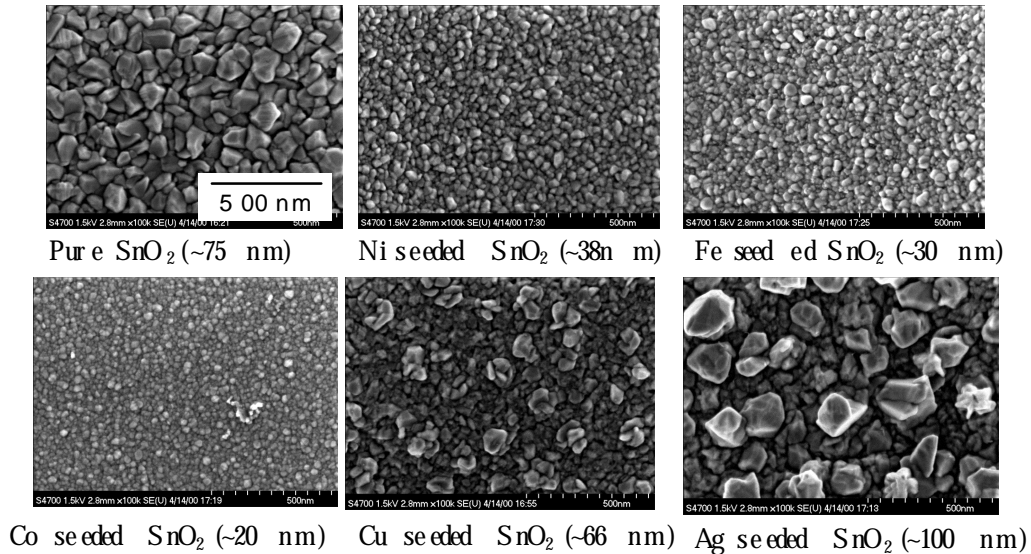


Figure 11. Microstructure of tin oxide grown with different seed layers. The average seed particle size used in the SnO_2 growth is given in parentheses. All images are at the same magnification.

We have also examined the performance of various surface-dispersed catalytic additives (on equivalent CVD SnO_2 films) using 36-element arrays. Catalysts were deposited by evaporation to nominal thicknesses of 3nm, and then the microhotplates were heated to affect the formation of a noncontinuous layer of catalyst particles on the SnO_2 surfaces. The 36-sample library created for this study is shown schematically in Figure 12, where the additive metal is labeled. Note again that each sample type is again produced six times, to examine process reproducibility. In all of these multiple element studies, the same array platform used to process the samples is used to measure a database of sensing responses. These outputs and their utility is the subject of the next section.

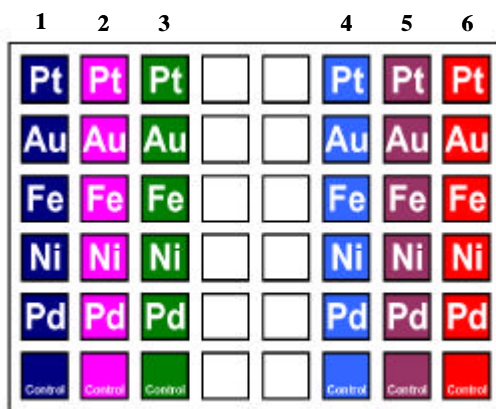


Figure 12. 36-element array layout employed for fabricating SnO₂ samples with metal additives and evaluating their sensing performance.

5c. Sensing Response Databases and Signal Processing

Temperature-dependent response data can be efficiently collected from the sensing materials deposited in microhotplate array formats. Signal processing studies of the rich data content from temperature-programmed individual microsensors and array elements enable analyte recognition and quantification.

Sensing Modes, Approaches and Sample Data

Sensing response data from individual sensors or multiple sensors within an array can be collected in a fixed temperature mode, or in a dynamic temperature programmed sensing (TPS) mode. We illustrate both types of data and the information that can be extracted from them in this section. We emphasize that by tuning the sensing films and operating modes, based upon information in the kinds of databases presented below, one can impact a range of applications. The goal of the enhanced selection and optimization capability offered by array studies, possible when one correlates materials processing (discussed in the last section) and materials performance (discussed in this section), is represented schematically in Figure 13. The important role of signal analysis is also emphasized in this section.

Sensor response databases were constructed in tests that used dilute concentrations (as low as ~ 100 ppb to ~500 ppm) of methanol, ethanol, benzene, hydrogen, carbon monoxide, dichloromethane, propane, trichloroethane, and butanone in dry air. We begin with illustrations from different sensing materials examined on 4-element arrays, then move to larger databases. The findings indicate trade-offs between sensitivity, stability and selectivity.

The first example of fixed temperature data is shown in Figure 14. Operation of a microsensor with spun-on nanoparticles at 350°C shows both high sensitivity, and increasing peak sizes which correspond to increased concentrations [36]. These films, operating at fixed temperature over long times, also show good stability, as indicated in Figure 15. Sensitivity as illustrated in Figure 14 (next section), but, more importantly, stable operation to repeated exposures of test gases. (These films also function well in a temperature-programmed sensing mode.)

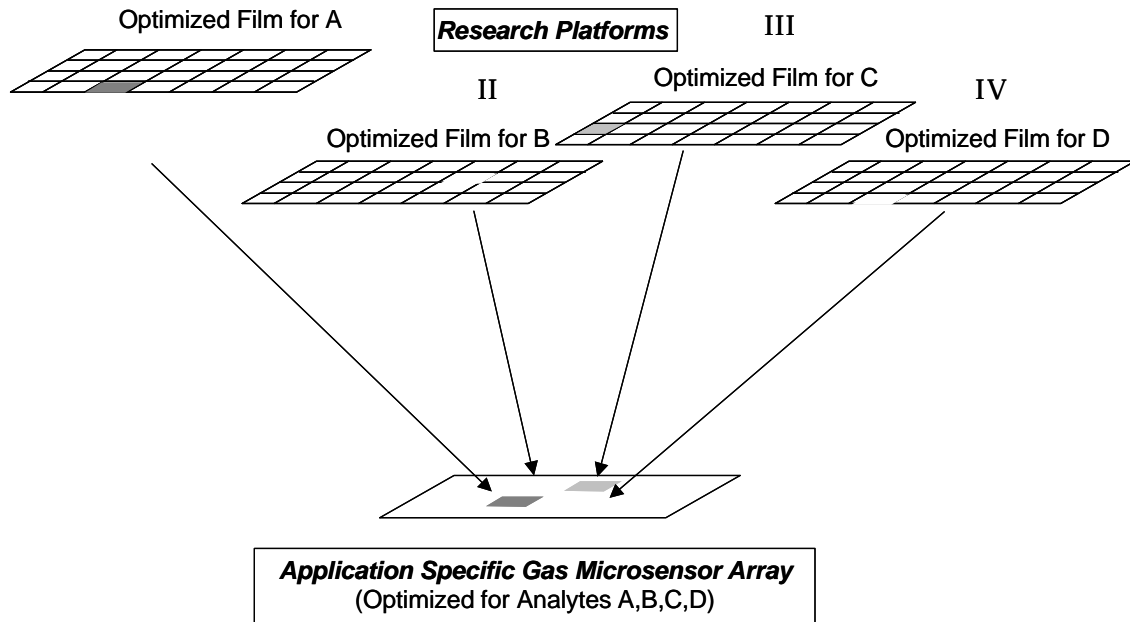


Figure 13. Schematic representation of the use of multi-element array studies to screen and select optimal films for a smaller (4-element) gas microsensor prototype.

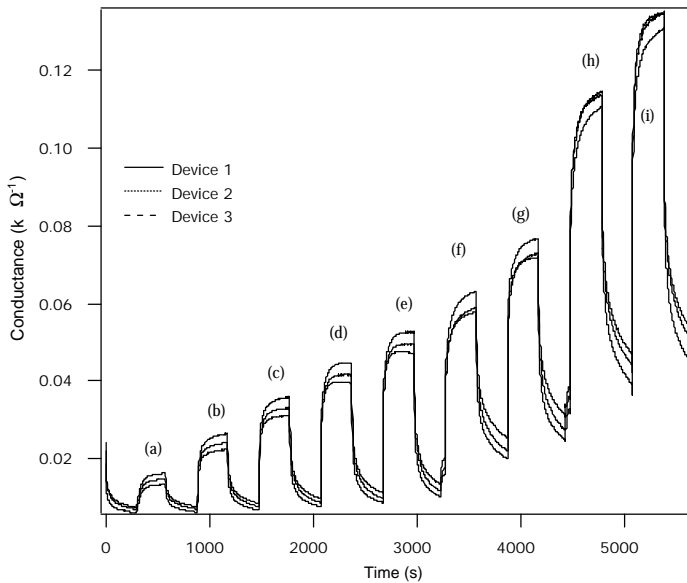


Figure 14. Response to methanol in dry air for the low concentration range: (a) 10 nmole/mole (10 ppb), (b) 20 nmole/mole (20 ppb), (c) 40 nmole/mole (40 ppb), (d) 80 nmole/mole (80 ppb), (e) 160 nmole/mole (160 ppb), (f) 320 nmole/mole (320 ppb), (g) 320 nmole/mole (320 ppb), (h) 640 nmole/mole (640 ppb), (i) 1.20

concentrations (a)-(e) the dilution flow rate was 5000 sccm; for (f) and (g) the dilution flow rate was 1250 sccm; for (h) and (i) the dilution flow rate was 325 sccm.

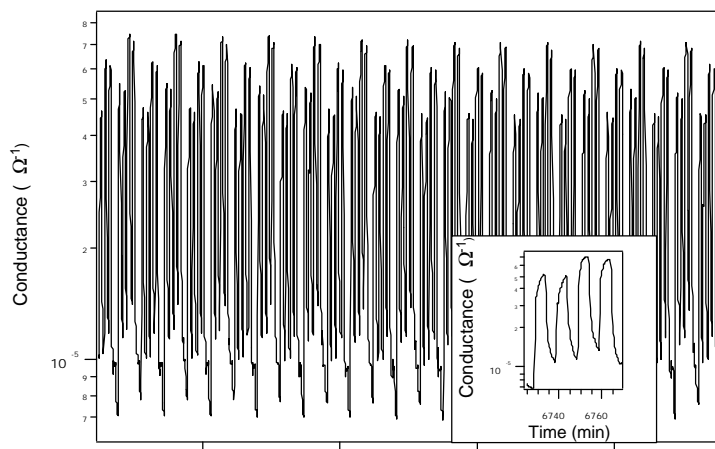


Figure 15. Stability test showing last 24 hours of a 120-hour run. The response to a sequence of ethanol and methanol exposures is presented. The inset shows a magnified section of the response to a set of four methanol exposures at about 112 hours of operation. The sensor operating temperature was 350 °C.

The fast heating/cooling characteristics of the microhotplates, as well as the built-in ability to control temperature with feedback, makes them ideal for variable temperature and pulsed sensor operation – a mode we call temperature programmed sensing (TPS) [30]. Temperature variation allows one to probe the temperature-dependent nature of gas phase interactions with the sensing film surface [23]. This approach dramatically increases the information content from a single microsensors. Pulsing can be used to access variable temperatures while also returning to a fixed base temperature when one records conductance values, so as not to introduce thermally-induced carriers (for the semiconducting oxides) into the measured response. Figure 16 shows an example of pulsed temperature programming consisting of temperature pulses from a base temperature to a subsequently lower temperature. Conductance measurements made at the base temperature provide information specific to the gas-sensor combination. Figure 17 shows two cycles of a temperature programmed experiment of sol-gel SnO₂ that has been coated with 20 Å of Cu. A different response pattern or “signature” is obtained for exposure to 100 ppm of four different gases (methanol, hydrogen, dichloromethane and trichloroethylene) when the base temperature is 350 °C. These time-dependent (temperature-dependent) patterns can provide unique capabilities for recognizing analytes [44].

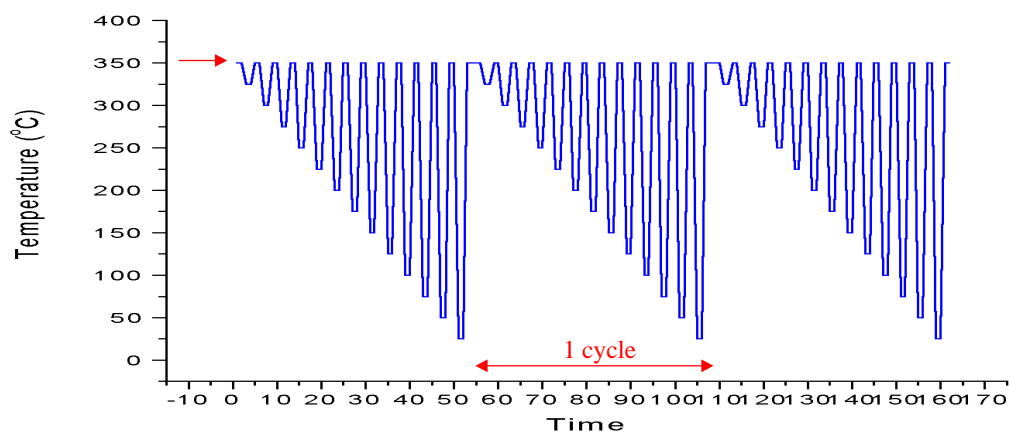


Figure 16: An example of pulsed Temperature Programming Sensing (TPS) cycles. The arrow indicates the base temperature where conductance is measured.

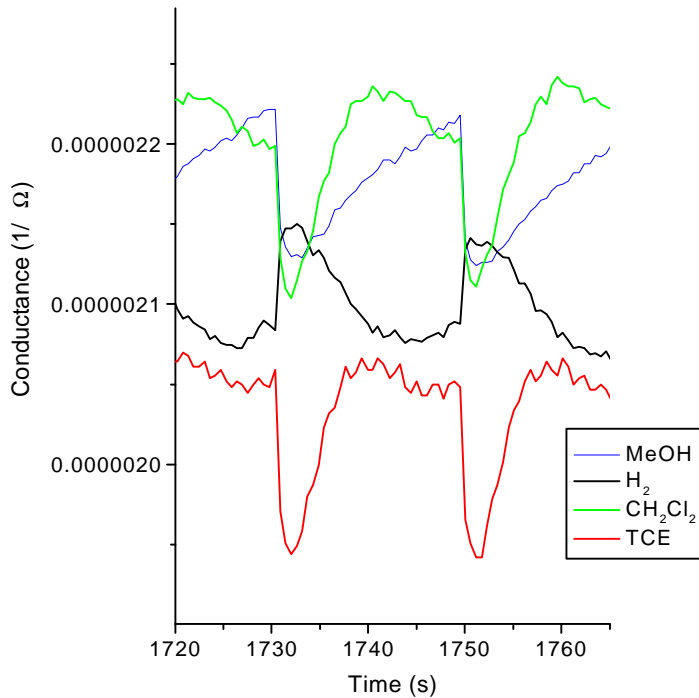


Figure 17: Temperature Programmed Sensing of sol-gel SnO_2 coated with 20 Å of Cu. The base temperature is 350 °C, with pulses going from 350 °C to room temperature.

Signal Processing of Microsensor Data

While microhotplate gas sensors provide sensitive, real-time data, converting data to recognize analytes and quantify concentrations requires analytical methods that can make use of the partially selective, non-linear information. These methods include a variety of chemometric and neural network approaches that have already been well developed for other applications, such as the analysis of infrared absorption spectra. The signal processing efforts highlight the need for selecting appropriate materials and operational conditions in order to obtain the best analytical information in the shortest time.

We first discuss chemometric signal processing methods applied to 4-element microsensor arrays where different sensing materials have been included. The first uses arrays of partially selective materials operated at fixed temperatures. An example of a two-component study on methanol and hydrogen test gas mixtures, in air, is shown in Figures 18 and 19. Figure 18 shows the raw response data taken during a training set defined matrix of mixed analyte concentrations indicated in Figure 19. The 4-element array for this study included the following sensing films:

- CVD TiO_2
- Spin-on nanoparticle SnO_2
- Ni-seed CVD SnO_2
- Ni-seed CVD SnO_2 with a surface-dispersed of Au

Figure 20 shows the distribution of samples within the scores plot of the 2 factor principal components analysis (PCA) coinciding with the distribution of samples within the experimental design. The slightly skewed positions of the points at higher analyte concentrations indicate that

the sensor response is nonlinear.

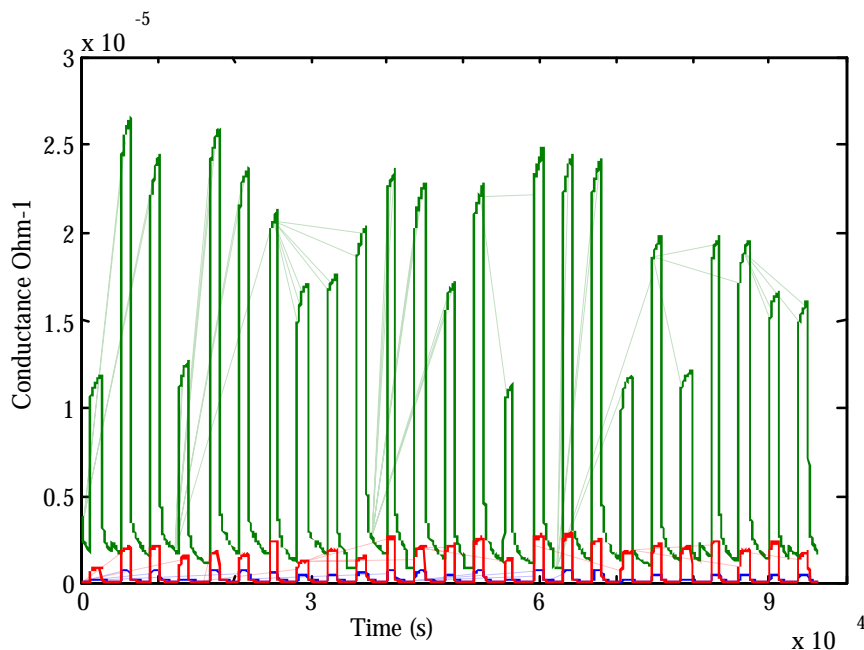


Fig 18. Measured conductance response of microsensors during a portion of the training and testing set within in Figure 19.

| | | Methanol | | | | | |
|----------|-----|----------|----|----|----|-----|-----|
| Conc | | 0 | 15 | 50 | 85 | 120 | 150 |
| Hydrogen | 0 | | 32 | 7 | 1 | 25 | 29 |
| | 15 | 9 | 31 | 6 | 10 | 4 | 3 |
| | 50 | 12 | 17 | 30 | 27 | 13 | 33 |
| | 85 | 15 | 2 | 8 | 23 | 34 | 21 |
| | 120 | 35 | 22 | 14 | 26 | 16 | 18 |
| | 150 | 19 | 24 | 28 | 5 | 11 | 20 |

Figure 19. Matrix of concentrations used for training and testing.

As indicated in Figure 19, this study used a fully crossed experimental design with concentrations at 15, 50, 85, 120, and 150 ppm. Data sets collected while the test mixture was exposed to the sensor array were unfolded to form a single consecutive vector response of all four sensors. Multivariate calibration methods were chosen in order to calibrate and predict the concentrations of the test analytes within a mixture. Among the methods used in calibrating the mixtures are a locally weighting method, locally weighted regression (LWR,) globally weighting methods:

alternating conditional expectations (ACE) and projection pursuit (PP,) and linear methods: partial least square (PLS,) and principal component regression (PCR.) Results obtained from certain analytical methods are summarized in Table 1.

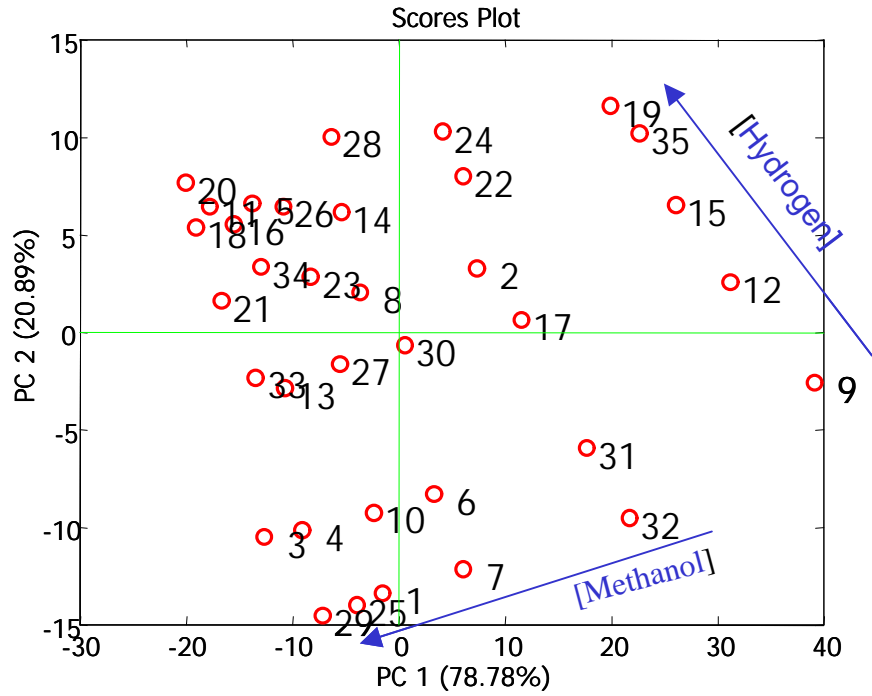


Figure 20. PCA Plot for experimental mixtures in Figure 19.

| | | | Alternating Conditional Expectation | | Projection Pursuit Reg | | Polynomial PLS | | Spline Partial Least Squares | | Locally Weighted Regression | |
|-------------------------|----------|----------------------|-------------------------------------|-----------|-------------------------|----------|-------------------------|----------|------------------------------|-----------|-----------------------------|-----------|
| | | Actual Concentration | Predicted Concentration | | Predicted Concentration | | Predicted Concentration | | Predicted Concentration | | Predicted Concentration | |
| Mixture | Methanol | Hydrogen | Methanol | Hydrogen | Methanol | Hydrogen | Methanol | Hydrogen | Methanol | Hydrogen | Methanol | Hydrogen |
| 1 | 120 | 50 | 122.50 | 51.43 | 118.08 | 62.41 | 118.08 | 62.41 | 118.81 | 70.68 | 118.78 | 65.26 |
| 2 | 15 | 150 | 24.10 | 130.80 | 9.36 | 151.89 | 9.36 | 151.89 | 8.78 | 160.01 | 13.85 | 147.78 |
| 3 | 50 | 85 | 51.87 | 100.64 | 56.28 | 77.20 | 56.28 | 77.20 | 57.64 | 71.96 | 60.47 | 69.56 |
| 4 | 120 | 120 | 120.93 | 120.87 | 121.37 | 120.08 | 121.37 | 120.08 | 119.06 | 114.36 | 120.42 | 124.26 |
| 5 | 85 | 120 | 86.11 | 125.05 | 85.25 | 127.53 | 85.25 | 127.53 | 83.08 | 129.28 | 82.26 | 139.20 |
| 6 | 150 | 15 | 131.47 | 28.01 | 143.11 | 24.43 | 143.11 | 24.43 | 162.20 | -6.69 | 142.71 | 21.78 |
| 7 | 15 | 85 | 15.47 | 92.42 | 17.16 | 75.85 | 17.16 | 75.85 | 14.41 | 77.34 | 21.55 | 69.17 |
| RMSEP | | | 7.91 ppm | 11.12 ppm | 4.29 ppm | 8.00 ppm | 4.29 ppm | 8.00 ppm | 6.00 ppm | 13.86 ppm | 5.55 ppm | 12.87 ppm |
| Mean % Error Prediction | | | 12.01% | 19.21% | 10.32% | 16.47% | 10.32% | 16.47% | 10.41% | 32.78% | 11.67% | 19.09% |

Table 1. Table of results from different multivariate methods applied to the methanol/hydrogen test data.

In order to increase efficiency, a central composite experimental design was used to better calibrate the non-linearity seen in the 2-factor PCA scores plot. Besides methanol vapors and hydrogen gas, more mixtures of gas and vapors were analyzed, including:

- methanol and ethanol,
- ethanol and acetone,
- methanol, ethanol and acetone,
- trichloroethylene (TCE) and dichloromethane (DCM)
- benzene and toluene

Improvements in the calibration come from the reduction in the number of required calibration samples and using a better description of the nonlinear analyte response.

A second approach uses temperature programming, as described above, to produce a time-periodic response from a single sensor. This periodic response has a characteristic shape that provides information about the composition and concentration. Figure 21 (a) shows the response pattern to a triangle ramp of temperature pulses in the presence of varying concentrations of methanol, hexane, and mixtures of the two. Hexane produces a peak at the maximum pulse temperature, while methanol produces a peak on the way up and on the way down from the maximum. Mixtures combine these effects. Partial least squares methods are used to deduce a concentration for test mixtures of the two, which correspond to the actual mixed values (see Figure 21b).

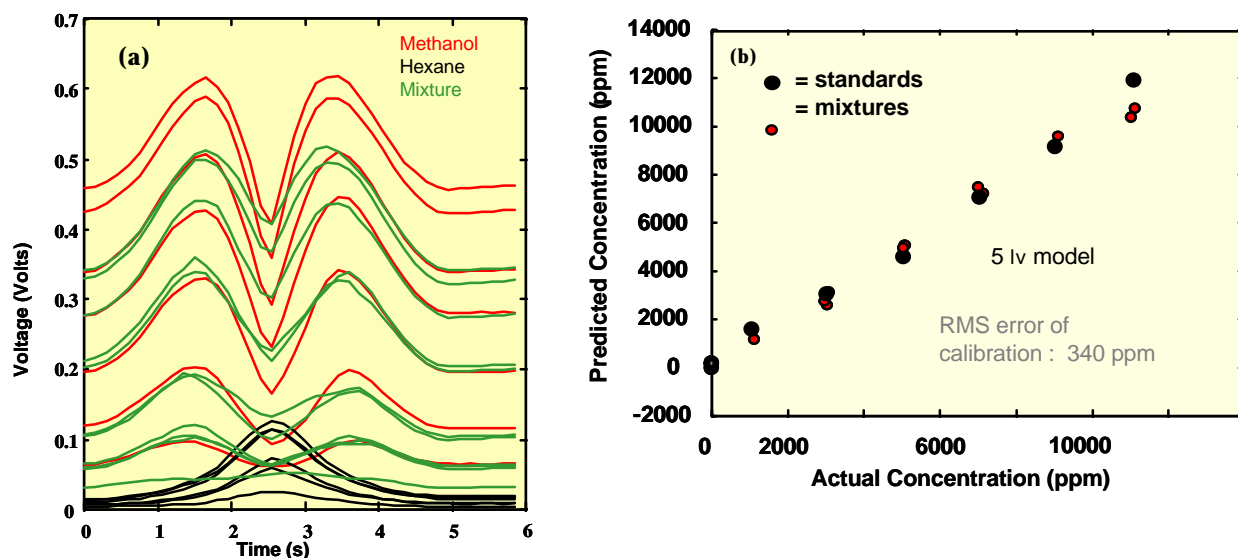


Figure 21. (a) Response to methanol, hexane and methanol/hexane mixtures. (b) Predicted concentration based on sensor data from a mixture vs. actual concentration.

Databases and Signal Processing for Large Microarrays

The discussion above indicated some of the approaches taken for data from single sensors and small arrays. Considerably larger databases for signal processing and response analysis are available from our work on large arrays. The results on simultaneous collection of sensor data from up to 36-elements was made possible by electronic hardware developed during the course of this project. In Figure 22, we show a web or radar plot obtained from samples in the 36-element seeding study on CVD-grown SnO_2 (see Figures 9 and 11). The data snapshot represents the relative sensitivities to various gases at 400 °C for the differing microstructures, but the full database obtained from this study provides such information sets at 50° increments from 200 °to 450 °C [42, 45]. Data from replicate samples in these arrays has been used both for averaging and obtaining statistical information on reproducibility.

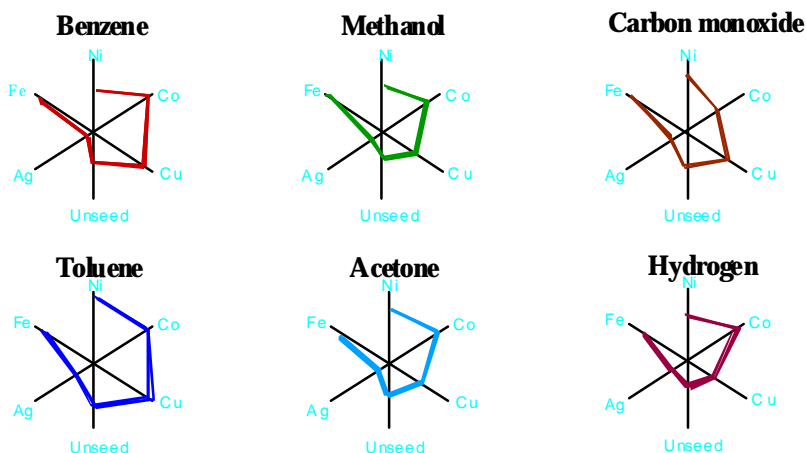


Figure 22. Response sensitivities to different gases from tin oxide sensing films grown with different ultrathin seed layers.

Another example of a 36-element study is the data from a study of response characteristics of SnO_2 with different surface-dispersed catalytic additives (Figure 23). Radar plots showing sensitivity results for operation at three fixed temperatures are shown [46]. The sensitivities represent an average response observed from the six samples of each type.

The full response data set from the 36-element array study of metal additives was used as input for an investigation in which two artificial neural networks (ANN) were trained from these data. The objective was to identify the minimal set of sensor types sufficient to correctly recognize the six gases: hydrogen, methanol, benzene, ethanol, acetone and methyl-benzene. The first ANN had 18 inputs, the responses by the “best” of each sensor type at all three temperatures. The second ANN had 6 inputs, consisting of only the “best” sensor types. In both of the ANN, 6 outputs were applied in successfully recognizing all test gases. The PCA-CG algorithm that calculates non-random initial connection weights trained the ANN models [47].

The inputs of the resulting ANN models were automatically pruned of the less-relevant inputs, and re-trained with the reduced input sets. After 7 such reductions of the first ANN, the minimal set needed to correctly identify all six gases were found to be Fe350, Ni350, Au250, Ni250, and Control (SnO_2) 250 (where the numbers indicate temperatures). The second ANN could identify all gases. A reduced ANN model, with only the Pt, Au, Ni and Pd sensors could identify all gases at the 350 °C and 300 °C, but could not identify acetone at the 250 °C. (see Table 2).

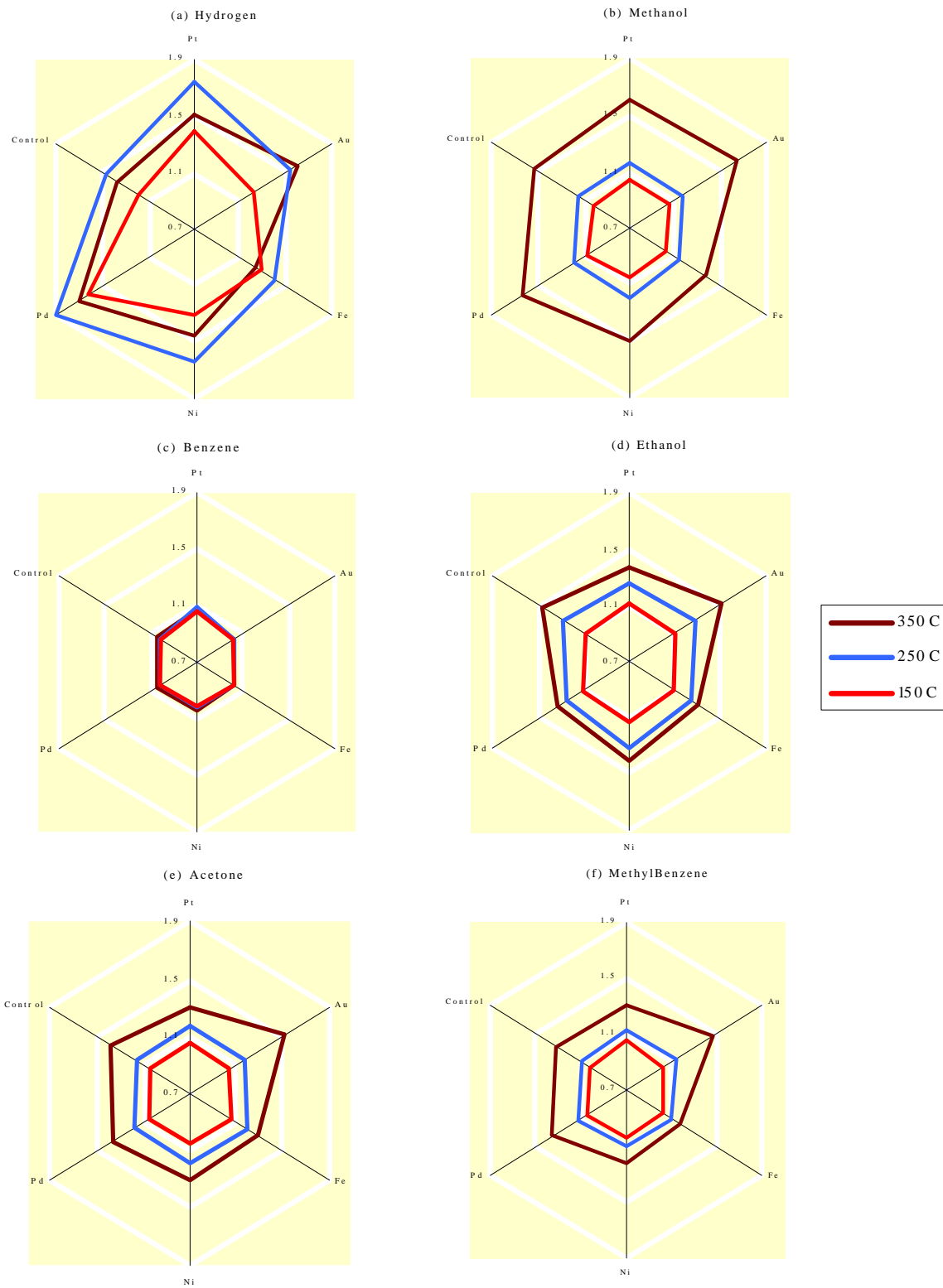


Figure 23. Radar plots from 36-element study of metallic additives on SnO₂.

| | Temperature Degrees C. | Hydrogen | Methanol | Benzene | Ethanol | Acetone | Methyl- Benzene |
|-----------------|---------------------------|-------------|-------------|-------------|-------------|-------------|--------------------|
| Hydrogen | 350 | 0.99 | 0.07 | 0.00 | 0.00 | 0.00 | 0.00 |
| Methanol | 350 | 0.02 | 0.94 | 0.00 | 0.00 | 0.00 | 0.04 |
| Benzene | 350 | 0.00 | 0.00 | 0.80 | 0.00 | 0.00 | 0.23 |
| Ethanol | 350 | 0.00 | 0.00 | 0.00 | 0.99 | 0.04 | 0.00 |
| Acetone | 350 | 0.00 | 0.00 | 0.00 | 0.02 | 0.97 | 0.01 |
| Methyl-Benzene | 350 | 0.00 | 0.09 | 0.00 | 0.00 | 0.01 | 1.00 |
| Hydrogen | 300 | 0.99 | 0.05 | 0.00 | 0.00 | 0.00 | 0.00 |
| Methanol | 300 | 0.00 | 0.93 | 0.00 | 0.03 | 0.04 | 0.00 |
| Benzene | 300 | 0.00 | 0.00 | 1.00 | 0.01 | 0.00 | 0.03 |
| Ethanol | 300 | 0.00 | 0.00 | 0.00 | 0.98 | 0.03 | 0.00 |
| Acetone | 300 | 0.00 | 0.00 | 0.00 | 0.06 | 0.95 | 0.00 |
| Methyl-Benzene | 300 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.87 |
| Hydrogen | 250 | 0.99 | 0.03 | 0.00 | 0.00 | 0.00 | 0.04 |
| Methanol | 250 | 0.00 | 0.84 | 0.00 | 0.09 | 0.00 | 0.16 |
| Benzene | 250 | 0.00 | 0.00 | 0.96 | 0.00 | 0.00 | 0.20 |
| Ethanol | 250 | 0.00 | 0.11 | 0.00 | 0.87 | 0.01 | 0.00 |
| Acetone | 250 | 0.00 | 0.06 | 0.02 | 0.01 | 0.00 | (0.27) |
| Methyl-Benzene | 250 | 0.00 | 0.02 | 0.21 | 0.00 | 0.00 | 0.47 |

Table 2: Listings that provide the classification matrix of the classification, using the Pt, Au, Ni and Pd sensors.

These results indicated that correct classifications could be achieved with a smaller number of sensors or temperatures, opening the way for more compact sensor arrays for a given application and quicker sampling procedures for fixed temperature gas detection. This analysis also demonstrates the importance of using both different materials and different temperatures as selected from our microarray databases. Recent work on TPS data from the 36-element array with ANN methods has indicated the power of coupling ANN methods with multiple materials to select out best samples for a given recognition/quantification problem [48].

5d. Research on Operational Effects and Detection Mechanisms

Temperature dependence of adsorption, desorption, reactions, and other phenomena are the basis on which temperature-dependent gas sensing is built. It is therefore important to understand thermal effects in sensing materials, at sensing interfaces, and near microsensing platforms to develop better microsensors.

Temperature-dependence that exists for adsorption, desorption, and reaction phenomena and the relationships that these dependencies have with electrical phenomena are the basis for conductometric gas sensing. As has been demonstrated already, temperature variations can be used to considerable advantage in tuning sensors. In the fixed temperature mode of operation, one may purposely switch from one temperature to another for a given microsensor in order to acquire different sensing information, while in temperature programmed sensing (TPS), rapid thermal modulation is applied to acquire even greater information density. We have performed research to better understand what effects temperature fluctuations produce both for the base sensing materials (such as SnO₂), and at the interfaces between the sensing materials and the gaseous environment being monitored.

Temperature Dependent Electronic Behavior of SnO₂

Before examining the role of temperature variations in controlling adsorbate concentrations, we conducted investigations (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. It has generally been observed that even in the absence of an analyte, the response to a repeated temperature cycles produced some baseline pattern, characteristic of the oxide sensing material. To establish a non-chemical (no analyte) environment, measurements were made in an argon background, and an air background. A model was developed based on the thermodynamics of the band-bending picture of Figure 24a [49]. Rate equations were developed for trap occupancy and carrier concentration as a function of time and temperature. Parameters for the model included donor density, trap density, trap depth, and dielectric constant. Examples of the model applied to a specific temperature sequence are shown in Figure 24b for argon and air. As can be seen, good agreement has been obtained between predictions and experimental measurements.

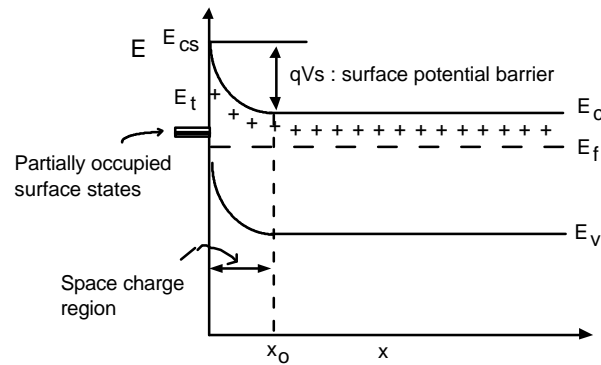


Figure 24a: Band diagram of surface states on a metal oxide sensing surface.

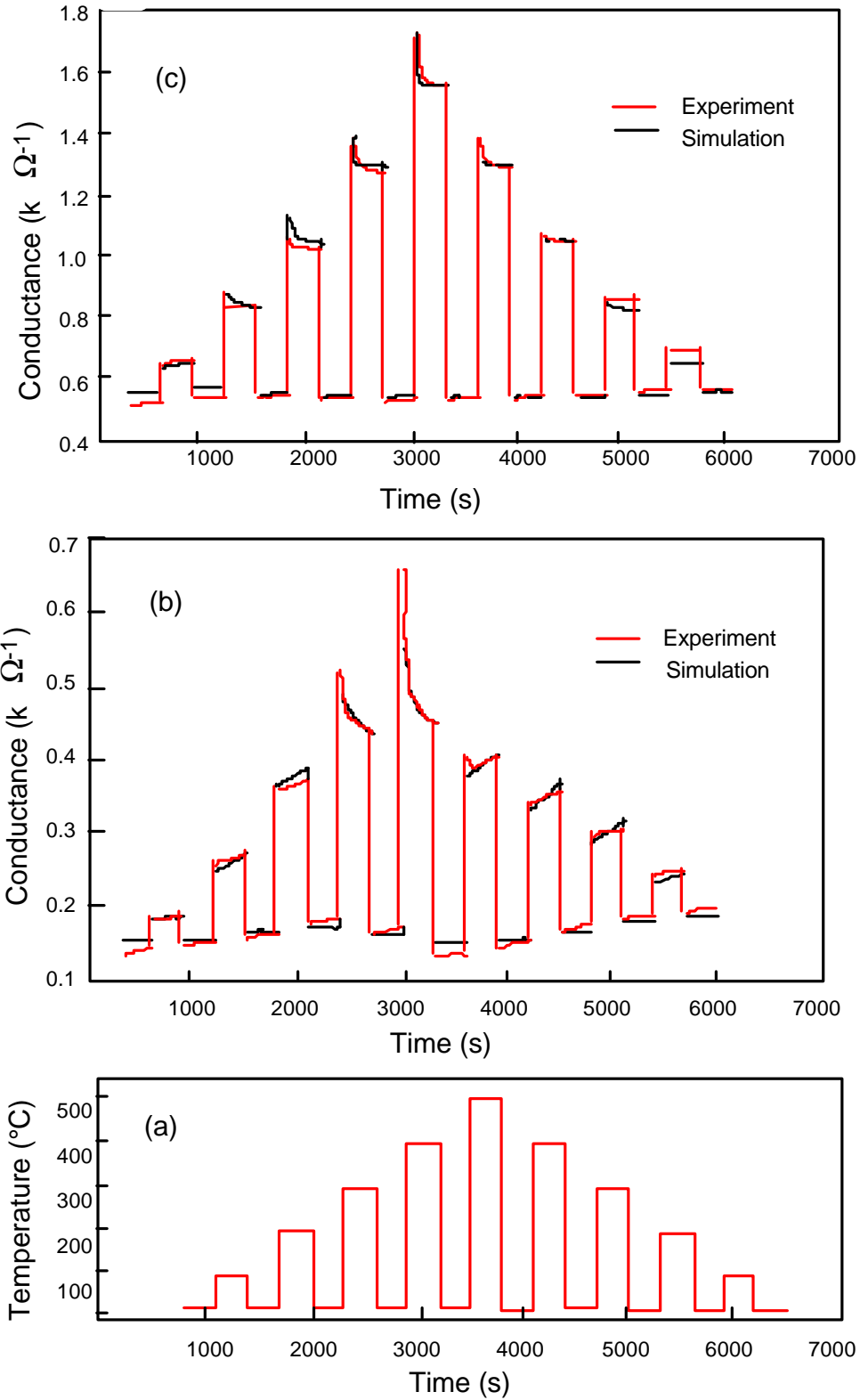


Figure 24b. Surface state model response simulations and measured sensor response to temperature profile (a) in an atmosphere of (b) air, and (c) argon.

Microarray Pulsed Desorption and Reaction Studies

In order to directly examine temperature-dependent transduction effects fundamental to gas sensing, a custom ultrahigh vacuum-based apparatus was constructed. The system, shown schematically in Figure 25, was designed to allow characterization of transient adsorption/desorption and reaction phenomena from an array of microhotplates, in vacuum and various gas environments, using a differentially pumped mass spectrometer [50].

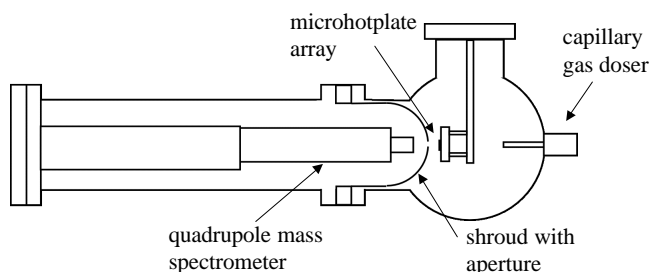


Figure 25: Schematic of temperature programmed desorption apparatus.

Multielement arrays have been used in combination with mass spectroscopic measurements in an effort to obtain kinetic information on adsorption and desorption, and to relate surface electronic effects to transient coverages of surface adsorbates. A specially-designed 340-element array for such work is shown in Figure 26. The $200\ \mu\text{m} \times 100\ \mu\text{m}$ microheater elements are closely spaced, and can be heated simultaneously to produce a sufficiently large desorption signal at an adjacent, apertured mass spectrometer mounted in an ultrahigh vacuum system (Figure 27). Samples of pure and metal-dosed SnO_2 sensing films were deposited on the 340-element arrays using the same processes as for fabricating microsensor prototypes. The low mass of the individual elements means that the *collective area can be temperature pulsed at rates in excess of $10^6\ \text{°C/s}$, with real time temperature monitoring*. Transient electrical conductance measurements (measured with a number of on-array electrical contacts) can be correlated with the coverage information derived from gas species evolved during heating pulses.

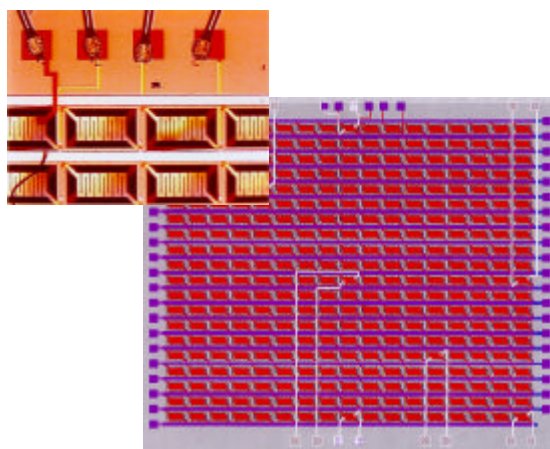


Figure 26: Schematic of microhotplate platform used for the pulsed temperature programmed desorption technique, and photomicrograph of individual elements (upper left). Each element has the dimensions of 100 microns x 200 microns.

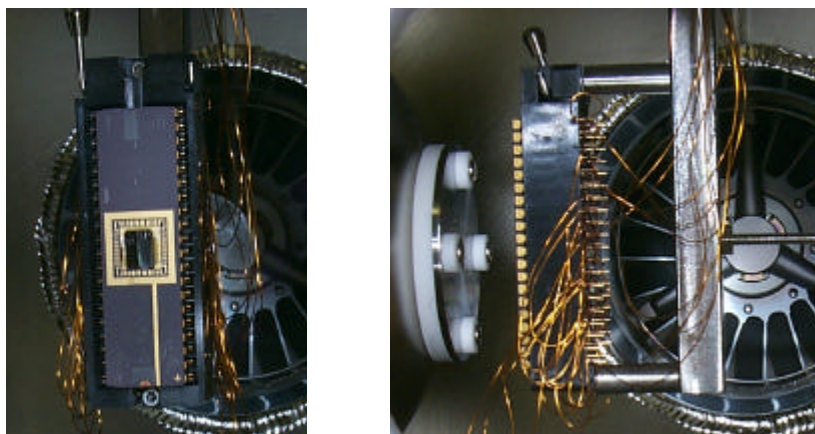


Figure 27. Left: 340-element array mounted in its package. Right: Sample facing aperture to mass spectrometer.

It is important to note that temperature programmed desorption (TPD) is a technique that is usually conducted at relatively low pressures ($<10^{-8}$ Torr), while gas sensors are typically operated at higher (atmospheric) pressures. However, because we are usually interested in detecting low concentrations of analytes, TPD experiments can be designed that probe pressure (molecular flux) regimes that are of interest in gas sensing applications. Using a combination of isothermal desorption [51], pulsed-TPD [52], and fractional desorption [53] techniques we have been able to conduct measurements under isobaric conditions. In experiments done under constant gas exposure, all of the microheater array elements are simultaneously subjected to square wave temperature pulses as short as 5 ms while gas evolution from the surface is monitored with the mass spectrometer.

A variety of adsorption/desorption phenomena can be easily examined using portions of the temperature sequence illustrated in Figure 28, which consists of: (1) a high-T (temperature) cleaning pulse, as high as 750 °C, (2) a low-T adsorption pulse, (3) an intermediate-T desorption pulse, and (4) a final high-T cleaning pulse. The time constants associated with the rates of adsorption and desorption are determined by varying the magnitude and duration of regions (2) and (3). Signal-to-noise is enhanced by averaging of repeated pulse sequences.

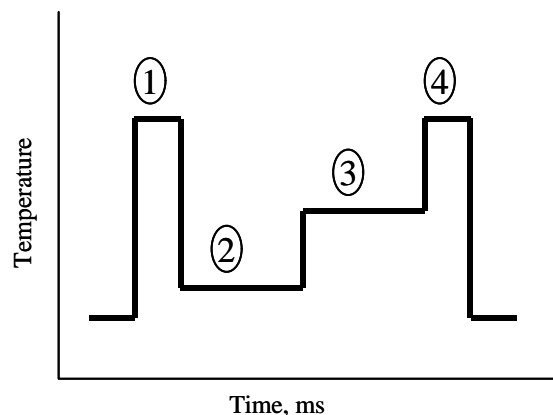


Figure 28: Schematic representation of temperature excursion sequence to probe various surface adsorption/desorption effects.

The pulsed-TPD technique has been used to map adsorption isotherms and extract kinetic parameters for methanol adsorption on CVD-deposited SnO₂ sensing films [50]. The equilibrium adsorption isotherms in Figure 29 were constructed from 185 individual pulsed-TPD experiments (each data point is the average of five experiments). In each experiment, the background methanol pressure was maintained at 1.7×10^{-8} Torr while the following program was applied: (1) T=450 °C for 200 ms, (2) T=25 °C for 5 minutes, (3) T=T_{equilibrium} for 500 ms, and (4) T=450 °C for 200 ms. Then, the surface coverage at T_{equilibrium} was determined by the integrated intensity of the mass spectrum desorption feature associated with region (4). The deviation of the measured adsorption isotherms from the calculated Langmuir isotherm at low surface coverage is consistent with an adsorption model that includes a distribution of methanol adsorption sites in which the most energetically favorable sites are preferentially occupied at low coverage.

By combining pulsed-TPD measurements with fractional desorption techniques, we have also measured isothermal desorption rates of methanol on SnO₂. The desorption transients (coverage, θ , versus time) in Figure 30 were constructed from a series of isobaric ($p_{\text{methanol}} = 9.2 \times 10^{-8}$ Torr) fractional desorption measurements described with the aid of the temperature profile in Figure 3 as follows: (1) the sample array was cleaned using an initial cleaning pulse (T=450°C for 200 ms); (2) the sample array was then maintained at room temperature to achieve saturation coverage (T=25°C for 5 minutes); (3) the array was heated to the isothermal desorption temperature for varying times (T=T_{desorption} for t_i ms); (4) a clearing pulse was applied to measure the remaining methanol coverage (T=450°C for 200 ms). The time, t_i , of the desorption pulse was varied from 5 ms to 500 ms. Note that at 500 ms, θ , is asymptotically approaching a finite coverage (equilibrium) at the higher temperatures.

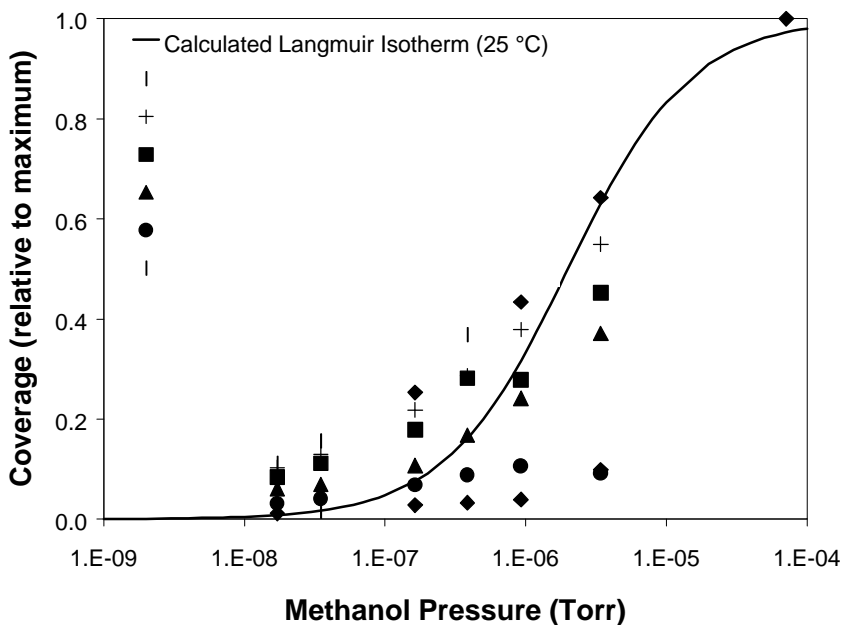


Figure 29: Equilibrium isotherms for methanol adsorption on SnO₂ measured by pulsed-TPD.

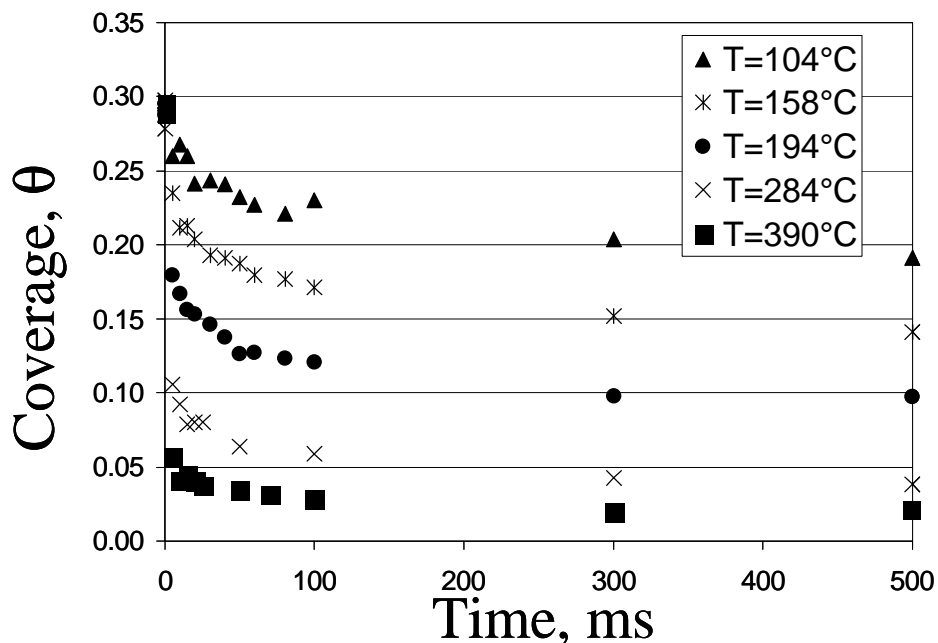


Figure 30: Transient dependence of methanol surface coverage, θ , on SnO_2 in response to a step increase in surface temperature.

In addition to measuring the adsorption kinetics of methanol on a SnO_2 sensor material, we have used isothermal pulsed temperature programmed reaction (TPR) techniques to investigate the reactions that might be occurring when the sensor is operating in an oxygen-containing environment [50]. In these experiments, the SnO_2 sample array was maintained in a constant background of 2×10^{-8} Torr of methanol and 1×10^{-6} Torr of oxygen. The initially clean array was maintained at room temperature for five minutes, then while monitoring the mass spectrometer signal corresponding to one of $m/z = 2, 18, 28, 31,$ or 44 , the following temperature program was applied: (1) $T=25^\circ\text{C}$ for 200 ms; (2) $T=400^\circ\text{C}$ for 400 ms; (3) $T=25^\circ\text{C}$ for 100 ms. The results of the experiments are displayed in the plot on the left of Figure 31, and indicate that the presence of oxygen has little effect on the adsorption or reaction of methanol on the pure SnO_2 sensor material at these gas pressures.

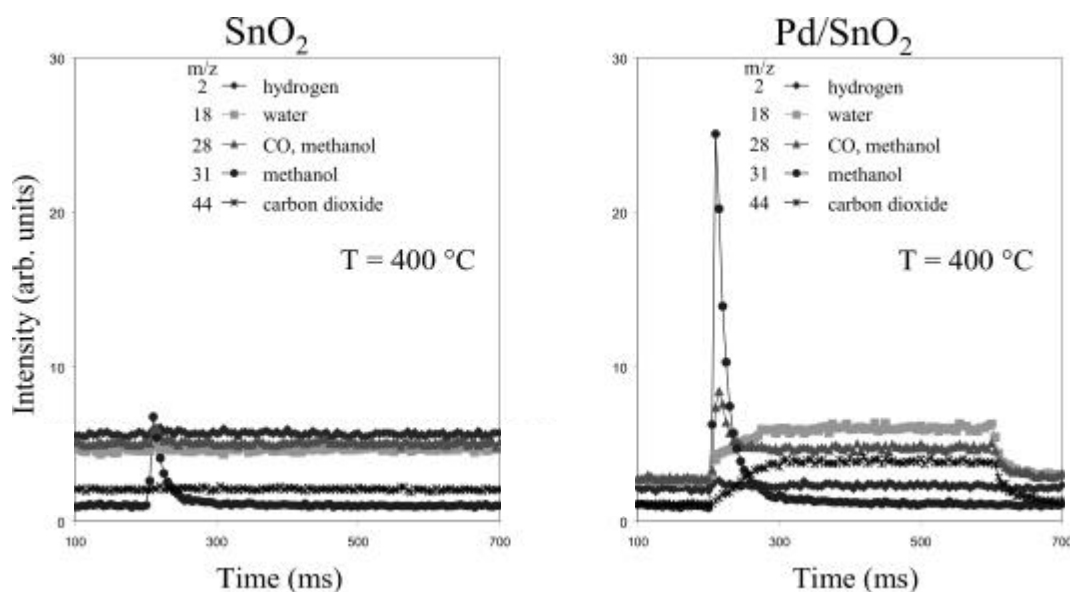


Figure 31: Pulsed temperature programmed reaction (TPR) experiment of methanol/oxygen coadsorption on SnO_2 and Pd-modified SnO_2 .

The sample array was then removed from the system, and the surface was modified by evaporating 60 nm of Pd onto the SnO₂. As already discussed above, metals such as Pd are commonly used to enhance the sensitivity and selectivity of SnO₂ sensors, and our intention was to probe the catalytic effect that addition of Pd might have on methanol adsorption and reaction. The results of the corresponding pulsed-TPR measurements on the Pd-modified SnO₂ array are shown in the plot on the right side of Figure 31. In addition to the prominent desorption features for $m/z = 31$ and $m/z = 28$ attributable to methanol, we observe oxidation products evolving that are not present in the experiments on unmodified SnO₂.

Research on Microcalorimeter Devices

The types of reaction effects that can be probed on short time scales using microheater platforms have also motivated additional work on a microcalorimetric device whose structure relates closely to the microhotplate. This device has the potential for applications in microchemical analysis, as either a chemical sensor, part of a microanalytical system, or for performing research on small samples. One version of the device is shown in the optical micrographs in Figure 32 [54]. It consists of a suspended rectangular microhotplate, with sample and reference zones at either end, each with a polysilicon microheater for temperature control. The temperature difference between the two zones is measured with a thermopile consisting of a series of successive polysilicon/metal junctions that alternate between the two zones. In a scanning differential calorimetry measurement, the two elements are heated simultaneously with a ramped temperature profile. The ramps to the two elements may be calibrated so that in the absence of any differences in thermal processes on the two elements, the output voltage of the thermopile is zero. [A thermal process zone is defined on one of the elements, for example, a catalyst for chemical sensing.] When temperature is scanned, the loss or gain of heat associated with the reaction or phase transition on the sample zone produces a difference signal on the thermopile. The microscale scanning differential calorimeter (μ DSC) device has a temperature range to 400 °C.

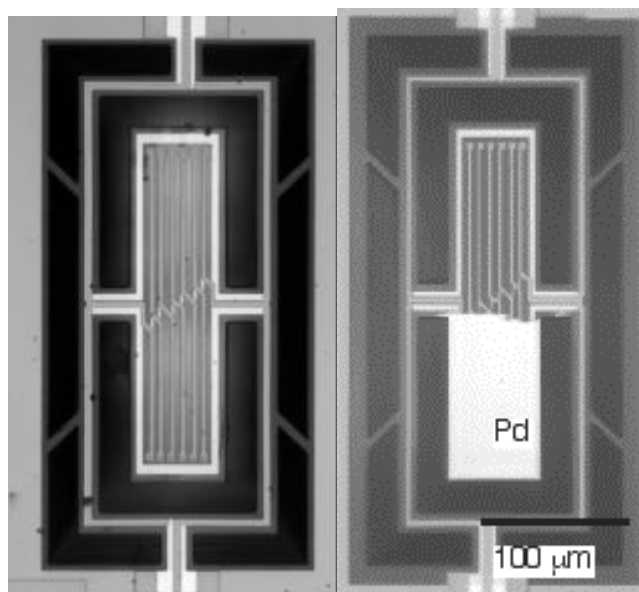


Figure 32: Micro-differential scanning calorimeter with sample and reference heaters and 5 thermopile junctions on each side (left), and with Pd on sample zone (right).

An example application for chemical sensing (Figure 33) shows the response to varying concentrations of methanol and acetone in air, while the microcalorimeter is operated with periodic ramps to 350 °C of duration 3.5 s. The thermopile responds with a periodic waveform that reflects the kinetics of the reaction of methanol and acetone over Pd in air. Different gases give different response patterns (similar to the conductometric TPS signatures), making possible pattern recognition analytical methods for gas identification.

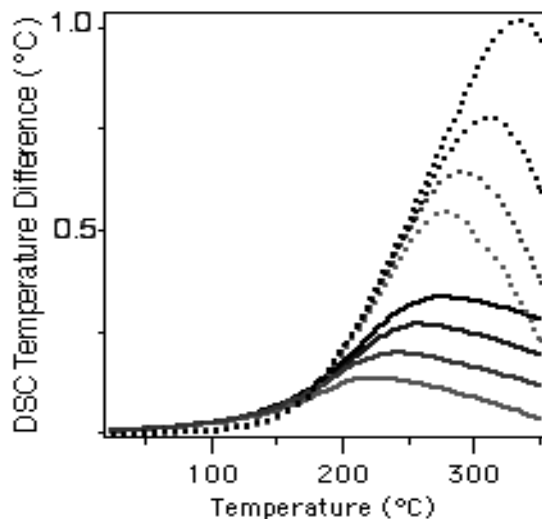


Figure 33: μ DSC response waveforms to 6, 12, 25, and 50 ppm (increasing darkness of line) of acetone (dashed) and methanol (solid), each in air.

Microhotplates as Oscillatory Reaction Probes

The occurrence of an oscillatory CO oxidation reaction on single crystal Pt is now well known, and has been widely studied by surface scientists [55, 56]. We were interested to see if a microsensor array approach could establish whether the effect occurs for supported (polycrystalline) Pt, and whether the use of multiple array devices, simultaneously operating at different temperatures, would help determine the conditions (surface temperature and gas phase partial pressure of CO in air) that create the oscillations. The detection scheme would involve having the oscillations that produce CO₂ periodically cause a reduction in the amount of adsorbed oxygen on Pt/SnO₂ microhotplate sensors, which would be expected to raise the conductance level for the given microsensor. We first studied the phenomenon with a 4-element array with the spacings between elements as shown in Figure 34a. Oscillations did occur, and the use of different microhotplate temperatures was effective in more efficiently attaining the conditions that caused them to develop [57]. We also found spatio-temporal synchronization that had been previously observed in the single crystal work. An example of three discrete Pt/SnO₂ microsensors oscillating in phase is shown in the results of Figure 35.

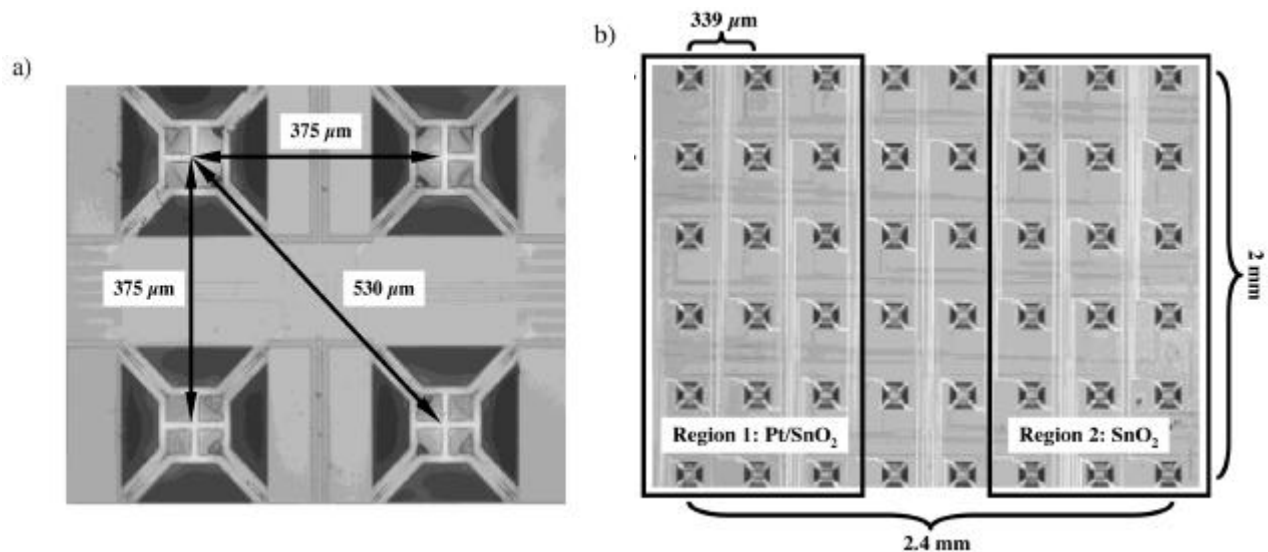


Figure 34a) 4-element array providing separation distances between elements. b) 48-element array for which two defined regions were covered with films to study proximal heating effects.

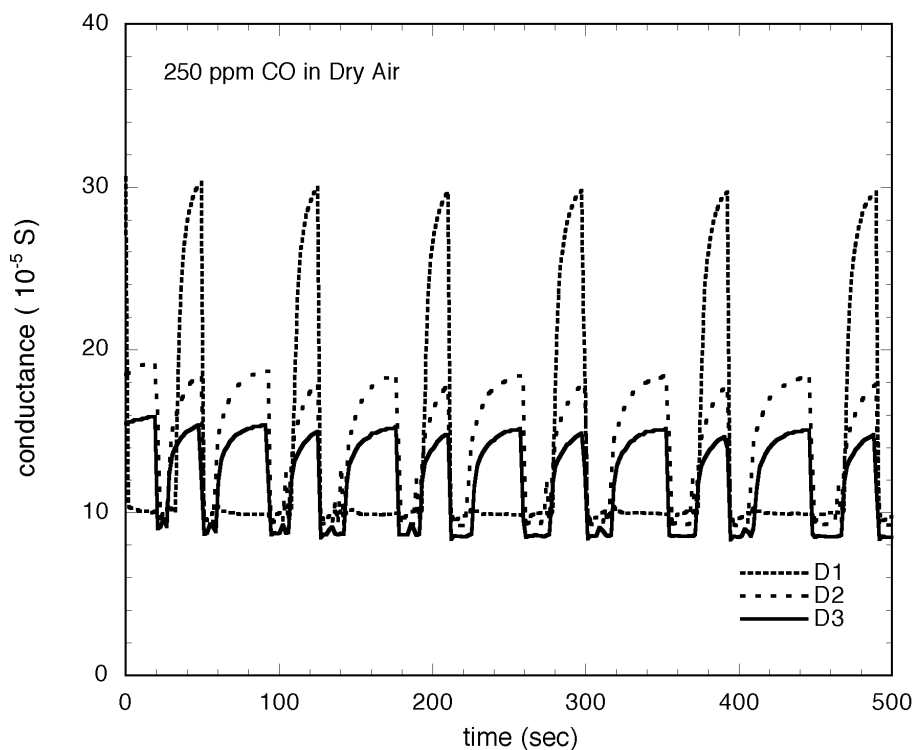


Figure 35. Synchronized CO oxidation oscillations observed on three conductometric microhotplate sensors within a 4-element array.

In an experiment where the CO partial pressure (in air) was steadily decreased, an oscillating microsensor was observed to change its oscillation frequency in a systematic (nearly linear) way, as illustrated by the data and plot of frequency vs. concentration in Figure 36 [58]. These results suggest the potential of using the Pt/SnO₂ conductometric sensors as CO detectors in certain situations (where the conditions allow oscillations to develop at an attainable temperature).

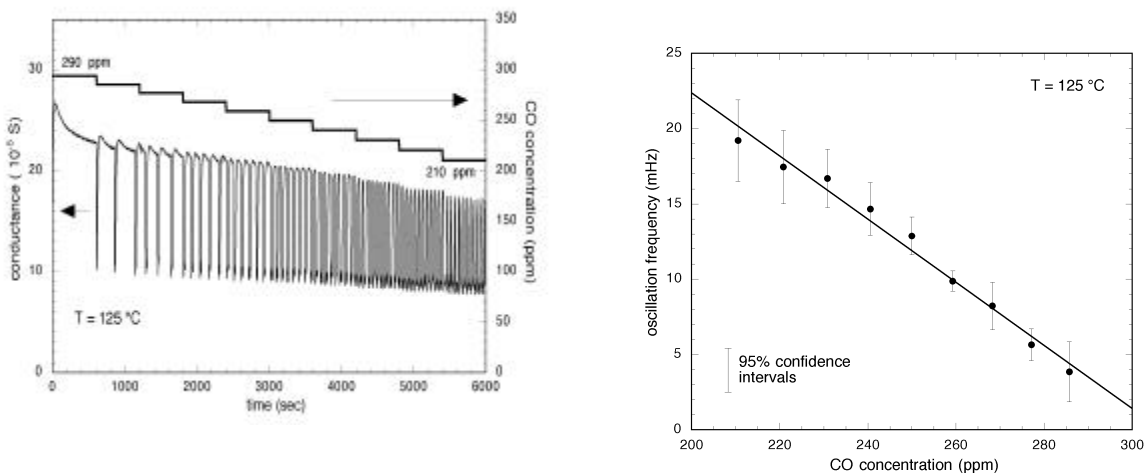


Figure 36. Left: Microsensor measurements of the oscillatory CO oxidation reaction under varied CO partial pressure. Right: Plot of oscillation frequency vs CO concentration.

Proximal Heating Effects in Microchemical Devices

In applying array methods with analytical microdevices containing microheaters (conductometric or microcalorimetric microsensors), one must be sure that the close proximity of the devices does not present crosstalk or depletion effects that will produce anomalous compositional readings on an environment. We employed portions of 36-element arrays (Pt treated side of Figure 34b) and the oscillatory CO oxidation reaction (discussed in the last subsection) to explore the magnitude of such effects [58]. The resultant effect of heating different sets of microhotplates on a single operating microsensor (Figure 37a) are summarized in Figure 37b. Other sensing situations (methanol and hydrogen, each in air) were also examined in similar experiments. Generally, the effect on the sensing signal of a microsensor when one is operating other (heated) devices ~ 300 to 500 microns away is 5% or less. The fact one can see an effect suggests that array microsensors can be improved by moving elements a bit further apart, or by operating the adjacent elements out of phase in time. It also suggests that properly implemented proximal thermal effects in microscale chemical systems can be utilized for other functions, such as releasing pre-concentrated gas from microscale pre-concentrators, or in activating on-board (reactive) filtering of test gas mixtures.

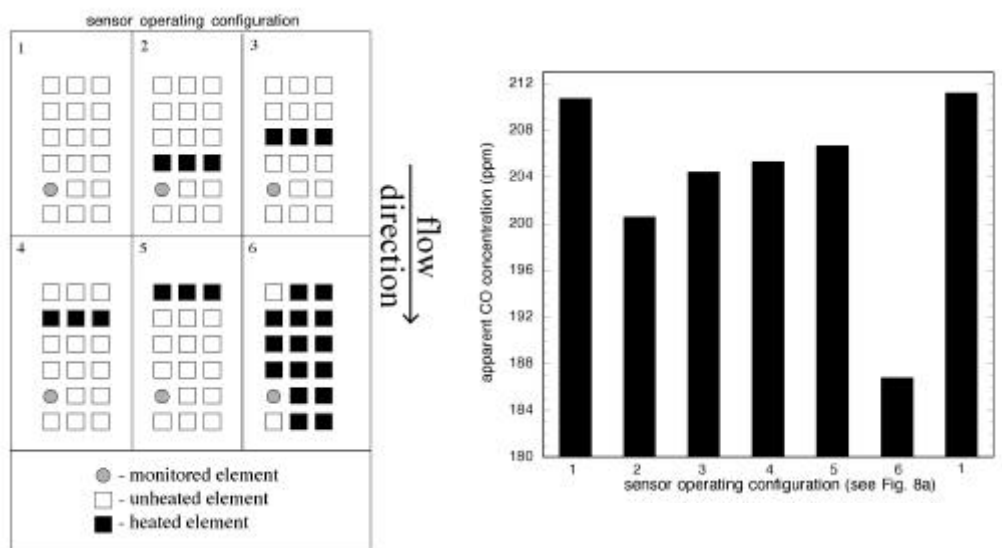


Figure 37. Results of experiments to determine the magnitude and range effects of heating proximal CO sensors. The left panel illustrates the device configurations in the Pt/SnO₂ region of the sensor array in Figure 34b. The bar graph presents the apparent concentration measured by the monitored sensor (maintained at 115 °C in a 210 μmol/mol, 210 ppm, (CO/dry air mixture) as neighboring devices were heated to 200 °C.

6. Relevance, Impact, and Technology Transfer

a. How does this new scientific knowledge focus on critical DOE environmental management problems

The primary DoE problem areas impacted by this project are monitoring of subsurface contamination (soil and groundwater), and waste storage tanks. Even as remediation progresses, continuous analysis of the site chemistry will remain a critical need for decades to come. Although adaptation of analytical techniques, e.g. gas chromatography, mass spectrometry, or FTIR, provide excellent chemical analyses, their ability to perform simultaneous measurements in many locations is limited by high cost per instrument, long analysis times, and the need for a well-trained operator. The technology described here is aimed at rapid waste characterization, and monitoring spatial variability and transport in the vadose zone, or tank headspaces, for analytes with sufficiently high vapor pressures.

The knowledge created by this project will provide the scientific basis for a less expensive, robust, miniaturized, and field-deployable alternative for chemical monitoring that consists of a generic device platform with sensing materials and operating modes that can be readily tailored to multiple site measurement needs. Our efforts establish a thin film interfacial and mechanistic science base, as well as a database of materials that will be used for specific sensing needs. The generic microsensor arrays would be materials- tunable and kinetically-tunable for a wide range of chemical (gas and vapor) measurement problems, with optimized materials selection, device operation and signal processing methods being drawn from the combination of materials studies and neural network modeling.

b. How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?

These microsensors have the potential to provide an important new measurement tool for continuous monitoring of a variety of DoE waste sites. Benefits of the technology include

- Simple electrical measurement
- Small size
- Low power requirements
- On-board circuitry
- Low-cost batch fabrication

Devices can be operated with telemetric control and interrogation as necessary, making them well suited to network deployment. The understanding of oxide and metal/oxide surfaces obtained will support development of soil and vapor-space monitors, but could also provide important methodology and data relevant to project extensions to personal protection and heavy metal sensing technology, as well as the surface chemistry of contaminated soil.

c. To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-driven applied technology development?

A key aspect of this specific project is that the science supports a wide range of applications; the technology development for a DoE site need follows as a optimization or tuning of the knowledge (operating principle, sensing material, data analysis scheme) for the given application. There are many uses for microchemical sensing, however, including for example, air quality monitors, automotive sensors, and chemical process monitors. Further, the generation of the adsorption/electronic characteristics database also impacts the catalytic community, which uses related oxide-supported systems. The demonstrated power of microsubstrate arrays for combinatorial studies should benefit other scientific/technological areas, e.g. catalysis, coatings, solar films, etc. Finally, methods of data analysis developed here can be used with a variety of sensor types to produce a system that can address a measurement situation

Meanwhile, the gases chosen for detection, such as hydrogen, ethanol, methanol, trichloroethylene, dichloromethane, benzene, methylbenzene, formaldehyde, acetone, toluene, CO, butanone, methyl ethyl ketone in concentrations to 1000 ppm in air, are important for DoE monitoring situations and so the materials and operating methods developed aim at those measurement needs.

- **What is the project's impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?**

New research methodology has been developed in this project which is of significant relevance to chemical sensor development, but also to other fields. The efficient microarray techniques for processing and characterizing materials is perhaps the approach that will be picked up on generally by universities and other research institutions. The MEMS sensor platforms and research tools we developed and utilized are already being applied by other research groups. The techniques described for studying adsorbate transients are sure to be of interest to members of the surface science community.

- **Now that the project is complete, what new capacity, equipment, or expertise has been developed?**

The project has facilitated two wafer runs of micromachined devices. With these fabrication runs, it has been possible to test a wide range of microhotplate-based designs for different device configurations. For example, we now have 48-element arrays for combinatorial studies of sensing materials, 340-element arrays for desorption studies, comb-contact structures for nanophase high-resistivity materials, and calorimetric structures for ultra-sensitive heat measurements. As part of the generation of these wafers, we have developed expertise in the design, processing and operation of a broad variety of micromachined structures. We are aware of factors that affect the success or failure of potential new designs, including robustness for long-term operation. Examples include mechanical effects on suspended devices, choice of contact materials, compatibility of metals with silicon etching procedures, and selection of sensing materials based on anticipated gas exposures. We are now at a stage where we can design and construct structures to be used for field tests to test performance and longevity.

- **How have the scientific capabilities of collaborating scientists been improved?**

Collaborating scientists on this project have worked in two important areas. The first area of signal analysis. While techniques for analyzing signals using chemometrics have been developed for other measurement problems, such as the analysis of FTIR signals, this is the first application for surface-micromachined, MEMS chemical sensing. Our collaborators learned how to operate sensors, set up test methods that explore the range sensor temperature and ambient concentrations so as to efficiently analyze and ultimately model and predict how a sensor is performing. An example is the work of J. Ding and T. MacAvoy, where signal analysis ultimately lead to the creation of a new microscopic model for the operation of a tin oxide sensor. The second area was materials synthesis. Coming from a background in engineering for MEMS, B. Panchapakesan and D. DeVoe developed knowledge of CVD growth of sensing materials, and the unique way this problem relates to this MEMS application.

- **How has this research advanced our understanding in the area?**

This project has shown a methodology for efficiently selecting and optimizing sensing materials. It also has demonstrated how important a role temperature control can play for enriching information from sensor signals. The development of methods to study adsorbate transients produced results that are fundamentally connected to adsorption – initiated transduction mechanisms.

- **What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?**

Issues that remain depend on the application. One model for proceeding would be to choose a specific measurement problem of interest to DoE-EM. From such a starting point the issues would be defined as 1) sensitivity to the desired level, 2) reproducibility, 3) stability of operation, which will depend on the anticipated frequency and duration of gas exposure, 4) the affect of additional gas phase components (such as humidity or interfering gases) on the response, and 5) the physical ruggedness of sensor in its operating package.

One area that could greatly enhance the utilization of the technology is to achieve higher chemical specificity using a microsystems approach, in which the microhotplate sensor is one component. Other components would be filters, chemically specific preconcentrators (i.e. - a high surface-area material with a chemically functionalized monolayer), and a microfluidic transport scheme. The science would be in the former two, while the third represents a microengineering problem. [See also Section 13.]

- **Have any other government agencies or private enterprises expressed interest in the project? Please provide contact information.**

In connection with our chemical microsensor program, we have (or have had) active contracts with government agencies (other than DoE), relating to other application sectors, as follows:

Defense Threat Reduction Agency (DTRA) – active
 Steve Semancik - PI
 Topic: Chemical warfare agent detection
 Program Manager: L. Pollack

NASA – active
 Steve Semancik – PI
 Topic: Detecting gases and trace gases in planetary atmospheres
 Program Contact: J. Landers

NIST (internal) – FY00 – FY01
 Steve Semancik – PI
 Topic: Microsensor research for detecting carbon – containing contaminants in hydrogen fuel streams for fuel cells
 Project Manager: G. Ceasar (NIST/ATP)

There are also Research Licenses and CRADAs that have developed from interest in our Chemical Microsensor Program (which has received supplemental (OA) funding through the DoE-EMSP support of this project).

Companies (and universities) that have interacted through such mechanisms during the course of this project include:

ATMI, Inc.
 Cyrano Sciences
 Boston MicroSystems
 University of Massachusetts/Lowell
 Williams Pyrotechnic, Inc.

(Contact information for these institutions is available from the Technology Partnerships Office at NIST.)

Others expressing interest:

J. Curtis Marines/CBRF 8/01
 Platforms for biosensing
 Inputs made to roadmapping workshop

R. Lareau FAA 7/01
 Microsensor capabilities for explosives detection

7. Project Productivity

As stated in Section 4, our objective in this project related to producing, and demonstrating the utility of, a scientific database for oxide conductometric gas/vapor sensing materials, in order to

develop a tunable, MEMS-based chemical sensing technology. Major goals indicated in our original proposal are listed and addressed below.

1) demonstrating the utility of micromachined, microhotplate arrays as highly efficient platforms for surveying the fabrication and properties of sensing materials

New 16-element and 36-element microarrays were designed, constructed, etched, packaged and used to conduct temperature-dependent experimentation. As temperature measurement and control, as well as microelectrodes for probing deposited films, can be individually-addressed at each element, these array platforms were very effective in carrying out *both* temperature-dependent processing and temperature-dependent sensing evaluation studies. The properties and performances of the materials can then be directly correlated.

2) establishing temperature-dependent databases for the adsorption/desorption/reaction characteristics of gases on sensing films, and relating measured interfacial conductance changes to adsorbate type and concentration.

Databases were constructed using the varied sample processing procedures developed in this project, in conjunction with our microarray materials/performance screening technology. We examined temperature-dependent CVD growth of TiO_2 , and SnO_2 deposited by a variety of methods, to create different microstructures. The work on SnO_2 involved nanoparticle seeding to affect nucleation, as well as the deposition of surface-dispersed metal additives on CVD SnO_2 . Large databases on parametric fixed-temperature and temperature programmed sensing (TPS) operation were assembled for both the seeded and additive SnO_2 , using 36-element arrays. As illustrated in Section 5c, portions of the very sizeable response data (temperature snapshots) were often plotted in radar plots.

3) utilizing adsorption/conductance databases with chemometric and neural network modeling as the basis for designing multi-element and temperature programmed gas sensors, with a microhotplate-based sensing demonstration

Signal processing was done using both chemometric and neural network methods. Both were found to be effective at recognizing analytes and in quantifying concentrations for single analytes, in air, for data taken in 4-element demonstrations, and for 36-element array databases. Analyses indicated the value of both materials/microstructure-based selectivity, and the rich content of temperature programmed sensing.

4) establishing the quality and potential of sensing performance as a function of oxide microstructure and additive metal loading and nucleation

In the course of this work, we consistently noted that fine-grained oxide films offered higher sensitivity. In particular, sol-gel and spun-on nanoparticle oxides were found to have the largest sensitivity factors. Metal additives, at appropriate low coverages (~ 30 Å deposition, annealed to form particles), also were shown to play an important selectivity role. When data from these sensing films was used in combination with signal processing, determinations could be made to indicate the subsets of sensors that were the most powerful for recognition and quantification functions. This type of guidance is particularly helpful in fabricating materials into sensing arrays for specific applications, such as would be encountered in field demonstrations.

We performed laboratory demonstrations on our sensing technology using a test gas set that included hydrogen, ethanol, methanol, trichloroethylene, dichloromethane, benzene, methylbenzene, formaldehyde, acetone, toluene, carbon monoxide, butanone, methyl ethyl ketone, in concentrations ranging primarily between 1 ppm and 200 ppm, but up to 1000 ppm, in air. Field demonstrations were discussed with DoE personnel at several sites, but we were not able to schedule field demonstrations inside the three year time frame of the project. As pointed

out in Section 14 below, field demonstrations are the obvious next step for testing our microsensor monitoring technology.

The project stayed very close to the schedule outlined in our original Research Plan. Two custom vacuum systems were constructed for the work, one for developing new sensing film processing methods, and the other for examining fast adsorbate transient phenomena through microarray-based desorption and mass spectrometry. Both systems were completed on time, and used extensively in the project. While signal processing efforts got started in Year 1, the level, as planned, ramped up considerably into Year 3. It was at that point that chemometric and neural network efforts dovetailed with the databases being produced to demonstrate both recognition and quantification capabilities on a variety of analytes (single and mixed), in air.

There were no major revisions to the work plan. We did emphasize the surface analytical efforts along fruitful thermal desorption directions, rather than using other spectroscopies, as the adsorbate transient studies were particularly relevant to temperature-pulsed microsensor operation. We also felt it important to add the microsensor-based examination of oscillatory reactions, which then fed nicely into our investigation of proximal chemical/heating effects in microscale arrays. There were some personnel modifications (additions) in the area of signal processing late in Year 2 and in Year 3, as researchers at Arizona State University and the Israel Atomic Energy Commission augmented the efforts from the University of Maryland.

8. Personnel Supported

Persons supported and /or associated with the research effort

Dr. Steve Semancik (PI)
Dr. Richard Cavicchi
Dr. Michael Tarlov
Dr. Thomas McAvoy (University of Maryland)
Dr. Don DeVoe (University of Maryland)
Dr. Karl Booksh (Arizona State University)
Mr Zvi Boger (Israel Atomic Energy Commission)
Dr. Robin Walton*
Dr. Clay Wheeler*
Dr. Nancy Savage*
Dr. Chuck Taylor*
Mike Carrier[s]
Maria Aquino-Class[s]
Jim Allen
Chip Montgomery
Jason Tiffany
Brian Dable (Arizona State University)[s]
Junhua Ding (University of Maryland)[s]
Balaji Panchapakesan (University of Maryland)[s]

Those listed here without a specific affiliation are (or were) employed at NIST during the course of the project. Those marked "*" contributed under the National Research Council (NRC)- NIST Postdoctoral Associateship Program. Those marked "[s]" were students in either B.S. (one), M.S. (one) or Ph.D. programs (three).

9. Publications

(a) Journal and Book Publications

1. 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.
2. R.E. Cavicchi, R.M. Walton, J.D. Allen, M. Aquino-Class and B. Panchapakesan, "Spin-On Nanoparticle Tin Oxide for Microhotplate Gas Sensors," Sensors and Actuators B: Chemical 77: 145-154 (2001).
3. M.C. Wheeler, R.E. Cavicchi, R.M. Walton and S. Semancik, "Chemical Crosstalk Between Heated Gas Microsensor Elements Operating in Close Proximity," Sensors and Actuators B: Chemical 77: 167-176 (2001).
4. S. Semancik, R.E. Cavicchi, C. Wheeler, J.E. Tiffany, G.E. Poirier, R.M. Walton, J.S. Suehle, B. Panchapakesan and D.L. DeVoe, "Microhotplate Platforms for Chemical Sensor Research," Sensors and Actuators B: Chemical 77: 579-591 (2001).
5. J. Ding, T.J. McAvoy, R.E. Cavicchi and S. Semancik, "Surface State Trapping Models for SnO₂-Based Microhotplate Sensors," Sensors and Actuators B: Chemical 77: 597-613 (2001).
6. B. Panchapakesan, D.L. DeVoe, R.E. Cavicchi and S. Semancik, "Nanoparticle Engineering and Control of Tin Oxide Microstructures for Chemical Microsensor Applications," Nanotechnology, 12: 336-349 (2001).

(b) Proceedings Publications

7. 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, (June 1999) Vol. 1, pp. 676-679.
8. 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.
9. 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.
10. 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.
11. J. Tiffany, R.E. Cavicchi and S. Semancik, "Microarray Study of Temperature Dependent Sensitivity and Selectivity of Metal/Oxide Sensing Interfaces," Proceedings of SPIE (2000) Vol 4205, pp. 240-247.

(c) Accepted Publications

12. S. Semancik and R.E. Cavicchi, "Micromachined Arrays as Sensor Platforms and Materials Research Tools," Proc. of the 3rd International Aviation Security Technology Symposium (Atlantic City, NJ, November 27-30, 2001).
13. C.J. Taylor and S. Semancik, "The Use of Microhotplates as Microdeposition Substrates for Materials Exploration," Chemistry of Materials.

Manuscripts in Preparation

1. B. Panchapakesan, D.L. DeVoe, R.E. Cavicchi and S. Semancik, "Sensitivity and Temperature Programmed Selectivity of Nanoparticle-Seeded SnO₂ Microsensors."
2. C. Kendrick, R.E. Cavicchi and S. Semancik, "Improved Performance of Polymer Microsensors Using Fast Thermal Conditioning."
3. M.C. Wheeler, R.M. Walton, R.E. Cavicchi and S. Semancik, "Tin Oxide Microsensor Arrays as Probes for the Oscillatory CO Oxidation Reaction on Supported Platinum."
4. M.C. Wheeler, R.E. Cavicchi and S. Semancik, "A Microarray Technique for Measuring Adsorption/Desorption Kinetics."
5. S. Semancik, "The Use of Micromachined Arrays for Combinatorial Studies of Temperature Dependent Materials Properties," – Invited chapter for the Marcel Dekker book Combinatorial Materials Synthesis Methods.
6. S. Semancik, "Microdevice Studies of Gas Sensing Materials and Concepts - Pages" article in Analytical Chemistry."
7. N. Ortins Savage, G. Gillen, M.J. Tarlov and S. Semancik, "Thermolithographic Patterning on Microhotplates Using Organosilanes."
8. C. Taylor, R.E. Cavicchi and S. Semancik, "Response Reversals for TiO₂-Based Gas Sensing Films."
9. B. Dable, K. Booksh, R.E. Cavicchi and S. Semancik, "Calibration of Microhotplate Conductometric Gas Sensors by Nonlinear Multivariate Regression Methods."
10. B. Dable, K. Booksh, R.E. Cavicchi and S. Semancik, "Microarray Studies of the Effects of Metal Additives on SnO₂ Sensing Response."
11. Z. Boger, S. Semancik and R.E. Cavicchi, "Artificial Neural Networks Method for Identification of the Most Relevant Inputs from Conductometric Microhotplate Sensors."

Web Publications

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

Web-based Document:

Poster from EMSP (Environmental Management Science Program) National Workshop in Atlanta, GA, Wed. April 25, 2000 "Microhotplate-Based Conductometric Gas Microsensors"
http://www.osti.gov/em52/NWS2000_Posters/id65421.pdf

10. Interactions

a. Participation / Presentations

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. "Microhotplate Array Studies of the Processing and Performance of Gas Sensing Materials," ATP Workshop on Combinatorial Methods for Materials Discovery, ATP 1998 Fall National Meeting, Atlanta, GA, November 18, 1998 [S. Semancik - **Invited**].
3. "Opportunities and Challenges in the Development of High Performance Materials for Gas Microsensors," Department of Materials Engineering Seminar, University of Maryland, College Park, MD, November 20, 1998 [S. Semancik - **Invited**].
4. "The Development of Tunable Gas Microsensors: Materials Research Issues," Department of Materials Science Seminar, University of Pennsylvania, Philadelphia, PA, January 28, 1999 [S. Semancik - **Invited**].
5. "Reaction Processes on Micromachined Arrays: The Fabrication and Operation of Gas Microsensors," Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, CA, March 4, 1999 [S. Semancik - **Invited**].
6. "Micromachined Array Studies of Tin Oxide Films: Nucleation, Structure and Gas Sensing Characteristics," MRS Spring National Meeting, San Francisco, CA, April 7, 1999 [B. Panchapakesan].
7. "Using Microhotplates to Optimize the Performance of Gas Sensing Materials," Joint Colloquium of the Materials Science and Chemical Engineering Departments, University of Michigan, Ann Arbor, MI, April 9, 1999 [S. Semancik - **Invited**].
8. "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, June 7, 1999 [R.M. Walton].
9. "The Development of Low Power, Solid State Gas Microsensors," Center for In Situ Exploration, Jet Propulsion Laboratory, Pasadena, CA, June 22, 1999 [S. Semancik - **Invited**].
10. "The Use of Micromachined Array Platforms for Tuning Oxide-Based Gas Sensing Materials," Gordon Research Conference on Solid State Studies in Ceramics", Meriden, NH, August 4, 1999 [S. Semancik - **Invited**].
11. "Modeling Microhotplate Gas Sensors," American Chemical Society National Meeting, New Orleans, August 24, 1999 [T.J. McAvoy].
12. "The Development of Temperature-Controlled Gas Microsensors: Using Microarrays as Sensor Platforms and Materials Research Tools," Annual Scientific and Industrial Affiliates

Meeting of the Northwestern University Center for Catalysis and Surface Science, Evanston, IL, September 14, 1999 [S. Semancik - **Invited**].

13. "Microhotplate Gas Sensor Arrays," SPIE International Symposium on Environmental and Industrial Sensing, Boston, MA, September 17-22, 1999 [R.E. Cavicchi].

14. "Solid State Gas Microsensors for Environmental and Industrial Monitor International Symposium on Industrial and Environmental Sensing, Boston, MA, September 17-22, 1999 [S. Semancik].

15. "Quantification of a Single Component Gas in Air with a Microhotplate Gas Sensor Using Partial Least Squares Techniques," SPIE International Symposium on Industrial and Environmental Sensing Boston, MA, September 22, 1999 [J. Ding].

16. "Investigations of Surface Reactions on Thin Film-Supported Catalysts Using Microhotplate Arrays," 46th International Symposium of the American Vacuum Society, Seattle, WA, October 28, 1999 [S. Semancik].

17. "Microhotplates: a Platform for Sensors and Materials Studies," University of Maine, Orono, ME, December 10, 2000 [R.E. Cavicchi – **Invited**].

18. "The Use of Chemical Kinetics Studies in Developing Improved Gas Microsensors," Gordon Research Conference on Chemical Sensors and Interfacial Design, Ventura, CA, January 23, 2000 [M.C. Wheeler].

19. "Silicon-based Gas Microsensor Arrays," IFPAC Symposium on Microanalytical Systems, Las Vegas, NV, January 24, 2000 [R.E. Cavicchi].

20. "Micromachined array studies of tin oxide films: nucleation, structure and gas sensing characteristics," Materials Research Society Spring 1999 Meeting, San Francisco, CA, April 7, 1999 [B. Panchepakesan].

21. "Tuning Microhotplate Arrays for Industrial and Environmental Monitoring," American Physical Society Meeting - Materials Advances for Chemical Sensing Applications Session, Minneapolis, MN, Minneapolis, MN, February 3, 2000 [R.E. Cavicchi - **Invited**].

22. "Using Chemical Kinetic Effects for Understanding Chemical Sensing Mechanisms," Sigma Xi Postdoctoral Poster Presentation, NIST, Gaithersburg, MD, February 17, 2000 [M.C. Wheeler].

23. "Microhotplate-Based Conductometric Gas Microsensors: The Challenges and Opportunities of Microarray Technology," PPG Glass Technology Center Seminar, Pittsburgh, PA, March 28, 2000, [S. Semancik - **Invited**].

24. "The Need for Real Time Thermal Pattern Measurements on Microarrays in Combinatorial Studies of Chemical Phenomena," NIST Internal Workshop on Non-Contact Thermometry, NIST, Gaithersburg, MD, April 14, 2000 [S. Semancik].

25. "Microhotplate-Based Conductometric Gas Microsensors," EMSP (Environmental Management Science Program) National Workshop, Atlanta, GA, Wed. April 25, 2000 [R.E. Cavicchi].

26. "Correlation of Chemisorption and Electronic Effects for Metal/Oxide Interfaces: Transducing Principles for Temperature-Programmed Gas Microsensors," DoE/EMSP National Workshop, Atlanta, GA, April 27, 2000 [R.E. Cavicchi].

27. "Micromachined Arrays for Combinatorial Materials Processing and Multisample Characterization," Materials Research Society National Meeting, San Francisco, CA, April 26, 2000 [S. Semancik – **Invited**].
28. "Microhotplate Arrays as Research and Sensor Platforms," Symyx Technologies, Santa Clara, CA, April 27, 2000 [S. Semancik - **Invited**].
29. "The Use of Micromachined Arrays for Efficient Sample Processing and Characterization," Combinatorial Materials Science: A National Dialogue Workshop Gaithersburg, MD, May 31, 2000 [S. Semancik].
30. "A Study of Interactions Between Heated Gas Microsensor Elements Operating in Closeth International Meeting on Chemical Sensors, Basel, Switzerland, July 4, 2000 [M.C. Wheeler].
31. "Spin-on Nanoparticle Tin Oxide for Microhotplate Gas Sensors," 8th International Meeting on Chemical Sensors, Basel, Switzerland, July 4, 2000 [R.E. Cavicchi].
32. "Microhotplate Platforms for Chemical Sensor Research," 8th International Meeting on Chemical Sensors, Basel, Switzerland, July 4, 2000 [S. Semancik].
33. "Microarray Devices for Research on Materials and Chemical Phenomena," Physical Electronics Laboratory Seminar, Swiss Federal Institute of Technology, Zurich, Switzerland, July 6, 2000 [S. Semancik - **Invited**].
34. "Microarray Study of Temperature Dependent Sensitivity and Selectivity of Metal/Oxide Sensing Interfaces," SPIE Proceedings of the Advanced Environmental and Chemical Sensing Technology, September, 2000. [J. Tiffany].
35. "A Microarray Technique for Measuring Adsorption/Desorption Kinetics," 47th International Symposium of the American Vacuum Society, Boston, MA, October 3, 2000 [M.C. Wheeler].
36. "Efficient Microarray Studies of Temperature-Dependent Materials Processing and Performance," NIST Non-Contact Thermometry National Workshop, NIST, Gaithersburg, MD, October 16, 2000 [S. Semancik].
37. "Microarray Studies of the Formation and Properties of Oxide Films and Metal/Oxidend International Workshop on Oxides, Taos, NM, January 15, 2001 [S. Semancik - **Invited**].
38. "Silicon-based Gas Microsensor Arrays," 14th International Forum on Process Analytical Chemistry-IFPAC, Las Vegas, NV, January 24, 2000 [R.E. Cavicchi].
39. "Microarray Studies for Efficient Processing, Testing, and Optimization of Sensing Materials," 8th International Symposium on Olfaction and the Electronic Nose, and the 199th Meeting of the Electrochemical Society, Washington, DC, March 27, 2001 [S. Semancik].
40. "Microhotplate Arrays as Microdeposition Substrates for Materials Exploration," Gordon Research Conference on Chemistry of Electronic Materials, Connecticut College, New London, CT, June 2001 [C.J. Taylor].
41. "Sol-Gel Tin Oxide Gas Sensors for the Detection of Trichloroethylene," 34th Middle Atlantic Meeting of the American Chemical Society, Towson, MD, June 1, 2001 [N.O. Savage].

42. "Development of an Application-Tunable Gas Microsensor Array Technology," Workshop on Aircraft Fire Detection, NIST, Gaithersburg, MD, March 29, 2001 [S. Semancik - **Invited**].
43. "Microarray Studies of Processing and Gas Sensing Performance for Oxide Films," American Ceramics Society, Indianapolis, IN, April 24, 2001 [S. Semancik - **Invited**].
44. "Microhotplate Array Studies of the Processing and Performance of Gas Sensing Thin Films," Industrial Candidates Meeting of the NIST Combinatorial Methods Center, Gaithersburg, MD, July 10, 2001 [S. Semancik].
45. "Microhotplate gas sensor arrays," 222nd American Chemical Society National Meeting, Chicago, IL, August 26-30, 2001 [R. Cavicchi].

b. Consultative and Advisory Functions to Other Labs and Agencies

Efforts were made to become familiar with the technical details of DoE measurement needs through participation in meetings, workshops and conferences, and through direct communications with DoE site personnel as outlined below. The communications were concentrated in Years 2 and 3 of the project.

DoE-related interactions during Year 2:

| | | |
|---|--------------------|------------|
| Roland Hirsh | DoE/Germantown | 10/99 |
| assistance with making site contacts for measurement needs information | | |
| Patrick Jackson | DoE/Savannah River | 10-11/99 |
| discussions on identification of target analytes and background conditions at Savannah River | | |
| Jim Hanson | DoE/Richland | 10-11/99 |
| discussions on identification of target analytes and background conditions at Richland | | |
| Virginia Rohay | DoE/Richland | 11/99-1/00 |
| discussion of CCl ₄ in vadose zone | | |
| discussion of other analytes of interest, including TCE, TCA, PCE, MEK | | |
| discussions of background conditions and relevant concentration levels | | |
| (these were utilized in designing our laboratory tests for database development on sensing films / target analytes) | | |

DoE-related interactions during Year 3:

| | | |
|--|-----------------------------|--------|
| Jack Corey | Westinghouse/Savannah River | 5/01 |
| discussion of possible site testing arrangements in connection with the Subsurface Contaminants Focus Area (SCFA) | | |
| Glenn Bastiaans | Ames Lab | 5-6/01 |
| discussions of long term monitoring technologies and the utility of our microsensors for problems in the Tank Focus Area (TFA) | | |
| Carolyn Purdy | CTC | 5-6/01 |
| discussion of field probing methods for subsurface deployment concepts and issues | | |

Participation in DoE/EMSP Workshops and National Meetings are noted in the listing of 10a. Participation in other Workshops, related to combinatorial methods, noncontact thermometry, and aircraft fire detection, are also noted there. In addition, written documentation was provided to the organizers for use in the June, 2001 DoE Workshop on Long Term Monitoring.

c. Collaborations

This project was centered in the Chemical Science and Technology Laboratory at NIST, but important contributions were made by other institutions in the various technical component areas. These contributions are summarized below.

MIT – Lincoln Laboratories: foundry runs to produce wafers of our device designs

University of Maryland: basic thermal response properties and microstructure engineering of oxide microsensors; signal processing by neural networks

Arizona State University: chemometric signal processing

Israel Atomic Energy Commission: neural network modeling

11. Transitions

a. see section 6i

b. Aspects of interest to the entities listed in Section 6i include microdevice designs, thermal control of microsensors, temperature-controlled materials processing, explosives detection, and thermal-based sensing.

12. Patents

1. R.E. Cavicchi, G.E. Poirier, J.S. Suehle, M. Gaitan and N.H. Tea, U.S. Patent 6,079,873 "Micron-Scale Differential Scanning Calorimeter on a Chip" (2000).

2. T. Kunt, R.E. Cavicchi, S. Semancik and T.J. McAvoy, U.S. Patent 6,095,681, "Method for Operating a Sensor to Differentiate Between Analytes in a Sample" (2000).

13. Future Work

This recently completed 3-year project dealt with several component studies, all aimed at advancing the capabilities of conductometric gas microsensor array technology. Research was conducted to develop processing methods for incorporating a range of sensor materials into tiny, MEMS platforms. Microarray studies developed databases for selecting and optimizing sensing films for detecting specific analytes in a range of monitoring applications. Research on interfacial phenomena as well as signal processing provided further insights on desired operational temperature schedules to produce the most useful data, and high information density signals. Collective findings from these studies have allowed us to advance a gas microsensor array technology in which the fast thermal characteristics of the microhotplates can be used to operate

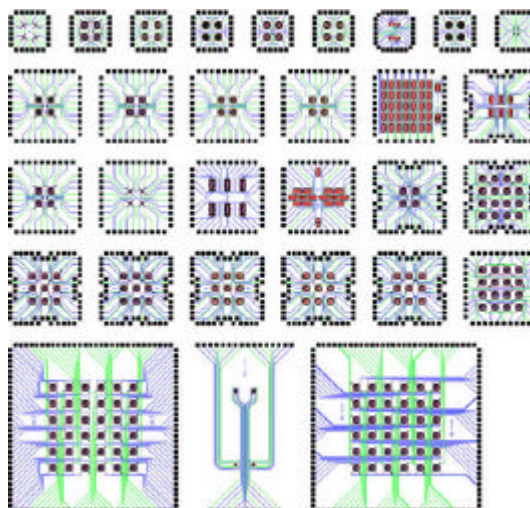
the low power devices in temperature programmed sensing modes. The scientific and technological efforts of the project have positioned us to move forward in two primary areas.

First, our findings have created a “detection tool” that is tunable for recognition and quantification for different analytes in different background conditions. This technology is now poised for field tests at one or more DoE waste sites. While our databases and laboratory demonstrations have involved an analyte set including trichloroethylene, dichloromethane, benzene, methylbenzene, fomaldehyde, acetone, toluene, methyl ethyl ketone, butanone, ethanol, methanol, carbon monoxide and hydrogen, the library can be easily extended to other chemicals using the methods we describe in this Report. Such tests would establish the feasibility of the NIST gas/vapor microsensor technology, and could encourage commercialization. By applying the microsensors at different sites, for different monitoring needs, the tunability aspect could also be clearly exhibited.

The results reported here involving 1) development of microscale platforms for microsensor prototypes and specialized research, 2) deposition methods for microsubstrate devices, and 3) the study of thermally-controlled (rapid) interfacial phenomena, have also positioned us well to extend our research toward the development of new microscale functionality. As described below, these new studies would enable the incorporation of our microhotplate conductometric detectors into microanalytical sensing systems.

Figure 38 shows the newest die design, completed in mid 2001. Through studies conducted with our MIT – Lincoln Laboratories collaborators, new metallizations have been developed for the foundry wafer runs with this die, which will improve the microelectrodes in our sensors. The die contains additional 4-element (and 9-element) arrays for fabricating microsensors for DoE field tests, as well as 16-element and 36-element arrays for developing and screening sensing films. However, it also includes a number of new thermally-controlled microdevice structures. Examples of two of the included structures, modular components for an integrated microanalytical sensing system, are illustrated in Figure 39. Figure 39a shows a research structure for examining reactive filtering effects on a test gas stream, while Figure 39b shows microheater platforms for preconcentration materials that would evolve collected gases/vapors to a central microsensor.

Figure 38. New die design
For wafer run at MIT –
Lincoln Laboratories.



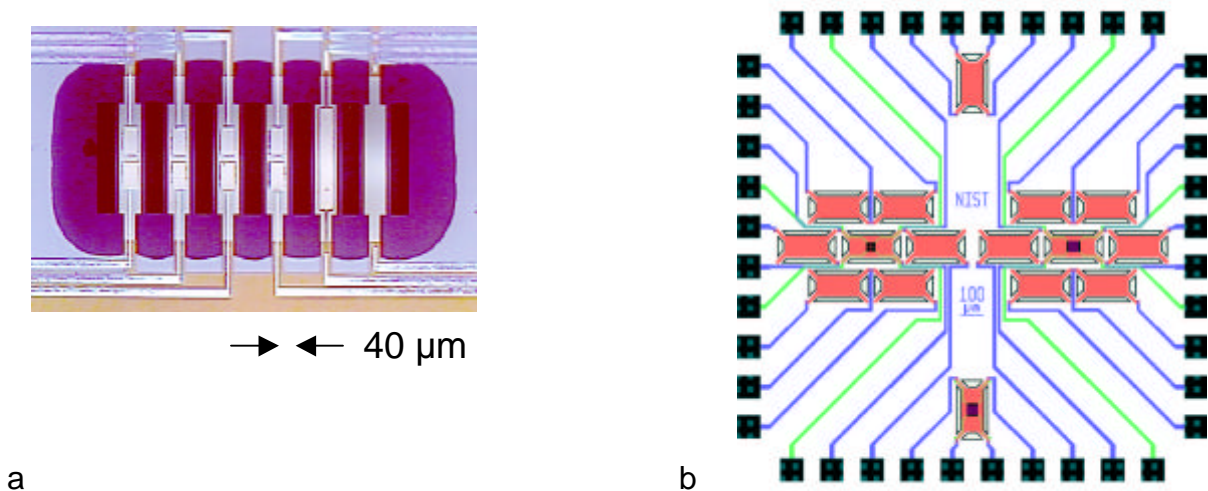


Figure 39. Designs of microscale devices to be studied for new functionality: (a) reactive filter and sensor bridges, (b) two preconcentrator platforms each surrounding a central sensor.

The die in Figure 38 also includes custom structures that would be examined for microfluidic (heat-driven gas and liquid) transport, and volatilizers to convert liquids to vapors, which could then be sensed using our developed conductometric sensors (or other new sensors like the microcalorimeter, mentioned in Section 5). A schematic diagram for a new microanalytical system, which includes microhotplate sensors, but also uses other fast microheaters for new functionality, is shown in Figure 40. Of course, new materials, other than conductometric sensing films, would also be required for realization of the new microscale functions. These would include catalysts for the filters, and high area materials for the preconcentrators. These types of materials could also be examined using the efficient methods we developed in this project. To use a “delayed activation” approach with sensor arrays, we would also develop coating materials that would protect sections of sensors until the coating was burned off to expose fresh replacement sensors; such an approach could extend device lifetimes for field deployment.

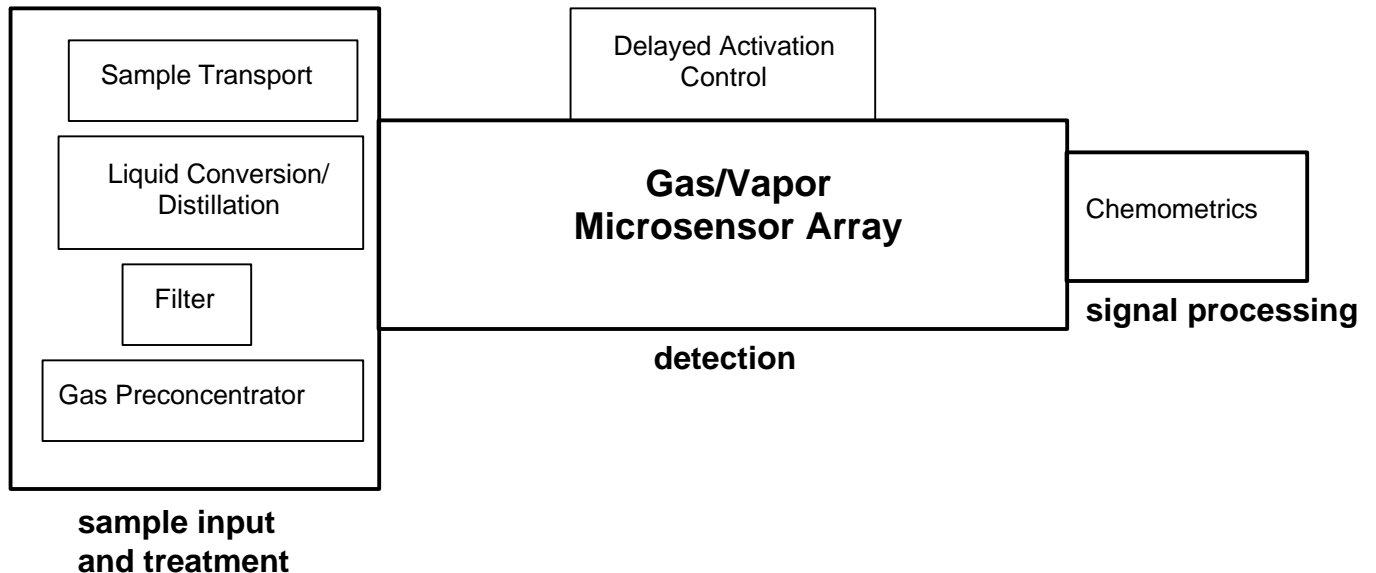


Figure 40. Schematic representation of microanalytical sensing system.

Clearly, there would be considerable synergy between the technical infrastructure we have already developed for producing a gas/vapor detector array and microarray research platforms, and the research that would underlie adding performance enhancing features (on-chip pre-filtering, sensitivity enhancing preconcentration, and delayed microsensor activation) to our detector arrays. The basic studies of volatilization (and heat-driven fluid movement) would open up the use of the of the same detector technology used for gases to liquids (which would be converted to vapors). This would greatly broaden the utility of the technology for network-deployed chemical monitoring at DoE sites.

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15. Feedback

n/a

16. Appendices

n/a

17. Quantities / Packaging

Microsoft Word 2000 was used to prepare this Report which is being submitted via email.