

Microhotplate platforms for chemical sensor research

S. Semancik^{a,*}, R.E. Cavicchi^a, M.C. Wheeler^a, J.E. Tiffany^a, G.E. Poirier^a,
R.M. Walton^{a,1}, J.S. Suehle^a, B. Panchapakesan^b, D.L. DeVoe^b

^aChemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

^bDepartment of Mechanical Engineering, University of Maryland, College Park, MD 20742, USA

Abstract

This paper describes the development and use of microdevices and microarrays in chemical sensor research. The surface-micromachined “microhotplate” structure common within the various platforms included here was originally designed for fabricating conductometric gas microsensor prototypes. Microhotplate elements include functionality for measuring and controlling temperature, and measuring the electrical properties of deposited films. As their name implies, they are particularly well-suited for examining temperature-dependent phenomena on a micro-scale, and their rapid heating/cooling characteristics has led to the development of low power sensors that can be operated in dynamic temperature programmed modes. Tens or hundreds of the microhotplates can be integrated within arrays that serve as platforms for efficiently producing processing/performance correlations for sensor materials. The microdevices also provide a basis for developing new types of sensing prototypes and can be used in investigations of proximity effects and surface transient phenomena. Published by Elsevier Science B.V.

Keywords: Catalyst; Gas microsensor; Microarray; Microhotplate; Micromachining; Statistically-designed experiments; Temperature dependence; Tin oxide

1. Introduction

The temperature of a sensing film can affect a variety of factors, including the film's base conductance, the quantity of gases it will adsorb, and the rates of reactions between adsorbates on its surface. As these effects can be important in producing response signals, temperature-controlled platforms have been used in developing gas sensors for many years. Increasingly, smaller device platforms have been fabricated recently in an attempt to achieve low power consumption when employing temperature control. The evolution of micromachining as a fabrication technology for chemical sensing has allowed miniaturization to progress toward a smaller scale with more convenient fabrication methods [1]. Micromachining of silicon to produce sensor platforms also provides the possibility for including on-chip circuitry, and replication of device structures into integrated arrays is straightforward.

Beginning in the early 1990s, the opportunities of silicon micromachining led to the fabrication of new types of microhotplate devices and arrays for gas sensing. These devices have been produced both by surface [2] and bulk

etching of silicon [3,4], and have been employed for developing gas microsensor prototypes [5]. The ability to locally heat miniature elements has been utilized both in fabricating gas microsensor films and in operating devices in rapid temperature-programmed modes [6]. For example, thermally-activated chemical vapor deposition (CVD) has been employed for depositing oxides and metals from gas phase precursors and reactants [7–9]. Such processes offer the benefit of self-lithography for incorporating sensing materials onto microdevice structures. Rapid thermal characteristics ($\tau \sim 5$ ms for the surface micromachined NIST microhotplates) also permit control of heating pulses in thermal programs that are capable of producing response signatures [6,10]. This approach has been demonstrated to increase signal information content and enable rapid analyte recognition [11]. Recently, the advantages of microhotplates as gas sensor platforms have been more broadly demonstrated [12–15].

While development efforts on microhotplate platforms for gas microsensor prototypes continue at NIST, we have also recognized that the characteristic features of these temperature-controllable platforms can be used to great advantage in conducting focused types of sensor research on temperature-dependent phenomena. In this paper we emphasize the adaptability of microhotplate fabrication methods for producing array configurations with functionalities that facilitate investigations of sensing materials, detection principles

* Corresponding author. Tel.: +1-301-975-2606; fax: +1-301-975-2643.
E-mail address: stephen.semancik@nist.gov (S. Semancik).

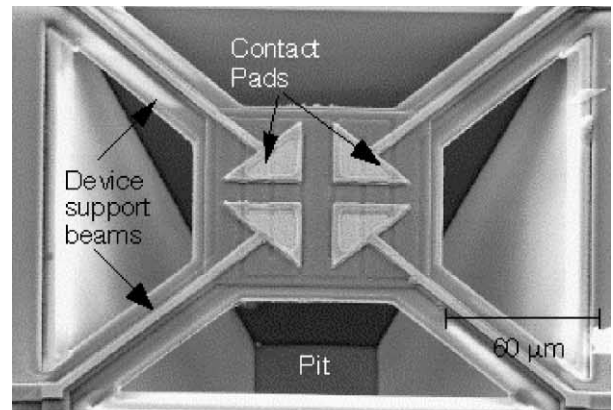
¹ Current address: Science and Technology Division, Corning Incorporated, Corning, NY 14831.

and mechanisms. Several examples are used to illustrate the value of such micro-platform studies for developing improved sensing films and operating modes.

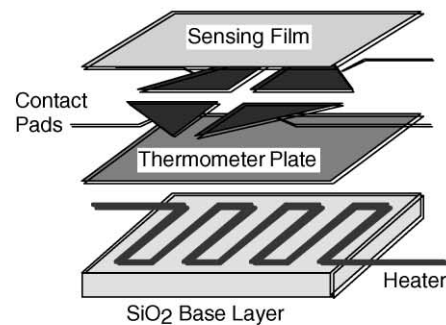
2. Microhotplate fabrication

The basic element we have used in fabricating gas micro-sensor prototypes and micro-scale research platforms is a multi-level, CMOS-compatible structure called a microhotplate, which has been described elsewhere [2]. The mask set originally used to create the microhotplates at silicon foundries was designed using the MAGIC CAD tool² [16]. (Other design tools such as those produced by Tanner Research, Inc.¹ or Cadence Design Systems¹ can also be used.) Regions of purposely exposed Si allow the devices to be surface micromachined in a manner that produces a thermally-isolated, suspended plate structure. (The necessary configuration of exposed substrate Si is defined by a modification in the design technology file called “open” [17]). We have had our microhotplate platforms manufactured at three different foundries, the Metal Oxide Semiconductor Implementation Service (MOSIS)¹ [18], Microelectronics Research Laboratory¹ [19], and MIT-Lincoln Laboratories¹ [20]. All offer certain advantages and certain limitations related to available types of materials, processing steps included, and delivery times and costs. In situ-processing etching steps (performed at NIST) involving various silicon etchants, including ethylene-diamine-pyrocatechol–water (EDP; anisotropic) [21], XeF₂ (isotropic) [22], or tetramethyl ammonium-hydroxide (TMAH) [23], have been used to produce the suspended microhotplates.

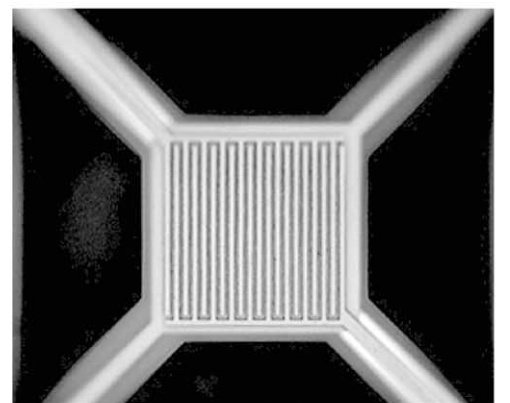
A single microhotplate element is illustrated in Fig. 1a. The most obvious features are the suspended plate, four support beams, and the etch pit. The device shown also has four arrow-shaped top electrodes that are used for measuring the electrical characteristics (conductance) of deposited sensing films. The layer structure within the suspended plate, shown in Fig. 1b, indicates other functionality within the basic microhotplate element. A serpentine polysilicon element embedded in SiO₂ serves as a resistive heater. Above the heater, separated by an insulating layer of SiO₂, is a metal plate that serves to conduct heat (generated by applying a current through the polysilicon heater) more evenly across the device. The temperature coefficient of resistance of this metal plate can be calibrated to provide temperature measurements; similarly, one may extract a temperature from the measured polysilicon resistance. To provide for measurement of the electrical characteristics of sensing films, the surface electrodes directly contact the sensing film while being isolated from the heat distribution layer by a SiO₂ layer. The suspended microhotplates are



(a)



(b)



(c)

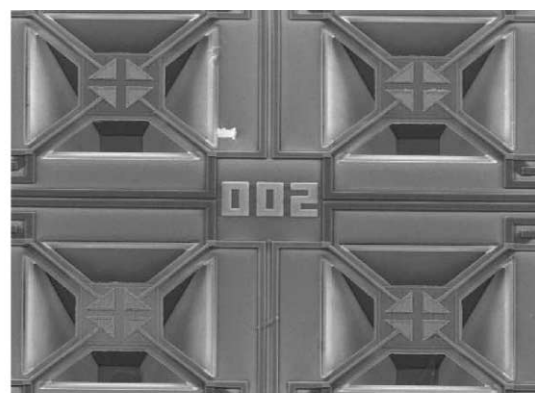
Fig. 1. (a) Micrograph of single microhotplate with four arrow-shaped electrodes, (b) schematic of functional layers in a surface-micromachined microhotplate, and (c) micrograph of another microhotplate with two interdigitated electrodes.

typically $\sim 100 \mu\text{m}$ across (although they can easily range from 30 to $>200 \mu\text{m}$), with a mass of $\sim 0.25 \mu\text{g}$. The low mass of the suspended structure gives thermal time constants of a few milliseconds. Maximum device temperatures are largely governed by the available type(s) of metallization at a given foundry. For Al metallization, the maximum temperature is approximately 500°C , and metal post processing is needed to produce more acceptable sensing film contact

² These suppliers are identified only to specify experimental procedures. Their mention in no way implies recommendation or endorsement by the National Institute of Standards and Technology.

composition (such as Ir over a Cr adhesion layer deposited on the foundry Al). When other metallizations, such as W or Ti–W are available at the foundry, devices can be heated as high as 750°C.

The use of computer-aided design in developing mask sets for foundry runs greatly simplifies the fabrication of multiple device variations. The size and geometry of contacts, for example, can be easily adjusted in the mask layout; Fig. 1c shows an interdigitated electrode structure produced by altering the section of the top layer metallization mask from that pattern which was used to fabricate the device pictured in Fig. 1a. Such interdigitated electrodes have proven particularly appropriate for studying devices with polymeric and nanoparticle sensing films. It is also straightforward to replicate the microhotplate structure to produce multi-element arrays in which the elements are thermally-isolated and individually addressable. We have employed primarily 4-element arrays as conductometric gas microsensor prototype platforms, an example of which is shown in Fig. 2. Expanding further upon that design, 48-element arrays have been developed and employed for efficient studies of sensing film processing/performance relationships. Arrays with 340-elements have been designed to attain maximized total surface area for desorption experiments aimed at investigating correlations between thin sensing film electrical properties and adsorbate coverages. Other modifications of the basic microhotplate structure and its configuration can be introduced to achieve related devices, such as microcalorimeters and catalytic filtering arrays, as well as to achieve specific required capabilities (smaller or bigger element size, faster thermal response, etc.). Examples of studies performed with various devices and arrays are described in Section 5 below. For certain applications, it may be desirable to raise the maximum temperature at which the device can be operated by removing any low melting point materials, while in other cases it may be necessary to adjust the scheme of wiring for electrical control and monitoring functions. The base structures illustrated in Fig. 1 use 8–10 electrical lines per device

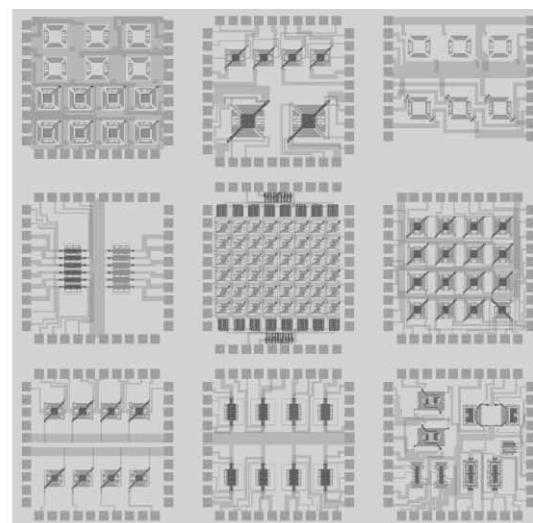


→ ← 100 μm

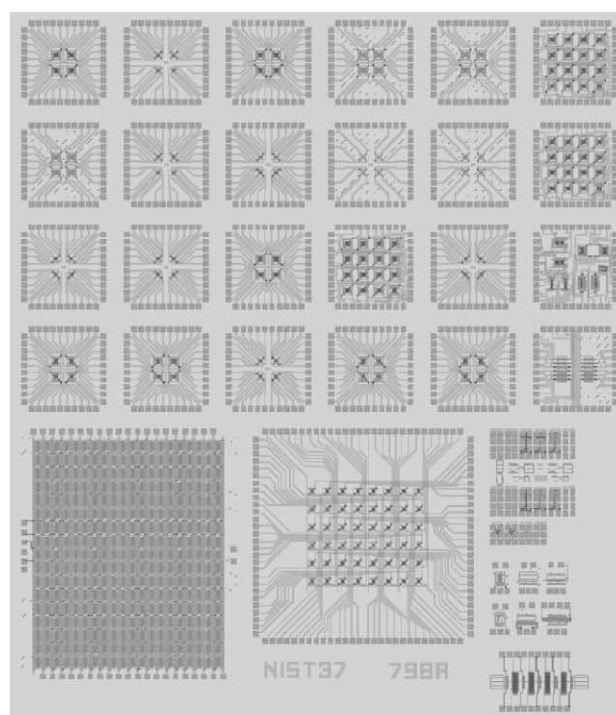
Fig. 2. Typical conductometric gas microsensor array prototype platform with 4 microhotplate elements.

element. The fact that the microhotplate design is CMOS compatible allows one to readily integrate various types of circuits on-chip. In a 48-element array, to avoid having 384–480 lines, we have introduced on-board multiplexer circuitry in one case, and a varied connectivity arrangement utilizing common bus lines in another.

To illustrate the variety of devices we have fabricated in single production runs at silicon foundries, Fig. 3 shows the design layout of two die. Fig. 3a is the layout for producing a die run at MOSIS¹, in which we procure one (7 mm \times 7 mm)



(a)



(b)

Fig. 3. (a) The 7 mm \times 7 mm die designed for a shared-wafer foundry production run, and (b) 13 mm \times 15 mm die designed for a repeated design on a 6 in. wafer foundry production run.

section on each of a number of wafers (typically 6–24). This layout has nine different designs that include varied microhotplate sizes, as well as field effect and microcalorimeter devices, and 16-element, multiplexed 48-element, and proximity arrays (see Fig. 8). The die layout in Fig. 3b shows 29 designs on a 13 mm × 15 mm die, which is replicated to fill each 6 in. wafer fabricated at MIT-Lincoln Laboratories¹ (a wafer run). Included in this run are varied types (and duplicates) of 4-element arrays, a (different) individually-addressable 48-element array (see Fig. 6), as well as a 340-element array (see Fig. 11). These die give an indication of how flexibly sensor prototypes and research platforms can be designed, and then fabricated. This approach provides a cost effective method for examining many of the different structures and functionalities required for sensor research and development.

3. Processing of sensing materials on micro-scale platforms

To study sensing materials and mechanistic phenomena of sensing using micro-scale devices and arrays, methods must be developed for compatibly incorporating the sensing materials of interest onto the miniature elements. As a variety of material types, and microstructures are used in gas sensing research and development, micro-scale processing onto microhotplates can present a considerable challenge. The sensing films of interest include oxides, metals and polymers that can be produced and tailored by a diverse spectrum of techniques. Typically, the films are deposited after silicon has been etched away to produce the thermally-isolated structures. Etching chemicals are usually too aggressive to properly maintain the integrity of pre-depos-

ited films. This means that one must deal with a 3-dimensional device structure during film deposition. The etch pits can be problematic, for example, when one attempts to use spin-on methods or for certain types of lift-off processing.

To demonstrate that a number of approaches can be adapted for depositing sensing materials onto single microhotplates or arrays of microhotplate elements, we present here a brief summary of techniques we have successfully employed for selective-area deposition. These techniques utilize local heating, local control of potential, lithography, and masking, and have been demonstrated successfully for registered deposition of SnO₂, ZnO, varied catalytic metals and polypyrrole. The deposition process can be continuously monitored electronically for sufficiently conductive films whenever the microdevice element includes top surface electrodes, as in Fig. 1a and c.

Two direct methods of self-lithographic deposition by electrical input to the microhotplate elements can be used. In the first case, a selected microhotplate in an array is addressed to carry a current through the device's integrated polysilicon heater. Due to the inherent thermal isolation, thermally-activated CVD will occur only on the area of the addressed hotplate. By selecting appropriate precursors and reactants, varied types of oxide and metal films can be deposited on one or more microhotplate elements. For example, we have used tetramethyltin in an oxygen background to deposit SnO₂ [7,8,24], diethylzinc in an oxygen background to deposit ZnO [6,25], and trimethyl(methylcyclopentadienyl)platinum in H₂ to deposit thin Pt films [26]. The growth monitoring capability of the microhotplates for over-deposited films is illustrated in Fig. 4, where the conductance traces follow the simultaneous formation of SnO₂ films on four microhotplates. For this deposition, the tetramethyltin precursor was held at –46°C, and flows of

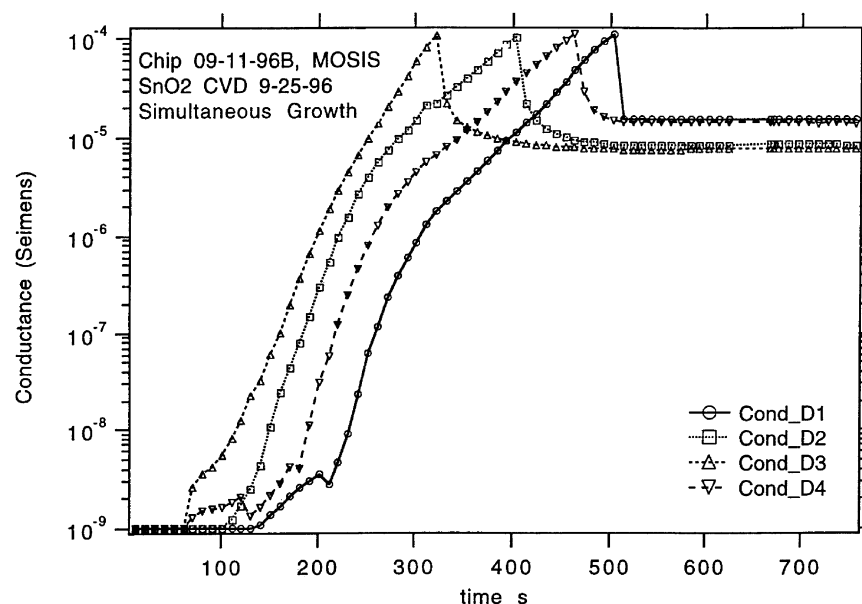


Fig. 4. Conductance monitoring for deposition of SnO₂ sensing films on four microhotplate elements within an array.

350 ml/min (350 sccm) and 300 ml/min (300 sccm) were used for the Ar carrier and oxygen reactant, respectively. The total pressure was 0.8 kPa (6.2 Torr), and the hotplates were held at 480°C. Time offsets between the conductance growth curves may arise from the differing nature of the random nucleation process in each case, as well as from possible small variations in absolute temperature between the elements.

Using an interdigitated electrode structure, similar to that shown in Fig. 1c, we have also deposited polypyrrole from solution onto elements of a microhotplate array using addressable electrochemistry [27,28]. The deposition solution consisted of anhydrous acetonitrile, 0.1 M LiClO₄, and 50 mM pyrrole. An electrode potential of +0.1 V was used for 5 min to obtain a polypyrrole film of ~10 μm thickness. The potential is switched to -0.5 V for 2 min after deposition to expel LiO₄ anions.

Localized heating of the microhotplates can also be used indirectly to assist deposition by “fixing” solids deposited from suspensions or sol-gels through controlled-rate drying [28]. Once the solution or sol-gel (dropped or spun on to the chip) has been heated to volatilize the carrier, and deposit a film out on selected hotplates, the solution or sol-gel can be rinsed from other sections of the chip. Heating can also be used in depositions that involve thermal lithography. Thermal resist materials, such as nitrocellulose, have been spun on to coat a chip, and then selectively vaporized by raising the temperature rapidly on a given microhotplate, thereby creating a window for a deposit and lift-off process [28].

It should be noted that we have also employed shadow masks that are carefully aligned with the packaged and wire-bonded arrays to deposit from the vapor phase. This procedure can work well for processes, such as evaporation or sputter deposition, but the small aperture size can be a problem for (liquid) spraying techniques, where particles and surface tension can clog the mask.

Finally, the localized temperature control available on individual elements (within an array) permits one to accomplish desired (variable) post-deposition anneals on the sensing materials being studied.

4. Temperature-dependent studies

The ability to control the temperatures of microarray elements allows efficient studies of temperature-dependent processing, temperature-dependent film properties, and temperature-dependent interfacial phenomena [29] critical to sensing. Some of the factors and effects that can be investigated are listed in Table 1.

Arrays of thermally-isolated and individually addressable microhotplate devices can provide matrices of temperature for highly efficient, parallel studies of processing/performance relationships for sensing materials. Statistically-designed (and combinatorial) experimentation can be used to systematically explore the phase space of deposition

Table 1
Some important temperature-dependent factors

Processing of films	Interfacial phenomena	Testing of performance
Substrate temperature	Vacancy formation	Sensitivity as $f(T)$
Annealing temperature	Adsorption as $f(T)$	Selectivity as $f(T)$
Anneal heating rate	Desorption as $f(T)$	Stability as $f(T)$
	Reaction as $f(T)$	

variables. In the case of CVD processing of oxides and metals, for example, microsamples can be formed not only with different hotplate temperatures, but also under differing precursor fluxes, carrier/precursor concentration ratios and pressures. Altering these variables can produce a variety of film stoichiometries, microstructures [24,30], defect densities, and degrees of interfacial dispersion and mixing (for metal/oxide systems). Microsamples with such varied properties can be expected to exhibit differing sensing characteristics. The differences are further enhanced if one deposits a different (catalytic) additive on the individual microsamples.

Once formed, the temperature-dependent performance evaluation of all the samples in the array can be efficiently completed using the same platform when it is exposed to test gases. For conductometric sensing microsamples, one uses the top surface electrodes on each element to monitor conductance changes in a given test gas as the temperatures are varied (incrementally or continuously) and recorded. Of course, the efficiency of the processing/performance study is amplified further, if the array of samples is exposed to a sequential set of test gases. Obviously, one can elect to use the multiple elements to conduct studies of processing reproducibility by dedicating columns of the array to samples all made under the same conditions (an additional practical benefit in prototype sensing arrays containing equivalent films is signal averaging). These types of approaches to process-performance correlations are illustrated in the first example of Section 5.

It should also be noted that arrays of microhotplates designed with closely positioned elements can also be used to examine the temperature dependence of proximal interactions or crosstalk effects, as well as catalyzed reactions activated purposefully (under thermal control) to modify the ambient gas composition to advantage in thermal filtering processes (see Section 5.2).

5. Microhotplate research platforms: examples and results

5.1. Multielement materials study

Although, there have been sensor arrays developed with tens of elements [31,32], much of the current developmental work on microsensor arrays involves configurations with less than 10-elements. Often recognition of analytes can be

performed using just a few different materials within an array format, along with chemometric analysis. More recently, the use of thermal programming of individual (microhotplate) elements has elevated the level of information content, so that selectivity is introduced for mixture analysis problems without necessarily using large numbers of differing films within an application-specific sensing array. However, it is important to note that the development of appropriate and optimized sensing materials (including their desired operating temperatures) represents a natural combinatorial problem, whether the microsensor device has 1, 4, or 40-elements. To achieve acceptable performance (and even a desired level of response orthogonality), one must properly correlate various sensing films, and the temperatures at which they are operated, to the varied types of analytes to be monitored. As part of this search process, it is necessary to consider the wide range of processing methods and conditions that can be used to alter film and interfacial composition and microstructure. Years of sensing research, almost exclusively carried out serially on single “macro-samples”, have demonstrated that these factors can profoundly affect the sensitivity (see, e.g. [33]), selectivity, and stability observed for sensing films.

We have adopted a more efficient approach to such materials selection and development studies that involves using microhotplate arrays of 16–48 elements to fabricate and test sensing films. Fig. 5 schematically, illustrates the concept of using arrays with many elements to more quickly screen for suitable and optimized films for use in a smaller array of microsensor elements which is capable of providing

the necessary signals for a given mixed analyte monitoring problem. To present this concept in a simplified manner, we have assumed that a 4-element array will be used to monitor 4 analytes: A, B, C, and D. As noted above, microarray studies on multiple microsamples allow highly efficient process/performance studies. Although, microarrays do present challenges to use processing methods that are platform compatible, the fabrication and testing is all done on one platform (for each analyte type A, B, C and D, in this example). The survey array has elements that are essentially the same as the basic elements which would be used in the ultimate microsensor array prototype. With individual temperature control of the elements, one can process and test the films on multiple elements in parallel under identical or different conditions, depending on the purpose of the given study.

To illustrate the approach, we describe experiments performed on 36-elements of a 48-element array, shown in Fig. 6. These experiments were part of an ongoing exploration of ultrathin metal seed layers for nanoengineering SnO₂ films produced by CVD [34]. Metal films of 16 Å thickness were evaporated on the six elements in each column using shadow masking; redundant samples were fabricated as a reproducibility check. Each of the six columns had a different type of nucleation material — Ni, Co, Fe, Cu, Ag and unseeded. Films were then grown on all elements using tetramethyltin and oxygen at 0.67 kPa (5 Torr) total pressure and a single growth temperature (set on each microhotplate) of 500°C. The resulting SnO₂ microstructures, measured with a Hitachi¹ Model 4700 SEM, are shown in Fig. 7a. It is

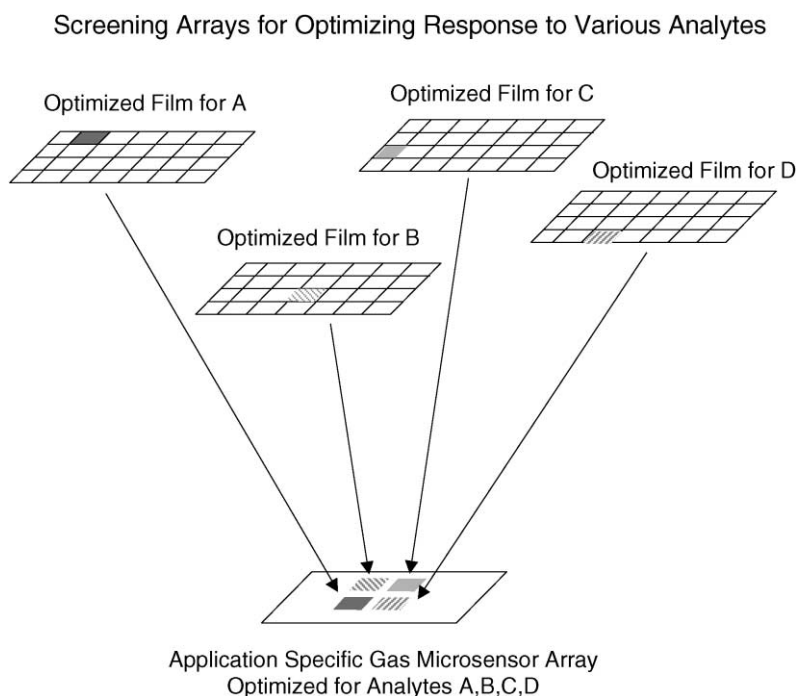


Fig. 5. Schematic representation of the use of multielement array studies of materials to screen and select optimal films for a smaller (4-element) gas microsensor array.

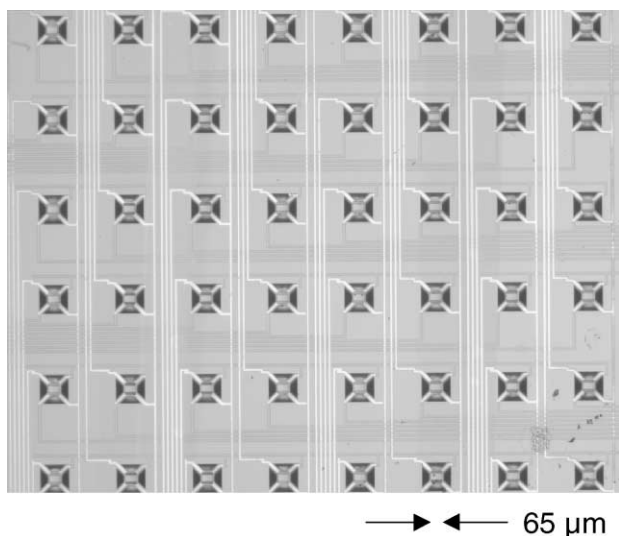


Fig. 6. 48-element microhotplate array used in efficient materials microstructure studies that correlate sensing film processing with performance.

noted that the nucleation sites created by the metals with higher melting points (Fe, Co, Ni for which $T_m = 1535$, 1495 , and 1453°C , respectively) produced finer and more uniformly-sized grains of SnO_2 . The redundant microsamples in each column showed very good reproducibility, as measured by both SEM micrographs and sensing performance. Once fabricated, the 36-elements were all subjected to sensing tests in which performance (sensitivity, stability) were examined with on-device conductance measurements as temperature was parametrically varied (100 , 200 , 300 and 400°C). Analytes including acetone, benzene, carbon monoxide, hydrogen, methanol and toluene — at concentrations varying from 10 to 90 ppm in air — were monitored. Data from the tests done at $T_{\text{test}} = 400^\circ\text{C}$, and 90 ppm analyte concentrations are presented in web plots in Fig. 7b. The data show that varying sensitivities are observed for the analytes as the microstructure is controlled by the different types of seed layers. The 36-element experiment was not only more efficient for this study of microstructure control by seeding, but also more systematic than single macro-sample trials more commonly used by sensor researchers. In addition, it was trivial to include reproducibility measurements, and the processing method transfers directly when one proceeds to incorporate the best films into microsensor array prototypes (with smaller numbers of elements, as indicated in Fig. 5). Obviously the methodology utilized could be adopted to look at many other variables that affect sensing film properties (e.g. oxide thickness, deposition temperature, pressure, reactant ratios) in statistically-designed experiments. We are also, for example, carrying out temperature-dependent performance evaluations on 36-element arrays in which a single type Ni-seeded CVD SnO_2 , deposited on all 36-elements, is modified by different surface-dispersed catalytic metal additives at variable loading values. A database of performance is then constructed for

different analytes (in air) at parametric microsensor temperatures.

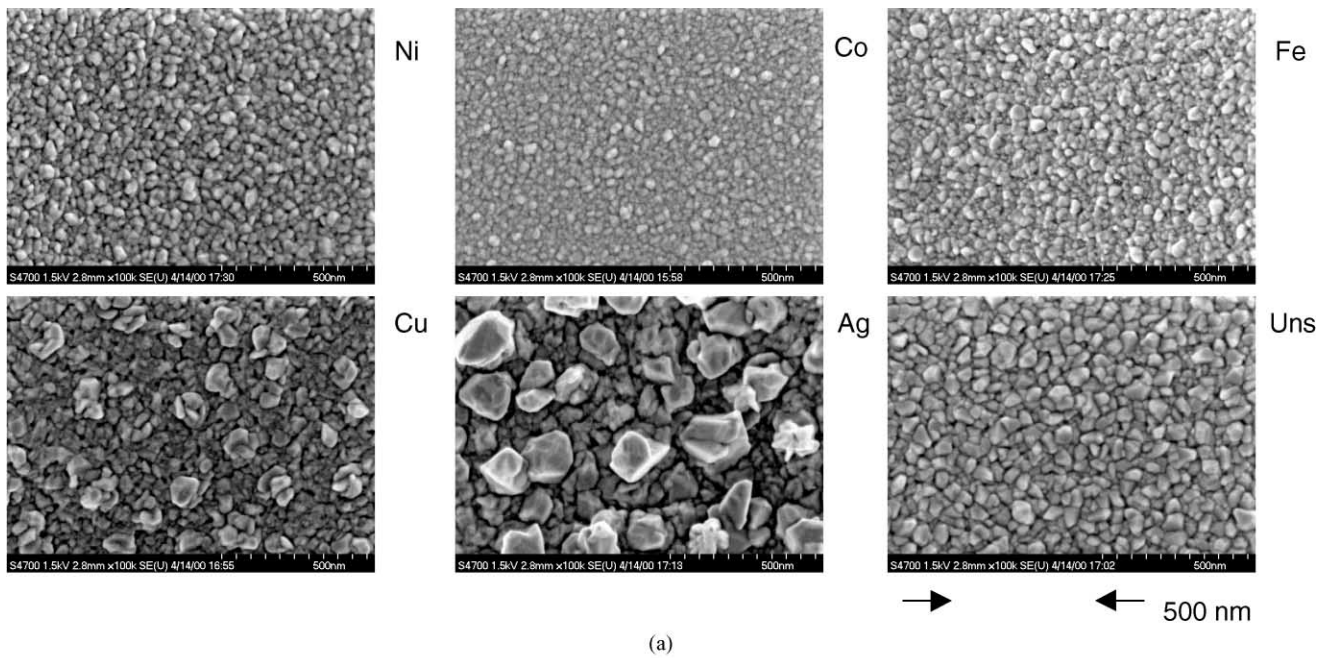
5.2. Studies of proximally-heated elements

We have used several types of microhotplate array configurations to examine possible benefits and problems of controlling chemical phenomena on the micro-scale. The proximity configuration shown in Fig. 8 was designed to investigate the feasibility of chemical filtering using heated catalytic elements placed near the microhotplate-based sensing elements. The array includes six adjacent $40\ \mu\text{m}$ wide bridge microheaters suspended over a single etch trough, with an edge-to-edge separation of $40\ \mu\text{m}$. The two bridges at the left are used to support catalytic metal films that can be heated to temperatures ranging from 20 to 500°C . The next four bridges, to the right, include heaters, and top-surface electrodes. In the basic experiments we have performed to date, CVD SnO_2 sensing films are deposited on the monitoring elements. The results of the demonstration experiment in Fig. 9 for saturated methanol in 20°C air show a conductance increase of nearly a factor of two above the background level is observed when an adjacent Pt-loaded element is heated. In this study the catalyst was switched from 20 to 480°C , and the nearby sensing element was operated at 400°C .

Such thermally-generated perturbations in the local chemical environment, while holding potential for filtering or separation functions, also suggest that studies must be done to insure that proximal heating of microhotplate elements does not produce any significant, undesirable shift in the signal level of a nearby sensor being operated at the same time. Obviously, the size and distance between elements would be expected to influence such shifts, and would determine the magnitude of any effect. The platform versatility allowed by having various types of arrays within a die design (see Fig. 3a, b) allows one to select arrays with differing intra-element and inter-element characteristics (size and spacing). Detailed studies on 4-element and 48-element arrays (as in Fig. 5) with different sizing/spacing have been performed, and are reported elsewhere [35]. As an example of our research into the magnitude of crosstalk effects produced by the operation of proximal microheaters, Fig. 10 presents results in which 15 nearby heaters produce a 4% shift in the conductance signal for a Pt/ SnO_2 sensing element near the center of an 18-element section of a 48-element array. Proximal effects for detection of other gases, including CO and methanol, are reported in reference [35].

5.3. Surface adsorbate studies

Interactions between gas phase molecules in an environment and the surface of sensing films initiate the transduction process by which analytes are detected. The concentration of adsorbed species and the charge transfer effects that occur between the adsorbing molecules and the



Gas Sensitivity For Seeded and Unseeded Elements

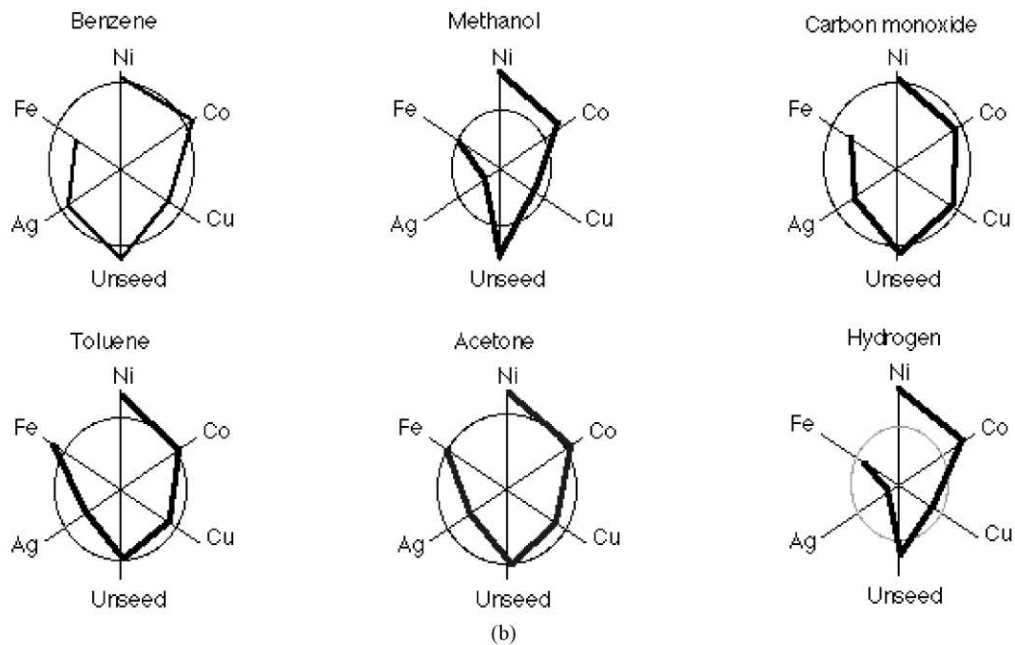


Fig. 7. (a) Micrographs showing varied microstructure produced when SnO_2 is deposited by CVD onto different types of metal seed layers, as labeled, and (b) web plots showing the relative sensitivity to six individual analytes in air of SnO_2 films engineered to have the six different microstructures presented in (a).

film surface determine the size of the signal observed. Surface reactions will alter the concentrations of adsorbates, and recently, we have used conductometric microhotplates to study the kinetics and spatial range of oscillatory CO oxidation on Pt/SnO_2 films [36]. For conductometric sensing, the relationship between conductance changes and adsorbed species was demonstrated in the 1970s by Yamazoe and co-workers [37] using thermal desorption measure-

ments from high area samples that involved heating rates $\sim 10^\circ\text{C/s}$. Microhotplate elements can be used in desorption studies for sensor materials. While a single microhotplate can be thermally ramped at rates as high as 10^6°C/s , it does not provide enough gas evolution to be readily measured with a mass spectrometer. Using arrays of hundreds of $\sim 100\ \mu\text{m} \times 100\ \mu\text{m}$ hotplates provides a total surface area large enough to desorb gases that can be easily monitored

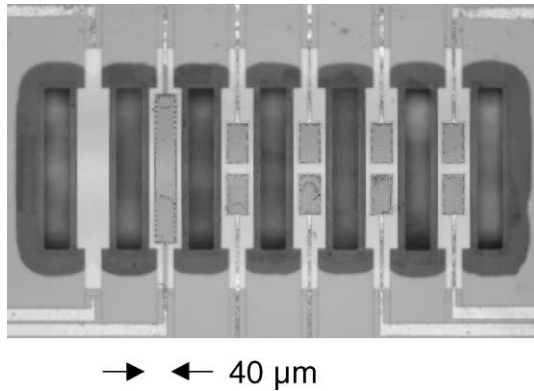


Fig. 8. Closely-spaced microhotplate bridges used to study the ability of heated catalysts to alter chemical composition sensed at adjacent elements.

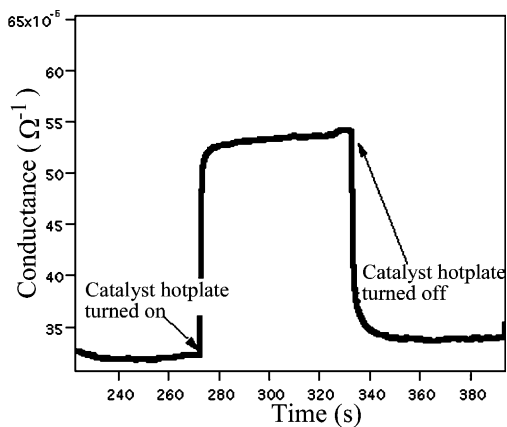


Fig. 9. The response measured at the third-element from the left in Fig. 8, operated at 400°C, when the leftmost element, coated with Pt, is heated from 20 to 480°C, and is then allowed to cool to 20°C.

with a mass spectrometer, while maintaining approximately the same rapid thermal characteristics for the “large” sample that exists for a single microhotplate. Experiments of this kind are conducted within a chamber that can be evacuated to ultrahigh vacuum conditions. By providing

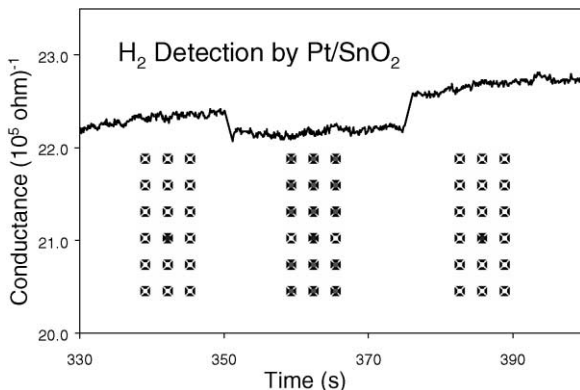


Fig. 10. Response perturbation observed at a centrally-located element, operated at 300°C, for hydrogen detection when the 15 nearby elements are heated to 300°C (heated elements are darkened in the inset schematics).

on-device electrical measurements, such platforms offer the opportunity to directly correlate surface adsorbate coverage (determined by desorption peak areas) with film conductance changes. The rapid thermal characteristics also allow transient phenomena to be studied on a time scale typically not accessible to macrosample ($\sim 1 \text{ cm}^2$ sample) desorption experiments.

Fig. 11 shows a 340-element microhotplate array designed specifically for desorption transient and sensing film electrical conductance studies. Each element is $100 \mu\text{m} \times 200 \mu\text{m}$. On-chip circuit lines allow all the elements to be heated in an equivalent manner simultaneously, producing desorption from an area of 6.8 mm^2 with a thermal time constant $\tau \sim 15 \text{ ms}$ dependent on the type of deposited metal (thermal gradients and τ are lower for metals than for oxides). Top surface electrodes for film electrical characterization are present on eight representative elements in various positions across the array. Thermal baths and non-contact infrared thermometry measurements have been used to correlate temperature with the thermal coefficient of electrical resistance of the microhotplate heaters.

Earlier work at NIST demonstrated the concept of using arrays with large numbers of microelements to measure desorption characteristics with thermal pulsing, and thereby, derive the prefactor and activation energy of desorption for CO from polycrystalline Pt [38]. More recently, arrays like that shown in Fig. 11, mounted in an ultrahigh vacuum chamber, have been used in isobaric coverage determinations on SnO₂ surfaces [39]. Tin oxide was deposited by CVD onto all 340 Ni-seeded microelements (in a manner similar to that described in Section 5.1 above). This “multi-part sample” was then exposed to methanol at a constant background pressure of $6.7 \times 10^{-6} \text{ Pa}$ ($5 \times 10^{-8} \text{ Torr}$). Dual-step temperature pulsing to temperatures T_{eq} and T_{d} was employed to measure the steady state adsorbate coverage reached after a time of $\sim 0.6 \text{ s}$ at T_{eq} , and then a 0.1 s pulse to a desorption temperature of $T_{\text{d}} = 425^\circ\text{C}$. As T_{eq} is raised from 20 to 365°C, desorption from the 340-element microhotplate array indicates that the steady state surface coverage of methanol on the SnO₂ drops, as expected. These results are shown in Fig. 12. In recent experiments, we have also demonstrated the transient in electrical conductance measured with on-element electrodes that is associated with such temperature pulsing [39]. Correlated measurements of the transient behaviors of adsorbate coverage and film conductance will be used to better understand the interfacial processes occurring in rapid temperature programmed sensing that has been used to increase the information content and selectivity of gas microsensors.

6. Prototype devices for sensing

While this paper and the examples just discussed have focused on the use of micromachined structures in sensor research, it is important to remember that similar platforms

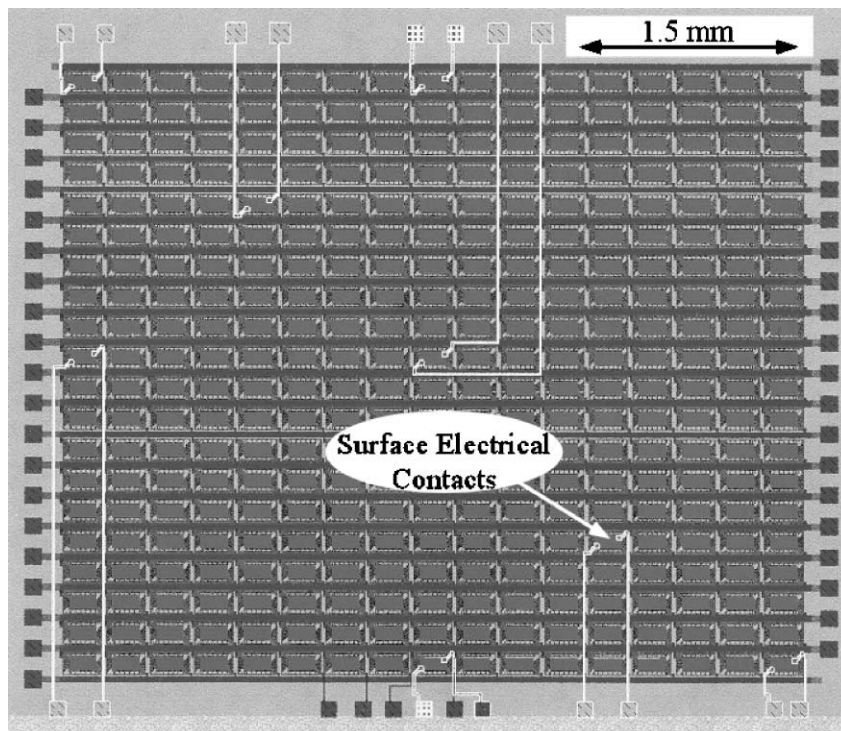


Fig. 11. Micrograph of 340-element array designed for adsorbate coverage (desorption) and film electrical conductance studies.

were initially used in developing microsensor prototypes. Four-element arrays like that in Fig. 2 have been our primary devices for developing micro-deposition methods, post-deposition film modification, and temperature programmed sensing.

The adaptation of the microhotplate structure into array research platforms has allowed us to more efficiently develop improved sensing films for our microsensor prototypes and explore new concepts, such as on-device thermal

filtering, and fast transient operation to enhance performance. It should also be noted that microhotplates can be easily modified to create new configurations and structures for sensing by principles other than the conductometric approach illustrated in this paper. One example of a microhotplate-related device is a differential microcalorimeter for detecting gases and chemical reactions [40]. This device includes 30 μm test (reactive) and reference (unreactive) suspensions (smaller thermal masses for greater sensitivity),

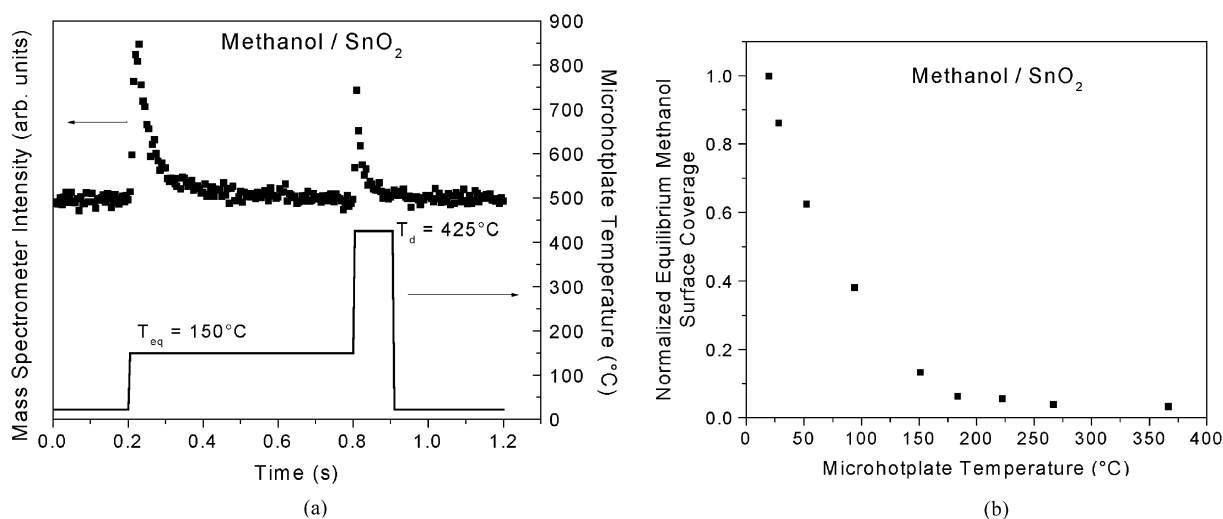


Fig. 12. (a) Results from a dual step procedure performed on a 340-element array, and the desorption features produced, with $T_{\text{eq}} = 150$ and $T_{\text{d}} = 425^\circ\text{C}$, for adsorption/desorption of methanol on/from Ni-seeded CVD SnO₂. (b) Methanol coverage results extracted from a set of such data.

each with their own polysilicon heater. An additional level of polysilicon lines has been added with Al lines to form a thermopile for sensitive temperature measurement.

The adaptation of the basic microhotplate for controlled-temperature sensing can be generalized not only to go from conductometric to thermal sensing, but also to make other types of layer structures and electrode configurations for measurements of, for example, capacitance. The ability to include multiple structures in a foundry run, as illustrated by the die in Fig. 3a and b, make it possible to test designs for new prototypes or research platforms in an efficient, and convenient manner. The foundry-compatible design process also insures that successful concepts can be entered into foundry production.

7. Summary

Micromachined silicon structures called microhotplates have been adapted to develop sensing device prototypes and micro-scale research platforms. The same features critical to temperature-controlled conductometric gas microsensor development and operation have been applied to advantage in producing arrays of elements designed as research tools. We have illustrated the use of such arrays in statistically-designed studies of conductometric sensing film process/performance correlations, for investigations of proximity effects, to observe the concept of catalytic filtering, and to collect data required for correlating electrical changes and changes in adsorbate coverages. The flexibility of silicon-based fabrication methods employed is important in making platforms for a range of prototype and systematic research studies.

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Biographies

Steve Semancik received his BS degree in Physics in 1974 from Rensselaer Polytechnic Institute, and his MSc and PhD degrees in Physics from Brown University during 1976 and 1980, respectively. He was then awarded a National Research Council Post-doctoral Associateship to do experimental studies in the Surface Science Division at the National Institute of Standards and Technology (NIST). In late 1982, he joined the Process Measurements Division at NIST as a Research Physicist and became Project Leader of NIST's program in solid state chemical sensing. Dr. Semancik's work has included research on oxide surfaces, thin film

growth, model catalytic systems, surface structural transitions, and the kinetics of fundamental surface reactions. His recent activities have been focused on developing improved materials for chemical sensing and combining active films with micromachined structures to realize advanced microsensor devices and operating modes. Dr. Semancik is a Fellow of the American Vacuum Society.

Richard E. Cavicchi is a physicist and co-project leader in chemical sensors at the National Institute of Standards and Technology. He received a BS in physics at MIT (1980) with a thesis on laser light scattering from colloidal crystals. At Cornell University he received a PhD in physics (1987) with a thesis on electron tunneling in small metal particles at low temperatures. While a post-doc at AT&T Bell Laboratories (1986–1988), he investigated carrier transport in quantum well devices. He joined NIST in 1989 where he has worked in the area of chemical sensors. This work includes the surface characterization of sensor interfaces, studies of sensor materials, micromachined device design, and novel sensing strategies.

M. Clayton Wheeler is a National Research Council Post-doctoral Research Associate at the National Institute of Standards and Technology in Gaithersburg, MD. He received his PhD in Chemical Engineering from The University of Texas at Austin in 1997. After graduation, he worked for two years as a Research Engineer for Texaco Inc., a global energy company, in Houston, Texas. He has been at his present position since 1999. His research interests include gas sensing mechanisms on oxide sensors, heterogeneous catalysis and microscale reaction phenomena.

Jason E. Tiffany received an MS in Chemical Engineering from Arizona State University in 1998. He has since worked in semiconductor manufacturing for Motorola and is currently investigating surface catalyst modifications for increased selectivity of tin oxide gas sensing arrays at the National Institute of Standards and Technology in Gaithersburg, MD.

Gregory E. Poirier completed his bachelor work at Indiana University, Bloomington, in 1986. His undergraduate research focused on time resolved fluorescence measurements of dyes in matrices. His graduate work, on ultra-high vacuum surface science and scanning tunneling microscopy studies of single crystal transition metal oxides, was conducted at the University of Texas, Austin, where he received his PhD in Physical Chemistry in 1991. The last summer of his PhD career was spent at Sandia National Laboratories where he investigated charge carrier dynamics in highly-excited semiconductor superlattices and quantum wells under the Outstanding Summer Student Program. Following his PhD, he spent two years at NIST as a National Research Council Post-doctoral Associate exploring oxygen depletion phenomena in nanoscale metal-oxide films using ultra high vacuum surface analytical tools. On completion of his post-doctoral tenure, he joined the NIST technical staff and conducted research on crystalline structures, assembly mechanisms, and phase transitions of alkanethiol molecular monolayers on noble metal surfaces.

Robin M. Walton received a PhD in Chemical Engineering from the University of Michigan in 1997. She was a National Research Council Post-doctoral Associate at the National Institute of Science and Technology from 1997–1999. She is currently, a senior research scientist at Corning Incorporated. Her research interests include chemical microsensors, biosensors, and planar lightwave circuits.

John S. Suehle received his PhD degree in Electrical Engineering from the University of Maryland, College Park, in 1988. In 1981, he received a Graduate Research Fellowship with the National Institute of Standards and Technology (NIST), Gaithersburg, MD. Since 1982, he has been working in the Semiconductor Electronics Division at NIST where he is leader of the Dielectric Reliability Metrology project. Dr. Suehle has over 16 years experience in research investigating the failure and wear-out mechanisms of semiconductor devices. He is also involved in developing CMOS-compatible micro-electro-mechanical-systems (MEMS) devices for inte-

grated sensor systems. Dr. Suehle is a senior member of IEEE and a member of Eta Kappa Nu.

Balaji Panchapakesan received a BS in Metallurgy & Materials science from Regional Engineering College in India. He is currently, a PhD student at the MEMS Laboratory in the Department of Mechanical Engineering at the University of Maryland, College Park. His current research interests include design, fabrication, and characterization of microsystems for MEMS based gas microsensor applications. His PhD work has involved development of new techniques for making nanostructured gas sensing materials that are fully compatible with the batch fabricated micro-machined structures.

Donald L. DeVoe is an Assistant Professor of Mechanical Engineering at the University of Maryland, College Park. Dr. DeVoe received his PhD in Mechanical Engineering from the University of California, Berkeley. In 1997, Dr. DeVoe joined the Department of Mechanical Engineering at the University of Maryland, where he has a joint appointment with the Institute for Systems Research. He is a founding Director of the Center for Micro Engineering at the University of Maryland, where his interests include novel silicon microfabrication technologies, bioMEMS, and thin film piezoelectric microsystems. Dr. DeVoe received the 1999 NSF Presidential Early Career Award for his work in micromechanism technology. He serves on the Executive Committee for the MEMS subdivision of the American Society of Mechanical Engineers.