

Kinetically Controlled Chemical Sensing Using Micromachined Structures

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Introduction

Microdevices produced by machining silicon can offer a variety of control functionality on a miniature scale,^{1,2} with general advantages connected to not only reduced size (less invasive), but also lower power requirements, lower cost, and reproducibility of manufacturing. Micromachining has already made impacts in a number of technical areas, and it promises to be an increasingly important and broadly applicable technology.

In the general field of sensors, micromachining has had its biggest impact, to date, in physical sensing. Commercialized devices include accelerometers and pressure sensors. This paper, however, focuses on the capabilities micromachined structures offer in the area of chemical sensing. It demonstrates how the inherently complex phenomena encountered in chemical sensing can be more completely probed using micromachined devices and arrays. The specific array devices described here consist of replicated low-mass suspensions we call “microhotplates”, where each element is covered with a sensing film. Two concepts are discussed. The first concept is the use of rapid heating of these low-mass devices to introduce “kinetic selectivity”. The second concept is the use of compositionally different surfaces and their varied interactions with gas phase molecules to introduce “materials selectivity”. While temperature control and the use of differing active materials (be they partially or highly selective) have been applied to chemical sensing for many years, what we wish to emphasize here is the enabling powers of these miniaturized structures and arrays in employing these concepts in entirely new ways. The approach provides a capability for “tuning”, through selection of film suites and operating programs, and thereby can address a wide range of gas and vapor sensing applications (in areas such as automated process control, environmental monitoring, and personal safety). The same generic base configuration can be used for varied applications, and fabrication aspects of the technology make it quite adaptable for manufacturing.

While other transduction modes may be considered for micromachined chemical sensors, for example, capacitance changes or calorimetric effects, we will focus on conductometric sensing. The approach is based on the technology that underlies Taguchi sensors developed decades ago. In our case, however, the semiconducting oxide materials such as SnO_2 and ZnO are applied as planar films, which are modified to enhance their sensing characteristics by surface-dispersing very low coverages of catalytic metals, for example, Pd and Pt.

The paper is structured as follows. First we indicate the basis for thermally controlled sensing by describing the importance of temperature-dependent processes in solid-state transduction. We next indicate the approach employed to

incorporate materials and kinetic selectivity to the microhotplates, and then describe the fabrication procedures as well as the characteristics of these micromachined devices. Self-lithographic chemical vapor deposition (CVD) is then presented as an efficient method for depositing active sensing films which lends itself readily to manufacturing. The next sections illustrate response characteristics (including temperature programmed analyte “signatures”) and an example of how training and predictive modeling are used to optimize performance. The closing sections then summarize benefits of the technology and indicate levels of adaptability and research needs.

Background

a. Temperature-Dependent Processes in Gas Sensing.

Many sensing principles and types of active materials have been used in chemical sensing;^{3,4} the accounts in this issue provide the reader with a sampling of a number of detection schemes with appropriate associated sensing materials. Figure 1 schematically depicts the types of interfacial components common for a variety of planar, solid-state gas sensing structures. Impinging gas molecules can enter into a progression of interaction phenomena at the sensing surface critical to transducing a chemical presence into a measurable electronic change. These effects include adsorption/desorption, molecular dissociation and reassociation, surface reaction, and surface, grain boundary, or bulk diffusion. All these phenomena (and other factors, such as microstructural and chemical stability of the active films) exhibit a significant temperature dependence which must be accounted for or controlled in sensing. The approach we take concentrates not only on controlling the temperature of microsensors, but actually using localized and modulated heating to great advantage in fabricating and operating the devices.

As indicated above, the sensing principle used to illustrate our microhotplate technology in this paper is adsorption-induced conductance change. Figure 2 indicates an example of the correlation of adsorption (and desorption), investigated with thermal desorption spectroscopy, with measured conductance changes.⁵ Since the bonding of adsorbates can modify the electronic transport properties at the surface of materials such as SnO_2 , temperature-dependent variation of the adsorbate concentration can be reflected in conductance changes.

b. Enabling Aspects of Micromachining.

The brevity of this publication does not allow any significant discussion of micromachining methods here. Therefore, we refer readers interested in learning more about this field to reviews on the subject.⁶⁻⁸ However, the paramount importance of micromachining in enabling our kinetically controlled microsensor approach, and the ease with which micromachined arrays can be fabricated and combined with on-board circuitry for sensing, certainly warrants special note here.

Isotropic and anisotropic etching of Si have been used to realize a variety of useful forms in Si-based structures: cantilevers, suspensions, tips, gears, tubes, etc. When

micromachining methods are cleverly combined with multilevel architecture, metallization, electrical insulation, and passivation layers can be designed to provide varied functionality within a device configuration. Additional details on the fabrication of our microsensor platforms are discussed in the Microhotplates section below.

Conductometric Sensing

a. Historical Background.

Conductometric sensing can be done using a variety of materials including polymers, oxides, and metals. The transduction mechanism depends on the class of material being used, but often adsorption or chemisorption creates a situation in which charge transfer occurs between the adsorbate molecules and the sensing surface. The form (molecular, dissociated, reacted) of the adsorbate and its concentration determine the extent to which the conductance is altered. The interreaction of coadsorbates also affects the concentration levels for individual adsorbates.

One of the oldest commercial sensors is the Taguchi gas sensor,⁹ which is based on conductometric changes that occur when gases adsorb on sintered semiconducting oxides, such as SnO_2 . In addition to the mechanistic effects mentioned above, band bending can accompany gas adsorption to produce conductance changes in semiconducting oxides, as can creation or removal of oxygen vacancies in the near-surface region.¹⁰ Over the years, Taguchi sensors have been applied for detecting reducing gases, primarily in alarm-type applications. Recently, researchers have recognized that temperature variations can be used in conjunction with such devices to enhance the amount of sensing information.¹¹ However, the size and construction of the Taguchi device place operational limits on this temperature modulation procedure.

b. Advanced Concepts.

Most research and development efforts on conductometric sensing are now focused toward (thin or thick) films. Planar processing of active sensing materials has the benefit of easier fabrication and the ability to obtain more reproducible films. Micromachining can be used to construct novel sensor platforms that include necessary functionality in a miniaturized format. Certain challenges may be encountered in combining thin film deposition techniques with the microsensor structures; however, important new capabilities and performance characteristics can be realized that motivate researchers to overcome technical barriers.

Planar processing and silicon micromachining offer excellent opportunities for compositional sensing in gas mixtures by providing direct methods for constructing integrated sensor arrays. Our microhotplate sensing technology,¹² described in the remainder of this paper, is an example of the enhanced performance possible when a straightforward and traditional method like conductometric sensing is combined with thin film deposition and micromachining.

While our approach takes advantage of the relative ease of constructing multielement arrays through micromachining, as for any sensor, a level of selectivity must be introduced into the device for identifying single or multiple analytes within gas mixtures. Two interrelated concepts are used in our conductometric microhotplates, “materials selectivity” and “kinetic selectivity”. These concepts are represented schematically in Figure 3. The materials selectivity we discuss here is introduced by depositing varied combinations of semiconducting oxides with surface-dispersed catalytic metal additives. Fabrication techniques for attaining such interfaces of varied composition are discussed in the Active Film Deposition section below. Additional selectivity is included for multiple elements by controlling their (fixed or dynamic) temperatures individually. The next section describes how micromachining can be employed to provide individually addressable, fast temperature control. Neural network modeling and recognition methods are taking on an increasingly important role in chemical sensing. In our work they are used to analyze and interpret response data, as well as to optimize operational modes for the microdevices.

Microhotplates

a. Fabrication. The microhotplate structures we use are designed in CMOS technology at NIST for fabrication at a Si foundry.^{13,14} The suspended microbridge structure for each of the elements is realized by chemical etching of certain areas (purposely left open to attack) by ethylene diamine pyrocatechol (EDP, anisotropic etch)¹⁵ or XeF₂ (isotropic etch). An etch pit beneath each element largely separates it from the surrounding material. A microhotplate is shown in the micrograph of Figure 4a. Temperature control for the miniature array elements is achieved through the multilevel design of our microhotplates presented in Figure 4b. Each element has a buried layer that includes an individually addressable heater. Additional functionality is included within the suspended layers for meeting sensing requirements. A metal “hotplate” layer is employed for heat distribution and temperature measurement (using the calibrated thermal coefficient of resistance), and four top-level contact pads allow conductance measurements to be made on the overdeposited sensing film. Electrical isolation layers of SiO₂ are also included in the suspension to separate the conducting layers.

b. Characteristics. The lateral dimension for our suspended hotplates is typically ~100 μm (as small as 30 μm), and the suspended mass is approximately 0.2 μg. The thermal isolation and low mass of the microbridge design mean that each element can be heated (and cooled) quickly without altering the temperature of surrounding materials. The thermal rise and fall times are between 2 and 5 ms, and the thermal efficiency is 8 °C/mW. Maximum temperature for the microhotplate depends on the details of its multi-level structure, including whether the metallization is Al or W. Microhotplates with Al can be operated to 500 °C, while those with W can be heated to ~800 °C, or higher. Aluminum metallization, which is provided in standard fabrication, also presents a challenge for attaining proper contact to the sensing film. Typically, we would postprocess more suitable metals over the four top-surface Al contact pads, but the W contacts have been used successfully without

modification. The rapid thermal switching and real time monitoring of temperature possible with these devices are critical for operating the devices in high-information content “kinetic selectivity” modes that are not possible with older (Taguchi or any other more massive sensor) technology. The results presented here are generally obtained from four-element, 2×2 array prototypes, as pictured in the micrograph in Figure 5.

Active Film Deposition

Efficient deposition of varied types of metal/oxide films only on the suspended $\sim 100 \mu\text{m} \times 100 \mu\text{m}$ areas in the microhotplate arrays presents a challenging lithographic problem. We have developed a direct method of locating and controlling the sensing films which uses thermally activated, chemical vapor deposition (CVD), and electrical monitoring of the growing films. The film growth procedure, which is self-lithographic, is indicated in Figure 6. Owing to the individually addressable heaters (and “thermometers”) in each element, films of semiconducting oxides and catalytic metals can be deposited, as desired, only on individually selected microhotplates purposely set at elevated temperatures. Using differing precursor and reactive gases allows films of varied composition to be located within an array.¹⁶ The SnO_2 , ZnO , and Pt films reported on here are grown using the following precursors and reactants respectively: tetramethyltin (TMT) and oxygen; diethylzinc (DEZ) and oxygen; and trimethyl(methylcyclopentadienyl)platinum ($\{\text{MeCp}\}\text{PtMe}_3$) and hydrogen. The four top-surface electrodes on each microhotplate provide a means to monitor the growth and relative thickness of films by measuring their conductance once they become continuous between probe electrodes.¹⁷

Figure 7 illustrates how differing oxides have been individually deposited on adjacent elements of a 2×2 array. Energy-dispersive X-ray analysis (EDS) indicates the presence of Zn in the two ZnO -covered devices on the left, and Sn in the two SnO_2 -covered devices on the right (the lower Zn EDS intensity in the top left film is because it is considerably thinner). Note that, despite the close proximity of the microdevices, the film processing can be performed without chemical cross-talk.

An additional challenge for the self-lithographic CVD method is the surface dispersion of catalytic metal additives on the oxide films. Ideally, the metals are to be deposited in the monolayer regime in the form of islands. In this low coverage, discontinuous form, metals can enhance the conductometric response, provide an additional basis for selectivity, and sometimes reduce the operating temperature for a sensor. (Note that a thicker, continuous metal overlayer would act to short out the semiconducting base layer, thereby eliminating the desirable larger dynamic signal range provided by the oxides.) Figure 8 shows the micrograph of small Pt islands on a SnO_2 film for a microhotplate sample in which selected area deposition of both the oxide and the low coverage Pt were carried out by our CVD processing.

Response Data

Having discussed fabrication methods for the micromachined device and its active overlayer sensing films, we now focus on operation of the microsensor device, and the conductance signature for each analyte in Figure 11b is consistently repeated as the temperature cycle is repeated, and that the discrete jumps within the signatures are real (not noise), and originate from the discrete nature of the temperature changes in the pulsed linear ramp sequence. The signatures for the linear ramp operation are all different for the four analytes tested, although the ethanol and methanol signatures are quite similar, owing to the similar chemistry of these two molecules. The operating mode and results shown here clearly indicate the basis for an approach for introducing selectivity and recognition (for single and multiple elements). Further work on recognition and optimization of the dynamic mode, using neural networks, is described in the next section.

Research Issues for Continued Advancements

a. Materials.

The heart of any chemical sensor relates to its active material and the chemo-electronic properties of that material under changing conditions. To be applicable to a range of gas and vapor monitoring problems, the sensing system must offer, inherently, an adaptability to match the richness of the analytes and environmental conditions that would be encountered. Primary issues to be addressed relate to understanding the influence of microstructural factors on performance and the development of active material suites of known utility for specific classes of analytes.

Microstructural characteristics and other factors, including film thickness, can have a profound effect on sensing action and must be better understood in order to construct superior sensing films with regard to stability, sensitivity, and speed. The micromachined arrays we have described as the platforms for our multielement sensors also provide an excellent tool for efficient materials processing/property survey studies.¹⁹ The utility of microsubstrate arrays is illustrated in Figure 12. The results there were obtained from a 2×2 array in an experiment designed to examine how CVD processing pressure and substrate temperature affect SnO_2 microstructure and, ultimately, the sensing performance.

The array survey concept is quite easy to generalize to larger arrays for examining processing parameter space in greater detail. To this end we are now developing 16 and 48-element arrays. The array concept is also of great value in response testing for developing databases on the temperature-dependent abilities of active films for sensing different types of analytes. While we have concentrated on robust metal/oxide sensing materials in this paper, the characterization approach could be extended directly, for example, to conducting polymers.

Finally, we note that research into entirely new film forms may eventually lead to performance breakthroughs. While certain performance improvements have been reported for sensing films composed of nanoparticle oxides,²⁰ we have looked into sensing aspects over a range of oxide microstructures, including epitaxial and ultrathin film configurations. The studies of epitaxial films, to date, were done on

macrosamples (not microhotplates) because atomically ordered substrates are required. Figure 13 shows the sensing responses to H₂ (in a vacuum) of epitaxial SnO₂ deposited on sapphire substrates to thicknesses of only 80, 40 and 15 Å, with one monolayer equivalent of Pd decoration.²¹ These types of constructs may eventually lead to faster and more stable sensing performance, since transduction phenomena are constrained to occur entirely at the near-surface region of a well-ordered material.

b. Modeling.

It is clear that the approach we have described, as illustrated by the results in Figure 11, will rapidly produce great quantities of time-dependent (and temperature-dependent) data. While large sets of response data may be required to deal with complex sensing problems, they are difficult to interpret directly for analyte identification and quantification. The problem becomes even more challenging when multiple sensors (with differing films) are operated at the same time to attain information for gas mixture analyses. Pattern recognition methods must be applied, and neural network and clustering methods can be particularly powerful for developing recognition algorithms.²² Neural net and wavelet modeling techniques can also be valuable in predicting the most useful dynamic temperature programs. The three panels in Figure 14 summarize the use of training sets to “learn” sensor response characteristics under a semi-random, segmented thermal program, and then formulate a predictive model for future performance. With such an approach, and training of a Pd/SnO₂ microsensor in both ethanol and methanol (note the similar response signatures for these vapors in Figure 11), iterative comparisons of an areal metric were performed to attain a single temperature program that would maximally separate the signatures for the two alcohols. Excellent agreement with the predicted signatures was obtained when the optimized temperature program was used in experimental measurements (Figure 14c).²³

Further modeling and recognition work is needed, especially for temperature-programmed operation of single and multiple sensors in concentration-varying gas mixtures. This work is now underway using our automated testing facility, which employs FTIR-based calibrations.

Benefits of the Microhotplate Technology

Concepts connected to the microhotplate arrays suggest a range of benefits that could be realized through further development efforts. Materials and kinetic tuning of our generic microhotplate array approach provides the potential for this technology to be developed across a range of application areas involving analyte detection/quantification in mixtures. For example, different suites of active films, with associated (but differing) temperature programs, could be developed (on the same base) for use in specific cases of process control, environmental and emissions monitoring, and detection of chemical hazards. Efficient array surveys, within the same micromachined technology, can be employed in developing, characterizing,

and optimizing the active materials sets. As indicated above, fabrication steps for the conductometric microhotplate sensors involve procedures that are readily adaptable for high volume manufacturing. The base platform, designed in CMOS, can be constructed by standard Si foundries. Deposition of certain classes of active films can be carried out self-lithographically and monitored in a way that allows these procedures to be automated. Planar processing of the active films also permits greater levels of reproducibility. Control and output electronics could be easily mated to the CMOS design of the microhotplates and, when beneficial, even directly integrated with them. The low power requirements connected with the microsize and pulsed operational modes for these microsensors means that packaging with small battery units is possible. These aspects, along with the relatively low manufacturing cost imply that portable devices based on the technology could be developed for personal “pocket-sensors” and for multiple (networked) deployment in industrial settings or for outdoor proximity measurements.

Using metal and oxide conductometric sensing materials such as those described in this article would permit sensing in somewhat harsh environments, as the robust films and device construction have the potential to hold up in moderately corrosive gases, and at elevated temperatures. The use of robust films also suggests that fouling of the sensors by reaction with environmental components might be prevented, or corrected, by periodic, high-temperature “burn-offs”. The ease with which elements could be replicated by planar and batch processing of the arrays and the multiple active films also provides a ready methodology for utilizing redundancy to prevent false readings, and to provide additional fresh sensors for delayed use. Manufacturability aspects and practical approaches for dealing with problems in operation make this microsensor technology attractive for a wide range of monitoring applications.

Concept Adaptability

The fact that temperature-dependent phenomena occur for many other transduction principles, in addition to conductometric methods, means that the concept of monitored temperature control on a microplatform offers immediate benefits for other sensing approaches. The benefits can be connected with fixed temperature operation, to help avoid drift, or with enhancements introduced by dynamic temperature programming, similar to those we have demonstrated here (see Figures 10, 11, and 14) for the conductometric technique. Within the conductometric approach, the utility of the microhotplate device with top-surface contacts (Figures 4a and 5) can be broadened by extending to other classes of sensing films, such as conducting polymers. The extension to depositing other types of materials will require development of materials processing methods compatible with the micromachined structures, but would provide the opportunity to use other sensing principles as well. To incorporate other sensing schemes, some modifications of the overall microhotplate element functionality would be required to permit different types of probing measurements (e.g., capacitance, work function, I-V, temperature, etc.). Most of these modifications could be designed into a

generally similar configuration, above the level of the heat-dispersing and monitoring layer.

Related hybrid device multielement structures could also be integrated with kinetically controlled conductometric sensors. In addition to having different classes of active films on the conductometric microhotplates, an assortment of detection principles could prove particularly powerful in certain applications. The local temperature control offered by microhotplate-like structures is also being examined for its utility in doing gas-phase separations, in conjunction with detection. Finally, the demonstrated use of CMOS technology and the flexibility for designing other types of micromachined structures suggest that physical sensors (temperature, flow, pressure) could also be integrated with temperature-controlled chemical gas sensors.

Summary

Micromachined devices called microhotplates have been developed as a temperature-controlled platform for conductometric gas sensing. These devices can be operated in static or dynamic (temperature-programmed) modes. In the dynamic mode, high-information content, time-dependent signatures are produced that provide an enhanced selectivity function and the basis for analyte recognition. Arrays of the devices can also be fabricated easily, and a self-lithographic CVD technique can be used to locally deposit varied types of active films to attain the response-variability needed for compositionally analyzing gas mixtures. The inherent tunability of the microhotplate and microhotplate array approach offers considerable potential for applying this technology to a spectrum of gas monitoring problems.

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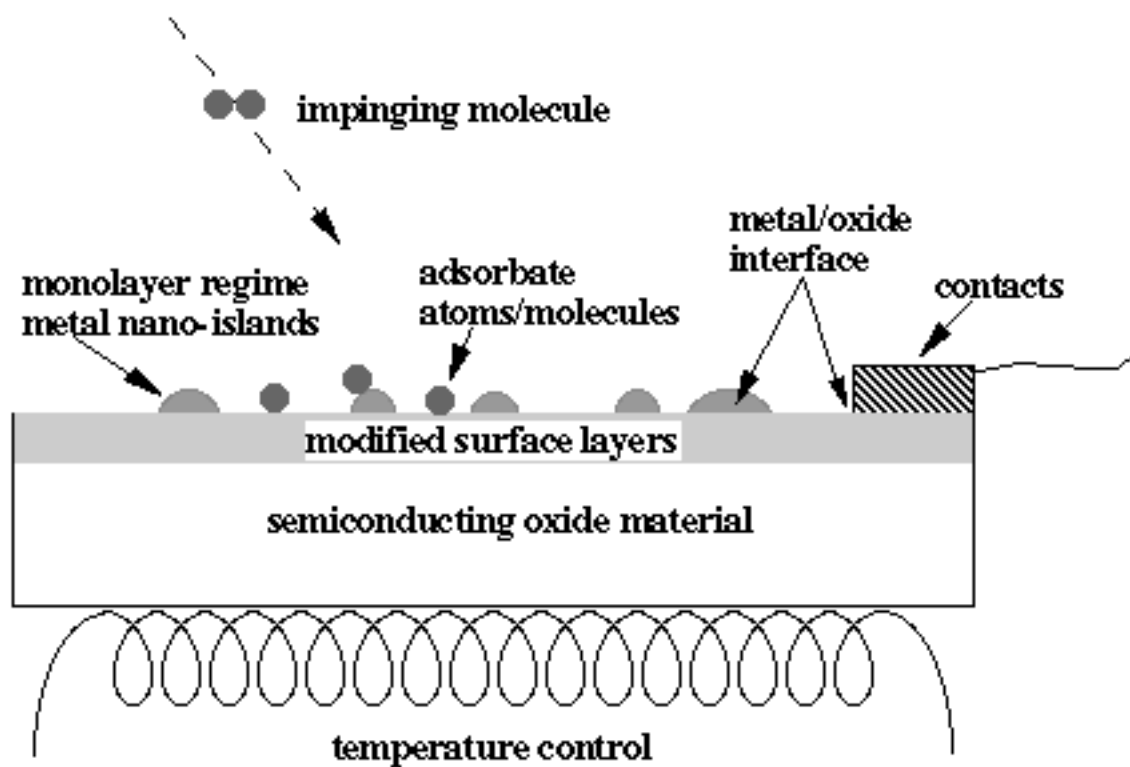


FIGURE 1. Generalized schematic of a planar gas sensing interface.

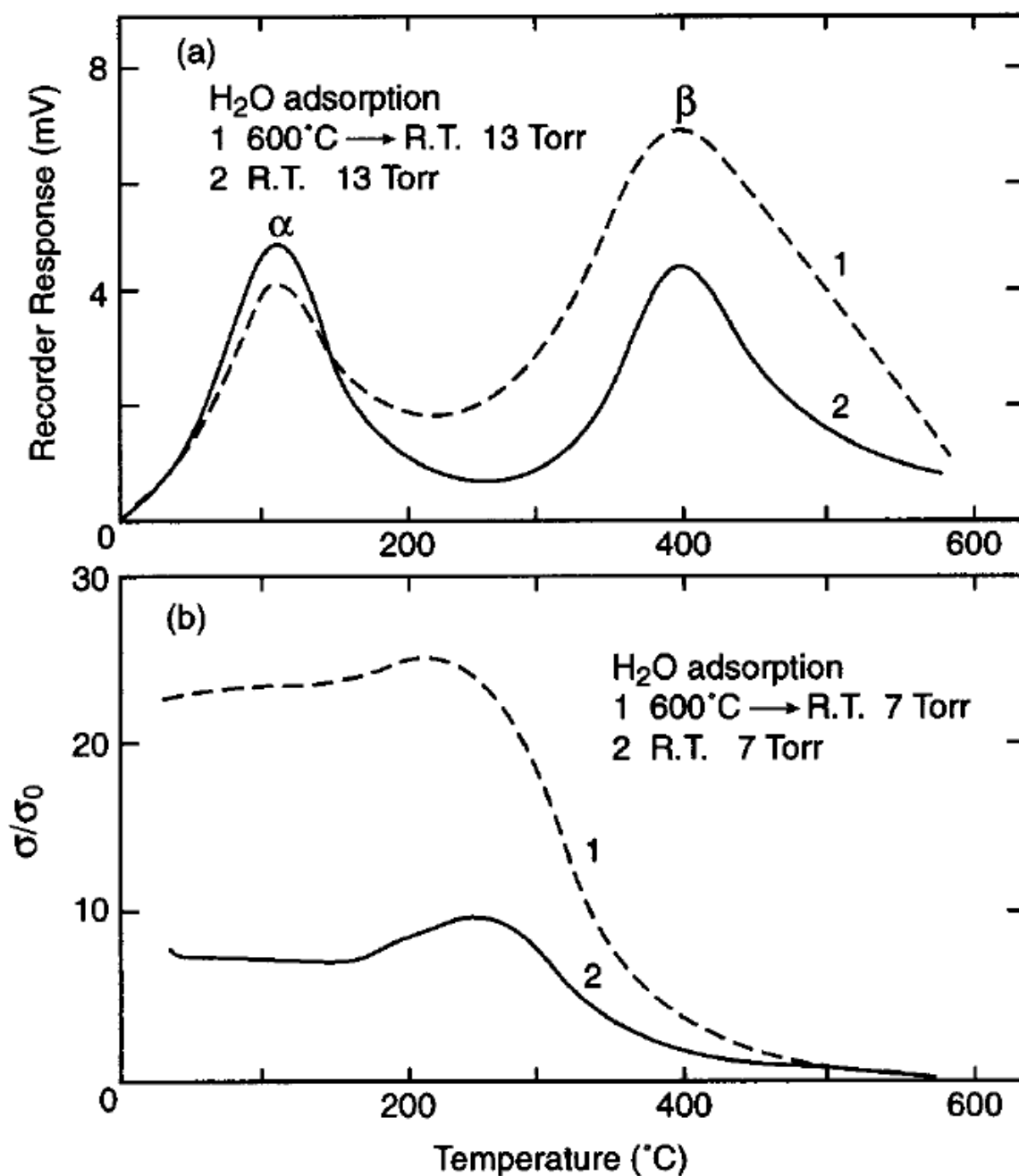


FIGURE 2. (a) Mass spectrometer output for thermal desorption of water from SnO_2 , and (b) effects of adsorbed water on the electrical conductivity of SnO_2 , for two cases of water exposure. Reprinted with permission from ref 5. Copyright 1979 Elsevier.

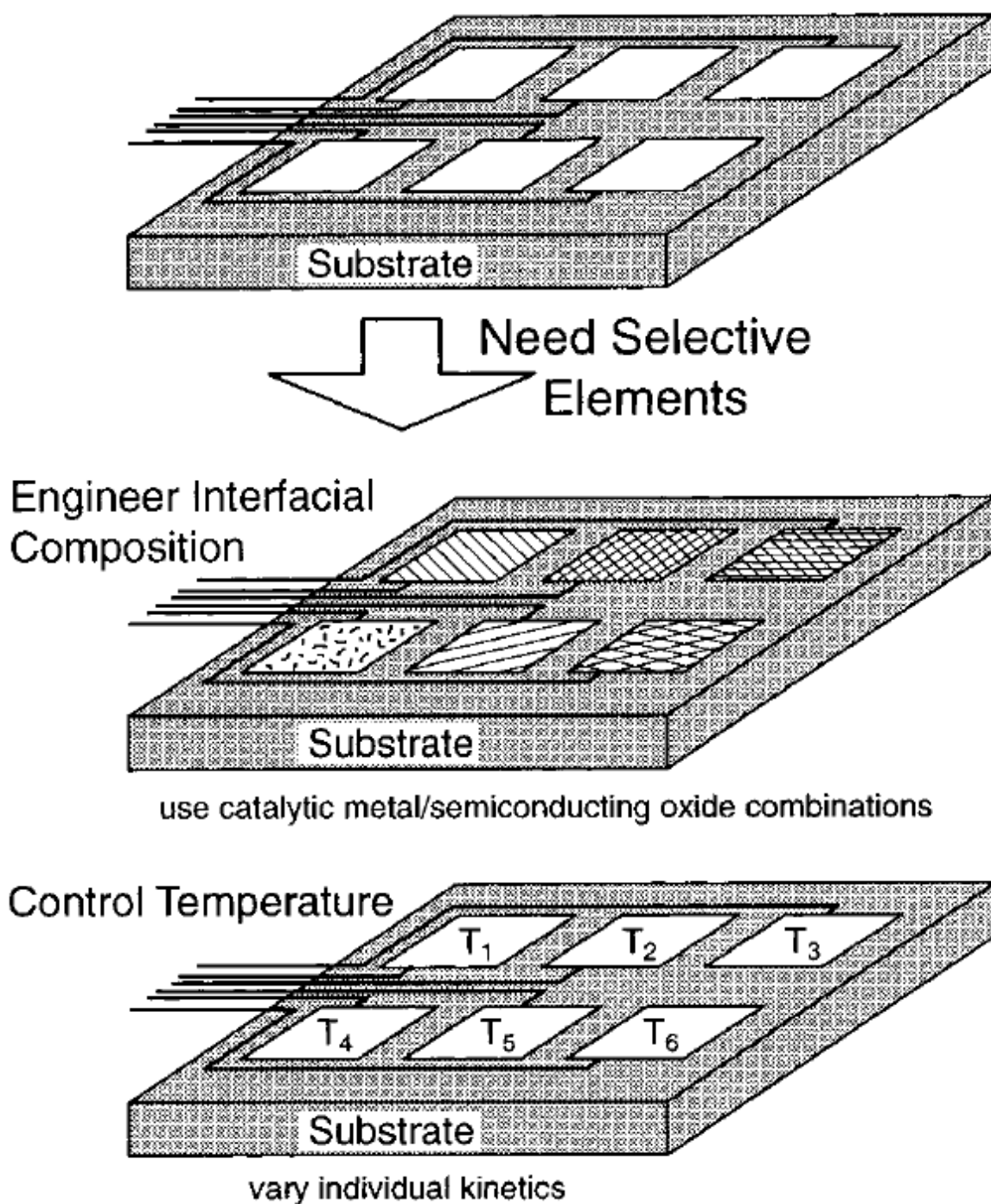


FIGURE 3. Concept for introducing materials selectivity and kinetic selectivity to a multielement array.

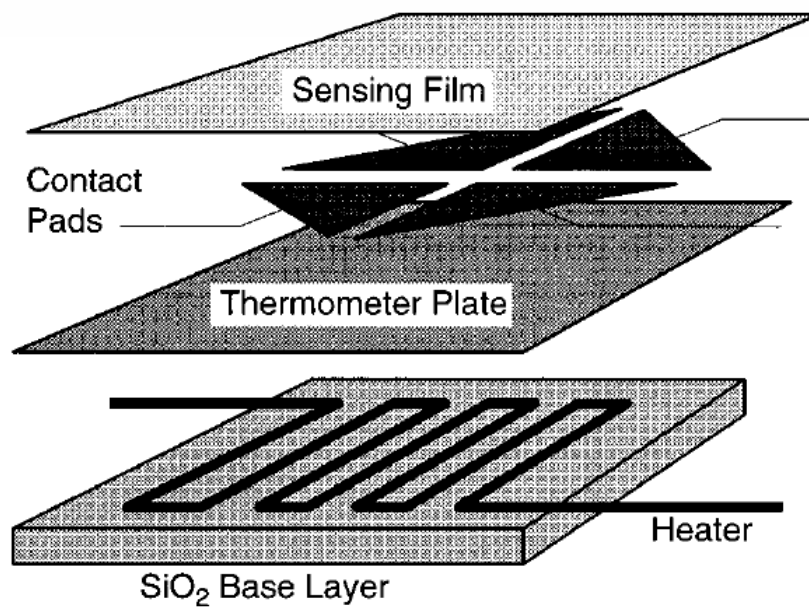


FIGURE 4. (a, top) Micrograph of a single microhotplate, and (b, bottom) representation of the functional components within the microhotplate structure. Note that, for clarity, electrically insulating SiO₂ layers, present above and below the thermometer plate, have been deleted.

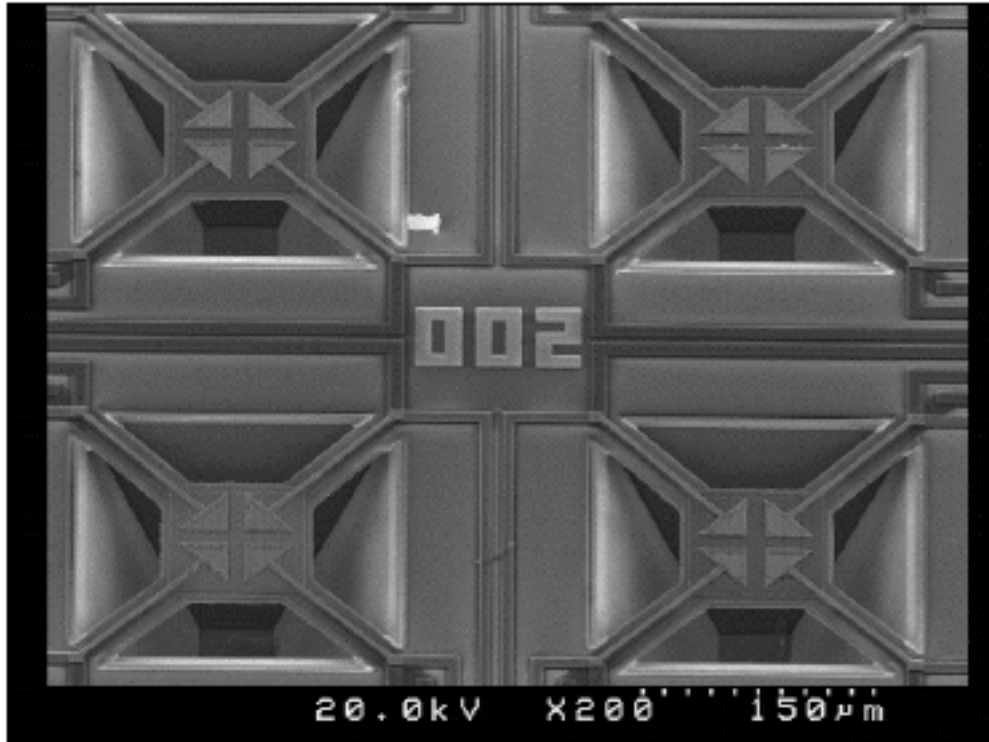


FIGURE 5. 2×2 microhotplate array.

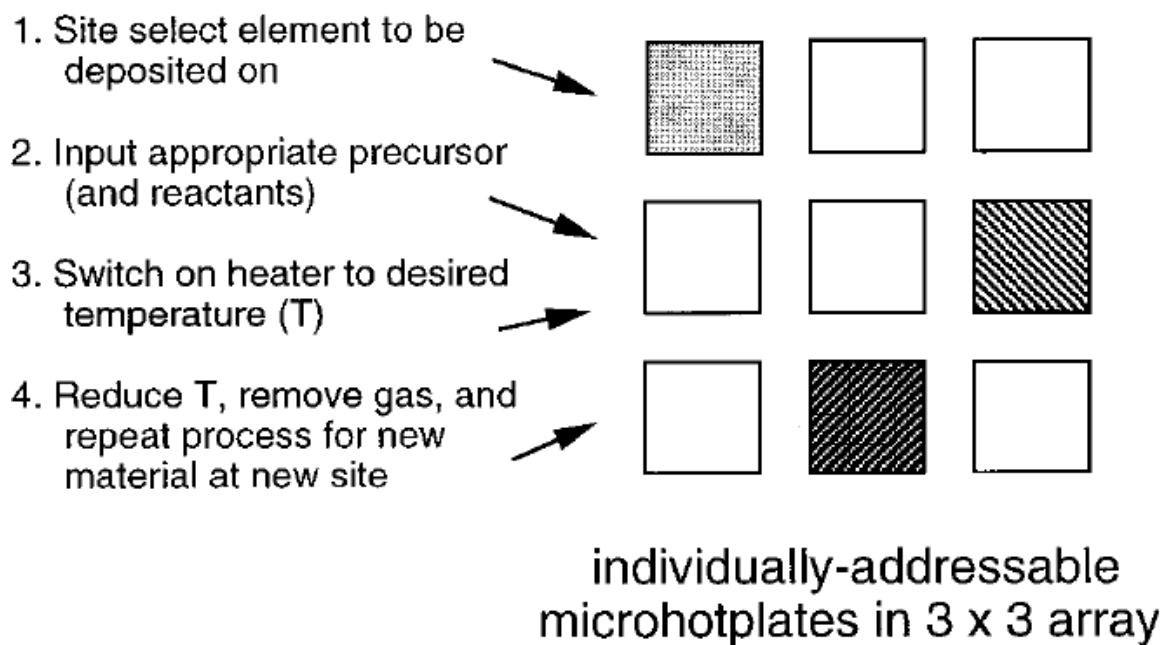


FIGURE 6. Procedural summary for CVD self-lithographic film growth on selected microhotplates within an array.

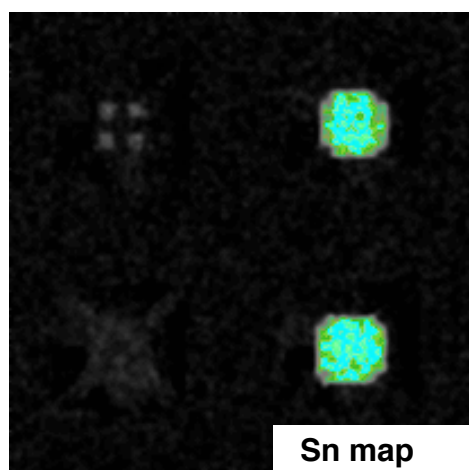
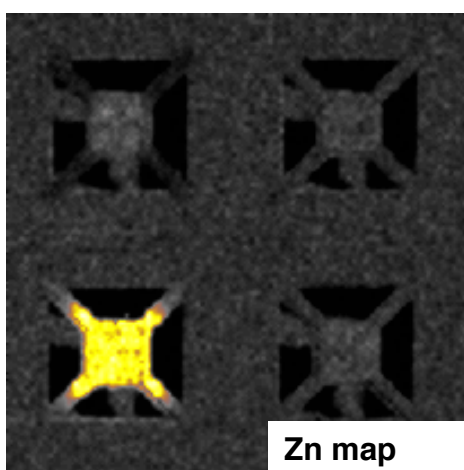
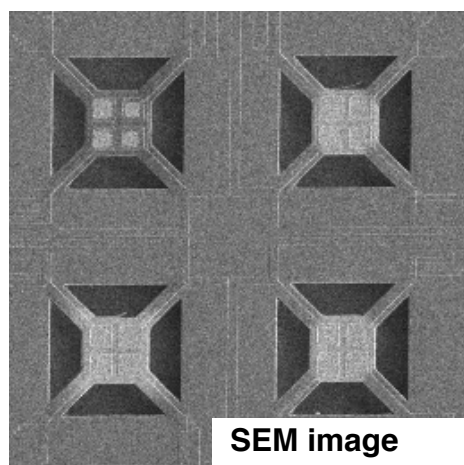


FIGURE 7. Energy-dispersive X-ray analyses indicating selected area deposition of Sn (in SnO_2) on the right elements, and Zn (in ZnO) on the left elements of a 2×2 array by self-lithographic, organometallic CVD. (The upper Zn signal is very weak due to the thinness of that ZnO film.)

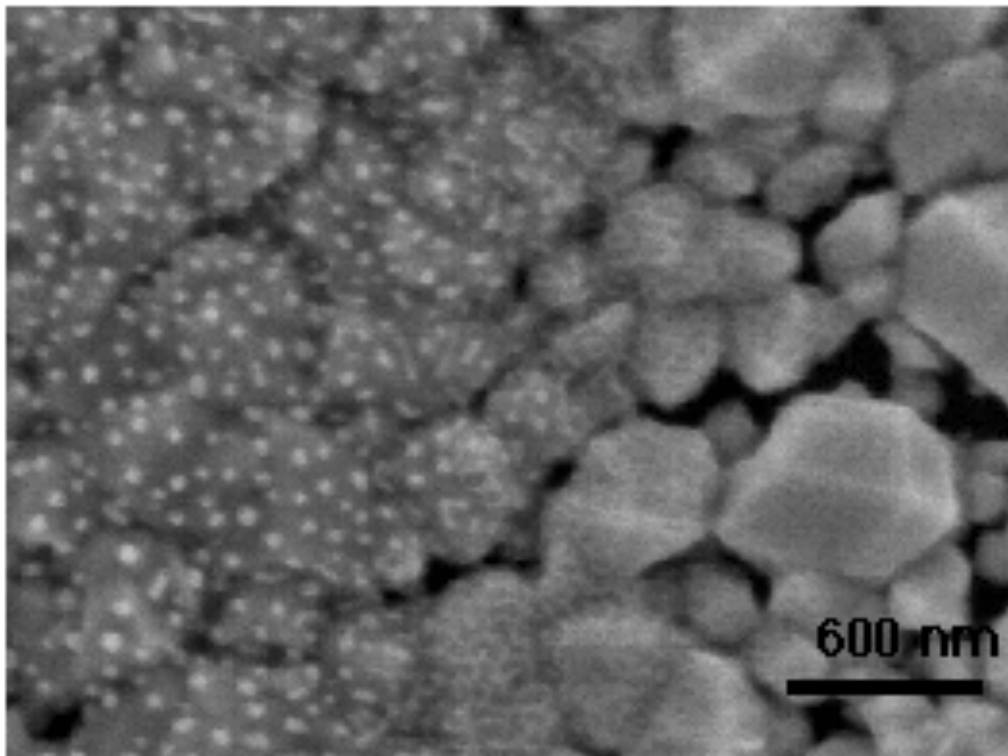


FIGURE 8. SEM micrograph showing Pt particles dispersed on the surface of a SnO_2 film. The oxide and overlying metal films were deposited sequentially onto a microhotplate using CVD. A region near the edge of the Pt deposit has been selected to more clearly illustrate microstructures in both the Pt/ SnO_2 (left) and SnO_2 films.

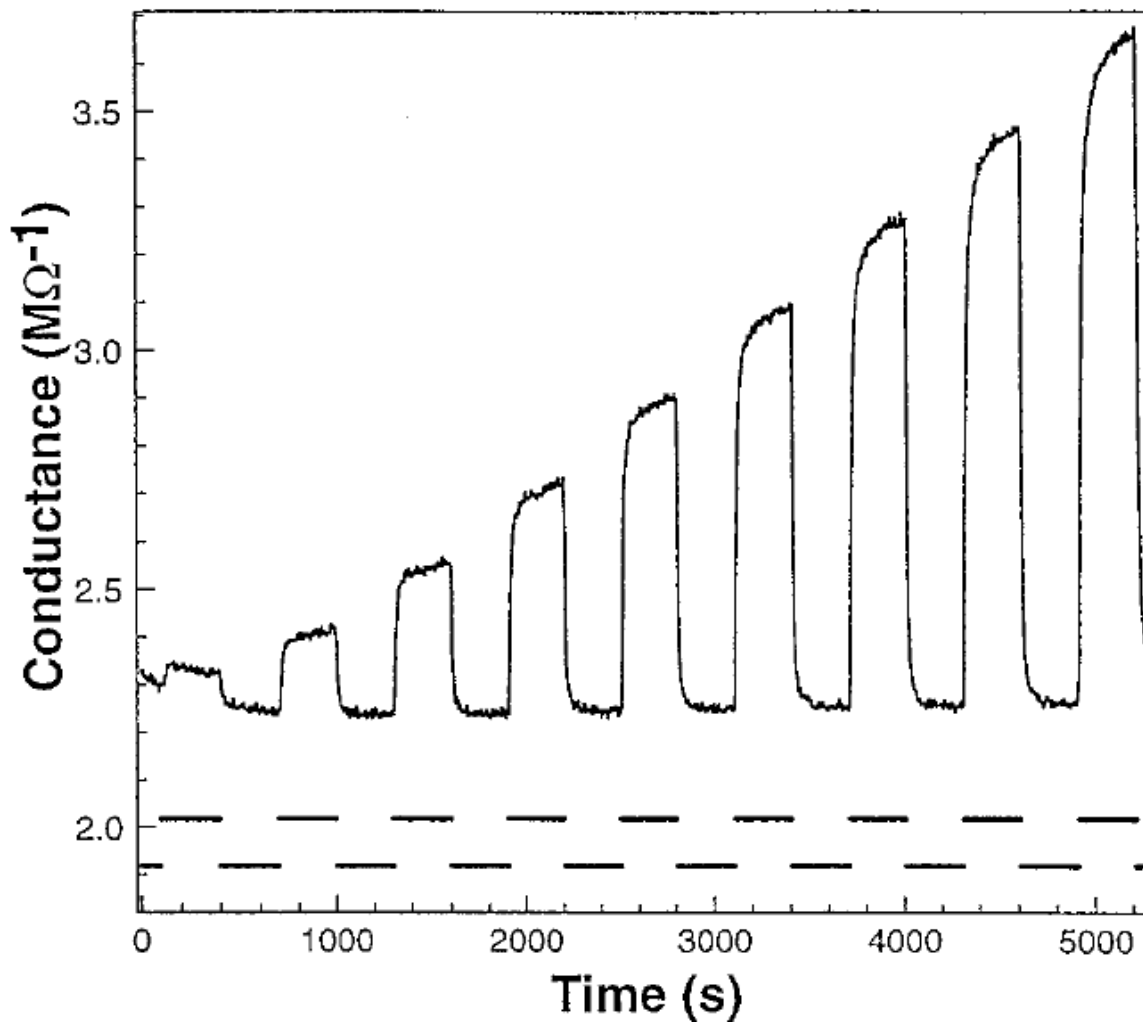


FIGURE 9. Static mode response at 130 °X of a Pt/SnO₂ microsensor to on/off CO exposures, into (dry) air, of increasing concentrations from 5 to 45 ppm.

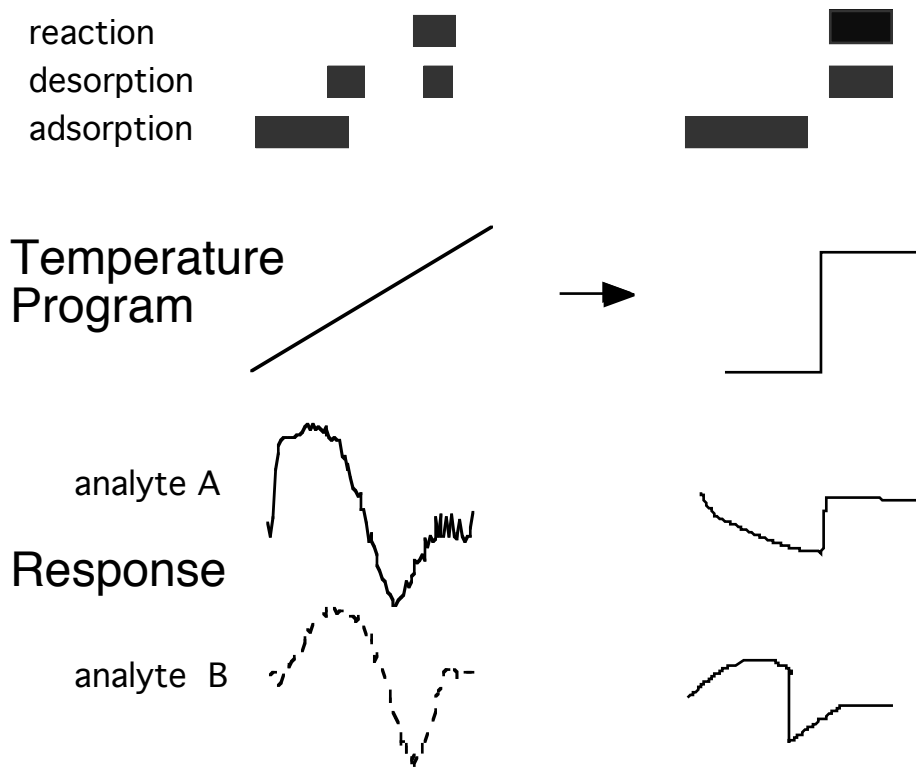


FIGURE 10. Concept of temperature-programmed sensing to produce response signatures.

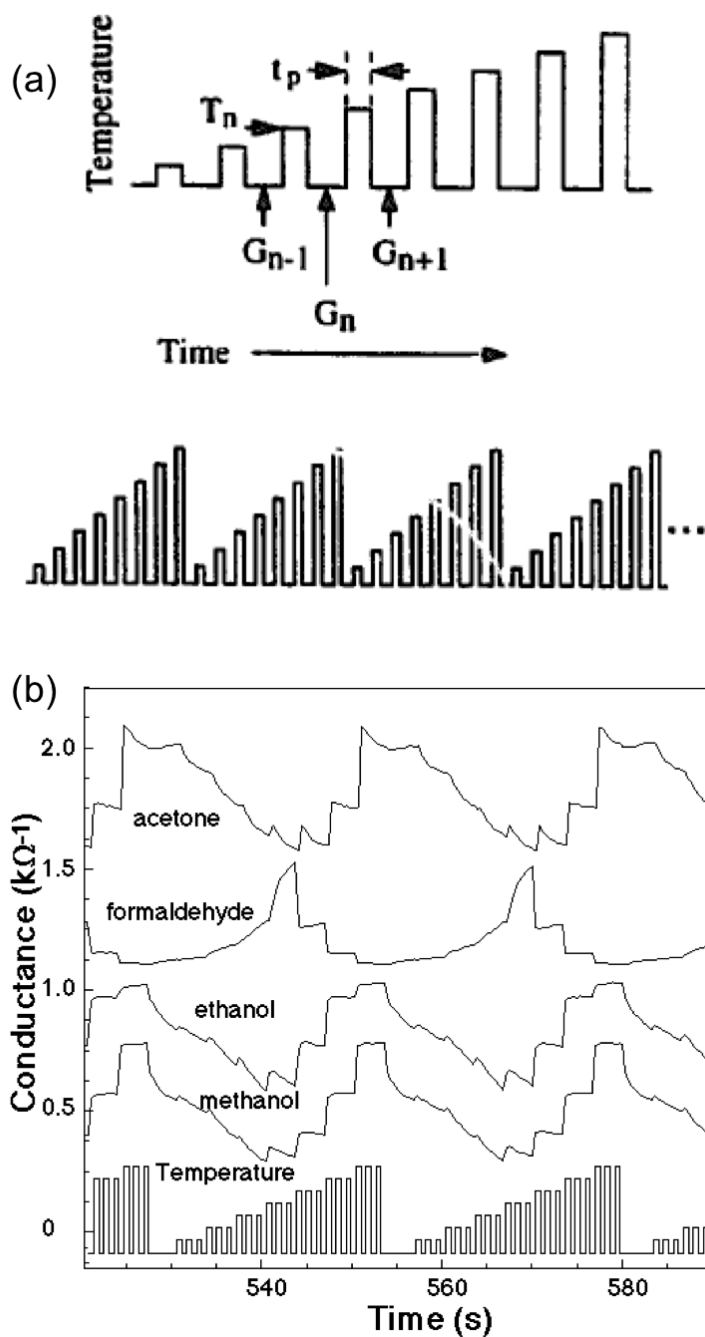
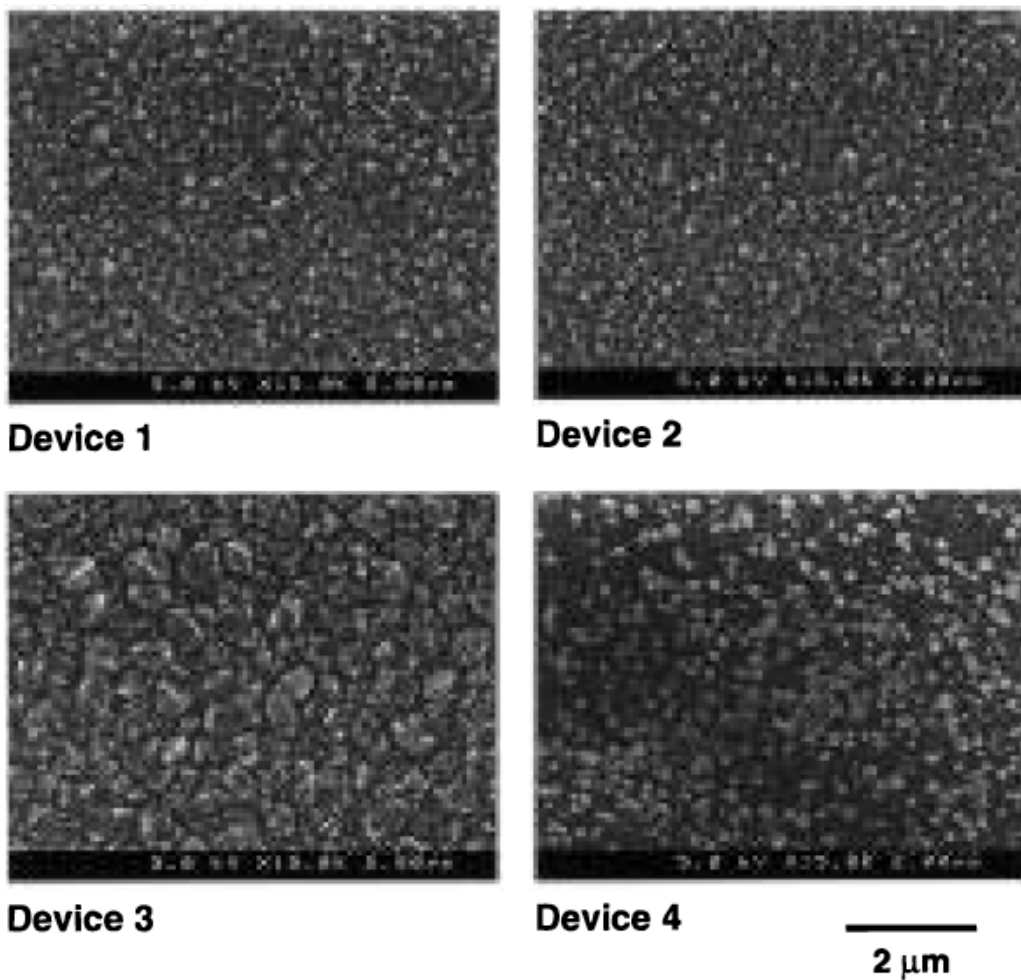


FIGURE 11. (a) Pulsing method used in dynamic temperature programming of a conductometric microsensor (to eliminate carrier concentration changes associated exclusively with temperature variation), and (b) response signatures measured for microsensor operation with a repeated, pulsed linear ramp temperature program for acetone, formaldehyde, ethanol, and methanol vapors in air.



Array Survey with 2 Pairs of Simultaneous Depositions:

devices 1 & 2 - high pressure (atmospheric) CVD at 480°C and 420°C
devices 3 & 4 - low pressure (10 Torr) CVD at 480°C and 420°C

FIGURE 12. Results of a 2×2 array survey relating film microstructure to CVD growth pressure and microsubstrate deposition temperature.

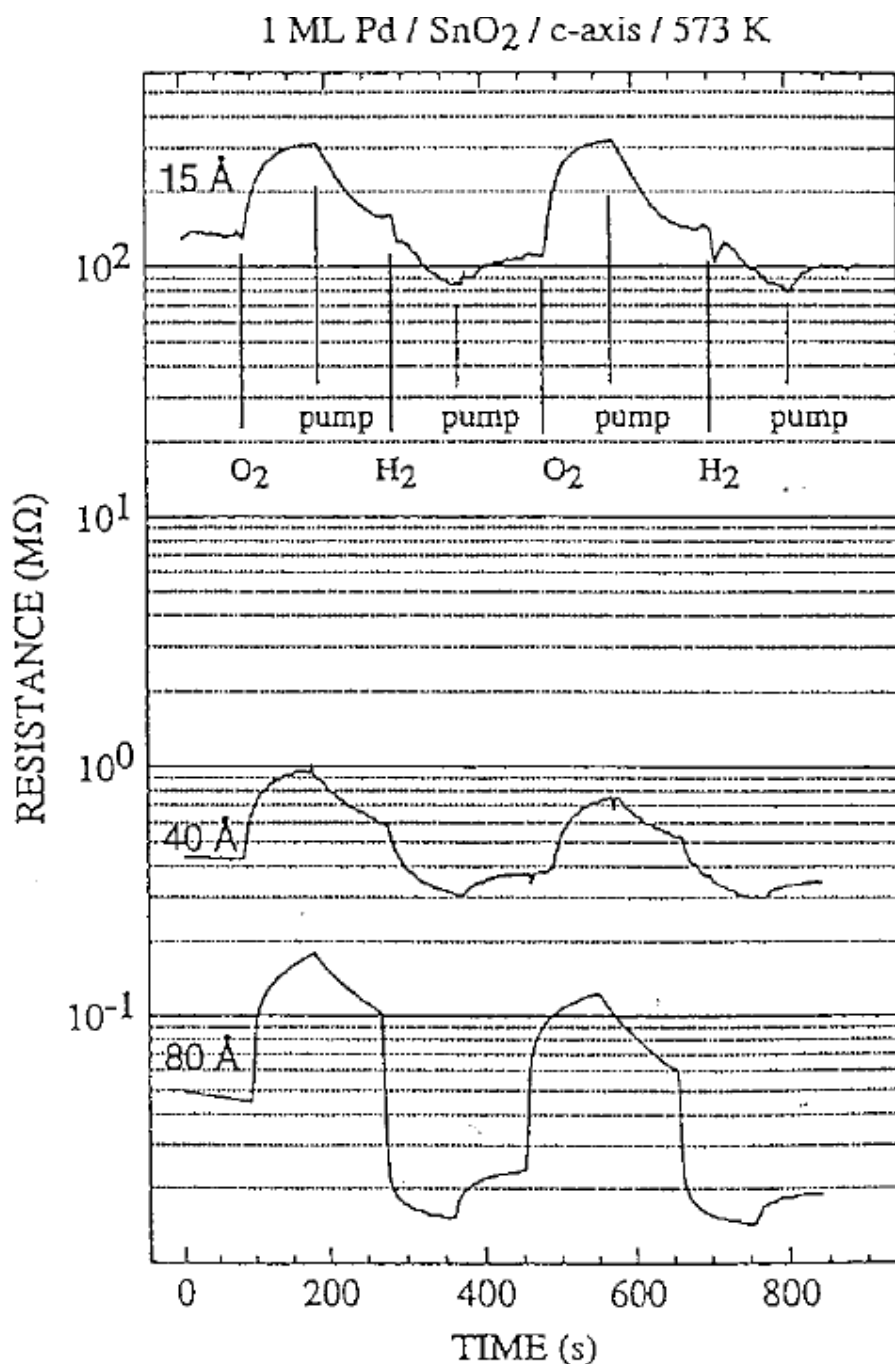


FIGURE 13. Research results for H₂ (injected in a vacuum) sensing with ultrathin, epitaxial SnO₂ films (thicknesses of 15, 40, and 80 Å) decorated with one monolayer (islands) of Pd.

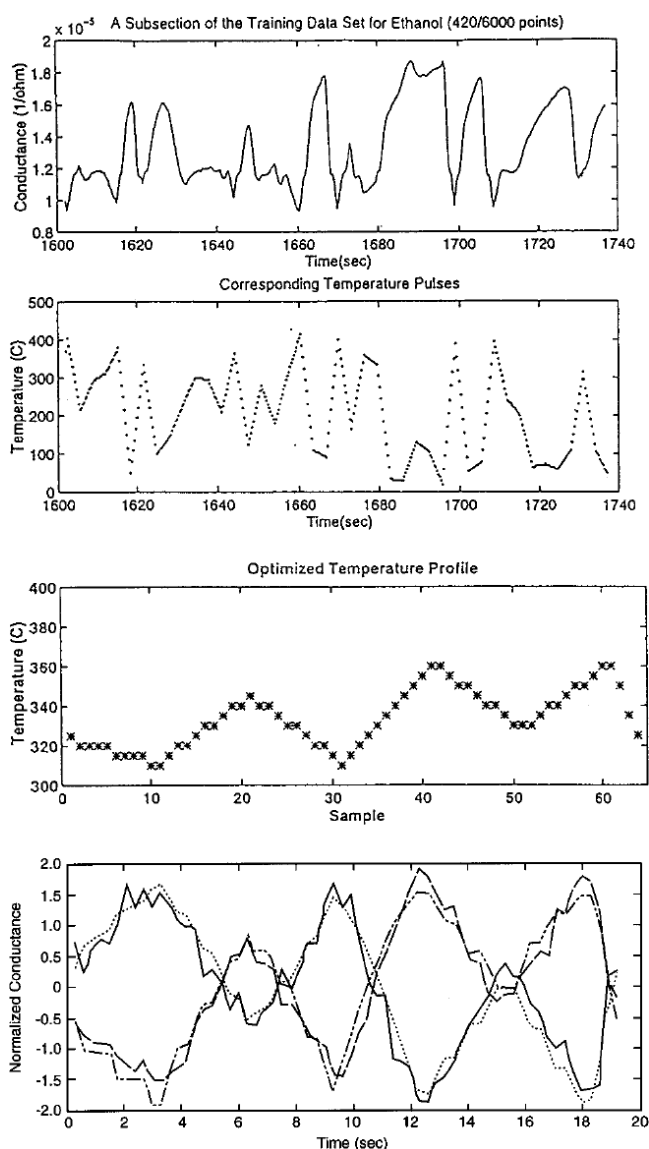


FIGURE 14. (a, top two panels) Portion of an ethanol (in air) training set in which conductometric responses for a Pd/SnO₂ microsensor are measured for a semi-random (pulsed) temperature program (only the temperature envelope is shown). The training data and similar data for methanol are used as inputs to construct predictive models for the microsensor response, as a function of temperature program, for the analytes. (b, third panel) Predicted temperature program which will maximize the response separation for the two vapors. (c, bottom) Predicted [ethanol, - - -; methanol, - - -] and experimentally-measured [ethanol, s; methanol, - -] responses to the temperature program (envelope) in (b).