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

Steve Semancik (PI) and Richard E. Cavicchi (Co-I), Process Measurements Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD

Thomas J. McAvoy (Co-PI), Department of Chemical Engineering, University of Maryland, College Park, MD

Other Contributors: M. C. Wheeler*, J. E. Tiffany* M. I. Aquino*, J. D. Allen*, M. J. Carrier*, J. Ding#, B. Panchapakesan#, D. L. DeVoe#

#University of Maryland , *National Institute of Standards and Technology

Environmental Management Needs Addressed

Primary Area

subsurface contamination

rapid waste characterization

monitoring spatial variability and transport in the vadose zone

(for analytes with sufficiently high vapor pressures)

Additional Areas

tank focus area

health/ecology/risk

Enabling Science and Technology

new insights into chemical sensor principles

database development for sensing films

fabrication of microdevice platforms

development of microarray research tools and methodology

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Research Objective

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

Approach

Monitoring capabilities will be centered on a generic, micromachined device structure that can measure conductance of active sensing films and also control their temperature. The core of this research program will involve experimental measurements to produce a direct correlation of interfacial conductance changes with the interfacial adsorption phenomena from which they result.

Implications and Advantages

Microsensor development evolving from this work will allow monitoring devices to be tailored for a range of Department of Energy hazardous waste sites. Advantages of the technology are:

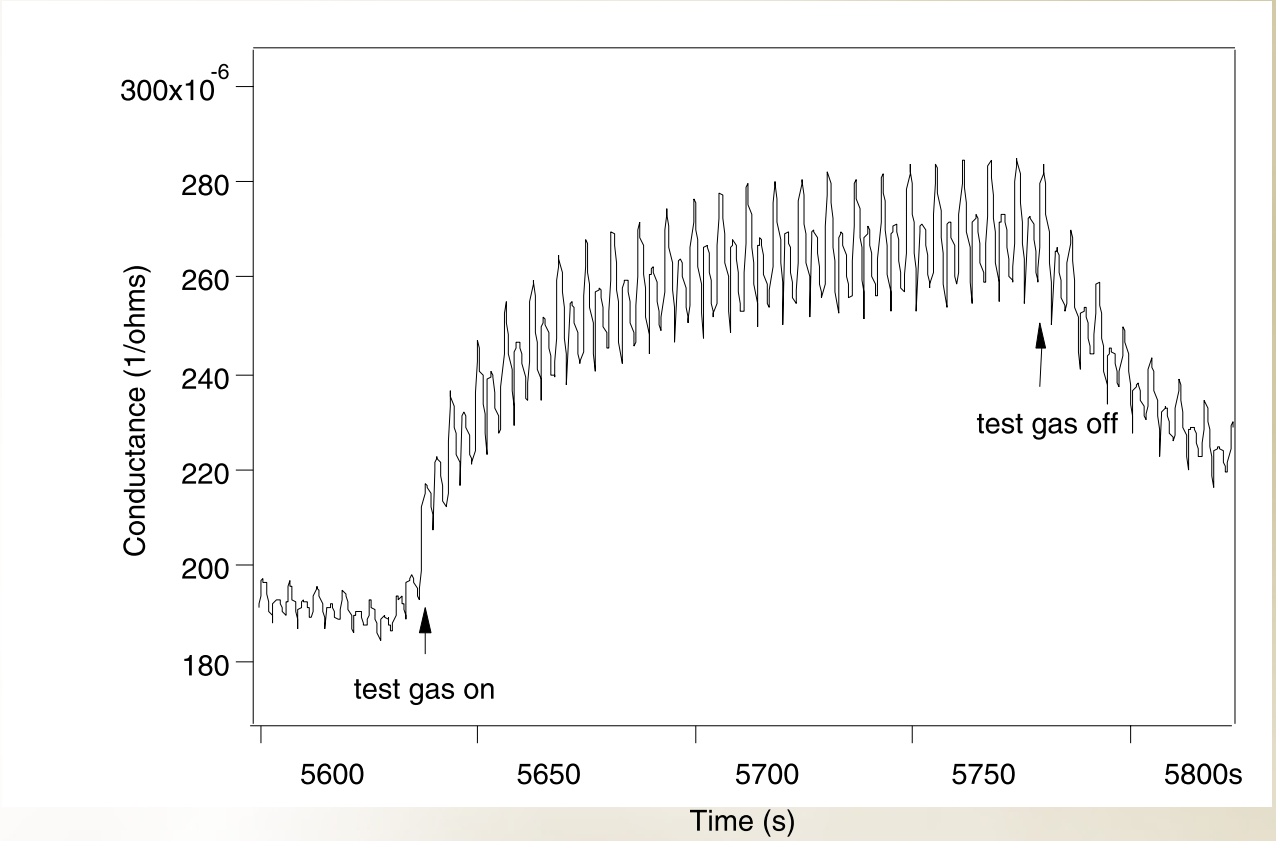
- inexpensive
- robust
- operable with low power
- field-deployable

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Research and Technology Overview

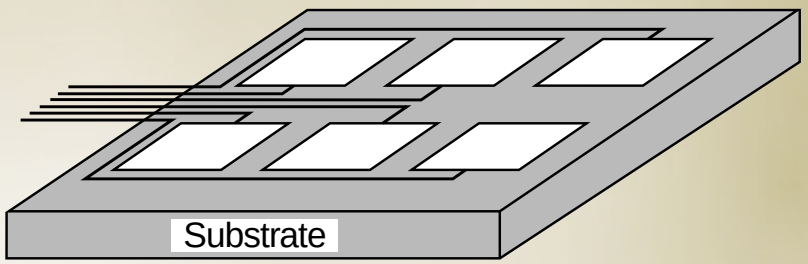
Conductometric Sensing

- adsorption-induced changes in electrical conductivity
- simple electrical measurement



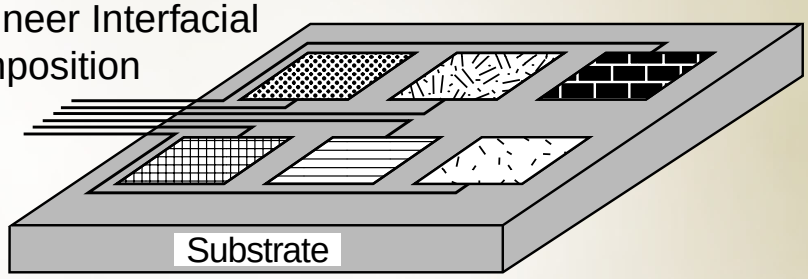
Response to 40 ppm methanol.Signal modulation is from temperature programming and isused for chemical identification.

Approach for Application- Specific Tunability



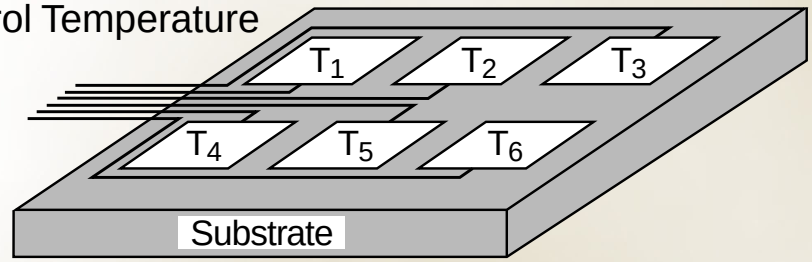
Need Selective Elements

Engineer Interfacial Composition



use catalytic metal/semiconducting oxide combinations

Control Temperature



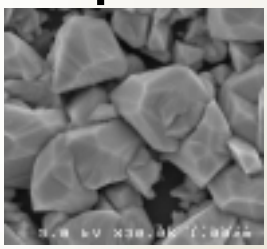
vary individual kinetics

Combinatorial Optimization Using Micromachined Microarrays

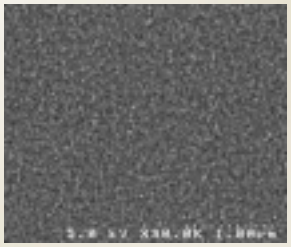
– sensing films being studied: metal oxides (SnO_2, ZnO, TiO_2 . . .) catalytic metals (Pd, Ni, Ag . . .)

48-element array of microhotplate gas sensors

Performance Correlations to Film Microstructure, Composition and Temperature



Large grain SnO_2 film



Fine grain SnO_2 produced by seeded CVD

NIST Chemical Microsensor Facilities

Microdevice Fabrication

dicing, etching, wirebonding

Chemical Vapor Deposition

self-lithographic deposition of sensing

Deposition and Characterization

sputter deposition, electrical characterization

Macrosample Preparation

Chemical vapor deposition of oxides

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

NIST Chemical Microsensor Facilities

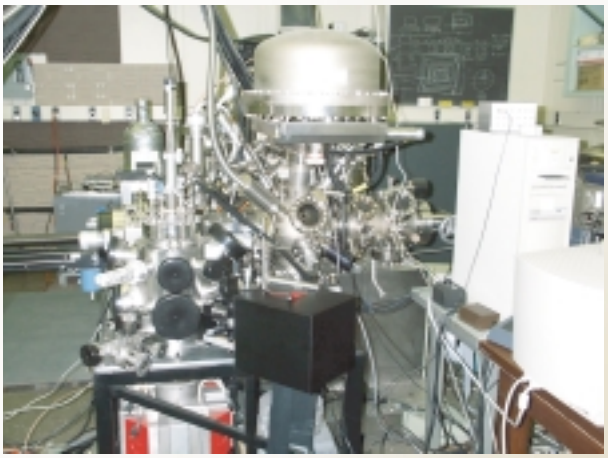
Scanning Electron Microscopy

device and film imaging, chemical analysis

Response Testing

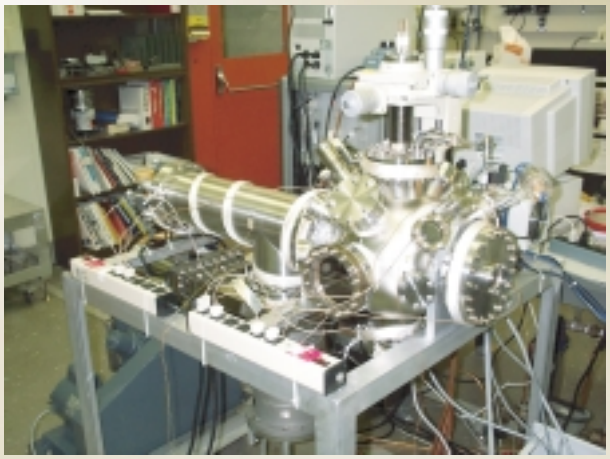
performance evaluation in flowing gas mixtures

Surface Analysis



surface characterization of macrosamples

Desorption Kinetics



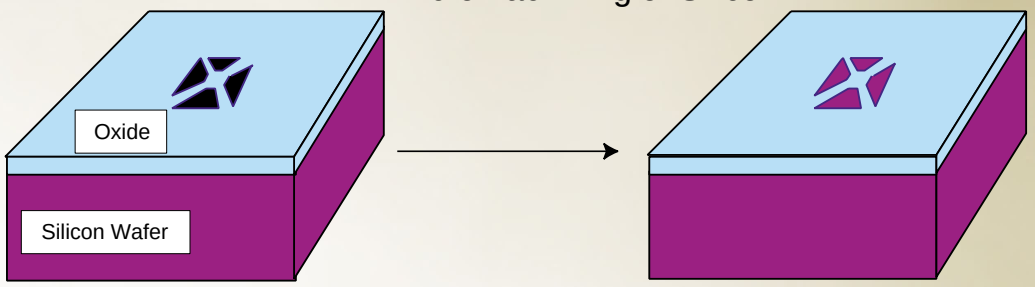
mechanistic studies on on sensor arrays

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Microdevice Platforms for Research and Sensing

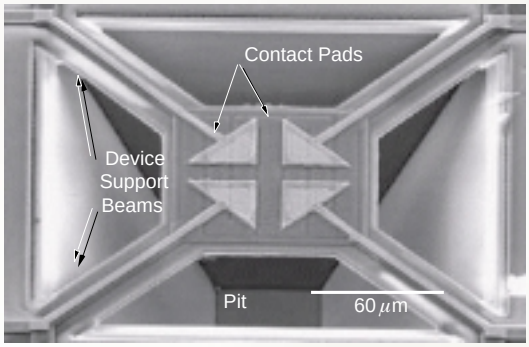
Micromachined Sensing Devices for LowPower, Portable Monitoring of Gases

Micromachining of Silicon



A) Pattern holes in the oxide first

B) Then, etch silicon underneath oxide to leave microbridge structure



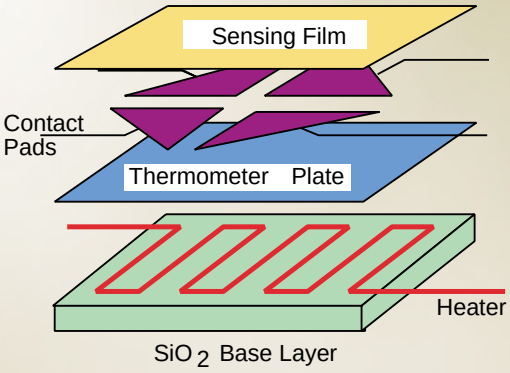
Sensing Device

The device platform we have developed at NIST is called a "microhotplate" since it provides tiny localized regions of controlled temperature.

Functionality

The multilevel structure includes layers that allow:

- remote control of a miniature heater
- measurement of the device's temperature
- measurement of the electronic conductance of an overlying (sensing) film



Specifications

- power consumption: 50 mW at 400 °C for 200 μm device
- size: 50-200 μm
- time constant: ~1 ms
- temperature range: 20-800 °C

Advantages

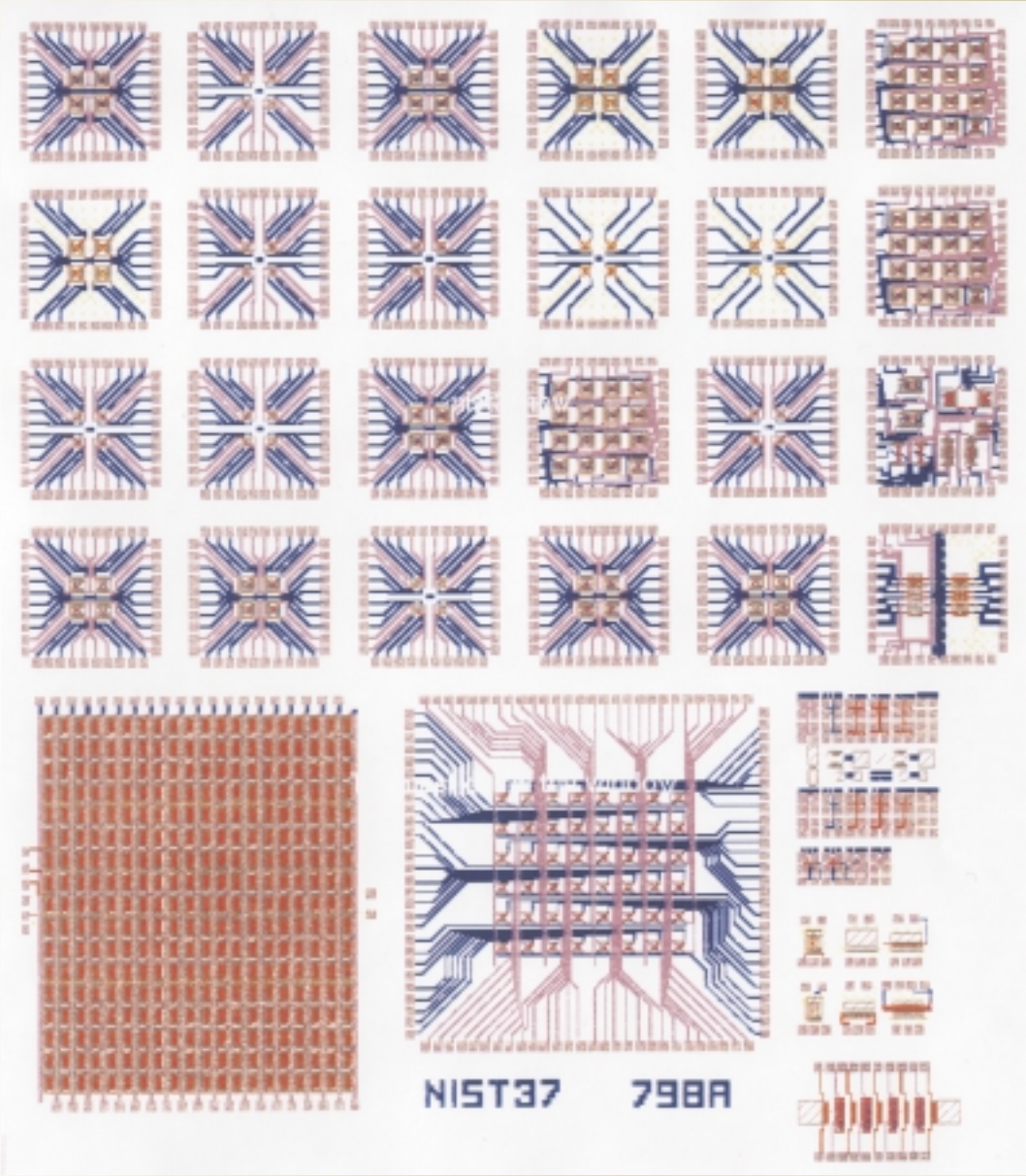
- rapid heating/cooling
- low power
- Si technology compatible (for on-board circuitry)
- inexpensive to fabricate many units

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

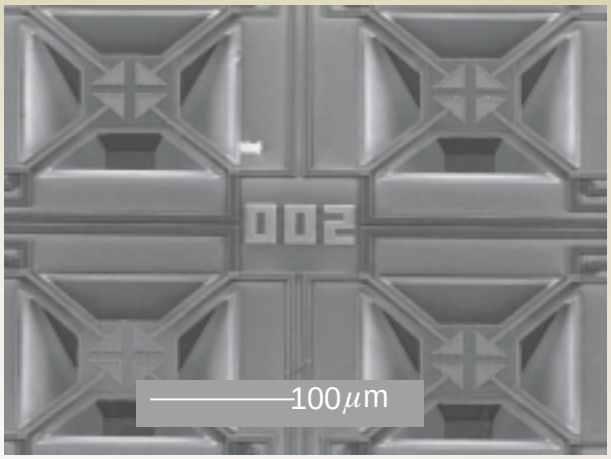
Layout of Microdevice Designs for Developing Varied Chemical Functionality

Wafer level runs at MIT – Lincoln Laboratories

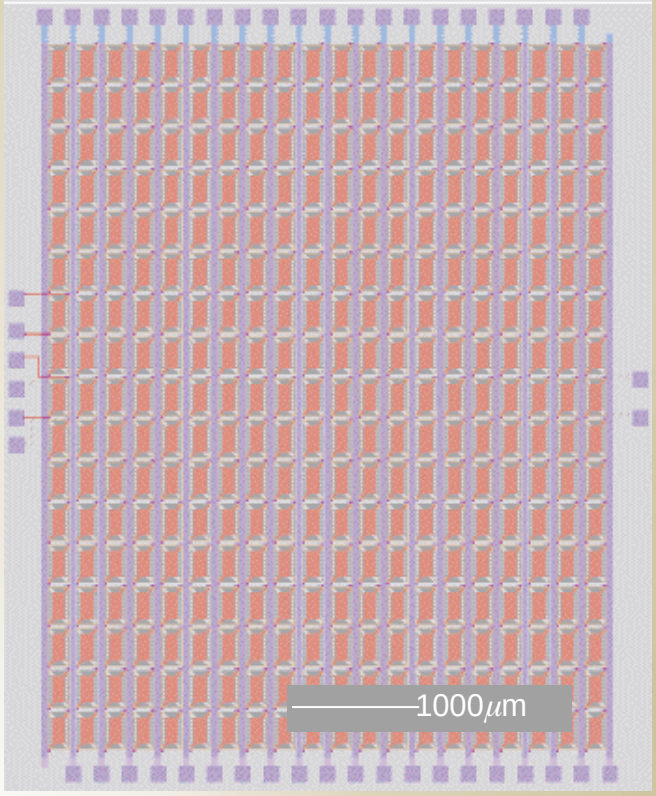
- Flat device topology (by chemical mechanical polishing)
- Improved metal contacts



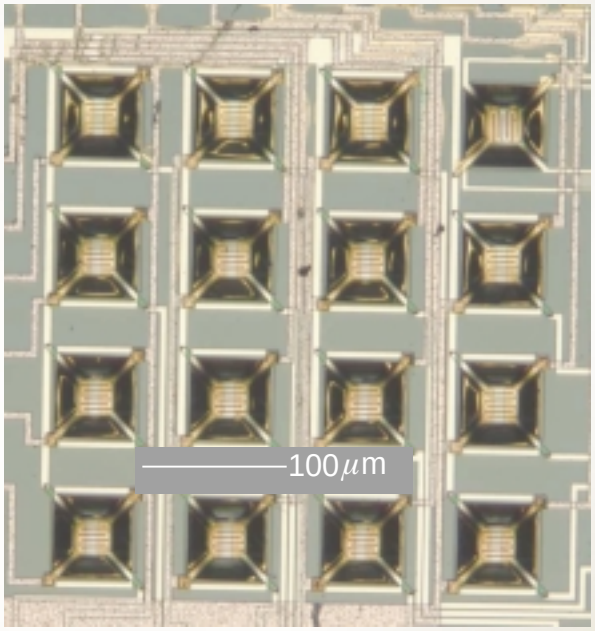
Different Microhotplate Designs



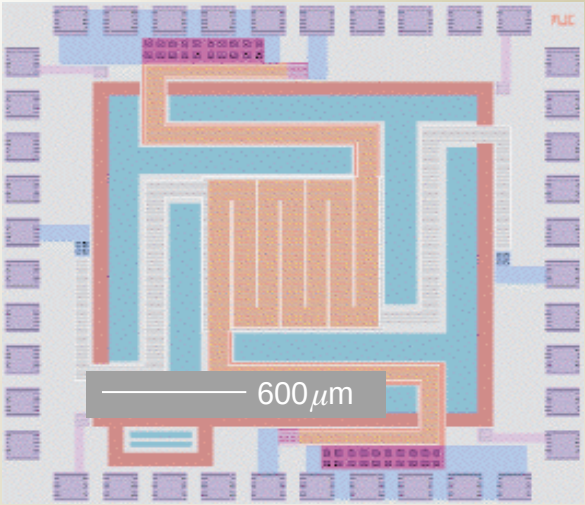
4-element microhotplate array used for initial materials studies and microsensor tests.



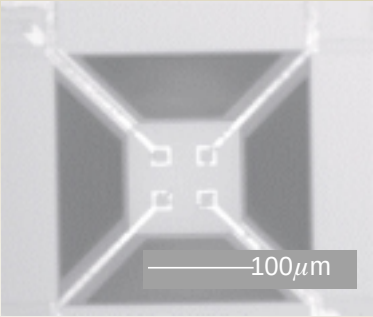
CAD design of large array of microhotplates for correlating adsorbate coverages with electrical changes.



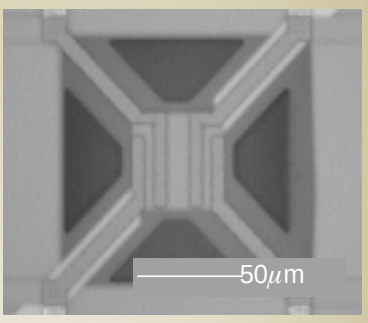
16-element array developed formore effective process-performance studies.



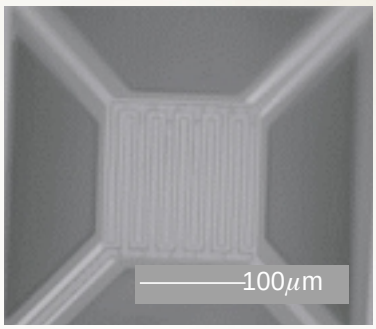
CAD design of large (600mm)microhotplate for surface analytical studies .



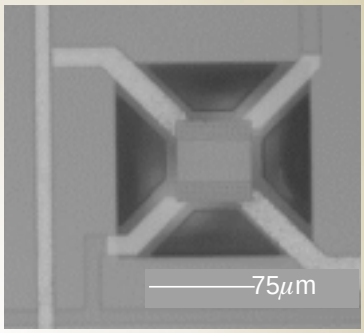
Four van der Pauw contacts for conductance measurement



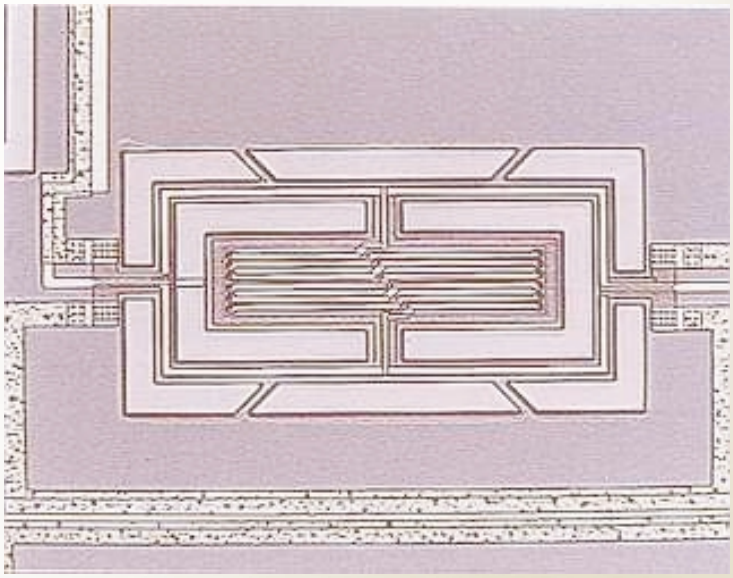
Four in-line contacts for 4-point conductance measurement



Comb-contacts for high-resistance sensing films



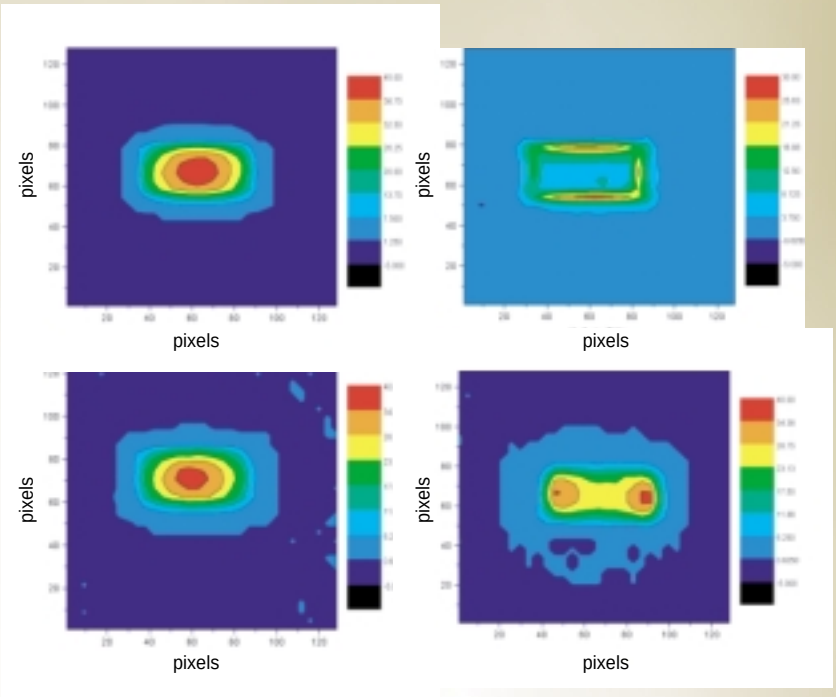
Two-contact device to be used in a large array

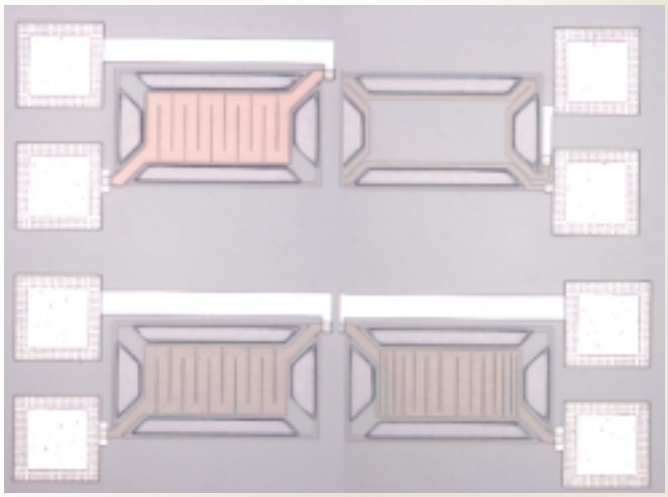


Differential Scanning Calorimeter with thermopile to measure the temperature difference between sample and micro-hotplate reference zones.

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Microheater Design Study for Temperature Uniformity





Varied heater designs are being examined to produce more uniform temperature across the microhotplates

Material Processing on Microplatforms

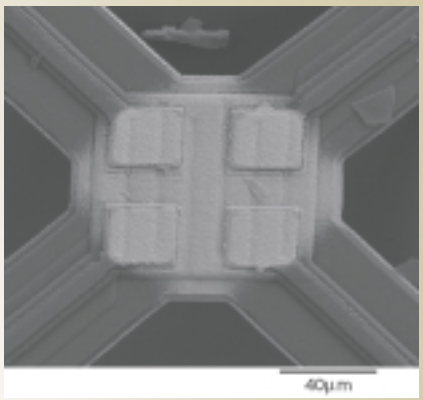
Film Growth on Microhotplates

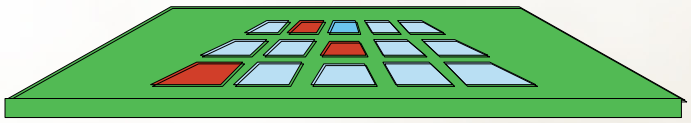
Chemical Vapor Deposition: Only heated microhotplates initiate the reactions to deposit a film. This self-lithography can be used to deposit different sensing materials on different microhotplates.

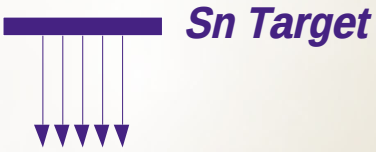
Organometallic, i.e. Tetramethyltin for tin oxide

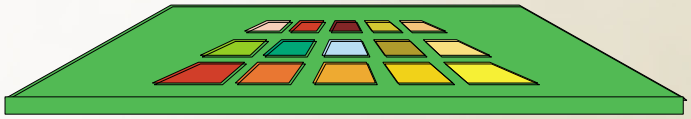
Oxygen

Argon





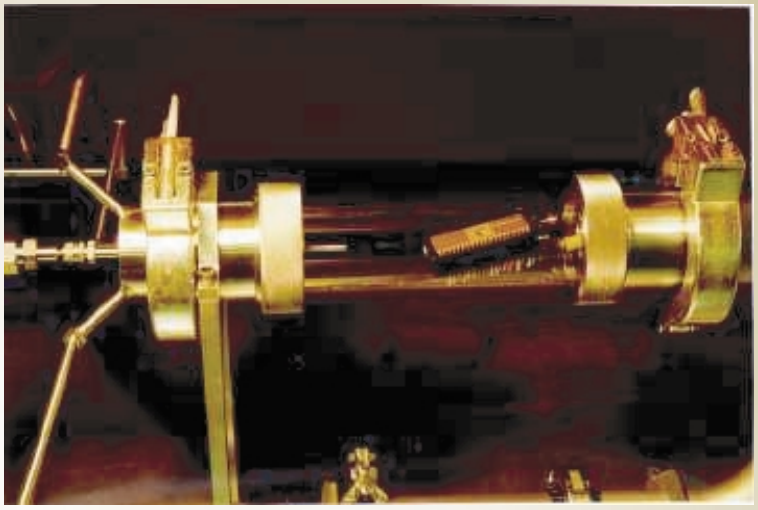


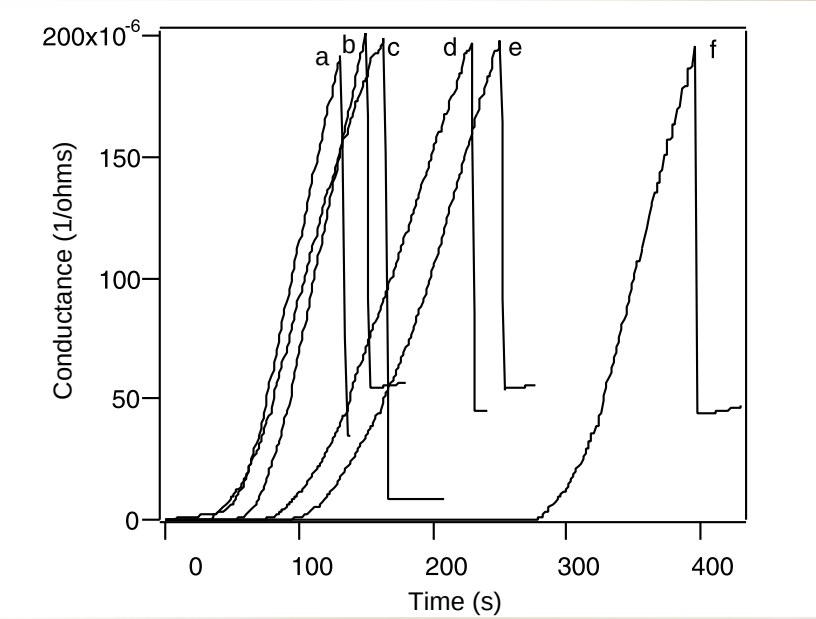


Reactive Sputter Deposition: Microstructure of the film on each microhotplate is controlled by the temperature.

Material Processing on Microplatforms

Electrical measurements in situ During CVD Growth





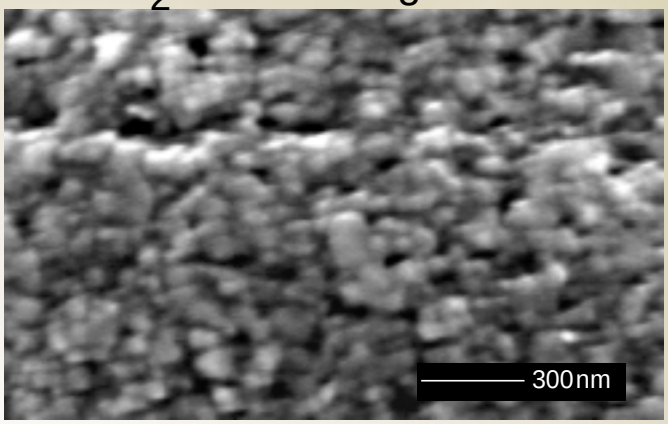
CVD conductance growth curves for various seeding of the microhotplates prior to tin oxide growth: (a) 16 Å Fe, (b) 16 Å Co, (c) 16 Å Cu, (d) 16 Å Ag,(e) 16 Å Ni, and (f) unseeded

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Material Processing on Microplatforms

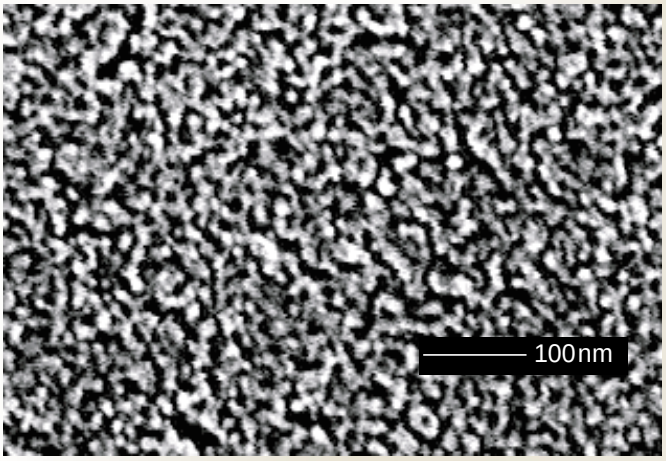
SnO_2 Films Prepared Using Wet Methods

SnO_2 from a sol-gel solution



A drop of sol-gel solution* is allowed to dry on a microhotplate (20 ^{o}C for two hours). Once the solution dries to form a film, the film is sintered with local heating of the microhotplate for 30 minutes at 500 ^{o}C.

* Solution consists of stannic acid, propanol,butanol and water



A drop of aqueous nanoparticle* solution is placed on a packaged microhotplate. The package is spun using a commercial spincoater. The films are then sintered with local heating of the microhotplate for 30 minutes at 500 ˚C.

*average particle size is 10 nm

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Film Performance Studies

Microarray studies are used to develop processing methods that optimize sensing films for varied performance characteristics. Studies of processing, properties, and performance are done efficiently on multielement microarrays. Often one is seeking a balance between sensitivity, stability and selectivity for the sensing films. We illustrate 2 case studies:

Seeded Oxides Study

- film morphologies (grain size, distribution, shape, orientation)
- enhanced selectivity
- improved sensitivity

Catalytic Metals Survey

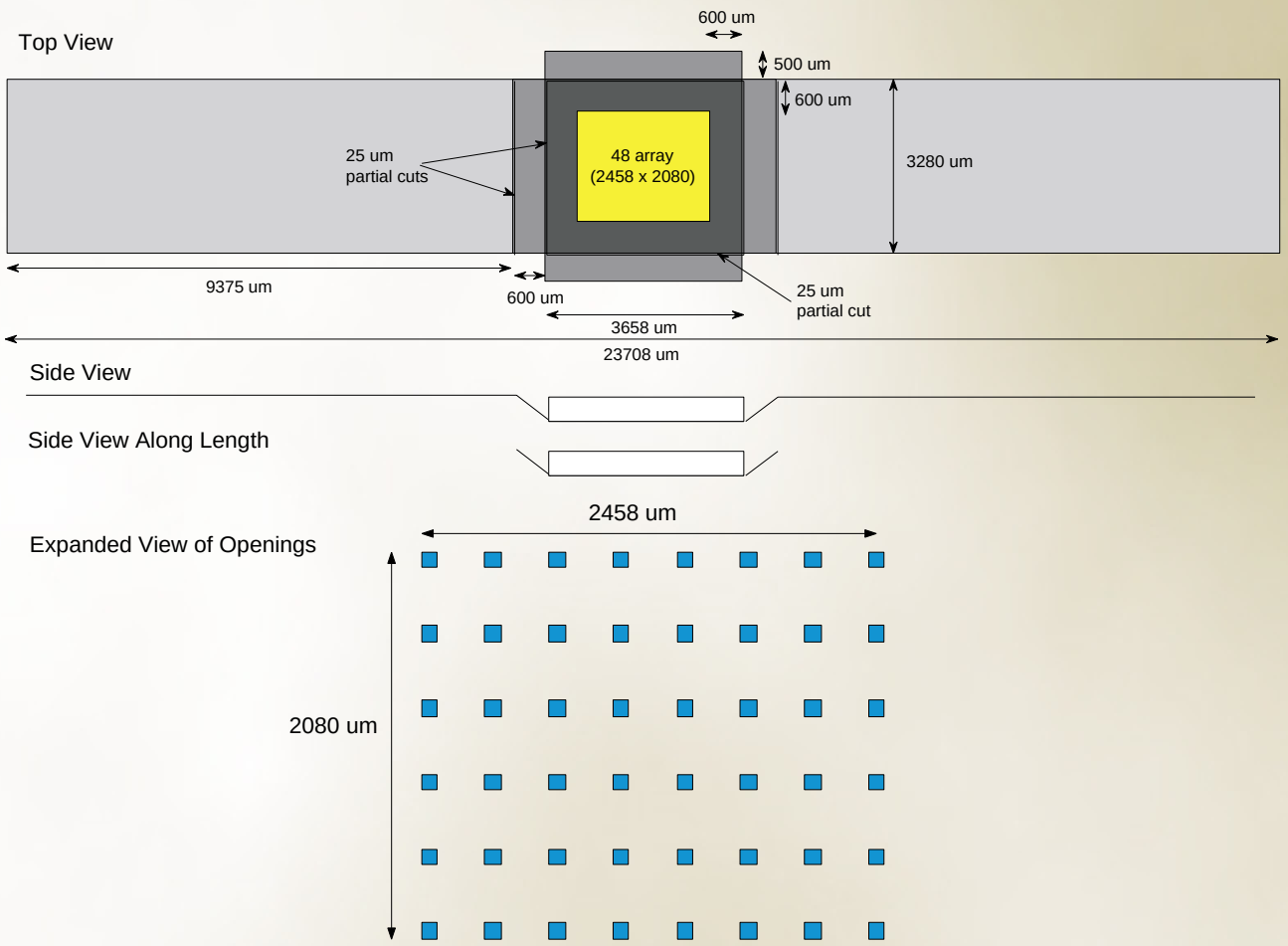
- catalyst type (Ni, Pd, Pt, Rh, Ru, Ir, Co, V, Cr, Zn, Cu, Ag)
- coverage of catalyst
- temperature dependence of catalyzed responses
- sensitivity and selectivity to a wide variety of gases

Film Performance Studies

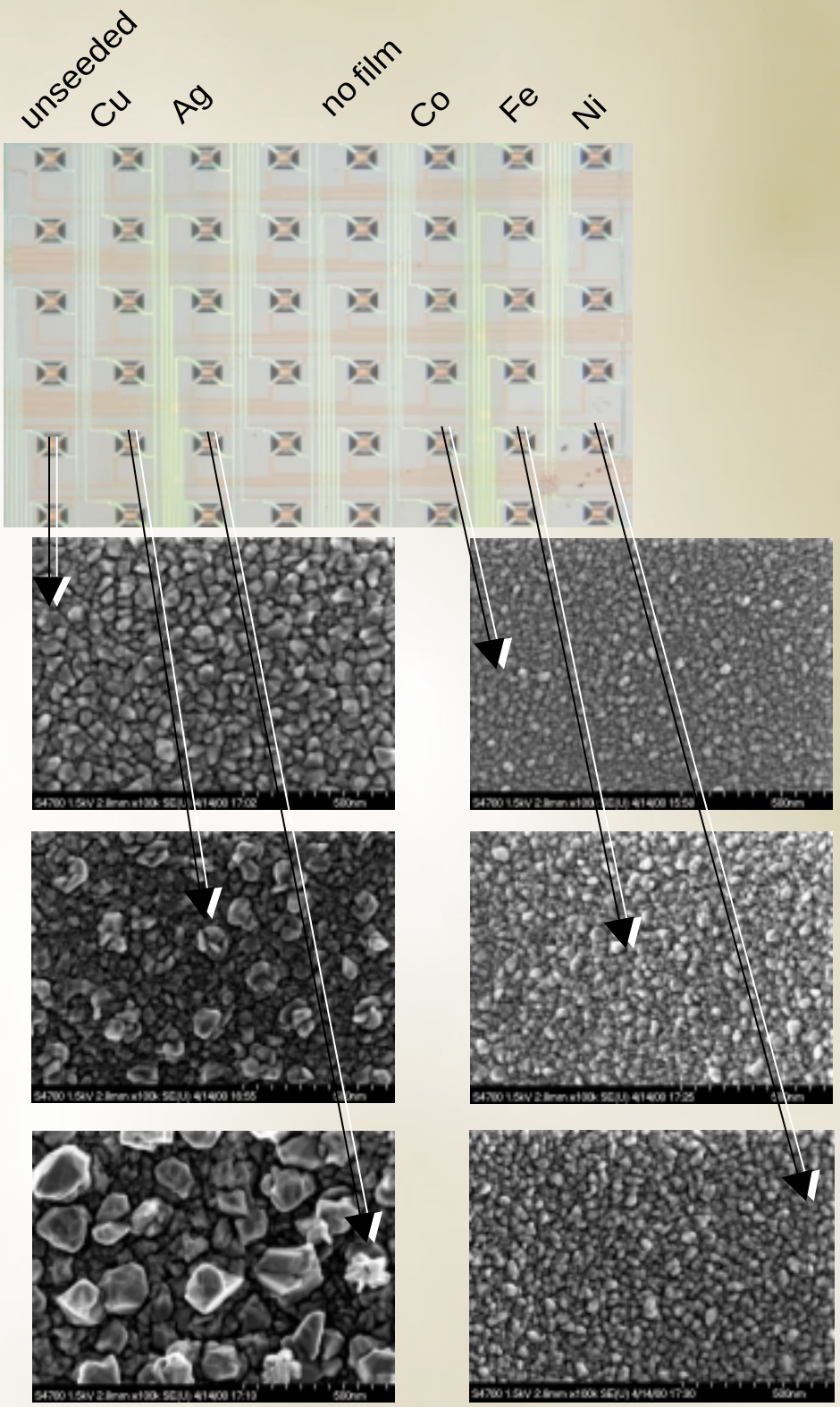
Evaporation Mask Design

Evaporation mask designed for physically masking selected elements of an array for metal deposition. These metals have been used for seeding tin oxide CVD and for catalytic surface studies.

Sputter/Evaporation Mask for 48 Element Array

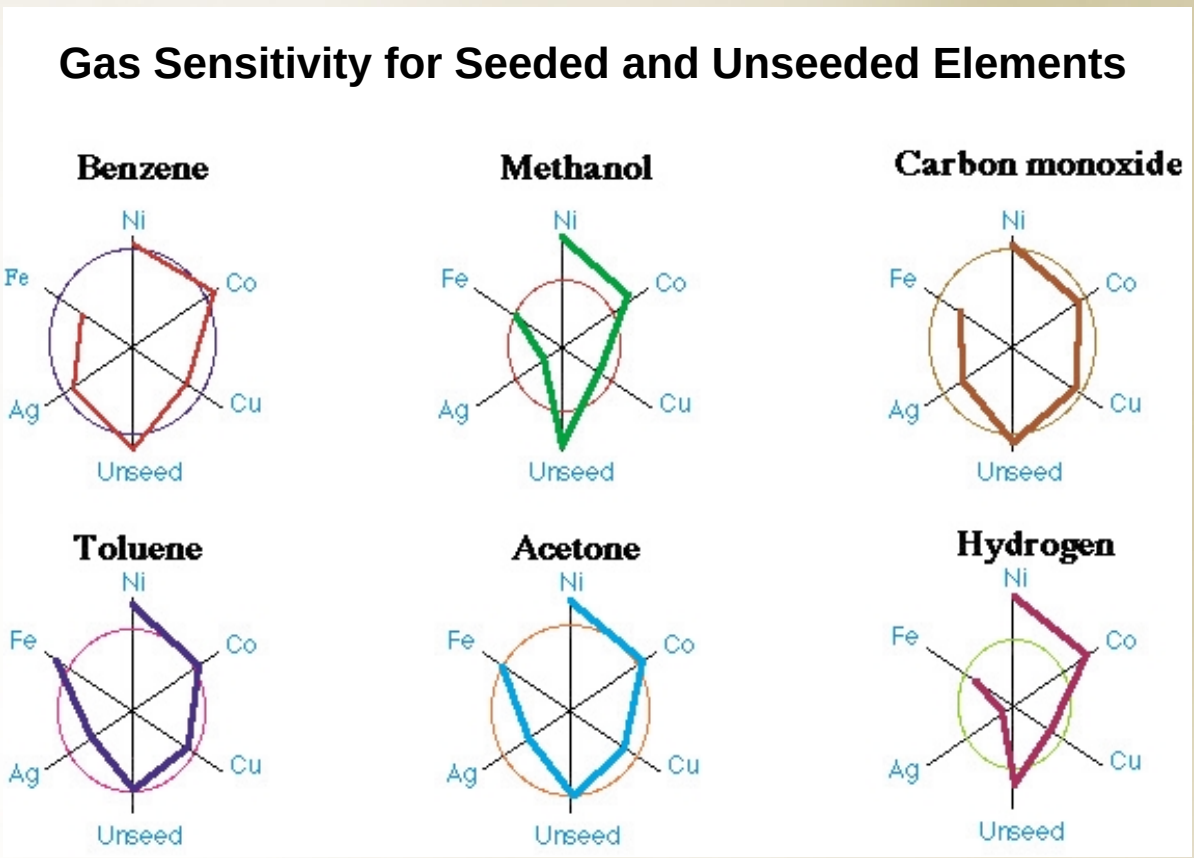


Seeded Oxides: A Combinatorial Study



NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Seeded Oxides: A Combinatorial Study

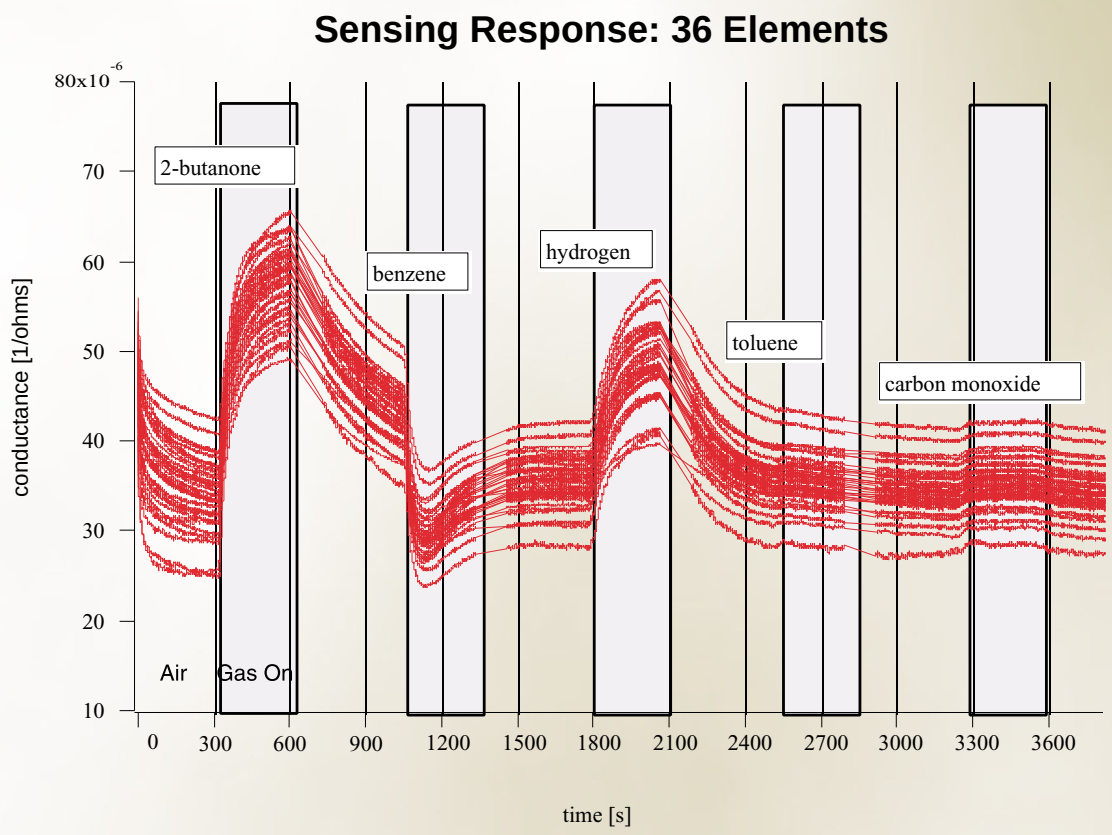


Catalytic Metals Survey

Catalyst Screening Survey: Initial Results- 36 elements of a 48 element array were used to investigate variables involved to reduce the experimental design space

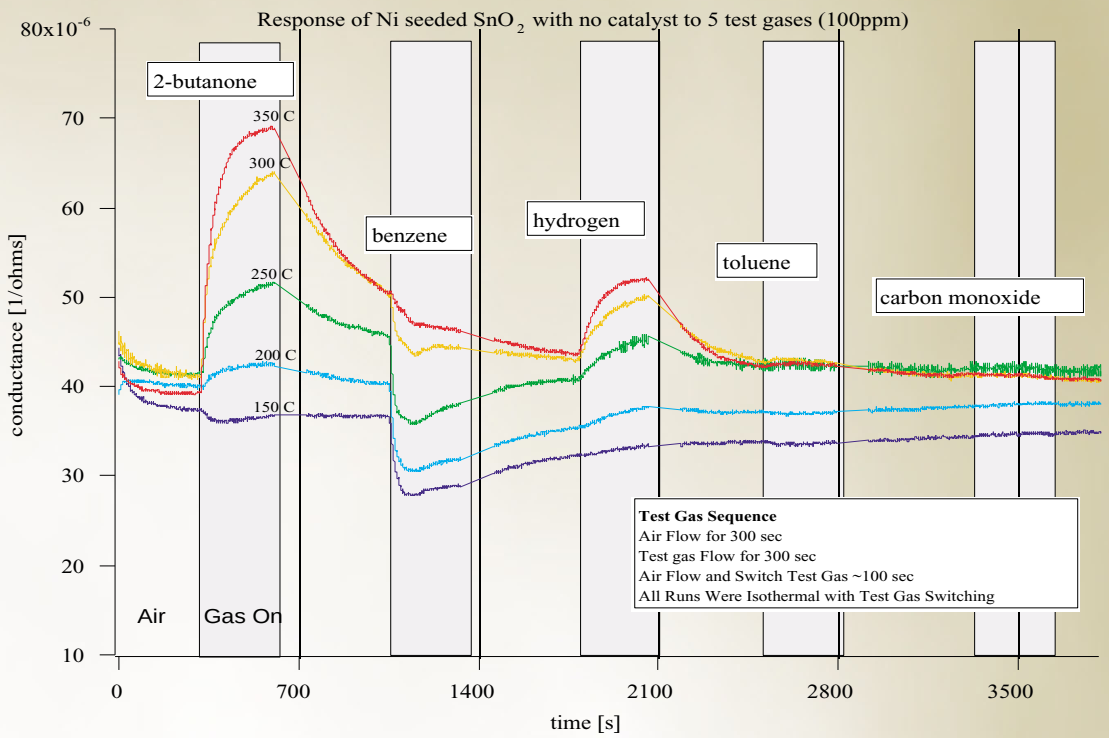
- Ni seeded SnO_2 films were grown
- Ni catalyst was deposited in 3 coverages (16Å, 32Å and 48Å)
- Sensors were tested in 5 gases before and after catalyst addition
- Sensing response of 36 elements to 5 gases demonstrates repeatibility of sensor platform for screening (see below)
- Before and after catalyst addition sensing results show an increase in 2-butanone sensitivity, and a decrease in both benzene and hydrogen sensitivity (see right)
- Catalyst coverage (16-48Å) not found to have a significant effect when compared to other factors

Response of Ni seeded SnO_2 with no catalyst to 5 gases (100ppm): All 36 elements

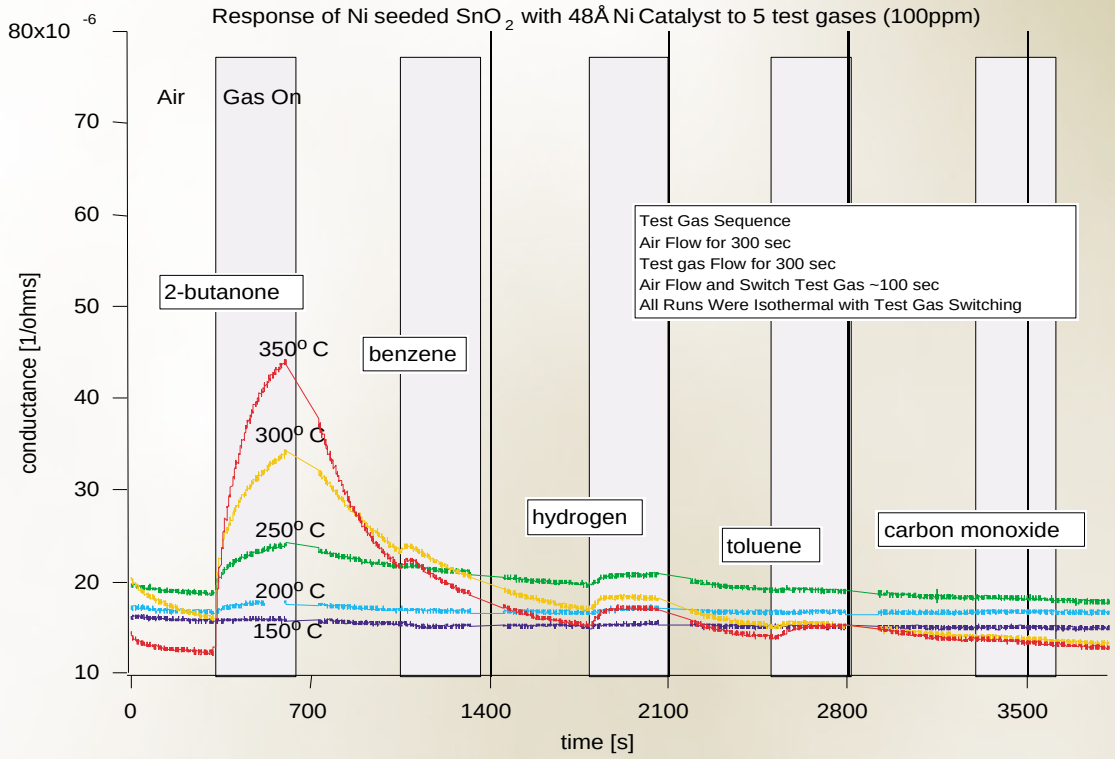


Catalytic Metals Survey

No Catalyst



With Catalyst

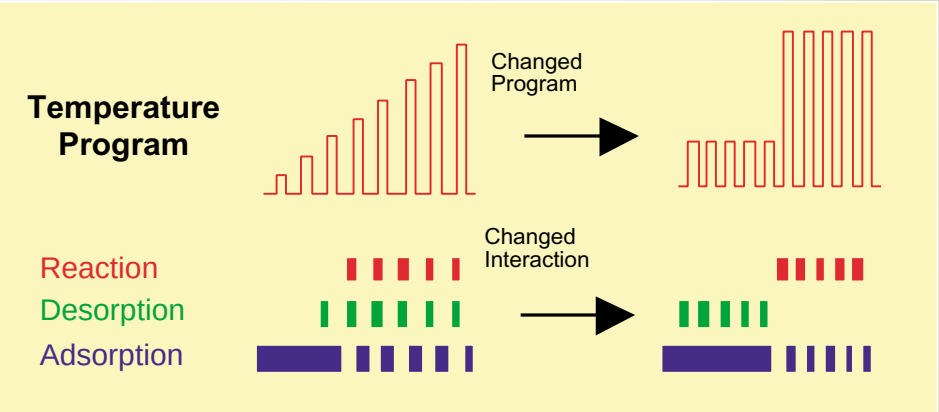


NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Signal Analysis and Transduction Principles

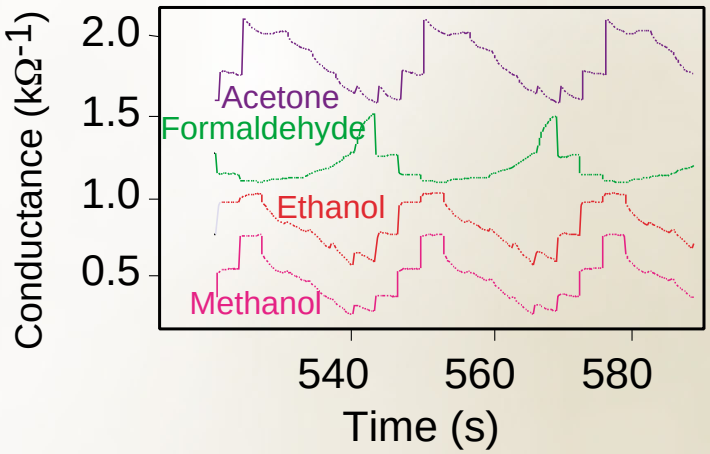
Temperature Programmed Operation for Selectivity

The temperature of a microhotplate can be easily and rapidly measured and controlled



Processes such as adsorption, desorption, diffusion, and reaction between gases and the sensing surfaces are temperature dependent

Rapid programming of the microhotplate temperature can be used to examine the characteristics of the interfacial interactions by making real time conductance measurements on the sensing films as the temperature is varied



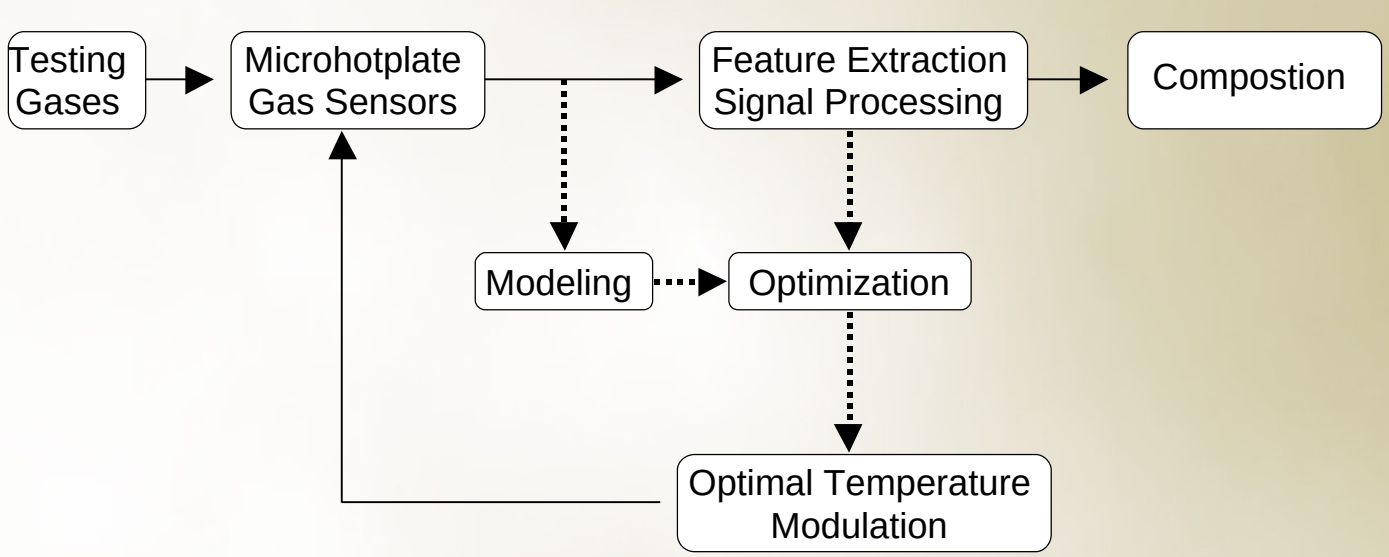
Response Signatures

Characteristic signatures for different chemical vapors in air are obtained by measuring the microsensor's conductance as a function of time (temperature)

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Signal Analysis

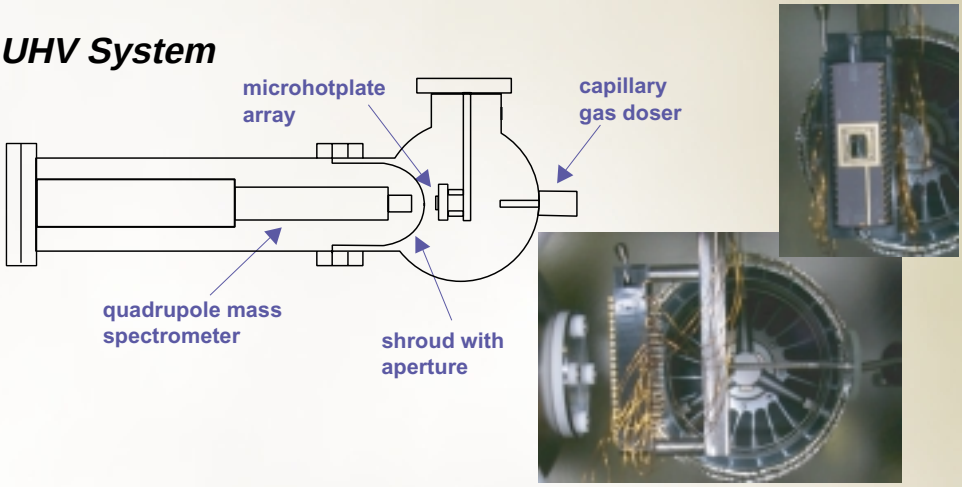
Temperature programming, combined with signals from an array of different sensing films, has the potential for producing an information-rich data set related to the gas environment. Wavelet neural networks are used to model device behavior and then optimize device operation (through the temperature program). Data processing, such as Partial Least Squares (PLS) methods are then used to convert complex data into useful forms.

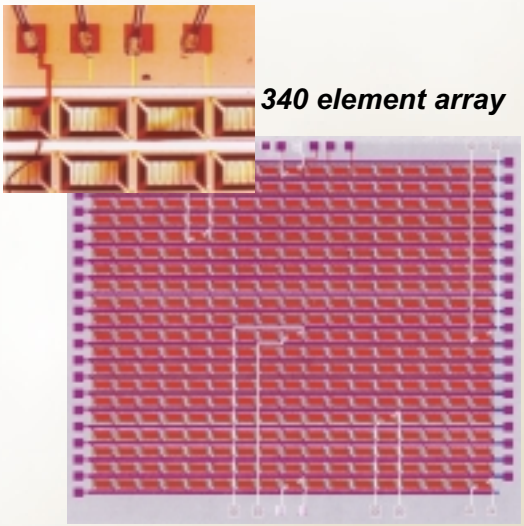


Mechanistic Studies of Adsorption/Desorption Transients

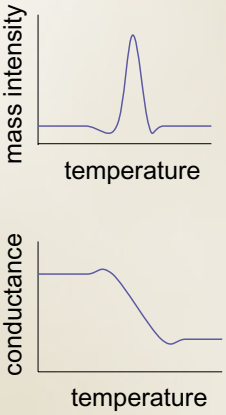
Objective: relate measured electrical changes to the type and concentration of adsorbed species.

UHV System

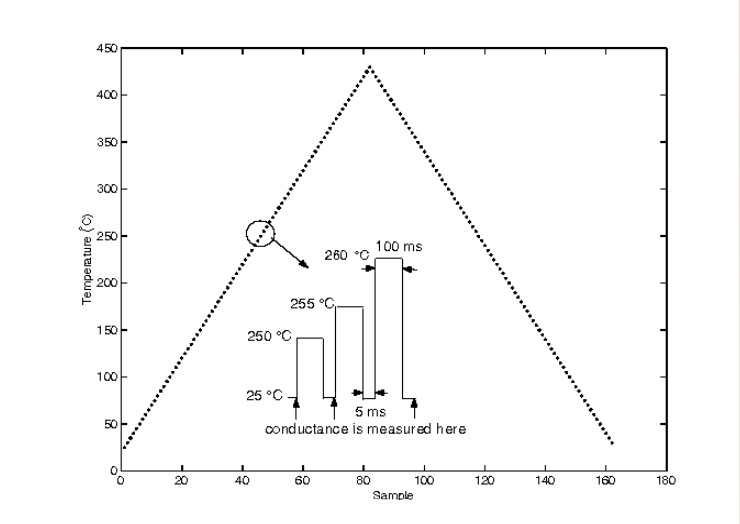




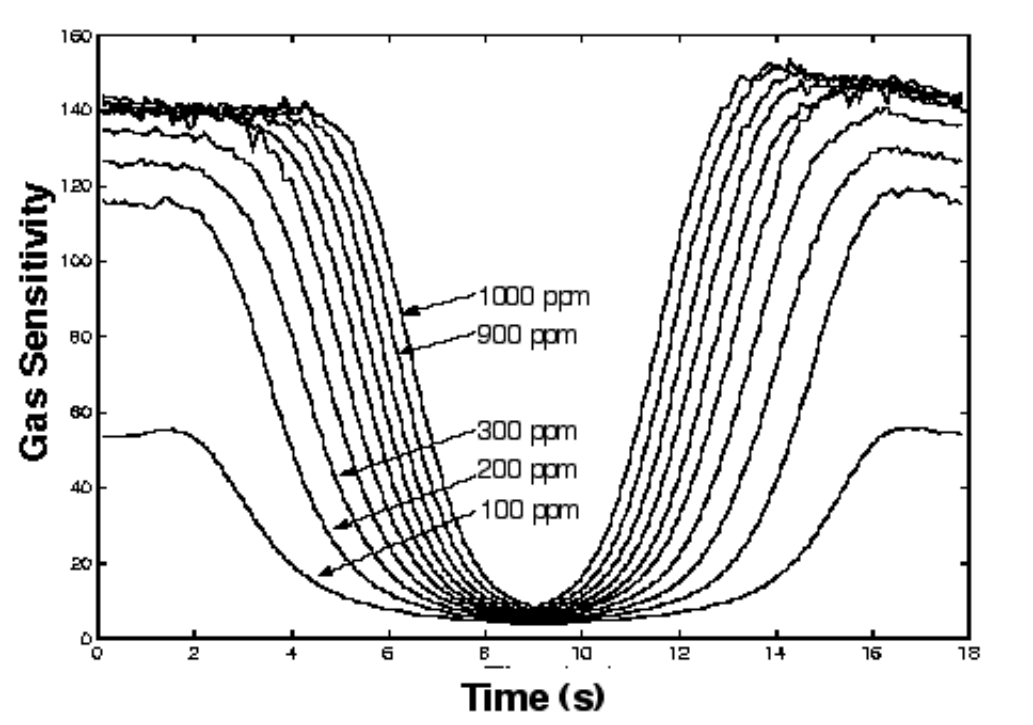
340 element array



Concentration Analysis



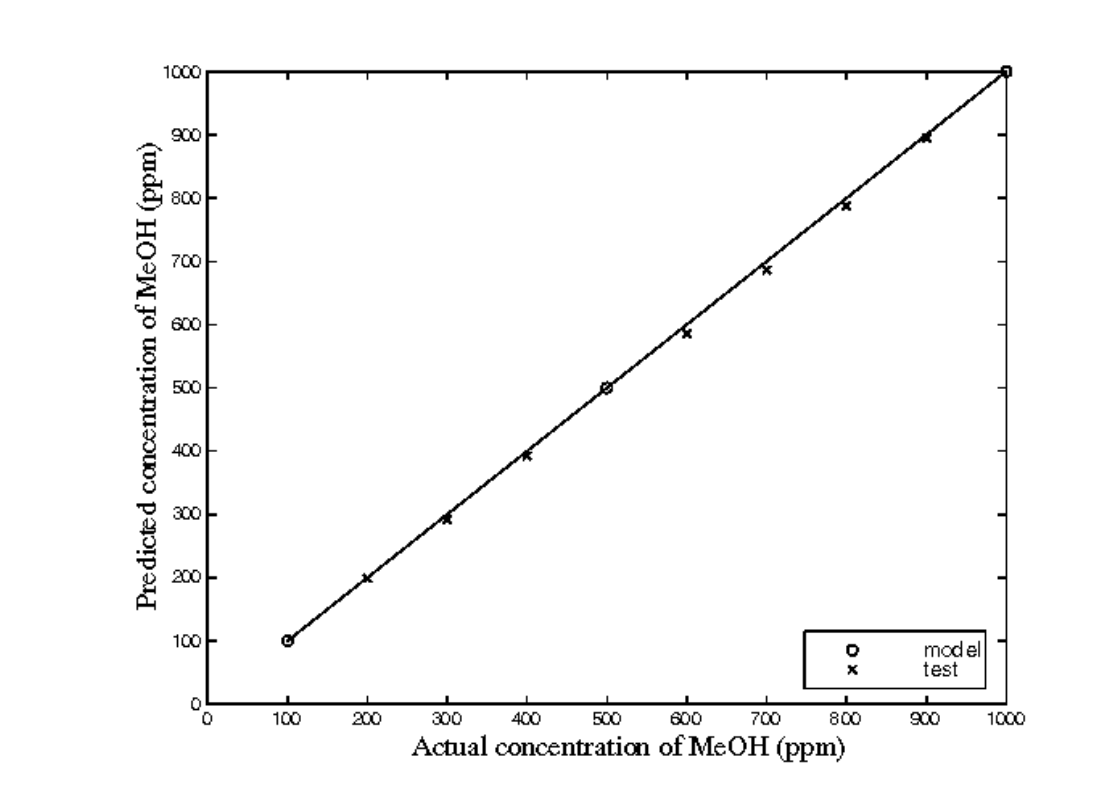
In this test, Temperature Program Sensing was used with a repeating triangle sequence of temperature pulses.Conductance was measured at 25°C between pulses.



Results were collected at several concentrations of methanol in air.

NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Concentration Analysis

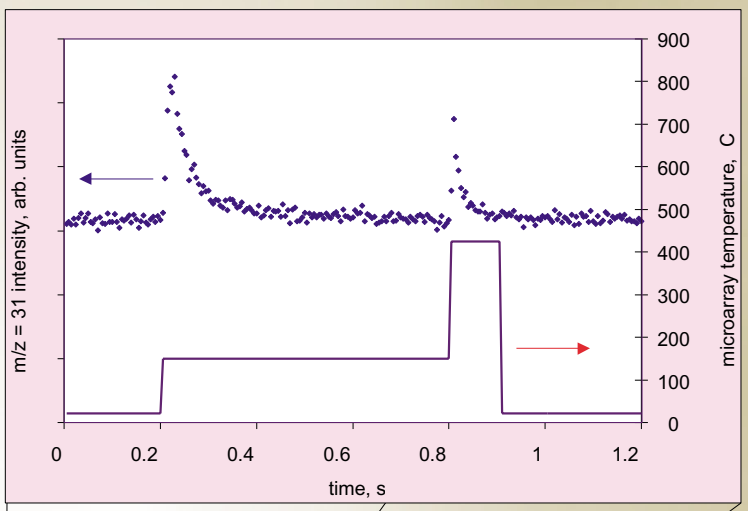


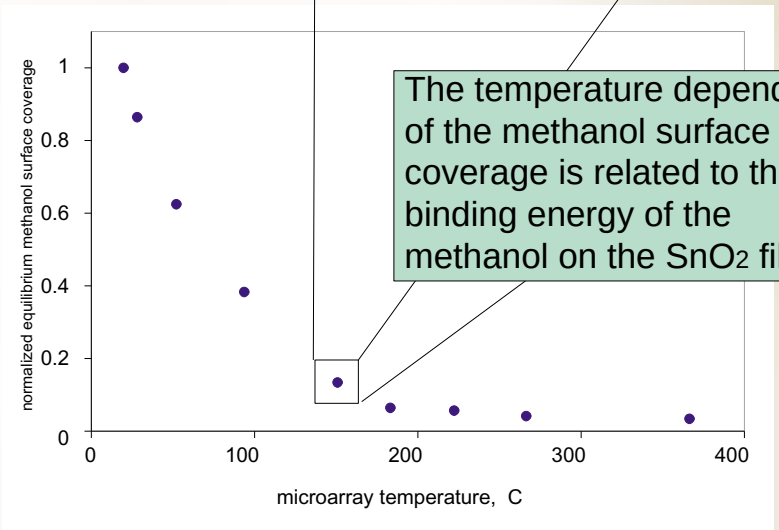
A Partial Least Squares calibration method was developed for the responses at 100, 500, and 1000 ppm Linearization is applied by taking the log of the input and output data before the PLS regression is performed. The model is used to predict the concentrations of the 7 shapes above not used in the calibration.

Example capability: pulsed desorption technique for measuring temperature dependence of equilibrium surface coverage for methanol on a SnO_2 sensor array.

Monitor desorption of methanol with mass spectrometer in a constant methanol pressure of $1x10^{-7}$ Torr.

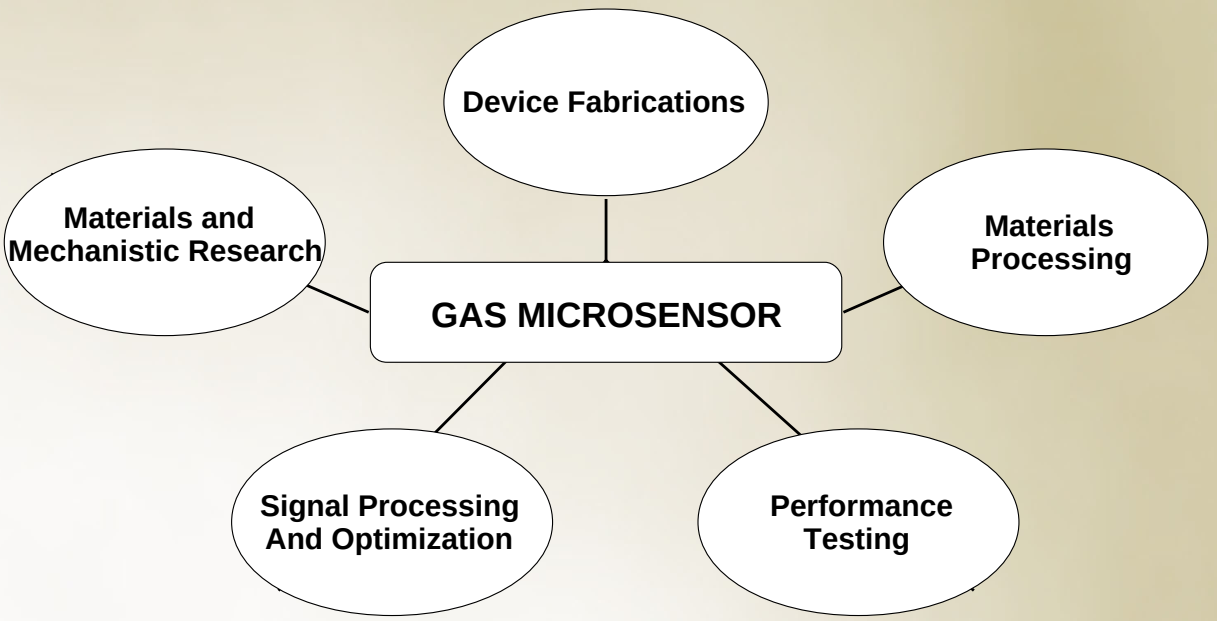
The area of the second peak relative to the total area is the normalized surface coverage at the initial pulse





The temperature dependence of the methanol surface coverage is related to the binding energy of the methanol on the SnO_2 film.

Summary



- Microhotplate conductometric gas sensors are a promising technology for low-cost, low-power measurements.

- Arrays of 36 or more elements with different sensing films provide a potentially rich source of data for enhanced chemical selectivity.

- Rapid thermal constants open up the possibility of Temperature Programmed Sensing, a new dimension of information for conductometric sensing

- Data-rich arrays will require development of analysis methods to reduce complex signals to concentration measurements.

Project #65421
Supported by DOE Grant #07-98 ER 62709