Micro-hotplate Gas Sensor

R. E. Cavicchi*, J. S. Suehle, P. Chaparala◊, K. G. Kreider,
M. Gaitan, and S. Semancik
National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

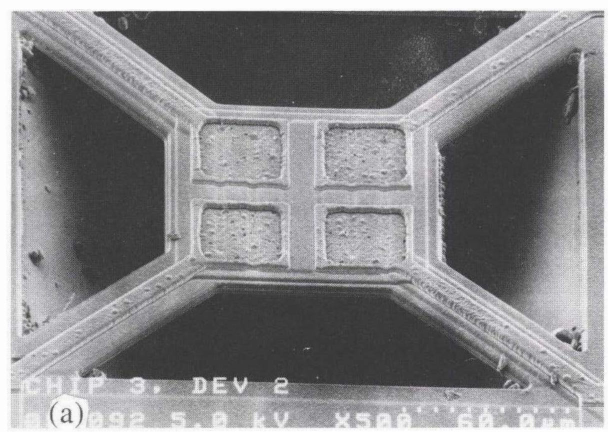
Micro-hotplates have been fabricated on a silicon wafer using CMOS technology. These micro-machined devices offer a wide range of temperature control, from 20 °C -550 °C or 1000 °C, depending on design materials, and a fast thermal response of about 1 ms. They may be fabricated in arrays with electrical circuitry on the same chip. To make sensors from CMOS chips or wafers requires a new technology for processing, which include anisotropic etching of Si, lithography, and film deposition. All process steps must be compatible with existing CMOS components and structures and must take into account the geometry and stability of micromachined structures. For gas sensors that use semiconducting oxides, the challenge is to make ohmic contacts that use a very small contact area and are rugged against thermal cycling. The micro-hotplate array can serve as a mini-laboratory for efficient process optimization using parallel experiments. The elements of a micro-hotplate array can be programmed with different temperature schedules through the process steps, and subsequently analyzed in one test/characterization cycle. An example of a film growth study is shown in which array elements are set to different temperatures during sputter deposition of tin oxide. The rapid thermal time constant of these structures offers opportunities for new modes of sensor operation which can reduce the power consumption and improve the selectivity of oxide sensors. Techniques that uses temperature pulses are demonstrated for low power sensing of H_2 in air and for distinguishing ethanol from methanol vapor.

Introduction

The development of gas sensors based on micromachined structures is a rapidly growing area of research. Potential advantages include low power consumption, lower cost and higher reliability via batch fabrication, improved selectivity through the use of arrays, and the development of "smart sensors" that incorporate on-chip electronics for data acquisition and signal processing. A key element for many applications is temperature-control. We have developed micromachined "micro-hotplate" arrays in which each element in the array performs the function of a conventional "hotplate" on a microscopic scale. The micro-hotplates may be used for heating during fabrication of the sensing films, for producing fixed temperature matrices and also fast temperature modulation during sensor operation, and for reconditioning of the active sensing films.

Figure 1 shows one design configuration of a micro-hotplate[1]. This device consists of a micromachined bridge which supports the following successive layers separated by insulation: 1) a polysilicon heater; 2) an aluminum hotplate with electrical connections for 4-point temperature measurement; and 3) open aluminum contact pads to make electrical contact to a deposited overlayer. This device has a temperature range from 20 to 550°C (limited by thermal migration of the aluminum), thermal time constant of 1 ms, and a temperature/power coefficient of 8 °C/mW. Other designs which use only polysilicon and no aluminum have temperature ranges to 1000 °C.

The basic micro-hotplates are fabricated using a combination of CMOS device fabrication and post-CMOS processing steps. The use of CMOS chips offers the advantages of high reliability, low-cost,



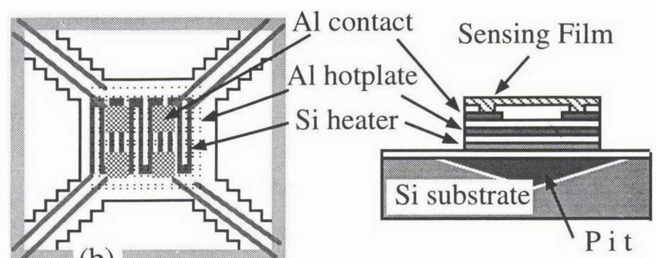


Figure 1. (a) SEM micrograph of suspended micro-hotplate structure with SnO_2 film coating. (b) Schematic illustrating the various layers comprising the structure.

and simple integration of on-chip electronics for multiplexing and signal processing. Chips received from the foundry are etched to realize the microbridge structures. Additional post-CMOS processing is required to optimize the electrical contacts to the sensing film, and to deposit selective sensor coatings on the individual micro-hotplates.

Development of these processing steps is an area where there remains much applied research to be done. Example technological issues are the ability of post-CMOS layers to withstand the harsh anisotropic etch, lift-off of photolithographically defined layers on micro-machined structures, surface cleaning procedures, formation of ohmic contacts to sensing films, the choice of top-side or bottom side contacts, calibration of temperature and the achievement of a uniform temperature distribution over the hotplate, and the thermal and mechanical stability of thin films and interfaces over small (10-100μm) length scales at the elevated temperatures and rapid thermal cycles that will be used during micro-hotplate device operation.

Gas sensors based on the conductance change of semiconducting oxides at elevated temperatures are traditionally operated at a fixed temperature in the range 300 °C to 700 °C. In this operating mode, many gases can give rise to a conductance change in the sensor, and the ability to determine the composition of the sensed gas is limited. Partial selectivity to a specific gas is obtained through the use of catalytic additives to the sensing film. Because of the rapid thermal time constants for micro-hotplate based sensors, other modes of sensing are possible. These modes will use the dynamic response at specific temperatures to characterize surface chemical reactions that are producing a sensing response. An example of one operating mode is a repetitive temperature pulse train in which the conductance is measured between pulses. The characteristic response to this pulse train can be analyzed using pattern recognition algorithms which can be incorporated into the CMOS electronics on the sensor chip. In principle, the device can use additional alternative pulse trains to furthur refine the compositional analysis.

Microscopic Thermal Processing of Materials

Solid state gas sensors commonly use catalyst-doped tin oxide as the active sensing medium. Sensing properties depend on the film microstructure, which in turn depends on the growth and subsequent thermal processing of the film. We use the micro-hotplate array to simultaneously set temperature process schedules for the individual micro-hotplates during tin oxide deposition. Experiments were done using both 36 and 4-element arrays. Using in-situ electrical measurements, and ex-situ scanning electron microscopy images (Figure 2), we were able to quantify the increase in electrical conductance and film microcrystal size with growth temperature. This technique has also been used in conjunction with chemical vapor deposition as a self-lithography. In

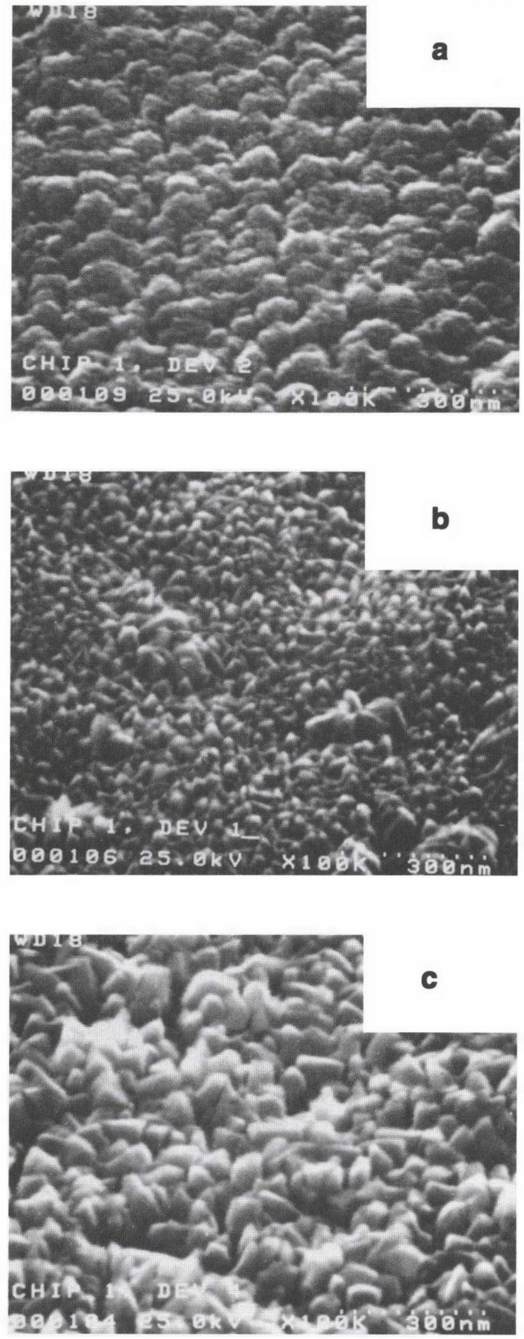


Figure 2. SEM micrographs of SnO_2 films grown on three micro-hotplates on the same chip. Each micro-hotplate was set to a different temperature during the growth as follows: (a) 25 °C, (b) 300 °C, (c) 500 °C.

this case, a film grows only on the hotplates that are heated to the deposition temperature required by a given chemical vapor. Such temperature-processing of sensing films can also be used to periodically recondition an operating sensor, for example, to eliminate the buildup of contamination during operation.

Temperature Pulsing for Sensor Operation

The very fast thermal response of micro-hotplates offers new opportunities for sensor operation. For reasons of lower cost and portability, sensors with reduced power requirements are desirable. Micro-hotplates used in our experiments require 47 mW to maintain 400°C, about ten times less power than a conventional Figaro sensor. Operation of sensors at much lower power levels is possible using temperature pulsing. As a demonstration, we have measured the response of SnO_2 to 0.1 % H_2 in air using 400°C, 10 ms temperature pulses every 1 s as shown in Figure 3. The power consumption of the device is only 470 µW. A sensor operating at this power level would run for nearly a year on an alkaline 9 V battery.

Transient phenomena can also be used for sensing. A tin oxide-coated micro-hotplate was subjected to a constant dose of water vapor (important for humidity effects on sensors). In Figure 4 is shown the electrical response to 500°C 10 ms desorption pulses and subsequent re-adsorption of H_2O. The data is shown for a dose at 1.3 Pa. The response amplitudes and transient characteristics have been measured at different pulse amplitudes, base temperature, and pulse durations to obtain adsorption/desorption kinetic parameters--a signature of the H_2O response. Response is easily detectable at 0.01Pa. Measurement of low partial pressures of water vapor in vacuum deposition environments is a critical issue that micro-hotplate technology may be able to address. Response at very low pressures may be obtainable using polymer films that are highly sensitive to water.

These sensors can also be operated in temperature-pulsed modes in which the amplitude of the temperature pulse is varied. Figure 5 shows an operating mode in which a series of increasing temperature pulses is applied, with a constant temperature increment. The conductance is measured between the pulses, while the micro-hotplate is at room temperature. The pulse cycle is repeated continuously. The response to admission of methanol and ethanol to air is shown in Figure 6. Both gases cause an increase in the tin oxide conductance. Conventional oxide sensors, operating at a fixed temperature would have difficulty in distinguishing the two gases, as both would give rise to a conductance increase. The patterns of response to the pulse sequence as shown in Figure 6 (b), a portion of the data in Figure 6 (a), reveals clear differences between the kinetic behavior of the two gases. A sensor operating with pattern recognition circuitry would be able to select which gas was being sensed. Pulse sequences in which the pulse width or duty cycle are also varied would provide additional selectivity enhancements.

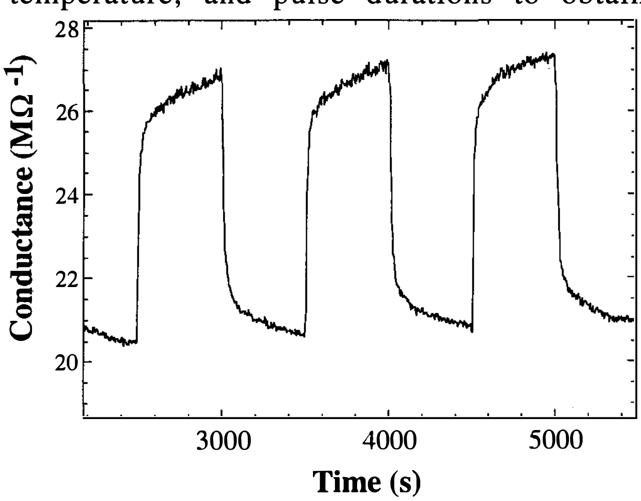


Figure 3. Response to exposure cycles of air injected with 0.1 % hydrogen every 500 s. Sample is operated using 10 ms pulses to 400 °C every 1.0 s. Conductance is measured at room temperature, between the pulses.

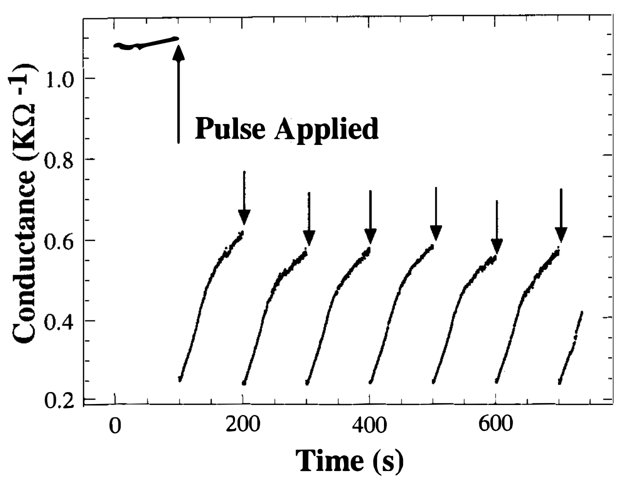


Figure 4. Pulsed desorption - adsorption sequence for H_2O on SnO_2 on a micro-hotplate. While dosing at 1.3Pa (10mT), and with a base temperature of 20°C, the sample was pulsed to 500°C for 10 ms, every 100 s.

Conclusions

Micro-hotplates have been fabricated from CMOS integrated circuit chips. The devices have a wide temperature range and fast thermal response. Processing CMOS-fabricated chips into smart sensors presents new challenges for process technology. The ability to thermally process materials on an array of devices allows for efficient optimization of some of these processes. The rapid thermal response of micro-hotplate based sensors offers new avenues for achieving selectivity to specific gases. Temperature-pulsed operating modes have been used to demonstrate the ability to distinguish two gases.

Acknowledgement

We would like to acknowledge Samuel Jones for the SEM images in this report.

*R. E. Cavicchi, Bldg 221 A303, NIST, Gaithersburg MD 20899
E-MAIL: dcav@enh.nist.gov

◊NIST Graduate Research Fellow at the Center for Reliability Engineering, Univ. MD.

1.) J. S. Suehle, R. E. Cavicchi, M. Gaitan, and S. Semancik, IEEE Electron Device Lett., Vol. 14, no. 3, pp. 118-120, 1993.

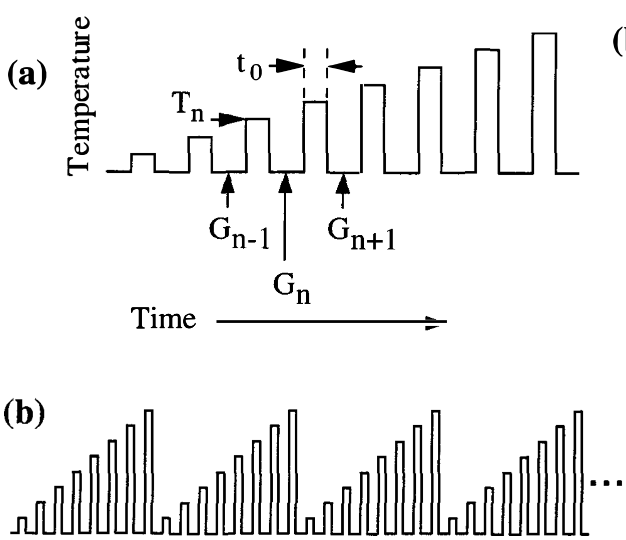


Figure 5. (a) Temperature pulse train applied to the micro-hotplate during sensor operation. Pulse width is t_0. Conductance G is measured between pulses, while the sample is at 30 °C. This pulse train is repeated as shown in (b).

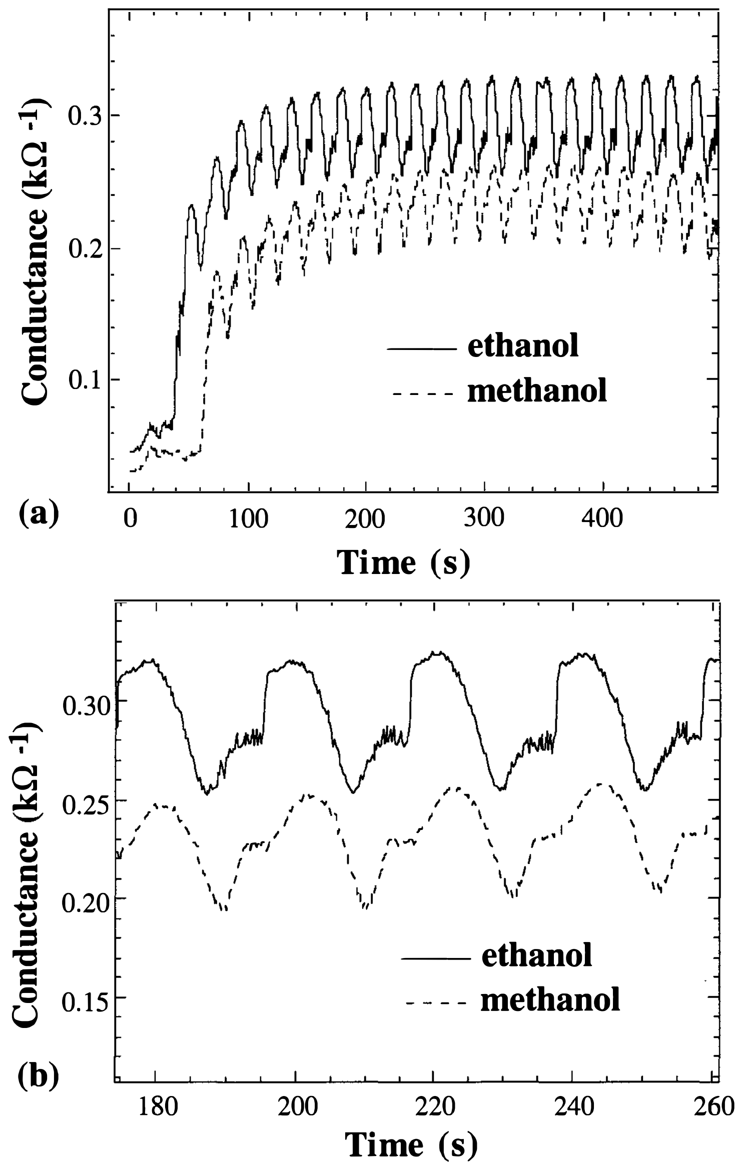


Figure 6. Response of a gas sensor using the repetative sequence of temperature pulses as described in Figure 5. The sample is a SnO_2 film on a micro-hotplate. The pulse temperature ranged from 30 to 450 °C in 5 °C steps. Pulse width was 100 ms. Conductance is measured between the pulses. (a) Response to the admission of ethanol or methanol vapor. (b) Detail from the data in (a), showing the response to four cycles of the temperature pulse sequence. The sample pulse is at 30 °C at 174 s and 450 °C at 194 s.