Optimized temperature-pulse sequences for the enhancement of chemically specific response patterns from micro-hotplate gas sensors

R. E . Cavicchi*, J. S. Suehle*, K. G. Kreider*, M. Gaitan*, and P. Chaparala†

*Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA
†University of Maryland, College Park, MD 20742, USA

Abstract

Micro-fabricated solid state gas sensors have been of continuing interest because of the potential for arrays of devices with low power consumption. Devices based on a micro-machined "hotplate" offer the additional advantage of a wide operating temperature range with a rapid thermal time constant of order 1 ms. By operating the device in a temperature-programmed mode, reaction kinetics on the sensing film surface are altered, producing a time-varying response signature that is characteristic of the gas being sensed. Approaches to optimize such temperature programs to maximize the differences in response signatures for gases of interest or to enhance the sensitivity of the device are discussed.

Introduction

Miniaturization using thin film technology continues to be an important area of research on solid state gas sensors. Microsensors; promise lower cost, due to batch fabrication, and lower power consumption. When produced as arrays, the generally poor chemical specificity of semiconductor gas sensors can be used to create a sensing chip with greatly improved analyzing performance by using pattern recognition algorithms in conjunction with the overlapping response signals of the array elements. A typical microsensor consist of an integrated heater, thermometer, and sensing film on a thermally isolated stage. A large part of the fabrication of the devices can be accomplished by conventional foundries of complementary metal oxide semiconductor (CMOS) chips, which reduces the cost and improves the reliability[1].

An additional benefit of micromachined devices, and the basis of the work reported here, is the extremely short thermal time constant. This is exploited in the use of a time-varying temperature program applied to the microsensor's heater. Cyclic alteration between two temperatures has been considered for the enhancement of sensitivity and selectivity, and minimization of the effects of humidity[2]-[6]. Hiranaka et al. describe the use of a single temperature pulse to create a transient response with a gas-dependent characteristic time constant[7]. While the temperature modulation for the above experiments is done on the time scale of seconds to minutes, the micro-hotplate devices can typically be heated to 550 °C or cooled from that temperature to room temperature in about a millisecond. This

makes possible rapid control of the reaction kinetics on the gas sensor surface and the production of chemically specific response patterns[8,9].

Experiment

The device used in these experiments is shown in Figure 1 and consists of a polysilicon heater, an aluminum hotplate that reduces thermal gradients and serves as a four-point resistance thermometer, and a set of four aluminum contacts. These conductive layers are separated by insulating layers of SiO_2. The microhotplate is fabricated by a commercial CMOS process followed by a simple etch to produce the micro-bridge structure[l]. An additional layer of Ta, Ti/Au, Ti/Pt, or Ti/Ir was deposited on the Al contact pads to improve electrical contact to the sensing film. The sensing film consisted of SnO_2 or Pd-dosed SnO_2. The SnO_2 film was deposited by reactive sputter deposition, with the micro-hotplate held at 450 °C by the micro-heater. The as deposited SnO_2 was electrically insulating. By heating the micro-hotplates in vacuum, the SnO_2 could be made conductive. Pd was deposited by evaporation, with the SnO_2 films held at room temperature. The temperature range of the device was 20 °C to 550 °C, limited by failure of Al at higher temperature. The thermal efficiency was 7.5 °C/mW. The thermal time constant for heating or cooling was 1 ms as measured by observing the transient in the heater resistance or Al plate resistance for step changes in voltage applied to the heater.

With the ability to change temperature rapidly, the sensor can be operated in a temperature-modulated mode. The simplest operating mode one might consider is a simple temperature ramp, essentially a temperature-programmed conductance. A drawback of this approach is that changes in mobility and/or carrier density in the sensing film caused by thermally activated processes can dominate surface chemical effects. Instead, we apply a sequence of temperature pulses of fixed duration t_p and increasing height T while monitoring the conductance G between pulses, while the sample is at room temperature. This is shown schematically in Figure 2. Changes in G following a pulse reflect only changes in the surface chemistry that occurred during that pulse.

Results

Figure 3 shows the response of the sensing film to this temperature pulse train when exposed to the room temperature saturated vapor pressures of acetone, formaldehyde, ethanol and methanol. The sensing film consisted of 1.2 nm Pd dispersed on a 100 nm SnO_2 film. Conductance was measured 5 ms after the trailing edge of the temperature pulse to ensure the sensing film was at room temperature. Greater detail in the patterns can be introduced by altering the temperature program, enhancing differentiation between patterns. For example, Figure 4 shows the sensor response to these same gases during a pulse sequence consisting of ten 100 ms pulses at each of eight temperatures ranging from 20 °C to 370 °C.

The timing of data acquisition is an important parameter in obtaining response patterns. A temperature pulse can cause desorption to occur, making sites available for adsorption during the period between pulses when the sensing film is at a lower temperature. Figure 5 shows a comparison in which the conductance is recorded both 5 ms and 200 ms after the application of each temperature pulse. Pulse temperatures above 220 °C begin to result in increased conductance values for the 200 ms delay compared to the 5 ms delay. The differences in the timed response can also be used as information to distinguish the response to two gases.

To optimize the selectivity of a temperature-modulated sensor it is desirable to obtain a relationship between a given pulse sequence and its conductance response in the presence of a specific gas. One approach is to do experiments to try to determine the surface chemistry that generates the response pattern. Measuring the response of pure gases dosed in a vacuum system is a first step in this process. Figure 6 shows the response of a Pd -dosed tin oxide film to a ramped sequence of 300 ms temperature pulses for three simple cases: (a) heating a vacuum-annealed film in oxygen, (b) heating in vacuum following the oxidation treatment of (a), and (c) heating a vacuum-annealed film in hydrogen. As expected, heating in oxygen reduces the conductance, both by reducing the number of oxygen vacancies created by previously heating in vacuum and by the appearance of chemisorbed oxygen. Heating in vacuum removes oxygen and increases the conductance. Heating in hydrogen produces a peak in the conductance near 400 °C. Heating the oxidized surface in vacuum removes oxygen and causes a conductance increase. By varying the pulse width, shifts in temperature of the features are observed which can be used to determine reaction kinetic parameters. Testing at atmospheric pressure in air introduces the complexity of a mixture of gases which, through their interaction, can effect the conductance response. An interesting example is shown in Figure 7 in which CO at 0.33 % concentration in air produces a step drop in the temperature-dependent conductance which is hysteretic. By determining the temperature changes where significant chemical events happen, a pulse sequence can be designed to exploit these changes.

An alternative approach is to use the ability to collect large amounts of data in a relatively short time to survey the operation of device over a wide range of temperature pulsing sequences. The conductance after a temperature pulse often depends both on the surface chemistry that has occurred during that pulse and the initial condition of the surface before the pulse was applied. This initial condition depends on the previous pulse history. A survey of pulse streams can be generated by applying a long sequence of randomly chosen temperature pulses as in Figure 8 and searching for maximal response differences between two gases. An improvement is to use such large data sets to generate phenomenological computer models which can be used to optimize temperature programs.

Conclusions

Temperature programming of micromachined sensors is a promising approach to selectivity. Future work will explore mechanisms for response characteristics, development of techniques for analyzing results from multiple sensors, and consideration of long-term stability and sample conditioning for this operating mode.

Acknowledgments

We would like to thank S. Semancik for encouragement and useful discussions and Dr. T. MacAvoy and T. Kunt for discussions relating to computer modeling of device response.

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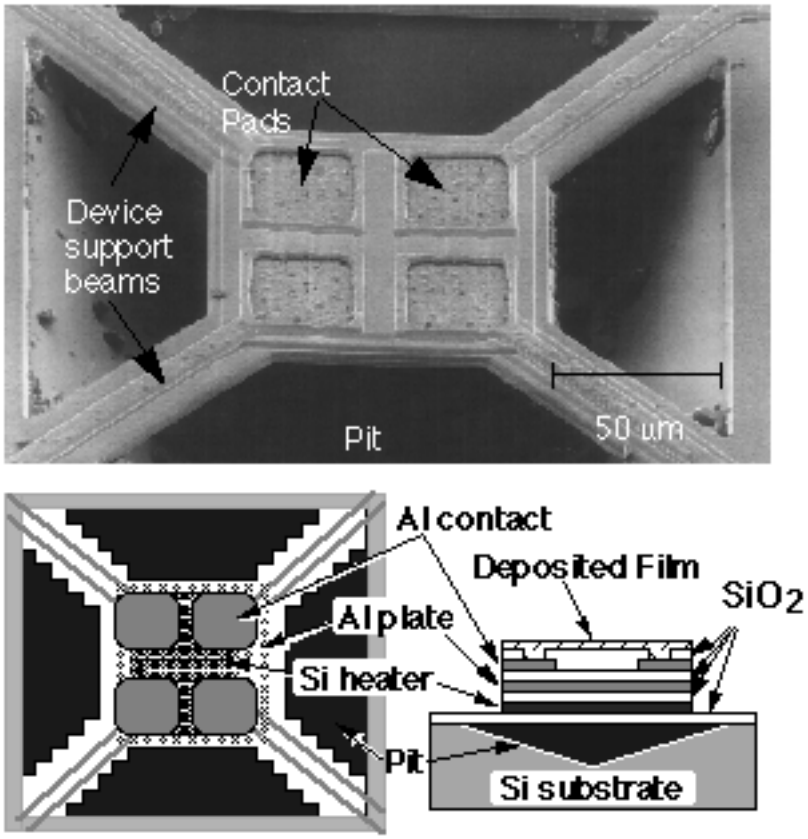

Figure I . Top: Scanning electron micrograph of a microhotplate. Bottom: Schematic top view (left) and side view (right) of the device.

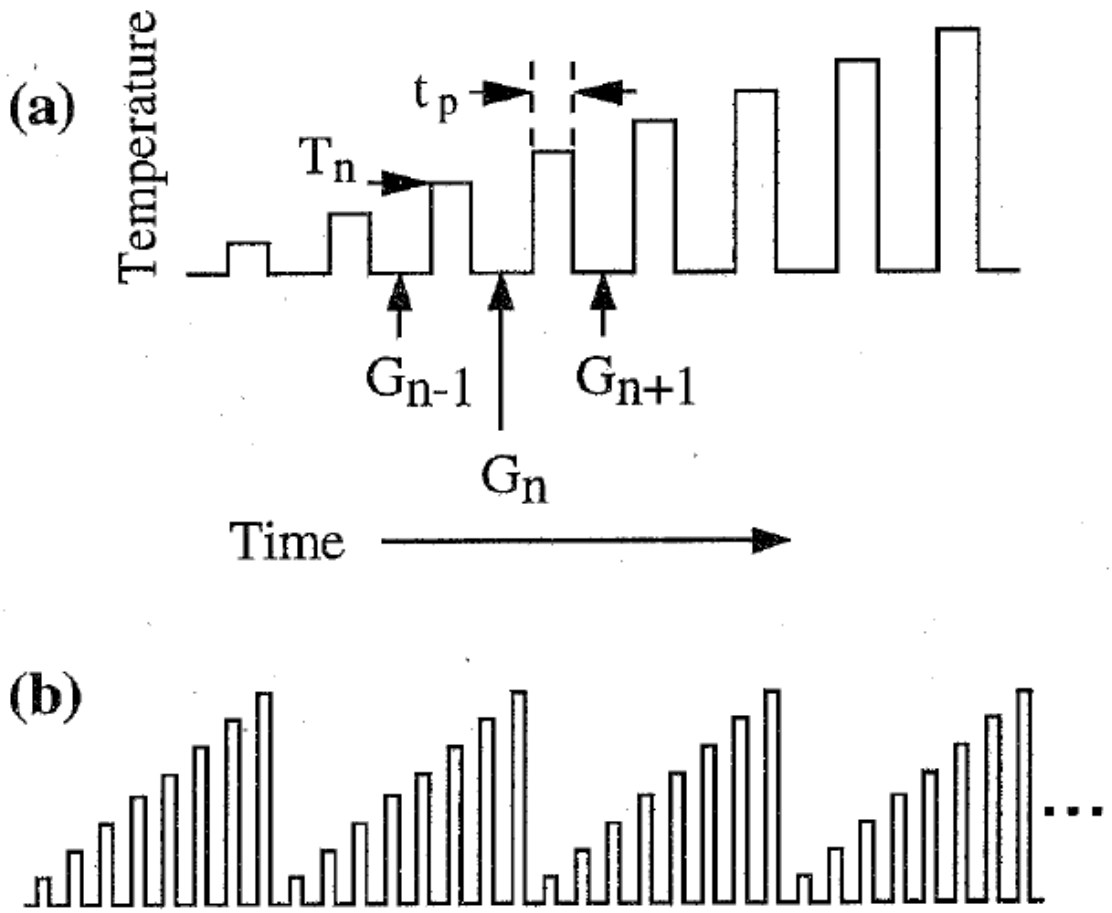

Figure 2. (a) Temperature pulse train applied to the micro-hotplate during sensor operation. Pulse width is t,,. Conductance G is measured between pulses, while the sample is at 20 °C. (6) Repetition of (a).

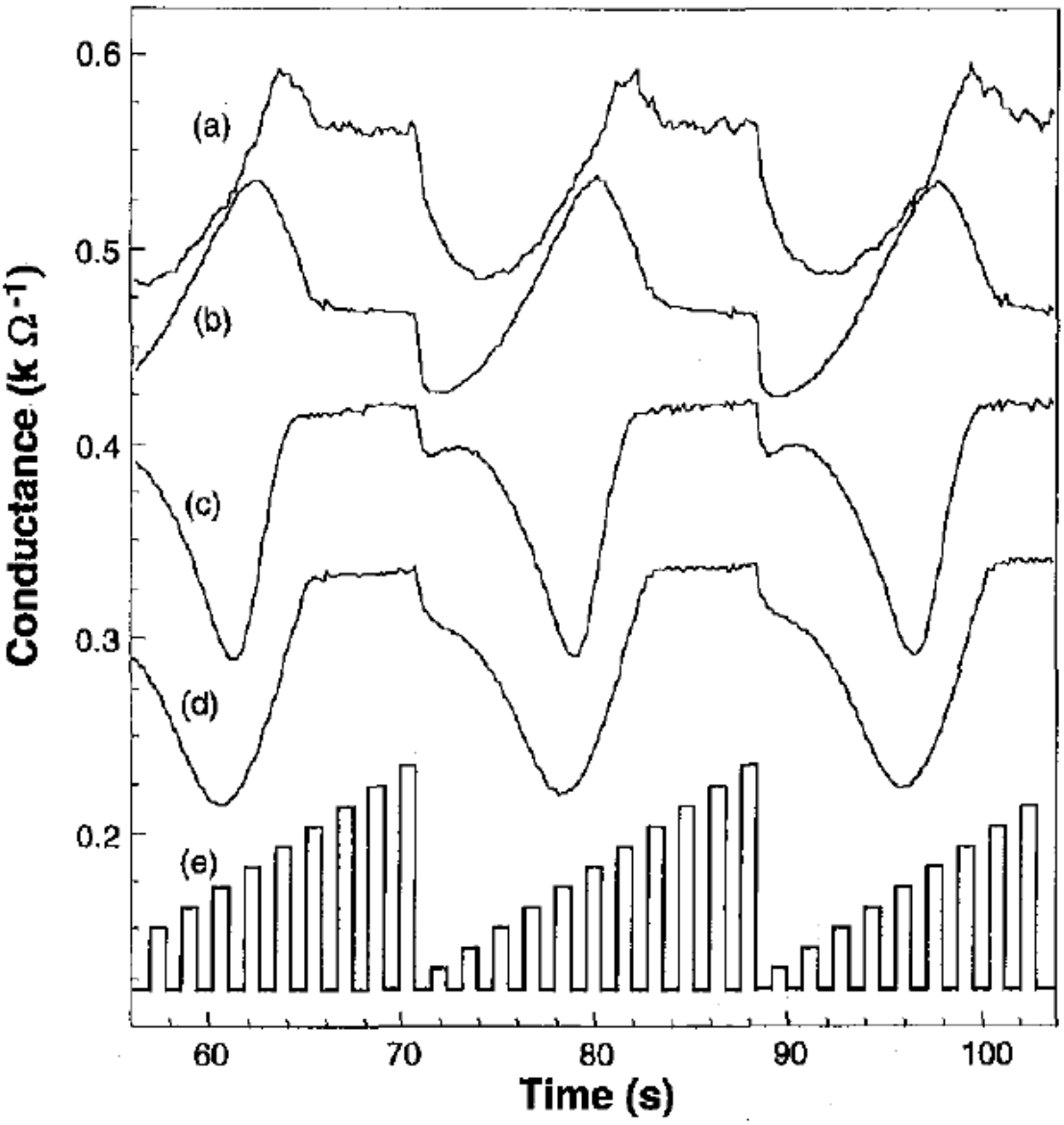

Figure 3. Conductance response of a Pd-dosed SnO_2 film to the 20°C saturated vapors of (a) acetone, (b) formaldehyde (c) ethanol, and (d) methanol during the repetitive temperature sequence schematically illustrated in (e). The temperature pulse sequence actually was much denser in time, consisting of 100 ms pulses ranging from 20°C to 450'C with a 5°C temperature increment. The conductance curves were scaled to fit on one graph as follows: (a) shown in 20G+0.2 $k\Omega^{-1}$, (b) 10G+0.27 $k\Omega^{-1}$, (c)G, and (d) 0.7G-0.05 $k\Omega^{-1}$.

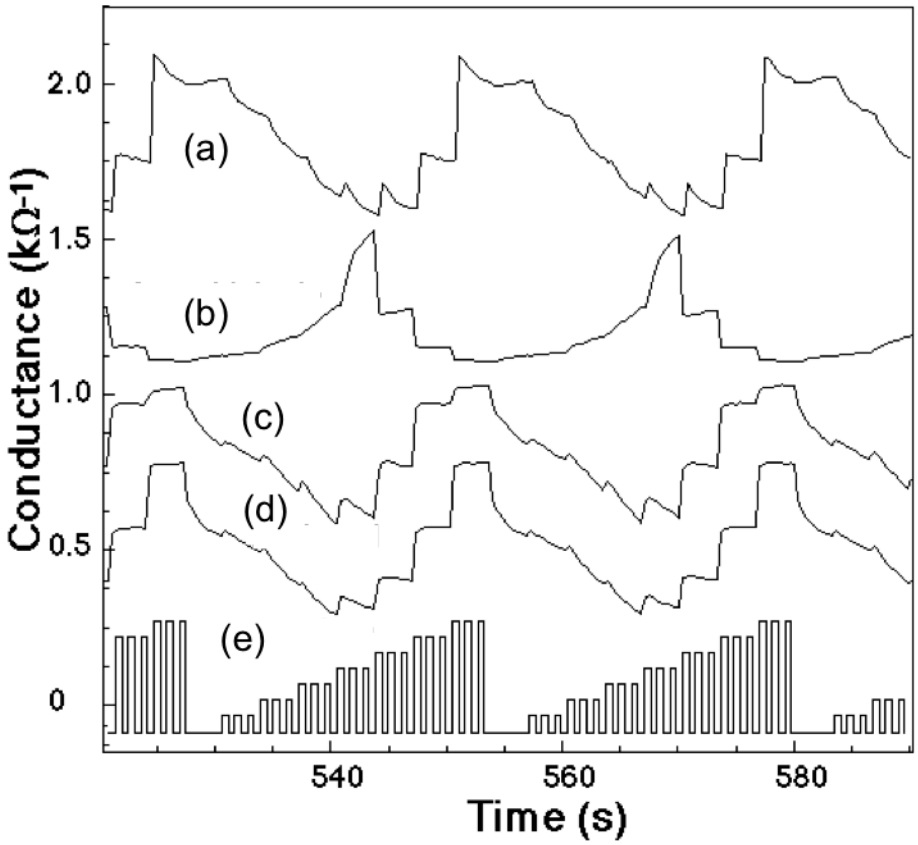

Figure 4. Conductance response of a Pd-dosed SnO_2 film to the 20°C saturated vapors of (a) acetone, (h) formaldehyde, (c) ethanol, and (d) methanol during the repetitive temperature sequence schematically illustrated in (e). Again, the temperature pulse sequence actually was much denser in time, consisting of ten 100 ms pulses at each of eight temperatures ranging from 20°C to 37OoC with a 50°C temperature increment. The conductance curves were scaled to fit on one graph as follows: (a) shown is 70G+ 0.6 $k\Omega^{-1}$, (b) 17G +1 $k\Omega^{-1}$, (c) G , and (d) G.

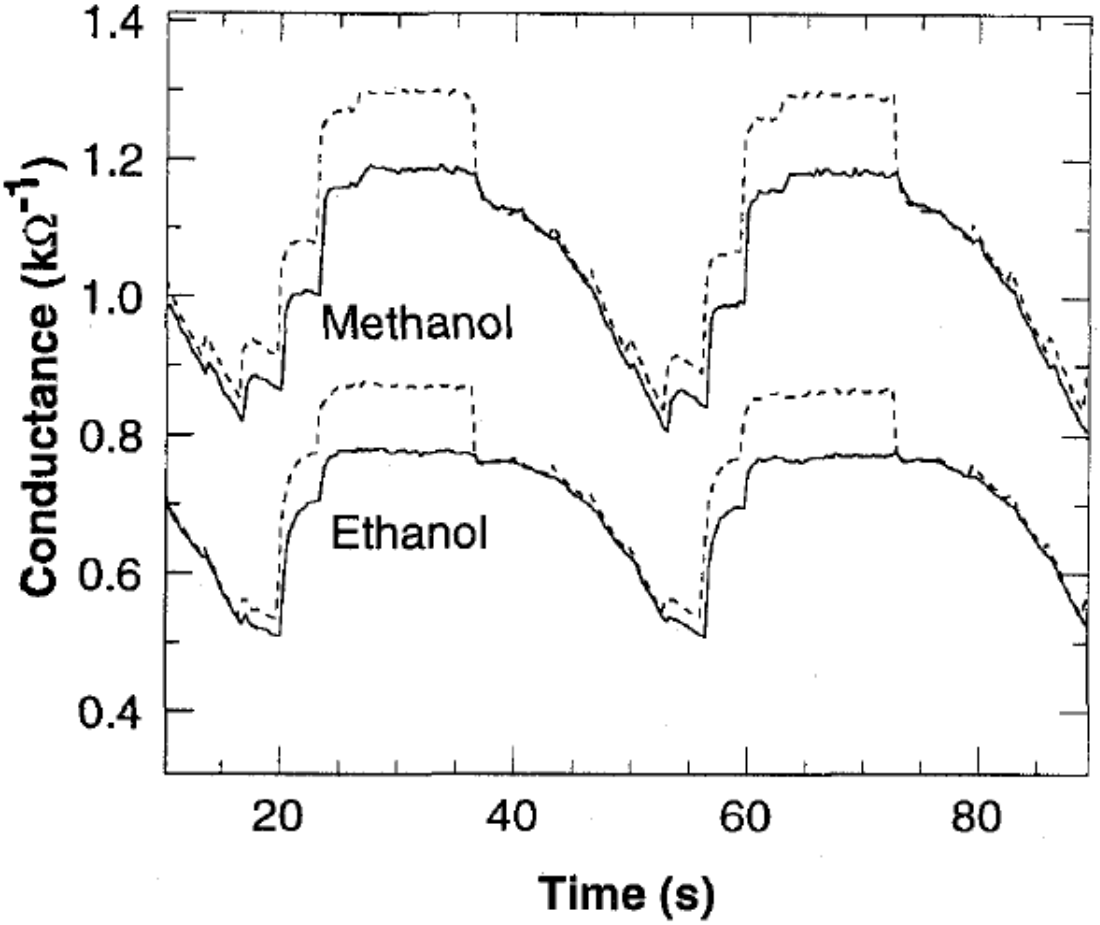

Figure 5. Conductance response to methanol and ethanol vapor (as labeled) during a temperature pulse sequence consisting of ten 100 ms pulses at each of I1 temperatures ranging from 20 °C to 520 °C. Solid and dashed curves are data collected 5 ms and 200 ms, respectively, after the pulse.

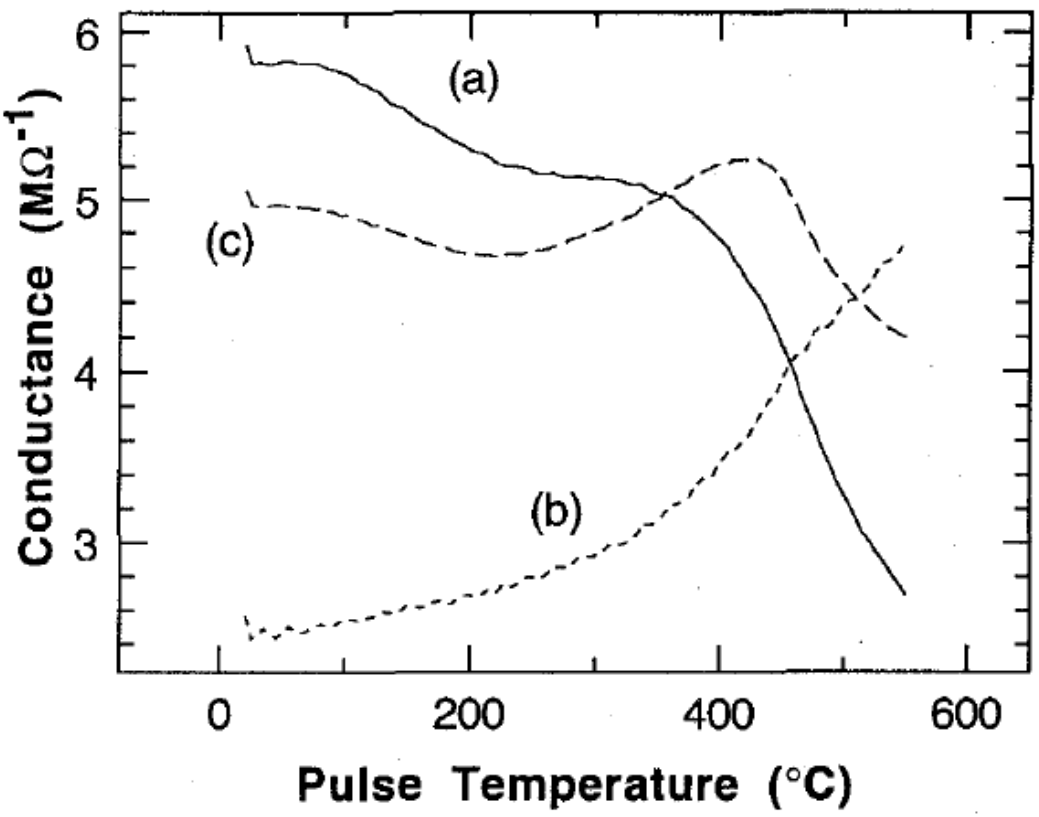

Figure 6. Response to a temperature pulse sequence consisting of 300 ms pulses ranging from 20 °C to 550 °C with a 5 °C temperature increment in the following test conditions: (a) 0.2 Pa 0, after heating in vacuum, (b) vacuum after treatment for curve (a), and (c) 0.5 Pa H, after heating in vacuum.

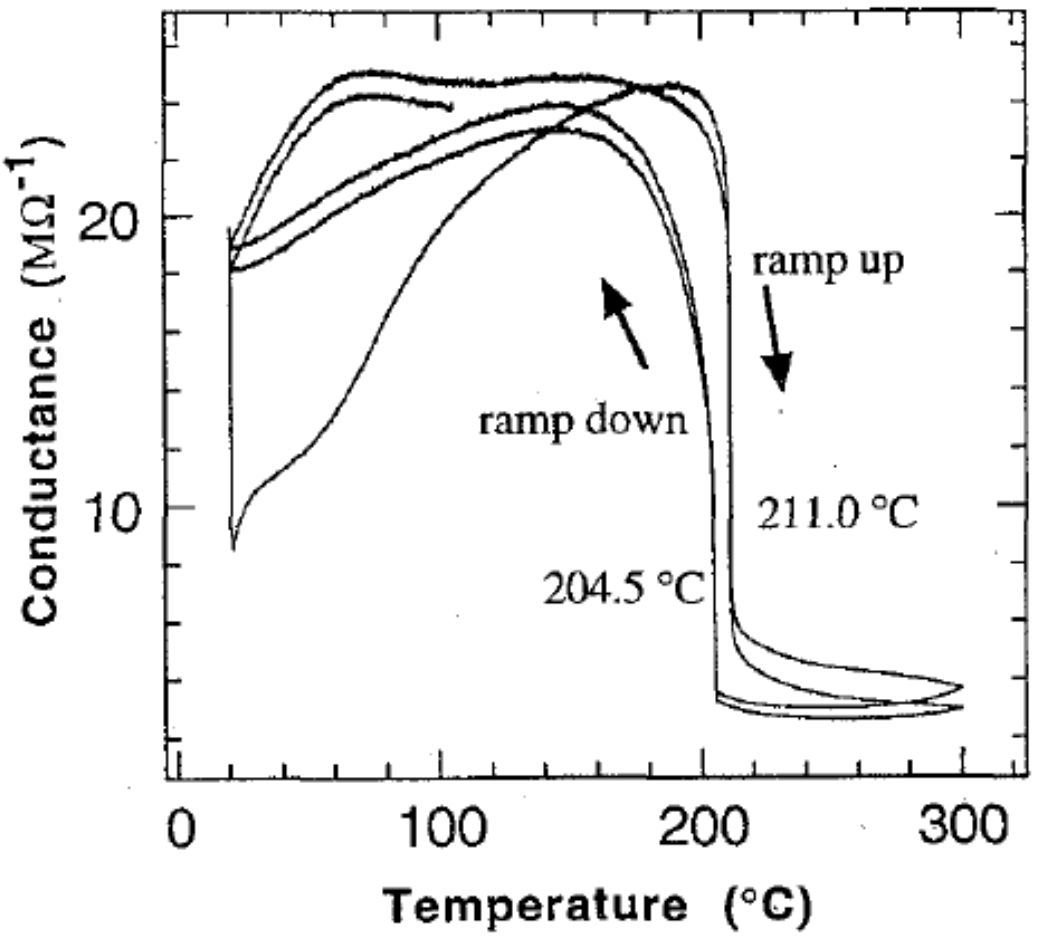

Figure. 7. Conductance as a function of temperature of a Pt-dosed SnO_2 film on a micro-hotplate in a concentration of 0.3% CO in air. The temperature was ramped between room temperature and 300°C at a rate of one cycle every 100 min.

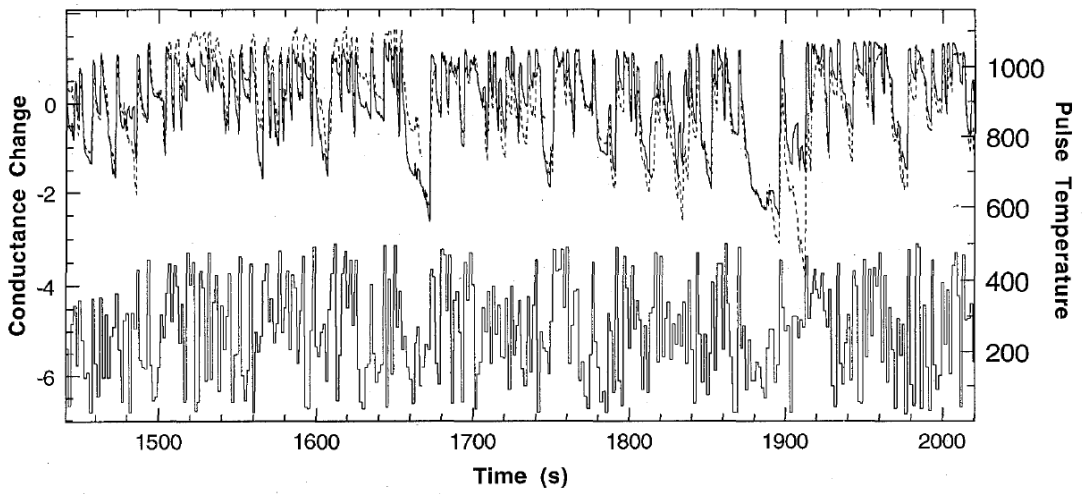

Figure 8. Normalized conductance change about the mean conductance during exposure to methanol (solid) and isopropanol (dashed) vapors during a long sequence of temperature pulses (lower trace). Larger response differences are seen near t = 1475 and 1925 s.