Fast Temperature Programmed Sensing Micro-Hotplate Gas Sensors

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Abstract-

We describe an operating mode of a gas sensor that greatly enhances the capability of the device to determine the composition of a sensed gas. The device consists of a micromachined hotplate with integrated heater, heat distribution plate, electrical contact pads, and sensing film. The temperature programmed sensing (TPS) technique uses millisecond timescale temperature changes to modify the rates for adsorption, desorption, and reaction of gases on the sensing surface during sensor operation. A repetitive train of temperature pulses produces a patterned conductance response that depends on the gas composition, as well as the temperature pulse width, amplitude, and specific sequence of pulses. Results are shown for the vapors of water, ethanol, methanol, formaldehyde, and acetone.

Semiconductor gas sensors are devices that can provide sensitive response to a gas of interest at moderate cost. The operating principle is a change in an electrical property of a sensing film, usually conductance, caused by a coverage of adsorbed or chemisorbed gas species. Semiconducting oxides such as SnO_2 are commonly used as a base sensing material. The devices typically operate at elevated temperatures to activate the reactions that produce a sensor response and to reduce the effects of humidity. One drawback of these devices is that a response may be produced by more than one gas. To enhance the "selectivity" of a device, catalytic metals are incorporated into the sensing material, and operating temperature ,is optimized to reduce the effects of competing reactions. While most devices in use today are discrete sensors, arrays of different sensors have been proposed as an additional means to enhance selectivity by using pattern recognition to analyze the overlapping responses of array elements.

An alternative route to selectivity is to take advantage of the temperature-dependence of surface kinetics by operating sensors in a dynamic mode, in which temperature is varied during operation. Cyclic alteration between two temperatures has been considered for the enhancement of sensitivity and selectivity, and minimization of the effects of humidity [1]-[5]. Hiranaka et al. describe the use of a single temperature pulse to create transient response which has a characteristic time that is gas-dependent [6] .Temperature-programmed desorption, in which the conductance is measured during a temperature ramp, has been used to investigate the desorption of 0_2 , H_2O, and H_2 from tin oxide [7] and the desorption of 0_2 from ultrathin metal films [8]. While the temperature modulation for the above

experiments is done on the time scale of seconds to minutes, with micro-machined structures it is possible to modulate temperature on a millisecond time scale [9].

This works describes a temperature-programmed sensing (TPS) technique that uses short temperature pulses applied to micro-hotplate gas sensors to produce response signatures that are specific to the gas being detected. A repeated temperature- pulse train is applied to the micro-heater, consisting of pulses with varying temperature, and controlled pulse width and separation. The conductance response is monitored between pulses, eliminating the interference resulting from thermally activated conductance in the sensing film. The pulses allow modification of the rates for desorption, reaction, and adsorption on the sensing surface during sensor operation. Response patterns specific to the vapors of water, ethanol, methanol, formaldehyde, and acetone are presented. These response patterns potentially can be combined with pattern recognition technology so that a sensor can specify the gas it is detecting.

The device, shown in Fig. 1, 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 micro-hotplate is fabricated by a commercial CMOS process followed by a simple etch to produce a micro-bridge suspended over a 1.4 μm pit [10]. An additional layer of Ti/Ir was deposited on the AI 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 was deposited by reactive sputter deposition, with the micro-hotplate held at 45O°C by the micro-heater. The SnO_2 was electrically insulating as deposited. By heating the micro-hotplates in vacuum, the SnO_2 was made conductive. A dispersed film of Pd clusters with a mean thickness of 12 Å was deposited on the surface by evaporation, with the SnO_2 films held at room temperature. After the Pd deposition, the film was annealed to 5OO°C to stabilize the film by inducing a further clustering of the Pd [11]. The temperature range of the device was 2O°C to 550 °C, limited by failure of AI 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 A1 plate resistance for step changes in voltage applied to the heater.

An example of a simple system that illustrates some of the principles of temperature-pulsing for sensors is the desorption of water from SnO_2 into vacuum (base pressure 10^{-6} Pa). Exposure of the SnO_2 to a 130 Pa-s dose of water increases the conductance. Heating the surface to a high enough temperature (above 200°C) causes desorption of water and a decrease in the room temperature conductance to the predosed value. A drawback of the temperature programmed conductance measurement for characterizing the desorption is that changes in mobility and/or carrier density 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, as shown in the inset of Fig. 2. Fig.

2 shows a set of step-shaped drops in conductance as a function of pulse temperature for different t_p. Application of this pulse sequence to surfaces without a water dose showed a constant conductance, independent of pulse temperature. The measured change in room temperature conductance from one pulse to the next on the water-dosed surface was only affected by desorption that occurred as a result of the previous pulse. A decrease in conductance was observed when the duration and height of a pulse are sufficient to cause a significant desorption from the film. For sequences with large t,, the conductance drop is shifted to lower temperature, compared to sequences with short t_p . The shift in the location of the conductance step with t_p can he used to determine the activation energy and rate constant for desorption.

The results in Fig. 2 illustrate one component, desorption, of the complex surface kinetics that take place during sensing. Other components, such as adsorption and surface reactions, can also affect the response G to the temperature pulse train. By applying a repeating train of temperature pulses, the conductance response to that train can represent a signature of the reaction kinetics that occur as a result of the interaction between a sensing film and a specific gas. Fig. 3 shows the response of a device to four different gases in air. The sensing film consisted of 1.2 nm Pd dispersed on a 100 nm SnO_2 film. The gases were the room temperature saturated vapor pressures of acetone, formaldehyde, ethanol, and methanol, The sequence of increasing temperature pulses is described in Fig. 3(e). The presence of these gases at saturated vapor pressure caused a Conductance increase by a factor of up to five hundred above the conductance in dry air. The response patterns showed clear differences between the various gases. As in Fig. 2, features in the pattern could be shifted to earlier times in the cycle (lower temperature) by using a longer pulse time. Greater detail in the patterns can be introduced by altering the temperature program, enhancing differentiation between patterns. For example, Fig. 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 2O°C to 370°C.

In conclusion, we have used temperature pulses to generate chemically-specific response patterns from sensing films on CMOS micro-hotplate gas sensors. These response patterns serve as a signature of the gas being detected. A smart sensor system would include an array of sensors with different sensing films, operating with temperature programs that may be adjusted by a central processor in real time. Response patterns from the device would be evaluated by pattern recognition algorithms in the processor to chemically analyze the detected gas.

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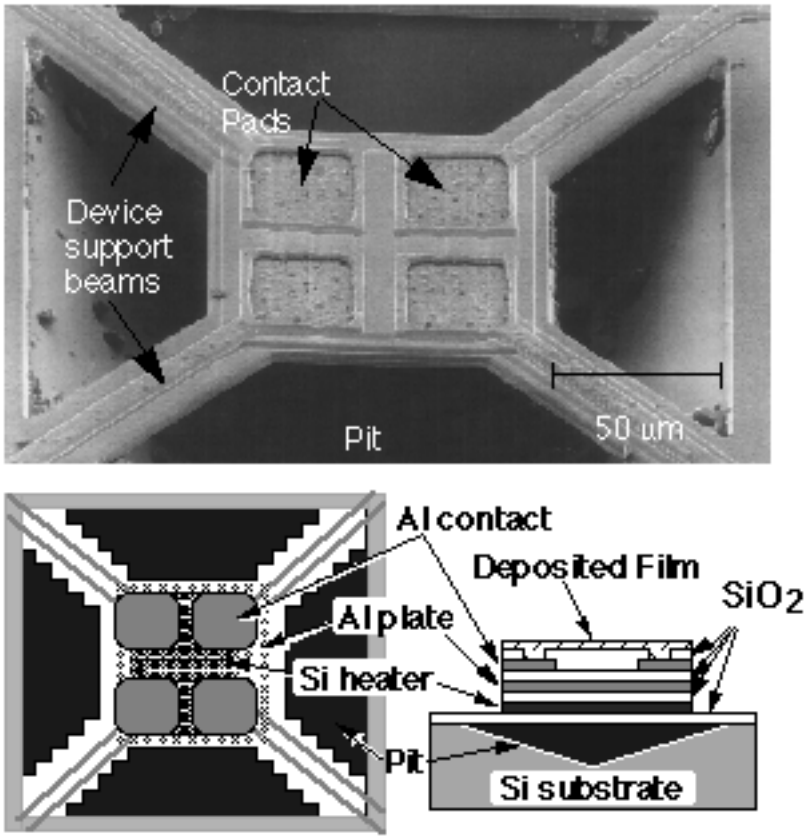

Fig. 1. Top: Scanning electron micrograph of a micro-hotplate. Bottom: Schematic top view (left) and side view (right) of the device.

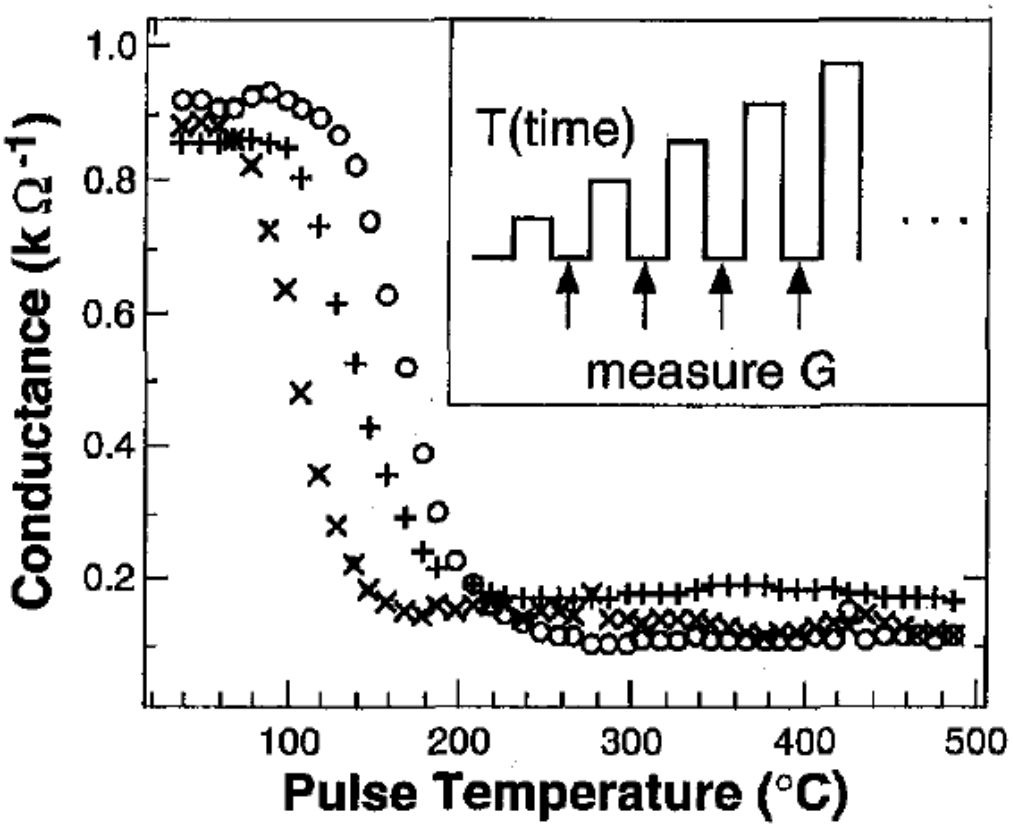

Fig. 2. Conductance measurement of the desorption of water from SnOa into vacuum. Shown is Conductance versus pulse temperature for three different pulse widths: circle 6 ms, plus 100 ms, and cross 300 ms. Inset shows the temperature pulse sequence used to desorb water and produce the data.

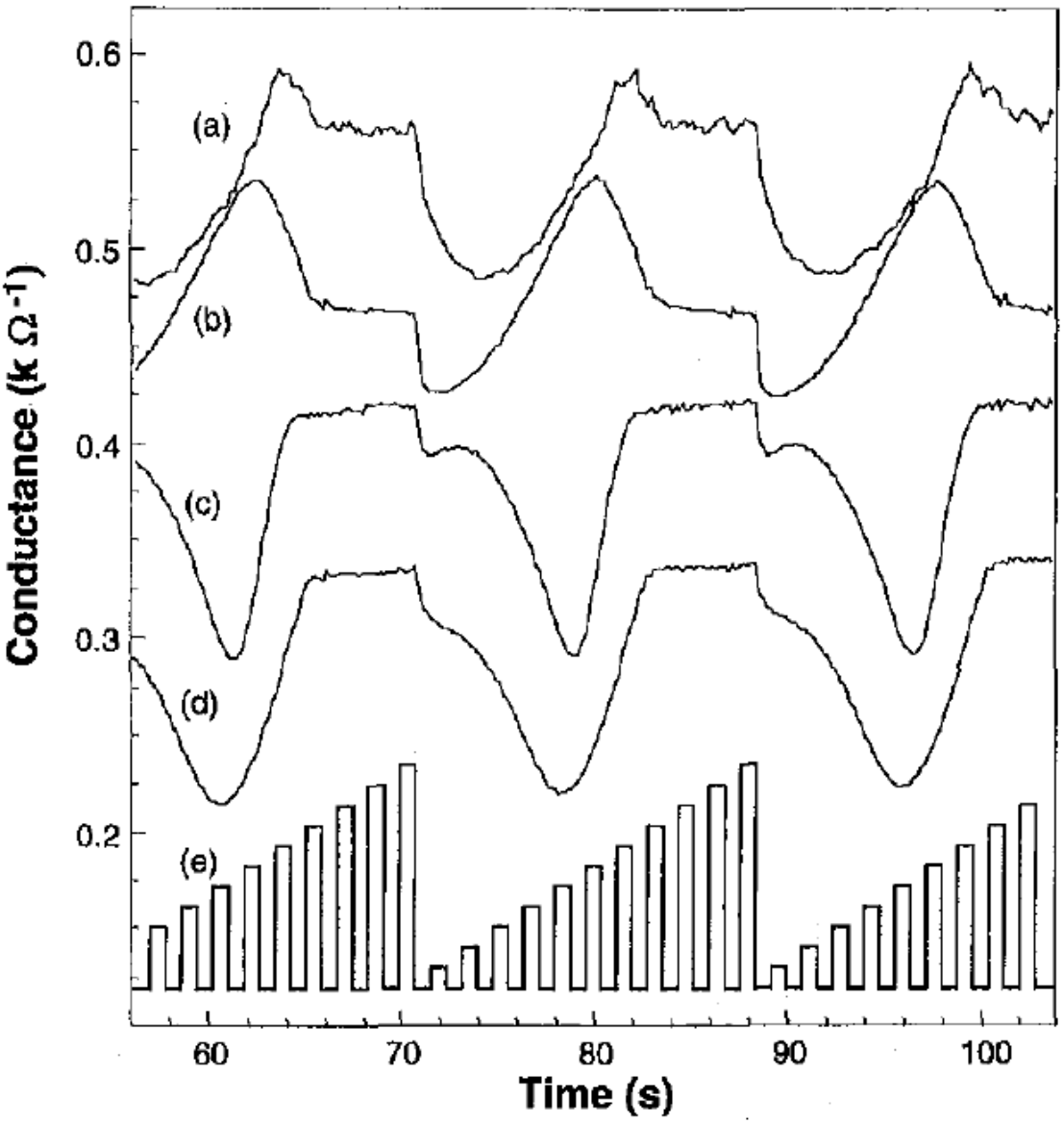

Fig. 3 Conductance response of a Pd-dosed SnO_2 film to the 20°C saturated vapors of (a) acetone, (b) formaldehyde (c) ethanol, and (d) methanol during the repetitive temperature sequence schematically illustrated in (e). The temperature pulse sequence actually was much denser in time, consisting of 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 $k\Omega^{-1}$.

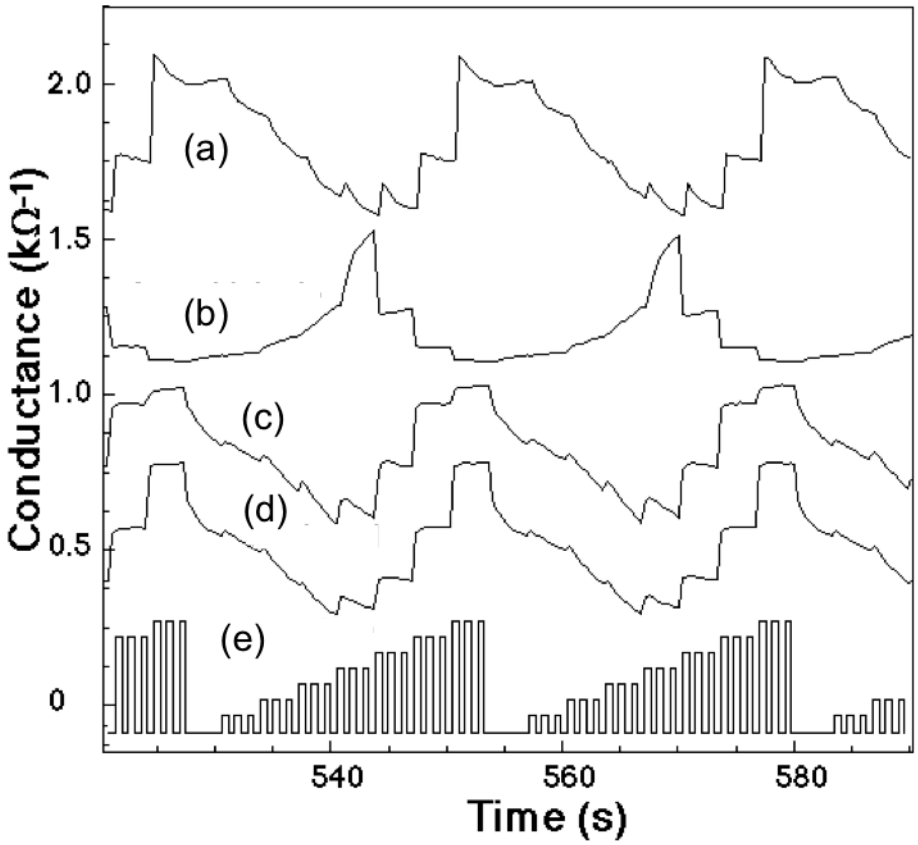

Fig. 4. Conductance response of a Pd-dosed SnO_2 film to the 20°C saturated vapors of (a) acetone, (h) formaldehyde, (c) ethanol, and (d) methanol during the repetitive temperature sequence schematically illustrated in (e). Again, the temperature pulse sequence actually was much denser in time, consisting 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.