Tin Oxide Gas Sensor Fabricated Using CMOS Micro-Hotplates and *In-Situ* Processing

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Abstract—**We report the first monolithic tin oxide (SnO_2) gas sensor realized by commercial CMOS foundry fabrication (MOSIS) and post-fabrication processing techniques. The device is composed of a sensing film that is sputter-deposited on a silicon micromachined hotplate. The fabrication technique requires no masking and utilizes *in-situ* process control and monitoring of film resistivity during film growth. Micro-hotplate temperature is controlled from ambient to 500°C with a thermal efficiency of 8°C / mW and thermal response time of 0.6 ms. Gas sensor responses of pure SnO_2 films to H_2 and O_2 with an operating temperature of 350°C are reported. The fabrication methodology allows integration of an array of gas sensors of various films with separate temperature control for each element in the array, and circuits for a low-cost CMOS-based gas sensor system.**

I. Introduction

THE methodology for the fabrication of micromechanical structures using commercial CMOS foundries, such as those available through the MOSIS service [1], with post-fabrication techniques has been recently reported [2], and a number of devices utilizing this methodology have been developed. The technique realizes a class of devices that are based on thermo-electro-mechanical effects and is compatible with existing VLSI circuit design techniques [3]–[6]. The devices consist of membranes composed of materials layers that are inherent in the CMOS process, namely, layers of polysilicon and aluminum encapsulated by SiO_2. The micromachining of the underlying silicon releases these surface layers forming membranes with high thermal isolation to realize devices based on thermo-electro-mechanical effects. The various layers can be designed to offer functions such as resistive heaters [3], resistive temperature sensors [4], thermal actuators [5], and thermoelectric sensors [6].

Advantages of this method include low cost, high yield, and easy integration of digital or analog electronics with the reliability of a standard integrated circuit process. The limited material layers available in a commercial IC process, which are optimized for integrated circuits, bound the specific class of micromechanical structures that can be realized. However, when additional materials layers are post-deposited and interconnected to existing circuitry, advanced sensor arrays and systems can be realized.

This letter reports on the successful fabrication of SnO_2 films on a commercially manufactured CMOS chip by reactive sputter deposition to produce an integrated gas sensor. Following a description of the micro-hotplate and the SnO_2 deposition process, the characteristics of the sensor when exposed to H_2 and O_2 are presented.

II. Device Description and Fabrication

The base element of the gas sensor is a micro-hotplate which is designed using the MAGIC CAD tool [7], [8]. The design is based on a modification to MAGIC's technology file that defines a new layer called *open* [9]. This layer opens a window to the silicon substrate. Designs are submitted to the MOSIS foundry service, and processed CMOS chips are then subjected to subsequent processing, referred to as post-fabrication processing. Ethylene diamine-pyrocatechol-water [10]–[12] (EDP), an anisotropic silicon etchant, is used to etch the exposed silicon defined by the layout of the *open* layer. Proper layout will form a pit under the suspended heater structure, giving high thermal isolation from the surrounding substrate. The SiO_2 passivation masks all other areas of the chip from the EDP solution providing a maskless process, requiring no photolithography. Aluminum hydroxide (AlOH) [13] is added to the EDP solution, and an etch temperature of 95°C is used to reduce attack on any exposed aluminum pads.

The heater structure is a sandwich of field and CVD oxides that encapsulate a polysilicon resistor for heating, an aluminum plate for temperature sensing, and four top aluminum contacts for connection to the SnO_2 film. Thin-film heaters for application to gas sensing have previously been manufactured in a custom semiconductor process [14]. The advantage of the micro-hotplate reported in this work is in the easy monolithic integration of electronics using commercial CMOS foundries.

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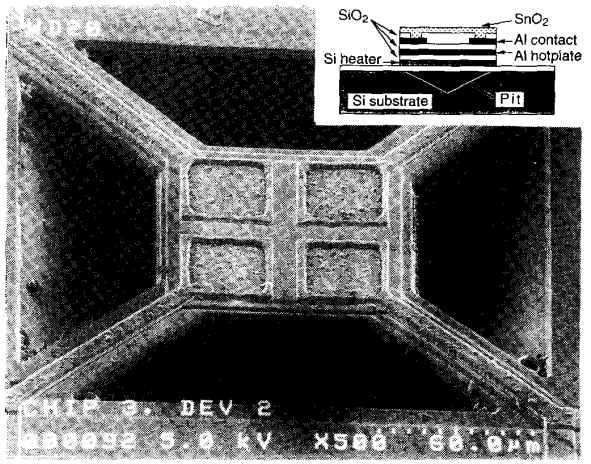

Fig. 1. SEM micrograph of suspended micro-hotplate structure with SnO_2 film coating. The inset shows a schematic illustrating the various layers comprising the structure.

Fig. 1 shows a SEM micrograph of one of the micro-hotplate structures which is 200 μm on a side. Connections to the polysilicon heater, aluminum temperature sensing resistor, and top film contacts are routed through the bridges that support the structure. The aluminum temperature sensor is designed as a square plate to more uniformly disperse the heat generated by the polysilicon resistor and to provide a four-point van der Pauw measurement [15] of aluminum film resistivity. The temperature of the structure for a given heater current is determined using the film's temperature coefficient of resistance (TCR) [16] which was determined to be $0.003657°C^{-1}$.

Films of SnO_2 were deposited onto the heated surface of the micro-hotplate using reactive sputter deposition in an ultrahigh vacuum-compatible chamber, which has been described elsewhere [17]. The chip was bonded, packaged, and fully wired within the deposition chamber such that each device in the array could be thermally controlled before, during, and after deposition. Different growth temperatures were utilized by selecting different temperatures (heater currents) for the polysilicon heater elements within the array of micro-hotplates. In this way, film properties could be optimized in an efficient manner. Indeed, SnO_2 films deposited on hotplates having increasingly higher temperatures exhibited correspondingly larger grain sizes and higher conductances [18]. The thermal array also facilitated the control of the microstructure and the composition of the SnO_2 films by allowing different post-annealing conditions for different device elements. The top aluminum pads on the micro-hotplate allowed the resistivity of the sensing films to be monitored as they were deposited.

The deposition of the SnO_2 films was also a maskless process that required no photolithograhy. Films deposited on nonheated surfaces had high resistivity and did not affect the operation of the active devices.

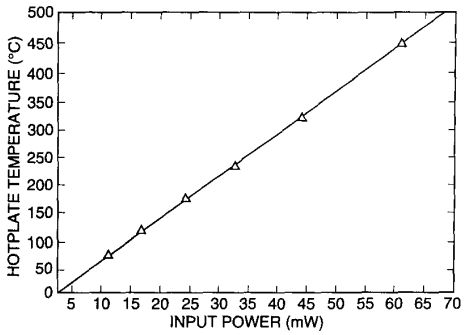

Fig. 2. Plot showing increase of micro-hotplate temperature over ambient versus input power applied to polysilicon heater.

III. Results and Discussion

A plot of the micro-hotplate's temperature versus input power applied to the polysilicon heater is shown in Fig. 2. This plot exhibits a thermal efficiency of about 8°C/mW for the hotplate in air. Temperatures as high as 500°C can be attained on the hotplate's surface. Much higher temperatures are achievable by the polysilicon heaters, but at these temperatures, the aluminum metallizations begin to have problems with stability. It is expected that most gas-sensing applications will require hotplate temperatures to be less than 400°C. The stability of the aluminum sensing resistor and the polysilicon heater was investigated by applying constant power of 47 mW to the polysilicon heater for over 6.5×10^5 s. This resulted in a hotplate temperature of 400°C. The change in sheet resistance was observed to be less than 4% for the aluminum and polysilicon films over this time period. The thermal and mechanical stability of the suspended polysilicon heater was also investigated in [3]. Transient measurements indicate that this device has a typical thermal response time of 0.6 ms.

An example of the gas-sensing response for one element in the fabricated device is shown in Fig. 3. These characteristics were obtained with the device mounted in the same vacuum system that was used to deposit the SnO_2 film. A current was forced through the polysilicon heater to produce a fixed 350°C temperature rise on the surface of a hotplate. This temperature activates the adsorptive processes that produce gas sensing responses from the film. The figure shows the conductance of the film as a function of time when it is exposed to two cycles of a sequence of H_2 exposure, evacuation, O_2 exposure, and evacuation. The individual gases were each introduced at a pressure of 1.3 Pa in the vacuum system. The value of conductance before these exposures is indicated by the values between $t = 0$ and 150 s. A conductance plateau region is observed following the removal of H_2 indicating that H_2 is remaining on the sensor's surface. The introduction of O_2 facilitates a reaction between O_2 and H_2 which decreases the conductance. Upon completion of one cycle the conductance is observed to return to a value close to the value at the beginning of the cycle. As

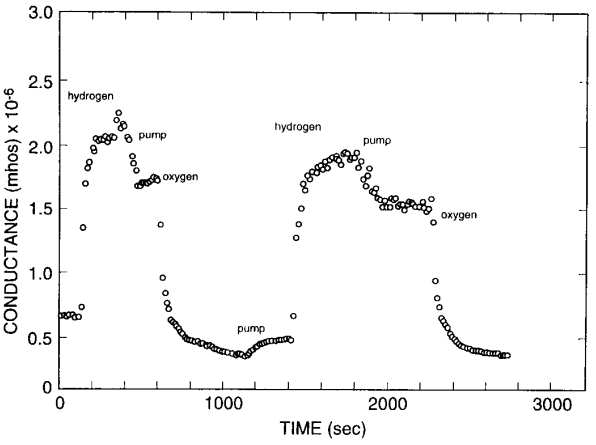

Fig. 3. Conductance of SnO_2 film versus time when exposed to a reducing gas, H_2, and an oxidizing gas, O_2, respectively, for two cycles. The individual gases were each introduced at a pressure of 1.3 Pa in the vacuum system.

shown by the figure, this microsensor exhibits a response time of about 200 s when exposed to a particular gas.

The gas selectivity, sensitivity, and response speed of the sensor elements can be varied by changing the temperature of the hotplates during sensing or by surface dispersing low coverages (monolayer regime) of additive metals, like Pt or Pd [19], [20]. This variability can be used to build an array of such sensors where each element would have a unique response when exposed to a mixture of gases. These signals can then be deconvoluted using pattern recognition procedures to determine the composition and concentrations of gases in the mixture.

IV. Conclusions

A monolithic SnO_2 gas sensor has been produced by micromachining a custom CMOS chip fabricated through the MOSIS foundry system and then sputter depositing a SnO_2 sensing film. A maskless micromachining technique was used in realizing a micro-hotplate array structure on the CMOS chip. The sensor exhibits a fivefold conductance change in response to H_2 and O_2 exposures in a vacuum, with a response time of less than 200 s. These sensing characteristics show promise in using the device with advanced (tailored) sensing materials in low-cost integrated sensor systems capable of gas mixture analysis.

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References

[1] C. Tomovich, "MOSIS—A gateway to silicon," *IEEE Circuits Devices*, vol. 4, no. 2, pp. 22–23, 1988.

[2] M. Parameswaran, H. P. Baltes, Lj. Ristic, A. C. Dhaded, and A. M. Robinson, "A new approach for the fabrication of micromachined structures," *Sensors and Actuators*, vol. 19, pp. 289–307, 1989.

[3] M. Parameswaran, A. M. Robinson, D. L. Blackburn, M. Gaitan, and J. Geist, "Micromachined thermal radiation emitter from a commercial CMOS process," *IEEE Electron Device Lett.*, vol. 12, no. 2, pp. 57–59, Feb. 1991.

[4] M. Parameswaran, A. M. Robinson, Lj. Ristic, K. Chau, and W. Allegretto, "A CMOS thermally isolated gas flow sensor," *Sensors and Materials*, vol. 2, pp. 17–26, 1990.

[5] D. Moser, O. Brand, and H. Baltes, "A CMOS compatible thermally excited silicon oxide beam resonator with aluminum mirror," in *Proc. Transducers '91*, pp. 547–550.

[6] J. Jaeggi, H. Baltes, and D. Moser, "Thermoelectric AC power sensor by CMOS technology," *IEEE Electron Device Lett.*, vol. 13, no. 7, p. 366, 1992.

[7] W. S. Scott, R. N. Mayo, G. Hamachi, and J. K. Ousterhout, "1986 VLSI tools: Still more works by the original artists," Comput. Sci. Div. (EECS), Univ. of California, Berkeley, Rep. UCB/CSD 86/272, Dec. 1985.

[8] J. K. Ousterhout, "The user interface and implementation of an IC layout editor," *IEEE Trans. Computer-Aided Design*, vol. CAD-3, no. 3, pp. 242–249, July 1984.

[9] J. C. Marshall, M. Parameswaren, M. E. Zaghoul, and M. Gaitan, "Methodology for the computer aided design of silicon micromachined devices in a standard CMOS process," National Inst. Standards Technol., Gaithersburg, MD, NIST Rep. 4845, May 1992.

[10] E. Bassos, "Fabrication of novel three-dimensional microstructures by the anisotropic etching of (100) and (110) silicon," *IEEE Trans. Electron Devices*, vol. ED-25, no. 10, pp. 1178–1185, 1978.

[11] A. Bohg, "Ethylene diamine–pyrocatechol–water mixture shows etching anomaly in boron doped silicon," *J. Electrochem. Soc.*, vol. 118, p. 401, 1971.

[12] K. E. Bean, "Anisotropic etching of silicon," *IEEE Trans. Electron Devices*, vol. ED-25, no. 10, pp. 1185–1192, 1978.

[13] M. Parameswaran, Simon Fraser Univ., Burnaby, B. C., Canada, private communication, 1991.

[14] N. Najafi, D. Wise, R. Merchant, and J. W. Schwank, "An integrated multi-element ultra-thin-film gas analyzer," in *Proc. IEEE Solid State Sensor and Actuator Workshop*, June 1992, pp. 19–22.

[15] L. J. van der Pauw, "A method of measuring the resistivity and Hall coefficient on Lamellae of arbitrary shape," *Philips Res. Rep.*, vol. 13, p. 1, 1958.

[16] H. A. Schafft and J. S. Suehle, "The measurement, use and interpretation of the temperature coefficient of resistance of metallizations," *Solid-State Electron.*, vol. 35, no. 3, p. 403, 1992.

[17] S. Semancik and R. E. Cavicchi, "The growth of thin, epitaxial SnO_2 films for gas sensing applications," *Thin Solid Films*, no. 206, pp. 81–87, 1991.

[18] R. E. Cavicchi, "Application of microsubstrates for materials processing," in preparation.

[19] T. B. Fryberger and S. Semancik, "Conductance response of $Pd/SnO_2(110)$ model gas sensors to H_2 and O_2," *Sensors and Actuators*, vol. B2, pp. 305–309, 1990.

[20] S. Semancik and T. B. Fryberger, "Fundamental studies of gas sensing response mechanisms: Pd on SnO_2 (110)," in *Proc. 3rd Int. Meeting Chemical Sensors* (Cleveland, OH), 1990, pp. 23–26.