High-temperature gas sensor using perovskite thin films on a suspended microheater

Grudin, O.; Marinescu, R.; Landsberger, L. M.; Kahrizi, M; Frolov, G.; Cheeke, D. J. N.; Chehab, S.; Post, Michael; Tunney, Jim; Du, Xiaomei; Yang, Dongfang; Segall, D.

Publisher's version / Version de l'éditeur:
https://doi.org/10.1116/1.1463072
Journal of Vacuum Science & Technology. A. Vacuum, Surfaces, and Films, 20, May 3, pp. 1100-1104, 2002-05

High-temperature gas sensor using perovskite thin films on a suspended microheater

O. Grudin, R. Marinescu, L. M. Landsberger,[a] M. Kahrizi, G. Frolov, and J. D. N. Cheeke
Department of Electrical and Computer Engineering, Concordia University, Montreal, Quebec H3G-1M8, Canada

S. Chehab, M. Post, J. Tunney, X. Du, and D. Yang
National Research Council of Canada, Institute for Chemical Process and Environmental Technology, Ottawa, Ontario K1A-0R6, Canada

D. Segall
The Armstrong Monitoring Corporation, 215 Colonnade Road South, Nepean, Ontario K2E 7K3, Canada

(Received 14 August 2001; accepted 28 January 2002)

Suspended microstructures consisting of a thin oxide/nitride diaphragm with embedded polysilicon heaters were designed and fabricated using a standard complementary metal–oxide–semiconductor process and simple postprocessing. Thin films of gas sensitive materials based on the $SrFeO_{2.5+x}$ nonstoichiometric perovskite family were deposited onto the diaphragms by room-temperature pulsed excimer laser deposition. Successful chemical sensor functionality was demonstrated. With applied power up to 30 mW, estimated temperatures of the gas sensor film up to 900 °C were reached. When the device was exposed to volatile organic compounds (VOCs) such as acetone and methanol, a reversible ten to 100-fold increase in sensor film resistance was observed, with response times from less than 1 s to a few minutes. Sensor response sensitivity depended on applied power and on the nature of the VOC analyte. This sensor device has the potential for use in multiarray configurations such as in an electronic nose. © *2002 American Vacuum Society.*
[DOI: 10.1116/1.1463072]

I. INTRODUCTION

The need for information about the chemical constitution of the environment continues to grow in many sectors. These range through indoor air quality, safety, spill detection, automotive, food, pharmaceutical, petrochemical, etc., where sensor technology is ever more important for determining real-time physical parameters and chemical concentration of complex analytes.

Among the increasing number of driving forces leading to the need for monitoring can be improvements in process control or efficiency, productivity, safety, and also addressing regulatory requirements. Of particular relevance in these areas is the fabrication of miniature devices by integration of chemical sensor materials with platforms, whereby the functionality of the created device is significantly improved. The approach is to provide a sensor which is compact, inexpensive, low power, low maintenance, and yet with a capability of real time response with analyses of multicomponents in a given environment. Such a device can be conveniently deployed in multipoint locations to satisfy a range of monitoring requirements over a large area.

One class of such a device is based upon silicon micromachined technology, with an integrated chemically responsive sensor material. These gas sensors use a suspended heater structure [i.e., microhotplate (MHP)] to thermally isolate a heated gas-sensing thin film from the bulk silicon and from on-board electronics. Typically,[1–5] such gas sensing structures operate at temperatures up to 300–350 °C. Also, they typically use a metal layer such as aluminum in the MHP to facilitate a more uniform thermal profile, and polysilicon/Al thermocouples for temperature monitoring.

The present research addresses the integration of thin films of complex metal oxides of the nonstoichiometric perovskite family, with the MHP, for sensing gases such as O_2, CO, H_2, and volatile organic compounds (VOCs). These sensor materials provide, by virtue of their chemical and structural characteristics,[6,7] a film with adjustable chemistry which is suitable for film array usage in gas sensing applications. In order to obtain sufficiently fast kinetics for film–gas chemistry and to provide a rapid sensor response, the thin film must be heated to approximately 500 °C or higher.[7] The electrical resistance of the film is then measured before, during, and after exposure to the analyte gas stream to yield a form of sensor transduction signal[8] which can then be simply monitored by on-board circuitry for analysis and processing. The effect of deposition conditions on film response is also described in Ref. 8. Effective use of MHPs at these unusually high temperatures raises practical issues[9] especially since, in order to allow for integration of an array of devices with powering and control circuitry on a single chip, implementation in a host standard process is desirable. Among others, the design must avoid the use of Al on the suspended MHP membrane.

This article reports on the implementation and characterization of a high-temperature gas sensor using perovskite thin films on a suspended microheater fabricated in a standard complementary metal–oxide–semiconductor (CMOS)

[a]Electronic mail: leslie@ece.concordia.ca

process, with postprocessing to release the microheaters and deposit the perovskite films.

II. DEVICE DESIGN, CHARACTERISTICS, AND FABRICATION

The device is designed to be integrated into a silicon chip, batch fabricated in a standard commercial host process (Mitel's 1.5 μm CMOS process), having a released suspended plate (membrane), thermally isolated from the silicon substrate, on which the gas-sensitive perovskite layer is deposited, and then operated at controllable high temperatures such as 500 °C or higher.

Figures 1(a) and 1(b) show schematically the main elements of the device. The gas-sensing device consists of a suspended microstructure, with imbedded polysilicon thermoresistors, Pt electrodes on the top surface, and a perovskite film. The resistance between the two Pt electrodes is monitored during high-temperature operation, for changes away from a quiescent (usually very high resistance) value. The heating element is thermally insulated from the silicon substrate by a bulk-micromachined cavity, and by the structural SiO_2 and SiN_x layers. Thermal isolation of the device is primarily limited by the thermal conductivity of the polysilicon heater lines, which must extend from the main power source onto the suspended structure

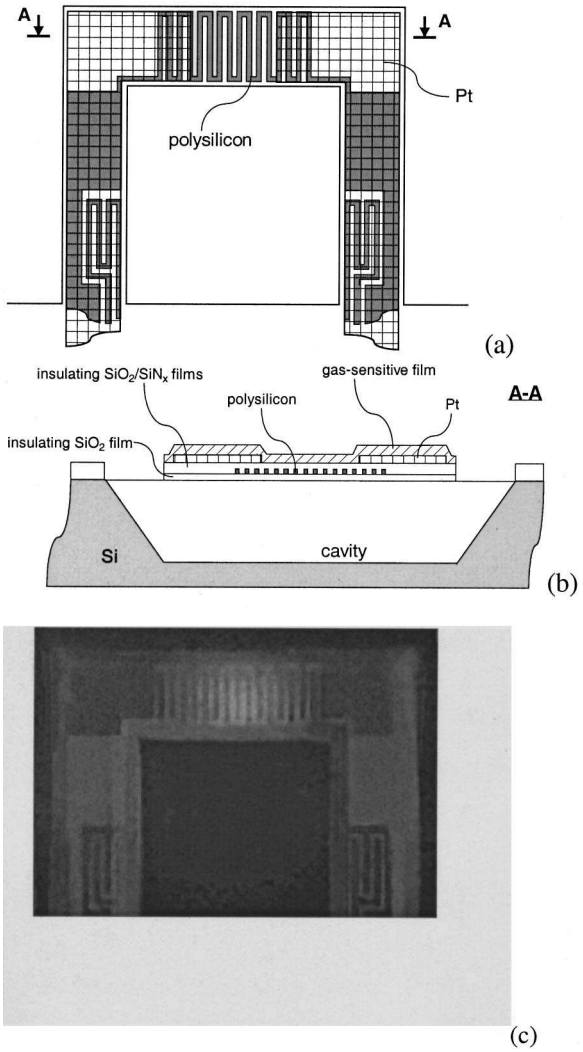

FIG. 1. (a) Top view schematic of a cantilever-type microheater. The active gas sensitive area is between the two Pt pads. (b) Schematic cross-sectional view of the structure through section A-A. (c) Optical micrograph of a glowing microheater in operation.

The devices are fabricated in the standard commercial process with several postprocess steps. Standard layers of field oxide, poly-1, contact, and intermetal oxides, and passivation oxide/nitride are patterned during the main CMOS process to form the plate and support arms. Subsequently, in a postprocess sequence, Pt is deposited and patterned by a liftoff procedure.

Bare silicon regions are obtained by alignment of openings in all of the layers, allowing bulk micromachining of a cavity underneath the microstructures by anisotropic etching. The release etch is done in a tetra-methyl ammonium hydroxide (TMAH) bath (25 wt % TMAH with added 15 vol % of isopropyl alcohol at 85°C). Deposition of the gas-sensing film is done by laser ablation using 25-μm-thick molybdenum shadow masks.

Several methods are available to protect the Al pads during the release etch. In this research, two methods were successfully applied: (1) a 0.2 μm SiN_x layer was deposited by plasma enhanced chemical vapor deposition and patterned using reactive ion etching, (2) SC-900 negative photoresist was applied and patterned.

The suspended plate (MHP) is designed to be approximately 50 μm$\times$150 μm, with a 30 μm$\times$30 μm active gas-sensitive area, as shown in Fig. 1. So far as sensor device fabrication and operation is concerned, the small size confers upon the structure two important characteristics. First, the duration of the release etch is reduced with consequent minimizing of potential damage to other die components. Second, the gas-sensitive area where the perovskite film is deposited is small enough such that the temperature nonuniformity within this area is also minimized. This results in a sensor film, which is relatively uniformly sensitive to gas concentrations over its whole surface, an important factor for accurate control of analyte selectivity in the film.

It was found that cantilever-type microstructures (one or two legged, clamped only on one side with the other side free to accommodate stresses) are preferable to fully clamped (four-legged) microstructures. These types of microstructures are preferred because: (i) the release etch process takes less time, (ii) much less damage is incurred during release etch, and (iii) much fewer (stress-induced) failures occur during high-temperature operation.

Typically, the power needed for the microheaters is in the range of tens of milliwatts. The heaters must be fabricated in one of the conductive layers included in the host process. In order for the power supply voltage to be reasonably low, the heaters have been patterned in the poly-1 layer, which has sheet resistance of 20 Ω/sq. (The Al interconnect layer, from which the contact pads are made, has sheet resistance 0.1 Ω/sq.). This allows the heater power to be supplied by a voltage under 15 V. Thermal isolation of $\sim$50 K/mW of the

microstructure from the substrate is achieved, comparing favorably with literature results[5] achieved on thermal microstructures.

Temperatures over 800 °C are reached, indicated by visible glowing of the microstructures. This is shown in Fig. 1(c). This required approximately 20 mW of power. Experimentally, it was found that above a power dissipation of roughly 30 mW, four-legged (fully clamped) structures failed (cracked due to stress).

Under these conditions of high-temperature operation, the polysilicon heater material is not stable enough[9] to be used simultaneously as both a heater and a temperature sensor. Accordingly, we used an additional temperature sensor, and also a polysilicon resistor, located on one of the supporting arms closer to the substrate at a lower temperature, which can be used for temperature control. It was found that at temperatures below a certain threshold, estimated to be between 400 and 500 °C, poly-1 was stable enough.[9]

Since it is expected that the heater resistive load will vary during the operation, a power supply integrated circuit delivering constant power is used in order to keep the temperature of the microhotplate constant. The power supply, based on an analog multiplier with feedback stages, delivers constant power within ±1% when the microheater resistance changes within ±50%, up to 40 mW on heater loads in the range 1–10 kΩ.

III. GAS-SENSITIVE FILM CHARACTERISTICS AND DEPOSITION

A. Cobalt substitution in $SrFe_{1-y}Co_yO_{2.5+x}$

For this research, the parent $SrFeO_{2.5+x}$ perovskite (SFO) compounds and their thin films have been chemically and morphologically modified to focus on the cobalt substituted series of the $SrFe_{1-y}Co_yO_{2.5+x}$ (abbreviated SFCO) family, for $0 \leqslant y \leqslant 1$.[10] The cobalt substitution confers upon these compounds a higher degree of mixed ionic/electronic conductivity[11] than is present in $SrFeO_{2.5+x}$. These attributes provide a more tunable sensor response with respect to the chemical-sensor orthogonality, and this facilitates the application of these modified materials with multielement MHP arrays to develop an electronic nose. Additionally, at ambient temperature the cobalt-substituted films have a measurable electrical resistance, allowing ready confirmation of electrical continuity prior to powering up the MHP.

B. Successful deposition by pulsed laser

Films of these $SrFe_{1-y}Co_yO_{2.5+x}$ materials are deposited by the pulsed laser deposition (PLD) technique, and characterization by x-ray diffraction (XRD) and inductively coupled plasma–Auger electron spectroscopy (ICP–AES) has shown them[11] to be single phase and with a well defined chemical composition, thus confirming congruent transfer during PLD. It was also determined that for the SFCO family, films could be successfully deposited by PLD onto substrates at ambient room temperature, (denoted SFCO–RT), with subsequent annealing during a preconditioning step to optimize sensor functionality (in contrast to the parent $SrFeO_{2.5+x}$). The avoidance of higher temperatures (i.e., $T > 300$ °C) during PLD is advantageous for minimizing the thermal stress experienced by the MHP and preserving its integrity. Investigation of the reduction–oxidation properties

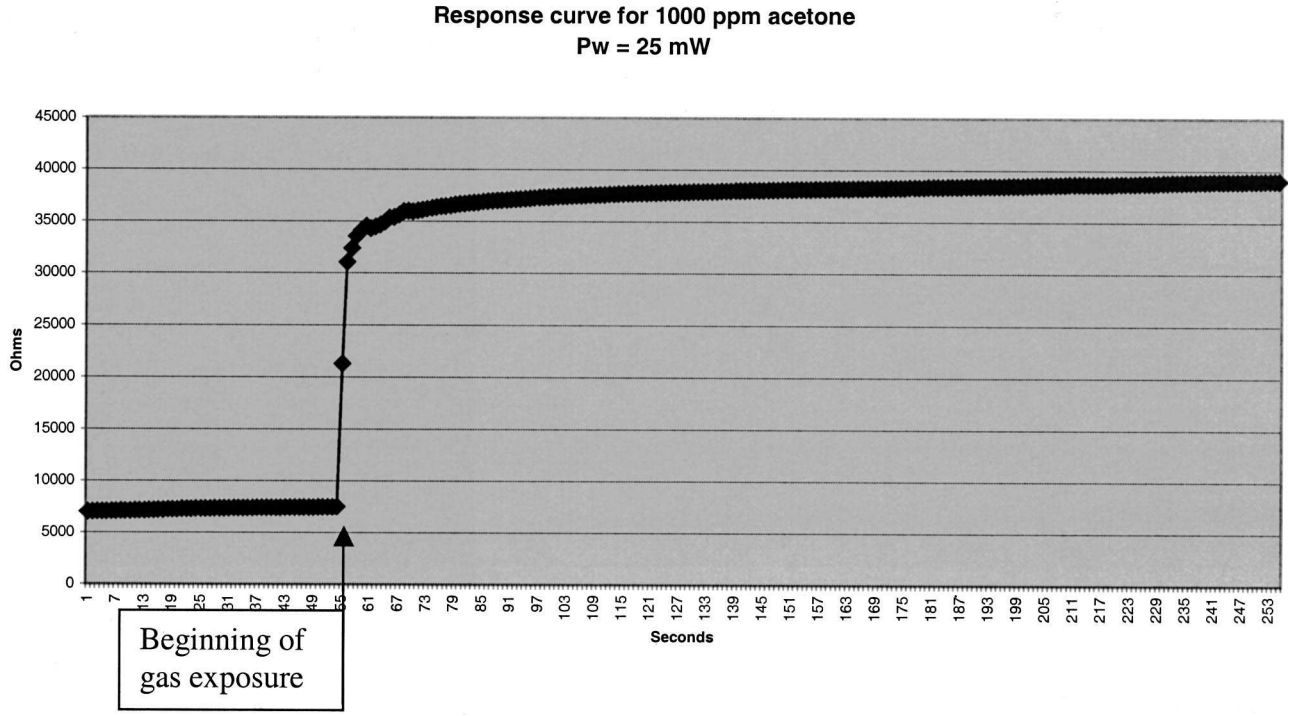

FIG. 2. Response to 1000 ppm acetone, of cantilever-type sensor with SFCO–RT, at 25 mW applied power (temperature estimated at 800–900 °C). The beginning of the gas exposure was at 56 s.

of the $SrFe_{1-y}Co_yO_{2.5+x}$ family[10,11] have determined that the optimum composition for enhanced sensing functionality is with $y=0.75$.

The SFCO films, deposited on microheaters by PLD over a range of temperatures from room temperature to 300 °C, were found to have the following characteristics:

(i) they adhered, and conformed to the surface on which they were deposited;
(ii) they have uniform thickness of approximately 200 nm;
(iii) they are single phase, with well-defined composition;
(iv) they are transparent to visible light; and
(v) they are *p*-type semiconducting.

IV. SENSOR CHARACTERIZATION RESULTS AND DISCUSSION

After deposition, electrical measurements of films on microheater structures showed that, at room temperature:

(i) SFO films were found to have sheet resistance greater than 220 MΩ/sq.; and
(ii) SFCO films were found to have sheet resistance in the range 30–40 MΩ/sq.

The sensor response data obtained in a calibrated gas exposure system of approximately 3 L volume, equipped with injection port and rapid mixing capability, are shown in the following figures. Figure 2 shows a response curve for a cantilever-type sensor with SFCO at 25 mW applied power, exposed to 1000 ppm of acetone; clearly greater than 95% response was achieved within less than 5 s. The SFCO film is 200 nm thick. A similar curve is obtained for 1000 ppm methanol, on the same sensor at the same 25 mW applied power. In this case, the curve begins at roughly 6 kΩ, rising to within 95% of its full response, roughly 25 kΩ, in less than 5 s. Several cycles were applied, with repeatability (reversibility) of the curves being within the noise of the measurement (estimated at better than ±5%).

The dynamic range with respect to analyte concentration was also examined for the same device at 25 mW of applied power. Figure 3 shows the resistance as a function of (separately applied) methanol and acetone concentrations. The methanol concentration ranged from 10 to 3000 ppm, and the acetone concentration ranged from 10 to 1510 ppm. For a given gas, although the sensitivity (slope of the R_s versus concentration, as seen in Fig. 3) decreases at higher concentrations, the sensitivity remains useful (e.g., roughly 5Ω/ppm for methanol at 2000 ppm).

Preliminary data have been collected to demonstrate the relative temperature sensitivity of response to these two analytes (acetone and methanol). The measurements in Fig. 4 were not done using the same gas handling apparatus as in Figs. 2 and 3. In this latter, and preliminary series of measurements, the sensor was exposed either to methanol or to acetone in an open system with a liquid source, allowing air flow to deliver the vapor to the sensor surface. Consequently, no precise vapor concentration at the sensor was known. However, the experimental apparatus was consistent enough that the analyte concentrations in Fig. 4(a) were closely duplicated in Fig. 4(b). From a knowledge of saturated vapor pressure at ambient temperatures, taken together with an assessment of air flow rate in the region of the sensor, the absolute concentrations are estimated to be a few vol %.

The data show that the sensitivity characteristics of the sensor can be controlled by varying the heater temperature. For example, at low temperatures, such as roughly 200 °C

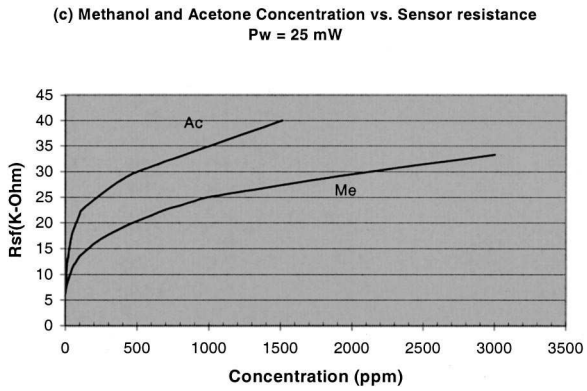

FIG. 3. SFCO–RT response curves for acetone and methanol, at optimum power (25 mW) for rapid response and high sensitivity. The results show good sensitivity even down to concentrations in the low ppm range.

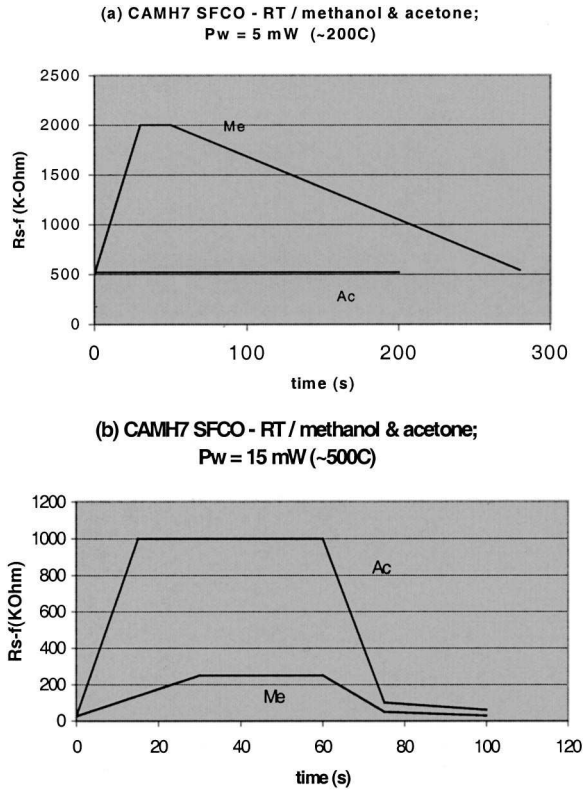

FIG. 4. (a) Sensor response to acetone and methanol (applied separately), at 5 mW applied power (roughly 200 °C). (b) Sensor response to acetone and methanol (applied separately), at 15 mW applied power (roughly 500 °C). For these measurements, the analyte concentrations were estimated at a few vol %.

obtained from the application of 5 mW, Fig. 4(a) shows that the resistance of the film changes very little upon exposure to acetone. Under the same operation conditions, however, the device shows a much higher sensitivity to methanol. At more elevated temperatures such as 500 °C resulting from the application of 15 mW to the MHP [Fig. 4(b)], the sensitivity to acetone is dramatically increased, allowing discrimination between these two components in a given gas mixture. This result is promising both for the use of the sensors in arrays, and for achieving an array-like performance from only a single sensor by suitable variation/control of the temperature.

Due to the *p*-type conductivity of the sensing film, certain interesting characteristics are obtained. For example, the resistance of the film increases in a reducing environment. This extends the measurement range of these films to concentrations beyond those accessible to commonly available conventional SnO_2 sensors, which are *n* type, and approach an $R=0\ \Omega$ (i.e., shorted) value at higher gas exposure concentrations. From preliminary observations, it is seen that under the temperature conditions of the exposure, the films have an affinity for organic solvents such as methanol, acetone, and toluene, and simultaneously a rejection of common interferents such as CO, halogens, and sulfur compounds.

V. CONCLUSION

Suspended microstructures consisting of a thin oxide/nitride diaphragm with embedded polysilicon heaters were designed and fabricated using a standard CMOS process and simple postprocessing. Thin films of gas sensitive materials based on the $SrFeO_{2.5+x}$ nonstoichiometric perovskite family were deposited onto the diaphragms by RT pulsed excimer laser deposition. Successful chemical sensor functionality was demonstrated. With applied power up to 30 mW, estimated temperatures of the gas sensor film up to 900 °C were reached. When the device was exposed to VOCs such as acetone and methanol, a reversible ten to 100-fold increase in sensor film resistance was observed, with response times from less than 1 s to a few minutes. Sensor response sensitivity depended on applied power and on the nature of the VOC analyte, thereby providing a means of discrimination by temperature programming. This sensor device has the potential for use in multiarray configurations such as in an electronic nose.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the services of the Canadian Microelectronics Corporation (CMC), Mitel, the Alberta Microelectronics Corporation, and the Laboratoire des Senseurs et Actuateurs (LISA) of École Polytechnique for the fabrication of samples. This work was partially supported by NSERC and the NRC/NSERC Collaborative Research Program.

[1] S. Wessel, M. Parameswaran, S. R. Morrison, and R. F. Frindt, Proceedings of the 1991 Canadian Conference on VLSI, Kingston, Ontario, August 1991, pp. 1.6.1–1.6.8.
[2] C. Rossi, P. Temple-Boyer, and D. Esteve, Sens. Actuators A **64**, 241 (1998).
[3] S. K. H. Fung, Z. Tang, P. C. H. Chan, J. K. O. Sin, and P. W. Cheung, Sens. Actuators A **54**, 482 (1996).
[4] S. Semancik, R. E. Cavicchi, M. Gaitan, and J. S. Suehle, U.S. Patent No. 5345213 (1994).
[5] Canadian Microelectronics Corporation Report, September 1995.
[6] M. L. Post, B. W. Sanders, and P. Kennepohl, Sens. Actuators B **13**, 272 (1993).
[7] M. L. Post, J. J. Tunney, D. Yang, X. Du, and D. L. Singleton, Sens. Actuators B **59**, 190 (1999).
[8] J. J. Tunney and M. L. Post, J. Electroceram. **5**, 63 (2000).
[9] O. Grudin, R. Marinescu, L. M. Landsberger, D. Cheeke, and M. Kahrizi, Canadian J. Electron. Comput. Eng. **25**, 29 (2000).
[10] M. Post, D. Yang, X. Du, and Z. Kassam, Proceedings of the Materials Research Society, Boston, MA, December 1999, abstract LL7.1.
[11] J. J. Tunney, M. L. Post, X. Du, and D. Yang, Proc.-Electrochem. Soc. **32**, 476 (2000).