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# Combinatorial libraries of semiconductor gas sensors as inorganic electronic noses

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We have fabricated thin-film combinatorial gas sensor libraries based on doped semiconducting $SnO_2$ thin films. Combinatorial pulsed-laser ablation was used to deposit compositionally varying arrays of sensor elements onto a prepatterned device electrode configuration. Using multiplexing electronics, we have demonstrated the detection of chloroform, formaldehyde, and benzene gases at concentrations down to 12.5 ppm through pattern recognition of signals from the arrays of sensors. This technique of fabricating gas sensor arrays as combinatorial libraries can be applied to the manufacturing of portable electronic noses. © *2003 American Institute of Physics.*
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Electrical properties of some semiconductive metal oxides are sensitive to the surrounding gas atmosphere. In particular, $SnO_2$ (Refs. 1–5) based semiconductors are commonly used for commercial gas sensors. Their low manufacturing cost, low operation power consumption, and high compatibility with microelectronic processing make semiconductive gas sensors ideal in a variety of settings including environmental monitoring, military applications, chemical industrial processes, food processing, and biomedical applications.[6–9]

The gas sensing mechanism of semiconducting metal oxide thin films involves interaction between surface adsorbates such as $O^-$, $O_2^-$, and $O^2$ and gas molecules of reactive chemical species. The reaction results in a change in the depletion layer thickness, which in turn changes the resistance of the film. Because the reaction takes place at the surface, microstructural details, such as grain size, grain boundaries, and the film thickness of the semiconductors are known to strongly affect their sensing properties.[10–14] The chemical composition of the semiconductor is also a key parameter that influences their sensing performance. In fact, composition by itself can affect the microstructure and, thus determine the sensing properties. It is known that a small amount of dopants, such as Pt and Pd, can boost the sensitivity of $SnO_2$ gas sensors by increasing the thickness of the space-charge layer, which enhances the consumption of oxygen adsorbates on the metal in addition to those on the $SnO_2$ surface. Gas sensing characteristics of a number of other metal oxides, including $In_2O_3$, ZnO, and $WO_3$, have also been previously reported.[15–18]

There is a continuing need to improve the sensitivity[19] and selectivity[19,20] of inorganic gas sensors. In particular, selectivity is a critical figure of merit, and ideal sensors would respond differently to different gas species. One strategy in pursuing the development of improved sensors is to systematically study a large number of compositionally varying sensor materials simultaneously. This can be performed using the combinatorial approach where a large number of samples with different compositions, as well as samples made with different synthesis parameters, can be screened for rapid optimization.[21]

An electronic nose is an instrument comprised of an array of different gas sensors and signal multiplexing electronics, capable of recognizing individual or mixtures of analytes through pattern recognition.[22–25] It is based on the multisensing principle in which the distributed response of an array is used to identify the constituents of a gaseous environment, emulating the olfactory sense. Individual sensor elements may or may not be selective to any one gas. But by using an array of different sensors, gases can be distinguished and identified by a distinct ‘‘fingerprint’’ each gas produces in the form of a pattern of measured electrical responses. Although various electronic noses, mostly composed of organic materials,[26–28] have been demonstrated to date, they have not enjoyed widespread use mainly because of their high cost of fabrication and energy consumption.[29,30]

We report here on the quick fabrication and characterization of thin-film combinatorial libraries of gas sensing metal oxides. The utility of combinatorial libraries is two fold: One is to search and optimize the compositions for high sensitivity and selectivity of gases, and the other is to make use of the natural array geometry of the libraries with different sensor elements for electronic noses. We have measured the library chips using sensitive wide-range balanced-bridge electronics, and demonstrated the detection of different gas species by pattern recognition.

For fabricating the gas sensor array chips, we have used our combinatorial pulsed-laser deposition system, which allows spatially selective deposition of compositionally varying discrete samples with arbitrary layout designs on 1 in. × 1 in. substrates using computer controlled two-dimensional physical shadow masks.[21] We have deposited 500 Å thick sensor films of different compositions on se-

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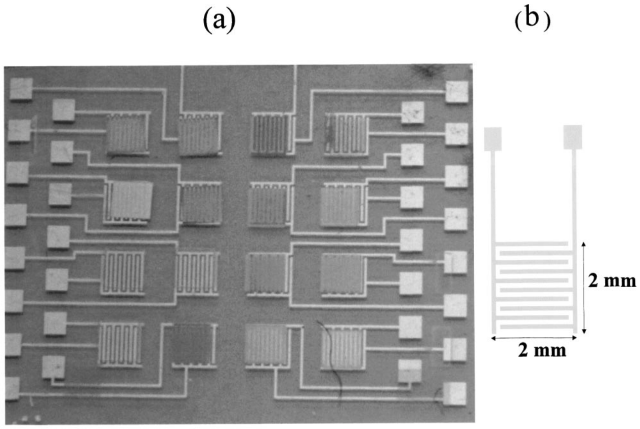

FIG. 1. (a) A photograph of a 16 member gas sensor library deposited on Au electrodes at 550 °C. Each sensor is $SnO_2$ doped with different concentrations of various dopants. The entire chip is approximately 1 in.×1 in. (b) A schematic of a set of interdigitated electrodes used for individual sensors.

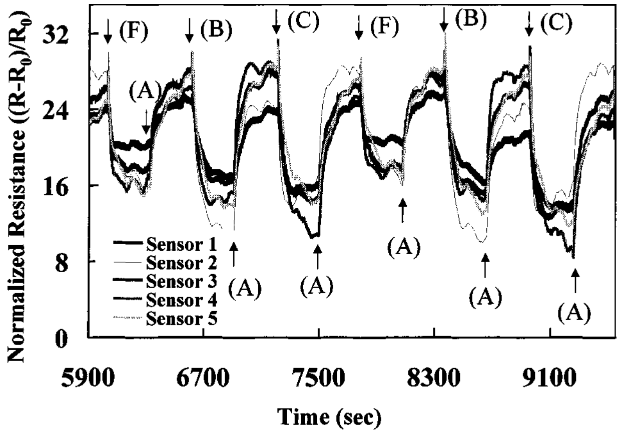

FIG. 2. Sensor response in resistance change $(R-R_o)/R_o$ at 400 °C for five sensors from the second library. Gases and refreshing air were introduced in an alternating manner. Each sensor exhibits a different time dependent response pattern for a given gas. The arrows indicate when different gases (F), (B), (C), and (A) were introduced in the chamber.

lected sites (each with a 2 mm×2 mm area) on two-terminal Au electrode patterns on $Al_2O_3$ (*c*-plane) substrates (Fig. 1). The Au patterns were fabricated using a photolithographic lift-off process prior to the sensor film deposition. Various semiconductor films were deposited at 550 °C in an oxygen partial pressure of $2\times10^{-3}$ Torr. Each sensor array consisted of 16 different compositions where $SnO_2$ was the host material and ZnO, $WO_3$, $In_2O_3$, Pt, and Pd were the dopants. The dopants were selected based on previous reports on single composition gas sensor studies.[19,20] In the first library, compositions of 16 sensors were pure $SnO_2$, $SnO_2+Pt$ (2.5 wt %), $SnO_2+Pd$ (2.8 wt %), $SnO_2+Pt$ (2.5 wt %)+Pd (2.5 wt %), $SnO_2+In_2O_3$ (5 wt %), $SnO_2+In_2O_3$ (5 wt %)+Pt (2.5 wt %), $SnO_2+In_2O_3$ (5 wt %)+Pd (2.8 wt %), $SnO_2+In_2O_3$ (5 wt %)+Pt (2.5 wt %)+Pd (2.5 wt %), $SnO_2+ZnO$ (5 wt %), $SnO_2+ZnO$ (5 wt %)+Pt (2.5 wt %), $SnO_2+ZnO$ (5 wt %)+Pd (2.8 wt %), $SnO_2+ZnO$ (5 wt %)+Pt (2.5 wt %)+Pd (2.5 wt %), $SnO_2+WO_3$ (50 wt %), $SnO_2+WO_3$ (50 wt %)+Pt (2.5 wt %), $SnO_2+WO_3$ (50 wt %)+Pd (2.8 wt %), and $SnO_2+WO_3$ (50 wt %)+Pt (2.5 wt %)+Pd (2.5 wt %). A photograph of a library chip is shown in Fig. 1.

To create thin films of selected chemical compositions, we deposited materials using a layer-by-layer process[31] where $SnO_2$ and other layers were deposited in an alternating manner. Each repeating layer of $SnO_2$ and its dopant material was less than 4 Å thick so that dopants were intimately mixed at a subnanometer level. Sixteen sensors were deposited one after another, and the total fabrication time of one library was $\leqslant$ 3 h, most of which was spent on moving and aligning the shadow masks.

The testing of the chips was performed in a cylindrical gas flow chamber (5 cm in diameter, 3.5 cm in height, and 2 ml in inside volume) where a chip could be heated up to 400 °C during measurements. All sensors were connected to the outside electronics to monitor their resistance change. Gases studied were chloroform (C), formaldehyde (F), and benzene (B), at concentrations of 100 ppm, 50 ppm, 25 ppm, and 12.5 ppm in air. To test the reproducibility and recovery of the sensor performance, responses of the sensors to multiple periods of a fixed gas flowing cycle were monitored. For each segment within a cycle, a gas was introduced in the chamber continuously for 300 s at 24 ml/min, and then air (A) was introduced for the same period of time. Depending on the dopant composition, the resistance *R* of the sensors in air, measured before exposing the chip to gases were in the range of 1 Ω to 20 MΩ which corresponded to the resistivity in the range from $10^{-3}$ Ω cm to 10 Ω cm.

Based on the results from the first library, we have selected compositions for the second library, which were focused down to different doping concentrations of Pt, Pd, and ZnO only. Every sensor on the second library was found to display significant responses to all gases. Here, we concentrate on five sensors whose responses were the most pronounced. Figure 2 shows a plot of $(R-R_o)/R_o$, where $R_o$ is the resistance at a fixed reference point prior to the gas flowing cycle for the five sensors measured at 400 °C. The compositions of the five sensors were $SnO_2+Pd$ (6 wt %) (sensor 1), $SnO_2+Pd$ (8 wt %) (sensor 2), $SnO_2+Pt$ (8 wt %) (sensor 3), $SnO_2+ZnO$ (5 wt %)+Pt (2 wt %) (sensor 4), and $SnO_2+Pt$ (8 wt %)+Pd (8 wt %) (sensor 5). Different gas species (at the concentration of 100 ppm) and refreshing air were introduced in an alternating manner. It can be seen that the sensors exhibit dissimilar time dependent responses for different gases, and the responses are reproducible from cycle to cycle. To further illustrate the dependence of response time on the chemical composition of the sensors, we replot data from Fig. 2 for two of the sensors from one gas flow cycle (Fig. 3).

In order to demonstrate the ability of sensor arrays to distinguish different gas species through a multichannel pattern recognition, averaged normalized responses from the five sensors at 400 °C are plotted in a radar plot, for responses to 100 ppm of chloroform, formaldehyde, and benzene (Fig. 4). Each curve in the plot of Fig. 4 represents data for one gas. It is clear that each gas produces a different response pattern with the five sensors. The variation of sensor responses to the same analyte was found to range typically from 0.3% to 1.6% from the average value, attesting to a high repeatability of the response, and yielding a well-defined pattern for each curve. The size of the response signal was found to be roughly proportional to the concentration

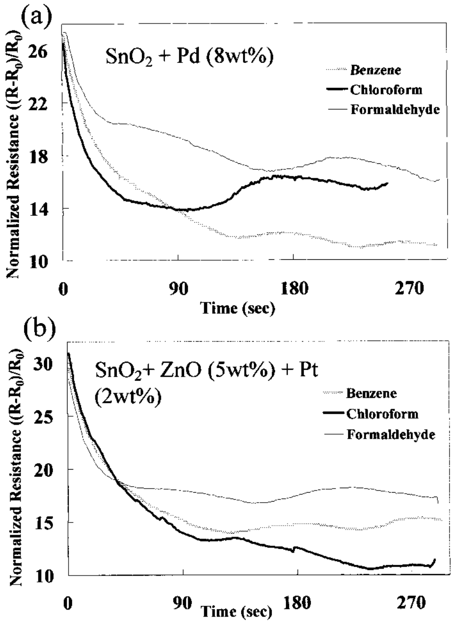

FIG. 3. Dependence of time response on gas introduced for two sensors. The responses were found to be reproducible from cycle to cycle.

of the analytes. We were able to discern response patterns for different gases down to 12.5 ppm. The sensors did not exhibit a ''memory'' of prior exposure to various analytes: Refreshing in air always brought the sensors back to approximately the same resistance. The average response time of the sensors were 600 s, 300 s, and 50 s for operation temperatures of 200 °C, 300 °C, and 400 °C, respectively.

In conclusion, we have used a combinatorial thin-film synthesis technique for fabricating inorganic gas sensor libraries of doped SnO$_2$ thin films. They were tested as electronic noses, and their ability to distinguish different analytes was demonstrated for concentrations down to 12.5 ppm with a high repeatability of response signals. The method described herein allows a fast and relatively inexpensive way of fabricating compact electronic nose devices.

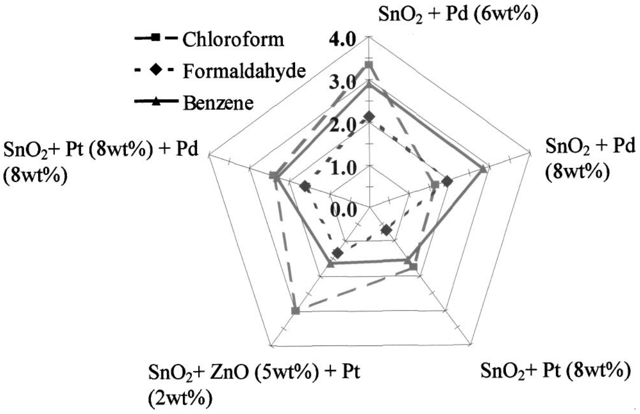

FIG. 4. A radar plot showing responses of the five sensors for different gases at 400 °C. The normalized resistance change corrected for drift is plotted on each axis for each sensor. Each curve represents a different analyte.

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