



Novel Carbon Dioxide Microsensor Based on Tin Oxide Nanomaterial Doped With Copper Oxide

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Abstract

Carbon dioxide (CO₂) is one of the major indicators of fire and therefore its measurement is very important for low-false-alarm fire detection and emissions monitoring. However, only a limited number of CO₂ sensing materials exist due to the high chemical stability of CO₂. In this work, a novel CO₂ microsensor based on nanocrystalline tin oxide (SnO₂) doped with copper oxide (CuO) has been successfully demonstrated. The CuO-SnO₂ based CO₂ microsensors are fabricated by means of microelectromechanical systems (MEMS) technology and sol-gel nanomaterial-synthesis processes. At a doping level of CuO: SnO₂ = 1: 8 (molar ratio), the resistance of the sensor has a linear response to CO₂ concentrations for the range of 1 to 4% CO₂ in air at 450 °C. This approach has demonstrated the use of SnO₂, typically used for the detection of reducing gases, in the detection of an oxidizing gas.

Introduction

Carbon dioxide (CO₂) gas is one of the most challenging gas species to detect due to its high chemical stability. However, there is a significant need for CO₂ sensors for aerospace and commercial applications, especially for low powered microsensors. These applications include low-false-alarm fire detection which detect chemical species indicative of a fire (e.g., CO and CO₂) (ref. 1), as well as for environmental and emissions monitoring (ref. 2). Due to the stable chemical properties of CO₂ gas, only a limited number of CO₂ sensing materials exist. Most existing CO₂ sensors are bulky in size and involve complicated fabrication processes (ref. 3 and 4). The high power consumption for the bulky CO₂ sensor is also a significant issue which needs to be addressed.

While actively working on miniaturizing CO₂ sensors using existing solid electrolyte sensing material (refs. 2, 5, and 6), we have also been aggressively exploring new CO₂ sensing materials. A novel CO₂ sensing material, nanocrystalline tin oxide (SnO₂) doped with copper oxide (CuO) has been successfully demonstrated for CO₂ detection. Contrary to traditional electrochemical-based CO₂ sensors, which involve a multiple-electrolyte structure (refs. 2 to 6) and are hard to miniaturize, the new sensing material is a solid-state resistor-based CuO and SnO₂ mixture allowing straightforward fabrication of the CO₂ microsensor.

Experimental

Sensor Fabrication

The CuO-SnO₂ nanomaterial-based CO₂ microsensors were fabricated utilizing the following process: First, platinum interdigitated electrodes (30 μm wide fingers and spacing) were microfabricated on a quartz substrate (250 μm in thickness) using photolithography and thin-film sputtering. Then, SnO₂ sol gel was synthesized through a water-based sol-gel process using tin chloride (SnCl₄) as a precursor to react with ammonium hydroxide (NH₄OH) (ref. 7). Freshly deposited CuO was produced by reacting copper chloride (CuCl₂) with potassium hydroxide (KOH), followed by removal of excess potassium and chloride ions in the solution. The SnO₂ sol gel was then homogeneously mixed with freshly deposited CuO in different ratios. The mixture was drop deposited on the interdigitated electrode area (1.10 by 0.99 mm). Finally, the sensors were heated at 700 °C for 2 hr to convert the doped sol-gel mixture into a nanocrystalline sensing material, with particle diameters smaller than 20 nm.

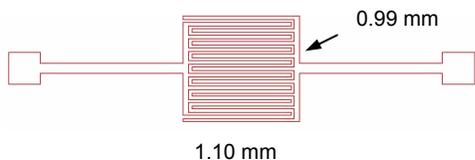


Figure 1.—AutoCAD drawing of the sensor structure, with an interdigitated electrode area of 1.10 by 0.99 mm, and two electrode contacts located at opposite sides.

Figure 1 is a drawing of the interdigitated electrodes showing the size of the electrode area. A wafer of around 50 mm diameter can be used to fabricate up to 100 sensors.

Sensor Testing

The CO₂ microsensors fabricated with different CuO/SnO₂ ratios were tested in a chamber on a heating stage and connected via probes to resistance meters. They were operated by measuring the electrical resistances of the sensor in various gases at a flow rate of 4000 sccm at a temperature of 450 °C.

Results and Discussion

Table 1 lists the CuO doping levels in SnO₂ as analyzed by X-Ray Photoelectron Spectroscopy (XPS), and the corresponding response of these materials to CO₂ gases. Results showed that only at a molar ratio of CuO: SnO₂ = 1: 8, does the microsensor respond to CO₂ at 450 °C.

TABLE 1.—XPS ANALYSIS OF CuO/SnO₂ NANOMATERIALS AND THEIR RESPONSES TO CO₂

Sample number	1	2	3	4	5
CuO: SnO ₂ (molar ratio)	1: 25.7	1: 15.4	1: 8.0	1: 3.4	1: 1.6
Response to CO ₂	No	No	Yes	No	No

Figure 2 shows the testing results of carbon dioxide microsensors (CuO: SnO₂ = 1: 8 in molar ratio) in different gases. The sensor resistance was measured in air, nitrogen (N₂), air (50%)/N₂ (50%), CO₂ (2%)/air (48%)/N₂ (50%) and CO₂ in air from 1 to 4% at 450 °C. Figure 3 is a linear fit of sensor resistance change (compared to the value measured in air) versus CO₂ concentrations from 1 to 4% in air.

Results from table 1, figures 2 and 3 show that linear responses to CO₂ from 1 to 4% in air were achieved at a doping level of CuO: SnO₂ = 1: 8 in molar ratio. No CO₂ response was seen at other doping levels. The baseline of the sensor drifted slightly in air. These observations are being further investigated.

The CuO-SnO₂ nanomaterial-based CO₂ microsensor is a resistor-type sensor, which is fundamentally different both in structure and in measurement approach from the traditional solid electrolyte CO₂ sensor. It can be integrated into a sensor

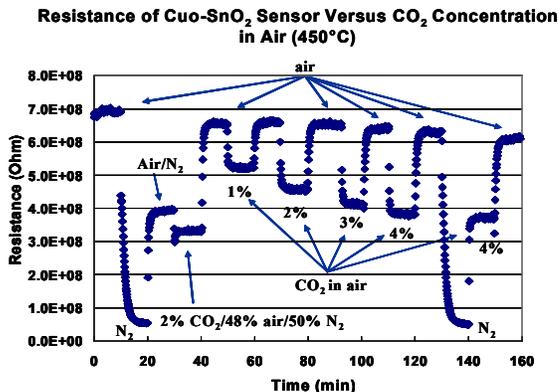


Figure 2.—Resistances of CuO-SnO₂ based microsensor (CuO: SnO₂ = 1: 8 in molar ratio) tested in air, N₂, air (50%)/N₂ (50%), CO₂ (2%)/air (48%)/N₂ (50%) and CO₂ in air from 1 to 4%, with a repeat measurement at 4% CO₂.

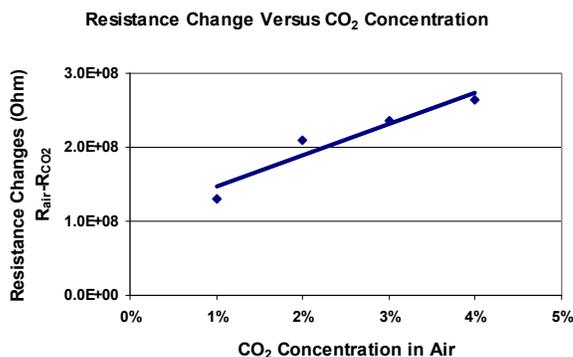


Figure 3.—Linear fitting of sensor resistance change versus CO₂ concentration tested from 1 to 4% CO₂ gases in air.

array to provide signals for aerospace and commercial applications such as fire detection, emission and environmental monitoring. This innovation is also scientifically significant because SnO₂ is an n-type sensing material that has been widely used for detecting reducing gases such as carbon monoxide, hydrogen, and hydrocarbons (ref. 8). This demonstration is the first time to our knowledge of a CuO-SnO₂ sensing material responding to CO₂ gas in a significant and consistent way. This development creates opportunities for the batch fabrication of simple and inexpensive CO₂ microsensors with low power consumption due to their small sizes. It could also lead to research that could alter fundamental knowledge of SnO₂ as a sensing material, leading to a wider range of detectable species. While there are some scientific speculations about the sensing mechanism, it is still not clear to us. Further exploration will include expanding the sensor detection range, improving the sensor baseline stability, and understanding the sensing mechanism.

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