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

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Abstract

Carbon dioxide (CO_2) 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 CO_2 sensing materials exist due to the high chemical stability of CO_2. In this work, a novel CO_2 microsensor based on nanocrystalline tin oxide (SnO_2) doped with copper oxide (CuO) has been successfully demonstrated. The CuO-SnO_2 based CO_2 microsensors are fabricated by means of microelectromechanical systems (MEMS) technology and sol-gel nanomaterial-synthesis processes. At a doping level of CuO: SnO_2 =1: 8 (molar ratio), the resistance of the sensor has a linear response to CO_2 concentrations for the range of 1 to 4% CO_2 in air at 450 °C. This approach has demonstrated the use of SnO_2, typically used for the detection of reducing gases, in the detection of an oxidizing gas.

Introduction

Carbon dioxide (CO_2) gas is one of the most challenging gas species to detect due to its high chemical stability. However, there is a significant need for CO_2 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 CO_2) (ref. 1), as well as for environmental and emissions monitoring (ref. 2). Due to the stable chemical properties of CO_2 gas, only a limited number of CO_2 sensing materials exist. Most existing CO_2 sensors are bulky in size and involve complicated fabrication processes (ref. 3 and 4). The high power consumption for the bulky CO_2 sensor is also a significant issue which needs to be addressed. While actively working on miniaturizing CO_2 sensors using existing solid electrolyte sensing material (refs. 2, 5, and 6), we have also been aggressively exploring new CO_2 sensing materials. A novel CO_2 sensing material, nanocrystalline tin oxide (SnO_2) doped with copper oxide (CuO) has been successfully demonstrated for CO_2 detection. Contrary to traditional electrochemical-based CO_2 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 SnO_2 mixture allowing straightforward fabrication of the CO_2 microsensor.

Experimental

Sensor Fabrication

The CuO-SnO_2 nanomaterial-based CO_2 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, SnO_2 sol gel was synthesized through a water-based sol-gel process using tin chloride ($SnCl_4$) as a precursor to react with ammonium hydroxide (NH_4OH) (ref. 7). Freshly deposited CuO was produced by reacting copper chloride ($CuCl_2$) with potassium hydroxide (KOH), followed by removal of excess potassium and chloride ions in the solution. The SnO_2 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.

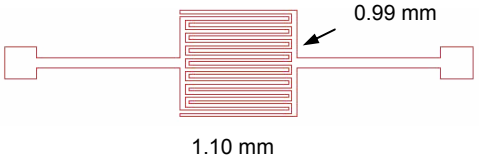

Figure 1.—AutoCAD drawing of the sensor structure, with an interdigitated electrode area of 1.10 by 0.99 mm, and two electrode contacts located at opposite sides.

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 CO_2 microsensors fabricated with different CuO/SnO_2 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 SnO_2 as analyzed by X-Ray Photoelectron Spectroscopy (XPS), and the corresponding response of these materials to CO_2 gases. Results showed that only at a molar ratio of CuO: SnO_2 = 1: 8, does the microsensor respond to CO_2 at 450 °C.

TABLE 1.—XPS ANALYSIS OF CuO/SnO_2 NANOMATERIALS AND THEIR RESPONSES TO CO_2

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: SnO_2 = 1: 8 in molar ratio) in different gases. The sensor resistance was measured in air, nitrogen (N_2), air (50%)/N_2 (50%), CO_2 (2%)/air (48%)/N_2 (50%) and CO_2 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 CO_2 concentrations from 1 to 4% in air.

Results from table 1, figures 2 and 3 show that linear responses to CO_2 from 1 to 4% in air were achieved at a doping level of CuO: SnO_2 = 1: 8 in molar ratio. No CO_2 response was seen at other doping levels. The baseline of the sensor drifted slightly in air. These observations are being further investigated.

The CuO-SnO_2 nanomaterial-based CO_2 microsensor is a resistor-type sensor, which is fundamentally different both in structure and in measurement approach from the traditional solid electrolyte CO_2 sensor. It can be integrated into a sensor

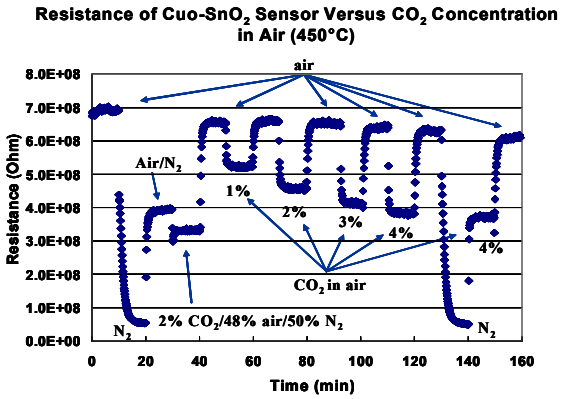

Figure 2.—Resistances of CuO-SnO_2 based microsensor (CuO: SnO_2 = 1: 8 in molar ratio) tested in air, N_2, air (50%)/N_2 (50%), CO_2 (2%)/air (48%)/N_2 (50%) and CO_2 in air from 1 to 4%, with a repeat measurement at 4% CO_2.

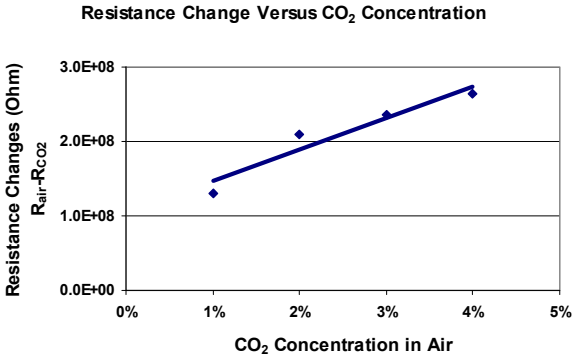

Figure 3.—Linear fitting of sensor resistance change versus CO_2 concentration tested from 1 to 4% CO_2 gases in air.

array to provide signals for aerospace and commercial applications such as fire detection, emission and environmental monitoring. This innovation is also scientifically significant because SnO_2 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-SnO_2 sensing material responding to CO_2 gas in a significant and consistent way. This development creates opportunities for the batch fabrication of simple and inexpensive CO_2 microsensors with low power consumption due to their small sizes. It could also lead to research that could alter fundamental knowledge of SnO_2 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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