Available online at www.sciencedirect.com
ScienceDirect
Sensors and Actuators B 120 (2006) 104–109
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Use of cobalt oxide CoOOH in a carbon monoxide sensor operating at low temperatures

Ren-Jang Wu [a,*], Jhih-Gan Wu [a], Tung-Kang Tsai [b], Chuin-Tih Yeh [c]

[a] Department of Applied Chemistry, Providence University, 200 Chungchi Road, Shalu, Taichung Hsien 433, Taiwan, ROC
[b] Center for Measurement Standards, Industrial Technology Research Institute, National Tsinghua University, Hsinchu 30043, Taiwan, ROC
[c] Department of Chemistry, National Tsinghua University, Hsinchu 30043, Taiwan, ROC

Received 1 August 2005; received in revised form 26 January 2006; accepted 26 January 2006
Available online 13 March 2006

Abstract

Cobalt oxide CoOOH was prepared from a $Co(NO_3)_2$ solution via a precipitation with NaOH and oxidation in air. The prepared samples were characterized by X-ray diffraction (XRD), temperature program reduction (TPR), and thermo-gravimetric/differential thermal analysis (TG/DTA) techniques. The resulting CoOOH was used as a sensing material in a semiconductor type CO sensor. The optimum CO detection working temperature was found to be 80 °C ($S = 6.7$) in this study, while the response time was short (~1 min). CoOOH has better response than Co_3O_4 at low temperatures and can detect CO concentration of 1 ppm. CoOOH offers high CO detection selectivity relative to H_2 ($S_{CO}/S_{H_2} \sim 4$) and good linearity ($R^2 = 0.9903$) for CO concentrations ranging from 1 to 1000 ppm. A probable explanation of the CO sensing characteristics of CoOOH is proposed.

Keywords: CoOOH; CO sensor; Response; TPR

1. Introduction

Carbon monoxide sensors are widely used in many roles, such as measuring the CO concentration of the indoor atmosphere, vehicle emissions, natural gas emissions, and industrial waste, etc. Several different sensing technologies, including electrochemical [1], optical [2], potentiometric [3,4], and resistive [5–15], have been employed to determine CO concentration. Among these types of sensors, the resistive method has the advantages of simplicity of construction and low cost of manufacture.

In recent years many types of sensing materials have been used in resistive CO sensors for various applications. For instance, micro-machining technology [5,6] and the oscillation amplitude method [7] allow SnO_2 CO sensors to achieve low power consumption. However, SnO_2 gas sensors still have the drawback of cross-sensitivity. A new type of platinum resistive film has been used in CO sensors using the principle of oscillation resistance [8]. Thin films of CuCl have been used [9] for CO sensors to sense H_2-rich streams in fuel cells. The foregoing types of CO sensors have high working concentrations in the range of 400–800 ppm [8] and 1000 ppm [9], respectively.

It has been found [17,18] that the catalyst Co_3O_4 can facilitate the rapid oxidation of CO at a temperature of 200 °C or less. By using cobalt oxides as a sensing material, Yamazoe and coworkers [10] improved the response ($S = 160$) of an In_2O_3-based CO sensor by the addition of 0.5 wt.% Co_3O_4 and 0.04 wt.% Au at 250 °C. The optimum working temperature of an In_2O_3-based CO sensor is about 200–250 °C. SnO_2–Co_3O_4 composite films [11] have been found to exhibit either n- or p-type response to CO and H_2 at 100–500 °C depending on the Co_3O_4 content, but there is a lack of interference effect data for this type of CO sensor. Co_3O_4-based films [12] on a silicon substrate used in GasFETs (field effect transistors) can be measured by the resistive method at 240 and 460 °C and the work function method at 30 and 130 °C. Co_3O_4 displays p-type semiconductor behavior and is cross-sensitive to gases CH_4, H_2, NH_3, CO, and NO_2. Since the relative response ratio of CO (50 ppm) to H_2 (100 ppm) is about 1.09 [12], the interference effect is large.

* Corresponding author. Tel.: +886 4 26328001/15212; fax: +886 4 26327554.
E-mail address: rjwu@pu.edu.tw (R.-J. Wu).

0925-4005/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2006.01.053

CoOOH is an active material used in conjunction with nickel hydroxide in Ni–H cells [16]. Cobalt oxide is coated on the positive electrodes of rechargeable alkaline nickel batteries to achieve high electrochemical efficiency. The high conductivity of CoOOH [16] makes it very suitable for use in resistance type gas sensors. In addition, CoOOH is non-stoichiometric and the Co is at a higher oxidation state (+3) than in Co_3O_4 (the oxidation states are +3, +3, +2 and the average is +8/3). Some studies on the oxidation of carbon monoxide [17,18] have shown that Cobalt Co^{+3} ions are active in this reaction. Our research team therefore prepared CoOOH and used it as a CO sensing material. Our results showed that CoOOH had a low working temperature and encountered little interference from other gases.

2. Experimental procedures

2.1. Sensing material

The synthesis of CoO_x in a basic environment is shown in Fig. 1 [19]. NaOH was slowly added to an appropriate amount of the starting material of $Co(NO_3)_2{\cdot}6H_2O$ to form a $Co(OH)_2$ precipitate. The pH value was kept below 9 during the mixing process, and the red color of the $Co(NO_3)_2{\cdot}6H_2O$ gradually changed to deep blue and finally to pink. When the pH was increased to $9 < pH < 14$, the color of the $Co(OH)_2$ precipitate turned brown with the formation $Co(OH)_3$.CoOOH was obtained from $Co(OH)_3$ by a hydrothermal method in air.

2.2. Sensor fabrication

A sensing material was prepared in the form of a paste by mixing an appropriate amount of glycerol, 5 g CoOOH powder, and 1 ml tetraethyl orthosilicate (TEOS) binder. The TEOS binder was a mixture of $Si(OC_2H_5)_4$:H_2O:C_2H_5OH in the weight ratio of 65:8:27. Fig. 2 shows the obverse side of an Al_2O_3 substrate (4 mm × 2.5 mm) with gold electrodes deposited with

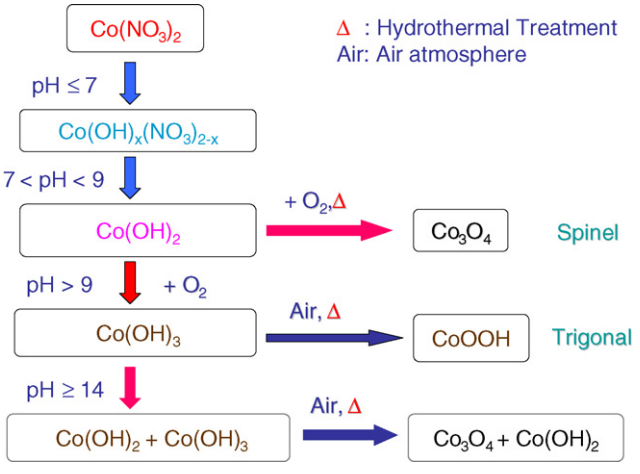
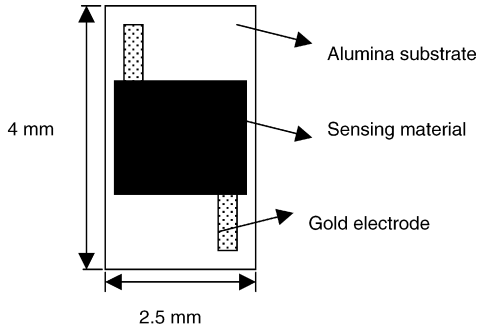
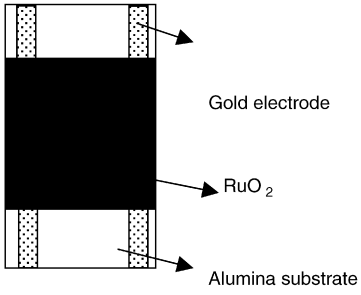


Fig. 1. Synthesis of CoO_x samples.



(a) Connection to measurement circuit



(b) Connection to heating circuit

Fig. 2. Structure of a sensing element: (a) obverse, (b) reverse.

screen-printing. The thick film CoOOH sensing material was also coated on the obverse of the substrate by screen-printing. The printed RuO_2 coating on the reverse of the substrate served to control the reaction temperature.

2.3. Sensing system

The CO sensing chamber employed a dynamic flow system. CO, H_2, CH_4, and NO_2 of 1000 ppm in pure air were used as standard gases. CO gas in the test system was diluted to different concentrations from 1 to 1000 ppm. The flow rate of the testing gas was fixed at 100 cm^3/min during measurements. Resistance signals from the sensor head were transformed to voltages by a simple circuit, and a computer performed data acquisition and processing. A single circuit was designed as follows in order to facilitate measurements. As seen in Fig. 3, the input voltage is V_s ($V_s = 4$ V), the cascade sensor head resistance is R_s, and the reference resistance is R_r. The input data consists of the voltage difference (V_m) across the reference resistance. The sensor resistance and gas response can be obtained from Eqs. (1)–(5):

$$I = \frac{V_s}{R_s + R_r} = \frac{V_m}{R_r} \quad (1)$$

$$R_s = R_r \times \frac{V_s - V_m}{V_m} \quad (2)$$

$$R_{air} = R_r \times \frac{V_s - V_{air}}{V_{air}} \quad (3)$$