

Fast response detection of H₂S by CuO-doped SnO₂ films prepared by electrodeposition and oxidization at low temperature

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ABSTRACT

Fast response detection of H₂S by CuO-doped SnO₂ films prepared by a simple two-step process: electrodeposition from aqueous solutions of SnCl₂ and CuCl₂, and oxidization at 600 °C. The phase constitution and morphology of the CuO-doped SnO₂ films were characterized by X-ray diffraction and scanning electron microscopy. In all cases, a polycrystalline porous film of SnO₂ was the product, with the CuO deposited on the individual SnO₂ particles. Two types of CuO-doped SnO₂ films with different microstructures were obtained via control of oxidation time: nanosized CuO dotted island doped SnO₂ and ultra-uniform, porous, and thin CuO film coated SnO₂. The sensor response of the CuO doped SnO₂ films to H₂S gas at 50–300 ppm was investigated within the temperature range of 25–125 °C. Both of the CuO-doped SnO₂ films show fast response and recovery properties. The response time of the ultra-uniform, porous, and thin CuO coated SnO₂ to H₂S gas at 50 ppm was 34 s at 100 °C, and its corresponding recovery time was about 1/3 of the response time.

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1. Introduction

H₂S, one of the combustion products of fuels, is a highly toxic and flammable gas. The fast monitoring of such toxic gases has therefore become extremely important. CuO doped SnO₂ has been found to be the most sensitive material to H₂S gas [1]. To improve the sensing properties of CuO doped SnO₂, various CuO–SnO₂ materials in such forms as thin/thick films, bulk CuO–SnO₂ [2–5], Cu–SnO₂ bilayers and heterostructures [6–8], and nano-CuO doped SnO₂ [9–13] have been prepared through different techniques, i.e., hydrothermal synthesis [10–12], sol–gel synthesis [11,14], aerosol deposition [15], thermal evaporation [5], sputtering [16], electrostatic spraying [17,18], and screen printing [20]. Although the response time of the CuO doped SnO₂ to the H₂S gas at 20–200 ppm could be decreased to less than 1 min, the recovery time was still long, about 4–8 min [2,17,19–21]. Therefore, it is very attractive to prepare CuO doped SnO₂ with fast response and recovery properties to H₂S gas.

In the present work, CuO doped SnO₂ porous and polycrystalline films have been prepared by an electrodeposition and oxidization method. It was grown different microstructures, like nanosized CuO dotted island doped SnO₂ and ultra-uniform, porous, and thin CuO film coated SnO₂. It has been made a sensor

structure and its gas response of the CuO doped SnO₂ films was found to be fast to H₂S gas at the low temperature.

2. Experimental

The CuO doped SnO₂ films were prepared by an electrodeposition and oxidation method. 1.75 g SnCl₂, 6.25 g Na₂C₆H₅O₇, and balanced distilled water were combined in a 250 mL flask, labeled as solution a. Solution b was prepared by the same method as solution a, except that the SnCl₂ was replaced by 0.1 g CuCl₂.

A piece of indium tin oxide (ITO) glass (10 mm × 20 mm) was dipped in 50 mL of solution a, and a 1 mA current was passed through the ITO glass for 3600 s using an EG&G M273 potentiostat, a platinum counter electrode (1 cm² in area), and a saturated calomel reference electrode, with the electrodes placed near the ITO glass. The same ITO glass was also dipped in 50 mL of solution b, and a 0.7 mA current was passed through it for 600 s using the same method. Tin and copper were nominally deposited on the ITO glass in the atomic ratio of 8.6:1, which was estimated from the electric charge passed.

After the electrodeposition, the ITO glass pieces were fired in air for 8–10 h at 500 °C and 600 °C and the copper and tin on the ITO glass were oxidized during the firing. X-ray diffraction (XRD) patterns of the oxidized films were collected using a Philips PW3040/60 diffractometer at a scanning rate of 0.03° min^{−1} for 2° in the range of 10–80°. Scanning electron microscope (SEM) images of the as-electrodeposited film and the oxidized films were captured using a scanning electron microscope (SSX-550) operated at an acceleration voltage of 30 kV.

Two platinum wires (0.5 mm in diameter) at a distance of 10 mm were fixed on the ITO glass. The platinum wires were fixed onto the ITO glass by a clamp to make a good electric connection. This assembly was then put in the bottom of a one ended and air-tight quartz tube (60 mm in inner diameter, 65 mm in outdiameter, 600 mm in height) and the quartz tube was heated in a vertical furnace. The H₂S gas was diluted in a container. According to the designed detection concentration, a certain amount of the diluted H₂S gas was taken and injected into the quartz tube. The resistance of the oxidized films was recorded by a multimeter (Aglient A34401) and a computer. The sensor response of the oxidized films to the H₂S gas at 50–300 ppm

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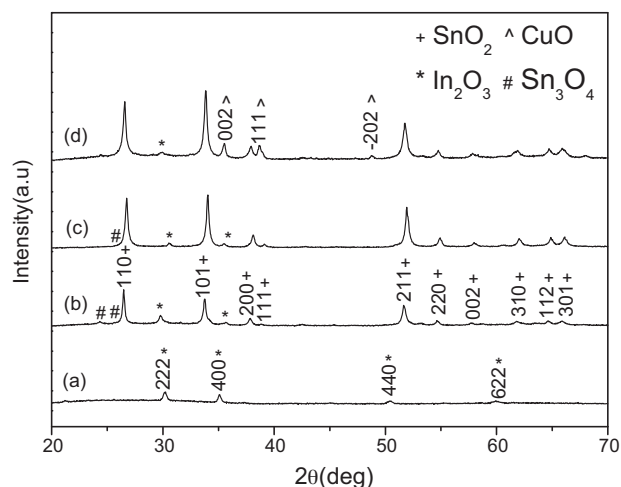


Fig. 1. XRD patterns of the ITO glass substrate and the oxidized films: (a) the ITO glass substrate, (b) tin oxide film fired at 500 °C for 8 h, (c) tin oxide film fired at 600 °C for 8 h, and (d) CuO doped SnO₂ film fired at 600 °C for 8 h.

was tested. When the response remained constant at a fixed operating temperature, air was let in immediately. The temperature of the furnace was controlled at 25, 50, 75, 100 and 120 °C, respectively, by a type N thermocouple and a DTC-2B temperature controller.

3. Results and discussion

The phase and purity of the oxidized films were determined by X-ray diffraction (XRD), and the diffraction patterns are shown in Fig. 1. The diffraction patterns of the ITO glass (In₂O₃ JCPDS card number 03-065-3170) were also collected for comparison. After 8 h firing at 500 °C and 600 °C in air, tin oxide films and CuO doped SnO₂ films were obtained. All the patterns of SnO₂ could be readily indexed to the tetragonal phase of SnO₂ (JCPDS card number 01-077-0447). However, the X-ray diffraction patterns of tin oxide film fired at 500 °C also show peaks corresponding to the triclinic phase of Sn₃O₄ (JCPDS card number 16-0737). With increasing temperature (from Fig. 1(b) and (c)) the intensity of the tetragonal SnO₂ phase increases significantly, while the intensity of the triclinic Sn₃O₄ phase is reduced. In the patterns of CuO doped SnO₂ film fired at 600 °C for 8 h, the diffraction peaks of CuO emerge (JCPDS card number 03-065-2309) (Fig. 1(d)).

Scanning electron microscope (SEM) images of the as-electrodeposited film and the oxidized films are shown in Fig. 2. As can be seen from Fig. 2(a), the as-electrodeposited film consisted of uniformly distributed irregular crystals, some of them presenting rectangular section. Both the average size of the crystals and the average size of the spaces between the crystals are about 3 μm. However, after the as-electrodeposited film was fired for 8 h at 600 °C in air, the as-electrodeposited irregular crystals was destroyed and instead consisted of porous, nanosized, CuO dotted islands on the SnO₂ particles in the film (Fig. 2(b)). The space that existed between the crystals in Fig. 2(a) was largely occupied by the growth of oxide particles. After further firing for 2 h at 600 °C, the nanosized CuO particles were transformed into an ultra-uniform, porous, and thin CuO film coating on the top of the porous SnO₂ particles (Fig. 2(c)).

Sensors were assembled by the CuO doped SnO₂ films connected separately with two platinum wires. The resistances of the sensors in air were first recorded in a few minutes and the H₂S gas at 50–300 ppm was ejected gradually after the resistances are constants and the sensing properties of the CuO doped SnO₂ films to the H₂S gas were measured within the temperature range of

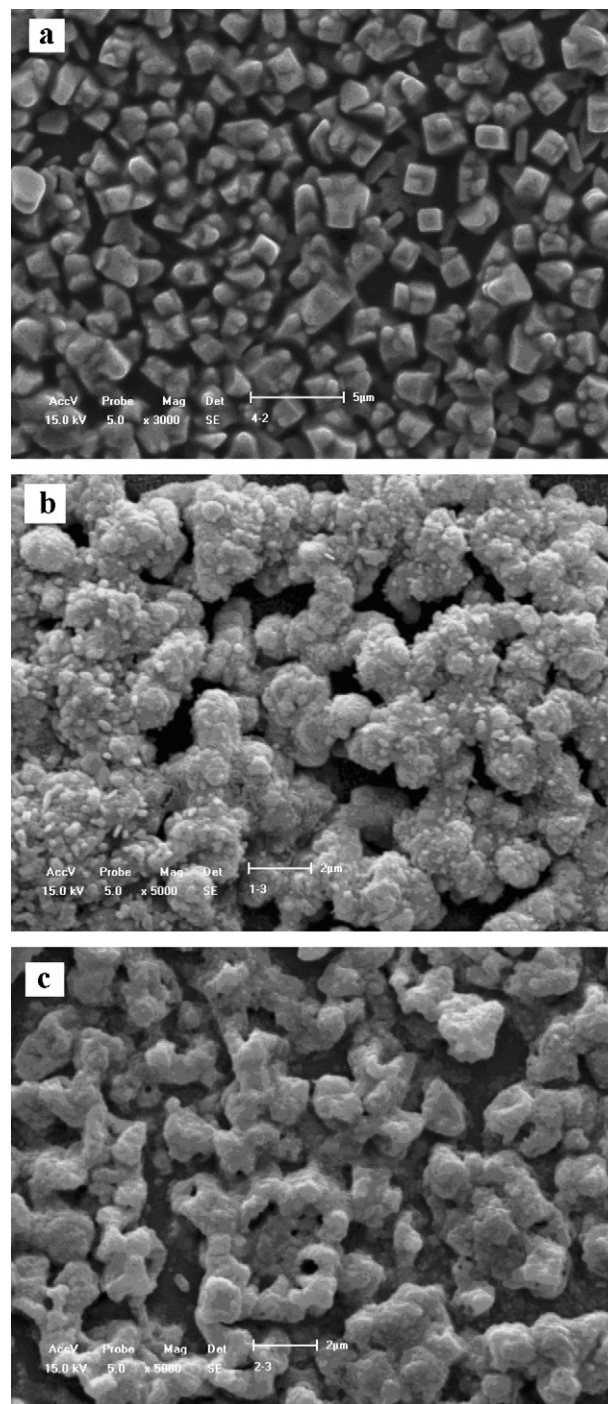


Fig. 2. SEM images of the as electrodeposited film and the oxidized films: (a) as-electrodeposited film with rectangular-shaped crystals, (b) nanosized CuO dotted island doped SnO₂ fired at 600 °C for 8 h, and (c) ultra-uniform, porous, and thin CuO film coated SnO₂ fired at 600 °C for 10 h.

25–125 °C. The sensitivity is defined as R_a/R_g , where R_a and R_g are the resistances in air and in the detected atmosphere, respectively.

Fig. 3 shows the baseline and sensitivities of the CuO doped SnO₂ film as functions of the concentration of H₂S gas and the operating temperature. The sensor resistance is stable before and after the ejection of 100 ppm H₂S gas. The ratio of the resistance before and after the gas ejection is around 3. The sensor response started at room temperature and reached maximum value at 100 °C. With increasing operating temperature, the response times of both the

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