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Highly sensitive and selective butanone sensors based on cerium-doped SnO_2 thin films

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ABSTRACT

Tin oxide (SnO_2) thin films, doped with different concentrations of cerium (Ce), were prepared via a simple sol–gel and dip-coating technique. The surface morphologies and microstructures of the thin films were characterized by field emission scanning electron microscope, atomic force microscopy, X-ray diffraction and Raman spectra. It was revealed that the Ce-doped SnO_2 thin films with rougher surface were composed of smaller crystallites compared with undoped ones. The disordered structures and boundaries of the Ce-doped SnO_2 thin films were also enhanced. Furthermore, the influence factors of gas-sensing properties for butanone, such as cerium concentration, calcination temperature, the layers of thin films and humidity, were investigated. The results indicated that four-layer 1 at% Ce-doped SnO_2 thin films calcined at 500 °C presented the best response. At the optimal working temperature of 210 °C, the response to 100 ppm of butanone vapor was about 181 in dry air. In addition, the gas sensor had a good selectivity for butanone. Finally, the possible mechanism of the Ce addition on the gas-sensing properties was also discussed.

1. Introduction

Recently, easily made drug chemicals have been seriously monitored and detected, because they could often be illegally used to produce drugs. Moreover, some of them, especially butanone and acetone, could cause some accidents in the public owing to their volatile and inflammability. Accordingly, the detection of butanone and acetone is not only important but also necessary for human health and safety. So far, acetone gas sensors have been widely reported. For example, many sensing materials such as $SmFe_{1-x}Mg_xO_3$ perovskite oxides [1], cobalt-doped SnO_2 thin films [2] and In_2O_3 nanowires [3] have been fabricated as gas sensors to detect acetone. However, there are few reports of gas sensors for the detection of butanone till now.

SnO_2 semiconductor gas sensors, especially thin film sensors, have been widely applied to the detection of various poisonous and combustible gases [4–6]. However, how to improve the sensitivity and selectivity of gas sensor is still a challenge for their practical application so far [7,8]. Doping as an efficient method to improve the sensing-performance of gas sensor was widely used. Many metals were doped into SnO_2, including Cu [9], Sb [10], La [11,12] and Pd [13]. Cerium (Ce) as a dopant has received great attention due to its peculiar properties arising from the availability of the 4f shell. For example, Ce-doped SnO_2 nanomaterials have been used to improve ethanol response selectivity in presence of CO, LPG and CH_4 [14]. Based on Ce-doped SnO_2 thin films by using $SnCl_2{\cdot}2H_2O$ and $Ce(NH_4)_2(NO_3)_6$ as precursors, Fang et al. [15] prepared a high sensitivity H_2S sensor at room temperature. Besides, Ce-doped ZnO thin-film gas sensors were also fabricated by dip-coating method, starting from $Zn(CH_3COO)_2{\cdot}2H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$, which exhibited good responses to volatile organic compounds [16]. Moreover, CeO_2 nanowires have been synthesized by a hydrothermal method and applied in fast detecting CO [17] and humidity [18].

Herein, highly sensitive and selective butanone sensor based on Ce-doped SnO_2 thin films was proposed. A series of SnO_2 thin films doped with different concentrations of cerium were prepared via a sol–gel method and dip-coating technique. The surface morphologies and microstructures of thin films were investigated in detail. The influence factors of gas-sensing properties, such as cerium concentration, calcination temperature, the layers of thin films and humidity, have been also investigated.

2. Experimental details

2.1. Preparation of thin films

All the reagents and solvents, which were purchased from Shanghai Chemical Reagent Ltd. Co., were analytical grade and

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used as received without further purification. Undoped and Ce-doped SnO_2 thin films were prepared by a sol–gel and dip-coating process using $SnCl_2{\cdot}2H_2O$ and $CeCl_3{\cdot}7H_2O$ as precursors. The starting sols of undoped and Ce-doped SnO_2 with five different molar concentrations (0.5, 1, 3, 5 and 10 at% cerium) were prepared by a simple procedure. A certain amount of $CeCl_3{\cdot}7H_2O$ and $SnCl_2{\cdot}2H_2O$ were dissolved in 20 ml ethanol. After refluxing at 100 °C for 8 h under magnetic stirring, homogeneous mixtures of precursors were formed. Then aging for two days at room temperature, the transparent sols were obtained. Subsequently, the sols were dip-coated on the ceramic substrate, then dried at 80 °C for 10 min, 150 °C for 20 min and 80 °C for 10 min step by step for the formation of initial thin films. After repeated several times for different layers (2, 3, 4 and 5 times corresponding to 2, 3, 4, and 5-layer, respectively), the samples were calcined in air at 400, 450, 500, 550 or 600 °C for 1 h via program heating, respectively. Finally, undoped and Ce-doped SnO_2 thin films were formed.

2.2. Physical characterization

The morphologies of as-prepared thin films were investigated with a Quanta 200 FEG environmental scanning electronic microscopy (ESEM) and a Veeco Autoprobe CP atomic force microscopy (AFM). The crystalline structural analysis was performed with a Philips X'Pert Pro X-ray diffractometer (XRD) with Cu Kα radiation (1.5418 Å). The Raman spectra of SnO_2 thin films doped with different concentrations of cerium were taken at room temperature in backscattering geometry. Thermo Fisher DXR Raman spectrometer with semiconductor laser beam was carried out at the excitation wavelength of 532 nm.

2.3. Gas-sensing measurement

The gas-sensing properties of thin films were performed with a gas-sensing measurement system similar to our previous reports [19–21]. All results shown in this paper were performed in a closed plastic box (1000 ml) equipped with appropriate inlets and outlets for gas flows. There is a gas container with air and target gases inputs which can be alternated for the requirement (air flow = 1800 ml/min). A Keithley 6487 picoammeter/voltage sourcemeter was employed to serve as both voltage source and current reader. The relative response was defined as:

$$S = \frac{R_a}{R_g}$$

where R_a is the resistance in atmospheric air and R_g is the resistance of the sensor device exposed in the detected gases. The results of the gas-sensing properties were obtained from the repeated measurements of three or more sensors of each type, which were shown in the form of Error bars standing for standard deviation. In addition, the response and recovery time were obtained by the time for 90% of final resistance change.

3. Results and discussion

3.1. Surface morphology and microstructure of thin films

After calcination at 500 °C in air, the surface morphologies of four-layer undoped and Ce-doped SnO_2 thin films were investigated by SEM, and the results were shown in Fig. 1(a)–(f). It was obvious that the Ce-doped SnO_2 thin films turned rougher than undoped ones. The particle sizes were slightly increased with the concentration of cerium increasing from 0 at% to 10 at%. Fur-

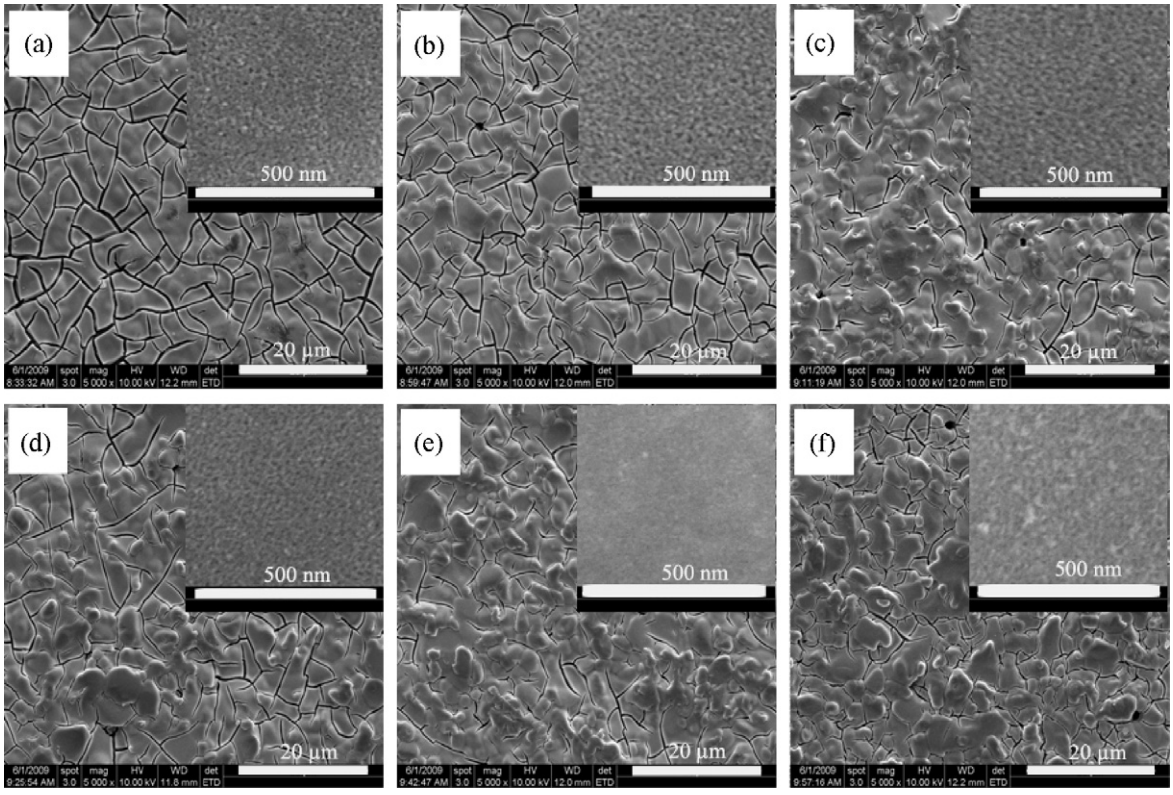

Fig. 1. Low-magnification and high magnification (shown in the insets) SEM images of four-layer SnO_2 thin films calcined at 500 °C with different concentrations of cerium doped: (a) undoped; (b) 0.5 at%; (c) 1 at%; (d) 3 at%; (e) 5 at%; (f) 10 at%.