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ScienceDirect
Sensors and Actuators B 120 (2007) 694–699
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Selective detection of HCHO gas using mixed oxides of ZnO/$ZnSnO_3$

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Received 22 November 2005; received in revised form 23 March 2006; accepted 24 March 2006
Available online 27 April 2006

Abstract

Mixed oxides of ZnO/$ZnSnO_3$ doped with Au element were prepared by a hydrothermal process. The crystal structure, composition and ceramic microstructure of the powders obtained were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The results show that the product is the mixture of ZnO/$ZnSnO_3$; its particle size is about 500 nm with good dispersivity in shape. The sensitivity, selectivity, response and recovery properties of the ZnO/$ZnSnO_3$-based sensors were investigated by mixing a target gas in air. It is found that the sensors have remarkable sensitivity to HCHO vapor and satisfactory selectivity to other gases.

Keywords: HCHO; Gas sensor; ZnO/$ZnSnO_3$; X-ray photoelectron spectroscopy (XPS)

1. Introduction

Formaldehyde, HCHO, is a known carcinogen found in (1) pathology laboratories due to vapors of formalin solutions (40 wt.% formaldehyde, 12.5 wt.% methanol and 47.5 wt.% water) used to preserve tissues, (2) industrial chemical processes, and (3) buildings as a result of condensation polymerization used for building materials, paint and carpets. The hazardous formaldehyde levels in air are mandated on a "long term exposure" basis, e.g. averaged over 1–2-week-period [1]. These factors may act separately or may supplement each other along with inadequate temperature, humidity, and lighting. The indoor air pollution caused by chemical contaminants contained in construction materials has become an important factor, because these compounds are strongly associated with sick building syndrome (SBS). Most indoor air pollution is caused by the sources inside the building. For example, adhesives, upholstery, carpeting, copy machines, manufactured wood products, cleaning agents and pesticides may emit volatile organic compounds (VOCs), including formaldehyde (HCHO). HCHO is a colorless, strong-smelling gas. Its most significant use in homes is as an adhesive resin in pressed wood products. In particular, HCHO is considered as a major cause of SBS [2]. But, there are no continuous electronic sensors available for detection of formaldehyde gas [3]. The demands of accurate and dedicated sensors to provide precise process control and automation in manufacturing processes, and also to monitor and control environmental pollution, which have accelerated the development of new sensing materials and sensor technology in the last decade. The focus was on the development of new sensing materials to improve sensitivity, selectivity and stability of sensors, and also on the development of new and better fabrication techniques to ensure reliability, safety, and reproducibility and to reduce the cost.

Zinc and tin compound oxides have recently attracted considerable attention because they exhibit interesting technological properties, such as high capacity anode material [4], which can also be used to oxygen separation acting as a photocatalyst under the action of visible light [5], and gas sensors [6,7]. For preparation of inorganic solids, a variety of methods have been proposed, such as low-temperature ion exchange, co-precipitation, sol–gel method, hydrolysis of metal alkoxides, etc. [6–9]. However, these methods have some disadvantages, such as complex operating procedures and the high price of raw materials. Furthermore, they generally need high-temperature treatment. On the other hand, a hydrothermal method has frequently been used for preparing ceramic powders for a variety of applications [10]. Perovskite-type $ZnSnO_3$ powder can be used as a new type of

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doi:10.1016/j.snb.2006.03.033

gas sensitive material for detecting reducing gases, such as *i*-C_4H_{10} and ethanol [11]. In the present work, mixed oxides of ZnO/$ZnSnO_3$ doped with Au element were prepared by the hydrothermal synthesis method. The experimental results indicate that the material is a new gas-sensing material for detecting formaldehyde. The ZnO/$ZnSnO_3$-based sensor shows satisfactory sensitivity and selectivity to formaldehyde.

2. Experimental procedure

2.1. Preparation and characterization of mixed oxides of ZnO/$ZnSnO_3$

Micron-sized ZnO/$ZnSnO_3$ particles were synthesized by using a mild hydrothermal method. The proper zinc acetate ($ZnAc_2{\cdot}2H_2O$, analytical grade) and tin tetrachloride ($SnCl_4{\cdot}5H_2O$, analytical grade) were used as starting materials without further purification. The mole ratio of Zn and Sn was 2:1 in the experiment. The raw materials were dissolved into distilled water to form two individual transparent solutions, and then these two solutions were mixed together. A sodium hydroxide (NaOH) solution was added dropwise into the mixture under magnetic stirring, and the solution of $HAuCl_4$ was dropped into the mixture at a mass ratio of about 1.0% Au to ZnO/$ZnSnO_3$. The final mixed solution was transformed into a Teflon-lined autoclave with 75% degree of fill, and the autoclave was sealed and heated at 200 °C for 24 h. The autoclave was cooled naturally to room temperature after the reaction. The white products on the bottom of the autoclave were collected, filtered and washed with distilled water. The samples were obtained after the powder was dried in air at 100 °C for 5 h.

The XRD patterns were recorded at room temperature by using a Philips (XPERT MPD) X-ray diffractometer employing the Cu Kα radiation (40 kV and 45 mA) with a 2θ scanning step of 0.02° and covering the angle range of 10°–70°. The lattice parameters were determined from the *d* values of XRD peaks by a standard least squares refinement method. The morphology (including grain size and distribution) of the samples was observed on a scanning electron microscopy (SEM) (JSM-5600LV) and transmission electron microscopy (TEM model JEM-100CX, JEOL Corporation). The composition of the sample was also characterized by an Axis Ultra X-ray photoelectron spectroscopy (XPS). Photoluminescence spectra were recorded on a UV–vis spectrophotometer (SPEX F212).

2.2. Measurement of the sensing characteristics

The final powders were mixed and ground with an adhesive in an agate mortar to form a gas-sensing paste. The paste was coated on a ceramic tube on which a pair of Au electrodes was previously printed, dried under IR light for several minutes in air, and then sintered at 400 °C for 1 h. At last, a Ni–Cr heating wire was inserted to form a side-heated gas sensor. It was shown in Fig. 1. In order to improve their stability and repeatability, the gas sensors were aged at 300 °C for 240 h in air. The response time is expected as the time required for the variation in conductance of a sample to reach 90% of the equilibrium value after injection of a test gas, and the recovery time is the time necessary for the sample to return to 10% above the original conductance in air after releasing the test gas. The gas sensing properties of ZnO/$ZnSnO_3$ micro-particles were tested in a glass test chamber, the volume of test chamber is 15 L. In general, the concentration of an organic steam tested, such as formaldehyde, benzene, ethanol and 90# petrol, was 50 ppm, while the concentration of other gases was 500 ppm, for example isobutene and hydrogen. The graphic measuring principle is shown in Fig. 2; a heating voltage (V_h) was supplied to the coil for heating the sensor, and a circuit voltage (V_c) was supplied across the sensor and the load resistor (R_L) connected to the sensor in series. The output voltage (V_{out}) across the load resister changed with the type and concentration of the gas measured. The gas response of a gas sensor is defined as $S = R_{air}/R_{gas}$, where R_{air} and R_{gas} are the resistance in air and in a test gas, respectively.

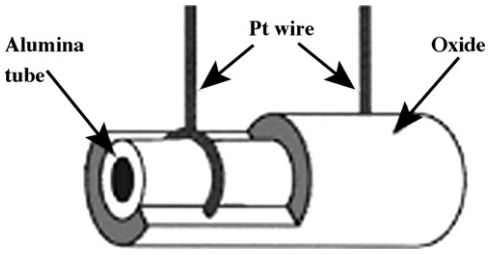

Fig. 1. The photography of gas sensor.

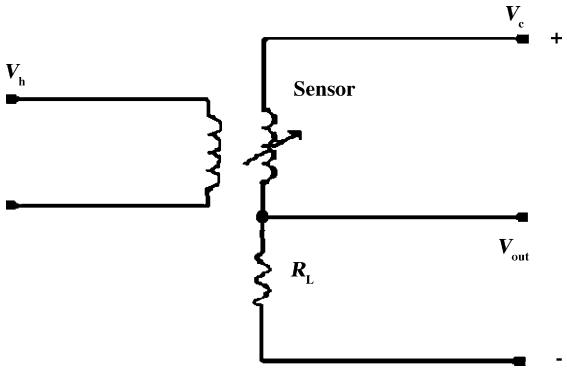

Fig. 2. The photography of testing principle.

3. Results and discussion

3.1. Phase and microstructure

The structure and crystal state of the mixed oxide powders were characterized by X-ray diffraction. Fig. 3 shows a representative XRD pattern of the micro-powder hydrothermally reacted at 200 °C for 24 h. The crystal phase of the material is the mixed oxide of ZnO and $ZnSnO_3$; most of the diffraction peaks can be indexed to face-centered perovskite $ZnSnO_3$, which is consistent with the standard data file 11-0274, and is marked with triangle symbols. The residual peaks marked with spherical symbols can be indexed to ZnO (JCPDS file No. 36-1451). These peaks of ZnO are much weaker than those of $ZnSnO_3$, indicating the presence of a small quantity of ZnO in the prepared sample. On