Sensors and Actuators B 145 (2010) 847–853

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Sensing characterization to NH_3 of nanocrystalline Sb-doped SnO_2 synthesized by a nonaqueous sol–gel route

Yude Wang*, Qiuying Mu, Guofeng Wang, Zhenlai Zhou

Department of Materials Science and Engineering, Yunnan University, 650091 Kunming, Yunnan Province, Peoples' Republic of China

ARTICLE INFO

Article history:
Received 11 October 2009
Received in revised form 21 January 2010
Accepted 29 January 2010
Available online 6 February 2010

Keywords:
Sb-doped SnO_2 nanoparticles
High-resolution electron microscopy
Gas sensor
Ammonia

ABSTRACT

Antimony-doped tin dioxide (ATO) nanoparticles with high crystallinity during solvothermal synthesis in alcohol were generated from the inorganic precursors ($SnCl_4$ and $Sb(OC_2H_5)_3$) and the cationic surfactant (cetyltrimethylammonium bromide, CTAB). The structural and morphological characterizations of the products were performed by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), N_2-sorption isotherm and X-ray photoelectron spectrum (XPS). The resulting particles were highly crystalline oxide particles in the nanometer range (10–14 nm). The indirect-heating sensors using ATO nanoparticles as sensitive materials were fabricated on an alumina tube with Au electrodes and platinum wires. The sensing properties of these sensors based on ATO nanoparticles were investigated. Compared to the original undoped sensor, the results show that the ATO nanoparticles have about 2.5 times increase in response and good dynamic response to NH_3 at low operating temperature (79 °C).

1. Introduction

The metal oxide semiconductor gas sensor is based on the conductivity change of the semiconductor material due to its interaction with gas. When gas molecules are adsorbed on the surface of a semiconductor, electron transfer occurs between the semiconductor and the adsorbates. If the electron affinity of the adsorbates is larger than the work function of the n-type semiconductor, the adsorbates accept electrons from the semiconductor. In the opposite case, the semiconductor accepts electrons from the adsorbates. This electron transfer continues until the Fermi level of the gas-adsorbed semiconductor surface becomes equal to that of the bulk [1]. As a result of this electron transfer, a depletion or accumulation of charges occurs near the semiconductor surface. Then, the accompanying variation of surface potential barrier induces a change in the electrical conductivity or resistivity [2]. Numerous metal oxide semiconductor materials were reported to be used as semiconductor gas sensors, such as ZnO, SnO_2, WO_3, TiO_2, α-Fe_2O_3, and In_2O_3. These candidates have microstructural defects, so free electrons originating from oxygen vacancies contribute to electronic conductivity [3]. The demands for accurate and dedicated sensors to provide precise process control and automation in manufacturing process, and also to monitor and control environmental pollutions, have accelerated the development of new sensing materials and sensors technology [4–9]. Most studies have focused on detecting the toxic and the flammable gases, present in the atmospheric composition in some environments, such as CO_2, CO, SO_2, O_2, O_3, H_2, NO_x, N_2, NH_3 and H_2O [6]. Ammonia is used largely to synthesize various materials in chemical industries. But it is a colorless gas with a special odor and is very harmful to the human body. The investigated results showed that NH_3 could stimulate eye and nose, and result in vomit and headache. Therefore, effective methods to monitor the ammonia have been demanded for atmospheric environmental measurements and control. The ammonia gas sensor is thought to be a desirable means for monitoring atmospheric composition in some environments.

It is believed that sensor sensitivity can be improved by the doping or the increasing specific surface area of the sensitive materials. It was demonstrated that a decrease in the size of the crystallites in the sensing layer leads to a considerable increase in sensitivity [5,10]. The materials will provide more surface sites available for oxygen to be adsorbed on them and to make contact with the surrounding gases [11,12]. The gas sensitivity properties can be greatly promoted by the doping with noble metals [13]. The positive effects of noble metals have been confirmed in many combinations of metals and semiconductors [14–18], and have been utilized extensively in the fabrication of practical gas-sensing devices. As an important member of transparent conductive oxides (TCOs), antimony-doped tin oxide exhibits high optical transmission, electrical conduction, stability and low cost. The synthesis of ATO is of great technological and scientific interests owing to the use of these materials as transparent electrodes, heat mirrors, displays, electrochromic windows, catalysts, rechargeable Li batteries, and energy storage devices and has potential uses in photovoltaic and optoelectronic

* Corresponding author.
E-mail address: ydwang@ynu.edu.cn (Y. Wang).

0925-4005/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.snb.2010.01.070

devices [19–22]. Other interesting features of ATO are their gas-sensing properties.

ATO powders reported previously in literature were prepared basically by high temperature solid-state reactions [23], wet chemical [24] and hydrothermal methods at 350 °C [25]. In these techniques, except for the hydrothermal routes, it is necessary for the samples to withstand a post-calcination at over 500 °C, so that Sb atoms can be incorporated into SnO_2 lattice. As a consequence, grain growth is unavoidable and generally leads to a larger crystallite size and to further agglomeration that results in particles with a low surface area. In view of these disadvantages, nonaqueous solvothermal procedures for crystalline metal oxide nanoparticles production are an alternative route to other processes because they offer several advantages, such as a better control over particle size, and a high crystallinity at relatively low temperature, as well as simplified synthesis parameters. In this work, ATO nanocrystals with a high specific surface area and sizes of about 12 nm were obtained by a facile nonaqueous solvothermal route at a low temperature. The cations (metal) are assembled within the template of CTAB surfactant micelles in a nonaqueous solution. The surfactant CTAB not only provides favorable sites for particulate assemblies growth but, it also influences the formation process, including nucleation, growth, coagulation and flocculation [26]. Surfactant plays an important role in the nanoparticles preparation and it has been succesfully used to prepare SnO_2 in an aqueous solution [27]. To investigate the sensing characteristics of the as-synthesized nanocrystals, the indirect-heating sensors using ATO nanoparticles were fabricated on an alumina tube with Au electrodes and platinum wires. Electrical and sensing properties of the sensors based on ATO nanoparticles to NH_3 in dry air were investigated.

2. Experimental

2.1. Synthesis

All the chemical reagents used in the experiments were obtained from commercial sources as guaranteed-grade reagents and used without further purification. In a typical synthesis of ATO nanoparticles, 1.2 mmol of CTAB, 5.10 mmol of tin chloride (99.0%, Aldrich) and 0.72 mmol of antimony(III) ethoxide ($Sb(OC_2H_5)_3$) were added to 12 mL of alcohol. The atomic Sb-to-Sn ratio is 14.12%. The reaction mixture was transferred into the autoclave (Parr Acid Digestion Bombs, Teflon cups with 45 mL inner volume) and heated at 200 °C for about 24 h. The resulting product was centrifuged, and the precipitate was thoroughly washed with ethanol and dried at room temperature. The undoped SnO_2 sample was also synthesized by the same process.

2.2. Characterization

Powder X-ray diffraction (XRD) data were carried out with a D8 diffractometer from Bruker instruments (Cu-Kα radiation) in reflection mode. The sample was scanned from 20° to 80° (2θ) in steps of 0.05°. The crystallite sizes (D) have been determined from XRD peaks by means of the Scherrer's equation: $D = 0.9\lambda/(\Delta W \cos\theta)$, where λ is the wavelength of X-ray ($\lambda = 0.15418$ nm), θ is the Bragg's diffraction angle, and ΔW is the true half-peak width of the X-ray diffraction lines. Nitrogen adsorption and desorption isotherms of various porous materials were all measured at 77 K with a Micromeritics ASAP 2010 automated sorption analyzer. Prior to the measurement, the sample was degassed at 150 °C overnight under vacuum. For the determination of the specific surface area, the BET method was used. The transmission electron micrographs (TEM) were obtained with a Zeiss EM 912 Ω instrument at an acceleration voltage of 120 kV, while high-resolution transmission electron microscopy (HRTEM) characterization was done using a Philips CM200-FEG microscope (200 kV, $C_s = 1.35$ mm). The samples for TEM were prepared by dispersing the final powders in ethanol; this dispersion was then dropped on carbon–copper grids. X-ray photoelectron spectroscopy (XPS) was measured at room temperature in ESCALAB 250. During XPS analysis, Al-Kα X-ray beam was adopted as the excitation source and power was set to 250 W. Vacuum pressure of the instrument chamber was 1×10^{-7} Pa. Measured spectra were decomposed into Gaussian components by a least-square fitting method. Bonding energy was calibrated with reference to C 1s peak (285.0 eV).

2.3. Detail of the simulating XRD powder pattern

The recorded XRD powder patterns were processed with the Rietveld method using the program FULLPROF. The details were performed as previously reported [28].

2.4. Calculation details of electronic structure

All the calculations in this paper were performed using the CASTEP software package in Material Studio 3.2. CASTEP is a quantum mechanics program based on density functional theory (DFT). The details are similar as previously reported [29].

2.5. Fabrication and testing of sensor elements

In order to prepare series of sensors, we elected the indirect-heating structure [30–32]. As-synthesized ATO nanoparticles used as sensitive layer with a thickness of about 0.6–0.8 mm were deposited on an alumina tube (4 mm in length and 1.2 mm in diameter) with Au electrodes and platinum wires. A Ni–Cr alloy crossed alumina tube was used as a heating resistor (R_H). This resistor ensured both substrate heating and temperature control with the different heating voltages (V_H). Before measuring the gas-sensing properties, the gas sensors were aged at 100 °C for 50 h in dry air. The gas-sensing properties were examined in a chamber through which air or a sample gas (NH_3, diluted in air) was allowed to flow at a rate of 160 cm^3/min. The electrical response of the sensor was measured with an automatic test system, controlled by a personal computer. The export signal of the sensor was measured by using a conventional circuit in which the element was connected with an external resistor in series at a circuit voltage of 10 V. The gas response was defined as R_{air}/R_{NH_3}, where R_{air} is the resistance in dry air, and R_{NH_3} in ammonia.

3. Results and discussion

The experimental X-ray powder diffraction (XRD) pattern of the as-synthesized nanoparticles, together with the calculated pattern obtained from Rietveld refinement and the difference profile are shown in Fig. 1. The experimental XRD pattern shows well-developed diffraction lines of cassiterite SnO_2 (ICDD PDF no. 88-0287), space group $P4_2/mnm$ (136). No other crystalline by-products such as Sb_2O_3 or Sb_2O_5 were found in the pattern, indicating that the as-synthesized sample had cassiterite structure. It implies that the antimony doping most probably occurs by substituting tin atom in crystal structure. For crystalline materials, the size of primary nanoparticles can be estimated by the amount by which the X-ray line is broadened; the crystallites size was about 12.8 nm, as estimated by using Scherrer's equation. The structure of the ATO nanocrystals was refined by the Rietveld method applied on the XRD powder pattern, and the values of unit cell param-