Journal of Alloys and Compounds 540 (2012) 21–26

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

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

Mesoporous three-dimensional network of crystalline WO_3 nanowires for gas sensing application

Yuxiang Qin *, Fei Wang, Wanjiang Shen, Ming Hu

School of Electronics and Information Engineering, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:
Received 10 December 2011
Received in revised form 13 June 2012
Accepted 14 June 2012
Available online 23 June 2012

Keywords:
Tungsten oxide
Nanowires
Gas sensor
Mesoporous oxide

ABSTRACT

Mesoporous three-dimensional (3D) network of crystalline WO_3 nanowires was prepared by nanocasting method using 3D SBA-15 silica with hexagonally ordered mesopores as hard template. After impregnation, mineralization and template removal, a mesoporous 3D framework of ordered crystalline WO_3 nanowires with high specific surface area and stable mesopore channels was formed through the randomly distributed bridging between the neighboring nanowires. The mesostructure of the product was confirmed by low-angle X-ray diffraction (XRD) and nitrogen physisorption measurements. High resolution transmission electron microscopy (HRTEM) images indicate the single crystal structure with different crystal orientation for mesoporous particles. The gas sensing properties of the mesoporous 3D WO_3 nanowires replica were investigated at 50 °C up to 200 °C over NO_2 concentration ranging from 15 to 500 ppb. The results indicate that the mesoporous 3D WO_3 nanowires exhibits high response, good selectivity and fast response–recovery characteristics in the detection of sub-ppm and ppb level NO_2 at the optimal operating temperature of 125 °C due to the stable mesopore channels, large surface area and perfect single-crystal structure.

1. Introduction

Semiconductor metal oxides have been widely used for sensing gases and vapors [1,2]. Their sensing mechanism lies in the changes of electrical conductivity in the presence of toxic gases and oxygen due to catalytic reduction/oxidation reactions occurring at the metal oxide surface. Therefore, the sensing response of oxide films is highly dependent on their surface structure and morphology [3,4]. For a high sensitivity and a fast response rate, sensing materials should exhibit large specific surface areas and high accessibility of gas molecules to the materials surface by diffusion. At present, various nanostructured metal oxide materials with one-dimensional or mesoporous features have been widely investigated as candidates for high performance gas sensors applications. Semiconductor metal oxides with one-dimensional nanostructure, such as nanowires, nanorods and nanobelts, can exhibit very good gas sensing properties at relative low operating temperature due to their large specific surface areas and dimensions comparable to Debye length [5,6]. In addition, nanostructured mesoporous oxides presenting well defined porosity and remarkably large surface areas are another class of sensing materials with wide application prospect [7,8].

Since the successful synthesis of MCM-41 [9], great efforts were made to prepare mesoporous oxide materials other than silica. Up to now, many mesoporous oxides such as Co_2O_3, Cr_2O_3, SnO_2, In_2O_3, MnO_x, etc. have been synthesized successfully by nanocasting method, i.e. hard template route [10–12]. In this method, the voids of a preformed mesoporous solid are used as templates for accommodating appropriate precursors by means of impregnation. Further mineralization of the precursors and removal of the solid templates leads to a mesostructured replica of the desired oxide. Usually, MCM-41, SBA-15, FDU-12 and SBA-16 are the most frequently used hard templates for preparing mesoporous metal oxides. Among various metal oxide semiconductors, tungsten oxide, which is a wide band-gap n-type semiconductor, has been considered as a promising sensing material for detection of toxic and dangerous gases such as NO_2, H_2, O_3, NH_3, H_2S [13,14]. Mesoporous WO_3 replica synthesized by using cubic KIT-6 or traditional SBA-15 as hard template have shown high sensitivity and response rate to NO_2 gas at the optimal operating temperature of 230 °C [15,16]. Of the used hard templates, great interests have been focused on SBA-15 due to its unique mesoporous system, i.e. hexagonal-ordered cylindrical pores with interconnected micropore channels in the walls [17]. The micropore channels between the hexagonally ordered 1D pores of the traditional SBA-15 can be expand to form 3D mesoporous network by rising the temperature of hydrothermally synthesis or adding organic cosolvents [18]. Thus, it is possible to synthesize 3D frameworks of crystalline nanowires with

* Corresponding author. Address: School of Electronics and Information Engineering, Tianjin University, No. 92, Weijin Road, Nankai District, Tianjin, China. Tel.: +86 22 27402372; fax: +86 22 27401233.
E-mail address: qinyuxiang@tju.edu.cn (Y. Qin).

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http://dx.doi.org/10.1016/j.jallcom.2012.06.058

stable mesopore structure and high specific surface area by choosing 3D SBA-15 as template. In this work, we prepared a semiconductor gas sensor based on the mesoporous 3D single crystalline WO_3 nanowires. The material was synthesized by a structure replication procedure from 3D SBA-15, which was prepared hydrothermally using butanol as organic cosolvent. The unique properties of the nanocasted 3D WO_3 nanowires, such as well defined porosity, highly stable mesoporous structure and large specific surface area, arise from its unique microstructure. The sensing properties of the material to NO_2 gas was investigated and found to be capable of NO_2 detection at ppb level with quick response–recovery characteristics and good selectivity.

2. Experiment

2.1. Synthesis and characterization

The synthesis of mesoporous 3D WO_3 nanowires network was accomplished by using mesoporous 3D SBA-15 silica as structure matrix.

3D SBA-15 was synthesized in acidic conditions by the modified process shown in the literature [18] using the pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$) as template and tetraethyl orthosilicate (TEOS) as silicon source. P123 and TEOS were all purchased from Aldrich Corporation. Five grams of P123 was dissolved in 181 ml deionized H_2O and 9.8 g of concentrated HCl (35%) at room temperature to form a solution. Then 4 g butanol was added into the above solution under vigorously stirring. After stirring for 1 h at 35 °C, 10.75 g of TEOS was added and continue to stir for 24 h at 35 °C. The resulted gel was transferred to and sealed in a Teflon-lined stainless steel autoclave. The hydrothermal treatment was conducted at 100 °C for 24 h in an electric oven. After that, the autoclave was cooled naturally to room temperature. The solid product was centrifuged and washed sequentially by deionized water and ethanol several times, and the obtained white powder was dried at room temperature and calcined at 550 °C for 4 h in air for the removal of the P123 block copolymer.

For the synthesis of mesoporous 3D WO_3 nanowires powder, the 3D SBA-15 silica got above was used as hard template and silicotungstic acid was used as precursor in a two-step impregnation process. In a typical synthesis, 2 g of silicotungstic acid was dissolved in 20 ml of ethanol, and then 1.2 g of silica template was added. After stirring for 6 h at room temperature, the mixture was centrifuged, dried and calcined at 300 °C for 1 h in air. In the second impregnation step, the resultant solution of the last centrifugation was used again and the same impregnation step was repeated. After drying at room temperature, the second calcination was performed at 600 °C for 4 h in air (heating rate 1°/min). Finally, the silica template was removed by stirring the SBA-15/WO_3 sample in 40 ml of 10% (v/v) HF solution for 6 h at room temperature. The WO_3 replica was thus obtained by centrifuging, washing sequentially with deionized water and ethanol, and then air-dried.

The morphology and crystalline structure of as-prepared samples are characterized with a field emission transmission electron microscopy (TEM, TECNAI G^2F-20) and an X-ray diffractometer (XRD, RIGAKU D/MAX 2500 V/PC, Cu Kα radiation). Brunauer–Emmett–Teller (BET) nitrogen physisorption measurement was performed on a Quantachrome NOVA automated gas–sorption system. Prior to measurement, sample was vacuum-dried at 200 °C for 10 h.

2.2. Sensor preparation and measurement

The gas sensing properties of the WO_3 replica was evaluated by measuring the change in resistance of the mesoporous 3D WO_3 nanowires based sensor under varying NO_2 concentration. The sensor was fabricated by spin coating the slurry of synthesized mesoporous WO_3 nanowires powder on the cleaned alumina substrates which were attached with a pair of interdigitated Pt electrodes. With the aid of a shadow mask, the patterned electrodes were deposited on the substrates by rf magnetron sputtering technique in a pure argon ambience, using a metallic Pt target (99.95%). The vacuum chamber was first evacuated to a base pressure of 4×10^{-4} Pa and then was kept at 2 Pa during Pt film deposition by controlling argon flow with a mass flow controller. After pre-sputtering about 10 min with the shutter closed, the deposition process was performed for 8 min under a fixed sputtering power of 100 W. The obtained Pt electrodes was about 100 nm in thickness. The coating slurry was prepared by ultrasonically mixing terpineol and tungsten oxide powders in appropriate quantity. For preparing the film, the spinning was controlled to 3000 rpm and the period of coating was 20 s. The coated sensing film was dried in air for 30 min and subsequently annealed at 300 °C for 1 h at ambient atmosphere in a program-controlled furnace to burn out the organic vehicle (i.e. terpineol) used in the preparation of the coating slurry as well as to enhance the adherence of the sensing film to the sensor substrate. Temperature was raised using a slow ramp of 2.5 °C/min in order to avoid the possible occurrences of cracks in the films.

To investigate the film thickness effects on the gas sensing properties, two other tungsten oxide film samples with the estimated film thickness of 500 and 1500 nm were prepared by increasing the number of spin-coatings to two and five times, respectively. When spin-coatings were repeated, the coated film was dried at 100 °C for 15 min before the next coating.

The gas-sensing measurements were carried out in a computer-controlled gas sensing testing system consisting of a test chamber, a flat heating plate, a professional digital multimeter and a data acquisition system [19]. The pure NO_2 gas was injected into the chamber directly to get the desired concentration. An UNI-T UT70D professional digital multimeter was used for continuously monitoring the resistance change of the sensors during the whole measurement process. The sampling interval was set to 1 s. The operating temperature changed from 50 to 200 °C by adjusting the temperature controller of the heating plate.

3. Results and discussion

3.1. Characterization of mesoporous WO_3

The powder WO_3 replica was investigated by X-ray diffraction (XRD). Fig. 1(a) shows the low-angle XRD of the sample obtained after two cycles of impregnation and oxide formation at 600 °C, as described in the experimental section. The inset is the low-angle XRD pattern of 3D SBA-15 silica. WO_3 replica exhibits characteristic peak of the same space groups as the silica template. The obvious diffraction peak appearing at low angle region, which can be assigned to the (100) reflection of the hexagonal SBA-15 silica matrix [20,21], revealed the formation of ordered mesoporous structure. However, in comparison to the XRD pattern of SBA-15 template shown in the inset in Fig. 1(a), the other two peaks with lower intensity below $2\theta = 2^o$, i.e. (110) and (200) diffraction peaks, could not be distinguished, indicating the relative lower overall nanostructural order of the WO_3 replica than the respective silica matrix. The wide-angle XRD pattern of the mesoporous WO_3 is shown in Fig. 1(b). All peaks are in agreement with the monoclinic phase of WO_3 with lattice parameters of $a = 7.297$ Å, $b = 7.539$ Å, $c = 7.688$ Å and $\beta = 90.91^o$ (JCPDS No. 43-1035). The

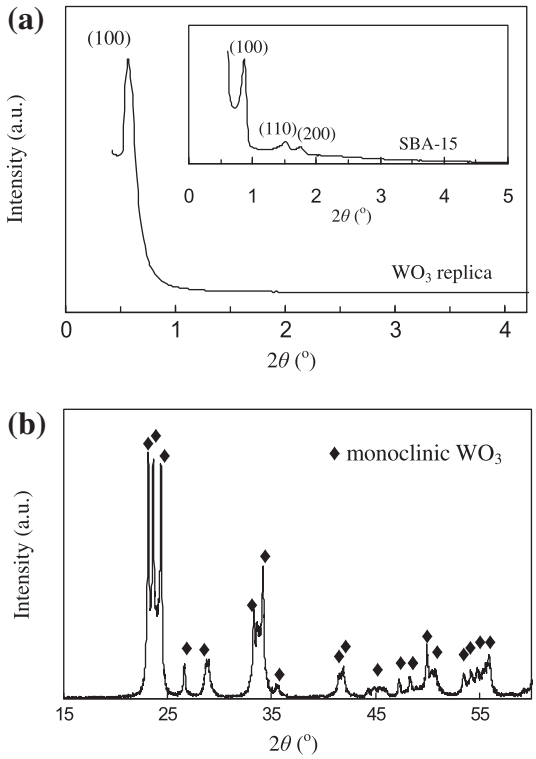

Fig. 1. Low-angle (a) and wide-angle (b) XRD patterns of tungsten oxide powder replicated from mesoporous 3D SBA-15 silica phase. The inset in (a) is the low-angle XRD pattern of 3D SBA-15.