Solid State Sciences 12 (2010) 1857–1860

Contents lists available at ScienceDirect

Solid State Sciences

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

Gas sensing selectivity of hexagonal and monoclinic WO_3 to H_2S

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ARTICLE INFO

Article history:
Received 22 November 2008
Received in revised form
9 November 2009
Accepted 10 January 2010
Available online 18 January 2010

Keywords:
Tungsten oxide
Hexagonal
Monoclinic
Gas sensor
Selectivity
H_2S

ABSTRACT

Hexagonal and monoclinic tungsten oxide (h- and m-WO_3) samples were produced by annealing hexagonal ammonium tungsten bronze, $(NH_4)_{0.07}(NH_3)_{0.04}(H_2O)_{0.09}WO_{2.95}$ at 470 and at 600 °C, respectively. Their structure, composition and morphology were analyzed by XRD, Raman, XPS, ^{1}H-MAS NMR and SEM. In order to study the effect of crystal structure on the gas sensitivity of tungsten oxides, h- and m-WO_3 were tested as gas sensors to CH_4, CO, H_2, NO and H_2S (1000 and 10 ppm) at 200 °C. Monoclinic WO_3 responded to all gases, but its gas sensing signal was two magnitudes greater to 10 ppm H_2S than to other gases, and it also detected H_2S even at 25 °C. Hexagonal WO_3 responded only to 10 ppm H_2S. Its sensitivity was smaller compared to m-WO_3, however, the response time of h-WO_3 was significantly faster. The gas sensing tests showed that while m-WO_3 had relative selectivity to H_2S in the presence CH_4, CO, H_2, NO; h-WO_3 had absolute selectivity to H_2S in the presence these gases.

1. Introduction

Several semiconductor oxides (e.g. SnO_2, In_2O_3, ZnO_2, TiO_2, etc.) are excellent gas sensors due to their high sensitivity to various gases (EtOH, H_2, NH_3, NO, CO, H_2S, O_3, H_2O, etc.) [1–4], though gas selectivity is still a great challenge. The different polymorphs of these materials may have different gas sensitivity (e.g. in the case of TiO_2, the anatase phase has better performance as gas sensor than the rutile phase [4]).

WO_3 is an n-type semiconductor, and it is one of the most studied oxide materials for gas sensing [5,6]. Generally the monoclinic (m-) polymorph of WO_3 is used in gas sensors. However, WO_3 has other (e.g. hexagonal, pyrochlore) polymorphs also [7] and recent studies showed that hexagonal (h-) WO_3 had considerable gas sensitivity [8–11]. Though h-WO_3 can be prepared in many ways (e.g. by hydrothermal treatment of alkali tungstates [8,9,12], by thermal evaporation and oxidation of tungsten metal [13], by thermal [11,14,15] or wet chemical [16] oxidation of hexagonal ammonium tungsten bronze, by thermal oxidation of ammonium polytungstates [17]), the most frequently used preparation method is the hydrothermal synthesis. Recently it was shown that the h-WO_3 sample prepared by annealing hexagonal ammonium tungsten bronze (HATB), $(NH_4)_xWO_3$, was more sensitive to NH_3, than the h-WO_3 sample prepared hydrothermally [8,9,11].

Since there were relatively few reports on the gas sensitivity of h-WO_3 [8–11], and mostly it was tested to NH_3, we intended to study it for sensing other gases. Our aim was to explore, if the hexagonal polymorph of WO_3 had different gas sensing properties than monoclinic WO_3 – similarly to TiO_2.

Therefore, we prepared h- and m-WO_3 by annealing HATB in air at 470 and at 600 °C, respectively. The use of the same precursor, and the similar preparation route ensured that h- and m-WO_3 had similar morphology and thus their gas sensing property could be compared in a reliable way. The structure, composition and morphology of h- and m-WO_3 were analyzed by X-ray powder diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), solid state ^{1}H-MAS (magic angle spinning) NMR spectroscopy and scanning electron microscopy (SEM). The gas sensitivity of tungsten oxides was tested to CH_4, CO, H_2, NO and H_2S (1000 and 10 ppm) at 200 °C.

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doi:10.1016/j.solidstatesciences.2010.01.019

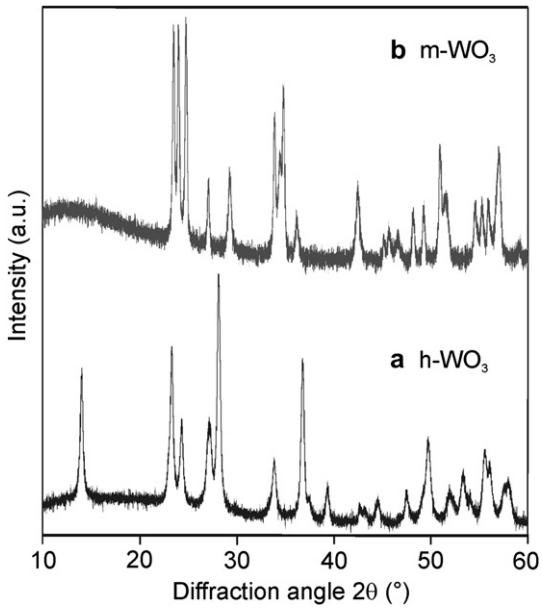

Fig. 1. XRD patterns of (a) h-WO_3; (b) m-WO_3.

2. Experimental

The h-WO_3 sample was prepared by annealing hexagonal ammonium tungsten bronze (HATB), $(NH_4)_{0.07}(NH_3)_{0.04}(H_2O)_{0.09}WO_{2.95}$ in air at 470 °C [11]. The m-WO_3 sample was prepared by annealing HATB in air at 600 °C [11]. The HATB precursor was prepared by annealing ammonium paratungstate tetrahydrate, $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$, in H_2 at 400 °C [18].

XRD pattern of h-WO_3 was obtained by a PANalytical X'pert Pro MPD X-ray diffractometer equipped with an X'Celerator detector using Cu K_α radiation.

Raman spectra were collected by a Jobin Yvon Labram instrument attached to an Olympus BX41 microscope. Frequency doubled Nd–YAG laser (532 nm) was applied as exciting source with 1 mW applied power.

XPS spectra were recorded on a VG Microtech instrument using Mg K_α radiation. The spectrometer was calibrated with the binding energy of the C1s line (284.5 eV).

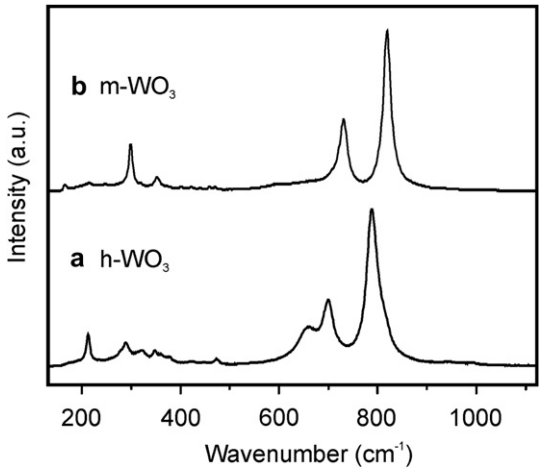

Fig. 2. Raman spectra of (a) h-WO_3; (b) m-WO_3.

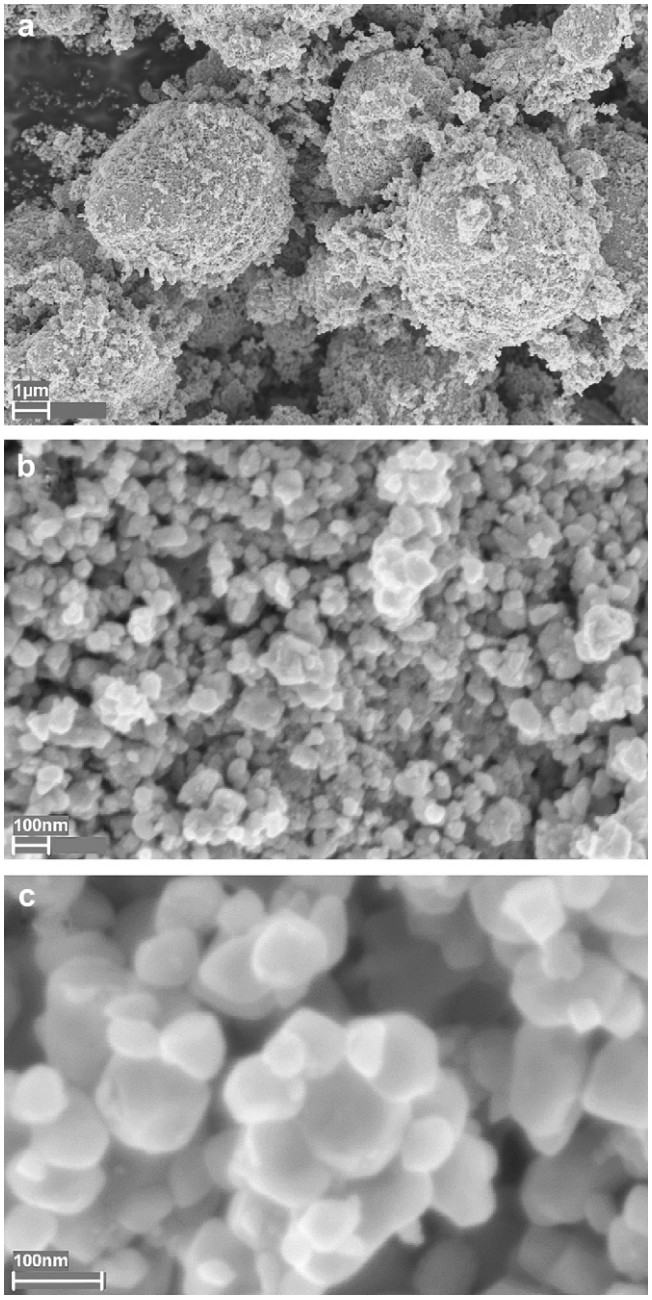

Fig. 3. SEM images of (a) micro-meter sized scale aggregated blocks of h-WO_3; (b) nanoparticles of h-WO_3; (c) nanoparticles of m-WO_3.

^{1}H-MAS NMR experiments were carried out on a VARIAN NMR SYSTEM spectrometer (600 MHz for ^{1}H) using a 3.2 mm HXY VARIAN/Chemagnetics probe. ^{1}H chemical shifts were referenced to adamantane ($\delta_{1H} = 0$ ppm). Spectra were recorded under the same experimental conditions. 16 transients were acquired at 12 kHz spinning rate and a recycle delay of 20 s was used. Background suppression DEPTH [19] was employed to remove signals from the probe.

SEM characterization was performed by a LEO-1550 FEG SEM instrument.

To measure the gas sensitivity, Al_2O_3 sensors sheets with Pt electrical contact were used. Sensing layers were produced by drop coating the sensor sheets with dispersions of h-WO_3 and m-WO_3 in ethanol. Sensing properties were tested to different