Sensors and Actuators B 268 (2018) 129–135

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

Gas sensing properties of p-type $CuBi_2O_4$ porous nanoparticulate thin film prepared by solution process based on metal-organic decomposition

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ARTICLE INFO

Article history:
Received 18 December 2017
Received in revised form 20 March 2018
Accepted 21 April 2018
Available online 22 April 2018

Keywords:
$CuBi_2O_4$
Thin film
Solution process
p-Type
Gas sensor

ABSTRACT

Exploring the novel semiconductor-type gas sensors based on complex oxides beyond binary oxides extends the degrees of freedom in chemical sensor research with structural and compositional versatility. In particular, such complex oxides have been reported to exhibit characteristic and promising gas sensing properties, which are mediated by chemical defects. In this work, $CuBi_2O_4$ has been prepared in the form of porous nanoparticulate thin film with high surface area-to-volume ratio and small amount of defect (Cu^+–oxygen vacancy ($V_O^\bullet$) complex) by the simple solution process based on metal-organic decomposition (MOD). The film exhibited high gas responses with the specific values of 10.8 toward C_2H_5OH, 4.2 toward H_2, and 2.2 toward CO when measured with 1000 ppm at 400 °C. The particularly high H_2S responses (4.7 with 1 ppm, 5.9 with 2 ppm, and 7.4 with 5 ppm) were obtained at 400 °C by the oxidation of H_2S on the $CuBi_2O_4$ surface. Upon exposure to the oxidizing NO_2 gas with low concentrations ($\leq$5 ppm), the resistance of $CuBi_2O_4$ thin film sensor was uncommonly increased.

1. Introduction

Metal-oxide semiconductor gas sensors have been widely studied because of the advantages of their low cost, flexible production and simple usability [1–5]. The performance of gas sensors is evaluated in terms of sensitivity, selectivity, and response/recovery time, and long-term stability [4,5]. Their gas sensing mechanism is demonstrated by three independent factors of receptor function, transducer function, and peculiarities of sensor construction [4]. In particular, the receptor function is mediated by the chemiresistive variation, which resulting from the change in width of electron depletion layer (n-type) or hole accumulation layer (p-type) in the near-surface region of sensor by the adsorption and desorption of atmospheric oxygen and target gas [6,7].

Most studies of the sensor materials have focused on binary oxides such as SnO_2, In_2O_3, NiO, and CuO owing to the facileness of preparation and structural modification, while their property control and performance improvement have been limited. Alternatively, the complex oxides with three or more elements can be explored as promising gas sensor materials with structural and compositional versatility, but their gas sensing properties are little known. Several attempts have been made to grasp the gas sensing characteristics of various perovskite oxides (ABO_3) such as $SrTiO_3$, $CaTiO_3$, $BaTiO_3$, $BaSnO_3$, $SrTi_{1-x}Fe_xO_{3-\delta}$, $LaFeO_3$, $LaCoO_3$, $YMnO_3$, and lathanoid oxides [8–16]. Also, a few studies were reported in delafossite (ABO_2) oxides such as $CuAlO_2$, $CuCrO_2$, and $CuFeO_2$ [17–19], and spinel oxides (AB_2O_4) such as $ZnFe_2O_4$, $CdFe_2O_4$, $MgFe_2O_4$, $NiFe_2O_4$, $CaFe_2O_4$, and $CuFe_2O_4$ [20–27]. Their gas sensing properties are suggested to be commonly modulated by the variations in cationic oxidation, stoichiometry, defect state, and charge carrier concentration.

Most recently, we have found that p-type $CuBi_2O_4$ with a tetragonal crystal structure (P4/ncc) exhibits promising gas sensing characteristics, depending on the defect condition, where it shows particularly high gas response toward ethanol (C_2H_5OH) [28]. In the first report on $CuBi_2O_4$ gas sensor, the $CuBi_2O_4$ has been prepared by the newly exploited powder synthesis technique using polymerized complex method (or Pechini process), and its intrinsic defect condition has been controlled by varying the calcinations temperature [28]. The powder-based $CuBi_2O_4$ gas sensors prepared with the particle size of 0.5–2.0 μm in diameter have provided room

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https://doi.org/10.1016/j.snb.2018.04.105
0925-4005/

for the performance improvement through thin-film processing or nanostructuration.

In the present work, the $CuBi_2O_4$ porous nanoparticulate thin film has been prepared by the simple solution process based on metal-organic decomposition (MOD) which was previously developed [29], and its gas sensing properties have been investigated. This work demonstrates the first examination of gas sensing properties of $CuBi_2O_4$ thin film, not previously known. Moreover, the solution process based on MOD possesses the advantages of easy composition tuning and simple rapid processing route with a minimal reactivity between precursor compounds [29]. This work shows the first successful use of the $CuBi_2O_4$ thin film prepared by such an advanced solution process as a gas sensor. As a consequence, it is found that the $CuBi_2O_4$ thin-film sensor exhibits high gas responses and fast response/recovery rates toward C_2H_5OH, H_2, and CO gases, which are superior to those of the powder-based counterpart due to its higher surface area-to-volume ratio and higher defect concentration. Toward H_2S and NO_2, the characteristic response behaviors were observed depending on gas concentration and operating temperature.

2. Experimental

2.1. Preparation of MOD precursor solution and $CuBi_2O_4$ thin film

The copper(II) acetylacetonate ($Cu(C_5H_7O_2)_2$, ≥99.99% purity) and bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$, ≥99.99% purity) were purchased from Sigma-Aldrich and used without a further purification. The solutions of 0.045 M copper(II) acetylacetonate and 0.15 M bismuth(III) nitrate pentahydrate in acetic acid (≥99.7%, Sigma-Aldrich) were prepared separately by stirring magnetically for 6 h at room temperature. Thereafter, the two solutions were mixed and 20 ml of acetylacetone (99% purity, Sigma-Aldrich) was further added to the solution, followed by stirring to show a transparent turquoise color. A 1:2 mol ratio between Cu(II) and Bi(III) was set in the solution. The solution was stable for 3 months under ambient conditions. The 30 μl precursor solution was dropped onto a SiO_2 (2 μm)/Si substrate, divided into five drops using a micropipette. The dropped solution was dried for 10 min in ambient air and this dropping-and-drying process was repeated once more. The dried solution film was calcined at 550 °C for 4 h in air using a box furnace and finally $CuBi_2O_4$ film on the SiO_2 (2 μm)/Si substrate was obtained.

2.2. Structural characterization

The film morphology and phase were observed by field-emission scanning electron microscope (FE-SEM, JEOL JSM-6500F) and the X-ray diffraction (XRD, D8-Advance, Bruker Miller Co.) using Cu Kα1 radiation (λ = 1.5406 Å), respectively. The chemical composition of film surface was investigated by X-ray photoelectron spectroscopy (XPS, SIGMA PROBE, ThermoVG, UK) with micro-focused monochromatized Al Kα radiation (1486.6 eV). The energy calibration was achieved by setting the hydrocarbon C1s line at 284.5 eV.

2.3. Fabrication and measurement of $CuBi_2O_4$ gas sensor

For the fabrication of gas sensor, a pair of comb-like Pt electrodes were deposited on the $CuBi_2O_4$ thin film (232 nm thickness) formed on the square area 1 cm × 1 cm of SiO_2/Si substrate by sputtering through a mask. The gap between Pt electrodes was 0.2 mm and the width was 8 mm. This was followed by firing for a short time at 550 °C without a change in the morphology or phase. Thereafter, Au wires were attached to the electrodes using Ag paste, and the samples were dried at 80 °C in a conventional oven. The sensor was placed in a quartz tube located inside an electrical tube furnace with a gas inlet/outlet system. The sensor responses were obtained by measuring the changes in the electrical resistance between gas flow (with varying concentrations) balanced with air and pure dry-air flow in the operating temperature range of 300–500 °C using a multimeter (Keithley 2002).

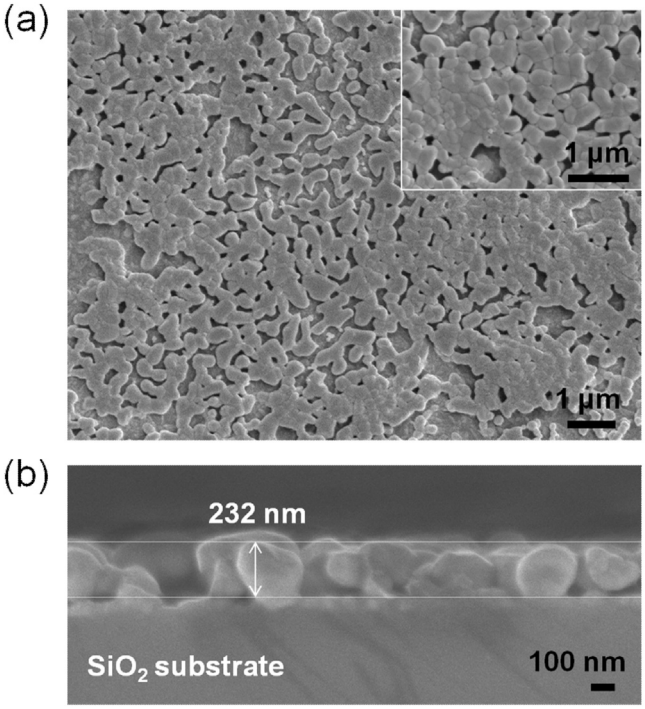

Fig. 1. (a) The surface and (b) cross-sectional FE-SEM images of $CuBi_2O_4$ thin film.

3. Results and discussion

The surface and cross-sectional morphologies of $CuBi_2O_4$ thin film prepared on a SiO_2/Si substrate by the MOD-based solution process, observed by FE-SEM, are shown in Fig. 1(a) and (b), respectively. The film morphology is defined by the interconnected structure among the particles with a diameter of 200–300 nm by means of necking, which gives rise to porous structure. The film thickness corresponds to an individual particle diameter. It is noticeable that this film morphology formed cohesively on a flat surface of SiO_2 substrate contrasts with the non-continuous, loosely packed particles formed on a faceted surface of SnO_2:F(FTO) substrate under the same processing condition, presumably due to their different adhesive/cohesive force ratio [29]. This porous nanoparticulate thin film with one-particle thickness holds high surface area-to-volume ratio leading to a high gas sensing performance [30]. In addition, the XRD pattern corresponding to the Joint Committee on Powder Diffraction Standards (JCPDS) no. 42-0334 corroborates that the prepared thin film is composed of a single phase polycrystalline $CuBi_2O_4$, as shown in Fig. 2.

The chemical composition of the $CuBi_2O_4$ thin film has been characterized by XPS, and the Cu2p, Bi4f, and O1 s core level spectra were acquired. As shown in Fig. 3a, the Cu2p spectra consist of the spin-orbit split $2p_{1/2}$ (954.1 eV) and $2p_{3/2}$ (934.0 eV) peaks with their respective shake-up satellite peaks in higher binding energies, indicating the characteristic of Cu(II) oxide in $CuBi_2O_4$ [5,28,29,31–33]. The $Cu2p_{3/2}$ spectrum was deconvoluted into three peaks where the principal peak at 934.1 eV and the second-highest peak at 932.7 eV arise from primary Cu(II) and minor Cu(I) components, respectively. The small peak at 935.4 eV is consid-