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Highly sensitive NO_2 sensors using lamellar-structured WO_3 particles prepared by an acidification method

Tetsuya Kida[a], Aya Nishiyama[b], Masayoshi Yuasa[a], Kengo Shimanoe[a,*], Noboru Yamazoe[a]

[a] *Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan*
[b] *Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Kasuga, Fukuoka, Japan*

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ABSTRACT

Tungsten trioxide (WO_3) was prepared by acidification of Na_2WO_4 with acid solutions such as H_2SO_4, HCl, and HNO_3 (pH 0.5 to −0.8) and tested for its NO_2 sensing properties. Acidification with strong acid solutions (pH −0.5, −0.8) was found to produce lamellar-structured WO_3 particles, which consisted of nano-sized crystalline plates that were 100–350 nm in lateral size and 20–50 nm in thickness, as observed by XRD and SEM analyses. The sizes of the primary and secondary particles were decreased by decreasing the pH of the acid solution used. This was accompanied by an increase in the specific surface area. The NO_2 responses of the prepared WO_3 lamellae were dependent on their morphology. The device using smaller WO_3 lamellae prepared with a H_2SO_4 solution (pH −0.8) had the highest sensor response, exhibiting a high sensor response ($S = 150–280$), even to dilute NO_2 (50–1000 ppb) in air at 200 °C. The use of smaller lamellae resulted in a decrease in the electrical resistance of the device, probably due to intimate contact between smaller lamellar particles, which allowed the detection of NO_2 in a rather wide concentration range. In addition, the developed device showed high NO_2 selectivity without substantial interference from NO.

1. Introduction

The continuous detection and monitoring of NO_2 in the atmosphere have become highly important because of its toxic effects on both animals and plants. There has been a high demand for compact, cheap, and preferably portable devices able to detect low levels (ppb level) of NO_2 in the atmosphere, since available analytical instruments based on Saltzman or chemiluminescence methods are large and expensive. Such a demand for high-performance NO_2 sensors is rapidly growing for other applications. It is envisaged that in the next few years, an automatic damper (ventilation) system will be introduced in cars. This system needs a compact sensor that can monitor NO_2 inside and outside in a rather wide concentration range, from ppb to several ppm levels. Thus far, several solid-state NO_2 sensors, such as resistive [1–6], potentiometric [7–9], amperometric [10–13], capacitive [14,15], optic [16,17], and surface acoustic wave (SAW) types [18] have been developed. In particular, resistive-type NO_2 sensors based on oxide-semiconductors are well-suited for the above applications due to their superior properties and simple structure, and as such they have been intensively studied for about 20 years [1–6]. Through an extensive search for NO_2-sensitive materials, tungsten trioxide (WO_3) has been found to show very promising NO_2 sensing properties [4,5]. Notably, WO_3-based sensors can detect dilute NO_2 in air without significant interference from CO_2, methane, CO, or H_2 at low temperatures like 200 and 300 °C [4]. It is important to note that the sensor response of WO_3 depends significantly on the preparation method. Many preparation routes for WO_3 sensors have been reported, including sputtering [19], vacuum evaporation [20], pulsed-laser deposition [21], sol–gel [22–25], pyrolysis [4,5,26], photochemical [27], and ion-exchange methods [28–31].

We have previously reported in a series of papers that thick and thin film devices using lamellar-structured WO_3 particles with nano-sized thickness, which were prepared by an ion-exchange method using a protonated cation-exchange resin and subsequent heat treatment, exhibited excellent NO_2 sensing properties at 200–300 °C [28–31]. It was found that the sensor response was significantly increased with a decrease in the thickness of the WO_3 lamellae and was well-correlated with its thickness [30]. Another important feature of the devices was the porous microstructure of the sensing layer packed with WO_3 lamellae with a high anisotropic shape. A sufficiently high sensor response was obtained, even to 10 ppb NO_2 in air, when WO_3 lamellae that were ca. 30 nm in thickness and 1 μm in lateral dimension were used for the sensing film [31]. However, the electrical resistance of the sensing film was fairly high, exceeding 10^8 Ω at 200 °C in response to even low concen-

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* Corresponding author. Tel.: +81 92 583 7876; fax: +81 92 583 7538.
E-mail address: simanoe@mm.kyushu-u.ac.jp (K. Shimanoe).

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trations of NO_2, e.g., 500 ppb [30]. Such a high electrical resistance makes measuring the sensor signal with the simple electric circuits that are typically used for commercial resistive sensors difficult, which hinders the detection of NO_2 at higher concentrations (sub ppm level). In addition, a high electrical resistance can sometimes be a source of noise in the sensor signal. Although the resistance can be decreased by raising the operation temperature, this is counterbalanced by a decrease in the sensor response. In this study, in order to decrease the sensor resistance and to extend the detectable concentration range, we prepared smaller WO_3 lamellae by the acidification of $WO_4{}^{2-}$ in a strong acid solution. We expected that nano-sized lamellae would contact more closely to each other than micro-sized lamellae, leading to a decrease in the sensor resistance. Acidification of W-polyanions is known to produce $WO_3{\cdot}2H_2O$ crystals, a precursor of WO_3 [32–35]. The acidification method was found to be able to tune the size of WO_3 lamellae by changing the pH of the acid solutions used, as described below.

2. Experimental

WO_3 particles were prepared by acidification of Na_2WO_4 and subsequent calcination of the resulting precipitates. A Na_2WO_4 solution was added drop by drop into an acidic solution under vigorous stirring. The two solutions were mixed so as to set the molar ratio of Na^+/H^+ at 1/10. The pH of the acidic solution was controlled with H_2SO_4, HNO_3, and HCl to be between 0.5 and −0.8. The mixing quickly produced a yellow gel (crystalline $WO_3{\cdot}2H_2O$), which was aged for 1 day at 30 °C. The gel was washed thoroughly with distilled water by centrifugation.

The structure of the fabricated sensor device is shown in Fig. 1. The obtained precipitates were mixed with water to form a paste. The resulting paste was screen-printed on an alumina substrate equipped with a pair of comb-type Au microelectrodes (line width: 180 μm; distance between lines: 90 μm; sensing layer area: 64 mm^2). The Au electrodes were also fabricated by a screen-printing method using a commercial Au paste followed by calcination at 850 °C. The paste deposited on the substrates was calcined at 300 °C for 2 h in air to form a WO_3 sensing layer via the dehydration of the precursor, $WO_3{\cdot}2H_2O$.

The surface morphology of the samples was analyzed with a field emission scanning electron microscope (FE-SEM). The thickness of the films was estimated to be 15–25 μm by FE-SEM observations. The crystal structure and specific surface area of the samples were measured using an X-ray diffractometer (XRD) with copper Kα radiation and a BET surface area analyzer, respectively. The NO_2 sensing properties of the devices were examined at an operating temperature of 200 °C in a concentration range of 50–1000 ppb in air. Measurements were performed using a conventional gas flow apparatus equipped with an electric furnace at a gas flow rate of 100 cm^3/min. The sensor response (*S*) was defined as the ratio of resistance in air containing NO_2 (R_g) to that in dry air (R_a) ($S = R_g/R_a$).

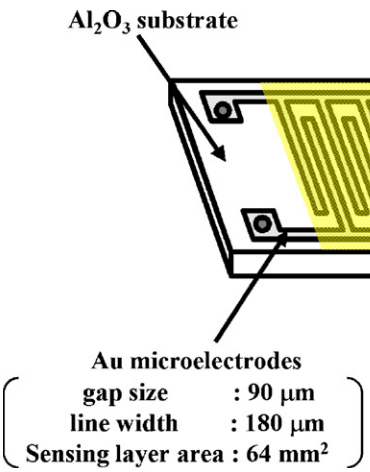

Fig. 1. Schematic structure of a NO_2 sensor device, in which a WO_3 thick film is deposited on an alumina substrate equipped with a pair of comb-type microelectrodes.

3. Results and discussion

3.1. Crystal structure and microstructure

Fig. 2 shows the XRD patterns of WO_3 particles prepared using the acidification method using H_2SO_4 with different pH solutions (pH 0.5 to −0.8) and subsequent calcination at 300 °C. All XRD peaks were assigned to monoclinic WO_3 (JCPDS 43–1035) for all samples. Other peaks are ascribable to Si, which was mixed with samples as an internal standard for the XRD measurements. It is noted that (0 0 1)-oriented WO_3 particles were formed when a H_2SO_4 solution with pH 0.5 was used. On the other hand, such a preferential orientation in the (0 0 1) plane became weak, i.e., the intensity of the (0 0 2) peak decreased with a decrease in the pH of the solution while those of the (0 2 0) and (2 0 0) peaks increased. In a previous report, we found that (0 0 1)-oriented WO_3 particles were formed by dehydrating (0 1 0)-oriented $WO_3{\cdot}2H_2O$ crystallites, which were prepared via the acidification of Na_2WO_4 with a protonated cation-exchange resin and repeated washing-centrifugation treatments [28]. Quite strikingly, the preferential orientation in layered $WO_3{\cdot}2H_2O$ was preserved even through the dehydration step leading to WO_3. Thus, in the present case, the observed (0 0 1) orientation in WO_3 at pH 0.5 also reflects the preferential (0 1 0) orientation in the precursor $WO_3{\cdot}2H_2O$. On the other hand, the observed loss in the crystal orientation at lower pH can be interpreted as follows: since $WO_3{\cdot}2H_2O$ is formed through the condensation of W-polyanions by acidification, the condensation rate, which depends on the pH of the precursor solution, may affect the orientation of the $WO_3{\cdot}2H_2O$ crystallites. It is thus suggested that with a significant decrease in pH of the solution from 0.5 to −0.8,

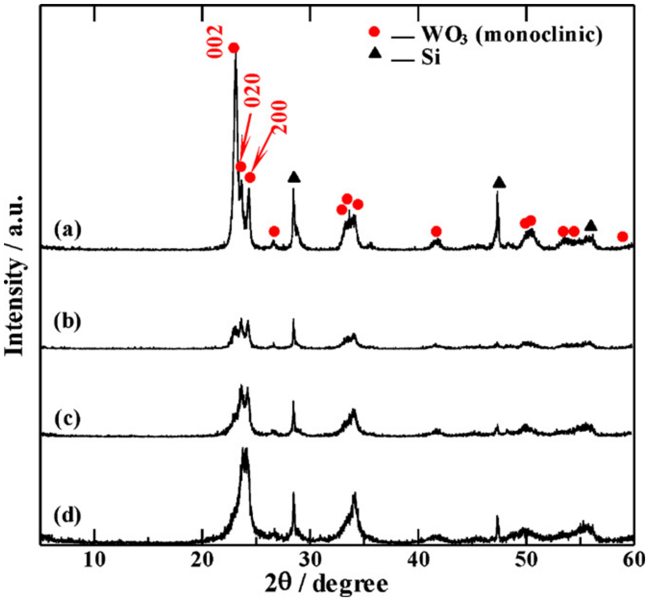

Fig. 2. XRD patterns of WO_3 particles prepared using H_2SO_4 solutions with different pH (a) 0.5, (b) 0, (c) −0.5, and (d) −0.8.