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Preparation of tungsten oxide nanowires and their application to NO_2 sensing

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ABSTRACT

Tungsten oxide nanowires were prepared by a vapor transport method using WO_3 powder as a raw material. The crystal structure and morphology of WO_3 nanowires were investigated by X-ray diffraction, scanning electron microscopy, and transmission electron microscopy. The obtained nanowires were hexagonal WO_3. The major factors that influenced the morphology were the furnace temperature and the substrate position. The diameter of the nanowires decreased as the distance of the substrate from the raw material increased. Sensors were fabricated by pouring a few drops of nanowire-suspended ethanol onto oxidized Silicon substrates equipped with a pair of interdigitated Pt electrodes. The sensor made of the nanowires as thin as 50 nm showed the highest response to NO_2 at a low operating temperature of 100 °C. The temperature dependence of the response was discussed in relation to the formation of NO_2^- and NO_3^- ions on the surface of WO_3. The response slightly increased with decreasing diameter if the nanowires are regional depleted in NO_2, while it largely increased if the nanowires are in volume depletion. A theoretical calculations based on assumptions were proposed in order to clarify the correlation between the nanowire response and their diameter.

1. Introduction

Nitrogen dioxide (NO_2) released from combustion facilities and automobiles is toxic and deteriorates the environment through acid rain and photochemical smog [1]. The threshold concentration of NO_2 in environmental monitoring is 3 ppm as listed in the safety standards by the American Conference of Governmental Industrial Hygienists. Therefore, the development of a sensor with high sensor response to low concentrations of NO_2 is necessary.

Various metal oxide semiconductors, such as tin oxide [2], zinc oxide [3], titanium oxide [4], molybdenum oxide [5], and tungsten oxide [6–11], have been studied as materials for NO_2 sensors. Of these oxide semiconductors, tungsten oxide (WO_3) is a promising material for detecting NO_2 [6,7]. The response of a sensor made of an oxide semiconductor is based on the change in its electrical resistance upon adsorption of a gas. Therefore, a larger surface area is desirable for attaining high response. Chung et al. [8] and Lee et al. [9] fabricated thick-film sensors using fine WO_3 particles formed by ball milling and calcinations of $W(OH)_6$ colloids, respectively. They reported that sensors with large surface areas showed high response to NO_2. Rossinyol et al. [10] reported that a mesoporous WO_3 sensor formed using a silica template showed high response to NO_2. Shen et al. [11] reported that the response of a porous sputtered film to NO_2 increased as the surface area of the film increased.

In recent years, nanowires of various oxide semiconductors with large surface-to-volume ratios have been studied as promising gas-sensing materials [12,13]. WO_3 nanowires have been synthesized by methods such as thermal evaporation [14,15], vapor transport [16,17], templating [18], solvothermal [19–21], and soft chemistry [22], and they have been studied as an NO_2-sensing material [15,16,19,22]. WO_3 nanowires formed by Ponzoni et al. [15] and Rout et al. [19] using thermal evaporation method and solvothermal method, respectively, showed high response to NO_2 in the range of parts per billion at high temperatures above 200 °C. WO_3 nanowires formed by Cao et al. [16] using the vapor transport method could detect NO_2 in the range of parts per billion at 180 °C. WO_3 nanowires formed by Polleux et al. [22] using soft chemistry showed high response to NO_2 in the range of parts per billion at 150 °C.

Although NO_2 sensors made of WO_3 nanowires have been studied by many researchers, as mentioned above [15,16,19,22], their properties at low temperatures have not been explored. Thus, in this paper, we examine their sensing properties over a wide range of temperatures, i.e., from room temperature to 300 °C. In addition, we investigate the dependence of the response on the diameter of the nanowires. Tamaki et al. [23] and the present authors [24] fabricated NO_2 sensors made of WO_3 particles with various sizes and showed that their response increased with decreasing size. However, there have been no reports on the relationship between the response and the diameter of WO_3 nanowires. In the present

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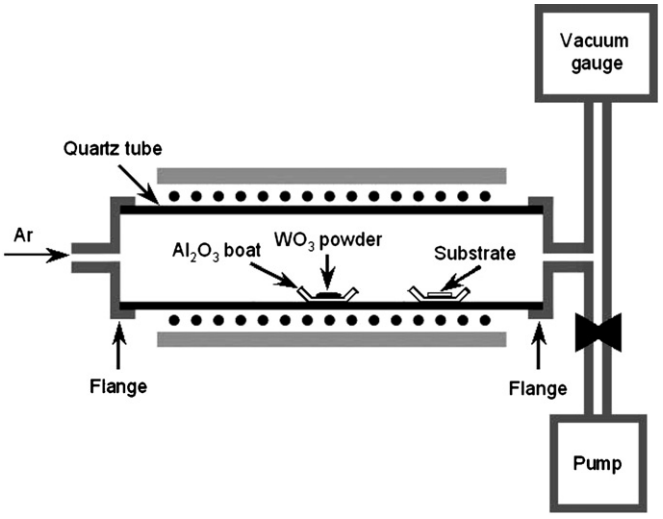

Fig. 1. Apparatus used for the formation of WO_3 nanowires.

study, we formed WO_3 nanowires by the vapor transport method and studied the NO_2-sensing properties of these nanowires. We found that the diameter of the nanowires depended on the furnace temperature and the substrate position. As the diameter of the nanowires decreased, the response increased. This result was explained by a theoretical calculation. We also discussed the temperature dependence of the response in relation to the formation of NO_2^- and NO_3^- ions on the surface of WO_3.

2. Experimental methods

WO_3 nanowires were formed by the vapor transport method using WO_3 powder as a raw material. The apparatus used for their formation is shown in Fig. 1. An alumina boat loaded with WO_3 powder (100 mg, 99.9% purity) was placed at the center of a quartz tube inserted in a horizontal electric furnace. A substrate on another alumina boat was placed 16, 17, or 17.5 cm away from the WO_3 powder. Our attempt to deposit a product on an oxidized Si substrate failed. Thus, an oxidized Si substrate coated with a 5-nm-thick Au film was used to deposit the product. After the quartz tube was evacuated to a pressure of approximately 30 Pa, Ar gas was introduced at a flow rate of 900 ml/min into the quartz tube, resulting in a pressure of 270 Pa. The furnace temperature was increased to 1050, 1100, or 1150 °C. After maintaining the furnace at this temperature for 2 h, the furnace was cooled naturally to room temperature. Thus, a layer of product was obtained on the substrate. Note that the temperature of the WO_3 powder during heating was equal to the furnace temperature, whereas the substrate temperature was lower than the furnace temperature. Table 1 shows the temperatures of the substrates placed 16, 17, or 17.5 cm away from the WO_3 powder at various furnace temperatures.

The structure of the products deposited on the substrates was investigated using an X-ray diffractometer (XRD, Shimadzu XRD-6100) with Cu Kα radiation, a field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F), and a transmission electron microscope (TEM, JEOL EM002B).

Sensors were fabricated by pouring a few drops of nanowire-suspended ethanol onto oxidized Si substrates equipped with a pair of interdigitated Pt electrodes with a gap length of 35 μm. The size of the sensing element was 9 mm × 10 mm. The weight of the nanowires used for a sensor was about 200 μg. Before measuring gas-sensing properties, the sensors were annealed in ambient air for half an hour at 350 °C. For measuring their NO_2-sensing properties, the sensors were placed in a quartz tube inserted into an electric furnace. After a dry synthetic air composed of N_2 and O_2 was introduced into the quartz tube at a flow rate of 200 ml/min, a prescribed concentration of NO_2 was introduced for a predetermined period of time. The change in the electrical resistance of the sensors was measured when NO_2 was introduced and exhausted at an operating temperature from room temperature 25 °C to 300 °C. The electrical resistance was determined by measuring the electric current flowing through the sensor at a voltage of 10 V applied between the interdigitated Pt electrodes. The sensor response was defined as R_g/R_a, where R_a and R_g are the electrical resistances in air and in air including NO_2, respectively.

Table 1
Substrate temperature at different furnace temperatures and substrate positions.

Furnace temperature (°C)	Substrate temperature (°C)		
	Position of 16 cm	Position of 17 cm	Position of 17.5 cm
1050	490	300	230
1100	520	330	250
1150	550	350	270

3. Results and discussion

3.1. Structure characterizations

FE-SEM images of the products are shown in Fig. 2. The morphology of the products depends on the furnace temperature and substrate position. We refer to all of the products as nanowires for convenience, although the products deposited at 1050 °C are better described as nanostrips. It was difficult to peel the nanowires deposited at 1050 °C from the substrate. The nanowires formed at 1100 and 1150 °C were in a powdered form, i.e., they were easily peeled from the substrates. The diameter of the nanowires decreased as the distance of the substrate from the WO_3 powder as a raw material increased. Thin nanowires were formed at a furnace temperature of 1100 °C. In this condition, the thinnest nanowires with a diameter of 50 nm were formed 17.5 cm away from the WO_3 powder.

Fig. 3(a) shows the XRD patterns of the nanowires deposited on the substrate at three different positions at a furnace temperature of 1100 °C, while Fig. 3(b) shows the XRD patterns of the nanowires deposited on a substrate 17.5 cm away from the WO_3 powder at three different furnace temperatures. These patterns agree with that of a hexagonal WO_3 listed in JCPDS card No. 85-2460. Note that this structure is different from those reported for the nanowires formed using the vapor transport method by other research groups. Cao et al. [16] reported WO_3 nanowires with a monoclinic structure. Hong et al. [17] reported $W_{18}O_{49}$ nanowires with a monoclinic structure. The hexagonal structure that we obtained agrees with that of the nanowires formed by a solvothermal method [21].

A high resolution TEM image (HRTEM) and a selected area electron diffraction pattern (SAED) observed for a nanowire deposited on a substrate 17.5 cm away from the WO_3 powder at a furnace temperature of 1100 °C are shown in Fig. 4(a) and (b), respectively. The side view of the nanowire is shown at the right hand side of Fig. 4(a). Since the lattice spacing of 0.38 nm indicated in Fig. 4(a) corresponds to the (0 0 2) plane of the hexagonal WO_3, the growth direction of the nanowires is [0 0 1].

3.2. Sensing properties of NO_2

Fig. 5 shows the temporal responses to 3 ppm NO_2 at the operating temperatures of 50, 150, and 250 °C measured for a sensor made of nanowires as thin as 50 nm, deposited on a substrate 17.5 cm