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Effect of micro-gap electrode on detection of dilute NO_2 using WO_3 thin film microsensors

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Abstract

The micro-gap electrodes with various gap sizes (0.1–1.5 μm) were fabricated on Si substrate by using MEMS techniques (photolithography and FIB) and the WO_3 thin film was deposited on the micro-gap by suspension dropping to be micro-gas sensor. The effect of gap size on sensing properties to dilute NO_2 (0.05–0.5 ppm) was investigated at 200 °C. The sensitivity to dilute NO_2 almost unchanged irrespective of gap size larger than 0.8 μm. On the other hand, the sensitivity tended to increase with decreasing gap size less than 0.8 μm. The sensitivity ($S = R_g/R_a$) to 0.5 ppm NO_2 was as high as 57 at gap size of 0.11 μm and was expected to increase further when the gap size was decreased less than 0.1 μm. The behavior was explained with the number of WO_3 grains in the micro-gap and the resistance changes at two kinds of boundaries (grain boundary and electrode–grain interface).

Keywords: WO_3; NO_2 sensing; Micro-gap; Microsensor; MEMS

1. Introduction

It is well known that WO_3 is an excellent sensing material for NO_x detection [1,2]. The conductivity-type sensors using WO_3 have enhanced their sensitivity to NO_2 by adopting thin film structure [3–5], by doping foreign oxides [6–10], and by using novel preparation method [11]. These WO_3 sensors can detect dilute NO_2 less than 1 ppm with high sensitivity. Recently, we found that WO_3 thin film sensor fabricated on Au comb-type microelectrode (line width 5 μm, distance between lines 5 μm) showed fairly high sensitivity to dilute NO_2 less than 0.1 ppm at 200 °C [12]. Further, the sensitivity to dilute NO_2 was improved by using disk-shaped WO_3 grains and by adopting optimized thick film, suggesting the possibility of environmental NO_2 monitoring [13,14]. Moreover, this WO_3 thick film sensor was hardly interfered by co-existing water vapor [14]. It was considered that the usages of microelectrode as well as disk-shaped WO_3 grains were responsible for high sensitivity. Thus, in this paper, we focused the effect of microelectrode on NO_2 sensitivity of WO_3 sensor. We fabricated micro-gap electrode with various gap sizes (0.1–1.5 μm) on Si substrate by using MEMS techniques (photolithography and FIB) and deposited WO_3 film on it to be micro-gas sensor. It is very interesting what happens if the distance between electrodes decreases down to grain size of oxide (a few tens to a few hundreds nanometers). The effect of gap size on dilute NO_2 sensing properties was investigated and novel design concept for high-sensitivity gas sensor was proposed on electrode design.

2. Experimental

The micro-gap electrodes with various gap sizes were fabricated by means of MEMS techniques (photolithography and FIB). At first, the Au line with width of 11–16 μm and thickness of 0.3 μm was deposited on Si substrate by photolithography, and then the Au line was etched by focused ion beam apparatus (FIB, Hitachi FB-2100) using Ga^+ ion

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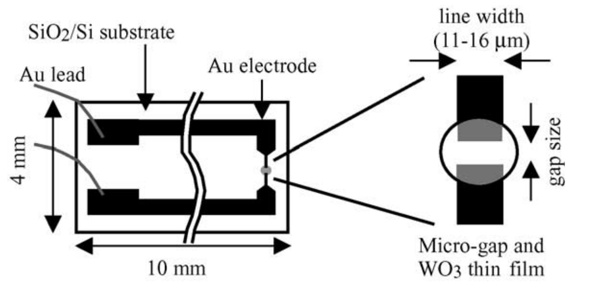

Fig. 1. Schematic drawing of WO_3 thin film microsensor equipped with micro-gap.

beam. As a result, the micro-gap electrodes with gap size of 0.1–1.5 μm and line width of 11–16 μm were obtained by these processes. Finally, the WO_3 thin film was deposited on micro-gap by the suspension dropping method to be micro-gas sensor as schematically drawn in Fig. 1.

The WO_3 powder was prepared from $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ by wet process. Aqueous solution of $(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$ was neutralized by dilute nitric acid solution. The precipitate obtained (H_2WO_4) was thoroughly washed with deionized water, dried, and dispersed into ethylene glycol to be a suspension. The micro-drop of suspension was dropped on micro-gap by using micromanipulator, dried, and calcined at 400 °C for 3 h. The surface morphology of microsensor was measured by means of SEM (JEOL JSM-6400).

The microsensor was set into a flow apparatus equipped with electric furnace and the sensing properties to dilute NO_2 (0.05–0.5 ppm) were measured at 200 °C. The gas sensitivity ($S = R_g/R_a$) was defined as a ratio of resistance in NO_2-containing atmosphere (R_g) to that in air (R_a).

3. Results and discussion

3.1. Fabrication of micro-gap

The micro-gaps were fabricated by means of FIB technique using Ga^+ ion beam. The beam conditions such as acceleration voltage, focusing current, and opening diameter were set constant. These values were 40 kV, 1 μA, and 40 μm, respectively. The set values were set for determining etching width and etching length. The etching width was changed from 0.05 to 1.0 μm in order to control the gap size, while the etching length was changed from 11 to 20 μm. Fig. 2 shows the resulting gap size as a function of set value. At the set value of 0.5 and 1.0 μm, the resulting gap size was one to two times larger than set value. On the other hand, the gap size was two to four times larger for the set values less than 0.2 μm. The deviation between the result and the set value was increased with decreasing set value, but the scattering of resulting gap size at the same set value was decreased with decreasing set value. Anyway, the gap sizes of 0.11–1.54 μm were obtained by FIB technique.

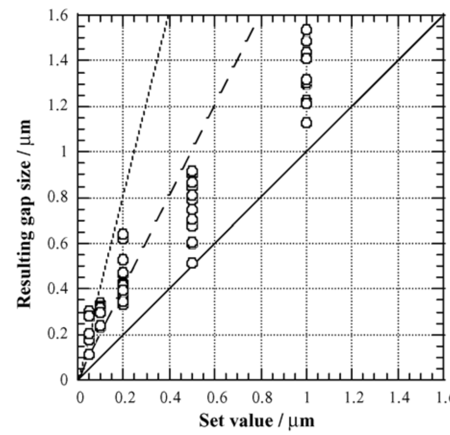

Fig. 2. Resulting gap size etched by FIB technique as a function of set value.

3.2. Surface morphology of micro-gap and microsensor

Fig. 3 shows SEM images of micro-gap and WO_3 microsensor. Fig. 3(a) depicts the typical micro-gap electrode without WO_3 film. The simple electrode structure with gap size of 5 μm and line width of 11 μm is seen. The WO_3 thin film deposited on micro-gap had a size with 130–150 μm in diameter (Fig. 3(b)). The film was also deposited on an area other than micro-gap. Since the gas sensing experiment was

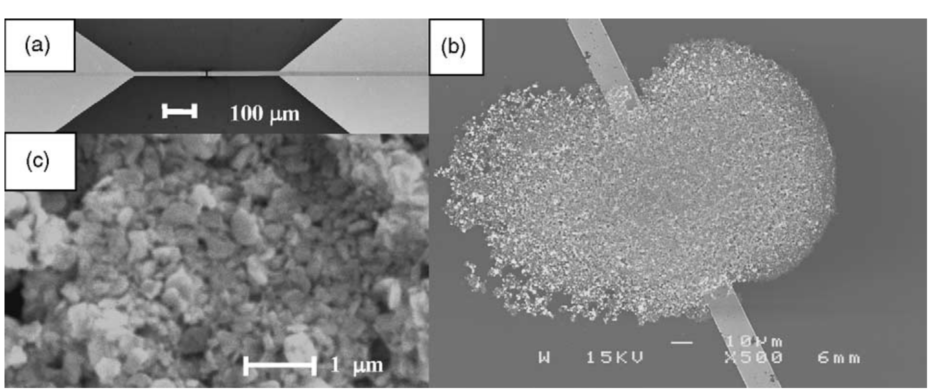

Fig. 3. SEM images of micro-gap electrode and WO_3 microsensor. (a) Micro-gap with 5 μm gap size without WO_3 thin film, (b) WO_3 thin film on micro-gap electrode, and (c) WO_3 grains in microsensor.