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Humidity-insensitive and low oxygen dependence tungsten oxide gas sensors

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Abstract

Gas sensing characteristics of WO_3 powder and its physical properties under different heat treatment conditions have been investigated. The WO_3 powder was synthesized by wet process from ammonium tungstate parapentahydrate and nitric solution. The precipitated product was then calcined at 300–800 °C for 2–12 h. The physical properties of the products were characterized by using X-ray diffractometer (XRD), scanning electron microscope (SEM), and BET method. It was found that the crystallite size, particle size and surface area of the WO_3 powders were in the range of 30–45 nm, 0.1–3.0 μm and 1.2–3.7 m^2/g, respectively. Calcination at higher temperature and longer time led to the increase of particle size by more than 300%, and reduction in specific surface area by more than 60%. However, the crystallite size was found to increase only by ∼30% under identical heat treatment. These results inferred that such heat treatment had more profound effect on crystallite aggregation than on crystallite growth. Gas sensing measurement showed that the largest change of output voltage to both ethyl alcohol and ammonia was obtained from the sensor calcined at 600 °C for 2 h, which had the highest surface area. However, the highest sensitivity which is defined as the ratio of sensor's resistance in air to that in the sample gas, R_{air}/R_{gas}, was obtained from the sensor calcined at 600 °C for 6 h due to its highest background resistance in air. Moreover, it was also found that the sensors were less sensitive to the oxygen content in the carrier gas and did not sensitive at all to water vapor.

Keywords: WO_3; Humidity; Oxygen; Ammonia; Ethyl alcohol; Calcination

1. Introduction

It is well known that electrical properties of metal oxide semiconductors were sensitive to a gas composition of surrounding atmosphere. By utilizing this phenomenon, tin oxide (SnO_2) and zinc oxide (ZnO) semiconductors were first demonstrated as gas sensing devices in early 1960s [1–2]. Since then the semiconductor sensors based on this property have been studied and used extensively for the chemical and gas detection. It was found that most metal oxide gas sensors were sensitive to relative humidity and oxygen content in background environment, which, in many cases, can interfere the sensor performance, particularly in the equatorial zone, which has high variation of humidity. Nevertheless, some oxides are so sensitive to humidity that they have been used as humidity sensor [3]. Therefore, it has been our prime interest to explore the materials, which, while show good response to targeted gases, are less sensitive to humidity.

Tungsten oxide (WO_3) was our first priority for this study since there have been many reports during the past decade on its sensing performance to many gases, such as nitrogen oxides [4–6] and sulfides [7]. The tungsten oxides have been prepared by various techniques, such as sol–gel [6], pyrolysis [7] and sputtering [8]. Like sensing behavior of other oxides, it was found that the tungsten oxides obtained from different preparation techniques resulted in different response characteristics. It was also known that the characteristics of the gas sensors depended strongly on base material as well as preparation conditions. In this paper, the response characteristics

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of the tungsten oxide prepared from precipitation method to ethyl alcohol and ammonia were investigated to study the effects of crystallite size, particle size, specific surface area and initial electrical resistance on sensing performance. The effects of humidity and oxygen content in the carrier gas were also reported.

2. Experimental

2.1. WO_3 synthesis and characterizations

The tungsten oxide (WO_3) powders were synthesized by precipitation technique from the precursor containing ammonium tungstate parapentahydrate ($(NH_4)_{10}W_{12}O_{41}\cdot 5H_2O$, Wako) and nitric acid (HNO_3, Carlo). A 0.1 M nitric acid was slowly added into a 3 mM ammonium tungstate solution pre-heated at 80 °C. After reaction completion, the yellowish precipitate was allowed to settle, separated by filtration and then dried at 200 °C for 2 h to remove the water. Finally, the dried precipitate was calcined in air at temperature ranging from 300 to 800 °C for 2, 6 and 12 h.

The crystal structures of the dried and calcined powders were identified using an X-ray diffractometer (XRD, JDX 3503). The crystallite size was estimated from peak broadening of the (2 0 0), (0 2 0) and (0 0 2) reflections using Scherrer approximation, which is defined as:

$$D = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where D is the crystallite size (Å), λ is the wavelength of the X-ray (1.5418 Å), B is the full width at half maximum (radian) and θ is the Bragg angle (degree). The microstructure was observed using a scanning electron microscope (SEM, JSM-5410). The specific surface area was measured based on nitrogen adsorption by Brunauer, Emmett and Tellet (BET) method using gas chromatography.

2.2. Sensor fabrication and characterizations

The calcined WO_3 powders were formed into paste by mixing the powders with ethyl alcohol, de-ionized water and dispersing agent (Dispex®). Thick-film sensors were formed by painting the paste onto the electrode coated on the glass substrate. The electrode was prepared by evaporating a 50 nm-thick titanium layer, followed by a 100 nm-thick platinum layer on the glass slide using electron beam evaporation (ULVAC, EBV-6DH).

The fabricated sensors were installed in a measuring chamber, which was specially designed so that six sensors were measured simultaneously under the identical conditions. Responses of the sensors towards ethyl alcohol and ammonia were characterized at operating temperatures of 150–400 °C. Nitrogen and oxygen with flow rates of 400 and 100 ml/min, respectively, were mixed together and used as carrier gas. For each measurement, a 50 μl of either ethyl alcohol or ammonium solution (0.01–100% (v/v) in de-ionized water) was injected into the injection port where it was instantly vaporized and transported into the chamber having working volume of 452 cm^3. Conductivity change of the sensor was measured using an operational amplifier measuring circuit (Fig. 1) to prevent the loading effect, which frequently occurs in the conventional voltage divider circuit. Detailed merit of this circuitry approach has been previously reported elsewhere [9]. A bias voltage (V_{in}) was fixed at 5 V. Note that R_s represents sensor's resistance while R_f is a resistor used to adjust the baseline output voltage (V_{out}). The output from the measuring circuit was sent to a PC and converted to a digital signal for monitoring and recording. Finally the effect of oxygen content in the carrier gas was also investigated by adjusting the flow rate ratio between nitrogen and oxygen gases at 0:500, 250:250 and 500:0 ml/min. In each measurement, the carrier gas was flowed into the chamber until the base line was stable before introducing the gas sample into the system.

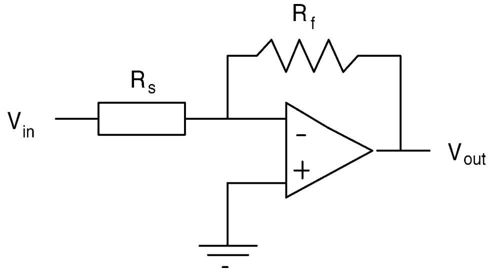

Fig. 1. Schematic illustration of the measuring circuit used in this study. R_s: sensor resistance; R_f: reference resistor used to adjust the baseline; V_{in}: input voltage and V_{out}: output voltage.

The sensor performance was compared by it sensitivity (S) which was defined as:

$$S = \frac{R_{air}}{R_{gas}} \tag{2}$$

where R_{air} is the resistance of the sensor in air environment, and R_{gas} is the sensor's resistance in gas sample. According to the illustration in Fig. 1,

$$R_{air} = -\frac{R_f V_{in}}{V_{out\text{-}air}} \tag{3}$$

and

$$R_{gas} = -\frac{R_f V_{in}}{V_{out\text{-}gas}} \tag{4}$$

where $V_{out\text{-}air}$ and $V_{out\text{-}gas}$ are the output voltage in air and the output voltage in gas, respectively. Hence, the sensitivity of the sensor could be derived directly from Eq. (5).

$$S = \frac{V_{out\text{-}gas}}{V_{out\text{-}air}} \tag{5}$$

This equation shows that the calculated sensitivity can be obtained directly from the output of the measuring circuit and it is not necessary to calculate the resistance of the sensors.