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Influences of microstructure on the gas sensing properties of ZnO/SnO_2 thin films

Masashi SHOYAMA and Masaki MURAYAMA
Industrial Research Division, Mie Science and Technology Promotion Center,
5-5-45 Takachaya, Tsu, Mie 514-0819, Japan

Fax: 81-59-234-3982, e-mail: shoyama@mie-iri.tsu.mie.jp

Hetero-layered ZnO/SnO_2 thin film and ZnO/SnO_2 composite thin film were prepared by the sol-gel method to compare the gas sensing properties. Gas sensing properties of ZnO/SnO_2 thin films were strongly affected by the microstructure of the film. The CO sensitivity and selectivity of the hetero-layered ZnO/SnO_2 thin film were drastically improved than that of the ZnO/SnO_2 composite thin film at a high operating temperature range from 300℃ to 500℃.

Key words: CO selectivity, ZnO/SnO_2, hetero-layer, composite, sol-gel

1. INTRODUCTION

Semiconductive gas sensors are important candidates to sense the toxic gases such as CO or NOx because of its high sensitivity and low cost performance. Generally, in the atmosphere, these toxic gases exist in a very low concentration, and various kinds of interference gases also co-exist. Therefore, the development of highly sensitive and highly selective sensor materials for a particular gas has been the subject of gas sensor technology.

Sensing properties of SnO_2 thin films for CO gas have been enhanced by the addition of noble metals such as Pt or Pd as a catalyst. But, the low sensitivity and slow response property caused by low operating temperature is the subject on the CO sensor material. In order to improve the sensitivity and selectivity of the sensor materials, various efforts such as doping [1-4] or hetero-coatings [5-7] have been reported in several methods. Among these methods, the sol-gel method is one of the best candidates to prepare high sensitive gas sensor thin films, because it results in high purity and high uniformity.

In this paper, dependence of gas sensing properties on the microstructure of the ZnO/SnO_2 thin film was reported. Two types ZnO/SnO_2 sensors of hetero-layered structure and mono-layered structure are fabricated by the sol-gel method to compare the gas sensing properties for CO and CH_4 gases.

2. EXPERIMENTAL

$SnCl_2$ (Wako Pure Chemical Industries, Ltd.) and $ZnCl_2$ (Wako Pure Chemical Industries, Ltd.) were used as raw materials, and 2methoxyethanol ($CH_3OCH_2CH_2OH$, Wako Pure Chemical Industries, Ltd.) was used as a solvent.

Figure 1 shows the preparation scheme of the hetero-layered ZnO/SnO_2 thin film and ZnO/SnO_2 composite thin film. In the case of hetero-layered ZnO/SnO_2 thin film, Sn- and Zn-precursor solutions were prepared in a dry N_2 atmosphere, independently. The concentrations of the Sn- and Zn-solution were both adjusted to 1.0mol/L. In the case of ZnO/SnO_2 composite thin film, Zn-Sn multi component precursor solution was prepared by the refluxing of the raw materials in the N_2-atmosphere. ZnO content in the ZnO/SnO_2 composite thin film was varied from 1 mol% to 50 mol%. The raw materials were mixed and refluxed at 124 ℃ for 3h to promote a poly-condensation reaction. The details of the preparation method of the precursor solution have been shown in previous papers. [8,9] Precursor solution was deposited on the Pt-passivated Al_2O_3 (5mm × 8mm) substrate three times by the spin-coating method, followed by baking at 300℃. Then, sensor thin films were obtained by the heating at 800℃ in air.

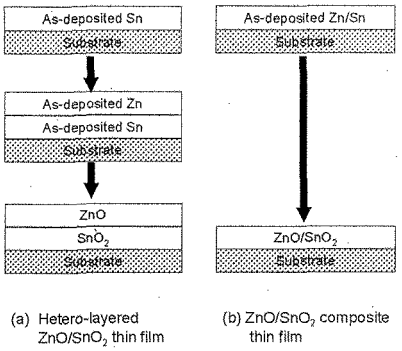

Figure1 Preparation scheme of the ZnO/SnO_2 thin films

The microstructure of the films was observed by a scanning electron microscope (SEM, Hitachi S-4100) and an X-ray diffraction (XRD, Rigaku RINT-2000/PC). The gas sensing properties of the films were evaluated for CO(100ppm) and CH_4(100ppm) gases respectively at operating temperatures from 200℃ to 500℃. The sensitivity of the films was determined by the ratio of the electric resistance in the air (Ra) and to that in the respective gas (Rg).

3. RESULTS AND DISCUSSIONS

3.1 Microstructure of ZnO/SnO_2 thin film

Figure 2 shows the SEM images of the surface of the hetero-layered ZnO/SnO_2 thin film heated at 800℃. It was clearly observed that columnar c-oriented ZnO crystals with a diameter of about 200nm grew perpendicular to the SnO_2 thin film surface. The growth of the c-oriented hexagonal ZnO crystal was clearly observed on the SnO_2 layer. The growth of the c-oriented ZnO crystal was not observed when the ZnO layer was deposited on the substrate directly. The lattice constant of the SnO_2 (tetragonal) is a=4.738A, c=3.187A, and the ZnO (hexagonal) is a=3.250A, c=5.207A. Therefore, the misfit of the c-axis of SnO_2 and the a-axis of ZnO was below 2%. Thus, it was considered that the c-oriented hexagonal ZnO layer was epitaxially grown onto the SnO_2 surface with the result of good fitting of the lattice constant between the a-axis of ZnO and the c-axis of SnO_2.

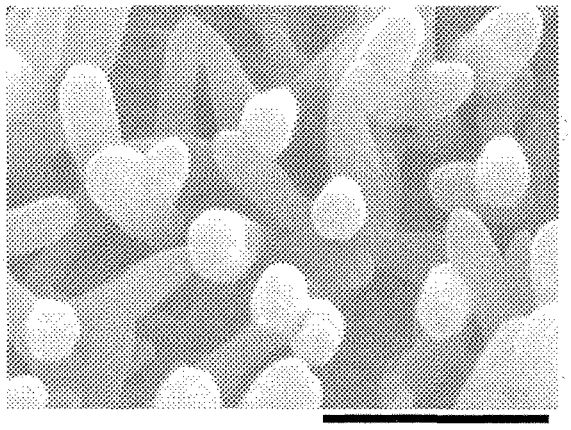

Figure2 SEM image of the hetero-layered ZnO/SnO_2 thin film (Bar: 1 μ m)

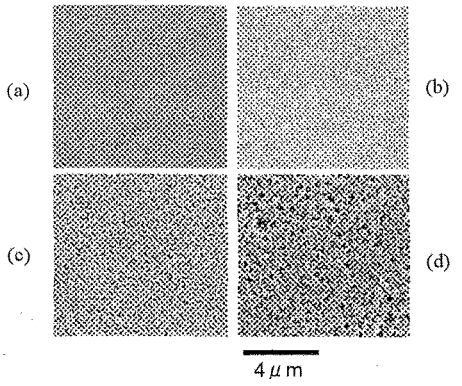

Figure3 SEM images of the ZnO/SnO_2 composite thin films
(a)ZnO 1mol% (b)ZnO 3mol%
(c)ZnO 25mol% (d) ZnO 50mol%

Figure 3 shows the SEM images of the surface of (a)ZnO 1mol%, (b) ZnO 3mol%, (c) ZnO 25mol% and (d) ZnO 50mol%-SnO_2 composite thin films heated at 800℃. The microstructure of the ZnO/SnO_2 composite thin film was apparently different from that of hetero-layered ZnO/SnO_2 thin films mentioned above. Any orientation was not observed in present ZnO/SnO_2 composite thin film. In addition, it was also confirmed that the microstructure of the film became coarse with increasing the ZnO content in the ZnO/SnO_2 composite thin film.

3.2 Gas sensitivity of ZnO/SnO_2 thin film

Figure 4 shows the operating temperature dependence of sensitivity of the hetero-layered ZnO/SnO_2 thin films for the four respective gases, CO and CH_4. The sensitivity of the hetero-layered ZnO/SnO_2 thin film for CO gas increased as the operating temperature increased, and the sensitivity for CH_4 gas of the hetero-layered ZnO/SnO_2 thin film slightly increased as the operating temperature increased. At an operating temperature of 500℃, the sensitivity of the hetero-layered ZnO/SnO_2 thin film for the CO gas was 584, which was about 10 times as large as the 59 of the CH_4 gas. From these results, it was also recognized that the hetero-layered ZnO/SnO_2 thin film has enough ability to detect CO gas reliably, even in the atmosphere where CH_4 co-exist with CO gas at high operating temperature between 300℃ to 500℃.

Conventionally, the CO sensor was used at a low operating temperature such as 100℃~200℃ to avoid influences from other gases, but slow response and recovery properties remain to be solved. A conventional CO sensor also has to remove the gases absorbed at the surface of the sensor material to maintain sensing ability by cyclic heating process (refresh operation). In contrast, hetero-layered ZnO/SnO_2 thin film can be used at a high temperature range such as 500℃. We can expect that the hetero-layered ZnO/SnO_2 thin film sensor does not need a refresh operation by the cyclic heating process, and that it shows fast response and recovery properties.

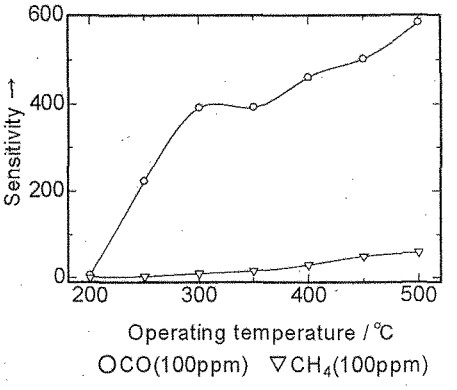

Figure4 Operating temperature dependence of sensitivity of the hetero-layered ZnO/SnO_2 thin films

Figure 5 shows the operating temperature dependence of sensitivity of ZnO/SnO_2 composite thin films (ZnO 50mol%) for CO gas(100ppm) and CH_4 gas (100ppm), respectively. The sensitivity for CO gas of the ZnO/SnO_2 composite thin film increased as operating temperature decreased, and showed maximum value of 587 was obtained at 200℃. In contrast, the sensitivity for CH_4 gas was hardly observed at respective operating temperatures, and it was stable in spite of the change of the operating temperature. From these results, it was recognized that the ZnO/SnO_2 composite thin film showed superior sensitivity and selectivity for CO gas at lower operating temperature, such as 200℃.

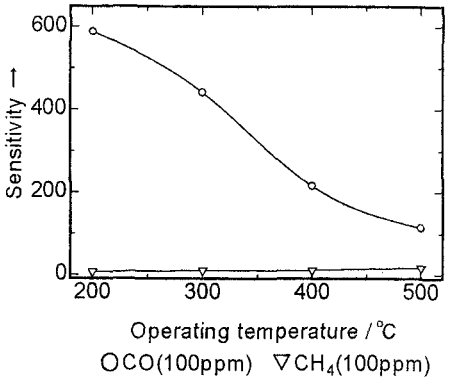

Figure5 Operating temperature dependence of sensitivity of the ZnO/SnO_2 composite thin films

3.3 Microstructure dependence of the gas sensing properties

As mentioned above, temperature dependence of the gas sensing properties are quite different each other. The CO sensitivity of the hetero-layered ZnO/SnO_2 thin film increased as operating temperature increased, while it decreased as operating temperature increased in the ZnO/SnO_2 composite thin film. It was considered that the difference in CO sensing property between the hetero-layered ZnO/SnO_2 thin film and the ZnO/SnO_2 composite thin film was caused by the difference of the contact oxide material to the Pt electrodes. In case of hetero-layered ZnO/SnO_2 thin film, SnO_2 layer contacted to the Pt electrodes, while ZnO/SnO_2 layer contacted in the ZnO/SnO_2 composite thin film. So, it was considered that the ZnO component affected the sensing properties of the films.

In addition, in the case of hetero-layered thin film, the microstructure of the ZnO layer coated onto the SnO_2 layer was very effective in reducing the CH_4 gases for the improvement of CO gas selectivity in the SnO_2 layer. It is considered that a nano-sized columnar ZnO layer could act as a filter to reduce the interference gases by the effective absorption with a high surface area, and could also pass the CO gas effectively to the intermediate SnO_2 layer without CO gas absorption. As a result, it is considered that the SnO_2 layer between the columnar ZnO layer and Pt electrode could sense CO gas with high selectivity even in the high temperature operation.

4 CONCLUSIONS

Highly CO selective ZnO/SnO_2 thin films were successfully prepared by the sol-gel method. It was recognized that the gas sensing properties of the ZnO/SnO_2 thin films were strongly affected by the difference of the microstructure. Hetero-layered ZnO/SnO_2 thin film showed high CO sensitivity and high CO selectivity at high operating temperature, while ZnO/SnO_2 composite thin film showed high CO sensitivity at low operating temperature.

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