Evaluation of sensor property for hydrogen and ethanol of zinc-doped tin-dioxide thin films fabricated by rf sputtering

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Zinc-doped Tin-dioxide thin (SnO₂) films were synthesized on c-alumina substrates by radio-frequency (rf) sputtering. To fabricate zinc-doped SnO₂ thin films with different concentrations of zinc, an insulating zinc-doped SnO₂ target was placed on a conductive non-doped target. Thin films were then deposited at different flow rates of argon gas. Zinc concentration in the deposited SnO₂ thin films increased with increasing flow rate of argon gas. Moreover, the SnO₂ thin film with a zinc concentration of 2.2 × 10¹⁹/cm³ showed the highest gas-sensor response. It is concluded that this rf-sputtering growth method is a useful tool for identifying suitable materials compositions for creating gas sensor with response for hydrogen and ethanol.

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1. Introduction

Utilizing oxide-based gas-sensor materials, such as tin dioxide (SnO₂) and zinc oxide (ZnO), for detecting several gases has been widely studied. These materials, which are n-type semiconductors, have been applied for detecting reducing gases, such as H₂, CO, CH₄, NO, NO₂, and ethanol. To exploit the characteristics of both materials, composite materials and doped materials were used previously. The present study focused on the gas-sensing property by the thin-film form of SnO₂. This material has been widely studied for use in solar cells and gas sensors and as an oxidation catalyst. While SnO₂ in gas sensors, in the form of thin films and porous nanosized SnO₂, has been extensively studied, and the conduction mechanism has been proposed. Generally, the established mechanism for sensing of a n-type oxide semiconductor is that oxygen is adsorbed on the oxide surface with conductivity, and it forms a depletion layer at the surface. By introduction of a reducing gas, the negatively charged oxygen oxidizes the reducing gas, and the depletion layer at the surface is annihilated. As a result, the conductivity of the surface is improved when a target gas is introduced.

In the case of film growth of SnO₂ by using physical techniques such as sputtering and the pulsed laser deposition, the dense SnO₂ target without additive is impossible to fabricate using the conventional growth technique. SnO₂ decomposes and its constituents evaporate during sintering. As a result, SnO₂ ceramics is usually porous form. In order to avoid above problem and to investigate the gas-sensing property, we used ZnO as additive into SnO₂. Previously, we reported that ZnO addition into SnO₂ is useful to fabricate the dense SnO₂ ceramics.

In this study, SnO₂ thin films doped with ZnO were fabricated by radio-frequency (rf) sputtering. In the ZnO–SnO₂ system, double targets (namely, non-doped SnO₂ and 0.5-mol. % ZnO-doped SnO₂) were used to grow the thin films. Moreover, the validity of using double targets to grow the thin film by rf-sputtering method and the possibility of applying their reaction product as a sensor material were demonstrated. The condition for thin film growth was optimized by controlling argon gas flow rate. After the thin films were characterized, their gas sensing property of thin films was evaluated.

2. Experimental methods

A conductive SnO₂ target (with diameter of 3 inches), purchased, was set at the target position in the chamber of the rf-sputtering apparatus. Another SnO₂ disk (with diameter of 20 mm) was also prepared as a target. This target was doped with 0.5-mol. % ZnO to suppress its conductivity. The features of a ZnO-doped SnO₂ disk are described in a previous paper. The arrangements of the different SnO₂ targets, namely, a non-doped SnO₂ target and an insulating SnO₂ target doped with ZnO, are shown in Fig. 1. The insulating SnO₂ target doped with ZnO was placed in the center of the conductive SnO₂ target. The ZnO-doped SnO₂ target was located at the front of the substrate. Zn-doped SnO₂ thin films were grown on a c-sapphire substrate under the different flow rates of Ar. Other conditions are listed in Table 1. The flow rate of argon gas influenced the amount of flux of sputtered target particles that reaches the substrate. Generally, it is considered that increasing the argon gas flow rate decreases the amount of flux of sputtered particles available for growing a thin film, thereby suppressing the growth rate of the film. The Zn-doped SnO₂ thin films fabricated in the study were listed in Table 2.

After the thin film was deposited, its thickness was measured.
by surface profiler (D-120, KLA Techno.). The deposited Zinc-doped thin films were characterized by Raman spectroscopy (to identify the thin film), atomic force microscopy (AFM) (to evaluate its surface morphology), and secondary-ion mass spectrometry (SIMS) (to evaluate zinc concentration). Secondary-ion signals were converted to concentration by referring a paper.16)

The gas-sensing properties for hydrogen (1000 ppm) and ethanol (50 ppm) were evaluated. Gold film (as an electrode) was deposited by sputtering it onto the thin film. To evaluate the gas-sensing property of thin film samples, a new evaluation tool was developed. This tool could be used to evaluate the gas-sensing property of four samples. The samples were set in a quartz tube in the furnace. Gas was injected into the inlet at the bottom of the quartz tube, and ejected from the outlet at the top of the quartz tube. The deposited gold film was used as an electrode. The gas-sensor response (Rair/Rgas) was defined as the ratio of the resistance of the gold electrode in air (Rair) to that in the target gas (Rgas).

3. Results and discussion

The zinc-doped SnO2 thin films were characterized by AFM (to observe the surface morphology) and Raman spectroscopy (to identify the crystal phase of the thin film). Surface morphology of the deposited thin films was observed by AFM. It seems that the thin films has a dense morphology in which particle size of the film increased with increasing argon gas flow rate.

Raman spectra obtained from the zinc-doped SnO2 thin films, and from single-crystal SnO2 and c-sapphire substrate as references, are shown in Fig. 2. A peak at 634 cm⁻¹ for SnO2 appears in the case of all the thin films. Broad peaks due to nano-sized SnO2 appear in the range of 400–800 cm⁻¹.17) These signals are remarkable features of the SnO2 thin films deposited at argon gas flow rates of 8 and 12 sccm. The signals in this range do not appear in the case of the zinc-doped SnO2 film deposited at argon gas flow rate of 15 sccm. Moreover, the thick film deposited at argon gas flow rate of 15 sccm shows a peak at 634 cm⁻¹ (identified as SnO2).

The measured zinc concentrations in three of the thin films are plotted in Fig. 3. Samples were measured by SIMS from surface to the film/substrate interface. It is clear from the figure that all the films contained zinc in the range of 4.2 × 10¹⁸ to 2.2 × 10¹⁹/cm³. And zinc concentration in the films increased with increasing of argon gas flow rate. The characterization of thin films described here demonstrates that argon gas flow rate is an effective parameter for controlling grain size, crystal quality in Raman spectrum, and zinc concentration.

The gas-sensing property of the fabricated thin films in regard to reducing gases (such as hydrogen and ethanol) were evaluated at the operating temperature in the range of 350 to 500°C for hydrogen and 400 to 500°C for ethanol. The evaluation results (gas-sensor response, Rair/Rgas) at 400°C are summarized in Fig. 4. It is clear from the figure that the SnO2 thin films deposited at argon gas flow rate of 15 sccm exhibit the best sensing property. The highest response (namely, a value of about 270) was shown for ethanol at 50 ppm. The response for 1000 ppm of hydrogen was about 75. In addition, the highest response for hydrogen was 120 at 450°C. These results indicate that SnO2 thin films doped with zinc can effectively detect ethanol and hydrogen.
The sensing property of SnO2-based materials has been widely studied. Recent reported values of gas-sensing response of Zn-doped SnO2 for ethanol and hydrogen are reported in papers. The sensor response of SnO2 for ethanol was summarized in previous paper. According to the paper, the sensor response of SnO2 for ethanol is in the value of 3 to 15 when the measurements were carried out under the following conditions: target gas concentration of 50 and 100 ppm and operating temperatures of 250 and 350°C. It is indicated that the response value for ethanol in our results is larger than those of previous results. The hydrogen response of Zn-doped SnO2 was also summarized in previous paper. The values of hydrogen response of Zn-doped SnO2 varies between 1.8 and 120 at hydrogen concentrations of 300 and 10,000 ppm and operating temperatures of 140 and 325°C. From the above, our result for hydrogen is comparable with previous value. Effect of Zn doping in SnO2 thin film on gas-sensing property for ethanol and hydrogen needs to study in details and then the mechanism behind these trends remains as our future work.

4. Summary

The effect of argon gas flow rate on a SnO2 thin film grown by rf-sputtering was studied by using “double” targets composed of non- and zinc-doped SnO2. The results of this study reveal that increasing argon gas flow rate during growth of the thin film improves the crystal quality in Raman spectrum by enhancing growth of SnO2 grains, increases zinc concentration in the thin film. Zinc doped SnO2 thin film improves the ethanol response while retaining the hydrogen response. These demonstrate that the rf-sputtering thin-film growth method used in this study is a useful tool for characterizing material compositions that attain gas sensing with high response.

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