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Self-Amplifying Effect on Gas Sensitivity of ZnO Thin Film by Oxygen Pumping through YSZ Substrate

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A ZnO thin film was fabricated on 8mol% yttria-stabilized zirconia (YSZ) substrate by R.F. magnetron sputtering, and was used as the cathode of YSZ. Effects of oxygen pumping through YSZ on gas sensing characteristics of the ZnO thin film were investigated. At 400-550°C and under the oxygen partial pressure between 0.21 and $10^{-2.5}$atm, sensitivities of the ZnO thin film for CO and CH_4 gases were much larger under the condition of oxygen pumping than that without oxygen pumping. It was confirmed that the oxygen pumping gives an amplification effect for ZnO gas sensitivity; that is, a decrease in ZnO resistance by reducing gases makes the oxygen pumping initiate, leading a further decrease in ZnO resistance. This mechanism was investigated in detail by using an equivalent circuit analysis. The ZnO gas sensitivity under oxygen pumping was found to be dependent on ambient oxygen partial pressure and ZnO cathode resistance.
Key words: gas sensor, ZnO, YSZ, oxygen pumping, reducing gas

1. INTRODUCTION

Zinc Oxide (ZnO) is widely known as a semiconducting gas sensor material, which can detect toxic and combustible gases by changes of the conductivity. The conductivity of n-type semiconductors such as ZnO and SnO_2 is dominated by surface adsorbed oxygens and oxygen defects in crystal lattice (1). The conductivity of ZnO increases by the reaction of combustible gases with surface adsorbed oxygen. Many studies concerning an enhancement in the sensitivity have been conducted through microstructure control and use of catalytic reaction (2, 3). Generally, the gas sensitivity becomes low at high temperatures as 500°C. In some cases as exhaust gas monitoring, gas sensors are required to work at high temperatures.

Yttria stabilized Zirconia (YSZ), a solid oxide electrolyte with high oxygen ion conductivity, can pump up oxygen by applied external voltage at high temperatures (4, 5).

The authors have reported the gas sensing characteristics of the ZnO thin film, which was fabricated on YSZ substrate and used as the cathode of YSZ (6). It was confirmed that the gas sensitivity of the ZnO thin film in ZnO/YSZ/Pt element to CO and CH_4 gases was much larger when it is operated under the condition of oxygen pumping through YSZ than that without oxygen pumping in air and at 400-550°C. The mechanism for the enhanced gas sensitivity was assumed as follows. A decrease in the resistance of ZnO by the introduction of CO and CH_4 triggers the oxygen pumping through YSZ. That is, ZnO starts to work as the cathode of YSZ. This leads to a lowering of oxygen activity at the interface between ZnO and YSZ, and the resistance of ZnO decreases further due to a decrease in surface adsorbed oxygen on ZnO and an increase in oxygen defects in ZnO lattice. However, it is not clear how the ZnO cathode resistance changes by oxygen pumping actually. In the present study, the dependence of gas sensitivity of the ZnO thin film on the oxygen partial pressure was examined with and without oxygen pumping, and the effect of oxygen pumping on the gas sensitivity was discussed by using results of equivalent circuit analysis.

2. EXPERIMENTAL

Powders of ZrO_2 with 8mol% Y_2O_3 were pressed into a disc under a pressure of 49MPa, and sintered at 1600 °C for 4h. Both surfaces of the YSZ disc (0.8mm diameter and about 0.3mm thickness) were polished by emery paper and diamond pastes. Platinum electrode was applied onto one surface of the YSZ disc by firing Platinum paste. A ZnO thin film (1.8μm thickness) was fabricated onto the other surface by using R.F. magnetron sputtering. The specimen was annealed at 700 °C for 10 h in air. Two gold electrodes were formed at both ends of the ZnO thin film by ion sputtering, and Pt wires were attached to each Au electrode for

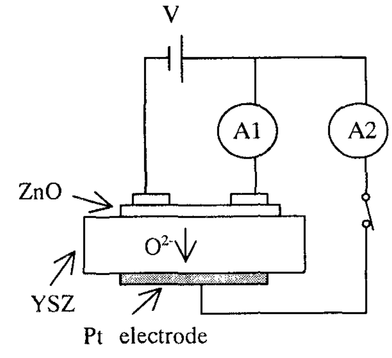

Fig.1 Schematic diagram of ZnO/YSZ/Pt element and electrical circuit

electrical measurements.

A parallel electrical circuit was set up, in which a DC voltage was applied both between two Au electrodes on the ZnO thin film and between one Au electrode and Pt electrode of YSZ, equally. A DC voltage was applied to the direction that oxide ions were pumped from the side of the ZnO thin film to the side of Pt electrode through YSZ. The voltage on YSZ was switched off for measurements without pumping. The schematic diagram of the sensor element and electrical circuit is shown in Figure 1. Currents running through ZnO and YSZ were monitored at A1 and A2, respectively. Under the condition of oxygen pumping, changes of the currents running through A1 and A2 by introducing test gases were measured. As a reference, a change of the current (A1) was also measured without oxygen pumping. The electrical measurements were carried out at 400-550 °C and under the oxygen partial pressure between 0.21 and $10^{-2.5}$atm. CO and CH_4 of 200-4000 ppm gases were used as test gases. The oxygen partial pressure was monitored by YSZ oxygen sensor. The gas sensitivity of the ZnO thin film (S_{ZnO}) was defined as the ratio of the currents (A1) before and after introducing test gases. Similarly, the sensitivity of YSZ (S_{YSZ}) was defined as the ratio of the currents (A2). Also, an amplifying degree of the gas sensitivity of the ZnO thin film by oxygen pumping was defined as the ratio of the sensitivities to test gases with and without oxygen pumping.

3. RESULTS AND DISSCUSSION

Figure 2 shows current changes of ZnO and YSZ by introducing 3300 ppm CO in 1% O_2-N_2 mixed gas with and without applying +0.5V to YSZ at 500°C. In both cases with and without oxygen pumping through YSZ, the currents running through ZnO increased by the introduction of CO. The gas sensitivity with oxygen pumping was much larger than that without oxygen pumping. Also, under the condition of oxygen pumping, it was confirmed that the ionic current running through YSZ increased just when CO was introduced. In other words, oxygen pumping through YSZ started by the introduction of CO. Figure 3 shows the dependence of the sensitivity of ZnO (S_{ZnO}) to CO gas on the concentration under the condition of oxygen pumping at 500°C. The sensitivity of YSZ (S_{YSZ}) is also represented in the figure. The S_{ZnO} and S_{YSZ} increased with the increase of the concentration of CO gas. It was confirmed that S_{YSZ} increased with the increase of S_{ZnO}. From these results, it is concluded that the enhancement of the gas sensitivity of the ZnO thin film was caused by oxygen pumping initiated by gas introduction. This phenomenon can be called as a self-amplifying effect on the gas sensitivity of ZnO thin film by oxygen pumping through YSZ.

Figure 4 shows the dependence of the sensitivity of ZnO and YSZ to 1000ppm CO on the oxygen partial pressure with and without oxygen pumping at 500°C.

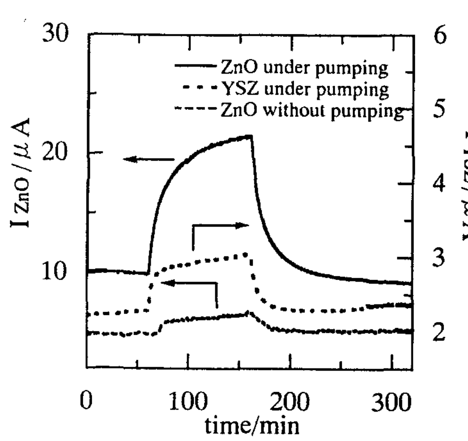

Fig.2 Current changes of ZnO and YSZ by 3300ppm CO in 1% O_2 -N_2 mixed gas with and without applying +0.5V to YSZ at 500°C

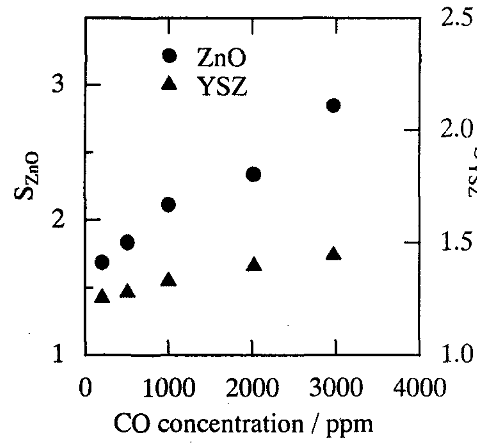

Fig.3 Dependence of sensitivity of ZnO and YSZ on CO concentration in air under the condition of oxygen pumping at 500°C

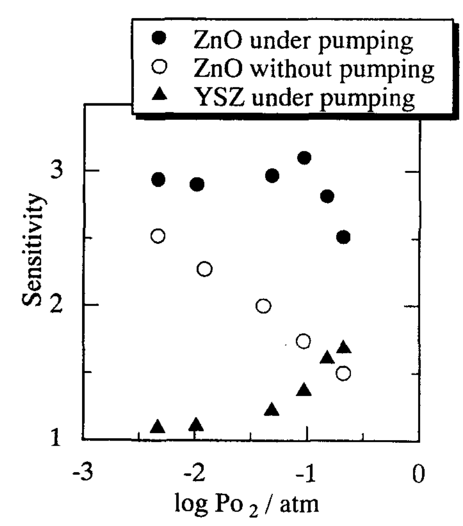

Fig.4 Po 2 dependence of sensitivity of ZnO and YSZ to 1000ppm CO with and without oxygen pumping at 500°C

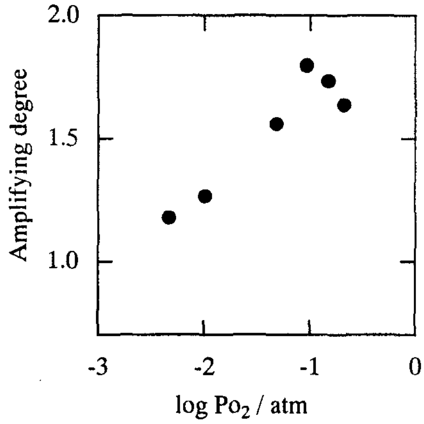

Fig.5 Po_2 dependence of amplifying degree of sensitivity of ZnO to 1000 ppm CO by oxygen pumping through YSZ at 500 °C

The gas sensitivity of ZnO without oxygen pumping increased gradually with a decrease in pO_2. On the other hand, the gas sensitivity of ZnO with oxygen pumping increased sharply with a decrease in pO_2, but didn't change so much under pO_2<10^{-1}atm. Also, the sensitivity of YSZ decreased with a decrease in pO_2. From this result, the amplifying degree of ZnO gas sensitivity was found to show the maximum at pO_2 of ≅10^{-1}atm, as shown in Figure 5. The resistance of YSZ is constant despite of a change of the oxygen partial pressure. The pO_2-dependent factors are the resistance of ZnO thin film and the electrode resistance of YSZ in the ZnO/YSZ/Pt element. Accordingly, it can be expected that they influence the pO_2 dependence of the amplifying degree of ZnO gas sensitivity.

In order to investigate how they influence the amplification of ZnO gas sensitivity actually, the resistance of the ZnO thin film and the electrode resistance of YSZ were examined by using an equivalent circuit, as shown in Figure 6. In the equivalent circuit, V is defined as the voltage equally applied to ZnO and YSZ. R_1 is defined as the resistance of the ZnO thin film. R_1' is the resistance of ZnO as the cathode of YSZ. R_2 is the sum of the bulk resistance of YSZ and Pt electrode as the anode of YSZ. I_1p,o and I_2,o are defined as the currents through ZnO and YSZ measured at A1 and A2 in carrier gases under oxygen pumping, respectively. I_1p,g and I_2,g are defined as the currents through ZnO and YSZ under oxygen pumping when reducing gases are introduced, respectively. Similarly, R_1p,o, R_2,o, R_1p,g and R_2,g are defined as using subscripts as p: under pumping, o: in carrier gas, g: in reducing gas. Here, for simplification of the calculation, two assumptions were constructed. Firstly, the bulk resistance and the resistance of Pt electrode (the anode of YSZ) do not change before and after the introduction of reducing gases. This is expressed as

$$R_2,o = R_2,g \qquad [1]$$

Secondly, since ZnO cathode resistance includes the resistance of ZnO thin film, it was assumed that their relationship can be expressed as

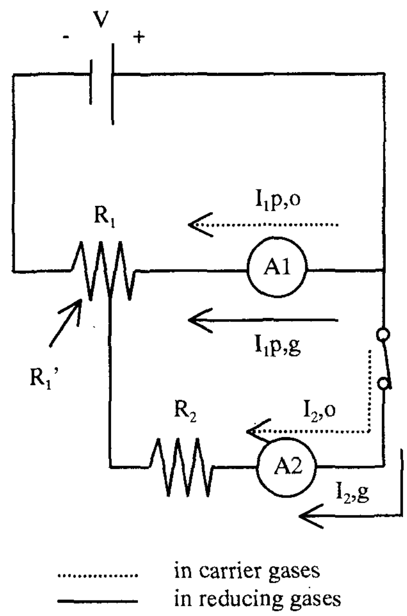

Fig.6 Equivalent circuit for ZnO/YSZ/Pt element (R_1: ZnO resistance, R_1': ZnO electrode resistance as cathode of YSZ, R_2: bulk resistance of YSZ + Pt electrode resistance)

$$R_1' = a\,R_1 \qquad [2]$$

where a is constant. In both cases in carrier gas and in reducing gas, the currents through ZnO and YSZ are also assumed to obey Ohm's law. Accordingly, following Eqs. 3, 4, 5, and 6 are formulated as below;

$$V = I_1p,o\ R_1p,o \qquad [3]$$

$$V = I_2,o\ (aR_1p,o + R_2) \qquad [4]$$

$$V = I_1p,g\ R_1p,g \qquad [5]$$

$$V = I_2,g\ (aR_1p,g + R_2) \qquad [6]$$

The gas sensitivity of the ZnO thin film (S_{ZnO}) and the sensitivity of YSZ (S_{YSZ}) are given by

$$S_{ZnO} = I_1p,g / I_1p,o = R_1p,o / R_1p,g \qquad [7]$$

$$S_{YSZ} = I_2,g / I_2,o = R_2,o / R_2,g \qquad [8]$$

From Eqs. 3 to 6, the correlation between S_{ZnO} and S_{YSZ} can be derived as

$$1/S_{ZnO} = (I_1p,o / aI_2,o)\,(1/S_{YSZ}) + 1-(I_1p,o / aI_2,o) \qquad [9]$$

Eq.9 represents that the correlation between $1/S_{ZnO}$ and $1/S_{YSZ}$ stands in a linear relationship.

Figure 7 shows the correlation between $1/S_{ZnO}$ and $1/S_{YSZ}$, measured for CO and CH_4 gases with various concentrations under the condition of oxygen pumping at 500°C. As expected from Eq.9, a linear relationship was confirmed in the correlation between $1/S_{ZnO}$ and

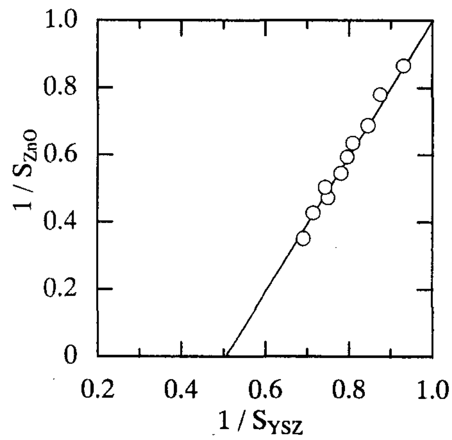

Fig.7 Correlation between sensitivity of ZnO (S_{ZnO}) and sensitivity of YSZ (S_{YSZ}) under the condition of oxygen pumping at 500°C

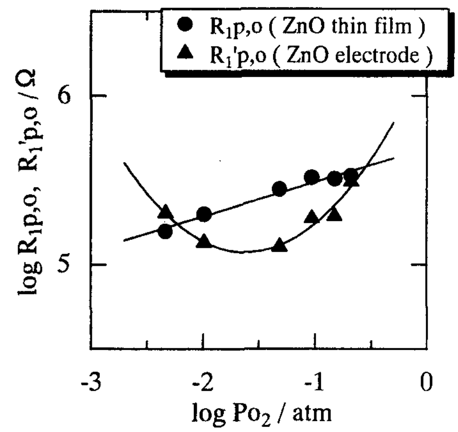

Fig.8 Po_2 dependence of R_1p,o (resistance of ZnO thin film) and R_1'p,o (resistance of ZnO cathode of YSZ) in carrier gas under oxygen pumping at 500°C

$1/S_{YSZ}$. Consequently, it could be said that the proposed equivalent circuit and assumptions of Eqs. 1 and 2 are valid as a model of ZnO/YSZ/Pt element in the present measurement condition. By using this equivalent circuit, the dependence of the amplifying degree of ZnO gas sensitivity on the oxygen partial pressure, as shown in Fig.5, can be discussed. The resistance of ZnO thin film (R_1p,o) and the resistance of ZnO cathode of YSZ (R_1',o) are given as follows, from Eqs.2 to 4 ;

$$R_1p,o = V/I_1p,o \qquad [10]$$

$$R_1',o = aV/I_2,o \qquad [11]$$

Figure 8 shows the dependence of R_1p,o and R_1',o on pO_2 in carrier gas under oxygen pumping. Firstly, the resistance of the ZnO thin film was proportional to the $pO_2^{1/4}$ in carrier gases under oxygen pumping, as is the case for the normal n-type semiconductor. This suggests that the resistance of the ZnO thin film is not much influenced by oxygen pumping through YSZ without reducing gases. Secondly, the resistance of ZnO cathode of YSZ decreased with a slope steeper than 1/4 with a decrease in pO_2, and increased with a decrease in pO_2 under $pO_2<10^{-1.5}$atm. Under $pO_2>10^{-1.5}$atm, it was considered that the ZnO cathode was greatly influenced by oxygen pumping even in carrier gases, so that the resistance of ZnO electrode decreased steeply with a decrease of the oxygen partial pressure. At low pO_2 under $<10^{-1.5}$atm, the oxygen pumping would become smaller due to an increased diffusion resistance of oxygen molecules in gas phase near the ZnO cathode. It seems that this pO_2 dependence of the resistance of ZnO cathode is reflected in that of the amplifying degree of ZnO gas sensitivity by oxygen pumping, shown in Figure 5. Under $pO_2>10^{-1}$atm, since a low electron conductance in ZnO film determines the cathodic reaction, i.e., the ionic current through YSZ, a lowering of ZnO resistance by introduction of reducing gases makes the ionic current through YSZ increase, leading to a high amplification degree. On the other hand, under $pO_2<10^{-1}$atm, since the diffusion of oxygen molecules near ZnO cathode determines mainly the ionic current through YSZ, a lowering of ZnO resistance by introduction of reducing gases will not contribute to an increase in the ionic current. In addition, an increase in gas sensitivity of ZnO film without pumping (as shown in Fig.4) will also make the pumping effect decrease. Therefore, the amplifying degree of ZnO gas sensitivity would be decreased with a decrease of pO_2, as is shown in Figure 5.

4. CONCLUSIONS

The gas sensitivity of the ZnO thin film in ZnO/YSZ/Pt element for CO and CH_4 gases was much larger when it is operated under the condition of oxygen pumping than that without oxygen pumping under the oxygen partial pressure between 0.21 and $10^{-2.5}$atm at 500°C. Oxygen pumping through YSZ was found to be much effective for the amplification of ZnO gas sensitivity at $pO_2>10^{-1}$atm. From the analysis of the equivalent circuit, oxygen pumping was suggested to be more effective when the rate determining step for the reaction at the interface between ZnO and YSZ is the electron diffusion through ZnO electrode as the cathode of YSZ.

5. REFERENCES

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