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APPLICATION OF A DUAL-DISC SEMICONDUCTORS TO A LEAN-BURN OXYGEN SENSOR

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A lean-burn oxygen sensor composed of two different sintered semiconductors was made by electrically contacting the discs of $SrAl_{0.01}Ti_{0.99}O_3$ and Cr_2O_3 with Pt mesh by mechanical pressing. The resistance-λ' characteristic of the connected device was investigated in the exhaust gas of oxygen-propane combustion, where λ' stands for the oxygen excess ratio. It was found that the $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device had promising properties for a lean-burn oxygen sensor, because the device exhibited a large change in the resistance in the lean-burn region with a negligible change in the rich-burn region.

Recently, there have been increasing interests in a lean-burn oxygen sensor which is useful for the improvement of energy effeciency in an engine system. Gas-diffusion-controlled oxygen sensors using solid-electrolyte have been investigated as a lean-burn oxygen sensor.[1-3] These sensors utilize the electrochemical pumping action. The output current, being limited by the diffusion rate of oxygen gas, was proportional to oxygen partial pressure and independent of the applied voltage. On the other hand, research and development of a semiconducting lean-burn oxygen sensor started with CoO[4] followed by the mixed oxides of CoO and MgO.[5] The semiconducting oxygen sensor has advantages of its simple structure, small size, and inexpensive price. From the stand point of feasibility for detecting the air to fuel ratio uniquely, whether the p-type semiconductivity of the oxide maintains in a rich-burn region or not is an important problem in application of semiconducting metal oxides to lean-burn oxygen sensors. We reported previously that $SrTiO_3$ exhibited p-type semiconductivity and high sensitivity to oxygen in the oxygen partial pressure range between 10^2 to 10^5 Pa.[6] However, the transition of semiconductivity of $SrTiO_3$ from p-type to n-type was found in the oxygen partial pressure of 10^{-2} Pa. In this study, we tried to search a new material which exhibited an excellent resistance-λ' characteristic using a connected device of semiconductors.

To prepare the device, Cr_2O_3 powder was pressed into discs of 10 mm in diameter and 2 mm thick, and it was sintered at 1200 °C for 6 h. The perovskite-type oxide, $SrAl_{0.01}Ti_{0.99}O_3$, was prepared by calcining the mixture of TiO_2, $SrCO_3$, and Al_2O_3 in the desired proportion at 1200 °C for 2 h. The resulting powder was ground and pressed into discs of 10 mm in diameter and 0.5 mm thick, and then sintered at 1200 °C for 6 h. The surfaces of both sintered discs were polished with fine emery paper. The Pt paste was applied to both sides of the disc and was fired at 1000 °C for 30 min. The characteristics of the elements thus prepared are summarized in

Table 1. Characteristics of the elements

No.	Sample	Sintering condition		Element size		Bulk density	Surface area
		Temp/°C	Time/h	Thick/mm	Electrode area/mm^2	g cm^{-3}	m^2 g^{-1}
1	$SrAl_{0.01}Ti_{0.99}O_3$	1200	6	0.4	50	3.38	1.2
2	Cr_2O_3	1200	6	1.9	7	2.49	1.6
3	$SrAl_{0.01}Ti_{0.99}O_3/Cr_2O_3$	——	—	0.4/1.8	50/7	——	——

Table 1. As shown in Fig. 1, the device was composed of $SrAl_{0.01}Ti_{0.99}O_3$, Cr_2O_3, and Pt mesh, the last being sandwitched by the two kinds of oxides. Electrical connection at the contact was ensured by mechanically pressing the oxides. The thickness and electrode area of each disc element used for the connected device were controlled in such a way that an excellent resistance-λ' characteistic of the device could be expected, as referred to the resistance-λ' characteristic of the constituent element. The resistance-λ' characteristics of $SrAl_{0.01}Ti_{0.99}O_3$, Cr_2O_3, and $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device were investigated under the exhaust gas of oxygen-propane combustion. The flow rate of 5 vol% propane diluted with nitrogen was maintained to be constant of 150 ml/min, and the flow rate of oxygen was controlled to obtain an appropriate ratio of oxygen to propane. The mixed gas was burned at 400 °C over a Pt/Al_2O_3 catalyst. Thus the oxygen excess ratio, λ', was defined by the following equation.

$$\lambda' = \frac{O_2/C_3H_8}{(O_2/C_3H_8)_{stoich}} \qquad (1)$$

Water vapor originating from the propane-oxygen combustion was trapped with a dry-ice and ethanol mixture before the exhaust gas was introduced into a test chamber. A calcia-stabilized zirconia (CSZ) oxygen sensor was used to measure the oxygen partial pressure in the exhaust gas.

Figure 2 shows the resistance-λ' characteristics of $SrAl_{0.01}Ti_{0.99}O_3$ and

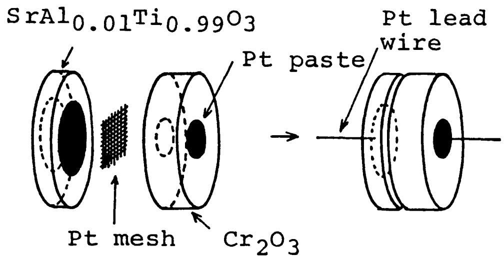

Fig. 1. Sensor structure of the $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device.

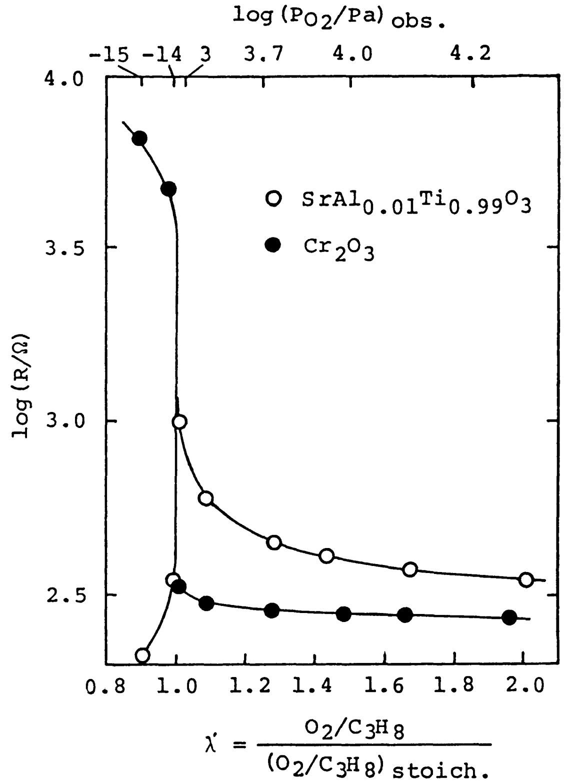

Fig. 2. Dependence of the resistance of the element on the λ' value at 973 K.

Cr_2O_3 at 700 °C. The observed oxygen partial pressure are plotted on the upper horizontal axis for reference. It is noticed here that the oxygen partial pressure increases abruptly from 10^{-14} to 10^3 Pa with increasing λ′ in the vicinity of λ′ = 1. In our previous paper,[6)] it was reported that the conduction mechanism of $SrTiO_3$ was p-type in an atmospheric environment and the conductivity was proportional to $P_{O_2}{}^{1/4}$ in the oxygen partial pressure range between 10^2 and 10^5 Pa. Further investigation of the electrical conductivity measurement in the oxygen partial pressure ranging 10^{-10} to 10^5 Pa suggested that the conduction mechanism of $SrTiO_3$ was changed into n-type at 10^{-2} Pa. The increase of the positive hole concentration by the partial substitution of aluminum for titanium was anticipated to maintain the p-type semiconduction even in a lower oxygen partial pressure. As shown in Fig. 2, the resistance-λ′ characteristic of $SrAl_{0.01}Ti_{0.99}O_3$ was similar to that of $SrTiO_3$, however, the p-type conduction mechanism was extended to a lower oxygen partail pressure than 10^{-2} Pa and the magnitude of the increase in the resistivity with increasing λ′ in the vicinity of λ′ = 1 was smaller than that of $SrTiO_3$.

It is well known that Cr_2O_3 exhibits p-type semiconductivity and is stable under reductive environment. As shown in Fig. 2, the result of the resistance-λ′ characteristic of Cr_2O_3 suggests that p-type semiconductivity is maintained in the oxygen partial pressure down to 10^{-15} Pa. The resistance of Cr_2O_3 decreased slightly with increasing λ′ up to λ′ = 1, decreased abruptly at λ′ = 1 and then decreased slightly with increasing λ′. This characteristic is in contrast to that of $SrAl_{0.01}Ti_{0.99}O_3$. The application of Cr_2O_3 device to a lean-burn oxygen sensor has a great disadvantage in a small oxygen sensitivity above λ′ = 1, that is, Cr_2O_3 exhibits only a small change in the resistance in the lean-burn region. From these results, it has become apparent that the combination of the resistance-λ′ characteristics of $SrAl_{0.01}Ti_{0.99}O_3$ in the lean-burn region and that of Cr_2O_3 in the rich-burn region exhibits a promising property for use of a lean-burn oxygen sensor.

The total resistance of the device of semiconductors connected in series as shown in Fig. 1 is controlled by the semiconductor which has a higher resistance than that of another one. Therefore, we investigated the resistance-λ′ characteristic of the $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device. An excellent resistance-λ′ characteristic can be obtained by employing the connected device, as shown in Fig. 3. It is obvious that the resistance-λ′ characteristic of the

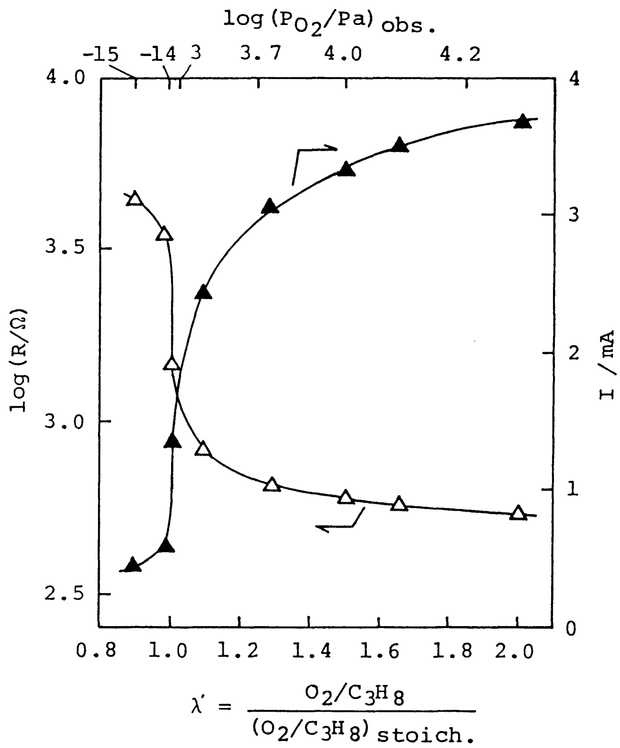

Fig. 3. The resistance-λ′ and current-λ′ characteristics of the $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device under the applied voltage of 2.0 V.

device in the lean-burn region is mainly dependent on that of $SrAl_{0.01}Ti_{0.99}O_3$. On the other hand, the resistance-λ' characteristic in the rich-burn region is mainly dependent on that of Cr_2O_3. Furthermore, one resistance value of the device corresponds to only one λ' value. The connected device exhibits a high sensitivity to oxygen in the lean-burn region and an apparent p-type semiconduction even in a lower oxygen partial pressure of 10^{-15} Pa. Figure 3 also shows the dependence of an electrical current measured in a closed circuit on the λ' value, in which the device was connected in series with a D. C. voltage supply and a picoammeter. It is confirmed that the connected device exhibits an excellent current-λ' characteristic. The current varies greatly with the λ' value in the lean-burn region, and the current in the rich-burn region is negligibly small.

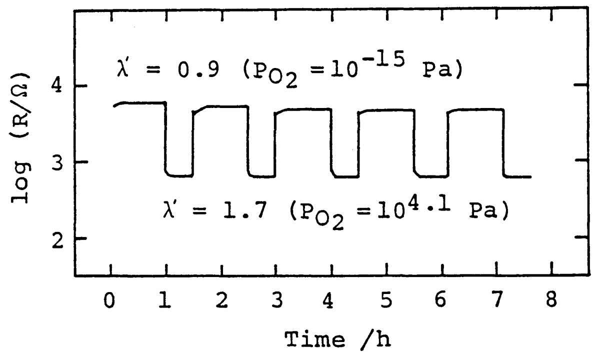

Fig. 4. Reproducibility of $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device at 973 K.

Figure 4 shows the reproducibility of the $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device when the oxygen excess ratio was changed abruptly from 0.9 to 1.7 and vice versa at 700 °C, where 0.9 and 1.7 of λ' value correspond to the oxygen partial pressures of 10^{-15} and $10^{4.1}$ Pa, respectively. It is confirmed that the device has a good reproducibility in its operation and a fairly good stability. The present results have proved that the $SrAl_{0.01}Ti_{0.99}O_3$-Cr_2O_3 device has promising properties for use of a lean-burn oxygen sensor.

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