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INVESTIGATION ON A LEAN-BURN OXYGEN SENSOR USING PEROVSKITE-TYPE OXIDES

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The oxygen sensitivity of $SrTiO_3$ doped with MgO has been investigated in the exhaust gas of propane-oxygen combustion as a function of the MgO content. Among the specimens studied, $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ appeared to be a suitable material for a lean-burn oxygen sensor, because it exhibited a high oxygen sensing performance in the lean-burn region and an excellent stability in the rich-burn region.

In recent years, there have been increased interests in oxygen sensors which can be used for monitoring and controlling combustion processes in an internal combustion engine of automobiles.[1,2] Oxygen sensors repored so far utilize changes in resistance of TiO_2 and those in the electromotive force of gas concentration cells using stabilized zirconia, both of which are induced by changes in oxygen concentration in engine exhaust gases. These sensors are useful to monitor the stoichiometric air to fuel ratio, and then are useful to eliminate the pollution with a help of three-way catalyst.[2,3] However, recent improvements of the engine system have made it possible to operate the engine under excess air (lean-burn) conditions, resulting in both high efficiencies for fuel combustion and depression of NO_x formation. The lean-burn oxygen sensors have drawn increasing interests.[4,5] Resistance measurements of a p-type semiconducting oxides, which are stable even in a rich-burn region, are useful for detecting the air excess ratio (λ), and such systems are advantageous in small size, simple structure, and low cost. We reported previously that $SrTiO_3$ exhibited a p-type semiconductivity and a high sensitivity to oxygen in the oxygen partial pressure of 10^2 - 10^5 Pa.[6] However, its usefulness was limited by the fact that change into n-type semiconductivity appears at oxygen partial pressure of 10^{-2} Pa. In this study attempts to substitute Mg^{2+} for Ti^{4+} in the $SrTiO_3$ were made to maintain the p-type semiconductivity even in an extremely low oxygen partial pressure.

Several samples of $SrTi_{1-x}Mg_xO_{3-\delta}$ were prepared by calcination of a mixture of $SrCO_3$, TiO_2, and MgO in a desired proportion at 1200 °C for 2 h. The calcined powders were ground and pressed into discs of 10 mm in diameter and 1 mm thick with 5 wt% methylcellulose, followed by sintering at 1200 °C for 6 h. The Pt paste was then applied on both faces of the discs, and fired at 1000 °C for 30 min. Measurements of resistivity-λ characteristics were carried out in a quartz tube at a temperature range between 600 °C and 800 °C. A stabilized zirconia (YSZ) oxygen sensor was set at a position close to the disc to monitor the oxygen partial pressure. Propane, oxygen, and nitrogen were mixed in an appropriate ratio to obtain a desired λ value, where λ is defined at the ratio of an actual (air/fuel) value to the stoichiometric one. The gas mixture was burned over a Pt/Al_2O_3 catalyst and the exhaust gas was introduced into the quartz tube.

The samples were identified by the X-ray diffraction method. As shown in Fig. 1, $SrTi_{1-x}Mg_xO_{3-\delta}$ (x = 0, 0.05, 0.1) has a cubic crystal structure with the lattice constant of 0.3905 nm. As for the specimen containing more than 20 mol% Mg, some new peaks appear in the X-ray diffraction patterns. The peaks marked by closed circles are MgO and others are unknown. In addition, a splitting of (110) peak is found in the diffraction patterns, suggesting that a transformation in the crystal structure is caused by the large amount of Mg content in $SrTiO_3$.

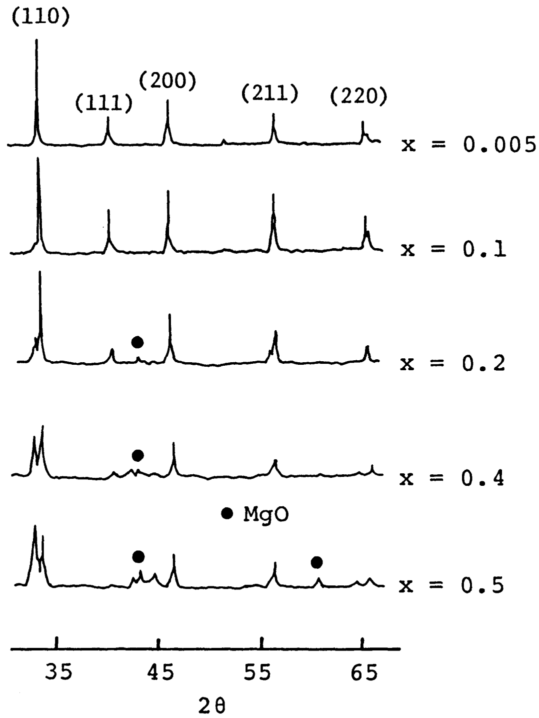

Fig. 1. X-Ray diffraction patterns of $SrTi_{1-x}Mg_xO_{3-\delta}$.

The resistivity-λ characteristics of $SrTi_{1-x}Mg_xO_{3-\delta}$ ($0 \leqq x \leqq 0.5$) in the exhaust gas of propane-oxygen combustion are shown in Fig. 2. The observed oxygen partial pressure determined by the YSZ oxygen sensor is given in the same figure. In the region of λ > 1, the resistivities of specimens increase with a decrease in the oxygen partial pressure, suggesting that all of them are p-type semiconductors. In this λ region, the resistivity decreases with an increase in the Mg content up to x = 0.4, but beyond that it seems to increase. Therefore, the smallest resistivity is achieved at $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$. The tendency of an increase in the resistivity with a decrease in the λ value becomes more marked with approaching to λ = 1, and the resistivity achieves its maximum in the vicinity of λ = 1 for all the samples investigated in this study. The degree of the increase in the resistivity around λ = 1 is most marked at $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$. In the region of λ < 1, the resistivity of

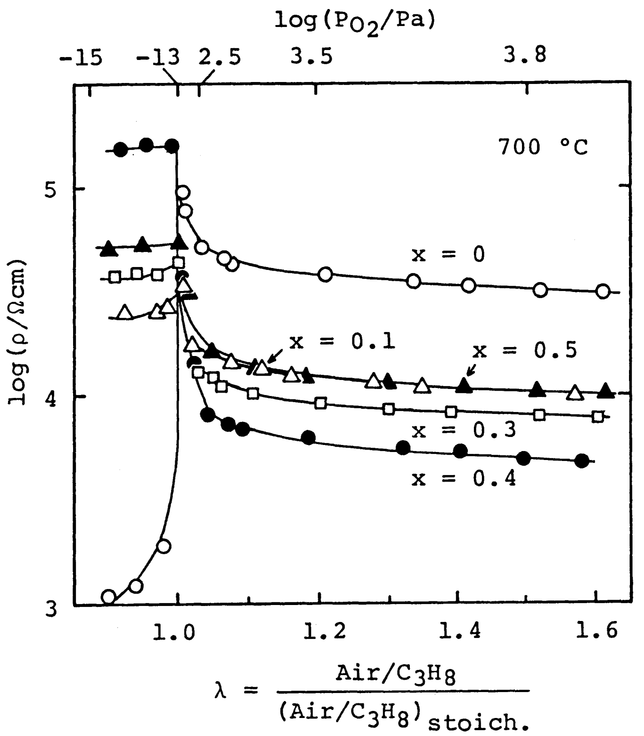

Fig. 2. Dependence of the resistivity of $SrTi_{1-x}Mg_xO_{3-\delta}$ on the air excess ratio.

$SrTiO_3$ decreases abruptly with a decrease in the λ value, suggesting that the semiconductivity of $SrTiO_3$ changes into n-type in the vicinity of λ = 1, as mentioned before. In contrast, $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ and $SrTi_{0.5}Mg_{0.5}O_{3-\delta}$ show a little decrease in their resistivities. The substitution of Mg^{2+} for Ti^{4+} makes an increase in the positive hole concentration, resulting in holding the p-type semiconductivity in a oxygen partial pressure lower than 10^{-2} Pa.

In general, the aim of lean-burn oxygen sensors is to monitor the λ value between 1.0 and 1.6. If $SrTi_{1-x}Mg_xO_{3-\delta}$ ($0 \leqq x \leqq 0.2$) specimens are put into practial use as lean-burn sensors, two different λ values, one of which is below unity and the other is above unity, are found at the same resistivity of the specimen. Therefore, an actual λ value is not determined correctly with the resistivity-λ characteristics of these specimens. In contrast, $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ exhibits the smallest resistivity in the region of λ > 1 and the largest resistivity in the region of λ < 1. Furthermore, it exhibits a little decrease in its resistivity with a decrease in the λ value below unity. Thus, one resistivity value of this specimen corresponds almost only one λ value. The above results have proved that $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ is the most suitable candidate for a lean-burn oxygen sensor among the specimens studied. In addition, $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ specimen could be operative in the temperature range between 600 °C and 800 °C with the constant sensitivity, as shown in Fig. 3.

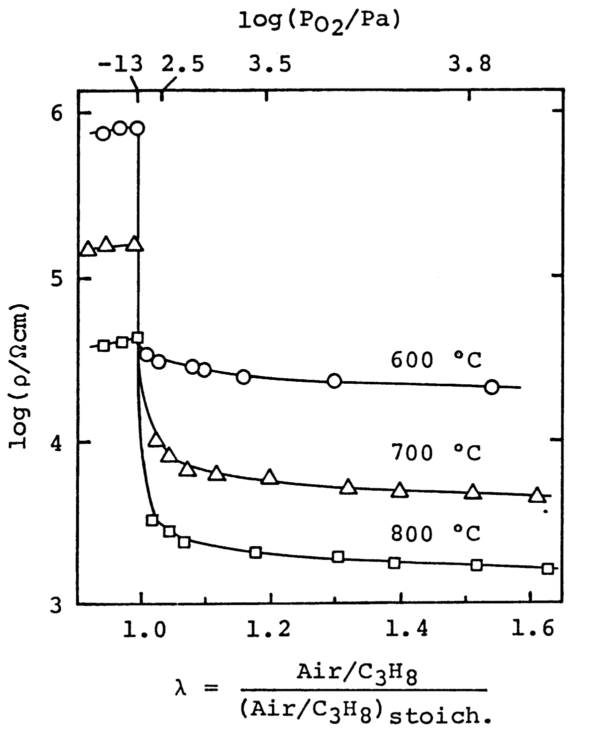

Fig. 3. Dependence of the resistivity of $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ on the air excess ratio at several temperatures.

In order to clarify the effect of the partial substitution of Mg^{2+} on the defect structure of $SrTiO_3$, the temperature programed desorption (TPD) of oxygen was carried out with the MgO doped specimens. The specimens were placed into the apparatus and preheated up to 800 °C in a flowing mixture of 20% oxygen and 80% helium at 40 cm^3min^{-1}

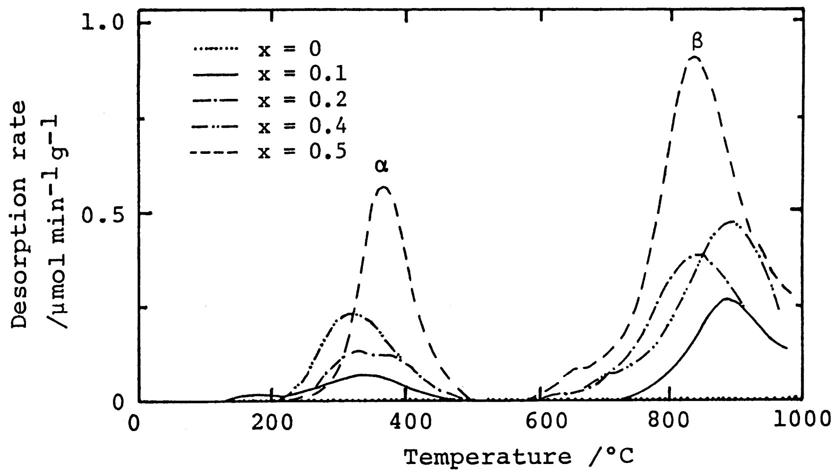

Fig. 4. TPD spectra of oxygen from $SrTi_{1-x}Mg_xO_{3-\delta}$.

Table 1. The amount of oxygen desorbed from $SrTi_{1-x}Mg_xO_{3-\delta}$

Sample	Surface area	Amount of desorbed oxygen					
		α	β	α	(θ_α)	β	(θ_β)
	m^2g^{-1}	$\mu mol\text{-}O_2/g$		$\mu mol\text{-}O_2/m^2$			
$SrTiO_3$	0.80	0	0	0	(0)	0	(0)
$SrTi_{0.9}Mg_{0.1}O_{3-\delta}$	3.20	1.42	4.43	0.44	(0.1)	1.38	(0.4)
$SrTi_{0.8}Mg_{0.2}O_{3-\delta}$	1.74	2.47	9.58	1.42	(0.4)	5.51	(1.4)
$SrTi_{0.6}Mg_{0.4}O_{3-\delta}$	1.64	3.61	8.62	2.20	(0.6)	5.26	(1.3)
$SrTi_{0.5}Mg_{0.5}O_{3-\delta}$	1.61	6.74	18.40	4.19	(1.1)	11.43	(2.9)

θ_α and θ_β denote surface coverages assuming 4.0 $\mu mol\text{-}O_2/m^2$ for the surface monolayer.

for 1 h, followed by cooling down to room temperature in the same atmosphere. Then, the TPD spectra of oxygen was carried out up to 1000 °C under helium flow at the same rate described above. Obtained spectra of these specimens are shown in Fig. 4. The spectra show two kinds of desorption peaks with peak maxima located at about 300 °C and about 900 °C, which are expressed by peak α and peak β, respectively. The amount of desorbed oxygen in these peaks together with the surface areas of the specimens are summarized in Table 1. With an increase in the Mg content from 10 mol% to 50 mol%, the amount of α oxygen increased from 1.42 μmol g^{-1}(0.44 μmol m^{-2}) to 6.74 μmol g^{-1}(4.19 μmol m^{-2}), whereas the surface area decreased from 3.20 m^2g^{-1} to 1.61 m^2g^{-1}. The surface coverage of α oxygen, θ_α, is beyond unity at 50 mol% Mg. It is thought from this result that a part of desorbed α oxygen is associated with oxygen vacancies produced by the substitution of Mg^{2+} for Ti^{4+}. Since the β peak was observed at high temperatures, the β oxygen could be assigned to the lattice oxygen. The introduction of MgO makes two opposite contribution to the resistivity of the specimen. First, it causes a decrease in the resistivity due to an increase of oxygen vacancy. Adsorbed oxygen on the oxygen vacancies in this case enhances the positive hole concentration. Secondly, the introduction of MgO above the solubility limit increases the resistivity due to the increased amount of undissolved MgO. As a result, $SrTi_{0.6}Mg_{0.4}O_{3-\delta}$ exhibited the smallest resistivity and the best sensitivity in the lean-burn region.

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