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Solid Electrolyte Oxygen Sensor Using LaF_3 Sputtered Film Workable at Room Temperature

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A solid-state sensor using a sputtered LaF_3 film was developed for detecting oxygen at room temperature. The EMF of the sensor varied logarithmically with the oxygen partial pressure. The response of the sensor was much improved by the water vapor treatment at 90 °C for 1 h: the 90% response time at 30 °C was as short as ca. 30 s. A sensing mechanism was proposed.

As one of the key components which govern various processes ranging from environmental or bio-related processes to industrial ones, oxygen has been a great, interesting target for chemical sensing. Although good solid electrolyte sensors such as zirconia oxygen sensor are now available for oxygen sensing at elevated temperatures usually above 500 °C, there is no commercial solid-state oxygen sensor operative at ambient temperatures in spite of its immeasurable importance in environmental and bio-related fields. Although electrochemical oxygen sensors using liquid electrolyte (oxygen electrode) are available for detection of oxygen at room temperature, they have several disadvantages such as leakage and corrosion associated with the use of liquid electrolyte.

Several attempts have been made to lower the operation temperature by using various ionic conductors.1-7) None of these attempts seem to have been so successful as to achieve an operation at room temperature with sufficient response rate. On this background, we are investigating new types of solid electrolyte oxygen sensors workable at room temperature. We recently reported that a sensor element using a LaF_3 single crystal could respond rather quickly to a change in oxygen partial pressure even at 25 °C.8) Subsequent studies have revealed that a sensor element using a sputtered LaF_3 film shows a faster response. This paper describes sensing performances and mechanism of the sputtered LaF_3 film sensor.

The sensor element was composed of the following electrochemical cell, its construction being illustrated schematically in Fig. 1.

(reference electrode) Sn, SnF_2 | LaF_3 film | Pt, O_2 (sensing electrode)

The LaF_3 film (ca. 5 um) was formed on a metallic tin plate (10 mm x 10 mm x 0.3 mm^t) in a RF sputtering instrument (NICHIDEN ANELVA, SPF-210HRF). Sputtering was carried out in Ar (5.3 Pa) for 20 h using a target of LaF_3 powder. X-Ray diffraction analysis revealed that the sputtered film was composed of poorly crystalline

LaF_3. As a sensing electrode, a sputtered Pt layer (ca. 200 nm) was attached on the LaF_3 layer. In order to produce SnF_2 at the interface between the Sn plate and the LaF_3 film, the sensor cell was subjected to an electrolysis at 24 V (at 1 μA) for 5 min in air at room temperature. Sample gases with various partial pressures of oxygen were prepared by mixing of oxygen with nitrogen and passed over the sensor element at a rate of 100 cm^3/min. As a sensor signal, the EMF of the sensor cell was measured by an electrometer.

In the sensor using a single crystalline LaF_3 previously reported,[8] the response (EMF) depended logarithmically on oxygen partial pressure (P_{O2}) as

$$E = \mathrm{Const.} + (RT/nF)\ln P_{O2} \qquad (1)$$

The constant n was close to 2 irrespective of temperature below 150 °C. The present sensor using a sputtered LaF_3 film was also found to show the same logarithmic dependence on P_{O2} at temperatures below 100 °C as shown in Fig. 2. The Nernstian slope of about 30 mV/decade indicated that n was also close 2, suggesting a following two-electron reduction of oxygen at the sensing Pt electrode.

$$O_2 + 2e^- = 2O^- \qquad (2)$$

It was noted that, before the sensors were subjected to the water vapor treatment described below (virgin sensors), the sputtered film sensor showed a faster response to a change in P_{O2} than the single crystal sensor. For example, the 90% response times of the former and the latter sensors were about 10 min and 90 min at 30 °C, respectively. We already reported[8] that the response rate of the single crystal sensor was much improved with a water vapor treatment, i.e., an exposure of the virgin element to an air stream containing water vapor. The highest response rate (the 90% response time of ca. 2 min) was achieved, for example, after a treatment at 150 °C for 12 h at water vapor pressure of 2 kPa. Such an effect of the water vapor treatment was also observed for the sputtered film sensor. However, the optimum treatment condition was found to be far milder. As shown in Fig. 3, the treatment at 90 °C for 1 h at water vapor pressure of 2 kPa was most effective to improve response rate of the sputtered film sensor, and the treatment at 150 °C was too heavy. It is quite notable that the sputtered film optimized in this way showed a surprisingly quick response even at 30 °C, i.e., the 90% response time as short as about 30 s. Such a quick response at room

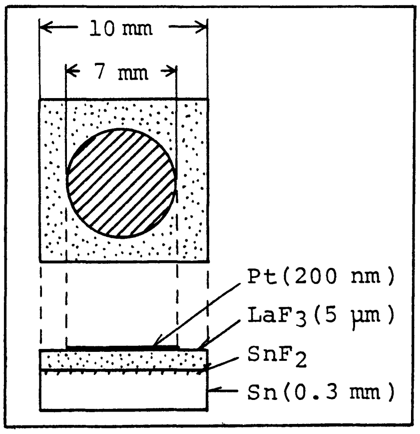

Fig. 1. Structure of the solid-state oxygen sensor using a sputtered LaF_3 film.

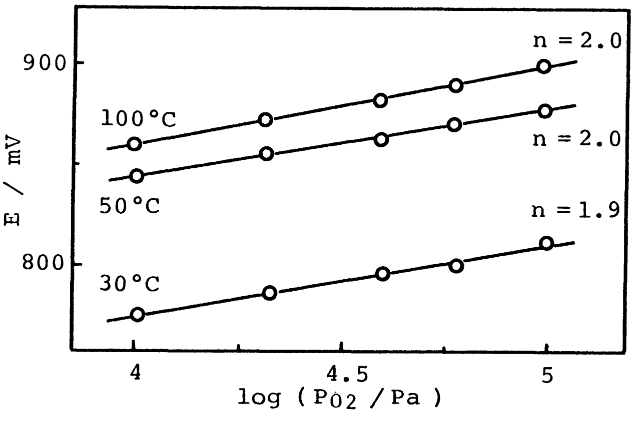

Fig. 2. Dependence of EMF of the sputtered LaF_3 sensor on oxygen partial pressure.

temperature have never been reported with other solid-state oxygen sensors. It was also found that, once optimized, both the response rate (90% response time to the change of P_{O2} from 21 kPa to 101 kPa) and the sensitivity (EMF change with an increase of P_{O2}) to oxygen were stable for the test period of about two months as shown in Fig. 4.

As described previously for the single crystal sensor,[8] the response (EMF) to oxygen is considered to be generated when the O^- ions formed by Reaction (2) are ion-exchanged with the lattice F^- ions of LaF_3 in the close vicinity of the sensing electrode as follows:

$$O^- + F_F^x = O_F^x + F^- \qquad (3)$$

where F_F^x and O_F^x stand for the F^- and O^- ions, sitting at F^- sites of LaF_3, respectively. Therefore, the overall reaction at the sensing electrode is given

$$O_2 + 2F_F^x + 2e^- = 2O_F^x + 2F^- \qquad (4)$$

On the other hand, the reference electrode reaction should be determined by

$$SnF_2 + 2e^- = Sn + 2F^- \qquad (5)$$

From Reactions (4) and (5), the total reaction in the sensor is given by

$$Sn + O_2 + 2F_F^x = SnF_2 + 2O_F^x \qquad (6)$$

Then, the EMF of the sensor can be expressed by the following equation as described before.[4]

$$E = E_{const} - \frac{RT}{2F}\ln\frac{a_{SnF2}\cdot(a_{O_F^x})^2}{a_{Sn}\cdot P_{O2}\cdot(a_{F_F^x})^2} \qquad (7)$$

where a stands for activity of each species. Since a_{Sn} and a_{SnF2} at the reference electrode should be constant, Eq. 7 can be rewritten as

$$E = E_{const} + \frac{RT}{2F}\ln P_{O2} + \frac{RT}{F}(\ln a_{F_F^x} - \ln a_{O_F^x}) \qquad (8)$$

In order to obtain a good linearity between E and $\ln P_{O2}$ as shown in Fig. 2, it is necessary to assume that both $a_{F_F^x}$ and $a_{O_F^x}$ are essentially constant as mentioned before.[3]

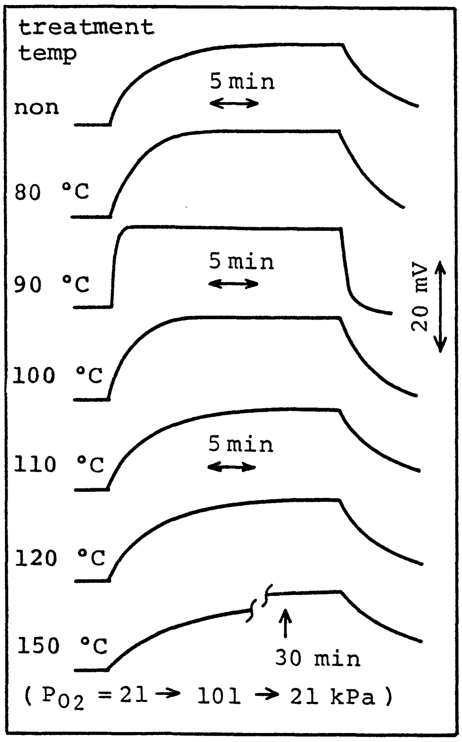

Fig. 3. Change of the response rate (at 30 °C) of the sputtered LaF_3 sensor with the water vapor treatment for 1 h.

The response rate of the sensor seems to be determined by the equilibration rate of Reaction (3), to which the water vapor treatment may be effective. As evaluated from XPS spectra of the sputtered LaF_3 film, the intensity ratio of O1s/F1s increased from 0.22 to 0.31 (or 0.55) with the water vapor treatment at 90 °C (or 150 °C) as shown in Fig. 5. The intensities of O1s signals in these spectra were not contributed by physisorbed water because they were not affected by evacuation at 150 °C. This increase suggests a partial hydroxylation (formation of OH group) of a surface of the LaF_3 film according to

$$F_F^x + H_2O = OH_F^x + HF \qquad (9)$$

where OH_F^x denotes OH^- ions sitting at the F^- site. At this moment, we consider that the ion exchange reaction (3) at the hydroxylated surface of the film proceeds in the following two steps, both steps being assumed to be rapid. Too much

$$O^- + OH_F^x = O_F^x + OH^- \qquad (10)$$

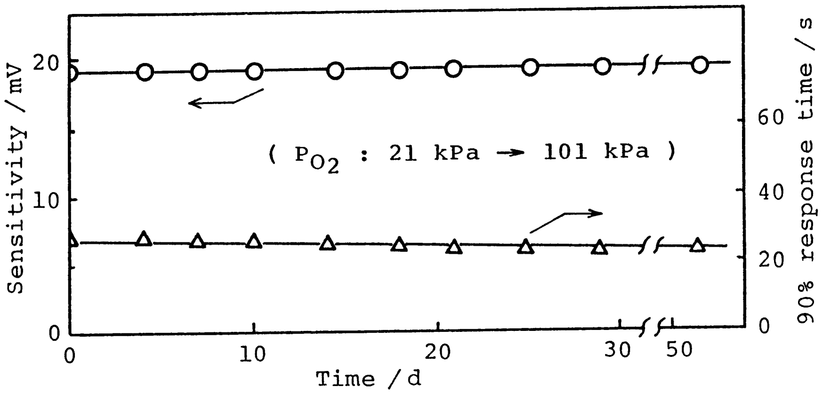

Fig. 4. Stability of the sensitivity (EMF change) and the response rate (90% response time) of the optimized oxygen sensor under an ambient atmosphere.

$$OH^- + F_F^x = OH_F^x + F^- \qquad (11)$$

hydroxylation of the surface of the LaF_3 film such as the water vapor treatment at 150 °C seems to give rise to an adverse effect on the equilibration rates of both Reactions (10) and (11).

In conclusion, the use of a LaF_3 sputtered film made it possible to fabricate a solid-state oxygen sensor which operated at room temperature with a short response time of ca. 30 s. Such a fast response at room temperature have never been achieved with the LaF_3 single crystal sensor or the other solid-state oxygen sensors reported so far. In addition adoption of a sputtered film instead of a single crystal offers also enormous advantages in sensor fabrication. Not only it reduces fabrication cost, but also it opens a way to micro-fabrication and sensor integration. However, further investigations are necessary as to the characterization of the sputtered film as well as the sensing mechanism.

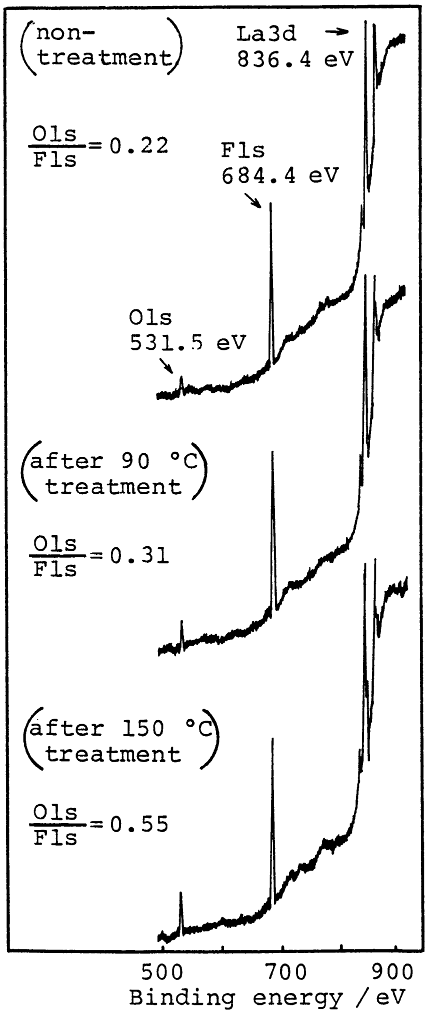

Fig. 5. Change of XPS spectra of a sputtered LaF_3 film with the water vapor treatment.

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