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Low temperature operation of thin-film limiting-current type oxygen sensor using graded-composition layer electrodes

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Abstract

A thin-film limiting-current type oxygen sensor incorporating graded-composition layers (GCL) was fabricated. The layers were formed by changing the sputtering power so that the mixing ratio of Pt and yttria-stabilized zirconia (YSZ) may changed continuously. The electrode interface resistance of the sensor has greatly decreased by inserting GCL between Pt electrode and YSZ electrolyte. In addition, the temperature dependence of the electrode interface resistance in the sensor with GCL has also become small. Therefore, even if the heat temperature of the sensor with GCL was decreased by 100–150 °C more than that of the sensor without GCL, the sensor with GCL could maintain the sensor output. It was demonstrated that the insertion of GCL was highly effective in decreasing the operating temperature of the thin-film limiting-current type sensor. Shortening of the warm-up time can be expected by using this electrode.

Keywords: Oxygen sensors; Zirconia; Thin-film; Limiting current

1. Introduction

The development of the reduction method of harmful emissions from automobiles might be an important concern of vehicle manufacturers. The development of a three-way catalyst system, which combines a three-way catalyst and an oxygen sensor, succeeded in a great decrease in the harmful exhaust components from the gasoline engine automobiles [1]. Thus during the past few decades, oxygen sensors for automobiles have been established as a key device for the emission control systems that decrease harmful components exhausted from automobiles. Most of the oxygen sensors used in automobiles are concentration-cell type and limiting-current type zirconia sensors. Since these sensors are used in exhaust atmospheres of several hundred degrees and are required to have high durability, the sensors are usually formed of sintered ceramics of yttria-stabilized zirconia (YSZ).

On the other hand, further reduction of the harmful emissions contained in the warm-up period has been urged in recent years for environmental and energy problems. To control the engine exhaust immediately from the start, an oxygen sensor with a short warm-up time is necessary. This requirement would be important in a limiting-current type oxygen sensor, which is used with an advanced three-way catalyst system for low emission vehicle (LEV) automobiles [2,3]. Various approaches are now being investigated to meet the demand: down-sizing of sensors with thin-film solid electrolytes [4–8], development of new electrolytes and new principales with low operating temperature [9–14], etc. However, these attempts could be still in the research phase.

A viable approach to shortening the start-up time should be to decrease the thermal capacity and/or the operating temperature of the sensor itself. As the thermal capacity of a small-sized sensor is small, a small-sized thin-film limiting-current type sensor might be promising. However, there is a hurdle that should be met to decrease the operating temperature of the thin-film limiting-current type sensor. When the sensor temperature is low, the limiting currents are not obtained at low voltages due to an increase in internal resistance of the sensor. Therefore, it is necessary to further decrease the internal resistance so that the sensor works practicably even if the sensor is not sufficiently heated up.

The internal resistance of a thin-film limiting-current type sensor is almost dominated by electrode interface resistance

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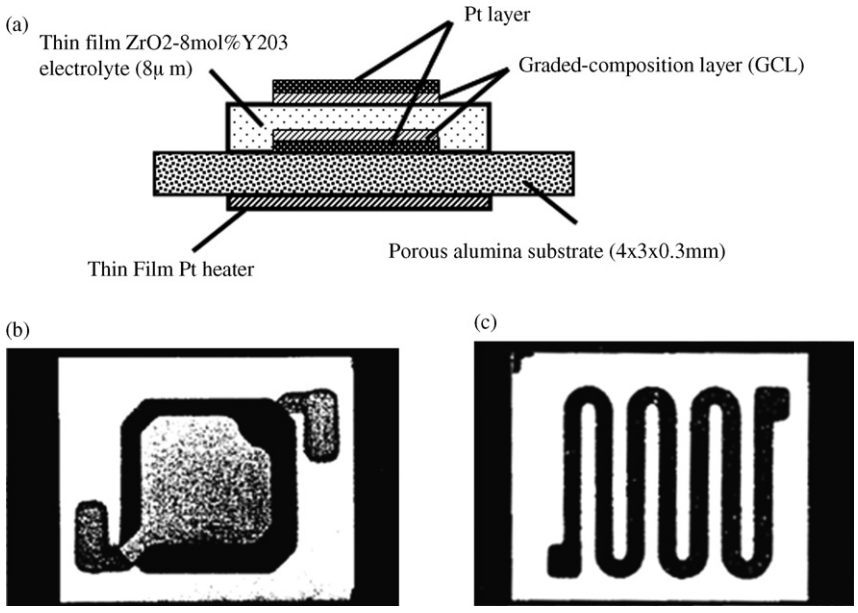

Fig. 1. (a) Structure of the limiting current type sensor, and detailed views of (b) sensor side and (c) heater side.

[15]. Therefore, the reduction technique of the electrode interface resistance has been investigated in this study. In order to decrease the operating temperature of the thin-film limiting-current type oxygen sensor, we have proposed a graded-composition layer (GCL) electrode in which the mixing ratio of Pt and YSZ varies continuously in the interface between Pt electrode and YSZ electrolyte.

2. Principles

A limiting-current type oxygen sensor consists of two parts: a diffusion-control layer where transporting rate of oxygen is controlled and a solid electrolyte cell with electrodes (Fig. 1). When a current is flowed through the solid electrolyte cell, the following electrochemical reactions occur, and oxygen moves from the cathode to the anode.

On the cathode side,

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (1)$$

while the anode side,

$$2O^{2-} \rightarrow O_2 + 4e^- \quad (2)$$

This phenomenon is well-known as 'electrochemical oxygen pumping'. If there is a diffusion-control layer on the cathode side, the solid electrolyte cell exhibits a saturated current–voltage characteristic. This saturation current is known as 'limiting current'.

When the gas transfer in the diffusion-control layer is subjected by the Knudsen diffusion, the limiting current I_{lim} is expressed as follows:

$$I_{lim} = \left(\frac{nFDS}{L}\right) C \quad (3)$$

where n is the number of electrons involved in the reactions (1) and (2), F is the Faraday constant, D is the diffusion coefficient of oxygen, S is the area of the cathode, L is the thickness of the diffusion layer, and C is the concentration of oxygen of the sensor ambience [16]. Since the limiting current is proportional to the oxygen concentration as shown in Eq. (3), the oxygen concentration can be estimated by measuring the magnitude of the current (limiting current) when a certain voltage is applied.

3. Experimental

3.1. Preparation of sensor

Fig. 1 shows a photograph and a cross-sectional view of a thin-film limiting-current type oxygen sensor. The detection part of this sensor has a multilayered structure; that is, a first electrode (Pt, graded-composition layer (GCL)), a solid electrolyte (YSZ), and a second electrode (Pt, GCL) are formed on one surface of a porous alumina substrate. A Pt heater is formed on the other surface of the porous alumina substrate. The substrate also functions as a diffusion-control layer.

A GCL was prepared using an ion beam sputtering (IBS) system (Commonwealth Scientific Corp.) with multiple ion guns. The layer was formed by controlling the power of the ion guns to continuously vary the composition ratio of Pt and YSZ. Table 1

Table 1
Preparation condition of GCL

Target	Pt and ZrO_2–8 mol% Y_2O_3 (YSZ)
Substrate temperature	Room temperature
Atmosphere	Ar
Pressure (Pa)	1.2×10^{-2}
Beam voltage (V)	500
Beam current (mA)	Pt: 100 ⇔ 50 YSZ: 30 ⇔ 80
Sputtering time (min)	20