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Ir–YSZ nano-composite electrodes for oxygen sensors

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Abstract

Iridium (Ir)–yttrium-stabilized zirconia (YSZ) nano-composite electrodes were prepared by MOCVD, and their electrode properties were examined. Ir–YSZ nano-composite electrodes consisted of amorphous YSZ and Ir particles of 5–10 nm in diameter. The interfacial conductivity for the Ir–YSZ electrodes was almost 1000 times higher than that of sputtered-Pt electrodes due to large contact area between YSZ and Ir in nano-composite electrodes and high catalytic activity of Ir nano-particles. The electro-motive-force values of the oxygen concentration cell constructed from the Ir–YSZ electrodes and YSZ electrolyte showed the Nernstian theoretical response within 10–20 s at 650 °C.

Keywords: Organometallic CVD; Iridium; Electrode; Oxygen sensor; AC impedance; Catalytic activity

1. Introduction

Oxygen sensors are playing an important role to control chemical processes and environmental monitoring because they can directly indicate the presence and concentration of oxygen in their environment. A Galvanic cell-type oxygen sensor is widely used, where yttrium-stabilized zirconia (YSZ) is commonly employed as a solid electrolyte due to high ionic conductivity and mechanical strength. Electrodes, on the other hand, should have high electronic conductivity, high chemical/thermal stability and catalytic activity for the dissociation of oxygen molecules [1–5]. Platinum group metals, particularly Pt, could satisfy these requirements, and then Pt has been generally applied to oxygen sensors. However, the operation temperature of a Pt/YSZ/Pt sensor is above 800 °C due to a low catalytic activity of Pt electrodes and a slow charge transfer reaction at the electrode/electrolyte/gas triple phase boundary.

Iridium (Ir) is a candidate material for the electrode, since Ir may have higher catalytic activity than Pt. In this study, Ir–YSZ nano-composite electrodes were prepared by MOCVD, and their microstructure and electrical properties were investigated.

2. Experimental

A horizontal hot-wall type MOCVD apparatus was used to prepare Ir–YSZ composite films in this study. $Ir(dpm)_3$, $Zr(dpm)_4$ and $Y(dpm)_3$ were used as precursors. Each precursor was vaporized and carried with argon gas separately, and all precursor vapors were mixed with oxygen gas in a quartz tube and conducted to the YSZ substrates through a hole of the mixing room. Compositions of the composite films were controlled by varying evaporation temperatures of precursors. Deposition conditions are summarized in Table 1.

The composition of the films was determined by electron probe microanalysis (EPMA). The microstructure was observed using scanning electron microscope (SEM), and their crystalline phase was investigated by X-ray diffraction (XRD). The electrical properties were measured by AC impedance spectroscopy with a two-probe method in the frequency range of 0.1 Hz to 10 MHz in air. The oxygen concentration cell was constructed using the composite electrodes and YSZ electrolyte. The

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Table 1
Deposition conditions

Deposition temperature, T_{dep}/K	923
Total gas pressure, P_{tot}/kPa	0.4
Precursor temperature	
$Zr(dpm)_4$, T_{Zr}/K	573
$Y(dpm)_3$, T_Y/K	423
$Ir(dpm)_3$, T_{Ir}/K	493–573
Gas flow rates	
Argon gas,	
$Zr(dpm)_4$, $FR_{Zr}/10^{-7}$ m^3 s^{-1}	8.0
$Y(dpm)_3$, $FR_Y/10^{-7}$ m^3 s^{-1}	4.0
$Ir(dpm)_3$, $FR_{Ir}/10^{-7}$ m^3 s^{-1}	8.0
Oxygen gas, $FR_{O2}/10^{-7}$ m^3 s^{-1}	3.2
Time, t/ks	9–12

composite film electrodes were attached to the both side of YSZ electrolyte.

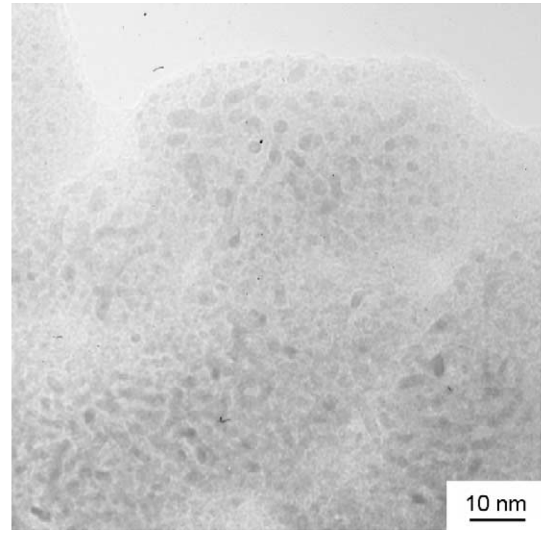

Fig. 2. TEM image of Ir–YSZ composite film.

3. Results and discussion

3.1. Structure

Fig. 1 shows a XRD pattern of Ir–YSZ nano-composite film (Ir=71 vol.%). A broad peak around 2θ=22° and some narrow peaks by Ir were observed, indicating the composite film would consists of crystalline Ir and amorphous YSZ. By changing precursor temperatures, compositions of Ir–YSZ composite films could be controlled from 3 to 71 vol.%. Amorphous YSZ contained 1–2 mol% Y_2O_3 in each film. Binding energies of Ir 4f electrons in composite films were almost the same to the reported values of Ir metal in agreement with the results of XRD.

Fig. 2 shows a TEM image of Ir–YSZ composite film (71 vol.%Ir). The average particle size of Ir (dark area in Fig. 2) was 3 nm, and they were dispersed in amorphous YSZ. Average particle sizes were not changed by varying Ir content.

3.2. Electrical properties

Fig. 3 demonstrates current–voltage characteristics of YSZ attached Ir–YSZ composite electrodes on both sides at 723 K in air. Current densities increased with Ir content, and the highest current density was twice that with conventional sputtered-Pt electrodes at 81 vol.%Ir. Since MOCVD can produce a film on a substrate with superior step coverage, the electrical resistivity of electrode/electrolyte interface could be smaller than sputtered-electrodes.

Fig. 4 depicts an AC impedance spectrum of YSZ with composite film electrode (71 vol.%Ir). There are three semicircles in the spectrum. The two semicircles near the original point were assigned to the bulk and the grain boundary responses of YSZ substrate, because they were independent of the kinds of electrodes and the associated capacitances were close to reported values [6]. The largest semicircle at the high Z' region was assigned to the response of Ir/YSZ interface (i.e., the charge transfer reaction at electrolyte/electrode/gas triple phase boundaries).

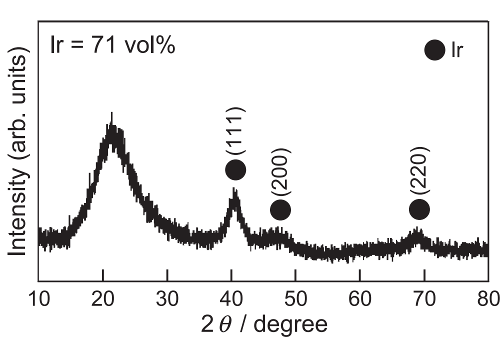

Fig. 1. XRD pattern of Ir–YSZ composite film prepared by MOCVD.

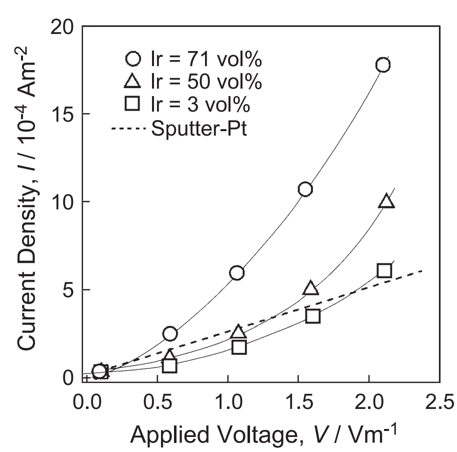

Fig. 3. Voltage–current characteristics of YSZ using Ir–YSZ composite electrodes.