Preparation of Ru-C Nano-composite Film by MOCVD and Electrode Properties for Oxygen Gas Sensor

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Abstract

Ru-C nano-composite films were prepared by MOCVD, and their microstructures and their electrode properties for oxygen gas sensors were investigated. Deposited films contained Ru particles of 5-20 nm in diameter dispersed in amorphous C matrix. The AC conductivities associating to the interface charge transfer between Ru-C composite electrode and YSZ electrolyte were 100-1000 times higher than that of conventional paste-Pt electrodes. The emf values of the oxygen gas concentration cell constructed from the nano-composite electrodes and YSZ electrolyte showed the Nernstian theoretical values at low temperatures around 500 K. The response time of the concentration cell was 900 s at 500 K.

Keywords : catalytic electrode, oxygen gas sensor, nano-composite, metal organic chemical vapor deposition, AC impedance spectroscopy

1. Introduction

Solid-electrolyte type oxygen sensors are widely used for monitoring oxygen concentration in exhaust gas of automobiles and chemical plants because of their relatively simple configuration and direct indication of oxygen content in ambient atmosphere. This type of oxygen sensors is mainly constructed from a solid electrolyte and electrodes. Yttria-stabilized zirconia (YSZ) is commonly used as a solid electrolyte due to high ionic conductivity and mechanical strength. Electrodes should have high electronic conductivity, high chemical/thermal stability and catalytic activity for the dissociation of oxygen molecules [1-3]. Since platinum group metals, particularly Pt, could satisfy these requirements, Pt electrodes have been generally applied to the oxygen sensors. The operation temperature of usual Pt/YSZ/Pt sensor is above 1000 K due to low catalytic activity of Pt and slow charge transfer at electrode/electrolyte/gas triple points at low temperatures. Since the low temperature operation of oxygen sensors is strongly required, a new electrode material with high catalytic activity at low temperatures should be developed.

Metal-organic chemical vapor deposition (MOCVD) can be suitable for preparing electrodes because of its controllability of microstructure of films by changing deposition conditions. Many kinds of metal films have been prepared by MOCVD, in which impurity C has been often contained degrading the electrical conductivity [4, 5]. On the other hand, the carbon phase has an advantage to hinder the grain growth of metals, and to form metal nano-particle dispersed composite films. The co-deposited C would often enhance the catalytic activity as reported in Pt-C catalysts. Thus, metal-C nano-composite electrodes having high catalytic activity can be prepared by MOCVD.

In this study, Ru-C composite electrodes were prepared by MOCVD, and their microstructures and electrode properties were investigated.

2. Experimental and Results

Ru-C films were prepared on silica glass and YSZ(8 mol%Y_2O_3-ZrO_2) substrates using a horizontal hot-wall type MOCVD apparatus [6]. $Ru(dpm)_3$ (dpm: dipivaloylmethanato) was used as precursors. Compositions and crystalline phases of films were analyzed by Auger electron spectroscopy(AES), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Microstructures were investigated with a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The electrical properties were studied by DC method and by AC impedance spectroscopy with a two-probe method in the frequency range between 0.1 Hz and 10^7 Hz. The oxygen concentration cell was constructed with the Ru-C nano-composite film electrodes and YSZ electrolyte. The electro-motive-force (emf) values were measured at temperatures from 500 to 773 K by changing the oxygen partial pressure ratio from 1 to 5**.**

Fig.1 shows TEM images of the film prepared at T_{sub}=673 K and $FR_{O2}=6.7\times10^{-8}$ m^3s^{-1}. Dark particles of 5-20 nm in size were dispersed in an amorphous matrix without pore or gap at the boundary.

Fig. 2 summarizes temperature dependence of the interfacial conductivity, which is related to the charge transfer process at the electrode/YSZ interface. The

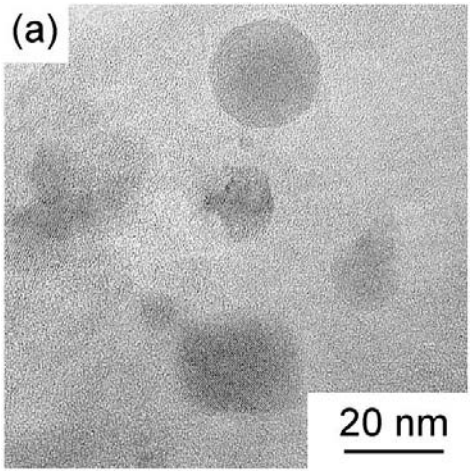

Fig. 1. TEM images of Ru-C composite film prepared at T_{sub}=673 K and FR_{O2}=6.7×10^{-8} m^{3}s^{-1}.

interfacial conductivity of Ru-C nano-composite electrode was 1000-10000 times higher than that of reported Pt electrode [7]. The high interfacial conductivities of the nano-composite electrodes could suggest the high catalytic activities of Ru nano-particles. The high interfacial conductivity of Ru-C nano-composite could be mainly caused of the large effective surface area of Ru particles in the nano-composite film without aggregation as shown in Fig, 1.

Fig. 3 shows the emf values of the oxygen gas concentration cells using the nano- composite electrodes. The Ru-C nano-composite electrodes showed the theoretical values even at 500 K. The response time of the oxygen gas concentration cells using Ru-C nano-composite electrodes. The response time of Ru-C electrode was 900 s at 500 K.

3. Summary

Ru-C nano-composite films were prepared by MOCVD. Ru particles of 5-20 nm in diameter were dispersed in amorphous C matrix. The AC interface electrical conductivities for Ru-C nano-composite electrodes were 1000-10000 times higher than that of reported Pt electrode. The emf values of the oxygen gas concentration cell constructed from Ru-C nano-composite electrodes showed the Nernstian theoretical values even at 500 K. The response time of the concentration cell was 900 s at 500 K for Ru-C nano-composite electrodes.

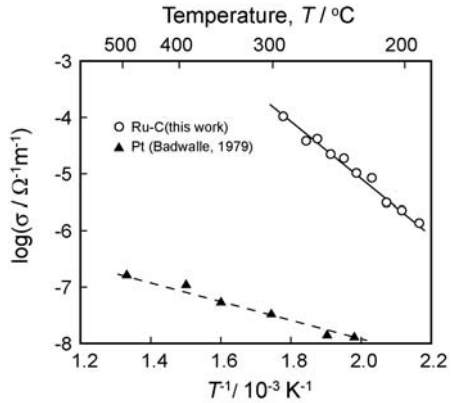

Fig. 2. Temperature dependence of Ru-C/YSZ interfacial conductivity.

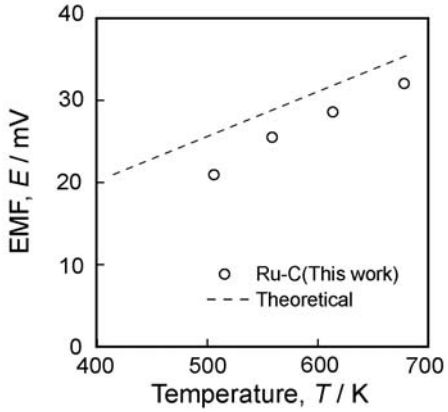

Fig. 3. EMF values of the oxygen concentration cell using the Ru-C nano-composite electrodes at 500 K.

4. References

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