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Ir Cluster Films Prepared by MOCVD as an Electrode for a Gas Sensor

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Iridium films were prepared by metal organic chemical vapor deposition (MOCVD) , and their properties as the electrode for an oxygen gas sensor were investigated. The Ir films consist of Ir clusters (1 to 3 nm in diameter) and amorphous carbon surrounding each Ir clusters. The charge transfer at the Ir cluster film electrode/electrolyte interface was about 100 times greater than that for other conventional platinum electrodes below 500℃. The emf values of the oxygen cell constructed from the Ir cluster film electrode and zirconia electrolytes showed the Nernstian theoretical values even at 300℃.

Key words: iridium, cluster, metalorganic chemical vapor deposition, electrode, gas sensor

1. INTRODUCTION

Platinum group metals are widely used as electrodes because of their high electrical conductivity and superior oxidation resistance. Since platinum group metals such as platinum (Pt) have also catalytic properties, they are applied to the electrode for oxygen sensors using oxide-ion conductors typically yttria-stabilized zirconia (YSZ). There are at least two kinds of oxygen gas sensors (i.e., electro-motive-force (emf) type and limiting-current type sensors). In those sensors, the operating temperature should be more than 500℃ due to sluggish charge transfer reactions at the electrode/YSZ interface[1]. In order to reduce the energy consumption and elongate the life time of the sensors, highly catalytic and porous electrodes should be developed to decrease the operating temperature because the charge transfer reactions proceed at the electrolyte/electrode/gas three phase interface.

Metalorganic chemical vapor deposition (MOCVD) is advantageous to control the microstructure by changing deposition parameters [2]. So far, many kinds of Pt [3] or Ir electrode films [4] have been prepared for microelectronic applications by MOCVD. However, the metals prepared by MOCVD often contain impurity carbon, which would degrade the electrical conductivity in the application to the semiconductor devices [5,6]. On the other hand, the carbon phase could hinder the grain growth of the metals, and no reaction takes place at less than 1500℃. In the present work, we found that Ir films containing carbon prepared by MOCVD had excellent performance as an electrode for YSZ solid electrolytes. In this paper, we report the microstructure and the electrochemical properties of the Ir films.

2. EXPERIMENTAL

A horizontal hot-wall type MOCVD apparatus made of mainly quartz glass tube was used in the present work. Fig. 1 represents the schematic diagram of the experimental set-up. Ir films were prepared on silica glass and yttria stabilized zirconia (YSZ; 8mol%Y_2O_3, 12mm in dia. by 1mm thick) substrates by using acetylacetonate precursor ($(CH_3COCHCOCH_3)_3Ir$). Pt films were also prepared by MOCVD for comparison. The precursor vapors were carried with argon gas at a

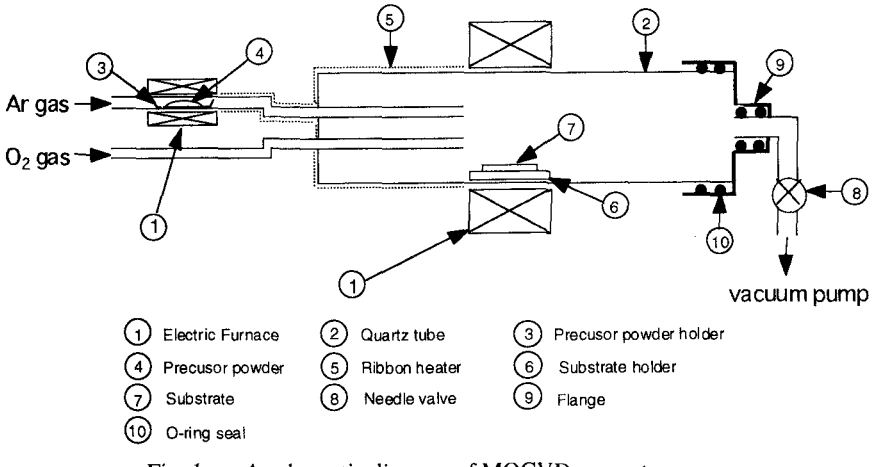

Fig. 1 A schematic diagram of MOCVD apparatus.

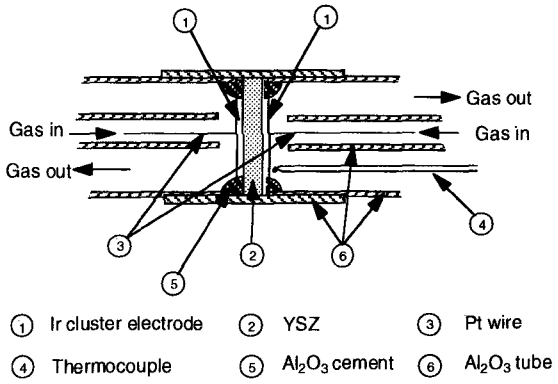

Fig. 2 A schematic diagram of oxygen concentration cell.

flow rate (FR_{AR}) of 8.3 to $10^{-7}m^3/s$. The precursor temperature (T_{prec}) was kept at 180℃, and the deposition temperature (T_{dep}) was changed between 500 and 700℃. The total gas pressure (P_{tot}) was maintained at 0.27kPa.

The composition of the deposits was analyzed by Auger electron spectroscopy (AES), and the microstructure was investigated with TEM, XRD and SEM. The electrical properties were investigated by a.c. impedance spectroscopy with a two-probe method in the frequency range between 0.05Hz and 20MHz in air. Fig. 2 depicts the schematic diagram of the oxygen concentration cell. The oxygen concentration cell was constructed using the Ir film as the electrode and YSZ as the solid electrolyte. The Ir film electrode was attached to the both side of the YSZ solid electrolyte. The voltage-current (V-I) characteristics of the YSZ solid electrolyte using the electrodes of the Ir film and the Pt sputtered film (that is now commercially applied to a limiting-current type oxygen sensor for automobiles) were measured. The electrical properties were measured in the temperature range between 250 and 600℃.

3. RESULTS AND DISCUSSION

3.1. Microstructure of MOCVD Ir films

Fig. 3 shows the XRD pattern of the Ir films (about 200nm thick) prepared on silica glass substrates. The Ir films were black having broad XRD peaks, and adhered well to the substrates. The calculations from the half-width of the X-ray peaks suggest that the Ir grains are about several nanometers in size.

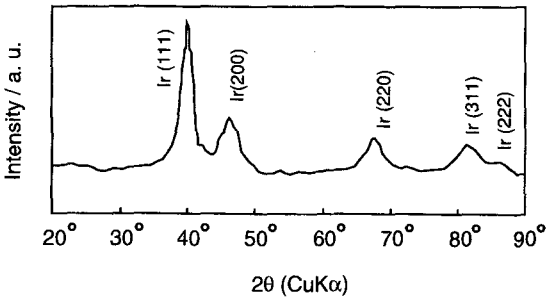

Fig. 3 XRD pattern of Ir cluster film (T_{dep}=600℃).

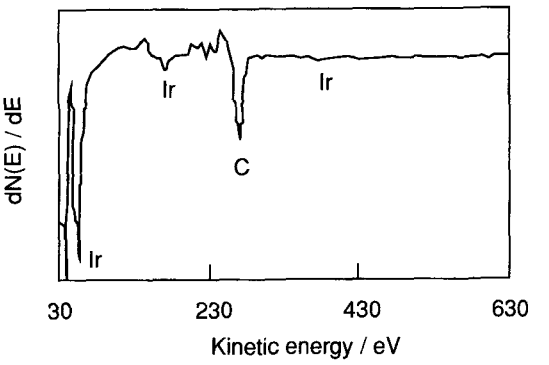

Fig. 4 AES spectrum of Ir cluster film after Ar etching (T_{dep}=600℃).

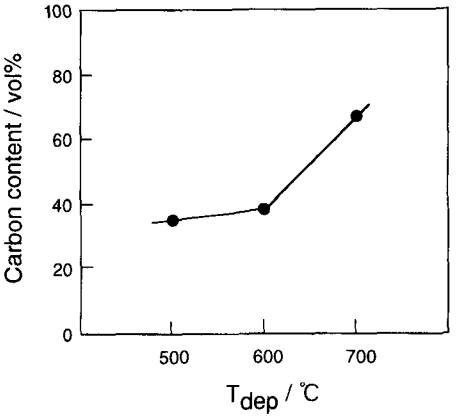

Fig. 5 Effect of deposition temperature (T_{dep}) on the carbon content in the Ir cluster film.

Fig. 4 depicts the AES spectrum of the Ir films after surface etching by Ar ions for 600s, which indicates that the Ir films contained carbon. The carbon content was estimated from the Ir to C intensity ratio of AES spectra. Fig. 5 shows the effect of T_{dep} on the carbon content in the films. The carbon content increased with increasing T_{dep}.

Fig. 6 shows the TEM micrographs of the Ir film. Ir crystallites (1 to 3nm in dia.) are surrounded by amorphous carbon. Each Ir crystallite consists of several tens to 100 atom clusters. The lattice image of (111) plane of Ir clusters can be observed in Fig. 6(b). Therefore, in this paper, we describe the Ir film as "Ir cluster film". The structure of MOCVD Pt films was similar to that of Ir cluster films.

3.2. Electrochemical properties of Ir cluster films

Fig. 7 depicts the a.c.impedance spectra for several kinds of electrodes deposited on the YSZ solid electrolytes. Carbon-free Ir and Pt films were also prepared as electrodes by adding O_2 gas(FR_{O2}=2 to $10^{-7}m^3/s$) for comparison. Small semicircles near the original point were independent of electrodes. They were assigned to the bulk (YSZ electrolyte) response because the associated capacitance was significantly small (3 to 10^{-11}F) [7]. The grain boundary response of

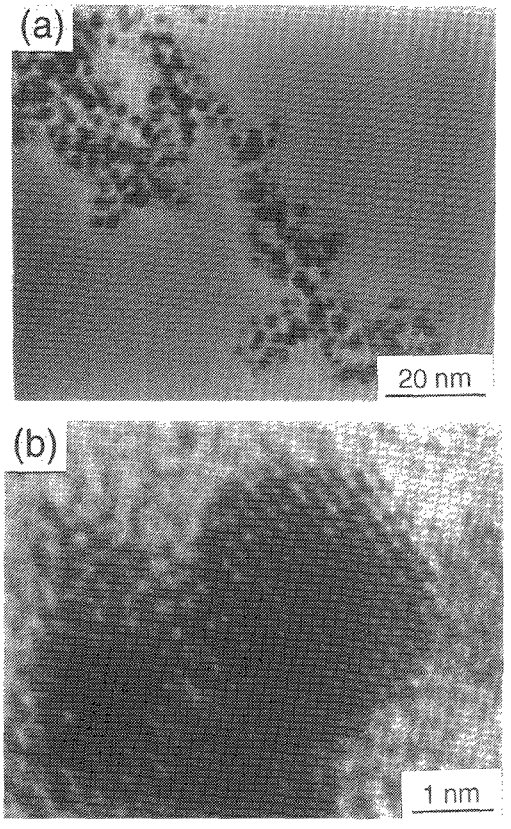

Fig. 6 TEM micrographs of the Ir cluster films (T_{dep}=600℃).
(b) is a higher magnification of (a).

the YSZ was not resolved because it was too small (about 1/100 times smaller than that of the bulk impedance). At lower frequencies (i.e., right-hand side of the bulk semicircles, the second semicircles appeared strongly depending on the kinds of electrodes. These dispersions must be caused by a YSZ/electrode/gas interface reaction because of a large associated capacitance (several to several tens μF) [8]. The semicircle for the Ir cluster film is magnified in the inserted figure because it is much smaller than that from other electrodes. This shows that the Ir cluster film is highly reversible and catalytic for the YSZ solid electrolyte.

Fig. 8 summarizes the conductivity associated with the interface process (interface conductivity). The figure includes the values from Pt paste electrode in a literature [9]. The activation energy for the interface conduction of Pt films were 130 to 140 kJ/mol which is almost in agreement with the dissociation of oxygen molecules accompanying the charge transfer reaction at the interface [10]. The interface conductivity of carbon-free MOCVD Pt electrode showed almost the same value of Pt paste electrode prepared by the present authors. The activation energies for these Pt electrodes were almost the same as the literature value. The activation energies of the Ir cluster electrode and carbon-free Ir electrode, 90 and 96 kJ/mol respectively, were smaller than those of Pt electrode. This suggests that dissociation of oxygen at the Ir electrode may be

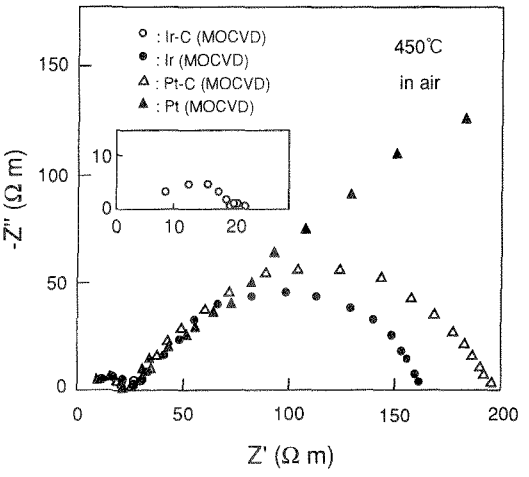

Fig. 7 A.C. impedance spectra for several kinds of electrodes deposited on the YSZ solid electrolyte.

slightly different from that at Pt electrode. It is known that the Ir electrode has better performance than Pt electrode for the electrolysis of water at the anode reaction due to a smaller oxygen over-voltage value [11]. The affinity between Ir and oxygen is stronger than Pt and oxygen, suggesting that the oxygen adsorption of Ir is more significant than that of Pt [12]. These features might have affected the difference of the interface conductivity between Ir and Pt electrodes. The Pt-C electrode showed low interface conductivity than that of carbon-free Pt electrode. This could have resulted from the weak adherence between Pt-C electrode and YSZ solid electrolyte. Once the temperature was raised to more than 600℃, the

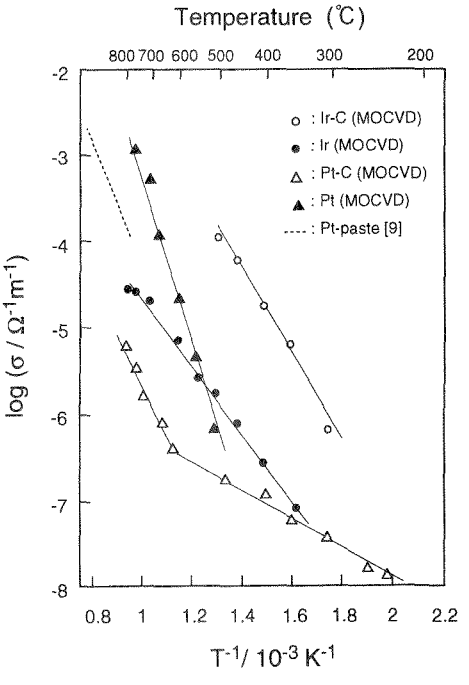

Fig. 8 Temperature dependence of conductivity associated with the interface reaction process.

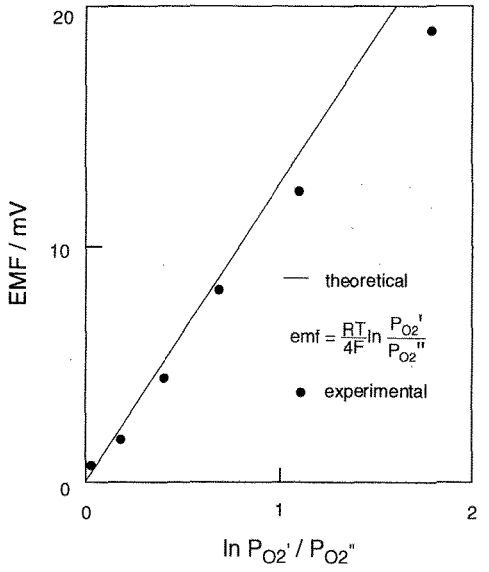

Fig. 9 Emf values of the oxygen concentration cell using the Ir cluster films.

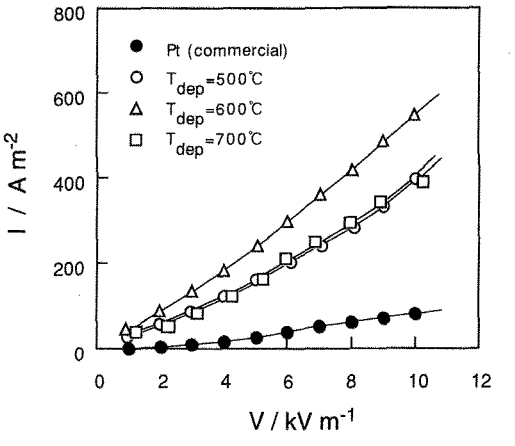

Fig. 10 Comparison of I-V characteristics between Ir cluster film and commercially used sputtered Pt film in the limiting-current type oxygen sensors at 500℃.

interface conductivity of the Ir cluster film decreased to the values as same as those of carbon-free Ir films. After the measurements in air at more than 600℃, the color of the Ir cluster film slightly changed from black to gray, and IrO_2 was identified by XRD. The degradation of the catalytic property could be mainly caused by the grain growth of the Ir clusters. It is reported that amorphous Ir-C composite films prepared by r.f.(radio frequency) sputtering were oxidized into IrO_x in air at 250℃ [13]; however, the present Ir cluster films seem stable in air up to 500℃.

Fig. 9 shows the emf values of the oxygen concentration cell using the Ir cluster films. The figure represents the relationship between oxygen partial pressure ratio (P_{O2}'/P_{O2}'') and emf values at 300℃, where P_{O2}' was fixed at 0.1MPa. The emf vs. (P_{O2}'/P_{O2}'') ratio was nearly to the theoretical value in the range between P_{O2}'/P_{O2}''=1.2 and 2.7. The emf values were quickly stabilized even at 300℃ within a few tens seconds. The response time became shorter with increasing temperature.

Fig. 10 represents the comparison of V-I characteristics between the Ir cluster film and the commercially operating Pt sputtered film in the oxygen sensor. In the limiting-current type sensor, the greater the current density, the higher the sensitivity to oxygen partial pressures. The Ir cluster film prepared at T_{dep}=600℃ showed the best performance, in which the current of the Ir film was about seven times as large as those of the commercial Pt sputtered film.

4. SUMMARY

Ir cluster films were prepared by MOCVD using an acetylacetonate precursor. Each Ir cluster, 1 to 3 nm in dia., was surrounded by amorphous carbon. The Ir cluster films deposited on YSZ solid electrolyte showed excellent electric and catalytic performance particularly at low temperatures below 500℃. The interface conductivity resolved from a.c. impedance spectra for the Ir cluster film electrodes was far greater than that of other Pt and Ir electrodes particularly at lower temperatures. The emf values of the oxygen concentration cell constructed with the Ir cluster film electrodes showed the theoretical Nernstian response even at 300℃. The electric current of the Ir cluster film was about seven times greater than that of Pt sputtered film that is used for automobile oxygen sensors.

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