

Application of plasma films prepared from manganese acetylacetonate for CO gas sensor device

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SUMMARY

The plasma polymerization of manganese acetylacetonate (MnAcAc) was carried out and the deposited plasma films were applied for CO gas sensor devices. The plasma polymerization of MnAcAc brought about the deposition of organic thin-films containing manganese oxides. The plasma films showed p-type-semiconductive properties and the response to CO gas with increases in resistivity. The CO gas sensor devices constructed from a sandwich structure of the plasma film (2000 - 3000 angstroms) and Pt catalyst layer (10 angstroms) is applicable for practical uses. The sensitivity of the sensor device to CO gas (1000 ppm) was 24.

INTRODUCTION

Most of chemical sensor devices for the determination of reducing gases, hydrocarbons, carbon oxide, nitrogen oxides, are composed of semiconductive metal oxides such as SnO_2 and TiO_2 [1]. The essential mechanism of the determination of the reducing gases by the devices is due to changes of SnO_2 and TiO_2 surfaces in electric conductivity when the surfaces are exposed to the reducing gases [1]. As the reducing gases reach the SnO_2 and TiO_2 surfaces, they eliminate the oxygen atoms which have been negatively-charged and adsorbed on the metal oxide surfaces. As a result, the electric conductivity of the metal oxides increases, and the reducing gases are oxidized [1]. Therefore the determination of the reducing gases are controlled by the factors of the adsorption of negatively-charged oxygen atoms adsorbed on the metal oxide surfaces, the elimination of the oxygen atoms from the metal oxide surface, and the oxidation reactions of the reducing gases on the metal oxide surface.

Manganese oxides, MnO , Mn_3O_4 , Mn_2O_3 , are p-type semiconductors, and carriers of the conduction are holes [2]. SnO_2 and TiO_2 are n-type semiconductors, and the carriers are electrons. Manganese oxides are different in electric properties from SnO_2 and TiO_2 . MnO_2 shows more powerful catalytic-activation in oxidation reactions of ^2CO than SnO_2 and TiO_2 [3]. Accordingly, we expect that manganese oxides could provide better surfaces for determination of the reducing gases than SnO_2 and TiO_2 .

Plasma polymerization is a thin-film process by which gaseous metal-containing compounds in a plasma zone are polymerized to yield polymer films containing fine particles of metal or metal oxides. Manganese acetylacetonate (MnAcAc) is dark-purple and solid material at room temperature, and is easy to sublimate in vacuum at low temperatures of 100 - 200 °C. When MnAcAc is sublimated in a plasma zone the plasma polymerization of MnAcAc will occur, and films containing manganese metal or oxides will deposit on substrate surfaces placed in the plasma polymerization reactor.

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From the viewpoint of above knowledges the plasma polymerization of MnAcAc was carried out in this study. The chemical composition of the deposited films was discussed by XPS and FT/IR spectroscopy, and the deposited films were applied for the CO gas sensor device.

EXPERIMENTAL

Plasma Polymerization

The plasma polymerization of manganese acetylacetonate (MnAcAc) was carried out with a home-made reactor which was a capacitively coupled system at a 20 kHz frequency. It consisted of a bell-jar (400 mm diameter, 470 mm height) with a quartz furnace for the sublimation of MnAcAc (15 mm diameter, 65 mm height), a pair of parallel electrodes (150 x 150 mm), an argon gas inlet, a stainless stage for mounting substrates (simultaneously, acting as an electrode for negative bias), a thickness monitor, and a vacuum system (the combination of a rotary pump (310 lit/min) and a diffusion pump (900 lit/sec)). The electrodes being 140 mm separate each other were perpendicularly positioned in the center of the bell-jar. The quartz furnace was placed just under the electrodes, and was 200 mm distance from the stage of substrates. A schema of the reactor is shown in Figure 1.

The experimental procedures for the plasma polymerization were as follows. The reaction system was evacuated to approximately 1.3×10^{-3} Pa, and then, the surface of substrates were exposed to argon plasma for 5 min to eliminate adsorbed water. Afterward, MnAcAc was sublimated from the furnace at 97 - 115 °C, and the pressure in the reaction chamber was adjusted to 2.0 Pa by introducing argon gas. The electric power (about 500 V) at a 20 kHz frequency was applied between the electrodes, and the negative bias of 300 V against the grounded electrode was applied on the stainless stage where the substrate was mounted. The plasma polymerization was performed at a constant current of 75 - 105 mA for a given duration. The application of the negative bias at 300 V is helpful in preventing the deposition of MnAcAc subjected to no plasma action [4].

Manganese acetylacetonate (MnAcAc) (more than 98 % purity) used as a starting material for the plasma polymerization was purchased from Tokyo Kasei Kogyo Co., and used without further purification.

Infrared Spectra

IR spectra for the plasma polymers prepared from MnAcAc were recorded by means of the KBr method on a Nihon Bunko Fourier transform spectrometer FT/IR-3. 500 Scans were recorded on each sample, and the spectral resolution was 2 cm^{-1} .

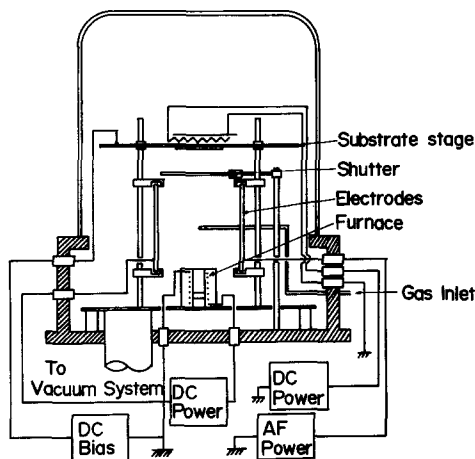


Fig. 1 Schema of Reaction Chamber for Plasma Polymerization.

XPS Spectra

XPS spectra for the plasma polymers deposited on Pyrex glass plates were recorded on an Ulvac-Phi Spectrometer model 5300 using a $MgK\alpha$ photon source (a voltage of 15 kV, a wattage of 400 W, and a background pressure of 1×10^{-7} Pa). The C_{1s} spectra were deconvoluted by fitting Gaussian functions to the experimental curve using a nonlinear, least-squares curve-fitting program supplied by Ulvac-Phi. The following sensitivity factors (S) for C_{1s} , O_{1s} , and $Mn_{2p3/2}$ core levels were used to calculate the relative atomic concentration on the plasma polymer surfaces: $S(C_{1s}) = 1.00$, $S(O_{1s}) = 2.40$, and $S(Mn_{2p3/2}) = 8.98$.

CO Gas Sensor Device and Sensitivity Measurement

CO gas sensor devices were the accumulative structure of Au electrode and plasma polymers deposited from MnAcAc. The Au comb electrodes were deposited onto quartz glass plate (15 x 15 x 1.0 mm) by the vacuum evaporation technique. The comb is 7.0 mm long and 0.5 mm wide, with a separation of 0.5 mm between adjacent teeth. The number of teeth of the comb is $4\frac{1}{2}$. The plasma polymers (2000 - 3000 angstroms) were deposited on the quartz glass plate and heated in air at temperatures of 200 - 500 °C. After the heat-treatment Pt or Pd film (10 angstroms), if necessary, was deposited on the top layer of the plasma films. Figure 2 shows the comb electrode and the schematic structure of the gas sensor devices (type I and II). The type I device was constructed from Au comb electrode and the plasma films of MnAcAc, and the type II device from the Au electrode, the plasma films of MnAcAc, and the Pt or Pd catalytic layers.

The ratio (R_{gas}/R_{air}) of the electric resistance in CO atmosphere (R_{gas}) to that in air (R_{air}) was estimated as CO gas sensitivity. An electric field of 10 V (DC) was applied between the combs, and the electric current between the combs was measured in a CO atmosphere (1000 ppm) with an Advantest electronmeter TR8652 as a function of the surface temperature of the sensor devices. From data of the electric current and the applied field between the combs the electric resistance (R_{gas} and R_{air}) was calculated.

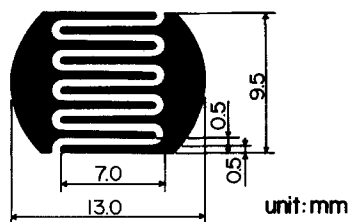
RESULTS AND DISCUSSION

Preparation and Chemical Composition of Plasma Polymer Films of MnAcAc

The plasma polymerization of MnAcAc yielded transparent, light-yellow films which were insoluble in ethylether. MnAcAc is soluble in ethylether, and its color is dark-purple. From these changes of the deposited plasma polymers in solubility and hue we assume that a part of the coordination bonds between manganese atom and acetylacetone molecule were cleaved by plasma actions to deposit polymeric films.

A typical IR spectrum of the plasma polymer films shows complex absorption peaks related to the coordination bonds between manganese atom and acetylacetone molecule (Figure 3). MnAcAc (spectrum A in Figure 3)

Comb Electrode



Sensor Device

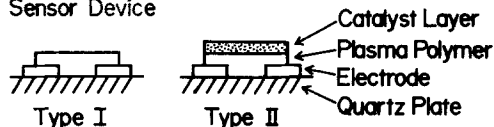


Fig. 2 Schema of CO Sensor Device.

shows strong absorption peaks at 1594, 1568, and 1510 ($\nu_{\text{C=O}} + \nu_{\text{C=C}}$) and 1255 cm^{-1} ($\nu_{\text{C-CH}_3} + \nu_{\text{C=C}}$) which are distinctive absorption peaks of the coordination between manganese atom and acetylacetonate molecule [5]. The plasma polymer films prepared from MnAcAc (spectrum B in Figure 3) show complex absorption peaks related to carbonyl moieties at 1700 (free C=O), 1585, 1520, 1510 (coordinated and conjugated C=O moieties), and 1400 cm^{-1} (δ_{CH_3}). And new strong absorption peaks appear at 3500 cm^{-1} (OH) and near 600 cm^{-1} (Mn-O) [6]. This spectrum indicates that the plasma polymer films contain not-coordinated carbonyl groups, hydroxyl groups, and manganese oxides in addition to the coordination between manganese and carbonyl moieties but the concentration of the coordination is low.

The XPS (C_{1s} and $\text{Mn}_{2p_{3/2}}$ core levels) spectra, which are not represented here because of sake of brief, explained the chemical composition of the deposited plasma polymers.

The C/Mn and O/Mn atomic ratios for the plasma polymers were 14.1 and 5.0, respectively, which are fairly lower than those for MnAcAc (the C/Mn and O/Mn atomic ratios are 15 and 6, respectively). The C_{1s} core level spectrum showed that the plasma polymers possessed five chemically-different carbon components; CH_x groups appearing at 285.0 eV, C-O groups at 286.4 eV, coordinated C=O groups at 287.6 eV, not-coordinated C=O groups at 288.6 eV, and C(O)-O groups at 290.1 eV. The relative concentration of these components was 16, 56, 12, 6, and 10 mol% of the total carbon atoms, respectively. The $\text{Mn}_{2p_{3/2}}$ core level spectrum appeared at 642.0 eV. The binding energy of the $\text{Mn}_{2p_{3/2}}$ core level is closely related to the oxidation state of manganese atoms; the binding energy appears at 641.0 eV for Mn, at 641.7 eV for MnO , at 641.8 eV for Mn_2O_3 , and at 642.4 eV for MnO_2 [7]. This reference indicates that manganese atoms of the plasma polymers are in highly-oxidized state (Mn_2O_3 or MnO_2). Either of the oxidation states (Mn_2O_3 or MnO_2) was not identified from the XPS data because of small chemical-shift of $\text{Mn}_{2p_{3/2}}$ core level. Conclusively, we expect a capability that the plasma polymers deposited from MnAcAc behave like a n-type semiconductor.

Sensitivity of Plasma Polymer Films to CO Gas

The plasma polymer films prepared from MnAcAc showed the response to CO gas. The electric resistance of the plasma polymer films increased when exposed to CO gas. The behavior of the plasma films in respect of the resistivity change by the CO exposure is in contrast to that of n-type-semiconductive sensor devices. The n-type semiconductors such as SnO_2 and TnO_2 , which are materials used frequently for gas sensor devices, show decreases in electric resistivity when exposed to CO gas. This indicates a possibility that the plasma films prepared from MnAcAc possess p-type semi-

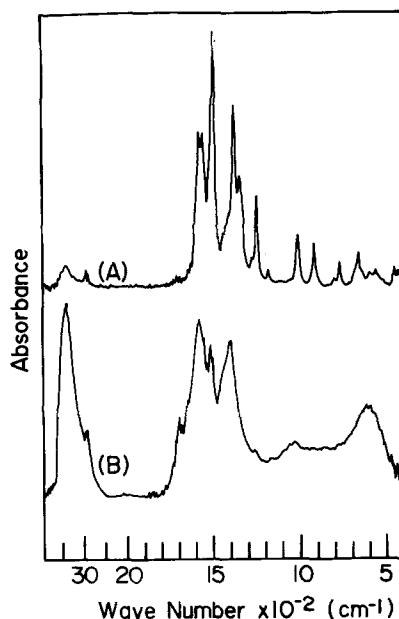


Fig. 3 IR Spectra of MnAcAc (A) and Plasma Polymers prepared from MnAcAc (B).

conductive properties.

The ratio ($R_{\text{gas}}/R_{\text{air}}$) of the electric resistance in CO atmosphere (1000 ppm) and in air was defined as the sensitivity to CO gas. The sensitivity of the sensor devices composed of the plasma polymer films deposited from MnAcAc was 2 which was too small for practical application of CO gas sensor device. It is necessary to make the resistivity of the plasma films low for practical uses.

The heat-treatment at 300 - 500 °C led to decreases in resistivity from 10^{-8} Ω-cm for the not-heat-treated plasma polymer films to 10^{-6} Ω-cm for the films heat-treated at 300 °C. The apparent activation energy₁ for the conduction was 0.43×10^1 eV for the films heat-treated at 400 °C. To obtain the sensor devices with higher sensitivity the catalyst layer of palladium (Pd) or platinum (Pt) (10 Å thick) was deposited on the surface of the plasma polymer films by vacuum deposition technique. The schematic structure of these sensor devices is the type II in Figure 2. Typical results of these sensor devices are represented in Figure 4, where the sensitivity ($R_{\text{gas}}/R_{\text{air}}$ ratio) is plotted as a function of the surface temperature of the devices. The Pt and Pd catalyst layers improve the sensitivity. The sensitivity increases with increasing with the surface temperature of the devices, reaches a maximum at a surface temperature of 150 °C, and then decreases. The sensitivity at a surface temperature of 150 °C is 24 and 5 for the sensor devices with the Pt and Pd catalyst layers, respectively. The Pt catalyst layer is more effective for the enhancement of the CO sensitivity than the Pd catalyst layer. Accordingly, the sensor devices composed of the plasma films deposited from MnAcAc and the Pt catalyst layer have enough high sensitivity for practical uses.

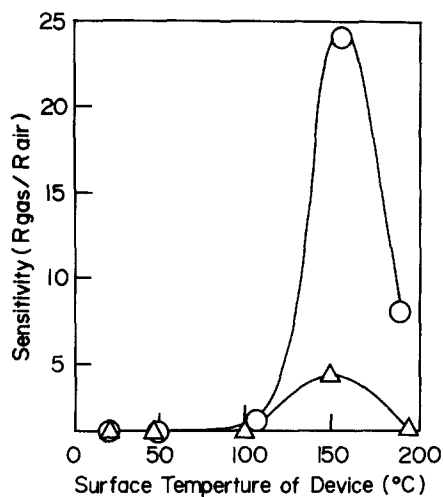


Fig. 4 Sensitivity of CO Sensor Device with Pt Catalyst Layer (○) and with Pd Catalyst Layer (△) to CO Gas (1000 ppm) as a function of Surface temperature of the Devices.

We have reported on the preparation of films containing tin oxides by the plasma polymerization of tetramethyltin ($\text{Sn}(\text{CH}_3)_4$) [8]. The plasma films deposited from $\text{Sn}(\text{CH}_3)_4$ showed n-type-semiconductive properties and the response to CO gas. The electric resistivity of the plasma films decreased when exposed to CO gas. TABLE I compares the sensitivity of the sensor devices composed of plasma films deposited from MnAcAc and $\text{Sn}(\text{CH}_3)_4$. The sensitivity to CO gas (1000 ppm) is 24 for the plasma films prepared from MnAcAc and 4 for those from $\text{Sn}(\text{CH}_3)_4$. This comparison indicates that the plasma film prepared from MnAcAc is a potential material for CO sensors, although the gas selectivity and durability should be examined prior to practical uses.

TABLE 1 The Sensitivity of Plasma Films to CO Gas

Plasma Film	Catalyst Layer	Operating Temperature (°C)	Sensitivity
MnAcAc	Pt	150	24*
Sn(CH ₃) ₄	PdCl ₃	300	4**

*, $R_{\text{gas}}/R_{\text{air}}$; **, $R_{\text{air}}/R_{\text{gas}}$.

In conclusion the plasma polymerization of MnAcAc brings about the deposition of thin films containing manganese oxides which show p-type-semi-conductive properties. The plasma film prepared from MnAcAc is a potential material for CO gas sensor devices. The equipment of the Pt catalyst layer on the surface of the plasma films is effective for the enhancement of the sensitivity to CO gas. The sensitivity of the sensor device with a sandwich structure of the plasma films and the Pt catalyst layer is 24.

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