Plasma Polymer Deposition from Indium Acetylacetonate and Its Application to Chemical Sensor Devices

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SYNOPSIS

Plasma polymerization of indium acetylacetonate (InAcAc) was investigated from the viewpoint of the material preparation for application to chemical sensor devices. The plasma polymerization of InAcAc resulted in the deposition of films, which were hydrocarbon-like polymers with fine particles of indium oxides. The deposition rate and the chemical composition of the deposited films were strongly influenced by the system pressure in operating the plasma polymerization, as well as by the substrate temperature. The deposited films possessed n-type semiconductive properties and responded to reducing gases, such as CO, H_2, C_3H_8, and C_2H_5OH, with increasing the conductivity. The sensor device composed of the films deposited from InAcAc showed extremely high sensitivity to CO and higher gas selectivity than the sensor devices consisting of SnO_2 and ZnO_2.

INTRODUCTION

Chemical sensor devices, used for determination of reducing gases involving carbon monoxide, nitrogen oxides, hydrogen, hydrocarbons, and alcohols, are of interest in the field of industrial engineering as well as in civil life. The essential mechanism for determining the gases is based upon the semiconductive properties of the sensor surface.[1] When the gas molecules approach the semiconductive surface of the sensor they eliminate oxygen atoms, which are adsorbed on the sensor surface, and then are oxidized themselves. As a result of the oxygen elimination from the semiconductive surface, the electric conductivity of the sensor surface increases or decreases depending upon the nature of the sensor surface, n-type or p-type semiconductor.[1] Most chemical sensor devices consist of tin oxide (SnO_2) and zinc oxide (ZnO_2) as a main component, which are n-type semiconductors. Indium oxide (In_2O_3) also is an n-type semiconductor, but it is rarely used as a material for the chemical sensor device. Some such sensor devices, however, have been found in patents.[2] Indium oxide is used mainly as a transparent, electrically-conductive electrode of liquid crystal displays. The basic requirements of the chemical sensor devices in the determination of reducing gases are sensitivity (how much the electric conductivity changes in exposing the reducing gases) and gas selectivity (how the sensor device distinguishes a desired gas from the mixture of many kinds of reducing gases).

Plasma polymerization is a thin-film process by which gaseous metal-containing compounds are polymerized to yield polymer films containing fine particles of metal or metal oxides.[3-8] Indium acetylacetonate (InAcAc), whose chemical structure is shown in Figure 1, is a complex between indium atom and acetylacetone as a ligand, and is solid at room temperature. The complex is easy to sublimate in a vacuum at low temperatures of 100–200°C. When InAcAc is sublimated in a plasma zone, the plasma polymerization of InAcAc will occur, and films containing indium metal or oxides will be created.

From the viewpoint of the above information, the plasma polymerization of InAcAc was carried out in this study. The chemical composition of the deposited films was investigated by XPS and FT/IR spectroscopy, and the application of the deposited films to chemical sensor devices was discussed.
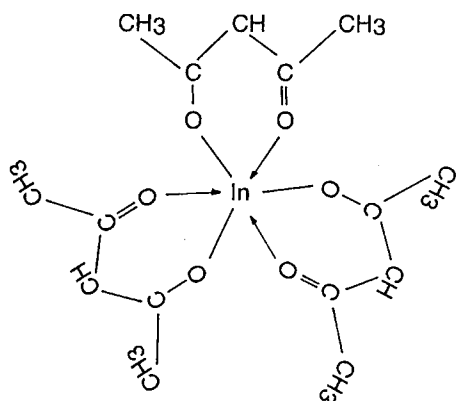
Figure 1   Chemical structure of indium acetylacetonate (InAcAc).

EXPERIMENTAL

Plasma Polymerization

The apparatus used in this study for the plasma polymerization of InAcAc was a homemade reactor that was a capacitively coupled system at a 13.56 MHz frequency. It consisted of a bell jar (400 mm in diameter, 470 mm in height) with a quartz furnace for sublimation of InAcAc (15 mm in diameter, 65 mm in height), a pair of parallel electrodes (mesh stainless electrodes), an electromagnetic coil for maintaining a discharge glow, a substrate stage with an electric heater, an argon gas inlet, a thickness monitor, and a vacuum system (the combination of a rotary and a diffusion pump). The conformation of the essential elements is schematically shown in Figure 2.

The mesh electrodes were horizontally positioned in the center of the bell jar with a gap of 65 mm. The electromagnetic coil was placed horizontally, 15 mm below the lower mesh electrode. The quartz furnace was placed 78 mm, just below the lower electrode. The substrate stage was positioned at 57 mm above the upper electrode.

The experimental procedures for the plasma polymerization of InAcAc follow. The reaction system was evacuated to less than 8×10^{-4} Pa, and the surface of substrate was exposed to argon plasma for 5 min to eliminate adsorbed water. Afterward, InAcAc was sublimated from the furnace at 97–115°C, and the pressure in the reaction chamber was adjusted to a given pressure by introducing argon gas. The electric power at 13.56 MHz frequency was applied between the electrodes. A magnetic field of 30 g was applied for maintaining a glow discharge at pressures of less than 10^{-2} Pa during the plasma

polymerization. The plasma polymerization was performed at a constant power of 60 or 20 W for a given duration.
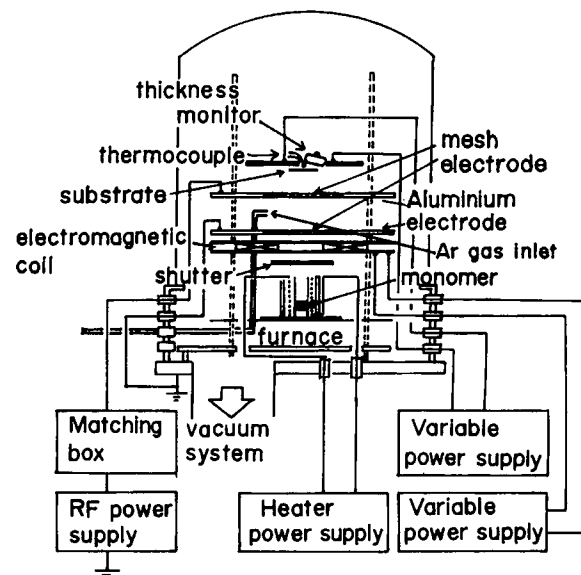
Mass Spectra

A mass spectrum of InAcAc was recorded on a JOEL AX-505W mass-spectrometer. The pressure of the analysis chamber was 1×10^{-4} Pa, the ionization voltage was 70 eV at 300 μA, and the acceleration voltage was 3 kV.
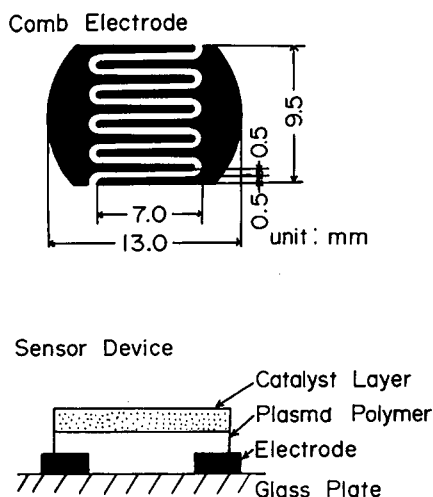
Infrared Spectra

IR spectra for the plasma polymers deposited on aluminum foils or Pyrex glass substrates were recorded by means of the ATR and KBr methods on a Nihon Bunko Fourier transform spectrometer FT/IR-3. A KRS-5 crystal prism was used for the ATR method. Five-hundred scans were recorded on each sample and the spectral resolution was 2 cm^{-1}.

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 (The anode power was 400 W at 15 kV and the background pressure was 1×10^{-7} Pa). The C$_{1s}$ spectra were deconvoluted by fitting Gaussian functions using a nonlinear, least-squares curve fitting program supplied by Ulvac-Phi. The sensitivity

Figure 2   Schematic illustration of plasma polymerization reactor.

Comb Electrode

7.0

13.0

9.5

0.5

0.5

0.5

unit : mm

Sensor Device

Catalyst Layer

Plasma Polymer

Electrode

Glass Plate

Figure 3 Schematic illustration of comb electrode and senor device.

factors (S) for core levels were $S(C_{1s})$ = 1.00, $S(In_{3d5/2})$ = 14.73, and $S(O_{1s})$ = 2.40.

Transmission Electron Microscope

Plasma polymers (800 Å thick) were deposited on KBr disks (1 mm thick). The disks were immersed in water, and the plasma polymer films were separated from the KBr layers. The films were used as specimens for observation with a transmission electron microscope, Hitachi model HS-7D. The magnification of transmission electron microscopy was 50,000 times.

Gas Sensor Device and Gas Sensitivity Measurement

Gas sensor devices were composed of the sandwich structure of three components: Au comb electrodes (1000 Å thick), plasma polymers deposited from InAcAc (2000–3000 Å thick), and a Pt catalytic layer (10 Å thick). First, the Au comb electrodes were deposited onto a quartz glass plate (15 × 15 × 1.0 mm) by vacuum evaporation technique. The comb with the 0.5 mm gap was 7.0 mm long and 0.5 mm wide. The comb had four and one-half teeth. Second, the plasma polymer film (2000–3000 Å thick) was deposited onto the Au comb electrodes and heated in air for 3 min at 350°C. Finally, a Pt film (10 Å thick) was deposited on the top layer of the heat-treated plasma films. Figure 3 shows a schematic representation of the comb electrode used for the gas sensor device and the schematic structure of the gas sensor device.

An electric field of 10 V (DC) was applied between the combs. The electric current between the combs

was measured, with an Advantest electronmeter TR8652, as being functions of gas atmosphere (CO, H_2, C_2H_5OH, and C_3H_8) (1000 ppm concentration) and the surface temperature of the sensor device. From the electric current data, the applied field values of the electric resistance in gas atmosphere (R_{gas}) and in air (R_{air}) were calculated. The ratio (R_{air}/R_{gas}) of the electric resistances in CO, H_2, C_2H_5OH, and C_3H_8 atmosphere (1000 ppm concentration), and in air (R_{air}), was estimated as gas sensitivity.

RESULTS AND DISCUSSION

Polymer Deposition from the Plasma Polymerization of InAcAc

Thin films were deposited from the plasma polymerization of InAcAc. The deposition rate depended largely upon the system pressure. In Figure 4, the deposition rate in the plasma polymerization of InAcAc at an rf power of 60 W is plotted against the system pressure, and it is shown that the deposition rate increases with decreasing the system pressure. The deposition rate at 6.6×10^{-2} Pa is 3.7 times faster than the rate at 6.6 Pa. This indicates that the deposition rate may be controlled by the magnitude of the mean-free path of InAcAc molecules. The distance of the mean-free path is estimated to be $ca.$ 1.5×10^{-1} cm at 6.6 Pa and 15 cm at 6.6×10^{-2} Pa. The magnitude of the rf power did not affect the deposition rate as much; the deposition rate was 2.96 $\mu g/cm^2$-min at 20 W rf power and 2.41 $\mu g/cm^2$-min at 60 W.

The transmission electron microscope picture (Fig. 5) shows that the deposited films are not ho-
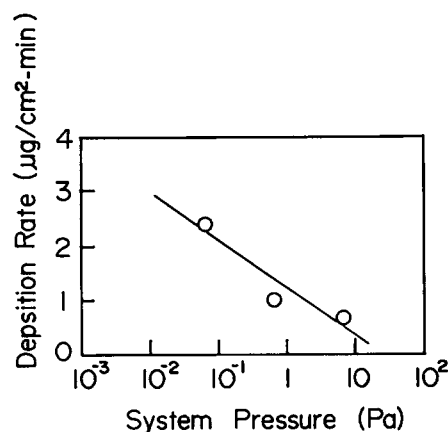
Figure 4 Deposition rate in plasma polymerization of InAcAc as a function of system pressure.
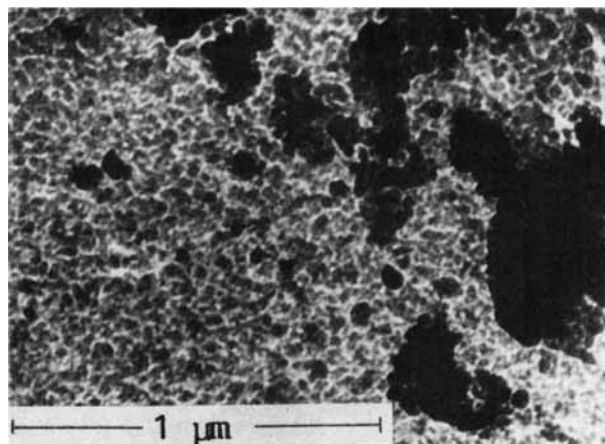
Figure 5 Transmission electron microscope picture of films deposited from InAcAc.

mogeneous. The films contain a plain layer, which transmits electrons, and the fine particles (0.2–0.6 μm in diameter), which do not transmit electrons. It is possible that the fine particles may be clusters of indium or indium oxides, which will be discussed later.

Chemical Composition of Deposited Films

A wide-scanning survey with XPS showed that the films deposited from the plasma polymerization of InAcAc were composed of carbon, oxygen, and indium elements. The elemental composition of the deposited films were different from that of InAcAc (C/In = 15, O/C = 0.4), and the composition depended upon plasma polymerization conditions, especially the system pressure and substrate temperature. Figure 6 shows that the atomic ratio (C/In and O/C) of the deposited films is a function of the system pressure. The C/In atomic ratio of the deposited films decreases greatly as the system pressure decreases, and the O/C atomic ratio increases slightly. The C/In atomic ratio decreases from 94.2 to 8.4 when the system pressure decreased from 6.6 to 6.6×10^{-2} Pa; the O/C atomic ratio increases from 0.32 to 0.45. The substrate temperature also influenced the chemical composition of the deposited films. When the substrate temperature rose from room temperature to 160 and 260°C, the C/In atomic ratio increased from 8.4 to 148 and 232, respectively, and the O/C atomic ratio decreased from 0.45 to 0.20 and 0.10, respectively. These changes in elemental composition suggest that InAcAc molecules would be fragmented mainly into organic and

indium moieties by the action of plasma (electron impact). Each of the moieties would then be plasma-polymerized and two kinds of plasma polymers, rich in carbon element and rich in indium element, would deposit at different deposition rates on the substrate surfaces.

The fragmentation processes in a discharge state are speculations based upon the mass spectrum of InAcAc. The fragmentation processes occurring in the chamber of a mass spectrometer are not exactly the same as those in the discharge state of plasma polymerization. This is because intermolecular interactions occur in plasma polymerization and no interaction occurs in mass spectrometry. The mass spectrum is, however, expected to offer useful information on the fragmentation of InAcAc in a discharge state. Figure 7 shows a mass spectrum of InAcAc in which the molecular weight is 412. There are characteristic peaks of the mass number 412, 313, 214, and 115, which are assigned to the parent ion of InAcAc (M^+), the fragment ions of the one-acetylacetone-eliminated (312), the ions of the two-acetylacetones-eliminated (214), and the ions of the three-acetylacetones-eliminated (115). This spectrum indicates that In—O bonds of InAcAc, rather than C—C and C—O bonds, are split off easily by the electron impact. Accordingly a theory proposing that InAcAc molecules in a discharge state are fragmented into organic moieties and indium moieties and then each of them is plasma polymerized independently is not unreasonable. The changes in elemental composition by the plasma polymerization conditions may be due to differences in the deposition rate of the plasma polymers from organic
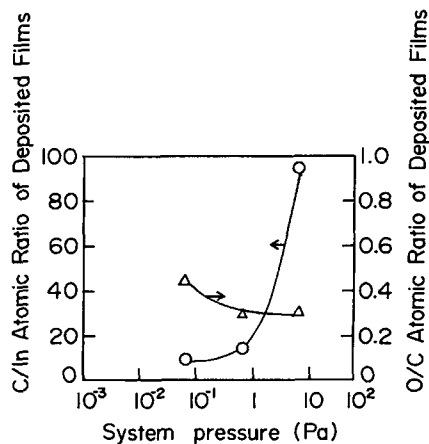
Figure 6 Elemental composition (C/In atomic ratio, ○; O/C, △) of the films deposited from InAcAc as a function of the system pressure.
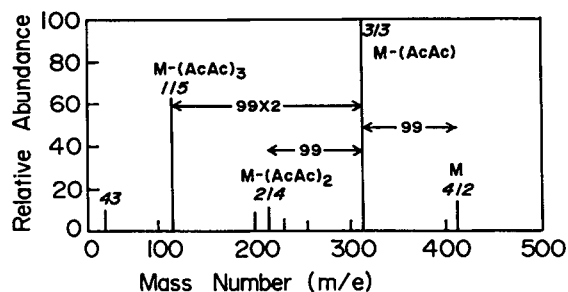
Figure 7 Mass spectrum of InAcAc (molecular weight of InAcAc = 412).

moieties and indium moieties, and in the sticking factor of the two plasma polymers rich in carbon and indium elements onto the substrate surfaces.

The XPS spectra of the deposited plasma polymer films reveal that the chemical features of carbon and indium atoms exist in the films. The plasma polymer films gave essentially similar C_{1s} spectra even when plasma polymerized at differing pressures from 6.6 to 6.6×10^{-2} Pa. Figures 8 and 9 show typical C_{1s} and In_{3d} core level spectra of the plasma polymer films as a function of the system pressure in the plasma polymerization. The C_{1s} spectra involve four components with different binding energies (285.0, 286.1–286.7, 287.8–288.2, and 289.0–289.2 eV), which are assigned to CH, C—O, coordinated or conjugated C=O, and not-coordinated or not-conjugated C=O groups, respectively.[9-11] The component due to CH groups reaches 70–75 mol % of the total of carbon atoms. The components due to C—O and C=O groups are 12–15 and 11–15 mol %, respectively. This indicates that the plasma polymer films are composed mainly of hydrocarbon-like chains with small amount of C—O and C=O groups. The appearance of free C=O groups (not-coordinated or not-conjugated) indicates that a part of the coordination between acetylacetone and indium atom was broken down by the action of plasma during the polymer-forming process.

The In_{3d} spectra (Fig. 9) show that the indium atoms incorporated into the plasma polymer films appear the 3d3/2 and 3d5/2 core levels at 445.3–445.8 and 452.9–453.2 eV, respectively. Generally the $In_{3d5/2}$ core level for indium metal appears at 444.8 eV, and that for In_2O_3 appears at 452.1 eV.[12] The comparison indicates that the indium atoms incorporated into the plasma polymer films are in a highly-oxidized state and are assigned to In_2O_3.

Figure 10 shows typical IR spectra of the plasma films and InAcAc. For InAcAc, characteristic ab-

sorption peaks related to the coordination bonds between acetylacetone and indium atom appear at 1580, 1530 ($\nu_{C-C} + \nu_{C-O}$), 1375 (δ_{CH_3}) 1270 ($\nu_{C-CH_3} + \nu_{C-C}$), 1025 (ρ_{CH_3}), and 933 cm^{-1} ($\nu_{C-C} + \nu_{C-O}$).[13,14] The plasma polymer films give complex absorption peaks at 1740–1700 cm^{-1} due to free C=O groups, 1655–1625 cm^{-1} due to C=C groups, 1560–1510 cm^{-1} due to CH_3, 1460–1400 cm^{-1} due to CH_2 groups, and 1060 cm^{-1} due to C—O groups.[13] The intensity of the absorption peaks at 1580, 1530, 1375, 1270, 1025, and 930 cm^{-1}, which are related to the coordination bonds, is low. This spectrum indicates that the greater part of coordination bonds between acetylacetone and the indium atom were degraded during the plasma polymerization.

From results of XPS and IR spectra we conclude that the plasma polymer films deposited from InAcAc are a mixture of hydrocarbon-like polymers with C—O and C=O groups and indium oxides (In_2O_3).

CO Chemical Sensor Devices Composed of Plasma Polymer Films of InAcAc

The plasma polymer films deposited from InAcAc are expected to have semiconductive properties be-
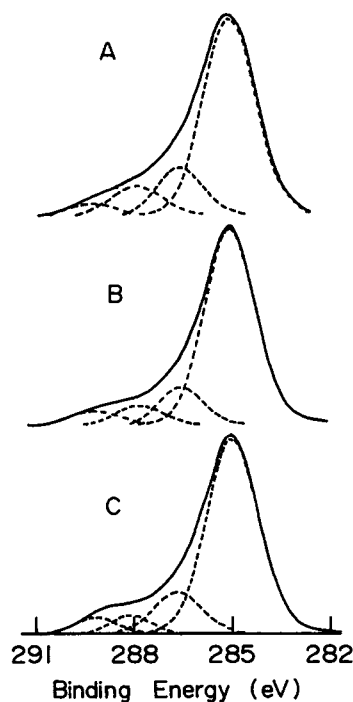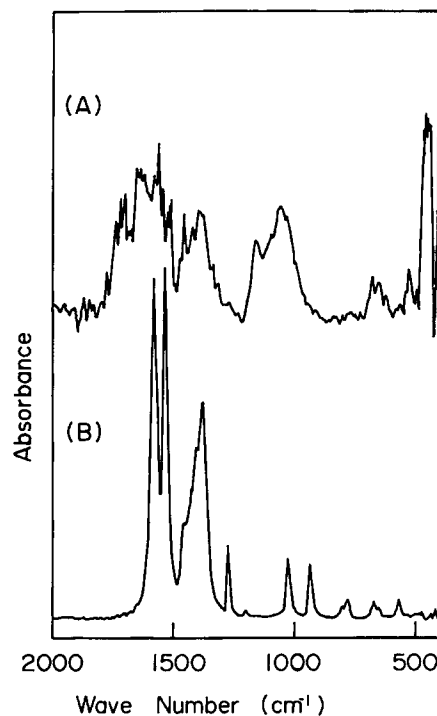

Figure 8 XPS (C_{1s}) spectra of films deposited from InAcAc as a function of the system pressure: (A) 6.6 Pa; (B) 6.6×10^{-1} Pa; (C) 6.6×10^{-2} Pa.
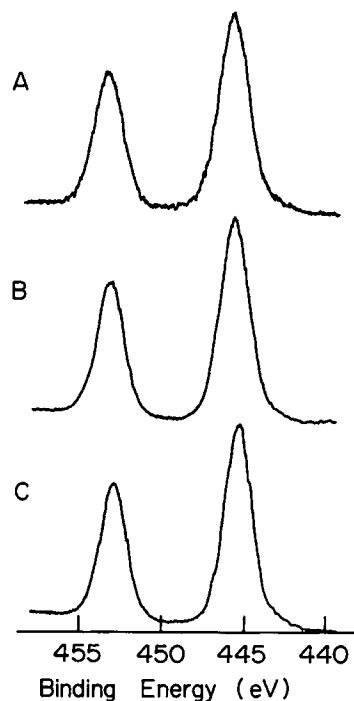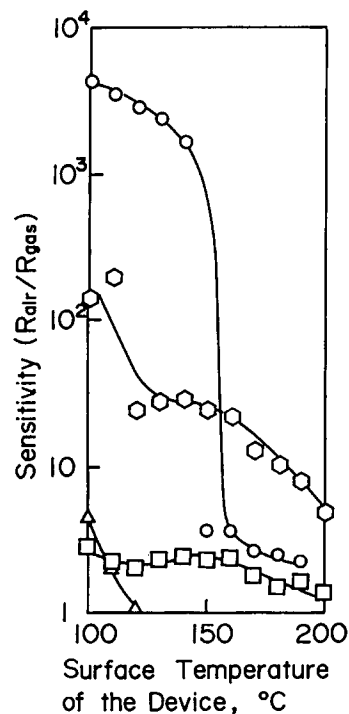
Figure 9 XPS (In$_{3d}$) spectra of films deposited from InAcAc as a function of the system pressure: (A) 6.6 Pa; (B) 6.6 × 10^{-1} Pa; (C) 6.6 × 10^{-2} Pa.

Figure 10 IR spectra of films deposited from InAcAc (A) and InAcAc (B).

cause of the incorporation of indium oxide (In$_2$O$_3$). The electric conductivity of the plasma polymer films was between 10^{-8} and 10^{-6} S cm^{-1}, depending upon the measuring temperature. The electric conductivity at 100°C was 1.0 × 10^{-8} S cm^{-1}, and the apparent activation energy for conduction was 0.29–0.3 eV. The heat-treatment of the deposited films at 350°C led to an increase in conductivity of between 10^{-5} and 10^{-4} S cm^{-1}. The electric conductivity at 100°C was 8.9 × 10^{-5} S cm^{-1}. The films responded to some reducing gases such as carbon monoxide, ethanol, hydrogen, and propane, and their resistivity decreased. Figure 11 shows the typical responses of the plasma polymer films to the gases as a function of the temperature of the plasma polymer films. The sensor device used in Figure 11 involved the plasma polymer films deposited from InAcAc, heat-treated at 350°C. It also involved a catalytic layer of platinum (10 Å thick) on the top layer of the heat-treated plasma polymer film. The Pt catalytic layer led to enhancement of the sensitivity by Pt catalytic actions. The electric resistivity of the plasma polymer films decreased when exposed to the gases. This indicates a capability that the heat-treated plasma polymer films, such as tin oxide and zinc oxide, operate as n-type semiconductors. The

Figure 11 Sensitivity (R_{air}/R_{gas}) as functions of reducing gases and surface temperature of devices: (O) CO; (o) C$_3$H$_8$; (□) C$_2$H$_5$OH; (△) H$_2$.

Table I Sensitivity and Selectivity of Gas Sensor Devices

Gas	Sensor Device Composed of Plama Films of InAcAc		Sensor Device[a] Composed of SnO_2		Sensor Device[a] Composed of ZnO_2	
	Sensitivity	Selectivity	Sensitivity	Selectivity	Sensitivity	Selectivity
CO	4309	1.0	16.1	1.0	1.8	1.0
H_2	4.07	1059	67.7	0.24	2.0	0.9
C_2H_5OH	2.88	1496	100	0.16	18	0.1
C_3H_8	146	29.5	—	—	12	0.15

[a] Taken from Ref. 15.

ratio of the electric resistance in air (R_{air}) and in the atmosphere containing carbon monoxide, ethanol, hydrogen, and propane of 1000 ppm concentration (R_{gas}) was used for the numeral evaluation of the response to the gases. The plasma polymer films, as shown in Figure 11, show high sensitivity (R_{air}/R_{gas} ratio) to carbon monoxide at relatively low temperatures of 100° to 150°C, and the value of the sensitivity reaches more than 1500. Note especially value 4309 at 100°C. The response to propane, hydrogen, and ethanol also are detectable with the plasma polymer films, however their sensitivity is extremely low compared with that of carbon monoxide. The value of the sensitivity at 100°C is 146, 4.07, and 2.88 for propane, hydrogen, and ethanol, respectively. The gas selectivity, which is defined as the sensitivity ratio of two gases, is high: the value of the selectivity at 100°C is 1 for carbon monoxide, 29.5 for propane, 1.06×10^2 for hydrogen, and 1.50×10^2 for ethanol (Table I). Most chemical sensor devices are composed mainly of tin oxide and zinc oxide, and they respond to such reducing gases as carbon monoxide, ethanol, hydrogen, and propane by exhibiting decreases in resistivity. Table I compares the sensitivity and selectivity of typical chemical sensor devices composed of tin oxide and zinc oxide.[15] This comparison emphasizes the high sensitivity to reducing gases and the selectivity of carbon monoxide for plasma polymer films deposited from InAcAc. The sensitivity to carbon monoxide is 4309 for the plasma polymer films, 16.1 for the SnO_2 sensor device, and 1.8 for the ZnO_2 sensor device. The selectivity between carbon monoxide and ethanol is 1.50×10^3 for the plasma polymer films, 0.16 for the SnO_2 sensor device, and 0.10 for the ZnO_2 sensor device. The In_2O_3 films that were deposited from indium metal by the vacuum evaporation technique and then were oxidized in air

also showed response to carbon monoxide, but the sensitivity was a lower value of 5. This comparison indicates that the high sensitivity of the plasma-polymerized film may be related to the larger surface area of easier gas diffusion, or to some participation of the plasma polymer directly in the carbon monoxide sensing. This is unclear at present and will be discussed further in a future article.

CONCLUSION

Plasma polymerization of InAcAc was investigated for the application of the plasma-polymerized films to chemical sensor devices. The deposition of the plasma polymerization of InAcAc produced films which contained hydrocarbon-like polymers with fine particles of indium oxides. The deposition rate and the chemical composition of the deposited films were strongly influenced by the system pressure in the plasma polymerization as well as by the substrate temperature. The deposited films possessed n-type semiconductive properties and they responded to reducing gases such as CO, H_2, C_3H_8, and C_2H_5OH. The sensor devices with the films deposited from InAcAc had extremely high sensitivity to CO, and selectivity between CO and other gases (H_2, C_3H_8, and C_2H_5OH) also was high. The plasma-polymerized film is a suitable material for the CO gas sensor device.

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