

# Plasma Polymerization of Metal Acetylacetonates and Application for Gas Sensor Devices

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## SYNOPSIS

Plasma polymerization of five metal acetylacetonates (MAcAc), aluminium acetylacetonate (AlAcAc), copper acetylacetonate (CuAcAc), titanium acetylacetonate (TiAcAc), zinc acetylacetonate (ZnAcAc), and magnesium acetylacetonate (MgAcAc), were investigated for the application of CO gas sensor devices. Plasma polymerization deposited thin films with metal elements as well as carbon and oxygen elements. The polymer deposition rate in the plasma polymerization was a function of the rf power, the system pressure, and the nature of the MAcAc. The elemental composition of the deposited films was fairly different from that of the starting materials, MAcAc. The complexing bonds of the MAcAc between acetylacetonate and the metal element occurred in the plasma zone. The cleavage was closely related to the delocalization of electrons on the complexing of the MAcAc. The plasma polymer films prepared from TiAcAc and ZnAcAc in the presence of Pt catalyst showed a response toward CO gas. The plasma polymer films, especially prepared from TiAcAc, are potential materials for a CO sensor device with both sensitivity and selectivity.

## INTRODUCTION

Polymer composites containing metal or metal oxide particles are interesting materials because of the electrical, magnetic, and optical properties of the particles. Many techniques for the preparation of the polymer composites have been proposed and some of the techniques are already used commercially.<sup>1</sup> Plasma polymerization is also one of the techniques for the preparation of these polymer composites. Metal-containing materials are plasma-polymerized to deposit thin films containing metal or metal oxide particles.<sup>2</sup> Polymer formation in a plasma polymerization process is accompanied by the fragmentation and rearrangement of the starting molecules.<sup>3</sup> The fragmentation as well as the rearrangement of the starting molecules is a factor for controlling the deposited plasma films. The fragmentation pattern is mainly dependent on the

chemical nature of the starting molecules. For this reason the choice of the starting materials is of importance in the plasma polymer formation with potential functionalities.

Li,<sup>4</sup> Morosoff,<sup>5</sup> and Osada<sup>6</sup> have each focussed their interest on various metal complexes including iron pentacarbonyl, complexes of cobalt with Schiff bases, *N,N'*-bis(salicylidene)ethylenediamino cobalt (II) (salcomine); *N,N'*-bis(salicylidene)-1,2-phenyl-enediamino cobalt (II); 5,10,15,20-tetra-phenyl-21H,23H-porphine cobalt (II) (cobalt TPP); copper 4,4',4'',4'''-tetraaza-29H,31H-phthalocyanine; and copper acetylacetonate. They investigated the plasma polymerization of metal complexes and the properties of the deposited films. We also have investigated the plasma polymerization of some metal acetylacetonates for application in a gas sensor device.<sup>7,8</sup> The thin films containing semiconductive metal oxide particles are potential materials because of the large surface area per volume of the metal oxide particles. This study focuses on the plasma polymerization of a series of metal acetylacetonates and their application in gas sensor devices.

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## EXPERIMENTAL

### Materials

Aluminum acetylacetonate [ $\text{Al}(\text{C}_5\text{H}_7\text{O}_2)_3$ , AlAcAc], copper acetylacetonate [ $\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ , CuAcAc], titanium acetylacetonate [ $\text{TiO}(\text{C}_5\text{H}_7\text{O}_2)_2$ , TiAcAc], zinc acetylacetonate [ $\text{Zn}(\text{C}_5\text{H}_7\text{O}_2)_2$ , ZnAcAc], and magnesium acetylacetonate [ $\text{Mg}(\text{C}_5\text{H}_7\text{O}_2)_2$ , MgAcAc], purchased from Tokyo Kasei Kogyo Co., were of analytical grade and were used as starting materials for the preparation of metal-containing plasma polymers without further purification.

### Plasma Polymerization and Apparatus

The apparatus used in this study for the plasma polymerization of MAcAc was a home-made reactor, capacitively coupled at a 13.56 MHz. It consisted of a bell-jar (400 mm diameter and 470 mm height) with a quartz furnace (15 mm diameter and 65 mm height) for the sublimation of MAcAc, a pair of parallel electrodes (mesh stainless electrodes), an electromagnetic coil for the maintenance of a glow discharge, a substrate stage with an electric heater, an argon gas inlet, a thickness monitor, and a vacuum system. A schema of the reaction system is shown in Figure 1.

The experimental procedures for the plasma polymerization of MAcAc were essentially same as reported elsewhere.<sup>8</sup> The reaction chamber was evacuated up to  $10^{-3}$  Pa, and then a given MAcAc was sublimated from the furnace at 97–115°C. The plasma polymerization was carried out at system pressures of  $6.65 \times 10^{-2}$ – $1.3 \times 10^{-1}$  Pa (adjusted by the introduction of argon gas), at rf (13.56 MHz) powers of 20–80 W, and under a magnetic field of 30 G, to maintain a glow discharge. The plasma polymer films deposited on aluminum foil, Pyrex glass, and quartz glass substrates were supplied for surface analyses and gas sensor devices.

### Surface Analysis

#### IR Spectra

The IR spectra for the plasma polymers were recorded by means of the attenuated total reflection (ATR) method on a Nihon Bunko Fourier transform spectrometer FT/IR-3. A KRS-5 crystal prism was used for the ATR method. For each sample 500 scans were recorded, and the spectral resolution was  $2 \text{ cm}^{-1}$ .

#### XPS Spectra

The XPS spectra for the plasma polymers were recorded on an Ulvac-Phi spectrometer model 5300

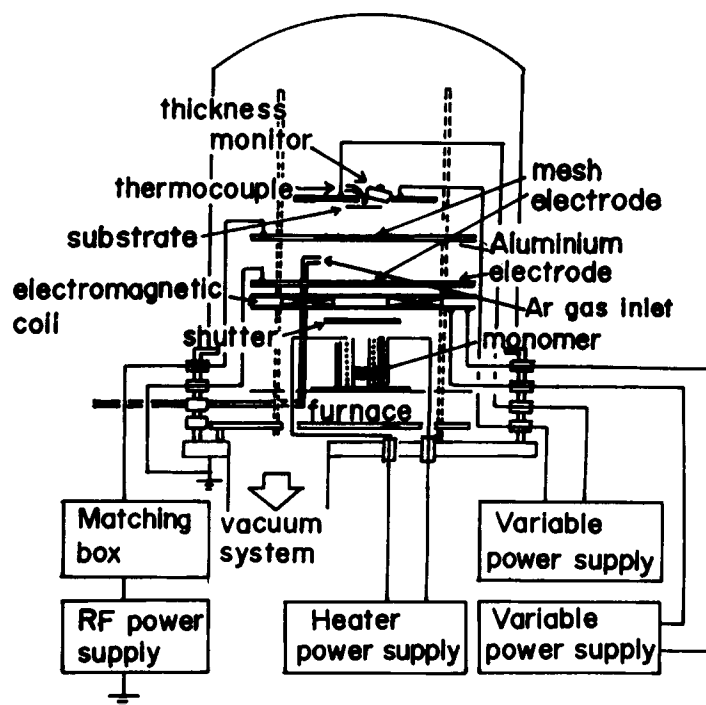


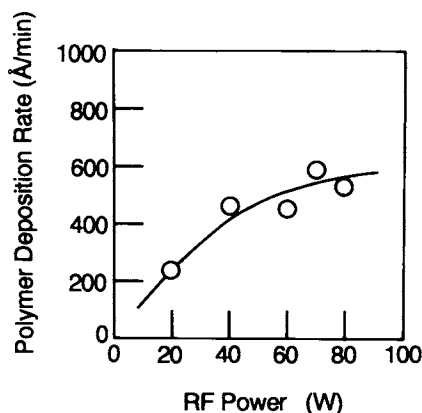
Figure 1 Schematic representation of reaction chamber.

using a  $MgK_{\alpha}$  photon source. The anode power was 400 W at 15 kV, and the background pressure was  $1 \times 10^{-7}$  Pa. The sensitivity factors ( $S$ ) for core levels were  $S(C_{1s}) = 1.00$ ,  $S(O_{1s}) = 2.40$ ,  $S(Al_{2p}) = 0.74$ ,  $S(Cu_{2p}) = 25.2$ ,  $S(Ti_{2p}) = 6.76$ ,  $S(Zn_{3p}) = 3.20$ , and  $S(Mg_{2s}) = 0.80$ .

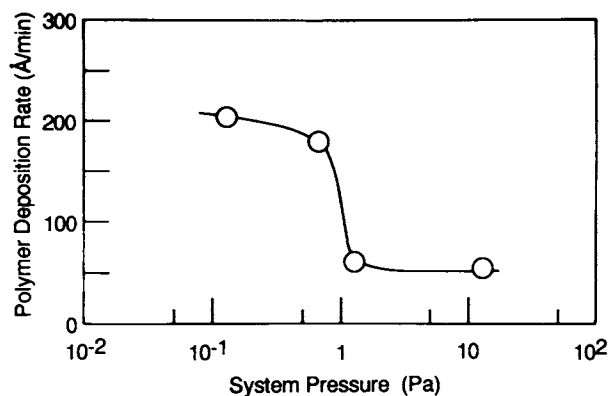
### Gas Sensor Device and Gas Sensitivity Measurement

Gas sensor devices were composed of a sandwich structure of three components, the plasma polymer films deposited from MAcAc (2000–3000 Å thick), a Pt or Pd catalytic layer (10 Å thick), and Au comb electrodes (100 Å thick). First, the plasma polymers (2000–3000 Å thick) were deposited on a quartz glass plate ( $15 \times 15 \times 1.0$  mm) from the plasma polymerization of MAcAc, and were heat-treated at 500°C for 1 min to decompose carbon residues in the films. Afterwards on the top layer of the heat-treated plasma films a Pt or Pd film (10 Å thick) was deposited by vacuum evaporation. Finally, Au comb electrodes (100 Å thick) were deposited by vacuum evaporation. The dimensions of the comb with 0.5 mm gap were 7.0 mm long and 0.5 mm wide. The number of the comb teeth was  $4 \frac{1}{2}$ .

The gas sensitivity for the gas sensor devices was evaluated by the ratio ( $R_{air}/R_{gas}$ ) of the electrical resistance ( $R_{gas}$ ) in a gas atmosphere and the resistance ( $R_{air}$ ) in air. An electric field of 10 V (DC) was applied between the combs, and the electric current between the combs was measured with an Advantest electrometer TR8652 as a function of gas atmosphere and the surface temperature of the sensor device. Carbon monoxide, CO, hydrogen,  $H_2$ , and



**Figure 2** Polymer deposition rate in plasma polymerization of ZnAcAc at  $6.65 \times 10^{-2}$  Pa as a function of rf power.



**Figure 3** Polymer deposition rate in plasma polymerization of TiAcAc at 20 W as a function of system pressure.

propane,  $C_3H_8$ , were used as gases for the determination of the gas sensitivity.

## RESULTS AND DISCUSSION

### Plasma Polymerization of Metal Acetylacetonates

The plasma polymerization of the five metal acetylacetonates—AlAcAc, CuAcAc, TiAcAc, ZnAcAc, and MgAcAc—deposited thin films that contained metal elements as well as carbon and oxygen elements. The polymer deposition rate in the plasma polymerization of the MAcAc was a function of the rf power, the system pressure, and the kind of MAcAc. When limited to a series of plasma polymerizations of ZnAcAc and TiAcAc, an increase in the rf power leads to an increase in the polymer deposition rate (Fig. 2) and an increase in the system pressure leads to a decrease in the polymer deposition rate (Fig. 3). These effects could be explained on the basis of the activation of MAcAc by electron collision and of the mean-free path of the sublimated molecules.

Table I shows the elemental composition of the plasma polymers, which was determined by XPS. The elemental composition of the deposited plasma polymers is completely different from that of the starting MAcAc used for the plasma polymerization. The plasma polymers, except for those plasma-polymerized from ZnAcAc, possess lower metal content and higher carbon content than the corresponding MAcAc. The difference in the elemental composition between the plasma polymers and the starting materials indicates a possibility that MAcAc molecules, when passing through the plasma zone, would be fragmented into at least two small molecules—one a metal-containing fragment and the other a frag-

**Table I** Elemental Composition of Plasma Polymers Prepared from Metal Acetylacetonates

Plasma Polymerization Conditions			Elemental Composition (atom %)		
Monomer	Pressure (Pa)	RF Power (W)	Carbon Content	Oxygen Content	Metal Content
AlAcAc	—	—	68.18	27.27	4.55
	0.0665	20	80.20	18.02	1.78
		60	67.77	31.19	1.05
CuAcAc	—	—	66.67	26.67	6.66
	0.133	20	66.66	29.23	4.10
		60	73.29	25.41	1.29
TiAcAc	—	—	62.50	31.25	6.25
	0.133	20	78.04	21.81	0.15
		60	68.93	28.58	2.50
ZnAcAc	—	—	66.67	26.67	6.66
	0.0665	20	67.01	24.56	8.43
		60	68.47	27.19	4.34
MgAcAc	—	—	66.67	26.67	6.66
	0.133	20	63.54	31.50	4.96
		60	70.68	26.02	3.30

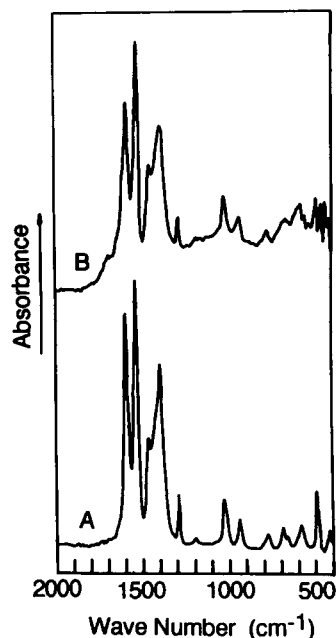
ment without metal element. Each of these fragments would be independently plasma-polymerized and deposited as polymers. Thus, the chemical composition of the deposited plasma polymers may be a complex of three processes, fragmentation, polymerization, and deposition. Here, fragmentation means how the starting MAcAc molecules are fragmented in the plasma zone, polymerization means how easily these fragments are polymerized, and deposition means how much the formed polymers stick on the substrate surface.

### Chemical Composition of Plasma Polymers

Metal acetylacetonates, MAcAc, show distinctive IR absorption peaks due to C=C, C=O, CH<sub>3</sub>, C—CH<sub>3</sub>, and M—O groups, in which the position is shifted to lower wave number than those of acetylacetonate, AcAc by the complexing with metal elements.<sup>9</sup> This shift is used for the determination of the presence of the complexing bonds between AcAc and the metal element. As discussed in a previous section the fragmentation reactions of MAcAc occur simultaneously with the polymerization process. We speculate that the fragmentation plays an important role in determining the elemental composition and properties of the deposited plasma polymers. From this viewpoint the nature of the fragmentation which occurs in a plasma zone, that is, which complexing bond of MAcAc is cleaved, is of interest.

The plasma polymers prepared from MAcAc showed two different patterns in the IR spectra: one

is for plasma polymers that contain strong absorption peaks due to the complexing bonds still present after the polymerization process, and the second is for plasma polymers that contain fewer absorption peaks due to complexing bonds but strong absorption peaks due to free (noncomplexed) C=O and C=C groups. Typical IR spectra are shown in Figures 4 and 5. The plasma polymer formed from AlAcAc belongs to the first pattern. Figure 4 shows the IR spectrum for the plasma polymers formed from AlAcAc at a system pressure of  $6.65 \times 10^{-2}$  Pa and an rf power of 20 W. The IR spectrum resembles that of the starting material, AlAcAc. Characteristic absorption peaks appear at 1595 ( $\nu$ C=C,  $\nu$ C=O), 1535 ( $\nu$ C=C,  $\nu$ C=O), 1460 ( $\delta$ CH<sub>3</sub>,  $\nu$ C—C), 1400 ( $\delta$ CH<sub>3</sub>), 1290 ( $\nu$ C—CH<sub>3</sub> +  $\nu$ C—CH<sub>3</sub>), 940 ( $\nu$ C=C,  $\nu$ C=O), and 495 cm<sup>-1</sup> ( $\nu$ Al—O +  $\nu$ C—CH<sub>3</sub>) which are due to complexing bonds, although the relative intensity of these absorptions is different from that of AlAcAc. In addition to these absorptions, a new absorption appears at 1125 cm<sup>-1</sup> and is assigned to a C—O stretching vibration in alcohol.<sup>10</sup> Comparison of the IR absorption of the plasma polymers and the starting material suggests that the plasma polymers prepared from AlAcAc possess a large amount of the complexing residues between aluminium and acetylacetonate. The plasma polymers prepared from TiAcAc and ZnAcAc belong to the second pattern. Figure 5 shows the IR spectra for the plasma polymers prepared from TiAcAc and ZnAcAc at an rf power of 20 W and at a system pressure of  $1.33 \times 10^{-1}$  and  $6.65 \times 10^{-2}$



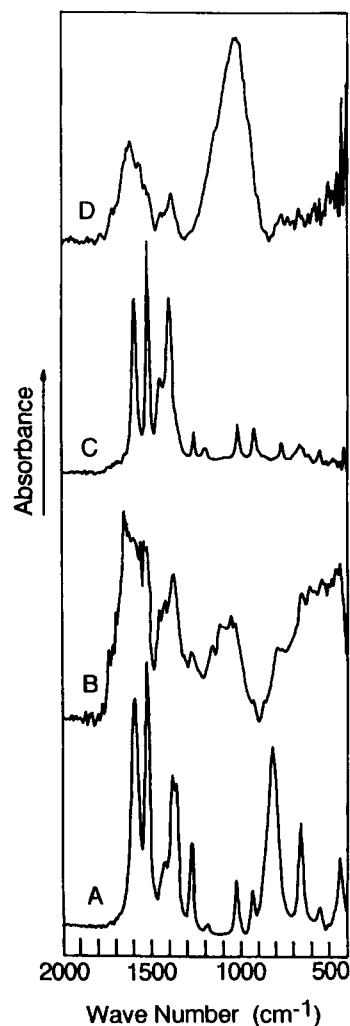
**Figure 4** IR spectra of plasma polymers prepared from AlAcAc: (a) starting material, AlAcAc; (b) plasma polymer.

Pa, respectively. The spectra are dissimilar to that of the starting materials, TiAcAc and ZnAcAc. TiAcAc and ZnAcAc give distinctive IR absorption peaks due to the complexing bonds at 1600, 1530, 1386, and 1280  $\text{cm}^{-1}$ ; and at 1600, 1520, 1460, and 1400  $\text{cm}^{-1}$ , respectively. However, the plasma polymers prepared from TiAcAc and ZnAcAc show complicated IR spectra with strong absorption peaks at 1730–1520  $\text{cm}^{-1}$  and 1150–1030  $\text{cm}^{-1}$ , although the absorption peaks due to the complexing bonds are still observed. The absorption peaks at 1730 and 1650  $\text{cm}^{-1}$  are assigned to C=O and C=C groups that are not complexed with the metal elements.<sup>10</sup> The complication of the absorption peaks due to C=O and C=C groups indicates that cleavage of the complexing bonds between AcAc and metal elements has occurred and that free C=O and C=C groups were formed in the plasma polymerization process.

This cleavage of the complexing bonds can be examined with respect to the binding energy of the metal element. The  $\text{Al}_{2p}$  and  $\text{Ti}_{2p}$  core level spectra for the plasma polymers prepared from AlAcAc and TiAcAc, which are not represented here for sake of brevity, appeared at 74.8 eV [the full width at half-maximum (FWHM) = 1.6 eV] and 458.7 eV (FWHM = 2.0 eV), respectively. The  $\text{Al}_{2p}$  peak position at 74.8 eV for the plasma polymers from

AlAcAc corresponds to that for Al metal at 74.0 eV. The  $\text{Ti}_{2p}$  peak position at 458.7 eV is higher than that for Ti metal at 455.0 eV. This peak position indicates that the Al in the plasma polymers is in the unoxidized state, because the  $\text{Al}_{2p}$  core level of metal appears at 74.0 eV, whereas the Ti in the plasma polymers is in an oxidized state, since the  $\text{Ti}_{2p}$  core level at 455.0 eV for Ti metal and at 489.0 eV for  $\text{TiO}_2$ .<sup>11</sup> This XPS measurement reveals the susceptibility of the complexing bonds to plasma. The complexing bonds between Al and AcAc are not cleaved during the plasma polymerization process but the complexing bonds between Ti or Zn and AcAc are cleaved.

The IR spectra provide valuable information on the complexing state between acetylacetonate and the



**Figure 5** IR spectra of plasma polymers prepared from ZnAcAc and TiAcAc: (a) starting material, ZnAcAc; (b) plasma polymer of ZnAcAc; (c) starting material, TiAcAc; (d) plasma polymer of TiAcAc.

**Table II** Stretching Vibration of C=C, C=O, and M—O Groups for Metal Acetylacetonates

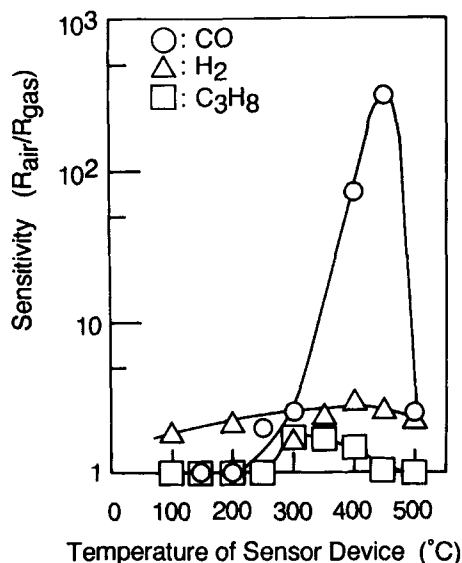
Complex	Metal	Stretching Vibration of C=C ( $\text{cm}^{-1}$ )	Stretching Vibration of C=O ( $\text{cm}^{-1}$ )	Stretching Vibration of M—O ( $\text{cm}^{-1}$ )
AlAcAc	Al(III)	1594	1533	494
CuAcAc	Cu(I)	1579	1532	450
TiAcAc	Ti(IV)	1571	1527	440
ZnAcAc	Zn(II)	1602	1518	421
MgAcAc	Mg(II)	1617	1521	418

metal element. Nakamoto et al. reported the absorption peaks of the C=C, C=O, and M—O stretching vibration for MAcAc. The absorption peaks due to the C=C and C=O stretching vibrations for acetylacetonate are shifted from 1626 and 1718  $\text{cm}^{-1}$ , to 1600 and 1530  $\text{cm}^{-1}$  respectively, by the complexing with metal elements, and the peak due to the M—O stretching vibration appears at near 450  $\text{cm}^{-1}$ . The position of the absorption peaks due to the C=C, C=O, and M—O stretching vibration is related to the delocalization of electrons on the complexing rings. Table II shows the IR absorption peaks due to C=C, C=O, and M—O stretching vibrations of MAcAc as a function of the metal elements.<sup>12</sup> The wave number of the absorption peaks of the C=C stretching vibration for MAcAc is in the order of Al < Cu < Ti < Zn < Mg, and that of the C=O stretching absorption is in the reverse order, indicating that the complexing state for MAcAc is strongly depended on the metal element. From this absorption shift the complexing bond between Al and AcAc could be used to predict its higher stability than TiAcAc and ZnAcAc. This stability may be related to the plasma susceptibility.

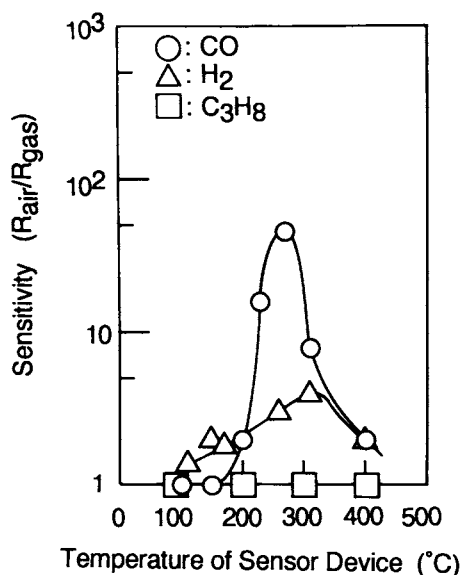
#### Gas Sensor Devices Prepared from Plasma Polymers

The results from IR and XPS measurements, as discussed in previous sections, suggest that the plasma polymers prepared from TiAcAc and ZnAcAc contain titanium or zinc oxides that possess *n*-type semiconductive properties. In general, the determination of reducing gases such as CO, H<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub> is based on the semiconductive properties of the sensor surface. When the reducing gas molecules reach the semiconductive surface they eliminate oxygen atoms adsorbed on the semiconductive surface and are oxidized themselves. As a result of the oxygen elimination the electric conductivity of the sensor surface increases.<sup>13</sup>

The plasma polymers deposited from the plasma polymerization of TiAcAc and ZnAcAc showed no response in electric conductivity when exposed to reducing gases including CO, H<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub>. However, in the presence of Pt or Pd catalysts the plasma polymers that were heat-treated in air at 400–500°C showed a response to the reducing gases. The sensor devices used for the sensitivity measurement were a sandwich structure composed of three layers, the plasma polymers (2000–3000 Å) that were subjected to heat treatment in air at 400–500°C for 1 min, the Pt or Pd catalyst layer (10 Å thick), and Au electrodes (100 Å thick). The Pt catalyst was more effective in the enhancement of the sensitivity than the Pd catalyst. Figures 6 and 7 show changes in the sensitivity of the two sensor devices with the sandwich structure of the three layers as a function of



**Figure 6** Sensitivity of sensor device prepared from plasma polymers of TiAcAc as a function of temperature of the sensor device and nature of the reducing gases: O, CO;  $\Delta$ , H<sub>2</sub>;  $\square$ , C<sub>3</sub>H<sub>8</sub>. The gas concentration was 1000 ppm.



**Figure 7** Sensitivity of sensor device prepared from plasma polymers of ZnAcAc as a function of temperature of sensor device and nature of the reducing gases:  $\circ$ , CO;  $\triangle$ ,  $H_2$ ;  $\square$ ,  $C_3H_8$ . The gas concentration was 1000 ppm.

temperature. Both sensor devices show high sensitivity toward CO but low sensitivity toward  $H_2$  and  $C_3H_8$ . The sensitivity at a CO concentration of 1000 ppm is 308 and 45.6 for the sensor devices made from the plasma polymers of TiAcAc and ZnAcAc, respectively. The sensor device made from the plasma polymers of TiAcAc is higher in CO sensitivity than that made from the plasma polymers of ZnAcAc. However, for the sensor device made from the plasma polymer of TiAcAc it is necessary to operate at high temperature ( $450^\circ C$ ) to obtain the maximum sensitivity, whereas the sensor device made from the plasma polymer of ZnAcAc shows maximum sensitivity operating at a temperature of

$270^\circ C$ . From a practical point of view, the operation at higher temperature may be inconvenient for the detection of CO gas.

Table III compares the performance of the CO gas sensor devices made from plasma polymers. The plasma polymers provided for the sensor devices are those plasma-polymerized from TiAcAc, ZnAcAc, InAcAc,<sup>8</sup> SnAcAc,<sup>7</sup> and tetramethyl tin,  $Ti(CH_3)_4$ .<sup>14</sup> All these plasma polymer films in the presence of Pt catalyst show a response toward the reducing gases. The sensitivity and selectivity, as shown in Table III, are strongly dependent on the plasma polymers. The selectivity is defined as the ratio of CO sensitivity compared to  $C_3H_8$  sensitivity and indicates how well the sensor device distinguishes CO from  $C_3H_8$ . The sensor device made from the plasma polymers of TiAcAc possesses both high sensitivity (308) and high selectivity (257). For the sensor device made from the plasma polymers of ZnAcAc the sensitivity is low but the selectivity high.

## CONCLUSION

Plasma polymerization of five metal acetoacetates—AlAcAc, CuAcAc, TiAcAc, ZnAcAc, and MgAcAc—were investigated for application as CO gas sensor devices. Plasma polymerization deposited thin films that contained metal elements as well as carbon and oxygen elements. The polymer deposition rate was a function of the rf power, the system pressure, and the nature of MAcAc. The elemental composition of the deposited films was fairly different from that of the starting material, MAcAc, and the difference indicates the fragmentation of MAcAc molecules in the plasma zone. The complexing bonds between acetylacetonate and the metal element were cleaved during the plasma polymerization process.

**Table III** Performance of CO Gas Sensor Devices Made from Plasma Polymers

Monomer Used for Plasma Polymerization	Catalyst	Sensitivity			Operating Temperature ( $^\circ C$ )	Reference
		CO	$C_3H_8$	Selectivity		
TiAcAc	Pt	308	1.2	257	450	This study
ZnAcAc	Pt	45.6	1.0	45.6	270	This study
InAcAc	Pt	4309	146	29.5	100	8
SnAcAc	Pt	210	335	0.63	—	7
$Sn(CH_3)_4$	—	1.2	5.0	0.36	300	14

Gas concentration is 1000 ppm.

Selectivity is  $R_{C_3H_8}/R_{CO}$ . (R = electrical resistance in a gas atmosphere.)

The cleavage is closely related to the delocalization of electrons on the complexing rings of MAcAc.

The plasma polymer films prepared from TiAcAc and ZnAcAc in the presence of a Pt catalyst showed a response toward CO gas. The plasma polymer films, especially those prepared from TiAcAc, were a good material for a CO sensor device, with both good sensitivity and selectivity.

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