CO Gas Sensor Devices Plasma-Polymerized from Tetramethyltin

N. INAGAKI, S. TASAKA, and T. MASE, *Laboratory of Polymer Chemistry, Faculty of Engineering, Shizuoka University, 3-5-1 Johoku, Hamamatsu, 432 Japan*

Synopsis

Thin films plasma-polymerized from tetramethyltin was applied for CO gas sensor device. The films formed from tetramethyltin contains alkyl chains with organic tin moieties, and pyrolysis of them at 350–500°C yields carbonized films with SnO_2 moieties. The electrical resistance for the films pyrolized at 350–500°C decreases in exposing to CO gas. The sensitivity, the ratio of the electrical resistance between in air and in CO atmosphere, is enhanced by catalytic actions of palladium chloride, specially in operation at low temperatures below 50°C. The gas sensitivity between CO and other gases such as ethanol, methane, and propane gases is good. The possible determination of CO gas concentration by the sensor device is in ranges from 10 to 1000 ppm.

INTRODUCTION

SnO_2 is an n-type semiconductor. The SnO_2 surface is of interest in electrochemical behavior. When the SnO_2 surface is exposed to reducible gases, the oxidation of them occurs at the SnO_2 surface, and, consequently, the electrical resistance of the SnO_2 surface decreases. This is a basic mechanism to detect propane gas with a gas sensor device.[1] Essentially, the detection of gases from decrease in electrical resistance of the SnO_2 surface is not restricted to propane gas, but is extend to other reducible gases. CO gas, which is a hazardous material because of rapid reactions with hemoglobin of human blood, is one of reducible gases.

Plasma polymerization is a polymer-forming process and has many characteristics including: (1) Volatile-organic molecules, even if they have no functional groups to be polymerized, are plasma-polymerized easily in the discharge state and (2) thin films deposit directly on the substrate surface without fabrication. Therefore, we are able to obtain films with many metals using plasma polymerization technique. The preparation and physical properties of plasma polymers containing metals were reported. They involve tin,[2-5] germanium,[6] copper.[7] Tin-containing polymers are obtained easily from plasma polymerization of tetramethyltin and show semiconductive properties.[5]

This study is a preliminary application of plasma films prepared from tetramethyltin to CO gas sensor device.

EXPERIMENTAL

Plasma Polymerization

The apparatus for plasma polymerization and the experimental procedures are similar to those reported elsewhere.[8] The reaction chamber (100 mm i.d.,

400 mm long) made of Pyrex glass is equipped with a monomer inlet, a pressure gauge, a vacuum system, and a matching network for the inductive coupling of a 13.56 MHz radio frequency (rf) source. Prior to performing plasma polymerization surfaces of the substrates on which plasma polymers would deposit were exposed to argon plasma for 10 min to eliminate water adsorbed on them. Afterwards plasma polymerization was performed under discharge conditions of an rf power of 25 W, a monomer flow rate of 1.87 cm^3 (STP)/min, and a pressure in the reaction chamber of 1.3 Pa. This operating condition of the plasma polymerization corresponds to a W/FM value of 100 MJ/kg, where W, F, and M are the input energy of the rf power (MJ/min), the flow rate of the monomer gas (mol/min), and the molecular weight of the monomer gas (kg/mol), respectively. The W/FM value is a measure of the apparent input energy per unit of the monomer gas.[9]

Tetramethyltin (TMT) (purchased from Alfa Products, 99.5% purity) was degassed by freeze thaw cycles and used as a monomer without further purification.

Infrared and ESCA Spectra

Infrared spectra of the plasma polymers which were deposited on glass plates and scraped from them were recorded with a Nihon Bunko FT/IR-3 Fourier Transform Infrared Spectrometer.

ESCA (C_{1s}, Sn_{3d}, and O_{1s} core levels) spectra of the plasma polymers deposited on silicon wafers were recorded with a Shimadzu ESCA 750 photoelectron spectrometer employing MgK_α exciting radiation which was operated at 8 kV and 30 mA. Furthermore, the obtained spectra were deconvoluted with a Shimadzu ESCAPAC 760 data system under the assumption that the observed spectra were the superposition of more than two Gaussian curves. Three parameters, the position and the height of the peaks and the full width at half-maximum (FWHM), were varied until the superposed curve corresponded roughly to the observed spectra. The FWHM value of all the resolved curves was less than 2.0 eV.

CO Sensor Device

Three types of the CO sensor device (Type I, II, and III) were manufactured to evaluate the sensitivity of the plasma polymers prepared from TMT toward CO gas. These CO sensor devices, as shown in Figure 1, are made up of Au comb electrodes, plasma layer, and catalytic layer, which were deposited onto quartz glass plate ($20 \times 15 \times 1.0$ mm) by the vacuum evaporation technique or plasma polymerization. The comb is 7.5 mm long and 0.27 mm wide, with a separation of 0.36 mm between adjacent teeth. The number of teeth in the comb is $4\frac{1}{2}$ [Fig. 1(A)].

Type I. The plasma polymer prepared from TMT (300–600 nm thick) was deposited on the quartz glass plate with the Au comb electrodes, and heated in air at temperatures from 350 to 500°C for 1 h [Fig. 1(B)].

Type II. The plasma polymer formed from TMT (300–600 nm thick) was deposited on the quartz glass plate with the Au comb electrodes, and, then, the catalytic layer (3–6 nm thick) of antimony, palladium, palladium chloride, and platinum was attached on the top surface of the plasma polymer by the
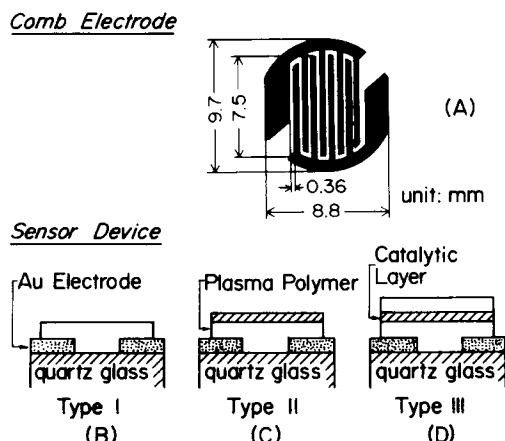
Comb Electrode

Sensor Device

Fig. 1. Schematic presentation of comb electrode as CO sensor device.

vacuum evaporation technique. Moreover, the plasma polymer deposited on the quartz glass plate was pyrolyzed in air at temperatures from 350 to 500°C for 1 h [Fig. 1(C)].

Type III. The CO sensor type III has sandwich structure composing of two layer of plasma polymer formed from TMT (300–600 nm thick) and the catalytic layer of palladium chloride (3–6 nm thick) [Fig. 1(D)]. First, the plasma polymer was deposited on the quartz glass plate with the Au comb electrodes, and then the catalytic layer (3–6 nm thick) was attached on the surface of the plasma polymer by the vacuum evaporation technique. Moreover, the catalytic layer was coated with the plasma polymer from TMT (300–600 nm thick). The plasma polymers deposited on the quartz glass plate was pyrolized in air at temperatures from 350 to 500°C for 1 h each time the plasma polymerization process was finished.

An electrical field of 10 V (dc) was applied between the combs, and the electrical current was measured with an Advatest electron meter TR8641 or TR8652 as function of the CO gas concentration and the surface temperature of the sensor device. Changes in the electrical resistance were estimated from the data of the changes in the electrical current. The sensitivity of the sensor device toward CO gas was defined as follows:

$$\alpha = R_{air}/R_{gas}$$

where R_{air} and R_{gas} mean electrical resistance of the sensor device in air and CO atmosphere, respectively.

RESULTS AND DISCUSSION

Chemical Composition of Plasma Polymers Prepared from TMT

Preliminary experiments showed that the polymer deposition rate in plasma polymerization of TMT and the appearance of the deposited products depended on a magnitude of the *W/FM* value. When plasma polymerization was performed at a constant rf power of 25 W, the polymer deposition rate

TABLE I
Atomic Ratio of Plasma Polymers Prepared from TMT

Pyrolysis (°C)	Atomic ratio	
	C/Sn	O/Sn
—	12.1	4.9
350	3.9	4.2
450	1.0	1.9
500	1.3	1.6

decreased with increasing the W/FM value, and the appearance of the deposited products changed from filmy to powdery. The plasma polymerization operated at a W/FM value of 100 MJ/kg gave good films for use of sensor devices: it is a colorless, transparent film having no crack. The polymer deposition rate was 8 $\mu g/cm^2$ min.

The C/Sn and O/Sn atomic ratios determined by ESCA for the plasma polymer prepared from TMT at a W/FM value of 100 MJ/kg were 12.1 and 4.9, respectively (Table I). The estimation of the atomic ratios from ESCA spectra allowed for correction of the cross section for photo-ionization but did not allow for correction of other factors such as the escape depth and the kinetic energy of electrons. Accordingly, the atomic ratios estimated here mean rather semiquantitative composition than quantitative composition at surface of the deposited polymer. The C/Sn atomic ratio of 12.1 is somewhat higher than that of the starting compound, TMT (C/Sn atomic ratio = 4), indicating that the formed polymer is rich in carbon atom. Similar formation of carbon-rich polymers by plasma polymerization of TMT has been reported by Kny et al.[3] They showed that the C/Sn atomic ratio varied from 2.2 to 31.4 and that the variation depended on the relative position between the rf energy input zone and the polymer deposition zone.

The pyrolysis at 350–500°C in air made the plasma polymers from transparent to brown, and also made the polymer poor in carbon and oxygen contents (Table I), especially the C/Sn atomic ratio decreased from 12.1 and 1.0 by pyrolysis at 350 and 450°C, respectively. This result indicates that the pryolized polymer may be composed of carbonized carbon with tin moieties.

IR spectra for the plasma polymer as deposited (Fig. 2) showed absorptions due to CH_3 and CH_2 groups at 2978, 2922, 1460, 1378, and 764 cm^{-1}, due to Sn—CH_3 groups at 1192 cm^{-1}, due to Sn—C moieties at 525 cm^{-1}, and due to OH groups at 3421 cm^{-1}. This indicates that the polymer is composed of alkyl chains with organic tin and hydroxyl moieties. The pryolized polymers showed IR spectra different from the former: Absorption peaks at 2958, 2922 due to stretching vibration of CH_2 and CH_3 groups, at 1460 and 1378 due to deformation vibration of CH_2 and CH_3 groups, at 1192 due to deformation vibration of Sn—CH_3 groups, and at 525 cm^{-1} due to stretching vibration of Sn—C moieties was weak. New absorptions at 1640 (C=C), 1400 (CH in —CH=CH—), 1073 (C—O and Sn—O), and 781–794 cm^{-1} (Sn—O—Sn) appeared.

Similar changes in chemical composition could be observed in ESCA spectra (Fig. 3). The C_{1s} spectra for the plasma polymer as deposited showed a sharp
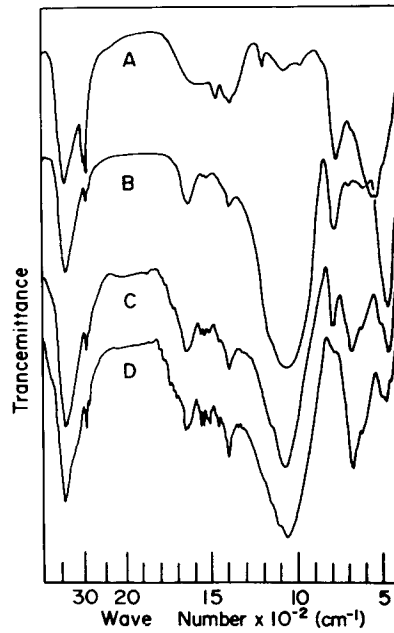
Fig. 2. IR spectra of plasma polymers: (A) not pyrolized; (B) pyrolized at 350°C; (C) at 450°C; (D) at 500°C.
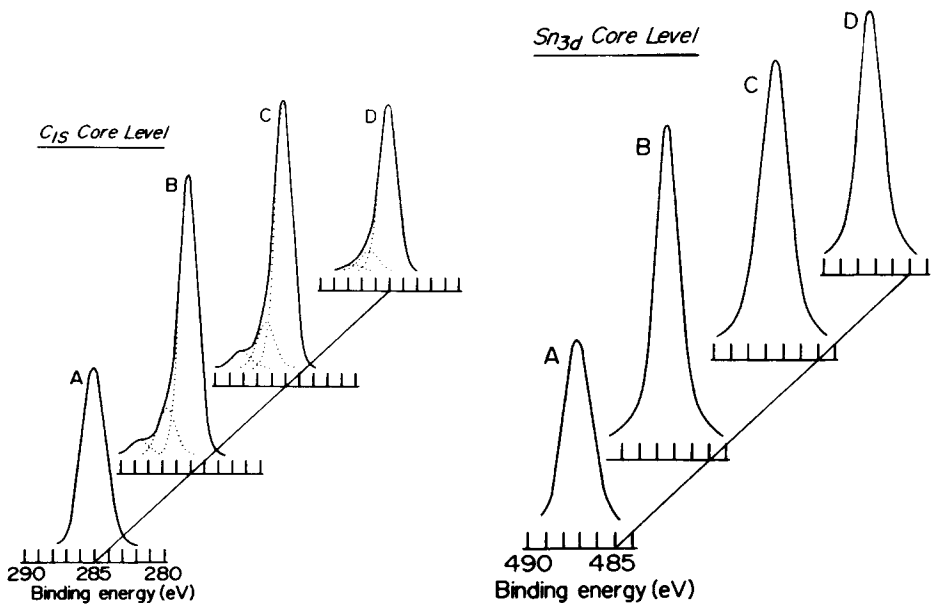

Fig. 3. ESCA (C_{1s} and Sn_{3d}) spectra of plasma polymers: (A) not pyrolized; (B) pyrolized at 350°C; (C) at 450°C; (D) at 500°C.

peak at 285.0 eV of which the FWHM value was 1.8 eV. The C_{1s} spectra for the pyrolized polymers widely distributed from 283 to 290 eV. These spectra were deconvoluted into $\underline{C}H_2$ (at 285.0 eV), $\underline{C}-O$ (at 286.6 eV), and $\underline{C}=O$ moieties (at 287.9 eV) of which the relative concentration was about 82–87, 11–14, and 3–6 mol %, respectively. The Sn_{3d} spectra showed a sharp peak at 487.3 eV with a FWHM value of 1.8 eV. It could be assigned SnO and/or SnO_2 features.

From these spectral results it could be concluded that the plasma polymer prepared from TMT is a mixture of alkyl and organic tin moieties. When the plasma polymers are pyrolized at 350–500°C, dehydration and oxidation occur to yield carbonized products containing much amount of tin oxides.

Sensitivity of Plasma Films Prepared from TMT toward CO Gas

The sensitivity of the plasma films toward CO gas was examined. The plasma films were prepared from TMT at a W/FM value of 100 MJ/kg and then pyrolized in air at 350–500°C. The sensitivity for the sensor device type I was evaluated as a ratio of the electrical resistance in air (R_{air}) and that in CO gas atmosphere of 1000 ppm (R_{gas}). The sensitivity depended on both pyrolysis temperature and surface temperature of the device (Fig. 4): At surface temperatures lower than 200°C, the sensitivity was very low; but above 200°C, the sensitivity increased with increasing the surface temperature of the device, and reached about 1.9 at a surface temperature of 350°C. However, a sensitivity of 1.9 was not enough to determine CO gas.

The catalytic action of metals was applied for improvement of the sensitivity. The catalytic layer (3–6 nm thick) was deposited like islands on the surface of the plasma films pyrolized at 450°C (sensor device type II). Antimony, palladium, palladium chloride, and platinum were chosen as catalysts. Figure 5 shows the sensitivity ratio at a CO concentration of 1000 ppm,
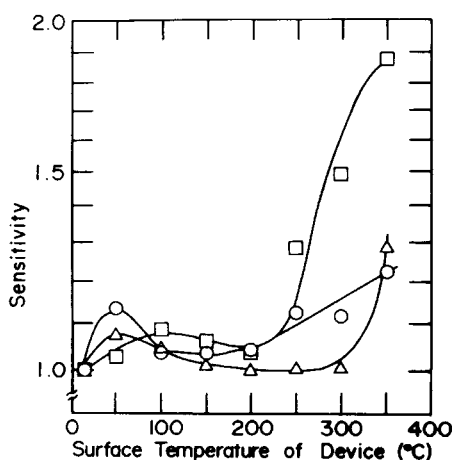

Fig. 4. CO sensitivity (at 1000 ppm CO) of sensor device type 1 as functions of pyrolysis temperature and surface temperature of device: (○) pyrolized at 350°C; (□) at 450°C; (△) at 500°C.
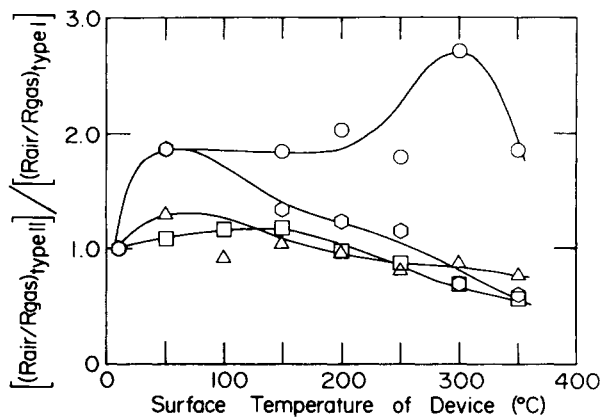
Fig. 5. CO sensitivity (at 1000 ppm CO) of sensor device type II as functions of catalytic layer and surface temperature of device: (○) $PdCl_2$; (⬡) Pd; (□) Pt; (△) Sb.

$[(R_{air}/R_{gas})_{type\ II}/(R_{air})/R_{gas})_{type\ I}]$, between in the presence of the catalyst $(R_{air}/R_{gas})_{type\ II}$ and in the absence of the catalyst $(R_{air}/R_{gas})_{type\ I}$ as functions of the catalyst and the surface temperature of the device. Significantly, a catalytic effect of palladium and palladium chloride could be observed, but antimony and platinum showed no effect. The catalytic effect of palladium chloride was more powerful than that of palladium. The sensitivity at a CO concentration of 1000 ppm reached 4.0 for the sensor device type II containing palladium chloride.
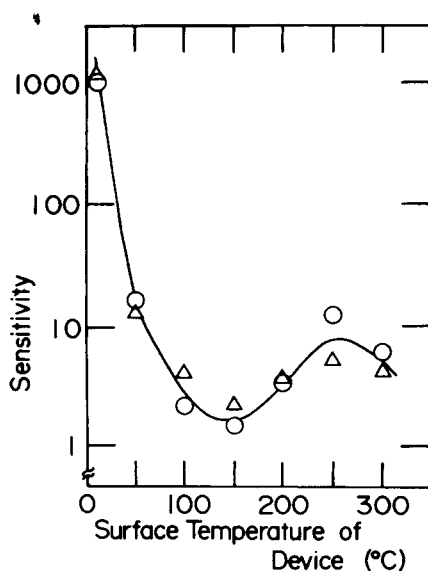
Fig. 6. CO sensitivity (at 1000 ppm CO) of sensor device type III as functions of plasma polymer thickness and surface temperature of device: (○) 310 nm thick; (△) 580 nm thick.

TABLE II
Sensitivity at 15 and 50°C toward Various Gases[a]

Gases	Sensitivity	
	At 15°C	At 50°C
CO	1060	16
H_2	40	45
CH_4	1.0	1.4
C_3H_8	1.0	1.2
C_2H_5OH	1.1	1.3

[a]The gas concentration was 1000 ppm.

Furthermore, to improve the sensitivity, the other type of the sensor device was applied. The sensor device type III is sandwich structure of three layers [see Fig. 1(D)]. Palladium chloride was used as a catalyst. Figure 6 shows the sensitivity at a CO concentration of 1000 ppm as functions of the surface temperature of the device and the plasma film thickness. The sensitivity for the sensor device type III was highly improved compared with that for the sensor device type I and II, and the film thickness showed no influence on the sensitivity. The sensor device showed higher sensitivity at lower temperature (the sensitivity was 16 at 50°C and 1060 at 10°C) rather than high temperatures (the sensitivity was 5 at 300°C), which may be applicable to practical use for determination of the CO concentration. The sensitivity toward ethanol, methane, and propane was less than one tenth as small as that toward CO gas: At 1000 ppm concentration of each gases and at a surface temperature of 50°C, the sensitivity was 1.2, 1.3, 1.4, and 45 toward propane, ethanol, methane, and hydrogen, respectively, compared with that of 16 toward CO gas (Table II). Therefore, the gas selectivity of the sensor device type III is good, although the selectivity against hydrogen is poor.

Finally, the relationship between the sensitivity and the CO concentration was illustrated in Figure 7. It is well known that when a surface of semiconductive SnO_2 films is exposed to reducible gases such as alcohol, hydrogen,
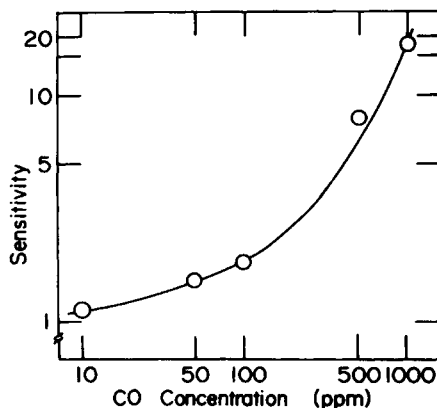

Fig. 7.   CO sensitivity at 50°C as a function of CO concentration.

methane, and propane, logarithm of (R_{air}/R_{gas}) is a linear function with logarithm of the gas concentration.[1] The sensor device type III did not show a linear relationship between logarithm of R_{air}/R_{gas} and logarithm of the CO concentration but a concave relationship.

Many investigators reported on the catalytic oxidation of CO molecules with precious metals. The reaction could be explained by the Langmuir–Hinshelwood mechanism of CO and oxygen molecules adsorbed chemically on the metal surface.[11] Such reports is helpful in understanding the sensing mechanism of CO molecules, but is not completely satisfied. Why palladium chloride in spite of palladium and platinum shows catalytic action, and what catalytic action palladium chloride operates at low temperatures below 50°C are important subjects to be resolved. These subjects are not yet clear at the present time. We can speculate that chloride atom of palladium chloride would play an important role in the catalytic reactions of CO oxidation. Omar et al.[11] reported that trace amount of chloride atom cocatalyzes oxidation reactions of ethylene. Kaji et al.[12] and Yoneyama et al.[13] separately reported similar catalytic reactions by palladium chloride.

CONCLUSION

Plasma polymerization of TMT was investigated by IR and ESCA spectra, and the plasma films was applied for sensor device of CO gas. Results are summarized as follows:

1. Plasma polymers prepared from TMT is a mixture of alkyl and organic tin moieties. Pyrolysis of the plasma polymers at 350–500°C yields carbonized films containing much amount of tin oxides.
2. Plasma films pyrolized at 350–500°C is sensitive to CO gas in CO concentration ranges from 10 to 1000 ppm. The electrical resistance of the films decreases in exposing it to CO atmosphere.
3. The sensitivity toward CO gas is enhanced by the presence of a trace amount of palladium chloride, and reaches 1060 and 16 at 10 and 50°C.
4. The selectivity against ethanol, methane, and propane is good, but that against hydrogen is poor.

References

1. T. Seiyama, J. Shiokawa, S. Suzukai, and K. Fueki, Eds., *Chemical Sensors*, Kodansha, Tokyo, 1982.
2. B. V. Tkachuk, N. Ya. Marusii, and Ye, P. Laurs, *Polym. Sci. USSR*, **15**, 2314 (1973).
3. E. Kny, L. L. Levenson, and W. J. James, *J. Vac. Sci. Technol.*, **16**, 359 (1979); *J. Phys. Chem.*, **84**, 1635 (1980).
4. R. K. Sadhir and W. James, *Thin Solid Films*, **97**, 17 (1982).
5. N. Inagaki, T. Nishio, and K. Katsuura, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 765 (1980); N. Inagaki, T. Yagi, and K. Katsuura, *Eur. Polym. J.*, **18**, 621 (1982); N. Inagaki and Y. Hashimoto, *J. Polym. Sci., Polym. Lett. Ed.*, **24**, 447 (1986); *Kobunshi Ronbunshu*, **43**, 711 (1986).
6. N. Inagaki and M. Mitsuuchi, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2887 (1983); *J. Polym. Sci., Polym. Lett. Ed.*, **22**, 391 (1984).
7. Y. Osada and A. Mizumoto, *J. Appl. Phys.*, **59**, 1776 (1986); Y. Osada and K. Yamada, *Kobunshi Ronbunshu*, **44**, 275 (1978); Y. Osada, K. Yamada, and I. Yoshizawa, *Thin Solid Films*, **151**, 71 (1987).

8. N. Inagaki and H. Katsuoka, *J. Membr. Sci.*, **34**, 297 (1987).

9. H. Yasuda, *Plasma Polymerization*, Academic, New York, 1985.

10. T. Matsushima, *Surf. Sci.*, **79**, 63 (1979).

11. A. Omar, G. D. Mariadassou, and F. B. Verduraz, *J. Catal.*, **60**, 295 (1979).

12. T. Kaji, H. Ohno, T. Nakayama, N. Yamazoe, and T. Seiyama, *Nippon Kagaku Kaishi*, **1980**, 1088.

13. H. Yoneyama, W. B. Li, and H. Tamura, *Nippon Kagaku Kaishi*, **1980**, 1580.