

Plasma Polymerization of Copper Phthalocyanines and Application of the Plasma Polymer Films to NO₂ Gas Sensor Device

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SYNOPSIS

Four copper phthalocyanines without substituent (CuPc) and with chlorine (CuPc-Cl), hydroxymethyl (CuPc-CH₂OH), and phthalimidomethyl substituents (CuPc-CH₂N-[C(O)]₂Ph) were plasma-polymerized to obtain amorphous and thin films having the extended π -electron system. The chemical composition of the plasma polymer films was discussed from the data of the electronic spectra, IR spectra, and XPS spectra. The application of the plasma polymer films was discussed with regard to the NO₂ sensitivity, the NO₂ selectivity, the response time, and the reversibility. Plasma polymerization of CuPc, CuPc-Cl, CuPc-CH₂OH, and CuPc-CH₂N[C(O)]₂Ph gives amorphous films having the extended π -electron system. In the plasma polymerization process, a part of the extended π -electron system is broken down. The CH₂OH and CuPc-CH₂N[C(O)]₂Ph substituents contribute to minimizing the degradation. The Cu atoms liberated from the chelation in the plasma polymerization process exist as CuO in the deposited films. The plasma polymer films of CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph show good sensitivity to NO₂ molecules. With regard to the sensitivity, the selectivity, the response time and the reversibility, the plasma polymer films are applicable materials to the NO₂ sensor device. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Copper phthalocyanine is one of the great interesting compounds having outstanding properties such as thermal and chemical stability, coloration, semi-conductivity, photoconductivity, catalytic actions, etc. Such functionalities are mainly due to the extended π -electron system in copper phthalocyanine. A gas sensor device of copper phthalocyanine is an interesting application of copper phthalocyanine and is able to detect NO₂, NH₃, and CO gas molecules from the conductivity change.^{1,2} Prior to the application of copper phthalocyanine to the gas sensor device, there are two issues to be considered: (1) How to prepare a thin film of copper phthalocyanine? and (2) How to stabilize the phase transition of crystalline copper phthalocyanine? Copper

phthalocyanine for the gas sensor device is used in the form of a single crystal, a pellet by pressing polycrystalline powders, and a film by vacuum sublimation. In many cases, the form of a film is convenient for the fabrication of the sensor device, but the sublimated film lacks resistance by mechanical stress and adhesion with the substrate surface for the sublimation. Copper phthalocyanine exists in at least two crystal modifications, α and β phases. The α phase is obtained as a polycrystalline powder or a film sublimated on cold substrate surface. The β phase is obtained in the form of a single crystal or in that of a film sublimated on hot substrate surface. The α phase transforms into the β phase by heating.³ Generally, the β phase of copper phthalocyanine shows higher gas sensitivity than the α phase.² The transformation is a knotty problem with respect to the stability and durability of the gas sensor device. If we could prepare a polymeric and amorphous film of copper phthalocyanine, it would solve the two issues at a stroke.

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Plasma polymerization is a unique film formation process. By the plasma polymerization, almost all organic molecules can be polymerized to deposit a thin and amorphous film. The plasma polymerization process may be a good technique to prepare the amorphous film of copper phthalocyanine. However, we are anxious that copper phthalocyanine, especially the extended π -electron system, may be broken down by the action of plasma. In this study, special derivatives of copper phthalocyanine are chosen as starting materials of the plasma polymerization for protecting the extended π -electron system from the plasma action. The derivatives are copper phthalocyanines with substituents such as chlorine, hydroxymethyl, and phthalimidomethyl groups. These substituents are susceptible to plasma. We expect that the plasma action may concentrate upon these substituents, and the substituents may be predominantly fragmented to form activated sites. As a result, the polymerization may be initiated from the activated sites to deposit an amorphous film. The preferential plasma attack at the substituents may minimize the damage of the extended π -electron system of the copper phthalocyanine structure.

From this concept, in this study we discuss the following subjects: Can the plasma polymerization

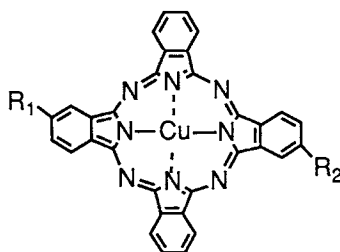
of the special copper phthalocyanines deposit an amorphous thin film? Can the substituents contribute to minimizing the degradation of the extended π -electron system by the plasma action? Can the deposited film show the NO_2 sensitivity?

EXPERIMENTAL

Plasma Polymerization

Four copper phthalocyanines without substituent and with chlorine, hydroxymethyl, and phthalimidomethyl substituents, which were kindly provided from Sanyo Color Workers, Ltd., were used as starting materials for plasma polymerization. The chemical structure and the abbreviation of the copper phthalocyanines are represented in Figure 1.

The reaction chamber used in this study for plasma polymerization of the phthalocyanines was essentially the same as reported elsewhere. The reaction chamber consisted of a bell jar (400 mm in diameter, 470 mm in height) in which a quartz furnace (15 mm in diameter, 65 mm in height) for the sublimation of the copper phthalocyanines, a pair of parallel, circular, and mesh electrodes (300 mm in diameter), a substrate stage temperature-con-



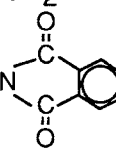
Compounds	R ₁ and R ₂ Substituents	Abbreviation
Copper phthalocyanine	R ₁ = R ₂ = H	CuPc
Copper chlorophthalocyanine	R ₁ = Cl, R ₂ = H	CuPc-Cl
Copper hydroxymethylphthalocyanine	R ₁ = R ₂ = CH ₂ OH	CuPc-CH ₂ OH
Copper phthalimidomethylphthalocyanine	R ₁ = CH ₂ -N  R ₂ = H	CuPc-CH ₂ N[C(O)] ₂ Ph

Figure 1 Copper phthalocyanines used as starting materials for plasma polymerization.

trolled with an electric heater, a thickness monitor positioned near the substrate stage (Ulvac Co., model CRTM-5), an argon gas inlet, and a pressure gauge were contained. The reaction chamber was directly connected through a butterfly valve to a vacuum system consisting of a combination of a diffusion pump (1200 L/s) and a rotary pump (300 L/min). A schematic diagram of the reaction chamber is shown in Figure 2.

The experimental procedures for the plasma polymerization were essentially the same as reported elsewhere.⁴ The copper phthalocyanines of a few grams were placed at the bottom of the quartz furnace. Silicon wafer of (111) plane for the measurement of infrared (IR) spectra, Pyrex glass for the measurement of X-ray photoelectron spectroscopy (XPS) spectra, and quartz glass for the measurement of electronic spectra and for the preparation of sensor devices were mounted at the surface of the substrate stage. The reaction chamber was evacuated to approximately 1.3×10^{-3} Pa, and the substrate stage was heated at a temperature of 60°C. Afterward, the surface of the electrodes and that of the substrate for the plasma polymer deposition were

exposed to argon plasma for 15 min to eliminate water molecules adsorbed at these surfaces. Finally, the copper phthalocyanines were sublimated from the furnace, which was kept at a constant temperature of 330°C, the reaction chamber was adjusted at a pressure of 1.3×10^{-1} Pa by introducing argon gas whose flow rate was controlled with a metering needle valve, and the glow discharge was initiated at a radio frequency (RF) power of 25 W at a given pressure. The RF generator at 13.56 MHz used in this study was a JOEL model JEH-015D whose maximum power was 1.5 kW. The deposition rate of plasma polymers was monitored with the thickness monitor (Ulvac, model CRTM-5) while the plasma polymerization process was in progress.

Electronic, IR, and XPS Spectra of Plasma Polymer Films

Electronic spectra of the plasma polymer films deposited on the quartz glass were recorded in a transmission mode on a Shimadzu spectrophotometer UV-160A in the wavelength range of 200 to 1100 nm.

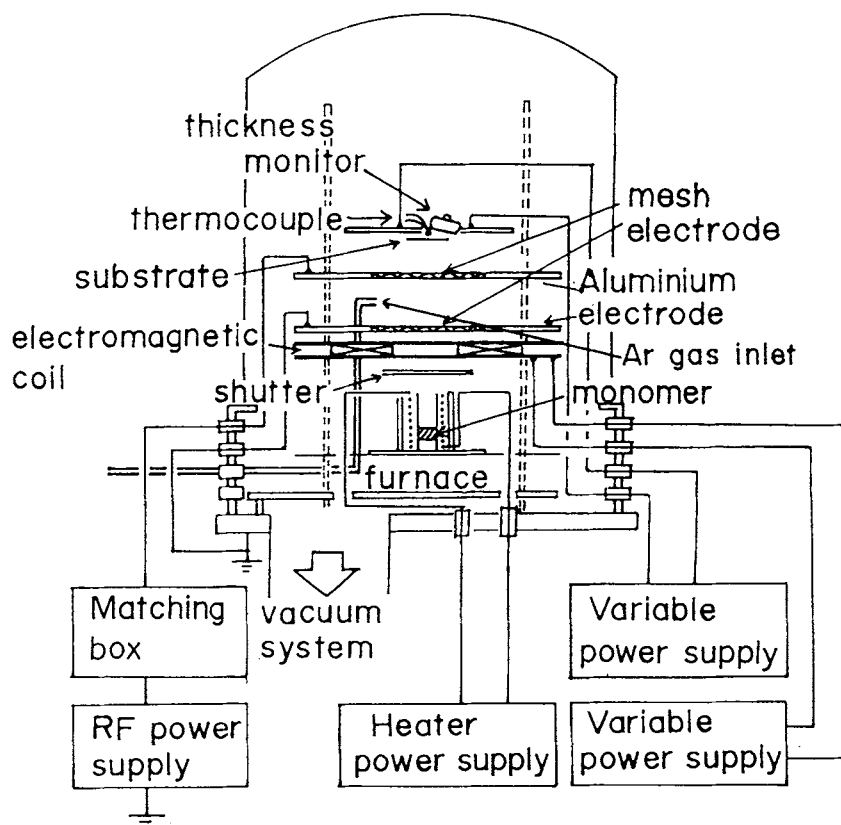


Figure 2 Schematic diagram of reaction chamber.

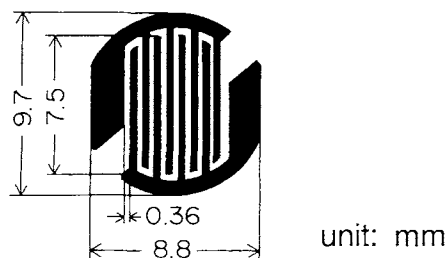
IR spectra of the plasma polymer films deposited at the surface of the silicon wafer were recorded in a transmission mode on a Horiba Fourier transform spectrometer FT300 with an MCT detector. The spectral resolution was 1.0 cm^{-1} and 500 scans were recorded on each sample.

XPS spectra of the plasma polymer films were obtained on an Ulvac-Phi spectrometer 5500 using a non-monochromatic MgK_α photon source. The anode voltage was 15 kV, the power 300 W, and the background pressure of the analytical chamber 4.7×10^{-7} Pa. The spot size of the X-ray irradiation was 7 mm in diameter, and the take-off angle of photoelectrons was 45 degrees with respect to the sample surface. Fifteen scans were recorded on each sample. The smoothing procedure of the observed spectra was not done. The atomic composition of the deposited plasma polymers was estimated from the relative peak area of the C_{1s} , N_{1s} , O_{1s} , and Cu_{2p} core levels and the sensitivity factor of these core levels. The sensitivity factor (S) for these core levels were $S(\text{C}_{1s}) = 1.00$, $S(\text{N}_{1s}) = 1.61$, $S(\text{O}_{1s}) = 2.4$, and $S(\text{Cu}_{2p}) = 18.0$. The spectra were referenced with respect to the 285.0 eV carbon 1s level observed for hydrocarbon to eliminate the charge effect. The C_{1s} , N_{1s} , O_{1s} , and Cu_{2p} spectra were decomposed by fitting a Gaussian-Lorentzian mixture function (the mixture ratio was 75 : 25) to an experimental curve using a nonlinear, least-squares curve-fitting program supplied by Ulvac.

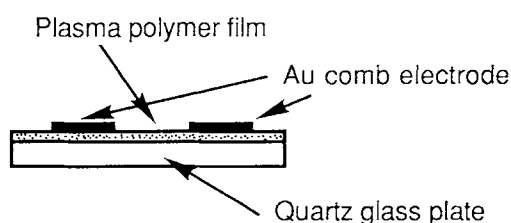
Gas Sensor Device and Gas Sensitivity Measurement

Gas sensor devices were in the sandwich structure of three components: quartz glass, plasma polymer films, and Au comb electrodes. First, a thin plasma polymer film (200 nm in thickness) was deposited at the surface of the quartz glass from the plasma polymerization of the copper phthalocyanines, and then Au comb electrodes (100 nm in thickness) were deposited by the vacuum evaporation technique. The size of the Au comb electrodes was 7.0 mm in length, 0.5 mm in width, and 0.5 mm gap between the electrodes. Figure 3 shows a schematic illustration of the gas sensor devices we made and the comb electrodes.

The gas sensor device was placed at the surface of the temperature-controlled stage in a stainless steel vessel (10 L), which contained a circulation fan, an inlet, and an outlet for test gas. In the dc electric field of 10 V between the comb electrodes, the electric current in dark between the comb electrodes was measured with an Advantest electrometer



Schematic illustration of Au comb electrode



Schematic illustration of gas sensor device

Figure 3 Schematic illustration of gas sensor device.

TR8652 as functions of gas atmosphere (NO_2 , NO , CO_2 , CO , H_2 , N_2 , O_2 , and C_3H_8) and the surface temperature of the gas sensor device. The electric resistance in dark (R_x and R_{air}) between the comb electrodes in the x gas atmosphere (1000 ppm concentration) and in air was calculated from data of the electric current and the dc electric field. The ratio of R_x in x gas atmosphere and R_{air} in air was evaluated as an x gas sensitivity.

$$\text{Gas sensitivity of } x \text{ gas} = \frac{R_x}{R_{\text{air}}} \quad (1)$$

RESULTS AND DISCUSSION

Electronic and IR Spectra of Plasma Polymer Films of Copper Phthalocyanines

In the polymer-forming process by the plasma polymerization, as described in an introduction, molecules introduced into a plasma zone are activated by the action of plasma energy, and two activated molecules (radicals in many cases) combine to form a larger molecule. The successive reactions of the

activation and combination lead to the formation of plasma polymers. This is a basic concept of the plasma polymerization process. In the plasma zone, generally, plasma makes not only the activation of the molecules but also the fragmentation of the molecules, the elimination of small moieties from the original molecules or the bond scission of the original molecules. Either of them occurs predominantly in the plasma zone, depending on the plasma susceptibility of the molecules and the energy level of the plasma.⁵ This dependence explains that plasma polymers are never composed of repeating of the starting molecule (monomer) and that the plasma polymerization operating at different power levels, even when the same starting molecule was used, gives us polymer films with different chemical composition. Copper phthalocyanine is one of most immune compounds against plasma but does not escape completely from the damage by plasma action. Some of the chemical bonds in the copper phthalocyanine molecule will be broken down.

Copper phthalocyanine shows interesting properties such as semiconductive, photoconductive, catalytic properties, etc. The ability of copper phthalocyanine in sensing NO_2 gas molecules is mainly due to semiconductive property. The property is related to highly extended π -electron system and highly delocalized π -electrons on carbon-nitrogen backbone. From the viewpoint of semiconductive property, whether plasma polymer films of copper phthalocyanine possess the π -electron system or not is an important factor in the application of the plasma polymer films to a gas sensor device. How to minimize the injury of the π -electron system in copper phthalocyanine by the plasma action is emphasized. We used special copper phthalocyanines with chlorine, hydroxymethyl, and phthalimido groups that were substituted with hydrogen atom in the benzene rings in copper phthalocyanine. These substituents are susceptible to plasma.⁵ We expected that the plasma action would be concentrated on the substituents to generate active sites. The polymer-forming reactions would be initiated from the active sites to deposit plasma polymers without fatal injury of the extended π -electron system. The chemical structure of the copper phthalocyanines used for plasma polymerization is represented in Figure 1. The effect of the substituents on minimizing the injury of the extended π -electron system was investigated from electronic spectra of the deposited plasma polymer films.

Preliminary experiments discussed operational conditions in the plasma polymerization of copper phthalocyanine, CuPc, for the deposition of smooth,

fine plasma polymer films, and led to the following conclusion: The sublimation temperature of CuPc was 330°C , the RF power 25 W, the pressure in the reaction chamber 1.3×10^{-1} Pa, and the substrate temperature for the deposition of plasma polymer films 60°C . Figure 4 shows typical electronic spectra of four plasma polymer films prepared from the four copper phthalocyanines, CuPc, CuPc-Cl, CuPc- CH_2OH , and CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$, under the above operational conditions. Copper phthalocyanine, as shown in spectrum A in Figure 4, shows characteristic optical absorptions at 345, 623, and 688 nm due to π - π^* transition.^{6,7} The position of these absorptions and their absorption intensity was used as the semiquantitative evaluation of the extended π -electron system in the copper phthalocyanines. All four plasma polymer films, as shown in Figure 4, show similar absorptions at 335, 630, and 690 nm to spectrum A, but by the plasma

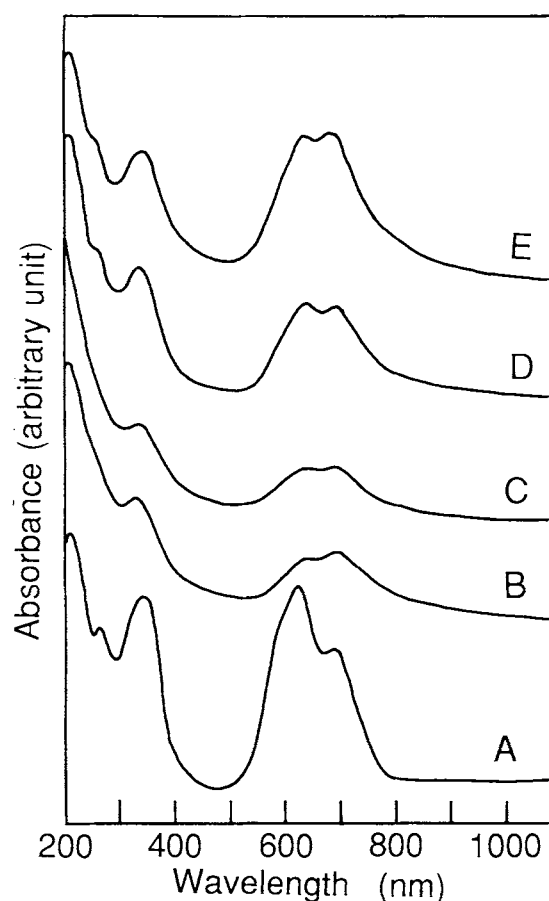


Figure 4 Electronic spectra of CuPc vacuum-deposited film (A), CuPc plasma-polymerized film (B), CuPc-Cl plasma-polymerized film (C), CuPc- CH_2OH plasma-polymerized film (D), and CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ plasma-polymerized film (E).

polymerization, the absorptions are broadened and the absorption intensity becomes weak compared with spectrum A. Furthermore, there is substituent effect in the absorption intensity: The plasma polymer films prepared from CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph show higher intensity at the absorption peaks due to π - π^* transition than those from CuPc and CuPc—Cl. These results indicate that the plasma polymer films possess the extended π -electron system, but the π -electron system after the plasma polymerization is not flawless. The plasma polymer films prepared from CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph possess higher concentration of the π -electron system than those from CuPc and CuPc—Cl.

The injury of the π -electron system by the plasma polymerization was investigated also from the IR spectra. Figure 5 compares IR spectra of the plasma polymer films prepared from CuPc and CuPc—CH₂OH. Copper phthalocyanine, as shown in spectrum C in Figure 5, shows strong absorption

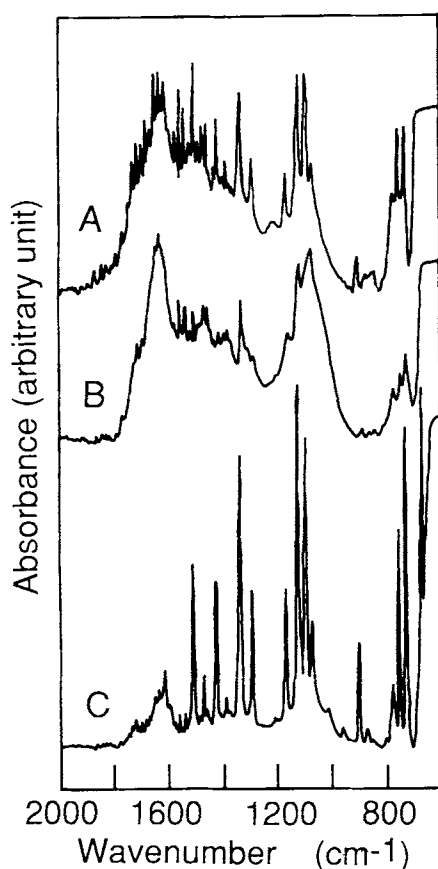


Figure 5 IR spectra of CuPc—CH₂OH plasma-polymerized film (A), CuPc plasma-polymerized film (B), and CuPc vacuum-deposited film (C).

peaks at 1513 and 1425 cm⁻¹ due to the C=C and C=N stretching vibration and at 1338, 1291, 1166, 1121, 1091, 1061, 903, 764, and 732 cm⁻¹ due to the skeletal stretching vibration of benzene ring and the C—H out-of-plane bending vibration.⁸⁻¹⁰ The plasma polymer films prepared from CuPc—CH₂OH (spectrum A in Fig. 5) and CuPc (spectrum B in Fig. 5) also show characteristic absorption peaks like spectrum C, but the background level in the range of 1700 to 1300 cm⁻¹ becomes high, the peak intensity becomes weak, and a broad absorption peak appears at 1730 to 1630 cm⁻¹ (C=O group). The peak broadening and the intensity weakening recognize the conclusion from the discussion of the electronic spectra: A part of the extended π -electron system in copper phthalocyanine is injured by the plasma polymerization. The CH₂OH substituent contributed to minimizing the injury.

In conclusion, the CH₂OH and CH₂N[C(O)]₂Ph substituents are effective in minimizing the injury of the extended π -electron system in the plasma polymerization. The plasma polymerization of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph deposits films with the extended π -electron system.

Chemical Composition of Plasma Polymer Films prepared from CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph

Plasma polymerization of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph operating at an RF power of 25 W deposited blue and transparent films. The X-ray diffraction analysis and the scanning electron microscopy (SEM) picture showed that the plasma polymer films were amorphous and their surfaces were smooth. Table I shows the atomic composition determined by XPS for the plasma-polymerized films deposited from CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph as well as the vacuum-deposited films. There are some differences in the atomic ratio between the plasma polymer film and the corresponding starting compounds. The N/C atomic ratio for the plasma polymers formed from CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph is 0.18, which is slightly smaller than that of the corresponding starting compounds (The N/C atomic ratio is 0.24 for CuPc—CH₂OH and 0.22 for CuPc—CH₂N[C(O)]₂Ph). The O/C atomic ratio for the plasma polymers is 0.24 and 0.25, respectively, which are greatly higher than that of the corresponding starting compounds (The O/C atomic ratio is 0.06 for CuPc—CH₂OH and 0.05 for CuPc—CH₂N[C(O)]₂Ph). The Cu/C atomic

Table I Atomic Composition of Plasma-Polymerized Films and Vacuum-Deposited Films from CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph

Copper Phthalocyanine	Method of Film Formation	Atomic Composition		
		N/C Atomic Ratio	O/C Atomic Ratio	Cu/C Atomic Ratio
CuPc-CH ₂ OH	Plasma polymerization	0.18	0.24	0.01
	Vacuum deposition	0.24 (0.24)	0.04 (0.06)	0.01 (0.03) ^a
CuPc-CH ₂ N[C(O)] ₂ Ph	Plasma polymerization	0.18	0.25	0.01
	Vacuum deposition	0.20 (0.22)	0.04 (0.05)	0.01 (0.02) ^b

^a Calculated from C₃₄H₂₀N₈O₂.^b Calculated from C₄₁H₂₁N₉O₂.

ratio (0.01) for the plasma polymers is almost equal to the corresponding starting compounds (0.03 for CuPc-CH₂OH and 0.02 for CuPc-CH₂N[C(O)]₂Ph) within measuring error. On the other hand, the vacuum-deposited films, as shown in Table I, possess almost the same atomic composition as the corresponding starting compounds: The N/C, O/C, and Cu/C atomic ratios for the vacuum-deposited films of CuPc-CH₂OH are 0.24 (0.24), 0.04 (0.06), and 0.01 (0.03), respectively; and the atomic ratios for the vacuum-deposited films of CuPc-CH₂N[C(O)]₂Ph are 0.20 (0.22), 0.04 (0.05), and 0.01 (0.02), respectively. The figure in parenthesis means the atomic ratio calculated from the structural formula of the starting copper phthalocyanines. The comparison in Table I indicates that the plasma polymerization led mainly to oxidation accompanying the polymer formation. The elimination of nitrogen moieties and copper atoms from the copper phthalocyanines occurred scarcely in the plasma polymerization process.

XPS spectra gave us important information on the chemical composition of the plasma polymer films. Figures 6 to 9 show C_{1s}, N_{1s}, O_{1s}, and Cu_{2p} core level spectra of the plasma polymer films formed from CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph as well as the vacuum-deposited films. These spectra were decomposed by fitting a Gaussian-Lorentzian mixture function. The C_{1s} core level spectra for all films, as shown in Figure 6, are asymmetric in shape and show a tailing in the higher energy side. The spectra were decomposed into five functions whose full width at half maximum (FWHM) was 1.5 eV for the plasma polymer films and was 1.0 eV for the vacuum deposition films. The results of the decomposition are illustrated in dotted lines in Figure 6. The peak position (in electron volts) of the decom-

posed functions and the relative peak area (in mole percent) are shown in Table II. The decomposed components are assigned to CH group (at 285.0 eV),

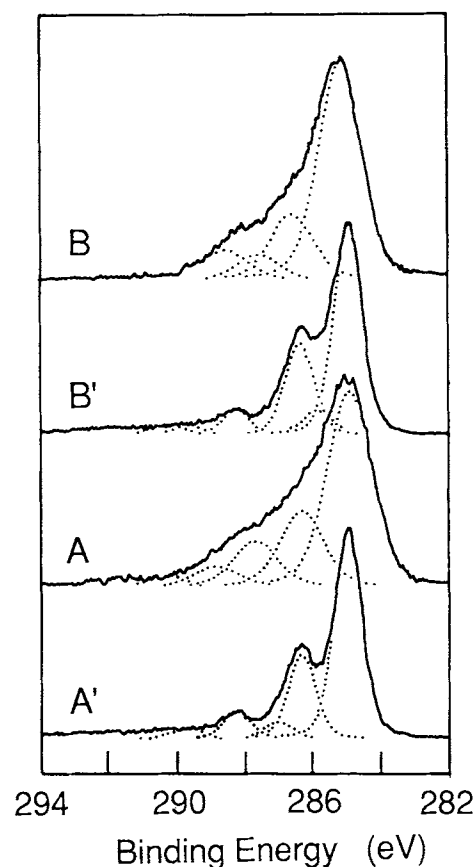


Figure 6 XPS (C_{1s}) spectra of CuPc-CH₂OH plasma-polymerized film (A), CuPc-CH₂OH vacuum-deposited film (A'), CuPc-CH₂N[C(O)]₂Ph plasma-polymerized film (B), and CuPc-CH₂N[C(O)]₂Ph vacuum-deposited film (B').

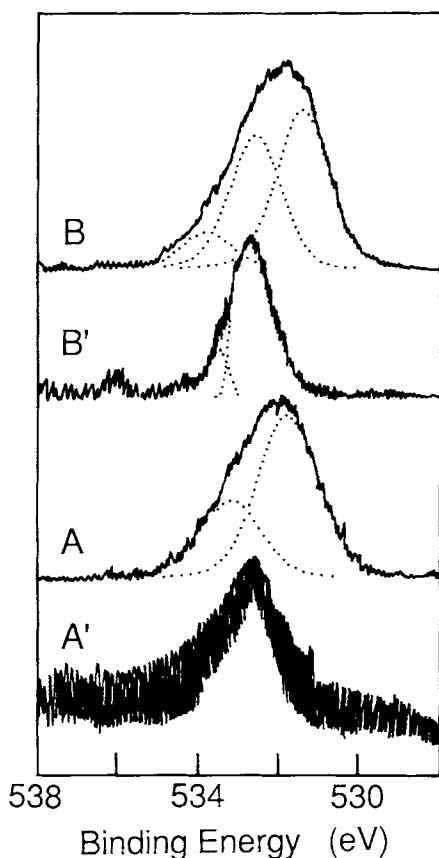


Figure 7 XPS (O_{1s}) spectra of CuPc-CH₂OH plasma-polymerized film (A), CuPc-CH₂OH vacuum-deposited film (A'), CuPc-CH₂N[C(O)]₂Ph plasma-polymerized film (B), and CuPc-CH₂N[C(O)]₂Ph vacuum-deposited film (B').

C—N group (at 285.9 eV), C=N and/or C—O group (286.4–286.5 eV), C=O group (at 287.1–287.7 eV), C(O)O and/or C(O)N group (at 288.3–288.9 eV), and π - π^* shake-up satellite (at 289.7–290.0 eV) in an increasing order of the binding energy.^{11–13} In the C_{1s} spectra of all films, a weak component due to π - π^* satellite can be observed, indicating that all plasma polymer films contain an extended π -electron system. The plasma polymer film of CuPc—CH₂OH, as shown in Table II, possesses four C_{1s} features except component 6. These are CH groups (component 1), C=N and/or C—O groups (component 3), C=O groups (component 4), and C(O)O and/or C(O)N groups (component 5). The C=O, C(O)O, and C(O)N groups are never contained in the starting compound of CuPc—CH₂OH, and are ones generated during the plasma polymerization process. In particular, the concentration of the C=O groups is higher than that of the C(O)O

and C(O)N groups. If the starting compound of CuPc—CH₂OH were plasma-polymerized without any degradation to form films, the CH groups and C=N and/or C—O groups should be estimated to be 76.5 and 29.4% of the total carbon atoms, respectively, from the chemical structure of CuPc—CH₂OH. The determined concentration of the CH groups in the plasma polymer of CuPc—CH₂OH is greatly lower than the estimation. This comparison indicates that the C=O formation in the plasma polymerization may occur at aromatic rings in phthalocyanine. The oxidation of aromatic rings is initiated not only by the plasma action but also by the thermal action because the vacuum deposition film of CuPc—CH₂OH also contains the C=O and C(O)O features in the C_{1s} spectra in Figure 6. The oxidation by the plasma action preponderates over that by the thermal action because of high O/C atomic ratio in the plasma polymer film.

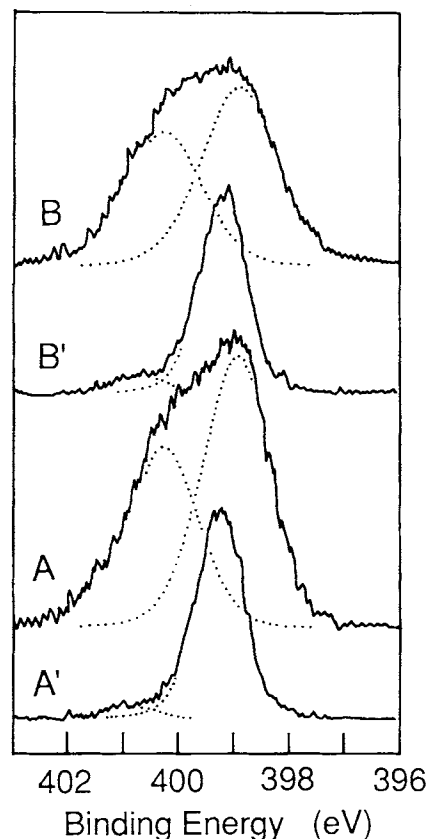


Figure 8 XPS (N_{1s}) spectra of CuPc-CH₂OH plasma-polymerized film (A), CuPc-CH₂OH vacuum-deposited film (A'), CuPc-CH₂N[C(O)]₂Ph plasma-polymerized film (B), and CuPc-CH₂N[C(O)]₂Ph vacuum-deposited film (B').

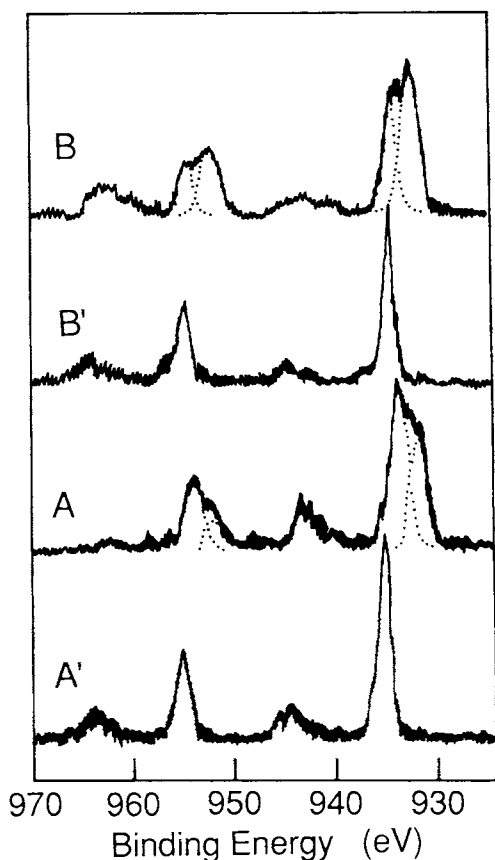


Figure 9 XPS (Cu_{2p}) spectra of CuPc- CH_2OH plasma-polymerized film (A), CuPc- CH_2OH vacuum-deposited film (A'), CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ plasma-polymerized film (B), and CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ vacuum-deposited film (B').

The plasma polymer film of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ shows a similar C_{1s} spectrum to that of CuPc- CH_2OH . The C_{1s} spectrum contains

five C_{1s} features, CH, C—O and/or C—N, C=O, C(O)O and/or C(O)N groups, and the π - π^* satellite. The oxidation is observed also in the plasma polymer film of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$, but the concentration of the oxidized residues, especially the C=O groups (7 mol %) in the plasma polymer film of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$, is lower than that in the plasma polymer film of CuPc- CH_2OH (14 mol %). The concentration of the CH groups (65 mol %) in the plasma polymer film of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ is higher than that in the film of CuPc- CH_2OH (58 mol %). From the viewpoint of the C_{1s} spectra, we can conclude that the plasma polymerization of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ rather than CuPc- CH_2OH deposits less oxidized films.

The O_{1s} core level spectra gave other information of the chemical composition, especially the oxidation state of the plasma polymer films. The observed O_{1s} spectra of the plasma polymer films of CuPc- CH_2OH and of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$, as shown Figure 7, are broad lines with a FWHM value of about 3 eV and their signal-noise ratio is poor. Especially, spectrum A' in Figure 7 is low signal intensity and noisy because of very low oxygen concentration in the film (as shown in Table I). The FWHM value (3 eV) of the plasma polymer films is greatly larger than that (1.3 eV) of the vacuum deposition film of CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ except the film of CuPc- CH_2OH . This broadening indicates that the plasma polymerization leads to complexity of the oxidation state. Although the decomposition of the O_{1s} spectra is difficult because of indistinctive spectra, we dared to decompose the O_{1s} spectra into two or three components. The result of the decomposition is shown in Figure 7 in dotted lines, and the peak position of the components and the relative peak area are tabulated in Table III. The decom-

Table II XPS (C_{1s}) Spectra of Plasma-Polymerized Films and Vacuum-Deposited Films from CuPc- CH_2OH and CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$

Copper Phthalocyanines	Method of Film Formation	C_{1s} Component ^a					
		Compt. 1	Compt. 2	Compt. 3	Compt. 4	Compt. 5	Compt. 6
CuPc- CH_2OH	Plasma polymerization	285.0 (58%)		286.4 (22%)	287.7 (14%)	288.9 (6%)	290.0
	Vacuum deposition	285.0 (62%)		286.4 (25%)	287.1 (5%)	288.3 (8%)	290.0
CuPc- $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$	Plasma polymerization	285.0 (65%)		286.5 (19%)	287.5 (7%)	288.4 (9%)	290.0
	Vacuum deposition	285.0 (60%)	285.9 (6%)	286.4 (27%)		288.3 (7%)	289.7

^a Binding energy in electron volts and relative concentration in mole percent.

Table III XPS (O_{1s}) Spectra of Plasma-Polymerized Films and Vacuum-Deposited Films from CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph

Copper Phthalocyanines	Method of Film Formation	O_{1s} Component ^a		
		Component 1	Component 2	Component 3
CuPc-CH ₂ OH	Plasma polymerization	531.8 (68%)		533.1 (32%)
	Vacuum deposition	Not decomposed because of poor <i>S/N</i> ratio		
CuPc-CH ₂ N[C(O)] ₂ Ph	Plasma polymerization	531.4 (49%)	532.6 (40%)	533.8 (11%)
	Vacuum deposition		532.4 (80%)	533.1 (20%)

^a Binding energy in electron volts and relative concentration in mole percent.

posed components of the oxygen features are assigned to C=O (component 1), C—O and/or C(O)N (component 2), and C(O)O groups (component 3) in an increasing order of the binding energy.¹¹ The result indicates there is a large difference between the plasma polymer films of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph. The plasma polymer film of CuPc—CH₂OH contains mainly C=O and C(O)O groups but no C—O group. This indicates that the hydroxyl substituent in CuPc—CH₂OH is completely oxidized to C=O and C(O)O groups. On the other hand, the plasma polymer film of CuPc—CH₂N[C(O)]₂Ph contains C=O, C(O)O, and C—O and/or C(O)N groups.

The N_{1s} core level spectra showed no difference between the plasma polymer films of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph, but distinguished between the plasma polymer films and the vacuum deposition films. The N_{1s} spectra are shown in Figure 8, and the result of the decompo-

sition is tabulated in Table IV. The N_{1s} spectra of the plasma polymer films of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph, as shown in Figure 8, distribute asymmetrically and broadly with a FWHM of more than 3 eV. These N_{1s} spectra were decomposed into two components whose peak positioned at 398.9 and 400.3 eV. While, the N_{1s} spectra of the vacuum deposition films distribute narrowly with a FWHM of 0.98–1.0 eV, and were decomposed into a large component at 399.2–399.3 eV and a small component at 400.7 eV.

Niwa et al.¹³ investigated effects of the copper chelation in phthalocyanine on the N_{1s} core level spectra. Their conclusion was that the copper chelation gave large effects on N_{1s} core level spectra. The pyrrole nitrogen atoms and aza nitrogen atoms in phthalocyanine appeared at a binding energy of 398.9 and 400.4 eV, respectively, but by the chelation with copper atoms, the pyrrole nitrogen atoms and aza nitrogen atoms became undiscriminated, and

Table IV XPS (N_{1s}) Spectra of Plasma-Polymerized Films and Vacuum-Deposited Films from CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph

Copper Phthalocyanines	Method of Film Formation	N_{1s} Component ^a	
		Component 1	Component 2
CuPc-CH ₂ OH	Plasma polymerization	398.9 (60%)	400.3 (40%)
	Vacuum deposition	399.3 (95%)	400.7 (5%)
CuPc-CH ₂ N[C(O)] ₂ Ph	Plasma polymerization	398.9 (57%)	400.3 (43%)
	Vacuum deposition	399.2 (92%)	400.7 (8%)

^a Binding energy in electron volts and relative concentration mole percent.

both of the nitrogen atoms appeared at 399.2 eV. The π - π^* shake-up satellite also was observed at a higher binding energy of 1.5 eV from the main peak. From Niwa's conclusion, components 1 and 2 decomposed from the N_{1s} spectra of the plasma polymer films can be assigned to pyrrole and aza nitrogen atoms, respectively, which are not chelated with copper atom. From this assignment we infer that all of the nitrogen-copper chelation in CuPcs were broken down by the plasma polymerization process, but the inference is not reasonable because characteristic electronic absorption, as shown in Figure 4, appear at 335, 630, and 690 nm. The plasma polymer films of CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph surely possess chelation. Therefore, we conclude that component 1 is a mixture of pyrrole and chelated nitrogen atoms. The conclusion is reasonable from the wide FWHM value of the component 1. The FWHM value is 1.7 eV for component 1 in the spectra *A* and *B*, and is 1.0 eV for the spectra *A'* and *B'*. Theoretically, component 1 should be decomposed further into two components due to pyrrole appearing at 398.9 eV and chelated nitrogen atoms at 399.2–399.3 eV, but the renewal decomposition of the N_{1s} spectra is impossible because the small difference (0.3–0.4 eV) between the chemical shift of pyrrole and chelated nitrogen atoms and the poor resolution of the N_{1s} spectra. Therefore, we perceive that component 1 is a mixture of pyrrole and chelated nitrogen atoms and component 2 is aza nitrogen atoms in phthalocyanines. The relative concentration of aza nitrogen atoms (component 2) means the relative concentration of nonchelated aza nitrogen in the plasma polymer films. The relative concentration of component 1 and 2 is 60 and 40 mol % for the plasma polymer films of CuPc-CH₂OH, respectively, and 57

and 43 mol % for the plasma polymer film of CuPc-CH₂N[C(O)]₂Ph, respectively. In conclusion, the plasma polymerization leads to degradation of chelation in CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph, and that the degradation reaches about 40%.

The Cu_{2p_{3/2}} core level spectra give us insight into the degradation of the chelation, too. Figure 9 shows Cu_{2p_{3/2}} and Cu_{2p_{1/2}} core level spectra of the plasma polymer films of CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph as well as the vacuum deposition films. In all four spectra, there are two main peaks (at about 935 eV for Cu_{2p_{3/2}} and at about 955 eV for Cu_{2p_{1/2}}) and two broad satellite peaks (at about 942–947 eV for Cu_{2p_{3/2}} and at about 962–967 eV for Cu_{2p_{1/2}}). The satellite peaks of Cu_{2p} core level is explained from the aspect of paramagnetic species in Cu atoms. Cu(II) atom has a paramagnetic 3d structure, while Cu(I) atom has a filled 3d orbital. As a result, Cu(II) atom has a satellite peak, and Cu(I) atom has no satellite peak.^{14–18} From this viewpoint, we conclude that the Cu atoms in the plasma polymer films as well as in the vacuum deposition films are in a state of Cu(II).

The Cu_{2p_{3/2}} core level spectra of the plasma polymer films, as shown in Figure 9, are composite distribution of more than two components, because of the appearance of a shoulder at near 933 eV; while the Cu_{2p_{3/2}} spectra of the vacuum deposition films are composed of a single component, because of symmetric and narrow distribution with a small FWHM of 1.1–1.2 eV. The Cu_{2p_{3/2}} spectra of the plasma polymer films were decomposed into two components, and the result of the decomposition is shown in Figure 9 in dotted lines and is summarized in Table V. The decomposed components appear at 932.7–932.8 eV and at 934.5–934.7 eV, which are

Table V XPS (Cu_{2p_{3/2}}) Spectra of Plasma-Polymerized Films and Vacuum-Deposited Films from CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph

Copper Phthalocyanines	Method of Film Formation	Cu _{2p_{3/2}} Component ^a		
		Component 1	Component 2	Satellite
CuPc-CH ₂ OH	Plasma polymerization	932.8 (35%)	934.5 (65%)	Yes
	Vacuum deposition		935.4 (100%)	Yes
CuPc-CH ₂ N[C(O)] ₂ Ph	Plasma polymerization	932.7 (51%)	934.7 (49%)	Yes
	Vacuum deposition		935.3 (100%)	Yes

^a Binding energy in electron volts and relative concentration in mole percent.

assigned to CuO and the chelated Cu atoms, respectively.¹⁴⁻¹⁸ The concentration of CuO in the plasma polymer films reaches 35–51% of the total Cu atoms. On the other hand, the vacuum deposition films show a simple $\text{Cu}_{2p_{3/2}}$ spectra at 935.3–935.4 eV which are assigned to the chelated Cu atoms. From results of the $\text{Cu}_{2p_{3/2}}$ spectra, we conclude that the plasma polymerization leads to degradation of the chelation structure between copper atom and nitrogen residues. The degradation reaches 35–51% of the total chelation. The Cu atoms liberated from the chelation are in the state of CuO in the plasma polymer films.

The degradation of the chelation occurring in the plasma polymerization, as described in a previous paragraph, is 40–43% from the estimation of the N_{1s} spectra, and that is 35–51% from the estimation of $\text{Cu}_{2p_{3/2}}$ spectra. Two estimations do not coincide exactly on the degradation of the chelation. The discordance is an inevitable result because of indefinite decomposition process of the N_{1s} and $\text{Cu}_{2p_{3/2}}$ spectra. In spite of the discordance, it is clear that the degradation (40% from estimation of N_{1s} spectra and 35% from the estimation of $\text{Cu}_{2p_{3/2}}$ spectra) in the plasma polymerization of $\text{CuPc}-\text{CH}_2\text{OH}$ is lower than that (43% from estimation of N_{1s} spectra and 51% from the estimation of $\text{Cu}_{2p_{3/2}}$ spectra) in the plasma polymerization of $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$. Therefore, the CH_2OH substituent shows more effective protection from the degradation of the chelation by plasma actions than the $\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ substituent.

In conclusion, we summarize the chemical composition of the plasma polymer films of $\text{CuPc}-\text{CH}_2\text{OH}$ and $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$.

1. The plasma polymers contain the extended π -electron system. Carbonyl and carboxyl groups are formed simultaneously with the plasma polymerization.
2. A part of the chelation with copper and nitrogen atoms is degraded in the plasma polymerization process. The degradation reaches 40–43% from the estimation of the N_{1s} spectra, and that is 35–51% from the estimation of $\text{Cu}_{2p_{3/2}}$ spectra.
3. The Cu atoms liberated from the chelation exist as CuO in the plasma polymer films.

NO_2 Sensitivity of Plasma Polymer Films of $\text{CuPc}-\text{CH}_2\text{OH}$ and $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$

The plasma polymer films of $\text{CuPc}-\text{CH}_2\text{OH}$ and $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ were not electrically con-

ductive, and the apparent activation energy for the dark electrical conduction, which was estimated from the Arrhenius plot, was 1.30 eV for the plasma polymer film prepared from $\text{CuPc}-\text{CH}_2\text{OH}$ and 1.37 eV for the plasma polymer from $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$. The estimation from the absorption position of the electronic spectra in Figure 4 (688 nm for the plasma polymer film prepared from $\text{CuPc}-\text{CH}_2\text{OH}$ and 690 nm for the plasma polymer from $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$) is expected to be 1.80 eV for the band gap. The activation energy estimated from the two plasma polymer films is larger than that of the crystalline copper phthalocyanine: The activation energy for the dark conductivity is 0.70 eV for the α -phase copper phthalocyanine in air and 1.0–1.1 eV for the β -phase copper phthalocyanine.¹⁹ These comparisons show that the plasma polymer film is less conductive than the crystalline copper phthalocyanine but is comparable to poly(*trans*-acetylene) (a band gap of 1.5 eV), which possesses the extended π -electron system of $-\text{CH}=\text{CH}-$ repeating unit.²⁰

The plasma polymer films of $\text{CuPc}-\text{CH}_2\text{OH}$ and $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ (200 nm in thickness) were deposited on the quartz glass plate and then on the surface of the films, the Au comb electrode in Figure 3 was vacuum-deposited. In this study we made a gas sensor device for the evaluation of gas sensitivity. The gas sensor device was exposed to eight gas atmospheres— NO_2 , NO, CO_2 , CO, H_2 , N_2 , O_2 , and C_3H_8 —and changes in the dark dc electric resistance of the sensor device before and after the exposure to the eight gas atmospheres were measured. The gas sensitivity was estimated from Eq. (1). The sensor device, when exposed to the atmosphere of the seven gasses (except NO_2) at a gas concentration of 100 ppm, showed somewhat an increase in the dc electrical resistance but the increase was not large. (The sensitivity was in the range of 1.1–1.9.) However, the exposure to the NO_2 atmosphere at a gas concentration of 100 ppm led to large increases in the electrical resistance. Table VI shows the NO_2 sensitivity (at 100 ppm NO_2 concentration) as a function of the temperature of the sensor surface. Both plasma polymer films, as shown in Table VI, show a large sensitivity to NO_2 (3.6–28.3), although the NO_2 sensitivity decreases with increasing temperature of the sensor surface. This indicates that the plasma polymer films of $\text{CuPc}-\text{CH}_2\text{OH}$ and $\text{CuPc}-\text{CH}_2\text{N}[\text{C}(\text{O})]_2\text{Ph}$ possess good selectivity with regard to NO_2 molecules.

To inspect the capability of the plasma polymer films to detect NO_2 molecules, the quantitative relationship, the response time, and the reversibility

Table VI NO₂ Gas Sensitivity of Plasma Polymer Films of CuPc-CH₂OH and CuPc-CH₂N[C(O)]₂Ph

Sensing Temperature (°C)	NO ₂ Sensitivity (R_{NO_2}/R_{air})	
	Plasma Polymer Films of CuPc-CH ₂ OH	Plasma Polymer Films of CuPc-CH ₂ N[C(O)] ₂ Ph
150	22.3	28.3
200	8.54	9.06
250	4.71	6.11
300	3.60	5.33

were investigated. Figure 10 shows a relationship between the sensitivity and the NO₂ concentration. The plasma polymer films prepared from CuPc-CH₂OH were used for the inspection, and the temperature of the sensor surface was 150°C. The NO₂ sensitivity, as shown in Figure 10, shows two linear relationships with the logarithm of the NO₂ concentration in the range of 5 to 50 ppm and of 50 to 1000 ppm. Therefore, the quantitative determination of the NO₂ molecules is possible in the low NO₂ concentration range of 5 to 50 ppm and high NO₂ concentration range of 50 to 1000 ppm. This indicates that there are two adsorption modes of NO₂ molecules at the surface of the plasma polymer films prepared from CuPc-CH₂OH. Why a

different adsorption mode operates in the low and high NO₂ concentration ranges is an interesting subject from the viewpoint of surface science, but we do not deal with it in this study. We direct our attention to the sensitivity in the high NO₂ concentration range, because of the high sensitivity and the wide range of determinable NO₂ concentration. Figure 11 shows the time dependence of the NO₂ sensitivity after the injection of NO₂ molecules and after sweeping out NO₂ molecules. The sensor device used for the inspection of the reversibility was the same as used for the inspection of the quantitative determination, but the temperature of the sensor surface was changed from 150 to 200°C. The sensitivity, as shown in Figure 11, increases rapidly

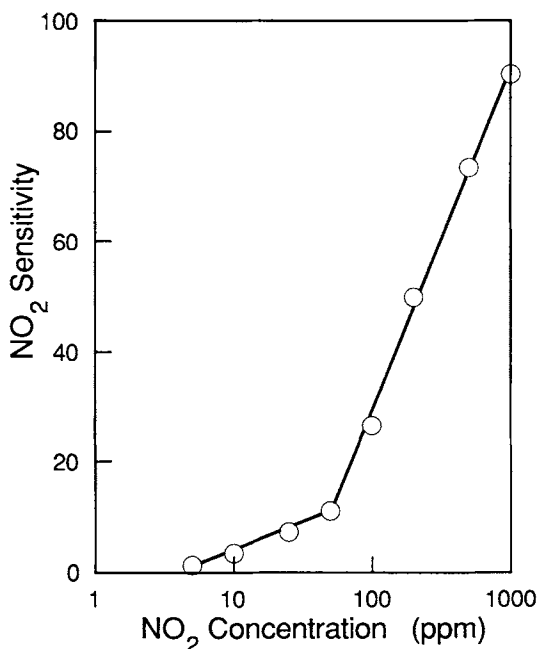


Figure 10 Relationship between NO₂ sensitivity and NO₂ concentration.

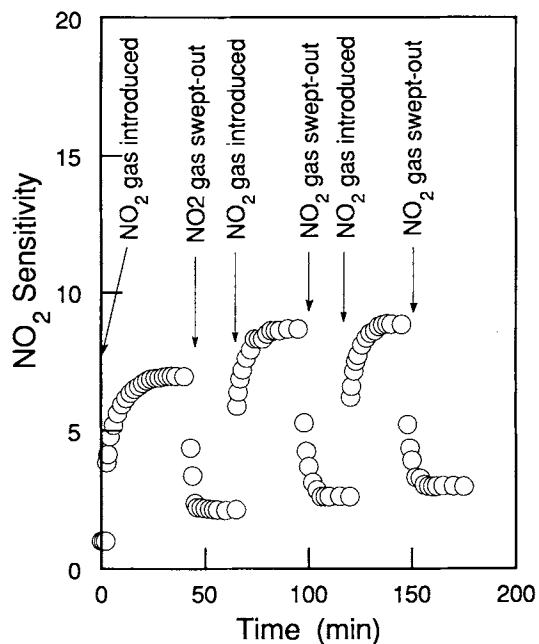


Figure 11 Time dependence of NO₂ sensitivity after NO₂ injection and after NO₂ sweeping-out.

within 5 min after the introduction of NO₂ molecule (the NO₂ concentration of 100 ppm) into the stainless steel vessel, and the gradual increase continues until 15 min after the introduction, and afterward, the NO₂ sensitivity becomes almost constant. When NO₂ molecules are swept out from the stainless steel vessel, the sensitivity decreases at once and comes back to the original level within 2 min. Except the first run, the reversibility of the NO₂ sensitivity, as shown in Figure 11, is good. Why the NO₂ sensitivity in the first run is lower than that in other runs is not yet clear.

Consequently, the plasma polymer films of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph possess good sensitivity to NO₂ molecules. With regard to the sensitivity, the selectivity, the response time, and the reversibility, the plasma polymer films are applicable materials to the NO₂ sensor device. However, prior to the application of the plasma polymer films to NO₂ sensor device, the stability and durability of the plasma polymer film and the sensitivity should be checked in comparison with those of the vacuum-deposited CuPc films. These factors are related to oxidative thermal degradation as well as the phase transition of the CuPc crystal. These will be investigated in the near future.

CONCLUSION

Four copper phthalocyanines without substituent (CuPc) and with chlorine (CuPc—Cl), hydroxymethyl (CuPc—CH₂OH), and phthalimidomethyl substituents (CuPc—CH₂N[C(O)]₂Ph) were plasma-polymerized to obtain amorphous and thin films having the extended π -electron system. The chemical composition of the plasma polymer films were discussed from the data of the electronic spectra, IR spectra, and XPS spectra. The application of the plasma polymer films was discussed with regard to the sensitivity, the selectivity, the response time, and the reversibility. The results are summarized as follows:

1. Plasma polymerization of CuPc, CuPc—Cl, CuPc—CH₂OH, and CuPc—CH₂OH gives amorphous and thin films.
2. A part of the extended π -electron system in copper phthalocyanines is broken down accompanying the plasma polymer formation.
3. The CH₂OH and CuPc—CH₂N[C(O)]₂Ph substituents contribute to minimizing the degradation of the extended π -electron system in the plasma polymerization process.

The degradation reaches 35–40% for the plasma polymerization of CuPc—CH₂OH and 43–51% for the plasma polymerization of CuPc—CH₂OH.

4. The Cu atoms liberated from the chelation exist as CuO in the plasma polymers.
5. The plasma polymer films of CuPc—CH₂OH and CuPc—CH₂N[C(O)]₂Ph show good sensitivity to NO₂ molecules. With regard to the sensitivity, the selectivity, the response time, and the reversibility, the plasma polymer films are applicable materials to the NO₂ sensor device.

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