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Plasma polymer thin films of zinc phthalocyanies for NO_2 gas sensor device

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Zinc phthalocyanines without substituent (ZnPc) and with hydroxymethyl (ZnOc-CH_2OH), and phthalimidomethyl substituents (ZnPc-$CH_2N[C(O)]_2Ph$) were plasma-polymerized and the application of the deposited plasma polymer films for NO_2 gas sensor device has been discussed. The chemical composition of the deposited plasma polymer films was analyzed by electronic spectroscopy and XPS. The electronic and XPS spectra showed that the plasma polymer films possessed the π-extended electron system and the zinc chelation, although a part of them was degraded by plasma. From the stability of the zinc chelation, the plasma polymer film of ZnPc was chosen as a suitable material for NO_2 gas sensor device. The NO_2 gas sensor device composing of the ZnPc plasma polymer film showed a sensitivity toward NO_2 gas in ranges of 100 to 1000 ppm.

Introduction

Metal phthalocyanine possesses functional groups such as an extended π-electron system and a metal chelation. The extended π-electron system in metal phthalocyanine can interact with electron acceptors, and makes a charge-transfer complex. On the other hand, metal atom in the metal phthalocyanine also can interact with electron donors, and makes a complex. As a result, these interactions lead to a large changes of electric conductivity. This is an essential process of sensing gas molecules. Many investigators have applied this process to gas sensor devices for NO_2, NH_3, and CO gas molecules (1, 2). This study is the thin film formation of metal phthalocyanine for NO_2 gas sensor device by plasma polymerization. Zinc phthalocyanine was used as a starting material for the plasma polymerization, because zinc phthalocyanine shows strong interaction with NO_2 molecules (3).

Plasma polymerization is a good manner to make thin films directly from monomers without fabrication process. In the plasma polymerization, two essential processes, polymerization from monomers and polymer deposition in a thin-film form, occur simultaneously (4). The polymerization is initiated by interactions between the monomer and electrons present in plasma. The interaction leads to transformation of the monomers into polymerizable products, in many cases radicals, and the polymerizable product is recombined stepwise with others to grow into a larger molecule. Finally, polymer molecules are formed by repeating such stepwise reactions. In addition to the polymerization, the interaction between the monomer and the electrons leads to degradation of the monomer. The degradation means split off some groups from the monomer. The degradation is an undesirable reaction for the formation of tailor-made plasma polymers. If the degradation rather than the polymerization occurs predominantly, functional groups will be split off from the monomer, and plasma polymers without functional groups will be deposited. Therefore, it is an important subject how to minimize the degradation of the monomer by plasma in order to obtain plasma polymer films with functional groups. In this study, the plasma polymer films of zinc phthalocyanines have been analyzed by electronic spectroscopy and

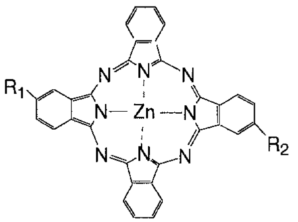
XPS, and whether the plasma polymer films are usable as a raw material for NO_2 gas sensor device or not is discussed from the viewpoint of the chemical composition.

Experimental

Plasma polymerization

Three zinc phthalocyanines without substituent and with hydroxymethyl, CH_2OH, and phthalimidomethyl substituents, $CH_2N[C(O)]_2Ph$, were kindly provided from Sanyo Color Workers, Ltd., and were used as starting materials for the plasma polymerization The chemical structure of the derivatives and the abbreviation used in this study are represented in Figure 1.

The reaction chamber used in this study for plasma polymerization of the zinc phthalocyanines was the same as reported elsewhere (5). Zinc phthalocyanines were placed at the bottom of a quartz furnace. The reaction chamber was evacuated to approximately 1.3 x 10^{-3} Pa, and a substrate stage for plasma polymer deposition was heated at 60°C. Afterward, the surface of electrodes and that of the substrate stage were exposed to argon plasma for 15 min to eliminate water molecules adsorbed at their surfaces. Finally, the zinc phthalocyanines were sublimated from the furnace at 330°C, the reaction chamber was adjusted at a pressure of 1.3 x 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 power of 25 W (13.56 MHz frequency). The plasma polymer deposition rate was monitored with a thickness monitor (Ulvac, model CRTM-5) during the plasma polymerization.



Chemical structure of zinc phthalocyanines

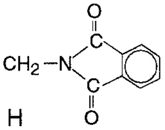
R_1 and R_2 substituents	Abbreviation
$R_1 = R_2 = H$	ZnPc
$R_1 = R_2 = CH_2OH$	ZnPc-CH_2OH
R_1 =  $R_2 = H$	ZnPc-$CH_2N[C(O)]_2Ph$

Figure 1 Chemical structure of zinc phthalocyanines and abbreviation

Electronic and XPS spectra of plasma polymer films

Electronic spectra of the deposited plasma polymer films 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.

XPS spectra of the plasma polymer films were obtained on an Ulvac-Phi spectrometer 5500 using a non-monochromatic MgKα photon source. The anode voltage was 15 kV, the power 300 W, and the background pressure of the analytical chamber 4.7 x 10^{-7} Pa. The sampling size was 7 mm in diameter, and the take-off angle of photoelectrons was 45° with respect to the sample surface. Fifteen scans were recorded for each sample. The smoothing procedure of the observed spectra was not done. The spectra were referenced to the 285.0 eV carbon 1s core level observed for hydrocarbon to eliminate the charge effect. The observed spectra were deconvoluted by fitting a Gaussian-Lorentzian mixture function (the mixture ratio was 75 : 25) to the observed curve using a nonlinear, least-squares curve fitting program supplied by Ulvac.

Gas sensor device and gas sensitivity measurement

Gas sensor devices were in a sandwich structure of three components; quartz glass, plasma polymer film (200 nm in thickness), and Au comb electrodes (100 nm in thickness). A 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. Detail of the gas sensor device configuration was reported elsewhere (5).

The NO_2 gas sensitivity was evaluated from the ratio of electric resistance between the comb electrodes in the NO_2 gas atmosphere from 100 to 1000 ppm concentration and that in air. The NO_2 sensitivity is defined by the following equation.

$$NO_2 \text{ sensitivity} = \frac{R_{NO_2}}{R_{air}} \qquad (1)$$

Results and discussion

Electronic spectra for plasma polymer films of zinc phthalocyanines

Plasma polymerization of ZnPc, ZnPc-CH_2OH, and ZnPc-$CH_2N[C(O)]_2Ph$ deposited transparent and blue thin films. Figure 2 compares electronic spectra among the three plasma polymer films and the vacuum-evaporated ZnPc film. All plasma polymer films show characteristic three absorption peaks related to the π-π* transition at 350, 615, and 650 nm. These π-π* transition peaks correspond to those for the vacuum-evaporated ZnPc. This comparison shows that all three plasma polymer films contain the extended π-electron system. However, the absorption peaks of the plasma polymer films are not so sharp as those of the vacuum-evaporated ZnPc film. The peak position of the π-π* transition and its width depend on not only the chemical structure but also the aggregation state, for example crystalline or non-crystalline (6). With respect to broadening the absorption peaks due to the π-π* transition for the plasma polymer films, there are two possible factors, degradation of the extended π-electron system by the plasma and a mixture of different aggregation states. We will discuss in a next section how much the extended π-electron system was injured by the plasma, but have no way how different the plasma polymer molecules aggregate themselves, although we know from x ray diffraction pattern that the plasma polymer films are amorphous, and the vacuum-evaporated ZnPc film is crystalline.

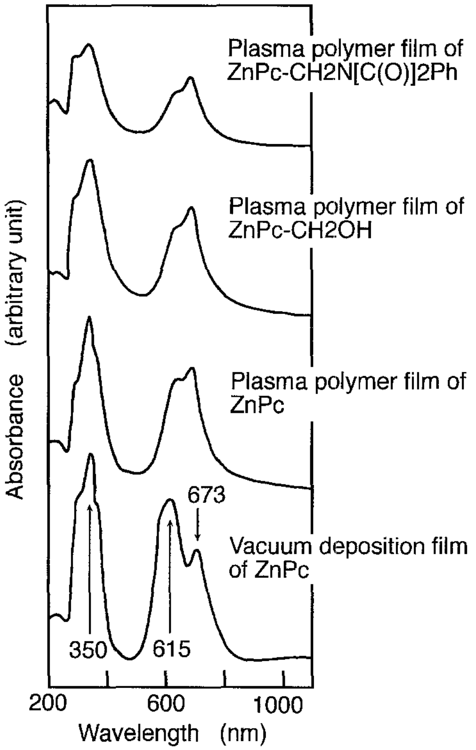


Figure 2 Electronic spectra for plasma polymer films of zinc phthalocyanines

Chemical composition of plasma polymer films of zinc phthalocyanines

The zinc chelation in the plasma polymer films was inquired from N_{1s} core level spectra and the injury by the plasma was evaluated. The N_{1s} core level spectra of the plasma polymer films in Figure 3 are decomposed into two components at 398.9 - 399.2 eV (component N1) and at 400.2 - 400.4 eV (component N2). The component N1 at 398.9 - 399.2 eV is assigned to nitrogen atoms chelated with zinc atom and not-chelated aza nitrogen atoms, and the component N2 at 400.2 - 400.4 eV is assigned to not-chelated pyrrole nitrogen atoms (7). Phthalocyanine has two types of nitrogen atoms, aza and pyrrole nitrogens, of which the N_{1s} photoelectrons appear at 398.2 and 400.2 eV, respectively (7). Metal chelation leads to simplifying the N_{1s} spectra with a single peak at 398.9 eV (7). The presence of the component N2 indicates that a part of the zinc chelation was degraded by the plasma. The relative concentration of the component N2 was calculated from the relative peak area of the N_{1s} core level spectra, and its value was 17, 21, and 28% of the total nitrogen atoms for the plasma polymers of ZnPc, $ZnPc-CH_2OH$, and $ZnPc-CH_2N[C(O)]_2Ph$, respectively (Table 1).

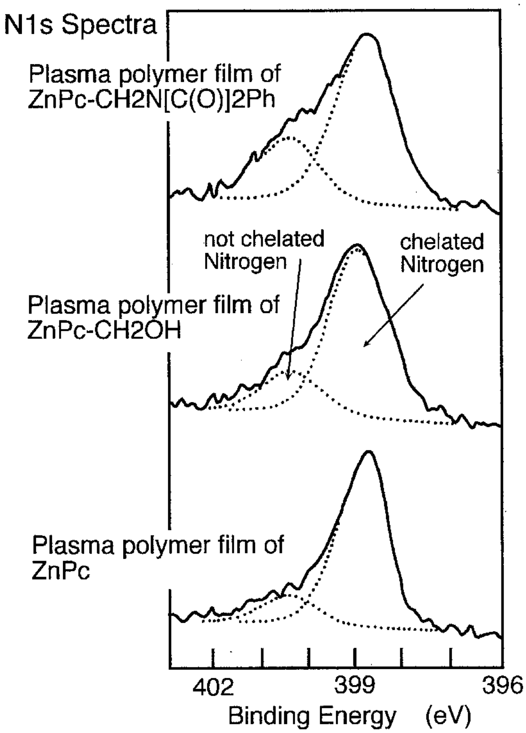


Figure 3 N_{1s} spectra for plasma polymer films of zinc phthalocyanines

Table 1 N_{1s} components of the plasma polymer films of ZnPc, $ZnPc-CH_2OH$, and $ZnPc-CH_2N[C(O)]_2Ph$

Plasma polymer	Relative concentration (%)	
	Component N1	Component N2
ZnPc	83	17
$ZnPc-CH_2OH$	79	21
$ZnPc-CH_2N[C(O)]_2Ph$	72	28

Components N1 and N2 are chelated and not-chelated nitrogen atoms, respectively.

From this estimation, we evaluate how much the zinc chelation still remain in the plasma polymer films even when these monomers are plasma-polymerized. The concentration of still remaining zinc chelation is 66% for ZnPc, 58% for $ZnPc-CH_2OH$, and 46% for $ZnPc-CH_2N[C(O)]_2Ph$. Therefore, the plasma polymer film of ZnPc possess the most chelation concentration of the three plasma polymer films. The CH_2OH and $CH_2N[C(O)]_2Ph$ substituents have no effect on minimizing the degradation of the zinc chelation by the plasma.

C_{1s} core level spectra gave us other information on the chemical composition of the plasma polymer films. The plasma polymer films of ZnPc, ZnPc-CH_2OH and ZnPc-$CH_2N[C(O)]_2Ph$ show similar C_{1s} spectra in Figure 4. Their C_{1s} spectra are decomposed into four components, which are assigned to CH group at 285.0 eV (component C1), a mixture of C=N and C-O group at 286.2 - 286.4 eV (component C2), a mixture of C(O)O and C(O)N group at 287.9 - 288.3 eV (component C3), and π-π* shake-up satellite at 289.7 - 290.1 eV (component C4) (8).

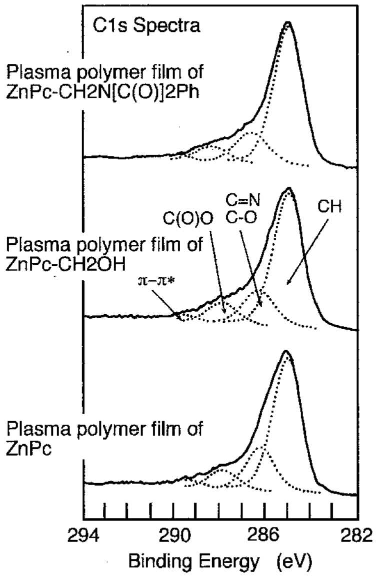


Figure 4 C_{1s} spectra for plasma polymer films of zinc phthalocyanines

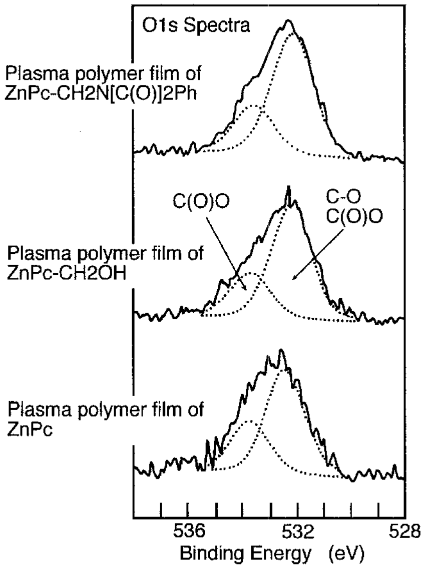


Figure 5 O_{1s} spectra for plasma polymer films of zinc phthalocyanines

Further, O_{1s} core level spectra give details of the oxygen functionalities in the plasma polymer films. The O_{1s} spectra in Figure 5 are decomposed into two components at 532.2 - 532.4 eV (component O1) and 533.6 - 533.8 eV (component O2), which are assigned to a mixture of C-O and C(O)$\underline{\text{O}}$ groups, and C($\underline{\text{O}}$)O groups, respectively (8). The underlined oxygen atom means the objective of the assignment. Figure 5 negatives the presence of C(O)N groups in the plasma polymer films, because the oxygen atom due to C(O)N groups will appear at lower binding energy near 531 eV. This indicates that C(O)N groups were completely split off from ZnPc-$CH_2N[C(O)]_2Ph$, when plasma-polymerized, to formed the plasma polymer film with no C(O)N group. From a combination of the C_{1s} and O_{1s} spectra, we conclude that C-O and C(O)O groups are formed as oxygen functionalities in the plasma polymer films by the plasma polymerization.

Table 2 and 3 show the relative concentration of each component composing the C_{1s} and O_{1s} spectra, respectively. These estimation was carried out from the peak area in these spectra. These tables indicate that there is not a large difference in the relative concentration of the oxygen functionalities among the three plasma polymer films. We cannot explain when and how such oxygen functionalities were formed, and what a source of oxygen used for the oxidation is. The formation of such oxygen functionalities may be due to a post-reaction after finishing the plasma polymerization rather than a coincident reaction with the polymerization. We believe that radicals remaining in the plasma polymer films would react with air to form such oxygen functionalities when the films were taken out from the plasma reactor after finishing the plasma polymerization.

Table 2 C_{1s} components of the plasma polymer films of ZnPc, ZnPc-CH_2OH, and ZnPc-$CH_2N[C(O)]_2Ph$

Plasma polymer	Relative concentration (%)		
	Component C1	Component C2	Component C3
ZnPc	68	22	10
ZnPc-CH_2OH	69	20	11
ZnPc-$CH_2N[C(O)]_2Ph$	72	19	9

Compnents C1, C2, and C3 are CH group, a mixture of C=N and C-O groups, and C(O)O groups, respectively.

Table 3 O_{1s} components of the plasma polymer films of ZnPc, ZnPc-CH_2OH, and ZnPc-$CH_2N[C(O)]_2Ph$

Plasma polymer	Relative concentration (%)	
	Component O1	Component O2
ZnPc	66	34
ZnPc-CH_2OH	71	29
ZnPc-$CH_2N[C(O)]_2Ph$	71	29

Component O1 and O2 are a mixture of C-O and C(O)$\underline{O}$ groups, and C($\underline{O}$)O group, respectively. The underlined oxygen atom is the objective of assignement.

$Zn_{2p3/2}$ spectra for the plasma polymer films also were analyzed, but results were not effective in revealing details of the films. The chemical shift of the $Zn_{2p3/2}$ core level by different electron energy state is very small: for example, when metal zinc is oxidized into zinc oxide, the binding energy of $Zn_{2p3/2}$ increases from 1021.7 eV for metal zinc to 1022.0 eV for zinc oxide, and the chemical shift is only 0.3 eV (9). Such small chemical shift is impossible to reveal in what state the zinc atoms in the plasma polymer films is present.

In conclusion, the discussion from XPS analysis shows that the plasma polymer films possess the extended π-electron system and zinc chelation. A part of the extended π-electron system and the zinc chelation is degraded by plasma. The stability of the zinc chelation is in the order of ZnPc > ZnPc-CH_2OH > ZnPc-$CH_2N[C(O)]_2Ph$. Oxidation also occurs during the plasma polymerization to form C-O and C(O)O groups in the plasma polymer films. Therefore, from the stability of the zinc chelation, the plasma polymer film of ZnPc is expected to be a sensitive material toward NO_2 gas.

NO_2 sensitivity of plasma polymer films of zinc phthalocyanine

The plasma polymer film of ZnPc, when exposed to the NO_2 gas, showed some increases in the DC electrical resistance. The NO_2 sensitivity is plotted as a function of the NO_2 concentration in Figure 6. The sensor device temperature was 200°C. The NO_2 sensitivity, as shown in Figure 6, increases linearly with increasing logarithms of the NO_2 concentration in ranges of 100 to 1000 ppm. This relationship shows that the plasma polymer film of ZnPc is an available material for a NO_2 gas sensor device. However, in prior to practical uses, the plasma polymer film of ZnPc should be inspected from viewpoints of the NO_2 response time, reproducibility, and durability.

Consequently, the plasma polymer films formed from ZnPc, ZnPc-CH_2OH, and ZnPc-$CH_2N[C(O)]_2Ph$ possessed the π-extended electron system and the zinc chelation, although a part of them was degraded by the plasma polymerization. From the stability of the zinc chelation, the plasma polymer film of ZnPc was chosen as a suitable material for NO_2 gas sensor device. The plasma polymer film of ZnPc was sensitive toward NO_2 gas. The sensitivity increased linearly with increasing logarithm of the NO_2 concentration in ranges of 100 to 1000 ppm.

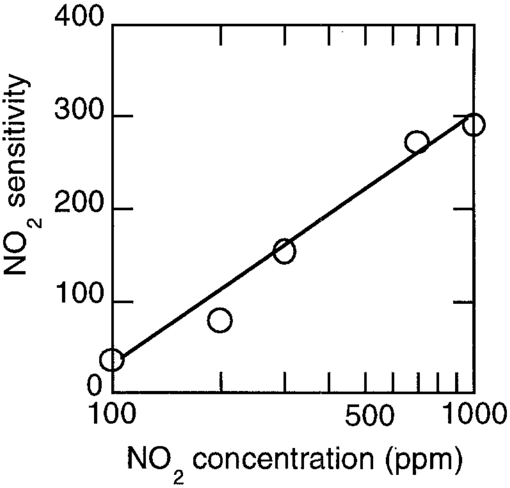


Figure 6 NO_2 sensitivity of plasma polymer film of zinc phthalocyanine as a function of NO_2 concentration

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