Effect of Adsorbed Oxidative Gases on Electrical Properties of Evaporated Films of Phthalocyanines

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The electrical conductivities of phthalocyanines (H_2Pc , $CuPc$, $FePc$ and $CoPc$) increased with the adsorption of NO_2 , NO and O_2 . In the thermal desorption spectra of the three gases between room temperature and $300^\circ C$ the first peak appeared in the temperature range $50\sim 100^\circ C$ for any gas-phthalocyanine system, whereas the second peak in the range $100\sim 250^\circ C$ were found only on $CoPc$ and $FePc$ on which NO_2 and NO had been adsorbed. Although the second peaks involved for far larger amounts of adsorbed gases, the electrical conductivities were found to be mostly affected by the gas adsorption responsible for the first peaks. The carrier (hole) may be produced by the interaction of ligand parts of phthalocyanine with NO_x and O_2 .

1 Introduction

It is well-known that ambient gases exert influence on the semiconductive properties of a number of organic compounds. The electrical conductivities of β -carotene¹⁾, metal-free phthalocyanine (H_2Pc)²⁾ and anthracene³⁾, for example, increase with the adsorption of electron acceptor type gases. Because of such gas-sensitive properties, phthalocyanines are being received interest as sensing material for detecting ambient gases^{4,5)}. We have reported^{6,7)} that some phthalocyanines are very sensitive to oxidative gases such as O_2 , NO and NO_2 . Despite extensive investigations published to date, however, the nature of gas adsorption on phthalocyanines have not been fully understood.

Metal phthalocyanine molecules have two possible sites for gas adsorption, *i. e.*, the central metal ions and the ligand π -electron systems. It has not been known on which sites gas molecules are actually adsorbed. It seems that the chemical properties of the two sites may change considerably depending on the central ions. Wolberg and Manassen⁸⁾ have reported that in the electrochemical oxidation of iron and cobalt phthalocyanine ($FePc$ and $CoPc$) the central metal ions are more easily oxidized than the

ligand π -electron system, while in the case of copper and hydrogen phthalocyanine ($CuPc$ and H_2Pc) the ligand part are oxidized. Such differences in chemical properties may be reflected on the adsorption properties of phthalocyanines toward oxidative gases.

In the present work, we have investigated the adsorption of NO_2 , NO and O_2 on four phthalocyanines (H_2Pc , $CuPc$, $CoPc$ and $FePc$) by means of thermal desorption technique and infrared spectroscopy. Efforts were concentrated especially on differentiating adsorption states and adsorption sites as well as on revealing how the respective adsorption states affect the electrical conductivities of phthalocyanine films.

2 Experimental

For electrical conductivity measurements, surface-type cells were prepared by vacuum evaporation⁹⁾. Each phthalocyanine (H_2Pc , $CuPc$, $CoPc$ or $FePc$) of α -form were deposited by vacuum evaporation from a Pyrex crucible onto a glass substrate ($1\times 1\text{cm}^2$). The film obtained was transformed into β -phthalocyanine by heating at $350^\circ C$ for 30 min under a nitrogen atmosphere. Then, two gold electrodes, separated by $200\ \mu\text{m}$ from each other, were deposited over the film. Electrical measurements were carried out with an electrometer (Takeda Riken, model TR 8651) and a d. c. power supply.

Thermal desorption spectra were obtained with β -form phthalocyanine powder (0.3 g) by means of a Pirani vacuum gauge (Nihonshinku, model GP-2 T) and/or a quadrupole mass spectrometer

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(Nihonshinku, model SM 800 A) which was connected to the sample tube through a capillary. After heat-treatment (150~250°C) under evacuation, the sample was exposed to O₂, NO or NO₂ (20~200 Torr) at room temperature. After evacuating to *ca.* 0.1 Torr or below, the sample was then heated up to 300°C at a constant rate under evacuation to record thermal desorption spectra. The gases used were of commercial origin (Takachiho); the purities of NO and NO₂ were 99.9% and 99.5%, respectively. Infrared spectra were recorded on a double beam spectrometer (JASCO model IR-G), by using β -form phthalocyanine films evaporated on KBr plates.

3 Results and Discussion

3.1 Thermal desorption spectra

Thermal desorption spectra for O₂, NO, and NO₂ were measured by using β -form phthalocyanines (H₂Pc, CuPc, CoPc and FePc). In each case, gas desorption went to completion below 300°C. The spectra, however, were found to change characteristically depending on the central metal ion of the phthalocyanines. With CoPc and FePc, the spectra for O₂ gave a single desorption peak which appeared in the range 50~100°C, whereas that of NO or NO₂ gave double peaks in the range 50~100°C and 100~250°C. In the latter case, desorption spectra were also recorded on a mass spectrometer to analyse desorbed gases. The partial pressures of NO₂ (*m/e* 46), N₂O (*m/e* 44), and NO (*m/e* 30) thus monitored are shown in Fig. 1^{*1}. Following NO adsorption, only NO was detected over the two desorption peaks. This means that NO is reversibly adsorbed. Following NO₂ adsorption, however, the situation was more complex. In addition to the desorption of NO₂ which took place in the ranges 50~100°C and 100~250°C. NO and N₂O were also found in the desorbed gas. The desorption of NO gave a chromatogram which was essentially the same as one obtained when NO was adsorbed. The N₂O desorption became significant above 150°C. These results show that a part of NO₂ undergo chemical changes to NO and N₂O. The IR

Fig. 1 Desorption spectra for NO_x adsorbed on CoPc

Heating rate: 10°C/min, Pressure of adsorption: 150 Torr (NO), 50 Torr (NO₂), (.....) *m/e* 30 for NO adsorption, (▲) *m/e* 46, (○) *m/e* 44, (●) *m/e* 30 for NO₂ adsorption

studies described later revealed that the adsorbed NO₂ on phthalocyanines exists as various types of adsorbates. It is considered that NO was formed from NO₂ in the course of adsorption while N₂O was formed by thermal decomposition of some adsorbates. Anyway, it is evident that NO and NO₂ are adsorbed on CoPc in at least two states, which are responsible for the occurrence of two desorption peaks.

In contrast, quite different chromatograms were obtained with CuPc and H₂Pc; desorption spectra after the adsorption of any of O₂, NO and NO₂ invariably showed only a single desorption peak in the temperature range 50~100°C. Desorption spectra for NO₂ adsorbed on H₂Pc is shown in Fig. 2^{*1}. NO₂ and N₂O were found in the desorbed gas with the ratio of desorbed N₂O to NO₂ being *ca.* 0.08 while that of desorbed NO and N₂O to NO₂ in CoPc *ca.* 0.3 and *ca.* 0.1, respectively.

Table 1 summarizes the temperature (*T_m*) at which the thermal desorption rate became maximum in each gas-phthalocyanine system. Obviously, the desorption in the lower temperature region (50~100°C, first peak) is common to all systems, while that in higher temperature region (100~250°C, second peak) is unique to the combinations between NO and NO₂ and CoPc and FePc. Such a difference among the

*¹ The relative sensitivity and the cracking pattern coefficient were used to estimate the partial pressure of each component.

Fig. 2 Desorption spectra for NO_2 adsorbed on H_2Pc

Heating rate: $10^\circ\text{C}/\text{min}$, Pressure of adsorption: 60 Torr, (Δ) m/e 46, ($\circ$) m/e 44

Table 1 Temperature of the peaks on desorption spectra

	$T_m/^\circ\text{C}$		
	O_2	NO	NO_2
H_2Pc	53	53	82
CuPc	63	77	57
CoPc	75	69 130	83 200
FePc	63	63 130	63 200

Heating rate: $10^\circ\text{C}/\text{min}$

gas-phthalocyanine systems seems to be related to the oxidation potential of the central metal ion. As stated earlier the central metal ions of FePc and CoPc are oxidized more easily than those of other phthalocyanines⁹⁾. We consider that the second peaks in FePc and CoPc are ascribed to the desorption of NO and NO_2 , which are adsorbed oxidatively on the central metal ions. Gas adsorption on the central metal ions have been proposed by Ercolani and Neri⁹⁾ and Mochida *et al.*¹⁰⁾ in NO -phthalocyanine systems. In the present study with FePc and CoPc , T_m of the second desorption peak for NO (130°C) is significantly lower than that for NO_2 (200°C). This suggests that NO_2 is bonded to the metal ions more strongly than NO , as expected from the order of electron affinity,

$\text{NO}_2 > \text{NO}$.

On the other hand, the first desorption peaks ($50\sim 100^\circ\text{C}$) may be ascribed to adsorbates bound to the ligand parts of phthalocyanines, not to metal ions. In order to confirm this assumption, the number of adsorbed molecules per unit weight of phthalocyanines N_{ad} for each gas-phthalocyanine system was estimated from an increase in pressure when the sample was heated up to 250°C in a closed system. The partial decomposition of NO_2 to NO and N_2O was neglected in this estimation. The results are shown in Table 2, where the value for N_2 under cor-

Table 2 The number of adsorbed molecules per unit weight of phthalocyanine (N_{ad})

	$(N_{\text{ad}}/\text{molecule}\cdot\text{g}^{-1})\times 10^{-9}$			
	N_2	O_2	NO	NO_2
H_2Pc	1	0.5	1	3
CuPc	3	1	2	6
CoPc	0.5	1	20	40
FePc	1	2	30	40

responding conditions is also included for comparison. As seen from this table, N_{ad} remains small for the cases where only the first desorption peaks appears, being comparable to that of N_2 adsorption. In contrast, N_{ad} is larger for NO and NO_2 on CoPc and FePc in which both desorptions participate; the molar ratio of the adsorbed $\text{NO}+\text{NO}_2$ to CoPc or FePc is estimated to be *ca.* $0.2\sim 0.3$ or 0.4 , respectively. In these systems, the desorption energies of O_2 , NO , and NO_2 obtained from thermal desorption spectra were much larger than the heats of condensation. Such an estimation leads to a picture that the adsorbates responsible for the first desorption peak are weakly bonded to the ligand parts of phthalocyanine, while those (NO and NO_2) responsible for the second peaks are bound to the central ions (Co and Fe).

3.2 IR spectra

The adsorption states of NO_2 on phthalocyanines were investigated by *IR* spectroscopy. As shown in Fig. 3, when NO_2 was adsorbed at room temperature on CoPc and CuPc , *IR* bands responsible to adsorbates appeared at; 1590, 1510, 1460, 1400, 1333*, 1265, 1050 and

Fig. 3 Infrared spectra for NO_2 adsorbed phthalocyanine
Pressure of adsorption: 50 Torr, (a) CuPc, (b) CoPc

1005 cm^{-1} for CoPc, 1460 and 1333 cm^{-1} *² for CuPc (the other bands observed in Fig. 3 are ascribed to the phthalocyanine substrate). With reference to the literature¹¹⁾, these bands could be assigned to various forms of adsorbates consisting of NO , NO_2 , and NO_3 groups as listed in Table 3. To know the thermal behavior of

Table 3 IR bands of phthalocyanine- NO_2

Wavenumber/ cm^{-1}	form
1590	M-NO nitrosyl and/or $\text{M}\langle\text{O}\rangle\text{NO}$ nitrato bidentate
1510, 1005	M-O- NO_2 nitrato monodentate
1460	M-O-NO nitrito
1400, 1050	NO_3^- free ion
1265	NO_2^- free ion

these adsorbates, the samples were heated stepwise up to 300°C at 50°C intervals *in vacuo*, with a heating period of 10 min at each temperature. The results are shown in Fig. 4. On CuPc, the bands at 1460 (nitrito) and 1333 cm^{-1} (nitro) disappeared below 100°C in agree-

*² The strong absorption band centered at 1333 cm^{-1} was also observed in phthalocyanine substrate.

Fig. 4 Variation of transmittance of each band in *vacuo* with heat-treatment temperature

Pressure of adsorption: 50 Torr, (--- $\blacktriangle$ ---) 1460 cm^{-1} , for CuPc, (— $\bullet$ —) 1510 cm^{-1} , (— $\blacktriangle$ —) 1460 cm^{-1} , (— $\triangle$ —) 1400 cm^{-1} , (— $\square$ —) 1265 cm^{-1} for CoPc

ment with the results of the thermal desorption experiments. On CoPc, heat-treatments up to 100°C have little or no effects on the band intensities. The bands at 1590 , 1510 , 1400 , 1333 , 1050 and 1005 cm^{-1} , assignable to nitrosyl, nitrato, nitro or free NO_3 , disappeared between 100 and 200°C , whereas those at 1460 and 1265 cm^{-1} , characteristics of nitrito or free NO_2^- , disappeared between 100 and 250°C . Judging from the desorption temperature, these adsorbates should be ascribed to the second peaks of the thermal desorption chromatograms.

3.3 Electrical conductivity

The electrical conductance (G) of pure phthalocyanine films after evacuation at 300°C was found to obey an exponential law in the temperature range $50\sim 280^\circ\text{C}$

$$G = G_0 \exp(-E/kT) \quad (1)$$

where E is the activation energy and G_0 the preexponential factor. The effects of gas adsorption on conductance were investigated by exposing the films to O_2 , NO , and NO_2 at room temperature followed by heating up to 300°C at a constant rate *in vacuo*. The results on H_2Pc and CoPc are shown in Figs. 5 and 6. The conductance of the films increased rapidly (within a minute) on exposure to the gases and decreased slightly on subsequent evacuation at

Fig. 5 Temperature dependence of conductance of H_2Pc in *vacuo*

Heating rate: $10^\circ C/min$, Adsorbed gas:
 (Δ) O_2 , 200 Torr, $(\bullet)$ NO , 150 Torr,
 $(\circ)$ NO_2 , 50 Torr, (a) after heating up
 to $300^\circ C$

Fig. 6 Temperature dependence of conductance of $CoPc$ in *vacuo*

Heating rate: $10^\circ C/min$, Adsorbed gas:
 (Δ) O_2 , 200 Torr, $(\bullet)$ NO , 150 Torr,
 $(\circ)$ NO_2 , 50 Torr, (a) after heating up
 to $300^\circ C$

room temperature. As seen from the figures, NO_2 exerts far more extensive influences on the conductance than NO or O_2 does. It is noted that when NO_2 is adsorbed the conductance of H_2Pc becomes *ca.* 10 times as large as that of

$CoPc$, although the amount of NO_2 adsorption is far less on H_2Pc than on $CoPc$ as described previously. This indicates that the conductance of the films cannot simply be correlated with the amount of adsorbed gas.

With raising temperature up to $300^\circ C$ in *vacuo*, the conductance went through a maximum. The most marked extremes were exhibited by the films on which NO_2 had been adsorbed. Such temperature dependences are of course associated with the thermal desorption of gases from the films. For the NO_2 -adsorbed H_2Pc , a steep decrease in conductance took place in the medium temperature range ($50 \sim 200^\circ C$), which coincided with the thermal desorption range of adsorbed NO_2 (Fig. 2). In the case of NO_2 -adsorbed $CoPc$, however, the conductance decreased in the similar temperature range, while the main desorption peak (second peak) appeared in the still higher temperature range (Fig. 1). The discrepancy of the two temperature ranges shows that the NO_2 adsorbates bonded to Co ions, which are responsible for the second desorption peak as mentioned earlier, do not affect the conductance significantly. In stead the NO_2 adsorbates bonded to the ligand parts are considered to be mainly associated with the conductance changes.

It has been reported^{6,7)} that the change in conductivity with gas concentration is interpretable on an extrinsic conduction model in which oxidative gas adsorption introduces an electron acceptor level in *p*-type phthalocyanine. For simplicity, it is assumed in the following discussion that hole mobility is not affected by gas adsorption, then the carrier (hole) concentration, p is given by,

$$p = (2 N_v N_a)^{1/2} \exp(-E_a/kT) \propto G \quad (2)$$

where N_v is the effective density of states in valence band, N_a the acceptor density and E_a the activation energy. p is expected to increase with an increase in amount of adsorbed oxidative gases as well as with a decrease in oxidation potential of phthalocyanines. For gas-phthalocyanine systems two mechanisms of hole creation may be considered: i) oxidation of central ions ($Me(II) Pc \rightarrow Me(III) Pc$) and ii) oxidation of ligand ($Pc \rightarrow Pc^+$ (cation radical)). As mentioned earlier, oxidation potential of the metal ions in $CoPc$ and $FePc$ is lower than that

of the ligand parts, whereas the ligand parts are oxidized in CuPc and H₂Pc. If the hole creation due to gas adsorption should occur by metal oxidation for CoPc and FePc and by ligand oxidation for H₂Pc and CuPc, p should be larger for CoPc and FePc than for H₂Pc and CuPc in the temperature range below ca. 200 °C, because the number of adsorbed NO₂ molecule on CoPc and FePc are much larger than that on H₂Pc and CuPc. On the contrary, if holes are created by ligand oxidation for all phthalocyanines, one can expect that p is larger for H₂Pc and CuPc than for CoPc and FePc, because the ligand oxidation potential is smaller for H₂Pc and CuPc than for CoPc and FePc while the numbers of adsorbed NO₂ corresponding to the first peak are comparable in all samples. In fact, it has been confirmed in the present study that H₂Pc and CuPc show larger conductance than CoPc and FePc when NO₂ is adsorbed. These results indicate that the enhancement of conductance resulting from gas adsorption can mainly be attributed to the NO₂ molecules weakly adsorbed on the ligand parts but not to those attached on metal ions having a vacant d_z^2 orbital.

Adsorbed NO₂ molecules on the ligand parts may act as a π -electron acceptor, and the in-

duced positive holes may wander by the resonance among the neighboring molecules.

The effect of NO or O₂ on conductivity was much smaller than that of NO₂. This difference in gas sensitivity corresponds well to the difference in electron affinity, NO₂ > NO and O₂, as described in the previous paper^{6,7)}.

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将来の技術革新は、今日までの長い間の技術の蓄積によるところ大であります。本シンポジウムのこれまでの講演論文をまとめて第1回から10回までの分を「第1集」、さらに第11回から15回までの分を「第2集」として刊行しましたが、今回その「第3集」として第16回(1979年5月)から第20回(1981年5月)までの分をまとめて、その内容についてより技術的に参考にし易いよう分類・再編集して刊行することになりました。本講演論文集が、今後この方面の研究・開発・生産を志す人々にとっても、またそれぞれの専門分野に携わっている人々にとっても良く参考になれば幸いです。なお、各集とも部数が限定されていますので早目にお申し込み下さい。

☆テーマⅠ. 結晶: Si, III-V, エピタキシー, 欠陥等, Ⅱ. プロセス 1: I², 拡散, CVD, 酸化等-主としてつける技術, Ⅲ. プロセス 2: Etching, 微細加工等-主としてとる技術, Ⅳ. デバイス: 素子の構造, 製法, 特性等, Ⅴ. 組立・実装: Bonding, 多層配線, パッケージ等, Ⅵ. 解析・評価: 材料解析, 評価, 測定等

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