

Development of new electronic devices
with organic semiconductors

1999

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CHAPTER 1

General Introduction

In recent years, the research and development of electronic devices with organic semiconductors such as phthalocyanines and perylene derivatives have attracted many investigators. Compared with inorganic semiconductors, organic semiconductors can be easily deposited on substrates as thin films and then make the low-cost fabrication of electronic devices be possible. In particular, organic thin films formed by electropolymerization are equivalent to inorganic materials in physical and chemical stability and can be applicable to various practical devices [1]. On the other hand, preparation of organic thin films by solvent casting are also possible, introducing the soluble substituent into the organic materials. Since the solvent casting do not need the special apparatus, the method for the most low-cost fabrication of devices can be offered [1].

In this study, it was confirmed that N,N'-2-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (2-hph-PTC), N,N'-3-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (3-hph-PTC), and N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (4-hph-PTC) were electrodeposited on indium tin oxide (ITO)-coated glass electrodes from the N,N-dimethylformamide (DMF) solutions containing hph-PTC and the supporting electrolyte of bivalent metal ion by cathodic polarization of the DMF solutions with a constant current. Perylene derivatives are generally known to be "n-" type semiconductors [2-6] while most organic semiconductors have p-type conduction properties. In chapters 2 and 4, p-n junction diodes were fabricated by the combination of perylene derivatives and phthalocyanines as p-type semiconductors and the electrical properties of the diodes were examined. In chapter 6, gas-sensors detectable to H₂S and mercaptan were fabricated with the electrodeposited perylene derivatives and sensing properties were

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evaluated. Moreover, it was reported that vacuum-deposited perylene derivatives had electrochromic property [7]. In chapter 9, electrochromic behavior of the electrodeposited perylene derivatives were examined and the mechanism of electrochromism were analyzed.

The electrodeposition of 2,9,16,23-tetracarboxyphthalocyaninato-cobalt(II) [Co(II)-taPc] on ITO electrode and the electrochromic behavior of the electrodeposited Co(II)-taPc film have reported previously [8]. In this study, it was confirmed that 2,9,16,23-tetracarboxyphthalocyaninato-copper(II) [Cu(II)-taPc] and 2,9,16,23-tetracarboxyphthalocyaninato-magnesium(II) [Mg(II)-taPc] were also electrodeposited on ITO electrodes by the method similar to that for Co(II)-taPc. These phthalocyanines are p-type semiconductors which form Schottky contacts at junctions with low work function metal such as aluminum [9]. In chapter 3, Schottky diodes based on electrodeposited Mg(II)-taPc film were fabricated and the electrical properties of the diodes were examined. Moreover, the electrical conductivity of phthalocyanines can be increased when electron acceptor gases adsorb on the surfaces of phthalocyanines because phthalocyanines have p-type conduction properties [10-26]. In chapter 5, gas-sensors based on electrodeposited Cu(II)-taPc or Co(II)-taPc film were fabricated and the sensing properties of the gas-sensors to NO₂ or SO₂ were examined.

In chapters 7 and 8, electronic devices based on soluble 2,9,16,23-tetra-(2,6-dimethylphenoxy)-metallophthalocyanine (TDMP-MPc) (in chapter 7) or N,N'-(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (dmp-PTC) (in chapter 8) and using interlocking electrodes and polyimide substrate were fabricated, respectively. The two electronic devices function as gas-sensors and optical sensors. The electrical conductivity of TDMP-MPc is increased if NO₂ or SO₂ as electron acceptor adsorbs on the surface of TDMP-MPc and decreased if O₂ depletes around the surface of TDMP-MPc since phthalocyanines are p-type semiconductors [10-26]. On the other hand, the electrical conductivity of dmp-PTC is increased if H₂S or CH₃SH as electron donor adsorbs on the surface of dmp-PTC since perylene derivatives are n-type semiconductors [2-6]. Moreover, the above two devices also function as optical sensors [27-29]. In this study, the effect of narrowing the gap between one tooth and the neighboring tooth on optical sensing properties was investigated.

The fabrication of the transistor constructed with only organic monomer semiconductors have not reported so far. The organic transistors reported previously were fabricated with combination of organic and inorganic semiconductors [30-34].

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In chapter 10, all-organic field effect transistors based on sublimed phthalocyanine as p-type semiconductor and N,N'-alkyl-3,4,9,10-perylenetetracarboxylic diimide (alkyl-PTC) as n-type semiconductor were fabricated and the transistor properties were examined. In this study, the method for stabilization of the transistor properties was investigated.

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CHAPTER 2

Fabrication of p-n junction diodes from phthalocyanine and electropolymerized perylene derivatives

Perylene derivative films, doped with metal ion, were deposited on indium/tin oxide (ITO) coated glass electrodes by electrodeposition from solutions of N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (hph-PTC) and CaCl₂, PbCl₂, ZnCl₂, or CoBr₂ as a supporting electrolyte in N,N-dimethylformamide (DMF). *P-n* junction diodes, consisting of a *p*-type phthalocyanine (Pc) sublimed film and an *n*-type hph-PTC electrodeposited film doped with metal ion, exhibited Zener-type breakdown and photocurrent enhancement. The device, which has a *p-n* junction consisting of a Pc sublimed film and a hph-PTC electrodeposited film doped with Ca²⁺, showed the largest amplification of photocurrent. The result suggests that the dopant ion in hph-PTC is an important factor for the preparation of *p-n* junction diodes.

2.1 INTRODUCTION

There has been a devoted material search for *n*-type pigments for the successful fabrication of all-organic *p-n* heterojunction diodes [1-6]. It has been confirmed that perylene derivatives behave as *n*-type semiconductors [1-5], especially Hiramoto et al. showed that perylene derivatives exhibited a large amplification of photocurrent [7].

In chapter 2, the author developed a method for preparation of hph-PTC thin films doped with bivalent metal ion on ITO electrodes by electrodeposition of hph-PTC with CaCl_2 , PbCl_2 , ZnCl_2 , or CoBr_2 as a supporting electrolyte in DMF.

This chapter describes the electrical properties of *p-n* junction diodes consisting of a *p*-type Pc sublimed film and an *n*-type hph-PTC electrodeposited film doped with metal ion. The dopant ion in hph-PTC electrodeposited film is an important factor for the preparation of *p-n* junction diodes.

2.2 EXPERIMENTAL

2.2.1 Materials

N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (hph-PTC) was prepared on the basis of the method by Rademacher et al [8]. A reaction mixture consisting of 0.68 g (1.7×10^{-3} mol) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 0.50 g (4.6×10^{-3} mol) of 4-aminophenol, and 0.50 g (2.4×10^{-3} mol) of zinc acetate suspended in 30 ml of quinoline was refluxed for 2 hours. The resulting precipitate was filtered off and recrystallized extractively from toluene. The red-purple crystalline hph-PTC was washed with methanol and dried *in vacuo* at room temperature.

Magnesium phthalocyanine (MgPc) was prepared according to the previous reported method [9]. A reaction mixture of MgCl_2 and ortho-phthalonitrile suspended in pentanol was refluxed for 48 hours. Evaporation of pentanol left a solid residue. The impurity in the residue was extracted with methanol. The blue crystalline MgPc was washed with methanol and dried *in vacuo* at room temperature. Metal-free phthalocyanine (H_2Pc) was purchased from Tokyo Kasei Co.

Ltd. MgPc and H₂Pc were purified by sublimation before fabrication of the devices. DMF was distilled under reduced pressure before use.

2.2.2 Deposition of hph-PTC Thin Films on ITO Electrodes

The hph-PTC thin films doped with metal ion on ITO electrodes were prepared by the method of cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of hph-PTC (5×10^{-4} M) and CaCl₂, PbCl₂, ZnCl₂, or CoBr₂ (1×10^{-3} M) as a supporting electrolyte in dry DMF was poured into the electrolytic cell including ITO working electrode and platinum counter electrode. The hph-PTC thin films doped with metal ion on the ITO electrodes were obtained by cathodical polarization of the solution with a constant current of -3.5×10^{-5} A/cm² for 30 min, stirring slowly the electrolytic solution. The resulting films were washed with acetone.

2.2.3 Preparation of p-n Junction Diodes

The p-n junction diodes were fabricated by vacuum deposition of Pc on a hph-PTC modified ITO glass electrodes under pressure conditions of 1.3×10^{-3} Pa. Finally, an opaque Ag electrode was formed on top of the Pc layer. The active electrode area was 5×10 mm².

2.2.4 Measurements

The film thicknesses of hph-PTC layer, Pc layer, and Ag layer were evaluated with a HITACHI S-2380N Scanning Electron Microscope. UV-VIS spectra of the Pc thin films on the hph-PTC modified ITO glass electrodes were measured with a Jasco UVIDEK-505 UV/VIS digital spectrophotometer. The current-voltage measurements were carried out using an Advantest R8340 ultra high resistance meter under irradiation of white light from a 300 W slide projector lamp. Elemental analyses were carried out with a HORIBA energy-dispersive X-ray microanalyzer, EMAX-5770W.

2.3 RESULTS AND DISCUSSION

The chemical structures of the pigments used in this chapter are shown in Figure 2.1. The present p-n junction diode is schematically depicted in Figure 2.2.

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The film thicknesses of hph-PTC layer, Pc layer, and Ag layer were evaluated about 100, 100, and 180 μm , respectively.

The hph-PTC is electropolymerizable because this compound has hydroxyphenyl groups [10]. Electrochemical polarization leads to dissociation of the terminal hydroxyl groups, and then the electropolymerization occurs on working electrode. However, heterogeneous hph-PTC films were deposited without stirring the electrolytic solution, since hph-PTC is poorly soluble in DMF. Therefore, the slow stirring of the electrolytic solution was essential to take homogeneous hph-PTC films.

Most of compounds which have hydroxyphenyl group are polymerized by anodical polarization. However, perylene derivatives are easily reduced because these compounds are *n*-type semiconductors whose electrical conductivity is increased by accepting electrons. Actually, hph-PTC electrodeposited films were prepared by cathodical polarization. This is explained by considering that high conductivity of monomers is necessary for electropolymerization [10]. The result suggests that these hph-PTC films doped with metal ion are *n*-type semiconductors in contrast with Pc which is *p*-type semiconductor. Therefore, it seems that the *p-n* junction interface is formed between hph-PTC electrodeposited film and Pc sublimed film. It is thought that both the rectification and the amplification of photocurrent described below are generated at this *p-n* junction interface, since it was confirmed by current-voltage measurements that both the hph-PTC film/TiO electrode interface and the Pc film/Ag electrode interface formed Ohmic contacts.

Absorption spectrum of the two-layered film consisting of a Pc sublimed film and a hph-PTC electrodeposited film doped with Ca^{2+} is shown in Figure 2.3. The absorption band in the region between 400 and 600 nm was assigned to hph-PTC. On the other hand, the bands in the region between 300 and 400 nm and the region between 600 and 700 nm were ascribed to B- and Q-band of MgPc, respectively. The fact that the two-layered films take up the light in almost all visible region would assist the large amplification of photocurrent described below.

The diode performances are summarized in Table 2.1. On a dark condition, all diodes exhibited Zener-type breakdown which is generated by the existence of a lot of impurities at *p-n* junction interface [11]. The result would be due to the existence of dopant metal ions in hph-PTC film, actually the existence of dopant metal ions was confirmed for each device by X-ray microanalyzer. Namely, it is thought that the dopant metal acts as impurity to generate Zener-type

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breakdown. The existence of M^{2+} ($M = \text{Ca}, \text{Pb}, \text{Zn}, \text{or } \text{Co}$) is reasonable because hph-PTC film was prepared by cathodical polarization.

In fact, many investigators reported that the devices using the semiconductors with dopant showed breakdown on reverse biased condition [12], while the devices without dopant did not show [1-4]. Therefore, it is thought that tunneling effect is generated at the *p-n* junction interface on reverse biased condition because of the decrease of distance between LUMO and HOMO [11].

In the previous reported diodes which were fabricated by only vacuum-deposition, the electric conductivity was low because of the high resistance of organic semiconductors [1-4]. The high conductivity of the present device is attributed to the dopant in hph-PTC films, since the electrodeposited films with dopant have a metallic high conductivity [13].

The Zener-type characteristic was stable for the diode doped with Ca^{2+} , Pb^{2+} or Zn^{2+} , but was unstable for the diode doped with Co^{2+} . The unstable current for the diode of a hph-PTC film doped with Co^{2+} would be explained by taking into account the various oxidation states of cobalt ion [14]. The dark current-voltage characteristic for the diode consisting of a hph-PTC film doped with Ca^{2+} and a MgPc sublimed film is shown in Figure 2.4. The breakdown voltage of this device was about -0.05 V. This low value is due to the existence of a great number of dopant as impurity. In conventional Zener-type diodes which use a combination of inorganic semiconductors, breakdown voltage is comparatively high since the number of dopants is easily controlled [11, 15]. However, the control of the number of dopants is usually difficult in the devices of organic semiconductors [13].

On a forward biased condition, the largest amplification of photocurrent was observed in the diode consisting of a hph-PTC film doped with Ca^{2+} and a MgPc sublimed film. Multiplication rate in Table 2.1 is the ratio of photocurrent to dark current at $+0.8$ V. This parameter indicates the efficiency of photogeneration of charge carriers. The device of a hph-PTC film doped with Zn^{2+} showed a large amplification comparable to that doped with Ca^{2+} . On the other hand, such a large amplification was not observed in the case of Pb^{2+} and Co^{2+} . These results suggest that the dopant metal ion in hph-PTC film is an important factor for charge carrier photogeneration. The effect of light irradiation on current for the diode consisting of a hph-PTC film doped with Ca^{2+} and a MgPc film is shown in Figure 2.5. The forward biased dark current of the device immediately after light irradiation is about 100 times that of dark

condition. When the device irradiated with light was allowed to stand on dark condition for 48 hours, the current drastically decreased. On the other hand, the reverse biased current was almost constant. Namely, it is clear that the current response of this device to light is reversible on a forward biased condition and the Zener-type characteristic is stable even under light.

Furthermore, the multiplication rate of the diode using H₂Pc as a *p*-type semiconductor was smaller than that of the diode using MgPc. UV-VIS spectra for MgPc and H₂Pc sublimed films are shown in Figure 2.6. Since both MgPc and H₂Pc have a fluorescence property [16], it can be expected that the diodes having MgPc or H₂Pc effectively respond to light irradiation.

In the UV-VIS spectra for phthalocyanines, the absorption peak at around 620 nm and that at around 690 nm are assigned to aggregates and non-aggregates, respectively [17]. Therefore, it is clear that aggregates of H₂Pc are easily formed in a sublimed film, while there are a lot of non-aggregates even in a sublimed film of MgPc. In the diode consisting of hph-PTC and MgPc, the charge transfer interaction between a hph-PTC molecule and a MgPc molecule would be stronger than in the diode consisting of hph-PTC and H₂Pc. Namely, in the diode of H₂Pc, it is thought that the aggregates of H₂Pc prevents the formation of uniform *p-n* junction interface between hph-PTC and H₂Pc. In fact, it was reported by Hiramoto et al. [4] that the charge transfer interaction between PTC molecule and Pc molecule was the most important factor for the performance of the diodes which are constructed by the PTC/Pc system. Thus, it is suggested that the photogenerated charge carriers are effectively transported between hph-PTC and MgPc.

2.4 CONCLUSION

The *p-n* junction diodes consisting of a hph-PTC electrodeposited film doped with metal ion and a sublimed Pc film exhibited Zener-type breakdown. In particular, the Zener-type characteristic was stable in the diode of hph-PTC film doped with Ca²⁺. The diode of hph-PTC film doped with Ca²⁺ also exhibited an excellent photo-conduction property. The amplification of photocurrent of the diode containing MgPc is larger than that of the diode of H₂Pc. Both the dopant metal ion in hph-PTC electrodeposited film and the existence of non-aggregate Pc

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molecules are important factors for the device characteristics. Finally, the present devices have potentially useful features for Zener-type diode or photomultiplier.

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Table 2.1 Performance of diodes.

Pigment combination	Electrical property	Stability	Multiplication rate of photocurrent
MgPc/hph-PTC (Ca ²⁺ doped)	Zener-type	stable	100
MgPc/hph-PTC (Pb ²⁺ doped)	non-linear symmetric	stable	1
MgPc/hph-PTC (Zn ²⁺ doped)	Zener-type	stable	30
MgPc/hph-PTC (Co ²⁺ doped)	Zener-type	unstable	10
H ₂ Pc/hph-PTC (Ca ²⁺ doped)	Zener-type	stable	30

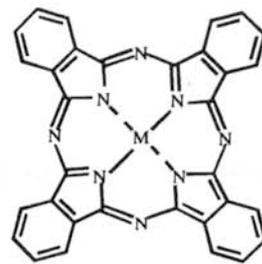
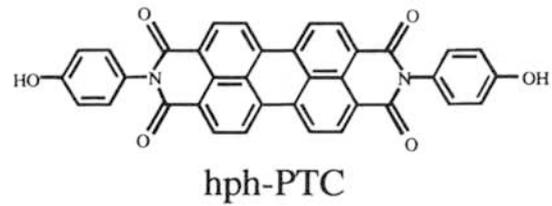


Figure 2.1 Molecular structures of hph-PTC and Pc.

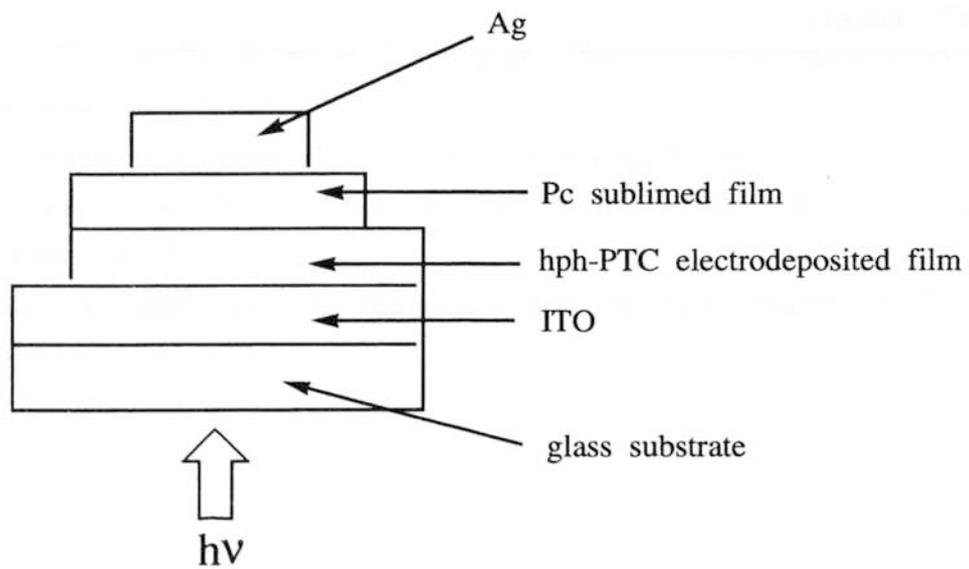


Figure 2.2 Schematic representation of diode.

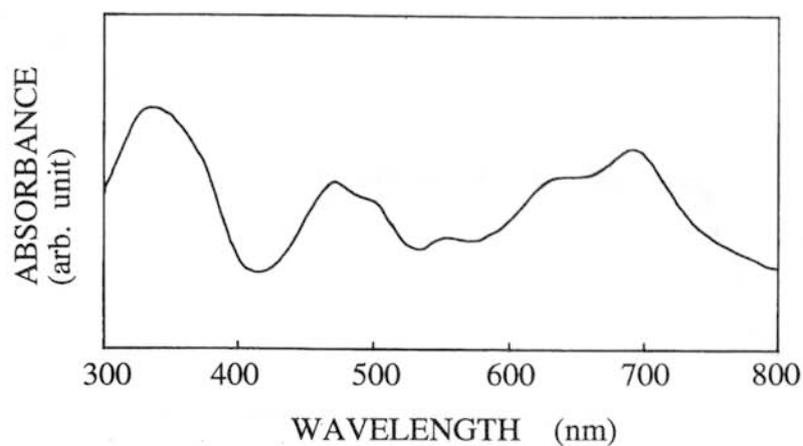


Figure 2.3 UV-VIS spectrum of two-layer film consisting of MgPc sublimed film and hph-PTC electrodeposited film doped with Ca^{2+} .

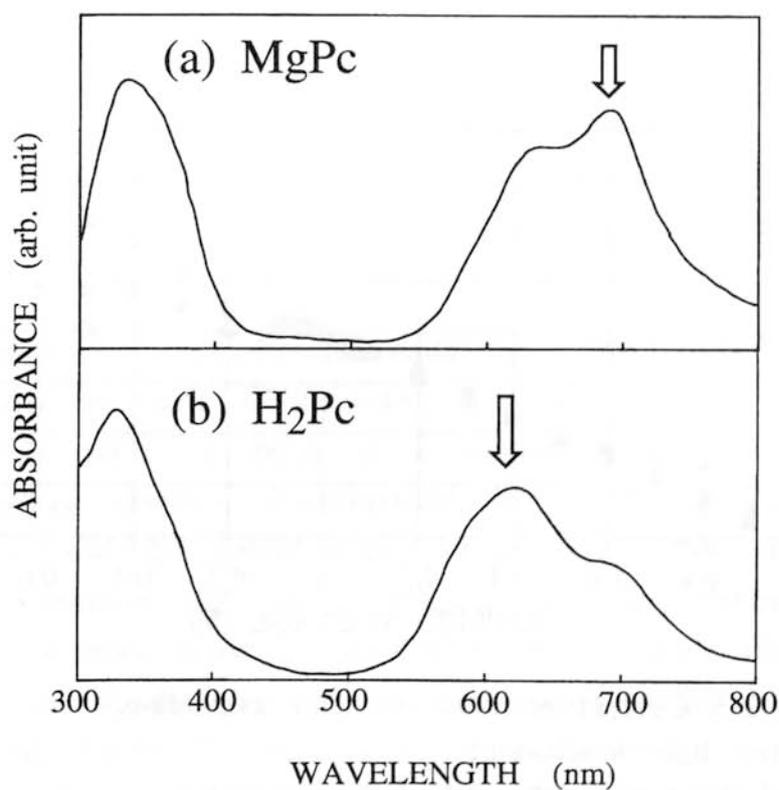


Figure 2.6 UV-VIS spectra of (a)MgPc and (b)H₂Pc sublimed films.

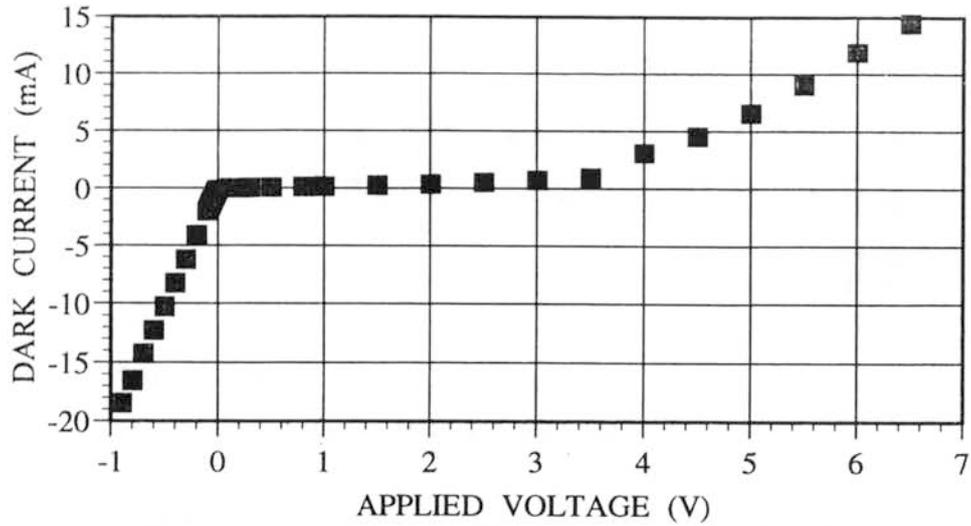


Figure 2.4 Dark current-voltage characteristic for diode consisting of MgPc and Ca^{2+} -doped hph-PTC.

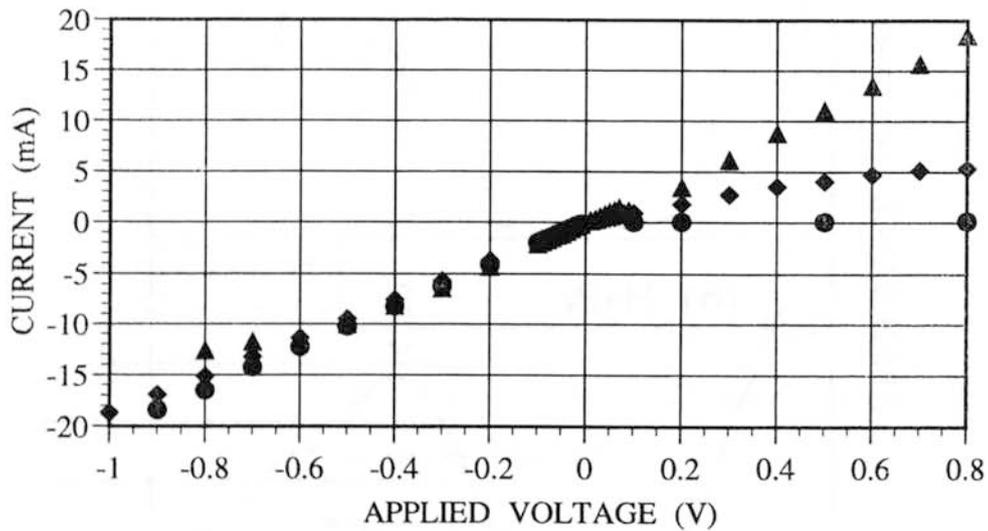


Figure 2.5 Current response to light irradiation.

- : before light irradiation;
- ▲: in dark immediately after light irradiation;
- ◆: after standing in dark for 48 h after light irradiation.

CHAPTER 3

Electrical properties of junctions between electrodeposited magnesium phthalocyanine and aluminum

2,9,16,23-Tetracarboxyphthalocyaninatomagnesium(II) [Mg(II)-taPc] films were obtained on indium/tin oxide (ITO) coated glass electrodes by electrodeposition, using MgCl₂, CaCl₂, CoCl₂, or ZnCl₂ as a supporting electrolyte. The electrical properties of junctions between electrodeposited Mg(II)-taPc film and aluminum electrode were evaluated by current-voltage measurements. The diode based on Mg(II)-taPc film containing Mg²⁺ as a bridging metal ion exhibited Zener-type breakdown, while the diode based on Mg(II)-taPc film containing Ca²⁺ or Zn²⁺ as a bridging metal ion showed almost symmetrical current-voltage characteristic. The diode based on Mg(II)-taPc film containing Co²⁺ as a bridging metal ion was electrically unstable. The diode based on Mg(II)-taPc film containing Mg²⁺, Ca²⁺, or Zn²⁺ as a bridging metal ion exhibited a photocurrent on forward biased condition.

3.1 INTRODUCTION

Metallophthalocyanines (Mt-Pc) attract considerable interest because of their high electrical conductivity [1-2], optical sensing properties [3-4], and *p*-type semiconduction [5-8]. Early research on solar cells having a Pc film has focused on the Schottky junction [9-13]. However, comparatively little has been done to investigate the fundamental aspects of junction interfaces between the film of phthalocyanine polymer doped with ion and metal electrode.

Shirai et al. reported a method for the preparation of 2,9,16,23-tetracarboxyphthalocyaninatocobalt(II) [Co(II)-taPc] films on indium/tin oxide coated (ITO) glass electrodes by electrodeposition [14]. In chapter 3, the author found that Mg(II)-taPc electrodeposited films can also be prepared on ITO electrode by similar method for Co(II)-taPc film. In this chapter, the author will report the fabrication of the Schottky-type diodes based on the junction interface between Mg(II)-taPc film containing bridging metal ions and aluminum electrode [15-17].

Since Mg-Pc shows strong fluorescence when exposed to ultraviolet or visible light [18], a device using a Mg-Pc film should be highly sensitive to light irradiation [4].

An ITO electrode is used as material which enables holes to enter semiconductor film, whereas the counter electrode is aluminum which has a low work function and enables electrons to enter the conduction band of Pc [19-20].

This chapter presents the electrical features of the junction interface between Mg-Pc film containing bridging metal ions and an aluminum electrode.

3.2 EXPERIMENTAL

3.2.1 Materials

Mg(II)-taPc was prepared according to the method for Co(II)-taPc [21]. A reaction mixture consisting of 3.00 g (1.6×10^{-2} mol) of trimellitic anhydride, 0.37 g (3.9×10^{-3} mol) of magnesium chloride, 10.0 g (1.7×10^{-1} mol) of urea, and 0.20 g (1.6×10^{-4} mol) of ammonium molybdate was poured into a separable flask and heated at 200°C for 20 min, stirring quickly the mixture. The residue was poured into 500 ml water and the solution was filtered off.

After extraction in a Soxhlet for 24 h with water, the residue was poured into 150 ml 50 wt% KOH aqueous solution and the solution was refluxed at 80°C for 24 h. The precipitate was filtered off and extracted with water. A 6 M HCl aqueous solution was dropped into the alkaline solution until the pH of the solution changed into 2, and the resulting precipitate was filtered off. After extraction in a Soxhlet for 24 h with methanol, the product was dried *in vacuo* at room temperature: yield 0.42 g (16 %); UV-VIS (DMF) λ_{max} 690 nm (Q-band for Pc); IR (KBr) 1698 cm^{-1} ($\nu_{\text{C-O}}$). Anal. Calcd for Mg in Mg(II)-taPc: Mg, 3.51%. Found: Mg, 3.22%.

N,N-Dimethylformamide (DMF) was distilled under reduced pressure before use. Supporting electrolytes, acetone, and aluminum were of analytical grade from commercial origin.

3.2.2 Fabrication of Devices Based on Mg(II)-taPc Film Containing Bridging Metal Ions

Mg(II)-taPc films containing bridging metal ions on ITO electrodes were prepared by cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of Mg(II)-taPc (3×10^{-4} M) and MgCl_2 , CaCl_2 , CoCl_2 , or ZnCl_2 (1×10^{-3} M) as supporting electrolyte in dry DMF was poured into the electrolytic cell containing an ITO working electrode and platinum counter electrode. Mg(II)-taPc films containing bridging metal ions on the ITO electrodes were prepared by cathodical polarization of the DMF solution containing Mg(II)-taPc and a supporting electrolyte with a constant current of $-35 \mu\text{A}/\text{cm}^2$ for 30 min. The deposited films were washed with acetone.

Aluminum electrodes were deposited on the Mg(II)-taPc modified ITO electrodes by sublimation at 1.3×10^{-3} Pa.

3.2.3 Measurements

IR spectrum for Mg(II)-taPc was measured with a JASCO FT/IR-7300 Fourier Transform Infrared Spectrometer using KBr disk. UV-VIS spectrum for Mg(II)-taPc was measured with a JASCO UV/DEC-505 UV/VIS Digital Spectrophotometer. Atomic absorption spectrometry for Mg in Mg(II)-taPc was carried out with a HITACHI 180-50 Atomic Absorption Spectrophotometer. Current-voltage characteristics were measured using an Advantest R8340 Ultra High Resistance Meter. Elemental analyses were carried out with a HORIBA energy-dispersive X-ray microanalyzer, EMAX-5770W. Photoconduction of devices was

measured under irradiation of white light from a 300 W slide projector lamp. Surface structures and thickness of the electrodeposited Mg(II)-taPc films containing bridging metal ions were examined with a HITACHI S-2380N Scanning Electron Microscope (SEM).

3.3 RESULTS AND DISCUSSION

Green thin films were obtained on ITO electrodes by constant current electrodeposition from DMF solutions containing Mg(II)-taPc and MgCl₂, CaCl₂, CoCl₂, or ZnCl₂ as a supporting electrolyte. When PbCl₂ was used as a supporting electrolyte, heterogeneous Mg(II)-taPc film containing Pb²⁺ as bridging metal ion was deposited on the ITO electrode. Films failed to form when FeCl₂ or CuCl₂ was used. These results suggest that the chemical stability of bridging metal ion is an important factor for the electrodeposition of Mg(II)-taPc film. Since Mg²⁺, Ca²⁺, and Zn²⁺ have closed shells of electron configurations, these bivalent ions are chemically stable [22-23]. Since Fe²⁺, Co²⁺, and Cu²⁺ have electron configurations whose d orbitals are not filled by electrons and Pb²⁺ has electron configuration whose p orbital is not filled by electrons, the valences of these metal ions can be changed. The electron configurations of these metals are listed in Table 3.1.

The chemical structure of Mg(II)-taPc film containing bridging metal ions is shown in Figure 3.1. The monomer of M(II)-taPc is polymerized by bridge formation with bivalent metal ion in the electrodeposited M(II)-taPc film [14].

The Schottky-type diodes were prepared by the formation of aluminum electrode on the Mg(II)-taPc film containing bridging metal ions. Since Pc derivatives are *p*-type semiconductors, Schottky-type or Mott-type barriers are formed by contact with low work function metal such as aluminum [15]. Mott-type barriers are likely to be formed because low work function metals are easily oxidized and a resistive thin layer is formed at the junction interface between semiconductor film and metal electrode. The device structure is shown in Figure 3.2.

The diode based on Mg(II)-taPc film containing Mg²⁺ as a bridging metal ion exhibited Zener-type breakdown generated by other molecules in the neighborhood of rectifying barriers. This would be due to the existence of

bridging metal ions in Mg(II)-taPc film. Actually, the existence of bridging metal ions was confirmed for each device by X-ray microanalyzer. It seems that the existence of the bridging metals causes the present devices to generate Zener-type breakdown. In fact, many investigators report that devices using the semiconductors with other molecules showed breakdown under the reverse biased condition [20], while the devices without other molecules did not [16]. It is thought that tunneling effect is generated at the interface of the Mg(II)-taPc film containing Mg^{2+} as a bridging metal ion and aluminum electrode under the reverse biased condition because of the decrease of gap between LUMO and HOMO [15, 24].

For previous Schottky-type diodes made by vacuum-deposition of organic semiconductors, high resistance of organic semiconductors decreased electric conductivity [16]. The high conductivity of the present device is attributed to bridging metal ions in Mg(II)-taPc films, since the electrodeposited films with ions have metallic high conductivity [25]. The dark current-voltage of the diode based on Mg(II)-taPc film containing Mg^{2+} as bridging metal ion is shown in Figure 3.3.

The low breakdown voltage of the device is due to the great number of bridging metal ions. In conventional Zener-type diodes constructed by an inorganic semiconductors, breakdown voltage is comparatively high since the number of dopants is easily controlled [15]. However, in the present devices, control of the number of metal ions is difficult because Mg(II)-taPc films are prepared by bridge formation with metal ions originating from supporting electrolytes in electrodeposition.

The current-voltage characteristic of the diode based on Mg(II)-taPc film containing Ca^{2+} or Zn^{2+} as bridging metal ion was almost symmetrical. The magnitude of applied voltage for turn-on of forward biased current was almost equal to that for breakdown of reverse biased current. The electrical properties of the devices of Mg(II)-taPc film containing Mg^{2+} , Ca^{2+} , or Zn^{2+} as bridging metal ion were reproducible. The results can be explained by the chemical stability of these metal ions which have closed shells of electron configurations [22-23].

The diode based on Mg(II)-taPc film containing Co^{2+} as bridging metal ion was electrically unstable. The reproducible values of current of the device were not obtained in any measurement. The electrical instability is due to the various oxidation states of cobalt ions [22-23].

The diode based on Mg(II)-taPc film containing Mg^{2+} , Ca^{2+} , or Zn^{2+} as

bridging metal ion exhibited photocurrent under the forward biased condition. The current after light irradiation was larger than that before light irradiation under the forward biased condition. Photocurrent/dark current, the ratio of photocurrent to dark current, of the present devices at applied voltage of +0.8 V is summarized in Table 3.1. The diode based on Mg(II)-taPc film containing Ca²⁺ as bridging metal ion showed the largest photocurrent/dark current, which indicates the efficiency of photogeneration of charge carriers. The Mg(II)-taPc film containing Ca²⁺ as bridging metal ion (350 μm) was thicker than the film containing Mg²⁺ or Zn²⁺ as bridging metal ion (250 μm). It is thought that the number of charge carriers in the film containing Ca²⁺ as bridging metal ion drastically increases by light irradiation because of the large absorbance of this thick film. UV-VIS spectra of Mg(II)-taPc film containing Mg²⁺ as bridging metal ion and that of Mg(II)-taPc film containing Ca²⁺ as bridging metal ion are shown in Figure 3.4. The absorbance of Mg(II)-taPc film containing Ca²⁺ as bridging metal ion was about 12 times that of Mg(II)-taPc film containing Mg²⁺ as bridging metal ion. The spectra show that these films especially take up light in the short wavelength region or high energy region.

The turn-on voltage of the diode based on Mg(II)-taPc film containing Mg²⁺ as bridging metal ion was high, while the breakdown voltage was very low (Figure 3.3). In the present devices in Table 3.1, more than 0.8 V applied voltage was necessary for the generation of photoconduction under the forward biased condition. These results suggest that Mott-type barriers, which would prevent the rising of forward biased current because of a thin resistive layer, are formed at the interface of semiconductor and aluminum [17, 20]. It is thought that applying high voltage is necessary for charge carrier transfer at the interface of the Mg(II)-taPc film containing bridging metal ions and aluminum electrode under the forward biased condition, while charge carriers are transferred by tunneling effect under the reverse biased condition.

It was confirmed by SEM observation that the film containing Mg²⁺ as bridging metal ion had a comparatively flat surface while the film containing Ca²⁺ as bridging metal ion and one containing Zn²⁺ as bridging metal ion had rough surfaces. The flatness of surface of film containing Mg²⁺ as bridging metal ion may promote effective tunneling of valence electrons at the junction between Mg(II)-taPc film containing Mg²⁺ as bridging metal ion and aluminum electrode under the reverse biased condition, since it can be expected that the barrier layer is thin enough for the tunneling effect.

3.4 CONCLUSION

Mg(II)-taPc films containing bridging metal ions were obtained from DMF solutions containing MgCl₂, CaCl₂, CoCl₂, or ZnCl₂ as supporting electrolyte. The present devices based on these Mg(II)-taPc films have potentially useful features for Zener-type diodes or photoelectric tubes. In particular, the diode based on Mg(II)-taPc film containing Mg²⁺, Ca²⁺, or Zn²⁺ as bridging metal ion exhibited reproducible electrical properties and photocurrent. The diode based on Mg(II)-taPc film containing Mg²⁺ as bridging metal ion exhibited a Zener-type breakdown on dark condition. This would be due to bridging metal ions in electrodeposited Mg(II)-taPc film. The diode based on Mg(II)-taPc film containing Ca²⁺ as bridging metal ion showed the largest photocurrent/dark current. These results suggest that the bridging metal ion in the Mg(II)-taPc film is an important factor for deposition of Mg(II)-taPc film and the diode performance.

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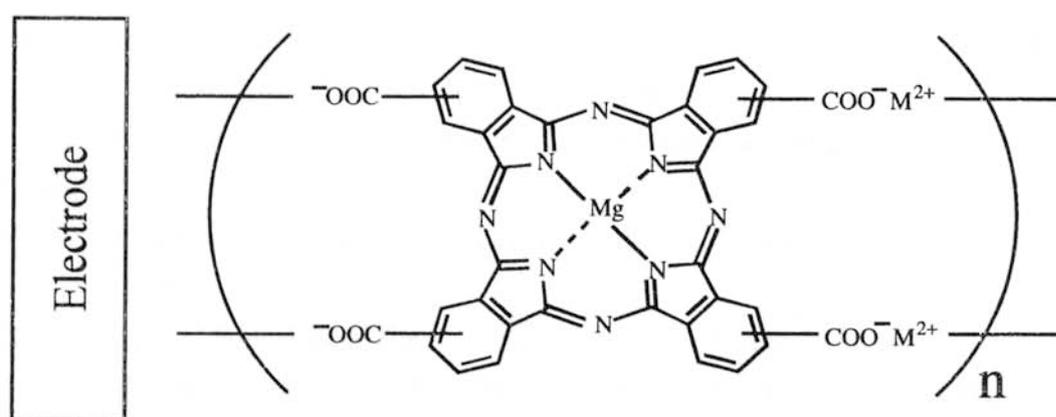
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Table 3.1 Diode performance.

Bridging metal (Electron configuration)	Aspect of film	Current-voltage characteristic	Photocurrent /dark current
Mg ([Ne] 3s ²)	homogeneous	Zener-type	8
Ca ([Ar] 4s ²)	homogeneous	symmetrical	118
Fe ([Ar] 3d ⁶ 4s ²)	not deposit	—————	—————
Co ([Ar] 3d ⁷ 4s ²)	homogeneous	unstable	1
Cu ([Ar] 3d ¹⁰ 4s)	not deposit	—————	—————
Zn ([Ar] 3d ¹⁰ 4s ²)	homogeneous	symmetrical	2
Pb ([Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ²)	heterogeneous	—————	—————



M = Mg, Ca, Co, or Zn

Figure 3.1 Molecular structure of Mg(II)-taPc film containing bridging metal ion.

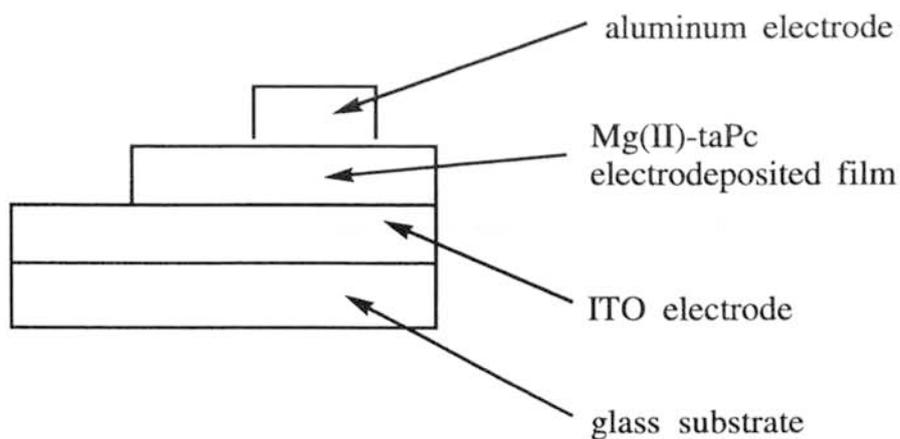


Figure 3.2 Schematic representation of the diode.

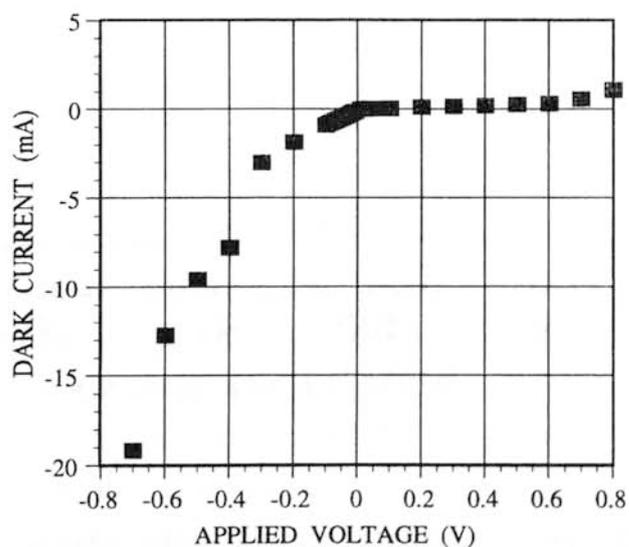


Figure 3.3 Dark current-voltage characteristic for diode based on Mg(II)-taPc film containing Mg^{2+} as bridging metal ion.

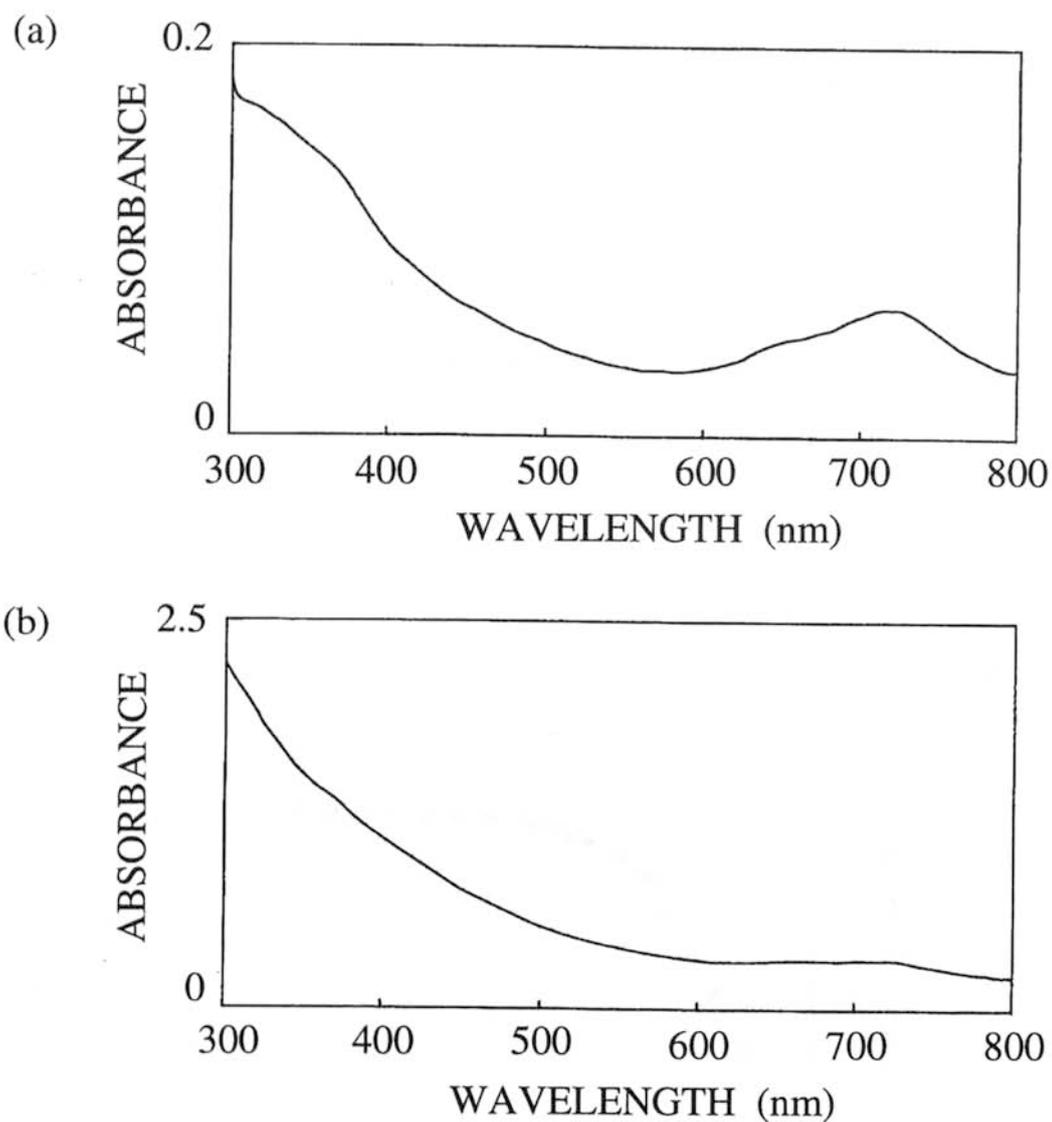


Figure 3.4 UV-VIS spectra of Mg(II)-taPc film containing (a)Mg²⁺ and (b)Ca²⁺ as bridging metal ion

CHAPTER 4

Preparation of electro-codeposited film consisting of phthalocyanine and perylene derivatives

A novel electro-codeposited film was homogeneously obtained on indium/tin oxide (ITO) coated glass electrode by cathodical polarization of a solution of 2,9,16,23-tetracarboxyphthalocyaninatomagnesium(II) [Mg(II)-taPc], N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (4-hph-PTC) and ZnCl₂ as a supporting electrolyte in N,N-dimethylformamide (DMF). The cyclic voltammogram for the codeposited film showed the reduction at -0.8 V vs. SCE which was assigned to the reduction of Mg(II)-taPc and that at -1.5 V vs. SCE which was assigned to the reduction of 4-hph-PTC. The device based on the codeposited film was prepared by the formation of aluminum electrode on the codeposited film. The device exhibited a rectification and a photoconduction. The results suggest that the codeposited film forms a number of *p-n* junction interfaces which were distributed on the ITO electrode.

4.1 INTRODUCTION

Magnesium phthalocyanines and perylene derivatives have attracted considerable interest because of the *p*-type and *n*-type semiconducting properties, respectively [1-7]. Since these compounds show strong fluorescence when exposed to ultraviolet or visible light [8-9], it can be expected that devices using these compounds are highly sensitive to light irradiation [7, 10].

The author confirmed that Mg(II)-taPc, Co(II)-taPc, 2-hph-PTC, 3-hph-PTC or 4-hph-PTC film on ITO electrode was prepared by the method of cathodic electrolytic deposition.

Recently we found that the codeposited film consisting of Mg(II)-taPc, 4-hph-PTC and Zn^{2+} as bridging metal ion on ITO electrode were prepared by galvanostat electrodeposition from the DMF solution containing Mg(II)-taPc, 4-hph-PTC and $ZnCl_2$ as a supporting electrolyte. This chapter concerns the preparation of the codeposited film and the electrical properties of the device based on the codeposited film.

4.2 EXPERIMENTAL

4.2.1 Materials

Mg(II)-taPc and Co(II)-taPc were prepared according to the literature [11]. A reaction mixture consisting of 3.00 g (1.6×10^{-2} mol) of trimellitic anhydride, 0.37 g (3.9×10^{-3} mol) of magnesium chloride or 0.37 g (2.8×10^{-3} mol) cobalt chloride, 10.0 g (1.7×10^{-1} mol) of urea and 0.20 g (1.6×10^{-4} mol) of ammonium molybdate was poured into a separable flask and heated at 200°C for 20 min, stirring quickly the mixture. The residue was poured into 500 ml of water and then the solution was filtered off. After extraction in a Soxhlet for 24 h with water, the residue was poured into 150 ml of 50 wt% KOH aqueous solution and then the solution was refluxed at 80°C for 24 h. The precipitate was filtered off and extracted with water. A 6 M HCl aqueous solution was dropped into the alkaline aqueous solution until the pH of the solution was changed into 2, and then the resulting precipitate was filtered off. After extraction in a Soxhlet for 24 h with methanol, the product was dried *in*

vacuo at room temperature.

2-, 3- and 4-hph-PTC were prepared on the basis of the method by Rademacher et al [9]. A reaction mixture consisting of 0.68 g (1.7×10^{-3} mol) of 3,4,9,10-perylenetetra-carboxylic dianhydride (PTCDA), 0.50 g (4.6×10^{-3} mol) of 2-, 3- or 4-aminophenol and 0.50 g (2.4×10^{-3} mol) of zinc acetate suspended in 30 ml of quinoline was refluxed for 2 h. The resulting precipitate was filtered off and recrystallized extractively from toluene. The red-purple crystalline 2-, 3- or 4-hph-PTC was washed with methanol and dried *in vacuo* at room temperature.

DMF was distilled under reduced pressure before use. CaCl_2 , ZnCl_2 and acetone were of analytical grade from commercial origin.

4.2.2 Preparation of devices based on codeposited films consisting of *M(II)-taPc*, *hph-PTC* and bridging metal ion

The codeposited films consisting of *M(II)-taPc* ($M = \text{Mg}$ or Co) and 2-, 3- or 4-hph-PTC were prepared on ITO electrodes by the method of cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of *M(II)-taPc* (3×10^{-4} M), *hph-PTC* (3×10^{-4} M) and ZnCl_2 or CaCl_2 (1×10^{-3} M) as a supporting electrolyte in dry DMF was poured into the electrolytic cell including ITO working electrode and platinum counter electrode. The codeposited films on the ITO electrodes were prepared by cathodical polarization of the DMF solution containing *M(II)-taPc*, *hph-PTC* and a supporting electrolyte with a constant current of $-35 \mu\text{A}/\text{cm}^2$ for 30 min, stirring slowly the solution. The deposited films were washed with acetone.

Finally, aluminum electrode was deposited on the codeposited film by sublimation under pressure of 1.3×10^{-3} Pa.

4.2.3 Measurements

UV-VIS spectra were recorded on a JASCO UVIDEK-505 UV/VIS Digital Spectrophotometer. Cyclic voltammetric measurements of the codeposited film on ITO electrodes were carried out in the DMF solution of 1×10^{-3} M CaCl_2 or ZnCl_2 with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode at a scan rate of 50 mV/s. Current-voltage characteristics were measured using an Advantest R8340 Ultra High Resistance Meter under irradiation of white light from a 300 W slide projector lamp. The surface structures and the thickness of the codeposited films were examined with

a HITACHI S-2380N Scanning Electron Microscope (SEM). A computer interfaced HEWLETT PACKARD 4192A LF Impedance Analyzer was used to measure the complex impedance, applying a voltage of +0.5 V to the device. Elemental analysis of electro-codeposited film was carried out with a HORIBA energy-dispersive X-ray microanalyzer, EMAX-5770W.

4.3 RESULTS AND DISCUSSION

The chemical structures of M(II)-taPc and hph-PTC are shown in Figure 4.1. The results of electro-codeposition are summarized in Table 4.1. The monomers of M(II)-taPc and hph-PTC would be polymerized by bridge formation with bivalent metal ion. Electrochemical polarization leads to dissociation of the terminal carboxyl or hydroxyl groups, and then the electropolymerization occurs on working electrode [12]. Actually, existence of Ca^{2+} or Zn^{2+} in electrodeposited films were confirmed by X-ray microanalysis. The chemical structures of electrodeposited Mg(II)-taPc and 4-hph-PTC are shown in Figure 4.2. Although the chemical structure of electrodeposited hph-PTC has not been confirmed, it is thought that the bridging way of the Zn ions with hph-PTC is similar to that with M(II)-taPc since hph-PTC was electrodeposited by the same method as M(II)-taPc.

In the electro-codeposition of Mg(II)-taPc and 4-hph-PTC using ZnCl_2 as a supporting electrolyte, a homogeneous film, in which small clusters of Mg(II)-taPc and those of 4-hph-PTC seemed to be almost uniformly distributed on ITO electrode, was obtained on ITO electrode. The slow stirring of the electrolytic solution was essential to take homogeneous codeposited film since heterogeneous film was deposited without stirring the electrolytic solution. The thickness of the codeposited film was evaluated about 100 μm . On the other hand, in the electro-codeposition using CaCl_2 as a supporting electrolyte, a heterogeneous film was obtained. It is suggested that supporting electrolyte is an important factor for the preparation of homogeneous codeposited film.

Shirai et al. have already reported that Co(II)-taPc film containing Ca^{2+} as bridging metal ion is homogeneously prepared on ITO electrode by electrodeposition [12]. Furthermore, 2-, 3- and 4-hph-PTC electrodeposited films were also homogeneously obtained on ITO electrodes by cathodical polarization of the DMF solution containing hph-PTC and CaCl_2 , PbCl_2 , ZnCl_2 or CoBr_2 as a supporting

electrolyte. However, Co(II)-taPc and 2-, 3- or 4-hph-PTC were separately deposited on ITO electrode when these two monomers co-existed in the DMF solution containing CaCl₂ as a supporting electrolyte. Namely, the resulting films were consisting of two regions: the region where only Co(II)-taPc film containing Ca²⁺ deposited and the region where only hph-PTC film containing Ca²⁺ deposited. In the cathodical polarization of the DMF solution containing ZnCl₂ as supporting electrolyte, Co(II)-taPc dominantly deposited on ITO electrode. It is thought that Co(II)-taPc prevented the electrodeposition of hph-PTC since the ability of electrodeposition of Co(II)-taPc is much higher than that of hph-PTC.

A homogeneous 2-hph-PTC film is easily obtained on ITO electrode since this compound is readily soluble in DMF compared with 3- or 4-hph-PTC. However, 2-hph-PTC and Mg(II)-taPc were separately deposited on ITO electrode when these two monomers co-existed in the DMF solution containing CaCl₂ or ZnCl₂ as a supporting electrolyte. That is, the resulting films were consisting of two regions: the region where only Mg(II)-taPc film containing Ca²⁺ deposited and the region where only 2-hph-PTC film containing Ca²⁺ deposited.

These results suggest that the compound which is readily deposited on ITO electrode is separately deposited from the other compound which co-exists in the DMF solution containing a supporting electrolyte. It is thought that the difficulty of electrodeposition of monomers is necessary to take homogeneous codeposited film, in which small clusters of phthalocyanine and those of perylene derivative seem to be uniformly distributed on ITO electrode.

Figure 4.3 shows the cyclic voltammogram of codeposited film consisting of Mg(II)-taPc, 4-hph-PTC and Zn²⁺ in the DMF solution of 1×10^{-3} M ZnCl₂. The reduction at -0.8 V vs. SCE and the reduction at -1.5 V vs. SCE were assigned to the reduction of electrodeposited Mg(II)-taPc and the reduction of electrodeposited 4-hph-PTC, respectively. Namely, the existence of both electrodeposited Mg(II)-taPc and 4-hph-PTC was confirmed.

The device based on the codeposited film consisting of Mg(II)-taPc, 4-hph-PTC and Zn²⁺ was fabricated by the formation of aluminum electrode on top of the codeposited film. The device structure is shown in Figure 4.4. The present device exhibited a rectifying characteristic under dark condition as shown in Figure 4.5. Since aluminum has a low work function and enables electrons to inject into the conduction band of semiconductor [13-14], an Ohmic contact is formed at the interface between aluminum and *n*-type semiconductor [15]. Therefore, aluminum electrode is usually used as cathode in electro-luminescent devices based

on *p-n* blend polymer [13-14], while ITO electrode is used as anode because ITO has a high work function and enables holes to inject into the valence band of semiconductor [13-14].

The results of current-voltage measurements for the present device suggest that a number of *p-n* junction interfaces are formed and distributed on the ITO electrode, since phthalocyanines and perylene derivatives are *p*-type and *n*-type semiconductors, respectively [1-7].

In the previously reported devices which were fabricated by vacuum-deposition of organic semiconductors, the high resistance of organic semiconductors decreased the electric conductivity [1-5]. In the present device, electric conductivity under the forward biased condition is between 1.54 and 4.06×10^{-4} S/cm. The high conductivity of the present device is attributed to the existence of bridging metal ion in the codeposited film since the electrodeposited film containing dopant have a metallic high conductivity [14].

Furthermore, in the present device, photoconduction and breakdown were observed when exposed to white light irradiation under forward and reverse biased condition, respectively. The current-voltage characteristic under light irradiation is shown in Figure 4.5. It is thought that charge carriers are newly generated by light irradiation and the tunneling effect is occurred by the decrease of depth of depletion layer which is formed at *p-n* junction interfaces. The decrease of depth of depletion layer is due to the existence of a great number of bridging metal ion [16-17]. Actually, the existence of Zn^{2+} as bridging metal ion in the codeposited film was confirmed by X-ray microanalyzer. UV-VIS spectrum of the codeposited film consisting of Mg(II)-taPc, 4-hph-PTC and Zn^{2+} is shown in Figure 4.6. The absorption bands in the region between 300 and 400 nm and the region between 670 and 750 nm were assigned to B- and Q-band of Mg(II)-taPc, respectively. On the other hand, the band between 400 and 550 nm was ascribed to 4-hph-PTC. The fact that the codeposited film takes up the light in almost all visible region would assist the effective photogeneration of charge carriers and explain that the cathodic photocurrent was due to tunneling effect at the *p-n* junction interfaces because excitation light was irradiated from ITO side.

In conventional double-layered *p-n* junction diodes, the excitation light is considerably absorbed by either *p*- or *n*-type semiconductor directed to light source before the light reaches to the *p-n* junction interface. On the other hand, in the present device, both *p* and *n*-type semiconductors absorb the excitation energy

Chapter 4 Preparation of electro-codeposited film

from light source. The direct reaching of excitation energy to both *p*- and *n*-type semiconductors would cause the effective excitation of charge carriers at *p-n* junction interface.

It was confirmed by SEM observation that the codeposited film consisting of Mg(II)-taPc, 4-hph-PTC and Zn²⁺ has a comparatively flat surface. Furthermore, in the measurement of complex impedance for the present device based on the codeposited film, the Cole-Cole plot converged to the origin on the complex impedance plane in high frequency region as shown in Figure 4.7. These results suggest that the contact resistance of the interface between aluminum electrode and the codeposited film is almost negligible. The low resistance of aluminum contact to the codeposited film would support the excellent rectification of the present device under dark condition.

4.4 CONCLUSION

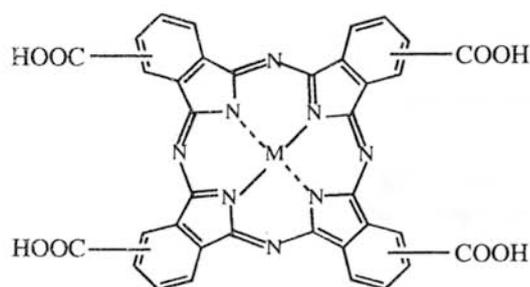
A homogeneous codeposited film consisting of Mg(II)-taPc, 4-hph-PTC and Zn²⁺ was obtained on ITO electrode by cathodical polarization of the DMF solution containing Mg(II)-taPc, 4-hph-PTC and ZnCl₂ as a supporting electrolyte. It was shown that both the bridging metal ion in codeposited film and the difficulty of electrodeposition of monomers were important factors for electro-codeposition. From UV-VIS spectrum of the codeposited film and the current-voltage characteristics of the present device, it was suggested that a number of *p-n* junction interfaces were distributed on the ITO electrode. The device based on the codeposited film exhibited photoconduction under both forward and reverse biased condition. It was suggested that the effective excitation of charge carriers were occurred by the directly reaching of excitation light to both *p*- and *n*-type semiconductors and tunneling effect was effectively occurred at *p-n* junction interfaces because of the decrease of depth of depletion layer.

4.5 REFERENCES

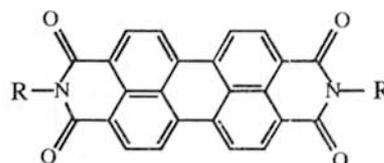
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Table 4.1. Aspects of codeposited films

Semiconductor combination	Supporting electrolyte	Bridging metal ion	Aspect
Mg(II)-taPc/2-hph-PTC	CaCl ₂	Ca ²⁺	two regions exist
Mg(II)-taPc/3-hph-PTC	CaCl ₂	Ca ²⁺	heterogeneous
Mg(II)-taPc/4-hph-PTC	CaCl ₂	Ca ²⁺	heterogeneous
Mg(II)-taPc/2-hph-PTC	ZnCl ₂	Zn ²⁺	two regions exist
Mg(II)-taPc/3-hph-PTC	ZnCl ₂	Zn ²⁺	heterogeneous
Mg(II)-taPc/4-hph-PTC	ZnCl ₂	Zn ²⁺	homogeneous
Co(II)-taPc/2-hph-PTC	CaCl ₂	Ca ²⁺	two regions exist
Co(II)-taPc/3-hph-PTC	CaCl ₂	Ca ²⁺	two regions exist
Co(II)-taPc/4-hph-PTC	CaCl ₂	Ca ²⁺	two regions exist
Co(II)-taPc/2-hph-PTC	ZnCl ₂	Zn ²⁺	only phthalocyanine exists
Co(II)-taPc/3-hph-PTC	ZnCl ₂	Zn ²⁺	phthalocyanine dominantly exists
Co(II)-taPc/4-hph-PTC	ZnCl ₂	Zn ²⁺	only phthalocyanine exists



Pc (M = Mg or Co)



hph-PTC (R = ,  or )

Figure 4.1 Molecular structures of M(II)-taPc and hph-PTC.

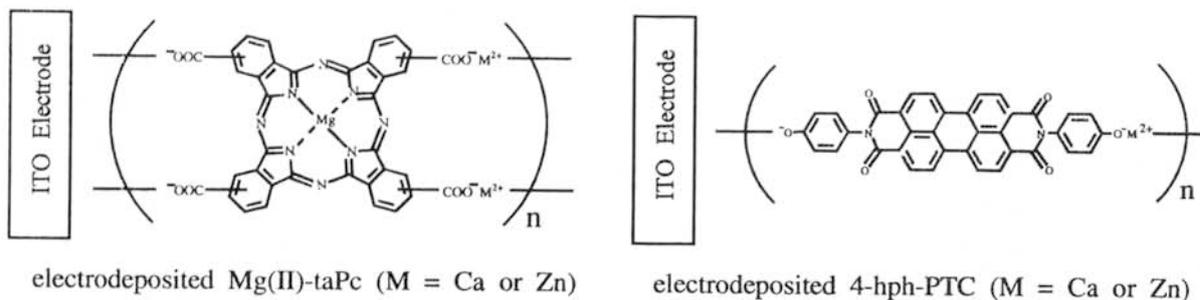


Figure 4.2 Chemical structures of electrodeposited Mg(II)-taPc and 4-hph-PTC.

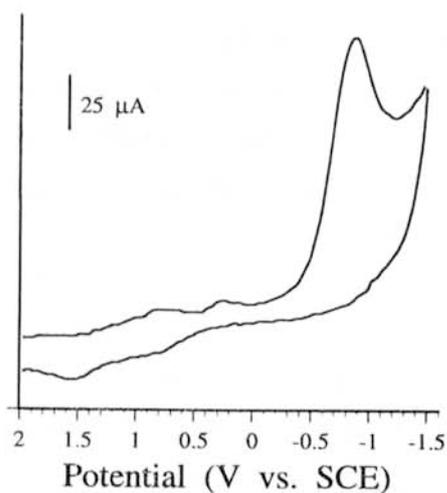


Figure 4.3 Cyclic voltammogram of codeposited film consisting of Mg(II)-taPc, 4-hph-PTC, and Zn²⁺ on ITO electrode in DMF solution of 1 × 10⁻³ M ZnCl₂ at a scan rate of 50 mV/s.

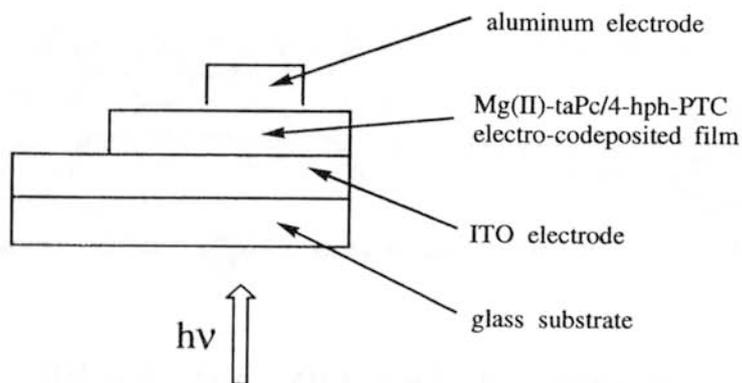


Figure 4.4 Schematic representation of device.

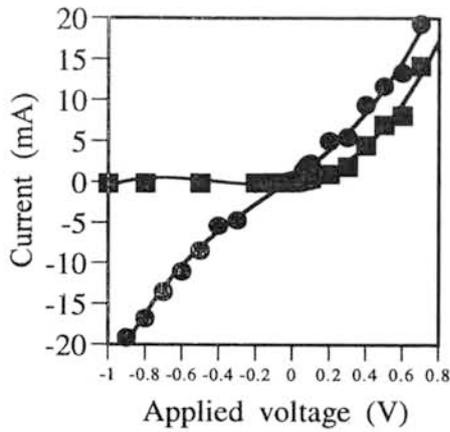


Figure 4.5 Current-voltage characteristic of the device based on codeposited film consisting of Mg(II)-taPc, 4-hph-PTC, and Zn^{2+} under dark condition (■) and light irradiation (●). The positive voltage is when aluminum is connected to a negative polarity.

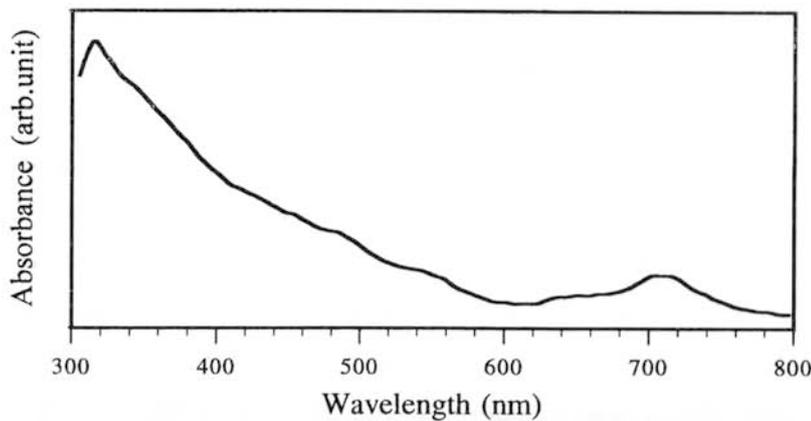


Figure 4.6 UV-VIS spectrum of codeposited film consisting of Mg(II)-taPc, 4-hph-PTC, and Zn^{2+} on ITO electrode.

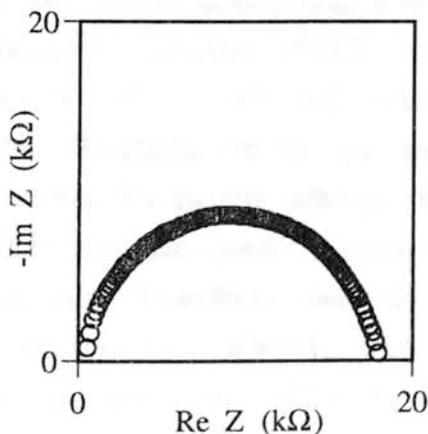


Figure 4.7 Cole-Cole plot of the device based on codeposited film consisting of Mg(II)-taPc, 4-hph-PTC, and Zn^{2+} , applying +0.5 V to the device. The positive voltage is when aluminum is connected to a negative polarity.

CHAPTER 5

Gas-sensors based on electrodeposited metallophthalocyanine film

2,9,16,23-Tetracarboxyphthalocyaninatocopper(II) [Cu(II)-taPc] and 2,9,16,23-tetracarboxyphthalocyaninatocobalt(II) [Co(II)-taPc] films on indium/tin oxide (ITO) coated glass electrodes were prepared by cathodical polarization of the electrolytic solution containing Cu(II)- or Co(II)-taPc and CaCl₂ as a supporting electrolyte with a constant current. Cu(II)-taPc film was deposited on ITO electrode from dimethyl sulfoxide (DMSO) solution containing Cu(II)-taPc and CaCl₂, while Co(II)-taPc film was deposited from N,N-dimethylformamide (DMF) solution containing Co(II)-taPc and CaCl₂. Gas-sensors based on M(II)-taPc film (M = Cu or Co) were fabricated by the formation of silver electrode on top of the M(II)-taPc film. The performance of the present gas-sensors is based on the change of electrical conductivity which is affected by the adsorption of acceptor gases such as NO₂ and SO₂ on the surface of the M(II)-taPc film. It was confirmed that the present gas-sensors were detectable to ppm levels of NO₂ or SO₂.

5.1 INTRODUCTION

Metallophthalocyanines (Mt-Pc) have attracted considerable interest because of their *p*-type semiconduction [1-5]. Electronic properties of Mt-Pc were the subject of numerous investigations, particularly their electronic conductivity [6-7], photovoltaic effects [1-2], electrochromic properties [8-10], and gas-detecting properties [11-27].

Many investigators have reported that the adsorption of gases on the surfaces of semiconductors can generate a marked effect on the electrical conductivity of semiconductors [28]. In particular, the electrical conductivity of organic semiconductors such as phthalocyanines can change by many orders of magnitude when a gas is adsorbed on the surfaces of organic semiconductors. The change of electrical conductivity makes the organic semiconductors be ideal for detecting very low concentrations of pollutants [14-15]. When an acceptor gas is adsorbed on the surface of *p*-type semiconductor, electron transfer from the *p*-type semiconductor to the acceptor gas can be occurred [28].

It is desirable, from the point of view of providing cheap instrumentation, that the fabrication of gas-sensors based on organic semiconductor such as phthalocyanine is easy and inexpensive.

Shirai et al. have already reported the method of the preparation of 2,9,16,23-tetracarboxyphthalocyanine film on indium/tin oxide (ITO) coated glass electrodes by electrodeposition [9]. This chapter concerns the gas-detecting properties of the gas-sensors based on 2,9,16,23-tetracarboxyphthalocyaninatocopper(II) [Cu(II)-taPc] or 2,9,16,23-tetracarboxyphthalocyaninatocobalt(II) [Co(II)-taPc] film on ITO electrode.

5.2 EXPERIMENTAL

5.2.1 Materials

Cu(II)- and Co(II)-taPc were prepared according to the method which was reported for Co(II)-taPc previously [29]. A reaction mixture consisting of 3.00 g (1.6×10^{-2} mol) of trimellitic anhydride, 0.50 g (3.7×10^{-3} mol) of copper chloride or 0.50 g (3.8×10^{-3} mol) of cobalt chloride, 10.0 g (1.7×10^{-1} mol) of urea, and 0.20 g (1.6×10^{-4} mol) of ammonium molybdate was

poured into a separable flask and heated at 200°C for 20 min, stirring quickly the mixture. The residue was poured into 500 ml of water and then the solution was filtered off. After extraction in a Soxhlet for 24 h with water, the residue was poured into 150 ml of 50 wt% KOH aqueous solution and then the solution was refluxed at 80°C for 24 h. The precipitate was filtered off and extracted with water. A 6 M HCl aqueous solution was dropped into the alkaline solution until the pH of the solution was changed into 2, and then the resulting precipitate was filtered off. After extraction in a Soxhlet for 24 h with methanol, the product was dried *in vacuo* at room temperature. Cu(II)-taPc: yield 0.40 g (14 %); UV-VIS (DMSO) λ_{\max} 340 (B-band for Pc), 620, and 680 nm (Q-band for Pc); IR (KBr) 1698 cm^{-1} ($\nu_{\text{C-O}}$). Anal. Calcd for Cu in Cu(II)-taPc: Cu, 8.78%. Found: Cu, 8.81%. Co(II)-taPc: yield 0.39 g (14 %); UV-VIS (DMF) λ_{\max} 330 (B-band for Pc) and 680 nm (Q-band for Pc); IR (KBr) 1698 cm^{-1} ($\nu_{\text{C-O}}$). Anal. Calcd for Co in Co(II)-taPc: Co, 8.21%. Found: Co, 8.28%.

Dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were distilled under reduced pressure before use. CaCl_2 , acetone, and silver were of analytical grade from commercial origin.

5.2.2 Preparation of Cu(II)- and Co(II)-taPc films on ITO electrodes

The Cu(II)-taPc film containing Ca^{2+} as bridging metal ion on ITO electrode was prepared by the method of cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of Cu(II)-taPc (3×10^{-4} M) and CaCl_2 (1×10^{-3} M) as a supporting electrolyte in dry DMSO was poured into the electrolytic cell including ITO working electrode and platinum counter electrode. The Cu(II)-taPc film containing Ca^{2+} as bridging metal ion on the ITO electrode was prepared by cathodical polarization of the DMSO solution containing Cu(II)-taPc and CaCl_2 with a constant current of $-35 \mu\text{A}/\text{cm}^2$ for 30 min, stirring slowly the electrolytic solution. The deposited film was washed with acetone.

The Co(II)-taPc film containing Ca^{2+} as bridging metal ion on ITO electrode was also prepared by the method of cathodic electrolytic deposition. A mixture of Co(II)-taPc (3×10^{-4} M) and CaCl_2 (1×10^{-3} M) as a supporting electrolyte in dry DMF was poured into the electrolytic cell including ITO working electrode and platinum counter electrode. The Co(II)-taPc film containing Ca^{2+} as bridging metal ion on the ITO electrode was prepared by cathodical polarization of the

DMF solution containing Co(II)-taPc and CaCl₂ with a constant current of $-35 \mu\text{A}/\text{cm}^2$ for 30 min, stirring slowly the electrolytic solution. The deposited film was washed with acetone.

5.2.3 Fabrication of gas-sensors based on Cu(II)- or Co(II)-taPc film

Gas-sensors based on Cu(II)- or Co(II)-taPc film were fabricated by the formation of silver electrode on top of the films. Silver was deposited by sublimation under pressure of $1.3 \times 10^3 \text{ Pa}$.

5.2.4 Measurements

UV-VIS spectra for Cu(II)- and Co(II)-taPc were measured with a JASCO UV/DEC-505 UV/VIS digital spectrophotometer. IR spectra for Cu(II)- and Co(II)-taPc were measured with a JASCO FT/IR-7300 Fourier Transform Infrared Spectrometer using KBr disk. Atomic absorption spectrometry for central metal in M(II)-taPc (M = Cu or Co) were carried out with a HITACHI 180-50 Atomic Absorption Spectrophotometer. The concentrations of NO₂ and SO₂ were controlled by GASTEC Permeator PD-1B, generating NO₂/N₂ or SO₂/N₂ mixtures with a GASTEC Permeation Tubes P-9-1 and P-5-H. The dependence of current change of the gas-sensors on the gas concentration was measured with an ADVANTEST R8340 Ultra High Resistance Meter. A computer interfaced Hewlett Packard 4192A LF Impedance Analyzer was used to measure the complex impedance of the gas-sensors, applying a bias voltage of 0.1 V to the gas-sensor. The surface structures and thickness of Cu(II)- and Co(II)-taPc films were examined with a HITACHI S-2380N Scanning Electron Microscope (SEM).

5.3 RESULTS AND DISCUSSION

The chemical structure of M(II)-taPc films on ITO electrodes is shown in Figure 5.1. The monomer of M(II)-taPc is polymerized by bridge formation with bivalent metal ion in the electrodeposited M(II)-taPc film [9].

The configuration of the present gas-sensors and the measurement system is schematically depicted in Figure 5.2. When acceptor gases such as NO₂ and SO₂ are adsorbed on the surface of M(II)-taPc film as *p*-type semiconductor, electron

transfer from the M(II)-taPc film to the acceptor gases can be occurred and the electric conductivity of the M(II)-taPc film is increased by the generation of holes which contribute to the electric conduction of *p*-type semiconductor [28]. It was confirmed by current-voltage measurements that both the junction interface between ITO electrode and M(II)-taPc film and the junction interface between M(II)-taPc film and silver electrode formed Ohmic contacts. The ohmic contacts are preferable for the detection of gases at low applied voltage since charge carriers are easily passed through the interface of semiconductor and electrode even at low applied voltage if Ohmic contact is formed at the junction interface between semiconductor and electrode. In the present gas-sensors, the contribution of ionic conduction by Ca^{2+} which is originated from supporting electrolyte in electrodeposition is negligible because Ca^{2+} acts as bridging metal ion in M(II)-taPc film. That is, Ca^{2+} as bridging metal ion cannot migrate in M(II)-taPc film. Actually, in the complex impedance measurements for the present devices, the resistance assigned to the ionic conductivity by Ca^{2+} was not observed. In the present gas-sensors, the mechanism of detection of gases which are adsorbed on the surface of M(II)-taPc film can be explained by only the charge transfer interaction between M(II)-taPc film and the adsorbed gases.

Cu(II)-taPc is soluble to DMSO but insoluble to DMF, while Co(II)-taPc is soluble to both solvents. Cu(II)-taPc film was deposited on ITO electrode from the DMSO solution containing Cu(II)-taPc and CaCl_2 , while Co(II)-taPc film was deposited from the DMF solution containing Co(II)-taPc and CaCl_2 . In the electrodeposition of Co(II)-taPc film, DMF was selected as electrolytic solvent because DMF has the higher conductivity than that of DMSO [30]. Actually, considerably homogeneous Co(II)-taPc film was obtained when DMF was used as electrolytic solvent. On the other hand, thin Co(II)-taPc film was obtained when DMSO was used as electrolytic solvent. In the device based on the Co(II)-taPc film deposited from DMSO solution, current was unstable and irreproducible.

The aspect of surface of Co(II)-taPc film deposited from DMF solution was more homogeneous than that of Cu(II)-taPc film. The thickness of these films was approximately 200 μm . It was confirmed that UV-VIS spectrum for Cu(II)-taPc in DMSO had the absorption peaks at around 620 and 690 nm on Q-band for phthalocyanine derivative, while that of Co(II)-taPc in DMF had only one peak at around 690 nm on Q-band. Since the absorption peak at around 620 nm and that at around 690 nm are assigned to aggregates and non-aggregates for phthalocyanine derivative [29], it seems that considerable amounts

of aggregates of Cu(II)-taPc existed in DMSO while non-aggregates of Co(II)-taPc dominantly existed in DMF. The formation of aggregates of Cu(II)-taPc in the DMSO solution would cause the difference in aspect between the surface of Cu(II)-taPc film and that of Co(II)-taPc film.

UV-VIS spectra for Cu(II)- and Co(II)-taPc films formed on ITO electrodes by electrodeposition are shown in Figure 5.3.

In both films, it was confirmed that the aggregates of M(II)-taPc dominantly existed on the electrodeposited films. The formation of the aggregates would assist the chemical stabilization of M(II)-taPc. That is, the sensing performance of the gas-sensors based on M(II)-taPc film to NO₂ or SO₂ gas was not degraded for several months even if the gas-sensors had been left in air.

The investigation of the effects of NO₂ and SO₂ gases on the conductivity of Cu(II)- and Co(II)-taPc films was carried out at room temperature, applying 0.1 V of voltage to the gas-sensor based on Cu(II)- or Co(II)-taPc film. The effects of low concentrations of NO₂ and SO₂ are shown in Figure 5.4. The dependence of current change on the concentrations of these acceptor gases were almost linear. It is thought that the current changes of the gas-sensors were not saturated since the concentrations of the acceptor gases were very low. The current increase of the gas-sensor based on Cu(II)-taPc film was larger than that of the gas-sensor based on Co(II)-taPc film.

In the previous gas-sensors which were fabricated by vacuum-deposition, solvent-casting, or Langmuir-Blodgett technique, the high resistance of organic semiconductors decreased the electric conductivity [12-20, 24, 26]. The electric conductivity of the present gas-sensors was about 10³ S/cm which is considerably higher than the value of electric conductivity of sublimed phthalocyanines [14]. The high conductivity of the present gas-sensors is attributed to the existence of considerable amounts of the bridging metal ion in M(II)-taPc films since the electrodeposited films with dopant have a metallic high conductivity [31].

The variations of current of the gas-sensors based on Cu(II)- or Co(II)-taPc film with time in introducing 3 ppm NO₂ or SO₂ were examined. The response time of the present gas-sensors to the gases was measured to be about 10 min. The comparatively long response time suggests that the adsorption of gas molecules on the surfaces of M(II)-taPc films are slower than that on the surfaces of sublimed or casted phthalocyanines [14, 19, 24].

After adsorbing the gases on the surfaces of M(II)-taPc films, heating the

gas-sensors at 100°C for 2 h was necessary for returning the current of the gas-sensors to that before adsorbing the gases. The result suggests that the current increase of the gas-sensors based on the M(II)-taPc film is effectively enhanced by the strong adsorption of NO₂ or SO₂ molecule on the surfaces of M(II)-taPc films.

From the SEM results of the surfaces of M(II)-taPc films, it was confirmed that considerable amounts of aggregates of M(II)-taPc existed in the electrodeposited films and the surfaces were rather rough. The rugged surfaces of M(II)-taPc films would cause the area of adsorption site for the gases to be wide.

5.4 CONCLUSION

The gas-sensors based on Cu(II)- or Co(II)-taPc film exhibited large current changes by the adsorption of NO₂ or SO₂ on the surfaces of Cu(II)- or Co(II)-taPc film at room temperature. It was confirmed that the present gas-sensors were suitable for detecting low concentrations of NO₂ or SO₂ gases. It was suggested that the current increase of the gas-sensors was effectively enhanced by the strong adsorption of NO₂ or SO₂ molecule on the surfaces of M(II)-taPc films. It is thought that the area of adsorption site for the gases are considerably wide since the surfaces of M(II)-taPc films are rough.

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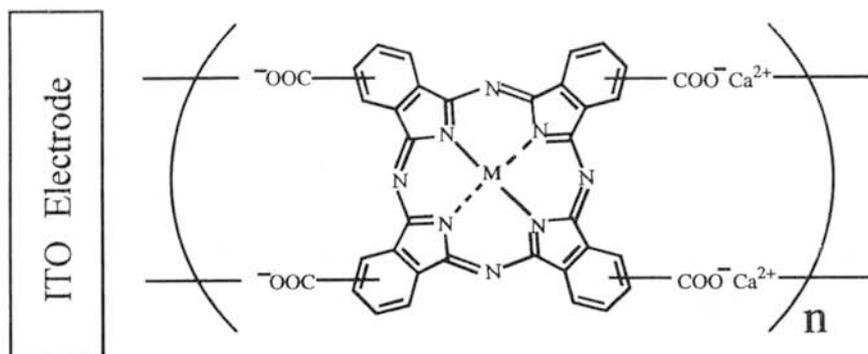


Figure 5.1 Molecular structure of electrodeposited M(II)-taPc film: M = Cu or Co.

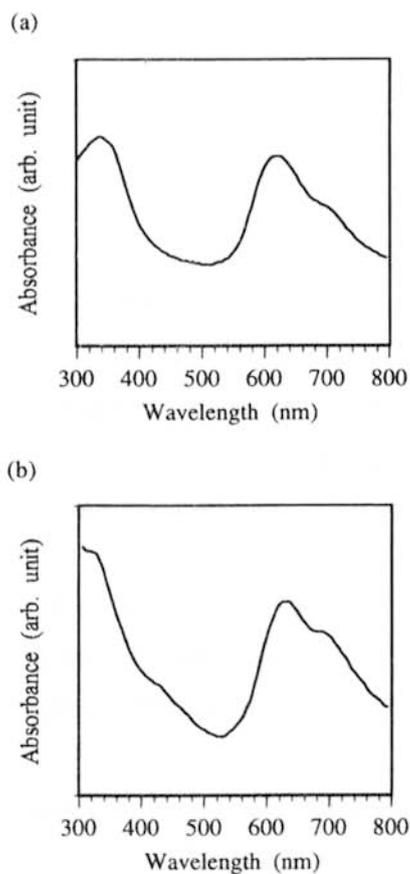


Figure 5.3 UV-VIS spectra of (a) Cu(II)-taPc film deposited from DMSO solution and (b) Co(II)-taPc film deposited from DMF solution.

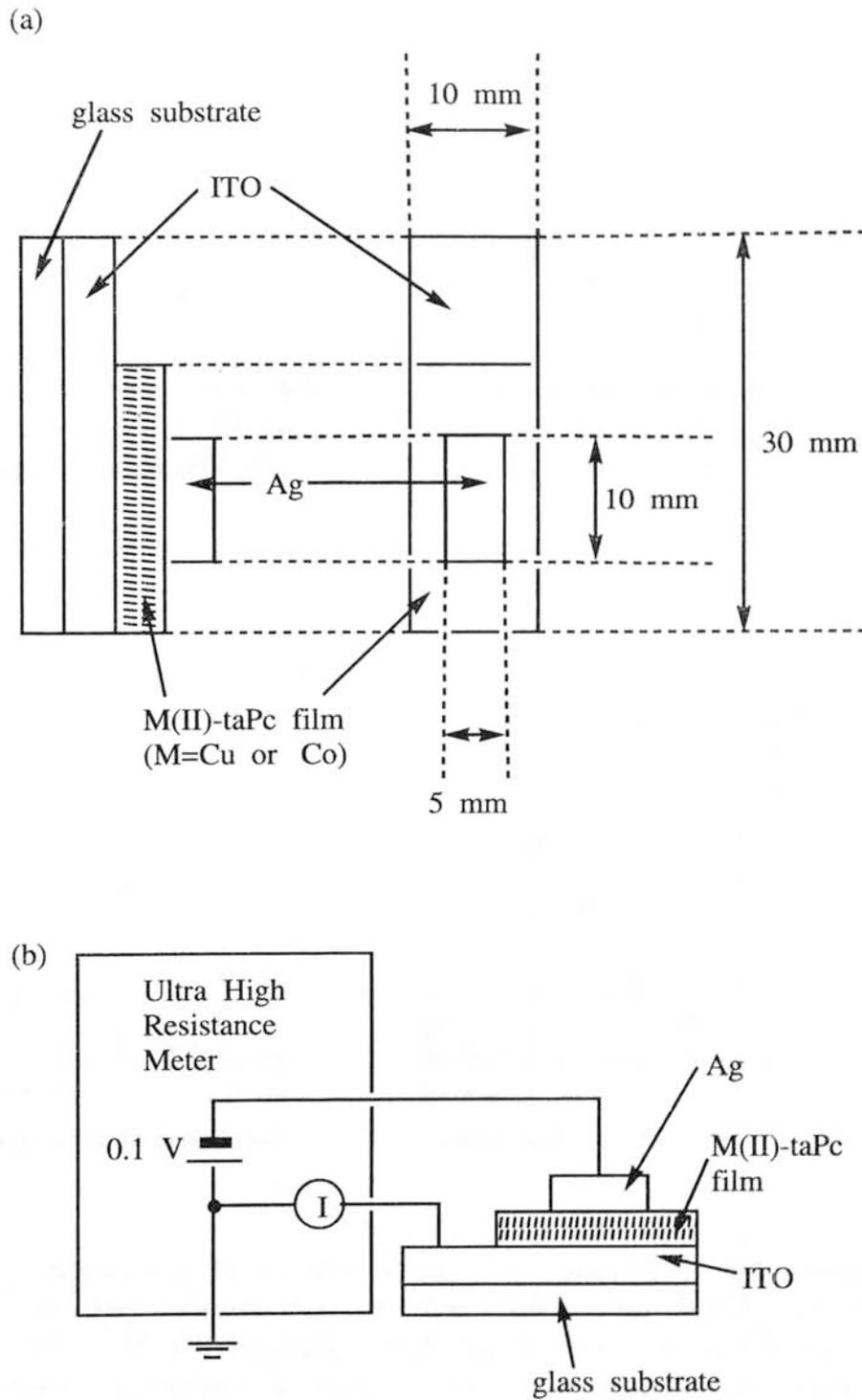


Figure 5.2 Schematic representation of (a) gas-sensor and (b) measurement system.

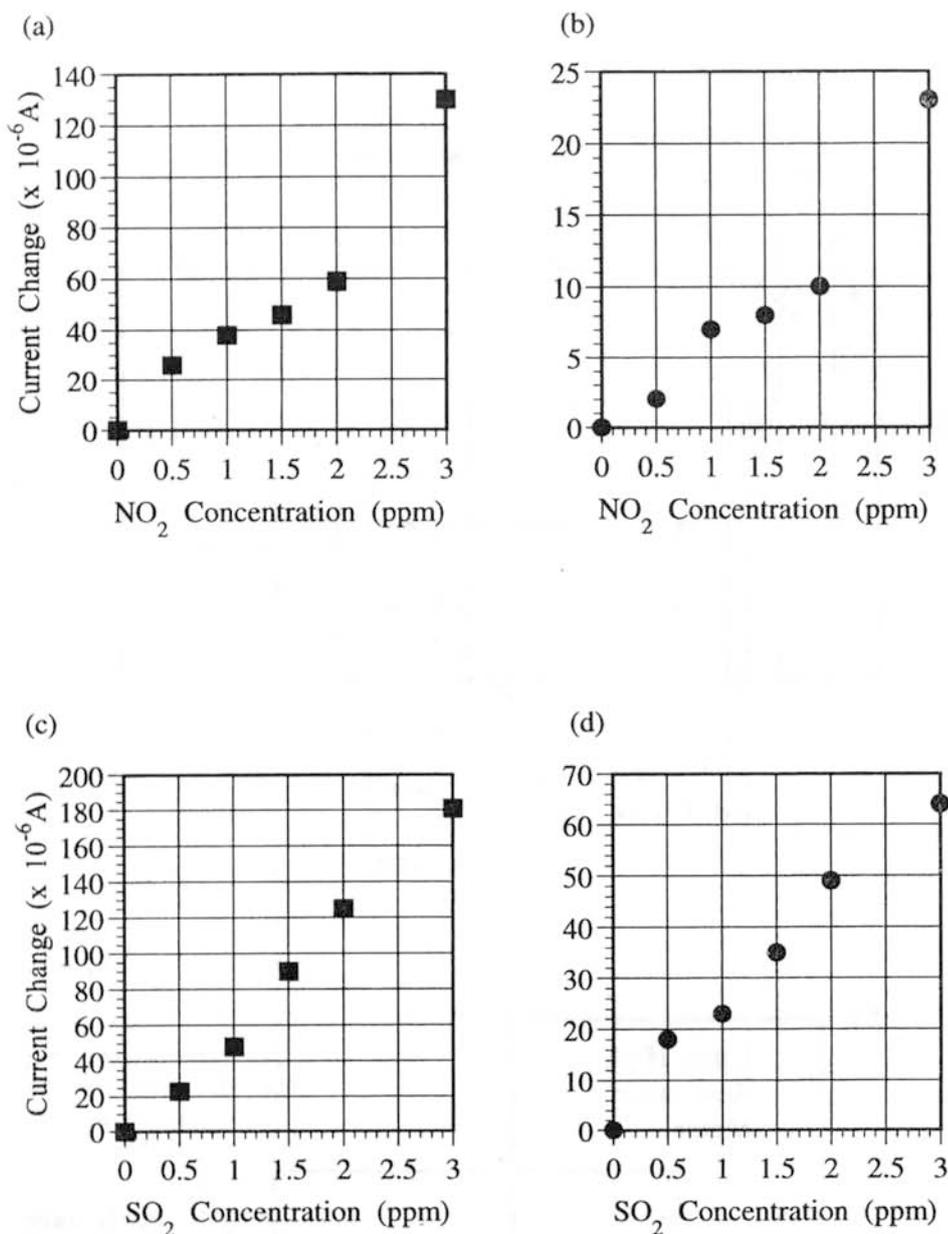


Figure 5.4 Dependence of current change of gas-sensors based on (a) Cu(II)-taPc film and (b) Co(II)-taPc film on NO₂ concentration at room temperature, applying 0.1 V to the gas-sensor; dependence of current change of gas-sensors based on (c) Cu(II)-taPc film and (d) Co(II)-taPc film on SO₂ concentration at room temperature, applying 0.1 V to the gas-sensor.

CHAPTER 6

Fabrication of gas-sensors based on electrodeposited perylene derivative

The films of perylene derivative containing the metal ions which originated from supporting electrolyte in electrodeposition, were obtained on indium/tin oxide (ITO) coated glass electrodes by cathodical polarization of the electrolytic solution of N,N'-2-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (2-hph-PTC), N,N'-3-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (3-hph-PTC), or N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (4-hph-PTC) and CaCl₂, ZnCl₂, PbCl₂, or CoBr₂ as a supporting electrolyte in N,N-dimethylformamide (DMF) with a constant current. Gas-sensors based on the electrodeposited hph-PTC film were fabricated by the formation of metal electrode on top of the hph-PTC film. The performance of the present gas-sensors is based on the change of electric conductivity which is affected by the adsorption of electron-donor gases such as H₂S and mercaptan on the surface of the hph-PTC film. It was confirmed that the present gas-sensors were detectable to low concentration of H₂S or mercaptan.

6.1 INTRODUCTION

Perylene derivatives have attracted considerable interest because of their *n*-type semiconduction [1-5] and amplification of photocurrent [6]. Since most organic pigments such as phthalocyanines act as *p*-type semiconductors [1-4], perylene derivatives as *n*-type semiconductors have attracted the attention of many investigators [1-5].

The films of the insoluble materials such as phthalocyanine and perylene derivatives have been prepared by vacuum evaporation [1-4], plasma polymerization [5], and micelle electrochemical deposition technique [7]. However, the above methods are expensive in comparison with the easier methods such as solvent casting or electrodeposition. In chapter 6, the author developed a new method for the preparation of films of perylene derivatives on indium/tin oxide (ITO) coated glass electrodes by electrodeposition from the N,N-dimethylformamide (DMF) solutions containing N,N'-hydroxyphenyl-3,4,9,10-perylenetetra-carboxylic diimide (hph-PTC) and supporting electrolyte.

Furthermore, the application of the electrodeposited hph-PTC films to electronic device was investigated. The gas-sensors based on the electrodeposited hph-PTC film were fabricated by the formation of metal electrode on the surface of the hph-PTC film. When electron-donor gases such as H₂S and mercaptan are adsorbed on the surface of *n*-type semiconductor, electron transfer from the donor gases to the *n*-type semiconductor can be occurred [8]. The gas-detecting performance of the present gas-sensors is originated from the electron transfer. That is, the electric conductivity of the present gas-sensors is increased by multiplication of conduction electrons which act as charge carriers in the hph-PTC film as *n*-type semiconductor.

This chapter concerns the preparation of electrodeposited hph-PTC films and the performance of the gas-sensors based on the hph-PTC film.

6.2 EXPERIMENTAL

6.2.1 Materials

N,N'-2-hydroxyphenyl-3,4,9,10-perylenetetra-carboxylic diimide (2-hph-PTC), N,N'-3-

hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (3-hph-PTC), and N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetracarboxylic diimide (4-hph-PTC) were prepared on the basis of the method by Rademacher et al [9]. A reaction mixture consisting of 0.68 g (1.7×10^{-3} mol) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 0.50 g (4.6×10^{-3} mol) of 2-, 3-, or 4-aminophenol, and 0.50 g (2.4×10^{-3} mol) of zinc acetate suspended in 30 ml of quinoline was refluxed for 2 h. The resulting precipitate was filtered off and recrystallized extractively from toluene. The red-purple crystalline 2-, 3-, or 4-hph-PTC was washed with methanol and dried *in vacuo* at room temperature.

DMF was distilled under reduced pressure before use. CaCl_2 , ZnCl_2 , PbCl_2 , CoBr_2 , acetone, aluminum and silver were of analytical grade from commercial origin.

6.2.2 Electrodeposition of hph-PTC films on ITO electrodes

The electrodeposited hph-PTC films on ITO electrodes were prepared by the method of cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of 2-, 3-, or 4-hph-PTC (5×10^{-4} M) and CaCl_2 , ZnCl_2 , PbCl_2 , or CoBr_2 (1×10^{-3} M) as a supporting electrolyte in dry DMF was poured into the electrolytic cell including ITO working electrode and platinum counter electrode. The 2-, 3-, and 4-hph-PTC films on the ITO electrodes were obtained by cathodical polarization of the electrolytic solution with a constant current of $-35 \mu\text{A}/\text{cm}^2$ for 30 min. The phenomena will be described with the reason in Results and Discussion. The deposited films were washed with acetone.

6.2.3 Fabrication of gas-sensors based on hph-PTC film

Gas-Sensors based on hph-PTC film were fabricated by the formation of metal electrode on top of the films. Aluminum or silver was deposited by vacuum evaporation under pressure of 1.3×10^{-3} Pa.

6.2.4 Measurements

UV-VIS spectra for hph-PTCs were measured with a Jasco UVVIDEC-505 UV/VIS digital spectrophotometer. Cyclic voltammetry for hph-PTCs were carried out in the electrolytic cell including ITO working electrode, platinum counter electrode and saturated calomel electrode (SCE) as a reference electrode, using a Yanaco P-1100 polarographic analyzer. Elemental analyses were carried out with a

HORIBA energy-dispersive X-ray microanalyzer, EMAX-5770W. The surface structure and thickness of the hph-PTC films on ITO electrodes were examined with a HITACHI S-2380N Scanning Electron Microscope (SEM). The concentrations of H₂S and CH₃SH were controlled by GASTEC Permeater PD-1B, generating diluted gases with a GASTEC Permeation Tubes P-4 and P-71-5. The dependence of current change of the gas-sensors on the gas concentration was measured with an ADVANTEST R8340 Ultra High Resistance Meter.

6.3 RESULTS AND DISCUSSION

The chemical structures of the monomers of hph-PTCs are shown in Figure 6.1.

The hph-PTCs are electropolymerizable because these compounds have hydroxyphenyl groups [10]. Electrochemical polarization leads to dissociation of the terminal hydroxyl groups, and then the electropolymerization can be occurred on the surface of working electrode. In the electrodeposition of 2-hph-PTC, homogeneous 2-hph-PTC films containing the metal ions which are originated from supporting electrolyte were obtained without stirring the electrolytic solution. On the other hand, in the electrodeposition of 3- or 4-hph-PTC, heterogeneous hph-PTC films were deposited when the electrolytic solution was not stirred since 3- or 4-hph-PTC are poorly soluble in DMF. Therefore, in the electrodeposition of 3- or 4-hph-PTC, the slow stirring of the electrolytic solution was essential to take homogeneous hph-PTC films.

Most of compounds which have hydroxyl group are polymerized by anodical polarization [10]. However, the electrodeposited hph-PTC films were prepared by not anodical but cathodical polarization. The result would be explained by the fact that perylene derivatives are easily reduced because these compounds are *n*-type semiconductors whose electrical conductivity is increased by accepting electrons. That is, high electric conductivity of monomers is necessary for electropolymerization [10]. Actually, hph-PTCs were easily reduced, but oxidation of hph-PTCs was not observed in the cyclic voltammograms for the DMF solutions containing hph-PTC and CaCl₂ as a supporting electrolyte. The reduction of hph-PTCs starts at about -0.5 V vs. SCE.

The cyclic voltammetric measurements for the hph-PTC films on ITO

electrodes were also carried out in order to expect the type of electrical conduction of the hph-PTC films. Only the reduction of hph-PTC films was observed and the oxidation was not observed in the cyclic voltammograms of hph-PTC films on ITO electrodes in the DMF solution of 1×10^{-3} M CaCl_2 . The results explain that the electrodeposited hph-PTC films are easily reduced to give the electrically conducting *n*-doped materials, but oxidation of hph-PTC films are not easy. Namely, it is thought that the hph-PTC films act as *n*-type semiconductors [11]. Actually, ohmic contact was formed at the junction interface between hph-PTC film and aluminum which has low work function, while rectifying barrier were formed at the interface between hph-PTC film and silver which has high work function.

UV-VIS spectra for the hph-PTC films on ITO electrodes were examined. It was confirmed that the spectra of the hph-PTC films had the absorption band in the region between 400 and 600 nm irrespective of the kinds of hph-PTC and metal ion in hph-PTC film. The result explains that the polymers of perylene derivatives were obtained on ITO electrodes by the electrodeposition [9].

The aspects of electrodeposited hph-PTC films on ITO electrodes are summarized in Table 6.1.

The 3-hph-PTC and 4-hph-PTC films were homogeneously prepared by cathodical polarization of the DMF solutions containing hph-PTC and CaCl_2 , ZnCl_2 , PbCl_2 , or CoBr_2 as a supporting electrolyte. On the other hand, in the electrodeposition of 2-hph-PTC, homogeneous hph-PTC film was obtained when CaCl_2 , ZnCl_2 , or CoBr_2 was used as a supporting electrolyte. Especially, the thick 2-hph-PTC film was obtained using CaCl_2 as a supporting electrolyte. The thickness of 2-hph-PTC film containing Ca^{2+} was about 200 μm , while the thickness of other hph-PTC films listed in Table 6.1 was about 100 μm . However, when PbCl_2 was used as a supporting electrolyte in electrodeposition, heterogeneous 2-hph-PTC film was deposited on ITO electrode. These results suggest that both the solubility of hph-PTC in DMF and the kind of metal ion which is originated from supporting electrolyte are important factors for the preparation of the homogeneous hph-PTC film. It is thought that the deposition of Pb^{2+} on ITO electrode is difficult since Pb is heavier and thus less movable. In the electrodeposition of 3- or 4-hph-PTC, it can be expected that the deposition of Pb^{2+} on ITO electrode is comparatively easy because Pb^{2+} is easily migrated by stirring the electrolytic solution. On the other hand, in the electrodeposition of 2-hph-PTC using PbCl_2 as a supporting electrolyte, the

deposition of Pb^{2+} on ITO electrode would be difficult since the electrodeposition is done without stirring the electrolytic solution. When the electrolytic solution containing 2-hph-PTC and $PbCl_2$ as a supporting electrolyte was stirred during the electrodeposition, heterogeneous 2-hph-PTC film was deposited on ITO electrode. It seems that 2-hph-PTC is diffused into the stirred electrolytic solution before deposits on ITO electrode. This would be due to the good solubility of 2-hph-PTC in DMF.

Since Ca, Zn, and Co are more reactive, it is thought that the supporting electrolytes containing one of these metals are appropriate for the electrodeposition. Actually, in the electrodeposition using $CaCl_2$, $ZnCl_2$, or $CoBr_2$ as a supporting electrolyte, homogeneous hph-PTC films were obtained on ITO electrodes irrespective of the kind of hph-PTC (Table 6.1).

Furthermore, hph-PTC film was not obtained on ITO electrode from the DMF solutions containing hph-PTC and a supporting electrolyte of univalent metal ion such as Li^+ and Na^+ . The result suggests that divalent metal ions are necessary for the electrodeposition of hph-PTC and the monomers of hph-PTC are cross-linked by the divalent metal ions at the peripheral hydroxyl groups in hph-PTC. The existence of M^{2+} ($M = Ca, Zn, Pb$ or Co) in hph-PTC films was confirmed for each film by X-ray microanalyzer.

The surfaces of the electrodeposited hph-PTC films were examined with SEM. The surfaces of the hph-PTC films containing Ca^{2+} were considerably rough, while those of the hph-PTC films containing other kind of metal ion were comparatively flat. It can be expected that the hph-PTC films containing Ca^{2+} are suitable for the application to the gas-sensor. The rough surfaces of the hph-PTC films containing Ca^{2+} would cause the actual surface areas for adsorption of gas to be wide.

The gas-sensors based on 2-, 3-, or 4-hph-PTC film containing Ca^{2+} were fabricated by the formation of aluminum or silver electrode on the surfaces of the hph-PTC films. Although rectifying barriers are formed at the junction interface between hph-PTC film and silver electrode as described above, silver as well as aluminum are able to be applied to the present gas-sensors because applied voltage to the gas-sensors was fixed on 0.1 V. Namely, the dependence on the value of applied voltage does not need to be taken into account. In order to prevent the degradation of gas-sensing properties, silver would be preferable as electrode material since silver is noble metal while aluminum can be easily oxidized. The configuration of the present gas-sensors is schematically

depicted in Figure 6.2.

The investigation of the effects of electron donor gases such as H₂S and mercaptan on the electric conductivity of hph-PTC films was carried out at room temperature, applying 0.1 V of voltage to the gas-sensors. The values of background current are 830 μ A for the device based on 2-hph-PTC film, 934 μ A for the device based on 3-hph-PTC film, and 1418 μ A for the device based on 4-hph-PTC film, applying 0.1 V to the devices.

The dependence of current changes of the gas-sensors based on 2-, 3-, or 4-hph-PTC film containing Ca²⁺ on the concentration of H₂S is shown in Figure 6.3. It is apparent that the dependence is almost linear irrespective of the kind of hph-PTC. It is thought that the current changes of the gas-sensors were not saturated since the concentration of H₂S was very low. The high electric conductivity of the present gas-sensors is attributed to the existence of considerable amounts of Ca²⁺ in hph-PTC films, since the electrodeposited films with dopant have a metallic high conductivity [12]. The response time of the gas-sensor based on 2-hph-PTC film to H₂S was about 10 min, while that of the gas-sensor based on 3- or 4-hph-PTC film was about 3 min. The difference of response time would be due to the difference of the surface among these hph-PTC films. Since the surface of 2-hph-PTC film was rougher than those of 3- and 4-hph-PTC films, the number of gas molecule which can adsorb on the surface of 2-hph-PTC film would be comparatively large. This would cause the time for saturation of current change of the gas-sensor based on 2-hph-PTC film to be long.

The dependence of the current changes of the present gas-sensors based on 2- or 3-hph-PTC film containing Ca²⁺ on the concentration of CH₃SH is shown in Figure 6.4. The response time of the gas-sensors to CH₃SH was about 3 min. On the other hand, the dependence of current change of the gas-sensor based on 4-hph-PTC film on the concentration of CH₃SH was not observed within the low concentration range, although the current of the gas-sensor was increased when 300 ppb CH₃SH was adsorbed on the surface of 4-hph-PTC film.

From these results, it seems that 2-hph-PTC film containing Ca²⁺ is suitable for the detection of both H₂S and mercaptan. The poor sensitivity of the gas-sensor based on 4-hph-PTC film would be due to the shortness of electrodeposited molecule. Namely, the number of gases which can adsorb on the surface of 4-hph-PTC film would be smaller than those on the surface of 2- or 3-hph-PTC film due to the weakness of adsorption of gases.

6.4 CONCLUSION

Electrodeposited hph-PTC films on ITO electrodes were obtained by cathodical polarization of the electrolytic solutions containing hph-PTC and supporting electrolyte. It was suggested that both the solubility of hph-PTC in DMF and the kind of metal ion in hph-PTC film were important factors for the electrodeposition of hph-PTC. It is thought that the electrodeposited hph-PTC films are *n*-type semiconductors. Furthermore, it was confirmed that the present hph-PTC films were suitable for the detection of H₂S or mercaptan. In particular, the gas-sensor based on 2-hph-PTC film containing Ca²⁺ exhibited an excellent property of the detection of gases. The rough surfaces of 2-hph-PTC film containing Ca²⁺ would assist the excellent gas-sensing property.

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Table 6.1 Aspects of electrodeposited hph-PTC films on ITO electrodes.

Supporting electrolyte	Monomer		
	2-hph-PTC	3-hph-PTC	4-hph-PTC
CaCl ₂	homogeneous and thick	homogeneous	homogeneous
ZnCl ₂	homogeneous	homogeneous	homogeneous
PbCl ₂	heterogeneous	homogeneous	homogeneous
CoBr ₂	homogeneous	homogeneous	homogeneous

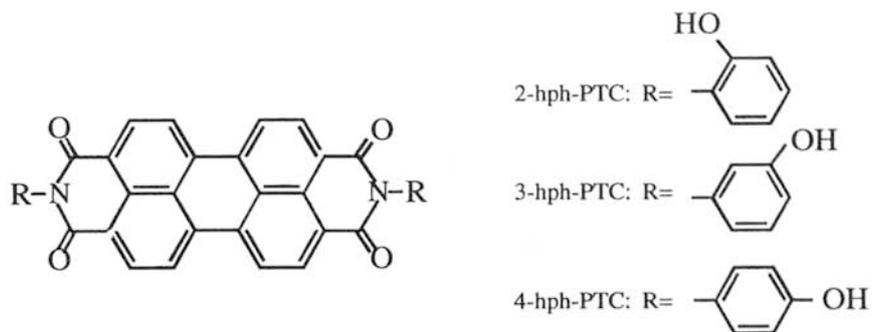


Figure 6.1 Molecular structure of hph-PTC.

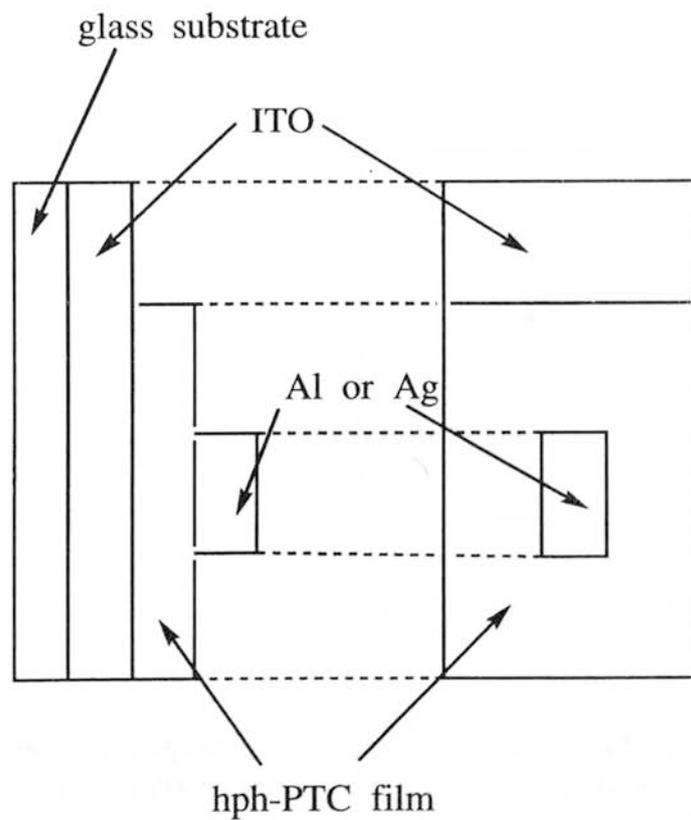


Figure 6.2 Schematic representation of gas-sensor.

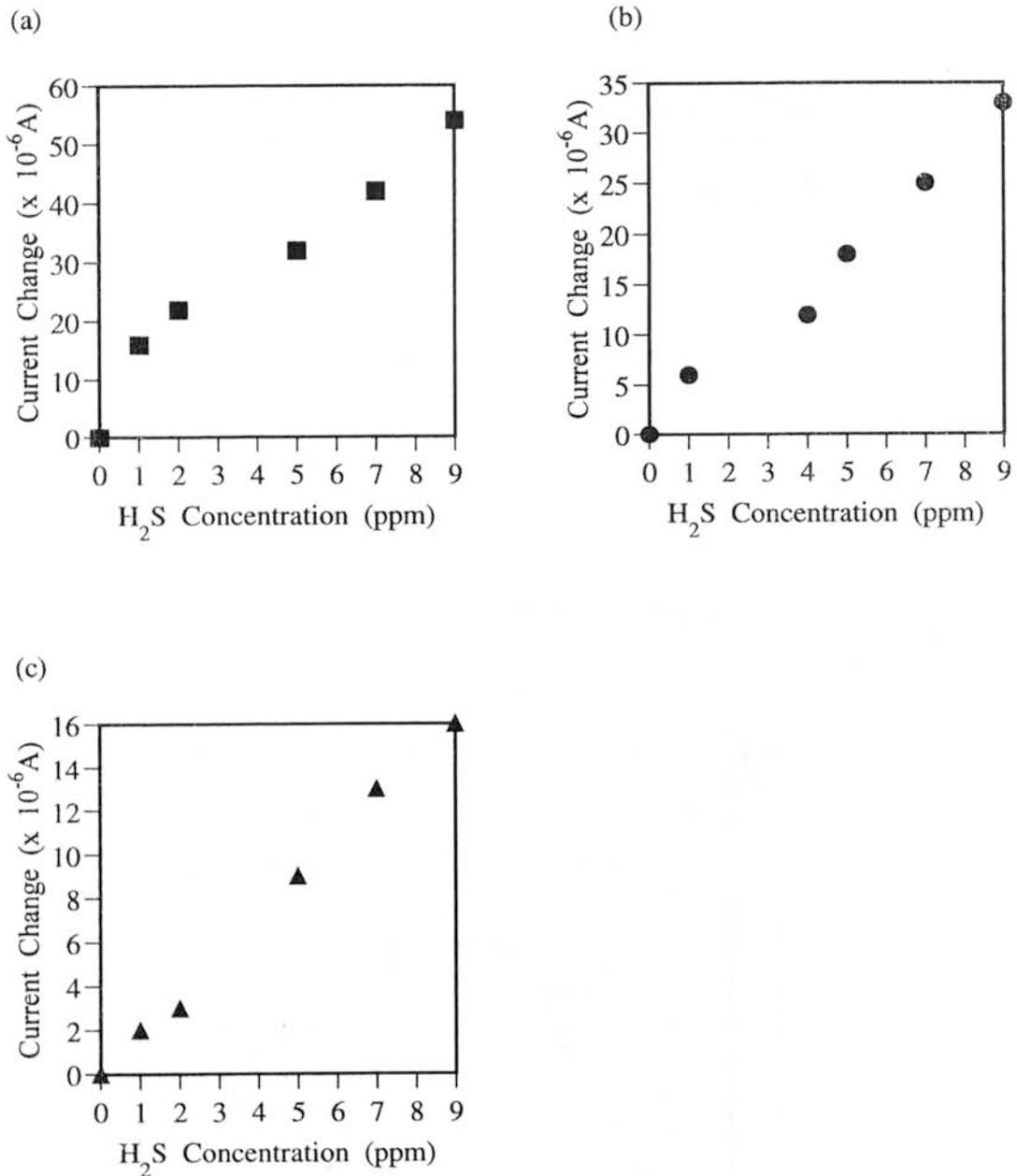


Figure 6.3 Dependence of current changes of gas-sensors based on (a) 2-hph-PTC film, (b) 3-hph-PTC film, and (c) 4-hph-PTC film on H_2S concentration at room temperature, applying 0.1 V to the gas-sensor. Silver is used as metal electrode and connected to a positive polarity.

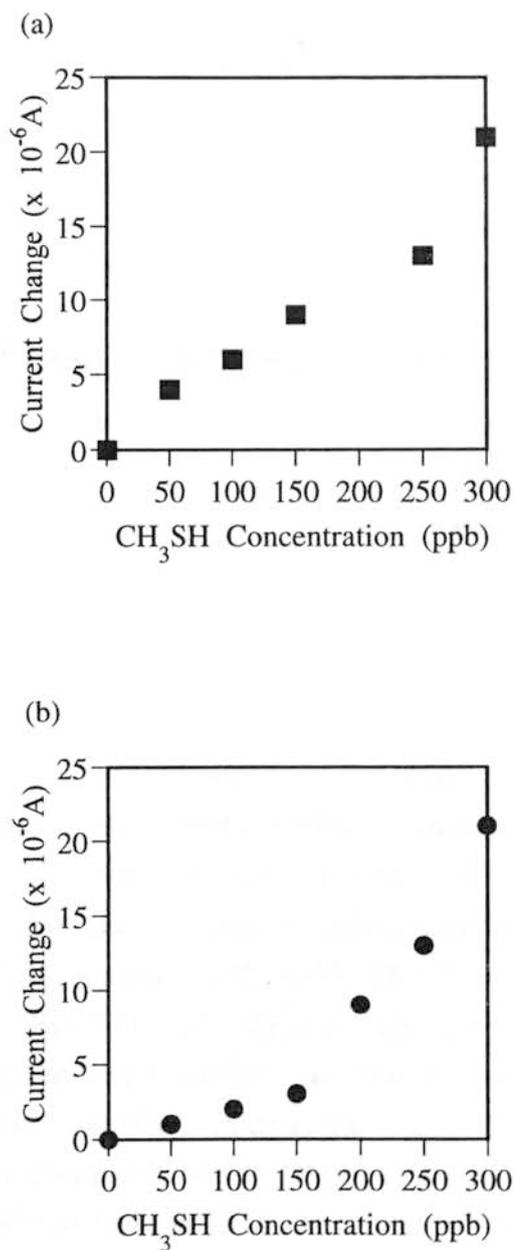


Figure 6.4 Dependence of current changes of gas-sensors based on (a) 2-hph-PTC film and (b) 3-hph-PTC film on CH₃SH concentration at room temperature, applying 0.1 V to the gas-sensor. Silver is used as metal electrode and connected to a positive polarity.

CHAPTER 7

Fabrication of electronic devices based on soluble phthalocyanine

The electronic devices based on 2,9,16,23-tetra-(2,6-dimethylphenoxy)metallophthalocyanine (TDMP-MPc) film on interlocking silver electrodes were fabricated by solvent casting from the chloroform solution containing 2,9,16,23-tetra-(2,6-dimethylphenoxy)copper, cobalt, or nickel phthalocyanine (TDMP-CuPc, TDMP-CoPc, or TDMP-NiPc). The sensing properties of the devices to the existence of NO₂ and the quantity of O₂ were investigated. It was confirmed that the gas-sensors based on TDMP-CuPc or TDMP-CoPc film were detectable to 1 ppm NO₂ at room temperature and the current responses to the existence of NO₂ and the depletion of O₂ were considerably quick. These results indicate that adsorption and desorption of NO₂ or O₂ on the surfaces of TDMP-MPc films are easily achieved at room temperature.

Moreover, the opto-electric conversion properties of the devices were also investigated. It was confirmed that narrowing the gap between one tooth and the neighbouring tooth in interlocking electrodes increased conductance and improved the opto-electric conversion property.

7.1 INTRODUCTION

The extended π -electron system in metallophthalocyanine can be interacted with electron acceptors such as NO_x and O_2 and formed charge-transfer complex [1]. Since phthalocyanines are p -type semiconductors, the electron transfer from semiconductor to gases leads to the increase of electric conductivity of phthalocyanines [2-15]. Many investigators have reported that lead, copper, cobalt, zinc, and nickel phthalocyanines are suitable for gas-sensors [7]. In this chapter, 2,9,16,23-tetra-(2,6-dimethylphenoxy)copper, cobalt, and nickel phthalocyanines (TDMP-CuPc, TDMP-CoPc, and TDMP-NiPc) were selected as the materials which respond to the presence of NO_2 or the depletion of O_2 because these phthalocyanines are easily synthesized and chemically stable.

Solvent casting is the easier and cheaper method to prepare the films of organic materials. Since TDMP-CuPc, TDMP-CoPc, and TDMP-NiPc are highly soluble to chloroform, the films of these phthalocyanines are easily prepared from the chloroform solutions of TDMP-MPc.

It has been reported that interlocking electrodes which are formed on substrates are suitable for various kinds of gas-sensors [6, 16]. However, in conventional gas-sensors which are constructed by inorganic semiconductor such as SnO_2 , sufficiently high adsorption and desorption rates of gas at room temperature have not been achieved [16-17].

In this chapter, it will be indicated that the gas-sensors based on TDMP-CuPc, TDMP-CoPc, or TDMP-NiPc film are quickly detectable to the existence of low concentration of NO_2 or the depletion of O_2 and the adsorbed gases desorb easily from the surfaces of the TDMP-MPc films at room temperature.

Moreover, phthalocyanines (Pc) attract considerable interest because of their high electrical conductivity [18-19] and optical sensing properties [20-26]. Photovoltaic cell, solar cell and photosensor based on Pc film have been fabricated by utilizing the optical sensing properties of Pc [20-26]. The electric conductivity of Pc is increased by photoexcitation because Pc is semiconductor and the number of charge carrier in Pc is increased by light irradiation [18].

It is well-known that interlocking electrodes are suitable for opto-electric conversion devices based on inorganic semiconductor such as cadmium sulfide, as for gas-sensors [16]. The length of the gap between one tooth and the neighbouring tooth in interlocking electrodes affects opto-electric conversion property.

In this chapter, the effect of narrowing the gap in interlocking electrodes on opto-electric conversion property of the devices based on TDMP-CuPc, TDMP-CoPc, or TDMP-NiPc will be described.

7.2 EXPERIMENTAL

7.2.1 Materials

4-(2,6-Dimethylphenoxy)-phthalonitrile was prepared on the basis of the method of Snow et al [27]. In a nitrogen atmosphere, 6.91 g (5.0×10^{-2} mol) of anhydrous K_2CO_3 was added to a solution of 6.11 g (5.0×10^{-2} mol) of 2,6-dimethylphenol and 4.33 g (2.5×10^{-2} mol) of 4-nitrophthalonitrile in 50 ml of dry N,N-dimethylformamide (DMF) by 1.38 g additions at 1-h intervals. The mixture was stirred for 20 h at room temperature under nitrogen. The reaction was worked up by filtering the undissolved salt and slowly adding the filtrate to a rapidly stirred 100 ml volume of water. The resulting precipitate was filtered with suction and washed with water. The crude product was recrystallized twice from methanol yielding large platelets: yield 4.35 g (70.2%); IR (KBr) 2924 (C-H in methyl), 2234 ($\nu_{C \equiv N}$), 1600 (phenyl), 1482 (phenyl), 1243 (ν_{C-O-C}), and 1086 (phenyl-O-phenyl) cm^{-1} . Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.42%; H, 4.84%; N, 11.29%. Found: C, 76.95%; H, 4.83%; N, 11.25%

TDMP-CuPc, TDMP-CoPc, and TDMP-NiPc were prepared on the basis of Wyler method [2-3, 18]. A reaction mixture consisting of 0.50 g (4.7×10^{-4} mol) of 4-(2,6-dimethylphenoxy)-phthalonitrile, 1.0 g (7.4×10^{-3} mol) of copper chloride, 1.0 g (7.7×10^{-3} mol) of cobalt chloride, or 1.0 g (7.7×10^{-3} mol) of nickel chloride, 5.0 g (9.0×10^{-2} mol) of urea, and 0.50 g (4.0×10^{-4} mol) of ammonium molybdate was poured into a separable flask and heated at 200°C for 20 min, stirring quickly the mixture. After extraction in a Soxhlet for 48 h with chloroform, chloroform was evaporated from the solution containing TDMP-MPc. The resulting residue was filtered with methanol and dried *in vacuo* at room temperature. TDMP-CuPc: yield 0.05 g (10.0%); UV-VIS (chloroform) λ_{max} 340 (B-band for Pc) and 680 (Q-band for Pc) nm; IR (KBr) 2922 (C-H in methyl), 1223 (ν_{C-O-C}), and 1093 (phenyl-O-phenyl) cm^{-1} . Anal. Calcd for Cu in TDMP-CuPc: Cu, 6.02%. Found: Cu, 6.08%. TDMP-CoPc: yield 0.04 g (8.30%); UV-VIS (chloroform) λ_{max} 330 (B-band for Pc) and 680 (Q-band for Pc) nm; IR (KBr) 2921 (C-H in methyl), 1224 (ν_{C-O-C}), and 1093 (phenyl-O-phenyl) cm^{-1} ;

^1H NMR (CDCl_3) δ 2.09 (s, 24H, methyl) and 7.50 (s, 24H, aromatic). Anal. Calcd for Co in TDMP-CoPc: Co, 5.61%. Found: Co, 5.67%. TDMP-NiPc: yield 0.06 g (10.6%); UV-VIS (chloroform) λ_{max} 360 (B-band for Pc) and 680 (Q-band for Pc) nm; IR (KBr) 2921 (C-H in methyl), 1223 ($\nu_{\text{C-O-C}}$), and 1092 (phenyl-O-phenyl) cm^{-1} ; ^1H NMR (CDCl_3) δ 2.48 (s, 24H, methyl) and 7.50 (s, 24H, aromatic). Anal. Calcd for Ni in TDMP-NiPc: Ni, 5.61%. Found: Ni, 5.68%.

7.2.2 *Formation of interlocking electrodes*

The masking plate which is made of stainless steel was prepared by wire electrical discharge machining to form interlocking electrodes on polyimide (Kapton®) substrates which were adhered on glass plates. Comb-shaped silver electrodes were formed on polyimide substrates by vacuum evaporation under pressure of 1.3×10^{-3} Pa through the masking plate. One comb of the interlocking electrodes has ten teeth, and the width of one tooth is 0.50 mm. The gap between one tooth and the neighboring tooth is 0.50, 0.20, or 0.13 mm. The overlap length of the interlocking electrodes is 4.5 mm.

7.2.3 *Fabrication of electronic devices based on TDMP-MPc film*

The electronic devices based on TDMP-MPc film were fabricated by casting the chloroform solutions containing 3.8×10^{-2} M TDMP-MPc on the interlocking silver electrodes. The thickness of the films was about 120 μm .

7.2.4 *Measurements*

UV-VIS spectra for TDMP-MPcs (M = Cu, Co, or Ni) were measured with a Jasco UVIDEc-505 UV/VIS digital spectrophotometer. IR spectra for compounds were measured with a JASCO FT/IR-7300 Fourier Transform Infrared Spectrometer using KBr disk. ^1H NMR spectra for TDMP-MPcs were measured with a JEOL JNM-FX90A Fourier Transform NMR Spectrometer using CDCl_3 and tetramethylsilane (TMS). Elemental analyses of C, H, and N were carried out with a PERKIN ELMER Series II CHNS/O Analyzer 2400. Atomic absorption spectrometry for central metal in TDMP-MPcs were carried out with a HITACHI 180-50 Atomic Absorption Spectrophotometer. The concentration of NO_2 was controlled by a GASTEC Permeator PD-1B, generating diluted NO_2 with a GASTEC Permeation Tube P-9-1. The dependence of current change on the existence or absence of gases was measured with an ADVANTEST R8340 Ultra High Resistance Meter. The surface structures and thicknesses of TDMP-MPc

films were examined with a HITACHI S-2380N Scanning Electron Microscope (SEM). The opto-electric conversion properties were examined with an ADVANTEST R8340 Ultra High Resistance Meter under irradiation of white light from a 300 W slide projector lamp.

7.3 RESULTS AND DISCUSSION

Since the compounds with 2,6-dimethylphenoxy substituent are highly soluble in chloroform [2], the TDMP-MPc films are easily prepared by solvent casting. The orientation of two methyl groups to 2- and 6-positions on the dimethylphenoxy substituent cause the compounds to be highly soluble. The high solubility of the compounds is preferable in solvent casting because film formation can be attainable with a small quantity of solvent. That is, although chloroform is suitable for solvent casting because the solvent can be volatile at room temperature without heating, the reduction of chloroform consumed should be taken into account because the solvent is carcinogenic agent.

The high solubility of the TDMP-MPcs in chloroform enables the inexpensive devices based on TDMP-MPc film to be fabricated. In fact, the conventional devices which have the film of phthalocyanine derivative have been fabricated by using more expensive instruments such as high vacuum evaporator and plasma polymerizer because most of phthalocyanine derivatives are insoluble in organic and inorganic solvent [3, 6-7, 9, 13-14]. The synthetic route to TDMP-MPcs are shown in Scheme 7.1.

Since many investigators have reported that interlocking electrodes which are formed on substrate and constructed by two comb-shaped electrodes are suitable for chemical and physical sensors [6, 16], the author fabricated the present devices with the interlocking silver electrodes on polyimide substrate.

In the present gas-sensors, polyimide film was selected as the substrate on which interlocking electrodes and TDMP-MPc film were deposited because of the strong adhesion of sublimed silver on the surface of polyimide film. Actually, the sublimed silver on polyimide film was not separated from the surface of the polyimide film even if the polyimide films on which sublimed silver was deposited were immersed in chloroform. When silver was sublimed on glass or zirconia plate and the chloroform was dropped onto the plate, the sublimed silver

was easily separated from the surface of the plate. The result suggests that plastic film such as polyimide is suitable for the fabrication of devices by the formation of casted film on sublimed silver electrodes. Polyimide film is particularly preferable to other plastic films because the dielectric strength and thermal resistance of polyimide are especially excellent [28]. However, since polyimide film is flexible, the fixation of polyimide film on the plate which has rigidity was necessary for the prevention of occurrence of cracks on TDMP-MPc film.

An Ohmic contact is formed at the interface between *p*-type semiconductor such as phthalocyanine derivative and silver which has a high work function [29]. The Ohmic contact is reasonable for the detection of gases at low applied voltage since current is easily flowed even at low applied voltage if Ohmic contact is formed at the interface between semiconductor and electrode. The shape of interlocking electrodes and the configuration of the present gas-sensors are shown in Figure 7.1.

UV-VIS spectra of TDMP-MPcs in chloroform and TDMP-MPc films on glass substrates were examined. The absorption peaks of TDMP-MPcs in chloroform at around 690 nm and those of TDMP-MPc films at around 620 nm were observed irrespective of the kind of central metal in TDMP-MPc. Since the absorption peak at around 620 nm and that at around 690 nm are assigned to aggregates and non-aggregates for phthalocyanine derivatives, it was confirmed that TDMP-MPcs were almost homogeneously dispersed in chloroform and considerable amounts of aggregates of TDMP-MPc existed in the films. The homogeneously dispersion of TDMP-MPc in chloroform which is used as the solvent for casting would cause the formation of the film in which TDMP-MPc molecules are almost homogeneously distributed. The formation of aggregates in TDMP-MPc films would assist the stabilization of TDMP-MPc films on substrates since bonding strength which is generated among the TDMP-MPc molecules would be strong. UV-VIS spectra of TDMP-MPc films are shown in Figure 7.2.

Since phthalocyanine derivatives are *p*-type semiconductors and NO₂ is an electron acceptor, electrons can be transferred from phthalocyanine to NO₂ when NO₂ is adsorbed on the surface of phthalocyanine film. The electron transfer cause the generation of holes in phthalocyanine and the increase of electric conductivity of phthalocyanine. The dependence of current changes of the gas-sensors based on TDMP-CuPc or TDMP-CoPc film on the concentration of NO₂ at applied voltage of 1 V are shown in Figure 7.3. The current change of the

gas-sensor based on TDMP-CuPc film was the largest. On the other hand, the dependence of current change of the gas-sensor based on TDMP-NiPc film on the concentration of NO₂ was not observed within the low concentration range, although the current of the gas-sensor was increased when 5 ppm NO₂ was adsorbed on the surface of TDMP-NiPc film. The result is consistent with the results reported for the NO_x sensors based on phthalocyanine film which was formed by vacuum-deposition [7]. Moreover, since the current of the present gas-sensors was able to be measured at applied voltage of 1 V, it can be expected that the electric power for driving the gas-sensor system was diminished.

The current response of the gas-sensor based on TDMP-CuPc film to 5 ppm NO₂ is shown in Figure 7.4 (a). In both NO₂ adsorption and desorption, the time for current changes of the gas-sensors is about 5 seconds. The response behavior of the gas-sensors based on TDMP-CoPc or TDMP-NiPc film was similar to that of the gas-sensor based on TDMP-CuPc. The result suggests that NO₂ adsorption and desorption are easily achieved and electron transfer from TDMP-MPc to NO₂ is rapidly occurred even at room temperature. That is, the present gas-sensors can be driven without controlling the temperature of the gas-sensors unlike the conventional devices which are constructed by inorganic semiconductor [16-17].

Furthermore, it was confirmed that the present gas-sensors were also detectable to the depletion of O₂ in air. Namely, the current of the present gas-sensors was rapidly decreased when introduced to nitrogen atmosphere and the value of current was returned to that before introducing to nitrogen atmosphere by carrying the gas-sensor to air. Since O₂ is also an electron acceptor, electrons can be transferred from phthalocyanine to O₂ in air. The electron transfer cause the increase of electric conductivity of phthalocyanine which is similar to that occurred by the adsorption of NO₂ on the surface of phthalocyanine. On the other hand, in the absence of O₂, the hole generation is prevented and phthalocyanine acts as intrinsic semiconductor whose electric conductivity is considerably smaller than that of extrinsic semiconductor. The current response of the gas-sensor based on TDMP-CuPc film to the absence of O₂ is shown in Figure 7.4 (b). In the gas-sensors based on TDMP-CoPc or TDMP-NiPc film, the similar response behavior to that of the gas-sensor based on TDMP-CuPc film was observed. It is thought that the adsorption of O₂ on the surfaces of TDMP-MPc films is weak and the adsorbed O₂ is easily separated from the surfaces of TDMP-MPc films by nitrogen flow. Moreover, since considerable

amounts of O_2 exist in air, O_2 can be adsorbed on the surfaces of TDMP-MPc when the gas-sensor is returned to air.

From the SEM observation of the surfaces of TDMP-MPc films, it was confirmed that the surface area under which the teeth of interlocking silver electrodes exist in parallel was flat. Namely, crack was not observed on the surfaces of the films and the gap region between one tooth and the neighboring tooth was continuous. The continuity of the gap region would assist the fast hole transfer in TDMP-MPc film to a tooth of cathode. The quick response of the present gas-sensors to the existence or absence of gases would be due to the continuity of the gap regions.

Dependence of conductance on the gap length in interlocking electrodes is shown in Figure 7.5. It is clear that conductance of device is increased by narrowing the gap between one tooth and the neighbouring tooth. The increase of conductance is due to the increase of charge carrier which reaches to counter electrode [16]. The mobility of charge carriers in TDMP-MPc is small because TDMP-MPc is an organic material. Narrowing the gap in interlocking electrodes enables the charge carriers which have small mobility to reach to counter electrode.

Phthalocyanines have absorption band in the region between 550 and 750 nm, as shown in Figure 7.2. The photo-excited charge carriers can be generated by irradiation of visible light since TDMP-MPc films are able to absorb visible light.

Photoconduction of the devices based on TDMP-NiPc is shown in Figure 7.6. The opto-electric conversion properties of the devices based on TDMP-CuPc or TDMP-CoPc were similar to that of the devices based on TDMP-NiPc. The ratio of photocurrent to dark current (= contrast) is summarized in Table 7.1. It is clear that narrowing the gap in interlocking electrodes enables contrast at the same applied voltage to be large. In particular, in the device having a gap length of 0.20 mm, contrast was drastically increased by applying more than 20 V to the device. The number of the charge carriers which are generated by light irradiation and reach to counter electrode would be increased by narrowing the gap in interlocking electrodes. Furthermore, current response of the present devices to light irradiation was reversible and reproducible irrespective of the value of applied voltage. However, response of the device having a gap length of 0.13 mm to light irradiation was slower than that of the device having a gap length of 0.50 or 0.20 mm. The response time of the former and latter

were about 5 min and 30 sec, respectively. Moreover, in the device having a gap length of 0.13 mm, current was irreproducible when more than 5 V was applied to the device. It is thought that applying high voltage to the device causes dielectric breakdown if gap length in interlocking electrodes is narrow.

7.4 CONCLUSION

It was confirmed that the devices based on TDMP-MPc films were detectable to low concentration (< 5 ppm) of NO_2 at room temperature. In particular, the device based on TDMP-CuPc film exhibited a good sensing performance. The responses of the present gas-sensors to the existence of NO_2 or the depletion of O_2 in air were considerably quick and reversible without heating process. The continuity of TDMP-MPc film in the gap regions of interlocking electrodes would assist the fast hole transfer to a tooth of cathode and the quick response to the existence or absence of gases.

Moreover, the opto-electric conversion properties of the present devices were also examined. It was confirmed that the contrast of photocurrent and dark current of the devices was increased by narrowing the gap between one tooth and the neighbouring tooth in interlocking electrodes. The present devices have potential useful features for photosensor since current response is reversible and reproducible.

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Table 7.1. Contrast of photocurrent and dark current of the devices based on TDMP-NiPc.

Applied voltage	Gap length (mm)		
	0.50	0.20	0.13
1	1.50	1.50	4.50
2	1.57	1.80	4.80
3	1.60	1.92	4.80
5	1.63	2.06	4.90
10	2.21	2.27	—
15	2.24	3.56	—
20	2.13	5.71	—
25	2.17	6.13	—

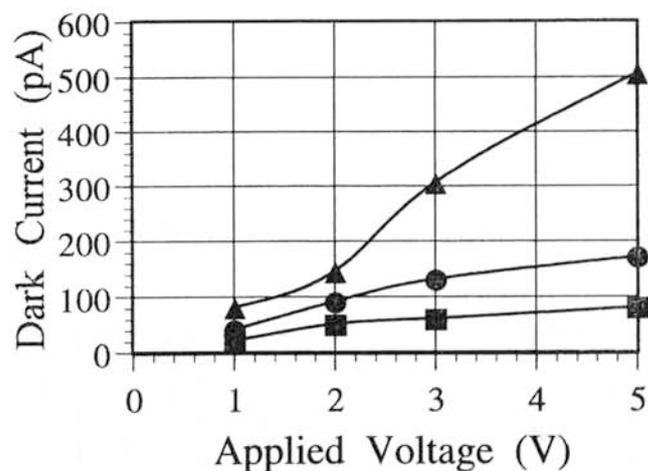
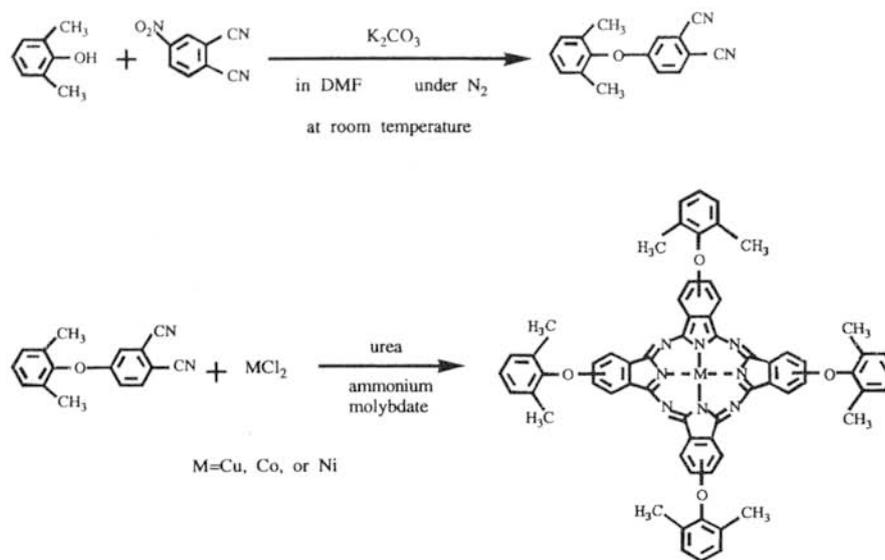


Figure 7.5 Conductance of the devices based on TDMP-NiPc under dark condition.

■ : gap length is 0.50 mm; ● : gap length is 0.20 mm; ▲ : gap length is 0.13 mm.



Scheme 7.1 Schematic diagram of synthetic route to TDMP-MPc (M = Cu, Co, or Ni).

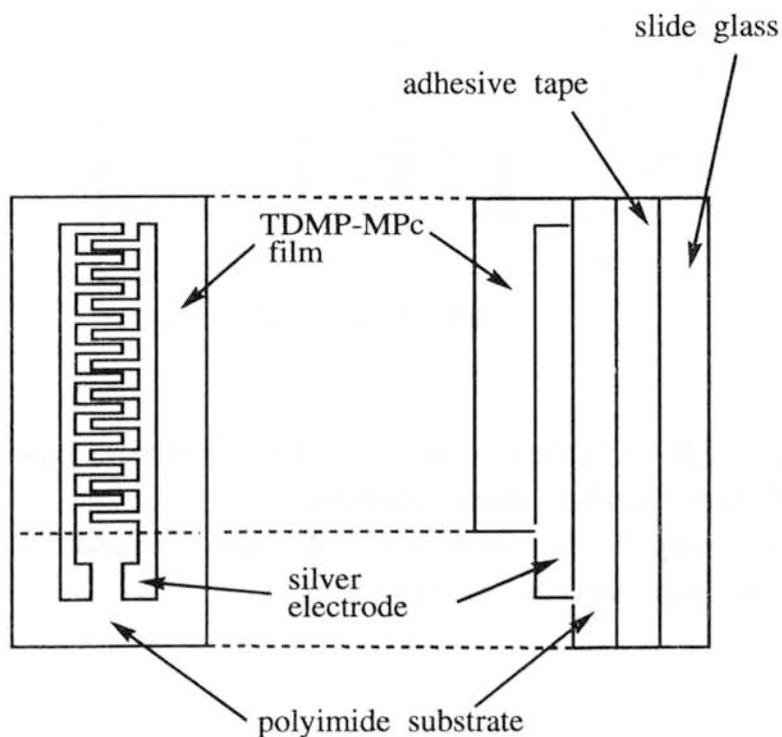


Figure 7.1 Schematic representation of electronic device.

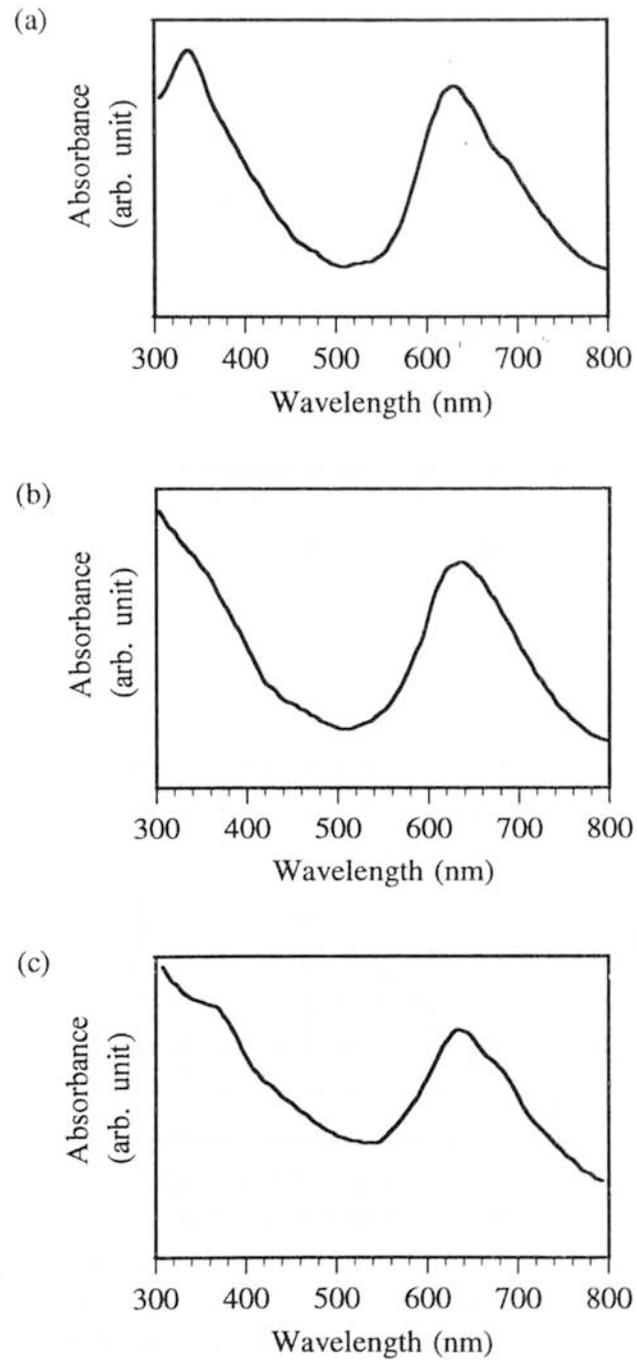


Figure 7.2 UV-VIS spectra of (a) TDMP-CuPc, (b) TDMP-CoPc, and (c) TDMP-NiPc films.

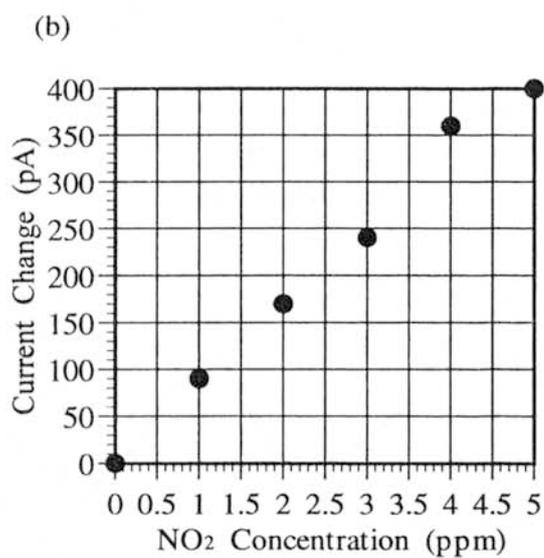
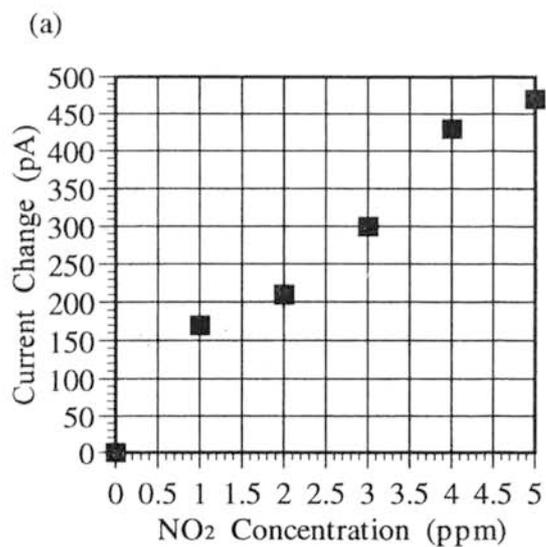


Figure 7.3 Dependence of current change of gas-sensors based on (a) TDMP-CuPc and (b) TDMP-CoPc on NO₂ concentration, applying 1 V to the gas-sensor.

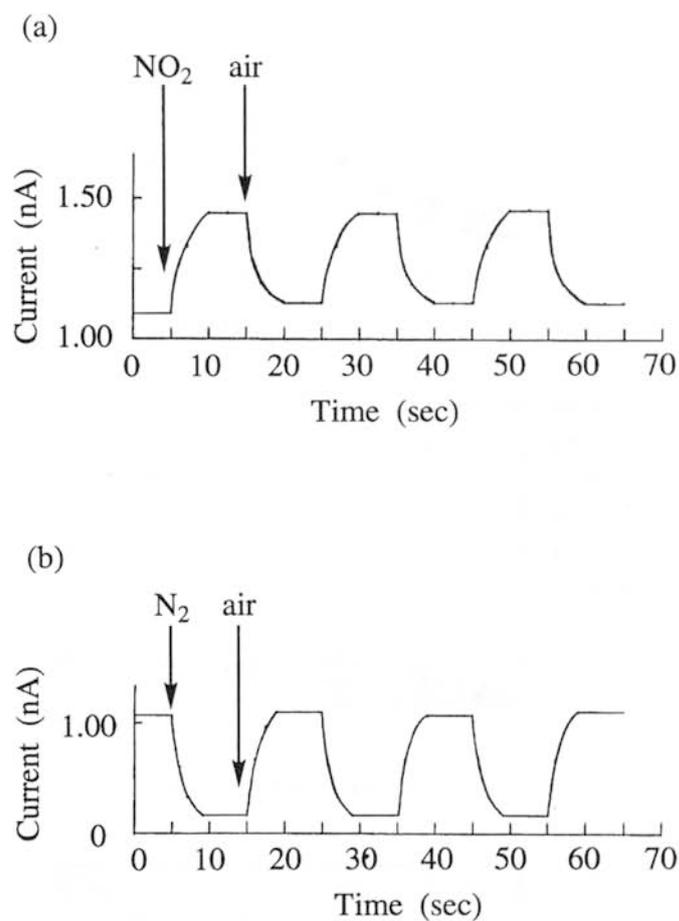


Figure 7.4 Current responses of the gas-sensor based on TDMP-CuPc film to (a) 5 ppm NO₂ and (b) the depletion of O₂, applying 1 V to the gas-sensor.

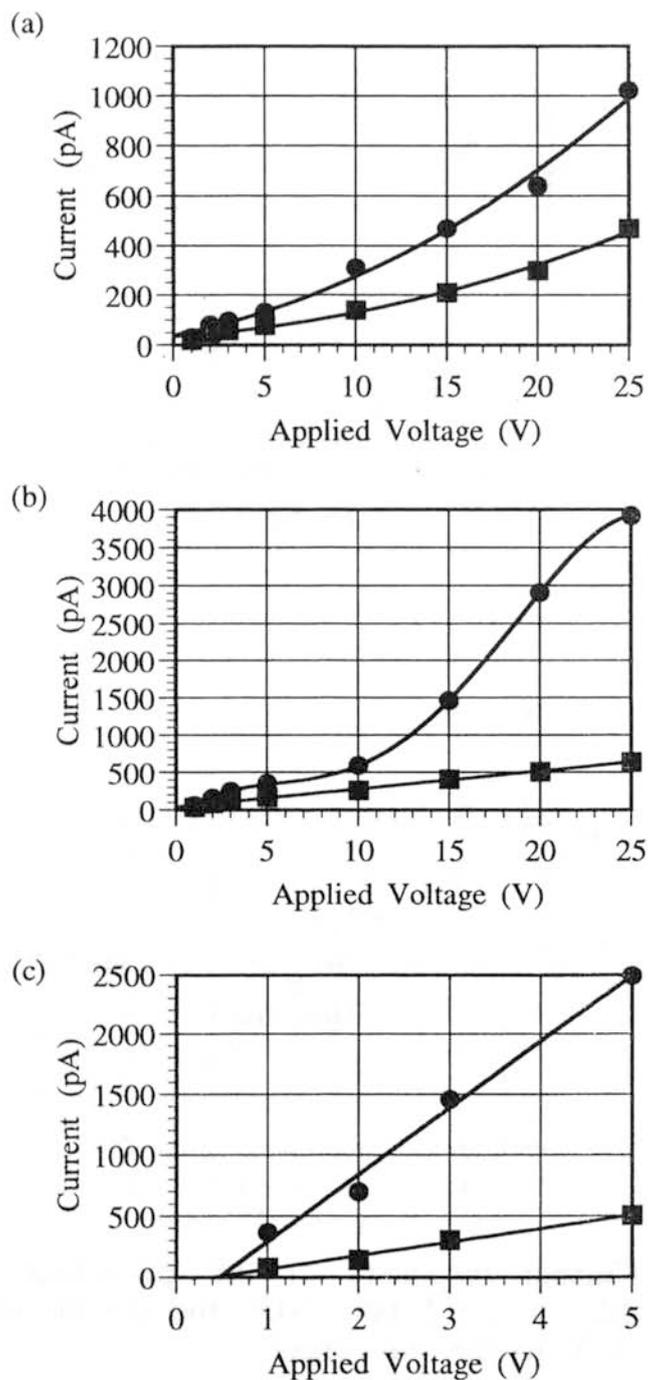


Figure 7.6 Photoconduction of the devices based on TDMP-NiPc and having a gap length of (a) 0.50, (b) 0.20, or (c) 0.13 mm in interlocking electrodes.

■: under dark condition; ●: under light irradiation.

CHAPTER 8

Fabrication of electronic devices based on soluble perylene derivative

The electronic devices based on N,N-(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (dmp-PTC) film on interlocking silver electrodes were fabricated by solvent casting from the chloroform solution containing dmp-PTC. The sensing properties to H₂S and mercaptan were investigated. It was confirmed that low concentrations of H₂S and mercaptan were detectable by the gas-sensor based on dmp-PTC at room temperature and the current responses to the existence of H₂S and mercaptan were considerably quick. These results suggest that adsorption and desorption of H₂S or mercaptan on the surfaces of dmp-PTC film is easily achieved at room temperature.

Moreover, the opto-electric conversion properties of the devices were also investigated. It was confirmed that narrowing the gap between one tooth and the neighbouring tooth in interlocking electrodes increased conductance and improved the opto-electric conversion property.

8.1 INTRODUCTION

Perylene derivatives have attracted considerable interest because the compounds are *n*-type organic semiconductors [1-5] and highly responsive to light irradiation [6]. Since most organic pigments such as phthalocyanines act as *p*-type semiconductors [1-4], perylene derivatives as *n*-type semiconductors have attracted the attention of many investigators [1-5].

Solvent casting is the easier and cheaper method to prepare the organic films. Since *N,N'*-(2,6-dimethylphenyl)-3,4,9,10-perylenetetracarboxylic diimide (dmp-PTC) is highly soluble to chloroform, the film of dmp-PTC is easily prepared by coating the chloroform solution of dmp-PTC.

It has been reported that interlocking electrodes which are formed on substrates are suitable for various kinds of gas-sensors [7-8]. However, in the previously reported gas-sensors which are constructed by inorganic semiconductor such as SnO₂, sufficiently high adsorption and desorption rates of gas at room temperature have not been achieved [9].

In this chapter, it will be indicated that the gas-sensor based on dmp-PTC film is quickly detectable to the existence of low concentration of H₂S or mercaptan and the adsorbed gases can desorb easily from the surfaces of the dmp-PTC film at room temperature.

Moreover, since perylene derivatives show strong fluorescence when exposed to ultraviolet or visible light [10], a device using a perylene derivative should be highly sensitive to light irradiation. In particular, Hiramoto et al. showed that *N,N'*-methyl-3,4,9,10-perylenetetracarboxylic diimide (Me-PTC) exhibited a large amplification of photocurrent [6].

It is well-known that interlocking electrodes are suitable for opto-electric conversion devices based on inorganic semiconductor such as cadmium sulfide, as for gas-sensors [8]. The length of the gap between one tooth and the neighbouring tooth in interlocking electrodes affects opto-electric conversion property.

In this chapter, the effect of narrowing the gap in interlocking electrodes on opto-electric conversion property of the device based on dmp-PTC will be described.

8.2 EXPERIMENTAL

8.2.1 Materials

Dmp-PTC was prepared on the basis of the method by Rademacher et al [10]. A reaction mixture consisting of 0.50 g (1.35×10^{-3} mol) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 0.33 g (2.70×10^{-3} mol) of 2,6-dimethylaniline, and 0.35 g (1.90×10^{-3} mol) of zinc acetate suspended in 5 ml of quinoline was refluxed for 24 h. After extraction with chloroform, chloroform was evaporated from the solution containing dmp-PTC. The resulting residue was recrystallized from toluene. The red crystalline dmp-PTC was washed with methanol and dried *in vacuo* at room temperature.

8.2.2 Formation of interlocking electrodes

The masking plate which is made of stainless steel was prepared by wire electrical discharge machining to form interlocking electrodes on polyimide (Kapton®) substrates which were adhered on glass plates. Comb-shaped silver electrodes were formed on polyimide substrates by vacuum evaporation under pressure of 1.3×10^{-3} Pa through the masking plate. One comb of the interlocking electrodes has ten teeth, and the width of one tooth is 0.50 mm. The gap between one tooth and the neighboring tooth is 0.50, 0.20, or 0.13 mm. The overlap length of the interlocking electrodes is 4.5 mm. The electrode thickness was about 100 μ m.

8.2.3 Fabrication of electronic devices based on dmp-PTC film

The electronic devices based on dmp-PTC film were fabricated by casting the chloroform solution containing 2.6×10^{-2} M dmp-PTC on the interlocking silver electrodes. The thickness of the film was about 125 μ m.

8.2.4 Measurements

The concentrations of H₂S and CH₃SH were controlled by a GASTEC Permeator PD-1B, generating diluted gases with a GASTEC Permeation Tubes P-4 and P-71-5. The dependence of current change on the existence of gases was measured with an ADVANTEST R8340 Ultra High Resistance Meter. The surface structure and thickness of the dmp-PTC film were examined with a HITACHI S-2380N Scanning Electron Microscope (SEM). UV-VIS spectrum of dmp-PTC film

was measured with a Jasco UV/DEC-505 UV/VIS digital spectrophotometer. The opto-electric conversion properties were examined with an ADVANTEST R8340 Ultra High Resistance Meter under irradiation of white light from a 300 W slide projector lamp.

8.3 RESULTS AND DISCUSSION

Since the compounds with 2,6-dimethylphenyl substituent are highly soluble in chloroform, the dmp-PTC film is easily prepared by solvent casting. The high solubility of the dmp-PTC in chloroform enables the inexpensive devices based on dmp-PTC film to be fabricated. The chemical structure of dmp-PTC is shown in Fig. 8.1.

Since many investigators have reported that interlocking electrodes which are formed on substrate and constructed by two comb-shaped electrodes are suitable for chemical and physical sensors [8], the author fabricated the present devices with the interlocking silver electrodes on polyimide substrate.

In the present gas-sensor, polyimide film was selected as the substrate on which interlocking electrodes and dmp-PTC film were deposited because of the strong adhesion of vacuum-deposited silver on the surface of polyimide film. Actually, the vacuum-deposited silver on polyimide film was not peeled from the surface of the polyimide film even if the polyimide films on which silver was vacuum-deposited were immersed in chloroform. When silver was vacuum-deposited on glass or zirconia plate and the chloroform was dropped onto the plate, the vacuum-deposited silver was easily peeled from the surface of the plate. The result suggests that plastic film such as polyimide is suitable for the fabrication of electronic devices by the formation of casted film on vacuum-deposited silver electrodes. Polyimide film is particularly preferable of plastic films because the dielectric strength and thermal resistance are especially high [11]. However, since polyimide film is flexible, the fixation of polyimide film on the plate which has rigidity was necessary to prevent the crack formation in dmp-PTC film.

The oxidation of metal used as electrode cause the degradation of the device because the electric resistance of the electrode is increased by the oxidation of the metal. Silver would be suitable for the electrode of the present gas-sensor since silver is chemically stable and highly conductive, although

Schottky barrier is formed at the interface between *n*-type semiconductor of perylene derivative and silver which has a high work function [12]. The rectification property at the interface between dmp-PTC and silver does not need to be taken into account because applied voltage to the present gas-sensor was fixed on 1 V. The shape of interlocking electrodes and the configuration of the present gas-sensor are shown in Fig. 8.2.

Since perylene derivatives are *n*-type semiconductors and H₂S and mercaptan are electron donors, electrons can be transferred from H₂S or mercaptan to perylene derivative when H₂S or mercaptan is adsorbed on the surface of the film of perylene derivative. The electron transfer cause the multiplication of conduction electrons in perylene derivative and the increase of electric conductivity of perylene derivative. The dependence of current change of the gas-sensor based on dmp-PTC film on the concentration of H₂S or CH₃SH at applied voltage of 1 V are shown in Fig. 8.3. The non linear dependence of change in current with respect to the change in gas concentration would be because of the poor sensitivity in low concentration region. The influence of humidity on the gas-sensing property was almost negligible if humidity was between 25% RH and 45% RH. It is thought that the interaction between dmp-PTC and H₂S or mercaptan is markedly stronger than that between dmp-PTC and water molecule.

The current response of the gas-sensor based on dmp-PTC film to 7 ppm H₂S or 300 ppb CH₃SH is shown in Fig. 8.4. In both gas adsorption and desorption, the time for current changes of the gas-sensors is about 5 seconds. The result suggests that adsorption and desorption of H₂S or CH₃SH are easily achieved and electron transfer from H₂S or CH₃SH to dmp-PTC is rapidly occurred even at room temperature. That is, the present gas-sensor can be driven without controlling the temperature of the gas-sensor unlike the previously reported devices which are constructed by inorganic semiconductor [9]. However, the recovery of current was not complete as shown in Fig. 8.4. This would be due to strongly adsorption of a small number of gas molecules during the initial introduction of the gas-sensor into the area in where H₂S or mercaptan exists since the current response to the gases was reproducible after second introduction. The incomplete recovery suggests that current of the present gas-sensors is changed by adsorption of sensing gas.

From the SEM observation of the surface of dmp-PTC film, it was confirmed that the surface area under which the teeth of interlocking silver electrodes exist in parallel was flat. Namely, crack was not observed on the

surface of the film and the gap region between one tooth and the neighbouring tooth was continuous. The continuity of the gap region would assist the fast electron transfer in dmp-PTC film to a tooth of anode. The quick response of the present gas-sensors to the existence or absence of gases would be due to the continuity of the gap regions.

Dependence of conductance on the gap length in interlocking electrodes is shown in Fig. 8.5. It is clear that conductance of device is increased by narrowing the gap between one tooth and the neighbouring tooth. The increase of conductance is due to the increase of charge carrier which reaches to counter electrode [8]. The mobility of charge carriers in dmp-PTC is small because dmp-PTC is an organic material. Narrowing the gap in interlocking electrodes enables the charge carriers which have small mobility to reach to counter electrode.

UV-VIS spectrum of dmp-PTC film is shown in Fig. 8.6. Perylene derivatives have absorption band in the region between 450 and 550 nm. The photo-excited charge carriers can be generated by irradiation of visible light since dmp-PTC film is able to absorb visible light.

Photoconduction of the present devices is shown in Fig. 8.7. The ratio of photocurrent to dark current (= contrast) is summarized in Table 8.1. It is clear that narrowing the gap in interlocking electrodes enables contrast at the same applied voltage to be large. In particular, in the device having a gap length of 0.13 mm, contrast was drastically increased by applying high voltage. The drastic turning-on of photocurrent would be attributed to the formation of rectifying barrier at the junction interface between dmp-PTC and silver electrode because perylene derivatives are *n*-type semiconductors and silver has a high work function [12]. The number of the charge carriers which are generated by light irradiation and reach to counter electrode would be increased by narrowing the gap in interlocking electrodes. Furthermore, current response of the present devices to light irradiation was reversible and reproducible irrespective of the value of applied voltage. However, response of the device having a gap length of 0.13 mm to light irradiation was slower than that of the device having a gap length of 0.50 or 0.20 mm. The response time of the former and latter were about 5 min and 30 sec, respectively.

8.4 CONCLUSION

It was confirmed that the devices based on dmp-PTC film was detectable to low concentration of H_2S or CH_3SH . The response of the present gas-sensor to the existence of H_2S or CH_3SH in air was considerably quick and reversible without heating process. The continuity of dmp-PTC film in the gap regions of interlocking electrodes would assist the fast electron transfer to a tooth of anode and the quick response to the existence or absence of gases.

Moreover, the opto-electric conversion properties of the present devices were also examined. It was confirmed that the contrast of photocurrent and dark current of the devices was increased by narrowing the gap between one tooth and the neighbouring tooth in interlocking electrodes. The present devices have potential useful features for photosensor since current response is reversible and reproducible.

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Table 8.1 Contrast of photocurrent and dark current.

Applied voltage (V)	Gap length (mm)		
	0.50	0.20	0.13
1	1.00	1.40	2.02
5	1.38	1.91	2.13
10	1.50	1.81	5.25
15	1.39	1.75	5.85

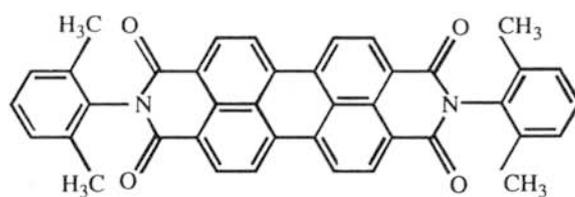


Figure 8.1 Molecular structure of dmp-PTC.

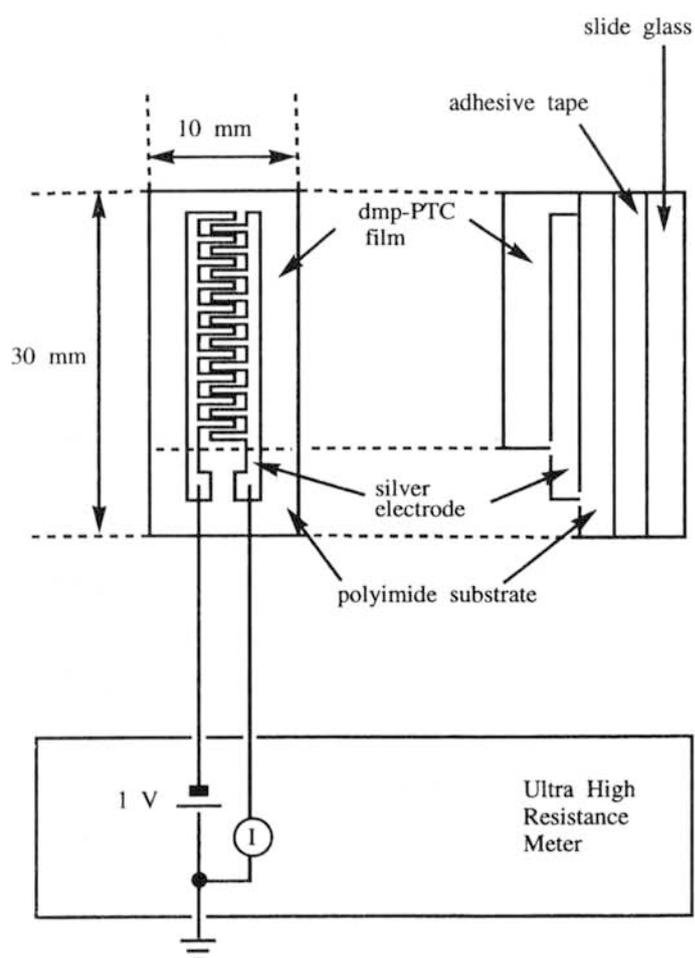


Figure 8.2 Schematic representation of electronic device.

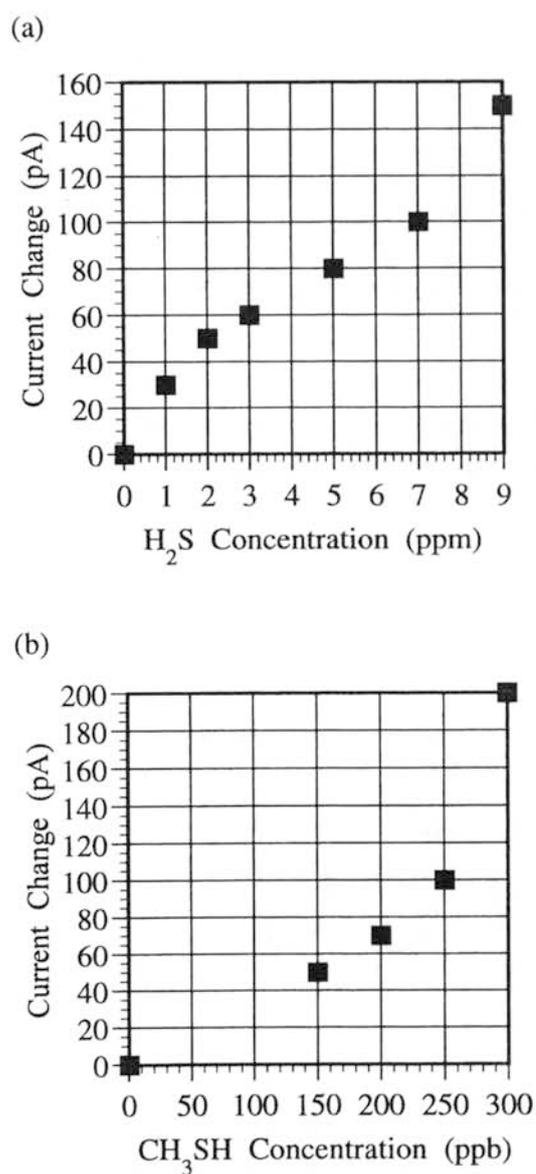


Figure 8.3 Dependence of current changes of gas-sensor based on dmp-PTC film on (a) H₂S and (b) CH₃SH concentration, applying 1 V to the gas-sensor.

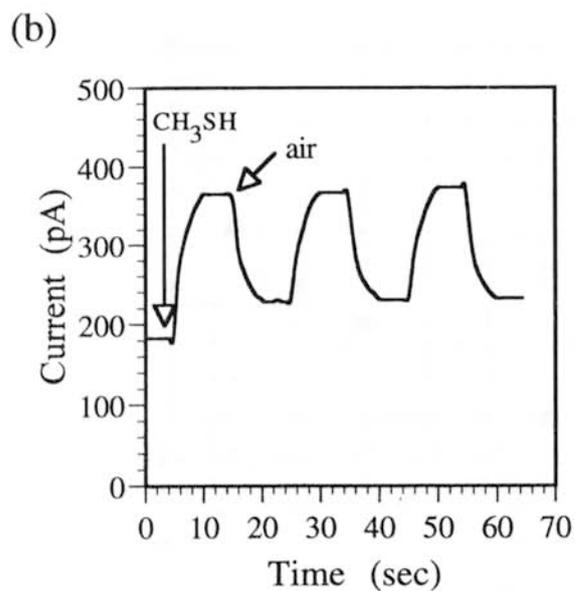
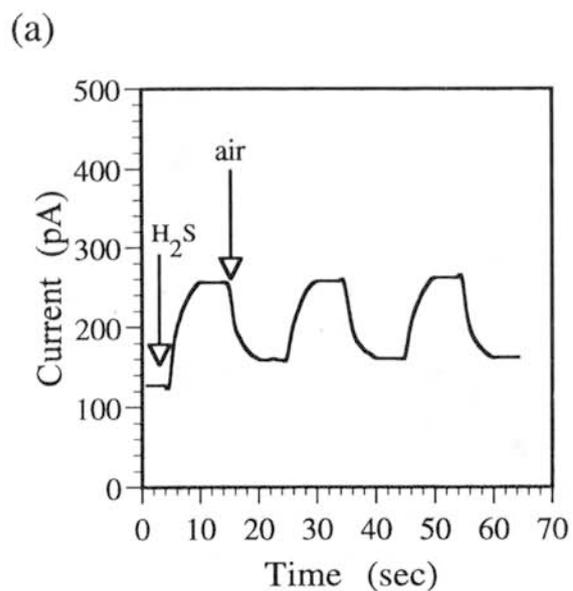


Figure 8.4 Current responses of the gas-sensor based on dmp-PTC film to (a) 7 ppm H₂S and (b) 300 ppb CH₃SH, applying 1 V to the gas-sensor.

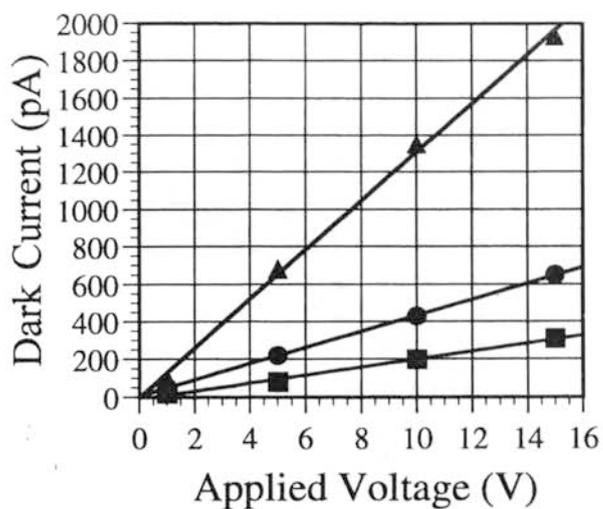


Figure 8.5 Conductance of the devices based on dmp-PTC under dark condition.

■: gap length is 0.50 mm; ●: gap length is 0.20 mm;
▲: gap length is 0.13 mm.

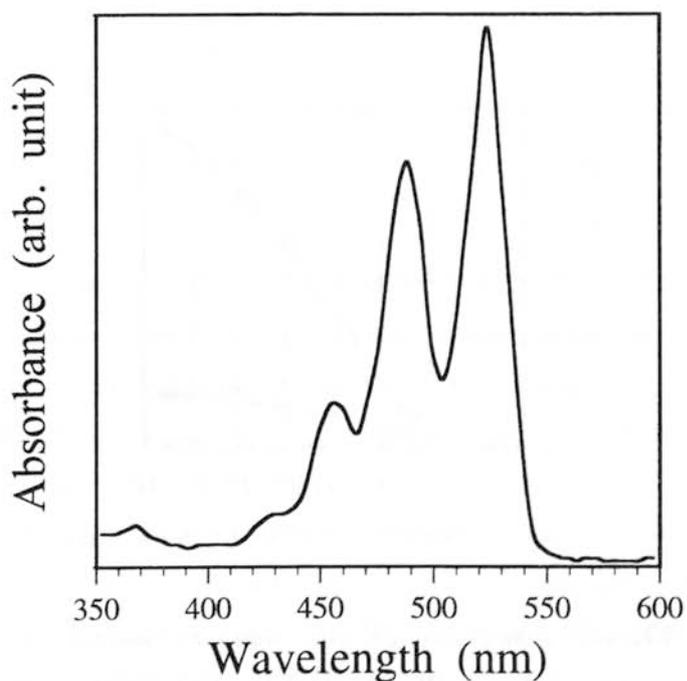


Figure 8.6 UV-VIS spectrum of dmp-PTC film.

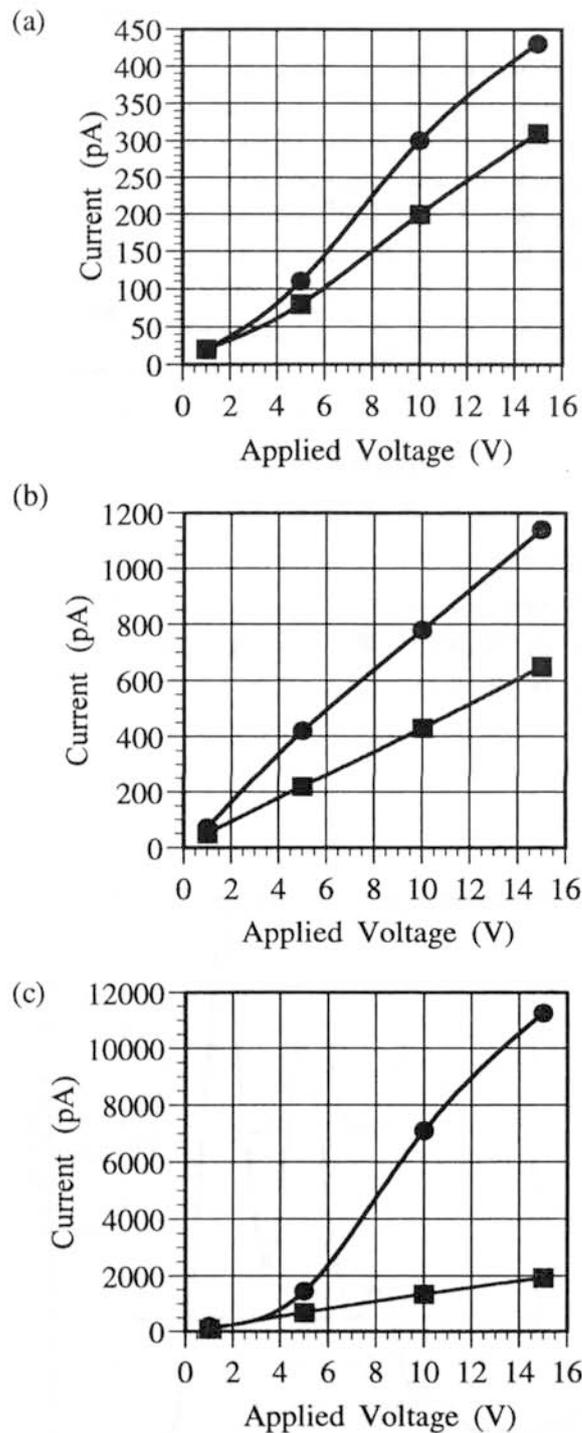


Figure 8.7 Photoconduction of the devices based on dmp-PTC and having a gap length of (a) 0.50, (b) 0.20, and (c) 0.13 mm in interlocking electrodes.

■: under dark condition; ●: under light irradiation.

CHAPTER 9

Electrochromic behavior of electro-deposited perylene derivative

It was found that perylene derivatives having hydroxyphenyl group as substituent are electro-deposited on indium-tin oxide (ITO) electrodes by cathodical polarization of the N,N-dimethyl-formamide (DMF) solution containing perylene derivative and supporting electrolyte having a bivalent metal with a constant current of $-35 \mu\text{A}/\text{cm}^2$. In this chapter, it was confirmed that electro-deposited film of N,N'-4-hydroxyphenyl-3,4,9,10-perylenetetra-carboxylic diimide (4-hph-PTC) exhibited an electrochromic behavior in aqueous solution containing supporting electrolyte when negative current was applied to 4-hph-PTC film on ITO electrode. The mechanism of electrochromic behavior of 4-hph-PTC film was investigated.

9.1 INTRODUCTION

Since power failure may be occurred by electric discharge if insulator for electrical supplying wire is degraded, the quick detection for leakage of electricity is necessary for preventing electrical trouble. Various electrochromic displays (ECD) are applied to monitoring for leakage of electricity because ECD can hold the changed colour caused by leak current for a long time [1].

It has been already reported by Tominaga et al. that vacuum-evaporated films of various perylene derivatives on ITO electrodes exhibit electrochromic behavior in aqueous solution containing NaNO_3 as a supporting electrolyte [2]. However, in general, vacuum-deposited film on ITO electrode can be easily peeled from the surface of the ITO electrode when immersed in aqueous solution even if current through ITO electrode is not applied to the vacuum-deposited film. In applying the film which has an electrochromic property to monitoring for leakage of electricity, strong adhesion of the film on the surface of electrode is required.

In chapter 9, it was found that a perylene derivative having 4-hydroxyphenyl group as substituent can be electro-deposited on ITO electrode and the electro-deposited film exhibits an electrochromic behavior in aqueous solution containing supporting electrolyte. The present electro-deposited film was not peeled from the surface of the ITO electrode in electrolytic solution if a current was not applied to the electro-deposited film.

In this chapter, it will be indicated that electro-deposited film of 4-hph-PTC would be applicable to monitoring for leakage of electricity.

9.2 EXPERIMENTAL

9.2.1 Materials

N,N' -phenyl-3,4,9,10-perylenetetra-carboxylic diimide (ph-PTC), N,N' -2-hydroxyphenyl-3,4,9,10-perylenetetra-carboxylic diimide (2-hph-PTC), N,N' -3-hydroxyphenyl-3,4,9,10-perylenetetra-carboxylic diimide (3-hph-PTC) and N,N' -4-hydroxyphenyl-3,4,9,10-perylenetetra-carboxylic diimide (4-hph-PTC) were prepared on the basis of the method by Rademacher et al [3]. A reaction mixture consisting of 0.68 g (1.7×10^{-3} mol) of 3,4,9,10-perylenetetra-carboxylic dianhydride (PTCDA), 0.92 g ($4.9 \times$

10^{-3} mol) of aniline or 0.50 g (4.6×10^{-3} mol) of 2-, 3- or 4-aminophenol and 0.50 g (2.4×10^{-3} mol) of zinc acetate suspended in 30 ml of quinoline was refluxed for 2 h. The resulting precipitate was filtered off and recrystallized extractively from toluene. The red-purple crystalline ph-, 2-hph-, 3-hph- or 4-hph-PTC was washed with methanol and dried *in vacuo* at room temperature. These PTCs were purified by sublimation before preparation of films.

DMF was distilled under reduced pressure before use. Supporting electrolytes used in this chapter were of analytical grade from commercial origin.

9.2.2 Formation of PTC films

The vacuum-evaporated PTC films on ITO electrodes were prepared by vacuum-deposition at a pressure of 1.3×10^{-3} Pa.

The electrodeposited hph-PTC films on ITO electrodes were prepared by the method of cathodic electrolytic deposition using a Hokuto-Denko HA-501 potentiostat/galvanostat. A mixture of 2-, 3- or 4-hph-PTC (5×10^{-4} M) and CaCl_2 (1×10^{-3} M) as a supporting electrolyte in dry DMF was poured into the electrolytic cell including ITO working electrode and platinum counter electrode. The 2-, 3- and 4-hph-PTC films on the ITO electrodes were obtained by cathodical polarization of the electrolytic solution with a constant current of $-35 \mu\text{A}/\text{cm}^2$ for 30 min. The deposited films were washed with acetone.

9.2.3 Measurements

UV-VIS spectra for hph-PTCs were measured with a Jasco V-570 UV/VIS/NIR Spectrophotometer. Cyclic voltammetry for hph-PTCs were carried out in the electrolytic cell including ITO working electrode, platinum counter electrode and saturated calomel electrode (SCE) as a reference electrode, using a Yanaco P-1100 polarographic analyzer. Elemental analyses were carried out with a HORIBA energy-dispersive X-ray microanalyzer, EMAX-5770W. The thickness of the hph-PTC films on ITO electrodes were examined with a HITACHI S-2380N Scanning Electron Microscope (SEM). Electrochromism of PTCs were observed by applying a constant current to PTC on ITO electrode with a Hokuto-Denko HA-501 potentiostat/galvanostat.

9.3 RESULTS AND DISCUSSION

The chemical structures of the monomers of PTCs are shown in Fig. 9.1.

The hph-PTCs are electropolymerizable because these compounds have hydroxyphenyl groups [4]. Electrochemical polarization leads to dissociation of the terminal hydroxyl groups, and then the electropolymerization can be occurred on the surface of working electrode. Actually, electrodeposition of ph-PTC which has not hydroxyl group was not observed when ph-PTC instead of hph-PTC existed in electrolytic solution. The existence of Ca^{2+} ions in the present electrodeposited films were confirmed by X-ray microanalysis. The similar phenomena were observed when CoBr_2 , ZnCl_2 or PbCl_2 instead of CaCl_2 was used as supporting electrolyte, although the amount of electro-deposited hph-PTC was smaller. The thickness of 2-hph-PTC film containing Ca^{2+} was about $200 \mu\text{m}$, while the thickness of 3- and 4-hph-PTC films containing Ca^{2+} was about $100 \mu\text{m}$. Furthermore, hph-PTC film was not obtained on ITO electrode from the DMF solutions containing hph-PTC and a supporting electrolyte of univalent metal ion such as Li^+ and Na^+ . These results suggest that divalent metal ions are necessary for the electrodeposition of hph-PTC and the monomers of hph-PTC are cross-linked by the divalent metal ions at the peripheral hydroxyl groups in hph-PTC. The expected chemical structures of electrodeposited hph-PTCs are shown in Fig. 9.2.

In the electrodeposition of 2-hph-PTC, homogeneous 2-hph-PTC films containing Ca^{2+} ions which originated from supporting electrolyte were obtained without stirring the electrolytic solution. On the other hand, in the electrodeposition of 3- or 4-hph-PTC, heterogeneous hph-PTC films were deposited when the electrolytic solution was not stirred since 3- or 4-hph-PTC are poorly soluble in DMF. Therefore, in the electrodeposition of 3- or 4-hph-PTC, the slow stirring of the electrolytic solution was essential to take homogeneous hph-PTC films.

Most of compounds which have hydroxyl group are polymerized by anodical polarization [4]. However, the electrodeposited hph-PTC films were prepared by not anodical but cathodical polarization. The result would be explained by the fact that perylene derivatives are easily reduced because these compounds are *n*-type semiconductors whose electrical conductivity is increased by accepting electrons [5-9]. That is, high electric conductivity of monomers is necessary for electropolymerization [4]. Actually, hph-PTCs were easily reduced, but oxidation of

hph-PTCs was not observed in the cyclic voltammograms for the DMF solutions containing hph-PTC and CaCl_2 as a supporting electrolyte. The reduction of hph-PTCs starts at about -0.5 V vs. SCE.

The ability of electrochromism for vacuum-deposited PTC monomers and electro-deposited hph-PTCs in 5.2×10^{-3} M NaNO_3 aqueous solution are summarized in Table 9.1. An applied electric current density of $-125 \mu\text{A}/\text{cm}^2$ was necessary for electrochromism of PTCs.

Electrochromic behavior of monomers and electro-deposited 4-hph-PTC [poly(4-hph-PTC)] was observed while that of electro-deposited 2- and 3-hph-PTC [poly(2-hph-PTC) and poly(3-hph-PTC)] was not. Furthermore, as shown in Table 9.2, the similar results were obtained when supporting electrolyte other than NaNO_3 was used. The colour of vacuum-deposited films and poly(4-hph-PTC) film was changed from vermilion into purple after applying negative current to the ITO electrode while the colour of poly(2-hph-PTC) and poly(3-hph-PTC) was purple both before and after cathodic polarization.

Poly(2-hph-PTC), poly(3-hph-PTC) and poly(4-hph-PTC) are prepared by electrical reduction of the corresponding monomer when electro-deposited. That is, it is thought that electro-deposited hph-PTCs have been reduced while vacuum-evaporated hph-PTCs have not. Electrochromism was clearly observed when PTCs were reduced while not observed when oxidized. These results suggest that electrochromism of PTCs is due to the reduction of oxidized PTC. Electrochromism of poly(4-hph-PTC) would be because the reduction of 4-hph-PTC is more difficult than that of 2- and 3-hph-PTC. UV-Vis spectra of poly(4-hph-PTC) before and after electrical reduction are shown in Fig. 9.3 (a) and (b), respectively. On the other hand, UV-Vis spectra of poly(2-hph-PTC) and poly(3-hph-PTC) are shown in Fig. 9.4 (a) and (b), respectively. UV-Vis spectrum of electrically reduced poly(4-hph-PTC) is similar to those of poly(2-hph-PTC) and poly(3-hph-PTC). This result suggests that 2- and 3-hph-PTC are sufficiently reduced when electro-deposited. The absorption peak at around 500 nm would be assigned to electrically reduced hph-PTC. On the other hand, the absorption peak at around 550 nm would be assigned to electrically oxidized hph-PTC since the ratio of the absorbance at around 550 nm to that at around 500 nm was increased when hph-PTC was oxidized.

The vacuum-deposited PTC films were easily peeled from the surface of ITO electrode in electrolytic solution even if current was not applied to the ITO electrode. On the other hand, the present electro-deposited PTC films were not

peeled from the surface of ITO electrode if current was not applied.

However, the electro-deposited films were peeled if electric current density of more negative than $-150 \mu \text{ A/cm}^2$ was applied to the ITO electrode. Furthermore, the electrochromic behaviour of poly(4-hph-PTC) was not reproducible. That is, the colour change of reduced poly(4-hph-PTC) film by oxidation was not observed, although the change of UV-Vis spectrum of the film was confirmed. These results imply that the present poly(4-hph-PTC) film can be applied to the memory for leakage of electricity.

9.4 CONCLUSIONS

The electro-deposited 2-, 3- and 4-hph-PTC films on ITO electrodes were obtained by cathodical polarization of the DMF solutions containing hph-PTC monomer and supporting electrolyte of divalent metal ion. Electrochromic behavior of electro-deposited 4-hph-PTC was observed in aqueous solution containing supporting electrolyte, while that of electro-deposited 2- or 3-hph-PTC was not. Electrochromism of PTCs would be due to the reduction of oxidized PTCs. Since the electro-deposited 4-hph-PTC film was not peeled from the surface of ITO electrode if current was not applied, the memory for leakage of electricity would be fabricated using the electro-deposited 4-hph-PTC film.

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Table 9.1 Ability of electrochromism for vacuum-deposited PTC monomers and electro-deposited PTCs in 5.2×10^{-3} M NaNO_3 aqueous solution.

PTC	electrochromism
ph-PTC	observed
2-hph-PTC	observed
3-hph-PTC	observed
4-hph-PTC	observed
poly(2-hph-PTC)	not observed
poly(3-hph-PTC)	not observed
poly(4-hph-PTC)	observed

Table 9.2 Ability of electrochromism for electro-deposited PTCs in aqueous solution of 5.2×10^{-3} M supporting electrolyte.

Supporting electrolyte	PTC		
	poly(2-hph-PTC)	poly(3-hph-PTC)	poly(4-hph-PTC)
LiNO_3	not observed	not observed	observed
NaNO_3	not observed	not observed	observed
KNO_3	not observed	not observed	observed
$\text{Mg}(\text{NO}_3)_2$	not observed	not observed	observed
$\text{Ca}(\text{NO}_3)_2$	not observed	not observed	observed
LiCl	not observed	not observed	observed
CH_3COOLi	not observed	not observed	observed
CaCl_2	not observed	not observed	observed

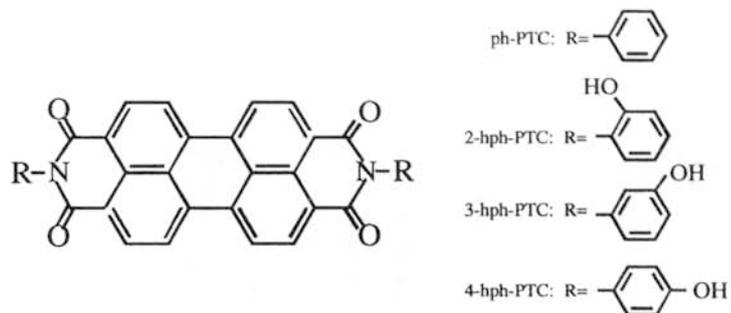


Figure 9.1 Molecular structures of PTC monomers.

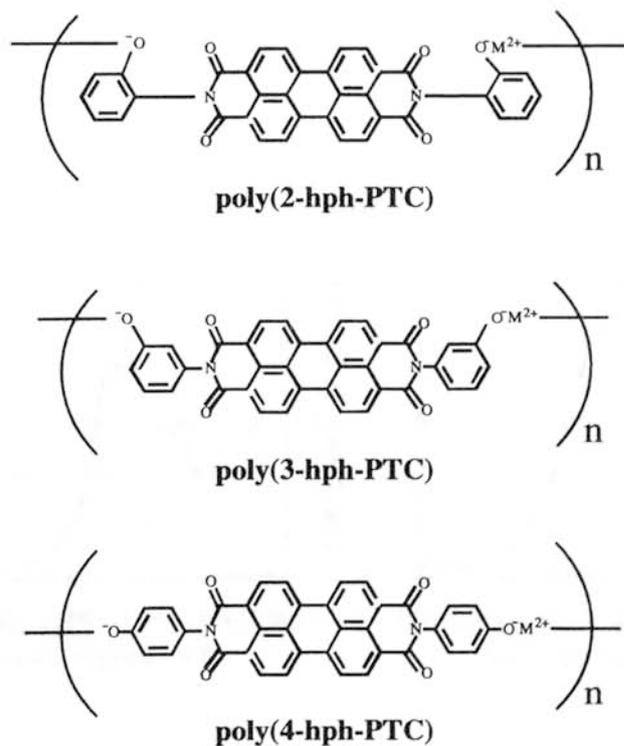


Figure 9.2 Chemical structures of electro-deposited PTCs.
M = Ca, Co, Zn, or Pb.

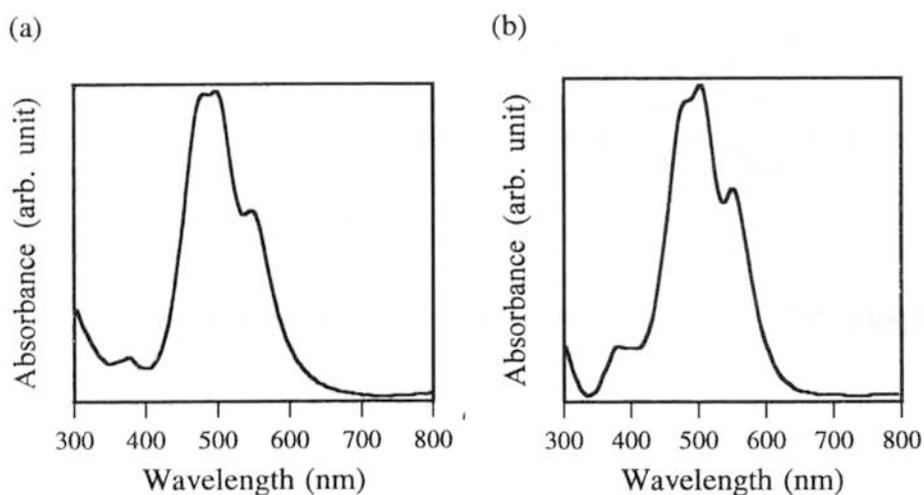


Figure 9.3 UV-Vis spectra of electro-deposited 4-hph-PTC film (a) before and (b) after electrical reduction.

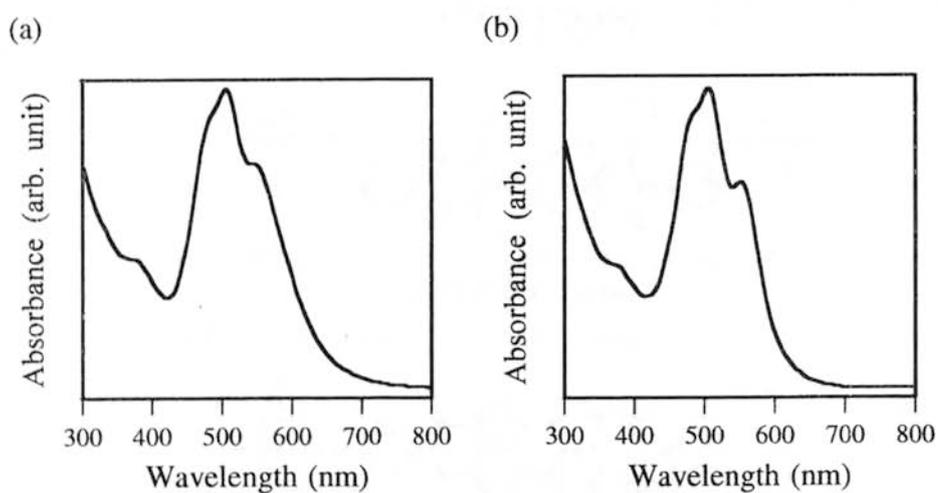


Figure 9.4 UV-Vis spectra of electro-deposited (a) 2- and (b) 3-hph-PTC film.

CHAPTER 10

Fabrication of all-organic field effect transistors based on phthalocyanine and perylene derivative

All organic field effect transistors based on thin films of phthalocyanine and perylene derivative were fabricated. It was confirmed that the gap length between source and drain electrodes was an important factor to stabilize transistor characteristics. Furthermore, the insertion of dielectric layer between channel and gate layers was observed to be effective for prevention of leakage of current.

10.1 INTRODUCTION

It has been shown that phthalocyanines and perylene derivatives are p- and n-type semiconductors, respectively [1-4]. All-organic p-n junction diodes have been fabricated with these materials and photo-voltaic effect of the diodes was observed [1-4].

However, fabrication of all-organic transistor has hardly been reported. Although recently Rogers et al. has reported the fabrication of all-organic field effect transistor consisting of semiconducting layer of poly(3-hexylthiophene) and dielectrics of polyimide [5], the fabrication of the transistor constructed with only organic monomer semiconductors have not reported so far. The organic transistors reported previously were fabricated with combination of organic and inorganic semiconductors [6-10].

In this chapter, the fabrication and characteristics of the field effect transistors with phthalocyanine and perylene derivative as monomer organic semiconductors will be described.

10.2 EXPERIMENTAL

10.2.1 Materials

Copper phthalocyanine (CuPc) and nickel phthalocyanine (NiPc) were prepared according to the previously reported method [11]. A reaction mixture of CuCl_2 or NiCl_2 and *ortho*-phthalonitrile suspended in pentanol was refluxed for 48 h. Evaporation of pentanol left a solid residue. The impurity in the residue was extracted with methanol. The blue crystalline CuPc and NiPc were washed with methanol and dried *in vacuo* at room temperature.

N,N'-Butyl-3,4,9,10-perylenetetracarboxylic-diimide (Bu-PTC) and *N,N'*-Octyl-3,4,9,10-perylenetetracarboxylic-diimide (Oct-PTC) were prepared on the basis of the method of Rademacher et al. [12]. A reaction mixture consisting of 0.68 g (1.7×10^{-3} mol) of 3,4,9,10-perylenetetracarboxylic dianhydride, 0.67 g (4.6×10^{-3} mol) of butylamine or 1.18 g (4.6×10^{-3} mol) of octylamine, and 0.50 g (2.4×10^{-3} mol) of zinc acetate suspended in 30 ml of quinoline was refluxed for 2 h. The resulting precipitate was filtered off and recrystallized extractively from toluene.

The red crystalline Bu-PTC and Oct-PTC were washed with methanol and dried *in vacuo* at room temperature.

CuPc, NiPc, Bu-PTC and Oct-PTC were purified by sublimation before fabrication of the devices.

10.2.2 Fabrication of field effect transistors

p-Channel type field effect transistor was fabricated by vacuum-deposition of silver as source and drain electrodes, CuPc as p-channel layer (100 μm), Oct-PTC as dielectric layer (200 μm), Bu-PTC as gate layer (200 μm) and silver as gate electrode on polyimide (Kapton[®]) substrate adhered to glass plate at a pressure of 1.3×10^{-3} Pa. On the other hand, n-channel type transistor was fabricated by vacuum-deposition of Oct-PTC as n-channel layer (200 μm), CuPc as dielectric layer (100 μm) and NiPc as gate layer (100 μm).

10.3 RESULTS AND DISCUSSION

CuPc, NiPc, Bu-PTC and Oct-PTC are preferable for applying to electronic devices because these compounds are chemically stable. Polyimide film is desirable as substrate for electronic device because the dielectric strength and thermal resistance are especially high [13]. However, since polyimide film is flexible, the fixation of polyimide film on the plate which has rigidity was necessary to prevent the crack formation in electrode and semiconductor films.

The present p- and n-channel type field effect transistors are shown in Fig. 10.1(a) and 10.1(b).

The appropriate gap length between source and drain electrodes was about 3 mm. The dielectric breakdown proceeded between source and drain electrodes if the gap length was shorter, while transistor property was unstable when a voltage was applied between source and gate electrodes if the gap length was longer.

Leakage of current between source and gate electrode was observed when dielectric layer did not exist. Transistor property was comparatively stable when dielectric layer existed between channel and gate layers. The result suggests that the insertion of dielectric layer was observed to be effective for prevention or relaxation of leakage of current.

The transistor property of the present p- and n-channel type field effect transistors is shown in Fig. 10.2(a) and 10.2(b). In both type transistors, drain-source current shifted to positive direction if gate was biased positively while shifted to negative direction if gate was biased negatively. Furthermore, drain-source current change by gate potential change was reproducible. That is, field effect on drain-source current was confirmed.

Conventional MISFETs reported previously were driven in enhancement mode [5-10, 14]. On the other hand, the present devices were driven in both enhancement and depletion modes. The result suggests that both electron and positive hole act as charge carriers within channel layer irrespective of the conduction type of semiconductor. This would be because phthalocyanines and perylene derivatives behave like intrinsic semiconductors since there is no dopant in the semiconductors.

10.4 CONCLUSION

All-organic field effect transistors with phthalocyanines and perylene derivatives which can be driven in both enhancement and depletion modes were fabricated. It was confirmed that the gap length between source and drain electrodes and the existence of dielectric layer between channel and gate layers were important factors for stabilization of transistor property.

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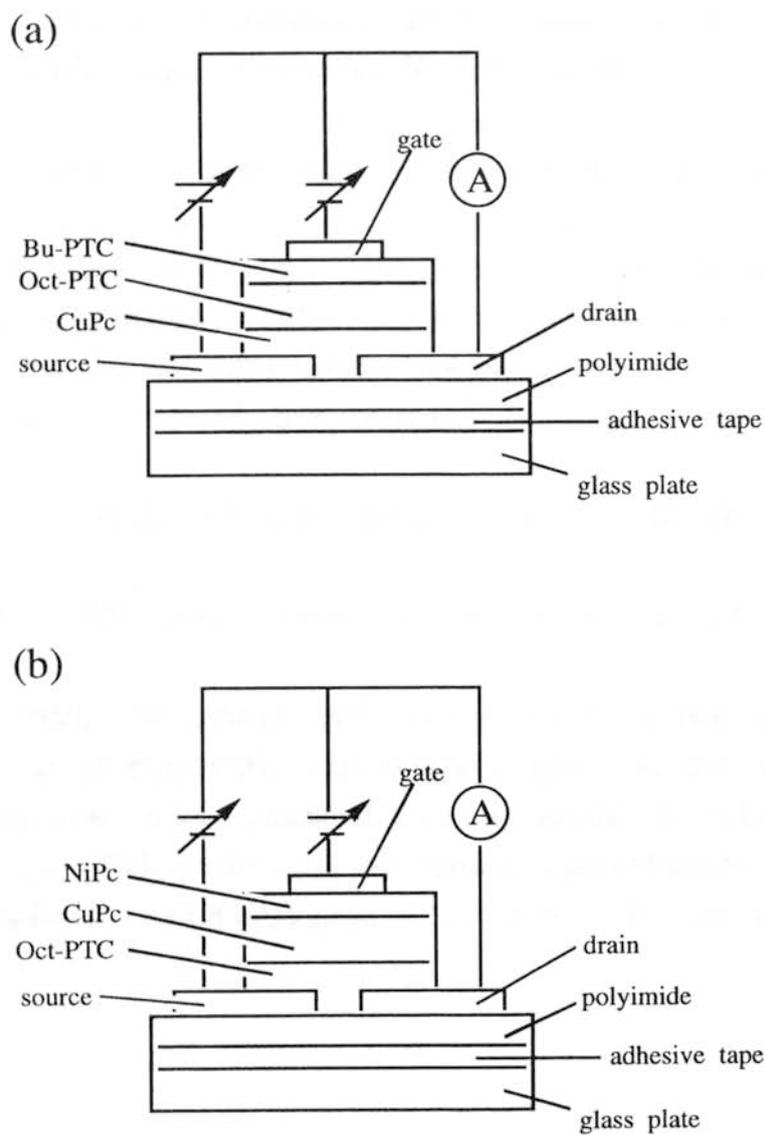


Figure 10.1 Schematic representation of (a) p- and (b) n-channel type field effect transistors.

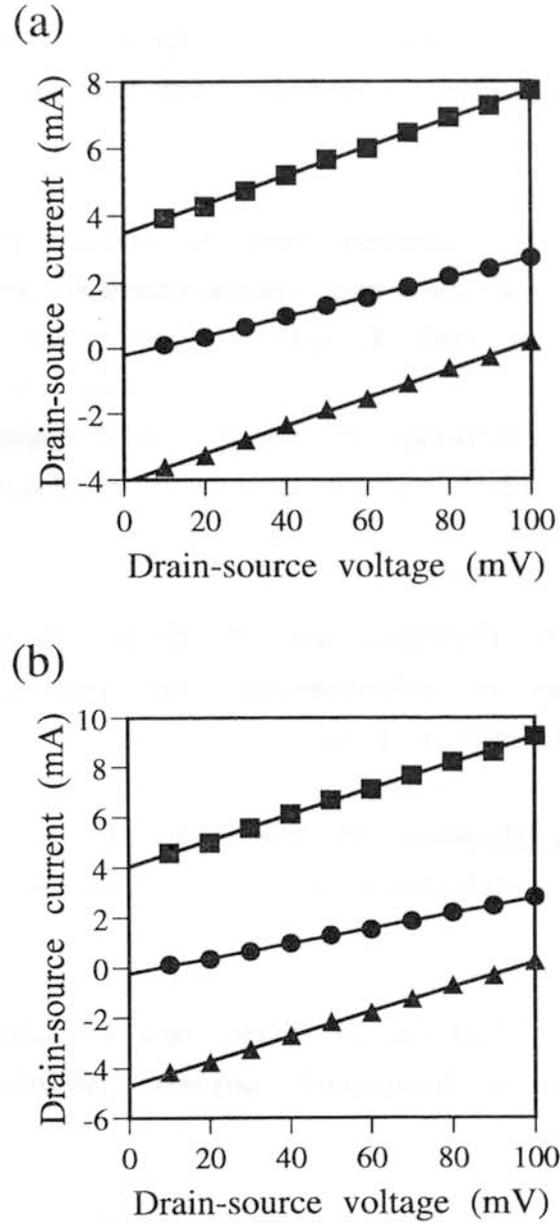


Figure 10.2 Drain-source current I_{DS} of (a) p- and (b) n-channel type field effect transistors as a function of the drain-source voltage V_{DS} for various gate-source voltage V_{GS} . \blacksquare : $V_{GS} = +90$; \bullet : $V_{GS} = 0$; \blacktriangle : $V_{GS} = -90$ mV.

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