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Effects of oxidizing gases on semiconductivity and thermal stability of phthalocyanine thin films

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The effects of oxidizing gases (O_2 and NO_2) on the p-type semiconductivity of the phthalocyanines H_2Pc, PbPc, ZnPc, CuPc, AlPcCl, AlPc–O–AlPc and $(AlPc)_n$ films treated in nitrogen at 350° C have been examined. The conductance increased in the presence of oxidizing gases. Reversible effects of oxidizing gases on the conductance were observed for PbPc, CuPc and ZnPc, all of which are thermally and/or chemically less stable than the other Pcs. For the latter, the conductance in nitrogen increased permanently after exposure to NO_2. The reversibility of the former may be related to the thermal and chemical stability of neutral and/or oxidized phthalocyanines. The conductivity is described by

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

The activation energy, E, decreased in the presence of oxidizing gases. The pre-exponential factor, G_0, was lowered by the introduction of NO_2 especially for PbPc, CuPc and ZnPc. It seems that the adsorption of NO_2 is limited to the surface of fine crystals and the increase in the conductance caused by exposure to NO_2 is strongly influenced by the crystallinity of phthalocyanine.

1. Introduction

It is well known that ambient gases affect the semiconductivity of a number of organic compounds. Phthalocyanines, in particular, have been studied as "prototypes" of organic semiconductors to use for toxic gas sensing. Metal-free, copper and lead phthalocyanine have received most attention [1–5]. Some phthalocyanines exhibit good thermal stability and are very sensitive to the presence of oxidizing gases. Most of them behave as p-type semiconductors. Their conductivity is increased by adsorption of oxidizing gases because majority carriers, i.e. holes, are produced by the formation of an adsorption complex. The sensitivity and thermal stability depend on the central cation species of phthalocyanine. The reversibility of the conductance change induced by adsorption and/or desorption of oxidizing gases and decomposition of molecular complexes depends on both the central cations and the crystal structure.

In this work, the effects of oxidizing molecules were examined on semiconductivity and thermal stability of "prototype" phthalocyanine thin films.

2. Experimental details

Metal-free (H_2Pc), lead (PbPc), copper (CuPc), zinc (ZnPc) and several aluminium phthalocyanines were used. Hydroxylaluminium phthalocyanine (AlPcOH) was made by refluxing chloroaluminium phthalocyanine (AlPcCl) with concentrated ammonium hydroxide and pyridine for 7 h. The resulting filtered solid was washed with pyridine, concentrated ammonium hydroxide and hot water [6]. Fluoroaluminium phthalocyanine (AlPcF) was prepared as follows: AlPcOH was evaporated to dryness on a steam bath with two separate portions of 48% hydrofluoric acid. The resulting solid was washed with water, methanol, pyridine, and acetone and was dried at 110° C [6]. All the samples were purified as follows: the solid was sublimed from a quartz crucible in vacuum (10^{-6} torr). The sublimed material was collected on a glass plate after the portion of sample sublimed in the initial periods had been deposited on another collector and removed without breaking the vacuum. With the exception of AlPcOH, the sublimed samples were assumed not to have decomposed although this could not be confirmed in detail. Oxo-aluminium phthalocyanine (AlPc–O–AlPc) was prepared by sublimation and condensation of AlPcOH in vacuum and its composition was confirmed by infrared spectroscopy. The thermogravimetric examination of sublimed samples was made under a flow of nitrogen, synthesized air, and synthesized air with 90% relative humidity at room temperature at a heating rate of 10° C $\min^{-1}$. The crystal structure was examined by standard X-ray diffractometry and infrared spectroscopy at room temperature.

The element for the electrical measurements was prepared by vacuum evaporation of purified phthalocyanine on to an alumina substrate over a pair of gold electrodes. The d.c. conductance was measured by using an electrometer and d.c. voltage supply (0.1 to 10 V) in flows of nitrogen, air and NO_2 diluted with air (10 p.p.m. NO_2) in the temperature range 50 to 300° C.

3. Results and discussion

3.1. Thermal stability

While the conductance of phthalocyanine used in this work was enhanced by exposure to oxidizing gases, the element must be maintained at a higher temperature in order to give satisfactory reversibility of the sorption–desorption process when used as a gas sensor. It is well known that some phthalocyanines have good thermal and chemical stability and sublime at 400° C or above in nitrogen, while little has been reported regarding the effect of ambient gas on the stability. If the decomposition and/or deformation of phthalocyanines is promoted by exposure to oxidizing gases and/or water vapour, the critical temperature at which weight loss occurs may be lowered because it is expected that the molecular weight of decomposed molecules is less than the initial one. In order to confirm the effects of ambient gases on the thermal stability, thermogravimetric analysis was used. Because of the limitations of the instrument, the measurements were only carried out in nitrogen, dry air, and air with 90% relative humidity at room temperature. The results are summarized in Table I. Characteristic temperatures for 5% and 10% weight loss are indicated. In nitrogen, the characteristic temperature for 5% weight loss of AlPc–O–AlPc and $(AlPcF)_n$ is considerably higher than that of the other samples. It is well known that the former is a μ-oxo-bridged compound and exists as a dimer while the latter exists as oligomer with (Al–F) backbones. The good stability observed in AlPc–O–AlPc and $(AlPcF)_n$ may be due to these special interactions between the monomers. For H_2Pc and AlPcCl, the decrease in the characteristic temperature of 5% weight loss on changing from nitrogen to air is less than 10° C. Larger decreases were observed for the other samples. The introduction of humid air induced a lack of thermal stability especially for PbPc and AlPcCl. It seems that the stability decreases further in the presence of NO_2 gas and hence the electrical measurements were limited to the temperature range below 300° C.

3.2. Crystal structure

It is well known that the phthalocyanines can take different crystal forms, and the phase transitions are strongly affected by minor impurities, ambient gases, and/or temperature. The polymorphism of some phthalocyanines has been studied widely. Ebert and Gottlieb [7] reported differences in infrared absorption spectra and X-ray diffraction patterns due to the dimorphism in H_2Pc, CuPc, ZnPc, etc. The temperature of the phase transition from the metastable α-form to the stable β-form is influenced by many factors, but the phase transition is achieved by heating to above 300° C and is irreversible for most of the phthalocyanines. The stable form of phthalocyanine thin films is preferred in studies of the effect of ambient gases in electrical conduction because the conductivity and the adsorbing power for gases are strongly affected by the crystal form and crystal size. Recently, Collins and Mohammed [8, 9] have reported the phase behaviour of CuPc, ZnPc, etc., and indicated that the growth of α-form microcrystallites into large crystals proceeded at lower temperatures. A fairly well-defined transition from α to β form was achieved by heating to 300° C or more. In addition, Sakaguchi *et al.* [10] have reported that the phase transition from α to β form was almost achieved by heating to 350° C, while the transition temperature was influenced by the ambient gases. In Table II, the main XRD peaks of phthalocyanine films before and after the heat treatment at 350° C in a flow of nitrogen are summarized. While the main peaks for H_2Pc, AlPcCl, AlPc–O–AlPc and $(AlPcF)_n$ were hardly affected by the heat treatment, the phase transition from the α to the β form was confirmed for CuPc and ZnPc. Furthermore, the intensity of peaks for PbPc was considerably lower than those for the other phthalocyanines and changed following the heat-treatments. It seems that the characteristics of phase transitions are influenced not only by the nature of the temperature but also by the substrate.

3.3. Electrical conductivity

Apparent irreversible temperature dependencies of the conductance in the range below 300° C were not

TABLE I Characteristic temperatures for 5 and 10 wt % weight loss for purified samples

Sample	Temperature for 5 wt % loss (° C)			Temperature for 10 wt % loss (° C)		
	N_2	Dry air	Humid air*	N_2	Dry air	Humid air*
H_2Pc	519	510	496	537	517	512
CuPc	551	416	423	573	443	443
ZnPc	530	485	500	550	515	520
PbPc	537	455	378	553	470	394
AlPcO–	608	459	466	627	500	500
AlPcCl	520	512	361	539	535	498
AlPcF	600	511	450	612	531	512

*Air with 90% relative humidity at room temperature.

TABLE II XRD patterns of sublimed phthalocyanines

	As-deposited		350° C/N_2	
	d (nm)	I/I_0	d (nm)	I/I_0
H_2Pc	1.340	91	1.339	90
	0.358	100	0.358	100
	0.337	100	0.339	88
AlPcCl	1.300	37	1.300	44
	0.330	100	0.330	100
AlPcF	1.320	100	1.310	100
	0.363	28	0.368	21
AlPcO–	1.300	100	1.300	100
	0.366	33	0.363	29
CuPc	1.310	100	1.290	62
	1.240	70		
	0.370	27	0.376	100
ZnPc	1.300	100	1.300	100
	1.065	78		
	0.966	55	0.966	88
	0.377	17	0.378	51
PbPc	1.210	100	1.300	52
	0.708	82	0.732	48
	0.358	21	0.365	100

observed for the sample annealed at 350° C under nitrogen. From these results, it is concluded that no apparent phase transitions and/or crystal growth take place during the electrical measuring procedures. Electrical conductance was measured in the temperature range below 300° C as the temperature was increased. The changes in ambient gases were affected as the temperature decreases and after the reversible temperature dependence of conductance was confirmed. For example, the results of PbPc are shown in Fig. 1. In this figure, N, A, and NO_2 indicate nitrogen, air and NO_2 diluted with air (10 p.p.m. NO_2). The order of measuring cycles is also indicated. For each measurement, the activation energy, E, and pre-exponential factor, G_0, were determined according to

$$G = G_0 \exp(-E/kT) \tag{1}$$

where k is the Boltzmann constant and T is absolute temperature. The correlation between the conductance at 150° C and its activation energy is shown in Figs 2 to 4 and summarized in Table III. The results indicated I and F in Figs 2 to 4 were obtained before and after the measurements under NO_2 ambient. For CuPc, the results fall on the two correlating straight lines drawn in Fig. 3. A similar correlation was found for PbPc and ZnPc.

The phase transition may be considered to be the reason for the deviation of the results observed in nitrogen from the straight line measured in the oxidizing gases. The phase transition, however, can be eliminated as the reason, because the characteristics were

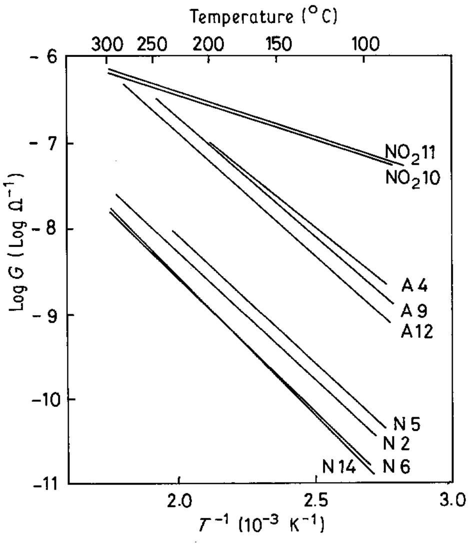

Figure 1 Temperature dependence of conductance of PbPc. N, in nitrogen, A, in air; NO_2, in NO_2/air (10 p.p.m.). The number of measuring cycles are indicated in the figure.

TABLE III Activation energy and conductance at 150° C

Sample	Condition	Before exposure to NO_2/air		After exposure to NO_2/air	
		E (eV)	log G (Ω^{-1})	E (eV)	log G (Ω^{-1})
H_2Pc	N_2	0.62	−9.84	0.41	−7.61
	air	0.59	−8.80	0.47	−7.46
	NO_2/air	0.42	−7.15		
PbPc	N_2	0.60	−9.33	0.64	−9.73
	air	0.50	−7.63	0.56	−7.90
	NO_2/air	0.21	−6.80		
ZnPc	N_2	0.75	−10.70	0.79	−10.10
	air	0.65	−8.56	0.64	−8.40
	NO_2/air	0.36	−6.96		
CuPc	N_2	0.84	−10.95	0.76	−10.22
	air	0.82	−8.89	0.73	−8.40
	NO_2/air	0.36	−7.20		
AlPcCl	N_2	0.84	−10.76	0.73	−8.89
	air	0.57	−8.40	0.61	−7.97
	NO_2/air	0.32	−6.21		
AlPcF	N_2	0.64	−10.09	0.36	−7.11
	air	0.35	−6.02	0.32	−5.60
	NO_2/air	0.15	−4.20		
AlPc–O	N_2	0.87	−10.98	0.72	−9.21
	air	0.63	−9.36	0.62	−8.15
	NO_2/air	0.29	−6.85		

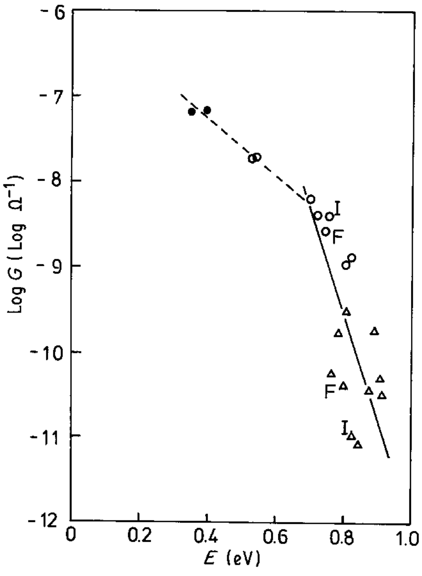

Figure 2 Relation between conductance at 150° C and activation energy for CuPc. (△) in nitrogen, (○) in air, (●) in NO_2/air. I and F indicate data obtained before and after exposure to NO_2/air, respectively.

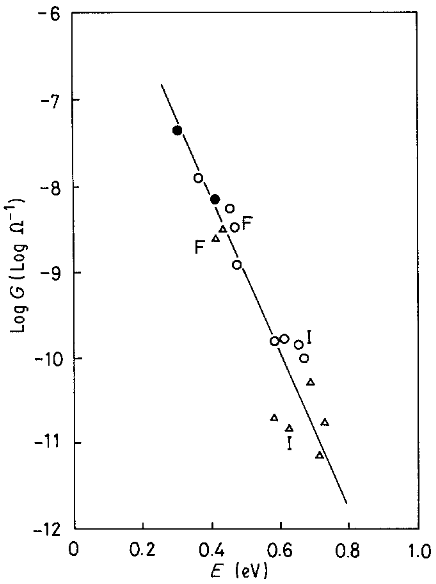

Figure 3 Relation between conductance at 150° C and activation energy for H_2Pc. Notations are explained in Fig. 2.

reproduced even after measurements in NO_2/air for CuPc, PbPc and ZnPc. The characteristics observed under each condition for PbPc, in particular, were directly dependent on the ambient conditions and tended to a given value for each condition, while some scatter was observed for CuPc and ZnPc. By assuming that the pre-exponential factor is independent of the ambient gas, the theoretical value of the slope in the relation between log G_0 and the activation energy, E, is estimated to be $-1/kT$. As summarized in Table IV, for H_2Pc, AlPcCl and AlPc-O-AlPc, the absolute value of the slope is slightly less than this theoretical value and all of the observed results can be represented by one straight line within experimental error. Furthermore, for $(AlPcF)_n$, the slope is in fairly good agreement with the theoretical value.

For the other phthalocyanines, the results observed under nitrogen and air, especially before exposure to NO_2, can be represented by one straight line for which the slope is comparable to the theoretical value, while the slope of the line obtained from the results in the presence of NO_2 and in air after exposure to NO_2 is considerably lower. A definite deviation from the form expressed in Equation 1 is observed only for PbPc, ZnPc and CuPc after exposure to NO_2. The deviation of NO_2 results may be caused by an irreversible oxidation reaction with the gas. But, as reported previously [11], the results observed for CuPc, NiPc and H_2Pc films formed on the transparent quartz substrates, under all conditions, are described by Equation 1 and the constant G_0 which is hardly influenced by the ambient gases, i.e. the slope of the correlation between log G at 150° C and activation energy is equal to $-1/kT$ within experimental error. Thus the differences must result from other reasons. One possibility is differences in the crystal form or crystal size in the evaporated film, because it has been already confirmed [12] that the crystal form and orientations are influenced not only by the evaporation rate and the substrate temperature during the evaporation procedure, but also by the crystallinity and/or flatness of the substrate. It seems that the crystallinity and/or crystal size in the films affect the concentration of adsorption sites and this results in less molecular adsorption and/or lower permeability. The molecular diameter of NO_2 is larger than that of O_2, and the electron affinity is considerably higher. By assuming that the adsorption of NO_2 is limited to the surface of fine crystals, it is realized that the conductance in NO_2 is considerably lower than the extrapolated value by using Equation 1 for a constant pre-exponential term determined from the results in N_2.

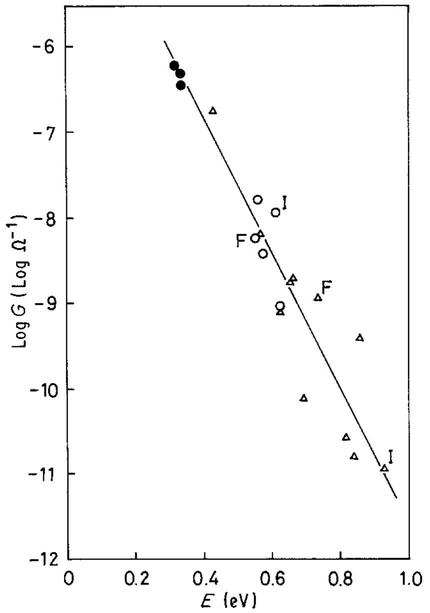

Figure 4 Relation between conductance at 150° C and activation energy for AlPcCl. Notations are explained in Fig. 2.

TABLE IV The slope of line confirmed in the relationship between log G at 150° C and activation energy in conduction

Sample	Befor exposure to NO_2/air	After exposure to NO_2/air
H_2Pc	−9.0	−9.0
PbPc	−11.9	−1.9
ZnPc	−11.7	−5.2
CuPc	−11.9	−3.4
AlPcCl	−7.8	−7.8
AlPcF	−11.6	−11.6
AlPcO	−7.1	−7.1

Theoretical slope ($-1/kT$) is $-11.91\,eV^{-1}$.
*Results observed in NO_2/air and air.

The conductance in air and nitrogen of H_2Pc and AlPc-O-AlPc measured after exposure to NO_2 was higher than that observed before exposure by a factor of 100 or more. In addition, for AlPcCl and (AlPcF), the conductance in nitrogen increased upon exposure to NO_2 while the conductance in air was the same after exposure. It seems that the differences in the reversibility of conduction are due to the chemical and/or thermal stability. As indicated in Table I, the characteristic temperature for 5% weight loss in air decreases in the order: AlPcCl-(AlPcF)*n*-H2Pc > ZnPc > (AlPc-O-AlPc)-PbPc > CuPc and, furthermore, the oxidation potentials compared to SCE have been estimated as 1.10 V (H_2Pc), 0.98 V (CuPc), 0.68 V (ZnPc) and 1.15 V (AlPcCl) [13, 14]. The reversibility of conductance confirmed for CuPc, PbPc and ZnPc may be caused by the decomposition and sublimation of the molecular complex being easier. Further experimental investigations on this subject are now in progress.

References

1. R. L. VAN EWYK, A. V. CHADWICK and J. D. WRIGHT, *J. Chem. Soc. Faraday I* **76** (1980) 2194.
2. C. L. HONEYBOURNE and R. J. EWIN, *J. Phys. Chem. Solids* **44** (1983) 216.
3. B. BOTT and T. A. JONES, *Sensors and Actuators* **5** (1984) 43.
4. T. A. JONES and B. BOTT, *ibid.* **9** (1986) 27.
5. Y. SADAOKA *et al.*, *Denki Kagaku* **50** (1982) 457.
6. J. P. LINSKY *et al.*, *Inorgan. Chem.* **19** (1980) 3131.
7. A. A. EBERT and H. B. GOTTLIEB, *J. Amer. Chem. Soc.* **74** (1952) 2806.
8. K. A. MOHAMMED and R. A. COLLINS, *Thermochim. Acta.* **104** (1986) 377.
9. R. A. COLLINS and K. A. MOHAMMED, *ibid.* **109**, (1987) 397.
10. M. SAKAGUCHI *et al.*, *J. Electrochem. Soc.* **127** (1980) 1872.
11. Y. SADAOKA, N. YAMAZOE and T. SEIYAMA, *Denki Kagaku* **46** (1978) 597.
12. Y. SADAOKA, unpublished results.
13. A. GIRAUDEAU, F. F. FAN and A. J. BARD, *J. Amer. Chem. Soc.* **102** (1980) 5137.
14. A. WOLBERG and J. MANASSEN, *J. Amer. Chem. Soc.* **92** (1970) 2982.

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