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Effects of morphology on NO_2 detection in air at room temperature with phthalocyanine thin films

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Lead phthalocyanine films freshly deposited on alumina and glass were found to consist of disordered phases and fine particles with mean diameter below 0.2 μm. Following annealing at 300° C, a transition to a crystalline form is obtained. The crystal size in the films annealed at 300° C or above is affected by the nature of the substrate, ambient atmosphere and annealing time. Following an optimized preparation procedure, the films exhibit response times of less than 20 sec and recovery times of the order of several minutes, independently of NO_2 concentration or exposure time, at room temperature. They consist of fine crystals with mean diameters of the order of 0.2 μm and amorphous phases are not observed. For zinc, copper, cobalt and nickel phthalocyanine films, some improvements in the response and recovery times are achieved by annealing but not sufficient to allow NO_2 detection at room temperature. For films of these phthalocyanines, fine crystals of the type formed in lead-phthalocyanine films were not produced in the conductive paths when the films were annealed at 300° C in air.

1. Introduction

It is well known that ambient gases can affect the semiconductivity of a number of organic compounds [1–5]. Several of the metal phthalocyanines are *p*-type semiconductors with good thermal and chemical stabilities. Their conductivity increases following adsorption of oxidizing molecules, because of the generation of hole carriers induced by the formation of charge transfer complexes at the surface of the phthalocyanine. Lead phthalocyanine films are superior to those of other phthalocyanines in terms of sensitivity, reproducibility and/or speed of response to changes in the concentration of the oxidizing species in air. Recently, Bott and Jones [6] reported that the ratio of the conductances observed in an atmosphere of NO_2 in air to those observed in air increased with the operating temperature in the range up to about 160° C and decreased at higher temperatures; in addition, both the response and recovery times decreased monotonically with an increasing operating temperature. For a sensor prepared by the usual vacuum sublimation technique, the operating temperature must be at above 150° C in order to give satisfactory reversibility. It is preferable not to operate at higher temperatures because the crystal size and/or crystal phase may be varied by operating at such temperatures and, furthermore, the lead phthalocyanine may react irreversibly with oxidizing molecules or may decompose [7, 8]. These factors can result in a lack of long-term stability of the sensing characteristics.

In this work, the feasibility of fabricating NO_2 gas sensors based on metal-substituted phthalocyanine thin films operable at room temperature was investigated and the correlation between the sensing characteristics and the film structures was examined. The oxidation of phthalocyanine and the changes in the film structure are less marked at lower operating temperatures.

2. Experimental procedure

Commercial lead phthalocyanine (PbPc) was initially purified by entrainer sublimation in a flow of nitrogen (100 ml min^{-1}). The entrainment used three temperature zones; a sublimation zone (ca. 520° C), a collection zone (220 to 320° C), and a lower temperature zone to collect impurities and decomposition products. The sample obtained in the collection zone was used to prepare the film. Films were formed on both alumina and glass substrates fitted with platinum electrodes. The substrate temperature during the

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evaporating procedure was maintained below 50° C. The film thickness was about 2 μm or less. The films with zinc phthalocyanine (ZnPc), copper phthalocyanine (CuPc), cobalt phthalocyanine (CoPc) and nickel phthalocyanine (NiPc) were prepared by vacuum sublimation using purified material.

D.c. resistance was measured at room temperature using an electrometer, in mixed flows of clean air and 10 p.p.m. NO_2 in air giving concentrations in the range from 0 to 10 p.p.m. The elements were located directly in the gas stream. The chamber, gas flow and mixing systems were made from PTFE and PVC, but metal-bodied mass flow controllers had to be used. Before carrying out electrical measurements, the elements were treated under appropriate conditions.

The elements were examined by scanning electron microscopy (SEM), Fourier transform-infrared (FT-IR) spectroscopy and X-ray photoelectron spectroscopy (XPS).

3. Results

3.1. Sensitivity and response to NO_2

3.1.1. Lead phthalocyanine

In Fig. 1, the changes in resistance at room temperature observed when the elements were exposed to air, switched to 10 p.p.m. NO_2/air then returned to air are shown for films formed on glass. For the fresh film, the response takes the form of an initial fast change followed by a slow drift to the steady state value. The second process can take a long time, especially in fresh films but is dramatically improved by annealing. For instance, the steady state is achieved within 2 min for the film annealed at 330° C in nitrogen. The recovery is similar in form. For the film annealed at 330° C, the original resistance is almost reached within the experimental measuring period. Similar effects of annealing on the sensing characteristics were confirmed for the film formed on alumina. The reproducibility and the repeatability of the sensing characteristics for films annealed at 330° C in nitrogen were, however, different from those for films formed on glass. In Fig. 2, the response and recovery curves observed for the first exposure to 10 p.p.m. NO_2/air and after five exposures are shown for films annealed at 330° C in nitrogen on glass and alumina. The drift in resistance of the film deposited on glass, especially in clean air, was considerably less than that of the film deposited on alumina, although the resistance in quasi-steady state in 10 p.p.m. NO_2/air was not influenced by the exposure times.

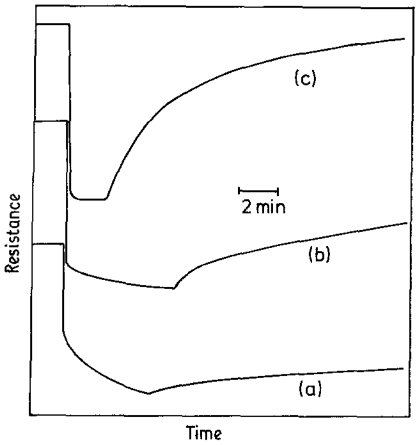


Figure 1 Response curves for PbPc films formed on glass and annealed in nitrogen for 3 h for the changes of ambient from clean air to 10 p.p.m. NO_2/air and vice versa. Annealing temperature: (a) 250° C, (b) 290° C, (c) 330° C.

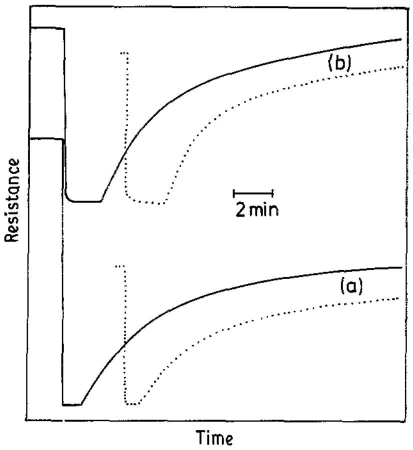


Figure 2 Response curves for PbPc films annealed at 330° C in nitrogen for 3 h. (a) Film formed on alumina, (b) formed on glass. (——) Initially observed results, (- - -) results following five consecutive exposures.

The response curves were influenced not only by the temperature but also the length of time for which the films were annealed. In Figs 3 and 4, the response curves for films deposited on glass and alumina and annealed at 300° C in air are shown. The slow approaches to the steady state in 10 p.p.m. NO_2/air are accelerated by increasing the annealing time, and the recovery times also become faster for both films. The recovery time is defined as the time to return to the critical value which corresponds to half of the resistance in air immediately before the exposure to 10 p.p.m. NO_2/air. By comparing the results for the films annealed at 300° C for 5 h in air and in nitrogen, it is apparent that the recovery time for the film annealed in nitrogen is longer than that for the film annealed in air. The recovery time for the film annealed in nitrogen increases with increasing period of exposure to 10 p.p.m. NO_2/air, while for the film

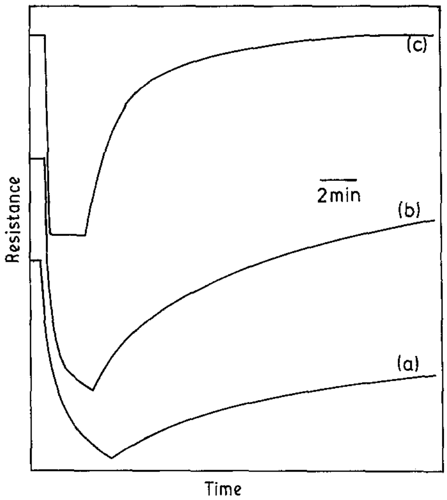


Figure 3 Response curves for PbPc films formed on glass. (a) Fresh film, (b) film annealed in air at 300° C for 3 h, (c) film annealed in air at 300° C for 5 h.

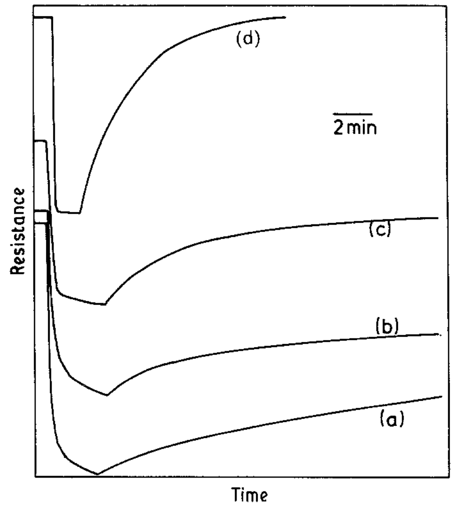


Figure 4 Response curves for PbPc films formed on alumina and annealed at 300° C in air. Annealing time: (a) 0 h, (b) 1 h, (c) 3 h, (d) 5 h.

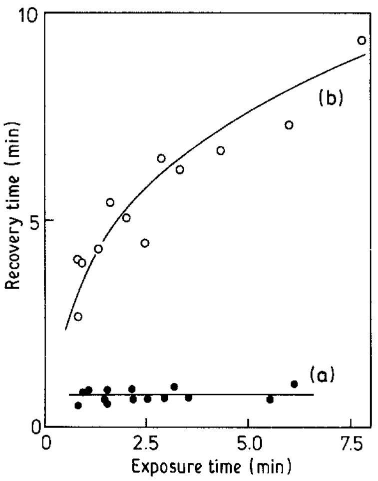


Figure 5 Exposure time dependence of the recovery time for PbPc films annealed at 300° C for 5 h. (a) Annealed in air, (b) annealed in nitrogen.

annealed in air the recovery time is not markedly influenced by the exposure time. The results are shown in Fig. 5.

The concentration dependence of the conductance for a film annealed at 300° C in air for 5 h is shown in Fig. 6; the resolution decreases with increasing concentration. The resistance values are summarized in Table I. The resistances in clean air and in 10 p.p.m. NO_2/air decreased following heat treatment at 250° C and increased with an increase in the annealing temperature above 250° C. For the films annealed at 300° C in air for 10 h, no detectable colour arising from the phthalocyanine ring can be observed. The resistance of these films is of the order of $1 \times 10^{10}\,\Omega$ and is not influenced by the ambient atmosphere.

3.1.2. Other phthalocyanines

For ZnPc, CuPc, CoPc and NiPc films, the response curves and the resistance values in clean air and in 10 p.p.m. NO_2/air at room temperature are shown in Figs 7 to 10 and Table II, respectively. For ZnPc film, the resistance decreases rapidly on exposure to NO_2 but the recovery time is slow. No significant improvements in the recovery characteristics are achieved by annealing at 300° C in air. For the CoPc film, the response takes the form of an initial fast change followed by a slow drift to the steady state and this second slow drift is also observed for the film annealed for 3 h. Annealing induces a distinct improvement in the response curve for CuPc films i.e. the extent of the slow drift is reduced and a fast recovery time is achieved, while the resistance in clean air is greater than $2 \times 10^{11}\,\Omega$. For NiPc films, different annealing effects from ZnPc, CoPc and CuPc were observed. The films prior to any heat treatment manifest fast response and recovery times, while the resistances in clean air decrease monotonically with repeated measuring cycles and the drift is enhanced by the heat treatment. For all the phthalocyanine films, the resistance in clean air increased with longer annealing times at 300° C in air.

3.2. Observation by SEM

It appears that the films prepared by the sublimation method consist of the α-phase and disordered phases. The heat treatment at 300° C induces the phase transition from the metastable α-phase to the β-phase. The

TABLE I The values of the resistance in air and in 10 p.p.m. NO_2/air at room temperature for lead phthalocyanine thin films

Annealing conditions			Substrate	Resistance (Ω)	
Temp. (° C)	Ambient	Time (h)		in air	in NO_2/air
Fresh			alumina	1.8×10^8	1.7×10^7
			glass	4.8×10^7	5.0×10^6
250	N_2	3	alumina	5.1×10^5	1.9×10^5
			glass	4.3×10^5	2.1×10^5
290	N_2	3	alumina	3.1×10^6	5.0×10^5
			glass	3.0×10^6	6.2×10^5
330	N_2	3	alumina	3.8×10^8	3.5×10^6
			glass	6.8×10^7	4.9×10^6
300	air	1	alumina	1.6×10^8	2.7×10^7
300	air	2	alumina	7.5×10^8	1.3×10^7
300	air	3	alumina	1.1×10^9	2.0×10^8
			glass	1.5×10^7	6.5×10^6
300	air	5	alumina	3.2×10^{10}	1.4×10^9
			glass	6.4×10^9	8.0×10^8
330	air	2	alumina	7.5×10^8	1.3×10^7
			glass	2.8×10^8	1.8×10^7
300	air	10	glass	3.0×10^{10}	3.0×10^{10}

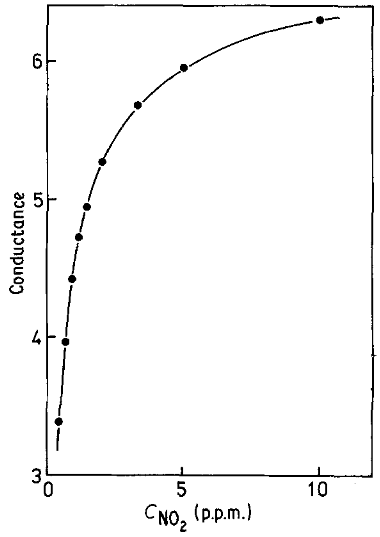


Figure 6 NO_2 concentration dependence of conductance for PbPc film annealed in air at 300° C for 5 h.

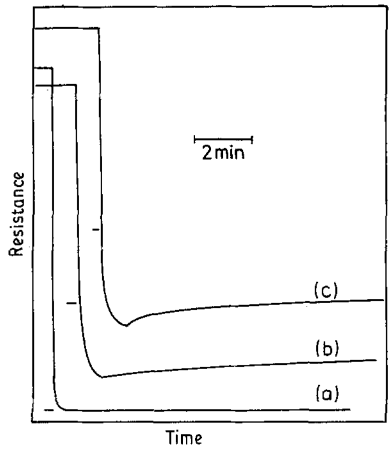


Figure 7 Response curves for ZnPc films formed on alumina and annealed in air at 300° C. (a) Fresh film, (b) film annealed for 3 h, (c) film annealed for 6 h.

change in geometrical structure is less simple and the crystal size especially is strongly influenced by the nature of the substrate, the ambient atmosphere and the central metal species of phthalocyanine.

3.2.1. Lead phthalocyanine

The geometrical structure of lead phthalocyanine films annealed in nitrogen is shown in Figs 11 and 12. The fresh films, prior to heat treatment formed on alumina and on glass consist of fine particles with a low degree of crystallinity and a disordered phase. No obvious differences in geometrical forms were observed in films formed on alumina and glass. Annealing at a higher temperature effected changes in the geometrical structures. For films annealed at 250 and 290° C in nitrogen, crystal growth and the presence of new single crystals formed on the film surface were observed.

The annealing at 330° C in nitrogen induced dramatic changes in the geometrical forms, i.e. larger crystals, 1 μm or more in thickness and length, were formed. The structure of the films was dependent on the substrates; for the films formed on alumina and annealed at 330° C, the larger single crystals formed by annealing were interconnected and smaller crystals were not formed (Fig. 11); films formed on glass and annealed at 330° C had a different film structure in which the larger crystals were isolated by layers consisting of very fine particles (Fig. 12).

The geometrical structure of the films was affected not only by the annealing temperature but also by the ambient atmosphere and the annealing time. In Figs 13 and 14, the micrographs for the films formed on alumina and glass and annealed at 300° C are shown as a function of the annealing time. During annealing at 300° C, the initial crystal growth was followed by the sublimation of molecules from the surface. The sharply defined crystals grown in the earlier periods became less clear with increasing annealing time. For the film annealed for 5 h, most of the large crystals disappeared and the films consisted only of fine crystals. This behaviour was also observed in the films formed on glass. Following annealing for 10 h or more in air, different forms of fine particles from those observed in the films annealed for 5 h were obtained as mentioned above, no clear colours arising from the phthalocyanine ring were detected in this film.

The observation that annealing in air at 300° C for 5 h induced the formation of only fine crystals is interpreted in terms of the formation of lead oxides on the particle surfaces. The oxygen molecules are adsorbed on the surface and diffuse into the crystals

TABLE II The values of the resistance in air and in 10 p.p.m. NO_2/air at room temperature for phthalocyanine thin films annealed in air

	Annealing time at 300° C (h)	Resistance (Ω)	
		in air	in NO_2/air
ZnPc	0 (fresh)	8.9×10^8	3.6×10^6
	3	9.3×10^9	1.8×10^9
	6	1.0×10^{10}	2.3×10^9
CuPc	0 (fresh)	7.5×10^6	1.5×10^6
	2	$> 2.0 \times 10^{11}$	$> 2.0 \times 10^{11}$
	4	$> 2.0 \times 10^{11}$	6.0×10^{10}
CoPc	0 (fresh)	1.3×10^8	6.5×10^6
	3	2.7×10^{10}	9.0×10^9
	6	6.7×10^9	2.1×10^9
NiPc	0 (fresh)	8.1×10^8	1.9×10^8
	3	1.3×10^{11}	3.0×10^{10}
	5	$> 2.0 \times 10^{11}$	2.0×10^{10}

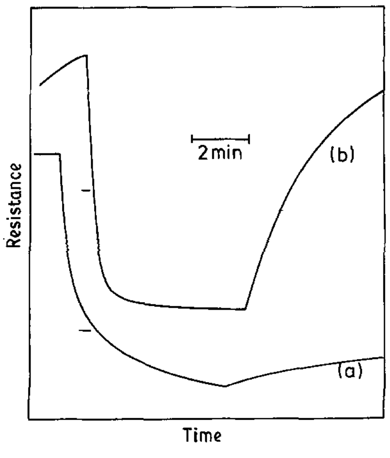


Figure 8 Response curves for CuPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 4 h.

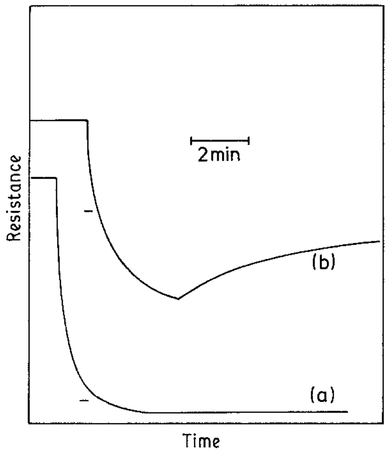


Figure 9 Response curves for CoPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 3 h.

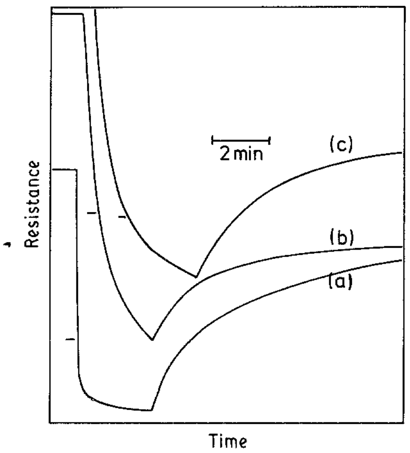


Figure 10 Response curves for NiPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 3 h, (c) film annealed at 300° C in air for 5 h.

along crystal imperfections and react with bulk PbPc during the annealing process. The surface lead oxides inhibit the growth of lead phthalocyanine crystals.

3.2.2. Zinc and cobalt phthalocyanine

No fine crystals were observed in the freshly deposited films as shown in Figs 15 and 16. The observed larger "cell" structure is that of the alumina substrate. For ZnPc films annealed at 300° C in air for 3 h, the crystallization was clearly observed and similar morphologies were observed for the films annealed for 3 and 6 h. The crystals have a direction of crystal growth which depends on the granular structure of the alumina substrate and crystals are connected to each other (Fig. 15). Similar annealing effects on the film structure were confirmed for CoPc films. The crystals grown in a direction perpendicular to the substrate were confined to limited areas of the CoPc films (Fig. 16).

3.2.3. Copper phthalocyanine

Freshly deposited films consist of very fine particles

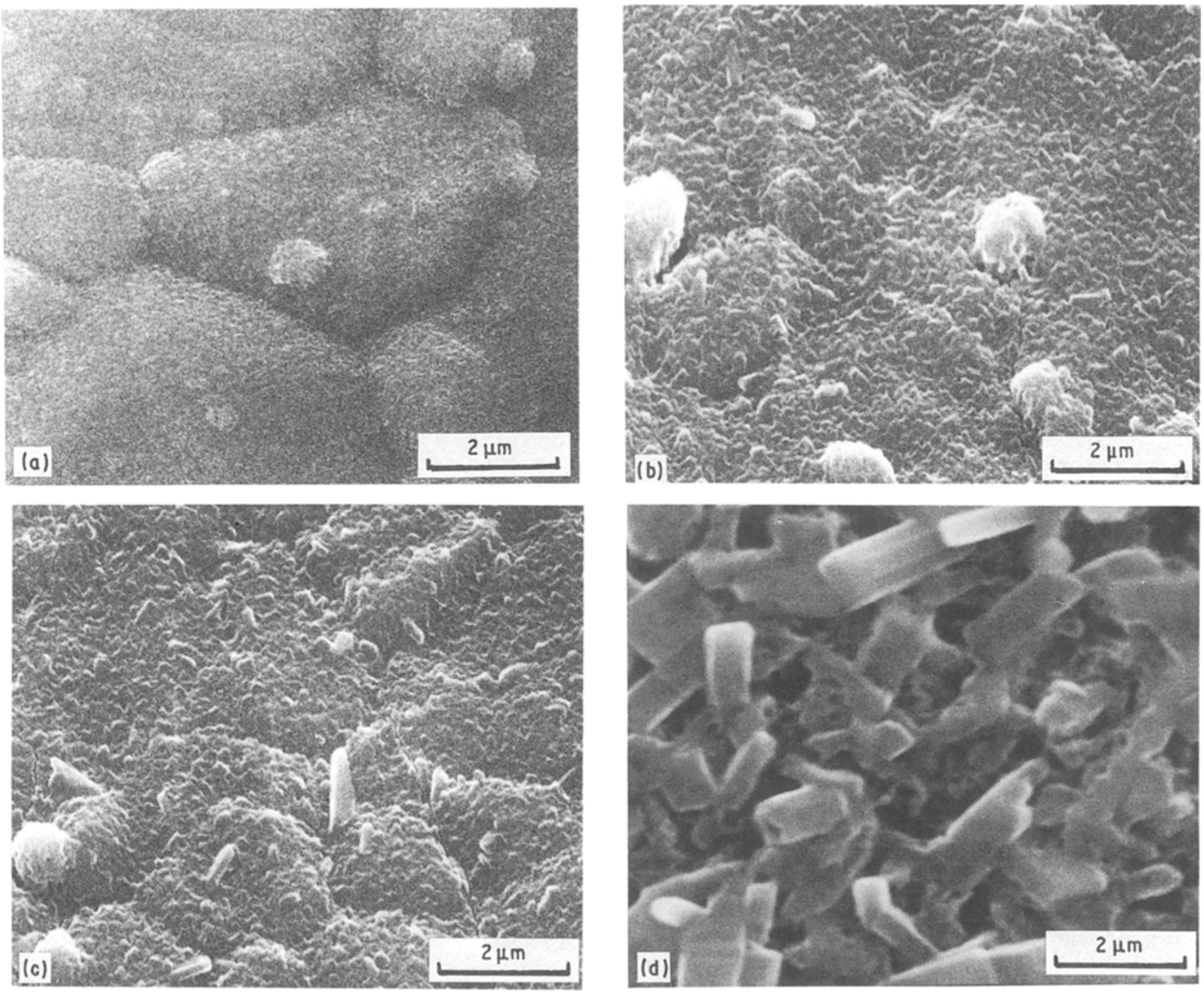


Figure 11 Scanning electron micrographs of PbPc films formed on alumina. (a) Fresh film, (b) film annealed at 250° C in nitrogen for 3 h, (c) film annealed at 290° C in nitrogen for 3 h, (d) film annealed at 330° C in nitrogen for 3 h.

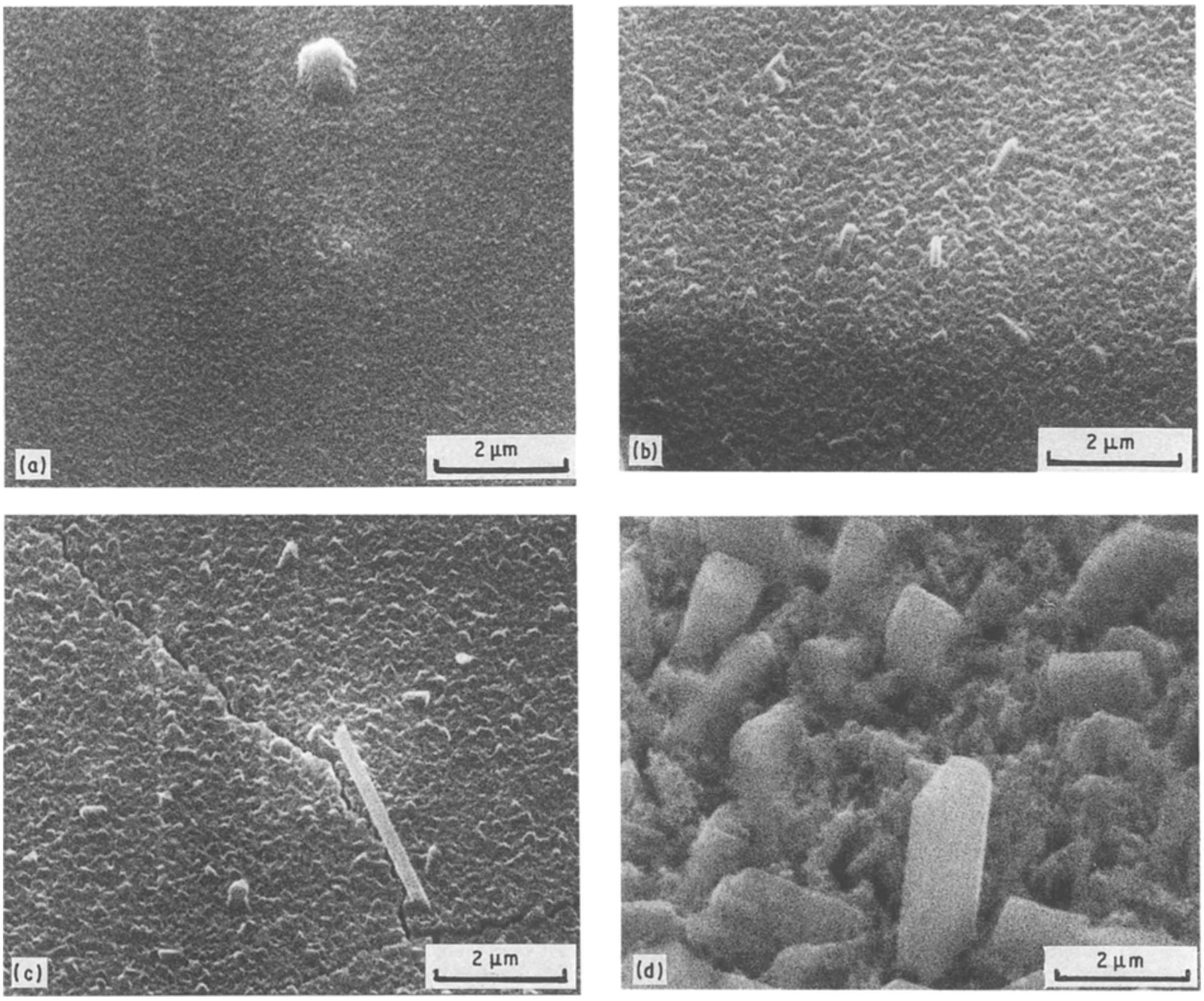


Figure 12 Scanning electron micrographs of PbPc films formed on glass. Notations as used in Fig. 11.

and amorphous phases which resemble the fresh PbPc films. Following annealing at 300° C for 2 h, a number of single crystals grew on the surface of the film in the direction perpendicular to the substrate. For the film annealed for 4 h, the growth of single crystals perpendicular to the substrate and the interconnection between the single crystals was extended (Fig. 17). On the flat faces of the alumina substrate, the porous layer in some areas consisted of fine crystals.

3.2.4. *Nickel phthalocyanine*

The morphology for the freshly deposited films was very similar to that of ZnPc and CoPc films (Fig. 18). The annealing at 300° C in air induces the formation of needle-like single crystals on the surface. These single crystals grew perpendicular to the substrate surface. It is concluded that these single crystals do not affect the sensitivity to ambient atmospheres.

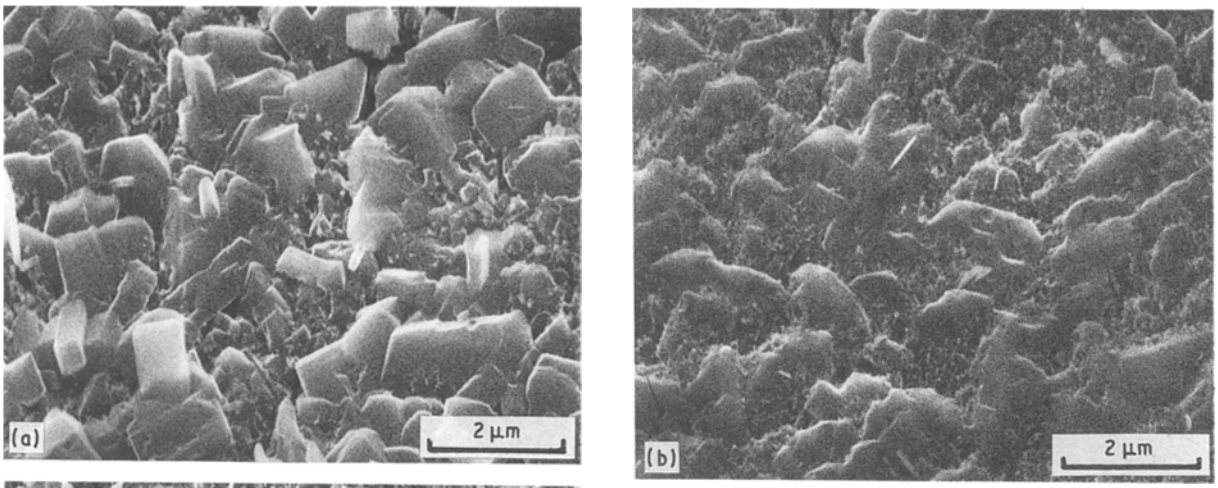
3.3. FT–IR spectra

Films prepared by sublimation on to substrates maintained at below 50° C during the process consisted of a mixture of the metastable α-form and an amorphous phase. It is well known that the conductance of the α-form of some phthalocyanines is more affected by absorption of oxygen than the β-form. The α-form is changed to the more stable β-form by heat treatment at or above 300° C and crystal growth proceeds at 150° C or lower. It is established that annealing of the film induces both crystal growth and a phase transition.

It was difficult to determine the crystal structure by X-ray diffraction for film thicknesses less than about 2 μm. An FT–IR investigation of the films formed on the substrate fitted with a pair of platinum electrodes was carried out. It is known [8, 9] that the infrared spectra in the region corresponding to the C–H stretch, C–H bend modes, etc., are influenced not only by the molecular structure but also by the crystalline phase of phthalocyanine. This method can, therefore, be used to obtain qualitative information relating to the phase transition.

3.3.1. *Lead phthalocyanine*

Following heat treatments at 290° C or below in nitrogen, the single peak at 720 cm^{-1} (C–H bending mode) was replaced by a doublet at 718 and 723 cm^{-1}. For the film annealed at 330° C in nitrogen, a single peak at 723 cm^{-1} was observed and the peak at 720 cm^{-1} disappeared. The peaks at 742 and 769 cm^{-1} were shifted to higher wavenumber and the ratio of the peak heights was changed by annealing. The peaks corresponding to the aromatic C–H stretching modes in the range from 3000 cm^{-1} were modified by heat treatment. The observed results may be consistent with the fresh films consisting of the α-form, the film



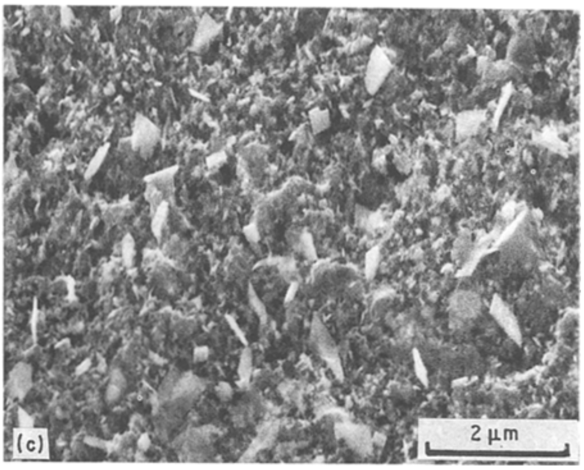


Figure 13 Scanning electron micrographs of PbPc films formed on alumina and annealed in air at 330° C. Annealing time: (a) 1 h, (b) 3 h, (c) 5 h.

annealed between 250 to 290° C of a mixture of α- and β-forms, and the film annealed at 330° C with β-form. However, because of its non-planar structure, there is considerable doubt as to the existence of α- and β-phases in PbPc, so that the observed changes may be due to other changes as a consequence of annealing; possibly a change from monoclinic to triclinic crystal form. Similar effects were observed for the film annealed in air. In addition, most of the main absorption peaks assigned to the PbPc molecules were observed.

3.3.2. *Other phthalocyanines*

For ZnPc film, the peaks at 718 and 768 cm^{-1} observed for the freshly deposited films were shifted to 726 and 780 cm^{-1} following annealing at 300° C in air. In addition, the peak at 887 cm^{-1} was observed for the untreated films and peaks at 879 and 890 cm^{-1} for the film annealed in air.

For CuPc film, the peaks at 726 cm^{-1} with shoulders at 720 and 770 cm^{-1} disappeared and a new peak appeared at 730 cm^{-1} following heat treatment at 300° C in air and the peak at 770 cm^{-1} shifted to 780 cm^{-1}. The new peak at 879 cm^{-1} was observed in

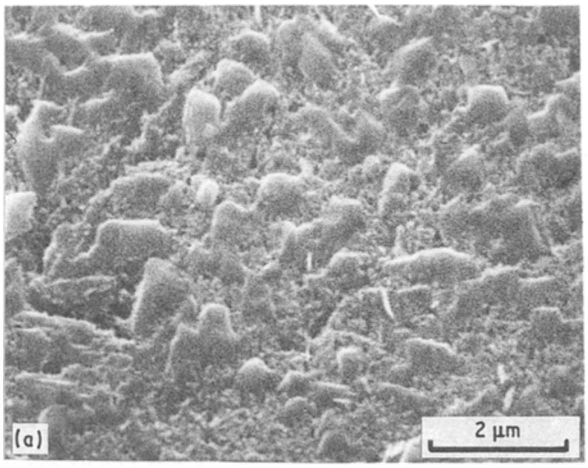
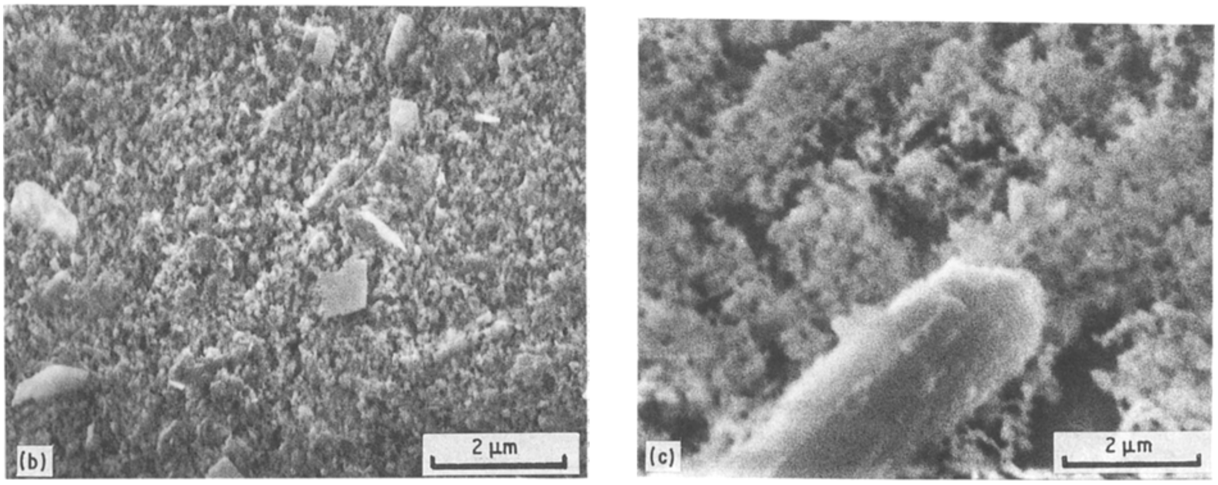
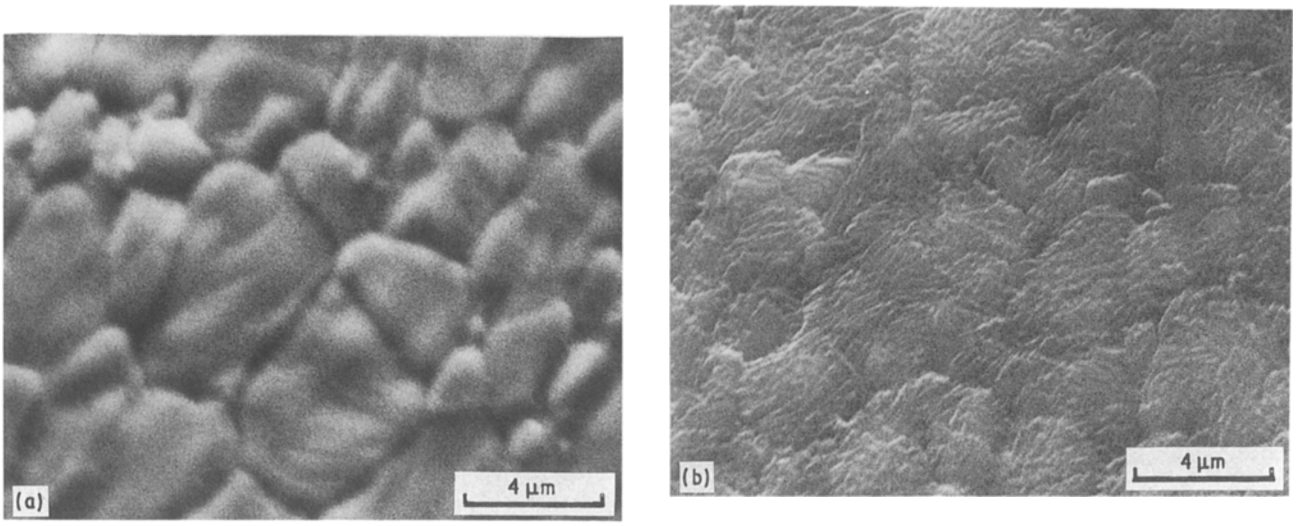


Figure 14 Scanning electron micrographs of PbPc films formed on glass and annealed in air at 300° C. Annealing time: (a) 3 h, (b) 5 h, (c) 12 h.





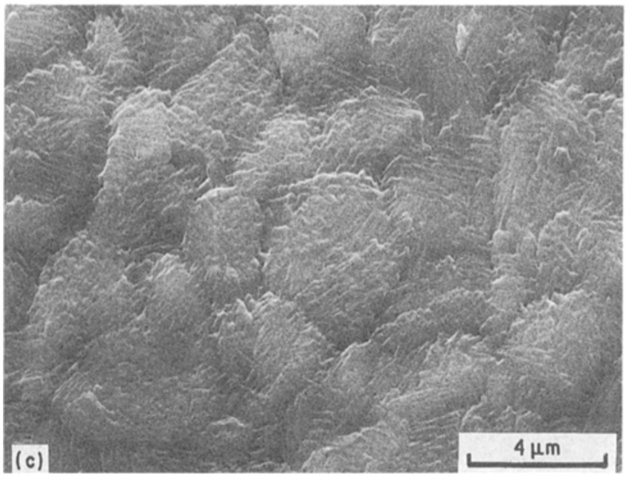


Figure 15 Scanning electron micrographs of ZnPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 3 h, (c) film annealed at 300° C in air for 6 h.

the annealed film. Although the peaks at 863 and 869 cm^{-1} were obtained, the one at 879 cm^{-1} was not detected.

For CoPc film, the absorption peaks at 723 and 771 cm^{-1} observed for the freshly deposited film were shifted to 732 and 780 cm^{-1}, respectively, by heat treatment at 300° C in air. A peak at 875 cm^{-1} was observed for the annealed film but not for the untreated film.

For fresh NiPc film, the peaks at 729 and 725 cm^{-1} were observed rather than the one at 719 cm^{-1} which corresponds to the α-form and the absorption at 941 cm^{-1} was very weak [9]. The ratio of the intensities at 729 and 725 cm^{-1} decreased following heat treatment. No absorption peaks assigned to the α-form were observed for NiPc films. It seems that the freshly deposited film consists of a mixture of the β-phase and an unknown phase. These observations indicate that the films annealed at 300° C in air consist probably of the β-phase.

3.4. X-ray photoelectron spectra (XPS)

3.4.1. Lead phthalocyanine

Lead phthalocyanine is stable in air at room temperature but sublimes and reacts with oxygen and/or water at temperatures above 300° C. In a previous paper [10], it was reported that the characteristic temperature for 5% weight loss in thermal gravimetry is lowered by changing the ambient from nitrogen to clean air or air at 90% r.h. at room temperature for many phthalocyanines. The observed lowering in this characteristic temperature is caused by decomposition and/or reaction with oxygen and/or water molecules. During the annealing procedures, the oxidation and/or the decomposition may proceed principally in the surface layers of the films. Surface analysis by XPS was used in an attempt to clarify the molecular structure of the surface layers. The films were deposited on alumina substrates over an evaporated platinum thin film. The observed binding energies were influenced by charging effects so that the measured values of the binding energies had to be corrected using the signals assigned to platinum as a measure of the energy shift.

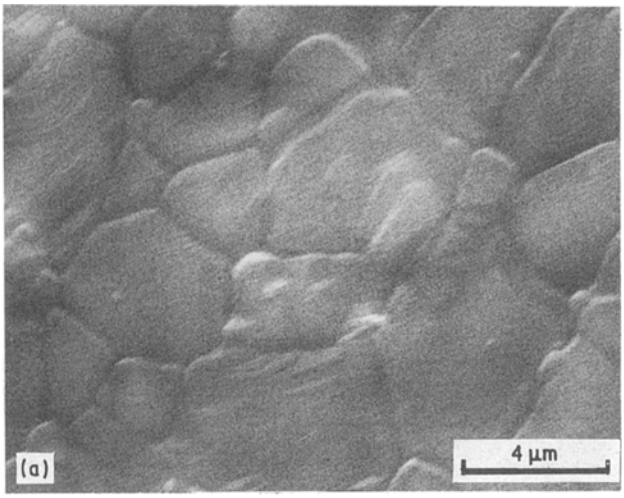
The corrected characteristic values are summarized in Table III. Even for the fresh film without any heat treatment and maintained in air, the oxygen peak (O1s) at a binding energy of 533 eV was observed. The ratio of the concentration of oxygen to lead decreased following heat treatment in both air and nitrogen from 5.6 to 1.8 ([O]/[Pb]). The ratio of the concentrations was computed from the peak heights and the

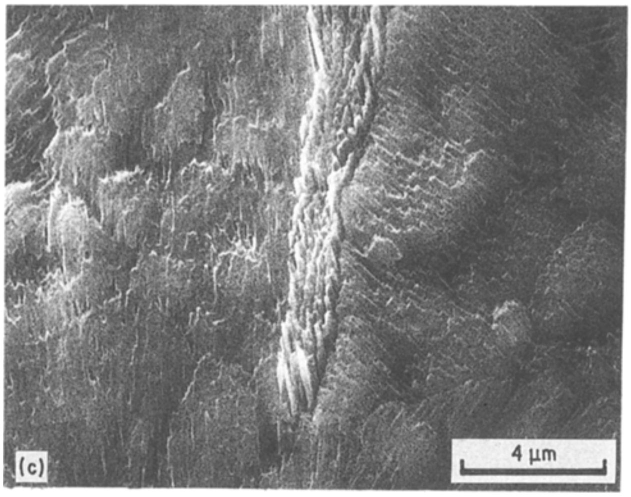
TABLE III Characteristics determined by XPS for PbPc films formed on alumina with thin platinum film

	Binding energy and FWHM(eV) for PbPc			
	Fresh	330° C, N$_2$ 3 h	330° C, air 2 h	300° C, air 5 h
P4 4f	138.1 (2.1)	138.7 (2.1)	139.3 (2.1)	141.1 (2.1)
	142.1	143.5	144.1	145.9
Pb 4d	414.6	414.6	414.6	416.4
C 1s	285.0 (3.0)	285.6 (3.3)	285.9 (4.2)	284.1 (2.1) 288.0 (3.0)
N 1s	398.7 (2.1)	399.0 (2.4)	399.9 (2.4)	402.0 (2.7)
O 1s	533.1 (5.1)	533.4 (4.8)	533.4 (4.8)	533.4 (5.7)
	Ratio of concentration*			
[C]$_4$/[N]†	4.4	5.4	2.5	3.2 (1.7, 1.5)
[C]$_{32}$/[Pb]†	26.7	21.6	10.8	13.8 (7.4, 6.4)
[N]/[Pb]	6.0	4.0	4.4	4.3
[O]/[Pb]	5.6	4.6	3.5	1.8

*Calculated values from the peak height and relative sensitivity for each element.

†Ideal values for PbPc.





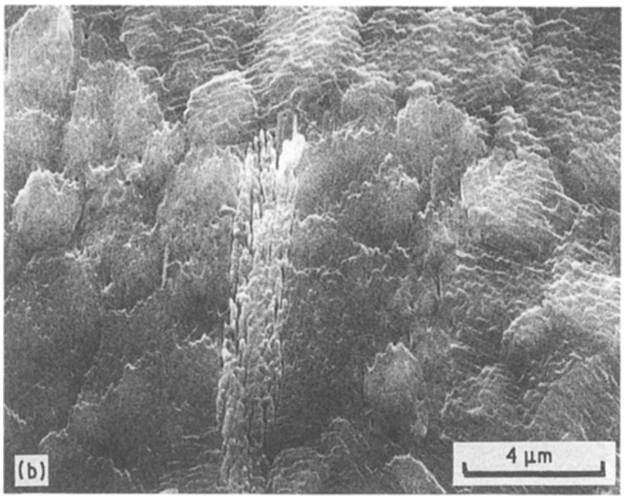


Figure 16 Scanning electron micrographs of CoPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 3 h, (c) film annealed at 300° C for 6 h.

specific sensitivity for each element. The oxygen peak was assigned to the chemisorbed O_2^- [11]. In lead phthalocyanine, it is thought that the central metal ion is the main oxygen adsorption site. These are not, however, the only sites because the observed ratio is too high for a simple single site adsorption model. The reduction in the ratio following heat treatment indicates that the concentration of the other adsorption sites decreases on heating.

The ratio of [C]/[N] was slightly decreased by heat treatment especially in air and similar tendencies were observed for [C]/[Pb] and [N]/[Pb] values, while the value of FWHM increased. It is apparent that the values of [C]/[Pb] and [N]/[Pb] are smaller than the values expected for the ideal molecular structure. It appears that the particles of phthalocyanine may be almost covered with lead oxides. In particular, the peak assigned to C1s at a binding energy of 285 eV was split to a doublet (284 and 288 eV) for the film annealed at 300° C in air for 5 h. This splitting indicates the existence of a higher valency of the central metal ion.

3.4.2. Other phthalocyanines

In Table IV, the binding energy, FWMH and the concentration ratio of the elements are summarized for the films formed on alumina over platinum electrodes. The values of [C]/[N] were between 3.2 and 5.3 while the theoretical value for lead phthalocyanine is 4.0. It seems that the surface of the film is phthalocyanine even after being annealed in air. In addition, a considerable amount of chemisorbed oxygen as observed in PbPc was detected for all the materials.

4. Discussion

Most metal-substituted phthalocyanines are p-type semiconductors so that their conductances increase following adsorption of oxidizing molecules and decrease following adsorption of reducing molecules. These characteristics in relation to molecular adsorption are interpretable in terms of an extrinsic conduction model in which oxidizing molecule adsorption induces an electron acceptor level in phthalocyanine. By assuming the validity of a simple band theory, the carrier concentration, p, is described by

$$p(p + N_D)/(N_A - (N_D + p)) = (N_V/2) \exp(-\Delta E/kT) \qquad (1)$$

TABLE IV Characteristics determined by XPS for some phthalocyanine films. Values in parentheses indicate FWHM. Annealing was done in air

	Binding energy and FWMH			[C]/[N]	[O]/[C]
	C 1s (eV)	N 1s (eV)	O 1s (eV)		
ZnPc:					
fresh	286.2 (2.3)	400.1 (1.2)	532.8 (3.0)	3.44	0.18
annealed 6 h	286.9 (2.0)	400.8 (1.2)	532.8 (2.6)	3.70	0.20
CuPc:					
fresh	284.2 (3.0)	397.8 (2.1)	531.0 (3.0)	4.54	0.21
annealed 4 h	287.4 (2.5)	402.4 (2.6)	532.6 (3.0)	3.22	0.13
CoPc:					
fresh	285.7 (2.5)	400.5 (1.5)	532.4 (2.4)	5.26	0.13
annealed 3 h	287.2 (2.5)	401.0 (1.5)	532.4 (2.6)	3.45	0.24
NiPc:					
fresh	286.7 (2.0)	400.7 (1.4)	533.0 (3.6)	4.54	0.15
annealed 5 h	286.9 (2.3)	400.8 (1.5)	532.8 (3.2)	5.26	0.20

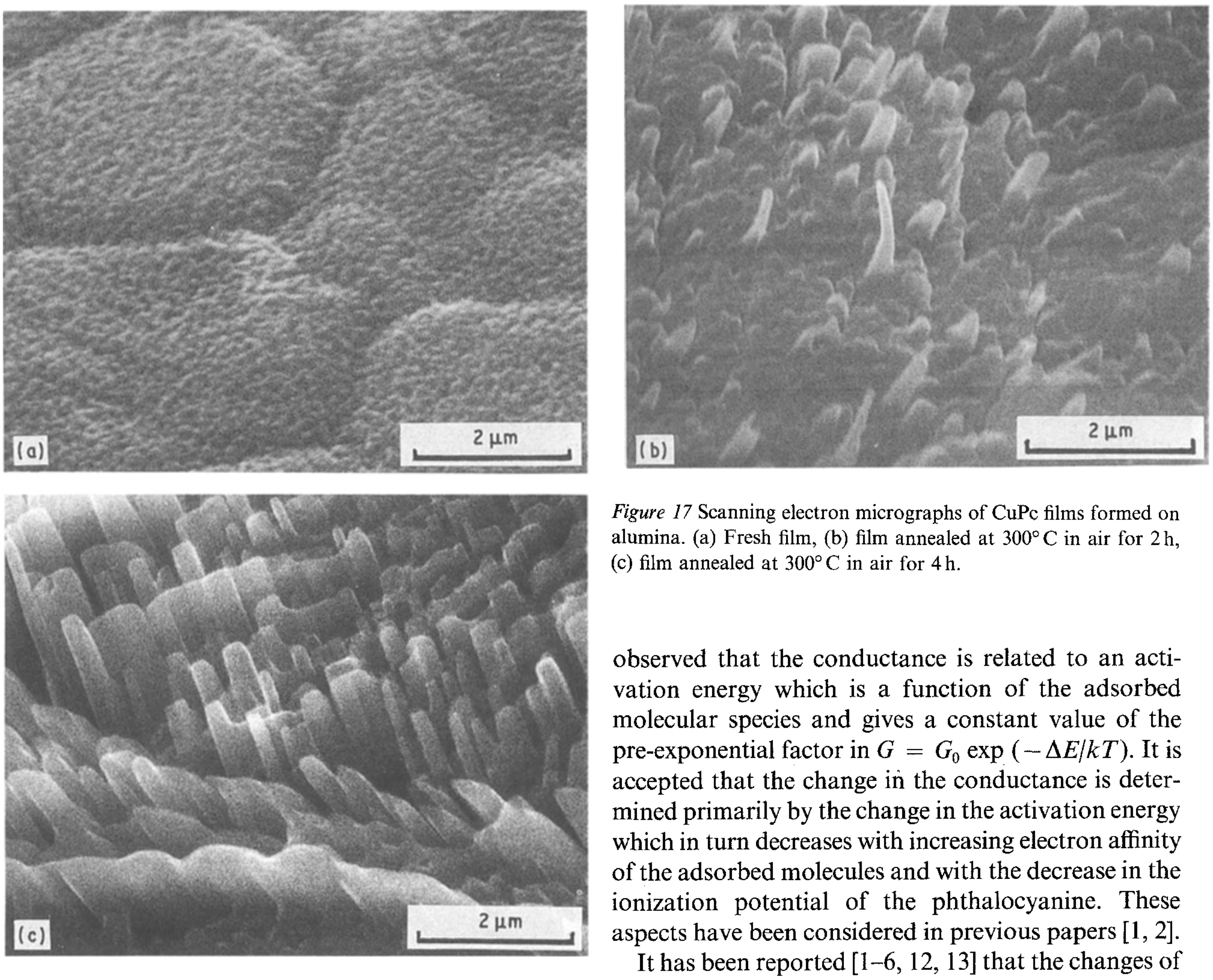


Figure 17 Scanning electron micrographs of CuPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 2 h, (c) film annealed at 300° C in air for 4 h.

where N_V is the effective density of states in the valence band, N_D the donor density, N_A the acceptor density and ΔE the difference between the valence band and the acceptor level. For p-type semiconductors, it is possible to ignore N_D and Equation 1 reduces to

$$p^2/(N_A - p) = (N_V/2) \exp(-\Delta E/kT) \quad (2)$$

Furthermore, by assuming $\Delta E/kT > 1$, i.e. $N_A > p$, Equation 3 is obtained

$$p = (N_V N_A/2)^{1/2} \exp(-\Delta E/2kT) \quad (3)$$

For some p-type phthalocyanine thin films, it has been observed that the conductance is related to an activation energy which is a function of the adsorbed molecular species and gives a constant value of the pre-exponential factor in $G = G_0 \exp(-\Delta E/kT)$. It is accepted that the change in the conductance is determined primarily by the change in the activation energy which in turn decreases with increasing electron affinity of the adsorbed molecules and with the decrease in the ionization potential of the phthalocyanine. These aspects have been considered in previous papers [1, 2].

It has been reported [1–6, 12, 13] that the changes of conductivity in phthalocyanines are strongly influenced not only by the central-metal species but also by the crystal structure and/or size. As is well known, phthalocyanine can take different crystal forms and the phase transitions are strongly affected by impurities, ambient atmosphere and temperature. The polymorphism of some phthalocyanines has been widely studied. For H_2Pc, CuPc, ZnPc, etc., the existence of the α- and β-phases is known and, for PbPc, monoclinic and triclinic crystal forms are known to exist. The α-phase is metastable and changes to the β-phase following appropriate heat treatment. Recently, Collins and Mohammed [14] have reported

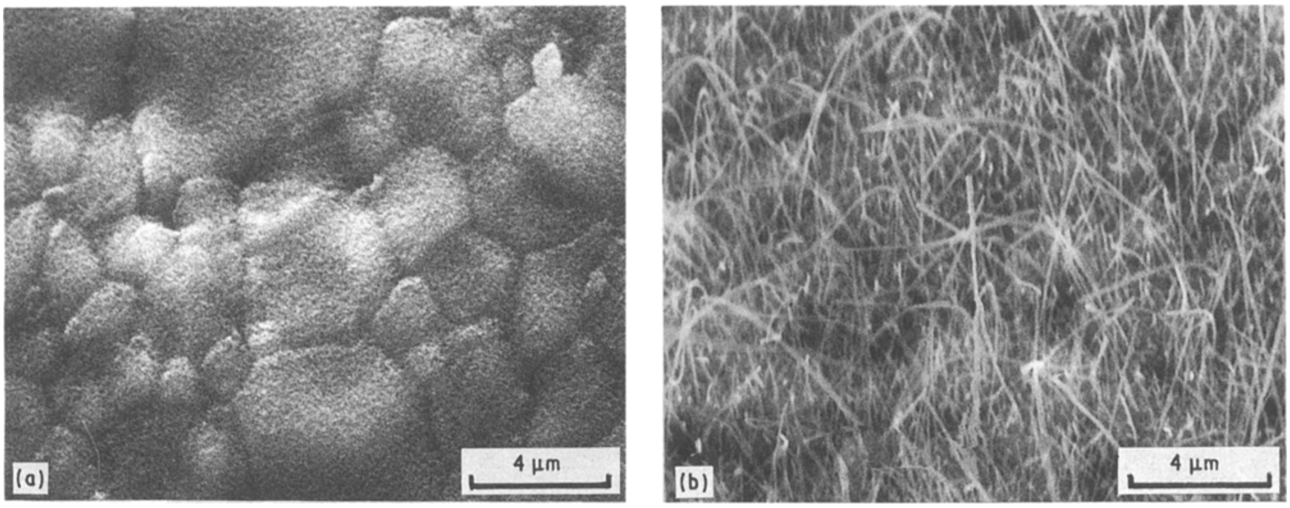


Figure 18 Scanning electron micrographs of NiPc films formed on alumina. (a) Fresh film, (b) film annealed at 300° C in air for 3 h.

the phase behaviour of CuPc, ZnPc, etc., and indicated that the growth of α-phase microcrystallites into large crystals proceeded at lower temperature below about 300° C and a fairly well-defined transition from the α-form to the β-form was achieved by heating at 300° C or more. For PbPc, changes induced by heat treatment have been observed for the evaporated thin film. In evaporated thin films, the existence of amorphous or disordered forms has been observed which is strongly influenced by the substrate temperature during the deposition procedure. It seems that the adsorption kinetics are strongly influenced by the film structure and the degree of crystallinity, especially in oxidizing atmospheres. For example, in H_2Pc and CuPc, the conductance in air of the α-form is much higher than that of the β-form because of the difference in the concentration of adsorbed oxygen. In this work, the existence of adsorbed oxygen on PbPc films under high vacuum conditions was observed and the concentration of the adsorbed oxygen decreased after annealing in air and in nitrogen (XPS results). This annealing reduces the presence of the amorphous phases, promotes crystal growth and induces the phase transition from the α-form to the β-form. So that to obtain a more detailed understanding of the mechanisms of gas sensitivity in the phthalocyanines, the influence of film structure and morphology on the adsorption kinetics must be elucidated.

For simplicity, it is assumed that the adsorption kinetics of oxidizing molecules is mainly influenced by the degree of stacking of the phthalocyanine molecule and the crystal size. In relation to this problem, H_2Pc and CuPc in film and whisker form have been studied [12]. In oxidizing ambients, i.e. in air and in NO_2, the activation energy of the resistance is almost independent on the form, i.e. film or whisker, but the value of the resistance for the whisker is considerably higher than that of the film. This means that the energy depth of the acceptor sites formed by the adsorption of oxidizing molecules is not significantly influenced by the crystal form. The conductive path for the whisker is probably limited to the surface, while the whole of the film may contribute to the conductive path.

Most electrophilic molecules (X) can interact with phthalocyanine. The molecule is initially adsorbed on the phthalocyanine surface (MPc_S) and subsequently diffuses into the bulk of the material (MPc_b). This behaviour and the carrier generation process can be expressed as follows.

$$MPc_s + X \rightarrow MPc_s^{\delta+}X^{\delta-} \quad (4)$$

$$MPc_s^{\delta+}X^{\delta-} + MPc_b \rightarrow MPc_s + MPc_b^{\delta+}X^{\delta-} \quad (5)$$

$$MPc_s^{\delta+}X^{\delta-} \rightarrow MPc_sX^- + \text{hole} \quad (6)$$

$$MPc_b^{\delta+}X^{\delta-} \rightarrow MPc_bX^- + \text{hole} \quad (7)$$

It seems that the rate of oxidizing molecule adsorption on the surface is very fast and not strongly influenced by the crystallinity. The rate of diffusion in the bulk may, however, be strongly affected by the crystallinity, the crystal size and the size of the oxidizing molecules. Under certain conditions in a concentration of NO_2 in air, the equivalent states for adsorption are established initially on the surface and subsequently in the bulk. The time to establish the equivalent states in the bulk depends on the degree of disorder and crystal size and would be expected to be in the order of amorphous < fine crystal < large crystal. It is assumed that the degree of crystallinity is independent of the crystal size.

These projected effects of morphology on the adsorption characteristics can be used to explain the observed response and recovery times. For simplicity, it is assumed that the film can consist of only three different forms, i.e. an amorphous phase, fine crystals or large crystals. For each component, the resistance is defined as R_a (amorphous phase), R_f (fine crystal) and R_l (large crystal), and additionally, R_g (grain boundary) and R_s (surface). The crystals of lead phthalocyanine are covered with a thin layer of lead oxides. The resistance component deriving from the lead oxides can be ignored for the equivalent circuits, because as previously stated the resistance of a film of lead oxides is not affected by exposure to NO_2. In considering equivalent circuits, the resistance components arising from the bulk are connected in parallel to those for the surface and the resistances of the grain boundary and the amorphous phases are in series with the other components. The capacitance component was not considered, because this model was applied only to d.c. resistance and to the response and recovery times for changes of the ambient atmosphere. The response time of each resistance component for changes in the NO_2 concentration in air is expected to be in the order of $R_s < R_a < R_f < R_l$, because the amorphous phase has a greater surface area to bulk ratio (which provides access to a greater proportion of the surface for the adsorbing molecules) than the crystal.

It appears that the value of R_s/R_l increases with crystal size and that the changes of the equivalent resistance is predominantly controlled by R_l for the annealed films. The fast response and recovery times of the resistance changes corresponding to changes in the ambient may be achieved when the films consist of fine crystals without either the amorphous phases or larger crystals.

This qualitative assumption is confirmed by the differences of the response and recovery times observed between the lead phthalocyanine films. The formation of "good" crystals, reduces the extent of the secondary slow drift to the steady state value. This is explained in terms of the reduction of the amorphous phases, and the contribution of the surface conductance to the equivalent resistance becomes more dominant than that of the bulk. In an NO_2-containing ambient, it is apparent that the resistance of the bulk is higher than that of the surfaces when the material consists mainly of fine crystals. Furthermore, if adsorption sites are limited to the surfaces and NO_2 cannot diffuse into the bulk of the crystal, it is likely that the response and recovery times will not be influenced by the crystal size. However, as mentioned earlier, the recovery time is influenced by the crystal size and by the exposure time, while the resistance in NO_2 is almost independent of these factors. These observed results indicate that the value of the resistance in NO_2 is mainly determined by the surface resistance and that the concentration of the adsorbed NO_2 on the surface reaches a steady state in a short period. In the desorption process, the concentration of NO_2 on the surface decreases more slowly because this is controlled by the rate of diffusion of NO_2 from bulk to the surface and this continues after the NO_2-containing atmosphere has been changed to clean air.

It is clear that the geometric structure, especially for the film annealed at 300° C in air, depends on the nature of the phthalocyanine, all of which take the β-phase where possible, as determined by infrared spectroscopy. The observed differences are attributed to the differences in thermal and chemical stabilities. In previous work [10], the effect of ambient on thermogravimetry have been examined. The characteristic temperatures for the 5% weight loss in nitrogen are 551, 530 and 537° C, for CuPc, ZnPc and PbPc, respectively. The characteristic temperatures were lowered to 416, 485 and 455° C in air, and 423, 500 and 378° C in air with 90% r.h. These results indicate that ZnPc film is the more stable of the three in air and PbPc and CuPc are more easy to sublime and/or to decompose in air. These differences may reflect the different geometrical structures of the annealed films, i.e. crystal growth predominantly in the direction perpendicular to the substrate is induced in PbPc and CuPc, and in ZnPc and CoPc, the growth tends to be parallel to the substrate and very little sublimation is observed at 300° C. Furthermore, the crystal size in the CuPc film annealed in air is considerably larger than that in the PbPc film. This is because the chemical stability of CuPc is superior to that of PbPc. These results indicate that the useful sensing characteristics for NO_2 observed in PbPc films are due at least in part to the special geometric structure. The formation of this structure is related to the instability of PbPc and the formation of lead oxides which suppress both the crystal growth and the fusion of the crystals.

While the crystallization and the disappearance of the disordered phases are effective in improving the sensing characteristics, the larger crystals formed in the conductive paths may be the cause of the slow recovery times and the irreproducibility.

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