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Effect of heat pretreatment on electrical conductance changes by NO_2 adsorption of lead phthalocyanine thin film

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The sensing characteristics of an NO_2 gas sensor using lead phthalocyanine thin film are influenced by heat-pretreatment time and ambient gas. The response behaviour of conductance for the change in ambient gas was characterized using Elovich's equation. The first stage in the adsorption and desorption kinetics reflects surface phenomena and the second stage the film diffusion. Both components were improved by heat treatment in air. The rising time in the NO_2 adsorption process was within 2 min, and the recovery time within 5 min at 130 °C for the film annealed in air for 1 h. The heat pretreatment induced the formation of a continuous layer of fine particles, ~ 0.1 μm in size, and larger single crystals isolated from each other, which formed on the continuous layer. The formation of the larger single crystals is not preferable in fabricating a sensor with fast rising and recovery times.

1. Introduction

The electrical conductivity changes which occur when electron donor or acceptor gases are adsorbed on the surfaces of metal phthalocyanine films are of increasing interest in chemical sensor applications [1–5]. When an electron acceptor molecule, such as NO_2, is adsorbed on to phthalocyanine film, charge transfer interactions occur, resulting in a large increase in conductivity. The charge transfer increases the conductivity by increasing the number of holes. Many kinds of metal phthalocyanines have been investigated. Lead phthalocyanine is the most promising for toxic gas sensor applications, because its electrical properties give it superior sensitivity, stability, and conductivity. For example, in an optimized film, the p.p.b. order of NO_2 gas can be detected and the operating temperature can be decreased [6]. In previous work [7], it was demonstrated that fast NO_2 detection could be achieved even at room temperature by using an optimized lead phthalocyanine thin-film structure annealed at 300 °C or more, in air. Similar behaviour was also observed for a film annealed in air at 300 °C or more, by Jones *et al.* [6], but these have not been studied in detail. Improvements in the response time by annealing at 150 °C in air for several hours have been reported by Archer *et al.* [8]. Annealing in nitrogen also improves repeatability [9]. These improvements are attributable to the crystallization of amorphous regions. Especially for the film annealed in air at 300 °C or more, the formation of a finer crystal phthalocyanine and decomposition proceed with the crystallization of amorphous regions. For the film annealed in air at 300 °C or more, the rising and recovering times for the changes in conductance following step changes from air to NO_2 diluted with air, are considerably shorter than those for the film annealed at a lower temperature.

The aim of the present study was to clarify the correlation between the heat-pretreatment condition and the rising and recovering time, i.e. the transient response for the changes of NO_2 concentration in ambient for the film annealed in air.

2. Experimental procedure

Commercial lead phthalocyanine powder was initially purified by an entrainer sublimation method in a flow of nitrogen (100 ml min^{-1}). The entrainer has three zones; the sublimation zone (520 °C), the collection zone (220–320 °C) and a lower temperature zone to collect impurities and decomposition products. The sample obtained in the collection zone was used to prepare a thin film about 5 μm thick. The thin film was formed on alumina and/or non-alkali glass substrates by vacuum sublimation by heating the purified sample (whisker) in a quartz crucible. Before sublimation of lead phthalocyanine on to the substrate, a pair of platinum electrodes 300 nm thick and 200 μm inter-electrode distance, prepared by a r.f. sputtering method, was fabricated on alumina and/or non-alkali glass substrates. Before carrying out electrical measurements, the elements were treated in nitrogen or synthesized air flows at 300 °C. D.c. conductance was measured using an electrometer in flows of air and NO_2-diluted air. The element was located directly in the gas stream. The chamber was made of quartz glass and the gas-flow system was made of polytetrafluoroethylene and polyvinylchloride. The NO_2 concentration was controlled by mixing air and 10 p.p.m.

NO_2/air. The gas-flow rates were set at 100 ml min^{-1} or less. The topography of the film was characterized by scanning electron microscopy (SEM) before and after electrical measurements.

3. Results and discussion

3.1. Temperature dependence of conductivity

The electrical conductance measurements commenced at a temperature just below 250 °C and continued as the temperature increased at a 5 °C min^{-1} heating rate. The changes in ambient gases were introduced at 50 °C or below, after the reversible temperature dependence of the conductance was confirmed. The time between measurements was set at 35–40 min because the time required to cool to 50 °C from 250 °C was approximately 30 min. For example, the results of the film formed on a glass substrate and annealed at 300 °C for 0.5 h in nitrogen are shown in Fig. 1. The conductance increased on changing the ambient of nitrogen (a) to air (b) or 3.3 p.p.m. NO_2/air (c). In a lower temperature region, the results can be expressed by

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

where G_0 is the pre-exponential factor which is influenced by the ambient, E is the activation energy, T the absolute temperature and k is Boltzmann's constant. The result (d) observed in nitrogen after measurement in 3.3 p.p.m. NO_2/air, is also shown in Fig. 1. Part of the sorbed oxygen and NO_2 was desorbed only by changing the ambient of NO_2/air to nitrogen at 50 °C or lower. The curve intercepted the result observed in air at 167 °C. At temperatures higher than 167 °C, the carrier concentration was less than that of the conductive state in air. The electrical characteristics were influenced by the time and ambient gas of the heat pretreatment. The results of the film formed on a glass substrate and annealed at 300 °C for 1 h in air are shown in Fig. 2. The degree of decrease in conductance at 50 °C on changing the ambient of NO_2/air (c) to nitrogen (d) is higher than that observed for the film on glass annealed in nitrogen for 0.5 h at 300 °C. For this element, the curve observed in nitrogen after measurement in NO_2/air intercepted the result in air at 127 °C, which was considerably lower than that for the sample annealed in nitrogen. The decrease in the critical temperature from 167 °C to 127 °C on changing the ambient from nitrogen to air convinced us that heat pretreatment in air is a preferable process to improve the response time in NO_2 gas sensing. In Table I, the activation energy and the conductance at 70 °C are summarized for several different heating pretreatments. The activation energy determined in NO_2/air for the film annealed in air was less than 0.1 eV and considerably lower than that for the film annealed in nitrogen, while the conductance of the former was less than that for the latter. This discrepancy may reflect the difference in the topography, as mentioned below. Furthermore, the activation energy in nitrogen and in air of the film annealed in air was slightly higher than that of the film annealed in nitrogen. This effect of heat-pretreatment condition on the activation energy may be interpreted by the partial decomposition of lead phthalocyanine and/or the difference of gas adsorption ability which is controlled by the crystal size and crystallinity.

3.2. Response time and/or reversibility

In Fig. 3, the changes in conductance with change of ambient from air to 3.3 p.p.m. NO_2/air at 130 °C are shown for the films annealed at 300 °C for 1 h with air annealing and nitrogen annealing, respectively. The response was measured with 2 min of NO_2/air and

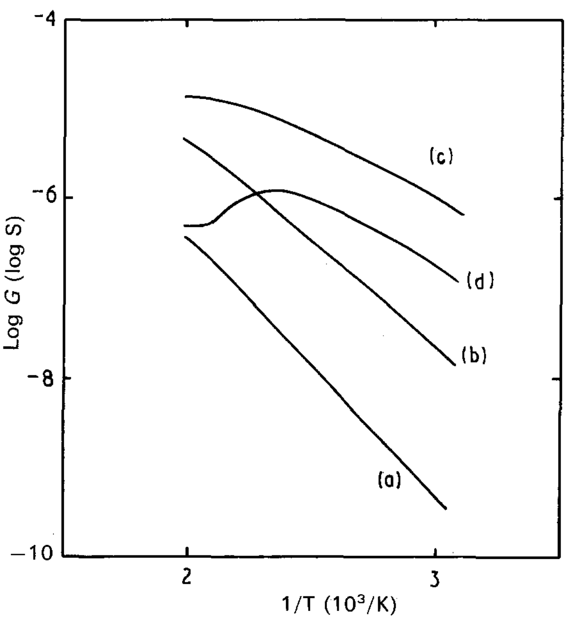

Figure 1 Temperature dependence of conductance of the film on glass annealed in nitrogen for 0.5 h at 300 °C in (a) nitrogen, (b) air, (c) 3.3 p.p.m. NO_2/air, (d) nitrogen after measuring in NO_2.

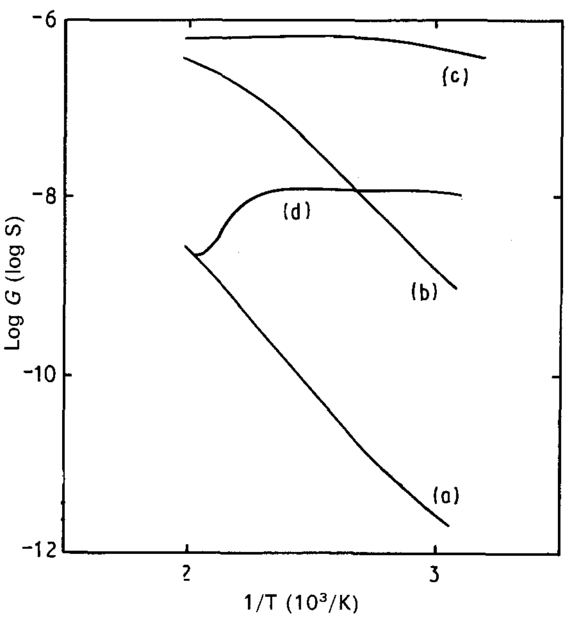

Figure 2 Temperature dependence of conductance of the film on glass annealed in air for 1.0 h at 300 °C in (a) nitrogen, (b) air, (c) 3.3 p.p.m. NO_2/air, (d) nitrogen after measuring in NO_2.

TABLE I Electrical characteristics of the film annealed at 300 °C

Annealing condition	Substrate	Ambient	E (eV)	G at 70 °C (S)
Air, 1 h	Glass	Nitrogen	0.65	3.3×10^{-12}
		Air	0.54	2.7×10^{-9}
		3 p.p.m. NO_2/air	0.10	6.4×10^{-7}
N_2, 0.5 h	Glass	Nitrogen	0.57	8.6×10^{-10}
		Air	0.46	3.6×10^{-8}
		3 p.p.m. NO_2/air	0.25	1.6×10^{-6}
Air, 1 h	Alumina	Nitrogen	0.64	1.1×10^{-12}
		Air	0.59	5.3×10^{-10}
		3 p.p.m. NO_2/air	0.06	8.4×10^{-7}
Air, 1.5 h	Alumina	Nitrogen	0.64	1.2×10^{-12}
		Air	0.56	5.0×10^{-10}
		3 p.p.m. NO_2/air	0.06	4.6×10^{-7}
N_2, 1 h	Alumina	Nitrogen	0.55	3.3×10^{-10}
		Air	0.41	2.9×10^{-8}
		3 p.p.m. NO_2/air	0.20	1.3×10^{-6}

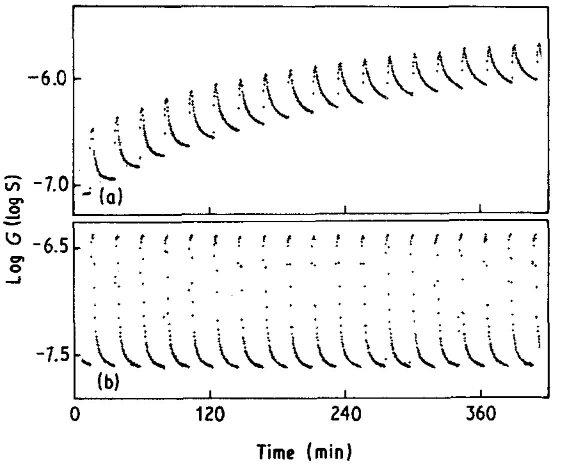

Figure 3 Transient responses of conductance with the change of air to 3.3 p.p.m. NO_2/air and inversed. (a) Annealed at 300 °C in nitrogen for 1 h. (b) Annealed at 300 °C in air for 1 h.

20 min of air, after the stationary state conductance was achieved in air. For the film annealed in nitrogen, the conductance observed in the initial stage, before the introduction of NO_2, was consistent with the value observed in the measurement of the temperature dependence of conductance in air. The introduction of NO_2 induced an increment in the conductance which did not stabilize within the NO_2 introduction period. In addition, in the recovery process the conductance did not return to the initial value. The conductance gradually increased with each cycle and the conductance in NO_2/air approached a reproducible value after a number of cycles. On the other hand, for the film annealed in air, good reproducibility was noted. The steady state in conductance was achieved within 100 s after the change of ambient from air to 3.3 p.p.m. NO_2/air and the conductance was recovered within 15 min after changing the ambient. In addition, no apparent gradual increases in the conductance with each cycle were observed (Fig. 3b). As reported previously [10, 11], the activation energy of the conductance is strongly influenced by ambient conditions such as gas species and its concentration. The conductance and/or the carrier (hole) concentration was not directly proportional to the concentration of adsorbed gas molecules. But for simplicity, as used in some other works [12, 13], it is assumed that the conductance is linearly proportional to the coverage of the objective gas molecule and the Elovich equation is applied to analyse the transient response.

$$\mathrm{d}\theta/\mathrm{d}t = a \exp(-b\theta) \qquad (2)$$

where a and b are time-independent constants and θ is the fraction of surface covered by gas molecules. Integrating this equation once gives

$$\begin{aligned} \theta &= (1/b)\ln(t/t_0 + 1) \\ &= \alpha G \end{aligned} \qquad (3)$$

where $t_0 = (ab)^{-1}$, α is a constant and G is the conductance. Recall that θ is assumed to be proportional to the conductivity change by the concentration of adsorbed NO_2 molecule. For the film annealed at 300 °C in air for 1 h, the correlation between the conductance ratio, G/G_0, and the time, t, observed in the NO_2 adsorption process is shown in Fig. 4 where G_0 is the conductance in NO_2/air in the stationary state. The conductance increased steeply at first for t

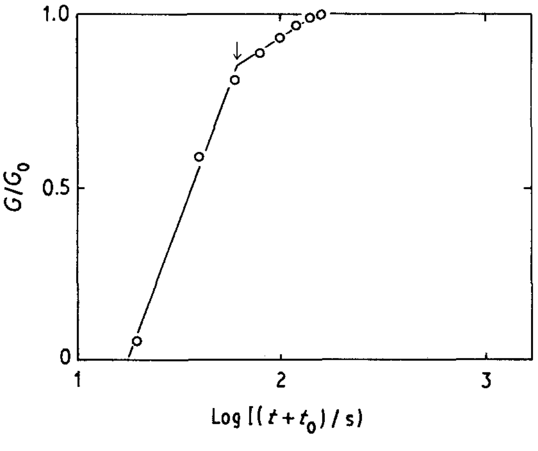

Figure 4 Conductance increment with adsorption of NO_2 of the film annealed at 300 °C in air for 1 h. Arrow indicates the cross point ($t = t_c$).

being small, then the slope decreased at t_c and G_c/G_o. This implies that NO_2 acts in at least two steps. In Table II, the characteristics of conductance change in the NO_2 adsorption process for the film annealed in air are summarized. The slope in the first stage increased and that in the second stage decreased with annealing time. In addition, G_c/G_o at the cross point ($t = t_c$), which is indicated by the arrow in Fig. 4, increased. When NO_2 is off, the reverse actions are surface desorption followed by diffusion out from the film, as shown in Fig. 5. The transient desorption characteristics in the NO_2 desorption process are also strongly influenced by annealing conditions and summarized in Table III. For the first stage in the desorption process, the slope increased with annealing time for the sample annealed in air and was considerably higher than that in nitrogen. The slope observed in the second process for the film annealed in air was less than that in nitrogen. Furthermore, the value of the cross point observed in the film annealed in air as denoted in Fig. 5 was very much less than that in nitrogen. It has been suggested that surface adsorption of NO_2 is a rapid process, whereas bulk effects, diffusion of NO_2 into the film, comprising absorption or reaction, are much slower. In this work, the reaction of NO_2 with phthalocyanine may be ruled out as the origin, because the conductance is completely recovered after NO_2 is turned off. Other work [14] on single crystals of phthalocyanine suggests that there is no absorption into the bulk of the crystal, because no conductance changes are observed on exposure to NO_2 when surface currents are eliminated by the use of a grounded guard-ring. It seems that the possibility of the diffusion of NO_2 is correlated to the imperfection of crystallinity and slow penetration into the bulk of the film via the grain is responsible for the second stage which is equally well described by a heterogeneous surface site model as denoted by Archer *et al.* [8]. Actually, the film annealed at 300 °C in air was very porous and was composed of fine particles and large crystals in which many damaged regions were observed on the surface of the large crystals.

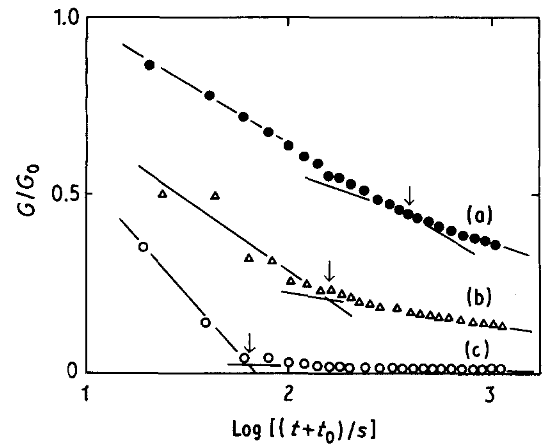

Figure 5 Conductance decrement with the desorption of NO_2. (a) Annealed at 300 °C in nitrogen for 1 h. (b) Annealed at 300 °C in air for 0.5 h. (c) Annealed at 300 °C in air for 2 h. Arrows indicate the cross point ($t = t_c$).

3.3. Topography and its effect on the electrical characteristics

In Fig.6, the topography of some films is shown. It is apparent that the as-deposited film on a glass substrate consists of fine particles and disordered phases.

TABLE II Transient response characteristics in NO_2 adsorption process for the film annealed in air

Annealing time (h)	Substrate	Slope 1st stage	Slope 2nd stage	G_c/G_o	t_c (s)
0.5	Glass	1.33	0.64	0.81	76
1.0	Glass	1.58	0.42	0.84	60
0.5	Alumina	1.54	0.33	0.85	52
1.0	Alumina	1.64	0.31	0.88	63
2.0	Alumina	1.79	0.22	0.92	62

TABLE III Transient response characteristics in NO_2 desorption process for the film

Annealing condition (h, ambient)	Substrate	Slope 1st stage	Slope 2nd stage	G_c/G_o	t_c (s)
0.5, air	Glass	0.83	0.062	0.12	101
1.0, air	Glass	0.88	0.039	0.09	76
0.5, N_2	Glass	0.45	0.27	0.51	530
1.0, N_2	Glass	0.36	0.19	0.46	630
0.5, air	Alumina	0.64	0.087	0.21	120
1.0, air	Alumina	0.92	0.036	0.06	85
2.0, air	Alumina	0.95	0.014	0.02	73
1.0, N_2	Alumina	0.38	0.20	0.45	360

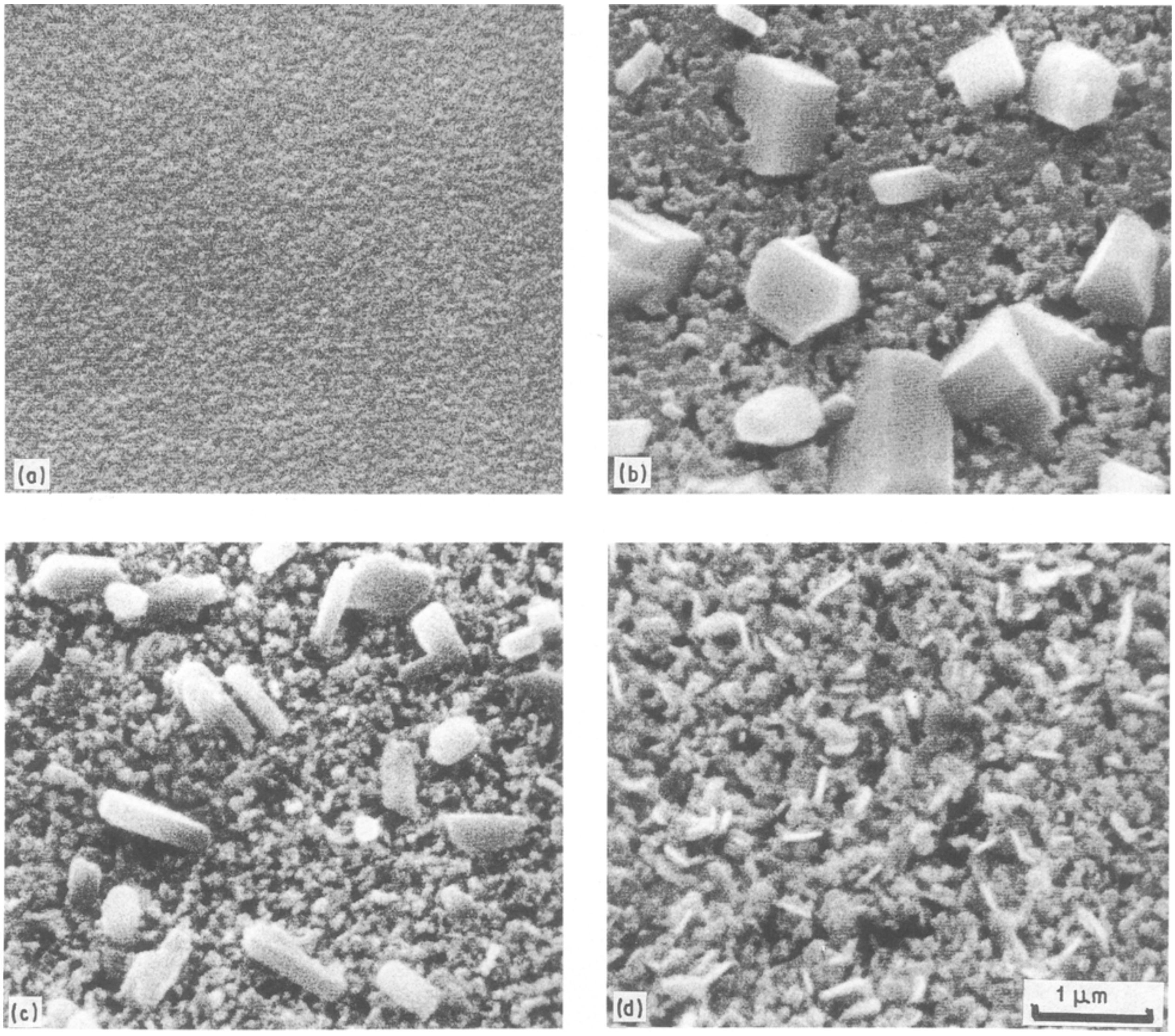

Figure 6 Scanning electron micrographs of the films formed on glass: (a) as-deposited: (b) annealed at 300 °C in nitrogen for 0.5 h; (c) annealed at 300 °C in air for 0.5 h; (d) annealed at 300 °C in air for 1.5 h.

Similar observations were also made for the as-deposited film on an alumina substrate. For the films annealed at 300 °C in nitrogen, the formation of single crystals, of ~ 1 µm size, was confirmed and these crystals were isolated by a region composed of smaller size particles. An additional annealing induced the growth and interconnection of the crystals, as reported [7]. Annealing in air also induced the formation of fine particles and well-defined larger single crystals. By prolonging the heat-pretreatment period, the size of the larger single crystals decreased and the fine particle layer became sharper, which may be a result of the crystallization of the disordered phase and the emaciation of the interparticle layer. The film annealed at 300 °C in air was very porous and was composed of fine particles and large crystals in which many damaged regions were observed on the surface of the large crystals while any damaged regions were not noted for the film annealed in nitrogen. The diminishing of larger crystals with heat-treatment period results from the sublimation and the oxidation (decomposition) of phthalocyanine. As reported previously [15], for the as-deposited film the oxygen signal was not detected and the Pb/C and N/C ratios determined by Auger spectroscopy were 0.09 and 0.31, respectively. The ratios are slightly influenced by the sublimation conditions used to prepare the film and the Pb/C and N/C ratios are higher and lower than the values for the ideal molecular structure, respectively. The decomposition of phthalocyanine partially proceeded in the sublimation process as reported by Mockert *et al.* [16]. Prolonging the exposure time in the atmosphere induced the formation of adsorbed O_2 and H_2O which could not be removed by pumping in a high vacuum. For the film annealed in air, the O/C ratio determined by Auger spectroscopy for the smaller particle surfaces was considerably higher than that for the larger single crystals. Annealing in air induced the oxidation of phthalocyanine and the crystal growth was depressed by the formation of lead oxide.

The decomposition of phthalocyanine molecules in air at 300 °C is also effective in forming fine particles.

The difference in topography influenced the response behaviour as mentioned previously. It seems that the conductance change induced by NO_2 adsorption is mainly controlled by the changes of the conductive behaviour of the small particle layer, because the applied voltage is parallel to the film surface and the larger single crystals are isolated from the conductive path, especially for the film formed on glass. Each fine particle for the film annealed in air is more isolated and/or separated than that in nitrogen, so it is expected that the response time in the conductance changes of the film annealed in air will be faster than that of the film annealed in nitrogen. In fact, the slope in the first stage observed in the desorption process of the film annealed in air is two- or three-fold higher than that of the film annealed in nitrogen. The other desorption characteristics summarized in Tables II and III can also be correlated. The increase in the slope in the first stage and the decrease in that in the second stage in the adsorption and desorption processes were achieved by heat pretreatment in air.

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