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INTERACTION BETWEEN COPPER TETRA-4(2,4-DI*TERT*-AMYLPHENOXY)PHTHALOCYANINE LANGMUIR–BLODGETT FILMS AS A GAS-SENSITIVE SENSOR AND NH_3

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Copper tetra-4-(2,4-di*tert*-amylphenoxy)phthalocyanine (tapCuPc) Langmuir–Blodgett (LB) films were deposited onto planar interdigital microelectrode arrays and the process of the interaction between the tapCuPc LB films and NH_3 was studied. The process of the interaction resulted in a large increase in the conductance of the LB film. The results of response and recovery processes were given when the tapCuPc LB films were exposed to 100 ppm NH_3 gas in air. It was suggested that the response process of the interaction between the tapCuPc LB films and NH_3 can be described by the relation $I = I_{\cdot} 1 - \exp(-t/\tau)$, and the recovery process of the tapCuPc LB film may be described by the relation $I = I \exp(-t/\tau^1)$. The two relations are in approximate agreement with the response and recovery curves measured in the experiment. From the two relations we can obtain that the response and recovery times are 32 s and 13 min respectively; the adsorption and the desorption probabilities are $3.12 \times 10^{-2} s^{-1}$ and $1.28 \times 10^{-3} s^{-1}$ respectively. The gas-sensitive sensor consisting of the tapCuPc LB film can detect NH_3 gas down to 2 ppm in air.

1. INTRODUCTION

The Langmuir–Blodgett (LB) technique is a method for depositing ultrathin high-order organic molecular films. In order to utilize this method in electronics, a large number of studies are now being undertaken. Because ultrathin films such as LB films have very high ratios of surface area to bulk volume, the use of organic gas-sensitive substances and the LB deposition technique shows a great potential for improving the performance of gas sensors. When gas molecules are adsorbed on the surface of the films and cause a physical or chemical action, the remarkable and rapid variation in physical or chemical parameters (such as conductivity) will arise. Therefore it can be expected to obtain an efficient and quick response gas sensor by using the LB film with a good molecular packing and with its gas-sensitive molecular groups aligned near the surface[1].

Many kinds of device structure have been utilized to study the gas-sensing abilities of LB films such as the field effect transistor sensor, planar interdigital

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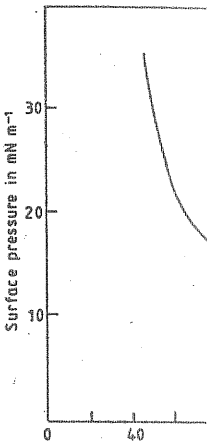
microelectrode arrays, the surface acoustic wave device and the piezoelectric crystal oscillator. Baker *et al.*[2] deposited asymmetrically substituted copper phthalocyanine onto a glass substrate with an interdigital aluminium electrode and obtained some results on the detection of NO_2. The response time was about 30 s and the detection sensitivity can attain a few parts per million. Wohltjen *et al.*[3] deposited higher quality LB films of the copper tetracumylphenoxyphthalocyanine and stearyl alcohol (1 : 1 mixture) onto a gold interdigital electrode and obtained a vapour-sensitive chemiresistor which could detect NH_3 down to 0.5 ppm with a response time of about 30 s at 30 °C. They also found a large response from this device on exposure to NO_2 at concentrations of around 1 ppm. Fu *et al.*[4] reported that asymmetrical axially substituted phthalocyanine LB films are sensitive to O_2, NH_3, NO_2 and Cl_2 gases. Tredgold *et al.*[5] studied metal complexes of mesoporphyrin IX and tetraarylporphyrin, in which the metals were copper, cobalt, nickel, magnesium and H_2, and the tested gases were CO, H_2S and NO_2 Barraud and coworkers[6] reported the gas sensitivity of their electrically conducting tetracyano-*p*-quinodimethane LB films. In this paper, we shall give a dynamical equation for the interaction between copper tetra-4-(2,4-di*tert*-amylphenoxy)phthalocyanine (tapCuPc) LB films and NH_3 and derive the dynamical relations on the variation in conductance with time. The relations are in agreement with experimental curves. From the two relations we can obtain the exact response and recovery times, and the adsorption and desorption probabilities.

2. EXPERIMENTAL DETAILS

The fabrication of a stable gas-sensitive sensor with organic semiconductors requires careful selection of the semiconductor material, film-forming technique, measurement electrode, measurement method etc. It is known that metal-substituted phthalocyanines are extremely stable to oxidation at high temperatures[3,7]. The central metal atoms have a profound effect on the conductivity and the gas-sensitive selectivity[3,8]. In order to form phthalocyanine monolayers using the LB film transfer technique, a peripherally substituted phthalocyanine derivative was needed. In this study, a new symmetrically substituted tapCuPc was synthesized by the method described in ref. 9. The details of the preparation and characterization of the material have been described elsewhere[10]. The molecular structure is shown in the inset of Fig. 1. This material can be dissolved easily in organic solvents such as chloroform, dichloromethane and methylbenzene and forms a stable monomolecular film spreading on the surface of water.

In this study, the tapCuPc LB films were deposited with a Joyce–Loebl constant-perimeter Langmuir trough. In order to spread a monolayer on water surface, firstly the solution was prepared by dissolving the tapCuPc in chloroform. The concentration of this solution was 1 mg cm^{-3}. The surface pressure–area isotherm for the tapCuPc molecule is shown in Fig. 1. A condensed-phase region was observed for this monolayer. The limiting molecular area was found to be about 67 $Å^2$. The monolayer on the water surface was transferred to the planar interdigital microelectrodes by repeatedly dipping the forming LB films. The LB film deposition parameters used in this study were as follows: the surface pressure was 20–25 mN^{-1},



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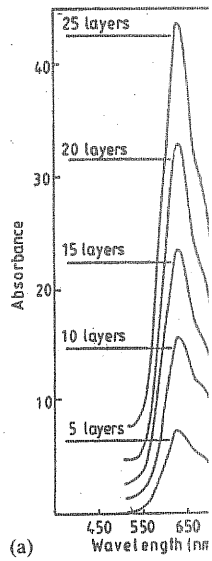

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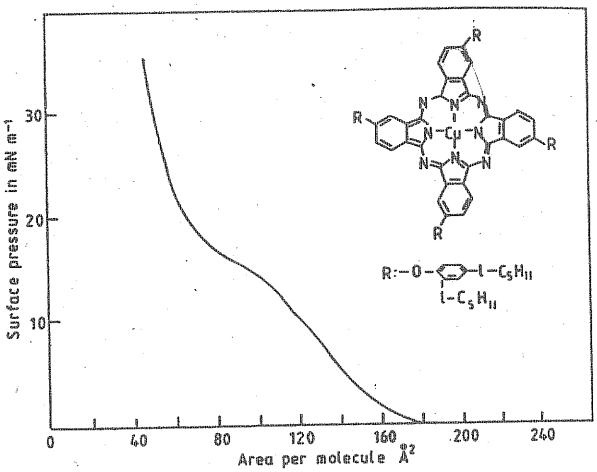

Fig. 1. Surface pressure–area isotherms of the tapCuPc. Its structure is shown in the inset.

the pH 8.5, the dipping speed 5 mm min^{-1} and the subphase temperature 20 °C. Z-type deposition was observed from the recording curves monitoring deposition processes.

Absorption spectra of the tapCuPc LB films were measured on UV–360 automatically recording UV–visible–near-IR spectrophotometer. The optical absorption spectra of tapCuPc LB films with different numbers of deposited layers are shown in Fig. 2(a). In comparison with the absorption spectra of asymmetrically

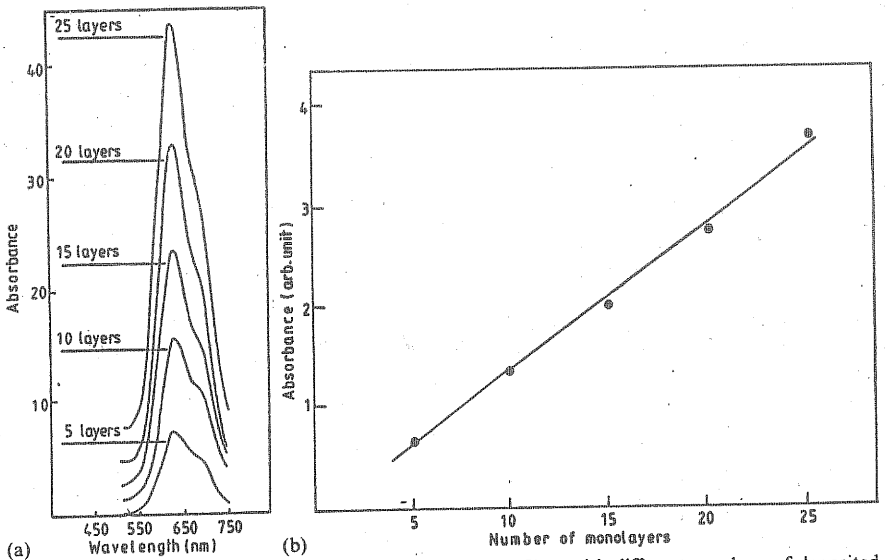

Fig. 2. (a). Optical absorption spectra of the tapCuPc LB films with different numbers of deposited layers. (b). Absorbance measured at 620 nm plotted against the number of layers for the tapCuPc LB films.

substituted copper phthalocyanine LB films reported previously[11], it can be regarded that the dominant peaks at 620 nm are caused by the formation of dimers or higher complexes and the small shoulders at 680 nm correspond to monomer formation. The optical absorbance at 620 nm is plotted in Fig. 2(b) as a function of the number of deposited layers. The linear relationship indicates a constant transfer ratio during sequential dipping of the glass substrate through the floating film.

Measurements of the conductance in the presence of different gas mixtures were performed by depositing the tapCuPc LB films onto a glass substrate on which an interdigital aluminium electrode pattern had been coated previously. The interdigital aluminium electrode in this work was lithographically patterned on a glass substrate. The glass substrates were clean and then deposited by evaporating a 200 nm aluminium film; they were patterned lithographically and etched to form 30 finger pairs of electrodes having a width of 100 μm, spaced 100 μm from the adjacent electrode. The measured sample was positioned in a sample chamber which was made of glass through which a variety of gas mixtures could be passed. The concentration of gas mixtures was controllable down to a few parts per million.

3. RESULTS AND DISCUSSION

3.1. Experimental results

It was found that the tapCuPc LB films have an excellent selectivity to the tested gases. Experimental results show that the conductivity of the tapCuPc LB film was not sensitive to NO_2, SO_2 and H_2S. There was no conductive change on exposure to 200 ppm of these gases in air at room temperature, but large increases in conductivity on exposure to NH_3 were observed. Figure 3 shows a linear relation between the conductive change and the NH_3 gas concentration for low concentrations. The detected sensitivity is around 2 ppm, but the conductive change tends

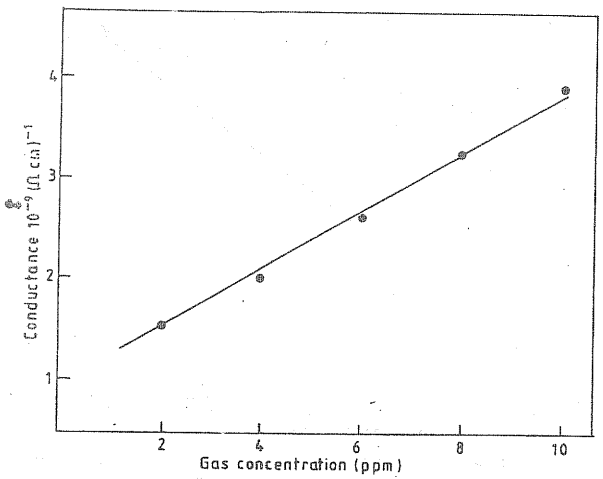

Fig. 3. Conductance change plotted against NH_3 gas concentration for 12-layer tapCuPc LB films deposited onto an aluminium interdigital electrode pattern.

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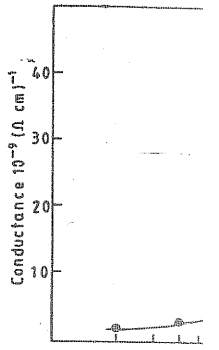

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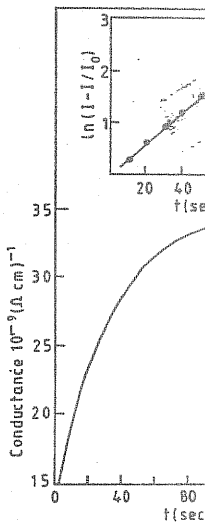

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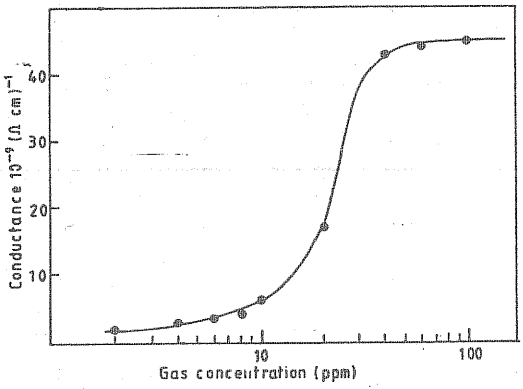

Fig. 4. Conductance change plotted against NH_3 gas concentration for 20-layer tapCuPc LB films at high concentrations.

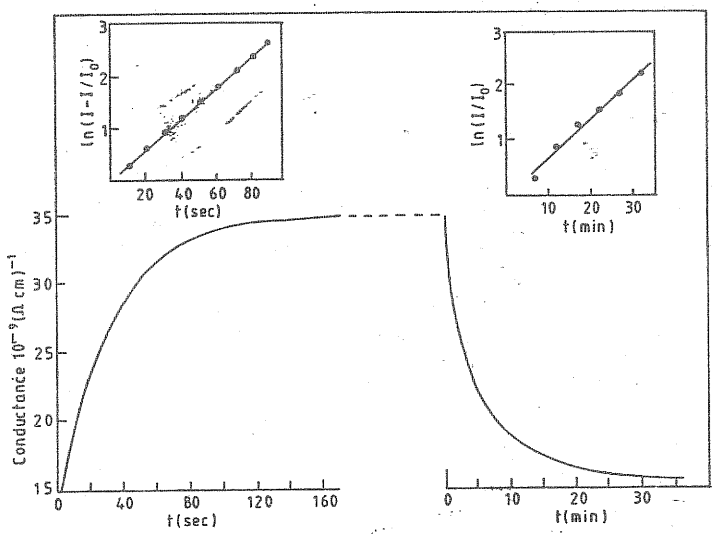

Fig. 5. Response and recovery processes of 12-layer tapCuPc LB films on exposure to 100 ppm NH_3 in air.

3.2. *Dynamical process*

The interaction process between the tapCuPc LB film gas-sensor and the adsorbed gas is a dynamical process. When the device is exposed to 100 ppm NH_3 in air, the adsorption and desorption processes will simultaneously occur. Having attained dynamic equilibrium, the number of the adsorbed gas molecules will be equal to the number of the desorbed gas molecules. Then the conductance of the

device attains a stable value. This process is called the response process. If the device is taken out of the air containing 100 ppm NH_3 and placed in the atmosphere, only the desorption process will occur. It is known that the change in conductivity I is directly proportional to the number N of adsorbed gas molecules:

$$dI \propto dN = \sigma (N_0 - N)\, dt + \sigma' N\, dt \tag{1}$$

where N_0 is the number of tapCuPc molecules on the surface of the LB film, N is the number of adsorbed gas molecules, σ is the adsorption probability of gas molecules per unit time and σ' is the desorption probability that gas molecules escape from the surface of the tapCuPc LB films per unit time. From eqn. (1) the adsorption relation can be described by

$$I = I_0 \left\{ 1 - \exp\left(-\frac{t}{\tau} \right) \right\} \tag{2}$$

and in the desorption process the first term in the eqn. (1) is zero; so the recovery relation is

$$I = I_0 \exp\left(-\frac{t}{\tau'} \right) \tag{3}$$

Here, $I_0 \propto \sigma N_0/(\sigma + \sigma')$ is the saturation conductance at dynamic equilibrium, and τ and τ' are response and recovery times respectively.

3.3. *Discussion of experimental results*

Figure 5 illustrates the increase in the conductance on exposure to NH_3 and the decrease in conductance on isolation from NH_3. The inset of Fig. 5 shows that the increase and decrease in conductance are in agreement with the adsorbed and recovery relations (2) and (3). From the inset, τ and τ' are obtained as equal to 32 s and 13 min respectively; the adsorption and desorption probabilities are equal to $3.12 \times 10^{-2}\ s^{-1}$ and $1.28 \times 10^{-3}\ s^{-1}$ respectively.

The larger the gas concentration, the larger is the probability of adsorbed gas molecules. σ' is constant. When the gas concentration is low ($\sigma \ll \sigma'$),

$$I \propto \frac{\sigma N_0}{(\sigma + \sigma')} = \frac{\sigma N_0}{\sigma'} \tag{4}$$

The conductance is directly proportional to the gas concentration; it is coincident with the experimental curve at the low concentration in Fig. 3. When the gas concentration is high ($\sigma \gg \sigma'$),

$$I \propto \frac{\sigma N_0}{(\sigma + \sigma')} = N_0 \tag{5}$$

The conductance tends towards saturation at high concentrations; it is in agreement with the experimental curve in Fig. 4.

On comparison of these experimental results with those of Baker *et al.* and of Wohltjen *et al.*, it seems that the different peripherally substituted groups affect the selectivity of the phthalocyanine derivatives. Copper tetracumylphenoxy phthalocyanine is sensitive to NH_3 and NO_2 [3]. It was reported that the tris(iso-

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4. CONCLUSION

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