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Study on the stability of a copper phthalocyanine Langmuir–Blodgett film gas-sensitive element

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Abstract

The stability of an asymmetrically substituted copper phthalocyanine (AsyCuPc) Langmuir–Blodgett (LB) film gas-sensitive element which showed good selective sensitivity to NH_3 in air was inspected by an aging test on the device. The reasons leading to the change in response characteristic with time are discussed. It is indicated that the change in gas-sensing response of the AsyCuPc LB film probably arises from the variation in film structure due to the influence of some external factor such as environmental temperature and vibration.

1. Introduction

Recent research progress shows that phthalocyanine (Pc) Langmuir–Blodgett (LB) films have become outstanding candidates for use as highly sensitive gas sensor [1–16]. Owing to their good chemical and thermal stabilities, their ultrathin nature and the ordering of the molecular arrangement, Pc LB film gas-sensitive elements show high gas-detecting sensitivity and speedy response and recovery characteristics. Therefore there has been wide interest in developing high sensitivity Pc LB film gas transducers [2, 3, 5].

Previously, our group reported some research results on the gas-sensing response of two copper phthalyocyanine derivatives to trace ammonia (NH_3) in the atmosphere by measuring the change in conductance and related properties of the LB films [6–8]. However, the stability of this LB film device is still a considerable problem. This paper describes the experimental research results on the stability of an asymmetrically substituted copper [tri-4-(2, 4-di-*t*-amylphenoxy)-mono-4-(2-methoxyethoxy)] phthalocyanine [$CuPc(C_3H_7O_2)$ ($C_{16}H_{25}O_3$)] (AsyCuPc) LB film has-sensitive element [8] which was obtained by an aging test on the device. The molecular structure of AsyCuPc is shown in Fig. 1. The reasons for the change in LB film conductance and gas-sensing response with time are discussed. The relationship between the film conductance and the structure of the membrane is investigated.

2. Experimental details

The synthesis of the AsyCuPc used in the present work has been reported elsewhere [9]. The surface-conducting type of gas-sensing element used in the aging test was constructed as follows: an AsyCuPc monolayer was spread from chloroform solution onto deionized water (resistivity, greater than 18 MΩ cm; pH > 8.0) at 293 K. A KSV-5000 twin-compartment LB instrument was used to study the monolayer behaviour of AsyCuPc and prepare the LB film. AsyCuPC LB films were deposited on a glass substrate with an interdigital electrode which consists of 50 finger pairs of electrodes (electrode width, 50 μm; gap, 50 μm). The normal dipping pressure was 20 mN m^{-1}; the dipping speed was 5 mm min^{-1}.

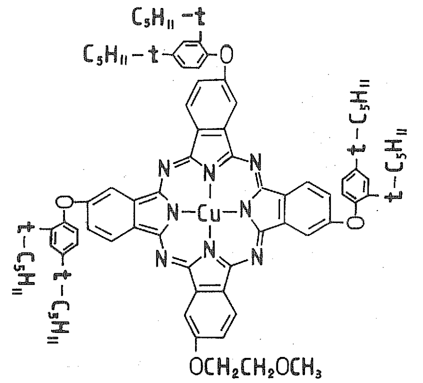

Fig. 1. Structure of the AsyCuPc derivative.

The lateral conductance of the LB film gas-sensing element and dynamic gas-sensing response characteristic were monitored using a current–voltage (*I–V*) measuring apparatus linked with a Teflon and glass gas-testing system consisted of inlets and flowmeters for the introduction of gases, a mixing chamber and a testing chamber, as shown in Fig. 2.

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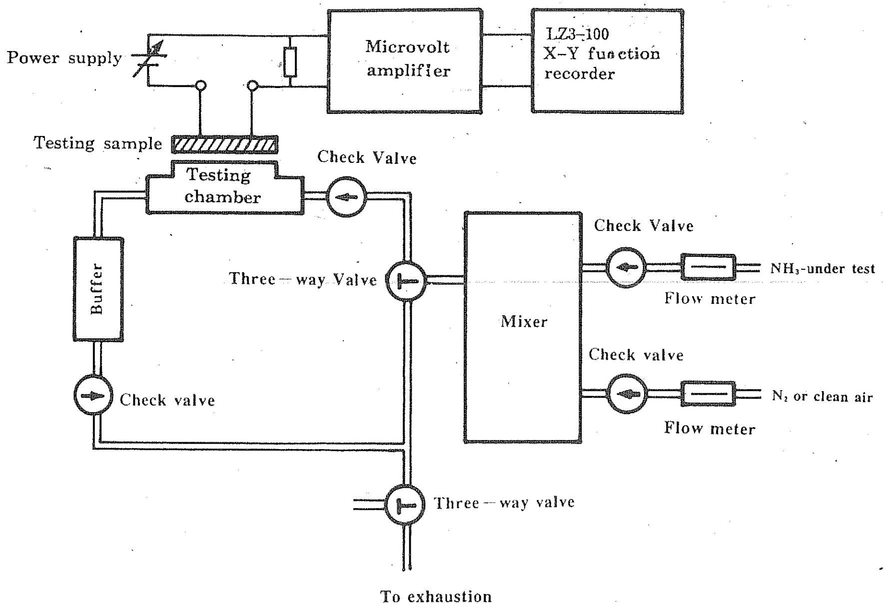

Fig. 2. Dynamic gas-sensing response testing apparatus.

3. Results and discussion

In order to study the stability of the gas-sensing response of the AsyCuPc LB film, the aging test was carried out using a reference sample. The gas-sensing elements were fabricated by the deposition of a 20-layer AsyCuPc LB film on a glass slide pre-covered with Au interdigital electrodes under a surface pressure of 20 mN m^{-1} and a dipping speed of 5 mm min^{-1}. The aging test on the AsyCuPc LB film gas-sensing element was carried out by observing the dependences of the initial conductance σ_0 the gas-sensing response time τ and the response intensity change $\Delta\sigma$ (i.e. the difference in the conductances before and after exposure) on the measuring interval as after exposure to 40 ppm NH_3 in air. Figure 3 shows the typical dynamic response curves for conductance σ with time which were measured at different intervals: Fig. 3(a) is for the as-deposited AsyCuPc LB film gas-sensing element, Fig. 3(b) after 9 days and Fig. 3(c) after 100 days. From the response curve, the response time τ is taken to be the time after a 50% change in the stationary signal. Figure 4 shows the aging testing result on a typical sample for 100 days. From Fig. 4 we can see that the response time increases gradually with increasing measuring interval. Both σ_0 and $\Delta\sigma$ decrease slightly with increase in measuring interval. The above results probably arise from the structural change in the LB films. With time the film structure can be affected by external factors such as environmental temperature and vibration. The molecular arrangement in LB film will relax easily so that the original ordered structure of LB film may be damaged to some extent. The fracture defect band and holes in film may be patched up; this is equivalent to adding a barrier layer to the gas-sensing film, leading to a reduction in the effective gas-adsorbed efficiency.

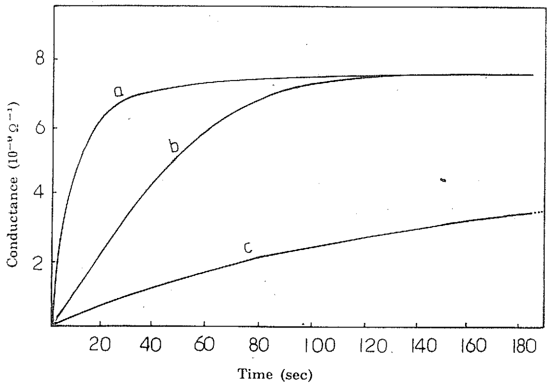

Fig. 3. Dynamic response curves measured at different intervals: (a) as-deposited AsyCuPc LB film gas-sensing element; (b) after 9 days; (c) after 100 days.

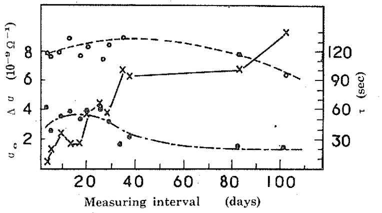

Fig. 4. The dependences of the initial conductance σ_0 (●), response time τ (×) and response intesnity change $\Delta\sigma$ (○) on the measuring interval for the AsyCuPc LB film gas-sensing element prepared at a surface pressure of 20 mN m^{-1}, on exposure to 40 ppm NH_3 in air (operating voltage, 10 V d.c.).

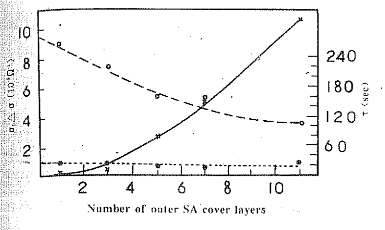

Fig. 5. The dependences fiof the initial conductance σ_0 (●), response time τ (×) and response intensity change $\Delta\sigma$ (○) on the number of outer SA cover layers for AsyCuPC monlayer covered by one-, three-, five- seven- and eleven-layer SA LB films, on exposure to 40 ppm NH_3 in air (operating voltage 10 V d.c.).

For comparison, we made a stearic acid (SA)-covered AsyCuPc LB film device. Firstly the AsyCuPc monolayer was deposited onto a Au interdigital electrode/glass substrate and then covered by a one-, three-, five-, seven- and eleven-layer SA LB film. The SA LB film has no sensitivity to NH_3 in air and plays the role of a barrier layer to gas penetration. Using the above samples we measured the dependence of σ_0, τ and $\Delta\sigma$ on the number of outer SA cover layers. The experimental results are shown in Fig. 5. It is indicated in Fig. 5 that the SA cover layer with a compact structure on the AsyCuPc monolayer really acts as a barrier layer to the penetration of NH_3. On the increase in the number of SA cover layers the gas-sensing response time increases and $\Delta\sigma$ has a tendency to decrease, whereas the initial conductance of the LB film is not affected by the SA cover layers. Therefore it is considered that the lateral conductance of the AsyCuPc LB film arises mainly from the conducting contribution of AsyCuPc sensing layer close to electrode layer; the effect of the outer film on conductance is minimal. The effect of the detected gas on the film conductance depends on the penetration of gas into the film. The compactness of the outer film directly affects the gas-sensing response time.

In summary, the aging test results on the gas-sensing response of the AsyCuPc LB film indicate that the stability of the LB film device needs to be further improved. On comparison of the aging test results on the AsyCuPc LB film gas-sensing element with the test results on the gas-sensing response of SA-covered AsyCuPC LB film device, it seems that the change in the gas-sensing response of the AsyCuPc LB film with time probably arises from the variation in film structure due to the influence of some external factors (such as environmental temperature and vibration). It is necessary to obtain experimental evidence which clarifies the reasons for the change in gas-sensing response. Further work on the structure analysis of films is in progress.

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