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Sensors and Actuators B 66 (2000) 207–209

SENSORS AND ACTUATORS B CHEMICAL

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Sensitivity and stability of substituted phthalocyaninato-polysiloxane Langmuir–Blodgett films and its gas sensor

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Received 30 July 1998; received in revised form 2 June 1999; accepted 29 January 2000

Abstract

The monolayer and Langmuir–Blodgett (LB) film deposition behavior of tetrakis-4-(2,4-di-*tert*-amylphenoxy) phthalocyaninato-polysiloxane (R_4PcPS) were studied. LB film gas-sensitive device was prepared by depositing R_4PcPS LB films on a glass substrate with aluminum interdigital electrodes. The results on dynamic gas sensing response characteristics showed that the R_4PcPS LB film gas-sensitive device has a higher detecting sensitivity on exposure to trace ammonia (1 ppm of NH_3) in air, as well as comparatively lower detecting sensitivity to NO_2 and I_2 (100 ppm) in air. On the other hand, the R_4PcPS LB film gas-sensitive device shows excellent stability. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sensitivity; Stability; Langmuir–Blodgett films

1. Introduction

In recent years, the numerous research results show that phthalocyanines (Pcs) Langmuir–Blodgett (LB) films are excellent candidates for developing high sensitive gas sensor [1–7]. Because their conductance change range can reach by orders of magnitude on exposure to certain gas, good chemical and thermal stability as well as thinness of Pc LB film and well-ordered layer structure, Pc LB film gas sensing elements have higher gas-detecting sensitivity and speedy response. For further improvement of device stability, researchers make an attempt at exploring appropriate polymeric materials with molecule recognition ability. P.D. Jeffery and Burr [2] reported a polymeric film of Si and Ge Pc, which could be used to make chemiresistive gas sensors as well as the results on detection of NO_2 and Cl_2. T. Sauer et al. [8] described the monolayer behavior of an unsymmetrically substituted phthalocyaninato-polysiloxane (PCPS) and the structure characteristic of PCPS LB film. W.H. Ko et al. [4] reported a gas microsensor for NO_2 and halogen fabricated by dimeric Si–Ge Pc LB film and their good operating stability.

The present paper describes the research results on the monolayer and LB film deposition behavior, gas-sensitive properties and stability of a tetrakis-4-(2,4-di-*tert*-amylphenoxy) phthalocyaninato-polysiloxane (R_4PcPS) LB film sensor.

2. Experimental

The synthesis of the R_4PcPS used in the present work has been previously reported by Y.J. Li [9]. The monolayer of R_4PcPS was spread from chloroform solution onto the surface of deionized water (with resistivity of more than 18 MΩ cm) at 293 K. A KSV-5000 Twin-compartment LB instrument was used to study the monolayer behavior of R_4PcPS and fabricate LB films. The R_4PcPS LB film gas-sensitive element used for measurement of conductance and sensitive property was fabricated by R_4PcPS LB film deposition onto a glass substrate with aluminum interdigital electrodes, which consist of 50 finger pairs of electrodes (electrode width is 50 μm; gap is 50 μm). The normal dipping pressure was 20–25 mN/m and the dipping speed was 5 mm/min. The lateral conductance of the LB film gas-sensitive element and dynamic gas-sensing response were measured on a current–voltage (I–V) measuring apparatus linked with a Teflon and glass gas testing system reported previously[6].

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PII: S0925-4005(00)00364-6

3. Results and discussion

3.1. Response properties of R_4PcPS LB film gas-sensitive device

The interaction process between the LB film and the detected gas is a dynamic process. When the LB film is exposed to detected gas, the adsorption and desorption process will simultaneously occur. When the number of adsorbed gas molecules is equal to the number of the desorbed gas molecules, the dynamic equilibrium is attained. Then the conductance of the LB film attains a saturation value. This process is called the response process. When the LB film gas sensor is taken out of the detected gas, only the desorption process will occur. The change in conductivity is directly proportional to the number of adsorbed gas molecules. The response and desorption processes can be described [3,5], respectively, by

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

$$I = I_0\exp\left(-\frac{t}{\tau'}\right) \tag{2}$$

where I_0 is saturation current, I is response current, t is time, τ and τ' are response and recovery time, respectively. The experimental results also show that the response and desorption processes are exponential relationship.

The response and desorption processes of a 15-layer R_4PcPS LB film to 100 ppm I_2 in air are shown in Fig. 1. It is observed from Fig. 1 that the response of R_4PcPS LB film to I_2 is very fast and the response time is less than 4 s. Fig. 2 shows the response and desorption processes of a 15-layer R_4PcPS LB film to 100 ppm NO_2 in air. The response time is very long and it is about 21 s. The response time to NO_2 is much longer than that of I_2. We consider that the ability of capturing electrons of I_2 (electronegativity of I_2) is larger than that of NO_2, so that I_2 is easy to be adsorbed onto surface of LB film and get electron from sensitive film. In other words, the adsorption

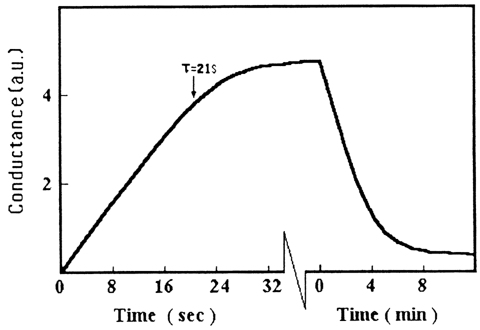

Fig. 2. Response and desorption of 100 ppm. NO_2 to R_4PcPS LB film.

probability of the sensitive film to I_2 is larger than that of NO_2. The response time is inversely proportional to the adsorption probability [3].

The response processes of R_4PcPS LB film sensor to 1, 10, and 100 ppm NH_3 in air are shown in Fig. 3. It can be observed that the response time is dependent on the gas concentration. The higher the gas concentration, the shorter the response time. The response time is inversely proportional to the number of the gas molecules to reach per unit area of sensitive film per unit time (expressed by N_s).

$$N_s = \int_0^{\infty} n v_x F(v_x)\,\mathrm{d}v_x. \tag{3}$$

Here v_x is the speed of gas molecular therm-motion; the $F(v_x)$ is Maxwell–Boltzmann distribution:

$$F(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{mv2}{2kT}}.$$

From Eq. (3) and Maxwell–Boltzmann distribution, N_s can be described by

$$\frac{1}{\tau} \propto N_s = \frac{1}{4} n\sqrt{\frac{8kT}{\pi m}}. \tag{4}$$

Here n is the number of gas molecules per unit volume. From Eq. (4), the same results can be obtained that the responding time decreases when the gas concentration increases. On the other hand, it can be seen that the responding time decreases when temperature increases.

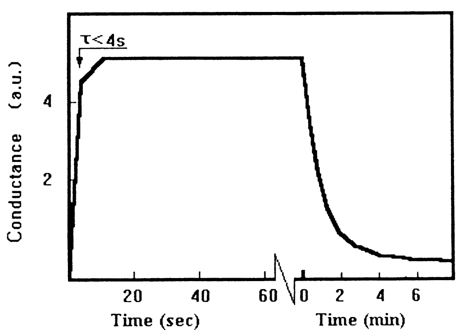

Fig. 1. Response and desorption of 100 ppm. I_2 to R_4PcPSLB film.

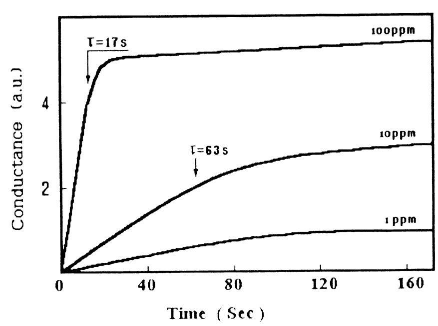

Fig. 3. Response of R_4PcPS LB film to 1, 10, and 100 ppm NH_3 in air.

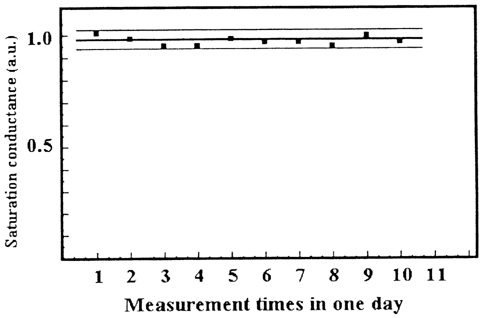

Fig. 4. The saturation conductance of repeated measurement to 20 ppm NO_2.

3.2. Stability of R_4PcPS LB film gas-sensitive device

We consider that the stability of LB film gas sensor means the difference of saturation conductance among repeated measurements in 1 day. Fig. 4 shows the saturation conductance of R_4PcPS LB film sensor to 20 ppm NH_3 in air. Ten-time measurements were finished within 1 day. The difference was obtained by following formula (5)

$$\delta = \frac{\Delta I}{\bar{I}} = \frac{I_{max} - I_{min}}{\bar{I}}. \quad (5)$$

Here ΔI is difference between the maximal and minimum saturation current at the same condition. It can be calculated that the difference (δ) of R_4PcPS LB film sensor is less than 4%. The gas sensor fabricated by R_4PcPS LB film is possessed of good stability.

Acknowledgements

The work was supported by The National Nature Science Foundation of China (59783005).

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