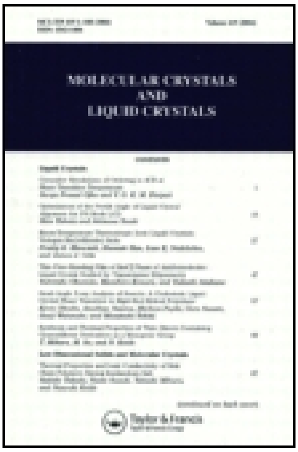

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GAS SENSING DEVICE BASED ON PHTHALOCYANINE LB FILMS

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Abstract. An investigation of the electrical conductivity of films consisting of multilayers of tetra-*t*-butyl-substituted copper phthalocyanine (TTBCuPc) films exposed to various levels of nitrogen oxides in air (within the ppm range) was carried out. The TTBCuPc films were deposited, using the Langmuir-Blodgett (LB) technique, onto glass substrates. Gold interdigital electrodes (ca. 2μm thick, 100 μm wide and 100 μm spaced) were evaporated on the top of the films. High reproducibility and reasonable sensitivity of the sensors to the nitrogen oxide at a relatively low temperature (313 K) suggest that TTBCuPc may be a viable material for gas sensing devices.

INTRODUCTION

It has been known for several years that adsorbed gases - either oxidizing or reducing - can substantially affect electrical and/or optical properties of phthalocyanines (see, e.g., Refs. 1-3 and references quoted therein). The changes in electrical conductivity of phthalocyanines can, in favourable cases, amount to several orders of magnitude. Such dramatic changes in electrical properties can be exploited for a number of chemical or gas sensor applications.

When a gas molecule is chemisorbed on the surface of a semiconductor, a charge transfer may occur between them, its direction depending upon the electronegativity of the gas and the work function of the solid. The charge transfer can either influence only the surface conductivity of the semiconductor or, following a reaction at the surface, carriers can be injected into the bulk causing changes in both the surface and bulk conductivities. Finally, the adsorbed species or products of the side reaction may diffuse into the sample's bulk, influencing its electrical properties.

As was demonstrated by van Ewyck et al,[4] changes in electrical conductivities of phthalocyanines caused by gases are confined to the surface of the crystals rather than to their bulk. It is therefore well founded that several phthalocyanine gas detectors described so far have been based on thin films.[5-9] Unfortunately, because of the polymorphism of crystals of many phthalocyanines, the morphology of phthalocyanine films can be quite complicated, making interpretation of results difficult. Moreover, the response and recovery times on such thin-film devices can also be very long, attempts to make them shorter resulting usually in operations at elevated temperatures (cf., e.g., Ref. 10).

One can hope that the LB technique, making possible to fabricate thin organic films with specific properties and to modify their surfaces in an organised and systematic way,[11] will enable one to overcome at least some of the problems mentioned above.

The present work reports on results of measurements of the effect of nitrogen oxides on phthalocyanine LB film gas sensor. We have monitored changes of the surface dark conductivity of sensors made of TTBCuPc films due to adsorption of nitrogen oxides.

EXPERIMENTAL

Sample preparation

Tetra-*t*-butyl Cu phthalocyanine was synthesized from o-xylene,[12] and purified on alumina chromatographic column. The purity of the product was checked by the thin-layer chromatography, and its molecular structure was confirmed by IR and UV-VIS spectroscopy as well as the elemental analysis.

Monomolecular films of TTBCuPc were spread from xylene solutions (c = 4.5 g/dm^3) on quartz-bidistilled water at 290 K. The films were compressed at the rate of 0.025 mm/s and the limiting area of about 0.6 nm^2 per molecule was confirmed.[13] The transfer of films onto glass substrates (Corning 2948, untreated or hydrofobized with dichloro-dimethylsilane) was carried out at a surface pressure of 20 mN/m. The deposited LB films were of the Y-type, the transfer ratio being only slightly lower than 100%. Films 3, 6 and 16 monomolecular layers thick were prepared and stored in a vaccum dessicator for 12 to 24 hours until 32 interdigital Au electrodes, 6 mm long, 100 μm wide and 100 μm spaced were vacuum-deposited onto their top side. Samples prepared in such a way were stored in air under a slightly reduced pressure.

Sensor studies.

NO_2 was obtained in the reaction of sodium nitrite with the nitric acid, and the NO_2- air mixtures used in this work and covering the concentration range from 0.1 to 15 mg/m^3, were prepared using a permeation tube located in glass enclosure kept at a constant temperature. A constant air flow over the permeation tube that could be varied between 1.5 and 4 cm^3/s provided a known concentration of NO_2 in the air. After each measurement session, the NO_2 concentration was checked according to the Polish National Health and Security standards, employing the Saltzman colorimetric method.

Detailed investigations of the temperature dependence of electrical conductivity of TTBCuPc LB films exposed to various NO_2 concentrations were carried out in order to optimise the operation conditions of phthalocyanine gas sensors. For relatively low concentrations of NO_2 (around 1 ppm), the conductivity was found to increase with temperature, passing through a maximum at ca. 320 K. A further heating resulted in an enhanced desorption and a decrease of the current until a value close to the initial one was reached again at ca. 370-380 K. The procedure of preparation of the sensors, adopted on the basis of these experiments, was as follows. Each sample was heated for two hours at 393 K in the stream of dry air, cooled down to 313 K and then exposed to NO_2- air mixture of a concentration at which the sensor was expected to work (between 0.25 and 30 ppm). The sample was subsequently cooled again to room temperature and stored in the air. The d.c. current-voltage characteristics, measured both prior to the admission of the nitrogen oxide and for all pressures of NO_2 were found linear over the entire voltage range covered by our experimens (up to 10 V).The temperature of the substrate was maintained constant during the calibration experiments (313 K in the experiments described in this paper).

RESULTS AND DISCUSSION

We measured the dependence of the surface conductivities of TTBCuPc sensors exposed to the air containing NO_2, its nominal concentration ranging between 0.129 mg/m^3 (0.28 ppm) and 14.7 mg/m^3 (31.3 ppm). The dependences were found slightly sub-linear with respect to the concentration of NO_2 , with some tendency toward a saturation at higher NO_2 concentrations.

If one assumes that the conductivity is directly related to the number of molecules of the active gas adsorbed on the sample surface, then, under a constant voltage, the shape of the $I(p)$ dependences can be described by the Freundlich isotherm[9]

$$\Delta I = I(p) - I(0) = k\, S(p) \,\square\, k\, p^{\gamma} , \qquad (1)$$

where $I(0)$ and $I(p)$ are the initial current measured prior to the admission of the active gas, and the current under the partial pressure of the active gas amounting to p, respectively, S is the fraction of the surface covered by the gas, and k and γ are constants.

Under a stationary flow of the nitrogen oxide - air mixture over the sensor, the proportionality of p to the total concentration of the active gas in the mixture should be fulfilled. It should be stressed here that a simple calculation shows that in the conditions of our experiments, the equilibrium is strongly shifted toward the formation of NO_2, the contents of other nitrogen oxides not exceeding 10^{-4}- 10^{-3}% of the total amount. Thus one should expect the ($\log \Delta I$ vs. $\log c$)

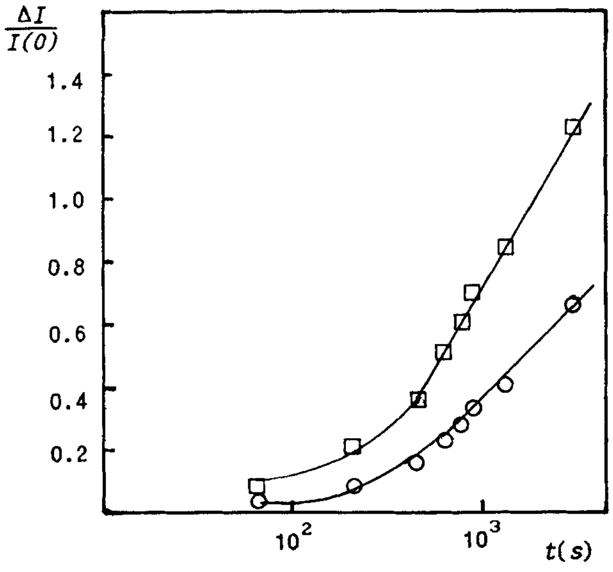

FIGURE 1 Variations of the relative surface conductivity of a TTBCuPc sensor measured 6 minutes after the exposure to various concentrations of NO_2 at 313 K.

dependence to be linear, its slope amounting to 1, as in the case of a non-dissociative adsorption. On the other hand, one cannot exclude a competition of adsorbed ubiquitous oxygen. Such a competition would explain the slopes slightly lower than unity, found in our experiments (cf. Fig. 1). The measurements carried out on vacuum-deposited polycrystalline phthalocyanines demonstrated that the 'oxygen effect' becomes apparent above 320 K, saturating above 370 K.[8]

The transient response characteristics for various concentrations of NO_2 are shown in Fig. 2. The characteristics have been plotted in the ($\Delta I/I(0)$ vs. log t) coordinates, resulting from the Elovich equation

$$dS/dt = a\exp(-\beta t) \ , \qquad (2)$$

often employed to describe the kinetics of chemisorption (see, e.g., Ref. 14). As one could expect, after an initial period the current becomes a linear function of log t.

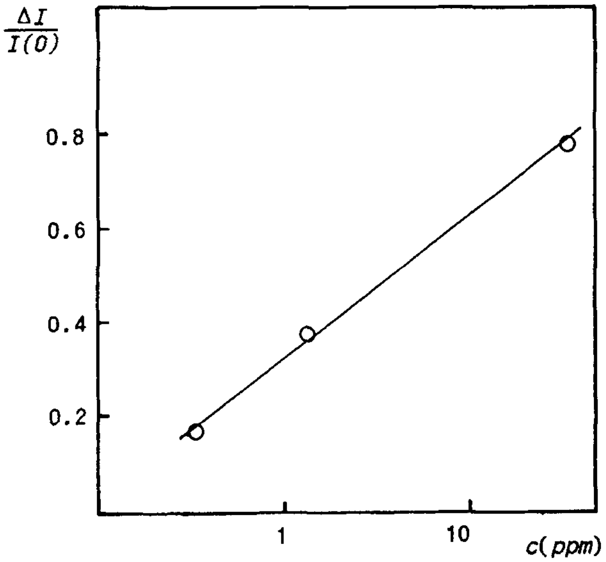

FIGURE 2 The Elovich plot measured on a TTBCuPc sensor at 313 K. The concentrations of NO2 amounted to 0.28 ppm (o) and 1.22 ppm (□)

Although the results presented in this paper reasonably well fulfil predictions of the model, the adsorption/desorption cycles, and in particular the first one, are not fully reversible, most probably due to an irreversible side reaction. However, after a proper ageing,[15] the characteristics become reasonably reversible, the resulting high reproducibility and stability of pre-treated sensors encouraging a further research on the use of phthalocyanine LB films as NO_2 sensors.

Both the sensitivity of the samples and the kinetics of their response to the presence of NO_2 were found to depend on their thickness and the electrode geometry. In our opinion, this behaviour is an evidence of a non-negligible role of bulk processes, associated probably with the diffusion of gases, and requiring further studies.

CONCLUSIONS

A gas sensor made of substituted phthalocyanine LB films was described, having a high sensitivity and a relatively short response time. In our opinion LB sensors, being significantly thinner and more ordered, may prove superior to those based on vacuum-deposited phthalocyanine films. Moreover, results presented in this paper demonstrate that the sensors based on phthalocyanine LB films are active at the temperature as low as 313 K, whereas most vacuum deposited films had to be used at much higher temperatures. We believe that the phthalocyanine LB films can be used, e.g., in monitoring low concentrations of NO_2 in protected areas, as cheap smog sensors, etc.

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