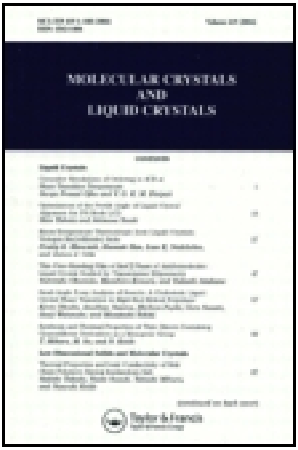

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APPLICATIONS OF ORGANIC SOLIDS TO CHEMICAL SENSING

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Abstract Experiments to evaluate several factors affecting the performance of organic semiconductors as gas sensors are reported. The influence of the strength of surface charge-transfer interactions on the magnitude, rate and reversibility of conductivity changes is reviewed and data presented on reversal rate as a function of temperature for NO_2 on lead phthalocyanine films, yielding a desorption energy of 76 kJ mol^{-1}. For copper phthalocyanine, surface heterogeneity prevents analysis of desorption rates in terms of a single desorption energy. Effects of the physical form of organic semiconductor surfaces on their gas sensing properties are reviewed and data presented showing these properties independent of film thickness for lead phthalocyanine on rough substrates. Studies of the effect of humidity on the response of lead phthalocyanine films to NO_2 are reported. At 12% relative humidity the conductivity increase is smaller than in dry conditions and proportional to NO_2 concentration up to 0.1 ppm, saturating thereafter. At 33% relative humidity, increases are smaller and saturate at lower NO_2 concentrations. These results are interpreted in terms of reaction of water with NO_2 in the gas phase and blocking of surface sites by water molecules, and demonstrate the need for careful calibration procedures.

INTRODUCTION

Many organic solids which are poor semiconductors exhibit large increases in surface semiconductivity on exposure to electron donor or acceptor gases. These effects, which arise from surface charge transfer interactions and consequent n- or p- type surface doping respectively, were first quantitatively studied using single crystals in high vacuum, with stepwise addition of small aliquots of pure samples of the gas to be detected[1]. Later, studies of the factors influencing the response speed, reversibility, reproducibility and sensitivity of sublimed films of metal phthalocyanines for use as gas detectors were reported[2] and the influence of the physical structure of the surface was demonstrated. These studies used mixtures of carefully dried air with nitrogen dioxide, and provided the basis for a prototype NO_2 sensor[3]. In this paper further investigations of three aspects of this application of organic solids to chemical sensing are reported. Firstly, the importance of the strength of the surface charge-transfer interactions in controlling the sensitivity, response speed and reversibility of the semiconductor sensor will be reviewed and data will be presented on one method for measuring the strengths of these interactions experimentally. Secondly, the influence of the physical structure of phthalocyanine films on their performance as NO_2 detectors will be summarised and data presented for the performance of films for varying thickness. Finally, quantitative data will be presented on the influence of water vapour on the performance of lead phthalocyanine films as NO_2 sensors.

EXPERIMENTAL

Metal phthalocyanines were synthesised from phthalonitrile[4] and purified by entrainer sublimation at least three times under oxygen-free nitrogen. Phthalocyanine films were sublimed in a vacuum of 10^{-2} Pa onto alumina substrates approximately 3mm square, fitted with a sputtered platinum interdigitated electrode assembly on one side and a sputtered platinum heater/resistance thermometer coil on the reverse side (Rosemount Engineering Co. E11268). Film mass per unit area was determined by simultaneous evaporation of films of known area on glass substrates, followed by dissolution of the film in tetrahydrofuran and spectrophotometric determination of the concentration of the resulting solution. Nitrogen dioxide concentrations in the range 0.04 - 1.4 ppm were obtained using a Tylan FC260 mass flow controller to control the flow of clean air over thermostatted gravimetrically-calibrated nitrogen dioxide permeation vials. Before passage over the permeation vials, this air was first dried with fresh silica gel or conditioned to standard humidity levels by bubbling through appropriate saturated solutions of metal salts.[5] Current-voltage characteristics with applied d.c. fields up to 10^5 v/m, and d.c. conductivity as a function of film temperature, NO_2 concentration and time, were measured using a computer-controlled apparatus described elsewhere.[6] Following earlier studies[2] which established the need for thermally-induced crystallisation of freshly-sublimed phthalocyanine films to develop the active sites necessary for adsorption, all new films were heated to at least 155°C for 12 hours before any electrical measurements were commenced.

RESULTS AND DISCUSSION

Effects of strength of surface charge-transfer interactions

Previous studies of variations in the magnitude, rate and reversibility of conductivity changes in a range of organic solids on exposure to different gases[1,2] suggest that the strength of surface charge-transfer interactions has a strong influence on each of these properties. Studies of the magnitude of the conductivity changes on exposure to different gases are best carried out using single crystal samples with high quality reproducible surfaces. In these conditions spurious effects on the magnitude of the changes, which might arise from variations in the physical quality of the surface and hence its density of active adsorption sites, are minimized. Experiments on such single crystal samples[1] have shown very large conductivity changes for phthalocyanines in NO_2 and for perylene in BF_3, but much smaller changes of conductivity of phthalocyanines in BF_3, perylene in NO_2 and tetracyanoquinodimethane in ammonia. The smaller change in phthalocyanine conductivity on exposure to BF_3 is accompanied by poor reversibility of the effect, which also saturates at a much lower pressure than the large effects of NO_2 on phthalocyanines or BF_3 on perylene. These observations all suggest that the charge-transfer interaction between phthalocyanines and BF_3 is too strong and localised, leading to a strong coulombic attraction between electron-hole pairs at the surface and consequently small conductivity increases, saturating at low pressures as the surface coverage rapidly reaches a monolayer, and difficult to reverse. Conversely, the small increases in conductivity on exposure of perylene to NO_2

and tetracyanoquinodimethane to ammonia are readily reversed and only saturate at high pressure, consistent with too weak charge-transfer interactions. The cases of NO_2 on phthalocyanine and BF_3 on perylene represent optimum strength of charge transfer interaction, with facile production of electron-hole pairs at the surface yet with sufficiently weak electron-hole attraction to permit charge migration. These single crystal experiments also suggested that the optimum strength of charge-transfer interaction is not highly critical, since a range of different phthalocyanines (Mn, Co, Ni, Cu, Zn, Pb and metal-free) with different electronic and geometric properties all show similar saturation surface conductivity in NO_2. However, studies of the rate of conductivity changes on exposure of heat treated phthalocyanine films to low concentrations of NO_2 in dry air show that this parameter is much more sensitive to the strength of surface charge-transfer interactions. Thus, films of lead phthalocyanine respond much more rapidly than those of other metal phthalocyanines (e.g. Figure 1), despite the

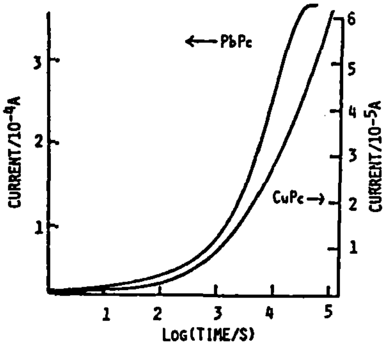

FIGURE 1. Response kinetics of lead and copper phthalocyanine films to NO_2.

fact that single crystal data show that the ultimate equilibrium conductivity in saturation conditions is the same for all the metal derivatives. The rates of response of films and single crystals to low partial pressures of NO_2 in air in a flow system are much slower than those for single crystals in high vacuum exposed to similar pressures of NO_2. This suggests that the rate of response in the flow system is determined by the rate of displacement of oxygen species from the phthalocyanine surface. This will be fastest for the most weakly-bound oxygen species, as well as faster in the absence of the high partial pressures of oxygen found in the flow system, where any displaced oxygen has a high probability of being replaced by another oxygen molecule from the air rather than by an NO_2 molecule. The faster response of lead phthalocyanine to NO_2 can thus be understood in terms of the weaker charge transfer interaction between lead phthalocyanine and oxygen arising from the non-planarity[7] of lead phthalocyanine. The non-planar Π electron system of lead phthalocyanine will be a poorer electron-donating system than the planar conjugated Π electron system of normal phthalocyanines, thus weakening the charge-transfer interaction and facilitating displacement of surface oxygen. The fastest response thus requires the weakest possible surface charge transfer interaction which will still provide a good magnitude of response. Similarly, in these conditions the conductivity changes produced by NO_2 are rapidly reversed on exposure to clean air, while strongly bound species (e.g. BF_3 on phthalocyanine) give effects which are slow to reverse. For a heterogeneous film surface with a range of different types of active site, this model explains the observed dependence of response rate and reversibility on surface coverage. Thus, for low NO_2 concentrations (and hence low surface coverages), only the most weakly bound oxygen species need be displaced from the surface and response is rapid and reverses rapidly[3], whereas for higher NO_2 concentrations successively more strongly-bound oxygen species must be displaced, leading to slower response and reversal[2].

Although all these observations may be rationalised in terms of the strength of surface charge-transfer interactions, very little quantitative information is available on the interaction energies in individual systems. Direct measurements of heats of adsorption on film or single crystal samples has not yet proved possible due to the low sample surface area and the sensitivity limitations of current microcalorimeters. In this work an attempt has been made to measure the heat of desorption by determining the rate of reversal of the conductivity change as a function of sample temperature. For weak chemisorption with a low adsorption activation energy, the desorption energy is approximately equal to the heat of adsorption. Figure 2 shows a plot of the log (time for 25% reversal of conductivity change) v. 1/T for a film of lead phthalocyanine. The slope of the line on this plot corresponds to an energy of 76 kJ mol^{-1}, which is of the expected order of magnitude for weak chemisorption.

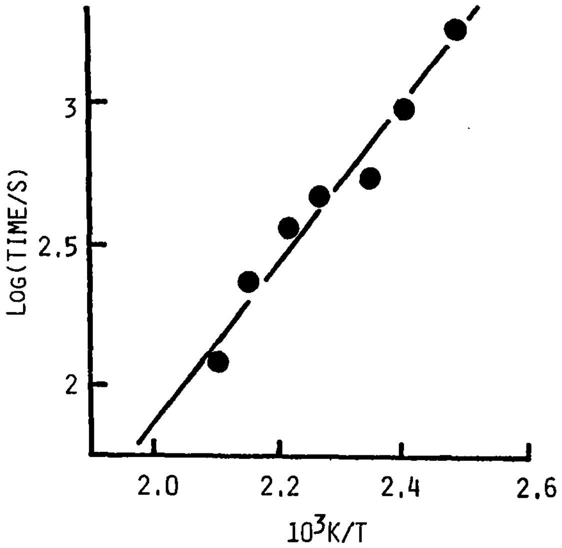

FIGURE 2. Time for 25% reversal as a function of temperature for NO_2 on a lead phthalocyanine film.

Unfortunately this method requires approximately constant surface coverage, since for a heterogeneous film any change in surface coverage will result in a change of heat of adsorption. For lead phthalocyanine this condition is satisfied as the duration of the exposure to NO_2 prior to reversal was sufficient to achieve equilibrium coverage, and the variation of equilibrium position with temperature is too small to affect the linearity of the plot. However, for other phthalocyanines the rate of response is much slower as mentioned above and the surface coverage at the end of the exposure (3½ h.) is thus limited by kinetic factors and hence much more variable as the temperature changes. The result (Figure 3) is a curved plot from which

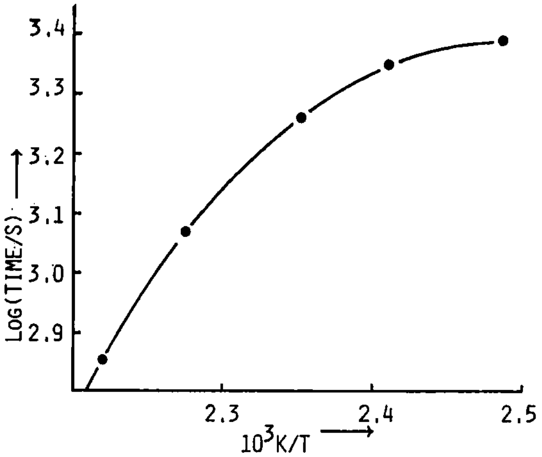

FIGURE 3. Time for 25% reversal as a function of temperature for NO_2 on a copper phthalocyanine film.

it is impossible to deduce any useful thermodynamic data. Further measurements of heats of adsorption using improved calorimetric techniques are of great importance to the quantitative understanding of organic solids as chemical sensors and are currently in progress in this laboratory.

Effects of physical structure of phthalocyanine films

Figure 3 clearly reflects the heterogeneity of adsorption sites on phthalocyanine films deposited on rough alumina substrates. Electron microscopy of the clean substrates revealed very rough surfaces, with undulations of the order of 1 µm. In contrast, previous work[2,8] has shown that phthalocyanine films deposited on smooth substrates are amorphous[9] and have the most uniform smooth surface when the substrate temperature is carefully controlled at approximately one-third of the boiling point of the phthalocyanine[10]. Such optimised films were found to display low sensitivity of conductivity towards NO_2, although heat treatment (150°C for 12 hours) increased the sensitivity to a reproducibly high level[2]. The main effect of this heat treatment has been shown to be thermally-induced crystallisation of the amorphous film, observable directly using high-resolution electron microscopy[9]. Active adsorption sites are believed to occur at crystallite surfaces and edges, and the observed heterogeneity is not surprising in view of the range of crystallite sizes and orientations together with the roughness of the underlying substrate. Phthalocyanine Langmuir-Blodgett films are believed to show more uniform surfaces, but the kinetics of the conductivity change on exposure to NO_2 in nitrogen suggest at least two types of adsorption site even in this case[11]. (The use of nitrogen as diluent for the NO_2 removes the competition by oxygen for surface sites and probably explains the apparent faster response of these LB films than that shown by sublimed films, exposed to NO_2 in air.) Despite the surface heterogeneity of sublimed phthalocyanine films, their sensitivity towards NO_2 following initial heat treatment has been shown[3] to be remarkably constant during the lifetime of the film, only falling off rapidly when the constant slow loss of surface molecules by sublimation has reduced the film thickness to a point where continuity is lost. This implies that the film NO_2 sensing properties are independent of film thickness when these rough substrates are used. Figures 4 - 6 show the results of measurements of magnitude, rate and reversal rate of the conductivity change on exposure to 0.04 ppm of NO_2 in air for lead phthalocyanine films of varying thickness at an operating temperature of 155°C. These results show that

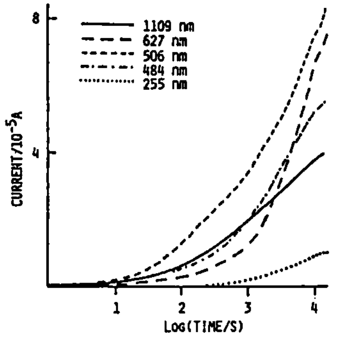

FIGURE 4. Response of lead phthalocyanine films of different thickness to 0.033 ppm NO_2 in dry air.

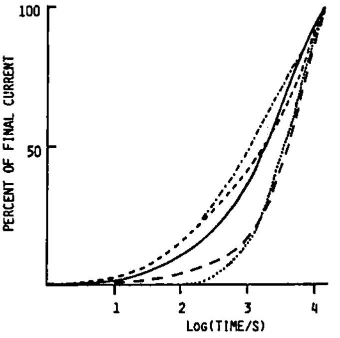

FIGURE 5. Rates of response of lead phthalocyanine films of different thickness to 0.033 ppm NO_2 in dry air. (Data of Figure 4 normalised to 100% at final point.)

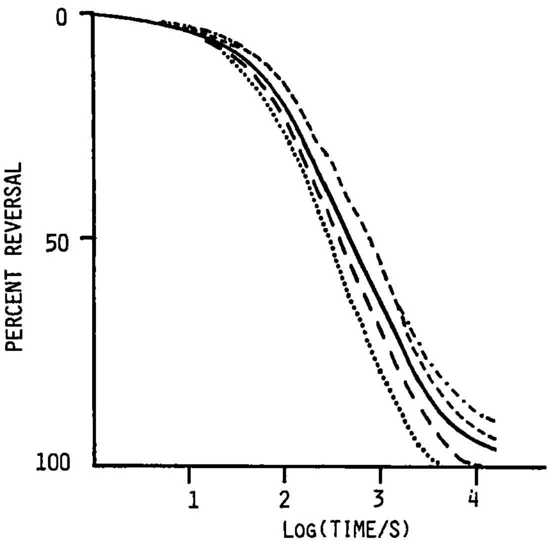

FIGURE 6. Rates of reversal of films in Figure 4 in clean dry air. (Data normalised to 100% at first point.)

although there are variations between different films, there is no systematic correlation with film thickness. Since the largest film thickness used was of the same order as the surface roughness, these results imply that the surface characteristics of these sensor films are dominated by the substrate structure. The importance of the result is that sensors of improved lifetime can be fabricated using thicker phthalocyanine films without risk of altering the sensor characteristics substantially.

Influence of water vapour on NO_2 sensing characteristics

During measurements of the conductivity of lead phthalocyanine films as a function of time and NO_2 concentration in dry air we observed that the onset of saturation of the drying agent (silica gel or molecular sieve) was reflected in a decrease in the conductivity. Since full sensitivity to NO_2 was restored when fresh drying agent was used, it was concluded that water vapour interfered with NO_2 detection either by reacting with the NO_2 to form nitric acid or by blocking adsorption sites on the phthalocyanine film surface. Experimentally it is impossible to study one of the latter effects in isolation. Furthermore, independent measurement of the concentration of free unreacted NO_2 in a moist NO_2/air mixture is difficult as many of the alternative methods of measuring free NO_2 are also affected by humidity to some extent. Nevertheless, quantitative studies of the magnitude of the interference as a function of humidity have been made to explore the possibility of compensating for the interference by using a combination of water vapour and phthalocyanine NO_2 sensors. Ideally, such a study would involve measuring the equilibrium conductivity of the phthalocyanine film as a function of NO_2 concentration and temperature in several different controlled standard humidity levels. Practically the time required to ensure final equilibrium values precludes this approach, and experiments were conducted exposing the sensor to 90s.pulses of NO_2/air mixtures of various concentrations and humidities, with reversal at 200°C in clean air between each pulse. Figure 7 shows the maximum current passing through the film as a function of NO_2 concentration for mixtures with air dried by silica gel and humidified to 12% and 33% relative humidity. In 12% humidity the conductivity change for NO_2 concentrations below about 0.1 ppm remains approximately linear with concentration although reduced in magnitude. Above 0.1 ppm a saturation effect is observed. At 33% humidity the sensitivity is still further reduced and saturation occurs at a lower NO_2 concentration.

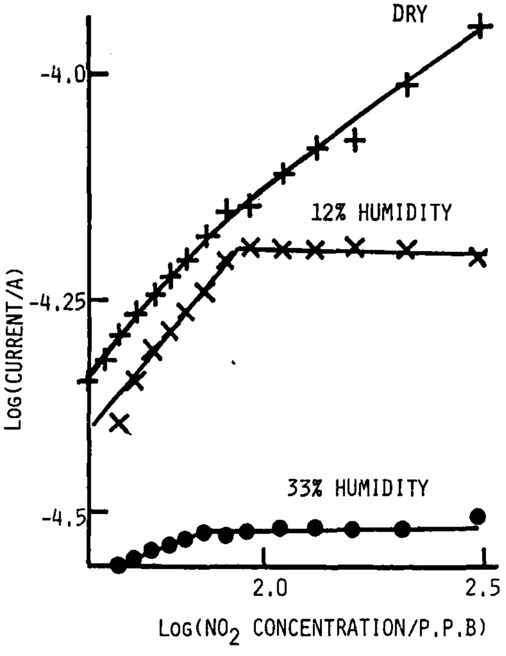

FIGURE 7. Lead phthalocyanine film conductance as a function of NO_2 concentration in air of different humidity levels.

Examination of the shape of the current v. time plot during the 90s. exposure to NO_2 (Figure 8) shows that the plots are more curved at high humidity (as well as at high temperature) reflecting as more rapid approach to final equilibrium in air of higher humidity. These results strongly suggest that water blocks some of the surface adsorption sites in addition to reacting with part of the free NO_2 prior to adsorption. They also show that although the interference effect on both the magnitude of response and the extent of the linearly proportional region of response is serious even for the relatively low atmospheric humidity of 33%, the sensor still retains a linear response region at the lower end of the concentration range. This

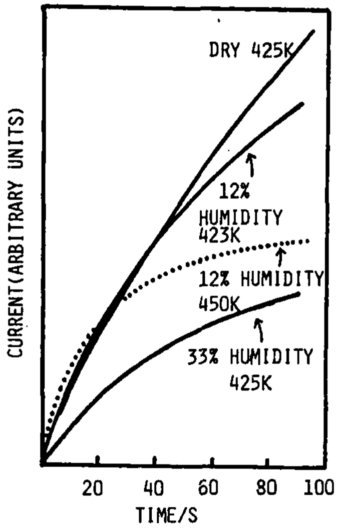

FIGURE 8. Initial response kinetics of a lead phthalocyanine film to NO_2 in air of different humidities.

is the region of most interest in atmospheric pollution monitoring. Hence calibrations of the type reported here, together with the use of combined water vapour and NO_2 sensors, are required if sensors of this type are to give reliable readings of NO_2 concentrations over the range of commonly-encountered atmospheric humidity.

CONCLUSIONS

This paper has shown the importance of optimising the strength of surface charge-transfer interactions between adsorbed gases and organic semiconductors in order to optimise the sensitivity, rate and reversibility of the resulting electrical conductivity changes for sensor applications. More quantitative data are needed on these interaction energies. The importance of careful study of the influence of the physical structure of the substrate and the semiconductor film, as well as calibration and measurement of response speed and reversibility in realistic conditions using low NO_2 concentrations in normal air of a range of humidities, is clearly demonstrated. Despite the complexity of several of the effects reported, lead phthalocyanine films still retain much of their strong potential as NO_2 sensing materials as reported earlier[3]. There is also considerable scope for extensive studies of this type on related materials, both from a fundamental point of view to characterise the nature of the adsorbed species by spectroscopic means as well as from the practical viewpoint of realistic evaluation of their sensing potential in practical environmental conditions.

ACKNOWLEDGEMENTS

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