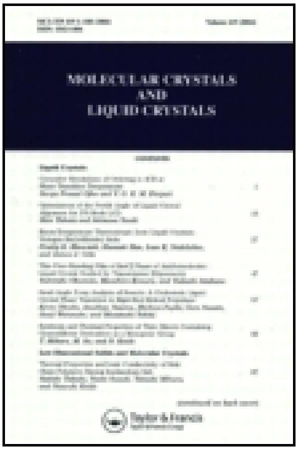

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Chemical and Structural Influences on Effects of Adsorbed Gases on Semiconductivity of Organic Films

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CHEMICAL AND STRUCTURAL INFLUENCES ON EFFECTS OF ADSORBED GASES ON SEMICONDUCTIVITY OF ORGANIC FILMS

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Abstract Effects of adsorbed NO_2 on surface semiconductivity of single crystals and sublimed films of metal phthalocyanines and hemiporphyrazines are reported. The magnitude and reversibility of conductivity increases are related to chemical factors, while data on the rate and reproducibility of the increases are interpreted in terms of the surface structure of the materials. The potential of organic semiconductors as electronic gas sensors is discussed.

INTRODUCTION

Electron donor-acceptor interactions between organic solid surfaces and adsorbed gases facilitate the production of charge carriers and can lead to large increases in surface semiconductivity. An example of this effect with considerable practical relevance to pollution monitoring is the detection of concentrations of NO_2 in air as low as 1 part in 10^9 by measuring semiconductivity changes in metal phthalocyanines[1]. Rapid response and reversibility are essential if such a system is to find practical use. Reversibility may be achieved by operating the semiconducting phthalocyanine sensor at elevated temperatures (e.g. 400K) and in practice this is most conveniently done using a thin film of phthalocyanine sublimed onto a suitable

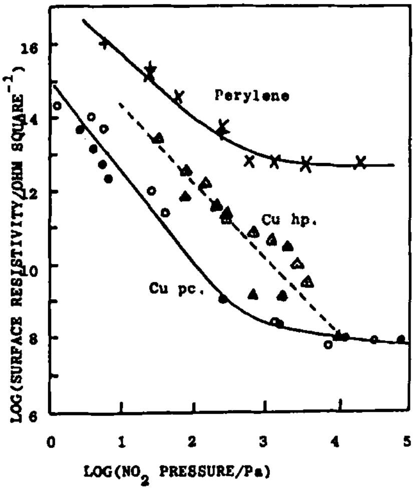

FIGURE 1

π electron system in hemiporphyrazine, with consequent slightly higher ionisation potential. Together with previous results[1] they lead to two general conclusions concerning sensitivity and reversibility of changes in surface semiconductivity of molecular crystals on exposure to electron donor or acceptor gases. Firstly, optimum sensitivity requires optimised strength of surface charge transfer interactions. If the interactions are too weak, small easily reversible conductivity increases occur. If the interactions are too strong or localised, strong coulombic attractions between oppositely charged solid surface and adsorbed gas molecules inhibit charge carrier movement and small irreversible conductivity increases saturating at very low gas concentrations are observed. Secondly, these semiconductvity enhancements can be reversed by heating or by treatment with a competing electron donor or acceptor gas, provided care is taken to avoid strong localised surface charge transfer interactions. This may be achieved by varying the chemical nature of the molecular crystal to control the surface ionisation potential and the availability of sites for localised charge transfer interactions. However, the sensitivity and reversibility of these gas effects cannot be completely described in terms of the strength of surface charge electrically heated substrate. However, the surface structure of evaporated films of organic solids is more complex and variable than that of single crystals and this is reflected in the electrical properties. In this paper the results of investigations of the factors affecting the response speed, reversibility, reproducibility and sensitivity of phthalocyanine films for use as NO_2 detectors will be reported, together with related results on the suitability of several other organic solid systems as gas sensor materials.

RESULTS AND DISCUSSION

Previous work[1] using single crystals has established that the magnitude of the increase in surface semiconductivity on exposure to a given concentration of NO_2 is similar for Mn, Co, Ni, Cu, Zn, Pb and metal-free phthalocyanines, but much smaller for perylene. In the present work, these studies have been extended to include the copper hemiporphyrazine complex (Cu hp) which is closely related to copper phthalocyanine (Cu pc), differing only in replacement of two of the four isoindole groups by pyridine rings[2,3]. The surface semiconductivity of this complex is slightly less sensitive to NO_2 than that of Cu pc (fig. 1), and requires NO_2 pressures approximately 10X larger than for phthalocyanine before saturating. Furthermore, evacuation at 304K reversed the effect whereas for Cu pc evacuation at 420K was required for such reversal. These results suggest that surface charge transfer interactions between Cu hp and NO_2 are weaker than those between Cu pc and NO_2, as expected in view of the smaller delocalised transfer interactions. For example, it has been shown[6] that a monolayer of relatively strongly adsorbed oxygen forms on a nickel phthalocyanine film surface exposed to 10^{-4} Pa O_2 in less than one minute at ambient temperatures. Since NO_2 is a stronger electron acceptor than O_2 it might be expected that monolayer coverage with NO_2 would be attained rather more rapidly than this at comparable pressures, yet the semiconductivity data of figure 1 show that saturation of the conductivity increase is not reached until approximately 10^3 Pa NO_2 pressure. Furthermore, from figure 2 it is clear that equilibrium surface coverage is only attained after exposure to NO_2 for times very much greater than the one minute required to form an oxygen monolayer. Figure 2 also shows that if exposure of a Pb pc film to NO_2 is stopped when only a small fraction of the surface has been covered with adsorbed NO_2, the resulting conductivity enhancement is reversible, while the enhancement produced by longer exposures and more complete surface coverage is not fully reversible. All these observations can be rationalised using a model which incorporates the fact that gases such as NO_2 must displace existing adsorbed oxygen from the molecular crystal surface before they can interact with that surface. Such a process differs from adsorption onto a clean surface in several important respects. The effective sticking probability will be much lower than for

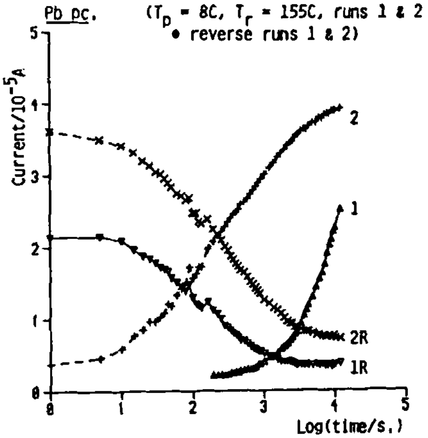

FIGURE 2

adsorption onto a clean surface since the incoming molecules must displace adsorbed oxygen in order to reach the adsorption sites. Oxygen on phthalocyanine surfaces can be relatively strongly adsorbed. For example, heating to 160C is required to remove oxygen from nickel phthalocyanine surfaces even in ultra high vacuum[4]. Displacement of this surface bound oxygen by incoming gases which are more strongly attracted to the surface will therefore be difficult and slow, accounting for the observed relatively slow rate of adsorption of, for example, NO_2. Similarly, the net free energy change on adsorption of NO_2 will be less favourable for adsorption onto a surface covered with adsorbed oxygen than for adsorption onto a clean surface, and the equilibrium surface coverage for a given pressure of NO_2 will be correspondingly less for adsorption onto an oxygen-covered surface. This explains why the conductivity increase when NO_2 is adsorbed on phthalocyanines only reaches saturation for high NO_2 pressures. Finally, for surfaces covered with oxygen, adsorption occurs first at those sites from which oxygen is most easily displaced, whereas in contrast adsorption onto clean surfaces tends to occur first at the most active sites on the surface. This implies that small amounts of NO_2 adsorb rapidly onto oxygen-covered surfaces, (since only the most weakly bound fraction of the adsorbed oxygen need be displaced) and that the adsorption is reversible (since the sites occupied are the least active sites). Adsorption of larger amounts of NO_2 inevitably requires displacement of more strongly bound oxygen, which is a slower and less reversible process, as observed.

The rate and reproducibility of conductivity changes in phthalocyanine films following exposure to 4 ppm NO_2 in air has been investigated for up to 16 films simultaneously using computer controlled apparatus. Ideally, for adsorption at a single set of sites, plots of conductivity v. log (time) should be linear ($d\theta/dt = ae^{-b\theta}$ - Elovich equation) and the response should be rapid. With some organic films this can be achieved (e.g. Figure 3). However,

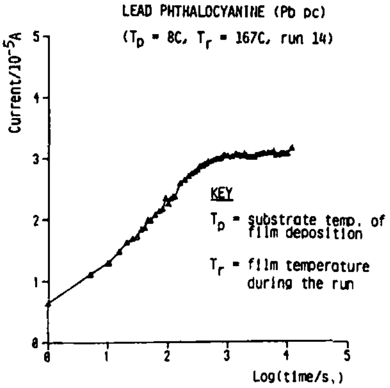

FIGURE 3

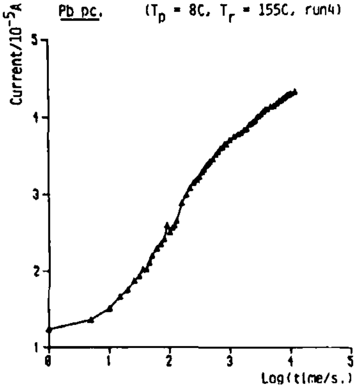

FIGURE 4

with other films curved plots or plots with two regions of different slope are obtained, showing complex surface structure with several types of adsorption site (e.g. Figure 4). Generally, the kinetics of conductivity change for a given film vary as the film ages, and always the initial response of a freshly prepared film to NO_2 has a long induction period. These effects are shown in figure 5 for successive cycles of exposure of a Pb pc film to 4 ppm of NO_2 in air alternating with reversal cycles in clean air. To determine whether the induction period involves the effect of heat or that of NO_2 on the films, the initial responses of two Pb pc films prepared simultaneously were compared, one film having been heated in clean air for the duration of one complete experimental cycle (7 h) at the normal operating temperature (155 C) while the other had been stored in air at room temperature (figure 6). The result shows clearly that heat treatment eliminates the initial induction period. High resolution electron microscopy[5] has shown that phthalocyanine films evaporated onto substrates near room temperature have a high amorphous content but crystallise on heating to temperatures of the same order as that of figure 6. The initiation period for new films may therefore be interpreted as generation of active sites as crystallisation proceeds. All these kinetic results suggest that surface structure and homogeneity influence the response of surface semiconductivity to adsorbed gases.

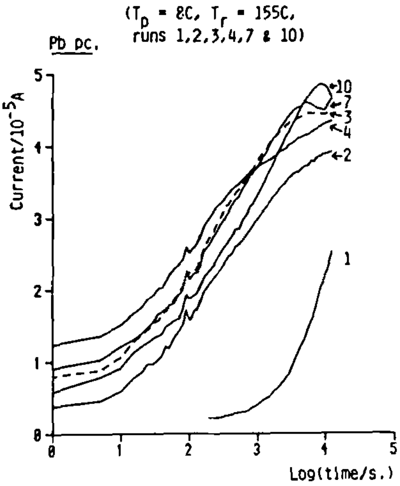

FIGURE 5

Previous workers[6] have shown that surface structure and homogeneity of evaporated films can be optimised by careful control of substrate temperature during film deposition. The optimum films are frequently obtained with substrates maintained at approximately 1/3 of the boiling point of the deposited material. In the case of metal free phthalocyanine, such optimisation produces a sharp discontinuity in the intensity of optical absorption due to electronic transitions in the visible region of the spectrum[7] which may conveniently be used as a criterion for optimisation. We have observed a similar phenomenon for Pb pc films (figure 7), the optimum substrate temperature in this case

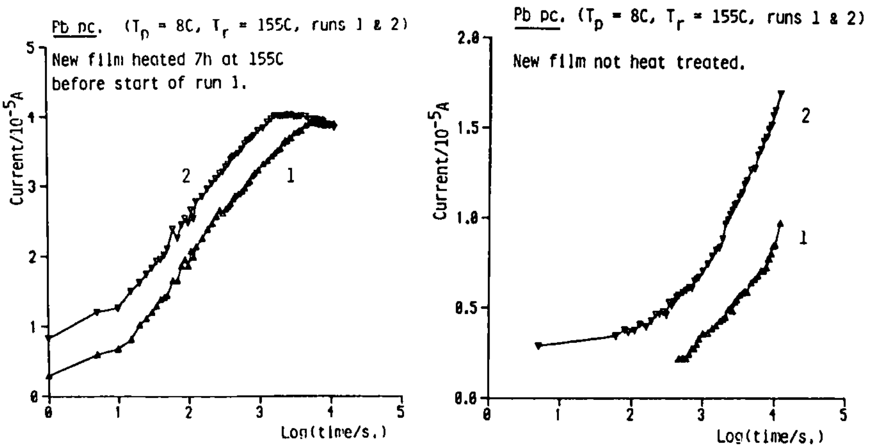

FIGURE 6

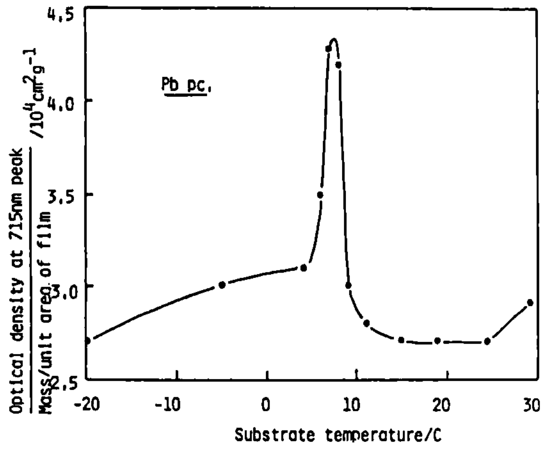

FIGURE 7

being 8 C. Comparison of the kinetics of response of such an optimised Pb pc film with a similar film prepared at a substrate temperature outside the optimum range shows that the initiation period for the new optimised film is substantially longer (figure 8). This is consistent with the view that the initiation process involves creation of

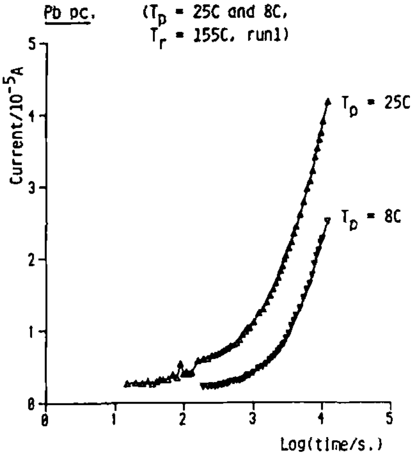

FIGURE 8

active sites by crystallisation of the film, since a high quality optimised film would possess less centres for initiation of crystallisation than would a rougher film surface. The interpretation of the detailed kinetic behaviour of such films on cycles after the initial one is very complex, since surface defect concentrations and proportions of crystalline and non-crystalline material or α and β phases are changing with time in addition to the fraction of surface covered by adsorbed NO_2. Thus, in some cases initial rapid conductivity changes occur as NO_2 is adsorbed and when these have reached equilibrium slower increases can be seen at longer times as structural and defect changes occur (figure 9). There is no evidence of any influence of initial film quality on the sensitivity or response speeds of aged phthalocyanine films towards NO_2.

Conclusions

Electronic gas sensors based on organic and organometallic semiconductors have high sensitivity and fast response in favourable cases. They provide a means of continuously monitoring the concentrations of, for example, atmospheric pollutants such as NO_2, and have the further advantage of small size and low power requirements. In principle this detection method is limited to electron donor or acceptor gases, and the semiconductor must be relatively involatile

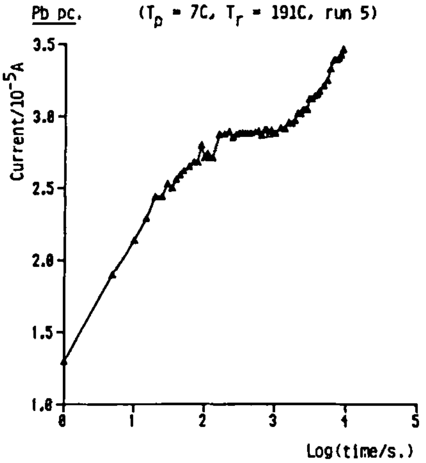

FIGURE 9

yet capable of forming coherent films by sublimation or deposition from solution, as well as preferably of very high purity and resistant to chemical degradation by atmospheric gases. The selectivity of the method towards gases present in mixtures has not been fully explored. The present work has shown that although sensitivity can be controlled by appropriate choice of organic semiconductor, the rate and reproducibility of conductivity changes following exposure to gases are influenced by the surface structure of the semiconductor. At temperatures high enough to ensure reversibility of the conductivity changes, this surface structure may show time dependence as crystallisation and/or phase changes occur, with associated changes in defect and active adsorption site densities. Studies of effects of gases on related materials are continuing in the light of these results.

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REFERENCES

1. R.L. van Ewyk, A.V. Chadwick and J.D. Wright, J.C.S. Faraday I, 76, 2194 (1980).
2. J.A. Elvidge and R.P. Linstead, J. Chem. Soc., 5008 (1952).
3. C.L. Honeybourne and P. Burchill, Inorganic Synthesis, 18, 47 (1978).
4. M.E. Musser and S.C. Dahlberg, Surface Science, 100, 605 (1980).
5. J.R. Fryer, 37th Ann. Proc. Electron Microscopy Soc. Amer., edited by G.W. Bailey (San Antonio, Texas, 1979), pp. 616-7.
6. G.G. Roberts, B.S. Keating, P.S. Vincett and W.A. Barlow, J. Phys. C, 11, 3847 (1978).
7. P.S. Vincett, Z.D. Popovic and L. McIntyre, Thin Solid Films, 82, 357 (1981).