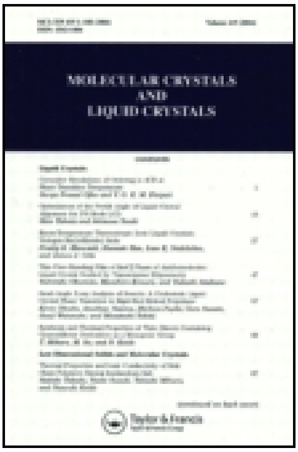

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Alan Wilson [a] & John D. Wright [a]
[a] Centre for Materials Research, University Chemical Laboratory, University of Kent, Canterbury, Kent, CT2 7NH, UK

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UNDERSTANDING AND OPTIMISING NO_2-SENSING USING SEMICONDUCTING PHTHALOCYANINE FILMS.

ALAN WILSON and JOHN D. WRIGHT*
Centre for Materials Research, University Chemical Laboratory,
University of Kent, Canterbury, Kent CT2 7NH, UK

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Abstract. This paper summarises recent progress in understanding the processes which lead to large increases in the semiconductivity of metal phthalocyanine films in the presence of even very small (sub-ppm) concentrations of nitrogen dioxide. A model, based on experimental data, for the kinetics of the adsorption process is described and its application in a microprocessor-controlled NO_2-sensing instrument is outlined. Chemical and morphological modification of the surfaces of lead phthalocyanine films by heat-treatment at 360° C in air is shown to lead to smaller but faster responses to NO_2 and possible origins of these effects are discussed with reference to data from electron microscopy, XPS and FTIR spectroscopy. Measurements of the strength of gas-surface interactions using a novel fibre-optic interferometric calorimeter are discussed with reference to the above data, and suggest that adsorption of NO_2 does not lead immediately to charge-carrier generation.

Keywords: phthalocyanines, semiconductors, gas-sensing, nitrogen dioxide, absorption, fibre-optic calorimetry

When electron acceptor gases such as NO_2 interact with solid organic or organometallic compounds having delocalised π-electron systems, charge transfer between the solid and the adsorbed gas leads to charge-carrier generation and large increases in electrical conductivity. This phenomenon, which has been known since the earliest investigations of organic semiconductors, has been widely studied with renewed vigour in recent years[1] following the realisation that it formed the basis of a class of highly-sensitive gas sensors. Metal phthalocyanine films are amongst the best materials for such sensors, having high chemical and physical stability and showing large conductivity increases which permit detection of ppb concentrations of NO_2 in air. However, this conductivity change is often slow, typically taking several hours to reach equilibrium after a change in NO_2 concentration, even when the film is maintained at temperatures above 150° C.

The response of freshly-prepared films is particularly slow, and experiments involving repeated cycles of exposure to 0.3ppm of NO_2 in dry air for over 3 hours with reversal in clean air between successive cycles have shown that the response rate increases with time (see for example figure 1). This phenomenon is discussed in detail in reference 2, and is a consequence of the fact that the adsorption of NO_2 necessarily involves desorption of oxygen species from the heterogeneous surface of the phthalocyanine film. It seems likely that part of the effect is due to morphological changes which occur on heating phthalocyanine films (for example, crystallisation of amorphous regions of the film leading to an increase in the surface area). However, the observation that a repeat process of initialisation is required after UHV treatment of a film which has undergone a sequence of exposure cycles such as shown in figure 1 shows that surface chemical changes are also involved.

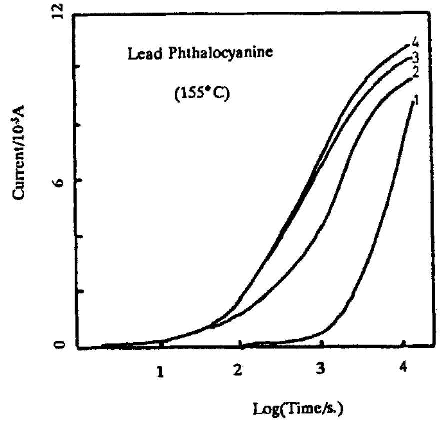

Figure 1

Electron acceptor gases undergo charge-transfer interactions with electron donor molecules such as phthalocyanines. The resulting partially charged species gain stabilisation by interacting with their polarisable surroundings, just as in the expression originally proposed by Lyons[3] for the energy (ΔE) required to generate a charge carrier in a molecular crystal:

$$\Delta E = IP - EA - P^{+} - P^{-}$$

where IP = ionisation potential
EA = electron affinity

and P^{+} and P^{-} are polarisation energies. Although IP and EA are molecular properties, the polarisation energies depend on the local environment of the adsorbed species and in particular will be larger at the base of steps on the surface, where ¾ of the volume surrounding the adsorbed molecule is polarisable material, and for species adsorbed in grain boundaries, which are entirely surrounded by polarisable material. The more favourable polarisation energy at such sites will lead to stronger charge-transfer chemisorption. Thus some adsorbed oxygen species will be much more difficult to displace than others, and this is believed to be the origin of the slow components in the response to NO_2. However, when NO_2 molecules succeed in displacing such strongly bound oxygen species, large surface dipoles are established between the phthalocyanine and the strongly electron-accepting NO_2. Electrostatic repulsions with these dipoles accelerate the desorption of neighbouring oxygen species and lead to the observed increase in response rate following the repeated cycling shown in figure 1.

This model has many implications. Firstly, it suggests that reproducible response kinetics for NO_2 sensors based on phthalocyanine films will only be obtained if the amount of strongly-bound residual adsorbed NO_2 at the start of a sampling pulse is constant. We have demonstrated that this is the case[4] by showing that the conductivity increase after 30-second exposures to 0.6ppm of NO_2 was dependent on the initial coverage with NO_2 as reflected in the initial conductivity. The higher the initial conductivity, the higher the response, as shown in figure 2. We have also used this result in a microprocessor-controlled instrument where the sampling pulse is automatically triggered when (and only when) the conductivity has reversed to a reference standard value after the preceding exposure pulse. Figure 3 illustrates the extremely reproducible responses which can be obtained in this way for a series of identical pulses of 2.1ppm NO_2 by ensuring reproducible response kinetics. This approach eliminates the need to wait until final equilibrium conductivity increases are achieved.

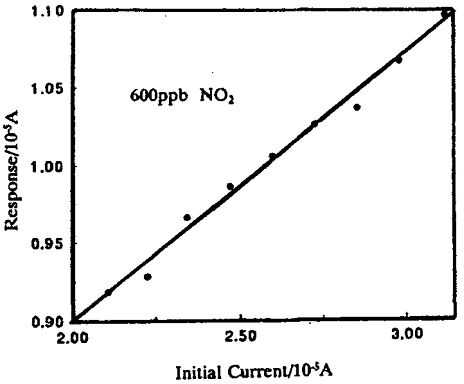

Figure 2

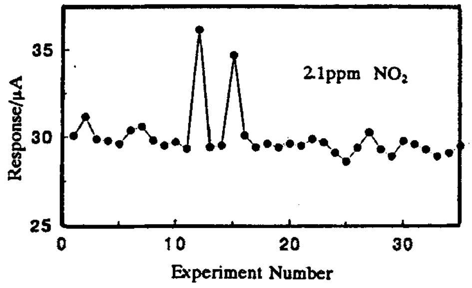

Figure 3

The second implication of the model is that the strong adsorption sites are the prime cause of slow response components. This in turn implies that uniform films are inherently preferable, that direct measurement of the strength of the adsorption as a function of surface coverage would be extremely valuable, and that a process which selectively removed the strongest adsorption sites from a phthalocyanine film might well yield a material whose electrical conductivity would respond more rapidly to changes in NO_2 concentration. We have explored all of these points. Since the strongest adsorption sites for acceptor gases are also most likely to lead to destructive oxidation of the phthalocyanine molecule, a promising approach to removing such sites should be to heat the films in air to high temperatures. This was first studied by Jones and co-workers[5] who showed that heating lead phthalocyanine to 360° C in air for one hour produced a film with a smaller but faster conductivity increase following exposure to NO_2. Figure 4 shows the effect of repeated exposure cycles, of the type used for figure 1, on the response of such heat-treated films. Clearly some strong adsorption sites remain after the heat treatment, and can become involved in the sensing process after traces of strongly-bound NO_2 have been accumulated on the surface as outlined above. This onset of a slow component to the response after several hours would represent an unacceptable drift in sensor performance in practice, but the model which explains its occurrence also suggests

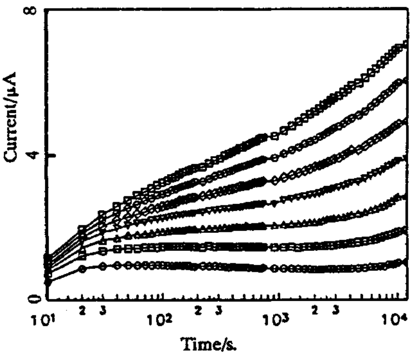

Figure 4

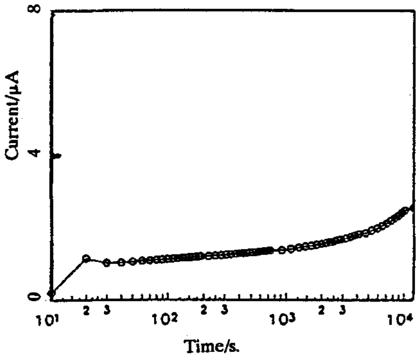

Figure 5

a remedy. Brief heating to 360°C (2 minutes) drives off the strongly-bound NO_2 which is responsible for the onset of the slow component of response, and returns the response characteristics to those observed after the initial heat treatment, as shown in figure 5. Such brief thermal purging after every few hours of operation is an acceptable price to pay for a reproducible fast-response material.

The mechanism proposed above for the effect of 360°C heat treatment on lead phthalocyanine films is supported by SIMS measurements[6] which show that some lead oxide is formed during the process, in marked contrast to films of other phthalocyanines (e.g. Cupc, Znpc). Furthermore, we have shown by XPS studies[7] that the non-planar lead phthalocyanine molecule fragments when sublimed above 400°C producing a change in film surface composition, suggesting that the non-planarity leads to lower stability of the conjugated ring system. This is further supported by FTIR spectra of lead phthalocyanine films before and after exposure to high concentrations of NO_2. After such exposure, the vibrational spectrum changes to resemble phthalimide, again consistent with oxidative ring cleavage[8]. None of these effects are observed for planar phthalocyanines, which show little increase in response rate to NO_2 on heating to 360°C. Thus, although electron microscopy shows a large increase in crystallite size after heat treatment, any effects of such morphological change cannot be the prime origin of the fast response since these effects are observed for all phthalocyanines. (One likely effect of increased crystallite size is an increase in the proportion of weak adsorption sites. In common with many other molecular crystals, phthalocyanines tend to grow fastest along the direction of strongest molecular interaction, i.e. along the molecular stacking axis. This has the effect of increasing the proportion of needle face adsorption sites [weak] and decreasing the proportion of needle end sites [strong].) These results illustrate the complexity of the processes involved in gas sensing by phthalocyanine films and the importance of thorough chemical and physical characterisation. Unfortunately, preliminary results suggest that the NO_2-sensing ability of these heat-treated lead phthalocyanine films is greatly impaired in humid conditions. Humidity effects are also observed for films which have not been heat-treated, but careful control of the pulse sampling conditions can reduce such effects to acceptable limits whereas there is no such possibility for the heat-treated materials operating in much simpler equilibrium conditions.

Much of the foregoing discussion has involved consideration of the strength of adsorption of gases on phthalocyanine films. A parameter which directly reflects such strengths is the heat of adsorption, but its measurement for films of organic solids has until recently been impossible since the quantity of heat is very small and the film must be supported by a substrate, whose heat capacity leads to extremely small temperature rises accompanying adsorption of gases. Recently we have developed a novel fibre-optic interferometric calorimeter capable of measuring these heats[9]. A Mach-Zehnder interferometer is constructed using single-mode fibre, and a short length of the active arm is coated with a film of the material under test. Adsorption of a gas onto this film, in an evacuated chamber, releases heat which changes the fibre refractive index and hence the optical path length. A compensating change in the reference arm is induced by mechanical stretching of the fibre using a piezoelectric cylinder with several turns of fibre tightly wound round it. The voltage which must be applied to this piezoelectric cylinder to maintain the interference fringes in a constant condition is directly proportional to the temperature rise in the sample arm. The instrument is calibrated using electrical heating pulses applied to a silver coating directly under the organic film under test, and has microjoule sensitivity. Figure 6 shows the temperature rise produced in a copper phthalocyanine film following exposure to 3 mbar of NO_2, as a function of elapsed time, while figure 7 shows the electrical conductivity of an identical film in the same sample chamber at the same time. Clearly, the heat release occurs much more rapidly than the electrical conductivity increase, and this suggests that the initial adsorption process is followed by one or more secondary process before the charge-carrier generation process is complete. The nature of these subsequent processes is not yet known. One possibility is that the initial adsorption occurs at the weakest adsorption sites, from which oxygen is most easily displaced, whereas migration to stronger sites (possibly down grain boundaries) must occur before effective carrier generation can occur. Although further studies with a wider range of materials and film preparation conditions are required before any general model of the processes can be established, we have recently confirmed by a totally independent mass measurement using a copper phthalocyanine film on a surface acoustic wave device, that the adsorption process is indeed complete in a few hundred seconds as indicated by the thermal measurements. The SAW technique permits direct measurement of the mass changes which occur as gas molecules adsorb on the film, with ng sensitivity. Measurement of the shaded area on the heat release curve of figure 4 gives the total heat released on adsorption. We have not yet been able to relate this to the heat of adsorption because this requires knowledge of the surface area of the film and of the fractional surface coverage. However work is in progress to determine these two quantities. The surface area will be determined using an electrochemical method. The initial stage in electrochemical oxidation of a phthalocyanine film involves surface oxidation, and can be identified from cyclic voltammetry. Measurement of the number of coulombs involved in this step will yield the surface area. With this information and SAW data on the mass of gas adsorbed, it will then be possible to determine the surface coverage. It is clear from electron microscopy that the film surface even on a smooth optical fibre substrate is not smooth but composed of microcrystallites, so even from the presently available data it is clear that the measured heat release

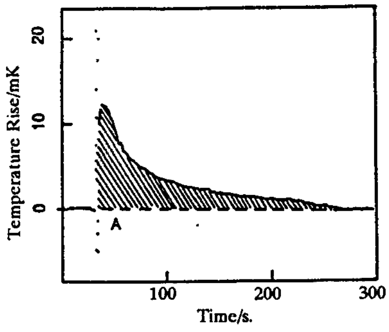

Figure 6

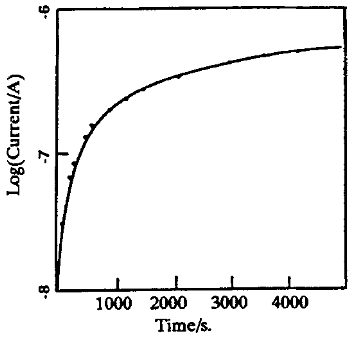

Figure 7

corresponds to a heat of adsorption of the right order for weak chemisorption. The calorimeter is currently being upgraded to operate with the sample and reference elements in an ultra high vacuum chamber as opposed to the chamber capable only of 10^{-6}mbar used for the experiments shown in figures 6 and 7. This will further simplify interpretation of the data and permit experiments with lower gas pressures, which are not yet possible with the existing apparatus due to the effect of adsorbed oxygen giving very slow adsorption rates when the pressure of added NO_2, for example, is very low.

Finally, we have explored the possibility that Langmuir-Blodgett films of substituted phthalocyanines might prove to have more uniform surfaces and hence improved response kinetics[4]. Comparison of L-B films of octa-pentyloxy metal-free phthalocyanine and tetra-cumylphenoxy copper phthalocyanine with conventional sublimed films of copper and lead phthalocyanine showed that at room temperature the performance of the L-B films was not significantly better than that of the sublimed films, the principal limitation in both cases being poor reversibility. The ultimate disadvantage for the L-B films is their very poor thermal stability, which prevents operation of sensors based on these films above about 40°C. Further experiments currently in progress aim to prepare uniform films by molecular beam epitaxial growth in the hope that these will prove to be more thermally stable.

The results reviewed in this paper show that although the adsorption of NO_2 on phthalocyanine films and the associated enhancement of charge-carrier generation is a complex process, detailed studies of this type can lead to models which can in turn be used to design optimised sensor materials and operating conditions. The availability of a range of surface characterisation techniques applicable to organic solids together with the wide current interest in gas sensor developments suggests that the surface chemistry of the organic solid state will assume an increasingly important role in future.

REFERENCES

1. J.D. Wright, Progress in Surface Science, **31**, 1-60 (1989).
2. P.B.M. Archer, A.V. Chadwick, J.J. Miasik, M. Tamizi and J.D. Wright, Sensors and Actuators, **16**, 379-92, (1989).
3. L.E. Lyons, J. Chem. Soc., (1957), 5001.
4. A. Wilson, J.D. Wright and A.V. Chadwick, Sensors and Actuators, **B4**, 499-504, (1991).
5. T.A. Jones, B.Bott and S.C. Thorpe, Sensors and Actuators, **17**, 467 (1989).
6. A.J. Eccles, P. Humphrey, T.A. Jones and J.C. Vickerman, Proc. SIMS VI Symposium, Versailles, (1987).
7. H. Mockert, K. Graf, D. Schmeisser, W. Göpel, Z.A. Ahmad, P.B.M. Archer, A.V. Chadwick and J.D. Wright, Sensors and Actuators, **B2**, 133 (1990).
8. H. Hobert, R.C. Weaver and J.D. Wright, Z. Chem., **29**, 454 (1989).
9. R.C. Weaver and J.D. Wright, Sensors and Actuators, **B4**, 505 (1991).
10. J.E. Darby, S.C. Thorpe and J.D. Wright, unpublished work.