NO$_2$ detection at room temperature with Copper Phthalocyanine thin film devices

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Abstract

In this work we report the effect of post deposition film treatment on the NO$_2$ sensing properties of CuPc thin films for room temperature operation. The gas sensitive response of the electrical conductivity to doping with NO$_2$, doping with oxygen (in air) and cooling to 77K in liquid nitrogen are reported. The pre-treatment with NO$_2$ is shown to improve the gas sensing properties by providing both an increase in the magnitude of the conductivity change for a given NO$_2$ concentration and a significant improvement in the recovery time. Data is analysed using an Elovich model, which suggests that the cooled devices have the best fit to this model; the data for the NO$_2$ doped devices suggest a Langmuir behaviour. For all devices, a simple time derivative of the change in current provides a measure of concentration for real time gas sensing applications.

keywords: phthalocyanine; nitrogen dioxide; thin film; gas sensor

Phthalocyanines are an extensively investigated class of weakly semiconducting organic dye materials. Their thermally stable nature makes them suitable for thin film deposition by thermal sublimation. An extensive review of these materials has been reported by Leznoff and Lever [1]. These materials have also shown promise for photoconductive and photovoltaic response of which the current state of research has also been extensively reviewed by Whitlock *et al* [2], Law [3] and Martin *et al* [4]. It has been widely reported that oxygen acts as a dopant in phthalocyanines and is also responsible for the formation of a space charge region near rectifying electrodes. As a consequence, many workers have used exposure to air for days before depositing the top metal contact in sandwich structures in order to oxygen dope the devices; after this time the oxygen doping is thought to be complete. Musser and Dahlberg [5] investigated the transient effect of oxygen adsorbed on to NiPc using the photovoltaic response and reported both reversible and irreversible effects.

Different metal substituted phthalocyanines have been shown to respond to the presence of highly reactive gases such as NO_2, NH_3 and Cl_2 [6-8]. Archer *et al* [9] extensively investigated the influence of heat treatment and gas-exposure history on NO_2 detection with MPc films. One of their conclusions was that the previous exposure of MPc films to different gases played a crucial role in the gas sensing response. Experiments using earthed guard rings by Archer *et al* [9] and VanEwyk *et al* [10] have suggested that changes in surface conductivity are responsible for the response to NO_2 rather than a bulk effect in single crystals however, slow

penetration into the bulk via regions between individual crystallites could be responsible for slow components in the kinetics. Hsieh et al [11] have shown that the effect of film structure is important in gas sensing properties and that an amorphous film shows the fastest response and recovery time to NO_2 exposure. The modelling of the adsorption/desorption of NO_2 on MPc thin films has more recently attracted interest [12,13]. Zhou and Gould have suggested that information about NO_2 concentration may be derived from the initial conductivity changes of a MPc film rather than from data obtained under saturation conditions. They have suggested that the initial response of CuPc films to NO_2 follow the Elovich equation: $d\theta/dt=a\exp(-b\theta)$ where $d\theta/dt$ represents the rate of change of surface coverage θ and a and b are constants. By assuming that the change in electrical conductivity is proportional to the change in surface coverage [14], the change in current ΔI under constant bias then gives $d\Delta I/dt=a'\exp(b'\Delta I)$ where the value of a' may be correlated to the NO_2 concentration.

In this work we compare the effect on the NO_2 gas sensing properties of initially doping CuPc films with NO_2 and alternatively, cooling in liquid nitrogen. heavy doping with NO_2 is designed to r... ...y contribution from diffusion into the bull. .. : _ _ ... .se dominated by the more rapid surface adsorption/desorptic... It will be demonstrated that this pre-treatment with NO_2 improves the gas sensing properties by providing both an increase in the magnitude of the conductivity change for a given NO_2 concentration and an improvement in the recovery time. Data from these devices will be analysed using the Elovich and Langmuir models.

Experimental

The devices used in these experiments consisted of interdigital transducers (IDTs) with a CuPc overlayer. The IDTs were made of gold on glass using photolithography and employed 20 finger pairs of length 2mm and equal finger widths and spaces of 25 μm. The CuPc was obtained from Fluka and purified by entrain sublimation prior to deposition; deposition was by thermal evaporation at a rate of 0.1 nm/s on to a room temperature substrate producing films in the alpha phase of approximate thickness 160-200nm. Immediately after deposition, the devices to be doped with NO_2 were placed in a 100ppm NO_2 in N_2 atmosphere for four weeks; these we will refer to as the doped devices. The other devices were stored in dry air for the same period. Half of the devices stored in dry air were immersed in liquid nitrogen for several minutes, these we will refer to as the cooled devices; the devices only stored in dry air will be referred to as untreated.

Conductivity changes in the CuPc films were measured by applying a constant bias of one Volt to each device and monitoring the current using Keithley model 485 picoammeters: the IDT geometry used produced an initial device resistance of typically 10MΩ to 15MΩ. The devices were mounted in a temperature controlled enclosure in an atmosphere of zero grade air (Air Products 2500 generator) provided at a constant flow rate of one litre/minute. The NO_2 was supplied by Air Products in the form of 100ppm NO_2 in N_2. The substrate temperature, gas flow controllers and electrical data collection were all controlled using a microcomputer: all data presented here are for room temperature measurements.

In Figure 1 we show the change in current (ΔI) of an untreated device for a sequence of 300 second exposures to NO_2 with a 1700 second recovery time for concentrations in the range 0.5 ppm to 5 ppm. Figure 2 shows the same sequence for a NO_2 doped device The doped device clearly shows an order of magnitude increase in the current change for the same NO_2 exposure and a significant improvement in recovery time. In Figure 3 we show the same sequence of exposures for the cooled device. There is a significant reduction in the conductivity for this device compared to the untreated. One possible explanation of this is that the cooling process causes microcracking on the film surface hence reducing the effective mobility but increasing the effective surface area of the film for gas adsorption.

Zhou and Gould [12] have reported that CuPc devices, under their test conditions, follow a simple Elovich model for surface coverage. In Figure 4 we show the NO_2 concentration as a function of the Elovich parameter a' for the data in Figures 1 (circles), Figure 2 (squares) and Figure 3 (triangles). Our data would suggest that, although we observe a similar relationship between NO_2 concentration and a' as that observed by Zhou and Gould, the linear region for the Elovich plot of the doped device is limited. To demonstrate this more clearly, in Figure 5 we show the effect of a much longer exposure (3000s) to 3ppm NO_2 for the cooled and the doped films; the untreated shows a similar response to the cooled device. Whilst the change in current for the cooled device (solid line) shows the same form as for

the short exposures, the current of the doped device (squares) begins to saturate at around 500 seconds. In Figure 6 we show the Elovich plot for the data in Figure 5 with the doped device represented by circles and the cooled device by squares. The Elovich model is clearly more applicable to the cooled device than to the doped indicating that for the cooled devices there is a change in activ.   . nergy dependant on surface cover:·· . Note that the minor change in gradient observed for the cooled film for ΔI between 0.9nA and 1nA is attributed to a small pressure change in the system due to the zero grade air generator compressor operation. An alternative analysis may be to assume a simple Langmuir model where the rate of surface coverage $d\theta/dt$ is proportional to $(1 - \theta)$. In Figure ′ we show the data from Figure 5 plotted as dI/dt as a function of ΔI for the cooled device (squares) and doped device (circles). A possible explanations for the linear slope for the doped device is that when we have such heavy doping with NO_2, only the most weakly binding surface sites dominated by a single activation energy are left free to take part in adsorption/desorption processes and hence providing more dynamic conductivity changes.

For real time gas sensing, a more appropriate analysis may be a simple time derivative of ΔI. In Figures 8, 9,10 we show the time derivative of the data in Figures 1, 2, 3 respectively. The peak values from these data have been extracted and are shown in Figure 11 as the log of the peak amplitude plotted as log of the concentration; the data for the untreated and cooled devices are multiplied by a factor of 20. From this data, the height of the differential peak would suggest to be

a measure of NO_2 concentration and following a similar power relationship for each type of device.

Conclusion

The effect on the NO_2 gas sensing properties of an initial doping of CuPc films with NO_2, oxygen (in air) and cooling to 77K in liquid nitrogen has been investigated for room temperature operation. The pre-treatment with NO_2 has been shown to improve the gas sensing properties by providing both an increase in the magnitude of the conductivity change for a given NO_2 concentration and a significant improvement in the recovery time. Data has been analysed using the Elovich equation which provides a relationship between NO_2 concentration and the Elovich parameter a'. The cooled devices clearly show the best Elovich response; however, the data for the doped devices would suggest a Langmuir model. For all devices, a simple time derivative of the change in current provides a measure of concentration for real time gas sensing applications.

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Biography

Michael Newton received a B.Sc.(Hons) degree in Physics in 1983 followed by a M.Sc. in Modern Electronics in 1985. In 1988 he received a Ph.D. for work on the interaction of acoustic waves with the two dimensional electron gas in a Si MOSFET from The University of Nottingham. He is currently a Senior Lecturer in the Department of Chemistry and Physics at The Nottingham Trent University. His research interests include applications of organic semiconductors and sensors based on acoustic wave devices.

Thomas Starke received a degree in Engineering Physics from Fachhochschule Munich in 1997. His Diploma thesis investigated Rayleigh-Benard convection in liquid gallium with work carried out at the Colorado University, Boulder USA. He is currently a Ph.D. student in the Department of Chemistry and Physics at The Nottingham Trent University researching into the application of surface acoustic wave devices and organic semiconductors as chemical sensors.

Dr. Martin Willis received his B.Sc. in Chemistry and Ph.D. from the University of Nottingham in 1957 and 1960, respectively. In 1960, he was appointed as an Assistant Lecturer to the University of Nottingham. Promotion to Lecturer and Senior Lecturer in Physical Chemistry followed in 1962 and 1971 and since 1976, Dr. Willis has held a position as a Reader in Physical Chemistry. He has during his career held Visiting Professorships and Research Appointments at The Institute for Solid State Physics, University of Tokyo, Japan, and The Institute for

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Glen McHale received a B.Sc.(Hons) degree in Mathematical Physics in 1983 and a Ph.D. in 1986 in Applied Mathematics from The University of Nottingham. From 1986 to 1989 he was a Research Assistant in Physics at The University of Nottingham and from 1989 to 1990 he was a Royal Society European Research Fellow at Universite de Pierre et Marie Curie in Paris. He is currently a Reader in the Department of Chemistry and Physics at The Nottingham Trent University. His main research interests are currently in the field of wetting and the interactions of surface acoustic waves with liquids.

Figure 1. Response of an untreated CuPc device to a sequence of 300 second exposures to NO_2 in the range 0.5 ppm to 5 ppm with 1700 seconds between each exposure.

Figure 2. Response of a NO_2 doped CuPc device to a sequence of 300 second exposures to NO_2 in the range 0.5 ppm to 5 ppm with 1700 seconds between each exposure.

Figure 3. Response of a cooled CuPc device to a sequence of 300 second exposures to NO_2 in the range 0.5 ppm to 5 ppm with 1700 seconds between each exposure.

Figure 4. a' plotted as a function of the NO_2 concentration for the untreated (circles multiplied by a factor of 20), the NO_2 doped (squares) devices and the cooled (triangles multiplied by a factor of 20).

Figure 5. The response of a NO_2 doped device (squares) and cooled device (continuous line multiplied by a factor of 30) to a 3000s exposure to 3ppm NO_2.

Figure 6. The Elovich plot of the data shown in Figure 5 for the NO_2 doped device (circles) and the cooled device (squares multiplied by a factor of 10).

Figure 7. The Langmuir plot of the data shown in Figure 5 for the NO_2 doped device (circles) and the cooled device (squares multiplied by a factor of 10)

Figure 8. The data from Figure 1 for the untreated device showing dI/dt as a function of time.

Figure 9. The data from Figure 2 for the NO_2 doped device showing dI/dt as a function of time.

Figure 10. The data from Figure 3 for the cooled device showing dI/dt as a function of time.

Figure 11. The log of the peak in the dI/dt data from Figure 8, Figure 9 and Figure 10 plotted as a function of log of NO_2 concentration for the untreated device (circles multiplied by a factor of 20), for the NO_2 doped device (squares) and for the cooled device (triangles multiplied by a factor of 20).