The influence of ammonia, chlorine and nitrogen dioxide on chloro-aluminium phthalocyanine thin films

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Abstract

Amperometric gas sensors were prepared by thermal evaporation of a chloro-aluminium phthalocyanine (ClAlPc) thin film onto inter-digital gold electrodes with 100 μm spacing. The behaviour of these thin films on exposure to NO_2, Cl_2 and NH_3 gases and the suitability of ClAlPc as a material for use in a practical gas sensors was investigated with zero grade air as the reference atmosphere. A change in resistivity of the ClAlPc thin film sensors was observed on exposure to ammonia and chlorine at several different temperatures. In particular, it was found that on increasing the temperature, the sensitivity of the ClAlPc thin film decreases a little, but the reversibility is greatly enhanced. This means that ClAlPc based toxic gas sensors could operate at lower temperatures than their mono-phthalocyanine counterparts. The temperature of maximum sensitivity (T_{max}) and the minimum temperature for good reversibility (T_{min}) have been determined for ClAlPc sensors 'doped' with Cl_2 and NO_2. It was found that these characteristic temperatures can provide information on the concentration and the nature of the gas to which the sensor is exposed and so could perhaps be used to distinguish between the different adsorbed species. Activation energies for conduction were also measured in the presence of the test gases. © 1997 Elsevier Science B.V.

1. Introduction

Metal phthalocyanines (MPc) are p-type organic semiconductors which exhibit high sensitivity to both electron acceptor gases such as Cl_2 and hole donor gases such as NH_3, even in low concentrations. It is well established that gas adsorption on the surface of crystals or films of MPcs is followed by charge transfer reactions which induce the generation of charge carriers and enhance the conductivity [1–4]. Recently, with the increase in atmospheric pollu-

tants, various metal phthalocyanines are now under intensive investigation to ascertain their suitability as viable, low-cost gas sensing materials. The performance of phthalocyanines as gas sensors is based on large changes (several orders of magnitude) in the dark conductivity which are directly related to the adsorption of ppm or even ppb levels of toxic gases such as NO_2, NH_3, Cl_2 etc. on the surface of MPc films. It is also well known that the structure and morphology of phthalocyanine thin films can strongly influence their gas-sensing characteristics [5,6]. Particular interest has been shown in PbPc films, primarily for NO_2 sensing. Bott and Jones [7] have described their use in a prototype multisensor system for monitoring toxic gases. CuPc has similar proper-

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ties to PbPc, but exhibits somewhat less sensitivity to NO_2 [8]. In addition CuPc thin films have been used as the basis of NH_3 and CCl_4 sensors [9,10]. A number of phthalocyanines (ZnPc, FePc, CoPc...) also exhibit a variation in DC conductivity when they are exposed to oxidising gases [11]. There is however relatively little information in the literature on ClAlPc which we expect to be a more sensitive and more stable material for gas sensor fabrication based on previous measurements of optical and thermogravimetric results [12]. The present work is a continuation of previous studies in our laboratory [13] and the object of this work was both to extend our knowledge of the role of the Cl_2, NH_3 and NO_2–ClAlPc interactions and to investigate the feasibility and advantages of utilising the electrical behaviour in viable ClAlPc based gas sensors for NO_2, Cl_2 and NH_3 detection. In particular, we studied the temperature dependence of the dark conductivity of ClAlPc thin films on exposure to NO_2 and Cl_2 with zero grade air as the reference atmosphere. The temperature of maximum and minimum dark conductivity is presented for ClAlPc on exposure to NO_2 and Cl_2. The significance to gas sensor design is also discussed.

2. Experimental procedures

Chloroaluminium phthalocyanine was prepared in our laboratory in the following way. A mixture of 40 g phthalonitrile, 10 g $AlCl_3$ and 200 ml quinoline (doubly distilled and deoxygenated under nitrogen atmosphere) was refluxed for 1.5 h. The resulting hot mixture was then filtered in a glass filter, it was then cooled to room temperature and filtered again. The solid thus isolated was washed sequentially with toluene, carbon tetrachloride and acetone, then dried in vacuum at 150°C.

Eight-finger interdigital gold electrodes with a 100 μm gap were fabricated photolithographically on pre-cleaned polyborosilicate glass substrates. The purified ClAlPc was thermally evaporated over the electrode arrays in vacuum at a pressure of 10^{-6} Torr. In this way ClAlPc thin films were produced which had chosen thicknesses in the range 50–250 nm deposited on substrates held at room temperature. The deposition rate was 0.1–0.2 nm s^{-1}. The thick-

nesses were monitored during deposition using a quartz crystal monitor.

A specially designed chamber was used to enable electrical characteristics to be measured over a wide temperature range. Thermofoil heaters (Minco HK913) were used to heat the devices. The whole assembly was mounted in the bell jar of a vacuum system together with gas inlet and outlet facilities. NH_3, Cl_2 and NO_2 gases were diluted with zero grade air (British Oxygen Company < 3 ppm (vol) H_2O, < 1 ppm CO_2) and then passed through the test chamber at a flow rate from 20 to 600 ml min^{-1} (the distance from the gas outlet to the surface of the sensor was approximately 1 cm). The resistance ratio (R_g/R_a) of the device was measured using a stabilised power supply and a Keithley 610C electrometer. A PC microcomputer was used to record the time profile and the dc dark current flowing through the ClAlPc sensor in response to various cycles of exposure to Cl_2 (500 ppm in zero grade air), NH_3 (500 ppm in zero grade air) and NO_2 (500 ppm in zero grade air).

3. Results and discussion

Freshly evaporated devices were left to stabilise in vacuum at a fixed bias (5 V) for 24 h. Zero grade air (BOC < 3 ppm (vol) H_2O, < 1 ppm CO_2 and 20% O_2) was then introduced and the change in dark current at a fixed bias was recorded over a period of 20 h as shown in Fig. 1. There is a rapid decrease in dark current during the first 40 min followed by a slower increase which continues for the whole of the 20 h period. Subsequently the thin film device was heated to 200°C in vacuum and a complete recovery was observed. This behaviour is of the same form as that observed for PbPc in oxygen [14]. The reason for the initial drop in current is not clear but may be associated with a surface process such as that proposed in Ref. [15]. They suggested that similar behaviour with CuPc was associated with a surface cleansing process whereby the initial exposure to oxygen generates volatile surface species. Appreciable oxygen absorption does not occur until after cessation of this process and the slow conductivity change is then associated with diffusion of oxygen into the bulk.
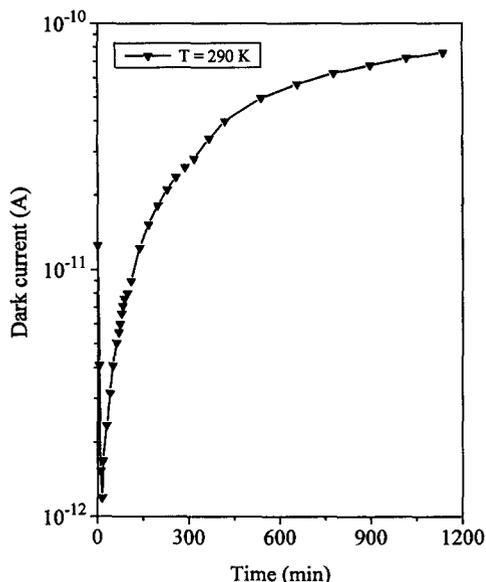
Fig. 1. Response of a ClAlPc thin film device to zero grade air (20% O_2) at room temperature.

Fig. 2 shows the change in the resistance ratio R_g/R_a (where R_g is the resistance in the presence of gas and R_a is the resistance in zero grade air (20%
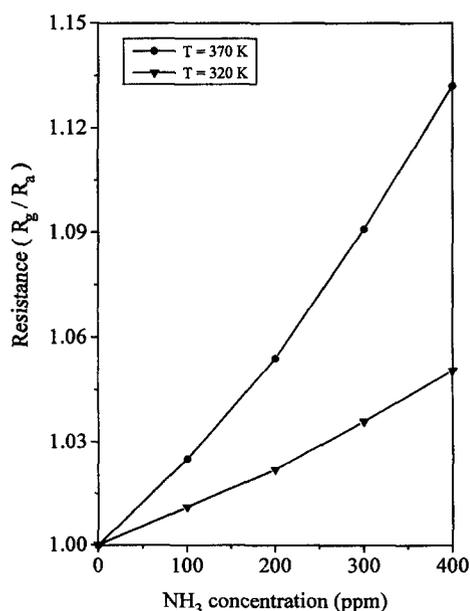

Fig. 2. Variation of resistance (R_g/R_a) of ClAlPc thin film versus ammonia gas concentration.

O_2)) on exposure to different concentrations of dry ammonia gas. For each selected concentration the ClAlPc thin film was exposed to the test gas for a duration of 10 min, which was sufficiently long to allow the dark current to reach a constant value. The concentration was increased in steps of 100 ppm in the range 0–400 ppm at a temperature of 320 K. The same measurements were then repeated at 370 K for another ClAlPc thin film sensor taken from the same batch of samples. As shown in Fig. 2 the resistance of the ClAlPc thin film devices increased with increasing sample temperature. The sensitivity (R_g/R_a) of the ClAlPc thin films was also observed to increase with increasing temperature. Physically, the reason for the increase in resistance of the device can be understood in terms of a change in the surface conductivity of the film. Such effects can be interpreted within the framework of band theory if we consider the adsorbed gases to produce appropriate donor or acceptor levels within the band gap of the material at the film surface. ClAlPc is a p-type organic semiconductor and it is well known that when a donor type gas such as ammonia is adsorbed onto a phthalocyanine film the surface conductivity is reduced [14]. This is because the NH_3 gas produces donor states in the near surface region of the ClAlPc which partially compensate the p-type ClAlPc by trapping positive holes. As shown in Fig. 3 the opposite response was obtained for Cl_2 which is an acceptor gas, using the same concentration and exposure times as before and it can be seen that the resistance now decreases with increasing concentration of Cl_2 gas as would be expected. This means that the ClAlPc thin film conductivity is enhanced by the creation of further positive holes in the surface region by the adsorbed Cl_2 gas. Fig. 3 also shows that the sensitivity of the sensor increases with increasing temperature up to 400 K.

In the present work we also tried to examine the reversibility of our ClAlPc thin film sensors with respect to exposure to NH_3 and Cl_2 gases at different temperatures (340 and 380 K). After the device to be tested had reached a stable state at the required temperature in a flow of zero grade air (20% O_2), which normally took 2 h, NH_3 gas was introduced into the test chamber for a period of 26 min. The flow of NH_3 was then switched off and the chamber was purged with zero grade air for 26 min. This
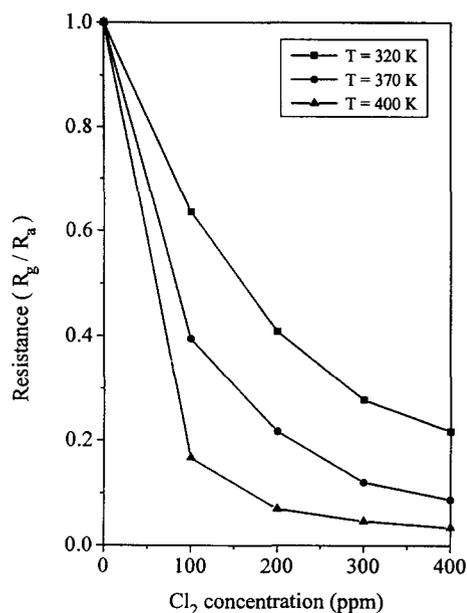
Fig. 3. Variation of resistance (R_g / R_a) of ClAlPc thin film versus chlorine gas concentration at several different temperatures.

Fig. 4. Resistance (R_g / R_a) versus time response of a ClAlPc thin film exposed to two cycles of 500 ppm ammonia at 340 and 380 K.

cycle was then repeated. As can be clearly seen from Fig. 4, by increasing the temperature from 340 to 380 K, the sensitivity (R_g/R_a) was reduced. However, the response of the ClAlPc sensor became much more reversible. This behaviour is in good agreement with the findings of other workers using mono-phthalocyanines as gas sensors [16]. We note that ClAlPc may have some important advantages since good reversibility is obtained at a much lower operating temperature (i.e. 107°C compared with 190°C in Ref. [16] for example). This offers reduced power consumption and increased operating lifetime since the film will not evaporate away in use. As shown in Fig. 5 the opposite response was obtained for Cl_2 gas, (because Cl_2 is an acceptor gas) R_g/R_a increased by increasing the temperature from 340 to 390 K and the overall sensitivity decreased. But, once again the ClAlPc thin film became more reversible.

In the present work we have also measured the response of ClAlPc to a continuous flow of 500 ppm Cl_2 at several different temperatures. As shown in Fig. 6 after the initial transient lasting about 20 min the resistance ratio (R_g/R_a) became constant. From the flat part of the characteristics it was observed
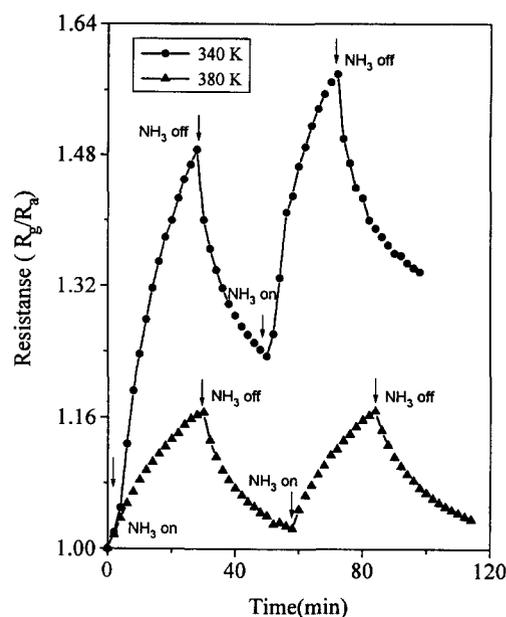
that the sensitivity of ClAlPc to Cl_2 increases with increasing temperature up to 353 K then decreases with increasing temperature. To obtain further infor-
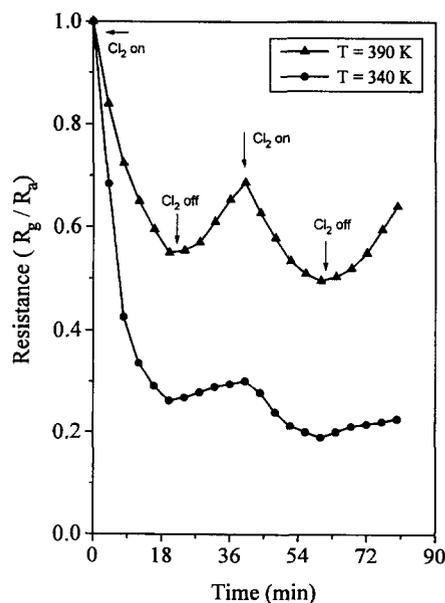

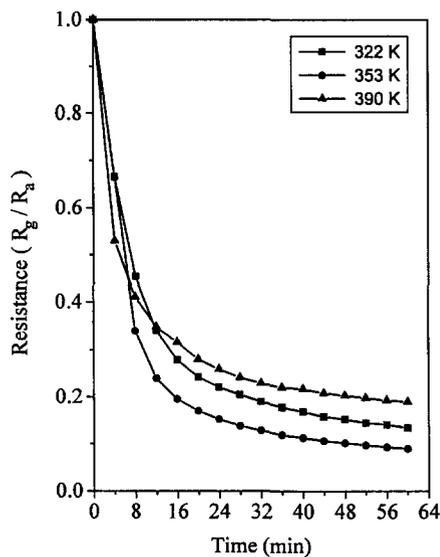Fig. 5. Resistance (R_g / R_a) versus time response for a ClAlPc thin film exposed to a cycles of 500 ppm chlorine.

Fig. 6. Variation of resistance (R_g / R_a) versus time for ClAlPc thin film exposed to 500 ppm chlorine at several different temperatures.

Fig. 7. Dark current versus temperature for a ClAlPc thin film gas sensor.

mation about the effects of temperature on gas adsorption two ClAlPc sensors were exposed to a continuous flow of either Cl_2 or NO_2 (500 ppm in zero grade air) for several hours to stabilise the film surface. The sensors were then heated up to 220°C and the resulting dark current was monitored. The temperature of the device was raised from room temperature to 220°C in steps of 10°C, each temperature step being of about 40 s duration. The dark current of the ClAlPc thin film was recorded at the end of each temperature step throughout the heating procedure. The relation between the dark current and the temperature are shown in Figs. 7 and 8 for the ClAlPc thin film sensor. We observed that under the present experimental conditions the dark current goes through a maximum at a temperature T_{max} = for NO_2 and Cl_2 gases, respectively. At $T < T_{max}$ the current increases with increasing temperature. If we assume that ClAlPc is a sufficiently good semiconductor then we can apply band theory. This means that the ClAlPc thin film was effectively 'doped' by the adsorbed gas (NO_2) which forms an acceptor level within the ClAlPc band gap. The film conductivity is thermally activated according to the equation $I = I_0 \exp(-E_{act}/KT)$, where $E_{act} = 0.15$ and 0.20 eV for ClAlPc 'doped' with Cl_2 (500 ppm) and NO_2,
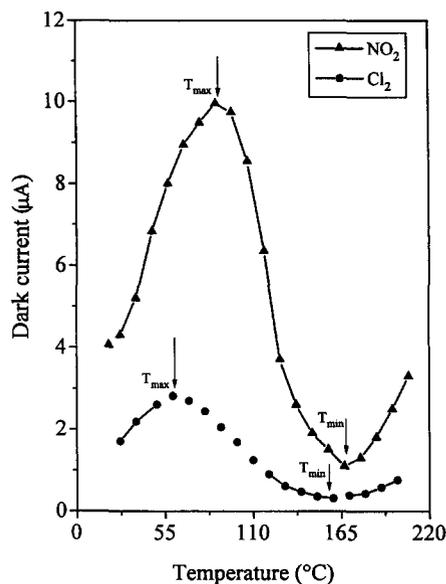
respectively, according to our measurements in Fig. 8. At temperatures $T > T_{max}$, the current decreases with increasing temperature. The higher temperature
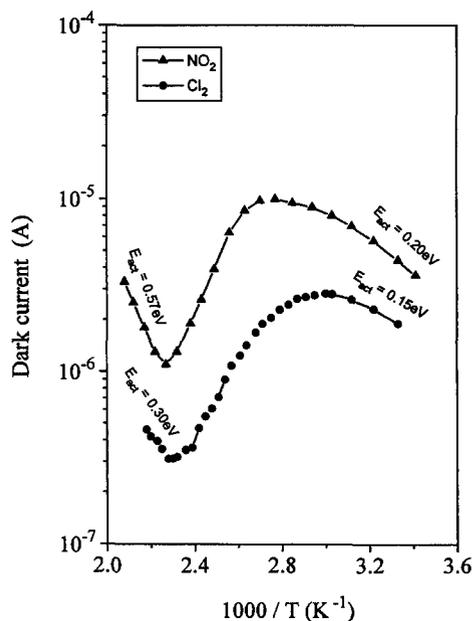

Fig. 8. The current–temperature curve of Fig. 7 plotted as log I versus $1/T$.

causes desorption of the adsorbed molecules and consequently a decrease in the number of extrinsic charge carriers and the conductivity of the ClAlPc thin film sensor. At temperatures > 197°C the dark current increases more rapidly with temperature which may be considered as intrinsic behaviour and is due to thermal activation energy of the intrinsic charge carriers from the valence band. From Fig. 8 E_{act} is found to be 0.57 and 0.30 eV for ClAlPc 'doped' with 500 ppm NO_2 in the presence of 20% O_2 and 500 ppm Cl_2 in the presence of 20% O_2, respectively. In fact both thermal activation (intrinsic conductivity) and gas desorption are active phenomena over the whole temperature range of 17 to 217°C, but at temperatures $T < T_{max}$ the semiconductor effect is dominant, whereas at temperatures $T > T_{max}$ desorption is dominant and this decreases the conductivity. Similar results have been reported for NO_2 in copper phthalocyanine and for chlorine in PbPc [8].

To further explain the information about localised levels created in the ClAlPc band gap as a result of adsorption of Cl_2 and NO_2, the $I–T$ data of Fig. 8 were analysed within the framework of the Roberts and Schmidlin model [17]. By using this model the extrinsic conductivity of the ClAlPc can be expressed in terms of the band gap and the absolute temperature as

$$\sigma_{ex} \propto \exp(E_v - E_h)/K_B T, \tag{1}$$

where E_h and E_v are the dominant hole (acceptor) level and valence band edge energies, respectively. So the activation energy for extrinsic conduction is thus $E_{ex} = E_h - E_v$. The corresponding pseudo-intrinsic conductivity σ_{pi} and activation energy E_{pi} are

$$\sigma_{pi} \propto \exp[(E_v - E_h) + 1/2(E_h - E_e)]/K_B T \tag{2}$$

and

$$E_{pi} = (E_h - E_v) + (E_e - E_h)/2 \tag{3}$$

respectively, where E_e is the dominant electron (donor) level.

The linearity of Fig. 8 at $T < T_{max}$ and $T > 470$ K may be attributed to extrinsic and pseudo-intrinsic conductivity, respectively. The region $T < T_{max}$ gives a satisfactory fit to Eq. (1) and the activation energy of 0.15 eV relates to the ionisation energy of the induced Cl_2 acceptor levels. This is less than the

value of 0.20 eV obtained for NO_2. The region $T > 470$ K can be described by Eq. (2). Substituting the experimental data obtained from regions $T < T_{max}$ and $T > 470$ K in Fig. 8 into Eqs. (1)–(3), $E_h - E_v$ and $E_e - E_h$ are found to be 0.20 and 0.80 eV, respectively, for ClAlPc 'doped' with NO_2.

The temperature T_{max} of the conductivity peak was determined for ClAlPc 'doped' with NO_2 and Cl_2 (Fig. 7). T_{max} represents a relative measure of the bonding energy between the gaseous doping molecules and the adsorption sites of the phthalocyanine film, although this energy can not be determined exactly from the value of T_{max}, which depends on the experimental conditions. The temperature T_{max} giving maximum conductivity of a phthalocyanine film was determined by subjecting the 'doped' film to increasing temperature steps. T_{max} could perhaps be used as a design parameter for a thin film gas sensor and the temperature at which it occurs could provide information on the concentration and nature of the gas the phthalocyanine film is exposed to. A maximum response is expected at this temperature.

4. Conclusions

ClAlPc thin film gas sensors were prepared which were stable and exhibited reversible increases in dark current on exposure to both Cl_2 and NO_2. These gases are adsorbed on the ClAlPc film surface where they induce surface acceptor states such that the ClAlPc can be considered to be 'doped' by Cl_2 and NO_2 which are both oxidising gases. On exposure to NH_3 surface donor states are produced and the conductivity change is in the opposite sense i.e. the dark current decreases. The temperature of maximum conductivity (T_{max}) was determined as, 57 and 87°C for ClAlPc after exposure to Cl_2 and NO_2, respectively, and the corresponding activation energies of the dominant acceptor levels were found to be 0.15 eV for Cl_2 and 0.20 eV for NO_2. Because the measured temperature values of maximum sensitivity (T_{max}) of our ClAlPc 'doped' films are different for different gases, the parameters T_{max} (and also T_{min}) must therefore be carefully considered and the appropriate operating temperature chosen accordingly in order to obtain a gas sensor with optimum characteristics.

ClAlPc is a thermally stable material and shows a good sensitivity when exposed to low levels (500 ppm) of acceptor gases such as NO_2 and Cl_2 as well as donor gases such as NH_3 at room temperature. These ClAlPc thin films therefore seem to possess some desirable properties as a practical gas sensor material. Although the sensors made in this work had a slow response speed they exhibited good reversibility at lower operating temperatures than is usually observed with mono-phthalocyanines.

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