The effects of exposure to oxygen and annealing on the conductivity of copper phthalocyanine thin films

The effects of exposure to oxygen and annealing on the conductivity of copper phthalocyanine thin films†

A K Hassan and R D Gould

Department of Physics, University of Keele, Keele, Staffs. ST5 5BG, UK

Abstract. It is well known that oxygen has a profound effect on the conductivity of the phthalocyanines. In the present work the conductivity of copper phthalocyanine thin films has been measured both after exposure to oxygen for several weeks and after annealing at temperatures up to 150 °C. At low voltages the conductivity was Ohmic with hole concentrations varying in the range 10^{14}–10^{20} m^{-3}. Higher values of hole concentration were derived for samples stored for longer periods, indicating that oxygen acts as an acceptor level, while annealed samples showed lower values consistent with the desorption of oxygen. At higher voltages samples stored for 2 weeks showed space-charge-limited conductivity dominated by a discrete trap level of concentration 7.3×10^{18} m^{-3} and activation energy 0.65 eV, which was attributed to oxygen incorporation within the films. Conversely, after annealing, an exponential trap distribution of concentration 1.5×10^{24} m^{-3} was detected which was similar to those observed in samples which had not undergone exposure to oxygen and thus confirmed the removal of oxygen during the annealing process.

1. Introduction

Copper phthalocyanine (CuPc) is an organic semiconductor with possible applications in gas-detecting systems, owing to its variation in conductivity in the presence of adsorbed gas molecules. The basic DC conduction properties of CuPc thin films have been widely investigated, revealing that the material has p-type properties. Ohm's law is followed at low voltages while, at higher voltages, space-charge-limited conductivity has been identified, dominated by either an exponential distribution of traps (Hamann 1968, Gould 1985) or by a uniform trap distribution (Müller *et al* 1971).

   The effects of oxygen on the conductivity of phthalocyanines have been investigated in the sense of both its doping effects (Sussman 1967b, Boudjema *et al* 1984, Twarowski 1982) and its role in the sensitivity of phthalocyanine films to other gases (Wilson and Collins 1986, Collins and Mohammed 1988). In the present work, we have undertaken a systematic study of the effects of oxygen incorporation on the conductivity and trap distribution of α-modification CuPc thin films.

† This is an amended version of a paper that was presented at the Eighth Interdisciplinary Surface Science Conference, University of Liverpool, 20–23 March 1989. A special supplement made up of papers from this conference will be issued on 30 October 1989, together with issue 43 of *Journal of Physics: Condensed Matter*.

2. Experimental details

The β-modification CuPc was obtained from Fluka AG. Elementary analysis revealed the following proportions of the elements by weight: carbon, 66.37% (calculated, 66.72%); nitrogen, 19.31% (calculated, 19.45%); hydrogen, 3.02% (calculated, 2.80%). There was thus a slight deficit in the proportions of carbon and nitrogen and a surplus of hydrogen. The remaining proportion by weight of 11.30% was mostly copper (calculated, 11.03%). X-ray fluorescence spectroscopy yielded the following counts ($\times 1000$) for the metallic elements listed: copper, 604; iron, 1.6; aluminium, 2.2; magnesium, 1.0; phosphorus, 1.0.

Samples were deposited on Corning 7059 microscope slides cleaned by ionic bombardment. Substrate temperatures were maintained at room temperature, resulting in the growth of α-modification CuPc films (Sharp and Abkowitz 1973). Gold electrodes were used as these provide Ohmic contacts to CuPc (Sussman 1967a). Evaporation rates were typically 0.5 nm s^{-1} for both the gold electrodes and the CuPc and deposition was carried out at pressures in the range 10^{-4}–10^{-3} Pa. The bottom gold electrode (thickness, typically 80 nm) and the CuPc layer (thickness, 5 μm) were evaporated sequentially without breaking the vacuum. Samples were then removed to a desiccator and stored in dry air for periods of up to 20 weeks, after which they were removed and the top gold electrode of thickness 80 nm and active area 1.2×10^{-5} m^2 deposited to complete the structure. Deposition rates were monitored using quartz crystal techniques and thicknesses accurately determined after deposition using a stylus instrument. Further details are given elsewhere (Gould 1985, Hassan and Gould 1989). Vacuum annealing was carried out in a subsidiary vacuum system, the samples being slowly heated over a period of several hours to a maximum temperature of 150 °C. After annealing, the temperature was slowly reduced to ambient.

Electrical measurements were carried out at a pressure of less than 10^{-3} Pa, using a stabilised power supply and a Keithley 480 picoammeter. Temperatures were controlled using a heater and liquid-nitrogen cooling facility over the approximate range 160–420 K, and measured using a Fluke 52 digital thermometer. Throughout this work, forward bias is defined as the situation when the bottom electrode is positive.

3. Results and discussion

In figure 1, typical forward- and reverse-bias current density–voltage (J–V) characteristics are shown for samples stored in air for different periods. Both samples show approximately Ohmic conduction at low voltages with J increasing more rapidly at higher voltages. For the sample stored for 2 weeks a clear power-law dependence of J on V is apparent, indicative of space-charge-limited conductivity. This type of behaviour has been studied in many previous studies (Delacote *et al* 1964, Sussman 1967a, b, Hamann 1968, Gould 1985). A drastic increase in conductivity is evident for the sample stored for the longer period. It is well known that oxygen acts as an acceptor in CuPc (Boudjema *et al* 1984, Wilson and Collins 1986), and the increased conductivity appears to be consistent with the longer period of exposure. On the assumption that conduction is primarily via holes (Sussman 1967a) the Ohmic conductivity may be expressed in the form

$$J = p_0 e \mu (V/d) \tag{1}$$

where p_0 is the concentration of thermally generated holes, e is the electronic charge, μ
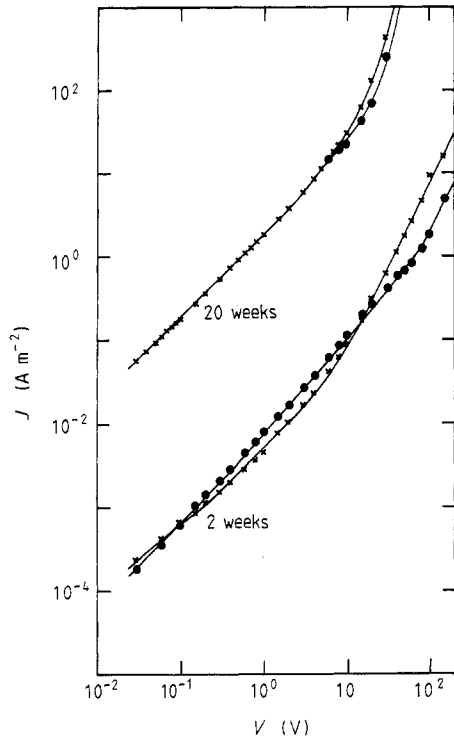
Figure 1. Current–voltage characteristics for samples stored in dry air for differing periods. Both forward-bias (×) and reverse-bias (●) characteristics are shown.

the hole mobility and d the film thickness. On the assumption of a value of $\mu = 5 \times 10^{-7}$ $m^2 V^{-1} s^{-1}$ as previously measured for samples prepared under similar conditions (Gould 1986), hole concentrations of approximately 5×10^{17} m^{-3} (2 weeks storage) and 10^{20} m^{-3} (20 weeks storage) were obtained.

At higher voltage levels the characteristic slope of the curves is 2 for the samples stored for 2 weeks, which indicates space-charge-limited conductivity controlled by a single dominant trap level. This behaviour may be expressed by the relationship (Lampert 1964)

$$J = \tfrac{9}{8}\varepsilon_r\varepsilon_0\mu\theta(V^2/d^3) \tag{2}$$

where $\varepsilon_r = 3.6$ (Gould 1986) is the relative permittivity of CuPc and ε_0 is the permittivity of free space. θ represents the ratio of free to trapped charge and is given by $\theta = (N_v/N_t)\exp(-E_t/kT)$ where N_v is the effective density of states in the valence band, N_t is the trap concentration, E_t is the activation energy of the hole traps, k is Boltzmann's constant and T is the absolute temperature. From equation (2) the value of θ is approximately 5.2×10^{-3} for forward bias, with a slightly lower calculated value for reverse bias. The high-voltage characteristics of the samples stored for 20 weeks were not investigated in detail but clearly show a deviation from Ohmic conductivity.

The results of the variation in J with temperature at fixed voltages under forward bias are shown in figure 2, for a sample stored for 2 weeks. The particular voltage levels used were chosen so that activation energies pertaining to both the Ohmic region (5 V) and the space-charge-limited region (50 V) could be derived. Both curves show a linear dependence of $\log J$ on $1/T$ over five decades of current. Deviations at higher temperatures are probably due to the desorption of oxygen at temperatures greater than
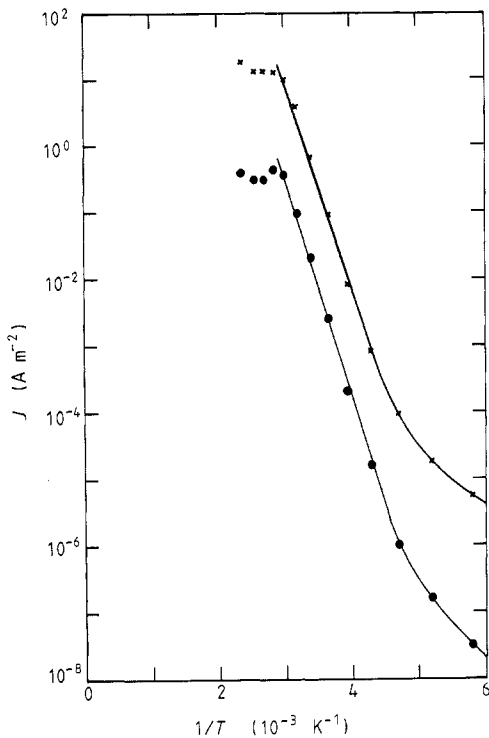
Figure 2. Temperature dependence of current density for conduction in the Ohmic region (5 V) (●) and in the space-charge-limited region (50 V) (×). Derived activation energies were 0.65 eV and 0.62 eV, respectively.

150 °C (Twarowski 1982) while at lower temperatures a hopping process, as suggested by Le Moigne and Even (1985), is a possible conduction mechanism. From figure 2 the activation energies obtained were 0.65 eV for Ohmic conduction and 0.62 eV for space-charge-limited conductivity; within experimental error these values may be considered equal and probably derive from the same cause. The activation energy derived for Ohmic conduction agrees well with the earlier measurements of Harrison and Ludewig (1966), who observed that samples exposed to air or oxygen generally yield activation energies of less than 0.7 eV. Clearly, oxygen impurities control the conductivity at low voltages by assuming the role of acceptor states which in turn control the hole concentration.

The activation energy in the space-charge-limited region may be identified with the energy E_t, which determines the ratio θ of free to trapped charge. The trap concentration is then given by $N_t = (N_v/\theta) \exp(-E_t/kT)$. Using $N_v = 10^{27}$ m^{-3} (Sussman 1967a) and $\theta = 5.2 \times 10^{-3}$ at room temperature, we obtain $N_t = 7.32 \times 10^{18}$ m^{-3}. This value is considerably lower than obtained in samples which have not been exposed to oxygen, and which normally show an exponential distribution rather than a discrete trapping level. It is thus concluded that exposure of the samples to air allows oxygen to be incorporated into the structure, resulting in the emergence of a dominant trap level. An alternative explanation in terms of an exponential trap distribution (Gould 1982) results in an unrealistically high trap concentration estimated at approximately 1.7×10^{29} m^{-3}.

Finally, in figure 3 the J–V characteristic is shown for a sample which had undergone annealing after storage in dry air for 2 weeks. The main features of this characteristic are that, in the Ohmic range, J is considerably reduced, while for higher voltages a well defined slope of value greater than 2 is obtained. In the Ohmic region a value of $p_0 \simeq 1.9 \times 10^{14}$ m^{-3} may be derived from equation (1). This very low value indicates that the
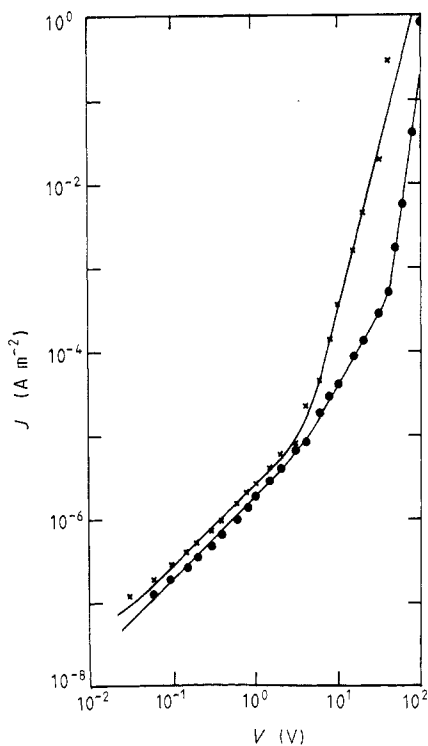
Figure 3. Current density–voltage characteristics for a sample after storage in dry air for 2 weeks and subsequent annealing at a maximum temperature of 150 °C. Both forward-bias (×) and reverse-bias (●) characteristics are shown.

annealing process has resulted in the removal of considerable quantities of oxygen acceptor impurities, as suggested by Twarowski (1982). At higher voltages under forward bias the slope of 3.7 indicates space-charge-limited conductivity dominated by an exponential distribution of trapping levels above the valence band edge described by $P(E) = P_0 \exp(-E/kT_t)$, where $P(E)$ is the trap density per unit energy at an energy E above the valence band edge, P_0 is the value of $P(E)$ at the valence band edge and T_t is a temperature parameter related to the power-law exponent. Detailed explanations have been given elsewhere (Gould 1985, Hassan and Gould 1989). Parameters derived from the forward-bias characteristic are $P_0 \simeq 1.38 \times 10^{44} \, \mathrm{J^{-1} \, m^{-3}}$, $T_t \simeq 816 \, \mathrm{K}$ and a total trap concentration N_t of about $1.55 \times 10^{24} \, \mathrm{m^{-3}}$; these values are comparable with those derived previously for samples which had been neither deliberately exposed to oxygen nor annealed (Gould 1985). It thus appears that annealing reverses the effects of exposure to oxygen and restores domination of the space-charge-limited conductivity by an exponential distribution of traps. The removal of oxygen by annealing may well be responsible for the disappearance of the single discrete trap level. The reverse-bias characteristic differs in detail from that for forward bias, but this is probably due to a variation in oxygen concentration as a function of distance from the surface of the film, resulting from the annealing process.

4. Summary and conclusions

In agreement with previous work, samples showed Ohmic conductivity at low voltages followed by space-charge-limited conductivity at higher voltages. In the Ohmic region

the hole concentration increased with prolonged exposure to oxygen and decreased with annealing, over an approximate range 10^{14}–10^{20} m^{-3}. Activation energies of 0.65 eV and 0.62 eV, respectively, for Ohmic and space-charge-limited conductivity were derived and indicate that oxygen impurities may play the dual role of both acceptors and trap levels. In contrast with many previous studies where the space-charge-limited conductivity was controlled by an exponential distribution of traps, samples exposed to oxygen appeared to be controlled by a single dominant level. On annealing, the exponential trap distribution was re-established, confirming that additional oxygen impurities are responsible for the modified behaviour.

Clearly the presence of incorporated oxygen profoundly influences the conductivity of CuPc thin films. Its role needs to be fully understood before the performance of gas detectors based on phthalocyanines may be fully optimised.

Acknowledgments

References

Boudjema B, Guillaud G, Gamoudi M, Maitrot M, André J-J, Martin M and Simon J 1984 *J. Appl. Phys.* **56** 2323–9
Collins R A and Mohammed K A 1988 *J. Phys. D: Appl. Phys.* **21** 154–61
Delacote G M, Fillard J P and Marco F J 1964 *Solid State Commun.* **2** 373–6
Gould R D 1982 *J. Appl. Phys.* **53** 3353–5
—— 1985 *Thin Solid Films* **125** 63–9
—— 1986 *J. Phys. D: Appl. Phys.* **19** 1785–90
Hamann C 1968 *Phys. Status Solidi* **26** 311–8
Harrison S E and Ludewig K H 1966 *J. Chem. Phys.* **45** 343–8
Hassan A K and Gould R D 1989 *J. Phys. D: Appl. Phys.* **22** 1162–8
Lampert M A 1964 *Rep. Prog. Phys.* **27** 329–67
Le Moigne J and Even R 1985 *J. Chem. Phys.* **83** 6472–9
Müller M A, Mihai I C and Müller L P 1971 *Phys. Status Solidi* a **4** 479–83
Sharp J H and Abkowitz M 1973 *J. Phys. Chem.* **77** 477–81
Sussman A 1967a *J. Appl. Phys.* **38** 2738–48
—— 1967b *J. Appl. Phys.* **38** 2748–52
Twarowski A 1982 *J. Chem. Phys.* **77** 4698–703
Wilson A and Collins R A 1986 *Phys. Status Solidi* a **98** 633–44