phys. stat. sol. (a) 123, 201 (1991)

Subject classification: 73.60; 73.40; S12

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# Ohmic and Space-Charge-Limited Conduction in Lead Phthalocyanine Thin Films

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The electrical characteristics of thermally evaporated triclinic lead phthalocyanine thin films are studied. A number of parameters is evaluated on the basis of the theory of space-charge-limited conduction and the following values are obtained: permittivity  $\varepsilon = 3.16 \times 10^{-11}$  F m<sup>-1</sup>; hole mobility  $\mu \approx 6.05 \times 10^{-10}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>; room temperature hole concentration  $p_0 \approx 1.60 \times 10^{18}$  m<sup>-3</sup>; concentration of traps per unit energy range at the valence band edge  $P_0 \approx 2.79 \times 10^{43}$  J<sup>-1</sup> m<sup>-3</sup>; temperature parameter of trapping distribution  $T_t \approx 770$  K; total trap concentration  $N_t \approx 2.97 \times 10^{23}$  m<sup>-3</sup>. The room temperature electrical conductivity  $\sigma = 1.55 \times 10^{-10}$  S m<sup>-1</sup>. C-U measurements confirm that the Au-PbPc interface does not form a Schottky barrier. At low temperatures the capacitance of Au-PbPc-Au devices is temperature insensitive, increasing rapidly above 300 K and saturating at about 400 K. Measurements of thermoelectric power confirm that semiconduction is p-type.

Die elektrischen Eigenschaften von thermisch aufgedampften dünnen triklinen Blei-Phtalozyaninschichten werden untersucht. Eine Anzahl von Parametern wird auf der Grundlage der Theorie des raumladungsgegrenzten Stromes berechnet und folgende Werte erhalten: Dielektrizitätskonstante  $\varepsilon = 3,16 \times 10^{-11}$  F m<sup>-1</sup>; Löcherbeweglichkeit  $\mu \approx 6,05 \times 10^{-10}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>; Raumtemperaturlöcherkonzentration  $p_0 \approx 1,60 \times 10^{18}$  m<sup>-3</sup>; Konzentration der Haftstellen pro Energieeinheit an der Valenzbandkante  $P_0 \approx 2,79 \times 10^{43}$  J<sup>-1</sup> m<sup>-3</sup>; Temperaturparameter der Haftstellenverteilung  $T_t \approx 770$  K; Gesamthaftstellenkonzentration  $N_t \approx 2,97 \times 10^{23}$  m<sup>-3</sup>. Die elektrische Leitfähigkeit bei Zimmertemperatur beträgt  $\sigma = 1,55 \times 10^{-10}$  S m<sup>-1</sup>. C-U-Messungen bestätigen, daß die Au-PbPc-Grenzfläche keine Schottky-Barriere bildet. Bei tiefen Temperaturen ist die Kapazität von Au-PbPc-Au-Bauelementen temperaturunabhängig, steigt oberhalb 300 K schnell an und sättigt bei etwa 400 K. Messungen der Thermospannung bestätigen den p-Halbleitungstyp.

## 1. Introduction

The electrical properties of metal-substituted phthalocyanines have assumed increasing importance in recent years, particularly in relation to the development of metal phthalocyanine (MPc) thin film gas sensors [1 to 5]. Recently Gould and co-workers have carried out systematic studies of the properties of CuPc using a variety of metal electrodes and under various regimes of annealing and gaseous exposure [6 to 9]. Other metal phthalocyanines have received relatively little attention in terms of their dc electrical properties. However, there is increasing evidence that PbPc may be the most suitable phthalocyanine for gas sensing, particularly for NO<sub>2</sub>. Jones and co-workers [3, 10, 11] have demonstrated fast response and recovery times for NO<sub>2</sub> detection using PbPc devices which have been thermally pre-heated to 300 °C and then operated at 170 °C. Studies by Archer [2] have led to a sensing model based on sensitization to NO<sub>2</sub> by a combination of thermally induced structural changes and the creation of strongly bonded NO<sub>2</sub> species. These have the effect of catalysing oxygen displacement from ad-sites. The p-type semiconductivity is thus strongly

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modified by gaseous adsorption but is also dependent on impurities [12, 13] and on film structure [14, 15].

In the present work we have extended our previous work on PbPc thin films [14 to 16] to studies of the dc electrical properties. Such studies of ohmic and space-charge-limited conductivity (SCLC) in organic semiconductors are capable of providing considerable insight into charge transport mechanisms and carrier trapping in these materials and such information is of particular importance in the development of viable thin film organic gas sensors.

## 2. Experimental

PbPc was prepared by boiling lead monoxide and phthalonitrile in chloronaphthalene in a refluxing condenser at a temperature of 180 to 200 °C for at least 80 min until the colour of the solution changed from pale yellow to dark blue. The product was filtered and then washed, firstly in chloronaphthalene and then in acetone, prior to vacuum drying at 60 °C for 12 h. The raw PbPc was then purified by entrainer sublimation in a three-zone tube furnace using a 0.51 min<sup>-1</sup> flow of zero-grade ( $\leq$  3 ppm H<sub>2</sub>O) argon (supplied by BOC Special Gases). The crystal form obtained, as determined by X-ray diffraction, depended on the temperature profile of the sublimation tube [14]. Thick plate-like single crystals of triclinic PbPc (coloured dark blue) grew in the intermediate temperature zone of the tube (300 to 350 °C) but thin needle-like monoclinic PbPc (coloured green) grew in the region of 250 to 300 °C.

The purified materials were subsequently thermally evaporated in vacuum onto  $5 \times 5$  cm<sup>2</sup> polyborosilicate glass substrates. Prior to vacuum evaporation the substrates were thoroughly cleaned by ultrasoneration in a 1:5 solution of Decon-90 in deionised water followed by an extended rinse in deionised water and were then blow-dried.

The structure of the samples was a Au-PbPc-Au sandwich in the configuration commonly used for such studies [17]. An edge thickening layer of SiO<sub>x</sub> was utilised to prevent edge emission or interelectrode short circuit effects [18]. Layers were thermally evaporated in vacuum at a pressure of  $10^{-4}$  Pa. The thicknesses of top and bottom gold electrodes were 50 nm and that of the edge thickening layer was about 100 nm. The sandwich layers of PbPc varied in thickness from 0.1 to 6 µm. Evaporation rates were maintained at 0.1 nm s<sup>-1</sup> for top and bottom gold electrodes, 0.3 nm s<sup>-1</sup> for SiO<sub>x</sub> layers, and 0.6 nm s<sup>-1</sup> for PbPc layers. The layer thicknesses were monitored during deposition using a quartz crystal monitor and were subsequently checked using a traversing stylus method. The bottom gold electrodes had dimensions  $45 \times 7$  mm<sup>2</sup> and the top gold electrodes were  $16 \times 2$  mm<sup>2</sup>. The electrodes were crossed such that there was an active area of  $1 \times 10^{-5}$  m<sup>2</sup> per device and each substrate incorporated twelve devices.

After fabrication the devices were mounted on a hollow copper block in a vacuum test chamber which could be evacuated to a pressure of the order of  $10^{-4}$  Pa. Electrical contacts to the devices were made with high conductivity silver paint (Electrodag 915). Temperatures down to about 150 K were achieved by the circulation of liquid nitrogen through the hollow copper block inside the chamber. Higher temperatures up to 475 K were achieved by means of a small thermofoil heater (Minco HK-913) directly beneath the substrate. Temperatures were monitored by a chromal/alumel thermocouple attached to the top surface of the substrate. Electrical measurements were made in the voltage range of 0 to 100 V using

a stabilised power supply and Keithly 610C electrometer for current measurements. For measurements of the capacitance a Wayne Kerr automatic component bridge was used.

Photoconductive effects were eliminated by shielding the samples from incident light for a minimum of 24 h prior to experimentation. Additionally, possible effects due to adsorbed water vapour and oxygen were minimised by heating devices to about 380 K for 12 h in a vacuum of  $10^{-6}$  Torr before measurements were made.

## 3. Results and Discussion

#### 3.1 Capacitance-voltage measurements

The depletion layer (space charge) capacitance associated with a p-n junction or Schottky barrier is given by

$$C^{2} = \frac{e \epsilon N A^{2}}{2(U_{b} - U)},$$
(1)

where N is the effective density of donors or acceptors, equal to the shallow level concentration compensated by any deep levels present, A is the area,  $\varepsilon$  the permittivity of the semiconductor, e the electronic charge, U the applied voltage, and  $U_b$  the barrier height. If one plots the experimentally obtained values of  $1/C^2$  versus reverse bias voltage, N and  $U_b$  may be determined from the slope and intercept on the abscissa, respectively [19]. This is applicable only if N is constant throughout the depletion region. If N is not a constant, the differential capacitance method can be used to determine the doping profile from the following equation [20]:

$$N = \frac{2}{e\varepsilon} \left\{ -\frac{1}{\mathrm{d}(1/C^2)/\mathrm{d}U} \right\}.$$
(2)

In Fig. 1 the variation of capacitance C with voltage U for forward bias (top Au positive) and reverse bias (bottom Au positive) are shown and it is clear that the capacitance C does not change with the variation of applied voltage U. This suggests that the total width of the PbPc layer is depleted and the system behaves as a simple capacitor of capacitance C given by

$$C = \frac{\varepsilon A}{d}.$$
(3)

Fig. 2 shows measurements of dc capacitance C as a function of reciprocal film thickness (1/d) of the PbPc. Clearly, the relationship between these two quantities is linear with the slope being  $\varepsilon A$ , where  $\varepsilon$  is the permittivity of the PbPc and A the effective sample area,  $1 \times 10^{-5} \text{ m}^2$ . The value of  $\varepsilon$  derived from Fig. 2 is  $3.6 \times 10^{-11} \text{ Fm}^{-1}$  (relative permittivity  $\varepsilon_r = 3.57$ ) which is in good agreement with the available literature values:  $3.19 \times 10^{-11} \text{ Fm}^{-1}$ [6, 7],  $2.5 \times 10^{-11} \text{ Fm}^{-1}$ [21],  $2.12 - 4.5 \times 10^{-11} \text{ Fm}^{-1}$ [22, 23] for CuPc, and  $1.77 \times 10^{-10} \text{ Fm}^{-1}$ [24] for ZnO/Sn composites. The derived value of  $\varepsilon$  will be used later in the following analysis.



Fig. 1. Variation of capacitance with voltage (at a frequency of 100 Hz) for various PbPc thicknesses: (a) 0.95, (b) 3.8, (c)  $5.55 \,\mu m$ 

Fig. 2. Dependence of capitance on reciprocal thickness

#### 3.2 Capacitance-temperature measurements

The continuous curves of capacitance as a function of temperature for different samples of varying thickness are illustrated in Fig. 3. At low temperatures (less than 300 K, which varies slightly from sample to sample) the capacitance C almost corresponds to the geometric capacitance and is practically temperature insensitive. Above 300 K there is a rapid increase in capacitance and finally at about 400 K, C saturates. Similar variation of C with T was observed by Simmons et al. [25] in the 250 to 400 K temperature range for MIM devices, but no such increase was observed by Machida et al. [26] for their M-PbPc-M samples. This difference may be due to the presence of organic impurities in the samples of Machida et al. as their PbPc had not been sublimed prior to evaporation.



Fig. 3. Capacitance C against temperature T for samples of different PbPc thickness: (a) 0.95, (b) 1.3, (c)  $2.0 \ \mu m$ 

According to Simmons et al., the temperatures at which the capacitance begins to increase and at which it saturates depend primarily on the activation energy of the dominant donors or acceptors in the bulk and to a lesser extent on resistance. Moreover, at higher temperatures where many impurity levels are ionised, the resistance of the semiconductor becomes sufficiently low as to shunt its capacitance. At low temperatures very few impurity levels are ionised and consequently the carrier density is low. Thus the resistance is large and does not allow the capacitance to be varied with the temperature. Twarowski [27] attributed this behaviour to the slow release of charge carriers from relatively deep traps.

#### 3.3 Ohmic current and SCLC measurements

Room temperature current density-voltage (J-U) characteristics are shown in Fig. 4 for Au-PbPc-Au sandwich structures with SiO<sub>x</sub> barrier layers at the interfaces for samples of varying thickness of PbPc ranging from 0.95 to 5.55 µm. There are two distinct regions in these characteristics: at low voltages the slopes of the lg J versus lg U plots are approximately equal to unity, while at higher voltages, above a well-defined transition voltage  $U_t$ , the slopes are approximately equal to 3.6. These plots are typical of ohmic conduction at voltages below  $U_t$  [6]. Therefore, at low voltages we expect Ohm's law, given by Lampert [28] as

$$J = e p_0 \mu \left(\frac{U}{d}\right),\tag{4}$$

will be observed and we assume that the ohmic conductivity is entirely due to holes. In the above equation J is the current density, U the applied voltage,  $p_0$  the concentration of thermally activated holes in the valence band, e the electronic charge,  $\mu$  the hole mobility, and d the top and bottom electrode spacing (the thickness of PbPc). According to Lampert the SCLC characteristics for a p-type semiconductor with an exponential distribution of trapping levels is given by

$$J = e\mu N_{v} \left(\frac{\varepsilon}{eP_{0}kT_{t}}\right)^{l} \frac{U^{l+1}}{d^{2l+1}},$$
(5)



Fig. 4. Dependence of current density J on applied voltage U for samples of different thickness: (a) 0.95, (b) 2.20, (c) 3.36, (d) 3.59, (e) 4.92, (f) 5.55  $\mu$ m

where  $N_v$  is the effective density of states in the valence band edge, k the Boltzmann constant,  $P_0$  the trap density per unit energy range at the valence band edge. U, e,  $\mu$ , d,  $\varepsilon$  have already been defined. The constant l is the ratio  $T_i/T$  where T is the room ambient and  $T_i$  is the temperature parameter describing the exponential trapping distribution P(E) equal to [7]

$$P(E) = P_0 \exp\left(\frac{-E}{kT_t}\right),\tag{6}$$

where P(E) is the trap density per unit energy range at an energy E above the valence band edge.

From (5) a slope of 3.6 implies that l = 2.6 and thus the temperature parameter is  $T_{\rm t} = 770$  K for T = 300 K.

The total density of traps  $N_t$  comprising the distribution is given by evaluating  $\int P(E) dE$  from the valence band edge to infinity, yielding the result as given by [24],

$$N_{t} = P_{0}kT_{t}, \tag{7}$$

while the transition voltage  $U_t$  between Ohmic conduction and SCLC is given by [6]

$$U_{t} = \left(\frac{p_{0}}{N_{v}}\right)^{1/l} \frac{d^{2}eN_{t}}{\varepsilon}.$$
(8)

The calculated values of  $U_t$  for different samples of varying thickness along with their experimental values from Fig. 4 are listed in Table 1.

Fig. 5 shows the dependence of transition voltage  $U_t$  on thickness d. The slope of 2 suggests good agreement with (8).

Shown in Fig. 6 are the thickness dependence of current density J for both ohmic current and SCLC regions at certain fixed values of voltages at room temperature. Each point corresponds to a different sample. The ohmic dependence (slope of  $\approx -1$ ) indicates that good ohmic contacts exist. Further, the relatively small scatter of points about this line indicates that the concentration of holes was relatively constant from sample to sample. The slope of  $\approx -6.2$  in the SCLC region verifies the space-charge-limited conduction dominated by an exponential distribution of traps. From (5) the slope in this region should be -(2l + 1) implying that  $l \approx 2.6$  is in excellent agreement with the values deduced from the J-U characteristics of Fig. 4.

Table 1

Calculated and experimental values of the transition voltage  $U_1$  between ohmic and SCLC regions for samples of various thicknesses

<i>d</i> (μm)	$U_{\rm t}$ (V)	
	experimental	theoretical
0.95	0.6	0.55
2	3	2.48
3.5	7	7.6
3.59	8	8
4.76	15	14
5.55	20	19.1



Fig. 5. Dependence of transition voltage  $U_t$  on thickness d (--- $\bigcirc$ --- theoretical,  $-\bullet$ - experimental values

Fig. 6. Dependence of current density J on thickness d for various constant voltages in the ohmic and SCLC regions. (a) 80, (b) 50, (c) 20, (d) 7, (e) 0.5, (f) 0.1 V

Temperature parameters allow us to obtain more information about the material under investigation. Fig. 7 shows lg J versus 1/T characteristics at constant voltages 20, 60, and 100 V, respectively, for a sample of thickness 5.55  $\mu$ m in the temperature range 200 to 400 K. For this temperature range the characteristics show quite linear segments and when extrapolated towards the negative value of 1/T intersected at a common point whose coordinates are [7]

$$\lg J = \lg \left( \frac{e^2 \mu d N_v N_t}{\varepsilon} \right) \quad \text{and} \quad \frac{1}{T} = -\frac{1}{T_t}.$$
(9)

The slopes of these lines are given by

$$S = \frac{d(\lg J)}{d(1/T)} = T_t \lg \left(\frac{\varepsilon U}{ed^2 N_t}\right)$$
(10)

and the intercept on the  $\lg J$  axis is given by

$$\lg J_0 = \lg \left(\frac{e\mu N_v U}{d}\right). \tag{11}$$

 $J_0$  represents the current density at infinite temperature (1/T = 0) and is thus a theoretical abstraction; however, it may readily be obtained graphically allowing the mobility to be determined from this equation (11).



Fig. 7. Dependence of current density J on reciprocal temperature 1/T as a function of applied voltage for a sample of PbPc, thickness = 5.55  $\mu$ m; (a) 100, (b) 60, (c) 20 V

Fig. 8. Derived trapping distribution, showing P(E) as a function of energy above the valence band edge of the PbPc

In order to determine the mobility  $\mu$  a value for  $N_v$  is required. In the literature an effective density of states  $N_v \approx 1 \times 10^{27} \text{ m}^{-3}$  has been used for different materials and device structures by several research workers. For example, Sussman [21], Gould [6, 7], and Chamberlain and Cooney [29] suggested  $N_v = 1 \times 10^{27} \text{ m}^{-3}$  for CuPc studies. Barbe and Westgate [30] used the same value of  $N_v$  for their  $\beta$ -phthalocyanine crystals and Schmidlin and Roberts [31] used  $N_v = 1.5 \times 10^{27} \text{ m}^{-3}$  in phthalocyanine analysis. Hartke [32] evaluated  $N_v$  equal to  $10^{26} \text{ m}^{-3}$  for his amorphous selenium films. Westgate and Warfield [33] measured  $N_v = (1.2 \text{ to } 2) \times 10^{27} \text{ m}^{-3}$  for the PbPc derivative of phthalocyanine. On the basis of these values,  $N_v = 1 \times 10^{27} \text{ m}^{-3}$  was used in the present work.

The intercepts extrapolated on the lg  $J_0$  axis are 5.6, 6, and 6.2 for 20, 60, and 100 V, respectively. Substituting the values of intercepts and  $N_v$  in (11), the measured values of mobilities are  $6.89 \times 10^{-10}$ ,  $5.77 \times 10^{-10}$ , and  $5.49 \times 10^{-10}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. For evaluation of parameters following we used an average value equal to  $\mu \approx 6.05 \times 10^{-10}$  m<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. The measured value of  $T_t$  from lg J versus 1/T plots was  $\approx 770$  K and is in good agreement with that obtained from the space-charge-limited characteristics of Fig. 4.

The measured slopes of the  $\lg J-1/T$  characteristics are -2560, -2280, and  $-2040 \text{ AK/m}^2$  for 20, 60, and 100 V, respectively. The total trapping concentration  $N_t$  was estimated from the measured slopes and by using (10), which yielded values of  $2.70 \times 10^{23}$ ,  $3.51 \times 10^{23}$ , and  $2.86 \times 10^{23} \text{ m}^{-3}$  for 20, 60, and 100 V, respectively. The average value  $N_t = 2.97 \times 10^{23} \text{ m}^{-3}$  was used in (7) for evaluating the trap concentration ( $P_0$ ) per unit energy range at the valence band edge and yields  $P_0 = 2.79 \times 10^{43} \text{ J}^{-1} \text{ m}^{-3}$ . The derived values of  $N_t = 2.97 \times 10^{23} \text{ m}^{-3}$  and  $P_0 = 2.79 \times 10^{43} \text{ J}^{-1} \text{ m}^{-3}$  appear to be reasonable in that they are of the same order as those deduced by Gould [6, 7] (i.e.  $N_t = 4 \times 10^{23} \text{ m}^{-3}$  and  $P_0 = 3.86 \times 10^{43} \text{ J}^{-1} \text{ m}^{-3}$  for CuPc). The exponential trap distribution of (6) associated with SCLC is thus completely specified and is shown in Fig. 8.

The room temperature concentration  $p_0$  of holes in the valence band can be calculated using the ohmic characteristics of Fig. 4 (i.e. U = 10 V and  $J = 0.028 \times 10^{-2}$  A m<sup>-2</sup>) and by substituting the derived value of mobility in (4). The calculated value is  $p_0 = 1.60 \times 10^{18}$  m<sup>-3</sup>, which is one order higher than that deduced by Gould [6, 7] for CuPc samples. It is not clear whether this difference is a property of PbPc or arises from different purification and preparation methods.

In the space-charge-limited region the average charge density Q is given by [28]

$$Q \approx e N_{\rm v} \left(\frac{\varepsilon U}{e d^2 N_{\rm t} k T_{\rm t}}\right)^l; \qquad l = \frac{T_{\rm t}}{T}.$$
 (12)

Substituting the derived values of parameters involved in (12), the estimated values of charge density Q range from 0.285 to 18.7 C m<sup>-3</sup> over the applied voltage range 20 to 100 V for the 5.55  $\mu$ m thick PbPc sample.

The conductivity of a semiconductor bar containing a uniform density of holes is given by

$$\sigma = e p_0 \mu \,. \tag{13}$$

Substituting the values of  $p_0$  and  $\mu$ , the calculated value of conductivity is  $\sigma = 1.55 \times 10^{-10} \text{ S m}^{-1}$ . Iyechika et al. [34] have reported that the electrical conductivity is very much lower in triclinic PbPc. The room temperature conductivity of triclinic PbPc is only about  $10^{-10} \text{ S m}^{-1}$  while that of monoclinic PbPc is about  $10^{-2} \text{ S m}^{-1}$ . Van Ewyk [35] evaluated the resistivity of PbPc as  $\varrho = 3 \times 10^8 \Omega \text{ m}$ , which would mean that  $\sigma = 3.33 \times 10^{-9} \text{ S m}^{-1}$ .

## 3.4 Determination of thermoelectric power

The Seebeck effect in PbPc at the vacuum pressure of  $\approx 10^{-6}$  Torr was investigated by measuring the small voltages  $\Delta U$  which developed across (001) faces of specimens bearing gold electrodes when a temperature difference  $\Delta T$  was established across them. Two calibrated chromal/alumel thermocouples were connected to the device, one on each side, for the measurement of the temperature difference  $\Delta T$ . This experiment was carried out to establish the sign of the majority carriers and to ascertain whether abrupt changes in this occurred as the temperature of the specimen was increased.

The smooth curves of Seeback coefficient  $S = \Delta U/\Delta T$  versus T are shown in Fig. 9. The observed values of S ranging from 0.017 to 0.115 mV K<sup>-1</sup> were obtained at a temperature difference  $\Delta T$  of 29 to 45 K (curve a in Fig. 9) and 0.005 to 0.095 mV K<sup>-1</sup> were taken at  $\Delta T = 9$  to 21 K (curve b in Fig. 9). The values of S are positive over the entire temperature range 315 to 470 K indicating p-type conduction in PbPc. The observed values of S are consistent with available literature values; +0.05 mV K<sup>-1</sup> for single CuPc [36] and 0.01 to 0.2 mV K<sup>-1</sup> for PbPc [37]. Curve c in Fig. 9 shows a plot at a temperature difference of 1 K and yields S = 0.1 to 56 mV K<sup>-1</sup>.



Fig. 9. The Seebeck coefficient S (thermoelectric power) of PbPc as a function of temperature; plots of different samples at temperature differences of 9 to 21 K (a) and 29 to 45 K (b) and at a temperature difference of  $\Delta T = 1$  K (c)

## 4. Conclusions

PbPc differs from the majority of metal phthalocyanines in having a non-planar molecule with two principal polymorphs. These are monoclinic and triclinic forms, characterised by different molecular stacking arrangements which in turn differ from the  $\alpha$  and  $\beta$  polymorphic phases of the Pc's with planar molecules (e.g. CuPc). The present measurements indicate that despite these structural differences the general electrical characteristics, including ohmic contacts with Au, and a conduction transition from ohmic to SCLC, are similar to observations for CuPc. Thus the basic conduction mechanisms seem to be the same as for CuPc and the specific differences in the electrical behaviour of PbPc-based gas sensors compared with other Pc's will clearly depend on other factors. These will include purity and preparation conditions, substrate parameters, thermal treatment, and gaseous exposure history. The effect of some of these is evident by comparing the present results with those of Mockert et al. [38] who deposited PbPc layers in UHV onto single-crystal  $SiO_2$  and Al<sub>2</sub>O<sub>3</sub> substrates. They generally obtained perfectly ohmic behaviour, but were unable to reproduce the switching effects which had been previously observed by Frauenheim et al. [39] in similar studies. It is apparent that systematic studies of structural and thermal factors will be necessary before the electrical properties of PbPc films can be fully characterised.

#### Acknowledgements

The authors would like to acknowledge the helpful advice of Dr. B. K. Jones. One of us (A. A.) would like to thank the Government of Pakistan for financial support.

### References

- [1] J. D. WRIGHT, Progr. Surface Sci. 31, 1 (1989).
- [2] P. B. M. ARCHER, PhD Thesis, University of Kent (1987).
- [3] T. A. JONES and B. BOTT, Sensors and Actuators 9, 27 (1986).
- [4] R. A. COLLINS and K. A. MOHAMMED, J. Phys. D 21, 154 (1988).
- [5] P. B. M. ARCHER, A. V. CHADWICK, J. J. MIASIK, M. TAMIZI, and J. D. WRIGHT, Sensors and Actuators 16, 379 (1989).
- [6] R. D. GOULD, Thin Solid Films 125, 63 (1985).
- [7] R. D. GOULD, J. Phys. D 9, 1785 (1986).
- [8] A. K. HASSAN and R. D. GOULD, J. Phys. D 22, 1162 (1989).
- [9] A. K. HASSAN and R. D. GOULD, J. Phys. Condens. Matter 1, 6679 (1989).
- [10] B. BOTT and T. A. JONES, Sensors and Actuators 9, 19 (1986).
- [11] WU RUIHUA and T. A. JONES, Sensors and Actuators B 12, 33 (1990).
- [12] R. A. COLLINS and K. A. MOHAMMED, Thin Solid Films 145, 133 (1986).
- [13] A. WILSON and R. A. COLLINS, Sensors and Actuators 12, 389 (1987).
- [14] R. A. COLLINS and A. BELGHACHI, Mater. Letters 8, 349 (1989).
- [15] R. A. COLLINS, K. R. STRICKLAND, M. J. JEFFERY, K. DAVIDSON, and T. A. JONES, Mater. Letters, in the press.
- [16] A. BELGHACHI and R. A. COLLINS, J. Phys. D 23, 223 (1990).
- [17] H. PAGNIA and N. SOTNIK, phys. stat. sol. (a) 108, 11 (1988).
- [18] P. J. DUNNE and R. A. COLLINS, Internat. J. Electronics 68, 373 (1990).
- [19] A. K. GOSH and T. FENG, J. appl. Phys. 44, 2781 (1973).
- [20] S. M. SZE, Physics of Semiconductor Devices, J. Wiley, New York 1981 (p. 249).
- [21] A. SUSSMANN, J. appl. Phys. 38, 2738 (1967).
- [22] C. HAMANN, phys. stat. sol. 26, 311 (1968).
- [23] W. MYCIELSKI, B. ZIOLKOWSKA, and A. LIPINSKI, Thin Solid Films 91, 335 (1982).
- [24] R. D. GOULD and M. S. RAHMAN, J. Phys. D 14, 79 (1981).
- [25] J. C. SIMMONS, G. S. NADKARNI, and M. C. LANCASTER, J. appl. Phys. 41, 538 (1970).
- [26] Y. MACHIDA, Y. SAITO, A. TAOMATO, K. NICHOGI, K. WARAGI, and S. ASAKAWA, Japan. J. appl. Phys. 28, 297 (1989).
- [27] A. TWAROWSKI, J. chem. Phys. 77, 4698 (1982).
- [28] M. A. LAMPERT, Rep. Progr. Phys. 27, 329 (1964).
- [29] G. A. CHAMBERLAIN and P. J. COONEY, Chem. Phys. Letters 66, 88 (1979).
- [30] D. F. BARBE and C. R. WESTGATE, J. chem. Phys. 52, 4046 (1970).
- [31] F. W. SCHMIDLIN and G. G. ROBERTS, Phys. Rev. B 9, 1578 (1974).
- [32] J. L. HARTKE, Phys. Rev. 125, 1177 (1962).
- [33] C. R. WESTGATE and G. WARFIELD, J. chem. Phys. 46, 537 (1967).
- [34] Y. IYECHIKA, K. YAKUSHI, I. IKEMOTO, and H. KURODA, Acta. cryst. B38, 766 (1982).
- [35] R. L. VAN EWYK, A. V. CHADWICK, and J. D. WRIGHT, J. Chem. Soc. Faraday Trans. I 76, 2194 (1980).
- [36] P. E. FIELDING and F. GUTMANN, J. chem. Phys. 26, 411 (1957).
- [37] H. YASUNAGA, K. KOJIMA, H. YOHDA, and K. TAKEYA, J. Phys. Soc. Japan 37, 1024 (1974).
- [38] W. MOCKERT, D. SCHMEISSER, and W. GOPEL, Sensors and Actuators 19, 159 (1989).
- [39] TH. FRAUENHEIM, C. HAMANN, and M. MÜLLER, phys. stat. sol. (a) 86, 735 (1984).

(Received September 27, 1990)