

## Conduction in lead phthalocyanine thin films with aluminium electrodes

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Electronic conduction has been investigated in evaporated lead phthalocyanine thin films with aluminium electrodes. In contrast to previously investigated samples where the injecting electrode was a gold ohmic contact, these samples did not exhibit space-charge-limited conductivity, but showed carrier excitation *via* a field-lowering mechanism with a  $\log J \propto V^{1/2}$  current density-voltage ( $J - V$ ) characteristic. Both polarities showed two regions in the  $J - V$  characteristics having different slopes, leading to the conclusion that conduction is *via* Schottky and Poole-Frenkel emission at lower and higher voltages respectively. In the presence of air there was a *decrease* in conductivity, which was attributed to the effects of oxygen at the electrodes.

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### 1. Introduction

The phthalocyanines are a class of organic materials which are generally thermally stable and may be deposited as thin films by vacuum evaporation without dissociation. They exhibit semiconducting behaviour and their electrical conductivity is affected by the presence of various gases. Wright has reviewed the particular gas sensing properties of phthalocyanines to various gases [1] and Yasunaga *et al* [2] have described some of the effects of oxygen on the conductivity of lead phthalocyanine (PbPc).

Gas detectors based on several different phthalocyanine films have been developed. Clarisse *et al* [3] described active field-effect transistors (FETs) based on a diphthalocyanine thin film while Burr *et al* [4] used PbPc as the gate material for FETs. The sensitivity of the latter device was claimed to be less than 20 ppb to NO<sub>2</sub>. More recently a copper phthalocyanine (CuPc) gas sensor has been described in which the concentration of NO<sub>2</sub> in air may be derived from initial exposure measurements rather than requiring equilibrium conditions [5]. However the sensitivity did not extend below 1 ppm in this case.

Although the use of phthalocyanines for gas detection is well appreciated, the basic electrical conduction processes observed in these materials depend on many factors including the phthalocyanine species, the phase of the microcrystallites comprising the film, the film thickness and the electrode materials. One of us has recently reviewed the conduction properties of phthalocyanine thin films over a wide range of systems [6].

Among the conductivity types observed are space-charge-limited (SCL) conductivity, field-lowering effects such as the Schottky and Poole-Frenkel effects, hopping, tunnelling and diode-type conductivity. In PbPc films

ohmic and SCL conductivity have been observed, particularly where both electrodes are Au ohmic contacts [7]. In Au-PbPc-Al samples there are literature reports of both field-lowering behaviour [8,9] and also diode-type conduction [9]. In the case of the field-lowering behaviour Schottky emission was identified at lower voltages, having a Schottky depletion region of thickness 50 nm and a barrier height of 1 eV.

Poole-Frenkel emission was identified at higher voltages [8]. Similar results were also reported by Ahmad and Collins [9], although they interpreted their higher voltage results as Schottky emission. To the authors' knowledge there are no reports on the electrical properties of simple PbPc structures in which *both* electrodes are Al and where the conduction process might be expected to be the same for both polarities. In the present work such measurements have been made in order to further probe the nature of the Al/PbPc contact and to investigate the conduction mechanisms in this structure. Measurements on the effects of exposure to oxygen are also reported, as these are relevant to the use of PbPc films in gas sensing systems.

### 2. Experimental

The PbPc used in this study was synthesised using the Linstead technique [10]. The substrates were of Corning 7059 borosilicate glass and were thoroughly cleaned before insertion into the deposition chamber, after which they were subjected to ion bombardment cleaning for a period of 5 min. Al-PbPc-Al sandwich structures were sequentially evaporated at a pressure of  $1.3 \times 10^{-3}$  Pa or below onto the substrates at room temperature, to give an active sample area of  $1.2 \times 10^{-5}$  m<sup>2</sup>. Each substrate supported six such samples. Deposition rates and film thicknesses were monitored during deposition using a

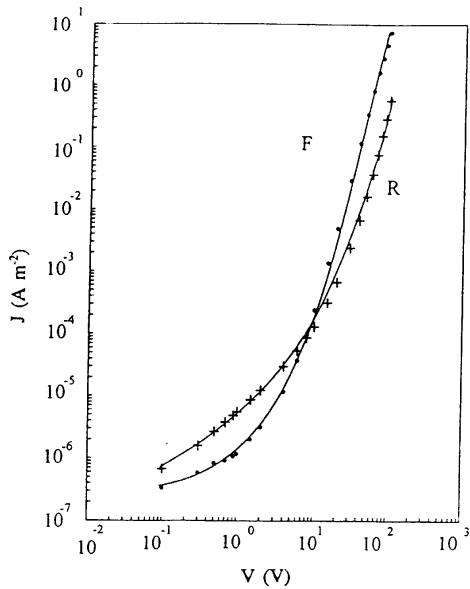


Figure 1. Dependence of current density on voltage for an Al-PbPc-Al sample under forward bias (F) and reverse bias (R) under vacuum.

quartz crystal system, and thickness was determined after deposition using a Planer Surfometer SF200 stylus instrument.

The Al electrodes were evaporated from a tungsten filament and deposited at a rate of 1 nm s<sup>-1</sup> to a thickness of typically 100 nm, while the PbPc was evaporated from a tantalum boat and deposited at a rate of 0.5 nm s<sup>-1</sup> to a thickness of 1 μm.

The electrical measurements were performed in a separate vacuum system, also maintained at room temperature and a pressure of less than 1.3 × 10<sup>-3</sup> Pa. Some measurements were made in air ambient. Current-voltage measurements were made using a Keithley 617 programmable electrometer with integral power supply. All samples were placed in the measurement chamber at least 24 hours before measurements were made, and kept in the dark, in order to eliminate photoelectric effects. Forward bias is defined as the situation when the top electrode is biased positively.

### 3. Results and discussion

#### 3.1 Current density-voltage characteristics

Fig. 1 shows a typical set of results of the dependence of current density *J* on applied voltage *V* for both forward (F) and reverse (R) polarities. This type of characteristic is in marked contrast to those observed in Au-PbPc-Au samples [7], where the characteristic has two regions. At lower voltages the slope of the logarithmic characteristic is 1 so that *J* ∝ *V* and the conductivity is ohmic; at higher voltages *J* ∝ *V*<sup>*n*</sup> where *n* ∼ 3.0 - 3.21, indicating SCL conductivity.

This type of conductivity is associated with the use

of ohmic contacts to the material. In the present case the forward-bias current density increases very slowly with voltage up to about 1.8 V, above which the increase is more rapid. The lower voltage region can no longer be treated as ohmic, as the slope is approximately 0.54. Above this voltage the slope approximates to 4.4. A similar trend is apparent for reverse bias, where the slopes are approximately 0.88 and 4.1 in the lower and higher voltage sections respectively.

The results were therefore analyzed in terms of the two field-lowering mechanisms, whose current density-voltage expressions are given by [11]

$$J = AT^2 \exp\left(-\frac{\Phi_S}{kT}\right) \exp\left(\frac{b_S V^{1/2}}{kTd^{1/2}}\right) \quad (1)$$

for the Schottky effect and by

$$J = J_0 \exp\left(\frac{b_{PF} V^{1/2}}{kTd^{1/2}}\right) \quad (2)$$

for the Poole-Frenkel effect. In these expressions *A* = 1.2 × 10<sup>6</sup> A m<sup>-2</sup> is the Richardson constant, *T* the absolute temperature, φ<sub>S</sub> the Schottky barrier height at the injecting electrode interface, *k* Boltzmann's constant, *d* the film thickness and *J*<sub>0</sub> (= σ<sub>0</sub>*F*) is the low-field current density. β<sub>S</sub> and β<sub>PF</sub> are respectively the Schottky and Poole-Frenkel field-lowering coefficients, which are related by

$$2b_S = b_{PF} = \left(\frac{e^3}{pe_r e_0}\right)^{1/2} \quad (3)$$

where *e* is the electronic charge, ε<sub>r</sub> the relative permittivity of the material and ε<sub>0</sub> the permittivity of free space. Since ε = ε<sub>r</sub>ε<sub>0</sub> = 3.54 × 10<sup>-11</sup> F m<sup>-1</sup> [7] the theoretical values of these coefficients are β<sub>S</sub> = 1.92 × 10<sup>-5</sup> eV m<sup>1/2</sup> V<sup>-1/2</sup> and β<sub>PF</sub> = 3.84 × 10<sup>-5</sup> eV m<sup>1/2</sup> V<sup>-1/2</sup>. In principle, therefore, the processes may be distinguished by determining a measured value of β from a plot of ln*J* against *V*<sup>1/2</sup>.

Figs. 2 and 3 show the dependence of log*J* on *V*<sup>1/2</sup> for the forward-bias and reverse-bias characteristics of Fig. 1. In both cases there are two linear regions. Values of β (Schottky or Poole-Frenkel) calculated from the lower voltage section of each plot are 6.1 × 10<sup>-5</sup> eV m<sup>1/2</sup> V<sup>-1/2</sup> (forward bias) and 6.9 × 10<sup>-5</sup> eV m<sup>1/2</sup> V<sup>-1/2</sup> (reverse bias). These values are 3.17 times the theoretical Schottky and 1.59 times the theoretical Poole-Frenkel value under forward bias. Under reverse bias the corresponding factors are 3.60 and 1.80. Previously several workers have interpreted lower-voltage data in terms of a Schottky depletion region of thickness *d*<sub>S</sub>, while assuming the theoretical value of β<sub>S</sub> in Eqn. (1) [8,9,12,13]. It can be shown that the depletion region thickness is then given by

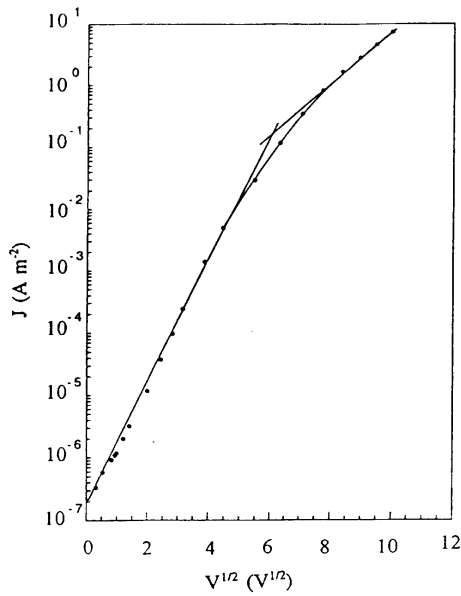


Figure 2. Forward bias characteristic of the sample of Fig. 1 showing a linear dependence of  $\log J$  on  $V^{1/2}$ . The lower voltage region was interpreted as Schottky emission with barrier height 1.03 eV and depletion region thickness 100 nm, while the higher voltage region was attributed to the Poole-Frenkel effect.

$$d_s = (\beta_s / \beta)^2 d \tag{4}$$

where  $\beta_s$  and  $\beta$  are the theoretical and measured values of the Schottky field-lowering coefficient respectively and  $d$  is the film thickness. This expression yields  $d_s$  values of 100 nm and 77 nm respectively for forward and reverse bias which are in reasonably good agreement with values of 50 nm measured in Au-PbPc-Al structures [8,9].

Using Eqn. (1) with  $T = 293$  K and the intercepts of the lower voltage sections on the  $J$  axis of Figs. 2 and 3 yields a value of the barrier height  $\phi_s = 1.03$  eV for both forward and reverse bias. Again this value is in good agreement with the values of 1 eV [8] and 1.11 eV [9] determined in Au-PbPc-Al structures.

Thus the lower voltage sections of the curves were ascribed to Schottky emission at the Al/PbPc interface. Additional evidence for the existence of Schottky barriers at this interface has previously been obtained from capacitance-voltage measurements [8] and from ac measurements [14].

region was attributed to the Poole-Frenkel effect.

In the higher voltage sections of Figs. 2 and 3 the calculated value of  $\beta$  is  $2.6 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$  (forward bias) and  $3.1 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$  (reverse bias). These values are reasonably close to the theoretical values of both  $\beta_s$  and  $\beta_{PF}$ . This is not inconsistent with the previous assignment of Poole-Frenkel behaviour in the higher voltage range in reverse-biased Au-PbPc-Al structures [8].

### 3.2 Effects of exposure to air

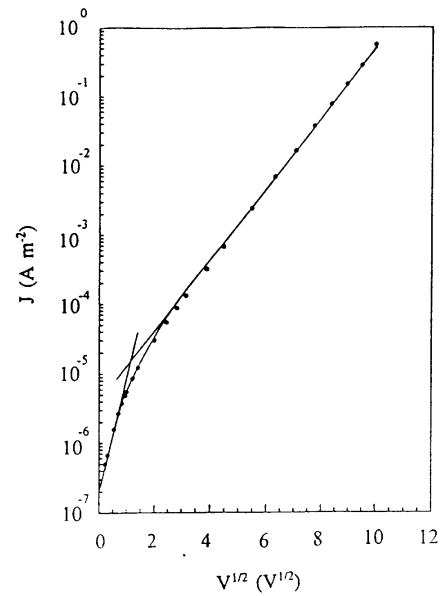


Figure 3. Reverse bias characteristic of the sample of Fig. 1 also showing a linear dependence of  $\log J$  on  $V^{1/2}$ . The lower voltage region was interpreted as Schottky emission with barrier height 1.03 eV and depletion region thickness 77 nm, while the higher voltage

Fig. 4 shows the dependence of  $J$  on  $V$  for a sample under forward bias under vacuum (a) and exposed to air (b). For lower voltages up to 2 V there is little difference in the current levels, but for higher voltage levels the  $J$  value is much higher for samples tested in vacuum than in air.

This is in direct contrast to samples having two Au electrodes where the oxygen enhances the conductivity by increasing the acceptor concentration. Although this effect is also likely to occur in the present samples, it is apparent that there is an additional effect peculiar to the electrode species used.

This is probably related to the formation of an interfacial region (possibly  $\text{Al}_2\text{O}_3$ ) which results in a further series impedance which reduces the current level.

Fig. 5 verifies that the current drawn is indeed very sensitive to the electrode characteristics. This shows the  $\log J - V^{1/2}$  characteristics of the same sample as in Fig. 4 in air for both forward bias (a) and reverse bias (b). A higher current density is observed for reverse bias than for forward bias even though the electrode configuration is symmetric. In this case the majority carriers (holes) are injected from the bottom electrode and the injection efficiency is likely to be higher than when they are injected from the top electrode, which may be more heavily degraded by the oxygen. The value of the field-lowering coefficient  $\beta$  calculated from the two curves is  $1.9 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$  (forward bias) and  $2.7 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$  (reverse bias). In the former case this is very close to the theoretical Schottky value, while in the latter it is intermediate between the Schottky and Poole-Frenkel values. This difference clearly indicates some asymmetry

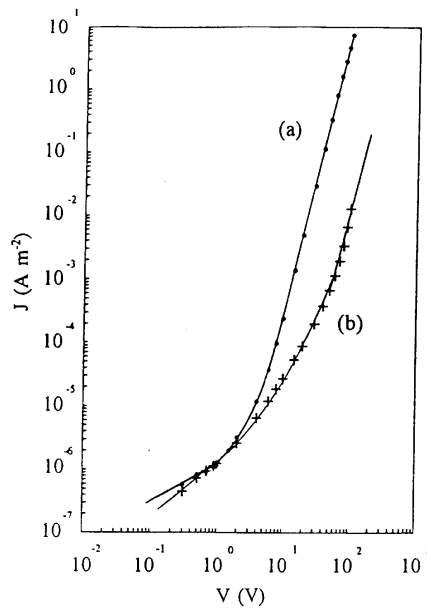


Figure 4. Dependence of current density on voltage for an Al-PbPc-Al sample under forward bias (a) under vacuum and (b) exposed to air. The lower current density when exposed to air was attributed to an interfacial region at one or both of the Al electrodes.

in the electrical properties, which is most likely dependent on potential barriers at the electrodes.

#### 4. Summary and conclusions

The electrical properties of PbPc thin film sandwich structures having two Al electrodes have been investigated. Samples showed field-lowering behaviour for both polarities, with the  $J$  -  $V$  characteristic exhibiting two regions in each case.

In the lower voltage region the behaviour was interpreted as Schottky emission with barrier height  $\phi_B = 1.03$  eV and depletion region thickness of typically 100 nm and 77 nm for forward and reverse bias respectively. This interpretation is consistent with earlier work on Al-PbPc-Au structures with hole injection at the Al electrode. In the higher voltage region Poole-Frenkel conductivity was indicated.

Samples showed higher current levels under forward bias when tested under vacuum than in air. This effect was related to the establishment of an interfacial region, resulting in an additional series impedance at one or both of the Al electrodes. It was also observed that a higher current density was drawn under reverse bias than under forward bias. It was suggested that this resulted from a higher injection efficiency for holes at the bottom electrode, which may be less heavily degraded by oxygen than the top electrode. It is clear that in sandwich-type samples it is unwise to assume symmetrical conductivity, even with electrodes of the same material.

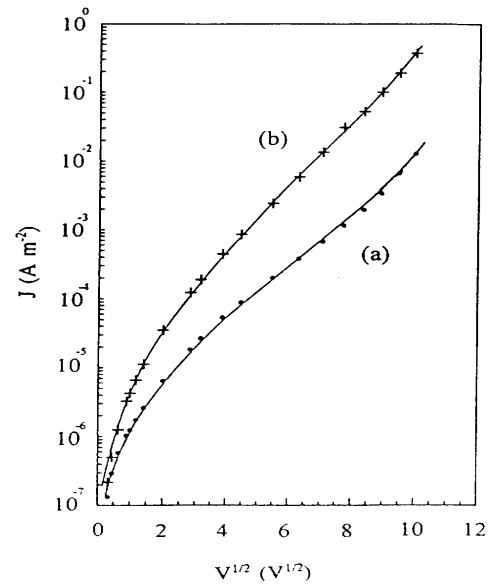


Figure 5. Dependence of current density for the sample of Fig. 4 under forward bias (a) and under reverse bias (b), both exposed to air. The lower current density under forward bias was attributed to a lower hole injection efficiency at the top electrode resulting from the oxygen exposure.

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