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Electrical conduction processes in as-deposited indium phthalocyanine chloride thin films using gold and aluminium electrode combination

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Abstract
Sandwich structures of the type (Au–InPcCl–Al) have been fabricated by successive vacuum deposition of indium phthalocyanine chloride (InPcCl) thin films and aluminium (Al) fingers onto Ohmic gold (Au) electrodes on glass substrates. Device characteristics of as-deposited Au/InPcCl/Al are obtained and found to show rectification properties. Current density–voltage characteristics under forward bias (aluminium electrode negative) are found to be due to Ohmic conduction at lower voltages. At higher voltages there is space charge limited conductivity (SCLC) controlled by an exponential trapping distribution above the valence edge. Transport properties of the material at ambient temperature have been obtained from the analysis of the samples in the Ohmic and SCLC regions. Under the reverse bias, Schottky emission is identified at lower voltages.

1. Introduction

Phthalocyanines (Pcs) are a class of organic compounds, having very high thermal and chemical stability, which are classified as p-type semiconductors characterized by low mobility and low carrier concentration [1]. They have potential advantages for use as active layers in electroluminescent devices [2], photovoltaics [3] and gas sensor devices [4], because they are easily processable in low cost and large area device fabrication. The basic electrical conduction processes observed in these materials depend on many factors including the phthalocyanine species, the film thickness, the film deposition temperature and the electrode materials [5]. The study of thin-film heterostructures of the metal/organic semiconductor/metal type gives useful information concerning the electrical conduction mechanism, transport properties, characteristics of metal–organic semiconductor interfaces etc [6–9]. Such information is of particular importance in the development of viable thin film devices. Among the various Pcs,

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indium phthalocyanine chloride (InPcCl) has received considerably less attention. Moreover, to the authors' knowledge there are no reports on the transport properties of as-deposited InPcCl. The object of this paper is to probe the electrical conduction processes of InPcCl sandwich structures using gold and aluminium electrodes. With most of the phthalocyanines, gold is found to form an Ohmic contact [1, 10, 11] and aluminium is found to form a blocking contact [12–14].

2. Experimental details

Indium phthalocyanine chloride (InPcCl) powder, procured from Aldrich Chemicals USA, is used as the source material. It is purified by the train-sublimation technique using nitrogen gas as a carrier [10, 14]. Sandwich samples are prepared by sequential vacuum thermal evaporation, using a 'Hind Hivac 12A4' evaporation plant at a base pressure of 1.3×10^{-3} Pa. For fabricating a three-layer structure, a thin layer of gold ($\sim$100 nm) is first vacuum deposited on pre-cleaned glass substrates, from an electrically heated tungsten spiral. Over this an InPcCl layer is deposited using an electrically heated molybdenum boat. Finally, an aluminium layer of thickness $\sim$100 nm is deposited using another tungsten spiral. All three layers are coated in a single vacuum cycle. The thickness of the films is measured using the Tolansky's multiple-beam interference technique [15]. The thickness of the InPcCl layer of the sandwich structure and its effective area are 230 ± 5 nm and 2.5×10^{-5} m^2 respectively. Current–voltage measurements are performed using a 'Keithley' electrometer (model No 617). The temperature of the sample is measured using a Chromel–Alumel thermocouple placed in close proximity to the specimen. To avoid contamination, measurements are performed in a subsidiary vacuum of 1.3×10^{-1} Pa. All the measurements are performed with the samples in dark to avoid any photoelectric effect. The capacitance is measured with a 'Hioki 3532 LCR Hi-tester'.

3. Results and discussion

The current–voltage (I–V) characteristics of the Au–InPcCl–Al device are shown in figure 1. The forward bias direction corresponds to the negative Al (top) electrode of the device. The behaviour as shown in figure 1 is due to the low work function of Al and high work function of Au electrodes and the p-type conduction of InPcCl. The electrode having the high work function forms an Ohmic contact with the InPcCl layer.

Detailed information about the transport mechanism through the organic thin film can be obtained from the analysis of forward current density–voltage (J–V) characteristics. The forward J–V characteristics are shown in figure 2. There are two distinct regions. At low voltages the slope of the log J versus log V plot is approximately equal to unity (0.95) and at higher voltages, above a well defined voltage V_X, the slope is 3.9. These values of slopes indicate Ohmic conductivity at lower voltages and SCLC mechanism controlled by an exponential distribution of traps at higher voltages. Shown in figure 3 is the thickness dependence of forward current density J at room temperature. The Ohmic dependence (slope of -1) indicates a good Ohmic contact exists.

The current density J within the Ohmic region is given by [16]

$$J = ep\mu\left(\frac{V}{d}\right) \tag{1}$$

where p is the concentration of thermally generated holes in the valence band, e is the electronic charge, μ is the hole mobility, V is the applied dc voltage and d is the thickness of the InPcCl

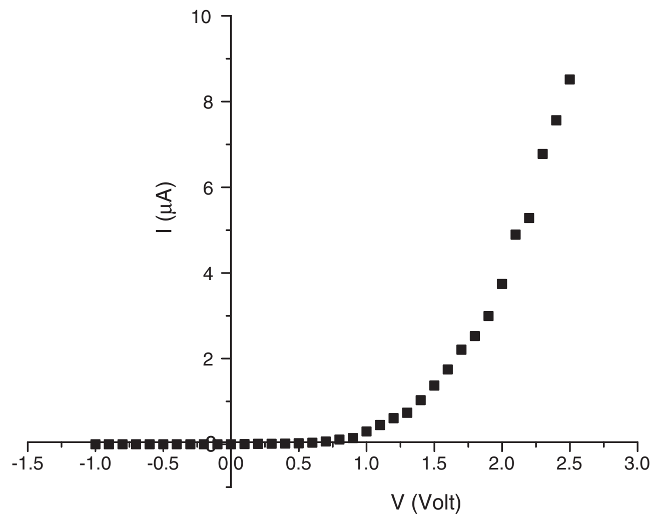

Figure 1. Forward and reverse current–voltage characteristics of the Au–InPcCl–Al device at room temperature.

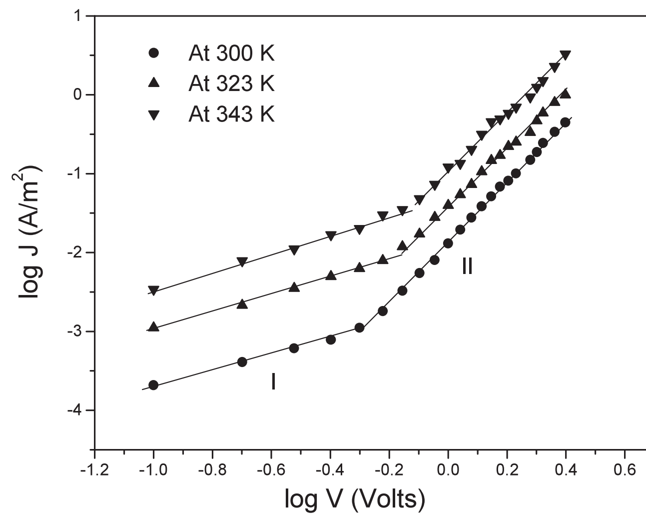

Figure 2. Plot of log J against log V at room temperature (300 K), 323 and 343 K. Region I corresponds to Ohmic conductivity and region II corresponds to SCLC.

thin film. Equation (1) can be written as

$$J = e\mu N_V \left(\frac{V}{d}\right) \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

where N_V is the effective density of states in the valence band, k is the Boltzmann constant, T is the absolute temperature and E_a is the activation energy. From the plot of ln J against $1/T$ for $V = 0.25$ V (figure 4), the activation energy $E_a = 0.59$ eV.

It is observed that whenever traps, distributed exponentially in energy, are governing the conduction in electrical materials, a Meyer–Neldel observation is expected [17]. Therefore, Arrhenius plots are straight lines that pass through or converge to a common point not coinciding

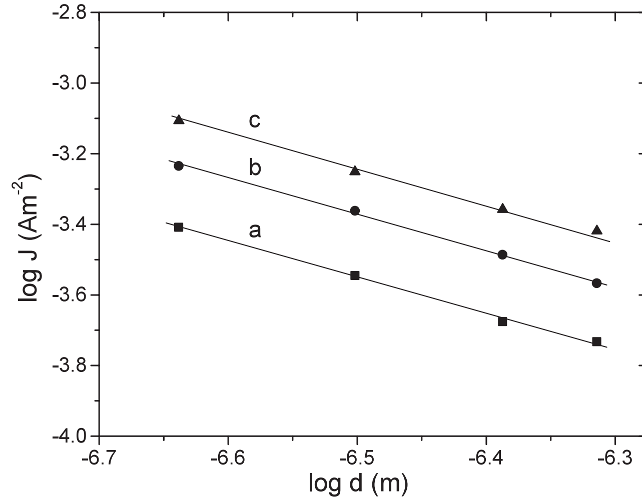

Figure 3. Dependence of J on thickness (d) for various applied voltages (at room temperature) in the Ohmic region: (a) 0.2 V, (b) 0.3 V, and (c) 0.4 V.

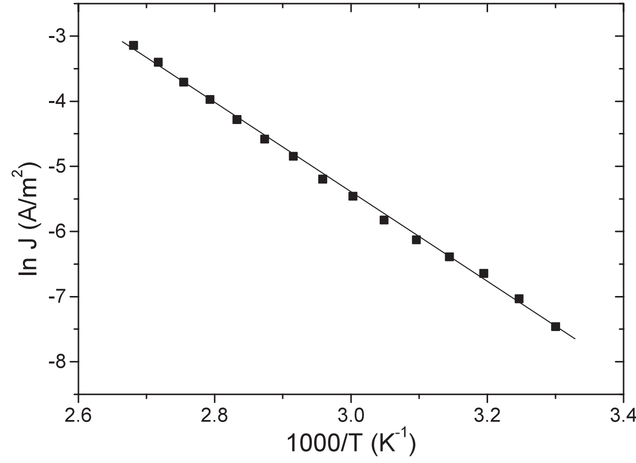

Figure 4. Variation of ln J with $1000/T$ in the Ohmic region.

with infinite temperature. The temperature dependence and the interdependence of activation energy and pre-exponential factor, as proposed by the Meyer–Neldel rule [18], have neither been experimentally tested nor been verified in our sample and thus the study presented in this paper is done by neglecting the temperature dependence and Meyer–Neldel rule.

Within the SCLC region the current density J is given by [14, 19]

$$J = e\mu N_{\mathrm{V}}\left(\frac{\varepsilon_{\mathrm{r}}\varepsilon_0}{ePkT_{\mathrm{t}}}\right)^L \frac{V^{L+1}}{d^{2L+1}} \tag{3}$$

where P is the trap density per unit energy range at the valence band edge, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_{r} is the relative permittivity of the sample ($\varepsilon_{\mathrm{r}} = 3.12$ is obtained from capacitance measurement) and L is the ratio T_{t}/T where T is the ambient temperature and T_{t} is the temperature parameter describing the exponential trapping distribution.

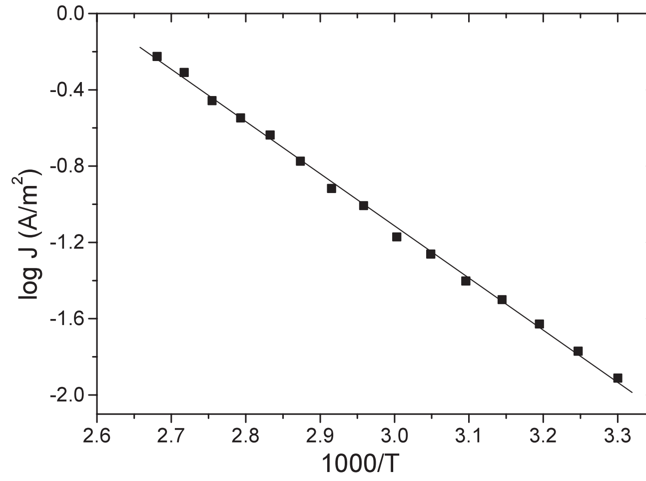

Figure 5. Variation of log J with $1000/T$ in the SCLC region.

The exponential trap distribution may be described in terms of T_t as [14, 19]

$$P_{(E)} = P\exp\left(\frac{-E}{kT_t}\right) \tag{4}$$

where $P_{(E)}$ is the trap concentration per unit energy range at an energy E above the valence band edge. The total concentration of the traps is given by [14, 19]

$$N_t = PkT_t. \tag{5}$$

From equation (3), a slope of 3.9 implies that $L = 2.9$ and thus the temperature parameter $T_t = 870$ K for $T = 300$ K. Figure 5 shows the variation of log J versus $1/T$ for $V = 1.0$ V (corresponding to region II in figure 2). For the temperature range within which the sample is investigated, the characteristics show quite a linear segment. The slope of this line is given by [16, 19]

$$S = T_t \log\left(\frac{\varepsilon_0\varepsilon_r V}{ed^2 N_t}\right) \tag{6}$$

from which the value of N_t is determined and is equal to 4.14×10^{24} m^{-3}. A trap concentration ranging from 10^{22}–10^{25} m^{-3} is found in phthalocyanine thin films [10, 20, 21]. The trap density per unit energy range at the valence band edge, $P = 3.45 \times 10^{44}$ J^{-1} m^{-3}, is obtained from equation (5). The intercept on the log J axis is given by

$$\log J_0 = \log\left(\frac{e\mu N_V V}{d}\right). \tag{7}$$

J_0 represents the current density at infinite temperature ($1/T = 0$) and gives μN_V. Assuming a temperature independent $N_V = 10^{27}$ m^{-3} [14, 16], the as-measured mobility $\mu = 2.87 \times 10^{-8}$ m^2 V^{-1} s^{-1}. Here, it is to be noted that a temperature and field dependent mobility is observed in several organic materials. But this paper does not contain a study on the temperature and field dependence of mobility.

The change-over from Ohmic to SCLC conduction takes place at a particular voltage V_x, known as the transition voltage, which is given by [16]

$$V_x = \left(\frac{p}{N_V}\right)^{\frac{1}{L}} \frac{eN_t d^2}{\varepsilon_0\varepsilon_r}. \tag{8}$$

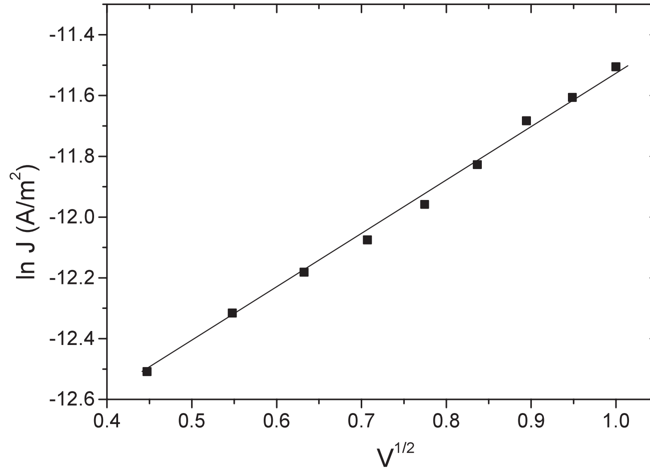

Figure 6. Reverse bias characteristics of the device.

Figure 2 indicates an increase in V_x with increase of temperature of the sample. At the ambient temperature $V_x = 0.5$ V. Using equation (8), the thermally generated carrier concentration of holes (p) at room temperature is 1.3×10^{17} m^{-3}.

The reverse bias I–V characteristics give information about the properties of the metal–semiconductor contact. Figure 6 shows the reverse bias data plotted in the form of ln J against $V^{1/2}$. The linear plot can be analysed in terms of the two field-lowering mechanisms, whose current density–voltage expressions are given by [22, 23]

$$J = A^* T^2 \exp\left(\frac{-\phi}{kT}\right) \exp\left(\frac{e\beta_{\mathrm{S}} V^{1/2}}{kTd^{1/2}}\right) \tag{9}$$

for the Schottky effect and by

$$J = J_{\mathrm{PF}} \exp\left(\frac{e\beta_{\mathrm{PF}} V^{1/2}}{kTd^{1/2}}\right) \tag{10}$$

for the Poole–Frenkel effect. In these expressions $A^* = 1.2 \times 10^{-6}$ A m^{-2} is the Richardson constant, T is the absolute temperature, ϕ is the Schottky barrier height at the injecting electrode interface, k is the Boltzmann constant, d is the film thickness and J_{PF} is the low-field current density. β_{S} and β_{PF} are respectively the Schottky and Poole–Frenkel field-lowering coefficients, which are related by [22]

$$2\beta_{\mathrm{S}} = \beta_{\mathrm{PF}} = \left(\frac{e}{\pi\varepsilon_0\varepsilon_{\mathrm{r}}}\right)^{1/2} \tag{11}$$

where e is the electronic charge. This gives $\beta_S = 2.15 \times 10^{-5}$ eV m$^{1/2}$ V$^{1/2}$ and $\beta_{\mathrm{PF}} = 4.3 \times 10^{-5}$ eV m$^{1/2}$ V$^{1/2}$. The value of β obtained from the slope of figure 6 is 2.23×10^{-5} eV m$^{1/2}$ V$^{1/2}$. This is in close agreement with the value of β_{S} obtained from equation (11). Thus in the case of the field-lowering behaviour, Schottky emission is identified for the voltage range in which the sample is studied. From the intercept on the ln J axis and using equation (9), the Schottky barrier height $\phi = 1.0$ eV has been obtained. Conduction by Schottky emission was also observed in the In/C1AIPc/1TO device [22] and in the A1/ZnPc/Au device [24] at low fields.

4. Conclusion

Fairly good rectification is observed in the device. Under forward bias, the electrical characteristics of as-deposited InPcCl thin films show Ohmic conduction at low voltages and space-charge limited conduction controlled by an exponential distribution of traps above the valence band edge at higher voltages. The transport parameters, derived at room temperature, are consistent with the reported values for other Pcs. Under reverse bias, Schottky emission is detected with a potential barrier $\phi = 1.0$ eV.

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