Electrical properties of hybrid phthalocyanines thin films using gold and lead electrodes

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Abstract. The electrical properties of mixed copper phthalocyanine (CuPc) and nickel phthalocyanine (NiPc) thin films devices with gold and lead electrodes have been investigated. The two phthalocyanines were co-evaporated and deposited on to a pre-cleaned glass substrate by thermal evaporation technique at room temperature. By the co-sublimation technique an integrated phthalocyanine sample was prepared. At low voltages the film showed an ohmic conduction whereas at higher voltage levels the conduction mechanisms were dominated by space charged limited conduction (SCLC). The value of mobility of holes were calculated as $\mu = 3.1 \times 10^{-8}$ m^2 V^{-1} s^{-1} which is lower for the mixed phthalocyanines whereas the trap concentrations $N_{t(e)} = 8.06 \times 10^{25}$ m^{-3} have increased in the SCLC region. Further the reverse conduction mechanisms have also been investigated. From the current limitations in the reverse condition a strong rectifying behaviour was evident.

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1 Introduction

Phthalocyanines are a class of organic semiconductors which have attracted considerable interest during the past few years. Because of its low cost and high thermal and chemical stability organic thin films were used in a variety of applications. They comprise of both metal free phthalocyanine, which contain two hydrogen atoms in the centre of the molecule and also the various metal substituted forms where the hydrogen atoms were replaced by a single metal atom. In the last two decades there has been considerable interest in the study of the electrical and optical properties of both types of phthalocyanine [1–3]. Phthalocyanine were widely used as gas sensors [4] liquid crystal colour display systems and photovoltaic devices [5,6]. The light absorbing properties of the phthalocyanine in the visible and in the infrared regions have attracted considerable attention in recent years because of the current interest in the conversion of solar to electrical energy [7] the electrical, optical and structural properties of many of these thin films prepared from different techniques have already been reported [8,9]. The electrical properties of these organic thin films largely depend on the evaporation rate, doping concentration, substrate temperature and post evaporation annealing [10,11]. The conduction mechanisms of organic semiconducting thin films depend on several factors such as the metallic contact to the semiconductor either an ohmic or blocking, the order of applied voltages across the film and its temperature [12,13]. Gold and silver electrodes have proved to be an effective ohmic contact to this type of materials whereas aluminium and indium were found to be blocking electrodes to many phthalocyanines [14,15]. Further the presence of oxygen [16] may also influence the conduction mechanisms in the organic thin films. The information of the barrier height at the interface between the electrodes and the organic layer is of significant importance for the study and fabrication of the organic semiconductor devices. It was reported earlier that the doping of organic semiconductors also [17] increase the order of conductivity considerably. There have been only few studies on mixed phthalocyanines with gold-lead electrode combination. In the present work the electrical properties of sandwiched device of the mixed copper phthalocyanine and nickel phthalocyanine with gold and lead electrodes have been investigated.

2 Experimental details

Pure phthalocyanine powders from Sigma-Aldrich Co Ltd were the base materials for the present study. With the help of a sensitive electronic balance 50 mg of copper phthalocyanine and 50 mg of nickel phthalocyanine were

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carefully weighed up. The two phthalocyanines were evaporated simultaneously from two tantalum boats which were kept side by side under a vacuum of approximately 10^{-5} torr. In order to get a uniform and fair mixing of the two phthalocyanines, the mixed vapour was passed through a tungsten helix filament, which was kept just above the boats. An additional power supply was used for heating this filament. Thin films of mixed phthalocyanines were deposited onto a pre-cleaned glass substrate, which was previously deposited with a gold film of about 50 nm thickness as the bottom electrode. During the evaporation process the pressure was kept steady by a diffusion pump backed by oil sealed rotary pump. The evaporation rate and the evaporation time were well monitored to get the different sample films with uniform thickness and with the two phthalocyanines almost in equal proportions. In order to get a multi layer structure over the organic layer, finally a lead top contact layer was also deposited from a tungsten coil. The thickness of this lead electrode later was found to be approximately 60 nm. Using a monochromatic light from a sodium vapour lamp the arrangement produces an interference pattern for the Fizeau fringes. From the fringe shift, thickness of the electrodes and the organic layers were measured by Tolansky's multiple beam interference technique [18]. To ensure the films of nearly equal proportions of the two phthalocyanines, samples that were kept very close and just above the boats were only used for study and further measurements. It was reported earlier from our lab [19,20] that the electrical and optical properties of phthalocyanine thin films very much depend on the substrate temperature, evaporation rate, annealing, film thickness and doping concentrations. Electrical conductivity measurements have been performed by a stabilized power supply and a Kethley programmable electrometer in a subsidiary vacuum system at a pressure of approximately 10^{-3} torr. Keeping the gold electrode as positive for the forward bias condition, current was measured for the different values of applied voltages ranging from 0 V to 10 V. Dependence of current in the forward bias and reverse bias for different applied voltage at room temperature has been measured. The forward current at a constant voltage of 0.3 V, 3.0 V, 6.0 V have been also measured in the 300–350 K temperature range. Temperature was measured by means of chromel/alumel thermocouple. In order to determine the value of the permittivity of the organic layer the capacitance of the device was also measured using a LCZ meter for different film thickness.

3 Results and discussion

There are various conduction methods and hence their corresponding theories depend upon the different materials used as the electrical contacts to the organic layer. In this paper the forward bias direction corresponds to the situation when the gold electrode was made positive. The thickness of the organic layer was measured as 800 nm and with an active area of 1.8×10^{-4} m^2. Figure 1 is the current density (J)-voltage (V) characteristics of the sandwiched device of gold-mixed Pc-lead sample measured in
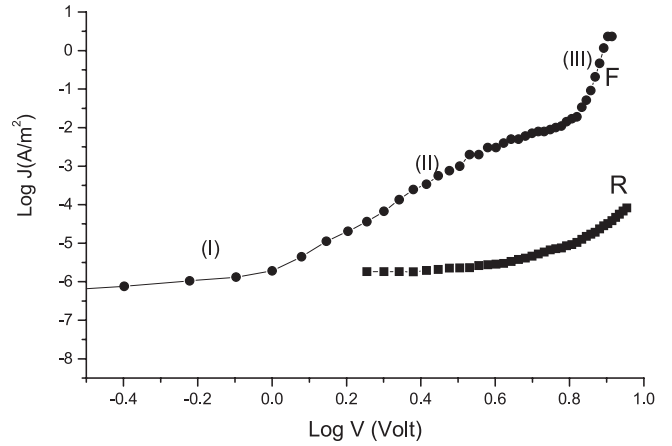

Fig. 1. J–V characteristics of the CuPc&NiPc mixed sample. F-Forward bias R-Reverse bias.

the voltage of 0.1 to 10 V range. The current was measured continuously varying the bias and interrupting the bias between each voltage step, but in both the cases yield the same results. In general, the J–V characteristics of the device is asymmetrical and the slope of the graph implies that the conduction mechanisms were different at the different voltage levels. From the order of the slopes it was identified that there are two distinct conduction processes involved. In the low voltage range up to 1 V the slope of the graph is in the order of unity and hence taken as an ohmic conduction between the organic layer and the electrodes. The extent of current in the low voltage region of mixed phthalocyanines was showing a significant deviation from its individual counterparts. This may be due to a change in the work function of the mixed phthalocyanines and may be due to increased p type conduction. The current density J within the ohmic region was described by the following equation

$$J = P_0 \, e\mu \frac{V}{d} \tag{1}$$

where e the electronic charge, μ the hole mobility, V the applied voltage across the film, d the thickness of the organic film and P_0 is the concentration of thermally generated holes in the valance band which given by

$$P_0 = N_v \exp\left(-\frac{E_f}{kT}\right) \tag{2}$$

where E_f is the position of the Fermi level above the valance band edge and the N_v the density of states in the valance band. Substituting the value of P_0 in equation (1)

$$J = N_v \, e\mu \, \frac{V}{d} \, \exp\left(-\frac{E_f}{kT}\right). \tag{3}$$

The value of $N_v = 10^{27}$ m^{-3} which corresponds to approximately one electronic state per molecule. Since this value of N_v was used for the pure Cu Pc and Ni Pc [21] the same value of N_v has been adopted for the mixed Pc in our calculations also. Figure 2 is the plot of Log J against
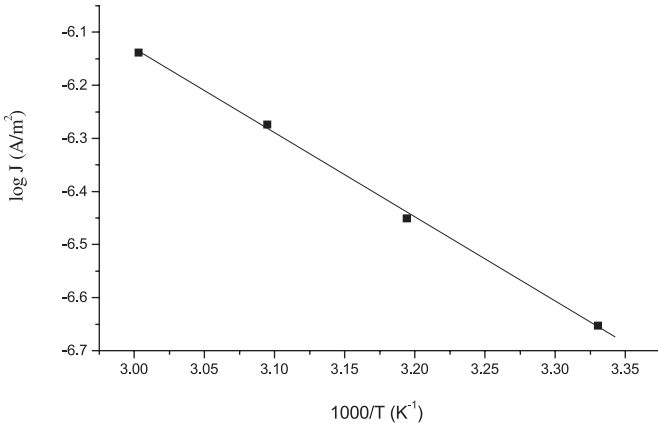
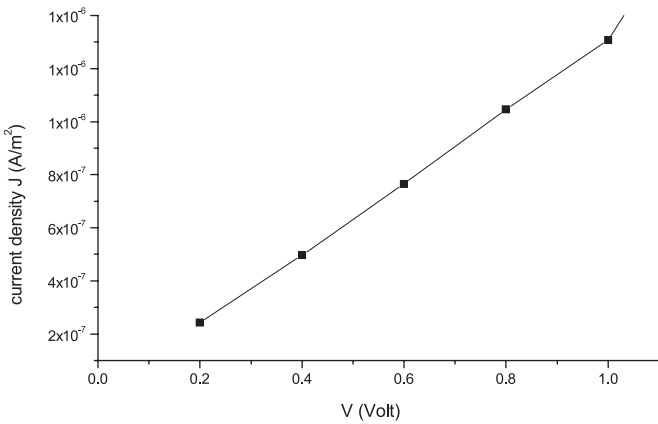**Fig. 2.** Variation of log J with $100/T$ in the ohmic region.

Fig. 3. J–V characteristics of mixed phthalocyanine diode device in the ohmic region.

Fig. 4. Variation of capacitance with inverse thickness.

$1000/T$ in the ohmic region in the 300–350 K temperature range at 0.3 V. The graph is almost a straight line where slope of the line the yields the value of E_f and the intercept will provide the value of the mobility of holes μ which were obtained as $E_f = 0.41$ eV and $\mu = 3.1 \times 10^{-8}$ m^2 V^{-1} s^{-1}. The value E_f suggests a shift in the Fermi level towards the valance edge and the value of mobility is lowered. Figure 3 is the J–V characteristics of the sample in the ohmic region that were re plotted. From the slope and using equation (1) the value $P_0 = 1.61 \times 10^{13}$ m^{-3} was obtained. These parameters in the ohmic region were at variance from the range of previously reported values of pure Ni Pc by Gould [22]. This difference may be related to the non uniform field within the mixed organic layer. At higher voltages in Figure 1 the slope of the J–V characteristics for the segment (II) and segment (III) are 2 and more suggesting that the current conduction is that of a space charged limited conduction (SCLC) which is characterized by a power law dependence in the form

$$J \alpha V^n \tag{4}$$

where 'n' is an index which has the values ≥ 2. The numerical value of this index was found to be associated with the nature of traps within the forbidden gap, the sample temperature and the bias direction. For the seg-
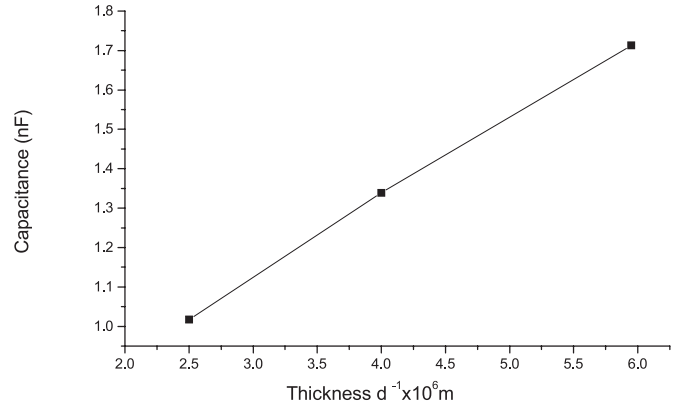
ment (2) of Figure 1 the slope is nearly 2 which suggests that the conduction is an SCLC charactistized by a single trap level situated at an energy level E_t above the valance band edge. The current density in this region was described by Rose [23]

$$J = \frac{9}{8}\varepsilon\mu\theta\frac{V^2}{d^3} \tag{5}$$

where θ measure of the ratio of free charges to trapped charges and

$$\theta = \frac{N_v}{N_{t(s)}}\exp\left(-\frac{E_t}{kT}\right) \tag{6}$$

where $N_{t(s)}$ is the total trap concentration at the energy level E_t. Hence

$$J = \left(\frac{9}{8}\right)\varepsilon\mu\frac{N_v}{N_{t(s)}}\frac{V^2}{d^3}\exp\left(-\frac{E_t}{kT}\right) \tag{7}$$

where ε and μ are the permittivity and the carrier mobility of the mixed phthalocyanines.

In order to find the permittivity of the mixed organic film the capacitance of a sandwich layer of the films were measured with different film thickness [24]. The effective value of the capacitance of the device was given by

$$C = \frac{\varepsilon_0\varepsilon_r\ A}{d} + Cp, \tag{8}$$

where ε_0 is the permittivity of free space and ε_r is the permittivity of organic layer C_p is a constant capacitance due to the instrument or the edge effects. The graph of capacitance C against inverse of thickness yields a linear plot and the slope of the curve is equal to $\varepsilon_0\varepsilon_r A$. Figure 4 shows the variation of capacitance of the films with the inverse of thickness at a constant frequency of 1 kHz. From the slope of the curve using equation (9) the absolute permittivity was calculated as 1.2×10^{-11} F/m. This value is slightly lower from the value of pure Cu Pc but comparable with the value of pure Ni Pc films which were reported earlier [14,19]. The lower value of the permittivity may be due to the lack of non-uniformity and low packing density of films. Figure 5 is the plot of Log J with
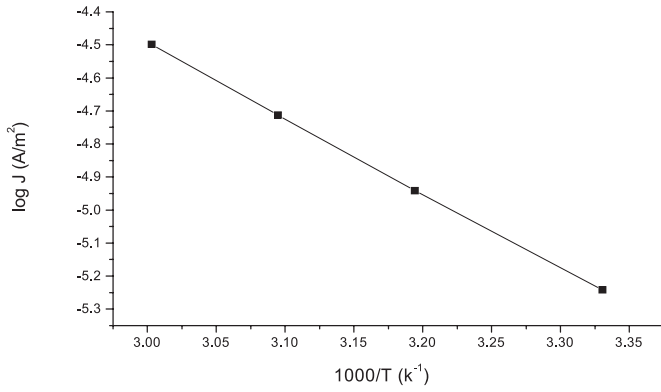
Fig. 5. Log J vs. $1000/T$ of segment (II) in the SCLC region at 3 V.

Fig. 6. Variation of Log J with $V^{1/2}$ for reverse bias region.

$1000/T$ in the segment (II) of the SCLC region, the slope and the intercept of this graph yield the values of E_t and $N_{t(s)}$. Using the values of N_v, ε and μ in equation (7) gives $E_t = 0.54$ eV and $N_{t(s)} = 2.23 \times 10^{23}$ m^{-3}.

The value $N_{t(s)}$ falls within the range of the values of Ni Pc and Cu Pc. For the higher voltage region in segment (III) of the Figure 1 the SCLC mechanism was governed by the equation

$$J = e\mu N_v \left(\frac{\varepsilon}{eP_0 kT_t} \right)^l \frac{V^{l+1}}{d^{2l+1}}. \qquad (9)$$

Besides the terms defined earlier P_0 is the trap concentration per unit energy range at the valance band edge, d the film thickness and the term $(l+1)$ represents the power exponent factor and $l = T_t/T$ where T_t is the temperature parameter measuring the exponential trap distribution given by

$$P(E) = P_0 \, \exp\left(\frac{-E}{kT_t} \right) \qquad (10)$$

where $P(E)$ is the concentration of traps per unit energy range and is a function of energy E above the valence band edge. The total concentration of traps $N_{t(e)}$ has been given by

$$N_{t(e)} = P_0 kT_t. \qquad (11)$$

The slope of the graph for the segment (III) in the Figure 1 was found to be 7 and hence the value of $l = 6$ and the temperature parameter $T_t = 1818$ K for $T = 303$ K. Taking the value of the density of states $N_v = 10^{27}$ m^{-3}, and the derived values of permittivity $\varepsilon = 1.2 \times 10^{-11}$ F/m, mobility $\mu = 3.1 \times 10^{-8}$ m^{-1} V^{-1} s^{-1} and using equation (9) and (11) the value of $P_0 = 5.76 \times 10^{44}$ J^{-1} m^{-3} and $N_{t(e)} = 8.06 \times 10^{25}$ m^{-3}. In the reverse bias condition the order of current was much lower than the forward current indicating a current limitation that can be explained as a Schottky or Poole-Frenkel type of conduction. The general equations [25] describing the reverse current density under these circumstances is given by

$$J = A^{**} T^2 \exp\left(-\frac{\Phi_s}{kT} \right) \exp\left(\frac{\beta_s V^{1/2}}{kT d^{1/2}} \right), \qquad (12)$$
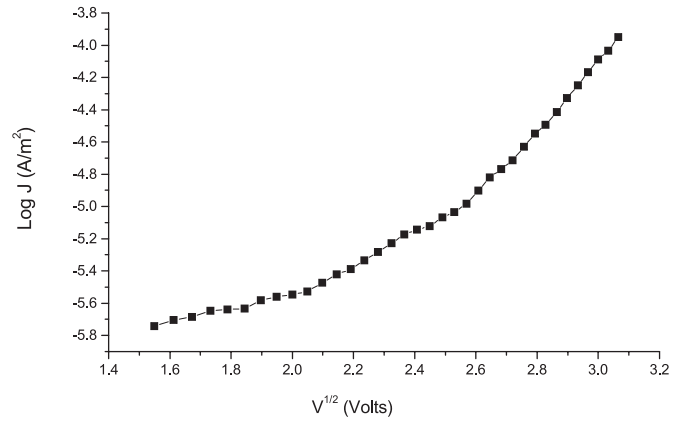
where $A^{**} = 1.3 \times 10^5$A m^2 K^2 is the Richardson constant and Φ_s is the Schottky barrier height at the injecting electrode interface, β_s is the Schotty field lowering coefficient. For the Schottky effect which is a field lowering of interfacial barrier at the injecting electrode, the current voltage relation is defined by

$$J = J_0 \exp\left(\frac{\beta_{PF} V^{1/2}}{kT d^{1/2}} \right) \qquad (13)$$

where J_0 is the low field current density and β_{PF} Poole-Frenkel field lowering coefficient. The two coefficients β_S and β_{PF} are related by the equation $2\beta_s = \beta_{PF} = \left(e^3/\pi\varepsilon\right)^{1/2}$ substituting the values of the permittivity $\varepsilon = 1.12 \times 10^{-11}$ F/m, the theoretical values of the field lowering coefficients were calculated as $\beta_{PF} = 6.74 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ and $\beta_s = 3.37 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$. In order to find the experimental values of these coefficients a graph of log J against $V^{1/2}$ is plotted in Figure 6.

This plot is having two linear portions and correspondingly there are two slopes. The two slopes give the values of the coefficients as $\beta_{PF} = 1.43 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ in the lower voltage range and $\beta_{PF} = 3.6\times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ in the higher voltage region. In the low voltage region the current conduction was originated from the contact interface rather than from the bulk material. The experimental values of β_{PF} in the high voltage region was in reasonable agreement with the theoretically calculated values β_{PF} The variation of β_{PF} in the low voltage region may be due the non uniformity and sub atomic structure of the mixture.

4 Conclusion

From the investigation of the current density characteristics of the mixed phthalocyanines we report that the in the low voltage region of the forward bias the conduction mechanism is almost ohmic in nature whereas at higher voltage the current transfer is space charged limited conduction. The lower value of E_f suggests that mixed Pc is

more efficient in conduction with the gold and lead electrode combination compared with the pure phthalocyanines. Again the experimental value of β_{PF} is in reasonable agreement with the theoretical values which suggests that the mixed phthalocyanines are having potential conduction capabilities rather than the pure Phthalocyanines. The reverse current was found to be much lower from the forward current indicating electrode limited conduction.

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