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Conduction in magnesium phthalocyanine thin films with aluminium electrodes

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Abstract. The various electrical properties and the nature of conduction mechanisms of magnesium phthalocyanine thin film devices with top and bottom aluminium electrodes have been investigated. The conduction mechanism was identified as injection limited essentially due to the electrode material. Even with the same electrode materials, the device showed asymmetric conduction behavior in the forward and reverse bias. In general the conduction was interpreted as a Schottky emission with barrier height $\Phi_s = 1.07$ eV for the forward bias and $\Phi_s = 1.09$ eV in the reverse bias. The effect of oxygen on the conductivity of the device has also been investigated. In the oxygen doped samples the conductivity is decreased which may be attributed to an interfacial layer between the electrode and the organic layer. Further in the oxygen doped sample while a Schottky emission is observed at lower voltages Poole-Frenkel conductivity was identified in the higher voltage region.

PACS. 73.50.Pz Photoconduction and photovoltaic effects – 73.61.At Metal and metallic alloys – 72.20.-i Conductivity phenomena in semiconductors and insulators – 84.32.Ff Conductors, resistors (including thermistors, varistors, and photoresistors)

1 Introduction

In recent years, organic semiconductors have attracted a great deal of attention due to their potential use in a wide range of technological applications. Due to their interesting physical properties combined with the low material cost make this particular family of organic compounds a strong candidate for the electronic and optoelectronic devices. Phthalocyanines are a class of organic dye material that are weakly semiconducting. They comprise of metal free phthalocyanine, which contain two hydrogen atoms in the centre of the molecule and the various metal substituted forms in which the hydrogen atoms are replaced by a single metal atom. Many of these materials incorporating different metals have been investigated for gas sensing [1] photovoltaic devices [2,3] thin film transistors [4] organic light emitting diodes [5] and schottky diodes [6]. The light absorbing properties of the phthalocyanines in the visible and in the infrared regions are of significant importance because of the current interest in the conversion of solar to electrical energy [7]. Most of the metal substituted phthalocyanines behave as p type semiconductors and its conductivity depends on the presence of oxygen and other acceptor impurities. The electrical, optical and structural properties of many of these organic thin films prepared from different techniques have already been reported [8–11]. The various electrical and optical properties of organic thin films mostly depend on their evaporation rate, doping concentration, substrate temperature and post evaporation annealing [12,13]. Further the conduction mechanism in the organic semi conducting thin films depend on the nature of the metallic contact to the semiconductor either as an ohmic or blocking and the order of applied voltage across the film [14,15]. Gold and indium tin oxide (ITO) electrodes have proved to be an effective ohmic contact to many such materials whereas aluminium and lead were found to be blocking electrodes that have different effects on the conductivity of phthalocyanines [16,17]. Among the conductivity types observed are space charged limited conduction (SCLC), field-lowering effects such as schottky or poole-frenkel effects, hopping, tunnelling and diode type conductivity. For the gold — aluminium and gold — lead electrode combinations a diode type of conduction and a field lowering behaviour also has been identified and reported for many phthalocyanines [18]. In magnesium phthalocyanine films ohmic conduction in the low voltage and space charged limited conductivity in the higher voltage has been observed with ohmic and blocking electrodes [6]. Relatively few studies have been conducted about thin film devices in which both electrodes are aluminium. In the present work the electrical properties of sandwich device of magnesium phthalocyanine (Mg Pc) thin films with both top and bottom electrodes as aluminium have been investigated. The

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various electrical parameters have been calculated to further probe into the nature of Al/Mg pc contact and to explore the conduction mechanisms of this structure. The effects of oxygen doping on the electrical conductivity of the device were also investigated as these are relevant to the use of Mg Pc films in gas sensing systems and solar cell applications.

2 Experimental details

Pure magnesium phthalocyanine powder from Sigma — Aldrich Co Ltd USA was the source material for the present study. To fabricate the multilayer device an aluminium film of approximately 60 nm thickness was deposited onto a pre cleaned glass substrate as the bottom electrode by thermal evaporation. Magnesium phthalocyanine layer was then deposited over the aluminium electrode at a base pressure of 10^{-5} Torr by thermal evaporation using a coating unit. During the evaporation process the pressure is kept steady by a diffusion pump backed by oil sealed rotary pump. In order to complete the device structure a top contact aluminium electrode was also deposited from a tungsten coil over the organic layer. For the oxygen doping some of the fresh samples were removed to a desiccator and stored in dry air for 30 days before the top aluminium electrode was deposited to complete the structure. Thickness of the magnesium phthalocyanine layer was measured as 550 nm by Tolansky's multiple beam interference technique [19]. The active area of the organic layer was calculated as 1.2×10^{-4} m^{-2}. Electrical conductivity measurements have been performed by a stabilized power supply and a Keithley programmable electrometer in a subsidiary vacuum system at a pressure of approximately 10^{-3} Torr. Both forward and reverse currents of the device were measured for the different values of applied voltages ranging from 0 V to 10 V at room temperature for the freshly prepared films and oxygen doped samples. Currents were measured continuously varying the bias and by interrupting the bias between each voltage step and in both cases, we found the same results.

3 Results and discussion

Conduction process in Al/Mg Pc/Al thin film devices were investigated by measuring the dark current density-voltage characteristics at room temperature. Figure 1 shows the typical current density against applied voltage ($J - V$) of the Mg Pc sandwich devices under forward and reverse bias of the freshly prepared and oxygen doped Al/Mg Pc/Al thin film devices. Forward bias is always defined as the situation when the top aluminium electrode is biased positively. In general, the $J - V$ characteristics of the device is asymmetrical and showed non-ohmic or rectifying behavior.

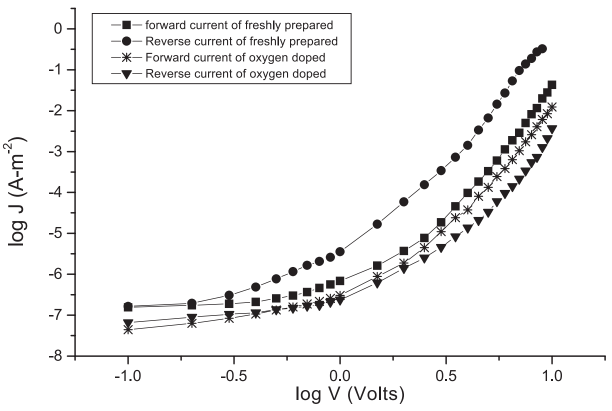

Fig. 1. $J - V$ charateristics of freshly prepared and oxygen doped Mg Pc device.

3.1 Freshly prepared Al/MgPc/Al device

The current-voltage characteristics of freshly prepared Al/MgPc/Al device (Fig. 1) showed different conduction mechanisms in different voltage levels. Forward current density of the device increases very slowly up to 0.8 V which neither fit with ohmic or rectifying characteristics and in the higher voltage region, the increase in current is more rapid. In the reverse bias also even though the current increases very slow in the lower region a transition is observed in the higher voltage region as in the forward bias. The variation of current in the forward and in the reverse bias is in contrast to the observed conductivity of Au/MgPc/Au and Au/MgPc/Al devices. Since the work function of aluminium is of the order 4.2 eV and that of Mg Pc is approximately 4.8 eV there will be barrier of roughly 0.6 eV for the carrier transport. The Schottky energy barrier (SEB) increases with aluminium electrode compared to gold electrodes. The current in the aluminium contact is injection limited at the contact interface due to SEB. The asymmetric conductivity of the Mg Pc/Al device could be explained as field lowering mechanisms either as a Schottky effect or a Poole-Frenkel effect, which are given by [20]

$$J = AT^2 \exp\left(-\frac{\Phi_s}{kT}\right) \exp\left(\frac{\beta_s\, V^{1/2}}{kTd^{1/2}}\right) \tag{1}$$

for the Schottky effect and

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

for the Poole-Frenkel effect where $A = 1.2 \times 10^5$ A m^{-2} K^{-2} is the effective Richardson constant, T is the absolute temperature Φ_s is the Schottky barrier height at the injecting electrode, k the Boltzmann constant d is the film thickness and J_0 is the low field current density β_s and β_{PF} are respectively Schottky and Poole-Frenkel field lowering coefficients which are related by $2\beta_s = \beta_{PF} = \left(e^3/\pi\varepsilon\right)^{1/2}$where ε is the absolute permittivity of the organic layer.

Substituting the values of the permittivity $\varepsilon = 3.87 \times 10^{-11}$ F/m which was measured earlier from our lab [6] the theoretical values of the field lowering coefficients were calculated as $\beta_s = 2.29 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ and $\beta_{PF} = 4.58 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$. Figure 2 is the graph of log J against $V^{1/2}$ for the Al/Mg Pc/Al thin film devices under forward and reverse bias of the freshly prepared and oxygen doped samples. The experimental values of the field lowering coefficients and the nature of conduction could be estimated from this plot. The variation of current is almost linear with a slope of 2.2 ± 0.01 for the forward and 2.5 ± 0.01 for the reverse bias. From the slope and using equation (2) the value of the field lowering coefficients for the forward and reverse bias curves were calculated as $\beta_s = 4.42 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ and $\beta_s = 5.12 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ respectively. The values of β_s for both forward and reverse bias is at variance from the theoretical values by 2.4 and 2.8 times. This discrepancy between experimental and theoretical values of β_s may be explained as a Schottky depletion region extending only for a small distance (d_s) and not across the entire organic layer. Hence even though the derived values for β_s is not in absolute agreement with the theoretical value it is reasonable to assume that the current conduction is originated from the contact interface rather than from the bulk material. This suggests that the conduction mechanism is controlled by Schottky emission as reported for many phthalocyanines. The value of the depletion region thickness (d_s) is given by

$$d_s = \left(\frac{\beta_s}{\beta}\right)^2 d \qquad (3)$$

where β_s and β are the theoretical and calculated values of Schottky field lowering coefficients and d is the film thickness. The depletion region thickness estimated from equation (3) yields a value of 97 nm for forward bias and 74 nm for reverse bias. These values are in good agreement with the previously reported values of similar materials [21]. From Figure 2 the extrapolated intercept of the linear portion of the graph with the J axis at $V = 0$ and using equation (2) the value of the barrier height Φ_s is calculated as 1.07 eV for forward bias and 1.09 eV for the reverse bias. These results are also in good agreement with the Mg Pc devices reported earlier [6].

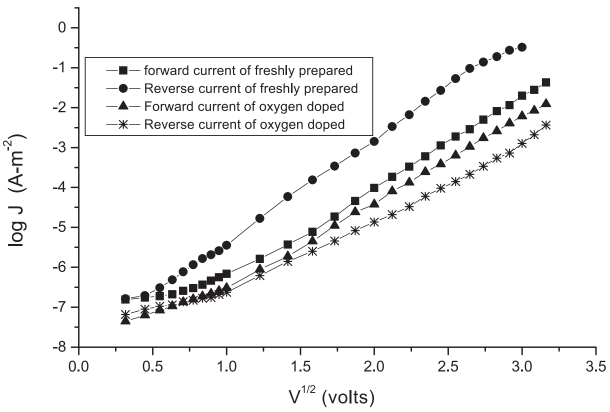

Fig. 2. Plot of log J vs. $V^{1/2}$ of freshly prepared and oxygen doped Mg Pc device.

3.2 Oxygen doped samples

log (J) − log (V) characteristics of the Al/Mg Pc/Al device exposed to dry air for 30 days is also plotted in Figure 1. The currents were slightly lower for oxygen-doped sample than the freshly prepared samples. Even though at the lower voltage levels modest difference exists in the current levels for forward and reverse bias, at higher voltages a considerable difference in current level exists. However, this in contrast with Mg Pc device with gold electrodes where oxygen significantly enhances the conductivity by increasing the acceptor concentrations. This may be explained as the formation of an interfacial layer at the contact interface, which is primarily the property of the contact electrode. This interfacial layer produces additional series impedance, which reduces the current level. A higher current density is observed for the reverse bias than for the forward bias even though the electrode configuration is same. In this case, the majority charge carrier (holes) are injected from the bottom electrode and the injection efficiency is higher than when the injection is from the top electrode, which may be more heavily degraded by oxygen. The nature of the current and the conductivity in the oxygen-doped sample was explored from the plot of log (J) against $V^{1/2}$ (Fig. 2).The curve consists of two distinct linear portions in the lower and in the higher voltage regions. The values of the field lowering constants were estimated from the slopes of linear portions of the forward and reverse curves. Thus the values $\beta_s = 2.29 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ for the forward bias and $\beta_s = 1.52 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ for the reverse bias in the lower voltage region were obtained. In the higher voltage region the values these values are obtained as $\beta = 4.32 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ for the forward bias and $\beta = 3.76 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ for the reverse bias respectively.

In the lower voltage range, the calculated values of the field lowering constants are 1.2 and 0.8 times the theoretical values of Schottky field lowering constant β_s for the forward and reverse bias. Such a variance is expected in the low voltage region as reported in many phthalocyanine devices [22]. The Schottky barrier height was also calculated for the oxygen-doped samples as 1.06 ± 0.01 eV for both forward and reverse bias. This type of the conduction behavior is in contrast to the reported behavior of magnesium phthalocyanine thin films with gold electrodes. This may be due to the formation of an interfacial oxide layer of aluminium in the electrode which produce a series resistance which reduce the current level. Hence there may be some deviation from the experimental values of the barrier height from the real values. The depletion region thickness was estimated as 104 nm and 137 nm for forward and reverse bias respectively. However, in the higher voltage region the values of the field lowering constants suggest a Poole-Frenkel type of conduction in the Mg Pc/Al devices.

4 Conclusion

In this paper, we have described the electrical properties of Al/MgPc/Al thin film device prior and after exposure to dry air. The analysis of the $J-V$ characteristics of the device showed an asymmetric behavior both under forward and reverse bias. The current in the device is sensitive to the electrode characteristics. The conduction mechanisms were identified as an electrode limited with a presence a Schottky barrier height $\Phi_s = 1.07$ eV for the forward bias and 1.09 eV for the reverse bias respectively. The depletion region thickness was calculated as 97 nm and 74 nm for the forward and reverse bias. In the oxygen doped samples the conductivity was decreased which may be attributed to the an interfacial layer between the electrode and the organic layer. Further in the oxygen doped sample a transition from the Schottky type of conduction to a Poole-Frenkel type of conduction was observed between lower and higher voltage regions.

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