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Richarson-schottky emission in Hypertemperature in PbPc and CuPc thin films

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ABSTRACT

The thin film of Lead Phthalocyanine (PbPc) and Cupper Phthalocyanine (CuPc) on glass are prepared by Vacuum deposition method. Deposition of PbPc and CuPc on pre-cleaned glass substrates under the pressure of 10^{-6} Torr are achieved by slowly varying the current. The rate of evaporation is properly controlled and maintained constant during all the evaporations. The thicknesses of the films are 150 nm, 300 nm and 450 nm on glass substrate. Current voltage conduction properties of Lead Phthalocyanine and Cupper Phthalocyanine thin films have been studied. At the higher temperatures, the slope of I –V curves indicates that the thermally generated carrier density exceeds that of the injected charges. In the case, it is observed that the slope of log (J) vs log (V) curves is about unity for 300 K. The region is considered as ohmic. The plots of In (J/T) versus 1000/ T at different voltages tend to be straight lines at higher temperatures. The straight line behaviour occurs at above 325 K. However the domination of the thermionic emission behaviour is observed at higher temperatures

Keywords: Phthalocyanine, Richarson – schottky (RS) emission, potential barrier, MSM structure.

INTRODUCTION

The search for materials suitable for low cost, versatile electronic devices has stimulated interest in organic thin film transistors[OTFTs] and sensors has led in recent years to an extensive investigation of a range of metal substituted phthalocyanines [1,2]. Application of OTFTs as chemical sensors has shown promise in the development of electronic noses and in nerve agent detection [3-5]. A key issue regarding the widespread production of OTFTs is the long term stability and device integrity in ambient operating conditions [6,7]. Among the small molecule based OTFTs, pentacene OTFTs have received significant attention regarding instability to ambient components such as oxygen and humidity [8-12]. Several mechanisms have been proposed to explain this instability in pentacene OTFTs, including water adsorption in grain boundaries [10,11] and oxygen generated impurities[13].

Phthalocyanines have potential applications in optical logic display devices, electrophotography, security printing, gas detectors [14], solar cells [15, 16], sensitisers and colour filters [17]. These materials are generally p-type semiconductors and have the advantage of being sufficiently stable towards chemicals and heat. They can be easily sublimed, resulting in high purity thin films without decomposition. The physicochemical properties can be altered by changing the metal ion. Film properties of this prototype organic semiconductor are dependent on the evaporation rate, substrate temperature and post-evaporation annealing [17, 18]. Photovoltaic devices made from organic pigments have reached power conversion efficiency of a few percent [19, 20] that is much lower than those of their inorganic combinations.

In the present work, we have characterized lead phthalocyanine (PbPc) and Copper phthalocyanine (CuPc) in the form of a Schottky barrier device and investigated the charge generation mechanism. We have studied the temperature dependent of current voltage characteristics of Cupc and PbPc thin film sandwiched between Al and A1 electrodes, with the aim to understand the charge generation mechanism.

MATERIALS AND METHODS

The powder of PbPc (80% dye, Sigma Aldrich company, Bangalore, India) is kept in a molybdenum boat (100 A current rating) heated with high current controlled by a transformer. The transformer is capable of supplying 150 amps at 20 volts which is used to provide the accessory current for heating the molybdenum source. It is used for the evaporation process. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for about 45 minutes with the closed shutter. Thin films of PbPc are deposited at room temperature on pre-cleaned glass substrates under the pressure of 10^{-6} Torr using a (12 A 4D Hind Hivac, India) coating unit. The rate of evaporation is properly controlled and maintained constant during all the evaporations. Rotary drive is employed to maintain uniformity in film thickness. The thicknesses of the films are 150 nm, 300 nm and 450 nm. The thickness of the films is measured by Quartz crystal monitor. The current voltage studies on PbPc and CuPc films are carried by forming Metal-Semiconductor-Metal (MSM) structures. The top electrode contact is made by evaporation of aluminum (A1) through an appropriate mask at a vacuum of 10^{-5} Torr. The resulting area of the device is about $1cm^2$. Electrical measurements are performed using a subsidiary vacuum system and maintained at a pressure of 1.3 x 10^{-3} Pa. This procedure is used for preparing PbPc and CuPc thin film on pre-cleaned glass substrate. For the current voltage (I-V) measurement, Keithley electrometer with built in power supply is used.

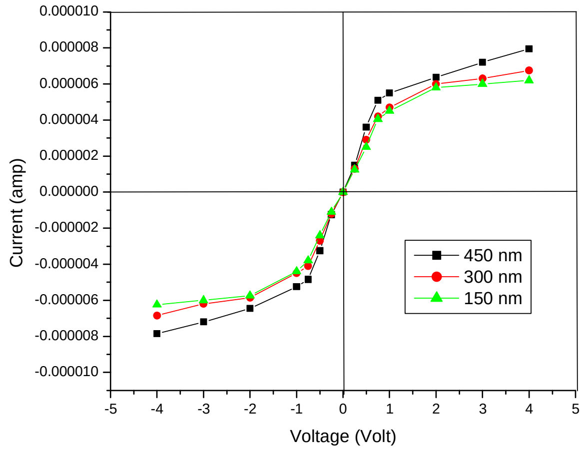

Figure 1. The current –voltage characteristics of PbPc Thin film on glass substrate for thickness

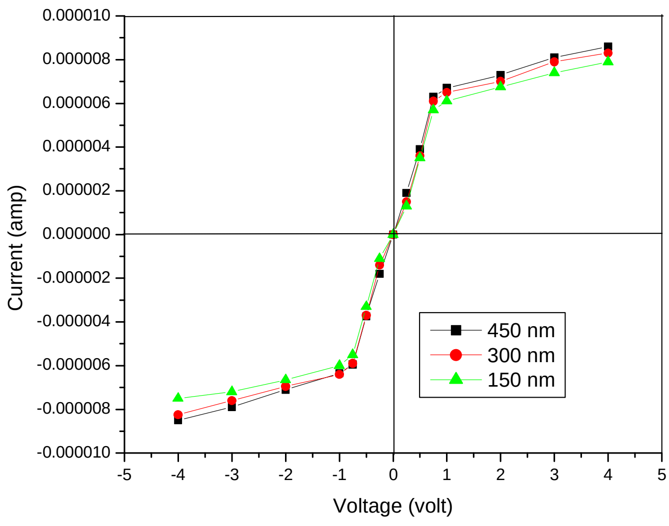

Figure 2. The current –voltage characteristics of CuPc Thin film on glass substrate for thickness

RESULTS AND DISCUSSION

Effect of Thickness

The Current-Voltage characteristic for a sandwich device of Al/PbPc/Al and Al/CuPc/Al structure of thickness 150 nm, 300 nm and 450 nm on glass substrates are shown in Figure 1 and 2. The applied voltage is changed from -4 to 4 V. In both forward and reverse bias region, the current is directly proportional to the applied voltage. The spectrum reveals that the current increases with increase in the voltage. The current increases rapidly upto saturation point, then increases slowly. From the Figure 1 and 2 the current increases with increase in the thickness of the film. As the thickness is increased, the number of injected carriers increases so that space charge accumulates limiting the current. The current density voltage characteristics of Au/PbPc/Au structure have identified an ohmic region followed by space charge limited conductivity [21].

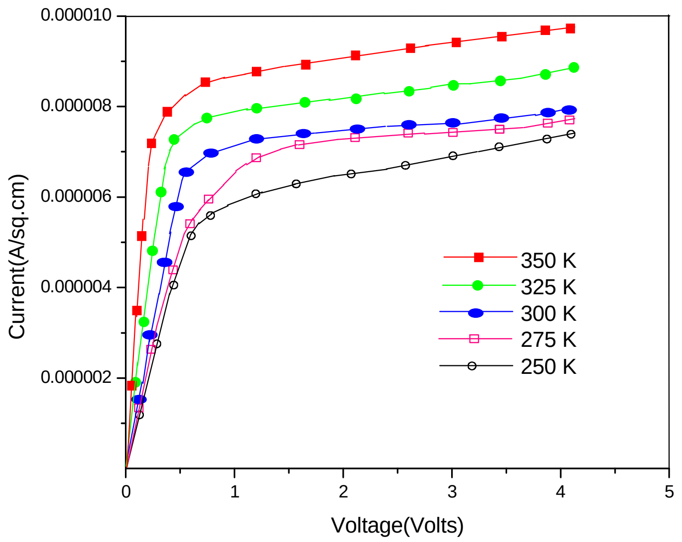

Figure 3. The current–voltage characteristics of PbPc Thin film of thickness 450 nm at different temperatures

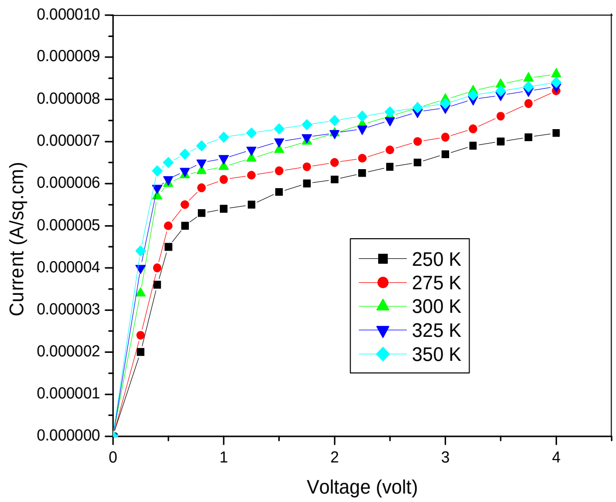

Figure 4. The current–voltage characteristics of CuPc Thin film of thickness 450 nm at different temperatures

Effect of Temperature

In I-V characteristics of Al/PbPc/A1 and Al/CuPc/Al devices recorded at different temperatures ranging from 250 to 350 K are shown in Figure 3 and 4. As MPc is a P type organic semiconductor, from Schottky barrier and nearly ohmic contact with PbPc, respectively and thus gives rise to asymmetrical nature of J-V characteristics i.e. rectification effect. It is observed from the above figures that the current increases with increase in the temperature in both spectrums. Rectification ratio defined as a ratio of forward to reverse current at the same voltages was equal to 1.2 for PbPc and 1.3 for CuPc [22]. Current increase in CuPc film is less than that of PbPc film with increase the temperature. The decrease in the nonlinearity coefficient with increase in the temperature may be firstly due to increase of conduction of depletion region formed in CuPc and Al interface and CuPc bulk region and secondly due to the increase of mobility of charge carriers (hopping mechanism of conduction). To explain the electrical behavior and the charge transport mechanism in organic semiconductor materials, the trapping model with a space charge limited current (SCLC) is used [23]. Traps at locations arise from disorders, dangling bonds, impurities, etc., and are called localized states that very often capture free charge carriers. Most frequently, an exponential distribution of traps in the energy band is assumed [23, 24].

Figure 5and 6 shows the typical forward bias I-V characteristics of Al/PbPc/A1 and Al/CuPc/Al devices in log–log plot at different temperatures. This situation corresponds hole injection in the HOMO of MPc through electrode into the film. It is observed in J-V characteristics of the devices at low temperatures below 300 K. At low voltage, the slope of the log (V) plots are approximately equal to unity, while at higher voltages above well defined transit voltage, the slope are approximately in between 2.0 and 2.5. These plots are typical of ohmic conduction at low voltage. It is well known that Metal Phthalocyanines (MPc's) are P type organic semiconductors; the condition is via holes only [25].

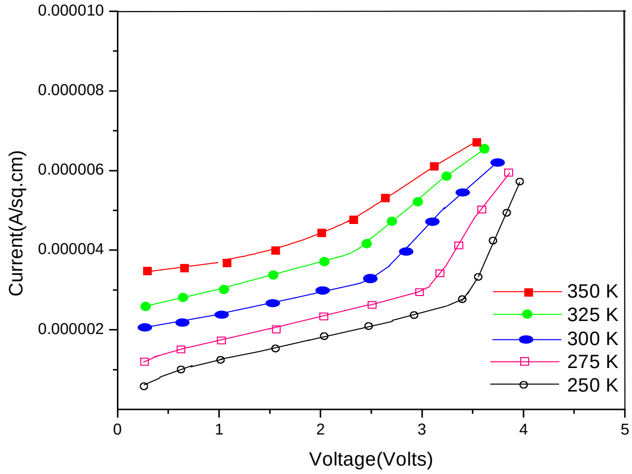

Figure 5. The current–voltage characteristics of PbPc Thin film on glass substrate for thickness 450 nm in log-log scale

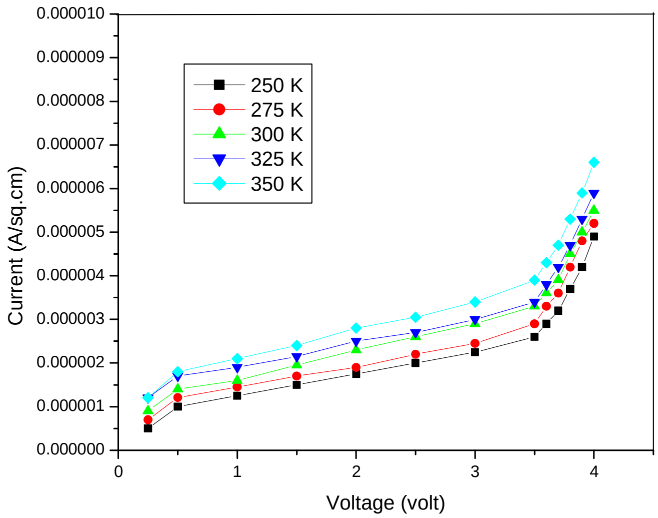

Figure 6. The current–voltage characteristics of CuPc Thin film on glass substrate for thickness 450 nm in log-log scale

The A1 contact with organic semiconductor form relatively high barrier at low temperatures and therefore thermally generated carriers are few and the injected charge density is small so that the overall behaviour becomes ohmic. As the voltage is increased, the number of injected carriers increases so that space charge accumulates limiting the current. The number of thermally generated carriers increases with temperature, therefore the current increases with temperature. The super linear behaviuor seen in the Figure 5 & 6 suggests that the injected charge carrier overcomes the transport capabilities of MPc, hence giving rise to the accumulation of positive charge near the A1 hole injecting electrode and the bulk properties of the organic layer control the J-V characteristics. In the case of PbPc, it is observed that the slope of log (J) vs. log (V) curves is about unity for 300 K. The region is considered as ohmic. For CuPc the curves is units about 285K.Above the ohmic region, the J – V characteristics may be fitted to the Richarson – Schottky (RS) emission model. At higher fields, the metal work function for the thermionic emission is reduced, thus lowering the Schottky barrier height.

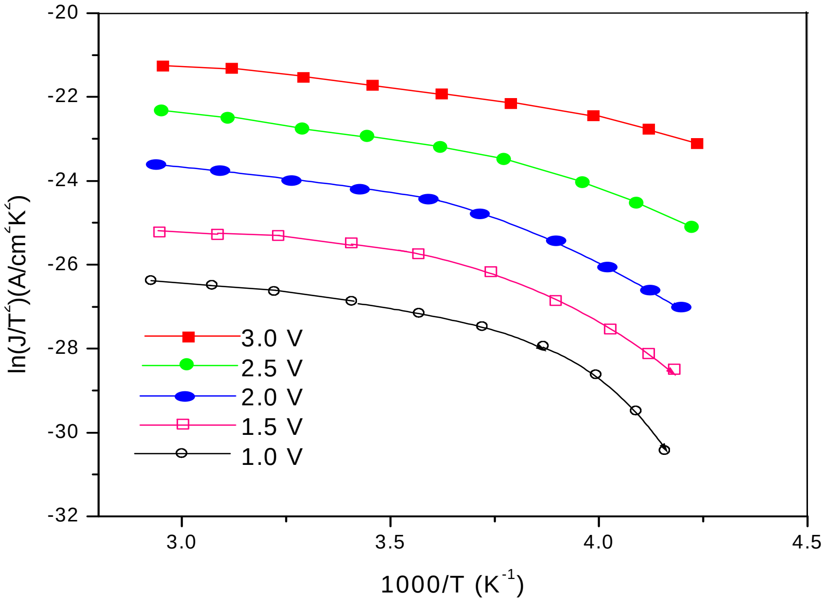

Figure 7. The current–voltage characteristics of PbPc Thin film on glass substrate for thickness 450 nm of In (J/T^2) vs 1000/T

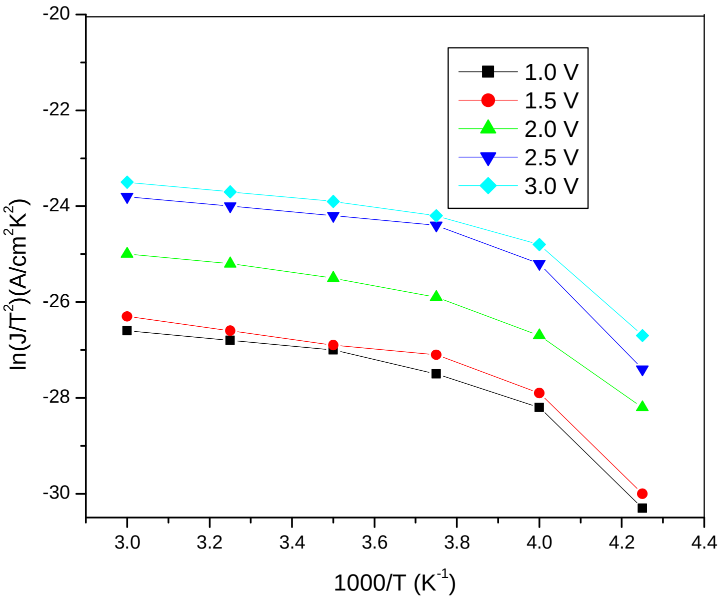

Figure 8. The current–voltage characteristics of CuPc Thin film on glass substrate for thickness 450 nm of In (J/T^2) vs 1000/T

As seen from Figure 7 and 8, the plots of In (J/T^2) versus 1000/ T at different voltages tend to be straight lines at higher temperatures. I-V characteristics in figure show linear or ohmic region, space-charge limited current region and traps region. Actually in space-charge limited current region shallow traps exchange by charge carriers from valence band (in the case of p-type semiconductor) and in transition from this region to trap region, deep traps are filled by charges causing a steep rise in the current [26].

The straight line behaviour occurs at above 325 K for PbPc and above 300 k for CuPc. However the domination of the thermionic emission behaviour is observed at higher temperature indicates that a higher hole injection barrier exits at Al/ PbPc interface, since more thermal energy is required to overcome the potential barrier height.

CONCLUSION

In Current-voltage characteristic, shows the applied voltage is changed from -4 to 4 V in both forward and reverse bias region, the current is directly proportional to the applied voltage. The current increases with increase in the thickness of the film. As the thickness is increased, the number of injected carriers increases so that space charge accumulates limiting the current. It is observed that current vary independently with substrate and current increases with increase in the temperature.

Rectifying characteristics are found as a function of temperature: rectification ratio, unlike to conventional p-n junction, increased with temperature. This can be associated with the generation of free carriers, detrapping of charges at elevated temperatures and with enhanced temperature assisted hopping in the organic films that decreases bulk resistance of the films. It is further observed that *I-V* characteristics of the samples follow space charge limited conduction model. With increase of temperature linear (ohmic) part of *I-V* characteristics extended into higher voltages, nonlinear part decreases in voltage scale and nonlinearity coefficient decreases as well. It was shown that trap factor, mobility and conductivity increase with temperature whereas the intrinsic concentration was approximately constant.

At low voltage, the slope of the Log (V) plots is approximately equal to unity. As the voltage is increased, the number of injected carriers increases so that space charge accumulates limiting the current. The numbers of thermally generated carriers increases with temperature, therefore the current increases with temperature. In this case, it is observed that the slope of log (J) vs log (V) curves is about unity at 300 K and 285 for PbPc and CuPc. This region is considered as ohmic. Above the ohmic region, the J – V characteristics may be fitted to the Richarson – Schottky (RS) emission model. The straight line behaviour occurs at above 325 K for PbPc and above 300 K for CuPc. The thermionic emission behaviour is observed at higher temperatures indicates that a higher hole injection barrier exits at Al/ PbPc and Al / CuPc interface, since more thermal energy is required to overcome the potential barrier height.

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