CHAPTER 9

CURRENT VOLTAGE CHARACTERISTICS

9.1 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. During the last couple of decades, much effort have been put into the development of solar cells based on organic electronic materials because of their low cost and ease of fabrication (Tang (1986)). In these molecular materials, the relevant molecules can be easily prepared and modified by rich chemical properties to meet the optical and electronics requirements. Among a variety of molecular materials, metal phthalocyanines (MPc’s) are well known stable materials with versatile functions (Gregg (2003), Peumans and Forrest (2001), Yakimov and Forrest (2002)).

Phthalocyanine contains four isoindoles units (a pyrrole ring conjugated with a benzene ring). A large family of Pc’s can be chemically modified by attaching various peripheral groups to the outer ring of isoindoles. Pc’s absorb the light in different spectral region in between 500-720nm. Photovoltaic devices made from organic pigments have reached power conversion efficiency of a few percent (Gregg (2003), Peumans and Forrest (2001)) that is much lower than those of their inorganic combinations. One of the possible improvements for this type of photovoltaic devices is the implementation of new materials which can absorb the red or near infrared part of the solar spectrum, where maximum photon flux of sun is present.
In the present work, we have characterized PbPc and CuPc in the form of a Schottky barrier device and investigated the charge generation mechanism. We have also studied the temperature dependence of Current Voltage (I-V) characteristics of PbPc and CuPc thin film sandwiched between Al and A1 electrodes i.e. A1/PbPc/A1, A1/CuPc/A1 with the aim to understand the charge generation mechanism. The variation of concentration of injected charge carriers and their mobility with temperature, bias voltage carrier trap density arising due to the defect and impurities are very important information required for improving the device performance. In the present work such measurements have been made in order to further probe the nature of the Al/PbPc/A1 and Al/CuPc/A1 contact and to investigate the conduction mechanisms in this structure.

9.2 THEORY OF CURRENT VOLTAGE STUDIES

In Current – Voltage characteristics, the forward bias was obtained with positive and negative bias to Al and A1 electrodes. The asymmetrical nature of curves is attributed to the difference in work function of the electrodes, implying different barriers at each electrode/PbPc and electrode/CuPc interface. As both PbPc and CuPc is P-type organic semiconductors, A1 and Al form Schottky barrier and nearly ohmic contact with PbPc and CuPc and thus give rise to asymmetrical nature of I-V characteristics i.e, rectification effect.

The Current – Voltage characteristics of Al/PbPc/A1 and Al/CuPc/A1 device at different temperatures give the charge generation mechanism. This situation corresponds to hole injection of PbPc and CuPc through one A1 electrode and electron injection through another Al into PbPc and CuPc. In each case two distinct regions were observed in I-V characteristics of the device 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 (i.e.) above well defined transit voltage, the slope is found to lie approximately between 2.0 and 2.5. These plots are typical of ohmic conduction at low voltage. Metal phthalocyanines (MPc’s) are P-type organic semiconductors, the conduction is via holes only, and the current is expressed in the form,

\[ I = P_h q \mu A \left( \frac{V}{d} \right) \]  

(9.1)

where \( P_h \) is the concentration of thermally generated holes, \( q \) is the electric charge, \( \mu \) is the hole mobility, \( V \) is the applied voltage and \( d \) is the thickness of the layer. At high voltage range, the power law dependence of \( I \) and \( V \) is indicative of Space Charge Limited Conductivity (SCLC) controlled by single dominant trapping.

I-V characteristics of metal – organic semiconductor devices are controlled by two basic processes:

(i) Injection of the charge carries from electrodes into organic semiconductor and vice versa

(ii) Transport of the charge carries in the bulk of film.

The Al 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. Due to super linear behaviour the injected charge carrier overcomes the transport capabilities of PbPc and CuPc, hence giving rise to the accumulation of positive charge near
the Al hole injecting electrode and the bulk properties of the organic layer control the I-V characteristics.

The injection of charge from Al into PbPc and CuPc is more due to the low barrier and the injected carrier density becomes so large that the field due to the carries themselves dominates over the applied field and then becomes space charge limited. SCLC occurs when the transit time of any excess injected carrier is less than the bulk relaxation time. Under these conditions, the trap filled space charge limited current (TFSCLC) takes place and is described by

\[ I_{SCLC} = \left( \frac{9}{8} \right) \varepsilon \mu V^2 / \alpha^3 \]  

where \( \mu \) the mobility of charge carrier, \( \varepsilon \) permittivity, \( V \) is applied voltage and \( \alpha \) is the thickness of the film layer. This behaviour is characterized by a quadratic dependence of the current on voltage i.e. slope of I-V curve. At the higher temperatures, the slope of I-V curves is between 1 and 2. This indicates that the thermally generated carrier density exceeds that of the injected charges.

The electric field at which the transition from ohmic to SCLC takes place increases with temperature. In forward bias, the Al/PbPc and Al/CuPc interface supplies high amount of charges in PbPc and CuPc bulk and the current is space charge limited in whole voltage and temperature range, suggesting the formation of ohmic contact for whole injection at the Al/PbPc interface.

The current density as a function of applied voltage in different range, shows a power law dependence of the form \( I \propto V^m \), where \( m = 2 \) indicating
that the current density in both PbPc and CuPc are a trap free space charge limited current. The current density in this region is given by equation (9.2).

The value of slope does not necessarily imply the absence of traps in the materials, but rather that they are all filled. All existing trapping centers are occupied by injected holes from the electrode and the material starts to resist any further injection. Since the mobility of the charge carrier in organic semiconductor is so low that the extra injected charges cannot be swept to the collecting electrode at same time at which they are being injected.

However, as the voltage increased the current density in the PbPc and CuPc layers are dominated by a single trapping level. The current density in this region is given by

\[
I = \left( \frac{9}{8} \right) \varepsilon \mu \theta AV^2 / d^3
\]

(9.3)

where \( \theta \) the trapping factor is given by

\[
\theta = \frac{N_v}{N_t} e^{-\frac{E_t}{kT}}
\]

(9.4)

where \( N_v \) and \( N_t \) are the effective density of states in the valence band and total trap concentration situated at energy level \( E_t \) above the valence band edge. The value of trap corresponding to difference temperature can be estimated from the intercept of the straight line of log \( (J) \) vs. log \( (V) \) on current axis in the space charge region.
9.3 MEASUREMENTS

The thin films of PbPc and CuPc were deposited on cleaned Al coated glass substrates by vacuum deposition technique. The Current Voltage studies on PbPc and CuPc films were carried by forming Metal-Semiconductor-Metal (MSM) structures. The rate of evaporation was properly controlled and maintained constant during all the evaporations. Rotary drive was employed to maintain uniformity in film thickness. The film thicknesses were controlled to be 150 nm, 300 nm and 450 nm by quartz crystal monitor. The top electrode contact was made by evaporation of aluminum (Al) through an appropriate mask at a vacuum of 10^{-5} Torr. The resulting area of the device was about 1cm^2. Electrical measurements were performed using a subsidiary vacuum system maintained at a pressure of 1.3×10^{-3} Pa. For the Current Voltage measurement, Keithley electrometer with built in power supply was used.

9.4 RESULTS AND DISCUSSION

9.4.1 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 9.1 and 9.2. 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 up to saturation point, then increases slowly. From the Figure 9.1 and 9.2 it is seen that 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 (Shafai and Gould (1990)).

9.4.2 Effect of Temperature

In I-V characteristics of Al/PbPc/A1 and Al/CuPc/A1 devices recorded at different temperatures ranging from 250K to 350K are shown in Figures 9.3 and 9.4 respectively. As MPc is a P-type organic semiconductor, form Schottky barrier and nearly ohmic contact with PbPc and thus gives rise to asymmetrical nature of J-V characteristics i.e. rectification effect. It is observed from the Figures 9.3 and 9.4 that the current increases with increase in the temperature for both films. 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 (Karimov KH. S.et al (2008)). Current increase in CuPc film is slightly less than that of PbPc film with increase in 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 behaviour and the charge transport mechanism in organic semiconductor materials, the trapping model with a space charge limited current (SCLC) is used (Moiz.S.A et al (2005)). 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 (Moiz.S.A et al (2005)).

Figures 9.5 and 9.6 show the typical forward bias I-V characteristics of Al/PbPc/A1 and Al/CuPc/A1 devices in log–log plot at different temperatures. This situation corresponds to 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 300K. 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 is found to lie approximately 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 and the conduction is via holes only (Lampert M.A. and Mark P (1970)).

Figure 9.1. The current–voltage characteristics of PbPc thin film on glass substrate for varied thickness

Figure 9.2. The current–voltage characteristics of CuPc thin film on glass substrate for varied thickness
Figure 9.3. The current–voltage characteristics of PbPc thin film of thickness 450 nm at different temperatures

Figure 9.4. The current–voltage characteristics of CuPc thin film of thickness 450 nm at different temperatures
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 behaviour seen in the Figures 9.5 and 9.6 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 at 300K and this region is considered as ohmic. For CuPc slope of the curves is about unity at 285K. Above the ohmic region, the J – V characteristics may be fitted to the Richardson – Schottky (RS) emission model. At higher fields, the metal work function for the thermionic emission is reduced, thus lowering the Schottky barrier height.

As seen from Figures 9.7 and 9.8, the plots of In (J/T^2) versus 1000/ T at different voltages tend to be straight lines at higher temperatures. I-V characteristics 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 (Epifanov and Moma (1986)). The straight line behaviour occurs at above 325K for PbPc and above 300K 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 (Shaji Varghese and Mercyiype (2011)).
9.5 CONCLUSION

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 measure of temperature, the rectification ratio is found to increase 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 is observed that trap factor, mobility and conductivity increase with temperature whereas the intrinsic concentration remained 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 number of thermally generated carriers increases with temperature, therefore the current increases with temperature. It is observed that the slope of log (J) vs log (V) curves is about unity at 300K and 285K for PbPc and CuPc respectively. This region is considered as ohmic. Above the ohmic region, the J–V characteristics may be fitted to the Richardson–Schottky (RS) emission model. The straight line behaviour occurs at above 325K for PbPc and above 300K for CuPc. The thermionic emission behaviour observed at higher temperatures indicates that a higher hole injection barrier exist at Al/ PbPc and Al / CuPc interface, since more thermal energy is required to overcome the potential barrier height.