Chapter 3

Current Injection Mechanism in Organic Molecular Semiconductor

3.1 Introduction.

There is currently tremendous research activities in the use of organic molecular semiconductor (OMS) based organic light emitting diodes for low cost, full color, large area flat panel display with viewing properties comparable to conventional cathode-ray and liquid crystal based display devices. The current conduction mechanism and operation of OMS based devices depend on metal/OMS and OMS/OMS heterojunctions. The interface properties of metal/OMS, which are extremely important for technology, are not well understood. Efficient injection of charge carriers across the interfaces requires increased control of the interface chemical and electronic properties. However, basic understanding of current injection and transport mechanisms in OELD still remains a crucial point for the development of highly efficient devices due to the complex nature of the electrical mechanisms involved in these materials. In the literature, this issue is being debated to understand the exact injection and transport mechanism involved using several models [65, 66, 67, 68, 69]. Analytical [22, 50, 70], as well as Monte-Carlo simulation[71, 72] have been developed concerning the charge carrier transport in these methods. Even the issue regarding the relative importance of charge injection as opposed to bulk transport is not settled and under debate [14, 20, 25]
in poly-p-phenylene vinylene (PPV) and its derivatives, which are the most widely investigated organic semiconductor (OS). Recently, we have shown [73] for small energy barrier contacts, current flow is due to space charge limited conduction (SCLC) in metal phthalocyanine (MePc). There are some reports on tris, 8-hydroxyquinoline Aluminum (Alq3) [74, 75], but so far, there is no systematic study on current injection and transport in molecular semiconductors, like MePc.

In this chapter, we present the investigation on current injection mechanism from metal contacts to MePc OMS using metal/OMS/metal (M/OMS/M) structures. In this case, by properly choosing contacting metals, current injection and transport due to holes have been investigated. Our approach is to begin with single layer devices based on MePc to understand the fundamental mechanism involved in metal/MePc/metal structures and it is also useful to consider only single carrier devices, which can be achieved by introducing a large energy barrier for one carrier type (for example, electron in this case) resulting insignificant injection. Here we have chosen copper phthalocyanine (CuPc) and zinc phthalocyanine (ZnPc) as the MePc, for its successful applications in organic devices. CuPc is a hole transport OMS with ionization potential and electron affinity [34] of 4.8eV and 3.1eV, respectively, so efficiency of hole injection depends on the work function ($\Phi$) of metal electrodes used as cathode or anode. In this study indium tin oxide (ITO) with $\Phi$ of 4.8eV, is kept fixed as cathode contact at one end to make an Ohmic contact for hole flow in CuPc and varied the other contact with metals with different work functions as different anodes to investigate the current injection mechanism. It has been shown [73, 74] that a barrier of $\phi_B e$ or $\phi_B h \geq 0.4eV$ is needed to observe the injection current in a simple single layer organic devices. Injection currents are explained through modified Schottky equation proposed by Scott and Malliaras [76] in case of carrier injection over a Schottky barrier between a disordered semiconductor and metal.
3.2 Fabrication of Single Layer Device based on OMS

The single layer organic devices in our study were prepared by sandwiching a thin active organic layer of MePc between Indium Tin Oxide (ITO) coated glass substrate and thermally evaporated metal electrodes of aluminum (Al), copper (Cu), and gold (Au). The devices were fabricated by vacuum deposition technique (described in Appendix C). We have studied the simple hole only devices with CuPc and ZnPc as thin organic layer, ITO as Ohmic hole injecting contact and Au, Cu, and Al are used for studying the barrier formation for holes at the metal/MePc interface. A schematic energy level diagram of different single layer devices using different contacting metals, used in this investigation are shown in Fig.3.1. Electrical studies were carried by continuously varying the bias and also by interrupting the bias between each voltage step, in both cases; we have observed the same results. The Current-voltage (J-V) characteristics for the ITO/MePc/metal (Au, Cu, Al) structures with different thicknesses of MePc layers were measured under vacuum and were reproducible at all temperatures and showed no hysteresis.

3.3 Validity of Vacuum Level Alignment in OMS

Though Alq3, perylenetetracarboxylic dianhydride (PCTDA), and 4,4'-bis[N-(1-napthyl) N-phenyl aminobiphenyl (NPD) are equally important for their application in opto-electronic devices, they show very poor contacts with metal electrodes[38, 39, 40] and devices based on these materials show degradation with time. The poor metal/molecular organic semiconductor (M/MOS) contacts can affect the bulk transport properties and defeat the main purpose of this investigation. In these materials, determination of barrier from the vacuum alignment of ionization potential (I) of molecular semiconductors and Fermi level of metal (E_F) at the M/MOS interface generally leads to the wrong results, because the barrier at M/MOS junction may be modified by the interaction of molecular materials with metal
Figure 3.1: Schematic illustration of the energy level diagram for the devices in use, showing the work function of the metals and the electron affinity ($\chi = 3.1\,\text{eV}$) and the ionization potential ($I = 4.8\,\text{eV}$) of MePc.

electrodes. It has been shown\cite{40} that Fermi level with respect to highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) edge of Alq3 is independent of work function of Mg and Au despite a large difference in the metal work function ($\Phi$), but we have shown\cite{41} that this is not the case in case of MePc. A schematic energy level diagram of the different single layer devices using different contacting metals, used in this investigation is shown in Fig.3.1. Fig.3.2. shows the measured J-V characteristics of a single layer CuPc devices in which cathode contact is fixed and anode contact is varied. We have observed that the current for devices with Cu anode is less than that of Au anode devices, which further decreases by using Al anode. This proves the validity of vacuum level alignment in these molecular based thin film devices. Physics of the M/OMS/M structures is assumed to be governed by the formation of barriers at the interfaces in the absence of Fermi level pinning. In the absence of surface states and a depletion region due to impurity
doping, the energy barriers that control the hole and electron injection are \( \phi_{Bh} = I - \Phi_{anode} \)
and \( \phi_{Be} = \Phi_{cathode} - \chi \), where I is the ionization potential and \( \chi \) is the electron affinity of
the organic material. The magnitude of \( \phi_{Bh} \) and \( \phi_{Be} \) take an important role in studying
the carrier injection, which can be varied by choosing the contacting metal of suitable work
function. For efficient charge injection, high work function metals must be used for hole
injecting contact and the low work function metal must be used for the electron injecting
contact. Since the work functions of Au, Cu and Al are 5.1eV, 4.6eV and 4.2eV respectively,
there will be no barrier for hole in ITO/CuPc/Au structure, but there will be barrier of
0.2eV and 0.6eV for holes at Cu/CuPc interface in ITO/CuPc/Cu and at Al/CuPc interface
in ITO/CuPc/Al structures, respectively. Since the work function of ITO(4.75eV) is close
to the ionization potential(4.8eV) of CuPc, giving rise to negligible barrier of 0.05eV at
the ITO/CuPc interface for holes, ITO is used for making Ohmic contact. Al, and Cu

Figure 3.2: Measured current density as a function of bias voltage for single layer hole only
CuPc devices with thickness of 200nm at room temperature. Cathode contact is fixed to be
ITO and anode contacts are Au, Cu and Al.
are used as hole blocking contacts in these devices, since the work function of Al(4.2eV) and Cu(4.6eV) are less than the ionization potential of CuPc. As the Schottky energy barrier (SEB) is increased from Au to Cu, the current at a given bias is reduced showing that contacts limiting the current flow. The current is further reduced when an Al contact is used, establishing that current is injection limited due to SEB. We have found[73] that current in ITO/CuPc/Au and ITO/CuPc/Cu is due to space charge limited current (SCLC) with field dependent mobility (discussed in Chapter-IV) and the current is injection limited in case of ITO/CuPc/Al structure, suggesting that ITO, Au, and Cu behave as Ohmic contacts to CuPc and Al, as Schottky contacts. This is consistent with the result of David et. al.[77] that for SEB less than about 0.3-0.4eV, the charge carrier conduction is due to SCLC.

3.4 Diode Like Asymmetric J-V Characteristics in ITO/MePc/Al Structures

Room temperature J-V characteristics of ITO/CuPc/Al structures are shown in Fig.3.3, which display a distinct diode like asymmetric J-V characteristic behavior. When positive bias is applied to ITO electrode (termed as forward bias), the current increases with bias by several order of magnitude compared to when ITO electrode is negatively biased (termed as reverse bias). In this case, holes can flow easily from the organic layer to Al electrode when ITO is forwardly biased. But, the holes can not flow easily from Al electrode to the organic layer due to the formation of a barrier height (~0.6eV) equal to the difference between the work function of Al and the ionization potential of MePcs, at the interface, when ITO is reversely biased. In the reverse direction, current is negligibly small and increases slowly with bias. The same asymmetric J-V characteristics are reproducible and have been observed on several devices with different thicknesses of MePcs and shown in Fig.3.3(for CuPc) and Fig.3.4(for ZnPc). The ratio of the forward current to the reverse current at the same bias is defined as rectification ratio ($\rho_r$). Fig.3.6 shows the rectification ratio ($\rho_r$) as a function of
Figure 3.3: Room temperature J-V characteristics of ITO/CuPc/Al devices with (a) 100nm, (b) 200nm, and (c) 400nm of CuPc layers in semilogarithmic representation. Open circles represents the forward (ITO as anode) current and open squares represent the reverse (ITO as cathode) current.
Figure 3.4: (a) J-V characteristics of an ITO/ZnPc/Al hole only device with thickness 200nm in semilogarithmic representation at room temperature. (b) shows the rectification ratio $\rho_r$ as a function of bias in semilogarithmic representation.

bias. It has been found that $\rho_r$ increases with bias and reaches $10^6$ for ITO/CuPc/Al (Fig. 3.6) and $10^3$ for ITO/ZnPc/Al devices (Fig. 3.4b). The forward current can be explained through the space charge limited current (SCLC) limited with field dependent mobility (discussed in Chapter-IV) and the reverse injection current can be explained by modified Schottky equation which will be discussed later.

Fig. 3.5 shows the J-V characteristics of ITO/MePc(200nm)/Cu structure, at room temperature. There is no significant difference in currents for the forward and reverse conditions. Here, the work functions of both electrodes (ITO and Cu) are close to the ionization potential of MePcs. It is already mentioned that, there are barriers $\phi_{Bh}$ of 0.05eV at ITO/CuPc and 0.2eV at Cu/CuPc interfaces respectively, to hole flow through the structure. This negligible barrier, gives rise to space charge limited current to flow through the device when either ITO or Cu is positively biased and we observe comparable current in both the forward and reverse biased conditions, resulting symmetric J-V characteristics in these devices.
Figure 3.5: J-V characteristics of ITO/MePc(200nm)/Cu hole only devices in semilogarithmic representation at room temperature. Symmetric behavior in current (no significant change in forward and reverse biased currents) is observed for (a) CuPc and (b) ZnPc based organic single layer devices.

3.5 Dependence of Diode Characteristics on Different Parameters

Fig.3.6 shows the variation of $\rho_r$ with bias for different thickness of CuPc layers in ITO/CuPc/Al structures. It is clear from this figure that $\rho_r$ increases from $\sim 10^1$ for 50nm samples to $\sim 10^8$ for thicknesses above 200nm, indicating that diodes of desired rectification for electronic applications can be achieved by controlling the thickness of the active organic layer in CuPc based single layer devices. Both forward SCLC current and reverse injection limited current depend on temperature leading to temperature dependence of $\rho_r$, as shown in Fig.3.7. $\rho_r$ decreases with temperature and maximum $\rho_r$ can be achieved at room temperature.
Figure 3.6: The rectification ratio $\rho_r$ of ITO/CuPc/Al devices at room temperature, as a function of bias in semilogarithmic representation for different thicknesses of CuPc layer.

Figure 3.7: The rectification ratio $\rho_r$ of an ITO/CuPc/Al device with thickness 400nm in semilogarithmic representation at various temperatures.
3.6 Different Current Injection Processes

Injection of charge carriers from a metal contact into a semiconductor is commonly described either by tunneling or by thermionic emission and the corresponding current conduction is explained through the following processes.

3.6.1 Fowler-Northeim Tunneling (FNT)

Electric transport through the thin insulating film is dominated by quantum mechanical tunneling and is characterized by observing the J-V characteristics. Fowler-Nordheim mechanism[78] is most commonly used to explain the experimental J-V characteristics dominated by tunneling current. Here, the analytical expression for current density is calculated by using W. K. B. approximation and considering a flat band structure,

\[ J_{FNT} = A F^2 \exp \left( -\frac{B}{F} \right) \]

where, \( A = \frac{e^3}{8 \pi \hbar \phi_B} \) and \( B = 4 \sqrt{2 m^* (e \phi_B)^{3/2}} / 3 e \hbar \), where \( F \) is the applied electric field, \( \phi_B \) is the barrier height formed at the junction, \( h \) is Planck's constant, \( e \) is the electronic charge and \( m^* \) is the effective mass of the charge carrier. FNT mechanism is most commonly used technique to explain the experimental J-V characteristics dominated by tunneling current. It has been found that FNT mechanism fails to fit the experimental data throughout the bias region. This model ignores the image-charge effects and is insensitive to temperature. The J-V characteristics of Metal-Insulator-Semiconductor (MIS), Metal-Insulator-Metal (MIM) and Metal-Semiconductor-Metal (MSM) structures are determined numerically by solving the time dependent Schrödinger equation, which can explain the experimental data over wide range of bias and is discussed in details in Appendix-G.
3.6.2 Richardson-Shottkey (RS) Emission Model

In the thermionic emission process, an electron from the metal contact can be injected once it has acquired a thermal energy sufficient to cross the barrier formed at the interface taking image force into account. Here tunneling is ignored. If the injection is thermally activated, then the thermionic emission over the barrier, describes the transport characteristics and is expressed by the RS formula

\[ J_{RS} = A^* T^2 e^\left( -\frac{\Phi_B - \sqrt{e^3/4\pi\epsilon}}{k_B T} F^{1/2} \right) \]  \hspace{1cm} (3.2)

where, \( A^* \) is the Richardson’s constant, \( T \) is the temperature, and \( k_B \) is the Boltzmann’s constant.

3.7 Charge Carrier Injection in Metal/OMS/Metal Structures

We have shown that ITO, Au and Cu behave as Ohmic contacts to CuPc and Al, as Schottky contact. Ohmic contact does not limit the current flow and supplies the space charge limited current, which is the maximum current density possible in OMS. But, in case of Schottky contacts, the current is injection limited and lower than space charge limited current. The experiment consisted of two parts. First: the current due to hole injection was measured by biasing Cu and Al electrodes positively and second: the current due to hole injection from ITO was measured by reversing the polarity of the bias voltage. It has been shown [73] that the current, for the case of ITO injecting contact, which has a 0.05eV barrier, is due to SCLC. Fig.3.5 shows the symmetric J-V characteristics in case of ITO/CuPc/Cu, in both cases (hole injection either from ITO, or from Cu electrodes). As it is already mentioned, This is because in both cases there are small energy barriers of 0.05eV(ITO/CuPc) and 0.2eV(Cu/CuPc), giving rise to SCLC when either ITO or Cu is positively biased. It has been shown [77], for SEB less than about 0.3-0.4eV, the current
flow is due to SCLC. But, in case of ITO/CuPc/Al devices, J-V characteristics displays asymmetric and rectification-like behavior (Fig. 3.3). Current density increases by almost five order of magnitude by reversing the polarity of bias. As discussed before, when ITO is positively biased, current is due to SCLC and when Al is positively biased, current is due to injection limited and reduced by several order of magnitude due to the existence of SEB of 0.6 eV at CuPc/Al contacts. Fig. 3.8 shows the J-V characteristics for ITO/CuPc/Al hole only devices at various temperatures (80K, 200K, and 320K) with Al as hole injecting contact for different CuPc thickness of 25, 50, 100, 200, and 400 nm. In this case, current density decreases with thickness. Campbell et al. [17] demonstrated a model for single layer OLEDs including the charge injection, transport and surface charge effects. At each contact there are three contributions for injection limited current: (i) thermionic emission, (ii) tunneling, and (iii) a backflowing interface recombination current, which is the time reversed process of thermionic emission. The hole current density at the contact (x = 0) is given by [17, 75]

\[ J(0) = J_{TH} + J_{TU} - J_{IR} \]  (3.3)

where \( J_{TH} \) is the thermionic current density, \( J_{TU} \) is the tunneling current density and \( J_{IR} \) is the interface recombination current density. The \( J_{TH} \) is calculated from the RS equation using an energy barrier that depends on the electric field at the interface because of the image force effect and is given by,

\[ \phi'_{B} = \phi_{B} - e \sqrt{\frac{e|F(L)|}{\epsilon}}. \]  (3.4)

where \( \phi_{B} \) is the Schottky energy barrier at zero field. The tunneling current is calculated using W. K. B. approximation for tunneling through a potential given by the image force model. The interface recombination current is

\[ J_{IR} = Sp(0) \]  (3.5)
Figure 3.8: Measured J-V characteristics for ITO/CuPc/Al(with Al hole injecting contacts) devices with CuPc thicknesses of 25, 50, 100, 200, and 400nm at three different temperatures. (a) 320K, (b)200K, and (c)80K.
where $S$ is the surface recombination velocity and $p(0)$ is the hole density at $x = 0$. Now the net current passing through the device[75, 17] is

$$J_p(0) = S[p_{QE}(F(0)) - p(0)] + J_{TU}$$

(3.6)

where $p_{QE}(0)$ is the quasi-equilibrium hole density calculated with the image force lowered energy, and is expressed as,

$$p_{QE}(F(0)) = p_0 exp(-\phi_B^\prime/k_BT)$$

(3.7)

In the hole only single layer devices the net device current density ($J_D$) is due to the hole current and also it is independent of position, i.e., $J_D = J_p(0)$. Campbell et al.[75, 17] have shown that the device current $J_D$ is too small to affect the hole density at the contact. Now the hole density at the contact can be given by,

$$p(0) = p_{QE} + \frac{J_{TU} - J_D}{S}$$

(3.8)

Depending on the thickness of the OMS in single layer and single carrier devices, two situations may arise.

**Case-I:** When the thermionic current density is large and tunneling current density is negligible (in thicker devices) and $p(0) = p_{QE}(0)$, which should be valid in devices ITO/CuPc/Al with 100, 200nm and 400nm thick CuPc (shown in Fig.3.8).

**Case-II:** When the tunneling current density is large compared to thermionic current density (in thinner devices) and $p(0) = J_{TU}/S$, which should be valid in devices ITO/CuPc/Al with 25nm and 50nm thick CuPc (shown in Fig.3.8.).

### 3.8 Schottky Energy Barrier and Charge Injection

The commonly observed charge injection mechanism at the metal-semiconductor interface[78] are predicted by assuming long range order in the semiconductor, where electrons are freely
propagating in the conduction band with thermal distribution of kinetic energies. But the fundamental aspects of the charge injection process for disordered OMS are not understood in details because of the difficulty in extending the calculations from a crystalline to a non-crystalline semiconductor, where the charge transport is due to hopping between localized states but not due to propagation in extended states. Scott and Malliaries[76] derive an expression considering injection(metal to organic) and recombination(organic to metal) processes simultaneously. Here, the effective Richardson's constant and the injection current are determined by assuming the surface recombination is a field-enhanced diffusion process, which is analogous to the Langevin bimolecular recombination in amorphous semiconductors[50, 79]. Langevin theory is applicable for the case where random, diffusive motion of charge carriers is dominant and drift can be viewed as a small bias in the time averaged displacement, the averaged electron-hole pair that approach each other within a distance such that their coulombic binding energy exceeds \( k_B T \) will ultimately recombine. The demarcation distance in a statistical sense is given by the Coulomb radius

\[
r_C = \frac{e^2}{4\pi\varepsilon_0 k_B T} \tag{3.9}
\]

The Langevin mechanism is justified in the present case by considering the attractive image potential acting on a charge carrier in the organic material as it approaches the metal contact[78]. Under an external electric field(\( F \)), the potential barrier is lowered by \( -eFx \), where \( x \) is the distance from the injection contact. The potential barrier, \( \phi(x) \), formed by the superposition of an external electric field and the coulomb field binding the carriers with its own image charge on the electrode is

\[
\phi(x) = \phi_B - eFx - \frac{e^2}{16\pi\varepsilon_0 x} \tag{3.10}
\]

where \( \phi_B \) is the Schottky barrier height(\( \phi_{Bh} \) for holes and \( \phi_{Be} \) for electrons) in the absence of both the external field and the image charge effect. \( \varepsilon \) is the dielectric constant of the organic
Figure 3.9: Potential energy at the metal/OMS interface. (a) shows the potential due to a uniform applied electric field. (b) shows the pure image potential in the absence of any applied field. (c) represents the average electrostatic energy of a charge carrier in the Coulombic field of the image charge and in the external electric field, which causes the reduction in barrier height by $\Delta \phi_B$

material. At zero electric field, the electron image binding energy is $k_B T$ at a distance $x_C = r_C/4$, which is larger than the intermolecular distance. As a result, the mean hopping distance (compared to mean free path) of the carrier is shorter than the Coulomb capture distance. This validates the diffusive transport and the recombination current at the $x = x_C$ can be given by

$$J_{REC} = n_0 e \mu F(x_C) = 16 \pi \epsilon (k_B T)^2 n_0 \mu / e^2$$  \hspace{1cm} (3.11)

where $n_0$ is the charge density at the interface (at $x_C$) and $\mu$ is the carrier mobility. This equation defines the surface recombination velocity as

$$S(0) = J_{REC} / n_0 e = 16 \pi \epsilon (k_B T)^2 \mu / e^3$$  \hspace{1cm} (3.12)

Let the injection current be $J_{INJ} = C \exp(-\phi_B / k_B T)$ in the absence of any applied electric field, there is a balance between thermally injected and surface recombination currents, which
gives

\[ J_{INJ} - J_{REC} = C[\exp(-\phi_B/k_BT) - n_0/N_0] = 0 \]  \hspace{1cm} (3.13)

\[ C = \left( \frac{16\pi \epsilon \epsilon_0 k^2 N_0 \mu}{e^2} \right) T^2 = A^*T^2 \]  \hspace{1cm} (3.14)

where \( N_0 \) is the density of the chargeable sites and \( A^* \) is the effective Richardson constant for metal-semiconductor cases.

The injection and recombination currents show an exponential electric field dependence which results from the consideration of lowering the energy barrier (Schottky barrier lowering) by an amount proportional to the square root of the applied field. The field dependent surface recombination velocity is determined by taking the Coulomb capture distance at which the energy is \( k_BT \) below the field-dependent maximum and is given by

\[ S(E) = \frac{1}{4} S(0) \left( \frac{1}{\psi^2} - f \right) \]  \hspace{1cm} (3.15)

where the reduced electric field is

\[ f = \frac{eFr_C}{k_BT} \]  \hspace{1cm} (3.16)

and \( \psi \) is a parameter that varies slowly with electric field and given by

\[ \psi(f) = f^{-1} + f^{-1/2} - f^{-1} \left( 1 + 2f^{1/2} \right)^{1/2} \]  \hspace{1cm} (3.17)

The net current due to thermionic and surface recombination is then given as

\[ J_{NET} = A^*T^2 \exp(-\phi_B/kT)\exp(f^{1/2}) - n_0 eS(E) \]  \hspace{1cm} (3.18)

Now by equating the net surface current to the bulk current leaving the interface (i.e., \( J = n_0e\mu E \)), an expression for the field dependence of the surface charge density can be given by

\[ n_0 = 4\psi^2 N_0 \exp(-\phi_B/kT)\exp(f^{1/2}) \]  \hspace{1cm} (3.19)

which is independent of mobility. Then the net current is expressed as

\[ J_{NET} = 4\psi^2 N_0 \mu e \exp \left( -\frac{\phi_B}{k_BT} \right) \exp(f^{1/2}) \]  \hspace{1cm} (3.20)
Figure 3.10: Temperature dependence of injected current density (when Al electrode is positively biased) as a function of electric field in ITO/CuPc/Al hole only devices with thickness of (a) 100nm and (b) 400nm, starting at 300K and then at the interval of 40K. The solid lines are theoretical prediction by Eq.3.20. Inset shows the Arrhenius plot of low field current versus temperature. Solid line is fit according to activation energy, $\phi_B=0.55eV$ for (a) and $\phi_B=0.57eV$ for (b).
Schottky barrier lowering due to image force is included by the factor $\exp(f^{1/2})$ in this equation.

Fig. 3.10 shows the temperature dependence of injection limited current in ITO/CuPc/Al structure with (a) 200nm and (b) 400nm of CuPc layers. In this case tunneling current can be neglected and the net injected current into the bulk of the CuPc is the difference between the injected flux due to thermionic emission over the Schottky barrier and the current due to interface recombination. The theoretical expression for the electric field dependence of thermionic injection current considering the Schottky barrier lowering due to image force explains the experimental J-V characteristics data shown in Fig. 3.10 and it is clear from this figure that injection limited current explains the variation of current with electric field quite well throughout the temperature range. Similar behavior of J-V characteristics has been observed\[80] in tetraphenyl diamine doped polycarbonate based single layer hole only devices. $\phi_B$ has been determined from the thermally activated behavior (shown in inset of Fig. 3.10) of the injected current at low field and has been found to be 0.55eV for 100nm and 0.57eV for 400nm devices, which is very close to ideal value of 0.6eV in case of CuPc/Al contact with the vacuum alignment consideration.

3.9 summary

The experimental observations of the J-V characteristics for MePc(CuPc and ZnPc) based single layer hole only ITO/MePc/Metal devices are presented. ITO, Au, and Cu behave as Ohmic contacts to CuPc for hole flow and Al as Schottky contact. It is demonstrated that diode-like asymmetric J-V characteristics with high rectification ratio of about $10^6$ can be achieved if an electrode with low work function is used. But, an electrode with high work function, comparable to the ionization potential of CuPc, results in negligible rectification. The rectification ratio strongly depend on temperature and thicknesses of the device. Diodes
with required rectification ratio are possible to achieve in single layer ITO/MePc/Metal devices by suitably controlling the thickness of the active organic layer.

The J-V characteristics in the forward direction (when ITO is positively biased) can be consistently described as bulk limited space charge current modified with field dependent mobility (discussed in detail in Chapter-IV). In the reverse direction (when ITO is negatively biased) the current conduction is injection limited due to the formation of barriers to hole flow at Metal/CuPc interface. The mechanism limiting the current flow in the device, depends on the device parameters such as Schottky energy barriers of the contacts, thickness of OMS, and the carrier mobility. A systematic investigation of the charge carrier injection is studied by varying the work function of the contacting metals. It has been demonstrated that structures having interface Schottky energy barriers to carrier (holes in ITO/CuPc/Al devices) less then 0.4 eV, shows the bulk transport limited current conduction. The contribution to injection currents from thermionic and tunneling have been varied by varying the thickness of the OMS layer. The injection current in case of devices based on thick CuPc layer has been found to follow the theoretically predicted analytic current-voltage relation.