Chapter 6

Effect of doping on the device characteristics of Schottky diodes fabricated from FePc, MgPc and NiPc
6.1 Introduction

In the thin film device fabrications film architectures place special emphasis and demands on charge carrier injection and transport through interfaces. Thin film devices often comprise multiple layers of organic materials and contacts for electron or hole injection, making metal–organic interfaces exceedingly important in terms of device fabrication and its performance. But there are still a few hurdles to overcome, in these interfaces or instead present real opportunities for improving device performance. For example, the large injection barriers often found between metals and large gap organic materials are serious impediments to charge injection, and can cause a variety of problems ranging from high turn-on voltages to device degradation. On the positive side, the advanced architecture of organic light emitting diodes and photovoltaic cells has been shown to make successful use of multiple organic layers with different energy gaps in engineering molecular level offsets across hetero junctions and blocking unwanted carrier transport or recombination of excitons, thus enhancing quantum efficiency. Given their obvious importance, these semiconductor interfaces have been the subject of multiple fundamental and phenomenological investigations aimed at understanding their electronic properties and at controlling interface energy barriers.\textsuperscript{1,2} In this chapter the various aspects of doping as a means of modifying or controlling metal semiconductor interfaces are studied. Doping of organic molecular films has been investigated relatively little as compared to doping of inorganic semiconductors at the same stage of development of these materials, but is now perceived as a key step for enhancing the performance and versatility of electronic and optoelectronic
devices. Doping is a simple and promising way to improve conductivity and carrier injection in the organic semiconductors. Further the shift in the Fermi level is another advantage of the controlled doping.\textsuperscript{3,4} Doping leads to considerably improved electrical properties of devices with organic layers, better ohmic or blocking contacts with metals or other conductive substrates, more efficient carrier transport and hence lower operating voltage in light emitting diodes.\textsuperscript{5,6} Basically doping of such layers is rather similar to inorganic semiconductors but the microscopic mechanisms seem to be different.\textsuperscript{7}

In this chapter we report the study of the electronic structure and the conduction mechanisms of the iodine doped Au/FePc/Al, Au/MgPc/Al and Au/NiPc/Al device from their dark current density–voltage characteristics. The electrical property of a mixed NiPc and CuPc device with gold and lead electrodes is also investigated and the results are given in this chapter.

### 6.2 Theory

The basic principle of doping in the organic semiconductors is similar to that in inorganic materials. However some preliminary observations may be made about doping in molecular materials. Molecules in the organic semiconductors are bound by weak Van der Waals forces; instead of strong inter atomic covalent bonds. Doping occurs by direct charge transfer of electrons from host to dopant for p-type and in the opposite direction for n-type, rather than by incorporation of the dopant via formation of covalent bonds and release of excess charge (electron or hole) to a band, as occurs in inorganic semiconductors.\textsuperscript{8} Second, the physics of charge transport in molecular films is dominated by localization and
polarization.\textsuperscript{9,10} The intermolecular overlap of wave functions is small and transport is by thermally activated hopping.\textsuperscript{11,12} By adding impurities to the organic semi conductors which either transfer electron to the electron conducting (LUMO) states (n-type doping) or remove an electron from the hole conducting (HOMO) states to generate a free hole.\textsuperscript{13} It has been shown that very high conductivities can be achieved when organic semiconductors with a weak donor character like the phthalocyanines are exposed to strongly oxidizing gases like bromine chlorine and sodium.\textsuperscript{14-17} However, such small dopants can easily diffuse in the organic layers, so this technique is suitable to prepare thermally stable bipolar devices such as pn or pin-junctions. Similar considerations hold for doping by other small atoms like lithium\textsuperscript{18} or small molecules like Lewis acids.\textsuperscript{19} The magnitude and the type of conduction depend upon number of factors such as electron affinity, polarization energy of acceptors, nature of electrodes\textsuperscript{16}, ionization potential of donors and concentration of acceptors.\textsuperscript{20-26}

Doping in the organic semiconductors creates a random distribution of dopant ions that will interact with carriers localized in intrinsic hopping sites. This coulomb interaction further increases the energy disorder. This effect is especially important in view of a small value of the dielectric constant and, concomitantly, long range of the Coulomb interaction typical for molecular semiconductors. Increasing energy disorder with increasing dopant concentration will lead to broadening of the effective density of states (DOS) distribution.\textsuperscript{27} Therefore, doping of a disordered organic semiconductor, on the one hand, increases the concentration of charge carriers and lifts up the Fermi level towards the transport
layer but, on the other hand, broadens the DOS distribution. While the former effect facilitates conductivity, the latter strongly suppresses the carrier hopping rate.\textsuperscript{28} The latter effect can dominate at some dopant concentrations such that doping appears to be even counterproductive as far as the carrier mobility is concerned. It is shown that doping shifts some intrinsic hopping sites to the deeper tail of the DOS distribution and, thus, creates additional deep traps for charge carriers. This leads to decreasing mobility at low dopant concentrations. At higher doping levels the filling of deep states takes over and causes a steeply increasing mobility at high dopant concentrations.

6.3 Experiment

Iron phthalocyanine, Magnesium phthalocyanine and Nickel phthalocyanine powder from Sigma- Aldrich USA is the base materials for the thin film device fabrication in the present study. Thin films of phthalocyanines are thermally evaporated from a tantalum boat at a pressure of about $10^{-6}$ Torr using a high precision thin film-coating unit as described in chapter II. Thin films are deposited onto a pre cleaned glass substrate, which is previously deposited with a gold film as the bottom electrode. Iodine is doped in to the organic layer by releasing iodine vapour from another boat containing pure iodine crystals. A separate power supply is used for this purpose. The device fabrication is completed with an aluminium top contact layer that is also deposited from a tantalum boat.

For fabricating a Mixed phthalocyanine device 50 mg of CuPc and 50 mg of NiPc are evaporated simultaneously from two separate tantalum boats which are kept side by side and using a thermal coating unit as explained earlier. In order to get a
uniform and fair mixing of the two phthalocyanines, the Mixed phthalocyanine vapour is passed through a tungsten helix filament, which is kept just above the boats. An additional power supply is used for heating this filament. Thin films of Mixed phthalocyanines are deposited onto a pre cleaned glass substrate, which is previously deposited with a gold electrode. The evaporation rate and the evaporation time are 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 is also deposited from a tungsten coil. To ensure the films of nearly equal proportions of the two phthalocyanines, samples that are kept very close and just above the boats are only used for study and further measurements.

Table 6.1  Device parameters of iodine doped FePc, MgPc and NiPc Schottky diodes with dissimilar electrodes.

<table>
<thead>
<tr>
<th>Device component</th>
<th>Gold electrode thickness (nm)</th>
<th>Aluminium/lead electrode thickness (nm)</th>
<th>Phthalocyanine layer thickness (nm)</th>
<th>Active area of phthalocyanine Layer (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/FePc/Al</td>
<td>60</td>
<td>60</td>
<td>640</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Au/MgPc/Al</td>
<td>60</td>
<td>68</td>
<td>600</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Au/NiPc/Al</td>
<td>50</td>
<td>60</td>
<td>600</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Au/Mixed Pc/Pb</td>
<td>50</td>
<td>60</td>
<td>600</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Electrical conductivity measurements of the iodine doped and Mixed phthalocyanine devices are performed by a stabilized digital power supply and a Kethley programmable electrometer in a subsidiary vacuum system at a pressure of
approximately $10^{-3}$ Torr as described in chapter 2.20. Keeping the gold electrode as positive for the forward bias condition, currents are measured for the different values of applied voltage ranging from 0V to 10V. Dependence of current in the forward bias and reverse bias for different applied voltage are measured at room temperature and also in the 300K –400K temperature range. Temperature is measured by means of chromel / alumel thermocouple. The permittivity of the Mixed phthalo cyanine is obtained from the capacitance measurement of the device with different film thickness using a Hioki LCR Hi-tester. The various device component dimensions are measured and listed in Table 6.1

6.4 Results and discussion

The effect of iodine doping on the electrical properties and the nature of conduction in the FePc, MgPc and NiPc thin film devices are studied.

6.4.1 Electrical Characteristics of Iodine doped Au/FePc/Al Schottky device.

The effect of iodine doping on the electrical conductivity of FePc thin films are investigated from the current density-voltage characteristics of the iodine doped Au/FePc/Al device. Keeping the gold electrode as positive for the forward bias condition, currents are measured for the different values of applied voltages ranging from 0V to 10V at room temperature. Currents are measured continuously varying the bias and also by interrupting the bias between each step and in each results are consistent.

Figure 6.1 is the plots of Ln (J) versus Ln (V) of the iodine doped Au/FePc/Al device from which the precise electrical conduction methods of the
device are evaluated. The graph shows two distinct conduction processes in the forward bias.

![Graph of forward and reverse J-V characteristics](image)

**Figure 6.1** Forward and reverse J-V characteristics of the iodine doped Au/FePc/Al device at room temperature.

The forward current is ohmic up to 0.7 V and thereafter changes to space charge conduction. Plotting \( \ln(J/V) \) against \((1000/T)\) in the ohmic region and using Equation 4.6, the values of thermally generated hole concentration \( E_f \) and the mobility of the holes are calculated from the slope and intercept. Figure 6.2 represents the variation of \( \ln (J/V) \) with inverse temperature in the ohmic region from which the various electrical parameters in the ohmic region are calculated and listed in Table 6.2. At higher voltages the slope of the J-V characteristics show a space charge limited conduction with an exponential trap level which may be
described by Equation 4.11. Using this equation the trap parameters in the SCLC region are evaluated and tabulated in Table 6.2

The nature of conduction under a reverse applied bias of the iodine doped Au/FePc/Al device is also investigated. From current voltage characteristics in Figure 6.1 under the reverse bias a current limitation in the device is observed. This may be explained as a electrode limited conduction which can be described as either a Schottky or Poole–Frenkel type of conduction governed by the Equation 4.15.

Table 6.2  Electrical conduction parameters of Iodine doped Au/FePc/Al device

<table>
<thead>
<tr>
<th>Characteristic region and nature of conduction</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic region</td>
<td>$E_f$</td>
<td>$0.55 \pm 0.01 \text{ eV}$</td>
</tr>
<tr>
<td></td>
<td>$\mu$</td>
<td>$1.43 \times 10^{-8} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P_0$</td>
<td>$6.09 \times 10^{-17} \text{ m}^{-3}$</td>
</tr>
<tr>
<td>Space charge limited conduction with an exponential trap level</td>
<td>$T_t$</td>
<td>1050 K</td>
</tr>
<tr>
<td></td>
<td>$P_t$</td>
<td>$9.4 \times 10^{-43} \text{ J}^{-1} \text{ m}^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$N_{t(e)}$</td>
<td>$1.36 \times 10^{-24} \text{ m}^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$V_t$</td>
<td>$0.61 \text{ V}$</td>
</tr>
<tr>
<td>Reverse bias</td>
<td>$\beta$</td>
<td>$4.14 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$</td>
</tr>
<tr>
<td></td>
<td>Barrier height</td>
<td>$0.97 \pm 0.01 \text{ eV}$</td>
</tr>
<tr>
<td></td>
<td>Depletion layer thickness</td>
<td>212 nm</td>
</tr>
</tbody>
</table>

The theoretical value of the Schottky field lowering coefficient is calculated as $\beta = 1.974 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$ Figure 6.3 shows the variation of current density against square root of applied voltage in the reverse bias of the iodine doped
Au/FePc/Al device. This is a linear plot and from the slope and intercept of this straight line the Schottky barrier height, the depletion layer thickness and the Schottky field lowering coefficients are calculated and tabulated in Table 6.2. The closeness of the theoretical and experimental values of the field lowering coefficient deduce to a Schottky field emission in the reverse bias. The slight variation of $\beta_s$ in the low voltage region may be attributed to the non uniformity of the doping. Further the Schottky depletion region is extending only for a small distance and not across the whole thickness of the organic layer.

Tsutomu etal\textsuperscript{29} investigated Copper phthalocyanine doped with TCNQ by co-evaporation technique and they reported increased values of electrical conductivity in doped device than that in undoped Copper phthalocyanine.

![Figure 6.2](image)

**Figure 6.2** Variation of Ln (J/V) with inverse temperature for the iodine doped Au/FePc/Al device in the ohmic region.
Figure 6.3 Semi logarithmic plot of reverse J vs. $V^{1/2}$ for the iodine doped Au/FePc/Al device at room temperature

M. Pfeiffer et al. reported the controlled p type and n type doping of Zinc phthalocyanine and reported that conductivities can be raised many orders of magnitude above the conductivity of nominally undoped materials.

6.4.2 Electrical characteristics of Iodine doped Au/MgPc/Al Schottky device.

Figure 6.4 is the plot of current density (J)-voltage (V) characteristics of the iodine doped Au/MgPc/Al sandwiched device measured in the voltage range of 0V to 10 volts at room temperature. The general behavior of the electrical conduction
of iodine doping in the Au/MgPc/Al device to the applied voltage is reflected in this graph.

Figure 6.4  Forward and reverse J-V characteristics of the iodine doped Au/MgPc/Al device at room temperature.

Generally the graph showed an asymmetric behavior and an enhanced conductivity after doping. From the order of the slopes it is considered that there are two distinct conduction processes involved in the forward bias. In the low voltage range nearly up to 1 V the slope of the logJ-logV characteristics of the forward bias is in the order of unity and hence can be considered as an ohmic conduction between the organic layer and the electrodes.
Figure 6.5  Variation of $\ln \left( \frac{J}{V} \right)$ with inverse temperature for the iodine doped Au/MgPc/Al device in the ohmic region.

Figure 6.6  Semi logarithmic plot of reverse $J$ vs. $V^{1/2}$ for the iodine doped Au/MgPc/Al device at room temperature
The various electrical properties in the ohmic range are calculated from the slope and intercept of the line in Figure 6.5 with Equation 4.6 and are reported in Table 6.3. Beyond 1V in the higher voltage range after iodine doping, the conduction is space charge limited with an exponential trap level and the trap parameters in this range of conduction are calculated using Equation 4.11 and reported in Table 6.3.

<table>
<thead>
<tr>
<th>Characteristic region and nature of conduction</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic conduction</td>
<td>$E_f$</td>
<td>$0.52 \pm 0.01$ eV</td>
</tr>
<tr>
<td></td>
<td>$\mu$</td>
<td>$2.58 \times 10^{-10}$ m$^2$ V$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P_0$</td>
<td>$1.56 \times 10^{18}$ m$^{-3}$</td>
</tr>
<tr>
<td>Space charged conduction with an exponential trap level</td>
<td>$T_t$</td>
<td>1060 K</td>
</tr>
<tr>
<td></td>
<td>$P_t$</td>
<td>$5.03 \times 10^{44}$ J$^{-1}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$N_{t(e)}$</td>
<td>$7.29 \times 10^{24}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$V_t$</td>
<td>1.1 V</td>
</tr>
<tr>
<td>Reverse bias</td>
<td>Lower voltage $\beta$</td>
<td>$2.39 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$</td>
</tr>
<tr>
<td></td>
<td>Higher voltage $\beta$</td>
<td>$2.68 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$</td>
</tr>
<tr>
<td></td>
<td>Barrier height</td>
<td>$1.03 \pm 0.01$ eV</td>
</tr>
</tbody>
</table>

The reverse bias current–voltage characteristics also give information about the changes in the electrical properties of metal-semiconductor after doping. The reverse current is much lower than the forward current indicating a current limitation that can be explained as a Schottky or Poole-Frenkel type of conduction. In order to find the experimental values of these coefficients a graph of
Ln J versus. $V^{1/2}$ is replotted as in Figure 6.6. This plot is having two distinct linear portions and correspondingly there are two slopes in the lower and in the higher voltage regions. The values of the field lowering coefficients $\beta$ in the two voltage regions are listed in Table 6.3. The result in the low field region suggests that the conduction mechanism is controlled by Schottky emission over the space charged region formed at the metal–organic semiconductor interface. In the low and high voltage region the value of $\beta$ is in reasonable agreement with the theoretical values of the Schottky field lowering coefficients suggesting an injection current at the metal organic interface.

Huanjun and Yongli have investigated cesium and sodium doping in Copper phthalocyanine and observed an energy level shift due to the Fermi level moving in the energy gap as a result of the doping of electrons from the alkaline metal to the organic, and significant modification of organic energy levels, such as the introduction of a new gap state, new core level components and a change of binding energies.

Taguchi et al. investigated magnetic properties of Manganese phthalocyanine after lithium doping and reported a gradual crossover of the intrachain exchange interactions from ferromagnetic to antiferromagnetic with the increase in doping level.

**6.4.3 Electrical characteristics of Iodine doped Au/NiPc/Al Schottky device.**

The nature of electrical conductivity and the various electrical parameters of the iodine doped Au/NiPc/Al device are investigated from the current density–voltage characteristics at room temperature. Figure 6.7 shows the variation of forward and
reverse $\ln(J)$ versus $\ln(V)$ of the iodine doped Au/NiPc/Al device at room temperature.

![Graph showing forward and reverse J-V characteristics](image)

**Figure 6.7** Forward and reverse J-V characteristics of the iodine doped Au/NiPc/Al device at room temperature.

The conductivity of the doped device is much higher than the undoped Au/NiPc/Al device. But the nature of conduction is not much deviated from its original nature even after doping. Slope of the graph implies that at different voltage levels the conduction mechanisms are different. From the order of the slopes it is concluded that there are three distinct conduction processes involved. In the low voltage range nearly up to 0.3 V for the segment (I) the slope of the J-V characteristics is in the order of two and hence can be considered as SCL conduction with a discrete
trap level described by Equation 4.10. Figure 6.8 is the plot of \( \ln \left( \frac{J}{V^2} \right) \) versus inverse temperature for the iodine doped Au/NiPc/Al device in the SCL range of segment (I). From the slope and intercept of the straight lines in this graph together with Equation 4.10 the various electrical parameters in the SCL range of conduction (segment I) are calculated and reported in Table 6.4.

![Graph showing variation of \( \ln \left( \frac{J}{V^2} \right) \) with inverse temperature](image)

**Figure 6.8**  Variation of \( \ln \left( \frac{J}{V^2} \right) \) with inverse temperature for the iodine doped Au/NiPc/Al device in the SCLC region.

At higher voltages above 0.3V for segment II and segment III the slope of the J-V characteristics in Figure 6.7 implies again SCL conduction with an exponential trap level at two different voltage levels governed by the Equation 4.11. Using this
equation the trap parameters in both SCLC regions are evaluated and tabulated in Table 6.4.

Figure 6.9  Semi logarithmic plot of reverse J vs. $V^{1/2}$ for the iodine doped Au/NiPc/Al device at room temperature
Table 6.4  Electrical conduction parameters of iodine doped Au/NiPc/Al device.

<table>
<thead>
<tr>
<th>Characteristic region and nature of conduction</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space charged limited conduction with a single trap level (Segment I)</td>
<td>$E_t$</td>
<td>$0.57 \pm 0.01$ eV</td>
</tr>
<tr>
<td></td>
<td>$N_{t(s)}$</td>
<td>$2.72 \times 10^{21}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$\theta$</td>
<td>$2.83 \times 10^{-4}$</td>
</tr>
<tr>
<td>Space charged conduction with an exponential trap level (Segment II)</td>
<td>$T_t$</td>
<td>640 K</td>
</tr>
<tr>
<td></td>
<td>$P_t$</td>
<td>$9.83 \times 10^{44}$ J$^{-1}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$N_{t(e)}$</td>
<td>$8.59 \times 10^{24}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$V_t$</td>
<td>0.3 V</td>
</tr>
<tr>
<td>Space charged conduction with an exponential trap level (Segment III)</td>
<td>$T_t$</td>
<td>1380 K</td>
</tr>
<tr>
<td></td>
<td>$P_t$</td>
<td>$3.23 \times 10^{42}$ J$^{-1}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$N_{t(e)}$</td>
<td>$6.16 \times 10^{22}$ m$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>$V_t$</td>
<td>1.9 V</td>
</tr>
<tr>
<td>Reverse bias Schottky conduction</td>
<td>$\phi_b$</td>
<td>$0.90 \pm 0.01$ eV</td>
</tr>
<tr>
<td></td>
<td>$\beta_s$</td>
<td>$2.29 \times 10^{-5}$ (eV m$^{1/2}$ V$^{-1/2}$)</td>
</tr>
</tbody>
</table>

Figure 6.9 shows the variation of current density with applied voltage in the reverse bias. This is a linear plot and from the slope and intercept of this line the Schottky barrier height and the Schottky field lowering coefficients are calculated and tabulated in Table 6.4. A change in the trap concentrations is observed for the NiPc after doping which enhances the electrical conductivity of the NiPc devices. Craciun$^{32}$ et al. have probed into the dependence of molecular orbitals and doping on the electrical conductivity of potassium intercalation in ZnPc, CuPc, NiPc, CoPc, FePc, and MnPc and reported that the nature of the molecular orbitals
produces observable effects in the doping dependence of the electrical conductivity of the materials.

**6.4.4 Electrical characteristics of Au/Mixed Pc/Al Schottky device.**

The electrical properties of mixed Copper phthalocyanine (CuPc) and Nickel phthalocyanine (NiPc) thin films devices with gold and lead electrodes is investigated. The two phthalocyanines are 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 mixed phthalocyanine sample is prepared.

Pakhomo and Drozdov\(^{33}\) have investigated the properties of thin films composed of planar metallophthalocyanines in various proportions of phthalocyanines prepared from vacuum sublimation. They reported the formation of stable solid solution from experimental data. Figure 6.10 shows the variation of capacitance of the Mixed phthalocyanine films against inverse of thickness at a constant frequency of 1 kHz. From the slope of the curve the absolute permittivity of the mixed organic layer is calculated\(^{34}\) as 1.2×10\(^{-11}\) F/m.

Figure 6.11 is the current density-voltage characteristics of the Schottky device of gold-Mixed Pc-lead sample measured in the voltage range of 0.1 to 10 volts. Current is measured continuously varying the bias and interrupting the bias between each voltage step, in both the cases yield the same results.
Figure 6.10  Variation of capacitance with inverse thickness of Au/Mixed Pc/Pb device at room temperature

Figure 6.11  Forward and reverse J-V characteristics of the iodine doped Au/Mixed Pc/Pb device at room temperature.
In general, the $J-V$ characteristics of the device is asymmetrical and the voltage variable slopes of the graph imply that the conduction mechanisms are different at the different voltage levels. From the order of the slopes it is 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 is 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 within the ohmic region is described by the Equation 4.6. The value of $N_v = 10^{27} \text{ m}^{-3}$ which corresponds to approximately one electronic state per molecule is used for the Mixed Pc in our calculations also. Figure 6.12 is the plot of Ln (J) against 1000/T in the ohmic region in the 300K-400K temperature range at 0.3 Volts. The graph is almost a straight line where slope and intercept of the line together with Equation 4.6 yields the various electrical parameter values in the ohmic region which are given in Table 6.5
Figure 6.12  Variation of Ln (J) with inverse temperature for the Al/Mixed Pc/Pb device.

The value of $E_f$ propose a shift in the Fermi level towards the valance edge and the mobility value suggests a lowering the mobility of the thermally generated holes. At higher voltages the slope of the J-V characteristics for the segment (II) and segment (III) are two and more suggesting a space charged limited conduction. Figure 6.12 also contain the plot of Ln (J) with 1000/T for the segment (II) of the SCLC region. From the slope and the intercept of this graph together with Equation 4.10 yield the values of $E_t$ and $N_{t(s)}$ for the segment (II) of the SCLC region. For the segment (III) in the higher voltage region of the SCLC conduction the trap parameters for the exponential trap distribution are calculated using Equation 4.11 and are tabulated in Table 6.5. In the reverse bias the current
limitation that can be explained as a Schottky or Poole-Frenkel type of conduction. Substituting the values of the permittivity of the Mixed phthalocyanine the theoretical values of the field lowering coefficients are calculated as \( \beta_{PF} = 6.74 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2} \) and \( \beta_s = 3.37 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2} \). In order to find the experimental values of these coefficients a graph of \( \ln(J) \) against \( V^{1/2} \) is re-plotted in Fig.6.13.

![Graph](image)

**Figure 6.13** Semi logarithmic plot of reverse J vs.\( V^{1/2} \) for the as deposited, iodine doped Au/Mixed Pc/Pb device at room temperature.

This plot is having two linear portions and correspondingly there are two slopes. The values of the field lowering coefficients from these two gradients are calculated and given in Table 6.5.
Table 6.5  Electrical conduction parameters of Au/ Mixed Pc/Pb Schottky device

<table>
<thead>
<tr>
<th>Characteristic region</th>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic region (Segment I)</td>
<td>$E_f$ (eV)</td>
<td>$0.41 \pm 0.01$</td>
</tr>
<tr>
<td></td>
<td>$\mu$ (m$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>$3.1 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>$P_0$ (m$^{-3}$)</td>
<td>$1.6 \times 10^{13}$</td>
</tr>
<tr>
<td>Space charged limited conduction with a single trap level (Segment II)</td>
<td>$E_t$ (eV)</td>
<td>$0.54 \pm 0.01$</td>
</tr>
<tr>
<td></td>
<td>$N_{t(s)}$ (m$^{-3}$)</td>
<td>$2.23 \times 10^{23}$</td>
</tr>
<tr>
<td></td>
<td>$\theta$</td>
<td>$3.63 \times 10^{-4}$</td>
</tr>
<tr>
<td>Space charged conduction with an exponential trap level (Segment III)</td>
<td>$T_t$ (K)</td>
<td>1818</td>
</tr>
<tr>
<td></td>
<td>$P_t$ (J$^{-1}$m$^{-3}$)</td>
<td>$5.76 \times 10^{44}$</td>
</tr>
<tr>
<td></td>
<td>$N_{t(e)}$ (m$^{-3}$)</td>
<td>$8.06 \times 10^{25}$</td>
</tr>
<tr>
<td>Reverse bias</td>
<td>Lower voltage $\beta$ (eVm$^{1/2}$V$^{-1/2}$)</td>
<td>$1.43 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Higher voltage $\beta$ (eVm$^{1/2}$V$^{-1/2}$)</td>
<td>$3.6 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>Barrier height (eV)</td>
<td>$1.03 \pm 0.01$</td>
</tr>
</tbody>
</table>

Both the calculated values of the field lowering coefficients in the low and in the higher voltage regions are at variance from the theoretical values. But it is reasonable to assume that the conduction in the lower voltage region is originated from the contact interface rather than from the bulk material or a Schottky emission whereas the higher voltage region suggests Poole-Frenkel conduction.

The discrepancy between the theoretical and calculated values of the field lowering coefficients may be explained as a thermally assisted tunneling field emission of charge carriers occurring close to the peak of the barrier where the potential width of the barrier is narrow. The variation of $\beta$ may also be attributed to the nonuniformity and sub atomic structure of the mixture.
6.5 Conclusion

We have investigated the effect of iodine doping on the electrical conductivities of Schottky device fabricated from FePc, MgPc and NiPc thin films. The electrical property of a mixed Copper phthalocyanine and Nickel phthalocyanine with gold and lead electrodes is also described in this chapter. Fabrications of device are carried out by thermal evaporation technique and doping by co evaporation. The results show that the conductivities can be raised by many orders of magnitude compared to the conductivity of undoped materials. This behavior is understood in terms of broadening of the transport manifold due to enhanced disorder coming from the dopants. The shift in the Fermi level position towards the valance band edge after doping causes an increase in the p type conductivity in the FePc, MgPc and NiPc thin films device. However, despite comparatively high doping ratios and high number of carriers generated, the achievable conductivities are still lower than that of doped inorganic semiconductors due to the much lower mobilities of the organic semiconductors. Although the basic effects of doping like Fermi level shifts can be well compared to the standard behavior of inorganic semiconductors, a detailed understanding of the dependence of conductivity on doping concentration requires models based on a subtle interplay of doping with localization and percolation effects.

It is observed that the iodine doped devices are more stable to the applied voltages despite the enhanced values of electrical conductivity. In the Mixed phthalocyanine device an ohmic conduction is observed with lead electrodes. This
could be explained on the basis of a change in the work function of the Mixed phthalocyanine.

Reference.


