Chapter 4

Studies on Design, Fabrication and Characteristics of Schottky diodes Using FePc MgPc and NiPc – Part I
4.1 Introduction

Organic materials are an important new class of semiconductor as they combine the virtues of plastics, which can be easily shaped, with those of semiconductors which are the basis of microelectronics and nanotechnology. Recently organic materials have received considerable attention as potential replacements for their inorganic counterparts in flat-panel-display driver circuitry, light-emitting elements, sensors and many other electronic devices.\textsuperscript{1-5} Organic materials have the key advantage of simple and low-temperature thin-film processing through inexpensive techniques such as spin coating, ink-jet printing, or stamping. In addition, the flexibility of organic chemistry enables the formation of organic molecules with useful luminescent and conducting properties.\textsuperscript{6-8} While very promising with regard to processing, cost, and weight considerations, organic compounds generally have some disadvantages, including lower thermal and mechanical stability. In addition, while electrical transport in organic materials has improved, the room-temperature mobility is fundamentally limited by the weak Van der Waals interactions between organic molecules. In the organic light emitting diodes, the stability and electrical transport characteristics of organic materials contribute to reduced device lifetime.\textsuperscript{9-11} For field effect transistors the inherent upper bound on electrical mobility translates to a cap on switching speeds and therefore on the types of applications that might employ the low-cost organic devices. If these issues could be adequately addressed, new technologies might be made possible by organic devices, including lightweight, flexible displays constructed entirely on plastics.\textsuperscript{12-14}
Boundaries of organic semiconductors with metals are the seats of many important phenomena such as rectification\textsuperscript{15,16} photovoltaic effects\textsuperscript{17,18} surface states,\textsuperscript{19} recombination of charge carriers and formation of space charge regions\textsuperscript{20,21} some of which have tremendous technological importance in the device applications. Metal-to-semiconductor (M-S) junctions\textsuperscript{22-24} is of great importance since they are present in every semiconductor device.

When a metal and a semiconductor are in contact there will be a flow of electrons from one to other due to the difference in their work function so that the Fermi level of both attains the same height or level. In the conduction band of the semiconductor a finite number of electrons exist and the number of these free electrons are dependent on the temperature and doping concentration or purity of the material. Similarly, there are a number of free electrons in the metal, and the numbers of such free electrons are dependent on the nature of metal and the temperature. When there is a flow of electrons, such an electron transfer will give rise to a depletion of electrons in one and an excess in the other thus resulting in the formation of a double charge layer of equal and opposite sign on the semiconductor and in metal surface. This flow of electron will continue until a thermodynamic equilibrium is established and the electric field developed by the two opposite but equal charges stops a further flow of electrons. The resultant potential or barrier height is known as Schottky barrier which is equal to the work function difference between the metal and semiconductor.
When a bias is applied to the junction, it can have one of two effects: it can make the barrier appear lower from the semiconductor side, or it can make it appear higher. The bias does not change the barrier height from the metal side. Hence the junction conducts for one bias polarity, but not the other. Almost all metal-semiconductor junctions will exhibit some of this rectifying behavior. But this rectifying behavior varies with the nature of the junction. Schottky contacts\textsuperscript{25-27} make good diodes, and are can even be used to make transistor, but for getting signals into and out of a semiconductor device, generally an ohmic contact is necessary. In the Ohmic contacts conduction is the same for both polarities and they usually obey Ohm's Law. There are two ways to make a metal-semiconductor contact as ohmic or designing the junction in the opposite makes them a good Schottky contact.

- Lower the barrier height

Barrier height is one of the factors which control the current in the metal semiconductor interface. The barrier height is the difference between the edge of the respective majority-carrier band of the semiconductor and the Fermi level at the interface. The barrier height is a property of the electrode materials used in the device. It is possible to use materials whose barrier height is small. Annealing can create an alloy between the semiconductor and the metal at the junction, which can also lower the barrier height. The knowledge of barrier heights at the interfaces between the electrodes and the active organic layers is of enormous importance for an understanding and improvement of organic semiconductor devices.\textsuperscript{28-30} Although the alignment of the Fermi levels ($E_F$) at organic/metal
interfaces and the possible formation of an interfacial electric dipole layer have been reported\textsuperscript{38,39} for many cases, the size and the nature of this dipole layer seems to depend on many factors and thus it is very difficult to predict the electronic interface properties from the well known bulk values. A reduction of the barrier height would significantly improve the device performance through lowering the power consumption. Several mechanisms may be used to tune the barrier heights of electrode contacts. In order to shed more light on the rules of the energy level alignment at organic/metal interfaces, systematic studies have to be carried out.

- Make the barrier very narrow

The electrons and holes can tunnel through barriers when they do not have enough energy to just cross over. The probability of tunneling becomes high for extremely thin barriers. Doping at a rate of $10^{19}$ dopant atoms/cm$^3$ or more is an effective method to narrow down barrier. Further research is needed to improve the mobility and environmental stability of organic semi conducting materials, as well as a fundamental understanding of electron injection, metal contact issues, electron transport, surface modification, and self-assembly. However, organic systems offer a great deal of flexibility in their synthesis, and as chemists develop new materials and learn how to better order and process them, it is hoped that performance and utility will continue to improve, perhaps reaching the standards of conventional semi conducting materials and expanding the applications of such materials for low-cost logic chips and in the nanotechnology realm.
This chapter contains an analysis and investigations of the electrostatics of the metal-semiconductor junctions, including the details of the charge carrier concentration, nature of the trapping states, and potential distribution within the device. Thermally evaporated thin films of Iron phthalocyanine, Magnesium phthalocyanine and Nickel phthalocyanine are the semiconductors used in our device fabrication. The electrical characteristics and device properties of Schottky diodes fabricated from FePc, MgPc and NiPc thin films in a sandwich structure with gold-gold and aluminium-aluminium electrodes combinations are investigated in this chapter. Schottky diodes of phthalocyanine with different electrodes and the effects of contact material on electrical properties, charge carrier mobility and the nature barrier potential are also discussed. The effect of oxygen and air annealing on the device permanence and its electrical characteristics are also studied and reported in this chapter.

4.2 Theory

4.2.1 Theory of metal-semiconductor contacts

The information about metal-semiconductor contacts was exposed in 1938 when both Schottky and Mott independently suggested a model for the current conduction mechanism in the metal-semiconductor junctions. They reported that the observed direction of current could be explained by supposing that electrons passed over a potential barrier through the normal process of drift and diffusion. The knowledge of barrier heights at interfaces between the electrodes and the active semiconductor layers is of enormous importance for an understanding and improvement of organic semiconductor devices.
The barrier height $\phi_b$, is defined as the potential difference between the Fermi energy of the metal and the band edge where the majority carriers reside. From the Schottky-Mott theory the barrier height is obtained as:

$$\phi_b = \phi_m - \chi_s \quad (4.1)$$

where,

$\phi_b = $ contact barrier height, at zero applied bias

$\phi_m = $ work function of the metal which is the energy required to remove an electron from the Fermi level of the metal to the vacuum outside the metal

$\chi_s = $ electron affinity of the semiconductor and is further expressed as

$$\chi_s = \phi_s - (E_c - E_f) \quad (4.2)$$

where $\phi_s$ work function of the semiconductor, $E_c$ is the conduction band energy in eV and $E_f=$ Fermi energy level in eV. The barrier encountered by electrons in the metal and the built in potential encountered by the electrons in the semiconductors $V_{bi}$ are related by the expression as

$$V_{bi} = \phi_m - \phi_s$$

$$= \phi_b - (E_c - E_f) \quad (4.3)$$

These experimental barrier heights often differ from the ones calculated using the above Equation 4.3. This is due to the detailed behavior of the metal-semiconductor interface. The ideal metal-semiconductor theory assumes that both materials are infinitely pure, that there is no interaction between the two materials and no unwanted interfacial layer. Chemical reactions between the metal and the semiconductor alter the barrier height as do interface states at the surface of the
semiconductor and interfacial layers. However some general trends can still be observed.

Figure 4.1 illustrates the band profile of a p-type semiconductor and a metal which are in out of contact with the metal whose work function $\phi_m$ is less than the work function $\phi_s$ of the semiconductor. In this case aligning the Fermi levels at equilibrium requires a positive charge on the metal side and a negative charge on the semiconductor side of the junction. This situation is illustrated in Figure 4.2.

As electrons are depleted from the metal, a net positive charge is created in the metal at the junction as shown in the figure. This positive charge will exert a force
on the electrons that opposes the diffusion current. Equilibrium is established when these two forces are equal.

Figure 4.2   Metal and p-type semiconductor junction at equilibrium

The semiconductor energy bands bend in response to the forces just described. The negative charge is accommodated by a depletion region $W$ in which ionized acceptors are left uncompensated by holes. It is within this region, called the depletion region, that all of the junction’s electrical properties are established. The amount of band bending is called the built-in potential $V_{bi}$. The potential barrier $V_{bi}$ retarding hole diffusion from the semiconductor to the metal is $\phi_s - \phi_m$ whereas an electron moving from the metal to the semiconductor must overcome the barrier potential $\phi_b$. The built-in potential can be decreased or increased by the application of either forward or reverse bias as in the case of p-n junction. It is
found that in most cases the barrier height is independent of the semiconductor properties, whereas built-in potential is dependent on the doping level.

If an external potential $V$ is applied across the junction, with the metal side as positive the added electric field will disturb the equilibrium conditions. This will create an electric field across the junction that is opposite to the electric field caused by the depleted semiconductor atoms. The built in potential is reduced from $V_{bi}$ to $V_{bi} - V$. The result is that the diffusion current will not be sufficiently opposed, and current will flow across the junction from metal to semiconductor. This gives rise to a forward current from metal to semiconductor through the junction. This is shown schematically in the Figure 4.3.

**Figure 4.3** Schottky barriers in the (a) forward bias (b) reverse bias.
If a negative voltage is applied to the metal, the external field will reinforce the electric field caused by the depleted carriers, increase the band bending at the junction, and prevent the diffusion current from flowing as shown in the Figure 4.3. The height of the barrier from the semiconductor side increases to $V + V_{bi}$. This increased barrier height impedes the flow of electrons from the semiconductor to the metal while the flow of electrons from the metal to semiconductor remains as before. Thus there is a net flow of current from the metal to semiconductor and the junction is said to have a reverse bias.

When a metal and a n type semiconductor contact is made and if $\phi_m > \phi_s$ as in Figure 4.4 the conduction electrons begin to flow from the semiconductor into the metal until the Fermi energies on both sides of the junction are equal. In the process, the surface of the metal becomes negatively charged and the surface of the semiconductor which is depleted of electrons becomes positively charged. As a result, a potential barrier is formed at the metal-semiconductor junction. Since, the Fermi energy on both sides has the same value; the energy levels in the bulk of the semiconductor are lowered by an amount $\phi_m - \phi_s$ as shown in Figure 4.5. After the equilibrium is reached, when a positive voltage is applied to the semiconductor side with respect to metal side, the height of the barrier from the semiconductor side increases while the barrier height from the metal side remains the same. This increased barrier height impedes the flow of electrons from the semiconductor into the metal while the flow of electrons from the metal into the semiconductor remains as before. Thus, there is a net flow of current from the metal to semiconductor and the semiconductor is said to have a reverse bias.
Figure 4.4  Band structure of disconnected metal and n-type semiconductor with $\phi_m > \phi_s$

Figure 4.5  Metal and n-type semiconductor junction at equilibrium
On the other hand when a negative voltage is applied to the semiconductor side with respect to the metal side then the barrier height is reduced and a flow of current begins from the semiconductor to the metal which is referred as a forward bias.

The two other cases with $\Phi_m < \Phi_s$ for the n type semiconductor and $\Phi_m > \Phi_s$ for p type semiconductor results in a non rectifying or ohmic contacts. The preceding description assumed ideal material conditions. Specifically, it is assumed that the semiconductor structure is uniform and perfect, even at the surface of the material. In practical cases, this may not be true. The atoms on the exposed surface do not have the required neighboring atom to complete all of the covalent bonds. Therefore, these surface atoms may either give up an electron and become a positively charged donor ion, or accept an electron and become a negatively charged acceptor ion. Surface states and their associated charge cause the energy bands of the semiconductor to bend even before the metal is introduced.

Furthermore, when the metal is brought into contact with the semiconductor, the surface states may be able to accommodate all of the charge movement required to equalize the free electrons between the two materials. When this occurs, the barrier potential is no longer dependent on the metal work function. Also, no additional band bending of the semiconductor occurs because of the metal–semiconductor contact. In other words, the junction characteristics are not dependent on the metal interface. Surface states can create severe reliability problems for semiconductor devices. Therefore, besides altering the
built-in voltage of the contact, surface states may also provide leakage paths for current. The critical points associated with the metal semiconductor junctions and the device reliability is,

- The sensitivity of its electrical characteristics to the semiconductor doping concentration.
- The interface barrier potential and
- The junction temperature.

Small changes in any of these parameters can greatly change the junction impedance and significantly influence the current that flows through the junction. While the circuit designer can control the junction temperature through proper packaging and heat sinking, the barrier potential and doping concentration may change unpredictably over the life of the junction.

### 4.2.2 Theory of Current transport Mechanisms

The current across a metal-semiconductor junction is mainly due to majority carriers. Three distinctly different mechanisms exist: diffusion of carriers from the semiconductor into the metal, thermionic emission of carriers across the Schottky barrier and quantum-mechanical tunneling through the barrier. The diffusion theory assumes that the driving force is distributed over the length of the depletion layer. The thermionic emission theory on the other hand postulates that only energetic carriers, those, which have an energy equal to or larger than the conduction band energy at the metal-semiconductor interface, contribute to the current flow. Quantum-mechanical tunneling through the barrier takes into
account the wave-nature of the electrons, allowing them to penetrate through thin barriers. In a given junction, a combination of all three mechanisms could exist. However, typically in metal organic semiconductor junctions very often only one current mechanism dominates. The physics of charge transport in molecular thin films is dominated by charge localization resulting from polarization of the medium and relaxation of molecular ions. These energies are much larger than transfer integrals or the temperature. Depending on the charge-injection conditions and applied fields, charge transport in these materials is described by space-charge-limited, trap-limited, or injection-limited models.

In the metal semiconductor interface the general nature of the electrical conduction and the influence of the electrode material can be studied from the device characteristics drawn from the dark current density with the applied bias voltage of the device both in the forward and reverse bias. Further the various electrical parameters including nature of traps, Schottky barrier heights and the depletion width are investigated from these characteristics. When the current conduction is ohmic in nature in a sandwich device of an organic semiconductor, the current density $J$ within the ohmic region for a p-type semi conducting material is described by Lampert$^{34}$ as

$$J = P_0 e \mu \frac{V}{d}$$  \hspace{1cm} (4.4)
where ‘e’ the electronic charge, ‘μ’ the hole mobility, V the applied voltage, ‘d’ the thickness of the organic film and P₀ is the concentration of thermally generated holes in the valance band which is given by

\[
P₀ = N_v \exp\left(\frac{-E_f}{kT}\right) \tag{4.5}
\]

where \(E_f\) is the position of Fermi level above the valance band edge, k the Boltzmann constant, T the absolute temperature and \(N_v\) the effective density of states in the valance band . Substituting for \(P₀\) in Equation 4.4

\[
J = N_v e \mu \left(\frac{V}{d}\right) \exp\left(\frac{-E_f}{kT}\right) \tag{4.6}
\]

By plotting \(\ln (J/V)\) against 1000/T the values of \(E_f\) and \(\mu N_v\) are calculated from the slope and intercept at the current axis at \(1/T=0\). Knowing the value of \(N_v\) the mobility of holes and the concentration of thermally generated holes in the valance band can be estimated. The value of \(N_v = 10^{27} \text{ m}^{-3}\) is applied generally for metal phthalocyanine which correspond to one state per molecule. The expression for current density described by the Equation 4.4 is true only for small applied voltages.

At higher applied voltages, the current density shows a power law exponent of the form,

\[
J \propto V^n \tag{4.7}
\]

where the value of ‘n’ defines the type of conduction. The numerical value of the index ‘n’ is found to be associated with the nature of traps and their distribution within the forbidden gap. When the current density varies in quadratic order
The current density dependence is described as a space charge limited conduction characterized by a single trap level situated at an energy level $E_t$ above the valance band edge. The current density in such circumstances are described by Rose

$$J = \frac{9}{8} q \mu \theta \frac{V^2}{d^3}$$

(4.8)

In addition to the terms described earlier, $\varepsilon$ is the permittivity of the organic layer and $\theta$ is the measure of the ratio of free charges to trapped charges where

$$\theta = \frac{N_t}{N_{t(s)}} \exp \left( -\frac{E_t}{kT} \right)$$

(4.9)

where $N_{t(s)}$ is the total trap concentration at the single energy level $E_t$ measured from the top of the valance band edge. Hence

$$J = \left( \frac{9}{8} q \mu \right) \frac{N_t}{N_{t(s)}} \frac{V^2}{d^3} \exp \left( -\frac{E_t}{kT} \right)$$

(4.10)

It is evident from Equation 4.10 that the plot of $\ln \left( \frac{J}{V^2} \right)$ against $\left( \frac{1}{T} \right)$ should yield a straight line. From the slope and the intercept on the current axis at $1/T=0$ of this graph the values of $E_t$ and $N_{t(s)}$ can be calculated. Substituting the values $E_t$ and $N_{t(s)}$ in Equation 4.9 the ratio of free to trapped charges is also calculated. When the current density variation with the applied voltage is much higher so that the index $n > 2$, the situation is termed as a space charge limited conduction with an exponential trap distribution. This is again described by Lampert and is given by

$$J = e\mu N_i \left( \frac{\varepsilon}{eFkT_i} \right) \frac{V^{1+n}}{d^{2+n}}$$

(4.11)
where $P_t$, the trap concentration per unit energy range at the valance band edge and $T$ the absolute temperature. The term $(l+1)$ represents the power exponent factor where $l = (T_t/T)$ and $T_t$ is the parameter characterizing trap distribution having the dimension of temperature, given by

$$P(E) = P_t \exp\left(\frac{-E}{kT}\right)$$  \hspace{1cm} (4.12)

where $P(E)$ is the concentration of traps per unit energy range and is a function of energy $E$ above the valence band edge. The total concentration of traps $N_{t(e)}$ is given by

$$N_{t(e)} = P_t kT_t$$  \hspace{1cm} (4.13)

Using Equation 4.11 and 4.13 the total concentration of traps and the other electrical parameters in the SCL conduction can be calculated. The transition voltage between Ohmic conduction and space charged limited conduction with an exponential trap distribution is described by

$$V_t = \left(\frac{P_t}{N_t}\right)^{1/2} \frac{eP_t kT_t}{\varepsilon} \, d^2$$  \hspace{1cm} (4.14)

When low work function materials are used as electrode to organic semiconductors the conduction is always through a barrier and conduction may be either a field lowering of the interfacial barrier at the injecting electrode as Schottky effect or a field assisted thermal excitations from the impurity centers as Poole-Frenkel effect.\textsuperscript{37} The general equations describing the current density under these circumstances is given by

$$J = A^{**}T^2 \exp\left(-\frac{\Phi_s}{kT}\right) \exp\left(\frac{\beta_s V^{1/2}}{kTd^{1/2}}\right)$$  \hspace{1cm} (4.15)
where $A^{**} = 1.3 \times 10^5 \text{A m}^2\text{K}^{-2}$ is the Richardson Constant and $\Phi_s$ is the Schottky barrier height at the injecting electrode interface, $\beta_s$ is the Schottky field lowering coefficient. For the Poole-Frenkel type of conduction which is a field lowering of interfacial barrier at the injecting electrode, the current voltage relation is defined by

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

(4.16)

where $J_0$ is the low field current density and $\beta_{PF}$ Poole-Frenkel field lowering coefficient. The two coefficients $\beta_s$ and $\beta_{PF}$ are related by the equation

$$2\beta_s = \beta_{PF} = \left( \frac{e^3}{\pi \epsilon} \right)^{1/2}$$

(4.17)

substituting the values of the permittivity $\epsilon$ of the organic layer, the theoretical values of the field lowering coefficients can be calculated. The experimental values of these coefficients may be calculated from the slope of the graph of $\ln J$ versus $V^{1/2}$. Further the barrier height at the injecting electrode and the width of the depletion layer can also be estimated from this graph using Equation 4.15.

The current transport through the device by emission over the barrier is essentially a two step process: first, the electrons have to be transported through the depletion region, and this is determined by the usual mechanisms of diffusion and drift; secondly, they must undergo emission over the barrier into the metal, and this is controlled by the number of electrons that impinge on unit area of the metal per second. This mode of current transport is commonly referred to as the thermionic emission current. This is represented by the diode equation as
\[ J = J_0 \left[ \exp \left( \frac{eV}{nkT} \right) - 1 \right] \]  

(4.18)

where \( e \) the electronic charge, \( V \) the D.C applied voltage across the device, \( k \) is the Boltzmann’s constant, \( T \) is the absolute temperature, \( n \) is a dimensionless parameter called the diode quality factor and \( J_0 \) is the saturation current that can be expressed as

\[ J_0 = A^* T^2 \exp \left( \frac{-\Phi_b e}{kT} \right) \]  

(4.19)

where \( A^* \) is the effective Richardson constant \( (1.3 \times 10^5 \text{A m}^{-2} \text{K}^{-2}) \) and \( \Phi_b \) is the barrier height encountered by electrons in the metal semiconductor interface. The ideality factor \( n \) gives a measure of the quality of the junction which is highly process dependent. For an ideal Schottky junction, \( n \) being equal to unity but in practice, larger values are obtained due to the presence of non-ideal effects or components to the current through the junction. From the current density-applied voltage characteristics the various parameters in the diode structure can be calculated.

4.3 Experiment

Pure FePc, MgPc and NiPc powder from Sigma-Aldrich USA is used as the base materials for the device fabrications. A schematic diagram of the thin film Schottky device structure is shown in Figure 4.6 Device fabrication begins with a careful cleaning of the glass substrates as described in chapter 2.13, because it is an important element in the performance of the devices. To fabricate a multilayer sandwich thin film device, a bottom electrode is first deposited onto
the pre-cleaned micro glass substrate by a Hind Hivac 12A4 coating unit by thermal evaporation technique as per the procedure described in section 2.14.

![Schematic diagram of the thin film device in sandwich configuration.](image)

Figure 4.6  Schematic diagram of the thin film device in sandwich configuration.

Phthalocyanine layer is then deposited over the bottom electrode at a base pressure of $10^{-6}$ Torr. During the evaporation process the pressure is kept steady by a diffusion pump backed by oil sealed rotary pump. In order to complete the device structure a top contact electrode is also deposited from a tungsten coil over the phthalocyanine layer. One sample is taken to a desiccator which is stored in dry air for 30 days for oxygen doping and another sample is annealed in air at 423K for one hour before evaporating the top electrode to complete the multilayer structure. Two different sets of Schottky device with a sandwich configuration of Al/Phthalocyanine/Al and Au/Phthalocyanine/Au are fabricated for FePc, MgPc and NiPc material. The effect of oxygen on the electrical properties of device is investigated with the former while the effect of heat treatment on the electrical conduction behaviour of the device with the later. Thickness of both electrodes and phthalocyanine layers are measured by Tolansky’s multiple beam interference
technique as described in section 2.17 of chapter 2. The active area of the phthalocyanine layer is also calculated. The values of the electrode thickness and the area of the active phthalocyanine layer of entire devices investigated in this chapter are given in Table 4.1. Electrical conductivity measurements are performed by a stabilized digital power supply and a Keithley programmable electrometer in a subsidiary vacuum system in light tight condition and at a pressure of approximately $10^{-3}$ Torr.

**Table 4.1** Device parameters of FePc, MgPc and NiPc Schottky diodes with similar electrodes.

<table>
<thead>
<tr>
<th>Device component</th>
<th>Gold/Aluminium electrode thickness (nm)</th>
<th>Gold/Aluminium electrode thickness (nm)</th>
<th>Phthalocyanine layer thickness (nm)</th>
<th>Active area of phthalocyanine Layer ($m^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/FePc/Au</td>
<td>80</td>
<td>90</td>
<td>500</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Al/FePc/Al</td>
<td>65</td>
<td>80</td>
<td>500</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Au/MgPc/Au</td>
<td>80</td>
<td>90</td>
<td>600</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Al/MgPc/Al</td>
<td>60</td>
<td>80</td>
<td>550</td>
<td>$1.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>Au/NiPc/Au</td>
<td>60</td>
<td>90</td>
<td>500</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Al/NiPc/Al</td>
<td>60</td>
<td>80</td>
<td>500</td>
<td>$1.5 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The electrode deposited initially in the device fabrication is always assigned a positive potential for the forward bias condition, currents are measured for the different values of applied voltages ranging from 0V to 10V at room temperature for the as deposited, air annealed films and oxygen doped samples. Currents are measured continuously varying the bias and also by interrupting the bias between each step to verify the stability of the device. The nature of the electrical
conductivity of the FePc, MgPc and NiPc thin film device with gold-gold and aluminium-aluminium electrode combinations are investigated in this chapter.

4.4 Results and Discussions

The device electrical characteristics of FePc, MgPc, NiPc thin films fabricated by bottom and top electrodes with the same electrodes materials are investigated. Gold and aluminium are the two electrodes used in the present device fabrications.

4.4.1 Electrical characteristics of Al/FePc/Al Device

The device having structural configuration of Al/FePc/Al is fabricated by depositing a thin film of FePc using vacuum evaporation technique on glass substrate which is previously deposited with a aluminium electrode. Another aluminium electrode is then deposited over the top of the FePc layer using the same technique. A typical dark current density against applied voltage (J–V) curve of the as deposited annealed and oxygen doped Al/FePc/Al sandwich devices measured at room temperature is shown in Figure 4.7.

In general, the J–V characteristics as deposited, annealed and oxygen doped thin film devices of Al/FePc/Al are asymmetrical and show non ohmic behaviour. The three samples showed approximately same response to the applied voltage. For the oxygen doped and annealed samples the currents are slightly lower compared to the as deposited samples. In the oxygen doped sample even though the oxygen acts as acceptor molecules which may enhance the conductivity the additional impedance produced at the aluminium interface reduce
the current level. In the case of the annealed samples heat treatment makes samples more orderly and thus reduces the current level.

![Graph showing current density versus voltage for as deposited, annealed, and oxygen doped Al/FePc/Al device at room temperature.](image)

**Figure 4.7** Current density (J) - Voltage (V) characteristics for the as deposited, annealed and oxygen doped Al/FePc/Al device at room temperature.

The forward current density of the device increases very slowly up to 0.6V which neither fit with ohmic or rectifying characteristics and the increase of current is more rapid in the higher voltage region. The current in the aluminium contact is injection limited at the contact interface due to a Schottky energy barrier. The asymmetric conductivity of the FePc/Al device could be explained as field lowering mechanisms either as a Schottky effect or a Poole-Frenkel effect, as
described in Equation 4.15. Substituting the values of the permittivity of FePc\textsuperscript{38} as $\varepsilon = 3.87 \times 10^{-11}$ F/m the theoretical value of the field lowering coefficients are calculated as $\beta_s = 2.29 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ and $\beta_{PF} = 4.58 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$.

Figure 4.8 is the graph of Ln (J) versus V$^{1/2}$ for the as deposited, annealed and oxygen doped samples. From the slope and the extrapolated intercept of the linear portions of this graph with the J axis at V=0 and using Equation 4.16 the value of the field lowering coefficients and values of the barrier height $\Phi$, are calculated and tabulated in Table 4.2.

![Figure 4.8](image_url)

**Figure 4.8**  Semi logarithmic plot of (J) versus V$^{1/2}$ for the as deposited, annealed and oxygen doped Al/FePc/Al device at room temperature.
Table 4.2  Electrical conduction parameters of as deposited, annealed and oxygen doped Al/FePc/Al thin film Schottky device.

<table>
<thead>
<tr>
<th>Al/FePc/Al Device</th>
<th>Field lowering coefficients $\beta_s$ (eV m$^{1/2}$ V$^{-1/2}$)</th>
<th>Schottky barrier height $\Phi_s \pm 0.01$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>$2.77 \times 10^{-5}$</td>
<td>1.04</td>
</tr>
<tr>
<td>Annealed</td>
<td>$2.54 \times 10^{-5}$</td>
<td>1.05</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>$2.43 \times 10^{-5}$</td>
<td>1.06</td>
</tr>
</tbody>
</table>

The field lowering coefficients of the as deposited, annealed and oxygen doped samples of FePc agree with the theoretical values of Schottky effect. These results suggest that the conduction mechanisms of the device structure are controlled by a Schottky emission between the metal and organic semiconductor interfaces. The barrier height is slightly higher for both oxygen doped and annealed samples. For the Al/FePc device oxygen is found to decrease the conductivity and an increased value of the barrier height.

Gould and Shafai$^{39}$ investigated the electronic conduction in evaporated Lead phthalocyanine thin films with aluminium electrodes. They reported a carrier excitation via a field lowering mechanism in low and higher voltage regions.

### 4.4.2 Electrical characteristics of Al/MgPc/Al Device

Conduction process in Al/MgPc/Al thin film devices are investigated by measuring the dark current density-voltage characteristics at room temperature for the as deposited, annealed and oxygen doped samples. Room temperature current density- voltage characteristics for the three samples of MgPc sandwich devices are shown in a logarithmic plot as in Figure 4.9. In general, the J–V characteristics
of the device is asymmetrical and showed two different stages of conduction. The forward current density of the device increases very slowly up to 1.2V which can no longer treated as ohmic since the slope of this region is approximately 0.52. Above this bias voltage the slope is about 5.3. The asymmetric conductivity of the MgPc/Al device could be explained as field lowering mechanisms either as a Schottky effect or a Poole-Frenkel effect. Substituting the values of the permittivity of MgPc as $\varepsilon = 3.87 \times 10^{-11} \text{ F/m}$ the theoretical value of the field lowering coefficients are calculated as $\beta_s = 2.29 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$ and $\beta_{PF} = 4.58 \times 10^{-5} \text{ eV m}^{1/2} \text{ V}^{-1/2}$.

![Figure 4.9](image)

**Figure 4.9** Current density (J) - Voltage (V) characteristics for the as deposited, annealed and oxygen doped Al/MgPc/Al device at room temperature.
Figure 4.10 is the semi logarithmic plot of Ln (J) versus V^{1/2} for the as deposited, annealed and oxygen doped samples. There are two linear portions for each graph and correspondingly there are two values for the field lowering coefficients for all the three samples. From the slope and the extrapolated intercept of the linear portions of the graph with the J axis at V=0 together with Equation 4.16 the value of the field lowering coefficients in the low and in the higher voltage regions and values of the barrier height Φ_s are estimated and reported in Table 4.3.

![Semi logarithmic plot of J versus V^{1/2} for the as deposited, annealed and oxygen doped Al/MgPc/Al device at room temperature.](image_url)
Table 4.3  Electrical conduction parameters of as deposited, annealed and oxygen doped Al/MgPc/Al thin film Schottky device at room temperature.

<table>
<thead>
<tr>
<th>Al/MgPc/Al Device</th>
<th>Field lowering coefficients $\beta$ (eV m $^{1/2}$ V$^{-1/2}$)</th>
<th>Schottky barrier height $\Phi_s \pm 0.01$(eV)</th>
<th>depletion region thickness $d_s$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower voltage</td>
<td>Higher voltage</td>
<td></td>
</tr>
<tr>
<td>As deposited</td>
<td>$4.45 \times 10^{-5}$</td>
<td>$3.83 \times 10^{-5}$</td>
<td>1.13</td>
</tr>
<tr>
<td>Annealed</td>
<td>$5.35 \times 10^{-5}$</td>
<td>$3.23 \times 10^{-5}$</td>
<td>1.15</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>$5.08 \times 10^{-5}$</td>
<td>$3.32 \times 10^{-5}$</td>
<td>1.14</td>
</tr>
</tbody>
</table>

The currents are slightly lower for oxygen-doped sample than the as deposited samples. This may be explained as the formation of an interfacial layer at the contact interface, which is primarily the property of the contact electrode. This interfacial layer produces additional series impedance, which reduces the current level. Currents in the annealed samples record the lowest value. The discrepancy between experimental and theoretical values of $\beta_s$ in the lower voltage region may be explained as a Schottky depletion region extending only for a small distance ($d_s$) and not across the entire organic layer. Hence even though the derived values for $\beta_s$ in the lower bias voltage is not in absolute agreement with the theoretical value it is reasonable to assume that the current conduction is originated from the contact interface rather than from the bulk material. This suggests that the conduction mechanism is controlled by Schottky emission as reported$^{39,41}$ for many phthalocyanines. The value of the depletion region thickness ($d_s$) is given by
\[ d_i = \left( \frac{\beta_s}{\beta} \right)^2 d \]

(4.20)

where \( \beta_s \) and \( \beta \) are the theoretical and calculated values of Schottky field lowering coefficients and \( d \) is the film thickness. The depletion region thickness estimated from Equation 4.20 are calculated and recorded in Table 4.3.

Senthilarasu et al.\(^{41}\) have studied the electrical properties of Al/ZnPc/Al thin film device prepared by the vacuum evaporation. From the current-voltage characteristics, they reported the charge transport conduction as Poole-Frankel type and the total number of interface states, which is responsible for the dispersion of capacitance, is increasing with increase in bias voltage.

### 4.4.3 Electrical characteristics of Al/NiPc/Al Device

Figure 4.11 is the Ln (J) - Ln (V) plot of Al/NiPc/Al device at room temperature for the as deposited, annealed and oxygen doped samples. Similar to the FePc and MgPc devices the characteristics of the Al/NiPc/Al device is also asymmetrical. The current density of the device increases very slowly up to 1.1V and thereafter, the current is increasing more rapidly. The oxygen doped sample showed a slightly higher order of conductivity than the as deposited sample. In heat treated sample a lower conductivity is exhibited.
Figure 4.11  Current density (J) - Voltage (V) characteristics for the as deposited, annealed and oxygen doped Al/NiPc/Al device at room temperature.

Figure 4.12 is the semi logarithmic variation of conductivity with bias voltage that is re plotted. From the slope and intercept together with Equation 4.16 the different electrical parameters are calculated and tabulated in Table 4.4. The value of the permittivity of NiPc is taken as $\varepsilon = 2.425 \times 10^{-11}$ F/m. In low voltage range the conduction is identified as a current through the Schottky barrier at the electrode interface and in the higher voltage region the derived values of $\beta$ (field lowering coefficient) is fairly in good agreement with that expected for the Poole-Frenkel effect suggesting a bulk limited conduction.
Figure 4.12  Semi logarithmic plot of $J$ versus $V^{1/2}$ for the as deposited, annealed and oxygen doped Al/NiPc/Al device at room temperature.

Table 4.4  Electrical conduction parameters of as deposited, annealed and oxygen doped the Al/NiPc/Al thin film Schottky device.

<table>
<thead>
<tr>
<th>Al/MgPc/Al Device</th>
<th>Field lowering coefficient $\beta$ (eV m $^{1/2}$ V$^{-1/2}$)</th>
<th>Schottky barrier height $\Phi_s$ ± 0.01(eV)</th>
<th>depletion region thickness $d_s$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower voltage</td>
<td>Higher voltage</td>
<td></td>
</tr>
<tr>
<td>As deposited</td>
<td>$5.49 \times 10^{-5}$</td>
<td>$10.3 \times 10^{-5}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Annealed</td>
<td>$5.49 \times 10^{-5}$</td>
<td>$10.1 \times 10^{-5}$</td>
<td>1.07</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>$5.63 \times 10^{-5}$</td>
<td>$9.51 \times 10^{-5}$</td>
<td>1.06</td>
</tr>
</tbody>
</table>
The values of field lowering constants, depletion layer thickness and the barrier height of the as deposited, annealed and the oxygen doped samples are estimated from Figure 4.12 are tabulated in Table 4.4.

Abu-Hilal et al.\textsuperscript{43} investigated the A.C electrical conductivity of thermally evaporated Zinc phthalocyanine with gold and aluminium contact electrodes in the temperature range of 180–430 K. They reported the conduction mechanism depends on the electrode material and free band conduction was observed in samples with aluminium electrodes.

\textbf{4.4.4. Electrical characteristics of Au/FePc/Au Device.}

Figure 4.13 is the plots of Ln (J) versus Ln (V) for FePc thin films device with gold electrodes for as deposited, annealed and oxygen doped films at room temperature. All the three samples show two distinct conduction mechanisms at different applied voltages. In the lower voltage region all the Au/FePc/Au samples showed an ohmic conduction whereas in the higher voltage a space charged limited conduction (SCLC) with an exponential trap distribution is identified.
Figure 4.13  Current density (J) - Voltage (V) characteristics for the as deposited, annealed and oxygen doped Au/FePc/Au device at room temperature.

Figure 4.14  Variation of \( \text{Ln} (J/V) \) with inverse temperature for the as deposited, annealed and oxygen doped Au/FePc/Au device in the ohmic region.
Oxygen doped samples show a higher order of conduction where as annealed samples record a lower value of currents both in the lower and higher voltage regions. The current density J within the ohmic region is described by Equation 4.4. Figure 4.14 is the plot of \( \ln(J/V) \) against \((1000/T)\) for the FePc thin films of as deposited, annealed and oxygen doped device within the ohmic region in the 300K-400K-temperature range. The slope of the lines in Figure 4.14 yield the value of position of the Fermi level from the valance band edge \((E_f)\) and the intercept will provide the mobility\((\mu)\) of holes and its concentration\((P_0)\). These values in the ohmic region for the Au/FePc/Au thin film device for the as deposited, annealed and oxygen doped samples are calculated and listed in Table 4.5.

<table>
<thead>
<tr>
<th>Au/FePc/Au device</th>
<th>(E_f \pm 0.01) (eV)</th>
<th>(\mu) ((m^2 V^{-1} s^{-1}))</th>
<th>(P_0) ((m^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>0.57</td>
<td>6.26\times10^{-9}</td>
<td>2.74\times10^{17}</td>
</tr>
<tr>
<td>Annealed</td>
<td>0.60</td>
<td>2.90\times10^{-9}</td>
<td>8.69\times10^{16}</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>0.53</td>
<td>8.22\times10^{-10}</td>
<td>1.51\times10^{18}</td>
</tr>
</tbody>
</table>

The electronic conduction by charge carrier hopping is dominated at low temperature. The current density of the oxygen doped samples is higher by nearly two orders of magnitude comparing with the fresh samples. This effect is known to rise from the high density of adsorbed oxygen which is responsible for the p-type conductivity of phthalocyanines. For applied voltages above 1V the
conduction is space charge limited (SCLC) characterized by an exponential trap distribution. In the SCLC range using Equation 4.11 the various parameters of the device are estimated and reported in Table 4.6.

**Table 4.6** Electrical conduction parameters of as deposited, annealed and oxygen doped Au/FePc/Au Schottky device in the SCLC region

<table>
<thead>
<tr>
<th>Au/FePc/Au device</th>
<th>T (K)</th>
<th>P (J m(^{-1}) m(^{-3}))</th>
<th>N(_{t(e)}) (m(^{-3}))</th>
<th>V(_t) ± 0.1 (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>1364</td>
<td>6.18×10(^{43})</td>
<td>1.21×10(^{24})</td>
<td>0.75</td>
</tr>
<tr>
<td>Annealed</td>
<td>1212</td>
<td>1.03×10(^{44})</td>
<td>2.03×10(^{24})</td>
<td>1.07</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>1406</td>
<td>3.98×10(^{43})</td>
<td>7.79×10(^{23})</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Sandwich structure of Au/FePc/Au show well defined ohmic conduction in the low voltages and SCLC behavior in the higher applied bias voltage. In the oxygen doped samples higher order of conductivity is observed whereas in the heat treated samples current density is lower. The change in the trap distribution within the band gap, as a result of heat treatment, may be understood leading to an improved crystallinity in terms of trap annealing process which results from a structural rearrangement of the molecular stacks of the phthalocyanine. The mobility of holes is slightly increased for annealed samples and the hole concentration is decreased compared to as deposited samples. But for the oxygen doped samples hole mobility has reduced whereas concentration of holes are increased. Again a change in the Fermi level is observed for both as deposited and annealed samples.

Shafai et al\(^{44}\) investigated the D.C electrical properties of Nickel phthalocyanine thin film structures with gold and indium electrodes. They reported a diode nature
at low voltages, while in the higher voltage levels; conduction is dominated by a space-charge-limited conduction.

4.4.5 Electrical characteristics of Au/MgPc/Au Device

Figure 4.15 is the J-V characteristics of the as deposited, heat treated and oxygen doped Au/MgPc/Au Schottky device at room temperature. There are two linear portions in each graph and correspondingly there are two modes of current conduction in each device. The slopes of the lines in the lower voltage segment are approximately unity and hence the current conduction is ohmic in nature. In the higher voltage region as the gradient of the line is more than two, the current density is space charge limited with an exponential trapping level.

Figure 4.15  Current density (J) - Voltage (V) characteristics for the as deposited, annealed and oxygen doped Au/MgPc/Au device at room temperature.
Table 4.7  Electrical conduction parameters of as deposited, annealed and oxygen doped Au/MgPc/Au Schottky device in the ohmic region.

<table>
<thead>
<tr>
<th>Au/MgPc/Au device</th>
<th>$E_f \pm 0.01$ (eV)</th>
<th>$\mu$ (m$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$P_o$ (m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>0.68</td>
<td>2.74×10$^{-7}$</td>
<td>3.42×10$^{15}$</td>
</tr>
<tr>
<td>Annealed</td>
<td>0.73</td>
<td>9.56×10$^{-7}$</td>
<td>5.05×10$^{14}$</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>0.65</td>
<td>1.22×10$^{-7}$</td>
<td>1.33×10$^{16}$</td>
</tr>
</tbody>
</table>

Oxygen doped samples shows a higher order of conduction where as annealed samples record a lower value of currents both in the lower and higher voltage regions. Figure 4.16 is the plot of $\ln (J/V)$ against $1000/T$ of the Au/MgPc/Au device within the ohmic region in the 300K-400K-temperature range. The various electrical parameters in the ohmic region of the as deposited, annealed and oxygen doped samples are calculated from Figure 4.16 and using the Equation 4.4. These values in the ohmic region are calculated and tabulated in Table 4.7. At higher voltages in the logJ-logV characteristics of Figure 4.15 suggesting a space charged limited conduction for all the three samples. From Equation 4.11 and Equation 4.13 the values of the electrical parameters in the SCLC region of the Au/MgPc/Au thin film device are calculated and reported in Table 4.8.

Generally Au/MgPc/Au device showed ohmic conduction in the lower voltage and SCL conduction with an exponential trapping level in the higher
voltage range. A transition voltage between ohmic and SCLC is observed for all the samples. This transition voltage is lowest for the oxygen doped samples.

![Graph showing the variation of \( \ln (J/V) \) with inverse temperature for as deposited, annealed, and oxygen doped Au/MgPc/Au device in the ohmic region.]

**Figure 4.16** Variation of \( \ln (J/V) \) with inverse temperature for the as deposited, annealed, and oxygen doped Au/MgPc/Au device in the ohmic region.

**Table 4.8** Electrical conduction parameters of as deposited, annealed, and oxygen doped Au/MgPc/Au Schottky device in the SCLC region

<table>
<thead>
<tr>
<th>Au/MgPc/Au device</th>
<th>( T_t ) (K)</th>
<th>( P_t ) (J(^{-1})m(^{-3}))</th>
<th>( N_{t(e)} ) (m(^{-3}))</th>
<th>( V_t \pm 0.1 ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>681</td>
<td>( 1.26 \times 10^{46} )</td>
<td>( 1.22 \times 10^{26} )</td>
<td>1.77</td>
</tr>
<tr>
<td>Annealed</td>
<td>610</td>
<td>( 3.85 \times 10^{47} )</td>
<td>( 3.22 \times 10^{27} )</td>
<td>2.1</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>665</td>
<td>( 1.09 \times 10^{46} )</td>
<td>( 9.95 \times 10^{25} )</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Nahass et al.\textsuperscript{45} investigated the A.C conductivity of Nickel phthalocyanine with evaporated gold electrodes in the frequency range from 20 kHz to 10 MHz and within the temperature range from 303 to 600 K. They reported the variations in the activation energy due to an extrinsic to intrinsic conduction mechanism.

4.4.6. Electrical characteristics of Au/NiPc/Au Device

The nature of the electrical conduction process in Nickel phthalocyanine thin film Schottky device is investigated from the current density-voltage characteristics of as deposited, annealed and oxygen doped NiPc thin film devices with gold electrodes. Figure 4.17 is the logarithmic plot of dark current density against applied voltage of the Au/NiPc/Au sandwich devices under forward bias for the as deposited, annealed and oxygen doped thin film devices. All the three curves consists of an ohmic region in the lower applied voltages as the slope in this region is approximately unity while at higher voltages the gradient is changed to three and above indicating a SCLC mechanism controlled by an exponential trap distribution. The later is mainly associated with imperfections of the NiPc introduced into the lattice during the deposition process. In order to estimate the different electrical parameters of the Au/NiPc/Au device in the ohmic region a plot of $\ln (J/V)$ versus $1000/T$ is plotted as in Figure 4.18. The values of concentration of thermally generated holes in the valance band, separation of Fermi level from the valance band edge and the mobility of holes are estimated and tabulated in Table 4.9. In the higher voltage region the various electrical parameters of the space charge conduction are calculated and given in table 4.10.
Figure 4.17  Current density (J) - Voltage (V) characteristics for the as deposited, annealed and oxygen doped Au/NiPc/Au device at room temperature.

Figure 4.18  Variation of Ln (J/V) with inverse temperature for the as deposited, annealed and oxygen doped Au/MgPc/Au device in the ohmic region.
Table 4.9  Electrical conduction parameters of as deposited, annealed and oxygen doped Au/NiPc/Au Schottky device in the ohmic region.

<table>
<thead>
<tr>
<th>Au/NiPc/Au device</th>
<th>$E_f \pm 0.01$ (eV)</th>
<th>$\mu$ ($m^2 V^{-1} s^{-1}$)</th>
<th>$P_0$ ($m^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>0.69</td>
<td>$2.41 \times 10^{-6}$</td>
<td>$2.69 \times 10^{15}$</td>
</tr>
<tr>
<td>Annealed</td>
<td>0.76</td>
<td>$1.6 \times 10^{-5}$</td>
<td>$1.71 \times 10^{14}$</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>0.63</td>
<td>$4.21 \times 10^{-7}$</td>
<td>$2.76 \times 10^{16}$</td>
</tr>
</tbody>
</table>

Table 4.10  Electrical conduction parameters of as deposited, annealed and oxygen doped Au/NiPc/Au Schottky device in the SCLC region

<table>
<thead>
<tr>
<th>Au/NiPc/Au device</th>
<th>$T_t$ (K)</th>
<th>$P_t$ ($J^{-1}m^{-3}$)</th>
<th>$N_{t(e)}$ ($m^{-3}$)</th>
<th>$V_t \pm 0.1$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>1170</td>
<td>$4.26 \times 10^{43}$</td>
<td>$6.32 \times 10^{23}$</td>
<td>1.1</td>
</tr>
<tr>
<td>Annealed</td>
<td>1090</td>
<td>$2.65 \times 10^{44}$</td>
<td>$5.62 \times 10^{24}$</td>
<td>1.3</td>
</tr>
<tr>
<td>Oxygen doped</td>
<td>1212</td>
<td>$1.19 \times 10^{43}$</td>
<td>$4.32 \times 10^{23}$</td>
<td>0.7</td>
</tr>
</tbody>
</table>

4.5 Conclusions

The electrical conduction mechanism of the as deposited, annealed and oxygen doped FePc, MgPc and NiPc Schottky devices with a structural configuration of Al/Metal Pc/Al and Au/Metal Pc/Au are investigated in this chapter. In general all the materials showed asymmetrical current conduction both in the lower and in the higher voltage regions. When both the electrodes are aluminium the device does not show any space charge limited conduction but showed carrier excitations through a field lowering mechanism. Iron phthalocyanine device shows Schottky conduction both in the lower and in the higher voltage levels whereas MgPc and FePc device show Schottky conduction in the lower voltage and a bulk limited conduction in the higher voltage region.
From the data of the depletion layer thickness MgPc is showing a non ideal Schottky device parameters. The lowest value of the barrier height is obtained for FePc while the highest value is for MgPc. After oxygen doping device with aluminium electrodes showed lesser value of current density except with NiPc in which current density slightly increases. After annealing a drop in the current density is observed in all the devices. In the oxygen doped samples the FePc and MgPc showed a marked reduction in the current levels whereas for the NiPc the effect of annealing and oxygen doping has only modest changes in the current levels. In the oxygen doped sample even though the oxygen acts as acceptor molecules which may enhance the conductivity the additional impedance produced at the aluminium interface reduce the current level. In the case of the annealed samples heat treatment makes samples more orderly and thus reduces the current level.

FePc, MgPc and NiPc thin film devices with gold electrodes showed ohmic conduction in the low voltage range whereas in the higher voltage range space charge limited conduction is identified. This suggests that gold can be used as an Ohmic contact to FePc, MgPc and NiPc thin films. The position of the Fermi level from the valance band edge is lowest for FePc and highest for MgPc. The transition voltage from the ohmic to SCLC is 0.75 V for FePc 1.77 V for MgPc and 1.1 V for NiPc. Significant changes in the trap parameters are observed after oxygen doping and annealing.
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