3.1 Introduction

Semiconductors are characterized by covalent bonding between atoms in the crystal. The basic property of semiconductors is its electrical conductivity, which depends on the mobility and concentration of charge carriers. Numerous studies have been conducted in the last few years to the properties of conducting organic materials in view of their application as active semiconducting films in electronic devices\(^1,2,3\). Organic compounds contain conjugated bonding, i.e. alternate single and double bonds\(^4\). The electrical conductivity and carrier concentrations and mobility of organic semiconductors are low in comparison with those of inorganic semiconductors\(^5\). In organic semiconductors, molecular units rather than ions control conduction. The electrons associated with the conjugate bonds are not localized on a particular atom but are associated with the entire molecule. These electrons are in the p-state and hence the \(\pi\)-electrons. The \(\pi\)-electrons is responsible for the conduction in organic semiconductors\(^6\). The intermolecular binding is weak-Vander Waals force, but the electrons within a molecule are tightly bound. If there is an intermolecular overlap of electronic wave functions, conduction still occurs yet, these molecular units make the conduction mechanism more complex. Electronic charge transport in organic semiconductors does not require perfect single crystals. A regular arrangement of atoms, ions or molecules over a distance of only
a few lattice spacing of the structural units is the only necessary and sufficient condition for conductivity in organic semiconductors.

Pcs are similar to the macrocyclic planar aromatic compounds, exhibiting semiconducting properties\textsuperscript{7}. Gutman and Lyons\textsuperscript{8} first addressed the major considerations for organic thin films, whether energy band model of conduction is applicable to them or not. Again Ahmad and Collins\textsuperscript{9} studied the same recently. In this regard the use of a mobility value of $10^{-4}$ m\textsuperscript{2} V\textsuperscript{-1}s\textsuperscript{-1}, give an electron mean free path orders of magnitude smaller than the intermolecular distance. Semiconducting behaviour was observed in MPcs in 1948 and it has attracted wide interest as a prototype organic semiconductor\textsuperscript{10}. These materials are generally p-type semiconductors; they can easily be sublimed resulting in high purity thin films without decomposition\textsuperscript{11}. Fan and Faulkner\textsuperscript{12} supported the view that most Pcs are p-type semiconductors. Zhenao Bao\textsuperscript{13} \textit{et al.} reported that CuPc semiconducting layer could function as $p$-channel accumulation-mode devices. The electrical properties of Pcs have considerable importance owing to their potential applications in electronic devices and sensor systems\textsuperscript{14}. Various electronic conduction processes are observed in Pc thin films. The electronic transport in Pcs shows ohmic conduction at low voltages and space charge limited conduction (SCLC) at high voltages\textsuperscript{15}. Traps control the conductivity. Traps normally are associated with crystal imperfections, dislocations, grain boundaries, and the surface of the material\textsuperscript{16}. Two types of carrier traps are found in Pcs: (i) traps with discrete energy levels in the forbidden energy gap of the material (ii) traps with quasi-continuous distribution of energy levels usually having maximum density at the edge of the conduction or valence bands\textsuperscript{8}.

Most MPcs show gas sensitivities, which are affected by the presence of oxygen, this behaviour being generally explicable in terms of interaction between the gaseous species or competition for adsorption sites\textsuperscript{17}. Gould\textsuperscript{15}
has recently reviewed the conduction properties of MPc thin films over a wide range of systems. The basic electrical conduction processes observed in these materials depend on many factors including the Pc species, the phase of the micro crystallites comprising the film, the film thickness and the electrode materials. Gould has investigated the conduction processes and confirmed the space charge limited conduction mechanism in Pcs. Among the conductivity types observed, space-charge-limited (SCL) conductivity, field-lowering effects such as the Schottky and Poole-Frenkel effects, hopping, tunneling and diode-type conductivity are reported in MPcs. The electronic conductivity in MPcs is found to vary with temperature. The study of the temperature dependence of ohmic and SCLC in CuPc, NiPc, and CoPc provides insight into the mechanism of charge transport and carrier trapping in organic semiconductors. Abdel-Malik and Cox obtained ohmic conduction and SCLC in NiPc crystals and determined the statistically important energy levels and their state densities. Gould and Blyth performed conductivity measurements in NiPc thin film and showed that the conductivity is ohmic at low voltages and SCLC at high voltages. Ohmic conduction is due to the presence of thermally excited free carriers where as SCLC occurs by direct carrier injection from suitable electrodes which can be either ohmic or Schottky barrier type. Varghese and Menon studied electrical properties of NiPc thin films using gold and lead electrodes and found that gold electrode acts as an ohmic contact and lead electrodes as a blocking contact to NiPc layer with the existence of a barrier region at the lead electrode side of the NiPc layer.

In ohmic contacts the energy band bending at the interface with the electrodes is such that there is a reservoir of charge carriers residing in the region of the contact, which is termed as the accumulation region. This charge reservoir is capable of supplying carriers to the material as required. Conversely, for Schottky barriers type, a depletion region is formed and
carriers are required to overcome a potential barrier between the Fermi level in the metal contact and the conduction or valence band edges in semiconductor. Ohmic currents increase linearly with the voltage. Space-charge-limited currents increase as the square or as some higher power of the voltage. The electrical properties at high fields are determined by an exponential trap distribution and the form of the distribution is determined from the SCLC values. The effects of unsaturated bonds and impurities at the interface can alter the shape and height of the interfacial barrier.

Conductivity can be correlated with the energy gap between the highest occupied orbitals and lowest unoccupied orbitals\textsuperscript{23}. The conductivity of these systems depends on the gap between HOMO and LUMO\textsuperscript{23}. A sudden change in carrier mobility could disrupt correlations between the HOMO-LUMO gap and conductivity\textsuperscript{23}. Conductivity of Pcs generally depends on hole concentration. The decrease in conductivity during a phase transition is being caused by inhibition of the carriers from transferring to the electrode due to temporarily thermal diffusion of constituent atoms\textsuperscript{24}. Vartanyan\textsuperscript{25} reported that the Pcs exhibit semiconducting behaviour and the presence of oxygen affects its electrical conductivity. The importances of the electrical properties in thin films have been stressed since the work of Wihksne and Newkirk\textsuperscript{26}. Aoyagi\textsuperscript{27} et al. have investigated electrical conductivity and magneto resistance effect of NiPc, CuPc, ZnPc and H2Pc single crystals. They observed that the central metal ion in the PCs changes the activation energy and mobility.

Collins and Mohammed\textsuperscript{28} have described much of the early work and were largely concerned with the role of electron-accepting species such as oxygen in determining the conductivity of H2Pc and CuPc. They have also reported the dark conductivity as a function of material purity, crystal phase transformation and temperature with regard to gas sensitivity in air. Assour and Harrison\textsuperscript{29} studied the electrical conductivity of H2Pc and CuPc
crystals and indicated that both surface and bulk conduction contribute to the electrical properties and are affected by oxygen atoms. Sadaoka\textsuperscript{30} et al. found that the enhancement of conductance during exposure to NO\textsubscript{2}, of evaporated films was mainly reflected in decreased activation energy.

In this chapter, the investigations are on the electrical conductivity of evaporated thin films of CuPc, NiPc and CoPc. Measurements on the electrical conductivity and the activation energies are given. These properties are found depended on evaporation rate, substrate temperature and post evaporation annealing.

3.2 Theory

The semi conducting properties are brought about by thermal excitation, impurities, lattice defects and non-stoichiometry. A pure semi conductor exhibits intrinsic conductivity. In semi conductors, as the temperature is increased from absolute zero, electrons are thermally excited from the valence band to the conduction band, leaving vacant sites called holes in the valence band. Holes in the valence band and electrons in the conduction band contribute to the electrical conductivity. The conductivity $\sigma$ due to electrons and holes is

$$\sigma = (n e \mu_e + p e \mu_h) \quad \text{-----------------3.2.1}$$

where $n$ and $\mu_e$ are the carrier concentration and mobility of the electrons respectively and $p$ and $\mu_h$ are the corresponding quantities for the holes, and $e$ is the electronic charge. In an intrinsic semiconductor, the number of electrons is equal to the number of holes. The expression for carrier concentration is given by

$$n_i = N_c \exp (E_F - E_C) / k_B T \quad \text{-----------------3.2.2}$$

$$p_i = N_v \exp (E_V - E_F) / k_B T \quad \text{-----------------3.2.3}$$
where \( N_c \) and \( N_v \) are the density of states in the conduction band and valence band respectively. \( E_C \) represents the bottom of the conduction band and \( E_V \), the top of the valence band. \( E_F \) is the Fermi energy level. \( k_B \) and \( T \) are the Boltzmann’s constant and absolute temperature respectively. \( N_c \) and \( N_v \) are given by

\[
N_c = \frac{2(2\pi m_e^* k_B T/h^2)^{3/2}}{3.2.4} \\
N_v = \frac{2(2\pi m_h^* k_B T/h^2)^{3/2}}{3.2.5}
\]

where \( m_e^* \) and \( m_h^* \) are the effective masses of the electrons and holes respectively. Since

\[
n_i = p_i, \text{ it follows from equations 3.2.2 and 3.2.3 that}
\]

\[
E_F = (E_C + E_V)/2 + 3/4 k_B T \ln(m_h^*/m_e^*)
\]

Substituting the values of \( E_F \) in to equation 3.2.2 and 3.2.3

\[
n_i = p_i = 2(2\pi k_B T/h^2)^{3/2} (m_e^* m_h^*)^{3/2} \exp (-E_a/2k_B T)
\]

\[
= A \exp (-E_a/2k_B T)
\]

where \( E_a \) represents the energy gap \( (E_C - E_V) \) and \( A \) is a constant.

If we assume that the variation of mobility of the electrons and holes in an electric field with temperature is small, then conductivity \( \sigma \), which is proportional to the number of carriers, has a variation of the form

\[
\sigma = \sigma_0 \exp (-E_a/2k_B T)
\]

where \( \sigma_0 \) is a constant. Such an exponential variation of electrical conductivity is known for semiconductors. Multiple donor levels exist within the forbidden energy gap and deeper levels can be frozen out as the temperature is increased.

Conductivity in phthalocyanines is due to both hopping of holes and charge transport via excited states. In such a case, the conductivity is given by
\[ \sigma = A \exp\left(-E_1/k_B T\right) + B \exp(-E_2/k_B T) + C \exp\left(-E_3/k_B T\right) + \ldots \]  

where \( E_1 \) is the pseudo intrinsic energy gap and \( E_2, E_3 \), the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band\(^{31}\). \( A, B, C \) are constants. The conductivity \( \sigma \) of a film of resistance \( R' \), length \( l' \) breadth \( b' \) and thickness \( t' \) is given by

\[ \sigma = l'/Rbt \]  

--- 3.2.10

The steady state transport properties of carriers in organic semiconductors are dominated by the presence and energy distribution of carrier trapping sites. At low voltages, the thermally generated carrier concentration exceeds the injected carrier concentration and the conductivity in the ohmic region can be described by the relation

\[ J = p_o e \mu (v/t) \]  

--- 3.2.11

where \( J \) is the current density, \( p_o \) is the thermally generated hole concentration, \( e \) is the electronic charge, \( \mu \) is the hole mobility, \( V \) is the applied voltage and \( t \) is the film thickness. When voltage is applied, majority carriers are injected into the material and when the injected carrier concentration exceeds that of the thermally generated carrier concentration, the SCLC current becomes dominant. However, the existence of traps within the extrinsic materials has the effect of immobilizing a large proportion of the injected carriers. If the trap is shallow and has an energy \( E_t \) above the valence band, the current density \( J \) in the SCLC region is given by the relation\(^{32}\).

\[ J = \frac{9}{8} \varepsilon_r \varepsilon_0 \theta \mu v^2/t^3 \]  

--- 3.2.12

where \( \varepsilon_r \) is the relative permittivity, \( \varepsilon_0 \) is the permittivity of free space, \( V \) is the applied voltage, \( \mu \) is the hole mobility and \( e \) is the ratio of free to trapped charge which is given by\(^{33}\)

\[ \theta = \frac{N_v}{N_i} \exp\left(-E_t/k_B T\right) \]  

--- 3.2.13
where \( N_v \) is the effective density of states in the valence band, \( N_t \) is the density of traps at an energy level \( E_t \).

A second type of conduction process is the Poole-Frenkel effect\(^{34}\). It is the field assisted lowering of the coulombic potential barrier between carriers at impurity levels and the edge of the conduction or valence bands. Poole-Frenkel effect is not observed in Pc thin films when an ohmic contact is used\(^{15}\).

A third type of conduction process, occurring in Pc thin films is known as hopping. In order that the carriers are transported through the material and to contribute to the conductivity, they perform a series of jumps or 'hops' from one localized energy level to another. Hopping occurs between various localized energy levels. According to Mott and Davis\(^ {35}\), in this type of conductivity \( \sigma \) exhibits different behaviour in different regions of \( \log \sigma \) versus \( 1/T \) characteristics. At higher temperature, thermal excitation of carriers to the band edges is possible while at lower temperatures, where less thermal energy is available, hopping can occur.

### 3.3 Experiment

Powdered samples of spectroscopically pure CuPc, NiPc and CoPc are obtained from Aldrich Chemical Company Inc., WI, USA and are used as the source materials. Glass substrates are cleaned physically and chemically to avoid contaminants from the glass surface. Thoroughly cleaned glass substrates of dimensions 75mm x 25mm x 1.35 mm are used for the evaporation. Resistive heating of CuPc, NiPc and CoPc powders from molybdenum boat is carried at the rate 15 - 20nm per minute. Thin films are prepared at a base pressure of \( 10^{-5} \) m.bar using a Hind-Hivac thermal evaporation plant (Model No.12A4) by thermal evaporation technique (2.2.5 of chapter 2). The substrate is placed 20cm away from the molybdenum boat of dimension 23x13x11mm. The thicknesses of the films
are measured using the Tolansky's multiple beam interference technique as described in section 2.4.1 of chapter 2.

To study the effect of thickness on conductivity, thin films of CuPc, NiPc and CoPc are deposited on the substrates with different thickness at room temperature. The thin films prepared at room temperature are annealed for one hour at different annealing temperatures in air to study effect of air annealing on its conductivity. Thin films of CuPc, NiPc and CoPc are also deposited at various substrate temperatures to study the effect of substrate temperature on conductivity. The temperature is monitored using a chromel-alumel thermocouple placed over the substrate. Current to the substrate heater is controlled by a variac. Silver coating is used as ohmic contact electrodes for conductivity measurements. Ohmic contact introduces little resistance to the flow of current. Wilson and Collins\textsuperscript{36} have reported that gold and silver are the best electrode materials for H\textsubscript{2}Pc and CuPc from their studies using Au, Ag, Ni and In as electrodes. Again Hassan and Gould\textsuperscript{34} reported Al, Au, Ag and Cu contacts to evaporated CuPc films for various polarity combinations and they concluded that Al forms blocking contacts, while the other metals form ohmic contacts. Wilson and Collins\textsuperscript{37} studied thin film interdigital metal-Pc-metal devices using H\textsubscript{2}Pc and CuPc, with regard to gas sensitivity. They also found that gold and silver are the best electrode materials with regard to linearity, reversibility and reproducibility.

Measurements on dark electrical conductivity are performed using a programmable Keithley electrometer (model No.617) in the constant current source mode. Room temperature deposited samples of metal substituted phthalocyanines CuPc, NiPc and CoPc are mounted on the sample holder of the conductivity cell given in section 2.6 of chapter 2. Electrical contacts are made using copper strands of diameter 0.6mm and are fixed to the specimen with silver paste.
To avoid contamination, measurements are performed in a subsidiary vacuum of $10^{-3}$ m.bar. Dark conductivity studies are done in the temperature range 320-500K. The electrical conductivity measurements are done for CuPc, NiPc and CoPc thin films deposited in various thicknesses at room temperature, thin films of equal thickness deposited at various substrate temperatures and thin films of above materials in the same thickness deposited at room temperature were air annealed at different temperature and conductivity studies are made. The error bars of thickness measurements are ± 10Å. The activation energies are calculated within an accuracy of ± 0.01 eV in all measurements.

3.4 Results and Discussion

Fielding and Gutman\textsuperscript{38} earlier studied the electrical properties of H$_2$Pc, CuPc, NiPc and CoPc, and confirmed their semiconducting nature and their activation energies were reported. Allen Twarowski\textsuperscript{39} reported that the ambient strongly influence dark conductivity and the photoconductivity of Pcs. Temperature dependent studies\textsuperscript{10-12} shows that a marked change occurs in the activation energy for dark conduction when phthalocyanine is exposed to oxygen. The dark conductivity at room temperature increases by 4 or 5 orders of magnitude when Pc is exposed to oxygen\textsuperscript{39}. Cox and Knight\textsuperscript{40} showed temperature dependence of dark electrical conductivity of β-metal-free phthalocyanine single crystals and find an electron trap level at 0.32eV below the conduction band edge. For temperature below 380K, the thermal activation energy in the ohmic region is interpreted as being equal to the energy separation of the localized electron level $E_m$ from the valence band $E_v$ and is characteristic of an extrinsic conduction process\textsuperscript{41}. Ahmad and Co11ins\textsuperscript{9} studied the effect of oxygen on the electrical properties of triclinic PbPc thin film and found that prolonged exposure to oxygen enhanced the conductivity and decreased the activation energy. The electrical properties of organic semiconductors are particularly dependent upon the crystal
modifications relating to the various dimorphic forms and there is much current interest in how these are affected by material preparation methods and subsequent thermal treatment\textsuperscript{42, 43}. The majority carriers in CuPc, NiPc and CoPc thin films are found to be holes and thus they are found to be p-type semiconductors\textsuperscript{11}.

3.4.1 Dependence of film thickness

Resistances of CuPc, NiPc and CoPc thin films deposited at room temperature are measured using the programmable Keithley electrometer in the temperature range 320-500K at intervals of 5K. The experimental setup is explained in section 2.5 and 2.6 of chapter-2. The corresponding electrical conductivity ($\sigma$) is estimated using the equation 3.2.10, knowing the length, breadth and thickness of the film. Plot of $\ln \sigma$ versus 1000/T yields different linear regions. The thermal activation energies of these samples are calculated from the slopes of the linear portions of the graphs using the relation 3.2.9. Figures 3.4.1, 3.4.2 and 3.4.3 show the plots of $\ln \sigma$ versus 1000/T for CuPc thin films of thicknesses 180nm, 301nm and 467nm.

![Graph](image)

**Figure 3.4.1:** $\ln \sigma$ versus 1000/T plot of CuPc thin film of thickness 180nm
The activation energies are tabulated in Table 3.4.1. It is observed that each sample has three linear regions giving three activation energy values.
Table 3.4.1: Variation of activation energy for CuPc thin films with different thickness

<table>
<thead>
<tr>
<th>Film Thickness t (nm)</th>
<th>Activation energy (eV) ± 0.01eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1</td>
</tr>
<tr>
<td>180</td>
<td>0.77</td>
</tr>
<tr>
<td>301</td>
<td>0.59</td>
</tr>
<tr>
<td>467</td>
<td>0.58</td>
</tr>
</tbody>
</table>

For CuPc thin film of thickness 180nm, 0.77eV, 0.44eV, 0.18eV are the activation energy values. Similar pattern of decrease in activation energies are obtained for other two thicknesses are shown in Table 3.4.1. The slope of the ln σ versus 1000/T plot is found varying with different temperature regions. The activation energy is higher at higher temperature region. Sussman\(^{43}\) has investigated conductivity, trap density and mobility of carriers as a function of voltage, temperature, thickness, illumination and different ambient gases on CuPc films. It has confirmed the existence of exponential trap distribution in CuPc films. Ambily\(^{10}\) et al. had similar observations for CuPc thin films and found a decrease in activation energy with increase in thickness. These types of observations are also reported for many other MPcs. From the present studies it is found that the activation energy reduced with increasing thickness of the film and hence the current increases as it is reported that the conductivity increases with increasing film thickness\(^{45}\). Hsieh\(^{46}\) et al. reported that the sensor current increases with the film thickness. It could be observed that the defects in the amorphous film localize the charges transported in the film and reduce the conductivity\(^{47}\). Harrison and Ludewig\(^{48}\) found high conductivity and low activation energy for the \(\alpha\) form of phthalocyanines when used as a gas sensor.

Figures 3.4.4, 3.4.5, 3.4.6 and 3.4.7 show the plots of ln σ versus 1000/T for NiPc thin films of thickness 94nm, 132nm, 156nm and 194nm respectively.
Figure 3.4.4: $\ln \sigma$ versus $1000/T$ plot of NiPc thin film of thickness 94nm

Figure 3.4.5: $\ln \sigma$ versus $1000/T$ plot of NiPc thin film of thickness 132nm
Figure 3.4.6: $\ln \sigma$ versus $1000/T$ plot of NiPc thin film of thickness 156nm

Figure 3.4.7: $\ln \sigma$ versus $1000/T$ plot of NiPc thin film of thickness 194nm

Thermal activation energies are calculated from the slopes of the linear portions of the graphs using the relation 3.2.9 and are tabulated in
Table 3.4.2. It is observed that each sample gives three linear regions resulting in three activation energy values.

**Table 3.4.2:** Variation of activation energy for NiPc thin films with different thickness

<table>
<thead>
<tr>
<th>Film Thickness (nm)</th>
<th>Activation energy (eV) ± 0.01eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1</td>
</tr>
<tr>
<td>94</td>
<td>0.79</td>
</tr>
<tr>
<td>132</td>
<td>0.76</td>
</tr>
<tr>
<td>156</td>
<td>0.71</td>
</tr>
<tr>
<td>194</td>
<td>0.69</td>
</tr>
</tbody>
</table>

For NiPc film of thickness 94nm, 0.79eV, 0.56eV, 0.02eV are the activation energy values. Same pattern of decrease in activation energies were observed in other three thicknesses of 132, 156 and 194nm. The slope of the ln $\sigma$ versus 1000/T plot is found varying with temperature for NiPc films also. The activation energy is higher at higher temperature region and is found decreased with film thickness. El-Nahass\(^49\) studied the transport properties of thermally evaporated NiPc thin films and measured dark electrical resistivity in the temperature range 298-423 K. He reported two activation energies $\Delta E1$ and $\Delta E2$. Room temperature measurements show a linear ohmic dependence at low voltages, followed by SCLC at higher voltage levels, dominated by an exponential distribution of traps. Abdel Malik\(^41\) et al. reported traps at 0.43 ± 0.02 ev for NiPc. Narayanan Unni\(^50\) et al. found three activation energies for NiPc thin films and reported decrease in activation energy with increase in thickness. Abdel Malik\(^20\) et al. also reported three activation energies for NiPc single crystals. These type observations are reported in CuPc and many other phthalocyanine compounds.

Figures. 3.4.8, 3.4.9 and 3.4.10 show the plots of ln $\sigma$ versus 1000/T for CoPc thin films of thickness 181nm, 301nm and 405nm respectively.
Figure 3.4.8: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film of thickness 181nm

Figure 3.4.9: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film of thickness 301nm
The ln $\sigma$ versus 1000/T plot for CoPc films shows three linear regions varying with temperature. Table 3.4.3 gives the variation of activation energy for CoPc thin films with film thicknesses. For thickness 181nm, 0.15eV, 0.17eV and 0.02eV are the activation energy values. The activation energy is found small at low temperature region. Almost similar pattern is obtained for other thickness as shown in Table 3.4.3. Ambily et al. also found three activation energies for CoPc thin films and reported decrease in
activation energy with increase in thickness. The experiments were repeated for films of different thickness and determined the activation energy values, which are found, decreased with increased thickness, similar to CuPc and NiPc. Thicker films may form a closely packed structure, which increases molecular overlapping and the diffusion. It is apparent that the sensor current increases with the film thickness because the number of adsorption sites increases with the thickness 46.

3.4.2 Dependence of substrate temperature

The resistance of the thin films prepared at different substrate temperatures are measured using the programmable Keithley electrometer in the temperature range 300-500K, at intervals of 5K. Corresponding electrical conductivity $\sigma$ is obtained using equation 3.2.10. To study the dependence of substrate temperature on the conduction mechanism, Arrhenius plots of $\ln \sigma$ versus $1000/T$ are made. The thermal activation energies of these samples are calculated from the slopes of the linear portions of the graphs using the relation 3.2.9. Figures. 3.4.11, 3.4.12, 3.4.13 and 3.4.14 give the $\ln \sigma$ versus $1000/T$ plots for CuPc thin films of thickness 330nm deposited at substrate temperatures 318, 363, 408 and 458K respectively.
Figure 3.4.11: In $\sigma$ versus 1000/T plot of CuPc thin film prepared at substrate temperature 318K.

Figure 3.4.12: In $\sigma$ versus 1000/T plot of CuPc thin film prepared at substrate temperature 363K.
Figure 3.4.13: \( \ln \sigma \) versus 1000/T plot of CuPc thin film prepared at substrate temperature 408K.

Figure 3.4.14: \( \ln \sigma \) versus 1000/T plot of CuPc thin film prepared at substrate temperature 458K.
The activation energies are calculated for the films prepared at different substrate temperatures from the Arrhenius plots and are given in Table 3.4.4

**Table 3.4.4:** Variation of activation energy for CuPc thin films with different substrate temperatures

<table>
<thead>
<tr>
<th>Substrate Temperature Ts (K)</th>
<th>Activation energy (eV) ± 0.01eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1</td>
</tr>
<tr>
<td>318</td>
<td>0.83</td>
</tr>
<tr>
<td>363</td>
<td>0.81</td>
</tr>
<tr>
<td>408</td>
<td>0.77</td>
</tr>
<tr>
<td>458</td>
<td>0.65</td>
</tr>
</tbody>
</table>

The ln $\sigma$ versus 1000/T plot for CuPc films shows two linear regions. The two linear regions are due to intrinsic extrinsic transitions. For substrate temperature 318K, 0.83eV and 0.02eV are the activation energy values. The activation energy is higher at higher temperature region and is found reduced in the lower temperature region. It is observed that as the substrate temperature increases, from 318K to 458K, the activation energy $E_1$ decreases from 0.83eV to 0.65eV. $E_2$ is trap level corresponding to the activation energy in the impurity scattering region. Higher substrate temperature leads to an increase in the size of the critical nucleus; and hence a decreased value of activation energy is expected. Hsieh et al. reported that crystal size play an important role in the conductivity. The increases in grain size are evidence from SEM studies (Figure 6.3 of chapter 6).

Figures 3.4.15, 3.4.16; 3.4.17 and 3.4.18 give the ln $\sigma$ versus 1000/T plots for NiPc thin films of thickness 330nm deposited at different substrate temperatures of 318, 363, 408 and 458K respectively.
Figure 3.4.15: In $\sigma$ versus 1000/T plot of NiPc thin film prepared at substrate temperature 318K.

Figure 3.4.16: In $\sigma$ versus 1000/T plot of NiPc thin film prepared at substrate temperature 363K.
Figure 3.4.17: In $\sigma$ versus 1000/$T$ plot of NiPc thin film prepared at substrate temperature 408K.

Figure 3.4.18: ln $\sigma$ versus 1000/$T$ plot of NiPc thin film prepared at substrate temperature 458K.
The activation energies are calculated from the ln σ versus 1000/T plots and are tabulated in the Table 3.4.5

**Table 3.4.5:** Variation of activation energy for NiPc thin films with different substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate Temperature Ts (K)</th>
<th>Activation energy (eV) ± 0.01 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1</td>
</tr>
<tr>
<td>318</td>
<td>0.81</td>
</tr>
<tr>
<td>363</td>
<td>0.69</td>
</tr>
<tr>
<td>408</td>
<td>0.60</td>
</tr>
<tr>
<td>458</td>
<td>0.54</td>
</tr>
</tbody>
</table>

The ln σ versus 1000/T plot for NiPc films shows three linear regions varying with temperature range. For substrate temperature 318K, the activation energy values are 0.81eV, 0.63eV and 0.03eV. The activation energy is higher at higher temperature region. It is observed that as the substrate temperature increases, from 318K to 458K, the activation energy E1, corresponding to the higher temperature region decreases from 0.81eV to 0.54eV. E2 and E3 are the activation energies corresponding to the impurity scattering region. Higher substrate temperature leads to an increase in the size of the critical nucleus and hence a decreased value of activation energy is expected\(^{52}\).

Figures. 3.4.19, 3.4.20, 3.4.21 and 3.4.22 are the ln σ versus 1000/T plots for CoPc thin films of thickness 330nm deposited at substrate temperatures 318, 363, 408 and 458K respectively.

The activation energies are calculated and are given in Table 3.4.6
**Figure 3.4.19:** $\ln \sigma$ versus $1000/T$ plot of CoPc thin film prepared at substrate temperature 318K.

**Figure 3.4.20:** $\ln \sigma$ versus $1000/T$ plot of CoPc thin film prepared at substrate temperature 363K.
Figure 3.4.21: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film prepared at substrate temperature 408K.

Figure 3.4.22: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film prepared at substrate temperature 458K.
Table 3.4.6: Variation of activation energy for CoPc thin films with different substrate temperatures.

<table>
<thead>
<tr>
<th>Substrate Temperature Ts (K)</th>
<th>Activation energy (eV) ± 0.01 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1</td>
</tr>
<tr>
<td>318</td>
<td>0.82</td>
</tr>
<tr>
<td>363</td>
<td>0.78</td>
</tr>
<tr>
<td>408</td>
<td>0.77</td>
</tr>
<tr>
<td>458</td>
<td>0.74</td>
</tr>
</tbody>
</table>

The ln $\sigma$ versus 1000/T plots for CoPc films show two linear regions varying with temperature. For substrate temperature 318K, the activation energy values are 0.82eV, 0.03eV. The activation energy is higher at higher temperature region and is found reduced in the lower temperature region. E2 is the trap level corresponding to the activation energy in the impurity scattering region. The activation energy is found reduced with increase in substrate temperature. Higher substrate temperature leads to an increase in the size of the critical nucleus and hence a decreased value of activation energy is expected$^{51}$. He observed that for certain PCs, the phase change occurs in two stages with a well-defined intermediate state. The FWHM values determined in chapter-5 also show low resistivity at high substrate temperature. It is reported that the larger the FWHM value the lower is the resistivity$^{53}$. SEM studies (Chapter 6) also support the observations.

3.4.3 Dependence of air - annealing

The role of oxygen in the bulk of the film is presumed to be the formation of acceptor states enhancing the p-type conductivity$^{28}$. Meyer$^{54}$ et al. observed that the conductivity increases by several orders of
magnitude in molecular semi conductors after heating and this led to the studies of annealing of thin films. Hooper\textsuperscript{55} et al. studied the electrical properties of NiPc sandwich devices and observed increase the conductivity due to air exposure. The desorption of oxygen which may be influenced intrinsic conductivity\textsuperscript{56} which leads to an increase in the resistance of the material\textsuperscript{57, 58}, thus proving the sensitivity of the electronic conduction of Pcs to the presence of oxygen. A constant specific conductivity was reached only after annealing at these temperatures for some hours. Examination of the conductivity of CuPc thin films provides evidence that oxygen absorption affects not only the surface conductivity but also the bulk conductivity. Gianluigi\textsuperscript{59} et al. studied effects of post deposition heat treatments on properties of CuPc films and found that part of the CuPc molecules decompose during heat treatments and formation of copper oxide take place. The replacement of CuPc by copper oxide in the heated films accounts for the change of their electrical conductance.

To study the effect of air annealing on the conduction mechanism and the activation energy, CuPc, NiPc and CoPc thin films prepared at room temperature are annealed in air for one hour. The resistances of the films are measured using the Keithley programmable electrometer in the temperature range 320-555K at intervals of 5K. Corresponding electrical conductivities are evaluated using equation 3.2.10. Figures. 3.4.23, 3.4.24, 3.4.25 and 3.4.26 show plots of \(\ln \sigma\) versus 1000/T for the as deposited CuPc thin films of thickness 130nm annealed in air for one hour at 313, 353, 393 and 433K respectively. The thermal activation energies of these samples are calculated from the slopes of the linear portions of the graphs using the relation 3.2.9. The values of activation energy are collected in Table 3.4.7.
Figure 3.4.23: $\ln \sigma$ versus $1000/T$ plot of CuPc thin film annealed 313K

Figure 3.4.24: $\ln \sigma$ versus $1000/T$ plot of CuPc thin film annealed 353K
Figure 3.4.25: \( \ln \sigma \) versus 1000/T plot of CuPc thin film annealed 393K

Figure 3.4.26: \( \ln \sigma \) versus 1000/T plot of CuPc thin film annealed 433K
Table 3.4.7: Variation of activation energy for CuPc thin films with different annealing temperatures

<table>
<thead>
<tr>
<th>Annealing Temperature Ta (K)</th>
<th>Activation energy (eV) ± 0.01 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E1</td>
</tr>
<tr>
<td>313</td>
<td>0.64</td>
</tr>
<tr>
<td>353</td>
<td>0.63</td>
</tr>
<tr>
<td>393</td>
<td>0.60</td>
</tr>
<tr>
<td>433</td>
<td>0.56</td>
</tr>
</tbody>
</table>

The $\ln \sigma$ versus 1000/T plot for CuPc films shows three linear regions. The three linear regions in the plot are due to extrinsic and intrinsic transitions. For the film annealed at 313K the activation energy values are 0.64 eV, 0.58eV and 0.26eV. The activation energy is decreased in the lower temperature region. It is observed that as the annealing temperature increases to 433K, the activation energy $E_1$, corresponding to the higher temperature region decreases from 0.64 eV to 0.56 eV. For the film annealed at 433K, the variation in the activation energy is marked. This change may be due to partial phase change or appearance of crystal defects during heat treatment as suggested by Amar$^{60}$ et al. Faassen and Kerp$^{61}$ found that CuPc, ZnPc and MnPc thin films absorb comparable quantities of oxygen by annealing, which distribute homogeneously through the bulk of the film.

Figures. 3.4.27, 3.4.28, 3.4.29 and 3.4.30 shows the plot of $\ln \sigma$ versus 1000/T for the NiPc thin films of thickness 130nm annealed in air for one hour at 313, 353, 393 and 433K respectively. The corresponding activation energies are collected in Table 3.4.8. Allen Twarowski$^{39}$ reported that oxygen induces acceptor states in Pcs while hydrogen removes them. Harrison and Ludewig$^{48}$ examined the conductivity of both phases of
thin films of CuPc under different atmospheric conditions and found that the larger α phase conductivity was due solely to the greater propensity of this phase for oxygen which acts as a dopant in Pc films. Sussman\textsuperscript{44} reported that both the position of the Fermi level and energy distributions of the trap levels is altered during annealing. From the conductivity-temperature data, they observed a transition from extrinsic to non-extrinsic conduction and the conductivity is found to be dependent on the presence of oxygen. Amar\textsuperscript{60} et al. studied the electrical properties of H\textsubscript{2}Pc thin films using gold electrodes. The results shows desorption of oxygen, re-growth of the phthalocyanine and appearance of crystal defects during heat treatment.

\begin{figure} 
\centering 
\includegraphics[width=\textwidth]{figure3.4.27.png} 
\caption{ln $\sigma$ versus 1000/T plot of NiPc thin film annealed at 313K} 
\end{figure}
Figure 3.4.28: $\ln \sigma$ versus $1000/T$ plot of NiPc thin film annealed at 353K

Figure 3.4.29: $\ln \sigma$ versus $1000/T$ plot of NiPc thin film annealed at 393K
The $\ln \sigma$ versus $1000/T$ plots for NiPc films show three linear regions. For annealing temperature 313K, the activation energy values are 0.91eV, 0.48eV and 0.02eV. The activation energy is found decreased in the low temperature region. It is observed that as the annealing temperature increases, from 313K to 433K, the activation energy E1 decreases from 0.91eV to 0.68eV. Higher substrate temperature leads to an increase in the size of the critical nucleus and hence a decreased value of activation energy is
expected. It is seen that the activation energy corresponding to the intrinsic conduction process $E_1$, decreases with annealing temperature. But for the film annealed at 433K, the variation in the activation energy is marked. This change may be due to the appearance of crystal defects during heat treatment as suggested by Amar et al. or due to the phase change.

Figures 3.4.31, 3.4.32, 3.4.33 and 3.4.34 show the plot of $\ln \sigma$ versus $1000/T$ for the CoPc thin films of thickness 130nm annealed in air for one hour at 313K, 353K, 393K and 433K and the corresponding activation energies are collected in Table 3.4.9.

![Figure 3.4.31: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film annealed at 313K.](image)

Figure 3.4.31: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film annealed at 313K.
Figure 3.4.32: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film annealed at 353K.

Figure 3.4.33: $\ln \sigma$ versus $1000/T$ plot of CoPc thin film annealed at 393K.
Figure 3.4.34: \( \ln \sigma \) versus 1000/T plot of CoPc thin film annealed at 433K.

Table 3.4.9: Variation of activation energy for CoPc thin films with different annealing temperatures

<table>
<thead>
<tr>
<th>Annealing Temperature Ta (K)</th>
<th>Activation energy (eV) ± 0.01 eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>E2</td>
</tr>
<tr>
<td>313</td>
<td>0.88</td>
</tr>
<tr>
<td>353</td>
<td>0.85</td>
</tr>
<tr>
<td>393</td>
<td>0.85</td>
</tr>
<tr>
<td>433</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The \( \ln \sigma \) versus 1000/T plots for CoPc films show two linear regions. For annealing temperature 313K the activation energy values are 0.88eV and 0.03eV. Low activation energy is found in the low temperature region. It is observed that as the annealing temperature increases, from 313K to 433K, the activation energy E1, corresponding to the higher temperature region decreases from 0.88 eV to 0.80 eV. Higher annealing
temperature leads to a reorientation of grains (Figure 17 in chapter 6). The size of the grains increases and a decreased value of activation energy is expected. It is seen that the activation energy corresponding to the intrinsic conduction decreases with increase in annealing temperature. This change may be due to crystal defects or the phase change activity. A fraction of the diffused oxygen molecules takes up an electron from the Pc system. The positively charged Pc+ units release a free hole, which establishes a p-type doping inside the material. As a consequence, the film conductivity is enhanced by several orders of magnitude. Twarowski reported an oxygen uptake of $10^{11}$ molecules/cm$^2$ s for CoPc and found this rate to be determined by diffusion of oxygen into the bulk of the CoPc film. In MPcs, the central metal atom is in a position of nearest approach to the nitrogen atoms in parallel pairs of molecules. Hence any crystal phase changes affect the energy gap between conduction and valence bands.

At room temperature, conductivity of $\beta$ phase is much lower than that of the oxygen doped $\alpha$ phase. It is due to the greater ability of the $\alpha$ phase to absorb oxygen. Szczepaniak and Bragiel from ab initio calculations, show that the HOMO-LUMO gap is narrowed in Mpcs on interaction with O$_2$. The p-type semi-conductivity is thus strongly modified by gaseous adsorption but is also dependent on impurities and on structure. An increase in temperature does not alter the total amount of space charge, but it increase the fraction of this space charge in the conduction band. The conduction is explained in terms of hopping through a band of localized states at lower temperatures and by free band conduction at higher temperatures. Grain boundaries play an important role in the electrical properties of a variety of ceramic materials. Fendrich et al. studied conductivity of CuPc and reported that the molecules may hop between adsorption sites due to thermal activation at room temperature. Grain boundaries act as barriers for the cross transport of charge carriers. The barrier character of the grain boundary is
pronounced in the low temperature regime. Under high temperature the resistive grain boundary barriers are reduced and that give rise to substantially field enhanced leakage currents through the components. It is known that over all grain boundaries resistance increases with the decreases in grain size due to the increase in number of boundaries per unit thickness. Ajith Kumar Mahapatro et al. studied grain-boundary-controlled current transport in CuPc and found anomalous temperature dependence of resistivity at low temperature in CuPc thin films. The prediction is based on the assumption that the thin film beyond a certain thickness is mainly polycrystalline, consisting of grains. Potential barriers at grain boundaries limited the transport.

Conclusion

Thin films of CuPc, NiPc and CoPc are prepared by thermal evaporation and their electrical conductivity measurements are done. The dependence of activation energy on film thickness, substrate temperature, and post deposition annealing are studied. The existence of activation energies corresponding to impurity scattering are confirmed by the presence of more than one linear portion in the \( \ln \sigma \) versus \( \ln000/T \) plots for CuPc, NiPc and CoPc thin films. From the slopes of the linear portions, values of activation energy are determined. The activation energy \( E_1 \) corresponding to the high temperature region is due to intrinsic carriers. This intrinsic activation energy arises from the intrinsic majority carriers whereas that in the extrinsic regions depends on the extrinsic conduction due to impurity states. From the present studies it is found that the activation energy is reduced with increasing thickness of the film in all the three Pcs. The activation energy was found reduced also with the increasing substrate temperatures and annealing temperatures in the three Pcs. The conjugation structure is an essential condition for intrinsic conductivity in Pcs. The Pcs show their intrinsic conductivity due to the partial charge transfer from Pc ring to the central ion. The charge distribution and its volume vary from
metal to metal. The central metal ion changes the activation energy and the conductivity of Pc. An extrinsic to intrinsic crossover for the activation energy is found in CuPc, NiPc and CoPc. The conduction processes in the three Pcs are found controlled by different trap levels present in the forbidden energy gap. Change in substrate temperature changes the intrinsic activation energy. From the studies it is found that oxygen doping is predominant in the case of films annealed in air.

References


