Chapter 4

4. ELECTRICAL CONDUCTIVITY STUDIES OF TTBPc, ZnTTBPc AND CuTTBPc THIN FILMS

4.1. Introduction

Phthalocyanine (Pc) or metallophthalocyanines (MPC) are aromatic compounds or complexes with semiconducting properties. Besides, they are chemically and thermally stable with the potential to be used as the hole transport layers or injection layers in the organic optoelectronic devices such as organic solar cells, gas sensors, field effect transistors and organic light emitting diodes (Mckeown, 1998), (Thomas, 1990), (Salzman and Forrest, 2005).

Most of the phthalocyanines are p-type due to the absorbed oxygen which creates an acceptor level in band gap (Gutman and Hyonv, 1967). The oxygen impurities, which are unavoidably introduced in the preparation of organic semiconductors (Martin and Simon, 1983) appear to play the dual role of both acceptors and trap levels (Ahamed and Collins, 1992). However, these impurities, as well as voids and defects give rise to extrinsic conductivity (Lewis, 1972) can be removed by heat treatment. The DC electrical properties of phthalocyanines have received considerable attention (Nalwa and Vasudevan, 1983), (James and Silver, 1992).

The molecular energy levels can be separated into two categories $\pi$ and $\pi^*$ orbital or bonding and anti-bonding orbitals. They form a band-like structure. The occupied $\pi$ levels are equivalent to valence band in crystalline semiconductors. Electrically active level is
the highest one and it is called Highest Occupied Molecular Orbital (HOMO), while the unoccupied $\pi-\pi^*$ levels are equivalent to conduction band. Here the electrically active level is called LUMO (Lowest Unoccupied Molecular Orbital). A band gap is formed between these two levels.

The experimental fact of negative temperature coefficient of carrier drift mobility has led to the development of Bloch band theory for carrier transport in organic crystals and is often obtained for organic semiconductors (Crowell and Sze, 1983). When an electric field is applied, a conductive path is formed and charge carriers are transported from one chain to another. The process of this transfer is commonly called intermolecular hopping and is a thermally assisted tunneling effect (Blom and Vissenberg, 2000). The conduction critically depends on the hopping between conjugated parts of the polymer material. The theories are also applicable to describe the charge transport in conducting and semiconducting organic materials such as conjugated polymers (Movaghar, 1992), (Abkowitz, 1992), (Tanase and de Leeuw, 2003), (Schein, 1992).

Metallophthalocyanine have been extensively studied due to their interesting electrical properties and their ability to form good quality thin films which are of particular interest in the study of low-dimensional metals and semiconductors. Although the conduction path in these systems has been described as originated from the $\pi-\pi$ overlapped of the stacked molecules, it has been noticed that the conductivity can be modified or enhanced by adding organic bridging ligands which allow electron migration from one metal atom to the other (Datz and Hanack, 1984). In particular, by using linear bi-dentate axial ligands coordinated to the metallophthalocyanine nuclei, low-dimensional electronic conduction within polymeric films has been achieved (Kim and Shigehara, 2000). The application of a band type model for
electronic conduction process in phthalocyanine films has been reported. (Gould, 1996). The photoconductivity behavior is similar to the electronic structure in terms of a semiconducting band model, indicating photo generation of free carriers via interband transition. After a fast initial decay, the excess of photo induced carriers approaches the equilibrium dark with a higher rate of decay. This effect was observed for VOPc (Santos and Mergnalhao, 2008). (A.M Saleh, 2012) studied the delegate response and electric porch is of organize semi conducting phthalocyanine thin films.

The metallophthalocyanines (MPc's) are well known by their semi conducting properties besides exhibiting thermal and chemical stability (Leznoff and Lever, 1993), (Shirota, 2000). The MPc's have been extensively applied in electronic devices such as sensors (Jakabik,2009), Solar cells, (Pfuetzner and Leo, 2009) nonlinear optics (Medina and Claessens, 2009), diodes (Kato and Pac, 2009), transistors (Rapp and Delaporte, 2009) and photo detectors. For instance, MPc's have been tested in P-N junctions for applications in solar cells, leading to excellent conversion efficiency (Ohmori, 2009), (Myers and Xue, 2009), (Ye and Mori, 2009). Morphology and electronic properties of Hybrid organic -Inorganic system: Ag nanoparticles Embedded into CuPc matrix (Aristova, 2012).

Electrical conductivity studies of Tetra-Tert-Butyl phthalocyanines (TTBPc), Zinc-Tetra-Tert-Butyl phthalocyanine (ZnTTBPc) and Copper-Tetra-Tert-Butyl phthalocyanine (CuTTBPc) thin films and their variation in electrical conductivity due to thickness, annealing in air and vacuum are studied.

4.2. Experimental details.

TTBPc, ZnTTBPc, CuTTBPc in the powder form are procured from Sigma Aldrich chemical company (USA). Thoroughly cleaned micro glass slides are used as substrates. The substrates are cleaned using the procedure described in the section 2.7 of chapter 2. The films are grown using the vacuum thermal evaporation technique using a Hind Hivac vacuum coating unit (Model No 12 A4D) at a base pressure of $10^{-5}$Torr. Molybdenum boat of the activation energies of TTBPc thin film are increasing with increase of air and
dimensions 2.9x1.2x0.5 cm is used for the evaporation. During evaporation the substrates are kept at a distance of 12 cm from the source. The rate of deposition is $1\text{A}^0/\text{sec}$. For electrical conductivity measurements, silver electrodes are pre-evaporated onto micro glass substrate and TTBPc of suitable thickness (285 nm $\pm$ 15 nm) are deposited in between the silver electrodes. Hot probe technique is used for finding the type of conductivity. Since phthalocyanines are photo sensitisers, all the conductivity measurements are performed in darkness and in a subsidiary vacuum system at a pressure of $10^{-3}$ mbar. Using a conductivity cell having temperature range 300-465 k, electrical measurements are done by standard two probe technique with a Keithley (Model 617) electrometer and a constant current source. Electrical contact are made using copper strands of diameter 0.6 mm and are fixed to the specimen with silver paste. Voltage is applied to the films from the internal voltage source of the electrometer. Samples are heated using resistive heating using the filament attached to the sample holder of the conductivity cell and the temperature in the conductivity cell is measured using a calibrated chromel-Alumel thermocouple.

In order to study the conductivity variation with film thickness, samples are prepared and each time, D.C electrical conductivity is measured. Air and vacuum annealing is also done.

4.3. Theory

The semi conducting properties are brought about by thermal excitation, impurities, lattice defects and non-stoichiometry. Structure of inorganic semiconductors is generally characterized by their strong covalent and ionic bonding between atoms in the lattice whereas in organic semiconductors the bonding is mainly due to the weak van der Waals or London
forces in between molecules. Electrons associated with the conjugate bonds are not localized on a particular atom in organic semiconductors but are associated with the entire molecule. In case of organic thin films, one of the major considerations is that whether the energy band model of conduction is applicable or not. In semiconductors, 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

\[
\sigma = (n_e \mu_e + p_e \mu_h)
\]  \hspace{1cm} (4.3.1)

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

\[
n_i = N_c \exp(E_F - E_C)/k_B T
\]  \hspace{1cm} (4.3.2)

\[
p_i = N_v \exp(E_V - E_F)/k_B T
\]  \hspace{1cm} (4.3.3)

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 level energy. \( k_B \) and \( T \) are the Boltzmann’s constant and absolute temperature respectively. \( N_c \) and \( N_v \) are given by

\[
N_c = 2(2\pi m_e^* k_B T/h^2)^{3/2}
\]  \hspace{1cm} (4.3.4)
\[ N_v = 2(2\pi m^*_h k_B T/h^2)^{3/2} \] (4.3.5)

Where \( m^*_e \) and \( m^*_h \) are the effective masses of the electrons and holes respectively. Since \( n_i = p_i \), it follows from equations 4.3.2 and 4.3.3 that

\[ E_F = (E_C + E_V)/2 + 3/4 k_B T \ln(m^*_h/m^*_e) \] (4.3.6)

Substituting the values of \( E_F \) in to equation 4.3.2 and 4.3.3

\[ n_i = p_i = 2(2\pi k_B T/h^2)^{3/2}(m^*_e m^*_h)^{3/2} \exp(-E_a/2k_B T) = A \exp(-E_a/2k_B T) \] (4.3.7)

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 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

\[ \sigma = \sigma_0 \exp(-E_a/2k_B T) \] (4.3.8)

Where \( \sigma_0 \) is a constant. Such an exponential variation of electrical conductivity is drawn by plotting \( \ln \sigma \) vs. \( 1000/T \) yields different linear regions known as Arrhenius plot (Muller and Mulle, 1971),(Law and Ng, 1997). 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

\[ \sigma = A \exp(-E_1/k_B T) + B \exp(-E_2/k_B T) + C \exp(-E_3/k_B T) + \ldots \] (4.3.9)

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. A, B, C
are constants. The conductivity ’$\sigma$’ of a film of resistance ’$R$’, length ’$l$’ breadth ’$b$’ and thickness ’$t$’ is given by

$$\sigma = \frac{l}{Rbt}$$

(4.3.10)

The activation energy is determined with an accuracy of $\pm 0.01$eV in all measurements according to the error analysis treatments suggested by Worsnop and Flint (Worsnop and Flint, 1931). The steady state transport properties of carriers in organic semiconductors are dominated by the presence and energy distribution of carrier trapping sites.

4.4. Results and Discussion

4.4.1. D. C. Electrical conductivity studies on TTBPc thin films

4.4.1.1 Effect of thickness Hot probe technique is used to study the type charge carriers in complex phthalocyanines, and is found to be electrons (Jaseentha, 2009). Figure 4.4.1, 4.4.2, 4.4.3 show the Arrhenius plot of TTBPc thin film with respect to thickness, 150 nm, 200nm and 250 nm. Conductivity is found to decrease with increase in thickness.

Figure 4.4.1: Plot of ln $\sigma$ vs.1000/T graph for TTBPc thin film having thickness 150 nm
Figure 4.4.2: Plot of $\ln \sigma$ vs. $1000/T$ graph for TTBPc thin film having thickness 200 nm.

Figure 4.4.3: Plot of $\ln \sigma$ vs. $1000/T$ graph for TTBPc thin film having thickness 250 nm.

Table 4.4.1: Variation of activation energy with thickness for TTBPc thin films.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Activation Energy $E_1$ (±0.01 eV)</th>
<th>Activation Energy $E_2$ (±0.01 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>200</td>
<td>0.08</td>
<td>0.02</td>
</tr>
<tr>
<td>250</td>
<td>0.05</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The linear dependence of $\ln \sigma$ versus $1000/T$ in the low temperature range allows us to determine the activation energy for each sample, the activation energy is tabulated in table 4.4.1. The behavior is consistent with the Arrhenius relation (Stevensen and Webe, 121).
It shows that the activation energy decreases with increase of film thickness in TTBPc thin film. Freshly prepared samples may contain different kinds of defects such as vacancies, grain boundaries and dislocations which can cause increase in its density on layer by layer deposition. Increase in thickness creates extra defect levels between Fermi level and conduction band edge which will in turn reduce the distance for band transition and require less energy for activation in TTBPc like N-type compounds. (Ling and Bao, 1996)

A similar behavior has been reported for NiPc thin film also (K.N. Unni Narayanan and Menon, 2000).

4.4.1.2 Effect of air annealing

Figures 4.4.4, 4.4.5, 4.4.6 shows the electrical conductivity of TTBPc film with thickness 285 nm, as a function of inverse temperature for different films. This figure shows two separate temperature regions characterized by different conductivity slopes. The activation energies of all the thin films are listed in Table 4.4.2.

![Figure 4.4.4: Plot of ln σ vs.1000/T graph for TTBPc thin film annealed at 323K](image)

Figure 4.4.4: Plot of ln σ vs.1000/T graph for TTBPc thin film annealed at 323K
These figures show two separate temperature regions characterized by different conductivity slopes. At low temperature range, the conduction mechanism due to carriers excited into the localized states at the edge of the band by hopping and at other range of temperature the conduction mechanism due to carriers into extended states beyond the mobility edge by thermal excitation (Davis and Mott, 1970).

Activation energies are calculated from the $\ln \sigma$ Vs 1000/T plots for TTBPc films in the temperature range 303-503K. The activation energies of all the thin films are listed in
Table 4.4.2. The activation energies for a film treated at higher annealing temperature are higher than those treated at lower annealing temperature. The increasing trend in E upon increasing annealing temperature is due to the decreasing voids, dangling bonds and localized states through energy gap which seems layer after heat treatment.

Table 4.4.2: Variation of activation energy with thickness 285nm air annealed at different temperatures.

<table>
<thead>
<tr>
<th>Air annealing(K)</th>
<th>Activation Energy $E_1(\pm0.01eV)$</th>
<th>Activation Energy $E_2(\pm0.01eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.2</td>
<td>0.01</td>
</tr>
<tr>
<td>373</td>
<td>0.4</td>
<td>0.02</td>
</tr>
<tr>
<td>423</td>
<td>0.46</td>
<td>0.07</td>
</tr>
</tbody>
</table>

4.4.1.3 Effect of vacuum annealing Vacuum annealing temperature are fixed to be 323K, 373K and 423K with a uniform annealing period of one hour. Annealing effects on various TTBPc thin films are plotted in figures 4.4.7, 4.4.8 and 4.4.9. The activation energies for all the samples are listed in Table 4.4.3. In the Arrhenius plot the low temperature region obeys hopping level conduction. $E_1$ is the activation energy corresponding to free band type conduction and $E_2$ that of extrinsic carrier conduction.

Figure 4.4.7: Plot of ln $\sigma$ Vs.1000/T graph for TTBPc thin film vacuum annealed at 323K
Multiple donor levels exist within the forbidden energy gap and the deeper levels can be frozen out as the temperature is increased. The conduction process is found to be controlled by different trapping levels present in the forbidden energy gap.

Table 4.4.3: Variation of activation energy with thickness 285nm of different temperatures.

<table>
<thead>
<tr>
<th>Vacuum annealing(K)</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1(\pm 0.01eV)$</td>
</tr>
<tr>
<td>323</td>
<td>0.2</td>
</tr>
<tr>
<td>373</td>
<td>0.3</td>
</tr>
<tr>
<td>423</td>
<td>0.39</td>
</tr>
</tbody>
</table>
Due to the polycrystalline nature of annealed samples, thermally activated conduction over potential barriers are formed at the grain boundaries. The change of activation energy from air to vacuum annealing is due to the difference in the distribution of trapping sites and unequal binding energies (Sussman, 1967).

4.4.2. D.C Electrical conductivity studies on ZnTTBPc thin films.

4.4.2.1 Effect of thickness  Resistance of ZnTTBPc thin film deposited at room temperature are measured using the programmable kiehlley electrometer is the temperature range 320-500 K. The experimental setup is explained in chapter 2.

Figure 4.4.10: Plot of ln $\sigma$ vs.1000/T graph for ZnTTBPc thin film with thickness 180nm

Figure 4.4.11: Plot of ln $\sigma$ vs.1000/T graph for ZnTTBPc thin film with thickness 205nm
Figure 4.4.12: Plot of \( \ln \sigma \) vs.1000/T graph for ZnTTBPc thin film with thickness 300nm

The corresponding electrical conductivity (\( \sigma \)) is extended using equation 5.3.7 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. Figures 4.4.10, 4.4.11 and 4.4.12 show the plot of \( \ln \sigma \) versus 1000/T for ZnTTBPc thin films of thicknesses 100 nm, 205 nm and 350 nm respectively.

Table 4.4.4: Variation of activation energy of ZnTTBPc thin films for different thicknesses.

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>Activation Energy $E_1(\pm0.01eV)$</th>
<th>Activation Energy $E_2(\pm0.01eV)$</th>
<th>Activation Energy $E_3(\pm0.01eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.53</td>
<td>0.47</td>
<td>0.04</td>
</tr>
<tr>
<td>205</td>
<td>0.52</td>
<td>0.42</td>
<td>0.03</td>
</tr>
<tr>
<td>300</td>
<td>0.52</td>
<td>0.41</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The activation energies are tabulated in table 4.4.4. It is observed that each sample has three activation energies. For thickness 180 nm, 0.53 eV, 0.47 eV and 0.04 eV are the activation energy respectively and is found to be smaller at low temperature region (Ambily and Menon, 1998). The experiment is repeated for films of different thicknesses and the
activation energy are determined, which are found to decrease with increase in thickness. Thicker films may form a closely packed structure which increase molecular overlapping and the diffusion. It is apparent that the sensor current increases with the film thickness because the number of absorption sites increases with the thickness. (Hsich and Ju, 1998)

4.4.2.2 Effect of air-annealing To study the effect of air annealing on the conduction mechanism and the activation energy, ZnTTBPc thin films prepared at room temperature have been annealed in air for one hour. The resistance of the film are measured using the Keithley programmable electrometer. Corresponding electrical conductivities are evaluated using equation 4.3.10

![Graph of ln σ Vs.1000/T](image)

Figure 4.4.13: Plot of ln σ Vs.1000/T graph for ZnTTBPc thin film having thickness 285nm air annealed at 373 K.
Figures 4.4.13, 4.4.14 and 4.4.15 shows a plot of ln σ versus 1000/T for the as deposited ZnTTBPc thin films of thickness 285 nm annealed in air for one hour at 373, 423, 473 K. The thermal activation energies of these samples are calculated from the slopes of the linear portions of the graphs using the relation 4.3.9. The values of activation energy are collected in table 4.4.5.
Table 4.4.5: Variation of activation energy of ZnTTBPc thin films having thickness 285nm air annealed at different temperatures.

<table>
<thead>
<tr>
<th>Air annealing(K)</th>
<th>Activation Energy $E_1$(±0.01eV)</th>
<th>$E_2$(±0.01eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.66</td>
<td>0.08</td>
</tr>
<tr>
<td>423</td>
<td>0.62</td>
<td>0.17</td>
</tr>
<tr>
<td>473</td>
<td>0.61</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The ln $\sigma$ versus 1000/T plot for ZnTTBPc films shows two linear regions. For the film annealed at 323 K the activation energy values are 0.66 eV and 0.08 eV. The activation energy is decreased in the lower temperature region. It is observed that as the annealing temperature increases to 473 K, the activation energy $E_1$, corresponding the higher temperature region decreases from 0.66 eV to 0.61 eV. This change may be due to partial phase change or occurrence of crystal defects during heat treatment as suggested by Amar et. al (Amar and Saleh, 1998). Fassen and Kerp (Fassen and Kerp, 2003) found that phthalocyanine thin films absorb comparable quantities of oxygen by annealing, which distribute homogenously through the bulk of the film.

4.4.2.3 Effect of vacuum annealing The conductivity changes are due to the creation or recombination of holes on the surface of the film. Sussman (Sussman, 1967) hence reported that the distribution of trapping sites is altered by annealing. Oxygen causes distribution of the trap levels altered by annealing giving two activation energies. Shihab and Gould (Shihab and Gould, 1996) have reported that annealing decreases the density of defects thereby changing the electrical conductivity.
Figure 4.4.16: Plot of ln $\sigma$ vs.1000/T graph for ZnTTBPc thin film having thickness 285nm vacuum annealed at 323K.

Figure 4.4.17: Plot of ln $\sigma$ vs.1000/T graph for ZnTTBPc thin film having thickness 285nm air annealed at 423K.
Figure 4.4.18: Plot of ln $\sigma$ vs.1000/T graph for ZnTTBPc thin film having thickness 285nm vacuum annealed at 473K.

To study the effect of vacuum annealing on the conduction mechanism and activation energy of ZTTBPc films, they are annealed in vacuum for one hour each. From 4.4.16, 4.4.17 and 4.4.18 gives the ln$\sigma$ versus 1000/T plots for ZnTTBPc thin films annealed in vacuum in the temperature range 323K to 473K. Two activation energy values corresponding to the slopes of two different linear regions in the graphs are obtained and are giving in table 4.4.6. As the annealing temperature increases from 323K to 473K the activating energy $E_1$ increases from 0.65eV to 0.8eV.

Table 4.4.6: Variation of activation energy of ZnTTBPc thin films having thickness 285nm vacuum annealed at different temperatures.

<table>
<thead>
<tr>
<th>Vacuum annealing(K)</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1$(±0.01eV)</td>
</tr>
<tr>
<td>323</td>
<td>0.65</td>
</tr>
<tr>
<td>373</td>
<td>0.61</td>
</tr>
<tr>
<td>473</td>
<td>0.80</td>
</tr>
</tbody>
</table>

The charge carrier conduction mechanism is interpreted as mainly of the free band type in the intrinsic region where as it is of the hopping type in the extrinsic region.
4.4.3. D.C Electrical conductivity studies of CuTTBPc thin films.

4.4.3.1 Effect of thickness  Resistances of CuTTBPc thin films deposited at room temperature are measured using the Programmable Keithley Electrometer. The corresponding electrical conduction $\sigma$ is estimated using the equation 4.3.10 knowing the length, breadth and thickness of the film.

Table 4.4.7: Variation of activation energy of CuTTBPc thin films with different thickness .

<table>
<thead>
<tr>
<th>Thickness(nm)</th>
<th>Activation Energy $E_1(\pm0.01eV)$</th>
<th>$E_2(\pm0.01eV)$</th>
<th>$E_3(\pm0.01eV)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>170</td>
<td>0.51</td>
<td>0.56</td>
<td>0.08</td>
</tr>
<tr>
<td>258</td>
<td>0.51</td>
<td>0.58</td>
<td>0.01</td>
</tr>
<tr>
<td>405</td>
<td>0.51</td>
<td>0.57</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 4.4.19: Plot of $\ln \sigma$ vs.1000/T graph for CuTTBPc thin film with thickness (a)170nm.
The temperature dependence of electrical conductivity shows an Arrhenius type relationship. Plot of $\ln \sigma$ versus $1000/T$ yields, different linear regions and are attributed to different charge conduction mechanisms. Figure 4.4.19, 4.4.20 and 4.4.21 shows the plots of $\ln \sigma$ versus $1000/T$ for CuTTBPc thin films deposited at thicknesses 170nm, 258nm and 405nm respectively. It is observed that the plot gives three linear regions resulting three activation energy. The activation energy for CuTTBPc thin films for various thicknesses are collected in table 4.4.8. Felix and Lawrence (Gutman and Lyons, 1981) reported an activation energy of 1.2eV. The difference in the activation energy may be due to the different deposition con-
ditions. Abdel-Malik and Cox (Abdel-Malik and Cox, 1977) reported that the plot of ln$\sigma$ versus 1000/T in semiconductors gives rise to one or more linear portions from which appropriate activation energies could be derived, providing details of the energy levels. Extrinsic conductivity for the CuTTBPc thin film of 405nm thickness is 0.1eV.

Table 4.4.8: Variation of activation energy of CuTTBPc thin films with different thickness.

<table>
<thead>
<tr>
<th>Air annealing(K)</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1(\pm0.01eV)$</td>
</tr>
<tr>
<td>170</td>
<td>0.51</td>
</tr>
<tr>
<td>258</td>
<td>0.51</td>
</tr>
<tr>
<td>405</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Low value of the activation energy is due to the creation of excitation level very near to conduction band due to the creation of more and more $\pi$ bonds (Krishnakumar and Menon, 1996). It is due to the creation of extra vacancies and defect sites on new layers that act as exitons for the free carrier conduction to conduction band which in turn reduces the activation energy between the bands. By increasing thickness, most of the defect centers disappear due to layer by layer deposition. So transport process like hopping conduction mechanism due to tunneling between far distance defect centers need more energy. It increases the value of hopping distance between the defect center where as in hopping mode, the charge carriers hoping from one localized state to another. When such defect centers decrease the density of charge carriers virtually trapped inside the potential well created due to atomic polarization decreases. This reduces the density of states for increase of thickness (Choudhuri and Goswami, 1983).
4.4.3.2 **Effect of air annealing**  To study the effect of air annealing on the conduction mechanism and on the activation energy, CuTTBPc thin films are annealed in air for one hour. The D.C electrical conductivity by making use of two probe method and their graph are plotted in figures 4.4.22, 4.4.23 and 4.4.24. From the graph, the activation energy for band transition is found out and listed in Table 4.4.9. For annealing temperature 323K, the activation energy values are 0.55eV, 0.63eV and 0.02eV. The activation energy is found decreased in the low temperature region. It observed that as the annealing temperature increases, from 323K to 473K, the activation energy $E_1$ decreases from 0.55eV to 0.26eV.

![Graph](image)

Figure 4.4.22: Plot of ln $\sigma$ vs.1000/T graph for CuTTBPc thin film having thickness 285nm air annealed at 423 K
Figure 4.4.23: Plot of ln $\sigma$ vs.1000/T graph for CuTTBPc thin film having thickness 285nm air annealed at 473 K

Figure 4.4.24: Plot of ln $\sigma$ vs.1000/T graph for CuTTBPc thin film having thickness 285nm air annealed at 523 K

Table 4.4.9: Variation of activation energy of CuTTBPc thin films having thickness 285nm air annealed at different temperatures.

<table>
<thead>
<tr>
<th>Air annealing(K)</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1(\pm 0.01eV)$</td>
</tr>
<tr>
<td>423</td>
<td>0.55</td>
</tr>
<tr>
<td>473</td>
<td>0.35</td>
</tr>
<tr>
<td>523</td>
<td>0.26</td>
</tr>
</tbody>
</table>

The decreases of activation energy may be due to the appearance of crystal defects during
heat treatment as suggested by Amar et al. (Amar and Saleh, 1998) or are due to the phase change.

4.4.3.3 Effect of vacuum annealing To study the effect of vacuum annealing on the conduction mechanism and activation energy of CuTTBPc films, they are annealed in vacuum for one hour each.

Figure 4.4.25: Plot of $\ln \sigma$ vs. $1000/T$ graph for CuTTBPc thin film having thickness 285 nm vacuum annealed at 373K

Figure 4.4.26: Plot of $\ln \sigma$ vs. $1000/T$ graph for CuTTBPc thin film having thickness 285 nm vacuum annealed at 473K
Figure 4.4.27: Plot of $\ln \sigma$ vs. $1000/T$ graph for ZnTTBPc thin film having thickness 285nm vacuum annealed at 523K.

Figures 4.4.25, 4.4.26 and 4.4.27 gives the $\ln \sigma$ versus $1000/T$ plots for CuTTBPc thin films vacuum annealed in the temperature range 373K to 523K.

Table 4.4.10: Variation of activation energy of CuTTBPc thin films having thickness 285nm vacuum annealed at different temperatures

<table>
<thead>
<tr>
<th>Vacuum annealing(K)</th>
<th>Activation Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_1(\pm 0.01eV)$</td>
</tr>
<tr>
<td>373</td>
<td>1.9</td>
</tr>
<tr>
<td>473</td>
<td>1.8</td>
</tr>
<tr>
<td>523</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Three activation energy corresponding to the slopes of three different linear regions in the graphs are obtained and are given in Table 4.4.10. As the annealing temperature is increased from 373K to 523K the activation energy $E_1$ decreases from 1.9 to 0.82.

4.5. Conclusions

Electrical studies of TTBPc, ZnTTBPc and CuTTBPc thin films are done by means of thickness, air and vacuum annealing temperatures. From these studies, it is concluded that
vacuum annealing temperature. Thin films of TTBPc, ZnTTBPc and CuTTBPc are prepared by thermal evaporation and their electrical conductivity measurements are done. The existence of activation energy corresponding to impurity scattering are confirmed by the presence of more than one linear portions in the lnσ versus 1000/T plots for TTBPc, ZnTTBPc, CuTTBPc thin films. From the slopes of the linear portions, values of activation energy are determined. The activation energy E1 corresponding to the high temperature region is due to intrinsic carriers, whereas that in the extrinsic region depends on the extrinsic conduction due to impurity states. From the present studies it is found that the activation energy of TTBPc is changes with thickness. But in case of ZnTTBPc and CuTTBPc the activation energy changes with thickness.

Metal addition to TTBPc increase the density of states near Fermi level and is highest for metal substituted Tetra-Tert-Butyl thin film due to the nature of central metal atom. At low temperature region of conduction, the only probability of seeing any free charge carriers the molecule is due to inter atomic bonding and anti-bonding mechanism and is larger for the presence of more unsaturated metal atom. Annealing of thin films influences the conductivity. In all the three films, the effect of annealing temperature changes the intrinsic thermal activation energy due to impurity conduction. Oxygen alters the distribution of trap levels during annealing. The adsorbed oxygen creates carriers and acts as impurity in the extrinsic conduction region. The variation the activation energies of the annealed thin films can be attributed to the change in the
distribution of trap levels and the removal of the trap levels during annealing of the film. By temperature application deeper energy levels are frozen out with the formation of trap levels near to conduction band. Drastic change in activation energy from room temperature thin film to annealed sample is due to the devoid of defects by partial annealing and the change in activation energy from air to vacuum annealing is due to the difference in the distribution of trapping sites and unequal binding energies in addition to the role of oxygen.
References


Davis E A and Mott N F 1970 Phil. Mag. 28 904.


Jakabik W P 2009 Thin solid films. 517 6188.


Medina A and Claessens C G 2009 J. Porphyrins Phthalocyanines. 13 446.


