CHAPTER 2

LITERATURE SURVEY

2.1 INTRODUCTION

The survey of past and ongoing research on PbPc and CuPc thin films help in better understanding of the materials. Metal phthalocyanine is one of the promising organic compounds due to the possibility of application in electro-optic devices, photoconducting agents, photovoltaic cell element, nonlinear optics, electro catalysis and other photo electric devices. Many researchers have developed and characterized thin films of PbPc and CuPc owing to its wide applications in numerous fields.

In this chapter, literature survey pertaining to

- Structural and compositional analysis,
- Surface Studies,
- Optical,
- Photoconduction studies,
- DC and AC Conduction studies and
- I-V studies of materials and characterization of metal phthalocyanine have been presented.

2.2 STRUCTURAL AND COMPOSITIONAL ANALYSIS

Simonyan et al (1987) have investigated the ESR, optical absorption and reflection spectra of monoclinic and triclinic modification of PbPc. Structural change is observed from monoclinic to triclinic modification of PbPc at 573 K. IR reflection spectra of PbPc within the 400 to 5000 cm\(^{-1}\) range are registered, the plasma edge and a group of lines associated with
symmetrical intermolecular vibration are found. The frequency dependence of the real and imaginary parts of dielectric constant is computed.

Hamann et al (1991) have developed PbPc thin films for NO$_2$ sensors, on different substrates. They have used different methods like FT-IR and IR spectroscopy, X-ray diffraction etc., to get reliable results. The NO$_2$ sensor shows defined behaviour for its characteristics and sensitivity depending on the temperature, applied voltage, humidity and annealing conditions.

The electrical characteristics of thermally evaporated triclinic PbPc thin films are studied by Ahmad and Collins (1991b). They evaluated the number of parameters on the basis of the theory of space charge limited conduction and they calculated the same space charge conduction.

FT-IR characterizations of triclinic PbPc have been studied by Ahmed and Collins (1991a). Infrared absorption spectra are presented for freshly evaporated PbPc, oxygen doped PbPc material which has been vacuum annealed. The spectra allow characterization of films for utilization in gas sensors and FET structures.

Response of PbPc to high NO$_2$ concentration was studied by Mrwa et al (1995). Depending on the gas concentration of NO$_2$ the electric and non-electric characteristics of PbPc gas sensors change reversibly or irreversibly. These processes have been investigated by IR spectroscopy and X-ray photoemission spectrosopes (XPS) to characterize the reasons for the irreversible response and to discuss the lifetime of the sensors.

Gulbinas et al (1995) have studied the excited state dynamics of phthalocyanine films. Femtosecond pump–probe transient absorption measurements were performed for thermally evaporated polycrystalline vanadyl and PbPc (VOPc and PbPc) films in order to obtain information
about the excitation energy migration and relaxation. The influence of local heating on the transient spectra is discussed.

Structural properties of evaporated PbPc films have been reported by Miyamoto et al (1995). They obtained films of pure monoclinic crystals, film consisting of mixed monoclinic and triclinic crystals in which the distribution was almost homogenous at a substrate temperature of 293 K and a pure triclinic crystal film at a substrate temperature of 373 K.

Campbell and Collins (1997) have studied the electrical conductivity and optical absorption for PbPc films exposed to nitrogen dioxide to assess their relative merits for the development of a PbPc-based thin film NO₂ sensor. Additionally, frequency variation of an oscillating quartz crystal during NO₂ adsorption together with Fourier transform infrared analysis have been used to investigate diffusion and bonding of NO₂ at the surface and in the bulk of the films. The results indicate that long-term exposure prevents film recovery.

Electrical conductivity, optical absorption and structural studies of thin films of PbPc were studied by Ambily and Menon (1998). The electrical conductivity, UV–visible spectrum analysis and structural investigations of thermally evaporated thin films of PbPc were carried out. Thermal activation energy and optical band gap were also determined.

Morphological characteristics of perylene-doped phthalocyanine thin films and their photovoltaic effect were studied by Rudiono et al (1999). The copper phthalocyanine (CuPc) thin films doped with perylene of various concentrations were prepared by co-evaporation and their morphology and photovoltaic characteristics were examined. The film morphology was characterized by using XRD, SEM and STM.
Rudolf Slota et al (2002) have investigated the crystals of free base phthalocyanine (H₂Pc) and its unsubstituted metal derivatives MPc (where M is Ni, Cu, Zn, Pb, and Pc =C₃₂H₁₆N₈²-phthalocyanine ligand) were examined after being exposed to NO₂ ambient gas. X-ray microprobe analysis (EDAX), UV analysis and FTIR spectroscopy as well as X-ray powder diffractometry (XRD) were applied to study the crystals. Elemental EDAX analyses performed at the materials surface have shown particular high concentrations of the oxygen atoms, in contrast to the pure (undoped) phthalocyanine crystals.

Naddaf et al (2002) investigated the PbPc tetracarboxylic acid prepared by chemical reaction from phthalic anhydride and urea was used as sensor element for sensing humidity and alcohol vapours. The surface was treated with electron cyclotron resonance (ECR) plasma consisting of 25% H₂ and 75% N₂. Remarkable improvement in the selectivity with respect to ethyl alcohol and reduction in the sensitivity for humidity was observed after this treatment. The response and recovery time for resistive sensing were of the order of 50 and 30 sec respectively. X-ray photoelectron spectroscopy and Fourier transformation infrared studies showed that the increased cross-linking of PC is responsible for the creation of new functional groups which have imparted the sensing of alcohol vapor through extrinsic doping.

Kiejin Lee et al (2005) have observed the dependence of the surface resistance of Copper Phthalocyanine (CuPc) thin films on substrate heating temperatures by using a near field scanning microwave microscope. The crystal structures of CuPc thin films due to different heating temperatures were observed by using X-ray diffraction. As the temperature increased from room temperature to 270°C, the crystal structure of CuPc thin films was transformed from α-phase to thermally stable β-phase.
Sub-monolayer and monolayer of PbPc deposited on InSb surface have been investigated by Angot et al (2004) using scanning tunneling microscopy and low energy electron diffraction. Molecules first adsorb on the indium rows of the structure in the (110) direction and diffuse at the surface in order to form two-dimensional islands. The molecule–substrate interaction stabilizes the PbPc molecules on the rows. It weakens the interaction between molecules located in adjacent rows resulting in numerous gliding planes between the molecular chains.

FTIR, TGA and DC electrical conductivity studies of phthalocyanine and its complexes were studied by Seoudi et al (2005). The absorption bands of phthalocyanines were compared with the spectral data of phthalocyanine and discussed in relation to its structure. Thermogravimetric (TG) analysis curves show that the main degradation step follows first order kinetics. The minor and major decomposition temperature and the activation energy of the main degradation step also were calculated.

PbPc, lead tetranitro phthalocyanine (PbTNP) and lead tetraamino phthalocyanine (PbTAP) are synthesized in pure state by Mohan kumar and Achar (2006b). These complexes are characterized using elemental analysis, UV–visible, IR-spectroscopy, X-ray crystallography and thermogravimetry. Kinetic and thermodynamic parameters associated with the thermal decomposition were calculated using thermogravimetric data. Electrical conductivity studies are done for all the three complexes using two-probe technique in the temperature range from 303 to 473 K. The relevant electrical conductivity data are reported.

UV–visible, electronic spectral study has been done on PbPc, lead tetranitro phthalocyanine and lead tetraamino phthalocyanine in dimethyl sulphoxide and H$_2$SO$_4$ media by Mohan kumar and Achar (2006a). The study has been extended to H$_2$Pc to compare the stability of phthalocyanine
structure with the PbPc complexes in H$_2$SO$_4$ medium. The decomposition reactions in H$_2$SO$_4$ media for H$_2$Pc, PbPc, PbTNP and PbTAP are followed spectrophotometrically and rate constants were calculated.

Rongbin Ye et al (2006) have reported on the correlation between morphology and electronic properties of fluorinated copper phthalocyanine (F$_{16}$CuPc) thin films deposited on SiO$_2$/Si substrates at different substrate temperatures. Highly ordered films with the 200 plane spacing of d$_{200}$ = 14.3 Å is observed. Increasing the substrate temperature significantly improves the molecular ordering of F$_{16}$CuPc, and the smallest FWHM was gained at a substrate temperature of 120°C.

Shafai and Gould (2006) analysed the conduction mechanism in p-type triclinic PbPc. The experimental data based on this model indicate that the current density increases with the reciprocal of temperature and furthermore shows three distinctive regions with hole concentration which are controlled by a different activation energy. The mobility of PbPc thin films were also determined using these temperature measurements.

Biswanath Mallik et al (2007) have investigated Molecular organization of copper phthalocyanine (CuPc) thin films deposited at room temperature on quartz and post annealed gold-coated quartz substrates have been studied. The thin films have been characterized by optical absorption, X-ray diffraction, atomic force microscopy and field emission scanning electron microscopy. The effects of substrates on the surface morphology, optical properties and the fractal dimension have been discussed.

Basova et al (2007) described the synthesis of new mesomorphic octakis substituted (alkylthio) phthalocyanines of Pb (II), using microwave irradiation with higher yield and heating without solvent methods. The Pb(II) Pcs were characterized using different spectroscopic techniques (NMR,
UV–Vis, FT-IR and MS). The microwave technique is a fairly novel approach for the synthesis of PbPcs. The Au/PbPc/Au structure, in which the film of PbPc is disordered at room temperature, shows I–V dependence close to symmetric and does not display any switching effect.

The structural and transport properties of evaporated fluorinated copper phthalocyanine organic field effect transistors with polymer dielectric layer polycarbonate were reported by Shizuyasu Ochiai et al (2008). X-ray diffraction shows a clear correlation between the morphology and structure of F_{16}CuPc film on the polycarbonate dielectric surface. X-ray diffraction results show that the crystallinity and orientation of F_{16}CuPc on polycarbonate thin film are enhanced with increasing surface temperature.

Kalpana S. Katti et al (2008) have investigated the molecular orientation of phthalocyanine films deposited on polycrystalline gold. The FTIR study suggests that each phthalocyanine film contains both α and β phases. H_{2}Pc based films demonstrate deposition method dependence on the molecular orientation, while the CuPc and CoPc films preserves their molecular orientation independent of deposition method.

Synthesis and evaluation of cationic phthalocyanine derivatives as potential inhibitors of telomerase were reported by Lixia Zhang et al (2008). They designed and synthesized novel and potent telomerase inhibitors. These phthalocyanine derivatives as inhibitors of telomerase were reported via modified telomerase repeat amplification protocol (TRAP) assay. The phthalocyanines derivatives binding to G-quadruplex enhance the block to DNA synthesis, primer extension reactions were carried out in the presence of phthalocyanines were discussed. These results indicate that the phthalocyanine derivatives might be potential lead compounds for the development of new telomerase inhibitor.
Orientation structure of vacuum deposited thin layer polyimide matrix in presence of copper phthalocyanine as a ‘‘guest’’, by means of polarization and derivative FTIR spectroscopy has been studied by Anton Georgiev et al (2008). FTIR analysis of spectra in the range of molecular vibration 1300–700 cm\(^{-1}\) demonstrates that polyimide films thermally treated at 473 K showed lower order structure than polyimide films treated at 573 K. After derivatization of the polyimide spectra two bands at 1125 cm\(^{-1}\) and 1116 cm\(^{-1}\) have appeared which are related to two types of C–N deformation vibration.

The synthesis, characterization, voltammetric and spectroelectrochemical properties of newly synthesized lead (II) phthalocyanine derivatives have been presented by Dincer et al (2008). The complexes showed ligand-based redox processes during the CV and DPV time scales, demetallization process was discussed during the spectroelectrochemical measurements. Different substituents of the complexes change the easy demetallization processes of the complexes.

Synthesis and photophysical properties of PbPcs film have been reported by Modibane and Nyokong (2008). They synthesized and characterized new nonperipheral and peripheral (phenoxy and 4-t-butylphenoxy) tetra-substituted and octa-substituted PbPc complexes. The fluorescence spectra were different from absorption spectra due to the loss of symmetry (due to demetallation) upon excitation. The high triplet quantum yields and low triplet lifetimes as the result of heavy atom (Pb) were discussed.

The phase and texture of a newly developed solution-processed copper phthalocyanine (CuPc) thin film have been investigated by Lulu Deng et al (2011). The phase and texture of a newly developed solution-processed copper phthalocyanine (CuPc) thin film have been investigated by two-dimensional grazing incidence X-ray diffraction. The results show that it has β phase.
crystalline structure, with crystallinity greater than 80%. The average size of the crystallites is found to be about 24 nm.

2.3 SURFACE STUDIES

PbPc as a prototype and NO₂ sensing were studied by Mockert et al. (1989). The crystal structure and size have been shown to vary with operating time at higher temperature. PbPc has been shown to be deformed following the reaction with oxidizing molecules.

Jones and Bott (1986) have studied the surface plasmon resonance phenomena of PbPc thin film. The study of lead phalocyanine indicates the sensitivity and the other characteristics were strongly influenced by the nature of the central metal species and also by the crystal structure and/or crystallinity.

Effect of Adsorbed Oxidative Gases on Electrical Properties of Evaporated Films of Phthalocyanines was studied by Sadaoka et al. (1982). The study of the structure is particularly important when coupled with data, concerning the film formation processes and with physico-chemical properties of the film surfaces obtained by atomic force microscopy.

Sadaoka et al. (1990) have studied the annealing effects on PbPc thin film as a toxic gas sensor. The topography and elemental analysis of the film surfaces were analysed by scanning electron microscopy and Auger electron spectroscopy (AES). FTIR measurements were also carried out.

Fast NO₂ detection at room temperature with optimized PbPc thin film structures were studied by Sadaoka et al. (1990). They observed films with response time of less than 20sec and recovery time of the order of some minutes, even at room temperature, after optimized preparation procedures.
The lack of reproducibility and a fast recovery time observed in the behaviour of these films were attributed to the presence of larger crystals in the conductive path.

Campbell and Collins (1995) have found that the visible and near infrared spectra of both the monoclinic and triclinic phases of PbPc thin films are affected significantly by the presence of the nitrogen dioxide. They are also calculated the values for the band gap of both phases from the absorption data.

Studies on the α to β phase transformations in phthalocyanine films, the dependence of structure and preferential orientation on film thickness and substrate temperature and observations of the monoclinic and triclinic phases in PbPc films are discussed by Gould (1996). AC and DC measurements on phthalocyanine films using both blocking and ohmic contacts were also described.

Effects of operating temperature and post deposition annealing, as well as the gas concentration and flow rate, on the response characteristics of the PbPc sensor are studied by Liu (1996). From the temperature dependence of the reciprocal of response time, the activation energy of the adsorption process Ea and that of the desorption process Ed has been calculated. It is also found that heat treatment of the PbPc film in air at 523 K for 3 hrs will reduce the activation energies and lead to faster sensor response.

Effects of film thickness and crystal morphology on the gas sensing characteristics of a chemiresistor-type NO₂ gas sensor based on the PbPc thin film are studied by Hsieh et al (1998). They found that the monoclinic PbPc film has the highest steady-state sensor current, followed by the amorphous film and triclinic film. They also reported that steady-state current, response
time and recovery time all increase with the film thickness and reach their maximal values at a limiting thickness.

Ottaviano et al (1998) deposited PbPc films at room temperature onto silicon substrates and then annealed in high vacuum at different temperatures. The samples have been analysed by X-ray diffraction as well as by atomic force microscopy in order to get structural and morphological information on the samples. The AFM topographic images suggest that at this temperature the triclinic crystallites evaporate, leaving wide holes in the films.

Andrzej Boguta et al (2002) have studied the morphology of semiconducting and metallic (Au) surfaces without organic dyes and when coated with the Langmuir–Blodgett (LB) dye layer was investigated with the Scanning Force Microscopy (SFM) technique. In the experiments the following dyes were used: magnesium tetracyanoquinodimethane (MgTNP), magnesium phthalocyanine (MgPc) and PbPc. On the ground of the AFM results the roughness parameter of the surfaces and its change upon dye deposition was estimated. It was shown that images of the surface morphology are closely connected with the relation between the magnitude of the substrate grains and the geometrical size of the dye molecules. The substrates of the large grains preserve their own topography after coating with the dye layer whereas the change in the morphology was observed for the substrate of low granularity.

The morphology of vacuum deposited copper phthalocyanine (CuPc) thin films deposited on Si (111) have been studied by Szuber et al (2003) using the contact mode Atomic Force Microscope (AFM). Experiments were showed the gradual increase of surface roughness (RMS), average and maximum grain height of in situ deposited CuPc thin films with increasing substrate temperature. For ex situ post-deposition UHV annealing of CuPc thin films these surface morphological parameters are evidently higher but
almost constant. The trend of increasing of the surface roughness, average and maximum grain height with temperature growing was in good correlations with an increase of the shift of Fermi level position in the band gap of CuPc thin films after exposition to molecular oxygen \( \text{O}_2 \).

Shinichiro Yanagiya et al (2003) reported annealing effects on the heteroepitaxial growth of Cu-phthalocyanine (CuPc) crystallites on KCl \{0 0 1\} substrate crystals. On the CuPc as-deposited surface, no clear contrast was observed by scanning electron microscopy (SEM). On the contrary, many needle-like crystallites could be observed after the annealing treatment. Those crystallites were oriented so that their long axis was parallel to the \( <1 0 0 > \) direction of the KCl substrate.

Yuh-Lang Lee et al (2003) investigated Copper tetra-tert-butyl Phthalocyanine (CuTTBPc) vacuum deposited onto substrates of hydrophilic glass, hydrophobic silanized-glass, and one layer CuTTBPc LB film. The effect of substrates on the growth behavior and film characteristics of CuTTBPc was studied by atomic force microscopy as well as XRD and dynamic contact angle analyzer. The XRD results demonstrate that the film grown on glass possess higher degree of crystallinity than the other films which resulted from the distinction of the initial growth stage. The hydrophilic glass surfaces possess very smooth topography. The root-mean-square roughness of this surface is estimated to be 0.35 nm. When a film of mean thickness of 1 nm is grown on the glass, outstanding islands of low density are found on the surface.

Effect of nitrogen dioxide and temperature on the properties of PbPc in polypyrrole films was analysed by Rungnapa Tongpool (2003) using spin coating technique. As the PbPc content in the films increased, the thickness, porosity and \( \text{NO}_2 \) sensitivity increased. The \( \text{NO}_2 \) sensitivity increased as the testing temperature increased up to 443 K, but decreased tremendously at
513 K due to appreciable desorption and chemical degradation. The films showed good recovery and fast response at high temperature, but were also susceptible to deterioration, as confirmed by SEM, XRD and UV-visible spectroscopy.

Tabuchi et al (2004) examined the property of PbPc films in relation to Ar ion sputtered and/or annealed sapphire faces were prepared by thermal deposition. The film structure and morphology were investigated by X-ray diffraction and atomic force microscopy, respectively. The interaction between the film and the substrate was evaluated from the viewpoint of the surface energy. The molecular orientation was dependent on the surface treatment where the ratio of the adhesion force to the cohesion force is derived from the hydrogen bond. They concluded that the sputtering treatment was effective in yielding a highly oriented PbPc film through the formation of a film-substrate interface possessing an appropriate balance between adhesion and cohesion forces.

The dielectric spectra of thin zinc phthalocyanine films equipped with interdigitated electrodes and the effect of annealing in dry N$_2$ were studied by Jarosz et al (2005). The measurements were performed in the frequency range $10^{-2}$–$10^5$ Hz. The electric properties of the films are not only affected by oxygen but also by water vapour, the presence which always leads to the drop in alternating current conductance.

Study of metallic-phthalocyanine by Transmission Electron Microscopy (TEM) and the Atomic Force Microscope (AFM) has been reported by Ponce et al (2005). In this work, powder and thin films of metallic-phthalocyanine (FePc, CoPc and PbPc) have been characterized by TEM, XRD and AFM. XRD and Selected Area Electron Diffraction (SAED) patterns were used to determine the crystalline structure of the phases in powder samples. The surface topography of the films had been characterized
by AFM and in needle like and granular features were found to be randomly oriented in the films.

Youngson Choe et al (2006) have Vacuum deposited copper phthalocyanine (CuPc) and placed it as a thin interlayer between indium tin oxide electrode and a hole transporting layer in a multi-layered organic light-emitting diode. The well-stacked CuPc layer increased the stability and efficiency of the devices. Thermal annealing after CuPc deposition and magnetic field treatment during CuPc deposition was performed to obtain a stacked-CuPc layer; the former increased the stacking density of the CuPc molecules and the alignment of the CuPc film. Thermal annealing at about 100°C increased the current flow through the CuPc layer by over 25%. Surface roughness decreased from 4.12 to 3.65 nm and spikes were lowered at the film surface.

Comparison of organic thin films deposited by supersonic molecular-beam epitaxy and organic molecular-beam epitaxy of titanyl phthalocyanine were studied by Walzer et al (2006). They found that the SuMBE deposition results in increased crystal quality of the deposited material. This is induced by the high kinetic energy of the molecular-beam in SuMBE, which leads to increased molecular mobility on the surface, resulting in larger crystal sizes and higher crystal quality. Alternatively, similar films as made by OMBE can be deposited by SuMBE at lower substrate temperatures. This temperature reduction may be of interest for the deposition of stacked organic devices on underlying heat sensitive layers, as they are quite common in organic electronic devices.

Maggioni. G et al (2005) investigated the deposition of copper phthalocyanine (CuPc) thin films for gas sensing applications by using a plasma-based method i.e. glow discharge-induced sublimation (GDS). Deposition rate of the CuPc molecules was measured by a quartz thickness
sensor. The properties of the deposited films were studied by FT-IR spectroscopy, RBS, ERDA, SEM and AFM.

Yamamoto et al (2008) have found clear correlation between PEEM contrast and the electronic structure measured by Micro-UPS. The correlation is very useful to understand the complicated PEEM contrast. The metastable islands consist of bilayer, but the molecular configuration may be different from that of the well-oriented bilayer film. For annealed submonolayer film, PbPc molecules are sparsely distributed and no islands or areas of bare HOPG were formed. They measured the same position of a sample using the high accuracy positioning stages in both measurements.

Zhongming Wei et al (2009) fabricated the bottom-contact CuPc monolayer thin-film transistors by inducing the Langmuir–Blodgett technology to construct monolayer transistors. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) images of the CuPc with a 1 µm channel length have been studied. CuPc formed a dense and smooth monolayer in the channel between two electrodes.

Michael Kraus et al (2010) investigated ambipolar charge transport in organic field-effect transistors (OFETs) with Copper-phthalocyanine (CuPc) as active material. They proved that charge carrier mobilities can be increased by at least one order of magnitude using the long-chain alkane tetratetracontane (TTC) as a passivation layer on top of silicon dioxide. TTC and CuPc films are characterized by atomic force microscopy and x-ray diffraction. TTC forms a highly crystalline layer that passivates electron traps on the SiO2 surface very efficiently and serves as a template for the growth of CuPc films with significantly improved crystallinity.

Wang Shi Rong et al (2011) analysed n-type organic thin film transistors (OTFTs) by employing Copper hexadecafluorophthalocyanine
(CuPcF\textsubscript{16}) as the active layer and para-hexaphenyl (p-6p) as the inducing layer. They employ para-hexaphenyl (p-6p) as the inducing layer to form well-organized CuPcF\textsubscript{16}/p-6p thin films by physical vapour deposition technique. The morphology and structure of these thin films were examined by XRD and SEM.

2.4 **OPTICAL PROPERTIES**

Van Ewyk et al (1980) have reported the quantitative studies of the magnitude, rate and reversibility of changes in surface semi-conductivity of single crystals of phthalocyanines, perylene, tetracyanoquinodimethane and molecular complexes as a function of ambient gas. They reported that semiconduction activation energies in the presence of gases enhancing conductivity are reduced to values comparable with those obtained from temperature dependence of photoconduction (0.1 - 0.2 eV). Conductivity changes are interpreted in terms of production of ionized states following weak chemisorptions involving donor acceptor interactions.

The optical properties of thin films of PbPc in both monoclinic and triclinic forms have been studied by Collins et al (1993). Optical parameters have been determined from both absorption and reflectivity data for wavelengths in the UV and visible regions. The observed results support the view that a band model analysis of this material is valid despite the very low mobility values found for both monoclinic and triclinic forms.

The aggregation of copper phthalocyanine dyes from sol to gel is effectively prevented by tethering them to sol-gel matrix were reported by Haiping Xia and Masayuki Nogami (2000). Tetracarboxyphthalocyaninato is incorporated in gel by sol-gel process using 3-aminopropyltriethoxysilane and 3-glycidoxypropyl-trimethoxysilane as precursors. The starting compound and
the gel are in the dimmer forms of copper phthalocyanine, which are identified from their UV/visible spectra.

Vacuum sublimed thin films of copper phthalocyanine were prepared at room temperature by Bahabri et al (2001). The optical properties of thin CuPc films have been investigated in the spectral range 200-2100 nm. The refractive index \( n \) as well as the absorption index \( k \) was calculated before and after annealing. It is obvious that the refractive index showed an anomalous dispersion in the absorption region as well as normal dispersion in the transparent region. The analysis of the spectral behaviour of the absorption coefficient, \( \alpha \) in the absorption region revealed direct transitions.

The Optical Limiting (OL) performances of the novel PbPc complex with the substituent group of octa-dodecaoxyl long chains in toluene were investigated by Shiliang Qu et al (2001). The experimental result shows that the OL clamped value of the compound is much lower than that of \( C_{60} \) in toluene. The agreement between the results and the simulations with phenomenological model considering only reverse saturable absorption (RSA) indicates that RSA is the main mechanism for OL.

Optical functions of copper phthalocyanine have been determined using spectroscopic ellipsometry in the spectral range from 1.55 to 4.1 eV. The samples have been prepared by evaporation on glass substrates. CuPc deposited on unheated and heated (373 K) substrates have been investigated by Djurisic et al (2002). The optical functions data were determined by point-to-point fit, as well as the conventional oscillator model and modified oscillator model. Atomic force microscopy images revealed considerable surface roughness of the films and hence surface roughness correction in determination of the optical functions have been performed.
Venugopal Rao and Narayana Rao (2002) presented their experimental results on the measurement of excited state dynamics in phthalocyanines (Pc, CuPc, FePc, and ZnPc) using degenerate four wave mixing with incoherent light. Three different timescales were observed, for all samples, in the phase conjugate signal recorded as a function of delay in probe beam in the standard backward geometry. The fastest component is associated to the phase relaxation in the Sn states and the slowest components to the vibration and population relaxation times from the $S_1$ state. The present results are compared with those obtained with shorter pulses and various techniques for similar molecules. The consequences of such short lifetimes are also discussed in view of the strong optical limiting properties of these molecules.

Pressure induced structural change in PbPc studied by infrared and UV-visible spectroscopy and theoretical calculation have been reported by Masafumi Sakata et al (2002). They measured infrared and UV-visible spectra for the PbPc crystal under high hydrostatic pressure and the IR spectrum result suggests a structural transformation of the PbPc molecule from the shuttle cock structure toward the planar structure with increasing pressure. In the UV-visible spectra, the peak intensity of the band at 2.7 eV was decreased, and the band at 1.5 eV was shifted to lower energy and broadened.

The Schottky barrier characteristics of evaporated $\alpha$-phase nickel phthalocyanine/lead ($\alpha$-NiPc/Pb) structures were investigated by Anthopoulos and Shafai (2004) using the small AC signal capacitance–voltage technique. It was established that for junctions fabricated and tested in situ at room temperature, detection of the barrier depletion layer is not possible. Voltage-dependent capacitance characteristics are detected only upon heating or after exposure of the devices to dry air for prolonged periods of time. The C–V response is attributed to the increase of carrier concentration; first due to
increased temperature and second due to p-type doping induced by oxygen absorption within the α-NiPc layer.

Salomon et al (2004) have measured the electronic transitions of PbPc thin films by means of optical absorption and reflection electron energy loss spectroscopy in the range from 1 to 20 eV. They compared the optical absorption spectrum with the loss spectra and discussed their similarity. They identified the loss structures and reported a new absorption band at 10 eV.

Jiayu Guo et al (2006) analysed an inorganic–organic hybrid silica gel glass with remarkable femtosecond optical Kerr effect in the order of the time-resolution of the experiment based on doped PbPc. In that materials, self-diffraction of the pumping beam by ultrafast transient grating dominates the Kerr signal, ensuring ultrafast response happens. A critical role for the design of novel ultrafast optical Kerr shutters in such low-cost silica based-nanocomposites with great flexibility was discussed.

Seoudi et al (2006) have studied the ultraviolet and visible spectroscopic spectrum of the phthalocyanine and its complexes thin films. Thin films of phthalocyanine and its complex (magnesium, manganese, iron, cobalt, zinc and PbPc) have been prepared by vacuum evaporation technique. The optical band gap, the extinction coefficient and the refractive indexes have been measured and discussed.

Rifat Capan et al (2007) reported about the characterisation and organic vapour sensing properties of Langmuir–Blodgett thin films of s-triazines bearing three oxygen-linked phthalocyanines incorporating Cu and Zn metals (CuPc and ZnPc). Surface pressure–area per molecule (π–A) isotherms of CuPc and ZnPc monolayers at room temperature shows that stable monolayers of both materials are formed at the air water interface. The LB film deposition processes of CuPc and ZnPc materials are characterized
by UV spectroscopy and a quartz crystal microbalance. The results indicate that high quality and uniform LB films can be prepared with the transfer ratio of over 0.95 and that the obtained LB films are significantly more sensitive to chloroform than other vapours. The response of the LB films is fast, large and reversible. These newly synthesised CuPc and ZnPc materials are promising sensing materials in the development of room temperature volatile organic vapour sensing devices for chloroform vapour.

The physical properties of polycarbonate blends containing the nonlinear optical dye lead tetracumylphenoxy phthalocyanines were characterized by Aditya Ranade et al (2007). Blends up to 20 wt % dye were prepared and characterized in terms of density, refractive index, glass transition temperature, loss modules, sub ambient relaxation behaviour and free volume hole size from position annihilation lifetime spectroscopy. They reported that the dye strongly affected the physical properties of the blend and it was present as a mixture of monomer, dimmer and higher aggregates.

Copper phthalocyanine (CuPc) thin films were prepared by Hanashriah Hassan et al (2010) using simple spin coating method. The films were annealed at 5 different temperatures (323, 373, 473, 523 and 573 K) for one hour in air. Optical properties study using the UV-Vis spectrophotometer showed that in the range of wavelength of 300-800 nm, all of the films have identical absorption coefficient patterns and there was no systematic change with respect to annealing temperature. The film annealed at 373 K showed the highest absorbance while the lowest absorbance was shown by the film annealed at 323 K. The film annealed at 373 K has the lowest optical energy gap. The results showed that the optical band gaps depended on the temperature.

Venugopal Rao et al (2011) have investigated the nonlinear optical properties, optical limiting thresholds and figure of merits for five different
phthalocyanine thin films, achieved through doping in PMMA, using the Z-scan technique at 800 nm with 2 ps laser pulses. From the open-aperture Z-scan data it was found that these molecules exhibit strong two photon absorption (2PA) with the nonlinear coefficients in the range of 15-200 cm/GW. They have also estimated the sign and magnitude of the real part of third order nonlinearity through the closed aperture scans. Their studies provide tangible evidence that these phthalocyanines are potential candidates for multi-photon imaging and optical limiting applications.

2.5 PHOTOCONDUCTION STUDIES

The photoelectrical behaviour of evaporated sandwich-type and coplanar-type cell copper phthalocyanine thin film were investigated by Toyohide Tanaka et al (1998) using a modulated photocurrent measurement technique. The modulated photocurrent sandwich-type cell showed a minimum value at the equilibrium point of photovoltage and applied voltage and a phase shift of the modulated photocurrent showed a drastic change of 180° in the vicinity of this point.

Ambily et al (1999) have prepared PbPc thin films (PbPc) by vacuum sublimation. Photoconductive studies as a function of applied voltage, intensity of incident light, temperature and wavelength were carried out. Photocurrent spectra as a function of wavelength indicate peaks around 1.54, 1.98, 2.4, 3.0 and 3.48 eV. These are interpreted as transitions at critical points. From the temperature dependence of photoconductivity measurements, the activation energies were studied for dark conductivity. Energy level diagrams of PbPc thin films from the photo response were discussed.

HeaYeon Lee et al (1999) prepared highly crystallized CuPc/PbTe multilayer are prepared at substrate temperature from room temperature to 300°C by pulsed laser deposition and thermal evaporation method. For
observation the interface effect of multilayer, they are measured the transverse current-voltage characteristics in the dark and under illumination. The photocarrier is generated in the CuPc layer and the electron-hole pairs are separated by the steep incline of the potential near the CuPc/PbTe interface. The CuPc/PbTe multilayers in the in-plane current-voltage curve exhibit larger photoconduction effect than that of CuPc single layer.

The electronic properties and thermal stability of PbPc thin film deposited on the InAs surface were studied by Giovanelli et al (2001) using synchrotron radiation core level and valance band photoelectron spectroscopy. The interaction between the over layer and the substrate was determined by analyzing the photoemission spectra of a thin film and of a single monolayer of adsorbed molecules.

Giovanelli et al (2001) used synchrotron radiation photoelectron spectroscopy to study the interface between a thin film and an ordered single monolayer of PbPc deposited on the clean InAs reconstructed surface. Analysis of the core level and valence band spectra information about the electronic properties of the interface was studied.

The interfacial properties of ultra thin films of lead-phthalocyanine deposited in situ onto InSb and InAs clean surfaces were studied by Papageorgiou et al (2001) using synchrotron radiation core level and valence band photoelectron spectroscopy. The interaction between the over layers and the substrates was determined upon analyzing the changes in the photoemission spectra between room and higher annealing temperatures, leading to ordered monolayer films.

Kohji Mizoguchi et al (2002) investigated the optoelectronic properties of orientation-controlled PbPc films on (001) sapphire and (001) KCl substrates prepared by vacuum deposition. The results obtained from XRD
measurement indicates that the orientations of the molecular planes in the PbPc films on the sapphire and KCl substrates are perpendicular and parallel to the substrate surface respectively. They also discussed the contribution of excitons to the photocarriers based on the results of the absorption and photocurrent spectra.

Gaoling Zhao et al (2003) investigated the optoelectronic properties of Copper-phthalocyanine (CuPc)/ Zincsulphide (ZnS) multilayer films prepared by vacuum-sublimation. The results showed that the photoconductive properties of the CuPc/ZnS multilayer films were better than that of the CuPc film. The effects of the pair number on the photoconductive properties of the multilayer films were studied. It was found that three-pair CuPc/ZnS multilayer film had the best photoconductive properties with the light sensitivity of 1 mW/cm$^2$ and residual potential of 17 V.

Yamane et al (2004) measured Ultraviolet photoelectron spectra for titanyl- and lead-phthalocyanine ultrathin films prepared on graphite in order to study effects of the electric dipole layer on the organic energy levels. They observed highest occupied molecular orbital (HOMO) band consisting of many peaks that could be assigned to different molecular orientations/aggregations. Difference of binding energy of HOMO bands between the oriented monolayer and the double layer in which molecular electric dipoles are cancelled, which is found to agree with the vacuum level shift for both molecules, leading to important conclusions that, (i) the molecular energy level with respect to the substrate Fermi level is changed when the molecule is in the dipole layer and (ii) the binding-energy shift corresponds with the vacuum level shift.

Jinsoo Joo et al (2008) have prepared a p-type and n-type organic thin film transistors (OTFTs) in the same experimental conditions by using hexadecahydro copper phthalocyanine (H$_{16}$CuPc) and hexadecafluoro copper
phthalocynine (F$_{16}$CuPc) molecules, respectively. The temperature dependence of the mobility and activation energy for both OTFTs was measured in saturation and linear regions of the drain-source current. He found that the activation energy of the F$_{16}$CuPc-based OTFTs was lower than that of H$_{16}$CuPc film. The gate voltage (Vg) dependence of the field-effect mobility measured in linear region for the F$_{16}$CuPc-based OTFTs was more stable, i.e., weaker variation of the field effect mobility with increasing Vg, than that of the H$_{16}$CuPc film.

Imran Murtaza et al (2010) investigated the optoelectronic properties of heterojunction thin film devices with ITO/CuPc/C$_{60}$/Al structure by analyzing their current–voltage characteristics, optical absorption and photocurrent. The experimental results show that in this device the total current density is a function of injected carriers at the electrode organic semiconductor surface, the leakage current through the organic layer and collected photo generated current that results from the effective dissociation of excitons.

A thin film of copper phthalocyanine (CuPc), a p-type semiconductor, deposited by thermal evaporation in vacuum on an n-type gallium arsenide (GaAs) single-crystal semiconductor substrate were studied by Khasan Sanginovich Karimov et al (2011). Photoconduction of the cell was measured in photoresistive and photodiode modes of operation. It was observed that with an increase in illumination, the photoresistance decreased in reverse bias while it increased in forward bias. The photocurrent was increased in reverse bias operation. In forward bias operation with an increase in illumination, the photocurrent showed a different behavior depending on the voltage applied.
2.6 DIELECTRIC AND AC CONDUCTION STUDIES

The influence of iodine on the electric conductivity and thermoelectric power of PbPc thin films was investigated by Witold Waclamek and Maria Zabkowska-waclawek (1987). For iodine doped samples, the electrical conductivity rises by seven to nine orders of magnitude. They reported that for these highly conducting materials a compensation rule for the conductivity is also valid. For some samples the mobility values and their temperature dependences are consistent with band model predictions.

The dark DC conductivity and spectroscopy of clean and gas doped thin films of various organic semiconductors have been studied in vacuum and in the presence of a wide range of gases by Colin Honeybourne and Ewen (1983). According to them only gases, which produce marked increase in the conductivity, were electron acceptors. The interactions of various groups and its derivatives were studied by conductivity measurements, UV / VIS and IR transmission spectroscopy and IR reflectance spectroscopy.

Shafai and Gould (1990) have studied the transport properties of PbPc thin films for use in FET structures. DC electrical measurements have been made for wide PbPc films of thickness range (d~0.5-5.0 µm). Measurements of capacitance as a function of inverse thickness revealed a low frequency relative permittivity ($\varepsilon_r \approx 3.9$). The observed results were accounted for in terms of an exponential distribution of traps of total concentration $2.8 \times 10^{25} \text{m}^{-3}$ within the band gap.

Azim-Araghi et al (1996) have studied the AC conduction mechanisms in thermally evaporated PbPc thin films over the frequency range $10^4$ to $4 \times 10^6$ Hz and the temperature range 160 to 440 K. In the high frequency region, the AC conductivity is proportional to $\omega^5$. The result obtained shows
the relative importance of the hopping model and band theory in describing the film conduction with regard to the operating conditions.

Kazuhiro Kudo et al (1997) have fabricated thin-film transistors consisting of the evaporated thin films of metal-free copper and PbPcs. They were also estimated the electrical parameters of the carrier mobility, carrier concentration and electrical conductivity by in situ field effect measurements. They were also investigated the effect of introducing oxygen gas into the vacuum chamber and of thermal annealing on the electrical parameters of the films. They found that the carrier concentration and carrier mobility are strongly influenced by the metals in the phthalocyanine molecules and by oxygen gas exposure.

Ray et al (1980) have reported conduction in partially monoclinic films of PbPc. The X-ray diffraction pattern of vacuum sublimed thin films of PbPc on glass substrates shows a partially monoclinic structure. The DC conduction is extrinsic, since the activation energy is much smaller than the energy band gap. AC conductivity $\sigma_{ac}$ follows a power law dependence on frequency ($f$) and this behaviour is believed to be due to correlated hopping of charge carrier.

Electrical conductivity and optical absorption of copper phthalocyanine (CuPc) substituted sodium borate glass were studied by Menon et al (2002). They carried out successfully prepared CuPc substituted sodium borate glass at $830^\circ$C and some preliminary studies on this glass are reported. Activation energy and optical band gap were determined for the glass from the Arrhenius plot of conductivity and optical absorption spectra are reported.

AC measurements on binary phthalocyanine films were studied by Pakhomov et al (2002). The impedance spectra of thin films composed of
PbPc and vanadyl phthalocyanine in various proportions were studied over a large range of frequencies. The experimental data were simulated with a serial RC network consisting of three terms. The behaviour of each term was analyzed as a function of film composition and ambient atmosphere. The applicability of known models has been evaluated.

Dielectric and Conductivity Studies on Cobalt Phthalocyanine Tetramers were studied by Anantharaman et al (2003). The permittivity study, AC conductivity was evaluated. The values of AC conductivity and DC conductivity were compared. Activation energy was calculated. To understand the conduction mechanism Mott’s variable range hopping model was applied to the system.

Electronic conduction in thermally evaporated thin films of organic semiconductor zinc phthalocyanine (ZnPc) has been investigated by Saleh.A.M. et al (2003) in a broad temperature range using gold Ohmic contacts. Electronic conduction by charge carrier hopping was dominated at low temperatures and higher voltages and space-charge-limited conduction (SCLC) has the dominant role, which was controlled by hole-trapping states distributed exponentially within the band gap.

Kuo-Chuan Hoa et al (2005) investigated the gas-sensing properties of ethanol-treated PbPc thin films, to be used in a chemiresistor-type nitric oxide gas sensor. The gas-sensing properties including current transient, sensitivity, and response time, were studied. The PbPc thin films post-treated with an ethanol vapour responded faster to NO gas both in adsorption and desorption processes, than PbPc thin films without any post-treatment was observed in this study.

Theodore Goodson et al (2006) have investigated the phthalocyanine dendritic system for strong dielectric response at high frequencies.
Measurements were carried out with both pressure compressed pellets and thin films of the Pc dendrimer system. The mechanism for this impressive high-frequency response with relatively small dispersion has been observed and can be due to a longrange polaron hopping mechanism.

The solution redox properties and spectroelectrochemical investigation of the novel PbPcs carrying chloro alkylthio and alkylmalonyl at periphery were studied by Atif Koca et al (2006) using various electrochemical techniques in DCM on a platinum electrode. Cyclic voltammetry and differential pulse voltammetry studies show that all of the complexes give up to five ligand-based diffusion controlled one-electron reversible redox couples. Spectroelectrochemical study reveals that PbPc complexes are demetallated during the controlled potential chronocoulometry measurement before the first reduction couple of the complexes.

Alternating current measurements of thermally evaporated triclinic PbPc thin films were studied by Shafai and Gould (2007). Electronic properties of thermally evaporated thin films of triclinic PbPc were reported employing symmetric gold ohmic electrodes in the frequency range of 100–20 kHz. Measurements on the dependence of capacitance on frequency (100–20 kHz) indicates that the capacitance is strongly frequency dependent and were found to decrease with increasing frequency at low frequency and less rapidly at higher frequencies were reported.

Device characterization and carrier transport properties of n-type fluorinated Copper phthalocyanine (F_{16}CuPc) organic thin-film transistors (OTFTs) were investigated using bottom gate device configuration with oxygen-plasma-treatment indium-tin-oxide (ITO) bottom source and drain (S/D) contact. Horng – Long Cheng et al (2008) suggest that the contact resistance between ITO electrodes and F_{16}CuPc plays an important role in current-voltage characteristics.
Wenping et al (2008) have reported organic compounds use as active semiconductor materials for OTFTs, among which phthalocyanine compounds have attracted considerable attention owing to their remarkable chemical and thermal stability as well as good field-effect performance.

2.7 CURRENT VOLTAGE STUDIES

The Current–Voltage characteristics of thin films of PbPc employing aluminium injecting electrodes were studied by Sakuri and Haya (1973). This result indicates a substantial deviation from the previous reports, where gold ohmic contacts were employed as the injecting electrodes. In his report they had calculated the coefficient $\beta$. For higher voltage region and under vacuum the coefficient $\beta$ is closely matched with that of Poole–Frenkel coefficients. Furthermore, it is noted that after exposure to air, the coefficient $\beta$ approaches closely to the value of theoretical Schottky coefficient. Variation in capacitance and conductance with frequency and temperature is also reported. The result is interpreted in terms of Simmons model. They calculated the value for the Schottky capacitance.

Verzimakha et al (1982) have reported photocells with organic semiconducting material. The affectivity and the sensitivity of photocells result from various optical and electrical properties of the active parts of these cells and their dependences on wavelength and intensity of incident light. They reported that nearly every metallic element of the periodic system may be used to synthesize.

IR response of phthalocyanine thin films to nitrogen dioxide has been studied by Schoch and Temofonte (1988). The IR transmission of nickel and PbPc thin films decreases dramatically after exposure to NO$_2$ at room temperature. This effect is caused by the creation of charge carriers and is
concurrent with increased electrical conductivity of the films. Both the effects can be reversed by heating the films to 160° C in vacuum.

The switching characteristics of a sandwich cell having a Au–PbPc–Au structure were studied by Machida (1989). Switching was observed in a film which was evaporated at a rate of 10 Å/s.

The electrical characteristics of thermally evaporated triclinic PbPc thin films were studied by Ahmed and Collins (1991c). A number of parameters like ε, μ, P₀, σ etc., were evaluated on the basis of the theory of space charge limited conduction. C-V measurements confirm that the Au-PbPc interface does not form a Schottky barrier. Measurements of thermoelectric power confirm that semiconductor is p-type.

Gas sensitivity measurements on NO₂ sensors based on PbPc thin films were studied by Heilmann et al (1991). The conductance response of NO₂ sensors based on PbPc thin films to NO₂, CO₂, SO₂ and to mixtures of these gases has been studied.

Ahmed and Collins (1992) have studied the electrical characteristics of triclinic PbPc thin films exposed to oxygen and dry air at atmospheric pressure for a period upto 25 weeks. Conductivity is found to be critically dependent upon the presence of oxygen, prolonged exposure enhancing conductivity and decreasing the conduction activation energies. Both ohmic and space-charge-limited conduction (SCLC) are observed together with a low temperature mechanism which may be variable range hopping.

Abass et al (1993) have studied the electrical behaviour of Au-PbPc-Au planar gas sensors as a function of exposure to I₂-air mixture. The changes in the I-V characteristics of PbPc thin films on exposure to iodine and after subsequent annealing in the vacuum at various temperatures
are investigated. It is found that iodine generates acceptor levels within the PbPc energy band gap. The dark current in the devices is studied as a function of temperature and film thickness at a constant bias voltage.

Abass et al (1993) have investigated changes in semiconductor behavior of PbPc thin film as a function of exposure to chlorine, annealing in chlorine, and subsequently in vacuum for a range of temperatures. It was found that Cl$_2$ generates acceptor levels within the band gap of the PbPc. They identified both ohmic and Space Charge Limited Conduction (SCLC).

Abass et al (1994) have studied the electrical characteristics of thin films of monoclinic PbPc as a function of substrate temperature during deposition, in situ under vacuum and after exposure to both oxygen and air. The effects of annealing in oxygen were also studied. Both ohmic and space charge limited conductivity were observed.

The responses of PbPc thin films upon encountering of NO$_2$ gas were studied by Ju et al (1999) both experimentally and theoretically. A surface adsorption/desorption and bulk diffusion mechanism was proposed to describe the response. Laplace Transform was employed to solve the resulting diffusion equation and an analytical solution was obtained. From the results of their study, it was concluded that the adsorption of NO$_2$ by PbPc is controlled by the surface adsorption and desorption with negligible diffusion resistance.

Menon.C.S and Ambily.S (1999) have studied vacuum sublimed thin films of copper phthalocyanine are prepared at room temperature and at different substrate temperatures. Post evaporation annealing is done at temperatures of 323, 373, 423 and 473 K. The electrical conductivity and optical absorption spectra of these films are studied.
Giovanelli et al (2001) have calculated the geometry and the electronic structure of the isolated PbPc molecule in its ground state. They have carried out all electron calculations including relativistic effects in the density-functional theory formalism using the DMOL3 code.

Jakubik et al (2001) presented the interaction of thin film layers of PbPc with trace amount of toxic gas NO\textsubscript{2} in a system with an acoustic surface wave on a LiNbO\textsubscript{3} substrate. The sensor properties dependence on changes in the differential frequency of the dual delay line configuration was discussed.

Electrical properties of both ClAlPc and CuPc were studied by Azim Araghi (2001). The activation energies of these materials were measured using both forward and reverse current-voltage characteristic and then they were compared. It was found that ClAlPc has lower activation energy than CuPc. Further, it was found that in ClAlPc, the activation energies evaluated using forward and reverse bias differ significantly at low temperatures while in CuPc this did not occur.

Electronic conduction has been investigated in evaporated PbPc thin films with aluminum electrodes by Gould and Shafai (2000). They reported that these samples did not exhibit space-charge-limited conductivity, but exhibited carrier excitation via a field-lowering mechanism with a \( \log J \propto V^{1/2} \) current density-voltage \((J-V)\) characteristic. Both polarities showed two regions in the \( J-V \) characteristics having different slopes, leading to the conclusion that conduction are via Schottky and Poole-Frenkel emission at lower and higher voltages respectively.

Pakhomov (2002) has reported conductivity measurements on thick films of PbPc in a sandwich cell with one pressure contact. The results obtained at different loads are discussed.
EL-Nahass.M.M et al (2002) have studied structural and transport properties of Copper Phthalocyanine (CuPc) thin films. The dark electrical resistivity and the thermoelectric power measurements were carried out at different temperatures in the range 300-450 K. Room temperature current density-voltage characteristics showed ohmic conduction in the lower voltage range and space charge limited conductivity (SCLC) in the relatively high voltage. The SCLC is controlled by an exponential distribution of traps above the valence band edge. The temperature dependence of current density allows the calculations of some essential parameters such as the hole mobility, the relative permittivity, the trap concentration, the characteristic temperature and the trap density.

Vibrational spectra of charge transfer complexes of PbPc were studied by Oza et al (2005). Infrared spectra of six charge transfer complexes of PbPc have been studied in the range of 400–4000 cm\(^{-1}\). Metal–ligand vibrations between 400 and 700 cm\(^{-1}\) lead to indirect transition between the valence and conduction bands. The phonon-mediated coupling between metal chains and the side chains were also studied.

Electrical transport properties of thermally evaporated phthalocyanine (H\(_2\)Pc) thin films were studied by El-Nahass et al (2005). The current density-voltage characteristics of H\(_2\)Pc at room temperature showed ohmic conduction mechanism at low voltages. At higher voltages the space-charge limited conduction (SCLC) accompanied by an exponential trap distribution was dominated. The temperature dependence of current density allows determination of some essential parameters such as the hole mobility, the total trap concentration, the characteristic temperature and the trap density.

Karimov.KH.S et al (2008) have reported P-type organic semi conducting Copper phthalocyananine (CuPc) thin films grown from its solution in benzene on nickel (Ni) substrates, at room temperature by vacuum
evaporation. To form Schottky junction Al/p-CuPc/Ni samples were fabricated, I-V characteristics were then evaluated at 24 °C and 64 °C. It was found that dark current-voltage characteristics of the Al / p-CuPc / Ni samples are non-linear and show rectification behavior. The dark I-V characteristics were simulated by space-charge limited current (SCLC) approach assuming the presence of deep trapping levels at energy above the valence band edge of the p-CuPc.

Zafar.Q et al (2011) have analysed the electrical properties of copper Phthalocyanine (CuPc) based organic field effect transistors (OFET) at temperatures from 300K to 400K. Thin films of organic semiconductor CuPc (40nm) and Semitransparent Al (20nm) were deposited in sequence, by vacuum evaporation on a glass substrate with previously deposited Ag source and drain electrodes with a gap of 40 μm. Under resistive mode of operation, where gate was suspended it was observed that drain-current of this organic field effect transistor (OFET) show an increase with temperature. While in grounded gate condition metal (aluminum) – semiconductor (Copper Phthalocyanine) Schottky junction dominated the output characteristics and device showed switching effect from low to high conduction states like Zener diode at higher bias voltages. This threshold voltage for switching effect has been found to be inversely proportional to temperature and shows an abrupt decrease after knee temperature of 360K. Change in dynamic resistance (Rd = dV/dI) with respect to temperature was observed to be -1%/K.

Shaji Varghese et al (2011) have carried out electrical conductivity studies separately on MnS, CuPc and multi layer MnS-CuPc thin films. Thermal activation energy of the as deposited and annealed samples is determined from the Arrhenius plot. It is found that the activation energy decreases with annealing temperature. This may be due to the reduction in trap sites during annealing.
Shahid M. Khan et al (2011) have investigated the temperature-dependent electrical properties of Tc-CuPc:PCBM bulk heterojunction (BHJ) under dark conditions. Rectifying nature of the BHJ was displayed by current-voltage (I-V) curves, recorded in dark and at various temperatures. At low voltages, conduction was ohmic succeeded by space-charge limiting current (SCLC) conduction at higher voltages in which exponential trap distribution was dominant.

Mutabar Shah et al (2011) have reported on the fabrication and investigation of a surface-type organic semiconductor copper phthalocyanine (CuPc) based diode. The current–voltage characteristics were measured at room temperature under dark conditions. At low voltages the device showed ohmic conduction where as the space charge limited current conduction mechanisms were dominated at higher voltages.