PREFACE

Thin films play an important role in present-day technological development. Thin film technology is based on three foundations: fabrication, characterization and applications.

Organic devices are already in market, most notably in the displays of several electronic appliances. Yet the future holds even greater promise for this technology, with an entirely new generation of ultra low-cost, lightweight and even flexible electronic devices, which will perform functions traditionally accomplished using much expensive components based on conventional semiconducting materials such as Silicon and Germanium.

Phthalocyanines (Pcs) are macro cyclic compounds characterized by conjugated bonding, i.e. alternate single and double bonds and they come under the class of organic semiconductors. Pcs are a representative of the p-type semiconducting materials that work as electron donors. π electrons are delocalised and are responsible for conduction in molecules having conjugated bonding. One of the important requirements of a solar cell material is its ability to transport the charge carriers. This property is commonly found for materials that have an extended delocalised π-electron system. Since the inter-molecular attraction is weak, the conduction band will be narrow and hence the mobility will be small. The major advantage of using organic semiconducting materials is their ability to modify their molecular structure and hence their electrical, optical and structural properties. Pcs form stable combination with many metals and semi-metal atoms. In combination with metals, which prefer a higher co-ordination number, square based pyramidal, tetrahedral or octahedral structures occur. In such cases, the central metal atom is co-ordinated with one or two axial ligands such as chlorine or pyridine. In general Pcs and metallo-phthalocyanines (MPcs) are classified as p-type semiconductors with low mobility and low carrier concentration. The molecular orbital of different molecules can be treated as isolated and hence the free electrons or carriers of the individual molecules stay in them rather than in between them. However, these electrons jump or hop from one site to another site due to perturbations caused by the neighbouring molecules. Because of high thermal and chemical stability, in contrast with many other organic compounds, the preparation of MPcs thin films by vacuum thermal evaporation is viable and feasible.

A large number of MPcs have been synthesized over the past few years and elaborate studies have been made. But no such detailed studies of halogenated MPcs have been reported yet. The optical, electrical and structural properties of phthalocyanine thin films depend on a number of material parameters including film morphology, which in turn is determined by the parameters, like deposition rate, substrate temperature and post deposition annealing. So the study of thin film properties is essential for the development of viable thin film devices. Among the properties, being tailored today for significant applications are: (1) optical band gap, (2) optical constants, reflectance and transmittance, (3) electrical conductivity and activation energy and (4) structure and surface morphological studies.

The thesis deals with the study of the optical, electrical and structural characterization of vacuum deposited Titanium phthalocyanine dichloride ($TiPcCl_2$), Silicon phthalocyanine dichloride ($SiPcCl_2$), Tin phthalocyanine dichloride ($SnPcCl_2$), and Tin phthalocyanine (SnPc) thin films. To probe the applicability of using $TiPcCl_2$, $SiPcCl_2$, $SnPcCl_2$ and SnPc thin films as radiation dosimeters, effects of gamma ray irradiation on these thin films have also been investigated. Chapter 1 introduces organic semiconductors and phthalocyanines. Also it gives a brief review of the earlier studies on the electrical, optical and structural properties of phthalocyanines thin films.

Chapter 2 focuses on the equipments and experimental techniques used in the present work. It also includes the various aspects of the thermal evaporation technique used for the thin film fabrication. Pc thin films prepared by subliming the source material in high vacuum system result in high purity thin films with excellent growth properties and chemical stability. Brief description of the UV-VIS-NIR spectrophotometer, electrical conductivity Cell, Keithley programmable electrometer, X-ray diffractometer and Scanning electron microscope are described in this chapter.

Chapter 3 gives the optical studies in thin films of $TiPcCl_2$, $SiPcCl_2$, $SnPcCl_2$ and SnPc. Optical properties include the analysis of absorption and reflection spectra and the determination of fundamental and excitonic energy gaps. The variations in energy band gap with post deposition annealing in air and vacuum and substrate temperature are also given. Refractive index n, extinction coefficient k and the real and imaginary parts of the dielectric constants ε_1 and ε_2 respectively are also presented in this chapter.

Chapter 4 emphasizes the electrical characterization of thin films of $TiPcCl_2$, $SiPcCl_2$, $SnPcCl_2$ and SnPc. The determination of the thermal activation energies and their dependence on film thickness, annealing temperature, in air and vacuum, and substrate temperature are included in this chapter.

The discussions on the structural and surface morphological studies of $TiPcCl_2$, $SiPcCl_2$, $SnPcCl_2$ and SnPc thin films are given in Chapter 5. It includes the indexing of X-ray powder diffraction pattern, determination of structural parameters viz. average grain size, micro strain, dislocation density and the effect of substrate temperature and post deposition annealing in air and vacuum. Scanning electron micrographs are analyzed to study the development of surface morphology of thin films during annealing.

Chapter 6 finds the applicability of using $TiPcCl_2$, $SiPcCl_2$, $SnPcCl_2$ and SnPc thin films as the gamma ray radiation dosimeters. The variation of optical energy gap and thermal activation energy on gamma ray irradiation for different dosages and exposure times are investigated in this chapter.

The thesis concludes with Chapter 7 where a summary of the investigations on the $TiPcCl_2$, $SiPcCl_2$, $SnPcCl_2$ and SnPc thin films are given. The future scope of this work is also presented in this chapter. Most of the work in this thesis have either been published in international journals or are presented in international conferences or are in the process of publication. A list of such publications is given below.