Emerging trends in modern organic electronics are growing towards Phthalocyanine type materials synthesis and characterizations. Naphthalocyanines are materials, which play an important role in the present day molecular electronics. Breakthrough products employed in commercial technologies include organic light-emitting diodes (OLEDs) and Organic field effect-transistors (OFETs) are and their efficiencies are improved with these materials. Tert-butyl addition to the fourth position of benzene ring in Naphthalocyanines gives excellent chemical and thermal stability in contrast to simple Naphthalocyanines. This appreciable feature makes them easily sublime to form thin films without undergoing decomposition. Apart from many other preparation techniques, vacuum sublimation is more feasible for the thin film fabrication of naphthalocyanines.

The versatility, architectural flexibility, the simplicity of processing and low cost make them eligible candidates for use in a wide range of technological applications. The major exploitation of thin film resides in micro electronics where the considerable efforts have been made towards the realization of various thin film devices like Photovoltaic cells, solar cells and fuel cells. Naphthalocyanies have long storage life and high read out times, for the use in optical storage systems. Class of naphthalocyanine compounds lies in organic dye categories since it absorbs light in visible and Infra-red regions and also used in the field of non-linear optics. On combining the environment friendly nature of naphthalocyanines with its good electrical sensitivity to adsorb impurities make them favourable for visible gas sensors and chemical sensors. Apart from phthalocyanines, some naphthalocyanines exhibit transparency and semi conducting property for a span of wave length in the visible region of the electromagnetic spectrum. This type of naphthalocyanine thin films is apt for the fabrication of laser windows for tuneable lasers.

It is observed that the electrical, optical and structural and surface morphological properties of organic semiconducting thin films critically depend on the film morphology, which is determined by the preparation parameters such as deposition rate, substrate temperature, post-deposition annealing and irradiation of high energy rays on the film. The electrical properties of semiconductors are decided by the type of conduction mechanism involved. For a desired film characterization, an understanding of its properties at various growth conditions is essential.

In this thesis the preparation of thin films of Metal free 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanines (TTBNc), Zinc 2,11,20,29 Tetra Tert-Butyl 2, 3 Naphthalocyanine (ZnTTBNc) and Vanadyl 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanine (VTTBNc) and the studies on electrical, optical, structural and surface morphological properties of these semiconductors are dealt with. The effect of central metal atom on TTBNc is also studied for each property of the materials thin films. The materials selected in the present work are class of Tetra tert- butyl 2,3 naphthalocyanines where the choice of materials are better on comparing with pure naphthalocyanines and their phthalocyanine counter parts due to better stability and coefficient of performance.

Chapter 1 gives a brief review of the earlier studies on the electrical, optical, structural and surface morphological properties of metal and metal free Tetra Tert-Butyl 2,3 Naphthalocyanines. A detailed description of physical and chemical properties, advantages and disadvantages with wide range of applications is also given here. The choice of materials like TTBNc, ZnTTBNc and VTTBNc is adequate for thin film fabrication on present scientific outlook due to the following reasons. The novelty of those classes of materials is so clear from the review papers and patent reports since both of them are very few in number. Though there are early reports on their use in photonic applications, the electrical studies both in high and low temperature region are scarce. Lack of available data in the structure and surface morphology of these classes of materials still exists as a hindrance in their applications for constructing single molecular devices and in nano technological applications. In this thesis a modest attempt has been made to study electrical, optical, structural and surface morphological properties on a class of tert-butyl substituted 2,3 Naphthalocyanines by varying different parameters like thickness, post deposition annealing temperature, substrate temperature and irradiation of gamma rays.

Chapter 2 gives the experimental techniques used in the present study. Methods of film preparation including the thermal evaporation technique, which is used in the present study, are given here. Purity rating of materials, substrate cleaning procedures, method of measuring film thickness, sample annealing mechanism, substrate heating set up details and gamma ray irradiation techniques are also mentioned in this chapter. Brief descriptions of the various characterization equipments like Keithley electrometer, UV-VIS-NIR spectrophotometer, X-ray diffractometer, Scanning electron microscope and Atomic force microscope used for the study of electrical, optical, structural and surface morphological analysis are also mentioned in this chapter.

Chapter 3 deals with the electrical conductivity studies of TTBNc, ZnTTBNc and VTTBNc thin films. All the three TTBNc thin films are found to be N-type materials with electrons as the majority charge carriers by hot probe analysis. Two probe D.C. electrical conductivity studies are carried out with the determination of electrical conductivity of thin films near room temperature and thermal activation energy. Variation of both intrinsic and extrinsic activation enthalpy with parameters like thickness of thin films, annealing temperatures in air and vacuum, substrate heating temperature and irradiation of gamma rays are well explained in the chapter by comparing the results among three different TTBNc thin films. The determination of Variable Range Hopping (VRH) conduction parameters are also given in this chapter. By analysing the electrical conductivity, VTTBNc thin film has larger conductivity for both in high and low temperature regions as compared with ZnTTBNc and metal free TTBNc thin films. VTTBNc thin films retain their higher value of conductivity even under the application of varying parameters on thin films. So Vanadyl Tetra Tert Butyl 2,3 Naphthalocyanine (VTTBNc) thin films are preferable to Zinc and metal free TTBNc thin films for thin film electronic applications.

The optical studies on TTBNc, ZnTTBNc and VTTBNc thin films are described in Chapter 4. All the optical parameters for freshly prepared thin film samples are determined. The optical band gaps and trap energy levels are determined and their variation with respect to thickness, annealing effects, substrate heating and gamma ray irradiations are well explained. The band gap energy found decreasing with all the varying parameters except for gamma ray irradiation where irradiation dosage goes on increasing with band gap energy for all the three TTBNc thin films. Band gap energy value is most reduced for maximum air and vacuum annealed VTTBNc thin films other than the metal free and Zn TTBNc thin films. So VTTBNc thin films are more preffered for the preparation of opto electronic devices with a high figure of merit compared with ZnTTBNc and metal free TTBNc thin films.

Structural studies like X-ray diffraction for TTBNc, ZnTTBNc and VTTBNc are given in Chapter 5. The effect of grain size distribution and micro crystalline strain produce in thin films due to the impact of homogenous layer by layer deposition, post deposition air and vacuum annealing, heating on glass substrate and irradiation with gamma rays are also given in this chapter. Thickness variation does not give crystalline property. Annealing results in the crystallization of thin films for all the three materials. Effect of oxygen varies the annealing results in air and vacuum conditions. The grain size of thin films is decreased much from the powdered sample due to the increase of internal stress during deposition in basic structural unit like bezoisoindole and it continuous for increase in annealing temperature. Substrate heating increases the mobility of atoms during deposition and it increases the size of critical nucleus of macro molecules. The effect produce an increase in grain size with less lattice deformations and thermal strain by defining well grain boundaries with expansion of thin film layer. Gamma irradiation effect on TTBNc, ZnTTBNc and VTTBNc thin films reduces the average grain size with out changing the basic structure. All the X-ray diffraction studies found no evidence of structural changes and distortions in all the three thin films with orthorhombic crystal type for TTBNc and VTTBNc while tetragonal for ZnTTBNc thin films. Metal TTBNc especially VTTBNc thin films having apt structural parameters like nano grain size, comparably less lattice dislocation density with thermal strain and presence of more secondary electrons with out disturbing the lattice structure. VTTBNc thin films are preferable to TTBNc and ZnTTBNc in its structural characteristics for electronics device fabrications.

Surface morphological studies like Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) studies are carried out for TTBNc, ZnTTBNc and VTTBNc are given in Chapter 6. In TTBNc, ZnTTBNc and VTTBNc thin films, under varied thickness and substrate heating increases the average grain size along with an increase in RMS surface roughness while the annealing process and gamma ray irradiation decreases the average grain size along with RMS surface roughness. High roughness clubbing with macro molecular grain size thin films are applicable for sensing applications while low roughness with reduced average grain size thin films are applicable for micro and nano electronics. On materials wise comparison

VTTBNc thin films are more suitable for using as gas sensors than Zinc or metal free TTBNc thin films with its improved morphological characteristics.

The summary and conclusion are given in Chapter 7. In conclusion, the central metal ion favours electrical, optical, structural and surface morphological properties of Tetra- Tert-Butyl 2,3 Naphthalocyanine tin films to a great extent. The transition metals with unfilled inner d-orbital like Vanadium has improved properties in the studies on comparing with Zinc and metal free TTBNc thin films due to the inner transition of majority charge carriers through the macro molecules. The future scope of this work is also indicated by combining the opto electronic features of class of TTBNc thin films with its nano regime; the materials for further investigations are suggested as interesting candidates for nano thin film device fabrications in the near future.

Most of the work presented in this thesis have either been published in journals or presented in International/ national conferences or are in the process of publications, a list of which is given below.

LIST OF PUBLICATIONS

1. Low temperature effects on electrical and optical properties of TTBNc thin films, I. Dhanya, T. G. Gopinathan, Nisha S Panicker and C.S. Menon, Journal of Non-Crystalline Solids, 356 (2010) 160-164.

2. Optical and electrical characterization of tin (II) 2,3- naphthalocyanines thin films coating containing agglomerated spherical particles, Nisha S Panicker, T. G. Gopinathan, I. Dhanya and C. S. Menon, Physica B, 405 (2010) 4556-4560.

3. Low temperature effects on electrical and optical properties of vacuum annealed Zinc Tetra-Tert-Butyl 2,3 Naphthalocyanine thin films, I. Dhanya and C. S. Menon, Journal of Nano and Electronic Physics, 3 (2011) 426-432.

4. Annealing effects on electrical, optical and structural properties of semiconducting transparent tetra- tert-butyl 2,3 naphthalocyanine thin films, I. Dhanya and C. S. Menon, Journal of Non-Crystalline Solids, 357 (2011) 3631-3636.

5. Effect of thickness on structural and optical properties of tetra- tert-butyl 2,3 naphthalocyanine thin films, I. Dhanya and C. S. Menon, E- Journal of Chemistry, 8(4) (2011) 0000-0000 (in press).

6. Surface morphological, structural, electrical and optical properties of annealed Vanadyl Tetra-Tert-Butyl 2, 3 Naphthalocyanine thin films, I. Dhanya and C. S. Menon, (accepted for publication in Vacuum).