Preface

Polymers and polymer based materials find enormous applications in the realm of electronics and optoelectronics. They are employed as both active and passive components in making various devices. Enormous research activities are going on in this area for the last three decades or so, and many useful contributions are made quite accidentally. Conducting polymers is such a discovery, and ever since the discovery of conducting polyacetylene, a new branch of science itself has emerged in the form of synthetic metals. Conducting polymers are useful materials for many applications like polymer displays, high density data storage, polymer FETs, polymer LEDs, photo voltaic devices and electrochemical cells. With the emergence of molecular electronics and its potential in finding useful applications, organic thin films are receiving an unusual attention by scientists and engineers alike. This is evident from the vast literature pertaining to this field appearing in various journals. Recently, computer aided design of organic molecules have added further impetus to the ongoing research activities in this area.

Polymers, especially, conducting polymers can be prepared both in the bulk and in the thin film form. However, many applications necessitate that they are grown in the thin film form either as free standing or on appropriate substrates. As far as their bulk counterparts are concerned, they can be prepared by various polymerisation techniques such as chemical routes and electrochemical means. A survey of the literature reveals that polymers like polyaniline, polypyrrole, polythiophene, have been investigated with a view to studying their structural electrical and optical properties. Among the various alternate techniques employed for the preparation of polymer thin films, the method of plasma polymerisation needs special attention in this context.

The technique of plasma polymerisation is an inexpensive method and often requires very less infra structure. This method includes the employment of ac, rf, dc, microwave and pulsed sources. They produce pinhole free
homogeneous films on appropriate substrates under controlled conditions. In conventional plasma polymerisation set up, the monomer is fed into an evacuated chamber and an ac/rf/dc/μw/pulsed discharge is created which enables the monomer species to dissociate, leading to the formation of polymer thin films. However, it has been found that the structure and hence the properties exhibited by plasma polymerized thin films are quite different from that of their counterparts produced by other thin film preparation techniques such as electrochemical deposition or spin coating. The properties of these thin films can be tuned only if the interrelationship between the structure and other properties are understood from a fundamental point of view. So very often, a through evaluation of the various properties is a pre-requisite for tailoring the properties of the thin films for applications. It has been found that conjugation is a necessary condition for enhancing the conductivity of polymer thin films. RF technique of plasma polymerisation is an excellent tool to induce conjugation and this modifies the electrical properties too. Both oxidative and reductive doping can be employed to modify the electrical properties of the polymer thin films for various applications. This is where organic thin films based on polymers scored over inorganic thin films, where in large area devices can be fabricated with organic semiconductors which is difficult to achieve by inorganic materials. For such applications, a variety of polymers have been synthesized such as polyaniline, polythiophene, polypyrrole etc. There are newer polymers added to this family every now and then.

There are many virgin areas where plasma polymers are yet to make a foray namely low-k dielectrics or as potential nonlinear optical materials such as optical limiters. There are also many materials which are not been prepared by the method of plasma polymerisation. Some of the materials which are not been dealt with are phenyl hydrazine and tea tree oil. The advantage of employing organic extracts like tea tree oil monomers as precursors for making plasma polymers is that there can be value addition to the already existing uses and
possibility exists in converting them to electronic grade materials, especially semiconductors and optically active materials for photonic applications.

One of the major motivations of this study is to synthesize plasma polymer thin films based on aniline, phenyl hydrazine, pyrrole, tea tree oil and eucalyptus oil by employing both rf and ac plasma polymerisation techniques. This will be carried out with the objective of growing thin films on various substrates such as glass, quartz and indium tin oxide (ITO) coated glass. There are various properties namely structural, electrical, dielectric permittivity, nonlinear optical properties which are to be evaluated to establish the relationship with the structure and the other properties. Special emphasis will be laid in evaluating the optical parameters like refractive index (n), extinction coefficient (k), the real and imaginary components of dielectric constant and the optical transition energies of the polymer thin films from the spectroscopic ellipsometric studies. Apart from evaluating these physical constants, it is also possible to predict whether a material exhibit nonlinear optical properties by ellipsometric investigations. So further studies using open aperture z-scan technique in order to evaluate the nonlinear optical properties of a few selected samples which are potential nonlinear optical materials is another objective of the present study. It will be another endeavour to offer an appropriate explanation for the nonlinear optical properties displayed by these films.

Doping of plasma polymers is found to modify both the electrical conductivity and optical properties. Iodine is found to modify the properties of the polymer thin films. However insitu iodine doping is tricky and the film often looses its stability because of the escape of iodine. An appropriate insitu technique of doping will be developed to dope iodine in to the plasma polymerized thin films. Doping of polymer thin films with iodine results in improved and modified optical and electrical properties. However it requires tools like FTIR and UV-Vis-NIR spectroscopy to elucidate the structural and optical modifications imparted to the polymer films. This will be attempted here to establish the role of iodine in the modification of the properties exhibited by
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the films. The main objectives of the present study can be summerised and are listed below.

Objectives of the present work

- Preparation of optical quality organic thin films by rf/ac plasma polymerisation techniques.
- Modification of the optical and electrical properties by \textit{insitu} doping of iodine.
- Evaluation of structural properties of these films by FTIR analysis.
- Morphological studies using scanning electron microscopy.
- Determination of the optical band gap of thin films and calculation of the defect levels from UV-Vis-NIR studies.
- Elucidation of the mechanism of conduction in these films for the fabrication of devices.
- Evaluation of permittivity and loss factor at various frequencies.
- Determination of the optical and thin film parameters using Spectroscopic Ellipsometric studies.
- Determination of the nonlinear optical properties of the films by z-scan technique.
- Study the effect of ultrafine coating on magnetic/ non magnetic nano particles on the electrical and structural properties.

This proposed thesis is entitled \textit{“Plasma Polymerised Organic Thin Films: A study on the Structural, Electrical, and Nonlinear Optical Properties for Possible Applications”} and consists of ten chapters.

\textit{Chapter I} contains a brief history and application potential of conducting polymers including plasma polymerisation and plasma polymerised thin films. The importance of the modification of the properties by doping is also described in this chapter. The motivation for the present study is brought out in this chapter.
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The theoretical aspects of the mechanism of conduction, the basic theory of the ellipsometric technique for thin film analysis and nonlinear optical properties of the polymers are discussed in Chapter II.

The experimental techniques used in the various stages of this study are briefly described in Chapter III. It deals with the preparation of the thin films by rf/ac plasma polymerisation, in situ doping with iodine, structural, optical and morphological studies, and the electrical characterisation. Also the techniques of spectroscopic ellipsometric and nonlinear optical characterization are described in detail.

The structural and optical characterisation of various plasma polymerized thin films is described in Chapter IV. FTIR studies gives a picture of the structural difference occurring during the process of plasma polymerisation and the optical band gap and the defect level calculation from the UV-Vis-NIR studies is described.

Chapter V gives a detailed analysis on the current voltage characterisation of plasma polymerized thin films. The various conduction models for different polymers and electrode configurations and the low temperature effects on the charge transport mechanism in plasma polymers are discussed.

The permittivity measurements carried out on various plasma polymers are described in Chapter VI. The low-k characteristics exhibited by different plasma polymers are described in this chapter.

Chapter VII deals with the spectroscopic ellipsometric characterisation of plasma polymerized poly aniline thin films in the pristine and doped form. The evaluation of the optical constants, dielectric constants and band gap are discussed in this chapter.

The nonlinear optical properties of plasma polymerized thin films are evaluated by z-scan technique. The nonlinear optical properties of plasma polymerized thin films in the pure and doped form is described in Chapter VIII.
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The effect of a thin polymer coating on inorganic nanocomposites by plasma polymerisation and modification of the permittivity and ac conductivity and the electrical properties of the composites are described in *Chapter IX*.

*Chapter X* is the concluding chapter where in the inference drawn out of the study are detailed. The scope of further work and the lacunae observed in this study are brought out.