Chapter 10
Conclusion

Polymers and polymeric materials are constantly playing a vital role in making new devices and thus paving the way for removing the obsolete. They play a lead role in making life more humane. The 20th century witnessed an exploding activity in this area. This has resulted in the birth of new disciplines like molecular electronics, synthetic metals, organic semiconductors, and plastic electronics. The advent of high-end workstations and supercomputers augmented the design of various molecules for specific applications. During the last 10 years or so, tremendous progress has been made in making new optoelectronic devices based on polymers like new display elements fluorescent materials, LEDs etc. Both bulk and thinfilms based on these polymers were synthesised/fabricated. Normally as far as the applications are concerned devices are thinfilm based and hence the preparation of polymer thinfilms assumes certain significance. Plasma polymerisation is a known technique for producing ultrathin films which are homogeneous, smooth and pinhole free. Both rf and ac plasma polymerisation techniques can be employed to prepare thinfilms. Polymers are increasingly finding new applications in the form of passivating medium for fuctionalization and as biocompatible materials for drug delivery and drug targeting. In plasma polymerisation, since the precursors are the monomers themselves, new polymers can be synthesised by using precursors like natural oils. This might lead to new electronic materials based on natural products or endup as value added products for biomedical applications. This thesis is thus an attempt towards this objective. The salient findings, conclusions drawn out of these studies and the scope for further investigations are listed in this concluding chapter.

It has been found that, by optimizing the process parameters namely, plasma current, monomer flow rate and monomer vapour pressure, good quality
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thinfilms could be fabricated using the technique of both rf and ac plasma polymerisation. Any study on polymer thinfilms is complete without structure-property correlation. Thus extensive spectroscopic investigations are carried out on polymer thinfilms. It has been found that in plasma polymerised aniline thinfilms the benzene ring is intact during plasma polymerisation. The optical band gap is modified by doping of iodine. An insitu method and an improvised setup for iodine doping has been fabricated indigenously. Elaborate studies were carried out on pristine and iodine doped samples. It was found that the insitu method of iodine doping could be modified and any dopant vapour could be admitted. Another feature of this setup is that the admittance of the dopant vapour can be monitored and the dopant concentration can be pre determined.

Engineers worldwide are struggling hard to cope up with the Moore’s law, to increase the component density in a chip. This has resulted in search for low-k materials. Though conventional low-k materials are based on silicon, search for non conventional low-k materials based on polymers are also on. It must be noted here that low-k materials are good inter layer dielectrics and thus enable to reduce the RC time constant which in turn help to decrease the crosstalk. This thesis is also an endavour to delve in to the fundamental aspects of the formation of plasma polymers based on aniline, phenyl hydrazine and tea tree oil. Emphasis was also laid in preparing plasma polymerised thinfilms based on tea tree oil.

Plasma polymer of phenyl hydrazine was never before investigated and it was found that thinfilms of plasma polymerised phenyl hydrazine is a potential candidate for applications such as low-k films. Spectroscopic investigations carried out on plasma polymerised natural oils like tea tree oil indicated that the plasma polymerised thinfilms based on tea tree oil contain optically active groups (species) like chromophers and can then be useful for device applications. The complexity of the structure and the presence of large groups like terpinen-4-ol, p-cymene, 4-iso-propyl toluene and para methyl cymene etc is a major impediment in clearly stating that a particular group is responsible for the properties exhibited by these films. Great amount of investigations is
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necessary to decipher the role of different groups with respect to a particular property. This needs further studies using FTIR and NMR. The presence of optically active groups like chromophores in plasma polymerised tea tree oil thin films increases the application potential as an active layer for the fabrication of the electroluminescent devices like polymer light emitting devices (PLEDs) etc.

Earlier investigations on plasma polymerised polyaniline and iodine doped polyaniline indicated that plasma polymerised polyaniline can be a potential low k material. However these studies were carried out in the low frequency regime. In order to revalidate these findings, spectroscopic ellipsometric experiments were performed. Pristine and iodine doped polyaniline thinfilms exhibited low k characteristics even at optical frequencies. This augurs well as well as applications are concerned. These experiments also establish the fact that rf plasma polymerisation is an effective tool for producing optically smooth films. It must be noted here that the findings on roughness by ellipsometric technique is in full conformity with that of the results obtained using AFM and SEM. The optical conductivity of these films was evaluated from spectroscopic ellipsometric data and has been found that the iodine doping increases the conductivity substantially. This is an important finding and in tune with the results obtained from the optical absorption studies.

Elaborate studies were carried out on the conducting properties of plasma polymerised thinfilms of aniline, phenyl hydrazine and tea tree oil in order to elucidate the possible conduction mechanism of these polymer thin films. It is found that the dominant conduction mechanism found in rf plasma polymerised aniline, phenyl hydrazine and tea tree oil is space charge limited conduction (SCLC), where as the ac plasma polymerised form of aniline exhibited Schottkey type conduction mechanism. Conductivity of all the plasma polymers subjected to the J-V measurements were found in the semiconducting regime.

Dielectric and ac conductivity studies on rf and ac plasma polymerised thin films of polyaniline, phenyl hydrazine and tea tree oil were carried out and the results are explained. All the films exhibit a ‘breakdown’ at higher
frequencies for an applied biasing voltage of 1 V between the electrodes. Up to this “breakdown frequency” the thinfilms show low-k properties. A hopping conduction at higher frequencies is observed in all films. The phonon frequencies corresponding to different frequencies for these films were evaluated. Inter electrode tunneling of carriers at high frequencies is observed in all films. The electric field induced polarisation and hopping of carriers at high frequencies were observed in all the plasma polymers subjected to the dielectric measurements.

Nonlinear optical studies of plasma polymerised thinfilms were carried out by employing the open aperture Z-scan technique. The optical and electrical studies carried out on plasma polymerised thinfilms of polyaniline and tea tree oil confirms a trap-controlled PR response. This indicates that these thinfilms are potential nonlinear optical materials. The z-scan studies revealed that polyaniline exhibited a saturable absorption and the tea tree oil exhibited a reverse saturable absorption which qualifies them as potential materials for optical limiting and optical switching respectively. Incorporation of iodine in the polymer network of these films modifies the nonlinear optical properties of these thinfilms considerably.

An indigenous method for surface passivation using rf plasma polymerisation of inorganic materials was developed. Initial experiments carried out on magnetic oxides indicate the passivation of oxide particles with an ultra thin polymer layer can easily be carried out by plasma polymerisation. A model based on Maxwell-Wagner theory of interfacial polarisation was applied to explain the observed enhancement of dielectric permittivity. This model can be applied for a bilayer or a trilayer coating and can be employed to tune the dielectric properties of oxide materials by surface modification.

There is huge scope for further work on plasma polymerised thinfilms, based on phenyl hydrazine and tea tree oil. Phenyl hydrazine based thinfilms are being investigated using plasma polymerisation technique for the first time. A complete evaluation of the structure of these polymer thinfilms with the help of FTIR spectroscopy in combinational with the NMR technique will shed light on
the structure of plasma polymerised phenyl hydrazine thinfilms. There is ample scope exists to investigate the electrical and photoconductive properties of these films. It has been found that the plasma polymerised tea tree oil films are semi conducting and transparent. They are bio compatible too. So scope exists to coat inorganic magnetic particles with tea tree oil films and functionalise them for drug delivery applications. These is also scope for carrying out a detailed investigation on the optical properties of plasma polymerised tea tree oil thinfilms for applications LEDs and active materials.