Chapter 8
Conclusions

8.1. Summary of the work

In last few years organic electronics have secured a position in modern era electronics due to its ability to provide low cost, large area and flexible alternative. Conjugated molecular semiconductors seems to be an able competitor to polymeric organic semiconductors as they possess a well defined molecular packing in comparison to amorphous character of polymeric thin films. The applicability is again limited by the polycrystalline nature of films as it is difficult to get the ordered films due to weaker van der Waals interaction among the molecules than their inorganic counterparts who have the ability to show large ordering in thin films owing to their strong covalent bonding. The performance of devices based on these molecular films is limited by the grain boundaries arise due to the incapability of producing long range order in thin films. The anisotropic shape of the molecules gives rise to the anisotropy in mobility. The mobility is high in the direction of $\pi-\pi$ overlap among the adjacent molecules. The anisotropic shape of the organic molecules leads to different morphological patterns, anisotropy in molecule-molecule and molecule-substrate interactions which controls the thin film morphology. Some particular patterns in thin film morphology enhance $\pi-\pi$ overlap and reduce the grain boundaries which are desired for optimized device performance. These two objectives can be achieved by having certain surface morphology. This leads to a need to understand a correlation between molecular structure, its effect on the evolution of a particular morphological pattern and their collective effect on device performance. Three organic molecules phthalocyanines (Pcs), Pentacene and Rubrene are chosen for their difference in molecular structure, anisotropicity and symmetry. Pcs consists of symmetric planar structure, Pentacene has a linear structure and Rubrene is non planar.

Chapter 2 summarizes the effect of all the growth parameters that play an important role to determine the optimized growth parameters for thin films to be used as active layers in devices such organic field effect transistor (OFET), organic light emitting diode (OLED), and organic solar cell (OSC). The thin film morphology of Pcs is quite sensitive to growth conditions and shows a large variation in morphology.
The films of metal free phthalocyanine (H$_2$Pc), iron phthalocyanine (FePc) and copper phthalocyanine (CuPc) achieve grainy structure to long molecular wires networks as the diffusion increases by increasing growth temperature. At very high deposition temperature, flat crystals are obtained but do not belong to the class of desired morphology. Apart from the deposition parameters the size and the valence electrons of central metal ion play an important role in deciding the film morphology. Zinc phthalocyanine (ZnPc) has been found unable to form elongated structures due to electronic structure of central metal ion with completely filled d orbital. We conclude that the higher substrate temperature can induce certain morphology and phase change in thin films and have a strong influence on device characteristics. This is confirmed by optical, AFM and XRD studies. Although deposition rate do not lead to any phase change however has a strong influence on the crystallinity and structural disorder in thin films. It is shown that the hydrophobic substrates provide a better template to enhance $\pi$- $\pi$ interaction among adjacent molecules lowering the molecule-substrate interaction. The incomplete unpaired d orbital leads to a better $\pi$- $\pi$ overlap thereby giving CuPc out of most of the metal phthalocyanines (MePcs) a better choice for the device application.

In chapter 3 we have investigated the effect of growth parameters on morphology of Pentacene thin films. Pentacene thin film consists of DLA type growth with pyramidal lateral growth that belongs to the ideal growth mode (layer by layer) for thin film transistor application. The high deposition rate disrupts island growth leading to small islands. The low substrate temperature is a favourable condition for large $\pi$-$\pi$ stacking and consequently layered growth. The high substrate temperature again hampers the island growth leading to the formation of small crystallites. Under optimized growth conditions of low deposition rate and low substrate temperature thin films of Pentacene shows ordered film growth consisting of both thin film and bulk phase leading to high mobility 0.3 cm$^2$/V$s$.

In chapter 4 we have studied the effect of growth conditions on morphology of thin films of Rubrene by optical, AFM and confocal microscopic images. Although the conformational change in Rubrene owing to its nonplanar structure in thin film evolution does not affect the absorption and morphological properties however the growth conditions effectively modify the structure at the interface. The films on SiO$_2$ substrates show spherulitic structure while on ITO substrate platelet like crystals are formed. High substrate temperature and high deposition rate are required to induce
high crystallization in Rubrene thin films. With high deposition rate, the films consist of stable polymorphs, orthorhombic and triclinic phases. This induced crystallization largely affects the transport properties of thin film. The two terminal devices consisting of spherulitic patterns with low deposition rate shows reversible switching effect.

Chapter 5 demonstrates the fabrication of organic Schottky diode and underlying physics. Growth conditions largely affect the performance. We have used a combination of $J$-$V$ and $C$-$V$ characteristics to establish unambiguously formation of Schottky junction in metal/organic /metal structure due to barrier at one metal/organic interface. Schottky barrier height can be determined from vacuum level alignment at metal/organic interfaces. The $J$-$V$ and $C$-$V$ characteristics provide evidences for existence of depletion region, band bending and flat band condition which are entirely determined by built-in-potential due to difference in work function between two electrodes. We have further shown that frequency dependence of capacitance of organic Schottky diode is powerful technique to study the charge dynamics in organic materials for determining carrier mobility.

We further extended our study for the identification and characterization of deep traps in organic thin films using capacitance based spectroscopy. The films grown with high deposition rates show a signature of deep traps due to structural disorder induced by high deposition rate. The non-monotonic nature of the $C$-$V$ characteristics in the forward bias and step in thermally stimulated capacitance (TSCAP) show a clear signature of deep traps. The peak in $C$-$V$ characteristics has been simulated by Gaussian distribution of traps. The value of the trap level obtained from simulation of $C$-$V$ characteristics matches well with that obtained directly from the TSCAP measurements. C-f characteristics have been shown to be useful method for to obtain energetic distribution of traps in organic semiconductors.

In chapter 6 microscopic explanation of charge carrier transport in organic molecular semiconductors have been achieved by a models which takes into account the temperature, electric field and carrier concentration dependence of charge carrier mobility. An excellent match between the microscopic parameters obtained from the theoretical simulation and the values directly measured by AFM and XRD establishes the applicability of the microscopic model for charge carrier transport in organic molecular semiconductors.
In chapter 7 we have tried to correlate the morphology and most discussed and debated charge transport mechanism multiple trapping and release (MTR) model proposed by Horowitz et al and percolation models proposed by Vissenberg and Matters. It has been believed that the MTR model holds good for polycrystalline thin films and PM model provides a better explanation for charge transport mechanism in disordered/amorphous systems. Here we have shown that not all the organic molecular semiconductors agree to common mechanism for charge transport in OFETs based on organic molecular semiconductors. The charge transport in Metal phthalocyanine based OFETs can be explained and modelled by MTR model. The grain boundaries can induce interface states which give rise to traps assisted conduction through these films. The Pentacne based OFETs show the highest molecular packing (layer by layer growth) and the charge transport is better explained by percolation model. Charge transport in Rubrene based OFETs showing least molecular packing with a polycrystalline spherulitic growth embedded in amorphous matrix can also be better explained with percolation model.

8.2. Future scope of the work

From the work presented in this thesis we have got fairly accurate understanding of the correlation between morphology and device performance and a glimpse of the role of molecular structure on their pattern formation. This sets a foundation for the future studies on following problems

1. How to achieve total control on the morphology of organic thin films to grow certain topological patterns including nanostructures on different substrates.
2. First principle explanation of different pattern formation in organic thin films.
3. To go beyond present “hit-trial-error” method for selecting molecular systems for achieving high performance device by thorough understanding of surface morphology and charge carrier mobility and their correlation.
4. How to design certain organic molecules, that could be anticipated to have certain thin film morphology for achieving stability of devices and high carrier mobility.