CHAPTER 6

GENERAL DISCUSSIONS AND CONCLUSIONS

Organic compounds have attracted great deal of interest in recent years because of their numerous potential applications such as optical mass memories, optoelectronic devices, gas sensors, display devices etc. Among these 9,10-anthraquinone based organic compounds seem to be promising materials due to their optical and photoconductive properties. Anthraquinones are thermally and photochemically stable and can be easily modified by substituents to exhibit wide range of properties.

In this direction, a series of organic compounds has been synthesised from 9,10-anthraquinone namely: 1,8-bis-(3-hydroxy propylamino)-9,10-anthraquinone 1-(3-hydroxy-propyl-amino)-9,10-anthraquinone; 1-(2-amino-ethylamino)-9,10-anthraquinone; 1,4-bis-(2-hydroxyethylamino)-9,10-anthraquinone and 1,4-bis-(2-dimethylaminoethylamino) -9,10-anthraquinone. The films of these newly synthesised materials have been prepared onto the glass substrate by thermal evaporation and hot wall techniques under different experimental conditions and are characterised for structural, electrical and optical properties.

The comparison of FTIR spectra of films deposited on KBr substrate, by and large show that compounds remain unaffected during vacuum deposition and annealing processes because of unchanged vibrational frequencies in their spectra.

The $^1$H NMR spectra of the samples obtained from the organic films appear to be same as that of the corresponding pure starting compound and do not show any
decomposition. Therefore, both IR and NMR spectral studies indicate that 9,10-anthraquinones based compounds do not undergo any change during film preparation.

Scanning electron microscopy investigations reveal that the thermally evaporated films of 1-(3-hydroxypropylamino)-9,10-anthraquinone; 1,8-bis-(3-hydroxypropylamino)-9,10-anthraquinone and 1-(2-amino-ethylamino)-9,10-anthraquinone exhibit long platelet type surface morphology. Whereas, elliptic crystallites and mesh of wires are noticed in case of thermally evaporated films of 1,4-bis-(2-dimethylaminoethylamino)-9,10-anthraquinone and 1,4-Bis-(2-hydroxyethylamino)-9,10-anthraquinone, respectively. An appreciable increase in crystallite size has been observed in organic films derived from 9,10-anthraquinone with increase in substrate temperature from 303 to 333 K. This may be due to the fact that at higher substrate temperatures, crystallites agglomerate to form bigger crystallites. Crystallite as large as 1.7 μm has been found in case of 1-(2-aminoethylamino)-9,10-anthraquinone film deposited at 333 K.

The XRD patterns obtained for thermally evaporated 9,10-anthraquinone based organic films show the presence of sharp and well resolved diffraction peaks, which confirm their crystalline behaviour. While the films deposited at higher substrate temperature show comparatively intense diffraction peaks and a decrease in full width measured at half maxima thus suggesting a higher degree of crystallinity and increase in particle size.

The SEM investigations of hot wall grown organic films derived from 9,10-anthraquinone show that these films are more ordered and the size of the crystallites are more than that obtained by thermally evaporated ones. X ray diffraction studies of hot wall grown films also indicate higher degree of crystallinity as compared to thermally evaporated ones. These remarkable changes in crystallinity of films may be due to the fact that adatoms undergo thermodynamic equilibrium conditions can find the most suitable arrangement before being incorporated into the crystal lattice resulting in highly ordered structure of deposited layers. Thus the substrate temperature and deposition techniques in turn influence the formation chemistry and adatoms mobility during growth.
The electrical resistivity of the 9,10-anthraquinone based films on the glass substrate has been studied as a function of temperature. Observations reveal that the electrical resistivity decreases with increase in temperature with in the experimental range investigated and can be represented by the equation

$$\rho = \rho_0 \exp(E_\rho/2kT)$$

where $E_\rho$ is the resistivity activation energy, $k$ is the Boltzmann's constant and $T$ is the absolute temperature. The results suggest that the organic films derived from 9,10-anthraquinone are essentially semiconductors. The electrical resistivity of films has been found to decrease with increase in the substrate temperature, which can be explained by Petritz’s barrier model. Since the crystallites do not grow sufficiently large at low temperature, the inter crystalline regions are wide, offering a high resistance to the movement of charge carriers. The formation of fewer nucleation centers at higher substrate temperature results in large crystallites, which ultimately decrease the barrier size. Thus charge carrier have to cross narrow inter-crystalline barriers and therefore may cause decrease in resistivity.

The studied organic films can be arranged as: 1-(2-aminoethylamino)-9,10-anthraquinone; 1-3-(hydroxypropylamino)-9,10-anthraquinone; 1,8-bis-(3-hydroxypropylamino)-9,10-anthraquinone; 1,4-bis-(2-dimethylaminoethyl amino)-9,10-anthraquinone and 1,4-bis-(2-hydroxyethylamino)-9,10-anthraquinone on the basis of decrease in resistivity. The electrical resistivity of 1,8-bis-(3-hydroxy propylamino)-9,10-anthraquinone and 1-(3-hydroxypropylamino)-910-anthraquinone films is nearly $10^4$ times less than that observed in case of ligand 9,10-anthraquinone based films. It implies that the position and nature of substituents can tune and tailor the properties of materials.

Interestingly the electrical resistivity of 9,10-anthraquinone based organic films deposited by hot wall technique decreases by an order of $10^2$-$10^3$ as compared to thermally evaporated ones.

The activation energy of charge carriers responsible for conduction has been evaluated using the Arhenius type log $\rho$ vs 1000/T plots and are found to lie in the range 0.2-0.6 eV. It is found that the activation energy decreases with increase in the
substrate temperature, thus indicating the formation of more ordered films at higher substrate temperatures.

The charge carrier concentration (n) is determined using the relation

\[ n = 2(2\pi m^+ kT/h^2)^{3/2}\exp(-E_g/2kT) \]

where \( m^+ \) is the effective mass of a charge carrier which is assumed to be equal to the real mass of a free electron and \( h \) is Planck's constant. It is observed that the carrier concentration of the films deposited on glass substrate increases with an increase in temperature with in the experimental range. Also the films prepared at higher substrate temperature show comparatively higher carrier concentration.

The UV–VIS spectra of 9,10-anthraquinone based organic films deposited onto the glass substrate kept at different temperatures has been recorded in the wavelength range 300-1100nm. The optical band gap of the films is evaluated from the absorption coefficients by fitting the data to the Bardeen et al relation

\[ \alpha hv = B(hv-E_g)^n \]

where \( hv \) is the incident photon energy, \( B \) is a constant and \( n \) is the exponent and \( E_g \) is the band gap. The extrapolation of the straight line in the spectral variation of absorption coefficients \( \alpha \) to \( (\alpha hv)^2 = 0 \) gives the value of optical band gap and found to lie in the range 1.33-1.94eV.

The extinction coefficient (k) and refractive index (n) of the films has been determined from absorption coefficient and refractivity of material respectively, using the relation

\[ \alpha = 4\pi k / \lambda \]

\[ T = (1-R) / (1+R) = 2n / (1+n^2) \]

Observations reveal that k and n of films show an increasing dependence on photon energy. Films deposited at higher substrate temperature show a decrease in k and n, which is in accordance with optical band gap data. The hot wall grown films show decrease in optical absorbance, n and k values as compared to thermally evaporated ones. These results are in agreement with SEM and XRD data.

Keeping in view the structural, electrical and optical properties of organic semiconducting films derived from 9,10-anthraquinone deposited on glass substrate kept at 333 K by hot wall technique have been selected for the fabrication of p-n
junction device for photovoltaic applications. In this direction FTO / 1-3-(hydroxypropylamino)-9,10-anthraquinone/Al; FTO / 1,4-bis-(2-hydroxyethylamino)-9,10-anthraquinone /Al and FTO / 1,4-Bis-(2-dimethylaminoethylamino)-9,10-anthraquinione /Al structure have been fabricated.

The J-V relationship of the devices are found to be in good agreement with standard diode equation

\[ J = J_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \]

The typical parameters such as open circuit voltage (Voc), short circuit current (JSC) and fill factor (FF) are calculated from J-V plots under illumination. It has been observed that Al/1,4-bis-(2(dimethylaminoethylamino)-9,10-anthraquinione/FTO structure shows comparatively larger value of JSC, lesser value of Voc and higher power conversion efficiency as compared to other ones.

Although there are numerous factors, which control the properties of the films and devices, yet it is hoped that present investigations providing data on structure, electronic and optical properties would be worth consideration for utilization in molecular electronic devices. A systematic study of the preparatory parameters on p-n junction devices would also contribute an interesting area of investigations. Hence, these investigations will not only help to synthesis and characterize the new materials but also pave way for the possible fabrications of electronic devices based on substituted anthraquinone compounds.